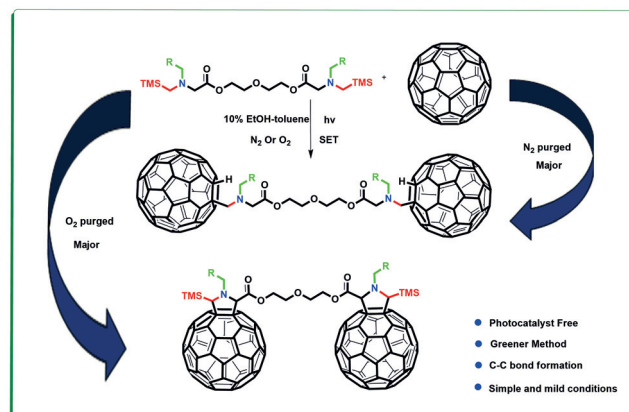


A Photocatalyst-Free, SET-Mediated Photochemical Approach for the Synthesis of Dumbbell-Like Amine-Functionalized Bis-C₆₀ Fullerene through C–C Bond Formation

Amol Balu Atar*

Department of Chemistry, Sejong University,
Seoul 143-747, Republic of Korea
amol.atar@sejong.ac.kr



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Abstract A novel method for the synthesis of dumbbell-like amine-functionalized bis-C₆₀ fullerene from simple bis-α-silyl tertiary benzyl amines and C₆₀ fullerene is described. The photoreactions between bis-α-silyl tertiary benzyl amines and C₆₀ furnished single-bonded bis-aminomethyl-1,2-dihydrofullerenes and double-bonded 1,2,5-trisubstituted bis-fulleropyrrolidines through 1,3-dipolar cycloaddition reactions of azomethine ylides under mild conditions.

Key words bis-C₆₀ fullerene, SET, photocatalyst free, 1,2-dihydrofullerenes, fulleropyrrolidines

Buckyball fullerenes, which are the most representative and abundant in terms of natural occurrence, possess unique physical and chemical properties that may be exploited for a wide variety of applications ranging from chemical sensors to superconductivity.¹ Functionalized fullerene derivatives have potential applications in the field of medicinal chemistry and have boosted the interest of the scientific community in these new molecular carbon allotropes.^{2,3} The broad range of physical and chemical properties of functionalized fullerenes makes them interesting building blocks for superconductors, photoconductors, and semiconductors, ferromagnetic, electronic and optical devices.^{4–10} Thus, dumbbell-like amine-functionalized bis-C₆₀ fullerene has attracted much attention in recent years because of its unique applications in molecular electronics and in the construction of photovoltaic devices.¹¹ The functionalized bis-C₆₀ fullerenes not only increase the solubility in common organic solvent but also tune the electronic

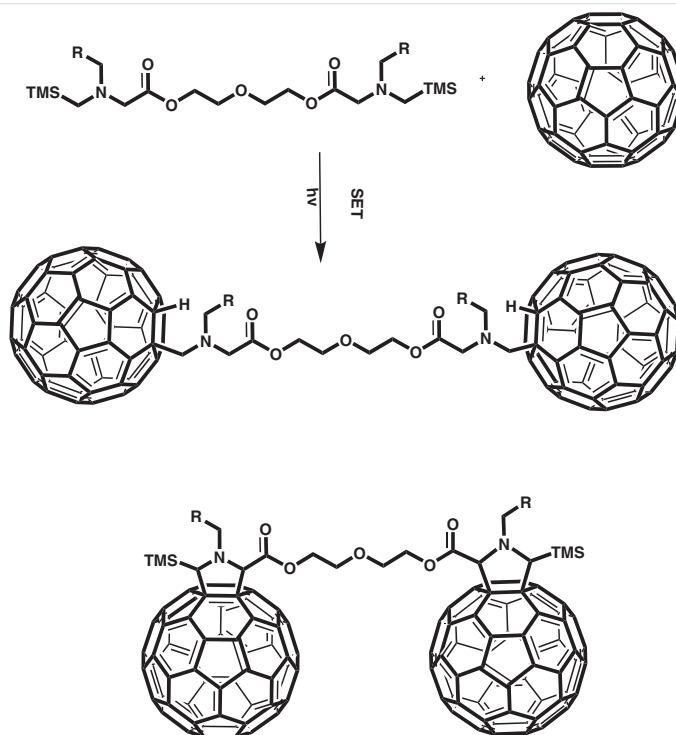
properties. The great solubility in common organic solvent enables desirable morphological properties of the functionalized bis-C₆₀ fullerenes to be developed.

Synthetic methods for the formation of dumbbell-like fullerene compounds have been reported by reaction of fullerene, carbonyl compounds, and diamines.^{12–16} The most common approach for the synthesis of amine functionalized C₆₀ fullerene derivatives through azomethine ylides was first reported by using the Prato reaction.¹⁷ Accordingly, A. S. Konev et al. developed the reaction of bisaziridines with C₆₀ fullerene to give dumbbell-like bis-C₆₀ fullerene triads.¹³ However, the reported methods have limited scope, harsh reaction conditions, require the use of transition-metal catalysts and additives, and involve tedious work-up processes and long reaction times, which strongly affect the economics as well as the environment-friendly nature of the reaction. The most common approaches derived for the preparation of dumbbell-like amine-functionalized bis-C₆₀ fullerenes involve thermal reaction. In contrast, photoinduced single-electron transfer (SET) reactions without using photocatalyst have become attractive for the preparation of substituted fullerenes because they can be carried out under environmentally benign conditions using visible light and because they generate unique products.^{18,19} The SET-promoted reaction involves reductive cleavage of a functional group without using any catalyst, and it is often utilized in modern organic reaction. The formation of a C–C bond through photoinduced SET reaction requires a radical ion pair in which the electron donor unit, such as tertiary amines, and electron acceptor, such as fullerene, result in the formation of complex organic molecules.

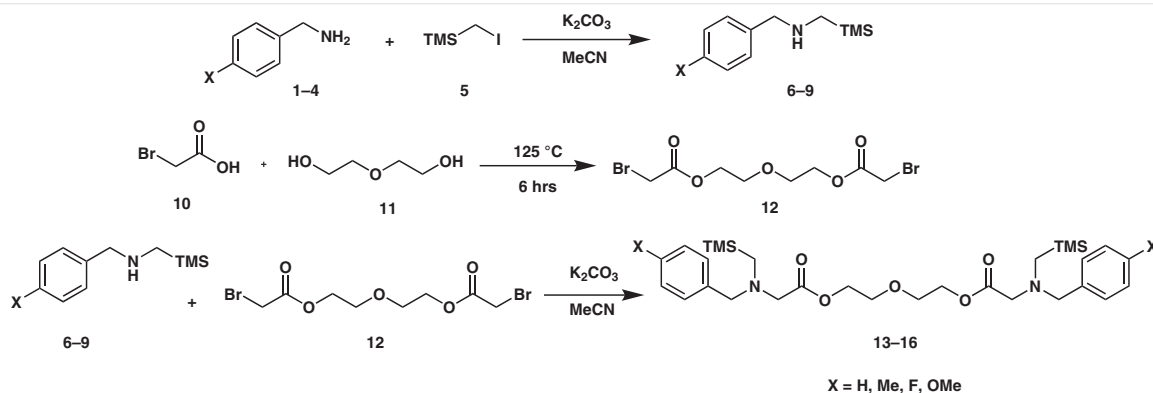
In the framework of our research concerning the development of new C–C and C–N bond-forming reactions for the synthesis of novel types of organic molecules,^{20–22} compounds with two bis- α -silyl tertiary benzyl amines connected by an aliphatic linker have been developed, which allow the construction of amine-functionalized bis- C_{60} fullerene. We present here the synthesis and characterization of bis- α -silyl tertiary benzyl amines, and the reaction with C_{60} fullerene for the preparation and characterization of novel dumbbell-like amine-functionalized bis- C_{60} fullerene derivatives by using photoinduced SET reactions (Scheme 1). The reaction is easy to perform and allows var-

ious amine-functionalized bis- C_{60} fullerenes to be synthesized. More importantly, the reaction was carried out in the absence of photocatalyst, which makes them green protocols. These reaction procedures are simple and can be used to isolate products with high purity and satisfactory yields. To our knowledge, this is the first report of a SET-mediated photochemical approach for the synthesis of dumbbell-like amine-functionalized bis- C_{60} fullerene through C–C bond formation.

The study was initiated by the synthesis of bis- α -silyl tertiary benzyl amines. The routes employed to prepare the bis- α -trimethylsilyl-substituted tertiary benzyl amines is



Scheme 1 Synthesis dumbbell-like amine-functionalized bis- C_{60} fullerene



Scheme 2 Synthesis of bis- α -silyl tertiary benzyl amines 13–16

outlined in Scheme 2. The α -silyl benzyl amines **6–9** were synthesized by employing potassium carbonate promoted substitution reactions of commercially available benzyl amines **1–4** with iodomethyltrimethylsilane **5** (Scheme 2).²³

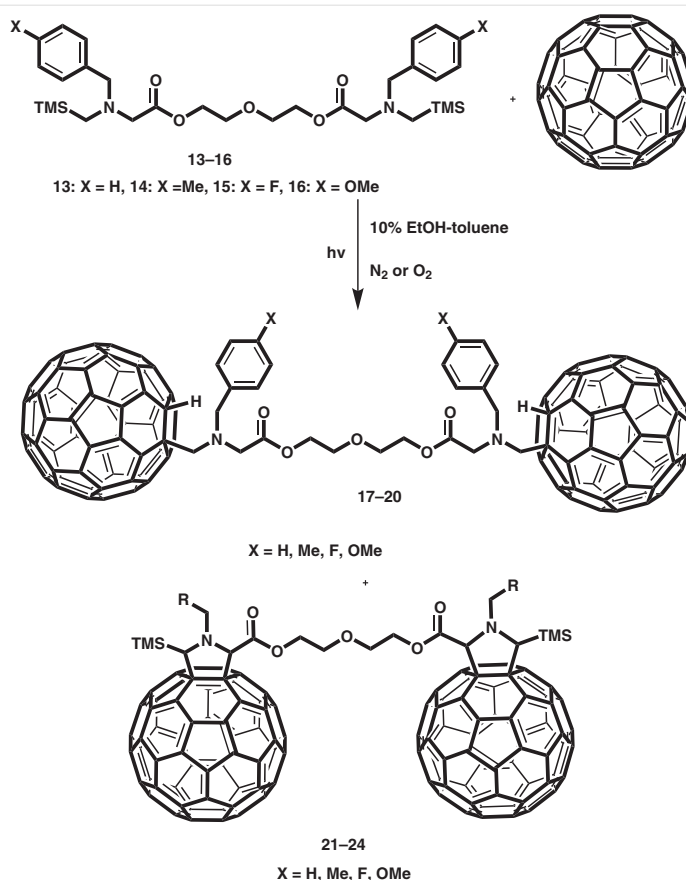
The known compound 2,2'-oxybis(ethane-2,1-diyl)bis(2-bromoacetate) (**12**) was easily prepared by adopting the literature precedent.²⁴ The diethylene glycol **11** was reacted with bromoacetic acid **10** under solvent-free conditions to yield the corresponding 2,2'-oxybis(ethane-2,1-diyl)bis(2-bromoacetate). The compounds with two bis- α -silyl tertiary benzyl amine units connected by an aliphatic linker have been developed by reaction of known α -trimethylsilyl-substituted secondary benzyl amines **6–9** with **12** in the presence of K_2CO_3 to yield the corresponding bis- α -silyl tertiary benzyl amines **13–16** in high yields (80–60%).²⁵

With bis- α -silyl tertiary benzyl amines **13–16** in hand, we next explored the photochemical reaction with C_{60} fullerene for the formation of dumbbell-like amine-functionalized bis- C_{60} fullerene derivatives. The yields and product distributions of photoreactions of C_{60} with the bis- α -trimethylsilyl-substituted tertiary benzyl amines **13–16**, which have various substituents on the *para*-position of the

phenyl ring, were determined (Scheme 3). All photochemical reactions were carried out by irradiation with a Hanovia medium-pressure mercury lamp (450 W) through a flint glass filter ($\lambda > 300$ nm) by using 10% EtOH-toluene solutions containing C_{60} (0.28 mmol) and bis- α -trimethylsilyl-substituted tertiary benzyl amines (0.56 mmol).²⁶

The photoproducts 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 pure photoproducts. Structural assignments to the photoproducts were made based on analysis of 1H and $^{13}CNMR$ and on HRMS analysis.

The results show that photoreactions of C_{60} with bis- α -trimethylsilyl-substituted tertiary amines **13–16**, carried out in N_2 -purged solution, generate two types of photoproducts, bis-aminomethyl-1,2-dihydrofullerenes **17–20**, and bis-fulleropyrrolidines **21–24** (Scheme 3). Clearly, 90 min irradiation of solutions of C_{60} and bis- α -trimethylsilyl-substituted tertiary benzyl amines **14** and **16** (0.56 mmol) possessing electron-donating groups (CH_3 and OCH_3) on the phenyl rings as well as the non-substituted analogue **13**, brings about high conversion of C_{60} and satisfactory yields



Scheme 3 Synthesis of dumbbell-like amine-functionalized bis- C_{60} -fullerene

Table 1 Products and Yields of Photoaddition Reactions of N₂-Purged Bis- α -silyl Tertiary Amines with C₆₀ in 10% EtOH–toluene^a

Entry	Amine	Irradiation time (min)	Conv. (%) ^b	Product (%) ^c
1	13	90	89	17 (49), 21 (4)
2	14	80	85	18 (51), 22 (3)
3	15	120	70	19 (34), 23 (5)
4	16	90	84	20 (53), 24 (2)

^a Bis- α -silyl tertiary benzyl amine/C₆₀ ratio 0.56:0.28 mmol in 220 mL of 10% EtOH–toluene.

^b Conversion was determined based on recovered C₆₀.

^c Isolated yield based on consumed C₆₀.

Table 2 Products and Yields of Photoaddition Reactions of O₂-Purged Bis- α -silyl Tertiary Amines with C₆₀ in 10% EtOH–toluene^a

Entry	Amine	Irradiation time (min)	Conversion (%) ^b	Product (%) ^c
1	13	90	90	17 (2), 21 (51)
2	14	80	90	18 (4), 22 (50)
3	15	120	72	19 (trace), 23 (42)
4	16	90	88	20 (3), 24 (47)

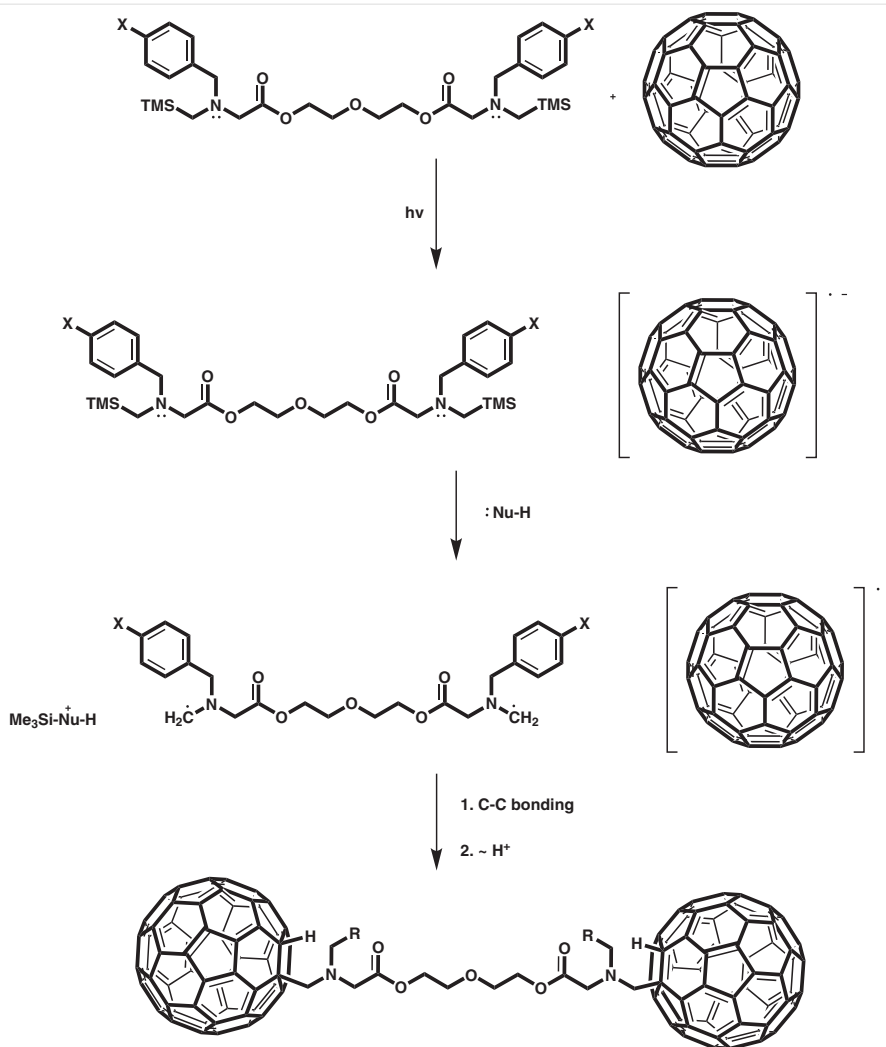
^a Bis- α -silyl tertiary benzyl amine/C₆₀ ratio 0.56:0.28 mmol in 220 mL of 10% EtOH–toluene.

^b Conversion was determined based on recovered C₆₀.

^c Isolated yield based on consumed C₆₀.

of formation of the corresponding bis-aminomethyl-1,2-dihydrofullerenes **17**, **18**, **20** predominantly, along with low yields of fulleropyrrolidines **21**, **22**, and **24** (Table 1, entries 1, 2, and 4). In contrast, photoreactions of C₆₀ with

electron-withdrawing group (F) substituted bis- α -trimethylsilyl-substituted tertiary amines **15** (entry 3) require longer irradiation times to bring about high C₆₀ conversions.

**Scheme 4** C₆₀ furnished single-bonded bis-aminomethyl-1,2-dihydrofullerenes

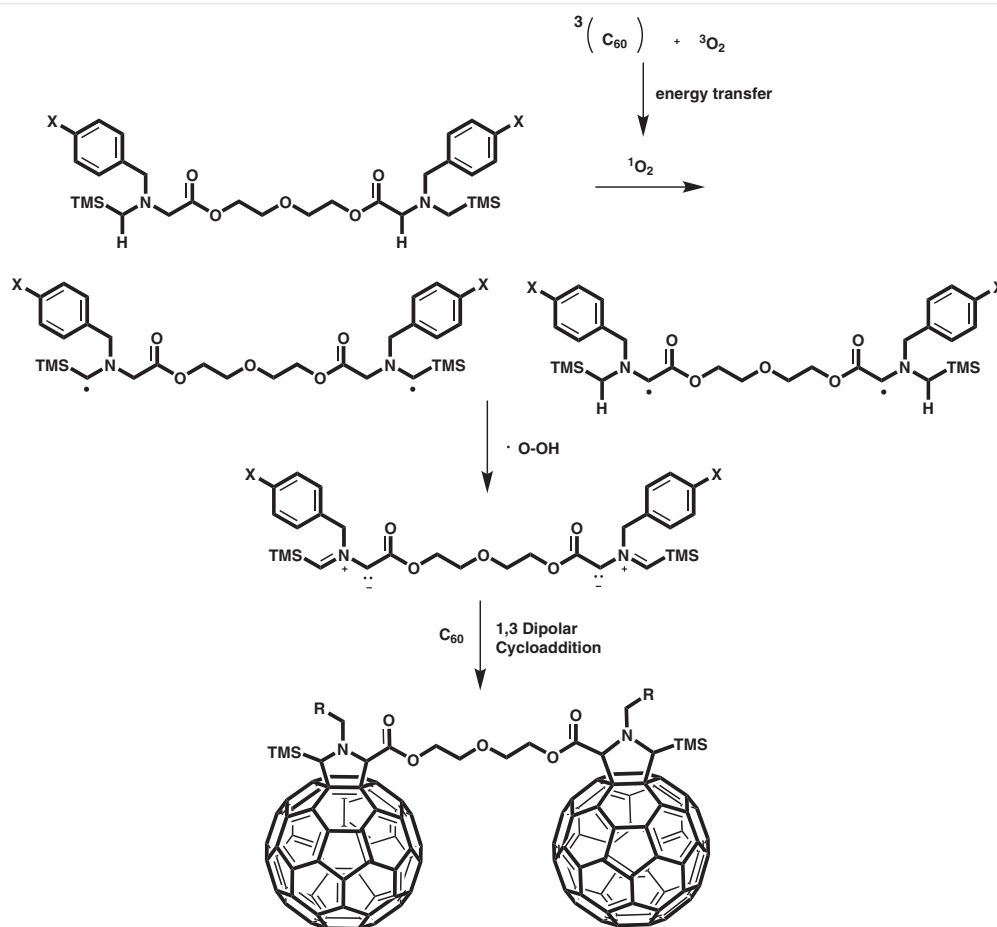
Significantly, these reactions occur in lower yield as compared with electron-donating group (CH_3 and OCH_3).

The effect of molecular oxygen on the photochemical processes was explored. The results show that irradiation of oxygenated 10% EtOH–toluene solutions containing C_{60} and bis- α -trimethylsilyl-substituted tertiary benzyl amines **13–16** under the same conditions as described above, leads to the exclusive formation of the corresponding bis-fulleropyrrolidines **21–24** (Table 2, entries 1–4) in modest yields. Longer irradiation times were also required for these photoreactions.

When photochemical addition of bis- α -trimethylsilyl-substituted tertiary benzyl amines to C_{60} was carried out in deoxygenated 10% EtOH–toluene, the major product obtained was the corresponding bis-adducts $\text{R-C}_{60}\text{H}$ (Scheme 4). In a similar manner to that of primary and secondary amines, the mechanism proposed for the photoreactions between C_{60} and tertiary amines starts with a SET from the bis- α -trimethylsilyl-substituted tertiary amines donor to triplet excited state of fullerene C_{60} to give a radical ion pair.^{17,18} This is followed by silophile (EtOH)-induced desilylation and formation of key α -amino radical intermediates.

Finally, radical ion pair fullerene radical anion ($\text{C}_{60}^{\cdot-}$) and α -amino radical combine to afford the final bis-adducts (Scheme 4). The photoreactions of C_{60} with electron-withdrawing group (F) substituted bis- α -trimethylsilyl-substituted tertiary amines **15** gave a lower yield, perhaps because the fluorine atom destabilizes the cationic nitrogen atom formed during single-electron transfer (Scheme 4).

Additionally, in the presence of molecular oxygen, a pathway is followed that involves singlet molecular oxygen ($^1\text{O}_2$) mediated generation of azomethine ylides, which are reactive intermediates that undergo 1,3-dipolar cycloadditions to fullerene to generate the respective bis-fulleropyrrolidines (Scheme 5). Thus, in the presence of molecular oxygen, the triplet state of C_{60} undergoes energy transfer and the formation of $^1\text{O}_2$. The singlet oxygen reacts with bis- α -trimethylsilyl-substituted tertiary benzyl amines by abstraction of the α -hydrogen atom to form α -carbon radicals (Scheme 5) along with hydroperoxy radical. Further hydrogen atom transfer generates the azomethine ylides, which undergo 1,3-dipolar cycloadditions to fullerene to generate the respective bis-fulleropyrrolidines. Similarly, the photoreactions of C_{60} with fluorine-substituted bis- α -trimethyl-



Scheme 5 C_{60} furnished double-bonded bis-fulleropyrrolidines

silyl-substituted tertiary amines **15** gave lower yield of the product, perhaps because the fluorine atom destabilizes the cationic nitrogen atom formed during single-electron transfer.

In summary, an efficient, expeditious, operationally simple, economical, and environmentally friendly method has been developed for the synthesis of dumbbell-like amine-functionalized bis-C₆₀ fullerene. In contrast to thermal and photochemical strategies developed previously, the new photochemical approach using bis- α -trimethylsilyl-substituted tertiary benzyl amines is both mild and efficient, and, as a result, should be useful in broadening the library of substituted dumbbell-like amine-functionalized bis-C₆₀ fullerene derivatives of type C₆₀-linker-C₆₀.

Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0037-1611862>.

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- General Procedure for Synthesis of Secondary N-Trimethylsilylmethyl-N-benzylamines 6–9**: The corresponding primary amine **1–4** (**1**, 5823 mg; **2**, 6586 mg; **3**, 6801 mg; **4**, 7455 mg, 54.35 mmol) was taken in acetonitrile (120 mL), and K₂CO₃ (11266 mg, 81.52 mmol) was added under argon. The reaction mixture was heated at 70 °C for 1 h and iodomethyltrimethylsilane **5** (9697 mg, 45.29 mmol) was added dropwise. The reaction mixture was stirred for 7 h at 70 °C. After completion of reaction (monitored by TLC), the mixture was concentrated in vacuo to give residues that were partitioned between water and CH₂Cl₂. The CH₂Cl₂ layers were dried and concentrated in vacuo to afford residues that were subjected to silica gel column chromatography (EtOAc/hexane = 1:1) to yield the corresponding secondary N-trimethylsilylmethyl-N-benzylamines **6** (8197 mg, 78%), **7** (9580 mg, 85%), **8** (6317 mg, 55%), and **9** (9712 mg, 80%). The spectral data matched exactly with reported data.
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- General Procedure for Synthesis of Bis- α -trimethylsilyl-Substituted Tertiary Amines 13–16**: The corresponding secondary amine **6–9** (**6**, 1160 mg; **7**, 1244 mg; **8**, 1268 mg; **9**, 1340 mg, 6 mmol) was taken in acetonitrile (120 mL), and K₂CO₃ (1243 mg, 9 mmol) was added under argon. The reaction mixture was heated at 70 °C for 1 h and 2,2'-oxy-bis(ethane-2,1-diyl)bis(2-bromoacetate) (**12**; 1043 mg, 3 mmol) was added dropwise. The reaction mixture was stirred for 7 h at 70 °C. After completion of reaction (monitored by TLC), the mixture was concentrated in vacuo to give residues that were partitioned between water and CH₂Cl₂. The CH₂Cl₂ layers were dried and concentrated in vacuo to afford residues that were subjected to silica gel column chromatography (diethyl ether/hexane = 1:8) to yield the corresponding symmetrical molecules **13** (1288 mg, 75%), **14** (1442 mg, 80%), **15** (1095 mg, 60%), and **16** (1481 mg, 78%).
2,2'-Oxybis(ethane-2,1-diyl)bis(2-(benzyl(trimethylsilyl)methyl)amino)acetate: ¹H NMR: δ = 0.08 (s, 18 H), 2.23 (s, 4 H), 3.32 (s, 4 H), 3.66 (t, *J* = 12.30 Hz, 4 H), 3.78 (s, 4 H), 4.34 (t, *J* = 12.24 Hz, 4 H), 7.37–7.21 (m, 10 H); ¹³C NMR: δ = -1.5, 41.4, 45.6, 56.7, 61.3, 63.5, 126.9, 128.1, 128.7, 139.2, 170.8.
- Detailed experimental procedures and characterization data are given in the Supporting Information.
General Procedure for Photoreactions of C₆₀ with Bis- α -trimethylsilyl-Substituted Tertiary Benzyl Amines: Preparative photochemical reactions were conducted with a 450 W Hanovia medium vapor pressure mercury lamp surrounded by a flint glass filter (>300 nm) in a water-cooled quartz immersion well surrounded by a solution consisting of 10% EtOH-toluene of C₆₀ (201.78 mg, 0.28 mmol), and bis- α -trimethylsilyl-substituted tertiary amines **13–16** (**13**, 320.81 mg; **14**, 336.52 mg; **15**, 340.96 mg; **16**, 354.44 mg, 0.56 mmol). Each solution was purged with nitrogen before and during irradiation, which was carried out for the time periods given for each substance below. The photoproducts were concentrated, and the generated residues were triturated with CHCl₃ to recover C₆₀. The tritirates

were concentrated in vacuo to generate residues that were subjected to silica gel column chromatography (eluants given below) to obtain the photoproducts.

Photoreaction of C₆₀ with 13: In N₂-saturated conditions: 90 min irradiation, 89% conversion, column chromatography (CS₂/CHCl₃, 5:1) to yield **17** (256 mg, 49%) and **21** (22 mg, 4%). O₂-saturated conditions: 120 min irradiation, 90% conversion, column chromatography (CS₂/CHCl₃, 5:1) to yield **17** (10 mg, 2%) and **21** (286 mg, 51%).

Compound 17: ¹H NMR: δ = 3.76 (t, *J* = 9.45 Hz, 4 H), 4.00 (s, 4 H), 4.48–4.53 (m, 8 H), 4.76 (s, 4 H), 6.90 (s, 2 H), 7.30–7.42 (m, 6 H), 7.62 (d, *J* = 6.60 Hz, 4 H); ¹³C NMR: δ = 41.6, 55.7, 58.0, 59.8, 64.17, 67.3, 68.4, 127.8, 128.7, 129.4, 136.0, 136.1, 138.15, 140.0, 140.2, 141.6 (2C), 141.7, 141.9, 142.0, 142.3, 142.5 (2C),

143.2, 144.4, 144.6, 145.3 (3C), 145.4, 145.8, 146.1 (2C), 146.3 (2C), 146.8, 147.2, 147.3, 154.3, 154.7, 171.1; HRMS (FAB): *m/z* [M + 1] calcd for C₁₄₄H₃₅N₂O₅: 1872.8212; found: 1872.9016.

Compound 21: ¹H NMR: δ = 0.51 (s, 18 H), 3.57–3.68 (m, 4 H), 4.37–4.45 (m, 2 H), 4.47–4.55 (m, 2 H), 4.60 (d, *J* = 12.15 Hz, 2 H), 5.28 (d, *J* = 12.18 Hz, 2 H), 5.39 (s, 2 H), 5.51 (s, 2 H), 7.28–7.48 (m, 6 H), 7.65 (d, *J* = 6.30 Hz, 4 H); ¹³C NMR: δ = 0.7, 41.3, 56.2, 64.5, 70.0, 77.2, 77.6, 77.9, 127.8, 128.6, 128.9, 134.9, 135.5, 135.6, 136.3, 138.7, 139.2, 139.6, 139.7, 140.1, 141.6, 141.7, 141.8, 141.9, 142.0, 142.1 (2C), 142.2, 142.3, 142.4, 142.6, 142.7, 143.0, 143.1, 144.2, 144.3, 144.4, 144.5, 144.9, 145.1, 145.2, 145.3, 145.5, 145.8, 145.9, 146.1 (2C), 146.2, 146.6, 146.9, 147.0, 152.4, 154.7, 156.4, 156.9, 170.3; HRMS (FAB): *m/z* [M + 1] calcd. for C₁₅₀H₄₇N₂O₅SiO₂: 2013.1516; found: 2013.2318.