

# Chemical Science

Volume 15  
Number 13  
7 April 2024  
Pages 4605–5038

rsc.li/chemical-science



ISSN 2041-6539

**EDGE ARTICLE**

Terumasa Kato, Yan Liu, Keiji Maruoka *et al.*  
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Cite this: *Chem. Sci.*, 2024, 15, 4757

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 21st December 2023

Accepted 21st February 2024

DOI: 10.1039/d3sc06857a

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# Synthetic utility of functionalized alkylsilyl peroxides for Fe-catalyzed and visible-light-promoted radical transformation†

Jiahao Liu,<sup>ab</sup> Shiyong Liu,<sup>ab</sup> Zhe Wang,<sup>ab</sup> Terumasa Kato,<sup>\*abc</sup> Yan Liu<sup>ID</sup><sup>\*ab</sup> and Keiji Maruoka<sup>ID</sup><sup>\*abc</sup>

$\alpha$ -Keto-,  $\beta$ -acetoxy- and  $\beta$ -amidoalkylsilyl peroxides are prepared from various precursors and utilized for Fe-catalyzed and visible-light-promoted radical functionalization with coupling partners under mild conditions with a broad substrate scope.

## Introduction

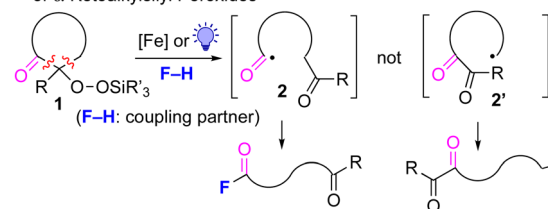
The generation of unstabilized, reactive alkyl radicals from appropriate organic precursors under mild conditions is very important and challenging in modern radical chemistry.<sup>1</sup> One of the most reliable approaches to generate such alkyl radicals is the  $\beta$ -scission of alkoxy radicals, which are generally prepared from the corresponding alkanols under strongly oxidative conditions.<sup>2</sup> However, due to the use of strong oxidants in this method, the choice of substrates is limited by the functional group tolerance and reaction conditions. Recently, the photocatalyzed generation of alkoxy radicals has also been reported with limited success.<sup>3</sup> In this context, we have recently reported the successful generation of alkyl radicals from alkylsilyl peroxides<sup>4</sup> under mildly reductive conditions (reductive  $\beta$ -scission strategy) using Cu, Fe or Ni catalysts; the *in situ*-generated alkyl radicals were then reacted with various coupling partners to furnish new C(sp<sup>3</sup>)-N,<sup>5</sup> C(sp<sup>3</sup>)-C(sp),<sup>6</sup> C(sp<sup>3</sup>)-B,<sup>7</sup> C(sp<sup>3</sup>)-Si,<sup>7</sup> C(sp<sup>3</sup>)-O,<sup>8</sup> C(sp<sup>3</sup>)-C(sp<sup>2</sup>),<sup>9</sup> and C(sp<sup>3</sup>)-C(sp<sup>3</sup>)<sup>10</sup> bonds.<sup>11</sup> Thus far, we have developed this radical chemistry using alkylsilyl peroxides without any functional groups. However, if various functional groups could be introduced into the carbon skeletons of the alkylsilyl peroxides, this radical chemistry would be further enhanced to a synthetically more useful level. In this work,  $\alpha$ -keto-substituted alkylsilyl peroxides of type 1 are prepared, and transformed into the more-stable acyl radicals 2,<sup>12,13</sup> rather than the alkyl radicals 2' using the reductive  $\beta$ -scission strategy (Fig. 1a). In a similar manner,  $\beta$ -acetoxy- and  $\beta$ -

amido-substituted alkylsilyl peroxides of types 3 and 5 are utilized for the generation of  $\alpha$ -acetoxyalkyl and  $\alpha$ -amidoalkyl radicals 4 and 6, respectively (Fig. 1b and c).<sup>14,15</sup> These functionalized carbon radicals, thus generated, are then utilized for subsequent transformation with various types of coupling partners (F-H), thereby providing more synthetically valuable products.

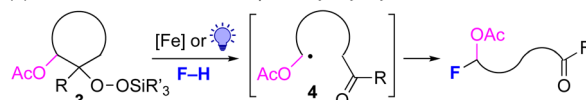
## Results and discussion

$\alpha$ -Ketoalkylsilyl peroxide 1a was conveniently prepared from 2-methylcyclohexanone *via* an initial hydroperoxylation and subsequent trimethylsilylation using a literature procedure (see ESI†). First, based on our previously reported conjugate addition–cyclization sequence,<sup>16,17</sup> reaction of  $\alpha$ -ketoalkylsilyl

(a) Fe-Catalyzed and Visible-Light Promoted Functionalization of  $\alpha$ -Ketoalkylsilyl Peroxides



(b) Radical Functionalization of  $\beta$ -Alkoxyalkylsilyl Peroxides



(c) Radical Functionalization of  $\beta$ -Amidoalkylsilyl Peroxides

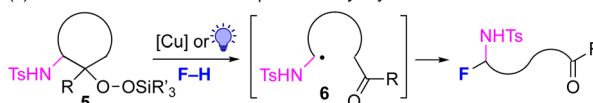


Fig. 1 Transformation of  $\alpha$ -ketoalkylsilyl peroxides 1 and  $\beta$ -acetoxyalkyl and  $\beta$ -amidoalkyl peroxides 3 and 5 for metal-catalyzed and visible-light-promoted functionalization.

<sup>a</sup>School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China. E-mail: terumasa.kato.j97@kyoto-u.jp; yanliu@gdut.edu.cn; maruoka.keiji.4w@kyoto-u.ac.jp

<sup>b</sup>Guangdong Provincial Key Laboratory of Plant Resources Biorefinery, Guangdong University of Technology, Guangzhou 510006, China

<sup>c</sup>Graduate School of Pharmaceutical Sciences, Kyoto University, Sakyo, Kyoto 606-8501, Japan

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3sc06857a>



peroxide **1a** as an alkyl radical source was carried out with methacrylamide **7** as a coupling partner. Thus, the reaction of  $\alpha$ -ketoalkylsilyl peroxide **1a** (1.2 equiv.) with methacrylamide **7** in dioxane in the presence of 20 mol% each of CuI and 1,10-phenanthroline (1,10-phen) at 80 °C for 4 h gave rise to desired conjugate addition–cyclization product **8a** exclusively in 11% yield (entry 1 in Table 1). The use of more-Lewis-acidic Cu(MeCN)<sub>4</sub>BF<sub>4</sub> under similar conditions afforded **8a** in slightly higher yield (entry 2). Replacing the Cu catalysts with Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O catalyst exhibited a similar low reactivity (entry 3). Interestingly, the addition of Fe catalysts such as FeCl<sub>2</sub> and Fe(acac)<sub>2</sub> enhanced the yield of **8a** to 42–53% yield (entries 4 and 5), although the use of FeCl<sub>3</sub> gave less satisfactory results (entry 6). Finally, the use of Fe(acac)<sub>3</sub> catalyst under similar conditions exhibited good yield (entry 7). Having identified Fe(acac)<sub>3</sub> as a suitable catalyst, the solvent effect was then examined. The use of DMSO solvent at low temperature afforded product **8a** in higher yield (69%) than MeCN, DCE, or benzene (entry 12 vs. 8–11). Furthermore, 95% of **8a** was obtained by using excess **1a** (2 equiv.) (entry 13). For more details of the reaction optimization, see Tables S1 and S2 in the ESI.†

With the optimized conditions for the Fe(acac)<sub>3</sub>-catalyzed conjugate addition–cyclization sequence of **1a** in hand, we subsequently examined the substrate scope of the Fe(acac)<sub>3</sub>-catalyzed radical functionalization of various  $\alpha$ -ketoalkylsilyl peroxides **1a–m** as shown in Table 2. Thus, the Fe(acac)<sub>3</sub>-

Table 1 Optimization of the synthesis of **8a** from  $\alpha$ -ketoalkylsilyl peroxide **1a** and **7**<sup>a</sup>

Entry	Metal catalyst	Solvent	Temp. (°C)	Yield <sup>b</sup> (%)
1	CuI	Dioxane	80	11
2	Cu(MeCN) <sub>4</sub> BF <sub>4</sub>	Dioxane	80	19
3	Ni(OAc) <sub>2</sub> ·4H <sub>2</sub> O	Dioxane	80	18
4	FeCl <sub>2</sub>	Dioxane	80	42
5	Fe(acac) <sub>2</sub>	Dioxane	80	53
6	FeCl <sub>3</sub>	Dioxane	80	28
7	Fe(acac) <sub>3</sub>	Dioxane	80	59
8	Fe(acac) <sub>3</sub>	MeCN	80	50
9	Fe(acac) <sub>3</sub>	DCE	80	42
10	Fe(acac) <sub>3</sub>	Benzene	80	50
11	Fe(acac) <sub>3</sub>	DMSO	80	65
12	Fe(acac) <sub>3</sub>	DMSO	40	69
13 <sup>c</sup>	Fe(acac) <sub>3</sub>	DMSO	40	95 <sup>d</sup>

<sup>a</sup> The reactions of **7** (0.2 mmol) and **1a** (0.24 mmol) were carried out in the presence of metal catalyst (0.04 mmol) and 1,10-phen ligand (0.04 mmol) in solvent (1 mL) at the indicated temperature for 4 h. <sup>b</sup> The yield of **8a** was determined by <sup>1</sup>H NMR spectroscopy using nitromethane as an internal standard. <sup>c</sup> **1a** (2.0 equiv.). <sup>d</sup> Isolated yield of **8a**.

Table 2 Substrate scope of the selective functionalization of various  $\alpha$ -ketoalkylsilyl peroxides **1** with methacrylamide **7**<sup>a</sup>

Entry	$\alpha$ -Ketoalkylsilyl peroxide <b>1</b>	Product <b>8</b>	Yield <sup>b</sup> (%)
1	<b>1b</b> ( <i>n</i> = 1)	<b>8b</b>	77
2	<b>1a</b> ( <i>n</i> = 2)	<b>8a</b>	95
3	<b>1c</b> ( <i>n</i> = 3)	<b>8c</b>	90
4	<b>1d</b> ( <i>n</i> = 4)	<b>8d</b>	84
5	<b>1e</b>	<b>8e</b>	65
6	<b>1f</b> (R = H)	<b>8f</b>	89
7	<b>1g</b> (R = Me)	<b>8g</b>	20 (15) <sup>c</sup>
8	<b>1g</b> (R = Me)	<b>8g</b>	57 <sup>d</sup> (40) <sup>c,d</sup>
9	<b>1h</b>	<b>8h</b>	18 (0) <sup>c</sup>
10			37 <sup>e</sup> (43) <sup>c,e</sup>
11	<b>1i</b>	<b>8i</b>	46 (99) <sup>e</sup>
12	<b>1j</b>	<b>8i</b>	52 (86) <sup>e</sup>
13	<b>1k</b>	<b>8k</b>	73
14	<b>1m</b>	<b>8m</b>	0 (27) <sup>f</sup>
	<b>9g</b>	<b>9h</b>	

<sup>a</sup> Unless otherwise specified, the reactions were carried out in the presence of **1** (0.4 mmol), **7** (0.2 mmol), Fe(acac)<sub>3</sub> catalyst (0.04 mmol), 1,10-phen ligand (0.04 mmol) in DMSO (1 mL) at 40 °C for 4 h. <sup>b</sup> Isolated yield. <sup>c</sup> The yield of decarbonylation product **9g** or **9h**. <sup>d</sup> For 24 h. <sup>e</sup> For 12 h. <sup>f</sup> At 80 °C for 16 h.



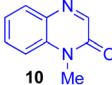
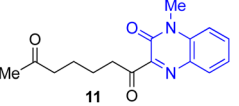

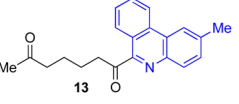
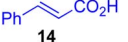
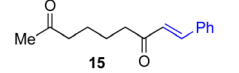
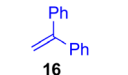
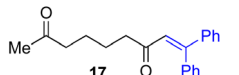
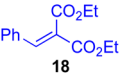
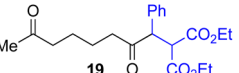
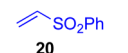
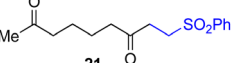
catalyzed reaction of 5–8-membered  $\alpha$ -ketoalkylsilyl peroxides **1a–d** with methacrylamide **7** furnished conjugate addition–cyclization products **8a–d** in high-to-excellent yield (entries 1–4). In a similar manner, aromatic-substituted  $\alpha$ -ketoalkylsilyl peroxide **1e** reacted with methacrylamide **7** to give product **8e** in good yield (entry 5). Acyclic  $\alpha$ -ketoalkylsilyl peroxide **1f** also worked well (entry 6), but decarbonylation of the intermediary acyl radical took place in the case of the more-substituted substrate **1g** to furnish a mixture of **8g** and decarbonylated **9g** in 20% and 15% yields, respectively (entry 7). Longer reaction time (24 h) enhanced the product yield of **8g** (entry 8). Similarly, facile decarbonylation was observed with more-substituted substrate **1h** (entries 9 and 10). Furthermore, the separate treatment of the diastereomers **1i** and **1j** of *L*-menthone-derived  $\alpha$ -ketoalkylsilyl peroxides with methacrylamide **7** afforded the same coupling product **8i** in high yield (entries 11 and 12). Ethyl-substituted **1k** afforded the corresponding ethyl ketone **8k**

in good yield (entry 13), though phenyl-substituted **1m** provided phenyl ketone **8m** in low yield (entry 14).

Next, we examined the substrate scope of various coupling partners (F–H) with  $\alpha$ -ketoalkylsilyl peroxide **1a**, as shown in Table 3. The Fe(acac)<sub>3</sub>-catalyzed reaction of  $\alpha$ -ketoalkylsilyl peroxide **1a** with 1-methylquinoxalin-2(1*H*)-one **10** furnished addition–rearomatization product **11** in high yield (entry 1). Although treatment of **1a** with 2-isocyano-5-methyl-1,1'-biphenyl **12** gave addition–cyclization product **13** in very low yield under the standard conditions, the use of DMF in place of DMSO afforded **13** in high yield (entry 2). In a similar manner, while the initial reaction of **1a** with cinnamic acid **14** provided the decarboxylated coupling product **15** in low yield, the use of excess **14** without the ligand 1,10-phen under otherwise similar conditions afforded **15** in good yield (entry 3). The reaction of **1a** with 1,1-diphenylethylene **16** under the standard condition also gave poor results, but the FeSO<sub>4</sub>·7H<sub>2</sub>O-catalyzed reaction in DMF at 80 °C with excess **16** (3.0 equiv.) afforded **17** in good yield (entry 4). Furthermore, treatment of **1a** with diethyl 2-benzylidenemalonate **18** produced the conjugate addition product **19** in moderate yield (entry 5).

By taking advantage of the generation of reactive acyl chloride intermediate **22** in a practical manner, several synthetically useful transformations were accomplished in a highly efficient manner, as shown in Fig. 2. Thus, treatment of the intermediary 6-oxoheptanoyl chloride (**22**) with BnNH<sub>2</sub>/NEt<sub>3</sub> or BnOH/DMAP afforded the corresponding amide **23** and ester **24**, respectively, in excellent yields. Even a one-mmol-scale experiment using **1a** afforded **23** in 84% yield. Friedel–Crafts acylation of **22** afforded the desired phenyl ketone **25** in moderate yield. These results demonstrate that our strategy is highly versatile due to the high synthetic utility of the acyl chloride intermediates **22**. A control experiment for the conjugate addition–cyclization reaction with **7** was carried out to obtain insight into the reaction mechanism: the results supported the hypothesized generation of acyl radical intermediates. Specifically, when the reaction of  $\alpha$ -

Table 3 Substrate scope of various coupling partners with  $\alpha$ -ketoalkylsilyl peroxide **1a**<sup>a</sup>

Entry	Coupling partner (F–H)	Product	Yield <sup>b</sup> (%)
1			91
2			9 (78) <sup>c</sup>
3			19 (56) <sup>c,d,e</sup>
4			<5 <sup>f</sup> (66) <sup>d,g,h,i</sup>
5			0 (43) <sup>d,g,h,j</sup>
6			<5 <sup>h</sup> (34) <sup>d,g,h</sup>

<sup>a</sup> Unless otherwise specified, the reactions were carried out in the presence of **1a** (0.4 mmol), coupling partner (0.2 mmol), Fe(acac)<sub>3</sub> (0.04 mmol), 1,10-phen (0.04 mmol) in DMSO (1 mL) at 40 °C for 4 h under argon atmosphere. <sup>b</sup> Isolated yield. <sup>c</sup> In DMF. <sup>d</sup> 1,10-Phen ligand was not used. <sup>e</sup> Use of **14** (5 equiv.) at 80 °C for 24 h. <sup>f</sup> NMR yield using nitromethane as an internal standard. <sup>g</sup> FeSO<sub>4</sub>·7H<sub>2</sub>O was used instead of Fe(acac)<sub>3</sub>. <sup>h</sup> In DMF at 80 °C. <sup>i</sup> Use of **1a** (0.2 mmol) and **16** (3.0 equiv.). <sup>j</sup> Use of **1a** (0.2 mmol) and **18** (2.0 equiv.).

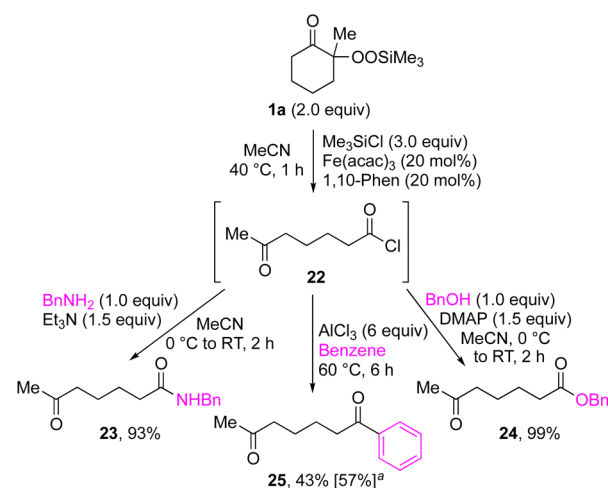


Fig. 2 Synthetic transformations of acyl chloride **22** derived from **1a**. <sup>a</sup> Generation of **22** with Me<sub>3</sub>SiCl (3.0 equiv.), Fe(acac)<sub>3</sub> (1 mol%), 1,10-phen (1 mol%) in CH<sub>2</sub>Cl<sub>2</sub> at 40 °C for 1 h.



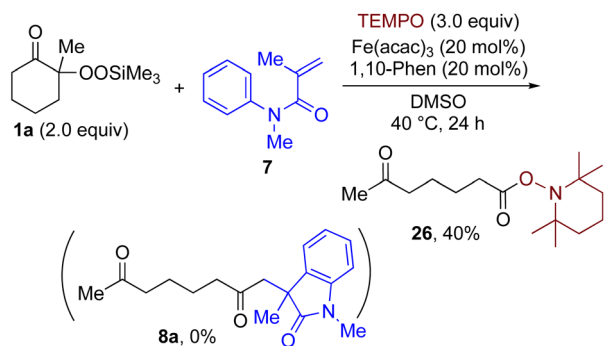


Fig. 3 Radical trapping experiment of **1a** with TEMPO.

ketoalkylsilyl peroxide **1a** and methacrylamide **7** with 20 mol% each of  $\text{Fe}(\text{acac})_3$  and 1,10-phen in DMSO was conducted at 40 °C for 24 h in the presence of a radical scavenger (2,2,6,6-tetramethylpiperidin-1-yl)oxy, TEMPO, the conjugate addition–cyclization reaction was significantly inhibited, and the acyl radical/TEMPO adduct **26** was obtained in 40% NMR yield (Fig. 3). This observation provides evidence that the *in situ*-generated acyl radical is most likely involved in this sequential transformation.

Based on our experimental results, a plausible reaction mechanism has been proposed for the  $\text{Fe}(\text{acac})_3$ -catalyzed conjugate addition–cyclization sequence of methacrylamide **9** with **1a** (Fig. 4). The use of  $\text{Fe}(\text{II})$  salts such as  $\text{FeCl}_2$ ,  $\text{Fe}(\text{acac})_2$ , and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  provided good to better results in the radical cleavage reaction of **1a** (entries 4 and 5 in Table 1; entries 4–6 in Table 3).<sup>16</sup> Thus, 1,10-phen-coordinated  $\text{Fe}(\text{II})$  species would cleave the O–O bond of **1a** *via* single-electron transfer (SET) process, leading to alkoxy radical **27** and trimethylsilanoxide. Oxy radical **27** then easily undergoes  $\beta$ -scission to generate the functionalized acyl radical **28**. This acyl radical **28** subsequently

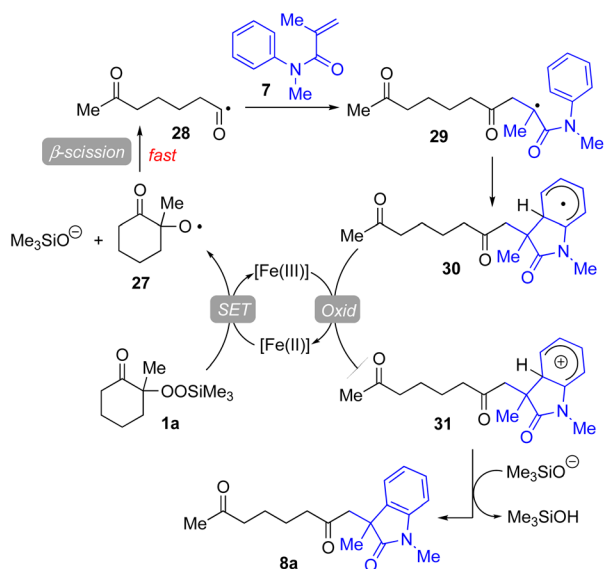


Fig. 4 Proposed reaction mechanism for  $\text{Fe}$ -catalyzed reaction of **1a** with **7**.

reacts with **7** to afford the intermediary carbon radical **29**, which further adds to the benzene ring to furnish the radical intermediate **30**. This radical is then oxidized by the  $\text{Fe}(\text{III})$  catalyst to give the corresponding carbocation species **31**, which is deprotonated by trimethylsilanoxide to afford the final product **8a**.

Attempted reactions of  $\beta$ -acetoxyalkylsilyl peroxides **32** with various coupling partners such as **7**, **10**, **12**, **16** and **20** resulted in producing none or very low yields of desired coupling products. In contrast, the choice of  $\text{Me}_3\text{SiN}_3$  as coupling partner gave the corresponding coupling product **33** in 85% yield (Fig. 5). In addition,  $\text{Fe}$ -catalyzed reactions of  $\beta$ -amidoalkylsilyl peroxides **34** with various coupling partners afforded none of desired coupling products. However, the  $\text{Cu}$ -catalyzed reaction of **34** with  $\text{Me}_3\text{SiCN}$  as coupling partner gave the corresponding coupling product **35** in 88% yield.

This approach is also applicable to our recently developed visible-light-promoted alkylation of electron-deficient alkenes with alkylsilyl peroxides.<sup>18</sup> Treatment of  $\alpha$ -ketoalkylsilyl peroxide **1a** with phenyl vinyl sulfone (**20**) and an equimolar

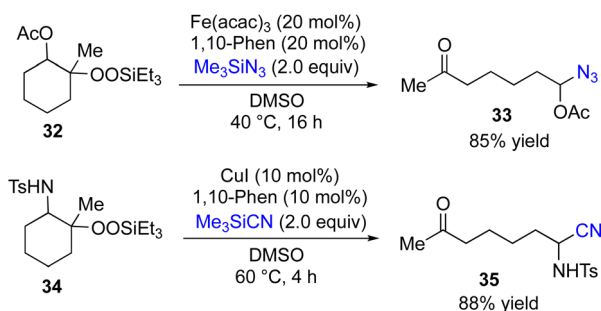


Fig. 5 Metal-catalyzed reactions of  $\beta$ -acetoxy, and  $\beta$ -amidoalkylsilyl peroxides.

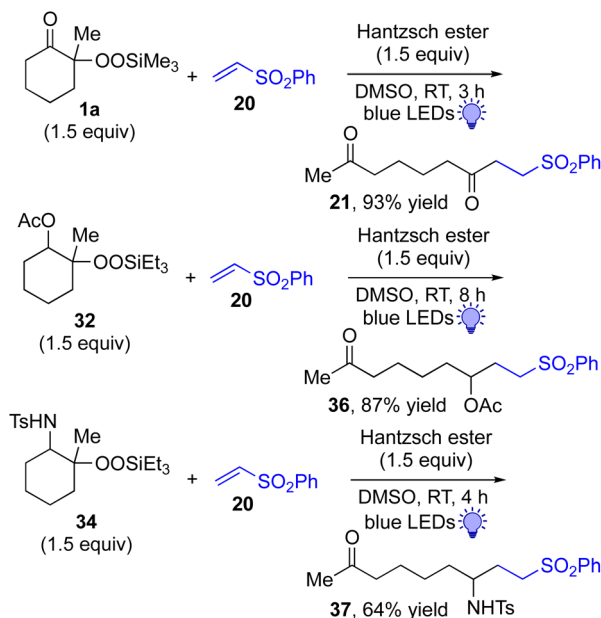


Fig. 6 Visible light-promoted reaction of  $\alpha$ -keto,  $\beta$ -acetoxy, and  $\beta$ -amidoalkylsilyl peroxides.



amount of Hantzsch ester in DMSO under blue light irradiation at room temperature for 3 h afforded the desired conjugate addition product **21** in 93% yield (Fig. 6). This approach can be further expanded to the visible-light-promoted alkylation of other functionalized alkylsilyl peroxides. For example, the reaction of  $\beta$ -acetoxy- and  $\beta$ -amidoalkylsilyl peroxides **32** and **34** (1.5 equiv.) with phenyl vinyl sulfone (**20**) and Hantzsch ester (1.5 equiv.) in DMSO under blue light irradiation at room temperature for 4–8 h gave rise to conjugate adducts **36** and **37**, respectively, in 87% and 64% yields (Fig. 6).<sup>19</sup>

## Conclusions

In summary, we have developed an Fe-catalyzed and visible-light-promoted radical transformations for functionalized alkylsilyl peroxides, such as  $\alpha$ -keto-,  $\beta$ -acetoxy-, and  $\beta$ -amidoalkylsilyl peroxides with several coupling partners under mild conditions and with a broad substrate scope. The synthetic utility of our approach is demonstrated by the facile generation of reactive acyl chloride intermediates, which can be easily transformed to the corresponding amides, esters, and phenyl ketones. A mechanistic study suggested the participation of intermediary acyl,  $\alpha$ -acetoxyalkyl, and  $\alpha$ -amidoalkyl radical species in the radical-promoted coupling reactions.

## Data availability

The datasets supporting this article have been uploaded as part of the ESI.†

## Author contributions

K. M. conceptualized the research. J. L. and S. L. performed the experiments. T. K. and K. M. prepared the manuscript and the ESI.† Z. W. and Y. L. edited the ESI.† K. M. supervised the project and edited the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21977019, 22101053, 22050410279, 22250710134) and JSPS KAKENHI Grant JP21H05026 and JP23H04910.

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