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Bismuth Triflate-Catalyzed Addition of Allylsilanes to *N*-Alkoxycarbonylamino Sulfones: Convenient Access to 3-Cbz-Protected Cyclohexenylamines

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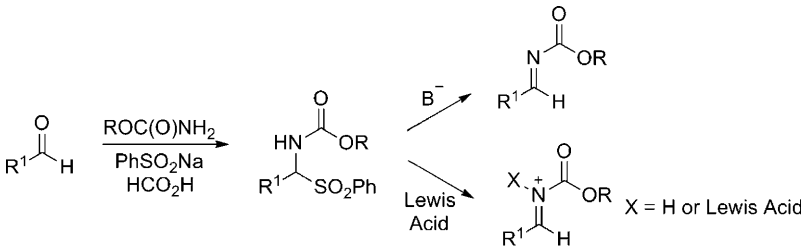
Abstract: Bismuth triflate was found to be an efficient catalyst in the Sakurai reaction of allyltrimethylsilanes with *N*-alkoxycarbonylamino sulfones. The reaction proceeded smoothly with a low catalyst loading of $Bi(OTf)_3 \cdot 4H_2O$ (2–5 mol%) to afford the corresponding protected homoallylic amines in very good yields (up to 96%). A sequential allylation reaction followed by ring-closing metathesis delivers 6–8 membered 3-Cbz-protected cycloalkenylamines.

Keywords: *N*-alkoxycarbonylamino sulfones; allylation; bismuth; ring-closing metathesis; Sakurai reaction; silanes

Introduction

The development of new methods for the synthesis of homoallylic amines is an important area of synthetic efforts. Homoallylic amines have attracted much synthetic effort and enjoy widespread use in natural product and bioactive molecule synthesis.[1] Among the variety of synthetic methods so far reported, the Lewis acid-catalyzed reaction of imines with silyl nucleophiles provides an efficient route for the synthesis of such compounds. However, the instability of carbamate-protected alkylimines has greatly hampered the development of catalytic reactions. Therefore, methods involving the *in situ* generation of imines are highly attractive, among which the one-pot allylation of imines has been proposed. Yet, most Lewis acids cannot be used in this reaction because they decompose or deactivate in the presence of the amine or water produced during imine formation. Very reactive *N*-acyliminium species, easily prepared from stable precursors, provide an attractive alternative.[2] Scheme 1 illustrates the preparation of the *N*-acylimine precursor from corresponding aldehydes.[2m] *N*-Alkoxycarbonylimines have been prepared by basic treatment of the *N*-alkoxycarbonylamino sulfones. The corresponding *N*-alkoxycarbonyliminium derivatives have been prepared by the use of a Lewis acid (Scheme 1). Over the past years, some elegant syntheses, including Sakurai and Mannich-type reactions, have been described, using *N*-alkoxycarbonylamino sulfones as substrates.[2] We wish to report herein the $Bi(OTf)_3 \cdot 4H_2O$-catalyzed Sakurai reaction of *N*-alkoxycarbonylamino sulfones. Alkoxycarbonyl-protected homoallylic amines were obtained efficiently in the presence of 2–5 mol% of $Bi(OTf)_3 \cdot 4H_2O$. Recently, synthetic methods involving Lewis acids such as



Scheme 1. Access to acylimines and iminium species from *N*-alkoxycarbonylamino aminosulfones.

$TiCl_4$, $SnCl_4$, $GaCl_3$, or $InCl_3$ have been reported.[3] However, the use of Ti(IV) and Sn(IV) salts in stoichiometric quantity or in large excess often restricts their utilization. The moisture sensitivity of these catalysts and the high cost of some of them restrain their use as well.

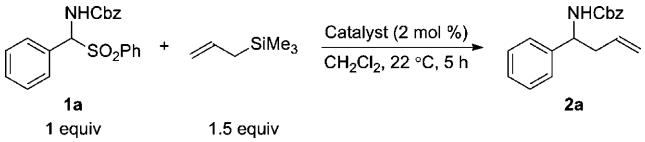
As a part of our ongoing interest in Bi(III)-catalyzed reactions involving silyl nucleophiles, we report herein a general $Bi(OTf)_3{\cdot}4H_2O$-catalyzed method for the addition of allylsilanes to *N*-alkoxycarbonylamino sulfones. Bismuth salts indeed provide a good alternative as they have recently attracted attention due to their low toxicity, low cost and environmentally benign character.[4] Bismuth salts have been reported as catalysts for the opening of epoxides,[5] Mukaiyama aldol reactions,[6] Mannich-type and Sakurai reactions,[7] formation and deprotection of acetals,[8] etherification reactions,[9] hydroamination reactions,[10] Friedel–Crafts reactions, and Fries and Claisen rearrangements.[11] $Bi(OTf)_3{\cdot}4H_2O$ is particularly attractive because it is commercially available or can be easily prepared from commercially available compounds. We recently reported the $Bi(OTf)_3{\cdot}4H_2O$-catalyzed Sakurai reaction of a variety of aldimines generated *in situ* using aldehydes, amines, and allylsilane in a three-component reaction.[12] A weakness of the one-pot Sakurai reaction could be the eventual formation of the homoallylic alcohol as a trace by-product. These results encouraged us to pursue an alternative approach using *N*-alkoxycarbonylamino sulfones as stable imine precursors.

In this paper, we wish to disclose our results in this area: the development of an efficient $Bi(OTf)_3{\cdot}4H_2O$-catalyzed reaction of *N*-alkoxycarbonylamino sulfones with allyltrimethylsilane. The corresponding amines were obtained efficiently in the presence of 2–5 mol% of $Bi(OTf)_3{\cdot}4H_2O$. Since the original communication of our work,[13] the scope and generality of the reaction have been broadened. A large selection of *N*-alkoxycarbonylamino sulfones and nucleophiles were chosen. In addition, further insights regarding the mechanism are reported.

Results and Discussion

Initially, the allylation reaction was studied with the *N*-benzyloxycarbonylamino sulfone derived from benzaldehyde and Cbz carbamate (Scheme 1, $R^1 = Ph$, $R = Bn$). This sulfone was kept as model sulfone for our initial studies. Various catalysts were screened for the allylation of benzyl phenyl(phenylsulfonyl)methylcarbamate **1a** with allyltrimethylsilane in dichloromethane (Table 1). Among the various Bi catalysts tested, $Bi(OTf)_3{\cdot}4H_2O$ was shown to be the most efficient one (Table 1, entry 5). $BiCl_3$, $BiBr_3$, $Bi(OAc)_3$ or $Bi(OCOCF_3)_3$ did not allow the reaction to proceed and starting material was recovered (Table 1, entries 1–4). Other metal triflates such as $Zn(OTf)_2$, $Sc(OTf)_3$, $Ga(OTf)_3$ or $Cu(OTf)_2$ also catalyzed this reaction but decreased yields were obtained (Table 1, entries 6–9). Interestingly, using allyltributylstannane as the nucleophile under the same conditions [2 mol% $Bi(OTf)_3{\cdot}4H_2O$, 22 °C] led only to traces of homoallylic amine **2a** (6%), albeit allyltrimethylgermane afforded the homoallylic amine **2a** in good yield (79%).

Table 1. Metal salt-catalyzed allylation of sulfone **1a** with allyltrimethylsilane.[a]



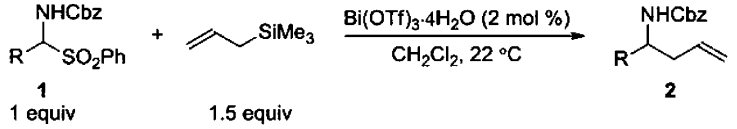
1a (1 equiv) + (1.5 equiv) → **2a**

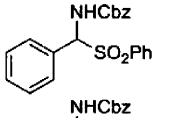
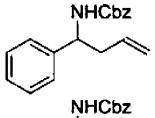
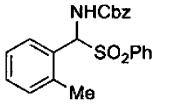
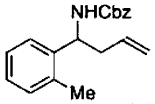
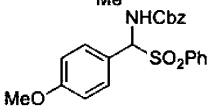
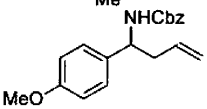
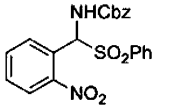
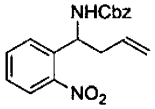
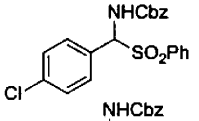
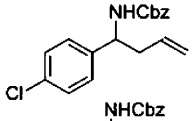
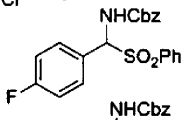
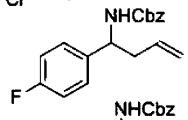
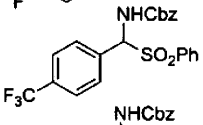
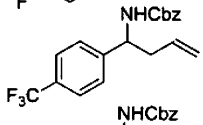
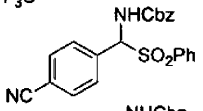
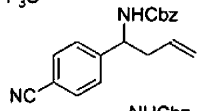
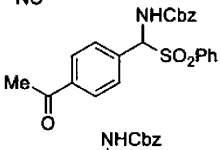
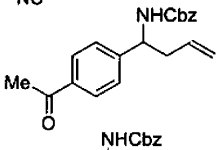
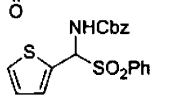
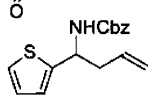
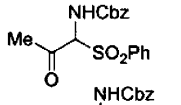
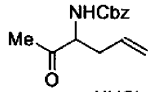
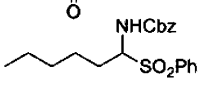
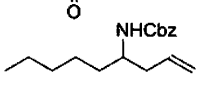
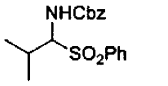
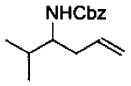
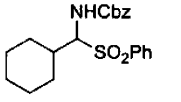
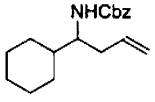
Entry	Catalyst	Yield of **2a** [%][b]
1	$BiCl_3$	–[c]
2	$BiBr_3$	–[c]
3	$Bi(OAc)_3$	–[c]
4	$Bi(OCOCF_3)_3$	–[c]
5	$Bi(OTf)_3{\cdot}4H_2O$	94
6	$Zn(OTf)_2$	35
7	$Sc(OTf)_3$	57
8	$Ga(OTf)_3$	71
9	$Cu(OTf)_2$	60[d]

[a] *Conditions:* benzyl phenyl(phenylsulfonyl)methylcarbamate **1a** (1.0 equiv.), allyltrimethylsilane (1.5 equiv.), metal salt (2 mol%) in dry CH_2Cl_2 at 22 °C for 5 h.
[b] Isolated yield.
[c] No trace of product according to ^1H NMR.
[d] Reaction time was 6.5 h.

In regard to the success obtained with sulfone **1a** derived from benzaldehyde, we studied the scope and limitations of this reaction with respect to the sulfone employed in the process [Scheme 1, $R^1 = Ar$, Alk, 1 equiv. $BnOC(O)NH_2$, H_2O-MeOH/THF, 22 °C, 22–140 h]. The results are summarized in Table 2. The addition of allyltrimethylsilane to various *N*-benzyloxycarbonylamino sulfones **1** proceeded readily employing $Bi(OTf)_3{\cdot}4H_2O$ as the Lewis acid [2–5 mol% $Bi(OTf)_3{\cdot}4H_2O$, CH_2Cl_2, 22 °C, 5–48 h]. Generally, the corresponding homoallylic amines **2** were obtained in moderate to good yields (Table 2, entries 1–18). Sulfones derived from electron-rich aromatic aldehydes, including those from *o*-substituted benzaldehydes, reacted smoothly to give the desired product in moderate to excellent yields (Table 2, entries 1–3). The reaction worked well with a variety of sulfones derived from electron-poor aromatic aldehydes and the corresponding homoallylic amines **2** were obtained in moderate to good yields (Table 2, entries 4–9). Benzyloxycarbonylamino sulfone **1i** could be selectively prepared from *p*-acetylbenzaldehyde and subsequently

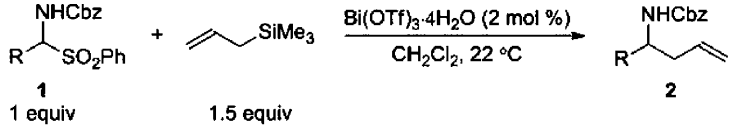
Table 2. $Bi(OTf)_3 \cdot 4H_2O$-catalyzed allylation of Cbz-amino sulfones **1** with allyltrimethylsilane.[a]

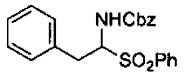
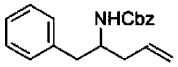
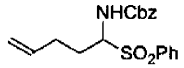
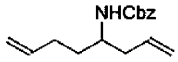
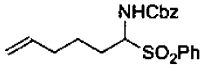
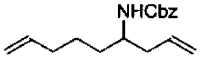
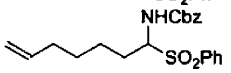
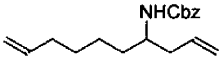


Entry	Sulfone **1**	Product **2**		Time (h)	Yield **2** (%)[b]
1			**2a**	5	94
2			**2b**	23	84
3			**2c**	12	86
4			**2d**	24	74
5			**2e**	26	78
6			**2f**	24	78
7			**2g**	43	58
8			**2h**	40	74[c]
9			**2i**	27	56
10			**2j**	23	46
11			**2k**	41	47[c]
12			**2l**	24	69
13			**2m**	28	74
14			**2n**	26	74

allylated to give **2i** with complete chemoselectivity (Table 2, entry 9). The same selectivity was observed for the reaction starting from 2-oxopropanal (Table 2, entry 11). In addition, heteroaromatic aldehyde-derived sulfones could also serve as substrates in this reaction, giving the corresponding homoallylic amines

Table 2. (Continued)



Entry	Sulfone **1**	Product **2**		Time (h)	Yield **2** (%)[b]
15			**2o**	22	76
16			**2p**	67	59
17			**2q**	48	61
18			**2r**	19	64

[a] *Conditions:* sulfone **1** (1.0 equiv.), allyltrimethylsilane (1.5 equiv.), $Bi(OTf)_3{\cdot}4H_2O$ (2 mol%) in CH_2Cl_2 at 22 °C.
[b] Isolated yield.
[c] The reaction was run with 2 mol% $Bi(OTf)_3{\cdot}4H_2O$ and 5.0 equiv allyltrimethylsilane at reflux in CH_2Cl_2.

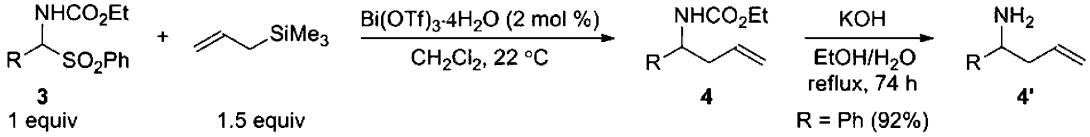
in moderate yields (Table 2, entry 10).[13] Aliphatic aldehydes led to moderate to good yields of **2** (Table 2, entries 11–18). For selected substrates, higher yields could be obtained using a catalyst loading of 5 mol% with 5 equiv. of allyltrimethylsilane in dichloromethane at reflux (Table 2, entries 8 and 11).

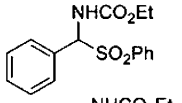
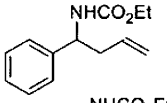
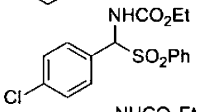
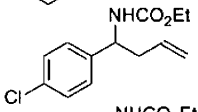
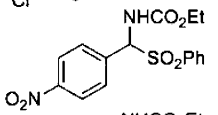
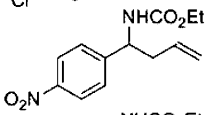
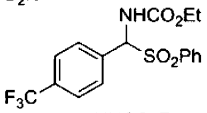
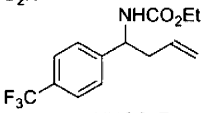
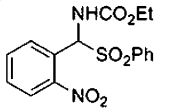
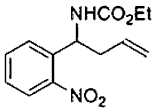
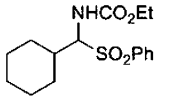
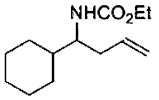
Next, the scope of this allylation reaction was evaluated with other *N*-alkoxycarbonylamino sulfones. Under the optimized reaction conditions, the allylation of ethyl carbamate-derived sulfones **3** was studied (Table 3). Generally, the allylation of such sulfones afforded good yields of the corresponding homoallylic carbamates **4**. Ethyl carbamate derivatives could then be deprotected using KOH (60 equiv. KOH, EtOH/H_2O, reflux, 74 h, 92% **4a′** from **4a**). Aromatic aldehyde-derived sulfones reacted smoothly to give **4** in moderate to good yields (Table 3, entries 1–5). With *N*-ethoxycarbonylamino sulfones derived from *p*-chloro- and *p*-nitrobenzaldehyde, the reaction did not proceed at room temperature. Upon reflux of dichloromethane and using 5 mol% $Bi(OTf)_3{\cdot}4H_2O$ and 5 equiv. allyltrimethylsilane, the expected homoallylic amines **4b** and **4c** could be obtained in good yields (Table 3, entries 2 and 3). The cyclohexylcarboxaldehyde-derived sulfone **3f** reacted smoothly to afford the expected product in good yield (Table 3, entry 6). Therefore, this Sakurai-type allylation could be extended to various carbamate-derived sulfones.

When the Boc carbamate-derived sulfone **5** was subjected to the $Bi(OTf)_3{\cdot}4H_2O$-catalyzed allylation conditions (Scheme 2), the cyclic carbamate **6** was obtained as the major product (36%, *dr* = 82:18), along with the corresponding allylation product **7**, albeit in low yield (16%). Such a cyclic carbamate resulting from the internal capture of an intermediate β-silyl cation with the Boc group and concomitant loss of isobutylene had already been reported in the literature with *tert*-butoxycarbonylpiperidine derivatives.[14]

In order to gain further insights into the allylation reaction, we decided to explore the mechanistic aspects of the $Bi(OTf)_3{\cdot}4H_2O$-catalyzed process in more detail. Given that the latter does not occur in the presence of N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamine proton sponge® [1 equiv. of **1a**, 1.5 equiv of allyltrimethylsilane, 2 mol% of $Bi(OTf)_3{\cdot}4H_2O$, 6 mol% of proton sponge®, 22 °C, 28 h, 99% recovery of **1a**],[7] or 2,6-di-*tert*-butylpyridine [(1 equiv. of **1a**, 1.5 equiv. of allyltrimethylsilane, 2 mol% of $Bi(OTf)_3{\cdot}4H_2O$, 6 mol% of 2,6-di-*tert*-butylpyridine, 22 °C, 19 h, 100% recovery of **1a**],[15] but still proceeds with K_2CO_3 used as a proton scavenger [1 equiv. of **1a**, 1.5 equiv. of allyltrimethylsilane, 2 mol% of $Bi(OTf)_3{\cdot}4H_2O$, 6 mol% K_2CO_3, 22 °C, 19 h, 62% of **2a**] does not indicate unambiguously that triflic acid is involved in the mechanism. Additionally, the allylation reaction does not occur using 2 mol% of HOTf or Me_3SiOTf. However, when HOTf (6 mol%) is used as the catalyst, the reaction proceeds to afford the expected product **2a**, indicating that HOTf is also an effective catalyst for the transformation (1 equiv. of **1a**, 1.5 equiv. of allyltrimethylsilane, 6 mol% of HOTf, 22 °C, 4 h, 67% of **2a**). In order to get further evidence on the role of HOTf as catalyst, the allylation of sulfones derived from both 3-pyridylcarboxaldehyde and 4-*N*,*N*-dimethylaminobenzaldehyde was at-

Table 3. $Bi(OTf)_3 \cdot 4H_2O$-catalyzed allylation of ethyl carbamate-derived sulfones **3** with allyltrimethylsilane.[a]

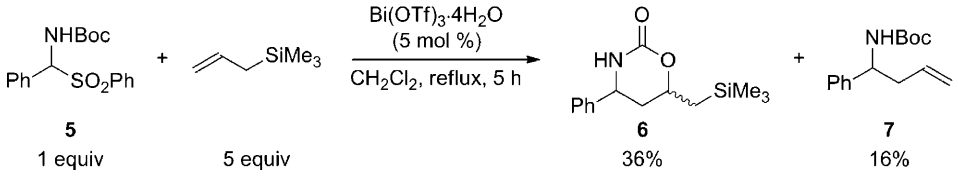


Entry	Sulfone **3**	Product **4**		Time (h)	Yield **4** (%)[b]
1			**4a**	3.5	69
2			**4b**	19	80[c]
3			**4c**	19	83[c]
4			**4d**	22	68
5			**4e**	62	80
6			**4f**	62	76

[a] *Conditions:* sulfone **3** (1.0 equiv.), allyltrimethylsilane (1.5 equiv.), $Bi(OTf)_3 \cdot 4H_2O$ (2 mol%) in CH_2Cl_2 at 22 °C.

[b] Isolated yield.

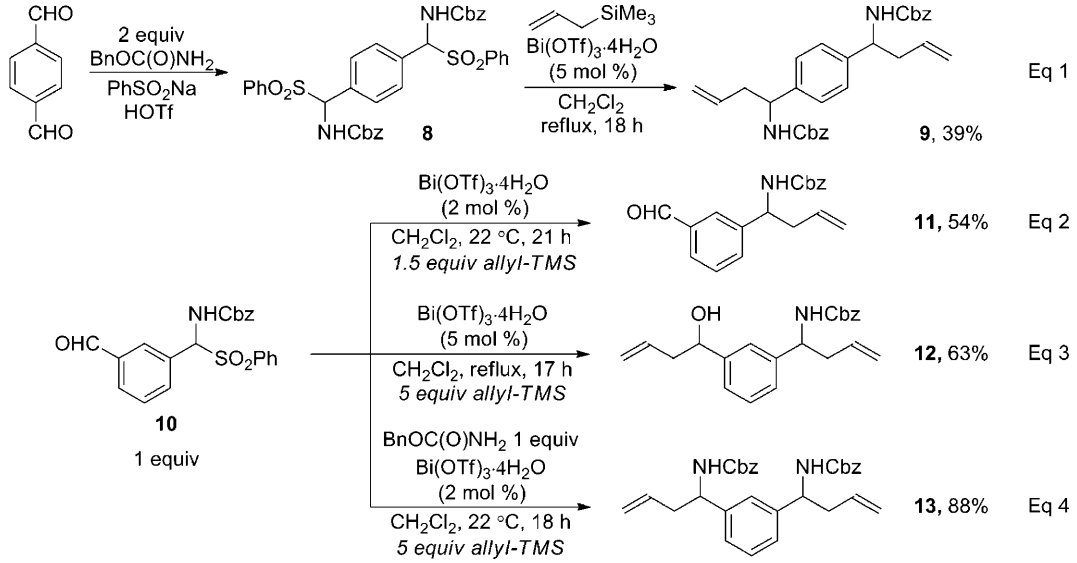
[c] Reaction was performed in CH_2Cl_2 at reflux in the presence of $Bi(OTf)_3 \cdot 4H_2O$ (5 mol%) with 5.0 equiv. allyltrimethylsilane.



Scheme 2. $Bi(OTf)_3 \cdot 4H_2O$ catalyzed allylation of Boc-amino sulfone **5** with allyltrimethylsilane.

tempted, but no conversion in expected homoallylic amine was observed. Moreover, Me_3SiOTf is an effective catalyst as well when used in 6 mol% (1 equiv. of **1a**, 1.5 equiv. of allyltrimethylsilane, 6 mol% of Me_3SiOTf, 22 °C, 5 h, 82% of **2a**). Since the allylation reaction does not occur using 2 mol% of HOTf or Me_3SiOTf and since the chemical yields of the 6 mol% HOTf- and Me_3SiOTf-catalyzed reactions are lower than when using 2 mol% $Bi(OTf)_3 \cdot 4H_2O$ (compare with Table 1, entry 5), a dual mechanism, namely Lewis and Brønsted acid catalysis, cannot be ruled out. Despite the fact that $Bi(OTf)_3 \cdot 4H_2O$, HOTf, and TMSOTf could co-exist as catalysts, practical use of $Bi(OTf)_3 \cdot 4H_2O$ makes our method particularly valuable since $Bi(OTf)_3 \cdot 4H_2O$ is neither corrosive nor difficult to handle.

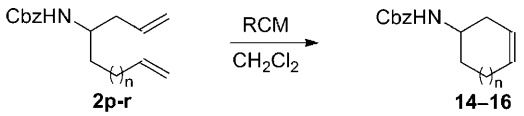
Encouraged by our previous results, we studied the allylation of bifunctional sulfones derived from dialdehydes such as terephthalaldehyde and isophthalaldehyde (Scheme 3). When the classical conditions for the preparation of sulfones were used with terephthalaldehyde, an equimolar mixture of mono and double sulfone (1:0.88) was formed. Unexpectedly, when triflic acid was used instead of formic acid, the double sulfone derived from terephthalaldehyde was obtained in high yield [5.0 equiv. of $PhSO_2Na$, 5.0 equiv.



Scheme 3. $Bi(OTf)_3{\cdot}4H_2O$ catalyzed allylation of bifunctional substrates.

of $BnOC(O)NH_2$, $THF/H_2O/HOTf$, 70 °C, 72 h, 87% of **8**]. Slight modifications of the conditions applied to isophthalaldehyde led to the monosulfone **10** as the only product [2.0 equiv. of $PhSO_2Na$, 2.0 equiv. of $BnOC(O)NH_2$, $THF/H_2O/HCO_2H$, 70 °C, 72 h, 85% of **10**]. Although the allylation of **8** afforded a poor yield of double homoallylic carbamate **9** [Scheme 3, Eq. (1)], monosulfone **10** could be advantageously used as a key precursor. Chemoselective mono-allylation of **10** using 1.5 equiv. of allyltrimethylsilane smoothly afforded aldehyde **11** [Scheme 3, Eq. (2)]. Subsequent allylation of the carbonyl group could be obtained by using excess of allyltrimethylsilane [Scheme 3, Eq. (3). Formation of the double homoallylic amine **13** could be possible *via* a $Bi(OTf)_3{\cdot}4H_2O$-catalyzed three-component reaction previously reported by our group [Scheme 4, Eq (4)].[12] However, the relative stereochemistry of products **8**, **9**, **12**, **13** could not be determined.

Our allylation method allows the straightforward formation of high value precursors for RCM. Our initial investigations focused on the reaction of terminal dienes prepared by our methodology with various metathesis catalysts (Scheme 4). Grubbs I catalysts allowed the smooth formation of 6- and 7-membered substituted Cbz carbamates. The corresponding cyclooctene derivative could be obtained using Grubbs II catalyst. 3-Cbz-protected cyclohexenylamine **14** has proven to be a valuable precursor of bicyclic urethanes after further cyclization involving electrophilic halogen atoms.[16]



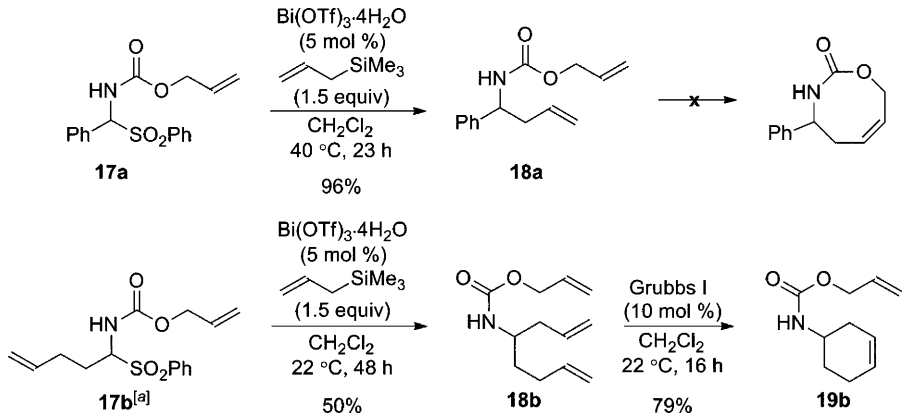
n = 1, **14** (93%) (5 mol % Grubbs I, 22 °C, 16 h)
n = 2, **15** (78%) (5 mol % Grubbs I, 22 °C, 45 h)
n = 3, **16** (35%, *Z*/*E* = 3.5:1) (5 mol % Grubbs II, reflux, 20 h)

Scheme 4. Ring-closing metathesis of terminal dienes.

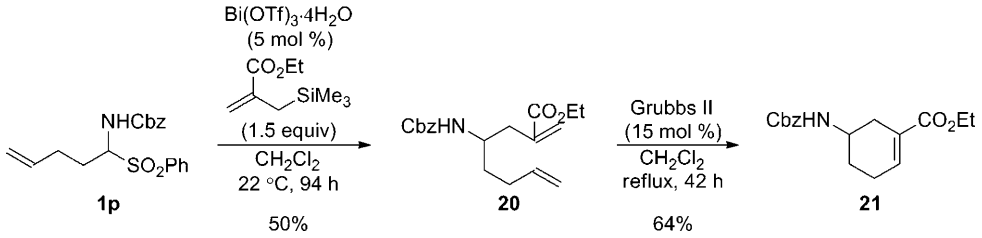
Other protecting groups could be used and Alloc-derived sulfones **17a** and **17b** could be allylated using our standard procedure (Scheme 5). At this point, use of Alloc instead of Cbz as the amine protecting group did not change the chemoselectivity of the RCM reaction since no RCM was observed with the Alloc group (Scheme 5). Compound **18a** indeed could not undergo RCM (Hoveyda–Grubbs II, CH_2Cl_2, reflux, 65 h, no conversion). On the other hand, Alloc-protected terminal diene **18b** afforded smoothly protected cyclohexenylamine **19b** (10 mol% Grubbs I, CH_2Cl_2, 22 °C, 16 h, 79%). The latter one could then be easily deprotected using standard Pd(0)-catalyzed procedure.[17]

In order to further extend the generality of our method, a functionalized allylsilane was also reacted with sulfone **1p**. Under the same optimized conditions, the corresponding homoallylic amine was obtained and subsequently subjected to ring-closing metathesis to afford compound **21** (Scheme 6). Albeit Grubbs II catalyst afforded the compound in moderate yield (64%), only the dimerization product could be obtained using Grubbs I catalyst (10% Grubbs I, PhMe, reflux, 16 h, 37% of dimerization product of **21′**, 6% of expected product **21**).

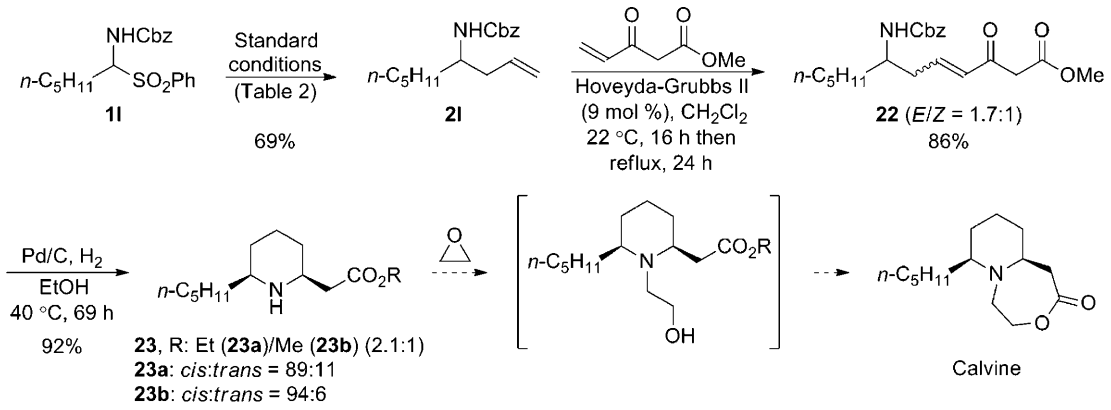
Our sequential allylation/ring-closing metathesis methodology was further applied to the preparation of a key intermediate in the synthesis of calvine



Scheme 5. Allylation of Alloc-derived sulfones and ring closing metathesis of an Alloc-protected homoallylic amine.[a] Purity of starting material **17b** was estimated to be 95% by ^{1}H NMR.



Scheme 6. $Bi(OTf)_3{\cdot}4H_2O$ catalyzed allylation using a functionalized allylsilane.



Scheme 7. Synthesis of calvine.

(Scheme 7). Homoallylic amine **2l** was obtained in a moderate yield according to our standard conditions (Table 2, entry 12). Cross-metathesis of **2l** with methyl 3-oxopent-4-enoate based on Blechert's work afforded compound **22** in a good yield (86% of **22**, E/Z = 1.7:1).[18,3d] *cis*-Disubstituted piperidine **23** was obtained with high yield and diastereoselectivity with partial transesterification occurring during the transformation. Further transformation of **23** into calvine has already been reported in the literature *via* ethylene oxide opening with **23b**, followed by ring-closing into the 7-membered lactone.[19]

Conclusions

In summary, we have found that the Sakurai reaction of *N*-benzyloxycarbonylamino sulfones proceed smoothly in the presence of a catalytic amount of $Bi(OTf)_3{\cdot}4H_2O$. This method offers several advantages including mild reaction conditions, low catalyst

loading (2–5 mol%), and no formation of by-products. Moreover, our process involves an environmentally benign, cheap, and easy to handle catalyst. The amines, already protected as Cbz derivatives, are smoothly obtained under mild conditions. Ring-closing metathesis allowed for rapid construction of diverse cyclic compounds with various carbamate substitution. Because of its numerous benefits, the $Bi(OTf)_3 \cdot 4H_2O$ protocol should find utility in the synthesis of biologically active compounds. Research is under way to demonstrate other significant applications of this $Bi(OTf)_3 \cdot 4H_2O$-catalyzed reactions with silyl nucleophiles.

Experimental Section

General Procedure for the $Bi(OTf)_3 \cdot 4H_2O$-Catalyzed Sakurai Reaction

Under an inert atmosphere of argon, allyltrimethylsilane (0.75 mmol) was added dropwise to a solution of $Bi(OTf)_3 \cdot 4H_2O$ (2 mol%) and *N*-alkoxycarbonylamino sulfone **1** (0.5 mmol) in dry CH_2Cl_2 (1.5 mL) at 22 °C. The mixture was stirred until the reaction was completed as indicated by TLC. The reaction was quenched with distilled H_2O and extracted with EtOAc. The combined organic phases were washed with H_2O, saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under vacuum (rotary evaporator). The crude product was purified by column chromatography (eluent hexanes/EtOAc 92:8 to 85:15, or toluene). Spectral data for **1a**,[20f] **1l**,[20h] **2a**,[20a] **2c**,[20a] **2e**,[20a] **2g**,[12] **2i**,[20b] **2l**,[20i] **2m**,[20c] **2n**,[20a] **2o**,[20c] **2p**,[20j] **3a**,[20d] **4a**,[20a] **4a′**,[20l] **5**,[20e] **7**,[20g] **14**,[20j] **15**,[20k] **18a**,[20m] and **19**[20n] agree with those previously reported in the literature.

Benzyl 1-[4-(trifluoromethyl)phenyl]but-3-enyl-carbamate (2g):[12] Using the gneral procedure above with the reagents benzyl phenylsulfonyl(4-(trifluoromethyl)phenyl)methylcarbamate **1g** (225 mg, 0.5 mmol), allyltrimethylsilane (120 μL, 0.75 mmol), $Bi(OTf)_3 \cdot 4H_2O$ (7.0 mg, 2 mol%). The reaction was stirred for 43 h at 22 °C. The crude product was purified by silica gel chromatography (hexanes/EtOAc = 90:10) to afford **2g** as a white solid; yield: 102 mg (58%); $R_f = 0.78$ (hexanes/EtOAc = 70:30); mp 65–67 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.54$ (d, $J = 8.0$ Hz, 2H), 7.14–7.41 (m, 7H), 5.60 (tdd, $J = 10.6$, 9.1, 7.1 Hz, 1H), 5.28 (d, $J = 7.2$ Hz, 1H), 4.95–5.16 (m, 4H), 4.72–4.88 (m, 1H), 2.37–2.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.8$, 146.3, 136.4, 133.1, 129.7 (q, $J = 32.6$ Hz), 128.7, 128.5, 127.8, 126.7, 125.8 (q, $J = 3.8$ Hz), 124.3 (q, $J = 272.7$ Hz), 119.4, 67.2, 54.3, 41.1; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -62.86$; IR (KBr): $\nu = 3283$, 1717, 1644 cm^{-1}; HR-MS: m/z = 350.1362, calcd. for $C_{19}H_{18}F_3NO_2$ $[M+H]^+$: 350.1368.

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