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Suk Hyun Lim, Dae Won Cho, Patrick S. Mariano

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Graphical Abstract



Catalyst Free, Visible-Light Promoted Photoaddition Reactions between C₆₀ and N-

Trimethylsilylmethyl-Substituted Tertiary Amines for Synthesis of Aminomethyl-1,2-

dihydrofullerenes

Suk Hyun Lim,¹ Dae Won Cho^{1*}, Patrick S. Mariano^{2*}

¹Department of Chemistry, Yeungnam University, Gyeongsan, Gyeongbuk 712-749, Korea

(dwcho00@yu.ac.kr)

²Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque,

New Mexico 97131, USA

(mariano@unm.edu)

Graphical Abstract



Abstract

An efficient and benign method for the preparation of aminomethyl-substituted fullerenes has been developed. The process, involving catalyst free, visible-light irradiation of 10% EtOH-toluene solutions containing fullerene C_{60} and *N*-trimethylsilylmethyl-substituted amines by using a 20 W compact fluorescent lamp, leads to formation of aminomethyl-substituted fullerene adducts in a highly efficient manner. The photoaddition reaction takes place *via* a pathway initiated by visible light absorption by C_{60} , followed by SET from the amine to the triplet excited state of C_{60} . Ethanolpromoted desilylation of the resulting aminium radical then generates the corresponding α -amino radical which couples with the C_{60} radical anion to form the anion precursor of the fullerene adducts. The new approach using visible-light takes place under mild conditions and it does not require the use of photocatalysts. Thus, the method developed in this effort could broadens the range of functionalized fullerene derivatives that can be readily prepared.

Introduction

Owing to the potential need for fullerene derivatives in many scientific research fields,¹⁻⁵ a number of studies have focused on the preparation of functionalized fullerene derivatives which not only maintain the unique photophysical and redox properties of the parent fullerenes but also have novel physical/chemical characteristics.⁶ For instance, addition reactions of diverse organic substances across the [6,6]-juncture (or [5,6]-juncture) of C_{60} have been shown to generate fullerene derivatives which have tunable properties,⁷ while maintaining high electron affinities,^{8,9} small reorganization energies^{10,11} and high electron transporting abilities.^{12,13}

The most common protocols developed to date to synthesize fullerene derivatives involve thermal cycloaddition reactions of 1,3-dipolar azomethine ylides (known as the Prato reaction),^{14,15} base/organometal-promoted nucleophilic additions,¹⁶⁻¹⁸ transition metal mediated free radical reactions^{19,20} and single electron transfer (SET)-promoted photoaddition reactions.²¹⁻²⁴ Owing to the excellent electron accepting ability of fullerene C₆₀ ($E_{red} = -0.42$ V vs SCE in PhCN), photoinduced SET-promoted reactions take place between excited states of fullerene C₆₀ and proper electron donating substrates under mild conditions with high quantum and chemical efficiencies.

Among the number of potentially available electron donating substances, tertiary aliphatic and aromatic amines (*ca.* $E_{ox} < +1$ V vs Ag/AgCl) have been utilized extensively in SET-promoted photoaddition reactions with C₆₀.^{21a,25-27} The results of these studies reveal that irradiation of C₆₀ in the presence of amines **1** leads to formation of aminomethyl-1,2-dihydrofullerenes **5** (*i.e.*, 1,2-

adducts) by a pathway involving thermodynamically favorable SET from the amines **1** to the triplet excited state of C_{60} (${}^{3}C_{60}^{*}$, $E_{red}({}^{3}C_{60}^{*}) = 1.56$ V), 11b,21b,28 formed by efficient intersystem crossing (ISC) from its singlet excited state of C_{60} (${}^{1}C_{60}^{*}$, $\Phi_{ISC} = 1$).²⁹ This process produces the radical anion of C_{60} (C_{60}^{\bullet}) (Scheme 1) and an amine radical cation **2**, the latter of which undergoes α -CH deprotonation (E = H) to form a carbon centered α -amino radical **3**, which couples with C_{60}^{\bullet} to form an anion (**6**) precursor of aminomethyl-substituted 1,2-adduct **5**. Alternatively, proton transfer can occur between the amine radical cation **2** (E = H) and C_{60}^{\bullet} to generate α -amino radical **4** and the hydrofullerene radical **3** (H- C_{60}^{\bullet}) which can then couple to generate the 1,2-adducts **4** directly.^{25a,30}

Scheme 1. Mechanistic pathway for SET-promoted photoaddition reactions between tertiary amines and C_{60} .



Recently, we explored SET-promoted photoaddition reactions of C_{60} with tertiary aliphatic amines that possess *N*-trimethylsilylmethyl substituents.³¹⁻³³ The results showed that photoreactions of C_{60} with the amines **1** (E = SiMe₃) gave rise to formation of 1,2-adducts **5** with much higher

efficiencies than photoreactions utilizing analogous, non- α -trimethylsilyl group containing amines **1** (E = H) (Scheme 1). The enhanced chemical efficiencies of photoreactions of *N*-trialkylsilylmethylsubstituted amines is a consequence of the fact that trimethylsilyl-substituted amine radical cations **2** (E = SiMe₃) undergo silophilic solvent-assisted desilylation much more rapidly than α -CH deprotonation of the non-trimethylsilyl analogs **1** (E = H).^{29–31}

Because photoaddition reactions of C₆₀ with amines are highly desirable processes to synthesize functionalized fullerene derivatives, we embarked on an effort to develop mild and eco-friendly conditions to conduct these reactions in an efficient manner. For the most part, these reactions have been promoted in the past using high energy UV-light.^{25,31,32a} However, visible light is advantageous as most organic compounds do not absorb in this region and product decomposition and unwanted side products are easily avoided. In addition, C₆₀ can absorbs light in the visible region and therefore no catalysts are necessary. As a result, we designed a study to explore the viability of these photoaddition reactions using visible light as the energy source. At the outset of this investigation, we were aware of studies by Nishibayashi and his coworkers^{31a} that demonstrated that visible-light could be utilized to promote iridium complex photocatalyzed reactions of C_{60} with Ntrimethylsilylmethyl-substituted arylamines (Me₃SiCH₂NAr₂, Ar = aryl) that produce aminomethylsubstituted fullerene derivatives. In addition, Troshin³⁵, Gan³⁶ and others^{26,37} showed that visiblelight initiated photoaddition reactions of C₆₀ with secondary/tertiary amines occurred to produce the corresponding fullerene derivatives. Although these reactions are simple and efficient, their wide use

is limited because highly intense light sources (high pressure Hg lamp equipped with a filter and cooling water bath or intense Xenon light bulb), and expensive and laboriously synthesized iridium (Ir) catalysts^{31a} are required. In the effort described below, we have shown that catalyst-free, direct visible-light promoted photoaddition reactions between C_{60} and *N*-trimethylsilylmethyl-substituted amines take place efficiently. To the best of our knowledge, the observations are the first that show that a methodology, in which a cheap and commercially available visible light source (and eventually even sunlight) is used, has great potential for the preparation of uniquely functionalized fullerenes.

Results and Discussion

The *N*-trimethylsilylmethyl-substituted tertiary amines used in this study were prepared using methods devised in our previous studies³¹ (see supplementary data). Photochemical reactions were performed by irradiation of N₂ purged, 10% EtOH-toluene (v/v) solutions (10 mL) containing C₆₀ (0.17 mM) and the amines (0.35 mM) using a 20 W commercial compact fluorescent lamp (CFL) for fixed time periods. (Emitted wavelength range and relative intensity of 20W CFL is shown in ESI) Photoproduct yields were determined by utilizing HPLC and UV-visible spectrometric analysis of the crude photolysates. Structural determination of photoproducts were made by comparison of ¹H and ¹³C NMR spectroscopic data to those previously reported.^{31,32}

Photoreactions of *N*-trimethylsilylmethyl-*N*,*N*-dialkylamines 7-12. Photoreactions of C_{60} with the *N*-trimethylsilylmethyl-*N*,*N*-dialkylamines 7-12^{31a} were explored first. The results, given in

Scheme 2 and Table 1, show that 5 h visible light irradiation of N₂-purged, 10% EtOH-toluene solutions containing C₆₀ and the *N*-trimethylsilylmethyl-substituted *N*,*N*-dialkylamines amines **7-11** led to production of the respective aminomethyl-substituted 1,2-adducts **13-17**^{31a} in high conversions, product yields and material recoveries (entries 1-5 in Table 1). In contrast, reaction of the *N*,*N*-di-carboxymethyl-substituted amine **12** formed the corresponding adduct **18**^{31a} in a low yield (27%, entry 6), which could be significantly improved by using much longer irradiation times (entries 7-8 in Table 1). Importantly, the aminomethylated 1,2-adducts were not generated when reactions were carried out by irradiation of either O₂-purged (entries 9-10 in Table 1) or pure toluene containing (entries 11-12 in Table 1) solutions. It is noteworthy that, in contrast to those of *N*-trimethylsilylmethyl-substituted amines, analogous non- α -trimethylsilyl-substituted amines (*N*-methyl in place of *N*-trimethylsilylmethyl) did not undergo photoaddition reactions with C₆₀ under these conditions even when much longer irradiation times (100 h) were utilized.

Scheme 2. Visible light promoted photoaddition reactions of C_{60} with *N*-trimethylsilylmethyl-*N*,*N*-dialkylamines 7-12.



Table 1. Products, conversions and yields of photoaddition reactions promoted by visible-light irradiation of N₂-purged 10% EtOH-toluene solutions containing C_{60} and *N*-trimethylsilylmethyl-*N*,*N*-dialkylamines **7-12**.

ontru	omino	\mathbf{P}^3	\mathbf{P}^4	irradiation	conversion	product
entry	annne	Κ	К	time (h)	$(\%)^{\mathrm{a}}$	(%)
1	7	$CH_2(CH_2)_4CH_3$	$CH_2(CH_2)_4CH_3$	5	100	13 (91)
2	8	$CH_2(CH_2)_4CH_3$	CH ₂ CH(Et)(CH ₂) ₃ CH ₃	5	88	14 (80)
3	9	$CH_2(CH_2)_4CH_3$	CH ₂ CH ₂ OCH ₃	5	86	15 (74)
4	10	CH ₂ CH(Et)(CH ₂) ₃ CH ₃	CH ₂ CH ₂ OCH ₂ CH ₂ OH	5	91	16 (79)
5	11	$CH_2(CH_2)_4CH_3$	CH ₂ CO ₂ CH ₂ CH ₃	5	68	17 (54)
6	12	CH ₂ CO ₂ CH ₂ CH ₃	CH ₂ CO ₂ CH ₂ CH ₃	5	35	18 (25)
7	12	CH ₂ CO ₂ CH ₂ CH ₃	CH ₂ CO ₂ CH ₂ CH ₃	10	58	18 (49)
8	12	CH ₂ CO ₂ CH ₂ CH ₃	CH ₂ CO ₂ CH ₂ CH ₃	24	91	18 (87)
9 ^b	7	$CH_2(CH_2)_4CH_3$	CH ₂ (CH ₂) ₄ CH ₃	24	n.r ^e	n.r ^e
10 ^b	11	$CH_2(CH_2)_4CH_3$	CH ₂ CO ₂ CH ₂ CH ₃	24	n.r ^e	n.r ^e
11 ^c	7	$CH_2(CH_2)_4CH_3$	CH ₂ (CH ₂) ₄ CH ₃	24	n.r ^e	n.r ^e
12 ^c	11	$CH_2(CH_2)_4CH_3$	CH ₂ CO ₂ CH ₂ CH ₃	24	n.r ^e	n.r ^e

^aDetermined based on recovered C_{60} . ^bPhotoreactions in O₂-purged 10% EtOH-toluene solution. ^cPhotoreaction in N₂-purged, pure toluene solution. ^eNo reaction

Photoreactions of *N*-trimethylsilylmethyl-*N*-alkyl-*N*-benzylamines 19-29. Photoreactions of C_{60} with *N*-trimethylsilylmethyl-substituted *N*-alkyl-*N*-benzylamines 19-29, ^{31a,32b} in which the alkyl substituents possess various functional groups, were performed using the conditions described above. As can be seen by viewing the data in Scheme 3 and Table 2, visible-light promoted photoreactions of C_{60} with amines 19-22, 24-25 and 28 took place to produce the corresponding 1,2-adducts 30-33^{31a}, 35-36^{31a,32b} and 39^{32b} with high conversions, product yields and material recoveries. In contrast, photoreactions of C_{60} with benzylamines 23 and 26-27, which possess either electron withdrawing

(CH₂CH₂CO₂CH₂CH₃ or *p*-F-Ph) or bulky (*t*-Bu) *N*-substituents, occurred to form the respective photoadducts 34^{31a} and $37-38^{32b}$ (65-79%) in only moderate to low yields. Moreover, reaction of C₆₀ with benzylamine 29, which possesses both an electron withdrawing *para*-F substituted phenyl ring and a bulky *N*-*tert*-butyl group, was highly inefficient as reflected in a low conversion (52%) and yield (33%) of adduct 40.^{32b} Here again, no 1,2-aminomethyl-adducts were produced when photoreactions of 19-29 were performed using either O₂-purged solutions or pure toluene as the solvent. Likewise, non- α -trimethylsilyl amine anologs of these substances (*N*-methyl in place of *N*trimethylsilylmethyl) did not undergo SET-promoted photoaddition reactions to C₆₀ when irradiated under the same conditions.

Scheme 3. Visible light promoted photoaddition reactions of C_{60} with *N*-trimethylsilylmethyl-*N*-alkyl-*N*-benzylamines **19-29**.



Table 2. Products, conversions and yields of photoaddition reactions promoted by visible-light irradiation of N₂-purged 10% EtOH-toluene solutions containing C_{60} with *N*-trimethylsilylmethyl-*N*-alkyl-*N*-benzylamines **19-29**.

entry	amine	R ⁵	X	irradiation time (h)	conversion (%) ^a	product (%)
1	19	$CH_2(CH_2)_4CH_3$	Н	5	85	30 (81)
2	20	CH ₂ (CH ₂) ₄ OH	Н	5	85	31 (73)
3	21	CH ₂ CH ₂ OCH ₂ CH ₂ OH	Н	5	82	32 (74)

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4	22	CH ₂ CH ₂ OCH ₂ CH ₂ OCH ₃	Н	5	82	33 (72)
5	23	CH ₂ CH ₂ CO ₂ CH ₂ CH ₃	Н	5	75	34 (65)
6	24	CH ₃	Н	5	99	35 (91)
7	25	CH ₃	CH ₃	5	99	36 (95)
8	26	CH ₃	F	5	91	37 (79)
9	27	<i>t</i> -Bu	Н	5	86	38 (69)
10	28	<i>t</i> -Bu	CH ₃	5	89	39 (75)
11	29	t-Bu	F	5	52	40 (33)

^aDetermined based on recovered C₆₀.

The products formed in the visible light promoted reactions described above are comparable to those generated using UV-irradiation of N₂-purged, 10% EtOH-toluene solutions of the same tertiary *N*-trimethylsilylmethyl-substituted amines and C_{60} (Table 3).^{31a,32b} Inspection of the data arising from the earlier study (Table 3) showed that while much shorter times were required to bring about high conversions of C_{60} when UV-irradiation was used, in most cases the yields of the 1,2-aminomethyl-adduct, reflected in much lower mass recoveries, were comparatively lower than those arising from visible light promoted reactions.

Table 3. Products and yields of photoaddition reactions promoted by UV-light irradiation of N2-
purged 10% EtOH-toluene solutions containing C_{60} and N-trimethylsilylmethyl amines 7-12 and 19-
29.^a29.^a

entry	amine	irradiation time (min)	conversion (%) ^b	product (%)
1^{c}	7	4	100	13 (92)
2^{c}	8	4	93	14 (90)
3°	9	4	69	15 (54)

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4 ^c	10	8	100	16 (51)	
5 ^c	11	60	85	17 (42)	
6 ^c	12	60	68	18 (23)	
7°	19	8	100	30 (47)	
8 ^c	20	8	100	31 (43)	
9°	21	8	88	32 (57)	
10	^c 22	8	93	33 (56)	
11	° 23	8	82	34 (54)	
12	° 24	8	100	35 (86)	
13	^d 25	15	94	36 (69)	
14	^d 26	60	84	37 (53)	
15	^d 27	30	89	38 (61)	
16	^d 28	30	91	39 (66)	
17	^d 29	120	77	40 (52)	

^aAmine/C₆₀ is 0.56:0.28 mmol in 220 mL of 10% EtOH-toluene and irradiated 450 W Hg lamp with a flint glass filter (>300 nm). ^bDetermined based on recovered C₆₀. ^cData from ref. 31a. ^dData from ref. 32b.

Photoreactions of *N*-trimethylsilylmethyl-*N*,*N*-dibenzylamines 41-53. Catalyst free, visiblelight promoted photoaddition reactions of C_{60} with *N*-trimethylsilylmethyl-*N*,*N*-dibenzylamines 41-53^{31b}, in which the arene ring on the benzyl groups contains various electron donating (CH₃, OCH₃) and electron withdrawing (F, CF₃) substituents, were carried out under the same conditions described above. As the results depicted in Scheme 4 and Table 4 show, in contrast to the parent phenyl group containing substrate 41 (entry 1, Table 3), irradiation of 10% EtOH-toluene solutions of amines 42-45, which possess either one or two electron donating phenyl substituents (*i.e.*, CH₃, OCH₃), underwent SET-promoted photoaddition reactions with C_{60} to produce the respective aminomethylsubstituted 1,2-adducts **55-58**^{31b} in high conversions and product yields (entries 1-5 in Table 4). However, photoreactions of amines **46-53**, containing one or two electron withdrawing phenyl substituents (*i.e.*, F, CF₃), took place less efficiently than the reaction of **41** to give the respective photoadducts **59-66**^{31b} (entries 6-13 in Table 3) even when a longer irradiation time (24 h) was used (entries 11-13 in Table 4). Another interesting observation was that 24 h irradiation of a solution of C_{60} and the two CF₃ group substituted benzylamine **53** led to formation of the aminomethyl adduct **66** along with the pyrrolidine-fused fullerene **67** (4%).^{31b}

Scheme 4. Visible-light promoted photoaddition reactions of C_{60} with *N*-trimethylsilylmethyl-*N*,*N*-dibenzylamines 41-53.



Table 4. Products, conversions and yields of photoaddition reactions promoted by visible-light irradiation of N₂-purged 10% EtOH-toluene solutions containing C_{60} and *N*-trimethylsilylmethyl-*N*,*N*-dibenzylamines **41-53**.

entry	amine	Х	Y	irradiation time (h)	conversion (%) ^a	product (%)
1	41	Н	Н	5	65	54 (58)

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2	42	Н	CH ₃	5	95	55 (88)
3	43	Н	OCH ₃	5	95	56 (84)
4	44	CH ₃	CH ₃	5	98	57 (92)
5	45	OCH ₃	OCH ₃	5	100	58 (94)
6	46	Н	F	5	30	59 (26)
7	47	Н	CF ₃	5	17	60 (11)
8	48	CH ₃	F	5	59	61 (54)
9	49	CH ₃	CF ₃	5	38	62 (22)
10	50	OCH ₃	CF ₃	5	42	63 (29)
11	51	F	F	24	54	64 (41)
12	52	F	CF ₃	24	28	65 (17)
13	53	CF ₃	CF ₃	24	22	66 (14), 67 (4)

^aDetermined based on recovered C₆₀.

Photoreactions of *N*-trimethylsilylmethyl-*N*-benzylglycinate esters 68-72. Observations made in an earlier study^{32a} demonstrated that UV-irradiation induced photoaddition reactions between C_{60} and *N*-trimethylsilylmethyl-*N*-benzyl substituted glycinate esters were unique in that the nature and distribution of photoproducts are highly dependent on reaction conditions. Specifically, while UV irradiation of N₂-purged, 10% EtOH-toluene solutions of C_{60} and these amines^{32a} for short time periods (1 h) leads to formation of expected aminomethyl-substituted 1,2-adducts^{32a} exclusively, irradiation of O₂-purged 10% EtOH-toluene solutions leads to exclusive formation of the corresponding fulleropyrrolidines.^{32a} In the current effort, we briefly explored catalyst free, visiblelight promoted reactions between C_{60} and *N*-trimethylsilylmethyl-*N*-benzylglycinate esters **68-72**

(Scheme 5 and Table 5). We observed that 20 W CFL irradiation of N₂-purged 10% EtOH-toluene solutions of C₆₀ and glycinates **68-72** led to production of the respective 1,2-aminomethyl adducts **73-77** solely. As anticipated (see above), the conversion and yield of the reaction of the p-CF₃ substituted substrate **72** were relatively low (Table 5).

Scheme 5. Visible-light promoted photoaddition reactions of C_{60} with *N*-trimethylsilylmethyl-*N*-benzylglycinate esters **68-72**.



Table 5. Products, conversions and yields of photoaddition reactions promoted by visible-light irradiation of N₂-purged 10% EtOH-toluene solutions containing C_{60} and *N*-trimethylsilylmethyl-*N*-benzylglycinate esters **68-72**.

entry	amine	Z	irradiation time (h)	conversion (%) ^a	product (%)
1	<mark>68</mark>	H	5	60	73 (56)
2	<mark>68</mark>	H	24	88	73 (86)
3	<mark>69</mark>	CH ₃	5	68	74 (66)
4	<mark>69</mark>	CH₃	24	90	74 (90)
5	<mark>70</mark>	<mark>OCH</mark> ₃	5	86	75 (72)
6	<mark>70</mark>	<mark>OCH</mark> ₃	24	94	75 (86)
7	<mark>71</mark>	F	5	41	76 (30)
8	<mark>71</mark>	F	24	64	76 (55)

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9	<mark>72</mark>	<mark>CF₃</mark>	5	9	77 (2)			
10	<mark>72</mark>	CF ₃	24	47	77 (43)			

^aDetermined based on recovered C₆₀.

Photoreactions of *N*-trimethylsilylmethyl-*N*-methylanilines **78-80**. Visible-light induced photoreactions of C_{60} with α -trimethylsilyl-substituted *N*-methylanilines **78-80**³⁸ were also explored by using the same irradiation conditions. (Scheme 6 and Table 6) As the data in Table 6 show, irradiation of N₂-purged 10% EtOH-toluene solutions containing C_{60} and anilines **78-80** gave rise to the corresponding aminomethyl-substituted 1,2-adducts **81-83**. In addition, both conversion and product yields were enhanced as the irradiation time increase. Finally, no aminomethyl photoadducts were produced when these processes were performed under O₂-purged irradiation conditions.

Scheme 6. Visible-light promoted photoaddition reactions of C_{60} with *N*-trimethylsilylmethyl-*N*-methylanilines 78-80.



Table 6. Products, conversions and yields of photoaddition reactions promoted by visible-light irradiation of N₂-purged 10% EtOH-toluene solutions containing C_{60} and *N*-trimethylsilylmethyl-*N*-methylanilines **78-80**.

time (h) $(\%)^a$	ontru	amina	v	irradiation	conversion	product (%)
	entry	amme	<u>Λ</u>	time (h)	$(\%)^{\mathrm{a}}$	product (%)

	1	ACCEPTE	D MANUS	SCRIPT	
1	<mark>78</mark>	H	5	65	81 (57)
2	<mark>78</mark>	H	7	76	81 (60)
3	<mark>78</mark>	H	10	87	81 (75)
4	<mark>79</mark>	CH₃	5	72	82 (59)
5	<mark>79</mark>	CH₃	7	81	82 (72)
6	<mark>79</mark>	CH₃	10	89	82 (79)
7	<mark>80</mark>	F	5	44	83 (32)
8	<mark>80</mark>	F	7	54	83 (46)
9	<mark>80</mark>	F	10	61	83 (49)

^aDetermined based on recovered C₆₀.

The results of studies with the *N*-trimethylsilylmethyl-substituted *N*-methylanilines are comparable to those observed arising from the work of Nishibayashi and co-workers.^{30a} This earlier effort showed that 9 h visible light (440 nm) irradiation (250W Hg lamp with filter) of a *o*-dichlorobenzene (ODCB)-H₂O (v/v = 200: 1) solution containing C₆₀ and the *N*-trimethylsilylmethyl-substituted aniline **78** in the absence of a photocatalyst (*i.e.*, iridium complex) gave rise to production of the 1,2-adduct **81** in a very low product yield (15 %). In addition, although photoreaction in the presence of an iridium photocatalyst occurred with an enhanced efficiency, the yield (36 %) was still low (Scheme 7).

Scheme 7. The results of Nishibayashi and co-workers' study of visible light promoted photoreaction of C_{60} with aniline 78 in the presence/absence of iridium photocatalyst.



Although it is not possible to compare the observations made earlier by Nishibayashi and by us in the current effort because different conditions (e.g., light sources, photochemical apparatus and reaction conditions) were employed, the largely different yields of the processes are most likely caused by the different solvents used. To explore how solvent governs the efficiencies of photoreactions of C_{60} with *N*-trimethylsilylmethyl-substituted anilines, N₂-purged 10% EtOH-ODCB solutions of C_{60} and anilines **78-80** were subjected to visible-light irradiation. As can be seen by reviewing the results in Table 7, although photoreactions in this solvent system took place to produce aminomethylated 1,2-adducts, the yields were dramatically lower than when the 10% EtOH-toluene solvent system was utilized. The differing in product yields depending on solvent system appear to be highly associated with chemoselectivity. In the HPLC analysis of photoproducts (see supplementary data), we found that while photoreactions of C_{60} with aniline derivatives **78-80** in 10% EtOH-toluene solution gave rise to formation of single products **81-83** (*i.e.*, one peak in HPLC data was observed), however, reactions in 10% EtOH-ODCB produced multiple products, in which one of them was aminomethyl 1,2-dihydrofullerenes **81-83** (*i.e.*, two or three peaks in HPLC data were observed).

Table 7. Products, conversions and yields of photoaddition reactions promoted by visible-light irradiation of N₂-purged 10% EtOH-ODCB solutions containing C_{60} and *N*-trimethylsilylmethyl-*N*-methylanilines **78-80**.

entry	amine	irradiation time (h)	conversion (%) ^a	product (%)
1	78	5	46	81 (22)
2	78	10	71	81 (34)
4	79	5	52	82 (25)
5	79	10	72	82 (35)
7	80	5	29	83 (16)
8	80	10	60	83 (36)

^aDetermined based on recovered C₆₀.

Conclusion

Visible-light promoted photochemical reactions have recently attracted great attention because of their wide application in organic synthesis and their use of sustainable and green energy sources. In the study described above, an efficient and environmentally benign method for the preparation of variously substituted aminomethyl-1,2-dihydrofullerenes has been developed. Observations made in this study show that photocatalyst free, visible-light promoted photoreactions of 10% EtOH-toluene solutions containing fullerene C_{60} and *N*-trimethylsilylmethyl-substituted amines generate aminomethyl substituted fullerene adducts in a highly efficient manner, although reactions with electron deficient amines give rise to limited conversion and product yields. Importantly, the results confirm our earlier observations that show that presence of an *N*-trimethylsilylmethyl group and the electronic nature of amine substrates play critical roles in governing the efficiencies of these photoaddition reactions. In comparison to typical thermal and photochemical methods developed previously for the preparation of aminomethylated fullerene derivatives, the new approach using visible-light takes place under mild conditions and it does not require the use of photocatalysts. Thus, the method developed in this study could broaden the scope of methods to functionalize fullerenes using amine substrates.

Experimental

General. Commercially available fullerene C_{60} (>99% HPLC pure) was used as received. ¹H and ¹³C NMR spectra (300 MHz) were recorded using CDCl₃ solutions, and chemical shifts are reported in parts per million relative to CHCl₃ (7.24 ppm for ¹H NMR and 77.0 ppm for ¹³C NMR) as an internal standard. High resolution (HRMS) mass spectra were obtained by using a quadrupole mass analyzer and electron impact ionization unless otherwise noted.

Synthesis of α -trimethylsilylamines 7-9 and 11.^{31a} Individual solutions of *N*-(trimethylsilyl)methyl-*N*-hexylamine (16 mmol) in MeCN (100 mL) containing K₂CO₃ (36 mmol) and alkyl halide (20 mmol of 1-hexyl bromide, 2-ethyl-1-hexyl iodide, and 2-methoxy-1-ethyl iodide, and ethyl 2-bromoacetate) were stirred for 12 h at room temperature and concentrated in vacuo to give residues that were in vacuo to afford residues, which were subjected to column chromatography (EtOAc: Hex = 1: 10) to yield 7 (85%), 8 (62%), 9 (68%) and 11 (80%).

Synthesis of α -trimethylsilylamine 10.^{31a} A 100 mL MeCN solution of *N*-(trimethylsilyl)methyl-*N*-hyroxyethoxyamine (10.5 mmol) containing K₂CO₃ (41.8 mmol) and 2-ethyl-1-hexyl bromide (15 mmol) was stirred for 12 h at room temperature and concentrated in vacuo

to give residue that was in vacuo to afford residues, which were subjected to column chromatography (EtOAc: Hex = 1: 5) to yield 10 (57%).

Synthesis of α -trimethylsilylamine 12.^{31a} A 100 mL MeCN solution of *N*,*N*-bisethylcarboxymethylamine (15.5 mmol) containing K₂CO₃ (41.8 mmol) and (iodomethyl)trimethylsilane (20 mmol) was stirred for 12 h at room temperature and concentrated in vacuo to give residue that was in vacuo to afford residues, which were subjected to column chromatography (EtOAc: Hex = 1: 8) to yield **10** (69%).

Synthesis of α -trimethylsilylamines 19 and 22-23.^{31a} Individual solutions of *N*-(trimethylsilyl)methyl-*N*-benzylamine (15.5 mmol) in MeCN (100 mL) containing K₂CO₃ (31 mmol) and alkyl halide (30 mmol of 1-hexyl bromide, 2-(2-methoxyethoxy)ethyl iodide, ethyl 2-bromopropionate) were stirred for 12 h at room temperature and concentrated in vacuo to give residues that were triturated with CH₂Cl₂. The triturates were dried and concentrated in vacuo to afford residues, which were subjected to column chromatography (EtOAc: Hex = 1: 8) to yield 19 (81%), 22 (90%) and 23 (44%).

Synthesis of α -trimethylsilylamine 20.^{31a} A 100 mL MeCN solution of *N*-5-hydroxypentyl-*N*-benzylamine (15.5 mmol) containing K₂CO₃ (41.8 mmol) and (iodomethyl)trimethylsilane (20 mmol) was stirred for 12 h at room temperature and concentrated in vacuo to give residue that was triturated with CH₂Cl₂. The triturate was dried and concentrated in vacuo to afford residues, which were subjected to column chromatography (EtOAc: Hex = 1: 8) to yield 20 (45%).

Synthesis of α -trimethylsilylamine 21.^{31a} A 100 mL MeCN solution of *N*-(trimethylsilyl)methyl-*N*-hydroxyethoxyamine (10.5 mmol) containing K₂CO₃ (41.8 mmol) and benzyl bromide (21 mmol) was stirred for 12 h at room temperature and concentrated in vacuo to give residue that was triturated with CH₂Cl₂. The triturate was dried and concentrated in vacuo to afford residues, which were subjected to column chromatography (EtOAc: Hex = 1: 5) to yield 21 (49%).

Synthesis of α -trimethylsilylamines 24-26.^{32b} Individual solutions of *N*-trimethylsilylmethyl-*N*-benzylamine derivatives (11 mmol) in MeCN (120 mL) containing K₂CO₃ (18 mmol) and methyl iodide (9.5 mmol) were stirred for 12 h at room temperature and concentrated in vacuo to give residues that were extracted with CH₂Cl₂. The extracts were dried and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (EtOAc/hexane = 1: 8) to yield corresponding amine substrates **24** (62%), **25** (76%) and **26** (75%).

Synthesis of α -trimethylsilylamines 27-29.^{32b} Individual solutions of *N*-(trimethylsilyl)methyl-*N*-*t*-butylamines (11 mmol) in MeCN (120 mL) containing K₂CO₃ (18 mmol) and *p*-substituted (H, Me, F) phenyl containing benzyl iodide (9 mmol) were stirred for 12 h at room temperature and concentrated in vacuo to give residues that were extracted with CH₂Cl₂. The extracts were dried and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (EtOAc/hexane = 1: 8) to yield **27** (89%), **28** (88%) and **29** (92%).

Synthesis of α -trimethylsilylamines 41-53.^{31b} Individual solutions of *N*-trimethylsilylmethyl-

N-benzylamine derivatives (13 mmol) in MeCN (120 mL) containing K_2CO_3 (20 mmol) and *p*-substituted benzyl halides (20 mmol) were stirred for 12 h at room temperature and concentrated in *vacuo* to give residues which were extracted with CH₂Cl₂. The extracts were dried and concentrated in *vacuo* to afford residues, which were subjected to silica gel column chromatography to yield **41** (72%), **42** (62%), **43** (68%), **44** (73%), **45** (47%), **46** (63%), **47** (87%), **48** (39%), **49** (96%), **50** (82%), **51** (71%), **52** (94%) and **53** (73%).

Synthesis of α -trimethylsilylamines 68-72.^{32a} Individual solutions of *N*-trimethylsilylmethyl-*N*-benzylamine derivatives (10 mmol) in MeCN (100 mL) containing K₂CO₃ (2.7 g, 19 mmol) and ethyl bromoacetate (12 mmol) were stirred for 12 h at room temperature and concentrated in *vacuo* to give residues which were triturated with CH₂Cl₂. The triturates were dried and concentrated in *vacuo* to afford residues, which were subjected to silica gel column chromatography (EtOAc: hexane = 1: 20) to yield **68** (66%), **69** (53%), **70** (70%), **71** (88%) and **72** (56 %).

Synthesis of α -trimethylsilylamines 78-80.³⁸ To individual solutions of *N*-methyl-*N*-phenylamine derivatives (9.3 mmol) in THF (30 mL) was added *n*-BuLi (12 mmol) at -78 °C. After stirred for 1 h, (iodomethyl)trimethylsilane (10.3 mmol) was added dropwise to the solutions and the resulting solutions were stirred for 5 h at room temperature. Then, the solutions were quenched by aq. NH₄Cl and triturated with CH₂Cl₂. The triturates were dried and concentrated in *vacuo* to afford residues, which were subjected to silica gel column chromatography (hexane) to yield **78** (75%), **79** (44%) and **80** (60%).

General procedure for photoreaction of C_{60} with tertiary α -trimethylsilylamines. Independent N₂-purged 10% EtOH-toluene (v/v) solutions (10 mL) containing C_{60} (0.17 mM) and α trimethylsilylamine (0.35 mM) in quartz tubes were simultaneously irradiated by using 20 W compact fluorescent lamp (CFL) in a merry-go-round apparatus for a certain period time. Each photolysate was subjected to HPLC analysis by comparison with authentic photoproducts. The results were summarized below.

amina	irradiation	conversion	product
amne	<mark>time (h)</mark>	<mark>(%)</mark>	<mark>(% yield)</mark>
7	<mark>5</mark>	<mark>100</mark>	13^{31a} (91)
<mark>8</mark>	<mark>5</mark>	<mark>88</mark>	14^{31a} (80)
<mark>9</mark>	<mark>5</mark>	<mark>86</mark>	15^{31a} (74)
<mark>10</mark>	<mark>5</mark>	<mark>91</mark>	16^{31a} (79)
<mark>11</mark>	<mark>5</mark>	<mark>68</mark>	17^{31a} (54)
12	<mark>5</mark>	<mark>35</mark>	18^{31a} (25)
	<mark>10</mark>	<mark>58</mark>	<mark>18</mark> (49)
	<mark>24</mark>	<mark>91</mark>	<mark>18</mark> (87)
<mark>19</mark>	5	<mark>85</mark>	30^{31a} (81)
<mark>20</mark>	<mark>5</mark>	<mark>85</mark>	31 ^{31a} (73)
<mark>21</mark>	<mark>5</mark>	<mark>82</mark>	32^{31a} (74)
<mark>22</mark>	<mark>5</mark>	<mark>82</mark>	33^{31a} (72)
<mark>23</mark>	5	<mark>75</mark>	34 ^{31a} (65)
<mark>24</mark>	<mark>5</mark>	<mark>99</mark>	35 ^{32b} (91)
25	<mark>5</mark>	<mark>99</mark>	<mark>36^{32b} (95)</mark>
<mark>26</mark>	<mark>5</mark>	<mark>91</mark>	37^{32b} (79)
27	<mark>5</mark>	<mark>86</mark>	38^{32b} (69)
<mark>28</mark>	<mark>5</mark>	<mark>89</mark>	39 ^{32b} (75)
<mark>29</mark>	<mark>5</mark>	<mark>52</mark>	40^{32b} (33)
<mark>41</mark>	<mark>5</mark>	<mark>65</mark>	54^{31b} (58)
<mark>42</mark>	<mark>5</mark>	<mark>95</mark>	55^{31b} (88)
<mark>43</mark>	<mark>5</mark>	<mark>95</mark>	56^{31b} (84)
<mark>44</mark>	<mark>5</mark>	<mark>98</mark>	57^{31b} (92)
<mark>45</mark>	<mark>5</mark>	<mark>100</mark>	58^{31b} (94)

46 5 30 59 ^{31b} (26) 47 5 17 60 ^{31b} (11)	
47 5 17 60 ^{31b} (11)	
48 5 59 61 ^{31b} (54)	
49 5 38 62 ^{31b} (22)	
50 5 42 63 ^{31b} (29)	
51 24 54 64 ^{31b} (41)	
52 24 28 65 ^{31b} (17)	
53 24 22 66 ^{31b} (14), 67 ³	^{1b} (4)
$\frac{5}{60} = \frac{5}{60} = \frac{73^{32a}}{73^{32a}} (56)$	
68 24 88 73 (86)	A Y
5 68 74^{32a} (66)	
24 90 74 (90)	
5 86 75 ^{32a} (72)	
24 94 75 (86)	
5 41 76 ^{32a} (30)	
24 64 76 (55)	
5 9 77 ^{32a} (2)	
24 47 77 (43)	

Photoreaction of C₆₀ with 78. In 10% EtOH-toluene solution: 5h irradiation, 65% conversion, HPLC analysis to yield 81 (57%); 7h irradiation, 76% conversion, HPLC analysis to yield 81 (60%); 10h irradiation, 87% conversion, HPLC analysis to yield 81 (75%). In 10% EtOH-ODCB solution: 5h irradiation, 46% conversion, HPLC analysis to yield 81 (22%); 10h irradiation, 71% conversion, HPLC analysis to yield 81 (34%). ¹H-NMR (CDCl₃) 3.52 (s, 3H), 5.34 (s, 2H), 6.49 (s, 1H), 6.78 (t, 1H, J = 7.2 Hz), 7.15-7.7.18 (m, 2H), 7.26-7.31 (m, 2H); ¹³C-NMR (CS₂+CDCl₃) 40.8, 57.8, 67.1, 67.5, 112.7, 118.0, 129.2, 135.2, 135.8, 139.8, 140.0, 141.3 (2H), 141.6 (2H), 141.8, 142.2, 142.8, 144.1, 144.2, 144.9, 145.0, 145.1, 145.3, 145.7, 145.8, 145.9, 146.0, 146.5, 146.6, 146.9, 148.9, 153.2, 153.9; HRMS (FAB) m/z 842.0966 (M+H, C₆₈H₁₂N require 842.0964).

Photoreaction of C₆₀ with 79. In 10% EtOH-toluene solution: 5h irradiation, 72% conversion,

HPLC analysis to yield **82** (59%); 7h irradiation, 81% conversion, HPLC analysis to yield **82** (72%); 10h irradiation, 89% conversion, HPLC analysis to yield **82** (79%). In 10% EtOH-ODCB solution: 5h irradiation, 52% conversion, HPLC analysis to yield **82** (25%); 10h irradiation, 72% conversion, HPLC analysis to yield **82** (35%). ¹H-NMR (CDCl₃) 2.3 (s, 3H), 3.5 (s, 3H), 5.3 (s, 2H), 6.51 (s, 1H), 7.09 (s, 4H); ¹³C-NMR (CS₂+CDCl₃) 20.4, 41.1, 57.9, 67.6, 67.7, 113.1, 126.8, 129.8, 135.3, 135.9, 139.9, 140.0, 141.4 (2H), 141.5, 141.7, 141.8, 141.9, 142.3, 142.9, 144.2, 144.3, 145.0, 145.1, 145.2, 145.5, 145.8, 145.9, 146.0, 146.1, 146.7 (2H), 147.0, 147.1, 153.4, 154.2; HRMS (FAB) m/z 856.1122 (M+H, C₆₉H₁₄N require 856.1121).

Photoreaction of C₆₀ with 80. In 10% EtOH-toluene solution: 5h irradiation, 44% conversion, HPLC analysis to yield 83 (32%); 7h irradiation, 54% conversion, HPLC analysis to yield 83 (46%); 10h irradiation, 61% conversion, HPLC analysis to yield 83 (49%). In 10% EtOH-ODCB solution: 5h irradiation, 29% conversion, HPLC analysis to yield 83 (16%); 10h irradiation, 60% conversion, HPLC analysis to yield 83 (36%). ¹H-NMR (CDCl₃) 3.49 (s, 3H), 5.29 (s, 2H), 6.47 (s, 1H), 6.95-7.01 (m 2H), 7.1-7.14 (m, 2H); ¹³C-NMR (CS₂+CDCl₃) 41.5, 58.0, 67.5, 68.0, 114.1 (d, $J_{C\cdot F} = 28.8$ Hz), 115.6 (d, $J_{C\cdot F} = 87.6$ Hz), 135.2, 135.9, 139.8, 140.1, 141.3, 141.4 (2H), 141.7 (2H), 141.8, 142.3, 142.7, 142.9, 144.1, 144.2, 145.0 (2H), 145.1, 145.4, 145.7 (2H), 145.8, 145.9, 146.0 (2H), 146.6 (2H), 146.9, 147.0, 153.1, 153.8, 155.7 (d, $J_{C\cdot F} = 949.2$ Hz); HRMS (FAB) m/z 860.0873 (M+H, C₆₈H₁₁F require 860.0870).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://

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