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m-$C_2B_{10}H_{11}HgCl$/AgOTf-Catalyzed Reaction for Reductive Deoxygenation

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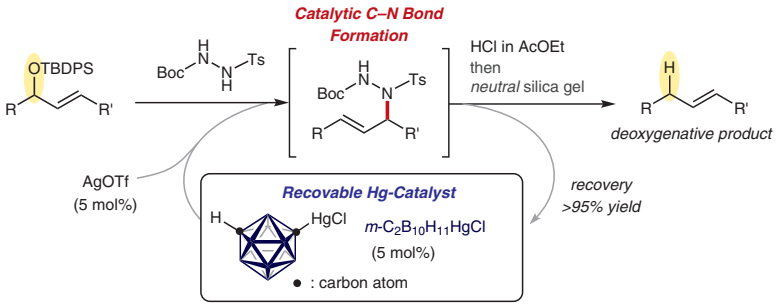

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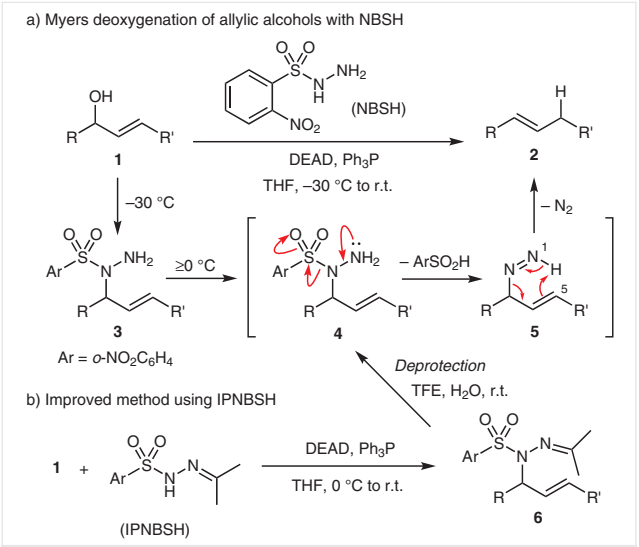
Abstract A *m*-$C_2B_{10}H_{11}HgCl$/AgOTf-catalyzed reaction of allyl silyl ethers with *N*-Boc-*N*′-tosylhydrazine has been developed. Under mild conditions, the resulting allyl hydrazine products were transformed into naked alkenes in good yield. Furthermore, the used *m*-$C_2B_{10}H_{11}HgCl$ could be recovered quantitatively.

Key words deoxygenation, *N*-Boc-*N*′-tosylhydrazine, allylic amination, allylic diazene, carbaborane, mercury, catalytic reaction



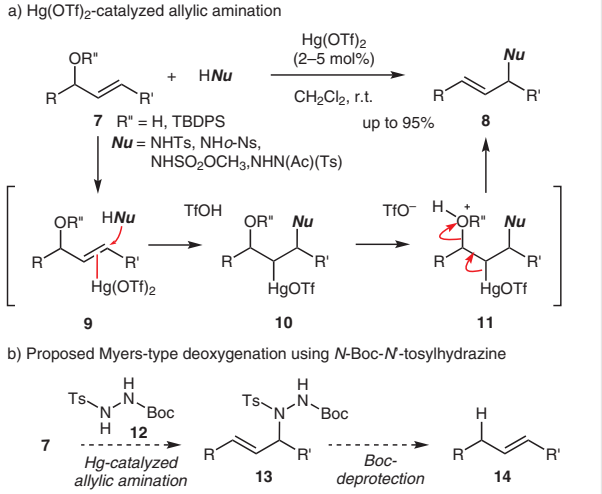
Scheme 1 Myers reductive deoxygenation of allylic alcohols with NBSH and the improved method using IPNBSH

The Myers reductive deoxygenation[1] of allylic alcohols with 2-nitrobenzenesulfonylhydrazine (NBSH) to furnish the corresponding naked alkenes is an important synthetic methodology in organic chemistry (Scheme 1, a).[2] This reaction is well-known to take place via a 1,5-sigmatropic rearrangement of allylic diazene intermediate **5**, which is smoothly formed from NBSH-substituted product **3** at 0 °C or more.

In 2006, Movassaghi and co-workers designed a thermally stable *N*-isopropylidene-*N*′-2-nitrobenzenesulfonyl hydrazine (IPNBSH) as a substitute for NBSH, and it was used for the total syntheses of (–)-acylfulvene and (–)-irofulven (Scheme 1, b).[3] Later, they demonstrated that IPNBSH provides high reactivity and ease of handling in the deoxygenative reaction.[4] Both the original Myers deoxygenation and the modified reaction using IPNBSH have played an important role in bioactive and natural product synthesis. Compounds **3** and **6**, which are the key precursors of **5**, have traditionally been prepared via a Mitsunobu reaction of allyl alcohols with hydrazine reagents in the presence of stoichiometric amounts of DEAD and Ph_3P.[5] There are only a few practical, carbon–nitrogen bond-forming reactions for the preparation of **3** and **6**, and very few catalytic reactions have been reported to date.[6] Herein, we wish to propose a novel bivalent mercury salt catalyzed allylic amination of allyloxy silanes with *N*-Boc-*N*′-tosylhydrazine, which is applicable to Myers-type deoxygenations.

Recently, we found that mercury trifluoromethanesulfonate [$Hg(OTf)_2$] catalyzed allylic aminations of allyl alcohols and their siloxy derivatives with soft nitrogen nucleophiles such as sulfonamides, sulfamates, and *N*,*N*-acyltosylhydrazines (Scheme 2, a).[7] These catalytic reactions proceeded smoothly at room temperature, giving the corresponding carbon–nitrogen adducts **8** via the demercuration reaction of mercury intermediate **10** with in situ generated TfOH. The observation that 'soft' nitrogen nucleophiles worked without impeding the catalytic cycle of $Hg(OTf)_2$ suggested that *N*-Boc-*N*′-tosylhydrazine (**12**) might also

function as an efficient nucleophile. Thus, we planned to use **12** for the mercury-catalyzed allylic amination with the aim of developing a Myers-type deoxygenation (Scheme 2, b). The probable product **13** could be expected to undergo nitrogen extrusion by removal of the Boc protecting group. Indeed, some researchers have previously demonstrated that the loss of *p*-toluenesulfinic acid took place from an *N*-allyl-*N*′-tosylhydrazine derivative to provide a corresponding alkene via allylic diazene intermediate **5**.[8]



Scheme 2 $Hg(OTf)_2$-catalyzed allylic aminations and our working hypothesis

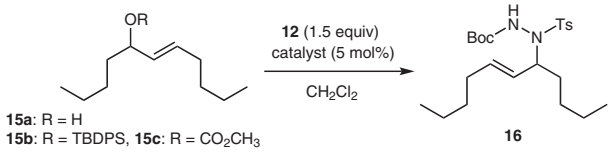
Initially, we examined the allylic amination of simple (*E*)-undec-6-en-5-ol (**15a**) with *N*-Boc-*N*′-tosylhydrazine (**12**,[9] Table 1). When using 5 mol% of $Hg(OTf)_2$ in CH_2Cl_2, the formation of the desired product **16** was limited to 30% yield even after 24 hours at room temperature (Table 1, entry 1). The substrate-dimerized ether was also formed as a byproduct in 20% yield.[10] Because CH_3CN and toluene gave similar results to that of CH_2Cl_2,[11] we decided that the siloxy functionality was used in the allylic amination. In 2012, we found that siloxy derivatives of allyl alcohols showed remarkable reactivity compared with the naked allyl alcohols for the $Hg(OTf)_2$-catalyzed allylic amination with *N*,*N*-acyltosylhydrazine.[7b] In particular, the *tert*-butyldiphenylsiloxy group exhibited a high leaving ability among the siloxy groups evaluated, giving the desired C–N adducts in good to excellent yields without the generation of a substrate-dimerized ether. The reaction of *tert*-butyldiphenylsilyl (TBDPS) derivative **15b** with **12** proceeded smoothly in CH_2Cl_2 at room temperature to completion within ten minutes. However, compound **16** was furnished in 41% yield along with the generation of complex byproduct mixtures (Table 1, entry 2). Compound **16** was obtained in 39% yield at 0 °C after 30 minutes (Table 1, entry 3), whereas the short-term reaction of five minutes at 0 °C furnished **16** in 46% yield (Table 1, entry 4). These findings (Table 1, entry 3 vs. 4) that the prolonged reaction time of 30 minutes decreased the yield of **16** suggested that **16** was decomposed by the $Hg(OTf)_2$ catalyst and/or very small amounts of in situ generated TfOH. Thus, we next examined a variety of mild catalytic conditions (Table 1, entries 5–9). Although a promising result was not obtained by using a 1:1 mixture of $Hg(OTf)_2$ and pyridine (Table 1, Entry 5), the 1:1 mixture of $Hg(OTf)_2$ and *N*,*N*,*N*′,*N*′-tetramethylurea (TMU)[12] gave **16** in 67% yield (Table 1, entry 6). The 1:3 mixture of $Hg(OTf)_2$ and TMU was less desirable as the reaction time was prolonged to six hours, giving **16** in 63% yield (Table 1, entry 7). The 1:0.1 combination of $Hg(OAc)_2$ and $Sc(OTf)_3$,[13] which acted as an effective catalyst in the cyclization of acid-sensitive 2-(4-pentynyl)furan, afforded **16** in low yield together with significant quantities of complex byproduct mixtures (Table 1, entry 8).

The 1:0.1 and 1:1 combinations of PhHgOAc and TfOH (Table 1, entries 9 and 10),[14] as well as the 1:1 combination of PhHgCl and AgOTf (Table 1, entry 11) also resulted in low yields. In contrast, the 1:1 combination of *m*-carbaboranyl mercuric chloride (*m*-$C_2B_{10}H_{11}HgCl$) and AgOTf (5 mol%)[15] exhibited significant reactivity, giving **16**[16] in 78% yield after ten minutes (Table 1, entry 12).[17] Fortunately, it was found that the used *m*-$C_2B_{10}H_{11}HgCl$ was recovered quantitatively (>96%) by quenching of the reaction mixture with saturated saline solution. This finding is particularly noteworthy in the context of green chemistry. The use of 3 mol% of *m*-$C_2B_{10}H_{11}HgCl$ and AgOTf was enough to complete the reaction within acceptable times, although the yield of **16** was slightly decreased to 69% (Table 1, entry 13). As shown in entries 14 and 15 (Table 1), the reaction using only *m*-$C_2B_{10}H_{11}HgCl$ or AgOTf resulted in almost quantitative recovery of starting material **15b**. Thus *m*-carbaboranyl mercuric trifrate (*m*-$C_2B_{10}H_{11}HgOTf$) was probably generated as the actual catalyst species through a salt metathesis between *m*-$C_2B_{10}H_{11}HgCl$ and AgOTf. Furthermore, it is conceivable that the *m*-carbaboranyl group on the catalyst acted as a bulky substituent to sterically inhibit the decomposition of the *N*-Boc moiety in product **16** as well as nucleophile **12**. Other conditions with gold,[18] indium,[19] and palladium[20] catalysts were also attempted; however, all yielded unsatisfactory results (Table 1, entries 16–19).

Next, we examined the nitrogen extrusion from **16** (Scheme 3, a). The selective cleavage of the Boc group in **16** was achieved by treating **16** with hydrogen chloride in AcOEt at room temperature.[21] The resulting *N*-tosylhydrazine **17** released sulfinic acid in the presence of neutral silica gel, giving the desired (*E*)-undecene (**19**) in 82% yield.

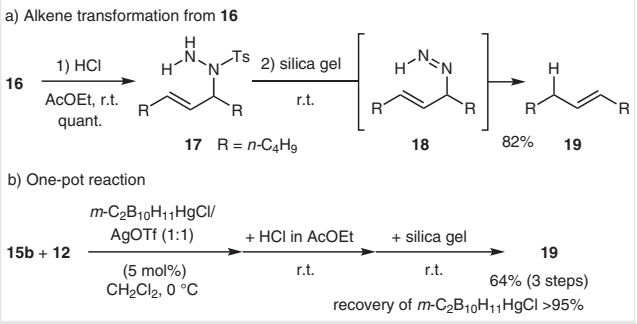
These sequences could be performed in one-pot by adding the requisite reagents to the reaction mixture (Scheme 3, b).[22] Additively, the used *m*-$C_2B_{10}H_{11}HgCl$ was also recovered without any trouble in the process of isolating **19** using column chromatography. Subsequently, the scope and limitations of the established procedure were investigated

Table 1 Optimization of the Reaction Conditions[a]



Entry	Substrate	Catalyst	Additive (mol%)	Temp (°C)	Time	Product (%)[b]
1	**15a**	$Hg(OTf)_2$	–	r.t.	24 h	30/20[c]
2	**15b**	$Hg(OTf)_2$	–	r.t.	10 min	41[d]
3	**15b**	$Hg(OTf)_2$	–	0	30 min	39[d]
4	**15b**	$Hg(OTf)_2$	–	0	5 min	46 (10)[e]
5	**15b**	$Hg(OTf)_2$	pyridine (5)	reflux	24 h	0 (96)[e]
6	**15b**	$Hg(OTf)_2$	TMU (5)	0	15 min	67[d]
7	**15b**	$Hg(OTf)_2$	TMU (15)	r.t.	6 h	63[d]
8	**15b**	$Hg(OAc)_2$	$Sc(OTf)_3$ (0.5)	0	24 h	38[d]
9	**15b**	PhHgOAc	TfOH (0.5)	0	24 h	10 (82)[e]
10	**15b**	PhHgOAc	TfOH (5)	0	24 h	17[d]
11	**15b**	PhHgCl	AgOTf (5)	0	24 h	24 (49)[e]
12[f]	**15b**	*m*-$C_2B_{10}H_{11}HgCl$	AgOTf (5)	0	10 min	78[d]
13[g]	**15b**	*m*-$C_2B_{10}H_{11}HgCl$	AgOTf (3)	0	1 h	69[d]
14	**15b**	*m*-$C_2B_{10}H_{11}HgCl$	–	0	24 h	0 (96)[e]
15	**15b**	–	AgOTf (5)	0	24 h	0 (92)[e]
16	**15b**	$AuCl_3$	–	0	1 h	trace[d]
17	**15b**	AuCl	–	0	10 min	30[d]
18	**15b**	$In(OTf)_3$	–	0	1 h	42[d]
19	**15c**	$Pd(PPh_3)_2Cl_2$	NEt_3 (20) Ph_3P (10)	reflux	8 h	12 (67)[e]

[a] Reactions were carried out using **15a–c** (0.3 mmol).
[b] Isolated yield after column chromatography.
[c] The yield (%) of a homodimer (ether) of **15a**.
[d] Substrate **15** was disappeared.
[e] Recovery (%) of starting substrate.
[f] Reaction was carried out using **15b** (2.6 mmol).
[g] *m*-$C_2B_{10}H_{11}HgCl$ (3 mol%) was used.



Scheme 3 Transformations to alkene

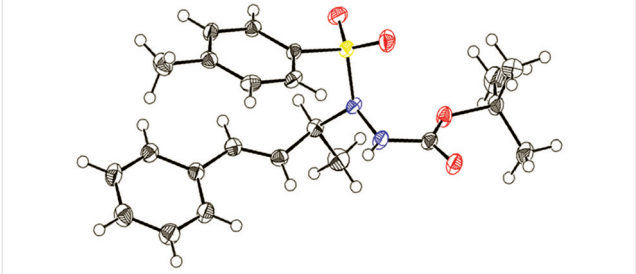
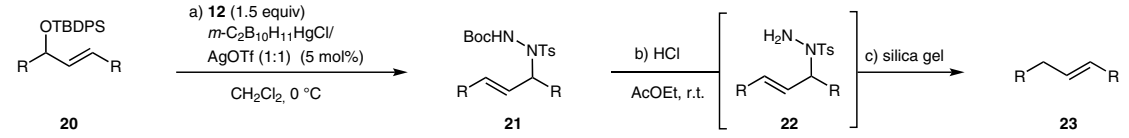


Figure 1 ORTEP plot of the molecular structure **21c**. The black, red, blue, and yellow colors in the structure indicate carbon, oxygen, nitrogen, and sulfur atoms, respectively.

in the synthesis of a wide variety of alkenes (Table 2). Compound **20a**, possessing phenyl groups at both terminal positions,[23] and cyclohex-2-en-1-ol derivative **20b** were good substrates to give single alkenes **23a** and **23b**, respectively (Table 2, entries 1 and 2). Unsymmetrical substrates were also examined in order to elucidate the regioselectivity of nitrogen nucleophile **12** in the catalytic amination. For (*E*)-1-phenylbut-2-en-1-ol derivative **20c**, complete regioselectivity was observed to give the conjugated **21c** as a single product in 81% yield (Table 2, entry 3). Because the isolated **21c** showed high crystallinity, the structural analysis was carried out using X-ray crystallography. The ORTEP plot of **21c** is illustrated in Figure 1;[24] **21c** was crystallized from a mixture of *n*-hexane and EtOAc (4:1).

Table 2 Scope for a) Allylic Amination and b) Nitrogen Removal Process[a]



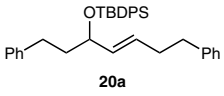
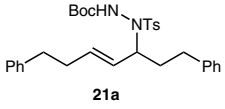
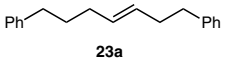
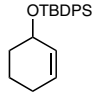
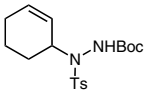
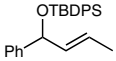
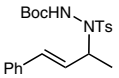
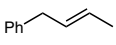
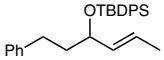
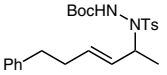
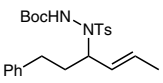
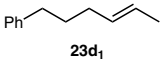
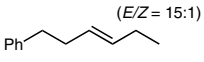
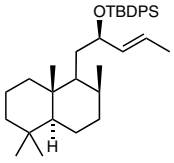
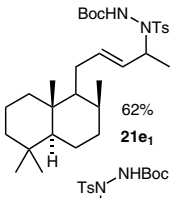
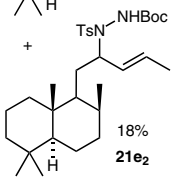
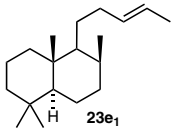
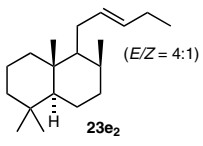
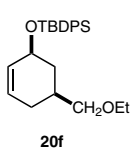
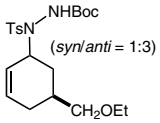
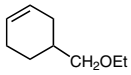
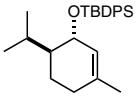
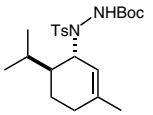
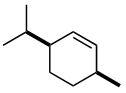
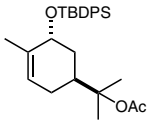
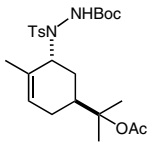
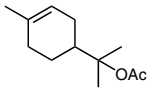
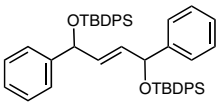
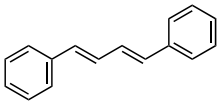
Entry	Reaction time and yield[b]				
	20		**21**		**23**
1	 **20a**	a) 1 h 84% >95%[c]	 **21a**	b) 8 h c) 5 h 75% (2 steps)	 **23a**
2	 **20b**	a) 1.5 h 74% >95%[c]	 **21b**	b) 18 h c) 36 h 86% (2 steps)	 **23b**
3	 **20c**	a) 15 min 81% >95%[c]	 **21c**	b) 72 h c) 32 h 43% (2 steps)	 **23c**
4	 **20d**	a) 3 h >95%[c]	 **21d$_1$** 57% +  **21d$_2$** 18%	b) 3 h c) 24 h 75% (2 steps) b) 6 h c) 24 h 72% (2 steps)	 **23d$_1$**  (*E*/*Z* = 15:1) **23d$_2$**
5	 **20e**	a) 3 h >95%[c]	 62% **21e$_1$** +  18% **21e$_2$**	b) 6 h c) 24 h 82% (2 steps) b) 12 h c) 24 h 80% (2 steps)	 **23e$_1$**  (*E*/*Z* = 4:1) **23e$_2$**

Table 2 (continued)

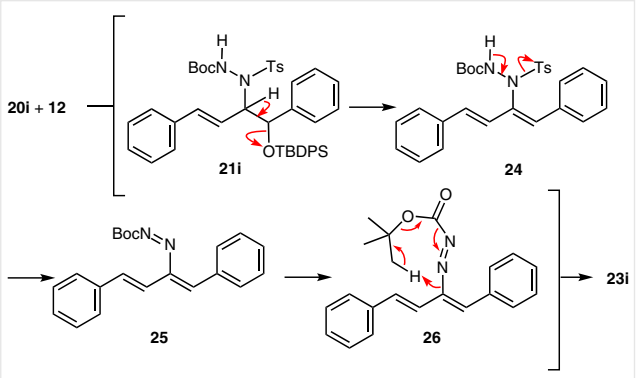
Entry	Reaction time and yield[b]				
	20		**21**		**23**
6	 **20f**	a) 6 h 79% >95%[c]	 **21f**	b) 18 h c) 24 h 86% (2 steps)	 **23f**
7	 **20g**	a) 1 h 77% >95%[c]	 **21g**	b) 14 h c) 24 h 79% (2 steps)	 **23g**
8	 **20h**	a) 4 h 82% >95%[c]	 **21h**	b) 48 h c) 12 h 87% (2 steps)	 **23h**
9	 **20i**	a) 4 h 62% >95%[c]	 **23i**		

[a] Reagents and conditions: a) **20** (0.3–0.4 mmol), b) HCl (20 equiv) in AcOEt (1.0 M), c) neutral silica gel (50 w/v%).
[b] Isolated yield after column chromatography.
[c] Recovery of used *m*-$C_2B_{10}H_{11}HgCl$ after column chromatography.

Although **21c** consists of a stable conjugated allyl-ene structure, the desired 1,5-sigmatropic rearrangement of hydrogen proceeded in a AcOEt solution of HCl followed by exposure to neutral silica gel, giving disconjugated **23c** as a major product. In the allylic amination from (*E*)-1-phenylhex-4-en-3-ol derivative **20d** (Table 2, entry 4), regioisomers $\mathbf{21d_1}$ and $\mathbf{21d_2}$ were formed in 57% and 18% yield, respectively. However, each product was easily separated by silica gel column chromatography, and the isolated $\mathbf{21d_1}$ and $\mathbf{21d_2}$ were converted into the corresponding alkenes. The conversion from $\mathbf{21d_1}$ into $\mathbf{23d_1}$ proceeded with complete *E* selectivity, while $\mathbf{21d_2}$ gave an *E*/*Z* (15:1) mixture of $\mathbf{23d_2}$.[25] Bicyclic-terpene-substituted **20e** also gave separable $\mathbf{21e_1}$ and $\mathbf{21e_2}$ in 62% and 18% yields, respectively (Table 2, entry 5). Thus, $\mathbf{21e_1}$ and $\mathbf{21e_2}$ were also isolated and then converted in good yields into $\mathbf{23e_1}$ and $\mathbf{23e_2}$, respectively. These transformations showed the same tendency as observed in the cases of $\mathbf{23d_1}$ and $\mathbf{23d_2}$. No trace of *Z* isomer in $\mathbf{23e_1}$ was detected by NMR spectroscopy, and $\mathbf{23e_2}$ was yielded as an *E*/*Z* mixture in a 4:1 ratio. When used diastereomerically pure *cis*-5-substituted **20f** (Table 2, entry 6), an inseparable diastereomer mixture **21f** (*syn*/*anti* = 1:3) was formed in 79% yield. Therefore, the mixture **21f** was directly subjected to alkene formation without separation. As the result of the attempt, **23f** was obtained as a single product in good yield. For **20g** and **20h** (Table 2, entries 7 and 8), allylic aminations proceeded smoothly to give **21g** and **21h** as single isomers in 77% and 82% yields, respectively. Transformations to corresponding alkenes were also successful, giving **23g** and **23h** in good yields.

One interesting finding from Table 2 was that *E*,*E*-diene product **23i** was directly formed in the reaction of disiloxy derivative **20i** with **12** at 0 °C for four hours (Table 2, entry 9). The plausible mechanism is shown in Scheme 4. The elimination of the *tert*-butyldiphenylsiloxy group from the hydrazine-monosubstituted product **21i** probably triggered the loss of sulfinic acid to provide **25** with a more extended conjugated structure. Eventually, denitrification from **25** took place via the cleavage of the *tert*-butyloxycarbonyl (Boc) group with loss of dinitrogen, giving the observed diene product **23i**. However, an alternative pathway to **23i**, in which double bond was formed by the concerted elimina-

tion of hydrazine and siloxy group, was also considered. Thus further study is necessary to prove our proposed mechanism.



Scheme 4 Proposed mechanism from **20i** to **23i**

In conclusion, we have developed a *m*-$C_2B_{10}H_{11}HgCl$/AgOTf-catalyzed carbon–nitrogen bond-forming reaction of allyl silyl ethers and *N*-Boc-*N*′-tosylhydrazine. In all cases, the reaction proceeded smoothly at 0 °C to furnish the hydrazine-substituted products in good yields. The used *m*-$C_2B_{10}H_{11}HgCl$ was recovered quantitatively. The observation that the resulting hydrazine-substituted products were effectively transformed into the corresponding alkenes under mild acidic conditions highlights the utility of the present catalytic reaction. We believe the present reaction will facilitate the synthesis of a variety of alkenes as a Myers-type reductive deoxygenation.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588554.

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(11) The reaction of **15a** with **12** in CH_3CN and toluene at r.t. for 1440 min gave **16** in 23% and 17% yield, respectively.
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(16) Product **16** was obtained as the mixture of rotamers; see Supporting Information.
(17) **Preparation of 0.1 M CH_2Cl_2 Solution of *m*-$C_2B_{10}H_{11}HgCl$/AgOTf**
To a suspension of AgOTf (38.5 mg, 0.150 mmol) in CH_2Cl_2 (1.5 mL) was added *m*-$C_2B_{10}H_{11}HgCl$ (56.9 mg, 0.150 mmol) at r.t., and the mixture was stirred at r.t. for 30 min.
Typical Procedure for the *m*-$C_2B_{10}H_{11}HgCl$/AgOTf-Catalyzed Allylic Amination (Table 1, Entry 12)
A solution of (*E*)-*tert*-butyldiphenyl(undec-6-en-5-yloxy)silane (**15b**, 1.08 g, 2.64 mmol) and *tert*-butyl 2-tosylhydrazine-1-carboxylate (**12**, 755 mg, 3.96 mmol) in CH_2Cl_2 (8.7 mL) was added to a dried two-neck flask under an atmosphere of argon. *m*-$C_2B_{10}H_{11}HgCl$/AgOTf in 0.1 M CH_2Cl_2 (1.32 mL) was added dropwise to the solution at 0 °C, and the mixture was stirred at 0 °C for 10 min. The reaction was quenched with sat. NaCl aq, and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (3 ×). The combined organic phase was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel chromatography (hexane/AcOEt = 20:1 to 4:1) to give **16** (902 mg, 2.06 mmol, 78%) along with *m*-$C_2B_{10}H_{11}HgCl$ (48.2 mg, 0.127 mmol, 96%).
Analytical Data for Compound 16
Colorless syrup. FT-IR (neat): 3313, 3238, 3138, 2957, 2929,

2857, 2856 cm^{-1}. ^1H NMR (500 MHz, DMSO, 70 °C): δ = 0.85 (6 H, m), 1.25 (20 H, m), 1.93 (3 H, m), 2.43 (3 H, s), 4.18 (1 H, br d, *J* = 6.0 Hz), 5.27 (1 H, m), 5.47 (1 H, m), 7.36 (2 H, d, *J* = 7.5 Hz), 7.79 (2 H, d, *J* = 7.5 Hz), 8.59 (NH, br s). ^{13}C NMR (125 MHz, DMSO, 70 °C): δ = 14.06, 21.36, 21.96, 22.18, 27.92, 28.13, 28.25, 28.47, 30.92, 31.68, 32.38, 62.06, 80.09, 128.22, 128.60, 129.55, 129.67, 143.80, 155.48. MS (CI): *m/z* = 437 $[M - H]^+$. HRMS (CI^+): *m/z* calcd for $C_{23}H_{39}N_2O_4S$: 437.2474; found: 437.2479.

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(21) **Typical Procedure for the Selective Cleavage of Boc-Protecting Group and the Transformation into Alkene (Scheme** 3, a**)**
A 1.0 M HCl in AcOEt (6.2 mmol, 6 mL) was added to a solution of **16** (156 mg, 0.310 mmol) in AcOEt (0.31 mL) at r.t. The reaction mixture was stirred for 5 h at r.t. It was diluted with Et_2O and then quenched with sat. $NaHCO_3$ aqueous solution. The aqueous phase was extracted with Et_2O (3 ×). The combined organic phase was dried over Na_2SO_4, and concentrated in vacuo to give **17** (105 mg, 0.310 mmol, quant.) as a crude product.
Analytical Data for Compound 17
Yellow syrup. FT-IR (neat): 3368, 3029, 2956, 2928, 2870, 2858 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (6 H, m), 1.13–1.33 (8 H, m), 1.52–1.67 (2 H, m), 1.86 (2 H, q, *J* = 6.6 Hz), 2.42 (3 H, s), 3.40 (NH_2, s), 4.39, (1 H, q, *J* = 7.5 Hz), 5.18 (1 H, ddd, *J* = 1.5 Hz, 7.5 Hz, 15.6 Hz), 5.50 (1 H, dt, *J* = 6.6 Hz, 15.6 Hz), 7.29 (2 H, d, *J* = 7.8 Hz), 7.73 (2 H, d, *J* = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.86, 14.00, 21.48, 22.11, 22.28, 28.28, 31.05, 31.65, 31.95, 60.35, 125.44, 128.25, 128.37, 134.54, 134.94, 143.51. MS (Cl): *m/z* = 339 $[M + H]^+$. HRMS (CI^+): *m/z* calcd for $C_{18}H_{31}N_2O_2S$: 339.3006; found: 339.2907.
Next, neutral silica gel (3.0 g) was added to a solution of **17** (105 mg, 0.310 mmol) in AcOEt (6 mL), and it was stirred for 6 h at r.t. It was filtrated and washed with hexane/AcOEt (100:1), and the filtrate was concentrated in vacuo. The residue was purified by silica gel chromatography (hexane/AcOEt = 100:1) to give (*E*)-undec-5-ene (**19**, 39.2 mg, 0.254 mmol, 82% from **16**).
Analytical Data for Compound 19
Colorless syrup. FT-IR (neat): 2957, 2931, 2871 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (6 H, m), 1.27 (10 H, m), 1.97 (4 H, m), 5.39 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.31, 14.43, 22.54, 22.90, 29.689, 31.75, 32.18, 32.64, 32.93, 130.64, 130.71. MS (Cl): *m/z* = 154 $[M]^+$. HRMS (CI^+): *m/z* calcd for $C_{11}H_{22}$: 154.1722; found: 154.1720.

(22) **One-Pot Synthesis of Alkene 19 from 15b (Scheme** 3, b**)**
A solution of **15b** (129 mg, 0.316 mmol) and **12** (136 mg, 0.474 mmol) in CH_2Cl_2 (0.85 mL) was added to a dried two-neck flask under an atmosphere of argon. *m*-$C_2B_{10}H_{11}HgCl$/AgOTf in 0.1 M CH_2Cl_2 (158 µL) was added dropwise to the solution at 0 °C, and it was stirred at 0 °C for 10 min. Subsequently, a 1.0 M HCl in AcOEt (5.0 mL) was added to the mixture at r.t., and it was stirred at r.t. until disappearance of **16**. Next, neutral silica gel (3.0 g) was added to the mixture, which was stirred for 24 h at r.t. The suspension was filtrated and washed with hexane/AcOEt (4:1). The filtrate was concentrated in vacuo. The residue was purified by silica gel chromatography (hexane/AcOEt = 100:1 to 4:1) to give **19** (31.2 mg, 0.202 mmol, 64% from **15b**) along with *m*-$C_2B_{10}H_{11}HgCl$ (5.9 mg, 15.6 µmol, 99%).

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