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可见光促进烯基硅化合物有氧氧化-叠氮化反应

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摘要 发展了一种在温和的反应条件下, 利用可见光促进烯基硅化合物与叠氮三甲基硅烷的有氧叠氮化反应合成 α-叠氮酮化合物的方法. 该方法可以放大到克级规模制备, 并且一系列自由基源, 如三氟甲基自由基、硫氰基自由基、溴自由基、氯自由基也能够有效地参与反应.

关键词 可见光催化; 有氧氧化; 烯基硅化合物; 叠氮化合物

Visible Light-Promoted Aerobic Oxo-azidation of Alkenyl Silanes

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Abstract A visible-light-enabled method for the synthesis of α-azidoketones has been developed via oxo-azidation of alkenyl silanes with trimethylsilylazide and molecular oxygen under mild conditions. The reaction could be carried out in gram scale. Various radical sources, including trifluoromethyl radical, thiocyanate radical, bromide radical, chlorine radical could participate effectively instead of azide radical in the reaction.

Keywords visible light catalysis; aerobic oxidation; alkenyl silanes; organic azides

1 Introduction

Organic azides are valuable intermediates in organic synthesis and as a result various methods have been developed for their synthesis.[1] Traditionally, α-azidoketones are prepared by direct nucleophilic substitution of α-halo ketone with azide ions.[2] Alternative methods are based on the reaction of an alkene or enol ether with an oxidizing agent in the presence of an azide source (Scheme 1).[3] However, most of these methods still require a large excess of expensive and hazardous oxidants, which would increase cost and environmental concerns, and limit their practical utility. From a green and sustainable points of view, the direct utilization of O_2 as both oxidant and oxygen source represents an ideal methodology for the construction of oxygen-containing compounds. In 2018, Yang and co-workers[4] reported a facile visible-light enabled method for the construction of α-azidoketones via metal-free Rose Bengal and $(PhSe)_2$ co-catalyzed oxyazidation of styrene with molecular oxygen. In 2021, Zhang and co-workers[5] reported an electrochemical synthetic route to access α-azido ketones from styrene with molecular oxygen. Although these two methods are relatively mild, the reaction substrates primarily focus on styrene derivatives and do not extend to alkyl-substituted olefins. Therefore, the development of a simple, efficient, and environmentally friendly method for the construction of various α-azidoketones is still highly desirable.

Alkenyl silanes are highly attractive intermediates due to their versatility in organic synthesis and materials science.[6] Since the presence of 3d empty orbitals of silicon atoms has the α-effect on stable α-C radical, alkenyl silanes can be regarded as effective radical acceptor.[7] In 1993, Isoe and co-workers[8] reported an electron-promoted aerobic oxythiolation of alkenyl silanes with PhSH to deliver the α-phenylthiol ketone. In 2003, Oshima and co-workers[9] reported that an Et_3B-promoted radical addition followed aerobic oxidation of alkenyl silanes with

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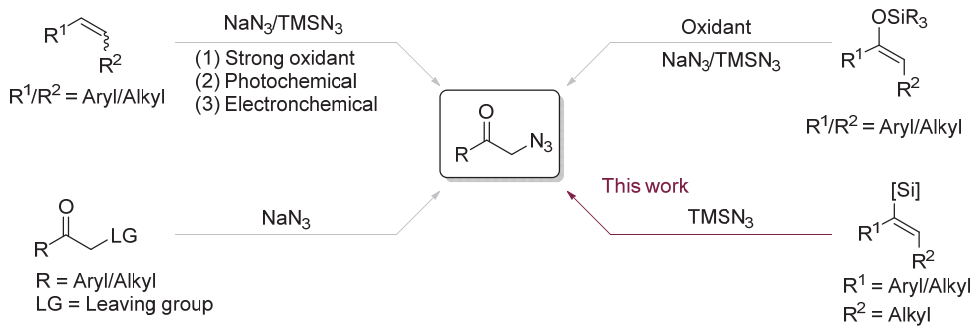


Scheme 1 Preparation methods of carbonyl azide compounds

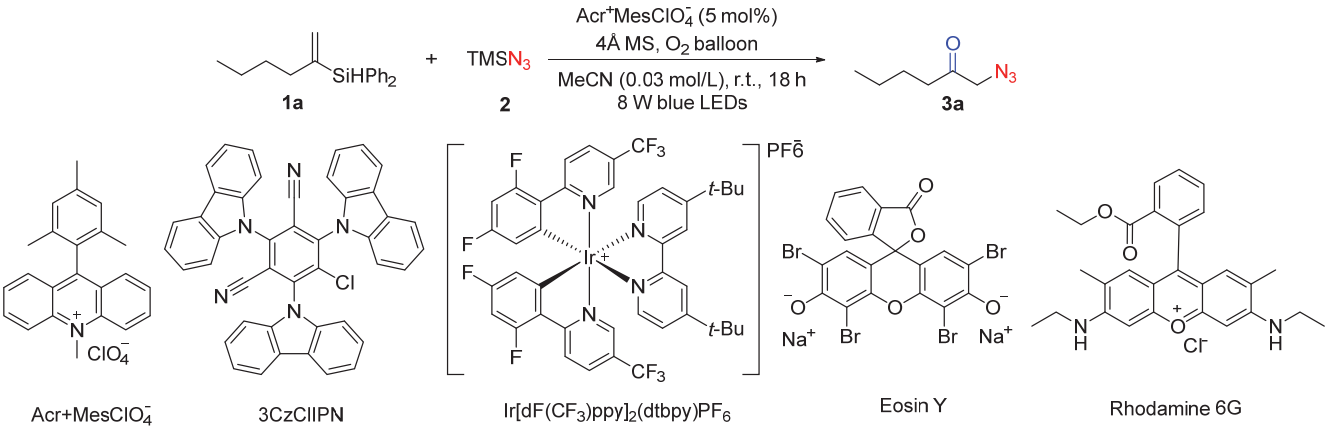
alkyl iodides to afford ketones. Although the oxygenation of alkenyl silanes to obtain the corresponding *α*-phenylthio carbonyl compounds and ketones has been reported, using alkenyl silanes as substrates to construct C—N bond has not been reported. Based on our previous efforts in the construction of the C—N bond and aerobic oxidation reactions,[10] herein, we report a visible light-promoted aerobic oxidation of alkenyl silanes with $TMSN_3$ to afford *α*-azidoketones.

2 Results and discussion

At the beginning of our study, hex-1-en-2-yldiphenylsilane (**1a**) was used as a model substrate, $TMSN_3$ as a nitrogen source, $Acr^+MesClO_4^-$ as a photocatalyst and MeCN as a solvent under the irradiation of 8 W blue LEDs for 18 h in the presence of an O_2 balloon. Initially, the reaction was conducted, delivering the final product in 71% yield (Table 1, Entry 1). However, screening a series of photocatalysts, the reactions afforded **3a** in 13%～53% yields (Entries 2～5). After the optimization of the solvents, no better results were obtained (Entries 6～8). The yield was slightly reduced to 63% when the loading of $Acr^+MesClO_4^-$ was decreased to 2 mol% (Entry 9). Although the yield of **3a** was increased to 80% with 10 mol% $Acr^+MesClO_4^-$, 5 mol% $Acr^+MesClO_4^-$ was chosen to further extend the application of this reaction (Entry 10).

Under the optimized conditions, the substrate scope was explored as shown in Table 2. The linear aliphatic vinyl-

Table 1 Variation of reaction conditions [a]

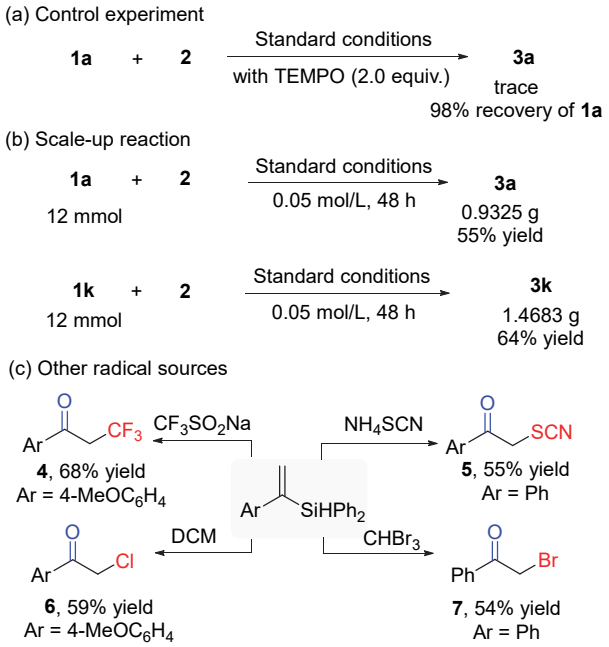


Entry	Variation from the standard conditions	Yield[b]/%
1	None	71 (63)
2	3CzClIPN as photocatalyst	53
3	$Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ as photocatalyst	32
4	Eosin Y as photocatalyst	13
5	Rhodamine 6G as photocatalyst	36
6	DCM as solvent	17
7	THF as solvent	0
8	DMF as solvent	0
9	2 mol% $Acr^+MesClO_4^-$	63
10	10 mol% $Acr^+MesClO_4^-$	80

[a] Reaction conditions: **1a** (0.3 mmol), **2** (2.0 equiv.), $Acr^+MesClO_4^-$ (5 mol%) in MeCN (0.03 mol/L) and irradiation with 8 W blue LEDs under the atmosphere of oxygen at room temperature for 18 h. [b] Yields were determined by ^1H NMR with TMSPh as an internal standard, and isolated yield was in the parenthesis.

silanes could be reacted to afford **3a**～**3e** in 50%～72% yields. (1-Cyclohexylvinyl)diphenylsilane could be converted to the desired products **3f** in 54% yield. It is worth noting that internal vinylsilanes could react smoothly to deliver the products **3g**～**3h** in 51%～54% yields. The diphenyl(1-phenylvinyl)silane with a methyl group on *para*-, *ortho*-positions could be tolerated giving the corresponding products **3i**～**3j** in 38%～42% yields. The methoxy group at *para*-position on aryl rings displayed moderate reactivity to afford the targeted products **3k** in 54% yield. Moreover, the reactions of disubstituted styryl silanes and heterocyclic silanes bearing 3-chloro-4-methylphenyl, 3-thienyl and benzo[*b*]thiophen-5-yl could react with $TMSN_3$ smoothly to produce the products **3l**～**3n** in 37%～46% yields. The substrate containing bioactive molecule such as niflumic acid **3o** could be also successfully accommodated, further demonstrating the utility of the approach. Furthermore, the various silane groups, such as dimethylphenyl silyl and diphenylmethyl silyl were found to be suitable for this transformation.

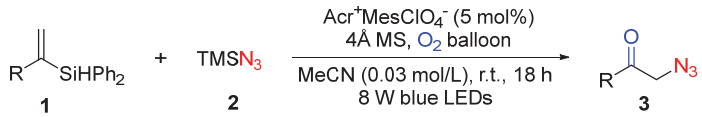
The reaction in the presence of 2,2,6,6-tetramethylpiperidinooxy (TEMPO) afforded a trace amount of **3a** with 98% recovery of **1a** (Scheme 2a), which indicated that the reaction likely proceeds through a radical process. In addition, to further explore the scalability of this protocol, the gram-scale reactions were conducted by reacting **1a** and **1k** with **2** to afford targeted compounds in 55% and 64% yields (Scheme 2b), respectively. To explore the diversity of the reaction types, various radical sources, including trifluoromethyl radical, thiocyanate radical, bromide radical, chlorine radical, participated well in the reaction, affording the carbonyl compounds **4**～**7** in 54%～68% yields (Scheme 2c).

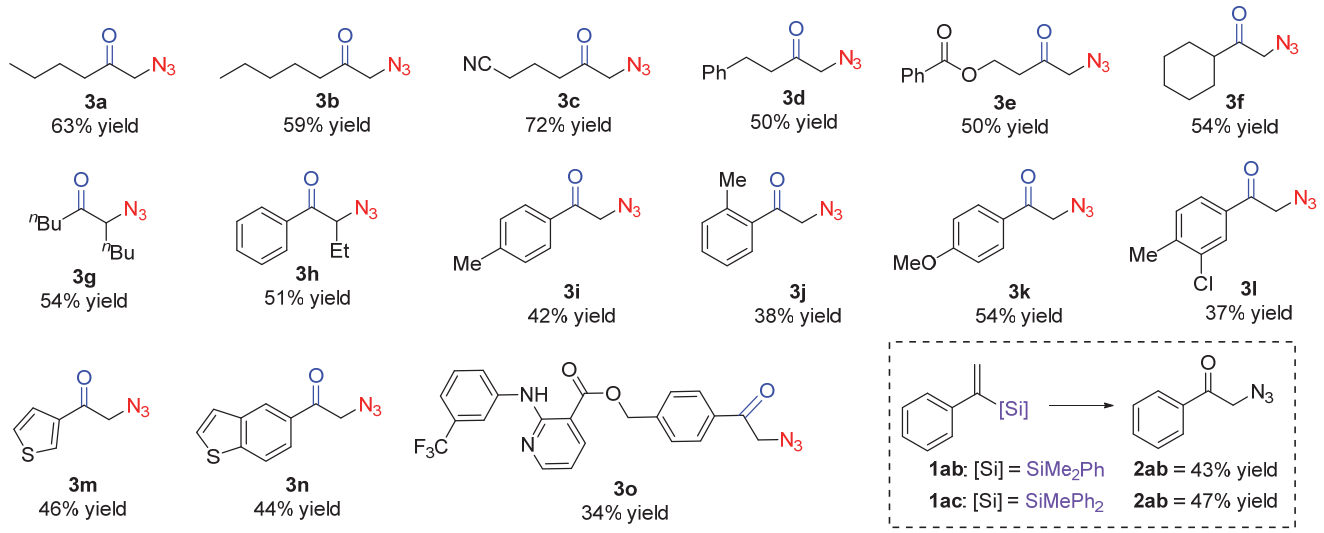


Scheme 2 The control experiment and synthetic applications

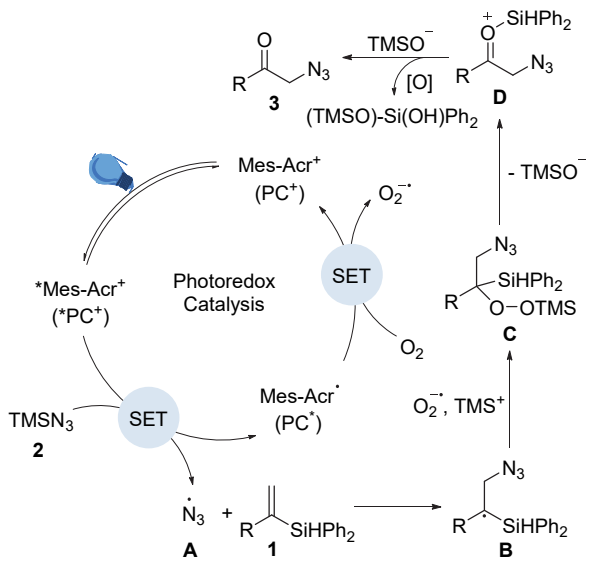
The plausible mechanisms for this transformation are proposed in Scheme 3. The photosensitizer (PC^+) absorbs visible light under the irradiation of 8W blue LEDs to generate its excited state ($^*PC^+$) which could oxidize $TMSN_3$ **2** to the azido radical **A**, which is then trapped by alkenyl silanes **1** to form **B** and the reduced species (PC^*).[11] Sub-

Table 2 Substrate scope[a]





[a] Reaction conditions: alkenyl silanes (0.3 mmol), $TMSN_3$ (2.0 equiv.), Acr^+ $MesClO_4^-$ (5 mol%) and 4 Å MS (w=100% based on **1**) in MeCN (0.03 mol/L) and irradiation with 8 W blue LEDs under the atmosphere of oxygen at room temperature for 18 h. Isolated yields were given.



Scheme 3 Proposed mechanism

sequently, PC^* could be oxidized by dioxygen to provide superoxide and regenerate the photocatalyst (PC^+). The radical **B** which then reacts with superoxide and TMS^+ to afford the peroxide **C**. Then peroxide **C** is then eventually converted into the carbonyl product through migration of the silyl group to the internal oxygen atom. Finally, desiliconization of intermediate **D** produces the desired product **3**.[12]

3 Conclusions

In summary, a convenient method for the construction of *α*-azidoketones has been developed. The conditions are mild, and a variety of alkenyl silanes participate efficiently in the reaction. The reaction could be easily carried out in gram scale. A variety of radical sources, including trifluoromethyl radical, thiocyanate radical, bromide radical, chlorine radical, were all effectively applicable in the sustainable reaction system. The products are easily derivatized further. Current efforts in our laboratory are underway to explore various reactions of alkenyl silanes.

4 Experimental section

4.1 General Information

MeCN, *N*,*N*-dimethylformamide (DMF), and CH_2Cl_2 were distilled from CaH_2 prior to use. 8 W blue LEDs were used as light source. The $Acr^+MesClO_4^-$ was prepared according to the literature.[13] NMR spectra were recorded on a Bruker-400 instrument or a Wuhan Zhongke-NiuJin-400 instrument. ^1H NMR chemical shifts were referenced to tetramethylsilane signal (δ 0). ^{13}C NMR chemical shifts were referenced to the solvent resonance (δ 77.00, $CDCl_3$). IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. High-resolution mass spectra (HRMS) were recorded on a Waters XEVOG2-S ESI-TOF mass spectrometer. Melting points were obtained using a WRR melting point apparatus (Laboratory Devices, Shanghai Precision & Scientific Instrument Co., Ltd.).

4.2 Procedure for the synthesis of starting materials

The synthesis of **1a**～**1o** was according to the previously reported method.[6a-6b]

4-(1-(Diphenylsilyl)vinyl)benzyl 2-((3-(trifluoromethyl)phenyl)amino)nicotinate (**1o**): White solid, m.p. 91.6～94.7 ℃ [*V*(petroleum ether, PE)∶*V*(ethyl acetate, EA)=10∶1]. ^1H NMR (400 MHz, $CDCl_3$) δ: 10.33 (s, 1H), 8.40 (dd, J=4.4, 1.6 Hz, 1H), 8.28 (dd, J=8.0, 2.0 Hz, 1H), 8.08 (s, 1H), 7.86 (d, J=8.0 Hz, 1H), 7.60～7.53 (m, 4H), 7.45～7.31 (m, 11H), 7.29～7.26 (m, 1H), 6.76 (dd, J=4.8, 2.8 Hz, 1H), 6.30 (d, J=1.2 Hz, 1H), 5.71 (d, J=2.4 Hz, 1H), 5.39 (s, 1H), 5.32 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.2, 155.8, 153.1, 145.4, 143.3, 140.34, 140.28, 135.7, 134.1, 132.8, 132.7, 131.1 (q, J_{C-F}=32.1 Hz), 129.9, 129.2, 128.4, 128.1, 127.0, 124.1 (q, J_{C-F}=272.7 Hz), 123.5, 119.0 (q, J_{C-F}=3.9 Hz), 117.1 (q, J_{C-F}=3.9 Hz), 114.1, 107.4, 66.8; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ: −62.6; IR (neat) ν: 2129, 1691, 1611, 1586, 1529 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{28}F_3N_2O_2Si$ ($M+H^+$) 581.1867, found 581.1865.

4.3 General procedure for the synthesis of *α*-azido ketones

To a 25 mL overdried Schlenk flask with magnetic stirrer were added **1** (0.3 mmol, 1.0 equiv.), $Acr^+MesClO_4^-$ (6.2 mg, 0.015 mmol, 5 mol%), 4 Å MS (w=100% based on **1**). Then, the tube was evacuated and backfilled with oxygen. Subsequently, **2** (80 μL, 2.0 equiv.) and dry MeCN (10 mL) were added by syringes. The reaction mixture was stirred under the irradiation of 8 W blue LEDs for 18 h. After that the reaction was quenched by petroleum ether, filtered through a short pad of silica and eluted with ethyl acetate. The combined filtrate was concentrated under reduced pressure and purified by flash column chromatography to afford the corresponding products **3a**～**3o** and **2ab**.

1-Azidohexan-2-one (**3a**): Colorless oil (26.7 mg, 63% yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 3.94 (s, 2H), 2.45 (t, J=7.6 Hz, 2H), 1.65～1.56 (m, 2H), 1.39～1.28 (m, 2H), 0.92 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.6, 57.4, 39.8, 25.5, 22.2, 13.7; IR (neat) ν: 2961, 2102, 1726, 1416, 1281 cm^{-1}; HRMS (ESI) calcd for $C_6H_{11}N_3NaO$ $(M+Na)^+$ 164.0794, found 164.0794.

1-Azidoheptan-2-one (**3b**):[14] Colorless oil (27.5 mg, 59% yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 3.93 (s, 2H), 2.44 (t, J=7.2 Hz, 2H), 1.67～1.59 (m, 2H), 1.36～1.27 (m, 4H), 0.90 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.6, 57.4, 40.0, 31.2, 23.1, 22.3, 13.8.

6-Azido-5-oxohexanenitrile (**3c**): Colorless oil (32.9 mg, 72% yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 3.99 (s, J=6.8 Hz, 2H), 2.67 (t, J=6.8 Hz, 2H), 2.47 (t, J=6.8 Hz, 2H), 2.04～1.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.8, 118.9, 57.4, 37.7, 18.8, 16.4; IR (neat) ν: 2918, 2105, 1728, 1419, 1277 cm^{-1}; HRMS (ESI) calcd for $C_6H_8N_4NaO$ $(M+Na)^+$ 175.0590, found 175.0588.

1-Azido-4-phenylbutan-2-one (**3d**):[14] Colorless oil (28.4 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32～7.26 (m, 2H), 7.24～7.15 (m, 3H), 3.86 (s, 2H), 2.95 (t, J=7.2 Hz, 2H), 2.76 (t, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 203.6, 140.2, 128.6, 128.3, 126.4, 57.6, 41.6, 29.4.

4-Azido-3-oxobutyl benzoate (**3e**): Colorless oil (35.0 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, J=7.6 Hz, 2H), 7.57 (t, J=7.2 Hz, 1H), 7.44 (t, J=8.0 Hz, 2H), 4.63 (t, J=6.0 Hz, 2H), 4.03 (s, 2H), 2.94 (t, J=6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.6, 166.3, 133.2, 129.64, 129.59, 128.4, 59.3, 57.8, 39.2; IR (neat) v: 3002, 2105, 1719, 1602, 1454 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{11}N_3NaO_3$ $(M+Na)^+$ 256.0693, found 256.0694.

2-Azido-1-cyclohexylethan-1-one (**3f**):[15] Colorless oil (27.1 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.99 (s, 2H), 2.45～2.37 (m, 1H), 1.87～1.77 (m, 4H), 1.72～1.64 (m, 1H), 1.45～1.17 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.2, 55.8, 48.3, 28.2, 25.6, 25.4.

6-Azidodecan-5-one (**3g**): Colorless oil (32.0 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.78 (dd, J=8.4, 4.8 Hz, 1H), 2.54～2.48 (m, 2H), 1.82～1.74 (m, 1H), 1.71～1.63 (m, 1H), 1.62～1.55 (m, 3H), 1.43～1.29 (m, 5H), 0.95～0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.8, 68.1, 39.3, 30.5, 27.9, 25.4, 22.3, 22.2, 13.8; IR (neat) v: 2959, 2875, 2100, 1722, 1605, 1453 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{19}N_3NaO$ $(M+Na)^+$ 220.1420, found 220.1419.

2-Azido-1-phenylbutan-1-one (**3h**):[14] Colorless oil (28.3 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, J=6.8 Hz, 2H), 7.62 (t, J=7.6 Hz, 1H), 7.50 (t, J=8.0 Hz, 2H), 4.54 (dd, J=8.4, 4.8 Hz, 1H), 2.06～1.95 (m, 1H), 1.93～1.82 (m, 1H), 1.08 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.7, 134.8, 133.9, 128.9, 128.5, 64.5, 24.8, 10.6.

2-Azido-1-(*p*-tolyl)ethan-1-one (**3i**):[4] White solid (22.1 mg, 42% yield), m.p. 60.7～62.7 ℃ ($CDCl_3$) (lit.[20] 60～61 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, J=8.4 Hz, 2H), 7.30 (d, J=8.0 Hz, 2H), 4.54 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz) δ: 192.8, 145.2, 131.9, 129.6, 128.0, 54.7, 21.7.

2-Azido-1-(*o*-tolyl)ethan-1-one (**3j**):[4] Colorless oil (20.0 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, J=7.6 Hz, 1H), 7.45 (t, J=7.6 Hz, 1H), 7.33～7.27 (m, 2H), 4.45 (s, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.3, 139.5, 134.3, 132.53, 132.49, 128.3, 125.9, 56.4, 21.5.

2-Azido-1-(4-methoxyphenyl)ethan-1-one (**3k**):[4] White solid (31.0 mg, 54% yield), m.p. 72.8～73.5 ℃ ($CDCl_3$) (lit.[20] 69～70 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, J=8.8 Hz, 2H), 6.96 (d, J=8.8 Hz, 2H), 4.51 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.6, 164.2, 130.3, 127.3, 114.1, 55.5, 54.5.

2-Azido-1-(3-chloro-4-methylphenyl)ethan-1-one (**3l**): White solid (23.8 mg, 37% yield), m.p. 78.7～80.1 ℃ (DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J=1.2 Hz, 1H), 7.69 (dd, J=8.0,1.6 Hz, 1H), 7.36 (d, J=8.0 Hz, 1H), 4.52 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.8, 143.0, 135.3, 133.5, 131.4, 128.6, 126.0, 54.8, 20.5; IR (neat) v: 2112, 1685, 1602, 1446, 1220 cm^{-1}; HRMS (ESI) calcd for $C_9H_8ClN_3NaO$ $(M+Na)^+$ 232.0248, found 232.0249.

2-Azido-1-(thiophen-3-yl)ethan-1-one (**3m**):[16] Colorless oil (23.1 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (s, 1H), 7.55 (d, J=4.0 Hz, 1H), 7.41～7.37 (m, 1H), 4.44 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.6, 139.0, 132.7, 127.1, 126.5, 55.4.

2-Azido-1-(benzo[*b*]thiophen-5-yl)ethan-1-one (**3n**): Colorless oil (28.7 mg, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (d, J=1.2 Hz, 1H), 7.97 (d, J=8.8 Hz, 1H), 7.88 (dd, J=8.4, 1.2 Hz, 1H), 7.57 (d, J=5.6 Hz, 1H), 7.45 (d, J=5.6 Hz, 1H), 4.65 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.0, 145.2, 139.4, 130.8, 128.4, 124.5, 123.9, 123.0, 122.8, 54.9; IR (neat) v: 2917, 2105, 1686, 1592, 1425 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_7N_3NaOS$ $(M+Na)^+$ 240.0202, found 240.0204.

4-(2-Azidoacetyl)benzyl 2-((3-(trifluoromethyl)phenyl)-amino)nicotinate (**3o**): Colorless oil (46.4 mg, 34% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.27 (s, 1H), 8.43 (dd, J=4.4,1.6 Hz, 1H), 8.32 (dd, J=8.0, 6.0 Hz, 1H), 8.06 (s, 1H), 7.95 (d, J=8.4 Hz, 2H), 7.87 (d, J=8.4 Hz, 1H), 7.57 (d, J=8.4 Hz, 2H), 7.43 (t, J=8.0 Hz, 1H), 7.29 (d, J=7.6 Hz, 1H), 6.81 (dd, J=7.6, 4.8 Hz, 1H), 5.44 (s, 2H), 4.56 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.7, 167.0, 155.8, 153.5, 141.8, 140.2, 140.1, 134.2, 131.0 (q, J_{C-F}=32.2 Hz), 129.7, 128.3, 128.2, 124.1 (q, J_{C-F}=273.0 Hz), 123.6, 119.1 (q, J_{C-F}=3.7 Hz), 117.1 (q, J_{C-F}=3.7 Hz), 114.1, 106.8, 86.0, 54.8; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ: −62.6; IR (neat) v: 2104, 1692, 1584, 1529, 1445 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{17}F_3N_5O_3$ $(M+H)^+$ 456.1278, found 456.1276.

2-Azido-1-phenylethan-1-one (**2ab**):[4] Colorless oil (20.8 mg, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, J=7.60 Hz, 2H), 7.63 (t, J=7.60 Hz, 1H), 7.51 (t, J=7.60 Hz, 2H), 4.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.2, 134.4, 134.1, 129.0, 127.9, 54.9.

4.4 Control experiment

Prepared according to the general procedure. To a 25 mL overdried Schlenk flask with magnetic stirrer was added **1a** (0.3 mmol, 80.1 mg), $Acr^+MesClO_4^-$ (6.2 mg, 0.015 mmol, 5 mol%), 4 Å MS (79.5 mg), and TEMPO (93.8 mg, 2 equiv.). Then, the tube was evacuated and backfilled with oxygen. Subsequently, **2** (80 μL, 2.0 equiv.) and dry MeCN (10 mL) were added by syringes. After 18 h, the reaction mixture was worked up, 2% yield of **3a** was monitored by ^{1}H NMR analysis.

4.5 Scale-up experiment

Prepared according to the general procedure. To a 500 mL overdried three-necked flask with a magnetic stirrer was added **1a** (3.1977 g, 12 mmol, 1.0 equiv.), $Acr^+MesClO_4^-$ (0.2477 g, 0.015 mmol, 5 mol%), 4 Å MS (3.2005 g). Then, the three-necked flask was evacuated and backfilled with oxygen. Subsequently, $TMSN_3$ (3.15 mL,

2.0 equiv.) and dry MeCN (240.0 mL) was added by syringes. The reaction mixture was stirred under the irradiation of 8 W blue LEDs for 48 h. After that the reaction was quenched by petroleum ether, filtered through a short pad of silica and eluted with ethyl acetate. The combined filtrate was concentrated under reduced pressure and purified by flash column chromatography [V(PE)∶V(EA)=10∶1] to afford 932.5 mg of **3a** with Colorless oil.

Prepared according to the general procedure. To a 500 mL overdried three-necked flask with a magnetic stirrer was added **1k** (3.7910 g, 12 mmol, 1.0 equiv.), Acr^+ $MesClO_4^-$ (0.2482 g, 0.015 mmol, 5 mol%), 4 Å MS (3.802 g). Then, the three-necked flask was evacuated and backfilled with oxygen. Subsequently, $TMSN_3$ (3.15 mL, 2.0 equiv.) and dry MeCN (240.0 mL) was added by syringes. The reaction mixture was stirred under the irradiation of 8 W blue LEDs for 48 h. After that the reaction was quenched by petroleum ether, filtered through a short pad of silica and eluted with ethyl acetate. The combined filtrate was concentrated under reduced pressure and purified by flash column chromatography [V(PE)∶V(EA)=10∶1] to afford 1.4683 g of **3k** with white solid.

4.6 Synthesis of 3,3,3-trifluoro-1-(4-methoxyphenyl)-propan-1-one (**4**)

To a 25 mL overdried Schlenk flask with a magnetic stirrer were added **1k** (0.3 mmol, 94.7 mg), Acr^+-$MesClO_4^-$ (6.2 mg, 0.015 mmol, 5 mol%), 4 Å MS (94.4 mg), and CF_3SO_2Na (187.7 mg, 4.0 equiv.). Then, the tube was evacuated and backfilled with oxygen. Subsequentl dry MeCN (10 mL) was added by syringes. Then reaction mixture was stirred under the irradiation of 8 W blue LEDs for 18 h. After that the reaction was quenched by petroleum ether, filtered through a short pad of silica and eluted with ethyl acetate. The combined filtrate was concentrated under reduced pressure and purified by flash column chromatography to afford the corresponding product. The combined filtrate was concentrated under reduced pressure and purified by flash column chromatography [V(PE)∶V(EA)=10∶1] to afford 3,3,3-trifluoro-1-(4-methoxyphenyl)propan-1-one (**4**):[17] Colorless oil (44.5 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, J=9.2 Hz, 2H), 6.97 (d, J=8.8 Hz, 2H), 3.89 (s, 3H), 3.74 (q, J=10.0 Hz, 2H); ^{19}F NMR: (376.5 MHz, $CDCl_3$) δ: −61.9; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.1 (q, J=2.2 Hz), 164.3, 130.8, 128.9, 125.5 (t, J=277.7 Hz), 114.1, 55.6, 41.8 (q, J_{C-F}=28.1 Hz); ^{19}F NMR: (376.5 MHz, $CDCl_3$) δ: −61.9.

4.7 Synthesis of 1-phenyl-2-thiocyanatoethan-1-one (**5**)

To a 25 mL overdried Schlenk flask with a magnetic stirrer were added diphenyl(1-phenylvinyl)silane (0.3 mmol, 86.4 mg), Acr^+ $MesClO_4^-$ (6.1 mg, 0.015 mmol, 5 mol%), 4 Å MS (94.4 mg), and NH_4SCN (46.7 mg, 2.0 equiv.). Then, the tube was evacuated and backfilled with oxygen. Subsequently dry MeCN (10 mL) was added by syringes. Then reaction mixture was stirred under the irradiation of 8 W blue LEDs for 18 h. After that the reaction was quenched by petroleum ether, filtered through a short pad of silica and eluted with ethyl acetate. The combined filtrate was concentrated under reduced pressure and purified by flash column chromatography to afford the corresponding product. he combined filtrate was concentrated under reduced pressure and purified by flash column chromatography [V(PE)∶V(EA)=10∶1] to afford 1-phenyl-2-thiocyanatoethan-1-one (**5**):[18] White solid (29.1 mg, 55% yield), m.p. 72.5～73.1 ℃ ($CDCl_3$) (lit.[21] 67.9～70.1 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96～7.93 (m, 2H), 7.68 (t, J=7.2 Hz, 1H), 7.54 (t, J=8.0 Hz, 2H), 4.75 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.8, 134.8, 133.9, 129.2, 128.4, 111.8, 43.0.

4.8 Synthesis of 2-chloro-1-(4-methoxyphenyl)-ethan-one (**6**)

To a 25 mL overdried Schlenk flask with a magnetic stirrer were added **1k** (0.3 mmol, 94.7 mg), Acr^+-$MesClO_4^-$ (6.3 mg, 0.015 mmol, 5 mol%), 4 Å MS (97.3 mg). Then, the tube was evacuated and backfilled with oxygen. Subsequently dry MeOH (0.8 mL) and dry dichloromethane (DCM, 9.2 mL) were added by syringes. Then reaction mixture was stirred under the irradiation of 8 W blue LEDs for 18 h. After that the reaction was quenched by petroleum ether, filtered through a short pad of silica and eluted with ethyl acetate. The combined filtrate was concentrated under reduced pressure and purified by flash column chromatography to afford the corresponding product. The combined filtrate was concentrated under reduced pressure and purified by flash column chromatography [V(PE)∶V(EA)=10∶1] to afford 2-chloro-1-(4-methoxyphenyl)ethan-1-one (**6**):[19] White solid (32.6 mg, 59% yield), m.p. 101.6～102.9 ℃ ($CDCl_3$) (lit.[22] 98～100 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, J=9.2 Hz, 2H), 6.97 (d, J=8.8 Hz, 2H), 4.66 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 189.7, 164.2, 130.9, 127.2, 114.1, 55.6, 45.6.

4.9 Synthesis of 2-bromo-1-phenylethan-1-one (**7**)

To a 25 mL overdried Schlenk flask with magnetic stirrer were added diphenyl(1-phenylvinyl)silane (0.3 mmol, 86.0 mg), Acr^+ $MesClO_4^-$ (6.3 mg, 0.015 mmol, 5 mol%), 4 Å MS (86.1 mg). Then, the tube was evacuated and backfilled with oxygen. Subsequently $CHBr_3$ (0.8 mL) and dry MeOH (9.2 mL) were added by syringes. Then reaction mixture was stirred under the irradiation of 8 W blue LEDs for 18 h. After that the reaction was quenched by petroleum ether, filtered through a short pad of silica and eluted with ethyl acetate. The combined filtrate was concentrated under reduced pressure and purified by flash column chromatography to afford the corresponding product. The combined filtrate was concentrated under reduced pressure and purified by flash column chromatography [V(PE)∶V(EA)=10∶1] to afford 2-bromo-1-phen- ylethan-1-one (**7**): White solid (32.1 mg, 54% yield), m.p. 48.7～50.2 ℃ ($CDCl_3$) (lit.[23] 49.9～52.6 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (d, J=8.0 Hz, 2H), 7.61 (t, J=

7.6 Hz, 1H), 7.50 (t, J=7.6 Hz, 2H), 4.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.3, 133.9, 128.9, 128.8, 30.9.

Supporting Information ^{1}H NMR, ^{13}C NMR spectra for the synthesized compounds **1o**, **3a**～**3o**, **2ab** and **4**～**7**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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