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Method for the Synthesis of Amine-Functionalized Fullerenes Involving SET-Promoted Photoaddition Reactions of α-Silylamines

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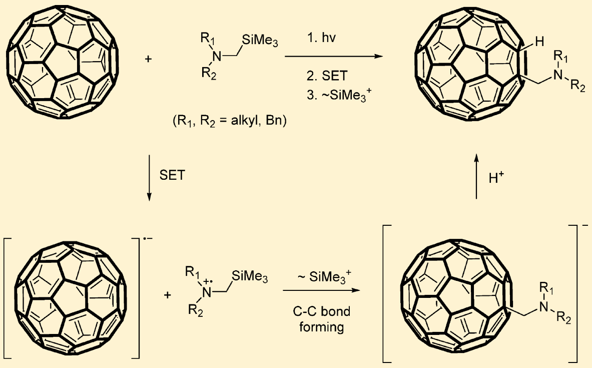
Ⓢ *Supporting Information*



ABSTRACT: A novel method for the preparation of structurally diverse fullerene derivatives, which relies on the use of single electron transfer (SET)-promoted photochemical reactions between fullerene C_{60} and α-trimethylsilylamines, has been developed. Photoirradiation of 10% EtOH−toluene solutions containing C_{60} and α-silylamines leads to high-yielding, regioselective formation of 1,2-adducts that arise through a pathway in which sequential SET-desilylation occurs to generate α-amino and C_{60} anion radical pair intermediates, which undergo C−C bond formation. Protonation of generated α-aminofullerene anions gives rise to formation of monoaddition products that possess functionalized α-aminomethyl-substituted 1,2-dihydrofullerene structures. Observations made in this effort show that the use of EtOH in the solvent mixture is critical for efficient photoproduct formation. In contrast to typical thermal and photochemical strategies devised previously for the preparation of fullerene derivatives, the new photochemical approach takes place under mild conditions and does not require the use of excess amounts of substrates. Thus, the method developed in this study could broaden the scope of fullerene chemistry by providing a simple photochemical strategy for large-scale preparation of highly substituted fullerene derivatives. Finally, the α-aminomethyl-substituted 1,2-dihydrofullerene photoadducts are observed to undergo photoinduced fragmentation reactions to produce C_{60} and the corresponding *N*-methylamines.

■ INTRODUCTION

Since the time of the first report describing its preparation using laser vaporization of graphite by Kroto et al.[1] and its large-scale synthesis,[2] fullerene (C_{60}) has received intense interest owing to its chemical and physical properties and its broad applications in the material[3−11] and biological[12−20] sciences. Of specific interest are [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) and fulleropyrrolidine, which have found widespread applications as n-type organic conducting materials in organic field effect transistor and organic photovoltaic devices. These applications are a consequence of the unique and useful electronic properties of fullerenes, such as high electron affinities,[21−23] small reorganization energies,[24−27] and high electron transporting abilities,[28] as well as their interesting physical properties including high solubility in common solvents.

The commonly employed synthetic approaches for the preparation of fullerene C_{60} derivatives involve 1,3-dipolar cycloadditions,[29−32] cyclopropanations,[33,34] addition of organometallic reagents,[35−42] base-promoted nucleophilic additions,[43,44] transition metal-mediated free radical reactions,[45−47] and photoinduced single electron transfer (SET) reactions.[48−52] The latter approach is of particular interest because in comparison to the others it relies on the use of more environmentally benign conditions. As mentioned above, fullerenes are excellent electron acceptors owing to the fact that they have high electron affinities associated with high reduction potentials (for C_{60}, E_{red} = −0.42 V vs SCE in PhCN).[53−55] In addition, the singlet excited state of fullerenes, generated by direct irradiation, undergoes highly efficient intersystem crossing (for $^1C_{60}$, Φ_{ISC} = 1)[56] to produce the corresponding triplet excited state. Importantly, the fullerene triplet has a relatively high reduction potential (for $^3C_{60}$, $^3E_{red}$ = 1.14 V vs SCE),[50] and, as a result, it should participate in rapid (diffusion controlled) SET with a wide variety of ground-state electron donors that possess oxidation potentials lower than ca. 1.1 V.

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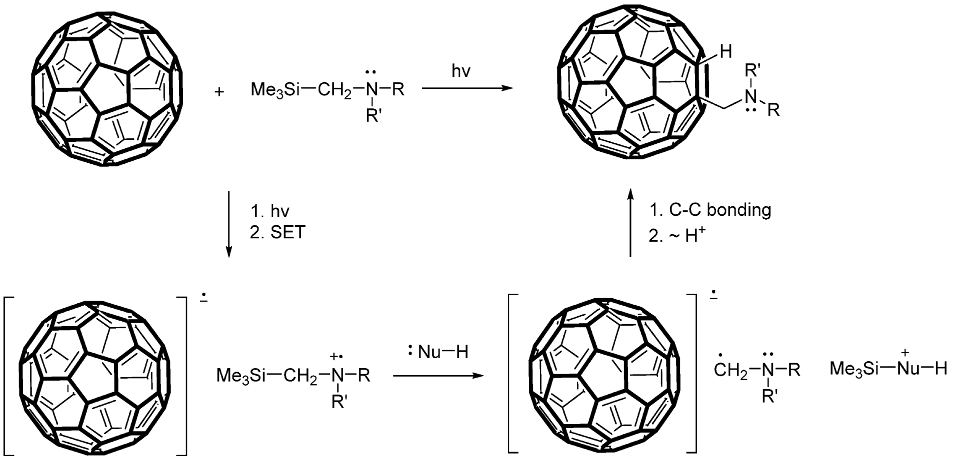
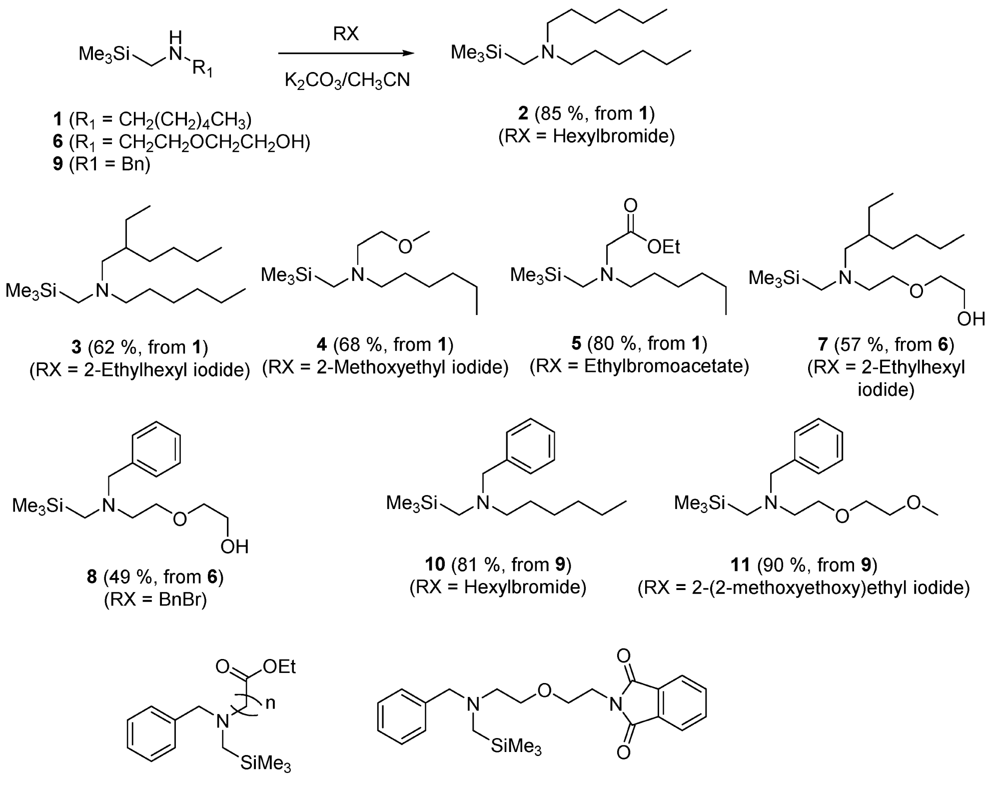
Scheme 1



Scheme 2



1 ($R_1 = CH_2(CH_2)_4CH_3$)
6 ($R_1 = CH_2CH_2OCH_2CH_2OH$)
9 (R1 = Bn)

2 (85 %, from **1**)
(RX = Hexylbromide)

3 (62 %, from **1**)
(RX = 2-Ethylhexyl iodide)

4 (68 %, from **1**)
(RX = 2-Methoxyethyl iodide)

5 (80 %, from **1**)
(RX = Ethylbromoacetate)

7 (57 %, from **6**)
(RX = 2-Ethylhexyl iodide)

8 (49 %, from **6**)
(RX = BnBr)

10 (81 %, from **9**)
(RX = Hexylbromide)

11 (90 %, from **9**)
(RX = 2-(2-methoxyethoxy)ethyl iodide)

12 (n =1, 52 %, from **9**)
(RX = Ethylbromoacetate)
13 (n = 2, 44 %, from **9**)
(RX = Ethylbromopropionate)

14 (61 %, from **9**)
(RX = N-(2-iodoethoxy)ethyl phthalimide)

Several reports already exist describing highly inefficient SET-promoted excited-state addition reactions of tertiary alkyl and aromatic amines to C_{60}.[57−60] These processes follow pathways in which SET occurs to form amine cation radicals (aminium radicals) and the fullerene radical anion ($C_{60}^{-\bullet}$). The low oxidation potentials of tertiary amines (E_{ox} <1 V vs Ag/AgCl)[55] and the relatively high reduction potential of the triplet state of C_{60} ($^3E_{red}$ = 1.19 V vs Ag/AgCl)[50] combine to make the free energy changes for SET in these cases negative ($\Delta G_{SET} < 0$ V) and, consequently, the rate constants for these processes (k_{SET}) nearly equal to that of diffusion (1×10^9 to 10^{10} M^{-1} s^{-1}).[55,61] Subsequent α-CH deprotonation of the formed aminium radicals takes place to form α-amino radicals that couple with $C_{60}^{-\bullet}$ to form the anion precursors of adducts. This mechanistic pathway mimics those that drive numerous excited-state reactions occurring between amines and a variety of electron acceptors, including cyanoarenes,[62] saturated[63−65] and α,β-unsaturated ketones,[66,67] and phthalimides.[68−72]

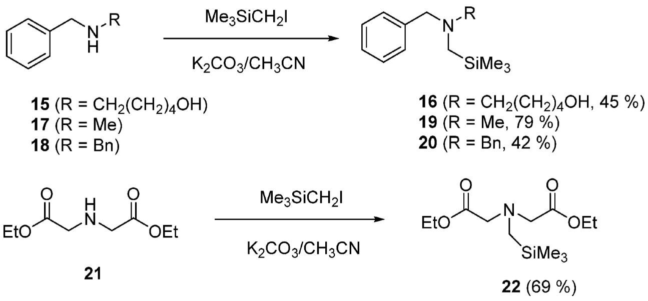
Among the tertiary amines that participate in these types of SET-promoted photochemical processes, those that possess α-trialkylsilyl substitution have unique features that enable them to undergo both highly regioselective and efficient SET photoadditions.[67] Specifically, trialkylsilyl-substituted amines are readily oxidized by SET to corresponding aminium ions owing to the fact that they have ca. 0.4 V lower oxidation potentials than their nonsilyl analogues. This property is a consequence of radical cation stabilization by overlap of the high-energy σ_{C-Si} orbital with the half-filled nitrogen p-orbital in these aminium radicals.[73−75] In addition, overlap of the $\sigma_{C-Si\text{-}p}$ and N p-orbital leads to weakening of the C−Si bond and an increase in the electron deficiency at Si in the α-trialkylsilylaminium radical, which combine to facilitate rapid transfer of the trialkylsilyl groups to silophiles, forming carbon-centered α-amino radicals. Importantly, the results of earlier laser flash photolysis (LFP) investigations[75,76] show that water- and alcohol-promoted desilylation reactions of α-trialkylsilylaminium radicals take place at much higher rates than do α-CH deprotonations of nonsilyl analogues, a feature that contributes to the high regioselectivities and efficiencies.

In early studies, we also demonstrated that SET-promoted photochemical addition and cyclization reactions of a number of α-trialkylsilyl substituted electron donors, including allyl- and benzyl-silanes[77−79] as well as silyl-ethers, -thioethers, and -amides,[68,69,80] take place regioselectively and efficiently and that these processes can be applied to the synthesis of interesting target molecules.[69b,79a,81] Owing to the growing importance of the need for functionalized fullerenes in current strategies employed to design photovoltaic devices, we have initiated a broad program to explore SET photoaddition reactions of a variety of α-trialkylsilyl-substituted electron donors to fullerenes with the aim of evaluating the scope and efficiency of the processes. In the initial phase of this long-range study, we explored photoaddition reactions of C_{60} with α-silyl tertiary amines. The results of this effort, presented below, demonstrate that these processes, following the pathway depicted in Scheme 1, take place with high chemical and quantum efficiencies; consequently, they constitute a potentially powerful and general method to synthesize novel fullerene derivatives.

■ RESULTS AND DISCUSSION

Preparation of α-Silyl Tertiary Amine Donors. Photoaddition reactions of fullerene (C_{60}) with a wide variety of α-trimethylsilyl-substituted tertiary amines were explored in this investigation. The routes employed to prepare the amines are outlined in Schemes 2−4. For example, the known α-trimethylsilyl-substituted secondary amines **1**,[82] **6**,[69c] and **9**[83] react with various types of alkyl halides in the presence of K_2CO_3 to yield the corresponding α-silyl tertiary amines **2**−**5**, **7**−**8**, and **10**−**14** in high yields (55−90%) (Scheme 2). α-Silyl amines **16**, **19**, **20**, and **22** are synthesized by employing base-promoted substitution reactions of commercially available secondary amines **15**, **17**, **18**, and **21** with iodomethyltrimethylsilane (Scheme 3).

Scheme 3



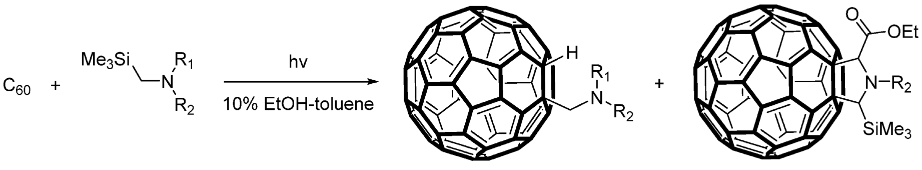
α-Silyl Tertiary Amine Oxidation Potentials. Prior to initiating studies of the photoaddition reactions of α-silyl tertiary amines with C_{60}, oxidation potential (E_{ox}) measurements were performed in order to ensure that SET from the amine donors to the excited state of C_{60} ($^3C_{60}$*) is thermodynamically favorable. As can be seen by viewing the data displayed in Table S1 (Supporting Information), all α-silyl tertiary amine donors have E_{ox} values in the range of 0.15−0.65 V (vs Ag/AgCl), which fall below the reduction potentials of $^3C_{60}$*. As a result, free energies for electron transfer from the amines to $^3C_{60}$*, calculated using the expression $\Delta G°_{SET} = E_{ox}(\alpha\text{-silylamine}) - E_{red}(^3C_{60}^*)$, are negative. Thus, as has been shown by Foote and co-workers utilizing other amine donors,[55] the rates of SET (k_{SET}) from the α-silyl tertiary amines to $^3C_{60}$* should be nearly equal to the diffusion-controlled limit.

Photoreactions of C_{60} with α-Silyl Tertiary Amines. Formation of Aminomethylfullerenes. Photoaddition reactions of C_{60} with the α-silyl tertiary amines were explored. As the results displayed in Scheme 4 and Table 1 show, irradiation (450 W Hanovia medium-pressure mercury lamp and uranium glass filter (λ > 330 nm)) of 10% EtOH−toluene solutions (220 mL, N_2 purged) containing C_{60} (0.28 mmol) and α-silyl tertiary amines **2**−**4** (0.56 mmol) for 4 min leads to production of the respective 1,2-adducts **23**−**25** as the sole products in high yields (54−94%). No polysubstituted photoadducts are generated in these processes even when high concentrations of the amines or long irradiation times are employed (Table 1, entry 2).

Irradiation of a solution of C_{60} and α-silylamine **5**, which contains an *N*-carboxymethyl moiety, gives rise to formation of photoadduct **26** in only a modest yield (36%) that is not significantly improved by using longer irradiation times (Table 1, entry 6). In reactions of hydroxyl group-containing α-silylamines **7** and **8**, 8 min irradiation brings about high conversion (100 and 88%, respectively) of the starting amine and moderate generation of the corresponding photoproducts **27** (51%) and **28** (57%). Similarly, photoreaction of *N*-hydroxypentyl-substituted α-silylamine **16** with C_{60} (Table 1, entry 15) produces **34** in modest yield (43%).

The photoreaction of C_{60} with α-silylamine **12**,[66b] which contains *N*-benzyl- and *N*-carboxymethyl substituents (Table 1, entries 11 and 12), is interesting in that the distribution of products formed is dependent on irradiation time. Specifically, while irradiation of a 10% EtOH−toluene solution of C_{60} and **12** for a shorter time period of 16 min produces the expected 1-aminomethyl-2-hydrofullerene **31** as the sole photoproduct (32%), irradiation for 1 h gives rise to formation of **31** (76%) along with fulleropyrrolidine **38** (12%). In a similar manner, photoreaction of C_{60} with *N*,*N*-dicarboxymethyl-substituted α-silylamine **22** also displays an irradiation time-dependent product distribution (Table 1, entries 19 and 20), with adduct **37**[84] being formed solely at a shorter (1 h) irradiation time and **37** and fulleropyrrolidine **39** produced at a longer (2 h) time. In contrast, photoreaction of the *N*-carboxyethyl-substituted α-silylamine **13** generates 1,2-photoadduct **32** as the sole product in modestly high yield (54%, Table 1, entry 13). In addition, photochemical reaction of C_{60} with *N*,*N*-dibenzyl-tethered α-silylamine **20** produces adduct **36** exclusively, even when a longer irradiation time is utilized (Table 1, entries 17 and 18).

Scheme 4



23-37

38 (R_2 = Bn)
39 (R_2 = CH_2CO_2Et)

Product	R_1	R_2
23	Hexyl	Hexyl
24	Hexyl	$CH_2CH(Et)CH_2CH_2CH_2CH_3$
25	Hexyl	$CH_2CH_2OCH_3$
26	Hexyl	CH_2CO_2Et
27	$CH_2CH(Et)CH_2CH_2CH_2CH_3$	$CH_2CH_2OCH_2CH_2OH$
28	Bn	$CH_2CH_2OCH_2CH_2OH$
29	Hexyl	Bn
30	Bn	$CH_2CH_2OCH_2CH_2OCH_3$
31	Bn	CH_2CO_2Et
32	Bn	$CH_2CH_2CO_2Et$
33	Bn	$CH_2CH_2OCH_2CH_2$-N-Phthalimide
34	Bn	$CH_2CH_2CH_2CH_2CH_2OH$
35	Bn	CH_3
36	Bn	Bn
37	CH_2CO_2Et	CH_2CO_2Et

Table 1. Products and Yields of Photoaddition Reactions of α-Silyl Tertiary Amines with C_{60}[a]

entry	amine	irradiation time (min)	conversion (%)[b]	product (%)[c]
1	**2**	4	100	**23** (92)
2	**2**[d]	4	100	**23** (94)
3	**3**	4	93	**24** (90)
4	**4**	4	69	**25** (54)
5	**5**	8	85	**26** (36)
6	**5**	60	85	**26** (42)
7	**7**	8	100	**27** (51)
8	**8**	8	88	**28** (57)
9	**10**	8	100	**29** (47)
10	**11**	8	93	**30** (56)
11	**12**	16	62	**31** (32)
12	**12**	60	100	**31** (76), **38** (12)
13	**13**	8	82	**32** (54)
14	**14**	8	100	**33** (67)
15	**16**	8	100	**34** (43)
16	**19**	8	100	**35** (86)
17	**20**	8	75	**36** (64)
18	**20**	60	100	**36** (91)
19	**22**	60	68	**37** (23)
20	**22**	120	78	**37** (36), **39** (4)

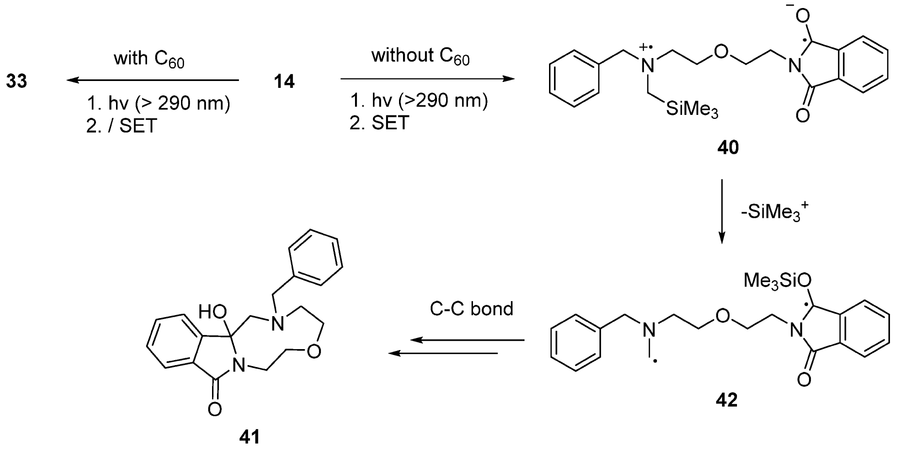
[a] α-Silyl amine/C_{60} is 0.56:0.28 mmol in 220 mL of 10% EtOH−toluene. [b] Conversion was determined by recovered C_{60}. [c] Isolation yields. [d] 5.6 mmol of **2** in 220 mL of 10% EtOH−toluene

Photoreaction of C_{60} with α-silylamine **14** was explored because the amine substrate possesses a phthalimide group that can also serve as an electron acceptor (Table 1, entry 12). It was expected that direct irradiation of a solution containing only **14** (λ_{max} = 290 nm) would promote intramolecular SET, leading to formation of the zwitterionic radical **40** (Scheme 5), which would undergo rapid desilylation followed C−C bond formation to generate cyclic amidol **41**. In accord with this expectation, irradiation of a solution of **14** in 10% EtOH−toluene does produce **41** (39%). However, when the reaction mixture contains both **14** and C_{60}, irradiation leads to formation of adduct **33** (67%) exclusively (Table 1, entry 14).

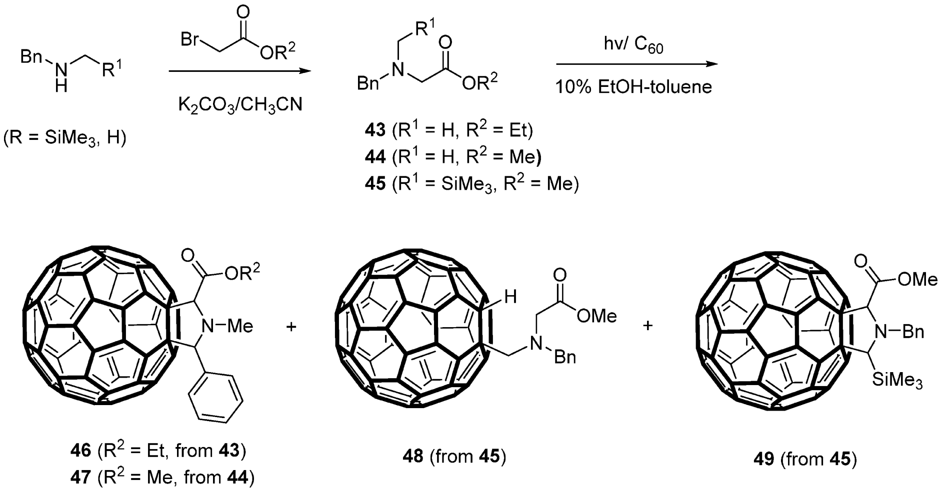
Structural assignments of the photoproducts described above were made by using ^1H and ^{13}C NMR, UV−visible spectroscopy, and HRMS (see Experimental Section and Supporting Information) as well as by comparing the data to those previously reported for related compounds. Diagnostic resonances are observed in the ^1H NMR spectra of 1,2-adducts **23**−**37** at 6.7−7.0 ppm, which correspond to the proton in each that is directly bonded to the C_{60} core and consequently experiences a characteristic deshielding effect.[57−60] In addition, the methylene protons on carbons that are bonded to both the C_{60} core and nitrogen in the adducts resonate in the 4.3−4.7 ppm region. In ^{13}C NMR spectra, the sp^3 fullerene core carbons of **23**−**37** appear at ca. 70 ppm, and the adjacent methylene carbons resonate at ca. 60 ppm. Importantly, the ^{13}C NMR spectral features of **23**−**37** exhibit patterns that correspond to mono-1,2-adducts of C_{60} arising by addition across the [6,6]-juncture rather than [5,6]-ring juncture.[57−60]

Owing to the presence of stereogenic carbons adjacent to the nitrogen atom in fulleropyrrolidine adduct **38**, the methylene protons in its ester ethoxy moiety appear in the ^1H NMR spectrum as an AB quartet at 4.19 and 4.28 ppm, and the benzylic protons appear as an AB quartet at 4.58 and 5.26 ppm. Analysis of the ^{13}C NMR and DEPT spectra of **38** shows that the quaternary sp^3 carbons in the fullerene core resonate at 77.7 and 78.0 ppm, the benzylic and ester ethoxy methylenes resonate at 56.2 and 60.9 ppm, and the chiral methine carbons appear at 70.2 and 77.2 ppm. Unfortunately, no information is available to aid the assignment of *cis* versus *trans* stereochemistry to the fulleropyrrolidine adducts. However, Gan's[85a] and Jørgensen's studies[85b] of the stereochemistry of 1,3-dipolar addition reactions of ylides to maleimides showed that *cis* isomers are produced predominantly. Finally, the UV−visible absorption spectra of photoproducts **23**−**37**, **38**, and **39** contain maxima at ca.

Scheme 5



Scheme 6



435 nm, which are characteristic of 1,2-adducts generated by addition across the [6,6]-juncture of C_{60}.[57−60]

The unusual behavior of **12** and **22** in photoreactions with C_{60} is also displayed by ester-containing, non-silylmethyl substituted amines **43**[66b] and **44**[86] (Scheme 6). Irradiation of 10% EtOH−toluene solutions of C_{60} containing these amines, prepared by the routes shown in Scheme 8, leads to exclusive formation of the respective fulleropyrrolidine adducts **46** and **47**. These reactions require substantially longer irradiation times (120 min, 44−53% conversion) than those needed to promote reaction with the silyl-substituted analogue **45** (30 min, 88% conversion), which efficiently forms 1,2-adduct **48** (64%) and fulleropyrrolidine adduct **49** (9%) (Scheme 6 and Table 2).

Table 2. Products and Yields of Photoaddition Reactions of Amines 43−45 with C_{60}[a]

amine	reaction time (min)	conversion (%)[b]	product (%)[c]
43	120	55	**46** (30)
44	120	43	**47** (39)
45	30	88	**48** (64), **49** (9)

[a] Amine/C_{60} is 0.56:0.28 mmol in 220 mL of 10% EtOH−toluene. [b] Conversion was determined by recovered C_{60}. [c] Isolation yields.

Solvent Effects. Because solvent polarity and silophilicity are also important factors that influence the efficiencies of SET photoreactions of α-silylamines,[63,66,67a] we have briefly explored the effects of variations in the EtOH content in the mixed EtOH−toluene solvent system on the efficiency of photoaddition of **20** to C_{60}. In earlier studies by Sun,[57] Nishimura,[58] and Cheng,[59] photoaddition reactions of C_{60} with non-silyl tethered aliphatic and aromatic tertiary amines were conducted in pure toluene and produced 1-hydroxy-2-aminomethyl fullerenes in low yields (5−16%). In the current effort, solutions of **20** and C_{60} in toluene containing volume percentages of EtOH ranging from 0 to 40% were simultaneously irradiated for 1 h. Product yields were then determined by using UV−visible spectroscopy (Figure S1, Supporting Information) and HPLC. The results summarized in the plot displayed in Figure S1 show that no photoproduct is generated in a 1 h (or even 3 h) photoreaction of **20** carried out in pure toluene. In addition, as the EtOH content of the EtOH−toluene solvent mixture is increased to 15%, the yield of photoadduct **36** increases and then decreases when the EtOH content exceeds 15%. The decrease in efficiencies taking place when high concentrations of EtOH are present might be a consequence of an increasing polarity effect that causes C_{60} complex formation.[87]

These findings show that the presence of polar protic EtOH enhances the efficiencies of these photoaddition reactions, which proceed through a mechanistic pathway involving sequential excited-state SET-aminium radical desilylation (see below). In this pathway, coupling of the α-amino radical formed by desilylation with the anion radical of C_{60} generates the adduct anion, which is protonated by the oxonium ion arising by EtOH-promoted desilylation. Evidence for this proposal comes from the observation that deuterium comprises ca. 75% of the fullerene core proton in 1,2-adduct **36** formed by photoreaction of C_{60} with **20** in toluene containing 10% EtOD.

Another important observation related to solvent effects arises in studies of photoaddition reactions of α-silylamines **12** and **22** with C_{60}. As can be seen by viewing the results displayed in Scheme 7 and Table 3, photoaddition reactions of C_{60} with **12** and **22**, carried out in toluene solutions containing low (10 and 15%) percent by volume contents of EtOH, produce the respective α-aminofullerenes **31** and **37** exclusively/predominantly. In contrast, irradiation of C_{60} and these amines in solutions having high contents (40%) of EtOH in toluene leads to formation of fulleropyrrolidine adducts **38** and **39** predominantly.

Scheme 7

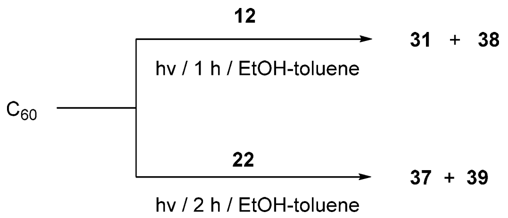


Table 3. Relative Ratios of Products Produced in Photoadditon Reactions of α-Silylamines 12 and 22 with C_{60}[a]

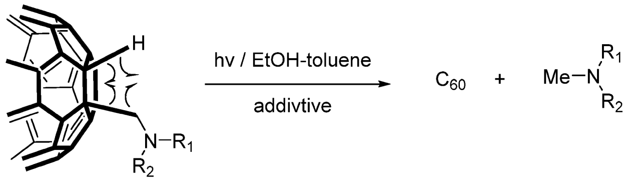
	relative product ratios derived from **12** and **22**[b]	
content (by volume) of EtOH in toluene (%)	**31:38**	**37:39**
10	1:0	1:0
15	16:1	17:1
40	1:2	1:6

[a] Ratio of reactants (α-silylamine/C_{60}) is 3.47:1.74 (10^{-3} mmol) in 10 mL of EtOH–toluene [b] Relative product ratios were determined by using HPLC.

Conversion Dependence of Photoreaction Efficiencies. In one approach to exploring the conversion dependencies of product distribution and yields, the progress of photoreaction of α-silylamine **5** with C_{60} was monitored as a function of time. For this purpose, deoxygenated 10% EtOH–toluene solutions containing **5** (0.35 mM) and C_{60} (0.17 mM) were irradiated for varying time periods ranging from 5 to 180 min while monitoring the formation photoproduct **26** by UV–visible spectroscopy (Figure S2, Supporting Information). The results, which show that the yield of **26** gradually increases during the irradiation period, are in accord with observations made in studies of the preparative photoreaction of this amine substrate that show that a mono adduct is generated exclusively (see above).

Next, a study was conducted to determine if 1,2-adducts **31**, **36**, and **37** undergo secondary photochemical reactions to form pyrrolidine-type products. Processes of this type have been invoked earlier to rationalize the formation of fulleropyrrolidines in photoreactions of C_{60} with tertiary amines.[57,59] Independent 10% EtOH–toluene solutions containing the three adducts and either $HClO_4$, pyridine, or no additive were irradiated while monitoring photolysate compositions using UV–visible spectroscopy and HPLC. The results (Figure S3, Supporting Information) show that photoreactions of these substrates under the different conditions lead, in all cases, to formation of C_{60} along with the respective amines *N*-methylamines (Scheme 8). In the absence of added acid or base, the photoreaction of **36** is more efficient than those of **31** and **37**. Moreover, the presence of 2 mol equiv of $HClO_4$ in solutions of each adduct enhances their photoconversions to form C_{60} and the corresponding amines, but pyridine has little effect on the efficiencies of these processes.

Scheme 8



31 (R_1 = Bn, R_2 = CH_2CO_2Et)
36 (R_1 = R_2 = Bn)
37 (R_1 = R_2 = CH_2CO_2Et)

Oxygen Effects on Fulleropyrrolidine Formation. To gain information about the mechanistic pathway that is responsible for the generation of the fulleropyrrolidine adducts, photoaddition reactions of C_{60} with α-silylamines **12**, **22**, and **45** in O_2 saturated 10% EtOH–toluene solutions were explored. The results (Table 4) show that photoaddition reactions in O_2 saturated solutions take place much less efficiently than those taking place in N_2 purged solutions. Second, in contrast to processes occurring in N_2 purged solutions, fulleropyrrolidines **38**, **39**, and **49** are generated exclusively in photoreactions in O_2 saturated solutions. These observations strongly indicate that oxygen is involved in the pathway that produces fulleropyrrolidines (see below).

Table 4. Products and Yields of Photoaddition Reactions of α-Silyl Tertiary Amines with C_{60} Carried out in O_2 Saturated 10% EtOH–Toluene Solutions[a]

substrate	irradiation time (h)	conversion (%)[b]	product (%)[c]
C_{60} + **12**	2	91	**38** (70)
C_{60} + **22**	10	10	**39** (8)
C_{60} + **45**	3	65	**49** (47)

[a] α-Silyl amine/C_{60} is 0.56:0.28 mmol in 220 mL of 10% EtOH–toluene. [b] Conversion was determined by recovered C_{60}. [c] Isolation yields.

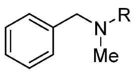
Factors Governing the Efficiencies of Photoaddition Reactions of Amines with C_{60}. As can be seen by viewing the data given in Tables 1 and 2, the nature of the amine substrate plays a significant role in governing the times required to bring about high-yielding formation of the C_{60} photoadducts. In order to gain more detailed information about factors governing the efficiencies of these processes, relative quantum yields (Φ_{rel}) were determined by measuring product yields for simultaneous, fixed-time, low-conversion photoreactions. For this purpose, deoxygenated 10% EtOH—toluene solutions (10 mL) containing 0.17 mM C_{60} and 0.35 mM amine were simultaneously irradiated for a fixed time period that promotes an average substrate conversion of ca. 10%. Product yields were then determined by utilizing HPLC analysis of crude photolyzates and transformed into relative quantum yields (Φ_{rel}) by setting the quantum yield for the reaction of **22** to be unity.

Inspection of the relative quantum efficiency data displayed in Table 5 clearly shows that photoaddition reactions of the non-carboxymethyl-substituted α-silylamines are higher than those of counterparts that either contain *N*-carboxymethyl groups (**5**, **12**, and **22**) or lack α-silyl substituents (**50** and **51**). Importantly, the differences in the efficiencies of these processes do not appear to be a consequence of varying rates of SET from the amines to $^3C_{60}$* because in all cases, even those of the non-silyl amines **50** ($E_{ox}(+)$ = 0.73 V vs Ag/AgCl) and **51** ($E_{ox}(+)$ = 0.23 V vs Ag/AgCl), the free energy for he telectron transfer step is negative, ensuring that SET is diffusion-controlled.

Table 5. Relative Quantum Efficiencies (Φ_{rel}) of Photoaddition Reactions of Tertiary Amines with C_{60}[a]

substrate	Φ_{rel}	substrate	Φ_{rel}
2	13.2	**13**	2.8
3	15.1	**14**	4.1
4	8.4	**16**	7.9
5	2.7	**19**	4.1
7	3.9	**20**	3.0
8	7.1	**22**	1
10	5.0	**50**	0.4
11	4.5	**51**	0.2
12	2.1		

[a] Fixed-time irradiations of N_2 purged 10% EtOH—toluene solutions with reactant concentrations being [α-silyl amine] = 0.35 mM and [C_{60}] = 0.17 mM.



50 (R = Me, $E_{ox}(+)$ = 0.73 V vs Ag/AgCl)
51 (R = Bn, $E_{ox}(+)$ = 0.26 V vs Ag/AgCl)

Mechanism for 1,2-Adduct and Fulleropyrrolidine Formation.

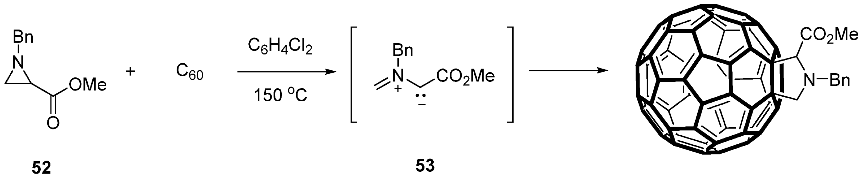
The mechanism depicted in Scheme 1 is responsible for formation of 1,2-adducts in photoreactions between the α-silyl tertiary amines and C_{60}. The pathway is initiated by SET from the amine donors to the triplet excited state of fullerene, which is followed by silophile (EtOH)-induced desilylation to generate key α-amino radical intermediates. This mechanism contrasts with an analogous route responsible for photoreactions of C_{60} with unsymmetric tertiary amines, which do not possess α-silyl groups, where SET is followed by proton transfer from the generated aminium radical. As a consequence of this difference, photoreactions of trimethylsilyl-substituted amines take place with higher efficiencies and exceptionally high and predictable levels of regioselectivity. Both of these outcomes are a result of the much larger rates of silophile-promoted desilylation compared to deprotonation of intermediate aminium radicals.[65,66,67a] As a result of this factor, site-selective formation of α-amino radicals takes place with rates that are more competitive with that of energy wasting (excited-state quenching) back SET between the amine cation radicals and fullerene anion radical.

The source of the quantum efficiency diminishing effect of *N*-carboxymethyl substitution on the α-silyl amines is not well understood at this point. However, it might not be a coincidence that the low relative quantum yields are associated with the same substrates that undergo competitive formation of fulleropyrrolidine photoadducts. Specifically, the low efficiencies of 1,2-adduct formation in these cases might enable a typically inefficient, pyrrolidine ring- forming reaction to become competitive. It should be noted that the low efficiencies and fulleropyrrolidine formation tendencies associated with photoreactions of *N*-carboxymethyl-substituted amines are not likely to be a consequence of a competition between deprotonation and desilylation of intermediate aminium cations. Support for this prediction comes from both an earlier observation that shows that carboxymethyl protons of the aminium cations are not more kinetically acidic (rapidly abstracted) than those present in simple alkyl groups[65,88] and the fact that the C_{60} radical anion formed by SET to $^3C_{60}$* is an extremely weak base.[21,89]

Although little evidence has been accumulated in this effort to address the issue, a reasonable mechanism for the fulleropyrrolidine-forming process can be proposed on the basis of earlier observations made by Prato and Foote. In a seminal investigation, Prato and co-workers[31b] showed that thermal reaction of aziridine **52** with C_{60} leads to exclusive production of fulleropyrrolidine **54** (Scheme 9). This process, which has gained great utility in the synthesis of fullerene derivatives that are employed in photovoltaic devices, likely takes place by sequential formation and dipolar cycloaddition of the intermediate azomethine ylide **53**. In addition, Foote[90] demonstrated that singlet oxygen is involved in pyrrolidine ring forming reactions of tertiary amines with C_{60}.

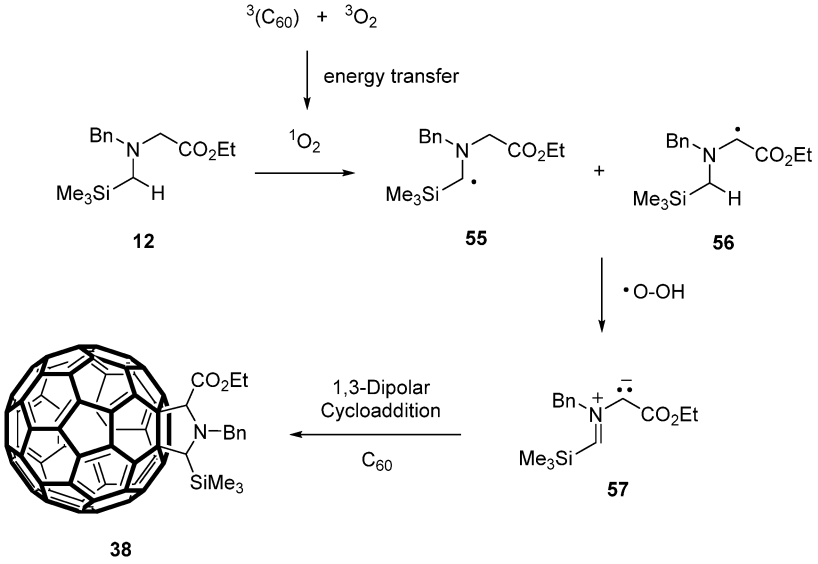
When combined, the results of these earlier investigations suggest that fulleropyrrolidine formation in photoreactions of *N*-carboxymethyl-substituted tertiary amines takes place via a route that involves singlet oxygen-mediated formation of azomethine ylides that then participate in dipolar cycloadditions to C_{60} (Scheme 10). Accordingly, in the presence of

Scheme 9



52 **53** **54** (73 %)

Scheme 10



$^3O_2$, the triplet excited state of C_{60} should undergo energy transfer ($k_q(O_2) = 2 \times 10^9$ M^{-1} s^{-1})[56a,91] to form $^1O_2$ and ground-state C_{60}, a process that effectively quenches formation of 1,2-photoadducts. As suggested by Foote,[90] reaction of $^1O_2$ with a *N*-carboxymethyl-*N*-*α*-silylmethyl amine (e.g., **12**, Scheme 10) likely involves *α*-hydrogen atom abstraction to form *α*-carbon radicals **55** and **56** along with the hydroperoxy radical.[92] Subsequent hydroperoxide forming reaction of either **55** or **56** through H-atom transfer generates the key azomethine ylide **57** that then undergoes dipolar cycloaddition with C_{60} to produce the fulleropyrrolidine adduct.

■ CONCLUSIONS

In this study, a novel, efficient, highly regioselective, and environmentally benign method for the preparation of variously substituted *α*-aminofullerene derivatives has been developed. The process, involving photoaddition of *α*-silyl tertiary amines to C_{60}, takes place via a mechanistic pathway involving formation of aminium radicals by SET from the amine to the triplet excited state of C_{60} followed by desilylation to generate *α*-amino radicals that couple with the C_{60} radical anion to form precursors of the 1,2-adducts. The high efficiencies of these reactions, which enable large-scale production of adducts in short time periods, are associated with the large rates of aminium radical desilylation promoted by the silophile EtOH incorporated as a solvent component. It is envisaged that this new strategy will find utility in the synthesis of new fullerene derivatives.

■ EXPERIMENTAL SECTION

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 >95% purity (by NMR analysis as well as HPLC trace) unless otherwise noted.

***α*-Silyl Tertiary Amines 2–5.** Individual solutions of *N*-trimethylsilyl-*N*-1-hexylamine **1** (3.0 g, 16 mmol) in acetonitrile (100 mL) containing K_2CO_3 (5.0 g, 36 mmol) and 20 mmol of the alkyl halide (3.3 g of 1-hexyl bromide for **2**, 4.8 g of 2-ethyl-1-hexyl iodide for **3**, 3.7 g of 2-methoxy-1-ethyl iodide for **4**, and 3.34 g of ethyl 2-bromoacetate for **5**) were stirred for 12 h at room temperature and concentrated in vacuo to give residues that were triturated with CH_2Cl_2. The triturates were dried and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (EtOAc/hexane = 1:10) to yield **2** (3.69 g, 85%), **3** (2.97 g, 62%), **4** (2.67 g, 68%), and **5** (3.5 g, 80%).

2: ^{1}H NMR 0.03 (s, 9H), 0.88 (t, 6H, *J* = 6.9 Hz), 1.16–1.30 (m, 12H), 1.32–1.44 (m, 4H), 1.90 (s, 2H), 2.32 (t, 4H, *J* = 7.2 Hz); ^{13}C NMR −1.2, 14.1, 22.7, 26.8, 27.2, 31.9, 45.9, 57.6; HRMS (FAB) *m/z* 272.2768 (M + 1, $C_{16}H_{38}NSi$ requires 272.2774).

3: ^{1}H NMR 0.00 (s, 9H), 0.79–0.88 (m, 9H), 1.23–1.35 (m, 17H), 1.82 (s, 2H), 2.06 (d, 2H, *J* = 5.7 Hz), 2.23 (t, 2H, *J* = 6.6 Hz); ^{13}C NMR −1.2, 10.9, 14.1 (2C), 22.7, 23.2, 24.4, 26.8, 27.2, 29.0, 31.2, 32.0, 37.4, 46.7, 57.8, 62.5; HRMS (FAB) *m/z* 300.3088 (M + 1, $C_{18}H_{42}NSi$ requires 300.3087).

4: ^{1}H NMR 0.02 (s, 9H), 0.85 (t, 3H, *J* = 6.9 Hz), 1.23–1.28 (m, 6H), 1.34–1.41 (m, 2H), 1.95 (s, 2H), 2.34 (t, 2H, *J* = 7.5 Hz), 2.56 (t, 2H, *J* = 6.3 Hz), 3.31 (s, 3H), 3.41 (t, 2H, *J* = 6.3 Hz); ^{13}C NMR −1.3, 14.0, 22.6, 26.8, 27.1, 31.8, 46.6, 56.6, 58.2, 58.8, 71.1; HRMS (FAB) *m/z* 246.2256 (M + 1, $C_{13}H_{32}NOSi$ requires 246.2253).

5: ^{1}H NMR 0.02 (s, 9H), 0.84 (t, 3H, *J* = 6.6 Hz), 1.21–1.25 (m, 6H), 1.34–1.41 (m, 2H), 2.11 (s, 2H), 2.52 (t, 2H, *J* = 7.2 Hz), 3.26 (s, 3H), 4.11 (q, 2H, *J* = 6.9 Hz); ^{13}C NMR −1.8, 13.8, 14.0, 22.4, 26.6, 27.3, 31.6, 45.5, 57.3, 57.6, 59.5, 170.9; HRMS (FAB) *m/z* 274.2200 (M + 1, $C_{14}H_{32}NO_2Si$ requires 274.2202).

***α*-Silyl Tertiary Amines 7–8.** Individual solutions of *N*-trimethylsilylmethyl-*N*-hydroxyethoxyamine **6** (2.0 g, 10.5 mmol) in acetonitrile (100 mL) containing K_2CO_3 (5.8 g, 41.8 mmol) and 21 mmol of the alkyl halide (4.0 g of 2-ethyl-1-hexyl bromide for **7**, 3.54 g of benzyl bromide for **8**) were stirred for 12 h at room temperature and concentrated in vacuo to give residues that were triturated with CH_2Cl_2. The triturates were dried and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (EtOAc/hexane = 1:5) to yield **7** (1.8 g, 57%) and **8** (1.44 g, 49%).

7: ^{1}H NMR 0.04 (s, 9H), 0.82–0.91 (m, 6H), 1.20–1.32 (m, 7H), 1.34–1.44 (m, 2H), 1.94 (s, 2H), 2.18 (d, 2H, diastereotopic, *J* = 6.6 Hz, 1.8 Hz), 2.54 (t, 2H, diastereotopic, *J* = 6.0 Hz, 1.8 Hz), 3.54 (t, 2H, *J* = 6.0 Hz), 3.56 (t, 2H, *J* = 4.5 Hz), 3.71 (t, 2H, *J* = 4.5 Hz); ^{13}C NMR −1.2, 10.8, 14.1, 23.2, 24.4, 28.9, 31.2, 37.5, 41.5, 57.3, 61.9, 63.2, 69.5, 72.2; HRMS (FAB) *m/z* 302.2520 (M − 1, $C_{16}H_{36}NO_2Si$ requires 302.2521).

8: ^{1}H NMR 0.07 (s, 9H), 2.04 (s, 2H), 2.59 (t, 2H, *J* = 6 Hz), 3.50 (t, 2H, *J* = 4.7 Hz), 3.20 (s, 1H), 3.56 (t, 2H, *J* = 6 Hz), 3.58

(s, 2H), 3.66 (t, 2H, *J* = 4.7 Hz), 7.22−7.35 (m, 5H); ^{13}C NMR −1.5, 46.5, 56.4, 61.5, 62.5, 69.1, 72.0, 126.7, 127.9, 128.0, 128.7, 139.2; HRMS (FAB) *m*/*z* 282.1891 (M + 1, $C_{15}H_{28}NO_2Si$ requires 282.1889).

***α*-Silyl Tertiary Amines 10−14 and 45.** Individual solutions of *N*-trimethylsilylmethyl-*N*-benzylamine **9** (3.0 g, 15.5 mmol) in acetonitrile (100 mL) containing K_2CO_3 (4.3 g, 31 mmol) and 30 mmol of the alkyl halide (4.95 g of 1-hexyl bromide for **10**, 6.9 g of 2-(2-methoxyethoxy)ethyl iodide for **11**, 5.0 g of ethyl 2-bromoacetate for **12**, 5.43 g of ethyl 2-bromopropionate for **13**, 10.35 g of *N*-(2-iodoethoxy)ethylphthalimide for **14**, and 4.9 g of methylbromoacetate for **45**) were stirred for 12 h at room temperature and concentrated in vacuo to give residues that were triturated with CH_2Cl_2. The triturates were dried and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (EtOAc/hexane = 1:8) to yield **10** (3.48 g, 81%), **11** (4.12 g, 90%), **12** (2.25 g, 52%), **13** (2.0 g, 44%), **14** (3.88 g, 61%), and **45** (2.6 g, 63%).

10: ^{1}H NMR 0.05 (s, 9H), 0.87 (t, 3H, *J* = 7.2 Hz), 1.24−1.30 (m, 6H), 1.32−1.44 (m, 2H), 1.93 (s, 2H), 2.31 (t, 2H, *J* = 6.9 Hz), 3.48 (s, 2H), 7.19−7.35 (m, 5H); ^{13}C NMR −1.3, 14.0, 22.6, 26.9, 27.0, 31.8, 45.8, 57.2, 62.1, 126.5, 128.0, 128.6, 140.6; HRMS (EI) *m*/*z* 277.2227 (M^+, $C_{17}H_{31}NSi$ requires 277.2226).

11: ^{1}H NMR 0.05 (s, 9H), 2.03 (s, 2H), 2.60 (t, 2H, *J* = 6.3 Hz), 3.34 (s, 3H), 3.48−3.56 (m, 8H), 7.16−7.33 (m, 5H); ^{13}C NMR −1.6, 46.4, 56.0, 58.7, 62.6, 69.6, 70.0, 71.7, 126.4, 127.8, 128.4, 139.9; HRMS (FAB) *m*/*z* 296.2042 (M + 1, $C_{16}H_{30}NO_2Si$ requires 296.2046).

12: ^{1}H NMR 0.01 (s, 9H), 1.20 (t, 3H, *J* = 7.2 Hz), 2.16 (s, 2H), 3.20 (s, 2H), 3.71 (s, 2H), 4.09 (q, 2H, *J* = 7.2 Hz), 7.17−7.31 (m, 5H); ^{13}C NMR −1.6, 14.2, 45.5, 56.9, 59.8, 61.4, 126.9, 128.1, 128.7, 139.4, 171.2.

13: ^{1}H NMR 0.01 (s, 9H), 1.18 (t, 3H, *J* = 7.2 Hz), 1.90 (s, 2H), 2.41 (t, 2H, *J* = 7.5 Hz), 2.67 (t, 2H, *J* = 7.2 Hz), 3.45 (s, 2H), 4.05 (q, 2H, *J* = 7.2 Hz), 7.17−7.22 (m, 5H); ^{13}C NMR −1.6, 14.0, 32.3, 45.6, 52.5, 60.1, 61.7, 126.7, 128.0, 128.5, 139.7, 172.5; HRMS (FAB) *m*/*z* 294.1885 (M + 1, $C_{16}H_{28}NO_2Si$ requires 294.1889).

14: ^{1}H NMR 0.04 (s, 9H), 1.93 (s, 2H), 2.51 (t, 2H, *J* = 6.0 Hz), 3.47 (s, 2H), 3.51 (t, 2H, *J* = 6.0 Hz), 3.63 (t, 2H, *J* = 5.7 Hz), 3.85 (t, 2H, *J* = 5.7 Hz), 7.14−7.7.24 (m, 5H), 7.66−7.69 (m, 2H), 7.79−7.82 (m, 2H); ^{13}C NMR −1.6, 37.4, 46.3, 56.1, 62.6, 67.5, 69.3, 123.1, 126.5, 127.9, 128.5, 132.0, 133.7, 140.1, 168.1; HRMS (FAB) *m*/*z* 411.2106 (M + 1, $C_{23}H_{31}N_2O_3Si$ requires 411.2104).

45: ^{1}H NMR 0.07 (s, 9H), 2.21 (s, 2H), 3.27 (s, 2H), 3.67 (s, 3H), 3.76 (s, 2H), 7.25−7.36 (m, 5H); ^{13}C NMR −1.6, 45.6, 50.9, 56.7, 61.3, 126.9, 128.1, 128.7, 139.3, 171.6; HRMS (FAB) *m*/*z* 266.1578 (M + 1, $C_{14}H_{24}NO_2Si$ requires 266.1576).

***α*-Silyl Tertiary Amines 16, 19, 20, and 22.** Individual solutions of 15.5 mmol of *N*-5-hydroxypentyl-*N*-benzylamine (3.0 g, for **16**), *N*-benzyl-*N*-methylamine (1.89 g, for **19**), *N*,*N*-dibenzylamine (3.06 g, for **20**), and *N*,*N*-bis-ethylcarboxymethylamine (2.93 g, for **22**) in acetonitrile (150 mL) containing K_2CO_3 (4.3 g, 31 mmol) and Me_3SiCH_2I (4.28 g, 20.0 mmol) were stirred for 12 h at room temperature and concentrated in vacuo to give residues that were triturated with CH_2Cl_2. The triturates were dried and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (EtOAc/hexane = 1:8) to yield **16** (1.95 g, 45%), **19** (2.54 g, 79%), **20** (1.85 g, 42%), and **22** (2.95 g, 69%).

16: ^{1}H NMR 0.03 (s, 9H), 1.26−1.34 (m, 2H), 1.41−1.54 (m, 4H), 1.92 (s, 2H), 2.31 (t, 2H, *J* = 6.9 Hz), 3.47 (s, 2H), 3.58 (t, 2H, *J* = 6.6 Hz); ^{13}C NMR −1.4, 23.2, 26.6, 32.4, 45.7, 56.9, 62.0, 62.5, 126.5, 127.9, 128.6, 140.1; HRMS (FAB) *m*/*z* 280.2094 (M + 1, $C_{16}H_{30}NOSi$ requires 280.2097).

19: ^{1}H NMR 0.07 (s, 9H), 1.92 (s, 2H), 2.19 (s, 3H), 3.44 (s, 2H), 7.23−7.32 (m, 5H).

20: ^{1}H NMR 0.20 (s, 9H), 2.10 (s, 2H), 3.63 (s, 4H), 7.33−7.56 (m, 10H); ^{13}C NMR −1.3, 45.8, 61.9, 126.6, 128.0, 128.6, 140.2; HRMS (FAB) *m*/*z* 284.1831 (M + 1, $C_{18}H_{26}NSi$ requires 284.1835).

22: ^{1}H NMR 0.00 (s, 9H), 1.19 (t, 3H, *J* = 7.2 Hz), 2.26 (s, 2H), 3.46 (s, 4H), 4.08 (q, 2H, *J* = 7.2 Hz); ^{13}C NMR −2.0, 14.0, 45.3, 57.7, 59.9, 170.7; HRMS (FAB) *m*/*z* 276.1633 (M + 1, $C_{12}H_{26}NO_4Si$ requires 276.1631).

General Procedure for Photoreactions of C_{60} with *α*-Silyl Tertiary Amines. Preparative photochemical reactions were conducted using an apparatus consisting of a 450 W Hanovia medium vapor pressure mercury lamp surrounded by a uranium glass filter in a water-cooled quartz immersion surrounded by the solution being irradiated, consisting of 10% EtOH−toluene (220 mL) containing C_{60} (0.28 mmol) and the *α*-silyl tertiary amines (0.56 mmol). The solutions being irradiated were purged with nitrogen before and during irradiations, and irradiations were carried out for time periods given below. The photolyzates 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 *α*-aminofullerenes. The purity of isolated products (>95%) was determined by HPLC traces as well as NMR analysis.

Formation of 23 from 2. Four minute irradiation, 100% conversion, column chromatography (toluene/hexane = 1:15) to yield **23** (237 mg, 92%).

23: ^{1}H NMR 0.94 (t, 6H, *J* = 6.9 Hz), 1.26−1.54 (m, 12H), 1.78−1.88 (m, 4H), 3.12 (t, 4H, *J* = 7.2 Hz), 4.43 (s, 2H), 6.88 (s, 1H); ^{13}C NMR 14.2, 22.9, 27.4, 27.8, 32.0, 55.7, 58.2, 67.6, 69.8, 135.7, 136.1, 139.9, 140.1, 141.5 (2C), 141.8 (2C), 141.9, 142.2, 142.4, 143.0, 143.1, 144.4, 144.6, 145.2, 145.3 (2C), 145.7, 146.0, 146.1, 146.2, 146.8, 147.0, 147.1 (2C), 154.5, 155.6; HRMS (FAB) *m*/*z* 920. 2378 (M + 1, $C_{73}H_{30}N$ requires 920.2373).

Formation of 24 from 3. Four minute irradiation, 93% conversion, column chromatography (toluene/cyclohexane = 1:30) to yield **24** (240 mg, 90%).

24: ^{1}H NMR 0.81−0.93 (m, 6H), 0.97 (t, 3H, *J* = 7.2 Hz), 1.23−1.78 (m, 16H), 2.84 (d, 2H, *J* = 6.9 Hz), 3.06 (t, 2H, *J* = 7.2 Hz), 4.38 (s, 2H), 6.80 (s, 1H); ^{13}C NMR 11.2, 14.1, 14.3, 22.7 (2C), 23.4, 24.8, 27.1, 27.3, 29.3, 29.4, 30.0, 31.6, 31.9 (2C), 32.7, 37.1, 38.3, 56.5, 58.4, 60.3, 135.8 (2C), 136.3 (2C), 139.9 (2C), 140.2, 141.6 (2C), 141.8, 142.0, 142.3 (2C), 142.5, 143.0, 143.2, 144.5, 144.6, 145.3 (3C), 145.9, 146.1, 146.2, 146.3, 147.1, 147.2, 147.3 (2C), 154.6, 155.8; HRMS (FAB) *m*/*z* 948.2695 (M + 1, $C_{75}H_{34}N$ requires 948.2691).

Formation of 25 from 4. Four minute irradiation, 69% conversion, column chromatography (toluene/hexane = 1:30) to yield **25** (136 mg, 54%).

25: ^{1}H NMR 0.80−0.90 (m, 3H), 1.22−1.50 (m, 6H), 1.75−1.82 (m, 2H), 3.14 (t, 2H, *J* = 7.5 Hz), 3.30 (t, 2H, *J* = 6 Hz), 3.46 (s, 3H), 3.82 (t, 2H, *J* = 6 Hz), 4.50 (s, 2H), 6.88 (s, 1H); ^{13}C NMR 14.0, 22.6, 27.1, 28.0, 31.9, 54.9, 56.7, 58.2, 59.0, 68.0, 70.2, 72.1, 135.9, 136.3, 140.0, 140.3, 141.6, 141.7, 141.9, 142.0, 142.1, 142.4, 142.6, 143.1, 143.3, 144.6, 144.7, 145.3, 145.4, 145.9, 146.2 (2C), 146.4, 147.0, 147.3, 147.4 (2C), 154.8, 155.8; HRMS (FAB) *m*/*z* 894.1854 (M + 1, $C_{70}H_{24}NO$ requires 894.1858).

Formation of 26 from 5. Eight minute irradiation, 85% conversion, column chromatography ($CHCl_3$/hexane = 1:5) to yield **26** (92 mg, 36%); 60 min irradiation, 85% conversion, column chromatography ($CHCl_3$/hexane =1:5) to yield **26** (108 mg, 42%).

26: ^{1}H NMR 0.84−0.89 (m, 3H), 1.23−1.44 (m, 9H), 1.72−1.82 (m, 2H), 3.14 (t, 2H, *J* = 7.6 Hz), 3.30 (t, 2H, *J* = 6 Hz), 4.00 (s, 2H), 4.31 (q, 2H, *J* = 7.2 Hz), 4.67 (s, 2H), 6.90 (s, 1H); ^{13}C NMR 14.2, 14.5, 22.7, 27.1, 28.6, 31.8, 56.0, 56.2, 58.1, 60.7, 67.8, 69.6, 136.0, 136.2, 140.0, 140.2. 141.6, 141.7, 141.8, 142.0, 142.1, 142.3, 142.5, 142.6, 143.2, 144.5, 144.7, 145.3, 145.4 (2C), 145.9, 146.1, 146.2, 146.4, 147.0, 147.2, 147.3, 147.4, 154.6, 155.2, 171.8; HRMS (FAB) *m*/*z* 922.1802 (M + 1, $C_{71}H_{24}NO_2$ requires 922.1807).

Formation of 27 from 7. Eight minute irradiation, 100% conversion, column chromatography ($CHCl_3$/EtOAc = 10:1) to yield **27** (134 mg, 51%).

27: ^{1}H NMR 0.88−0.99 (m, 6H), 1.28−1.51 (m, 5H), 1.62−1.74 (m, 2H), 1.76−1.84 (m, 2H), 2.94 (d, 2H, *J* = 6.9 Hz), 3.34 (t, 2H, *J* = 5.8 Hz), 3.64 (t, 2H, *J* = 4.3 Hz), 3.77 (t, 2H, *J* = 4.3 Hz), 3.88

(t, 2H, J = 5.8 Hz), 4.48 (s, 2H), 6.81 (s, 1H); ^{13}C NMR 11.1, 14.3, 23.3, 24.6, 29.2, 31.5, 38.3, 55.4, 58.2, 61.1, 61.9, 67.6, 69.9, 70.8, 72.3, 135.8, 135.9, 136.2 (2C), 139.8 (2C), 140.2, 141.5, 141.6, 141.7, 141.9 (2C), 142.2 (2C), 142.5, 143.1, 144.5, 144.6, 145.2, 145.3 (2C), 145.8, 146.0, 146.1, 146.3, 146.9, 147.1, 147.3, 154.4, 155.4; HRMS (FAB) m/z 952.2274 (M + 1, $C_{73}H_{30}NO_2$ requires 952.2277).

Formation of 28 from 8. Eight minute irradiation, 88% conversion, column chromatography (CHCl$_3$) to yield **28** (149 mg, 57%).

28: ^{1}H NMR 1.98 (t, 1H, J = 6 Hz), 3.33 (t, 2H, J = 5.6 Hz), 3.66 (t, 2H, J = 4.5 Hz), 3.80 (t, 2H, J = 4.5 Hz), 3.95 (t, 2H, J = 5.6 Hz), 4.37 (s, 2H), 4.61 (s, 2H), 6.86 (s, 1H), 7.31 (t, 1H, J = 7.2 Hz), 7.40 (t, 2H, J = 7.2 Hz), 7.64 (d, 2H, J = 6.9 Hz); ^{13}C NMR 54.7, 58.1, 60.9, 61.9, 67.3, 69.1, 70.3, 72.2, 127.4, 128.4, 129.2, 135.8, 136.0, 138.9, 139.9, 140.1, 141.5 (2C), 141.7, 141.8, 141.9, 142.2, 142.4, 142.9, 143.1, 144.4, 144.5, 145.1, 145.2, 145.7, 146.0 (2C), 146.2, 146.6, 147.1, 154.4, 155.0; HRMS (FAB) m/z 930.1492 (M + 1, $C_{72}H_{20}NO_2$ requires 930.1494).

Formation of 29 from 10. Eight minute irradiation, 100% conversion, column chromatography (hexane) to yield **29** (122 mg, 47%).

29: ^{1}H NMR 0.81−0.88 (m, 3H), 1.21−1.48 (m, 6H), 1.84−1.92 (m, 2H), 3.06 (t, 2H, J = 7.3 Hz), 4.26 (s, 2H), 4.46 (s, 2H), 6.74 (s, 1H), 7.32 (t, 1H, J = 7.3 Hz), 7.41 (t, 2H, J = 7.3 Hz), 7.64 (d, 2H, J = 7.2 Hz); ^{13}C NMR 14.1, 22.7, 27.1, 27.4, 31.8, 55.8, 58.3, 60.1, 67.3, 68.7, 127.4, 128.5, 129.4, 135.9, 136.2, 139.3, 139.9, 140.2, 141.6 (2C), 141.8, 141.9, 142.0, 142.3, 142.5, 143.0, 143.2, 144.5, 144.6, 145.2, 145.3, 145.8, 146.1 (2C), 146.3, 146.8, 147.2, 147.3 (2C), 154.5, 155.4; HRMS (FAB) m/z 926.1911 (M + 1, $C_{74}H_{24}N$ requires 926.1909).

Formation of 30 from 11. Eight minute irradiation, 93% conversion, column chromatography (CHCl$_3$/hexane = 1:3) to yield **30** (149 mg, 56%).

30: ^{1}H NMR 3.32 (t, 2H, J = 5.5 Hz), 3.39 (s, 3H), 3.62 (t, 2H, J = 4.8 Hz), 3.72 (t, 2H, J = 4.8 Hz), 3.94 (t, 2H, J = 5.5 Hz), 4.37 (s, 2H), 4.63 (s, 2H), 6.89 (s, 1H), 7.30 (t, 1H, J = 7.2 Hz), 7.39 (t, 2H, J = 7.2 Hz), 7.65 (d, 2H, J = 7.2 Hz); ^{13}C NMR 54.6, 58.2, 59.1, 60.9, 67.4, 69.2, 70.5 (2C), 72.0, 127.4, 128.5, 129.3, 135.9, 136.1, 139.1, 139.9, 140.1, 141.5, 141.8, 141.9 (2C), 142.3, 142.4, 143.1, 144.4, 144.6, 145.2, 145.3, 145.7, 146.0, 146.1, 146.2, 146.7, 147.1, 147.2, 154.6, 155.2; HRMS (FAB) m/z 944.1656 (M + 1, $C_{73}H_{22}NO_2$ requires 944.1651).

Formation of 31 and 38 from 12. Sixteen minute irradiation, 62% conversion, column chromatography (CHCl$_3$/hexane = 1:3) to yield **31** (83 mg, 32%); 60 min irradiation, 100% conversion, column chromatography (CHCl$_3$/hexane = 1:3) to yield **31** (197 mg, 76%) and **38** (33 mg, 12%).

31: ^{1}H NMR 1.35 (t, 3H, J = 7.2 Hz), 3.93 (s, 2H), 4.23 (q, 2H, J = 7.2 Hz), 4.53 (s, 2H), 4.75 (s, 2H), 6.95 (s, 1H), 7.31 (t, 1H, J = 6.9 Hz), 7.39 (t, 2H, J = 6.9 Hz), 7.62 (d, 2H, J = 6.9 Hz); ^{13}C NMR 14.4, 56.0, 58.1, 59.9, 60.7, 67.4, 68.5, 127.7, 128.7, 129.4, 136.1, 136.2, 138.5, 140.1, 140.3, 141.7 (2C), 141.9, 142.0, 142.1, 142.4, 142.6, 143.1, 143.3, 144.5, 144.7, 145.3, 145.4, 145.5, 145.9, 146.2, 146.4, 146.9, 147.3 154.5, 154.9, 171.6; HRMS (FAB) m/z 928.1343 (M + 1, $C_{72}H_{18}NO_2$ requires 928.1338).

38: ^{1}H NMR 0.48 (s, 9H), 1.15 (t, 3H, J = 7.2 Hz), 4.19 (q, 1H, J = 7.2 Hz), 4.28 (q, 1H, J = 7.2 Hz), 4.58 (d, 1H, J = 13.5 Hz), 5.26 (d, 1H, J = 13.5 Hz), 5.38 (s, 1H), 5.44 (s, 1H), 7.35 (t, 1H, J = 6.9 Hz), 7.43 (t, 2H, J = 6.9 Hz), 7.63 (d, 2H, J = 6.9 Hz); ^{13}C NMR 0.7, 14.1, 56.2, 60.9, 70.2, 77.2, 77.7, 78.0, 127.7, 128.6, 128.8, 134.9, 135.6, 135.7, 136.2, 139.0, 139.2, 139.5, 139.6, 140.1, 141.7 (2C), 141.8, 141.9, 142.1 (2C), 142.2 (2C), 142.3, 142.4, 142.6, 142.7, 143.0, 143.1, 144.2, 144.4 (2C), 144.5, 145.0, 145.1, 145.2, 145.3, 145.5, 145.8, 145.9, 146.1 (2C), 146.3, 146.4, 146.7, 146.9, 147.0, 152.8, 155.0, 156.6, 157.3, 170.6; HRMS (FAB) m/z 998.1580 (M + 1, $C_{75}H_{24}NO_2Si$ requires 998.1576).

Formation of 32 from 13. Eight minute irradiation, 82% conversion, column chromatography (CHCl$_3$/hexane = 1:5) to yield **32** (142 mg, 54%).

32: ^{1}H NMR 1.25 (t, 3H, J = 6.9 Hz), 2.84 (t, 2H, J = 7.2 Hz), 3.46 (t, 2H, J = 7.2 Hz), 4.15 (q, 2H, J = 6.9 Hz), 4.30 (s, 2H), 4.50 (s, 2H), 6.71 (s, 1H), 7.31 (t, 1H, J = 7.2 Hz), 7.39 (t, 2H, J = 7.2 Hz), 7.60 (d, 2H, J = 7.2 Hz); ^{13}C NMR 14.2, 32.9, 51.4, 58.1, 59.9, 60.7, 67.0, 68.4, 127.6, 128.5, 129.4, 135.9, 136.1, 138.4, 139.9, 140.2, 141.5, 141.6, 141.8, 141.9, 142.0, 142.2, 142.5, 143.1, 144.4, 144.6, 145.2, 145.3 (2C), 145.7, 146.1 (2C), 146.3, 146.7, 147.1, 154.3, 154.9, 172.3; HRMS (FAB) m/z 942.1497 (M + 1, $C_{73}H_{20}NO_2$ requires 942.1494).

Formation of 33 from 14. Eight minute irradiation, 100% conversion, column chromatography (CHCl$_3$/hexane = 2:1) to yield **33** (196 mg, 67%).

33: ^{1}H NMR 3.27 (t, 2H, J = 5.1 Hz), 3.81 (t, 2H, J = 5.4 Hz), 3.89 (t, 2H, J = 5.1 Hz), 4.01 (t, 2H, J = 5.4 Hz), 4.29 (s, 2H), 4.56 (s, 2H), 6.74 (s, 1H), 7.25 (t, 1H, J = 6.9 Hz), 7.33 (t, 2H, J = 6.9 Hz), 7.56 (d, 2H, J = 7.2 Hz), 7.64−7.67 (m 2H), 7.79−7.82 (m, 2H); ^{13}C NMR 37.6, 54.4, 58.2, 60.4, 67.5, 68.0, 69.1, 70.0, 123.2, 127.3, 128.4, 129.2, 132.0, 133.9, 135.8, 136.1, 139.0, 139.8, 140.1, 141.5 (2C), 141.7, 141.9 (2C), 142.2, 142.4 (2C), 143.1, 144.4, 144.6, 145.1, 145.2, 145.7, 146.0, 146.1, 146.2, 146.8, 147.1, 147.2154.5, 155.3, 168.2; HRMS (FAB) m/z 1059.1713 (M + 1, $C_{80}H_{23}N_2O_3$ requires 1059.1709).

Formation of 34 from 16. Eight minute irradiation, 100% conversion, column chromatography (CHCl$_3$/hexane = 1:30) to yield **34** (112 mg, 43%).

34: ^{1}H NMR 1.46−1.63 (m, 4H), 1.86−1.94 (m, 2H), 3.06 (t, 2H, J = 7.5 Hz), 3.64 (t, 2H, J = 6 Hz), 4.25 (s, 2H), 4.46 (s, 2H), 6.70 (s, 1H), 7.30 (t, 1H, J = 6.9 Hz), 7.39 (t, 2H, J = 6.9 Hz), 7.61 (d, 2H, J = 7.2 Hz); ^{13}C NMR 23.6, 27.3, 32.7, 55.7, 58.4, 60.3, 62.9, 67.3, 68.7, 127.4, 128.5, 129.5, 135.9, 136.2, 139.2, 139.9, 140.2, 141.6 (2C), 141.8, 142.0 (2C), 142.3, 142.5, 143.0, 143.2, 144.5, 144.6, 145.3 (2C), 145.8, 146.1, 146.2, 146.3, 146.8, 147.2 (2C), 147.3, 154.4, 155.3; HRMS (FAB) m/z 928.1699 (M + 1, $C_{73}H_{22}NO$ requires 928.1701).

Formation of 35 from 19. Eight minute irradiation, 100% conversion, column chromatography (CHCl$_3$/hexane = 1:30) to yield **35** (206 mg, 86%).

35: ^{1}H NMR 2.9 (s, 3H), 4.24 (s, 2H), 4.42 (s, 2H), 6.92 (s, 1H), 7.34 (t, 1H, J = 6.9 Hz), 7.44 (t, 2H, J = 6.9 Hz), 7.65 (d, 2H, J = 6.9 Hz); ^{13}C NMR 29.6, 45.0, 58.1, 63.8, 67.2, 71.0, 127.4, 128.5, 129.2, 136.0, 136.1, 138.8, 140.0, 140.1, 141.5 (2C), 141.7, 141.9 (2C), 142.2, 142.4 (2C), 143.1, 144.4, 144.6, 145.2 (2C), 145.3, 145.7, 146.0 (2C), 146.2, 146.6, 147.1, 147.2, 154.4, 155.2; HRMS (FAB) m/z 856.1132 (M + 1, $C_{69}H_{14}N$ requires 856.1126).

Formation of 36 from 20. Eight minute irradiation, 75% conversion, column chromatography (hexane) to yield **36** (167 mg, 64%); 60 min irradiation, 100% conversion, column chromatography (hexane) to yield **36** (237 mg, 91%).

36: ^{1}H NMR 4.22 (s, 4H), 4.48 (s, 2H), 6.44 (s, 1H), 7.34 (t, 1H, J = 7.2 Hz), 7.44 (t, 2H, J = 7.2 Hz), 7.67 (d, 2H, J = 7.2 Hz); ^{13}C NMR 58.4, 60.3, 66.8, 67.3, 127.7, 128.6, 129.7, 135.9, 136.1, 138.9, 139.9, 140.2, 141.6, 141.8, 141.9, 142.0, 142.3, 142.5, 143.0, 143.1, 144.5, 144.6, 145.2, 145.3, 145.8, 146.1 (2C), 146.3, 146.7, 147.2 (3C), 147.3, 154.3, 155.0; HRMS (FAB) m/z 932.1434 (M + 1, $C_{75}H_{18}N$ requires 932.1439).

Formation of 37 and 39 from 22. Sixty minute irradiation, 68% conversion, column chromatography (CHCl$_3$/hexane = 1:1) to yield **37** (59 mg, 23%); 120 min irradiation, 78% conversion, column chromatography (CHCl$_3$/hexane = 1:1) to yield **37** (93 mg, 36%) and **39** (11 mg, 4%).

37: ^{1}H NMR 1.32 (t, 6H, J = 7.2 Hz), 4.20 (s, 4H), 4.26 (q, 4H, J = 7.2 Hz), 4.77 (s, 2H), 7.06 (s, 1H); ^{13}C NMR 14.0, 14.3, 57.0, 57.6, 60.9, 67.5, 68.7, 135.9, 136.2, 139.9, 140.2, 141.5, 141.6 (2C), 141.9, 142.0, 142.3, 142.4, 142.5, 143.0, 143.1, 144.4, 144.6, 145.2, 145.3 (2C), 145.4, 145.7, 146.0, 146.1, 146.3 (2C), 146.8, 147.1, 147.2, 147.3, 154.5, 171.2; HRMS (FAB) m/z 924.1236 (M + 1, $C_{69}H_{18}NO_4$ requires 924.1230).

39: ^{1}H NMR 0.40 (s, 9H), 1.16 (t, 3H, J = 7.2 Hz), 1.37 (t, 3H, J = 7.2 Hz), 4.18−4.37 (m, 5H), 4.64 (d, 1H, J = 19.2 Hz), 4.80 (s, 1H), 5.78 (s, 1H); ^{13}C NMR 0.7, 14.2, 14.3, 49.5, 60.6, 61.7, 65.8, 74.2, 74.4, 76.0, 125.2, 128.2, 129.0, 135.9, 136.2, 137.3, 137.5, 138.7, 138.8, 139.4, 141.4, 141.6, 141.7, 141.9, 142.0, 142.1, 142.2, 142.7 (2C), 142.9, 143.0, 143.1, 144.4 (2C), 144.6, 144.7, 145.1, 145.2, 145.3, 145.4, 145.8 (2C), 145.9, 146.0, 146.2, 146.3, 146.4, 146.9, 147.2 (2C), 152.4, 153.6 (2C), 154.4, 169.6, 171.1; HRMS (FAB) *m*/*z* 994.1473 (M + 1, $C_{72}H_{24}NO_4Si$ requires 994.1475).

Formation of 48 and 49 from 45. Thirty minute irradiation, 88% conversion, column chromatography (CS_2) to yield **48** (164 mg, 64%) and **49** (26 mg, 9%).

48: ^{1}H NMR 3.82 (s, 3H), 3.93 (s, 2H), 4.54 (s, 2H), 4.76 (s, 2H), 6.99 (s, 1H), 7.24−7.32 (m, 1H), 7.37(t, 1H, *J* = 6.9 Hz), 7.59 (d, 2H, *J* = 6.9 Hz); ^{13}C NMR 51.2, 55.2, 57.9, 59.6, 67.1, 68.3, 127.6, 128.5, 129.1, 135.8, 135.9, 138.0, 139.8, 140.1, 141.4 (2C), 141.5, 141.7, 141.8, 142.1, 142.3, 143.0, 144.2, 144.4, 145.1, 145.2, 145.5, 145.9 (2C), 146.1, 146.5, 147.0, 154.1, 154.4, 171.2; HRMS (FAB) *m*/*z* 914.1177 (M + 1, $C_{71}H_{16}NO_2$ requires 914.1176).

49: ^{1}H NMR 0.51 (s, 9H), 3.75 (s, 3H), 4.59 (d, 1H, *J* = 13.5 Hz), 5.28 (d, 1H, *J* = 13.5 Hz), 5.40 (s, 1H), 5.50 (s, 1H), 7.35−7.40 (m, 1H), 7.46 (t, 1H, *J* = 6.9 Hz), 7.65 (d, 2H, *J* = 6.9 Hz); ^{13}C NMR 0.8, 51.7, 56.3, 70.2, 77.2, 77.7, 77.9, 127.8, 128.7, 128.9, 134.9, 135.6, 135.7, 136.2, 138.8, 139.3, 139.6, 140.2, 141.7, 141.8 (2C), 141.9, 142.1, 142.2, 142.3, 142.4, 142.7 (2C), 143.0, 143.2, 144.2, 144.4, 144.5, 144.6, 145.0, 145.1, 145.2, 145.5, 145.8, 146.0 (2C), 146.1, 146.2, 146.3, 146.7, 147.0, 171.2; HRMS (FAB) *m*/*z* 984.1418 (M + 1, $C_{74}H_{22}NO_2Si$ requires 984.1420).

General Procedures of Photoreaction of C_{60} with Non-silyl Tertiary Amines 43 and 44. A nitrogen purged 10% EtOH−toluene solution (220 mL) containing C_{60} (0.28 mmol) and non-silyl tertiary amines (0.56 mmol) was irradiated with uranium filtered light for a certain period of time. Concentration of the photolyzates in vacuo gave residues that were washed with $CHCl_3$ followed by filtration to recover C_{60}. The filtrate was concentrated in vacuo to give residues that were subjected to silica gel column chromatography to yield fulleropyrrolidines.

Photoreaction of C_{60} with 43: Formation of 46. One-hundred twenty minute irradiation, 55% conversion, column chromatography (CS_2/hexane = 1:1) to yield **46** (77 mg, 30%).

46: ^{1}H NMR 1.34 (t, 3H, *J* = 7.2 Hz), 2.88 (s, 3H), 4.35 (q, 1H, *J* = 7.2 Hz), 4.44 (q, 1H, *J* = 7.2 Hz), 5.62 (s, 1H), 6.36 (s, 1H), 7.29 (t, 1H, *J* = 7.2 Hz), 7.38 (t, 2H, *J* = 7.2 Hz), 7.75 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR (CS_2 + $CDCl_3$) 14.4, 34.8, 60.8, 70.6, 76.6, 77.3, 128.3, 128.4, 136.0, 136.7, 139.8, 141.7 (2C), 141.8, 141.9 (2C), 142.3 (2C), 142.4, 144.0, 144.2, 144.3, 144.4, 144.9 (2C), 145.0 (2C), 145.2, 145.3 (2C), 145.6, 145.8, 146.1, 147.0, 147.1, 150.5, 153.4, 153.6, 155.5, 170.4; HRMS (FAB) *m*/*z* 926.1184 (M + 1, $C_{72}H_{16}NO_2$ requires 926.1181).

Photoreaction of C_{60} with 44: Formation of 47. One-hundred twenty minute irradiation, 43% conversion, column chromatography (CS_2/hexane = 1:1) to yield **47** (99 mg, 39%).

47: ^{1}H NMR 2.87 (s, 3H), 3.91 (s, 3H), 5.67 (s, 1H), 6.33 (s, 1H), 7.29 (t, 1H, *J* = 7.2 Hz), 7.38 (t, 2H, *J* = 7.2 Hz), 7.76 (d, 2H, *J* = 6 Hz); ^{13}C NMR (CS_2 + $CDCl_3$) 35.0, 51.5, 70.6, 75.8, 76.9, 77.3, 128.3, 128.5, 135.7, 136.0, 136.1, 136.6, 139.8, 141.3, 141.4, 141.5, 141.6, 141.7, 141.8 (3C), 141.9 (2C), 142.3, 142.4, 142.5, 144.1, 144.2, 144.3, 144.4, 144.9 (3C), 145.0 (2C), 145.1, 145.2, 145.3 (2C), 145.4, 145.6, 145.7, 145.8, 145.9 (2C), 146.0, 146.1 (2C), 146.2, 146.4, 150.5, 153.3, 153.6, 155.4, 171.0; HRMS (FAB) *m*/*z* 912.1021 (M + 1, $C_{71}H_{14}NO_2$ requires 912.1025).

Photoreactions of α-Silyl Tertiary Amine 14. Preparative photochemical reaction was conducted using an apparatus consisting of a 450 W Hanovia medium vapor pressure mercury lamp surrounded by a Pyrex glass filter (>290 nm) in a water-cooled quartz immersion surrounded by the solution being irradiated, consisting of a 10% EtOH−toluene solution (220 mL) containing α-silyl tertiary amine **14** (0.487 mmol). The solutions being irradiated were purged with nitrogen before and during irradiations, and irradiation was carried out for 1 h. The photolysates were concentrated in vacuo to generate residues, which were subjected to silica gel column chromatography to yield cyclic amidol **41** (64 mg, 39%).

41: ^{1}H NMR 2.49 (m, 2H), 3.62−3.88 (m, 7H), 4.03−4.11 (m, 2H), 4.49−4.59 (m, 1H), 6.40 (d, 1H, *J* = 7.8 Hz), 7.05−7.10 (m, 1H), 7.26−7.29 (m, 3H), 7.30−7.43 (m, 4H), 7.61 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR 42.2, 71.3, 71.7, 71.7, 74.6, 77.2, 92.9, 122.9, 124.3, 127.8, 128.0, 129.1, 130.7, 131.3, 135.3, 146.0, 168.1; HRMS (EI) *m*/*z* 338.1628 (M^+, $C_{20}H_{22}N_2O_3$ requires 338.1630).

Relative Quantum Yields of Photoreaction of C_{60} with α-Silyl Tertiary Amines. Independent N_2 purged 10% EtOH−toluene solutions containing each α-silyl tertiary amine (3.47×10^{-4} M) with C_{60} (1.74×10^{-4} M) in 10 mL in quartz tubes were simultaneously irradiated using uranium filtered light in a merry-go-round apparatus for 5 min (below 15% conversion). Each photolysate was subjected to HPLC analysis.

Cyclic Voltammetry. Electrochemical experiments using a three-electrode one-compartment cell were conducted using a potentiostat (CH Instruments, Model 630C). The electrochemical measurements were conducted using an Ag/AgCl reference electrode, a coiled platinum counter electrode, and a glassy carbon electrode (Bioanalytical Systems Inc., *A* = 0.071 cm^2). The potential range of cyclic voltammetry was between −1.2 and 3.0 V (vs Ag/AgCl), with a scan rate of 0.1 V/s. Square-wave voltammograms (SWV) were registered in the potential interval −1.2 to 3.0 V (vs Ag/AgCl) under the following conditions: potential increment, 5 mV; pulse frequency, 15 Hz (which was optimized in relation to the peak definition).

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of all previously unidentified compounds, UV−visible spectra, and oxidation potentials of amine donors. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ REFERENCES

(1) Kroto, H. W.; Health, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 163.

(2) Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(3) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* **1990**, *350*, 600.

(4) Anthopoulos, T. D.; Tanase, C.; Setayesh, S.; Meijer, E. J.; Haummelen, J. C.; Blom, P. W. M.; de Leeuw, D. M. *Adv. Mater.* **2004**, *16*, 2174.

(5) Yang, Y. *Nature* **1992**, *356*, 585.

(6) Allemand, P. M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Konovan, S.; Gruner, G.; Thompson, J. D. *Science* **1991**, *253*, 301.

(7) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.

(8) Bendikov, M.; Wudl, F. *Chem. Rev.* **2004**, *104*, 4891.

(9) Matsuo, Y.; Ichiki, T.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 9932.

(10) Brunetti, F. G.; Kumar, R.; Wudl, F. *J. Mater. Chem.* **2010**, *20*, 2934.

(11) Mateo-Alonso, A.; Iliopoulos, K.; Couris, S.; Prato, M. *J. Am. Chem. Soc.* **2008**, *130*, 1534.

(12) Takenaka, S.; Yasmashita, K.; Takagi, N.; Hatta, T.; Tsuge, O. *Chem. Lett.* **1999**, 321.

(13) Friedman, S. H.; DeCamp, D. L.; Sijbesma, R. P.; Srdanov, G.; Wudl, F.; Keyton, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6506.

(14) Cataldo, F.; Da Ros, T. *Medicinal Chemistry and Pharmacological Potential of Fullerenes and Carbon Nanotubes*; Springer: Dordrecht, The Netherlands, 2008.

(15) Sun, D.; Zhu, Y.; Liu, Z.; Liu, G.; Guo, X.; Zhan, R.; Liu, S. *Chin. Sci. Bull.* **1997**, *42*, 748.

(16) Boutorine, A.; Tokuyama, H.; Takasugi, M.; Isobe, H.; Nakamura, E.; Helene, C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2462.

(17) Tokuyama, H.; Yamago, S.; Nakamura, E.; Shiraki, T.; Sugiura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 7918.

(18) Kato, S.; Aoshima, H.; Saitoh, Y.; Miwa, N. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 5293.

(19) Yang, J.; Alemany, L. B.; Driver, J.; Hartgerink, J. D.; Barron, A. R. *Chem.—Eur. J.* **2007**, *13*, 2530.

(20) Partha, R.; Conyers, J. L. *Int. J. Nanomed.* **2009**, *4*, 261.

(21) Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075.

(22) Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* **1991**, *254*, 1183.

(23) McEwen, C. N.; McKay, R. G.; Larsen, B. S. *J. Am. Chem. Soc.* **1992**, *114*, 4412.

(24) Guldi, D. M.; Neta, P.; Asmus, K.-D. *J. Phys. Chem.* **1994**, *98*, 4617.

(25) Imahori, H.; Sakata, Y. *Adv. Mater.* **1997**, *9*, 537.

(26) Imahori, H.; Hagiwara, K.; Akiyama, T.; Aoki, M.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *Chem. Phys. Lett.* **1996**, *263*, 545.

(27) Guldi, D. M.; Prato, M. *Acc. Chem. Res.* **2000**, *33*, 695.

(28) Singh, T. B.; Marjanović, N.; Matt, G. J.; Günes, S.; Sariciftci, N. S.; Ramil, A. M.; Andreev, A.; Sitter, H.; Schwödiauer, R.; Bauer, S. *Org. Electron.* **2005**, *6*, 105.

(29) Wudl, F. *Acc. Chem. Res.* **1992**, *126*, 157.

(30) Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khemani, K.; Wudl, F.; Leonetti, J.; Little, R. D.; White, T.; Richborn, B.; Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1993**, *115*, 1594.

(31) (a) An, Y.-Z.; Anderson, H.; Rubin, Y. *J. Org. Chem.* **1993**, *58*, 4799. (b) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798.

(32) (a) Maroto, E. E.; Filippone, S.; Suárez, M.; Martínez-Álvarez, R.; de Cózar, A.; Cossío, F. P.; Martín, N. *J. Am. Chem. Soc.* **2014**, *135*, 705. (b) Filippone, S.; Maroto, E. E.; Martín-Domenech, A.; Suarez, M.; Martín, N. *Nat. Chem.* **2009**, *1*, 578.

(33) Bingel, C. *Chem. Ber.* **1993**, *126*, 1957.

(34) Hirsch, A.; Lamparth, I.; Karfunkel, H. R. *Angew, Chem. Int. Ed. Engl.* **1994**, *33*, 437.

(35) Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697.

(36) Hirsch, A.; Soi, A.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 766.

(37) Komatsu, K.; Murata, Y.; Takimoto, N.; Mori, S.; Sugita, N.; Wan, T. S. M. *J. Org. Chem.* **1994**, *59*, 6101.

(38) Keshavarz, M. K.; Knight, B.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 11371.

(39) Timmerman, P.; Anderson, H. L.; Faust, R.; Nierengarten, J.-F.; Habicher, T.; Seiler, P.; Diederich, F. *Tetrahedron* **1996**, *52*, 4925.

(40) Fujiwara, F.; Murata, Y.; Wan, T. S. M.; Komatsu, K. *Tetrahedron* **1998**, *54*, 2049.

(41) Champeil, E.; Crean, C.; Larraya, C.; Pescitelli, G.; Proni, G.; Ghosez, L. *Tetrahedron* **2008**, *64*, 10319.

(42) Zhang, Y.; Matsuo, Y.; Li, C.-Z.; Tanaka, H.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 8086.

(43) (a) Meier, M. S.; Bergosh, R. G.; Gallagher, M. E.; Spielmann, H. P.; Wang, Z. *J. Org. Chem.* **2002**, *67*, 5946. (b) Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697. (c) Lu, S.; Jin, T.; Bao, M.; Yamamoto, Y. *Org. Lett.* **2012**, *14*, 3466.

(44) (a) Naim, A.; Shevlin, P. B. *Tetrahedron Lett.* **1992**, *33*, 7097. (b) Husebo, L. O.; Sitharaman, B.; Furukawa, K.; Kato, T.; Wilson, L. J. *J. Am. Chem. Soc.* **2004**, *126*, 12055. (c) Wang, G.-W.; Li, F.-B.; Chen, Z.-X.; Wu, P.; Cheng, B.; Xu, Y. *J. Org. Chem.* **2007**, *72*, 4779.

(45) (a) Hashiguchi, M.; Obata, N.; Maruyama, M.; Yeo, K. S.; Ueno, T.; Ikebe, T.; Takahashi, I.; Matsuo, Y. *Org. Lett.* **2012**, *14*, 3276. (b) Liu, T.-X.; Li, F.-B.; Wang, G.-W. *Org. Lett.* **2011**, *13*, 6130.

(46) (a) Yeh, W.-Y. *Chem. Commun.* **2011**, *47*, 1506. (b) Toh, K. K.; Wang, Y.-F.; Ng, E. P. J.; Chiba, S. *J. Am. Chem. Soc.* **2011**, *133*, 465.

(47) (a) Matsumoto, F.; Iwai, T.; Moriwaki, K.; Takao, Y.; Ito, T.; Mizuno, T.; Ohno, T. *J. Org. Chem.* **2012**, *77*, 9038. (b) Lu, S.; Si, W.; Bao, M.; Yamamoto, Y.; Jin, T. *Org. Lett.* **2013**, *15*, 4030. (c) Tzirakis, M. D.; Orfanopoulos, M. *Org. Lett.* **2008**, *10*, 873.

(48) Fujitsuka, M.; Ito, O. *Encyclopedia of Nanoscience and Nanotechnology*; Nalwa, H. S., Ed.; American Scientific Publishers: Stevenson Ranch, CA; Vol *8*, pp 593−615.

(49) (a) Akasaka, T.; Maeda, Y.; Wakahara, T.; Okamura, M.; Fujitsuka, M.; Ito, O.; Kobayashi, K.; Nagase, S.; Kato, M.; Nakadaira, Y.; Horn, E. *Org. Lett.* **1999**, *1*, 1509. (b) Akasaka, T.; Suzuki, T.; Maeda, Y.; Ara, M.; Wakahara, T.; Kobayashi, K.; Nagase, S.; Kato, M.; Nakadaira, Y.; Fujitsuka, M.; Ito, O. *J. Org. Chem.* **1999**, *64*, 566.

(50) Mikami, K.; Matsumoto, S.; Ishida, A.; Takamuku, S.; Suenobu, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **1995**, *117*, 11134.

(51) (a) Siedschlag, C.; Luftmann, H.; Wolff, C.; Mattay, J. *Tetrahedron* **1997**, *53*, 3587. (b) Krusic, P. J.; Wasserman, E.; Parkinson, B. A.; Malone, B.; Holler, E. R. *J. Am. Chem. Soc.* **1991**, *113*, 6274. (c) Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.* **1999**, 2445.

(52) Miyake, Y.; Ashida, Y.; Nakajima, K.; Nishibayashi, Y. *Chem.—Eur. J.* **2014**, *20*, 6120.

(53) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364.

(54) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773.

(55) Arbogast, J. W.; Foote, C. S.; Kao, M. *J. Am. Chem. Soc.* **1992**, *114*, 2277.

(56) (a) Arbogast, J. W.; Darmanyan, A. O.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11. (b) Terazima, M.; Hirota, N.; Shinohara, H.; Saito, Y. *J. Phys. Chem.* **1991**, *95*, 9080.

(57) Lawson, G. E.; Kiaygorodskiy, A.; Ma, B.; Bunker, C. E.; Sun, Y.-P. *J. Chem. Soc., Chem. Commun.* **1995**, 2225.

(58) Nakamura, Y.; Suzuki, M.; O-kawa, K.; Konno, T.; Nishimura, J. *J. Org. Chem.* **2005**, *70*, 8472.

(59) Liou, K.-F.; Cheng, C.-H. *Chem. Commun.* **1996**, 1423.

(60) Lawson, G. E.; Kitaygorodskiy, A.; Sun, Y.-P. *J. Org. Chem.* **1999**, *64*, 5913.

(61) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(62) Brumfield, M. A.; Yoon, U. C.; Hasegawa, E.; Mariano, P. S. *J. Org. Chem.* **1988**, *53*, 5435.

(63) (a) Cohen, S. G.; Parola, A. H.; Parsons, G. H., Jr. *Chem. Rev.* **1973**, *73*, 141. (b) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 1048.

(64) (a) Padwa, A.; Eisenhardt, W.; Gruber, N.; Pashayan, D. *J. Am. Chem. Soc.* **1969**, *91*, 1857. (b) Cohen, S. G.; Chao, H. M. *J. Am. Chem. Soc.* **1968**, *90*, 165. (c) Cohen, S. G.; Cohen, J. I. *J. Phys. Chem.* **1968**, *72*, 3782.

(65) (a) Bartholomew, R. F.; Davidson, R. S.; Lambeth, P. F.; McKeller, J. F.; Turner, P. H. *J. Chem. Soc., Perkin Trans. 2* **1972**, 577. (b) Shaefer, C. G.; Peters, K. S. *J. Am. Chem. Soc.* **1980**, *102*,

7566. (c) Pak, C.; Sakurai, H.; Tosa, T. *J. Chem. Soc., Chem. Commun.* **1970**, 1311.

(66) (a) Yoon, U. C.; Kim, J. U.; Hasegawa, E.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 4421. (b) Yoon, U. C.; Kim, Y. C.; Choi, J. J.; Kim, D. U.; Mariano, P. S.; Cho, I. S.; Jeon, Y. T. *J. Org. Chem.* **1992**, *57*, 1422.

(67) (a) Xu, W.; Jeon, Y. T.; Hasegawa, E.; Yoon, U. C.; Mariano, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 406. (b) Yoon, U. C.; Kim, J. U.; Hasegawa, E.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 4421. (c) Hasegawa, E.; Wu, X.; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *J. Am. Chem. Soc.* **1988**, *110*, 8099.

(68) (a) Yoon, U. C.; Kim, J. W.; Ryu, J. Y.; Cho, S. J.; Oh, S. W.; Mariano, P. S. *J. Photochem. Photobiol., A* **1997**, *106*, 145. (b) Yoon, U. C.; Oh, S. W.; Lee, J. H.; Park, J. H.; Kang, K. T.; Mariano, P. S. *J. Org. Chem.* **2001**, *66*, 939. (c) Cho, D. W.; Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **2011**, *44*, 204.

(69) (a) Cho, D. W.; Quan, C.; Park, H. J.; Choi, J. H.; Kim, S. R.; Hyung, T. G.; Yoon, U. C.; Kim, S. H.; Jin, Y. X.; Mariano, P. S. *Tetrahedron* **2010**, *66*, 3173. (b) Yoon, U. C.; Jin, Y. X.; Oh, S. W.; Park, C. H.; Park, J. H.; Campana, C. F.; Cai, X.; Duesler, E. N.; Mariano, P. S. *J. Am. Chem. Soc.* **2003**, *125*, 10664. (c) Yoon, U. C.; Kwon, H. C.; Hyung, T. G.; Choi, K. H.; Oh, S. W.; Yang, S.; Zhao, Z.; Mariano, P. S. *J. Am. Chem. Soc.* **2004**, *126*, 1110. (d) Cho, D. W.; Choi, J. H.; Oh, S. W.; Quan, C.; Yoon, U. C.; Wang, R.; Yang, S.; Mariano, P. S. *J. Am. Chem. Soc.* **2008**, *130*, 2276.

(70) (a) Griesbeck, A. G.; Thomas, H.; Oelgemoeller, M.; Molis, A.; Heidtmann, A. *Helv. Chim. Acta* **2002**, *85*, 4561. (b) Griesbeck, A. G.; Heinrich, T.; Oelgemoeller, M.; Lex, J.; Molis, A. *J. Am. Chem. Soc.* **2002**, *124*, 10972.

(71) Coyle, J. D.; Newport, G. L. *Tetrahedron Lett.* **1977**, *18*, 899.

(72) (a) Kanaoka, Y.; Migita, Y. *Tetrahedron Lett.* **1974**, *15*, 3693. (b) Machida, M.; Takechi, H.; Kanaoka, Y. *Heterocycles* **1980**, *14*, 1255.

(73) (a) Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaya, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962. (b) Yoshida, J.; Matsunaga, S.; Murata, T.; Isoe, S. *Tetrahedron* **1991**, *47*, 615.

(74) (a) Cooper, B. E.; Owen, W. J. *J. Organomet. Chem.* **1971**, *29*, 33. (b) Pitt, C. G. *J. Organomet. Chem.* **1973**, *61*, 49.

(75) Zang, X. M.; Yeh, S.-R.; Hong, S.; Freccero, M.; Albini, A.; Falvey, D. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1994**, *116*, 4211.

(76) Su, Z.; Mariano, P. S.; Falvey, D. E.; Yoon, U. C.; Oh, S. W. *J. Am. Chem. Soc.* **1998**, *120*, 10676.

(77) (a) Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213. (b) Ullrich, J. W.; Chiu, F. T.; Harding, T.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 220. (c) Chen, S. F.; Ullrich, J. W.; Mariano, P. S. *J. Am. Chem. Soc.* **1983**, *205*, 6160.

(78) (a) d'Alessandro, N.; Albini, A.; Mariano, P. S. *J. Org. Chem.* **1993**, *58*, 937. (b) Ohga, K.; Mariano, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 617.

(79) (a) Dai-Ho, G.; Mariano, P. S. *J. Org. Chem.* **1988**, *53*, 5113. (b) Cho, I. S.; Tu, C. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1990**, *112*, 3594. (c) Park, H. J.; Choi, J. H.; Park, B. N.; Yoon, U. C.; Cho, D. W.; Mariano, P. S. *Res. Chem. Intermed.* **2012**, *38*, 847.

(80) (a) Yoon, U. C.; Oh, S. W.; Lee, C. W. *Heterocycles* **1995**, *41*, 2665. (b) Yoon, U. C.; Mariano, P. S. *Bull. Korean Chem. Soc.* **2006**, *27*, 1099. (c) Hasegawa, E.; Brumfield, M. A.; Mariano, P. S.; Yoon, U. C. *J. Org. Chem.* **1988**, *53*, 5435.

(81) (a) Ahmed-Schofield, R.; Mariano, P. S. *J. Org. Chem.* **1985**, *50*, 5667. (b) Wang, R.; Zhao, Z.; Mariano, P. S.; Choi, K. H.; Kim, S. H.; Yoon, U. C. *J. Photochem. Photobiol., A* **2005**, *175*, 232. (c) Maeda, H.; Tierney, D. L.; Mariano, P. S.; Banerjee, M.; Cho, D. W.; Yoon, U. C. *Tetrahedron* **2008**, *64*, 5268.

(82) Katritzky, A. R.; Koeditz, J.; Lang, H. *Tetrahedron* **1994**, *50*, 12571.

(83) Wang, R.; Chen, C.; Duesler, E.; Mariano, P. S.; Yoon, U. C. *J. Org. Chem.* **2004**, *69*, 1215.

(84) Gan, L.; Jiang, J.; Zhang, W.; Su, Y.; Shi, Y.; Huang, C.; Pan, J.; Lu, M.; Wu, Y. *J. Org. Chem.* **1998**, *63*, 4240.

(85) (a) Zhang, S.; Gan, L.; Huang, C.; Lu, M.; Pan, J.; He, X. *J. Org. Chem.* **2002**, *67*, 883. (b) Gothelf, K. V.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 863.

(86) Soheili, A.; Tambar, U. K. *J. Am. Chem. Soc.* **2011**, *133*, 12956.

(87) (a) Sun, Y.-P.; Ma, B.; Bunker, C. E.; Liu, B. *J. Am. Chem. Soc.* **1995**, *117*, 12705. (b) Yeo, S. J.; Pode, R.; Ahn, J. S. *J. Korean Phys. Soc.* **2009**, *55*, 322.

(88) Xu, W.; Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 1431.

(89) Sawamura, M.; Nagahama, N.; Toganoh, M.; Hackler, U. E.; Isobe, H.; Nakamura, E.; Zhou, S.-Q.; Chu, B. *Chem. Lett.* **2000**, *29*, 1098.

(90) Bernstein, R.; Foote, C. S. *J. Phys. Chem. A* **1999**, *103*, 7244.

(91) Sension, R. J.; Phillips, C. M.; Szarka, A. Z.; Romanow, W. J.; McGhie, A. R.; MaCauley, J. P., Jr.; Smith, A. B., III; Hochstrasser, R. M. *J. Phys. Chem.* **1991**, *95*, 6075.

(92) Cheng, H.; Gan, L.; Shi, Y.; Wei, X. *J. Org. Chem.* **2001**, *66*, 6369.