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Letter

Formal Hydrotrimethylsilylation of Styrenes with Anti-Markovnikov Selectivity Using Hexamethyldisilane

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Cite This: *Org. Lett.* 2022, 24, 8735−8740

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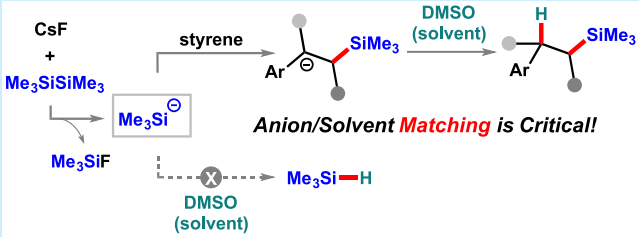
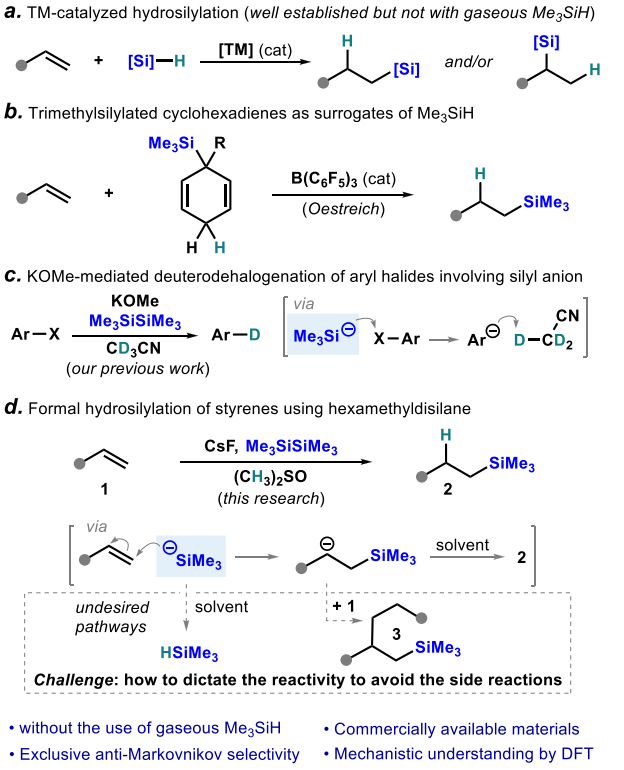
ABSTRACT: A combination of CsF and hexamethyldisilane in DMSO enabling an anti-Markovnikov formal hydrotrimethylsilylation of styrenes is reported. Mechanistic investigations detail the reaction pathways, including in situ generation of a silyl anion, the addition of this silyl anion onto the alkene to form a carbanion, and this carbanion is then protonated by DMSO. The choice of the solvent to match its reactivity with the carbanion and silyl anion is key to the success of this reaction.



Hydrosilylation of alkenes is a direct and powerful route to access organosilicon compounds that are widely utilized in the fields of synthetic chemistry, organic photonics and electronics, and material sciences.[1,2] There are substantial reports using transition-metal (TM) catalysts to achieve controllable selectivity and reactivity (Scheme 1a).[2,3] In these reactions, a variety of hydrosilanes can be used to realize hydrosilylation. But to synthesize TMS-substituted products, gaseous trimethylsilane (Me_3SiH) has to be applied, which brings tremendous operational inconvenience and safety issues.[4] Therefore, new approaches employing readily available and safe reagents for trimethylsilylation, ideally under transition-metal-free conditions, are of practical importance and environmental meaningfulness.

Scheme 1. Hydrotrimethylsilylation of Alkenes



Breakthroughs were made by the use of trimethylsilylated cyclohexadiene as sources of both the trimethylsilyl and H incorporated into alkenes.[5,6] The Studer group initially designed a radical chain process using silylated cyclohexadiene as the corresponding silyl radical and H atom donors.[5] Remarkable achievements by Oestreich et al. realized an ionic transfer hydrosilylation of alkenes in the presence of a $B(C_6F_5)_3$ catalyst (Scheme 1b).[6] Contrary to the Lewis acid catalyzed pathway,[6,7] base-promoted olefin silylation was reported involving the formation of a silyl anion but with only limited information disclosed.[8] An inspirational fluoride-catalyzed 1,4-disilylation of 1,3-dienes using disilanes was reported by Hiyama when HMPA was used as the solvent.[8a]

Recently, our group developed a deuterodehalogenative strategy using a combination of hexamethyldisilane ($Me_3SiSiMe_3$) and potassium methoxide (KOMe) at room temperature (Scheme 1c).[9] In this transformation, the trimethylsilyl anion is slowly generated upon treatment of hexamethyldisilane with methoxide. This silyl anion spontaneously attacks the aryl halide to form an aryl carbanion which

Received: September 17, 2022
Published: November 24, 2022

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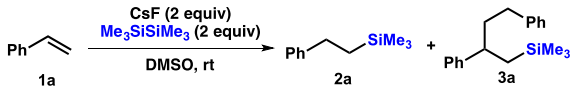
https://doi.org/10.1021/acs.orglett.2c03170
Org. Lett. 2022, 24, 8735−8740

is then quenched by CD_3CN to provide the deuterated product. Based on this, we speculated that the trimethylsilyl anion would add onto the carbon−carbon double bond of styrenes **1** to form a benzyl anion,[10] followed by in situ protonation to achieve a formal hydrotrimethylsilylation products **2** with anti-Markovnikov selectivity (Scheme 1d). The realization of this design will offer a new synthetic tool for organosilanes that is desirable from the standpoint of green chemistry.

Considering the nucleophilic and basic properties of the silyl anion and carbanion involved, a precise match of reaction conditions to (1) avoid the initially generated trimethylsilyl anion being quenched by the solvent and (2) prevent secondary addition of the carbanion to styrene that forms byproduct **3** or oligomers is key to the success. In turn, we found the judicious choice of the base and the solvent enabled the proposed transformation. Here, we report our study of the formal hydrotrimethylsilylation of styrenes using hexamethyldisilane as a pronucleophile. The detailed mechanism of this unprecedented reaction revealed through experimental and computational investigations is also delivered.

A preliminary result was obtained by the use of CsF as a base and DMSO as a solvent, accessing a 56% yield of the anti-Markovnikov product **2a** and 34% yield of a byproduct **3a** (Table 1, entry 1). Detailed investigations of the reaction

Table 1. Optimization of the Reaction Conditions



entry[a]	deviation	2a (%)[b]	3a (%)[b]
1	none	56	34
2	LiF, NaF, or KF instead of CsF	<5	<5
3[c]	KF/18-C-6 instead of CsF	45	18
4	KOMe instead of CsF	31	15
5	MeCN instead of DMSO	N.R.	N.R.
6	THF or toluene instead of DMSO	N.R.	N.R.
7	w/o CsF	N.R.	N.R.
8[d]	CsF (standard conditions)	79 (72)[e]	21

[a]Reaction conducted with **1a** (0.2 mmol, 0.4 mol/L) at rt for 12 h; N.R., no reaction. [b]GC yield. [c]With 2 equiv of 18-crown-6. [d]With **1a** (0.13 mol/L), CsF (3 equiv) and $Me_3SiSiMe_3$ (3 equiv). [e]Isolated yield.

parameters were then carried out (see Supporting Information (SI)), and the selected results were highlighted in Table 1. The reaction with other fluoride salts, such as LiF, NaF, and KF, produced a trace amount of **2a** (entry 2). Intriguingly, the addition of 18-crown-6 ether to the reaction in the presence of KF dramatically improved the reactivity, likely due to the coordination of the crown ether to the potassium cation to release the naked fluoride, which can then facilitate the formation of pentacoordinate silicon species.[11] Alkoxides were reported to cleavage the Si−Si bond of hexamethyldisilane.[12] In our reaction, the use of KOMe delivered **2a** and **3a** in 31% and 15% yield, respectively (entry 4). The choice of solvents was crucial for the hydrosilylation, and no desired product was observed in MeCN, THF, or toluene (entries 5 and 6). In the absence of any base, no product was generated (entry 7). To increase the yield of **2a**, various reaction parameters including the concentration of the substrate and the ratio of base and silane were further screened (see Table S1). To our delight, the desired product **2a** could be isolated in 72% yield, when the loadings of CsF and the disilane were increased to 3 equiv, and a diluted concentration of **1a** (0.13 mol/L) was applied meanwhile (entry 8).

During the investigation of the substrate scope, we applied the optimal conditions shown in Scheme 2. But slightly modified reaction conditions were employed for some substrates with varying electronic nature (Table S1). Electron-rich styrenes are found to be less reactive and require a higher concentration and elevated conditions. For instance, 2-, 3-, and 4-methyl styrenes (**1b**−**1d**) delivered the corresponding hydrosilylation products **2b**−**2d** in 80−96% yields when the reactions were conducted at 80 °C in higher concentration (0.7 M). We were delighted to find that the reaction was amenable to scale up and **2d** (1.88 g) was accessed in 98% yield. 4-Methoxy- and 3,4,5-trimethoxy-substituted styrenes (**1f** and **1m**) were also hydrosilylated to afford **2f** and **2m** in 60% and 74% yields, respectively. For electron-deficient substrates, dropwise addition of the styrenes using a syringe pump was critical to suppress polymerization. Styrenes bearing a variety of functional groups, including halogens (**1g**, **1h**), cyano (**1i**), and phenyl (**1j**), were successfully tolerated. Vinylnaphthalene and vinylbenzothiophene were feasible substrates, delivering **2n** and **2o** in moderate yields. Notably, substrates possessing trimethylsilyl (**1k**), boronic esters (**1l**), and heterocycles (**1p** and **1q**) were tolerated and provided moderate yields ranging from 40% to 79% yields. 1,1-Disubstituted (**1r** and **1s**) and 1,2-disubstituted (**1t** and **1u**) olefins were also capable of the hydrosilylation reaction. In particular, when vinylsilanes were employed as substrates, geminal disilyl compounds (**2t**, **2u**) were smoothly obtained. These products are important synthons due to their bifunctional reactivity.[13] To further demonstrate the generality of this method, $Ph_3SiSiPh_3$ was examined under the optimized conditions, and the corresponding formal hydrotriphenylsilylation products (**2v**−**2z**) were isolated in 50−81% yields. In general, the reactions using $Ph_3SiSiPh_3$ as a pronucleophile resulted in lower yields in comparison with $Me_3SiSiMe_3$, probably due to the fact that the triphenylsilyl anion is less nucleophilic than the trimethylsilyl anion. We also investigated the reaction with $PhMe_2SiSiMe_2Ph$, but it failed to deliver the corresponding product.[14]

To gain insights into the mechanism, both experimental and computational investigations were carried out. A cyclopropane-containing substrate **1aa** was subjected to the standard reaction conditions, and the hydrosilylation product **2aa** was obtained in 76% yield (Scheme 3a). No ring-opening product was detected, suggesting a benzyl radical species is less likely to be involved.[15] An isotope labeling experiment using DMSO-d_6 as the solvent was then carried out. Deuterium incorporation at the benzylic positions of both **2d** and the byproduct **3d** was observed (Scheme 3b), indicating the involvement of a benzyl anion. It is worth pointing out that this exclusive deuterium incorporation reaction is of synthetic significance to access precisely β-deuterated silanes by avoiding the preparation of deuterosilanes in conventional hydrosilylation reactions.[16,17] It was reported that the Si−Si bond of disilanes can be cleaved by treatment with fluoride to produce a nucleophilic silyl anion in an aprotic polar solvent.[8a] Based on our experimental results and the literature precedent, a polar mechanism was proposed as shown in Scheme 3c. Coordination of fluoride to $Me_3SiSiMe_3$ generates a trimethylsilyl anion. This anion attacks the styrene to form a benzyl anion, which then

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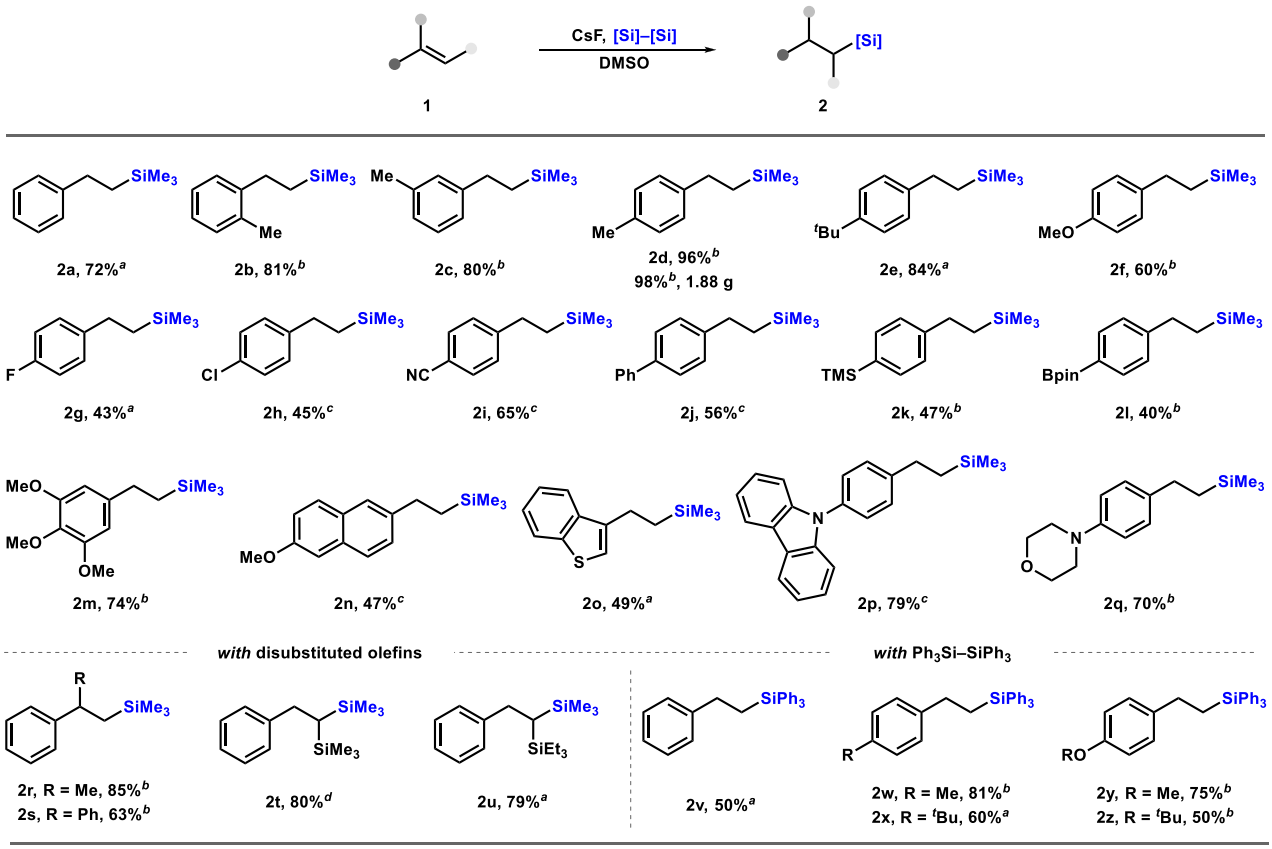
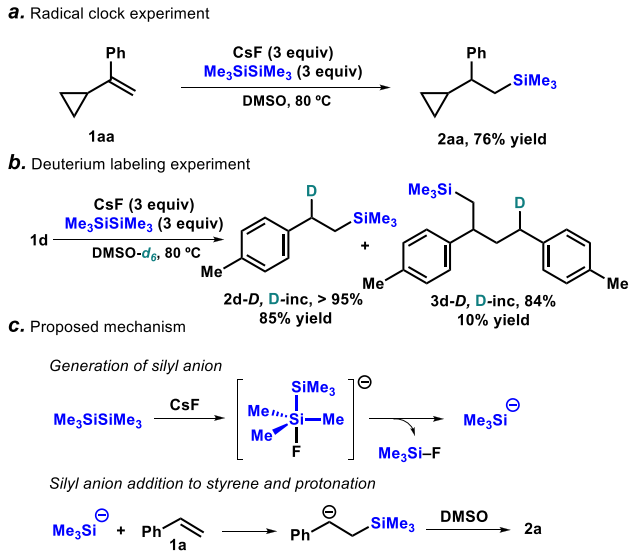
Scheme 2. Substrate Scope



Reactions conducted with **1** (1 equiv), CsF (3 equiv), and disilane (3 equiv) in DMSO. [a]With **1** (0.13 mol/L) in DMSO, rt. [b]With **1** (0.7 mol/L) in DMSO at 80 °C. [c]**1** (0.1 mol/L) in DMSO added in 2 h using a syringe pump, rt. [d]With **1t** (0.4 mol/L), CsF (2 equiv), and disilane (2 equiv) in DMSO at 40 °C. See SI for details.

Scheme 3. Mechanistic Studies



abstracts a proton from DMSO to provide the desired product **2a**.

We further conducted a computational study to understand the proposed mechanism above (Figure 1). Coordination of fluoride to hexamethyldisilane forms a pentacoordinate silicon anionic complex **CP1**.[18] This bimolecular process is endergonic by 14.0 kcal/mol. Subsequently, a highly reactive trimethylsilyl anion (**IN1**) is formed upon the cleavage of the Si−Si bond via transition state **TS1**, requiring 8.5 kcal/mol (from **CP1** to **TS1**). The formation of the trimethylsilyl anion is not a fast process (from reactants of hexamethyldisilane and fluoride to **TS1**, 22.5 kcal/mol), resulting in a low concentration of trimethylsilyl anion in the reaction system. We then computed how the trimethylsilyl anion acts as a nucleophile to react with styrene (Path A, the green line). The addition of the trimethylsilyl anion to styrene via transition state **TS2** gives a benzyl anion **IN2**, which spontaneously forms a complex **CP2** with DMSO. Since DMSO is used as the solvent (the concentration of pure DMSO is 14.1 mol/L), there is negligible entropy change here for forming **CP2**. With this assumption, the free energy change in this process is estimated to be 6.1 kcal/mol. After the formation of **CP2**, the carbanion then abstracts a proton from DMSO via **TS3**, requiring $\Delta G^{\ddagger}$ = 15.9 kcal/mol.[19] During the condition optimization, we found that a moderate yield of the present reaction was achieved even with 20 mol% of CsF (Table S1). In this case, we proposed that the dimethyl sulfoxide anion generated above can then react with hexamethyldisilane to generate the TMS anion again to turn over the reaction, as supported by our detailed DFT calculations (Figure S2). As a competition, the trimethylsilyl anion could be quenched by DMSO. Computationally, this process starts from the formation of a complex **CP3**, which is followed by abstracting a proton via **TS2′** (Path B, the red line). We have also assumed

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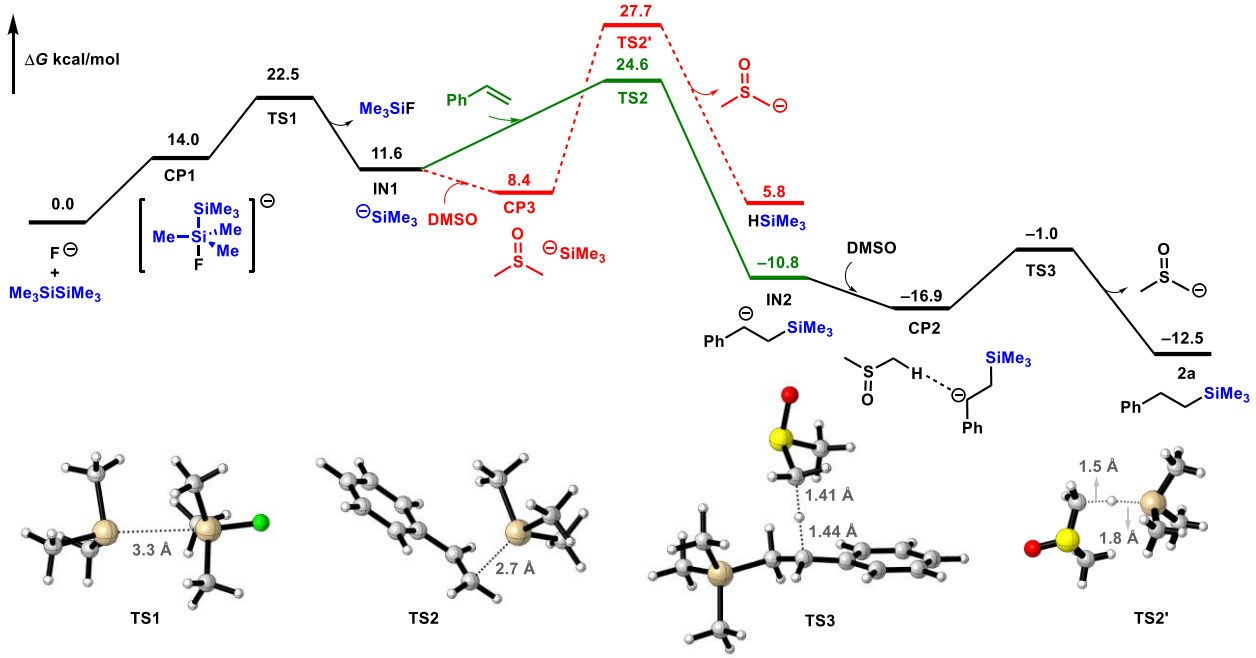

Figure 1. Reaction pathway in DMSO and free energy profile calculated at the SMD(DMSO)/M06-2X/6-311+G(d,p)//SMD(DMSO)/M06-2X/6-31+G(d,p) level.

that the formation of **CP3** from the silyl anion and large excess of DMSO has a small change in entropy. The abstraction of a proton by the silyl anion requires $\Delta G^{\ddagger}$ = 19.3 kcal/mol (from **CP3** to **TS2′**). **TS2′** in pathway B is higher than **TS2** in pathway A by 3.1 kcal/mol, indicating that the trimethylsilyl anion quenched by DMSO is much slower than its addition onto the styrene. In comparison, the activation free energy of abstracting a proton from MeCN by the trimethylsilyl anion is 1.1 kcal/mol, which is lower than path A (see SI). Therefore, the quench of the silyl anion is feasible in MeCN. These results are consistent with our experiments that no hydrosilylation product was observed when MeCN was used as the solvent.

Finally, the mechanism for the formation of the byproduct **3a** was also studied (Figure 2). The addition of **IN2** to another styrene via **TS4** requires an activation free energy of 12.8 kcal/mol. This is not favored more than the quenching of **IN2** by DMSO solvent via **TS3** by 3.0 kcal/mol. However, if the concentration of styrene is increased, the formation of **3a** could become favored because this is a bimolecular process, which can explain the experimental results when styrene was used in high concentration.

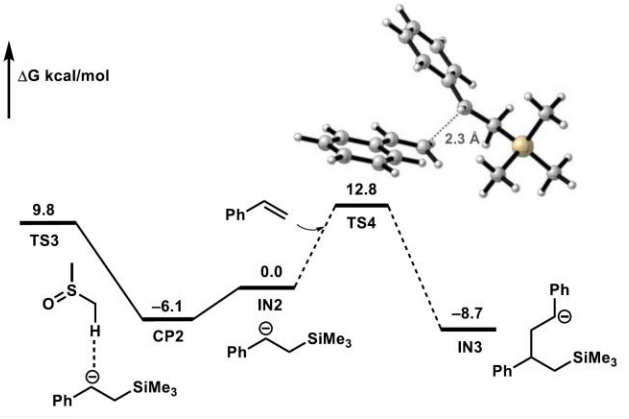

Figure 2. Free energy barriers of benzyl anion addition to alkene and protonation by DMSO. All were calculated at the SMD(DMSO)/M06-2X/6-311+G(d,p)//SMD(DMSO)/M06-2X/6-31+G(d,p) level.

In summary, we have developed a formal hydrosilylation of alkenes with exclusive anti-Markovnikov selectivity. This method employs hexamethyldisilane as a safe and readily available trimethylsilylation reagent to access alkyl trimethyl silanes. Mechanistic studies via experimental and DFT investigations revealed this reaction adopts a polar reaction pathway involving a silyl anion and a carbanion. As a proton source, the use of DMSO solvent is crucial to the success of the hydrosilylation reaction. This study provides an alternative to synthesize organosilanes in an environmentally benign manner, by obviating the use of transition-metal catalysts and gaseous silylation reagents.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its online Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.2c03170.

Experimental procedures, characterization data and NMR spectra for new compounds, calculation details, Cartesian coordinates and energies of computed stationary points (PDF)

https://doi.org/10.1021/acs.orglett.2c03170
Org. Lett. 2022, 24, 8735−8740

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the National Natural Science Foundation of China (21971198, 21933003, 22222111), the Natural Science Foundation of Hubei Province (Grant 2020CFA036), and the Fundamental Research Funds for the Central Universities (2042021kf0193) for financial support. We thank Mr. Weiming Shi (Peking University) for helping with the calculations regarding the reaction of dimethyl sulfoxide anion with Me_3Si-$SiMe_3$.

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