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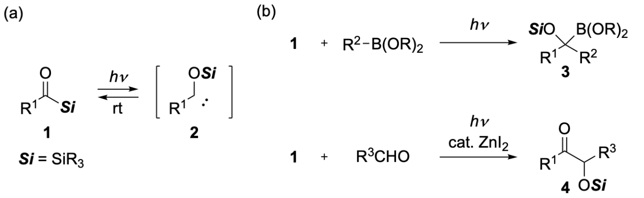
Efficient Generation and Synthetic Applications of Alkyl-Substituted Siloxycarbenes: Suppression of Norrish-type Fragmentations of Alkanoylsilanes by Triplet Energy Transfer

Kento Ishida[a], Hokuto Yamazaki[a], Chihiro Hagiwara[a], Manabu Abe[b], Hiroyuki Kusama*[a]

Abstract: Acylsilanes have been known to undergo isomerization to siloxycarbenes under photoirradiation and thus-generated carbenes can be utilized for various synthetic reactions. But this carbene formation is not necessarily efficient with some kinds of alkanoylsilanes because Norrish-type fragmentations compete, which limit synthetic utility of alkanoylsilanes as carbene precursors. In this study, generation of siloxycarbenes from alkanoylsilanes by visible-light-induced energy transfer was examined by using an Ir complex, [Ir{dF(CF_3)ppy}$_2$(dtbpy)]PF_6, and was successfully applied to the C-C coupling reactions with boronic esters or aldehydes. This methodology efficiently suppressed undesired Norrish-type reactions and broadened synthetic utility of alkanoylsilanes.

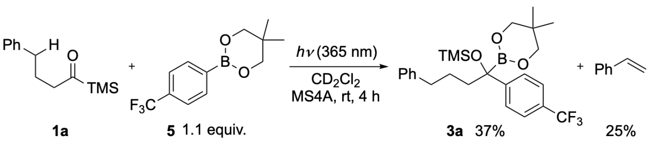
Photocatalytic organic transformations have attracted significant attentions in current synthetic chemistry. Photoredox process involving radical intermediate is one of the hot topics in this field.[1] Another interesting aspect of photocatalytic reactions is triplet energy transfer processes which enable generation of triplet-excited states of organic substrates through energy transfer from photo-excited catalysts.[1b,1c,1e,2] From a synthetic point of view, triplet energy transfer is considered to have some benefits[3] as compared to direct photoexcitation of organic substrates: (i) highly energetic singlet-excited states of substrates, which sometimes induce undesired reactions, can be skipped, and (ii) it enables excitation of substrates with longer-wavelength light than the inherent absorption band of substrates.

It has been known that triplet-excited states of acylsilanes **1** undergo a 1,2-silyl migration to generate transient and nucleophilic siloxycarbene intermediates **2** (Scheme 1a).[4] Since Brook and co-workers originally discovered this photoisomerization through reactions of siloxycarbene intermediates **2** with polar compounds such as alcohols over fifty years ago,[5] various synthetic reactions utilizing photochemically-generated siloxycarbenes **2** have been developed by several groups[6] including us.[7] However, in contrast to the reactions of aroylsilanes (**1**, R^1 = aryl), the use of alkanoylsilanes (**1**, R^1 = alkyl) has been quite limited.[8]



Scheme 1. (a) Photochemical generation of siloxycarbenes (b) Photo-induced coupling reactions between acylsilanes and electrophiles (our previous works)

We have already reported intermolecular coupling reactions of photochemically-generated siloxycarbenes **2** with boronic esters or aldehydes under neutral or Lewis acidic conditions (Scheme 1b).[7] During the course of these studies, we noticed that serious undesired photochemical processes competed with the siloxycarbene formation in the reactions with some kinds of alkanoylsilanes. For example, UV-irradiation (365 nm) to a mixture of 4-phenylbutanoylsilane **1a**[9] and boronic ester **5** gave styrene along with the desired coupling product **3a** in low yield (Scheme 2). The formation of styrene clearly indicated that Norrish type II fragmentation[10][11] competed with the desired photochemical isomerization to siloxycarbene **2** from excited states of alkanoylsilane **1a**.



Yields were determined by ^{1}H-NMR analysis.

Scheme 2. Photochemical reaction with **1a** and **5**

Similarly, photo-irradiation to a mixture of α-branched alkanoylsilane **1b** and boronic ester **5** afforded a decarbonylated product **6** as a major product (Scheme 3). In this case, a Norrish type I fragmentation[12] apparently competed with siloxycarbene formation.

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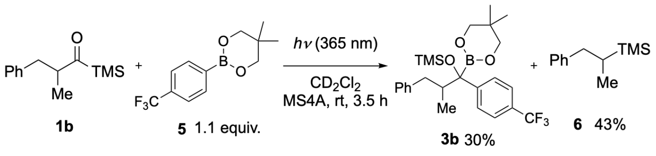
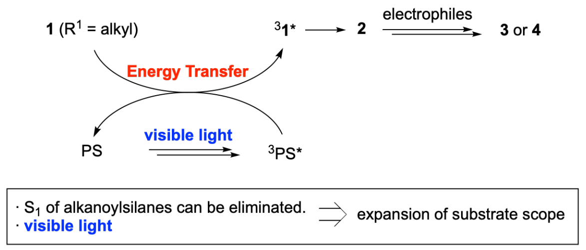


Yields were determined by ^{1}H-NMR analysis.

Scheme 3. Photochemical reaction with **1b** and **5**

These results clearly indicate that Norrish type fragmentation reactions are serious problems to expand synthetic applicability of photochemically-generated siloxycarbenes. Generally, Norrish type fragmentations are known to take place both from singlet and triplet excited states of carbonyls, but, in the reactions of alkanoylsilanes, clear evidence about which excited state is involved in Norrish type reactions is not available in literatures. If the above Norrish reactions took place from the singlet-excited-state of the alkanoylsilanes, triplet energy transfer methodology would be a reasonable solution to realize efficient generation of siloxycarbenes. Thus, we decided to develop the generation of siloxycarbenes **2** from alkanoylsilanes **1** through triplet energy transfer[13] and tried to suppress undesired Norrish type fragmentations to expand synthetic utility of alkanoylsilanes.

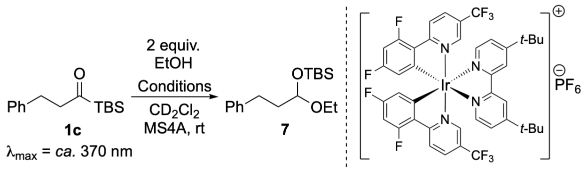
Strategy for the generation of siloxycarbenes **2** via triplet sensitization is shown in Scheme 4. A photosensitizer (PS) having its absorption band in visible region would be a reasonable candidate to prevent the direct photo-excitation of co-existing alkanoylsilanes **1**, because the n-π* absorption of **1** lies around 360-370 nm. Triplet energy of PS should be comparable or larger than that of an alkanoylsilane **1** to realize energy transfer from a triplet-excited state of PS (^{3}PS*) to the ground state of the alkanoylsilane **1**. With these requirements, the triplet-excited state of the alkanoylsilane **1** (^{3}**1***) can be generated without the formation of its singlet-excited-state, and generation of the corresponding siloxycarbene **2** will be realized efficiently. By using this strategy, undesired reactions from singlet-excited state of alkanoylsilanes **1** can be eliminated.



Scheme 4. Generation of siloxycarbenes from alkanoylsilanes by visible-light-induced energy transfer (this work)

With this in mind, we tried to find an appropriate photosensitizer by using an alkanoylsilane **1c** as a model substrate. To estimate efficiency of siloxycarbene formation, ethanol was employed as a carbene trapping reagent because the reaction of photochemically-generated siloxycarbenes with alcohols have been known to be facile (Table 1).[5] At first, photo-irradiation was conducted with a 500W super-high-pressure Hg lamp through a 365 nm band pass filter in the absence of photosensitizers (direct photo-excitation condition). An acetal **7** was obtained in good yield, which confirmed that the siloxycarbene actually reacted with ethanol smoothly (entry 1). On the other hand, no reaction occurred with photoirradiation through a 436 nm band pass filter, indicating that the formation of siloxycarbene from **1c** did not proceed at all under these conditions (entry 2). Then, we examined reactions with various photosensitizers under 436 nm photo-irradiation conditions and found that the use of 2 mol% of an iridium catalyst **8** afforded the desired acetal **7** in quantitative yield (entry 3).[14] Since the triplet energies of the Ir complex **8** and the alkanoylsilane **1c** are almost same (**8**: 60.8 kcal/mol[15], **1c**: 60.6 kcal/mol[16]), this result suggested that expected triplet energy transfer proceeded efficiently.

Table 1. Examination of photosensitizers by using ethanol as a siloxycarbene-trapping reagent



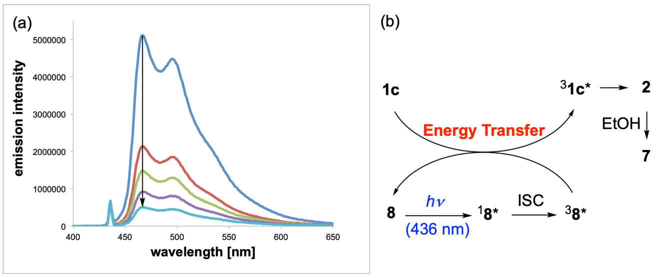
[Ir{dF(CF_3)ppy}$_2$(dtbpy)]PF_6 (**8**)

entry	Conditions	Time	Yield of 7 [%][a]
1	hν (365 nm)	1 h	65
2	hν (436 nm)	5 h	-
3	hν (436 nm) + **8** (2 mol%)	1 h	quant

[a] Determined by ^{1}H-NMR analysis.

To confirm the energy transfer between a triplet-excited state of **8** (^{3}**8***) and a ground state of **1c**, quenching experiments were conducted by measuring luminescence spectra of **8** under various concentration of the alkanoylsilane **1c**. As shown in Scheme 5a, the emission intensity decreased with increasing the concentration of alkanoylsilane **1c**. These data indicated that the triplet-excited state of **8** (^{3}**8***) was quenched by **1c** through triplet energy transfer.[17]

A plausible mechanism of this reaction is described in Scheme 5b. The Ir complex **8** is photo-excited under visible-light irradiation conditions and the resulting singlet-excited state of **8** (^{1}**8***) is smoothly converted to its triplet-excited state (^{3}**8***) by intersystem crossing. Then, energy transfer from ^{3}**8*** to the ground state of **1c** occurs to give a triplet-excited state of **1c** (^{3}**1c***). ^{3}**1c*** undergoes a 1,2-silyl migration to generate siloxycarbene **2**,[18] which reacts with ethanol to afford the acetal **7**.



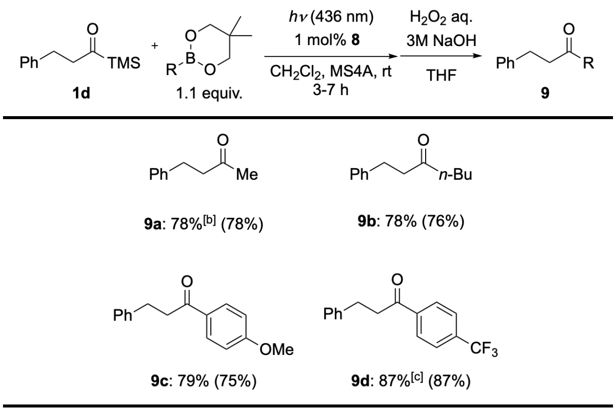
Conditions : CH_2Cl_2, 20 °C, excited at 436 nm, [**8**] = 36.5 μM
[**1c**] : ▬ 0 mM, ▬ 4.95 mM, ▬ 10.3 mM, ▬ 19.9 mM, ▬ 39.2 mM

Scheme 5. (a) Quenching experiment of the Ir complex **8** under various concentration of **1c** (b) Plausible reaction mechanism

With the energy transfer conditions in hands, we then turned our attention into applicability of this methodology to the carbon-carbon bond-forming reactions using boronic esters or aldehydes. We first examined the reactions of alkanoylsilane **1d** without a reactive γ-hydrogen with boronic esters (Table 2). Gratifyingly, visible-light-irradiation to mixtures of alkanoylsilane **1d** and various boronic esters in the presence of 1 mol% of the Ir complex **8** afforded the desired coupling products, which could be converted to the corresponding ketones **9a-d**. Yields of the products **9a-d** were comparable to those obtained under direct photo-excitation conditions with UV light.[7a]

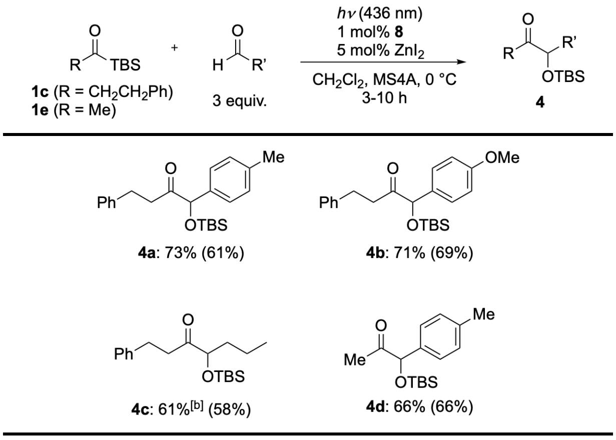
This methodology was also applicable to the reactions with aldehydes (Table 3). Visible-light-irradiation to mixtures of alkanoylsilanes **1** and aldehydes in the presence of 1 mol% of the Ir complex **8** and 5 mol% of zinc iodide afforded the desired α-siloxyketones **4a-d** in good yields. Again, yields of the products **4a-d** were comparable to those obtained under direct photo-excitation conditions.[7b]

Table 2. Application to the coupling reaction with boronic esters[a]



[a] Isolated yields. Yields in the parentheses are those obtained under direct photo-excitation conditions. (see ref. 7a) [b] 2 equiv. of boronic ester were employed. [c] The crude material of photochemical reaction was treated with 1M HCl aq. under air.

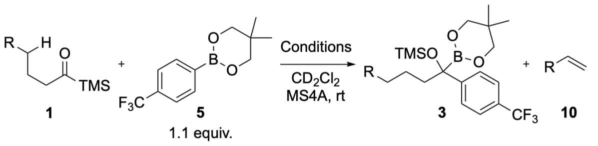
Table 3. Application to the coupling reaction with aldehydes[a]



[a] Isolated yields. Yields in the parentheses are those obtained under direct photo-excitation conditions. (see ref. 7b) [b] 5 equiv. of butyraldehyde were employed.

Thus, the energy transfer methodology could be successfully applied to the reactions of the alkanoylsilanes **1c-e** with boronic esters or aldehydes. Then, we tried to suppress the serious side reaction in the reaction of 4-phenylbutanoylsilane **1a**. As described in the beginning, the reaction of **1a** with the boronic ester **5** under UV-irradiation conditions afforded styrene as a byproduct through Norrish type II fragmentation (Scheme 2). But, under the triplet sensitization conditions, formation of styrene was significantly suppressed and the yield of the desired coupling product **3a** was improved to 83% yield (Table 4, entry1).

Table 4. Coupling reactions with alkanoylsilanes bearing weak C-H bonds at the γ position

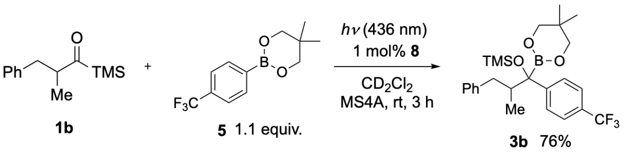


entry	R	Conditions[a]	Time [h]	Yield of **3** [%][b]	Yield of **10** [%][b]
1	Ph (**1a**)	B	4.5	83 (**3a**)	7
2	OBn (**1f**)	A	4	33 (**3c**)	19
3	OBn (**1f**)	B	4	87 (**3c**)	N.D.
4	vinyl (**1g**)	A	2	11 (**3d**)	23
5	vinyl (**1g**)	B	5	73 (**3d**)	trace

[a] A: $h\nu$ (365 nm), B: $h\nu$ (436 nm) + 1 mol% **8** [b] Yields were determined by ^{1}H-NMR analysis.

This kind of improvement was also observed with other alkanoylsilanes bearing a reactive γ-hydrogen. UV-irradiation to alkanoylsilanes bearing a benzyloxy or a vinyl group at γ-position (**1f** or **1g**) in the presence of boronic ester **5** resulted in complex mixtures including fragmentation products **10**, and the yields of the desired coupling products **3c** and **3d** were quite low (entries 2 and 4). In contrast, under triplet sensitization conditions, formation of the fragmentation products **10** was almost completely suppressed in both cases, and the yields of the coupling products **3c** and **3d** were dramatically improved to 87 and 73%, respectively (entries 3 and 5). These results indicated that Norrish type II fragmentation of alkanoylsilanes mainly proceeded from the singlet-excited states and, from the triplet-excited states, isomerization to siloxycarbenes was much faster than the fragmentation reaction.

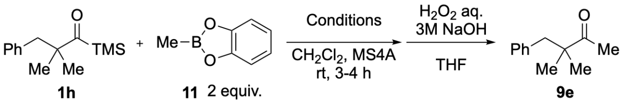
Then, we turned our attention to the reactions of the α-branched alkanoylsilane **1b**. As already mentioned in Scheme 3, direct photoexcitation of **1b** with UV-light afforded the decarbonylated compound **6** as a major product through Norrish type I fragmentation. With this substrate, the energy transfer conditions again worked nicely, and the desired coupling product **3b** was obtained in 76% yield without accompanying the decarbonylated product **6** (Scheme 6). Thus, Norrish type I fragmentation of **1b** took place from its singlet-excited state, and the triplet sensitization methodology completely eliminated this undesired process. To our knowledge, this is the first successful C-C coupling reaction of photochemically-generated siloxycarbenes derived from a *sec*-alkyl silyl ketone.



The yield was determined by ^{1}H-NMR analysis.

Scheme 6. Coupling reaction between α-branched acylsilane **1b** and boronic ester **5** under triplet sensitization conditions

This methodology could be also applied to the reaction of α-tertiary alkanoylsilane **1h**, which was highly susceptible to Norrish I fragmentation. The desired coupling reaction between **1h** and a boronic ester **11** proceeded well under triplet sensitization conditions, while the same reaction under direct photo-excitation conditions gave a poor result (Scheme 7).[19] Thus, triplet sensitization methodology efficiently suppressed Norrish type fragmentation reactions of alkanoylsilanes, thereby enhancing the synthetic utility of alkanoylsilanes as siloxycarbene precursors.

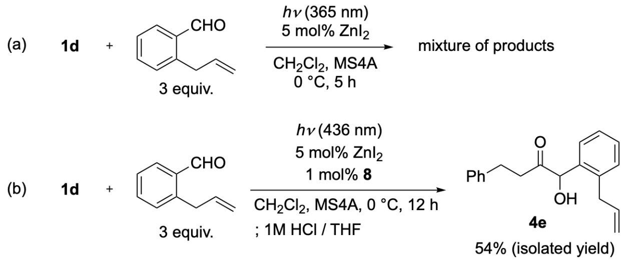


Conditions	Yield of **9e**[a]
$h\nu$ (365 nm)	8%
$h\nu$ (436 nm) + 1 mol% **8**	69%

[a] Isolated yield.

Scheme 7. Coupling reaction between *tert*-alkyl silyl ketone **1h** and boronic ester **11**

From a synthetic point of view, visible light-induced energy transfer process has another merit that can be utilized for the reaction with UV-labile compounds. For example, UV-irradiation (365 nm) to a mixture of alkanoylsilane **1d** and 2-allylbenzaldehyde in the presence of 5 mol% of zinc iodide resulted in complex mixture (Scheme 8a). In this case, formation of 2-(1-propenyl)benzaldehydes was observed. This means photo-enolization[20] of 2-allylbenzaldehyde by γ-hydrogen abstraction took place because this aldehyde also absorbed UV-light. But the triplet sensitization conditions promoted the desired coupling reaction, giving an α-hydroxyketone **4e** in good yield without accompanying isomerization of 2-allylbenzaldehyde (Scheme 8b). Considering the triplet energies of substrates (alkanoylsilanes : ca. 60 kcal/mol, aromatic aldehydes : ca. 70 kcal/mol[21]), this result is attributed to chemoselective energy transfer from the triplet-excited state of **8** to the ground state of **1d**.



Scheme 8. Photochemical reactions with **1d** and 2-allylbenzaldehyde

In summary, we have realized the generation of siloxycarbenes from various kinds of alkanoylsilanes by visible-light-induced energy transfer[13], and this methodology was successfully applied to the C-C coupling reactions with boronic esters or aldehydes. Noteworthy is that Norrish type fragmentations of alkanoylsilanes were clarified to proceed mainly from singlet-excited states and these undesired reactions were significantly suppressed by triplet sensitization. We believe that the present results clearly show the synthetic utility of alkanoylsilanes as siloxycarbene precursors.

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Keywords: acylsilanes • energy transfer • photochemistry • siloxycarbenes • triplet sensitizer

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[13] Quite recently, triplet sensitization to alkanoylsilanes was reported by Glorius *et al.* See: J.-H. Ye, L. Quach, T. Paulisch, F. Glorius, *J. Am. Chem. Soc.* **2019**, *141*, 16227-16231. But no information on Norrish type reactions was available in this report. We independently studied the triplet energy transfer methodology and its synthetic applications. We have reported the present work in 14th International Kyoto Conference on Organic Chemistry (IKCOC14), November 13th, 2018.

[14] For details of the examination, see SI.

[15] M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, Jr., G. G. Malliaras, S. Bernhard, *Chem. Mater.* **2005**, *17*, 5712-5719.

[16] The triplet energy of alkanoylsilane **1c** was determined by measuring a phosphorescence spectrum (See SI).

[17] Single electron transfer (SET) reactions between a triplet-excited state of Ir complex **8** (^{3}**8***) and a ground state of alkanoylsilane **1c** are thermodynamically disfavored according to their redox potentials (**1c**: E_{Red} = -1.13 V, E_{Ox} = + 1.66 V (see SI); ^{3}**8***: $E_{Ir(III)*/Ir(IV)}$ = -0.89 V, $E_{Ir(III)*/Ir(II)}$ = +1.21 V (see ref. 1c) (vs SCE)). Therefore, the decrease of emission intensity of Ir complex **8** is attributed to energy transfer. For redox chemistry of acylsilanes, see: L. Capaldo, R. Riccardi, D. Ravelli, M. Fagnoni, *ACS Catal.* **2018**, *8*, 304-309.

[18] Initially generated siloxycarbene is triplet, but this must be readily converted to its singlet state and then reacts with ethanol because ground state of siloxycarbene is singlet.

[19] Reactions of **1h** with other boronic esters such as **5** were unsuccessful even under triplet sensitization conditions probably due to the bulky *tert*-alkyl substituent. The use of less sterically hindered catecholate was important.

[20] a) K. C. Nicolaou, D. L. F. Gray, J. Tae, *J. Am. Chem. Soc.* **2004**, *126*, 613-627; b) B. Grosch, C. N. Orlebar, E. Herdtweck, M. Kaneda, T. Wada, Y. Inoue, T. Bach, *Chem. Eur. J.* **2004**, *10*, 2179-2189.

[21] M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi*, HANDBOOK OF PHOTOCHEMISTRY THIRD EDITION*, CRC Press, Boca Raton, FL, **2006**.

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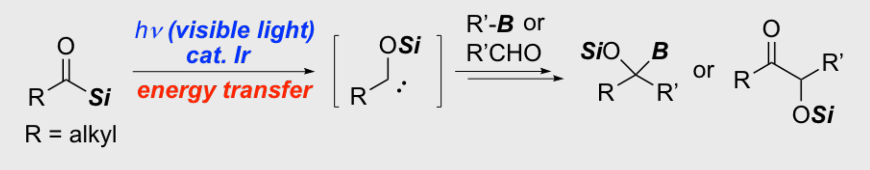

Enhancement of the utility of alkanoylsilanes: Generation of siloxycarbenes from alkanoylsilanes by triplet energy transfer was examined by using an Ir complex and was successfully applied to C-C coupling reactions with boronates or aldehydes. This methodology efficiently suppressed undesired Norrish-type fragmentation reactions and broaden synthetic utility of alkanoylsilanes.

*K. Ishida, H. Yamazaki, C. Hagiwara, M. Abe, H. Kusama**

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Efficient Generation and Synthetic Applications of Alkyl-Substituted Siloxycarbenes: Suppression of Norrish-type Fragmentations of Alkanoylsilanes by Triplet Energy Transfer