Letter

Rare-Earth-Catalyzed Regioselective Hydrosilylation of Aryl-Substituted Internal Alkenes

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Rare-Earth-Catalyzed Regioselective Hydrosilylation of Aryl-Substituted Internal Alkenes

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ABSTRACT: Rare-earth-catalyzed regioselective hydrosilylation of internal alkenes with an ene-diamido samarium alkyl as precatalyst has been described. The samarium alkyl complex $LSmCH_2SiMe_3(THF)_2$ (**2**, L = DipNC(Me)C(Me)NDip, Dip = 2,6-iPr$_2$C$_6$H$_3$) enabled highly regioselective hydrosilylation of aryl-substituted internal alkenes with primary silanes, leading to the selective formation of a series of secondary silanes in high yields.

KEYWORDS: *rare-earth complex, hydrosilylation, internal alkene, metal hydride, samarium, catalysis*

Catalytic hydrosilylation of alkenes represents the most powerful and selective protocol for the synthesis of organosilanes, which have wide applications in synthetic chemistry and for the production of various silicon materials both in industry and academia.[1,2] Although metal-catalyzed hydrosilylation of terminal alkenes have been extensively studied,[3] selective hydrosilylation of internal alkenes is still a challenge and has been rarely reported because of their slow coordination-insertion process and poor regioselectivity in the case of unsymmetric alkenes (Scheme 1).[4,5] On the other hand, transition metal catalysts may suffer from serious side reactions such as isomerization,[4d-f,6] and dehydrogenative silylation due to the steric effects of internal alkenes.[7]

Hydrosilylation of terminal alkenes, *extensively studied*
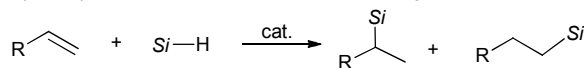
Hydrosilylation of internal alkenes, *very limited reports*
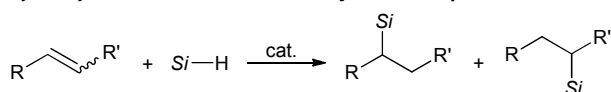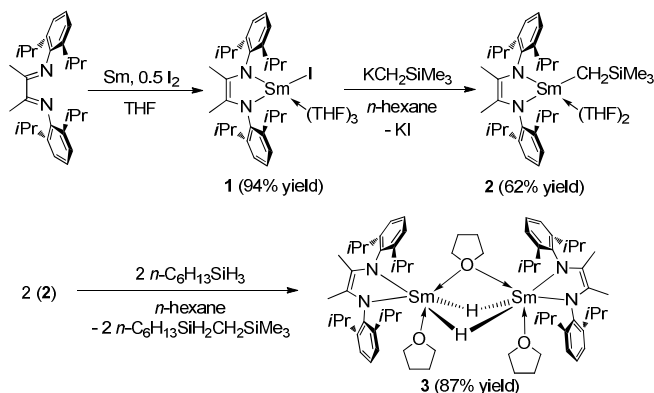

Scheme 1. Hydrosilylation of Terminal and Internal Alkenes

So far, only a few transition metal complexes and main group metal complexes have been reported to catalyze hydrosilylation of a few of internal alkenes, but they exhibited poor regioselectivity and required harsh conditions, and sometimes led to isomerization products. It has been reported that palladium complexes could catalyze hydrosilylation of β-alkylstyrenes with trichlorosilane only.[4a,b] Several catalysts based on Fe, Co and Ni are only viable for the hydrosilylation of cyclic alkenes such as norbornene, cyclopentene, and cyclohexene.[4c-f] The catalysts based on main group metals were reported to be less reactive and selective.[4g-i] Very recently, iron-catalyzed regioselective hydrosilylation of *trans-β*-substituted styrenes was reported by Zhu, et al.[5] Since internal alkenes widely exist in natural products and are versatile start-

ing materials in synthetic chemistry, their selective hydrosilylation is of considerable interest for their further conversions.

Rare-earth-catalyzed hydrofunctionalization of alkenes has emerged as a powerful strategy for the creation of carbon-heteroatom bonds.[8,9] The reaction could offer distinctive catalytic sequences and reaction patterns from other catalysts because of the large electropositivity and inaccessibility of oxidative-addition process of rare-earth ions.[10] Besides their unique regioselectivity, the hydrosilylation of alkenes with primary silanes could selectively yield secondary silanes, which are key intermediates for cyclosiloxane materials, silanediols and polysilanes.[11] Although a number of rare-earth complexes have been reported to catalyze hydrosilylation of alkenes,[12-14] rare-earth-catalyzed hydrosilylation of internal alkenes has been virtually unexplored. We report here the synthesis and characterization of the ene-diamido samarium alkyl (**2**, Scheme 2) and hydride (**3**), which enabled highly regioselective hydrosilylation of a range of aryl-substituted internal alkenes even in the presence of bulky groups.

Samarium-catalyzed hydrosilylation of terminal alkenes have been extensively investigated with well-defined samarium complexes supported by cyclopentadienyl (Cp) ligands.[12l-q] A couple of samarium catalysts with multiple dentate ligands based on N, O and S donors have also been reported.[12r,14e] Our group reported earlier that a dimeric ene-diamido samarium methoxide exhibited high regioselectivity in the hydrosilylation of terminal alkenes.[14f] The detailed mechanistic studies by DFT calculations disclosed the initial formation of a samarium hydride intermediate. However, the hydride could not be directly isolated and detected by the reaction of the samarium methoxide with silanes. It is envisioned that the ene-diamido samarium halides could be suitable precursors for the corresponding alkyls and hydrides via substitution reaction with an alkylpotassium and the subsequent σ-bond metathesis. It is expected that the highly reactive alkyls and hydride may offer increased activity and broad substrate scopes by taking advantage of the unique properties of the bulky ene-diamido ligand. Thus, the preparation of the samarium halides and alkyls has been explored.

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Scheme 2. Synthesis of Ene-Diamido Samarium Complexes

The samarium iodide **1** could prepared in good yield (94%) by the three-component reaction of the corresponding diimine, samarium and iodine in THF.[15] The samarium alkyl complex LSmCH$_2$SiMe$_3$(THF)$_2$ (**2**, L = DipNC(Me)C(Me)NDip, Dip = 2,6-iPr$_2$C$_6$H$_3$] was obtained as brown crystals in 62% yield by the reaction of **1** with KCH$_2$SiMe$_3$ in n-hexane. Reactions of **2** with PhSiH$_3$ and RSiH$_3$ (R = n-C$_6$H$_{13}$) have been investigated for the preparation of the hydride. The reaction with PhSiH$_3$ led to a mixture arising from the cleavage of both the Si–C and Si–H bonds, whereas reaction with RSiH$_3$ at room temperature resulted in the clean formation of the hydride bridged dimer L(THF)Sm(μ-H)$_2$(μ-THF)Sm(THF)L (**3**) in high yield (87%) in 5 minutes. The excess of RSiH$_3$ also led to the clean reaction, and the other possible side-products such as metal silyl complex could not be detected, indicating the rapid and selective σ-bond metathesis of the Sm–C bond with the silane.[16] The selective and rapid formation of the hydride **3** in this case demonstrated the potentials of this class of compounds for hydrosilylation reactions. Complexes **1**–**3** are paramagnetic and display broad NMR signals. Their structures have been determined by X-ray single crystal analysis.
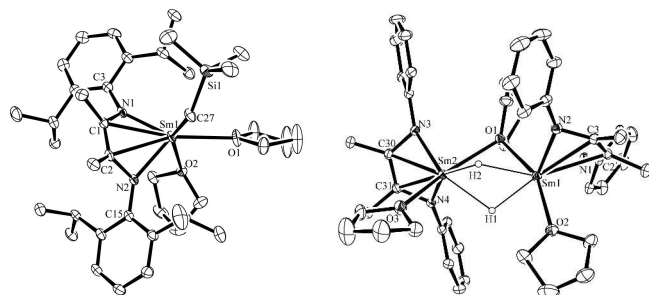

Figure 1. Molecular structure of complexes **2** (left) and **3** (right) with 30 % ellipsoid probability. Hydrogen atoms except the ones on the samarium atoms and the iPr groups on the phenyl rings have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **2**: Sm1–C27 2.508(3), Sm1–N1 2.241(2), Sm1–N2 2.236(2), Sm1–C1 2.682(3), Sm1–C2 2.681(2), Sm1–O1 2.682(3), Sm1–O2 2.5447(19), N1–C1 1.425(3), N2–C2 1.419(3), C1–C2 1.380(4). **3**: Sm1–N1 2.241(3), Sm1–N2 2.226(3), Sm1–C2 2.695(3), Sm1–C3 2.703(4), Sm1–H1 2.29(4), Sm1–H2 2.26(4), Sm1–O1 2.651(2), Sm1–O2 2.439(2), Sm1–Sm2 3.6296(3), N1–C2 1.419(4), N2–C3 1.413(5), C2–C3 1.375(5); N1–Sm1–N2 79.74(11), Sm1–O1–Sm2 87.23(7), H1–Sm1–H2 64.2(13).

The molecular structures of **2** and **3** are shown in Figure 1, and that of **1** is given in Figure S1 in the Supporting Infor-

mation. The alkyl complex **2** is monomeric in the solid state, whereas the hydride **3** features a dimeric structure with two bridging hydride ligands and one bridging THF molecule. The Sm−N bond lengths (2.226−2.241(3) Å) in **2** and **3** are similar to those reported,[14f] while the distances between the samarium atoms to the carbon atoms in the ligand backbone in **2** and **3** (2.681(2)−2.704(4) Å) are much shorter than those found in the previously reported dimeric samarium methoxide (av. 2.821 Å), indicating the strong η^4 bonding of the ligand to the samarium atom. The dihedral angles between the N−Sm−N and N−C−C−N planes are 124.1° in **2** and av. 126.6° in **3**, which are smaller than that in dimeric samarium methoxide (132.2°). The bridged Sm−H bond distances of 2.23−2.29(4) Å are shorter than those in {[(Me$_3$Si)$_2$NC(NiPr)$_2$]$_2$Sm(μ-H)}$_2$ (av. 2.36(2) Å).[17] The Sm−Sm distance of 3.6296(3) Å in **3** is shorter than those found in {[(Me$_3$Si)$_2$NC(NiPr)$_2$]$_2$Sm(μ-H)}$_2$ (3.8102(2) Å) and [(C$_5$Me$_5$)$_2$Sm(μ-H)]$_2$ (3.905(3) Å).[18]

With the alkyl and hydride **2** and **3** in hand, we are interested in the investigation of their catalytic hydrosilylation reactions with the aim to broaden their applications. It is envisioned that the highly reactive alkyl and hydride could be viable for more challenging substrates. In the first place, the hydrosilylation of styrene and 1-hexene with complex **2** as precatalyst were examined (Table S1, entry 17 and 18 in SI) for comparison. As expected, 3 mol% of **2** exhibited high regioselectivity for the two substrates with primary silanes, similar to the previously reported methoxide catalyst.[14f] The catalytic behaviors of the hydride **3** are comparable to those of **2**, indicating the similar mechanism (Table S1, entry 19 and 20 in SI). As catalytic hydrosilylation of terminal alkenes has been extensively studied, we turned our attention to hydrosilylation of internal alkenes, which are much less studied.

Table 1. Optimization Reaction Conditions[a]

entry	solvent	T (°C)	time (h)	yield (%)[b]	regiosel. (%)[b]
1	THF	25	1	10	>99
2	toluene	25	1	85	>99
3[c]	toluene	25	1	43	>99
4	toluene	25	4	93	>99
5	toluene	60	3	90	>99
6[d]	toluene	60	3	99	>99

[a]Reaction conditions: n-C$_6$H$_{13}$SiH$_3$ (0.5 mmol), alkene (0.5 mmol), **2** (0.015 mmol, 3 mol%) and 0.1 mL solvent. [b]Determined by GC-MS with the crude mixture. [c]PhSiH$_3$ was used. [d]0.55 mmol of silane.

At the outset, we probed the catalytic hydrosilylation of β-methylstyrene PhCH=CHMe with 3 mol% of **2** as catalyst and commercially available PhSiH$_3$ and n-C$_6$H$_{13}$SiH$_3$ (RSiH$_3$) as silylation reagents. As shown in Table 1, the reaction in THF with one equivalent of RSiH$_3$ at room temperature only led to 10% yield in 1 h (entry 1), whereas the same reaction in toluene yielded the hydrosilylation product in 85% yield in 1 h (entry 2), indicating the significant solvent effects and consistent with the coordination-insertion mechanism. However, the hydrosilylation with PhSiH$_3$ in toluene only afforded the desired product in 43% yield under the same conditions (entry

3), because of the complicated σ-bond metathesis of **2** with PhSiH$_3$ that involves both of the Si–H and Si–C bond cleavage as noted above. Prolonged reaction time with RSiH$_3$ resulted in the improved yield to 93% (entry 4). It was found that the reaction with one equivalent of RSiH$_3$ at 60 °C only gave the desired secondary silane in 90% yield in 3 h, along with the formation of a small amount of the tertiary silane due to the double addition of the silane to two equivalents of the alkene (entry 5). However, the yield was increased to 99% under the similar conditions with slightly excess of RSiH$_3$ (entry 6). Although these reaction parameters have noticeable effects on the reaction rate and yields, the regioselectivity maintained excellent (>99%) in all of the cases. It has been observed that efficient hydrosilylation of β-methylstyrene with other silanes such as Ph$_2$SiH$_2$ and PhMeSiH$_2$ did not occur under our catalytic conditions.

**Table 2. Samarium-Catalyzed Hydrosilylation of Internal Alkenes**[a]

4a, 3 h, 60 °C
86% (> 99%)

4b, 8 h, 60 °C
89% (> 99%)

4c,[b,c] 24 h, 80 °C
41% (97%)

4d, 3 h, 60 °C
91% (> 99%)

4e, 3 h, 60 °C
88% (> 99%)

4f,[b] 12 h, 60 °C
89% (> 99%)

4g,[b] 12 h, 60 °C
85% (> 99%)

4h, 10 h, 60 °C
86% (> 99%)

4i, 10 h, 60 °C
88% (> 99%)

4j,[b] 12 h, 60 °C
82% (> 99%)

4k,[b,c,d] 12 h, 80 °C
87%

4l,[c] 12 h, 80 °C
84% (> 99%)

4m,[c] 12 h, 80 °C
91% (> 99%)

4n,[b,c] 24 h, 80 °C
33% (93%)

4o,[b,c] 24 h, 80 °C
41% (> 99%)

4p,[c] 10 h, 60 °C
75%
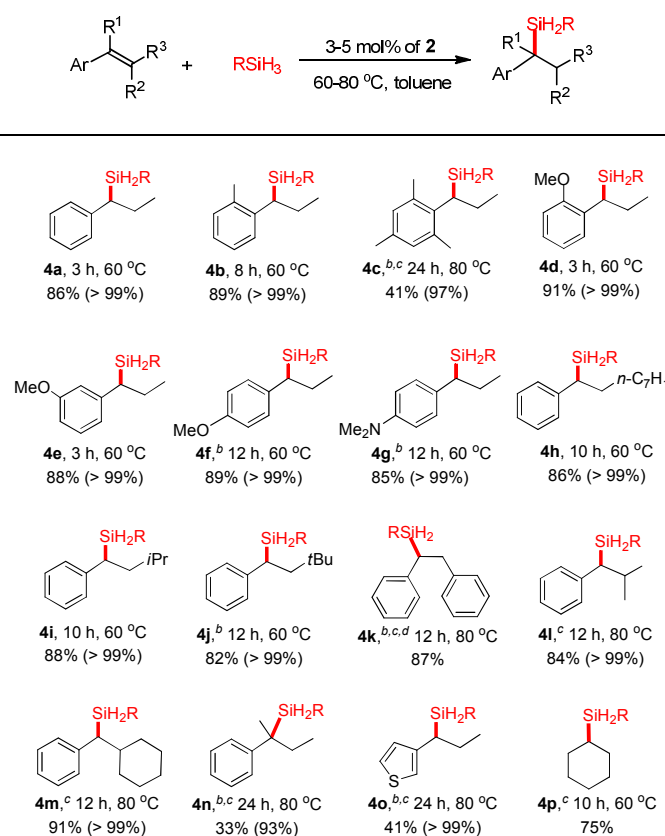
[a]Reaction conditions: 0.015 mmol of **2** (3 mol%), 0.5 mmol of alkenes and 0.55 mmol of RSiH$_3$ (R = n-C$_6$H$_{13}$) in 0.1 mL of toluene; The yield (%) referred to the isolated yields and the percent in parentheses referred the regioselectivity determined by GC-MS measurement of the crude products. [b]1 mmol silane. [c]0.025 mmol of **2** (5 mol%). [d]0.3 mL toluene.

Under the optimized conditions with slightly excess of RSiH$_3$ as silylation reagent, a range of β-substituted styrene derivatives were examined with 3–5 mol% of **2** in toluene. As shown in Table 2 (for details see Table S1 in SI), the β-substituted styrenes with Me, OMe and NMe$_2$ substitutents on the phenyl rings can be hydrosilylated smoothly to give the corresponding regioselective products (**4b** and **4d**–**g**) in good

yields. The bulky 2,4,6-trimethylphenyl-substituted internal alkene required 5 mol% loading of **2** and 80 °C to give the hydrosilylation product **4c** in 41% yield, a relatively low yield due to the steric effects. The hydrosilylation of β-substituted styrenes with a long chain alkyl, bulky iPr and tBu groups proceeded at 60 °C to give highly regioselective (>99%) products (**4h**–**j**) in good yields. Notably, the catalytic reaction is also effective for trisubstituted alkenes with 5 mol% loading of **2** at 80 °C, leading to the formation of the hydrosilylation products (**4l** and **4m**) in good yields. Even more interesting, the regioselective hydrosilylation also took place at the disubstituted alkene carbon atom to give the product **4n** in 33% yield. The 1,2-diphenyl was smoothly hydrosilylated to yield the product **4k** in high yield. In addition, thiophene substituted and cyclic internal alkenes also yielded the hydrosilylation products (**4o** and **4p**) in modest to good yields. For comparison, the hydrosilylation of two terminal alkenes, styrene and 1-hexene, was also studied under the similar conditions: styrene was exclusively converted to the corresponding Markovnikov product **4q** in 89% yield in 1 h (Table S1, entry 17 in SI) while 1-hexene yielded anti-Markovnikov product **4r** in 78% yield in 2 h (Table S1, entry 18 in SI). The regioselectivity observed for **4q** and **4r** is well correlated with that catalyzed by the ene-diamido samarium methoxide reported previously, indicating the similar mechanistic pathway. However, the samarium methoxide is almost inactive for hydrosilylation of β-methylstyrene, very likely due to the high energy barrier for the formation of the active hydride from the methoxide plus high barrier for the coordination-insertion of the internal alkene.

Although the high regioselectivities were observed for β-substituted styrenes, the catalytic hydrosilylation of aliphatic internal alkenes and halogen-substituted styrenes under the similar conditions proved to be sluggish, yielding a mixture containing several products which cannot be separated and identified definitely (Table S2 in SI). This indicated that the aryl group on alkenes plays significant roles for the directing regioselectivity. This feature can be attributed to the unique η^3 bonding of styrene derivatives to the rare-earth ion.[14f] Comparison of the results for the different alkenes indicated that the substrate dependence of reaction rate roughly follows terminal > 1,2-disubstituted > trisubstituted alkenes. Steric effects are noticeable as observed for the formation of **4c** and **4l**–**n**. We also observed that the catalytic hydrosilylation of diphenylacetylene is faster than 1,2-diphenylethene as indicated by NMR and GC analysis in the hydrosilylation of their 1:1 mixture with RSiH$_3$.
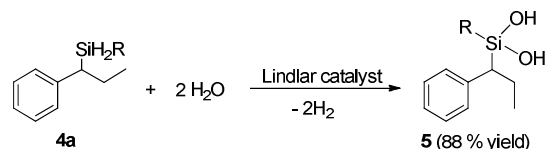
Scheme 3. Palladium-Catalyzed Hydrolytic Oxidation of Dihydrosilanes for the Synthesis of Silanediol

Catalytic hydrolytic oxidation of hydrosilanes presents the most efficient and atom-economic protocol for synthesis of silanols.[19] To demonstrate the synthetic potentials of the dihydrosilanes, palladium-catalyzed hydrolytic oxidation of **4a** with Lindlar catalyst has been conducted (Scheme 3). The catalytic reaction gave the corresponding silanediol in 88%

yield. It can be expected that the resulting dihydrosilanes are useful for the preparation of a series of silanediols. It is noted that silanediols have been employed as hydrogen bond donor catalysts and for molecular sensing and drug discovery.[20]

Kinetic studies (Table S4 and Figure S2 in SI) on the hydrosilylation of β-methylstyrene PhCH=CHMe with n-$C_6H_{13}SiH_3$ in toluene roughly disclosed the first order dependence on **2**, the alkene and the silane. The result is distinct from that reported for hydrosilylation of terminal alkenes by the ene-diamido samarium methoxide, which follows the first order dependence on the catalyst and an alkene but zero order on phenylsilane. This inconsistence is very likely due to the different rate-limiting step in the catalytic cycle arising from the different steric effects of internal and terminal alkenes. For terminal alkenes, the coordination-insertion of an alkene has been proposed as the rate-limiting step.[14f] Based on the coordination-insertion of the alkene to the metal hydride intermediate followed by σ-bond metathesis mechanism disclosed by DFT calculations previously,[14f] the present kinetic studies suggested that the σ-bond metathesis in the cycle is the rate-limiting step. The relatively slow σ-bond metathesis in this case can be attributed to the steric effects of the bulky alkyl group attached to the samarium atom generated via the insertion of the internal alkene.[21] As shown in Scheme 4, the regioselectivity of the internal alkene insertion into the Sm−H bond via **TS1** to form **B** is controlled by the stabilizing η^3 coordination mode of the styrene fragment. The subsequent rate-limiting σ-bond metathesis of **B** with $RSiH_3$ via **TS2** led to the formation of hydrosilylation products and regeneration of the active hydride **A**.
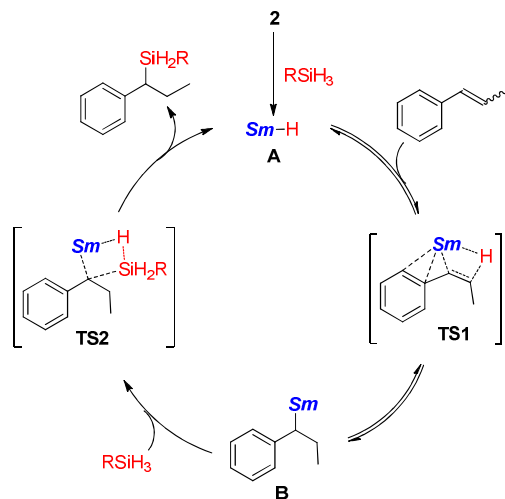
Scheme 4. Proposed Mechanism for the Regioselective Hydrosilylation

In summary, we have disclosed the first rare-earth catalytic system that enabled highly regioselective hydrosilylation of aryl-substituted internal alkenes. The high regioselectivity can be attributed to the unique stabilizing η^3 coordination mode of the styrene fragment to the rare-earth ion in the four-membered transition state. The kinetic studies suggested that the last step σ-bond metathesis is the rate-limiting step, indicating the reaction is sensitive to the steric effects of alkene substrates. The results demonstrated the potentials of ene-diamido rare-earth catalysts for the regioselective addition of element-hydrogen bond to unsaturated molecules. Further studies of the catalytic system for broad applications are currently in progress.

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

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> Experimental procedures, crystallographic data, and spectroscopic data.

Accession Codes

CCDC 1544763−1544765 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Table of Contents

RSiH₃ + Internal Alkenes → (product)

3 mol% [SmR]

[SmH]

[SmR]

16 examples
Up to 91% yield
Up to 99% regioselectivity
Isolated active species [SmH]