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Me₃SI-promoted chemoselective deacetylation: a general and mild protocol†

 Aakanksha Gurawa,‡ Manoj Kumar‡ and Sudhir Kashyap *

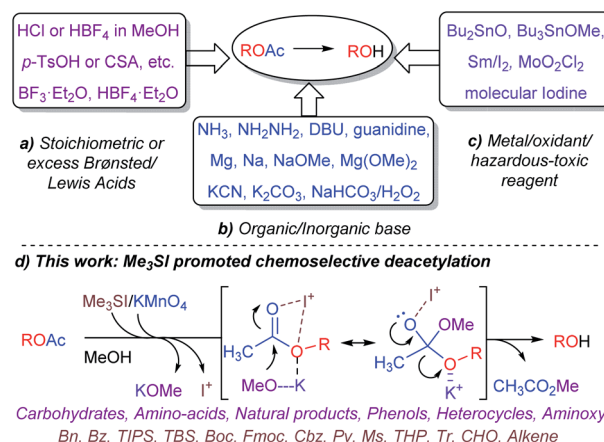
A Me₃SI-mediated simple and efficient protocol for the chemoselective deprotection of acetyl groups has been developed *via* employing KMnO₄ as an additive. This chemoselective deacetylation is amenable to a wide range of substrates, tolerating diverse and sensitive functional groups in carbohydrates, amino acids, natural products, heterocycles, and general scaffolds. The protocol is attractive because it uses an environmentally benign reagent system to perform quantitative and clean transformations under ambient conditions.

The divergent protection–deprotection approach and extensive functional group manipulation continues to serve as an important chemical tool to access biologically potent molecules and complex natural products.¹ In particular, the hydroxyl moieties and their derivatives are ubiquitous in natural products and recognized as renowned scaffolds because of the overwhelming number of chemical and biological applications that they can be used in.^{2,3} The selective and orthogonal protection–deprotection of free hydroxyl group(s) are significant chemical transformations and frequently employed in target-oriented synthesis (TOS).⁴ Due to the widespread use and relative ease of protection–deprotection, introduction of an *O*-Ac group to mask the hydroxyl-moiety has remained as a highly reliable and convenient strategy, especially in synthetic carbohydrate chemistry.^{1–3} However, the chemoselective deprotection of *O*-Ac in the presence of analogous and sensitive *O*-protective groups such as benzoyl (Bz) or pivaloyl (Pv) is a notoriously challenging yet important task.^{1–3}

Thus, considerable effort has been devoted to developing robust and selective methods for the deprotection of the acetate ester. As outlined in Scheme 1, the cleavage of *O*-Ac is conventionally performed under a homogeneous reagent system including: (a) Brønsted acids/Lewis acids such as HCl/MeOH,⁵ HBF₄·Et₂O,⁶ BF₃·Et₂O,⁷ *p*-TsOH or CSA,⁸ (b) inorganic/organic basic conditions employing Zemplén hydrolysis (NaOMe/MeOH),¹ ammonia solution,⁹ hydrazine/AcOH/pyridine,¹⁰ DBU/PhH,¹¹ guanidine/EtOH/DCM,¹² Mg–metal or Mg(OMe)₂,¹³ KCN/EtOH,¹⁴ K₂CO₃/MeOH/H₂O,¹⁵ NaHCO₃/H₂O,¹⁶ (c) metallic compounds or oxidants such as MoO₂Cl₂,¹⁷ molecular iodine/

MeOH,^{18a} Sm/I₂,^{18b} Bu₂SnO/heating,^{19a} Bu₃SnOMe/DCE.^{19b} Although, the use of heterogeneous catalysts such as CuFe₂O₄ nanoparticles²⁰ and enzymes²¹ have also been demonstrated for deacetylation with limited substrate scope. Recently, a tetranuclear zinc cluster, Zn₄(OCOFC₃)₆O has been investigated for use in trans-esterification and deacylation with discriminate selectivity.²²

Despite the synthetic challenges and demands placed on modern chemistry, advancing green chemical syntheses employing milder and environmentally benign reagent systems remains a constant motivation and is actively pursued. In this context and our continued interest²³ developing versatile and selective protocols inspired the development of a simple and chemoselective deacetylation method with remarkable and distinctive synthetic applicability. Recently the dual-reactivity of KMnO₄ for selective deacetylation and one-pot deacetylation–oxidation of benzyl-*O*-acetates under controlled reaction conditions was successfully investigated.^{23a}



Carbohydrate Chemistry Research Laboratory (CCRL), Department of Chemistry, Malaviya National Institute of Technology Jaipur, (MNIT), Jaipur-302017, India. E-mail: skashyap.chy@mnit.ac.in; skr.kashyap@gmail.com

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‡ Aakanksha Gurawa and Manoj Kumar contributed equally.

Scheme 1 Previous advances, and the Me₃SI-catalyzed chemoselective deacetylation developed in this work.



Emerging from these precedents, the Me₃SI-catalyzed, simple and chemoselective removal of *O*-acetate, an elegant and promising alternative approach for the deprotection of the acetate ester (Scheme 1d) is presented herein. Inspired by recent research,^{23f} an initial experiment employing Me₃SI(OAc)₂, generated *in situ* oxidative transfer of the acetyl groups from PhI(OAc)₂ to Me₃SI, which gave the regioselective 2-iodoglycosylation of enol ether functionality in 3,4,6-tri-*O*-acetyl-*D*-glucal (**1a**) with methanol together with traces of the deacetylated product **1** (Table 1, entry 1). The preliminary results led to the exploration of the possibility of using sulfonium iodate salts in the selective removal of the *O*-acetyl protection group. As summarized in Table 1, subsequent optimization of the reaction was performed by altering the reagents and solvent systems. Accordingly, the reactions of TOAc-glucal **1a** using varying amounts of Me₃SI and NaIO₄ in the presence of MeOH facilitated the smooth deacetylation providing the desired product **1** with excellent efficiency under ambient conditions (Table 1, entries 2–5). It is worth noting, that the use of Me₃SI in combination with NaIO₄ in MeOH as the solvent, promoted the deprotection of acetates in a chemoselective manner, however the direct 1,2-addition product, 2-deoxy-glycoside was not

detected.^{23f,g} Meanwhile, the reaction using 0.2 equiv. of both Me₃SI and NaIO₄ was found to suffice for obtaining the complete deacetylation of **1a** after 40 min (Table 1, entry 4).

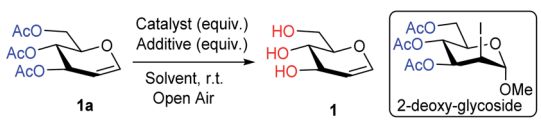
Consequently, TOAc-glucal **1a** was subjected to various complementary halide salts employing NaIO₄ (0.1 equiv.) in MeOH under ambient reaction conditions (Table 1, entries 6–12). Use of the catalytic *n*-Bu₄Ni and KI provided the desired product with good to modest transformation, 90% and 50% yields, respectively (Table 1, entries 6 and 7 vs. 5). It was found that NaI can efficiently promote the deacetylation in improved yields (90%) after 16 h under the present conditions (Table 1, entry 8). In contrast, Me₃SOI and bromide salts such as Me₃SBr, *n*-Bu₄NBr, and KBr failed to deliver the deacetylated product even after increasing the amount of the salts and additive NaIO₄ to 1.0 equiv. and a prolonged reaction time (Table 1, entries 9–12). Remarkably, switching to KMnO₄ (0.1 equiv.) as the additive in a Me₃SI-catalyzed reaction led to simple deacetylation of **1a** with almost quantitative yields (100%), within 5 min (Table 1, entry 13). A rapid screening of common organic solvents including CH₃CN, toluene, THF or CH₂Cl₂ were unsuccessful and did not give any desired transformations (Table 1, entries 14–17). Further optimization employing analogous additives such as K₂S₂O₈, oxone, KBrO₃, NaBO₃·H₂O, and Na₃BO₃ were found to be too sluggish or resulted in poor conversions (Table 1, entries 18–22).

Having improved and optimized the reagent system, the generality and limitation of Me₃SI-catalyzed selective deacetylation protocol was investigated next, and the results are summarized in Scheme 2. Of the particular note, diverse and commonly used *O*-protecting groups in *D*-glucal comprising benzoyl (**1b**), benzyl (**1c**), methyl (**1d**), and *tert*-butyldimethylsilyl ether (**1e**) were fully tolerated, thus unambiguously establishing the potential synthetic applicability of the representative chemoselective procedure. Subsequently, the selective deacetylation of several per-*O*-acetylated glycals: *D*-galactal (**2a**), *D*-rhamnal (**3a**), *L*-rhamnal (**4a**), *D*-xylal (**5a**), *D*-arabinal (**6a**) and *L*-arabinal (**7a**), also disaccharide derived glycals bearing 1,4-glycosidic linkages, for example *D*-lactal (**8a**) and *D*-maltal (**9a**), were performed successfully to obtain the corresponding products **2–9** in excellent yields.

Furthermore, the substrates bearing *O*-TIPS (**10a**), *O*-Bn (**11a–13a**), and 4,6-*O*-benzylidene (**14a**) in carbohydrate substrates were uniformly sustained under selective deacetylation conditions giving the hydroxyl products **10–14**, respectively, (up to 98% yields). Indeed, the glycosides comprising sensitive *O*-isopropylidene linkages in *D*-galactopyranose (**15a**), *D*-glucofuranose (**16a**), *D*-ribose (**17a**), and unprotected uridine (**18a**) were selectively deacetylated to generate the corresponding free-hydroxyl compounds **15–18** in good yields. Importantly, the amino acid derivatives **19a–23a** including relatively subtle or labile substituents such as *tert*-butylcarbamate (Boc), fluorenylmethoxycarbonyl (Fmoc) carbobenzoxy (Cbz), and methyl ester (–CO₂Me), underwent efficient chemoselective deacetylation giving the desired products **19–23** in good to excellent yields.

Encouraged by these results, the scope of the selective protocol was extended by performing the systematic

Table 1 The screening and optimization of the deacetylation reagent system^a

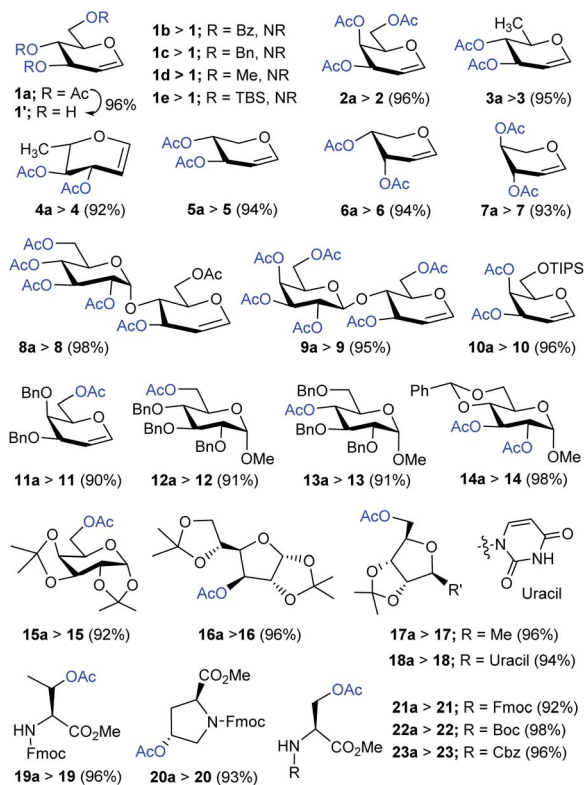


Entry	Catalyst (equiv.)	Additive (equiv.)	Solvent	Time	Yield ^b
1	Me ₃ SI (1.0)	PhI(OAc) ₂ (1.0)	MeOH	24 h	Trace
2	Me ₃ SI (1.0)	NaIO ₄ (1.0)	MeOH	10 min	100%
3	Me ₃ SI (0.4)	NaIO ₄ (0.4)	MeOH	30 min	100%
4	Me ₃ SI (0.2)	NaIO ₄ (0.2)	MeOH	40 min	100%
5	Me ₃ SI (0.1)	NaIO ₄ (0.1)	MeOH	12 h	95%
6	<i>n</i> -Bu ₄ Ni (0.1)	NaIO ₄ (0.1)	MeOH	12 h	90%
7	KI (0.1)	NaIO ₄ (0.1)	MeOH	12 h	50%
8	NaI (0.1)	NaIO ₄ (0.1)	MeOH	16 h	90%
9 ^c	Me ₃ SOI (0.1)	NaIO ₄ (0.1)	MeOH	12 h	NR
10 ^c	Me ₃ SBr (0.1)	NaIO ₄ (0.1)	MeOH	12 h	NR
11 ^c	<i>n</i> -Bu ₄ NBr (0.1)	NaIO ₄ (0.1)	MeOH	12 h	NR
12 ^c	KBr (0.1)	NaIO ₄ (0.1)	MeOH	12 h	NR
13	Me₃SI (0.1)	KMnO₄ (0.1)	MeOH	5 min	100%
14	Me ₃ SI (0.1)	KMnO ₄ (0.1)	MeCN	24 h	NR
15	Me ₃ SI (0.1)	KMnO ₄ (0.1)	Toluene	24 h	NR
16	Me ₃ SI (0.1)	KMnO ₄ (0.1)	THF	24 h	NR
17	Me ₃ SI (0.1)	KMnO ₄ (0.1)	DCM	24 h	NR
18	Me ₃ SI (0.1)	K ₂ S ₂ O ₈ (0.1)	MeOH	12 h	Trace
19	Me ₃ SI (0.1)	Oxone (0.1)	MeOH	12 h	Trace
20	Me ₃ SI (0.1)	KBrO ₃ (0.1)	MeOH	12 h	Trace
21	Me ₃ SI (0.1)	NaBO ₃ ·H ₂ O (0.1)	MeOH	12 h	40%
22	Me ₃ SI (0.1)	Na ₃ BO ₃ (0.1)	MeOH	12 h	Trace

^a Reaction conditions: **1a** (1.0 equiv.), salt (0.1 to 1.0 equiv.), additive (0.1 to 1.0 equiv.), solvent (1 mL) in open-air at room temperature.

^b The isolated and unoptimized yields, based on the starting material **1a**. ^c Increasing the amount of both salt and additive up to 1.0 equiv., 24 h. NR = no reaction.

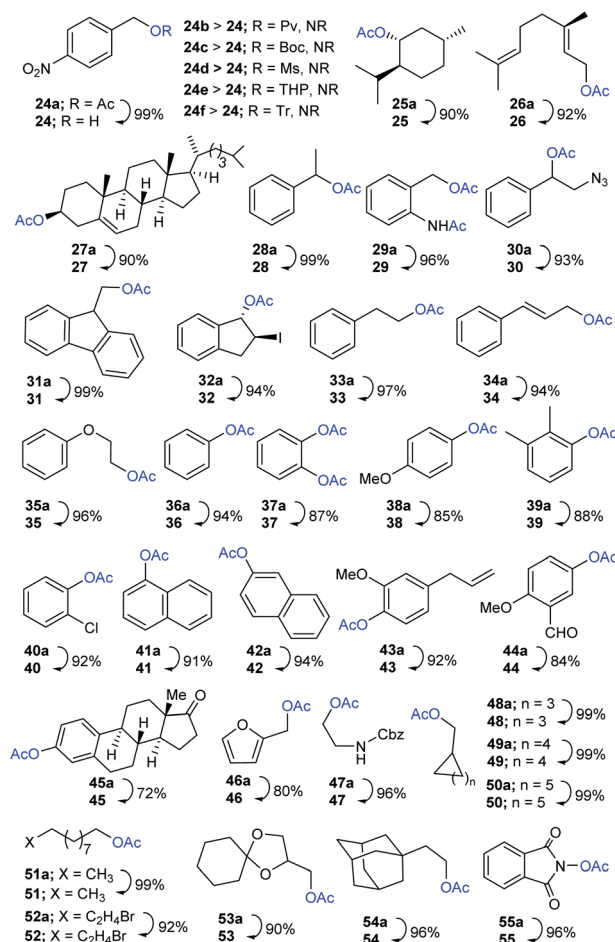




Scheme 2 The study of the substrate scope and a functional group compatibility investigation for the chemoselective deacetylation. Reaction conditions: **1a**–**23a** (1.0 equiv.), Me₃SI (0.1 equiv.), additive (0.1 equiv.), MeOH (1 mL), 25 °C under atmospheric pressure, 1–12 h. The isolated and unoptimized yields are shown.

deacetylation of substrates involving benzylic, alkylic, allylic, phenolic, naphthyl, heterocyclic, alicyclic, spirocyclic, natural-products, long chain aliphatic, and aminoxy moieties. As illustrated in Scheme 3, a series of substrates enclosing comparatively susceptible and electronically diverse *O*-protecting groups (*O*-Ac; **24a** vs. *O*-Piv; **24b**, *O*-Boc; **24c**, *O*-Ms; **24d**, *O*-THP; **24e**, *O*-Tr; **24f**) were well protected under present conditions, further confirming the effectiveness of the chemoselective method. The Me₃SI-catalyzed simple removal of acetyl groups, in menthyl (**25a**), geranyl (**26a**), cholesteryl (**27a**), and diversely substituted aryl substrates **28a**–**35a**, was conducted to efficiently obtain the desired products **25**–**35** in good-to-excellent yields (90–99%). It is worth noting, that the selective deacetylation for a substrate consisting of two electronically different acetates was accomplished successfully (cleavage of *O*-acetate vs. *N*-acetate in **29a**).

Next, the diversely substituted phenolic or naphthyl *O*-acetates **36a**–**42a**, eugenyl **43a**, vanillyl **44a**, and estrone acetate **45a** were subjected, under ambient conditions, to access the corresponding free-phenols **36**–**45** in acceptable yields (72–96%). Likewise, the reaction employing heterocyclic furfuryl acetate (**46a**), 2-amino-(Cbz)-ethyl acetate (**47a**), and alicyclic substrates with different ring sizes (five, six, or seven) **48a**–**50a** proceeded smoothly providing the corresponding products **46**–**50** (80–99% yields). Additionally, long chain aliphatic acetates **51a** and **52a**, a spirocycle bearing sensitive dioxa moiety **53a**,



Scheme 3 Extended scope of the Me₃SI-catalyzed selective deacetylation. Reaction conditions: **24a**–**55a** (1.0 equiv.), Me₃SI (0.1 equiv.), additive (0.1 equiv.), MeOH (1 mL), 25 °C under atmospheric pressure, 1–12 h. The isolated and unoptimized yields are shown.

sterically hindered adamantyl **54a**, and aminoxy-*O*-acetate **55a** were competent, when used in the applied protocol, of producing their corresponding hydroxyls **51**–**55** in satisfactory yields (90–99%).

To gain further insight into the Me₃SI-promoted deacetylation, the reaction of TOAc-glucal **1a** was performed with equimolar amounts of trimethylsulfonium iodide and an additive (0.1 equiv. each) employing deuterated methanol (CD₃OD) as the solvent (Fig. 1). The ¹H-NMR analyses of the crude reaction mixture revealed the presence of a distinctive resonance which was due to an anomeric proton (δ 6.42 dd, J_{1-2} = 6.10, 1.4 Hz, H-1) and other characteristic chemical shifts which conformed with that of the desired product **1'** (tri-*O*-²H-D-glucal).

With no variance, the acetyl protons of methyl acetate (CH₃CO-OCD₃) were found at δ 2.10 (s, 9H) which potentially resulted from the methanolysis of the acetate groups with CD₃OD. In addition, substantial amounts of trimethylsulfonium hydroxide species were observed consistently at δ 3.05 as a singlet (vs. Me₃SI at δ 1.56),²⁴ and this established the role of trimethylsulfonium iodide in selective and simple cleavage of acetates. A set of control experiments were performed to



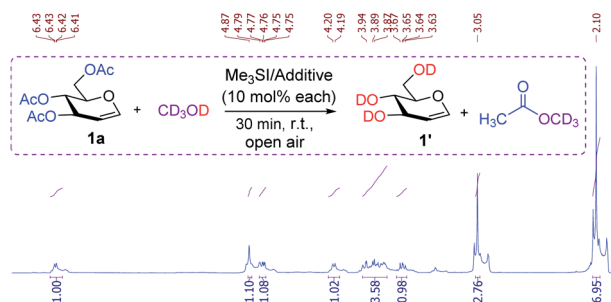


Fig. 1 Experiments with deuterated methanol and ^1H -NMR analyses, used to provide mechanistic rationalization for Me_3SI -promoted deacetylation.

identify the possible intermediate iodine species in this transformation. The studies revealed the absence of molecular iodine in the present reaction conditions as confirmed by a negative starch solution test (the color did not change to an intense blue color).²⁴ Indeed, the standard Me_3SI -mediated deacetylation reaction employing a common radical scavenger such as TEMPO (a stable aminoxy radical) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) preceded smoothly, and further ruled out a radical pathway in the process. Although, attempting a reaction of TOAc-glucal **1a** using a catalytic amount of iodine in methanol solvent was inconsistent (50–60% conversion) resulting in the mono-deacetylation of the primary acetate (6-OAc) even after a prolonged reaction time (48 h).^{18a} It is worth noting that the characteristic Lewis acidity of molecular iodine (I_2) has been exploited in the selective *O*-Ac as well *N*-Boc protection of diverse substrates.²⁵

Based on the previously mentioned experimental observations and with reference to precedents in the literature, a plausible mechanistic rationalization for a Me_3SI -catalyzed reaction is postulated in Scheme 4. Initially, KMnO_4 showed rapid disproportionation, resulting in permanganic acid ($\text{HMnO}_4 \leftrightarrow \text{H}^+ + \text{MnO}_4^-$) and potassium methoxide ($\text{KOMe} \leftrightarrow \text{K}^+ + \text{MeO}^-$) ions in the presence of methanol, which was attributed to the reducing behavior of methanol in the present system.²⁶ The main oxidizing reagent $\text{Mn}(\text{VII})\text{O}_4^-$ was capable of inverting the

polarity of the reactivity of the halide salt Me_3SI in slightly acidic conditions which resulted in the iodate (I^+) species [A], and was disproportionate to $\text{Mn}(\text{IV})\text{O}_2$ and H_2O . The reduced $\text{Mn}(\text{IV})$ species would then readily oxidize back to the higher $\text{Mn}(\text{VI})\text{O}_4^-$ in a slightly basic medium ($\text{KOMe}/\text{H}_2\text{O}$) under the normal atmosphere^{26c} and this was likely to facilitate the release of trimethylsulfonium hydroxide. Meanwhile, the incipient electrophilic intermediate [A] initiated from the oxidation of Me_3SI coordinated with the oxygen atoms of the carbonyl functionality (CH_3CO_2^-) in the acetate compound [1a] to generate a transient species [B].^{25b,25c,27} This significantly induced the polarization of the $\text{C}=\text{O}$ double bond and increased the electrophilicity of the carbonyl carbon as well contributing towards the bond lengthening of the carbonyl $\text{C}=\text{O}$ moiety in [B].

Subsequent coordination of the K^+ ion with alkyl-oxygen (RO^-) and attack of methoxide (MeO^-) as the nucleophile on the electrophilic carbon in [B], would then eventually produce the tetrahedral intermediate [C]. Following the elimination of the penultimate transient species [D] and simultaneously trapping of the respective alkoxide ion (RO^-) in a hydrolytic environment would unambiguously lead to the formation of the respective alcohol (ROH) [1] with the liberation of potassium methoxide. The proposed intermediate [D] finally displaced the corresponding methyl acetate ($\text{CH}_3\text{CO}_2\text{Me}$) by releasing the required iodate species [A] which presumably participated in another catalytic cycle *en route* to the selective deacetylation process.

In summary, a catalytic and practical procedure for chemoselective deacetylation with a general substrate scope employing environmentally benign reagents under ambient reaction conditions is reported. It is worth noting that the catalytic protocol is broadly applicable to numerous substrates, including carbohydrates, amino acids, and natural products, tolerating orthogonal and sensitive groups (esters, ethers, silyl ethers, carbamates, carboxybenzyl, mesyl, 2-tetrahydropyranyl, trityl, aldehydes, and also alkenes). Furthermore, the method is advantageous as it involves a safe and convenient reaction, ensuring smooth and quantitative conversion as well as preventing trans-esterification.

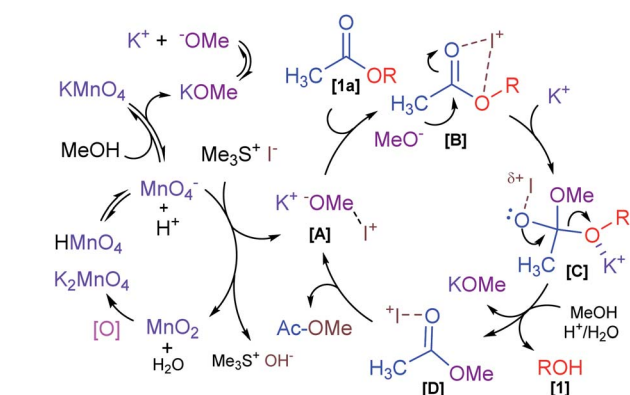
Experimental

Representative procedure for chemoselective deacetylation

To a previously prepared solution of acetate substrate (50 mg, 1.0 equiv.) in MeOH (1 mL) was added Me_3SI (0.1 equiv.) and KMnO_4 (0.1 equiv.). The mixture was stirred at room temperature in an open-air environment and the reaction progress was monitored by TLC. After the complete consumption of the starting material had occurred, typically 5 min to 12 h, the reaction mixture was filtered and washed with EtOAc (10 mL). The filtrate was treated with saturated aqueous NaHCO_3 (5 mL), and the aqueous layer was extracted with EtOAc (3×30 mL). The combined organic layers were then washed with water and brine, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo* to obtain the analytically pure products.

Conflicts of interest

There are no conflicts to declare.



Scheme 4 A plausible mechanism for Me_3SI -promoted selective deacetylation.



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