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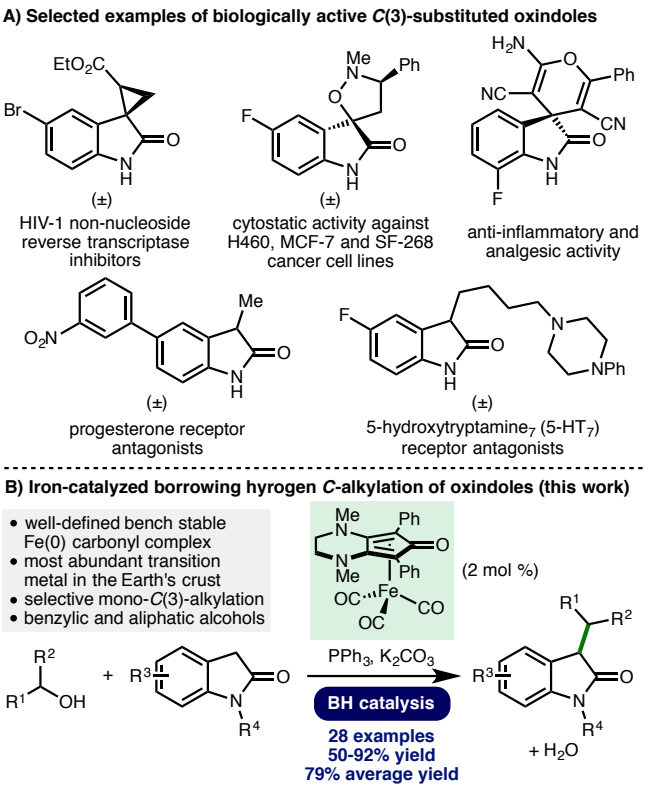
Iron-Catalyzed Borrowing Hydrogen *C*-Alkylation of Oxindoles Using Alcohols

Mubarak B. Dambatta,[a] Kurt Polidano,[a] Alexander D. Northey,[a] Jonathan M. J. Williams,[b] and Louis C. Morrill*[a]

Abstract: A general and efficient iron-catalyzed *C*-alkylation of oxindoles has been developed. This borrowing hydrogen approach employs a (cyclopentadienone)iron carbonyl complex (2 mol %) and exhibits a broad reaction scope, allowing benzylic and simple primary and secondary aliphatic alcohols to be employed as alkylating agents. A variety of oxindoles undergo selective mono-*C*(3)-alkylation in good to excellent isolated yields (28 examples, 50-92% yield, 79% average yield).

The oxindole framework is present in a diverse array of naturally occurring compounds.[1] Furthermore, oxindoles that are mono- or disubstituted at the *C*(3) position are commonly employed in drug discovery programmes,[2] with examples including the development of HIV-1 non-nucleoside reverse transcriptase inhibitors, spircocyclic compounds with anti-cancer and anti-inflammatory properties, and antagonists of progesterone and 5-hydroxytryptamine$_7$ (5-HT$_7$) receptors (Scheme 1A). The traditional method for alkylation of unprotected oxindoles employs toxic alkyl halides and exhibits poor selectivity (mono- vs. dialkylation, *C*- vs. *N*-alkylation) alongside the generation of stoichiometric quantities of undesired byproducts.[3] An alternative approach employs the borrowing hydrogen (BH) principle, also known as hydrogen autotransfer, which allows bench stable and inexpensive alcohols to be used as alkylating agents, generating water as the sole byproduct.[4] Recent progress in this area has provided alternatives to commonly employed precious metal catalysts through the development of catalysts based on earth-abundant first row transition metals.[5]

The BH alkylation of oxindoles using alcohols, which selectively produces mono-*C*(3)-alkylation products, has been reported using heterogeneous catalysis,[6] and by employing homogeneous precious metal catalyst systems based on ruthenium and iridium.[7] However, with respect to earth-abundant first row transition metal catalysis, only sporadic examples appear in the literature, in each case forming only a minor component of a broader study.[8] As such, the development of a general catalytic BH *C*-alkylation of oxindoles using well-defined complexes based on earth-abundant first row transition metals is required and would represent a valuable addition to the synthetic toolbox. To this end, herein we report the use of a bench stable (cyclopentadieneone)iron(0) carbonyl complex (2 mol %) for the selective mono-*C*(3)-alkylation of various oxindoles using both benzylic and simple primary and secondary aliphatic alcohols as alkylating agents (Scheme 1B).[9]



Scheme 1. Oxindole importance and project overview work.

To commence our studies, we selected the *C*(3)-benzylation of oxindole **2** with benzyl alcohol **1** (1.2 equiv.) as a model system (Table 1). After extensive optimization,[10] it was found that a BH system composed of bench stable (cyclopentadieneone)iron(0) carbonyl complex **3** (2 mol %),[11] triphenylphosphine (4 mol %) to form the active catalyst, K_2CO_3 (0.5 equiv.) as base in xylenes ([**2**] = 0.5 M) at 150 °C for 24 h, enabled the efficient *C*-benzylation of **2**, giving **4** in 97% NMR yield and 90% isolated yield (entry 1).[12] Importantly, only 1.2 equivalents of the alkylating agent and substoichiometric quantities of base were required for complete conversion, giving a high atom economy process.[13] No alkylation occurs in the absence of iron precatalyst **3** (entry 2), with only 26% conversion observed in the absence of K_2CO_3 (entry 3). The PPh_3-bound [Fe] precatalyst **5** could be employed, accessing **4** in 95% NMR yield (entry 4), verifying it as a plausible catalytic intermediate (c.f. Scheme 3). Interestingly, from the iron complexes employed

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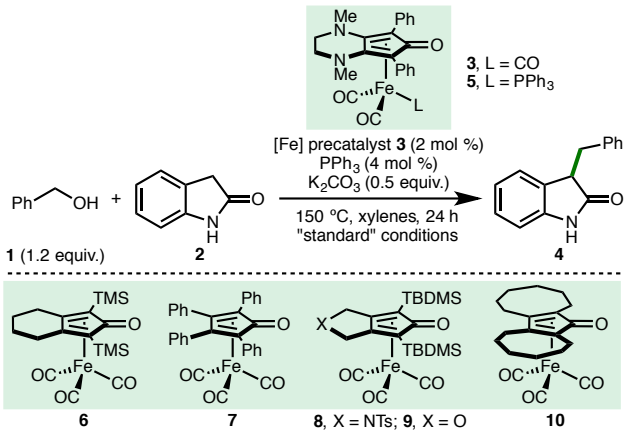
Information about the data that underpins the results presented in this article, including how to access them, can be found in the Cardiff University data catalogue at under: http://XXXX (accessed XXXX)

Table 1: Optimization of the Fe-catalyzed oxindole *C*-benzylation.[a]



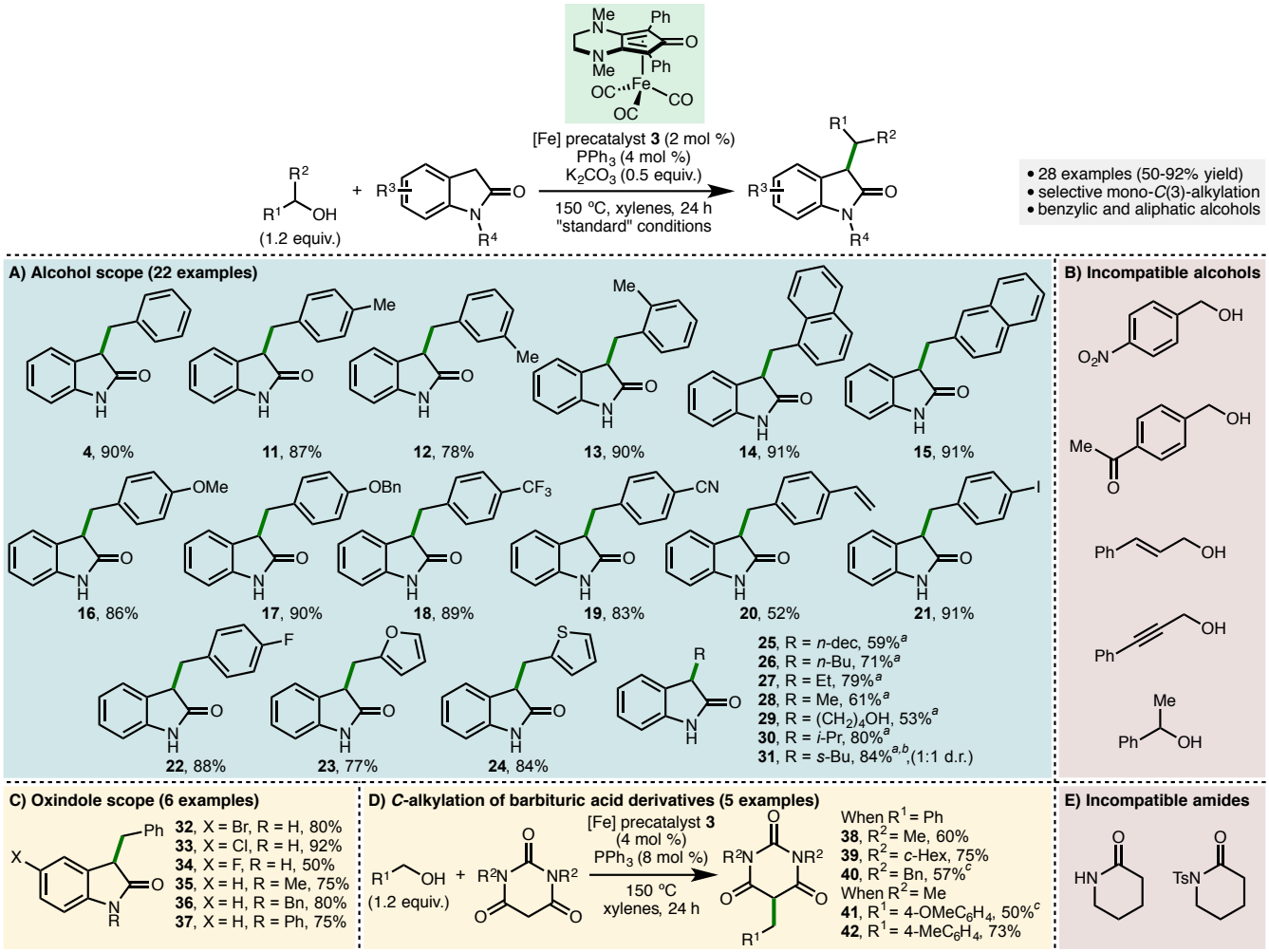
entry	variation from "standard" conditions	yield[b] (%)
1	**none**	**97 (90)**
2	no [Fe] precatalyst **3**	< 2
3	no K_2CO_3	26
4[c]	**5** (2 mol %) instead of **3**	95
5	**6** (2 mol %) instead of **3**	18
6	**7** (2 mol %) instead of **3**	5
7	**8** (2 mol %) instead of **3**	5
8	**9** (2 mol %) instead of **3**	5
9	**10** (2 mol %) instead of **3**	5
10	no PPh_3 activator	90
11	Me_3NO (4 mol %) instead of PPh_3	92
12	Cs_2CO_3 (0.5 equiv) instead of K_2CO_3	85
13	K_2CO_3 (0.1 equiv)	88
14	toluene instead of xylenes	91
15	[**2**] = 1 M	93
16	130 °C	86
17	reaction time = 6 h	92
18[d]	[Fe] precatalyst **3** (1 mol %)	73

[a] Reactions performed using 1 mmol of oxindole **2** and bench-grade xylenes. [**2**] = 0.5 M. [b] Yield after 24 h as determined by ^{1}H NMR analysis of the crude reaction mixture with 1,3,5-trimethylbenzene as the internal standard. Isolated yield given in parentheses. [c] no PPh_3. [d] 2 mol % of PPh_3.

in this study, it was found that (cyclopentadienone)iron carbonyl precatalysts **3** and **5**, which contain a more electron-rich cyclopentadienone framework, were uniquely effective for the desired transformation, with the use of alternative iron precatalysts **6**-**10** resulting in low to negligible formation of alkylated oxindole **4** (entries 5-9).[14] The reaction can be performed in the absence of PPh_3, albeit in a slightly diminished yield, indicating thermal activation of the precatalyst occurs at 150 °C (entry 10).[11] Substituting triphenylphopshine for trimethylamine *N*-oxide (4 mol %),[15] also had a slightly negative impact on the reaction (entry 11). Employing Cs_2CO_3 as base resulted in lower conversion to **4** (entry 12). Lowering the quantity of K_2CO_3 (entry 13), highlighted that catalytic quantities of base (10 mol %) can be employed, accessing **4** in 88% NMR yield. Employing toluene as solvent (entry 14), increasing the reaction concentration (entry 15), lowering reaction temperature (entry 16), reducing reaction time (entry 17), or reducing the catalyst loading (entry 18), all lowered the efficiency of the iron-catalyzed mono-*C*(3)-benzylation of **2**.

The full scope of the Fe-catalyzed BH *C*(3)-alkylation of oxindoles was explored, starting with the *C*-alkylation of oxindole **2** (Scheme 2A/B).[16] Using the optimized reaction conditions (Table 1, entry 1) a variety of substituted benzylic alcohols can be employed as alkylating agents, giving the corresponding mono-*C*(3)-alkylated oxindoles in excellent isolated yields (products **4** and **11**−**24**, 52-91% yield). Within the alcohol, sterically encumbered aryl units such as *o*-tolyl and 1-naphthyl were tolerated in addition to electron-donating (4-OMe, 4-OBn) and electron-withdrawing (4-CF_3, 4-CN) substituents. The catalytic system exhibits chemoselectivity, tolerating the reducible nitrile and alkene moieties present within products **19** and **20**. 4-Iodobenzyl alcohol was employed as the alkylating agent, incorporating an additional functional handle into oxindole **21** for subsequent elaboration *via* established cross-coupling methods.[17] Furan-2-ylmethanol and thiophene-2-ylmethanol were both compatible with this methodology, incorporating an additional heterocycle into products **23** and **24**, which were formed in 77% and 84% isolated yield, respectively. We were pleased to discover that less activated simple aliphatic alcohols can also be employed as alkylating agents in this process (products **25**−**31**, 53-84% yield). In each case, the alcohol was used as solvent in order to obtain high isolated yields of the mono-*C*(3)-alkylated oxindoles. Under otherwise identical reaction conditions, decan-1-ol, butan-1-ol, ethanol and methanol were all successfully utilized as alkylating agents. 1,4-Butanediol was also employed as the alkylating agent, accessing mono-*C*(3)-alkylated oxindole **29** in 53% isolated yield, with no dialkylation products observed. Remarkably, it was found that unactivated secondary alcohols propan-2-ol and butan-2-ol, were also tolerated, giving alkylated oxindoles **30** and **31** in excellent isolated yields. This is a rare example of secondary alcohol compatibility as alkylating agents in BH catalysis employing earth-abundant first row transition metal catalysts.[18] Unfortunately, despite examining a range of alternative reaction conditions, benzylic alcohols containing nitro or ketone functional groups, allylic alcohols, propargylic alcohols and bulkier secondary alcohols (e.g. 1-phenylethan-1-ol) were found to be incompatible with this *C*-alkylation procedure.

Next, we explored the scope of the reaction with respect to variation within the oxindole component (Scheme 2C). Employing the optimized reaction conditions (Table 1, entry 1) a variety of substituted oxindoles undergo efficient and selective mono-*C*(3)-alkylation with benzyl alcohol (products **32**−**37**, 50-92% yield). Oxindoles containing halogen substitution at the 5-position (5-Br, 5-Cl and 5-F) in addition to *N*-methyl, *N*-benzyl and *N*-phenyl substitution were all well tolerated. Barbituric acids are a class of activated amide that have been shown to participate as competent nucleophiles in homogeneous BH alkylation processes employing precious metal catalysts.[19] Using [Fe] precatalyst **3** (4 mol %), it was found that a selection



Scheme 2. Scope of the Fe-catalyzed *C*-alkylation of oxindoles. Reactions performed using 1 mmol of oxindole starting material and bench-grade xylenes. All yields are isolated yields after chromatographic purification. Reagents and conditions: [a] alcohol used as solvent; [b] [Fe] precatalyst **3** (4 mol %), PPh_3 (8 mol %); [c] K_2CO_3 (0.5 equiv.).

of *N*-alkyl barbituric acid derivatives undergo efficient *C*(5)-monoalkylation, giving products **38**−**42** in 50-75% isolated yield (Scheme 2D). This iron-catalyzed process is the first example of a BH alkylation of barbituric acid derivatives employing an earth-abundant transition metal catalyst. Unfortunately, piperdin-2-one and 1-tosylpiperdin-2-one were found to be incompatible with this protocol, with complex reaction mixtures obtained across a range of reaction conditions explored.

To obtain insight into the reaction mechanism, α,β-unsaturated amide **43** was synthesized and subjected to the "standard" *C*-alkylation reaction conditions, which produced **4** in 71% NMR yield, indicating that **43** is a plausible reaction intermediate (Scheme 3A). In line with this observation, and previous related investigations,[11] a plausible reaction mechanism initiates with CO decoordination of [Fe] precatalyst **3** by PPh_3 to form the active iron complex, which abstracts hydrogen from benzyl alcohol in the presence of base to form the required transient reactive benzaldehyde intermediate (Scheme 3B). Subsequent nucleophilic attack of oxindole **2** generates β-hydroxy amide **44** that undergoes rapid base-catalyzed E1cB dehydration to form α,β-unsaturated amide **43**. Finally, reduction of **43** by the iron-hydrogen complex gives *C*(3)-alkylated product **4** with regeneration of the active iron complex.

In conclusion, we have developed a general and efficient Fe-catalyzed *C*-alkylation of oxindoles using benzylic and simple primary and secondary aliphatic alcohols as alkylating agents *via* the borrowing hydrogen approach. A variety of oxindoles undergo selective mono-*C*(3)-alkylation in excellent isolated yields (28 examples, 50-92% yield, 79% average yield). Ongoing studies are focused on further applications of earth-abundant first row transition metals in catalysis and these results will be reported in due course.

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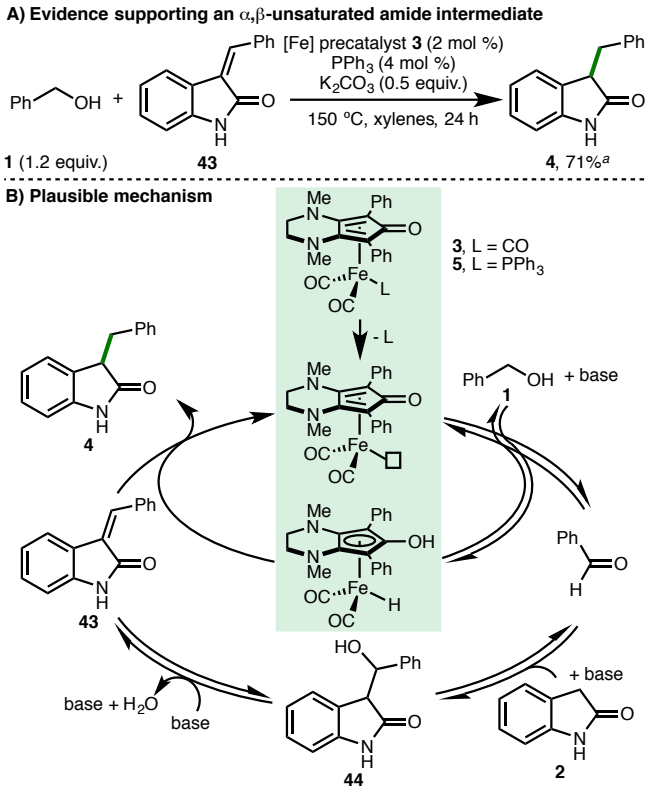
Conflict of interest

The authors declare no conflict of interest



Scheme 3. Mechanistic considerations. [a] Yield after 24 h as determined by ^{1}H NMR analysis of the crude reaction mixture with 1,3,5-trimethylbenzene as the internal standard.

Keywords: iron catalysis • borrowing hydrogen • alkylation • oxindoles • alcohols

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[10] See the Supporting Information for full experimental details.

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[12] When **4** was employed as starting material using the optimized reaction conditions, 100% of **4** was returned after 24 h.

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[18] For selected examples, see: a) A. J. Rawlings, L. J. Diorazio, M. Wills, *Org. Lett.* **2015**, *17*, 1086-1089; b) H.-J. Pan, T. W. Ng, Y. Zhao, *Chem. Commun.* **2015**, *51*, 11907-11910; c) G. Di Gregorio, M. Mari, F. Bartoccini, G. Piersanti, *J. Org. Chem.* **2017**, *82*, 8769-8775; d) T. J. Brown, M. Cumbes, L. J. Diorazio, G. J. Clarkson, M. Wills, *J. Org. Chem.* **2017**, *82*, 10489-10503; e) P. Yang, C. Zhang, Y. Ma, C. Zhang, A. Li, B. Tang, J. S. Zhou, *Angew. Chem. Int. Ed.* **2017**, *56*, 14702-14706.

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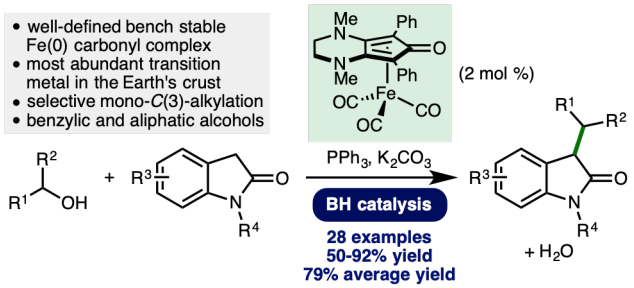
Entry for the Table of Contents

Layout 2:

COMMUNICATION



I'm only borrowing it!: A general and efficient iron-catalyzed *C*-alkylation of oxindoles has been developed. This borrowing hydrogen approach employs a (cyclopentadienone)iron carbonyl complex (2 mol %) and exhibits a broad reaction scope, allowing benzylic and simple primary and secondary aliphatic alcohols to be employed as alkylating agents. A variety of oxindoles undergo selective mono-*C*(3)-alkylation in good to excellent isolated yields (28 examples, 50-92% yield, 79% average yield).

*Mubarak B. Dambatta, Kurt Polidano, Andrew D. Northey, Jonathan M. J. Williams and Louis C. Morrill**

Page No. – Page No.

Iron-Catalyzed Borrowing Hydrogen *C*-Alkylation of Oxindoles Using Alcohols