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Iron-Catalyzed Minisci Type Acetylation of *N*-Heteroarenes Mediated by CH(OEt)₃/TBHP

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Abstract: Iron-catalyzed acetylation of electron deficient *N*-heteroarenes has been reported using triethylorthoformate as robust and inexpensive acetyl source. This new method is

successfully applied for the acetylation of quinolines, isoquinoline, quinoxalines, arylpyridines, bipyridines, and benzothiazole.

Introduction

N-heterocycles, such as quinoline and isoquinoline derivatives, are key structural motifs of natural products and biologically active scaffolds. In particular, quinoline alkaloids have attracted great interest, due to their antitussive, antipsychotic, antispasmodic, anxiolytic, antibacterial, antifungal and anticancer activities.^[1] Consequently, design of synthetic approaches allowing rapid and straightforward access to these compounds from simple and non-prefunctionalized precursors is an attractive research field. In this context, Minisci reaction,^[2] implying radical C–H functionalization of electron deficient *N*-heteroarenes established itself as a method of choice to install alkyl or acyl moieties. Following this seminal work, a variety of protocols allowing radical acylation of electron-deficient *N*-heteroarenes have been devised.^[2] Accordingly, α -keto acids,^[2b] aldehydes,^[2c] benzylamines,^[2d] aryl methanes^[2e] etc., have proven to be appealing coupling partners to rapidly introduce aromatic and aliphatic acyl moieties. In clear contrast, direct installation of the acetyl moiety is much more challenging. Indeed, acetylation is not possible when toluene derivatives or benzylamines substrates are used as aldehyde source and when 2-oxopropanoic acid is selected as acetyl precursor, use of a silver salt in combination with strong oxidants and additives are needed.^[2] Zhu and co-workers discovered that gold is also promising catalyst for such reaction, allowing a radical coupling between a large panel of *N*-heterocycles and ethanol.^[3] Recently, silver-catalyzed acetylation mediated by a mild Selectfluor oxidant was dis-

closed by Baxter.^[4] In parallel, a metal-free acetylation of isoquinoline was achieved using α -keto acids as coupling partner, in combination with potassium persulfate oxidant.^[5] A rare example of mild protocol employing formaldehyde as coupling partner was disclosed by Antonchick.^[6] However, efficiency of this strategy and its generality need for PIFA oxidant and TMSN₃ might be limiting. Finally, an original electrocatalytic approach has been conceived very recently, delivering acetylated heteroarenes in a presence of pyruvic acid.^[7]

Considering the importance of functionalized *N*-heterocycles, we surmised that design of new routes towards a large panel of acetylated products, using cheap and abundant metal-catalyst is a challenging research field. Accordingly, herein we report an alternative strategy for acetylation of *N*-heterocycles, using for the first time triethylorthoformate in combination with TBHP as robust and inexpensive acetyl radical source. Remarkably, the desired reactivity is achieved with a cheap and abundant iron catalyst and the coupling occurs without the need of external solvent, since triethylorthoformate is used as self-solvent: This work follows our previous contribution on the iron catalyzed oxidative cross coupling reactions.^[8–11]

Results and Discussion

We initiated our experimental work by establishing optimal reaction conditions for acetylation of 2-methylquinoline **1a** with triethylorthoformate **2**. Rapidly it was discovered that when **1a** (1 mmol) was treated with an excess amount of **2** in the presence of **3** (3 equiv. of TBHP 70 % aq solution) at 100 °C, 4-acetyl-2-methyl quinoline **4a** was formed in 74 % yield (Table 1, entry 1). By varying the temperature to 90 °C or 110 °C, the efficiency of the coupling was decreased to 61 % and 65 % respectively (Table 1, entries 2 and 3). Subsequently, it was determined that 4 equivalents is an optimal amount of TBHP oxidant (Table 1, entries 4,5). Increasing catalyst loading, 20 mol-%, had slightly harmful impact on the reaction (Table 1 entry 6). By changing the oxidation state of Fe^{III} to Fe^{II} the yield of the product **4a** has decreased to 62 % (Table 1, entry 7). Other Fe^{III} catalysts such as ferric chloride hexahydrate or simple ferric chloride

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delivered **4a** in lowered yields of 58 % and 54 % respectively (Table 1, entries 8 and 9). Altering the oxidation state of the catalyst from Fe^{III} to Fe^{II} drastically hampered the reaction [**4a** isolated in 42 % with FeCl₂ and 20 % with Fe(acac)₂ respectively; Table 1, entries 10 and 11]. The absence of water in TBHP (TBHP in Decane) did not improve the yield of the product **4a** (Table 1, entry 12). No enhancement was achieved by changing the oxidant from TBHP to DTBP (Di *tert*-butyl peroxide), TBPB (*tert*-butyl peroxybenzoate), DCP (Dicumyl peroxide) and H₂O₂ (Table 1, entries 13–16). The product **4a**, was not detected neither in the absence of Fe^{III} perchlorate catalyst nor TBHP (Table 1, entries 17 and 18).

Table 1. Screening of reaction conditions.^[a]

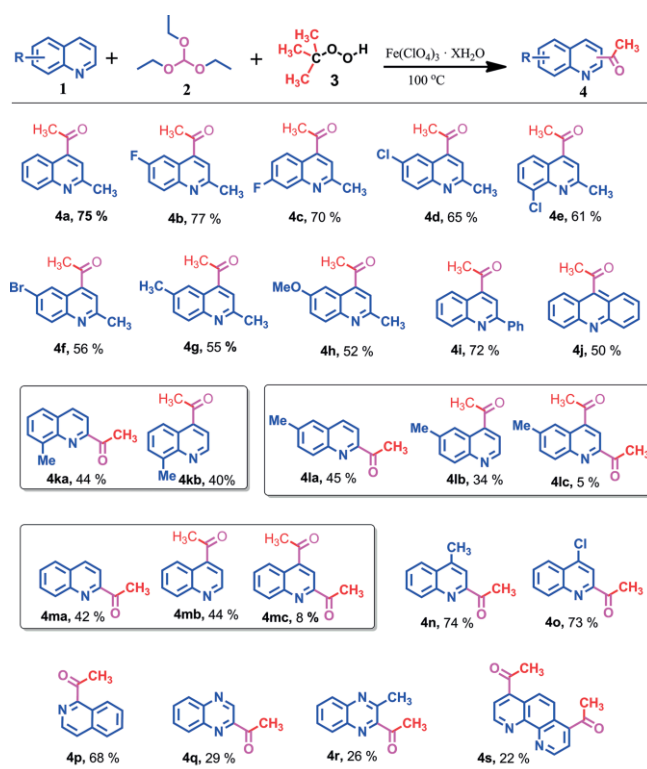
Entry	Catalyst (mol-%)	Oxidant [equiv.]	Temp [°C]	Yield [%] ^[b]
1	Fe(ClO ₄) ₃ ·xH ₂ O (10)	TBHP (3)	100	74
2	Fe(ClO ₄) ₃ ·xH ₂ O (10)	TBHP (3)	90	61
3	Fe(ClO ₄) ₃ ·xH ₂ O (10)	TBHP (3)	110	65
4	Fe(ClO₄)₃·xH₂O (10)	TBHP (4)	100	78
5	Fe(ClO ₄) ₃ ·xH ₂ O (10)	TBHP (5)	100	78
6	Fe(ClO ₄) ₃ ·xH ₂ O (20)	TBHP (4)	100	77
7	Fe(ClO ₄) ₃ ·xH ₂ O (10)	TBHP (4)	100	62
8	FeCl ₃ ·6H ₂ O (10)	TBHP (4)	100	58
9	FeCl ₃ (10)	TBHP (4)	100	54
10	FeCl ₂ (10)	TBHP (4)	100	42
11	Fe(acac) ₂ (10)	TBHP (4)	100	20
12	Fe(ClO ₄) ₃ ·xH ₂ O (10)	TBHP in Dec (3)	100	56
13	Fe(ClO ₄) ₃ ·xH ₂ O (10)	DTBP (3)	100	NR
14	Fe(ClO ₄) ₃ ·xH ₂ O (10)	TBPB (3)	100	NR
15	Fe(ClO ₄) ₃ ·xH ₂ O (10)	DCP (3)	100	NR
16	Fe(ClO ₄) ₃ ·xH ₂ O (10)	H ₂ O ₂ (3)	100	NR
17	–	TBHP (4)	100	NR
18	Fe(ClO ₄) ₃ ·xH ₂ O (10)	–	100	NR

[a] Reaction conditions: **1** (1 mmol), **2** (2 mL), **3** (70 % TBHP in water), time 12 h. [b] Isolated yields after column chromatography.

The generality and substrate scope of the reaction was evaluated using various N-heteroarenes as shown in the Table 2, **4a–4s**. Particularly 2-methyl quinolines reacted well with triethylorthoformate and TBHP in the presence of Fe^{III} perchlorate·xH₂O and afforded the corresponding acetyl quinolines from moderate to good yields (52–75 % yields, Table 2, **4a–4h**).

Electron withdrawing halogen substitution at positions 6, 7 and 8 of 2-methyl quinolines furnished the corresponding acetylated products **4b–4f** in high yields. Slightly lower efficiency is observed for electron-rich substrates bearing methyl or methoxy motifs at 6 position of 2-methyl quinoline (55 % and 52 % Table 2, **4g** and **4h**). Acetylation of 2-phenyl quinoline furnished the corresponding product **4i** in 72 % yield and the fused aromatic acridine afforded **4j** in moderate yield (50 %). Notably, the mixtures of acetylated products were obtained using “not biased” quinoline congeners, with a comparable rate at both, C2 and C4 positions. When 8-methyl quinoline (**1k**) underwent the acetylation, both regioisomers **4ka** (2-acetyl-8-methyl quinoline) and **4kb** (4-acetyl-8-methyl quinoline) were delivered in

Table 2. Substrate scope of quinolines, isoquinoline, quinoxaline.^[a]

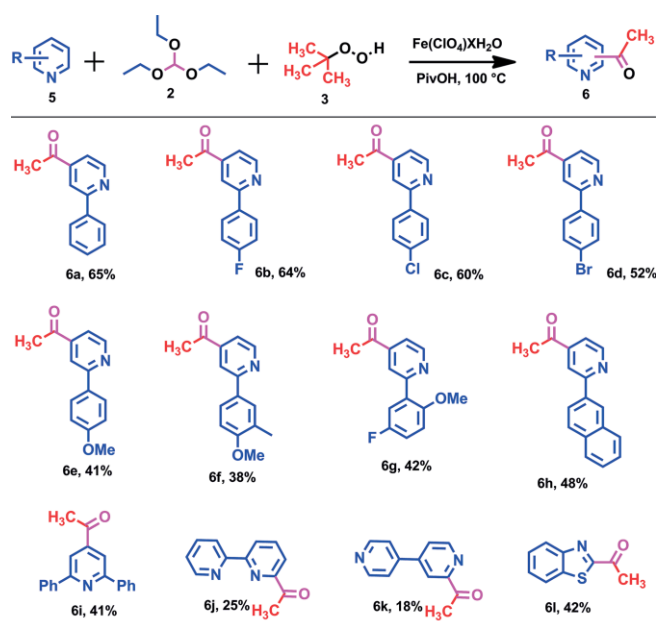


[a] Reaction Conditions: **1** (1 mmol), **2** (2 mL), **3** TBHP (4 equiv.), Fe(ClO₄)₃·xH₂O (0.1 mmol), 100 °C, Isolated yields after column chromatography.

44 % and 40 % yields respectively. When 6-methyl quinoline (**1l**) was subjected to the standard reaction conditions, the mixture of 2-acetylated, 4-acetylated and 2,4-diacetylated products (**4la–4lc**) were formed. The regioisomers **4la** (2-acetyl-6-methyl quinoline) and **4lb** (4-acetyl-6-methyl quinoline) were generated in 45 % and 34 % yields respectively. The diacetylated product **4lc** was isolated only as a minor product in 5 % yield. In the case of simple quinoline, two regioisomers **4ma** (2-acetyl quinoline) and **4mb** (4-acetyl quinoline) were delivered in 42 % and 44 % yield, while the diacetylated product **4mc** was separated as a minor compound in 8 % yield (Table 2, entries **4ma–4mc**). Comparable results were obtained starting from quinolines having the electron donating and electron withdrawing groups at C4 position of quinoline giving 4-methyl-2-acetyl quinoline (**4n**) and 4-chloro-2-acetyl quinoline (**4o**) (Table 2, **4n**, 74 % and **4o**, 73 %). When isoquinoline was subjected to the reaction, only 1-acetyl isoquinoline was afforded in good yield (Table 2, **4p**). In contrast, acetylation of quinoxaline and 2-methyl quinoxaline turned out to be less efficient, furnishing the corresponding functionalized products **4q** and **4r** in 29 % and 26 % yield respectively. Challenging diacetylation of phenanthroline gave C2-symmetric **4s** isolated in low, 22 % yield (Table 2).

The substrate scope was extended to pyridines, bipyridines and benzothiazole (Table 3, **6a–6l**). When 2-phenyl pyridine **5a** was subjected to the standard reaction conditions, **6a** was obtained regioselectively but in moderate 37 % yield.^[12] Rewardingly, addition of 1 equiv. of pivalic acid enabled drastic im-

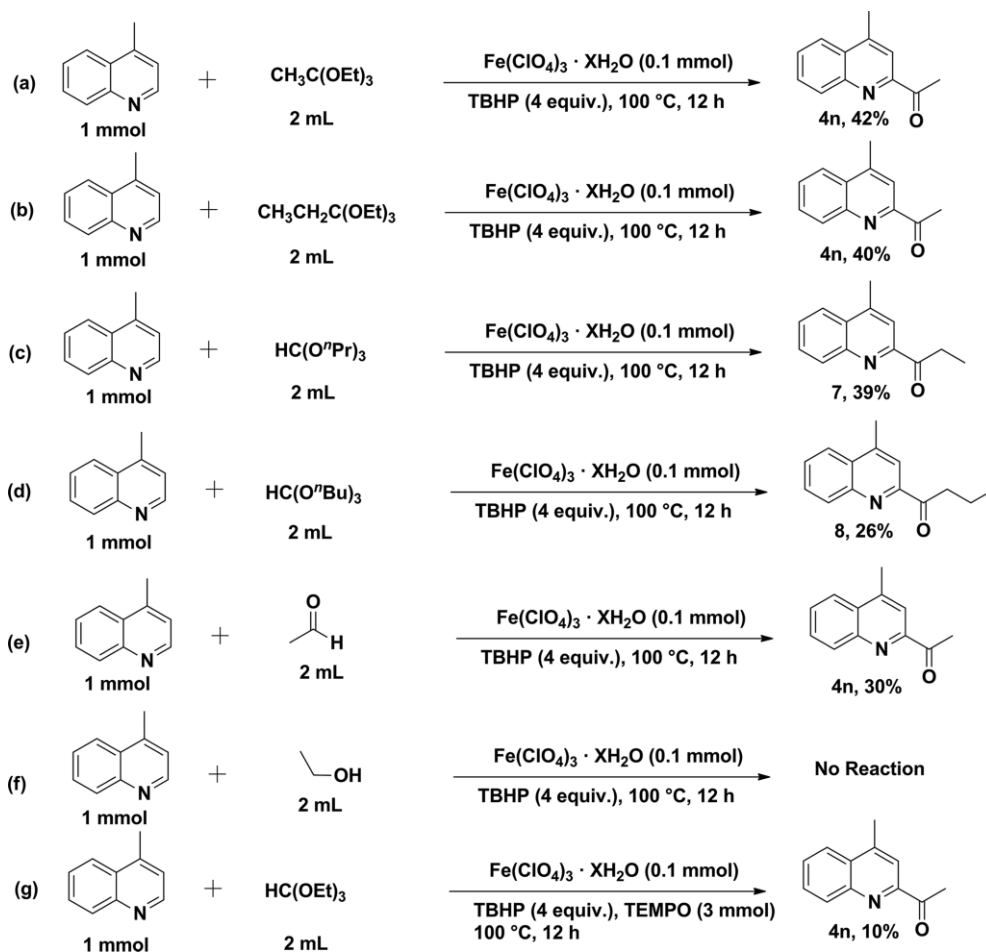
Table 3. Acetylation of pyridines, bipyridines and benzothiazole.^[a]



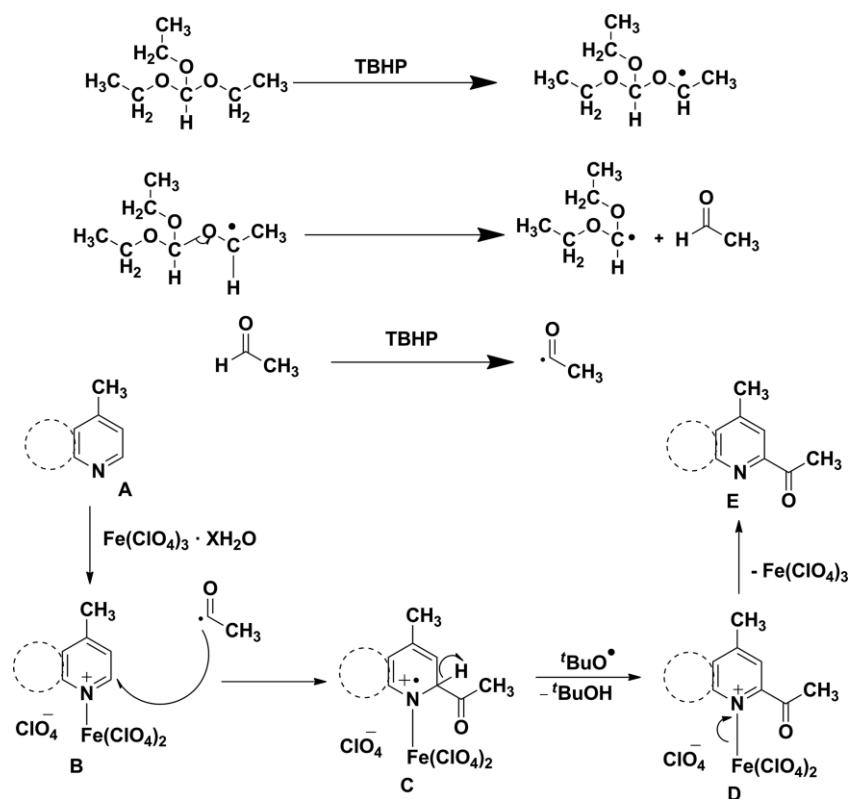
[a] Reaction Conditions: **5** (1 mmol), **2** (2 mL), **3** TBHP (4 equiv.), $\text{Fe}(\text{ClO}_4)_3 \cdot \text{XH}_2\text{O}$ (0.1 mmol), PivOH (1 equiv.), 100 °C, Isolated yields after column chromatography.

provement in the reaction efficiency, providing the desired product in 65 % yield. This modified protocol was further employed for acetylation of an array of N-heterocycles (Table 3, entries **6a–6l**).

Pyridines bearing *para*-halogen substituted phenyl moieties underwent the reaction smoothly; 4-F-C₆H₄, 4-Cl-C₆H₄, 4-Br-C₆H₄ pyridines furnished the corresponding products **6b–6d** in better yields than electron rich substrates containing motifs such as 4-OMe-C₆H₄ and 3-Me-4-OMe-C₆H₃ groups (Table 3, **6e** and **6f**). When 2-OMe-5-F-C₆H₃ was reacted under standard acetylation conditions, the expected product **6g** was accessed in 42 % yield. 2-naphthyl pyridine was converted into the functionalized product 4-acetyl-2-naphthyl pyridine (**6h**) in 48 % yield (Table 3, **6h**). Acetylation of the disubstituted substrate 2,6-diphenyl pyridine delivered 4-acetyl-2,6-diphenyl pyridine **6i** in 41 % yield and 2,2-bipyridine and 4,4-bipyridines were converted into the expected products **6j** and **6k** sluggishly. Under the standard reaction conditions, benzothiazole underwent the acetylation and afforded the 2-acetyl benzothiazole in moderate yield 42 % (Table 3, **6l**). However, acetylation of 4-nitrophenyl pyridine, 2-methyl pyridine and simple pyridine failed. Up on successful acetylation on benzothiazole, then benzoxazole was also subjected to the standard reaction conditions but deceptively no desired product was formed.



Scheme 1. Control experiments.



Scheme 2. Proposed mechanism.

In order to find out acetyl source as well as mechanism, several control experiments were carried out (Scheme 1). Reactions with triethylorthoacetate (Scheme 1a) and triethylorthopropionate (Scheme 1b) under optimized reaction conditions with 4-methyl quinoline, provided the same 2-acetyl-4-methyl quinoline (**4n**). Similarly tripropylorthoformate (Scheme 1c) and tributylorthoformate (Scheme 1d) under similar conditions resulted in 2-propionylated and 2-butanoylated products respectively. The above reactions suggest that acyl functionality is generated from the respective alkoxy groups of the orthoformates. For example we assume that HC(OEt)₃ generates the acetaldehyde in situ, and further converts into acetyl radical in presence of TBHP (Scheme 2). This was further established with the reaction with acetaldehyde where the desired product (**4n**) in 30 % yield was observed (Scheme 1e). The formation of desired product was not observed with Ethanol (Scheme 1f). Radical mechanism was established by radical scavenger (TEMPO) where the desired product (**4n**) was isolated only 10 % yield (Scheme 1g).

Based on the control experiments and literature precedents,^[13] the following mechanism is proposed. Triethylorthoformate generates the acetyl radical in presence of TBHP (Scheme 2). In parallel, iron perchlorate co-ordinates *N*-atom of heteroarene **A** and forms more electron deficient intermediate **B**. The acetyl radical present in the reaction medium attacks at the more electrophilic C1 position of the heteroarene intermediate **B** to provide the corresponding radical cation **C**. The hydrogen abstraction from the radical cation **C** by the *t*BuO radical which releases from TBHP followed by elimination of

*t*BuOH leads to the rearomatized intermediate **D**.^[14] Furthermore, the final product **E** is furnished together with the regeneration of catalyst **D** (Scheme 2).

In conclusion, we have developed an iron-catalyzed acetylation of quinolines, isoquinolines and quinoxalines using triethylorthoformate/TBHP system as acetyl source. This novel acetylation method is extended to pyridines, bipyridines and benzothiazole. We have demonstrated an operationally simple method using commercially available and cheaper catalyst Fe(ClO₄)₃ as well as robust triethylorthoformate and TBHP.

Experimental Section

General Procedure for Iron Catalyzed Acetylation of **4a–4s** with Triethylorthoformate and *tert*-Butyl Hydroperoxide:

In a reaction vessel, Fe(ClO₄)₃·xH₂O (0.1 mmol) and *N*-heteroarenes (**1a–s**) (1 mmol) were dissolved in 2 mL of triethylorthoformate (**2**). To the above mixture *tert*-butyl hydroperoxide 70 % aq solution (4 equiv.) was added slowly over a period of 2 minutes. The reaction mixture was stirred at 100 °C for 12 hours. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was allowed to come to room temperature and extracted with ethyl acetate. The organic layer was washed with brine, water and dried with anhydrous Na₂SO₄. The organic layer was concentrated under reduced pressure and afforded the crude product. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (4:1 ratio) mixture as eluent and the pure product was analyzed by ¹H NMR, ¹³C NMR and ESI-HRMS.

General Procedure for Iron Catalyzed Acetylation of 6a–6l with

Triethyl Orthoformate and tert-Butyl Hydroperoxide: In a reaction vessel, Fe(ClO₄)₃·xH₂O (0.1 mmol), Pivalic acid (1.1 mmol) and 2-aryl pyridines (**5a–i**) or bipyridines **5j** and **5k** or benzothiazole **5l** (1 mmol) were dissolved in 2 mL of triethyl orthoformate (**2**). To the above mixture tert-butyl hydroperoxide 70 % aq solution (4 equiv.) was added slowly over a period of 2 minutes. The mixture was stirred at 100 °C for 12 hours. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was allowed to come to room temperature and extracted with ethyl acetate. The organic layer was washed with brine, water and dried with anhydrous Na₂SO₄. The organic layer was concentrated under reduced pressure and afforded the crude product. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (4:1 ratio) mixture as eluent. The pure products were analyzed by ¹H NMR, ¹³C NMR and ESI-HRMS.

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Keywords: Acetylation · Iron catalyst · N-heteroarenes · Triethylorthoformate · TBHP

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