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An Inexpensive Catalyst, $Fe(acac)_3$, for Regio/Site-Selective Acylation of Diols and Carbohydrates Containing a 1,2-*cis*-diol

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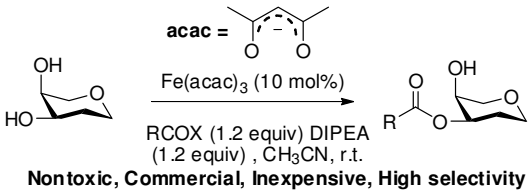
This work describes the [$Fe(acac)_3$] (acac = acetylacetonate)-catalyzed, regio/site-selective acylation of 1,2- and 1,3-diols and glycosides containing a *cis*-vicinal diol. The iron(III) catalysts initially formed cyclic dioxolane-type intermediates with substrates between the iron(III) species and vicinal diols, and the efficient and selective acylation of one hydroxyl group was subsequently achieved by adding acylation reagents in the presence of diisopropylethylamine (DIPEA) under mild conditions. This reaction generally produced high selectivities and highly isolated yields with the same protection pattern as that achieved with dibutyl tinoxide-mediated schemes.

Regio/site-selective protection strategy under mild and sustainable conditions remains a central challenge in carbohydrate chemistry due to the requirements for the preparation of value-added carbohydrate chemicals and for the construction of building blocks for oligosaccharide synthesis.[1] Previously, organotin reagents, which play key roles in selective protection strategies, were identified as the best reagents and were thus widely used.[2] These strategies used stoichiometric amounts of dibutyl tinoxide, and the origin of the resulting selectivities was attributed to stannylene intermediates through mechanism studies. However, organotin compounds are potentially inherently toxic, a significant drawback.[3] For this reason, protection strategies involving reduced amounts of organotin species or nontoxic alternatives are attractive, assuming that good selectivities can be achieved. In 2011, Taylor and colleagues reported an organoboron catalyst, a diarylborinic acid derivative (Taylor's catalyst).[4] This nontoxic catalyst has since been successfully used for the selective acylation and alkylation of carbohydrates. In 2012, we challenged the conception that the selectivities originated from complex stannylene dimer or polymer by mechanism studies and proposed that the selectivity is more likely controlled by stereoelectronic effects of the parent substrate structure.[5] Guided by this principle, we have developed several methods based on nontoxic alternatives to organotin[6] or reduced amount of organotin species[7] for selective protection. Particularly, in 2016, our group identified an iron(III)-catalyst, [$Fe(dibm)_3$] (dibm= diisobutyrylmethane), which yielded high regio/site-selectivities with very broad substrate scope in the alkylation of diols and polyols.[8] As iron is inexpensive, highly abundant, nontoxic, and generally environmentally benign, we wished to expand the use of this iron(III)-based catalyst to selective acylation. This challenge has been addressed in the present study, where an iron(III)-based catalyst was used for selective acylation of 1,2-diols, 1,3-diols, and glycosides containing a *cis*-vicinal diol (Scheme 1), leading to highly selective acylation of primary and equatorial hydroxyl groups. Comparison of this method with all previous reported selective acylation methods that avoided the use of stoichiometric amounts of dibutyl tinoxide, including methods using reduced amounts of organotins,[9] heavy metal-based complexes,[10] chiral catalysts[11] and other nonmetallic catalysts[4b,12] and reagents,[13] the reported [$Fe(acac)_3$] (acac = acetylacetonate) catalyst herein can be more easily acquired from commercial sources at a lower cost, and the method is environment-friendly and associated with more convenient manipulation, higher efficiency and selectivity, better yields and broad substrate scope.



Nontoxic, Commercial, Inexpensive, High selectivity

Scheme 1. Iron(III)-catalyzed regioselective acylation of carbohydrates containing a *cis*-vicinal diol.

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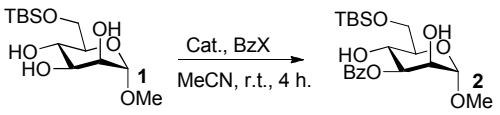
Initially, we expected $Fe(dibm)_3$ would also catalyze acylation as it catalyzed alkylation reported by us.[8] Therefore, methyl-6-*O*-(tertbutyldimethylsilyl)-α-D-mannopyranoside **1** was chosen as the first substrate with which to verify this hypothesis (Table 1). As expected, compound **1** was treated with 1.2 equiv. of BzCl in the presence of 0.1 equiv. of $Fe(dibm)_3$ and 1.5 equiv. of diisopropylethylamine (DIPEA) in acetonitrile at room temperature, leading to high regioselectivity for the 3-*O*-benzoated product **2** (Entry 1, 85% isolated yield). Compared with $Fe(dibm)_3$, $Fe(acac)_3$ is more easily acquired from commercial sources and is less expensive. However, the use of $Fe(acac)_3$ for alkylation is inefficient due to the instability of the acetylacetonate ligand at high reaction temperature (80 °C).[8] To our delight, the use of 0.1 equiv. of $Fe(acac)_3$, instead of $Fe(dibm)_3$, led to an identical result for acylation (Entry 2, 85% isolated yield of **2**). An increase in the catalyst load to 0.2 equiv. of $Fe(acac)_3$ led to an 86% isolated yield of **2** (Entry 3), whereas a decrease in the catalyst load to 0.05 equiv. of $Fe(acac)_3$ still produced an 80% yield of **2** (Entry 4). Little or no conversion was observed with no catalyst or when $FeCl_3$ was used as the catalyst (Entries 5 and 6). Various bases, including K_2CO_3, Ag_2O, TEA, TMEDA, DEA and pyridine, were also tested in the acylation reaction with 0.1 equiv. of $Fe(acac)_3$ (Entries 7 - 12). A good result was also observed with the use of TEA (Entry 9, 83% isolated yield of **2**). The use of Bz_2O as the acylation reagent produced a 76% isolated yield of **2** (Entry 13). Replacement of the solvent acetonitrile by DMF, along with the use of Bz_2O as the acylation reagent, produced a 55% isolated yield of **2** (Entry 14). The results of conversion and selectivity indicated that $Fe(acac)_3$ mainly improved the acylation rate of compound **1**.

Table 1. Comparison of results achieved under various conditions.[a]



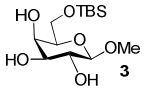
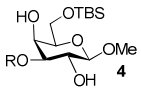
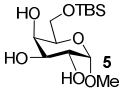
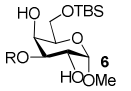
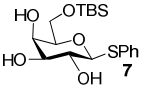
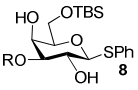
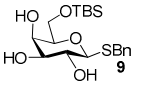
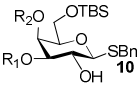
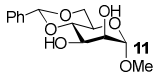
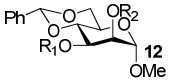
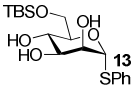
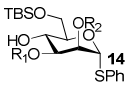
X stands for Cl, OBz

Entry	Various Conditions	IsolatedYield % (**2**/side-product)	Conversion %
1	0.1 eq. $Fe(dibm)_3$, DIPEA	85/-	>95
2	0.1 eq. $Fe(acac)_3$, DIPEA	85/-	>95
3	0.2 eq. $Fe(acac)_3$, DIPEA	86/-	>95
4	0.05 eq. $Fe(acac)_3$, DIPEA	80/-	>90
5	Without cat., DIPEA	29/6	38
6	0.1 eq. $FeCl_3$, DIPEA	-	0
7	0.1 eq. $Fe(acac)_3$, K_2CO_3	32/-	39
8	0.1 eq. $Fe(acac)_3$, Ag_2O	47/15	65
9	0.1 eq. $Fe(acac)_3$, TEA	83/-	>90
10	0.1 eq. $Fe(acac)_3$, TMEDA	45/-	49
11	0.1 eq. $Fe(acac)_3$, DEA	-	0
12	0.1 eq. $Fe(acac)_3$, Pyridine	43/	50
13[b]	0.1 eq. $Fe(acac)_3$, DIPEA	76/8	85
14[c]	0.1 eq. $Fe(acac)_3$, DIPEA	55/8	64

[a] Reactant (100 mg), BzCl (1.2 eq.), catalyst (0.05 – 0.2 eq.), base (1.5 eq.), MeCN (1 mL), r.t., 4 h. [b] Bz_2O (1.2 eq.) used instead of BzCl. [c] Bz_2O (1.2 eq.) and DMF (1 mL) used instead of BzCl and MeCN.

The scope of this method was further evaluated using other substrates containing a *cis*-diol moiety with AcCl as the acylation reagent (Table 2). TEA as a base was initially excluded in the method due to the low conversions of substrates **3** and **5**. To our delight, when using DIPEA as the base, all tested substrates were selectively acylated at the equatorial hydroxyl groups in yields of 70–85%. High yields (82-85%) were obtained for the acylation of galacto-type compounds **3**, **5**, and **7** (Entries 1–3). However, the benzoylation of the galacto-type compound **9** and manno-type compounds **11** and **13** yielded more side-products with acylated axial hydroxyl groups (Entries 4–6, 13-21% yields). The method using stoichiometric amounts of organotin gives much better regioselectivity for some of these compounds.[14]

Table 2. [$Fe(acac)_3$]-catalyzed regioselective acylation of substrates containing *cis*-diol.[a]

Entry	Substrate	Product	Isolated Yields %
1			**4a**: R=Bz 85 **4b**: R=Ac 83
2			**6a**: R=Bz 82 **6b**: R=Ac 85
3			**8a:** R=Bz 83 **8b:** R=Ac 84
4			**10a**: R_1=Bz R_2=H 76 **10b**: R_1=H R_2=Bz 13
5[b]			**12a**: R_1=Bz R_2=H 73 **12b**: R_1=H R_2=Bz 21
6[b]			**14a**: R_1=Bz R_2=H 70 **14b**: R_1=H R_2=Bz 20

[a] Reactant (100 mg), BzCl or AcCl (1.2 eq.), $Fe(acac)_3$ (0.1 eq.), DIPEA (1.5 eq.), MeCN (1 mL), r.t., 4-8 h. [b] Reaction at 15 °C.

Acyl group migration is often found in carbohydrate chemistry.[5,15] For carbohydrates containing a *cis*-diol, an equatorial acyl group equilibrates with its axial counterpart under basic conditions and axial substitution is preferred.[5,15b] Accordingly, we suspected that the poor selectivities for the acylation of **9**, **11**, and **13** originated from acyl group migrations in the presence of excess amounts of DIPEA. Acetyl group is more prone to acyl migration. Thus, with acetyl chloride as the acylation reagent instead of benzoyl chloride (73/21 selectivity, entry 5 in Table 2), a poorer selectivity (57/38) was obtained from the acetylation of **11**. This hypothesis was further confirmed, as shown in Table 3. The selectivities for the acylation of **9**, **11**, and **13** improved considerably when the amounts of DIPEA were reduced to 1.2 equiv (Entries 1 – 3). As most of the base DIPEA may form acyl

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ammonium intermediate with equimolecular amount of acyl chloride instantly, the acyl group migration was suppressed due to the lack of base catalysis. To further verify the effects of acyl group migrations on the reaction, the benzoylation of **13** was compared at various reaction temperatures (Entries 4-6). Accordingly, the ratio of **14a**/**14b** decreased to 56/33 at 25°C, 48/45 at 50 °C and 36/62 at 70 °C, indicating the migration accelerates as the reaction temperature is increased. The yield of **14a** only increased to 85% in the presence of 1.2 equiv of DIPEA when 1.5 equiv of BzCl was used in the benzoylation of **13** (Entry 7). To minimize the effect of benzoyl group migration on the selectivity, a mixture of 1.2 equiv of DIPEA and 1.2 equiv of BzCl was added dropwise into the reaction solution of **13**, which yielded the best selectivity (Entry 8, **14a**/**14b**: 90/-). These experiments indicate that the regioselectivity in this method can be improved by suppressing acyl group migration via reducing the amount of DIPEA, decreasing the reaction temperature, and improving the DIPEA feed method.

Table 3. Selectivities affected by acyl group migration.[a]

Entry	Substrate	Various Conditions	Isolated Yield %
1	**9**	1.2 eq. DIPEA, 1.2 eq. BzCl, 25 °C	**10a/10b** (91/-[c])
2	**11**	1.2 eq. DIPEA, 1.2 eq. BzCl, 25 °C	**12a/12b** (81/13)
3	**13**	1.2 eq. DIPEA, 1.2 eq. BzCl, 25 °C	**14a/14b** (83/11)
4	**13**	1.5 eq. DIPEA, 1.2 eq. BzCl, 25 °C	**14a/14b** (56/33)
5	**13**	1.5 eq. DIPEA, 1.2 eq. BzCl, 50 °C	**14a/14b** (48/45)
6	**13**	1.5 eq. DIPEA, 1.2 eq. BzCl, 70 °C	**14a/14b** (35/62)
7	**13**	1.2 eq. DIPEA, 1.5 eq. BzCl, 25 °C	**14a/14b** (85/10)
8[b]	**13**	1.2 eq. DIPEA, 1.2 eq. BzCl, 25 °C	**14a/14b** (90/-[c])

[a] Reactant (100 mg), $Fe(acac)_3$ (0.1 eq.), MeCN (1 mL), 4 h. [b] The mixture of DIPEA and BzCl added dropwise over 2 h. [c] No or trace amount.

After comprehensive consideration of reaction efficiency and manipulation methodology, further tests of our method were conducted with the following substrates containing *cis*-diols **7**, **9**, **15**, **17**, **19**, **21**, **23**, **25**, **27**, **29**, **31**, **33**, **35**, and **37**, DIPEA and acylation reagents were simply mixed with the acetonitrile solution of the substrate in the presence of 0.1 equiv of $Fe(acac)_3$ catalysts. These reactions were then allowed to proceed at room temperature for 2 – 8 h (Figure 1). Most tested substrates were selectively acylated at the equatorial hydroxyl groups in high yields (> 80%). The acylation of the free methyl glycosides **39**, **41**, and **43** with 1.2 equiv. of DIPEA and 1.2 equiv. of acylation reagents led to mixtures of 3-OBz/OAc, 6-OBz/OAc and 3,6-di-OBz/OAc products. Therefore, 4 equiv. of DIPEA and 4 equiv. of acylation reagents were allowed to react with **39**, **41**, and **43** in the presence of 0.1 equiv of $Fe(acac)_3$, which produced moderate yields of 3,6-di-OBz/OAc products **40**, **42**, and **44** (Figure 1, 68 - 80%). This method was also tested using the 1, 2- and 1, 3-diols **45**, **47**, **49**, **51**, **53**, **55**, and **57,** where the primary hydroxyl groups were selectively acylated in high yields (Figure 1, 76 - 94%).

The cyclic dioxolane/dioxane-type intermediates play key roles in the catalytic mechanism of the regio/site-selective acylation (Figure **2**), analogous to the proposed mechanism of $Fe(dibm)_3$ catalyzed regioselective alkylation.[8] Once the intermediate **a** has formed between the *cis*-diol and $Fe(acac)_3$ in the presence of DIPEA, **a** would further react with the acylating reagent to yield intermediate **b**, where the equatorial position is acylated and the axial position is occupied by the Fe species. The intermediate **b** would subsequently undergo ligand exchange with a second *cis*-diol in the presence of DIPEA, either directly or *via* acac, thus regenerating the cyclic intermediate **a** and a product with an acylated equatorial position. However, in the presence of excess DIPEA, the acyl group is favored to migrate from the equatorial to the axial position *via* the five-membered ring tetrahedral intermediate **c**,[5] thereby decreasing the selectivity of acylation.

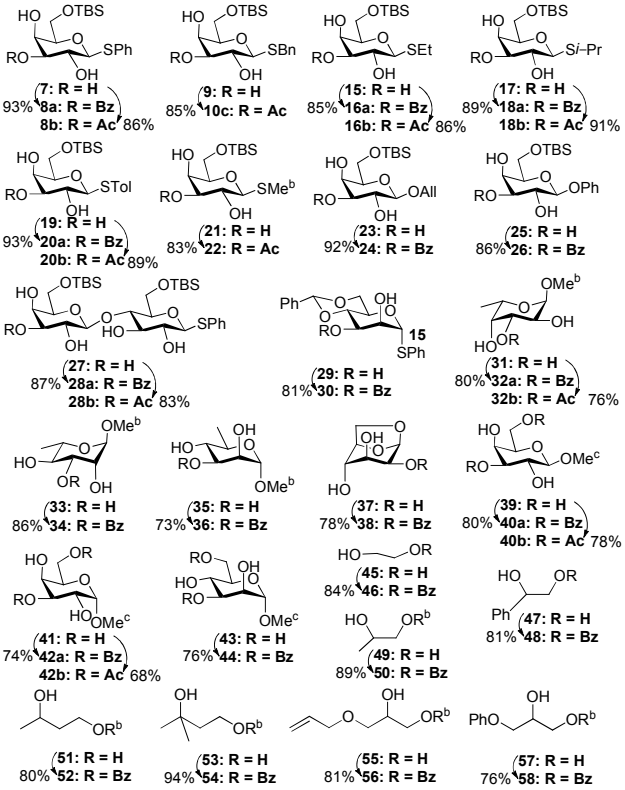

Fig. 1 [$Fe(acac)_3$]-catalyzed regioselective acylation of substrates containing *cis*-, 1,2-, and 1,3-diols.[a] Reaction conditions: [a] BzCl or AcCl (1.2 eq.), $Fe(acac)_3$ (0.1 eq.), DIPEA (1.2 eq.), MeCN (1 mL), r.t., 2-8 h., [b] BzCl or AcCl (1.5 eq.), $Fe(acac)_3$ (0.1 eq.), DIPEA (1.5 eq.), MeCN (1 mL), r.t., 2-8 h. [c] BzCl or AcCl (4 eq.), $Fe(acac)_3$ (0.1 eq.), DIPEA (4 eq.), MeCN (1 mL), r.t., 2-8 h.

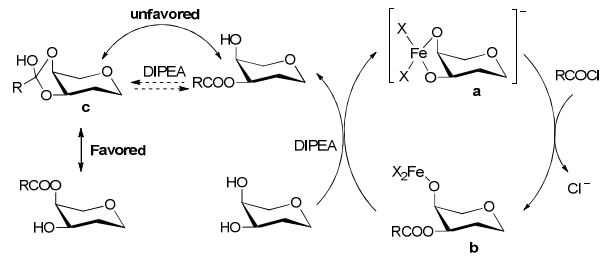

Figure 2. Proposed catalytic mechanism.

The selective protection of carbohydrates containing a *trans*-

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diol is a challenge when using alternatives to stoichiometric amounts of dibutyl tinoxide, because a *trans*-diol is difficult to form a cyclic dioxolane-type intermediate with catalysts.[7a] As $Fe(dibm)_3$ was found to be able to catalyze the selective benzylation of carbohydrates containing a *trans*-diol,[8] we expected that Fe(III) catalysts would also catalyze the selective acylation of these type of compounds. Unfortunately, our attempt failed, possibly due to the same reason, the formation of a cyclic dioxolane-type intermediate being difficult.

In conclusion, $Fe(acac)_3$ was successfully applied as a catalyst for regio/site-selective acylation of 1,2-diols, 1.3-diols, and carbohydrates containing *cis*-diols. The acylation reaction is proposed to proceed through a cyclic dioxolane-type intermediate between a diol and $Fe(acac)_3$ under base conditions. The resulting selectivities exhibited the same product pattern as for traditional dibutyl tinoxide-mediated approaches. Despite the effects of acyl group migration during the reaction, high selectivities were obtained in most cases through suppressing the migration. Our method proved straightforward, representing an affordable, green and benign alternative to Taylor's catalyst. Additionally, $Fe(acac)_3$ is a much less expensive catalyst, which at approximately is only one-fourth (for the price per mole) as expensive as Taylor's catalyst.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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