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Iron promoted C3–H nitration of 2*H*-indazole: direct access to 3-nitro-2*H*-indazoles†

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An efficient C3–H functionalization of indazole has been demonstrated. Notably, this method involves chelation-free radical C–H nitration on 2*H*-indazole. The radical mechanism was confirmed by control experiments and quantum chemical calculations. The synthetic utility has been proven by the synthesis of bio-relevant benzimidazoindazoles *via* reductive cyclization.

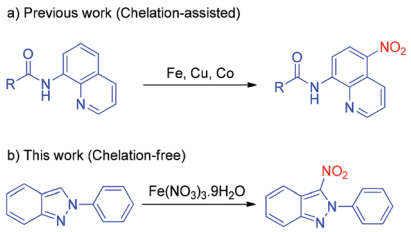
Introduction

Direct C–H functionalization has become a reliable and robust method for various transformations,[1] *i.e.* the carbon–hydrogen bond to the carbon–carbon and carbon–heteroatom bonds to construct complex molecules due to its high step- and atom-economy.[2] Recently, direct C–H functionalization *via* a radical pathway has become a rapidly expanding area of research and has emerged as a promising and sustainable approach towards molecular construction often complementary to traditional methods.[3] Despite these developments selective C–H functionalization *via* a radical pathway is still in its infancy and controlling the reactivity and chemo/regioselectivity of radical species for the selective C–H functionalization requires efforts to find more mild and suitable methods which poses many opportunities and challenges to address.[4]

Owing to the ubiquitous nature of heteroarenes in agrochemicals and pharmaceuticals,[5] the direct C–H functionalization of heteroarenes is a highly attractive strategy providing a concise route for complex molecules as well as for late-stage functionalization (LSF) of bioactive molecular scaffolds and hence offers tremendous opportunities for chemists.[6] Among them, C–H functionalization of heteroarenes *via* a radical pathway is one of the most appealing and straightforward strategies.[7]

Heteroaromatic nitro compounds are of great significance due to their importance as key precursors in organic synthesis[8] and their potential for further transformations. In recent years, several chemists have achieved a transition-metal-catalyzed radical C–H nitration on arenes/heteroarenes by using various nitro sources,[9] such as $AgNO_2$,[9a–d] ^tBuONO,[9e,f] $Cu(NO_3)_2$[9h,i] and $Fe(NO_3)_3{\cdot}9H_2O$.[11d] Among all metal nitrates, $Fe(NO_3)_3{\cdot}9H_2O$ as a non-toxic, inexpensive and green reagent is well known for various radical nitration strategies such as nitration on olefins,[10a–c] allenes[10d] and imines.[10e] However, its application in aromatic nitration is rare, except for a recent nitration on 8-aminoquinoline.[11d] Hence, there is a broad scope for the development of strategies for radical nitration of arenes and heteroarenes (Scheme 1).[11]

As an important class of heteroarenes, indazole motifs are embedded in pharmaceuticals with a broad range of biological activities,[12,13] including antitumor,[14] antimicrobial,[15] anti-inflammatory,[16] and HIV-protease inhibition.[17] Hence, there have been extensive efforts directed towards the synthesis of indazole derivatives. Due to the recent emergence of radical C–H functionalization as a new paradigm in contemporary chemistry and as a part of our research program on C–H functionalization and indazole chemistry,[18] we were interested in developing radical C–H functionalization as a new approach for func-



Scheme 1 Radical C–H nitration of heteroarenes.

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tionalized indazoles. Recently, Wu *et al.* have demonstrated the regioselective C–H functionalization of 8-aminoquinoline through theoretical data calculations.[7e] Accordingly, we planned to support our findings on radical C–H functionalization through quantum chemical calculations. Herein, we are delighted to disclose for the first time a radical C–H functionalization of 2*H*-indazole through $Fe(NO_3)_3{\cdot}9H_2O$ promoted C3–H nitration.

Results and discussion

To achieve our goal, we initiated our preliminary experiments with 2*H*-indazole (**1a**) as a model substrate and $Fe(NO_3)_3{\cdot}9H_2O$ as a nitro source in MeCN as a solvent at 80 °C under an oxygen atmosphere (Table 1, entry 1). As expected, a C3-nitro functionalized product (**2a**) was obtained albeit in very poor yield. Inspired by this result, we screened various nitro sources (Table 1, entries 2–8). However, we did not observe any satisfactory yields.

Next, we turned to the use of the oxidant (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) in the reaction. Surprisingly, we observed the expected product in very good yield in the presence of TEMPO (Table 1, entry 9). Furthermore, our attempts of replacing TEMPO with other oxidants went in vain (Table S1, ESI†).

Furthermore we also screened the reaction with different solvents (Table 1, entries 10–18) and varying temperatures (Table S2, ESI†). Interestingly, we have observed the formation of the product with very good yield in the case of DCE as a solvent (Table 1, entry 10). Notably, when we performed the reaction in open air, we observed the formation of the expected product with moderate yield (Table 1, entry 19). Subsequently, we screened the reaction with different equivalents of nitro sources and oxidants (Tables S1 & S3, ESI†). From these experiments we concluded that 2 equiv. of nitro source and 1 equiv. of oxidant are necessary for the complete conversion of the starting materials.

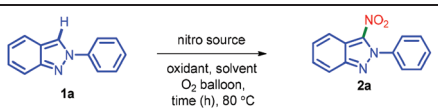
With the optimized conditions in hand, we next examined the scope of this methodology with different substituted 2*H*-indazole systems (Table 2). The methylenedioxy substitution gave good yield when compared to halo substitution at the 5th, 6th and 7th positions of 2*H*-indazoles **2c–g**.

Next, we examined the scope of substrates with various substitutions (halogen, alkyl, alkoxy) on the amine partner of 2*H*-indazoles resulting in desired products with moderate to good yields. Having the benzyl group in place of aryl at the 2nd position of 2*H*-indazoles **2w** & **x** did not show any improvement in the yield.

Unfortunately, amine partner bearing electron withdrawing groups, such as nitro, nitrile and ester groups did not afford the desired products **2aa–ac**. In addition, 2*H*-indazoles with alkyl substitution at the 2nd position of **2ad** & **ae** could not afford the nitration product. Furthermore, our attempts to carry out nitration on other heteroarenes (indole, imidazole, 1*H*-indazole) went in vain.

Based on the experiments performed for the optimization of reaction conditions shown in Table 1, we observed that other nitro sources failed to give any nitro product, hence in order to prove the role of $Fe(NO_3)_3{\cdot}9H_2O$, we planned to examine the reaction with metal free nitro sources, however, in the presence of Fe/Cu as a promotor which resulted in good yield (Scheme 2b), thus indicating the dual role of $Fe(NO_3)_3{\cdot}9H_2O$. Furthermore, the reaction in the absence of any promotor with metal-free nitrate (TBN) did not afford the desired product (Scheme 2c). Hence, the promotor is necessary for the nitration of indazole at the C3 position. To prove the radical pathway, we performed HR-MS analysis of the crude reaction mixture, which showed 2,2,6,6-tetramethylpiperidin-1-ol. To know the role of oxygen, we have conducted a couple of control experiments. We obtained the desired product in 10% and 15% yield when the reaction was carried out in the absence of O_2 and TEMPO respectively (Scheme 2e & d). However, these experiments are not conclusive. When we performed the reaction in the presence of an excess amount of TEMPO (2 equiv.) under an argon atmosphere, 80% yield of the desired product was obtained (Scheme 2f). This indicates that the presence of oxygen reduces the amount of TEMPO significantly (optimized conditions *i.e.* 1 equiv. of TEMPO under an oxygen atmosphere). From these experiments, we can conclude that 'O_2' might involve either in the recycling of TEMPO (TEMPOH to TEMPO) or in the direct oxidation of intermediate **B** to intermediate **C**. Finally, to confirm the C3-functionalization of 2*H*-indazole, we performed the reaction with C3 sub-

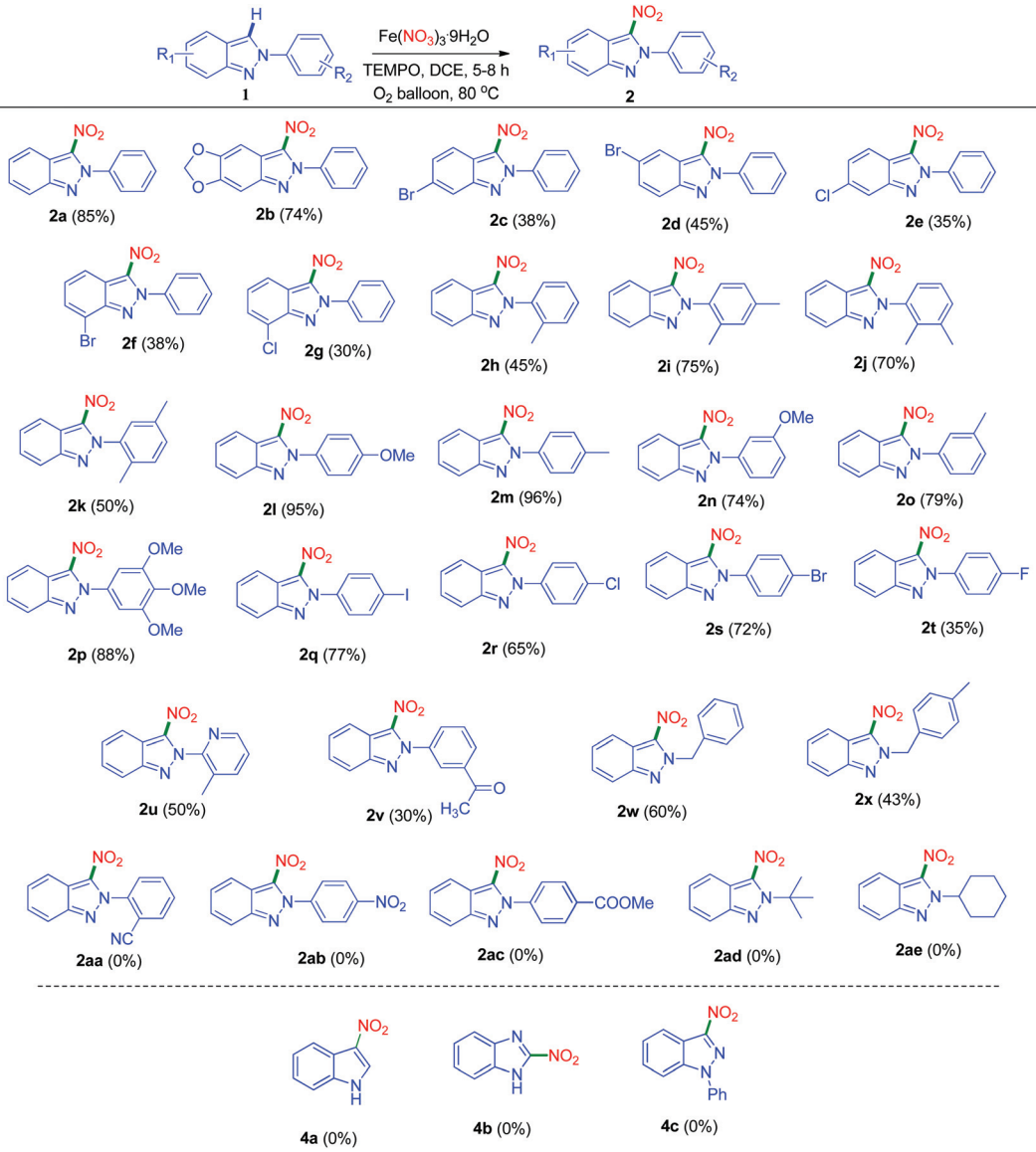
Table 1 Optimization of reaction conditions for the synthesis of **2a**[a]



Entry	Nitro source	Oxidant	Solvent	Time (h)	Yield[b] (%)
1	$Fe(NO_3)_3{\cdot}9H_2O$	—	MeCN	5	15
2	$Ni(NO_3)_2{\cdot}6H_2O$	—	MeCN	5	Trace
3	CAN	—	MeCN	5	Trace
4	^tBuONO	—	MeCN	5	n.d.[c]
5	$AgNO_3$	—	MeCN	5	n.d.[c]
6	$AgNO_2$	—	MeCN	5	n.d.[c]
7	$NaNO_2$	—	MeCN	5	n.d.[c]
8	$Cu(NO_3)_2{\cdot}3H_2O$	—	MeCN	5	10
9	$Fe(NO_3)_3{\cdot}9H_2O$	TEMPO	MeCN	5	65
10	**$Fe(NO_3)_3{\cdot}9H_2O$**	**TEMPO**	**DCE**	**5**	**85**
11	$Fe(NO_3)_3{\cdot}9H_2O$	TEMPO	$CHCl_3$	5	55
12	$Fe(NO_3)_3{\cdot}9H_2O$	TEMPO	DMF	12	nr[d]
13	$Fe(NO_3)_3{\cdot}9H_2O$	TEMPO	DMSO	12	n.d.[c]
14	$Fe(NO_3)_3{\cdot}9H_2O$	TEMPO	Dioxane	12	n.d.[c]
15	$Fe(NO_3)_3{\cdot}9H_2O$	TEMPO	Toluene	12	n.d.[c]
16	$Fe(NO_3)_3{\cdot}9H_2O$	TEMPO	H_2O	12	n.d.[c]
17	$Fe(NO_3)_3{\cdot}9H_2O$	TEMPO	EtOH	12	n.d.[c]
18	$Fe(NO_3)_3{\cdot}9H_2O$	TEMPO	MeOH	12	n.d.[c]
19	$Fe(NO_3)_3{\cdot}9H_2O$	TEMPO	DCE	5	60.[d]

[a] Reaction conditions: **1a** (1 mmol), nitro source (2 mmol), oxidant (1 mmol), solvent (1 mL), oxygen balloon, 80 °C, 5–12 h. [b] Isolated yield of chromatographically pure products. [c] Starting materials recovered. [d] Reaction carried out in open air.

Table 2 Substrate scope for the C3-nitration of 2*H*-indazole[a,b]



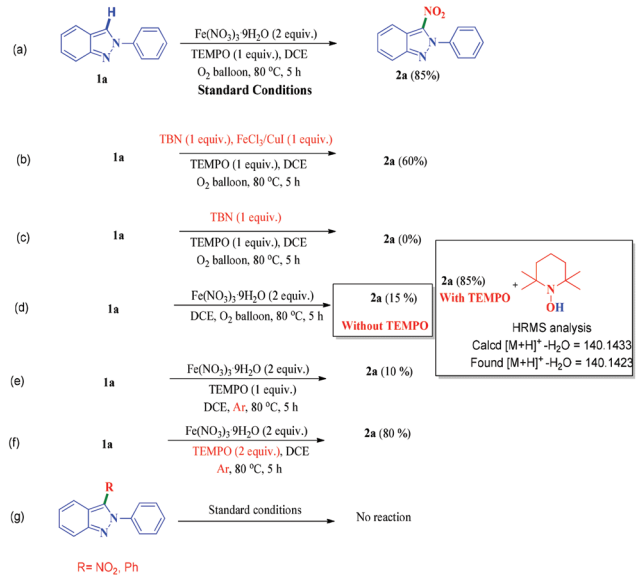
[a] Conditions: **1a** (1 mmol), $Fe(NO_3)_3{\cdot}9H_2O$ (2 mmol), TEMPO (1 mmol), DCE (2 mL), oxygen balloon, 80 °C, 5–8 h. [b] Isolated yield of chromatographically pure products.

stituted 2*H*-indazole under standard conditions (Scheme 2g), which did not afford any nitro substituted 2*H*-indazole. The X-ray crystallography analysis of compound **2t** further supports the nitration at the C3 position.

To further support our finding, we carried out quantum chemical calculations[7e] to investigate the charge distribution on indazole. The theoretical data of atoms (C3, C4, C6) on the Fe coordinated indazole intermediate **A** are shown in Table 2. The charges of the C3, C4 and C6 as calculated were found to be −0.025, −0.027 and −0.037 respectively (Table 3).

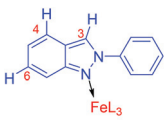
The charges include the contribution from all valance electrons and based on the literature precedence[7e] the p_z orbital occupancy would be a more effective way to assess the reactivity of a specific atom. Among various atoms, the largest p_z orbital occupancy at the C3 carbon atom implicates that C3 may be the most likely electrophilic reactive site. Thus the theoretical calculations support the only C3–H nitration on 2*H*-indazole.

Based on the control experiments, literature reports[7e,9a,11d] and quantum chemical calculations, we have proposed a plausible mechanism for the synthesis of 3-nitro-2-phenyl-2*H*-indazole as depicted in Scheme 3. Initially, coordination of 2-phenyl-2*H*-indazole with $Fe(NO_3)_3{\cdot}9H_2O$ led to the formation of intermediate **A**. Meanwhile, the nitro radical ($NO_2^{\bullet}$) generated from $Fe(NO_3)_3{\cdot}9H_2O$ under thermal conditions[19] would react at the electrophilic reactive site of the intermediate **A** in

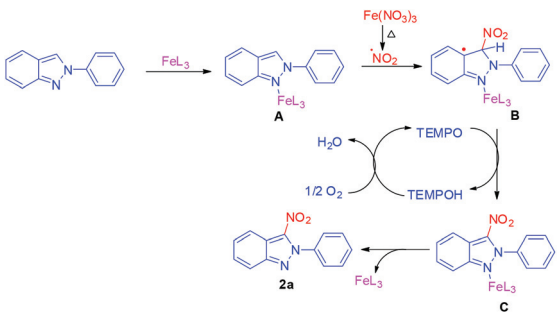


Scheme 2 Control experiments.

Table 3 Charge distribution and p_z orbital occupancy of the C3, C4 and C6 atoms in structure A

	Atom	Hirshfeld	p_z orbital occupancy
	C3	−0.025	0.997
	C4	−0.037	0.990
	C6	−0.027	0.980

A

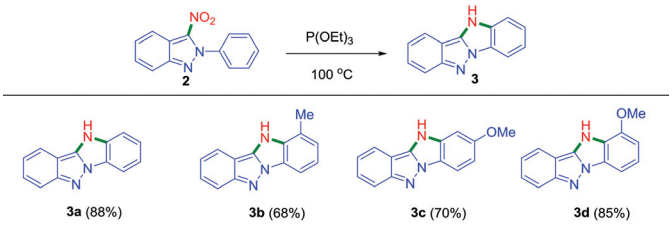


Scheme 3 Plausible mechanism.

order to generate an intermediate **B**. The combination of TEMPO/O_2 is involved in oxidation by the abstraction of a hydrogen radical[20] from the C3 position of intermediate **B** leading to the formation of intermediate **C**, which eventually provides the desired product **2a**.

After we synthesized various C3-nitro 2*H*-indazoles, we successfully demonstrated the synthetic utility of nitro indazoles by the synthesis of bio-relevant benzimidazoindazoles through reductive cyclization (Table 4).

Table 4 Synthesis of benzimidazoindazoles[a,b]



[a] Reaction conditions: **2a** (0.1 mmol), $P(OEt)_3$ (1 mL), 100 °C, 1 h. [b] Isolated yield of chromatographically pure products.

Conclusions

In conclusion we have developed a novel protocol for the radical C–H nitration of 2*H*-indazoles. This method offers chelation-free C–H nitration on 2*H*-indazole by using the inexpensive and nontoxic $Fe(NO_3)_3{\cdot}9H_2O$ under mild conditions. Moreover, the mechanistic pathway was inferred on the basis of control experiments and quantum chemical calculations. The synthetic utility of nitroindazoles was demonstrated by the synthesis of bio-relevant benzimidazoindazoles. This unique radical C–H nitration of 2*H*-indazoles should open new avenues for the C–H functionalization of 2*H*-indazoles and studies in this direction are currently underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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