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Visible-Light-Mediated Regioselective Allylation, Benzylation, and Silylation of Methylene-Malononitriles via Photoredox-Induced Radical Cation Fragmentation

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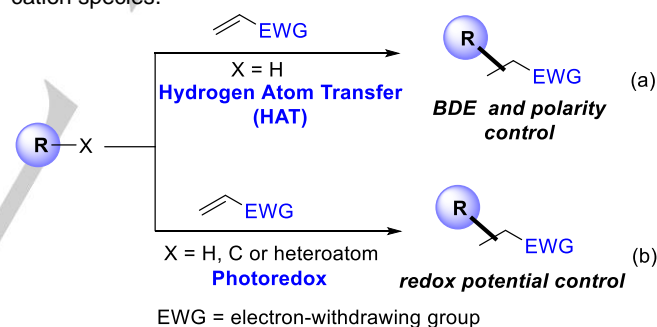
Abstract: Visible-light-mediated regioselective allylation, benzylation, and silylation of methylene-malononitriles using allylic/benzylic silane and disilane reagents have been developed, delivering the corresponding allylated, benzylated, and silylated products in moderate to excellent yields. These reactions proceed smoothly with exclusive regioselectivity by employing only an organo-photoredox catalyst under mild conditions. A photoredox-induced radical cation fragmentation is proposed for the generation of the key allylic, benzylic, and silyl radicals.

Introduction

The rapidly growing field of visible-light photocatalysis offers a valuable platform for the design and discovery of new synthetic transformations, enabling numerous new bond formations via open-shell radical species.^[1] In this context, the direct addition of photo-generated radicals to C=C bonds represents an attractive approach for the construction of C–C or C–heteroatom bonds.^[2] In general, the photo-induced generation of radicals for conjugate addition proceeds in two reaction modes: a) via hydrogen atom transfer (HAT); b) via photoredox process. The HAT process affords the radical species directly from C–H substrates through hydrogen atom abstraction, offering enormous opportunities for C–H activations. The efficiency of HAT is controlled by the relative bond dissociation energies (BDEs) and the polarity of the HAT catalyst and the substrates involved (Scheme 1, a).^[3] On the other hand, photoredox catalysis can generate radicals from both C–H and C–heteroatom substrates via either single electron oxidation or reduction, which is effectively controlled by the corresponding redox potentials of the photocatalyst and the substrates (Scheme 1, b).^[1,2] Over the past decade, significant developments have been made in both HAT and photoredox catalysis.

Radical cation species generated from photoredox catalysis have been frequently used in many important transformations.^[4] Radical cation can undergo fragmentation to directly afford

radicals for further transformations.^[5] Recently, we have developed a metal-free direct alkylation of allylic/benzylic sp³ C–H bonds via photoredox-catalyzed π -C–H⁺ type radical cation deprotonation.^[6] By employing 9-mesityl-10-methylacridinium perchlorate (Mes-Acr⁺ClO₄[−]), an organo-photoredox catalyst, a broad array of substrates including tetra-, tri-, and disubstituted alkenes and toluenes could serve as effective radical precursors to smoothly couple with electron deficient alkenes. However, efforts to extend this methodology to terminal alkenes and electron-poor toluenes were not successful, mainly due to the higher oxidative potentials associated with these substrates (e.g. $E_{1/2}^{ox} = +2.50$ V vs SCE in MeCN for 2-methylpent-1-ene).^[7] We envisioned that introducing an electroauxiliary group such as a trimethylsilyl (TMS) group to the allylic/benzylic substrates may significantly lower their oxidative potentials (e.g. $E_{1/2}^{ox} = +1.58$ V vs Ag/Ag⁺ in MeCN for allyltrimethylsilane).^[8g] This will thus enable an effective photoredox-induced single electron transfer (SET) to generate the radical cation, and the subsequent fragmentation will deliver a reactive carbon radical and a silyl cation species.



Scheme 1. Two modes of photo-induced generation of radicals for conjugate addition

Notably, the use of organosilicon compounds in photo-induced reactions such as allylation, benzylation, and silylation have been developed since the late 1980s.^[8] However, the reported examples required high catalyst loading (20–50 mol%), use of equipment-demanding UV light, or suffered from poor selectivity.^[8] Recently, Melchiorre and co-workers reported an elegant enantioselective catalytic β -alkylation of enals with alkyltrimethylsilanes under visible-light irradiation, through carbon radicals generation from organosilicon compounds under mild visible-light conditions.^[9] Moreover, Molander and coworkers have developed novel dual nickel/photoredox cross-couplings by use of a new class of hypercoordinate silicates, which acts as an effective radical precursor under visible-light photoredox catalysis.^[10] Inspired by these pioneering work and

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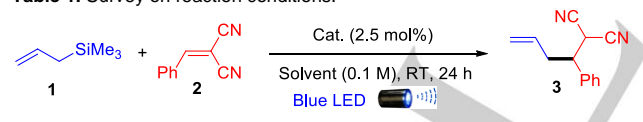
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also as our continuous interest on visible-light photocatalysis,^[11] we herein report visible-light-mediated allylation, benzylation, and silylation of methylene-malononitriles with allylsilanes, benzylsilanes, and disilanes by utilizing only an organo-photocatalyst via photoredox-induced σ -C-Si⁺ or σ -Si-Si⁺ type radical cation fragmentation.

Results and Discussion

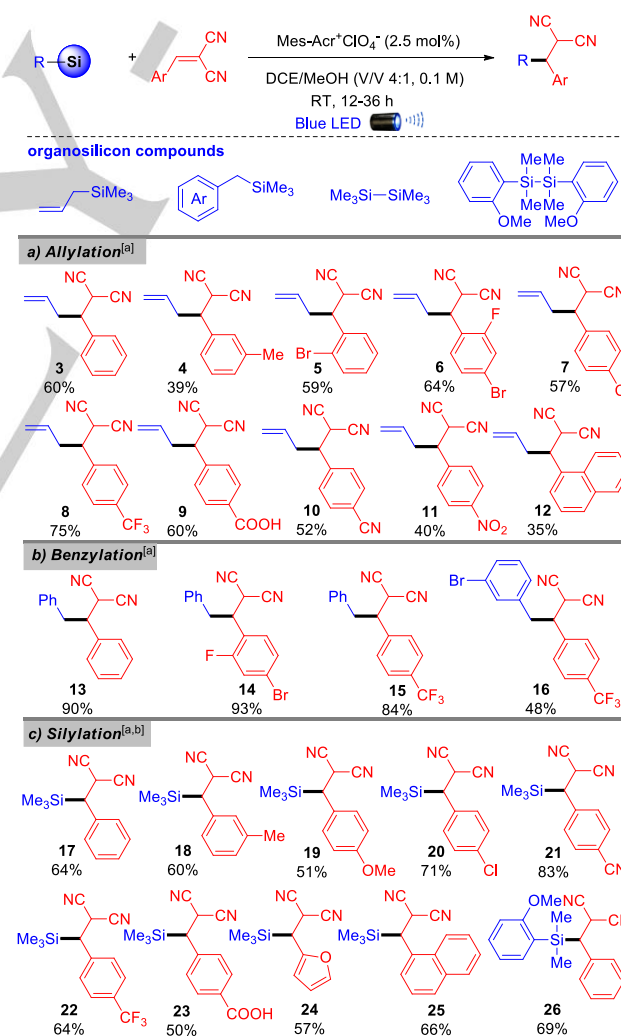
We initiated our study with the reaction between allyltrimethylsilane **1** and benzylidenemalononitrile **2** in the presence of Mes-Acr⁺ClO₄⁻ (2.5 mol%) in 1,2-dichloroethane (DCE, 0.1 M) under blue LED irradiation (λ_{max} = 470 nm). To our delight, the expected allylation product **3** was achieved in 38% yield, with no other regioisomers detected (Table 1, entry 1). A systematic survey on the reaction conditions was conducted to further improve the efficiency using **1** and **2** as the model substrates. Among several common photocatalysts investigated, Mes-Acr⁺ClO₄⁻ proved to be the most effective one (entries 1-5). The organo-photocatalyst 2,4,6-tri(*p*-tolyl)pyrylium tetrafluoroborate gave an inferior result, while Ir(III) and Ru(II) based catalysts were completely ineffective, probably due to their lower excited-state oxidizing ability ($E_{1/2}^{\text{red}^*}$ = +1.21, +1.14, +0.77 V vs SCE in MeCN for the catalysts used in entries 3-5, respectively). Screening of the reaction medium indicated that a mixed DCE/MeOH was the most suitable medium for this transformation, probably due to a nucleophile-assisted silane radical cation fragmentation (entries 6-15).^[12] The volume ratio of the two solvents influenced the reaction to a certain extent, and the optimal ratio was found to be DCE/MeOH as 4/1 (entries 12-15). A declined yield was obtained when the reaction solution was more concentrated (entry 16). Finally, no reaction occurred in the absence of either light or photocatalyst, highlighting the necessity of both components (entry 17).

Table 1. Survey on reaction conditions.^[a]

			
Entry	Catalyst	Solvent	Yield (%) ^[b]
1	Mes-Acr ⁺ ClO ₄ ⁻	DCE	38
2	2,4,6-tri(<i>p</i> -tolyl)pyrylium tetrafluoroborate	DCE	5
3	Ir[dF(CF ₃)ppy] ₂ (dtbpy)PF ₆	DCE	0
4	Ir(dFppy) ₂ (dtbpy)PF ₆	DCE	0
5	Ru(bpy) ₃ Cl ₂ ·6H ₂ O	DCE	0
6	Mes-Acr ⁺ ClO ₄ ⁻	DCM	24
7	Mes-Acr ⁺ ClO ₄ ⁻	MeCN	22
8	Mes-Acr ⁺ ClO ₄ ⁻	Acetone	20

9	Mes-Acr ⁺ ClO ₄ ⁻	DMF	5
10	Mes-Acr ⁺ ClO ₄ ⁻	DMSO	0
11	Mes-Acr ⁺ ClO ₄ ⁻	MeOH	23
12	Mes-Acr ⁺ ClO ₄ ⁻	DCE/MeOH (V/V 3/1)	49
13	Mes-Acr ⁺ ClO ₄ ⁻	DCE/MeOH (V/V 4/1)	65(60)
14	Mes-Acr ⁺ ClO ₄ ⁻	DCE/MeOH (V/V 5/1)	55
15	Mes-Acr ⁺ ClO ₄ ⁻	DCE/MeOH (V/V 10/1)	45
16	Mes-Acr ⁺ ClO ₄ ⁻	DCE/MeOH (V/V 4/1)	39 ^[c]
17	Mes-Acr ⁺ ClO ₄ ⁻	no light or photocatalyst	0

[a] General conditions: allyltrimethylsilane **1** (63 μ L, 0.4 mmol), benzylidenemalononitrile **2** (31 mg, 0.2 mmol), and photocatalyst (0.005 mmol) in solvent (2.0 mL), irradiated by 18 W blue LED. [b] Yields were determined by the crude ¹H NMR spectra using 1,3,5-trimethoxybenzene as an internal standard, and data in parentheses are isolated yields. [c] 1.0 mL of solvent was used.



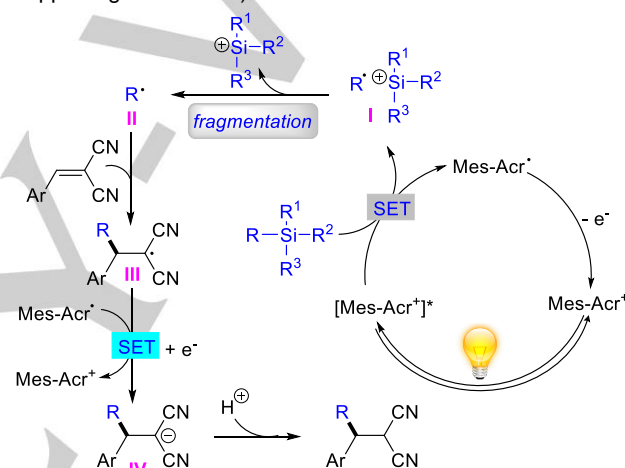
Scheme 2. Scope of the visible-light-mediated allylation, benzylation, and silylation reactions. [a] General conditions: silane (0.4 mmol), methylene-

malononitrile (0.2 mmol), and Mes-Acr⁺ClO₄⁻ (2.1 mg, 0.005 mmol) in DCE/MeOH (2.0 mL, V/V 4/1), irradiated by 18 W blue LED. Isolated yields. [b] DCE (2.0 mL) was used as the solvent.

With the optimal conditions in hand (Table 1, entry 13), we sought to investigate the generality of this protocol (Scheme 2). Employing allyltrimethylsilane **1** as a representative substrate, a variety of methylene-malononitriles bearing different electronic and steric properties were first investigated (Scheme 2a). Allylation reactions of allyltrimethylsilane **1** with an array of methylene-malononitriles, bearing either electron-neutral, electron-rich, or electron-poor aromatic rings, proceeded smoothly to afford the corresponding products **3–11** in moderate to good yields. The protocol was found to tolerate functional groups such as halogens, trifluoromethyl groups, acids, nitriles, and nitro groups. A sterically demanding naphthyl group was also accommodated, albeit the yield of product **12** was relatively lower. However, alkene with a hetero-aryl moiety such as 2-furyl substituted methylene-malononitrile was ineffective for this allylation. Furthermore, this radical cation fragmentation protocol could be extended to benzylsilanes, leading to the benzylation of methylene-malononitriles (Scheme 2b). Under the optimal conditions, the benzylation of arylidene-malononitriles with the representative benzylsilanes, benzyltrimethylsilane and (4-bromobenzyl)trimethylsilane, occurred smoothly to afford their corresponding products **13–16** in moderate to excellent yields. Notably, disilanes were also a competent class of compounds for this protocol (Scheme 2c). In all the examined cases, disilanes such as hexamethyldisilane and 1,2-bis(2-methoxyphenyl)-1,1,2,2-tetramethyldisilane participated in the reaction smoothly to give the corresponding silylated products **17–26** in moderate to good yields, with methylene-malononitriles bearing either electron-rich, electron-poor aryl, heteroaryl, or sterically hindered aryl group. It is also worth noting that although transition-metal-catalyzed hydrosilylation of electron-rich alkenes has been extensively studied,^[13] the hydrosilylation of electron-deficient alkenes is scarce due to their low reactivity and poor selectivity toward most of the existing catalysts.^[14] This study thus represents an example of metal-free hydrosilylation of electron-deficient alkenes under mild conditions.^[11e,15] Remarkably, only one regioisomer was obtained for all the substrates examined, highlighting the regioselective process.

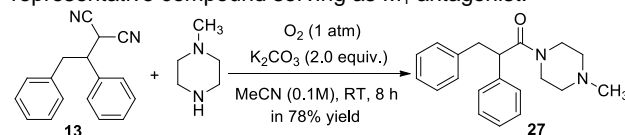
A plausible mechanism for the allylation, benzylation, and silylation reactions was proposed based on all experimental results and our previous related studies (Scheme 3).^[6] Initial visible-light excitation of the acridinium photoredox catalyst generates its excited-state [Mes-Acr⁺]^{*} ($E_{1/2}^{\text{red}^*} = +2.06$ V vs SCE in MeCN),^[6] which is sufficiently oxidizing to oxidize the silane ($E_{1/2}^{\text{ox}} = +1.58$ V vs Ag/Ag⁺ in MeCN for allyltrimethylsilane)^[8g] to its radical cation **I** via SET. Luminescence quenching experiments indicate that the silanes such as allyltrimethylsilane **1** can quench the excited state of acridinium ([Mes-Acr⁺]^{*}), whereas methylene-malononitrile such as benzylidenemalononitrile **2** are unable

to (See Supporting Information Fig. S1 and S2). This supports the proposed SET between the silane and the light-excited photocatalyst. Fragmentation of radical cation **I** yields the corresponding carbon or silicon radical **II**.^[5,16] Nucleophilic addition of radical **II** to electron-deficient methylene-malononitrile gives radical **III**. The addition of radical **II** to the C=C bond occurred exclusively at the β -position to the cyano group due to the formation of a more stable radical intermediate **III**.^[17] Single-electron reduction of the radical **III** by the reduced form of the acridinium catalyst ($E_{1/2}^{\text{ox}} = -0.57$ V vs SCE in MeCN) delivers the anion intermediate **IV** and regenerates the photocatalyst. Protonation of anion **IV** by solvent produces the corresponding allylation, benzylation, or silylation product. Furthermore, no reaction occurred when radical scavengers such as TEMPO and hydroquinone were added, supporting the above radical-based process (See Supporting Information).



Scheme 3. Plausible mechanism for the allylation, benzylation, and silylation reactions

Importantly, the malononitrile moiety in the products can be transformed to acid,^[18] ester,^[19] amide,^[20] and other functionalities in a convenient manner. As exemplified in Scheme 4, the benzylation product **13** could be easily converted to the bioactive compound **27** in one-step, a representative compound serving as M₁ antagonist.^[21]



Scheme 4. Synthetic transformation of the benzylation product **13**

Conclusions

In conclusion, we have developed visible-light-mediated allylation, benzylation, and silylation of methylene-malononitriles using organosilanes as the radical precursors by employing an organo-photoredox catalyst, affording the corresponding products in moderated to excellent yields with exclusive regioselectivity. A photoredox-catalyzed radical cation fragmentation process was proposed to generate the key allyl, benzyl, and silyl radicals to couple with methylene-malononitriles. The reactions benefit from their redox economy, mild conditions, and good selectivity. The synthetic utility of the methodology was demonstrated by facile synthesis of a bioactive compound. Future efforts in our laboratory will be directed towards further application of the visible-light-induced radical cation fragmentation protocol for synthesis of other value-added molecules.

Experimental Section

Typical procedure for the allylation and benzylation reactions

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst Mes-Acr⁺ClO₄⁻ (2.1 mg, 0.005 mmol), and methylene-malononitrile (0.2 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequently backfilled with argon for three times. After that, anhydrous DCE and methanol (2.0 mL, V/V 4/1), and silane (0.4 mmol) were added sequentially using a syringe. The reaction setup was placed under blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 12-36 hrs. After completion as monitored by TLC, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel via gradient elution with hexane / ethyl acetate (15:1-3:1) give the allylation or benzylation product.

2-(1-Phenylbut-3-en-1-yl)malononitrile (**3**)

Prepared according to the typical procedure, allyltrimethylsilane (63 μ L, 0.4 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol) were employed to give **3** (23.5 mg, 60% yield) as a pale yellow liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.45 – 7.32 (m, 5H), 5.76 – 5.59 (m, 1H), 5.31 – 5.11 (m, 2H), 4.02 (d, *J* = 5.6 Hz, 1H), 3.29 (td, *J* = 7.6, 5.7 Hz, 1H), 2.79 – 2.69 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 136.3, 132.9, 129.2, 128.9, 127.9, 119.9, 111.8, 111.5, 45.9, 36.4, 28.9 ppm; HRMS-ESI [M-H]⁻ calculated for C₁₃H₁₁N₂ 195.0922, found 195.0928.

2-(1-(*m*-Tolyl)but-3-en-1-yl)malononitrile (**4**)

Prepared according to the typical procedure, allyltrimethylsilane (63 μ L, 0.4 mmol) and 2-(3-methylbenzylidene)malononitrile (33.6 mg, 0.2 mmol) were employed to give **4** (16.4 mg, 39% yield) as a pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (t, *J* = 7.9 Hz, 1H), 7.16 (dd, *J* = 20.6, 6.5 Hz, 3H), 5.72 – 5.61 (m, 1H), 5.25 (dd, *J* = 17.1, 1.2 Hz, 1H), 5.17 (d, *J* = 10.1 Hz, 1H), 4.00 (d, *J* = 5.7 Hz, 1H), 3.25 (dd, *J* = 13.4, 7.5 Hz, 1H), 2.80 – 2.68 (m, 2H), 2.38 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) 138.9, 136.3, 133.1, 129.7, 129.1, 128.6, 124.8, 119.7, 111.9, 111.5, 45.9, 36.5, 28.9, 21.5 ppm; HRMS-ESI [M-H]⁻ calculated for C₁₄H₁₃N₂ 209.1079, found 209.1084.

2-(1-(2-Bromophenyl)but-3-en-1-yl)malononitrile (**5**)

Prepared according to the typical procedure, allyltrimethylsilane (63 μ L, 0.4 mmol) and 2-(2-bromobenzylidene)malononitrile (46.6 mg, 0.2 mmol) were employed to give **5** (32.5 mg, 59% yield) as a pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.25 (m, 5H), 5.77 – 5.63 (m, 1H), 5.30 – 5.18 (m, 2H), 4.13 – 4.04 (m, 2H), 2.88 – 2.83 (m, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃) 135.3, 133.7, 132.3, 130.2, 128.2, 125.1, 119.8, 111.6, 111.1, 43.6, 35.0, 27.7 ppm; HRMS-ESI [M-H]⁻ calculated for C₁₃H₁₀BrN₂ 273.1412, found 273.0033.

2-(1-(4-Bromo-2-fluorophenyl)but-3-en-1-yl)malononitrile (**6**)

Prepared according to the typical procedure, allyltrimethylsilane (63 μ L, 0.4 mmol) and 2-(4-bromo-2-fluorobenzylidene)malononitrile (50.2 mg, 0.2 mmol) were employed to give **6** (37.5 mg, 64% yield) as a pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.34 (ddd, *J* = 11.6, 9.1, 1.6 Hz, 2H), 7.25 – 7.21 (m, 1H), 5.67 – 5.55 (m, 1H), 5.20 (dd, *J* = 17.1, 1.2 Hz, 1H), 5.15 (dd, *J* = 10.2, 0.7 Hz, 1H), 4.03 (d, *J* = 6.5 Hz, 1H), 3.66 (dd, *J* = 15.1, 6.8 Hz, 1H), 2.71 (ddd, *J* = 31.1, 14.3, 7.1 Hz, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 160.4 (d, *J* = 250.8 Hz), 132.2, 129.9 (d, *J* = 4.3 Hz), 128.4 (d, *J* = 3.6 Hz), 123.4 (d, *J* = 10.1 Hz), 122.7 (d, *J* = 13.7 Hz), 120.3, 119.9 (d, *J* = 25.7 Hz), 111.3, 111.2, 38.9, 35.4, 27.6 ppm; HRMS-ESI [M-H]⁻ calculated for C₁₃H₉BrFN₂ 290.9933, found 290.9939.

2-(1-(4-Chlorophenyl)but-3-en-1-yl)malononitrile (**7**)

Prepared according to the typical procedure, allyltrimethylsilane (63 μ L, 0.4 mmol) and 2-(4-chlorobenzylidene)malononitrile (37.7 mg, 0.2 mmol) were employed to give **7** (26.3 mg, 57% yield) as a pale yellow liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.42 – 7.27 (m, 5H), 5.71 – 5.58 (m, 1H), 5.27 – 5.18 (m, 2H), 4.02 – 4.00 (m, 1H), 3.31 – 3.24 (m, 1H), 2.75 – 2.69 (m, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃) 134.9, 134.7, 132.5, 129.4, 129.2, 120.1, 111.6, 111.1, 45.2, 36.3, 28.7; HRMS-ESI [M-H]⁻ calculated for C₁₃H₁₀ClN₂ 229.0533, found 229.0538.

2-(1-(4-(Trifluoromethyl)phenyl)but-3-en-1-yl)malononitrile (**8**)

Prepared according to the typical procedure, allyltrimethylsilane (63 μ L, 0.4 mmol) and 2-(4-(trifluoromethyl)benzylidene)malononitrile (44.4 mg, 0.2 mmol) were employed to give **8** (39.6 mg, 75% yield) as a pale yellow liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 5.74 – 5.58 (m, 1H), 5.32 – 5.17 (m, 2H), 4.06 (d, *J* = 5.5 Hz, 1H), 3.42 – 3.31 (m, 1H), 2.85 – 2.68 (m, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃) 140.1, 132.3, 131.3 (q, *J* = 33.0 Hz), 128.5, 126.2 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.3 Hz), 120.5, 111.5, 110.1, 45.6, 36.3, 28.5 ppm; HRMS-ESI [M-H]⁻ calculated for C₁₄H₁₀F₃N₂ 263.0796, found 263.0802.

4-(1,1-Dicyanopent-4-en-2-yl)benzoic acid (**9**)

Prepared according to the typical procedure, allyltrimethylsilane (63 μ L, 0.4 mmol) and 4-(2,2-dicyanovinyl)benzoic acid (39.6 mg, 0.2 mmol) were employed to give **9** (28.8 mg, 60% yield) as an orange liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 5.72 – 5.57 (m, 1H), 5.24 (dd, *J* = 21.7, 13.6 Hz, 2H), 4.06 (d, *J* = 5.7 Hz, 1H), 3.42 – 3.35 (m, 1H), 2.85 – 2.70 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) 170.9, 142.1, 132.3, 131.1, 128.2, 120.4, 111.6, 111.1, 45.8, 36.3, 28.5 ppm; HRMS-ESI [M-H]⁻ calculated for C₁₄H₁₁N₂O₂ 239.0821, found 239.0826.

2-(1-(4-Cyanophenyl)but-3-en-1-yl)malononitrile (**10**)

Prepared according to the typical procedure, allyltrimethylsilane (63 μ L, 0.4 mmol) and 2-(4-cyanobenzylidene)malononitrile (35.8 mg, 0.2 mmol) were employed to give **10** (23 mg, 52% yield) as a yellow liquid. ¹H NMR

(300 MHz, CDCl₃) δ 7.74 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 7.7 Hz, 2H), 5.72 – 5.56 (m, 1H), 5.32 – 5.19 (m, 2H), 4.08 (dd, J = 5.4, 1.7 Hz, 1H), 3.36 (dd, J = 13.3, 7.3 Hz, 1H), 2.85 – 2.66 (m, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃) 141.3, 132.9, 131.9, 128.9, 120.7, 117.9, 113.2, 111.3, 110.8, 45.6, 36.1, 28.3 ppm; HRMS–ESI [M–H][–] calculated for C₁₄H₁₀N₃ 220.0875, found 220.0880.

2-(1-(4-Nitrophenyl)but-3-en-1-yl)malononitrile (**11**)

Prepared according to the typical procedure, allyltrimethylsilane (63 μ L, 0.4 mmol) and 2-(4-nitrobenzylidene)malononitrile (39.8 mg, 0.2 mmol) were employed to give **11** (19.3 mg, 40% yield) as an orange liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 5.72 – 5.59 (m, 1H), 5.32 – 5.22 (m, 2H), 4.09 (d, J = 5.5 Hz, 1H), 3.46 – 3.40 (m, 1H), 2.85 – 2.71 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) 143.1, 131.8, 129.1, 124.3, 120.9, 111.2, 110.7, 45.4, 36.2, 28.3 ppm; HRMS–ESI [M–H][–] calculated for C₁₃H₁₀N₃O₂ 240.0773, found 240.0779.

2-(1-(Naphthalen-1-yl)but-3-en-1-yl)malononitrile (**12**)

Prepared according to the typical procedure, allyltrimethylsilane (63 μ L, 0.4 mmol) and 2-(naphthalen-1-ylmethylene)malononitrile (40.8 mg, 0.2 mmol) were employed to give **12** (17.2 mg, 35% yield) as a brown liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.87 (m, 3H), 7.65 – 7.60 (m, 1H), 7.59 – 7.51 (m, 3H), 5.76 – 5.65 (m, 1H), 5.32 – 5.24 (m, 1H), 5.16 (dd, J = 10.2, 1.3 Hz, 1H), 4.32 (dd, J = 13.1, 7.1 Hz, 1H), 4.16 (d, J = 5.6 Hz, 1H), 2.97 (t, J = 7.1 Hz, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) 134.4, 132.9, 132.2, 131.2, 129.9, 129.7, 127.5, 126.4, 125.6, 124.8, 121.6, 120.1, 112.3, 111.8, 38.2, 36.2, 28.7 ppm; HRMS–ESI [M–H][–] calculated for C₁₇H₁₃N₂ 245.1079, found 245.1084.

2-(1,2-Diphenylethyl)malononitrile (**13**)

Prepared according to the typical procedure, benzyltrimethylsilane (76 μ L, 0.4 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol) were employed to give **13** (44.3 mg, 90% yield) as a yellow liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.47 – 7.27 (m, 8H), 7.22 – 7.17 (m, 2H), 3.85 (d, J = 5.1 Hz, 1H), 3.47 (td, J = 7.8, 5.2 Hz, 1H), 3.31 – 3.23 (m, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃) 136.5, 136.4, 129.1, 129.0, 128.9, 128.8, 127.9, 127.5, 111.9, 111.3, 48.3, 38.5, 28.4 ppm; HRMS–ESI [M–H][–] calculated for C₁₇H₁₃N₂ 245.1079, found 245.1084.

2-(1-(4-Bromo-2-fluorophenyl)-2-phenylethyl)malononitrile (**14**)

Prepared according to the typical procedure, benzyltrimethylsilane (76 μ L, 0.4 mmol) and 2-(4-bromo-2-fluorobenzylidene)malononitrile (50.2 mg, 0.2 mmol) were employed to give **14** (63.8 mg, 93% yield) as a yellow liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.38 – 7.24 (m, 6H), 7.15 (d, J = 6.2 Hz, 2H), 3.95 (d, J = 6.3 Hz, 1H), 3.87 (dd, J = 14.4, 7.3 Hz, 1H), 3.30 (dd, J = 14.0, 7.8 Hz, 1H), 3.18 (dd, J = 14.0, 7.6 Hz, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃) 160.3 (d, J = 251.1 Hz), 135.8, 129.9 (d, J = 4.0 Hz), 129.1, 128.8, 128.3 (d, J = 3.6 Hz), 127.7, 123.3 (d, J = 10.1 Hz), 122.7 (d, J = 13.4 Hz), 119.9 (d, J = 25.7 Hz), 111.4, 111.2, 41.1, 37.6, 27.4 ppm; HRMS–ESI [M–H][–] calculated for C₁₇H₁₁BrF₂N₂ 341.0090, found 341.0095.

2-(2-Phenyl-1-(4-(trifluoromethyl)phenyl)ethyl)malononitrile (**15**)

Prepared according to the typical procedure, benzyltrimethylsilane (76 μ L, 0.4 mmol) and 2-(4-(trifluoromethyl)benzylidene)malononitrile (44.4 mg, 0.2 mmol) were employed to give **15** (52.8 mg, 84% yield) as a yellow liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.70 (d, J = 8.2 Hz, 2H), 7.54 (d, J =

8.2 Hz, 2H), 7.39 – 7.27 (m, 3H), 7.20 (d, J = 6.5 Hz, 2H), 3.89 (d, J = 5.0 Hz, 1H), 3.58 – 3.49 (m, 1H), 3.28 (dd, J = 7.8, 3.6 Hz, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃) 140.3, 135.9, 131.4 (q, J = 32.8 Hz), 129.3, 128.8, 128.6, 127.8, 126.2 (q, J = 3.7 Hz), 123.7 (q, J = 272.1 Hz), 111.7, 111.0, 48.0, 38.3, 28.1 ppm; HRMS–ESI [M–H][–] calculated for C₁₈H₁₂F₃N₂ 313.0953, found 313.0958.

2-(2-(3-Bromophenyl)-1-(4-(trifluoromethyl)phenyl)ethyl)malononitrile (**16**)

Prepared according to the typical procedure, benzyltrimethylsilane (97.2 mg, 0.4 mmol) and 2-(4-(trifluoromethyl)benzylidene)malononitrile (44.4 mg, 0.2 mmol) were employed to give **16** (37.7 mg, 48% yield) as a yellow liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.69 (d, J = 8.3 Hz, 2H), 7.47 (dd, J = 11.4, 8.3 Hz, 4H), 7.04 (d, J = 8.3 Hz, 2H), 3.89 (d, J = 5.3 Hz, 1H), 3.56 – 3.46 (m, 1H), 3.33 – 3.16 (m, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃) 139.8, 134.8, 132.4, 131.6 (q, J = 33.0 Hz), 130.5, 128.5, 126.3 (q, J = 3.8 Hz), 124.7 (d, J = 277.1 Hz), 121.8, 111.4, 110.9, 47.8, 37.8, 28.4 ppm; HRMS–ESI [M–H][–] calculated for C₁₈H₁₁BrF₃N₂ 391.0058, found 391.0063.

Typical procedure for the silylation reactions

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst Mes-Acr⁺ClO₄[–] (2.1 mg, 0.005 mmol), and methylene-malononitrile (0.2 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequently backfilled with argon for three times. After that, anhydrous DCE (2.0 mL), and silane (0.4 mmol) were added sequentially using a syringe. Then the reaction was placed under blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 12–36 hrs. After completion as monitored by TLC, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel via gradient elution with hexane / ethyl acetate (15:1–3:1) give the allylation or benzylation product.

2-(Phenyl(trimethylsilyl)methyl)malononitrile (**17**)

Prepared according to the typical procedure, hexamethyldisilane (81.7 μ L, 0.4 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol) were employed to give **17** (29.2 mg, 64% yield) as a yellow liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.41 – 7.32 (m, 2H), 7.32 – 7.24 (m, 1H), 7.22 – 7.14 (m, 2H), 4.08 (d, J = 7.8 Hz, 1H), 2.64 (d, J = 7.8 Hz, 1H), 0.16 (s, 9H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 137.2, 129.2, 127.8, 127.4, 113.2, 113.1, 37.8, 25.2, -2.1 ppm; HRMS–ESI [M–H][–] calculated for C₁₈H₁₅N₂Si 227.1010, found 227.1010.

2-(*m*-Tolyl(trimethylsilyl)methyl)malononitrile (**18**)

Prepared according to the typical procedure, hexamethyldisilane (81.7 μ L, 0.4 mmol) and 2-(3-methylbenzylidene)malononitrile (33.6 mg, 0.2 mmol) were employed to give **18** (29 mg, 60% yield) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.12 – 7.04 (m, 1H), 6.92 (d, J = 7.6 Hz, 1H), 6.81 (d, J = 7.6 Hz, 2H), 3.90 (d, J = 8.0 Hz, 1H), 2.44 (d, J = 8.0 Hz, 1H), 2.19 (s, 3H), 0.00 (s, 9H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 138.8, 137.1, 128.9, 128.6, 128.1, 124.7, 113.3, 113.2, 37.7, 25.2, 21.5, -2.1 ppm; HRMS–ESI [M–H][–] calculated for C₁₄H₁₇N₂Si 241.1166, found 241.1161.

2-((4-Methoxyphenyl)(trimethylsilyl)methyl)malononitrile (**19**)

Prepared according to the typical procedure, hexamethyldisilane (81.7 μ L, 0.4 mmol) and 2-(4-methoxybenzylidene)malononitrile (36.8 mg, 0.2 mmol) were employed to give **19** (26.3 mg, 51% yield) as a yellow semi-solid. ¹H NMR (300 MHz, CDCl₃) δ 7.12 (d, J = 8.6 Hz, 2H), 6.89 (d, J =

8.6 Hz, 2H), 4.03 (d, $J = 7.5$ Hz, 1H), 3.81 (s, 3H), 2.58 (d, $J = 7.6$ Hz, 1H), 0.16 (s, 9H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 158.8, 129.1, 128.9, 114.6, 113.3, 113.1, 55.2, 36.9, 25.5, -2.1 ppm; HRMS-ESI $[\text{M}-\text{H}]^-$ calculated for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{OSi}$ 257.1116, found 257.1116.

2-((4-Chlorophenyl)(trimethylsilyl)methyl)malononitrile (20)

Prepared according to the typical procedure, hexamethyldisilane (81.7 μL , 0.4 mmol) and 2-(4-chlorobenzylidene)malononitrile (37.7 mg, 0.2 mmol) were employed to give **20** (37.2 mg, 71% yield) as a yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.35 (d, $J = 8.4$ Hz, 2H), 7.14 (d, $J = 8.4$ Hz, 2H), 4.06 (d, $J = 7.5$ Hz, 1H), 2.63 (d, $J = 7.5$ Hz, 1H), 0.17 (s, 9H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 135.6, 133.3, 129.4, 129.2, 113.0, 112.8, 37.3, 25.1, -2.2 ppm; HRMS-ESI $[\text{M}-\text{H}]^-$ calculated for $\text{C}_{13}\text{H}_{14}\text{ClN}_2\text{Si}$ 261.0620, found 261.0620.

2-((4-Cyanophenyl)(trimethylsilyl)methyl)malononitrile (21)

Prepared according to the typical procedure, hexamethyldisilane (81.7 μL , 0.4 mmol) and 2-(4-cyanobenzylidene)malononitrile (35.8 mg, 0.2 mmol) were employed to give **21** (42 mg, 83% yield) as a yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.3$ Hz, 2H), 4.13 (d, $J = 7.5$ Hz, 1H), 2.75 (d, $J = 7.5$ Hz, 1H), 0.18 (s, 9H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 142.8, 132.9, 128.5, 118.2, 112.8, 112.5, 111.4, 38.2, 24.5, -2.3 ppm; HRMS-ESI $[\text{M}-\text{H}]^-$ calculated for $\text{C}_{14}\text{H}_{14}\text{N}_3\text{Si}$ 252.0962, found 252.0967.

2-((4-(Trifluoromethyl)phenyl)(trimethylsilyl)methyl)malononitrile (22)

Prepared according to the typical procedure, hexamethyldisilane (81.7 μL , 0.4 mmol) and 2-(4-(trifluoromethyl)benzylidene)malononitrile (44.4 mg, 0.2 mmol) were employed to give **22** (37.9 mg, 64% yield) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 4.11 (d, $J = 7.5$ Hz, 1H), 2.74 (d, $J = 7.5$ Hz, 1H), 0.18 (s, 9H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 141.3, 129.7 (q, $J = 32.7$ Hz), 128.1, 126.2 (q, $J = 3.7$ Hz), 123.9 (q, $J = 272.0$ Hz), 112.9, 112.7, 37.9, 24.8, 25.5, -2.2 ppm; HRMS-ESI $[\text{M}-\text{H}]^-$ calculated for $\text{C}_{14}\text{H}_{14}\text{F}_3\text{N}_2\text{Si}$ 295.0884, found 295.0889.

4-(2,2-Dicyano-1-(trimethylsilyl)ethyl)benzoic acid (23)

Prepared according to the typical procedure, hexamethyldisilane (81.7 μL , 0.4 mmol) and 4-(2,2-dicyanovinyl)benzoic acid (39.6 mg, 0.2 mmol) were employed to give **23** (27 mg, 50% yield) as a white semi-solid. ^1H NMR (300 MHz, CDCl_3) δ 8.12 (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 4.14 (d, $J = 7.8$ Hz, 1H), 2.79 (d, $J = 7.8$ Hz, 1H), 0.19 (s, 9H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 170.9, 143.5, 131.1, 128.4, 127.8, 112.9, 112.7, 38.2, 24.7, -2.2 ppm; HRMS-ESI $[\text{M}-\text{H}]^-$ calculated for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_2\text{Si}$ 271.0908, found 271.0919.

2-(Furan-2-yl(trimethylsilyl)methyl)malononitrile (24)

Prepared according to the typical procedure, hexamethyldisilane (81.7 μL , 0.4 mmol) and 2-(furan-2-ylmethylene)malononitrile (28.8 mg, 0.2 mmol) were employed to give **24** (24.8 mg, 57% yield) as a yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.22 (dd, $J = 5.0, 0.8$ Hz, 1H), 7.04 – 6.99 (m, 2H), 4.03 (d, $J = 6.6$ Hz, 1H), 2.96 (d, $J = 6.6$ Hz, 1H), 0.23 (s, 9H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 138.3, 127.6, 126.1, 124.6, 112.8, 112.7, 32.9, 26.4, -2.2 ppm; HRMS-ESI $[\text{M}-\text{H}]^-$ calculated for $\text{C}_{11}\text{H}_{13}\text{N}_2\text{OSi}$ 217.0803, found 217.0808.

2-(Naphthalen-1-yl(trimethylsilyl)methyl)malononitrile (25)

Prepared according to the typical procedure, hexamethyldisilane (81.7 μL , 0.4 mmol) and 2-(naphthalen-1-ylmethylene)malononitrile (40.8 mg, 0.2 mmol) were employed to give **25** (36.7 mg, 66% yield) as a yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.3$ Hz, 1H), 7.90 (d, $J = 7.5$ Hz, 1H), 7.79 (d, $J = 8.2$ Hz, 1H), 7.62 – 7.45 (m, 3H), 7.38 (d, $J = 7.2$ Hz, 1H), 4.24 (d, $J = 9.0$ Hz, 1H), 3.73 (d, $J = 9.0$ Hz, 1H), 0.15 (s, 9H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 134.2, 134.0, 131.5, 129.3, 127.8, 126.6, 126.1, 125.3, 123.9, 122.5, 113.4, 113.3, 30.8, 25.4, -1.9 ppm; HRMS-ESI $[\text{M}-\text{H}]^-$ calculated for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{Si}$ 277.1166, found 277.1166.

2-((2-Methoxyphenyl)dimethylsilyl)(phenyl)methyl)malononitrile (26)

Prepared according to the typical procedure, 1,2-bis(2-methoxyphenyl)-1,1,2,2-tetramethyldisilane (132 mg, 0.4 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol) were employed to give **26** (55 mg, 69% yield) as a yellow solid. ^1H NMR (300 MHz, CDCl_3) δ 7.55 – 7.45 (m, 1H), 7.40 – 7.31 (m, 4H), 7.25 – 7.17 (m, 2H), 7.05 (t, $J = 7.3$ Hz, 1H), 6.98 (d, $J = 8.3$ Hz, 1H), 4.18 (d, $J = 7.1$ Hz, 1H), 3.97 (s, 3H), 3.03 (d, $J = 7.1$ Hz, 1H), 0.45 (s, 3H), 0.37 (s, 3H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 163.8, 136.9, 136.2, 132.4, 128.9, 128.4, 127.2, 122.2, 121.4, 113.6, 113.5, 110.0, 55.2, 37.2, 25.5, -2.7, -3.9 ppm; HRMS-ESI $[\text{M}-\text{H}]^-$ calculated for $\text{C}_{19}\text{H}_{19}\text{N}_2\text{OSi}$ 319.1272, found 319.1278.

Typical procedure for synthesis of bioactive compound 27

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added 1-methylpiperazine (40 mg, 0.4 mmol), benzylolation product **13** (49.2 mg, 0.2 mmol), K_2CO_3 (55.2 mg, 0.4 mmol), and CH_3CN (2.0 mL). The resulting mixture was stirred at room temperature with an oxygen balloon until the compound **13** was completely consumed as monitored by TLC. The solution was filtered, then concentrated and purified through column chromatography on silica gel by gradient elution with hexane / ethyl acetate / methanol to give the compound **27** (48 mg) as a colorless oil in 78% yield. A known compound and the data are in accordance with those reported in the literature.^[20] ^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.32 (m, 2H), 7.32 – 7.25 (m, 5H), 7.25 – 7.20 (m, 1H), 7.18 – 7.12 (m, 2H), 4.08 – 4.00 (m, 1H), 3.82 – 3.71 (m, 1H), 3.65 – 3.51 (m, 2H), 3.46 – 3.33 (m, 2H), 3.02 (dd, $J = 13.5, 6.7$ Hz, 1H), 2.39 – 2.30 (m, 1H), 2.31 – 2.23 (m, 1H), 2.21 (s, 3H), 2.10 – 2.02 (m, 1H), 1.88 – 1.80 (m, 1H) ppm.

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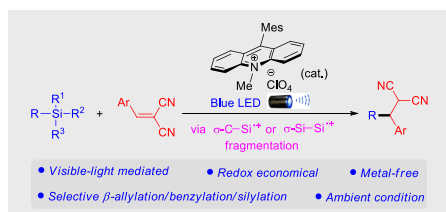
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Layout 2:

FULL PAPER



Visible-light-mediated regioselective allylation, benzylation, and silylation of methylene-malononitriles with silanes have been realized. The reactions proceed via a photoredox-catalyzed σ -C-Si $^{+\bullet}$ or σ -Si-Si $^{+\bullet}$ type radical cation fragmentation.

Rongfang Liu, Shane Pui Mun Chia, Yi Yiing Goh, Han Wen Cheo, Binbin Fan, Ruifeng Li, Rong Zhou*, Jie Wu*

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