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Photoaddition reactions of *N*-benzylglycinates containing α-trimethylsilyl group with dimethyl acetylenedicarboxylate: competitive formation of pyrroles *vs.* β-enamino esters†

Suk Hyun Lim,[a] Amol B. Atar,[a] Gunoh Bae,[b] Kyung-Ryang Wee[b] and Dae Won Cho *[a]

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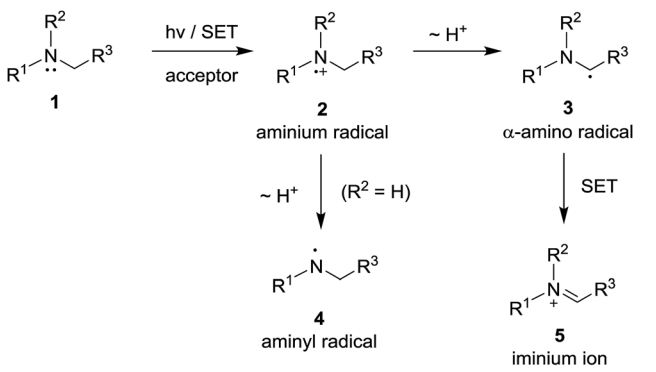
A study was conducted to gain insight into the preparative potential of photosensitized reactions of acyclic *N*-benzylglycinates containing an α-trimethylsilyl group with dimethyl acetylenedicarboxylate (DMAD). The photosensitizers employed in the reactions include 9,10-dicyanoanthracene (DCA), 1,4-dicyanonaphthalene (DCN), rose bengal (RB) and fullerene C_{60}. The results show that photoirradiation of oxygenated solutions containing the photosensitizers, glycinates and dimethyl acetylenedicarboxylate leads to competitive formation of pyrroles and β-enamino-esters. The distributions of pyrrole and β-enamino-ester products formed in these reactions are highly influenced by the electronic nature of the phenyl ring substituent on the benzylglycinates and the photosensitizer used. These photoaddition reactions take place *via* mechanistic pathways involving competitive formation of azomethine ylides and secondary amines, generated by a mechanistic routes involving initial SET from the benzylglycinates to photosensitizers.

Introduction

Photoinduced single electron transfer (SET), occurring between a variety of electron donating and accepting pairs, is now recognized to be one of the most important events taking place in mechanistically interesting and preparatively useful photochemical reactions.[1–6] Among a wide variety of electron donating substances that participate in these processes, aliphatic/aromatic amines have perhaps been among the most widely explored.[7–10] In photoinduced SET reactions of aliphatic/aromatic amines **1**, aminium radicals **2** (*i.e.*, amine radical cations) serve as key reactive intermediates (Scheme 1). The most common reaction pathways open to aminium radicals are base-promoted deprotonation from either nitrogen to produce either aminyl radicals **4** (in the cases of primary and secondary aminium radicals)[11,12] or α-carbon to form α-amino radicals **3** (in the case of tertiary aminium radicals).[7,9b,13] The radical intermediates generated in this manner take part in a variety of addition reactions with electron deficient alkenes, alkynes and unsaturated carbonyl compounds.[8,10a,12–15] In addition, owing to their extremely low oxidation potential,[16] α-amino radicals **3** undergo ready secondary SET oxidation in the presence of appropriate oxidants to form iminium ions **5**.[8a,17]

Among the interesting photochemical reactions that take place through the sequential SET – α-CH deprotonation pathway are those involving tertiary amines, which possess *N*-carboxymethyl groups (*i.e.*, glycinates).[18] Tertiary glycinate esters undergo unique cycloaddition reactions with alkenes/alkynes, which take place *via* the intermediacy of 1,3-dipolar azomethine ylides. An interesting example was uncovered in early studies by Xiao[18a] and Rueping,[18b] which showed that photoirradiation of solutions of ethyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetate derivatives **6** and electron deficient alkenes/



Scheme 1 Photoinduced single electron transfer (SET) reaction pathways opened for amine substrates.

[a]*Department of Chemistry, Yeungnam University, Gyeongsan, Gyeongbuk 38541, Republic of Korea. E-mail: dwcho00@yu.ac.kr*

[b]*Department of Chemistry, Daegu University, Gyeongsan, Gyeongbuk 38453, Republic of Korea*

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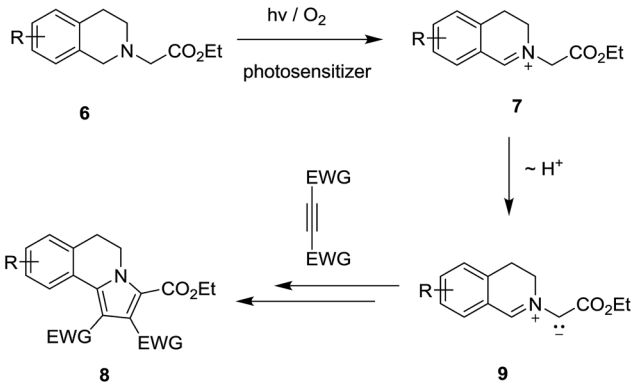


Scheme 2 SET-promoted 1,3-dipolar cycloaddition reactions of ethyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetate **6** with dipolarophile.

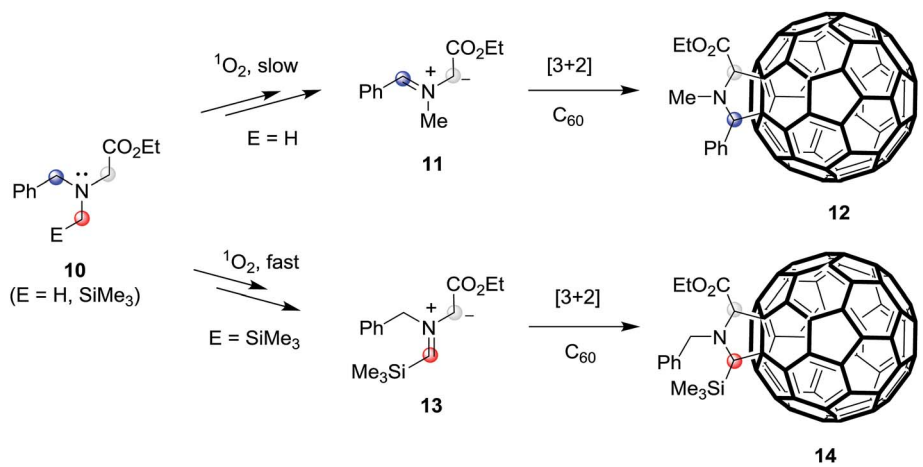
alkynes, containing a photosensitizer and molecular oxygen, gives rise to generation of pyrrolo[2,1-*a*]isoquinoline products **8** (Scheme 2). This process likely occurs through a mechanistic pathway entailing deprotonation of an intermediate iminium ion **7** produced by a route (see Scheme 1) that begins with SET from **6** to the electronic excited state of the photosensitizer. The azomethine ylide intermediate **9**, generated in this way, undergoes 1,3-dipolar cycloaddition reactions with alkene/alkyne substrates.

In recent studies aimed at exploring photoaddition reactions of tertiary amines with fullerene C_{60}, we also observed that *N*-benzylglycinates **10** (E = H) could serve as precursors of azomethine ylides (Scheme 3).[10c,19] Specifically, irradiation of solutions of *N*-benzylglycinates **10** (E = H) and C_{60} in the presence of molecular oxygen gives rise to formation of pyrrolidine ring-fused fullerene derivatives **12** (fulleropyrrolidines) (Scheme 3). In this process, C_{60} serve as both the photosensitizer as well as reactive dipolarophile. Moreover, we found that irradiation of oxygenated solutions of C_{60} and *N*-benzylglycinates **10**, which possess α-trimethylsilyl groups (E = $SiMe_3$), promotes generation of trimethylsilyl group containing fulleropyrrolidines **14** in a much more efficient manner.[19] These observations suggested that the routes for formation of these products begin with the generation of singlet oxygen ($^1O_2$) *via* energy transfer from the triplet state ($^3C_{60}^*$) of the photosensitizer.[20] Following the suggestion made earlier by Foote and his coworkers,[20c] the formed $^1O_2$ abstract H-atom from the benzylic position of benzylglycinate **10** (E = H), lacking the α-trimethylsilyl group, followed by SET oxidation to form iminium precursor of azomethine ylides **11**, which then cycloadd to C_{60} to form **12**. However, in photoreactions of the α-trimethylsilyl group containing *N*-benzylglycinate **10** (E = $SiMe_3$), H-atom abstraction mediated by $^1O_2$ takes place more efficiently at the α-trimethylsilyl substituted carbon position to produce azomethine ylides **13** that cycloadd to C_{60} to generate **14**.

Although a variety of photosensitized 1,3-dipolar cyclization reactions of either cyclic *N*-carboxyalkyl substituted tetrahydroisoquinolines[21a] or iminoester derivatives[21b] with dipolarophiles have been mainly performed so far, to the best of knowledge, cyclization reactions utilizing acyclic *N*-carboxyalkyl substituted benzylamine substrates are not common. Thus, the observations made in the investigation described above suggested that azomethine ylides generated from acyclic *N*-benzylglycinates containing α-trimethylsilyl group might participate in photosensitized cycloaddition reactions with a variety of electron deficient dipolarophiles to produce five membered ring *N*-heterocycles. In order to assess this proposal, we explored photosensitized addition reactions of dimethyl acetylenedicarboxylate (DMAD) with *N*-α-trimethylsilyl-*N*-benzylglycinates, possessing a variety of substituents on the arene ring of the benzyl group. The photosensitizers (PS) employed in these processes include 9,10-dicyanoanthracene (DCA), 1,4-dicyanonaphthalene (DCN), rose bengal (RB) and fullerene C_{60}. The results arising from this effort show that two competitive pathways are followed in these reactions, one of which involves cycloaddition to form pyrroles and the other generates β-enamino-esters. In addition, the photoproduct distributions (*i.e.*, pyrrole/β-enamine ester ratios) are influenced by the electronic nature of the glycinate substrates and photosensitizer used.

Results and discussion

N-α-Trimethylsilyl-*N*-benzylglycinates **16a–16g**, in which the benzyl moieties contain various substituents on the phenyl ring,



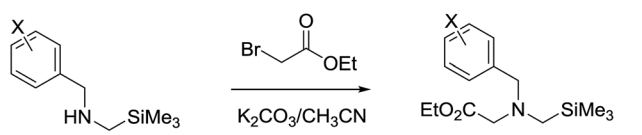
Scheme 3 SET-promoted 1,3-dipolar cycloaddition reactions of tertiary *N*-benzylglycinates **10** (E = H, $SiMe_3$) with fullerene C_{60}.

were prepared using an earlier developed synthetic protocol[10c,19,22] (Scheme 4). Photochemical reactions were carried out using O_2-purged MeCN or toluene solutions containing **16a–16g** (3.2 mM) and DMAD (**17**, 3.2 mM) in the presence of SET photosensitizer. The solutions were irradiated for time periods that bring about 100% conversion of the starting glycinates by using a 450 W Hanovia mercury lamp equipped with a glass filter (λ > 310 nm). In all cases, the photolysates were concentrated and the residues were subjected to column chromatography to produce pure samples of the respective photoproducts.

DCA-promoted photochemical reactions

Prior to carrying out DCA promoted photochemical reactions, oxidation potentials (E_{ox}) of the glycinate substrates **16a–16g** were determined in order to ascertain whether SET from the glycinates to the singlet excited state of the SET photosensitizer DCA (^{1}DCA) is thermodynamically favorable. In addition, the rate constants for quenching of the fluorescence of DCA by glycinates **16a–16g** in MeCN were determined in order to derive the rate constants (k_{SET}) for SET. As can be seen viewing the data in Table 1, the glycinates have E_{ox} values in the range of 0.83–0.91 V (*vs.* SCE), which are below the reduction potential of singlet state of DCA (^{1}DCA) ($^1E_{red}$(DCA) = 1.99 V *vs.* SCE). As a result, free energy changes for SET (ΔG_{SET}) from all glycinates to ^{1}DCA are negative, suggesting that the rates of these processes should be near the diffusion controlled limit. Stern–Volmer analysis of plots of fluorescence intensities of DCA *vs.* glycinate concentrations (Fig. S1, ESI†), showed that the rates of fluorescence quenching by SET from the glycinates **16a–16g** to ^{1}DCA are near that of diffusion in MeCN.

Photochemical reactions of *N*-benzylglycinates **16a–16g** with DMAD (**17**) were performed in O_2-purged MeCN solutions in the presence of DCA for the time periods given in Table 2. Concentration of the photolysates followed by chromatographic separation gave the products shown in Scheme 5 and the yields listed in Table 2. As can be seen by viewing the results, 5 min irradiation of O_2-purged MeCN solutions containing DCA, acetylene **17** and glycinates **16a–16d**, which possess H and electron donating groups (Me, OMe) on the phenyl ring of the benzyl substituent, gave rise to production of the respective β-enamino-esters **19a–19d**, along with minor amounts of the corresponding substituted pyrroles **18a–18d** (entries 1–4, Table 2). In contrast,



15a (X = H)
15b (X = *p*-Me)
15c (X = o,*p*-di-Me)
15d (X = *p*-OMe)
15e (X = *p*-F)
15f (X = o,*p*-di-F)
15g (X = *p*-CF_3)

16a (X = H, 70%)
16b (X = *p*-Me, 66%)
16c (X = o,*p*-di-Me, 66%)
16d (X = *p*-OMe, 51%)
16e (X = *p*-F, 74%)
16f (X = o,*p*-di-F, 68%)
16g (X = *p*-CF_3, 55%)

Scheme 4 Synthesis of *N*-α-trimethylsilyl-*N*-benzylglycinates **16a–16g**.

Table 1 Oxidation potentials (E_{ox}), free energy changes for SET (ΔG_{SET}) and rate constants for DCA fluorescence quenching by *N*-α-trimethylsilyl-*N*-benzylglycinates **16a–16g** in MeCN solutions

Glycinate	E_{ox}(+) (V *vs.* SCE)	ΔG_{SET}[a] (V)	$k_{SET} \times 10^{-10}$ (M^{-1} s^{-1})
16a	0.84	−1.15	1.1
16b	0.83	−1.16	1.0
16c	0.83	−1.16	—[b]
16d	0.84	−1.15	—[b]
16e	0.80	−1.19	0.99
16f	0.89	−1.10	—[b]
16g	0.91	−1.08	0.86

[a] Determined by using $\Delta G_{SET} = E_{ox}$ (glycinate) − E_{red} (DCA) − E_{ex} (DCA), where E_{red} (DCA) is −0.91 V (*vs.* SCE) (ref. 23) and E_{ex} (DCA) is 2.90 V (ref. 23). [b] Not measured.

Table 2 Products and yields of DCA-photosensitized reactions of oxygen purged MeCN solutions containing glycinates **16a–16g** and acetylene **17**[a]

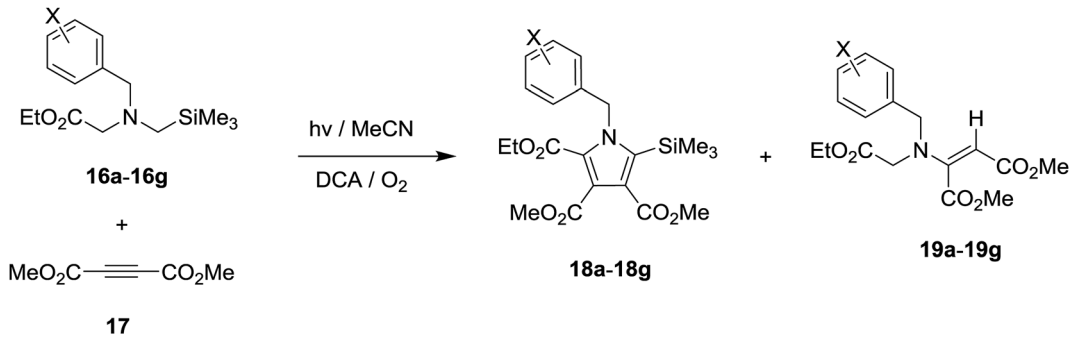
Entry	Amine	X	Irradiation time (min)	Product[b] (%)
1	**16a**	H	5	**18a** (6), **19a** (50)
2	**16b**	*p*-Me	5	**18b** (4), **19b** (51)
3	**16c**	o,*p*-di-Me	5	**18c** (trace), **19c** (48)
4	**16d**	*p*-OMe	5	**18d** (trace), **19d** (45)
5	**16e**	*p*-F	10	**18e** (21), **19e** (31)
6	**16f**	o,*p*-di-F	10	**18f** (24), **19f** (33)
7	**16g**	*p*-CF_3	20	**18g** (32), **19g** (22)
8[c]	**16a**	H	300	n.r[d]
9[e]	**16a**	H	300	n.r[d]

[a] 220 mL of MeCN solutions containing glycinates **16a–16g** (3.2 mM), acetylene **17** (3.2 mM) and DCA (0.27 mM). [b] Isolated yields. [c] Photoreaction in N_2-purged MeCN solution. [d] No reaction. [e] Photoreaction in O_2-purged MeCN solution without DCA.

10 min irradiation of solutions containing the mono- and difluoro substituted phenyl containing glycinates **16e–16f**, **17** and DCA produced *ca.* 1 : 1.5 ratios of pyrroles (**18e–18f**) and β-enamino-esters (**19e–19f**) (entries 5 and 6, Table 2). Finally, DCA-promoted photoreaction of the *para*-CF_3-phenyl containing glycinate **16g** with **17** took place to produce both trimethylsilyl-substituted pyrrole **18g** (32%) and β-enamino-ester **19g** (22%) by 20 min irradiation (entry 7 in Table 2). Importantly, the concentration of DCA in all photoreactions was kept constant and control experiments (entries 8 and 9 in Table 2) revealed that both molecular oxygen and DCA are necessary for reactions to take place.

DCN-promoted photochemical reactions

DCN was also utilized as a SET photosensitizer to promote reactions of the glycinates with acetylene **17**. Similar to the case of DCA, the calculated free energy changes (ΔG_{SET}) for SET from the glycinates to the singlet state of DCN ($^1E_{red}$ = 2.3 V *vs.* SCE)[23] were negative. In addition, the results of fluorescence quenching experiments showed that the glycinates quench the singlet



Scheme 5 DCA-promoted photochemical reactions of *N*-benzylglycinates **16a–16g** with DMAD **17**.

state of DCN (^{1}DCN) with near diffusion controlled rates (Fig. S2 of ESI†).

The results of photochemical reactions of *N*-α-trimethylsilyl-*N*-benzylglycinates **16a**, **16b**, **16e** and **16g** with acetylene **17** in O_2-purged MeCN solutions in the presence of DCN are shown in Table 3. As the data show, the DCN-promoted photoreactions took place to produce pyrroles and β-enamino-esters but, in contrast to the DCA-photosensitized reactions, they required much longer irradiation times to bring about complete conversion of glycinate substrates. For example, 60 min irradiation of an oxygenated MeCN solution containing **16a**, **17** and DCN gave rise to formation of β-enamino-ester **19a** (40%), along with pyrrole **18a** (11%) (entry 1 in Table 3). Moreover, 60 min photochemical reaction of the *p*-Me-phenyl substituted glycinate **16b** and **17** in the presence of DCN produced β-enamino-ester **19b** exclusively (entry 2 in Table 3), and photoreactions of the *p*-F- (**16e**) and *p*-CF_3-substituted (**16g**) glycinates with **17** occurred to produce *ca.* 1 : 3 and 2 : 3 respective ratios of pyrroles (**18e** and **18g**) and the respective enamino-esters (**19e** and **19g**) by much longer irradiation (entries 3 and 4 in Table 3).

RB-promoted photochemical reactions

RB-promoted photoaddition reactions of *N*-α-trimethylsilyl-*N*-benzylglycinates with acetylene **17** were also investigated. Similar to the cases of DCA and DCN, the free energy changes for SET occurring between glycinates and RB ($^{S1}E_{red}$ = 1.18 V, $^{T1}E_{red}$ = 1.02 V *vs.* SCE)[24] are all negative.

The results displayed in Table 4 show that RB-promoted photochemical reactions O_2-purged MeCN solutions of glycinates **16a**, **16b**, **16e** and **16g** with acetylene **17** take place efficiently to produce pyrroles and β-enamino-esters. Specifically, 5 min irradiation of RB solutions containing **16a–16b** and **17** produced a *ca.* 1 : 4 ratios of the corresponding pyrroles **18a–18b** (11–12%) and β-enamino-esters **19a–19b** (47–49%) (entries 1 and 2 in Table 4). Interestingly, in contrast to those photosensitized by DCA, RB-promoted reactions of the *p*-F- (**16e**) and *p*-CF_3- (**16g**) phenyl substituted glycinates with **17** produced higher yields of the respective β-enamino-esters **19e** and **19g** (41–45%) than pyrroles **18e** and **18g** (11–12%) (entries 3 and 4 in Table 4).

C_{60}-promoted photochemical reactions

A consideration of redox potentials suggests that C_{60} ($^3E_{red}$ = 1.14 V *vs.* SCE)[25] should serve as a SET-photosensitizer for reactions between the glycinates and DMAD. Owing to the generally low solubility of fullerene C_{60} in MeCN, toluene was used as the solvent for C_{60}-promoted photoaddition reactions of *N*-α-trimethylsilyl-*N*-benzylglycinates **16a–16g** with acetylene **17**. Inspection of the results summarized in Table 5 showed that the product distributions patterns arising from these photochemical reactions are comparable with those from DCA-, DCN- and RB-promoted photochemical reactions of these substrates. Specifically, irradiation of O_2-purged toluene solutions containing glycinates **16a–16g**, **17** and C_{60} produced pyrroles **18a–**

Table 3 Products and yields of DCN-photosensitized reactions of O_2-purged MeCN solutions containing glycinates (**16a**, **16b**, **16e** and **16g**) and acetylene **17**[a]

Entry	Glycinate	Irradiation time (min)	Product[b] (%)
1	**16a**	60	**18a** (11), **19a** (40)
2	**16b**	60	**18b** (4), **19b** (49)
3	**16e**	90	**18e** (12), **19e** (40)
4	**16g**	180	**18g** (21), **19g** (32)

[a] 220 mL of MeCN solutions containing glycinates (**16a**, **16b**, **16e** and **16g**, 3.2 mM), acetylene **17** (3.2 mM) and DCN (0.32 mM). [b] Isolated yields.

Table 4 Products and yields of RB-photosensitized reactions of O_2-purged MeCN solutions containing glycinates (**16a**, **16b**, **16e** and **16g**) and acetylene **17**[a]

Entry	Glycinate	Irradiation time (min)	Product[b] (%)
1	**16a**	5	**18a** (11), **19a** (49)
2	**16b**	5	**18b** (12), **19b** (47)
3	**16e**	10	**18e** (12), **19e** (45)
4	**16g**	30	**18g** (11), **19g** (41)

[a] 220 mL of MeCN solution containing glycinate (3.2 mM), acetylene (3.2 mM) and RB (0.32 mM). [b] Isolated yields.

Table 5 Products and yields of C_{60}-photosensitized reactions of O_2-purged toluene solutions containing glycinates **16a–16g** and acetylene **17**[a]

Entry	Glycinate	Irradiation time (min)	Product[b] (%)
1	**16a**	10	**18a** (38), **19a** (21)
2	**16b**	10	**18b** (41), **19b** (19)
3	**16c**	10	**18c** (38), **19c** (16)
4	**16d**	10	**18d** (39), **19d** (18)
5	**16e**	20	**18e** (35), **19e** (20)
6	**16f**	20	**18f** (32), **19f** (21)
7	**16g**	30	**18g** (31), **19g** (21)

[a] 220 mL of toluene solution containing glycinate (3.2 mM), acetylene (3.2 mM) and C_{60} (016 mM). [b] Isolated yields.

18g as major photoproducts and β-enamino-esters **19a–19g** as minor products (Table 5). Noticeably, no photoproduct arising from addition reactions between glycinates and C_{60} were observed.[19]

N-trimethylsilyl- and ester-substituent effects on photochemical reactions

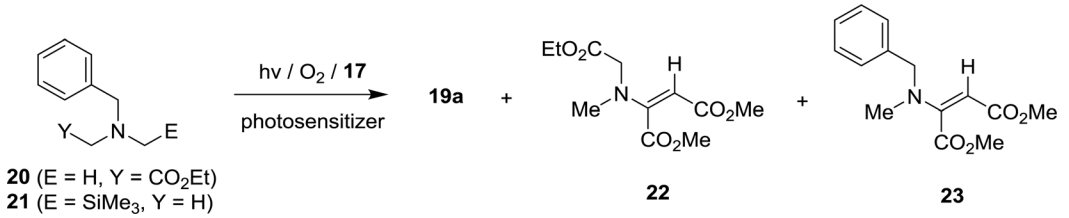
In order to gain additional information about how *N*-substituents on the glycinates (*e.g.*, trimethylsilyl and ester groups) influence the efficiencies and product distributions, we probed SET photosensitized reactions of acetylene **17** with the non-trimethylsilyl and non-ester group containing *N*-benzylamine substrates, **20** (ref. 19) and **21**,[10c] respectively. As the results depicted in Table 6 show, in the photoreactions of non-trimethylsilyl substituted amine **20** with acetylene **17**, mixtures of several types of β-enamino-esters, **19a**, **22** and **23**,[26] were produced and no pyrrole products are generated (entries 1–4 in Table 6). In contrast, photoreactions of non-ester group substituted amine **21** with **17** gave rise to β-enamino-ester **23** as a single photoadduct (entries 5–8 in Table 6). Thus, it appears that the presence of both the trimethylsilyl and ester groups in the *N*-benzylamine substrates are essential for these SET-photosensitized reactions to produce pyrrole adducts.

Mechanistic pathways

The SET-photosensitized reactions described above most likely follow the pathways outlined in Scheme 6, which are terminated either by Michael addition of secondary amines **37** to DMAD to generate β-enamino-esters **40** or by dipolar cycloaddition of azomethine ylides **36** to DMAD to produce precursors of the pyrroles **39**. In these processes, the secondary amines (**37**) and ylides (**36**) could be formed from the *N*-α-trimethylsilyl-*N*-benzyl glycinates (**GL**) through a number of different routes. However, it is nearly certain that the β-enamino-ester and pyrrole forming photoreactions are both initiated by SET from the glycinates to the excited states of the sensitizers ($^{S1\text{ or }T1}$Sens). This proposal is based on the results of the fluorescence quenching studies described above and a consideration of the concentrations of the glycinates used. Accordingly, the rates of the SET processes (k_{SET} [glycinate], where $k_{SET} = k_{diff} = ca.\ 1 \times 10^9\ M^{-1}\ s^{-1}$ and [glycinate] $= 3.2 \times 10^{-3}$ M) should far exceed those for excited state sensitizer decay and energy transfer to molecular oxygen (k_{ET} [O_2], where $k_{ET} = ca.$ 1.9–7.5 $\times 10^9\ M^{-1}\ s^{-1}$ and [O_2] $\ll$ [glycinate]).[20a,27]

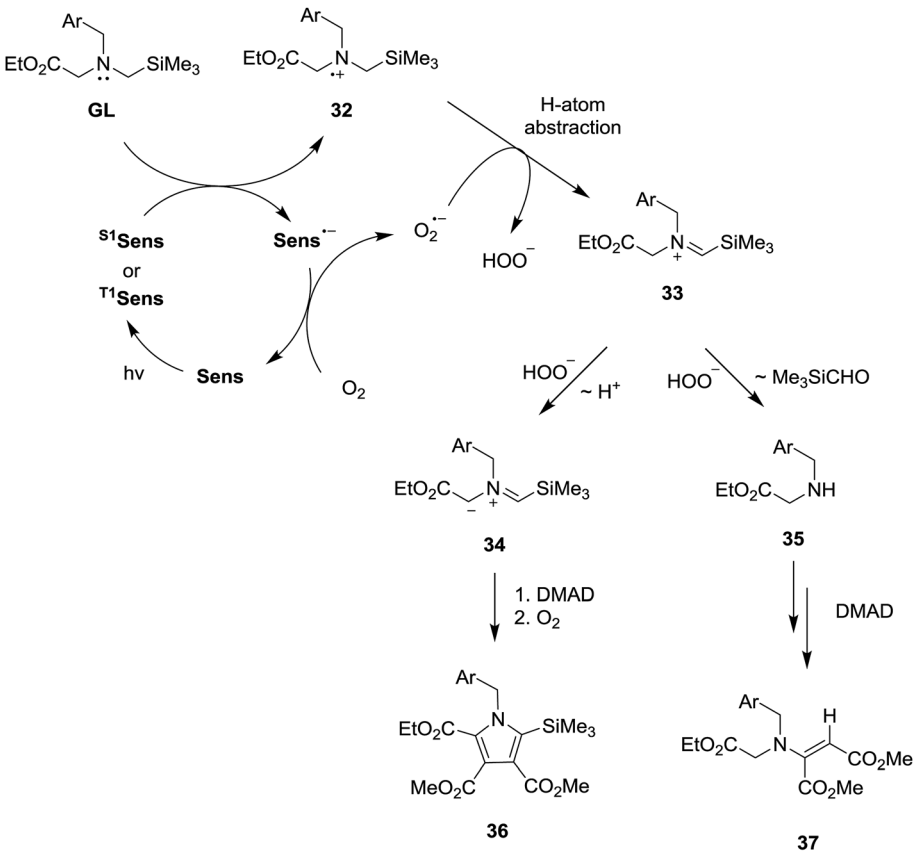
SET from **GL** to $^{S1\text{ or }T1}$Sens in the mechanistic pathway generates a glycinate derived aminium radical **32** and a radical anion of the photosensitizer (Sens$^{\bullet-}$), the former of which serves as a key intermediate in the pathways that produce the pyrrole and β-enamino-ester products. The generated radical

Table 6 Products and yields of SET-photosensitized reactions of *N*-benzylamines **20–21** with acetylene **17**[a]



Entry	Amine	Reaction condition	Irradiation time (min)	Product[b] (%)
1	**20**	DCA in MeCN	10	**19a** (10), **22** (34), **23** (10)
2	**20**	DCN in MeCN	60	**19a** (14), **22** (32), **23** (10)
3	**20**	RB in MeCN	10	**19a** (17), **22** (29), **23** (11)
4	**20**	C_{60} in toluene	30	**19a** (42), **22** (19)
5	**21**	DCA in MeCN	5	**23** (61)
6	**21**	DCN in MeCN	60	**23** (60)
7	**21**	RB in MeCN	5	**23** (58)
8	**21**	C_{60} in toluene	10	**23** (78)

[a] 220 mL of MeCN or toluene solutions containing *N*-benzylamines (3.2 mM), acetylene (3.2 mM) and photosensitizer (DCA (0.27 mM), DCN (0.32 mM), RB (0.32 mM) and C_{60} (0.16 mM)). [b] Isolated yields.



Scheme 6 Proposed mechanistic pathways.

anion of the photosensitizer is oxidized by $^3O_2$ to ground state of photosensitizer (Sens) and $O_2^{\bullet-}$ is generated at the same time. While a number of pathways are possible for conversion of **32** to secondary amine **35** and ylide **34**, an initial route involving $O_2^{\bullet-}$ promoted H-atom abstraction of the aminium radical **32** (leading to **33**) is most plausible based on observations made in earlier studies.[18,28] Then, generated silyl containing iminium ion **33** undergo hydrolytic cleavage by hydrogen peroxide anion (HOO^-) to form secondary amine **35**, which add to DMAD to yield β-amino-ester **37**. Competitively, deprotonation of silyl group containing iminium ion **33** produces azomethine ylide **34**, which cycloadd to DMAD, followed aromatization, to form pyrrole **36**.

While conforming to observations made in this study, it is difficult to explain the regioselectivity for H-atom abstraction process from **32** (leading to iminium ion **33**) and, in particular, why loss of benzylic or α-ester hydrogen do not take place competitively. However, it is clear that in contrast to non-regioselectivity of aminium radical **38** derived from non-silyl amine analog **21** (Scheme 7), a presence of electrofugal group (*i.e.*, $SiMe_3$) in the aminium radicals **32** might lead to regioselective H-atom abstraction process.

Conclusion

In this study, photoaddition reactions of *N*-α-trimethylsilyl-*N*-benzylglycinates, which contain various kinds of substituents on arene ring, with electron deficient dimethyl acetylenedicarboxylate (DMAD) in the presence of various kinds of SET-photosensitizers were explored in order to assess the preparative utility of trimethylsilyl group containing acyclic *N*-benzylglycinates as substrates in azomethine ylide dipolar cycloaddition reactions.

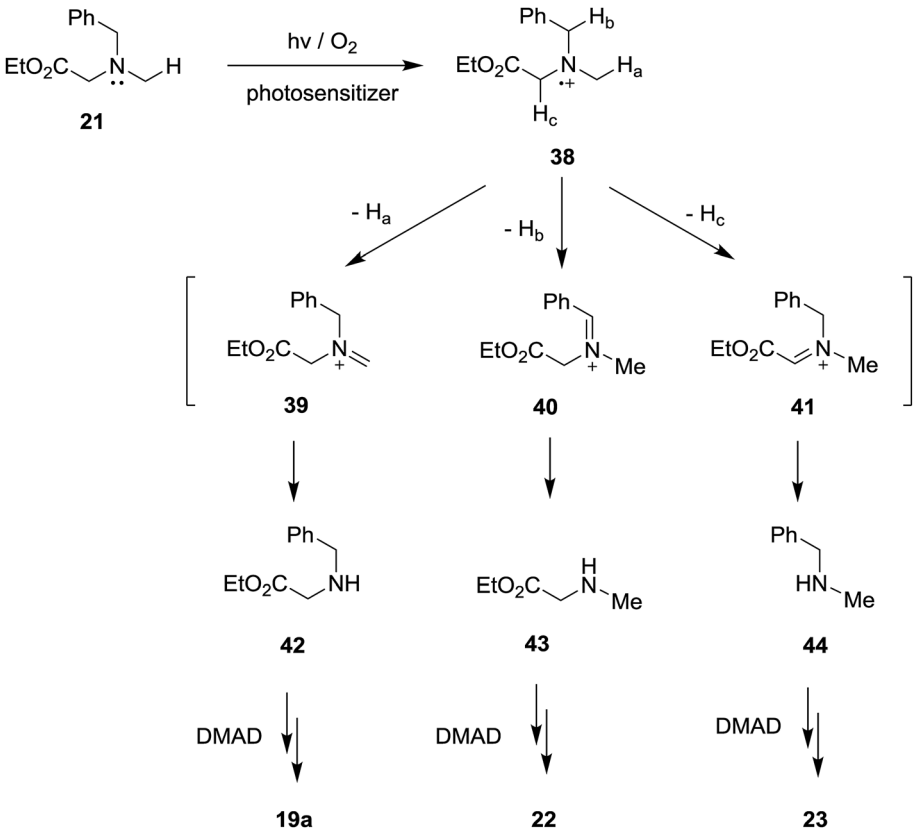
The results showed that two competitive pathways are followed in these reactions, one of which involves cycloaddition to form pyrroles *via* azomethine ylides and the other generates β-enamino-esters *via* secondary amines. Importantly, the photoproduct distributions (*i.e.*, pyrrole/β-enamine ester ratios) are influenced by the electronic nature of the glycinate substrates and photosensitizer used.

Finally, a plausible mechanistic pathway has been proposed for SET-promoted oxidation reactions of tertiary amines. This proposal along with other interesting features of these reactions will guide the design of future mechanistic and preparative studies.

Experimental

General

The ^1H (300 MHz) and ^{13}C NMR (75 MHz) spectra 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 use of quadrupole mass



Scheme 7 Non-regioselective formation of iminium ions 39–41 from non-silyl amine analog 21.

analyzer and electron impact ionization unless otherwise noted. All new compounds described were isolated as oils unless noted otherwise.

Synthesis of *N*-α-trimethylsilyl-*N*-benzylglycinates 16a–16g

Individual solutions of *N*-α-trimethylsilyl-*N*-benzylamines **15a–15g** (ref. 22*a*) (10 mmol) in acetonitrile (100 mL) containing K_2CO_3 (42 mmol) and ethyl bromoacetate (30 mmol) were stirred for 12 h at room temperature and concentrated *in vacuo* to give residues that were triturated with CH_2Cl_2. The triturates were dried and concentrated *in vacuo* to afford residues, which were subjected to silica gel column chromatography (EtOAc/hexane = 1 : 5 to 1 : 8) to yield **16a** (ref. 10*c*) (70%), **16b** (ref. 19) (66%), **16c** (66%), **16d** (ref. 19) (51%), **16e** (ref. 19) (74%), **16f** (68%) and **16g** (ref. 19) (55%) respectively.

16c (yellow liq). ^{1}H-NMR 0.05 (s, 9H), 1.26 (t, 3H, J = 6.9 Hz), 2.24 (s, 2H), 2.30 (s, 3H), 2.34 (s, 3H), 3.25 (s, 2H), 3.75 (s, 2H), 4.14 (q, 2H, J = 6.9 Hz), 6.95 (d, 1H, J = 7.5 Hz), 6.96 (s, 1H), 7.19 (d, 1H, J = 7.5 Hz); ^{13}C-NMR −1.6, 14.2, 19.0, 20.9, 45.5, 56.4, 59.8, 126.0, 129.8, 130.9, 134.0, 136.4, 137.3, 171.3; HRMS (EI) m/z 307.1965 (M^+, $C_{17}H_{29}NO_2Si$ requires 307.1968).

16f (yellow liq). ^{1}H-NMR 0.01 (s, 9H), 1.22 (t, 3H, J = 7.2 Hz), 2.16 (s, 2H), 3.22 (s, 2H), 3.73 (s, 2H), 4.12 (q, 2H, J = 7.2 Hz), 6.68–6.75 (m, 1H), 6.76–6.82 (m, 1H), 7.36–7.43 (m, 1H); ^{13}C-NMR −1.7, 14.2, 45.6, 53.6, 57.0, 60.1, 103.4 (t, J = 25.5 Hz), 110.9 (dd, J = 20.8 Hz, 3.8 Hz), 121.9 (dd, J = 14.3 Hz, 3.6 Hz), 131.8 (dd, J = 9.4 Hz, 6.2 Hz), 161.2 (dd, J = 246.9 Hz, 11.8 Hz), 162.0 (dd, J = 245.9 Hz, 12 Hz), 171.1; HRMS (EI) m/z 315.1465 (M^+, $C_{15}H_{23}F_2NO_2Si$ requires 315.1466).

General procedure of photoreactions of *N*-α-trimethylsilyl-*N*-benzylglycinates and dimethyl acetylenedicarboxylate (DMAD) in the presence of photosensitizer

Preparative photochemical reactions were conducted using an apparatus consisting of a 450 W Hanovia medium vapor pressure mercury lamp equipped with a flint glass filter (>310 nm) in a water-cooled quartz immersion well surrounded by the solution being irradiated, consisting of solution (220 mL) containing glycinate (0.7 mmol, 3.2 mM), acetylene **17** (0.7 mmol, 3.2 mM), and photocatalyst (DCA (0.27 mM), DCN (0.32 mM), RB (0.32 mM), C_{60} (0.16 mM)). The solution being irradiated was purged with oxygen before and during irradiations for the time periods given below. The photolysates were concentrated *in vacuo* to yield residues, which were subjected to silica gel column chromatography to isolate the pure photoproducts.

Photoreactions of oxygenated solution of 16a and 17

In MeCN solution of DCA: 5 min irradiation, column chromatography (EtOAc : hexane = 1 : 5) to yield **18a** (18 mg, 6%) and **19a** (117 mg, 50%). In MeCN solution of DCN: 60 min irradiation, column chromatography to yield **18a** (32 mg, 11%) and **19a** (94 mg, 40%). In MeCN solution of RB: 5 min irradiation, column chromatography to yield **18a** (32 mg, 11%) and **19a**

(115 mg, 49%). In toluene solution of C_{60}: 20 min irradiation, column chromatography to yield **18a** (111 mg, 38%) and **19a** (49 mg, 21%).

18a (yellow liq). ^{1}H-NMR 0.26 (s, 9H), 1.19 (t, 3H, $J = 7.2$ Hz), 3.80 (s, 3H), 3.88 (s, 3H), 4.12 (q, 2H, $J = 7.2$ Hz), 5.77 (s, 2H), 6.78 (d, 2H, $J = 7.2$ Hz), 7.18–7.31 (m, 3H); ^{13}C-NMR 1.2, 14.0, 51.5, 51.8, 52.6, 61.1, 122.7, 124.4, 125.2, 126.7, 127.3, 128.8, 138.4, 145.6, 159.6, 164.4, 166.9; HRMS (FAB) *m*/*z* 418.1680 (M + 1, $C_{21}H_{28}NO_6Si$ requires 418.1686).

19a (yellow liq). ^{1}H-NMR 1.23 (t, 3H, $J = 6.9$ Hz), 3.59 (s, 3H), 3.70 (s, 2H), 3.89 (s, 3H), 4.16 (q, 1H, $J = 6.9$ Hz), 4.38 (s, 2H), 4.70 (s, 1H), 7.22–7.34 (m, 5H); ^{13}C-NMR 14.2, 50.2, 51.1, 53.2, 55.2, 61.7, 87.0, 128.1, 128.3, 129.0, 134.9, 154.5, 165.9, 167.9, 168.3; HRMS (FAB) *m*/*z* 336.1445 (M + 1, $C_{17}H_{22}NO_6$ requires 336.1447).

Photoreactions of oxygenated solution of 16b and 17

In MeCN solution of DCA: 5 min irradiation, column chromatography (EtOAc : hexane = 1 : 5) to yield **18b** (12 mg, 4%) and **19b** (125 mg, 51%). In MeCN solution of DCN: 60 min irradiation, column chromatography to yield **18b** (12 mg, 11%) and **19b** (120 mg, 49%). In MeCN solution of RB: 5 min irradiation, column chromatography to yield **18b** (36 mg, 12%) and **19b** (115 mg, 47%). In toluene solution of C_{60}: 10 min irradiation, column chromatography to yield **18b** (124 mg, 41%) and **19b** (46 mg, 19%).

18b (yellow liq). ^{1}H-NMR 0.27 (s, 9H), 1.19 (t, 3H, $J = 6.9$ Hz), 2.28 (s, 3H), 3.79 (s, 3H), 3.87 (s, 3H), 4.12 (q, 2H, $J = 6.9$ Hz), 5.72 (s, 2H), 6.67 (d, 2H, $J = 7.8$ Hz), 7.06 (d, 2H, $J = 7.8$ Hz); ^{13}C-NMR 1.1, 13.9, 21.1, 51.3, 51.8, 52.5, 61.0, 122.5, 124.3, 125.0, 126.5, 129.4, 135.3, 136.8, 145.5, 159.5, 164.4, 166.8; HRMS (FAB) *m*/*z* 432.1841 (M + 1, $C_{22}H_{30}NO_6Si$ requires 432.1842).

19b (yellow liq). ^{1}H-NMR 1.23 (t, 3H, $J = 7.2$ Hz), 2.31 (s, 3H), 3.61 (s, 3H), 3.69 (s, 2H), 3.90 (s, 3H), 4.16 (q, 1H, $J = 7.2$ Hz), 4.34 (s, 2H), 4.70 (s, 1H), 7.13 (s, 4H); ^{13}C-NMR 14.3, 21.3, 50.0, 51.1, 53.2, 55.0, 61.7, 86.8, 128.2, 129.7, 131.8, 138.2, 154.5, 165.9, 167.9, 168.4; HRMS (FAB) *m*/*z* 350.1603 (M + 1, $C_{18}H_{24}NO_6$ requires 350.1604).

Photoreactions of oxygenated solution of 16c and 17

In MeCN solution of DCA: 5 min irradiation, column chromatography (EtOAc : hexane = 1 : 5) to yield **18c** (3 mg, 1%) and **19c** (121 mg, 48%). In toluene solution of C_{60}: 10 min irradiation, column chromatography to yield **18c** (120 mg, 38%) and **19c** (40 mg, 16%).

18c (yellow liq). ^{1}H-NMR 0.21 (s, 9H), 1.18 (t, 3H, $J = 7.2$ Hz), 2.24 (s, 3H), 2.25 (s, 3H), 3.79 (s, 3H), 3.88 (s, 3H), 4.11 (q, 2H, $J = 7.2$ Hz), 5.63 (s, 2H), 5.98 (d, 1H, $J = 7.8$ Hz), 6.82 (d, 1H, $J = 7.8$ Hz), 6.95 (s, 1H); ^{13}C-NMR 0.8, 13.8, 18.8, 20.9, 49.9, 51.6, 52.4, 60.9, 122.3, 123.5, 124.0, 126.6, 127.1, 130.8, 133.3, 133.8, 136.5, 145.8, 159.4, 164.2, 166.9; HRMS (EI) *m*/*z* 445.1922 (M^+, $C_{23}H_{31}NO_6Si$ requires 445.1921).

19c (yellow liq). ^{1}H-NMR 1.23 (t, 3H, $J = 6.9$ Hz), 2.18 (s, 3H), 2.27 (s, 3H), 3.60 (s, 3H), 3.63 (s, 2H), 3.88 (s, 3H), 4.15 (q, 1H, $J = 6.9$ Hz), 4.33 (s, 2H), 4.76 (s, 1H), 6.94–7.06 (s, 3H); ^{13}C-NMR 14.1, 18.8, 20.9, 49.4, 50.9, 52.3, 53.0, 61.4, 87.2, 126.9, 128.6, 129.0, 131.5, 136.7, 138.0, 154.4, 165.7, 167.8, 168.5; HRMS (EI) *m*/*z* 363.1680 (M + 1, $C_{19}H_{25}NO_6$ requires 363.1682).

Photoreactions of oxygenated solution of 16d and 17

In MeCN solution of DCA: 5 min irradiation, column chromatography (EtOAc : hexane = 1 : 5) to yield **18d** (3 mg, 1%) and **19d** (115 mg, 45%). In toluene solution of C_{60}: 10 min irradiation, column chromatography to yield **18d** (123 mg, 39%) and **19d** (46 mg, 18%).

18d (yellow liq). ^{1}H-NMR 0.27 (s, 9H), 1.19 (t, 3H, $J = 7.2$ Hz), 2.28 (s, 3H), 3.74 (s, 3H), 3.78 (s, 3H), 3.86 (s, 3H), 4.12 (q, 2H, $J = 7.2$ Hz), 5.68 (s, 2H), 6.70 (d, 2H, $J = 8.7$ Hz), 6.78 (d, 2H, $J = 8.7$ Hz); ^{13}C-NMR 1.0, 13.8, 50.8, 51.6, 52.3, 55.1, 60.9, 114.0, 122.4, 124.2, 126.2, 126.3, 130.1, 145.2, 158.6, 159.4, 164.2, 166.6; HRMS (EI) *m*/*z* 447.1717 (M + 1, $C_{22}H_{29}NO_7Si$ requires 447.1713).

19d (yellow liq). ^{1}H-NMR 1.23 (t, 3H, $J = 7.2$ Hz), 3.61 (s, 3H), 3.67 (s, 2H), 3.77 (s, 3H), 3.90 (s, 3H), 4.16 (q, 1H, $J = 7.2$ Hz), 4.31 (s, 2H), 4.70 (s, 1H), 6.84 (d, 2H, $J = 8.7$ Hz), 7.17 (d, 2H, $J = 8.7$ Hz); ^{13}C-NMR 13.8, 50.6, 52.7, 54.2, 54.9, 61.2, 86.2, 113.9, 126.3, 128.9, 129.2, 154.1, 159.2, 165.5, 167.5, 167.9; HRMS (EI) *m*/*z* 365.1477 (M + 1, $C_{18}H_{23}NO_7$ requires 365.1475).

Photoreactions of oxygenated solution of 16e and 17

In MeCN solution of DCA: 10 min irradiation, column chromatography (EtOAc : hexane = 1 : 5) to yield **18e** (65 mg, 21%) and **19e** (77 mg, 31%). In MeCN solution of DCN: 90 min irradiation, column chromatography to yield **18e** (38 mg, 12%) and **19e** (99 mg, 40%). In MeCN solution of RB: 10 min irradiation, column chromatography to yield **18e** (37 mg, 12%) and **19e** (111 mg, 45%). In toluene solution of C_{60}: 20 min irradiation, column chromatography to yield **18e** (107 mg, 35%) and **19e** (49 mg, 20%).

18e (yellow liq). ^{1}H-NMR 0.27 (s, 9H), 1.19 (t, 3H, $J = 7.2$ Hz), 3.79 (s, 3H), 3.87 (s, 3H), 4.13 (q, 2H, $J = 7.2$ Hz), 5.72 (s, 2H), 6.73–6.78 (m, 2H), 6.96 (t, 2H, $J = 8.7$ Hz); ^{13}C-NMR 1.3, 14.0, 51.0, 51.9, 52.6, 61.2, 115.8 (d, $J = 21.6$ Hz), 122.9, 124.2, 126.9 (d, $J = 8$ Hz), 134.1 (d, $J = 3.2$ Hz), 145.6, 159.6, 161.8 (d, $J = 244.1$ Hz), 164.3, 166.8; HRMS (FAB) *m*/*z* 436.1589 (M + 1, $C_{21}H_{27}FNO_6Si$ requires 436.1592).

19e (yellow liq). ^{1}H-NMR 1.14 (t, 3H, $J = 6.9$ Hz), 3.50 (s, 3H), 3.64 (s, 2H), 3.80 (s, 3H), 4.07 (q, 1H, $J = 6.9$ Hz), 4.27 (s, 2H), 4.60 (s, 1H), 6.92 (t, 2H, $J = 8.7$ Hz), 7.14–7.18 (m, 2H); ^{13}C-NMR 13.8, 49.8, 50.6, 52.7, 54.2, 61.3, 86.8, 116.0 (d, $J = 21.5$ Hz), 129.4 (d, $J = 8.2$ Hz), 130.4 (d, $J = 3.1$ Hz), 153.9, 162.8 (d, $J = 245.6$ Hz), 165.4, 167.3, 168.8; HRMS (FAB) *m*/*z* 354.1355 (M + 1, $C_{17}H_{21}FNO_6$ requires 354.1353).

Photoreactions of oxygenated solution of 16f and 17

In MeCN solution of DCA: 10 min irradiation, column chromatography (EtOAc : hexane = 1 : 5) to yield **18f** (76 mg, 24%) and **19f** (86 mg, 33%). In toluene solution of C_{60}: 20 min irradiation, column chromatography to yield **18f** (102 mg, 32%) and **19f** (55 mg, 21%).

18f (yellow liq). ^{1}H-NMR 0.25 (s, 9H), 1.20 (t, 3H, $J = 7.2$ Hz), 3.79 (s, 3H), 3.87 (s, 3H), 4.14 (q, 2H, $J = 7.2$ Hz), 5.71 (s, 2H),

6.24–6.32 (m, 1H), 6.70–6.84 (m, 2H); ^{13}C-NMR 0.7, 13.7, 46.0, 51.6, 52.4, 61.0, 103.7 (t, J = 25.1 Hz), 111.4 (dd, J = 21.2 Hz, 3.7 Hz), 121.8 (dd, J = 14.6 Hz, 3.8 Hz), 122.7, 123.9, 126.7, 126.8 (dd, J = 9.7 Hz, 5.6 Hz), 145.6, 158.8 (dd, J = 247.1 Hz, 11.7 Hz), 159.1, 162.0 (dd, J = 247.1 Hz, 11.6 Hz), 163.9, 166.4; HRMS (EI) m/z 453.1421 (M^+, $C_{21}H_{25}F_2NO_6Si$ requires 453.1419).

19f (yellow liq). ^{1}H-NMR 1.21 (t, 3H, J = 7.2 Hz), 3.57 (s, 3H), 3.74 (s, 2H), 3.86 (s, 3H), 4.14 (q, 2H, J = 7.2 Hz), 4.37 (s, 2H), 4.67 (s, 1H), 6.73–6.86 (m, 2H), 7.24–7.31 (m, 1H); ^{13}C-NMR 14.0, 48.2 (d, J = 3.8 Hz), 50.8, 50.9, 53.0, 61.6, 87.6, 103.9 (t, J = 25.3 Hz), 111.7 (dd, J = 21.2 Hz, 3.8 Hz), 117.8 (dd, J = 14.3 Hz, 3.7 Hz), 130.65 (dd, J = 9.4 Hz, 5.2 Hz), 153.8, 160.7 (dd, J = 248.0 Hz, 11.9 Hz), 162.6 (dd, J = 248.4 Hz, 11.9 Hz), 165.5, 167.4, 167.9; HRMS (EI) m/z 371.1182 (M^+, $C_{17}H_{19}F_2NO_6$ requires 371.1180).

Photoreactions of oxygenated solution of 16g and 17

In MeCN solution of DCA: 20 min irradiation, column chromatography (EtOAc : hexane = 1 : 5) to yield **18g** (108 mg, 32%), **19g** (64 mg, 22%). In MeCN solution of DCN: 180 min irradiation, column chromatography to yield **18g** (71 mg, 21%) and **19g** (90 mg, 32%). In MeCN solution of RB: 30 min irradiation, column chromatography to yield **18g** (36 mg, 11%) and **19g** (115 mg, 41%). In toluene solution of C_{60}: 30 min irradiation, column chromatography to yield **18g** (105 mg, 31%) and **19g** (59 mg, 21%).

18g (yellow liq). ^{1}H-NMR 0.26 (s, 9H), 1.18 (t, 3H, J = 7.2 Hz), 3.80 (s, 3H), 3.87 (s, 3H), 4.12 (q, 2H, J = 7.2 Hz), 5.81 (s, 2H), 6.91 (d, J = 8.1 Hz), 7.53 (d, J = 8.1 Hz); ^{13}C-NMR 1.0, 13.7, 51.1, 51.7, 52.4, 61.0, 122.8, 123.8, 125.3, 125.7 (q, J = 3.7 Hz), 126.9, 142.3, 145.5, 159.3, 164.0, 166.5; HRMS (EI) m/z 485.1479 (M^+, $C_{22}H_{26}F_3NO_6Si$ requires 485.1482).

19g (yellow liq). ^{1}H-NMR 1.24 (t, 3H, J = 7.2 Hz), 3.61 (s, 3H), 3.74 (s, 2H), 3.89 (s, 3H), 4.18 (q, 2H, J = 7.2 Hz), 7.38 (d, 2H, J = 8.4 Hz), 7.59 (d, 2H, J = 8.4 Hz); ^{13}C-NMR 14.0, 50.7, 51.0, 53.1, 54.7, 61.7, 87.8, 125.8 (q, J = 3.7 Hz), 127.9, 139.0, 153.9, 165.5, 167.4, 168.0; HRMS (EI) m/z 403.1244 (M^+, $C_{18}H_{20}F_3NO_6$ requires 403.1243).

Photoreactions of oxygenated solution of 20 and 17

In MeCN solution of DCA: 10 min irradiation, column chromatography (EtOAc : hexane = 1 : 5) to yield **19a** (29 mg, 10%), **22** (62 mg, 34%) and **23** (18 mg, 10%). In MeCN solution of DCN: 60 min irradiation, column chromatography to yield **19a** (41 mg, 14%), **22** (58 mg, 32%) and **23** (18 mg, 10%). In MeCN solution of RB: 10 min irradiation, column chromatography to yield **19a** (50 mg, 17%), **22** (53 mg, 29%) and **23** (20 mg, 11%). In toluene solution of C_{60}: 30 min irradiation, column chromatography to yield **19a** (123 mg, 42%) and **22** (34 mg, 19%).

22 (yellow liq). ^{1}H-NMR 1.25 (t, 3H, J = 7.2 Hz), 2.91 (s, 3H), 3.60 (s, 3H), 3.81 (s, 2H), 3.87 (s, 3H), 4.18 (q, 2H, J = 7.2 Hz), 4.65 (s, 1H); ^{13}C-NMR 14.1, 39.2, 50.9, 53.0, 54.0, 61.6, 86.9, 154.3, 165.7, 167.7, 168.4; HRMS (EI) m/z 259.1052 (M^+, $C_{11}H_{17}NO_6$ requires 259.1056).

23 (yellow liq). ^{1}H-NMR 2.72 (s, 3H), 3.61 (s, 3H), 3.90 (s, 3H), 4.27 (s, 2H), 4.65 (s, 1H), 7.19–7.34 (m, 5H); ^{13}C-NMR 36.8, 50.7, 52.9, 56.3, 84.6, 127.3, 127.8, 128.7, 135.5, 154.9, 166.0, 168.0; HRMS (EI) m/z 263.1154 (M^+, $C_{14}H_{17}NO_4$ requires 263.1158).

Photoreactions of oxygenated solution of 21 and 17

In MeCN solution of DCA: 5 min irradiation, column chromatography (EtOAc : hexane = 1 : 5) to yield **23** (112 mg, 61%). In MeCN solution of DCN: 60 min irradiation, column chromatography to yield **23** (111 mg, 60%). In MeCN solution of RB: 5 min irradiation, column chromatography to yield **23** (107 mg, 58%). In toluene solution of C_{60}: 10 min irradiation, column chromatography to yield **23** (144 mg, 78%).

Conflicts of interest

There are no conflict of interest to declare.

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