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SYNTHESIS OF FUNCTIONALIZED FULLERENES BY PHOTOADDITION OF *N*-α-TRIMETHYLSILYL-*N*-CARBOXYMETHYL-*N*-BENZYLAMINES TO C_{60}

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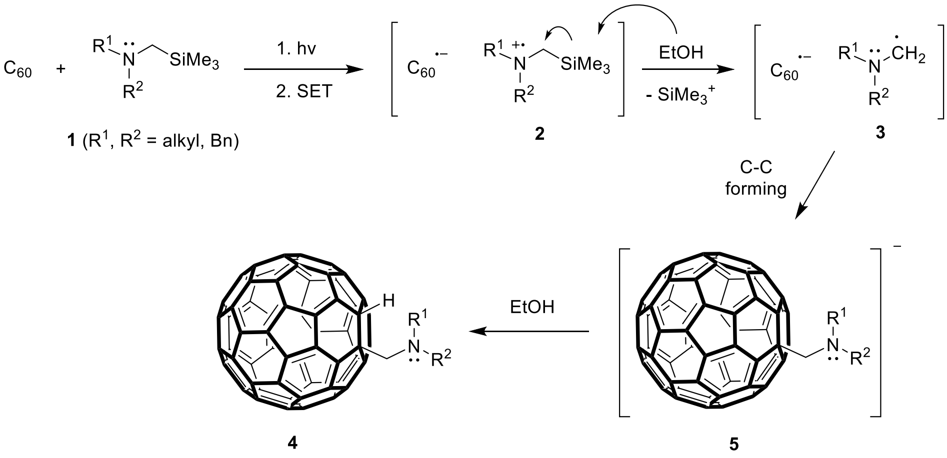
Abstract – Photoaddition reactions of fullerene C_{60} with *N*-α-trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines, which contain various para-substituents, were explored in order to evaluate factors governing efficiencies of this potentially useful method for preparing functionalized fullerene derivatives. Observations made in this study show that two reaction pathways are followed in these photoreactions. The first involves initial formation of α-trimethylsilyl-aminium radicals and the C_{60} anion radical by SET from the amines to the triplet excited state of C_{60}. This step is followed by desilylation to produce α-amino radicals. Coupling of these radicals with the anion radical of C_{60} followed by protonation or with the hydrofullerene radical generated by protonation of the anion radical of C_{60} then produces aminomethyl-1,2-dihydrofullerenes. When limited amounts of $^3O_2$ are present in the reaction medium, fulleropyrrolidines are generated in low yields by a competitive pathway involving formation of singlet oxygen, which undergoes sequential H-atom abstractions from the *N*-α-trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines to produce azomethine ylide intermediates. Dipolar cyloaddition of the ylides to C_{60} then produces fulleropyrrolidines. Photoreactions of the C_{60} and the amines in the presence of high $^3O_2$ concentrations exclusively produce fulleropyrrolidine. In addition, the results show that photoreactions of non-silicon substituted, *N*-methyl-*N*-carboxymethyl-*N*-benzylamines with C_{60} form fulleropyrrolidines

independent of the concentration of $^3O_2$ present in the media.

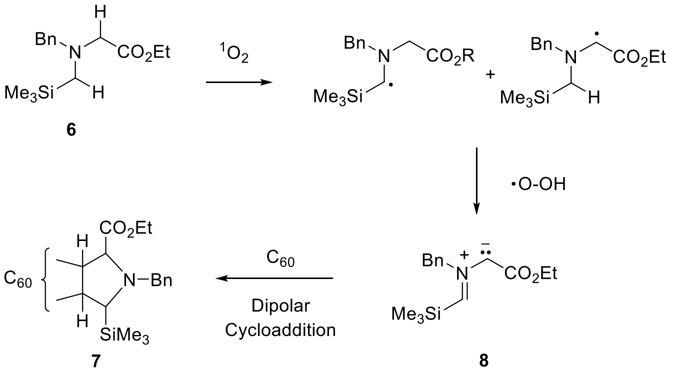
INTRODUCTION

Thermal and photochemical reactions of fullerenes have been broadly explored in order to develop methods to prepare novel substituted fullerenes that can potentially serve as unique electron accepting materials.[1-6] The most common approaches employed for the preparation of these substances involve 1,3-dipolar cycloaddition,[7-9] cyclopropanation[10,11] and radical coupling reactions.[12,13] In addition, single electron transfer (SET) promoted photochemical reactions between fullerene and electron donating substances[14-17] also serve as useful methods for synthesizing substituted fullerenes. These reactions are driven by the high electron affinities[18] and relatively high reduction potential ($^3E_{red}(C_{60})$ = 1.14 V vs SCE)[19] of the triplet excited state of C_{60}. Observations made in earlier studies[17] show that SET promoted photoaddition reactions take place between tertiary amines and fullerene to produce aminomethyl substituted 1,2-dihydrofullerene derivatives. Moreover, when α-trimethylsilyl substituted tertiary amines (**1**, Scheme 1) are used as electron donor substrates, photoaddition reactions with C_{60} generate aminomethyl-1,2-dihydrofullerenes **4** in a highly efficient manner. The mechanistic pathway operating in these photoaddition reactions involves initial SET from the amine to the excited state of fullerene to form the corresponding amine radical cations **2** (*i.e.*, aminium radicals) and fullerene radical anion. Subsequent desilylation of the formed aminium radical occurs to produce an α-amino radical **3** that couples with the fullerene radical anion (or the corresponding protonated hydrofullerenyl radical) to generate the anion precursor **5** of the fullerene-adduct (or directly the fullerene-adduct).



Scheme 1

Recently, we observed that the efficiencies of photoaddition reactions of amines with C_{60} are highly dependent on the electronic nature of the amine substrates.[17] For instance, photoreactions of deoxygenated 10% EtOH-toluene solutions containing C_{60} and *N*-α-trimethylsilyl-*N*,*N*-dibenzylamines that contains electron donating substituents (*e.g.*, Me, OMe) on the phenyl rings, take place efficiently to form the corresponding aminomethyl substituted 1,2-dihydrofullerene adducts in modestly high yields. In contrast, photoreactions of *N*-α-trimethylsilyl-*N*,*N*-dibenzylamines, which contain electron withdrawing phenyl substituents (*i.e.*, F, CF_3), require longer irradiation times and produce 1,2-adducts in low yields.[17b] In addition, photoreactions of deoxygenated solutions of C_{60} and benzylamines, which contain electron withdrawing *N*-carboxymethyl groups (*e.g.* **6** in Scheme 2), not only require longer irradiation times and they produce either low yields of aminomethyl-1,2-dihydrofullerene adducts (under N_2 purged 10% EtOH-toluene) or fulleropyrrolidines (*e.g.* **7** in Scheme 2) exclusively (oxygenated 10% EtOH-toluene).[17a] These results show that photoreactions of *N*-carboxymethyl substituted amines in the presence of molecular oxygen take place via a pathway that involves singlet molecular oxygen ($^1O_2$) mediated generation of azomethine ylides (*e.g.* **8** in Scheme 2), reactive intermediates that undergo 1,3-dipolar cyloadditions to fullerene.[7-9,17]

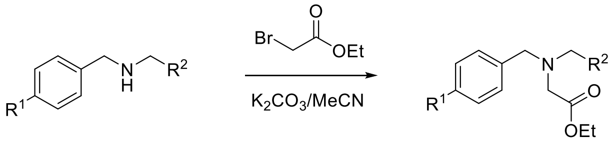


Scheme 2

The unique effects of *N*-carboxymethyl substituents on the nature of photochemical reactions of amines with C_{60} and substituent effects on efficiencies of SET promoted photochemical reactions of C_{60} with tertiary *N*-α-trimethylsilyl-*N*-benzylamines are interesting in that they help guide the design of methods to prepare variously functionalized fullerenes. To gain more information about the preparative utility of these processes, an investigation was designed to explore photochemical reactions of fullerene C_{60} with electron donating and withdrawing *para*-phenyl substituted *N*-carboxymethyl-*N*-α-trimethylsilyl-*N*-benzylamines and analogs not containing trimethylsilyl groups. The major goal of this effort was to elucidate if and how the electronic nature of the amine substituents, the presence of α-trimethylsilyl groups and photoreaction conditions affect the efficiencies and nature of these processes. Observation made in this study, summarized below, show that two competitive photochemical pathways are followed in these systems, one involving formation of aminium radicals by SET from the amine to the triplet excited state of C_{60} followed by desilylation leading to formation of aminomethyl-1,2-dihydrofullerenes and the other involving formation of azomethine ylides by singlet oxygen mediated H-atom abstraction from amine followed by cycloaddition to lead to formation of fulleropyrrolidine adducts. The relative importance of these pathways depends on both the nature of phenyl ring substituents, the presence or absence of α-trimethylsilyl groups and high concentrations of $^3O_2$.

RESULTS AND DISCUSSION

Synthesis of *N*-α-trimethylsilyl-N-carboxymethyl-*N*-benzylamines. The *N*-α-trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines, **6** and **19-22**, utilized in this study were readily prepared by using substitution reactions between available *N*-α-trimethylsilyl-*N*-benzylamines **9-13** and ethyl bromoacetate in the presence of K_2CO_3 in MeCN (Scheme 3). In addition, in order to elucidate the effect of trimethylsilyl groups on these photoreactions, non-trimethylsilyl containing benzylamine analogs, **23-27**, were also prepared using similar processes (Scheme 3).

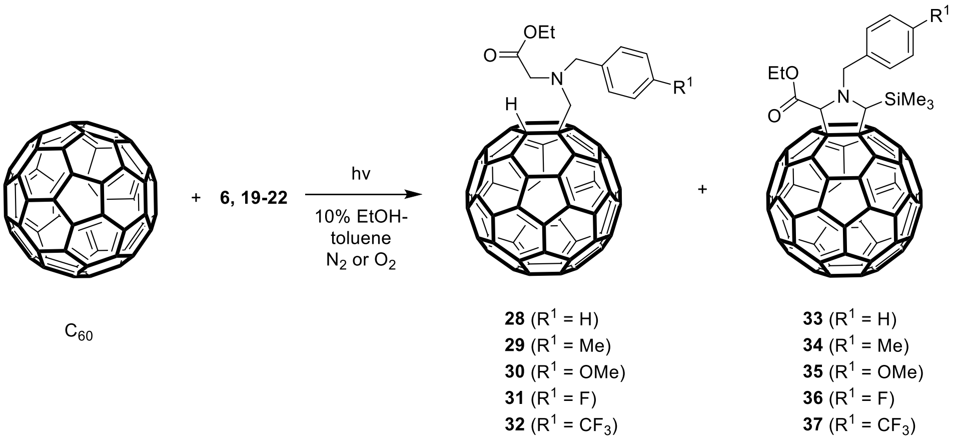


Substrates	R_1	R_2	Benzylamines
9	H	$SiMe_3$	**6**
10	Me	$SiMe_3$	**19**
11	OMe	$SiMe_3$	**20**
12	F	$SiMe_3$	**21**
13	CF_3	$SiMe_3$	**22**
14	H	H	**23**
15	Me	H	**24**
16	OMe	H	**25**
17	F	H	**26**
18	CF_3	H	**27**

Scheme 3

Photoreactions of C_{60} with *N*-α-trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines and non-trimethylsilyl containing counterparts. The yields and product distributions of photoreactions of C_{60} with the silyl/non-silyl benzylamines **6** and **19-22**, which have various substituents at *para* position of the phenyl rings, were determined. All photochemical reactions were carried out by irradiating (450 W Hanovia medium pressure mercury lamp and flint glass filter $\lambda > 300$ nm) 10% EtOH-toluene solutions containing C_{60} (0.28 mmol) and benzylamines (0.59 mmol). The photolysates were triturated with $CHCl_3$ to recover C_{60} and the triturates were concentrated in vacuo to generate residues, which were subjected to silica gel column chromatography to obtain pure photoproducts. Structural assignments to the photoproducts were made based on analysis of ^1H and ^{13}C NMR, and UV-visible spectra, and by using HRMS (see Experimental and Supporting data), as well as by comparing the data to those previously reported[17a] for related compounds.

The results show that photoreactions of C_{60} with α-trimethylsilyl containing benzylamines **6**, and **19-22**, carried out on N_2 purged solutions, generate two types of photoproducts, including aminomethyl-1,2-dihydrofullerenes **28-32** and fulleropyrrolidines **33-37** (Scheme 4 and Table 1). Specifically, 1 h irradiation of solutions of C_{60} and amines **19** and **20** (0.59 mmol) possessing electron donating substituted (Me and OMe) phenyl rings as well as the unsubstituted analog **6**, brings about high conversion of C_{60} and modestly high yielding formation of the corresponding aminomethyl-1,2-dihydrofullerenes **28-30** predominantly, along with low yielding generation of fulleropyrrolidines **33-35** (Table 1, entries 1-3). In contrast, photoreactions of C_{60} with electron withdrawing group (F and CF_3) substituted benzylamines **21** and **22** (entries 4-5, Table 1) require longer irradiation times to bring about high C_{60} conversions. Significantly, these reactions occur in lower yields and they generate fulleropyrrolidnes **36** and **37** in relatively larger amounts. Furthermore, the results of previous studies,[17a] showing that aminomethyl-1,2-dihydrofullerene **28**[17a] is not converted to fulleropyrrolidine **33**[17a] upon prolonged photoirradiation, demonstrate that two types of adducts formed in these photoreactions arise by independent pathways.



Scheme 4

Table 1. Products and yields of photoaddition reactions of N_2 purged 10% EtOH-toluene solutions containing C_{60} and **6** and **19-22**.

Entry	Amine	Irradiation Time (h)	Conversion (%)^b	Product (%)^c
1	**6**	1	95	**28** (68), **33** (10)
2	**19**	1	100	**29** (69), **34** (2)
3	**20**	1	100	**30** (70), **35** (3)
4	**21**	3	89	**31** (57), **36** (10)
5	**22**	3	77	**32** (40), **37** (10)

6[d]	**6**	1	100	**28** (76), **33** (12)

[a]α-Silylamines (0.56 mmol) and C_{60} (0.28 mmol) in 220 mL of 10% EtOH-toluene.

[b]Conversions determined based on recovered C_{60}. [c]Yields of isolated products. [d]Previous result (ref. 17a)

We postulated that the small yet finite amounts of O_2, which are present in photoreaction mixtures that are purged with nitrogen, are responsible for formation of the fulleropyrrolidine adducts (see below). In order to explore this proposal, photoreaction of C_{60} with α-trimethylsilyl benzylamine **6** was carried out using a completely deoxygenated solution (by using a freeze-pump-thaw method). Specifically, a 10% EtOH-toluene solution (7 mL) containing C_{60} (1.74×10^{-4} M) and benzylamine **6** (3.46×10^{-4} M) was added to Schlenk flask and then subjected to a repetitive freeze-pump-thaw degassing process to remove O_2 completely. Irradiation of this solution under a N_2 atmosphere was carried out for 2.5 h and the photolysate was analyzed by using HPLC. Importantly, analysis of chromatogram showed that the aminomethyl-1,2-difullerene adduct **28** (retention time 6.3 min) is produced exclusively and that none of the fulleropyrrolidine **33** is formed (retention time 11.9 min) (See Supporting Data).

The effect of molecular oxygen on these processes was explored next. The results show that irradiation of oxygenated 10% EtOH-toluene solutions containing C_{60} and benzylamines **6**, **19**-**22** under the same conditions as described above leads to exclusive formation of the corresponding fulleropyrrolidines **33**-**37** in modestly high yields (Table 2). Longer irradiation times are required for these photoreactions regardless of the nature of the benzylamine substituent.

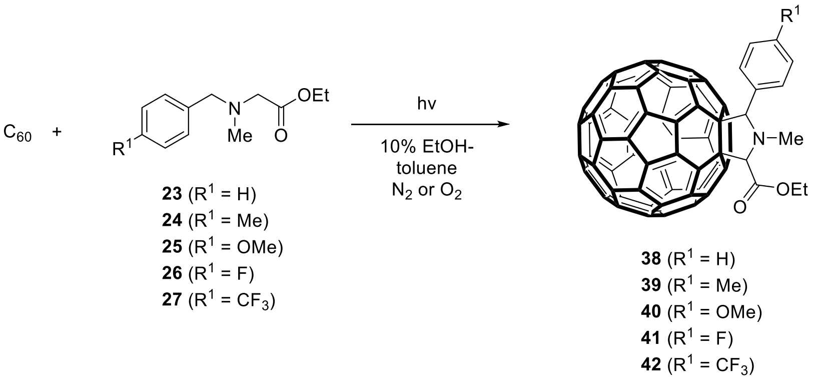
Table 2. Products and yields of photoaddition reactions of O_2 purged 10% EtOH-toluene solutions containing C_{60} and **6** and **19**-**22**.

Entry	Amine	Irradiation Time (h)	Conversion (%)[b]	Product (%)[c]
1	**6**	2	89	**33** (57)
2	**19**	2	90	**34** (56)
3	**20**	2	90	**35** (57)
4	**21**	2	68	**36** (41)
5	**21**	4	85	**36** (56)
6	**22**	2	56	**37** (32)
7	**22**	4	81	**37** (51)
8[d]	**6**	2	91	**38** (70)

[a]α-Silylamines (0.56 mmol) and C_{60} (0.28 mmol) in 220 mL of 10% EtOH-toluene.

[b]Conversions determined based on recovered C_{60}. [c]Yields of isolated products. [d]Previous result (ref. 17a)

To investigate the effect of the trimethylsilyl group in the amine substrates on the nature and efficiencies of the photoreaction, nitrogen or oxygen purged 10% EtOH-toluene solutions solutions of C_{60} and the non-trimethylsilyl containing benzylamines **23-27** were irradiated. The results (Scheme 5 and Tables 3 and 4) show that these photoreactions, taking place under both conditions, require longer irradiation times and yield fulleropyrrolidine adducts **38-42** exclusively.



Scheme 5

Table 3. Products and yields of photoaddition reactions of N_2 purged 10% EtOH-toluene solutions containing C_{60} and **23-27**.

Entry	Amine	Irradiation Time (h)	Conversion (%)[b]	Product (%)[c]
1	**23**	2	59	**38** (37)
2	**24**	2	60	**39** (35)
3	**25**	2	60	**40** (38)
4	**26**	5	76	**41** (40)
5	**27**	5	72	**42** (42)
6[d]	**23**	2	55	**38** (30)

[a]Amines (0.56 mmol) and C_{60} (0.28 mmol) in 220 mL of 10% EtOH-toluene.

[b]Conversions determined based on recovered C_{60}. [c]Yields of isolated products. [d]Previous result (ref. 17a)

Table 4. Products and yields of photoaddition reactions of O_2 purged 10% EtOH-toluene solutions containing C_{60} and **23-27**.

Entry	Amine	Irradiation Time (h)	Conversion (%)[b]	Product (%)[c]
1	**23**	5	66	**38** (35)
2	**24**	5	67	**39** (35)

3	**25**	5	70	**40** (42)
4	**26**	5	60	**41** (32)
5	**27**	5	57	**42** (32)
6	**27**	8	85	**42** (50)

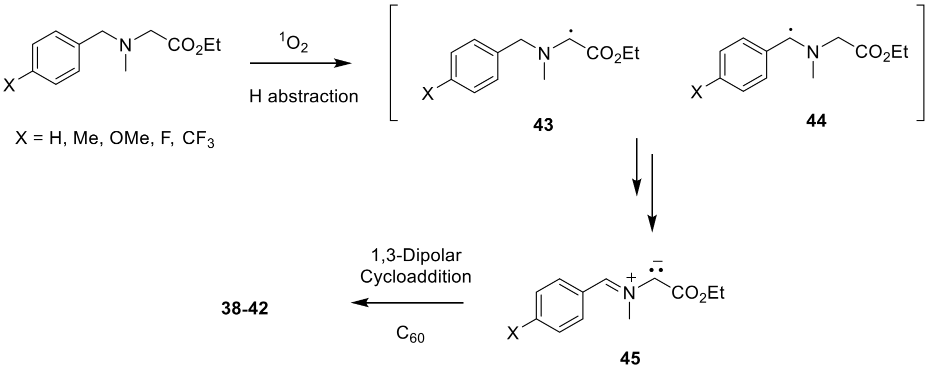
[a]Amines (0.56 mmol) and C_{60} (0.28 mmol) in 220 mL of 10% EtOH-toluene.

[b]Conversions determined based on recovered C_{60}. [c]Yields of isolated products.

Effect of amine substituents and structures on photoaddition reaction efficiencies. As can be seen from viewing the data given in Tables 1 and 2, the electronic nature of the *p*-phenyl substituent in *N*-α-trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines plays a surprisingly important role in governing efficiencies of photoaddition reactions with C_{60}. The results show that photoaddition reactions of non- and electron-donating group substituted amine substrates take place more efficiently than those of the electron withdrawing group substituted analogs. Moreover, it is clear that two independent processes occur when solutions of C_{60} and the amines are irradiated. One produces aminomethyl-1,2-dihydrofullerenes **28-32** and the other fulleropyrrolidines **33-37**. Consequently, two competing, mechanistically different pathways are followed in these reactions. The route leading to 1,2-dihydrofullerenes **28-32** is almost certainly initiated by SET from the amines to the triplet excited state of C_{60}, produced by direct excitation followed by rapid intersystem crossing.[20] Because the rates of SET from all benzylamines to the triplet excited state of C_{60} are predicted to be near equal to that of diffusion control,[17a,19] differences in the efficiencies of 1,2-dihydrofullerene formation need to be associated with the rates of EtOH promoted desilylation of intermediate aminium radicals which competes with energy wasting/efficiency diminishing back SET from the aminium radicals to the anion radical of C_{60}. Alternatively, the substituents could influence the rates of α-amino radical coupling with the anion radical of C_{60} or its protonated conjugate acid. Frankly, as discussed earlier,[17b] both of these possibilities are difficult to understand because of the remoteness of the location of the substituents relative to the centers participating in aminium radical desilylation and amino radical coupling.

In contrast, the pathway followed in fulleropyrrolidine forming photoreactions of *N*-α-trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines is more firmly understood. Specifically, this process takes place via a route that involves singlet oxygen mediated formation of azomethine ylides that then undergo familiar[7-9] dipolar cycloadditions to C_{60} (Scheme 2). As suggested by Foote[20a] earlier, the triplet excited state of C_{60} should undergo energy transfer to $^3O_2$ to form $^1O_2$ and ground-state C_{60}, a process that competes with or dominates over SET from the amine depending upon on the concentration of $^3O_2$. In the manner described by Foote,[20a] $^1O_2$ then reacts with the *N*-carboxymethyl-*N*-α-trimethylsilyl-*N*-benzylamine through sequential α-hydrogen atom abstractions to form the key azomethine ylide (Scheme 2). This proposal is helpful in explaining why fulleropyrolidines are formed in increased amounts relative to the aminomethyl-1,2-dihydrofullerenes in photoreactions of electron withdrawing group substituted substrates in deoxygenated solutions. In these cases, $^1O_2$ is produced from small amounts of $^3O_2$ present under these conditions. Owing to the fact that aminomethyl-1,2-dihydrofullerene production is highly inefficient in these cases, fullerpyrrolidine formation would become more competitive.

Another observation made in this effort has both preparative and mechanistic significance. As can be seen from viewing the data in Tables 3 and 4, photoreactions of C_{60} with non-trimethylsilyl substituted benzylamines require much longer irradiation times to bring about high conversions of C_{60}. In addition, these processes generate fulleropyrrolidines **38-42** exclusively. Of equal interest is the structural nature of generated fulleropyrrolidines. As discussed above, azomethine ylide intermediates formed in photoreactions of the *N*-α-trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines involving the intermediacy of $^1O_2$ arise by H-atom abstractions pathways. The nature of the cycloadducts dictates that loss of hydrogens in these processes takes place exclusively from the trimethylsilyl and alkoxycarbonyl substituted α-carbons and not the benzylic position of the amines (see Scheme 2). However, in $^1O_2$ promoted reactions of the non-trimethylsilyl substituted amines H-atom abstractions occurs at the amine alkoxycarbonyl and aryl substituted α-centers exclusively to generate α-amino radicals **43** and **44** and, eventually, azomethine ylide **45** (Scheme 6).



Scheme 6

In this study, photochemical reactions of fullerene C_{60} with *N*-α-trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines that contain various substituents at *para* position on the phenyl ring were carried out. Observation made in this study show that two competitive photochemical pathways are followed in these reactions, one involving formation of aminium radicals by SET from the amine to the triplet excited state of C_{60} followed by desilylation leading to formation of aminomethyl-1,2-dihydrofullerenes and the other involving formation of azomethine ylides by singlet oxygen mediated H-atom abstraction from amine followed by cycloaddition to form fulleropyrrolidines.

The relative importance of these pathways depends on both the nature of phenyl ring substituents, the presence or absence of α-trimethylsilyl groups and the concentration of $^3O_2$.

EXPERIMENTAL

General Procedure ^{1}H and ^{13}C NMR spectra were recorded on $CDCl_3$ solutions and chemical shifts are reported in parts per million 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 using a quadrupole mass analyzer and electron impact ionization unless otherwise noted. All starting materials used in the photoreactions derived from commercial sources. All new compounds described were isolated as oils in >90% purity (by NMR analysis) unless noted otherwise.

***N*–α-Trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines 19-22.** Individual solutions of *N*-α-trimethylsilyl-*N*-benzylamines **10-13** (2.0 g, 9.6 mmol of **10**, 2.0 g, 9 mmol of **11**, 2.1 g, 9.9 mmol of **12**, and 1.5 g, 5.7 mmol of **13**) in MeON (100 mL) containing K_2CO_3 (2.7 g, 19 mmol) and ethyl bromoacetate (1.8 g for **10**, 2.5 g for **11**, 4.3 g for **12**, and 1.2 g for **13**) were stirred for 12 h at room temperature and concentrated in vacuo to give residues which 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: 20) to yield **19** (1.5 g, 53%), **20** (1.9 g, 70%), **21** (2.6 g, 88%), and **22** (1.2 g, 56%).

19: ^{1}H-NMR 0.06 (s, 9H), 1.25 (t, 3H, J = 7.2 Hz), 2.20 (s, 2H), 2.31 (s, 3H), 3.23 (s, 2H), 3.72 (s, 2H), 4.13 (q, 2H, J = 7.2 Hz), 7.09 (d, 2H, J = 7.8 Hz), 7.22 (d, 2H, J = 7.8 Hz); ^{13}C-NMR -1.7, 14.0, 20.8, 45.3, 56.4, 59.7, 60.8, 128.6, 129.5, 135.6, 136.3, 170.8; HRMS (EI) *m/z* 293.1812 (M, $C_{16}H_{27}NO_2Si$ requires 293.1811).

20: ^{1}H-NMR 0.05 (s, 9H), 1.24 (t, 3H, J = 7.2 Hz), 2.17 (s, 2H), 3.21 (s, 2H), 3.67 (s, 2H), 3.77 (s, 3H), 4.12 (q, 2H, J = 7.2 Hz), 6.82 (d, 2H, J = 8.7 Hz), 7.24 (d, 2H, J = 8.7 Hz); ^{13}C-NMR -1.5, 14.3, 45.5, 55.1, 56.8, 59.9, 60.7, 113.5, 129.9, 131.4, 158.6, 171.4; HRMS (EI) *m/z* 309.1757 (M, $C_{16}H_{27}NO_3Si$ requires 309.1760).

21: ^{1}H-NMR 0.03 (s, 9H), 1.24 (t, 3H, J = 7.2 Hz), 2.15 (s, 2H), 3.22 (s, 2H), 3.69 (s, 2H), 4.12 (q, 2H, J = 7.2 Hz), 6.97 (t, 2H, J = 8.7 Hz), 7.26-7.31 (m, 2H); ^{13}C-NMR -1.7, 14.1, 45.3, 56.8, 59.8, 60.6, 114.8 (d, J = 83.7 Hz), 130.1 (d, J = 31.5 Hz), 135.1 (d, J = 12 Hz), 161.8 (d, J = 972.3 Hz), 171.7; HRMS (EI) m/z 297.1562 (M, $C_{15}H_{24}FNO_2Si$ requires 297.1560).

22: ^{1}H-NMR 0.04 (s, 9H), 1.25 (t, 3H, J = 7.2 Hz), 2.19 (s, 2H), 3.26 (s, 2H), 3.82 (s, 2H), 4.14 (q, 2H, J = 7.2 Hz), 7.46 (d, 2H, J = 8.1 Hz), 7.54 (d, 2H, J = 8.1 Hz); ^{13}C-NMR -1.7, 14.2, 45.5, 56.9, 60.1, 61.1, 125.1 (q, J = 14.7 Hz), 128.8, 143.7, 171.0; HRMS (EI) *m/z* 347.1527 (M, $C_{16}H_{24}F_3NO_2Si$ requires 347.1528).

Photoreactions of C_{60} with Amines. Preparative photochemical reactions were conducted using an apparatus consisting of a 450 W Hanovia medium vapor pressure mercury lamp surrounded by a glass filter (>300 nm) in a water-cooled quartz immersion well surrounded by the solution being irradiated, consisting of 10% EtOH-toluene solution (220 mL) containing C_{60} (0.28 mmol) and the amine (0.56 mmol). The solution being irradiated was purged with either nitrogen or oxygen before and during irradiations for the time periods given below. The photolysates were triturated with $CHCl_3$ to recover C_{60} and the triturates were concentrated in vacuo to generate residues, which were subjected to silica gel column chromatography to generate the pure photoproducts.

Photoreaction of C_{60} with Amine 6. Formation of 28 and 33. N_2 saturated condition. 1 h irradiation, 95% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **28** (175 mg, 68%) and **33** (27 mg, 10%). O_2 saturated condition. 2 h irradiation, 88% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **33** (157 mg, 57%).

Photoreaction of C_{60}+19. Formation of 29 and 34. N_2 saturated condition. 1 h irradiation, 100% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **29** (179 mg, 69%) and **34** (7 mg, 2%). O_2 saturated condition. 2 h irradiation, 90% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **34** (158 mg, 56%).

29: ^{1}H-NMR 1.35 (t, 3H, *J* = 7.2 Hz), 2.36 (s, 3H), 3.90 (s, 2H), 4.28 (q, 2H, *J* = 7.2 Hz), 4.48 (s, 2H), 4.74 (s, 2H), 6.99 (s, 1H), 7.17 (d, 2H, *J* = 7.8 Hz), 7.48 (d, 2H, *J* = 7.8 Hz); ^{13}C-NMR ($CDCl_3$+CS_2) 14.4, 21.2, 55.3, 57.9, 59.4, 60.4, 67.1, 68.2, 129.1, 129.2, 135.0, 135.8, 135.9, 137.0, 139.9, 140.1, 141.4 (2C), 141.6, 141.7, 141.8, 142.1, 142.3 (2C), 143.0, 144.3, 144.5, 145.1 (3C), 145.2, 145.6, 145.9 (2C), 146.1 (2C), 146.5, 147.0 (2C), 147.1, 154.3, 154.6, 170.7; HRMS (FAB) *m/z* 942.1491 (M+1, $C_{73}H_{20}NO_2$ requires 942.1494).

34: ^{1}H-NMR 0.51 (s, 9H), 1.17 (t, 3H, *J* = 7.2 Hz), 2.40 (s, 3H), 4.17 (q, 1H, J = 7.2 Hz), 4.28 (q, 1H, *J* = 7.2 Hz), 4.53 (d, 1H, *J* = 13.2 Hz), 5.30 (d, 1H, *J* = 13.2 Hz), 5.37 (s, 1H), 5.43 (s, 1H), 7.23 (d, 2H, *J* = 7.8 Hz), 7.50 (d, 2H, *J* = 7.8 Hz); ^{13}C-NMR ($CDCl_3$+CS_2) 0.7, 14.1, 21.2, 55.7, 60.6, 69.8, 76.2, 77.2, 77.8, 128.5, 129.4, 134.7, 135.5, 135.6, 135.7, 136.0, 137.1, 139.1, 139.3, 139.4, 140.0, 141.5, 141.6, 141.7, 141.8, 141.9, 142.0 (3C), 142.1 (2C), 142.3, 142.5 (3C), 142.6, 142.9, 143.0, 144.1, 144.2, 144.3, 144.4, 144.9 (2C), 145.0 (2C), 145.1 (3C), 145.3, 145.4, 145.7, 145.8 (2C), 145.9 (2C), 146.0, 146.1, 146.2, 146.5, 146.8 (2C), 152.6, 154.8, 156.4, 157.1, 170.2; HRMS (FAB) *m/z* 1012.1729 (M+1, $C_{76}H_{26}NO_2Si$ requires 1012.1733).

Photoreaction of C_{60}+20. Formation of 30 and 35. N_2 saturated condition. 1 h irradiation, 100% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **30** (186 mg, 70%) and **35** (8 mg, 3%). O_2 saturated condition. 2 h irradiation, 90% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **35** (163 mg, 57%).

30: ^{1}H-NMR 1.36 (t, 3H, *J* = 6.9 Hz), 3.80 (s, 3H), 3.90 (s, 2H), 4.29 (q, 2H, *J* = 6.9 Hz), 4.46 (s, 2H), 4.74 (s, 2H), 6.90 (d, 2H, *J* = 8.1 Hz), 6.97 (s, 1H), 7.50 (d, 2H, *J* = 8.1 Hz); ^{13}C-NMR ($CDCl_3$+CS_2) 14.4, 55.0, 55.5, 58.0, 59.1, 60.5, 67.3, 68.2, 113.9, 130.1, 130.4, 135.9, 136.0, 139.9, 140.1, 141.5 (2C), 141.7, 141.8, 141.9, 142.2, 142.4 (2C), 143.1, 144.4, 145.2 (3C), 145.3, 145.7, 146.0 (2C), 146.2 (2C), 146.7, 147.1 (2C), 147.2, 154.3, 154.7, 159.0, 171.1; HRMS (FAB) *m/z* 958.1447 (M+1, $C_{73}H_{20}NO_3$ requires 958.1443).

35: ^{1}H-NMR 0.50 (s, 9H), 1.16 (t, 3H, *J* = 7.2 Hz), 3.84 (s, 3H), 4.19 (q, 1H, *J* = 7.2 Hz), 4.29 (q, 1H, *J* = 7.2 Hz), 4.50 (d, 1H, *J* = 12.9 Hz), 5.19 (d, 1H, *J* = 12.9 Hz), 5.36 (s, 1H), 5.44 (s, 1H), 6.96 (d, 2H, *J* = 8.7 Hz), 7.53 (d, 2H, *J* = 8.7 Hz); ^{13}C-NMR ($CDCl_3$+CS_2) 0.7, 14.1, 55.0, 55.4, 60.7, 69.8, 76.1, 77.5, 77.8, 114.1, 129.7, 130.7, 134.8, 135.5, 135.6, 136.0, 139.1, 139.3, 139.5, 140.1, 141.6 (2C), 141.7, 141.8, 141.9, 142.0 (2C), 142.1 (2C), 142.2, 142.3, 142.5 (2C), 142.6 (2C), 142.9, 143.0, 144.1, 144.3 (2C), 144.4, 144.9, 145.0 (2C), 145.1 (3C), 145.4, 145.7, 145.8 (2C), 145.9, 146.0 (2C), 146.1, 146.3, 146.5, 146.8, 146.9152.7, 154.9, 156.4, 157.2, 159.1, 170.3; HRMS (FAB) *m/z* 10.28.1685 (M+1, $C_{76}H_{26}NO_3Si$ requires 1028.1682).

Photoreaction of C_{60}+21. Formation of 31 and 36. N_2 saturated condition. 3 h irradiation, 89% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **31** (151 mg, 57%) and **36** (29 mg, 10%). O_2 saturated condition. 2 h irradiation, 68% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **36** (116 mg, 41%); 4 h irradiation, 85% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **36** (147 mg, 56%).

31: ^{1}H-NMR 1.37 (t, 3H, *J* = 7.2 Hz), 3.89 (s, 2H), 4.29 (q, 2H, *J* = 7.2 Hz), 4.50 (s, 2H), 4.75 (s, 2H), 6.96 (s, 1H), 7.05 (t, 2H, *J* = 8.4 Hz), 7.57 (t, 2H, *J* = 8.4 Hz); ^{13}C-NMR ($CDCl_3$+CS_2) 14.3, 55.2, 57.8, 58.8, 60.5, 67.0, 68.3, 115.3 (d, *J* = 84 Hz), 130.6 (d, *J* = 30.9 Hz), 133.7 (d, *J* = 12.9 Hz), 135.8 (d, *J* = 18 Hz), 139.8, 140.1, 141.4 (2C), 141.5, 141.7, 141.8, 142.0, 142.3 (2C), 143.0, 144.2, 144.4, 145.1, 145.2, 145.5, 145.9 (2C), 146.1 (2C), 146.4, 146.9, 147.1, 154.0, 154.3, 162.0 (d, *J* = 982.2 Hz), 170.4; HRMS (FAB) *m/z* 946.1245 (M+1, $C_{72}H_{17}NO_2F$ requires 946.1243).

36: ^{1}H-NMR 0.51 (s, 9H), 1.18 (t, 3H, *J* = 7.2 Hz), 4.20 (q, 1H, *J* = 7.2 Hz), 4.27 (q, 1H, *J* = 7.2 Hz), 4.55 (d, 1H, *J* = 13.2 Hz), 5.23 (d, 1H, *J* = 13.2 Hz), 5.37 (s, 1H), 5.40 (s, 1H), 7.13 (t, 2H, *J* = 8.7 Hz), 7.58-7.63 (m, 2H); ^{13}C-NMR ($CDCl_3$+CS_2) 0.6, 14.1, 55.2, 60.6, 69.6, 76.1, 77.3, 77.6, 115.5 (d, *J* = 84.9 Hz), 129.9 (d, *J* = 31.2 Hz), 134.3 (d, *J* = 12 Hz), 134.6, 135.4 (2C), 136.0, 139.1, 139.3, 139.4, 140.0, 141.5 (2C), 141.6 (2C), 141.7, 141.8, 141.9 (2C), 142.0 (2C), 142.2, 142.4 (2C), 142.5 (2C), 142.8, 142.9, 144.0, 144.1, 144.2, 144.3, 144.7, 144.9 (2C), 145.0 (4C), 145.2, 145.6, 145.7, 145.9 (2C), 146.0, 146.1, 146.3, 146.7, 146.8, 152.4, 154.5, 156.1, 156.9, 162.1 (d, *J* = 980.1 Hz), 169.8; HRMS (FAB) *m/z* 1016.1485 (M+1, $C_{75}H_{23}FNO_2Si$ requires 1016.1482).

Photoreaction of C_{60}+22. Formation of 32 and 37. N_2 saturated condition. 3 h irradiation, 77% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **32** (112 mg, 40%) and **37** (30 mg, 10%). O_2 saturated condition. 2 h irradiation, 56% conversion, column chromatography (CS_2:hexane = 1: 1) to yield **37** (96 mg, 32%); 4 h irradiation, 81% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **37** (141 mg, 51%).

32: ^{1}H-NMR 1.37 (t, 3H, *J* = 7.2 Hz), 3.89 (s, 2H), 4.30 (q, 2H, *J* = 7.2 Hz), 4.63 (s, 2H), 4.79 (s, 2H), 6.99 (s, 1H), 7.63 (d, 2H, *J* = 8.1 Hz), 7.76 (d, 2H, *J* = 8.1 Hz); ^{13}C-NMR ($CDCl_3$+CS_2) 14.3, 55.5, 57.9, 59.1, 60.7, 67.0, 68.7, 125.5 (d, *J* = 14.7 Hz), 129.2, 135.8, 135.9, 139.9, 140.2, 141.4, 141.5, 141.6, 141.8, 141.9, 142.1, 142.3, 142.4 (2C), 143.0, 144.3, 144.5, 145.2 (2C), 145.3, 145.5, 146.0 (2C), 146.1, 146.2, 146.4, 146.9, 147.0, 147.2, 153.9, 154.2, 170.5; HRMS (FAB) *m/z* 996.1210 (M+1, $C_{73}H_{17}F_3NO_2$ requires 996.1211).

37: ^{1}H-NMR 0.5 (s, 9H), 1.18 (t, 3H, *J* = 7.2 Hz), 4.20 (q, 1H, *J* = 7.2 Hz), 4.28 (q, 1H, *J* = 7.2 Hz), 4.65 (d, 1H, *J* = 13.8 Hz), 5.33 (d, 1H, *J* = 13.8 Hz), 5.37 (s, 1H), 5.39 (s, 1H), 7.70 (d, 2H, *J* = 8.4 Hz), 7.78 (d, 2H, *J* = 8.4 Hz); ^{13}C-NMR ($CDCl_3$+CS_2) 0.7, 14.2, 55.8, 61.0, 70.0, 76.7, 77.0, 77.7 125.7 (q, *J* = 14.7 Hz), 128.6, 134.7, 135.6 (d, *J* = 16.5 Hz), 136.2, 139.2, 139.5, 139.6, 140.2, 141.7, 141.8 (2C), 141.9, 142.0, 142.1 (2C), 142.2 (2C), 142.4, 142.6 (2C), 142.7 (2C), 143.0, 143.1, 144.2, 144.3, 144.4, 144.5, 144.8, 145.1 (2C), 145.2 (3C), 145.4, 145.8, 145.9 (2C), 146.1 (2C), 146.2, 146.5, 146.9, 147.0, 152.4, 154.6, 156.2, 156.9, 170.1; HRMS (FAB) *m/z* 1066.1447 (M+1, $C_{76}H_{23}$ F_3NO_2Si requires 1066.1450).

Photoreaction of C_{60}+23. Formation of 38.[17a] N_2 saturated condition. 2 h irradiation, 59% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **38** (96 mg, 37%). O_2 saturated condition. 5 h irradiation, 66% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **38** (91 mg, 35%).

Photoreaction of C_{60}+24. Formation of 39. N_2 saturated condition. 2 h irradiation, 60% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **39** (91 mg, 35%). O_2 saturated condition. 5 h irradiation, 67% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **39** (92 mg, 35%). ^{1}H-NMR 1.34 (t, 3H, *J* = 7.2 Hz), 2.34 (s, 3H), 2.87 (s, 3H), 4.35 (q, 1H, *J* = 7.2 Hz), 4.44 (q, 1H, *J* = 7.2 Hz), 5.62 (s, 1H), 6.32 (s, 1H), 7.18 (d, 2H, *J* = 8.1 Hz), 7.63 (d, 2H, *J* = 8.1 Hz); ^{13}C-NMR ($CDCl_3$+CS_2) 14.4, 21.3, 35.0, 61.0, 70.8, 76.0, 76.8, 77.3, 129.3, 133.8, 136.0, 138.0, 139.4, 139.9 (2C), 141.4, 141.5, 141.6, 141.7, 141.9 (3C), 142.0 (2C), 142.1 (2C), 142.4, 142.5 (2C), 142.6, 144.2, 144.4, 144.5, 145.0, 145.1 (3C), 145.2, 145.3, 145.4 (2C), 145.5 (2C), 145.8 (2C), 146.0 (2C), 146.2, 146.5, 146.6, 150.8, 153.8, 155.7, 170.9; HRMS (FAB) *m/z* 940.1339 (M+1, $C_{73}H_{18}NO_2$ requires 940.1338).

Photoreaction of C_{60}+25. Formation of 40. N_2 saturated condition. 2 h irradiation, 60% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **40** (101 mg, 38%). O_2 saturated condition. 5 h irradiation, 70% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **40** (112 mg, 42%). ^{1}H-NMR 1.34 (t, 3H, *J* = 7.2 Hz), 2.86 (s, 3H), 3.79 (s, 3H), 4.35 (q, 1H, *J* = 7.2 Hz), 4.44 (q, 1H, *J* = 7.2

Hz), 5.63 (s, 1H), 6.32 (s, 1H), 6.91 (d, 2H, *J* = 8.7 Hz), 7.68 (d, 2H, *J* = 8.7 Hz); ^{13}C-NMR ($CDCl_3$+CS_2) 14.4, 34.8, 54.8, 60.8, 70.6, 76.1, 76.7, 77.2, 113.8, 128.7, 130.4, 135.8, 135.9, 136.1, 137.4, 139.4, 139.9 (2C), 141.4, 141.5 (2C), 141.6, 141.8 (2C), 141.9 (2C), 142.0 (3C), 142.4 (2C), 142.5, 142.8, 144.1, 145.0 (2C), 145.1 (2C), 145.3 (3C), 145.4 (2C), 145.7 (2C), 145.9 (2C), 146.0, 146.2, 146.4, 146.5, 153.7, 153.9, 155.7, 159.4, 170.5; HRMS (FAB) *m/z* 956.1290 (M+1, $C_{73}H_{18}NO_3$ requires 956.1287).

Photoreaction of C_{60}+26. Formation of 41. N_2 saturated condition. 5 h irradiation, 76% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **41** (106 mg, 40%). O_2 saturated condition. 5 h irradiation, 60% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **41** (85 mg, 32%). ^{1}H-NMR 1.32 (t, 3H, *J* = 7.2 Hz), 2.86 (s, 3H), 4.35 (q, 1H, *J* = 7.2 Hz), 4.44 (q, 1H, *J* = 7.2 Hz), 5.63 (s, 1H), 6.36 (s, 1H), 7.07 (t, 2H, *J* = 8.7 Hz), 7.76 (t, 2H, *J* = 8.7 Hz); ^{13}C-NMR ($CDCl_3$+CS_2) 14.3, 34.8, 60.9, 70.5, 75.7, 76.6 (2C), 115.4 (d, *J* = 87.6 Hz), 130.8 (d, *J* = 30.2 Hz), 132.5 (2C), 135.8, 136.0 (d, *J* = 20.7 Hz), 137.3, 139.3, 139.4, 139.9 (2C), 141.3, 141.4, 141.5, 141.7, 141.8, 141.9 (4C), 142.3, 142.4, 142.5, 142.9, 144.1, 144.2, 144.3, 144.4, 144.9, 145.0 (2C), 145.1, 145.2, 145.3 (3C), 145.4, 145.5, 145.7 (2C), 145.9 (3C), 146.0, 146.1, 146.2, 147.0, 147.2, 150.4, 153.2, 153.3, 155.4, 162.4 (d, *J* = 985.8 Hz), 170.5; HRMS (FAB) *m/z* 944.1089 (M+1, $C_{72}H_{15}FNO_2$ requires 944.1087).

Photoreaction of C_{60}+27. Formation of 42. N_2 saturated condition. 5 h irradiation, 72% conversion, column chromatography (CS_2: hexane = 1: 1) to yield **42** (117 mg, 42%). O_2 saturated condition. 5 h irradiation, 57% conversion, column chromatography (CS_2:hexane = 1: 1) to yield **42** (89 mg, 32%); 8 h irradiation, 85% conversion, column chromatography (CS_2:hexane = 1: 1) to yield **42** (139 mg, 50%). ^{1}H-NMR 1.34 (t, 3H, *J* = 7.2 Hz), 2.87 (s, 3H), 4.36 (q, 1H, *J* = 7.2 Hz), 4.44 (q, 1H, *J* = 7.2 Hz), 5.54 (s, 1H), 6.45 (s, 1H), 7.65 (d, 2H, *J* = 8.4 Hz), 7.92 (d, 2H, *J* = 8.4 Hz); ^{13}C-NMR ($CDCl_3$+CS_2) 14.4, 29.7, 34.9, 61.1, 70.8, 75.6, 76.8, 77.2, 125.4 (q, *J* = 14.7 Hz), 129.7, 136.0 (2C), 136.2, 137.3, 139.4, 139.5, 140.0, 141.2, 141.5 (2C), 141.6 (2C), 141.7, 141.8, 141.9, 142.0 (2C), 142.5 (2C), 142.6, 142.9 (2C), 143.0, 144.2, 144.3, 144.4 144.9, 145.0, 145.1 (2C), 145.2, 145.3, 45.4, 145.5, 145.8 (2C), 146.0 (2C), 146.1 (2C), 146.2 (2C), 147.2, 147.3, 150.4, 152.8, 153.0, 155.3, 170.7; HRMS (FAB) *m/z* 994.1052 (M+1, $C_{73}H_{15}F_3NO_2$ requires 994.1055).

Photoreactions of C_{60} with Amine 6 in a completely deoxygenate solution. A 10% EtOH-toluene solution (7 mL) containing C_{60} (1.73 x 10^{-4} M) and amine **6** (3.46 x 10^{-4} M) was added to a Schlenk flask. The flask containing the solution immersed in liquid nitrogen evacuated using a vaccum and pump for 20 min. The solution was thawed and then subjected to 3 repeated freeze-pump-thaw cycles until evolution of gas during thawing was not observed. The flask was filled with N_2 gas and then sealed. Irradiation (>300 nm) for 2.5 h gave a photolysate that was subjected to HPLC analysis. The results show that a single peak corresponding to aminomethyl-fullerene **28** is present in the chromatogram.

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