



Photoredox Catalysis

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

Rongfang Liu,^[a] Shane Pui Mun Chia,^[b] Yi Yiing Goh,^[b] Han Wen Cheo,^[b] Binbin Fan,^[a] Ruifeng Li,^[a] Rong Zhou,^{*,[a]} and Jie Wu^{*,[b]}

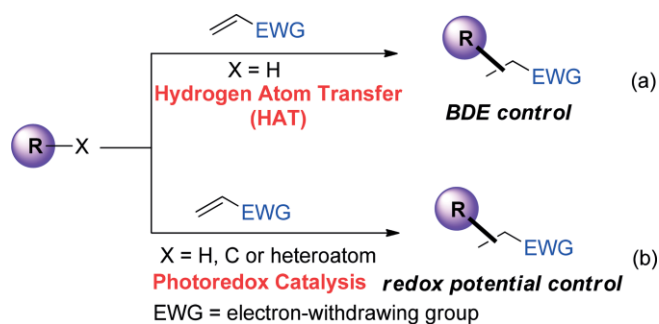
Abstract: Visible-light-mediated regioselective allylation, benzylation, and silylation of methylene-malononitriles using allylic/benzylic silane and disilane reagents have been developed, delivering the corresponding allylated, benzylated, and silylated products in moderate to excellent yields. These reactions pro-

ceed smoothly with exclusive regioselectivity by employing only an organo-photoredox catalyst under very 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] Generally, the photo-induced generation of radicals for conjugate addition proceeds in two modes: a) via hydrogen atom transfer (HAT); b) via photoredox catalysis. The HAT process affords the radical species directly from C–H substrates through hydrogen atom abstraction, offering enormous opportunities for C–H activations. However, the efficiency of this process is controlled by the relative bond dissociation energies (BDE) 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–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] Furthermore, they can undergo radical cation fragmen-



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

tation to directly afford radicals for further transformations.^[5] Recently, we have developed a metal-free direct alkylation of allylic/benzylic sp^3 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 therefore enable an effective photoredox mediated single electron transfer (SET) to generate the radical cation, which undergoes radical cation fragmentation to form the corresponding carbon radical for conjugate addition.

[a] College of Chemistry and Chemical Engineering,
Taiyuan University of Technology
Taiyuan 00024, P.R. China
E-mail: zhourong@tyut.edu.cn

[b] Department of Chemistry, National University of Singapore
3 Science Drive 3, Singapore 117543, Republic of Singapore
E-mail: chmjie@nus.edu.sg
<https://www.wujiegroupnus.com>

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under <https://doi.org/10.1002/ejoc.201900902>.

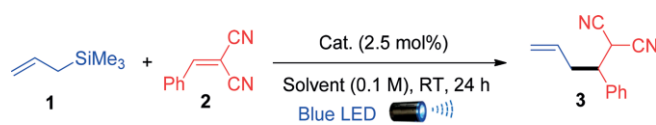
Notably, the use of organosilicon compounds in photo-induced reactions such as allylation, benzylation, and silylation have been developed since the late 1980s.^[8] However, the reported examples required high catalyst loading (20–50 mol-%), use of harmful and equipment-demanding UV light, or suffered from poor selectivity.^[8] Recently, Melchiorre and co-workers reported an elegant enantioselective catalytic β -allylation of enals with alkyltrimethylsilanes under visible-light irradiation, presenting a rare method of carbon radical generation from organosilicon compounds under mild visible-light conditions.^[9] Moreover, Molander and co-workers 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 also as our continuous studies on visible-light photocatalysis for activation of inert chemical bonds,^[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 DCE (0.1 M) under blue LED irradiation ($\lambda_{\text{max}} = 470$ nm). To our delight, the expected allylation product **3** was afforded 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 the reaction between **1** and **2** as a model. Among several common photocatalysts investigated, Mes-Acr⁺ClO₄[−] proved to be the most effective (entries 1–5). The organophotocatalyst 2,4,6-tri(*p*-tolyl)pyrylium tetrafluoroborate gave a 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 4:1 (entries 12–15). A decline in the yield was observed 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 every component (entry 17).

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

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

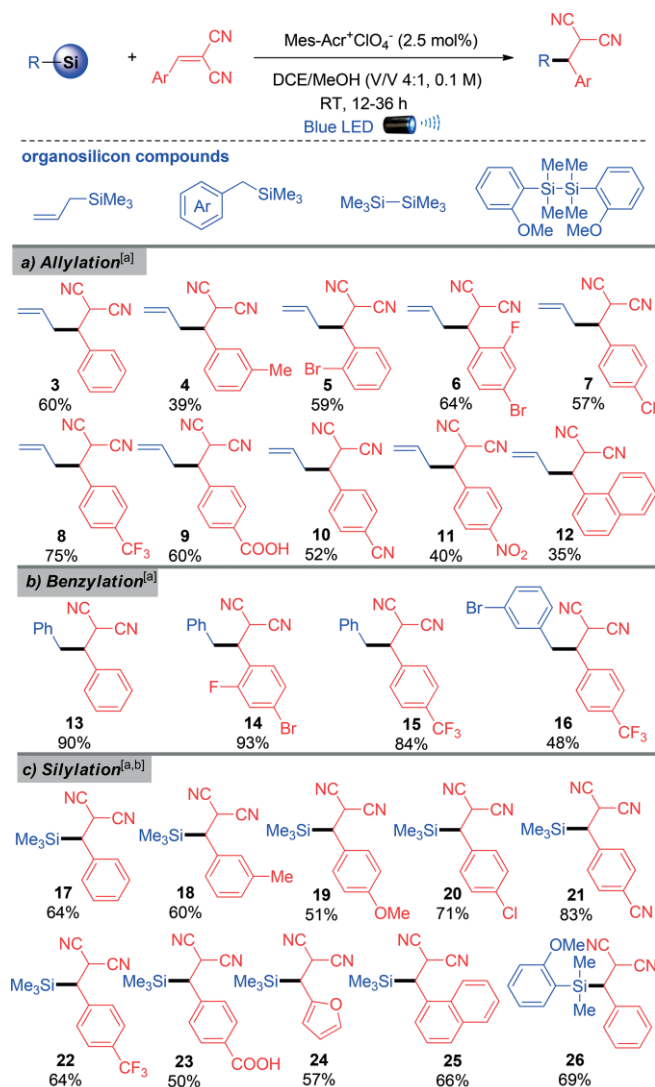


Entry	Catalyst	Solvent	Yield [%] ^[b]
1	Mes-Acr ⁺ ClO ₄ [−]	DCE	38
2	2,4,6-Tri(<i>p</i> -tolyl)pyrylium tetrafluoroborate	DCE	5
3	Ir[dF(CF ₃)ppy] ₂ (dtbpy)PF ₆	DCE	0
4	Ir(dFppy) ₂ (dtbpy)PF ₆	DCE	0
5	Ru(bpy) ₃ Cl ₂ ·6H ₂ O	DCE	0
6	Mes-Acr ⁺ ClO ₄ [−]	DCM	24
7	Mes-Acr ⁺ ClO ₄ [−]	MeCN	22
8	Mes-Acr ⁺ ClO 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 crude ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard, and data in parentheses are isolated yields. [c] 1.0 mL of solvent was used.

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 yielding the product **12** in relatively lower yield. However, hetero-aryl such as 2-furyl substituted methylene-malononitrile was ineffective for this allylation reaction. Furthermore, this radical cation fragmentation protocol could be extended to benzylsilanes, and thus, lead to the benzylation of methylene-malononitriles (Scheme 2b). Under the standard 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. Interestingly, the use of pure DCE as the reaction medium for these reactions led to a higher reaction efficiency than when a mixed solvent system was employed. 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 a rare example of metal-free hydrosilylation of electron-

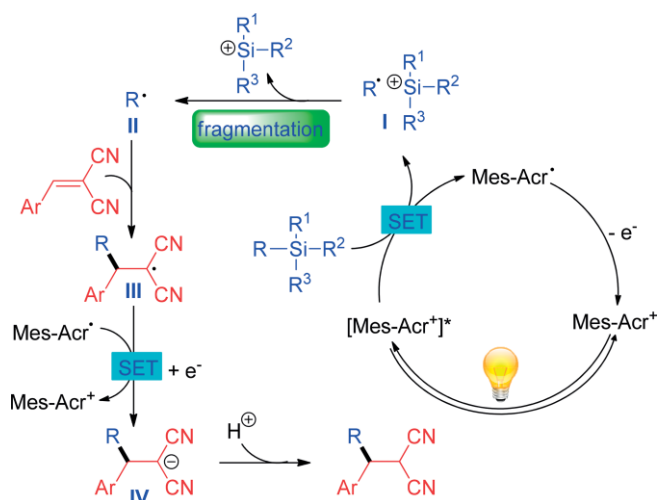
deficient alkenes under mild conditions.^[11e,15] Remarkably, only one regioisomer was obtained for all the substrates examined, highlighting a highly regioselective process.



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 mol) 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.

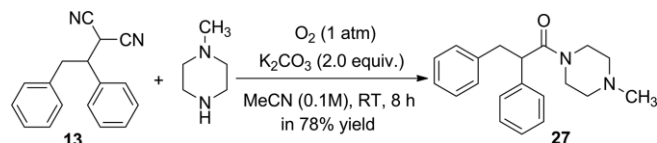
A plausible mechanism for the allylation, benzylation, and silylation reactions was proposed based on all experimental results and our previous closely related studies (Scheme 3).^[6] Initial visible-light excitation of the acridinium photoredox catalyst generates its excited-state [Mes-Acr⁺]^{*} ($E_{1/2}^{\text{red}*} = +2.06$ 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-malononitriles such as benzylidenemalononitrile **2** are unable to (See Supporting Information Fig S1 and S2). This supports the proposed SET from the silane to the light-excited photocatalyst. Fragmentation of radical cation **I** yields the corre-

sponding 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] This results in the exclusive regioselectivity of the above reactions, which is distinguished from the reported UV light-mediated radical-radical coupling processes that show low regioselectivity and chemoselectivity.^[8] 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, suggesting 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 facily converted to the bioactive compound **26** 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 silanes by employing only one organo-photoredox catalyst, which provide the corresponding products in moderate 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 h. 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 benzyldenemalononitrile (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, CDCl_3) 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; ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{M} - \text{H}]^-$ calculated for $\text{C}_{17}\text{H}_{13}\text{N}_2$ 245.1079, found 245.1084.

2-(1,2-Diphenylethyl)malononitrile (13): Prepared according to the typical procedure, benzyltrimethylsilane (76 μL , 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, CDCl_3) 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; ^{13}C NMR (75 MHz, CDCl_3) 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 $[\text{M} - \text{H}]^-$ calculated for $\text{C}_{17}\text{H}_{13}\text{N}_2$ 245.1079, found 245.1084.

2-[1-(4-Bromo-2-fluorophenyl)-2-phenylethyl]malononitrile (14): Prepared according to the typical procedure, benzyltrimethylsilane (76 μL , 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, CDCl_3) 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; ^{13}C NMR (75 MHz, CDCl_3) 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 $[\text{M} - \text{H}]^-$ calculated for $\text{C}_{17}\text{H}_{11}\text{BrFN}_2$ 341.0090, found 341.0095.

2-[2-Phenyl-1-[4-(trifluoromethyl)phenyl]ethyl]malononitrile (15): Prepared according to the typical procedure, benzyltrimethylsilane (76 μL , 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, CDCl_3) 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; ^{13}C NMR (75 MHz, CDCl_3) 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 $[\text{M} - \text{H}]^-$ calculated for $\text{C}_{18}\text{H}_{12}\text{F}_3\text{N}_2$ 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, CDCl_3) 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; ^{13}C NMR (75 MHz, CDCl_3) 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 $[\text{M} - \text{H}]^-$ calculated for $\text{C}_{18}\text{H}_{11}\text{BrF}_3\text{N}_2$ 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 $^+\text{ClO}_4^-$ (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 h. 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 μL , 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, CDCl_3) 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; ^{13}C NMR (75 MHz, CDCl_3) δ = 137.2, 129.2, 127.8, 127.4, 113.2, 113.1, 37.8, 25.2, –2.1 ppm; HRMS-ESI $[\text{M} - \text{H}]^-$ calculated for $\text{C}_{18}\text{H}_{15}\text{N}_2\text{Si}$ 227.1010, found 227.1010.

2-[m-Tolyl(trimethylsilyl)methyl]malononitrile (18): Prepared according to the typical procedure, hexamethyldisilane (81.7 μL , 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, CDCl_3) 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; ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{M} - \text{H}]^-$ calculated for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{Si}$ 241.1166, found 241.1161.

2-[(4-Methoxyphenyl)(trimethylsilyl)methyl]malononitrile (19): Prepared according to the typical procedure, hexamethyldisilane (81.7 μL , 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, CDCl_3) 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 [$M - H$] $^-$ 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 [$M - H$] $^-$ 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 [$M - H$] $^-$ calculated for $\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_2\text{Si}$ 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 [$M - H$] $^-$ calculated for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{Si}$ 277.1166, found 277.1166.

2-[[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 benzyldienemalononitrile (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 [$M - H$] $^-$ calculated for $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_2\text{Si}$ 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), benzylation 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.

Acknowledgments

We are grateful for the financial support provided by National Natural Science Foundation of China (Grant No. 21702142, 21871205), and the Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi (Grant No. 201802024).

Keywords: Radical cations · Fragmentation · Allylation · Benzylation · Silylation

- [1] For selected reviews, see: a) N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075; b) D. Ravelli, S. Protti, M. Fagnoni, *Chem. Rev.* **2016**, *116*, 9850; c) K. L. Skubi, T. R. Blum, T. P. Yoon, *Chem. Rev.* **2016**, *116*, 10035; d) R. Brimioulle, D. Lenhart, M. M. Maturi, T. Bach, *Angew. Chem. Int. Ed.* **2015**, *54*, 3872; *Angew. Chem.* **2015**, *127*, 3944; e) C. K. Prier, D. A. Rankin, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322; f) J. Xuan, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2012**, *51*, 6828; *Angew. Chem.* **2012**, *124*, 6934; g) J. M. R. Narayanam, C. R. Stephenson, *Chem. Soc. Rev.* **2011**, *40*, 102.
- [2] For reviews, see: a) Y. Zhao, Y. Lv, W. Xia, *Chem. Rev.* **2019**, *19*, 424; b) J. Streuff, A. Gansäuer, *Angew. Chem. Int. Ed.* **2015**, *54*, 14232; *Angew. Chem.* **2015**, *127*, 14438; c) M. Fagnoni, D. Dondi, D. Ravelli, A. Albin, *Chem. Rev.* **2007**, *107*, 2725.
- [3] For reviews, see: a) L. Capaldo, D. Ravelli, *Eur. J. Org. Chem.* **2017**, 2056; b) S. Protti, M. Fagnoni, D. Ravelli, *ChemCatChem* **2015**, *7*, 1516.
- [4] For selected recent examples, see: a) N. A. Romero, K. A. Margrey, N. E. Tay, D. A. Nicewicz, *Science* **2015**, *349*, 1326; b) D. J. Wilger, J.-M. M. Grandjean, T. R. Lammert, D. A. Nicewicz, *Nat. Chem.* **2014**, *6*, 720; c) D. S. Hamilton, D. A. Nicewicz, *J. Am. Chem. Soc.* **2012**, *134*, 18577; d) S. Lin, M. A. Ischay, C. G. Fry, T. P. Yoon, *J. Am. Chem. Soc.* **2011**, *133*, 19350; e) M. A. Ischay, Z. Lu, T. P. Yoon, *J. Am. Chem. Soc.* **2010**, *132*, 8572.
- [5] a) M. Schmitt, A. Burghart, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2550; *Angew. Chem.* **1997**, *109*, 2658; b) A. Albin, M. Mella, M. Freccero, *Tetrahedron* **1994**, *50*, 575.
- [6] R. Zhou, H. Liu, H. Tao, X. Yu, J. Wu, *Chem. Sci.* **2017**, *8*, 4654.
- [7] H. G. Roth, N. A. Romero, D. A. Nicewicz, *Synlett* **2016**, 27, 714.
- [8] For selected examples: a) S. Montanaro, D. Ravelli, D. Merli, M. Fagnoni, A. Albin, *Org. Lett.* **2012**, *14*, 4218; b) T. Hayamizu, H. Maeda, K. Mizuno, *J. Org. Chem.* **2004**, *69*, 4997; c) T. Hayamizu, M. Ikeda, H. Maeda, K. Mizuno, *Org. Lett.* **2001**, *3*, 1277; d) T. Hayamizu, H. Maeda, M. Ikeda, K. Mizuno, *Tetrahedron Lett.* **2001**, *42*, 2361; e) K. Mizuno, K. Nakanishi, J.-i. Chosa, Y. Otsuji, *J. Organomet. Chem.* **1994**, *473*, 35; f) K. Mizuno, K. Nakanishi, J.-i. Chosa, T. Nguyen, Y. Otsuji, *Tetrahedron Lett.* **1989**, *30*, 3689; g) K. Mizuno, M. Ikeda, Y. Otsuji, *Chem. Lett.* **1988**, *17*, 1507.
- [9] M. Silvi, C. Verrier, Y. P. Rey, L. Buzzetti, P. Melchiorre, *Nat. Chem.* **2017**, *9*, 868.
- [10] a) J. A. Milligan, J. P. Phelan, S. O. Badir, G. A. Molander, *Angew. Chem. Int. Ed.* **2019**, *58*, 6152; *Angew. Chem.* **2019**, *131*, 6212; b) M. Jouffroy, D. N. Primer, G. A. Molander, *J. Am. Chem. Soc.* **2016**, *138*, 475.
- [11] a) X.-Z. Fan, J.-W. Rong, H.-L. Wu, Q. Zhou, H.-P. Deng, J. D. Tan, C.-W. Xue, L.-Z. Wu, H.-R. Tao, J. Wu, *Angew. Chem. Int. Ed.* **2018**, *57*, 8514; *Angew. Chem.* **2018**, *130*, 8650; b) H.-P. Deng, Q. Zhou, J. Wu, *Angew. Chem. Int. Ed.* **2018**, *57*, 12661; *Angew. Chem.* **2018**, *130*, 12843; c) J. Hou, A. Ee, H. Cao, H.-W. Ong, J.-H. Xu, J. Wu, *Angew. Chem. Int. Ed.* **2018**, *57*, 17220; *Angew. Chem.* **2018**, *130*, 17466; d) H. Deng, X. Fan, Z. Chen, Q. Xu, J. Wu, *J. Am. Chem. Soc.* **2017**, *139*, 13579; e) R. Zhou, Y. Y. Goh, H. Liu, H. Tao, L. Li, J. Wu, *Angew. Chem. Int. Ed.* **2017**, *56*, 16621; *Angew. Chem.* **2017**, *129*, 16848.
- [12] J. P. Dinnozenzo, S. Farid, J. L. Goodman, I. R. Gould, W. P. Todd, S. L. Mattes, *J. Am. Chem. Soc.* **1989**, *111*, 8973.
- [13] For selected hydrosilylation reviews, see: a) X.-Y. Du, Z. Huang, *ACS Catal.* **2017**, *7*, 1227; b) J. Sun, L. Deng, *ACS Catal.* **2016**, *6*, 290; c) E. Malacea, R. Poli, E. Manoury, *Coord. Chem. Rev.* **2010**, *254*, 729; d) B. Marciniak, *Hydrosilylation: A Comprehensive Review on Recent Advances*, Springer, **2009**.
- [14] a) T. J. Steiman, C. Uyeda, *J. Am. Chem. Soc.* **2015**, *137*, 6104; b) N. Kamine, M. Abe, R. Suda, M. Hirano, *Organometallics* **2015**, *34*, 432; c) K.

- Taheshita, Y. Seki, K. Kawamoto, S. Murai, N. Sonoda, *J. Org. Chem.* **1987**, 52, 4864.
- [15] a) H. Qrareya, D. Dondi, D. Ravelli, M. Fagnoni, *ChemCatChem* **2015**, 7, 3350; b) See ref.^[14b]; c) H. Dong, Y. Jiang, H. Berke, *J. Organomet. Chem.* **2014**, 750, 17.
- [16] The methoxytrimethylsilane byproduct was detected using GC-Mass analysis of the crude mixture of the reaction between allyltrimethylsilane **1** and benzylidenemalononitrile **2** under the standard conditions, which further supports the radical cation fragmentation process.
- [17] H. Zipse, *Radical Stability-A Theoretical Perspective in Topics in Current Chemistry*, Vol. 263 (Ed.: A. Gansäuer), Springer, Berlin, Heidelberg, **2006**, pp. 163–189.
- [18] D. Yang, H. Yang, H. Fu, *Chem. Commun.* **2011**, 47, 2348–2350.
- [19] S. Förster, O. Tverskoy, G. Helmchen, *Synlett* **2008**, 18, 2803–2806.
- [20] J. Li, M. J. Lear, Y. Hayashi, *Angew. Chem. Int. Ed.* **2016**, 55, 9060; *Angew. Chem.* **2016**, 128, 9206.
- [21] M. S. Poslusney, C. Sevel, T. J. Utley, T. M. Bridges, R. D. Morrison, N. R. Kett, D. J. Sheffler, C. M. Niswender, J. S. Daniels, P. J. Conn, C. W. Lindsley, M. R. Wood, *Bioorg. Med. Chem. Lett.* **2012**, 22, 6923.

Received: June 25, 2019