JOC The Journal of Organic Chemistry

Article

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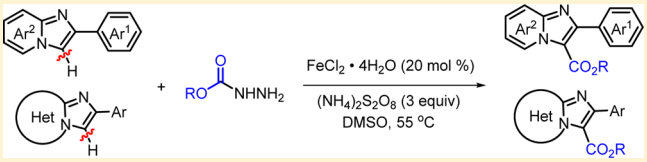
Iron-Catalyzed Regioselective Alkoxycarbonylation of Imidazoheterocycles with Carbazates

Yongyuan Gao, Weiye Lu, Ping Liu,* and Peipei Sun*

College of Chemistry and Materials Science, Jiangsu Provincial Key Laboratory of Material Cycle Processes and Pollution Control, Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, Nanjing Normal University, Nanjing 210023, China

Supporting Information

ABSTRACT: A regioselective alkoxycarbonylation of imidazoheterocycles using carbazates as ester group sources in DMSO was developed, in which an inexpensive $FeCl_2·4H_2O$ was used as the catalyst and $(NH_4)_2S_2O_8$ was the oxidant. The reaction proceeded smoothly under an air atmosphere to give the 3-alkoxycarbonylated products in moderate to good yields.



INTRODUCTION

The ester group is a versatile and important building block in natural products as well as in organic synthesis, since it can be converted into diverse functional groups such as hydroxymethyl, carbonyl, amide, etc. For the synthesis of esters, besides the traditional esterification of carboxylic acids and alcohols, the direct introduction of an ester group to organic molecules doubtlessly represents a very important strategy. The incorporation of CO and alcohols provided a reliable approach for the alkoxycarbonylation of alkyl or aryl halides.[1] Palladium-catalyzed alkoxycarbonylation of alkenes and alkynes using CO and alcohols as the sources of ester groups has also become an important synthetic protocol for the synthesis of esters.[2] Even so, new strategies for alkoxycarbonylation without toxic gas and a noble metal are always desired. In the past few years, elegant advances have been made in the development of using carbazates as the precursors of alkoxycarbonyl radicals. In 2010, Taniguchi and co-workers developed an iron-catalyzed oxidative addition of an alkoxycarbonyl radical to alkenes using methyl carbazate as the radical source.[3] Alkoxycarbonylation of terminal alkenes or *N*-vinylacetamides had also been well developed by Tian, Loh, and Li.[4] Du and Yu independently reported the alkoxycarbonylation/cyclization reaction of *N*-aryl acrylamides with carbazates.[5] Recently, the convenient syntheses of phenanthridine-6-carboxylates via a radical alkoxycarbonylation of 2-isocyanobiphenyls and carbazates were investigated by several groups.[6]

On the other hand, the structural modification of imidazo[1,2-*a*]pyridine is synthetically attractive since this structural motif exists in many pharmaceuticals, such as Zolpidem, Alpidem, Saripidem, Zolimidine, etc. (Figure 1). In 2006, Sames reported a palladium-catalyzed regioselective 3-position arylation of the imidazo[1,2-*a*]pyridine with aryl halides.[7] Recent advances of the 3-position functionalization of the imidazo[1,2-*a*]pyridine scaffolds are proposed to occur via three main manners: (i) a carbometalation process followed by coupling reactions,[7,8] (ii) direct electrophilic attack on the 3-position,[9] or (iii) a radical pathway.[10] Very recently, we have successfully developed an efficient method for the regioselective monofluorination of imidazo[1,2-*a*]pyridine with Selectfluor under aqueous conditions.[9h] As a continuous study by our group on the selective direct C−H bond functionalization of an electron-rich aryl ring or heterocyclic compounds,[9h,11] we herein report a highly regioselective alkoxycarbonylation of imidazopyridines and some other imidazoheterocycles by using carbazates as the source of an ester group and $FeCl_2·4H_2O$ as the catalyst.

RESULTS AND DISCUSSION

We began our investigation by using 2-phenylimidazo[1,2-*a*]pyridine (**1a**) and methyl carbazate (**2a**) as model substrates (Table 1). TBAI (tetrabutylammonium iodide) was tested as the catalyst considering its low cost and low toxicity, and TBHP (*tert*-butyl hydroperoxide) was used as the oxidant. We were delighted to find that, after the reaction proceeded in DMSO at 80 °C under an air atmosphere for 6 h, the desired alkoxycarbonylation product methyl 2-phenylimidazo[1,2-*a*]-pyridine-3-carboxylate (**3a**) was obtained in 44% yield. However, a byproduct 3-*tert*-butoxy-2-phenyl imidazo[1,2-*a*]pyridine was also isolated in 21% yield (entry 1). Other oxidants such as BPO (benzoyl peroxide), $K_2S_2O_8$, and $(NH_4)_2S_2O_8$ were tested, among which $(NH_4)_2S_2O_8$ gave the best result, but BPO showed no activity for this transformation (entries 2−4). Without the catalyst, the reaction could not take place at all (entry 5). In order to further improve the catalytic efficiency, several iron and copper catalysts including $Fe(acac)_2$, $FeCl_3$, FePc (iron phthalocyanine), $FeCl_2·4H_2O$, and $Cu(OTf)_2$ were examined. When $FeCl_2·4H_2O$ (20 mol %) was used, the highest yield of 82% was obtained (entries 6−10); reducing the catalyst loading to 10 mol % led to a lower yield of 70% (entry 11). The reaction proceeded efficiently in DMSO. Other solvents such as DMF, MeCN, 1,4-dioxane, and DCE, however, significantly decreased the yields (entries 12−15). By

Received: January 8, 2016
Published: February 26, 2016

DOI: 10.1021/acs.joc.6b00046
J. Org. Chem. 2016, 81, 2482−2487

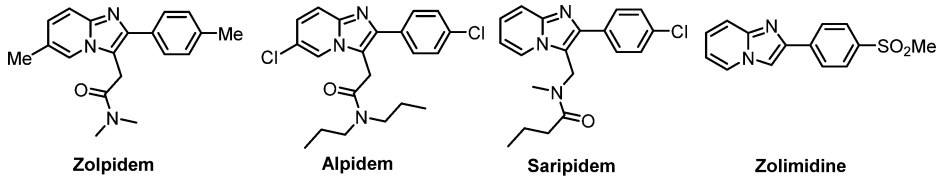
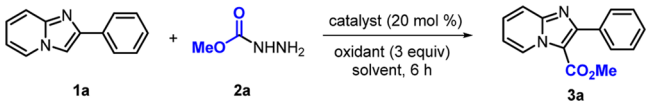


Figure 1. Some pharmaceuticals in imidazo[1,2-*a*]pyridine family.

Table 1. Optimization of Reaction Conditions[a]



1a 2a 3a

entry	catalyst	oxidant	solvent	temp (°C)	yield (%)
1	TBAI	TBHP	DMSO	80	44 (21)[b]
2	TBAI	BPO	DMSO	80	n.r.
3	TBAI	$K_2S_2O_8$	DMSO	80	48
4	TBAI	$(NH_4)_2S_2O_8$	DMSO	80	51
5	–	$(NH_4)_2S_2O_8$	DMSO	80	0
6	$Fe(acac)_2$	$(NH_4)_2S_2O_8$	DMSO	80	74
7	$FeCl_3$	$(NH_4)_2S_2O_8$	DMSO	80	53
8	FePc	$(NH_4)_2S_2O_8$	DMSO	80	68
9	$FeCl_2{\cdot}4H_2O$	$(NH_4)_2S_2O_8$	DMSO	80	82
10	$Cu(OTf)_2$	$(NH_4)_2S_2O_8$	DMSO	80	0
11[c]	$FeCl_2{\cdot}4H_2O$	$(NH_4)_2S_2O_8$	DMSO	80	70
12	$FeCl_2{\cdot}4H_2O$	$(NH_4)_2S_2O_8$	DMF	80	45
13	$FeCl_2{\cdot}4H_2O$	$(NH_4)_2S_2O_8$	MeCN	80	15
14	$FeCl_2{\cdot}4H_2O$	$(NH_4)_2S_2O_8$	1,4-dioxane	80	35
15	$FeCl_2{\cdot}4H_2O$	$(NH_4)_2S_2O_8$	DCE	80	60
16	$FeCl_2{\cdot}4H_2O$	$(NH_4)_2S_2O_8$	DMSO	55	83
17	$FeCl_2{\cdot}4H_2O$	$(NH_4)_2S_2O_8$	DMSO	rt	62
18[d]	$FeCl_2{\cdot}4H_2O$	$(NH_4)_2S_2O_8$	DMSO	55	68
19[e]	$FeCl_2{\cdot}4H_2O$	$(NH_4)_2S_2O_8$	DMSO	55	81

[a]Unless otherwise specified, the reactions were carried out in the presence of **1a** (0.2 mmol), **2a** (0.4 mmol), catalyst (20 mol %), oxidant (0.6 mmol), and solvent (2 mL) under an air atmosphere for 6 h. [b]The yield of 3-*tert*-butoxy-2-phenyl imidazo[1,2-*a*]pyridine in parentheses. [c]10 mol % catalyst was used. [d]In the presence of 0.4 mmol of $(NH_4)_2S_2O_8$. [e]Under an Ar atmosphere.

lowering the reaction temperature to 55 °C, the yield had no obvious change (entry 16), but at room temperature, a lower yield of 62% was obtained (entry 17). The appropriate amount of the oxidant was 3 equiv. Reducing it to 2 equiv led to a decrease in the yield to 68% (entry 18). In addition, the result had no obvious difference if the reaction was performed in an Ar atmosphere (entry 19).

With the optimized reaction conditions in hand, we evaluated the scope and limitations of this transformation. Gratifyingly, a wide range of substituted 2-arylimidazo[1,2-*a*]pyridines can be used in the reaction to give the desired 3-alkoxycarbonylation products (Table 2). The electronic effect of the substituent groups on the benzene ring had a slight influence on the reaction, and good yields could be obtained in the presence of either the electron-donating groups, such as methyl and methoxyl, or the electron-withdrawing groups, such as halogen, nitro, and mesyl (**3b**–**3h**). Moreover, the reaction of a heterocycle substituted reactant 2-thienylimidazo[1,2-*a*]pyridine with methyl carbazate also proceeded smoothly and gave a 3-carbomethoxy product (**3i**) in 92% yield. We then examined the effect of the substituents on the pyridine ring. The results revealed that when methyl, as well as halogen, was substituted on the pyridine ring, the reaction took place normally and gave moderate to good yields (**3j**–**3m**). Similar results could also be obtained from the multisubstituted reactants (**3n**–**3q**). In line with our expectation, when ethyl carbazate was employed as the ester group source, the ethoxycarbonylation also proceeded well to afford ethyl 2-phenylimidazo[1,2-*a*]pyridine-3-carboxylate (**3r**) in 78% yield. For *tert*-butyl carbazate, however, only trace *tert*-butoxycarbonylation product (**3s**) was observed.

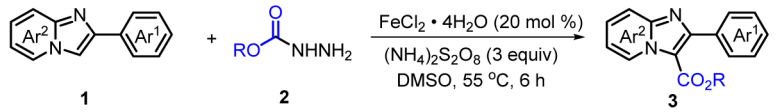
Unfortunately, the 2-alkyl substituted substrates 2-methyl or 2-isobutylimidazo[1,2-*a*]pyridines seemed inactive to the alkoxycarbonylation process (Scheme 1), which is consistent with the trifluoromethylation of imidazoheterocycles reported by Hajra et al.[10b] To our delight, an alkoxycarbonylation product **3v** was obtained in 57% yield when an electron-withdrawing group, ethoxycarbonyl, was substituted on the 2-position of imidazo[1,2-*a*]pyridine, which provided the possibility of diverse transformation since two ester groups were linked on one imidazo ring of the product.

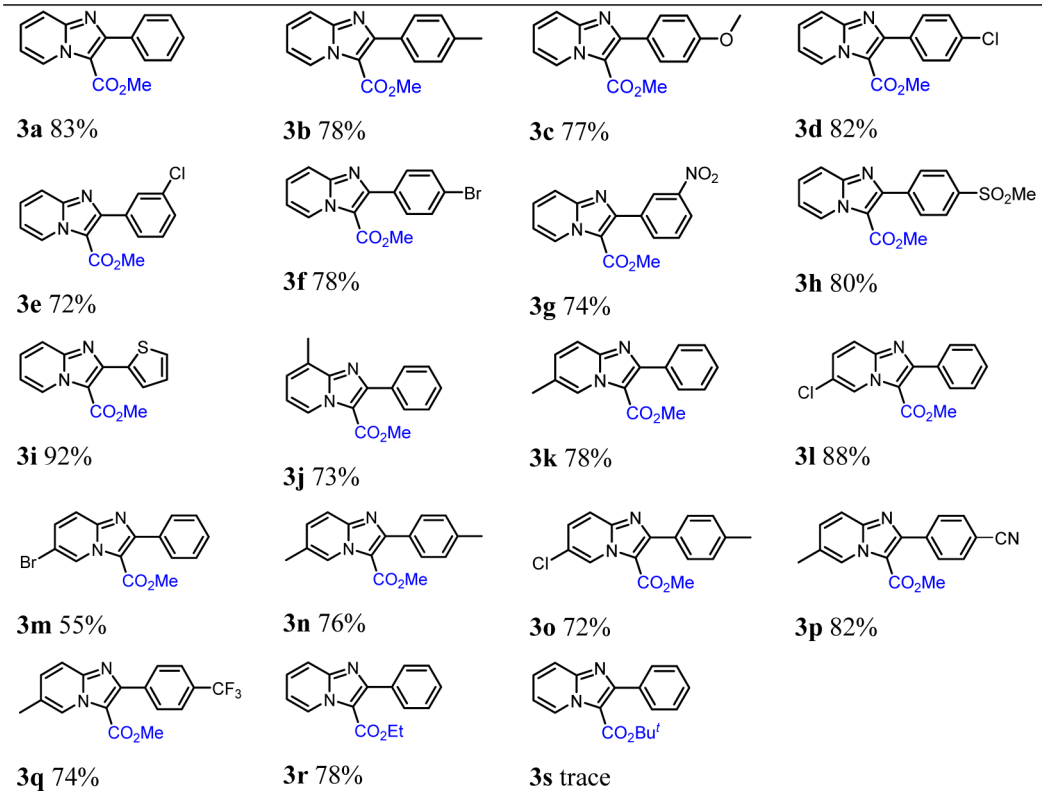
Subsequently, to extend the scope of the alkoxycarbonylation reaction, our attention turned to identifying other imidazoheterocycles such as imidazo[1,2-*a*]pyrimidine, benzo[*d*]imidazo[2,1-*b*]thiazole, and imidazo[2,1-*b*]thiazole derivatives (Scheme 2). The selective 3-position alkoxycarbonylation of 2-phenylimidazo[1,2-*a*]pyrimidine (**4a**) was particularly noteworthy. An alkoxycarbonylation similarly took place on the 3-position of 2-phenylbenzo[*d*]imidazo[2,1-*b*]thiazole. The reactions of 2-arylbenzo[*d*]imidazo[2,1-*b*]thiazoles with various substituents, such as methyl, methoxyl, and chloro, on the benzene ring were then studied. From these reactants, the corresponding alkoxycarbonylation products were obtained in good yields (**7a**–**7d**). However, the reaction of 6-phenylimidazo[2,1-*b*]thiazole only gave a lower yield of 32% (**7e**) and the substrate was recovered in 55% yield.

To understand the mechanism of the reaction, some control experiments were performed (Scheme 3). Notably, the addition of a radical inhibitor TEMPO (2 equiv) to the alkoxycarbonylation reaction resulted in no conversion of 2-phenylimidazo[1,2-*a*]pyridine (**1a**). This result suggested that the above-mentioned reaction referred to a radical pathway (eq 1). Although the particular regioselectivity in the electrophilic fluorinating process of imidazo[1,2-*a*]pyridines was proven,[9h] we were still curious about whether the same result would appear in the radical alkoxycarbonylation. From imidazo[1,2-*a*]pyridine (**8a**), only C3-substituted product methyl imidazo[1,2-*a*]pyridine-3-carboxylate (**9a**) was obtained under the standard reaction conditions (eq 2). Also, from 3-phenylimidazo[1,2-*a*]pyridine (**10a**), we failed to obtain C2 selective product **11a** (eq 3). In addition, it should be pointed out that, under an Ar atmosphere, there was no obvious decrease in the yield (Table 1, entry 19), which indicated that the oxygen might not be involved in the iron catalytic cycle.

DOI: 10.1021/acs.joc.6b00046
J. Org. Chem. 2016, 81, 2482–2487

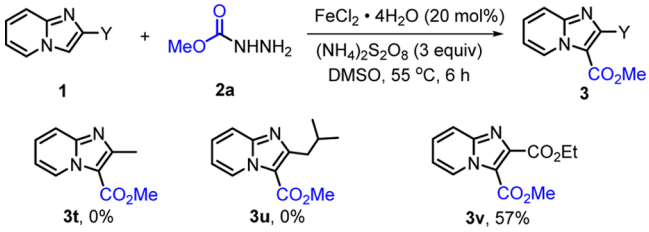
Table 2. Alkoxycarbonylation of 2-Arylimidazo[1,2-*a*]pyridines[a]



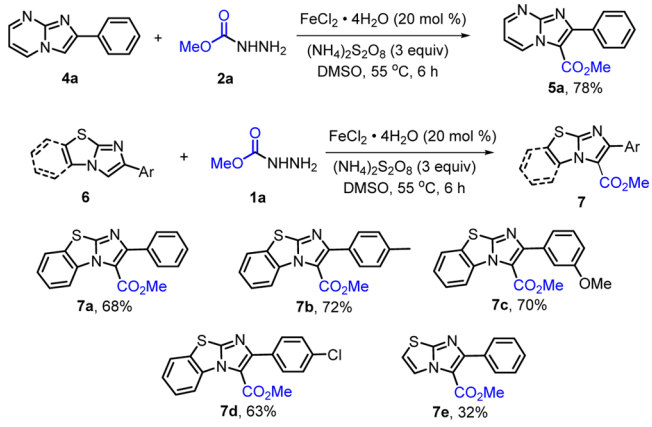


[a]Reaction conditions: **1** (0.20 mmol), **2** (0.40 mmol), $(NH_4)_2S_2O_8$ (0.60 mmol), and $FeCl_2{\cdot}4H_2O$ (20 mol %) in DMSO (2 mL) were stirred at 55 °C for 6 h.

Scheme 1. Alkoxycarbonylation of Alkyl or Ethoxycarbonyl Substituted Imidazo[1,2-*a*]pyridines



Scheme 2. Regioselective Alkoxycarbonylation of Imidazoheterocycles



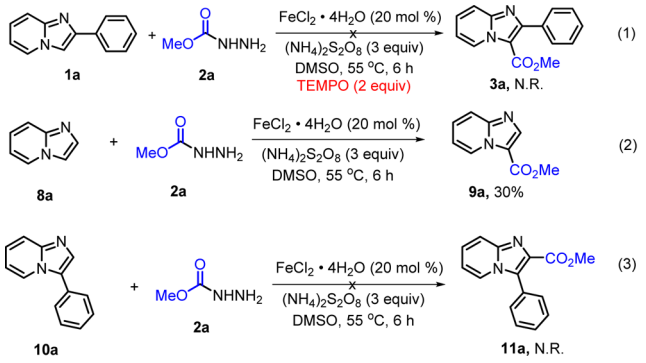
Based on the above-mentioned results and the related reports,[10] a possible reaction mechanism for the alkoxycarbonylation is illustrated in Scheme 4. Initially, in the presence of Fe(II) and $S_2O_8^{2-}$, a cation radical **A** was generated by the single-electron transfer between methyl carbazate (**2a**) and an Fe(III) species; the subsequent deprotonation of **A** yielded the radical intermediate **B**. The sequential single-electron transfer and deprotonation, followed by the release of molecular nitrogen, formed alkoxycarbonyl radical **E**.[3,6c] The addition of **E** to imidazo[1,2-*a*]pyridine (**1a**) generated another radical intermediate **F**, which was oxidized by $S_2O_8^{2-}$ to form the unstable carbocation intermediate **G**.[10d,f] Finally, deprotonation took place to afford the alkoxycarbonylation product **3a**.

CONCLUSIONS

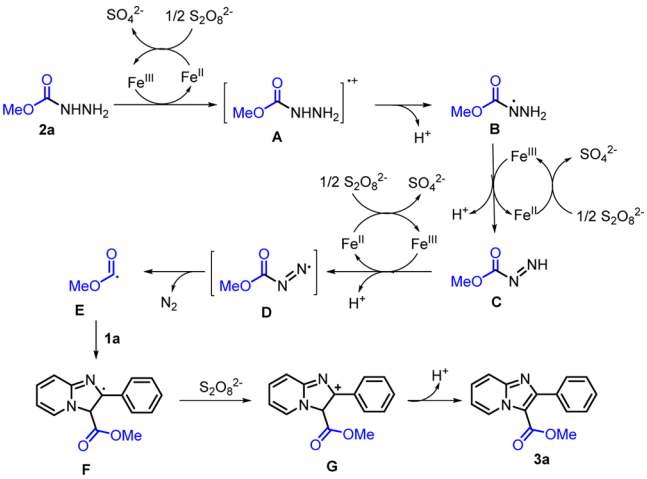
In summary, we have described a regioselective alkoxycarbonyl reaction of imidazo[1,2-*a*]pyridines. In this process carbazates served as ester group sources. Both electron-donating and -withdrawing groups at different positions of imidazo[1,2-*a*]pyridines are tolerated in the reaction, and other imidazoheterocycles such as imidazo[1,2-*a*]pyrimidine, benzo[*d*]-

DOI: 10.1021/acs.joc.6b00046
J. Org. Chem. 2016, 81, 2482−2487

Scheme 3. Control Experiments



Scheme 4. Plausible Mechanism for Alkoxycarbonylation of Imidazo[1,2-*a*]pyridines



imidazo[2,1-*b*]thiazole, and imidazo[2,1-*b*]thiazole are suitable for the transformation. The protocol is distinguished by usage of a cheap catalyst, practicability in ambient air, a broad substrate scope, and high regioselectivity, as well as good yields. The method may gain application in the pharmaceutical synthesis.

EXPERIMENTAL SECTION

General. All reactions were run in a sealed tube with a Teflon lined cap under ambient air. Unless otherwise indicated, all starting materials purchased from commercial suppliers were used without further purification. Imidazo[1,2-*a*]pyridines and imidazoheterocycles were prepared according to the literature procedures.[12] The NMR spectra were recorded at 400 MHz (^{1}H) and 100 MHz (^{13}C{^{1}H} NMR) in $CDCl_3$ or DMSO-d_6 using TMS as an internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, td = triplet of doublet, q = quartet, m = multiplet. Melting points are uncorrected. Q-TOF was used for the HRMS measurements.

General Experimental Procedures for the Alkoxycarbonylation Reaction. A mixture of 2-phenylimidazo[1,2-*a*]-pyridine **1a** (38.8 mg, 0.2 mmol), methyl carbazate (36.0 mg, 0.4 mmol, 2.0 equiv), $(NH_4)_2S_2O_8$ (136.9 mg, 0.6 mmol, 3.0 equiv), and $FeCl_2{\cdot}4H_2O$ (8.0 mg, 0.04 mmol, 20 mol %) in DMSO (2 mL) was stirred at 55 °C under ambient air for 6 h. After cooling to room temperature, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ solution (5 mL) and extracted with DCM (15 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel (300−400 mesh) column chromatography using hexane/EtOAc (3:1, v/v) or hexane/acetone (5:1, v/v) as eluent to afford the desired product **3a**.

*Methyl 2-Phenylimidazo[1,2-a]pyridine-3-carboxylate (**3a**).* Yellow solid (41.9 mg, 83% yield); mp 127−128 °C (lit.[13] 130−131 °C) ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.42 (d, J = 7.0 Hz, 1H), 7.77 (dd, J = 11.4, 5.4 Hz, 3H), 7.51−7.37 (m, 4H), 7.05 (t, J = 6.8 Hz, 1H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.5, 153.6, 147.2, 134.4, 130.1, 128.8, 128.4, 128.1, 127.7, 117.5, 114.2, 111.7, 51.3.

*Methyl 2-(p-Tolyl)imidazo[1,2-a]pyridine-3-carboxylate (**3b**).* Yellow solid (41.5 mg, 78% yield); mp 125−126 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.41 (d, J = 7.0 Hz, 1H), 7.74 (d, J = 8.9 Hz, 1H), 7.68 (d, J = 8.1 Hz, 2H), 7.51−7.40 (m, 1H), 7.32−7.22 (m, 2H), 7.03 (t, J = 6.6 Hz, 1H), 3.83 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.6, 153.7, 147.1, 138.7, 131.3, 130.0, 128.5, 128.4, 128.0, 117.4, 114.1, 111.5, 51.3, 21.5; HRMS-ESI (m/z): calcd for $C_{16}H_{14}N_2O_2Na$ [M + Na]$^+$ 289.0948, found 289.0956.

*Methyl 2-(4-Methoxyphenyl)imidazo[1,2-a]pyridine-3-carboxylate (**3c**).* Yellow solid (43.5 mg, 77% yield); mp 98−99 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.39 (d, J = 7.0 Hz, 1H), 7.75 (ddd, J = 15.0, 7.4, 5.9 Hz, 3H), 7.48−7.36 (m, 1H), 7.07−6.91 (m, 3H), 3.87 (s, 3H), 3.84 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.6, 160.1, 153.5, 147.1, 131.5, 128.4, 128.0, 126.7, 117.3, 114.0, 113.2, 111.3, 55.3, 51.3; HRMS-ESI (m/z): calcd for $C_{16}H_{14}N_2O_3Na$ [M + Na]$^+$ 305.0897, found 305.0895.

*Methyl 2-(4-Chlorophenyl)imidazo[1,2-a]pyridine-3-carboxylate (**3d**).* Yellow solid (47.0 mg, 82% yield); mp 125−126 °C (lit.[14] 130−132 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.40 (dt, J = 7.0, 1.1 Hz, 1H), 7.77−7.68 (m, 3H), 7.49−7.38 (m, 3H), 7.06 (td, J = 6.9, 1.2 Hz, 1H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.3, 152.4, 147.2, 134.9, 132.9, 131.5, 128.4, 128.3, 128.0, 117.5, 114.4, 111.8, 51.4.

*Methyl 2-(3-Chlorophenyl)imidazo[1,2-a]pyridine-3-carboxylate (**3e**).* Yellow solid (41.3 mg, 72% yield); mp 123−124 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.41 (dt, J = 7.0, 1.1 Hz, 1H), 7.78 (d, J = 1.9 Hz, 1H), 7.75 (d, J = 9.0 Hz, 1H), 7.66 (dt, J = 6.8, 1.8 Hz, 1H), 7.50−7.43 (m, 1H), 7.43−7.34 (m, 2H), 7.07 (td, J = 6.9, 1.2 Hz, 1H), 3.84 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.2, 152.0, 147.2, 136.1, 133.6, 130.2, 129.0, 128.8, 128.4, 128.3, 117.6, 114.4, 111.9, 51.4; HRMS-ESI (m/z): calcd for $C_{15}H_{11}ClN_2O_2Na$ [M + Na]$^+$ 309.0401, found 309.0415.

*Methyl 2-(4-Bromophenyl)imidazo[1,2-a]pyridine-3-carboxylate (**3f**).* Yellow solid (51.7 mg, 78% yield); mp 127−128 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.39 (d, J = 7.0 Hz, 1H), 7.73 (d, J = 8.9 Hz, 1H), 7.67−7.64 (m, 2H), 7.61−7.56 (m, 2H), 7.49−7.40 (m, 1H), 7.05 (td, J = 6.9, 1.0 Hz, 1H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.3, 152.4, 147.2, 133.3, 131.7, 130.9, 128.4, 128.3, 123.2, 117.5, 114.4, 111.7, 51.4; HRMS-ESI (m/z): calcd for $C_{15}H_{11}BrN_2O_2Na$ [M + Na]$^+$ 352.9897, found 352.9904.

*Methyl 2-(3-Nitrophenyl)imidazo[1,2-a]pyridine-3-carboxylate (**3g**).* White solid (44.0 mg, 74% yield); mp 136−137 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) 9.34 (dt, J = 7.0, 1.1 Hz, 1H), 8.72−8.60 (m, 1H), 8.34−8.27 (m, 2H), 7.90−7.86 (m, 1H), 7.78 (t, J = 8.0 Hz, 1H), 7.68−7.63 (m, 1H), 7.31 (td, J = 6.9, 1.2 Hz, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz): δ (ppm) 160.8, 150.1, 147.8, 147.0, 137.0, 136.1, 129.8, 129.6, 128.8, 125.0, 123.9, 117.9, 115.7, 112.4, 52.0; HRMS-ESI (m/z): calcd for $C_{15}H_{11}N_3O_4Na$ [M + Na]$^+$ 320.0642, found 320.0646.

*Methyl 2-(4-(Methylsulfonyl)phenyl)imidazo[1,2-a]pyridine-3-carboxylate (**3h**).* Yellow solid (52.9 mg, 80% yield); mp 146−147 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.43 (d, J = 7.0 Hz, 1H), 8.01 (td, J = 8.6, 6.6 Hz, 4H), 7.77 (d, J = 9.0 Hz, 1H), 7.53−7.48 (m, 1H), 7.12 (td, J = 7.0, 1.2 Hz, 1H), 3.85 (s, 3H), 3.11 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.0, 151.3, 147.3, 140.4, 140.1, 131.1, 128.6, 128.5, 126.8, 117.8, 114.8, 112.3, 51.5, 44.6; HRMS-ESI (m/z): calcd for $C_{16}H_{14}N_2O_4SNa$ [M + Na]$^+$ 353.0567, found 353.0580.

*Methyl 2-(Thiophen-2-yl)imidazo[1,2-a]pyridine-3-carboxylate (**3i**).* White solid (47.5 mg, 92% yield); mp 87−88 °C (lit.[15] 75.5−77 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.32 (dt, J = 7.0, 1.0

DOI: 10.1021/acs.joc.6b00046
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Hz, 1H), 8.01 (dd, J = 3.8, 1.1 Hz, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.47 (dd, J = 5.1, 1.1 Hz, 1H), 7.39 (ddd, J = 8.9, 6.9, 1.2 Hz, 1H), 7.14 (dd, J = 5.1, 3.8 Hz, 1H), 6.96 (td, J = 7.0, 1.2 Hz, 1H), 3.98 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.1, 146.9, 146.8, 136.6, 129.8, 128.4, 128.3, 128.3, 127.5, 117.1, 114.0, 110.5, 51.3.

*Methyl 8-Methyl-2-phenylimidazo[1,2-a]pyridine-3-carboxylate (**3j**).* Yellow solid (38.9 mg, 73% yield); mp 97−98 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.26 (d, J = 6.7 Hz, 1H), 7.79−7.71 (m, 2H), 7.47−7.40 (m, 3H), 7.24−7.19 (m, 1H), 6.93 (t, J = 7.0 Hz, 1H), 3.79 (s, 3H), 2.68 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$,100 MHz) δ (ppm) 161.7, 153.2, 147.4, 134.8, 130.1, 128.6, 127.7, 127.5, 126.9, 126.1, 114.1, 112.1,51.2, 17.1; HRMS-ESI (m/z): calcd for $C_{16}H_{14}N_2O_2Na$ $[M + Na]^+$ 289.0948, found 289.0956.

*Methyl 6-Methyl-2-phenylimidazo[1,2-a]pyridine-3-carboxylate (**3k**).* Yellow solid (41.5 mg, 78% yield); mp 95−96 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.22 (s, 1H), 7.77−7.73 (m, 2H), 7.64 (d, J = 9.1 Hz, 1H), 7.47−7.39 (m, 3H), 7.30 (dd, J = 9.1, 1.6 Hz, 1H), 3.81 (s, 3H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.6, 153.4, 146.2, 134.5, 131.0, 130.0, 128.6, 127.7, 126.2, 124.1, 116.7, 111.4, 51.2, 18.5; HRMS-ESI (m/z): calcd for $C_{16}H_{14}N_2O_2Na$ $[M + Na]^+$ 289.0948, found 289.0955.

*Methyl 6-Chloro-2-phenylimidazo[1,2-a]pyridine-3-carboxylate (**3l**).* Yellow solid (50.5 mg, 88% yield); mp 104−105 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.52 (s, 1H), 7.80−7.74 (m, 2H), 7.74−7.69 (m, 1H), 7.49−7.41 (m, 4H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.2, 153.8, 145.3, 133.7, 130.0, 129.5, 129.1, 127.8, 126.4, 122.7, 117.7, 112.1, 51.5; HRMS-ESI (m/z): calcd for $C_{15}H_{11}ClN_2O_2Na$ $[M + Na]^+$ 309.0407, found 309.0415.

*Methyl 6-Bromo-2-phenylimidazo[1,2-a]pyridine-3-carboxylate (**3m**).* Yellow solid (36.4 mg, 55% yield); mp 96−97 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.60 (d, J = 1.4 Hz, 1H), 7.76−7.74 (m, 2H), 7.64 (d, J = 9.4 Hz, 1H), 7.52 (dd, J = 9.4, 1.8 Hz, 1H), 7.48−7.43 (m, 3H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.3, 153.8, 145.5, 133.8, 131.5, 130.0, 129.0, 128.5, 127.8, 118.0, 112.0, 109.1, 51.5; HRMS-ESI (m/z): calcd for $C_{15}H_{11}BrN_2O_2Na$ $[M + Na]^+$ 352.9897, found 352.9903.

*Methyl 6-Methyl-2-(p-tolyl)imidazo[1,2-a]pyridine-3-carboxylate (**3n**).* Yellow solid (42.6 mg, 76% yield); mp 139−140 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.22 (s, 1H), 7.65 (t, J = 7.5 Hz, 3H), 7.34−7.20 (m, 3H), 3.82 (s, 3H), 2.42 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.7, 153.4, 146.1, 138.6, 131.5, 131.0, 129.9, 128.4, 126.3, 124.0, 116.6, 111.3, 51.1, 21.4, 18.5; HRMS-ESI (m/z): calcd for $C_{17}H_{16}N_2O_2Na$ $[M + Na]^+$ 303.1104, found 303.1106.

*Methyl 6-Chloro-2-(p-tolyl)imidazo[1,2-a]pyridine-3-carboxylate (**3o**).* White solid (43.3 mg, 72% yield); mp 122−123 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.50 (d, J = 1.7, 1H), 7.67 (t, J = 9.5, 3H), 7.41 (dd, J = 9.4, 1.9 Hz, 1H), 7.33−7.22 (m, 2H), 3.85 (s, 3H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.3, 154.0, 145.3, 139.1, 130.8, 129.9, 129.4, 128.6, 126.4, 122.5, 117.6, 112.0, 51.5, 21.4; HRMS-ESI (m/z): calcd for $C_{16}H_{13}ClN_2O_2Na$ $[M + Na]^+$ 323.0558, found 323.0566.

*Methyl 2-(4-Cyanophenyl)-6-methylimidazo[1,2-a]pyridine-3-carboxylate (**3p**).* Yellow solid (47.8 mg, 82% yield); mp 162−163 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.24−9.17 (m, 1H), 7.91−7.84 (m, 2H), 7.76−7.70 (m, 2H), 7.69−7.62 (m, 1H), 7.38−7.32 (m, 1H), 3.83 (s, 3H), 2.47−2.42 (m, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.0, 151.1, 146.3, 139.2, 131.6, 131.5, 130.5, 126.3, 124.8, 118.9, 116.9, 112.2, 111.9, 51.4, 18.6; HRMS-ESI (m/z): calcd for $C_{17}H_{13}N_3O_2Na$ $[M + Na]^+$ 314.0900, found 314.0899.

*Methyl 6-Methyl-2-(4-(trifluoromethyl)phenyl)imidazo[1,2-a]-pyridine-3-carboxylate (**3q**).* White solid (49.5 mg, 74% yield); mp 118−119 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.22 (s, 1H), 7.88 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 9.0 Hz, 1H), 7.33 (d, J = 8.6 Hz, 1H), 3.82 (s, 3H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.3, 151.8, 146.3, 138.2, 131.4, 130.6 (q, J = 32.2 Hz), 130.5, 126.3, 124.6 (q, J = 3.4 Hz), 124.3 (q, J = 270.5 Hz), 116.9, 111.84, 51.4, 18.6; HRMS-ESI (m/z): calcd for $C_{17}H_{13}F_3N_2O_2Na$ $[M + Na]^+$ 357.0821, found 357.0835.

*Ethyl 2-Phenylimidazo[1,2-a]pyridine-3-carboxylate (**3r**).* Yellow oil (41.5 mg, 78% yield); (lit.[14] mp 66−67 °C) ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.44 (d, J = 7.0 Hz, 1H), 7.82−7.74 (m, 3H), 7.50−7.41 (m, 4H), 7.06 (td, J = 6.9, 1.1 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.1, 153.6, 147.1, 134.5, 130.2, 128.7, 128.4, 127.9, 127.6, 117.5, 114.1, 112.0, 60.5, 14.0.

*Dimethyl Imidazo[1,2-a]pyridine-2,3-dicarboxylate (**3v**).* Yellow oil (28.3 mg, 57% yield); ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.27 (d, J = 7.0 Hz, 1H), 7.79 (d, J = 9.0 Hz, 1H), 7.53−7.46 (m, 1H), 7.12 (t, J = 6.9 Hz, 1H), 4.50 (q, J = 7.1 Hz, 2H), 3.97 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 163.7, 160.3, 146.5, 143.3, 128.6, 127.9, 118.4, 115.4, 114.1, 62.0, 52.0, 14.2; HRMS-ESI (m/z): calcd for $C_{12}H_{12}N_2O_4Na$ $[M + Na]^+$ 271.0690, found 271.0694.

*Methyl 2-Phenylimidazo[1,2-a]pyrimidine-3-carboxylate (**5a**).* Light green solid (39.5 mg, 78% yield); mp 110−111 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.68 (d, J = 6.3 Hz, 1H), 8.74 (d, J = 2.0 Hz, 1H), 7.86 (dd, J = 6.4, 2.7 Hz, 2H), 7.53−7.37 (m, 3H), 7.12 (dd, J = 6.3, 3.9 Hz, 1H), 3.86 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.2, 155.0, 152.7, 149.8, 136.2, 133.5, 130.3, 129.3, 127.8, 110.4, 110.2, 51.6; HRMS-ESI (m/z): calcd for $C_{14}H_{11}N_3O_2Na$ $[M + Na]^+$ 276.0744, found 276.0745.

*Methyl 2-Phenylbenzo[d]imidazo[2,1-b]thiazole-3-carboxylate (**7a**).* Red solid (41.9 mg, 68% yield); mp 111−112 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.80 (dd, J = 8.4, 0.6 Hz, 1H), 7.75−7.68 (m, 3H), 7.48−7.42 (m, 4H), 7.40−7.35 (m, 1H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.0, 154.8, 152.1, 134.3, 133.8, 130.0, 129.7, 128.6, 127.8, 126.4, 125.4, 123.8, 117.5, 117.3, 51.7; HRMS-ESI (m/z): calcd for $C_{17}H_{12}N_2O_2SNa$ $[M + Na]^+$ 331.0512, found 331.0515.

*Methyl 2-(p-Tolyl)benzo[d]imidazo[2,1-b]thiazole-3-carboxylate (**7b**).* Red solid (46.4 mg, 72% yield); mp 125−126 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.81 (d, J = 8.4 Hz, 1H), 7.72 (dd, J = 7.9, 1.0 Hz, 1H), 7.64 (d, J = 8.1 Hz, 2H), 7.53−7.47 (m, 1H), 7.44−7.37 (m, 1H), 7.27 (d, J = 8.6 Hz, 2H), 3.86 (s, 3H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.1, 154.8, 152.0, 138.6, 133.9, 131.2, 130.0, 129.6, 128.5, 126.4, 125.3, 123.8, 117.5, 117.1, 51.6, 21.4; HRMS-ESI (m/z): calcd for $C_{18}H_{14}N_2O_2SNa$ $[M + Na]^+$ 345.0668, found 345.0676.

*Methyl 2-(3-Methoxyphenyl)benzo[d]imidazo[2,1-b]thiazole-3-carboxylate (**7c**).* Red solid (47.4 mg, 70% yield); mp 101−102 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.76 (dd, J = 8.4, 0.7 Hz, 1H), 7.68 (dd, J = 8.0, 1.0 Hz, 1H), 7.46 (ddd, J = 8.6, 7.4, 1.3 Hz, 1H), 7.39−7.31 (m, 2H), 7.30−7.26 (m, 2H), 6.97 (ddd, J = 8.1, 2.6, 1.2 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.1, 159.2, 154.4, 151.9, 135.5, 133.8, 130.1, 128.7, 126.4, 125.4, 123.8, 122.3, 117.4, 117.4, 114.8, 114.8, 55.4, 51.7; HRMS-ESI (m/z): calcd for $C_{18}H_{14}N_2O_3SNa$ $[M + Na]^+$ 361.0617, found 361.0622.

*Methyl 2-(4-Chlorophenyl)benzo[d]imidazo[2,1-b]thiazole-3-carboxylate (**7d**).* Red solid (43.2 mg, 63% yield); mp 168−169 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.79 (d, J = 8.4 Hz, 1H), 7.70 (dd, J = 7.8, 0.7 Hz, 1H), 7.68−7.60 (m, 2H), 7.53−7.44 (m, 1H), 7.44−7.35 (m, 3H), 3.83 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.7, 153.5, 152.2, 134.7, 133.8, 132.7, 131.1, 130.1, 128.0, 126.5, 125.5, 123.8, 117.6, 117.4, 51.7; HRMS-ESI (m/z): calcd for $C_{17}H_{11}ClN_2O_2SNa$ $[M + Na]^+$ 365.0122, found 365.0126.

*Methyl 6-Phenylimidazo[2,1-b]thiazole-5-carboxylate (**7e**).* Red solid (16.5 mg, 32% yield); mp 100−101 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.18 (d, J = 4.4 Hz, 1H), 7.85 (dd, J = 7.9, 1.4 Hz, 2H), 7.54−7.38 (m, 3H), 6.97 (d, J = 4.4 Hz, 1H), 3.86 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.4, 154.1, 153.0, 133.7, 129.8, 128.8, 127.8, 121.8, 114.5, 113.5, 51.6; HRMS-ESI (m/z): calcd for $C_{13}H_{10}N_2O_2SNa$ $[M + Na]^+$ 281.0355, found 281.0357.

*Methyl Imidazo[1,2-a]pyridine-3-carboxylate (**9a**).* Yellow solid (10.6 mg, 30% yield); mp 67−68 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.84 (s, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.80−7.78 (m, 2H), 7.24 (dd, J = 8.8, 7.2 Hz, 1H), 4.02 (s, 3H) ; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.3, 146.0, 134.8, 125.7, 122.9, 122.2, 118.9, 114.8, 52.8; HRMS-ESI (m/z): calcd for $C_9H_8N_2O_2Na$ $[M + Na]^+$ 199.0478, found 199.0474.

DOI: 10.1021/acs.joc.6b00046
J. Org. Chem. 2016, 81, 2482−2487

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00046.

^{1}H and ^{13}C NMR spectra for all products (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: sunpeipei@njnu.edu.cn.
*E-mail: pingliu@njnu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Projects 21272117, 21502097), the Natural Science Foundation of the Education Department of Jiangsu province (15KJB150015), and the Priority Academic Program Development of Jiangsu Higher Education Institutions. The authors also thank Mr. Hailong Liu for the determination of HRMS.

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