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Facial Synthesis of π-Conjugated Quinazoline-Substituted Ethenes from 2-Ethynylanilines and Benzonitriles under Transition-Metal-Free Conditions

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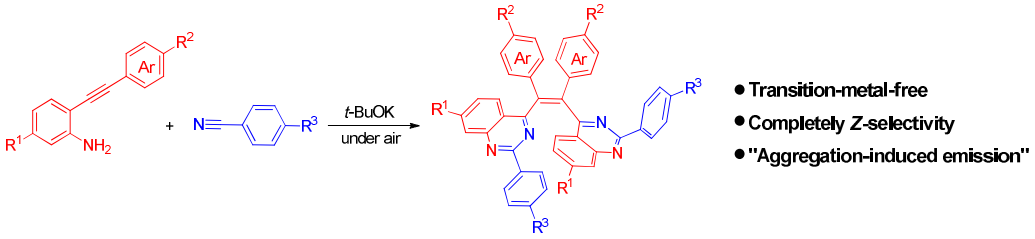


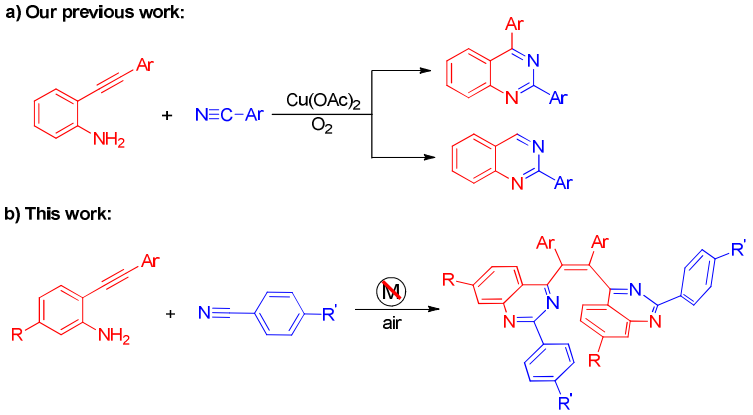
Abstract: A new transition-metal-free version for the synthesis of π-conjugated quinazoline-substituted ethene derivatives from readily available starting materials has been developed. Quinazoline-substituted ethenes were obtained in moderate to high yields with completely *Z*-selectivity, and the resulting quinazoline-substituted ethenes show typical aggregation-induced emission (AIE) properties.

INTRODUCTION

Conjugated organic π-systems containing arenes and heteroarenes have gained increasing interest owing to their potential utility in materials sciences.[1] Due to the

great value, the development of novel strategies for rapid synthesis of π-conjugated organic molecules are critically important. In this respect, the common methods for constructing π-conjugated compounds are transition-metal-catalyzed reactions,[2-6] such as well-known Heck coupling reaction,[7] Negishi coupling reaction,[8] Sonogashira coupling reaction[9] and Suzuki coupling reaction.[10] In recent years, transition-metal-free reactions are gradually recognized as an indispensable tool in organic synthesis,[11] which are not only less costly and more environmentally friendly but also can avoid potential transition metal contamination in the heterocyclic products. However, controlling chemoselectivity and regioselectivity in chemical reactions under transition-metal-free conditions still remains challenging, owing to the intrinsic mechanistic limitation.[11a] From environmental and economic perspectives, design and implementation of an efficient synthetic approach to construct π-conjugated molecules under transition-metal-free conditions is still highly desirable.

Scheme 1. Different Reaction Pathways of Benzonitriles with 2-Ethynylanilines



More recently, we have reported a copper-catalyzed process for the synthesis of substituted quinazolines from benzonitriles and 2-ethynylanilines under O_2 atmosphere (Scheme 1a).[12] Inspired by this previous work and in continuation of our

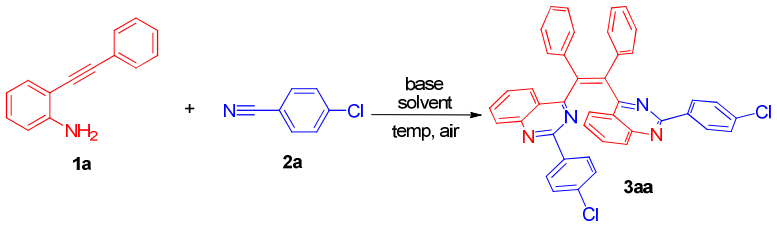
interest in the transformation of nitriles,[13] we herein report a transition-metal-free catalytic route for chemoselective synthesis of π-conjugated quinazoline-substituted ethenes from 2-ethynylanilines and benzonitriles (Scheme 1b), which exhibit typical aggregation-induced emission (AIE) properties[14] with adjustable emission color.

RESULTS AND DISCUSSION

Initially, 2-(phenylethynyl)aniline (**1a**) and 4-chlorobenzonitrile (**2a**) were chosen as the model substrates to optimize the reaction conditions (Table 1). Fortunately, the desired product (*Z*)-1,2-bis(2-(4-chlorophenyl)quinazolin-4-yl)-1,2-diphenylethene (**3aa**) was obtained in 7% yield with *t*-BuOK as base in toluene at 110 °C for 24 h (entry 1). Subsequent investigation on the effect of the reaction temperature proved that 120 °C was appropriate for this reaction (entries 1 vs 2-4). The initial substrate ratio for this transformation was also investigated, and the reaction with **1a**/**2a** (1:2) gave the best result (entries 1 vs 5-6). Then, various bases were tested, and trace amount of **3aa** was detected when other bases such as *t*-BuONa and *t*-BuOLi were employed (entries 7-8). No product was found with NEt_3, NaOH, K_2CO_3 and K_3PO_4 as bases (entries 9-12), where *t*-BuOK turned out to be the most appropriate. Large amount of unreacted starting material was recovered in all cases. Among the different solvents that we screened (entries 13-17), when DMA was used as solvent, although the yield was increased to 47% (entry 17), the intramolecular cyclization product 2-phenyl-1*H*-indole was also found. Gratifyingly, an improvement of the yield (73%) and a shorter reaction time (2 h) were observed for conducting the reaction with the combination of DMA and toluene (4:1) as solvent (entry 20). Further reduction of

t-BuOK to 2 equiv led to a sharp decrease in yield to 27% (entry 22). Finally, we attempted the reaction under a N_2 atmosphere, however, the corresponding product **3aa** could not be obtained (entry 23).

Table 1. Optimization of reaction conditions[a,b]



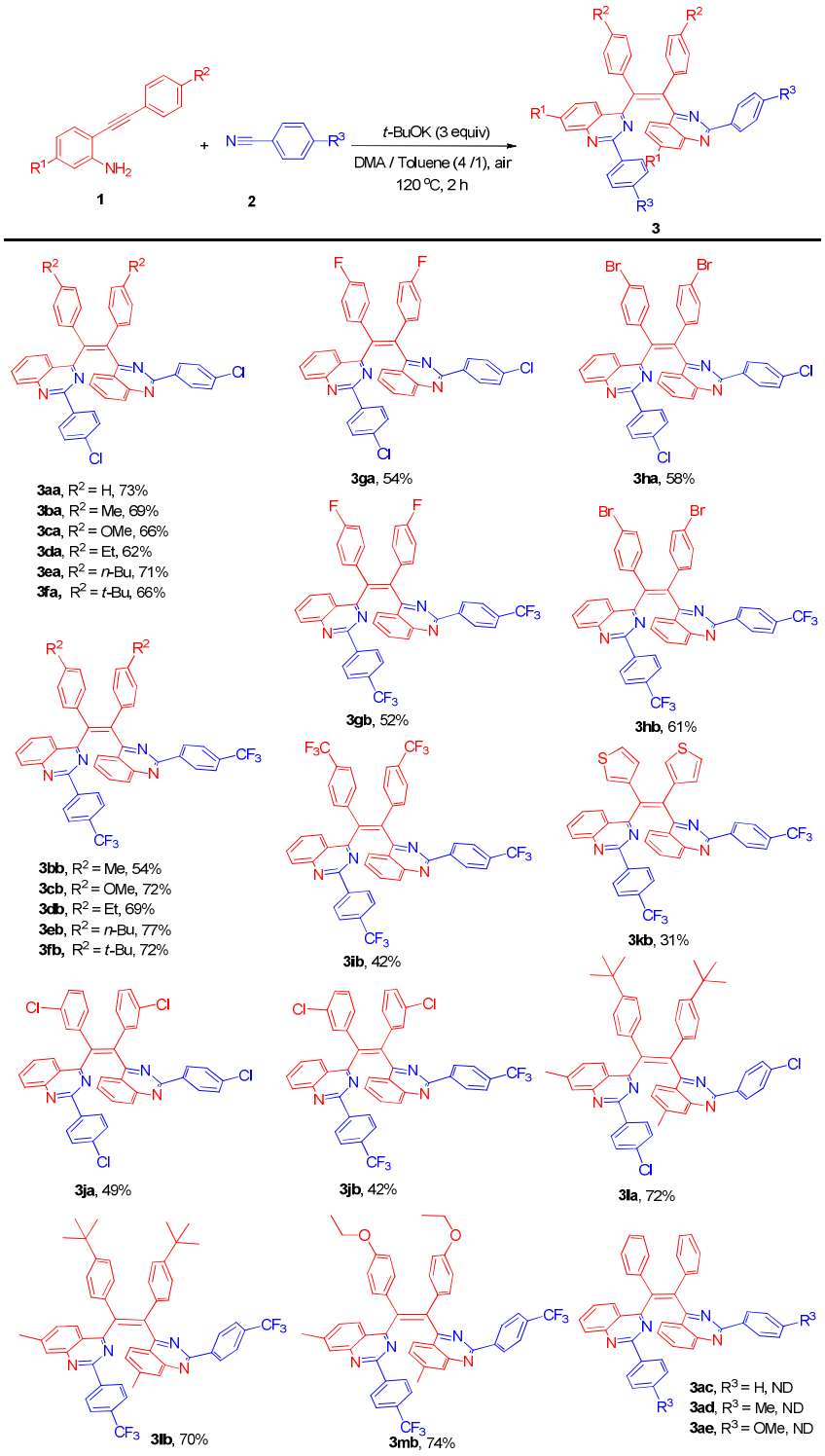
entry[a]	base (equiv)	solvent	temp (°C)	yield (%)[b]
1	*t*-BuOK (3)	toluene	110	7
2	*t*-BuOK (3)	toluene	100	trace
3	*t*-BuOK (3)	toluene	115	9
4	*t*-BuOK (3)	toluene	120	13
5[c]	*t*-BuOK (3)	toluene	120	6
6[d]	*t*-BuOK (3)	toluene	120	8
7	*t*-BuONa (3)	toluene	120	trace
8	*t*-BuOLi (3)	toluene	120	trace
9	NEt_3 (3)	toluene	120	ND
10	NaOH (3)	toluene	120	ND
11	K_2CO_3 (3)	toluene	120	ND
12	K_3PO_4 (3)	toluene	120	ND
13	*t*-BuOK (3)	1,4-dioxane	100	ND
14	*t*-BuOK (3)	MeCN	80	ND
15	*t*-BuOK (3)	DMSO	120	21
16	*t*-BuOK (3)	DMF	120	32
17	*t*-BuOK (3)	DMA	120	47
18	*t*-BuOK (3)	DMA/toluene (1/1)	120	53
19	*t*-BuOK (3)	DMA/toluene (2/1)	120	67
20	*t*-BuOK (3)	DMA/toluene (4/1)	120	74 (73)[e]
21	*t*-BuOK (3)	DMA/toluene (5/1)	120	52
22	*t*-BuOK (2)	DMA/toluene (4/1)	120	27
23[f]	*t*-BuOK (3)	DMA/toluene (4/1)	120	ND

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), base (3 equiv) and solvent (1 mL), under air, 24 h. [b]Isolated yields. ND = not detected. [c]**1a** (0.4 mmol), **2a** (0.2 mmol). [d]**1a** (0.2 mmol), **2a** (0.2 mmol). [e]2 h. [f]Under N_2 atmosphere.

With the optimal reaction conditions in hand, we then started to examine the scope

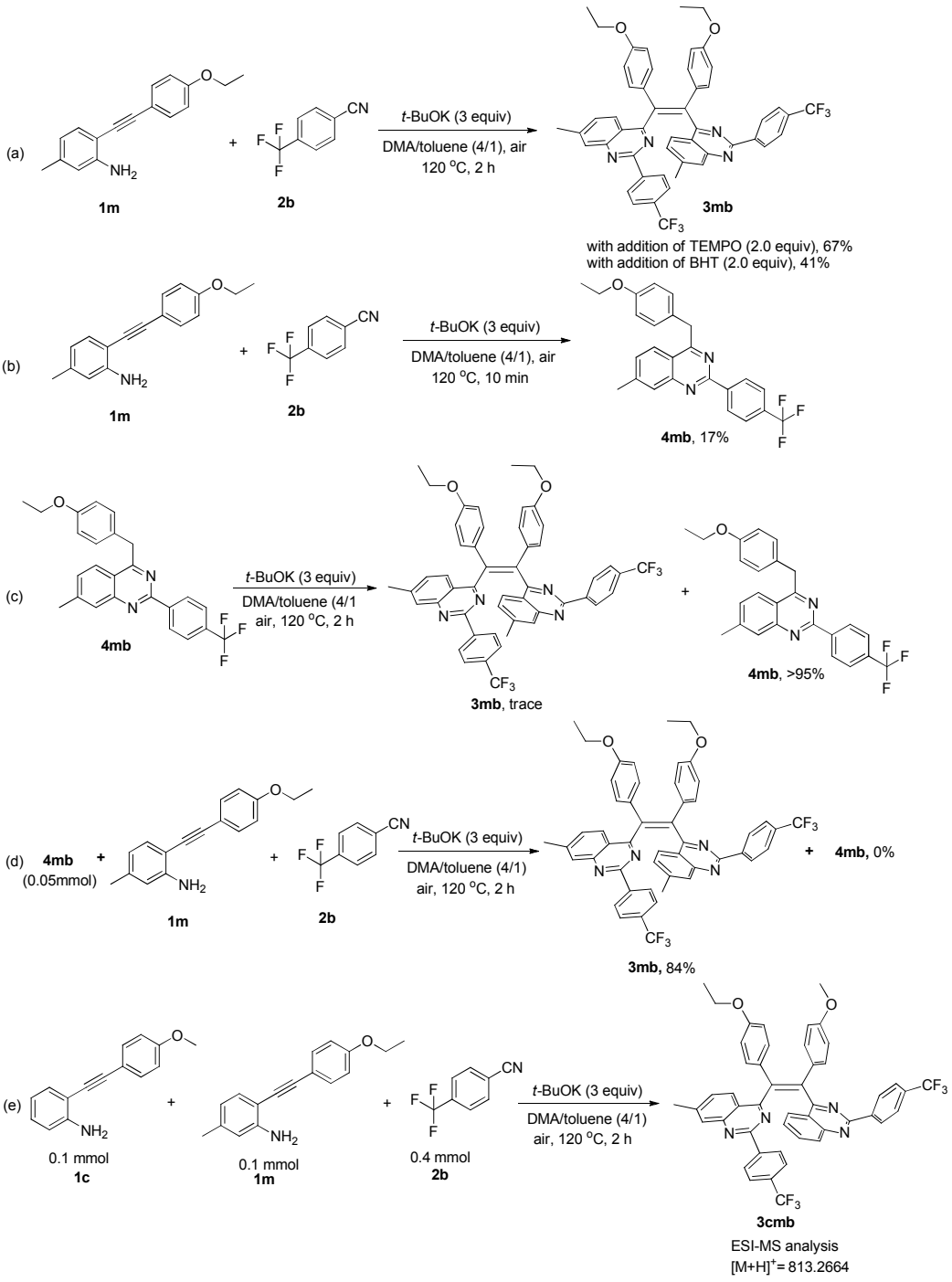
of quinazoline-substituted ethenes of this reaction (Scheme 2). It was observed that a series of selected 2-(phenylethynyl)anilines and benzonitriles were applied to the reaction, resulting in the generation of the desired products in moderate to good yields with complete (*Z*)-configuration. 2-(Phenylethynyl)anilines bearing electron-rich substituents at *para* position of benzene ring, such as -Me, -Et, -*n*-Bu, -*t*-Bu and -OMe groups, transferred to the target products **3ba-3fb** in 54-77% yields. The reactions of substrates **1g**, **1h** and **1i** possessing an electron-withdrawing group at *para*-position of aryl ring, including -F, -Br and -CF_3 groups, gave the desired products **3ga-3ib** in 42-61% yields. Obviously, 2-(phenylethynyl)anilines with an electron-donating group at the benzene ring furnished the desired products in higher yields than those bearing electron-withdrawing group. 2-(Phenylethynyl)aniline (**1j**) with a substituent at the *meta*-position reacted smoothly and converted to the products **3ja** and **3jb** in 42% and 49% yields. Delightfully, 2-(thiophen-3-ylethynyl)aniline (**1k**) was also transferred to the expected product **3kb** in 31% yield. In addition, the 2-(phenylethynyl)anilines bearing an electron-donating group at R^1 position, such as -CH_3, also provided the desired products **3la-3mb** in high yields. Unfortunately, unsubstituted benzonitrile or benzonitriles substituted with an electron-donating group failed to transformed to the corresponding products **3ac-3ae** under the optimized conditions. Other benzonitriles presumably are not conducive to the formation of intermediate Ⅱ (Scheme 4).

Scheme 2. Synthesis of Quinazoline-Substituted Ethenes 3[a,b]



[a]Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), *t*-BuOK (3 equiv) in 1 mL of DMA/toluene (4/1), under air, 120 °C, 2 h. [b]Isolated yields. ND = not detected.

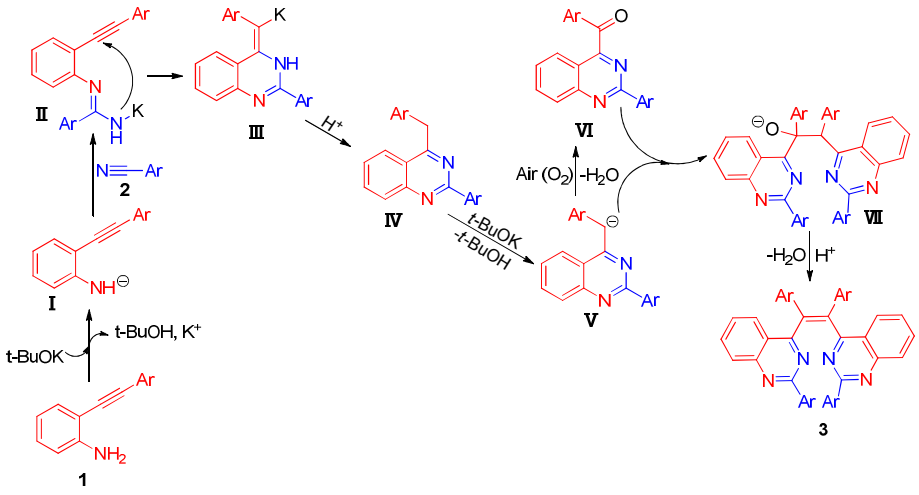
Scheme 3. Control Experiments



To gain more mechanistic insight into this transformation, some control experiments were carried out (Scheme 3). When 2.0 equiv of the radical scavengers such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) or BHT (3,5-di-*tert*-butyl-4-hydroxytoluene) were added to this system under standard

conditions, 67% and 41% yields of **3mb** were smoothly obtained (Scheme 3a), respectively, which suggested that this transformation might not undergo a radical process. The reaction of 2-((4-ethoxyphenyl)ethynyl)-5-methylaniline (**1m**) with 4-(trifluoromethyl)benzonitrile (**2b**) under the standard conditions for 10 min gave **4mb** in 17% yield (Scheme 3b). Subsequently, **4mb** was subjected to the optimized reaction conditions, and **3mb** was detected in a trace yield with large amounts of unreacted **4mb** was found (Scheme 3c). When 0.05 mmol of **4mb** was added to this system under standard conditions, an 84% yield of **3mb** was obtained and the species **4mb** was not detected (Scheme 3d). These results demonstrated that **4mb** should be an intermediate in the current reaction. In addition, **3cmb** ($[M+H]^+$ = 813.2664) could be detected in the reaction mixture by ESI-MS (Scheme 3e), suggesting that **3cmb** was formed through a cross-coupling reaction between compounds Ⅴ and Ⅳ (see Scheme 4).

Scheme 4. Plausible Mechanism



Based on the above results and previous reports,[12,15] we proposed a plausible reaction mechanism for this transformation detailed in Scheme 4. The initial step is

the deprotonation of **1** in the presence of *t*-BuOK to form anion intermediate **I** which could selectively attack the cyano group to give the amidine intermediate □. Then, intramolecular cyclization of alkynes and amidine produces intermediate □, which would undergo protonation to generate intermediate □. Further deprotonation of □ gives carbanion □ and subsequent oxidation affords □, followed by the attack of □ to give species □. Finally, elimination of one molecule of water leads to the desired product **3**. The benzene ring at the 2-position of quinazoline influences the stereoselectivity of the reaction, leading to stereoregular product configuration.[16]

More encouragingly, all these products exhibited a marked solid luminescence phenomenon. Obviously, the products with trifluoromethyl (-CF_3) substituents at the benzene ring show better luminescence intensity than which possessed chloro (-Cl) substituents on the benzene ring. To further evaluate the optical properties, **3bb**, **3cb**, **3fb**, and **3gb** were selected as the representatives, which were investigated by the UV-vis absorption and PL spectra in dilute THF solution (1×10^{-5} mol/L) and thin films. As shown in Table 2, all the selected compounds have the similar two absorption peaks (Figure 1A), with the dominant one at 260 nm and a shoulder at 340 nm in pure THF solution, which should be attributed to the π-π* transition of the conjugated skeleton and the intramolecular charge transfer (ICT) between donor and acceptor moieties. The molar absorptivities (ε) for **3bb**, **3cb**, **3fb**, and **3gb** were determined to be 48900, 73700, 47500 and 38200 $L\cdot mol^{-1}\cdot cm^{-1}$ at 340 nm, respectively. The absorption capacity for the compounds featuring the electron-donating substituents at the phenyl ring was better than those of the

electron-withdrawing aryl substituted ones. This trend might be due to the increased π-π* transition. As can be seen from their PL spectra (Figure 1B), the emission maximum for **3gb** is located at 470 nm, while **3bb** and **3fb** show similar emission bands at 493 nm. Compared to **3gb**, the emission maximum of **3cb** was red-shifted for 60 nm, indicating the stronger donor-acceptor interaction. These results show that substituents with different electronic properties results in different intramolecular charge transfer (ICT) effects. The fluorescence quantum yield ($\Phi_{F,film}$) values were determined to be 16.1%, 52.3%, 9.7% and 5.4% for **3bb**, **3cb**, **3fb** and **3gb** in thin films, respectively (Table 2). The quantum yields ($\Phi_{F,soln}$) of **3bb**, **3cb**, **3fb** and **3gb** in THF solutions (1×10^{-5} mol/L) were also measured to be 1.4%, 3.4%, 3.6%, and 3.3%, respectively. Therefore, the AIE factor ($\alpha_{AIE} = \Phi_{F,film}/\Phi_{F,soln}$) of **3bb**, **3cb**, **3fb** and **3gb** were calculated to be 11.5, 15.4, 2.7, and 1.6, respectively. These data clearly showed that **3bb**, **3cb**, **3fb** and **3gb** are AIE active molecules. Furthermore, the fluorescence lifetimes (τ_{film}) were also investigated and they were 3.18 ns, 8.12 ns, 2.85 ns and 1.84 ns for **3bb**, **3cb**, **3fb**, and **3gb**, respectively. Obviously, the molecules bearing a strong electron-donating group at aryl ring, such as the -OCH_3 group, exhibited stronger AIE effect than others.

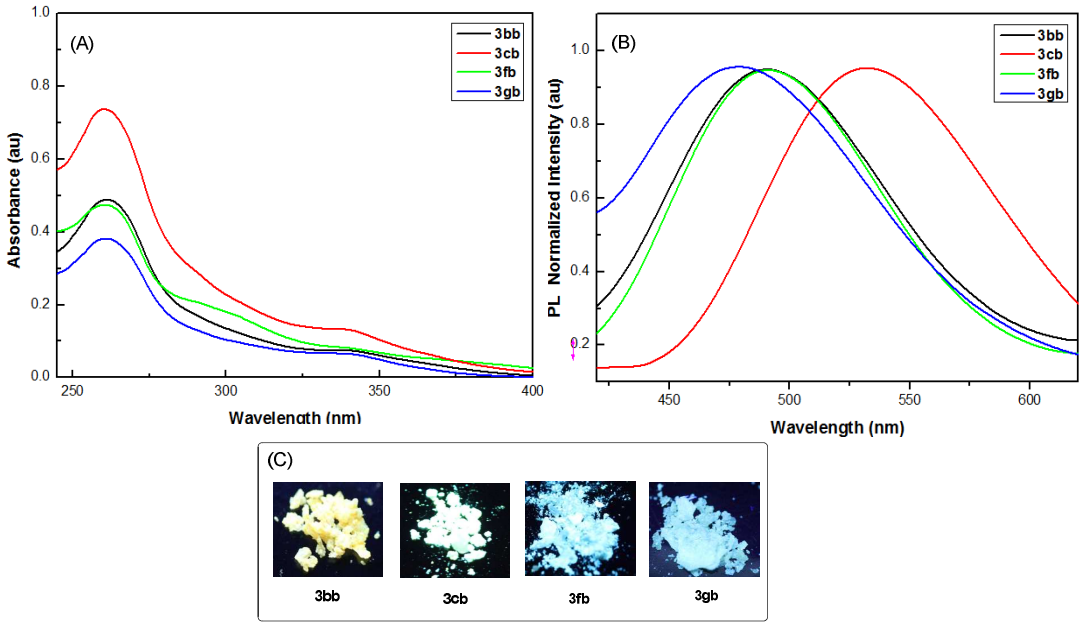


Figure 1. (A) The absorption spectra of **3bb**, **3cb**, **3fb**, and **3gb** in THF solutions (10^{-5} M). (B) The emission spectra of **3bb**, **3cb**, **3fb**, and **3gb** in thin films. (C) **3bb**, **3cb**, **3fb** and **3gb** taken under the irradiation of 365 nm light.

Table 2. Photophysical properties of 3bb, 3cb, 3fb, and 3gb

comp.	λ_{max} abs.[a] (nm)	ε[a] $(M \cdot cm)^{-1}$	λ_{max} em.[b] (nm)	$\Phi_{F,soln}$[a]	$\Phi_{F,film}$[b]	τ_{film}[b] (ns)	α_{AIE}[c]
3bb	261 342	48900	493	1.4%	16.1%	3.18	11.5
3cb	261 341	73700	530	3.4%	52.3%	8.12	15.4
3fb	260 340	47500	493	3.6%	9.7%	2.85	2.7
3gb	261 341	38200	470	3.3%	5.4%	1.84	1.6

[a]In THF solutions (10^{-5} M). [b]In thin films. [c]$\alpha_{AIE} = \Phi_{F,film}/\Phi_{F,soln}$

Density functional theory (DFT) calculation was carried out to help understand the relationship between electronic structures and photophysical properties (Figure 2). The lowest unoccupied molecular orbital (LUMO) of **3bb**, **3cb**, **3fb** and **3gb** exhibits a strong electron clouds distribution at the quinazoline ring (see Supporting Information for details). The electron distribution of the highest occupied molecular

orbital (HOMO) of **3bb** and **3fb** are located mainly on the phenyl unit and vinyl core, partly on the quinazoline ring. The electron density of the HOMO of **3gb** is almost spread to the whole molecule. In contrast to **3cb**, the spatial distributions of the HOMO and the LUMO are less overlapped, ascribed to the relatively strong ICT effect. These results are consistent with their expected intramolecular charge transfer process.

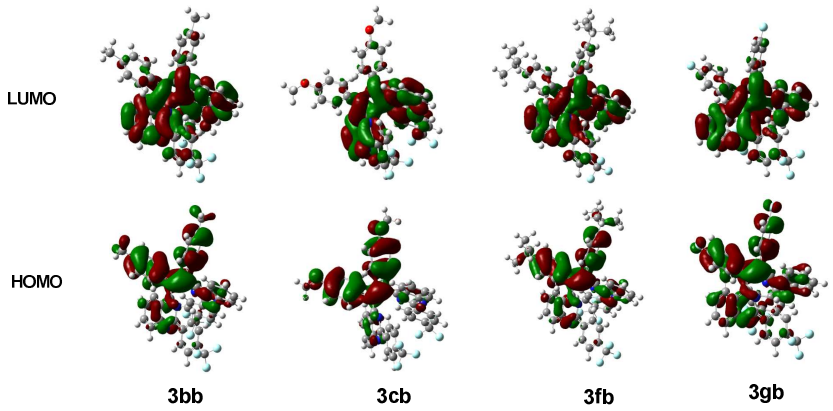


Figure 2. The optimal structure and HOMO and LUMO distributions of **3bb**, **3cb**, **3fb** and **3gb**

To further verify the AIE character, the fluorescence properties of **3bb**, **3cb**, **3fb** and **3gb** in water/THF mixtures of various ratios are shown in Figure 3. It is noteworthy that the changing trends in luminescence of these compounds were similar. As an example, the photoluminescence intensity of **3bb** were almost continued to decline until the water fraction (f_w) reached 90%, and a red shift of about 110 nm to 490 nm was also observed. This can be attributed to an intramolecular charge-transfer (ICT) process. Afterwards, with the increase of f_w from 90% to 99%, a significantly enhanced emission intensity could be detected, which should be associated with the formation of nanoaggregates, since increasing water content will reduce the ability to

dissolve, demonstrating AIE activity.

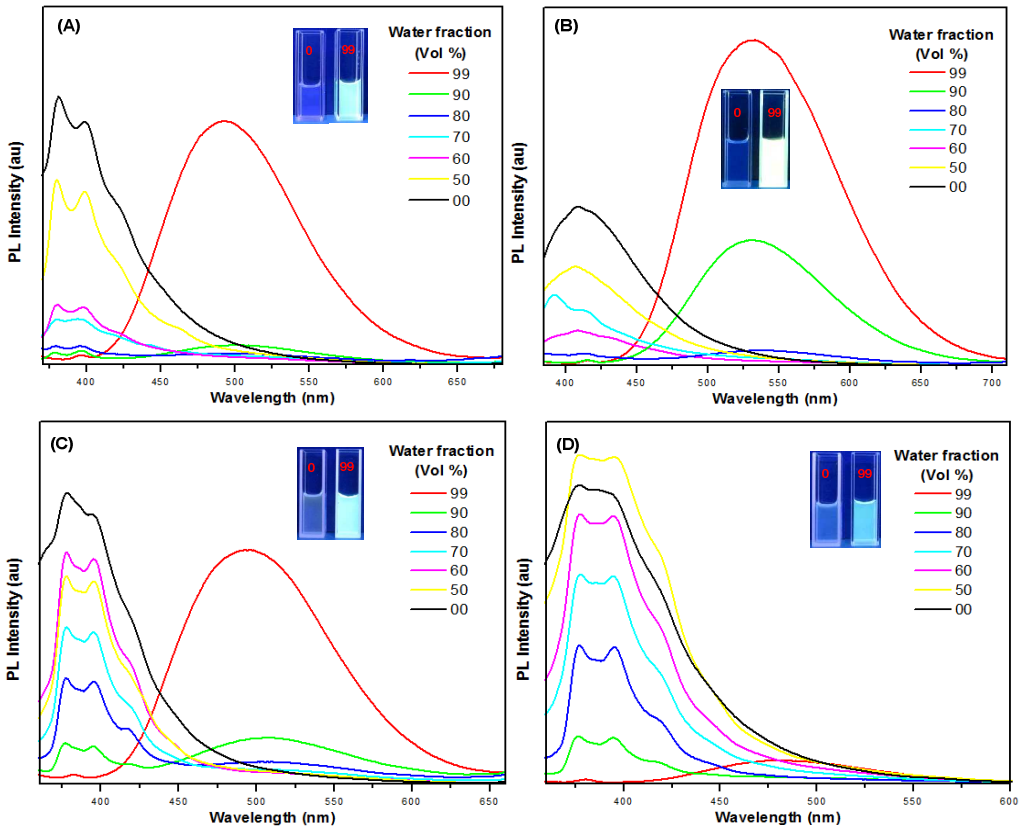


Figure 3. Fluorescence spectra of (A) **3bb**, (B) **3cb**, (C) **3fb** and (D) **3gb** in THF/water mixtures with different water content (10^{-5} mol/L).

To better explain and understand the AIE behaviors, single crystals of **3bb**, **3cb**, **3fb** and **3gb** were grown through their slow crystallization in absolute alcohol and analyzed by X-ray diffraction crystallography. Three kinds of aromatic ring in compounds **3** are named as ϕ_1, ϕ_2 and ϕ_3. The four molecules exhibited the folded *Z*-isomer (Figure 4), and the dihedral angle between the two phenyl groups (ϕ_1) in **3bb**, **3cb**, **3fb** and **3gb** were observed as 54.37°, 61.67°, 47.49° and 59.66°. The dihedral angles between the two quinazoline moieties (ϕ_2) were 70.04°, 69.55°, 62.60° and 69.50°, respectively. Moreover, the quinazoline moieties (ϕ_2) and the phenyl groups (ϕ_3) are located in an almost parallel manner. Thus, these molecules exhibited

a highly twisted configuration, and no obvious intramolecular interactions occurred.

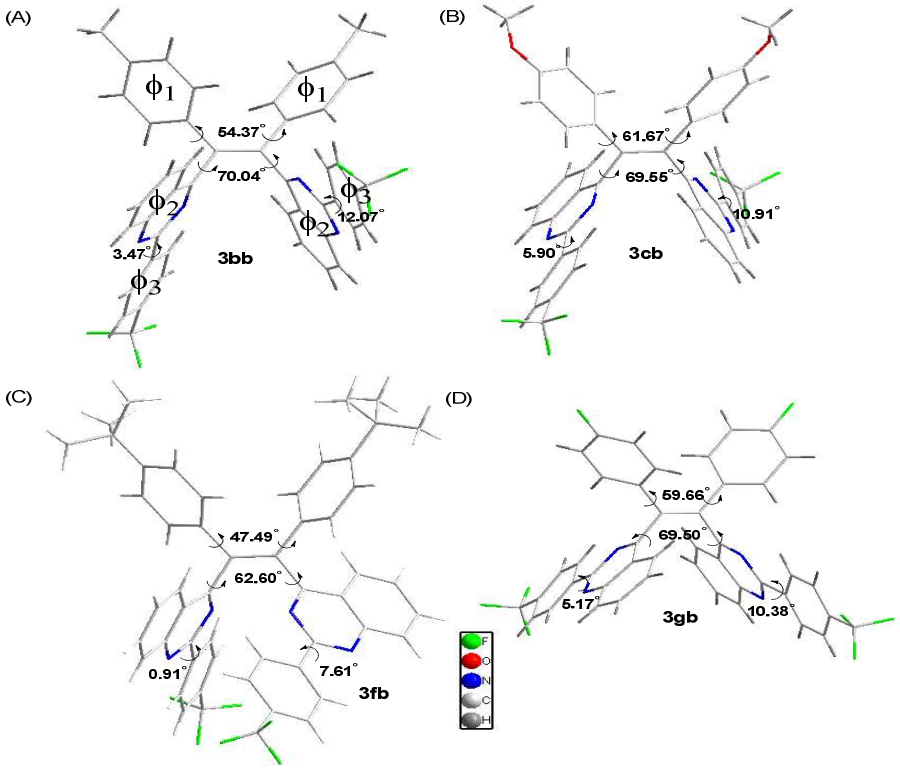


Figure 4. (A, B, C and D) Basic unit structure of the **3bb**, **3cb**, **3fb** and **3gb** crystal.

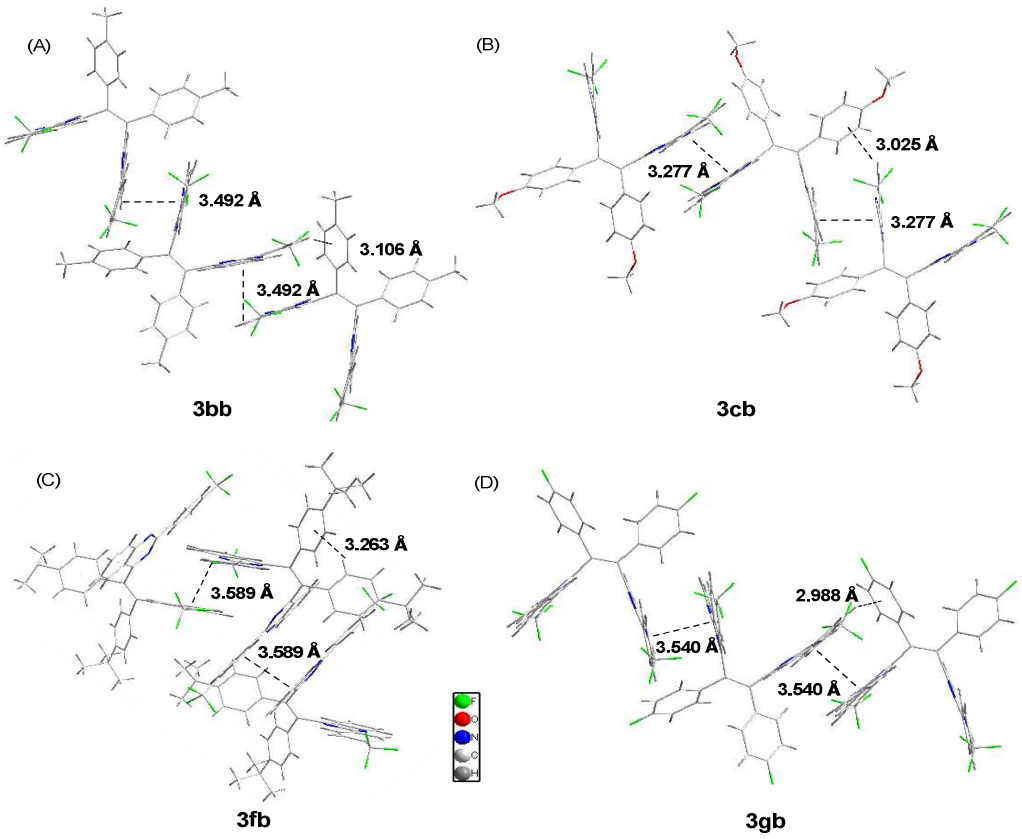


Figure 5. (A, B, C and D) C-H···π hydrogen bonds and π-π interactions with indicated distances (Å) between the adjacent molecules of **3bb**, **3cb**, **3fb** and **3gb** in the crystal state.

The intermolecular effects of crystals were also investigated. As shown in Figure 5, similar modes of intermolecular interactions were observed in the four molecules. Quinazoline moieties (ϕ_2) from two neighboring molecules in **3bb**, **3cb**, **3fb** and **3gb** are stacked in a roughly parallel manner and approximately half of their surfaces are overlapped. The distance between two overlapped quinazoline planes were in the range of 3.277-3.589 Å, indicating the presence of intermolecular π-π stacking interactions. In addition to π-π stacking interactions, multiple C-H···π hydrogen bonds from adjacent molecules were also found, and the shortest distances of these C-H···π bonds were in the range of 2.988-3.263 Å. So the intermolecular C-H···π and

π-π stacking interactions together help to rigidify the molecular conformation and lock the intramolecular rotations of the phenyl (ϕ_1) and quinazoline rings (ϕ_2) against the vinyl core.

CONCLUSION

In conclusion, we have successfully developed a flexible and rapid route to synthesize a series of π-conjugated quinazoline-substituted ethene derivatives from 2-ethynylanilines and benzonitriles. The new reaction tolerated many functional groups and obtained the corresponding products exhibiting typical AIE properties in moderate to high yields. The relationship between structure and luminescence properties of these compounds was investigated in detail.

EXPERIMENTAL SECTION

General Information: NMR spectra were obtained using a Bruker Avance 400 spectrometer (^{1}H at 400 MHz, and ^{13}C at 101 MHz). Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: δ 77.0 ppm). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a spectrometer. HRMS was obtained with a LCMS-IT-TOF mass spectrometer. Single crystal X-ray diffraction analyses were done on Bruker polycrystal X-ray diffraction and Rigaku Oxford Diffraction Supernova Dual Source. UV-vis absorption spectra were obtained using Shimadzu UV-2600 spectrophotometer.

Photoluminescence spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. Solution and thin film fluorescence quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus-QY. Fluorescence lifetimes were determined with a Hamamatsu C11367-11 Quantaurus-Tau time-resolved spectrometer. The ground-state geometries of **3bb**, **3cb**, **3fb** and **3gb** were optimized using the density function theory (DFT) method with B3LYP hybrid functional at the basis set level of 6-31G (d, p). All the calculations were performed using Gaussian 09 package. Benzonitriles were all commercial available. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

General Procedure for the Preparation of Compound 3: A mixture of 2-ethynylanilines **1** (0.2 mmol), nitriles **2** (0.4 mmol), *t*-BuOK (3 equiv) were added to 1 mL DMA/toluene (4:1, v/v). The mixture was stirred in a tube under open air at 120 ^{o}C for 2 h and monitored periodically by TLC. Upon completion, the reaction mixture was diluted with water (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water and brine, dried over Na_2SO_4 and filtered. The solvent was removed under vacuum. The residue was purified by flash column chromatography to afford quinazoline-substituted ethenes **3**.

General Procedure for the Preparation of Compound 1: a mixture of 2-iodoanilines (2 mmol), CuI (2 mol %), $PdCl_2(PPh_3)_2$ (1mol %), and Et_3N (5 mL) were added successively under N_2 and then alkynes (2.4 mmol) were added via syringe. The mixture was stirred at room temperature for 5 h and monitored

periodically by TLC. Upon completion, the reaction mixture was diluted with water (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water and brine, dried over Na_2SO_4 and filtered. The solvent was removed under vacuum. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate 10/1 v/v).

General Procedure for the Preparation of Compound 4mb: A mixture of 2-ethynylaniline **1m** (0.2 mmol), nitrile **2b** (0.4 mmol), *t*-BuOK (3 equiv) were added to 1 mL DMA/toluene (4:1, v/v). The mixture was stirred in a tube under open air at 120 ^oC for 10 min, the reaction mixture was diluted with water (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water and brine, dried over Na_2SO_4 and filtered. The solvent was removed under vacuum. The residue was purified by flash column chromatography to afford **4mb**.

(*Z*)-1,2-Bis(2-(4-chlorophenyl)quinazolin-4-yl)-1,2-diphenylethene (3aa): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 73% (47.8 mg) as a white solid: 210-212 ^oC. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.22-8.15 (m, 2H), 7.89-7.80 (m, 6H), 7.76-7.71 (m, 2H), 7.50-7.43 (m, 2H), 7.42-7.35 (m, 4H), 7.28-7.22 (m, 6H), 7.20-7.12 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 169.8, 158.8, 151.2, 141.9, 138.8, 136.3, 136.2, 133.4, 130.3, 129.5, 128.9, 128.6, 128.4, 128.3, 127.3, 126.9, 122.9. **IR** (KBr, cm^{-1}): 2930, 1722, 1539, 1337, 1038, 759. **HRMS** (ESI) m/z: calcd for $C_{42}H_{26}Cl_2N_4Na$ $[M + Na]^+$ 679.1427; found 679.1433.

(*Z*)-1,2-Bis(2-(4-chlorophenyl)quinazolin-4-yl)-1,2-di-*p*-tolylethene (3ba):

Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 69% (47.1 mg) as a white solid: 282-284 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.15 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.73-7.70 (m, 6H), 7.49-7.41 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 4H), 7.16-7.11 (m, 4H), 7.04 (d, *J* = 8.0 Hz, 4H), 2.31 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 170.2, 158.8, 151.1, 141.5, 138.1, 136.2, 136.1, 136.0, 133.3, 130.2, 129.5, 129.3, 128.9, 128.3, 127.4, 126.9, 123.0, 21.4. **IR** (KBr, cm^{-1}): 2928, 1723, 1543, 1345, 1038, 850. **HRMS** (ESI) m/z: calcd for $C_{44}H_{30}Cl_2N_4Na$ $[M + Na]^+$ 707.1740; found 707.1743.

(*Z*)-1,2-Bis(2-(4-chlorophenyl)quinazolin-4-yl)-1,2-bis(4-methoxyphenyl)ethene (3ca): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 66% (47.2 mg) as a white solid: 304-306 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.12 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.74 (dd, *J* = 13.4, 8.0 Hz, 6H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.28-7.24 (m, 4H), 7.12 (d, *J* = 8.4 Hz, 4H), 6.77 (d, *J* = 8.6 Hz, 4H), 3.78 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 170.4, 159.3, 158.8, 151.1, 140.8, 136.2, 133.3, 131.6, 131.5, 129.4, 128.9, 128.3, 127.4, 126.9, 123.1, 114.1, 55.2. **IR** (KBr, cm^{-1}): 2924, 1726, 1539, 1386, 1026, 756. **HRMS** (ESI) m/z: calcd for $C_{44}H_{31}Cl_2N_4O_2$ $[M + H]^+$ 717.1819; found 717.1824.

(*Z*)-1,2-Bis(2-(4-chlorophenyl)quinazolin-4-yl)-1,2-bis(4-ethylphenyl)ethene (3da): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 62% (44.1 mg) as a white solid: 262-264 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.16 (d, *J* = 8.3 Hz, 2H), 7.84-7.70 (m, 8H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 4H), 7.14 (d, *J* = 8.5 Hz, 4H), 7.05 (d, *J* = 8.0 Hz, 4H), 2.62 (q, *J*

= 7.6 Hz, 4H), 1.21 (t, *J* = 7.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 170.2, 158.8, 151.1, 144.3, 141.3, 136.3, 136.2, 136.1, 133.3, 130.2, 129.5, 128.8, 128.3, 128.0, 127.5, 126.8, 123.0, 28.6, 15.1. **IR** (KBr, cm^{-1}): 2923, 1729, 1539, 1386, 1082, 757. **HRMS** (ESI) m/z: calcd for $C_{46}H_{35}Cl_2N_4$ $[M + H]^+$ 713.2233; found 713.2239.

(*Z*)-1,2-Bis(4-butylphenyl)-1,2-bis(2-(4-chlorophenyl)quinazolin-4-yl)ethene (3ea): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 71% (54.5 mg) as a white solid: 238-239 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.53 (d, *J* = 8.3 Hz, 4H), 8.26 (d, *J* = 8.3 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.78 (t, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 6H), 7.07 (d, *J* = 7.8 Hz, 4H), 6.72 (d, *J* = 8.0 Hz, 4H), 2.30 (t, *J* = 7.6 Hz, 4H), 1.32-1.26 (m, 4H), 1.08-0.99 (m, 4H), 0.73 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 170.1, 159.2, 151.3, 142.5, 140.6, 136.7, 133.7, 130.0, 129.1. 128.8, 128.7, 128.1, 127.4, 126.7, 122.6, 35.1, 33.0, 22.0, 13.8. **IR** (KBr, cm^{-1}): 2929, 1722, 1538, 1343, 1037, 754. **HRMS** (ESI) m/z: calcd for $C_{50}H_{42}Cl_2N_4Na$ $[M + Na]^+$ 791.2679; found 791.2681.

(*Z*)-1,2-Bis(4-(*tert*-butyl)phenyl)-1,2-bis(2-(4-chlorophenyl)quinazolin-4-yl)ethene (3fa): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 66% (50.6 mg) as a white solid: 278-280 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.24 (d, *J* = 7.8 Hz, 2H), 7.90-7.82 (m, 6H), 7.73 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 2H), 7.51-7.46 (m, 2H), 7.36-7.30 (m, 4H), 7.29-7.25 (m, 4H), 7.22-7.17 (m, 4H), 1.32 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 170.0, 158.7, 151.2, 151.1, 141.0, 136.3, 136.2, 135.7, 133.2, 129.8, 129.5, 128.8, 128.3, 127.5, 126.7, 125.3, 122.9, 34.6, 31.2. **IR** (KBr, cm^{-1}): 2956, 1720, 1539, 1392, 1088, 757. **HRMS** (ESI)

m/z: calcd for $C_{50}H_{42}Cl_2N_4Na$ $[M + Na]^+$ 791.2679; found 791.2673.

(*Z*)-1,2-Bis(2-(4-chlorophenyl)quinazolin-4-yl)-1,2-bis(4-fluorophenyl)ethene (3ga): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 54% (37.4 mg) as a white solid: 234-236 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.12 (d, *J* = 8.3 Hz, 2H), 7.84 (t, *J* = 9.4 Hz, 6H), 7.78-7.69 (m, 2H), 7.50-7.46 (m, 2H), 7.39-7.29 (m, 4H), 7.17 (d, *J* = 8.6 Hz, 4H), 6.97 (t, *J* = 8.6 Hz, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 169.3, 162.7 (d, *J* = 248.4 Hz), 158.8, 151.3, 141.0, 136.5, 136.1, 134.5(d, *J* = 3.5 Hz), 133.6, 132.1 (d, *J* = 8.2 Hz), 1295, 129.1, 128.4, 127.0 (d, *J* = 28.5 Hz), 122.6, 116.0, 115.8. **IR** (KBr, cm^{-1}): 2930, 1723, 1596, 1388, 1038, 767. **HRMS** (ESI) m/z: calcd for $C_{42}H_{24}Cl_2F_2N_4Na$ $[M + Na]^+$ 715.1238; found 715.1233.

(*Z*)-1,2-Bis(4-bromophenyl)-1,2-bis(2-(4-chlorophenyl)quinazolin-4-yl)ethene (3ha): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 58% (47.2 mg) as a white solid: 308-309 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.09 (d, *J* = 8.2 Hz, 2H), 7.83 (dd, *J* = 12.4, 8.6 Hz, 6H), 7.75 (t, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 4H), 7.23 (d, *J* = 8.5 Hz, 4H), 7.17 (d, *J* = 8.6 Hz, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 168.9, 158.8, 151.3, 141.3, 137.3, 136.5, 136.0, 133.7, 132.1, 131.8, 129.5, 129.1, 128.4, 127.1, 126.9, 122.9, 122.5. **IR** (KBr, cm^{-1}): 2932, 1725, 1537, 1349, 1040, 752. **HRMS** (ESI) m/z: calcd for $C_{42}H_{24}Cl_2Br_2N_4Na$ $[M + Na]^+$ 834.9637; found 834.9652.

(*Z*)-1,2-Bis(3-chlorophenyl)-1,2-bis(2-(4-chlorophenyl)quinazolin-4-yl)ethene (3ja): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum

ether, yielding 49% (35.5 mg) as a white solid: 224-226 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.17 (d, *J* = 8.3 Hz, 2H), 7.89 (t, *J* = 8.5 Hz, 6H), 7.82-7.74 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 1.7 Hz, 2H), 7.33-7.29 (m, 4H), 7.28-7.19 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 168.5, 158.8, 151.3, 141.3, 139.9, 136.6, 136.0, 134.7, 133.7, 130.0, 129.9, 129.5, 129.1, 128.8, 128.4, 128.3, 127.2, 126.9, 122.4. **IR** (KBr, cm^{-1}): 2925, 1719, 1540, 1399, 1037, 757. **HRMS** (ESI) m/z: calcd for $C_{42}H_{24}Cl_4N_4Na$ $[M + Na]^+$ 747.0647; found 747.0652.

(*Z*)-1,2-Bis(4-(*tert*-butyl)phenyl)-1,2-bis(2-(4-chlorophenyl)-7-methylquinazolin-4-yl)ethene (3la): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 72% (57.3 mg) as a white solid: 283-285 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.00-7.94 (m, 6H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.48 (dd, *J* = 8.6, 1.8 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 4H), 7.24-7.18 (m, 8H), 2.42 (s, 6H), 1.28 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 169.0, 158.0, 151.1, 149.7, 140.1, 136.8, 136.6, 136.1, 135.6, 129.8, 129.5, 128.3, 126.3, 125.2, 122.6, 34.6, 31.3, 21.9. **IR** (KBr, cm^{-1}): 2925, 1723, 1539, 1402, 1036, 834. **HRMS** (ESI) m/z: calcd for $C_{52}H_{46}Cl_2N_4Na$ $[M + Na]^+$ 819.2992; found 819.2994.

(*Z*)-1,2-Di-*p*-tolyl-1,2-bis(2-(4-(trifluoromethyl)phenyl)quinazolin-4-yl)ethene (3bb): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 54% (40.6 mg) as a yellow solid: 270-271 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.75 (dd, *J* = 18.3, 8.3 Hz, 6H), 7.63 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 4H), 7.11 (d, *J* = 7.7 Hz, 4H), 6.92 (d, *J* = 7.9 Hz, 4H), 2.18 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) δ

170.4, 158.4, 151.1, 141.5, 138.3, 135.9, 133.5, 131.6 (q, J = 32.0 Hz), 130.2, 129.4, 129.1, 128.3, 127.4, 127,3, 125.01 (q, J = 3.7 Hz), 123.8 (q, J = 270.6 Hz), 123.3, 21.4. **IR** (KBr, cm^{-1}): 2922, 1729, 1538, 1321, 1078, 756. **HRMS** (ESI) m/z: calcd for $C_{46}H_{31}F_6N_4$ $[M + H]^+$ 753.2447; found 753.2451.

(*Z*)-1,2-Bis(4-methoxyphenyl)-1,2-bis(2-(4-(trifluoromethyl)phenyl)quinazolin-4-yl)ethene (3cb): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 72% (56.4 mg) as a white solid: 272-274 ^oC. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.16 (d, J = 8.2 Hz, 2H), 7.88 (t, J = 6.8 Hz, 6H), 7.79 (t, J = 7.6 Hz, 2H), 7.52 (t, J = 7.5 Hz, 2H), 7.39 (d, J = 8.2 Hz, 4H), 7.27 (d, J = 8.9 Hz, 4H), 6.78 (d, J = 8.7 Hz, 4H), 3.79 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 170., 159.4, 158.4, 151.1, 141.0, 140.9, 133.5, 133.2 (q, J = 32.0 Hz), 131.9, 131.4, 129.0, 128.3, 127.4, 127.3, 125.2 (q, J = 270.7 Hz), 123.3, 122.8 (q, J = 3.5 Hz), 114.1, 55.2. **IR** (KBr, cm^{-1}): 2922, 1733, 1507, 1320, 1067, 758. **HRMS** (ESI) m/z: calcd for $C_{46}H_{30}F_6N_4NaO_2$ $[M + Na]^+$ 807.2165; found 807.2166.

(*Z*)-1,2-Bis(4-ethylphenyl)-1,2-bis(2-(4-(trifluoromethyl)phenyl)quinazolin-4-yl)ethene (3db): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 69% (53.8 mg) as a white solid: 236-238 ^oC. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.21 (d, J = 8.3 Hz, 2H), 7.93 (d, J = 8.2 Hz, 4H), 7.86 (d, J = 8.4 Hz, 2H), 7.77 (t, J = 7.6 Hz, 2H), 7.52 (t, J = 7.6 Hz, 2H), 7.42 (d, J = 8.3 Hz, 4H), 7.27 (d, J = 8.1 Hz, 4H), 7.07 (d, J = 8.0 Hz, 4H), 2.63 (q, J = 7.6 Hz, 4H), 1.22 (t, J = 7.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 170.3, 158.3, 151.1, 144.4, 141.4, 141.0, 136.0, 133.4, 131.5(q, J = 32.1 Hz), 130.2, 129.0, 128.3,

128.0, 127.4, 127.3, 125.0 (q, J = 3.5 Hz), 124.0 (q, J = 268.3 Hz), 123.2, 28.5, 15.0. **IR** (KBr, cm^{-1}): 2925, 1726, 1540, 1321, 1068, 761. **HRMS** (ESI) m/z: calcd for $C_{48}H_{35}F_6N_4$ $[M + H]^+$ 781.2760; found 781.2762.

(*Z*)-1,2-Bis(4-butylphenyl)-1,2-bis(2-(4-(trifluoromethyl)phenyl)quinazolin-4-yl)ethene (3eb): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 77% (64.4 mg) as a white solid: 136-138 ^oC. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.20 (d, J = 8.2 Hz, 2H), 7.94 (d, J = 8.1 Hz, 4H), 7.87 (d, J = 8.4 Hz, 2H), 7.76 (t, J = 7.3 Hz, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.42 (d, J = 8.2 Hz, 4H), 7.27-7.23 (m, 4H), 7.05 (d, J = 8.0 Hz, 4H), 2.63-2.52 (m, 4H), 1.64-1.52 (m, 4H), 1.38-1.28 (m, 4H), 0.92 (t, J = 7.3 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 170.3, 158.3, 151.1, 143.2, 141.5, 141.0, 136.1, 133.5, 131.6 (q, J = 31.9 Hz), 130.1, 129.0, 128.6, 128.4, 127.4, 127.3, 125.01 (q, J = 3.8 Hz), 123.3, 122.8 (q, J = 270.5 Hz), 35.4, 33.2, 22.3, 14.0. **IR** (KBr, cm^{-1}): 2975, 1666, 1542, 1320, 1068, 758. **HRMS** (ESI) m/z: calcd for $C_{52}H_{43}F_6N_4$ $[M + H]^+$ 837.3386; found 837.3393.

(*Z*)-1,2-Bis(4-(*tert*-butyl)phenyl)-1,2-bis(2-(4-(trifluoromethyl)phenyl)quinazoli n-4-yl)ethene (3fb): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 72% (60.2 mg) as a white solid: 231-233 ^oC. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.26 (d, J = 8.2 Hz, 2H), 8.00 (d, J = 8.1 Hz, 4H), 7.87 (d, J = 8.4 Hz, 2H), 7.76 (t, J = 7.6 Hz, 2H), 7.53 (t, J = 7.6 Hz, 2H), 7.46 (d, J = 8.1 Hz, 4H), 7.29 (dd, J = 19.4, 8.3 Hz, 8H), 1.31 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 170.3, 158.4, 151.4, 151.1, 141.1, 135.7, 133.5, 131.6 (q, J = 31.9 Hz),

129.9, 129.0, 128.4, 127.6, 127.3, 125.4, 125.0 (d, J = 3.7 Hz), 123.2, 122.8 (q, J = 270.5 Hz), 34.7, 31.3. **IR** (KBr, cm^{-1}): 2958, 1727, 1541, 1320, 1067, 759. **HRMS** (ESI) m/z: calcd for $C_{52}H_{42}F_6N_4Na$ $[M + Na]^+$ 859.3206; found 859.3218.

(*Z*)-1,2-Bis(4-fluorophenyl)-1,2-bis(2-(4-(trifluoromethyl)phenyl)quinazolin-4-yl)ethene (3gb): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 52% (39.5 mg) as a white solid: 216-218 ^oC. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.16 (d, J = 8.2 Hz, 2H), 7.97 (d, J = 8.2 Hz, 4H), 7.89 (d, J = 8.4 Hz, 2H), 7.83-7.76 (m, 2H), 7.54 (t, J = 7.4 Hz, 2H), 7.44 (d, J = 8.3 Hz, 4H), 7.36 (dd, J = 8.7, 5.3 Hz, 4H), 6.98 (t, J = 8.6 Hz, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 169.4, 162.5 (d, J = 258.4 Hz), 158.4, 151.2, 141.1, 140.8, 134.5 (d, J = 3.5 Hz), 133.7, 132.0 (d, J = 9.3 Hz), 131.8 (q, J = 32.0 Hz), 129.3, 128.3, 127.5, 127.0, 125.2 (q, J = 3.6 Hz), 124.3 (q, J = 270..6 Hz), 122.8, 116.0 (d, J = 2.2 Hz). **IR** (KBr, cm^{-1}): 2924, 1604, 1543, 1320, 1067, 760. **HRMS** (ESI) m/z: calcd for $C_{44}H_{25}F_8N_4$ $[M + H]^+$ 761.1946; found 761.1954.

(*Z*)-1,2-Bis(4-bromophenyl)-1,2-bis(2-(4-(trifluoromethyl)phenyl)quinazolin-4-yl)ethene (3hb): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 61% (53.7 mg) as a white solid: 247-249 ^oC. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) δ 8.01 (d, J = 8.3 Hz, 2H), 7.85 (d, J = 8.1 Hz, 4H), 7.78 (d, J = 8.4 Hz, 2H), 7.69 (t, J = 7.4 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.3-7.2 (m, 8H), 7.13 (t, J = 6.5 Hz, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) δ 169.1, 158.4, 151.3, 141.4, 140.7, 137.2, 133.8, 132.2, 131.9 (q, J = 32.1 Hz), 131.7, 129.3, 128.3, 127.6, 126.9, 125.5 (q, J = 3.6 Hz), 124.4 (q, J = 270.0 Hz),123.0, 122.8. **IR** (KBr,

cm^{-1}): 2923, 1726, 1541, 1320, 1068, 760. **HRMS** (ESI) m/z: calcd for $C_{44}H_{25}Br_2F_6N_4$ $[M + H]^+$ 881.0345; found 881.0345.

(*Z*)-1,2-Bis(4-(trifluoromethyl)phenyl)-1,2-bis(2-(4-(trifluoromethyl)phenyl)quinazolin-4-yl)ethene (3ib): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 42% (36.1 mg) as a white solid: 212-214 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) δ 8.15 (d, *J* = 8.3 Hz, 2H), 8.05 (d, *J* = 8.1 Hz, 4H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.81 (t, *J* = 7.7 Hz, 2H), 7.60-7.44 (m, 14H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) δ 168.5, 158.4, 151.3, 141.9, 141.5, 140.6, 134.0, 131.9 (q, *J* =32.1 Hz), 130.9 (q, *J* =33.0 Hz),130.5, 129.4, 128.4, 127.8, 126.7, 125.9 (q, *J* = 3.7 Hz), 125.1 (q, *J* = 3.7 Hz), 124.0 (q, *J* =270.5 Hz), 123.3 (q, *J* =206.1 Hz), 122.5. **IR** (KBr, cm^{-1}): 2926, 1724, 1540, 1321, 1067, 758. **HRMS** (ESI) m/z: calcd for $C_{46}H_{24}F_{12}N_4Na$ $[M + Na]^+$ 883.1702; found 883.1710.

(*Z*)-1,2-Bis(3-chlorophenyl)-1,2-bis(2-(4-(trifluoromethyl)phenyl)quinazolin-4-yl)ethene (3jb): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 42% (33.2 mg) as a white solid: 259-261 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.09 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 4H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.71 (t, *J* = 7.3 Hz, 4H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 4H), 7.26 (s, 2H), 7.21-712 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 167.7, 157.4, 150.2, 140.4, 139.7, 138.8, 133.7, 132.9, 130.7 (q, *J* = 32.1), 129.0, 128.9, 128.2, 127.9, 127.3, 126.6, 125.8, 124.0 (q, *J* = 3.8 Hz), 123,7 (q, *J* = 270.0 Hz), 121.7. **IR** (KBr, cm^{-1}): 2922, 1722, 1543, 1320, 1069, 755. **HRMS** (ESI) m/z: calcd for $C_{44}H_{25}Cl_2F_6N_4$ $[M + H]^+$ 793.1355; found 793.1351.

(*Z*)-1,2-Di(thiophen-3-yl)-1,2-bis(2-(4-(trifluoromethyl)phenyl)quinazolin-4-yl) ethene (3kb): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 31% (22.8 mg) as a white solid: 224-226 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.12 (d, *J* = 8.3 Hz, 2H), 7.96-7.87 (m, 6H), 7.80 (t, *J* = 7.7 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 4H), 7.31 (s, 2H), 7.18 (s, 2H), 7.07 (d, *J* = 4.9 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) δ 169.5, 158.4, 151.1, 140.8, 139.3, 136.4, 133.7, 131.7 (q, *J* = 32.0 Hz) , 129.1, 128.4, 128.3, 127.4, 127.1, 127.0, 125.9, 125.1 (q, *J* = 3.4 Hz), 124.2 (q, *J* = 271.3 Hz), 123.1. **IR** (KBr, cm^{-1}): 2922, 1729, 1541, 1320, 1068, 756. **HRMS** (ESI) m/z: calcd for $C_{40}H_{22}F_6N_4NaS_2$ $[M + H]^+$ 759.1082; found 759.1073.

(*Z*)-1,2-Bis(4-(*tert*-butyl)phenyl)-1,2-bis(7-methyl-2-(4-(trifluoromethyl)phenyl) quinazolin-4-yl)ethene (3lb): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 70% (60.5 mg) as a white solid: 266-268 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.13 (d, *J* = 8.2 Hz, 4H), 8.01 (s, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.55 – 7.48 (m, 6H), 7.33 (d, *J* = 8.5 Hz, 4H), 7.25 (d, *J* = 8.6 Hz, 4H), 2.45 (s, 6H), 1.30 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 169.1, 157.6, 151.2, 149.7, 140.2, 137.3, 135.7, 135.6, 132.0 (q, *J* = 32.0 Hz), 129.8, 128.5, 128.3, 126.2,125.2, 125.0 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 270.5 Hz), 122.8, 34.6, 31.2, 21.9. **IR** (KBr, cm^{-1}): 2957, 1687, 1543, 1319, 1067, 755. **HRMS** (ESI) m/z: calcd for $C_{54}H_{47}F_6N_4$ $[M + H]^+$ 865.3699; found 865.3707.

(*Z*)-1,2-Bis(4-ethoxyphenyl)-1,2-bis(7-methyl-2-(4-(trifluoromethyl)phenyl)qui nazolin-4-yl)ethene (3mb): Purified *via* flash column chromatography with 40%

ethyl acetate/petroleum ether, yielding 74% (62.2 mg) as a white solid: 135-136 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.01 (d, *J* = 8.1 Hz, 4H), 7.96 (s, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 4H), 7.28 (d, *J* = 8.5 Hz, 4H), 6.77 (d, *J* = 8.5 Hz, 4H), 4.01 (q, *J* = 6.9 Hz, 4H), 2.46 (s, 6H), 1.40 (t, *J* = 6.9 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 169.6, 158.7, 157.7, 149.7, 141.3, 134.0, 137.4, 135.7, 131.6, 131.2, 131.0 (q, *J* = 32.4 Hz), 128.6, 128.3, 126.1, 125.5, 124.9 (q, *J* = 3.6 Hz), 124.2 (q, *J* = 270.7 Hz), 123.0, 114.5, 21.9, 14.8. **IR** (KBr, cm^{-1}): 2923, 1723, 1545, 1319, 1029, 755. **HRMS** (ESI) m/z: calcd for $C_{50}H_{38}F_6N_4NaO_2$ $[M + Na]^+$ 863.2791; found 863.2805.

(*Z*)-4-(1-(4-ethoxyphenyl)-2-(4-methoxyphenyl)-2-(2-(4-(trifluoromethyl)phenyl)quinazolin-4-yl)vinyl)-7-methyl-2-(4-(trifluoromethyl)phenyl)quinazoline (3cmb): **HRMS** (ESI) m/z: calcd for $C_{48}H_{35}F_6N_4O_2$ $[M + H]^+$ 813.2659; found 813.2664.

4-(4-Ethoxybenzyl)-6-methyl-2-(4-(trifluoromethyl)phenyl)quinazoline (4mb): Purified *via* flash column chromatography with 40% ethyl acetate/petroleum ether, yielding 17% (14.3 mg) as a yellow solid: 107-109 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, δ ppm) 8.72 (d, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.89 (s, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.65 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.57 (s, 2H), 3.97 (d, *J* = 7.0 Hz, 2H), 2.52 (s, 3H), 1.36 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ ppm) 169.1, 158.1, 157.8, 149.6, 141.7, 137.7, 135.9, 131.8 (q, *J* = 31.7. Hz), 129.9, 129.7, 129.2, 128.7, 125.3 (q, *J* = 3.8. Hz), 124.3 (q, *J* = 270.5 Hz), 123.9, 122.7, 114.7, 63.4, 40.4, 22.0, 14.8. **IR** (KBr, cm^{-1}): 2928, 1719,

1508, 1321, 1121, 828. **HRMS** (ESI) m/z: calcd for $C_{25}H_{22}F_3N_2O$ $[M + H]^+$ 423.1679; found 423.1683.

ASSOCIATED CONTENT

Supporting Information

Copies of NMR spectra for all compounds, X-ray crystallographic data for **3bb**, **3cb**, **3fb** and **3gb**, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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