Organic & Biomolecular Chemistry

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DOI: 10.1039/C5OB00823A

Journal Name

ARTICLE

Rhodium(III)-Catalyzed Cascade Oxidative Annulation Reactions of Aryl Imidazolium Salts with Alkynes involving Multiple C–H Bond Activation

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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The cascade oxidative annulation reactions of aryl imidazolium salts with alkynes proceed efficiently in the presence of $[Cp^*RhCl_2]_2$ and $Cu(OAc)_2·H_2O$ to give substituted imidazo[1,2-*a*]-quinolinium salts and benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salts. The reactions were through the normal and abnormal N-heterocyclic carbenes (NHCs)- directed cyclometalation, alkynes insertion into the Rh–C bond, and reductive elimination of alkenyl and NHC ligands. The reactions are highly regioselective with unsymmetrical alkynes and can be achieved stepwise by controlling the reaction conditions. This provides a new application of NHCs as directing groups and substrates in synthesis of fused N-heterocyclic compounds. The N-substituting group of the benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salts could be removed successfully with pyridine to afford benzo[ij]imidazo[2,1,5-de]quinolizines in excellent yields. Moreover, some of the benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salts exhibit intense fluorescence which might be useful in organic electronic materials.

Introduction

N-heterocyclic carbenes (NHCs) have been extensively used as ligands in transition metal catalysis and organometallic chemistry due to their σ-electron-donating capability and steric effects.[1] Typical transition-metal NHC complexes show "normal" binding at C2 position of the imidazole ring.[2] Crabtree and co-workers firstly reported an "abnormal" NHC (*a*NHC) complex in which the metalation is at the C5 position of the NHC ring.[3] Blocking C2 position with a substituent, such as Me or Ph group, will also encourage bonding in the C5 position.[4] The Achilles' heel in (NHC)M-catalyzed reactions is the tendency for NHC reductive elimination to the imidazolium salt $[NHC\text{-}R]^+$.[5] Reductive elimination is a key step of transition metal catalyzed C–C or C–heteroatom coupling reactions. Generally, it involves two anionic ligands and hence reductive elimination of a neutral molecule. If the reductive elimination is from an anionic and a neutral ligand such as NHC, the product is a salt. As a major catalyst decomposition pathway for NHC transition metal complexes, the reductive eliminations of alkyl, aryl, or acyl transition metal–NHC complexes have been much studied.[2,6-8] However, most works about NHCs and *a*NHCs have focused on their mechanism and prevention of reductive elimination. There are only a few reports on annulation reactions of NHC or *a*NHC-based cyclometalated complexes, and there are rare reports about transition-mental catalyzed C–H bond activation reaction from NHCs or imidazolium salts.[9] More recently, the direct C–H activation of non-NHC based (hetero)arene substrates without the coordination assistance from directing group has attracted growing attention.[10] For example, Miura[10a,10e,10g] and Chen[10b,10d] have developed Rh(III)-catalyzed C–H activation to synthesize polycyclic aromatics. Hua[10f] and co-workers reported synthesis of multisubstituted 2-aminoquinolines via Rh(III)-catalyzed annulation reaction between tetrazoles and internal alkynes. Significantly, the structures of imidazo[1,2-*a*]-quinolinium and benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium moieties are similar to aza-fused heterocyclic frameworks such as imidazophenanthridinium (IPs) and dihydroimidazophenanthridinium derivatives (DIPs) (Chart 1) which exist in many compounds that express diverse physical, chemical, and biological properties.[11,12,13] Additionally, these molecules with extended conjugated π-systems display fluorescence property which might be useful in organic electronic materials.[14]

On the basis of our previous work on NHC complexes[15] and transition-metal-catalyzed C–H bond activation processes,[16] we devote to explore the synthesis of polyheteroaromatic

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† Electronic Supplementary Information (ESI) available: For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x

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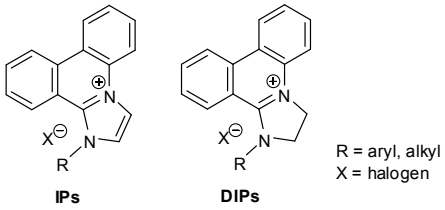
compounds through double or multiple C–H bond activation and annulation. Herein, we report an efficient Rh(III)-catalyzed C–H bond activation and annulation reaction from aryl imidazolium salts and alkynes with the normal and abnormal NHCs as directing groups leading to imidazo[1,2-*a*]quinolinium salts and benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salts. During the preparation of our manuscript, Choudhury reported a similar work.[17] Different from our conditions, AgOTf was used in their system and all products contained TfO^- as the anion. But in our cases the chloride anion of aryl imidazolium salts was remained in the final products. A different catalytic intermediate was isolated and characterized by us. Furthermore, we also demonstrated that two different alkynes could be introduced in the annulation reaction and the *N*-substituent at the benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salts could be removed successfully with pyridine to afford benzo[ij]imidazo[2,1,5-de]quinolizines in excellent yields.

Chart 1.



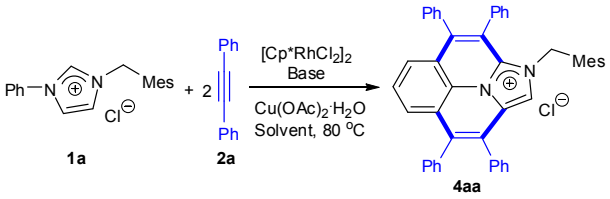
IPs DIPs

Results and discussion

Our study began by investigating the potential reaction of phenylimidazolium salt **1a** and diphenylacetylene **2a** to form benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salt **4aa** in which two alkyne units were incorporated. As shown in Table 1, treatment of **1a** (0.2 mmol) with diphenylacetylene (**2a**, 0.4 mmol) in the presence of $[Cp^*RhCl_2]_2$ (5 mol %), $Cu(OAc)_2{\cdot}H_2O$ (0.8 mmol), and Cs_2CO_3 (0.8 mmol) in *t*-AmOH (2 mL) at 80 °C for 12 h led to the desired product **4aa** in 88% yield (Table 1, entry 2). Compound **4aa** was characterized by ^1H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry (HRMS). The reaction also could proceed in CH_3CN (Table 1, entry 4). But only trace of the annulation product was observed when *t*-AmOH was replaced by MeOH or CH_2Cl_2 (Table 1, entries 1 and 3). Moreover, the reaction could proceed smoothly without any bases (Table 1, entry 5). Pleasingly, when the amount of **1a** was increased slightly, the reaction completed in 4 h with 96% yield (Table 1, entries 8 and 10). The yields had tiny reduction owing to the reduced amount of catalyst (Table 1, entry 9). When the reaction was carried out in the absence of the rhodium catalyst or oxidant, no product was observed (Table 1, entries 6 and 7). Finally, we chose 5 mol % of $[Cp^*RhCl_2]_2$ and 0.8 mmol of $Cu(OAc)_2{\cdot}H_2O$ in *t*-AmOH (2 mL) at 80 °C under argon as the standard reaction conditions.

With the optimal reaction conditions established, various substituted phenylimidazolium salts **1a–j** were treated with diphenylacetylene (**2a**) to give the corresponding products **4** in great yields (Table 2). When the substituents were located at the *para* position of the phenyl imidazolium moiety, 4-fluoro, 4-chloro, and 4-bromophenyl imidazolium salts **1b–d** afforded benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salts **4ba–da** in good yields (76–85%). 4-Methyl, 4-*tert*-butyl substituted and electron-rich substrates **1e–h** reacted nicely with **2a** to give the corresponding products **4ea–ha** in excellent yields (80–97%). In contrast, electron-withdrawing 4-nitrophenyl imidazolium salt **1i** provided **4ia** only in 53% yield. *N*-Phenyl and *N*-methyl substituted imidazolium substrates **1j** and **1l** also could provide the corresponding products (**4ja** and **4la**) in good yields. Aside from **2a**, other symmetrical alkynes were also tested for the present reaction. Gratifyingly, substituted diphenylacetylenes both with electron-rich or electron-deficient groups could give high yields (87–99%). 3-Hexyne could react with **1a** to give the expected product, however, the pure compound could not be isolate mainly from the one molecule of alkyne annulation by-product by column chromatography or recrystallization. Surprisingly, 1-phenyl-1-propyne (**2i**) and 1-phenyl-1-butyne (**2j**) provided single regioisomeric products of **4ai** and **4aj** in high yields, respectively. The structure of **4aj** was confirmed by single-crystal X-ray diffraction analysis (Figure 1). It was regrettable that phenylacetylene could not react with phenylimidazolium salt **1a** to produce the expected product.

Table 1. Optimization of reaction conditions [a]



1a 2a 4aa

Entry	Equiv of **1a**	Base	Solvent	Yields[b] (%)
1	1	Cs_2CO_3	MeOH	trace
2	1	Cs_2CO_3	*t*-AmOH	88%
3	1	Cs_2CO_3	CH_2Cl_2	trace
4	1	Cs_2CO_3	CH_3CN	87%
5	1	-	*t*-AmOH	87%
6[c]	1	-	*t*-AmOH	N.D.
7[d]	1	-	*t*-AmOH	N.D
8	1.1	-	*t*-AmOH	96%
9[e]	1.1	-	*t*-AmOH	93%
10[f]	1.1	-	***t*-AmOH**	**96%**

[a]Reaction conditions: **1a**, **2a** (0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (0.8 mmol, 4.0 equiv), Base (0.8 mmol, 4.0 equiv), solvent (2 mL), 80 °C, under Ar atmosphere, for 12 h. [b]Isolated yield. [c]Without $[Cp^*RhCl_2]_2$. [d]Without $Cu(OAc){\cdot}H_2O$. [e]$[Cp^*RhCl_2]_2$ (2.5 mol%). [f]Reaction time 4 h. N.D.= no detected.

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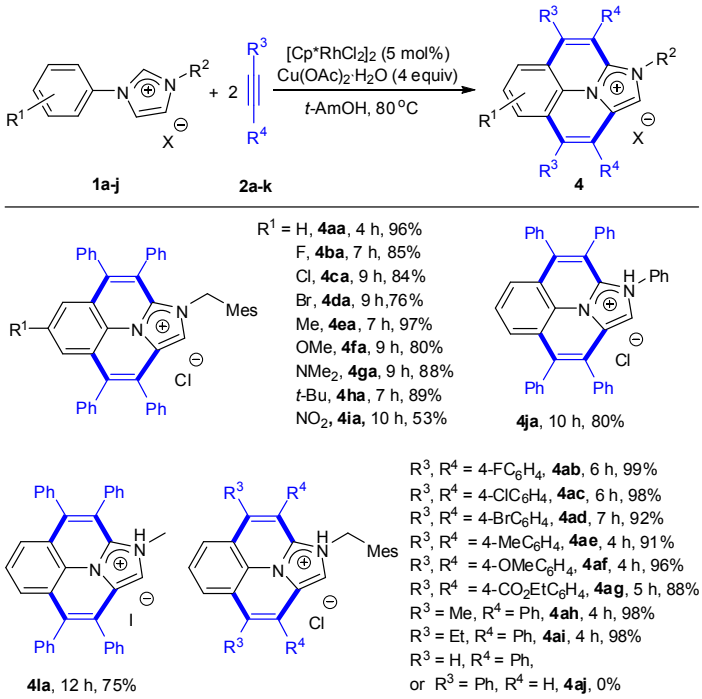
Table 2. Substrate scope of rhodium-catalyzed cascade oxidative annulation with alkynes [a,b]



[a]Reaction conditions: **1** (0.22 mmol, 1.1 equiv), **2** (0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol %), $Cu(OAc)_2{\cdot}H_2O$ (0.8 mmol, 4.0 equiv), *t*-AmOH (2.0 mL), 80 °C, Ar atmosphere, TLC monitored. [b]Isolated yields are given.

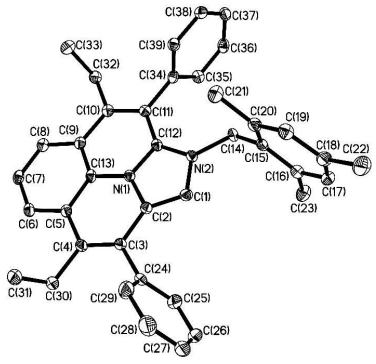


Figure 1. Molecular structure of **4ai**.

To further demonstrate the efficiency and practicality of this cascade reaction, a scale-up reaction was performed. Thus, gram-scale synthesis of **4aa** was achieved in 76% yield.

In addition, when reducing by half the amount of $[Cp^*RhCl_2]_2$ and $Cu(OAc)_2{\cdot}H_2O$, **1a** underwent the oxidative annulation reaction with one molecule of diphenylacetylene **2a** in MeOH leading to imidazo[1,2-*a*]-quinolinium salt **3aa**. The scope of the imidazolium salts and alkynes for the reaction to form imidazo[1,2-*a*]-quinolinium salts was next briefly explored (Table 3). It was found that substituted phenylimidazolium salts bearing electron-rich and electron-deficient groups were fully tolerated in this transformation, and the corresponding products were isolated in good to high yields (**3aa–ia**). *N*-Phenyl substituted imidazolium substrate **1j** also could provide the corresponding product (**3ja**) in good yield. Benzimidazolium substrate **1k** provided **3ka** in 91% yield. And the alkyne substrates **2b–j** also smoothly completed the reaction in excellent yields (88–98%). Similarly, 1-phenyl-1-propyne (**2i**) and 1-phenyl-1-butyne (**2j**) provided single regioisomeric products. As expected, the imidazo[1,2-*a*]-quinolinium salts **3** could further react with one molecule of alkyne to form benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salts **4** (Scheme 1a). If the second alkynes are different from **2a**, e.g. 1,2-di-p-tolylacetylene and 1,2-bis(4-methoxyphenyl)acetylene, the annulation products **4aae** and **4aaf** with two different alkynes were obtained in nearly quantitative yields. Following this line, 2-methyl imidazolium salt **1m** could react with diphenylacetylene to form the desired product **4ma** (Scheme 1b).

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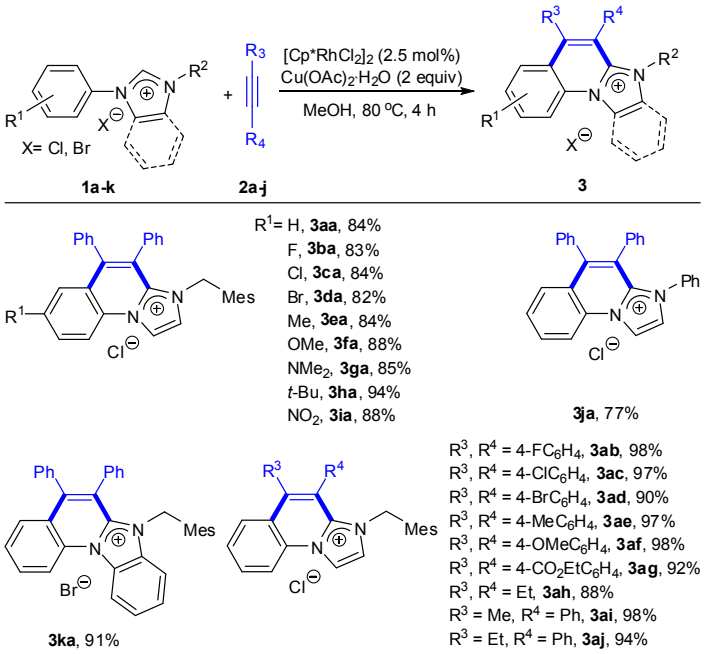
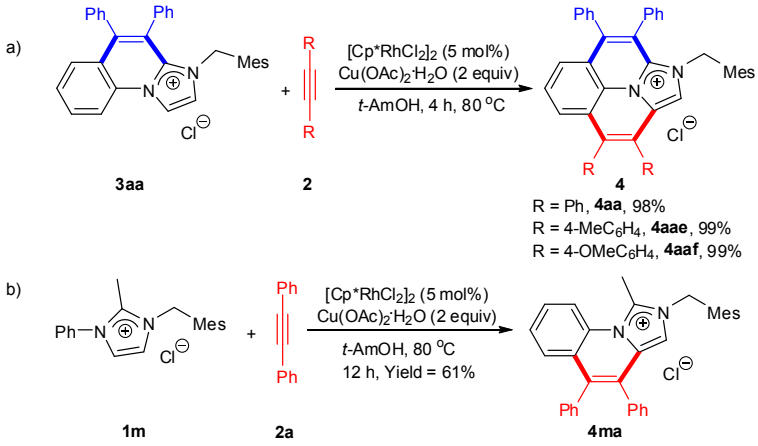
Table 3. Substrate scope of rhodium-catalyzed 1:1 oxidative annulation with alkynes [a,b]



[a]Reaction conditions: **1** (0.2 mmol, 1.0 equiv), **2** (0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (2.5 mol %), $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol, 2.0 equiv), MeOH (2.0 mL), 80 °C, Ar atmosphere. [b]Isolated yields are given.



Scheme 1. *a*NHCs-directed C-H bond activation and annulation reactions

To gain more insight into the mechanism of this reaction, the rhodacycle intermediates **A** and **B** were isolated by the reactions of **1a** and **3aa** with $[Cp^*RhCl_2]_2$ and NaOAc, respectively (Schemes 2a and 3a). They have been fully characterized by ^1H and ^{13}C NMR spectra and HRMS. The structure of intermediate **B** was further confirmed by single-crystal X-ray diffraction analysis (Figure 2). The stoichiometric reactions of **A** and **B** with **2a** at 80 °C were performed and the final products **3aa** and **4aa** were obtained in 74% and 53% yields, respectively (Schemes 2b and 3b). Then **A** and **B** were used as the catalyst instead of $[Cp^*RhCl_2]_2$ in the reactions of **1a** and **3aa** with **2a** under the standard reaction conditions to form **3aa** and **4aa** in 92% and 97% yields, respectively (Schemes 2c and 3c).

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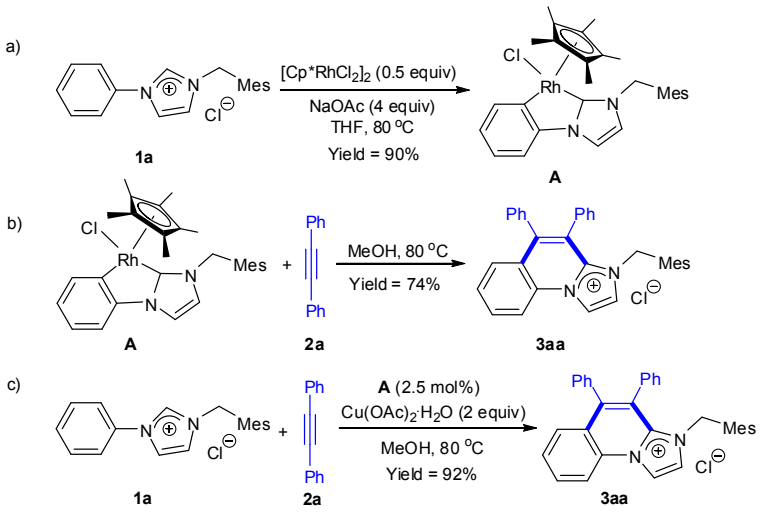
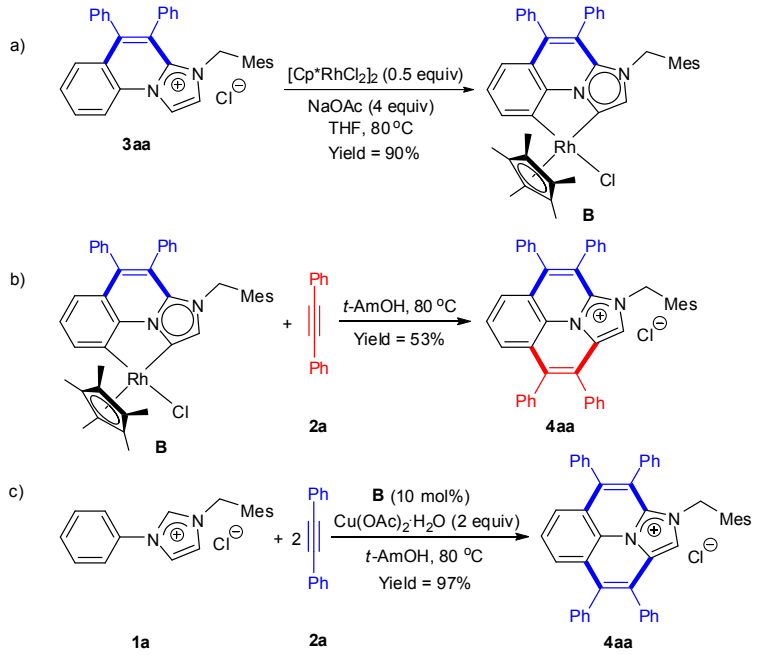


Scheme 2. Synthesis of the intermediate **A** and its use as either the reactant or catalyst in the annulation reaction



Scheme 3. Synthesis of the intermediate **B** and its use as either the reactant or catalyst in the annulation reaction

To afford the structurally diverse neutral compounds, we tried to remove the trimethylbenzyl group from the benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salts. Upon treatment of **4aa** in pyridine at 140 °C,[20e,20f,25] the corresponding benzo[*ij*]imidazo[2,1,5-*de*]quinolizine **5aa** was obtained in 99% yields (Table 4). According to this method, we obtained various benzo[*ij*]imidazo[2,1,5-*de*]quinolizine **5** with diverse substituent patterns incorporated and demonstrated the high-throughput of the methodology.

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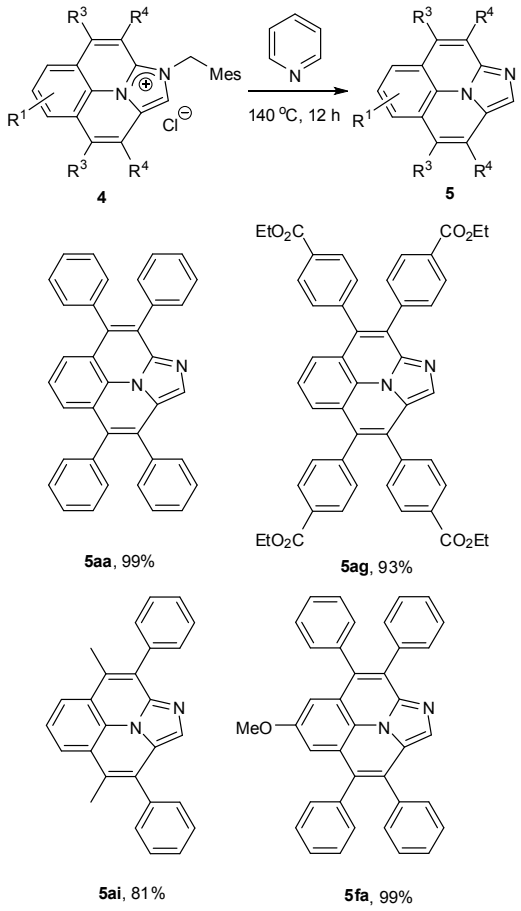
Table 4. Deionization of benzo[ij]imidazo[2,1,5-*de*]quinolizinium salts



[a]Reaction conditions: **4** (0.1 mmol), pyridine (1.0 mL), 140 °C. [b]Isolated yields are given.

Most of the benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salts **4** obtained above exhibited intense fluorescence in a range of 470–479 nm (Figure 3). Notably, **4ag** was found to exhibit the most intense luminescence (λ_{emis} = 479 nm), and the intensity of **4ag** was almost seven times stronger than that of benzo[*ij*]imidazo[2,1,5-*de*]quinolizine **5ag**, and was much stronger than the intensity of tris(8-quinolinolato)aluminum (**Alq3**) in the preliminary estimation. The molecular structure of **4ai** (Figure 1) shows that the cyclic framework is coplanar with the mean deviation of 0.0171 Å from the plane. The presence of *N*-substituent in the benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salts **4** has important effect on the luminescence property by increasing the donor-accepter effect. The electron-donor group at the *N*-phenyl ring and the electron-withdrawing group at the phenyl ring of the diarylacetylene unit may also increase the donor-accepter effect and the luminescence intensity.

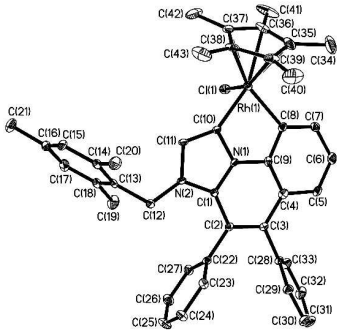


Figure 2. Molecular structure of intermediate **B**.

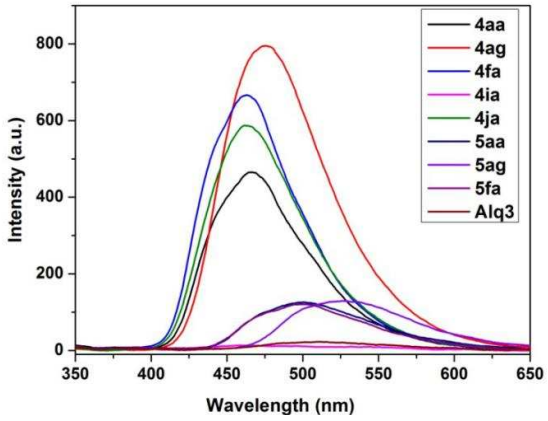


Figure 3. Fluorescence spectra of selected compounds **4**, **5**, and Alq3 at a concentration of 1×10^{-5} M in CH_2Cl_2.

Moreover, we tested a series of kinetic isotope effect (KIE) experiments shown in the Scheme 5. For the annulation reaction with one molecule of alkyne to form **3**, the k_H/k_D value of ~1.2 indicated that cleavage of the C–H bond of the phenyl ring, in which normal NHC acted as directing group, was not involved in the rate-determining step (Scheme 4a). Interestingly, the KIE experiments for the cascade reaction and the second step reaction gave different results. The k_H/k_D values of ~6.7 and ~2.8 indicated that cleavage of the C–H bond of the phenyl ring, in which abnormal NHC participated as directing group, was involved in the rate-determining step (Scheme 4b and 4c).[18]

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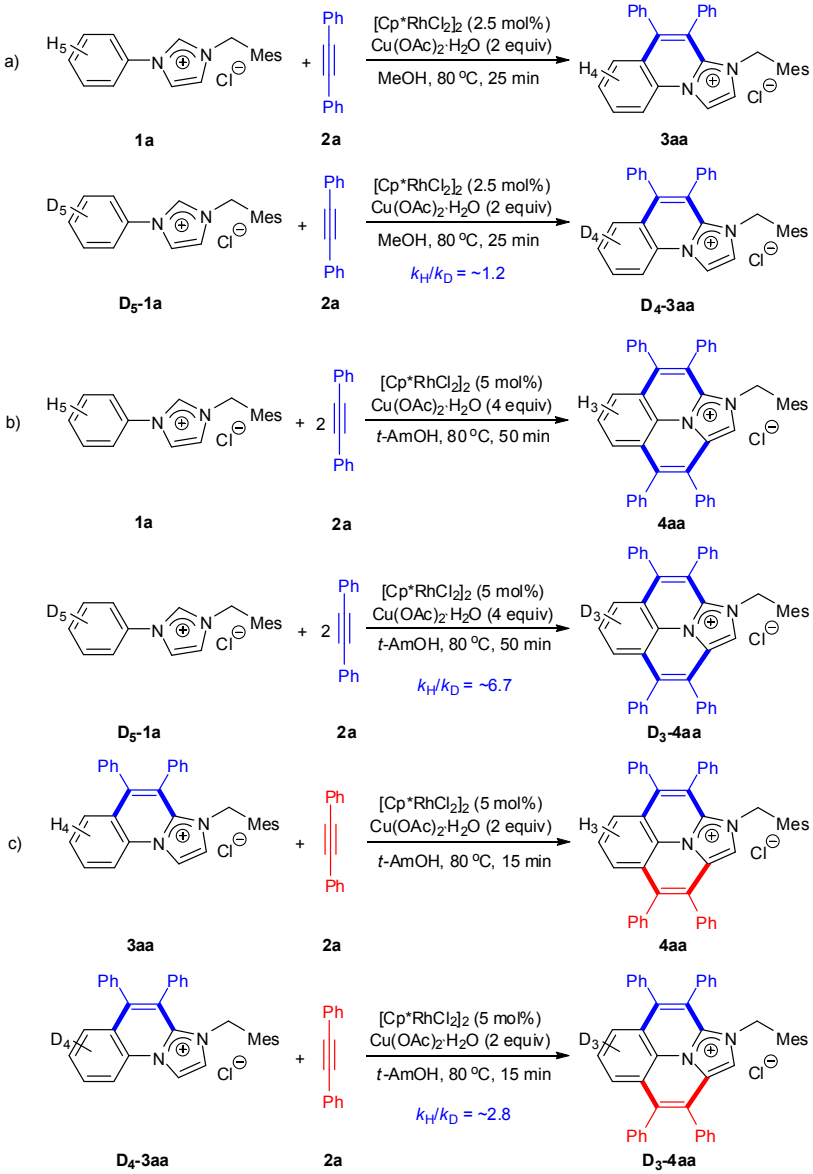

Scheme 4. Kinetic isotope effect experiments

Based on the above experimental results and the relating references,[19,20] a possible mechanism is proposed for the present catalytic reaction (Figure 4). The first step is likely to be a C–H bond activation process thus affording the five-membered cyclometalated intermediate **A**. Then an alkyne coordinates following by inserting the coordinated alkyne into the Rh–C bond to give the seven-membered rhodacycle **I** or **I'**. Then, **I** or **I'** reacts with $Cu(OAc)_2 \cdot H_2O$ and HCl to give **3** and

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regenerates the rhodium(III) species. Compound **3** continuously proceeded C–H bond activation affording the cyclometalated intermediate **B**. Similar to **A**, the alkyne coordinates and inserts to generate **II** or **II'**. Subsequent reductive elimination from **II** or **II'** affords the annulation product **4** and the rhodium(III) species which continues the catalytic cycle.

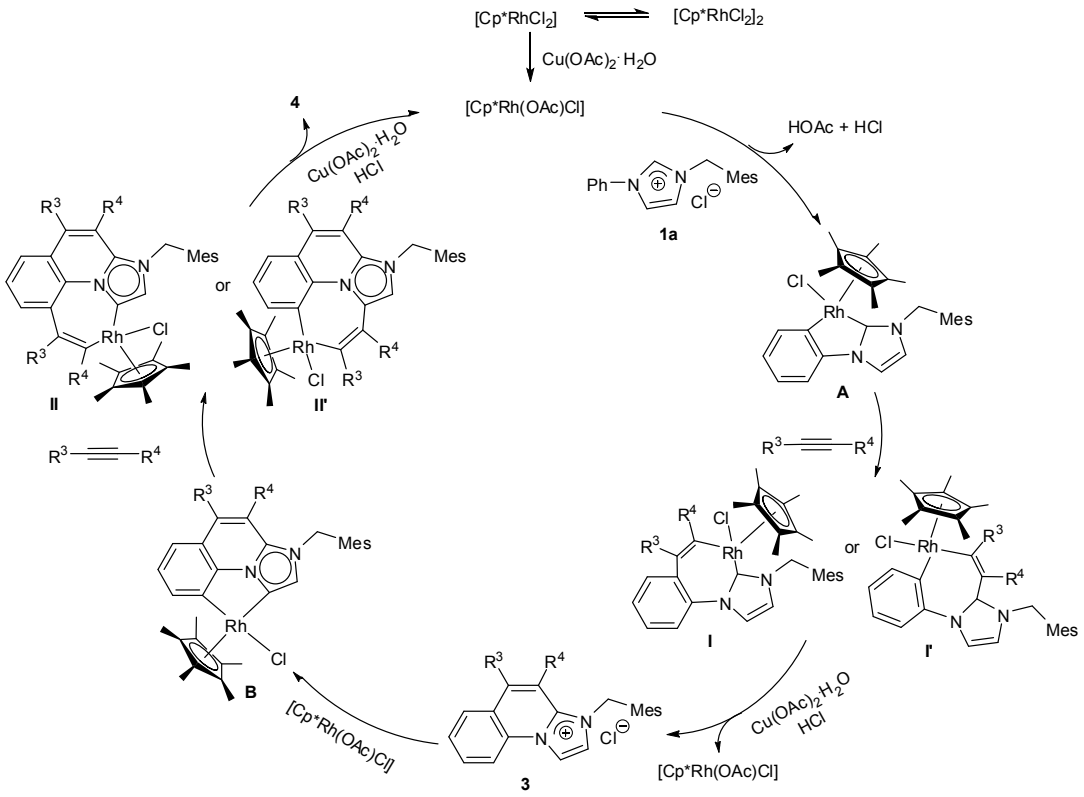

Figure 4. Proposed mechanistic pathway of the annulation reaction.

Conclusions

In conclusion, we have successfully developed a new method for efficient synthesis of imidazo[1,2-*a*]quinolinium salts and benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salts via rhodium(III)-catalyzed cascade oxidative annulation reaction of aryl imidazolium salts with alkynes, in which normal and abnormal NHCs participated as directing group in C–H bond activation. The reactions are highly regioselective with unsymmetrical alkynes and can be achieved stepwise by controlling the reaction conditions. Notably, two catalytically competent five-membered rhodacycles have been characterized, thus revealing two key active species in the catalytic cycle. This provides a new application of NHCs as directing groups and substrates in synthesis of fused N-heterocyclic compounds. The N-substituting group of the benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salts could be removed successfully with pyridine to afford benzo[ij]imidazo[2,1,5-de]quinolizines in excellent yields. Moreover, some of the benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salts exhibit intense fluorescence which might be useful in organic electronic materials. Further investigations and applications on the catalytic reactions of the aryl-substituted imidazolium salts with alkynes are currently underway in our laboratory.

Experimental

General Information

All the reactions were carried out under argon atmosphere using standard Schlenk technique. ^{1}H NMR (400 MHz), ^{19}F (376 M Hz), and ^{13}C NMR (101 MHz) were recorded on a NMR spectrometer with DMSO-d_6 and $CDCl_3$ as solvent. Column chromatography was performed on silica gel 200–300 mesh or alumina 200–300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. IR spectra were recorded as KBr disks on a FT-IR spectrometer. High-resolution mass spectrometry (HRMS) was done on a FTICR-mass spectrometer. $[Cp^*RhCl_2]_2$ was prepared

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from $RhCl_3 \cdot xH_2O$ following a literature procedure.[21] The *N*-arylimidazoles,[22] 1,3-diphenylimidazolium chloride,[23] and arylimidazolium salts[15d,24] were prepared following the literature procedures. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available without any further purification.

General procedure for Rh(III)-catalyzed oxidative annulation

Reaction of aryl imidazolium salts with one molecule of alkynes.

A mixture of substituted arylimidazolium salts **1** (0.2 mmol, 1.0 equiv.), alkyne **2** (0.2 mmol, 1.0 equiv.), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), and $Cu(OAc)_2 \cdot H_2O$ (80.0 mg, 0.4 mmol, 2.0 equiv,) were weighted in a Schlenk tube equipped with a stir bar. Dry MeOH (2.0 mL) was added and the mixture was stirred at 80 °C for 4 h under Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was absorbed onto a small amount of alumina. Products **3** were isolated by column chromatography on an alumina using CH_2Cl_2/MeOH (50/1) as eluant.

4,5-Diphenyl-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3aa)

White solid, 82.3 mg (84%). M.p.: 184 – 185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.73 (s, 1H), 9.38 (d, *J* = 8.5 Hz, 1H), 7.99 (t, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.28 (m, 8H), 7.17 – 7.12 (m, 2H), 7.02 (s, 1H), 6.88 (s, 2H), 4.50 (s, 2H), 2.26 (s, 3H), 2.04 (s, 6H). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.32 (s, 1H), 8.91 (d, *J* = 8.5 Hz, 1H), 8.09 (t, *J* = 7.0 Hz, 1H), 7.79 (t, *J* = 6.5 Hz, 1H), 7.57 (d, *J* = 6.1 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 20.2 Hz, 7H), 7.25 (d, *J* = 6.0 Hz, 2H), 6.96 (s, 2H), 4.45 (s, 2H), 2.24 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.0, 138.9, 138.2, 136.7, 134.4, 132.7, 131.9, 131.0, 130.5, 129.7, 129.4, 129.2, 128.4, 128.2, 128.1, 125.7, 123.8, 123.5, 123.4, 117.0, 114.5, 47.7, 20.6, 19.0. HRMS (ESI) *m/z* Calcd for $C_{33}H_{29}N_2$ $[M\text{-}Cl]^+$ 453.2331, found 453.2322. IR (cm^{-1}) ν 3014, 2859, 1603, 1548, 1491, 1442, 1349, 1231, 1137, 1030, 851, 754, 702.

7-Fluoro-4,5-diphenyl-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3ba)

White solid, 84.0 mg (83%). M.p.: 207 – 208 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.35 (s, 1H), 9.04 (dd, *J* = 9.1, 4.2 Hz, 1H), 8.07 (td, *J* = 9.3, 2.8 Hz, 1H), 7.57 (d, *J* = 6.6 Hz, 2H), 7.44 – 7.33 (m, 7H), 7.28 – 7.23 (m, 2H), 7.08 (dd, *J* = 9.5, 2.7 Hz, 1H), 6.96 (s, 2H), 4.44 (s, 2H), 2.24 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ161.5, 159.0, 144.2, 139.0, 138.2, 136.5, 133.9, 132.5, 130.8, 129.6, 129.4, 129.3, 128.4, 128.2, 127.4, 125.5, 124.7, 123.6, 120.6, 120.4, 120.2, 120.1, 114.8, 112.7 ($J_{C\text{-}F}$ = 24.4 Hz), 47.7, 20.6, 19.0. ^{19}F NMR (DMSO-d_6) δ –111.2 (s). HRMS (ESI) *m/z* Calcd for $C_{33}H_{28}FN_2$ $[M\text{-}Cl]^+$ 471.2237, found 471.2234. IR (cm^{-1}) ν 3016, 2859, 1613, 1549, 1488, 1442, 1379, 1277, 1214, 1178, 850,759, 728, 701.

7-Chloro-4,5-diphenyl-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3ca)

White solid, 88.0 mg (84%). M.p.: 209 – 210 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.34 (d, *J* = 2.5 Hz, 1H), 8.99 (d, *J* = 9.2 Hz, 1H), 8.20 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.56 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.41 (dd, *J* = 12.5, 5.0 Hz, 5H), 7.37 – 7.34 (m, 3H), 7.28 – 7.24 (m, 2H), 6.97 (s, 2H), 4.45 (s, 2H), 2.25 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.9, 139.0, 138.1, 136.6, 133.7, 132.5, 132.3, 131.8, 130.8, 129.6, 129.3, 128.5, 128.2, 126.8, 125.4, 125.2, 124.8, 123.7, 119.3, 114.7, 47.7, 20.5, 18.9. HRMS (ESI) *m/z* Calcd for $C_{33}H_{28}ClN_2$ $[M\text{-}Cl]^+$ 487.1941, found 487.1931. IR (cm^{-1}) ν 3006, 2859, 1607, 1541, 1487, 1442, 1351, 1220, 1140, 825, 760, 704.

7-Bromo-4,5-diphenyl-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3da)

White solid, 93.4 mg (82%). M.p.: 215 – 216 °C. ^{1}H NMR (DMSO-d_6,, 400 MHz) δ 9.34 (d, *J* = 2.4 Hz, 1H), 8.92 (d, *J* = 9.1 Hz, 1H), 8.30 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.55 (d, *J* = 6.5 Hz, 2H), 7.49 (d, *J* = 2.1 Hz, 1H), 7.44 – 7.33 (m, 7H), 7.28 – 7.23 (m, 2H), 6.96 (s, 2H), 4.44 (s, 2H), 2.24 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.8, 139.0, 138.2, 136.7, 134.5, 133.8, 132.4, 130.8, 129.9 129.7, 129.6, 129.4, 128.5, 128.3, 125.5, 124.8, 123.7, 120.8, 119.5, 114.7, 47.8, 20.6, 19.0. HRMS (ESI) *m/z* Calcd for $C_{33}H_{28}BrN_2$ $[M\text{-}Cl]^+$ 531.1436, found 531.1425. IR (cm^{-1}) ν 3003, 2859, 1605, 1538, 1487, 1442, 1352, 1216, 1139, 1029, 823, 759, 703.

7-Methyl-4,5-diphenyl-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3ea)

White solid, 84.4 mg (84%). M.p.: 200 – 201 °C.^{1}H NMR (DMSO-d_6,, 400 MHz) δ 9.34 (d, *J* = 2.1 Hz, 1H), 8.86 (d, *J* = 8.7 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.57 (d, *J* = 6.9 Hz, 2H), 7.42 – 7.32 (m, 6H), 7.30 – 7.21 (m, 4H), 6.96 (s, 2H), 4.44 (s, 2H), 2.42 (s, 3H), 2.24 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.0, 139.1, 138.3, 138.0, 136.5, 134.5, 133.5, 132.9, 131.1, 129.8, 129.5, 129.3, 128.8, 128.3, 128.2, 127.5, 125.8, 123.9, 123.5, 123.4, 116.9, 114.2, 47.70, 21.0, 20.9, 19.1. HRMS (ESI) *m/z* Calcd for $C_{34}H_{31}N_2$ $[M\text{-}Cl]^+$ 467.2487, found 467.2484. IR (cm^{-1}) ν 3017, 2857, 1606, 1549, 1488, 1442, 1354, 1234, 1139, 1031, 822, 758, 700.

7-Methoxy-4,5-diphenyl-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3fa)

White solid, 91.1 mg (88%). M.p.: 192 – 193 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.32 (s, 1H), 8.91 (d, *J* = 9.3 Hz, 1H), 7.75 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.58 (d, *J* = 7.4 Hz, 2H), 7.37 (dt, *J* = 7.1, 6.0 Hz, 6H), 7.29 – 7.24 (m, 3H), 6.96 (s, 2H), 6.76 (d, *J* = 2.5 Hz, 1H), 4.43 (s, 2H), 3.73 (s, 3H), 2.24 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.0, 139.1, 138.3, 138.0, 136.5, 134.5, 133.5, 132.97, 131.1, 129.8, 129.5, 129.3, 128.8, 128.3, 128.2, 127.5, 125.8 123.9, 123.5, 123.4, 116.9, 114.2, 47.7, 21.0, 20.7, 19.1. HRMS (ESI) *m/z* Calcd for $C_{34}H_{31}N_2O$ $[M\text{-}Cl]^+$ 483.2436, found 483.2434. IR (cm^{-1}) ν 3017, 2859, 1734, 1614, 1550, 1488, 1442, 1379, 1278, 1178, 1030, 823, 728, 702.

7-(Dimethylamino)-4,5-diphenyl-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3ga)

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DOI: 10.1039/C5OB00823A

White solid, 90.8 mg (85%). M.p.: 156 – 157 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.20 (d, J = 2.2 Hz, 1H), 8.71 (d, J = 9.4 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.41 – 7.31 (m, 6H), 7.25 (d, J = 6.9 Hz, 2H), 7.20 (d, J = 2.2 Hz, 1H), 6.95 (s, 2H), 6.36 (d, J = 2.5 Hz, 1H), 4.40 (s, 2H), 2.86 (s, 6H), 2.24 (s, 3H), 2.05 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.0, 144.4, 138.8, 138.1, 135.1, 134.8, 133.0, 131.0, 129.5, 129.3, 129.04 128.1, 128.0, 125.8, 125.3, 123.2, 123.0, 122.1, 118.4, 117.6, 113.5, 106.4, 47.4, 20.6, 19.0. HRMS (ESI) *m/z* Calcd for $C_{35}H_{34}N_3$ [M-Cl]$^+$ 496.2753, found 496.2751. IR (cm^{-1}) ν 3021, 2919, 1612, 1543, 1489, 1443, 1381, 1340, 1222, 815, 756, 701.

7-(*tert*-Butyl)-4,5-diphenyl-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3ha)

White solid, 103.0 mg (94%). M.p.: 174 – 175 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.34 (d, J = 2.4 Hz, 1H), 8.86 (d, J = 9.0 Hz, 1H), 8.19 (dd, J = 9.0, 2.0 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.44 – 7.34 (m, 7H), 7.32 (d, J = 2.3 Hz, 1H), 7.29 – 7.23 (m, 2H), 6.96 (s, 2H), 4.45 (s, 2H), 2.24 (s, 3H), 2.06 (s, 6H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.6, 145.2, 138.9, 138.1, 136.5, 134.5, 132.8, 131.0, 130.2, 129.7, 129.4, 129.2, 128.7, 128.2, 128.0, 125.8, 123.5, 123.4, 123.2, 116.8, 114.3, 47.6, 34.7, 30.5, 20.6, 19.0. HRMS (ESI) *m/z* Calcd for $C_{37}H_{37}N_2$ [M-Cl]$^+$ 509.2957, found 509.2955. IR (cm^{-1}) ν 3023, 2961, 1603, 1546, 1465, 1442, 1365, 1258, 1207, 1140, 848, 762, 701.

7-Nitro-4,5-diphenyl-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3ia)

White solid, 93.7 mg (88%). M.p.: 205 – 206 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.48 (s, 1H), 9.20 (d, J = 9.0 Hz, 1H), 8.84 (d, J = 9.2 Hz, 1H), 8.21 (s, 1H), 7.59 (d, J = 6.7 Hz, 2H), 7.42 (s, 7H), 7.30 (d, J = 6.2 Hz, 2H), 6.97 (s, 2H), 4.48 (s, 2H), 2.25 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.9, 144.7, 139.1, 138.2, 137.6, 133.5, 133.4, 132.2, 130.8, 129.9, 129.5, 129.4, 129.3, 128.8, 128.4, 128.3, 125.7, 125.4, 124.2, 124.0, 123.8, 119.2, 115.4, 48.0, 20.6, 19.0. HRMS (ESI) *m/z* Calcd for $C_{33}H_{28}N_3O_2$ [M-Cl]$^+$ 498.2182, found 498.2182. IR (cm^{-1}) ν 3019, 2966, 1604, 1524, 1443, 1348, 1269, 1117, 850, 748, 704.

3,4,5-Triphenylimidazo[1,2-*a*]quinolinium chloride (3ja)

White solid, 66.9 mg (77%). M.p.: 262 – 263 °C. ^{1}H NMR (DMSO-d_6,, 400 MHz) δ 9.67 (s, 1H), 9.03 (d, J = 8.2 Hz, 1H), 8.59 (s, 1H), 8.17 (t, J = 7.5 Hz, 1H), 7.83 (t, J = 7.3 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.31 (s, 3H), 7.23 (d, J = 6.7 Hz, 3H), 7.14 (s, 4H), 6.93 (d, J = 6.8 Hz, 2H), 6.85 (d, J = 7.4 Hz, 1H), 6.80 (d, J = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.7, 136.9, 135.3, 134.4, 132.1, 131.0, 130.9, 130.4, 129.8, 129.2, 128.6, 128.5, 128.4, 128.1, 128.0, 127.6, 127.1, 127.0, 124.0, 123.6, 117.0, 114.2. HRMS (ESI) *m/z* Calcd for $C_{29}H_{21}N_2$ [M-Cl]$^+$ 397.1705, found 397.1703. IR (cm^{-1}) ν 2989, 1593, 1538, 1497, 1443, 1343, 1260, 1097, 1021, 801, 761, 697.

5,6-Diphenyl-7-(2,4,6-trimethylbenzyl)benzo[4,5]imidazo[1,2-*a*]quinolinium bromide (3ka)

White solid, 106.1 mg (91%). M.p.: 240 – 241 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.41 (d, J = 8.8 Hz, 1H), 9.30 (d, J = 8.7 Hz, 1H), 8.25 (dd, J = 11.7, 4.1 Hz, 1H), 7.86 (dt, J = 19.4, 7.8 Hz, 2H), 7.69 (t, J = 7.9 Hz, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.50 (dd, J = 6.3, 2.7 Hz, 2H), 7.42 – 7.31 (m, 6H), 7.29 (d, J = 7.7 Hz, 2H), 7.12 (d, J = 8.5 Hz, 1H), 6.84 (s, 2H), 5.08 (s, 2H), 2.19 (s, 3H), 1.92 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.3, 141.9, 137.9, 136.5, 134.5, 133.4, 132.9, 132.7, 131.0, 129.8, 129.4, 129.3, 129.1, 128.5, 128.3, 128.0, 127.9, 126.7, 126.5, 124.3, 123.0, 118.0, 117.3, 113.7, 47.8, 20.4, 19.6. HRMS (ESI) *m/z* Calcd for $C_{37}H_{31}N_2$ [M-Br]$^+$ 503.2487, found 503.2482. IR (cm^{-1}) ν 3020, 2920, 1592, 1526, 1490, 1445, 1335, 1282, 1234, 1019, 855, 760, 701.

4,5-Bis(4-fluorophenyl)-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3ab)

White solid, 101.7 mg (98%). M.p.: 212 – 213 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.32 (d, J = 2.4 Hz, 1H), 8.92 (d, J = 8.5 Hz, 1H), 8.16 – 8.04 (m, 1H), 7.80 (dd, J = 11.5, 4.1 Hz, 1H), 7.62 (dd, J = 8.6, 5.5 Hz, 2H), 7.50 (dd, J = 8.3, 0.9 Hz, 1H), 7.35 (d, J = 2.4 Hz, 1H), 7.27 (d, J = 8.8 Hz, 6H), 6.98 (s, 2H), 4.51 (s, 2H), 2.26 (s, 3H), 2.08 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.1($J_{C\text{-}F}$ = 57.0 Hz), 160.7($J_{C\text{-}F}$ = 56.3 Hz), 144.6, 138.9, 138.2, 136.6, 133.2, 133.1, 132.1, 132.0, 131.9, 130.7, 130.5, 129.4, 129.0, 128.3, 125.7, 123.7, 123.5, 123.0, 116.9, 115.6, 115.4, 115.1, 114.4, 47.9, 20.6, 19.0. ^{19}F NMR (DMSO-d_6) δ –111.5 (s), –113.2 (s). HRMS (ESI) *m/z* Calcd for $C_{33}H_{27}F_2N_2$ [M-Cl]$^+$ 489.2142, found 489.2136. IR (cm^{-1}) ν 3016, 1610, 1596, 1510, 1457, 1354, 1225, 1158, 826, 754.

4,5-Bis(4-chlorophenyl)-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3ac)

White solid, 109.3 mg (98%). M.p.: 199 – 201 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.36 (d, J = 2.0 Hz, 1H), 8.94 (d, J = 8.6 Hz, 1H), 8.10 (t, J = 7.8 Hz, 1H), 7.80 (t, J = 7.7 Hz, 1H), 7.62 (d, J = 8.3 Hz, 2H), 7.50 (dd, J = 14.9, 7.1 Hz, 5H), 7.36 (s, 1H), 7.27 (d, J = 8.3 Hz, 2H), 6.98 (s, 2H), 4.53 (s, 2H), 2.26 (s, 3H), 2.08 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.0, 138.9, 138.2, 136.4, 134.1, 133.2, 132.8, 132.1, 131.6, 130.5, 129.3, 128.4, 125.7, 123.4, 122.6, 117.2, 114.7, 47.9, 20.6, 19.1. HRMS (ESI) *m/z* Calcd for $C_{33}H_{27}Cl_2N_2$ [M–Cl]$^+$ 521.1546, found 521.1554. IR (cm^{-1}) ν 3009, 2856, 1607, 1546, 1491, 1348, 1258, 1088, 1018, 813, 755.

4,5-Bis(4-bromophenyl)-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3ad)

White solid, 116.3 mg (90%). M.p.: 193 – 195 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.44 (s, 1H), 8.97 (d, J = 8.6 Hz, 1H), 8.09 (t, J = 7.8 Hz, 1H), 7.79 (t, J = 7.7 Hz, 1H), 7.64 (t, J = 7.7 Hz, 4H), 7.58 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.2 Hz, 1H), 7.33 (d, J = 2.2 Hz, 1H), 7.22 (d, J = 8.3 Hz, 2H), 6.97 (s, 2H), 4.54 (s, 2H), 2.25 (s, 3H), 2.08 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.0, 139.0, 138.2, 136.3, 133.6, 133.1, 132.2, 131.9, 131.3, 130.5, 129.4, 128.3, 125.7, 123.4, 122.9, 122.5, 121.8, 117.1, 114.6, 47.9, 20.6, 19.1. HRMS (ESI) *m/z* Calcd for $C_{33}H_{27}Br_2N_2$ [M–Cl]$^+$ 609.0536, found 609.0541. IR (cm^{-1}) ν 3009, 2857, 1604, 1544, 1488, 1388, 1348, 1208, 1135, 1069, 1013, 815, 756.

4,5-Di-*p*-tolyl-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3ae)

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DOI: 10.1039/C5OB00823A

White solid, 100.1 mg (97%). M.p.: 174 – 176 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.35 (d, J = 2.4 Hz, 1H), 8.91 (d, J = 8.5 Hz, 1H), 8.06 (dd, J = 11.5, 4.2 Hz, 1H), 7.77 (t, J = 7.8 Hz, 1H), 7.46 (d, J = 7.8 Hz, 3H), 7.31 (d, J = 2.3 Hz, 1H), 7.26 – 7.17 (m, 4H), 7.13 (d, J = 8.0 Hz, 2H), 6.96 (s, 2H), 4.45 (s, 2H), 2.30 (s, 3H), 2.25 (s, 6H), 2.06 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.2, 138.9, 138.5, 138.2, 137.4, 136.8, 131.8, 131.6, 130.8, 130.4, 129.8, 129.6, 129.4, 128.8, 128.7, 128.4, 128.1, 125.8, 124.0, 123.5, 123.4, 116.8, 114.3, 47.6, 20.8, 20.7, 20.6, 19.0. HRMS (ESI) *m/z* Calcd for $C_{35}H_{33}N_2$ $[M\text{-}Cl]^+$ 481.2644, found 481.2643. IR (cm^{-1}) ν 3016, 2918, 1602, 1549, 1509, 1456, 1351, 1234, 1137, 849, 753.

4,5-Bis(4-methoxyphenyl)-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3af)

White solid, 108.0 mg (98%). M.p.: 178 – 180 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.34 (s, 1H), 8.90 (d, J = 8.5 Hz, 1H), 8.06 (t, J = 7.7 Hz, 1H), 7.78 (t, J = 7.7 Hz, 1H), 7.55 – 7.44 (m, 3H), 7.28 (d, J = 1.9 Hz, 1H), 7.17 (d, J = 8.5 Hz, 2H), 6.96 (s, 6H), 4.50 (s, 2H), 3.74 (d, J = 16.6 Hz, 6H), 2.25 (s, 3H), 2.08 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.4, 158.7, 145.4, 138.9, 138.2, 137.1, 132.4, 131.8, 131.1, 130.4, 129.4, 128.5, 128.1, 126.6, 125.9, 124.7, 124.2, 123.6, 123.3, 116.9, 114.3, 113.7, 113.6, 55.0, 47.7, 20.6, 19.1. HRMS (ESI) *m/z* Calcd for $C_{35}H_{33}N_2O_2$ $[M\text{-}Cl]^+$ 513.2542, found 513.25. IR (cm^{-1}) ν 2933, 2836, 1609, 1543, 1506, 1458, 1290, 1248, 1178, 1026, 816, 761.

4,5-Bis(4-(ethoxycarbonyl)phenyl)-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3ag)

White solid, 116.2 mg (92%). M.p.: 206 – 208 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.37 (s, 1H), 8.95 (d, J = 8.6 Hz, 1H), 8.11 (t, J = 7.8 Hz, 1H), 7.96 (d, J = 8.0 Hz, 4H), 7.78 (dd, J = 16.5, 8.0 Hz, 3H), 7.43 (t, J = 7.0 Hz, 3H), 7.37 (s, 1H), 6.96 (s, 2H), 4.48 (s, 2H), 4.34 – 4.20 (m, 4H), 2.24 (s, 3H), 2.07 (s, 6H), 1.29 (dt, J = 14.3, 7.0 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.0, 143.9, 139.1, 138.9, 138.2, 137.3, 136.2, 132.2，131.5, 130.6, 130.4, 130.3, 129.6, 129.3, 128.9, 128.2, 125.6, 123.5, 123.2, 122.5, 117.1, 114.8, 60.9, 47.9, 20.5, 19.0, 13.9. HRMS (ESI) *m/z* Calcd for $C_{39}H_{37}N_2O_4$ $[M\text{–}Cl]^+$ 597.2748, found 597.2760. IR (cm^{-1}) ν 2982, 1718, 1606, 1547, 1461, 1401, 1368, 1274, 1105, 1022, 853, 755.

4,5-Diethyl-3-(2,4,6-trimethylbenzyl)-3-imidazo[1,2-*a*]quinolinium chloride (3ah)

White solid, 69.0 mg (88%). M.p.: 173 – 175 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.11 (s, 1H), 8.73 (d, J = 8.4 Hz, 1H), 8.39 (d, J = 8.1 Hz, 1H), 7.96 (t, J = 7.5 Hz, 1H), 7.85 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 15.6 Hz, 3H), 5.78 (d, J = 13.4 Hz, 2H), 3.42 (d, J = 7.0 Hz, 2H), 3.30 (d, J = 7.2 Hz, 2H), 2.33 (s, 3H), 2.27 (s, 6H), 1.46 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.1, 138.9, 138.5, 137.9, 130.8, 130.1, 129.4, 127.9, 126.1, 123.6, 122.5, 117.2, 114.0, 48.1, 20.6, 20.2, 19.1, 15.6, 14.9. HRMS (ESI) *m/z* Calcd for $C_{25}H_{29}N_2$ $[M\text{–}Cl]^+$ 357.2325, found 357.2333. IR (cm^{-1}) ν 2925, 2867, 1601, 1544, 1517, 1456, 1341, 1198, 1049, 854, 761.

5-Methyl-4-phenyl-3-(2,4,6-trimethylbenzyl)imidazo[1,2-*a*]quinolinium chloride (3ai)

White solid, 84.0 mg (98%). M.p.:197 – 199 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.26 (d, J = 1.5 Hz, 1H), 8.85 (d, J = 8.5 Hz, 1H), 8.42 (d, J = 8.2 Hz, 1H), 8.08 (t, J = 7.7 Hz, 1H), 7.92 (t, J = 7.7 Hz, 1H), 7.70 (d, J = 3.9 Hz, 5H), 7.19 (d, J = 1.3 Hz, 1H), 6.95 (s, 2H), 4.42 (s, 2H), 2.50 (s, 3H), 2.23 (s, 3H), 2.05 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 141.0, 138.9, 138.1, 136.7, 133.4, 131.8, 130.5, 130.3, 129.8, 129.3, 129.2, 128.1, 127.0, 125.8, 123.4, 122.9, 122.7, 117.0, 114.0, 47.4, 20.6, 19.0, 16.2. HRMS (ESI) *m/z* Calcd for $C_{28}H_{27}N_2$ $[M\text{-}Cl]^+$ 391.2174, found 391.217. IR (cm^{-1}) ν 3015, 2916, 1613, 1547, 1467, 1366, 1238, 1206, 1005, 853, 752, 706.

5-Ethyl-4-phenyl-3-(2,4,6-trimethylbenzyl)-3-dihydroimidazo[1,2-*a*]quinolinium chloride (3aj)

White solid, 83.2 mg (94%). M.p.: 194 – 197 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (d, J = 1.6 Hz, 1H), 8.90 (d, J = 8.5 Hz, 1H), 8.45 (d, J = 8.3 Hz, 1H), 8.07 (t, J = 7.7 Hz, 1H), 7.93 (t, J = 7.6 Hz, 1H), 7.75 (d, J = 7.0 Hz, 2H), 7.72 – 7.61 (m, 3H), 7.15 (d, J = 1.6 Hz, 1H), 6.95 (s, 2H), 4.39 (s, 2H), 2.92 (dd, J = 14.2, 6.8 Hz, 2H), 2.24 (s, 3H), 2.05 (s, 6H), 1.17 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.7, 138.7, 138.1, 136.6, 133.0, 131.6, 130.6, 130.3, 129.8, 129.2, 129.0, 128.1, 126.6, 125.6, 122.6, 122.1, 117.4, 114.2, 47.3, 22.1, 20.5, 19.0, 14.8. HRMS (ESI) *m/z* Calcd for $C_{29}H_{29}N_2$ $[M\text{–}Cl]^+$ 405.2325, found 405.2331. IR (cm^{-1}) ν 2967, 2924, 1604, 1544, 1454, 1372, 1233, 1178, 1028, 849, 755, 707.

General procedure for Rh(III)-catalyzed cascade oxidative annulation reaction of aryl imidazolium salts with two molecules of alkynes

A mixture of aryl substituted imidazolium salts **1** (0.22 mmol, 1.1 equiv.), alkyne **2** (0.4 mmol, 2.0 equiv.), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (160.0 mg, 0.8 mmol, 4.0 equiv.) were weighted in a Schlenk tube equipped with a stir bar. Dry *t*-AmOH (2.0 mL) was added and the mixture was stirred at 80 °C under Ar atmosphere. The reaction process was monitored by TLC. After the reaction finished, the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure, and the residue was absorbed onto a small amount of alumina. Products **4** were isolated by column chromatography on an alumina using CH_2Cl_2/MeOH (80/1–50/1) as eluant.

3,4,8,9-Tetraphenyl-1-(2,4,6-trimethylbenzyl)-1-dihydrobenzo[*ij*]imidazo[2,1,5-*de*] quinolizinium chloride (4aa)

Yellow-green solid, 128.5 mg (96%). M.p.: >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.2 Hz, 2H), 7.66 – 7.60 (m, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.37 – 7.23 (m, 12H), 7.18 (d, J = 8.8 Hz, 6H), 6.88 (s, 1H), 6.78 (s, 2H), 4.98 (s, 2H), 2.16 (s, 3H), 2.10 (s, 6H). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (t, J = 8.0 Hz, 1H), 7.63 (d, J = 7.2 Hz, 2H), 7.57 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 8.2 Hz, 1H), 7.49 – 7.37 (m, 9H), 7.36 – 7.21 (m, 9H), 6.90 (s, 2H), 6.68 (s, 1H), 4.69 (s, 2H), 2.17 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.7, 139.2, 138.2, 136.0, 134.2, 133.5, 132.9, 132.1, 130.9, 129.8, 129.3, 129.1, 128.8, 128.7, 128.6, 128.4, 128.1, 127.9, 127.5, 125.7, 125.3, 125.0, 124.7, 124.6, 124.5, 124.1, 114.5, 47.9, 20.5, 18.9. HRMS (ESI) *m/z* Calcd for $C_{47}H_{37}N_2$ $[M\text{–}Cl]^+$ 629.2951, found

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DOI: 10.1039/C5OB00823A

629.2967. IR (cm^{-1}) ν 3053, 2921, 1608, 1553, 1486, 1444, 1339, 1174, 1028, 851, 764, 705.

6-Fluoro-3,4,8,9-tetraphenyl-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4ba)

Yellow-green solid, 116.4 mg (85%). M.p.: >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.61 (s, 2H), 7.53 – 7.39 (m, 9H), 7.37 – 7.15 (m, 11H), 6.91 (s, 2H), 6.78 (s, 1H), 4.71 (s, 2H), 2.18 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.4, 158.9, 144.0, 139.3, 138.2, 135.4, 133.7, 133.1, 132.5, 131.8, 130.8, 129.8, 129.5, 129.3, 129.1, 129.0, 128.8, 128.7, 128.5, 128.3, 128.2, 126.6, 126.5, 125.9, 125.2, 125.0, 124.7, 115.5, 111.7 ($J_{C\text{-}F}$ = 26.7 Hz), 109.6 ($J_{C\text{-}F}$ = 25.3 Hz), 48.1, 20.5, 18.9. ^{19}F NMR (376 MHz, DMSO-d_6) δ –108.8 (s). HRMS (ESI) *m/z* Calcd for $C_{47}H_{36}FN_2$ $[M–Cl]^+$ 647.2857, found 647.2868. IR (cm^{-1}) ν 3053, 2923, 2856, 1608, 1577, 1515, 1442, 1404, 1338, 1188, 1122, 1026, 857, 800, 712.

6-Chloro-3,4,8,9-tetraphenyl-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4ca)

Yellow-green solid, 117.7 mg (84%). M.p.: >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (t, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.1 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.49 – 7.38 (m, 9H), 7.34 (m, 2H), 7.30 – 7.23 (m, 6H), 6.90 (s, 2H), 6.69 (s, 1H), 4.72 (s, 2H), 2.17 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.7, 139.3, 138.2, 136.0, 134.2, 133.5, 132.9, 132.1, 130.9, 129.8, 129.3, 129.2, 128.8, 128.7, 128.6, 128.4, 128.2, 127.9, 127.5, 125.7, 125.3, 125.0, 124.7, 124.6, 124.5, 124.1, 114.5, 47.9, 20.5, 18.9. HRMS (ESI) *m/z* Calcd for $C_{47}H_{36}ClN_2$ $[M–Cl]^+$ 663.2562, found 663.2556. IR (cm^{-1}) ν 3052, 2921, 2857, 1621, 1554, 1485, 1444, 1336, 1173, 1026, 764, 706.

6-Bromo-3,4,8,9-tetraphenyl-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4da)

Yellow-green solid, 113.7 mg (76%). M.p.: >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (m, 1H), 7.61 (s, 3H), 7.45 (d, *J* = 2.7 Hz, 9H), 7.29 (t, *J* = 19.1 Hz, 9H), 6.91 (s, 2H), 6.68 (s, 1H), 4.69 (s, 2H), 2.18 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.6, 139.1, 138.1, 135.9, 134.2, 133.5, 132.8, 132.1, 130.9, 129.8, 129.3, 129.2, 129.1, 128.7, 128.6, 128.5, 128.3, 127.9, 127.4, 125.7, 125.3, 125.0, 124.6, 124.5, 124.0, 114.5, 47.9, 20.4, 18.9. HRMS (ESI) *m/z* Calcd for $C_{47}H_{36}BrN_2$ $[M–Cl]^+$ 707.2056, found 707.2051. IR (cm^{-1}) ν 3051, 2921, 2857, 1609, 1551, 1485, 1443, 1335, 1172, 1026, 854, 764, 705.

6-Methyl-3,4,8,9-tetraphenyl-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4ea)

Yellow-green solid, 131.8 mg (97%). M.p.: >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.63 (s, 2H), 7.53 – 7.20 (m, 20H), 6.90 (s, 2H), 6.65 (s, 1H), 4.68 (s, 2H), 2.42 (s, 3H), 2.17 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.3, 139.2, 138.2, 137.9, 135.8, 134.2, 133.5, 132.6, 132.1, 130.9, 129.8, 129.3, 129.2, 128.8, 128.7, 128.6, 128.3, 127.6, 126.3, 125.7, 125.3, 124.8, 124.7, 124.6, 123.9, 114.5, 47.8, 21.7, 20.4, 18.9. HRMS (ESI) *m/z* Calcd for $C_{48}H_{39}N_2$ $[M–Cl]^+$ 643.3108, found 643.3121. IR (cm^{-1}) ν 3052, 2921, 2857, 1612, 1578, 1485, 1443, 1334, 1196, 1161, 1027, 856, 797, 710.

6-Methoxy-3,4,8,9-tetraphenyl-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4fa)

Yellow-green solid, 111.4 mg (80%). M.p.: >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.65 (d, *J* = 6.4 Hz, 2H), 7.43 (dd, *J* = 20.9, 5.8 Hz, 9H), 7.35 (d, *J* = 6.7 Hz, 2H), 7.27 (d, *J* = 14.9 Hz, 7H), 7.02 (s, 1H), 6.89 (s, 3H), 6.68 (s, 1H), 4.69 (s, 2H), 3.65 (s, 3H), 2.17 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.1, 143.9, 139.1, 138.2, 135.4, 134.1, 133.4, 132.1, 130.9, 129.7, 129.3, 129.1, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.4, 126.1, 125.3, 125.1, 124.4, 123.2, 114.9, 111.8, 107.1, 55.5, 47.8, 20.4, 18.9. HRMS (ESI) *m/z* Calcd for $C_{48}H_{39}N_2O$ $[M–Cl]^+$ 659.3057, found 659.3071. IR (cm^{-1}) ν 3054, 2918, 1610, 1578, 1469, 1408, 1369, 1298, 1208, 1133, 1032, 845, 796, 707.

6-(Dimethylamino)-3,4,8,9-tetraphenyl-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4ga)

Yellow-green solid, 124.3 mg (88%). M.p.: >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 – 7.58 (m, 2H), 7.42 (d, *J* = 20.2 Hz, 9H), 7.35 – 7.18 (m, 9H), 6.89 (s, 2H), 6.81 (s, 1H), 6.55 (d, *J* = 7.9 Hz, 2H), 4.62 (s, 2H), 2.74 (s, 6H), 2.17 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.0, 143.7, 139.1, 138.1, 135.7, 134.5, 134.4, 133.7, 132.4, 131.3, 130.9, 129.7, 129.2, 129.1, 128.8, 128.6, 128.5, 128.3, 127.5, 126.7, 125.9, 125.4, 124.6, 124.1, 120.7, 114.4, 109.0, 104.9, 47.6, 20.4, 18.9. HRMS (ESI) *m/z* Calcd for $C_{49}H_{42}N_3$ $[M–Cl]^+$ 672.3373, found 672.3387. IR (cm^{-1}) ν 3052, 2918, 1609, 1577, 1484, 1443, 1375, 1185, 1130, 1027, 847, 791, 708.

6-(*tert*-Butyl)-3,4,8,9-tetraphenyl-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4ha)

Yellow-green solid, 128.8 mg (89%). M.p.: >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (d, *J* = 7.1 Hz, 2H), 7.60 (s, 1H), 7.48 (d, *J* = 6.9 Hz, 7H), 7.44 – 7.36 (m, 5H), 7.35 – 7.22 (m, 7H), 6.88 (s, 2H), 6.70 (s, 1H), 4.74 (s, 2H), 2.15 (s, 3H), 2.08 (s, 6H), 1.14 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.4, 144.7, 139.1, 138.1, 136.0, 134.2, 133.5, 132.7, 132.1, 130.9, 129.8, 129.3, 129.1, 128.8, 128.7, 128.5, 128.4, 128.3, 127.5, 126.3, 125.6, 125.4, 124.8, 124.6, 124.3, 121.8, 120.2, 114.5, 47.8, 34.9, 30.7, 20.4, 18.9. HRMS (ESI) *m/z* Calcd for $C_{51}H_{45}N_2$ $[M–Cl]^+$ 685.3577, found 685.3610. IR (cm^{-1}) ν 3054, 2960, 1617, 1514, 1483, 1442, 1267, 1169, 1026, 851, 770, 708.

6-Nitro-3,4,8,9-tetraphenyl-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4ia)

Pale brown solid, 75.7 mg (53%). M.p.: 154 – 156 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (d, *J* = 4.7 Hz, 2H), 7.67 (t, *J* = 8.0 Hz, 2H), 7.58 – 7.44 (m, 9H), 7.42 – 7.25 (m, 9H), 6.92 (s, 2H), 6.87 (s, 1H), 4.78 (s, 2H), 2.18 (s, 3H), 2.08 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.8, 144.7, 139.4, 138.3, 135.5, 133.6, 133.4, 133.3, 132.9, 131.6, 130.8, 130.1, 129.9, 129.7, 129.6, 129.5, 129.3, 129.1, 128.9, 128.8, 128.7, 128.5, 127.0, 126.7, 125.2, 125.1, 118.4, 117.9, 116.2, 48.4, 20.4, 19.0. HRMS (ESI) *m/z* Calcd for $C_{47}H_{36}N_3O_2$ $[M–Cl]^+$

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DOI: 10.1039/C5OB00823A

674.2802, found 674.2801. IR (cm^{-1}) ν 3053, 2918, 2852, 1636, 1513, 1457, 1341, 1261, 1174, 1027, 802, 756, 704.

1,3,4,8,9-Pentaphenyl-1H-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4ja)

Yellow-green solid, 97.2 mg (80%). M.p.: 190 – 193 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.52 (t, 1H), 7.94 (t, 1H), 7.68 – 7.07 (m, 22H), 6.93 (dd, J = 33.1, 11.8 Hz, 5H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.9, 136.0, 134.8, 134.4, 134.2, 133.5, 132.9, 130.6, 130.0, 129.6, 129.4, 128.9, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.7, 127.2, 127.0, 125.9, 124.8, 124.7, 124.1, 120.9. HRMS (ESI) *m/z* Calcd for $C_{43}H_{29}N_2$ $[M–Cl]^+$ 573.2325, found 573.2330. IR (cm^{-1}) ν 3054, 2922, 1624, 1548, 1494, 1442, 1342, 1180, 1039, 765, 703.

1-methyl-3,4,8,9-tetraphenyl-benzo[*ij*]imidazo[2,1,5-de]quinolizinium iodide (4la)

Yellow-green solid, 95.9 mg (75%). M.p.: >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.71 – 7.62 (m, 2H), 7.56 – 7.47 (m, 3H), 7.42 (d, J = 7.3 Hz, 2H), 7.33 (dt, J = 15.6, 7.8 Hz, 12H), 7.26 – 7.18 (m, 4H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 136.3, 134.3, 133.8, 133.3, 132.0, 131.0, 130.9, 129.9, 129.6, 129.3, 129.1, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.5, 126.3, 125.2, 125.0, 124.7, 124.5, 124.1, 120.7, 39.0. HRMS (ESI) *m/z* Calcd for $C_{38}H_{27}N_2$ $[M–Cl]^+$ 511.2169, found 511.2184. IR (cm^{-1}) ν3054, 2908, 1708, 1629, 1558, 1441, 1238, 1073, 752, 701.

1-Methyl-4,5-diphenyl-2-(2,4,6-trimethylbenzyl)-2-imidazo[1,5-*n*]quinolinium chloride (4ma)

White solid, 61.5 mg (61%). M.p.: 112 – 115 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.71 (d, J = 8.5 Hz, 1H), 7.87 (t, J = 7.6 Hz, 1H), 7.68 (t, J = 7.3 Hz, 1H), 7.37 (dd, J = 14.5, 7.9 Hz, 4H), 7.24 (s, 3H), 7.17 (d, J = 7.9 Hz, 4H), 6.96 (s, 2H), 6.54 (s, 1H), 5.63 (s, 2H), 3.46 (s, 3H), 2.22 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.9, 138.9, 138.3, 134.8, 134.6, 133.9, 130.3, 130.2, 129.6, 129.4, 129.3, 128.3, 128.1, 128.0, 127.9, 126.5, 126.4, 125.5, 118.8, 112.1, 47.3, 20.5, 19.1, 15.2. HRMS (ESI) *m/z* Calcd for $C_{34}H_{31}N_2$ $[M–Cl]^+$ 467.2482, found 467.2484. IR (cm^{-1}) ν 3055, 2919, 1620, 1560, 1479, 1444, 1378, 1305, 1183, 1085, 1028, 853, 766, 702.

3,4,8,9-Tetrakis(4-fluorophenyl)-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4ab)

Yellow-green solid, 146.8 mg (99%). M.p.: >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (t, J = 7.1 Hz, 1H), 7.68 (s, 2H), 7.60 (d, J = 7.7 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.33 (t, J = 12.7 Hz, 12H), 7.19 (t, J = 7.9 Hz, 2H), 6.92 (s, 2H), 6.79 (s, 1H), 4.78 (s, 2H), 2.19 (s, 3H), 2.08 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ163.3 ($J_{C\text{-}F}$ = 56.9 Hz), 160.8 ($J_{C\text{-}F}$ = 55.3 Hz), 144.4, 139.2, 138.2, 133.1, 133.0, 132.8, 132.2, 132.1, 131.7, 131.6, 131.5, 130.3, 129.7, 129.3, 128.4, 128.2, 127.0, 125.6, 125.4, 124.9, 124.5, 124.3, 124.1, 116.1, 115.9, 115.7, 114.7, 48.2, 20.5, 18.9. ^{19}F NMR (376 MHz, DMSO-d_6) δ –111.1 (s), –111.9 (s), –112.7 (s), –112.8 (s). HRMS (ESI) *m/z* Calcd for $C_{47}H_{33}F_4N_2$ $[M–Cl]^+$ 701.2574, found 701.2576. IR (cm^{-1}) ν 3041, 2920, 1604, 1503, 1406, 1226, 1158, 1014, 820, 770.

3,4,8,9-Tetrakis(4-chlorophenyl)-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4ac)

Yellow-green solid, 157.4 mg (98%). M.p.: >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (s, 1H), 7.61 (d, J = 39.2 Hz, 10H), 7.47 – 7.20 (m, 8H), 6.89 (d, J = 20.5 Hz, 3H), 4.79 (s, 2H), 2.19 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.0, 139.2, 138.2, 135.3, 134.4, 133.6, 133.4, 133.3, 132.8, 132.6, 132.1, 131.8, 131.3, 131.1, 130.7, 129.3, 129.1, 128.9, 128.7, 128.4, 127.9, 126.7, 125.3, 125.0, 124.7, 124.2, 123.7, 115.0, 48.3, 20.5, 19.0. HRMS (ESI) *m/z* Calcd for $C_{47}H_{33}Cl_4N_2$ $[M–Cl]^+$ 765.1392, found 765.1390. IR (cm^{-1}) ν 3019, 2962, 2921, 1622,1487, 1396, 1341, 1174, 1090, 1015, 814, 765.

3,4,8,9-Tetrakis(4-bromophenyl)-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4ad)

Yellow-green solid, 179.8 mg (92%). M.p.: >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 – 7.88 (m, 1H), 7.69 (m, 6H), 7.56 (m, 6H), 7.34 – 7.15 (m, 6H), 6.90 (d, J = 18.7 Hz, 3H), 4.77 (s, 2H), 2.20 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.9, 139.2, 138.2, 135.3, 133.2, 132.9, 132.6, 132.4, 132.1, 132.0, 131.8, 131.9, 131.5, 131.4, 131.1, 129.4, 128.5, 127.9, 126.7, 125.3, 125.2, 125.1, 124.7, 124.5, 124.2, 123.6, 123.1, 122.3, 122.1, 122.0, 115.0, 48.3, 20.5, 19.0. HRMS (ESI) *m/z* Calcd for $C_{47}H_{33}Br_4N_2$ $[M–Cl]^+$ 940.9372, found 940.9366. IR (cm^{-1}) ν 3017, 1628, 1586, 1484, 1389, 1339, 1173, 1070, 1010, 813, 765.

3,4,8,9-Tetra-*p*-tolyl-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4ae)

Yellow-green solid, 131.7 mg (91%). M.p.: >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (t, J = 7.3 Hz, 1H), 7.51 (dd, J = 19.5, 10.8 Hz, 4H), 7.34 – 7.05 (m, 14H), 6.90 (s, 2H), 6.69 (s, 1H), 4.69 (s, 2H), 2.30 (d, J = 15.8 Hz, 9H), 2.19 (d, J = 17.4 Hz, 6H), 2.07 (s, 6H).. ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.8, 139.2, 138.7, 138.2, 138.1, 137.6, 137.5, 135.9, 133.0, 131.5, 131.4, 130.8, 130.7, 129.7, 129.5, 129.3, 129.2, 129.1, 128.0, 127.8, 127.3, 125.9, 125.5, 125.1, 124.7, 124.0, 114.4, 47.9, 20.8, 20.6, 20.5, 19.0. HRMS (ESI) *m/z* Calcd for $C_{51}H_{45}N_2$ $[M–Cl]^+$ 685.3577, found 685.3584. IR (cm^{-1}) ν 3021, 2918, 2860, 1618, 1557, 1502, 1457, 1338, 1175, 1022, 853, 769, 728.

3,4,8,9-Tetrakis(4-methoxyphenyl)-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4af)

Yellow-green solid, 151.3 mg (96%). M.p.: >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.89 (t, J = 7.6 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 7.4 Hz, 3H), 7.24 (d, J = 7.8 Hz, 2H), 7.17 (t, J = 9.0 Hz, 4H), 7.03 (s, 6H), 6.92 (s, 2H), 6.86 (d, J = 6.9 Hz, 2H), 6.71 (s, 1H), 4.74 (s, 2H), 3.78 (s, 6H), 3.75 (s, 3H), 3.70 (s, 3H), 2.19 (s, 3H), 2.09 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.5, 159.0, 158.8, 145.0, 139.3, 138.2, 135.5, 133.2, 132.2, 131.2, 130.7, 130.5, 129.3, 127.9, 127.7, 127.2, 126.4, 126.1, 125.7, 125.6, 125.2, 124.9, 124.6, 124.5, 124.1, 124.0, 114.3, 114.0, 113.8, 55.0, 48.0, 20.5, 19.0. HRMS (ESI) *m/z* Calcd for $C_{51}H_{45}N_2O_4$ $[M–Cl]^+$ 749.3374, found 749.3388. IR (cm^{-1}) ν 2927, 2836, 1611, 1510, 1461, 1291, 1248, 1176, 1028, 816, 771.

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DOI: 10.1039/C5OB00823A

3,4,8,9-Tetrakis(4-(ethoxycarbonyl)phenyl)-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4ag)

Yellow-green solid, 168.6 mg (88%). M.p.: 125 – 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 5.8 Hz, 8H), 7.83 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.9 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 8.1 Hz, 1H), 7.40 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 7.27 (d, J = 9.7 Hz, 2H), 6.88 (s, 1H), 6.78 (s, 2H), 5.01 (s, 2H), 4.41 – 4.24 (m, 8H), 2.16 (s, 3H), 2.13 (s, 6H), 1.34 (dd, J = 15.3, 7.7 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 144.6, 139.7, 138.9, 138.6, 138.5, 137.8, 136.6, 136.0, 132.7, 131.6, 131.4, 130.63, 130.5, 130.1, 129.8, 129.6, 128.8, 127.7, 127.4, 125.9, 125.3, 125.0, 124.7, 124.4, 116.2, 61.2, 61.1, 49.5, 20.9, 19.8, 14.1. HRMS (ESI) *m/z* Calcd for $C_{59}H_{53}N_2O_8$ $[M–Cl]^+$ 917.3796, found 917.3811. IR (cm^{-1}) ν 2977, 1717, 1611, 1518, 1465, 1402, 1274, 1177, 1104, 1020, 866, 767, 719.

4,8-Dimethyl-3,9-diphenyl-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4ai)

Yellow-green solid, 108.3 mg (98%). M.p.: 119 – 121 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.46 (d, J = 8.1 Hz, 1H), 8.37 (d, J = 7.7 Hz, 1H), 8.23 (t, J = 7.9 Hz, 1H), 7.78 – 7.66 (m, 5H), 7.60 – 7.49 (m, 3H), 7.45 (d, J = 7.0 Hz, 2H), 6.89 (s, 2H), 6.50 (s, 1H), 4.65 (s, 2H), 2.57 (s, 3H), 2.46 (s, 3H), 2.17 (s, 3H), 2.03 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.6, 139.1, 138.1, 133.9, 132.9, 132.2, 130.8, 130.3, 129.9, 129.3, 129.2, 129.1, 128.1, 126.8, 126.4, 125.4, 125.3, 124.5, 123.7, 123.6, 123.5, 123.0, 112.8, 47.6, 20.5, 18.9, 16.3, 15.4. HRMS (ESI) *m/z* Calcd for $C_{37}H_{33}N_2$ $[M–Cl]^+$ 505.2638, found 505.2642. IR (cm^{-1}) ν 3021, 2921, 1700, 1617, 1516, 1446, 1278, 1170, 1023, 854, 768, 706.

4,8-Diethyl-3,9-diphenyl-1-(2,4,6-trimethylbenzyl)-1-benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4aj)

Yellow-green solid, 111.6 mg (98%). M.p.: 160 – 162 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.48 (d, J = 8.2 Hz, 1H), 8.40 (d, J = 7.4 Hz, 1H), 8.21 (t, J = 7.9 Hz, 1H), 7.79 – 7.67 (m, 5H), 7.61 – 7.50 (m, 3H), 7.40 (d, J = 6.6 Hz, 2H), 6.88 (s, 2H), 6.35 (s, 1H), 4.57 (s, 2H), 2.99 (d, J = 7.1 Hz, 2H), 2.92 – 2.81 (m, 2H), 2.17 (s, 3H), 2.01 (s, 6H), 1.27 – 1.16 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.7, 139.1, 138.2, 136.4, 133.7, 132.5, 132.3, 130.2, 130.0, 129.2, 128.6, 128.2, 127.9, 126.3, 125.2, 124.8, 124.3, 123.5, 123.4, 123.0, 122.7, 112.8, 47.4, 22.5, 21.4, 20.4, 18.8, 13.6, 13.3. HRMS (ESI) *m/z* Calcd for $C_{39}H_{37}N_2$ $[M–Cl]^+$ 533.2951, found 533.2959. IR (cm^{-1}) ν 3051, 2925, 1617, 1557, 1450, 1315, 1278, 1169, 1024, 853, 770, 707.

General procedure for preparation of benzo[*ij*]imidazo[2,1,5-*de*]quinolizine from benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salts

A Schlenk tube with a magnetic stir bar was charged with benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium salts (0.1 mmol) and pyridine (1.0 mL). The reaction mixture was heated at 140 °C for 12 h. The reaction mixture was then allowed to cool to room temperature, diluted with 10–15 mL of dichloromethane. The pyridine was evaporated under reduced pressure, and the resulting residue was absorbed onto a small amount of alumina. Products **5** were isolated by column chromatography on an alumina using CH_2Cl_2/MeOH (500/1) as eluant.

3,4,8,9-Tetraphenylbenzo[*ij*]imidazo[2,1,5-*de*]quinolizine (5aa)[20e,20f,25]

Yellow-green solid, 49.2 mg (99%). M.p.: >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.37 (d, J = 6.9 Hz, 2H), 7.34 (s, 1H), 7.33 – 7.26 (m, 8H), 7.21 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 136.6, 136.5, 135.9, 134.6, 132.2, 130.7, 130.6, 130.5, 130.4, 129.8, 128.8, 128.6, 128.5, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 126.5, 126.4, 125.6, 125.2, 124.9, 121.9, 121.3. HRMS (ESI) *m/z* Calcd for $C_{37}H_{25}N_2$ $[M+H]^+$ 497.2018, found 497.2021. IR (cm^{-1}) ν 3052, 2922, 1599, 1551, 1486, 1441, 1413, 1333, 1179, 1071, 811, 756, 700.

Tetraethyl 4,4',4'',4'''-benzo[*ij*]imidazo[2,1,5-*de*]quinolizine-3,4,8,9-tetrayl) tetrabenzoate (5ag)[20e,20f,25]

Yellow-green solid, 72.9 mg (93%). M.p.: 256 – 258 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.2, 3.5 Hz, 4H), 7.98 (dd, J = 8.3, 2.1 Hz, 4H), 7.71 (s, 1H), 7.51 – 7.44 (m, 3H), 7.42 (dt, J = 6.7, 2.6 Hz, 3H), 7.38 – 7.31 (m, 5H), 4.38 (m, 8H), 1.44 – 1.35 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 166.1, 166.0, 141.1, 140.9, 140.2, 139.2, 135.2, 131.4, 130.8, 130.7, 130.6, 130.5, 130.2, 130.1, 130.0, 129.9, 129.8, 129.7, 129.4, 128.7, 127.0, 126.1, 125.8, 125.1, 124.6, 122.0, 121.2, 61.1, 60.9, 14.3. HRMS (ESI) *m/z* Calcd for $C_{49}H_{41}N_2O_8$ $[M+H]^+$ 785.2863, found 785.2877. IR (cm^{-1}) ν 2979, 1718, 1608, 1456, 1401, 1367, 1274, 1177, 1104, 1021, 867, 766, 719.

4,8-Dimethyl-3,9-diphenylbenzo[*ij*]imidazo[2,1,5-*de*]quinolizine (5ai)[20e,20f,25]

Yellow-green solid, 30.3 mg (81%). M.p.: 212 – 214 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 1H), 7.76 (d, J = 4.4 Hz, 2H), 7.56 (dd, J = 4.9, 3.8 Hz, 6H), 7.53 (d, J = 2.2 Hz, 3H), 7.52 – 7.49 (m, 1H), 7.49 – 7.46 (m, 1H), 2.54 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 136.6, 135.5, 130.3, 129.6, 129.4, 129.1, 128.8, 128.6, 128.5, 128.1, 128.0, 126.1, 126.0, 125.2, 124.9, 124.8, 119.4, 118.7, 16.1, 15.5. HRMS (ESI) *m/z* Calcd for $C_{27}H_{21}N_2$ $[M+H]^+$ 373.1705, found 373.1697. IR (cm^{-1}) ν 3048, 2911, 1598, 1568, 1487, 1441, 1416, 1364, 1173, 1074, 763, 703.

6-Methoxy-3,4,8,9-tetraphenylbenzo[*ij*]imidazo[2,1,5-*de*]quinolizine (5fa)[20e,20f,25]

Yellow-green solid, 52.1 mg (99%). M.p.: >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.31 (d, J = 7.7 Hz, 2H), 7.29 – 7.24 (m, 5H), 7.23 – 7.14 (m, 13H), 6.86 (dd, J = 6.6, 2.2 Hz, 2H), 3.57 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 136.8, 136.5, 136.1, 135.4, 134.9, 131.5, 130.7, 130.6, 130.5, 129.8, 128.6, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 126.6, 126.4, 126.1, 107.9, 106.1, 55.5. HRMS (ESI) *m/z* Calcd for $C_{38}H_{27}N_2O$ $[M+H]^+$ 527.2123, found 527.2117. IR (cm^{-1}) ν 3055, 2960, 1602, 1560, 1446, 1416, 1261, 1205, 1070, 1018, 780, 709.

Preparation of 4 from 3aa

A mixture of **3aa** (97.8 mg, 0.2 mmol), alkyne **2** (0.2 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), and $Cu(OAc)_2 \cdot H_2O$ (80.0 mg, 0.4 mmol) were weighted in a Schlenk tube equipped with a stir bar.

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DOI: 10.1039/C5OB00823A

Dry *t*-AmOH (2.0 mL) was added and the mixture was stirred at 80 °C for 4 h under Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was absorbed onto a small amount of alumina. Products **4** were isolated by column chromatography on an alumina using CH_2Cl_2/MeOH (80/1–50/1) as eluant.

8,9-diphenyl-3,4-di-*p*-tolyl-1-(2,4,6-trimethylbenzyl)-

benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4aae)

Yellow-green solid, 137.0 mg (99%). M.p.: >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.5 Hz, 2H), 7.64 (q, J = 7.8 Hz, 2H), 7.53 (d, J = 7.2 Hz, 1H), 7.40 – 7.27 (m, 8H), 7.18 – 7.05 (m, 6H), 6.99 (d, J = 7.3 Hz, 2H), 6.93 (s, 1H), 6.82 (s, 2H), 5.03 (s, 2H), 2.35 (s, 3H), 2.25 (s, 3H), 2.21 (s, 3H), 2.14 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 139.6, 138.3, 137.9, 136.8, 134.0, 132.3, 131.9, 131.4, 131.1, 130.6, 129.7, 129.6, 129.4, 129.2, 129.1, 128.5, 128.4, 128.3, 127.6, 126.7, 125.9, 125.5, 124.9, 124.5, 124.4, 115.4, 49.0, 21.1, 21.0, 20.8, 19.7. HRMS (ESI) *m/z* Calcd for $C_{49}H_{41}N_2$ $[M–Cl]^+$ 657.3264, found 657.3284. IR (cm^{-1}) ν 3021, 2917, 1618, 1555, 1493, 1444, 1337, 1272, 1173, 933, 854, 763, 705.

3,4-bis(4-methoxyphenyl)-8,9-diphenyl-1-(2,4,6-trimethylbenzyl)-

benzo[*ij*]imidazo[2,1,5-*de*]quinolizinium chloride (4aaf)

Yellow-green solid, 143.5 mg (99%). M.p.: >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.3 Hz, 2H), 7.66 (d, J = 4.7 Hz, 2H), 7.56 – 7.49 (m, 1H), 7.42 – 7.27 (m, 8H), 7.17 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 7.6 Hz, 2H), 6.94 (s, 1H), 6.89 (d, J = 7.5 Hz, 2H), 6.83 (s, 2H), 6.74 (d, J = 7.7 Hz, 2H), 5.05 (s, 2H), 3.81 (s, 3H), 3.75 (s, 3H), 2.22 (s, 3H), 2.16 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 159.1, 146.0, 139.6, 138.2, 136.3, 134.0, 132.2, 131.9, 131.1, 130.6, 129.6, 129.4, 129.3, 128.5, 128.4, 128.3, 127.6, 127.4, 126.7, 126.5, 125.9, 125.8, 125.4, 125.3, 124.9, 124.4, 124.3, 115.3, 114.1, 113.8, 55.0, 49.0, 20.8, 19.7. HRMS (ESI) *m/z* Calcd for $C_{49}H_{41}N_2O_2$ $[M–Cl]^+$ 689.3123, found 689.3186. IR (cm^{-1}) ν 2923, 1714, 1613, 1495, 1460, 1290, 1175, 830, 766, 705.

Gram-scale synthesis of 4aa

A mixture of imidazolium salt **1a** (1.0 g, 3.2 mmol), diphenylacetylene (**2a**) (1.036 g, 5.8 mmol), $[Cp^*RhCl_2]_2$ (90.1 mg, 0.145 mmol, 5 mol%), and $Cu(OAc)_2\cdot H_2O$ (2.326 g, 11.6 mmol) were weighted in a Schlenk tube equipped with a stir bar. Dry *t*-AmOH (29 mL) was added and the mixture was stirred at 80 °C for 4 h under Ar atmosphere. Then the mixture was cooled to room temperature, diluted with CH_2Cl_2 and transferred to a round bottom flask. Alumina was added to the flask and the solvents were evaporated under reduced pressure. After purification by flash column chromatography on alumina, 1.6 g (76%) of **4aa** was obtained.

Preparation of d_5-iodobenzene

The d_5-iodobenzene was prepared by following a similar procedure for the synthesis of iodobenzene according to the published procedure.[26] A mixture of d_6-benzene (0.46 mL, 5 mmol), AgOTf (1.284 g, 5 mmol), and iodine (1.27 g, 5 mmol) in dry CH_2Cl_2 (20 mL) was stirred for 15 min at room temperature in dark condition. Then the reaction mixture was passed through a short Celite pad and washed with CH_2Cl_2. The combined filtrates were washed with dilute NH_4OH solution, dilute Na_2SO_3, and water, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The resulting residue was utilized directly for further reaction purpose.

Preparation of *N*-(d_5-phenyl)imidazole[23]

A mixture of CuI (53.8 mg, 0.28 mmol), Cs_2CO_3 (1.84 g, 5.6 mmol), imidazole (269.4 mg, 3.9 mmol), and d_5-iodobenzene (591 mg, 2.8 mmol) in DMF (60 mL) was stirred for 30 min at room temperature under Ar, and then heated at 120 °C for 40 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, filtered through a pad of silica gel, and washed with water. Then the organic phase was dried over anhydrous Na_2SO_4 and the filtrate was evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel with EtOAc/petroleum (1/1) to provide the desired product (209 mg, 50%).

Preparation of 1-(d_5-phenyl)-3-(2,4,6-trimethylbenzyl)imidazolium

chloride (1a-d_5)

A mixture of the *N*-(d_5-phenyl)imidazole (435.4 mg, 2.9 mmol) and 2-(chloromethyl)-1,3,5-trimethylbenzene (492.3 mg, 2.9 mmol) in THF (10 mL) were refluxed overnight in a round-bottom flask equipped with a condenser. After cooling to room temperature, **1a**-d_5 (645.0 mg, 70%) was obtained as a white solid by filtered, washed with hexane, and dried. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (s, 1H), 8.15 (s, 1H), 6.85 (s, 1H), 6.81 (s, 2H), 5.66 (s, 2H), 2.18 (s, 9H).

Preparation of 3aa-d_4

A mixture of **1a**-d_5 (47.0 mg, 0.15 mmol), diphenylacetylene (26.7 mg, 0.15 mmol), $[Cp^*RhCl_2]_2$ (2.4 mg, 0.0037 mmol), and $Cu(OAc)_2\cdot H_2O$ (60.0 mg, 0.3 mmol) were weighted in a Schlenk tube equipped with a stir bar. Dry MeOH (1.5 mL) was added and the mixture was stirred at 80 °C for 4 h under Ar atmosphere. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was absorbed onto a small amount of alumina. Purification by column chromatography on an alumina with CH_2Cl_2/MeOH (50/1) afforded **3aa**-d_4 (69.4 mg) in 94% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.36 (d, J = 2.1 Hz, 1H), 7.58 (d, J = 6.8 Hz, 2H), 7.37 (ddd, J = 20.6, 10.2, 4.3 Hz, 7H), 7.25 (d, J = 6.8 Hz, 2H), 6.96 (s, 2H), 2.25 (s, 3H), 2.07 (s, 6H).

KIE experiments

(a) A mixture of **1a** (31.3 mg, 0.1 mmol) or **1a**-d_5 (31.8 mg, 0.1 mmol), diphenylacetylene (17.8 mg, 0.1 mmol), $[Cp^*RhCl_2]_2$ (1.6 mg, 0.0025 mmol), and $Cu(OAc)_2\cdot H_2O$ (40.0 mg, 0.2 mmol) were weighed in a Schlenk tube equipped with a stir bar. Dry MeOH (1.0 mL) was added and the mixture was stirred at 80 °C for 25 min under Ar atmosphere. Afterward, the two independent reaction mixtures were poured into a same round flask. The solvent was evaporated under reduced pressure, and the residue was absorbed to a small amount of alumina. The purification was performed by column chromatography on an alumina using CH_2Cl_2/MeOH (50/1) as eluant.

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(b) A mixture of **1a** (17.2 mg, 0.055 mmol) or **1a**-d_5 (17.5 mg, 0.055 mmol), diphenylacetylene (17.8 mg, 0.1 mmol), $[Cp^*RhCl_2]_2$ (1.6 mg, 0.0025 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (40 mg, 0.2 mmol) were weighed in a Schlenk tube equipped with a stir bar. Dry *t*-AmOH (0.5 mL) was added and the mixture was stirred at 80 °C for 50 min under Ar atmosphere. Afterward, the two independent reaction mixtures were poured into a same round flask. The solvent was evaporated under reduced pressure, and the residue was absorbed to a small amount of alumina. The purification was performed by column chromatography on an alumina using CH_2Cl_2/MeOH (80/1–50/1) as eluant.

(c) A mixture of **3aa** (24.5 mg, 0.05 mmol) or **3aa**-d_4 (24.7 mg, 0.05 mmol), diphenylacetylene (8.9 mg, 0.05 mmol), $[Cp^*RhCl_2]_2$ (1.6 mg, 0.0025 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (20 mg, 0.1 mmol) were weighed in a Schlenk tube equipped with a stir bar. Dry *t*-AmOH (0.5 mL) was added and the mixture was stirred at 80 °C for 15 min under Ar atmosphere. Afterward, the two independent reaction mixtures were poured into a same round flask. The solvent was evaporated under reduced pressure, and the residue was absorbed to a small amount of alumina. The purification was performed by column chromatography on an alumina using CH_2Cl_2/MeOH (80/1–50/1) as eluant.

Preparation of intermediate A

A mixture of imidazolium salt **1a** (15.6 mg, 0.05 mmol), $[Cp^*RhCl_2]_2$ (15.4 mg, 0.025 mmol, 0.5 equiv), NaOAc (16.4 mg, 0.2 mmol), and THF (2 mL) in a Schlenk tube equipped with a stir bar was stirred at 80 °C for 8 h. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was absorbed onto a small amount of alumina. After purification by column chromatography on an alumina with EtOAc/petroleum (1/6) column as eluant, intermediate **A** (25.6 mg, 93%) was obtained as an orange-red solid. M.p.: 228 – 230 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (s, 1H), 7.70 (s, 1H), 7.36 (s, 1H), 6.97 (s, 4H), 6.50 (s, 1H), 5.46 (dd, J = 32.3, 13.2 Hz, 2H), 2.27 (s, 9H), 1.70 (s, 15H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.6, 146.0, 138.2, 137.8, 137.2, 129.0, 128.0, 124.2, 122.1, 119.5, 115.3, 111.1, 97.0, 47.2, 20.5, 19.6, 9.7, 9.4. HRMS (ESI) *m/z* Calcd for $C_{28}H_{33}N_2Rh$ $[M–Cl]^+$ 513.1777, found 513.1782. IR (cm^{-1}) ν 3015, 2919, 1603, 1548, 1442, 1349, 1231, 1137, 1030, 851, 754, 702.

Stoichiometric reaction of intermediate A with diphenylacetylene

A mixture of intermediate **A** (27.5 mg, 0.05 mmol), diphenylacetylene (8.9 mg, 0.05 mmol), and MeOH (2 mL) in a Schlenk tube equipped with a stir bar was stirred at 80 °C for 4 h. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was absorbed onto a small amount of alumina. After purification by column chromatography on an alumina with CH_2Cl_2/ MeOH (50/1) as eluant, 18.2 mg (74%) of **3aa** was obtained.

Catalytic reaction with intermediate A

A mixture of imidazolium salt **1a** (0.2 mmol, 1.0 equiv.), alkyne **2a** (0.2 mmol, 1.0 equiv), intermediate **A** (5.5 mg, 0.01 mmol, 5 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (80.0 mg, 2.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry MeOH (2.0 mL) was added and the mixture was stirred at 80 °C for 4 h under Ar atmosphere. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was absorbed onto a small amount of alumina. After purification by column chromatography on an alumina with CH_2Cl_2/ MeOH (50/1) as eluant, 91.6 mg (92%) of **3aa** was obtained.

Preparation of intermediate B

A mixture of imidazolium salt **3aa** (24.5 mg, 0.05 mmol), $[Cp^*RhCl_2]_2$ (15.4 mg, 0.025 mmol, 0.5 equiv), NaOAc (16.4 mg, 0.2 mmol), and THF (2 mL) in a Schlenk tube equipped with a stir bar was stirred at 80 °C for 12 h. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was absorbed onto a small amount of alumina. After purification by column chromatography on an alumina with EtOAc/petroleum (1/4) as eluant, intermediate **B** (32.6 mg, 90%) was obtained as an orange-red solid. M.p.: >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 (s, 1H), 7.59 – 7.44 (m, 3H), 7.34 (s, 7H), 7.22 (m, 1H), 7.04 (s, 1H), 6.96 (s, 2H), 6.68 (s, 1H), 4.59 (d, J = 14.1 Hz, 1H), 4.50 (d, J = 13.2 Hz, 1H), 2.25 (s, 3H), 2.08 (s, 6H), 1.72 (s, 15H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.9, 153.6, 144.1, 144.0, 143.5, 138.4, 138.2, 137.5, 135.6, 135.0, 133.1, 131.0, 129.9, 129.1, 128.6, 128.1, 128.0, 127.8, 127.7, 127.6, 127.3, 127.2, 124.3, 121.9, 121.6, 121.1, 100.7, 46.1, 20.5, 18.9, 9.0. HRMS (ESI) *m/z* Calcd for $C_{43}H_{42}N_2Rh$ $[M–Cl]^+$ 689.2403, found 689.2412. IR (cm^{-1}) ν 2918, 2852, 1605, 1513, 1457, 1375, 1341, 1261, 1175, 1101, 1027, 802, 757, 704.

Stoichiometric reaction of intermediate B with diphenylacetylene

A mixture of intermediate **B** (36.3 mg, 0.05 mmol), diphenylacetylene (8.9 mg, 0.05 mmol), and *t*-AmOH (2 mL) in a Schlenk tube equipped with a stir bar was stirred at 80 °C for 4 h. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was absorbed onto a small amount of alumina. After purification by column chromatography on an alumina with CH_2Cl_2/MeOH (80/1–50/1) as eluant, 17.5 mg (53%) of **4aa** was obtained.

Catalytic reaction with intermediate B

A mixture of imidazolium salt **1a** (0.22 mmol, 1.1 equiv.), alkyne **2a** (0.4 mmol, 2.0 equiv), intermediate **B** (7.3 mg, 0.01 mmol, 10 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (80.0 mg, 2.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry *t*-AmOH (2.0 mL) was added and the mixture was stirred at 80 °C for 4 h under Ar atmosphere. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was absorbed onto a small amount of alumina. After purification by column chromatography on an alumina with CH_2Cl_2/MeOH (80/1–50/1) as eluant, 129.0 mg (97%) of **4aa** was obtained.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (Nos 21372122 and 21421062) for financial support.

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DOI: 10.1039/C5OB00823A

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