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SET-Promoted Photoaddition Reactions of Fullerene C_{60} with Tertiary *N*-Trimethylsilylmethyl Substituted α-Aminonitriles. Approach to the Synthesis of Fulleropyrrolidine Nitriles

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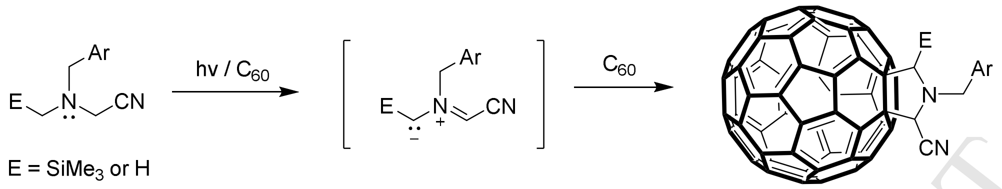
Graphical Abstract



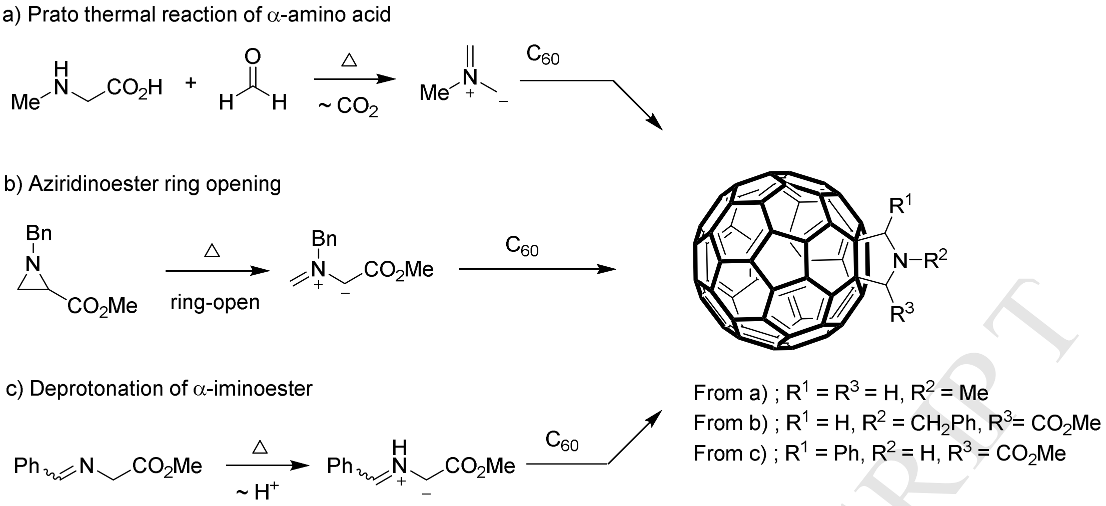
Abstract

Photoaddition reactions of C_{60} with tertiary *N*-arylmethyl-*N*-trimethylsilylmethyl substituted α-aminonitriles were explored. The results show that these photoreactions produce both trimethylsilyl- and cyano group containing fulleropyrrolidines as major products through pathways involving 1,3-dipolar cycloadditon of azomethine ylide intermediates. The ylides are formed either by SET from α-aminonitriles to the triplet excited state of C_{60} (in N_2-purged solutions) followed by desilylation or deprotonation, or by hydrogen atom abstraction by singlet oxygen (in O_2-purged solutions). In contrast, photoreactions of C_{60} with analogous amines that do not contain trimethylsilyl group form fulleropyrrolidines that contain aryl- and cyano substitutents on the pyrrolidine ring. The efficiencies of these photoaddition reactions are influenced by several factors including reaction condition (N_2 or O_2-purged), solvent polarity, the electronic and structural nature of α-aminonitriles and additive. The presence of trimethylsilyl group in the α-aminonitrile substrates plays a crucial role in enhancing the efficiencies of the fulleropyrrolidine forming reactions.

Introduction

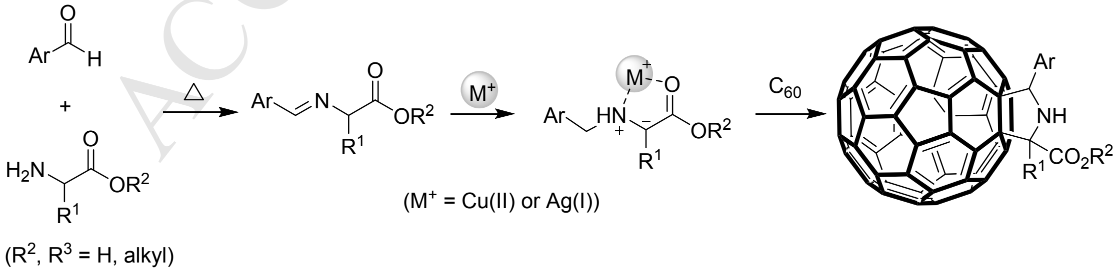
Chemical transformation of fullerenes to organofullerene derivatives, which possess unique photochemical and photophysical properties, is required for potential applications in the fields of material and biological sciences.[1-7] Among a number of organofullerene families probed so far, those containing appended amine functionality have attracted interests owing to their synthetic accessibility and well-defined structures. Especially interesting in this regard are fulleropyrrolidines in which the fullerene ring system is fused to a five-membered *N*-heterocyclic ring.[8-14] A variety of thermal, metal-catalyzed and photochemical methods using α-amino acid derivatives have been developed for the preparation of fulleropyrrolidines. For instance, the pioneering work of Prato and co-workers[7a,7b,8] led to the development of thermally promoted 1,3-dipolar cycloaddition reactions of fullerene C_{60} with azomethine ylides. The ylide serving as the intermediate in this process is generated through condensation reaction of *N*-methylglycine with formaldehyde followed by decarboxylation. Since that time, related approaches have been devised to prepare fulleropyrrolidines using a variety of other azomethine ylide precursors such as a combination of α-amino acids and aldehydes,[15] aziridinoesters[8] and α-iminoesters (Scheme 1).[13,14] Recently, during an exploration of Prato type thermal reactions of C_{60}, Wang and co-workers[10a] discovered that α-amino acids and α-aminoesters undergo sequential deamination-decarboxylation to generate aldehydes, which then react in situ with the starting α-amino acids/esters to form azomethine ylides that add to C_{60} to form fulleropyrrolidines. More recently, Liu and co-workers[9] reported that thermal reactions of C_{60} with mixtures of arylmethylamines ($ArCH_2NHR$, R = H, alkyl) and arylaldehydes (ArCHO) give rise to stereoselective formation of 2,5-diaryl substituted pyrrolidine containing fullerene adducts.

Scheme 1.



Metal-catalyzed cycloaddition reactions of amines with C_{60} also have been employed to prepare fulleropyrrolidines. Martin and co-workers[14] revealed that α-iminoesters, derived by reactions of arylaldehydes with primary α-aminoesters, add to C_{60} in the presence of Cu(II) or Ag(I) at room temperature to generate mixtures of diasteromeric fulleropyrrolidines (Scheme 2). Interestingly, when these processes were conducted in the presence of chiral organic additives, stereoselective and enantioselective formation of fulleropyrrolidine adducts took place. In addition, the results of a study by Liu and co-workers[12a] showed that Fe(III)-catalyzed reactions of primary and secondary arylmethylamines ($ArCH_2NHR$, R = H, alkyl) with C_{60} occur to produce fulleropyrrolidines stereoselectively.

Scheme 2.

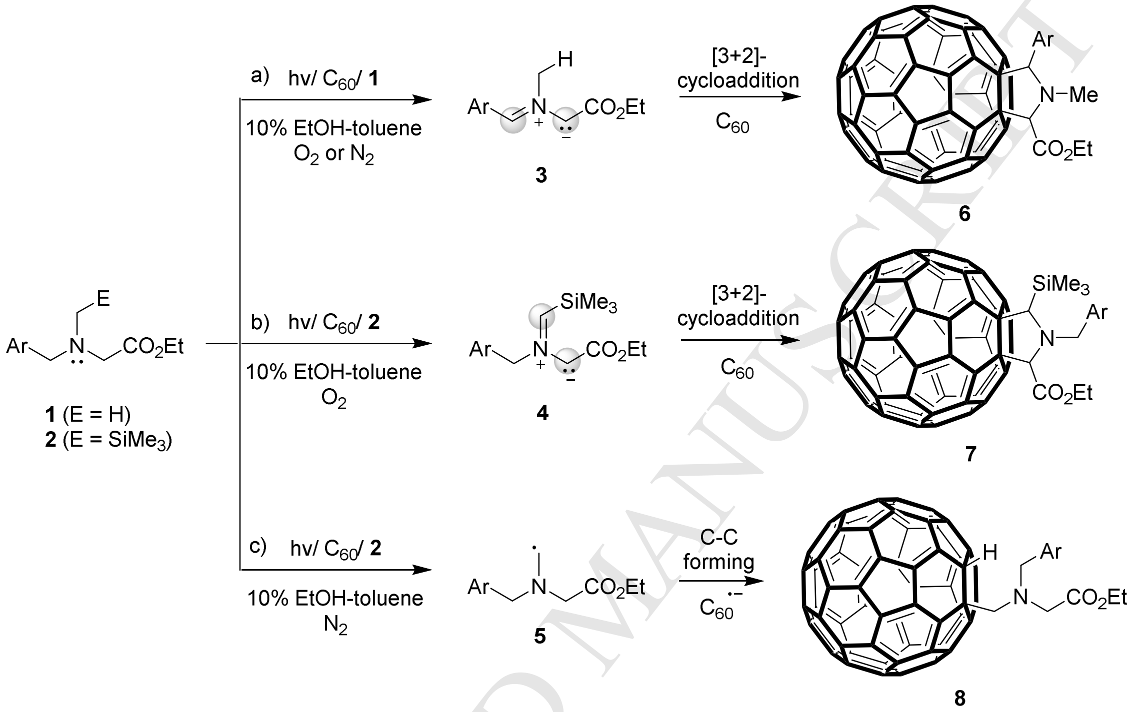


In addition to these efforts, earlier studies by Foote,[16] Gan[11] and others[10b,10c,10d] showed that irradiation of oxygenated (O_2-purged or air-saturated) solutions of C_{60} containing aliphatic amines possessing α-hydrogens gives rise to formation of fulleropyrrolidine adducts through pathways involving singlet oxygen ($^1O_2$) and/or single electron transfer (SET) steps. In recent studies exploring photochemical reactions of C_{60}, we observed that irradiation of both O_2 and N_2-purged 10% EtOH-toluene (v/v) solutions of C_{60} and tertiary α-aminoesters **1** ($MeN(ArCH_2)CH_2CO_2Et$, Ar = *para*-substituted phenyl) gives rise to formation of fulleropyrrolidines **6** *via* [3+2]-dipolar cycloaddition between C_{60} and in situ generated azomethine ylides **3** (a in Scheme 3).[17] More interesting results came from an investigation of the photoreactions of C_{60} with α-aminoesters possessing the trimethylsilyl group (**2** ($Me_3SiCH_2N(ArCH_2)CH_2CO_2Et$, Ar = *para*-substituted phenyl). Specifically, irradiation of O_2-purged 10% EtOH-toluene solutions containing C_{60} and α-aminoesters **2** resulted in the formation of fulleropyrrolidines **7** (b in Scheme 3). Importantly, these reactions were more efficient than those of the related non-trimethylsilyl substituted α-aminoester analogs **1**. In contrast, photoreaction of N_2-purged solutions of C_{60} and trimethylsilyl substituted α-aminoesters **2** led to predominant/exclusive formation of 1-aminomethyl-1,2-dihydrofullerenes **8**, *via* addition of α-amino radicals **5** to fullerene radical anions ($C_{60}^{\bullet-}$), formed by SET from **2** to the excited state of C_{60}.[17] (c in Scheme 3) These observations show that O_2 plays an important role in governing pathways followed in these photochemical processes.

Another interesting observation made relates to the different substitution patterns in the fulleropyrrolidine adducts **6** and **7** that arise from photoreactions of non-trimethylsilyl- (**1**) and trimethylsilyl (**2**) substituted α-aminoesters. Specifically, while irradiation of C_{60} in the presence of non-trimethylsilyl containing α-aminoesters **1** ($MeN(ArCH_2)CH_2CO_2Et$) led to formation of products **6** arising from cycloaddition of ethoxycarbonyl- and aryl substituted azomethine ylides **3**, irradiation of C_{60} in solutions containing trimethylsilyl substituted α-aminoesters **2**

($Me_3SiCH_2N(ArCH_2)CH_2CO_2Et$) brought about formation of fulleropyrrolidines **7**, derived from ethoxycarbonyl- and trimethylsilyl substituted ylides **4** (Scheme 3).

Scheme 3.

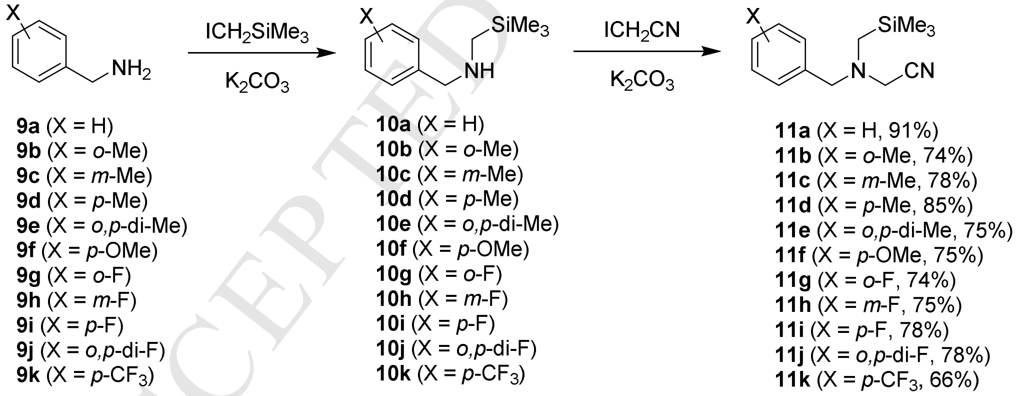


In a continuing research program aimed at exploring the nature and range of photoaddition reactions employed for the synthesis of fulleropyrrolidines, we designed, prepared and probed photoaddition reactions of C_{60} with *N*-arylmethyl and *N*-trimethylsilylmethyl substituted tertiary α-aminonitriles ($Me_3SiCH_2N(ArCH_2)CH_2CN$), in which the aryl groups contain either electron donating or withdrawing substituents. Despite the simplicity of their preparation and their high utility as potential azomethine ylide precursors,[18] to the best of our knowledge, these amines have only rarely been utilized in photochemical reactions. Because α-aminonitriles bearing α-hydrogens (pK_a ca. 25) can potentially serve as chemical equivalents of α-aminoesters (pK_a ca. 25), they should be useful substrates in photocycloaddition reactions leading to fulleropyrrolidines. Observation made in studies with these substances, summarized below, show that photoaddition reactions of trimethylsilyl group containing α-aminonitriles with C_{60} occur stereoselectively to form fulleropyrrolidines in a highly efficient manner, even when conducted using N_2-purged conditions.

Results and Discussion

Synthesis and photochemistry. The *N*-arylmethyl and *N*-trimethylsilylmethyl substituted tertiary α-aminonitriles **11a-11k**, employed as substrates in photoreactions with C_{60}, were prepared by using sequences beginning with well-known base-catalyzed substitution reactions of commercially available substituted benzylamines **9a-9k** and iodomethyltrimethylsilane (ICH_2SiMe_3). (Scheme 4) These processes produced secondary *N*-trimethylsilylmethyl-*N*-benzylamines **10a-10k**,[19] which then reacted with iodoacetonitrile (ICH_2CN) in the presence of base (K_2CO_3) to form the target tertiary α-aminonitriles **11a-11k** (66-91 %).

Scheme 4.



Photoreactions were performed by irradiation (450W Hanovia medium pressure Hg lamp and flint glass filter (>300 nm)) of 10% EtOH-toluene (v/v) and 10% EtOH-*o*-dichlorobenzene (ODCB) solutions (220 mL, N_2 or O_2 purged condition) containing the α-aminonitriles (0.59 mmol) and C_{60} (0.28 mmol). The concentrated photolysates were then subjected to column chromatography to give the products and yields displayed in Scheme 5 and Tables 1-4.

Scheme 5.

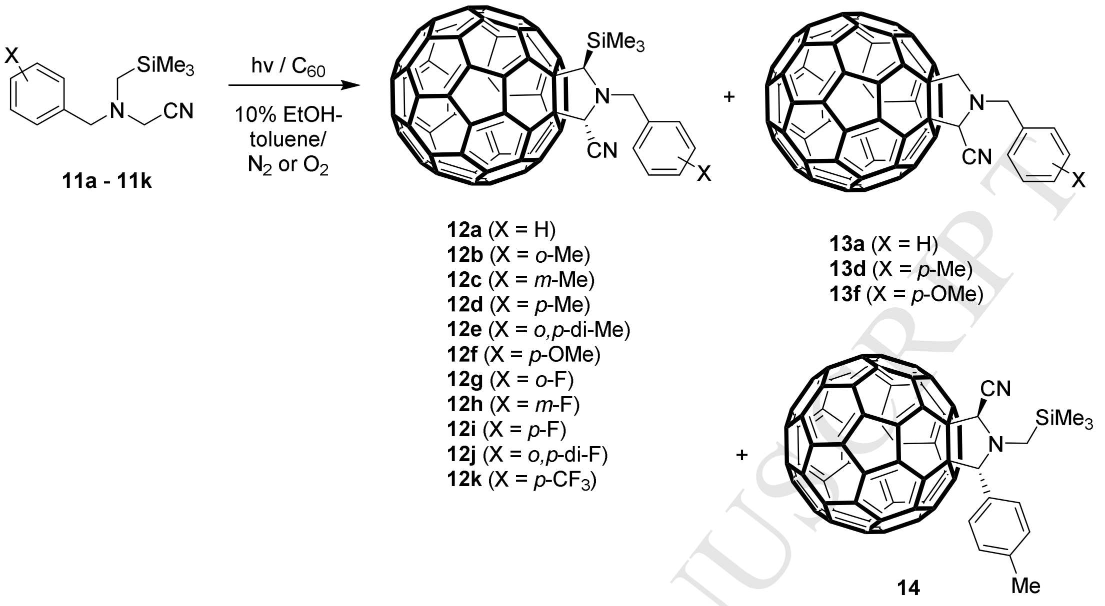


Table 1. Products and yields of photoaddition reactions of C_{60} with α-aminonitriles **11a-11k** in N_2-purged 10% EtOH-toluene solutions.

entry	amine	irradiation Time (h)	conversion (%)[a]	product (%)[b]
1	**11a**	2	83	**12a** (42), **13a** (13)
2[c]	**11a**	2	83	**12a** (41), **13a** (13)
3	**11b**	2	85	**12b** (40)
4	**11c**	2	85	**12c** (42)
5	**11d**	2	86	**12d** (42), **13d** (17), **14** (4)
6	**11e**	2	87	**12e** (50)
7	**11f**	2	85	**12f** (43), **13f** (15)
8	**11g**	6	81	**12g** (39),

9	**11h**	6	84	**12h** (41)
10	**11i**	6	69	**12i** (40)
11	**11j**	8	85	**12j** (44)
12	**11k**	8	80	**12k** (40)

[a] Determined based on recovered C_{60}. [b] Isolated yields.
[c] Excess of α-amino nitrile **11a** (2.95 mmol) is used.

As the results in Scheme 5 and Table 1 show, 2 h irradiation of a N_2-purged 10% EtOH-toluene solution containing C_{60} and α-aminonitrile **11a** gave rise to formation of the *N*-benzyl, trimethylsilyl- and cyano group substituted fulleropyrrolidine **12a** as the major photoadduct, along with a minor amount of cycloadduct **13a** that does not contain the trimethylsilyl group (entry 1 in Table 1). No change in the percent conversion or product ratio occurred when a molar excess of **11a** (2.95 mmol) was used (entry 2 in Table 1). Similar product distributions arose from photoreactions of *p*-Me (**11d**) and *p*-OMe (**11f**) substituted analogs (entries 5 and 7 in Table 1). Interestingly, reaction of **11d** with C_{60} also generated the *N*-trimethylsilyl, toluyl- and cyano group substituted fused pyrrolidine **14** as a minor photoproduct. Moreover, photoreactions of C_{60} in the presence of α-aminonitriles **11b**, **11c**, **11e** and **11g-11k** generated the corresponding trimethylsilyl- and cyano group substituted fulleropyrrolidines **12** as sole photoadducts (39-44%) (entries 3, 4, 6, 8-12 in Table 1). Notably, in contrast to those of *p*-H and *p*-electron donating group substituted analogs **11a-11f** (2 h), photoreactions of electron withdrawing (F and CF_3) group substituents containing cyanoamines **11g-11k** with C_{60} required much longer irradiation times (6-8 h) to bring about high conversions of C_{60}.[17-18]

It is noteworthy to compare the product profiles of photoreactions of the α-aminonitriles with those arising from α-aminoesters (c in Scheme 3). While photoreactions of trimethylsilyl containing α-aminoesters **2** (Scheme 3) occurred under anaerobic conditions to produce 1-aminomethyl-1,2-

dihydrofullerenes **8** predominantly,[17] those of the corresponding α-aminonitriles produced fulleropyrrolidines solely. (Scheme 5) It should be noted that photoreactions of C_{60} with all of the α-aminonitriles examined in this effort led to stereoselective formation of *trans*-isomers of the fulleropyrrolidines **12a-12k** (see below).

Studies were carried out to assess the nature of photoaddition reactions of oxygenated (O_2-purged) 10% EtOH-toluene solutions containing C_{60} and α-aminonitriles **11a-11k**. As can be seen by viewing the results in Scheme 5 and Table 2, the product distributions of these reactions were quite similar to those arising from reactions in N_2-purged solutions. However, relatively shorter irradiation times were required in all cases to bring about high conversion of C_{60} (> 90%) and modest product yields (39-50%). Moreover, photoreactions of respective α-aminonitriles **11a**, **11d** and **11f** gave rise to exclusive formation of trimethylsilyl- and cyano group substituted fulleropyrrolidines **12a**, **12d** and **12f** (entries 1, 4 and 6 in Table 2).

Table 2. Products and yields of photoaddition reactions of C_{60} with α-aminonitriles **11a-11k** in O_2-purged 10% EtOH-toluene.

entry	amine	Irradiation Time (h)	Conversion (%)[a]	Product (%)[b]
1	**11a**	1	94	**12a** (44), **13a** (3)
2	**11b**	1	95	**12b** (47)
3	**11c**	1	96	**12c** (50)
4	**11d**	1	96	**12d** (44), **13d** (5), **14** (1)
5	**11e**	1	96	**12e** (49)
6	**11f**	1	96	**12f** (49), **13f** (5)

7	**11g**	3	93	**12g** (48)
8	**11h**	3	94	**12h** (48)
9	**11i**	3	86	**12i** (43)
10	**11j**	5	90	**12j** (53)
11	**11k**	5	91	**12k** (44)

[a]Determined based on recovered C_{60}. [b]Isolated yields.

We observed earlier that solvent polarity is an important factors in governing the efficiencies of SET-promoted photochemical reactions of C_{60} with amines.[10b,10c,17,19-21] As a result, photoaddition reactions of C_{60} with **11a-11k** in the 10% EtOH-*o*-dichlorobenzene (ODCB), which is less polar solvent system than 10% EtOH-toluene, were explored. Photoreactions of N_2-purged 10% EtOH-ODCB solutions containing C_{60} and **11a-11k** took place less efficiently than those of N_2-purged 10% EtOH-toluene solutions to produce fulleropyrrolidines exclusively (Table 3). For example, even 10 h irradiation of solutions containing *o*,*p*-di-F (**11j**) and *p*-CF_3 (**11k**) aryl ring substituted α-aminonitriles resulted in low conversion of C_{60} (entries 10-11 in Table 3). Another interesting observation was that photoreactions of C_{60} with **11a**, **11d** and **11f** produce the trimethylsilyl- and cyano group containing fulleropyrrolidines **12a**, **12d** and **12f** exclusively. The product distributions were comparable to those from reactions of N_2-purged 10% EtOH-toluene solutions containing the same α-aminonitriles.

Table 3. Products and yields of photoaddition reactions of C_{60} with α-aminonitriles **11a-11k** in N_2-purged 10% EtOH-ODCB.

Entry	amine	irradiation	conversion (%)[a]	product (%)[b]

		Time (h)		
1	**11a**	3	87	**12a** (39), **13a** (3)
2	**11b**	3	80	**12b** (35)
3	**11c**	3	79	**12c** (35)
4	**11d**	3	80	**12d** (37), **13d** (5)
5	**11e**	3	82	**12e** (43)
6	**11f**	3	89	**12f** (46), **13f** (trace)
7	**11g**	6	65	**12g** (26)
8	**11h**	6	62	**12h** (30)
9	**11i**	6	62	**12i** (33)
10	**11j**	10	52	**12j** (26)
11	**11k**	10	41	**12k** (23)

[a]Determined based on recovered C_{60}. [b]Isolated yields.

Photoreactions of O_2-purged 10% EtOH-ODCB solutions containing C_{60} and **11a-11k** were also conducted (Table 4). Interestingly, the results showed that photoreactions of all of α-aminonitriles, including **11a**, **11d** and **11f**, take place efficiently and give rise to trimethylsilyl- and cyano group containing fulleropyrrolidiens **12a-12k** solely. Moreover, photoreactions of the respective *o*,*p*-di-F (**11j**) and *p*-CF_3 (**11k**) substituted α-aminonitriles took place with increased conversion efficiencies and chemical yields (entries 10-11 in Table 4).

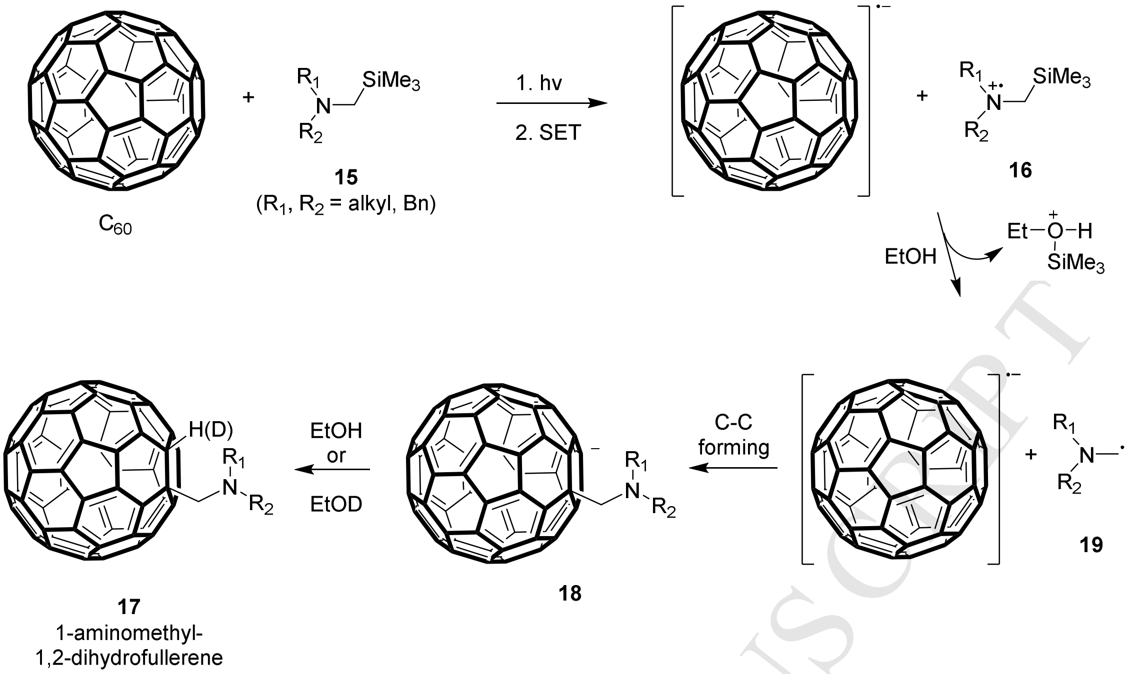
Table 4. Products and yields of photoaddition reactions of C_{60} with α-aminonitriles **11a-11k** in O_2-purged 10% EtOH-ODCB.

entry	amine	irradiation Time (h)	conversion (%)[a]	product (%)[b]
1	**11a**	2	85	**12a** (45)
2	**11b**	2	83	**12b** (39)
3	**11c**	2	82	**12c** (39)
4	**11d**	2	84	**12d** (44)
5	**11e**	2	93	**12e** (46)
6	**11f**	2	96	**12f** (52)
7	**11g**	5	89	**12g** (43),
8	**11h**	5	86	**12h** (46)
9	**11i**	5	88	**12i** (46)
10	**11j**	10	76	**12j** (39)
11	**11k**	10	74	**12k** (37)

[a] Determined based on recovered C_{60}. [b] Isolated yields.

Solvent effect. In earlier studies,[17a] we explored the effects of the EtOH content in EtOH-toluene solvent systems on the efficiencies of SET-promoted photoaddition reactions between tertiary *N*-α-silylamines **15** and C_{60}. The results showed that the presence of EtOH in the mixed solvent system was essential for formation of 1-aminomethyl-1,2-dihydrofullerenes **17** (Scheme 6). This observation is consistent with the sequential SET-desilylation mechanism for these photoreactions (Scheme 6).

Scheme 6.



The earlier findings stimulated us to probe the effect of EtOH content in toluene or ODCB solutions on photoreactions of C_{60} with α-aminonitriles **11a**-**11k**. For this purpose, photoreactions of C_{60} with two α-aminonitriles **11a** and **11d** were performed in N_2 or O_2-purged pure toluene solutions (Table 5). While photoreactions of N_2-purged pure toluene solutions of **11a** and **11d** (entries 1-2 in Table 5) took place less efficiently than those in 10% EtOH-toluene solutions (see entries 1 and 5 in Table 1), no significant differences existed in the photoreactions of O_2-purged pure (entries 3-4 in Table 5) and EtOH-toluene mixed solutions (entries 1 and 4 in Table 2).

Table 5. Products and yields of photoaddition reactions of C_{60} with α-amino nitriles **11a** and **11d** in pure toluene.

entry	amine	reaction condition	irradiation time (h)	conversion (%)[a]	product (%)[b]
1	**11a**	N_2	2	77	**12a** (32), **13a** (2)

2	**11d**	N_2	2	77	**12d** (26), **13d** (8)
3	**11a**	O_2	1	93	**12a** (46), **13a** (2)
4	**11d**	O_2	1	95	**12d** (42), **13d** (10)

[a]Determined based on recovered C_{60}. [b]Isolated yields.

The same probes were made in photoaddition reactions of C_{60} with α-aminoesters **20**-**21** in O_2-purged pure toluene solutions (Scheme 7 and Table 6). In a previous study,[17b] we found that photoaddition reactions of α-aminoesters **20**-**21** in O_2-purged 10% EtOH-toluene solutions give rise to fulleropyrrolidines **22**-**23**, respectively (entries 1-2 in Table 6). While the reactions of **20**-**21** in O_2-purged pure toluene solutions also produced **22**-**23**, they required much longer irradiation times to bring about the same conversions.

Scheme 7.

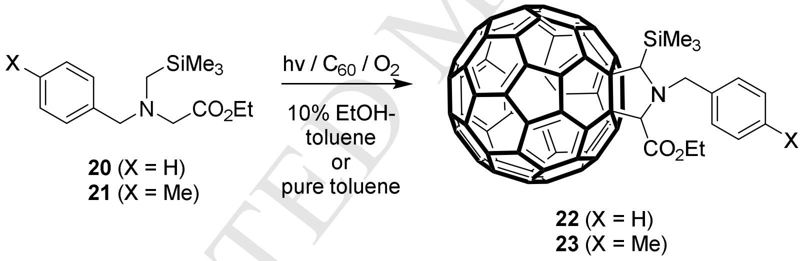


Table 6. Products and yields of photoaddition reactions of C_{60} with α-aminoesters **20**-**21** in O_2-purged 10% EtOH-toluene or pure toluene solutions.

entry	amine	irradiation time (h)	conversion (%)[a]	product (%)[b]
1[c]	**20**	2	89	**22** (57)
2[c]	**21**	2	90	**23** (56)

3^d	**20**	5	85	**22** (50)
4^d	**21**	5	87	**23** (50)

[a]Determined based on recovered C_{60}. [b]Isolated yields. [c]Reaction in 10% EtOH-toluene. [d]Reaction in pure toluene

Effect of trimethylsilyl group. As mentioned above (Scheme 3), not only the efficiencies but also the product distributions of photoaddition reactions of α-aminoesters to C_{60} are highly dependent on the presence of a α-trimenthylsilyl group.[17] To explore if this effect also plays a role in photoreactions with α-aminonitriles, we prepared and explored the photochemistry of the non-trimethylsilyl α-aminonitrile analogs **24**-**26**[22] (Scheme 8). The results showed that photoreactions of **24-26** with C_{60} are comparable to those of the trimethylsilyl group containing α-aminonitriles. For example, no photoreactions took place when N_2-purged 10%-EtOH solutions of **24-26** were irradiated even for long irradiation period (entries 1, 4 and 7 in Table 7). In contrast, photoreactions of **24-26** did occur upon prolonged irradiation of O_2-purged 10% EtOH-toluene solutions to form *trans*- and *cis*-diastereomeric mixtures of the corresponding fulleropyrrolidines **27-29**, along with **13a** (from **24**) and **13d** (from **25**).

Scheme 8.

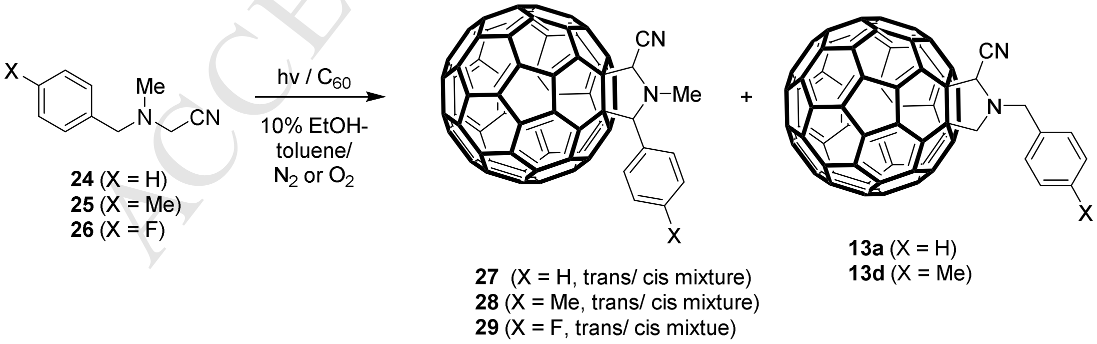


Table 7. Products and yields of photoaddition reactions of C_{60} with non-trimethylsilyl containing α-

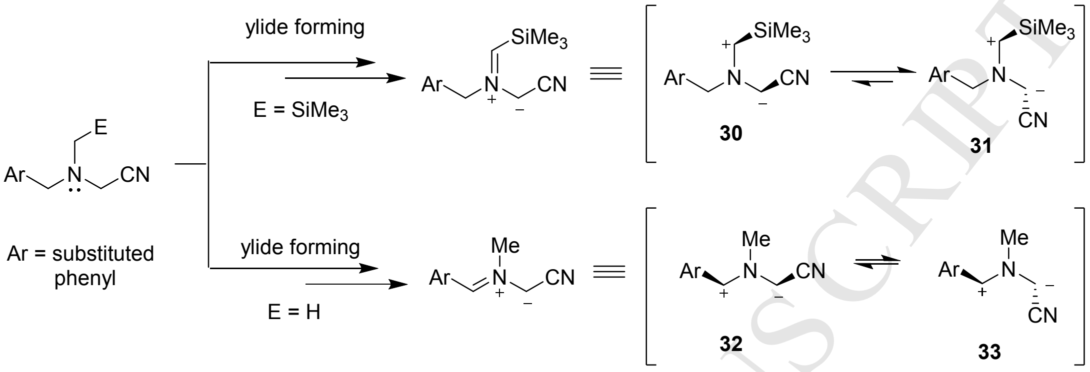
aminonitriles **24-26** in 10% EtOH-toluene solutions.

entry	amine	reaction condition	irradiation time (h)	conversion (%)[a]	product (% yield, *trans*:*cis* ratio)[b]
1	**24**	N_2	8	-[c]	-[c]
2	**24**	O_2	8	54	**27** (38, 1: 0.7), **13a** (2)
3	**24**	O_2	15	77	**27** (44, 1: 0.7), **13a** (4)
4	**25**	N_2	8	-[c]	-[c]
5	**25**	O_2	8	53	**28** (33, 1: 0.3), **13d** (4)
6	**25**	O_2	15	78	**28** (46, 1: 0.3), **13d** (8)
7	**26**	N_2	15	-[c]	-[c]
8	**26**	O_2	15	10	**29** (4, 1: 0.9)
9	**26**	O_2	40	28	**29** (14, 1: 0.9)

[a]Determined based on recovered C_{60}. [b]Isolated yields and *trans*:*cis* isomer molar ratio. [c]No reaction

Another interesting observation concerned the stereochemistry features of photoproducts **27-29**. Specifically, in contrast to the *trans*-specific formation of fulleropyrrolidines (**12a**, **12d** and **12i**) in photoreactions of the trimethylsilyl group containing α-aminonitriles **11a**, **11d** and **11i**, photoreactions of the non-trimethylsilyl counterparts **24-27** produced *trans*- and *cis*- isomeric mixtures of fulleropyrrolidines products **27-29**. A possible explanation for the lack of stereoselectivity observed in photoreactions of C_{60} with the non-trimethylsilyl containing α-aminonitriles comes from a proposal made by Liu and co-workers[9a,12a] that the conformation of in-situ formed azomethine ylides are responsible for stereochemistry of these photoreactions of fulleropyrrolidines. Accordingly, azomethine ylides generated from trimethylsilyl group containing α-aminonitriles should prefer to have conformation **31**, which minimizes steric repulsion between the sterically bulky benzyl, cyano and trimethylsily groups. In contrast, the conformations **32** and **33** of ylides generated from non-trimethylsilyl containing α-aminonitriles **24-26** are energetically more similar. (Scheme 9)

Scheme 9.



Structural and stereochemical assignments. Structural assignments of the fulleropyrrolidines photoproducts formed in the reactions described above were made by using ^{1}H and ^{13}C NMR, FT-IR, UV-visible spectroscopy and HRMS (see Experimetnal Section and Supplementary data), as well as by comparing the data to those previously reported for related fulleropyrrolidines.[9a,12a,14,16-19] In ^{1}H NMR spectra of fulleropyrrolidines **12a-12k**, the presence of two stereogenic carbons adjacent to the nitrogen atom caused the the benzyl protons to appear as AB quartets in the *ca*. 4.0-5.0 ppm region. In addition, the two methine protons on carbons bearing trimethylsilyl and cyano groups appeared as singlet peaks at *ca*. 4.3-4.4 and 5.3-5.4 ppm region, respectively. In the ^{13}C NMR spectra of **12a-12k**, the quaternary sp^3 carbons in the hydro-C$_{60}$ core resonated at *ca*. 68-74 ppm region and the methine carbons possessing the trimethylsilyl and cyano groups resonated at *ca*. 66-67 ppm. Importantly, cyano carbon resonated at *ca*. 114-115 ppm in all cases. FT-IR spectra of **12a-12k** also clearly contained characteristic absorptions at 2260 cm^{-1} for cyano stretching vibrations. Fulleropyrrolidines **13a**, **13d**, **13f** contain one chiral center and, as a result, ^{1}H NMR showed that their methylene protons appear as AB quartets at *ca*. 4.2-4.6 ppm and their benzyl protons appear at *ca*. 4.5-4.7 ppm as AB quartets. In addition, the ^{13}C NMR spectra of **13a**, **13d**, **13f** contained peaks that correspond to two quaternary sp^3 carbons, two methylene carbons and one methine carbon. The UV-visible absorption spectra of all of photoproducts contained maxima at *ca*. 431-433 nm, which are characteristic of 1,2-adducts formed by addition across the [6,6]-juncture of C_{60}.[10b,10c,17-21] Finally, spectroscopic data for the isomeric mixtures of **27-29** and comparisons of these data with those for **12a-12k** and **14** enabled assignments of their structures of photoproducts. These data clearly showed the characteristic peaks corresponding to fulleropyrrolidines **27-29**.

It should be noted that ^{1}H and ^{13}C NMR spectral data provide no information to enable assignments of stereochemistry (*trans* versus *cis*) to the generated fulleropyrrolidines. In addition, despite repeated attempts to obtain clear x-ray crystallographic data on photoproducts, we met with failure. We recently became aware of studies by Liu and co-workers[9a,12a] in which the stereochemistry of isomeric fulleropyrrolidines was assigned by using NOESY. As a result, we utilized this technique to assign stereochemistry of **12a-12k**. Based on the results of previous studies,[9a,12a] we expected that while the methine protons in *trans*-fulleropyrrolidines would display no correlation NOE peaks owing to their great spatial separation, the analogous *cis*-fulleropyrrolidines would display strong NOE correlation peaks between the two methine protons. In fact, NOESY spectra of *trans*-fulleropyrrolidines **12a**, **12d** and **14** did not display any NOE correlation peaks for the two methine protons on the trimethylsilyl and cyano substituted carbons (Supporting Information). Analysis of NOESY data for the isomers of fulleropyrrolidines **27-29**, produced by photoreactions of C_{60} with non-trimethylsilyl containing α-aminonitriles **24-26**, support the proposal that the absence or presence of NOE correlation peaks would be decisive in assigning stereochemistry. Although separation of the *cis* and *trans* isomers of fulleropyrrolidines **27-29** was exceedingly difficult, it was possible to isolate isomerically pure *cis*-**27** and *trans*-**28**. The results of NOESY analysis of these substances showed that, as expected, *cis*-**27** displays strong NOE correlation peaks and *trans*-**28** does not (Supporting Information).

Additive effect. To gain information about factors governing the efficiencies of photoaddition reactions leading to formation of the trimethylsilyl (**12a-12k**) and non-trimethylsilyl (**13a**, **13d** and **13f**) containing fulleropyrrolidines, photoreactions of N_2 and O_2-purged pure toluene solutions containing C_{60} and α-aminonitriles **11a** and **11d** along with pyridine were explored. In the absence of pyridine, 2 h irradiation of N_2-purged solutions of **11a** and **11d** brought about high conversion of C_{60} (77%) and relatively low yields of fulleropyrrolidines (**12a**+**13a** (34%), **12d**+**13d** (34%), entries 1-2 in Table 5). Interestingly, in the presence of pyridine (1.26 mM), 2 h photoreactions of these substances occurred with higher conversions (> 94%), higher yields (> 54%) and greater degrees of chemoselectivity favoring the trimethylsilyl group containing adducts (entries 1-2 in Table 8). However, pyridine had no significant effects on both the conversions (C_{60}) and yields (**12a**+**13a** and **12d**+**13d**) on photoreactions of oxygenated toluene solutions containing these substrates (entries 3-4 in Table 5 and Table 8), a finding that has mechanistic implications.

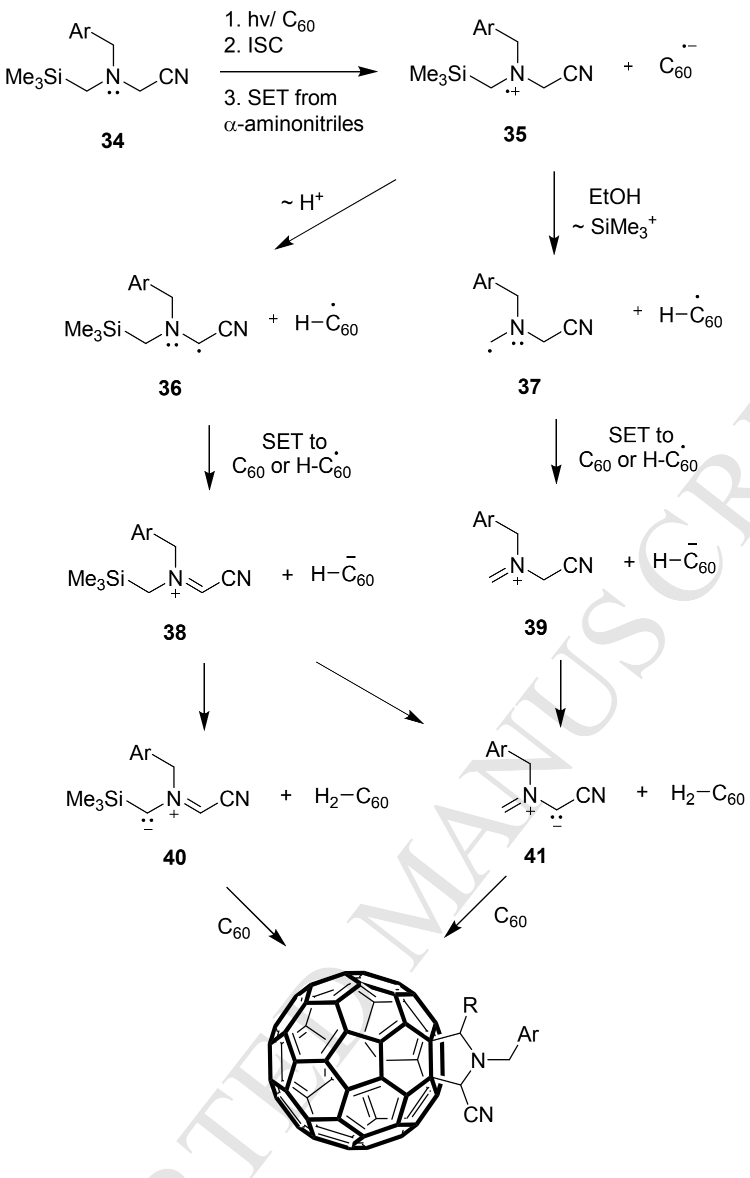
Table 8. Products and yields of photoaddition reactions of pure toluene solutions containing C_{60} and α-aminonitriles **11a** and **11d** in the presence of pyridine (1.26 mM).

entry	amine	reaction condition	irradiation time (h)	conversion (%)[a]	product (%)[b]
1	**11a**	N_2	2	94	**12a** (54)
2	**11d**	N_2	2	95	**12d** (55)
3	**11a**	O_2	1	95	**12a** (50), **13a** (3)
4	**11d**	O_2	1	96	**12d** (53), **13d** (2)

[a]Determined based on recovered C_{60}. [b]Isolated yields.

Mechanistic analysis. The observations outlined above enabled the proposal of feasible mechanistic pathways for formation of the trimethylsilyl and non-trimethylsilyl containing fulleropyrrolidines formed in the photoreactions of C_{60} with the α-aminonitriles. The routes for reactions taking place in N_2 purged solutions (Scheme10) are initiated by SET from the α-aminonitrile **34** to the triplet excited state of C_{60} ($^3C_{60}^*$), generated by efficient intersystem crossing of $^1C_{60}^*$ (Φ_{ISC} = 1).[23] This process forms a radical ion pair consisting of the fullerene radical anion radicals ($C_{60}^{\bullet-}$) and aminium radicals **35**. The generated aminium radicals undergo competitive α-CH deprotonation by $C_{60}^{\bullet-}$ vs ethanol promoted desilylation to give the respective trimethylsilyl and non-trimethylsilyl containing α-amino radicals **36** and **37**, along with the hydrofullerene radical (H-$C_{60}^{\bullet}$). Although it is known that typical α-silyl substituted aminium radicals undergo solvent assisted desilylation with rates that exceed those of α-CH deprotonation,[24-25] the latter process could overwhelm desilylation when, like in the current case, the acidity of the aminium radicals is enhanced by α-substituents. The α-amino radicals **36** and **37**, generated by deprotonation or desilylation, are oxidized by SET to either H-$C_{60}^{\bullet}$ or C_{60}, to form the respective iminium ions **38** and **39** along with the hydrofullerene anion (H-C_{60}^{-}). Deprotonation of **38** and **39** then produces the respective ylides **40** and **41**. Alternatively, desilylation of **38** can also generate **41**. The processes are then terminated by [3+2]-dipolar cycloaddition to give fulleropyrrolidine adducts **42**. If a much stronger base such as pyridine (pK_a *ca*. 5.2) rather than H-C_{60}^{-} (pK_a *ca*. 4.7) is present, deprotonation of aminium radical **35** occurs more rapidly, explaining why the reaction efficiency increases and the products arising from azomethine ylides **40** are more predominant.

Scheme 10.



42 (R =SiMe$_3$ or H)

In photoreactions occurring in O$_2$-purged solutions, the triplet excited state of C$_{60}$ ($^3C_{60}{}^*$) participates in energy transfer to form singlet oxygen ($^1O_2$).[23] As suggested by Foote,[16b] reactions of $^1O_2$ with amines take place through α-H atom abstraction to generate α-amino radicals **36**. This process with α-aminonitriles generates α-amino radicals **36** along with the hydroperoxy radicals (HOO$^•$) in pathways leading to the production of the key azomethine ylides **40** and **41**, which cycloadd to C$_{60}$ to produce fulleropyrrolidines **42**.

Conclusion

In the study described above, photoaddition reactions of C_{60} with *N*-arylmethyl-*N*-trimethylsilylmethyl substituted tertiary α-aminonitriles were explored. The results show that photoreactions of C_{60} with trimethylsilyl group containing α-aminonitriles produce predominantly trimethylsilyl and cyano group containing pyrrolidine ring fused fullerenes in a *trans*-stereoselective manner through a pathway involving azomethine ylide intermediates. The azomethine ylides, generated by either SET process or H-atom abstraction, cycloadd to C_{60} at [6,6]-juncture positions to form fulleropyrrolidines. In contrast, photoreaction of C_{60} with non-trimethylsilyl containing amine analogs give rise to inefficient formation of *trans*- and *cis* isomers of phenyl- and cyano group containing pyrrolidine ring fused fullerenes. Importantly, the efficiencies of photoaddition reactions of C_{60} with α-aminonitriles are influenced by several factors including reaction condition (N_2 or O_2-purged), solvent polarity, the electronic and structural nature of the α-aminonitriles and additive. For example, photoreactions occurring in either oxygenated (O_2 purged) or 10% EtOH-toluene solutions, rather than either deoxygenated (N_2-purged) or 10% EtOH-ODCB solutions, require much shorter irradiation times to bring about high conversions of C_{60} as well as high product yields. In addition, short period irradiation of solutions containing C_{60} and α-aminonitriles, possessing arene rings that are either un-substituted or substituted with electron donating groups (H, Me and OMe), promotes high conversions and product yields. Finally, presence of trimethylsilyl group in α-aminonitrile substrates plays a crucial role in enhancing reaction efficiencies.

Finally, in contrast to thermal and photochemical strategies developed previously for fulleropyrrolidine synthesis, the currently developed SET-promoted photoaddition reactions of C_{60} with trimethylsilyl group containing amine substrates are mild and efficient, and as a results they should be highly useful in preparing a broader library of functionalized fulleropyrrolidines.

Experimental

General Procedure ^1H and ^{13}C NMR spectra were recorded using $CDCl_3$ solutions and chemical shifts are reported in parts per million 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 electrospray ionization unless otherwise noted. All starting materials used in the synthetic routes came from commercial sources. All new compounds described were isolated in >90% purity (by NMR analysis) unless noted otherwise.

General procedure for synthesis of *N*-arylmethyl-*N*-trimethylsilylmethyl substituted α-aminonitriles 11a-11k. Individual solutions of secondary *N*-α-trimethylsilylmethyl-*N*-benzylamines[19] (5 mmol) in acetonitrile (100 mL) containing K_2CO_3 (10 mmol) and 2-iodoacetonitrile (4.5 mmol) were stirred for 12 h at room temperature and concentrated in vacuo to give residues that were partitioned between water and CH_2Cl_2. The CH_2Cl_2 layers were dried and concentrated in vacuo to afford residues that were subjected to silica gel column chromatography (EtOAc/hexane = 1: 15 - 1: 30) to yield corresponding α-aminonitiriles **11a**[18] (91%), **11b** (74%), **11c** (78%), **11d** (85%), **11e** (75%), **11f** (75%), **11g** (74%), **11h** (75%), **11i** (78%), **11j** (78%) and **11k** (66%).

11a (liq): ^1H-NMR 0.12 (s, 9H), 2.18 (s, 2H), 3.40 (s, 2H), 3.62 (s, 2H), 7.27-7.34 (m, 5H).

11b (liq): ^1H-NMR 0.13 (s, 9H), 2.20 (s, 2H), 2.40 (s, 3H), 3.36 (s, 2H), 3.63 (s, 2H), 7.17-7.21 (m, 3H), 7.29-7.32 (m, 1H); ^{13}C-NMR -1.9, 18.9, 44.1, 46.2, 60.0, 114.5, 125.6, 127.5, 129.7, 130.3, 135.1, 137.4; HRMS (ESI) *m/z* 269.1449 (M+Na, $C_{14}H_{22}N_2SiNa$ requires 269.1450).

11c (liq): ^1H-NMR 0.15 (s, 9H), 2.18 (s, 2H), 2.36 (s, 3H), 3.39 (s, 2H), 3.58 (s, 2H), 7.09-7.15 (m, 3H), 7.20-7.25 (m, 1H); ^{13}C-NMR -1.8, 21.2, 44.7, 46.3, 61.0, 114.5, 125.7, 128.2, 128.3, 129.3, 137.3, 137.9; HRMS (ESI) *m/z* 269.1461 (M+Na, $C_{14}H_{22}N_2SiNa$ requires 269.1450).

11d (liq): ^{1}H-NMR 0.10 (s, 9H), 2.14 (s, 2H), 2.32 (s, 3H), 3.36 (s, 2H), 3.54 (s, 2H), 7.12 (d, 2H, J = 8.1 Hz), 7.20 (d, 2H, J = 8.1 Hz); ^{13}C-NMR -1.1, 21.6, 45.3, 46.9, 61.4, 115.1, 129.3, 129.7, 135.0, 137.7; HRMS (ESI) *m/z* 269.1473 (M+Na, $C_{14}H_{22}N_2SiNa$ requires 269.1450).

11e (liq): ^{1}H-NMR 0.15 (s, 9H), 2.20 (s, 2H), 2.33 (s, 3H), 2.37 (s, 3H), 3.35 (s, 2H), 3.60 (s, 2H), 6.97-6.70 (m, 2H), 7.19 (d, 1H, J = 7.5 Hz); ^{13}C-NMR -1.9, 18.8, 20.7, 43.9, 46.2, 59.8, 114.4, 126.2, 129.8, 131.1, 132.0, 137.0, 137.2; HRMS (FAB) *m/z* 283.1609 (M+Na, $C_{15}H_{24}N_2SiNa$ requires 283.1606).

11f (liq): ^{1}H-NMR 0.10 (s, 9H), 2.12 (s, 2H), 3.33 (s, 2H), 3.50 (s, 2H), 3.75 (s, 3H), 6.83 (d, 2H, J = 8.7 Hz), 7.21 (d, 2H, J = 8.7 Hz); ^{13}C-NMR -1.9, 44.4, 46.0, 54.8, 60.3, 113.6, 114.4, 129.3, 129.7, 158.8; HRMS (FAB) *m/z* 285.1397 (M+Na, $C_{14}H_{22}N_2OSiNa$ requires 285.1399).

11g (liq): ^{1}H-NMR 0.09 (s, 9H), 2.15 (s, 2H), 3.39 (s, 2H), 3.64 (s, 2H), 6.98-7.04 (m, 1H), 7.06-7.11 (m, 1H), 7.20-7.28 (m, 1H), 7.32-7.37 (m, 1H); ^{13}C-NMR -1.9, 44.9, 46.3, 54.2, 114.5, 115.4 (d, $J_{C\text{-}F}$ = 86.7 Hz), 123.9 (d, $J_{C\text{-}F}$ = 14.1 Hz), 124.2 (d, $J_{C\text{-}F}$ = 56.4 Hz), 129.3 (d, $J_{C\text{-}F}$ = 32.7 Hz), 130.9 (d, $J_{C\text{-}F}$ = 16.5 Hz), 161.2 (d, $J_{C\text{-}F}$ = 985.8 Hz); HRMS (FAB) *m/z* 273.1196 (M+Na, $C_{13}H_{19}FN_2SiNa$ requires 273.1199).

11h (liq): ^{1}H-NMR 0.09 (s, 9H), 2.13 (s, 2H), 3.38 (s, 2H), 3.57 (s, 2H), 6.90-6.96 (m, 1H), 7.01-7.08 (m, 2H), 7.22-7.29 (m, 1H); ^{13}C-NMR -1.9, 44.8, 46.1, 60.6, 114.3, 114.4 (d, $J_{C\text{-}F}$ = 76.5 Hz), 115.2 (d, $J_{C\text{-}F}$ = 85.2 Hz), 124.1 (d, $J_{C\text{-}F}$ = 11.1 Hz), 129.9 (d, $J_{C\text{-}F}$ = 32.7 Hz), 140.1 (d, $J_{C\text{-}F}$ = 28.2 Hz), 162.8 (d, $J_{C\text{-}F}$ = 978.6 Hz); HRMS (FAB) *m/z* 273.1193 (M+Na, $C_{13}H_{19}FN_2SiNa$ requires 273.1199).

11i (liq): ^{1}H-NMR 0.09 (s, 9H), 2.13 (s, 2H), 3.37 (s, 2H), 3.55 (s, 2H), 6.97-7.04 (m, 2H), 7.25-7.30 (m, 2H); ^{13}C-NMR -2.3, 44.2, 45.6, 60.1, 113.9, 114.8 (d, $J_{C\text{-}F}$ = 84.6 Hz), 129.9 (d, $J_{C\text{-}F}$ = 31.5 Hz), 133.0 (d, $J_{C\text{-}F}$ = 12.9 Hz), 161.7 (d, $J_{C\text{-}F}$ = 977.1 Hz); HRMS (FAB) *m/z* 273.1221 (M+Na, $C_{13}H_{19}FN_2SiNa$ requires 273.1199).

11j (liq): ^{1}H-NMR 0.06 (s, 9H), 2.11 (s, 2H), 3.37 (s, 2H), 3.58 (s, 2H), 6.70-6.84 (m, 2H), 7.26-7.34 (m, 1H); ^{13}C-NMR -2.1, 44.7, 46.0, 53.7, 10.7 (t, J_{C-F} = 101.7 Hz), 111.0 (dd, J_{C-F} = 83.6 Hz, 15Hz), 114.3, 120.2 (dd, J_{C-F} = 57.5 Hz, 14.7 Hz), 131.7 (dd, J_{C-F} = 38.1 Hz, 23.1 Hz), 161.2 (dd, J_{C-F} = 996.5 Hz, 47.1 Hz), 162.2 (dd, J_{C-F} = 989.1 Hz, 47.4 Hz); HRMS (FAB) *m/z* 291.1104 (M+Na, $C_{13}H_{18}F_2N_2SiNa$ requires 291.1105).

11k (liq): ^{1}H-NMR 0.10 (s, 9H), 2.16 (s, 2H), 3.39 (s, 2H), 3.65 (s, 2H), 7.44 (d, 2H, J = 7.8 Hz), 7.57 (d, 2H, J = 7.8 Hz); ^{13}C-NMR -1.8, 45.0, 46.3, 60.8, 114.3, 125.4 (q, J_{C-F} = 15 Hz), 128.9, 141.7; HRMS (FAB) *m/z* 301.1333 (M+H, $C_{14}H_{20}F_3N_2Si$ requires 301.1342).

General procedure of photoreactions of C_{60} with α-aminonitriles 11a-11k. Photochemical reactions were conducted using an apparatus consisting of a 450 W Hanovia medium vapor pressure mercury lamp surrounded by a flint glass filter (>300 nm). Nitrogen or oxygen-purged 10% EtOH-toluene or 10% EtOH-ODCB solutions (220 mL) containing C_{60} (0.278 mmol, 1.26 mM) and the α-aminonitriles **11a-11k** (0.555 mmol, 2.5 mM) were irradiated for a fixed time period given below. Photolysates were concentrated in vacuo and the unreacted C_{60} was recovered by filtration using $CHCl_3$ to determine conversion yields. Photoproducts were separated by using silica gel column chromatographic isolation (CS_2) of crude photolysates.

Photoreaction of C_{60} with 11a. *In N_2-purged, 10% EtOH-toluene solution*: 2 h irradiation (83% conversion), column chromatography (CS_2) to yield **12a** (42%) and **13a** (13%). *In O_2-purged, 10% EtOH-toluene solution*: 1 h irradiation (94% conversion), column chromatography (CS_2) to yield **12a** (44%) and **13a** (3%); *In N_2-purged, 10% EtOH-ODCB solution*: 3 h irradiation (87% conversion), column chromatography (CS_2) to yield **12a** (39%) and **13a** (3%). *In O_2-purged, 10% EtOH-ODCB solution*: 2 h irradiation (85% conversion), column chromatography (CS_2) to yield **12a** (45%).

12a (sol, mp > 400 ^{o}C): ^{1}H-NMR 0.58 (s, 9H), 4.04 (d, 1H, J = 12.3 Hz), 4.37 (s, 1H), 4.90 (d, 1H, J = 12.3 Hz), 5.34 (s, 1H), 7.35-7.40 (m, 1H), 7.43-7.48 (m, 2H), 7.70 (d, 1H, J = 7.2 Hz); ^{13}C-

NMR ($CDCl_3$ + CS_2) 0.5, 55.7, 66.6, 66.8, 73.1, 74.2, 114.8, 128.2, 128.6, 129.1, 136.3, 136.4, 136.6, 137.3, 138.7, 138.8, 139.8, 139.9, 141.3, 141.4, 141.6 (2C), 141.8, 141.9, 142.0, 142.4, 142.5, 142.8, 142.9, 144.1, 144.2, 144.4, 144.9, 145.0, 145.1, 145.3 (2C), 145.4, 145.8 (2C), 146.1, 146.7, 147.0; HRMS (MALDI-TOF) *m/z* 949.1163 (M-H, $C_{73}H_{17}N_2Si$ requires 949.1166).

13a (sol, mp > 400 °C): ^{1}H-NMR 4.30 (d, 1H, *J* = 12.9 Hz), 4.57 (d, 1H, *J* = 9.9 Hz), 4.58 (d, 1H, *J* = 12.9 Hz), 4.71 (d, 1H, *J* = 9.9 Hz), 5.44 (s, 1H), 7.37-7.42 (m, 1H), 7.46-7.51 (m, 2H), 7.72 (d, 1H, *J* = 6.9 Hz); ^{13}C-NMR ($CDCl_3$ + CS_2) 55.5, 64.2, 65.5, 68.6, 71.9, 114.4, 128.1, 128.7, 128.9, 135.5, 135.8, 136.3, 136.9, 137.8, 139.7, 139.8, 140.0, 140.1, 141.5 (2C), 141.6 (2C), 141.7 (3C), 141.8, 141.9, 142.0, 142.3, 142.4, 142.5, 142.8, 144.1, 144.2, 144.7 (2C), 145.1, 145.2 (2C), 145.4 (2C), 145.5, 145.6, 145.8, 145.9, 146.0, 146.1 (2C), 147.1, 147.2, 149.3, 151.6, 151.9, 154.0; HRMS (MALDI-TOF) *m/z* 877.0775 (M-H, $C_{70}H_9N_2$ requires 877.0771).

Photoreaction of C_{60} with 11b. *In N_2-purged, 10% EtOH-toluene solution*: 2 h irradiation (85% conversion), column chromatography (CS_2) to yield **12b** (40%). *In O_2-purged, 10% EtOH-toluene solution*: 1 h irradiation (95% conversion), column chromatography (CS_2) to yield **12b** (47%); *In N_2-purged, 10% EtOH-ODCB solution*: 3 h irradiation (80% conversion), column chromatography (CS_2) to yield **12b** (35%). *In O_2-purged, 10% EtOH-ODCB solution*: 2 h irradiation (83% conversion), column chromatography (CS_2) to yield **12b** (39%) (sol, mp > 400 °C). ^{1}H-NMR 0.58 (s, 9H), 2.76 (s, 3H), 4.11 (d, 1H, *J* = 12 Hz), 4.37 (s, 1H), 4.89 (d, 1H, *J* = 12 Hz), 5.23 (s, 1H), 7.28-7.32 (m, 3H), 7.68-7.71 (m, 1H); ^{13}C-NMR ($CDCl_3$ + CS_2) 0.8, 19.9, 54.9, 66.9, 72.9, 74.2, 115.1, 126.4, 128.4, 130.1, 131.0, 134.3, 136.1, 136.2, 137.3, 137.4, 138.6, 138.8, 139.7, 141.3, 141.4, 141.5 (2C), 141.7, 141.8 (2C), 141.9, 142.0, 142.4 (2C), 142.5, 142.7, 142.8, 144.1 (2C), 144.3 (2C), 144.4, 144.9, 145.0 (2C), 145.1, 145.2, 145.3, 145.4 (2C), 145.7 (2C), 145.8, 146.1, 146.9, 147.0, 150.3, 151.9, 153.2, 153.8; HRMS (MALDI-TOF) *m/z* 963.1331 (M-H, $C_{74}H_{19}N_2Si$ requires 963.1323).

Photoreaction of C_{60} with 11c. *In N_2-purged, 10% EtOH-toluene solution*: 2 h irradiation (85%

conversion), column chromatography (CS_2) to yield **12c** (42%). *In O_2-purged, 10% EtOH-toluene solution*: 1 h irradiation (96% conversion), column chromatography (CS_2) to yield **12c** (50%); *In N_2-purged, 10% EtOH-ODCB solution*: 3 h irradiation (79% conversion), column chromatography (CS_2) to yield **12c** (35%). *In O_2-purged, 10% EtOH-ODCB solution*: 2 h irradiation (82% conversion), column chromatography (CS_2) to yield **12c** (39%) (sol, mp > 400 ^oC). ^{1}H-NMR 0.58 (s, 9H), 2.46 (s, 3H), 4.01 (d, 1H, *J* = 12.3 Hz), 4.38 (s, 1H), 4.88 (d, 1H, *J* = 12.3 Hz), 5.38 (s, 1H), 7.19 (d, 1H, *J* = 7.5 Hz), 7.35 (t, 1H, *J* = 7.5 Hz), 7.48 (s, 1H), 7.54 (d, 1H, *J* = 7.5 Hz); ^{13}C-NMR ($CDCl_3$ + CS_2) 0.6, 21.4, 55.7, 66.7, 66.8, 73.1, 74.3, 115.0, 125.7, 129.0 (2C), 129.4, 136.4, 136.6, 138.5, 138.7, 138.8, 139.8, 141.4 (2C), 141.5, 141.6 (2C), 141.8, 141.9, 142.0 (2C), 142.4, 142.5, 142.8, 144.1 (2C), 144.3, 144.4 (2C), 145.1, 145.2, 145.3 (2C), 145.4 (2C), 145.7, 145.8 (2C), 146.1, 146.7, 147.0 (2C), 150.5, 152.2, 153.1, 153.5; ; HRMS (MALDI-TOF) *m/z* 963.1333 (M-H, $C_{74}H_{19}N_2Si$ requires 963.1323).

Photoreaction of C_{60} with 11d. *In N_2-purged, 10% EtOH-toluene solution*: 2 h irradiation (86% conversion), column chromatography (CS_2) to yield **12d** (42%), **13d** (17%) and **14** (4%). *In O_2-purged, 10% EtOH-toluene solution*: 1 h irradiation (96% conversion), column chromatography (CS_2) to yield **12d** (44%), **13d** (5%) and **14** (1%); *In N_2-purged, 10% EtOH-ODCB solution*: 3 h irradiation (80% conversion), column chromatography (CS_2) to yield **12d** (37%) and **13d** (5%). *In O_2-purged, 10% EtOH-ODCB solution*: 2 h irradiation (84% conversion), column chromatography (CS_2) to yield **12d** (44%).

12d (sol, mp > 400 ^oC): ^{1}H-NMR 0.58 (s, 9H), 2.43 (s, 3H), 4.02 (d, 1H, *J* = 12.3 Hz), 4.38 (s, 1H), 4.88 (d, 1H, *J* = 12.3 Hz), 5.38 (s, 1H), 7.28 (d, 2H, *J* = 7.8 Hz), 7.61 (d, 2H, *J* = 7.8 Hz); ^{13}C-NMR ($CDCl_3$ + CS_2) 0.6, 21.2, 55.4, 66.6, 66.7, 73.0, 74.3, 115.0128.6, 129.7, 133.6, 136.3, 136.4, 137.8, 138.7 (2C), 139.8, 141.2, 141.3, 141.4, 141.5 (2C), 141.7 (2C), 141.9, 142.0, 142.3, 142.4, 142.5, 144.1, 144.3 (2C), 144.4, 144.8, 145.0, 145.1 (2C), 145.2, 145.3 (2C), 145.4, 145.7 (2C), 145.8, 146.1 (2C), 146.7, 147.0 (2C), 150.4, 152.1, 153.1, 153.5; HRMS (MALDI-TOF) *m/z* 963.1322 (M-H, $C_{74}H_{19}N_2Si$ requires 963.1323).

13d (sol, mp > 400 ^oC): ^{1}H-NMR 2.42 (s, 3H), 4.25 (d, 1H, *J* = 12.9 Hz), 4.54 (d, 1H, *J* = 12.9 Hz), 4.55 (d, 1H, *J* = 9.9 Hz), 4.69 (d, 1H, *J* = 9.9 Hz), 5.43 (s, 1H), 7.29 (d, 2H, *J* = 7.8 Hz), 7.60 (d, 2H, *J* = 7.8 Hz); ^{13}C-NMR ($CDCl_3$ + CS_2) 21.2, 55.3, 64.2, 65.5, 68.7, 72.0, 114.8, 128.8, 129.6, 132.8, 137.8, 137.9, 140.2, 141.6, 141.7 (3C), 141.8 (3C), 142.0 (2C), 142.1 (2C), 142.5, 142.6, 142.9, 144.2, 144.3, 144.5, 144.8, 144.9, 145.0, 145.1, 145.2, 145.3 (2C), 145.4, 145.5, 145.6 (2C), 145.7, 145.8, 145.9, 146.0, 146.1, 146.2 (2C), 147.2, 147.3, 149.5, 151.7, 152.1, 154.2; ; HRMS (MALDI-TOF) *m/z* 891.0930 (M-H, $C_{71}H_{11}N_2$ requires 891.0928).

14 (sol, mp > 400 ^oC): ^{1}H-NMR 0.40 (s, 9H), 2.36 (s, 3H), 2.40 (d, 1H, *J* = 14.7 Hz), 2.81 (d, 1H, *J* = 14.7 Hz), 5.35 (s, 1H), 5.82 (s, 1H), 7.20 (d, 2H, *J* = 7.5 Hz), 7.58 (s, 2H); ^{13}C-NMR ($CDCl_3$ + CS_2) -1.6, 21.2, 39.3, 67.7, 70.3, 74.6, 81.5, 114.6, 132.3, 135.6, 136.0, 136.9, 137.5, 138.4, 139.4, 139.8 (2C), 141.4 (2C), 141.5, 141.6 (3C), 141.7, 141.8, 141.9, 142.0, 142.3, 142.4, 142.5, 142.8 (2C), 144.1 (2C), 144.2, 144.4, 144.5, 144.8, 144.9, 145.1, 145.2 (2C), 145.3, 145.5 (2C), 145.8, 145.9, 146.0, 146.1, 146.2, 147.2, 151.7, 152.4, 152.7; HRMS (MALDI-TOF) *m/z* 963.1327 (M-H, $C_{74}H_{19}N_2Si$ requires 963.1323).

Photoreaction of C_{60} with 11e. *In N_2-purged, 10% EtOH-toluene solution*: 2 h irradiation (87% conversion), column chromatography (CS_2) to yield **12e** (50%). *In O_2-purged, 10% EtOH-toluene solution*: 1 h irradiation (96% conversion), column chromatography (CS_2) to yield **12e** (49%); *In N_2-purged, 10% EtOH-ODCB solution*: 3 h irradiation (82% conversion), column chromatography (CS_2) to yield **112e** (43%). *In O_2-purged, 10% EtOH-ODCB solution*: 2 h irradiation (93% conversion), column chromatography (CS_2) to yield **12e** (46%) (sol, mp > 400 ^oC). ^{1}H-NMR 0.57 (s, 9H), 2.37 (s, 3H), 2.72 (s, 3H), 4.05 (d, 1H, *J* = 12 Hz), 4.35 (s, 1H), 4.85 (d, 1H, *J* = 12 Hz), 5.23 (s, 1H), 7.09 (d, 1H, *J* = 8.1 Hz), 7.10 (s, 1H), 7.56 (d, 1H, *J* = 8.1 Hz); ^{13}C-NMR ($CDCl_3$ + CS_2) 0.8, 19.8, 21.0, 54.7, 66.9 (2C), 72.9, 74.2, 115.2, 127.0, 130.2, 131.2, 131.9, 136.1, 136.2, 137.2, 138.0, 138.6, 138.8, 139.8 (2C), 141.3, 141.5 (3C), 141.7, 141.8 (2C), 141.9, 142.0, 142.4, 142.5 (2C), 142.8, 144.3 (2C), 144.4, 145.0 (2C), 145.1, 145.2, 145.3, 145.4, 145.5, 145.7, 145.8 (2C), 146.1 (2C), 146.9, 147.0 (2C), 150.4, 152.0, 153.3, 153.9; HRMS (MALDI-TOF) *m/z* 977.1475 (M-H, $C_{75}H_{21}N_2Si$ requires 977.1479).

Photoreaction of C_{60} with 11f. *In N_2-purged, 10% EtOH-toluene solution*: 2 h irradiation (85% conversion), column chromatography (CS_2) to yield **12f** (43%) and **13f** (15%). *In O_2-purged, 10% EtOH-toluene solution*: 1 h irradiation (96% conversion), column chromatography (CS_2) to yield **12f** (49%) and **13f** (5%); *In N_2-purged, 10% EtOH-ODCB solution*: 3 h irradiation (89% conversion), column chromatography (CS_2) to yield **12f** (46%) and **13f** (trace). *In O_2-purged, 10% EtOH-ODCB solution*: 2 h irradiation (96% conversion), column chromatography (CS_2) to yield **12f** (52%).

12f (sol, mp > 400 ^{o}C): ^{1}H-NMR 0.57 (s, 9H), 3.84 (s, 3H), 4.00 (d, 1H, J = 12 Hz), 4.35 (s, 1H), 4.84 (d, 1H, J = 12 Hz), 5.36 (s, 1H), 6.97 (d, 2H, J = 8.4 Hz), 7.61 (d, 2H, J = 8.4 Hz); ^{13}C-NMR ($CDCl_3$ + CS_2) 0.6, 54.8, 55.1, 66.5, 66.7, 73.0, 74.3, 114.3, 115.0, 128.5, 129.8, 136.3, 136.4, 138.7, 139.8, 141.3 (2C), 141.4, 141.5, 141.6, 141.7, 141.8, 141.9, 142.0, 142.4 (2C), 142.5 (2C), 142.8, 144.1, 144.3, 144.4, 144.9, 145.1 (2C), 145.2, 145.3 (2C), 145.4, 145.7 (2C), 145.8 (2C), 146.1 (2C), 146.7, 147.0 (2C), 150.5, 152.2, 153.2, 153.5, 159.3; HRMS (MALDI-TOF) *m/z* 979.1278 (M-H, $C_{74}H_{19}N_2OSi$ requires 979.1272).

13f (sol, mp > 400 ^{o}C): ^{1}H-NMR 3.85 (s, 3H), 4.22 (d, 1H, J = 12.9 Hz), 4.51 (d, 1H, J = 12.9 Hz), 4.55 (d, 1H, J = 9.6 Hz), 4.68 (d, 1H, J = 9.6 Hz), 5.39 (s, 1H), 6.97 (d, 2H, J = 8.7 Hz), 7.61 (d, 2H, J = 8.7 Hz); ^{13}C-NMR ($CDCl_3$ + CS_2) 54.8, 54.9, 64.1, 65.3, 68.6, 71.8, 114.2, 127.6, 128.0, 128.7, 129.9, 135.5, 136.3, 136.9, 137.8, 139.7, 139.8, 140.0, 140.1, 141.5 (2C), 141.6 (2C), 141.7 (2C), 141.8, 141.9, 142.0, 142.3, 142.4, 142.8, 144.1, 144.4, 144.7, 145.1, 145.2 (3C), 145.4 (2C), 145.6, 145.9, 146.0, 146.1 (2C), 147.1, 147.2, 151.6, 152.0, 154.1, 159.3; HRMS (MALDI-TOF) *m/z*

907.0874 (M-H, $C_{71}H_{11}N_2O$ requires 907.0877).

Photoreaction of C_{60} with 11g. *In N_2-purged, 10% EtOH-toluene solution*: 6 h irradiation (81% conversion), column chromatography (CS_2) to yield **12g** (39%). *In O_2-purged, 10% EtOH-toluene solution*: 3 h irradiation (93% conversion), column chromatography (CS_2) to yield **12g** (48%); *In N_2-purged, 10% EtOH-ODCB solution*: 6 h irradiation (65% conversion), column chromatography (CS_2) to yield **12g** (26%). *In O_2-purged, 10% EtOH-ODCB solution*: 5 h irradiation (89% conversion), column chromatography (CS_2) to yield **12g** (43%) (sol, mp > 400 ^oC). ^1H-NMR 0.57 (s, 9H), 4.21 (d, 1H, J = 12.6 Hz), 4.41 (s, 1H), 4.97 (d, 1H, J = 12.6 Hz), 5.39 (s, 1H), 7.16-7.22 (m, 1H), 7.26-7.31 (m, 1H), 7.38-7.46 (m, 1H), 7.78-7.83 (m, 1H); ^{13}C-NMR ($CDCl_3$ + CS_2) 0.5, 49.3, 67.0 (2C), 73.3, 74.2, 115.0, 115.9 (d, J_{C-F} = 84.9 Hz), 123.6 (d, J_{C-F} = 56.4 Hz), 124.5 (d, J_{C-F} = 15 Hz), 125.1, 128.0, 128.7, 130.0 (d, J_{C-F} = 32.1 Hz), 130.7 (d, J_{C-F} = 14.7 Hz), 136.4, 136.5, 137.2, 138.7, 139.7, 139.8, 141.3, 141.4, 141.5, 141.6, 141.8, 141.9, 142.0, 142.4, 142.5, 142.8 (2C), 144.1 (2C), 144.3, 144.9, 145.0, 145.1, 145.2, 145.3 (2C), 145.4, 145.6, 145.7, 145.8 (2C), 146.1, 146.7, 147.0, 150.4, 152.2, 152.9, 153.4, 161.3 (d, J_{C-F} = 917.4 Hz); HRMS (MALDI-TOF) *m/z* 967.1076 (M-H, $C_{73}H_{16}FN_2Si$ requires 967.1072).

Photoreaction of C_{60} with 11h. *In N_2-purged, 10% EtOH-toluene solution*: 6 h irradiation (84% conversion), column chromatography (CS_2) to yield **12h** (41%). *In O_2-purged, 10% EtOH-toluene solution*: 3 h irradiation (94% conversion), column chromatography (CS_2) to yield **12h** (48%); *In N_2-purged, 10% EtOH-ODCB solution*: 6 h irradiation (62% conversion), column chromatography (CS_2) to yield **12h** (30%). *In O_2-purged, 10% EtOH-ODCB solution*: 5 h irradiation (86% conversion), column chromatography (CS_2) to yield **12h** (46%) (sol, mp > 400 ^oC). ^1H-NMR 0.59 (s, 9H), 4.07 (d, 1H, J = 12.3 Hz), 4.38 (s, 1H), 4.90 (d, 1H, J = 12.3 Hz), 5.35 (s, 1H), 7.06-7.11 (m, 1H), 7.40-7.52 (m, 3H); ^{13}C-NMR ($CDCl_3$ + CS_2) 0.4, 55.1, 66.5, 66.7, 73.0, 74.0, 114.4, 115.1 (d, J_{C-F} = 58.2 Hz), 115.4 (d, J_{C-F} = 59.4 Hz), 124.0 (d, J_{C-F} = 11.7 Hz), 130.5 (d, J_{C-F} = 31.5 Hz), 136.3, 136.5, 137.2, 138.6, 138.7, 139.1 (d, $J_{C\text{-}F}$ = 27.6 Hz), 139.7, 141.2, 141.3 (2C), 141.4, 141.5, 141.7 (2C), 141.8, 142.0, 142.3, 142.4, 142.7, 142.8, 144.0, 144.1, 144.2, 144.3, 144.8, 144.9, 145.0, 145.1, 145.2, 145.3, 145.4, 145.6, 145.7 (2C), 145.8, 146.1, 146.5, 146.9 (2C), 150.2, 151.9, 152.8, 162.9 (d, $J_{C\text{-}F}$ = 1002 Hz); HRMS (MALDI-TOF) *m/z* 967.1072 (M-H, $C_{73}H_{16}FN_2Si$ requires 967.1072).

Photoreaction of C_{60} with 11i. *In N_2-purged, 10% EtOH-toluene solution*: 6 h irradiation (69% conversion), column chromatography (CS_2) to yield **12i** (40%). *In O_2-purged, 10% EtOH-toluene solution*: 3 h irradiation (86% conversion), column chromatography (CS_2) to yield **12i** (43%); *In N_2-purged, 10% EtOH-ODCB solution*: 6 h irradiation (80% conversion), column chromatography (CS_2) to yield **12i** (33%). *In O_2-purged, 10% EtOH-ODCB solution*: 5 h irradiation (88% conversion), column chromatography (CS_2) to yield **12i** (46%) (sol, mp > 400 ^oC). ^{1}H-NMR 0.58 (s, 9H), 4.06 (d, 1H, *J* = 12.3 Hz), 4.38 (s, 1H), 4.88 (d, 1H, *J* = 12.3 Hz), 5.34 (s, 1H), 7.13-7.19 (m, 2H), 7.69-7.73 (m, 2H); ^{13}C-NMR ($CDCl_3$ + CS_2) 0.5, 54.9, 66.7, 66.8, 73.1, 74.2, 114.9, 116.0 (d, $J_{C\text{-}F}$ = 85.2 Hz), 130.2 (d, $J_{C\text{-}F}$ = 31.8 Hz), 132.4 (d, $J_{C\text{-}F}$ = 12.6 Hz), 136.3 (2C), 136.5, 137.2, 138.7, 138.8, 139.8, 139.9, 141.3, 141.4, 141.6 (2C), 141.8, 141.9, 142.0, 142.4, 142.5, 142.8, 142.9, 144.1 (2C), 144.3, 144.9, 145.0, 145.1, 145.2, 145.3 (2C), 145.4, 145.7 (2C), 145.8, 145.9, 146.1, 146.7, 147.0 (2C), 150.3, 152.0, 153.0, 153.4, 162.4 (d, $J_{C\text{-}F}$ = 978.6 Hz); HRMS (MALDI-TOF) *m/z* 967.1076 (M-H, $C_{73}H_{16}FN_2Si$ requires 967.1072).

Photoreaction of C_{60} with 11j. *In N_2-purged, 10% EtOH-toluene solution*: 8 h irradiation (85% conversion), column chromatography (CS_2) to yield **12j** (44%). *In O_2-purged, 10% EtOH-toluene solution*: 5 h irradiation (90% conversion), column chromatography (CS_2) to yield **12j** (53%); *In N_2-purged, 10% EtOH-ODCB solution*: 10 h irradiation (52% conversion), column chromatography (CS_2) to yield **12j** (26%). *In O_2-purged, 10% EtOH-ODCB solution*: 10 h irradiation (76% conversion), column chromatography (CS_2) to yield **12j** (39%) (sol, mp > 400 ^oC). ^{1}H-NMR 0.57 (s, 9H), 4.17 (d, 1H, *J* = 12.6 Hz), 4.38 (s, 1H), 4.92 (d, 1H, *J* = 12.6 Hz), 5.36 (s, 1H), 6.90-7.05 (m, 2H), 7.75-7.82 (m, 1H); ^{13}C-NMR ($CDCl_3$ + CS_2) 0.5, 48.9, 66.8, 66.9, 73.2, 74.1, 104.4 (t, $J_{C\text{-}F}$ = 100.5 Hz), 111.6 (dd, $J_{C\text{-}F}$ = 84.2 Hz, 15.3 Hz), 114.8, 119.6 (dd, $J_{C\text{-}F}$ = 57.8 Hz, 15.6 Hz), 131.6 (dd, $J_{C\text{-}F}$ = 37.8 Hz, 21.6 Hz), 136.3, 136.4 (2C), 137.2, 138.7, 139.7, 139.8, 141.3 (2C), 141.5 (2C), 141.6, 141.7 (2C), 141.8 (2C), 142.0, 142.4 (2C), 142.5, 142.7, 142.8, 144.0, 144.1, 144.2, 144.3 (2C), 144.8, 144.9, 145.0, 145.1, 145.2 (2C), 145.3, 145.4, 145.5, 145.7 (2C), 145.8 (2C), 146.1, 146.5, 146.9, 147.0, 150.2, 152.0, 152.7, 153.2, 161.3 (dd, $J_{C\text{-}F}$ = 1023.9 Hz, 46.2 Hz), 162.8 (dd, $J_{C\text{-}F}$ = 999.9 Hz, 46.2 Hz); HRMS (MALDI-TOF) *m/z* 985.0977 (M-H, $C_{73}H_{15}F_2N_2Si$ requires 985.0978).

Photoreaction of C_{60} with 11k. *In N_2-purged, 10% EtOH-toluene solution*: 8 h irradiation (80% conversion), column chromatography (CS_2) to yield **12k** (40%). *In O_2-purged, 10% EtOH-toluene solution*: 5 h irradiation (91% conversion), column chromatography (CS_2) to yield **12k** (44%); *In N_2-purged, 10% EtOH-ODCB solution*: 10 h irradiation (41% conversion), column chromatography (CS_2) to yield **12k** (23%). *In O_2-purged, 10% EtOH-ODCB solution*: 10 h irradiation (74% conversion), column chromatography (CS_2) to yield **12k** (37%) (sol, mp > 400 ^{o}C). ^{1}H-NMR 0.58 (s, 9H), 4.17 (d, 1H, *J* = 12.9 Hz), 4.41 (s, 1H), 4.97 (d, 1H, *J* = 12.9 Hz), 5.33 (s, 1H), 7.74 (d, 2H, *J* = 8.1 Hz), 7.88 (d, 2H, *J* = 8.1 Hz); ^{13}C-NMR ($CDCl_3$ + CS_2) 0.4, 55.2, 66.7 (2C), 73.0, 74.0, 114.5, 125.9 (q, J = 14.7 Hz), 128.8, 136.2 (2C), 138.7 (2C), 139.8, 140.6, 141.2, 141.3, 141.4, 141.5 (2C), 141.6, 141.7, 141.9 (2C), 142.4 (2C), 142.5, 142.7, 144.0, 144.1, 144.2 (2C), 144.8, 144.9, 145.0 (2C), 145.1, 145.2 (3C), 145.3, 145.4, 145.5, 145.7 (2C), 145.8 (2C), 146.1, 146.5, 146.9, 150.0, 151.8, 152.7, 153.1; HRMS (MALDI-TOF) *m/z* 1017.1050 (M-H, $C_{74}H_{16}F_3N_2Si$ requires 1017.1040).

General procedure for synthesis of *N*-arylmethyl-*N*-methyl substituted α-aminonitriles 24-26. Individual solutions of secondary *N*-methyl-*N*-benzylamines (5 mmol) in acetonitrile (100 mL) containing K_2CO_3 (10 mmol) and 2-iodoacetonitrile (4.5 mmol) were stirred for 12 h at room temperature and concentrated in vacuo to give residues that were partitioned between water and

CH_2Cl_2. The CH_2Cl_2 layers were dried and concentrated in vacuo to afford residues that were subjected to silica gel column chromatography (EtOAc/hexane = 1: 10 - 1: 20) to yield corresponding α-aminonitriles **24**[22] (81%), **25**[22] (77%) and **26** (70%).

24 (liq): ^{1}H-NMR 2.42 (s, 3H), 3.43 (s, 2H), 3.59 (s, 2H), 7.30-7.33 (m, 5H).

25 (liq): ^{1}H-NMR 2.33 (s, 3H), 2.42 (s, 3H), 3.42 (s, 2H), 3.55 (s, 2H), 7.14 (d, 2H, J = 7.8 Hz), 7.20 (d, 2H, J = 7.8 Hz).

26 (liq): ^{1}H-NMR 2.34 (s, 3H), 3.38 (s, 2H), 3.51 (s, 2H), 6.93-6.99 (m, 2H), 7.22-7.27 (m, 2H); ^{13}C-NMR 41.8, 43.8, 58.9, 114.2, 115.1 (d, $J_{C\text{-}F}$ = 84.9 Hz), 130.3 (d, $J_{C\text{-}F}$ = 32.4 Hz), 132.5 (d, $J_{C\text{-}F}$ = 12.3 Hz), 162.0 (d, $J_{C\text{-}F}$ = 977.1 Hz); HRMS (FAB) m/z 179.0981 (M+H, $C_{10}H_{12}N_2F$ requires 179.0979).

General procedure of photoreactions of C_{60} with α-aminonitiriles 24-26. Photochemical reactions were conducted using an apparatus consisting of a 450 W Hanovia medium vapor pressure mercury lamp surrounded by a flint glass filter (> 300 nm). Nitrogen or oxygen-purged 10% EtOH-toluene (220 mL) containing C_{60} (0.278 mmol, 1.26 mM) and the *N*-cyanomethyl-*N*-methyl-*N*-benzylamines **24-26** (0.555 mmol, 2.5 mM) were irradiated for a fixed time period given below. Photolysates were concentrated in vacuo and the unreacted C_{60} was recovered by filtration using $CHCl_3$. Photoproducts were then isolated by using silica gel column chromatographic isolation (CS_2) of crude photolysates.

Photoreaction of C_{60} with 24. *In O_2-purged, 10% EtOH-toluene solution*: 8 h irradiation (54% conversion), column chromatography (CS_2) to yield *trans*-**27** (22%) and *cis*-**27** (16%); 15 h irradiation (77% conversion), column chromatography (CS_2) to yield *trans*-**27** (26%) and *cis*-**27** (18%).

trans-**27** (sol, mp > 400 ^{o}C): ^{1}H-NMR 2.95 (s, 3H), 5.41 (s, 1H), 5.87 (s, 1H), 7.33-7.45 (m, 3H), 7.70-7.90 (m, 2H); ^{13}C-NMR ($CDCl_3$ + CS_2) 36.4, 68.3, 70.1, 75.1, 79.2, 114.5, 128.7, 128.8, 134.7, 135.1, 135.7, 136.0, 139.7, 139.8, 140.0, 141.2, 141.3, 141.4, 141.5 (2C), 141.6 (2C), 141.7, 141.8, 141.9, 142.0, 142.3 (2C), 142.4, 142.7, 144.0 (2C), 144.3, 144.4, 144.9, 145.0 (2C), 145.1, 145.3 (2C), 145.6, 145.7, 145.8 (2C), 146.0, 146.1, 147.0, 147.2, 149.4, 151.3, 151.9, 152.3; HRMS (MALDI-TOF) *m/z* 877.0773 (M-H, $C_{70}H_9N_2$ requires 877.0771).

cis-**27** (sol, mp > 400 ^oC): ^{1}H-NMR 2.97 (s, 3H), 5.01 (s, 1H), 5.07 (s, 1H), 7.35-7.45 (m, 3H), 7.60-7.80 (m, 2H); ^{13}C-NMR ($CDCl_3$ + CS_2) 38.6, 68.7, 70.0, 74.8, 82.1, 115.7, 128.8, 134.8, 135.0, 135.7, 136.1, 137.3, 139.3, 139.7 (2C), 140.0, 141.1, 141.3, 141.4 (2C), 141.5, 141.7 (2C), 141.8, 141.9, 142.0, 142.3 (2C), 142.4, 142.6, 142.7, 143.9, 144.2, 144.3, 144.8, 144.9 (2C), 145.0, 145.2, 145.3, 145.6 (2C), 145.7, 145.8, 145.9; HRMS (MALDI-TOF) *m/z* 877.0770 (M-H, $C_{70}H_9N_2$ requires 877.0771).

Photoreaction of C_{60} with 25. *In O_2-purged, 10% EtOH-toluene solution*: 8 h irradiation (53% conversion), column chromatography (CS_2) to yield *trans*-**28** (25%) and *cis*-**28** (8%); 15 h irradiation (78% conversion), column chromatography (CS_2) to yield *trans*-**28** (35%) and *cis*-**28** (11%).

trans-**28** (sol, mp > 400 ^oC): ^{1}H-NMR 2.36 (s, 3H), 2.93 (s, 3H), 5.36 (s, 1H), 5.85 (s, 1H), 7.21 (d, 2H, J = 7.8 Hz), 7.55-7.70 (m, 2H); ^{13}C-NMR ($CDCl_3$ + CS_2) 21.2, 36.4, 68.3, 70.1, 75.3, 79.1, 114.6, 129.4, 131.7, 135.7, 138.5, 139.4, 139.8, 141.4, 141.5 (2C), 141.6 (2C), 141.7, 141.8, 141.9 (2C), 142.0, 142.3, 142.5, 142.7, 142.8, 144.1 (2C), 144.2, 144.4 (2C), 145.0 (2C), 145.1, 145.2 (3C), 145.3, 145.4 (2C), 145.5, 145.7 (2C), 145.8, 145.9, 146.0, 146.1 (2C), 149.5, 151.6, 152.1, 152.4; HRMS (MALDI-TOF) *m/z* 891.0927 (M-H, $C_{71}H_{11}N_2$ requires 891.0928).

cis-**28** (sol, mp > 400 ^oC): ^{1}H-NMR 2.38 (s, 3H), 2.93 (s, 3H), 4.97 (s, 1H), 5.05 (s, 1H), 7.21 (d, 2H, J = 7.8 Hz), 7.60-7.70 (m, 2H); ^{13}C-NMR ($CDCl_3$ + CS_2) 21.1, 36.2, 68.5, 69.8, 74.7, 81.8, 115.7, 129.2, 131.6, 134.9, 135.5, 135.8, 136.7, 137.2, 138.3, 139.2 (2C), 139.6 (2C), 141.0, 141.2 (2C), 141.3 (2C), 141.4, 141.5, 141.6, 141.7, 141.8, 142.1, 142.2 (3C), 143.8 (2C), 143.9 (2C), 144.1 (2C), 144.2 (2C), 144.6, 144.7, 144.8 (3C), 145.0, 145.1, 145.3, 145.5, 145.6, 145.7 (2C), 145.8, 145.9, 146.0, 146.9 (2C), 149.8, 150.5, 151.1, 151.4; HRMS (MALDI-TOF) *m/z* 891.0925 (M-H, $C_{71}H_{11}N_2$ requires 891.0928).

Photoreaction of C_{60} with 26. *In O_2-purged, 10% EtOH-toluene solution*: 15 h irradiation (10% conversion), column chromatography (CS_2) to yield *trans*-**29** (2%) and *cis*-**29** (2%); 40 h irradiation (28% conversion), column chromatography (CS_2) to yield *trans*-**29** (7%) and *cis*-**29** (7%).

trans-**29** (sol, mp > 400 ^oC): ^{1}H-NMR 2.94 (s, 3H), 5.39 (s, 1H), 5.84 (s, 1H), 7.08-7.14 (m, 2H), 7.65-7.85 (m, 2H); ^{13}C-NMR ($CDCl_3$ + CS_2) 36.4, 68.3, 70.1, 75.1, 78.5, 115.9, 130.6 (d, J_{C-F} = 12.6 Hz), 135.8, 136.3, 136.9, 137.5, 139.9, 140.1, 141.4, 141.6 (2C), 141.8 (2C), 141.9, 142.0, 142.1, 142.4 (3C), 142.9, 144.0 (2C), 144.4, 144.8, 144.9, 145.0, 145.2, 145.3, 145.4, 145.6, 145.7 (2C), 145.9 (2C), 146.1, 146.2, 146.3, 147.1, 147.2, 149.3, 151.0, 151.1 (2C), 162.7 (d, J_{C-F} = 993 Hz); HRMS (MALDI-TOF) *m/z* 895.0678 (M-H, $C_{70}H_8FN_2$ requires 895.0677).

cis-**29** (sol, mp > 400 ^oC): ^{1}H-NMR 2.95 (s, 3H), 5.00 (s, 1H), 5.07 (s, 1H), 7.08-7.14 (m, 2H), 7.65-7.85 (m, 2H); ^{13}C-NMR ($CDCl_3$ + CS_2) 38.7, 68.8, 70.0, 74.8, 81.4, 114.3, 130.7 (d, J_{C-F} = 12.6 Hz), 135.2, 135.7, 136.2, 137.3, 139.5, 139.8, 141.5 (2C), 141.6, 141.7 (3C), 141.8, 142.0, 142.4 (3C), 142.5, 142.7, 142.8, 144.0, 144.2, 144.3, 144.9 (2C), 145.1 (2C), 145.3, 145.4 (2C), 145.5, 145.7, 145.8, 146.0 (2C), 146.1 (2C), 147.1, 147.2, 149.8, 150.6, 151.6, 152.2, 162.7 (d, J_{C-F} = 993 Hz); HRMS (MALDI-TOF) *m/z* 895.0678 (M-H, $C_{70}H_8FN_2$ requires 895.0677).

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Appendix A. Supplementary data

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

^{1}H and ^{13}C NMR spectra of all previously unidentified compounds, NOESY spectra of **12a**, **12d**, *cis*-**27** and *trans*-**28**, and UV-visible spectra of synthesized fulleropyrrolidines

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