Letter

A Facile Access to Primary Alkylamines and Anilines via Ir(III)-Catalyzed C-H Amidation by Using Azidoformates

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A Facile Access to Primary Alkylamines and Anilines via Ir(III)-Catalyzed C–H Amidation by Using Azidoformates

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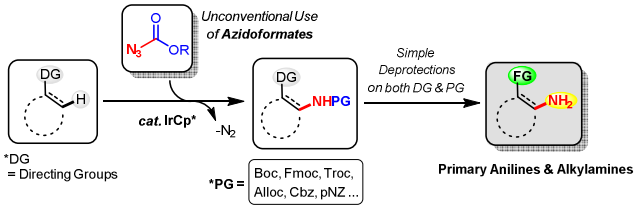
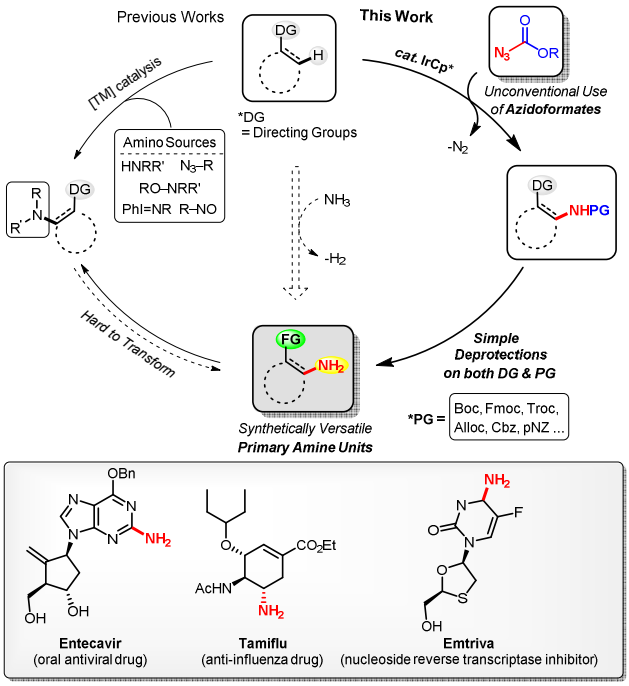
ABSTRACT: Described herein is the development of Ir(III)-catalyzed direct C–H amidation using azidoformates as a readily deprotectable amino source. Substrates with unactivated methyl C(sp^3)–H and aromatic or olefinic C(sp^2)–H bonds were smoothly reacted by the iridium-based catalyst system to provide the corresponding *primary alkylamines and anilines* upon the subsequent removal of N-protecting groups such as Boc, Fmoc, Cbz, pNZ, or Troc. A brief mechanistic study and synthetic applications are also presented.



KEYWORDS: C–H amidation, iridium catalysis, azidoformates, primary alkylamines, primary anilines

Installation of a primary amino group (–NH_2) into hydrocarbons has been the focus of intensive research in synthetic chemistry. The main grounds for these efforts are attributed to the crucial role of primary amino functionality in displaying biological and pharmaceutical activities in natural or synthetic compounds in addition to their high coordination ability toward metal centers.[1] Although an approach of immediate choice toward the preparation of primary amines is the coupling of ammonia with organic (pseudo)halides,[1a–c,2] challenges are still present in the direct use of ammonia. This can be ascribed mainly to the high bond strength of N–H bonds (107 kcal/mol)[2c] and strong coordination of ammonia to transition metals, thus easily leading to the catalyst deactivation.[3–5]

Direct C–H amidation/amination of sp^2 (aryl or vinyl) and sp^3 (alkyl) C–H bonds has been developed with the formation of *N*-substituted secondary or tertiary aryl-, alkenyl-, and alkylamines by using the corresponding amino precursors.[6] However, mainly due to the robustness of those aminating reagents, subsequent conversion of initially formed (secondary or tertiary) amino products to *primary* amines is not feasible in most cases (Scheme 1, upper left).[6] In this regard, Glorius'[7] and our group[8] independently presented effective routes accessing a range of primary anilines by using *O*-substituted carbamates as the amino precursors in the C–H amidation of arenes. Upon the successful amidation of arene C–H bonds, carbamate protecting groups can readily be removed to deliver the desired aniline products.[9] In addition, Ackermann *et al.* also very recently reported a Ru-catalyzed C–H imidation of arenes to afford *ortho*-imidophenones which eventually give rise to primary anilines upon removal of *N*-phthalyl group with hydrazine.[10]

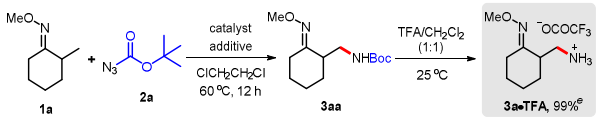


Scheme 1. Iridium-Catalyzed C–H Amidation with Azidoformates: A Facile Access to Primary Amines.

In spite of these progresses towards efficient preparation of primary anilines, to the best of our knowledge, there is no report applicable to sp^3 C–H bond amidation that subsequently leads to primary alkylamines. Therefore, it is still in high demand of developing an inclusive methodology that allows both sp^2 and sp^3 C–H bonds to be transformed to primary amines with broad applicability as demonstrated in a variety of synthetic, medicinal, and coordination chemistry (Scheme 1, bottom).[1d–i]

Continuing our efforts on the development of mild and efficient C–H amination/amidation with organic azides as the amino source,[6g,11] we now present that C–H amidation can be achieved by using *azidoformates* as both an amino source and an internal oxidant via N–N_2 bond cleavage (Scheme 1, upper right). Although azidoformates were previously utilized as a nitrenoid precursor under thermal or photochemical conditions,[12a–h] the synthetic utilization has not been much explored especially in the C–H amidation reactions.[12i–j] It needs to be noted that, quite recently, Zhang *et al.* reported the use of 2,2,2-trichloroethoxycarbonyl azide as a carbamoyl source in the Ir-catalyzed *cyclization* of benzamides to afford quinazoline-2,4(1*H*,3*H*)-diones.[12k] Herein we describe a bench scale preparation of a range of synthetically valuable azidoformates,[13] and their use in the C–H amidation of both C(sp^2)–H and C(sp^3)–H bonds to eventually provide the corresponding primary anilines and alkylamines.

Table 1. Optimization of the Reaction Parameters[a]

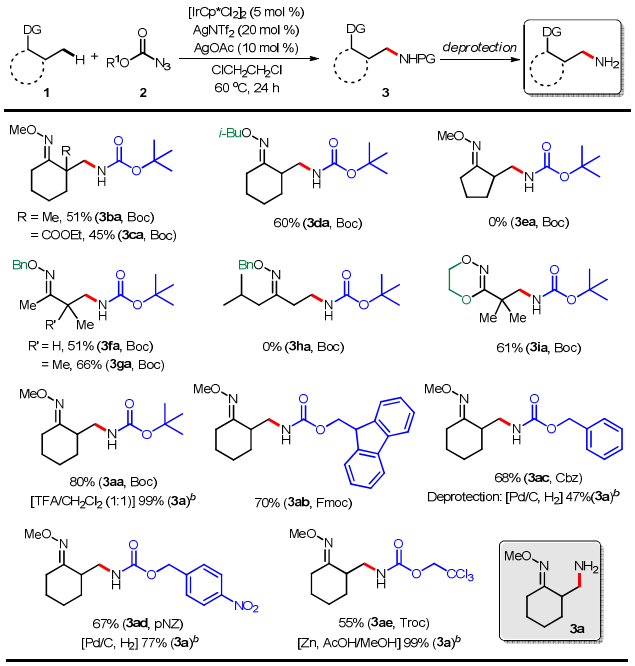


Entry	Catalyst (mol %)	Additive (mol %)	Yield (%)[b]
1	$[IrCp^*Cl_2]_2$ (5)/$AgNTf_2$ (20)	-	<1
2	$[IrCp^*Cl_2]_2$ (5)/$AgNTf_2$ (20)	NaOAc (10)	<1
3	$[IrCp^*Cl_2]_2$ (5)/$AgNTf_2$ (20)	LiOAc (10)	<1
4	$[IrCp^*Cl_2]_2$ (5)/$AgNTf_2$ (20)	CsOAc (10)	10
5	$[IrCp^*Cl_2]_2$ (5)/$AgNTf_2$ (20)	AgOAc (10)	71
6	$[IrCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	AgOAc (10)	<1
7[c]	**$[IrCp^*Cl_2]_2$ (5)/$AgNTf_2$ (20)**	**AgOAc (10)**	**81 (80)**
8	$[IrCp^*Cl_2]_2$ (2.5)/$AgNTf_2$ (10)	AgOAc (10)	53
9[c,d]	$[IrCp^*Cl_2]_2$ (5)/$AgNTf_2$ (20)	AgOAc (10)	39
10	$[RhCp^*Cl_2]_2$ (5)/$AgNTf_2$ (20)	AgOAc (10)	<1
11	$[Ru(p\text{-cymene})Cl_2]_2$ (5)/$AgNTf_2$ (20)	AgOAc (10)	<1
12	$[CoCp^*Cl_2]_2$ (5)/$AgNTf_2$ (20)	AgOAc (10)	<1

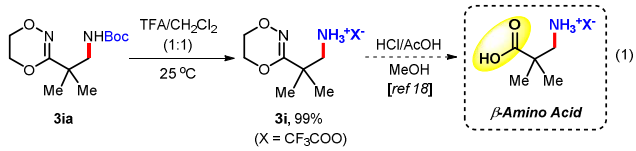
[a]**1a** (0.20 mmol), **2a** (0.40 mmol), catalyst, and additive in 1,2-dichloroethane (0.5 mL). [b]Yields of **3aa** based on ^{1}H NMR analysis of the crude mixture using 1,1,2,2-tetrachloroethane as an internal standard (isolated yield in parentheses). [c]For 24 h. [d]At 25 °C. [e]**3aa** (0.10 mmol) in CF_3COOH (1.0 mL) and CH_2Cl_2 (1.0 mL).

At the outset of our investigation, optimal amidation conditions for the unactivated sp^3 C–H bonds were examined by using azidoformates. In this line, ketoxime **1a** was chosen as a model substrate to react with *tert*-butyl azidoformate (Boc–N_3) **2a** (Table 1). With a cationic Ir^{III} catalyst generated *in situ* from $[IrCp^*Cl_2]_2$ with $AgNTf_2$, no significant conversion was observed (entry 1). However, a catalytic amount of acetate additive (10 mol %) facilitated the desired C–H amidation (entries 2–5). Among various acetates screened (see Supporting Information for full data), AgOAc enhanced the reaction efficiency most dramatically to give the desired product in good yield at 60 °C for 12 h (entry 5). Interestingly, a cationic iridium species generated from $[IrCp^*Cl_2]_2$ with $AgSbF_6$ instead of $AgNTf_2$ was ineffective (entry 6). The elongation of reaction time (24 h) slightly increased the product yield (entry 7) while the reaction efficiency was diminished with lower catalyst loading (entry 8). Notably, the amidation took place even at room temperature albeit with decreased efficiency (entry 9). It should be mentioned that Rh,[14] Ru[15] and Co[16] catalyst systems which were previously applied in the C–H amidation/amination reactions were totally unsuccessful for the present reaction (entries 10–12). We then explored conditions to remove *tert*-butyl carbamate (Boc) group in the amidated product (**3aa**) to find that it was readily deprotected by trifluoroacetic acid to give primary alkylamine salt (**3a·TFA**) in quantitative yield.

Table 2. Substrate Scope of C(sp^3)–H Bond Amidation[a]



[a]**1** (0.20 mmol) and **2** (0.40 mmol) in 1,2-dichloroethane (0.5 mL). [b]Yields of the deprotected **3a** based on ^{1}H NMR analysis of the crude mixture using CH_2Br_2 as the internal standard.

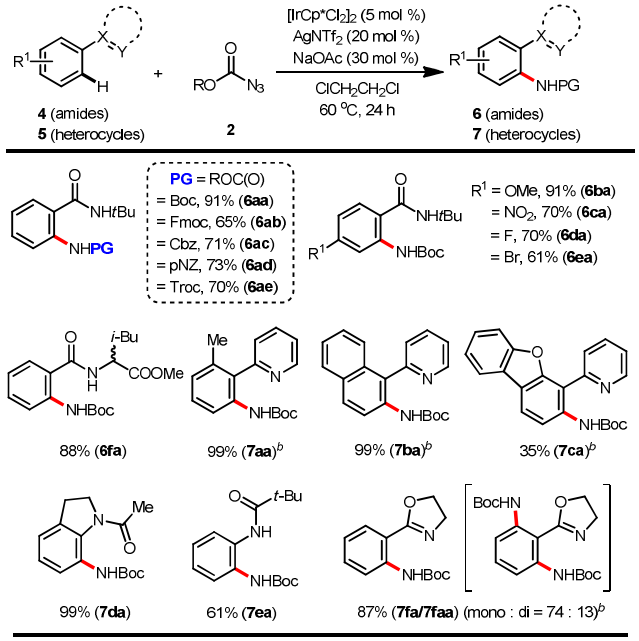


With the above optimized catalytic conditions for the sp^3 C–H bond amidation with *tert*-butyl azidoformate (**2a**), we next examined the scope of various ketoxime substrates (Table 2). The reaction readily took place with α,α-disubstituted ketoximes (**1b–c**) albeit with moderate product yields. Notably, an ester group did not affect the present C–H amidation (**3ca**). Variation at the *O*-alkyl substituent of ketoximes was found to be facile (**3da**). However, the amidation of 2-methylcyclopentanone *O*-methyl oxime (**1e**) was not occurred, implying that the reaction efficiency was sensitive to the type of substrates' structure. In addition, it was revealed that acyclic ketoximes (**1f–g**), which can be considered to be more challenging due to the structural flexibility,[17] also smoothly

participated in the present reaction without difficulty. However, a substrate that does not have any substituents alpha to the ketoxime directing group (**1h**) was totally ineffective with the present amidation protocol. We were pleased to see that the current amination was successful with a substrate possessing 5,6-dihydro-[1,4,2]dioxazine as a directing group (**3ia**), which can be utilized for further applications especially in the synthesis of *β*-amino acid derivatives (eq 1).[18] In order to make the present approach to be synthetically more valuable and flexible, a range of additional azidoformates, readily prepared from the corresponding chloroformates,[13] were examined in the sp^3 C–H amidation. Gratifyingly, the desired amidation took place efficiently with diverse azidoformates bearing Fmoc (**3ab**), Cbz (**3ac**), pNZ (**3ad**), and Troc groups (**3ae**). It should be noted that carbamate products were readily deprotected under the known conditions leading to corresponding primary alkylamine (**3a**).[9]

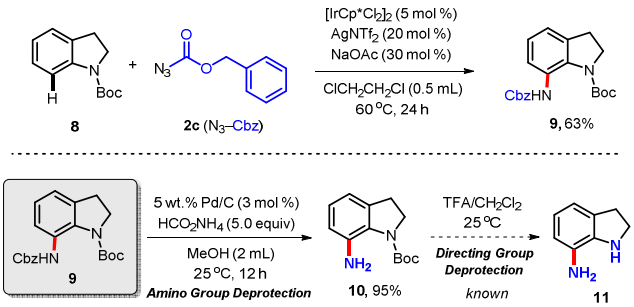
To examine the generality of the current protocol, we subsequently tried to expand the scope of the Ir-catalyzed C–H amidation to aromatic compounds to obtain *N-protected anilines* (Table 3). We chose *N*-(*tert*-butyl)benzamide as a model substrate to react with various azidoformates bearing synthetically valuable functional groups. Pleasingly, when 30 mol % of NaOAc was employed in lieu of AgOAc, the amidated products were obtained in good to excellent yields irrespective of the type of azidoformates (**6aa–ae**). The electronic property in benzamide substrates did not significantly affect the reaction efficiency (**6ba–ea**). In addition, a benzamide substrate derived from α-amino ester underwent the C–H amidation in high yield (**6fa**). An additional array of heterocyclic directing groups was also tested (**5aa–fa**) to reveal that they worked also effectively to drive the C–H amidation at the *ortho*-position under slightly modified conditions using 1.0 equiv of NaOAc. *N*-Acetylindoline was highly facile to install the NH–Boc group (**7da**). While benzanilide underwent the C–H amidation with Boc–N_3 (**7ea**), a reaction of 2-phenyloxazoline gave a mixture of mono- and bis-amidated products (**7fa**/**7faa**, 74:13).

Table 3. Scope of Arene C(sp^2)–H Bond Amidation[a]



[a]**4** or **5** (0.20 mmol) and **2** (0.30 mmol) in 1,2-dichloroethane (0.5 mL). [b] NaOAc (1.0 equiv) was used.

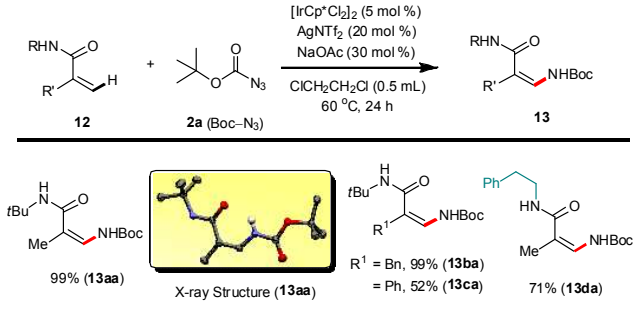
Considering the fact that heterocycles bearing amino groups are important pharmacophores,[1d–i] the present protocol was examined to see whether it would be effective for the preparation of aminated heterocycles. Pleasingly, C7-aminoindoline, a prevalent bioactive scaffold,[19] was proved to be readily accessible (Scheme 2). A selective C-7 amidation of *N*-Boc-indoline (**8**) with Cbz–N_3 (**2c**) was performed under the present conditions to afford **9** in acceptable yield. Selective deprotection of Cbz group was achieved with Pd-catalyzed transfer hydrogenation to give **10** in high yield. It needs to be mentioned that 7-aminoindoline **11** is known to be accessible upon the removal of *N*-Boc group of **10**.[19d]



Scheme 2. A Facile Route to 7-Aminoindoline (10 → 11: Ref 19d**)**

Given that enamides serve as a versatile synthetic building unit and potent pharmacophore, a stereoselective access to *N*-protected enamine fragments is highly desirable.[20] In this context, we attempted to apply the present conditions for the *olefinic* C–H amidation (Table 4). Methacrylamide (**12a**) was smoothly reacted with azidoformate (**2a**) to afford *Z*-enamide **13aa** in quantitative yield. Significantly, an X-ray crystallographic analysis of **13aa** revealed the presence of an intramolecular H-bond between carbonyl oxygen of acrylamide and the newly introduced NH–Boc group, with the verification of *Z*-enamide stereoisomer.[21] Acrylamides bearing other than methyl substituent at the α-position also underwent the desired selective amidation (**13ba–ca**). Moreover, variation at the *N*-alkyl amido group did not much affect the reaction efficiency (**13da**).

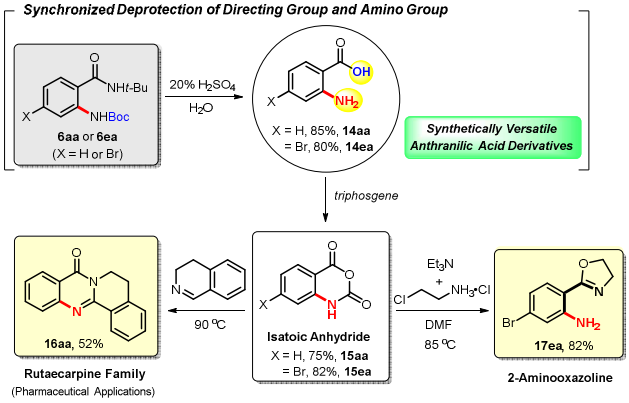
Table 4. Scope of Olefin C(sp^2)–H Bond Amidation[a]



[a]**12** (0.20 mmol) and **2** (0.30 mmol) in 1,2-dichloroethane (0.5 mL).

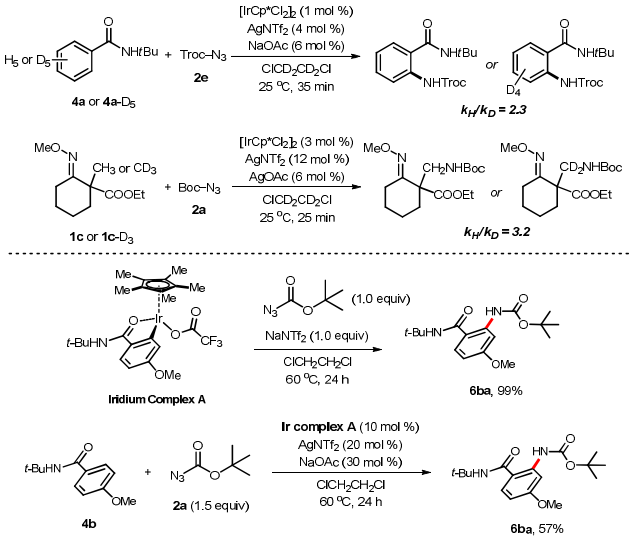
Amidated benzamides obtained through the present C–H amidation protocol could easily be transformed to synthetical-

ly versatile anthranilic acid derivatives (Scheme 3).[22] Upon acidic treatment of **6aa** or its bromo-substituted analogue **6ea**, both amide directing group and newly introduced NH–Boc moiety were removed to give anthranilic acids (**14aa** and **14ea**, respectively) in good yields. Subsequent conversion to cyclic isatoic anhydrides (**15aa** and **15ea**) offered a variety of synthetic opportunities. For example, a derivative of natural alkaloid rutaecarpine (**16aa**) was obtained from **15aa** in 52% yield. It should be mentioned that parent rutaecarpine exhibits interesting biological activities such as anti-platelet aggregation, vasorelaxing, antiobesity and cytoxity.[22b] In addition, a bromo derivative of 2-oxazolinylaniline (**17ea**), known to have an effective chelating ability,[23] was readily accessible in good yield that can be further functionalized by cross-coupling reactions.



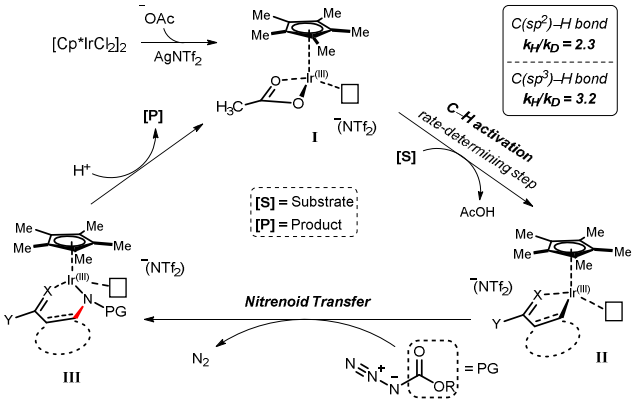
Scheme 3. Access to Anthranilic Acid and Its Derivatization

To shed light on the mechanistic details, we conducted a series of preliminary experiments (Scheme 4). A significant level of primary kinetic isotope effect was measured in both sp^2 and sp^3 C–H amidations (k_H/k_D = 2.3 and 3.2, respectively), thus suggesting that the C–H bond cleavage is likely to be involved in the rate-limiting stage. It was notable that an isolated iridacyclic complex **A**, prepared according to our previous procedure,[6e] performed a stoichiometric amidation to yield **6ba** (99%). In addition, the iridacycle **A** was shown to catalyze the amidation in lieu of $[IrCp^*Cl_2]_2$ precursor to indicate that this iridacyclic complex is an active species in the catalytic cycle.



Scheme 4. Preliminary Mechanistic Investigation

On the basis of the above experimental results and precedent literature,[6g,11,24] a plausible mechanistic pathway is depicted in Scheme 5. First, a cationic iridium species **I** bound to acetate is generated upon the chloride abstraction from the dimeric iridium precursor. It induces the C–H bond cleavage of substrates to generate a cyclometalated Ir(III) complex (**II**), likely via a base-assisted concerted metalation-deprotonation (CMD) process.[24g–h] The azidoformate would then coordinate to a vacant site of **II** and subsequently transfers its imido group into the Ir–C bond with concomitant release of N_2 to afford an Ir-amido complex (**III**). Foretold by our precedent studies to this process including DFT calcuations in rhodium catalysis,[24e] a stepwise nitrenoid insertion pathway is believed to be more likely while a concerted pathway cannot be completely excluded. Finally, protodemetalation of complex **III** will liberate the desired amidated product with the regeneration of a catalytically active iridium species (**I**).



Scheme 5. Plausible Mechanistic Pathway

In conclusion, an efficient and selective Ir-catalyzed $C(sp^3)$–H and $C(sp^2)$–H amidation using a range of synthetically valuable azidoformates as an amino source has been developed. This process turned out to be a facile route to the corresponding *primary* alkylamines and anilines upon

deprotection of the carbamate groups in the initially generated amidated products.

ASSOCIATED CONTENT

Supporting Information.

The following file is available free of charge on the ACS Publications website at http://pubs.acs.org.

General experimental procedures; characterization details; and ^{1}H, ^{13}C and ^{19}F NMR spectra of new compounds (PDF)

X-ray crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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