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Note

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Preparation of *N*-Arylquinazolinium Salts via a Cascade Approach

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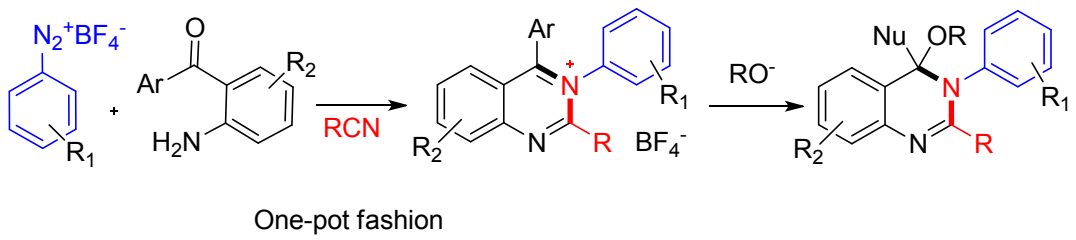
Graphic Abstract (TOC)



ABSTRACT. An easy manipulation method for the preparation of *N*-arylquinazolinium salts is described from readily available aryldiazonium salts, nitriles and 2-aminoarylketones in a one-pot operation. This method relies on the *in situ* generation of *N*-arylnitrilium intermediate from the reaction of aryldiazonium salt with nitrile, which undergoes amination/cascade cyclization/aromatization leading to *N*-arylquinazolinium salts in excellent yields. Nucleophilic addition of alkoxide to these *N*-arylquinazolinium salts provides functionalized dihydro-*N*-arylquinazoline.

KEYWORDS. Quinazolinium, Diazonium, Cascade reaction, Nitrilium.

Quinazoline and its derivatives represent a potential class of heterocyclic scaffolds found in drugs exerting unique pharmacological activities including antiasthmatic,[1] antitubercular,[2] antiviral,[3] anticancer,[4] antimalarial,[5] antihypertensive[6] and anticonvulsant[7] properties. In addition, quinazolines exhibit excellent photophysical properties[8] and act as potential ligands in asymmetric transformations.[9] Consequently, numerous synthetic routes have been developed to access this ubiquitous core.[10]

Despite the skeletal diversity in quinazoline, cationic quinazolinium derivatives have rarely been found in literature.[11] Figure 1 summarizes some known quinazolinium species and most of them are prepared by *N*-substitution reactions. A chelated palladacycle was used as the substrate to render the *N*-arylquinazolinium salts **IV** in low yields *via* an insertion of alkyne followed by depalladation.[11d]

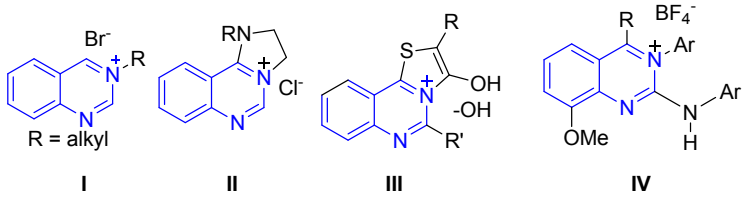
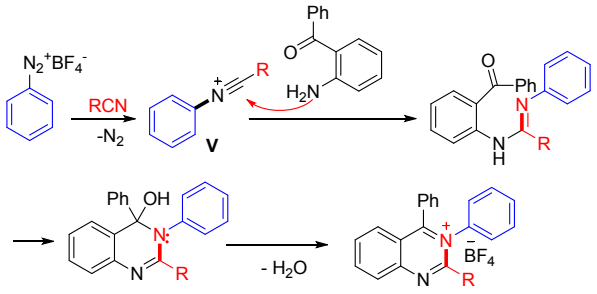


Figure 1. Some known quinazolinium salts

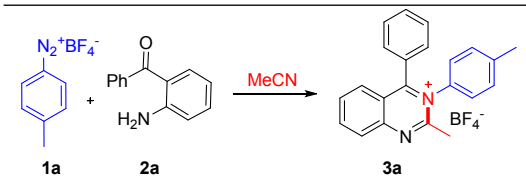
Aryldiazonium salts are prerogative reagents in synthetic uses.[12] In recent years, the use of *N*-arylnitrilium intermediates, generated *in situ* from aryldiazonium salts and nitriles, has received significant attention due to the applications in the synthesis of various heterocycles.[13-14] We envisioned the possibility of developing a one-pot preparation of substituted *N*-arylquinazolinium salts. The unprecedented synthesis was expected to proceed via an initial formation of *N*-arylnitrilium intermediate (**V**) followed by a tandem amination/cyclization/elimination sequences as shown in Scheme 1.

Scheme 1. Proposed Synthetic Approach to *N*-arylquinazolinium salts.



To explore this feasibility, we investigated the reaction of **1a** with **2a** in anhydrous MeCN under various conditions (Table 1). When the reaction was carried out at 80 °C for 2 h, the desired product **3a** was isolated in 52% yield by the addition of ether to the mixture followed by a filtration (Table 1, entry 1). To our delight, significant improvement in yield was observed upon increasing the temperature to 120 °C (Table 1, entries 3-5). Conducting the reaction for a longer period led to no further improvement (Table 1, entry 6). Unfortunately, our attempts to reduce the amount of nitrile in the presence of co-solvents such as DCE, DMSO and toluene were unfruitful (Table 1, entries 7-10). It is noticed that the yield does not improved by addition of molecular sieves (Table 1, entry 11) due to the decomposition.

Table 1. Reaction Optimization[a]



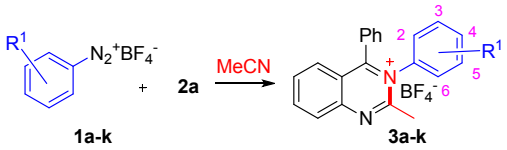
entry	solvent	T (°C)	*t* (h)	Yield (%)[b]
1	MeCN	80	2	52
2	MeCN	80	12	48
3	MeCN	100	3	66
4	MeCN	100	5	63
5	MeCN	120	5	81
6	MeCN	120	12	78
7[c]	MeCN/DMSO	120	12	ND[d]
8[c]	MeCN/DCE	120	12	47
9[e]	MeCN/ DCE	120	12	15
10[c]	MeCN/toluene	120	12	38
11[f]	MeCN	120	12	10

[a]Reaction conditions: a mixture of **1a** (0.48 mmol), **2a** (0.53 mmol), and anhydrous MeCN (2 mL) were heated in a sealed tube. [b]isolated yields. [c]MeCN (1 mL) in solvent (2 mL). [d]ND = Not detected. [e]MeCN (0.5 mL) in solvent (2 mL). [f]With addition of 1.5 g of molecular sieve.

With the optimal conditions, we explored the reaction scope by treating **2a** with aryldiazonium salts of diverse steric and electronic characteristics in anhydrous MeCN (Table 2). A wide range of substituted aryldiazonium salts were readily participated in the reaction and provided the corresponding *N*-arylquinazolinium salts in good to excellent yields (Table 2, entries 1-9). It was noted that the difference in the substitution pattern of the aromatic ring had no influence on the conversion. In particular, 2,4,6-trimethylphenyldiazonium and 3,4,5-trimethoxyphenyldiazonium

salts proceeded smoothly in the reaction and furnished the corresponding salts in good yields (Table 2, entries 10-11). For a practical utility, treatment of **1j** (0.6 g) with 2-aminobenzophenone (0.56 g) in acetonitrile (12 mL) furnished **3j** (0.83 g) in 75% yield.

Table 2. Reaction scope with various aryldiazonium salts[a]

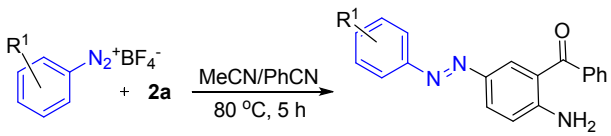


Entry	R^1 =	Product (yield)
1	R^1 = 4-Me	**3a** (81%)
2	R^1 = H	**3b** (62%)
3	R^1 = 3-Me	**3c** (74%)
4	R^1 = 2-Me	**3d** (84%)
5	R^1 = 2-MeS	**3e** (72%)
6	R^1 = 3-MeO	**3f** (71%)
7	R^1 = 3,4-$(Me)_2$	**3g** (82%)
8	R^1 = 3,5-$(Me)_2$	**3h** (77%)
9	R^1 = 2,6-$(Me)_2$	**3i** (74%)
10	R^1 = 2,4,6-$(Me)_3$	**3j** (88%)
11	R^1 = 3,4,5-$(MeO)_3$	**3k** (76%)

[a]Reaction conditions: a mixture of diazonium salt (0.52 mmol) and **2a** (0.57 mmol) in acetonitrile (2mL) at 120 °C for 5 h. Yields given refer to isolated yields.

On the other hand, aryldiazonium salts with electron-withdrawing functional groups underwent rapid azo-coupling with **2a** leading to 5-(aryldiazenyl)-substituted 2-aminobenzophenones (Scheme 2).[15] Intriguingly, these azo-coupled products (**3aa-3ac**) could be accessed under mild conditions.

Scheme 2. Reactions of **2a** with $ArN_2^+BF_4^-$ bearing electron-withdrawing groups.

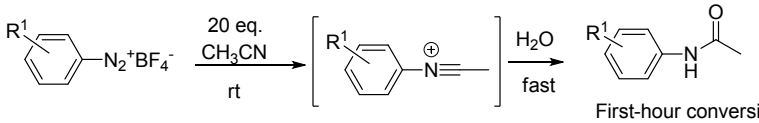


1l, R^1 = 3-Br
1m, R^1 = 4-CO_2Et
1n, = R^1 = 4-COPh

3aa, R^1 = 3-Br, 48%
3ab, R^1 = 4-CO_2Et, 56%
3ac, R^1 = 4-COPh, 43%

Next, we probed the reactivity difference of aryldiazonium salts **1a**, **1j**, and **1o** bearing substituents in a different electronic nature (Scheme 3). It is known that the hydrolysis of nitrilium ion into the corresponding amide is a rapid reaction.[13c] Thus, the measurement of the amount of amide formation is able to compare the relative rate of reactions. It was observed that compound **1a** and **1j** readily reacted with MeCN at room temperature and resulted in a significant amount of amide upon quenching with water (Scheme 3). Furthermore, the reactivity of **1j** is more active than that of **1a** due to the three methyl groups on the ring. In case of **1o** with a fluoro substituent, no amide product (**1oA**) was observed. These results indicate the formation of *N*-arylnitrilium intermediate highly depends on the electronic nature of the aryldiazonium components. Presumably, the electron withdrawing group at 4-position readily destabilizes the cationic nature for the substitution.

Scheme 3. Comparison of reactivity of various $ArN_2^+BF_4^-$ toward acetonitrile



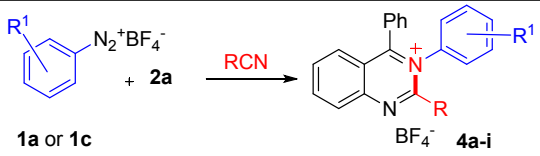
1a, R^1 = H,
1j, R^1 = 2,4,6-Me_3
1o, R^1 = 4-F

1aA, R^1 = H, 36%
1jA, R^1 = 2,4,6-Me_3 53%
1oA, R^1 = 4-F 0%

Further, we investigated this reaction with a variety of nitriles in combination with aryldiazonium salts and **2a** (Table 3). The reaction proved efficiently with a series of 1°, 2°, 3° and cyclic aliphatic nitriles furnishing the corresponding 2-alkylated-3,4-diarylquinazolinium salts in moderate to excellent yields (Table 3, entries 1-8). Sterically demanding pivalonitrile led to no desired product upon treating 2,4,6-trimethylphenyldiazonium salt (Table 3, entry 6).

However, the product **4g** was successfully isolated albeit with a diminished yield (Table 3, entry 7). To our delight, adiponitrile was also amenable for this transformation to afford the desired *N*-arylquinazolinium salt in 82% yield (Table 3, entry 8). Notably, the sensitive cyano group on the aliphatic chain remains unaffected. Furthermore, benzylnitrile was also participated well in the reaction and afforded the desired product **4i** in moderate yield (entry 9).

Table 3. Reaction scope with various aliphatic nitriles[a]

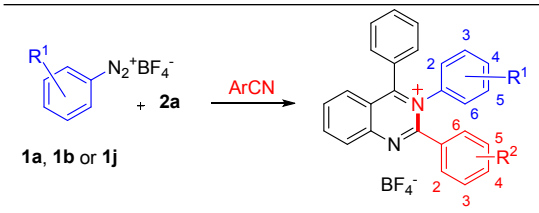


entry	substituents	yield[b]
1	R^1 = 2,4,6-$(Me)_3$, R = *n*-Pr	**4a**, 84%
2	R^1 = 2,4,6-$(Me)_3$, R = CH_2CH_2OMe	**4b**, 44%
3	R^1 = 2,4,6-$(Me)_3$, R = *i*-Pr	**4c**, 76%
4	R^1 = 2,4,6-$(Me)_3$, R = *c*-Pr	**4d**, 78%
5	R^1 = 2,4,6-$(Me)_3$, R = *c*-C_6H_{11}	**4e**, 41%
6	R^1 = 2,4,6-$(Me)_3$, R = *t*-Bu	**4f**, 0
7	R^1 = 3-Me, R = *t*-Bu	**4g**, 31%
8	R^1 = 2,4,6-$(Me)_3$, R = $(CH_2)_4CN$	**4h**, 82%
9	R^1 = 2,4,6-$(Me)_3$, R = CH_2Ph	**4i**, 52%

[a]Reaction conditions: a mixture of diazonium salt (0.52 mmol) and **2a** (0.57 mmol) in nitrile (2mL) at 120 °C for 5 h. [b]Yields given refer to isolated yields.

On the other hand, various substituted benzonitriles were also successfully utilized in this reaction to furnish 2,3,4-triarylated quinazolinium salts in yields ranging from 49-71% (Table 4). Together, these unprecedented and diverse *N*-arylquinolinium salts may find potential implications for drug library and material applications.[16]

Table 4. Reaction scope with various aromatic nitriles[a]

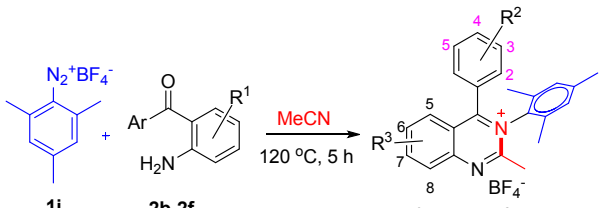


entry	substituents	yield[b]
1	R^1 = H, R^2 = H	**4j**, 54%
2	R^1 = H, R^2 = 2-Me	**4k**, 44%
3	R^1 = 4-Me, R^2 = 2-Me	**4l**, 71%
4	R^1 = 2,4,6-$(Me)_3$, R^2 = 2-Me	**4m**, 41%
5	R^1 = H, R^2 = 4-Me	**4n**, 66%
6	R^1 = H, R^2 = 3-Br	**4o**, 67%
7	R^1 = 2,4,6-$(Me)_3$, R^2 = 4-F	**4p**, 49%

[a]Reaction conditions: a mixture of diazonium salt (0.52 mmol) and **2a** (0.57 mmol) in an aromatic nitrile (2 mL) at 120 °C for 5 h. [b]Yields given refer to isolated yields.

Finally, we probed the scope with variously substituted 2-aminoarylketones (Scheme 4). It was noted that, 2-aminoaryl ketone bearing halogens (Cl, F) at various positions of the aromatic ring were participated in the reaction and conveniently led to the corresponding product in good yields (Scheme 4, **5a**-**5c**). Notably, multi-halogenated *N*-arylquinazolinium salt **5e** was also obtained in excellent yield.

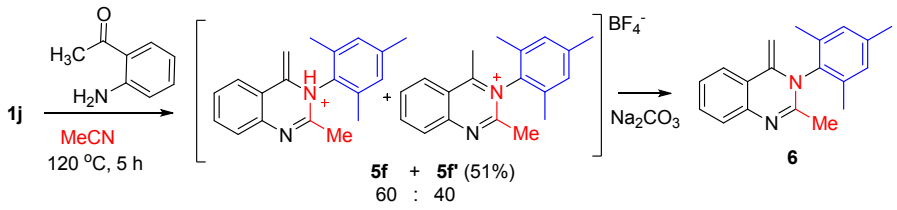
Scheme 4. Reaction of **1j** with various 2-aminoarylketones



5a, R^3 = 6-Cl, R^2 = H, 77%
5b, R^3 = 6-Br, R^2 = H, 74%
5c, R^3 = H, R^2 = 4-F, 78%
5d, R^3 = H, R^2 = 4-Me, 78%
5e, R^3 = 6-Cl, R^2 =2'-Cl, 73%

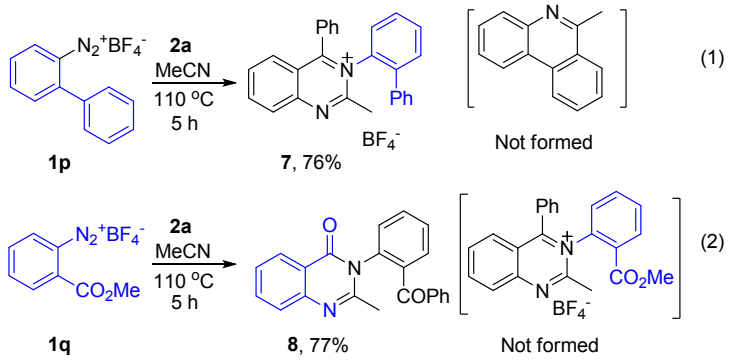
Interestingly, when 2-aminoacetophenone was treated with **1j** in MeCN, an inseparable mixture (60:40) of **5f** and **5f'**were observed in CD_3CN (Scheme 5). However, upon base treatment, this mixture readily converted into one isomeric form **6.**

Scheme 5. Reaction of **1j** with 2-aminoacetophenone



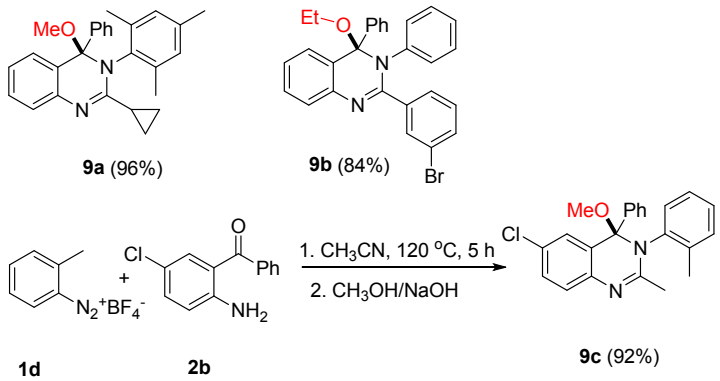
In contrary to our earlier observations,[14a,14d,14f] aryldiazonium salt **1p** with adjacent phenyl group, reacted with **2a** and MeCN to give **7** in good yield in lieu of 6-methylphenanthridine (Scheme 6, Eq. 1). Apparently, *N*-arylnitrilium intermediate is reactive towards amino nucleophile rather than adjacent phenyl group leading to **7**. On the other hand, aryldiazonium salt with *o*-ester functionality expeditiously resulted in the formation of **8** (Scheme 6, Eq. 2), unlike compound **3ab** presumably due to the steric hindrance preventing the diazo coupling. Seemingly, the rate of intramolecular amidation is faster than that of the intermolecular amination/tandem cyclization/elimination sequences.

Scheme 6. Reactions of **2a** with *o*-functionalized aryldiazonium salts



Further synthetic application using these quinazolinium salts is demonstrated by the nucleophilic addition of alkoxides leading to the dihydroquinazolines. Typically, reaction of **4d** with sodium methoxide gave **9a** in 96% yield. Similarly, compound **4o** reacted with ethoxide in ethanol under ambient temperature provided **9b** in 84% yield (Scheme 7). Furthermore, this dihydroquinazoline could be obtained from a sequential treatment without the isolation of quinazolinium salt (Scheme 7). Thus, reaction of *o*-toluenediazonium tetrafluoroborate and 2-amino-5-chlorbenzophenone in acetonitrile at 120 °C for 5 h led to the desired quinazolinium salts, which was stirred in a basic methanol/water solution at room temperature for 12 h to yield the dihydroquinazoline **9c**.

Scheme 7. Structures of **9a-b** and direct preparation of **9c**.



In summary, we have disclosed an efficient method to prepare diversely substituted *N*-arylquinazolinium salts from readily accessible aryldiazonium salts, nitriles and 2-amino arylketones in a one-pot manner. Nucleophilic addition of alkoxide toward these quinazolinium salts giving the dihydroquinazoline derivative provides an alternative to prepare various quinazolines.

Experimental Section

General information. ^{1}H and ^{13}C NMR were recorded in a 400 MH_Z spectrometer in $CDCl_3$ and CD_3CN referenced to TMS. All the nitriles were dried over activated 4Å molecular sieves and solid nitriles were purchased and used without any further drying. All the anilines were commercially purchased and used for diazotization without further purification. Other chemicals were used as purchased. Flash chromatography was performed using silica gel 230-400 mesh. Aryldiazonium salts were prepared according to the literature procedure. In cases of known compounds, their spectral data were compared with the literature values. Melting points were determined on a Fargo MP-1D instrument. Unless otherwise noted, all the reactions were performed without any special precautions. Compound **2c** was prepared according to the literature method,[17a] whereas **2a**-**2b** and **2d**-**2f** were purchased.

General procedure for preparing aryldiazonium tetrafluroborate:

All the substituted aryldiazonium salts were synthesized by following the reported methods. Spectral data of the compounds are in agreement with those reported in the literature. A typical procedure for preparing benzenediazonium tetrafluroborate is shown below. The corresponding aniline (0.93 g, 10 mmol) was dissolved in a mixture of water (4 mL) and 50% aqueous hydrofluroboric acid (3.3 mL, 19.3 mmol, 1.92 equiv.). The mixture was cooled to 0 ^{o}C and a solution of $NaNO_2$ (0.69 g, 10 mmol in 1.5 mL of water) was added slowly. The resulting reaction mixture was stirred at 0 ^{o}C for 30 min. and the precipitate was collected by filtration.

The solid product was dissolved in minimum acetone and re-precipitated using diethyl ether to yield aryldiazonium tetrafluroborate which was dried under vacuum without further purification.

General procedure for the synthesis of *N*-arylquinazolinium tetrafluoroborates:

In a dry 10 mL glass sealed tube, aryldiazonium salt (100 mg, 0.52 mmol) and 2-aminobenzophenone (113 mg, 0.57 mmol, 1.1 eq.) were suspended in 2 mL of anhydrous nitrile. The tube was sealed with a Teflon screw cap and heated in an oil bath (120 ^{O}C) for 5 h. After cooling to room temperature, reaction mixture was added dropwise to diethyl ether (30 mL) under vigorous stirring. Resulting solid was filtered and dried under high vacuum to obtain the title compound.

*2-Methyl-3,4-diphenylquinazolin-3-ium tetrafluoroborate (**3a**).*

124 mg, 62%, off-white solid: mp 228-229 ^{o}C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.47 (ddd, *J* = 15.4, 7.8, 1.2 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 7.94 (t, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.53-7.50 (m, 3H), 7.49-7.48 (m, 3H), 7.47-7.43 (m, 2H), 7.40-7.38 (m, 2H), 2.70 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 169.6, 156.6, 152.5, 143.0, 139.5, 132.6, 132.4, 132.2, 132.1, 131.2, 130.4, 130.2, 129.5, 129.3, 128.1, 123.4, 25.1; HRMS (ESI-TOF) calcd. For $C_{21}H_{17}N_2$ $(M)^+$ m/z = 297.1392, found 297.1382.

*2-Methyl-4-phenyl-3-(p-tolyl)quinazolin-3-ium tetrafluoroborate (**3b**).*

156 mg, 81%, off-white solid: mp 248-249 ^{o}C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.45 (t, *J* = 8.0 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.93 (t, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.69 (s, 3H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 169.7, 156.8, 152.4, 142.9, 142.6, 137.1, 132.5, 132.3, 132.0, 131.5, 130.4, 129.5, 129.4, 129.3, 127.7, 123.5, 25.1, 21.2; HRMS (ESI-TOF) calcd. For $C_{22}H_{19}N_2$ $(M)^+$ m/z = 311.1548, found 311.1551.

*2-Methyl-4-phenyl-3-(m-tolyl)quinazolin-3-ium tetrafluoroborate (**3c**).*

142 mg, 74%, off-white solid: mp 216-217 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.46 (t, *J* = 7.6 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 7.94 (t, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.54-7.51 (m, 1H), 7.46 (t, *J* = 6.8 Hz, 2H), 7.42-7.40 (m, 2H), 7.38-7.34 (m, 1H), 7.31-7.24 (m, 3H), 2.72 (s, 3H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 169.5, 156.6, 152.4, 142.9, 141.8, 139.4, 132.6, 132.5, 132.3, 132.0, 130.8, 130.4, 129.4 (2C), 129.3, 128.4, 124.9, 123.4, 25.0, 21.1; HRMS (ESI-TOF) calcd. For $C_{22}H_{19}N_2$ $(M)^+$ m/z = 311.1548, found 311.1552.

*2-Methyl-4-phenyl-3-(o-tolyl)quinazolin-3-ium tetrafluoroborate (**3d**)*.

162 mg, 84%, off-white solid: mp 214-215 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.49 (ddd, *J* = 15.6, 7.6, 1.6 Hz, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 7.96 (ddd, *J* = 15.6, 7.8, 1.2 Hz, 1H), 7.80 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.57-7.51 (m, 1H), 7.50-7.47 (m, 2H), 7.46-7.42 (m, 3H), 7.41-7.40 (m, 1H), 7.38-7.32 (m, 2H), 2.67 (s, 3H), 2.03 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 169.4, 156.4, 152.9, 143.3, 138.4, 134.4, 133.1, 132.8, 132.7, 132.4, 132.2, 130.9, 129.5, 129.46, 129.41, 129.1, 128.7, 123.7, 24.5, 17.7; HRMS (ESI-TOF) calcd. For $C_{22}H_{19}N_2$ $(M)^+$ m/z = 311.1548, found 311.1558.

*2-Methyl-3-(2-(methylthio)phenyl)-4-phenylquinazolin-3-ium tetrafluoroborate (**3e**)*.

129 mg, 72%, pale yellow solid: mp 263-264 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.50 (t, *J* = 7.6 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.96 (t, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.59-7.55 (m, 2H), 7.53-7.49 (m, 2H), 7.47-7.43 (m, 3H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 2.71 (s, 3H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 170.5, 156.6, 152.7, 143.7, 136.8, 136.3, 132.9, 132.8, 132.4, 130.8, 129.5, 129.3, 129.0 (2C), 128.4, 128.1, 127.3, 123.4, 24.2, 15.2; HRMS (ESI-TOF) calcd. For $C_{22}H_{19}N_2S$ $(M)^+$ m/z = 343.1269, found 343.1271.

*3-(3-Methoxyphenyl)-2-methyl-4-phenylquinazolin-3-ium tetrafluoroborate (**3f**)*.

133 mg, 71%, orange solid: mp 186-187 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.47 (ddd, *J* = 15.4, 7.6, 1.6 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.94 (ddd, *J* = 15.6, 8.0, 0.8 Hz, 1H), 7.79-7.76 (m,

1H), 7.54-7.50 (m, 1H), 7.49-7.41 (m, 3H), 7.40-7.36 (m, 2H), 7.07-7.01 (m, 3H), 3.74 (s, 3H), 2.75 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN) δ 169.8, 161.9, 156.9, 152.8, 143.3, 140.6, 132.8, 132.7, 132.4, 132.3, 130.7, 129.7, 129.6, 129.5, 123.6, 120.4, 118.2, 113.9, 56.9, 25.2; HRMS (ESI-TOF) calcd. For $C_{22}H_{19}N_2O$ $(M)^+$ m/z = 327.1497, found 327.1496.

*3-(3,4-Dimethylphenyl)-2-methyl-4-phenylquinazolin-3-ium tetrafluoroborate (**3g**)*.

153 mg, 82%, off-white solid: mp 218-219 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.45 (ddd, *J* = 15.4, 7.6, 1.6 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 7.93 (ddd, *J* = 15.6, 7.8, 1.2 Hz, 1H), 7.76-7.73 (m, 1H), 7.52-7.50 (m, 1H), 7.48-7.43 (m, 2H), 7.42-7.39 (m, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.15 (dd, *J* = 8.0, 2.4 Hz, 1H), 2.70 (s, 3H), 2.21 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN) δ 169.9, 157.2, 152.7, 143.2, 141.5, 140.5, 137.5, 132.8, 132.6, 132.4, 132.1, 130.7, 129.7 (2C), 129.6, 128.9, 125.4, 123.8, 25.3, 20.1, 19.9; HRMS (ESI-TOF) calcd. For $C_{23}H_{21}N_2$ $(M)^+$ m/z = 325.1705, found 325.1697.

*3-(3,5-Dimethylphenyl)-2-methyl-4-phenylquinazolin-3-ium tetrafluoroborate (**3h**)*.

144 mg, 77%, off-white solid: mp 225-226 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.45 (t, *J* = 7.2 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 7.93 (t, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.54-7.51 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.42-7.40 (m, 2H), 7.12 (s, 1H), 7.07 (s, 2H), 2.72 (s, 3H), 2.25 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN) δ 169.4, 156.7, 152.4, 142.8, 141.4, 139.3, 133.1, 132.4, 132.3, 132.0, 130.4, 129.3 (2C), 125.4, 123.4 (2C), 24.9, 21.1; HRMS (ESI-TOF) calcd. For $C_{23}H_{21}N_2$ $(M)^+$ m/z = 325.1705, found 325.1705.

*3-(2,6-Dimethylphenyl)-2-methyl-4-phenylquinazolin-3-ium tetrafluoroborate (**3i**)*.

138 mg, 74%, off-white solid: mp 224-225 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.51 (ddd, *J* = 15.4, 7.8, 1.2 Hz, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 8.00-7.96 (m, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.48-7.46 (m, 2H), 7.42-7.37 (m, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 2H), 2.66 (s, 3H), 2.04 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN) δ 169.0, 156.1, 153.3,

143.5, 137.7, 134.7, 133.2, 132.8, 132.6, 132.3, 130.2 (2C), 129.5 (2C), 128.3, 123.9, 23.8, 18.3 (2C); HRMS (ESI-TOF) calcd. For $C_{23}H_{21}N_2$ $(M)^+$ m/z = 325.1705, found 325.1715.

*3-Mesityl-2-methyl-4-phenylquinazolin-3-ium tetrafluoroborate (**3j**)*.

160 mg, 88%, off-white solid: mp 233-234 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.50 (t, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.97 (t, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.04 (s, 2H), 2.65 (s, 3H), 2.26 (s, 3H), 1.99 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 169.6, 156.7, 153.6, 143.8, 143.1, 135.7, 134.6, 133.4, 133.1, 132.9, 131.6, 129.9, 129.86, 129.82, 128.7, 124.3, 24.2, 21.3, 18.5 (2C); HRMS (ESI-TOF) calcd. For $C_{24}H_{23}N_2$ $(M)^+$ m/z = 339.1861, found 339.1863.

When the reaction was carried out in a scale of mesitylenediazonium tetrafluoronorate (0.6 g) and 2-aminobenzophenone (0.56 g) in acetonitrile (12 mL), the desired compound **3j** was obtained (0.83 g) in 75% yield.

*2-Methyl-4-phenyl-3-(3,4,5-trimethoxyphenyl)quinazolin-3-ium tetrafluoroborate (**3k**)*.

127 mg, 76%, green solid: mp 176-177 °C;^{1}H NMR (400 MHz, CD_3CN) δ: 8.46 (t, *J* = 7.2 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.94 (t, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.57-7.54 (m, 1H), 7.51-7.44 (m, 4H), 6.78 (s, 2H), 3.71 (s, 6H), 3.69 (s, 3H), 2.82 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 169.8, 157.0, 154.9, 152.4, 143.0, 140.3, 134.6, 132.5, 132.3, 132.1, 130.4 (2C), 129.3 (2C), 123.2, 106.2, 61.1, 57.1 (2C), 24.7; HRMS (ESI-TOF) calcd. For $C_{24}H_{23}N_2O_3$ $(M)^+$ m/z = 387.1709, found 387.1709.

*(E)-(2-Amino-5-((3-bromophenyl)diazenyl)phenyl)(phenyl)methanone (**3aa**)*.

67 mg, 48%, orange solid: mp 137-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 1.6 Hz, 1H), 7.94 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.90 (s, 1H), 7.73-7.69 (m, 3H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 3H), 7.30 (t, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 9.2 Hz, 1H), 6.65 (brs, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.7, 153.7, 153.6, 142.7, 139.4, 134.9, 132.5, 131.5, 130.2, 129.1,

128.3, 125.7, 124.1, 123.0, 122.4, 117.7, 117.0; HRMS (ESI-TOF) calcd. For $C_{19}H_{15}{}^{79}BrN_3O$ $(M+H)^+$ m/z = 380.0398, found 380.0375; HRMS (ESI-TOF) calcd. For $C_{19}H_{15}{}^{81}BrN_3O$ $(M+H)^+$ m/z = 382.0378, found 382.0353.

*Ethyl (E)-4-((4-amino-3-benzoylphenyl)diazenyl)benzoate (**3ab**)*.

78 mg, 56%, orange solid: mp 136-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.4 Hz, 1H), 8.12-8.08 (m, 2H), 7.97 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.80-7.77 (m, 2H), 7.71-7.69 (m, 2H), 7.56 (ddd, *J* = 14.6, 7.2, 2.4 Hz, 1H), 7.51-7.47 (m, 2H), 6.79 (d, *J* = 9.2 Hz, 1H), 6.68 (brs, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.7, 166.1, 155.3, 153.9, 143.0, 139.4, 135.2, 131.5, 131.2, 130.4, 129.1, 128.3, 125.7, 122.1, 117.7, 117.0, 61.1, 14.3; HRMS (ESI-TOF) calcd. For $C_{22}H_{20}N_3O_3$ $(M+H)^+$ m/z = 374.1505, found 374.1489.

*(E)-(4-((4-amino-3-benzoylphenyl)diazenyl)phenyl)(phenyl)methanone (**3ac**)*.

58 mg, 43%, orange solid: mp 141-142 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 2.0 Hz, 1H), 8.00 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.89-7.83 (m, 4H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.60-7.55 (m, 2H), 7.51-7.45 (m, 4H), 6.80 (d, *J* = 9.2 Hz, 1H), 6.71 (brs, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.7, 196.0, 154.9, 153.9, 143.0, 139.4, 138.1, 137.5, 135.3, 132.4, 131.5, 131.0, 129.9, 129.1, 128.4, 128.3, 125.7, 122.1, 117.7, 117.0; HRMS (ESI-TOF) calcd. For $C_{26}H_{20}N_3O_2$ $(M+H)^+$ m/z = 406.1556, found 406.1544.

*3-Mesityl-4-phenyl-2-propylquinazolin-3-ium tetrafluoroborate (**4a**)*.

162 mg, 84%, off-white solid: mp 149-150 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.50 (ddd, *J* = 15.6, 7.8, 1.2 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.96 (ddd, *J* = 15.6, 8.0, 0.8 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.62-7.58 (m, 1H), 7.50-7.46 (m, 2H), 7.38 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.03 (s, 2H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.62 (s, 3H), 2.07-2.00 (m, 2H), 1.97 (s, 6H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 169.2, 158.5, 153.1, 143.4, 142.8, 134.8, 134.5, 133.1,

132.7, 132.5, 131.3, 129.6, 129.5, 129.4, 128.6, 123.8, 37.1, 21.0, 20.1, 18.3 (2C), 13.5; HRMS (ESI-TOF) calcd. For $C_{26}H_{27}N_2$ $(M)^+$ m/z = 367.2174, found 367.2166.

*3-Mesityl-2-(2-methoxyethyl)-4-phenylquinazolin-3-ium tetrafluoroborate (**4b**)*.

88 mg, 44%, pale yellow solid: mp 121-122 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.52 (ddd, *J* = 15.4, 7.6, 1.6 Hz, 1H), 8.37 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.00-7.96 (m, 1H), 7.84-7.82 (m, 1H), 7.62-7.58 (m, 1H), 7.51-7.46 (m, 2H), 7.42-7.39 (m, 2H), 7.03 (s, 2H), 4.00 (t, *J* = 5.6 Hz, 2H), 3.29 (s, 3H), 2.99 (t, *J* = 6.0 Hz, 2H), 2.26 (s, 3H), 1.98 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 169.3, 157.0, 152.9, 143.6, 142.9, 134.8, 134.7, 133.1, 132.9, 132.6, 131.2, 129.6, 129.5, 128.6, 127.0, 123.9, 69.1, 59.1, 35.7, 21.0, 18.3 (2C); HRMS (ESI-TOF) calcd. For $C_{26}H_{27}N_2O$ $(M)^+$ m/z = 383.2123, found 383.2116.

*2-Isopropyl-3-mesityl-4-phenylquinazolin-3-ium tetrafluoroborate (**4c**)*.

147 mg, 76%, pale yellow solid: mp 226-227 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.50 (ddd, *J* = 15.6, 7.8, 1.2 Hz, 1H), 8.35 (d, *J* = 8.8 Hz, 1H), 7.96 (ddd, *J* = 15.4, 7.8, 1.2 Hz, 1H), 7.80 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.62-7.57 (m, 1H), 7.50-7.46 (m, 2H), 7.39-7.36 (m, 2H), 7.02 (s, 2H), 3.01 (hept, *J* = 6.4 Hz, 1H), 2.25 (s, 3H), 1.99 (s, 6H), 1.39 (d, *J* = 6.4 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 168.9, 164.1, 153.5, 143.4, 142.7, 134.9, 134.7, 133.0, 132.8, 132.4, 131.2 (2C), 129.4 (2C), 128.8, 123.9, 34.0, 22.8 (2C), 21.0, 18.6 (2C); HRMS (ESI-TOF) calcd. For $C_{26}H_{27}N_2$ $(M)^+$ m/z = 367.2174, found 367.2179.

*2-Cyclopropyl-3-mesityl-4-phenylquinazolin-3-ium tetrafluoroborate (**4d**)*.

150 mg, 78%, pale yellow solid: mp 193-194 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.42 (ddd, *J* = 15.6, 7.6, 1.6 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.87 (ddd, *J* = 15.4, 7.8, 1.2 Hz, 1H), 7.75-7.37 (m, 1H), 7.61-7.57 (m, 1H), 7.48 (ddd, *J* = 13.8, 7.2, 1.6 Hz, 2H), 7.41-7.38 (m, 2H), 7.03 (s, 2H), 2.25 (s, 3H), 2.03 (s, 6H), 1.87-1.81 (m, 1H), 1.56-1.53 (m, 2H), 1.29-1.24 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 168.5, 160.9, 153.8, 143.3, 142.7, 135.1, 134.9, 133.0,

132.3, 132.0, 131.1, 129.5, 129.1, 128.7 (2C), 123.5, 21.0(2C), 18.4 (2C), 14.6 (2C); HRMS (ESI-TOF) calcd. For $C_{26}H_{25}N_2$ $(M)^+$ m/z = 365.2018, found 365.2008.

*2-Cyclohexyl-3-mesityl-4-phenylquinazolin-3-ium tetrafluoroborate (**4e**)*.

86 mg, 41%, off-white solid: mp 230-231 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.49 (ddd, *J* = 15.6, 7.8, 1.2 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.94 (dt, *J* = 15.4, 1.2 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.38-7.36 (m, 2H), 7.02 (s, 2H), 2.66-2.59 (m, 1H), 2.26 (s, 3H), 1.98 (s, 6H), 1.90-1.88 (m, 4H), 1.84-1.79 (m, 2H), 1.70-1.68 (m, 1H), 1.39-1.28 (m, 1H), 1.16-1.05 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 168.9, 162.8, 153.5, 143.3, 142.7, 134.9, 134.7, 133.0, 132.8, 132.4, 131.1 (2C), 129.5 (2C), 128.9, 123.9, 44.0, 33.3(2C), 26.4(2C), 26.0, 21.0, 18.7 (2C); HRMS (ESI-TOF) calcd. For $C_{29}H_{31}N_2$ $(M)^+$ m/z = 407.2487, found 407.2481.

*2-(tert-Butyl)-4-phenyl-3-(m-tolyl)quinazolin-3-ium tetrafluoroborate (**4g**)*.

68 mg, 31%, off-white solid: mp 236-237 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.45 (ddd, *J* = 15.6, 7.8, 1.2 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 7.93 (ddd, *J* = 15.2, 7.6, 0.8 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.48-7.39 (m, 3H), 7.37-7.27 (m, 4H), 7.25-7.24 (m, 2H), 2.27 (s, 3H), 1.38 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 171.8, 163.8, 151.9, 143.2, 140.5, 139.8, 133.1, 132.9, 132.1, 132.0, 131.5, 130.5, 130.4, 129.8, 129.4, 129.3, 128.1, 123.7, 43.6, 31.8, 21.3; HRMS (ESI-TOF) calcd. For $C_{25}H_{25}N_2$ $(M)^+$ m/z = 353.2018, found 353.2016.

*2-(4-Cyanobutyl)-3-mesityl-4-phenylquinazolin-3-ium tetrafluoroborate (**4h**)*.

175 mg, 82%, off-white solid: mp 148-149 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.51 (ddd, *J* = 15.4, 7.8, 1.2 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 7.97 (ddd, *J* = 15.6, 7.8, 1.2 Hz, 1H), 7.81 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.62-7.58 (m, 1H), 7.50-7.46 (m, 2H), 7.39-7.37 (m, 2H), 7.02 (s, 2H), 2.77 (t, *J* = 7.2 Hz, 2H), 2.45 (t, *J* = 6.8 Hz, 2H), 2.25 (s, 3H), 2.16-2.08 (m, 2H), 1.97 (s, 6H), 1.76-1.68 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 169.4, 157.9, 153.1, 143.5, 142.9, 134.7,

134.5, 133.2, 132.9, 132.6, 131.4, 129.7, 129.6, 129.5, 128.6, 123.9, 121.1, 34.7, 25.7, 25.1, 21.1, 18.4(2C), 17.5; HRMS (ESI-TOF) calcd. For $C_{28}H_{28}N_3$ $(M)^+$ m/z = 406.2283, found 406.2269.

*2-Benzyl-3-mesityl-4-phenylquinazolin-3-ium tetrafluoroborate (**4i**)*.

111 mg, 52%, off-white solid: mp 188-189 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.51 (t, *J* = 7.2 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.98 (t, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.30-7.26 (m, 3H), 7.00 (d, *J* = 6.4 Hz, 2H), 6.95 (s, 2H), 4.26 (s, 2H), 2.27 (s, 3H), 1.72 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 169.7, 157.2, 153.0, 143.5, 143.0, 135.0, 134.6, 134.2, 133.1, 133.0, 132.6, 131.2, 130.5, 129.7 (2C), 129.6, 129.4, 128.8, 128.5, 124.1, 42.5, 21.0, 18.2 (2C); HRMS (ESI-TOF) calcd. For $C_{30}H_{27}N_2$ $(M)^+$ m/z = 415.2174, found 415.2180.

*2,3,4-Triphenylquinazolin-3-ium tetrafluoroborate (**4j**)*.

125 mg, 54%, brown solid: mp 220-221 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.52 (ddd, *J* = 15.4, 7.8, 1.2 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.03 (ddd, *J* = 15.4, 7.8, 1.2 Hz, 1H), 7.89 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.54-7.46 (m, 4H), 7.44-7.39 (m, 4H), 7.36-7.31 (m, 4H), 7.23-7.17 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 169.9, 156.0, 152.2, 143.3 (2C), 139.8, 134.2, 133.3, 132.4, 132.2, 131.5, 131.4, 130.8, 130.4, 130.1, 129.9, 129.6, 129.5, 129.2, 123.7; HRMS (ESI-TOF) calcd. For $C_{26}H_{19}N_2$ $(M)^+$ m/z = 359.1548, found 359.1535.

*3,4-Diphenyl-2-(o-tolyl)quinazolin-3-ium tetrafluoroborate (**4k**)*.

150 mg, 63%, brown solid: mp 217-218 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.54 (ddd, *J* = 15.6, 8.0, 1.6 Hz, 1H), 8.44-8.41 (m, 1H), 8.06 (ddd, *J* = 15.4, 8.0, 0.8 Hz, 1H), 7.95-7.92 (m, 1H), 7.55-7.51 (m, 2H), 7.48-7.38 (m, 3H), 7.33-7.28 (m, 3H), 7.28-7.23 (m, 2H), 7.20-7.13 (m, 3H), 7.11-7.09 (m, 1H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 170.3, 155.8, 152.0, 143.3 (2C), 139.4, 137.8, 133.5, 132.5, 132.3, 131.6, 131.5 (2C), 130.9, 130.6, 130.1, 129.9, 129.5

(2C), 129.4, 126.3, 124.0, 20.1; HRMS (ESI-TOF) calcd. For $C_{27}H_{21}N_2$ $(M)^+$ m/z = 373.1705, found 373.1710.

*4-Phenyl-2-(o-tolyl)-3-(p-tolyl)quinazolin-3-ium tetrafluoroborate (**4l**)*.

163 mg, 71%, off-white solid: mp 197-198 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.53 (ddd, *J* = 15.4, 7.8, 1.2 Hz, 1H), 8.41 (d, *J* = 8.4 Hz. 1H), 8.05 (ddd, *J* = 15.4, 7.8, 1.2 Hz. 1H), 7.91 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.56-7.54 (m, 2H), 7.52-7.48 (m, 3H), 7.35-7.28 (m, 2H), 7.25-7.19 (m, 2H), 7.12 (t, *J* = 7.2 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 2.34 (s, 3H), 2.12 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 170.4, 155.9, 151.9, 143.1 (2C), 141.9, 137.7, 137.0, 133.6, 133.4, 132.4, 132.2 (2C), 131.4 (2C), 130.9, 130.6, 130.4, 129.8 (2C), 126.3, 124.0, 21.0, 20.1; HRMS (ESI-TOF) calcd. For $C_{28}H_{23}N_2$ $(M)^+$ m/z = 387.1861, found 387.1876.

*3-Mesityl-4-phenyl-2-(o-tolyl)quinazolin-3-ium tetrafluoroborate (**4m**)*.

87 mg, 41%, off-white solid: mp 191-192 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.56 (t, *J* = 7.6 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.07 (t, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.51-7.46 (m, 4H), 7.42-7.34 (m, 2H), 7.02-6.93 (m, 2H), 6.77 (s, 2H), 2.44 (s, 3H), 2.10 (s, 3H), 1.98 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 170.3, 154.8, 152.6, 143.5, 142.1, 139.4, 135.6, 135.3, 133.6, 133.2, 132.7, 132.6, 131.9, 131.7, 130.5, 130.1, 130.0, 129.7, 129.4, 128.8, 126.0, 124.0, 20.8, 20.4, 18.9 (2C); HRMS (ESI-TOF) calcd. For $C_{30}H_{27}N_2$ $(M)^+$ m/z = 415.2174, found 415.2182.

*3,4-Diphenyl-2-(p-tolyl)quinazolin-3-ium tetrafluoroborate (**4n**)*.

157 mg, 66%, off-white solid: mp 201-202 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.52 (ddd, *J* = 15.6, 8.0, 1.6 Hz, 1H), 8.42-8.39 (m, 1H), 8.02 (ddd, *J* = 15.4, 7.6, 0.8 Hz, 1H), 7.88-7.86 (m, 1H), 7.53-7.48 (m, 1H), 7.46-7.43 (m, 4H), 7.42-7.37 (m, 2H), 7.34-7.31 (m, 2H), 7.26-7.21 (m, 3H), 7.20-7.16 (m, 2H), 1.92 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 170.3, 156.6, 152.7, 143.5 (2C), 142.6, 140.2, 133.6, 132.7, 132.5, 131.7, 131.2, 130.8, 130.4, 130.3, 130.2, 129.8,

129.3 (2C), 124.0, 21.7; HRMS (ESI-TOF) calcd. For $C_{27}H_{21}N_2$ $(M)^+$ m/z = 373.1705, found 373.1705.

*2-(3-Bromophenyl)-3,4-diphenylquinazolin-3-ium tetrafluoroborate (**4o**)*.

185 mg, 67%, grey solid: mp 240-241 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.55 (ddd, *J* = 15.4, 7.6, 1.6 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.06 (ddd, *J* = 15.6, 7.8, 1.2 Hz, 1H), 7.92 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.66 (t, *J* = 1.6 Hz, 1H), 7.60-7.57 (m, 1H), 7.56-7.52 (m, 1H), 7.49-7.43 (m, 5H), 7.36-7.34 (m, 2H), 7.29-7.22 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 170.1, 154.3, 152.1, 143.4, 139.5, 136.0, 134.5, 133.6, 133.4, 132.5, 132.3, 131.6, 131.2, 130.5, 130.3, 130.0, 129.7, 129.5, 129.4, 129.2, 123.8, 122.5; HRMS (ESI-TOF) calcd. For $C_{26}H_{18}{}^{79}BrN_2$ $(M)^+$ m/z = 437.0653, found 437.0643; HRMS (ESI-TOF) calcd. For $C_{26}H_{18}{}^{81}BrN_2$ $(M)^+$ m/z = 439.0633, found 439.0718.

*2-(4-Fluorophenyl)-3-mesityl-4-phenylquinazolin-3-ium tetrafluoroborate (**4p**)*.

130 mg, 49%, pale yellow solid: mp 205-206 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.56 (t, *J* = 8.0 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 8.05 (t, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.53-7.48 (m, 4H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.13 (t, *J* = 8.8 Hz, 2H), 6.83 (s, 2H), 2.15 (s, 3H), 1.95 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 169.8, 166.3, 163.8, 154.8, 153.2, 143.7, 142.7, 135.5, 135.1, 133.6, 133.3 (d, *J* = 7.4 Hz), 132.7, 130.8 (2C), 130.2, 129.9, 129.4 (d, *J* = 19 Hz), 128.4, 124.1, 116.5 (d, *J* = 22 Hz), 20.9, 18.8 (2C); HRMS (ESI-TOF) calcd. For $C_{29}H_{24}FN_2$ $(M)^+$ m/z = 419.1924, found 419.1964.

*6-Chloro-3-mesityl-2-methyl-4-phenylquinazolin-3-ium tetrafluoroborate (**5a**)*.

152 mg, 77%, off-white solid: mp 225-226 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.43 (dd, *J* = 9.2, 2.4 Hz, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 2.0 Hz, 1H), 7.61 (ddd, *J* = 15.4, 8.2, 1.2 Hz, 1H), 7.51-7.48 (m, 2H), 7.40 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.04 (s, 2H), 2.65 (s, 3H), 2.25 (s, 3H), 1.98 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 168.7, 157.0, 152.2, 143.7, 143.0, 138.2,

135.3, 134.2, 133.4, 131.5, 131.4, 130.5, 129.7, 129.6, 128.0, 125.0, 23.9, 21.0, 18.2 (2C); HRMS (ESI-TOF) calcd. For $C_{24}H_{22}{}^{35}ClN_2$ $(M)^+$ m/z = 373.1472, found 373.1475; HRMS (ESI-TOF) calcd. For $C_{24}H_{22}{}^{37}ClN_2$ $(M)^+$ m/z = 375.1442, found 375.1443.

*6-Bromo-3-mesityl-2-methyl-4-phenylquinazolin-3-ium tetrafluoroborate (**5b**)*.

160 mg, 74%, grey solid: mp 222-223 °C; ^{1}H NMR (400 MHz, CD_3CN) δ: 8.55 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.25 (d, *J* = 9.2 Hz, 1H), 7.95 (d, *J* = 2.0 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.41-7.38 (m, 2H), 7.04 (s, 2H), 2.63 (s, 3H), 2.25 (s, 3H), 1.98 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 168.6, 157.1, 152.3, 146.2, 143.0, 135.2, 134.2, 133.9, 133.4, 131.3 (2C), 129.7, 129.6, 127.9, 126.2, 125.3, 23.9, 21.0, 18.2 (2C); HRMS (ESI-TOF) calcd. For $C_{24}H_{22}{}^{79}BrN_2$ $(M)^+$ m/z = 417.0966, found 417.0963; HRMS (ESI-TOF) calcd. For $C_{24}H_{22}{}^{81}BrN_2$ $(M)^+$ m/z = 419.0946, found 419.0948.

*4-(4-Fluorophenyl)-3-mesityl-2-methylquinazolin-3-ium tetrafluoroborate (**5c**)*.

147 mg, 78%, off-white solid: mp 238-239 °C; ^{1}H NMR (400 MHz, CD_3CN) δ: 8.51 (ddd, *J* = 15.4, 7.8, 1.2 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.99 (ddd, *J* = 15.6, 8.0, 0.8 Hz, 1H), 7.87 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.46-7.42 (m, 2H), 7.26-7.21 (m, 2H), 7.06 (s, 2H), 2.66 (s, 3H), 2.27 (s, 3H), 1.97 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 168.3, 166.7, 164.2, 156.5, 153.3, 143.6, 142.9, 135.2, 134.2, 132.7 (d, *J* = 55 Hz), 132.5, 131.4, 129.5, 124.6 (d, *J* = 3 Hz), 124.0, 116.9 (d, *J* = 23 Hz), 23.9, 21.0, 18.1 (2C); HRMS (ESI-TOF) calcd. For $C_{24}H_{22}FN_2$ $(M)^+$ m/z = 357.1767, found 357.1768.

*3-Mesityl-2-methyl-4-(p-tolyl)quinazolin-3-ium tetrafluoroborate (**5d**)*.

151 mg, 80%, off-white solid: mp 253-254 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.49 (ddd, *J* = 15.4, 7.6, 1.6 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 7.96 (ddd, *J* = 15.4, 8.0, 0.8 Hz, 1H), 7.83 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.32-7.27 (m, 4H), 7.05 (d, *J* = 0.8 Hz, 2H), 2.62 (s, 3H), 2.37 (s, 3H), 2.27 (s, 3H), 1.98 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 169.5, 156.3, 153.1, 144.1, 143.3

(2C), 142.8, 135.4, 134.3, 132.7, 131.3, 130.1, 129.8, 129.4, 125.5, 124.0, 23.9, 21.5, 21.0, 18.2 (2C); HRMS (ESI-TOF) calcd. For $C_{25}H_{25}N_2$ $(M)^+$ m/z = 353.2012, found 353.2018.

*6-Chloro-4-(2-chlorophenyl)-3-mesityl-2-methylquinazolin-3-ium tetrafluoroborate (**5e**)*.

154 mg, 73%, off-white solid: mp 317-318 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.46 (dd, *J* = 9.2, 2.0 Hz, 1H), 8.38 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 2.0 Hz, 1H), 7.66-7.58 (m, 2H), 7.41-7.37 (m, 1H), 7.27 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.12 (s, 1H), 7.00 (s, 1H), 2.69 (s, 3H), 2.26 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 165.8, 158.0, 152.1, 144.3, 143.0, 139.0, 135.3, 135.2, 134.8, 134.3, 133.1, 132.1, 131.9, 131.5, 131.3, 131.2, 129.8, 128.6, 126.8, 124.5, 24.1, 21.0, 18.4, 18.1; HRMS (ESI-TOF) calcd. For $C_{24}H_{21}{}^{35}Cl_2N_2$ $(M)^+$ m/z = 407.1082, found 407.1066; HRMS (ESI-TOF) calcd. For $C_{24}H_{21}{}^{37}Cl_2N_2$ $(M)^+$ m/z = 409.1052, found 409.1042.

*3-Mesityl-2-methyl-4-methylene-3,4-dihydroquinazoline (**6**)*.

60 mg, 51%, viscous oil: ^{1}H NMR (400 MHz, CD_3CN) δ 7.54 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.34 (td, *J* = 15.0, 1.6 Hz, 1H), 7.28 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.14 (td, *J* = 15.0, 1.6 Hz 1H), 7.00 (s, 2H), 4.52 (d, *J* = 2.0 Hz, 1H), 3.38 (d, *J* = 2.4 Hz, 1H), 2.32 (s, 3H), 2.14 (s, 6H), 1.88 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 154.1, 140.9, 140.7, 138.7, 135.4, 134.9, 130.3, 130.1, 125.6, 125.4, 122.9, 121.7, 80.3, 22.7, 21.0, 17.2 (2C); HRMS (ESI-TOF) calcd. For $C_{19}H_{21}N_2$ $(M+H)^+$ m/z = 277.1705, found 277.1697.

*3-([1,1'-Biphenyl]-2-yl)-2-methyl-4-phenylquinazolin-3-ium tetrafluoroborate (**7**)*.

123 mg, 76%, off-white solid: mp 305-306 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.44 (ddd, *J* = 15.6, 7.8, 1.2 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 7.89-7.83 (m, 2H), 7.68-7.63 (m, 3H), 7.53 (tt, *J* = 15.2, 1.2 Hz, 1H), 7.49-7.47 (m, 1H), 7.37-7.32 (m, 2H), 7.30-7.20 (m, 4H), 6.72-6.70 (m, 2H), 6.33 (dd, *J* = 7.4, 1.3 Hz, 1H), 2.96 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 169.3, 157.2, 152.5, 143.4, 137.9, 136.5, 136.3, 133.2, 133.0, 132.9, 132.2, 131.6, 130.5, 130.2, 130.1, 129.8,

129.6, 129.5, 129.2, 129.1, 128.0, 122.7, 25.9; HRMS (ESI-TOF) calcd. For $C_{27}H_{21}N_2$ $(M)^+$ m/z = 373.1705, found 373.1707.

*3-(2-Benzoylphenyl)-2-methylquinazolin-4(3H)-one (**8**)*.[17b]

104 mg, 77%, pale yellow solid: mp 161-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.71-7.58 (m, 3H), 7.56-7.51 (m, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.39-7.30 (m, 4H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.0, 162.0, 154.7, 147.5, 137.0, 136.6, 134.4, 133.2, 132.2, 130.7 (2C), 130.3, 129.6, 128.6, 128.3, 126.9, 126.8, 126.2, 120.4, 24.3; HRMS (ESI-TOF) calcd. For $C_{22}H_{17}N_2O_2$ $(M+H)^+$ m/z = 341.1290, found 341.1284.

*2-Cyclopropyl-3-mesityl-4-methoxy-4-phenyl-3,4-dihydroquinazoline (**9a**)*.

Compound **4d** was dissolved in anhydrous methanol (10 mL) under N_2. NaOMe (weighed in glove box) (60 mg, 5eq) was added in one portion. Resulting mixture was stirred for 12h and the excess methanol was removed under reduced pressure. Residue was diluted with DCM (40 mL) and washed with water (10 mL) and brine (10 mL). Removal of solvents and purification by silica gel column chromatography (5% to 10%-EA : Hexane) provided the **9a** (84 mg, 96%) as off-white solid. mp 139-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 4H), 7.06-6.97 (m, 4H), 6.87 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.76 (s, 1H), 6,42 (s, 1H), 2.99 (s, 3H), 2.57 (s, 3H), 2.10 (s, 3H), 1.64 (s, 3H), 1.33-1.25 (m, 1H), 1.17-1.12 (m, 1H), 1.00-0.94 (m, 1H), 0.71-0.64 (m, 1H), 0.55-0.49 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.3, 144.4, 140.6, 138.0, 137.6, 136.9, 136.8, 129.2, 129.0, 128.7, 128.6, 127.4, 126.1, 124.0, 123.1, 122.6, 93.1, 50.1, 20.6, 20.2, 18.9, 13.6, 8.8, 7.9; HRMS (ESI-TOF) calcd. For $C_{27}H_{29}N_2O$ $(M+H)^+$ m/z = 397.2280, found 397.2288.

*2-(3-Bromophenyl)-4-ethoxy-3,4-diphenyl-3,4-dihydroquinazoline (**9b**)***.**

The procedure is similar to that for **9a** except using **4o** and sodium ethoxide as reagents. 62 mg, 84%, brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.63 (m, 1H), 7.45-7.43 (m, 1H), 7.38-7.34 (m, 2H), 7.32-7.27 (m, 2H), 7.26-7.21 (m, 2H), 7.08-7.00 (m, 5H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.86-6.80 (m, 2H), 6.79-6.71 (m, 1H), 6.32-6.30 (d, *J* = 6.0 Hz, 1H), 3.77-3.69 (m, 1H), 3.28-3.20 (m, 1H), 1.27 (t, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.0, 144.2, 142.0, 140.9, 139.2, 132.2, 131.5, 130.5, 130.0, 129.1, 129.0, 128.5, 128.1, 127.9, 127.7, 127.1, 126.3, 125.5, 124.9, 124.6, 121.8, 91.6, 57.7, 15.0; HRMS (ESI-TOF) calcd. For $C_{28}H_{24}{}^{79}BrN_2O$ $(M+H)^+$ m/z = 483.1072, found 483.1059; HRMS (ESI-TOF) calcd. For $C_{19}H_{15}{}^{81}BrN_3O$ $(M+H)^+$ m/z = 485.1052, found 485.1044.

*6-Chloro-4-methoxy-2-methyl-4-phenyl-3-(o-tolyl)-3,4-dihydroquinazoline (**9c**)*.

In a dry 10 mL glass sealed tube, 2-toluenediazonium tetrafluoroborate (100 mg, 0.48 mmol) and 5-chloro-2-aminobenzophenone (123 mg, 0.53mmol, 1.1 eq.) were suspended in anhydrous acetonitrile (2 mL). The tube was sealed with a Teflon screw cap and heated in an oil bath (120 ^{o}C) for 5 h. After cooling, diethyl ether (50 mL) was added dropwise to the reaction mixture. The quinazolinium salt was obtained by filtration and the solid was then dissolved in methanol (6 mL) with NaOH (85 mg, 2.12 mmol). After stirring at room temperature for 12 h, solvents were removed under reduced pressure and the residue was extracted with DCM (30 mL x 2). Organic layer was washed with water (10 mL) and brine (10 mL). The organic layer was dried over $MgSO_4$. Removal of solvents and purification by silica gel column chromatography (5% to 10%-EA:Hexanes) provided **9c** (71mg, 92%) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 4H), 7.13 (ddd, *J* = 15.2, 8.2, 1.2 Hz, 1H), 7.07-7.03 (m, 3H), 7.02-6.99 (m, 2H), 6.84 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.80-6.79 (m, 1H), 3.12 (s, 3H), 1.93 (s, 3H), 1.68 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.2, 142.0, 141.4, 138.1, 136.2, 130.5, 130.0, 129.7, 129.2, 128.2, 128.1, 127.7, 126.5 (2C),

126.2, 125.0, 124.5, 91.3, 49.6, 23.6, 17.6; HRMS (ESI-TOF) calcd. For $C_{23}H_{22}{}^{35}ClN_2O$ $(M+H)^+$ m/z = 377.1421, found 377.1426; HRMS (ESI-TOF) calcd. For $C_{23}H_{22}{}^{37}ClN_2O$ $(M+H)^+$ m/z = 379.1391, found 379.1400.

ASSOCIATED CONTENT

Supporting Information

Spectra for all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.xxxxxx

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Notes

The authors declare no competing financial interest.

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