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# Alkyl Formates as Transfer Hydroalkylation Reagents and Their Use in the Conversion of Imines to Alkylamines

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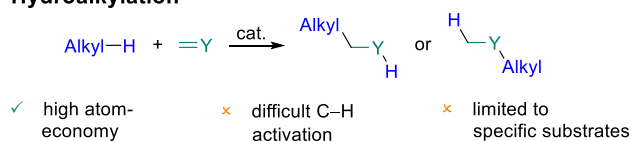
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**Abstract:** Easily accessible *via* a simple esterification of alcohols with formic acid, alkyl formates are used as a novel class of transfer hydroalkylation reagents, CO<sub>2</sub> acting as a traceless linker. As a proof-of-concept, their reactivity in the transfer hydroalkylation of imines is investigated, using a ruthenium-based catalyst and LiI as promoter to cleave the C–O  $\sigma$ -bond of the formate scaffold. Providing tertiary amines, the reaction displays a reverse and complementary regioselectivity compared to previously reported transfer hydroalkylation strategies.

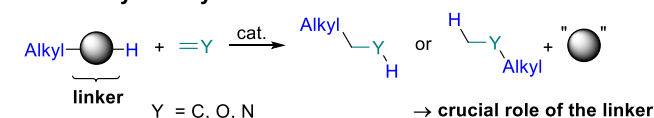
Hydrofunctionalizations of unsaturated bonds, such as carbonyl, imines, alkenes or alkynes, provide a rapid and atom-economic access to functionalized molecules.<sup>[1]</sup> Among these processes, hydroalkylation, which formally adds an alkane R–H across a C=C, C=O, or C=N bond, is particularly attractive, as hydrocarbons are readily available. This strategy however requires to activate strong C–H alkyl bonds and has only been applied to very specific substrates such as 1,2-dicarbonyl derivatives<sup>[2]</sup> or alkylamines<sup>[3]</sup> – for the so-called hydroaminoalkylation reaction – bearing activated C–H bonds. To avoid the intrinsic difficulty of selective C–H activation and the use of sacrificial donors, transfer hydroalkylations have been explored, in a similar approach as transfer hydrogenation<sup>[4]</sup> (Scheme 1). They rely on the use of bifunctional reagents<sup>[5]</sup> from which both a hydrogen atom and an alkyl group, bounded by a linker, can be transferred across unsaturated bonds. The nature of the linker directly governs the reactivity of the transfer hydroalkylation agent and its release is the driving force of the process. For instance, Oshima and coworkers used bulky ketones as linkers and made use of the retro-allylation (or allenylation) of homoallyl and allenyl alcohols to promote the transfer allylation or allenylation of aldehydes and imines under Rh or Cu-catalysis (Scheme 1a).<sup>[6]</sup> Inspired by transfer hydrogenation reactions and biological hydrogen donors, the group of Tang thereafter designed alkyl-donors based on Hantzsch esters or benzothiazoles as linkers (Scheme 1b).<sup>[7]</sup> These derivatives were successfully applied in the transfer hydroalkylation of aldehydes, imines, alkynes, activated alkenes and azo compounds,<sup>[8]</sup> under thermal<sup>[9]</sup> or photochemical conditions<sup>[10]</sup>. In these examples, the reaction is driven by the rearomatization of the pyridine linker. Interestingly, the group of Li sought after the use of N<sub>2</sub> as a gaseous linker and employed hydrazones as transfer hydroalkylating reagents for imines in presence of a Ru-based catalyst (Scheme 1c).<sup>[11]</sup> The authors then extended the scope of the unsaturated coupling partner, using carbonyl,<sup>[12]</sup> activated alkenes,<sup>[13]</sup> or alkynes.<sup>[14]</sup> Although interesting from an atom-

economical point of view, the handling of hydrazone might however limit its use on large-scale syntheses.

## Hydroalkylation



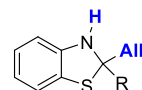
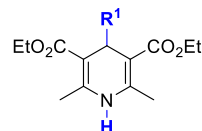
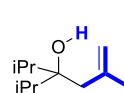
## Transfer hydroalkylation



### Organic linkers - low atom economy and organic wastes

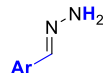
a) Oshima et al. - homoallyl alcohols

b) Tang et al. - Hantzsch esters and benzothiazoles

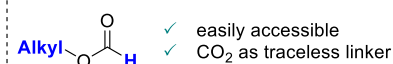


### Gaseous linkers - higher atom economy and easily removable

c) Li et al. - hydrazones



d) This work - alkyl formates



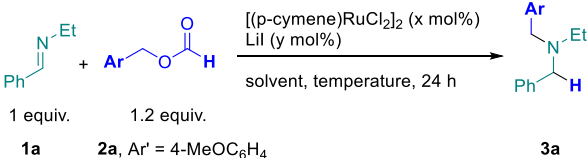
**Scheme 1.** Hydroalkylation and transfer hydroalkylation strategies, a) with homoallyl alcohols, b) with Hantzsch esters and benzothiazoles, c) with hydrazones, and d) with alkyl formates (*this work*)

Herein, we wish to report the proof-of-concept for the use of alkyl formates, HCO<sub>2</sub>R, as transfer hydroalkylation agents, where CO<sub>2</sub> is used as a gaseous and traceless linker (Scheme 1d). These compounds are easily accessible *via* an esterification of alcohols with formic acid. Based on our work on transfer hydrosilylation with silyl formates as hydrosilane surrogates,<sup>[15]</sup> we indeed envisaged that alkyl formates could act as bifunctional reagents<sup>[5]</sup> with a formyl hydrogen showing a hydride character, combined to an electrophilic alkyl group. The transfer hydroalkylation of imines was hence targeted, under transition-metal catalysis.

To test our hypothesis, *N*-ethyl imine **1a** was reacted with 4-methoxybenzyl formate (**2a**, 1.2 equiv.) in the presence of a transfer hydrogenation catalyst, [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (2.5 mol%) in

THF at 120 °C. Under these conditions, no reaction was detected (Table 1, entry 1). Reasoning that the concentration of formate anions should be increased to facilitate the formation of a hydride ligand in the coordination sphere of the Ru-catalyst, the influence of Lil as a co-catalyst (25 mol%) was evaluated, to promote the cleavage of the C–O in the formate reagent.<sup>[16]</sup> It allowed the formation of amine **3a** in 80 % yield at 100 °C (Table 1, entry 2). Pleasingly, no product resulting from the previously reported protodecarboxylation or decarbonylation of the benzyl formate could be detected.<sup>[17]</sup> The formation of **3a** is hence the first demonstration of the ability of alkylformates to act as transfer hydroalkylation agent. Interestingly, they can promote a reversed and complementary regioselectivity compared to other reported alkyl donor reagents (Scheme 1), as the hydride character of the formate directs the formation of C–H and N–C bonds in place of N–H and C–C bonds.

**Table 1.** Influence of the reaction conditions on the transfer hydroalkylation of anisyl formate (**1a**) with imine **2a** (see Table S2 Supporting Information for a more exhaustive table)<sup>[a]</sup>



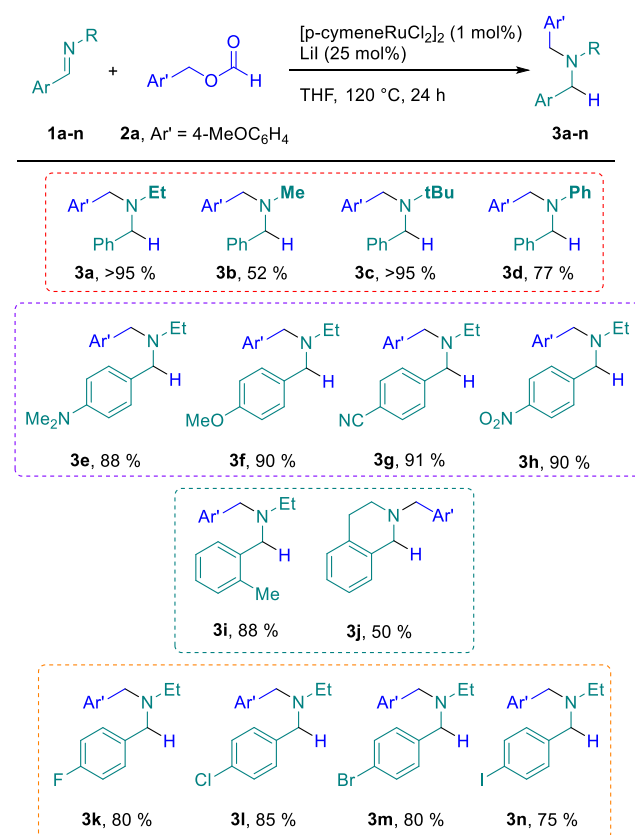
Entry	x	y	Solvent	T (°C)	Yield (%)
1	2.5	-	THF-d <sub>8</sub>	120	0
2	2.5	25	THF-d <sub>8</sub>	100	80
3	-	25	THF-d <sub>8</sub>	120	0
4	2.5	25	CD <sub>3</sub> CN	100	25
5	2.5	25	Toluene-d <sub>8</sub>	100	0
6	2.5	25	THF-d <sub>8</sub>	80	15
7	2.5	25	THF-d <sub>8</sub>	120	90
8	2.5	25	THF-d <sub>8</sub>	150	65
9	2.5	5	THF-d <sub>8</sub>	120	Traces
10 <sup>[b]</sup>	2.5	50	THF-d <sub>8</sub>	120	>95
11 <sup>[c]</sup>	2.5	100	THF-d <sub>8</sub>	120	>95
12	1	25	THF-d <sub>8</sub>	120	>95

[a] Standard reaction conditions: **1a** (0.20 mmol, 1 equiv.), **2a** (0.24 mmol, 1.2 equiv.), solvent (0.5 mL), temperature. Yields were measured by <sup>1</sup>H NMR (internal standard: mesitylene). [b] Reaction completed in 5 h. [c] Reaction completed in 2 h.

The use of [Ir] or [Rh] precursors or *N,N*- or *N,O*-ligands, known to promote reactions with formic acid,<sup>[4,18]</sup> showed no significant or deleterious effect on the reactivity (see Table S1 in Supporting Information for more details). The ruthenium catalyst was necessary for the reaction to proceed (Table 1, entry 3). Using the more coordinating solvent MeCN (Table 1, entry 4) reduced the yield to 25 %. Apolar and non-coordinating solvents such as toluene (Table 1, entry 5) completely inhibited the reactivity, most likely because of the low solubility of both lithium iodide and the ruthenium catalyst in these solvents. At 80 °C (Table 1, entry 6),

the conversion dropped and a yield of 15 % was observed. Increasing the temperature at 120 °C furnished the desired amine in 90 % yield (Table 1, entry 7), whereas at higher temperature (150 °C) side-products were detected, such as 4-methoxytoluene, resulting from the protodecarboxylation of formate **2a**, and 1,2-bis(4-methoxyphenyl)ethane from the homocoupling of the formate, leading to a decrease in yield (65 %, Table 1, entry 8). We also observed that the amount of the Lil promotor had a strong effect on the reaction rate. Only traces of product **3a** were detected with 5 mol% of Lil within 20 h, when complete conversion was noticed with 25 mol%, 50 mol% or 100 mol% within 24 h, 5 h or 2 h, respectively (Table 1, entries 2 and 9-11). To avoid excess salts in the reaction mixture, we selected the conditions with 25 mol% of Lil, and the [Ru]-catalyst loading could be lowered to 1 mol% (Table 1, entry 12).

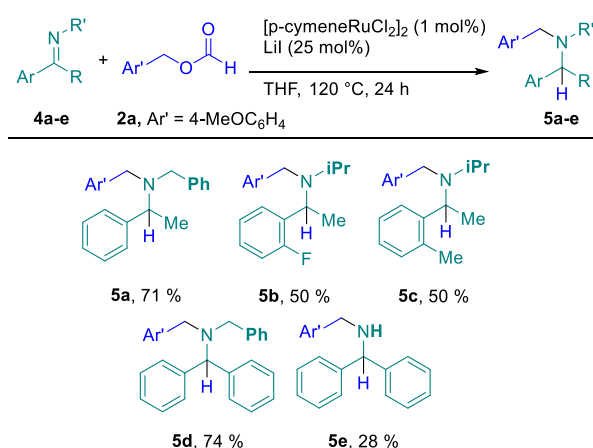
With these conditions in hands, the influence of the *N*-substitution of aldimine **1** was first investigated. *N*-methyl substituted imine **2b** gave the desired amine **3b** in a moderate yield of 52%.<sup>[19]</sup> Interestingly, the reaction is not sensitive to sterically hindered imines, *N*-*tert*-butyl amine **3c** being obtained in quantitative yield. Aniline derivatives such as **3d** can also be formed, in 77 % yield, certainly due to a less nucleophilic nitrogen. Electron-donating or withdrawing substituents on the aryl moiety of aldimine **1** were both tolerated, and benzyl amines **3e-h** were obtained in 88–91 % yields. Remarkably, a nitrile (**3g**) and a nitro (**3h**) functional groups, which are usually sensitive towards reduction, remained untouched here. Despite the steric hindrance induced by the methyl *ortho*-substituent on the aromatic ring of **2i**, amine **3i** was



**Scheme 2.** Substrate scope in aldimine **1**. Reaction conditions: aldimine **1** (0.20 mmol, 1.0 equiv.), anisyl formate (**2a**, 0.24 mmol, 1.2 equiv.), Lil (50 μmol, 25 mol%) [(p-cymene)RuCl<sub>2</sub>]<sub>2</sub> (2 μmol, 1 mol%), THF (0.5 mL), 120 °C, 24 h. Yields were measured by <sup>1</sup>H NMR (internal standard: mesitylene).

obtained in 88 % yield. 3,4-Hydroisoquinoline (**1j**) underwent hydroalkylation under the same conditions, leading to the alkylated tetrahydroisoquinoline **3j** in 50 % yield. Halide substituents (F, Cl, Br, I) were also tolerated, giving compounds **3k-n** in 80 – 85 % yields, thereby allowing further downstream derivatizations by a cross-coupling reaction (Scheme 2).

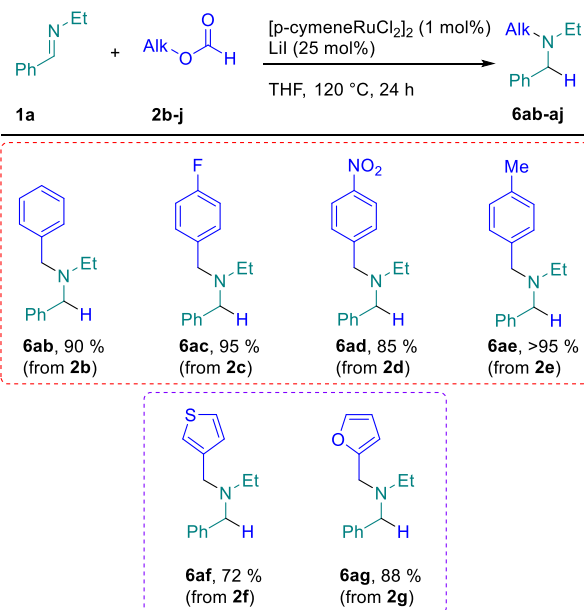
Ketimines also reacted under these conditions. Trisubstituted amine **5a** was obtained in 71 % yield. Ortho-substituted imines **4b** and **4c** both furnished the corresponding amines **5b** and **5c** in 50 % yield. In case of **4c**, the product of hydrogenation was observed, which explains the loss of yield. The bulky benzophenone imine **4d** also reacted under the optimized conditions, giving amine **5d** in 74 % yield. In contrast, the secondary amine **5e**, resulting from the reaction of diphenylmethanimine (**4e**), was obtained in only 28 % yield, showing a drastic effect of the imine substituent (Scheme 3).<sup>[19]</sup>



**Scheme 3.** Substrate scope in ketamine **4**. Reaction conditions: ketimine **4** (0.20 mmol, 1.0 equiv.), anisyl formate (**2a**, 0.24 mmol, 1.2 equiv.), Lil (50  $\mu$ mol, 25 mol%) [p-cymeneRuCl<sub>2</sub>]<sub>2</sub> (2  $\mu$ mol, 1 mol%), THF (0.5 mL), 120 °C, 24 h. Yields were measured by <sup>1</sup>H NMR (internal standard: mesitylene).

To appreciate the influence of the stereoelectronics of the transfer hydroalkylation agent on the reactivity, a range of different alkylformates was tested (Scheme 4). Electron-poor and electron-rich benzyl formates **2b-e** were subjected to the reaction conditions in presence of aldimine **1a** and gave tertiary amines **6ab-ae** in 85–95 % yield. Remarkably, a nitro group was tolerated, without being reduced (**6ad**, 85 % yield). Thiophenyl and furanyl derivatives **6af** and **6ag** were obtained in good yields, 72 % and 88 %, respectively. The reaction with furanyl formate is especially interesting, as it is a bio-sourced building block, formed through the condensation of formic acid and furanyl alcohol. Under the described reaction conditions, other methyl, ethyl, or isopropyl derivatives proved unproductive, the desired products being only observed as traces. Adding more Lil promotor proved ineffective (see SI for more details).

To better understand how alkylformates can serve as bifunctional agents for transfer hydroalkylation, the mechanism of this reaction was further investigated via a kinetic study coupled to control reactions. The rate law of the reaction was determined using the Burés method for the ruthenium<sup>[20]</sup> and a flooding method for the other reactants, giving the following partial orders  $v = k[\mathbf{1}]^0[\mathbf{2}]^1[\text{Ru}]^{0.3}[\text{Lil}]^1$  (with  $k = 0.84 \text{ s} \cdot \text{L}^{-1.3} \cdot \text{mol}^{-1.3}$ ). The rate law showed no influence of the imine substrate on the reactivity, as

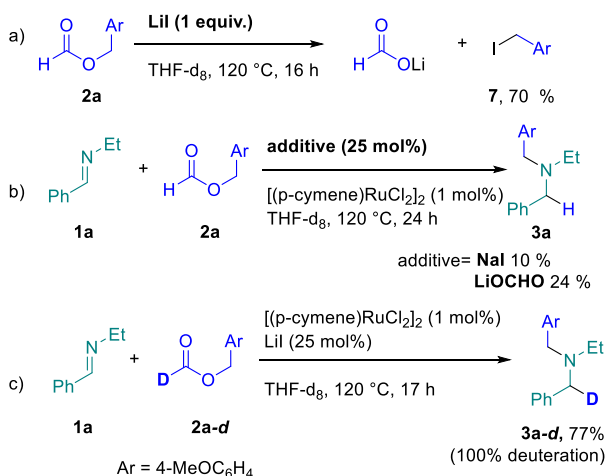


**Scheme 4:** Substrate scope in formate **2**. Reaction conditions: aldimine **1a** (0.20 mmol, 1.0 equiv.), formate **2** (0.24 mmol, 1.2 equiv.), Lil (50  $\mu$ mol, 25 mol%) [p-cymeneRuCl<sub>2</sub>]<sub>2</sub> (2  $\mu$ mol, 1 mol%), THF (0.5 mL), 120 °C, 24 h. Yields were measured by <sup>1</sup>H NMR (internal standard: mesitylene).

already inferred from the substrate scope, where the electronic and steric parameters of the imine had a limited influence on the reaction outcome (Scheme 2). The concentration of the ruthenium catalyst has a marginal impact on the kinetics because of a low partial order of 0.3. In contrast, the concentrations of alkyl formate **2** and Lil are decisive, suggesting that the activation of the alkyl formate by Lil is rate-determining.

Formate **2a** was thus reacted with 1 equivalent of Lil under the reaction conditions. After 16 h at 120°C, benzyl iodide **7** was obtained in 70 % yield (Scheme 5a), showing that Lil promotes the cleavage of the C–O  $\sigma$ -bond to form the iodinated electrophile **7** and lithium formate. Control experiments, using NaI or LiOCHO instead of Lil, provided **3a** in 10 and 24 % yields, respectively (Scheme 5b), pointing to the crucial role of both the lithium and iodide. The absence (or traces of) benzyl iodide **7** in the reaction mixture in the course of the reaction, confirmed that the cleavage of the C–O  $\sigma$  bond is indeed rate-determining. Finally, isotopic labeling confirmed the H-transfer from the formate (Scheme 5c).

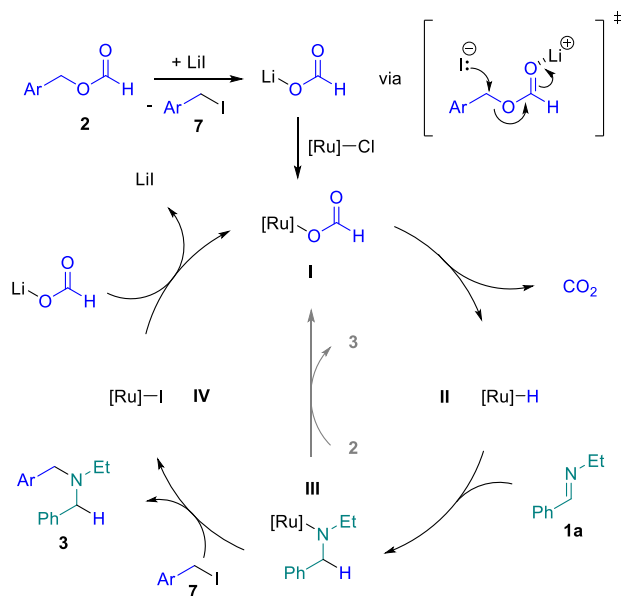
All together, these data support a mechanism where the alkyl formate reagent HCO<sub>2</sub>R is pre-activated by the Lil co-catalyst to generate a strong electrophile (RI) and a formate salt [Li][HCO<sub>2</sub>] (Scheme 6). The Lewis acidity of lithium(I) is key to facilitate this C–O bond cleavage. The release of the CO<sub>2</sub> linker is catalyzed by the ruthenium complex **I** which is able to decarboxylate a formate ligand into a hydride, and the presence of CO<sub>2</sub> was confirmed by the GC analysis of the gas phase (Supporting Information S3.1.6). The resulting hydride complex **II** is a potent reductant, able to reduce imine **1** by forming a C–H bond. The formation of the N–C bond in the final amine product (**3**) then arises from the alkylation of ruthenium amide **III** with benzyl iodide **7**. An alternative pathway could consist in the direct reaction of amide **III** with benzyl formate **2**, serving as the electrophile. Nevertheless, this route seems



**Scheme 5:** Mechanistic control experiments. Yields were measured by <sup>1</sup>H NMR (internal standard: mesitylene).

much slower, as replacing the Lil co-catalyst with lithium formate significantly hampered the kinetics of the catalytic reaction (Scheme 5b). A last transmetalation from ruthenium iodide complex **IV** with lithium formate regenerates ruthenium formate **I**.

In summary, we have developed a new class of easily accessible transfer reagents for hydroalkylation, namely alkyl formates, and demonstrated their utility in the transfer hydroalkylation of imines, as a proof-of-concept. Using a ruthenium catalyst in combination with Lil as a co-catalyst, the CO<sub>2</sub> linker in the alkyl formate is released and the resulting hydride nucleophile and alkyl electrophile enable the conversion of the imine to the functionalized amine product. These results pave the way to the development of new transfer hydroalkylations on unsaturated substrates, currently under investigation in our laboratory, using formates as bio-available and recyclable transfer reagents.



**Scheme 6:** Proposed mechanism for the conversion of imines to amines, using alkyl formates as transfer hydroalkylation agents.

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**Keywords:** alkyl formates • decarboxylation • transfer hydroalkylation • ruthenium catalysis • imines

- [1] a) *Hydrofunctionalization*, Vol. 43, Springer Berlin Heidelberg, Berlin, Heidelberg, **2013**; b) S. W. M. Crossley, C. Obradors, R. M. Martinez, R. A. Shenvi, *Chem. Rev.* **2016**, *116*, 8912–9000.
- [2] a) T. Pei, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2001**, *123*, 11290–11291; b) X. Yao, C.-J. Li, *J. Am. Chem. Soc.* **2004**, *126*, 6884–6885; c) K. Motokura, N. Fujita, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *Angew. Chem. Int. Ed.* **2006**, *45*, 2605–2609; *Angew. Chem.* **2006**, *118*, 2667–2671; d) M. Rueping, B. J. Nachtsheim, A. Kuenkel, *Synlett* **2007**, 2007, 1391–1394; e) T. Sawano, K. Ogihara, J. Sagawa, M. Ono, R. Takeuchi, *Org. Lett.* **2020**, *22*, 6187–6191; f) G. Lei, M. Xu, R. Chang, I. Funes-Ardoiz, J. Ye, *J. Am. Chem. Soc.* **2021**, *143*, 11251–11261.
- [3] a) P. M. Edwards, L. L. Schafer, *Chem. Commun.* **2018**, *54*, 12543–12560; b) J. Hannedouche, E. Schulz, *Organometallics* **2018**, *37*, 4313–4326; c) L. Gonnard, A. Guérinot, J. Cossy, *Tetrahedron* **2019**, *75*, 145–163.
- [4] a) J. S. M. Samec, J.-E. Bäckvall, P. G. Andersson, P. Brandt, *Chem. Soc. Rev.* **2006**, *35*, 237–248; b) O. Saidi, J. M. J. Williams, in *Iridium Catalysis* (Ed.: P. G. Andersson), Springer, Berlin, Heidelberg, **2011**, p. 77–106; c) M. Yoshimura, M. Kitamura, in *Organic Reactions*, John Wiley & Sons, Ltd, **2019**, p. 329–382.
- [5] H.-M. Huang, P. Bellotti, J. Ma, T. Dalton, F. Glorius, *Nat. Rev. Chem.* **2021**, *5*, 301–321.
- [6] a) Y. Takada, S. Hayashi, K. Hirano, H. Yorimitsu, K. Oshima, *Org. Lett.* **2006**, *8*, 2515–2517; b) M. Sai, H. Yorimitsu, K. Oshima, *Angew. Chem. Int. Ed.* **2011**, *50*, 3294–3298.
- [7] G. Li, R. Chen, L. Wu, Q. Fu, X. Zhang, Z. Tang, *Angew. Chem. Int. Ed.* **2013**, *52*, 8432–8436; *Angew. Chem.* **2013**, *125*, 8590–8594.
- [8] P.-Z. Wang, J.-R. Chen, W.-J. Xiao, *Org. Biomol. Chem.* **2019**, *17*, 6936–6951.
- [9] K. Nakajima, Y. Zhang, Y. Nishibayashi, *Org. Lett.* **2019**, *21*, 4642–4645.
- [10] a) F. F. de Assis, X. Huang, M. Akiyama, R. A. Pilli, E. Meggers, *J. Org. Chem.* **2018**, *83*, 10922–10932; b) T. van Leeuwen, L. Buzzetti, L. A. Perego, P. Melchiorre, *Angew. Chem. Int. Ed.* **2019**, *58*, 4953–4957; *Angew. Chem.* **2019**, *131*, 5007–5011; c) G. Goti, B. Bieszczyk, A. Vega-Peñalosa, P. Melchiorre, *Angew. Chem. Int. Ed.* **2019**, *58*, 1213–1217; d) T. Uchikura, K. Moriyama, M. Toda, T. Mouri, I. Ibáñez, T. Akiyama, *Chem. Commun.* **2019**, *55*, 11171–11174; e) T. Uchikura, M. Toda, T. Mouri, T. Fujii, K. Moriyama, I. Ibáñez, T. Akiyama, *J. Org. Chem.* **2020**, *85*, 12715–12723.
- [11] N. Chen, X.-J. Dai, H. Wang, C.-J. Li, *Angew. Chem. Int. Ed.* **2017**, *56*, 6260–6263; *Angew. Chem.* **2017**, *129*, 6356–6359.
- [12] H. Wang, X.-J. Dai, C.-J. Li, *Nat. Chem.* **2017**, *9*, 374–378.
- [13] X.-J. Dai, H. Wang, C.-J. Li, *Angew. Chem. Int. Ed.* **2017**, *56*, 6302–6306; *Angew. Chem.* **2017**, *129*, 6399–6403.
- [14] L. Yu, L. Lv, Z. Qiu, Z. Chen, Z. Tan, Y.-F. Liang, C.-J. Li, *Angew. Chem. Int. Ed.* **2020**, *59*, 14009–14013; *Angew. Chem.* **2020**, *132*, 14113–14117.
- [15] a) C. Chauvier, P. Thuery, T. Cantat, *Angew. Chem. Int. Ed.* **2016**, *55*, 14096–14100; *Angew. Chem.* **2016**, *128*, 14302–14306; b) C. Chauvier, T. Godou, T. Cantat, *Chem. Commun.* **2017**, *53*, 11697–11700; c) T. Cantat, T. Godou, C. Chauvier, P. Thuéry, *Synlett* **2017**, *28*, 2473–2477; d) R. M. Romero, N. Thyagarajan, N. Hellou, C. Chauvier, T. Godou, L. Anthore-Dalio, T. Cantat, *Chem. Commun.* **2022**.
- [16] G. Jenner, *Appl. Catal.*, **A** **1995**, *121*, 25–44.
- [17] a) J. S. Matthews, D. C. Ketter, R. F. Hall, *J. Org. Chem.* **1970**, *35*, 1694–1695; b) T. Kondo, S. Tantayanon, Y. Tsuji, Y. Watanabe, *Tetrahedron Lett.* **1989**, *30*, 4137–4140.
- [18] a) Y. Watanabe, T. Ohta, Y. Tsuji, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2441–2444; b) N. Uematsu, A. Fujii, S. Hashiguchi, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 4916–4917; c) N. Menashe, E. Salant, Y. Shvo, *J. Organomet. Chem.* **1996**, *514*, 97–102; d) Y. Gao, M. C. Jennings, R. J. Puddephatt, *Can. J. Chem.* **2001**, *79*, 915–921; e) C. P. Casey, S. W. Singer, D. R. Powell, *Can. J. Chem.* **2001**, *79*, 1002–1011.
- [19] Statistical redistribution of the N-substituents were observed leading to a medium yield (See Supporting information for more details)
- [20] J. Burés, *Angew. Chem. Int. Ed.* **2016**, *55*, 2028–2031; *Angew. Chem.* **2016**, *128*, 2068–2071.