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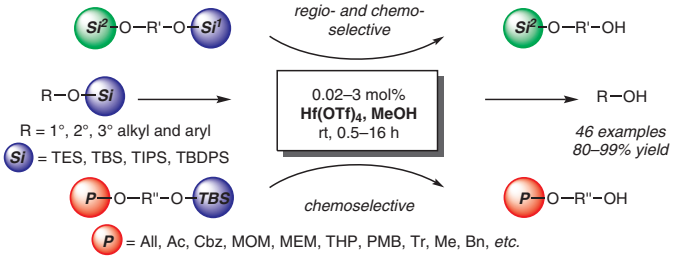
Hafnium Triflate as a Highly Potent Catalyst for Regio- and Chemoselective Deprotection of Silyl Ethers

Xiu-An Zheng
Rui Kong
Hua-Shan Huang
Jing-Ying Wei
Ji-Zong Chen
Shan-Shan Gong*
Qi Sun*

Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, 605 Fenglin Avenue, Nanchang, Jiangxi 330013, P. R. of China
gongshanshan@jxstnu.edu.cn
sunqi@jxstnu.edu.cn



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Abstract As a Group IVB transition metal Lewis acid, hafnium triflate [$Hf(OTf)_4$] exhibited exceptionally high potency in desilylations. Since the amounts of $Hf(OTf)_4$ required for the deprotection of 1°, 2°, 3° alkyl and aryl *tert*-butyldimethylsilyl (TBS) ethers are significantly different, ranging from 0.05 mol% to 3 mol%, regioselective deprotection of TBS could be easily implemented. Moreover, chemoselective cleavage of different silyl ethers or removal of TBS in the presence of most hydroxyl protecting groups was also accomplished. NMR analyses of silyl products from TBS deprotection indicated that $Hf(OTf)_4$-catalyzed desilylation may proceed via different mechanisms, depending on the solvent used.

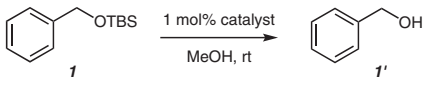
Key words hafnium triflate, desilylation, regioselectivity, chemoselectivity, mechanism

Silyl ethers, such as triethylsilyl (TES), *tert*-butyldimethylsilyl (TBS), triisopropylsilyl (TIPS), and *tert*-butyldiphenylsilyl (TBDPS), are one of the most prominent hydroxyl protecting groups in organic synthesis. Acidic and fluoride-based reagents have long been recognized for their capability in silyl ether deprotection. In addition, many basic, reducing, and oxidizing reagents have also been employed for the same purpose.[1,2] However, these methods have obvious limitations. Typically, excess of these reagents is required for desilylation. Therefore, selective deprotection of silyl ether protected polyhydroxy compounds, which is crucial for specific modification of individual hydroxyl groups, has always been a challenging task for these conventional methods.[3]

In recent years, metal Lewis acid based methods have emerged as a promising approach for the purpose of efficient and selective deprotection of silyl ethers. Though metal Lewis acids, such as $Sc(OTf)_3$,[4] $InCl_3$,[5] $Ce(OTf)_4$,[6] $ZnBr_2$,[7] $ZrCl_4$,[8,9] $SbCl_5$,[10] $SnCl_2{\cdot}6H_2O$,[11] $NiCl_2{\cdot}6H_2O$,[12] phosphomolybdic acid,[13] $CuBr_2$,[14] $FeCl_3$,[15] $Fe(OTs)_3$,[16] $SmCl_3$,[17] $CuSO_4{\cdot}5H_2O$,[18] $AlCl_3{\cdot}6H_2O$,[19] $Bi(OTf)_3$,[20] $NaAuCl_4{\cdot}2H_2O$,[21] and $Zn(OTf)_2$,[22] have been reported effective for desilylation, it should be noted that, typically, 5–30 mol% of these catalysts is required for the removal of 1° alkyl TBS ethers. Among these metal Lewis acids, only $Sc(OTf)_3$ and the recently reported $NaAuCl_4{\cdot}2H_2O$ are capable of cleaving TBS ethers at a level lower than 1 mol%. As the most potent metal Lewis acid for desilylation to date, generally only 0.5 mol% $NaAuCl_4{\cdot}2H_2O$ is needed to cleave 1° alkyl TBS ethers at room temperature. Moreover, the high catalytic activity further enhanced its regio- and chemoselectivity in TBS deprotection. However, the high cost of $NaAuCl_4{\cdot}2H_2O$ limits its practical applications. In this paper, we report the discovery of hafnium triflate [$Hf(OTf)_4$] as an even more potent, but much less expensive, catalyst for highly selective desilylation.

In our ongoing research on Group IVB transition metal Lewis acid catalysts, we have found that Hf(IV) salts exhibit superior activity than the closely related Zr(IV) salts in many reactions.[23,24] Therefore, we were curious to know whether Hf(IV) Lewis acids are more potent than $ZrCl_4$ in cleaving silyl ethers. In a preliminary experiment, the desilylation of benzyl TBS ether (**1**) in MeOH (AR grade) was used as a model to evaluate the catalytic activity of a series of Group IVB transition metal Lewis acids at 1 mol% level. The concentration of **1** was fixed at 0.15 M. The data in Table 1 show that all Zr(IV) salts tested were effective, but a reaction time of 1–6 hours was required. This result indicated that the catalytic activity of $ZrCl_4$ in desilylation has been undervalued in previous reports, possibly due to the unsuitable solvents used.[8,9] Interestingly, we observed that the desilylation reactions catalyzed by $HfCl_4$ and $Hf(OTf)_4$ were much faster than those catalyzed by Zr(IV) salts. As the most potent catalyst, $Hf(OTf)_4$ afforded nearly quantitative desilylation in only 10 minutes.

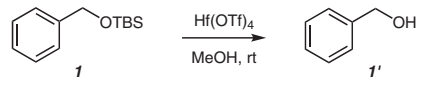
Table 1 Catalytic Activity of Group IVB Transition Metal Lewis Acids in TBS Deprotection



Entry	Catalyst	Reaction time	Isolated yield of **1′** (%)
1	$ZrCp_2Cl_2$	6 h	94
2	$ZrO(NO_3)_2$	4 h	95
3	$Zr(NO_3)_4$	3 h	95
4	$ZrOCl_2{\cdot}8H_2O$	1.5 h	96
5	$ZrCl_4$	1 h	96
6	$HfCp_2Cl_2$	2 h	94
7	$HfCl_4$	30 min	96
8	$Hf(OTf)_4$	10 min	98

To evaluate the potency of $Hf(OTf)_4$, we gradually reduced its amount from 1 mol% to 0.01 mol%. As listed in Table 2, when the equivalents of catalyst were reduced to as low as 0.05 mol%, $Hf(OTf)_4$ still resulted in high-yield deprotection of **1** in 12 hours. However, further lowering the catalyst amount to 0.01 mol% led to incomplete desilylation. The solvent effect on $Hf(OTf)_4$-catalyzed desilylation of **1** was also investigated. As shown in Table 3, 0.1 mol% $Hf(OTf)_4$ exhibited limited catalytic activity in most tested solvents. Only the reaction in CH_3CN resulted in a comparable yield and reaction rate to those in MeOH. However, there was always a trace amount of **1** left unreacted (*ca.* 5%) at the end of the reaction in CH_3CN.

Table 2 Effect of $Hf(OTf)_4$ Amount on TBS Deprotection

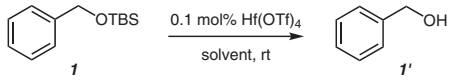


Entry	$Hf(OTf)_4$ (mol%)	Reaction time	Isolated yield of **1′** (%)
1	1	10 min	98
2	0.5	1 h	97
3	0.1	4 h	97
4	0.05	12 h	96
5	0.01	24 h	56[a]

[a] The reaction proceeded no further after 24 h.

In the subsequent research, we tested the catalytic effect of 0.1 mol% $Hf(OTf)_4$ on a diversity of *para*-substituted benzyl TBS ethers in MeOH. The data in Table 4 show that electron-donating groups (EDG; **2**, **3**) accelerated the cleavage of TBS ether, whereas electron-withdrawing groups (EWG; **4**–**7**) decelerated the desilylation process. The deprotection of 1° allylic TBS ethers **8**, **9** was much faster than

Table 3 Solvent Effect on $Hf(OTf)_4$-Catalyzed TBS Deprotection



Entry	Solvent	Reaction time (h)	Isolated yield of **1′** (%)
1	toluene	12	10[a]
2	DMF	12	15[a]
3	THF	12	21[a]
4	DCM	12	22[a]
5	acetone	12	35[a]
6	*i*PrOH	12	67[a]
7	CH_3CN	4	92
8	MeOH	4	97

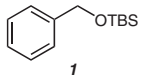
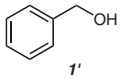
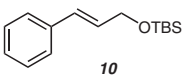
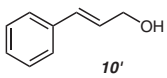
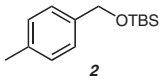
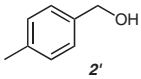
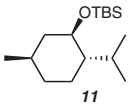
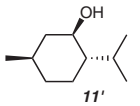
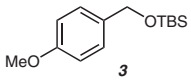
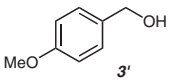
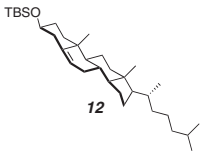
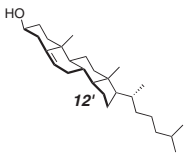
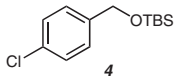
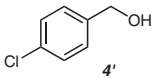
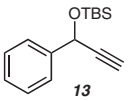
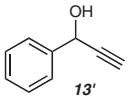
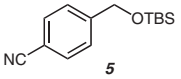
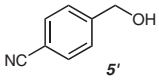
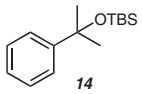
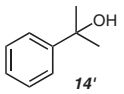
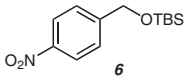
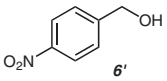
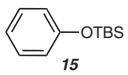
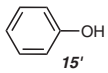
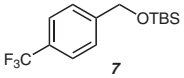
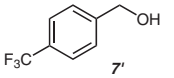
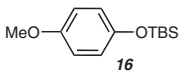
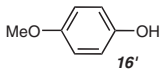
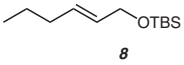
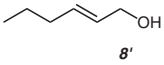
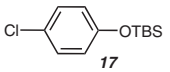
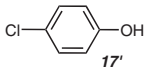
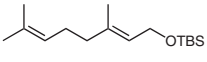
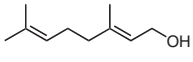
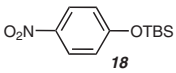
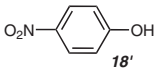
[a] The reaction was not complete and stopped after 12 h.

that of **1**, while the reaction of cinnamyl TBS ether (**10**) was similar to that of **1**. For the desilylation of 2° TBS ethers **11**–**13**, $Hf(OTf)_4$ needed to be increased to 0.4–0.6 mol% and the reactions took 4–8 hours. For 3° TBS ether **14**, 3 mol% $Hf(OTf)_4$ was needed to complete the deprotection in 5 hours. The effects of EDG and EWG on desilylation of phenolic substrates **15**–**18** were similar to those of *para*-substituted benzyl silyl ethers **2**–**7**. Compared to aliphatic TBS ethers, phenolic TBS ethers required 1–3 mol% $Hf(OTf)_4$ and 7–10 hours for desilylation in MeOH.

The significant differences in the amounts of $Hf(OTf)_4$ needed for the deprotection of 1°, 2°, 3° alkyl and aryl TBS ethers allowed us to achieve regioselective desilylation in substrates with multiple TBS groups (**19**–**26**, Table 5). Generally, 0.1 mol% $Hf(OTf)_4$ was ideal to selectively remove 1° alkyl TBS ether in the presence of 2°, 3° alkyl and aryl TBS ethers. However, the presence of other functional groups such as carbamate (**20**, **21**, **24**) required elevated amounts of $Hf(OTf)_4$ for regioselective removal of 1° or 2° alkyl TBS ether. As an extension of this method, the 5′-*O*-TBS of fully TBS protected uridine (**25**) and thymidine (**26**) was smoothly and selectively removed in high yield with 0.5 mol% $Hf(OTf)_4$.

In order to chemoselectively cleave different silyl ethers, such as TES, TBS, TIPS, and TBDPS, we first determined that the optimal amounts of $Hf(OTf)_4$ for deprotection of BnOTES (**27**), BnOTIPS (**28**), and BnOTBDPS (**29**) were 0.02 mol%, 1 mol%, and 3 mol%, respectively (Table 6). Therefore, 0.02 mol% $Hf(OTf)_4$ was ideal to remove 1° TES in the presence of 1° TBS (**30**), and 0.05 mol% $Hf(OTf)_4$ was used to cleave 1° TBS in the presence of 1° TIPS (**31**) and TBDPS (**32**) with high selectivity. In addition, 1 mol% $Hf(OTf)_4$ cleaved TIPS without affecting TBDPS (**33**). In our attempt to obtain **34′** from di-TBS-protected substrate, we found that ~50% of the 3° TBS was cleaved along with 2° TBS in the presence of even 0.5 mol% $Hf(OTf)_4$. This abnormal result suggested that, in this specific substrate, the interaction of 2° TBS with

Table 4 Deprotection of 1°, 2°, 3° Alkyl and Aryl TBS Ethers Catalyzed by $Hf(OTf)_4$ in MeOH

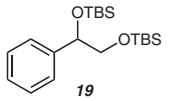
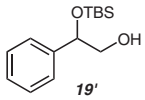
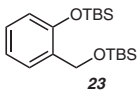
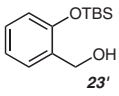
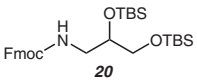
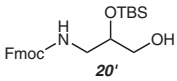
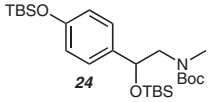
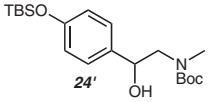
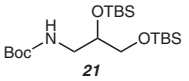
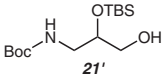
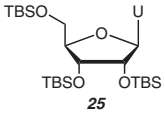
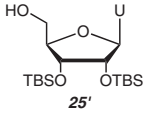
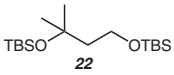
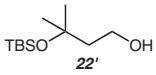
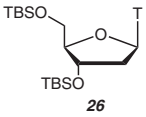
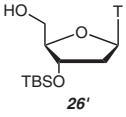
Substrate	Product	$Hf(OTf)_4$ (mol%)	Reaction time (h)	Isolated yield (%)	Substrate	Product	$Hf(OTf)_4$ (mol%)	Reaction time (h)	Isolated yield (%)
 **1**	 **1′**	0.1	4	97	 **10**	 **10′**	0.1	4	96
 **2**	 **2′**	0.1	3	96	 **11**	 **11′**	0.4	6	96
 **3**	 **3′**	0.1	3	97	 **12**	 **12′**	0.4	8	95
 **4**	 **4′**	0.1	7	95	 **13**	 **13′**	0.6	4	95
 **5**	 **5′**	0.1	9	96	 **14**	 **14′**	3	5	93
 **6**	 **6′**	0.1	12	95	 **15**	 **15′**	1	10	97
 **7**	 **7′**	0.1	12	94	 **16**	 **16′**	1	7	95
 **8**	 **8′**	0.1	1	96	 **17**	 **17′**	3	8	96
 **9**	 **9′**	0.1	1	96	 **18**	 **18′**	3	10	96

$Hf(OTf)_4$ may bring the 3° TBS to the vicinity of the Hf(IV) catalytic center. To solve this problem, the 2° TBS was replaced with TES in substrate **34**. The selectivity of 2° TES over 3° TBS in **34** was achieved by using only 0.02 mol% $Hf(OTf)_4$.

Finally, we explored the possibility to cleave TBS ethers in the presence of other commonly used hydroxyl protecting groups (substrates **35**–**46**). The results in Table 6 show that allyl (All), acetyl (Ac), carboxybenzyl (Cbz), and especially acid-labile methoxymethyl (MOM), (2-methoxyethoxy)methyl (MEM), 2-tetrahydropyranyl (THP), *p*-methoxybenzyl (PMB), isopropylidene, methyl/benzyl glycosides, and even trityl (Tr) could be maintained under the conditions for desilylation of 1° TBS. Only dimethoxytrityl (DMT) was cleaved along with 1° TBS due to its ultrahigh sensitivity to acids. It is noteworthy that in the presence of certain functional groups or in more complicated substrates, such as nucleosides and saccharides, elevated amounts of $Hf(OTf)_4$ were needed to deprotect 1° TBS.

In several previous research efforts on metal Lewis acid catalyzed TBS deprotection, the catalytic activity was simply ascribed to the Brønsted acid generated *in situ*.[12,13] To test this point, we added 0.5 mol% triflic acid (TfOH) to a MeOH solution of **1**. After 12 hours, only a trace amount of TBS was cleaved. To reveal the interactions of $Hf(OTf)_4$ and **1**, we attempted to see whether addition of $Hf(OTf)_4$ to **1** could cause complex formation and result in notable changes in either the ^1H or ^{13}C NMR data. Due to the fact that CD_3CN is nonreactive in this reaction and contains only a trace amount of water, it should be easier to catch the intermediate complex than in MeOH-d_4. Unfortunately, from the NMR tracing experiments, we did not observe formation of

Table 5 Regioselective Deprotection of TBS Ethers Catalyzed by $Hf(OTf)_4$

Substrate	Product	$Hf(OTf)_4$ (mol%)	Reaction time (h)	Isolated yield (%)	Substrate	Product	$Hf(OTf)_4$ (mol%)	Reaction time (h)	Isolated yield (%)
 **19**	 **19′**	0.1	4	95	 **23**	 **23′**	0.1	6	94
 **20**	 **20′**	0.3	8	97	 **24**	 **24′**	0.8	16	83
 **21**	 **21′**	0.3	7	96	 **25**	 **25′**	0.5	6	85
 **22**	 **22′**	0.1	2	82	 **26**	 **26′**	0.5	6	88

any stable complex like that we have seen in another $Hf(OTf)_4$-catalyzed reaction,[24] when we gradually added 0.1 mol% to 2 mol% $Hf(OTf)_4$ to **1** in CD_3CN. Therefore, the coordination/dissociation of **1** with Hf(IV) seems to be an ultrafast process.

Instead, at this point, we noticed that 45% of **1** had been desilylated by the trace amount of H_2O in the reaction system, with a single silyl product. However, after 1.5 equivalents of H_2O were added, interestingly, a substantial amount of a second silyl product was observed (Figure 1, A). By a comparison with literature data[25,26] and authentic samples, the first silyl product formed during the addition of catalyst was identified as $(TBS)_2O$ ($Si(CH_3)_2$: –2.6 ppm), while the second silyl product formed after the addition of 1.5 equivalents of H_2O was TBSOH ($Si(CH_3)_2$: –3.3 ppm).

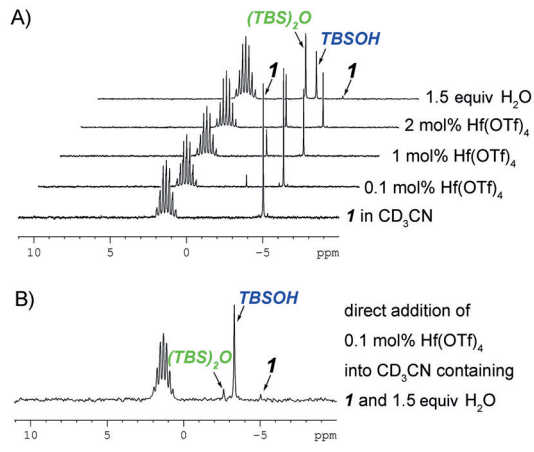


Figure 1 ^{13}C NMR analysis of the $Hf(OTf)_4$-catalyzed desilylation of **1** in CD_3CN ([**1**] = 0.3 M)

This result was surprising to us, because TBSOH is supposed to be the major product, if the desilylation proceeds via direct hydrolysis as proposed in a previous report[13] (Figure 2, Path B). Because of the bulky size and very small quantity, further reaction of TBSOH with Hf(IV)-activated **1** via S_N2-type alcoholysis should not be easy. The presence of $(TBS)_2O$ as the sole product in the presence of a trace amount of H_2O indicates that a highly reactive TBS species, TBSOTf,[27] is very possibly generated via a fast ligand-exchange process (Figure 2, Path A).[20,28,29] The subsequent hydrolysis of TBSOTf consumes the trace amount of H_2O and yields TBSOH, which immediately reacts with the highly reactive TBSOTf to generate $(TBS)_2O$ as the sole product. To mimic the conditions for desilylation in AR grade CH_3CN, we directly performed the reaction in CD_3CN containing 1.5 equivalents of H_2O. The NMR data showed that $(TBS)_2O$ and TBSOH were obtained in a ratio of 1:10 (determined by ^1H NMR) due to the competitive hydrolysis of TBSOTf by more

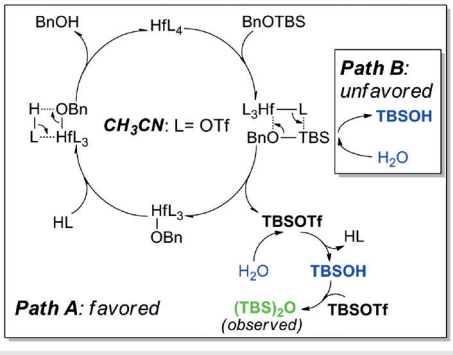
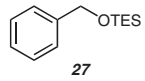
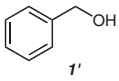
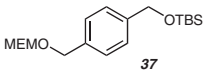
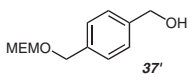
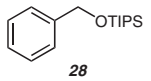
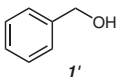
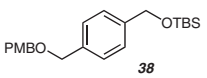
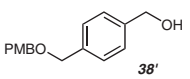
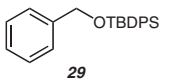
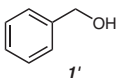
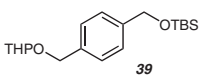
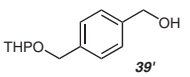
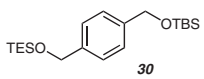
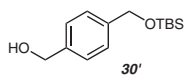
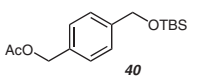
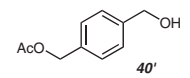
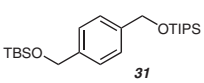
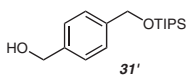
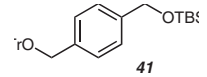
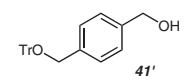
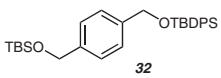
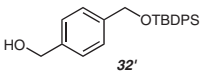
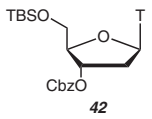
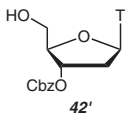
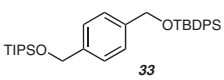
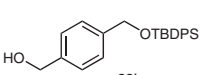
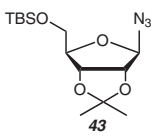
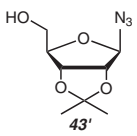
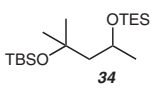
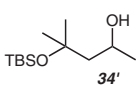
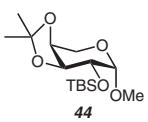
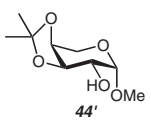
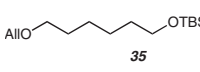
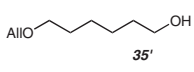
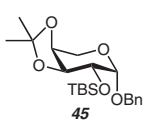
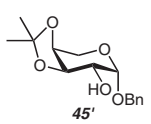
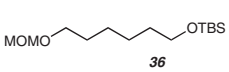
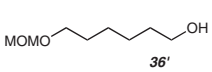
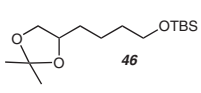
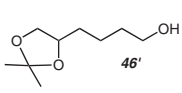


Figure 2 Proposed mechanism for $Hf(OTf)_4$-catalyzed desilylation in AR grade CH_3CN

Table 6 Chemoselective Deprotection of Silyl Ethers Catalyzed by $Hf(OTf)_4$

Substrate	Product	$Hf(OTf)_4$ (mol%)	Reaction time (h)	Isolated yield (%)	Substrate	Product	$Hf(OTf)_4$ (mol%)	Reaction time (h)	Isolated yield (%)
 **27**	 **1′**	0.02	4	99	 **37**	 **37′**	0.1	3	96
 **28**	 **1′**	1	3	96	 **38**	 **38′**	0.1	6	98
 **29**	 **1′**	3	3	97	 **39**	 **39′**	0.3	8	93
 **30**	 **30′**	0.02	0.5	90	 **40**	 **40′**	0.3	10	95
 **31**	 **31′**	0.05	12	95	 **41**	 **41′**	0.3	16	80
 **32**	 **32′**	0.05	12	94	 **42**	 **42′**	0.5	16	84
 **33**	 **33′**	1	5	95	 **43**	 **43′**	0.4	12	95
 **34**	 **34′**	0.02	3	85	 **44**	 **44′**	0.4	10	94
 **35**	 **35′**	0.1	1	96	 **45**	 **45′**	0.4	10	92
 **36**	 **36′**	0.1	1	97	 **46**	 **46′**	0.1	2	97

H_2O molecules in this case (Figure 1, B). In CH_3CN, the direct hydrolysis pathway (Figure 2, Path B) should be unfavored, because H_2O is largely outnumbered by solvent molecules. Therefore, the fast ligand exchange within the transient Hf(IV) coordinate should be dominant (Figure 2, Path A). It is worth mentioning that both ^1H and ^{13}C NMR data showed that ~5% of **1** was left unreacted even after prolonged time, suggesting that the desilylation reaches an equilibrium due to the limited amount of H_2O in CH_3CN, which is in good agreement with our experimental result (Table 3, entry 7).

In contrast to the reaction in CH_3CN, $Hf(OTf)_4$-catalyzed desilylation in MeOH proceeds more completely. It is understandable that direct alcoholysis of activated **1** should no longer be neglected as a minor pathway in the presence of a large excess of MeOH (Figure 3, Path B). In addition, $Hf(OTf)_4$ is also transformed into a more complicated complex ($HfL_nL'_m$) due to ligand insertion/exchange by MeOH.[30] The fast ligand exchange of coordinated **1** with MeO^- (L′) or TfO^- (L) should generate TBSOMe or TBSOTf. But, we could envision that the formation of TBSOTf is no longer a major pathway because a substantial amount of TfO^- (L) has been

exchanged by MeO^- (L′) and competition from MeOH (solvent) and MeO^- (L′) may significantly suppress TBS transfer to TfO^- (L). Due to the presence of a large excess of MeOH, the very small amount of TBSOTf generated should be immediately quenched as TBSOMe (Figure 3, Path A).

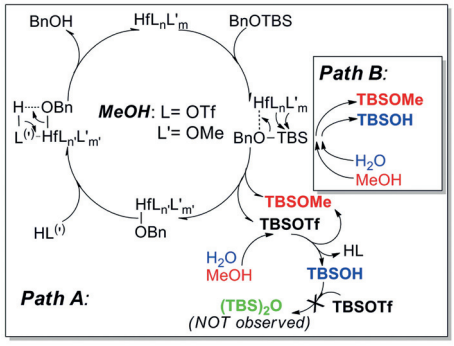


Figure 3 Proposed mechanism for $Hf(OTf)_4$-catalyzed desilylation in AR grade MeOH

In a previous report,[11] H_2O had been intentionally added to alcohol solvent to facilitate metal Lewis acid catalyzed desilylation. Therefore, ^1H and ^{13}C NMR spectroscopy were employed to analyze the $Hf(OTf)_4$-catalyzed desilylation of **1** in MeOH-d_4 with various amounts of H_2O (0.3, 1.5, 3.0, and 9.0 equiv). The experiments showed that $(TBS)_2O$ was not observed as a silyl product in any of these cases, while TBSOH ($Si(CH_3)_2$: –3.7 ppm) and TBSOMe ($Si(CH_3)_2$: –5.9 ppm) were the only two silyl products generated, which is in good agreement with the mechanism proposed above. With an increasing amount of H_2O, the ratio of TBSOH/TBSOMe was elevated from 5:95 to 66:34 (Figure 4). Surprisingly, the desilylation decelerated (1 to 6 h) with an increasing amount of H_2O (0.3 to 9 equiv). Though addition of more H_2O provides a higher number of stronger nucleophiles, it seems that enhanced interaction of Hf(IV) with more H_2O molecules may significantly lower its interaction rate with **1** at the same time. Another interesting result was that upon completion of desilylation, the ratio of TBSOH/TBSOMe in all four cases no longer changed any more, indicating that TBSOMe was not eventually converted into TBSOH as described in a previous report.[18] Our results indicate that $Hf(OTf)_4$-catalyzed desilylation in MeOH is essentially a fast-equilibrating silyl transfer from **1** to both MeOH and H_2O promoted by Hf(IV). We conclude that it is unwise to add extra H_2O to promote $Hf(OTf)_4$-catalyzed desilylation in MeOH, since it will not benefit the desilylation with regard to either reaction rate or equilibrium.

In summary, $Hf(OTf)_4$ was identified as an extremely potent metal Lewis acid catalyst for the deprotection of silyl ethers. Cleavage of the most labile 1° alkyl TES ether only required 0.02 mol% $Hf(OTf)_4$ in MeOH at ambient temperature. When the amount of catalyst was gradually increased from 0.05 mol% to 3 mol%, $Hf(OTf)_4$ could efficiently cleave 1°, 2°, 3° alkyl and aryl TBS ethers, and 1° TIPS and TBDPS ethers, and enabled both regio- and chemoselective desilylation in a diversity of multisilylated substrates. Moreover, the deprotection of 1° TBS ethers at mol‰ level is orthogonal to most hydroxyl protecting groups, thereby making this $Hf(OTf)_4$-based method applicable to the synthesis of complicated multifunctional molecules. With the assistance of NMR analysis, it was proposed that desilylation in CH_3CN mainly proceeds via fast ligand exchange within the transient Hf(IV) coordinate, whereas desilylation in MeOH may involve both direct alcoholysis and ligand-exchange pathways.

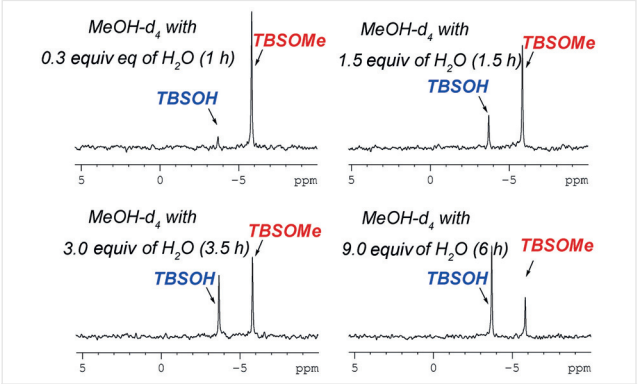


Figure 4 ^{13}C NMR analysis of the $Hf(OTf)_4$-catalyzed desilylation of **1** in MeOH-d_4 ([**1**] = 0.3 M)

General chemical reagents and solvents were obtained from commercial suppliers. Compounds **1**–**46** were prepared according to methods described in the literature.[1,2,21] All reactions were monitored by TLC on plates coated with 0.25 mm silica gel 60 F_{254}. TLC plates were visualized by UV irradiation (254 nm) or staining with *p*-anisaldehyde. Flash column chromatography employed silica gel (particle size 32–63 μm). Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. NMR spectra were obtained with a Bruker AV-400 instrument; chemical shifts are reported in parts per million (ppm, δ) and referenced to $CDCl_3$, DMSO-d_6, or D_2O. Low- and high-resolution mass spectra are reported as *m*/*z* values and were obtained with a Bruker amaZon SL mass spectrometer and a Bruker Daltonics micrOTOF-Q II spectrometer, respectively.

$Hf(OTf)_4$-Catalyzed Desilylation; General Procedure

To a solution of silyl ether in MeOH (AR grade) was added $Hf(OTf)_4$ (0.02–3 mol%). The reaction ([substrate] = 0.15 M) was stirred at room temperature for 0.5–16 h and monitored by TLC. Upon completion, excess triethylamine was added to neutralize the Lewis acid. The solution was concentrated *in vacuo*. Flash column chromatography on silica gel afforded desilylated product in pure form.

2-((*tert*-Butyldimethylsilyl)oxy)-2-phenylethanol (19′)

Colorless oil; yield: 478 mg (95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.32 (m, 4 H), 7.32–7.25 (m, 1 H), 4.82–4.77 (m, 1 H), 3.65–3.57 (m, 2 H), 2.30–2.24 (m, 1 H), 0.95 (s, 9 H), 0.10 (s, 3 H), 0.06 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6, 128.4 (×2), 127.8, 126.4 (×2), 76.0, 69.0, 26.0 (×3), 18.3, –4.4, –4.8.

MS (ESI): *m*/*z* = 253.2 $[M + H]^+$.

9*H*-Fluoren-9-ylmethyl 2-((*tert*-butyldimethylsilyl)oxy)-3-hydroxypropylcarbamate (20′)

Colorless oil; yield: 827 mg (97%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.5 Hz, 2 H), 7.62–7.56 (m, 2 H), 7.44–7.38 (m, 2 H), 7.35–7.28 (m, 2 H), 5.08 (t, *J* = 6.2 Hz, 1 H), 4.50–4.37 (m, 2 H), 4.22 (t, *J* = 6.8 Hz, 1 H), 3.88–3.79 (m, 1 H), 3.54–3.38 (m, 3 H), 3.25–3.14 (m, 1 H), 2.76–2.65 (m, 1 H), 0.91 (s, 9 H), 0.09 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 144.0 (×2), 141.5 (×2), 127.9 (×2), 127.2 (×2), 125.2, 125.1, 120.2 (×2), 71.3, 67.0, 63.5, 47.4, 43.5, 26.0 (×3), 18.2, –4.5, –4.6.

MS (ESI): *m*/*z* = 428.2 $[M + H]^+$.

***tert*-Butyl 2-((*tert*-butyldimethylsilyl)oxy)-3-hydroxypropylcarbamate (21′)**

Colorless oil; yield: 585 mg (96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.85 (t, *J* = 6.1 Hz, 1 H), 3.83–3.76 (m, 1 H), 3.52–3.37 (m, 3 H), 3.13–3.01 (m, 2 H), 1.43 (s, 9 H), 0.88 (s, 9 H), 0.08–0.05 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 80.0, 71.6, 63.4, 43.2, 28.5 (×3), 26.0 (×3), 18.2, –4.5, –4.6.

MS (ESI): *m*/*z* = 306.2 $[M + H]^+$.

3-((*tert*-Butyldimethylsilyl)oxy)-3-methylbutan-1-ol (22′)

Colorless oil; yield: 357 mg (82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83–3.76 (m, 2 H), 3.20–3.14 (m, 1 H), 1.69 (t, *J* = 5.8 Hz, 2 H), 1.28 (s, 6 H), 0.84 (s, 9 H), 0.13–0.09 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 75.5, 60.1, 45.8, 30.0 (×2), 26.0 (×3), 18.1, –1.8 (×2).

MS (ESI): *m*/*z* = 219.2 $[M + H]^+$.

(2-((*tert*-Butyldimethylsilyl)oxy)phenyl)methanol (23′)

Colorless oil; yield: 447 mg (94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.30 (m, 1 H), 7.22–7.15 (m, 1 H), 7.00–6.94 (m, 1 H), 6.83 (d, *J* = 6.4 Hz, 1 H), 4.68 (d, *J* = 6.2 Hz, 2 H), 2.36 (t, *J* = 6.3 Hz, 1 H), 1.04 (s, 9 H), 0.27 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.5, 131.6, 128.9, 128.7, 121.5, 118.5, 61.9, 25.9 (×3), 18.3, –4.0 (×2).

MS (ESI): *m*/*z* = 239.1 $[M + H]^+$.

***tert*-Butyl 2-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-2-hydroxyethyl(methyl)carbamate (24′)**

White solid; yield: 632 mg (83%); mp 41–42 °C.

IR (KBr): 3253, 2912, 1725, 1675, 1394, 1215, 1030 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 8.2 Hz, 2 H), 6.80 (d, *J* = 8.2 Hz, 2 H), 4.86–4.82 (m, 1 H), 4.16–4.13 (m, 1 H), 3.51–3.30 (m, 2 H), 2.80 (s, 3 H), 1.45 (s, 9 H), 0.97 (s, 9 H), 0.17 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 155.3, 135.2, 127.1 (×2), 120.1 (×2), 80.3, 73.4, 57.6, 36.5, 28.5 (×3), 25.8 (×3), 18.3, –4.3 (×2).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{36}NO_4Si$: 382.2408; found: 382.2404.

2′,3′-Di-*O*-(*tert*-butyldimethylsilyl)uridine (25′)

White solid; yield: 802 mg (85%); mp 226–228 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.35 (s, 1 H), 7.94 (d, *J* = 8.1 Hz, 1 H), 5.80 (d, *J* = 5.6 Hz, 1 H), 5.68 (d, *J* = 8.1 Hz, 1 H), 5.28–5.21 (m, 1 H), 4.28–4.21 (m, 1 H), 4.16–4.11 (m, 1 H), 3.88 (s, 1 H), 3.71–3.61 (m, 1 H), 3.60–3.51 (m, 1 H), 0.88 (s, 9 H), 0.82 (s, 9 H), 0.11–0.05 (m, 6 H), 0.04–0.01 (m, 6 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.9, 150.7, 140.3, 102.0, 86.9, 85.5, 74.6, 71.8, 60.4, 25.7 (×3), 25.6 (×3), 17.7, 17.6, –4.7, –4.8, –4.9, –5.1.

MS (ESI): *m*/*z* = 473.2 $[M + H]^+$.

3′-*O*-(*tert*-Butyldimethylsilyl)thymidine (26′)

White solid; yield: 627 mg (88%); mp 95–97 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.53 (br, 1 H), 7.41 (s, 1 H), 6.15 (t, *J* = 6.7 Hz, 1 H), 4.51–4.44 (m, 1 H), 3.94–3.86 (m, 2 H), 3.77–3.69 (m, 1 H), 3.18 (br, 1 H), 2.35–2.27 (m, 1 H), 2.23–2.16 (m, 1 H), 1.87 (s, 3 H), 0.87 (s, 9 H), 0.06 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 150.6, 137.2, 111.1, 87.8, 86.8, 71.7, 62.0, 40.7, 25.9 (×3), 18.1, 12.6, –4.6, –4.7.

MS (ESI): *m*/*z* = 357.2 $[M + H]^+$.

(4-(((*tert*-Butyldimethylsilyl)oxy)methyl)phenyl)methanol (30′)

Colorless oil; yield: 453 mg (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (s, 4 H), 4.74 (s, 2 H), 4.64 (d, *J* = 5.1 Hz, 2 H), 2.13–2.07 (m, 1 H), 0.95 (s, 9 H), 0.11 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0, 139.7, 127.1 (×2), 126.4 (×2), 65.3, 64.9, 26.1 (×3), 18.6, –5.1 (×2).

MS (ESI): *m*/*z* = 253.2 $[M + H]^+$.

(4-(((Triisopropylsilyl)oxy)methyl)phenyl)methanol (31′)

Colorless oil; yield: 558 mg (95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.30 (m, 4 H), 4.84 (s, 2 H), 4.66 (d, *J* = 5.3 Hz, 2 H), 1.88 (t, *J* = 5.6 Hz, 1 H), 1.24–1.14 (m, 3 H), 1.13–1.07 (m, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.4, 139.5, 127.1 (×2), 126.1 (×2), 65.4, 65.0, 18.2 (×6), 12.2 (×3).

MS (ESI): *m*/*z* = 295.2 $[M + H]^+$.

(4-(((*tert*-Butyldiphenylsilyl)oxy)methyl)phenyl)methanol (32′)

Colorless oil; yield: 705 mg (94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.74 (m, 4 H), 7.51–7.35 (m, 10 H), 4.83 (s, 2 H), 4.70 (s, 2 H), 2.09 (s, 1 H), 1.16 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.7, 139.7, 135.7 (×5), 133.6, 129.9 (×2), 127.9 (×4), 127.1 (×2), 126.4 (×2), 65.5, 65.3, 27.0 (×3), 19.5.

MS (ESI): *m*/*z* = 377.2 $[M + H]^+$.

4-((*tert*-Butyldimethylsilyl)oxy)-4-methylpentan-2-ol (34′)

Colorless oil; yield: 394 mg (85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.31 (s, 1 H), 4.21–4.12 (m, 1 H), 1.71–1.65 (m, 1 H), 1.42–1.37 (m, 1 H), 1.34 (s, 3 H), 1.30 (s, 3 H), 1.14 (d, *J* = 6.2 Hz, 3 H), 0.87 (s, 9 H), 0.15 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 76.2, 65.2, 52.0, 32.2, 28.2, 26.0 (×3), 23.9, 18.1, –1.8 (×2).

MS (ESI): *m*/*z* = 233.2 $[M + H]^+$.

6-(Allyloxy)hexan-1-ol (35′)

Colorless oil; yield: 303 mg (96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.91–5.78 (m, 1 H), 5.24–5.16 (m, 1 H), 5.13–5.07 (m, 1 H), 3.92–3.87 (m, 2 H), 3.56–3.50 (m, 2 H), 3.36 (t, *J* = 6.6 Hz, 2 H), 2.63–2.49 (br, 1 H), 1.59–1.44 (m, 4 H), 1.37–1.26 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.1, 116.7, 71.8, 70.4, 62.6, 32.7, 29.7, 26.0, 25.7.

MS (ESI): *m*/*z* = 159.1 $[M + H]^+$.

6-(Methoxymethoxy)hexan-1-ol (36′)

Colorless oil; yield: 315 mg (97%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.65–4.59 (m, 2 H), 3.64–3.59 (m, 2 H), 3.50 (t, *J* = 6.6 Hz, 3 H), 3.34 (s, 2 H), 1.72–1.66 (br, 1 H), 1.61–1.53 (m, 4 H), 1.40–1.35 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 96.6, 67.9, 63.0, 55.2, 32.9, 29.8, 26.2, 25.7.

MS (ESI): *m*/*z* = 163.1 $[M + H]^+$.

(4-((2-Methoxyethoxy)methoxymethyl)phenyl)methanol (37′)

Colorless oil; yield: 435 mg (96%).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.31–7.26 (m, 4 H), 5.18 (t, *J* = 5.7 Hz, 1 H), 4.76 (d, *J* = 10.8 Hz, 1 H), 4.69 (s, 1 H), 4.53 (d, *J* = 13.5 Hz, 2 H), 4.48 (d, *J* = 5.7 Hz, 2 H), 3.65–3.60 (m, 2 H), 3.49–3.44 (m, 2 H), 3.25 (t, *J* = 6.3 Hz, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 141.7, 136.3, 127.4 (×2), 126.3 (×2), 94.0, 71.2, 68.3, 66.3, 62.6, 58.0.

MS (ESI): *m*/*z* = 227.1 $[M + H]^+$.

(4-((4-Methoxybenzyloxy)methyl)phenyl)methanol (38′)

Colorless oil; yield: 505 mg (98%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.23 (m, 6 H), 6.87 (d, *J* = 7.6 Hz, 2H), 4.58 (s, 2 H), 4.49 (s, 2 H), 4.45 (s, 2 H), 3.77 (s, 3 H), 2.44 (br, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 140.5, 137.7, 130.3, 129.5 (×2), 128.1 (×2), 127.1 (×2), 113.9 (×2), 71.7, 71.6, 64.9, 55.3.

MS (ESI): *m*/*z* = 259.1 $[M + H]^+$.

(4-(Tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl)methanol (39′)

Colorless oil; yield: 413 mg (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.31 (m, 4 H), 4.77 (d, *J* = 12.0 Hz, 1 H), 4.69 (t, *J* = 3.4 Hz, 1 H), 4.66 (s, 2 H), 4.49 (d, *J* = 12.0 Hz, 1 H), 3.95–3.87 (m, 1 H), 3.58–3.50 (m, 1 H), 2.10 (s, 1 H), 1.88–1.81 (m, 1 H), 1.77–1.69 (m, 1 H), 1.68–1.50 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.4, 137.9, 128.2 (×2), 127.2 (×2), 97.9, 68.7, 65.2, 62.3, 30.7, 25.6, 19.5.

MS (ESI): *m*/*z* = 223.1 $[M + H]^+$.

(4-(Acetoxymethyl)phenyl)methanol (40′)

Colorless oil; yield: 343 mg (95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.30 (m, 4 H), 5.07 (s, 2 H), 4.65 (s, 2 H), 2.40–2.32 (br, 1 H), 2.08 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 141.2, 135.3, 128.6 (×2), 127.2 (×2), 66.2, 64.9, 21.1.

MS (ESI): *m*/*z* = 181.1 $[M + H]^+$.

(4-(Trityloxymethyl)phenyl)methanol (41′)

Colorless oil; yield: 609 mg (80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.48 (m, 6 H), 7.42–7.22 (m, 13 H), 4.68 (s, 2 H), 4.17 (s, 2 H), 1.65 (br, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3 (×3), 139.9, 138.8, 128.9 (×6), 128.0 (×6), 127.4 (×3), 127.2 (×4), 87.2, 65.7, 65.4.

MS (ESI): *m*/*z* = 381.2 $[M + H]^+$.

3′-*O*-(Benzyloxycarbonyl)thymidine (42′)

White solid; yield: 630 mg (84%); mp 65–67 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.18 (s, 1 H), 7.45 (s, 1 H), 7.41–7.33 (m, 5 H), 6.21–6.14 (m, 1 H), 5.32–5.28 (m, 1 H), 5.17 (s, 2 H), 4.17 (s, 1 H), 3.96–3.85 (m, 2 H), 3.01 (s, 1 H), 2.56–2.39 (m, 2 H), 1.90 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9, 154.7, 150.6, 136.8, 134.9, 129.0, 128.9 (×2), 128.6 (×2), 111.5, 86.9, 85.1, 78.4, 70.3, 62.8, 37.2, 12.7.

MS (ESI): *m*/*z* = 377.1 $[M + H]^+$.

2,3-*O*-Isopropylidene-β-D-ribofuranosyl 1-Azide (43′)

Colorless oil; yield: 407 mg (95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.53 (s, 1 H), 4.76 (d, *J* = 5.9 Hz, 1 H), 4.51 (d, *J* = 5.9 Hz, 1 H), 4.39 (dd, J_1 = J_2 = 4.6 Hz, 1 H), 3.76 (dd, J_1 = 12.2 Hz, J_2 = 4.0 Hz, 1 H), 3.67 (dd, J_1 = 12.2 Hz, J_2 = 5.1 Hz, 1 H), 2.42 (br, 1 H), 1.49 (s, 3 H), 1.31 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.2, 98.2, 88.7, 86.1, 81.8, 63.8, 26.7, 25.1.

MS (ESI): *m*/*z* = 216.1 $[M + H]^+$.

Methyl 3,4-*O*-isopropylidene-β-L-arabinopyranoside (44′)

Colorless oil; yield: 383 mg (94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.61 (d, *J* = 3.3 Hz, 1 H), 4.13–4.07 (m, 2 H), 3.83 (s, 2 H), 3.68–3.64 (m, 1 H), 3.34 (s, 3 H), 3.01 (s, 1 H), 1.43 (s, 3 H), 1.26 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.1, 99.0, 76.1, 73.0, 70.1, 59.3, 55.6, 27.9, 26.0.

MS (ESI): *m*/*z* = 205.1 $[M + H]^+$.

Benzyl 3,4-*O*-isopropylidene-β-L-arabinopyranoside (45′)

Colorless oil; yield: 515 mg (92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.31 (m, 5 H), 4.93 (d, *J* = 3.6 Hz, 1 H), 4.79 (d, *J* = 11.8 Hz, 1 H), 4.55 (d, *J* = 11.8 Hz, 1 H), 4.25–4.18 (m, 2 H), 4.04–3.98 (m, 1 H), 3.96–3.90 (m, 1 H), 3.83–3.77 (m, 1 H), 2.25 (br, 1 H), 1.53 (s, 3 H), 1.36 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.2, 128.7 (×2), 128.2 (×3), 109.4, 97.1, 76.1, 73.1, 70.1, 70.0, 60.2, 28.0, 26.1.

MS (ESI): *m*/*z* = 281.1 $[M + H]^+$.

4-(2,2-Dimethyl-1,3-dioxolan-4-yl)butan-1-ol (46′)

Colorless oil; yield: 338 mg (97%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.12–3.99 (m, 2 H), 3.67–3.59 (m, 2 H), 3.51 (t, *J* = 7.3 Hz, 1 H), 1.70 (s, 1 H), 1.66–1.44 (s, 5 H), 1.40 (s, 3 H), 1.35 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 108.9, 76.2, 69.6, 62.8, 33.4, 32.8, 27.1, 25.9, 22.2.

MS (ESI): *m*/*z* = 175.1 $[M + H]^+$.

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Supporting Information

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