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Fullerene C_{60} promoted photochemical hydroamination reactions of an electron deficient alkyne with trimethylsilyl group containing tertiary *N*-alkylbenzylamines†

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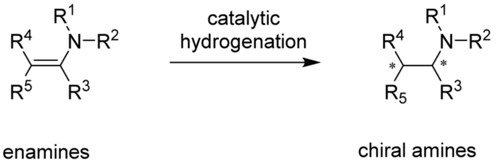
C_{60}-promoted photoaddition reactions of both trimethylsilyl- and a variety of alkyl group containing tertiary benzylamines (*i.e.*, *N*-α-trimethylsilyl-*N*-alkylbenzylamines) with dimethyl acetylenedicarboxylate (DMAD) were carried out to explore the synthetic utility of trimethylsilyl group containing tertiary amines as a substrate in the photochemical hydroamination reactions with dimethyl acetylenedicarboxylate (DMAD). The results showed that photoreactions of all the trimethylsilyl containing *N*-alkylbenzylamines with DMAD, under an O_2-purged environment, produced non-silyl containing enamines efficiently through a pathway involving addition of secondary amines to DMAD, the former of which are produced by hydrolytic cleavage of *in situ* formed iminium ions. Exceptionally, five-membered N-heterocyclic rings, pyrroles, could be produced competitively in photoreaction of bulky alkyl (*i.e.*, *tert*-butyl) group substituted benzylamines through a pathway involving 1,3-dipolar cycloaddition of azomethine ylides to DMAD. Furthermore, C_{60}-sensitized photochemical reactions of non-silyl containing benzylamines with DMAD under oxygenated conditions took place in a less efficient and non-regioselective manner to produce enamine photoadducts. The observations made in this study show that regioselectivity of C_{60}-promoted photochemical reactions of *N*-α-trimethylsilyl-*N*-alkylbenzylamines, leading to formation of secondary amines, can be controlled by the presence of the trimethylsilyl group, and that these trimethylsilyl containing tertiary amines can serve as a precursor of secondary amines for hydroamination reactions with a variety of electron deficient acetylenes.

Introduction

The development of synthetic protocols for enamines possessing biologically interesting properties and their chemical manipulation have been a promising research topic in pharmaceutical and organic chemistry fields.[1–3] In particular, because enamine moieties can be readily converted to valuable chiral amine moieties in asymmetric catalytic hydrogenation reactions of unsaturated compounds, enamines have served as useful intermediates in natural product synthesis.[4] (Scheme 1).

Among the well-known enamine synthetic methods, inter- or intramolecular hydroamination reactions of alkynes with primary- or secondary amine substrates seem to be atom and step-economic transformations because of direct addition of the N–H moiety of amines to an alkyne substrate.[5] Typically, hydroamination reactions through nucleophilic addition of amines to electron sufficient C–C multiple bonds are not readily available due to the repulsion between non-bonding electron on a nitrogen atom and π-electron on alkyne. To overcome these thermodynamic and kinetic constraint, a number of catalytic hydroamination reactions using a variety of metal catalysts[5–8] and alkali bases[9] have been employed, in which the use of metals facilitate amines to be readily added to electron-rich alkyne *via* metal–amine complex insertion to alkyne, while the alkali bases deprive proton to endow more nucleophilic ability. Although these metals and alkali base exhibit efficient catalytic activities for hydroamination reactions of alkynes, a cost-effective and



Scheme 1 Chiral amine synthesis *via* asymmetric catalytic hydrogenation of enamines.

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toxic waste-free strategy amenable for the large scale applications are still remained.

In the studies exploring application of amine SET photochemistry for the synthesis of nitrogen-containing compounds, interesting observation was made in our recent studies aiming at exploring photochemical behaviors of both α-trimethylsilyl and α-alkoxycarbonyl group containing *N*-benzylamines (*i.e.*, *N*-α-trimethylsilyl-*N*-benzylglycinates).[10] The results showed that photoirradiation of *N*-α-trimethylsilyl-*N*-benzylglycinates in the presence of molecular oxygen (O_2) and photosensitizer (PS) could convert starting tertiary amines to non-silyl containing secondary amines *via* hydrolytic cleavage of *in situ* formed iminium ions. This investigation suggested that α-trimethylsilyl group substituted tertiary amines can participate in photochemical hydroamination reactions with alkynes to produce enamine derivatives predominantly. To the best of knowledge, hydroamination reactions of alkynes with tertiary amines as a reaction substrates are not common.[11]

To explore substrate scope and synthetic utility of α-trimethylsilyl group containing tertiary aliphatic amines in the photochemical hydroamination reactions of C–C multiple bonds, in current study, we have prepared (trimethylsilyl) methyl and a variety of alkyl group substituted tertiary *N*-benzylamines (*i.e.*, *N*-α-trimethylsilyl-*N*-alkylbenzylamines) and then, the photochemical reactions of them with dimethyl acetylenedicarboxylate (DMAD) in the presence of fullerence C_{60} were carried out. Since fullerene C_{60} is excellent electron acceptor owing to its high electron affinity and relatively high reduction potentials (for $^3C_{60}$, $^3E_{red}$ = 1.14 V *vs.* SCE),[12,13] fullerene C_{60} as a photosensitizer can participate in rapid and efficient SET process with a variety of amine electron donors possess oxidation potentials lower than *ca.* 1.1 eV. The results of this study, presented below, showed that in contrast to those of non-silyl containing tertiary amines, aminium radicals generated by SET processes undergo H-atom abstraction regioselectively at α-carbons next to trimethylsilyl substituent to produce iminium ions, which are hydrolyzed to secondary amines. Then, generated secondary amines are added to alkyne to produce enamines. Especially, when the bulky alkyl group like *tert*-butyl is present on nitrogen atom, not only secondary amine but azomethine ylide intermediates could be formed.

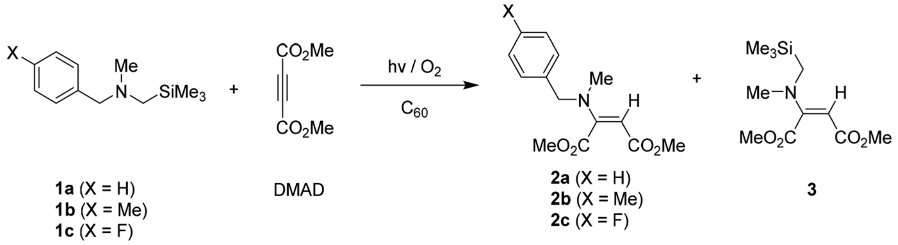
Results and discussion

C_{60}-promoted photoaddition reactions of *N*-α-trimethylsilyl-*N*-alkylbenzylamines and DMAD

A variety of alkyl (*i.e.*, methyl, ethyl, isopropyl, and *tert*-butyl) and (trimethylsilyl)methyl substituted *N*-benzylamines, where phenyl group within benzyl moiety possesses a substituent like H, Me and F at *para*-position, were readily prepared by using earlier reported synthetic procedure.[14,15] With these tertiary benzylamines in hand, photoaddition reactions of toluene solutions (220 mL) containing benzylamines (0.7 mmol, 1 equiv.), dimethyl acetylenedicarboxylate (DMAD) (1.4 mmol, 2 equiv.) and fullerene (C_{60}) photosensitizer (0.035 mmol, 0.05 equiv.) were performed by irradiation (450 W Hanovia medium pressure mercury lamp equipped with flint glass filter (>310 nm)) under oxygenated (O_2-purged) conditions. The photolysates were then purified by column chromatography to determine photoproducts and their yields.

First, C_{60}-promoted photoaddition reactions of *N*-α-trimethylsilyl-*N*-methylbenzylamines **1a–1c** with DMAD in the oxygenated toluene were conducted. As shown in Table 1, 10 min photoirradiation of toluene solutions containing **1a–1b** and DMAD gave rise to formation of high yielding of enamines **2a–2b** as the sole adduct. In the photoreaction of *para*-fluoro

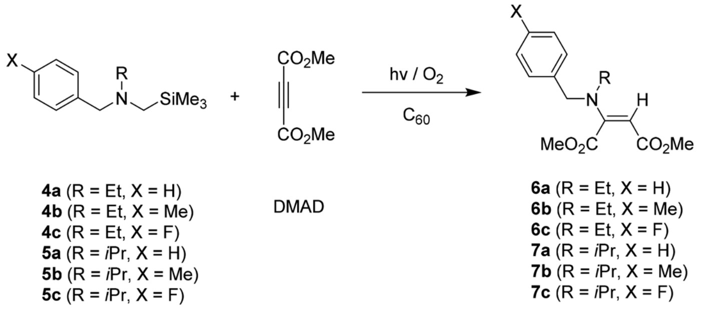
Table 1 Products and their yields in the C_{60}-promoted photoaddition reactions of benzylamines **1a–1c** with DMAD under the oxygenated condition



Entry	Amine	Irradiation time (min)	Conversion[a] (%)	Product[b] (%)
1	**1a**	10	100	**2a** (78)
2	**1b**	10	100	**2b** (73)
3	**1c**	10	93	**2c** (60), **3** (19)
4[c]	**1a**	30	—[d]	—[d]
5[e]	**1a**	30	—[d]	—[d]

[a] Conversion was determined based on recovered amine. [b] Isolation yields. [c] Photoreaction in deoxygenated (using freeze–pump–thaw degassing) condition. [d] No reaction. [e] Photoreaction in the absence of C_{60}.

Table 2 Products and their yields in the C_{60}-promoted photoaddition reactions of benzylamines **4a–4c** and **5a–5c** with DMAD under the oxygenated condition



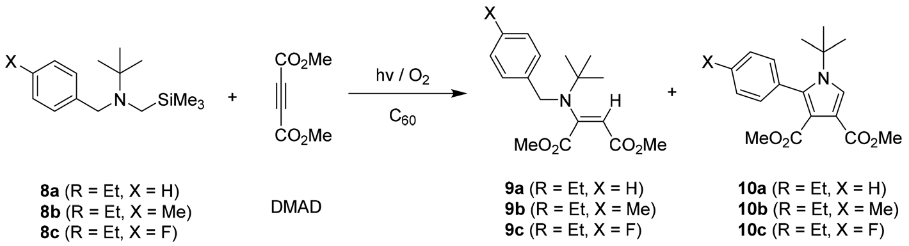
Entry	Amine	Irradiation time (min)	Conversion[a] (%)	Product[b] (%)
1	**4a**	10	100	**6a** (65)
2	**4b**	10	100	**6b** (76)
3	**4c**	10	90	**6c** (60)
4	**5a**	10	34	**7a** (18)
5	**5a**	30	96	**7a** (51)
6	**5b**	10	39	**7b** (21)
7	**5b**	30	100	**7b** (53)
8	**5c**	10	11	**7c** (6)
9	**5c**	50	100	**7c** (53)

[a] Conversion was determined based on recovered amine. [b] Isolation yields.

phenyl containing amine **1c**, non-silyl enamine **2c** was produced as a major product, along with silyl group containing enamine **3** as a minor adduct. Importantly, control experiments (entries 4 and 5 in Table 1) revealed that photoreaction did not take place in cases that the reactions were conducted under the either deoxygenated (freeze–pump–thaw degassing) condition or absence of C_{60} photosensitizer.

Similarly, photoreactions of *N*-α-trimethylsilyl-*N*-ethylbenzylamines **4a–4c** with DMAD in the presence of C_{60} produced the same types of enamines **6a–6c** as a single product even in the reaction of *para*-fluoro substituted amine **4c**. (Table

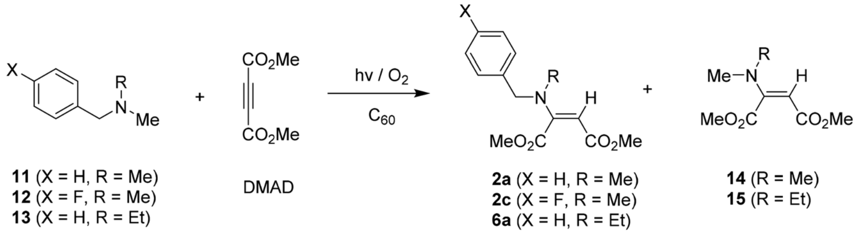
Table 3 Products and their yields in the C_{60}-promoted photoaddition reactions of benzylamines **8a–8c** with DMAD under the oxygenated condition



Entry	Amine	Irradiation time (min)	Conversion[a] (%)	Product[b] (%)
1	**8a**	10	19	**9a** (10)
2	**8a**	30	60	**9a** (19), **10a** (19)
3	**8b**	10	15	**9b** (8)
4	**8b**	30	63	**9b** (25), **10b** (8)
5	**8c**	10	6	**9c** (3)
6	**8c**	90	73	**9c** (36), **10c** (9)

[a] Conversion was determined based on recovered amine. [b] Isolation yields.

Table 4 Products and their yields in the C_{60}-promoted photoaddition reactions of benzylamines **11–13** with DMAD under the oxygenated condition



Amine	Irradiation time (min)	Conversion[a] (%)	Product[b] (%)
11	10	60	**2a** (15), **14** (22)
11	20	100	**2a** (28), **14** (42)
12	10	35	**2c** (14), **14** (9)
12	20	79	**2c** (35), **14** (21)
13	10	58	**6a** (16), **15** (15)
13	20	100	**6a** (35), **15** (30)

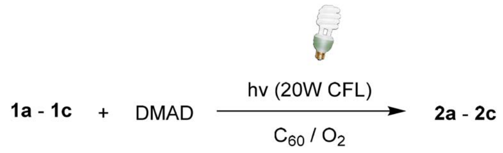
[a] Conversion was determined based on recovered amine. [b] Isolation yields.

2) When *N*-alkyl substituent of amine substrates was changed from ethyl (*N*-ethyl, **4a–4c**) to isopropyl (*N*-isopropyl, **5a–5c**) group, enamines **7a–7c** were also produced. However, conversion yields of amine substrates **5a–5c** and their photoproduct yields were much lower than those from **4a–4c**. Especially, in case of photoreactions of *para*-fluoro phenyl tethered amine **5c**, much longer irradiation time was required to bring about high conversion of starting amine **5c** and high yielding of photoproduct **7c**. (entries 8 and 9 in Table 2).

The results of photoreactions of *tert*-butyl group containing benzylamines **8a–8c** with DMAD in the presence of C_{60} were quite different from those of less alkyl group containing benzylamines **1a–1c** (*N*-methyl), **4a–4c** (*N*-ethyl), **5a–5c** (*N*-isopropyl) in terms of both photoreaction efficiency and photoproduct distribution pattern. As shown in Table 3, the photoaddition reactions of **8a–8c** with DMAD took place much less efficiently and, moreover, the least reaction efficiency was made in the photoreaction using both *tert*-butyl and *para*-fluoro phenyl groups containing benzylamine **8c** (see Tables 1 and 2). More interesting observation made in these reactions was that when much longer irradiation time was employed for the reactions, not only enamines **9a–9c** but also the highly substituted pyrrole derivatives **10a–10c** were produced, albeit relatively low yield. Considering our previous studies,[10] it is likely that 1,3-dipolar cycloaddition reactions of *in situ* formed azomethine ylides from **8a–8c** to DMAD are responsible for the formation of five membered *N*-heterocycles. In here, it is noteworthy to mention that the generation of non-stabilized azomethine ylides stimulated by sterically hindered N-substituent is quite unusual.

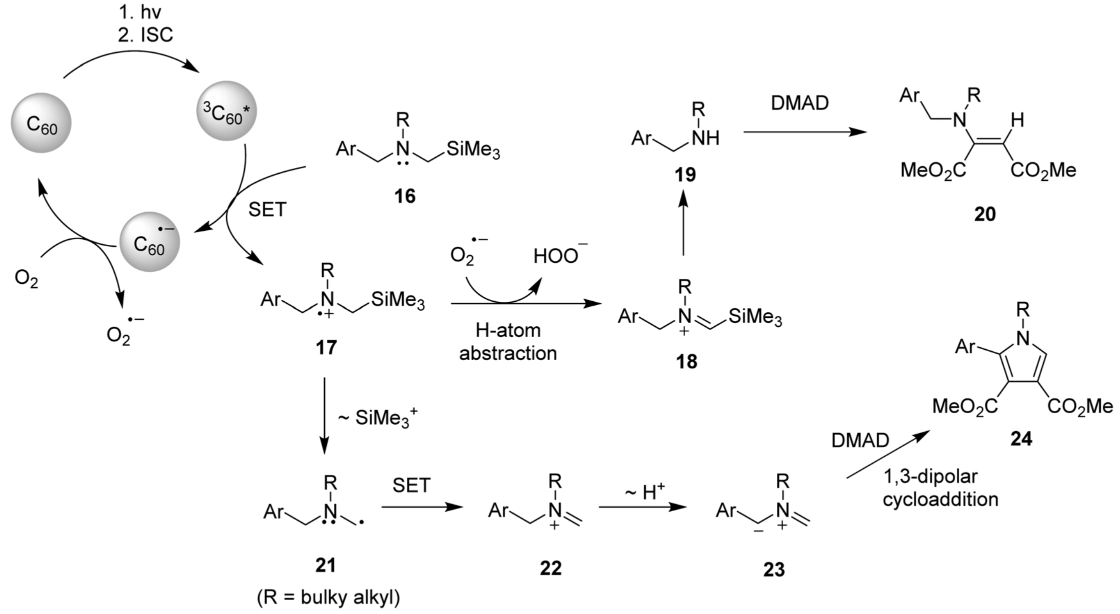
In order to evaluate how the trimethylsilyl group on the amine influence the reaction efficiencies and photoproduct distributions, we probed C_{60}-promoted photoaddition reactions of non-silyl containing benzylamines **11–13**. As described in Table 4, in contrast those of silyl group containing amine analogs (see Tables 1 and 2), photoreactions of non-silyl group tethered amines **11–13** with acetylene (DMAD) led to competitive formation of two types of enamine mixtures, **2a**, **2c**, **6a** and **14–15** inefficiently. These observation reveal that silyl group resided on nitrogen atom is likely to be responsible for regioselective secondary amine formation. Especially, silyl group tethered aminium radicals undergo H-atom abstraction at α-carbons adjacent to silyl moiety regioselectively to form precursors of secondary amines (see reaction mechanism). In addition, considering irradiation time *vs.* conversion of amine substrates, silyl group on amines seem to be able to enhance the reaction efficiencies.

Table 5 Products and their yields in the visible light irradiated, C_{60}-promoted photoaddition reactions of benzylamines **1a–1c** with DMAD under the oxygenated condition



Amine	Irradiation time (h)	Conversion[a] (%)	Product[b] (%)
1a	20	47	**2a** (32)
1a	40	100	**2a** (70)
1b	20	51	**2b** (36)
1b	40	100	**2b** (73)
1c	20	20	**2c** (10)
1c	40	48	**2c** (28)
1c	60	80	**2c** (45)

[a] Conversion was determined based on recovered amine. [b] Isolation yields.



Scheme 2 Plausible mechanistic pathways for the enamine and pyrrole photoadducts.

Visible light irradiated, C_{60}-promoted photoaddition reactions of *N*-α-trimethylsilyl-*N*-alkylbenzylamines **1a–1c** with DMAD

Visible-light promoted photochemical reactions have attracted great attention because of their wide application in organic synthesis and their use of sustainable and green energy sources. Especially, utilization of visible light is highly advantageous as most organic compounds do not absorb in this region and product decomposition and unwanted side products are readily avoided. Because fullerene C_{60} can absorbs light in the visible region as well as serve as an efficient electron acceptor, as a preliminary study, we explored viability of photoreactions of *N*-α-trimethylsilyl-*N*-alkylbenzylamines **1a–1c** with DMAD using visible light. For this purpose, C_{60}-promoted photoaddition reactions of benzylamines **1a–1c** with DMAD under the O_2-purged condition were performed by irradiation using commercially available 20 W compact fluorescent lamp (CFL) for fixed time periods (information about emitted wavelengths and their relative intensity from 20 W fluorescent lamp is available in ESI†). The results, given in Table 5, show that 20 h visible light irradiation of toluene solutions containing **1a–1c** and DMAD led to production of the respective enamines **2a–2c**, although reactions of *para*-fluorophenyl containing amine **1c** gave rise to lower conversion and product yield. Definitely, employing much longer visible light irradiation time could enhance the conversion and photoproduct yields in the photoreactions of **1a–1c** with DMAD.

Reaction mechanism

On the basis of observation made in earlier studies,[10,16,17] plausible mechanistic pathways can be suggested. (Scheme 2) Enamine formation in these reactions seems to occur *via* Michael addition of formed secondary amines **19** to DMAD. Specifically, right after the excitation of ground state of fullerene C_{60} to singlet state of C_{60}, followed rapid and efficient intersystem crossing ($\Phi_{\text{ISC}} = 1$) processes, the SET process from benzylamines **16** to triplet state of fullerene C_{60} ($^3C_{60}^*$) takes place initially to generate aminium radicals **17** and radical ions of C_{60} ($C_{60}^{\bullet-}$), latter of which are oxidized by molecular oxygen (O_2) to ground state of C_{60} and radical anions of molecular oxygen ($O_2^{\bullet-}$). Among the several pathways open to aminium radicals **17**, $O_2^{\bullet-}$-promoted regioselective H-atom abstraction of the aminium radicals seems to be the most feasible pathway.[16] Then, generated iminium ions **18** undergo hydrolytic cleavage by hydrogen peroxide anions (HOO^-) to produce non-silyl containing secondary benzylamines **19**, which add to DMAD to form enamine adducts **20**.[5] When the sterically bulky *N*-substituent is present on the starting amine substrates, another photochemical process takes place competitively. A mechanistic pathway for this process, which is compatible with the results of photoreactions, is 1,3-dipolar cycloaddition reactions of *in situ* formed azomethine ylides to DMAD to produce *N*-heterocyclic pyrrole photoadducts. As shown in Scheme 2, the key step in this route is that aminium radicals **17** undergo desilylation to form α-amino radicals **21**, which are consecutively converted to iminium ions **22** through a pathway involving second SET owing to the much lower oxidation potential of α-amino radicals in the range of -1 V (*vs.* SCE). Non-silyl containing iminium ions **22** formed in this manner then lose proton from benzyl position to produce 1,3-dipolar azomethine ylides **23** which serve as a precursor of pyrrole photoadducts **24**.

Conclusion

In current study, C_{60}-promoted photoaddition reactions of both trimethylsilyl- and a variety of alkyl group containing tertiary benzylamines (*i.e.*, *N*-α-trimethylsilyl-*N*-alkylbenzylamines) with dimethyl acetylenedicarboxylate (DMAD) were carried out to explore synthetic utility of trimethylsilyl group containing tertiary amines as substrates in the photochemical hydroamination reactions with C–C multiple bonds. The results showed that photoreactions of all of trimethylsilyl containing *N*-alkylbenzylamines with DMAD under O_2-purged environment, produced non-silyl containing enamines efficiently through a pathway involving addition of secondary amines to DMAD, former of which are produced by hydrolytic cleavage of *in situ* formed iminium ions. Exceptionally, five-membered *N*-heterocyclic ring, pyrroles, were also produced competitively in photoreaction of those of less bulky alkyl group (*i.e.*, *tert*-butyl) substituted benzylamines through a pathway involving 1,3-dipolar cycloaddition of azomethine ylides to DMAD. Furthermore, photoreactions of non-silyl containing benzylamines with DMAD under oxygenated conditions took place less efficient and non-regioselective manner to produce enamine photoadducts.

The observation made in this study show that regioselectivity of C_{60}-promoted photochemical reactions of *N*-α-trimetylsilyl-*N*-alkylbenzylamines, leading to formation of secondary amines, can be controlled by the presence of trimethylsilyl group, and that this silyl containing tertiary amines can serve a precursor of secondary amines for the hydroamination reactions with electron deficient acetylenes.

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. 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 (aceglass cat. # 7825-34), a power supply (aceglass cat. # 7830-61), a water-cooled quartz immersion well (aceglass cat # 7874-27), a borosilicate reaction vessel (agceglass cat. # 7841-03) and a flint glass filter (>310 nm). Detail information about UV lamps used in this study are provided on ESI.†

General procedure of C_{60}-promoted photoreactions of *N*-α-trimethylsilyl-*N*-alkylbenzylamines with DMAD.

The toluene solutions (220 mL) containing benzylamines (0.7 mmol, 1 equiv.), dimethyl acetylenedicarboxylate (1.4 mmol, 2 equiv.), and C_{60} (0.035 mmol, 0.05 equiv.) that were purged with O_2 before and during irradiation were irradiated with a 450 W 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. Then, photolysates were concentrated *in vacuo* and then the resulting mixture were separated by using silica gel column chromatographic isolation to give photoadducts.

Photoreaction of 1a

10 min irradiation (100% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **2a**[10] (144 mg, 78%). ^1H-NMR δ 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 δ 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).

Photoreaction of 1b

10 min irradiation (100% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **2b** (142 mg, 73%). ^1H NMR δ 2.30 (s, 3H), 2.70 (s, 3H), 3.61 (s, 3H), 3.90 (s, 3H), 4.22 (s, 2H), 4.64 (s, 1H), 7.07–7.14 (m, 4H); ^{13}C NMR δ 21.0, 36.7, 50.7, 52.9, 56.2, 84.6, 127.4, 129.4, 132.5, 137.6, 155.0, 166.1, 168.1; HRMS (EI) *m*/*z* 277.1313 (M^+, $C_{15}H_{19}NO_4$ requires 277.1314).

Photoreaction of 1c

10 min irradiation (93% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **2c** (119 mg, 78%) and **3** (34 mg, 19%).

2c: ^1H NMR δ 2.68 (s, 3H), 3.58 (s, 3H), 3.88 (s, 3H), 4.2 (s, 2H), 4.62 (s, 1H), 6.94–7.0 (m, 2H), 7.15–7.19 (m, 2H); ^{13}C NMR δ 36.5, 50.6, 52.8, 55.5, 84.7, 115.5 (d, J_{C-F} = 21.5 Hz), 128.9 (d, J_{C-F} = 8.1 Hz), 131.1 (d, J_{C-F} = 3.1 Hz), 154.6, 160.5, 162.1 (d, J_{C-F} = 245 Hz), 165.9, 167.8; HRMS (EI) *m*/*z* 28101066 (M^+, $C_{14}H_{16}FNO_4$ requires 281.1063).

3: ^1H NMR δ 0.08 (s, 9H), 2.68 (s, 2H), 2.84 (s, 3H), 3.57 (s, 3H), 3.88 (s, 3H), 4.44 (s, 1H); ^{13}C NMR δ −1.6, 50.5, 52.7, 82.5, 154.7, 166.1, 168.2; HRMS (EI) *m*/*z* 259.1242 (M^+, $C_{11}H_{21}NO_4Si$ requires 259.1240).

Photoreaction of 4a

10 min irradiation (100% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **6a** (127 mg, 78%). ^1H NMR δ 1.05 (t, 3H, *J* = 7.2 Hz), 3.12 (q, 2H, *J* = 7.2 Hz), 3.55 (s, 3H), 3.87 (s, 3H), 4.26 (s, 2H), 4.62 (s, 1H), 7.18–7.28 (m, 5H); ^{13}C NMR δ 50.4, 52.7, 77.2, 83.9, 126.9, 127.5, 128.5, 135.4, 154.0, 165.9, 168.0; HRMS (EI) *m*/*z* 277.1312 (M^+, $C_{15}H_{19}NO_4$ requires 277.1314).

Photoreaction of 4b

10 min irradiation (100% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **6b** (156 mg, 76%). ^1H NMR δ 1.06 (t, 3H, *J* = 7.2 Hz), 2.28 (s, 3H), 3.12 (q, 2H, *J* = 7.2 Hz), 3.57 (s, 3H), 3.88 (s, 3H), 4.23 (s, 2H), 4.63 (s, 1H), 7.09 (s, 4H); ^{13}C NMR δ 20.9, 50.5, 52.7, 77.2, 83.8, 127.0, 129.2, 132.4, 137.2, 154.1, 166.0, 168.1; HRMS (EI) *m*/*z* 291.1474 (M^+, $C_{16}H_{21}NO_4$ requires 291.1471).

Photoreaction of 4c

10 min irradiation (90% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **6c** (125 mg, 60%). ^1H NMR δ 1.03 (t, 3H, *J* = 6.9 Hz), 3.09 (q, 2H, *J* = 6.9 Hz), 3.53 (s, 3H), 3.85 (s, 3H), 4.2 (s, 2H), 4.58 (s, 1H), 6.91–6.97 (m, 2H), 7.13–7.17 (m, 2H); ^{13}C NMR δ 50.6, 52.8, 77.2, 84.2, 115.5 (d, J_{C-F} = 21.4

Hz), 128.7 (d, $J_{\text{C–F}} = 8$ Hz), 131.2, 153.9, 160.4, 162.1 (d, $J_{\text{C–F}} = 244.5$ Hz), 165.9, 168.0; HRMS (EI) *m*/*z* 295.1221 (M^+, $C_{15}H_{18}FNO_4$ requires 295.1220).

Photoreaction of 5a

10 min irradiation (34% conversion), column chromatography (EtOAc : hexane = 1 : 6) to yield **7a** (36 mg, 18%); 30 min irradiation (96% conversion), column chromatography (EtOAc : hexane = 1 : 6) to yield **7a** (105 mg, 51%). ^1H NMR δ 1.17 (d, 6H, $J = 6.3$ Hz), 3.53 (s, 3H), 3.79 (septet, 1H, $J = 6.3$ Hz), 3.92 (s, 3H), 4.31 (s, 2H), 4.47 (s, 1H), 7.18–7.24 (m, 3H), 7.27–7.32 (m, 2H); ^{13}C NMR δ 20.9, 47.1, 50.7, 52.8, 52.9, 85.7, 126.0, 127.1, 128.6, 136.1, 154.5, 166.3, 168.2; HRMS (EI) *m*/*z* 291.1472 (M^+, $C_{16}H_{21}NO_4$ requires 291.1471).

Photoreaction of 5b

10 min irradiation (39% conversion), column chromatography (EtOAc : hexane = 1 : 6) to yield **7b** (45 mg, 21%); 30 min irradiation (100% conversion), column chromatography (EtOAc : hexane = 1 : 6) to yield **7b** (114 mg, 53%). ^1H NMR δ 1.15 (d, 6H, $J = 6.6$ Hz), 2.28 (s, 3H), 3.52 (s, 3H), 3.75 (septet, 1H, $J = 6.6$ Hz), 3.91 (s, 3H), 4.26 (s, 2H), 4.46 (s, 1H), 7.04–7.11 (m, 4H); ^{13}C NMR δ 20.8, 21.0, 46.9, 50.6, 52.7, 52.9, 85.4, 125.9, 129.2, 133.0, 136.6, 154.5, 166.3, 168.2; HRMS (EI) *m*/*z* 305.1624 (M^+, $C_{17}H_{23}NO_4$ requires 305.1627).

Photoreaction of 5c

10 min irradiation (11% conversion), column chromatography (EtOAc : hexane = 1 : 6) to yield **7c** (12 mg, 6%); 50 min irradiation (100% conversion), column chromatography (EtOAc : hexane = 1 : 6) to yield **7c** (116 mg, 53%). ^1H NMR δ 1.14 (d, 6H, $J = 6.6$ Hz), 3.51 (s, 3H), 3.74 (septet, 1H, $J = 6.6$ Hz), 3.89 (s, 3H), 4.24 (s, 2H), 4.43 (s, 1H), 6.93–6.98 (m, 2H), 7.12–7.17 (m, 2H); ^{13}C NMR δ 20.7, 46.4, 50.6, 52.7, 52.8, 85.9, 115.5 (d, $J_{\text{C–F}} = 21$ Hz), 127.6 (d, $J_{\text{C–F}} = 8.3$ Hz), 131.7 (d, $J_{\text{C–F}} = 3$ Hz), 154.3, 160.1, 161.7 (d, $J_{\text{C–F}} = 244.5$ Hz), 166.1, 167.9; HRMS (EI) *m*/*z* 309.1378 (M^+, $C_{16}H_{20}FNO_4$ requires 309.1376).

Photoreaction of 8a

10 min irradiation (19% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **9a** (21 mg, 10%); 30 min irradiation (60% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **9a** (41 mg, 73%) and **10a** (41 mg, 19%).

9a: ^1H NMR δ 1.37 (s, 9H), 3.59 (s, 3H), 3.80 (s, 3H), 4.43 (s, 2H), 4.96 (s, 1H), 7.18–7.33 (m, 5H); ^{13}C NMR δ 28.8, 50.8, 52.8, 53.0, 59.5, 91.1, 126.5, 127.0, 128.5, 138.5, 154.1, 167.2, 167.8; HRMS (EI) *m*/*z* 305.1629 (M^+, $C_{17}H_{23}NO_4$ requires 305.1627).

10a: ^1H NMR δ 1.38 (s, 9H), 3.52 (s, 3H), 3.78 (s, 3H), 7.32–7.38 (m, 5H), 7.46 (s, 1H); ^{13}C NMR δ 31.3, 51.3, 51.5, 59.0, 112.3, 118.1, 124.4, 127.4, 128.6, 131.9, 132.9, 136.2, 164.2, 165.6; HRMS (EI) *m*/*z* 315.1471 (M^+, $C_{18}H_{21}NO_4$ requires 315.1471).

Photoreaction of 8b

10 min irradiation (15% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **9b** (18 mg, 8%); 30 min irradiation (60% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **9b** (55 mg, 25%) and **10b** (18 mg, 8%).

9b: ^1H NMR δ 1.36 (s, 9H), 2.30 (s, 3H), 3.59 (s, 3H), 3.80 (s, 3H), 4.38 (s, 2H), 4.95 (s, 1H), 7.08–7.15 (m, 4H); ^{13}C NMR δ 28.8, 50.8, 52.8, 90.8, 126.4, 129.1, 135.4, 136.6, 154.1, 167.2, 167.9; HRMS (EI) *m*/*z* 319.1786 (M^+, $C_{18}H_{25}NO_4$ requires 319.1784).

10b: ^1H NMR δ 1.39 (s, 9H), 2.37 (s, 3H), 3.55 (s, 3H), 3.78 (s, 3H), 7.14 (d, 2H, $J = 7.8$ Hz), 7.22 (d, 2H, $J = 7.8$ Hz), 7.45 (s, 1H); ^{13}C NMR δ 21.4, 31.5, 51.3, 51.6, 59.0, 112.4, 118.2, 124.4, 128.3, 129.9, 131.9, 136.5, 138.6, 164.4, 165.9; HRMS (EI) *m*/*z* 329.1625 (M^+, $C_{19}H_{23}NO_4$ requires 329.1627).

Photoreaction of 8c

10 min irradiation (6% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **9c** (7 mg, 3%); 90 min irradiation (73% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **9c** (82 mg, 36%) and **10c** (21 mg, 9%).

9c: ^1H NMR δ 1.35 (s, 9H), 3.58 (s, 3H), 3.78 (s, 3H), 4.37 (s, 2H), 4.94 (s, 1H), 6.94–7.0 (m, 2H), 7.19–7.22 (m, 2H); ^{13}C NMR δ 28.8, 50.8, 52.1, 52.8, 59.4, 91.9, 115.4 (d, $J_{\text{C–F}} = 21$ Hz), 128.1 (d, $J_{\text{C–F}} = 8.3$ Hz), 134.2 (d, $J_{\text{C–F}} = 3$ Hz), 153.7, 161.8 (d, $J_{\text{C–F}} = 243.8$ Hz), 167.1, 167.7; HRMS (EI) *m*/*z* 323.1530 (M^+, $C_{17}H_{22}FNO_4$ requires 323.1533).

10c: ^1H NMR δ 1.39 (s, 9H), 3.55 (s, 3H), 3.79 (s, 3H), 7.01–7.07 (m, 2H), 7.3–7.34 (m, 2H), 7.46 (s, 1H); ^{13}C NMR δ 31.5, 51.4, 51.6, 112.6, 114.7 (d, $J_{\text{C–F}} = 21.8$ Hz), 118.6, 124.7, 129.0 (d, $J_{\text{C–F}} = 3.8$ Hz), 133.9 (d, $J_{\text{C–F}} = 7.5$ Hz), 135.1, 162.9 (d, $J_{\text{C–F}} = 247.5$ Hz), 164.3, 165.6; HRMS (EI) *m*/*z* 333.1378 (M^+, $C_{18}H_{20}FNO_4$ requires 333.1376).

General procedure of C_{60}-promoted photoreactions of non-silyl containing *N*-alkylbenzylamines with DMAD

Under the same reaction conditions employed above, the photoreactions of non-silyl containing each benzylamine **11–13** with DMAD were carried out. Then, photolysates were concentrated *in vacuo* and then the resulting mixture were separated by using silica gel column chromatographic isolation to give photoadducts.

Photoreaction of 11 with DMAD

10 min irradiation (60% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **2a** (28 mg, 15%) and **14** (ref. 10) (29 mg, 22%); 20 min irradiation (100% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **2a** (52 mg, 28%) and **14** (55 mg, 42%).

Photoreaction of 12 with DMAD

. 10 min irradiation (35% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **2c** (28 mg, 14%) and **14** (12 mg, 9%); 20 min irradiation (79% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **2c** (69 mg, 35%) and **14** (28 mg, 21%).

14: ^{1}H NMR δ 2.79 (s, 6H), 3.54 (s, 3H), 3.84 (s, 3H), 4.50 (s, 1H); ^{13}C NMR δ 39.6, 50.5, 52.7, 84.2, 155.1, 165.9, 168.0; HRMS (EI) *m*/*z* 187.0845 (M$^+$, $C_8H_{13}NO_4$ requires 187.0845).

Photoreaction of 13 with DMAD

10 min irradiation (60% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **6a** (31 mg, 16%) and **15** (21 mg, 15%); 20 min irradiation (100% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **6a** (68 mg, 35%) and **15** (43 mg, 30%).

15: ^{1}H NMR δ 1.09 (t, 3H, *J* = 7.2 Hz), 2.75 (s, 3H), 3.11 (q, d, *J* = 7.2 Hz), 3.55 (s, 3H), 3.86 (s, 3H), 4.51 (s, 1H); ^{13}C NMR δ 36.6, 47.7, 50.6, 52.7, 83.6, 154.5, 166.0, 168.1; HRMS (EI) *m*/*z* 201.1002 (M$^+$, $C_9H_{15}NO_4$ requires 201.1001).

Visible light irradiated, C_{60}-promoted photoreactions of *N*-α-trimethylsilyl-*N*-alkylbenzylamines 1a–1c with DMAD

The O_2-purged toluene solutions (70 mL) containing each benzylamine **1a–1c** (0.18 mmol, 1 equiv.), dimethyl acetylenedicarboxylate (0.35 mmol, 2 equiv.) and C_{60} (0.009 mmol, 0.05 equiv.) were simultaneously irradiated with a 20 W compact fluorescence lamp for fixed time periods (20, 40 and 60 h respectively). Then, photolysates were concentrated *in vacuo* and then the resulting mixture were separated by using silica gel column chromatographic isolation to give photoadducts.

Photoreaction of 1a

20 h irradiation (47% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **2a** (15 mg, 32%); 40 h irradiation (100% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **2a** (32 mg, 70%).

Photoreaction of 1b

20 h irradiation (51% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **2b** (18 mg, 36%); 40 h irradiation (100% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **2b** (36 mg, 73%).

Photoreaction of 1c

20 h irradiation (20% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **2b** (5 mg, 10%); 40 h irradiation (48% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **2c** (14 mg, 28%); 60 h irradiation (80% conversion), column chromatography (EtOAc : hexane = 1 : 5) to yield **2c** (23 mg, 45%).

Conflicts of interest

There are no conflicts of interest to declare.

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