PAPER

Check for updates

Direct intramolecular double cross-dehydrogentive-coupling (CDC) cyclization of N-(2-pyridyl)amidines under metal-free conditions†

Fengping Yi, Chao Fu, Qihui Sun, Huazhen Wei, Genfa Yu [ID] * and Weiyin Yi [ID] *

A facile transition-metal-free protocol to form 2-iminoimidazo[1, 2-a]-pyridines bearing a −CHBr$_2$ group and an aza-quaternary carbon center at the 3 position from N-(2-pyridyl)amidines substrates, in which the new heterocyclic skeletons constructed from amidines *via* radical reactions or nucleophilic substitution reactions are promoted only by CBr$_4$ under mild conditions, is demonstrated. The reactions were realized by intramolecular CDC reaction involving C−N and C−C bond formation *via* the sequential C(sp^3)−H bifunctionalization mode on the same carbon atom under mild conditions. Moreover, this work also provides an excellent and representative example for CBr$_4$ as an efficient reagent to initiate radical reactions under initiator-free conditions or to give rise to nucleophilic substitution reactions only by base.

Introduction

C–H functionalization, especially sp^3 C–H bond functionalization, to efficiently construct C–X (X = C, N, O, S, *etc.*) bonds has been one of the most researched topics in the field of organic chemistry because the formation of C–X (X = C, N, O, S, *etc*) bonds is a fundamental organic reaction.[1] Previous reports on C–H functionalization to build new C–X (X = C, N, O, S, *etc*) bonds required the prefunctionalization of the substrates, which caused unnecessary waste, great costs, and laborious experimental handling. Moreover, some cross-coupling reactions generally needed transition-metal catalysts and special ligands,[2] which would also cause heavy metal contamination for underground water and soil. Therefore, it is still highly desirable to further develop new atom- and step-economic, greener approaches to construct C–X (X = C, N, O, S, *etc*) bonds by direct C–H functionalization. More recently, cross-dehydrogenative-coupling (CDC) reactions,[3] especially transition-metal-free CDC reaction, which can introduce a substituent through the direct cleavage of a C–H bond under redox conditions without the introduction of a leaving group,[4] have emerged as a valuable tool for this transformation and have also gained significant attention because this strategy presented a non-metallic, environmentally friendly, and concise way compared to other previous available methods. For example, the formation of C–X (X = C, N, O, S, *etc*) bonds can be achieved by the metal-free CDC

reaction under only oxidants such as peroxides,[5] quinones[6] and hypervalent iodine reagents,[7] O$_2$,[8] or KO^{t}Bu/DMF.[9] Though every above-mentioned metal-free CDC protocol has its own advantages, further exploitation of more simple, efficient and metal-free CDC approaches to forge C–X (X = C, N, O, S, *etc*) bonds using various novel mediators under mild conditions is still the goal pursuit by many scientific workers.

Carbon tetrabromide (CBr$_4$), as a commercially available and cheap reagent, which has been utilized as a organocatalyst or a stoichiometric reagent for a variety of organic transformations, has attracted considerable attention from chemists.[10] Some literature surveys showed that CBr$_4$ was used to catalyze the deprotection of trialkylsilyl esters and *b*-(trimethylsilyl)ethoxymethyl ethers,[10b,11] esterifications,[10h] expoxide ring opening,[12] the acetalization of aldehydes,[13] the Friedel–Crafts alkylation indoles with carbonyl compounds,[14] the carboxylation of indoles with CBr$_4$/MeOH,[15] and esterification of methyl aromatic,[16] *etc*. Furthermore, most importantly, it has been found that CBr$_4$ also played an extremely important role in the formation of C–X (X = C, N, O, S, *etc*) bonds in the field of cross-dehydrogenation coupling (CDC) reactions to construct the physiological and biological active compounds *via* C–H functionalization under metal-free conditions.[17] For example, Huang's group developed an efficient and facile CBr$_4$-mediated CDC reaction to form the C–O bond and C–S bond under metal-free conditions.[17a,b] Equally, the Huo and other groups have also demonstrated a series of the CBr$_4$-promoted CDC and DOD reactions *via* C–C bond and C–N bond formation to construct successfully complex heterocyclic compounds such as imidazo[1, 2-a]pyridines, imidazo[1, 2-a]pyrimidines and imidazoles.[17c-k] The advancements of these reactions clearly showed that CBr$_4$ had great potential in organic synthesis. Therefore, it

School of Perfume and Aroma Technology, Shanghai Institute of Technology, Shanghai 201418, P. R. China. E-mail: yiwy@sit.edu.cn; shyugenfa@163.com

Paper

is an urgent mission for organic chemists to further develop its greater potential in organic chemistry at present.

As an important class of organic synthons, amidines have been frequently applied in the synthesis of various heterocyclic ring systems such as quinazolines,[18] quinazolinones,[19] pyrimidines,[20] triazoles,[21] and benzimidazoles.[22] Especially importantly, *N*-(2-pyridyl) amidines, as one of the most important *N*-aryl amidines, have also been employed for the formation of different biological active compounds bearing nitrogen-containing heterocyclic skeletons, including 1, 2, 4-triazoles and imidazo[1, 2-*a*]-pyridines, by the direct C–H functionalization for N–N and C–N bond formation in the presence of a catalyst and oxidant. For example, when a large variety of oxidants were used, including air,[23a,g] PIFA (phenyliodinebis(trifluoroacetate)),[23b] NaClO,[23c] Pb(OAc)$_4$,[23e,g] and I$_2$,[23f] 1,2,4-triazoles with various substituents can be afforded by intramolecular oxidative N–N bond formation from *N*-(2-pyridyl)amidines substrates (Scheme 1a). Significantly, in 2016, Chang's group[24] reported one example for the synthesis of 2-aminoimidazo[1, 2-*a*]-pyridines from *N*-(2-pyridyl)amidines *via* intramolecular oxidative C–N bond formation using I$_2$/KI as reagent (Scheme 1b), in which the bonding mode of reaction was completely different from a previously reported one by Chang and co-workers[23g] even under the same reaction conditions. These reports, as a consequence, indicated clearly that the results of the reaction could be greatly affected by the structure of the substrates and the reaction conditions. Although great progress has already been made in this area, there is still an urgent requirement to develop highly efficient and environmentally benign synthetic methods to construct the diverse core framework in structure *via* oxidative CDC strategies on account of the increasing demands of structural novelty and diversity in both biomedical research and drug discovery. Accordingly, in view of our continuous interest in amidines and ketenimines,[25] we herein report a transition-metal-free oxidative CDC cyclization reaction of *N*-(2-pyridyl)amidines *via* the sequential dual C–H functionalization of the C(sp^3)–H bond on the same carbon atom involving C–N and C–C bond formation, in which the new heterocyclic skeletons constructed from amidines *via* radical reactions or nucleophilic substitution reactions are promoted only by CBr$_4$ under mild conditions.

Results and discussion

The desire to create novel and diverse compounds in structure continues to activate us to investigate the reaction process of amidines by using CBr$_4$. Firstly, the oxidative cyclic conditions for the CDC strategy were optimized. To our delight, the reaction of *N*-(2-pyridyl)amidine (**1a**) and CBr$_4$ (**2**) was carried out at room temperature for 10 h in the presence of K$_2$CO$_3$ under N$_2$, giving the corresponding imidazo[1, 2-*a*]-pyridine core-like product in 25% yield (Table 1, entry 1). **3a** had been confirmed by ^{1}H NMR, ^{13}C NMR, and HRMS. Morever, we also observed that when the reaction temperature was elevated to 60 °C, the yield of **3a** was also increased to 37% accordingly (Table 1, entry 2). To further increase the yield of **3a**, the reactions were performed under different bases. As shown in Table 1 (Table 1, entries 2–7), it was found that K$_2$CO$_3$ turned out to be the best base in improving the yield of CDC reaction (entry 2, 37%). However, when TEA and DBU as bases were employed, two reactions furnished **3a** only in trace amounts (entries 4 and 7). We, subsequently, attempted to perform the reaction in various commonly used solvents. It was shown that, in contrast to DCM, the use of other solvents was found to be less effective (Table 1, entry 2 and entries 8–12). To render further improve the yield of the transformation, a change in the amount of reaction substrates was also investigated. The results indicated that the molar ratio of **1a** : **2** was enhanced to 1 : 1.2, the yield of reaction products was the best (Table 1, entries 13–19). However, it could be found that if the amount of CBr$_4$ was

previous work

a. previous examples for the synthesis of 1,2,4-triazoles from *N*-(2-pyridyl)amidines [ref 23]

R^2= aryl and alkyl
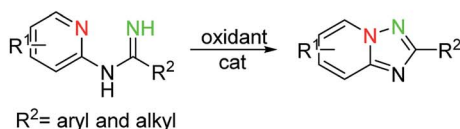
b. previous example for the synthesis of 2-amino-imidazo[1,2-a]pyridines from *N*-(2-pyridyl)amidines [ref 24]
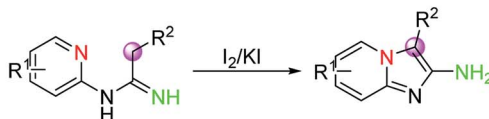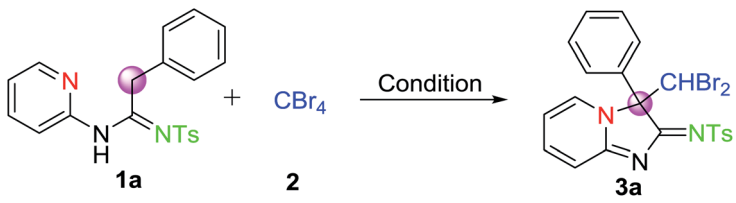

this work
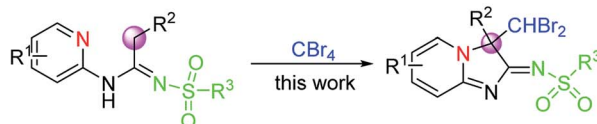
Scheme 1 Previous works on the oxidative cyclization of *N*-(2-pyridyl)amidines and this work.

Table 1 Optimization of the reaction conditions [a]

Entry	Catalyst	Solvent	Temp/°C	Yield[b] [%]
1	K_2CO_3	DCM	rt	25
2	K_2CO_3	DCM	60	37
3	Cs_2CO_3	DCM	60	30
4	TEA	DCM	60	Trace
5	LiO^{t}Bu	DCM	60	22
6	KO^{t}Bu	DCM	60	24
7	DBU	DCM	60	Trace
8	K_2CO_3	THF	60	Trace
9	K_2CO_3	DMF	60	Trace
10	K_2CO_3	MeCN	60	34
11	K_2CO_3	DMSO	60	Trace
12	K_2CO_3	Dioxane	60	28
13	K_2CO_3	DCM	60	41
14	K_2CO_3	DCM	60	45
15	K_2CO_3	DCM	80	57
16	K_2CO_3	DCM	100	68
17	K_2CO_3	DCM	120	66
18[c]	K_2CO_3	DCM	100	78
19[d]	K_2CO_3	DCM	100	74

[a] Reaction conditions: entries 1–12, **1a** (0.2 mmol), **2** (0.2 mmol), base (0.4 mmol) in solvent (2 mL), stirred at room temperature for 10 hours under N_2; entry 13, the molar ratio of **1a** : **2** = 1 : 1.5, the amount of other conditions is unchanged. Entries 14–20, the molar ratio of **1a** : **2** = 1 : 1.2, the amount of other conditions is unchanged. [b] An isolated yield of **3a** is given, **1a** is used as a reference. [c] The reaction was carried out for 12 hours. [d] The reaction was carried out for 14 hours.

further increased, the yield of the product **3a** would decrease (Table 1, entry 13, 31% yield). In addition, it was noteworthy that the longer reaction time and the more suitable higher temperature were required for the formation of **3a** (Table 1, entries 16–19). Finally, the optimized reaction conditions were obtained as follows: the CDC reaction system with the ratio of 1 : 1.2 (**1a** : **2**) was carried out at 100 °C in DCM for 12 h in the presence of K_2CO_3 under N_2.

Under the optimized conditions given above, the scope and generality of the reaction in regard to different N-(2-pyridyl) amidines (**1**), which were furnished from the reaction of 2-amino pyridines, terminal alkynes and sulfonyl azides under Cu(I) and base,[25,26] were investigated, and the results are summarized in Table 2. All tested amidines reacted smoothly with CBr_4 were efficiently transformed into their corresponding products (Table 2, **3a–3ad**) with moderate to good yields, reflecting wide scope of this CDC reaction system. The structure of product **3a** was also further confirmed by single-crystal X-ray diffraction, as also shown in Table 2. Moreover, it was found that the yields remained relatively stable and only N-(2-pyridyl) amidines derived from terminal alkynes with electron-withdrawing group on phenyl rings afforded slightly lower yields of products than those from other terminal alkynes

(Table 2, **3a–3i**). Meanwhile, the effect of different N-(2-pyridyl) amidines from sulfonyl azides was surveyed too. The results indicated that the yields of products derived from sulfonyl azides bearing electron-donating group on phenyl rings were obviously higher than those of products without substituents on phenyl rings of sulfonyl azides, for example, **3a** and **3x** or **3b** and **3y**.

From the results of the investigation in Table 2, we found that an appropriate temperature rise for the reaction would contribute to the formation of the products **3**. To further gain mechanistic insights into this transformation, a series of control experiments were performed under the envisaged conditions. However, when the reaction was carried out in the dark according to eqn (1) in Scheme 2 under the reaction conditions of entry 1 (Table 1), the yield is equal to that of entry 1. Similarly, the reaction was performed in the dark according to eqn (2) in Scheme 2 under standard reaction conditions, the desired product **3a** was also isolated in 76% yield, which was also close to that of the reaction in Table 1 (entry 18, 78%). These results indicated that the visible light was not essential for the successful completion of the reaction. In addition, the reaction of **1a** and **2** was conducted in the presence of 1 equiv. of TEMPO as a radical scavenger under the optimized conditions,

Table 2 Substrate scopes of CDC reaction system for the formation of **3** [a]
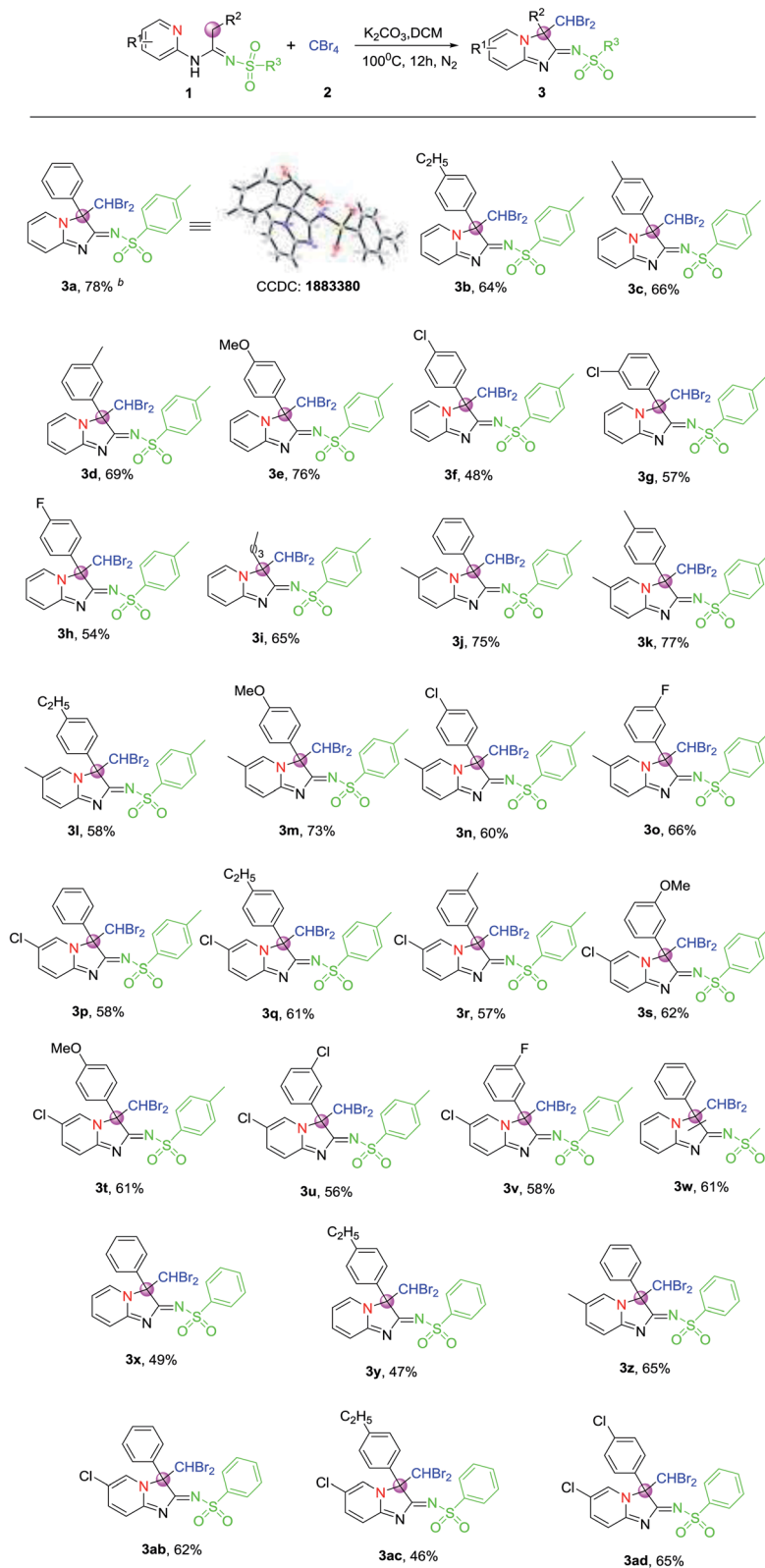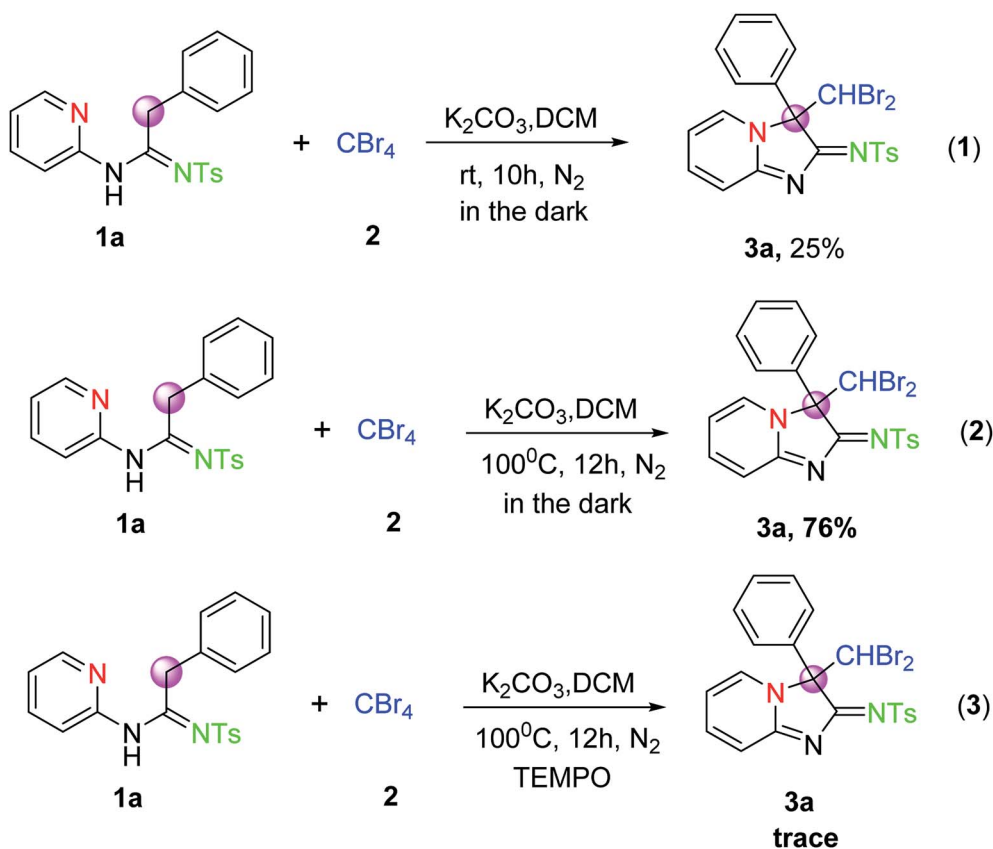
Scheme 2 Control experiments.

only the trace amount of **3a** was observed. This result suggested that radical processes might be involved in the CDC reaction system.

Based on these facts mentioned above and previous literatures,[17] a tentative mechanism for the transformation of **1a** and CBr$_4$ into **3a** is proposed, as depicted in Scheme 3. Initially, substrate **1a** can easily tautomerize into intermediate **1a′** in the presence of the α-hydrogen of the amidine group under such reaction conditions. And then, a hydrogen atom of intermediate **1a′** is abstracted by CBr$_3$ radical, which is derived from the homolytic cleavage of the C–Br bond of CBr$_4$ upon heating accompanied by the formation of Br radical, to deliver the radical intermediate **A**. Intermediate **A** reacts rapidly with Br radical to afford intermediate **B**. Subsequently, a base-promoted intramolecular nucleophilic substitution of intermediate **C**, which is achieved from intermediate **B** in the presence of base, will occur to provide intermediate **D**. Intermediate **D** will tautomerize into intermediate **D′** again. Finally, the desired product **3a** *via* intermediate **E** will be provided by the nucleophilic substitution of intermediate **D′** with CHBr$_3$ under base. Meanwhile, we can also not rule out another possible mechanism route that experienced a base promoted nucleophilic substitution. Thus, another possible mechanism process is also described by us (see ESI†).

In conclusion, we have demonstrated a facile metal-free strategy to form 2-iminoimidazo[1, 2-*a*]-pyridines by CBr$_4$-

mediated intramolecular CDC reaction under mild conditions, in which the new heterocyclic skeletons were constructed from amidines by the sequential C(sp^3)–H bifunctionalization mode on the same carbon atom involving C–N and C–C bond formation. The surveys could better reveal that the results of the reaction depended greatly on the structure of the substrates and the reaction conditions. Moreover, this approach further indicates that amidines have abundant reactivity under various reaction conditions again. This work also provides an excellent example for CBr$_4$ as an efficient reagent to initiate radical reactions under initiator-free conditions or to give rise to nucleophilic substitution reactions only by base.

Experimental section

General remarks

All reagents were purchased from commercial suppliers, and were used without further purification. All solvents were treated according to standard procedures. The progress of reactions was monitored by TLC. For chromatographic purifications, 200–300 mesh silica gel was used. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra were recorded with tetramethylsilane as an internal standard. HRMS measurements were carried out using the ESI ionization technique with an FT-ICR analyzer. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling
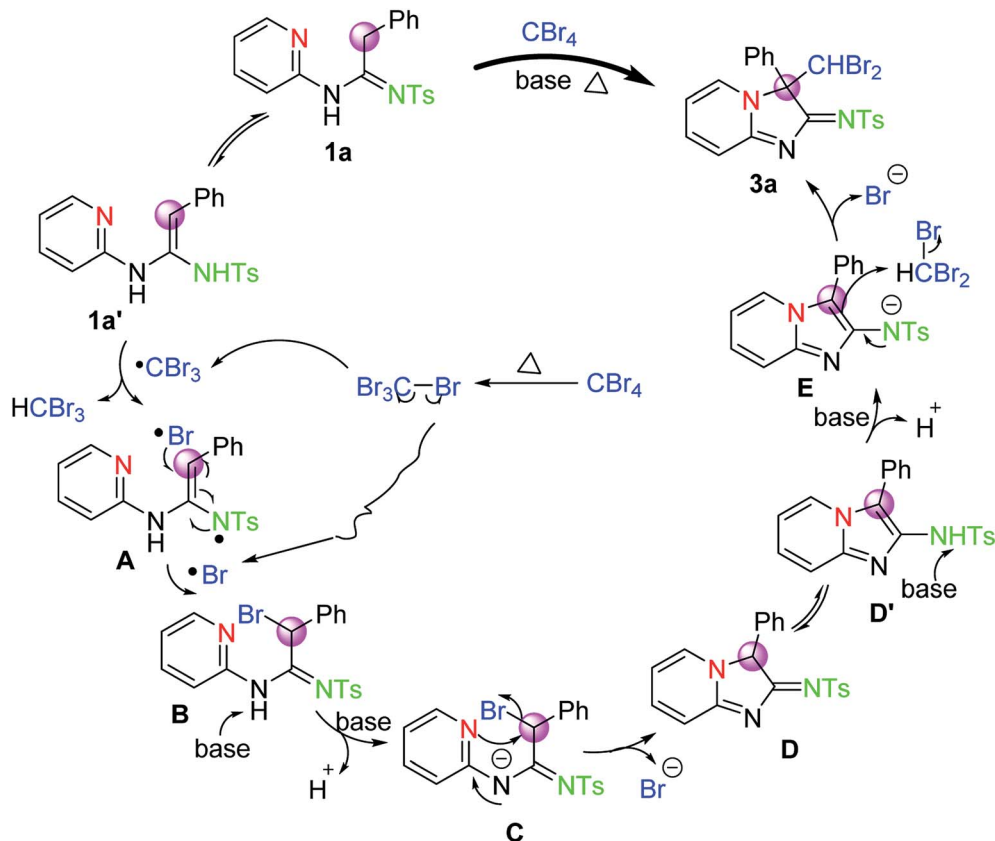
Scheme 3 The tentative mechanistic pathway for the formation of **3a**.

constants (Hz) and integration. CCDC (for **3a**) contains the supplementary crystallographic data for this paper.

Procedure for generation of *N*-(2-pyridyl)amidines 1

N-(2-Pyridyl)amidines (**1**) were prepared as reported in the literature[1f,26a] according to the reaction equation (see ESI†) or are commercially available.

General procedure for the synthesis of 3

Under N$_2$, a mixture of *N*-(2-pyridyl)amidines (**1**) (0.2 mmol), CBr$_4$ (**2**) (0.24 mmol), K$_2$CO$_3$ (0.3 mmol), in dry DCM (2 mL) was added to a sealed tube. And then, the mixture was stirred at 100 °C for 12 h. The reaction mixture was then cooled to room temperature. The solvent was removed under reduced pressure to give a residue. The crude product was purified on silica gel column chromatography using ethyl acetate and petroleum ether as the eluent to afford the desired products **3**.

Characterization data for 3

N-(3-(Dibromomethyl)-3-phenylimidazo[1,2-*a*]pyridin-2(3*H*)-ylidene)-4-methylbenzenesulfonamide (3a). A yellow solid (78%). Mp: 216–218 °C. ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.42 (d, *J* = 6.4 Hz, 1H), 8.02 (t, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 3H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 3H), 6.59 (s, 1H), 2.35 (s, 3H). ^{13}C

NMR (126 MHz, chloroform-*d*) δ 176.06, 165.89, 145.29, 142.25, 138.75, 135.34, 133.92, 129.73, 129.33, 128.62, 127.61, 125.53, 117.68, 114.59, 81.42, 45.46, 21.53. HRMS: calcd for C$_{21}$H$_{17}$-Br$_2$N$_3$O$_2$S [M + H]$^+$ 533.9481; found 533.9486.

N-(3-(Dibromomethyl)-3-(4-ethylphenyl)imidazo[1,2-*a*]pyridin-2(3*H*)-ylidene)-4-methylbenzenesulfonamide (3b). A light yellow solid (64%). Mp: 227–229 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.42 (d, *J* = 6.5 Hz, 1H), 8.00 (t, *J* = 7.7 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.18 (t, *J* = 9.4 Hz, 4H), 7.06 (t, *J* = 6.8 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.58 (s, 1H), 2.65 (q, *J* = 7.5 Hz, 2H), 2.36 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 176.28, 166.01, 146.12, 144.77, 142.12, 138.89, 135.34, 131.23, 128.78, 128.56, 127.68, 127.54, 125.47, 117.70, 114.00, 81.36, 45.66, 28.40, 21.52, 15.15. HRMS: calcd for C$_{23}$H$_{21}$Br$_2$N$_3$O$_2$S [M + H]$^+$ 563.9774; found 563.9783.

N-(3-(Dibromomethyl)-3-(*p*-tolyl)imidazo[1,2-*a*]pyridin-2(3*H*)-ylidene)-4-methylbenzenesulfonamide (3c). A light yellow solid (66%). Mp: 182–184 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.40 (d, *J* = 6.5 Hz, 1H), 8.01 (t, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 4H), 7.07 (t, *J* = 6.8 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.56 (s, 1H), 2.34 (d, *J* = 8.2 Hz, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 176.27, 165.95, 144.96, 142.15, 139.95, 138.89, 135.35, 131.07, 129.99, 128.58, 127.67, 125.39, 117.68, 114.19, 81.33, 45.70, 21.54, 21.10. HRMS: calcd for C$_{22}$H$_{19}$Br$_2$N$_3$O$_2$S [M + H]$^+$ 549.9617; found 549.9625.

N-(3-(Dibromomethyl)-3-(m-tolyl)imidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3d). A yellow solid (69%). Mp: 178–180 °C ^{1}H NMR (500 MHz, chloroform-d) δ 8.40 (d, J = 6.5 Hz, 1H), 8.01 (t, J = 7.7 Hz, 1H), 7.84 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.8 Hz, 1H), 7.24 (t, J = 7.7 Hz, 1H), 7.19–7.14 (m, 3H), 7.08 (t, J = 6.8 Hz, 1H), 6.85 (d, J = 6.8 Hz, 2H), 6.57 (s, 1H), 2.32 (d, J = 19.1 Hz, 6H). ^{13}C NMR (126 MHz, chloroform-d) δ 176.09, 166.01, 144.82, 142.15, 139.24, 135.33, 133.91, 130.53, 129.16, 128.57, 127.64, 127.51, 126.00, 122.65, 117.68, 114.02, 81.37, 45.55, 21.61, 21.52. HRMS: calcd for $C_{22}H_{19}Br_2N_3O_2S$ [M + H]$^+$ 549.9617; found 549.9627.

N-(3-(Dibromomethyl)-3-(4-methoxyphenyl)imidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3e). A light yellow solid (76%). Mp: 155–157 °C ^{1}H NMR (500 MHz, chloroform-d) δ 8.42 (d, J = 6.5 Hz, 1H), 8.00 (t, J = 7.7 Hz, 1H), 7.88 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.8 Hz, 1H), 7.18 (d, J = 7.9 Hz, 2H), 7.04 (dd, J = 16.4, 7.8 Hz, 3H), 6.88 (d, J = 8.8 Hz, 2H), 6.55 (s, 1H), 3.82 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, chloroform-d) δ 176.59, 166.11, 160.59, 144.79, 142.27, 139.03, 135.41, 128.70, 127.81, 127.05, 126.06, 117.86, 114.78, 114.04, 81.17, 55.54, 46.00, 21.64. HRMS: calcd for $C_{22}H_{19}Br_2N_3O_3S$ [M + H]$^+$ 565.9567; found 565.9573.

N-(3-(4-Chlorophenyl)-3-(dibromomethyl)imidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3f). A light yellow solid (48%). Mp: 172–174 °C ^{1}H NMR (500 MHz, chloroform-d) δ 8.41 (s, 1H), 7.84 (d, J = 7.4 Hz, 2H), 7.58 (s, 1H), 7.42–7.37 (m, 2H), 7.33–7.30 (m, 2H), 7.18 (d, J = 7.4 Hz, 2H), 7.05–7.02 (m, 2H), 6.57 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, chloroform-d) δ 175.69, 165.56, 145.58, 142.56, 138.54, 136.09, 135.24, 132.50, 129.61, 129.10, 128.80, 127.60, 127.31, 127.07, 118.01, 114.93, 81.07, 45.19, 21.59. HRMS: calcd for $C_{21}H_{16}Br_2ClN_3O_2S$ [M + H]$^+$ 569.9070; found 569.9074.

N-(3-(3-Chlorophenyl)-3-(dibromomethyl)imidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3g). A yellow solid (57%). Mp: 161–163 °C ^{1}H NMR (500 MHz, chloroform-d) δ 8.42 (d, J = 6.5 Hz, 1H), 8.04 (t, J = 7.7 Hz, 1H), 7.86 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.8 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.9 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.10 (t, J = 7.6 Hz, 2H), 7.02 (s, 1H), 6.53 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, chloroform-d) δ 175.21, 165.38, 145.62, 142.12, 138.24, 135.63, 135.05, 130.42, 129.64, 129.07, 128.39, 127.15, 125.77, 125.51, 123.82, 117.32, 80.73, 44.85, 21.14. HRMS: calcd for $C_{21}H_{16}Br_2ClN_3O_2S$ [M + H]$^+$ 569.9070; found 569.9070.

N-(3-(Dibromomethyl)-3-(4-fluorophenyl)imidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3h). A yellow solid (54%). Mp: 203–205 °C ^{1}H NMR (500 MHz, chloroform-d) δ 8.42 (d, J = 6.5 Hz, 1H), 8.02 (t, J = 8.1 Hz, 1H), 7.87 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.9 Hz, 1H), 7.19 (d, J = 7.9 Hz, 2H), 7.14–7.10 (m, 2H), 7.08 (d, J = 7.7 Hz, 3H), 6.55 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, chloroform-d) δ 175.79, 165.67, 145.39, 142.17, 138.62, 135.19, 129.86, 128.47, 127.70, 127.64, 127.37, 117.42, 116.29, 116.11, 114.74, 80.83, 45.37, 21.33. HRMS: calcd for $C_{21}H_{16}Br_2FN_3O_2S$ [M + H]$^+$ 553.9367; found 553.9376.

N-(3-Butyl-3-(dibromomethyl)imidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3i). A light yellow solid (65%). Mp: 185–187 °C ^{1}H NMR (500 MHz, chloroform-d) δ 8.27 (d, J = 6.4 Hz, 1H), 7.94 (dd, J = 21.5, 7.9 Hz, 3H), 7.41 (d, J = 8.8 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.04 (t, J = 6.8 Hz, 1H), 5.99 (s, 1H), 2.34 (s, 3H), 2.20 (s, 2H), 2.06 (s, 2H), 1.15–1.11 (m, 2H), 0.69 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, chloroform-d) δ 176.65, 165.67, 144.34, 142.32, 138.73, 133.60, 128.59, 127.96, 117.47, 114.64, 79.27, 46.09, 38.38, 25.17, 22.15, 21.52, 13.52. HRMS: calcd for $C_{19}H_{21}Br_2N_3O_2S$ [M + H]$^+$ 515.9774; found 515.9787.

N-(3-(Dibromomethyl)-6-methyl-3-phenylimidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3j). A yellow solid (75%). Mp: 146–148 °C ^{1}H NMR (500 MHz, chloroform-d) δ 8.21 (s, 1H), 7.86 (t, J = 8.4 Hz, 3H), 7.45 (d, J = 9.0 Hz, 1H), 7.39 (d, J = 7.6 Hz, 3H), 7.17 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 6.9 Hz, 2H), 6.61 (s, 1H), 2.40 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, chloroform-d) δ 176.01, 164.56, 147.34, 142.03, 134.11, 133.07, 129.78, 129.64, 129.27, 128.86, 128.73, 128.54, 127.87, 127.63, 125.60, 124.73, 121.09, 117.20, 81.68, 45.60, 21.51, 18.04. HRMS: calcd for $C_{22}H_{19}Br_2N_3O_2S$ [M + Na]$^+$ 571.9437; found 571.9442.

N-(3-(Dibromomethyl)-6-methyl-3-(p-tolyl)imidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3k). A yellow solid (77%). Mp: 211–213 °C ^{1}H NMR (500 MHz, chloroform-d) δ 8.18 (s, 1H), 7.86 (t, J = 8.3 Hz, 3H), 7.44 (d, J = 9.0 Hz, 1H), 7.16 (d, J = 5.2 Hz, 4H), 6.95 (d, J = 7.9 Hz, 2H), 6.57 (s, 1H), 2.38 (s, 3H), 2.34 (d, J = 4.2 Hz, 6H). ^{13}C NMR (126 MHz, chloroform-d) δ 176.26, 164.44, 147.42, 141.98, 139.80, 133.09, 131.19, 129.92, 128.52, 127.62, 125.49, 124.80, 117.13, 81.62, 45.74, 21.51, 21.08, 18.03. HRMS: calcd for $C_{23}H_{21}Br_2N_3O_2S$ [M + H]$^+$ 563.9774; found 563.9780.

N-(3-(Dibromomethyl)-3-(4-ethylphenyl)-6-methylimidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3l). A light yellow solid (58%). Mp: 190–192 °C ^{1}H NMR (500 MHz, chloroform-d) δ 8.20 (s, 1H), 7.86 (d, J = 8.2 Hz, 3H), 7.45 (d, J = 9.0 Hz, 1H), 7.18 (dd, J = 16.2, 8.1 Hz, 4H), 6.98 (d, J = 8.3 Hz, 2H), 6.60 (s, 1H), 2.65 (q, J = 7.5 Hz, 2H), 2.37 (d, J = 17.3 Hz, 6H), 1.24 (s, 3H). ^{13}C NMR (126 MHz, chloroform-d) δ 176.26, 164.55, 147.14, 146.00, 141.95, 133.13, 128.73, 128.50, 127.65, 125.57, 124.50, 117.16, 81.66, 45.73, 28.39, 21.50, 18.02, 15.14. HRMS: calcd for $C_{24}H_{23}Br_2N_3O_2S$ [M + Na]$^+$ 599.9750; found 599.9789.

N-(3-(Dibromomethyl)-3-(4-methoxyphenyl)-6-methylimidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3m). A yellow solid (73%). Mp: 148–150 °C ^{1}H NMR (500 MHz, chloroform-d) δ 8.18 (s, 1H), 7.85 (d, J = 8.0 Hz, 3H), 7.43 (d, J = 9.0 Hz, 1H), 7.16 (d, J = 7.9 Hz, 2H), 7.00 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.55 (s, 1H), 3.79 (s, 3H), 2.36 (d, J = 15.9 Hz, 6H). ^{13}C NMR (126 MHz, chloroform-d) δ 176.49, 164.33, 160.37, 147.39, 142.05, 133.10, 129.50, 128.56, 127.57, 127.06, 126.33, 125.98, 117.17, 114.61, 81.47, 55.42, 45.85, 21.49, 18.03. HRMS: calcd for $C_{23}H_{21}Br_2N_3O_3S$ [M + H]$^+$ 579.9723; found 579.9725.

N-(3-(4-Chlorophenyl)-3-(dibromomethyl)-6-methylimidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3n). A yellow solid (60%). Mp: 151–153 °C ^{1}H NMR (500 MHz, chloroform-d) δ 8.17 (s, 1H), 7.88 (d, J = 8.7 Hz, 1H), 7.84 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 9.0 Hz, 1H), 7.34 (d, J = 8.7 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.6 Hz, 2H), 6.53 (s, 1H), 2.37 (d, J

= 15.7 Hz, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 175.57, 164.54, 147.66, 142.21, 132.80, 132.67, 131.04, 129.45, 129.01, 128.96, 128.60, 128.08, 127.61, 127.08, 120.99, 117.32, 117.24, 81.19, 45.25, 21.51, 18.05. HRMS: calcd for $C_{22}H_{18}Br_2ClN_3O_2S$ [M + H]$^+$ 583.9226; found 583.9229.

N-(3-(Dibromomethyl)-3-(3-fluorophenyl)-6-methylimidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3o). A yellow solid (66%). Mp: 127–129 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.16 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 9.0 Hz, 1H), 7.34–7.29 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.82 (t, *J* = 7.0 Hz, 2H), 6.48 (s, 1H), 2.32 (d, *J* = 16.8 Hz, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 174.68, 163.35, 147.50, 141.36, 138.09, 135.55, 132.30, 130.27, 130.20, 128.51, 127.78, 126.64, 125.28, 120.76, 116.12, 112.81, 112.61, 80.55, 44.50, 20.65, 20.59, 17.13. HRMS: calcd for $C_{22}H_{18}Br_2FN_3O_2S$ [M + H]$^+$ 567.9523; found 567.9528.

N-(6-Chloro-3-(dibromomethyl)-3-phenylimidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3p). A yellow solid (58%). Mp: 144–146 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.40 (s, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 9.5 Hz, 1H), 7.40 (d, *J* = 7.4 Hz, 3H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 6.9 Hz, 2H), 6.55 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 175.93, 164.80, 145.90, 142.44, 138.67, 133.58, 132.83, 129.96, 129.63, 129.50, 129.04, 128.71, 127.91, 127.57, 125.38, 118.51, 81.91, 45.09, 21.54. HRMS: calcd for $C_{21}H_{16}Br_2ClN_3O_2S$ [M + H]$^+$ 569.9070; found 569.9075.

N-(6-Chloro-3-(Dibromomethyl)-3-(4-ethylphenyl)imidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3q). A yellow solid (61%). Mp: 149–151 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.41 (s, 1H), 7.97–7.93 (m, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 9.5 Hz, 1H), 7.21 (dd, *J* = 16.9, 8.1 Hz, 4H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.55 (s, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.38 (s, 3H), 1.24 (d, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 176.21, 164.75, 146.36, 145.80, 142.36, 132.90, 130.83, 129.55, 128.95, 128.67, 128.50, 127.95, 127.60, 125.36, 121.33, 118.44, 81.91, 45.22, 28.39, 21.53, 15.12. HRMS: calcd for $C_{23}H_{20}Br_2ClN_3O_2S$ [M + H]$^+$ 597.93834; found 597.93830.

N-(6-Chloro-3-(dibromomethyl)-3-(m-tolyl)imidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3r). A yellow solid (57%). Mp: 183–185 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.40 (s, 1H), 7.99 (d, *J* = 9.3 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 9.5 Hz, 1H), 7.28–7.26 (m, 1H), 7.20 (dd, *J* = 16.1, 7.7 Hz, 3H), 6.88 (s, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.54 (s, 1H), 2.36 (d, *J* = 13.9 Hz, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 176.01, 164.77, 146.12, 142.40, 139.46, 138.80, 133.51, 132.79, 130.75, 129.31, 128.69, 127.50, 125.86, 122.51, 121.41, 118.60, 81.91, 45.09, 21.63, 21.54. HRMS: calcd for $C_{22}H_{18}Br_2ClN_3O_2S$ [M + H]$^+$ 583.9226; found 583.9231.

N-(6-Chloro-3-(dibromomethyl)-3-(3-methoxyphenyl)imidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3s). A yellow solid (62%). Mp: 145–147 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.42 (s, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 9.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 6.51 (s, 1H), 3.77 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 175.79, 164.72, 160.20, 145.92, 142.47, 138.73, 134.88, 132.86, 130.54, 128.73,

127.53, 121.32, 118.47, 117.45, 114.84, 112.03, 81.74, 55.51, 45.03, 21.52. HRMS: calcd for $C_{22}H_{18}Br_2ClN_3O_3S$ [M + H]$^+$ 597.9196; found 597.9191.

N-(6-Chloro-3-(dibromomethyl)-3-(4-methoxyphenyl)imidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3t). A yellow solid (61%). Mp: 134–136 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.40 (s, 1H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.52 (s, 1H), 3.81 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 176.48, 164.59, 160.57, 145.97, 142.50, 132.87, 131.08, 128.75, 127.53, 126.87, 125.38, 121.49, 118.48, 114.83, 81.72, 55.49, 45.35, 21.54. HRMS: calcd for $C_{22}H_{18}Br_2ClN_3O_3S$ [M + H]$^+$ 597.9196; found 597.9192.

N-(6-Chloro-3-(3-chlorophenyl)-3-(dibromomethyl)imidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3u). A light yellow solid (56%). Mp: 231–233 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.41 (s, 1H), 7.98 (d, *J* = 9.4 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 9.5 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.37 (t, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.06 (s, 2H), 6.49 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 175.16, 164.92, 145.94, 142.60, 135.59, 135.47, 132.50, 130.78, 130.26, 128.77, 127.56, 125.52, 123.75, 121.48, 118.62, 81.23, 44.59, 21.54. HRMS: calcd for $C_{21}H_{15}Br_2Cl_2N_3O_2S$ [M + H]$^+$ 603.8679; found 603.8678.

N-(6-Chloro-3-(dibromomethyl)-3-(3-fluorophenyl)imidazo[1,2-a]pyridin-2(3H)-ylidene)-4-methylbenzenesulfonamide (3v). A yellow solid (58%). Mp: 145–147 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.39 (s, 1H), 8.02 (d, *J* = 9.3 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 9.4 Hz, 1H), 7.37 (q, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.11 (t, *J* = 6.8 Hz, 1H), 6.87 (t, *J* = 9.8 Hz, 2H), 6.48 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 175.31, 164.81, 163.89, 161.91, 146.28, 142.63, 138.49, 135.72, 132.54, 131.30, 128.77, 127.55, 121.72, 121.18, 118.70, 117.08, 113.18, 112.98, 81.31, 44.61, 21.54. HRMS: calcd for $C_{21}H_{15}Br_2ClFN_3O_2S$ [M + H]$^+$ 585.8997; found 585.8999.

N-(3-(Dibromomethyl)-3-phenylimidazo[1,2-a]pyridin-2(3H)-ylidene)methanesulfonamide (3w). A yellow solid (61%). Mp: 256–258 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.50 (d, *J* = 6.4 Hz, 1H), 8.09 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.41 (d, *J* = 5.7 Hz, 3H), 7.15 (d, *J* = 5.6 Hz, 3H), 6.66 (s, 1H), 3.15 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 176.80, 165.98, 145.12, 135.43, 129.89, 129.46, 125.50, 117.58, 114.24, 81.37, 45.89, 39.93. HRMS: calcd for $C_{15}H_{13}Br_2N_3O_2S$ [M + H]$^+$ 457.9167; found 457.9168.

N-(3-(Dibromomethyl)-3-phenylimidazo[1,2-a]pyridin-2(3H)-ylidene)benzenesulfonamide (3x). A yellow solid (49%). Mp: 139–141 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.43 (d, *J* = 4.3 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 5.9 Hz, 5H), 7.54 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.1 Hz, 3H), 7.25 (s, 1H), 7.09 (d, *J* = 6.5 Hz, 3H), 6.60 (s, 1H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 176.20, 165.73, 145.51, 143.23, 135.47, 131.98, 129.54, 129.28, 128.79, 127.93, 127.42, 126.08, 125.51, 117.46, 114.89, 81.53, 45.33. HRMS: calcd for $C_{20}H_{15}Br_2N_3O_2S$ [M + Na]$^+$ 543.9124; found 543.9128.

N-(3-(Dibromomethyl)-3-(4-ethylphenyl)imidazo[1,2-a]pyridin-2(3H)-ylidene)benzenesulfonamide (3y). A yellow solid

(47%). Mp: 147–149 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.42 (d, *J* = 6.1 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.0 Hz, 2H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.07 (dd, *J* = 14.5, 7.5 Hz, 2H), 6.98 (d, *J* = 6.8 Hz, 2H), 6.58 (s, 1H), 2.65–2.62 (m, 2H), 1.21 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 176.48, 165.92, 146.16, 145.06, 135.39, 131.69, 128.81, 128.22, 127.93, 127.63, 125.47, 117.63, 114.34, 81.47, 45.52, 28.39, 15.17. HRMS: calcd for $C_{22}H_{19}Br_2N_3O_2S$ [M + H]$^+$ 549.9617; found 549.9619.

N-(3-(Dibromomethyl)-6-methyl-3-phenylimidazo[1,2-*a*]pyridin-2(3*H*)-ylidene)benzenesulfonamide (3z). A light yellow solid (65%). Mp: 121–123 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.19 (s, 1H), 7.90 (d, *J* = 7.2 Hz, 3H), 7.42 (dd, *J* = 17.0, 7.9 Hz, 3H), 7.37–7.33 (m, 4H), 7.08–7.04 (m, 2H), 6.62 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 175.93, 163.62, 147.96, 143.26, 141.20, 133.60, 133.05, 131.62, 129.38, 129.01, 128.53, 127.71, 127.00, 125.68, 125.43, 116.49, 81.72, 45.21, 17.63. HRMS: calcd for $C_{21}H_{17}Br_2N_3O_2S$ [M + H]$^+$ 535.9461; found 535.9470.

N-(6-Chloro-3-(dibromomethyl)-3-phenylimidazo[1,2-*a*]pyridin-2(3*H*)-ylidene)benzenesulfonamide (3ab). A yellow solid (62%). Mp: 141–143 °C. ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.41 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 9.1 Hz, 1H), 7.49–7.43 (m, 2H), 7.42–7.38 (m, 4H), 7.09 (d, *J* = 6.9 Hz, 2H), 6.56 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 176.05, 164.62, 145.97, 141.20, 133.32, 132.80, 131.89, 129.93, 129.45, 129.00, 128.02, 127.80, 127.41, 125.27, 118.40, 81.93, 44.82. HRMS: calcd for $C_{20}H_{14}Br_2ClN_3O_2S$ [M + Na]$^+$ 577.8733; found 577.8738.

N-(6-Chloro-3-(dibromomethyl)-3-(4-ethylphenyl)imidazo [1,2-*a*]pyridin-2(3*H*)-ylidene)benzenesulfonamide (3ac). A yellow solid (46%). Mp: 135–137 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.40 (s, 1H), 7.94 (d, *J* = 6.6 Hz, 2H), 7.61–7.51 (m, 2H), 7.48–7.43 (m, 2H), 7.38 (s, 2H), 7.23–7.19 (m, 2H), 7.00–6.97 (m, 1H), 6.57 (s, 1H), 2.68–2.61 (m, 2H), 1.22 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 176.45, 164.67, 146.47, 146.03, 141.35, 133.03, 132.38, 131.99, 130.68, 129.54, 129.04, 129.00, 128.14, 127.53, 126.35, 125.42, 118.49, 82.12, 45.06, 28.42, 15.16. HRMS: calcd for $C_{22}H_{18}Br_2ClN_3O_2S$ [M + H]$^+$ 583.9226; found 583.9229.

N-(6-Chloro-3-(4-chlorophenyl)-3-(dibromomethyl)imidazo [1,2-*a*]pyridin-2(3*H*)-ylidene)benzenesulfonamide (3ad). A yellow solid (65%). Mp: 160–162 °C ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.39 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 9.4 Hz, 1H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 8.2 Hz, 3H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.54 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 180.53, 169.20, 151.07, 145.74, 144.01, 140.77, 137.44, 137.31, 136.78, 136.64, 134.30, 132.81, 132.07, 131.67, 126.73, 123.01, 116.37, 86.31, 82.41, 49.37. HRMS: calcd for $C_{20}H_{13}Br_2Cl_2N_3O_2S$ [M + H]$^+$ 589.8522; found 589.8528.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

Notes and references

1 Selected literatures for C–H functionalization: (*a*) V. Ritleng, C. Sirlin and M. Pfeffer, *Chem. Rev.*, 2002, **102**, 1731–1770; (*b*) D. Alberico, M. E. Scott and M. Lautens, *Chem. Rev.*, 2007, **107**, 174–238; (*c*) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy and J. F. Hartwig, *Chem. Rev.*, 2010, **110**, 890–931; (*d*) J. Wencel-Delord, T. Dröge, F. Liu and F. Glorius, *Chem. Soc. Rev.*, 2011, **40**, 4740–4761; (*e*) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord and F. Glorius, *Angew. Chem., Int. Ed.*, 2012, **51**, 10236–10254; (*f*) F. P. Yi, S. X. Zhang, L. R. Zhang, W. Y. Yi and R. Yu, *Asian J. Org. Chem.*, 2017, **6**, 1808–1817; (*g*) J. Xie, H. L. Jiang, Y. X. Cheng and C. J. Zhu, *Chem. Commun.*, 2012, **48**, 979–981.

2 R. Jana, T. P. Pathak and M. S. Sigman, *Chem. Rev.*, 2011, **111**, 1417–1492.

3 Selected literatures for CDC reactions, see: (*a*) C. J. Li, *Acc. Chem. Res.*, 2009, **42**, 335–344; (*b*) S. A. Girard, T. Knauber and C. J. Li, *Angew. Chem., Int. Ed.*, 2014, **53**, 74–100; (*c*) M. Klussmann and D. Sureshkumar, *Synthesis*, 2011, 353–369.

4 R. G. Bergman, *Nature*, 2007, **446**, 391–393.

5 Selected literatures for the formation of C–X (X = C, N) bonds *via* CDC reactions using peroxides as oxidant, see: (*a*) L. K. Jin, J. Feng, G. P. Lu and C. Cai, *Adv. Synth. Catal.*, 2015, **357**, 2105–2110; (*b*) Z. H. Jia, T. Nagano, X. S. Li and A. S. C. Chan, *Eur. J. Org. Chem.*, 2013, 858–861; (*c*) R. Xia, H. Y. Niu, G. R. Qu and H. M. Guo, *Org. Lett.*, 2012, **14**, 5546–5549; (*d*) W. P. Mai, H. H. Wang, Z. C. Li, J. W. Yuan, Y. M. Xiao, L. R. Yang, P. Mao and L. B. Qu, *Chem. Commun.*, 2012, **48**, 10117–10119; (*e*) T. He, L. Yu, L. Zhang, L. Wang and M. Wang, *Org. Lett.*, 2011, **13**, 5016–5019; (*f*) W. Liu, S. Liu, H. Xie, Z. Qing, J. Zenga and P. Cheng, *RSC Adv.*, 2015, **5**, 17383–17388; (*g*) M. Wan, H. X. Lou and L. Liu, *Chem. Commun.*, 2015, **51**, 13953–13956.

6 Selected literatures for the formation of C–X (X = C, N) bonds *via* CDC reactions using quinones as oxidant, see: (*a*) S. S. Kong, L. Q. Zhang, X. L. Dai, L. Z. Tao, C. S. Xie, L. Shi and M. Wang, *Adv. Synth. Catal.*, 2015, **357**, 2453–2456; (*b*) K. Kawasumi, Q. Y. Zhang, Y. Segawa, L. T. Scott and K. Itami, *Nat. Chem.*, 2013, **5**, 739–744; (*c*) K. Alagiri, P. Devadig and K. R. Prabhu, *Chem. – Eur. J.*, 2012, **18**, 5160–5164; (*d*) S. H. Gwon and S. G. Kim, *Tetrahedron : Asymmetry*, 2012, **23**, 1251–1255; (*e*) A. S. K. Tsang, P. Jensen, J. M. Hook, A. S. K. Hashmi and M. H. Todd, *Pure Appl. Chem.*, 2011, **83**, 655–665; (*f*) D. Ramesh, U. Ramulu, S. Rajaram, P. Prabhakar and Y. Venkateswarlu, *Tetrahedron Lett.*, 2010, **51**, 4898–4903; (*g*) L. Y. Zhai, R. Shukla, S. H. Wadumethrige and R. Rathore, *J. Org. Chem.*, 2010, **75**, 4748–4760; (*h*) X. G. Liu, Z. L. Meng, C. K. Li, H. X. Lou and L. Liu, *Angew. Chem., Int. Ed.*, 2015, **54**, 6012–6015; (*i*) X. G. Liu, S. T. Sun, Z. L. Meng, H. X. Lou and L. Liu, *Org. Lett.*, 2015, **17**, 2396–

2399; (j) Z. L. Meng, S. T. Sun, H. Q. Yuan, H. X. Lou and L. Liu, *Angew. Chem., Int. Ed.*, 2014, **53**, 543–547.

7 Selected literatures for the formation of C–X (X = C, N) bonds *via* CDC reactions using hypervalent iodine reagents as oxidant, see: (a) A. P. Antonchick and L. Burgmann, *Angew. Chem., Int. Ed.*, 2013, **52**, 3267–3271; (b) K. Morimoto, T. Dohi and Y. Kita, *Eur. J. Org. Chem.*, 2013, 1659–1662; (c) K. Matcha and A. P. Antonchick, *Angew. Chem., Int. Ed.*, 2013, **52**, 2082–2086; (d) J. W. Wang, Y. C. Yuan, R. Xiong, D. Zhang-Negrerie, Y. F. Du and K. Zhao, *Org. Lett.*, 2012, **14**, 2210–2213; (e) T. Dohi, M. Ito, I. Itani, N. Yamaoka, K. Morimoto, H. Fujioka and Y. Kita, *Org. Lett.*, 2011, **13**, 6208–6211; (f) K. Morimoto, N. Yamaoka, C. Ogawa, T. Nakae, H. Fujioka, T. Dohi and Y. Kita, *Org. Lett.*, 2010, **12**, 3804–3807.

8 Selected literatures for the formation of C–X (X = C, N) bonds *via* CDC reactions using O₂ as oxidant, see: (a) H. Ueda, K. Yoshida and H. Tokuyama, *Org. Lett.*, 2014, **16**, 4194–4197; (b) Á. Pintér, A. Sud, D. Sureshkumar and M. Klussmann, *Angew. Chem., Int. Ed.*, 2010, **49**, 5004–5007; (c) B. Schweitzer-Chaput, A. Sud, Á. Pintér, S. Dehn, P. Schulze and M. Klussmann, *Angew. Chem., Int. Ed.*, 2013, **52**, 13228–13232; (d) C. D. Huo, Y. Yuan, M. X. Wu, X. D. Jia, X. C. Wang, F. A. Chen and J. Tang, *Angew. Chem., Int. Ed.*, 2014, **53**, 13544–13547; (e) J. Liu, F. Liu, Y. Z. Zhu, X. G. Ma and X. D. Jia, *Org. Lett.*, 2015, **17**, 1409–1412; (f) X. D. Jia, Y. Z. Zhu, Y. Yuan, X. W. Zhang, S. W. Lv, L. Zhang and L. L. Luo, *ACS Catal.*, 2016, **6**, 6033–6036; (g) X. D. Jia, F. F. Peng, C. Qing, C. D. Huo and X. C. Wang, *Org. Lett.*, 2012, **14**, 4030–4033.

9 Selected literatures for the formation of C–X (X = C, N) bonds *via* CDC reactions using KO*t*Bu–DMF as reagents see: (a) W. T. Wei, X. J. Dong, S. Z. Nie, Y. Y. Chen, X. J. Zhang and M. Yan, *Org. Lett.*, 2013, **15**, 6018–6021; (b) Y. Y. Chen, X. J. Zhang, H. M. Yuan, W. T. Wei and M. Yan, *Chem. Commun.*, 2013, **49**, 10974–10976.

10 Selected literatures for CBr₄ as organocatalyst, see: (a) P. R. Schreiner, O. Lauenstein, I. V. Kolomitsyn, S. Nadi and A. A. Fokin, *Angew. Chem., Int. Ed.*, 1998, **37**, 1895–1897; (b) M. Y. Chen and A. S. Y. Lee, *J. Org. Chem.*, 2002, **67**, 1384–1387; (c) Y. L. Zhong, J. Lee, R. A. Reamer and D. Askin, *Org. Lett.*, 2004, **6**, 929–931; (d) M. T. Crimmins and K. A. Emmitte, *Org. Lett.*, 1999, **1**, 2029–2032; (e) J. Wu, W. Sun, X. Sun and H. G. Xia, *Green Chem.*, 2006, **8**, 365–367; (f) M. Y. Chen, K. C. Lu, A. S. Y. Lee and C. C. Lin, *Tetrahedron Lett.*, 2002, **43**, 2777–2780; (g) A. S. Y. Lee, Y. J. Hu and S. F. Chu, *Tetrahedron*, 2001, **57**, 2121–2126; (h) L. Zhang, Y. Luo, R. Fan and J. Wu, *Green Chem.*, 2007, **9**, 1022–1025; (i) T. Sugai and A. Itoh, *Tetrahedron Lett.*, 2007, **48**, 9096–9099; (j) S. Hirashima, T. Nobuta, N. Tada, T. Miura and A. Itoh, *Org. Lett.*, 2010, **12**, 3645–3647; (k) T. Keshari, V. P. Srivastavaa and L. D. S. Yadav, *RSC Adv.*, 2014, **4**, 5815–5818.

11 A. S. Y. Lee and F. Y. Su, *Tetrahedron Lett.*, 2005, **46**, 6305–6309.

12 J. S. Yadav, B. V. S. Reddy, K. Harikishan, C. Madan and A. V. Narsaiah, *Synthesis*, 2005, 2897–2900.

13 C. D. Huo and T. H. Chan, *Adv. Synth. Catal.*, 2009, **351**, 1933–1938.

14 C. D. Huo, C. G. Sun, C. Wang, X. D. Jia and W. J. Chang, *ACS Sustainable Chem. Eng.*, 2013, **1**, 549–553.

15 Q. Q. Yang, M. Marchini, W. J. Xiao, P. Ceroni and M. Bandini, *Chem. – Eur. J.*, 2015, **21**, 18052–18056.

16 S. I. Hirashima, T. Nobuta, N. Tada, T. Miura and A. Itoh, *Org. Lett.*, 2010, **12**, 3645–3647.

17 Selected literatures for CBr₄ as cross-dehydrogenation coupling reagent, see: (a) J. Tan, F. S. Liang, Y. M. Wang, X. Cheng, Q. Liu and H. J. Yuan, *Org. Lett.*, 2008, **10**, 2485–2488; (b) X. X. Liu, J. H. Pu, X. L. Luo, X. F. Cui, Z. Y. Wu and G. S. Huang, *Org. Chem. Front.*, 2018, **5**, 361–365; (c) Z. C. Shen, P. Yang and Y. Tang, *J. Org. Chem.*, 2016, **81**, 309–317; (d) C. D. Huo, H. S. Xie, M. X. Wu, X. D. Jia, X. C. Wang, F. J. Chen and J. Tang, *Chem. – Eur. J.*, 2015, **21**, 5723–5726; (e) F. J. Chen, Y. J. Wang, S. J. Zhao, W. Jiang and C. D. Huo, *Org. Biomol. Chem.*, 2017, **15**, 7710–7714; (f) J. Tang, S. J. Zhao, Y. Y. Wei, Z. J. Quan and C. D. Huo, *Org. Biomol. Chem.*, 2017, **15**, 1589–1592; (g) C. D. Huo, H. S. Xie, F. J. Chen, J. Tang and Y. J. Wang, *Adv. Synth. Catal.*, 2016, **358**, 724–730; (h) C. D. Huo, M. X. Wu, F. J. Chen, X. D. Jia, Y. Yuan and H. S. Xie, *Chem. Commun.*, 2015, **51**, 4708–4711; (i) C. D. Huo, J. Tang, H. S. Xie, Y. J. Wang and J. Dong, *Org. Lett.*, 2016, **18**, 1016–1019; (j) X. Q. Zhou, H. J. Ma, C. Shi, Y. X. Zhang, X. X. Liu and G. S. Huang, *Eur. J. Org. Chem.*, 2017, 237–240; (k) X. G. Zhang, P. Wu, Y. J. Fu, F. D. Zhang and B. H. Chen, *Tetrahedron Lett.*, 2017, **58**, 870–873.

18 Y. Ohta, Y. Tokimizu, S. Oishi, N. Fujii and H. Ohno, *Org. Lett.*, 2010, **12**, 3963–3965.

19 B. Ma, Y. Wang, J. L. Peng and Q. Zhu, *J. Org. Chem.*, 2011, **76**, 6362–6366.

20 (a) E. D. Anderson and D. L. Boger, *J. Am. Chem. Soc.*, 2011, **133**, 12285–12292; (b) E. D. Anderson and D. L. Boger, *Org. Lett.*, 2011, **13**, 2492–2494.

21 G. M. Castanedo, P. S. Seng, N. Blaquiere, S. Trapp and S. T. Staben, *J. Org. Chem.*, 2011, **76**, 1177–1179.

22 J. S. Peng, M. Ye, C. J. Zong, F. Y. Hu, L. T. Feng, X. Y. Wang, Y. F. Wang and C. X. Chen, *J. Org. Chem.*, 2011, **76**, 716–719.

23 Selected literatures for the synthesis of 1,2,4-triazoles from *N*-(2-pyridyl)amidines substrates, see: (a) S. Ueda and H. Nagasawa, *J. Am. Chem. Soc.*, 2009, **131**, 15080–15081; (b) Z. S. Zheng, S. Y. Ma, L. L. Tang, D. Zhang-Negrerie, Y. F. Du and K. Zhao, *J. Org. Chem.*, 2014, **79**, 4687–4693; (c) V. J. Grenda, R. E. Jones, G. Gal and M. Sletzinger, *J. Org. Chem.*, 1965, **30**, 259–261; (d) K. T. Potts, H. R. Burton and J. Bhattacharyya, *J. Org. Chem.*, 1966, **31**, 260–265; (e) J. D. Bower and G. R. Ramage, *J. Chem. Soc.*, 1957, 4506–4510; (f) L. N. Song, X. H. Tian, Z. G. Lv, E. T. Li, J. Wu, Y. X. Liu, W. Q. Yu and J. B. Chang, *J. Org. Chem.*, 2015, **80**, 7219–7225; (g) X. Meng, C. Yu and P. Zhao, *RSC Adv.*, 2014, **4**, 8612–8616.

24 X. H. Tian, L. Song, M. M. Wang, Z. G. Lv, J. Wu, W. Q. Yu and J. B. Chang, *Chem. – Eur. J.*, 2016, **22**, 7617–7622.

25 (a) F. P. Yi, Q. H. Sun, J. Sun, C. Fu and W. Y. Yi, *J. Org. Chem.*, 2019, **81**, 6780–6787; (b) Y. Huang, W. Y. Yi, Q. H. Sun and

F. P. Yi, *Adv. Synth. Catal.*, 2018, **360**, 3074–3082; (*c*) Y. Huang, W. Y. Yi, Q. H. Sun, L. R. Zhang and F. P. Yi, *RSC Adv.*, 2018, **8**, 74–79; (*d*) F. P. Yi, S. X. Zhang, Y. Huang, L. R. Zhang and W. Y. Yi, *Eur. J. Org. Chem.*, 2017, 102–110.

26 Selective literatures for the Synthesis of amidines by Cu-catalyzed MCRs.(*a*) I. Bae, H. Han and S. Chang, *J. Am. Chem. Soc.*, 2005, **127**, 2038–2039; (*b*) S. L. Cui, J. Wang and Y. G. Wang, *Org. Lett.*, 2008, **10**, 1267–1269; (*c*) J. J. Wang, P. Lu and Y. G. Wang, *Org. Chem. Front.*, 2015, **2**, 1346–1351; (*d*) D. P. Chauhan, S. J. Varma, A. Vijeta, P. Banerjee and P. Talukdar, *Chem. Commun.*, 2014, **50**, 323–325; (*e*) D. Zhang, I. Nakamura and M. Terada, *Org. Lett.*, 2014, **16**, 5184–5187; (*f*) W. Choi, J. Kim, T. Ryu, K. B. Kim and P. H. Lee, *Org. Lett.*, 2015, **17**, 3330–3333; (*g*) J. J. Wang, J. Y. Liu, H. L. Ding, J. Wang, P. Lu and Y. G. Wang, *J. Org. Chem.*, 2015, **80**, 5842–5850; (*h*) J. Kim, Y. Lee, J. Lee, Y. Do and S. Chang, *J. Org. Chem.*, 2008, **73**, 9454–9457 and the cited references.