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Cascade Skeletal Rearrangement of Gold Carbene Intermediates: Synthesis of Medium-Sized Pyrimidine-Fused Benzolactones

Ali Wang,[a] Xiaoping Hu,[a] Xin Xie,[a] and Yuanhong Liu[a,*]

[a] State Key Laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, People's Republic of China
E-mail: yhliu@sioc.ac.cn

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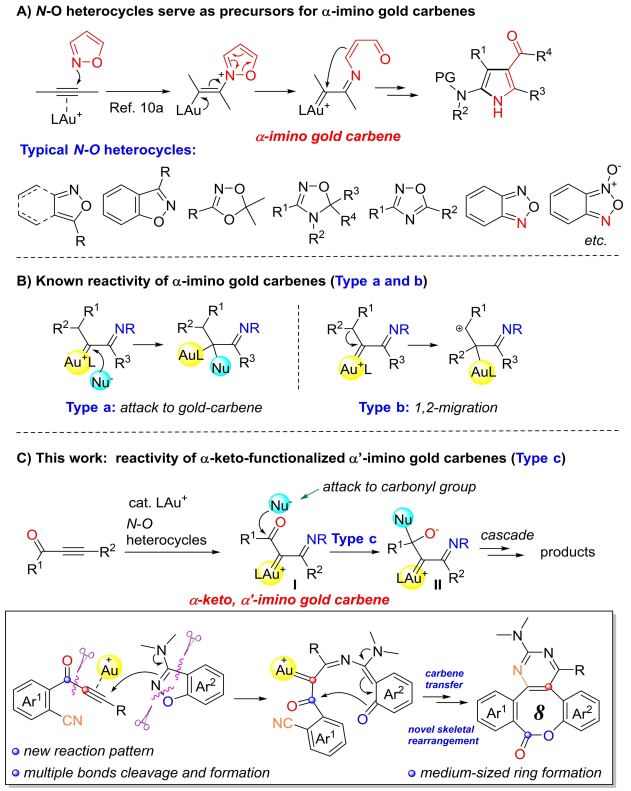
Abstract: A gold-catalyzed cyclization/cascade skeletal rearrangement of *o*-cyanophenylalkynones with 3-amino-benzo[*d*]-isoxazoles has been developed, which provides an approach for synthesizing medium-sized benzolactones. Based on the experimental results, we postulate that the initial nucleophilic attack occurs preferentially at the keto moiety instead of the gold-carbene. This reactivity initiates an attractive cascade process involving carbene transfer, 1,2-aryl migration, cycloaddition, ring-expansion etc. resulting in multiple bonds cleavage of the initial substrates.

Keywords: gold catalysis; ynones; benzo[*d*]-isoxazoles; gold carbene; skeletal rearrangement

Transition-metal-catalyzed reactions involving C–C bonds cleavage have attracted significant attention not only because they can offer efficient and rapid amplification of molecular complexity through reorganization of organic skeletons, but also due to their intriguing reaction mechanisms.[1] Because of the inherent strength and stability of C–C bond (83–85 kcal mol-1),[2] the cleavage of C–C bonds has emerged as one of the most challenging and valuable targets in organic synthesis. In this context, gold-catalyzed skeletal rearrangements via cationic or gold-carbene intermediates have been proved to be a powerful tool for the cleavage of C–C bonds as well as C–X bonds.[3] Owing to the distinguished reactivities and excellent selectivities of these highly electrophilic intermediates, C–C or C–X bond cleavage reactions (e. g., via 1,2-migration) have been widely invoked in gold-catalyzed transformations such as in 1,n-enyne cycloisomerization,[4] 1,2-acyloxy migration of propargyl carboxylates,[5] furan-yne cyclizations,[6] the retro-Buchner reaction of cyclo-heptatrienes,[7] oxygen[8] and nitrene transfer[9] reactions etc. However, the reactions involving three or more than three chemical bonds cleavage are quite rare in gold-catalyzed rearrangement reactions.

N–O-containing heterocycles such as isoxazoles[10] and benzo[*c*]isoxazoles (anthranils)[11] are easily available heterocyclic compounds. Since the pioneering studies by Ye, Hashmi, Liu, et al., these heterocycles have been disclosed to be efficient nitrene transfer reagents for the generation of α-imino gold-carbene intermediates. The related catalytic reactions are usually initiated through the nucleophilic attack of the N–O-heterocycles to the gold-activated alkyne followed by ring-opening to give an α-imino gold-carbene intermediate (Scheme 1A). Generally, the subsequent reactions tend to occur at the carbene center via nucleophilic attack (type **a**), or 1,2-C–C bond migration (type **b**) (Scheme 1B). As our continuous interests in the development of the new strategies for the synthesis of heterocycles, we recently found that 1,4,2-dioxazoles,[12a] 4,5-dihydro-1,2,4-oxadiazoles,[12b] benzo[*d*]iso-xazoles,[12c,d] benzofurazans[12e] and benzofurazans *N*-oxides[12e] (see Scheme 1A) could also be used as efficient nitrene transfer reagents[12,13] to promote gold-catalyzed cycloaddition reactions with ynamides. During our studies on ynones,[14] we envisioned that α-keto, α'-imino gold carbenes **I** would be generated from ynones. It is possible that both of the keto and gold-carbene moiety might be attacked by a nucleophile. The chemoselectivity should be highly dependent on the substitution pattern of the substrates. The reaction with the keto moiety would result in the formation of a new gold-carbene intermediate **II** poised for further C–X bond formations (Scheme 1C, type **c**). However, such reaction pattern has not been reported yet. We postulate that the reactivity of the

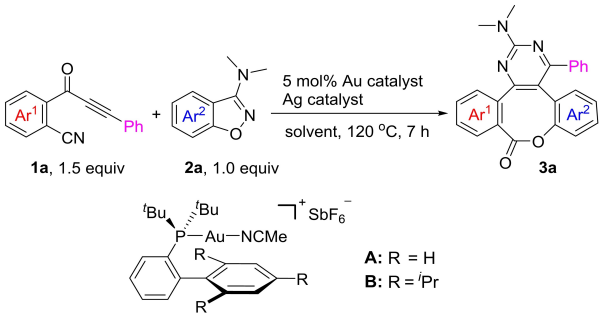


Scheme 1. Gold-catalyzed reactions involving α-imino gold carbenes.

keto moiety might be greatly enhanced by an electron-poor R^1 group. Herein, we report a gold-catalyzed reaction of cyano-functionalized ynones with 3-amino-benzo[*d*]isoxazoles. To our surprise, the ensuing catalytic reaction proceeds via an unprecedent cascade skeletal rearrangement with cleavage of two C–C bonds and one C–O bond of the starting substrates, furnishing pyrimidine-fused dibenzo[*b*,*f*]oxocin-6-one derivatives with wide functional group compatibility. The method offers an efficient and straightforward access for the synthesis of medium-sized heterocycles.

Our studies began with the optimization of gold-catalyzed reactions of *o*-cyanophenylalkynone **1a** with *N*,*N*-dimethylbenzo[*d*]-isoxazol-3-amine **2a**. Gratifyingly, in the presence of 5 mol% JohnphosAu(MeCN)SbF_6 (catalyst **A**), an eight-membered pyrimidine-fused benzolactone **3a** with blue fluorescent was formed in 34% yield in DCE at 120 °C for 7 h (Table 1, entry 1). The structures of **3a** and its analogs **3c** and **3n** (vide infra) were unambiguously confirmed by X-ray crystallography.[15] Interestingly, these molecules adopt a highly bent saddle shape, wherein two of the phenyl rings are in a *syn* orientation. Based on the X-ray structures of **3c** and **3n**, we could define that the Ar^1 and Ar^2 ring in **3a** come from the ynone and benzoisoxazole, respectively. The results also indicates that ring-opening of benzoisoxazole occurs during the

Table 1. Optimization of the reaction conditions.



Entry	Au catalyst	Ag catalyst (mol %)	Solvent	Yield (%)[a]
1	catalyst **A**	–	DCE	34
2	catalyst **B**	–	DCE	6
3	PPh_3AuNTf_2	–	DCE	10
4	$IPrAuNTf_2$	–	DCE	53
5	$AuBr_3$	–	DCE	3
6	**IPrAuCl**	**$AgNTf_2$ (10)**	**DCE**	**63**
7	IPrAuCl	$AgNTf_2$ (20)	DCE	65
8	IPrAuCl	$AgNTf_2$ (5)	DCE	48
9	$(ArO)_3PAuCl$[b]	$AgNTf_2$ (10)	DCE	27
10	IPrAuCl	$AgNTf_2$ (10)	Toluene	51
11	IPrAuCl	$AgNTf_2$ (10)	1,4-dioxane	43
12	IPrAuCl	$AgNTf_2$ (10)	MeCN	36
13	IPrAuCl	$AgNTf_2$ (10)	$MeNO_2$	13
14	IPrAuCl	$AgSbF_6$ (10)	DCE	61
15	IPrAuCl	$AgBF_4$ (10)	DCE	60
16	IPrAuCl	AgOTf (10)	DCE	60
17	IPrAuCl	AgOTs (10)	DCE	18
18	IPrAuCl	AgOAc(10)	DCE	0
19	IPrAuCl	–	DCE	0
20	–	$AgNTf_2$ (10)	DCE	0

[a] The yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.
[b] Ar = (2,4-di^{t}Bu)C_6H_3.

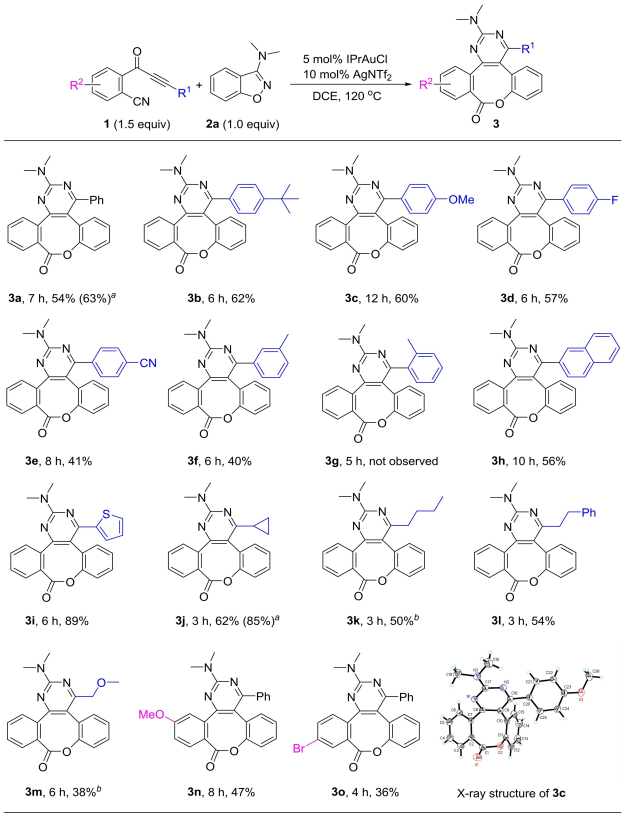
process, and the cyano group in **1a** is incorporated into the newly-formed pyrimidine ring. The use of more hindered ^{t}BuXPhosAuMeCNSbF$_6$ (catalyst **B**) led to only 6% of **3a** (entry 2). Screening of the gold catalysts revealed that *N*-heterocyclic carbene gold(I) complex $IPrAuNTf_2$ (IPr = 1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene) provided **3a** in a higher yield of 53% (entry 4). When the reaction was conducted with 5 mol% IPrAuCl and 10 mol% $AgNTf_2$, the yield could be further improved to 63% (entry 6). Increasing the amount of $AgNTf_2$ did not improve the product yield apparently (entry 7). However, reducing the amount of $AgNTf_2$ afforded **3a** in lower yield (48%, entry 8). Other solvents such as toluene, 1,4-dioxane etc. could not improve the reaction efficiency (entries 10–13). The counter anions such as SbF_6^-, BF_4^- or OTf^- were also effective for this transformation, while OTs^- and OAc^- were

significantly less efficient (entries 14–18). The use of IPrAuCl or $AgNTf_2$ alone failed to catalyze the reaction (entries 19–20).

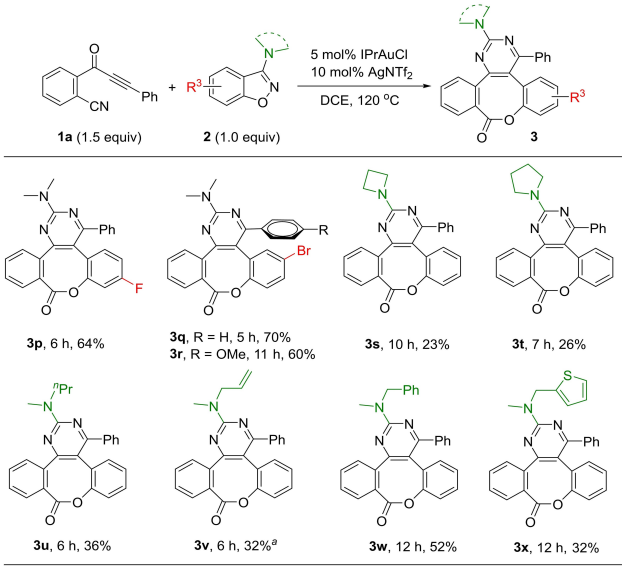
We next investigated the substrate scope of this reaction under the conditions shown in Table 1, entry 6. First, the scope of ynones bearing different functionalities at their alkyne terminus was examined using **2 a** as the reaction partner (Scheme 2). Substrates bearing either electron-donating (*p*-^{t}Bu, *p*-OMe) or electron-withdrawing (*p*-F, *p*-CN) groups on the aryl rings proceeded smoothly to give **3 b**–**3 e** in 41–62% yields. A 3-Me substituent on the phenyl ring was compatible (**3 f**). When a sterically demanding *o*-methylphenyl-substituted alkyne was employed, no desired product was formed (**3 g**). However, less hindered 2-naphthyl-substituted alkyne cyclized efficiently to provide **3 h** in 56% yield. The results indicate that the reaction is sensitive to the steric effect. Reaction of the heteroaryl-substituted alkyne such as 2-thienyl-substituted one proceeded cleanly to furnish **3 i** in excellent yield. Substrate with a cyclopropyl group also showed a high reactivity (**3 j**). Due to the poor solubility of **3 j**, the NMR yield of this product was also provided. Aliphatic alkynes with n-butyl or phenylethyl substituent converted to **3 k**–**3 l** in 50–54% yields. With a methoxy group on the alkyl chain, 38% yield of **3 m** was observed. Substrates bearing methoxy or bromo group on the parent aryl ring were also compatible (**3 n**–**3 o**). However, when free amine of benzo[*d*]isoxazol-3-amine was used as a substrate, complicated reaction mixture was observed.

Next, the scope of benzo[*d*]isoxazoles **2** was examined (Scheme 3). The method was general for various benzoisoxazoles. The fluoro or bromo substituent on the phenyl ring were compatible (**3 p**–**3 r**). Especially, **3 q** and **3 r** with a bromo substituent can be further elaborated via cross-coupling reactions. The amino moiety could be azacycles such as azetidine or pyrrolidine (**3 s**, **3 t**). *N*-propyl, *N*-allyl, *N*-benzyl or *N*-thiophen-2-ylmethyl substrates turned out to be suitable (**3 u**–**3 x**). These results demonstrated the diversity and flexibility of this method. Pyrimidines and their fused derivatives exist as key structures in numerous natural products and pharmaceutical agents.[16] Therefore, the development of efficient route to pyrimidines is highly demanded.

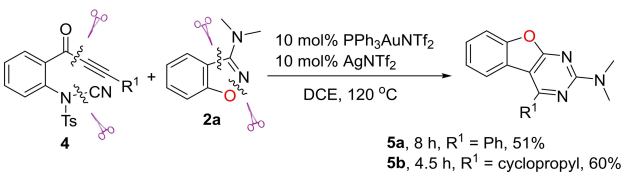
The above results prompted us to investigate the reactivity of other type of ynone-nitriles. Benzofuro[2,3-*d*]pyrimidine derivatives **5** were formed in 51–60% yields from the reactions of ynone-cyanamides **4** with **2 a** (Scheme 4). Among them, **5 a** displays strong



Scheme 2. Scope of ynones. [a] NMR yield. [b] 2.5 equiv. ynone was used.



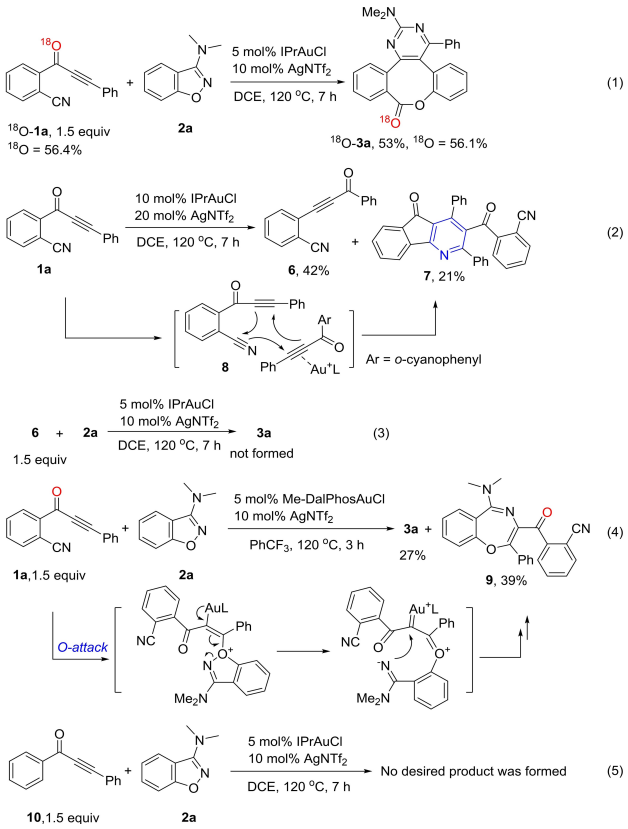
Scheme 3. Scope of benzo[*d*]isoxazoles. [a] 2.5 equiv. **1 a** was used.



Scheme 4. Reaction of ynone-cyanamides with **2 a**.

blue fluorescent. Interestingly, during the process, four chemical bonds of the substrates were cleaved including two C–C bonds, one C–N bond and one N–O bond.

To understand the reaction mechanism, various control experiments were performed (Scheme 5). It was found that ^{18}O-labeled substrate ^{18}O-**1a** converted to the corresponding lactone ^{18}O-**3a** in 53% yield under the standard conditions. The result implies that the carbonyl oxygen in the product come from ynone **1a** (Scheme 5, eq 1). It was reported that ynones could undergo 1,3-oxygen transposition under gold catalysis.[17] In fact, in the absence of benzoisoxazole, the transposed product **6** was formed from **1a**, along with a pyridine derivative **7** through cyclodimerization via **8** (Scheme 5, eq 2). However, the desired product **3a** was not formed via gold-catalyzed reaction of **6** with **2a**, indicating that **6** is not the intermediate for **3a** (Scheme 5, eq 3). To learn if the gold-carbene is formed or not during the process, we tried to isolate the possible intermediates or byproducts under various reaction conditions. Attempt to trap the gold carbene intermediate by adding styrene failed to obtain the desired products. To our delight, when Me–DalPhosAuCl was used as the pre-catalyst, the desired **3a** was obtained in 27% yield in $PhCF_3$, along with [5+2] cycloaddition product **9** (Scheme 5, eq 4). The product

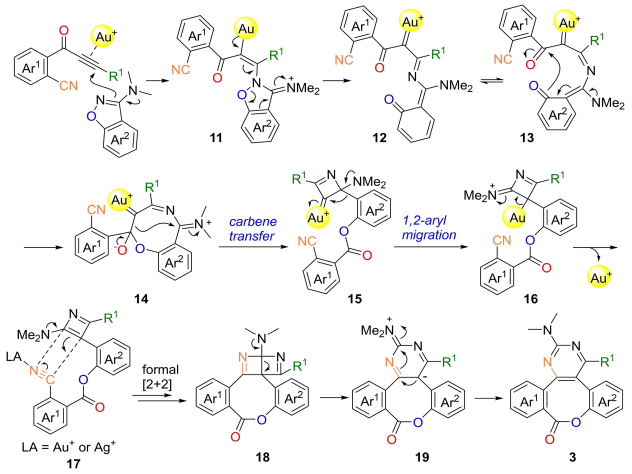


Scheme 5. Control experiments.

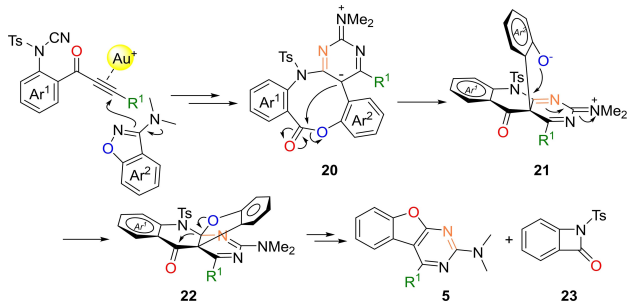
9 is possibly formed via *O*-attack of benzo[*d*]isoxazole to ynone followed by nucleophilic attack of the nitrogen moiety to the gold-carbene. Recently, *O*-attack of benzisoxazoles to propiolates was reported by Liu et al., which is assumed to be reversible with that of *N*-attack. The *O* or *N*-attack in these reactions led to α-imino gold carbenes.[10e,11c] Possibly, both *N*-attack and *O*-attack are involved in the reaction shown in eq 4. The results also imply that α-imino gold carbene may also be formed in our reaction process. By comparison, we also investigated the reactivity of the ynone **10** without a cyano group. In this case, most of the substrates remained, and no desired product was formed (Scheme 5, eq 5). The result emphasizes the important role of the cyano group, which can enhance the ynone reactivity by increasing the polarity of the alkyne triple bond.

Based on the above results and our previous work,[12c] we tentatively propose the following reaction mechanism for this reaction (Scheme 6). Initially, attack of benzo[*d*]isoxazole to gold-activated ynone affords vinyl gold intermediate **11** regiospecifically, which fragmentizes into the α-imino gold-carbene **12.** **12** isomerizes to **13**. Then the newly formed carbonyl group attacks the keto moiety to give the cyclized intermediate **14**. Subsequently, carbene transfer via C–C bond cleavage followed by 1,2-aryl migration[18] generates the intermediate **16**. Elimination of gold catalyst gives **17.** **17** undergoes formal [2+2] cycloaddition to deliver ring-fused intermediate **18**. Ring-enlargement of **18** affords the final product **3**.

When cyanamides **4** are used as the substrates, the nine-membered heterocyclic intermediate **20** is generated through the similar reaction pathway. This is followed by the ring-closure and rearrangement to afford the products **5** (Scheme 7). The byproduct **23** could not be isolated due to no clean byproducts were



Scheme 6. Possible reaction mechanism for the formation of **3**.



Scheme 7. Possible reaction mechanism for the formation of **5**.

observed according to TLC analysis. Possibly, **23** was unstable under the current conditions.

In summary, we have disclosed for the first time a new reaction pattern of α-keto, α'-imino gold-carbene intermediates generated from *o*-cyanophenylalkynones and 3-aminobenzo[*d*]-isoxazoles. Based on the experimental results, we postulate that the initial nucleophilic attack occurs preferentially at the keto moiety instead of the gold-carbene due to the high electrophilicity of the keto moiety bearing a strong electron-withdrawing group. This unprecedented reactivity induces an attractive cascade process involving carbene transfer, 1,2-aryl migration, cycloaddition, ring-expansion etc. Further studies on the detailed reaction mechanism and extension of the synthetic utility are currently in progress in our laboratory.

Experimental Section

Typical Procedures for the Synthesis of Pyrimidine-Fused Benzolactones (3)

To a sealed tube (volume: 10 mL) were added **1a** (0.45 mmol, 104.1 mg), DCE (3 mL), **2a** (0.3 mmol, 48.7 mg), IPrAuCl (0.015 mmol, 9.3 mg) and $AgNTf_2$ (0.03 mmol, 11.6 mg) under argon. Then the tube was sealed. After the reaction mixture was stirred at 120 °C for 7 h as monitored by thin-layer chromatography, the reaction mixture was filtered through a pad of silica gel and washed with DCM. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (wet loading, eluent: petroleum ether: ethyl acetate = 30:1 to 20:1 to 15:1) to afford **3a** in 54% yield (63.5 mg) as a white solid. M.p. 252–253 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 (s, 6H), 6.56 (d, J = 7.6 Hz, 1H), 6.75–6.78 (m, 1H), 7.06–7.09 (m, 1H), 7.15–7.24 (m, 4H), 7.33–7.45 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.0, 114.0, 120.8, 126.0, 126.9, 127.8, 128.8, 129.0, 129.1, 129.3, 129.6, 130.9, 131.1, 131.5, 132.0, 136.5, 138.3, 151.3, 161.8, 165.3, 165.4, 169.1. IR (neat): 3055, 2917, 2869, 1739, 1583, 1560, 1516, 1483, 1442, 1409, 1375, 1240, 1211, 1189, 1104, 1094, 1068, 1040, 996, 898, 766, 749, 690, 652 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{20}N_3O_2$ 394.1550; found 394.1544.

Acknowledgements

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