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Silver(I)-promoted intramolecular addition of *N*-heterocyclic carbenes towards unsaturated esters in water

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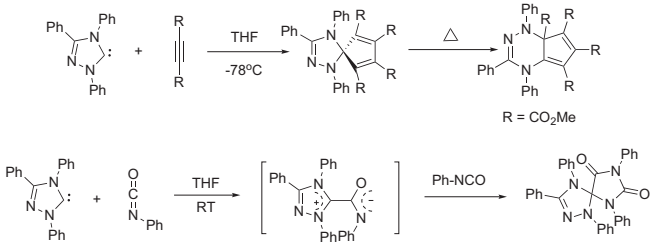
ABSTRACT

Silver(I)-promoted intramolecular addition reaction between *N*-heterocyclic carbene and unsaturated esters in water is described. The reaction leads to 1*H*-imidazo[1,2-*a*]indole derivatives in moderate to excellent yields.

1. Introduction

N-Heterocyclic carbenes (NHCs) have found impressive uses not only as ligands in the catalysis and organometallic chemistry[1] due to their strong σ-donating ability but also as powerful organocatalysts in molecular chemistry[2] and precision polymer synthesis in macromolecular chemistry.[3] The reactivity of stable diaminocarbenes towards C–C multiple bonds have been studied by Enders and co-workers.[4,5] The reactions of triazolylidene with dimethyl fumarate, *N*-alkyl or *N*-aryl maleimides and benzyl bromide generate the methylene triazoline derivatives. The reaction of triazolylidene with dimethyl acetylenedicarboxylate afforded the spiro compounds (Scheme 1) via nucleophilic addition of the carbene to the triple bond and subsequent 1,3-dipolar cycloaddition, which rearranges to the more stable bicyclic compound upon heating.[6] Triazolylidene can also react with an excess of phenyl isocyanate to generate the spiro compound (Scheme 1).[6] The [4+1] cyclization of NHCs with vinyl isocyanates, vinyl ketenes and diphenyltetrazine has also been reported leading to hydroindolone derivatives.[7] The multicomponent reactions of NHCs towards activated acetylenes and aldehydes are also known.[8] Besides, intramolecular addition of NHC to imines giving access to new heterocycles with the formation of six- and seven-membered rings,[9] C–H insertion reaction of NHC with the methyl group to



Scheme 1. The spiro compounds formed via the NHC addition.

generate the aminal[10] and NHC bearing push–pull substituents and aromatic aldehydes or acrylates resulting in the formation of imidazole derivatives[11] have also been reported. More recently, Bielawski and co-workers described the synthesis of a variety of cyclopropanes, epoxides and diamidocyclopropenes by combining DAC (*N*,*N*′-diamidocarbene) with a range of structurally and electronically diversed olefins, aldehydes and alkynes.[12] In these reactions, DAC is used as a readily accessible and isolable [2+1] cycloaddition reagent.

NHCs are often generated through deprotonation of azolium salts with NaH, KH, or KO*t*-Bu in THF.[13] However, these methods suffer from the drawbacks, such as sensitivity to air and moisture and limited tolerance to various functionalities. The generation of free NHCs through thermal decomposition of masked NHCs is a good choice.[14] The masked NHCs, such as 5-alkxytriazolines,[4]

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imidazolium-2-carboxylate,[15] imidazolium-2-thioisocyanates,[16] Ag(I)–NHC complexes,[17] 2-alkoxy,[18] 2-trichloromethyl,[19] 2-pentafluorophenyl imidazolidines[20] have been reported. Silver oxide can easily react with imidazolium salts to give silver–NHC complexes in which the Ag–C bonds are labile, thus the nucleophilic addition of NHCs would proceed in the presence of basic silver compounds. As an extension of our NHC chemistry,[21] here, we report a silver(I)-promoted intramolecular addition of NHC towards unsaturated esters in water.

2. Results and discussion

Initially, we treated imidazolium salt **2a** with 0.5 equiv of Ag_2O in THF at 65 °C, and **3a** was produced in 78% yield. As shown in Table 1, the yield decreased to 29% when 0.1 equiv of Ag_2O was used in the reaction. Obviously, 0.5 equiv Ag(I) is needed in this reaction. A few other silver(I) salts were then screened in subsequent experiments. When $AgNO_3$ and AgOTf were used, the reaction did not proceed at all, whereas when Ag_2CO_3 was used as the deprotonation agent, the yield of **3a** was increased to 82%. AgOAc is also efficient. The reaction initially gave an unidentified product, but it quickly transformed to **3a** after flash column chromatography in 80% yield. The effect of solvents was also examined, and the results were summarized in Table 1. The results indicated that when the solvent THF was replaced by acetonitrile, DMF and toluene, the yield of **3a** was sharply decreased to less than 40%. Surprisingly, the reaction could proceed smoothly in water, and the yield is comparable to that in THF. Thus we finally chose water as the solvent owing to its environmental-friendly feature for further studies. For comparison, the commonly used bases like NaH and KO*t*-Bu were also examined, and the desired product was obtained in 51% and 36% yields, respectively.

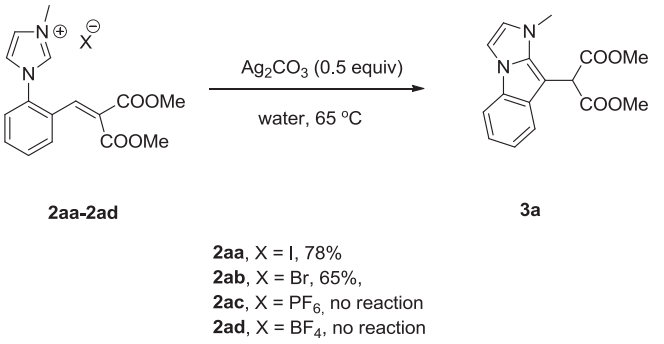
Table 1
Optimization of the reaction conditions

2a **3a**

Entry	Base (equiv)	Solvent	*T* (°C)	Yield (%)
1	Ag_2O (0.5)	THF	65	78
2	Ag_2O (0.1)	THF	65	29
3	AgOAc (1.0)	THF	65	80
4	Ag_2CO_3 (0.5)	THF	65	82
5	$AgNO_3$ (1.0)	THF	65	No reaction
6	AgOTf (1.0)	THF	65	No reaction
7	Ag_2CO_3 (0.5)	Toluene	65	37
8	Ag_2CO_3 (0.5)	CH_3CN	65	39
9	Ag_2CO_3 (0.5)	DMF	65	31
10	Ag_2CO_3 (0.5)	H_2O	65	78
11	Ag_2CO_3 (0.5)	H_2O	100	49
12	KO*t*-Bu (1.5)	THF	65	36
13	NaH (1.5)	THF	65	51

All reactions were carried out with **2** (0.5 mmol) for 18 h.

As shown in Scheme 2, imidazolium bromide **2ab** and imidazolium iodide **2aa** reacted smoothly with Ag_2CO_3 giving corresponding imidazo[1,2-*a*]indoles in 65% and 78% yields, respectively. However, under the same conditions, the PF_6^- and BF_4^- salts are inactive, and no imidazo[1,2-*a*]indole was isolated. Probably, $[Ag(NHC)_2]^+$ species generated from the PF_6^- and BF_4^- salts are inert whereas imidazolium halides [Ag(NHC)X] are more labile.



2aa-2ad **3a**

2aa, X = I, 78%
2ab, X = Br, 65%,
2ac, X = PF_6, no reaction
2ad, X = BF_4, no reaction

Scheme 2. The effect of anion on the reaction. [a]All reactions were carried out with **2** (0.5 mmol), Ag_2CO_3 (0.5 equiv) in water (2.5 mL) at 65 °C for 18 h under nitrogen. [b]Yield of isolated product after flash column chromatography.

Under the optimized condition, a series of substrates were subjected to the reaction and the results are summarized in Table 2. All the imidazolium and benzoimidazolium salts in the presence of Ag_2CO_3 could be converted to their corresponding products in moderate to excellent yields. The reaction of isopropyl esters afforded the best yield in up to 91%, whereas *tert*-butyl esters gave relatively lower yield (Table 2, entries 4–6). In addition, the reactions of benzoimidazonium salt showed lower activity compared to similar imidazolium salt (entry 7). The reaction of 2-imidazoliumylcinnamic ester with Ag_2CO_3 did not yield the desired product suggesting that only more electron-deficient double bond could receive nucleophilic addition of NHC.

A plausible mechanism was tentatively proposed shown in Scheme 3. The Ag(I)–NHC complex A was firstly formed upon treatment of the imidazolium salt with Ag_2CO_3. The dynamic dissociation of Ag–C bond would generate free NHC species **B**, and silver–olefin interaction would increase the electrophilicity of the double bond. The subsequent [2+1] cycloaddition of the carbene with the double bond might generate the cyclopropane derivative **C**,[6a] which would undergo rapid ring opening to afford the zwitterionic intermediate **D**. Direct Michael addition of NHC towards the double bond giving zwitterionic **D** is also possible.[22] Finally, [1,2]-hydrogen shift form intermediate **E**, which quickly transferred to the final product **F**.

3. Conclusions

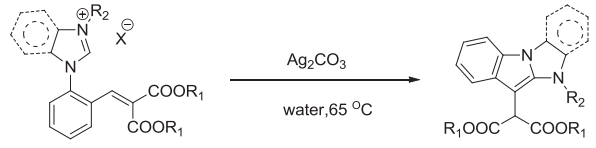
In summary, we have developed a silver-assisted intramolecular cyclization of 2-imidazoliumylcinnamic esters selectively to 1*H*-imidazo[1,2-*a*]indole derivatives in good to excellent yields. The reaction was performed in water and the starting materials are easily available. So far the synthesis and uses of imidazo[1,2-*a*]indoles has remained undeveloped.[23] The present reaction offers a reliable synthetic approach of the fused heterocyclic compounds (Scheme 3).

4. Experimental section

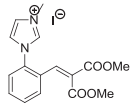
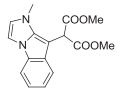
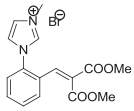
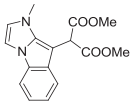
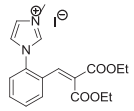
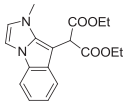
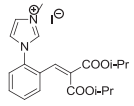
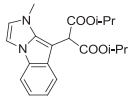
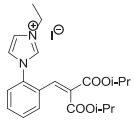
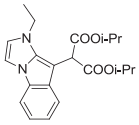
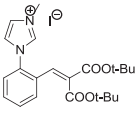
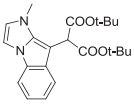
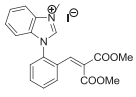
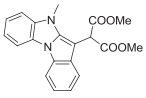
4.1. General

The materials and solvents were purchased from commercial suppliers and used without additional purification. NMR spectra were recorded on a Bruke Avance operating at for ^1H NMR at 400 MHz, and ^{13}C NMR at 100 MHz. Chemical shifts were given relative to $CDCl_3$ (7.26 ppm for ^1H NMR, 77.0 ppm for ^{13}C NMR) and DMSO-d_6 (2.50 ppm for ^1H NMR, 39.5 ppm for ^{13}C NMR). Mass spectrometry data of the products were collected on an HRMS-TOF instrument or a low-resolution MS instrument using

Table 2
The scope of the reaction[a]



2 3

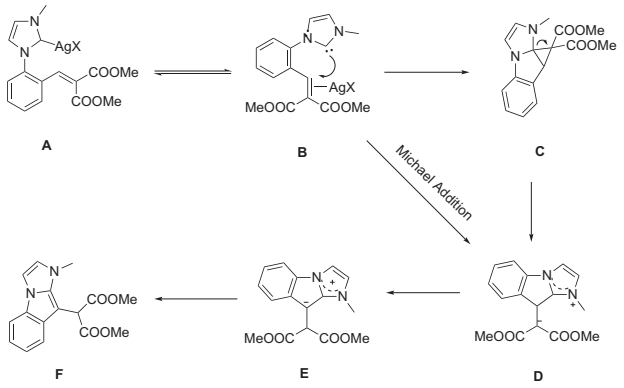
Entry	Reactant	Product	Yield[b] (%)
1	 2a	 3a	78
2	 2b	 3a	66
3	 2c	 3c	74
4	 2d	 3d	91
5	 2e	 3e	81
6	 2f	 3f	63
7	 2g	 3g	68

[a] All reactions were carried out with **2** (0.5 mmol), Ag_2CO_3 (0.5 equiv) in water (2.5 mL) at 65 °C for 18 h under nitrogen.
[b] Yield of isolated product after flash column chromatography.

EI (Agilent 5975) or ESI (Bruker Esquire 3000^{plus}) ionization. Infrared spectra were recorded on a Bruker ATR-FTIR spectrometer. Melting points were measured with a WRS-1A digital point apparatus.

4.2. General procedure for synthesis of 2a–h

Alkyl halide (5.0 equiv) was added to a solution of substituted imidazole or benzoimidazole (3.0 mmol) in toluene (10 mL). The mixture was stirred at 80 °C overnight. Then the solvent was removed in vacuo and recrystallized by diethylether to afford the final imidazolium or benzoimidazolium salts.



Scheme 3. A proposed mechanism.

*4.2.1. 1-(2-(3-Methoxy-2-(methoxycarbonyl)-3-oxoprop-1-en-1-yl) phenyl)-3-methyl-1H-imidazol-3-ium iodide (**2a**).* ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.53 (s, 1H), 7.98 (s, 1H), 7.93 (s, 1H), 7.73 (d, J=8.8 Hz, 3H), 7.65 (s, 1H), 7.51 (d, J=6.8 Hz, 1H), 3.97 (s, 3H), 3.76 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ 165.0, 163.0, 138.1, 137.7, 133.5, 131.7, 131.0, 129.8, 128.9, 128.8, 127.0, 124.2, 123.6, 53.0, 52.8, 36.2; ESI-MS: m/z=300.9 (positive ion, MeOH), m/z=127.2 (negative ion, MeOH); IR (neat): 3092, 3018, 2957, 1715, 1361, 1260, 1236, 1066 cm^{-1}.

*4.2.2. 1-(2-(3-Methoxy-2-(methoxycarbonyl)-3-oxoprop-1-en-1-yl) phenyl)-3-methyl-1H-imidazol-3-ium bromide (**2b**).* ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.58 (s, 1H), 8.00 (s, 1H), 7.93 (s, 1H), 7.70–7.75 (m, 3H), 7.65 (s, 1H), 7.51 (d, J=6.8 Hz, 1H), 3.98 (s, 3H), 3.77 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.1, 163.1, 138.1, 137.8, 133.6, 131.7, 131.0, 129.8, 129.0, 128.8, 127.0, 124.2, 123.7, 53.0, 52.8, 36.2; ESI-MS: m/z=300.9 (positive ion, MeOH), m/z=81.3 (negative ion, MeOH); IR (neat): 3095, 2891, 1718, 1443, 1363, 1263, 1237, 1070 cm^{-1}.

*4.2.3. 1-(2-(3-Ethoxy-2-(ethoxycarbonyl)-3-oxoprop-1-en-1-yl)phenyl)-3-methyl-1H-imidazol-3-ium iodide (**2c**).* ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.54 (s, 1H), 7.95 (d, J=10.8 Hz, 1H), 7.67–7.80 (m, 3H), 7.63 (s, 1H), 7.54 (d, J=6.8 Hz, 1H), 4.13–4.27 (m, 4H), 3.98 (s, 3H), 1.22 (t, J=6.8 Hz, 3H), 1.09 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.5, 162.6, 138.1, 137.3, 133.5, 131.6, 130.9, 130.6, 129.1, 129.0, 126.9, 124.2, 123.7, 61.8, 61.6, 36.2, 13.9, 13.6; ESI-MS: m/z=329.0 (positive ion, MeOH), m/z=127.1 (negative ion, MeOH); IR (neat): 3080, 2980, 1721, 1256, 1219, 1072, 1016 cm^{-1}.

*4.2.4. 1-(2-(3-Isopropoxy-2-(isopropoxycarbonyl)-3-oxoprop-1-en-1-yl)phenyl)-3-methyl-1H-imidazol-3-ium iodide (**2d**).* ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.50 (s, 1H), 7.94 (d, J=11.2 Hz, 2H), 7.68–7.77 (m, 3H), 7.52–7.59 (m, 2H), 4.96–5.08 (m, 2H), 3.97 (s, 3H), 1.23 (d, J=5.6 Hz, 6H), 1.16 (d, J=6.0 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.2, 162.1, 138.1, 136.3, 133.6, 131.6, 131.3, 130.9, 129.1, 129.0, 127.0, 124.2, 123.7, 69.6, 69.5, 36.2, 21.4, 21.1; ESI-MS: m/z=357.0 (positive ion, MeOH), m/z=127.2 (negative ion, MeOH); IR (neat): 3064, 2982, 1734, 1718, 1274, 1262, 1210, 1101, 1061 cm^{-1}.

*4.2.5. 3-Ethyl-1-(2-(3-isopropoxy-2-(isopropoxycarbonyl)-3-oxoprop-1-en-1-yl)phenyl)-1H-imidazol-3-ium iodide (**2e**).* ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.60 (s, 1H), 8.10 (d, J=1.2 Hz, 1H), 7.95 (d, J=1.6 Hz, 1H), 7.68–7.81 (m, 3H), 7.52–7.59 (m, 2H), 4.96–5.07 (m, 2H), 4.33 (q, J=7.2 Hz, 2H), 1.51 (t, J=7.2 Hz, 3H), 1.22 (d, J=5.2 Hz, 6H), 1.15 (d, J=5.2 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.1, 162.1, 137.3, 136.4, 133.6, 131.6, 131.1, 130.9, 129.0, 129.0, 127.0, 123.9,

122.8, 69.5, 69.4, 44.8, 21.4, 21.1, 15.0; ESI-MS: *m*/*z*=359.0 (positive ion, MeOH), *m*/*z*=127.1 (negative ion, MeOH); IR (neat): 2987, 2901, 1707, 1375, 1241, 1106, 1071 cm^{-1}.

*4.2.6. 1-(2-(3-(tert-Butoxy)-2-(tert-butoxycarbonyl)-3-oxoprop-1-en-1-yl)phenyl)-3-methyl-1H-imidazol-3-ium iodide (**2f**).* ^1H NMR (400 MHz, DMSO-d_6): δ 9.54 (s, 1H), 7.99 (s, 1H), 7.88 (s, 1H), 7.69–7.76 (m, 3H), 7.58–7.64 (m, 1H), 7.40 (s, 1H), 3.98 (s, 3H), 1.45 (s, 9H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.9, 161.8, 138.0, 134.7, 133.5, 133.3, 131.4, 130.8, 129.3, 129.2, 127.0, 124.2, 123.5, 82.8, 82.4, 36.3, 27.6, 27.4; ESI-MS: *m*/*z*=385.0 (positive ion, MeOH), *m*/*z*=127.0 (negative ion, MeOH); IR (neat): 2987, 2901, 1704, 1394, 1249, 1067 cm^{-1}.

*4.2.7. 1-(2-(3-Methoxy-2-(methoxycarbonyl)-3-oxoprop-1-en-1-yl) phenyl)-3-methyl-1H-benzo[d]imidazol-3-ium iodide (**2g**).* ^1H NMR (400 MHz, DMSO-d_6): δ 10.06 (s, 1H), 8.17 (d, *J*=8.0 Hz, 1H), 7.75–7.87 (m, 4H), 7.65–7.73 (m, 1H), 7.57–7.64 (m, 2H), 7.46 (d, *J*=8.4 Hz, 1H), 4.21 (s, 3H), 3.76 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.3, 163.0, 144.3, 138.4, 132.1, 131.7, 131.6, 131.5, 130.3, 129.6, 129.3, 128.4, 127.3, 126.9, 114.1, 113.0, 52.9, 52.9, 33.6; ESI-MS: *m*/*z*=351.0 (positive ion, MeOH), *m*/*z*=127.0 (negative ion, MeOH); IR (neat): 2987, 2901, 1719, 1406, 1394, 1241, 1067 cm^{-1}.

4.3. General procedure for synthesis of 2ac

To the saturated solution of ammonium hexafluorophosphate (5.0 equiv), imidazolium or imidazolium halide dissolved in water was added slowly, the white precipitate was produced immediately. The product was filtrated and dried.

2ac: ^1H NMR (400 MHz, DMSO-d_6): δ 9.50 (s, 1H), 7.94 (s, 2H), 7.69–7.76 (m, 3H), 7.64 (s, 1H), 7.50–7.53 (m, 1H), 3.97 (s, 3H), 3.77 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.1, 163.1, 138.1, 137.7, 133.6, 131.7, 131.0, 129.9, 129.0, 128.8, 127.0, 124.2, 123.7, 53.0, 52.8, 36.1; ESI-MS: *m*/*z*=300.9 (positive ion, CH_3CN), *m*/*z*=144.8 (negative ion, CH_3CN); IR (neat): 2987, 2901, 1406, 1394, 1250, 1229, 1066, 1056 cm^{-1}.

4.4. General procedure for synthesis of 2ad

To the saturated solution of sodium fluoroborate (5.0 equiv), imidazolium or benzoimidazolium salt dissolved in water was added slowly, the white precipitate was produced immediately. The pure product was obtained after filtration and drying.

2ad: ^1H NMR (400 MHz, DMSO-d_6): δ 9.48 (s, 1H), 7.93 (s, 2H), 7.71–7.76 (m, 3H), 7.64 (s, 1H), 7.62 (d, *J*=7.2 Hz, 1H), 3.96 (s, 3H), 3.77 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.1, 163.1, 138.1, 137.7, 133.6, 131.8, 131.0, 130.0, 129.0, 128.9, 127.0, 124.2, 123.8, 53.0, 52.8, 36.2; ESI-MS: *m*/*z*=300.9 (positive ion, CH_3CN), *m*/*z*=87.2 (negative ion, CH_3CN), IR (thin film): 2987, 2901, 1706, 1406, 1193, 1051 cm^{-1}.

4.5. General procedure for synthesis of 3a–g

Silver carbonate (0.5 equiv) was added to the solution of **2** (0.5 mmol) in water (2.5 mL) at 65 °C under nitrogen in the Schlenk tube. The mixture was stirred for 18 h. After the completion of the reaction detected by TLC, it was extracted by ethyl acetate. The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The product was purified by column chromatography.

*4.5.1. Dimethyl 2-(1-methyl-1H-imidazo[1,2-a]indol-9-yl)malonate (**3a**).* Green solid, mp=111–116 °C, yield: 78%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J*=8.0 Hz, 1H), 7.52 (d, *J*=8.0 Hz, 1H), 7.19–7.29 (m, 2H), 7.02 (t, *J*=8.0 Hz, 1H), 6.64 (s, 1H), 5.19 (s, 1H), 3.78 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 140.9, 132.0, 123.5, 121.9, 120.9, 116.6, 116.0, 109.8, 104.7, 73.7, 52.7, 47.9, 34.5; IR (neat): 2987, 2901, 1727, 1250, 1066, 1056 cm^{-1}; MS (EI): *m*/*z* (%): 300 (M^+, 20), 241 (100), 181 (50); HRMS (EI-TOF) calcd for $C_{16}H_{16}N_2O_4$ (M^+): 300.1110, found: 300.1110.

*4.5.2. Diethyl 2-(1-methyl-1H-imidazo[1,2-a]indol-9-yl)malonate (**3c**).* Green solid, mp=135–138 °C, yield: 74%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J*=8.4 Hz, 1H), 7.49 (d, *J*=8.0 Hz, 1H), 7.15–7.26 (m, 2H), 6.98 (t, *J*=7.6 Hz, 1H), 6.60 (d, *J*=2.0 Hz, 1H), 5.11 (s, 1H), 4.13–4.29 (m, 4H), 3.75 (s, 3H), 1.26 (t, *J*=7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 140.9, 132.1, 123.6, 121.9, 120.8, 116.9, 115.9, 109.7, 104.7, 74.0, 61.6, 48.4, 34.6, 14.1; IR (neat): 2987, 2901, 1741, 1714, 1255, 1057, 1028 cm^{-1}; MS (EI): *m*/*z* (%): 328 (M^+, 29), 255 (100), 227 (55), 181 (38); HRMS (EI-TOF) calcd for $C_{18}H_{20}N_2O_4$ (M^+): 328.1423, found: 328.1425.

*4.5.3. Diisopropyl 2-(1-methyl-1H-imidazo[1,2-a]indol-9-yl)malonate (**3d**).* Green solid, mp=120–125 °C, yield: 91%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J*=8.0 Hz, 1H), 7.47 (d, *J*=8.4 Hz, 1H), 7.12–7.26 (m, 2H), 6.97 (t, *J*=7.6 Hz, 1H), 6.60 (d, *J*=2.0 Hz, 1H), 4.99–5.11 (m, 3H), 3.75 (s, 3H), 1.18–1.30 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 141.0, 132.2, 123.6, 121.9, 120.6, 117.2, 115.8, 109.6, 104.7, 74.1, 69.1, 49.0, 34.7, 21.6; IR (neat): 2986, 2924, 1723, 1568, 1096 cm^{-1}; MS (EI): *m*/*z* (%): 356 (M^+, 23), 269 (63), 227 (100), 181 (39), 149 (22); HRMS (EI-TOF) calcd for $C_{20}H_{24}N_2O_4$ (M^+): 356.1736, found: 356.1739.

*4.5.4. Diisopropyl 2-(1-ethyl-1H-imidazo[1,2-a]indol-9-yl)malonate (**3e**).* Brown oil, yield: 81%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J*=8.0 Hz, 1H), 7.48 (d, *J*=8.0 Hz, 1H), 7.13–7.26 (m, 2H), 6.97 (t, *J*=7.6 Hz, 1H), 6.67 (s, 1H), 5.00–5.13 (m, 2H), 5.00 (s, 1H), 4.10 (q, *J*=7.2 Hz, 2H), 1.44 (t, *J*=7.2 Hz, 3H), 1.15–1.35 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 140.2, 131.9, 123.8, 120.6, 119.3, 118.2, 115.8, 109.5, 105.0, 73.9, 69.0, 49.2, 42.0, 21.7, 21.6, 15.1; IR (neat): 2979, 1720, 1574, 1098 cm^{-1}; MS (EI): *m*/*z* (%): 370 (M^+, 37), 283 (81), 241 (100), 195 (42); HRMS (EI-TOF) calcd for $C_{21}H_{26}N_2O_4$ (M^+): 370.1893, found: 370.1888.

*4.5.5. Di-tert-butyl 2-(1-methyl-1H-imidazo[1,2-a]indol-9-yl)malonate (**3f**).* Green solid, mp=107–109 °C, yield: 63%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J*=8.0 Hz, 1H), 7.49 (d, *J*=7.6 Hz, 1H), 7.23 (d, *J*=0.8 Hz, 1H), 7.18 (t, *J*=8.0 Hz, 1H), 6.98 (t, *J*=7.6 Hz, 1H), 6.63 (s, 1H), 4.96 (s, 1H), 3.79 (s, 3H), 1.49 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 132.3, 129.8, 128.1, 121.9, 120.5, 117.6, 115.7, 115.5, 109.5, 104.6, 81.5, 50.7, 34.8, 29.7, 28.0, 27.7; IR (neat): 2974, 2923, 1738, 1720, 1126, 1066 cm^{-1}; MS (EI): *m*/*z* (%): 384 (M^+, 81), 283 (28), 227 (100), 183 (72); HRMS (EI-TOF) calcd for $C_{22}H_{28}N_2O_4$ (M^+): 384.2049, found: 384.2048.

*4.5.6. Dimethyl 2-(10-methyl-10H-benzo[4,5]imidazo[1,2-a]indol-11-yl)malonate (**3g**).* Green solid, mp=124–126 °C, yield: 68%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J*=8.0 Hz, 1H), 7.65 (d, *J*=8.0 Hz, 1H), 7.53 (d, *J*=8.0 Hz, 1H), 7.03–7.22 (m, 5H), 5.13 (s, 1H), 3.74 (s, 3H), 3.70 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 142.6, 138.3, 132.5, 127.1, 125.8, 122.3, 121.3, 120.1, 118.4, 117.2, 110.3, 109.9, 107.9, 76.4, 52.8, 47.8, 31.0; IR (neat): 2987, 2901, 1731, 1255, 1066, 1055 cm^{-1}; MS (EI): *m*/*z* (%): 350 (M^+, 63), 291 (100), 233 (42); HRMS (EI-TOF) calcd for $C_{20}H_{18}N_2O_4$ (M^+): 350.1267, found: 350.1272.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.02.031.

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