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A novel atom-economic synthesis of functionalized imidazolidines through copper(I)-catalyzed domino three-component coupling and cyclization reactions

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ABSTRACT

An interesting approach to functionalized imidazolidines is described. These compounds are obtained in a copper(I)-catalyzed domino three-component coupling and cyclization reaction involving two formaldehyde-derived imine units and a terminal alkyne. Alternatively, imidazolidines can be obtained from propargylamines and formaldehyde-derived imines. This strategy provides a straightforward and atom-economic pathway to construct imidazolidines with high yields and benefits from readily available starting materials, convenient one-pot operations.

1. Introduction

Heterocyclic compounds embedded with nitrogen have attracted considerable interest over the years because they form the core structures, and are key intermediates, of natural products, such as alkaloids.[1] Among the nitrogen heterocycles, imidazolidine nucleus is a prominent motif that exists in numerous natural products and synthetic bioactive compounds.[2] One of the conventional methods for the synthesis of imidazolidines relies upon the condensation of aldehydes with 1, 2-diamines.[3] Imidazolidines can also be prepared by dipolar cycloaddition of azomethine ylides and imines.[4] The main two routes to imidazolidines have some defects, such as limited source of starting materials, limited diversity of the target molecules, harsh reaction conditions, and cumbersome operation, etc. Therefore, more efficient methods to acquire such heterocycles, in particular highly functionalized imidazolidines, remains an attractive goal.

In recent years, multicomponent reactions (MCRs) have become an efficient means for assembling heterocyclic frameworks from simple starting materials by virtue of their convergent nature.[5] Unlike traditional multistep processes, these reactions allow formation of several bonds via a cascade of irreversible chemical reactions in a single step with greater efficiency and atom economy.

Our efforts are recently directed toward the development of atom-economical reactions (multicomponent domino reactions and hydroamination[6]) for the efficient construction of heterocycles. During our work in assembling acetylides with aldimines into synthetically versatile propargylamines from which an array of nitrogen compounds can be accessed,[7] an interesting product, (*E*)-methyl 2-(1,3-diphenylimidazolidin-4-ylidene)acetate (**4a**) was unexpectedly obtained in 87% yield calculating from **1a** (Scheme 1). Treatment of *N*-methyleneaniline (**1a**, 1.0 equiv) with methyl propiolate (**2a**, 1.0 equiv) in the presence of copper(I) chloride (0.2 equiv) in toluene at rt gave neat **4a** without the attempted **3a** observed. The yield of **4a** was so excellent that a simple solvent rinsing is enough to provide the analytic sample. This reaction would involve a coupling reaction of alkyne **2a** with imine **1a** to form propargylamine **3a**, and under the help of cationic Cu(I), a subsequent cyclization of another **1a** molecule with activated **3a** to form **4a** (Scheme 1). To the best of our knowledge, this one-pot three-component reaction is the first route to imidazolidines from two imines and one alkyne. Thereby, a copper-catalyzed domino three-component reaction is established by us for substituted imidazolidines synthesis.

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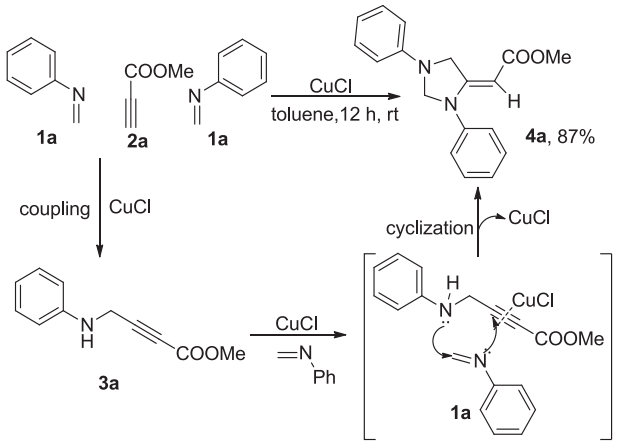
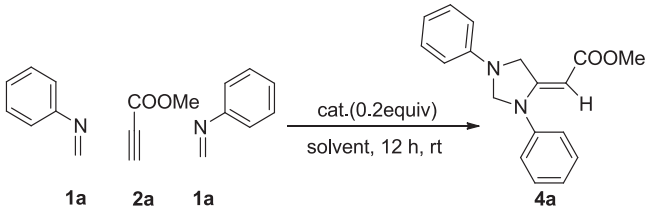


Scheme 1. A sequential copper(I)-catalyzed coupling and cyclization reaction for the synthesis of imidazolidines.

2. Results and discussion

With imine **1a** and methyl propiolate **2a** as model substrates, the original reaction conditions (**1a**, 1.0 equiv; **2a**, 1.0 equiv; CuCl, 0.2 equiv) were optimized, and the loading of **2a** was increased to 2.0 equiv giving **4a** with a comparable yield (89%). We then examined the process with various catalysts and solvents, and the results are described in Table 1. A variety of copper salts were examined for this reaction in toluene at rt (Table 1, entries 1–5). CuCl, CuBr, and $CuCl_2$ were effected to generate the corresponding products in moderate to good yields, but CuCl gave the best result (Table 1, entries 1 and 2, 4). However, no desired **4a** was observed in the presence of CuI or $CuSO_4$. AgCl, or Ag_2CO_3 was also used exhibiting no activation on this reaction (Table 1, entries 6 and 7). Subsequently, we tried to improve the yields by examining different solvents. Toluene, CH_2Cl_2, dioxane, *N*,*N*-dimethylformamide (DMF), and acetonitrile (MeCN) were all tolerant for this reaction, whereas CH_2Cl_2 proved to be the best one (Table 1, entries 1, 8–11). Furthermore, the control experiments revealed that no product was formed in the absence of CuCl (Table 1, entry 12).

Table 1
Optimization of reaction conditions[a]

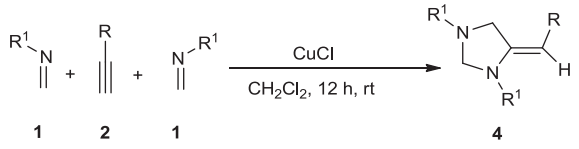


Entry	Catalyst	Solvent	Yield[b] (%)
1	CuCl	Toluene	89
2	CuBr	Toluene	84
3	CuI	Toluene	0
4	$CuCl_2$	Toluene	70
5	$CuSO_4$	Toluene	0
6	AgCl	Toluene	0
7	$AgCO_3$	Toluene	0
8	CuCl	CH_2Cl_2	93
9	CuCl	Dioxane	88
10	CuCl	DMF	65
11	CuCl	MeCN	53
12	—	CH_2Cl_2	0

[a] Reaction conditions: imine **1a** (10.0 mmol), methyl propiolate **2a** (5.0 mmol), catalyst (1.0 mmol), solvent (15 mL), under an ambient atmosphere.
[b] Isolated yield based on imine **1a**.

With the optimal conditions in hand (0.2 equiv CuCl, CH_2Cl_2, rt, 12 h), the scope of imines was investigated (Table 2). Aromatic imines **1b**, **1d**–**g** containing electron-donating groups on the benzene ring reacted all smoothly with **2a** to give **4b** (98% yield), **4d** (95% yield), **4e** (90% yield), **4f** (75% yield), and **4g** (89% yield), respectively (Table 2, entries 2, and 4–7). The reaction was also applicable to **1c** bearing an electron-withdrawing halogen atom on the benzene ring to provide **4c** in 93% yield (Table 2, entry 3). The lowered yield of **4f** seemly indicates that ortho-bulky groups on imines exert a slightly adverse effect on the reaction. Then aliphatic imines were also examined for this process. Imines **1h** and **1i** were successfully converted into the corresponding products (Table 2, entries 8 and 9), which really illustrates *N*-alkylformaldimines are also tolerant for this reaction. Next, we investigated the scope of terminal alkynes. To our delight, the electron-deficient alkynes, such as ethyl propiolate (**2b**) and 3-butyn-2-one (**2c**), were both applicable for this reaction to afford the imidazolidines **4j**–**n** in high yields (Table 2, entries 10–14). When phenylacetylene (**2d**) and trimethylsilylacetylene (**2e**) were employed instead of **2a**, only the propargylamine intermediates were found without generation of desired imidazolidines. Among obtained imidazolidines, the fine crystal of **4b** was carefully cultivated through volatilization of its dichloromethane solution for X-ray crystallography, and the result confirmed well the structure of **4b** as *E* configuration shown in Fig. 1. The decreased steric effect between Ha with Hb well explains the thermodynamic stability of the *E* configuration prior to the *Z* configuration (Scheme 2).

Table 2
Copper(I)-catalyzed reaction of imines and alkynes[a]



Entry	R^1	R	4	Yield[b] (%)
1[c]	**1a**: Ph	**2a**: COOMe	**4a**	93
2[c]	**1b**: 4-$MeOC_6H_4$	**2a**: COOMe	**4b**	98
3[c]	**1c**: 4-ClC_6H_4	**2a**: COOMe	**4c**	93
4[c]	**1d**: 4-MeC_6H_4	**2a**: COOMe	**4d**	95
5	**1e**: 3-MeC_6H_4	**2a**: COOMe	**4e**	90
6	**1f** : 2-MeC_6H_4	**2a**: COOMe	**4f**	75
7	**1g**: 3,5-$(Me)_2C_6H_3$	**2a**: COOMe	**4g**	89
8	**1h**: benzyl	**2a**: COOMe	**4h**	86
9	**1i**: cyclohexyl	**2a**: COOMe	**4i**	85
10	**1a**: Ph	**2b**: COOEt	**4j**	88
11	**1b**: 4-$MeOC_6H_4$	**2b**: COOEt	**4k**	90
12	**1a**: Ph	**2c**: COMe	**4l**	87
13	**1b**: 4-$MeOC_6H_4$	**2c**: COMe	**4m**	88
14	**1c**: 4-ClC_6H_4	**2c**: COMe	**4n**	85
15	**1a**: Ph	**2d**: Ph	—	0
16	**1a**: Ph	**2e**: Me_3Si	—	0

[a] Reaction conditions: imine **1** (10.0 mmol), alkyne **2** (5.0 mmol), CuCl (1.0 mmol), CH_2Cl_2 (15 mL), under an ambient atmosphere.
[b] Yield of isolated product.
[c] No chromatographic procedures were required for purification of the product.

As a matter of course, the imine scope was tentatively extended to other aldimines. When imine **5a** (2.0 equiv) was treated with methyl propiolate **2a** (1.0 equiv) under the optimal conditions, only a propargylamine adduct **6a** was obtained just as the literature described (Scheme 3).[8] Even after refluxing for 24 h, imidazolidine formation was still not observed. It is probably the steric hindrance and/or the low reactivity of imine **5a** that inhibit the following cyclization of **5a** with **6a**. Prompted by the proposed mechanism, we wondered whether *N*-methyleneaniline (**1a**) could perform the cyclization with the propargylamine **6a**. Thus, **6a** was isolated and

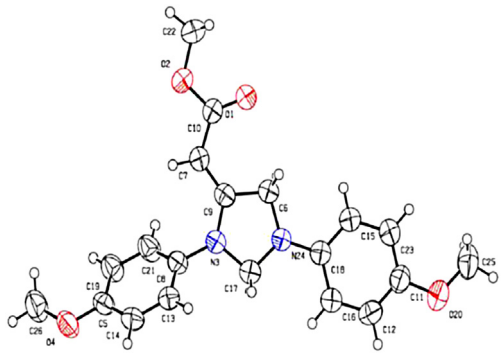
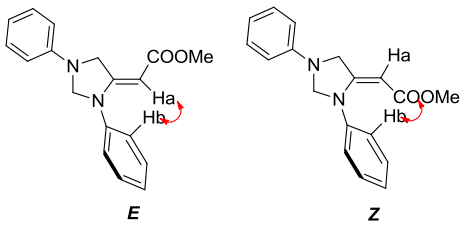
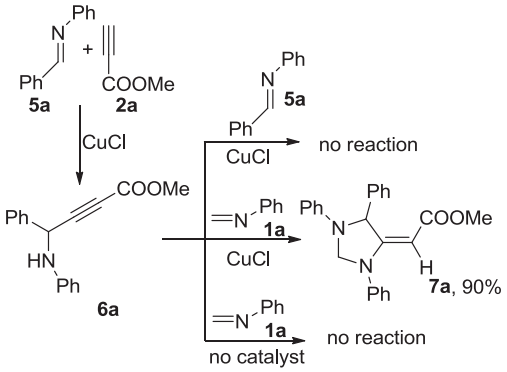


Fig. 1. X-ray crystal structure for **4b**.



Scheme 2. The thermodynamic stability of the *E* configuration prior to the *Z* configuration.

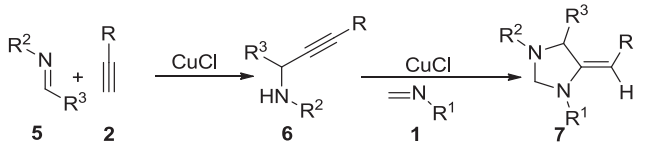
treated with imine **1a** in the presence of CuCl in CH_2Cl_2 at rt for 12 h, and **7a** was successfully obtained with 90% yield (Scheme 3). Next, a control experiment was carried out and revealed that no reaction was observed in the absence of CuCl (Scheme 3). This newly-discovered method is of great value because it can not only allow us to achieve high molecular diversity of imidazolidines, but also give a credible exemplification on the proposed mechanism (Scheme 1). Although the cyclization of propargylamines to form heterocycles has been widely reported,[7c,9] the reaction of propargylamines with imines to assemble substituted imidazolidines is disclosed for the first time.



Scheme 3. Imidazolidine from propargylamine and formaldimine.

To expand the reaction scope, a variety of formaldimines were treated with propargylamine **6**, and the results are shown in Table 3. Five *N*-arylformaldimines (**1a**–**d**, and **1g**), no matter the electron nature of substituents on the benzene ring, reacted smoothly to give the corresponding imidazolidines **7a**–**e** in excellent yields (Table 3, entries 1–5). Especially, the above-mentioned reactions generated no any observable undesired byproduct from TLC analysis. Notably, when *N*-alkylformaldimine **1i** and **1j** were used as the substrates, good yields of desired **7f** and **7g** were obtained (Table 3, entries 6 and 7). Then, with **1a** fixed as the second imine moiety, imines **5b**–**g** were checked for this copper-catalyzed

Table 3
Imidazolidines from two different imines and one alkyne[a]



Entry	Imine **1**: R^1	Imine **5**: R^2, R^3	Alkyne	**7**, yield[b] (%)
1[c]	**1a**: Ph	**5a**: Ph, Ph	**2a**	**7a**, 90
2[c]	**1b**: 4-$MeOC_6H_4$	**5a**: Ph, Ph	**2a**	**7b**, 98
3[c]	**1c**: 4-ClC_6H_4	**5a**: Ph, Ph	**2a**	**7c**, 91
4[c]	**1d**: 4-MeC_6H_4	**5a**: Ph, Ph	**2a**	**7d**, 95
5	**1g**: 3,5-$(Me)_2C_6H_3$	**5a**: Ph, Ph	**2a**	**7e**, 88
6	**1i**: cyclohexyl	**5a**: Ph, Ph	**2a**	**7f**, 88
7	**1j**: isopropyl	**5b**: 4-$MeOC_6H_4$, Ph	**2a**	**7g**, 86
8[c]	**1a**: Ph	**5b**: 4-$MeOC_6H_4$, Ph	**2a**	**7h**, 93
9[c]	**1a**: Ph	**5c**: 4-MeC_6H_4, Ph	**2a**	**7i**, 94
10	**1a**: Ph	**5d**: Ph, 4-ClC_6H_4	**2a**	**7j**, 87
11	**1a**: Ph	**5e**: Ph, 4-MeC_6H_4	**2a**	**7k**, 89
12	**1a**: Ph	**5f** : Ph, 2-furyl	**2a**	**7l**, 88
13	**1a**: Ph	**5g**: Ph, 2-thienyl	**2a**	**7m**, 85
14	**1a**: Ph	**5a**: Ph, Ph	**2b**	**7n**, 88
15	**1a**: Ph	**5a**: Ph, Ph	**2c**	**7o**, 85

[a] Reaction conditions: imine **5** (10.0 mmol), CuCl (1.0 mmol), alkyne **2** (10.0 mmol), CH_2Cl_2 (15 mL), 12 h, imine **1** (10.0 mmol), 12 h, under an ambient atmosphere.
[b] Yield of isolated product.
[c] No chromatographic procedures were required for purification of the product.

process. When *N*-arylbenzaldimines **5b**–**e** were utilized, the reactions proceeded well to produce **7h**–**k** in excellent yields (Table 3, entries 8–11). Imines **5f** and **5g** can also be employed for this reaction to furnish **7l** and **7m** both in excellent yields (Table 3, entries 12–13). It is noteworthy that the halide and methoxyl groups on these products offer the opportunity for further functionalization.[10] Electron-deficient alkynes **2b** and **2c** were also adopted to give the corresponding imidazolidines **7n** and **7o** in good yields (Table 3, entries 14 and 15). The structure of **7f** was confirmed unambiguously by X-ray diffraction analysis (Fig. 2), which was in accordance with ^1H NMR, ^{13}C NMR, and HRMS spectra.

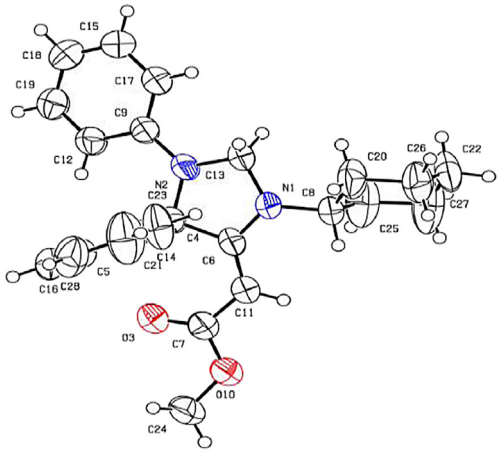


Fig. 2. X-ray crystal structure for **7f**.

3. Conclusion

In conclusion, we have developed a novel and efficient method for the preparation of functionalized imidazolidines through copper(I)-catalyzed domino three-component reactions of alkynes and imines. During the reaction, one carbon–carbon bond and two carbon–nitrogen bonds are formed with 100% atom economy.

Readily available starting materials, operational simplicity, and mild conditions make it very promising for both experimental synthesis and large-scale preparation. In addition, a new stereocenter is generated in the imidazolidine ring (**7a**–**o**) in this metal-catalyzed procedure, which offers the opportunity for further asymmetric investigation. Furthermore, the presented method is another exemplification of alkynes as increasingly attractive building blocks for developing MCRs.[11] Studies in this direction are also underway in our laboratory.

4. Experimental section

4.1. General

All the reagents were purchased from commercial suppliers, and were used without further purification. Column chromatography was carried out on silica gel. The ^{1}H NMR and ^{13}C NMR spectra were performed with a Varian Unity Plus spectrometer in $CDCl_3$ using TMS as internal standard. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standards (δ 7.26 for ^{1}H, δ 77.0 for ^{13}C). Coupling constants (J) are reported in Hertz (Hz). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), m (multiplet). Melting points were measured on microscopic melting point apparatus. High-resolution mass spectral analysis (HRMS) data were recorded by Electro-Spray Ionization (ESI).

4.2. General procedures for the synthesis of imidazolidines

*4.2.1. General procedures for the preparation of imidazolidines (**4a**–**n**).* Procedures for the synthesis of **4a**–**d**: CuCl (1.0 mmol) was added to a solution of imine **1** (10.0 mmol) and alkyne **2** (5.0 mmol) in dichloromethane (15 mL), and the reaction mixture was stirred at rt for 12 h. Then the reaction mixture was filtered and the solvent was removed under vacuum to give white or light yellow solid, which was rinsed with n-hexane to give analysable imidazolidines **4**. Compounds **4a**–**d** were synthesized according to this procedure and the spectral data of these compounds were given below.

Procedures for the synthesis of **4e**–**n**: CuCl (1.0 mmol) was added to a solution of imine **1** (10.0 mmol) and alkyne **2** (5.0 mmol) in dichloromethane (15 mL), and the reaction mixture was stirred at rt for 12 h. After filtration of the CuCl, the crude product was concentrated in vacuo and purified by chromatography on silica gel (hexane/ethyl acetate 10:1–5:1) yielding the imidazolidine **4**. Compounds **4e**–**n** were synthesized according to this procedure and the spectral data of these compounds were given below.

*4.2.2. General procedures for the synthesis of functionalized imidazolidines (**7a**–**o**).* Procedures for the synthesis of **7a**–**d** and **7h**–**i**: CuCl (1.0 mmol) was added to a solution of imine **5** (10.0 mmol) and alkyne **2** (10.0 mmol) in dichloromethane (15 mL). The reaction mixture was stirred at rt for 12 h. Then imine **1** (10.0 mmol) was added and the mixture was stirred at rt for 12 h. After filtration of the CuCl, the crude product was concentrated in vacuo to yield a white or yellow solid, which was washed with *n*-hexane to analysable imidazolidines **7**. Compounds **7a**–**d** and **7h**–**i** were synthesized according to this procedure and the spectral data of these compounds were given below.

Procedure for the synthesis of **7e**–**g** and **7j**–**o**: CuCl (1.0 mmol) was added to a solution of imine **5** (10.0 mmol) and alkyne **2** (10.0 mmol) in dichloromethane (15 mL). The reaction mixture was stirred at rt for 12 h. Then imine **1** (10.0 mmol) was added and the mixture was stirred at rt for 12 h. After filtration of the CuCl, the crude product was concentrated in vacuo and purified by chromatography on silica gel (hexane/ethyl acetate 10:1–5:1) yielding the imidazolidine **7**. Compounds **7e**–**g** and **7j**–**o** were synthesized according to this procedure and the spectral data of these compounds were given below.

4.3. Characterization

*4.3.1. (E)-Methyl 2-(1,3-diphenylimidazolidin-4-ylidene)acetate (**4a**).* White solid, mp: 132–133 °C, 1.37 g, 4.65 mmol, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, J=7.7 Hz, 2H), 7.40–7.27 (m, 5H), 6.85 (t, J=7.3 Hz, 1H), 6.66 (d, J=8.0 Hz, 2H), 5.08 (s, 2H), 5.01 (s, 1H), 4.87 (s, 2H), 3.66 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.32, 158.32, 144.86, 138.57, 129.88, 129.54, 127.14, 124.83, 118.15, 112.13, 80.92, 70.03, 53.59, 50.48 ppm. HRMS (EI$^+$) 294.1368 (calcd for $C_{18}H_{18}N_2O_2$ 294.1368).

*4.3.2. (E)-Methyl 2-(1,3-bis(4-methoxyphenyl)imidazolidin-4-ylidene)acetate (**4b**).* Light yellow solid, mp: 159–160 °C, 1.74 g, 4.9 mmol, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.23 (m, 2H), 6.99–6.94 (m, 2H), 6.89 (d, J=9.0 Hz, 2H), 6.60 (d, J=9.0 Hz, 2H), 4.96 (s, 2H), 4.80 (s, 3H), 3.84 (s, 3H), 3.78 (s, 3H), 3.64 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.40, 159.67, 158.65, 152.55, 139.73, 131.10, 126.87, 115.12, 113.30, 79.97, 71.20, 55.80, 55.57, 54.19, 50.38 ppm. HRMS (EI$^+$) 354.1582 (calcd for $C_{20}H_{22}N_2O_4$ 354.1580).

*4.3.3. (E)-Methyl 2-(1,3-bis(4-chlorophenyl)imidazolidin-4-ylidene) acetate (**4c**).* White solid, mp: 177–178 °C, 1.68 g, 4.65 mmol, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J=8.8 Hz, 2H), 7.29 (d, J=8.8 Hz, 2H), 7.25 (d, J=7.5 Hz, 2H), 6.56 (d, J=8.9 Hz, 2H), 5.00 (d, J=7.2 Hz, 3H), 4.82 (d, J=0.9 Hz, 2H), 3.66 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.03, 156.55, 142.23, 135.94, 131.61, 129.08, 128.39, 124.98, 122.30, 112.16, 80.81, 68.77, 52.49, 49.58 ppm. HRMS (EI$^+$) 362.0591 (calcd for $C_{18}H_{16}Cl_2N_2O_2$ 362.0589).

*4.3.4. (E)-Methyl 2-(1,3-di-p-tolylimidazolidin-4-ylidene)acetate (**4d**).* White solid, mp: 120–121 °C, 1.53 g, 4.75 mmol, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J=2.7 Hz, 2H), 7.24–7.20 (m, 2H), 7.11 (d, J=8.2 Hz, 2H), 6.57 (d, J=8.5 Hz, 2H), 5.01 (s, 2H), 4.92 (s, 1H), 4.82 (s, 2H), 3.64 (s, 3H), 2.38 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.42, 158.88, 142.90, 137.18, 135.90, 130.41, 130.03, 127.37, 124.85, 112.24, 80.38, 70.46, 53.84, 50.41, 21.11, 20.38 ppm. HRMS (EI$^+$) 322.1679 (calcd for $C_{20}H_{22}N_2O_2$ 322.1681).

*4.3.5. (E)-Methyl 2-(1,3-di-m-tolylimidazolidin-4-ylidene)acetate (**4e**).* Light yellow solid, mp: 134–135 °C, 1.45 g, 4.5 mmol, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.30 (m, 1H), 7.23–7.09 (m, 4H), 6.67 (d, J=7.5 Hz, 1H), 6.49 (s, 1H), 6.45 (d, J=8.0 Hz, 1H), 5.05 (s, 2H), 4.98 (s, 1H), 4.85 (d, J=1.1 Hz, 2H), 3.66 (s, 3H), 2.39 (s, 3H), 2.34 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.43, 158.56, 144.94, 139.95, 139.44, 138.47, 129.63, 129.37, 127.96, 125.38, 121.87, 119.06, 112.94, 109.28, 80.63, 70.15, 53.66, 50.46, 21.74, 21.41 ppm. HRMS (EI$^+$) 322.1679 (calcd for $C_{20}H_{22}N_2O_2$ 322.1681).

*4.3.6. (E)-Methyl 2-(1,3-di-o-tolylimidazolidin-4-ylidene)acetate (**4f**).* Viscous liquid, 1.21 g, 3.75 mmol, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (dd, J=6.2, 3.7 Hz, 3H), 7.22–7.13 (m, 3H), 7.04 (dd, J=17.2, 7.4 Hz, 2H), 4.81 (dd, J=28.3, 10.9 Hz, 4H), 4.37 (s, 1H), 3.61 (s, 3H), 2.39 (s, 3H), 2.19 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.51, 160.95, 148.21, 136.91, 136.28, 131.67, 128.58, 127.58, 127.16, 126.77, 123.59, 118.53, 79.81, 74.00, 57.49, 50.32, 19.26, 17.69 ppm. HRMS (EI$^+$) 322.1679 (calcd for $C_{20}H_{22}N_2O_2$ 322.1681).

*4.3.7. (E)-Methyl 2-(1,3-bis(3,5-dimethylphenyl)imidazolidin-4-ylidene)acetate (**4g**).* Light yellow solid, mp: 159–159 °C, 1.56 g, 4.45 mmol, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94 (d, J=4.6 Hz, 3H), 6.50 (s, 1H), 6.29 (s, 2H), 5.02 (s, 2H), 4.97 (s, 1H), 4.83

(d, *J*=1.1 Hz, 2H), 3.66 (s, 3H), 2.34 (s, 6H), 2.30 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.51, 158.74, 145.02, 139.64, 139.27, 138.38, 128.87, 122.42, 120.09, 110.12, 80.36, 70.25, 53.74, 50.44, 21.60, 21.31 ppm. HRMS (EI$^+$) 350.1997 (calcd for $C_{22}H_{26}N_2O_2$ 350.1994).

*4.3.8. (E)-Methyl 2-(1,3-dibenzylimidazolidin-4-ylidene)acetate (**4h**).* Viscous liquid, 1.39 g, 4.3 mmol, 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.27 (m, 7H), 7.21 (d, *J*=7.2 Hz, 3H), 4.75 (s, 1H), 4.28 (d, *J*=20.4 Hz, 4H), 4.03 (s, 2H), 3.70 (s, 2H), 3.62 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.36, 161.12, 137.81, 135.52, 128.75, 128.56, 128.39, 127.65, 127.33, 127.19, 78.16, 73.00, 59.20, 58.89, 50.07, 48.56 ppm. HRMS (EI$^+$) 322.1684 (calcd for $C_{20}H_{22}N_2O_2$ 322.1681).

*4.3.9. (E)-Methyl 2-(1,3-dicyclohexylimidazolidin-4-ylidene)acetate (**4i**).* Viscous liquid, 1.31 g, 4.25 mmol, 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.50 (s, 1H), 4.06 (d, *J*=4.0 Hz, 4H), 3.59 (s, 3H), 3.32 (s, 1H), 2.21 (s, 1H), 1.76 (dd, *J*=47.1, 18.5 Hz, 10H), 1.26 (dd, *J*=25.6, 8.0 Hz, 10H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.54, 160.68, 76.22, 67.12, 61.70, 56.72, 53.90, 49.95, 31.28, 29.47, 25.79, 25.49, 24.46 ppm. HRMS (EI$^+$) 306.2309 (calcd for $C_{18}H_{30}N_2O_2$ 306.2307).

*4.3.10. (E)-Ethyl 2-(1,3-diphenylimidazolidin-4-ylidene)acetate (**4j**).* White solid, mp: 127–129 °C, 1.36 g, 4.4 mmol, 88% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 (t, *J*=7.6 Hz, 2H), 7.41–7.28 (m, 5H), 6.85 (t, *J*=7.2 Hz, 1H), 6.66 (d, *J*=7.9 Hz, 2H), 5.07 (s, 2H), 5.01 (s, 1H), 4.87 (s, 2H), 4.13 (q, *J*=7.1 Hz, 2H), 1.26 (t, *J*=7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.87, 158.11, 144.87, 138.62, 129.81, 129.46, 127.03, 124.83, 118.07, 112.08, 81.36, 69.95, 58.88, 53.54, 14.55 ppm. HRMS (EI$^+$) 308.1527 (calcd for $C_{19}H_{20}N_2O_2$ 308.1525).

*4.3.11. (E)-Ethyl 2-(1,3-bis(4-methoxyphenyl)imidazolidin-4-ylidene) acetate (**4k**).* White solid, mp: 141–142 °C, 1.66 g, 4.5 mmol, 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 (d, *J*=8.6 Hz, 2H), 6.96 (d, *J*=8.8 Hz, 2H), 6.88 (d, *J*=8.9 Hz, 2H), 6.59 (d, *J*=8.9 Hz, 2H), 4.94 (s, 2H), 4.79 (s, 3H), 4.10 (dd, *J*=14.2, 7.1 Hz, 2H), 3.80 (d, *J*=19.2 Hz, 6H), 1.24 (t, *J*=7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.96, 159.46, 158.61, 152.52, 139.75, 131.15, 126.86, 115.09, 113.25, 80.41, 71.12, 58.75, 55.62, 54.14, 14.56 ppm. HRMS (EI$^+$) 368.1739 (calcd for $C_{21}H_{24}N_2O_4$ 368.1736).

*4.3.12. (E)-1-(1,3-Diphenylimidazolidin-4-ylidene)propan-2-one (**4l**).* Yellow solid, mp: 107–108 °C, 1.21 g, 4.35 mmol, 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (t, *J*=7.6 Hz, 2H), 7.42–7.27 (m, 5H), 6.84 (t, *J*=7.3 Hz, 1H), 6.66 (d, *J*=8.0 Hz, 2H), 5.47 (s, 1H), 5.07 (s, 2H), 4.90 (s, 2H), 2.06 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.51, 158.10, 144.75, 129.90, 129.47, 127.43, 125.02, 118.06, 112.09, 91.53, 69.74, 54.31, 30.55 ppm. HRMS (EI$^+$) 278.1416 (calcd for $C_{18}H_{18}N_2O$ 278.1419).

*4.3.13. (E)-1-(1,3-Bis(4-methoxyphenyl)imidazolidin-4-ylidene) propan-2-one (**4m**).* Light yellow solid, mp: 148–150 °C, 1.49 g, 4.4 mmol, 88% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30–7.23 (m, 2H), 7.00 (d, *J*=8.9 Hz, 2H), 6.89 (d, *J*=8.9 Hz, 2H), 6.60 (d, *J*=9.0 Hz, 2H), 5.27 (s, 1H), 4.94 (s, 2H), 4.83 (s, 2H), 3.85 (s, 3H), 3.77 (s, 3H), 2.02 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.31, 159.41, 158.83, 152.51, 139.63, 130.88, 126.90, 115.13, 113.25, 90.95, 70.90, 55.64, 54.93, 30.45 ppm. HRMS (EI$^+$) 338.1633 (calcd for $C_{20}H_{22}N_2O_3$ 338.1630).

*4.3.14. (E)-1-(1,3-Bis(4-chlorophenyl)imidazolidin-4-ylidene) propan-2-one (**4n**).* White solid, mp: 180–182 °C, 1.47 g, 4.25 mmol, 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 (d, *J*=8.6 Hz, 2H), 7.27 (dd, *J*=18.9, 8.8 Hz, 4H), 6.55 (d, *J*=8.8 Hz, 2H), 5.44 (s, 1H), 4.99 (s, 2H), 4.83 (s, 2H), 2.05 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.66, 157.45, 143.19, 133.07, 130.20, 129.38, 126.31, 123.27, 113.17, 92.07, 69.52, 54.26, 30.62 ppm. HRMS (EI$^+$) 346.0643 (calcd for $C_{18}H_{16}Cl_2N_2O$ 346.0640).

*4.3.15. (E)-Methyl 2-(1,3,5-triphenylimidazolidin-4-ylidene)acetate (**7a**).* White solid, mp: 161–165 °C, 3.33 g, 9.0 mmol, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J*=7.3 Hz, 2H), 7.48–7.42 (m, 2H), 7.37 (d, *J*=7.4 Hz, 2H), 7.31 (d, *J*=7.2 Hz, 2H), 7.23–7.16 (m, 4H), 6.72 (t, *J*=7.3 Hz, 1H), 6.66 (d, *J*=8.0 Hz, 2H), 6.56 (s, 1H), 5.28 (d, *J*=4.4 Hz, 1H), 5.21 (dd, *J*=4.3, 1.1 Hz, 1H), 5.03 (s, 1H), 3.54 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.88, 160.64, 143.36, 140.48, 138.68, 130.00, 129.36, 128.22, 127.63, 126.95, 124.72, 117.96, 112.39, 82.89, 69.10, 64.75, 50.45 ppm. HRMS (EI$^+$) 370.1677 (calcd for $C_{24}H_{22}N_2O_2$ 370.1681).

*4.3.16. (E)-Methyl 2-(3-(4-methoxyphenyl)-1,5-diphenylimidazolidin-4-ylidene)acetate (**7b**).* White solid mp: 147–148 °C, 3.92 g, 9.8 mmol, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.52 (m, 2H), 7.35–7.28 (m, 4H), 7.19 (dd, *J*=8.6, 7.6 Hz, 3H), 6.99 (d, *J*=8.9 Hz, 2H), 6.72 (t, *J*=7.3 Hz, 1H), 6.64 (d, *J*=7.9 Hz, 2H), 6.54 (s, 1H), 5.22 (s, 2H), 4.78 (s, 1H), 3.84 (s, 3H), 3.53 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.91, 161.94, 158.72, 143.32, 140.53, 131.08, 129.33, 128.22, 127.58, 127.06, 117.84, 115.25, 112.31, 81.71, 69.78, 64.73, 55.61, 50.35 ppm. HRMS (EI$^+$) 400.1789 (calcd for $C_{25}H_{24}N_2O_3$ 400.1787).

*4.3.17. (E)-Methyl 2-(3-(4-chlorophenyl)-1,5-diphenylimidazolidin-4-ylidene)acetate (**7c**).* Light yellow solid, mp: 137–138 °C, 3.68 g, 9.1 mmol, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J*=7.3 Hz, 2H), 7.47–7.42 (m, 2H), 7.36–7.27 (m, 4H), 7.25–7.17 (m, 3H), 6.74 (t, *J*=7.3 Hz, 1H), 6.66 (d, *J*=8.0 Hz, 2H), 6.54 (s, 1H), 5.27 (d, *J*=4.2 Hz, 1H), 5.20 (dd, *J*=4.2, 1.1 Hz, 1H), 5.01 (s, 1H), 3.56 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.69, 160.26, 143.26, 140.34, 137.28, 132.25, 130.17, 129.39, 128.36, 128.07, 127.73, 125.85, 118.13, 112.43, 83.68, 68.95, 64.63, 50.56 ppm. HRMS (EI$^+$) 404.1288 (calcd for $C_{24}H_{21}ClN_2O_2$ 404.1292).

*4.3.18. (E)-Methyl 2-(1,5-diphenyl-3-(p-tolyl)imidazolidin-4-ylidene) acetate (**7d**).* Light yellow solid, mp: 124–126 °C, 3.65 g, 9.5 mmol, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.53 (m, 3H), 7.29 (t, *J*=7.5 Hz, 3H), 7.23–7.14 (m, 5H), 6.71 (dd, *J*=8.9, 5.7 Hz, 1H), 6.64 (d, *J*=7.9 Hz, 2H), 6.54 (s, 1H), 5.24 (d, *J*=4.4 Hz, 1H), 5.20 (dd, *J*=4.4, 1.4 Hz, 1H), 4.93 (d, *J*=0.6 Hz, 1H), 3.53 (s, 3H), 2.38 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.93, 161.12, 143.35, 140.52, 137.15, 135.93, 130.57, 129.34, 128.22, 127.59, 124.91, 117.87, 112.34, 82.31, 69.34, 64.76, 50.39, 21.13 ppm. HRMS (EI$^+$) 384.1832 (calcd for $C_{25}H_{24}N_2O_2$ 384.1838).

*4.3.19. (E)-Methyl 2-(3-(3,5-dimethylphenyl)-1,5-diphenylimidazolidin-4-ylidene)acetate (**7e**).* White solid, mp: 161–162 °C, 3.5 g, 8.8 mmol, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.53 (m, 2H), 7.31 (t, *J*=7.5 Hz, 2H), 7.21 (td, *J*=8.7, 7.5 Hz, 3H), 7.00 (s, 2H), 6.95 (s, 1H), 6.73 (t, *J*=7.3 Hz, 1H), 6.66 (d, *J*=7.9 Hz, 2H), 6.54 (s, 1H), 5.28 (d, *J*=4.4 Hz, 1H), 5.21 (dd, *J*=4.4, 1.4 Hz, 1H), 4.98 (d, *J*=0.7 Hz, 1H), 3.55 (s, 3H), 2.35 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.95, 160.88, 143.37, 140.57, 139.83, 138.43, 129.32, 128.79, 128.22, 127.58, 122.40, 117.83, 112.33, 82.51, 69.27, 64.79, 50.40, 21.33 ppm. HRMS (EI$^+$) 398.1990 (calcd for $C_{26}H_{26}N_2O_2$ 398.1994).

*4.3.20. (E)-Methyl 2-(3-cyclohexyl-1,5-diphenylimidazolidin-4-ylidene)acetate (**7f**).* White solid, mp: 151–152 °C, 3.31 g, 8.8 mmol, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J*=7.3 Hz, 2H), 7.23 (d, *J*=7.7 Hz, 2H), 7.17 (dd, *J*=10.6, 5.2 Hz, 3H), 6.69 (t, *J*=7.3 Hz, 1H), 6.60 (d, *J*=8.1 Hz, 2H), 6.43 (s, 1H), 4.99 (dd, *J*=4.5, 1.5 Hz, 1H), 4.89 (d, *J*=4.6 Hz, 1H), 4.63 (s, 1H), 3.56 (s, 3H), 2.14 (d,

J=12.0 Hz, 1H), 2.06 (d, *J*=11.7 Hz, 1H), 1.92 (t, *J*=12.8 Hz, 2H), 1.76 (d, *J*=13.0 Hz, 1H), 1.60 (qd, *J*=12.3, 3.4 Hz, 2H), 1.50–1.31 (m, 3H), 1.29–1.20 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.97, 161.26, 143.26, 140.35, 129.23, 128.11, 127.38, 117.52, 112.15, 78.69, 64.93, 63.67, 54.15, 50.24, 30.50, 28.37, 25.75, 25.56, 25.43 ppm. HRMS (EI^+) 376.2151 (calcd for $C_{24}H_{28}N_2O_2$ 376.2151).

*4.3.21. (E)-Methyl 2-(3-isopropyl-1-(4-methoxyphenyl)-5-phenylimidazolidin-4-ylidene)acetate (**7g**).* Light yellow solid, mp: 180–181 °C, 3.15 g, 8.6 mmol, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.35 (m, 2H), 7.24 (dd, *J*=8.5, 4.6 Hz, 2H), 7.19–7.13 (m, 1H), 6.80–6.72 (m, 2H), 6.62–6.54 (m, 2H), 6.38 (s, 1H), 4.92 (dd, *J*=4.7, 1.7 Hz, 1H), 4.78 (d, *J*=4.7 Hz, 1H), 4.65 (s, 1H), 4.01–3.92 (m, 1H), 3.69 (s, 3H), 3.55 (s, 3H), 1.41 (d, *J*=6.7 Hz, 3H), 1.30 (d, *J*=6.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.07, 161.47, 152.30, 140.27, 138.28, 128.10, 127.35, 114.91, 113.94, 79.06, 66.01, 63.45, 55.67, 50.20, 45.76, 19.96, 18.12 ppm. HRMS (EI^+) 366.1940 (calcd for $C_{22}H_{26}N_2O_{23}$ 366.1943).

*4.3.22. (E)-Methyl 2-(1-(4-methoxyphenyl)-3,5-diphenylimidazolidin-4-ylidene)acetate (**7h**).* White solid, mp: 148–149 °C, 3.72 g, 9.3 mmol, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.50 (m, 2H), 7.50–7.44 (m, 2H), 7.41–7.36 (m, 2H), 7.30 (ddd, *J*=7.3, 4.8, 1.4 Hz, 3H), 7.22 (dd, *J*=8.3, 6.4 Hz, 1H), 6.83–6.76 (m, 2H), 6.71–6.64 (m, 2H), 6.49 (s, 1H), 5.19 (s, 2H), 5.06 (d, *J*=0.7 Hz, 1H), 3.72 (s, 3H), 3.54 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.02, 160.74, 152.74, 140.17, 138.85, 138.61, 129.95, 128.21, 127.60, 126.82, 124.63, 114.96, 114.61, 82.82, 69.96, 66.23, 55.67, 50.43 ppm. HRMS (EI^+) 400.1783 (calcd for $C_{25}H_{24}N_2O_3$ 400.1787).

*4.3.23. (E)-Methyl 2-(3,5-diphenyl-1-(p-tolyl)imidazolidin-4-ylidene)acetate (**7i**).* White solid, mp: 159–160 °C, 3.61 g, 9.4 mmol, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J*=7.5 Hz, 2H), 7.47 (t, *J*=7.7 Hz, 2H), 7.39 (d, *J*=7.7 Hz, 2H), 7.30 (t, *J*=7.4 Hz, 3H), 7.21 (t, *J*=7.3 Hz, 1H), 7.01 (d, *J*=8.1 Hz, 2H), 6.59 (d, *J*=8.2 Hz, 2H), 6.53 (s, 1H), 5.24 (dd, *J*=22.8, 4.1 Hz, 2H), 5.04 (s, 1H), 3.55 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.95, 160.76, 141.38, 140.47, 138.78, 129.93, 128.22, 127.59, 127.28, 126.87, 124.68, 112.72, 82.81, 69.36, 65.13, 50.45, 20.36 ppm. HRMS (EI^+) 384.1834 (calcd for $C_{25}H_{24}N_2O_2$ 384.1838).

*4.3.24. (E)-Methyl 2-(5-(4-chlorophenyl)-1,3-diphenylimidazolidin-4-ylidene)acetate (**7j**).* White solid, mp: 149–150 °C, 3.52 g, 8.7 mmol, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.45 (m, 4H), 7.41–7.35 (m, 2H), 7.34–7.27 (m, 2H), 7.27–7.24 (m, 1H), 7.21 (dd, *J*=8.6, 7.4 Hz, 2H), 6.76 (t, *J*=7.4 Hz, 1H), 6.63 (d, *J*=7.9 Hz, 2H), 6.52 (s, 1H), 5.30 (d, *J*=4.4 Hz, 1H), 5.23 (dd, *J*=4.3, 1.5 Hz, 1H), 5.02 (d, *J*=0.8 Hz, 1H), 3.56 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.88, 160.27, 143.10, 139.11, 138.52, 133.37, 130.05, 129.49, 128.49, 127.08, 124.66, 118.23, 112.38, 83.02, 69.09, 64.10, 50.52 ppm. HRMS (EI^+) 404.1295 (calcd for $C_{24}H_{21}ClN_2O_2$ 404.1292).

*4.3.25. (E)-Methyl 2-(1,3-diphenyl-5-(p-tolyl)imidazolidin-4-ylidene)acetate (**7k**).* White solid, mp: 157–158 °C, 3.42 g, 8.9 mmol, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.42 (m, 4H), 7.39 (d, *J*=7.4 Hz, 2H), 7.30 (t, *J*=7.3 Hz, 1H), 7.20 (t, *J*=7.9 Hz, 2H), 7.11 (d, *J*=7.9 Hz, 2H), 6.73 (t, *J*=7.3 Hz, 1H), 6.66 (d, *J*=8.0 Hz, 2H), 6.52 (s, 1H), 5.30 (d, *J*=4.3 Hz, 1H), 5.25–5.17 (m, 1H), 5.02 (s, 1H), 3.55 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.91, 160.83, 143.35, 138.73, 137.52, 137.25, 129.97, 129.33, 129.03, 128.01, 126.89, 124.69, 117.86, 112.39, 82.76, 69.01, 64.48, 50.44, 21.20 ppm. HRMS (EI^+) 384.1842 (calcd for $C_{25}H_{24}N_2O_2$ 384.1838).

*4.3.26. (E)-Methyl 2-(5-(furan-2-yl)-1,3-diphenylimidazolidin-4-ylidene)acetate (**7l**).* Light yellow solid, mp: 141–142 °C, 3.17 g, 8.8 mmol, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, *J*=7.8 Hz, 2H), 7.40 (dd, *J*=8.5, 1.2 Hz, 2H), 7.30 (d, *J*=7.4 Hz, 1H), 7.24–7.20 (m, 3H), 6.81–6.70 (m, 4H), 6.55 (d, *J*=3.0 Hz, 1H), 6.26 (dd, *J*=3.2, 1.8 Hz, 1H), 5.22 (d, *J*=4.2 Hz, 1H), 5.18 (dd, *J*=4.2, 1.0 Hz, 1H), 4.99 (s, 1H), 3.59 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.10, 158.39, 151.76, 143.26, 141.87, 138.80, 129.92, 129.27, 127.11, 125.08, 118.47, 112.88, 110.07, 109.29, 82.11, 68.81, 58.66, 50.47 ppm. HRMS (EI^+) 360.1472 (calcd for $C_{22}H_{20}N_2O_3$ 360.1474).

*4.3.27. (E)-Methyl 2-(1,3-diphenyl-5-(thiophen-2-yl)imidazolidin-4-ylidene)acetate (**7m**).* Light yellow solid, mp: 144–145 °C, 3.20 g, 8.5 mmol, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.36 (m, 2H), 7.32–7.27 (m, 3H), 7.23–7.16 (m, 3H), 7.08 (dd, *J*=5.1, 1.1 Hz, 1H), 6.98 (s, 1H), 6.85 (dd, *J*=5.1, 3.6 Hz, 1H), 6.74 (t, *J*=7.4 Hz, 1H), 6.65 (d, *J*=7.8 Hz, 2H), 5.18 (d, *J*=4.6 Hz, 1H), 5.05 (dd, *J*=4.5, 1.1 Hz, 1H), 5.01 (s, 1H), 3.58 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.16, 160.03, 143.08, 142.67, 138.64, 129.96, 129.45, 127.00, 126.45, 124.78, 118.61, 113.01, 82.85, 68.11, 60.51, 50.59 ppm. HRMS (EI^+) 376.1247 (calcd for $C_{22}H_{20}N_2O_2S$ 376.1245).

*4.3.28. (E)-Ethyl 2-(1,3,5-triphenylimidazolidin-4-ylidene)acetate (**7n**).* White solid, mp: 108–110 °C, 3.38 g, 8.8 mmol, 88% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, *J*=7.3 Hz, 2H), 7.49 (t, *J*=7.6 Hz, 2H), 7.41 (d, *J*=7.4 Hz, 2H), 7.32 (t, *J*=7.3 Hz, 3H), 7.27–7.16 (m, 3H), 6.82–6.65 (m, 3H), 6.61 (s, 1H), 5.28 (dd, *J*=22.1, 3.8 Hz, 2H), 5.05 (s, 1H), 4.04 (dd, *J*=8.7, 7.3 Hz, 2H), 1.17 (t, *J*=7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.46, 160.43, 143.43, 140.51, 138.75, 129.92, 129.29, 128.14, 127.52, 126.80, 124.67, 117.91, 112.39, 83.32, 69.04, 64.65, 58.87, 14.43 ppm. HRMS (EI^+) 384.1835 (calcd for $C_{25}H_{24}N_2O_2$ 384.1838).

*4.3.29. (E)-1-(1,3,5-Triphenylimidazolidin-4-ylidene)propan-2-one (**7o**).* White solid, mp: 166–168 °C, 3.01 g, 8.5 mmol, 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (d, *J*=7.4 Hz, 2H), 7.54 (t, *J*=7.7 Hz, 2H), 7.46–7.30 (m, 5H), 7.21 (t, *J*=7.8 Hz, 3H), 6.78–6.65 (m, 4H), 5.46 (s, 1H), 5.37–5.22 (m, 2H), 1.94 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.87, 160.20, 143.21, 140.33, 138.47, 129.99, 129.26, 128.16, 127.36, 124.94, 117.85, 112.29, 92.31, 68.95, 64.98, 30.87 ppm. HRMS (EI^+) 354.1735 (calcd for $C_{24}H_{22}N_2O$ 354.1732).

Supplementary data

Experimental procedures, characterization data, and copies of the ^{1}H NMR and ^{13}C NMR spectra for the products are available. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.03.063.

References and notes

1. (a) Iinuma, Y.; Kozawa, S.; Ishiyama, H.; Tsuda, M.; Fukushi, E.; Kawabata, J.; Fromont, J.; Kobayashi, J. *J. Nat. Prod.* **2005**, *68*, 1109–1110; (b) Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2008**, *41*, 1013–1025; (c) Zhang, C.; De, C. K.; Mal, R.; Seidel, D. *J. Am. Chem. Soc.* **2008**, *130*, 416–417; (d) Gil, C.; Brase, S. *J. Comb. Chem.* **2009**, *11*, 175–197; (e) Bhandari, M. R.; Yousufuddin, M.; Lovely, C. J. *Org. Lett.* **2011**, *13*, 1382–1385; (f) Chattopadhyay, B.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2012**, *51*, 862–872; (g) Gulevich, A. V.; Dudnik, A. S.; Chernyak, N.; Gevorgyan, V. *Chem. Rev.* **2013**, *113*, 3084–3213.
2. (a) Molinski, T. F.; Ko, J.; Reynolds, K. A.; Lievens, S. C.; Skarda, K. R. *J. Nat. Prod.* **2011**, *74*, 882–887; (b) Neves, J. K. A. L.; Lima, M. C. A.; Pereira, V. R. A.; Melo, C. M. L.; Peixoto, C. A.; Pitta, I. R.; Albuquerque, M. C. P. A.; Galdino, S. L. *Exp. Parasitol.* **2011**, *128*, 82–90; (c) Ye, Z.; Xia, S.; Shao, X.; Cheng, J.; Xu, X.; Xu, Z.; Li, Z.; Qian, X. *J. Agric. Food Chem.* **2011**, *59*, 10615–10623; (d) Nishiwaki, H.; Kuriyama, M.; Nagaoka, H.; Kato, A.; Akamastu, M.; Yamauchi, S.; Shuto, Y. *Bioorg. Med. Chem.* **2012**, *20*, 6305–6312; (e) Xie, H.; Liu, J. C.; Wu, L.; Ding, M. W. *Tetrahedron* **2012**, *68*, 7984–7990.
3. (a) Boca, M.; Baran, P.; Boca, R.; Fuess, H.; Kickelbick, G.; Linert, W.; Renz, F.; Svoboda, I. *Inorg. Chem.* **2000**, *39*, 3205–3212; (b) Katritzky, A. R.; Suzuki, K.; He, H. Y. *J. Org. Chem.* **2002**, *67*, 3109–3114; (c) Brefuel, N.; Lepetit, C.; Shova, S.; Dahan, F.; Tuchagues, J. P. *Inorg. Chem.* **2005**, *44*, 8916–8928; (d) Arai, T.; Mishiro, A.; Yokoyama, N.; Suzuki, K.; Sato, H. *J. Am. Chem. Soc.* **2010**, *132*, 5338–5339.

4. Viso, A.; Pradilla, R. F.; Garcir, A.; Guerrero-Strachan, C.; Alonso, M.; Tortosa, M.; Flores, A.; Martinez-Ripoll, M.; Fonseca, I.; Andre, I.; Rodriguez, A. *Chem.—Eur. J.* **2003**, *9*, 2867–2876.
5. (a) Armstrong, R. W.; Combs, A. P.; Tempest, P. A.; Brown, S. D.; Keating, T. A. *Acc. Chem. Res.* **1996**, *29*, 123–131; (b) Domling, A. *Chem. Rev.* **2006**, *106*, 17–89.
6. Shen, X.; Bu, H.; Shi, J.; Wu, Z.; Ma, H.; Li, Y. *Tetrahedron Lett.* **2013**, *54*, 3937–3939.
7. (a) Black, D. A.; Arndtsen, B. A. *Org. Lett.* **2004**, *6*, 1107–1110; (b) Whiting, M.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2006**, *45*, 3157–3161; (c) Ohno, H.; Ohta, Y.; Oishi, S.; Fujii, N. *Angew. Chem., Int. Ed.* **2007**, *46*, 2295–2298; (d) Black, D. A.; Beveridge, R. E.; Arndtsen, B. A. *J. Org. Chem.* **2008**, *73*, 1906–1910; (e) Ohta, Y.; Chiba, H.; Oishi, S.; Fujii, N.; Ohno, H. *J. Org. Chem.* **2009**, *74*, 7052–7058; (f) Barluenga, J.; Gomez, A.; Santamaria, J.; Tomas, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 1306–1308; (g) Wang, Y.; Zhang, W. X.; Wang, Z.; Xi, Z. *Angew. Chem., Int. Ed.* **2011**, *50*, 8122–8126; (h) Suresh, R.; Muthusubramanian, S.; Senthilkumaran, R.; Manickam, G. *J. Org. Chem.* **2012**, *77*, 1468–1476.
8. (a) Huffman, M. A.; Yasuda, N.; Decamp, A. E.; Grabowski, E. J. J. *J. Org. Chem.* **1995**, *60*, 1590–1594; (b) Gommermann, N.; Koradin, C.; Polborn, K.; Knochel, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 5763–5766; (c) Magueur, G.; Crousse, B.; Delpon, D. B. *Tetrahedron Lett.* **2005**, *46*, 2219–2221; (d) Colombo, F.; Benaglia, M.; Orlandi, S.; Usuelli, F.; Celentano, G. *J. Org. Chem.* **2006**, *71*, 2064–2070.
9. (a) Wipf, P.; Aoyama, Y.; Benedum, T. E. *Org. Lett.* **2004**, *6*, 3593–3595; (b) Li, S.; Li, Z.; Yuan, Y.; Peng, D.; Li, Y.; Zhang, L.; Wu, Y. *Org. Lett.* **2012**, *14*, 1130–1133; (c) Senadi, G. C.; Hu, W. P.; Hsiao, J. S.; Vandavasi, J. K.; Chen, C. Y.; Wang, J. J. *Org. Lett.* **2012**, *14*, 4478–4481; (d) Hu, Y.; Wang, C.; Wang, D.; Wu, F.; Wan, B. *Org. Lett.* **2013**, *15*, 3146–3149.
10. (a) Yu, D.-G.; Li, B.-J.; Shi, Z.-J. *Acc. Chem. Res.* **2010**, *43*, 1486–1495; (b) Tobisu, M.; Shimasaki, T.; Chatani, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 4866–4869.
11. (a) Nair, V.; Bindu, S.; Sreekumar, V.; Rath, N. P. *Org. Lett.* **2003**, *5*, 665–667; (b) Ma, C.; Yang, Y. *Org. Lett.* **2005**, *7*, 1343–1345; (c) Nair, V.; Sreekumar, V.; Bindu, S.; Suresh, E. *Org. Lett.* **2005**, *7*, 2297–2300; (d) Lee, P. H.; Lee, K.; Kang, Y. *J. Am. Chem. Soc.* **2006**, *128*, 1139–1146; (e) Xu, X.; Cheng, D.; Li, J.; Guo, H.; Yan, J. *Org. Lett.* **2007**, *9*, 1585–1587; (f) Zhang, M.; Jiang, H.; Liu, H.; Zhu, Q. *Org. Lett.* **2007**, *9*, 4111–4113; (g) Ding, Q.; Wu, J. *Org. Lett.* **2007**, *9*, 4959–4962; (h) Galliford, C. V.; Scheidt, K. A. *J. Org. Chem.* **2007**, *72*, 1811–1813; (i) Barluenga, J.; Suero, M. G.; Campa, R. D.; Florez, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 9720–9724; (j) Ruijter, E.; Scheffelaar, R.; Orru, R. V. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 6234–6246; (k) Erver, F.; Hilt, G. *Org. Lett.* **2012**, *14*, 1884–1887.