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Controlled Regiodivergent C−H Bond Activation of Imidazo[1,5-*a*]pyridine via Synergistic Cooperation between Aluminum and Nickel

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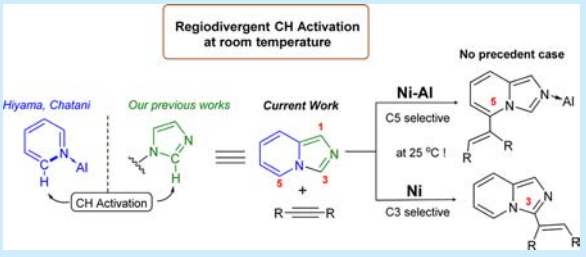
Supporting Information

ABSTRACT: The catalytic method features a cooperative interaction between Ni and Al imparting remote C−H alkenylation at the C5 position of imidazo[1,5-*a*]pyridine with alkynes at mild conditions. Exclusion of $AlMe_3$ switches the selectivity to the C3 position. Reactions with styrene and other olefinic substrates affording C5-adducts by Ni/Al catalysis are also included.



Over the past decade, transition metal promoted C−H bond activation has emerged as a powerful synthetic strategy, avoiding additional steps associated with prefunctionalized coupling partners.[1] In this context, direct C−H activation of heteroarenes like imidazo[1,5-*a*]pyridines has synthetic merits and importance due to their potential applications in electronic and photoresponsive materials,[2] carbene-like ancillary ligand,[3] and various bioactive agents.[4] Although significant progress has been witnessed in Pd-mediated C−H activation of heterocyclic motifs, such as pyridines, indoles, caffeines, azoles, and furans,[5] work related to C−H functionalization of imidazo[1,5-*a*]pyridine are scarce at this stage, for which the majority of their reactivities occurred exclusively at the C3 and C1 positions (Scheme 1).[6] Yet, no single example has been reported on direct C5 functionalization of imidazo[1,5-*a*]pyridine. Therefore, a new paradigm for C5−H bond activation would be highly desirable from academic curiosity and synthetic perspective.

The use of nickel, a benign and low-cost transition metal, to mediate C−H bond functionalization is less common, particularly for the heteroarene moiety.[7] More recently, our group,[8] Nakao, Hiyama,[9] and Chatani[10] utilized bifunctional catalysts consisting of Ni and a Lewis acid to derivatize the C−H bond of pyridines and azoles in a regioselective manner. Particularly, Driver and co-workers reported the C7-functionalization of triazolopyridine by nickel in the presence of $AlMe_3$.[7h] Encouraged by these previous successes, we hypothesized that the addition of Lewis acid $AlMe_3$ would act cooperatively with nickel to invoke an C−H alkenylation selectively at C5 position (Scheme 1). At the same time, we expected that C−H activation can be switched back to the C3 position without $AlMe_3$. Herein, we report regiodivergent C−H alkenylation between C5 and C3 sites of imidazo[1,5-*a*]pyridine and derivatives using bimetallic Ni/Al catalysis. The synthetic scope encompasses a myriad of imidazo[1,5-*a*]pyridines, alkynes, and alkenes.

To test our initial hypothesis for C−H activation at the C3 position, we first examined alkenylation of imidazo[1,5-*a*]-pyridine (**1a**) with 4-octyne (**2a**) in the presence of 10 mol % of $Ni(cod)_2$ in toluene at 40 °C with various supporting ligands (entries 1−6 in Table 1). Phosphine ligands $PtBu_3$ and PPh_3 were completely ineffective (entries 1−2). Both IMes and PCy_3 showed the best yield (99%) to afford C3 and C5 alkenylated products (**3aa** and **4aa**) in a high selectivity of 4:1 ratio (entries 3 and 6). Encouragingly, such high efficiency and C3 selectivity can still be maintained when the catalyst loading was further reduced to 5 mol % (entry 7). It should be noted that this direct C−H functionalization of imidazo[1,5-*a*]pyridine was performed under very mild conditions at ambient temperature. Finally,

Scheme 1. New Conceptual Approach

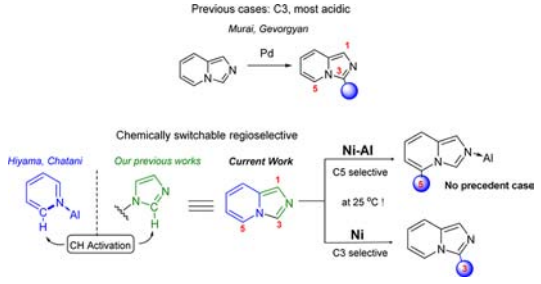


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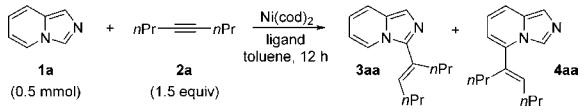
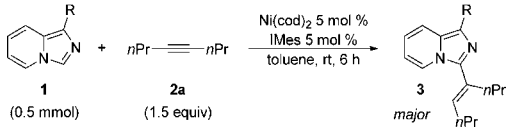
Table 1. Optimization Process for C3-Alkenylation of 1a[a]



entry	[Ni] (mol %)	ligand (mol %)	T (°C)	yield (%)[b]	ratio (3:4)
1	10	$PtBu_3$ (10)	40	N.R.	
2	10	PPh_3 (20)	40	N.R.	
3	10	PCy_3 (20)	40	99	4:1
4	10	amino-NHC[c] (10)	40	99	2:1
5	10	IPr (10)	40	78	3:1
6	10	IMes (10)	40	99	4:1
7[d]	5	IMes (5)	rt	99 (96)	4:1

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.5 equiv), $Ni(cod)_2$, and ligand in toluene (2 mL) for 12 h. [b]Determined by ^1H NMR using mesitylene as the internal standard; isolated yield given in parentheses. [c]Amine-linked NHC.[11] [d]Run for 6 h.

Table 2. C3-Alkenylation of 1 with 2a[a]



entry	1	yield %[b] (3:4)	major	E/Z[c] (3)
1	**1a**: R = H	96 (4:1)	**3aa**	98:2
2	**1b**: R = H	99 (5:1)	**3ba**	99:1
3	**1c**: R = Me	97 (5:1)	**3ca**	99:1
4	**1d**: R = *t*Bu	90 (5:1)	**3da**	99:1
5	**1e**: R = NMe_2	82 (4:1)	**3ea**	99:1
6	**1f**: R = OMe	52 (4:1)	**3fa**	83:17
7	**1g**: R = F	95 (5:1)	**3ga**	99:1
8	**1h**: R = CF_3	97 (5:1)	**3ha**	99:1
9	**1i**: R = CO_2Et	97 (5:1)	**3ia**	99:1
10	**1j**: R = Ph	23 (7:1)	**3ja**	93:7
11	**1k**: Ar = Mesityl	71 (3:1)	**3ka**	92:8
12	**1l**: Ar = 2-Naph	46 (4:1)	**3la**	99:1
13[d]	**1m**: Ar = 2-Thienyl	86 (6:1)	**3ma**	99:1
14[d]	**1n**: Ar = 2-Furanyl	82 (5:1)	**3na**	99:1
15	**1o**: Ar = Ph	97 (5:1)	**3oa**	99:1
16	**1p**: Ar = 4-MeC_6H_4	69 (5:1)	**3pa**	99:1
17	**1q**: Ar = 4-FC_6H_4	84 (5:1)	**3qa**	99:1

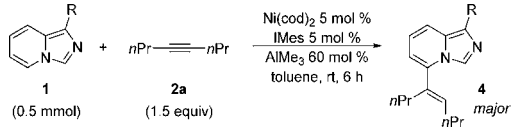
[a]Reaction conditions: **1** (0.5 mmol), **2a** (1.5 equiv), $Ni(cod)_2$ (5 mol %), and IMes (5 mol %) in toluene (2 mL) at rt for 6 h. [b]Isolated yield. [c]Determined by ^1H NMR. [d]Run with **2a** (1.1 equiv).

control experiments performed in the absence of nickel or IMes did not afford any C−H alkenylated products.

With the optimized reaction conditions in hand, we examined the reaction scope with various imidazo[1,5-*a*]pyridines (Table 2). Excellent yields with high C3 regioselectivity were observed for **1a**, **1b**, and **1k**, illustrating the nonsensitivity of the reaction toward different substituents at C1 site of imidazo[1,5-*a*]pyridines. At this stage, we wanted to examine the viability of this catalytic reaction with various 1-aryl-imidazo[1,5-*a*]pyridine, which may be useful for our future study in photosensitive materials (entries 2−10, **1b−j**).[12] Overall, excellent yields (~90%) were observed for substrates bearing electron-donating groups (**1c−e**) with high C3 regioselectivity, but a moderate yield (52%) was observed with a methoxy group (**1f**). Derivatives containing electron-withdrawing groups like fluoro (**1g**), CF_3 (**1h**), and ester (**1i**) were suitable with good yields and regioselectivity. Such a catalysis promoted by nickel can also be extended to heterocyclic-based substrates like thienyl (**1m**, 86%) and furanyl (**1n**, 82%) with high efficiency except for the naphthyl group (**1l**, 46%). Finally, imidazo[1,5-*a*]pyridines bearing different styryl groups **1o−q** (entries 15−17) gave the corresponding products **3oa−3qa** in moderate to good yields.

On the basis of our previous experience with Ni−Al cooperative catalysis in C−H bond activation, introducing bulky Lewis acid should in principle invoke a steric blockade around C3's vicinity of imidazo[1,5-*a*]pyridine, thus imparting a possible activity at C5. Our initial screening efforts have focused on few potential Lewis acids.[13] We found $AlMe_3$ was particularly effective to direct C−H bond activation of **1a** remotely at the C5 position with **2a**, affording **4aa** in a 98% yield with excellent regioselectivity at room temperature (10:1 = **4aa**:**3aa**) (entry 1, Table 3). High yields (~90%) with high C5 selectivity (average

Table 3. C5-Alkenylation of 1 with 2a[a]



entry	1	yield (%)[b] (3:4)	major	E/Z[c] (4)
1	**1a**: R = H	98 (1:10)	**4aa**	99:1
2	**1b**: R = H	99 (1:7)	**4ba**	95:5
3	**1c**: R = Me	82 (1:9)	**4ca**	96:4
4	**1d**: R = *t*Bu	99 (1:8)	**4da**	99:1
5[d]	**1e**: R = NMe_2	97 (1:9)	**4ea**	99:1
6[d]	**1f**: R = OMe	97 (1:10)	**4fa**	94:6
7	**1g**: R = F	99 (1:7)	**4ga**	93:7
8	**1h**: R = CF_3	97 (1:5)	**4ha**	90:10
9	**1i**: R = CO_2Et	98 (1:5)	**4ia**	99:1
10	**1j**: R = Ph	83 (1:11)	**4ja**	94:6
11[d]	**1k**: Ar = Mesityl	98 (1:10)	**4ka**	99:1
12	**1l**: Ar = 2-Naph	96 (1:11)	**4la**	99:1
13[e]	**1m**: Ar = 2-Thienyl	95 (1:6)	**4ma**	99:1
14[e]	**1n**: Ar = 2-Furanyl	92 (1:14)	**4na**	99:1
15	**1o**: Ar = Ph	83 (1:11)	**4oa**	80:20
16	**1p**: Ar = 4-MeC_6H_4	89 (1:6)	**4pa**	94:6
17[d]	**1q**: Ar = 4-FC_6H_4	95 (1:10)	**4qa**	99:1

[a]Reaction conditions: **1** (0.5 mmol), **2a** (1.5 equiv), $Ni(cod)_2$ (5 mol %), IMes (5 mol %), and $AlMe_3$ (60 mol %) in toluene (2 mL) at rt for 6 h. [b]Isolated yield. [c]Determined by ^1H NMR. [d]At 60 °C for 12 h. [e]Run with **2a** (1.1 equiv).

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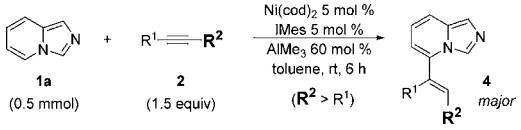
~1:9 = **3**:**4**) were witnessed for substrates bearing various alkyl substituted 1-aryl-imidazo[1,5-*a*]pyridines (**1b**–**d**). Electron-withdrawing groups consisting of fluoro (**1g**), CF_3 (**1h**), CO_2Et (**1i**), and Ph (**1j**) gave excellent yields with high selectivity (entries 7–10). Electron-donating groups like NMe_2 (**1e**) and OMe (**1f**) also afforded the corresponding products **4ea** and **4fa** with high yields albeit at higher temperature 60 °C (entries 5–6). In general, electronic perturbation of substrates did not seem to affect much of the regioselectivity for C5 position. Likewise, such C–H bond activation at C5 position could also be extended to a more π-conjugated system like 1-naphthyl (**1l**), 1-heterocyclic (**1m** and **1n**), and 1-styryl (**1o**–**q**) groups with good yields and regioselectivity. To the best of our knowledge, this protocol can be considered as the first example of remote C5–H bond activation for imidazo[1,5-*a*]pyridine, compared with the reported Pd-catalyzed C3 and C1 arylation.[6]

To further demonstrate its catalytic utility, we expanded the scope of this Ni–Al bimetallic protocol to other alkyne derivatives (Table 4). Good yields with high C5 selectivity

Table 4. C5-Alkenylation of 1a with Various Alkynes[a]



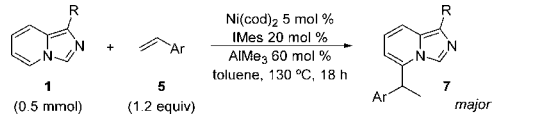
entry	2: R^1, R^2	yield %[b] (C3:C5)	major	r.r.[c,d] (C5)	E/Z[d] (4)
1	**2a**: *n*Pr, *n*Pr,	98 (1:10)	**4aa**		99:1
2	**2b**: Et, Et	90 (1:10)	**4ab**		96:4
3[e]	**2c**: Ph, Ph	53 (1:3)	**4ac**		87:13
4	**2d**: Me, *i*Pr	83 (1:16)	**4ad**	91:9	99:1
5	**2e**: Me, *t*Bu	93 (1:11)	**4ae**	99:1	99:1
6[e]	**2f**: Ph, *t*Bu	96 (1:8)	**4af**	99:1	99:1
7[e,f]	**2g**: *n*Bu, TMS	98 (1:8)	**4ag**	99:1	38:62
8[e,f]	**2h**: Ph, TMS	82 (1:20)	**4ah**	99:1	58:42

[a]Reaction conditions: **1a** (0.5 mmol), **2** (1.5 equiv), $Ni(cod)_2$ (5 mol %), IMes (5 mol %), and $AlMe_3$ (60 mol %) in toluene (2 mL) at rt for 6 h. [b]Isolated yield. [c]Regioisomeric ratio. [d]Determined by ^1H NMR. [e]Run with IMes (20 mol %) at 130 °C. [f]Run with **2** (1.05 equiv).

were observed in symmetrical alkynes **2a** and **2b**, but the addition across diphenylacetylene (**2c**) was sluggish with favorable regioselectivity for C5 (entry 3). Unsymmetrical dialkyl-alkynes like **2d**, **2e**, and phenylalkyl-alkyne **2f** (entries 4–6) proved to be competent alkynes for this reaction with high yields and superior C5 selectivity. Alkynes bearing a trimethylsilyl group (**2g**–**h**) proceeded efficiently at a higher temperature (130 °C) to afford **4ag** and **4ah** adducts with high C5 regioselectivity. Nevertheless, formation of *E* and *Z* stereoisomeric mixtures was observed due to a facile self-isomerization process.[9b] In general, reactions of unsymmetrical alkynes were highly selective to give the corresponding adducts bearing a smaller substituent on the same side with imidazopyridine (entries 4–8). Finally, we were pleased to witness that excluding $AlMe_3$ additive in the catalytic reaction would switch the selectivity back to the C3 position.[13]

Encouraged by the successful C5–H activation manifold, we were curious whether the viability of this manifold could be applied to styrenes and different olefinic substrates other than alkynes. Positively, hydroheteroarylation of styrenes occurred selectively at C5 position with various imidazo[1,5-*a*]pyridines in good to moderate yields (entries 1–8, Table 5). Generally, the addition of imidazo[1,5-*a*]pyridine occurred exclusively at α-

Table 5. Hydroheteroarylation of Olefins with 1[a]



entry	1	5	yield (%)[b] (7)
1	**1a**: R = H	**5a**: Ar = 4-MeC_6H_5	**7aa**, 92
2	**1b**: R = Ph		**7ba**, 88
3	**1c**: R = 4-MeC_6H_4		**7ca**, 74
4	**1f**: R = 4-$OMeC_6H_4$		**7fa**, 76
5	**1g**: R = 4-FC_6H_4		**7ga**, 55
6	**1h**: R = 4-$CF_3C_6H_4$		**7ha**, 52
7	**1j**: R = 4-PhC_6H_4		**7ja**, 64
8	**1l**: R = 2-Naph		**7la**, 58
9	**1a**: R = H	**5b**: Ar = 3-MeC_6H_4	**7ab**, 96
10		**5c**: Ar = 2-MeC_6H_4	**7ac**, 27
11		**5d**: Ar = Ph	**7ad**, 83
12		**5e**: Ar = 4-$OMeC_6H_4$	**7ae**, 89
13		**5f**: Ar = 4-FC_6H_4	**7af**, 53
14		**5g**: Ar = 2-Naph	**7ag**, 88
15[c]		**5h**: R = C_8H_{17}	**7ah**, 83
16[c]		**5i**: R = $(CH_2)_2OTBS$	**7ai**, 70

[a]Reaction conditions: **1** (0.50 mmol), **5** (0.60 mmol), $Ni(cod)_2$ (5 mol %), IMes (20 mol %), and $AlMe_3$ (60 mol %) in toluene (2 mL) at 130 °C for 18 h. [b]Isolated yield. [c]Run with $Ni(cod)_2$ (10 mol %), IPr (20 mol %), $AlMe_3$ (30 mol %), and **5** (1.5 equiv).

position of styrene to afford 1,1-diaryl ethane adducts (**7**). Likewise, a high level of C5-regioselectivity and yields were consistently observed with a myriad of styrenes bearing different functional groups, except those with sterically hindered *ortho*-methyl (**5c**) and strong electron-withdrawing fluoro groups (**5f**) (entries 9–14). To our delight, such method can also be extended to other aliphatic olefinic reagents (**5h**,**i**) with high efficiency and selectivity (entries 15–16). This simplified methodology of affording linear C5-alkylated imidazo[1,5-*a*]pyridines like **7ai** would be a representative example to prepare the related biological active compounds like thromboxane A_2 synthetase inhibitor.[14]

To gain insights into the reaction mechanism, the following experiments were conducted. Reaction of **1a**-d_2 with **2a** was examined in the presence and absence of $AlMe_3$. As revealed by ^1H NMR analysis, the cleaved deuterium was inserted into **2a** in syn manner to give **3aa**-d_2 and **4aa**-d_2, respectively (eqs 1 and 2, Scheme S1).[13] The kinetic isotope effect (KIE) was investigated by an intermolecular competition between **1a** and **1a**-d_2. A notable KIE value of 3.8 obtained in C3-alkenylation suggested C–H bond cleavage may be significant with respect to the rate-determining step (eq 3). Intriguingly, a KIE value of 1.1 was observed in C5-alkenylation (eq 4), illustrating that C–H bond cleavage was fast. These labeling results indicated C3- and C5-alkenylation involved two different operating mechanistic pathways. Further studies are necessary to investigate the mechanistic details.

In summary, without resorting to directing group installment on the substrate, we have disclosed a novel regiodivergent C–H bond functionalization of imidazo[1,5-*a*]pyridine and derivatives. The catalytic method features a cooperative interaction between Ni and Al to invoke remote C–H activation via alkenylation at the C5 position of imidazo[1,5-*a*]pyridine, which is unprecedented. Exclusion of $AlMe_3$ cocatalyst switches the reaction to the C3 site. Ongoing work seeks to gain a detailed mechanistic understanding of the synergism offered by Ni–Al bimetallic catalysis. Such mechanistic insights will be crucial for

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developing bimetallic catalysis on the scope of the reaction in the future. In addition, the possibilities to functionalize the C8 position of imidazo[1,5-*a*]pyridine are currently under exploration in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization of all new compounds are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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