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Full Paper

Synthesis of Quinolinium Salts from *N*-Substituted Anilines, Aldehydes, Alkynes, and Acid: Theoretical Understanding of the Mechanism and Regioselectivity

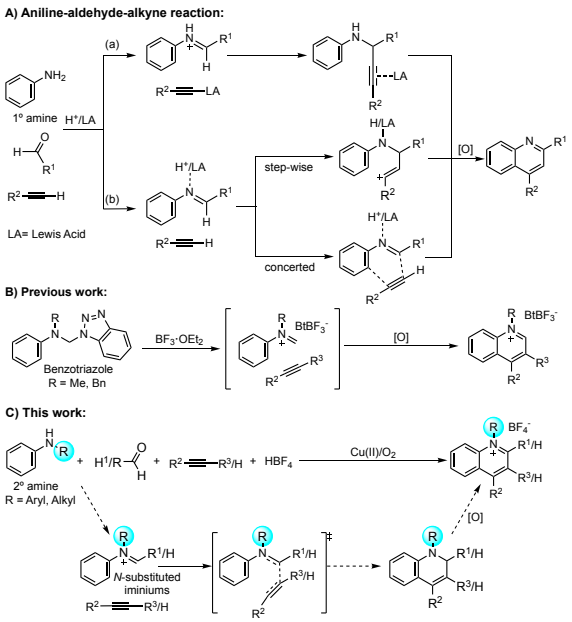
Lin-Chieh Cheng‡[a], Wei-Chen Chen‡[a], Rajagopal Santhoshkumar[a], Tzu-Hsuan Chao[b], Mu-Jeng Cheng*[b], and Chien-Hong Cheng*[a,c]

Abstract: Secondary anilines were first utilized in the four-component coupling of aniline, aldehyde, alkyne, and acid to synthesize a variety of *N*-substituted quinolinium salts. This method was carried out under mild reaction conditions and exhibited excellent chemo- and regioselectivities. DFT calculation was performed to analyze the cyclization step, where the interaction/distortion model provided better insight into the singular selectivity of terminal/internal alkynes in reaction.

Introduction

N-heteroaromatic cations are essential skeletons found in many bioactive molecules, pharmaceuticals, and material applications.[1] In particular, quinolinium salts are notable due to their bioactivity in medical researches.[2] The easily convertible electrophilic 2 and 4 positions of the arene promise quinolinium salts an useful precursor in the synthesis of *N*-heterocyclic derivatives.[3] Due to its strong oxidizing ability at singlet excited state and long fluorescence lifetimes,[4] quinolinium salts serve as potent photoredox catalysts, which have been utilized in benzene C–H functionalizations and benzylic cleavage/cyclization reactions.[5] Although the basic and nucleophilic nitrogen of quinolines provides direct access to quinoliniums with electrophiles,[6] this strategy limits the substrate scopes to *N*-alkyl products. In 1950s, Pilyugin first developed a series of cascade reactions of diarylamine, formaldehyde, acetone, and acid to access *N*-aryl quinolinium salts,[7] which addressed the disadvantages of substitution approach. However, these methods suffered from harsh reaction conditions and offered poor product yields. Except for Pilyugin's works, report of synthesis and application of *N*-aryl quinolinium salts is rare.[8]

In contrast to lack of synthetic methods for quinolinium salts, several approaches have been developed to synthesize quinolines.[9] A well-established route to acquire multi-substituted quinolines is through Bronsted/Lewis acid activated aniline-aldehyde-alkyne reaction (A^3 reaction)[10] (Scheme 1A). There are generally two different pathways involved in the reaction. In one path, a propargylamine generated from nucleophilic addition of terminal alkyne to imine undergoes cyclization and oxidation to afford quinoline motif.[11] Another path is a variant of Povarov reaction with acetylenes used as dienophiles to cyclize with aromatic aldimines.[12] In this path, the hypothetical mechanism of [4+2] cyclization reactions have been proposed through a concerted process or a step-wise manner, but the real mechanism remained unclear. Though synthesis of quinoline from imines and alkynes are widely-known, there has been only one report, which proposed an *in situ* formed *N*-substituted iminium ions reacting with alkynes. In 1998, Katritzky utilized benzotriazole derivatives as starting materials to synthesize the quinolinium salts (Scheme 1B),[13] but this method needed the prefunctionalization of secondary anilines and only offered *N*-alkyl products with low atom-economy. Based upon this background and our continued interest in quaternary ammonium salt synthesis,[14] we are highly interested in developing a rapid and efficient method to furnish *N*-aryl and -alkyl quinolinium salts. Herein, we describe a four-component coupling of aniline, aldehyde, alkyne, and acid to synthesize *N*-substituted quinolinium salts. To better explain the mechanism and regioselectivity, theoretical studies were carried out for the key cyclization step.



Scheme 1. Strategies for the synthesis of quinolines and quinoliniums

Results and Discussion

We commenced our investigation by the reaction of aniline **1a**, phenylacetylene **2a**, paraformaldehyde **3a**, and HBF_4 in acetonitrile under an oxygen balloon at room temperature for 1 h. The reaction produced quinolinium salt **4aa** in 43% yield and tertiary aniline **5a** in 48% yield (Table 1, entry 1). The formation of tertiary aniline **5a** is consistent with previous research that imines could act as hydrogen acceptor.[11a, 15] In this case, iminium ion **I-**

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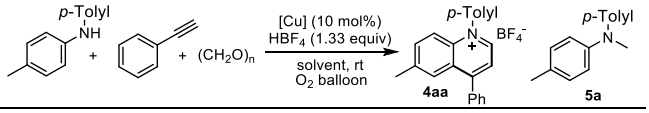
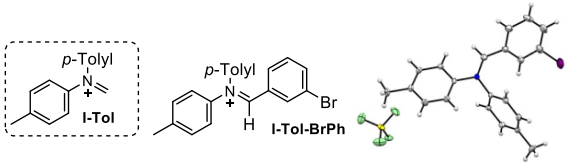
Tol played the role in oxidizing hydroquinoline to form quinolinium salts. Though isolation of **I-Tol** was unsuccessful due to the short lifetime, fortunately, we separated **I-Tol-BrPh**[16] by recrystallization, which confirmed the iminium ion produced *in situ*. In order to prevent depletion of reactive intermediate, catalysts featuring strong oxidizing efficiency were considered.

Table 1. Optimization studies[a][b]



Entry	[Cu]	Solvent	Yield (%)
1	-	CH_3CN	43
2	$CuBF_4{\cdot}6H_2O$	CH_3CN	52
3	$Cu(OTf)_2$	CH_3CN	54
4	$Cu(OAc)_2$	CH_3CN	56
5	$CuSO_4$	CH_3CN	69
6	$CuCl_2$	CH_3CN	87
7	CuCl	CH_3CN	81
8	CuI	CH_3CN	49
9	$CuCl_2$	CH_3NO_2	72
10	$CuCl_2$	AcOH	68
11	$CuCl_2$	$CHCl_3$	80
12	$CuCl_2$	DCE	71
13[c]	$CuCl_2$	CH_3CN	52
14[d]	$CuCl_2$	CH_3CN	93

[a] Unless otherwise mentioned, all reactions were carried out with aniline **1a** (0.30 mmol), alkyne **2a** (0.30 mmol), paraformaldehyde **3a** (0.40 mmol), cat. [Cu] (0.030 mmol), HBF_4 (0.40 mmol, 50% in water), and solvent (3.0 mL) at rt under an O_2 balloon. [b] Isolated yields. [c] Reaction under an air balloon. [d] Reaction with alkyne **2a** (0.40 mmol) and CH_3CN (2.0 mL). AcOH = acetic acid, DCE = 1,2-dichloroethane.



Copper reagent, which has been employed in aerobic dehydrogenation reaction,[17] was applied to this system. Different copper salts were tested (Table 1, entries 2–8), in which $CuCl_2$ provided **4aa** in 87% yield (Table 1, entry 6). When the reaction was performed in other solvents, such as CH_3NO_2, CH_3COOH, $CHCl_3$, and DCE, there was no improvement in the efficiency (Table 1, entries 9–12). The reaction in the presence of an air balloon was not effective (Table 1, entry 13). Increasing alkyne **2a** to 0.40 mmol in 0.15 M acetonitrile showed the best performance (Table 1, entry 14).

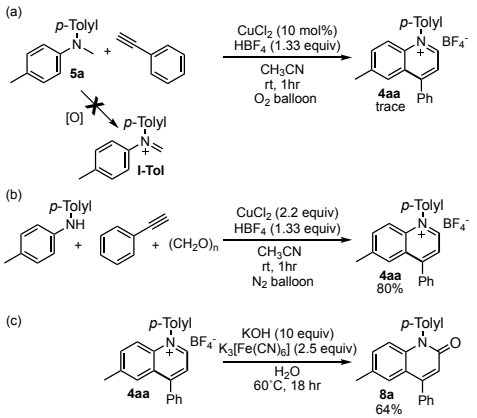
With the optimized conditions, we explored the scope of the reaction. The results revealed that a variety of *N*-substituted anilines, alkynes, and aldehydes were viable in the transformation in good to excellent yields (Scheme 2). Different substituted *N*-aryl anilines **1a**-**d** underwent tandem cyclization to afford *N*-aryl quinolinium salts **4aa**-**da**. The structure of **4aa** was unambiguously confirmed by X-ray crystallographic analysis. It is noteworthy that unsymmetrical diarylamine **1e** furnished product **4ea** with a chemo-isomeric ratio of 69:31. The results illustrated that the electron-rich aryl group favored the reaction. In addition, *N*-methyl anilines with electron donating (**1g**, **1l**), halogen (**1i**-**j**), and electron withdrawing (**1k**) substitution proceeded smoothly to yield *N*-alkyl products **4fa**-**la**. *N*-heterocyclic compounds, indoline **1m** and tetrahydroquinoline **1n**, participated in the reaction to build multicyclic quinolinium motifs **4ma**-**na** in good yields. *N*-Benzyl aniline **1o** is also an effective reagent in the reaction.

Regarding alkyne substrates, both terminal and internal acetylenes proceeded in the reaction with high efficacy to provide single regioisomeric products. The regioselectivity of the quinolinium salts **4aa**-**ay** is consistent with preceding reports.[18] Phenylacetylenes with substituents at *para* (**2b**-**2g**), *meta* (**2h**-**2i**), and *ortho* (**2j**) positions all underwent the reaction efficiently. Sterically hindered tri-substituted substrate **2k** also participated in the reaction affording **4ak** in 91% yield. Alkynes with thiophene **2l** and naphthyl **2m** groups delivered products **4al**-**am** in good yields. Aliphatic alkynes **2n**-**o** were tolerated well to provide salt products **4an**-**ao**. Unfortunately, methyl propiolate was incapable to react in our conditions. Symmetrical alkynes, 3-hexyne **2p** and diphenylacetylenes **2q**-**s** could be used in the reaction but gave decreased yields. This was probably due to evenly distributed electronic structure which slower the cyclization step and allowed side reaction. Unsymmetrical alkynes **2t**-**y** were also examined to give 3-alkyl quinolinium salts **4at**-**av**. Surprisingly, less nucleophilic ynone **2w** and phenyl propiolates **2x**-**y** could also be functionalized to afford desired salts **4aw**-**ay**. The structures of **4aw**-**ay** were confirmed by either X-ray crystallographic analysis or NOE nuclear magnetic resonance spectroscopic analysis (see supporting information).

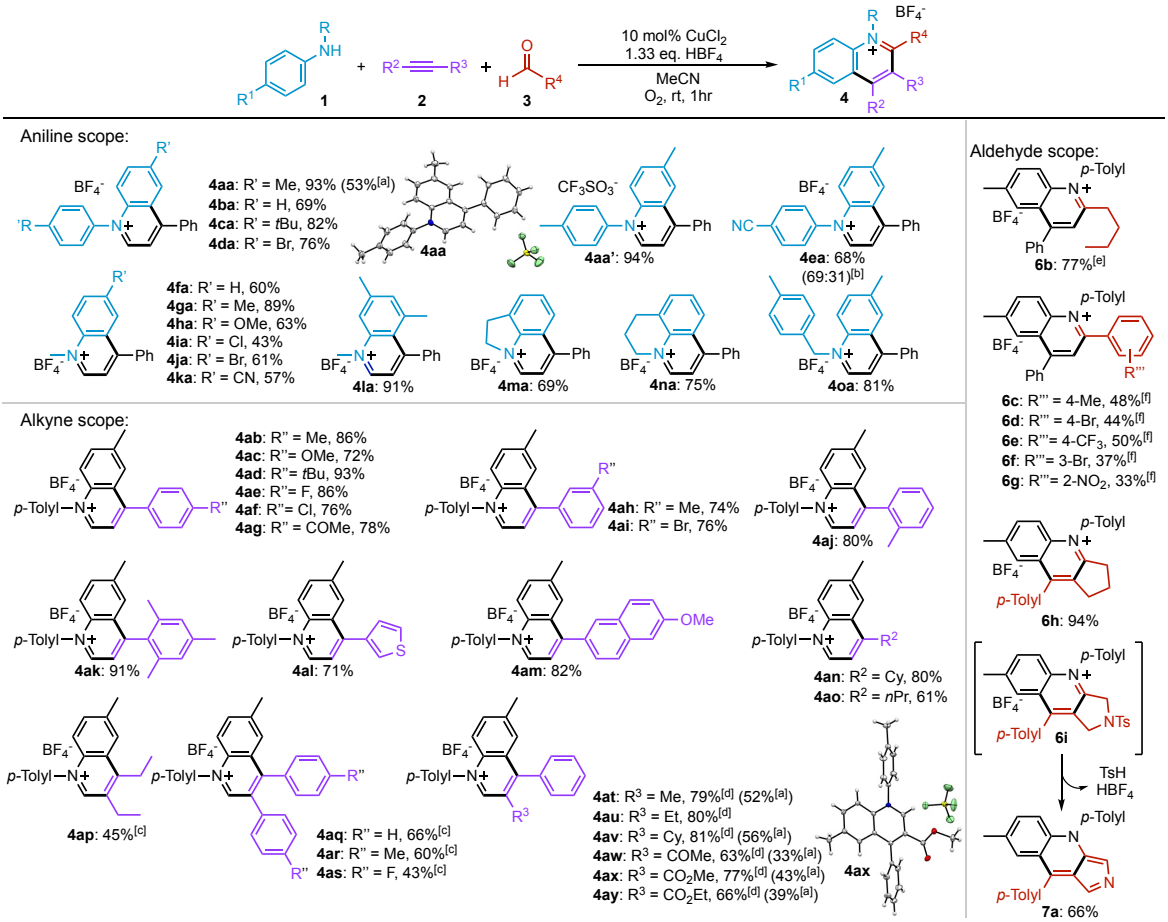
As for aldehydes, the present reaction was not limited to formaldehyde; it is also suitable for aliphatic and aryl aldehydes. Valeraldehyde **3b** was able to yield salt product **6b**. Aromatic aldehydes **3c**-**g** required higher temperature and longer time to conquer the steric hindrance in the condensation step. Disappointingly, these substrates offered quinolinium salts **6c**-**g** in low yields. Ynal **3h** combining alkyne and aldehyde groups in one reagent directly furnished tricyclic product **6h**. *N*-tethered ynal **3i** was also examined, but produced quinoline **7a**. This product might result from salt **6i** through elimination reaction of tosyl group,[19] but the exact mechanism was unclear.

Furthermore, with hydrohalic acid and acetic acid, the isolation of quinolinium salts with these anions was unsuccessful. To our delight, CF_3SO_3H provided a good complementary ion and triflate salt **4aa'** could be isolated in 94% yield.

To elucidate the role of copper catalyst, we carried out several control experiments. The moderate product yields of internal alkynes **2t**-**y** under condition without copper catalyst preclude alkyne complexation by Cu(II) (Scheme 2, condition a). Previously, $CuCl_2$ have been reported to oxidize *N*,*N*-dimethylanilines under aerobic condition.[17d] To test the possibility, tertiary amine **5a** was treated with **2a** in the presence of $CuCl_2$ (Scheme 3a). Only a trace amount of **4aa** was observed in the reaction, indicating **5a** could not be reactivated to iminium ion **I-Tol** under our conditions. In addition, stoichiometric $CuCl_2$ was used under condition without oxygen, and gave good yield (Scheme 3b). This confirmed the $CuCl_2$ could compete with iminium ions in the oxidation step.



Scheme 3. (a) Reaction of tertiary amine with Cu(II). (b) Reaction with stoichiometric Cu(II) under N_2. (c) Synthesis of quinolinone.

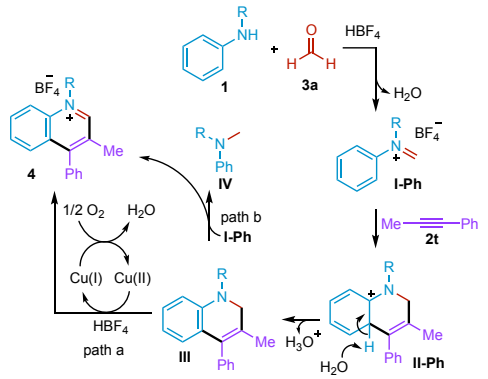


Scheme 2. Scope of the reaction. Conditions: anilines **1** (0.30 mmol), alkyne **2** (0.40 mmol), paraformaldehyde **3a** (0.40 mmol), $CuCl_2$ (0.03 mmol), HBF_4 (0.40 mmol, 50% in water) and MeCN (2.0 mL) at rt under O_2 balloon for 1 h. Yields of isolated products are given. [a] without $CuCl_2$. [b] Regioisomers were determined from ^1H NMR analysis of crude product. [c] Alkynes **2** (0.60 mmol), paraformaldehyde **3a** (0.50 mmol) at 60 °C. [d] Alkynes **2** (0.60 mmol) and paraformaldehyde **3a** (0.33 mmol) at rt. [e] Alkyne **2a** (0.60 mmol), valeraldehyde **3b** (0.40 mmol) at 60 °C. [f] Aldehydes **3c-g** (0.40 mmol) at 60 °C for 24 h.

Moreover, quinolinium salts were easily transformed into corresponding 2-quinolones by oxidation. For example, quinolinium salt **4aa** was treated with $K_3[Fe(CN)_6]$ in water to give 2-quinolones **8a** in 64% yield (Scheme 3c).

A plausible mechanism for the present reaction is proposed in Scheme 4. The reaction starts with the formation of iminium ion **I-Ph** from aniline **1** and aldehyde **3a** in the presence of HBF_4. Then, [4+2] cycloaddition of **2t** with **I-Ph** followed by aromatization affords intermediate **III**. Finally, the oxidation of **III** by Cu(II) produces the desired salt **4** and Cu(I) (path a). The Cu(I) was reoxidized to Cu(II) by oxygen for the next oxidation step. Alternatively, the oxidation of **III** could be conducted by iminium ion **I-Ph** (path b), which is suppressed in the presence of Cu(II).

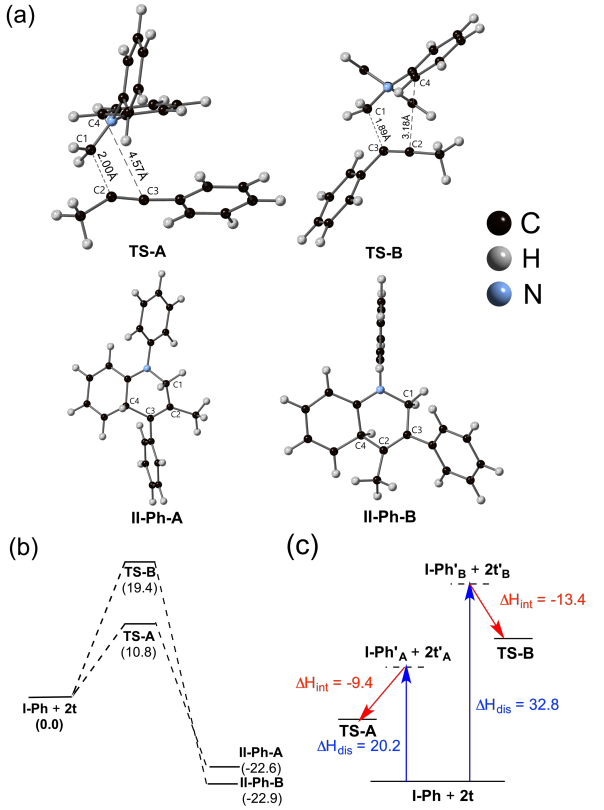
Density functional theory (DFT, the B3LYP function)[20] combined with the CPCM implicit solvation model[21] was used to investigate the [4+2] cycloaddition of iminium intermediate **I-Ph** with **2t** (methylphenylacetylene) to form **II-Ph**, the key step in the proposed mechanism. The reaction is found to proceed through a concerted and yet asynchronous transition state with one C–C distance (C1-C2: 2.00 Å for **TS-A** and C1-C3: 1.89 Å for **TS-B**, (Scheme 5a)) that is much shorter than the other (C4-C3: 4.57 Å for **TS-A** and C4-C2: 3.18 Å for **TS-B**, (Scheme 5a)), as confirmed by the intrinsic reaction coordinate (IRC) calculations. The $\Delta H^{\ddagger}/\Delta H$ is 10.8/-22.6 kcal/mol for the formation of **II-Ph-A** and 19.4/-22.9 kcal/mol for **II-Ph-B** (Scheme 5b), which is qualitatively consistent with our experimental results showing that **II-Ph-A** is the only product. Similar results were obtained when terminal -CH_3 of **2t**, was replaced by -H, -C(O)CH_3, and -C(O)OCH_3 (see supporting information).



Scheme 4. A plausible mechanism.

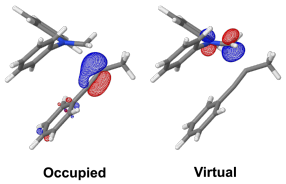
The energy decomposition scheme proposed by Head-Gordon et al.[22] was used to analyze the transition state to identify the roles that **I-Ph** and **2t** play in the reaction. This approach has been utilized by Goddard et al. to characterize the role of metal complexes in methane C–H activation.[23] From the charge transfer (CT) term, we find that much more electron density was transferred from **2t** to **I-Ph** (0.558 e^- for **TS-A** and 0.522 e^- for **TS-B**) than from **I-Ph** to **2t** (0.006 e^- for **TS-A** and 0.019 e^- for **TS-B**),

suggesting that **2t** is a nucleophile whereas **I-Ph** is an electrophile. Moreover, the most significant CT interaction is from the HOMO of **2t** to the LUMO of **I-Ph** (Scheme 6). The results support that when the terminal -Me is replaced by more electron-withdrawing groups, -C(O)CH_3 and -C(O)OCH_3, $\Delta H^{\ddagger}$ increases from 10.2 to 11.3 and 13.0 kcal/mol, respectively (see supporting information).



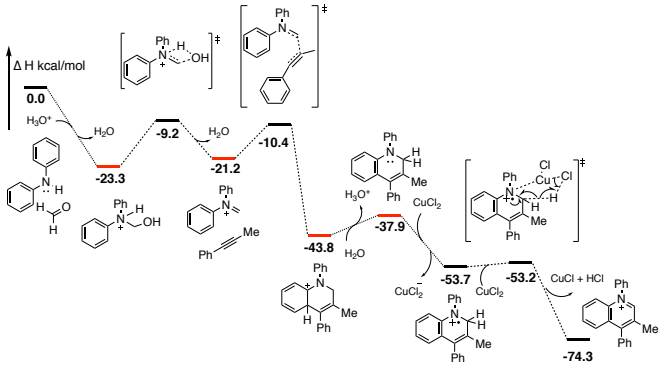
Scheme 5. (a) The optimized structures for all stationary points along the two pathways. Carbon, nitrogen, and hydrogen are colored by black, blue, and gray, respectively. (b) The enthalpic reaction profiles for the [4+2] cycloaddition of **I-Ph** and **2t.** (c) Schematic description of the decomposition of the $\Delta H^{\ddagger}$ into the distortion energy (ΔH_{DIS}, the energy cost to distort the two isolated reactants into the corresponding geometries in the transition state, e.g., **I-Ph** → **I-Ph'$_A$** and **2t** → **2t'$_A$**) and the interaction energy (ΔH_{INT}, the energy gain from bringing the two distorted reactants together to form the final transition state structure, e.g., **I-Ph'$_A$** + **2t'$_A$** → **TS-A**). The units are kcal/mol for energy and Å for bond length.

To understand the driving force for the regioselectivity, each $\Delta H^{\ddagger}$s was decomposed into the distortion and interaction energy ($\Delta H^{\ddagger} = \Delta H_{DIS} + \Delta H_{INT}$, Scheme 5c). Our calculations show that ΔH_{DIS} for Path-A (20.2 kcal/mol) is much smaller than ΔH_{DIS} for Path-B (32.8 kcal/mol), whereas the ΔH_{INT}s values for the two pathways are relatively similar (-9.4 and -13.4 kcal/mol for Path-A and Path-B, respectively). This result means that the lower $\Delta H^{\ddagger}$ for Path-A is due to the lower energy cost to distort the reactants. Further analysis shows that this is contributed by both fragments (ΔH_{DIS}, **I-Ph**, and ΔH_{DIS}, **2t** are 10.2 and 10.0 kcal/mol for Path-A compared with 16.9 and 15.9 kcal/mol for Path-B).



Scheme 6. Complementary Occupied-Virtual Pair interaction for HOMO of **2t** with LUMO of **I-Ph** based on the EDA-ALMO scheme. Blue, gray, and white represent nitrogen, carbon, and hydrogen, respectively.

In addition to the key step, the energetics for the other steps in the proposed mechanism were also calculated (Scheme 7). It was found that all of the kinetic barriers are less than 15.0 kcal/mol and that most of the reaction energies are downhill, with only two being slightly uphill (2.1 and 5.9 kcal/mol, colored by red). This finding demonstrates that the overall reaction is facile and validates the proposed mechanism (Scheme 4).



Scheme 7. Calculated $\Delta H^{\ddagger}$ and ΔH for each step in the proposed mechanism.

Conclusion

In summary, we have successfully developed an efficient method for the synthesis of quinolinium salts from secondary anilines, alkynes, aldehydes, and acid. The four-component coupling reaction was combined with Cu-catalyzed aerobic oxidation to offer a highly atom-economical process. A wide range of substrates, including terminal/internal alkynes and aliphatic/aromatic aldehydes, was converted into quinolinium salts under ambient temperature. The DFT calculations confirm that the reaction proceeds through a concerted asynchronous [4+2] cycloaddition of an iminium ion with alkyne, which occurs in polar Diels-Alder fashion with the iminium ion acting as the acceptor and alkyne as the donor. The distortion/interaction model shows that the regioselectivity of alkynes is controlled by the distortion energy for easy interaction. Further investigation into highly atom-economical synthetic methods using Cu(II)/O_2 is underway.

Experimental Section

General procedure for the synthesis of quinolinium salts 4aa-4oa, 4aa', 4ab-4ao. A sealed tube fitted with a rubber septum was charged with $CuCl_2$ (4.0 mg, 0.03 mmol), aniline (0.30 mmol), alkyne (0.40 mmol) and paraformaldehyde (12 mg, 0.4 mmol), then, the septum was secured with parafilm. The tube was evacuated to remove air and O_2 balloon inserted. Subsequently, MeCN (2 mL) and Acid (0.40 mmol) were added to the tube via syringe. (If aniline or alkyne were liquid, they were added with syringe following the insertion of MeCN.) The resulting mixture was stirred at 20 ˚C for 1 h. Then, the reaction was diluted with CH_2Cl_2 (10 mL), filtered through celite pad, and washed three times with CH_2Cl_2 (3×20 mL). The combined filtrate was concentrated under vacuum. (i) The residue was purified by chromatography using MeOH and CH_2Cl_2 as eluent to afford **4aa-4ha, 4aa', 4la-4oa, 4ab-4ao**. (ii) The residue was dissolved in minimal CH_2Cl_2, and Et_2O was added dropwise. The precipitate

was collected and washed with Et_2O three times (3×10 mL). The solid was recrystallized in MeOH and $CHCl_3$ to afford quinolinium salts **4ia**-**ka**.

6-Methyl-4-phenyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4aa). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford quinolinium salts **4aa** as pale yellow solid (110 mg, 93%). mp: 185-187°C. IR (neat): 1616, 1600, 1523, 1508, 1368, 1055 (υ $_{B-F}$), 846, 823, 763, 704 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 9.05 (d, *J* = 6.0 Hz, 1H), 8.05 (d, *J* = 6.0 Hz, 1H), 8.00 (s, 1H), 7.78 (d, *J* = 9.0 Hz, 1 H), 7.65-7.64 (m, 2H), 7.60-7.59 (m, 4H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 2.53 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.5 (C), 147.4 (*C*H), 142.2 (C), 141.1 (C), 138.4 (C), 137.2 (C), 137.2 (*C*H), 134.9 (C), 131.1 (2*C*H), 130.8 (*C*H), 129.7 (2*C*H), 129.2 (2*C*H), 128.3 (C), 127.3 (*C*H), 126.0 (2*C*H), 122.8 (*C*H), 119.9 (*C*H), 21.7 (CH_3), 21.3 (CH_3). ^{11}B NMR (160 MHz, $CDCl_3$): δ -1.21. ^{19}F NMR (470 MHz, $CDCl_3$): δ -152.90, -152.96. HRMS (FAB, $[M]^+$) for $C_{23}H_{20}N$ calcd 310.1590; found 310.1593.

6-Methyl-4-phenyl-1-(*p*-tolyl)quinolin-1-ium trifluoromethanesulfonate (4aa'). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford quinolinium salts **4aa'** as brown solid (130 mg, 94 %). mp: 130-132 °C. IR (neat): 1610, 1600, 1523, 1508, 1369 (υ $_{S=O}$), 1261, 1224, 1154, 1030 (υ $_{S=O}$), 824, 762, 734 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 9.11 (d, *J* = 6.0 Hz, 1H), 8.04 (d, *J* = 6.0 Hz, 1H), 7.99 (s, 1H), 7.79 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.65-7.58 (m, 6H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 2.52 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3 (C), 147.3 (*C*H), 142.1 (C), 141.0 (C), 138.2 (C), 137.2 (*C*H), 137.0 (C), 134.6 (C), 131.0 (2*C*H), 130.6 (*C*H), 129.5 (2*C*H), 129.1 (2*C*H), 128.1 (C), 127.1 (*C*H), 125.9 (2*C*H), 122.6 (*C*H), 120.4 (q, *J* = 317.8 Hz, *C*F_3), 119.8 (*C*H), 21.8 (CH_3), 21.4 (CH_3). ^{19}F NMR (470 MHz, $CDCl_3$): δ -78.27. HRMS (FD, $[M]^+$) for $C_{23}H_{20}N$ calcd 310.1590; found 310.1592.

1,4-Diphenylquinolin-1-ium tetrafluoroborate (4ba). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford quinolinium salts **4ba** as olive solid (83 mg, 69%). mp: 194-196 °C. IR (neat): 1604, 1590, 1525, 1492, 1396, 1308, 1055 (υ $_{B-F}$), 764, 707 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 9.06 (d, *J* = 6.0 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 6.0 Hz, 1H), 7.96-7.93 (m, 1H), 7.84-7.81 (m, 1H), 7.67-7.54 (m, 11H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.5 (C), 148.2 (*C*H), 139.6 (C), 139.5 (C), 135.3 (*C*H), 134.6 (C), 131.6 (*C*H), 130.8 (*C*H), 130.6 (2*C*H), 130.1 (*C*H), 129.8 (2*C*H), 129.1 (2*C*H), 128.6 (*C*H), 128.0 (C), 126.3 (2*C*H), 122.5 (*C*H), 119.9 (*C*H). HRMS (FAB, $[M]^+$) for $C_{21}H_{16}N$ calcd 282.1277; found 282.1287.

6-(*tert*-Butyl)-1-(4-(*tert*-butyl)phenyl)-4-phenylquinolin-1-ium tetrafluoroborate (4ca). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford quinolinium salts **4ca** as olive solid (119 mg, 82%). mp: 217-219 °C. IR (neat): 2965, 1608, 1578, 1517, 1373, 1050 (υ $_{B-F}$), 843, 764, 705. ^1H NMR (500 MHz, $CDCl_3$): δ 9.15 (d, *J* = 6.0 Hz, 1H), 8.22 (d, *J* = 1.5 Hz, 1H), 8.17 (d, *J* = 6.0 Hz, 1H), 8.04 (dd, *J* = 9.0, 1.5 Hz, 1H), 7.70-7.67 (m, 5H), 7.63-7.62 (m, 3H), 7.57 (d, *J* = 8.5 Hz, 2H), 1.40 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8 (C), 155.1 (C), 153.6 (C), 147.4 (*C*H), 138.2 (C), 137.0 (C), 134.8 (C), 134.1 (*C*H), 130.9 (*C*H), 129.7 (2*C*H), 129.1 (2*C*H), 127.9 (C), 127.5 (2*C*H), 125.8 (2*C*H), 123.5 (*C*H), 122.8 (*C*H), 119.9 (*C*H), 35.4 (C), 35.0 (C), 31.0 (3*C*H_3), 30.5 (3*C*H_3) cm^{-1}. HRMS (FAB, $[M]^+$) for $C_{29}H_{32}N$ calcd 394.2529, found 394.2523.

6-Bromo-1-(4-bromophenyl)-4-phenylquinolin-1-ium tetrafluoroborate (4da). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford quinolinium salts **4da** as apricot solid (120.mg, 76%). mp: 262-264 °C. IR (neat): 1602, 1513, 1485, 1360, 1057 (υ $_{B-F}$), 838, 763, 731, 710 cm^{-1}. ^1H NMR (500 MHz, $(CD_3)_2CO$): δ 9.63 (d, *J* = 6.0 Hz, 1H), 8.52 (s, 1H), 8.39 (d, *J* = 6.0 Hz, 1H), 8.33 (d, *J* = 9.5 Hz, 1H), 8.07 (d, *J* = 7.5 Hz, 2H), 7.97-7.93 (m, 3H), 7.84-7.83 (m, 2H), 7.78 (m, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 160.5 (C), 150.3 (*C*H), 140.2 (C), 140.2 (C), 139.2 (*C*H), 135.6 (C), 134.6 (2*C*H), 132.1 (*C*H), 131.1 (*C*H), 130.8 (2*C*H), 130.3 (2*C*H), 130.2 (C), 129.8 (2*C*H), 126.4 (C), 125.0 (C), 124.4 (*C*H), 123.5 (*C*H). HRMS (FAB, $[M]^+$) for $C_{21}H_{14}Br_2N$ calcd 437.9488; found 437.9485.

1-(4-Cyanophenyl)-6-methyl-4-phenylquinolin-1-ium tetrafluoroborate (4ea). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford products **4ea+4ea'** as cream yellow solid (83 mg, 68%). mp: 217-219 °C. IR (neat): 1599, 1557, 1524, 1503, 1388, 1304, 1283, 1059 (υ $_{B-F}$), 852, 823, 788, 764, 705 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 9.04 (d, *J* = 6.0 Hz, 1H), 8.02 (s, 1H), 7.97 (d, *J* = 6.0 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.80 (dd, *J* = 9.0, 1.0 Hz, 1H), 7.66-7.60 (m, 5H), 7.46 (d, *J* = 9.0, 1H), 2.53 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.7 (C), 147.2 (*C*H), 142.7 (C), 141.4 (C), 137.9 (C), 137.7 (*C*H), 134.8 (C), 134.5 (2*C*H), 131.0 (*C*H), 129.7 (2*C*H), 129.3 (2*C*H), 128.4 (C), 128.0 (2*C*H), 127.7 (*C*H), 122.7 (*C*H), 119.2 (*C*H), 117.0 (C), 115.9 (C), 21.7 (CH_3). HRMS (FAB, $[M]^+$) for $C_{23}H_{17}N_2$ calcd 321.1386; found 321.1388

6-Cyano-4-phenyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4ea'). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford products **4ea+4ea'** as cream yellow solid (83 mg, 68%). mp: 251-253 °C. IR (neat): 2236 (υ $_{C\equiv N}$), 1608, 1564, 1516, 1365, 1307, 1284, 1055 (υ $_{B-F}$), 830, 787, 763 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 9.15 (d, *J* = 6.5 Hz, 1H), 8.55 (s, 1H), 8.13 (d, *J* = 6.0 Hz, 1H), 8.01 (dd, *J* = 9.5, 1.0, 1H), 7.79 (d, *J* = 9.5 Hz, 1H), 7.69-7.61 (m, 5H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.3 (C), 150.9 (*C*H), 142.8 (C), 141.1 (C), 136.8 (C), 135.1 (*C*H), 134.4 (*C*H), 133.8 (C), 131.6 (*C*H), 131.3 (2*C*H), 130.0 (2*C*H), 129.6 (2*C*H), 128.0 (C), 126.1 (2*C*H), 124.3 (*C*H), 122.0 (*C*H), 116.5 (C), 114.0 (C), 21.4 (CH_3). HRMS (FAB, $[M]^+$) for $C_{23}H_{17}N_2$ calcd 321.1386; found 321.1394.

1-Methyl-4-phenylquinolin-1-ium tetrafluoroborate (4fa). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 6:94) to afford quinolinium salts **4fa** as white solid (56 mg, 60%). mp: 147-149 °C. IR (neat): 1604, 1531, 1448, 1398, 1368, 1056 (υ $_{B-F}$), 859, 791, 768, 706 cm^{-1}. ^1H NMR (500 MHz, $(CD_3)_2CO$): δ 9.51 (d, *J* = 5.5 Hz, 1H), 8.69 (d,*J* = 9.0 Hz, 1H), 8.35-8.32 (m, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 5.5 Hz, 1H), 8.07-8.04 (m, 1H), 7.71-7.70 (m, 5H), 4.86 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 159.7 (C), 150.0 (*C*H), 140.2 (C), 136.2 (*C*H), 135.9 (C), 131.4 (*C*H), 131.0 (*C*H), 130.6 (2*C*H), 130.0 (2*C*H), 129.3 (*C*H), 128.6 (C), 123.1 (*C*H), 120.2 (*C*H), 46.3 (*C*H_3). HRMS (FAB, $[M]^+$) for $C_{16}H_{14}N$ calcd 220.1121; found 220.1129.

1,6-Dimethyl-4-phenylquinolin-1-ium tetrafluoroborate (4ga). Following the general procedure for the synthesis of quinolinium

salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 7:93) to afford quinolinium salts **4ga** as white solid (86 mg, 89%). mp: 172-174 °C. IR (neat): 1613, 1536, 1452, 1346, 1234, 1055 (υ B-F), 851, 810, 769, 705 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 9.28 (s, 1H), 8.35 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.89 (s, 1H), 7.79 (s, 1H), 7.56-7.55 (m, 3H), 7.50-7.49 (m, 2H), 4.69 (s, 3H), 2.50 (s, 3H). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 9.45 (d, *J* = 5.2 Hz, 1H), 8.49 (d, *J* = 8.8 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 5.2 Hz, 1H), 7.94 (s, 1H), 7.67 (m, 5H), 4.67 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.2 (C), 147.6 (*C*H), 140.9 (C), 137.7 (*C*H), 137.5 (C), 134.7 (C), 130.5 (*C*H), 129.4 (2*C*H), 129.0 (2*C*H), 127.9 (C), 127.1 (*C*H), 122.1 (*C*H), 118.6 (*C*H), 45.6 (CH_3), 21.5 (CH_3). HRMS (FAB, $[M]^+$) for $C_{17}H_{16}N$ calcd 234.1277; found 234.1287.

6-Methoxy-1-methyl-4-phenylquinolin-1-ium tetrafluoroborate (4ha). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 7:93) to afford quinolinium salts **4ha** as purple solid (64 mg, 63%). mp: 168-170 °C. IR (neat): 1620, 1532, 1474, 1447, 1383, 1286, 1247, 1054 (υ B-F), 852, 786, 761, 711 cm^{-1}. ^1H NMR (500 MHz, $(CD_3)_2CO$): δ 9.36 (d, *J* = 5.5 Hz, 1H), 8.64 (d, *J* = 9.5 Hz, 1H), 8.07 (d, *J* = 5.5 Hz, 1H), 7.95 (dd, *J* = 9.5, 2.5 Hz, 1H), 7.79-7.77 (m, 2H), 7.71-7.70 (m, 3H), 7.61 (d, *J* = 3.0 Hz, 1H), 4.85 (s, 3H), 3.94 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): 161.0 (C), 157.9 (C), 147.2 (*C*H), 136.3 (C), 136.0 (C), 131.4 (*C*H), 130.6 (C), 130.4 (2*C*H), 130.2 (2*C*H), 127.9 (*C*H), 123.5 (*C*H), 122.0 (*C*H), 107.1 (*C*H), 56.5 (CH_3), 46.4 (CH_3). HRMS (FAB, $[M]^+$) for $C_{17}H_{16}NO$ calcd 250.1226; found 250.1228

6-Chloro-1-methyl-4-phenylquinolin-1-ium tetrafluoroborate (4ia). Following the general procedure for the synthesis of quinolinium salts and purification by recrystallization in MeOH/$CHCl_3$ (slow evaporation in air) to afford quinolinium salts **4ia** as pale yellow solid (44 mg, 43%). mp: 167-169 °C. IR (neat): 1610, 1586, 1523, 1456, 1438, 1368, 1057 (υ B-F), 856, 825, 783, 761 cm^{-1}. ^1H NMR (500 MHz, $(CD_3)_2CO$): δ 9.58 (d, *J* = 6.0 Hz, 1H), 8.77 (d, *J* = 9.5 Hz, 1H), 8.34 (dd, *J* = 9.5, 2.0 Hz, 1H), 8.27 (d, *J* = 2.5 Hz, 1H), 8.23 (d, *J* = 6.0 Hz, 1H), 7.78-7.75 (m, 2H), 7.74-7.73 (m, 3H), 4.91 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): 159.1 (C), 150.6 (*C*H), 139.1 (C), 136.8 (C), 136.3 (*C*H), 135.6 (C), 131.8 (*C*H), 130.7 (2*C*H), 130.2 (2*C*H), 129.8 (C), 127.9 (*C*H), 124.3 (*C*H), 122.7 (*C*H), 46.6 (CH_3). HRMS (FAB, $[M]^+$) for $C_{16}H_{13}ClN$ calcd 254.0731; found 254.0737.

6-Bromo-1-methyl-4-phenylquinolin-1-ium tetrafluoroborate (4ja). Following the general procedure for the synthesis of quinolinium salts and purification by recrystallization in MeOH/$CHCl_3$ (slow evaporation in air) to afford quinolinium salts **4ja** as white solid (71 mg, 61%). mp: 203-205 °C. IR (neat): 1608, 1584, 1520, 1454, 1434, 1365, 1229, 1050 (υ B-F), 839, 782, 762, 727, 710 cm^{-1}. ^1H NMR (500 MHz, $(CD_3)_2CO$): δ 9.60 (d, *J* = 5.5 Hz, 1H), 8.69 (d, *J* = 9.0 Hz, 1H), 8.45 (d, *J* = 9.0 Hz, 1H), 8.42 (d, *J* = 1.5 Hz, 1H), 8.22 (d, *J* = 5.0 Hz, 1H), 7.77-7.76 (m, 2H), 7.73-7.72 (m, 3H), 4.90 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 158.9 (C), 150.6 (*C*H), 139.3 (C), 138.9 (*C*H), 135.6 (C), 131.7 (*C*H), 131.2 (*C*H), 130.7 (2*C*H), 130.2 (2*C*H), 130.0 (C), 124.9 (C), 124.3 (*C*H), 122.6 (*C*H), 46.6 (CH_3). HRMS (FAB, $[M]^+$) for $C_{16}H_{13}BrN$ calcd 298.0226; found 298.0230.

6-Cyano-1-methyl-4-phenylquinolin-1-ium tetrafluoroborate (4ka). Following the general procedure for the synthesis of quinolinium salts and purification by recrystallization in MeOH/$CHCl_3$ (slow evaporation in air) to afford quinolinium salts **4ka** as yellow solid (56 mg, 57%). mp: 184-186 °C. IR (neat): 1610, 1587, 1527, 1458, 1441, 1370, 1058 (υ B-F), 854, 835, 787, 765, 704 cm^{-1}. ^1H NMR (400 MHz, $(CD_3)_2CO$): δ 9.68 (d, *J* = 6.0 Hz, 1H), 8.91 (d, *J* = 9.2 Hz, 1H), 8.80 (d, *J* = 2.0 Hz, 1H), 8.58 (dd, *J* = 9.2, 2.0 Hz, 1H), 8.31 (d, *J* = 6.0 Hz, 1H), 7.82-7.79 (m, 2H), 7.75-7.72 (m, 3H), 4.93 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ 160.2 (C), 152.4 (*C*H), 141.4 (C), 136.3 (*C*H), 135.1 (*C*H), 135.0 (C), 131.8 (*C*H), 130.7 (2*C*H), 130.1 (2*C*H), 128.2 (C), 124.5 (*C*H), 122.0 (*C*H), 117.3 (C), 114.5 (C), 46.7 (CH_3). HRMS (FAB, $[M]^+$) for $C_{17}H_{13}N_2$ calcd 245.1073; found 245.1075.

1,5,7-Trimethyl-4-phenylquinolin-1-ium tetrafluoroborate (4la). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 7:93) to afford quinolinium salts **4la** as golden solid (91 mg, 91%). mp: 176-178 °C. IR (neat): 1621, 1608, 1571, 1456, 1347, 1056 (υ B-F), 855, 771, 708 cm^{-1}. ^1H NMR (500 MHz, $(CD_3)_2CO$): δ 9.39 (d, *J* = 6.0 Hz, 1H), 8.40 (s, 1H), 7.90 (d, *J* = 6.5 Hz, 1H), 7.73 (s, 1H), 7.62-7.61 (m, 3H), 7.52-7.51 (m, 2H), 4.82 (s, 3H), 2.71 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 160.4 (C), 148.1 (*C*H), 147.9 (C), 141.7 (C), 140.7 (C), 139.4 (C), 136.3 (*C*H), 130.4 (*C*H), 129.5 (2*C*H), 129.0 (2*C*H), 126.8 (C), 124.2 (*C*H), 117.6 (*C*H) 46.9 (CH_3), 24.4 (CH_3), 22.1 (CH_3). HRMS (FAB, $[M]^+$) for $C_{18}H_{18}N$ calcd 248.1434; found 248.1443.

8-Methyl-6-phenyl-1,2-dihydropyrrolo[3,2,1-*ij*]quinolin-3-ium tetrafluoroborate (4ma). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on alumina (MeOH:CH_2Cl_2, 0:100 to 3:97) to afford quinolinium salts **4ma** as white solid (66 mg, 69%). mp: 203-205 °C. IR (neat): 1629, 1523, 1438, 1393, 1336, 1222, 1052 (υ B-F), 859, 781, 764, 710 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 10.08 (d, *J* = 5.6 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.86-7.83 (m, 2H), 7.77-7.73 (m, 1H), 7.52 (m, 5H), 5.66 (t, *J* = 6.8 Hz, 2H), 3.83 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3 (C), 143.6 (*C*H), 141.8 (C), 136.3 (C), 133.9 (C), 131.6 (*C*H), 130.6 (*C*H), 129.1 (2*C*H), 129.0 (2*C*H), 128.6 (*C*H), 125.5 (C), 123.2 (*C*H), 122.9 (*C*H), 56.7 (CH_2), 27.6 (CH_2). HRMS (FAB, $[M]^+$) for $C_{17}H_{14}N$ calcd 232.1121; found 232.1123.

9-Methyl-7-phenyl-2,3-dihydro-1*H*-pyrido[3,2,1-*ij*]quinolin-4-ium tetrafluoroborate (4na). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on alumina (MeOH:CH_2Cl_2, 0:100 to 3:97) to afford quinolinium salts **4na** as pale yellow solid (75 mg, 75%). mp: 197-199 °C. IR (neat): 1611,1570, 1539, 1450, 1419, 1370, 1274, 1238, 1054 (υ B-F), 859, 821, 770, 714 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 9.31 (d, *J* = 6.0 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.88-7.86 (m, 2H), 7.76-7.72 (m, 1H), 7.59-7.57 (m, 3H), 7.55-7.52 (m, 2H), 5.07 (t, *J* = 5.6 Hz, 2H), 3.36 (t, *J* = 6.0 Hz, 2H), 2.50 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 158.8 (C), 147.3 (*C*H), 136.3 (C), 134.9 (C), 133.7 (*C*H), 130.5 (*C*H), 130.1 (C), 129.4 (2*C*H), 129.2 (*C*H), 129.1 (2*C*H), 128.4 (C), 126.5 (*C*H), 122.0 (*C*H), 57.3 (CH_2), 27.4 (CH_2), 20.8 (CH_2). HRMS (FAB, $[M]^+$) for $C_{18}H_{16}N$ calcd 246.1277; found 246.1284.

6-Methyl-1-(4-methylbenzyl)-4-phenylquinolin-1-ium tetrafluoroborate (4oa). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford quinolinium salts **4oa** as pink solid (100 mg, 81%). mp: 122-124 °C. IR (neat): 1606, 1585, 1569, 1529, 1446, 1433, 1375, 1239, 1056 (υ B-F), 820, 786, 763 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 9.36 (d, *J* = 6.0 Hz, 1H), 8.36 (d, *J* = 9.0 Hz, 1H), 7.90-7.85 (m, 3H), 7.57-7.56 (m, 3H), 7.50-7.50 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.11 (s, 2H), 2.44 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.7 (C), 147.1 (*C*H), 140.9 (C), 139.0 (C), 137.6 (*C*H), 136.8 (C), 134.7 (C), 130.6 (*C*H), 129.8 (2*C*H), 129.4 (2*C*H),

129.4 (C), 129.1 (2*C*H), 128.4 (C), 127.5 (2*C*H), 127.3 (*C*H), 122.2 (*C*H), 119.1 (*C*H), 60.8 (CH_2), 21.4 (CH_3), 20.8 (CH_3). HRMS (FAB, $[M]^+$) for $C_{24}H_{22}N$ calcd 324.1747; found 324.1754.

6-Methyl-1,4-di-*p*-tolylquinolin-1-ium tetrafluoroborate (4ab). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 4:96) to afford quinolinium salts **4ab** as brown solid (106 mg, 86%). mp: 196-198 °C. IR (neat): 1598, 1523, 1508, 1369, 1056 (υ $_{B-F}$), 819, 735 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 9.02 (d, *J* = 5.5 Hz, 1H), 8.03-8.01 (m, 2H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 2.52 (s, 3H), 2.46 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6 (C), 147.1 (*C*H), 142.1 (C), 141.4 (C), 141.0 (C), 138.3 (C), 137.2 (*C*H), 137.1 (C), 131.9 (C), 131.1 (2*C*H), 129.9 (2*C*H), 129.7 (2*C*H), 128.1 (C), 127.3 (*C*H), 125.9 (2*C*H), 122.4 (*C*H), 119.8 (*C*H), 21.6 (CH_3), 21.3 (CH_3), 21.2 (CH_3). HRMS (FAB, $[M]^+$) for $C_{24}H_{22}N$ calcd 324.1747; found 324.1757.

4-(4-Methoxyphenyl)-6-methyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4ac). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 4:96) to afford quinolinium salts **4ac** as brown solid (92 mg, 72%). mp: 220-222 °C. IR (neat): 1539, 1509, 1368, 1285, 1256, 1182, 1057 (υ $_{B-F}$), 826 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.95 (d, *J* = 6.0 Hz, 1H), 8.07 (s, 1H), 8.01 (d, *J* = 6.0 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.47-7.43 (m, 4H), 7.10 (d, *J* = 8.5 Hz, 2H), 3.88 (s, 3H), 2.53 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.9 (C), 159.2 (C), 146.8 (*C*H), 142.1 (C), 140.9 (C), 138.4 (C), 137.1 (C), 137.1 (*C*H), 131.7 (2*C*H), 131.1 (2*C*H), 127.9 (C), 127.4 (*C*H), 126.9 (C), 126.0 (2*C*H), 122.2 (*C*H), 119.7 (*C*H), 114.8 (2*C*H), 55.5 (CH_3), 21.6 (CH_3), 21.2 (CH_3). HRMS (FAB, $[M]^+$) for $C_{24}H_{22}NO$ calcd 340.1696; found 340.1703.

4-(4-(*tert*-Butyl)phenyl)-6-methyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4ad). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 4:96) to afford quinolinium salts **4ad** as khaki solid (126 mg, 93%). mp: 88-90 °C IR (neat): 1605, 1597, 1524, 1507, 1368, 1057 (υ $_{B-F}$), 824, 735 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 9.05 (d, *J* = 5.5 Hz, 1H), 8.08 (s, 1H), 8.05 (d, *J* = 5.5 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.63-7.59 (m, 4H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 2.54 (s, 3H), 2.47 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6 (C), 154.5 (C), 147.2 (*C*H), 142.1 (C), 141.0 (C), 138.3 (C), 137.2 (*C*H), 137.2 (C), 131.9 (C), 131.1 (2*C*H), 129.7 (2*C*H), 128.1 (C), 127.4 (*C*H), 126.2 (2*C*H), 126.0 (2*C*H), 122.6 (*C*H), 119.8 (*C*H), 34.9 (C), 31.1 (3CH_3), 21.6 (CH_3), 21.2 (CH_3). HRMS (FAB, $[M]^+$) for $C_{27}H_{28}N$ calcd 366.2216; found 366.2225.

4-(4-Fluorophenyl)-6-methyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4ae). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 4:96) to afford quinolinium salts **4ae** as pale yellow solid (107 mg, 86%). mp: 219-220 °C. IR (neat): 1599, 1509, 1368, 1233, 1165, 1057 (υ $_{B-F}$), 825 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 9.00 (d, *J* = 6.0 Hz, 1H), 8.02 (d, *J* = 5.5 Hz, 1H), 7.93 (s, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.68-7.65 (m, 2H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.28-7.24 (m, 2H), 2.52 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164 (d, *J* = 252.6 Hz, C), 158.2 (C), 147.2 (*C*H), 142.1 (C), 141.2 (C), 138.3 (C), 137.3 (*C*H), 137.2 (C), 131.9 (d, *J* = 8.7 Hz, 2*C*H), 131.0 (2*C*H), 130.9 (d, *J* = 3.3 Hz, C), 128.1 (C), 126.9 (*C*H), 126.0 (2*C*H), 122.7 (*C*H), 119.9 (*C*H), 116.4 (d, *J* = 22.0 Hz, 2*C*H), 21.6 (CH_3), 21.2 (CH_3). ^{11}B NMR (160 MHz, $CDCl_3$): δ -1.29. ^{19}F NMR (470 MHz, $CDCl_3$): δ -108.62, -152.82, -152.87. HRMS (FAB, $[M]^+$) for $C_{23}H_{19}FN$ calcd 328.1496; found 328.1504.

4-(4-Chlorophenyl)-6-methyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4af). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 4:96) to afford quinolinium salts **4af** as pale yellow solid (98 mg, 76%). mp: 225-227 °C. IR (neat): 1603, 1592, 1522, 1508, 1368, 1055 (υ $_{B-F}$), 822, 735 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.99 (d, *J* = 6.0 Hz, 1H), 8.01 (d, *J* = 6.0 Hz, 1H), 7.92 (s, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.58-7.99 (m, 3H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 2.52 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.9 (C), 147.1 (*C*H), 142.1 (C), 141.3 (C), 138.3 (C), 137.3 (*C*H), 137.1 (C), 136.9 (C), 133.2 (C), 131.0 (2*C*H), 131.0 (2*C*H), 129.3 (2*C*H), 128.0 (C), 126.7 (*C*H), 125.9 (2*C*H), 122.5 (*C*H), 119.8 (*C*H), 21.5 (CH_3), 21.1 (CH_3). HRMS (FAB, $[M]^+$) for $C_{23}H_{19}ClN$ calcd 344.1201; found 344.1202.

4-(4-Acetylphenyl)-6-methyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4ag). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 4:96) to afford quinolinium salts **4ag** as coffee brown solid (103 mg, 78%). mp: 219-221 °C. IR (neat): 1684 (υ $_{C=O}$), 1601, 1523, 1508, 1480, 1365, 1266, 1055 (υ $_{B-F}$), 823, 733 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.99 (d, *J* = 6.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 2H), 8.01 (d, *J* = 5.5 Hz, 1H), 7.85 (s, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 2.63 (s, 3H), 2.49 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.4 (*C*O), 158.0 (C), 147.3 (*C*H), 142.1 (C), 141.4 (C), 1391. (C), 138.3 (C), 138.1 (C), 137.4 (*C*H), 137.1 (C), 131.0 (2*C*H), 129.9 (2*C*H), 128.7 (2*C*H), 128.0 (C), 126.7 (*C*H), 125.9 (2*C*H), 122.6 (*C*H), 119.9 (*C*H), 26.7 (CH_3), 21.5 (CH_3), 21.2 (CH_3). HRMS (FD, $[M]^+$) for $C_{25}H_{22}NO$ calcd 352.1696; found 352.1691.

6-Methyl-4-(*m*-tolyl)-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4ah). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 4:96) to afford quinolinium salts **4ah** as brown solid (92 mg, 74%). mp: 172-174 °C. IR (neat): 1598, 1523, 1508, 1369, 1057 (υ $_{B-F}$), 826, 801, 711 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 9.07 (d, *J* = 3.5 Hz, 1H), 8.04 (d, *J* = 3.5 Hz, 1H), 7.99 (s, 1H), 7.79 (d, *J* = 9.0 Hz, 1H), 7.59 (d, *J* = 9.0 Hz, 1H), 7.51-7.40 (m, 8H), 2.52 (s, 3H), 2.47 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7 (C), 147.2 (*C*H), 142.1 (C), 141.0 (C), 139.1 (C), 138.2 (C), 137.3 (*C*H), 137.1 (C), 134.7 (C), 131.4 (*C*H), 131.0 (2*C*H), 130.1 (*C*H), 128.9 (*C*H), 128.2 (C), 127.2 (*C*H), 126.8 (*C*H), 126.0 (2*C*H), 122.6 (*C*H), 119.8 (*C*H), 21.6 (CH_3), 21.3 (CH_3), 21.2 (CH_3). HRMS (FAB, $[M]^+$) for $C_{24}H_{22}N$ calcd 324.1747; found 324.1757.

4-(3-Bromophenyl)-6-methyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4ai). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 4:96) to afford quinolinium salts **4ai** as olive solid (109 mg, 76%). mp: 83-85 °C. IR (neat): 1612, 1596, 1556, 1523, 1508, 1369, 1055 (υ $_{B-F}$), 826, 799, 744 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 9.01 (d, *J* = 6.0 Hz, 1H), 7.96 (d, *J* = 6.0 Hz, 1H), 7.87 (s, 1H), 7.79 (d, *J* = 9.0 Hz, 1H), 7.74 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.51-7.45 (m, 3H), 7.43 (d, *J* = 8.0 Hz, 2H), 2.52 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.4 (C), 147.4 (*C*H), 142.2 (C), 141.4 (C), 138.3 (C), 137.4 (*C*H), 137.2 (C), 136.8 (C), 133.5 (*C*H), 131.9 (*C*H), 131.0 (2*C*H), 130.7 (*C*H), 128.4 (*C*H), 128.1 (C),

126.7 (*C*H), 126.0 (2*C*H), 123.0 (C), 122.7 (*C*H), 119.9 (*C*H), 21.6 (*C*H$_3$), 21.2 (*C*H$_3$). HRMS (FAB, [M]$^+$) for $C_{23}H_{19}BrN$ calcd 388.0695; found 388.0704.

6-Methyl-4-(*o*-tolyl)-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4aj). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford quinolinium salts **4aj** as brown solid (99 mg, 80%). mp: 194-196 °C. IR (neat): 1610, 1521, 1509, 1374, 1055 (υ $_{B-F}$), 824, 765, 731 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.08 (d, *J* = 6.0 Hz, 1H), 7.95 (d, *J* = 5.5 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.57-7.51 (m, 3H), 7.47-7.43 (m, 3H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.28(d, *J* = 7.5 Hz, 1H), 2.47 (s, 6H), 2.10 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.1 (C), 147.5 (*C*H), 142.1 (C), 141.3 (C), 137.9 (C), 137.5 (*C*H), 137.1 (C), 135.5 (C), 134.3 (C), 131.0 (2*C*H), 130.7 (*C*H), 130.1 (*C*H), 129.1 (*C*H), 128.9 (C), 126.9 (*C*H), 126.1 (*C*H), 126.0 (*C*H), 126.0 (*C*H), 123.2 (*C*H), 119.9 (*C*H), 21.5 (*C*H$_3$), 21.2 (*C*H$_3$), 19.9 (*C*H$_3$). HRMS (FAB, [M]$^+$) for $C_{24}H_{22}N$ calcd 324.1747; found 324.1754.

4-Mesityl-6-methyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4ak). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford quinolinium salts **4ak** as khaki solid (126 mg, 91%). mp: 278-280 °C. IR (neat): 1611, 1508, 1490, 1374, 1057 (υ $_{B-F}$), 823, 733 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.12 (d, *J* = 5.5 Hz, 1H), 7.91 (d, *J* = 5.5 Hz, 1H), 7.8 (d, *J* = 9.0 Hz, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.56 (d, *J* = 7.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.44 (s, 1H), 7.02 (s, 2H), 2.47 (s, 6H), 2.37 (s, 3H), 1.89 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.9 (C), 148.2 (*C*H), 142.2 (C), 141.6 (C), 139.6 (C), 137.9 (C), 137.7 (*C*H), 137.1 (C), 135.2 (2C), 131.1 (2*C*H), 131.0 (C), 129.2 (C), 128.8 (2*C*H), 126.2 (*C*H), 126.1 (2*C*H), 123.9 (*C*H), 120.1 (*C*H) , 21.5 (*C*H$_3$), 21.2 (*C*H$_3$), 21.1 (*C*H$_3$), 20.2 (2*C*H$_3$). HRMS (FAB, [M]$^+$) for $C_{26}H_{26}N$ calcd 352.2060; found 352.2069.

6-Methyl-4-(thiophen-3-yl)-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4al). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford quinolinium salts **4al** as camel solid (86 mg, 71%). mp: 217-219 °C. IR (neat): 1597, 1563, 1524, 1507, 1056 (υ $_{B-F}$), 847, 819, 777, 732 cm^{-1}. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.37 (d, *J* = 6.0 Hz, 1H), 8.47 (s, 1H), 8.38 (d, *J* = 2.0 Hz, 1H), 8.31 (d, *J* = 6.5 Hz, 1H), 8.07 (d, *J* = 9.0 Hz, 1H), 7.94 (dd, *J* = 4.8, 3.0 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.76-7.74 (m, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 2.66 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 154.4 (C), 148.5 (*C*H), 142.9 (C), 142.3 (C), 139.9 (C), 138.9 (C), 138.3 (*C*H), 136.6 (C), 131.8 (2*C*H), 131.7 (*C*H), 129.6 (*C*H), 129.4 (*C*H), 128.6 (C), 127.8 (*C*H), 127.3 (2*C*H), 122.5 (*C*H), 121.1 (*C*H), 21.5 (*C*H$_3$), 21.2 (*C*H$_3$). HRMS (FAB, [M]$^+$) for $C_{21}H_{18}NS$ calcd 316.1154; found 316.1162.

4-(6-Methoxynaphthalen-2-yl)-6-methyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4am). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford quinolinium salts **4am** as brown sticky solid (118 mg, 82%). mp: 117-119 °C. IR (neat): 1626, 1598, 1524, 1506, 1487, 1392, 1364, 1271, 1222, 1205, 1166, 1057 (υ $_{B-F}$), 854, 820,733 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.00 (d, *J* = 6.0 Hz, 1H), 8.10-8.08 (m, 2H), 8.07 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.76 (dd, *J* = 9.0, 1.0 Hz, 1H), 7.66 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.21-7.19 (m, 2H), 3.94 (s, 3H), 2.50 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7 (C), 159.4 (C), 147.0 (*C*H), 142.1 (C), 141.0 (C), 138.7 (C), 137.2 (C), 137.1 (*C*H), 135.6 (C), 131.1 (2*C*H), 130.4 (*C*H), 130.2 (*C*H), 129.9 (C), 128.4 (C), 128.2 (C), 127.8 (*C*H), 127.5 (*C*H), 126.9 (*C*H), 126.0 (2*C*H), 122.7 (*C*H), 120.2 (*C*H), 119.8 (*C*H), 105.7 (*C*H), 55,4 (*C*H$_3$), 21.6 (*C*H$_3$), 21.2 (*C*H$_3$). HRMS (FAB, [M]$^+$) for $C_{28}H_{24}NO$ calcd 390.1852; found 390.1861.

4-Cyclohexyl-6-methyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4an). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford quinolinium salts **4an** as brown solid (96 mg, 80%). mp: 198-200 °C. IR (neat): 2932, 2859, 1600, 1528, 1507, 1452, 1367, 1057 (υ $_{B-F}$), 828 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.02 (d, *J* = 6.0 Hz, 1H), 8.19 (s, 1H), 8.12 (d, *J* = 6.0 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 3.55 (m, 1H), 2.65 (s, 3H), 2.48 (s, 3H), 2.04 (m, 2H), 1.96 (m, 2H), 1.84 (m, 1H), 1.70 (m, 2H), 1.58 (m, 2H), 1.37 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.1 (C), 147.6 (*C*H), 142.0 (C), 140.9 (C), 137.3 (C), 137.1 (C), 137.0 (*C*H), 131.0 (2*C*H), 128.0 (C), 125.9 (2*C*H), 123.9 (*C*H), 120.2 (*C*H), 119.6 (*C*H), 40.4 (*C*H), 32.9 (2*C*H$_2$), 26.2 (2*C*H$_2$), 25.5 (*C*H$_2$), 21.7 (*C*H$_3$), 21.2 (*C*H$_3$). HRMS (FAB, [M]$^+$) for $C_{23}H_{26}N$ calcd 316.2060; found 316.2061.

6-Methyl-4-propyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4ao). Following the general procedure for the synthesis of quinolinium salts and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford quinolinium salts **4ao** as brown solid (67 mg, 61%). mp: 137-139 °C. IR (neat): 2952, 1608, 1526, 1507, 1374, 1050 (υ $_{B-F}$), 826 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.93 (d, *J* = 5.5 Hz, 1H), 8.14 (s, 1H), 8.02 (d, *J* = 5.5 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 3.29 (t, *J* = 8.0 Hz, 2H), 2.60 (s, 3H), 2.44 (s, 3H), 1.88 (qt, *J* = 8.0, 7.0 Hz, 2H), 1.07 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.7 (C), 147.0 (*C*H), 142.0 (C), 141.0 (C), 137.2 (C), 137.2 (*C*H), 136.9 (C), 130.9 (2*C*H), 128.6 (C), 125.8 (2*C*H), 124.6 (*C*H), 122.0 (*C*H), 119.9 (*C*H), 35.0 (*C*H$_2$), 22.9 (*C*H$_2$), 21.5 (*C*H$_3$), 21.1 (*C*H$_3$), 13.9 (*C*H$_3$). HRMS (FAB, [M]$^+$) for $C_{20}H_{22}N$ calcd 276.1747; found 276.1755.

Optimized condition for the synthesis of quinolinium salts 4ap-4as. To a solution of $CuCl_2$ (4.0 mg, 0.03 mmol), di-*p*-tolylamine (59.2 mg, 0.30 mmol), alkyne (0.60 mmol) and paraformaldehyde (15.0 mg, 0.50 mmol) in MeCN (2 mL), HBF_4 (0.40 mmol, 50% in water) was added under O_2 balloon. The resulting mixture was heated to 60 °C and stirred for 1 h. After cooling, the reaction was diluted with CH_2Cl_2 (10 mL), filtered through celite pad, and washed three times with CH_2Cl_2 (3×20 mL). The combined filtrate was concentrated under vacuum and the residue was purified by chromatography on using MeOH and CH_2Cl_2 as eluent to afford quinolinium salts **4ap-4as**.

3,4-Diethyl-6-methyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4ap). Following the optimized procedure for the synthesis of quinolinium salts **4ap-4as** and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford quinolinium salts **4ap** as brown solid (51 mg, 45%). mp: 138-140 °C. IR (neat): 2982, 2933, 1528, 1509, 1375, 1269, 1053 (υ $_{B-F}$), 821, 733 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.11 (s, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.50-7.45 (m, 5H), 3.36 (q, *J* = 7.6 Hz, 2H), 3.08 (q, *J* = 7.6 Hz, 2H), 2.63 (s, 3H), 2.49 (s, 3H), 1.44 (t, *J* = 7.6 Hz, 3H), 1.39 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9 (C), 147.3 (*C*H), 141.9 (C), 140.6 (C), 137.1 (C), 136.4 (C), 136.2 (C), 135.9 (*C*H), 130.9 (2*C*H), 128.5 (C), 126.1 (2*C*H), 124.4 (*C*H), 120.0 (*C*H), 23.9 (*C*H$_2$), 22.7 (*C*H$_2$), 22.0

(CH_3), 21.4 (CH_3), 14.7 (2CH_3). HRMS (FD, $[M]^+$) for $C_{21}H_{24}N$ calcd 290.1903; found 290.1905.

6-Methyl-3,4-diphenyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4aq). Following the optimized procedure for the synthesis of quinolinium salts **4ap-4as** and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 4:96) to afford quinolinium salts **4aq** as brown solid (93 mg, 66%). mp: 237-239 °C. IR (neat): 1523, 1509, 1372, 1347, 1269, 1055 (υ_{B-F}), 820, 784, 732, 703 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 7.74-7.69 (m, 4H), 7.57 (d, *J* = 9.6 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.42-7.34 (m, 5H), 7.33-7.30 (m, 2H), 7.22-7.18 (m,3H), 2.50 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2 (C), 147.1 (*C*H), 141.9 (C), 140.8 (C), 137.5 (C), 137.3 (C), 136.8 (*C*H), 135.0 (C), 133.8 (C), 133.4 (C), 130.9 (2*C*H), 130.0 (2*C*H), 129.8 (2*C*H), 129.6 (C), 129.2 (*C*H), 128.3 (*C*H), 128.3 (2*C*H), 128.3 (2*C*H), 127.7 (*C*H), 126.2 (2*C*H), 119.5 (*C*H), 21.8 (CH_3), 21.4 (CH_3). HRMS (FD, $[M]^+$) for $C_{29}H_{24}N$ calcd 386.1903; found 386.1893.

6-Methyl-1,3,4-tri-*p*-tolylquinolin-1-ium tetrafluoroborate (4ar). Following the optimized procedure for the synthesis of quinolinium salts **4ap-4as** and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 4:96) to afford quinolinium salts **4ar** as brown solid (91 mg, 60%). mp: 101-103 °C. IR (neat): 1608, 1510, 1371, 1346, 1269, 1056 (υ_{B-F}), 820, 734 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.73 (s, 1H), 7.74 (s, 1H), 7.71 (d, *J* = 9.5 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.24-7.17 (m, 6H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.49 (s, 3H), 2.47 (s, 3H), 2.39 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2 (C), 146.9 (*C*H), 141.8 (C), 140.6 (C), 139.3 (C), 138.1 (C), 137.3 (C), 137.2 (C), 136.6 (*C*H), 134.8 (C), 130.9 (C), 130.8 (2*C*H), 130.3 (C), 129.7 (2*C*H), 129.7 (2*C*H), 129.5 (C), 129.0 (2*C*H), 129.0 (2*C*H), 127.6 (*C*H), 126.1 (2*C*H), 119.4 (*C*H), 21.7 (CH_3), 21.4 (CH_3), 21.3 (CH_3), 21.1 (CH_3). HRMS (FD, $[M]^+$) for $C_{31}H_{28}N$ calcd 414.2216; found 414.2213.

3,4-Bis(4-fluorophenyl)-6-methyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4as). Following the optimized procedure for the synthesis of quinolinium salts **4ap-4as** and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 4:96) to afford quinolinium salts **4as** as brown solid (66 mg, 43%). mp: 119-121 °C. IR (naet): 1604, 1509, 1371, 1346, 1268, 1228, 1163, 1056 (υ_{B-F}), 845, 819, 734 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.70 (s, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.65 (s, 1H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.36-7.30 (m, 4H), 7.07 (t, *J* = 8.5 Hz, 2H), 6.88 (t, *J* = 8.5 Hz, 2H), 2.48 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8 (d, *J* = 248.3 Hz, C), 162.3 (d, *J* = 247.1 Hz, C), 156.4 (C), 147.0 (*C*H), 141.9 (C), 140.9 (C), 137.6 (C), 137.3 (C), 136.7 (*C*H), 134.2 (C), 132.1 (d, *J* = 8.3 Hz, 2*C*H), 131.8 (d, *J* = 8.3 Hz, 2*C*H), 130.8 (2*C*H), 129.9 (d, *J* = 3.4 Hz, C), 129.6 (C), 129.3 (d, *J* = 3.5 Hz, C), 127.4 (*C*H), 126.2 (2*C*H), 119.5 (*C*H), 115.7 (d, *J* = 21.7 Hz, 2*C*H), 115.4 (d, *J* = 21.6 Hz, 2*C*H), 21.8 (CH_3), 21.4 (CH_3). HRMS (FAB, $[M]^+$) for $C_{29}H_{22}F_2N$ calcd 422.1715; found 422.1719.

Optimized condition for the synthesis of quinolinium salts 4at-4ay. To a solution of $CuCl_2$ (4.0 mg, 0.03 mmol), di-*p*-tolylamine (59.2 mg, 0.30 mmol), alkyne (0.60 mmol) and paraformaldehyde (9.9 mg, 0.33 mmol) in MeCN (2 mL), HBF_4 (0.40 mmol, 50% in water) was added under O_2 balloon. The resulting mixture was stirred at 20 °C for 1 h. Then, the reaction was diluted with CH_2Cl_2 (10 mL), filtered through celite pad, and washed three times with CH_2Cl_2 (3×20 mL). The combined filtrate was concentrated under vacuum and the residue was purified by chromatography using MeOH and CH_2Cl_2 as eluent to afford quinolinium salts **4at-4ay**.

3,6-Dimethyl-4-phenyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4at). Following the optimized procedure for the synthesis of quinolinium salts **4at-4ay** and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 4:96) to afford quinolinium salts **4at** as green solid (98 mg, 79%). mp: 88-90°C. IR (neat): 1526, 1508, 1373, 1340, 1271, 1056 (υ_{B-F}), 822, 763, 733, 705 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.89 (s, 1H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.59-7.56 (m, 5H), 7.49 (d, *J* = 9.0 Hz, 1H), 7.46-7.45 (m, 3H), 7.38 (d, *J* = 6.5 Hz, 2H), 2.48 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1 (C), 148.6 (*C*H), 141.9 (C), 140.4 (C), 137.2 (C), 136.7 (C), 135.9 (*C*H), 133.7 (C), 131.7 (C), 130.9 (2*C*H), 129.4 (*C*H), 129.4 (C), 128.9 (2*C*H), 128.2 (2*C*H), 126.9 (*C*H), 126.1 (2*C*H), 119.3 (*C*H), 21.8 (CH_3), 21.4 (CH_3), 18.1 (CH_3). HRMS (FAB, $[M]^+$) for $C_{24}H_{22}N$ calcd 324.1747; found 324.1745.

3-Ethyl-6-methyl-4-phenyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4au). Following the optimized procedure for the synthesis of quinolinium salts **4at-4ay** and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 4:96) to afford quinolinium salts **4au** as green solid (102 mg, 80%). mp: 94-96 °C. IR (neat): 3068, 2928, 1614, 1525, 1509, 1374, 1054 (υ_{B-F}), 821, 761, 733 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.85 (s, 1H), 7.66 (dd, *J* = 9.0, 1.5 Hz, 1H), 7.61-7.58 (m, 5H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.41-7.39 (m, 3H), 2.78 (q, *J* = 7.5 Hz, 2H), 2.49 (s, 3H), 2.42 (s, 3H), 1.15 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7 (C), 147.6 (*C*H), 141.8 (C), 140.5 (C), 137.2 (C), 136.8 (C), 136.7 (C), 136.1 (*C*H), 133.3 (C), 130.8 (2*C*H), 129.6 (C), 129.3 (*C*H), 128.7 (2*C*H), 128.2 (2*C*H), 126.9 (*C*H), 126.0 (2*C*H), 119.2 (*C*H), 24.5 (CH_2), 21.7 (CH_3), 21.4 (CH_3), 14.5 (CH_3). HRMS (FAB, $[M]^+$) for $C_{25}H_{24}N$ calcd 338.1903; found 338.1902

3-Cyclohexyl-6-methyl-4-phenyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4av). Following the optimized procedure for the synthesis of quinolinium salts **4at-4ay** and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 4:96) to afford quinolinium salts **4av** as green solid (116 mg, 81%). mp: 74-76 °C. IR (neat): 2923, 2853, 2364, 2345, 1525, 1508, 1267, 1055 (υ_{B-F}), 818, 767, 733 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.71 (s, 1H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.63-7.59 (m, 5H), 7.51-7.49 (m, 3H), 7.41-7.40 (m, 2H), 7.38 (s, 1H), 2.69-2.64 (m, 1H), 2.51 (s, 3H), 2.42 (s, 3H), 1.94-1.91 (m, 2H), 1.74-1.72 (m, 2H), 1.61-1.58 (m, 1H), 1.49-1.41 (m, 2H), 1.22-1.09 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6 (C), 145.7 (*C*H), 142.0 (C), 140.5 (C), 139.8 (C), 137.6 (C), 136.8 (C), 136.3 (*C*H), 133.4 (C), 130.9 (2*C*H), 129.9 (C), 129.3 (*C*H), 128.7 (2*C*H), 128.2 (2*C*H), 127.3 (*C*H), 126.1 (2*C*H), 119.4 (*C*H), 39.7 (*C*H), 33.6 ($2CH_2$), 26.4 ($2CH_2$), 25.4 (CH_2), 21.8 (CH_3), 21.4 (CH_3). HRMS (FD, $[M]^+$) for $C_{29}H_{30}N$ calcd 392.2373; found 392.2375.

3-Acetyl-6-methyl-4-phenyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4aw). Following the optimized procedure for the synthesis of quinolinium salts **4at-4ay** and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 4:96) to afford quinolinium salts **4aw** as brown solid (83 mg, 63%). mp: 113-115 °C. IR (neat): 1696 ($\upsilon_{C=O}$), 1653, 1615, 1507, 1372, 1235, 1057 (υ_{B-F}), 822 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.92 (s, 1H), 7.78 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.73 (s, 1H), 7.68-7.60 (m, 5H), 7.57-7.55 (m, 3H), 7.47 (d, *J* = 8.4 Hz, 2H), 2.51 (s, 3H), 2.49 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8 (*C*O), 156.7 (C), 146.9 (*C*H), 142.2 (C), 141.4 (C), 138.2 (C), 138.0 (*C*H), 137.2 (C), 133.5 (C), 133.0 (C), 130.9 (2*C*H), 130.6 (*C*H), 129.3 (2*C*H), 129.2 (C), 129.1 (2*C*H), 128.2 (*C*H), 126.1 (2*C*H), 119.8 (*C*H), 29.9 (CH_3), 21.9 (CH_3), 21.5 (CH_3). HRMS (FD, $[M]^+$) for $C_{25}H_{22}NO$ calcd 352.1696; found 352.1696.

3-(Methoxycarbonyl)-6-methyl-4-phenyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4ax). Following the optimized procedure for the synthesis of quinolinium salts **4at-4ay** and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford quinolinium salts **4ax** as brown solid (106 mg, 77%). mp: 233-235 °C. IR (neat): 1747, 1721 (υ $_{C=O}$), 1617, 1525, 1509, 1438, 1379, 1269, 1242, 1208 (υ $_{C-O}$), 1140, 1054 (υ $_{B-F}$), 823, 732, 716 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 9.39 (s, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.66-7.64 (m, 3H), 7.61-7.56 (m, 4H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.45 (dd, *J* = 7.5, 1.0 Hz, 2H), 3.69 (s, 3H), 2.52 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3 (*C*O), 161.0 (C), 148.2 (*C*H), 142.3 (C), 141.5 (C), 138.7 (*C*H), 138.6 (C), 137.2 (C), 133.5 (C), 131.0 (2*C*H), 130.1 (C), 129.5 (*C*H), 129.0 (*C*H), 128.2 (2*C*H), 128.1 (2*C*H), 126.1 (2*C*H), 123.8 (C), 119.8 (*C*H), 53.3 (*C*H_3), 21.9 (*C*H_3), 21.5 (*C*H_3). HRMS (FAB, $[M]^+$) for $C_{25}H_{22}NO_2$ calcd 368.1645; found 368.1646.

3-(Ethoxycarbonyl)-6-methyl-4-phenyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (4ay). Following the optimized procedure for the synthesis of quinolinium salts **4at-4ay** and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 4:96) to afford quinolinium salts **4ay** as brown solid (93 mg, 66%). mp: 162-164 °C. IR (neat): 1741, 1718 (υ $_{C=O}$), 1616, 1525, 1377, 1268, 1240, 1206 (υ $_{C-O}$), 1140, 1057 (υ $_{B-F}$), 824, 733 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 9.35 (s, 1H), 7.82 (dd, *J* = 9.0, 1.5 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.62 (s, 1H), 7.60-7.53 (m, 4H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.45 (dd, *J* = 8.0, 1.5 Hz, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 2.51 (s, 3H), 2.46 (s, 3H), 0.96 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0 (*C*O), 160.4 (C), 148.1 (*C*H), 142.2 (C), 141.5 (C), 138.7 (*C*H), 138.5 (C), 137.0 (C), 133.7 (C), 130.9 (2*C*H), 130.0 (C), 129.3 (*C*H), 128.7 (*C*H), 128.1 (2*C*H), 128.0 (2*C*H), 126.0 (2*C*H), 124.1 (C), 119.7 (*C*H), 62.5 (*C*H_2), 21.8 (*C*H_3), 21.4 (*C*H_3), 13.4 (*C*H_3). HRMS (FD, $[M]^+$) for $C_{26}H_{24}NO_2$ calcd 382.1802; found 382.1807.

Optimized condition for the synthesis of quinolinium salts 6b. To a solution of $CuCl_2$ (4.0 mg, 0.03 mmol), di-*p*-tolylamine (59.2 mg, 0.30 mmol), phenylacetylene (61.2 mg, 0.60 mmol) and valeraldehyde (50.4 mg, 0.4 mmol) in MeCN (2 mL), HBF_4 (0.40 mmol, 50% in water) was added under O_2 balloon. The resulting mixture was heated to 60 °C and stirred for 1 h. After cooling, the reaction was diluted with CH_2Cl_2 (10 mL), filtered through celite pad, and washed three times with CH_2Cl_2 (3×20 mL). The combined filtrate was concentrated under vacuum and the residue was purified by chromatography gel using MeOH and CH_2Cl_2 as eluent to afford quinolinium salts **6b**.

2-Butyl-6-methyl-1,4-di-*p*-tolylquinolin-1-ium tetrafluoroborate (6b). Following the optimized procedure for the synthesis of quinolinium salts **6b** and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 2:98) to afford quinolinium salts **6b** as black sticky solid (105 mg, 77%). mp: 57-59 °C. IR (naet): 2961, 2926, 1598, 1566, 1508, 1457, 1378, 1270, 1056 (υ $_{B-F}$), 822, 768, 704 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.79 (s, 1H), 7.68-7.66 (m, 2H), 7.62 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.59-7.58 (m, 3H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 9.0 Hz, 1H), 2.90 (t, *J* = 8.0 Hz, 2H), 2.52 (s, 3H), 2.46 (s, 3H), 1.71-1.65 (m, 2H), 1.30-1.23 (m, 2H), 0.77 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.1 (C), 158.4 (C), 142.0 (C), 139.9 (C), 139.7 (C), 136.4 (*C*H), 135.1 (C), 134.4 (C), 131.5 (2*C*H), 130.3 (*C*H), 129.5 (2*C*H), 129.0 (2*C*H), 127.0 (*C*H), 126.8 (C), 126.6 (2*C*H), 123.6 (*C*H), 120.3 (*C*H), 34.8 (*C*H_2), 30.8 (*C*H_2), 22.4 (*C*H_2), 21.4 (*C*H_3), 21.3 (*C*H_3), 13.3 (*C*H_3). HRMS (FAB, $[M]^+$) for $C_{27}H_{28}N$ calcd 366.2216; found 366.2214.

Optimized condition for the synthesis of quinolinium salts 6c-g. To a solution of $CuCl_2$ (4.0 mg, 0.03 mmol), di-*p*-tolylamine (59.2 mg, 0.30 mmol), phenylacetylene (40.8 mg, 0.40 mmol) and aldehyde (0.4 mmol) in MeCN (2 mL), HBF_4 (0.40 mmol, 50% in water) was added under O_2 balloon. The resulting mixture was heated to 60 °C and stirred for 24 h. After cooling, the reaction was diluted with CH_2Cl_2 (10 mL), filtered through celite pad, and washed three times with CH_2Cl_2 (3×20 mL). The combined filtrate was concentrated under vacuum and the residue was purified by chromatography on silica gel using MeOH and CH_2Cl_2 as eluent to afford quinolinium salts **6c-g**.

6-Methyl-4-phenyl-1,2-di-*p*-tolylquinolin-1-ium tetrafluoroborate (6c). Following the optimized procedure for the synthesis of quinolinium salts **6c-g** and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 6:94) to afford quinolinium salts **6c** as brown solid (71 mg, 48%). mp: 88-90 °C. IR (neat): 1610, 1592, 1560, 1509, 1494, 1388, 1365, 1266, 1050 (υ $_{B-F}$), 821, 769, 736, 704 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.81 (s, 1H), 7.72-7.69 (m, 3H), 7.59-7.58 (m, 3H), 7.40 (d, *J* = 9.0Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 2.51 (s, 3H), 2.39 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7 (C), 157.6 (C), 141.0 (C), 140.8 (C), 140.1 (C), 139.6 (C), 136.8 (*C*H), 135.2 (C), 135.1(C), 130.5 (2*C*H), 130.3 (*C*H), 129.9 (C), 129.6 (2*C*H), 129.5 (2*C*H), 129.1 (2*C*H), 128.9 (2*C*H), 127.8 (2*C*H), 127.5 (C), 127.1 (*C*H), 125.2 (*C*H), 120.4 (*C*H), 21.7 (*C*H_3), 21.4 (*C*H_3), 21.4 (*C*H_3). HRMS (FAB, $[M]^+$) for $C_{30}H_{26}N$ calcd 400.2060; found 400.2067.

2-(4-Bromophenyl)-6-methyl-4-phenyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (6d). Following the optimized procedure for the synthesis of quinolinium salts **6c-g** and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 6:94) to quinolinium salts **6d** as brown solid (73 mg, 44%). mp: 111-113 °C. IR (neat): 1592, 1560, 1507, 1492, 1386, 1365, 1057 (υ $_{B-F}$), 1011, 818, 769, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.76 (s, 1H), 7.72-7.67 (m, 3H), 7.57-7.55 (m, 3H), 7.40-7.36 (m, 7H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.50 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2 (C), 156.1 (C), 141.2 (C), 140.3 (C), 139.7 (C), 137.0 (*C*H), 135.0 (C), 135.0 (C), 131.8 (C), 131.5 (2*C*H), 131.1 (2*C*H), 130.6 (2*C*H), 130.3 (*C*H), 129.6 (2*C*H), 128.9 (2*C*H), 127.8 (C), 127.7 (2*C*H), 127.2 (*C*H), 125.1 (C), 124.9 (*C*H), 120.4 (*C*H), 21.7 (*C*H_3), 21.4 (*C*H_3). HRMS (FD, $[M]^+$) for $C_{29}H_{23}BrN$ calcd 464.1008; found 464.1003.

6-Methyl-4-phenyl-1-(*p*-tolyl)-2-(4-(trifluoromethyl)phenyl)quinolin-1-ium tetrafluoroborate (6e). Following the optimized procedure for the synthesis of quinolinium salts **6c-g** and purification by chromatography on silica gel (MeOH:CH_2Cl_2, 0:100 to 6:94) to quinolinium salts **6e** as brown solid (81 mg, 50%). mp: 110-112 °C. IR (neat): 1591, 1564, 1508, 1324, 1168, 1126, 1066 (υ $_{B-F}$), 1018, 850, 818, 771 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.76 (s, 1H), 7.72-7.68 (m, 3H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.59-7.54 (m, 3H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 9.0 Hz, 1H), 7.23 (d, *J* = 6.5 Hz, 2H), 2.49 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4 (C), 155.5 (C), 141.3 (C), 140.4 (C), 139.7 (C), 137.1 (*C*H), 136.4 (d, *J* = 1.3 Hz, C), 135.0 (C), 134.9 (C), 131.8 (q, *J* = 32.6 Hz, C), 130.6 (2*C*H), 130.3 (*C*H), 130.1 (2*C*H), 129.6 (2*C*H), 128.8 (2*C*H), 127.9 (C), 127.7 (2*C*H), 127.2 (*C*H), 125.1 (q, *J* = 3.7 Hz, 2*C*H), 124.8 (*C*H), 123.2 (q, *J* = 270.2 Hz, *C*F_3), 120.4 (*C*H), 21.7 (*C*H_3), 21.3 (*C*H_3). HRMS (FAB, $[M]^+$) for $C_{30}H_{23}F_3N$ calcd 454.1777; found 454.1786.

2-(3-Bromophenyl)-6-methyl-4-phenyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (6f). Following the optimized procedure

for the synthesis of quinolinium salts **6c-g** and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 6:94) to quinolinium salts **6f** as brown solid (61 mg, 37%). mp: 101-103 °C. IR (neat): 2926, 1685, 1568, 1506, 1440, 1418, 1314, 1288, 1262, 1068 (υ_{B-F}), 814, 748, 707 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.79 (s,1H), 7.73-7.70 (m, 3H), 7.58-7.57 (m, 3H), 7.55 (s, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.31-7.39 (m, 3H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 2.51 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ159.4 (C), 155.4 (C), 141.3 (C), 140.4 (C), 139.7 (C), 137.1 (*C*H), 135.0 (C), 134.9 (C), 134.6 (C), 133.2 (*C*H), 131.7 (*C*H), 130.5 (2*C*H), 130.3 (*C*H), 130.0 (*C*H), 129.6 (2*C*H), 128.9 (2*C*H), 128.6 (*C*H), 127.9 (C), 127.7 (2*C*H), 127.2 (*C*H), 124.7 (*C*H), 122.0 (C), 120.4 (*C*H), 21.8 (CH_3), 21.4 (CH_3). HRMS (FAB, $[M]^+$) for $C_{29}H_{23}BrN$ calcd 464.1008; found 464.1016.

6-Methyl-2-(2-nitrophenyl)-4-phenyl-1-(*p*-tolyl)quinolin-1-ium tetrafluoroborate (6g). Following the optimized procedure for the synthesis of quinolinium salts **6c-g** and purification by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 5:95) to quinolinium salts **6g** as reddish brown solid (51 mg, 33%). mp: 261-263 °C. IR (neat): 1590, 1564, 1527, 1507, 1380, 1366, 1345, 1267, 1056 (υ_{B-F}), 787, 772, 733 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.5, 1H), 8.01 (s, 1H), 7.76-7.72 (m, 5H), 7.63 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.6-7.57 (m, 4H), 7.32 (d, *J* = 9.0 Hz, 1H), 7.23 (d, *J* = 9.5 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.04 (dd, *J* = 8.0, 1.5 Hz, 1H), 2.53 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4 (C), 154.7 (C), 145.2 (C), 141.6 (C), 140.6 (C), 139.7 (C), 137.1 (*C*H), 135.0 (*C*H), 134.7 (C), 134.7 (C), 132.8 (*C*H), 131.8 (*C*H), 131.0 (*C*H), 130.3 (*C*H), 130.2 (*C*H), 129.6 (*C*H), 129.6 (*C*H), 128.8 (2*C*H), 128.3 (*C*H), 127.9 (C), 127.9 (C), 127.2 (*C*H), 124.7 (*C*H), 124.5 (*C*H), 123.0 (*C*H), 120.2 (*C*H), 21.7 (CH_3), 21.3 (CH_3). HRMS (FAB, $[M]^+$) for $C_{29}H_{23}N_2O_2$ calcd 431.1754; found 431.1755.

Synthesis of ynal 6-(p-tolyl)hex-5-ynal **3h** and 4-methyl-*N*-(2-oxoethyl)-*N*-(3-(*p*-tolyl)prop-2-yn-1-yl)benzenesulfonamide **3i** can be found in supporting information.

Synthesis of 7-Methyl-4,9-di-*p*-tolyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinolin-4-ium tetrafluoroborate (6h). To a solution of $CuCl_2$ (4.0 mg, 0.03 mmol) and di-*p*-tolylamine (59.2 mg, 0.30 mmol) in MeCN (1.0 mL), solution of 6-(p-tolyl)hex-5-ynal **3h** (74.5 mg, 0.40 mmol) in MeCN (1.0 mL) and HBF_4 (0.4 mmol, 50% in water) were added via syringe under O_2 balloon. The mixture was left stirring at 20 °C for 1 h. Then, the reaction was diluted with CH_2Cl_2 (10 mL), filtered through celite pad, and washed three times with CH_2Cl_2 (3×20 mL). The combined filtrate was concentrated under vacuum. The residue was purified by chromatography on silica gel ($MeOH:CH_2Cl_2$, 0:100 to 3:97) as eluent to afford quinolinium salt **6h** as green solid (126.6 mg, 94 %). mp: 102-104 °C. IR (neat): 1597, 1510, 1407, 1054 (υ_{B-F}), 813, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.52 (dd, *J* = 9.2, 1.0 Hz, 1H), 7.48-7.44 (m, 4H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 9.2 Hz, 1H), 3.13 (t, *J* = 7.2 Hz, 2H), 3.11 (t, *J* = 7.2 Hz, 2H), 2.49 (s, 3H), 2.46 (s, 3H), 2.41 (s, 3H), 2.24-2.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0 (C), 153.0 (C), 141.5 (C), 139.5 (C), 139.0 (C), 138.0 (C), 138.0 (C), 135.0 (*C*H), 134.6 (C), 131.2 (2*C*H), 130.7 (C), 129.3 (2*C*H), 128.5 (2*C*H), 128.0 (C), 126.7 (*C*H), 125.7 (2*C*H), 118.9 (*C*H), 34.9 (CH_2), 31.2 (CH_2), 22.6 (CH_2), 21.4 (CH_3), 21.4 (CH_3), 21.3 (CH_3). HRMS (FAB, $[M]^+$) for $C_{27}H_{26}N$ calcd 364.2060; found 364.2061.

Synthesis of 7-methyl-4,9-di-*p*-tolyl-4*H*-pyrrolo[3,4-*b*]quinoline (7a). To a solution of $CuCl_2$ (4.0 mg, 0.03 mmol) and di-*p*-tolylamine (59.2 mg, 0.30 mmol) in MeCN (1.0 mL), solution of 4-methyl-*N*-(2-oxoethyl)-*N*-(3-(*p*-tolyl)prop-2-yn-1-yl)benzenesulfonamide **3i** (136.6 mg, 0.4 mmol) in MeCN (1.0 mL) and HBF_4 (0.4 mmol, 50% in water) were added via syringe under O_2 balloon. The mixture was left stirring at 20 °C for 1 h. Then, the reaction was diluted with CH_2Cl_2 (10 mL), filtered through celite pad, and washed three times with CH_2Cl_2 (3×20 mL). The combined filtrate was concentrated under vacuum. The residue was purified by chromatography on alumina ($MeOH:CH_2Cl_2$, 0:100 to 2:98) to afford quinoline **7a** as purple solid (72 mg, 66 %). mp: 58-60 °C. IR (neat): 1605, 1570, 1560, 1509, 1456, 1364, 1252, 1159, 1134, 1020, 813, 732 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.73 (s,1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.37-7.35 (m, 3H), 7.15 (d, *J* = 8.8 Hz, 1H), 6.76 (s, 1H), 2.52 (s, 3H), 2.52 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4 (C), 139.5 (C), 139.2 (C), 137.3 (C), 136.7 (C), 133.8 (*C*H), 132.1 (C), 131.7 (C), 131.0 (2*C*H), 130.4 (C), 129.7 (2*C*H), 129.1 (2*C*H), 129.0 (*C*H), 128.1 (*C*H), 127.3 (2*C*H), 126.2 (C), 118.8 (C), 115.6 (*C*H), 109.7 (*C*H), 21.5 (CH_3), 21.4 (CH_3), 21.0 (CH_3). HRMS (FD, $[M]^+$) for $C_{26}H_{22}N_2$ calcd 362.1783; found 362.1771.

Synthesis of *N*,4-dimethyl-*N*-(*p*-tolyl)aniline (5a). Following the general procedure for the synthesis of quinolinium salts, reaction between di-*p*-tolylamine (59.2 mg, 0.30 mmol), phenylacetylene (30.6 mg, 0.30 mmol) and paraformaldehyde (12.0 mg, 0.40 mmol) were performed without copper under N_2 balloon. Purification by chromatography on silica gel (CH_2Cl_2) to afford **5a** as pale yellow liquid (27 mg, 43%). IR (neat): 1610, 1510, 1336 (υ_{C-N}), 1253 (υ_{C-N}), 1124, 1109, 871, 808, 722 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.0 Hz, 4H), 6.90 (d, *J* = 8.5 Hz, 4H), 3.25 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0 (2C), 130.4 (2C), 129.6 (4*C*H), 120.3 (4*C*H), 40.4 (CH_3), 20.5 (2CH_3). HRMS (EI, $[M]^+$) for $C_{15}H_{17}N$ calcd 211.1361; found 211.1356.

Synthesis of *N*-(3-Bromobenzylidene)-4-methyl-*N*-(*p*-tolyl)benzenaminium tetrafluoroborate (I-Tol-BrPh). A sealed tube fitted with a rubber septum was charged with and di-*p*-tolylamine (59.2 mg 0.30 mmol) and septum was secured with parafilm. Subsequently, 3-bromobenzaldehyde (55.5 mg, 0.30 mmol), $CHCl_3$ (0.5 mL), and HBF_4 (0.40 mmol, 50% in water) were added via syringe under an atmosphere of N_2. The mixture was left stirring at 60 °C for 3 h. The organic layer of the crude solution was collected. The recrystallization was performed with vapor diffusion of dried Et_2O into the crude solution. The precipitate was washed quickly with Et_2O several times to afford **I-Tol-BrPh** as moisture sensitive marigold solid (14 mg,13%). mp: 216-218 ºC. IR (neat): 2364, 2341, 1663, 1617, 1559, 1507, 1285, 1212, 1190, 1068 (υ_{B-F}), 1022, 817, 801, 733 cm^{-1}. ^1H NMR (500 MHz, CD_3CN) δ 9.20 (s, 1H), 7.89 (d, *J* = 7.0 Hz, 1H), 7.56 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.45-7.41 (m, 6H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.48 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, CD_3CN): δ 170.5 (*C*H), 144.6 (C), 144.3 (C), 143.5 (C), 140.9 (*C*H), 138.2 (C), 137.8 (*C*H), 134.3 (*C*H), 132.8 (2*C*H), 132.4 (*C*H), 131.7 (2*C*H), 130.7 (C), 126.3 (2*C*H), 124.6 (2*C*H), 123.6 (C), 21.5 (CH_3), 21.3 (*C*H_3). HRMS (FAB, $[M]^+$) for $C_{21}H_{19}BrN$ calcd 364.0695; found 364.0693.

Synthesis of 6-Methyl-4-phenyl-1-(*p*-tolyl)quinolin-2(1*H*)-one (8a). To an aqueous solution of $K_3[Fe(CN)_6]$ (469.2 mg 1.4 mmol, 0.2 M) in ice bath, an aqueous solution of KOH (319.8 mg, 5.7 mmol, 0.7 M) was added dropwise. Then, **4aa** (227.7 mg, 0.57 mmol) was added in portions to the mixture. The reaction was allowed to warm to room temperature and left stirring for 1 h. After that, the suspension was stirred at 60 ºC for 18 h. After cooling to room temperature, the reaction was partitioned with H_2O and CH_2Cl_2. The aqueous layer was extracted three times with CH_2Cl_2

(3×20 mL). The collected organic layer was concentrated under vacuum. Purification by chromatography on alumina (CH_2Cl_2) to afford **8a** as pale yellow liquid (120 mg, 64%). IR (neat): 1657 (υ C=O), 1590, 1559, 1511, 1305 (υ C-N), 874, 815, 776 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54-7.41 (m, 5H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.34 (s, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.14 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.73 (s, 1H), 6.67 (d, *J* = 8.8 Hz, 1H), 2.47 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (*C*O), 151.1 (C), 139.3 (C), 138.4 (C), 136.9 (C), 134.8 (C), 131.3 (C), 131.1 (*C*H), 130.6 (2*C*H), 128.5 (2*C*H), 128.4 (*C*H), 128.3 (2*C*H), 128.2 (2*C*H), 126.6 (*C*H), 121.4 (*C*H), 119.7 (C), 116.1 (*C*H), 21.3 (CH_3), 20.7 (CH_3). HRMS (FAB, $[M]^+$) for $C_{23}H_{19}NO$ calcd 325.1467; found 325.1466.

Computational detail:
The geometry optimizations zero-point vibrational energies (ZPVEs) were calculated using the B3LYP/6-31G** level of theory combined with the CPCM implicit solvation model to simulate acetonitrile. Singlet point energy calculations with B3LYP/6-311++G** were performed on the B3LYP/6-31G** optimized structures to obtain more accurate electronic energies. The energy discussed throughout the manuscript is enthalpy calculated as $H = E_{SCF} + ZPVE + H_{vib} + 4RT$. All the calculations were performed by using Gaussian 09.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aza-Diels-Alder reaction • quinolinium salts • distortion energy • energy decomposition analysis (EDA)

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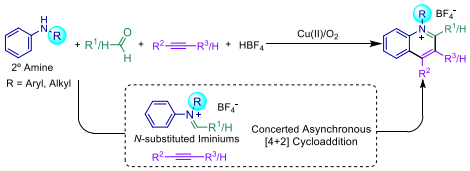
A^3 reaction with secondary aniline: Secondary anilines were first utilized in coupling with aldehydes, and alkynes to synthesize corresponding *N*-substituted quinolinium salts. DFT calculation was performed to understand the [4+2] cycloaddition mechanism and the singular regioselectivity of the reaction.



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Synthesis of Quinolinium Salts from *N*-Substituted Anilines, Aldehydes, Alkynes, and Acid: Theoretical Understanding of the Mechanism and Regioselectivity