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

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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/

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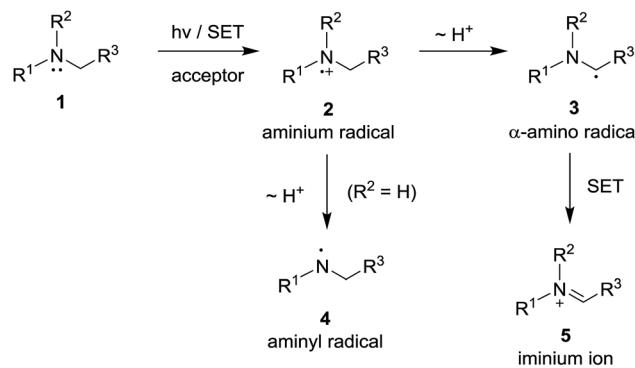
Scheme 1 Photoinduced single electron transfer (SET) reaction pathways opened for amine substrates.
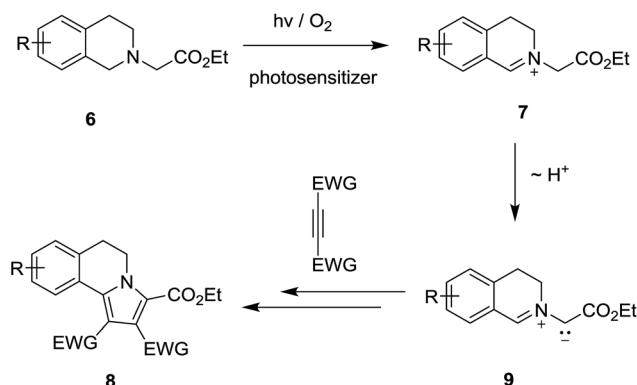
Scheme 2 SET-promoted 1,3-dipolar cycloaddition reactions of ethyl 2-(3,4-dihydroisoquinolin-2(1H)-yl)acetate **6** with dipolarophile.

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,
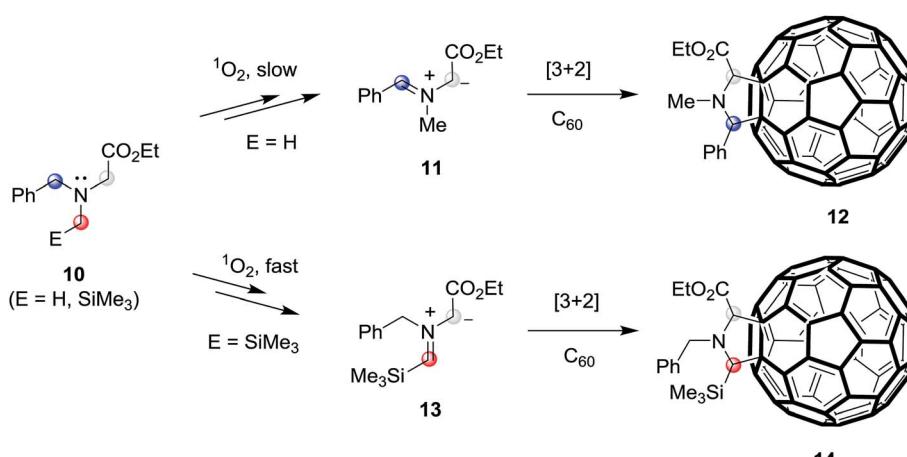
Scheme 3 SET-promoted 1,3-dipolar cycloaddition reactions of tertiary N-benzylglycinates **10** (E = H, SiMe$_3$) with fullerene C_{60}.

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 ($\lambda > 310$ 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,

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)	$\Delta G_{SET}{}^a$ (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.
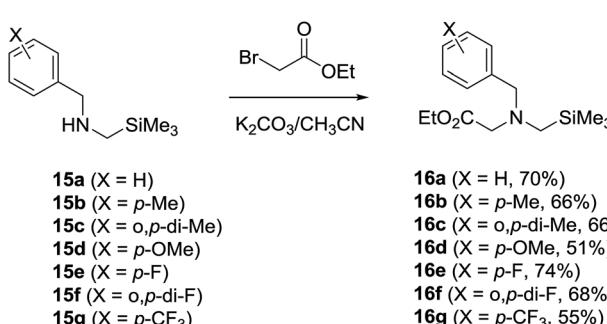
DCN-promoted photochemical reactions

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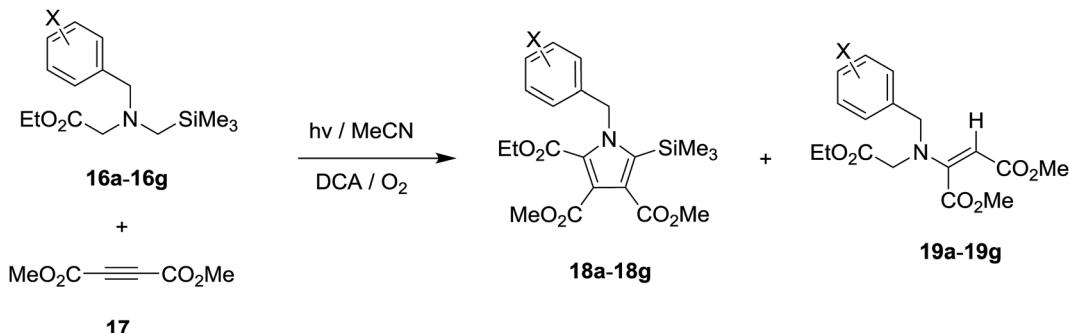
Scheme 5 DCA-promoted photochemical reactions of N-benzylglycinates **16a–16g** with DMAD **17**.

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 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 $k_{SET} = k_{diff} = ca.$ 1×10^9 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 or T1]Sens in the mechanistic pathway generates a glycinate derived aminium radical **32** and a radical anion of the photosensitizer (Sens[•−]), 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]

20 (E = H, Y = CO_2Et)
21 (E = $SiMe_3$, Y = H)
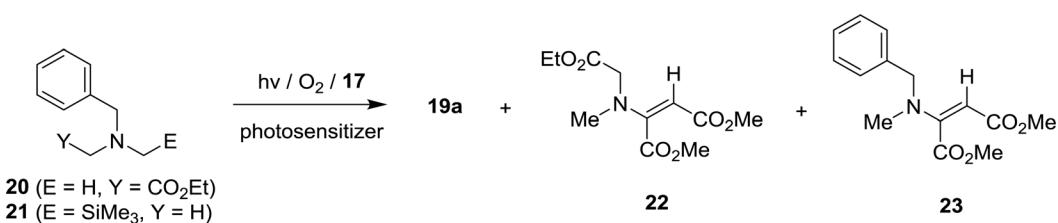
Entry	Amine	Reaction condition	Irradiation time (min)	Product[b] (%)
1	**20**	DCA in MeCN	10	**19a** (10), **22** (34), **23** (10)
2	**20**	DCN in MeCN	60	**19a** (14), **22** (32), **23** (10)
3	**20**	RB in MeCN	10	**19a** (17), **22** (29), **23** (11)
4	**20**	C_{60} in toluene	30	**19a** (42), **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.
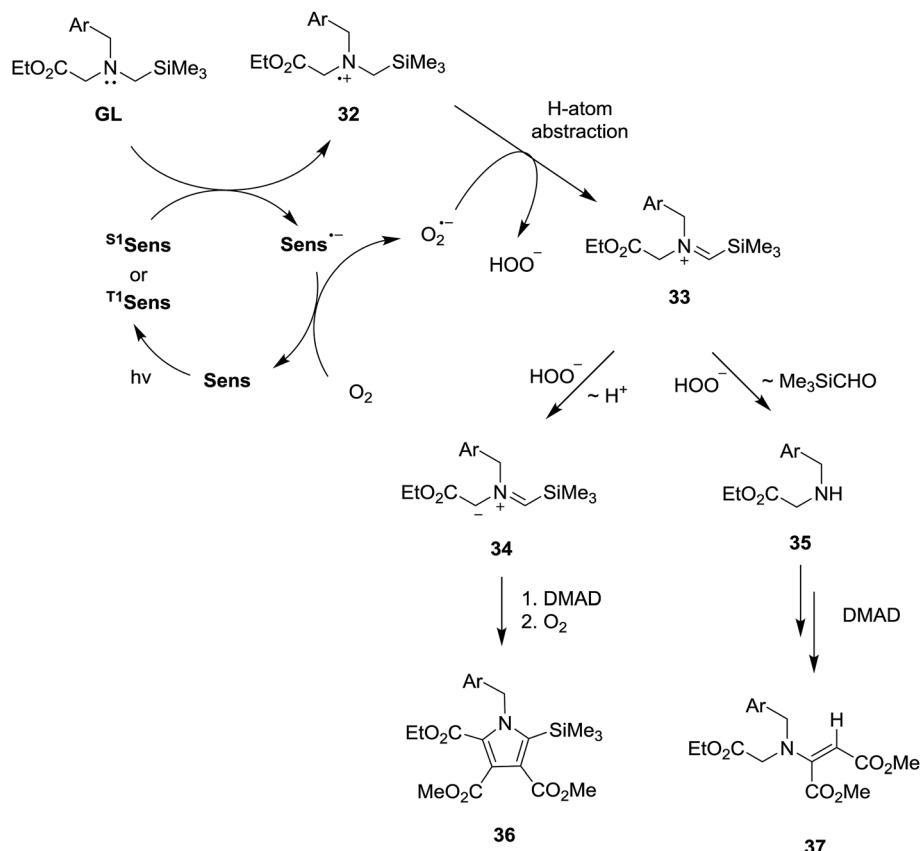
Scheme 6 Proposed mechanistic pathways.

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*-benzyl-glycinates 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 ^{1}H (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 ^{1}H and 77.0 ppm for ^{13}C) as an internal standard. High resolution (HRMS) mass spectra were obtained by use of quadrupole mass
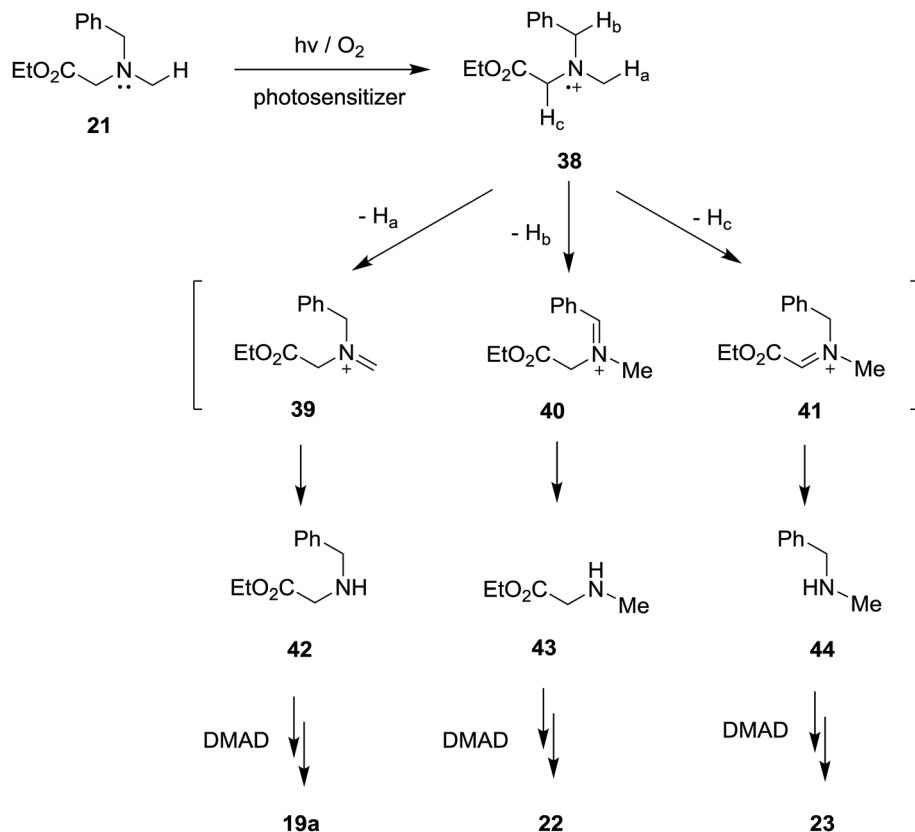
Scheme 7 Non-regioselective formation of iminium ions **39–41** from non-silyl amine analog **21**.

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. 22a) (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. 10c) (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.

Acknowledgements

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