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Control of Chemoselectivity of SET-Promoted Photoaddition Reactions of Fullerene C_{60} with α-Trimethylsilyl Group Containing *N*-alkylglycinates Yielding Aminomethyl-1,2-dihydrofullerenes or Fulleropyrrolidines

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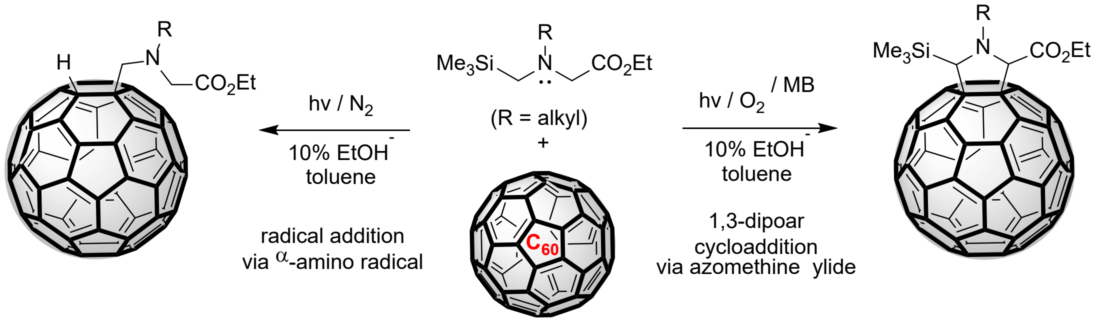
Graphical Abstract



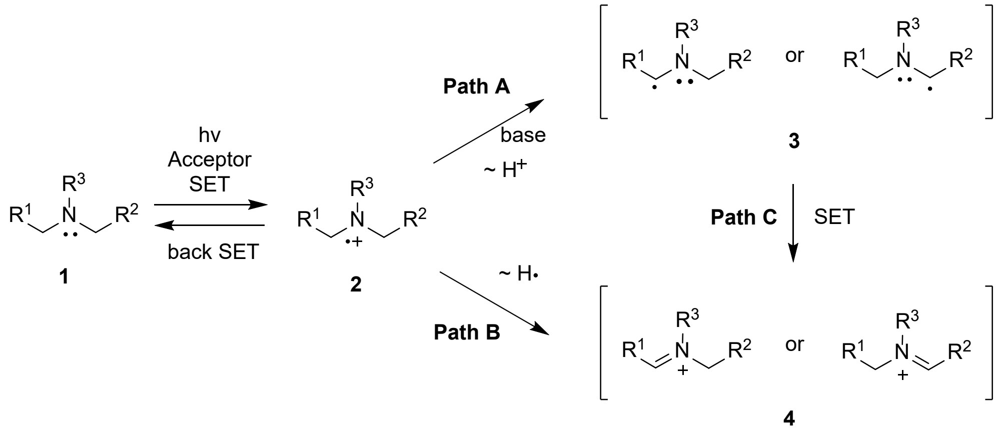
Abstract

Knowledge about factors that govern chemoselectivity is pivotal to the design of reactions that are utilized to produce complex organic substances. In the current study, SET-promoted photoaddition reactions of fullerene C_{60} with both trimethylsilyl and various alkyl group containing glycinates, ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates were explored to evaluate how the nature of *N*-alkyl substituents of glycinate substrates and reaction conditions govern the chemoselectivity of reaction pathways followed. The results showed that photoreactions of C_{60} with glycinates, performed in deoxygenated conditions, produced aminomethyl-1,2-dihydrofullerenes efficiently through a pathway involving addition of α-amino radical intermediates that are generated by sequential SET- solvent-assisted desilylation of glycinate substrates to C_{60}. Under oxygenated conditions, photoreactions of the glycinate substrates, except *N*-benzyl substituted analogs, did not take place efficiently owing to quenching of $^3C_{60}^*$ by oxygen. Interestingly, *N*-benzyl substituted glycinates did react under these conditions to form fulleropyrrolidines through a pathway involving 1,3-dipolar cycloaddition of in situ formed azomethine ylides to C_{60}. The ylide intermediates were formed by regioselective H-atom transfer from glycinates by singlet oxygen. Furthermore, methylene blue (MB) photosensitized reactions of C_{60} with glycinates under oxygenated conditions took place efficiently to produce fulleropyrrolidines independent of the nature of the *N*-alkyl substituents of glycinates.

Introduction

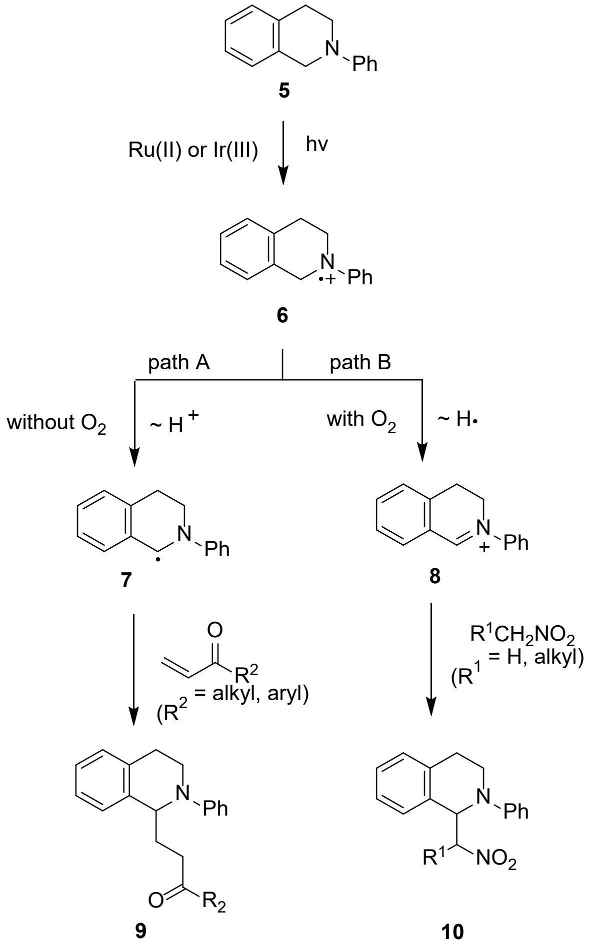
Among the variety of organic substances that participate in photoinduced single electron transfer (SET) processes, aliphatic/aromatic amines have a long abundant history as readily oxidized (E_{ox} < 1 V vs SCE) electron donors that undergo photoaddition reactions with a host of different electron acceptors.[1-5] In these photochemical reactions, amine radical cations **2** (*i.e.*, aminium radicals) generated by SET from amines serve as key reactive intermediates,[1,3b,5] that undergo diverse reactions including energy-wasting back-SET to reform ground state of donors and acceptors[6] and base-promoted deprotonation at α-carbons to form α-amino radicals **3-4** (Path A in Scheme 1).[1b,3a,7,8] Electron rich α-amino radicals formed in this manner participate in radical coupling or nucleophilic addition to electron deficient olefins, cyanoarenes, and α,β-unsaturated ketones.[4,5,9,10] Another common viable route of aminium radicals **2** is hydrogen atom transfer (HAT) from α-carbons to produce iminium ions **5-6**. (Path B in Scheme 1),[5,11,12] which also arise by SET from the readily oxidized α-amino radical intermediates **3-4** (E_{ox} = *ca.* - 1 V)[13] (Path C in Scheme 1). Owing to the electrophilic nature of iminium ions, they are readily captured by a wide range of nucleophiles *via* carbon-carbon or carbon-heteroatom bond forming processes.[11,12,14]

Scheme 1. Reaction pathways followed in SET-promoted photochemical reactions of amines



Since each of pathways that are followed in SET photochemical reactions of amines have the capability of generating interesting products, amine-based photochemical reactions have high preparative potential, but only if approaches are available to gain control over regioselectivity and chemoselectivity.[11a,8b,15] Several strategies have been developed thus far to control these features, especially in SET photosensitized oxidation reactions of tertiary amines where intermediate aminium radicals generally undergo α-CH deprotonation to produce α-amino radicals[7,8] or H-atom transfer (HAT) to external oxidant such as molecular oxygen (O_2) to form iminium ions.[5,11,12,15] Combined with this protocol, selection of appropriate trapping agents capable of intercepting generated intermediates is inevitable to complete reactions. Pertinent examples are found in early studies by Stephenson and König, which showed that photosensitizer-catalyzed photoreactions of *N*-phenyltetrahydroisoquinoline **5** with nitromethane ($R^1CH_2NO_2$, Nu^-) or enone ($CH_2{=}CHCOR^2$, E^+).[11a,12a,15a] As depicted in Scheme 2, when the transition metal complex sensitized photoreactions of **5** were performed in the presence of both molecular oxygen and nucleophiles like nitromethane, product formation took place through a pathway involving iminium ions **8**. In contrast, the reactions of **7** with electrophilic enone conducted in oxygen-free condition led to final photoadduct **9** through addition of α-amino radicals **7** to enone.

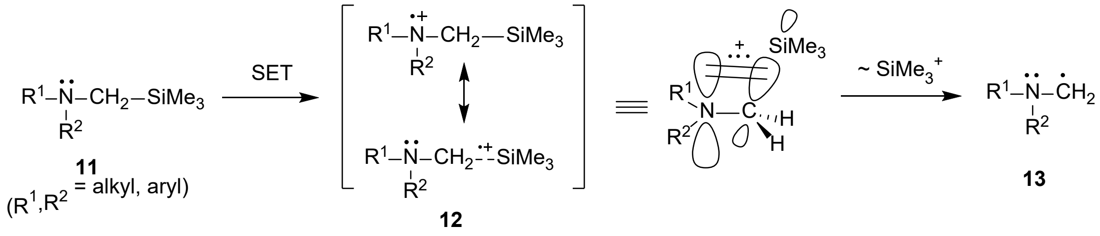
Scheme 2. Photoreactions of *N*-phenyltetrahydroisoquinoline with nitromethane/ enone



One another excellent approach to govern both regioselectivity and chemoselectivity of tertiary amines was developed in earlier independent investigation by Mariano, and Yoon,[3,4a,7a,4c,16] which showed that α-trimethylsilyl substituted tertiary amines serve as useful precursors of α-amino radicals owing to the fact that α-trimethylsilyl group greatly lowers oxidation potentials of amines and the resulting aminium radicals undergo rapid and selective desilylation to form α-amino radicals **13**.[7a,17]

(Scheme 3) Based on this strategy, several photoaddition and photocyclization reactions has been employed to prepare amine-functionalized photoproducts.[4a,4c]

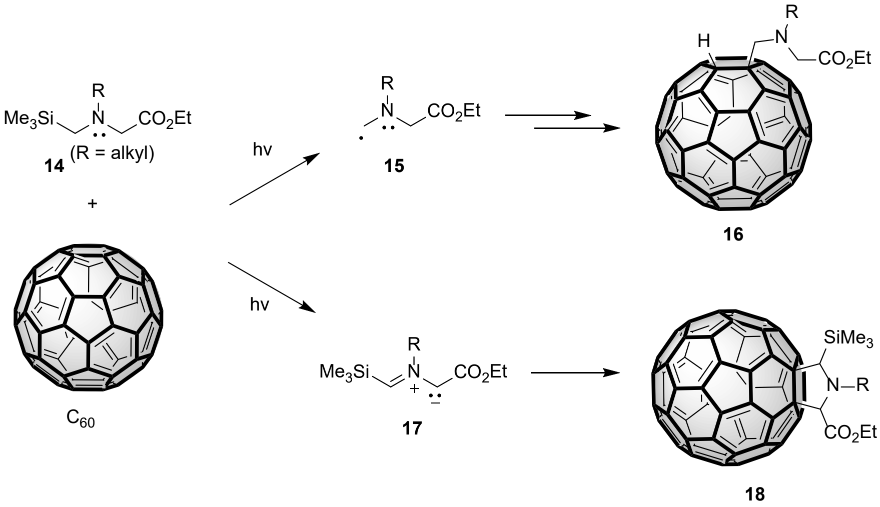
Scheme 3. Selective SET- desilyation process of α-trimethylsilyl substituted tertiary amines



1,3-dipolar cycloaddition reactions are a highly useful and reliable synthetic method that lead to construction of five-membered heterocycles.[18] In particular, the reaction using azomethine ylides with dipolarophiles is a powerful method for the synthesis of diversely substituted pyrrolidines. Classical azomethine ylide forming reactions involve deprotonation (or decarboxylation) of intermediates in situ generated by the reaction of aldehydes with a secondary amines bearing an electron-withdrawing group, ring opening reactions of aziridines, and metal-catalyzed α-iminoesters. Besides these thermal synthesis, recent development of photoredox catalysis reactions also was able to provide an efficient photochemical method for the generation of 1,3-dipolar azomethine ylide intermediates through deprotonation of photochemically generated iminium ions.[11]

In our studies aimed at exploring application of amine SET photochemistry to the synthesis of functionalized fullerenes,[19,20] we observed that photoreaction of C_{60} with α-trimethylsilyl substituted amines in deoxygenated condition promotes formation of aminomethyl-1,2-dihydrofullerenes *via* exclusive generation and addition of α-amino radicals produced by sequential SET-desilylation processes from α-trimethylsilyl amines. More recently, we found that both α-trimethylsilyl and α-alkoxycarbonyl groups containing amines **14** (*i.e.*, ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates) serve as precursors of not only α-amino radicals **15** but also azomethine ylides **17**. (Scheme 4) What made these reactions especially interesting was that photochemical reaction pathways open to glycinates **14** can be effectively governed by reaction conditions employed and, in addition, resulting intermediates can be captured by common fullerene C_{60} through either radical addition of α-amino radicals (leading to aminomethyl-1,2-dihydrofullerenes **15**) or 1,3-dipolar cycloaddition of ylides (leading to fulleropyrrolidines **18**). Thus, in the current study described below, we thoroughly explored how *N*-alkyl substituents of glycinate substrates (i.e., *N*-aliphatic alkyl, *N*-phenethyl and *N*-benzyl moieties) and reaction conditions (*i.e.*, N_2 vs O_2-purged condition, presence/absence of a photosensitizer) govern the chemoselectivity of SET-promoted photoaddition reactions of fullerene C_{60} with ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates.

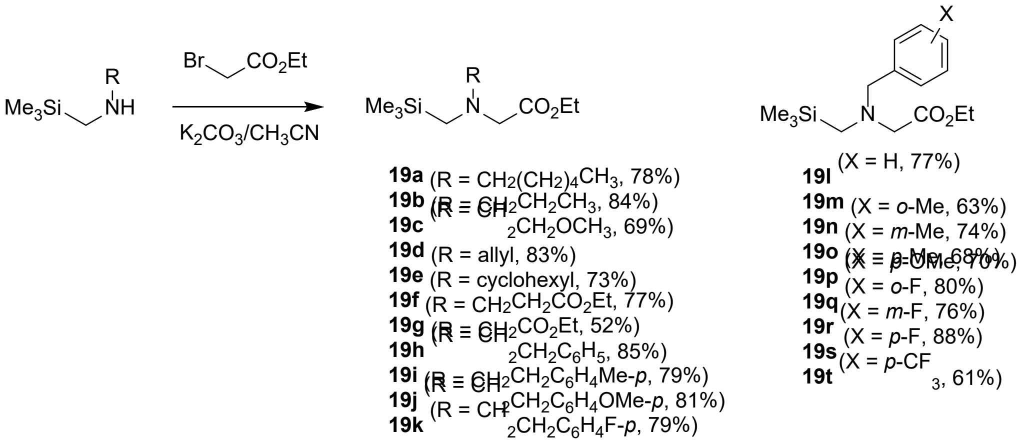
Scheme 4. Photoaddition reaction of C_{60} with ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates



Results and Discussion

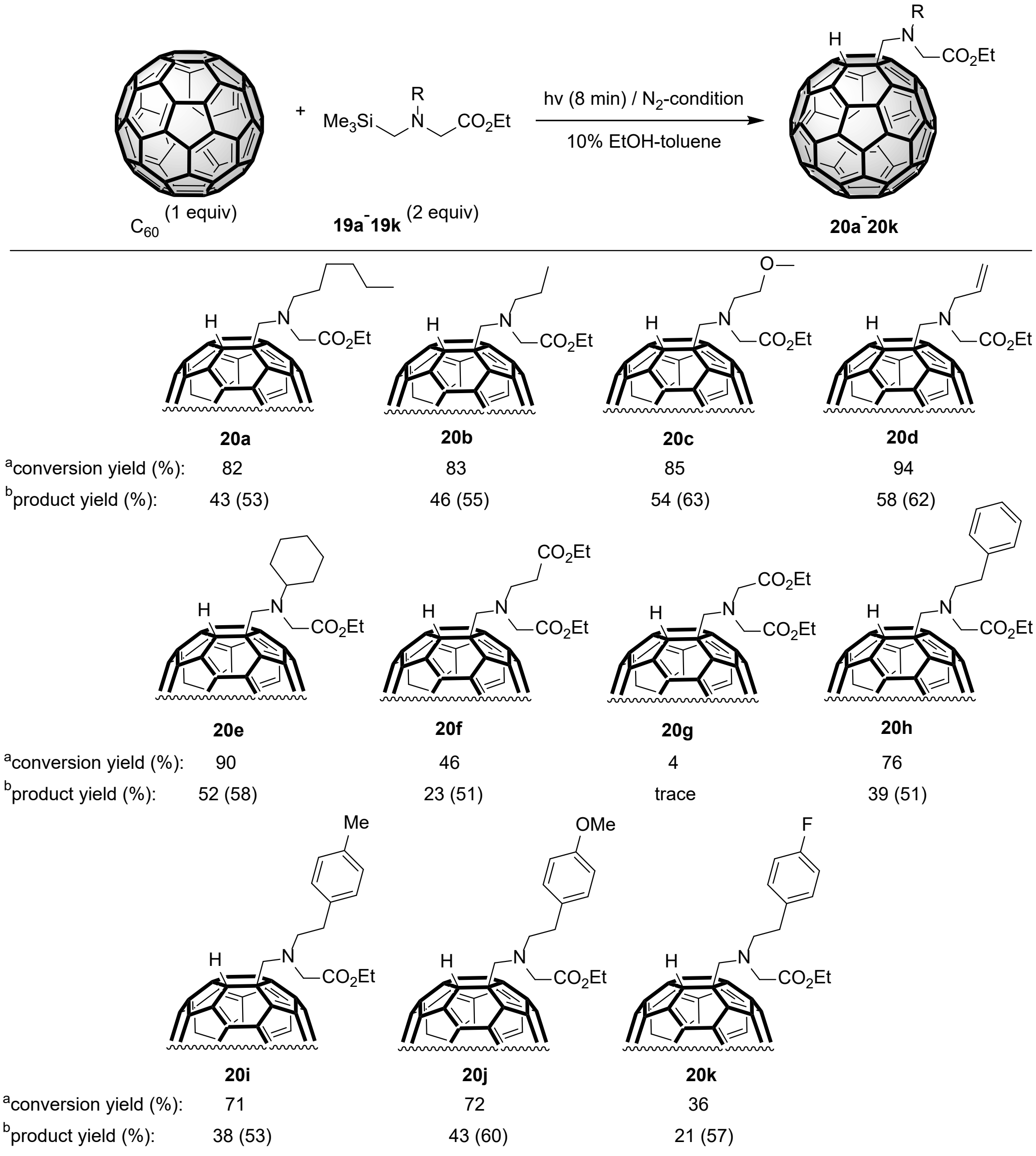
Photoreactions of C₆₀ with ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates in deoxygenated condition. A variety of alkyl- and trimethylsilyl group substituted glycinates **19a-19t** used to explore photoreactions with C_{60} were prepared by using the general synthetic procedures shown in Scheme 5, involving base-catalyzed alkylation of respective secondary trimethylsilyl group containing *N*-alkylamines[19a,21a] with ethyl bromoacetate ($BrCH_2CO_2Et$).[21d]

Scheme 5. Synthesis of ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl))glycinates **19a-19t**



Photoaddition reactions of 10% EtOH-toluene (v/v) solutions containing C_{60} (0.28 mmol, 1 equiv) and **19a-19t** (0.56 mmol, 2 equiv) were performed by irradiation (450 W Hanovia medium pressure mercury lamp equipped with flint glass filter (> 310 nm)) under deoxygenated (N_2-purged) conditions. The photolysates were then purified by column chromatography to determine conversion of C_{60} and photoproducts yields.

Scheme 6. Photoreactions of C_{60} with ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates **19a-19k**



	20a	20b	20c	20d
[a]conversion yield (%):	82	83	85	94
[b]product yield (%):	43 (53)	46 (55)	54 (63)	58 (62)

	20e	20f	20g	20h
[a]conversion yield (%):	90	46	4	76
[b]product yield (%):	52 (58)	23 (51)	trace	39 (51)

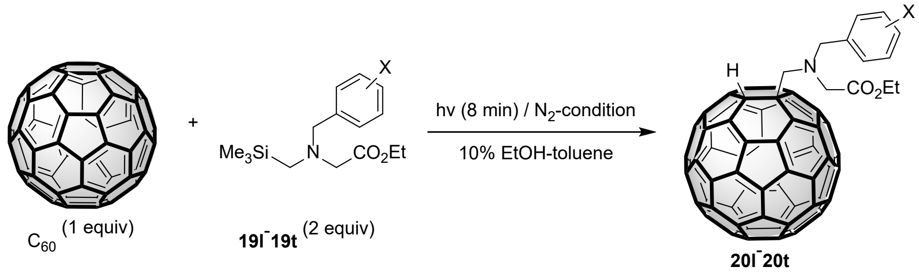
	20i	20j	20k
[a]conversion yield (%):	71	72	36
[b]product yield (%):	38 (53)	43 (60)	21 (57)

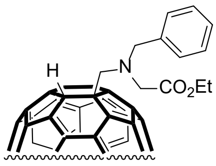
[a]Conversion yields were determined by recovered C$_{60}$. [b]Product yields were determined after isolation. Those in parentheses were determined based on consumed C$_{60}$. Reaction condition: N$_2$-purged, 10% EtOH-toluene (v/v) solutions (220 mL) containing C$_{60}$ (0.278 mol, 1.26 mM) and glycinate (0.556 mmol, 2.53 mM) were irradiated for 8 min.

First, photoreactions of C$_{60}$ with alkyl group containing glycinates **19a-19k** in the N$_2$-purged environment were conducted. As can be seen by viewing the results in Scheme 6, 8 min irradiation of solutions containing C$_{60}$ and **19a-19e** brought about high conversion of C$_{60}$ (*ca.* 82-94%) and efficient formation of aminomethyl-1,2-dihydrofullerenes **20a-20e** as the sole adduct. Similarly, photoreactions of C$_{60}$ with *N*-phenethyl substituted glycinates **19h-19j** promoted by 8 min irradiation produced the same types of photoproducts **20h-20j**, albeit relatively lower conversion and product yields than those of **19a-19e**. It is noteworthy to mention that no photoproducts of multi-addition of the amines to C_{60} were formed even under conditions where an excess of glycinates (2.8 mmol, 10 equiv) was employed and, in addition, photoreactions did not take place even by much longer irradiation time in the absence of EtOH from the reaction medium.[19a] These observations show that polar protic EtOH enhances the efficiencies of these photoaddition reactions, which proceed through a mechanistic route involving sequential SET-desilylation of α-silylamines as well as protonation of photoadduct precursors, aminomethylated fullerene anions, in the final reaction process (see below mechanistic reaction pathways). In contrast to those of **19a-19e** and **19h-19j**, photoreactions using **19f**, **19g** and **19k** took place much less efficiently, mainly due to the electronic nature of electron withdrawing group near the nitrogen atom. Especially, when electron withdrawing ethoxycarbonyl group (-CO_2Et) as an alkyl substituent was closer to nitrogen atom (**19g**), both conversion and product yields were much lowered than that of further to nitrogen atom (**19f**).

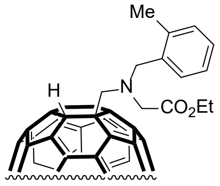
The results of photoreactions of C_{60} with *N*-benzyl substituted glycinates **19l-19t**, in which benzyl groups contain Me, OMe, F and CF_3 substituted phenyl rings,[21a] are shown in Scheme 7. Again, 8 min irradiation of 10% EtOH-toluene solutions containing C_{60} and **19l-19p**, where phenyl rings possess non (H)- or electron donating group (Me, OMe), led to formation of aminomethylated fullerenes **20l-20p** as single photoadducts. Likewise, presence of EtOH in the reaction medium was required to produce photoproducts. However, conversion of C_{60} and product yields were much lower than those from **19a-19e** and **19h-19j**. Especially, in case of photoreactions using F and CF_3 substituted phenyl containing glycinates **19q-19t**, no adducts were generated by using 8 min irradiation time and still low conversions and product (**20q-20t**) yields occurred even after a 60 min irradiation time.

Scheme 7. Photoreactions of C_{60} with ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates **19l-19t**

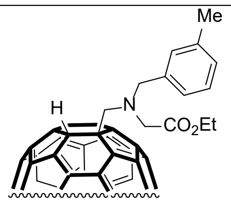




20l

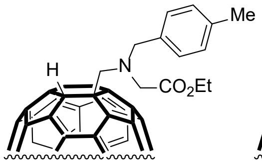


20m

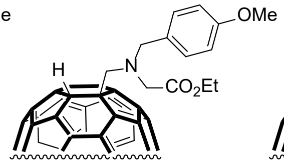


20n

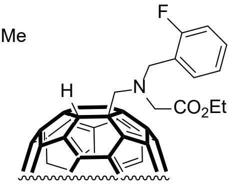
	20l	**20m**	**20n**
irradiation time :	8 min	8 min	8 min
[a]conversion yield (%):	34	35	35
[b]product yield (%):	18 (53)	18 (51)	17 (49)



20o

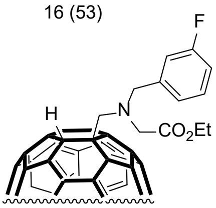


20p

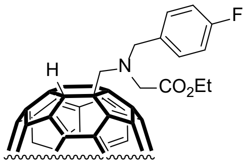


20q

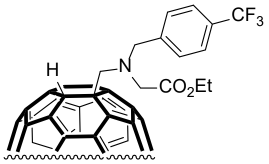
	20o	**20p**	**20q**
irradiation time :	8 min	8 min	60 min
[a]conversion yield (%):	30	32	18
[b]product yield (%):	16 (53)	18 (56)	7 (39)



20r



20s



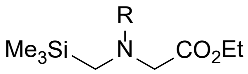
20t

	20r	**20s**	**20t**
irradiation time :	60 min	60 min	60 min
[a]conversion yield (%):	20	22	19
[b]product yield (%):	8 (40)	9 (39)	7 (38)

[a]Conversion yields were determined by recovered C$_{60}$. [b]Product yields were determined after isolation. Those in parentheses were determined based on consumed C$_{60}$. Reaction condition: N$_2$-purged 10% EtOH-toluene (v/v) solutions (220 mL) containing C$_{60}$ (0.278 mol, 1.26 mM) and glycinate (0.556 mmol, 2.53 mM) were irradiated for 8 min (for **19l¯19p**) or 60 min (for **19q¯19t**).

The results of photoreactions described above clearly show that the reaction efficiencies are largely influenced by the nature of *N*-alkyl substituents on glycinate substrates. To obtain semi-quantitative information about the substituent effects on reaction efficiencies, relative reaction quantum yields (Φ_{rel}) for photoreactions of C$_{60}$ with selected glycinates were determined. For this purpose, N_2-purged 10% EtOH-toluene solutions (10 mL) containing C_{60} (1.7 mmol) and each glycinates (3.5 mmol) were simultaneously irradiated for a fixed time period that promotes an average substrates conversion below *ca*. 10%. Photoproduct yields were then determined by using HPLC analysis of crude photolysates and transformed into relative reaction quantum yields (Φ_{rel}) by setting the Φ_{rel} for reaction of **19l** to be unity ($\Phi_{rel} = 1$). As the results summarized in Table 1 show, the reaction efficiencies for photoreactions of electronically neutral and electron donating group substituted *N*-alkyl glycinates like *N*-propyl **19b**, *N*-phenethyl **19h**, *N*-benzyl **19l, 19o** and **19p** analogs were much larger than those containing electron withdrawing groups like **19g**, **19s** and **19t**. Interestingly, in spite of the presence of an electron withdrawing group in glycinate **19f**, the reaction efficiency of **19f** was nearly equal to that of **19l**. Especially, the least reaction efficiency was made in the photoreaction of C_{60} with glycinate **19g**, possessing electron withdrawing ethoxycarbonyl (CO_2Et) group at much close to nitrogen atom.

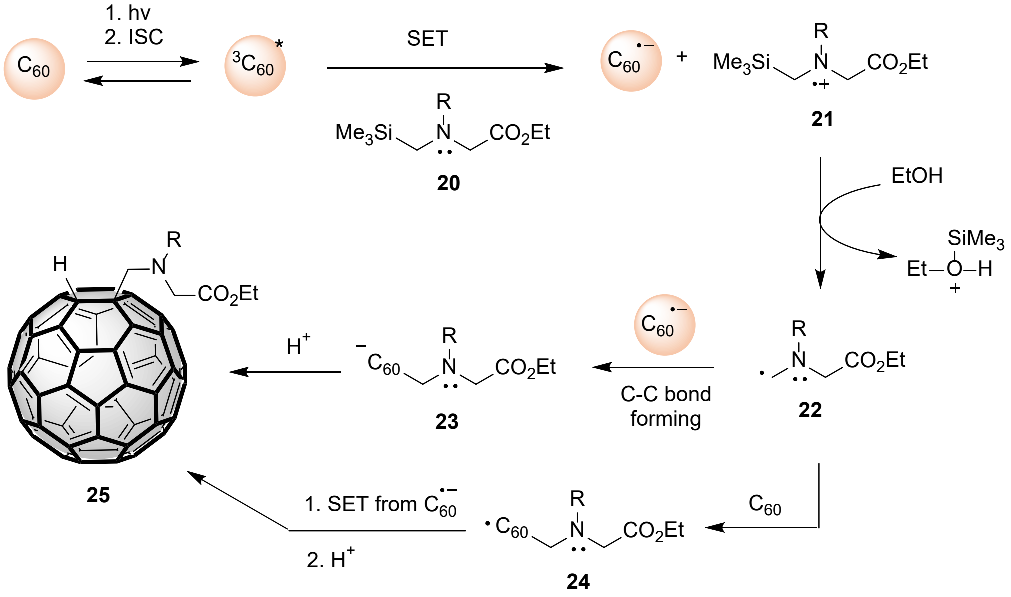
Table 1. Relative reaction quantum yields (Φ_{rel}) of photoreactions of C_{60} with ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates in deoxygenated 10% EtOH-toluene solutions.

	Φ_{rel}
19b (R = $CH_2CH_2CH_3$)	2.4
19f (R = $CH_2CH_2CO_2Et$)	1.1
19g (R = CH_2CO_2Et)	0.05
19h (R = $CH_2CH_2C_6H_5$)	1.5
19l (R = $CH_2C_6H_5$)	1.0
19o (R = $CH_2C_6H_4Me$-*p*)	1.2

19p (R = $CH_2C_6H_4OMe$-*p*)	1.2
19s (R = $CH_2C_6H_4F$-*p*)	0.2
19t (R = $CH_2C_6H_4CF_3$-*p*)	0.1

The mechanism for formation of the aminomethyl-1,2-dihydrofullerenes seem to follow the pathway suggested earlier by our studies[19] (Scheme 8). It is assumed that because the singlet excited state of fullerene ($^1C_{60}^*$) undergoes rapid and efficient intersystem crossing (Φ_{ISC} = 1) to form the triplet excited state of C_{60} ($^3C_{60}^*$)[22,23] and, moreover, the concentrations of the glycinates are in the 2.5 mM range and their oxidation potentials (E_{ox} < 1 V vs SCE) are lower than the reduction potential of $^3C_{60}^*$ ($^3E_{red}$ = 1.14 V vs SCE),[22] (see Table S1 in Supporting Information) it is likely bimolecular SET from glycinates to $^3C_{60}^*$ take place favorably to form aminium radicals **21**. Then, EtOH-assisted desilylation from **21**, occurring in competition with back SET, forms α-amino radicals **22** that can couple with the radical anions of C_{60} ($C_{60}^{\bullet -}$), followed by protonation of the formed anions **23** to generate the aminomethyl-1,2-dihydrofullerenes **25**. Evidence for this proposal comes from the observation that photoreactions of C_{60} with *N*,*N*-dibenzyl-1-(trimethylsilyl)methanamine ($(C_6H_5CH_2)_2NCH_2SiMe_3$) performed in the deuterated 10% EtOD-toluene solution give rise to formation of deuterium-incorporated fullerene products exclusively.[19a] Alternatively, α-amino radical **22** can be added to C_{60} to form fullerene radicals **24** which are then transformed to **25** by SET from $C_{60}^{\bullet -}$, followed by protonation.

Scheme 8. Mechanistic pathways leading to formation of aminomethyl-1,2-dihydrofullerenes from photoreactions of C_{60} and ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates



Based on consideration of this scenario, it is possible to evaluate possible origins of the observed *N*-substituent effects on reaction efficiencies. First, it is unlikely that the effects are a consequence of different rates of EtOH-promoted desilylation of intermediate aminium radicals **21**. Specifically, in earlier laser flash photolysis (LFP) studies with anilinium radicals originating from *N*-α-trimethylsilyl-*N*-alkylanilines ($C_6H_5NRCH_2SiMe_3$), it was found that *N*-electron withdrawing groups (R = CO_2Et and COMe) containing anilinium radicals cause a significant enhancement of the rates of desilylation, compared to *N*-electron donating group (R = Me) tethered analog, owing to the fact that *N*-electron withdrawing group make the oxidation potential of anilinium radicals increased to accelerate the destabilization of anilinium radicals, resulting in a rapid desilylation process.[24] However, this trend is not in accord with those observed in photoreactions of C_{60} with ethyl *N*-alkyl-*N*-

((trimethylsilyl)methyl)glycinates. As an alternative, we consider *N*-substituent can control of the rates of SET from glycinates to $^3C_{60}{}^*$. To address this possibility, ionization potential (IP) of each ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates in ethanol and toluene were calculated by using density functional theory (DFT) with B3LYP hybrid exchange correlation function and the 6-311++G(d,p) basis set. As can be seen from Figure 1, ethoxycarbonyl containing glycinate **19g**, showing the least Φ_{rel} (Φ_{rel} = 0.05), has the highest IPs (5.31 eV in ethanol and 5.91 eV in toluene) whereas the propyl containing glycinate **19b**, showing the highest value (Φ_{rel} = 2.4), has the lowest IPs (5.04 eV in ethanol and 5.68 eV in toluene). These DFT calculation results demonstrate that the reaction efficiency trends of glycinates (Φ_{rel}) parallel with IPs in both solvents, where reaction efficiencies increase as the IPs of the glycinate substrates decrease.

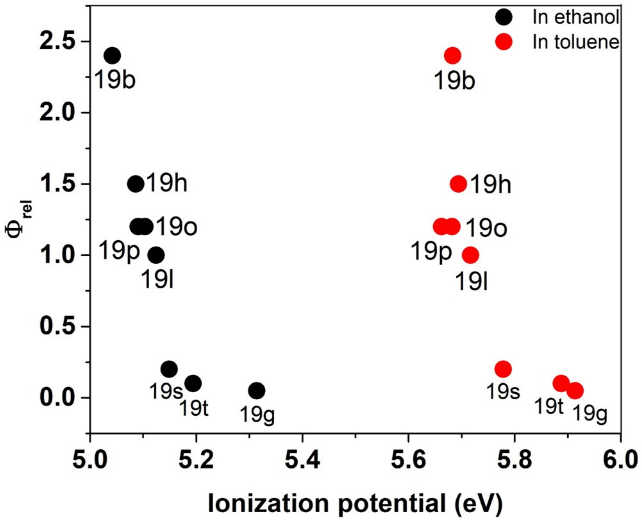
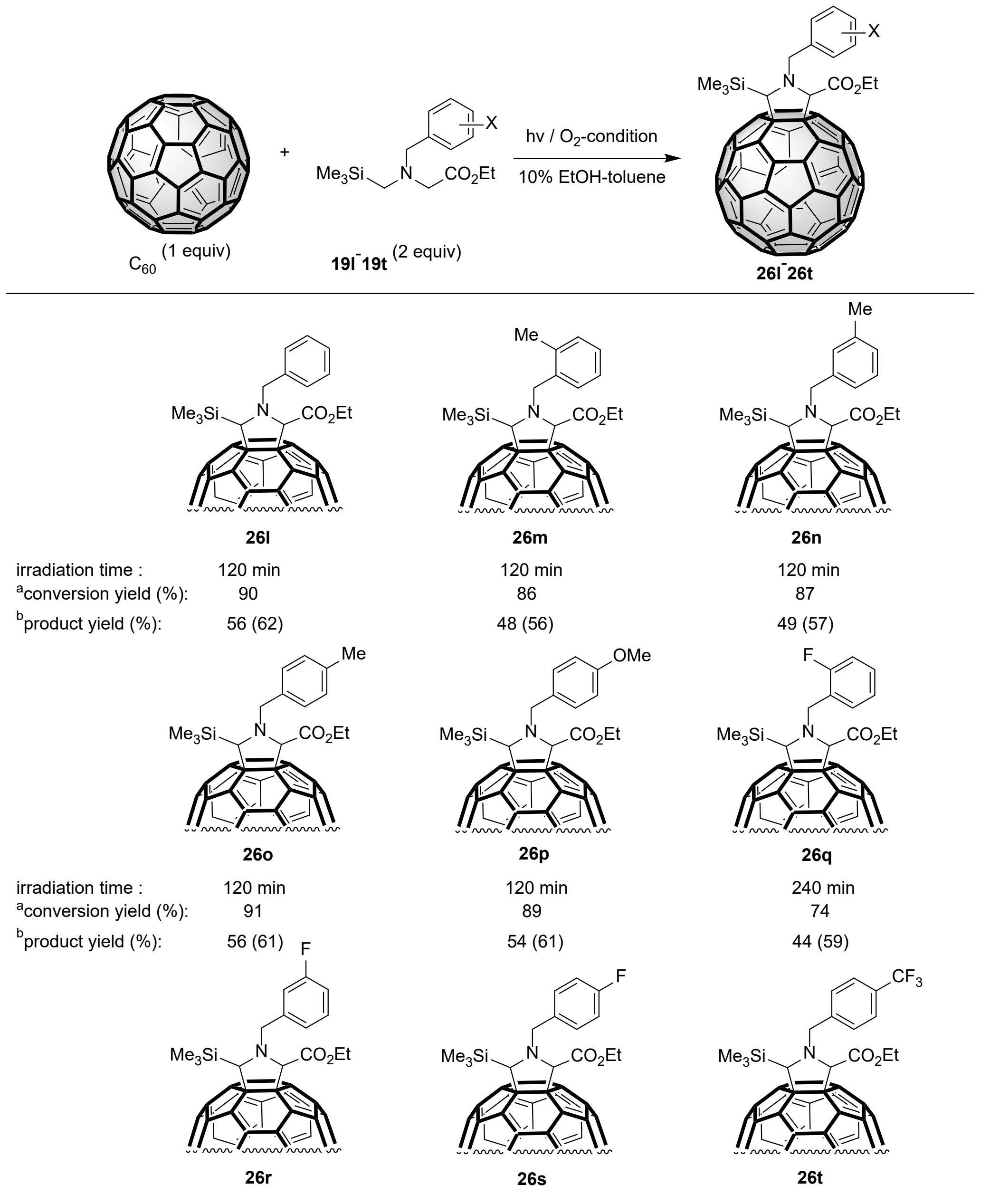


Figure 1. The correlation plot of DFT-calculated ionization energies (IP) of ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates vs their Φ_{rel}. The ionization potentials (IP) were calculated in both ethanol (black dot) and toluene (red dot).

Photoreactions of C_{60} with ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates in oxygenated condition. To assess the effects of oxygen, photoreactions of C_{60} with glycinates **19a-19t** were conducted in the O_2-purged solutions under otherwise identical conditions. At the outset, we expected that the efficiencies of the processes would be decreased by the presence of molecular oxygen (O_2) owing to rapid quenching of $^3C_{60}{}^*$.[22a,25] Indeed, irradiation of O_2-purged solutions of C_{60} and *N*-alkyl or *N*-phenethyl substituted glycinates **19a-19k** did not promote formation of any products even when a much longer irradiation time (8 h) was used. In contrast, the *N*-benzyl substituted glycinates **19l-19t** did react under these conditions, but only inefficiently (*i.e.*, relatively long irradiation times required),[21a] and interestingly, the reactions of **19l-19t** with C_{60} produced pyrrolidine ring fused fullerenes (fulleropyrrolidines **26l-26t**) rather than the corresponding aminomethyl-1,2-dihydrofullerenes **20l-20t** (Scheme 9).

Scheme 9. Photoreactions of C_{60} with ethyl *N*-benzyl-*N*-((trimethylsilyl)methyl)glycinates **19l-19t**



	26l	26m	26n
irradiation time :	120 min	120 min	120 min
[a]conversion yield (%):	90	86	87
[b]product yield (%):	56 (62)	48 (56)	49 (57)

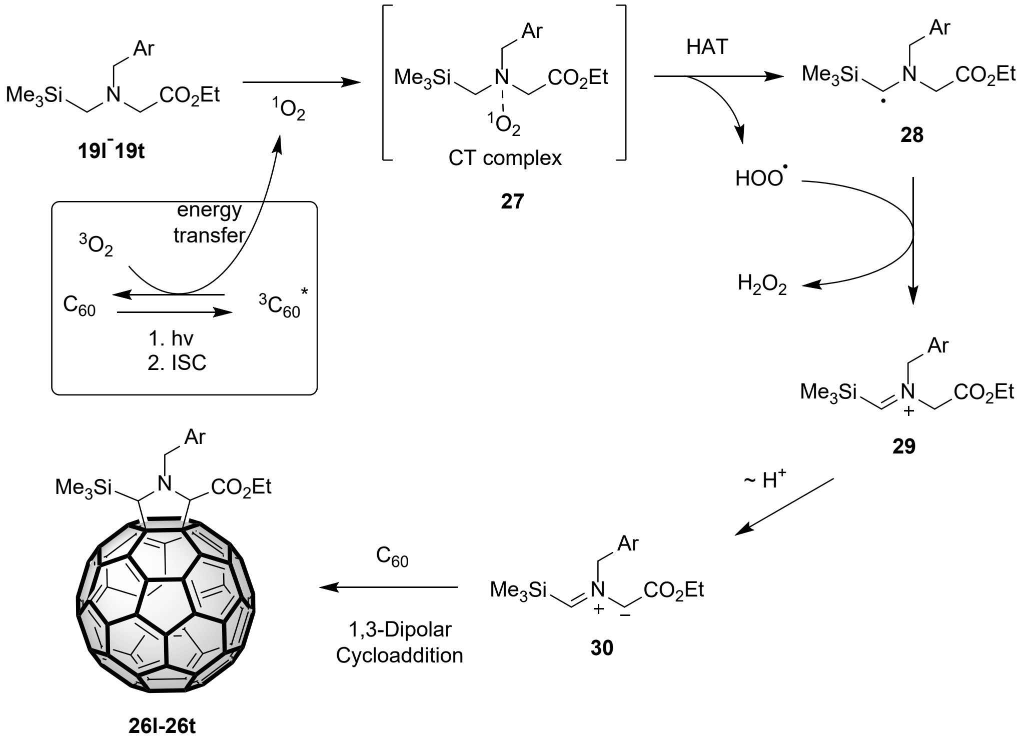
	26o	26p	26q
irradiation time :	120 min	120 min	240 min
[a]conversion yield (%):	91	89	74
[b]product yield (%):	56 (61)	54 (61)	44 (59)

	26r	26s	26t
irradiation time :	240 min	240 min	240 min
[a]conversion yield (%):	76	82	80
[b]product yield (%):	43 (57)	51 (62)	50 (62)

[a]Conversion yields were determined by recovered C_{60}. [b]Product yields were determined after isolation. Those in parentheses were determined based on consumed C_{60}. Reaction condition: O_2-purged 10% EtOH-toluene (v/v) solutions (220 mL) containing C_{60} (0.278 mol, 1.26 mM) and glycinate (0.556 mmol, 2.53 mM) were irradiated for 120 min (for **19l¯19p**) or 240 min (for **19q¯19t**).

On the basis of observation made in earlier studies by Prato[26] as well as by Foote[22c,27] and Baciocchi,[28] plausible mechanistic pathways responsible can be suggested. Fulleropyrrolidine formation in these reactions seems to occur via 1,3-dipolar cycloaddition of azomethine ylide intermediates, generated by singlet oxygen ($^1O_2$) promoted reaction of *N*-α-trimethylsilyl substituted glycinates. (Scheme 10) In this route, photochemically generated $^3C_{60}^*$ participates in energy transfer with $^3O_2$ (k_{ET} (O_2) = 2×10^9 $M^{-1}s^{-1}$)[22a,23a] to generate singlet oxygen ($^1O_2$), which bind to glycinates to form charge-transfer complexes (CT-complex) **27**.[29,30] Regioselective H-atom transfer (HAT) in the complexes occur to form the α-amino radicals **28** and hydroperoxy radicals ($HOO^\bullet$).[28] Oxidation of **28** produces the iminium ions **29** which undergo deprotonation to form the key ylides **30**, serving as the precursor of fulleropyrrolidine **26l-26t**.

Scheme 10. Mechanistic route involving formation of fulleropyrroldines **26l-26t** in oxygenated condition



This mechanistic route proposed for fulleropyrrolidine formation gains support from experiments carried out using the known single oxygen quencher 1,4-diazabicyclo[2.2.2]octane (DABCO). [28,29] As depicted in Figure 2, when the oxygenated 10% EtOH-toluene solutions of C_{60} and **19l** were irradiated for 2 h in the presence of DABCO, the presence of increasing concentrations (0-63 mM) of DABCO caused a continuous decrease in both conversion of C_{60} and yields of **26l**. These features represents that $^1O_2$ serve as a major participant in photoreactions taking place in the oxygenated condition.

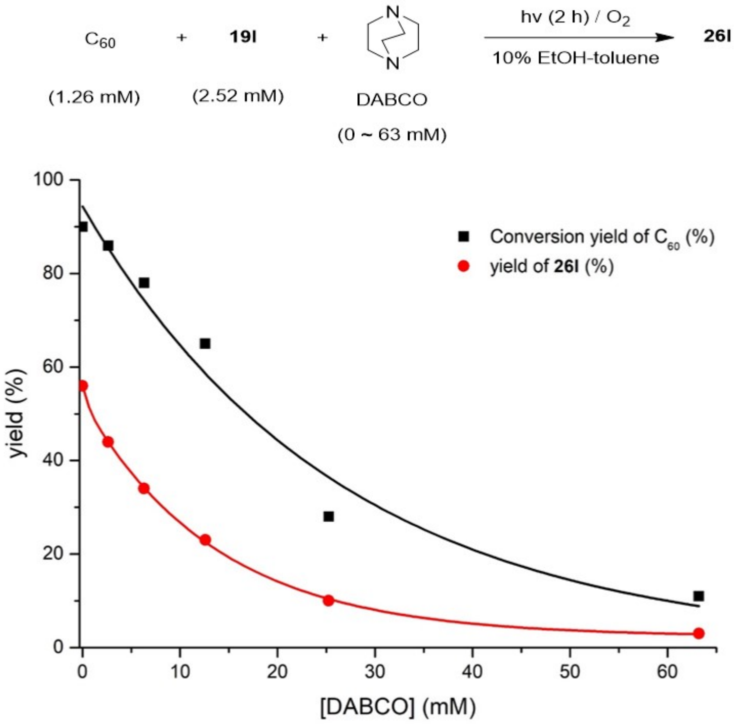
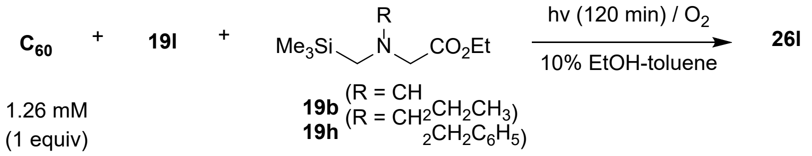


Figure 2. Plots of the both conversion- (black square) and product (red circle) yields as function of concentration of DABCO in the photoreactions of C_{60} with **19l**.
Reaction condition: O_2-purged 10% EtOH-toluene (v/v) solutions (220 mL) containing C_{60} (1.26 mM, 1 equiv) and glycinate **19l** (2.52 mM, 2 equiv) were irradiated for 2 h.

The result of $^1O_2$ quenching experiment using DABCO provided us useful information to guess the reason for why, in contrast to those of glycinates **19l-19t**, photoreactions of C_{60} with *N*-alkyl or *N*-

phenethyl substituted glycinates **19a-19k** did not produce any photoproducts under oxygenated condition. To figure out the reason, photoreactions of oxygenated 10% EtOH-toluene solutions containing C_{60} and glycinate **19l** (2.5 mM) were performed in the presence of *N*-propyl (**19b**) or *N*-phenethyl (**19h**) glycinate (0, 6.3 and 12.6 mM respectively). As can be seen in Table 2, in the presence of 6.3 mM of **19b** or **19h**, both conversion of C_{60} and yields of **26l** arisen from reactions of C_{60} and **19l** were largely decreased. (entries 3 and 5 in Table 2) Moreover, much significant decreases in both conversion and product yields were observed when much higher concentration of **19b** or **19h** (12.6 mM) were present in the solution. (entries 4 and 6 in Table 2) Clearly, no photoproducts derived from the reactions of C_{60} with **19b** or **19h** were observed. These experimental results show that *N*-alkyl (**19a-19g**) or *N*-phenethyl (**19h-19k**) substituted glycinates can serve as a singlet oxygen quencher in the same manner as does DABCO and possibly that they form complexes with $^1O_2$ that do not produce the key ylide intermediates.[29]

Table 2. Product yields changes in the photoreactions of C_{60} with glycinate **19l** under the oxygenated condition.[a]



Entry	reaction condition	conversion (%)[b]	yield of **26l** (%)[c]
1	**19l** (2.5 mM, 2 equiv)	90	56 (62)
2	**19l** (6.3 mM, 5 equiv)	90	56 (62)
3	**19l** (2.5 mM, 2 equiv), **19b** (6.3 mM, 5 equiv)	51	25 (49)

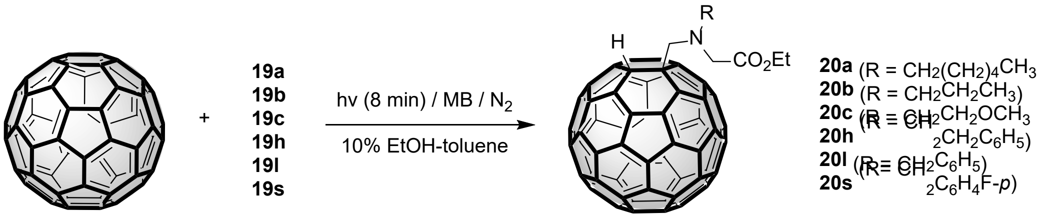
4	**19l** (2.5 mM, 2 equiv), **19b** (12.6 mM, 10 equiv)	13	5 (41)
5	**19l** (2.5 mM, 2 equiv), **19h** (6.3 mM, 5 equiv)	46	23 (50)
6	**19l** (2.5 mM, 2 equiv), **19h** (12.6 mM, 10 equiv)	8	3 (38)

[a]220 ml of oxygenated 10% EtOH-toluene solutions containing C_{60} (1.26 mM, 1eq.) and varying concentration of glycinate **19l** (2.5-25 mM) and additive (**19b** or**19h**) [b]Conversion was determined by recovered C_{60}. [c]Isolation yields. Those in parentheses were based on consumed C_{60}.

Methylene blue (MB) sensitized photoreactions of C_{60} with ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates. Based on the proposal that aminomethyl-1,2-dihydrofullerenes and fulleropyrrolidines forming reactions take place via pathways involving either SET from glycinates to $^3C_{60}{}^*$ or HAT by singlet oxygen, we explored whether these processes could be promoted using typical triplet photosensitizers. For this purpose, we utilized an organic photosensitizer, methylene blue (MB). As a well-known triplet photosensitizer (Φ_{ISC} ($^1MB^*$) = 0.52, $\tau_{triplet}$ = 32 μs),[31] MB has been widely used to generate singlet oxygen and has a high excited state reduction potential ($^3E_{red}$ = 1.6 V vs SCE),[32] which enable SET from amines to $^3MB^*$ to take place efficiently.[33] Indeed, Stern-Volmer plots derived from MB luminescence quenching experiments show that triplet excited state of MB ($^3MB^*$) is efficiently quenched by glycinates (E_{ox} < 1 V vs SCE) even in oxygenated solution. (see Supporting Information)

Prior to performing the reactions under the oxygenated conditions, MB sensitized photoreactions of C_{60} with representative glycinates **19a-19c**, **19h, 19l** and **19s** were carried out in the deoxygenated conditions. As the results depicted in Table 3 show, very little difference existed in photoreactions of the glycinates **19a**-**19c**, **19h**, **19l**, and **19s**, carried out in the absence and presence of MB. These results can be understood that because relative concentration of C_{60} (1.26 mM) is much higher than that of MB (0.063 mM) and most of wavelengths emitted from medium pressure Hg lamp (*i.e.*, 313, 365, 404, 435 and 546 nm) are absorbed by C_{60}, SET taking place from glycinates and $^3C_{60}{}^*$ seems to overwhelm $^3MB^*$ involved excited state deactivation processes.

Table 3. Products and yields in MB-sensitized photoreactions of C_{60} with glycinate **19a**-**19c**, **19h**, **19l**, and **19s** under the deoxygenated condition.[a]



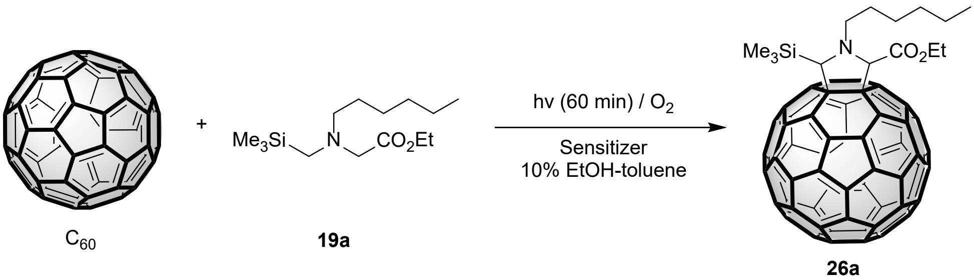
entry	Substrate and MB	conversion (%)[b]	yields (%) of **20**[c]
1	**19a** with MB (0.063 mM)	83	44 (53)
2[d]	**19a** without MB	82	43 (53)
3	**19b** with MB (0.063 mM)	83	45 (54)
4[d]	**19b** without MB	83	46 (55)
5	**19c** with MB (0.063 mM)	85	55 (65)
6[d]	**19c** without MB	85	54 (63)
7	**19h** with MB (0.063 mM)	75	38 (50)
8[d]	**19h** without MB	76	39 (51)
9	**19l** with MB (0.063 mM)	34	17 (49)
10[e]	**19l** without MB	34	18 (53)
11	**19s** with MB (0.063 mM)	22	10 (43)

12[e]	**19s** without MB	22	9 (39)

[a] 220 ml of 10% EtOH-toluene solutions containing C_{60} (1.26 mM, 1eq.), glycinate (2.53 mM, 2 eq.) and MB (5 mol %) was irradiated for 8 min. [b] Conversion was determined by recovered C_{60}. [c] Isolation yields. Those in parentheses were based on consumed C_{60}. [d] Data from Scheme 6. [e] Data from Scheme 7

MB sensitized photoreactions of C_{60} with glycinates under oxygenated condition showed highly interesting results. As shown in Table 4, in contrast to photoreactions of C_{60} with **19a** in the absence of MB, which did not produce any photoadduct (entry 7 in Table 4), the MB sensitized reaction of **19a** in O_2-purged 10% EtOH-toluene solution did occur to produce fulleropyrrolidine **26a** in a highly efficient manner. (entry 1 in Table 4) Notably, both the conversion of C_{60} and yield of **26a** were not affected by using high concentration of MB (from 0.063 to 0.25 mM) or **19a** (from 2.53 to 6.3 mM) (entries 2-4 in Table 4). Moreover, other sensitizers like rose Bengal (RB) (entry 5) and eosin Y (entry 6) also promoted photoinduced conversion of **19a** to **26a**.

Table 4. Product and yield in MB sensitized photoreactions of C_{60} with **19a** under oxygenated condition[a]



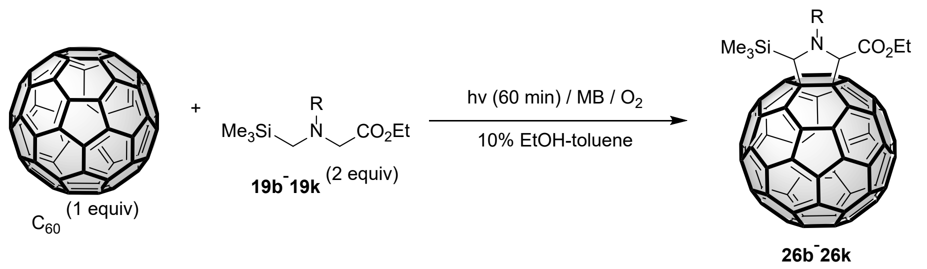
entry	amine and sensitizer	conversion (%)[b]	yields (%) of **26a**[c]
1	**19a** (2.53 mM), MB (0.063 mM)	82	48 (59)
2	**19a** (6.3 mM), MB (0.063 mM)	81	50 (62)
3	**19a** (2.53 mM), MB (0.126 mM)	80	43 (53)

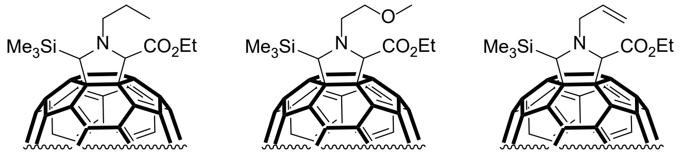
4	**19a** (2.53 mM), MB (0.25 mM)	81	43 (53)
5	**19a** (2.53 mM), RB (0.063 mM)	80	42 (53)
6	**19a** (2.53 mM), EY (0.063 mM)	76	40 (55)
7	**19a** (2.53 mM), no MB	n.r[d]	n.r[d]

[a] 220 ml of 10% EtOH-toluene solutions containing C_{60} (1.26 mM), glycinate (2.53-6.3 mM) and photosensitizer like MB, RB and EY (0.063-0.25 mM) was irradiated for 60 min. [b] Conversion was determined by recovered C_{60}. [c] Isolation yields. Those in parentheses were based on consumed C_{60}. [d] No reaction

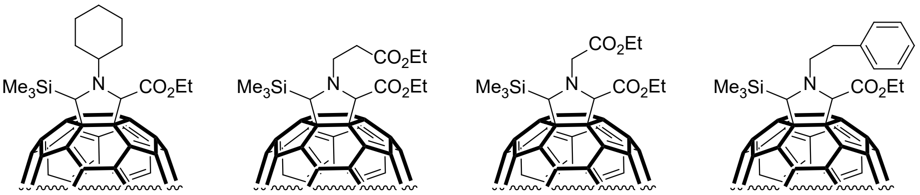
With the results of MB sensitized reaction of **19a** in hand, we next examined the scope and generality of these reaction protocols. As described in Scheme 11, 60 min irradiation of oxygenated 10% EtOH-toluene solutions containing C_{60} and glycinates **19b-19k** in the presence of MB led to formation of fulleropyrrolidines **26b-26k** as sole photoadducts.

Scheme 11. MB-sensitized photoreactions of C_{60} with ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates **19b-19k**

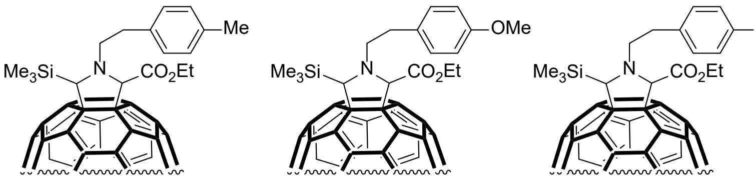




	26b	26c	26d
ᵃconversion yield (%):	83	81	87
ᵇproduct yield (%):	49 (59)	45 (55)	53 (61)



	26e	26f	26g	26h
ᵃconversion yield (%):	75	66	51	52
ᵇproduct yield (%):	42 (46)	33 (50)	27 (53)	31 (59)



	26i	26j	26k
ᵃconversion yield (%):	58	52	56
ᵇproduct yield (%):	33 (56)	31 (61)	29 (52)

[a] Conversion yields were determined by recovered C_{60}. [b] Product yields were determined after isolation. Those in parentheses were determined based on consumed C_{60}. Reaction condition: N_2-purged 10% EtOH-toluene (v/v) solutions (220 mL) containing C_{60} (0.278 mol, 1.26mM), glycinate (0.556 mmol, 2.53 mM) and methylene blue (MB, 0.063 mM) were irradiated for 60 min.

Likewise, MB-catalyzed photoreactions of C_{60} with **19l-19t** in oxygenated condition took place with efficiencies that far exceed those of **19a-19k**. (Table 5) Specifically, 15 min irradiation of oxygenated solutions of C_{60} and non- (**19l**) or electron donating (*ortho*-Me (**19m**), *meta*-Me (**19n**), *para*-Me (**19o**) and *para*-OMe (**19p**)) group containing glycinates in the presence of MB gave rise to high yielding production of fulleropyrrolidines **26l-26p**. (entries 1-5 in Table 5) Although MB sensitized reactions with electron withdrawing (*ortho*-F (**19q**), *meta*-F (**19r**), *para*-F (**19s**) and *para*-CF_3 (**19t**)) group containing glycinates took place less efficiently than those of **19l-19p** (entries 6-7 in Table 5), just 30 min irradiation of solutions containing C_{60} and **19q-19t** brought about high conversion of starting C_{60} as well as high yielding of photoproducts **26q-26t**. (entries 7-13 in Table 5)

Table 5. Product and yield in MB sensitized photoreactions of C_{60} with glycinates **19l-19t** in oxygenated condition.[a]

$$\mathbf{C_{60}} + \mathbf{19l\text{-}19t} \xrightarrow[\text{10\% EtOH-toluene}]{\text{hv / MB / }O_2} \mathbf{26l - 26t}$$

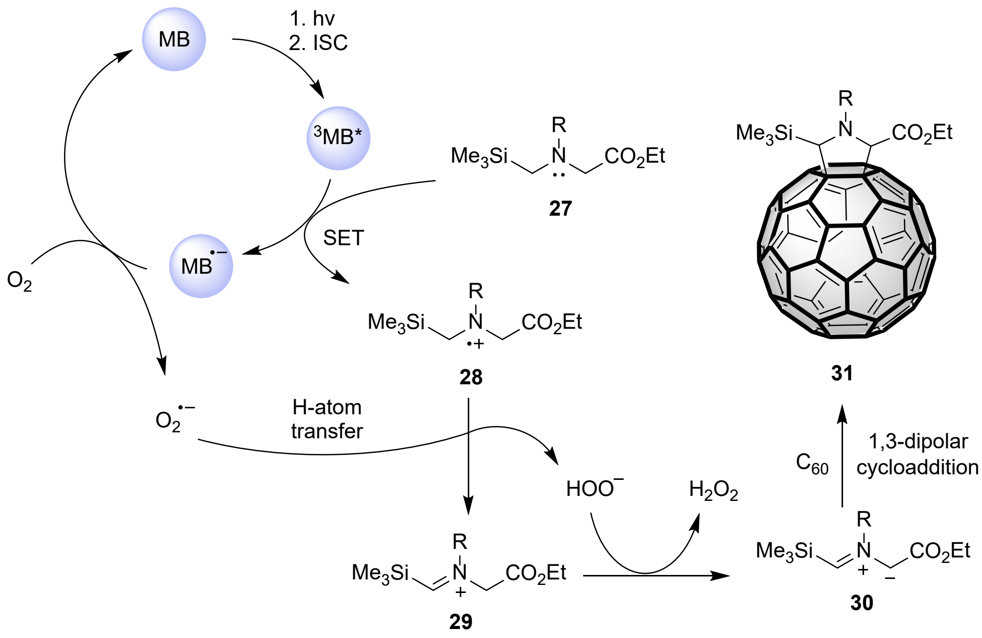
entry	amine	irradiation time (min)	conversion (%)[b]	yields (%) of **26**[c]
1	**19l**	15	100	65
2	**19m**	15	91	47 (51)
3	**19n**	15	94	48 (51)
4	**19o**	15	100	58
5	**19p**	15	100	60
6	**19q**	15	32	16 (51)
7	**19q**	30	73	42 (58)
9	**19r**	30	75	43 (58)
11	**19s**	30	79	49 (62)
13	**19t**	30	73	42 (60)

[a] 220 ml of 10% EtOH-toluene solutions containing C_{60} (1.26 mM, 1eq.), glycinate (2.53 mM, 2 eq.) and MB (0.063 mM). [b] Conversion was determined by recovered C_{60}. [c] Isolation yields. Those in parentheses were based on consumed C_{60}.

On the basis of observation made in amine SET photochemistry using photosensitizer[31,32a] and photoproduct distribution profiles obtained from current reactions, feasible mechanistic pathways for

MB sensitized photoreactions of C_{60} with ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates under oxygenated condition can be suggested in Scheme 12. Initial photochemical event appears to SET from glycinates **27** to photochemically generated $^3MB^*$ to generate aminium radicals **28** and radical anions of MB ($MB^{\bullet-}$),[31,33] latter of which subsequently undergo SET oxidation processes with O_2 to reform ground state of MB and radical anions of O_2 ($O_2^{\bullet-}$). In here, it is likely that competitive SET between glycinates and $^3C_{60}^*$ also take place rapidly. However, this event might be hampered via fast and efficient deactivation of $^3C_{60}^*$ by molecular oxygen, resulting in reforming ground state of C_{60}. Aminium radicals **28** formed in this manner undergo $O_2^{\bullet-}$ catalyzed HAT processes to form iminium intermediates **29**, followed by deprotonation from α-carbon located between nitrogen atom and ethoxycarbonyl group (*e,g.*, CO_2Et) by hydroperoxy anion (HOO^-) to produce azomethine ylides **30**. Finally, in situ generated ylides **30** are added to C_{60} to form photoproducts **31**.

Scheme 12. Reaction mechanism of MB sensitized photoreactions of C_{60} and ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates in the oxygenated condition.



It is noteworthy to mention about possibility of $^1O_2$-promoted azomethine ylides formation because, similarly with C_{60}, MB can serve as an efficient singlet oxygen generator ($\Phi(^1O_2) = 0.52$).[31,34] In order to clarify whether $^1O_2$ is involved in ylide forming processes, we carried out MB sensitized photoreactions of C_{60} with **19l** in the presence of DABCO (0-20 mM). As the results described in Figure 3 show, there was a slight decrease in conversion of C_{60} and yields of **26l** in the presence of DABCO (2.53 mM), compared to reactions carried out in the absence of DABCO. However, the presence of increasing concentration of DABCO did not cause any continuous decreases in both yields. Especially, in case of MB sensitized reactions of C_{60} with *N*-propyl substituted glycinate **19b** in the absence and presence of DABCO, very little difference exist in both conversion of C_{60} and yields of **26b**. (see Figure S8 in Supporting Information) These observations indicate that $^1O_2$ should not be a major participant in MB sensitized photoreactions of C_{60} with ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates under oxygenated condition.

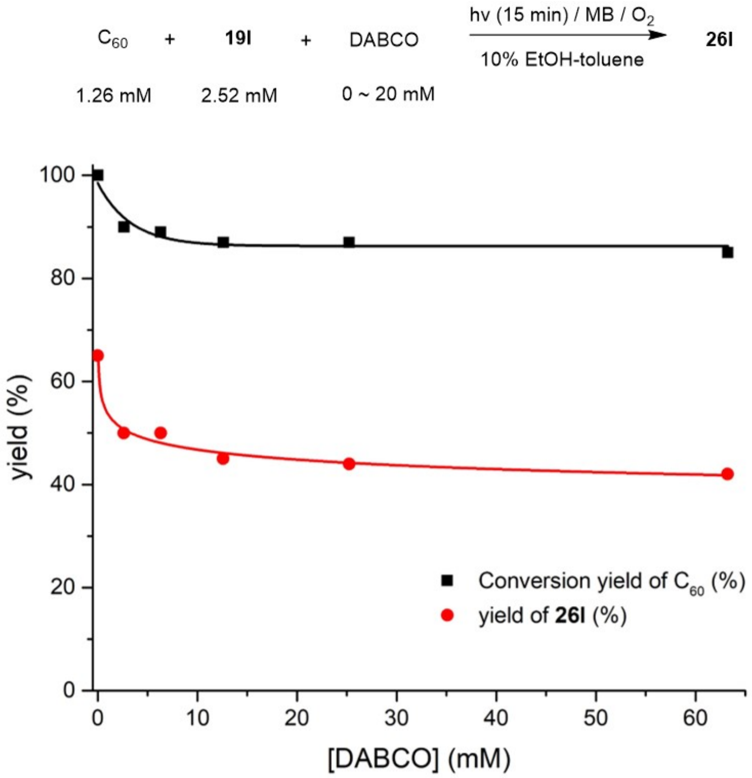


Figure 3. Plots of the both conversion of C_{60} (black square) and yields of **26l** (isolation yield, red circle) as function of concentration of DABCO in the MB sensitized photoreactions of C_{60} with **19l**. Reaction condition: O_2-purged 10% EtOH-toluene (v/v) solutions (220 mL) containing C_{60} (1.26 mM), glycinate **19l** (2.52 mM) and varying concentration of DABCO (0, 2.53, 6.3, 12.6 and 63 mM) were irradiated for 15 min.

Conclusion

In the current study, SET-promoted photoaddition reactions of fullerene C_{60} with both trimethylsilyl- and a variety of alkyl group containing glycinates were explored to evaluate how the nature of *N*-alkyl substituents and reaction conditions affect chemoselectivity. The results showed photoreactions of C_{60} with all trimethylsilyl group containing *N*-alkylglycinates, performed under deoxygenated (N_2-purged) conditions, produced aminomethyl-1,2-dihydrofullerenes efficiently through a pathway involving α-amino radical intermediates that are generated by sequential SET-solvent-assisted desilylation (~ $SiMe_3$+) of glycinate substrates. Except for the *N*-benzyl analogs, the same glycinate substrates did not undergo photoreactions under oxygenated (O_2-purged) conditions. Moreover, pyrrolidine ring fused fullerene derivatives, fulleropyrrolidines, were produced exclusively in photoreaction of *N*-benzyl analogs through a pathway involving [3+2] cycloaddition of 1,3-dipolar azomethine ylides to C_{60}. The ylide intermediates were formed by regioselective H-atom transfer from glycinates by $^1O_2$. Furthermore, methylene blue (MB) sensitized photochemical reaction of C_{60} with ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates under oxygenated conditions took place efficiently to produce fulleropyrrolidines independent of the nature of the *N*-alkyl substituents.

The combined observation made in this study conclusively show that chemoselectivity of photochemical reactions of C_{60} with ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates can be selectively controlled by the nature of *N*-alkyl substituents, and that this photochemical methodology is ideally suited to the synthesis of functionalized fullerenes, aminomethyl-1,2-dihrofullerenes and fulleropyrrolidines.

Experimental

General. The ^1H (300 MHz) and ^{13}C NMR (75 MHz) spectra (obtained by using Bruker DPX300) were recorded on $CDCl_3$, and chemical shifts were reported in parts per million (δ, ppm) relative to

$CHCl_3$ (7.24 ppm for ^1H and 77.0 ppm for ^{13}C) as an internal standard. High resolution (HRMS) mass spectra were obtained by using an EI or ESI-TOF. All starting materials used in the synthetic routes came from commercial sources. Photochemical reactions were conducted by using an immersion-well photochemical apparatus, consisting of a 450 W Hanovia medium pressure mercury vapor UV lamp (Ace Glass cat. # 7825-34), a power supply (Ace Glass cat. # 7830-61), a water-cooled quartz immersion well (Ace Glass cat # 7874-27), a borosilicate reaction vessel (Ace Glass cat. # 7841-03) and a flint glass filter (> 310 nm). Detail information about UV lamps used in this study are provided on Supporting Information.

General procedure for synthesis of tertiary ethyl *N*-alkyl-*N*-((trimethylsilyl)methyl)glycinates 19a-19t. Individual solutions of corresponding secondary *N*-(trimethylsilyl)methyl substituted amines (5 mmol) in acetonitrile (100 mL) containing K_2CO_3 (10 mmol) and ethyl bromoacetate (4.5 mmol) were stirred for 12 h at room temperature and concentrated in vacuo to give residues that were partitioned between water and CH_2Cl_2. The CH_2Cl_2 layers were dried and concentrated in vacuo to afford residues that were subjected to silica gel column chromatography (EtOAc/hexane = 1: 15 for **19b-19e** and **19l-19t**, EtOAc/hexane = 1: 10 for **19f-19g**, EtOAc/hexane = 1: 20 for **19h-19k**) to yield corresponding glycinates, **19a**[19a] (1.0 g, 78%), **19b** (970 mg, 84%), **19c** (854 mg, 69%), **19d** (952 mg, 83%), **19e** (990 mg, 73%), **19f** (1.11 g 77%), **19g**[19a] (716 mg, 52%), **19h** (1.25 g, 85%), **19i** (1.21 g, 79%), **19j** (1.31 g, 81%), **19k** (1.23 g, 79%), **19l**[19a] (1.08 g, 77%), **19m** (924 mg, 63%), **19n** (1.09 g, 74%), **19o**[21a] (998 mg, 68%), **19p**[21a] (1.08 g, 70%), **19q** (1.19 g, 80%), **19r** (1.13 g, 76%), **19s**[21a] (1.31 g, 88%) and **19t**[21a] (1.06 g, 61%)

To evaluate the practical utility of above synthetic method, large scale synthesis using secondary amines, *N*-((trimethylsilyl)methyl)propan-1-amine (4 g, 27.5 mmol) and 2-methoxy-*N*-((trimethylsilyl)methyl)ethan-1-amine (4 g, 24.8 mmol), were carried out according to the same synthetic procedures mentioned above. These large scale reactions finally yielded glycinate **19b** (5.1 g, 80%) and **19c** (4.29 g, 70%) respectively.

19b (liquid/oil): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.13 (q, 2H, *J* = 7.2 Hz), 3.29 (s, 2H), 2.52 (t, 2H, *J* = 7.2 Hz), 2.14 (s, 2H), 1.40-1.47 (m, 2H), 1.24 (t, 3H, *J* = 7.2 Hz), 0.84 (t, 3H, *J* = 7.5 Hz), 0.03 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 171.0, 59.6, 59.2, 57.6, 45.4, 20.4, 14.0, 11.3, -1.8; HRMS (EI) *m/z*: M^+ Calcd for $C_{11}H_{25}NO_2Si$ 231.1655; Found 231.1654.

19c (liquid/oil): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.10 (q, 2H, *J* = 7.2 Hz), 3.42 (t, 2H, *J* = 6 Hz), 3.39 (s, 2H), 3.28 (s, 3H), 2.79 (t, 2H, *J* = 6 Hz), 2.19 (s, 2H), 1.22 (t, 3H, *J* = 7.2 Hz), 0.01 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 171.1, 71.0, 59.6, 58.3, 57.9, 56.3, 46.0, 14.0, -1.8; HRMS (EI) *m/z*: M^+ Calcd for $C_{11}H_{25}NO_3Si$ 247.1604; Found 247.1605.

19d (liquid/oil): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.72-5.86 (m, 1H), 5.06-5.16 (m, 2H), 4.11 (q, 2H, *J* = 7.2 Hz), 3.25 (s, 2H), 3.18 (d, 2H, *J* = 6.6 Hz), 2.12 (s, 2H), 1.22 (t, 3H, *J* = 7.2 Hz), 0.02 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 170.8, 135.7, 117.2, 60.2, 59.6, 57.0, 45.2, 14.0, -1.8; HRMS (EI) *m/z*: M^+ Calcd for $C_{11}H_{23}NO_2Si$ 229.1498; Found 229.1496.

19e (liquid/oil): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.09 (q, 2H, *J* = 7.2 Hz), 3.23 (s, 2H), 2.38-2.45 (m, 1H), 2.12 (s, 2H), 1.21 (t, 3H, *J* = 7.2 Hz), 0.98-1.18 (m, 6H), 0.00 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 172.3, 62.3, 59.8, 54.2, 42.3, 29.1, 26.1, 25.8, 14.1, -1.7; HRMS (EI) *m/z*: M$^+$ Calcd for $C_{14}H_{29}NO_2Si$ 271.1968; Found 271.1968.

19f (liquid/oil): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.05-4.15 (m, 4H), 3.31 (s, 2H), 2.93 (t, 2H, *J* = 7.2 Hz), 2.41 (t, 2H, *J* = 7.2 Hz), 2.15 (s, 2H), 1.19-1.25 (m, 6H), 0.00 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 172.1, 170.8, 59.9, 59.7, 52.9, 44.9, 33.0, 14.0, 13.9, -1.9; HRMS (EI) *m/z*: M$^+$ Calcd for $C_{13}H_{27}NO_4Si$ 289.1709; Found 289.1707.

19h (liquid/oil): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.15-7.29 (m, 5H), 4.16 (q, 2H, *J* = 7.2 Hz), 3.38 (s, 2H), 2.83-2.88 (m, 2H), 2.73-2.78 (m, 2H), 2.24 (s, 2H), 1.27 (t, 3H, *J* = 7.2 Hz), 0.06 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 171.1, 140.2, 128.6, 128.1, 125.7, 59.9, 59.3, 57.8, 45.6, 34.0, 14.2, -1.6; HRMS (EI) *m/z*: M$^+$ Calcd for $C_{16}H_{27}NO_2Si$ 293.1811; Found 293.1807.

19i (liquid/oil): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.07 (s, 4H), 4.15 (q, 2H, *J* = 7.2 Hz), 3.36 (s, 2H), 2.79-2.83 (m, 2H), 2.67-2.72 (m, 2H), 2.30 (s, 3H), 2.22 (s, 2H), 1.26 (t, 3H, *J* = 7.2 Hz), 0.05 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 171.0, 137.0, 135.0, 128.8, 128.4, 59.8, 59.4, 57.8, 45.5, 33.5, 20.8, 14.1, -1.6; HRMS (EI) *m/z*: M$^+$ Calcd for $C_{17}H_{29}NO_2Si$ 307.1968; Found 307.1966.

19j (liquid/oil): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.08 (d, 2H, *J* = 8.4 Hz), 6.79 (d, 2H, *J* = 8.4 Hz), 4.13 (q, 2H, *J* = 7.2 Hz), 3.76 (s, 3H), 3.34 (s, 2H), 2.75-2.80 (m, 2H), 2.64-2.69 (m, 2H), 2.20 (s, 2H), 1.24 (t, 3H, *J* = 7.2 Hz), 0.03 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 171.1, 157.7, 132.2, 129.5, 113.5, 59.9, 59.5, 57.9, 55.0, 45.6, 33.0, 14.2, -1.6; HRMS (EI) *m/z*: M$^+$ Calcd for $C_{17}H_{29}NO_3Si$ 323.1917; Found 323.1915.

19k (liquid/oil): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.09-7.14 (m, 2H), 6.89-6.95 (m, 2H), 4.13 (q, 2H, J = 7.2 Hz), 3.33 (s, 2H), 2.76-2.81 (m, 2H), 2.66-2.71 (m, 2H), 2.19 (s, 2H), 1.24 (t, 3H, J = 7.2 Hz), 0.02 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 170.8, 161.0 (d, $J_{C\text{-}F}$ = 967.5 Hz), 135.7 (d, $J_{C\text{-}F}$ = 12.6 Hz), 129.8 (d, $J_{C\text{-}F}$ = 30.9 Hz), 114.6 (d, $J_{C\text{-}F}$ = 83.7 Hz), 59.7, 59.1, 57.5, 45.4, 33.1, 14.0, -1.8; HRMS (EI) *m/z*: M$^+$ Calcd for $C_{16}H_{26}FNO_2Si$ 311.1717; Found 311.1716.

19m (liquid/oil): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.28-7.3 (m, 1H), 7.12-7.14 (m, 3H), 4.12 (q, 2H, J = 7.2 Hz), 3.75 (s, 2H), 3.23 (s, 2H), 2.34 (s, 3H), 2.21 (s, 2H), 1.25 (t, 3H, J = 7.2 Hz), 0.02 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 170.9, 137.3, 137.0, 129.9, 129.6, 126.8, 125.3, 60.0, 59.5, 56.3, 45.3, 19.0, 14.1, -1.7; HRMS (EI) *m/z*: M$^+$ Calcd for $C_{16}H_{27}NO_2Si$ 293.1811; Found 293.1809.

19n (liquid/oil): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.12-7.21 (m, 3H), 7.03-7.05 (m, 1H), 4.13 (q, 2H, J = 7.2 Hz), 3.71 (s, 2H), 3.24 (s, 2H), 2.32 (s, 3H), 2.19 (s, 2H), 1.25 (t, 3H, J = 7.2 Hz), 0.05 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 171.1, 139.3, 137.5, 129.4, 127.9, 127.5, 61.3, 56.9, 45.5, 21.2, 14.2, -1.6; HRMS (EI) *m/z*: M$^+$ Calcd for $C_{16}H_{27}NO_2Si$ 293.1811; Found 293.1812.

19q (liquid/oil): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.41-7.46 (m, 1H), 7.16-7.21 (m, 1H), 7.05-7.10 (m, 1H), 6.95-7.01 (m, 1H), 4.13 (q, 2H, J = 6.9 Hz), 3.80 (s, 2H), 3.25 (s, 2H), 2.20 (s, 2H), 1.25 (t, 3H, J = 6.9 Hz), 0.03 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 170.8, 161.1 (d, $J_{C\text{-}F}$ = 245 Hz), 130.9 (d, $J_{C\text{-}F}$ = 4.4 Hz), 128.2 (d, $J_{C\text{-}F}$ = 8.1 Hz), 125.9 (d, $J_{C\text{-}F}$ = 14 Hz), 123.6 (d, $J_{C\text{-}F}$ = 3.3 Hz), 114.9 (d,

$J_{C\text{-}F}$ = 22 Hz), 59.7, 56.9, 53.8, 45.5, 14.0, -1.8; HRMS (EI) *m/z*: M$^+$ Calcd for $C_{15}H_{24}FNO_2Si$ 297.1560; Found 297.1559.

19r (liquid/oil): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.17-7.21 (m, 1H), 7.04-7.06 (m, 2H), 6.85-6.90 (m, 1H), 4.10 (q, 2H, *J* = 7.2 Hz), 3.71 (s, 2H), 3.22 (s, 2H), 2.14 (s, 2H), 1.22 (t, 3H, *J* = 7.2 Hz), 0.06 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 170.8, 162.8 (d, $J_{C\text{-}F}$ = 243.8 Hz), 142.4 (d, $J_{C\text{-}F}$ = 6.9 Hz), 129.4 (d, $J_{C\text{-}F}$ = 8 Hz), 124.0 (d, $J_{C\text{-}F}$ = 2.3 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.2 Hz), 113.6 (d, $J_{C\text{-}F}$ = 21.1 Hz), 60.9 (d, $J_{C\text{-}F}$ = 1.4 Hz), 59.8, 56.8, 45.3, 14.1, -1.7; HRMS (EI) *m/z*: M$^+$ Calcd for $C_{15}H_{24}FNO_2Si$ 297.1560; Found 297.1561.

General procedure of photoreactions of C_{60} with *N*-α-trimethylsilyl-*N*-alkylglycinates 19a-19t. The 10% EtOH-toluene (v/v) solutions (220 mL) containing C_{60} (0.278 mmol, 1.26 mM) and each glycinates **19a-19t** (0.555 mmol, 2.53 mM) with/without methylene blue (MB, 5 mol %) that were purged with N_2 or O_2 before and during irradiation were irradiated with a 450W Hanovia medium pressure Hg lamp surrounded by a flint glass filter (> 310 nm) in a water-cooled quartz immersion well for time periods given below. The photolysates were concentrated in vacuo and the unreacted C_{60} was recovered by filtration using $CHCl_3$ to determine conversion yields. Photoproducts were separated by using silica gel column chromatographic isolation of crude photolysates.

Photoreaction of C_{60} with 19a. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (82% conversion), column chromatography (CS_2: $CHCl_3$ = 1: 1) to yield **20a**[19a] (112 mg, 43% (53% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 60 min irradiation

(82% conversion), column chromatography ((CS_2: $CHCl_3$ = 1: 2) to yield **26a** (133 mg, 48% (59% based on consumed C_{60})).

26a: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 5.64 (s, 1H), 5.23 (s, 1H), 4.18-4.39 (m, 2H), 3.91-4.0 (m, 1H), 3.25-3.34 (m, 1H), 1.83-1.93 (m, 2H), 1.52-1.60 (m, 2H), 1.42-1.46 (m, 4H), 1.27 (t, 3H, *J* = 6.9 Hz), 0.95-1.0 (m, 3H), 0.45 (S, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$+CS_2, 75 MHz) δ 169.8, 156.8, 156.0, 154.6, 152.4, 146.7, 146.6, 146.4, 146.1, 145.9, 145.8 (2C), 145.7, 145.6, 145.5, 145.2, 144.9 (2C), 144.7, 144.2, 144.1, 143.9, 142.8, 142.7, 142.4, 142.3, 142.1, 141.9 (2C), 141.8, 141.7, 141.6, 141.5 (2C), 141.4, 141.3, 139.9, 139.2 (2C), 138.9, 136.3, 135.4, 134.8, 76.2, 70.3, 60.6, 52.3, 31.9, 30.2, 26.9, 22.9, 14.2, 0.7; HRMS (MALDI-TOF) *m/z* $[M + H]^+$ Calcd for $C_{74}H_{30}NO_2Si$ 992.2040; Found 992.2047.

Photoreaction of C_{60} with 19b. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (83% conversion), column chromatography (CS_2) to yield **20b** (113 mg, 46% (55% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 60 min irradiation (83% conversion), column chromatography (CS_2) to yield **26b** (133 mg, 49% (59% based on consumed C_{60})).

20b: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 6.92 (s, 1H), 4.66 (s, 2H), 4.27 (q, 2H, *J* = 7.2 Hz), 3.98 (s, 2H), 3.27 (t, 2H, *J* = 7.5 Hz), 1.78-1.85 (m, 2H), 1.38 (t, 3H. *J* = 7.2 Hz), 1.09 (t, 3H, *J* = 7.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$+CS_2, 75 MHz) δ 170.2, 154.6, 154.1, 146.9, 146.8 (2C), 146.4, 145.9 (2C), 145.8, 145.7, 145.4, 145.1, 144.9, 144.3, 144.1, 142.8, 142.2, 142.1, 141.9, 141.6 (2C), 141.4, 141.2

(2C), 139.9, 139.7, 135.7, 135.6, 69.1, 67.2, 60.2, 57.6, 57.4, 55.3, 22.0, 14.4, 11.9; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{68}H_{18}NO_2$ 880.1338; Found 880.1339

26b: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 5.65 (s, 1H), 5.25 (s, 1H), 4.22-4.38 (m, 2H), 3.90-3.99 (m, 1H), 3.25-3.34 (m, 1H), 1.88-1.96 (m, 2H), 1.27 (t, 3H, *J* = 7.2 Hz), 1.19 (t, 3H, *J* = 7.2 Hz), 0.46 (S, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$+CS_2, 75 MHz) δ 169.8, 156.8, 156.0, 154.7, 152.4, 146.7, 146.6, 146.5, 146.2, 146.0, 145.9, 145.8 (2C), 145.7, 145.6, 145.5, 145.3, 145.0, 144.9 (2C), 144.8 (2C), 144.3, 144.2, 144.1, 144.0, 142.9, 142.8, 142.5, 142.4 (3C), 142.2, 142.0 (2C), 141.9 (3C), 141.7 (2C), 141.6, 141.5 (2C), 141.4, 139.9, 139.3, 139.2, 139.0, 136.4, 135.5, 134.9, 76.1, 70.1, 60.7, 53.9, 23.5, 14.2, 11.7, 0.7; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{71}H_{24}NO_2Si$ 950.1576; Found 950.1573.

Photoreaction of C_{60} with 19c. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (85% conversion), column chromatography (CS_2: $CHCl_3$ = 1: 2) to yield **20c** (134 mg, 54% (63% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 60 min irradiation (81% conversion), column chromatography (CS_2: $CHCl_3$ = 1: 2) to yield **26c** (120 mg, 45% (55% based on consumed C_{60})).

20c: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 6.96 (s, 1H), 4.74 (s, 2H), 4.27 (q, 2H, *J* = 7.2 Hz), 4.11 (s, 2H), 3.79 (t, 2H, *J* = 4.8 Hz), 3.51 (t, 2H, *J* = 4.8 Hz), 3.4 (s, 3H), 1.37 (t, 3H, *J* = 7.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$+CS_2, 75 MHz) δ 170.9, 154.6, 154.3, 147.1, 147.0, 146.9, 146.6, 146.1 (2C), 145.9 (2C), 145.5, 145.2, 145.1 (2C), 144.4, 144.2, 143.0, 142.3 (2C), 142.1, 141.8, 141.7, 141.5, 141.4 (2C), 140.0, 139.8, 135.8, 135.7, 72.6, 69.4, 67.4, 60.4, 58.6, 57.6, 57.0, 55.3, 14.4; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{68}H_{17}NO_3Na$ 918.1106; Found 918.1105.

26c: ^1H NMR ($CDCl_3$+CS_2, 300 MHz) δ 5.81 (s, 1H), 5.25 (s, 1H), 4.26-4.34 (m, 1H), 4.16-4.23 (m, 2H), 3.71-3.83 (m, 2H), 3.54-3.61 (m, 1H), 3.46 (s, 3H), 1.25 (t, 3H, *J* = 7.2 Hz), 0.47 (S, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$+CS_2, 75 MHz) δ 169.3, 145.9, 145.7, 145.6, 145.5, 145.4 (2C), 145.2, 145.0 (2C), 144.7, 144.6 (2C), 144.5, 144.0, 143.9, 143.8, 143.7, 142.6, 142.5, 142.2, 142.1 (2C), 141.9, 141.7, 141.6, 141.5 (2C), 141.3 (2C), 141.2, 141.1, 139.6, 139.0, 138.9, 138.7, 135.7, 135.2, 135.1, 134.5, 72.9, 70.5, 60.2, 58.4, 51.9, 14.0, 0.4; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{71}H_{23}NO_3SiNa$ 988.1345; Found 988.1335.

Photoreaction of C_{60} with 19d. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (94% conversion), column chromatography (CS_2: $CHCl_3$ = 1: 1) to yield **20d** (142 mg, 58% (62% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 60 min irradiation (87% conversion), column chromatography (CS_2: $CHCl_3$ = 1: 1) to yield **26d** (141 mg, 53% (61% based on consumed C_{60})).

20d: ^1H NMR ($CDCl_3$+CS_2, 300 MHz) δ 6.95 (s, 1H), 6.05-6.19 (m, 1H), 5.45 (d, 1H, *J* = 17.1 Hz), 5.32 (d, 1H, *J* = 10.2 Hz), 4.28 (q, 2H, *J* = 7.2 Hz), 3.99 (s, 2H), 3.95-3.99 (m, 2H), 1.38 (t, 3H, *J* = 7.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$+CS_2, 75 MHz) δ 170.3, 154.4, 154.1, 146.9, 146.8 (2C), 146.4, 146.0, 145.9, 145.8, 145.7, 145.4, 145.1, 145.0, 144.3, 144.1, 142.8, 142.2, 142.1, 141.9, 141.7, 141.6, 141.4, 141.3, 141.2, 139.9, 139.7, 135.7, 135.6, 135.2, 118.3, 68.1, 67.1, 60.3, 58.4, 57.6, 55.1, 14.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{68}H_{15}NO_2Na$ 900.1000; Found 900.0992.

26d: ^1H NMR ($CDCl_3$+CS_2, 300 MHz) δ 6.10-6.24 (m, 1H), 5.68 (s, 1H), 5.52 (d, 1H, *J* = 17.1 Hz), 5.39 (d, 1H, *J* = 10.2 Hz), 5.29 (s, 1H), 4.66-4.73 (m, 1H), 4.16-4.39 (m, 2H), 4.03-4.08 (m, 1H), 1.25 (t, 3H, *J* = 7.2 Hz), 0.49 (S, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$+CS_2, 75 MHz) δ 169.5, 145.9, 145.8, 145.7, 145.6, 145.5, 145.2, 144.9 (2C), 144.8 (2C), 144.7, 144.2, 144.1 (2C), 143.9, 142.8, 142.7, 142.4 (2C), 142.3, 142.1, 141.9 (3C), 141.8, 141.7 (2C), 141.6, 141.5, 141.4, 139.9, 139.3, 139.2, 139.0, 136.0, 135.6, 135.3, 134.6, 118.3, 76.3, 69.9, 60.5, 55.2, 14.2, 0.5; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{71}H_{21}NO_2SiNa$ 970.1239; Found 970.1238.

Photoreaction of C_{60} with 19e. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (90% conversion), column chromatography (CS_2: $CHCl_3$ = 1: 1) to yield **20e** (133 mg, 52% (58% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 60 min irradiation (75% conversion), column chromatography (CS_2: $CHCl_3$ = 1: 1) to yield **26e** (116 mg, 42% (46% based on consumed C_{60})).

20e: ^1H NMR ($CDCl_3$+CS_2, 300 MHz) δ 7.04 (s, 1H), 4.69 (s, 2H), 4.22 (q, 2H, *J* = 6.9 Hz), 3.95 (s, 2H), 3.22-3.29 (m, 1H), 2.23-2.27 (m, 2H), 1.92-1.96 (m, 2H), 1.72-1.76 (m, 2H), 1.41-1.53 (m, 4H), 1.34 (t, 3H, *J* = 6.9 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$+CS_2, 75 MHz) δ 171.3, 154.9, 154.3, 146.8, 146.7, 146.5, 145.9 (2C), 145.7 (2C), 145.4, 145.0, 144.9, 144.3, 144.0, 142.8, 142.1 (2C), 141.9, 141.6, 141.5, 141.3, 141.2 (2C), 139.9, 139.6, 135.6, 135.4, 67.5, 65.8, 62.3, 60.2, 57.4, 52.1, 30.6, 26.4, 26.3, 14.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{71}H_{21}NO_2Na$ 942.1470; Found 942.1472.

26e: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 5.61 (s, 1H), 5.52 (s, 1H), 4.18-4.41 (m, 2H), 3.38-3.46 (m, 1H), 2.22-2.91 (m, 2H), 1.76-2.06 (m, 6H), 1.44-1.52 (m, 2H), 1.29 (t, 3H, *J* = 7.2 Hz), 0.45 (S, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$+CS_2, 75 MHz) δ 172.2, 155.9, 154.0, 151.7, 147.0, 146.6 (2C), 146.2, 145.9, 145.8 (2C), 145.7, 145.6, 145.5 (2C), 145.2 (2C), 144.9 (2C), 144.8 (2C), 144.7, 144.3, 144.2, 144.0, 143.9, 142.8, 142.7, 142.6, 142.3 (2C), 142.1, 142.0, 141.9 (2C), 141.7, 141.6 (2C), 141.5, 141.4, 141.3, 141.1, 139.7, 139.1, 138.8, 138.5, 136.8, 136.0, 135.3, 128.7, 128.0, 71.4, 67.5, 60.5, 58.9, 34.9, 33.4, 26.9, 26.0, 0.5; HRMS (MALDI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{74}H_{27}NO_2SiNa$ 1012.1709; Found 1012.1696.

Photoreaction of C_{60} with 19f. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (46% conversion), column chromatography (CS_2) to yield **20f** (60 mg, 23% (51% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 60 min irradiation (66% conversion), column chromatography (CS_2) to yield **26f** (92 mg, 33 (50% based on consumed C_{60})).

20f: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 6.76 (s, 1H), 4.7 (s, 2H), 4.26 (q, 2H, *J* = 7.2 Hz), 4.11 (q, 2H, *J* = 7.2 Hz), 4.03 (s, 2H), 3.63 (t, 3H, *J* = 6.9 Hz), 2.75 (t, 2H, *J* = 6.9 Hz), 1.35 (t, 3H, *J* = 7.2 Hz), 1.25 (t, 3H, *J* = 7.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$+CS_2, 75 MHz) δ 171.3 (2C), 170.6, 170.5, 154.3, 154.0, 147.0, 146.9, 146.8, 146.5, 146.1, 146.0, 145.9, 145.8, 145.5, 145.2, 145.0, 144.4, 144.2, 142.9, 142.3, 142.2, 142.0, 141.8, 141.7, 141.5, 141.4, 141.3, 140.0, 139.7, 135.8, 135.7, 69.0, 67.2, 60.5, 60.4, 57.6, 55.5, 51.7, 34.1, 14.3, 14.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{70}H_{19}NO_4Na$ 960.1212; Found 960.1198.

26f: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 5.67 (s, 1H), 5.2 (s, 1H), 4.29-4.40 (m, 1H), 4.14-4.28 (m, 4H), 3.62-3.71 (m, 1H), 2.84 (t, 3H, *J* = 7.5 Hz), 1.24-1.34 (m, 6H), 0.46 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$+CS_2, 75 MHz) δ 170.8, 169.4, 156.4, 155.7, 154.4, 152.2, 146.7, 146.6, 146.4, 146.1, 146.0, 145.8, 145.5, 145.2 (2C), 145.0 (2C), 144.9 (3C), 144.8, 144.7, 144.3, 144.2, 144.1, 144.0, 142.8, 142.7, 142.4 (3C), 142.3, 142.1, 141.9 (3C), 141.8, 141.7, 141.5 (2C), 141.4, 141.3, 139.9, 139.2 (2C), 138.9, 136.4, 135.5 (2C), 134.8, 75.9, 69.8, 60.7, 60.4, 48.1, 35.4, 14.2, 0.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{73}H_{26}NO_4Si$ 1008.1626; Found 1008.1628.

Photoreaction of C_{60} with 19g. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (4% conversion), column chromatography (CS_2: $CHCl_3$ = 1: 1) to yield **20g**[19a] (trace). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 60 min irradiation (51% conversion), column chromatography (CS_2) to yield **26g**[19a] (75 mg, 27 % (53% based on consumed C_{60})).

Photoreaction of C_{60} with 19h. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (76% conversion), column chromatography (CS_2: $CHCl_3$ = 1: 1) to yield **20h** (102 mg, 39% (51% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 60 min irradiation (52% conversion), column chromatography (CS_2: $CHCl_3$ = 1: 1) to yield **26h** (87 mg, 31% (59% based on consumed C_{60})).

20h: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 7.22-7.24 (m, 4H), 7.10-7.16 (m, 1H), 6.86 (s, 1H), 4.70 (s, 2H), 4.29 (q, 2H, *J* = 7.2 Hz), 4.05 (s, 2H), 3.58 (t, 2H, *J* = 7.8 Hz), 3.09 (t, 2H, *J* = 7.8 Hz), 1.41 (t, 3H. *J* = 7.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$+CS_2, 75 MHz) δ 169.9, 154.4, 154.0, 146.8, 146.7 (2C), 146.3, 145.9, 145.8, 145.7, 145.6, 145.3, 145.0, 144.9 (2C), 144.2, 144.0, 142.8, 142.1 (2C), 141.9, 141.6, 141.5, 141.3, 141.2 (2C), 139.8, 139.6, 138.9, 135.5, 128.5, 128.3, 126.0, 69.1, 67.1, 60.2, 57.4, 57.3, 55.4, 35.4, 14.4; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{73}H_{19}NO_2Na$ 964.1313; Found 964.1313.

26h: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 7.30-7.32 (m, 4H), 7.20-7.23 (m, 1H), 5.69 (s, 1H), 5.25 (s, 1H), 4.18-4.39 (m, 3H), 3.57-3.66 (m, 1H), 3.17 (t, 3H, *J* = 7.5 Hz), 1.29 (t, 3H, *J* = 7.2 Hz), 0.42 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$+CS_2, 75 MHz) δ 169.5, 146.1, 145.9, 145.8 (2C), 145.6, 145.5, 145.2, 144.9 (2C), 144.8, 144.6, 144.2, 144.1 (2C), 143.9, 142.8, 142.7, 142.4, 142.3, 142.1, 142.0, 141.9 (2C), 141.8, 141.7 (2C), 141.6, 141.5, 141.4, 141.3, 139.9, 139.3, 138.9 (2C), 136.3, 135.4, 135.3, 134.7, 128.7, 128.4, 126.3, 70.7, 60.7, 54.5, 37.3, 14.2, 0.6; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{76}H_{25}NO_2SiNa$ 1034.1552; Found 1034.1543.

Photoreaction of C_{60} with 19i. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (71% conversion), column chromatography (CS_2: $CHCl_3$ = 2: 1) to yield **20i** (100 mg, 38% (53% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 60 min irradiation (58% conversion), column chromatography (CS_2: $CHCl_3$ = 2: 1) to yield **26i** (93 mg, 33% (56% based on consumed C_{60})).

20i: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 7.13 (d, 2H, *J* = 7.8 Hz), 7.03 (d, 2H, *J* = 7.8 Hz), 6.08 (s, 1H), 4.68 (s, 2H), 4.31 (q, 2H, *J* = 6.9 Hz), 4.07 (s, 2H), 3.56 (t, 2H, *J* = 7.2 Hz), 3.04 (t, 2H. *J* = 7.2 Hz), 2.26 (s, 3H), 1.40 (t, 3H, *J* = 6.9 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$+CS_2, 75 MHz) δ 170.6, 154.7, 154.3, 147.0, 146.9 (2C), 146.5, 146.1, 146.0, 145.9, 145.8, 145.5, 145.2, 145.1, 145.0 (2C), 144.4, 144.2, 143.0, 142.3 (2C), 142.0, 141.8, 141.7, 141.4 (2C), 141.3, 139.9, 139.8, 136.1, 135.8, 135.7, 135.3, 129.2, 128.6, 69.3, 67.3, 60.5, 57.6, 55.5, 34.9, 21.0, 14.4; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{74}H_{21}NO_2Na$ 978.1470; Found 978.1463.

26i: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 7.2 (d, 2H, *J* = 7.8 Hz), 7.11 (d, 2H, *J* = 7.8 Hz), 5.68 (s, 1H), 5.25 (s, 1H), 4.23-4.41 (m, 2H), 4.14-4.23 (m, 1H), 3.55-3.64 (m, 1H), 3.13 (t, 2H, *J* = 7.5 Hz), 2.35 (s, 3H), 1.29 (t, 3H, *J* = 7.2 Hz), 0.43 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$+CS_2, 75 MHz) δ 169.7, 156.7, 155.9, 154.6, 152.4, 146.7, 146.6, 146.3, 146.1, 146.0, 145.8 (2C), 145.7, 145.5, 145.2, 145.0, 144.9 (2C), 144.8 (2C), 144.7, 144.3, 144.2, 144.1, 144.0, 142.9, 142.8, 142.4 (2C), 142.3, 142.2, 142.0 (2C), 141.9, 141.8 (2C), 141.7, 141.6, 141.5, 141.4 (2C), 139.9, 139.3 (2C), 139.0, 136.3, 135.8, 135.4, 134.7, 129.1, 128.6, 70.8, 60.7, 54.6, 36.9, 21.1, 14.3, 0.7; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{77}H_{27}NO_2SiNa$ 1048.1709; Found 1048.1704.

Photoreaction of C_{60} with 19j. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (72% conversion), column chromatography (CS_2: $CHCl_3$ = 1: 2) to yield **20j** (116 mg, 43% (60% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 60 min irradiation (52%

conversion), column chromatography (CS_2: $CHCl_3$ = 1: 2) to yield **26j** (91 mg, 31% (61% based on consumed C_{60})).

20j: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 7.15 (d, 2H, *J* = 8.4 Hz), 6.8 (s, 1H), 6.75 (d, 2H, *J* = 8.4 Hz), 4.68 (s, 2H), 4.31 (q, 2H, *J* = 7.2 Hz), 4.06 (s, 2H), 3.69 (s, 3H), 3.54 (t, 2H. *J* = 7.8 Hz), 3.02 (t, 2H. *J* = 7.8 Hz), 1.39 (t, 3H, *J* = 7.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$+CS_2, 75 MHz) δ 170.7, 157.8, 154.7, 154.3, 147.1, 147.0, 146.9, 146.5, 146.1 (2C), 145.9, 145.8, 145.5, 145.2, 145.1 (2C), 145.0, 144.4, 144.2, 143.0, 142.3 (2C), 142.0, 141.8, 141.7, 141.5, 141.4, 141.3, 140.0, 139.8, 135.8, 131.1, 129.6, 113.8, 69.4, 67.3, 60.5, 57.6, 55.6, 54.7, 34.4, 14.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{74}H_{22}NO_3$ 972.1594; Found 972.1586.

26j: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 7.21 (d, 2H, *J* = 8.1 Hz), 6.82 (d, 2H, *J* = 8.1 Hz), 5.66 (s, 1H), 5.24 (s, 1H), 4.13-4.41 (m, 3H), 3.78 (s, 3H), 3.53-3.62 (m, 1H), 3.10 (t, 3H, *J* = 7.5 Hz), 1.28 (t, 3H, *J* = 6.9 Hz), 0.42 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$+CS_2, 75 MHz) δ 169.6, 157.9, 156.6, 155.9, 154.5, 152.3, 146.6, 146.5, 146.3, 146.1, 145.9, 145.8, 145.7 (2C), 145.6, 145.5, 145.2, 144.9 (2C), 144.8 (2C), 144.7, 144.6, 144.2, 144.1, 144.0, 143.9, 142.8, 142.7, 142.4 (2C), 142.3 (2C), 142.1, 141.9 (3C), 141.8, 141.7, 141.6, 141.5 (2C), 141.3, 139.8, 139.2, 138.9, 136.3, 135.3 (2C), 134.7, 130.8, 129.6, 113.7, 70.7, 60.6, 54.6 (2C), 36.4, 14.2, 0.6; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{77}H_{27}NO_3SiNa$ 1064.1658; Found 1064.1661.

Photoreaction of C_{60} with 19k. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (36% conversion), column chromatography (CS_2: $CHCl_3$ = 1: 2) to yield **20k** (55 mg, 21% (57% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 60 min irradiation (56% conversion), column chromatography (CS_2: $CHCl_3$ = 1: 2) to yield **26k** (83 mg, 29% (52% based on consumed C_{60})).

20k: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 7.18-7.22 (m, 2H), 6.89-6.94 (m, 2H), 6.81 (s, 1H), 4.69 (s, 2H), 4.3 (q, 2H, J = 7.2 Hz), 4.04 (s, 2H), 3.55 (t, 2H. J = 7.2 Hz), 3.06 (t, 2H. J = 7.2 Hz), 1.39 (t, 3H, J = 6.9 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$+CS_2, 75 MHz) δ 170.5, 161.2 (d, $J_{C\text{-}F}$ = 243.9 Hz), 154.5, 154.1, 147.1, 146.9 (2C), 146.5, 146.1 (2C), 145.9 (2C), 145.5, 145.2, 145.1, 144.4, 144.2, 143.0, 142.3, 142.0, 141.8, 141.7, 141.4 (2C), 141.3, 140.0, 139.8, 135.7, 134.8 (d, $J_{C\text{-}F}$ = 3 Hz), 130.0 (d, $J_{C\text{-}F}$ = 7.7 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21 Hz), 69.4, 67.2, 60.5, 57.7, 57.5, 55.8, 34.7, 14.4; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{73}H_{18}FNO_2Na$ 982.1219; Found 982.1217.

26k: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 7.28-7.33 (m, 2H), 7.01 (t, 2H, J = 8.4 Hz), 5.65 (s, 1H), 5.25 (s, 1H), 0.4 (s, 9H), 4.18-4.42 (m, 3H), 3.57-3.66 (m, 1H), 3.15 (t, 3H, J = 7.2 Hz), 1.28 (t, 3H, J = 7.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$+CS_2, 75 MHz) δ 169.6, 161.3 (d, $J_{C\text{-}F}$ = 244.1 Hz), 156.6, 155.8, 154.5, 152.2, 146.7, 146.3, 146.1, 146.0, 145.8 (3C), 145.6, (2C), 145.5, 145.2, 145.0, 144.9 (2C), 144.8 (2C), 144.6, 144.1 (2C), 143.9, 142.9 (2C), 142.8, 142.4 (2C), 142.3, 142.1, 142.0, 141.9 (2C), 141.8 (2C), 141.7 (2C), 141.6, 141.5, 141.4, 139.3 (2C), 139.0, 136.3, 135.3 (d, $J_{C\text{-}F}$ = 7.5 Hz), 134.6 (3C), 130.2 (d, $J_{C\text{-}F}$ = 7.7 Hz), 115.1 (d, $J_{C\text{-}F}$ = 20.9 Hz), 70.8, 60.8, 54.4, 36.4, 14.2, 0.6; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{76}H_{24}FNO_2SiNa$ 1052.1458; Found 1052.1446.

Photoreaction of C_{60} with 19l. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (34% conversion), column chromatography (CS_2) to yield **20l**[19a] (47 mg, 18% (53% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution without MB*: 120 min irradiation (90% conversion), column chromatography (CS_2) to yield **26l**[21a] (156 mg, 56% (62% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 15 min irradiation (100% conversion), column chromatography (CS_2) to yield **26l** (179 mg, 65%).

Photoreaction of C_{60} with 19m. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (35% conversion), column chromatography (CS_2) to yield **20m** (46 mg, 18% (53% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution without MB*: 120 min irradiation (86% conversion), column chromatography (CS_2) to yield **26m** (135 mg, 48% (56% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 15 min irradiation (91% conversion), column chromatography (CS_2) to yield **26m** (131 mg, 47% (51% based on consumed C_{60})).

20m: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 7.65-7.67 (m, 1H), 7.16-7.27 (m, 3H), 6.61 (s, 1H), 4.77 (S, 2H), 4.48 (s, 2H), 4.3 (q, 2H, J = 6.9 Hz), 3.99 (s, 2H), 2.53 (s, 3H), 1.36 (t, 3H, J = 6.9 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$+CS_2, 75 MHz) δ 170.7, 154.4, 154.0, 147.1, 146.9, 146.5, 146.1 (2C), 145.9 (2C), 145.5, 145.2, 145.1 (2C), 144.4, 144.2, 142.9, 142.3 (2C), 142.0, 141.8, 141.7, 141.5, 141.4, 141.3, 140.0, 139.7, 137.4, 136.1, 135.9, 135.8, 130.5, 130.0, 127.8, 126.1, 67.9, 67.0, 60.4, 58.0, 57.8, 56.1, 19.7, 14.4; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{73}H_{19}NO_2Na$ 964.1313; Found 964.1311.

26m: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 7.55-7.58 (m, 1H), 7.24-7.25 (m, 3H), 5.38 (s, 1H), 5.25 (s, 1H), 5.19 (d, 1H, J = 12.6 Hz), 4.54 (d, 1H, J = 12.9 Hz), 4.12-4.36 (m, 2H), 2.62 (s, 3H), 1.18 (t, 3H, J = 7.2 Hz), 0.53 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$+CS_2, 75 MHz) δ 169.9, 157.0, 156.1, 154.5, 152.5, 146.8, 146.7, 146.6, 146.2, 146.0, 145.9 (2C), 145.8, 145.7, 145.6, 145.3, 145.0 (2C), 144.9, 144.7, 144.4, 144.2, 144.1, 144.0, 142.9, 142.8, 142.5, 142.4, 142.1, 142.0, 141.9 (2C), 141.7 (2C), 141.5, 141.4, 139.9, 139.3, 139.2, 138.9, 137.1, 136.0, 135.9, 135.5, 134.6, 130.6, 129.4, 127.7, 126.1, 75.6, 68.9, 60.5, 54.3, 19.8, 14.1, 0.9; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{76}H_{25}NO_2SiNa$ 1034.1552; Found 1034.1544.

Photoreaction of C_{60} with 19n. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (35% conversion), column chromatography (CS_2) to yield **20n** (45 mg, 17% (49% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution without MB*: 120 min irradiation (87% conversion), column chromatography (CS_2) to yield **26n** (139 mg, 49% (57% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 15 min irradiation (94% conversion), column chromatography (CS_2) to yield **26n** (134 mg, 48% (51% based on consumed C_{60})).

20n: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 7.39-7.44 (m, 2H), 7.24-7.29 (m, 1H), 7.10-7.12 (m, 1H), 7.02 (s, 1H), 4.77 (s, 2H), 4.5 (s, 2H), 4.30 (q, 2H, J = 7.2 Hz), 3.92 (s, 2H), 2.39 (s, 3H), 1.40 (t, 3H, J = 7.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$+CS_2, 75 MHz) δ 170.2, 154.4, 154.1, 147.0, 146.9 (2C), 146.8, 146.4, 146.0 (2C), 145.8 (2C), 145.5, 145.1, 145.0, 144.4, 144.2, 142.9, 142.2 (2C), 142.0, 141.7, 141.6, 141.5, 141.3 (2C), 140.0, 139.7, 137.9, 137.7, 135.8, 135.7, 129.8, 128.4, 128.2, 126.1, 68.2, 67.0, 60.3, 59.6, 57.8, 55.3, 21.4, 14.4; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{73}H_{19}NO_2Na$ 964.1313; Found 964.1305.

26n: ^1H NMR ($CDCl_3$+CS_2, 300 MHz) δ 7.38-7.43 (m, 2H), 7.27-7.32 (m, 1H), 7.12-7.15 (m, 1H), 5.42 (s, 1H), 5.38 (s, 1H), 5.19 (d, 1H, *J* = 12.9 Hz), 4.52 (d, 1H, *J* = 13.2 Hz), 4.12-4.34 (m, 2H), 2.43 (s, 3H), 1.18 (t, 3H, *J* = 6.9 Hz), 0.54 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$+CS_2, 75 MHz) δ 169.7, 157.0, 156.2, 154.6, 152.5, 146.7, 146.6, 146.4, 146.1, 146.0, 145.9, 145.8, 145.7 (2C), 145.6, 145.5, 145.2, 145.0, 144.9, 144.8, 144.7, 144.3, 144.2, 144.1, 144.0, 142.9, 142.8, 142.4 (2C), 142.3, 142.1, 142.0, 141.9 (3C), 141.7 (2C), 141.5 (2C), 141.4, 139.9, 139.3, 139.2, 139.0, 138.5, 137.9, 135.9, 135.4 (2C), 134.6, 129.1, 128.6, 128.3, 125.5, 77.6, 77.3, 76.1, 69.6, 60.4, 55.9, 21.5, 14.1, 0.6; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{76}H_{25}NO_2Si$ Na 1034.1552; Found 1034.1539.

Photoreaction of C_{60} with 19o. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (30% conversion), column chromatography (CS_2) to yield **20o**[21a] (41 mg, 16% (53% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution without MB*: 120 min irradiation (91% conversion), column chromatography (CS_2) to yield **26o**[21a] (157 mg, 56% (61% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 15 min irradiation (100% conversion), column chromatography (CS_2) to yield **26o** (162 mg, 58%).

Photoreaction of C_{60} with 19p. *In N_2-purged, 10% EtOH-toluene solution*: 8 min irradiation (32% conversion), column chromatography (CS_2) to yield **20p**[21a] (48 mg, 18% (56% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution without MB*: 120 min irradiation (89% conversion), column chromatography (CS_2) to yield **26p**[21a] (155 mg, 54% (61% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 15 min irradiation (100% conversion), column chromatography (CS_2) to yield **26p** (171 mg, 60%).

Photoreaction of C_{60} with 19q. *In N_2-purged, 10% EtOH-toluene solution*: 60 min irradiation (18% conversion), column chromatography (CS_2) to yield **20q** (19 mg, 7% (39% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution without MB*: 240 min irradiation (74% conversion), column chromatography (CS_2) to yield **26q** (124 mg, 44% (59% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 15 min irradiation (32% conversion), column chromatography (CS_2) to yield **26q** (46 mg, 16% (51% based on consumed C_{60})); 30 min irradiation (73% conversion), column chromatography (CS_2) to yield **26q** (119 mg, 42% (58% based on consumed C_{60})).

20q: ^1H NMR ($CDCl_3$+CS_2, 300 MHz) δ 7.70-7.75 (m, 1H), 7.26-7.33 (m, 1H), 7.14-7.19 (m, 1H), 7.02-7.08 (m, 1H), 6.93 (s, 1H), 4.78 (s, 2H), 4.56 (s, 2H), 4.29 (q, 2H, J = 6.9 Hz), 3.93 (s, 2H), 1.38 (t, 3H, J = 6.9 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$+CS_2, 75 MHz) δ 170.2, 161.3 (d, $J_{C\text{-}F}$ = 245.5 Hz), 154.3, 154.1, 147.0, 146.9, 146.5, 146.0 (2C), 145.9, 145.8, 145.5, 145.2, 145.0 (2C), 144.4, 144.2, 142.9, 142.3, 142.2, 142.0, 141.7 (2C), 141.5, 141.4, 141.3, 140.0, 139.7, 135.8 (d, $J_{C\text{-}F}$ = 5.9 Hz), 131.3 (d, $J_{C\text{-}F}$ = 4 Hz), 129.2 (d, $J_{C\text{-}F}$ = 8 Hz), 124.9 (d, $J_{C\text{-}F}$ = 14 Hz), 124.1 (d, $J_{C\text{-}F}$ = 3.6 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.8 Hz), 68.3, 67.0, 60.4, 57.7, 55.4, 52.6 (d, $J_{C\text{-}F}$ = 2.1 Hz), 14.4; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{72}H_{16}FNO_2Na$ 968.1063; Found 968.1073.

26q: ^{1}H NMR (CDCl$_3$+CS$_2$, 300 MHz) δ 7.76-7.81 (m, 1H), 7.29-7.37 (m, 1H), 7.21-7.26 (m, 1H), 7.05-7.12 (m, 1H), 5.37 (s, 1H), 5.35 (s, 1H), 5.25 (d, 1H, *J* = 13.9 Hz), 4.54 (d, 1H, *J* = 13.5 Hz), 4.13-4.35 (m, 2H), 1.20 (t, 3H, *J* = 7.2 Hz), 0.52 (s, 9H); ^{13}C{^{1}H} NMR (CDCl$_3$+CS$_2$, 75 MHz) δ 169.3, 160.7 (d, $J_{C\text{-}F}$ = 246.5 Hz), 156.5, 155.7, 154.3, 152.2, 146.6, 146.5, 146.2, 145.9, 145.8, 145.7 (3C), 145.5 (2C), 145.4, 145.1 (2C), 144.9, 144.8, 144.7, 144.5, 144.2, 144.0 (2C), 143.8, 142.7, 142.6, 142.3, 142.2 (2C), 142.0, 141.9, 141.8 (2C), 141.7, 141.5, 141.4, 141.2, 139.8, 139.1 (2C), 138.8, 136.0, 135.5, 135.4, 134.7, 130.2 (d, $J_{C\text{-}F}$ = 4 Hz), 128.9 (d, $J_{C\text{-}F}$ = 8 Hz), 125.4 (d, $J_{C\text{-}F}$ = 13.5 Hz), 124.2 (d, $J_{C\text{-}F}$ = 3.5 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.4 Hz), 76.5, 76.1, 69.2, 60.5, 48.5 (d, $J_{C\text{-}F}$ = 2.6 Hz), 14.0, 0.4; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{75}H_{22}FNO_2SiNa$ 1038.1302; Found 1038.1304.

Photoreaction of C_{60} with 19r. *In N_2-purged, 10% EtOH-toluene solution*: 60 min irradiation (20% conversion), column chromatography (CS$_2$) to yield **20r** (21 mg, 8% (40% based on consumed C$_{60}$)). *In O_2-purged, 10% EtOH-toluene solution without MB*: 240 min irradiation (76% conversion), column chromatography (CS$_2$) to yield **26r** (122 mg, 43% (57% based on consumed C$_{60}$)). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 30 min irradiation (75% conversion), column chromatography (CS$_2$) to yield **26r** (122 mg, 43% (58% based on consumed C$_{60}$)).

20r: ^{1}H NMR (CDCl$_3$+CS$_2$, 300 MHz) δ 7.30-7.4 (m, 3H), 6.97 (s, 1H), 6.95-7.01 (m ,1H), 4.76 (s, 2H), 4.54 (s, 2H), 4.29 (q, 2H, *J* = 6.9 Hz), 3.91 (s, 2H), 1.37 (t, 3H, *J* = 6.9 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$+CS$_2$, 75 MHz) δ 170.6, 162.8 (d, $J_{C\text{-}F}$ = 245.9 Hz), 154.3, 154.0, 147.1, 147.0, 146.5, 146.2, 146.1, 146.0, 145.9, 145.6, 145.3, 145.2 (2C), 144.5, 144.3, 143.0, 142.4 (2C), 142.1, 141.9, 141.8, 141.6, 141.5, 141.4, 140.9, 140.8, 140.1, 139.9, 135.9 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.0 (d, $J_{C\text{-}F}$ = 8 Hz), 124.5 (d, $J_{C\text{-}F}$ = 2.8 Hz), 115.8 (d, $J_{C\text{-}F}$ = 21.2 Hz), 114.4 (d, $J_{C\text{-}F}$ = 20.9 Hz), 68.5, 67.0, 60.6, 59.1, 57.9, 55.5, 14.3; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{72}H_{17}FNO_2$ 946.1243; Found 946.1247.

26r: ^{1}H NMR ($CDCl_3$+CS_2, 300 MHz) δ 7.33-7.40 (m, 3H), 7.0-7.06 (m, 1H), 5.37 (s, 2H), 5.24 (d, 1H, J = 13.5 Hz), 4.56 (d, 1H, J = 13.5 Hz), 4.14-4.35 (m, 2H), 1.20 (t, 3H, J = 7.2 Hz), 0.53 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$+CS_2, 75 MHz) δ 169.4, 162.9 (d, $J_{C\text{-}F}$ = 246.3 Hz), 156.7, 155.9, 154.4, 152.2, 146.7, 146.2, 146.0 (2C), 145.9, 145.8, 145.6, 145.5, 145.2, 145.0, 144.9 (3C), 144.8, 144.6, 144.2, 144.1 (2C), 143.9, 142.8 (2C), 142.4 (2C), 142.3, 142.1, 142.0, 141.9 (2C), 141.8, 141.7, 141.6 (2C), 141.5 (2C), 141.4, 141.3, 140.0, 139.3, 139.2, 139.0, 136.0, 135.5, 135.3, 134.5, 130.1 (d, $J_{C\text{-}F}$ = 8 Hz), 123.7 (d, $J_{C\text{-}F}$ = 2.8 Hz), 115.1 (d, $J_{C\text{-}F}$ = 21.4 Hz), 114.5 (d, $J_{C\text{-}F}$ = 20.9 Hz), 77.4, 77.1, 76.2, 69.5, 60.6, 55.5 (d, $J_{C\text{-}F}$ = 1.4 Hz), 14.1, 0.5; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{75}H_{22}FNO_2SiNa$ 1038.1302; Found 1038.1304.

Photoreaction of C_{60} with 19s. *In N_2-purged, 10% EtOH-toluene solution*: 60 min irradiation (22% conversion), column chromatography (CS_2) to yield **20s**[21a] (23 mg, 9% (39% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution without MB*: 240 min irradiation (82% conversion), column chromatography (CS_2) to yield **26s**[21a] (144 mg, 51% (62% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 30 min irradiation (79% conversion), column chromatography (CS_2) to yield **26s** (139 mg, 49% (62% based on consumed C_{60})).

Photoreaction of C_{60} with 19t. *In N_2-purged, 10% EtOH-toluene solution*: 60 min irradiation (19% conversion), column chromatography (CS_2) to yield **20t**[21a] (20 mg, 7% (38% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution without MB*: 240 min irradiation (80% conversion), column chromatography (CS_2) to yield **26t**[21a] (148 mg, 50% (62% based on consumed C_{60})). *In O_2-purged, 10% EtOH-toluene solution with MB (5 mol %)*: 30 min irradiation (73% conversion), column chromatography (CS_2) to yield **26t** (123 mg, 42% (60% based on consumed C_{60})).

Cyclic Voltammetry. Oxidation potentials of glycinate substrates were determined by cyclic voltammetry (CV) using a platinum working electrode, platinum-wire counter electrode, and Ag/Ag+ reference electrode. Measurements were performed under Ar gas; a dichloromethane solution containing tetrabutylammonium tetrafluoroborate (0.1 M) was used as a supporting electrolyte, and the scan rate was 50 mV s^{-1} at room temperature.

Associated Content

Supporting Information

The Supporting Information is available free of charge at http://pubs.acs.org/0000000000.

· Oxidation potentials of selected glyciantes and MB luminescence quenching by glycinates

· Copies of ^1H and ^{13}C NMR spectra of synthesized compounds **19a-19t**, **20a-20t**, **26a-26t**

· DFT-optimized geometry of neutral and radical cations for ethyl *N*-alkyl-*N*-((trimethylsilyl) methyl)glycinates **19b**,**19g**, **19h**, **19l**, **19o**, **19p**, **19s**, **19t**

FAIR data is available as Supporting Information for publication and include the primary NMR FID files for synthesized compounds **19a-19t**, **20a-20t**, **26a-26t**

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References

1. (a) Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. Nonaromatic Aminium Radicals. *Chem. Rev*. **1978**, *78*, 243-274. (b) Dinnocenzo, J. P.; Banach, T. E. Deprotonation of Tertiary Amine Cation Radicals. A Direct Experimental Approach. *J. Am. Chem. Soc*. **1989**, *111*, 8646-8653.

2. (a) Lewis, F. D.; Ho, T.-I. Selectivity of Tertiary Amine Oxidations. *J. Am. Chem. Soc*. **1980**, *102*, 1751-1752. (b) Lewis, F. D.; Ho, T. -I.; Simpson, J. T. Photochemical Addition of Tertiary Amines to Stilbene. Free-Radical and Electron-Transfer Mechanisms for Amine Oxidation. *J. Am. Chem. Soc*. **1982**, *104*, 1924-1929.

3. (a) Xu, W.; Zhang, X. M.; Mariano, P. S. Single Electron Transfer Promoted Photocyclization of (Aminoalkyl)cyclohexenones. Mechanistic and Synthetic Features of Processes Involving the Generation and Reactions of Amine Cation and α-Amino Radicals. *J. Am. Chem. Soc*. **1991**, *113*,

8863-8878. (b) Mariano, P. S.; Stavinoha, J. L. Synthetic Aspects of Photochemical Electron Transfer Reactions. In Synthetic Organic Photochemistry; Horspool, W. M., Ed.; Plenum Press: New York, 1984,; pp 145-257.

4. (a) Yoon, U. C.; Mariano, P. S. Mechanistic and Synthetic Aspects of Amine-Enone Single Electron Transfer Photochemistry. *Acc. Chem. Res*. **1992**, *25*, 233-240. (b) Miyake, Y.; Nakajima, K.; Nishibayashi, Y. Visible-Light-Mediated Utilization of α-Aminoalkyl Radicals: Addition to Electron-Deficient Alkenes Using Photoredox Catalysts. *J. Am. Chem. Soc*. **2012**, *134*, 3338. (c) Cho, D. W.; Yoon, U. C.; Mariano, P. S. Studies leading to the Development of a Single Electron Transfer (SET) Photochemical Strategy for Syntheses of Macrocyclic Polyethers, Polythioethers, and Polyamides. *Acc. Chem. Res*. **2011**, *44*, 204.

5. (a) Beatty, J. W.; Stephenson, R. J. Amine Functionalization via Oxidative Photoredox Catalysis: Methodology Development and Complex Molecule Synthesis. *Acc. Chem. Res.* **2015**, *48*, 1474-1484. (b) Hu, J.; Wang, J.; Nguyen, T. H.; Zheng, N. The Chemistry of Amine Radical Cations Produced by Visible Light Photoredox Catalysis. *Beilstein. J. Org. Chem*. **2013**, *9*, 1977-2001.

6. Kavarnos, G. J.; Turro, N. J. Photosensitization by Reversible Electron Transfer: Theories, Experimental Evidence, and Examples. *Chem. Rev*. **1986**, *86*, 401-449.

7. (a) Zhang, X.; Yeh, S. -R.; Hong, S.; Freccero, M.; Albini, A.; Falvey, D. E.; Mariano, P. S. Dynamics of α-CH Deprotonation and α-Desilylation Reactions of Tertiary Amine Cation Radicals. *J. Am. Chem.*

Soc. **1994**, *116*, 4211-4220. (b) Parker, V. D.; Tilset, M. Facile Proton Transfer Reactions of *N*,*N*-Dimethylaniline Cation Radicals. *J. Am. Chem. Soc*. **1991**, *113*, 8778-8781.

8. (a) Lewis, F. D. Proton-Transfer Reactions of Photogenerated Radical Ion Pairs. *Acc. Chem. Res.* **1986**, *19*, 401-405. (b) Shi, L.; Xia, W. Photoredox Functionalization of C-H Bonds Adjacent to a Nitrogen Atom. *Chem. Soc. Rev.* **2012**, *41*, 7686-7697.

9. (a) Dai, X.; Cheng, D.; Guan, B.; Mao, W.; Xu, X.; Li, X. The Coupling of Tertiary Amines with Acrylate Derivatives via Visible-Light Photoredox Catalysis. *J. Org. Chem*. **2014**, *79*, 7212-7219. (b) Zhang, X. M.; Mariano, P. S. Mechanistic details for SET-Promoted Photoadditions of Amines to Conjugated Enones Arising from Studies of Aniline-Cyclohexenone Photoreactions. *J. Org. Chem.* **1991**, *56*, 1655-1660. (c) Nakajima, K.; Miyake, Y.; Nishibayashi, Y. Synthetic Utilization of α-Aminoalkyl Radicals and Related Species in Visible Light Photoredox Catalysis. *Acc. Chem. Res.* **2016**, *49*, 1946-1956.

10. (a) Kohls, P.; Jadhav, D.; Pandey, G.; Reiser, O. Visible Light Photoredox Catalysis: Generation and Addition of *N*-Aryltetrahydroisoquinoline-Derived α-Amino Radicals to Michael Acceptors. *Org. Lett*. **2012**, *14*, 672-675. (b) McManus, J. B.; Onuska, N. P. R.; Nicewicz, D. A. Generation and Alkylation of α-Carbamyl Radicals via Organic Photoredox Catalysis. *J. Am. Chem. Soc*. **2018**, *140*, 9056-9060. (c) Espelt, L. R.; Wiensch, E. M.; Yoon, T. P. Bronsted Acid Cocatalysts in Photocatalytic Radical Addition of α-Amino C–H Bonds across Michael Acceptors. *J. Org. Chem*. **2013**, *78*, 4107. (d) Bertrand, S.; Hoffmann, N.; Pete, J. P. Highly Efficient and Stereoselective Radical Addition of

Tertiary Amines to Electron Deficient Alkenes - Application to the Enantioselective Synthesis of Necine Bases. *Eur. J. Org. Chem*. **2000**, 2227-2238.

11. (a) Freeman, D. B.; Frust, L.; Condie, A. G.; Stephenson, C. R. J. Functionally Diverse Nucleophilic Trapping of Iminium Intermediates Generated Utilizing Visible Light. *Org. Lett*. **2012**, *14*, 94-97. (b) Rueping, M.; Leonori, D.; Poisson, T. Visible Light Mediated Azomethine Ylide Formation - Photoredox Catalyzed [3+2] Cycloadditions. *Chem. Commun.* **2011**, *47*, 9615-9617. (c) Vila, C.; Lau, J.; Rueping, M. Visible-Light Photoredox Catalyzed Synthesis of Pyrroloisoquinolines via Organocatalytic Oxidation/[3+2] Cycloaddition/Oxidative Aromatization Reaction Cascade with Rose Bengal. *Beilstein J. Org. Chem*. **2014**, *10*, 1233-1238. (d) Zou, Y. -Q.; Lu, L. -Q.; Fu, L.; Chang, N.-J.; Rong, J.; Chen, J. -R. Xiao, W. -J. Visible-Light-Induced Oxidation/[3+2] Cycloaddition/Oxidative Aromatization Sequence: A Photocatalytic Strategy to Construct Pyrrolo[2,1-a]isoquinolines. *Angew. Chem. Int. Ed*. **2011**, *50*, 7171-7175.

12. (a) Hari, D. P.; Konig, B. Eosin Y Catalyzed Visible Light Oxidative C-C and C-P Bond Formation. *Org. Lett*. **2011**, *13*, 3852-3855. (b) Yadav, A. K.; Yadav, L. D. S. Visible-Light-Driven Electocyclization of Activated Allylic Amines via Azomethine Ylide Formation. *Tetrahedron Lett*. **2015**, *56*, 686-689.

13. (a) Wayner, D. D. M.; McPhee, D. J.; Griller, D. Oxidation and Reduction Potentials of Transient Free Radicals. *J. Am. Chem. Soc.* **1988**, *110*, 132-137. (b) Burkey, T. J.; Castelhano, A. L.; Griller, D.; Lossing, F. P. Heats of Formation and Ionization Potentials of Some α-Aminoalkyl Radicals. *J. Am.*

Chem. Soc. **1983**, *105*, 4701. (c) Wayner, D. D. M.; Dannenberg, J. J.; Griller, D. Oxidation Potentials of α-Aminoalkyl Radicals: Bond Dissociation Energies for Related Radical Cations. *Chem. Phys. Lett*. **1986**, *131*, 189.

14. (a) Rueping, M. Zhu, S.; Koenigs, R. M. Photoredox Catalyzed C-P Bond Forming Reactions - Visible Light Mediated Oxidative Phosphonylations of Amines. *Chem. Commun*. **2011**, *47*, 8679-8681. (b)

15. (a) Zhu, S.; Das, A.; Bui, L.; Zhou, H.; Curran, D. P.; Rueping, M. Oxygen Switch in Visible-Light Photoredox Catalysis: Radical Additions and Cyclizations and Unexpected C-C Bond Cleavage Reactions. *J. Am. Chem. Soc*. **2013**, *135*, 1823-1829. (b) Bartling, H.; Eisenhofer, A.; Konig, B.; Gschwind, R. M. The Photocatalyzed Aza-Henry Reaction of *N*-Aryltetrahydroisoquinolines: Comprehensive Mechanism, $H^\bullet$- versus H^+-Abstraction, and Background Reactions. *J. Am. Chem. Soc*. **2016**, *138*, 11860-11871.

16. Yoon, U. C.; Kwon, H. C.; Hyung, T. G.; Choi, K. H.; Oh, S. W.; Yang, S.; Zhao, Z.; Mariano, P. S. The Photochemistry of Polydonor-Substituted Phthalimides: Curtin-Hammet Type Control of Competing Reactions of Potentially Interconverting Zwitterionic Biradical Intermediates. *J. Am .Chem. Soc*. **2004**, *126*, 1110-1124.

17. (a) Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaga, S. Electrochemical Oxidation of Organosilicon Compounds. The Origin of the β-Silicon Effect in Electron Transfer Reactions of Silicon Substituted Heteroatom Compounds. Electrochemical and Theoretical Studies. *J. Am. Chem.*

Soc. **1990**, *112*, 1962-1970. (b) Cooper, B. E.; Owen, W. J. Silicon Carbon Bond Hyperconjugation in Cation Radicals. Lower Oxidation Potentials of *N*-(Trimethylsilylmethyl) Aromatic Amines. *J. Organometal. Chem.* **1971**, *29*, 33-40. (c) Yoshida, J.; Isoe, S. Electrochemical Oxidation of Organo-Silicon Compounds. Electrochemical Oxidation of α-Silylcarbamates. *Tetrahedron Lett.* **1987**, *28*, 6621. (d) Pitt, C. G. Hyperconjugation and Its Role in Group IV Chemistry. *J. Organometal. Chem.* **1973**, *61*, 49-70.

18. (a) Coldham, I.; Hufton, R. Intramolecular Dipolar Cycloaddition Reactions of Azomethine Ylides. *Chem. Rev*. **2005**, *105*, 2765-2809. (b) Hashimoto, T.; Maruoka, K. Recent Advances of Catalytic Asymmetric 1,3-Dipolar Cycloadditions. *Chem. Rev*. **2015**, *115*, 5366-5412.

19. (a) Lim, S. H.; Yi, J.; Moon, G. M.; Ra, C. S.; Nahm, K.; Cho, D. W.; Kim, K.; Hyung, T. G.; Yoon, U. C.; Lee, G. Y.; Kim, S.; Kim, J.; Mariano, P. S. Method for the Synthesis of Amine-Functionalized Fullerenes Involving SET-Promoted Photoaddition Reactions of α-Silylamines. *J. Org. Chem.* **2014**, *79*, 6946-6958. (b) Lim, S. H.; Yi, J.; Ra, C. S.; Nahm, K.; Cho, D. W.; Lee, G. Y.; Kim, J.; Yoon, U. C.; Mariano, P. S. SET-Promoted Photoaddition Reactions of *N*-α-Trimethylsilylmethyl-*N*,*N*-dibenzylamines with Fullerene C_{60}. Electronic Factors that Govern Photoaddition Efficiencies. *Tetrahedron Lett*. **2015**, *56*, 3014-3018.

20. (a) Jeong, H. C.; Lim, S. H.; Sohn, Y.; Kim, Y. -I.; Jang, H.; Cho, D. W.; Mariano, P. S. Electronic and Steric Effects Controlling Efficiencies of Photoaddition Reactions of Fullerene C_{60} with *N*-α-Trimethylsilyl-*N*-Alkyl-*N*-Benzylamines. *Tetrahedron Lett*. **2017**, *58*, 949-954. (b) Lim, S. H.; Cho, D.

W.; Mariano, P. S. Catalyst Free, Visible-Light Promoted Photoaddition Reactions between C_{60} and *N*-Trimethylsilylmethyl-Substituted Tertiary Amines for Synthesis of Aminomethyl 1,2-Dihydrofullerenes. *Tetrahedron* **2018**, *74*, 383-391.

21. (a) Lim, S. H.; Cho, D. W.; Mariano, P. S. Synthesis of Functionalized Fullerenes by Photoaddition of *N*-α-Trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines to C_{60}. *Heterocycles* **2016**, *93*, 202-217. (b) Lim, S. H.; Jeong, H. C.; Sohn, Y.; Kim, Y. -I.; Cho, D. W.; Woo, H. -J.; Shin, I. -S.; Yoon, U. C.; Mariano, P. S. Single Electron Transfer-Promoted Photochemical Reactions of Secondary *N*-Trimethylsilylmethyl-*N*-benzylamines Leading to Aminomethylation of Fullerene C_{60}. *J. Org. Chem.* **2016**, *81*, 2460-2473. (c) Jeong, H. C.; Lim, S. H.; Cho, D. W.; Kim, S. H.; Mariano, P. S. Single Electron Transfer Promoted Photoaddition Reactions of α-Trimethylsilyl Substituted Secondary *N*-Alkylamines with Fullerene C_{60}. *Org. Biomol. Chem*. **2016**, *14*, 10502-10510. (d) Lim, S. H.; Atar, A. B.; Bae, G.; Wee, K. -R.; Cho, D. W. Photoaddition Reactions of *N*-Benzylglycinates Containing α-Trimethylsilyl group with Dimethyl Acetylenedicarboxylate: Competitive Formation of Pyrroles vs. β-Enamino Esters. *RSC Adv*. **2019**, *9*, 5639-5648.

22. (a) Arbogast, J. W.; Darmanyan, A. O.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. Photophysical Properties of C_{60}. *J. Phys. Chem*. **1991**, *95*, 11-12. (b) Hung, R. R.; Grabowski, J. J. A Precise Determination of the Triplet Energy of C_{60} by Photoacoustic Calorimetry. *J. Phys. Chem*. **1991**, *95*, 6073-6075. (c) Arbogast, J. W.; Foote, C. S.; Kao, M. Ekectron Transfer to Triplet C_{60}. *J. Am. Chem. Soc*. **1992**, *114*, 2277-2279.

23. (a) Sension, R. J.; Phillips, C. M.; Szarka, A. Z.; Romanow, W. J.; McGhie, A. R.; McCauley Jr, J. P.; Smith III, A. B.; Hochstrasser, R. M. Transient Absorption Studies of C_{60} in Solution. *J. Phys. Chem*. **1991**, *95*, 6075-6078. (b) Ebbesen, T. W.; Tanigaki, K.; Kuroshima, S. Exicted-State Properties of C_{60}. *Chem. Phys. Lett.* **1991**, *181*, 501-504. (c) Fraelich, M. R.; Weisman, R. B. Triplet State of C_{60} and C_{70} in Solution: Long Intrinsic Lifetimes and Energy Pooling. *J. Phys. Chem*. **1993**, *97*, 11145-11147.

24. Su, Z.; Mariano, P. S.; Falvey, D. E.; Yoon, U. C.; Oh, S. W. Dynamics of Anilinium Radical α-Heterolytic Fragmentation Processes. Electrofugal Group, Substituent, and Medium Effects on Desilylation, Decarboxylation, and Retro-Aldol Cleavage Pathways. *J. Am. Chem. Soc*. **1998**, *120*, 10676.

25. Mikami, K.; Matzumoto, S.; Ishida, A.; Takamuku, S.; Suenobu, T.; Fukuzumi, S. Addition of Ketene Silyl Acetals to the Triplet Excited State of C_{60} via Photoinduced Electron Transfer Leading to the Fullereneacetates. *J. Am. Chem. Soc*. **1995**, *117*, 11134.

26. (a) Guldi, D. M.; Prato, M. Excited-State Properties of C_{60} Fullerene Derivatives. *Acc. Chem. Res*. **2000**, *33*, 695-703. (b) Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khemani, K.; Wudl, F.; Leonetti, J.; Little, R. D.; White, T.; Rickborn, B. [3+2] and [4+2] Cycloadditions of C_{60}. *J. Am. Chem. Soc*. **1993**, *115*, 1594-1595. (c) Maggini, M.; Scorrano, G.; Prato, M. Addition of Azomethine Ylides to C_{60}: Synthesis, Characterization, and Functionalization of Fullerene pyrrolidines. *J. Am. Chem. Soc*. **1993**, *115*, 9798-9799.

27. Bernstein, R.; Foote, C. S. Singlet Oxygen Involvement in the Photochemical Reaction of C_{60} and

Amines. Synthesis of an Alkyne-Containing Fullerene. *J. Phys. Chem. A* **1999**, *103*, 7244.

28. (a) Baciocchi, E.; Giacco, T. D.; Lanzalunga, O.; Lapi, A.; Raponi, D. The Singlet Oxygen Oxidation of Chlorpromazine and Some Phenothiazine Derivatives. Products and Reaction Mechanism. *J. Org. Chem*. **2007**, *72*, 5912-5915. (b) Baciocchi, E.; Giacco, T. D.; Lapi, A. Oxygenation of Benzyldimethylamine by Singlet Oxygen. Products and Mechanism. *Org. Lett*. **2004**, *6*, 4791-4794. (c) Baciocchi, E.; Giacco, T. D.; Lapi, A. Dual Pathways for the Desilylation fo Silylamines by Singlet Oxygen. *Org. Lett*. **2006**, *8*, 1783-1786.

29. (a) Ouannes, C.; Wilson, T. Quenching of Singlet Oxygen by Tertiary Aliphatic Amines. Effect of DABCO. *J. Am. Chem. Soc*. **1968**, *90*, 6527-6528. (b) Ogryzlo, E. A.; Tang, C. W. Quenching of Oxygen ($^1\Delta_g$) by Amines. *J. Am. Chem. Soc*. **1970**, *92*, 5034-5036.

30. (a) Darmanyan, A. P.; Jenks, W. S.; Jardon, P. Charge-Transfer Quenching of Singlet Oxygen $O_2(^1\Delta_g)$ by Amines and Aromatic Hydrocarbons. *J. Phys. Chem. A* **1998**, *102*, 7420-7426. (b) Young, R. H.; Martin, R. L. On the Mechanism of Quenching of Singlet Oxygen by Amines. *J. Am. Chem. Soc.* **1972**, *94*, 5183-5185.

31. (a) Pitre, S. P.; McTiernan, C. D.; Ismaili, H.; Scaiano, J. C. Mechanistic Insights and Kinetic Analysis for the Oxidative Hydroxylation of Arylboronic Acids by Visible Light Photoredox Catalysis: A Metal-Free Alternative. *J. Am. Chem. Soc*. **2013**, *135*, 13286-13289. (b) Pitre, S. P.; McTiernan, C. D.; Ismaili, H.; Scaiano, J. C. Metal-Free Photocatalytic Radical Trifluoromethylation Utilizing Methylene Blue and Visible Light Irradiation. *ACS Catal*. **2014**, *4*, 2530-2535.

32. (a) Romero, N. A.; Nicewicz, D. A. Organic Photoredox Catalysis. *Chem. Rev*. **2016**, *116*, 10075-10166. (b) Shen, T.; Zhao, Z. -G.; Yu, Q.; Xu, H. -J. Photosensitized Reduction of Benzil by Heteroatom-Containing Anthracene Dyes. *J. Photochem. Photobiol. A*. **1989**, *47*, 203-212.

33. Kayser, R. H.; Young, R. H. The Photoreduction of Methylene Blue by Amines-I. A Flash Photolysis Study of the Reaction between Triplet Methylene Blue and Amines. *Photochem. Photobiol*. **1976**, *24*, 395-401.

34. (a) Usui, Y.; Kamogawa, K. A Standard System to Determine the Quantum Yield of Single Oxygen Formation in Aqueous Solution. *Photochem. Photobiol*. **1974**, *19*, 245-247. (b) DeRosa, M. C.; Crutchley R. J. Photosensitized Singlet Oxygen and Its Applications. *Coord. Chem. Rev*. **2002**, *233-234*, 351-371.