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Studies aimed at elucidating factors involved in the control of chemoselectivity in single electron transfer promoted photoreactions of branched-polydonor substituted phthalimides

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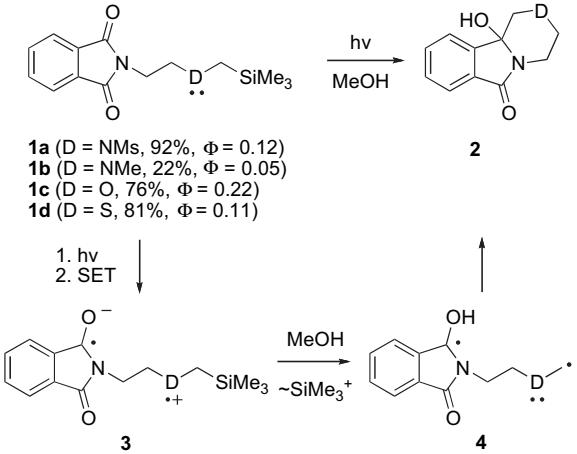
This paper is dedicated to the memory of late Professor Chi Sun Hahn

ABSTRACT

Factors that govern the chemical selectivities and efficiencies of SET-promoted photocyclization reactions of acceptor–polydonor substrates were explored by using systems comprised of phthalimide acceptors linked via polymethylene or polyethylenoxy chains to α-silylether and thioether donors. A number of linear and branched substrates of this type were prepared and their photochemical behavior was explored. The results of this effort have led to the identification of several key factors that govern the chemoselectivities and efficiencies of the competitive reaction pathways followed. The observations suggest that the length and nature of the chain linking the phthalimide acceptor and α-silyl donor sites are important factors in controlling the rates of formation of zwitterionic biradicals that serve as penultimate intermediates in routes for product formation. In addition, the rates of methanol promoted desilylation at cation radical centers in intermediate zwitterionic biradicals also play important roles especially in cases where chain length/type is not a factor. The results are discussed in terms of both their mechanistic and synthetic significance.

1. Introduction

In past studies,[1,2] we have explored the factors involved in determining the efficiencies of single electron transfer (SET) promoted, intramolecular photochemical reactions of linked acceptor–polydonor systems. In addition to providing mechanistic insight, these efforts have uncovered useful information that has guided the design of synthetically useful photochemical processes.[3,4] For example, in earlier investigations we showed that α-trimethylsilyl substituted amines, amides, ethers, and thioethers serve as precursors of the corresponding donor-substituted, carbon centered free radicals.[5] Processes in which these radical forming transformations operate are exemplified by photocyclization reactions of the silyl-substituted phthalimides **1** shown in Scheme 1.[5] In these reactions, the α-silyl cation radicals, as part of zwitterionic biradicals **3**, are formed by intramolecular SET and undergo methanol promoted desilylation to produce carbon centered radical components of biradical precursors of cyclic amidol products **2**. The high chemical yields and quantum efficiencies (Φ) generally seen with these photoreactions are a consequence of the large bimolecular rate constants of methanol induced, cation radical desilylation (except for the NMe system **1b**),[6,7]



1a (D = NMs, 92%, Φ = 0.12)
1b (D = NMe, 22%, Φ = 0.05)
1c (D = O, 76%, Φ = 0.22)
1d (D = S, 81%, Φ = 0.11)

2

3

4

Scheme 1.

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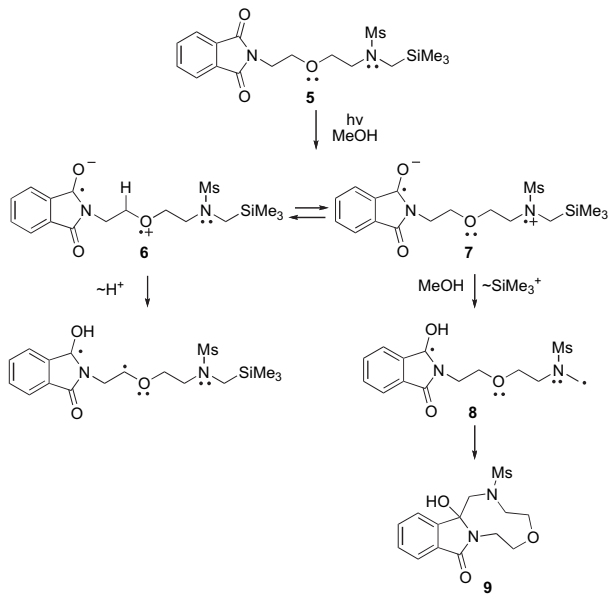
a process that competes with other reactions (e.g., α-deprotonation) and decay modes (e.g., back single electron transfer (BSET)) available to the intermediate zwitterionic biradicals. It should be noted that related α-amino acid cation radicals present as components of related zwitterionic biradicals undergo rapid decarboxylation to efficiently generate 1,*n*-biradicals and that this process has been used in Griesback's design of preparatively useful photomacrocyclization reactions.[8]

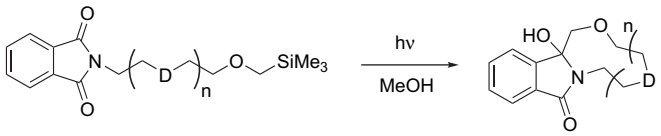
Continuing investigations have provided data that support the conclusion that desilylation reactions of α-silyl-donor derived cation radicals take place at high rates. For example, methanol promoted desilylation reactions of α-silyl anilinium $[PhNMeCH_2SiMe_3]^{+\bullet}$ and related amide $[PhNAcCH_2SiMe_3]^{+\bullet}$ cation radicals were found to have respective bimolecular rate constants of 7.0×10^5 and 6.0×10^7 M^{-1} s^{-1}. In addition, a later study carried out by Baciocchi and his co-workers[9] showed that the bimolecular rate constant for methanol induced desilylation of the α-silylthioanisole cation radical $[PhSCH_2SiMe_3]^{+\bullet}$ is 3.5×10^6 M^{-1} s^{-1}. It is interesting that the results of these and other efforts[10] demonstrate that the rate constants for heterolytic cleavage of the C–Si bond in radical cations derived from structurally similar α-silyl substituted electron donors are dependent upon the stabilities of the charged radicals, which is reflected in the oxidation potentials of the corresponding electron donors. As a consequence of this relationship, it is predicted that the rate constants for nucleophile assisted desilylation of cation radicals derived from D-CH_2SiMe_3 would be D=RO and RNMs>RNAc>RS>RNMe.

In more recent studies,[1,2] we have attempted to gain information about the factors that control the nature and efficiencies of intramolecular SET-promoted photoreactions in linked acceptor–polydonor systems. In studies with α-silylether terminated phthalimides,[1] attention was given to elucidating the effects of chain length, the number and types of the intervening donor sites, and the nature of the cation radical fragmentation reaction on chemical and quantum yields. One important finding arising from this effort is that the major pathway followed in these photoreactions involves generation and cation radical desilylation of ω-zwitterionic biradical intermediates, independent of the existence of other competitively formed zwitterionic biradicals and other types of cation radical reactions of these intermediates. For example, irradiation of the phthalimido α-silylsulfonamide **5** (Scheme 2) gives rise to high yielding (91%) and quantum efficient (Φ=0.14) formation of a single cyclic product **9**. Importantly, two zwitterionic biradicals **6** and **7** can be formed by photoinduced SET and both are capable of undergoing α-heterolytic fragmentation reactions, including inter- or intra-molecular deprotonation in **6** and methanol promoted desilylation of **7**. However, methanol promoted desilylation of **7** occurs exclusively to produce the biradical **8** that serves as the precursor of **9**. This and a number of other observations led us to conclude that a major factor governing the nature and efficiencies of SET-reactions of linked acceptor–polydonor systems is the reactivity of cation radical sites in the potentially interconverting intermediate zwitterionic biradicals.



Scheme 2.

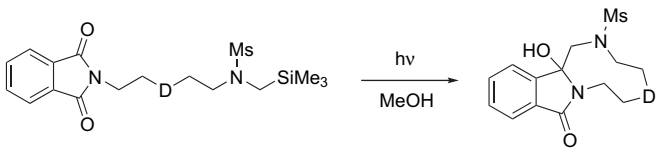
The results of additional investigations[2] show that the length and type of chain linking the acceptor and the reactive donor site have a pronounced impact on the efficiencies of SET-photocyclization reactions. Observations supporting this conclusion were made in studies with the related α-silylether terminated phthalimides **10**–**14** displayed in Scheme 3. We observed that photocyclization reactions take place more efficiently in substrates that contain shorter rather than longer polyethylenoxy or polymethylene chains linking the phthalimide acceptor and α-silylether donor centers and when the donor acceptor pairs are linked by polyethylenoxy rather than polymethylene chains. These findings suggest that chain length and type govern the rates of formation of the key ω-zwitterionic biradicals, processes that compete with energy wasting decay by BSET.



10 (n=0; D=-; 80%, Φ=0.22)
11 (n=3; D=O; 64%, Φ=0.11)
12 (n=4; D=O; 60%, Φ=0.07)
13 (n=3; D=CH_2; 40%, Φ=0.04)
14 (n=4; D=CH_2; 56%, Φ=0.02)

Scheme 3.

Finally, the nature of other donors, located between the phthalimide acceptor and reactive, terminal α-silyl-substituted donor groups, plays an important role in governing the quantum efficiencies of photocyclization reactions proceeding via sequential SET-desilylation pathways. As demonstrated by observations made in investigations with the related phthalimido α-silylsulfonamides **15**–**19** shown in Scheme 4, photocyclization quantum yields increase when the donor within the chain is varied in the series D=NMe and S, <NMs, O, and $^+$NHMe. This trend was explained by considering energy profiles for desilylation reactions of rapidly interconverting pairs of zwitterionic biradicals, in which the activation energies for desilylation (a process competing with decay by BSET) are governed by the energies of the lowest energy zwitterionic biradical intermediate.



15 (D=NMe; Φ=0.04)
16 (D=S; Φ=0.02)
17 (D=NMs; Φ=0.12)
18 (D=O; Φ=0.14)
19 (D=NHMs; Φ=0.34)

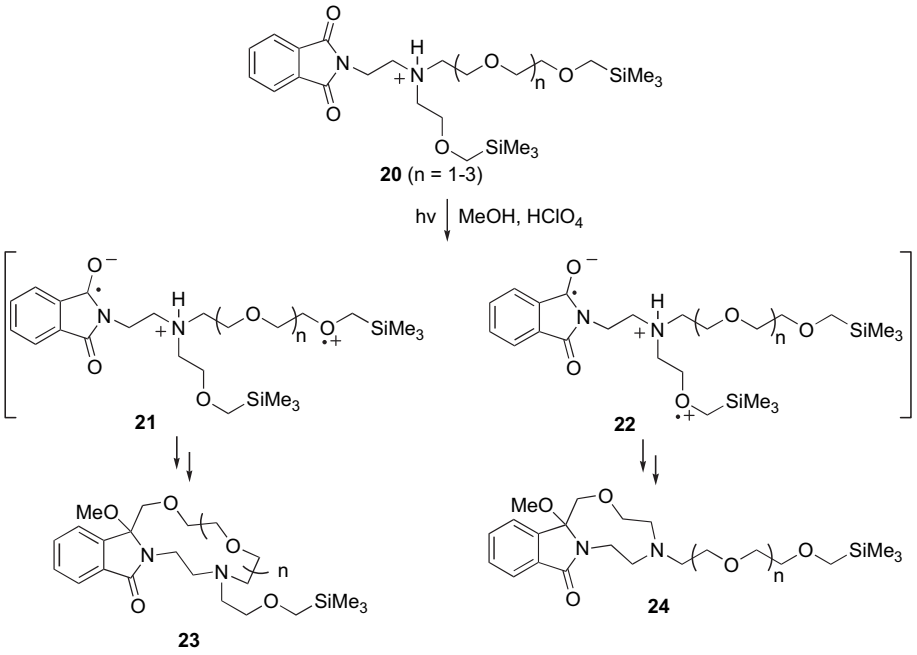
Scheme 4.

The results arising from these studies have been applied to the design of photoreactions that can be used to prepare novel lariat[3,4] and bis-type crown[4] ethers as part of pathways for the preparation of heavy metal ion fluorescence sensors. At a point where we felt confident that the trends observed could be used to predict the SET-photochemical behavior of acceptor–polydonor systems, counter-intuitive observations were made in studies of the bis-tethered phthalimides **20** (Scheme 5).[2] Specifically, in a manner opposite to that predicted based on the distance dependencies seen in other systems, SET-promoted photoreactions of **20** were observed to take place either exclusively (n=1) or predominantly (n=2 and 3) at the more remote silylether center to produce the macrocyclic amidol ethers **23** rather than analogs **24**. These observations were rationalized in terms of the effect of ammonium cations in the linking chains on the relative energies of the intermediate zwitterionic biradicals **21** and **22**.

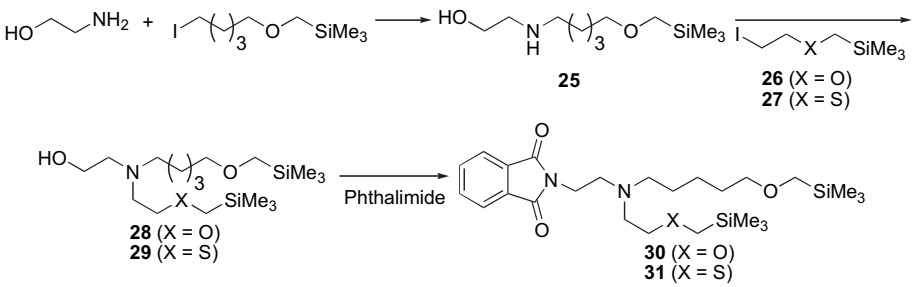
In order to gain a deeper understanding of the factors that govern the chemical selectivities and efficiencies of SET-promoted photocyclization reactions of acceptor–polydonor substrates, in the current effort we have addressed additional issues in studies with phthalimide linked polyether and thioether systems. For this purpose, a number of linear and branched silylether terminated phthalimides were prepared and their photochemical behavior was explored. The results have led to a more complete picture of these processes as well as information that will be useful in guiding the design and synthesis of new lariat-type crown ethers.

2. Results

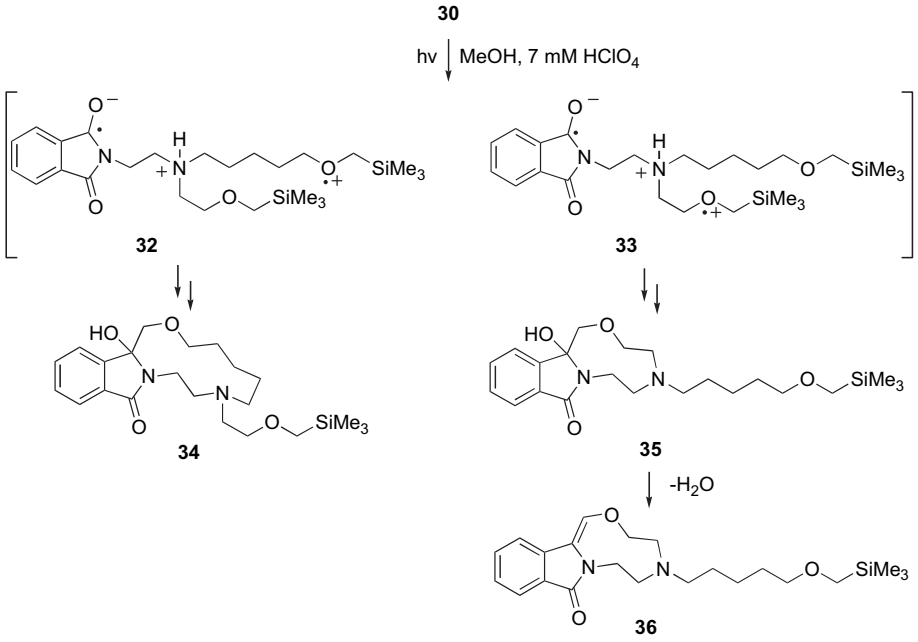
In one phase of the current effort, we investigated the photochemical reactivity of the ethylenoxy- and polymethylene-linked, bis-silylether **30**, in which the long polyethylenoxy chain in **20** (n=1) (Scheme 5) is replaced by a polymethylene chain. If like with **20** (n=1), charge repulsion governs the relative energies and, therefore, populations of the intermediate zwitterionic biradicals **32** and **33**, photocyclization of **30** is expected to produce the macrocyclic amidol **34** rather than **35** (Scheme 7). However, in contrast to the behavior of **20** (n=1), **30** prepared by the route given in Scheme 6, is transformed to **36** exclusively (76%, Φ=0.21) when irradiated in a methanol solution containing 7.0 mM $HClO_4$. In this case, product formation follows a pathway in which reaction takes place at the α-silylether center, that is, closest to the linking ammonium cation group to form cyclic amidol **35**. As observed earlier,[2] the initially formed cyclic amidol **35** undergoes dehydration to generate the enamide **36** under the acidic condition employed in the photoreaction.



Scheme 5.



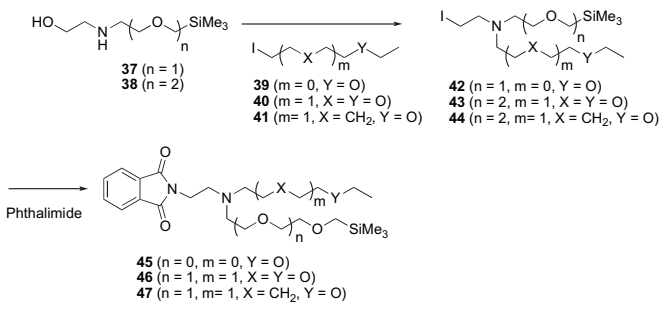
Scheme 6.



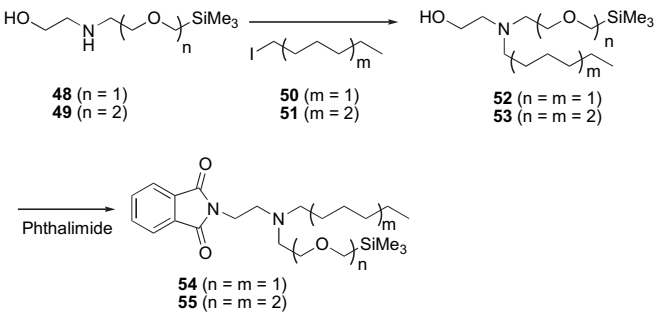
Scheme 7.

It is important to note that, despite following different regiochemical courses, photoreactions of **20** (n=1) and **30** occur with near equal chemical yields (72 and 76%, respectively) and high quantum efficiencies of 0.39 and 0.21, respectively. Moreover, similar chemical and quantum efficiencies attend photocyclization reactions of the branched phthalimides **45**–**47**, **54**, and **55**, prepared by the sequences shown in Schemes 8 and 9. These substances produce the corresponding amido-ethers **56**–**60** upon irradiation in methanol containing 6.6 mM $HClO_4$ (Scheme 10). As observed before,[1,2] the initially formed cyclic amidols are transformed to the corresponding amido-ethers under the acidic methanol condition employed in the photoreaction. Thus, it appears that the rates of formation of the reactive zwitterionic biradicals (e.g., **21** in Scheme 5 and **33** in Scheme 7) (competing with excited state decay) and those of methanol induced desilylation that produces biradical precursors of the observed products (competing with BSET) are nearly the same for processes participating in the formation of **23** from **20**, **35** from **30**, and **56**–**58** from **45**–**47**, and **59**, **60** from **54** and **55**.

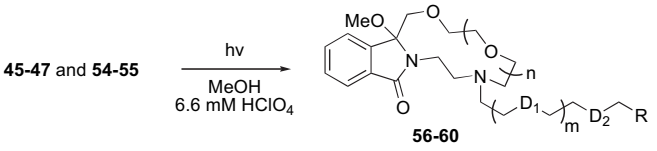
This is a remarkable result considering the fact that a variety of other donor sites are present in these substances and that cation radical centers in the reactive zwitterionic biradicals are located at different positions relative to the ammonium cation center. Additional information about this issue has come from studies with the α-silylthioether **31**, the sulfur analog of **30** (Scheme 7). As



Scheme 8.



Scheme 9.

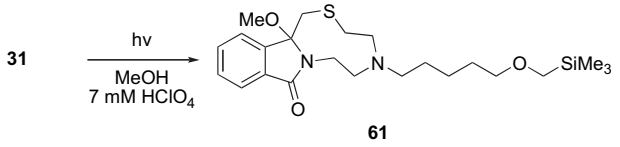


Substrate	n	m	D_1	D_2	R	Product	%Yield	Φ
45	0	0	-	O	CH_3	**56**	67	0.21
46	1	1	O	O	CH_3	**57**	48	0.14
47	1	1	CH_2	O	CH_3	**58**	52	0.15
54	0	0	-	CH_2	H	**59**	62	0.21
55	1	1	CH_2	CH_2	H	**60**	58	0.19

Scheme 10.

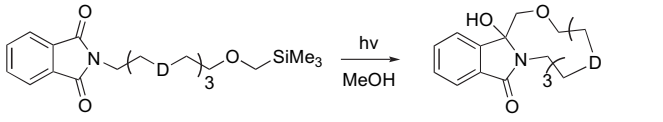
mentioned in the introduction section, cation radicals arising from SET oxidation of α-silylthioethers should undergo methanol promoted desilylation at lower rates than those of their silylether counterparts.[9] Consequently, if a mixture of sulfur containing zwitterionic biradicals analogous to **32** and **33** (Scheme 7) is formed via intramolecular SET and if rates of cation radical

desilylation govern the preference for biradical and product formation, photoreaction of **31** should generate the cyclic product arising by reaction at the α-ether center. Yet, irradiation of a methanol solution of **31**, produced by the route given in Scheme 6, containing 7 mM $HClO_4$ promotes exclusive formation of the cyclic amido ether **61** (73%, Φ=0.31), which arises by desilylation of the zwitterionic biradical containing the thioether cation radical center (Scheme 11).



Scheme 11.

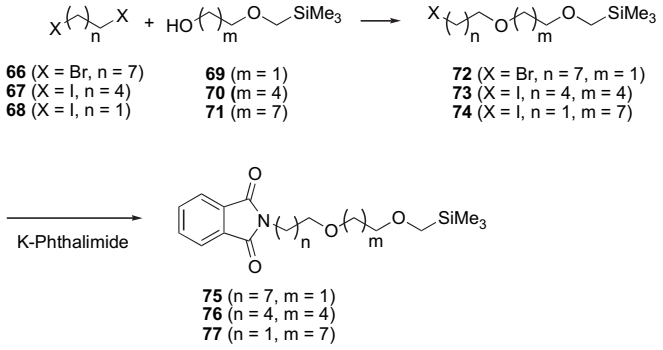
The results from studies with the branched α-silylether and thioether terminated phthalimides described above could indicate that the presence of a polymethylene chains linking the silyl substituted donors and phthalimide acceptors impact the rates of formation of zwitterionic biradicals. Thus, a plausible explanation for these observations is that SET in the excited states of **30** and **31** takes place more rapidly over short distances to produce zwitterionic biradicals that undergo desilylation more rapidly than they interconvert with the zwitterionic biradicals in which long polymethylene chains separate the charged radical centers. This explanation is consistent with findings made in our earlier investigations[1] with polyethylenoxy and polymethylene linked α-silylether substrates (Scheme 3) and with donor–acceptor dyads. Moreover, current studies with the linked phthalimido-silylethers **75**–**77** (Scheme 14) along with previous work carried out with **62**



62 (D = O)
63 (D = CH_2)

64 (D = O, 64%, Φ = 0.11)
65 (D = CH_2, 40%, Φ = 0.02)

Scheme 12.



66 (X = Br, n = 7)
67 (X = I, n = 4)
68 (X = I, n = 1)

69 (m = 1)
70 (m = 4)
71 (m = 7)

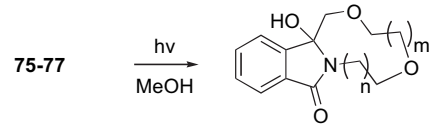
72 (X = Br, n = 7, m = 1)
73 (X = I, n = 4, m = 4)
74 (X = I, n = 1, m = 7)

75 (n = 7, m = 1)
76 (n = 4, m = 4)
77 (n = 1, m = 7)

Scheme 13.

and **63** (Scheme 12) provide additional insight into the bridge type/length issue. Earlier,[2] we showed that photoreactions of the polyethylenoxy and polymethylene linked phthalimido-silylethers **62** and **63**, although producing similar types of cyclization products (**64** and **65**, respectively), take place with greatly different quantum efficiencies (0.11 vs 0.02). These observations were attributed to the larger rates of formation of ω-zwitterionic biradicals in systems where oxygen donor sites are present in near equal length chains linking the phthalimide acceptor and α-silylether donor.

More information about the control of chain type comes from the results of current studies probing photocyclization reactions



78-80

Substrate	n	m	Product	%Yield	Φ
75	7	1	**78**	63	0.01
76	4	4	**79**	68	0.08
77	1	7	**80**	52	0.03

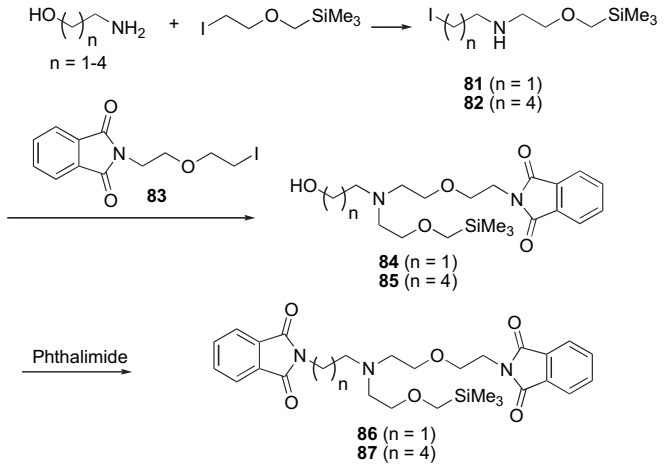
Scheme 14.

of the alternately polymethylene-oxo-polymethylene linked substrates **75**–**77**, generated by the sequence given in Scheme 13. Like with **63** and **62**, these substances, containing near equal length chains separating the phthalimide and silylether centers, undergo SET-promoted photocyclization in MeOH to produce the corresponding macrocyclic amidols **78**–**80** in comparable chemical yields (Scheme 14). However, reactions of **75** and **77**, which contain seven-carbon methylene chains between either the phthalimide ring and the terminal ethylenoxy-silylether group or the near ethylenoxy and terminal silylether groups, have low quantum efficiencies (Φ=0.01 and 0.03, respectively) that match that of the photoreaction of the polymethylene tethered substrate **63**. In contrast, the monoether linked, phthalimido-silylether **76** undergoes photocyclization with a quantum yield (Φ=0.08), that is, near equal to that of the polyethylenoxy substrate **62**.

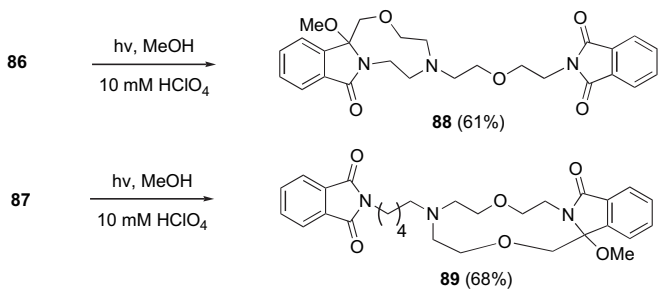
Importantly, it is highly doubtful that changes in the rates of ω-zwitterionic biradical desilylation are responsible for the different efficiencies of these processes since in all cases this process takes place at α-silylether cation radical centers that exist in roughly the same environments. As a consequence of these observations, it is reasonable to conclude that not only does the number but also the position of oxygens in the chain linking phthalimide acceptor and silylether donor sites play an important role in governing the rates of SET events that transform initial formed phthalimide excited states into the key reactive ω-zwitterionic biradical intermediates.

Another manifestation of the chain length/type control of SET-photocyclization reactions of linked α-silylether–phthalimide substrates is seen in the chemoselectivities of photochemical reactions of the bis-phthalimides **86** and **87**, which were prepared by the routes displayed in Scheme 15. The effect in reactions of these substrates is displayed in the form of competitive SET from a single silylether donor site to two competitively formed excited phthalimide acceptors that are linked either by a short polymethylene chain and a longer ethylenoxy chain (as in **86**) or by near equal length polymethylene and ethylenoxy chains (as in **87**). Studies of the photoproducts produced in photoreactions of **86** and **87** (Scheme 16) show that in each case the preferred pathway followed results from selective SET from the silylether to the phthalimide, that is, either linked by a shorter (formation of **88** from **86**) or an ethylenoxy chain (formation of **89** from **87**).

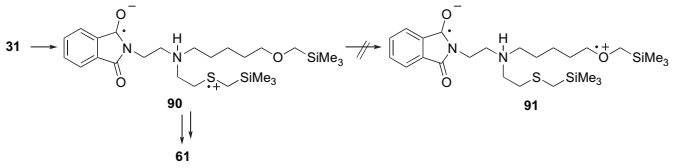
Factors other than distance and chain type can play a role in governing the chemoselectivities of these processes. For example, reaction of the branched bis α-silylthioether α-silylether substrate **31** could be controlled by the rates of formation and/or the relative populations of the two possible zwitterionic biradicals **90** and **91** (Scheme 17) that arise by SET from the thioether and ether centers.



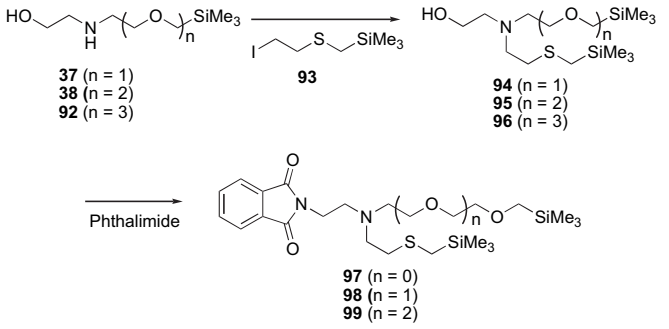
Scheme 15.



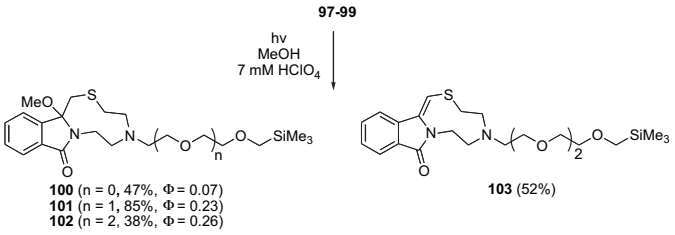
Scheme 16.



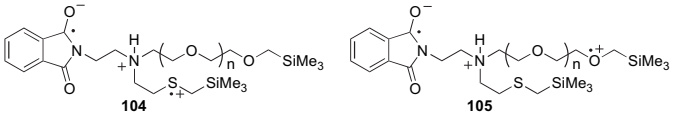
Scheme 17.



Scheme 18.



Scheme 19.



Scheme 20.

If, owing to its ca. 10 kcal/mol lower energy, the α-silylthioether cation radical containing zwitterionic biradical **90** is formed more rapidly and if the rate of its conversion to the higher energy zwitterionic biradical **91** is slow relative to desilylation, the photocyclization process, reaction of **31** would take place via desilylation of **90** to yield **61**.

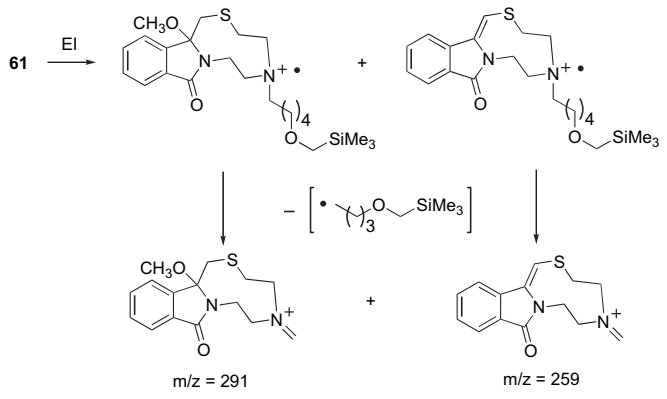
A clear test of whether or not the low energy of the α-silylthioether cation radical plays a contributing role in controlling the chemoselectivity of the photocyclization reaction of **31** is found in studies of systems where chain length/type is not the sole contributing factor. This issue was explored in studies with the branched bis α-silylthioether—α-silylether substituted phthalimides **97**–**99**, produced by the sequence outlined in Scheme 18. As can be seen by viewing the results included in Scheme 19, irradiation of each of these substrates in MeOH containing 7 mM $HClO_4$ brings about exclusive formation of the respective cyclic products **100**, **101**, and **102**+**103** that arise by generation and desilylation of α-silylthioether containing zwitterionic biradicals **104** (Scheme 20). Moreover, as demonstrated conclusively by the transformation of **97** to **100**, chain length is not the exclusive control element in governing these processes. Thus, despite its expected lower desilylation reactivity (see above), the low energy of zwitterionic biradical **104** relative to **105** plays an important role in determining the chemoselectivity of this photocyclization reaction.

2.1. Structure assignments

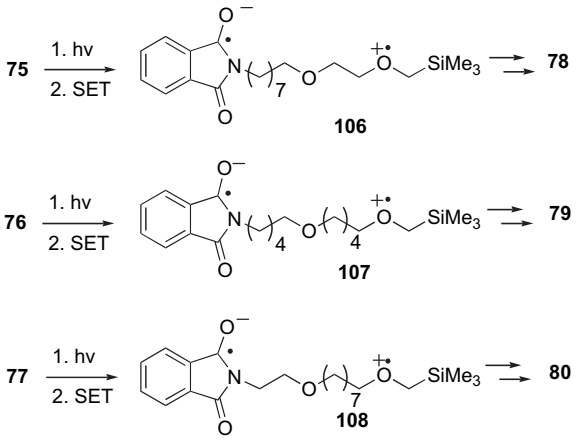
Assignments of the structures of several products (**61**, **88**–**89**, and **100**–**102**) is complicated by ambiguities associated with the interpretation of NMR data. Specifically, although the existence of the phthalimide derived amido ether or enamide groups in these substances is demonstrated by the presence of characteristic ^{1}H and ^{13}C NMR resonances, distinction between the formed rings and residual side chains can not be made by employing spectroscopic methods. Like before,[2] we have used electron-impact (EI) mass spectrometry to make unambiguous structural assignments to **61**, **88**–**89**, and **100**–**102**. The key assumption in employing the mass spectrometry data for this purpose is that EI-promoted cleavage of the external carbon–carbon bond adjacent to nitrogen in the parent ion for each photoproduct and the ion resulting from loss of CH_3OH would take place efficiently to yield iminium ions having m/z values that are characteristic of the nature of formed-ring and external-side chain (exemplified for **61** in Scheme 21). The results of EI-mass spectrometric analysis of the photoproducts **61**, **88**–**89**, and **100**–**102** are shown in Table 1.

3. Discussion

The results of the investigation described above have provided interesting information about the factors that influence the regiochemical courses and efficiencies of photocyclization reactions of diverse polydonor linked-phthalimide systems. In previous work,[1,2] we have shown that sequential SET-desilylation is a key pathway followed in photochemical reactions of polydonor linked-phthalimide and that the chain length and types of polydonor greatly influence the efficiencies of the photomacrocyclization reactions. These observations have been explained by employing



Scheme 21.



Scheme 22.

a reaction pathway in which initial SET to the electronically excited phthalimide moiety takes place from the nearest electron donor site to generate the zwitterionic biradical intermediate. Consecutive intrachain SET (ISET) causes equilibration of all possible donor atom-centered zwitterionic biradicals. Of course, this 'electron hopping' pathway might simply be a formalism for an 'electron super exchange mechanism' in which the intervening donor lone pair electrons play a role.[11] Alternatively, it is possible that long-range SET from distant electron donor sites to the excited phthalimide chromophore also takes place to form the 1,ω-zwitterionic biradical directly. Finally, silophile assisted desilylation take place in the 1,ω-zwitterionic biradical to generate the 1,ω-biradical, which serves as the precursor of the photoproduct.

The results from studies of the photocyclization reactions of phthalimides **75**–**77**, summarized in Scheme 14, provide interesting and important information that supports the significant role played by oxygen donor sites in the chain interconnecting the phthalimide acceptor and the terminal trimethylsilymethyl ether donor. Phthalimides **75**–**77** differ in the length of the chain between internal and terminal oxygen atoms. Although photoreactions of these substances give similar types of photoproducts in similar chemical yields (63% of **78**, 68% of **79** and 52% **80**), their quantum yields decrease in the order **76** (Φ=0.08)>**77** (Φ=0.03)>**75** (Φ=0.01). This trend is well rationalized in terms of distance dependence of the rates of SET promoted formation of the key terminal zwitterionic biradicals **106**–**108**. It is expected that when the lengths of the polymethylene chains in these systems increase the rates of SET decrease. Consequently, the relatively shorter chain that exists between the near oxygen donor site and the phthalimide acceptor group in **76** vs **75** and between the internal and terminal oxygen sites in **76** versus **77** causes the overall rate of formation of the terminal zwitterionic biradical **107** to be faster than that of either **106** or **108** (Scheme 22).

As described above, the bis-polyether and bis-thioether tethered phthalimides **97**–**99** (Scheme 19) were studied in order to probe intramolecularly competitive SET-photocyclization reactions of substrates that contain two α-silyl donor sites having different oxidation potentials. The findings of previous studies with bis-short and -long polyethylenoxy tethered phthalimides (**20**, Scheme 5) showed that products arising by cyclization through the longer polyether chain are formed either exclusively or predominantly. These surprising results were explained by considering of the charge states of photoreactants (i.e., ammonium salts **20**) and invocation of a charge repulsive interactions present in shorter chain zwitterionic biradicals **22** that cause them to be higher in energy than the longer chain analogs **21**.

On the basis of this conclusion, it is anticipated that replacement of the shorter trimethylsilylmethyl ether terminated chains in these substances by trimethylsilylmethyl thioether chains, as in **97**–**99** (Scheme 20), would alter the relative energies of the short (**104**) versus long (**105**) chain zwitterionic biradicals. This effect would be a consequence of the much lower oxidation potential of thioether donors versus their oxygen analogs.[5b,9] If this reasoning is correct, irradiation of **97**–**99** should bring about regioselective formation of products resulting from photocyclization involving the thioether chain. Indeed, the results of photoreactions of **97**–**99**, showing that sulfur containing azathioether products **100**–**103** are produced as sole products and in high yields (Scheme 19), clearly support this proposal.

The quantum yields of photocyclization reactions of **97**–**99** reveal that the efficiencies of these processes are governed by the number of oxygen atoms present in the polyethylenoxy chains (e.g., **97** (Φ=0.07), **98** (Φ=0.23) and **99** (Φ=0.26)). Moreover, the quantum efficiency for photocyclization of **20** (n=1) (Φ=0.34), the all oxygen analog of **98**, is much higher than that of thioether **16** (Scheme 4), which does not contain an intervening tertiary amine moiety or an external polyethylene chain. Although requiring further support, it is clear that trends seen in the quantum yields of photocyclization reactions of **97**–**99** vs **16** and **20** are associated with the availability of slow or non-productive SET pathways as a consequence of the presence of multiple oxygen donor sites. In addition, the comparably lower quantum yield for photocyclization of **98** versus the oxygen analog **20** (n=1, Scheme 5) must be associated with the lower rate of desilylation (vs BSET) of the α-silylthioether cation radical **104** (Scheme 20) arising from **98** as compared to that of the α-silylether cation radical **21** (Scheme 4) arising from **20** (n=1).[9,12]

Table 1
Major fragment ions in EI mass spectra of photoproducts **73**, **100**,–**101**, and **112**–**114**

Photoproduct	Fragment ion			
	m/z Observed (% rel intens.)	*m/z* Calculated/Molec. Form.	*m/z* Observed (% rel intens.)	*m/z* Calculated/Molec. Form.
61	291.1163 (11)	291.1167/$C_{15}H_{19}N_2O_2S$	259.0904 (100)	259.0905/$C_{14}H_{15}N_2OS$
88	275.1300 (14)	275.1396/$C_{15}H_{19}N_2O_3$	243.1133 (100)	243.1134/$C_{14}H_{15}N_2O_2$
89	489.2260 (91)	489.2264/$C_{28}H_{31}N_3O_5$		
100	291.1163 (7)	291.1167/$C_{15}H_{19}N_2O_2S$	259.0903 (100)	259.0905/$C_{14}H_{15}N_2OS$
101	291.1165 (6)	291.1167/$C_{15}H_{19}N_2O_2S$	259.0909 (100)	259.0905/$C_{14}H_{15}N_2OS$
102	291.1170 (7)	291.1167/$C_{15}H_{19}N_2O_2S$	259.0909 (100)	259.0905/$C_{14}H_{15}N_2OS$

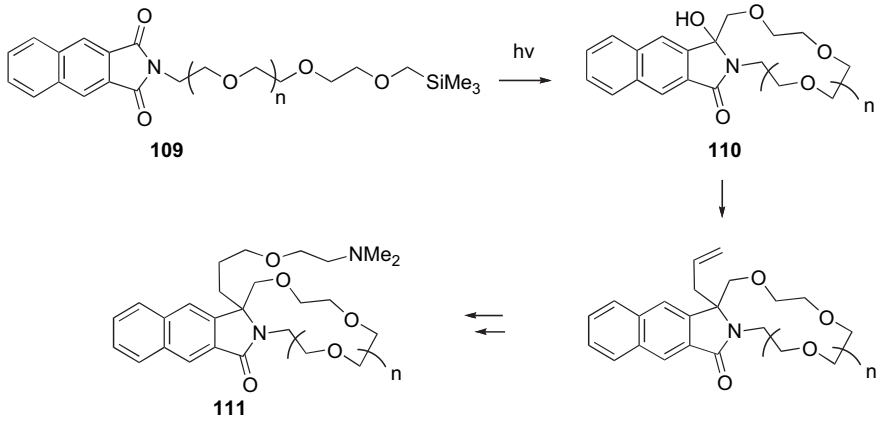
An important step whose rate governs the quantum efficiencies of the excited state SET-photocyclization reactions is desilylation, which generates the biradical precursors of the cyclic photoproducts. The desilylation reaction competes with BSET that occurs from all of possible zwitterionic biradicals formed by SET. Due to the relatively higher stability (or lower reactivity) of the thioether zwitterionic biradical **104** (Scheme 20), BSET becomes more competitive giving a lower quantum yield but still retaining a high chemical efficiency. In a similar fashion, low quantum yields but high regioselectivities are observed to accompany photoreaction of phthalimides **30** (Φ=0.21, Scheme 7) and **31** (Φ=0.31, Scheme 11). The phenomenon described above is consistent with expectations based on the well-known Curtin–Hammett principle,[13] which proposes that product ratios arising from rapidly equilibrating reactants or intermediates are governed by the relative rates of their respective reactions.

Other interesting observations have been made in the current investigation. Methanol promoted desilylation of α-silyl cation radicals is a highly efficient (rapid) process that favorably competes with cation radical deactivation by BSET or other reaction modes. In contrast, owing to a high neutral state C–H bond dissociation energy ($B\Delta E_{C-H}$=ca. 105 kcal/mol) vs that of the C–Si bond ($B\Delta E_{C-Si}$=ca. 89 kcal/mol), which are known to parallel those of cation radicals,[14] zwitterionic biradicals arising by SET from non-trialkylsilyl containing donors do not typically undergo rapid, regioselective deprotonation in the absence of strong bases to generate 1,ω-biradicals. As expected on the basis of these considerations, irradiation of phthalimides **45**–**47**, **54** and **55** (Scheme 10) promotes efficient reactions that take place via sequential SET-desilylation pathways exclusively and that lead to regioselective production of the respective crown ethers **56**–**60**.

Another question addressed in this effort concerns how the presence of non-trimethylsilyl terminated polyethylenoxy- or polymethylene-chains that are not involved in the photocyclization processes influence the efficiencies of photocyclization reactions. This question was probed in studies with **45**–**47**, **54** and **55**. Quantum yield measurements made on photoreactions of these substances provide important information about this issue. Comparisons of the quantum yields of the photoreactions of **45** (Φ=0.21) with that of **54** (Φ=0.21), **46** (Φ=0.14) with that of **55** (Φ=0.19), and **47** (Φ=0.15) with that of **55** (Φ=0.19) show that the nature of the auxiliary chains have small but consistent effects on the efficiencies of these processes. A possible explanation for these observations is that the ethoxy terminated polyether chains present in phthalimides **45**–**47** possess oxygen donor sites that could participate in competitive SET to form non-reactive zwitterionic biradicals. This competition would result in additional pathways for deactivation of the non-reactive zwitterionic biradicals by BSET. In contrast, the polymethylene chains present in phthalimides **54** and **55** cannot participate in competitive SET and, as a result, no additional pathways exist for formation of zwitterionic biradicals that can return to ground states of the substrates by BSET. The above results demonstrate that all electron donor sites can contribute to the control of quantum efficiencies of photoreactions of acceptor–polydonor systems regardless of whether or not SET from all or one of the donors is on the pathway for product formation.

Several studies in our laboratories have been carried out to explore the intricate features controlling the chemical and quantum efficiencies of SET-promoted photocyclization reactions of acceptor–polydonor systems. We anticipated that an investigation of SET photoreactions of mono-donor tethered bis-acceptor substrates would provide similar information about how reactivity profiles are governed by the type and length of chains connecting donor and acceptor sites. By design, the bis-phthalimide **86** (Scheme 15) contains two different types of linkers connecting the two phthalimide acceptors with the terminal trimethylsilylmethyl ether site. One is a two-atom methylene linker and the other a longer five-atom oxygen containing linker. It is interesting that photoreaction of bis-phthalimide **86** in methanol containing $HClO_4$ yields a single product **88**, which is generated by an SET route that takes place via the shorter methylene rather than longer oxygen containing chain. This result suggests that the length of the chain between the electron donor and electron acceptor is a more important factor governing the efficiencies of SET photocyclization. In contrast, the bis-phthalimide **87** differs from **86** in that it contains a five atom polymethylene and a five-atom oxygen containing chain linking the two phthalimide moieties to the terminal trimethylsilylmethyl ether site. In this case, photoreaction follows a route that involves SET through the oxygen containing chain to produce **89**. Thus, when chain length is not a factor, the regiochemical course of the reaction appears to be governed by presence of an oxygen donor site, which can facilitate SET routes for formation of the key zwitterionic biradical that undergoes desilylation to produce the 1,ω-biradical precursor of the observed product.

A final point worthy of discussion concerns the synthetic significance of the observations made in this effort. As has been demonstrated in our earlier studies in this area, photocyclization reactions of polydonor linked, α-silylether, -thioether, and -amide terminated, phthalimides and naphthalimides serve as useful methods to prepare new families of crown and bis-crown ethers and their thia- and amido-analogs.[3,4,15,16] Of particular interest are the results of investigations in which we have outlined a new strategy for synthesis of lariat-type crown ethers[17] that can be employed as selective metal cation fluorescence sensors.[3,4a] The design developed in the earlier work relies on introduction of a functionalized side chain into an amidol intermediate (e.g., **110** in Scheme 23) generated by photocyclization of a naphthalimide



Scheme 23.

precursor (e.g., **109**), employing *N*-acyliminium ion-allylsilane chemistry. Ether, amine or thioether groups are then introduced into the side chain in order to construct the appropriate lariat-type crown ether (e.g., **111**).

While being novel, this approach suffers from the need for post-photocyclization chemistry to install the lariat side chain. In contrast, regiocontrolled photocyclization reactions of bis polydonor tethered phthalimides and naphthalimides can be used to directly produce lariat-type crown ethers, as exemplified by the conversion of **46** to **57** (Scheme 10).

4. Conclusions

The results described above provide a wealth of information about factors that govern the nature and quantum efficiencies of excited state SET-promoted photochemical reactions of acceptor–polydonor and polyacceptor–donor systems. The findings show that reactions of the trimethylsilylmethyl-ether and -thioether terminated, electron donor tethered phthalimides take place by SET pathways that lead to generation of key 1,ω-zwitterionic biradicals that undergo methanol-induced desilylation to form biradical precursors of macrocyclic products. The efficiencies of these processes are regulated by chain length, type and the distance between the donor sites within electron donor chain. In addition, the rates of the desilylation reactions that convert 1,ω-zwitterionic biradicals to corresponding biradical also play a key role in governing the efficiencies of these processes.

In summary, the excited state electron transfer photochemistry of polydonor-phthalimides has been an exceptionally fruitful area for studies designed to explore the factors involved in controlling the nature and efficiencies of the types of SET-promoted photochemical reactions of complex, polyfunctionalized substrates that play a useful role in the synthesis of macrocyclic compounds.

5. Experimental section

5.1. General procedures

^{1}H- and ^{13}C NMR spectra were recorded on $CDCl_3$ solutions and the chemical shifts of resonances are reported in parts per million relative to the ^{1}H and ^{13}C resonances of $CHCl_3$ serving as an internal standard unless noted otherwise. Preparative photochemical reactions were conducted with an apparatus consisting of a 450 W Hanovia medium vapor pressure mercury lamp surrounded by a Pyrex glass filter in a water-cooled quartz immersion well surrounded by the solution being irradiated. The photolysis solutions were purged with nitrogen before and during irradiations. The photolysates were concentrated under reduced pressure giving residues, which were subjected to silica gel column chromatography. All starting materials used in the photoreactions derived from commercial sources. All new compounds described are isolated as oils in >90% purity (by NMR analysis) unless noted otherwise.

5.2. Quantum yield measurements

The actinometer used for measurements of the quantum yields for disappearance of the phthalimide substrates are the TMS-substituted *N*-methanesulfonamide (Φ=0.12).[2] Solutions (ca. 6×10^{-4} M, 10 mL) of the substrates and actinometer in MeOH, whose concentrations were adjusted to bring about equal absorbances at 287–293 nm, were simultaneously irradiated using Rayonet photoreactor with 3000 Å light in a merry-go-round apparatus. Aliquots of the photolysates were removed periodically over a 2–20 min interval, and their absorbances at 293 nm were determined. The quantum yields for product formation given in the manuscript were calculated by taking into account the quantum yields for starting material disappearance, determined by comparing the percent disappearance of the substrate to that of the actinometer for photoreactions run at low conversion (<30%, and averaged of three independent measurements) and the yields of products.

5.3. Preparation of photochemical substrates

*5.3.1. Preparation of **25**.* A solution of ethanolamine (30.0 g, 491 mmol) in CH_3CN 80 mL containing K_2CO_3 (22.5 g, 163 mmol) was stirred at 80 °C for 30 min. The known trimethylsilylmethoxypentyl iodide[18] (5.0 g, 17 mmol) was added dropwise and the resulting solution was stirred at 120 °C for 13 h. Concentration in vacuo gave a residue, which was diluted with CH_2Cl_2 and extracted water. The extracts were dried over Na_2SO_4, filtered and concentrated in vacuo to yield **25** (3.3 g, 80%). ^{1}H NMR ($CDCl_3$) δ −0.02 (s, 9H), 1.25–1.56 (m, 6H), 2.60 (t, 2H, *J*=7.2 Hz), 2.73 (t, 2H, *J*=5.4 Hz), 3.02 (s, 2H), 3.24–3.35 (m, 4H), 3.62 (t, 2H, *J*=5.4 Hz); ^{13}C NMR ($CDCl_3$) δ −3.1, 23.7, 29.2, 49.2, 51.0, 60.3, 64.7, 75.0, 75.1; HRMS (FAB) *m*/*z* 234.1892 (M+1, $C_{11}H_{28}NO_2Si$ requires 234.1889).

*5.3.2. Preparation of **28** and **29**.* Solutions of aminoalcohols **25** (1.0 g, 4 mmol) in CH_3CN 80 mL containing K_2CO_3 (0.9 g, 6 mmol) were stirred at 80 °C for 30 min. The known trimethylsilylmethoxyethyl iodide **26**[2,18] (1.5 g, 6.0 mmol) and trimethylsilylmethylthioethyl iodide **27**[16] (1.6 g, 6.0 mmol) were added dropwise and the resulting solutions were stirred at 120 °C for 10 h. Concentration of solutions in vacuo gave residues, which were diluted with CH_2Cl_2 and extracted with water. The extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to yield **28** (0.8 g, 51%) and **29** (0.9 g, 55%).

Compound **28**: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 18H), 1.22–1.54 (m, 6H), 2.49 (t, 2H, *J*=7.2 Hz), 2.58–2.65 (m, 4H), 3.04 (s, 2H), 3.06 (s, 2H), 3.34 (t, 2H, *J*=6.6 Hz), 3.41 (t, 2H, *J*=5.7 Hz), 3.48 (t, 2H, *J*=5.4 Hz); ^{13}C NMR ($CDCl_3$) δ −3.2, −3.1, 23.7, 27.2, 29.3, 53.1, 54.9, 55.9, 59.0, 64.6, 65.3, 74.0, 75.2; HRMS (FAB) *m*/*z* 364.2707 (M+1, $C_{17}H_{42}NO_3Si_2$ requires 364.2703).

Compound **29**: ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 9H), 0.08 (s, 9H), 1.27–1.58 (m, 8H), 1.76 (s, 2H), 2.47 (t, 2H, *J*=7.2 Hz), 2.58 (t, 2H, *J*=5.1 Hz), 2.68 (t, 2H, *J*=6.9 Hz), 3.06 (s, 2H), 3.34 (t, 2H, *J*=6.6 Hz), 3.51 (t, 2H, *J*=5.1 Hz); ^{13}C NMR ($CDCl_3$) δ −3.3, −2.0, 18.2, 23.6, 26.7, 29.0, 34.0, 52.4, 53.8, 55.4, 58.5, 64.3, 74.8; HRMS (FAB) *m*/*z* 380.2474 (M+1, $C_{17}H_{42}NO_2Si_2S$ requires 380.2475).

*5.3.3. Preparation of **30** and **31**.* Solutions of aminoalcohols **28** and **29** (2.5 g, 7 mmol) in THF 60 mL containing phthalimide (1.5 g, 10 mmol) and PPh_3 (2.7 g, 10 mmol) were stirred at room temperature for 30 min. DIAD (2.1 g, 10 mmol) was added dropwise in the dark to each solution followed by stirring at room temperature for 12. Concentration of solutions in vacuo gave residues, which were triturated with hexane. The solutions were filtered and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (1:5 EtOAc/*n*-hexane) to afford **30** (2.6 g, 69%) and **31** (2.1 g, 63%).

Compound **30**: ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 9H), 0.01 (s, 9H), 1.15–1.46 (m, 6H), 2.49 (t, 2H, *J*=7.5 Hz), 2.69 (t, 2H, *J*=6.0 Hz), 2.75 (t, 2H, *J*=6.6 Hz), 3.02 (s, 2H), 3.06 (s, 2H), 3.25 (t, 2H, *J*=6.6 Hz), 3.43 (t, 2H, *J*=6.0 Hz), 3.74 (t, 2H, *J*=6.6 Hz), 7.69 (q, 2H, *J*=2.4 Hz), 7.82 (q, 2H, *J*=2.7 Hz); ^{13}C NMR ($CDCl_3$) δ −3.2, 23.6, 27.2, 29.2, 36.2, 51.9, 53.1, 54.7, 64.4, 65.0, 74.0, 75.1, 122.9, 132.1, 133.6, 168.1; HRMS (EI) *m*/*z* 492.2841 (M^+, $C_{25}H_{44}N_2O_4Si_2$ requires 492.2840).

Compound **31**: ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9H), 0.06 (s, 9H), 1.17–1.49 (m, 8H), 1.77 (s, 2H), 2.44–2.53 (m, 4H), 2.67–2.74 (m, 4H), 3.25 (t, 2H, *J*=6.6 Hz), 3.74 (t, 2H, *J*=6.9 Hz), 7.68 (q, 2H, *J*=2.1 Hz), 7.82 (q, 2H, *J*=2.4 Hz); ^{13}C NMR ($CDCl_3$) δ −3.2, −1.9, 18.3, 23.6, 27.0, 29.2, 33.4, 36.0, 51.2, 53.4, 53.9, 64.4, 75.0, 122.9, 132.0, 133.6, 168.0; HRMS (EI) *m*/*z* 508.2614 (M^+, $C_{25}H_{44}N_2O_3Si_2S$ requires 508.2611).

*5.3.4. Preparation of **41**.* A solution of 5-ethoxypentanol (2.7 g, 21 mmol) in ether 80 mL containing triethylamine (2.2 g, 22 mmol) was stirred at 0 °C for 30 min. Methanesulfonyl chloride (2.5 g, 22 mmol) was added dropwise and the resulting solution was stirred at room temperature for 10 h. Concentration of solution in vacuo gave a residue, which was diluted with ether and extracted with water. The extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to yield a residue. A solution of residue in acetone 100 mL containing sodium iodide (5.0 g, 33 mmol) was stirred at 80 °C for 12 h. Concentration of solution in vacuo gave a residue, which was diluted with ether and extracted water. The extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to yield **41** (4.7 g, 94%). ^{1}H NMR ($CDCl_3$) δ 1.20 (t, 3H, J=7.2 Hz), 1.43–1.51 (m, 2H), 1.55–1.62 (m, 2H), 1.80–1.90 (m, 2H), 3.19 (t, 2H, J=6.9 Hz), 3.39–3.50 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 6.6, 15.1, 27.1, 28.5, 33.2, 65.9, 70.0; HRMS (EI) m/z 242.0164 (M^+, $C_7H_{15}IO$ requires 242.0168).

*5.3.5. Preparation of **43**.* A solution of aminoalcohol **38**[2] (2.1 g, 9 mmol) in CH_3CN 70 mL containing K_2CO_3 (6.3 g, 45 mmol) was stirred at 80 °C for 30 min. 1-Ethoxyethyleneoxyethyl iodide **40**[19] (2.4 g, 10 mmol) was added dropwise and the resulting solution was stirred at 120 °C for 15 h. Concentration in vacuo gave a residue, which was diluted with CH_2Cl_2 and extracted with water. The extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to give **43** (2.8 g, 88%). ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9H), 1.16 (t, 3H, J=7.2 Hz), 2.67 (t, 2H, J=4.8 Hz), 2.74 (q, 4H, J=5.4 Hz), 3.10 (s, 2H), 3.44–3.57 (m, 14H); ^{13}C NMR ($CDCl_3$) δ −3.1, 15.0, 54.1, 54.2, 56.7, 59.3, 65.3, 66.5, 69.6, 69.7, 70.1, 70.3, 74.5; HRMS (FAB) m/z 352.2521 (M+1, $C_{16}H_{38}NO_5Si$ requires 352.2519).

*5.3.6. Preparation of **44**.* A solution of aminoalcohol **38** (0.8 g, 4 mmol) in CH_3CN 70 mL containing K_2CO_3 (2.5 g, 18 mmol) was stirred at 80 °C for 30 min. Ethoxypentyl iodide **41** (1.0 g, 4 mmol) was added dropwise and the resulting solution was stirred at 120 °C for 15 h. Concentration of solution in vacuo gave a residue, which was diluted with CH_2Cl_2 and extracted with water. The extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to afford a residue, which was subjected to silica gel column chromatography (1:2 EtOAc/*n*-hexane) to afford **44** (0.8 g, 65%). ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 9H), 1.19 (t, 3H, J=6.9 Hz), 1.30–1.38 (m, 2H), 1.43–1.62 (m, 4H), 2.54 (t, 2H, J=7.5 Hz), 2.65 (t, 2H, J=4.8 Hz), 2.70 (t, 2H, J=6.0 Hz), 3.14 (s, 2H), 3.39 (t, 2H, J=6.6 Hz), 3.47 (t, 2H, J=7.2 Hz), 3.52–3.59 (m, 8H); ^{13}C NMR ($CDCl_3$) δ −3.1, 15.2, 23.9, 27.1, 29.7, 53.3, 55.0, 56.2, 59.0, 65.5, 66.0, 69.8, 70.2, 70.5, 74.6; HRMS (FAB) m/z 350.2724 (M+1, $C_{17}H_{40}NO_4Si$ requires 350.2727).

*5.3.7. Preparation of **46**.* A solution of aminoalcohol **43** (1.4 g, 4 mmol) in anhydrous THF 60 mL containing phthalimide (0.7 g, 5 mmol) and PPh_3 (1.3 g, 5 mmol) was stirred at room temperature for 10 min. DIAD (1.0 g, 5 mmol) was added dropwise in the dark at room temperature and the resulting solution was stirred for 8 h at room temperature. Concentration of solution in vacuo gave a residue, which was rinsed with hexane. The solution was filtered and concentrated in vacuo to afford a residue, which was subjected to silica gel column chromatography (1:5 EtOAc/*n*-hexane) to afford **46** (1.5 g, 78%). ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9H), 1.18 (t, 3H, J=7.2 Hz), 2.76–2.86 (m, 6H), 3.11 (s, 2H), 3.45–3.53 (m, 14H), 3.75 (t, 2H, J=6.9 Hz), 7.66–7.72 (m, 2H), 7.79–7.84 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −3.2, 15.0, 36.2, 52.5, 53.9, 54.0, 65.3, 66.4, 69.6, 69.7, 70.0, 70.3, 74.4, 122.9, 132.1, 133.6, 168.1; HRMS (FAB) m/z 481.2731 (M+1, $C_{24}H_{41}N_2O_6Si$ requires 481.2734).

*5.3.8. Preparation of **47**.* A solution of **44** (1.4 g, 4 mmol) in anhydrous THF 60 mL containing phthalimide (0.7 g, 5 mmol) and PPh_3 (1.3 g, 5 mmol) was stirred at room temperature for 20 min. DIAD (1.0 g, 5 mmol) was added dropwise in the dark and the resulting solution was stirred for 8 h at room temperature. Concentration of solution in vacuo gave a residue, which was rinsed with hexane. The solution was filtered and concentrated in vacuo to afford a residue, which was subjected to silica gel column chromatography (1:6 EtOAc/*n*-hexane) to afford **47** (1.3 g, 70%). ^{1}H NMR ($CDCl_3$) δ 0.02 (s 9H), 1.17 (t, 3H, J=6.9 Hz), 1.24 (t, 2H, J=4.5 Hz), 1.33–1.53 (m, 4H), 2.51 (t, 2H, J=7.5 Hz), 2.69–2.78 (m, 4H), 3.12 (s, 2H), 3.29 (t, 2H, J=6.6 Hz), 3.41 (q, 2H, J=6.9 Hz), 3.48–3.55 (m, 6H), 3.75 (t, 2H, J=6.9 Hz), 7.68–7.70 (m, 2H), 7.81–7.84 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −3.1, 15.1, 23.8, 27.1, 29.6, 36.2, 51.9, 53.4, 54.7, 65.3, 65.9, 69.7, 70.1, 70.5, 74.5, 123.0, 132.2, 133.7, 168.2; HRMS (FAB) m/z 479.2943 (M+1, $C_{25}H_{43}N_2O_5Si$ requires 479.2941).

*5.3.9. Preparation of **52** and **53**.* The solutions aminoalcohol (1.2 g, 5 mmol of **48**,[2] 1.7 g, 6 mmol of **49**[2]) in CH_3CN 70 mL containing K_2CO_3 (3.5 g, 25 mmol for **48**, 4.0 g, 29 mmol for **49**) were stirred at 80 °C for 20 min, respectively. Alkyl iodide (1.3 g, 7 mmol of **50**, 1.5 g, 6 mmol of **51**) was added, respectively and the resulting solutions were stirred at 120 °C for 15 h. Concentration in vacuo gave residues, which were diluted with CH_2Cl_2 and extracted with water. The each extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to yield **52** (1.0 g, 75%) and **53** (1.8 g, 93%).

Compound **52**: ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9H), 0.89 (t, 3H, J=7.5 Hz), 1.24–1.35 (m, 4H), 1.41–1.51 (m, 2H), 2.53 (t, 2H, J=7.8 Hz), 2.63–2.71 (m, 4H), 3.10 (s, 2H), 3.46 (t, 2H, J=5.1 Hz), 3.53 (t, 2H, J=5.1 Hz); ^{13}C NMR ($CDCl_3$) δ −3.2, 14.0, 22.6, 27.0, 29.4, 53.1, 55.0, 59.0, 74.0; HRMS (EI) m/z 261.2126 (M^+, $C_{13}H_{31}NO_2Si$ requires 261.2124).

Compound **53**: ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9H), 0.87 (t, 3H, J=6.9 Hz), 1.22–1.30 (m, 10H), 1.40–1.49 (m, 2H), 2.51 (t, 2H, J=7.8 Hz), 2.64 (t, 2H, J=5.4 Hz), 2.69 (t, 2H, J=6.0 Hz), 3.14 (s, 2H), 3.52–3.59 (m, 8H); ^{13}C NMR ($CDCl_3$) δ −3.2, 13.9, 22.5, 27.1, 27.2, 29.1, 29.4, 31.7, 53.3, 55.0, 56.1, 59.0, 65.3, 69.7, 70.1, 74.5; HRMS (FAB) m/z 348.2932 (M+1, $C_{18}H_{42}NO_3Si$ requires 348.3934).

*5.3.10. Preparation of **54** and **55**.* The solutions of aminoalcohol (1.0 g, 4 mmol of **52**, 1.4 g, 4 mmol of **53**) in anhydrous THF 60 mL containing phthalimide (0.7 g, 5 mmol for **52** and **53**) and PPh_3 (1.3 g, 5 mmol for **52** and **53**) were stirred at room temperature for 20 min, respectively. DIAD (1.0 g, 5 mmol for **52** and **53**) was added dropwise and the each resulting solutions were stirred in the dark for 8 h. Concentration of solution in vacuo gave residues, which were rinsed with hexane. The each solution were filtered and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (1:20 EtOAc/*n*-hexane for **54**, 1:10 for **55**) to afford **54** (1.3 g, 80%) and **55** (1.3 g, 68%).

Compound **54**: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9H), 0.77 (t, 3H, J=7.2 Hz), 1.11–1.36 (m, 6H), 2.49 (t, 2H, J=7.5 Hz), 2.70 (t, 2H, J=6.0 Hz), 2.76 (t, 2H, J=6.9 Hz), 3.07 (s, 2H), 3.44 (t, 2H, J=6.0 Hz), 3.75 (t, 2H, J=6.6 Hz), 7.68–7.71 (m, 2H), 7.81–7.84 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −3.1, 14.0, 22.6, 27.2, 36.4, 52.1, 53.2, 54.9, 65.2, 74.1 123.0, 132.3, 133.7, 168.3; HRMS (FAB) m/z 391.2416 (M+1, $C_{21}H_{35}N_2O_3Si$ requires 391.2417).

Compound **55**: ^{1}H NMR ($CDCl_3$) δ 0.02 (s 9H), 0.85 (t, 3H, J=6.9 Hz), 1.12–1.38 (m, 12H), 2.49 (t, 2H, J=7.5 Hz), 2.69–2.78 (m, 4H), 3.13 (s, 2H), 3.48–3.54 (m, 6H), 3.75 (t, 2H, J=6.6 Hz), 7.67–7.70 (m, 2H), 7.81–7.84 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −3.2, 13.9, 22.5, 27.2, 27.3, 29.1, 29.4, 31.7, 36.1, 51.8, 53.4, 54.8, 65.2, 69.7, 70.0, 74.4, 122.9, 132.1, 133.6, 168.1; HRMS (FAB) m/z 477.3147 (M+1, $C_{26}H_{45}N_2O_4Si$ requires 477.3149).

*5.3.11. Preparation of **72**.* A solution of trimethylsilylmethoxyethanol **69**[5b] (2.0 g, 14 mmol) in anhydrous THF 50 mL containing Na (0.4 g, 15 mmol) was stirred at 110 °C for 5 h. 1,8-Dibromooctane **66** (4.1 g, 15 mmol) was added dropwise and the resulting solution

was stirred for 15 h at 130 °C. Concentration of solution in vacuo gave a residue, which was diluted with pentane and extracted with water. The extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to afford a residue, which was subjected to silica gel column chromatography (1:5 EtOAc/*n*-hexane) to afford **72** (3.4 g, 72%). ^{1}H NMR −0.04 (s, 9H), 1.18–1.50 (m, 10H), 1.72–1.81 (m, 2H), 3.08 (s, 2H), 3.31 (t, 2H, *J*=6.9 Hz), 3.38 (t, 2H, *J*=6.6 Hz), 3.47 (s, 4H); ^{13}C NMR −3.2, 25.8, 27.9, 28.5, 29.1, 29.5, 32.6, 33.6, 65.1, 69.7, 71.2, 74.5; HRMS (ES) *m*/*z* 361.1169 (M+Na, $C_{14}H_{31}BrO_2SiNa$ requires 361.1174).

5.3.12. Preparation of ***73****.* A solution of trimethylsilylmethoxypentanol **70**[18] (5.0 g, 26 mmol) in anhydrous THF 50 mL containing Na (0.7 g, 30 mmol) was stirred at 110 °C for 15 h. 1,5-Diiodopentane **67** (9.8 g, 30 mmol) was added dropwise and the resulting solution was stirred for 20 h at 120 °C. Concentration of solution in vacuo gave a residue, which was diluted with pentane and extracted with water. The extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to afford a residue, which was subjected to silica gel column chromatography (1:1:10 EtOAc/$CHCl_3$/*n*-hexane) to afford **73** (6.8 g, 67%). ^{1}H NMR ($CDCl_3$) δ −0.04 (s, 9H), 1.27–1.56 (m, 10H), 1.73–1.82 (m, 2H), 3.00 (s, 2H), 3.12 (t, 2H, *J*=7.2 Hz), 3.29–3.34 (m, 6H); ^{13}C NMR ($CDCl_3$) δ −3.1, 22.6, 27.1, 28.5, 29.2, 29.4, 33.2, 64.5, 70.3, 70.7, 75.0; HRMS (FAB) *m*/*z* 387.1215 (M+1, $C_{14}H_{31}IO_2Si$ requires 387.1216).

5.3.13. Preparation of ***74****.* A solution of trimethylsilylmethoxyoctanol **71**[18] (5.0 g, 22 mmol) in anhydrous THF (50 mL) containing Na (0.5 g, 22 g) was stirred at 110 °C for 15 h. 1,2-Diiodoethane **68** (6.5 g, 23 mmol) was added dropwise and the resulting solution was stirred for 12 h at 130 °C. Concentration of solution in vacuo gave a residue, which was diluted with pentane and extracted with water. The extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (1:10 EtOAc/*n*-hexane) to afford **74** (5.0 g, 60%). ^{1}H NMR ($CDCl_3$) δ −0.00 (s, 9H), 1.22–1.33, 1.47–1.53 (m, 12H), 3.03 (s, 2H), 3.20 (t, 2H, *J*=6.0 Hz), 3.32 (q, 4H, *J*=6.6 Hz), 3.43 (t, 2H, *J*=6.3 Hz), 3.64 (t, 2H, *J*=6.6 Hz); ^{13}C NMR ($CDCl_3$) δ −3.0, 26.0, 29.4 (multiple resonances), 71.0, 71.4, 75.3; HRMS (FAB) *m*/*z* 387.1213 (M+1, $C_{14}H_{31}IO_2Si$ requires 387.1216).

5.3.14. Preparation of ***75****–****77****.* Solutions of **72** (3.0 g, 9 mmol), **73** (3.0 g, 8 mmol), and **74** (3.9 g, 10 mmol) each containing potassium phthalimide (1.6 g, 9 mmol for **72**, 1.9 g, 10 mmol for **73**, 2.8 g, 15 mmol for **74**) in 80 mL DMF were stirred for 16 h at 120 °C. Concentration of the solutions in vacuo gave residues, which were diluted with methylene chloride and extracted with water. The extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (1:5 EtOAc/*n*-hexane for **75** and **76** and 1:7 EtOAc/*n*-hexane for **77**) to afford **75** (2.4 g, 68%), **76** (2.5 g, 79%), and **77** (3.6 g, 86%).

Compound **75**: ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9H), 1.23–1.35 (m, 8H), 1.52 (t, 2H, *J*=6.6 Hz), 1.63 (t, 2H, *J*=6.3 Hz), 3.12 (s, 2H), 3.41 (t, 2H, *J*=6.6 Hz), 3.52 (s, 4H), 3.64 (t, 2H, *J*=6.6 Hz), 7.66–7.69, 7.80–7.83 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −3.2, 25.8, 26.5, 26.6, 28.4, 28.9, 29.1, 29.5, 37.8, 65.1, 69.6, 71.2, 74.4, 122.9, 131.9, 133.6, 168.1; HRMS (ES) *m*/*z* 428.2229 (M+Na, $C_{22}H_{35}NO_4SiNa$ requires 428.2233).

Compound **76**: ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 9H), 1.26–1.41, 1.46–1.71 (m, 12H), 3.03 (s, 2H), 3.31 (m, 6H), 3.64 (t, 2H, *J*=7.2 Hz), 7.65–7.68, 7.78–7.81 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −3.2, 22.6, 23.4, 28.3, 29.1, 29.4, 37.8, 64.5, 70.3, 70.7, 75.0, 122.9, 132.0, 133.7, 168.2; HRMS (FAB) *m*/*z* 406.2414 (M+1, $C_{22}H_{36}NO_4Si$ requires 406.2414).

Compound **77**: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9H), 1.15–1.23, 1.44–1.48 (m, 12H), 3.03 (s, 2H), 3.31 (t, 2H, *J*=6.6 Hz), 3.40 (q, 2H, *J*=6.9 Hz), 3.63 (t, 2H, *J*=5.7 Hz), 3.85 (t, 2H, *J*=5.7 Hz); ^{13}C NMR ($CDCl_3$) δ −3.2, 25.7, 25.8, 29.1, 29.2, 29.3, 37.2, 64.4, 67.1, 70.7, 75.1, 123.0, 131.9, 133.7, 167.9; HRMS (FAB) *m*/*z* 406.2414 (M+1, $C_{22}H_{36}NO_4Si$ requires 406.2414).

5.3.15. Preparation of ***82****.* A solution of 5-amino-1-pentanol (9.3 g, 90 mmol) in CH_3CN 130 mL containing K_2CO_3 (12 g, 89 mmol) was stirred at 80 °C for 20 min. The known trimethylsilylmethoxyethyl iodide[2,18] (4.6 g, 18 mmol) was added dropwise and the resulting solution was stirred at 120 °C for 14 h. Concentration in vacuo gave a residue, which was diluted with CH_2Cl_2 and extracted with water. The extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to yield **82** (2.9 g, 68%). ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 9H), 1.38–1.63 (m, 6H), 1.85 (br s, 1H), 2.62 (t, 2H, *J*=6.9 Hz), 2.73 (t, 2H, *J*=5.4 Hz), 3.11 (s, 2H), 3.50 (t, 2H, *J*=5.7 Hz), 3.63 (t, 2H, *J*=6.3 Hz); ^{13}C NMR ($CDCl_3$) δ −3.3, 23.3, 29.4, 32.3, 48.8, 49.3, 61.5, 64.9, 73.8; HRMS (FAB) *m*/*z* 234.1891 (M+1, $C_{11}H_{28}NO_2Si$ requires 234.1889).

5.3.16. Preparation of ***84*** *and* ***85****.* Solutions of aminoalcohols **81** (2.5 g, 13 mmol) and **82** (2.5 g, 11 mmol) in CH_3CN 120 mL containing K_2CO_3 (9.0 g, 65 mmol for **81**, 7.0 g, 51 mmol for **82**) were stirred at 80 °C for 20 min, respectively. Iodide **83**[20] (4.7 g, 14 mmol for **81**, 3.9 g, 11 mmol for **82**) was added dropwise and the resulting solutions were stirred at 110 °C for 16 h, respectively. Concentration of solution in vacuo gave residues, which were diluted with CH_2Cl_2 and extracted with water. The extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to afford **84** (4.1 g, 78%) and **85** (3.4 g, 71%).

Compound **84**: ^{1}H NMR ($CDCl_3$) δ −0.03 (s, 9H), 2.59–2.71 (m, 6H), 3.00 (s, 2H), 3.35 (t, 2H, *J*=5.7 Hz), 3.39 (t, 2H, *J*=5.1 Hz), 3.49 (t, 2H, *J*=5.7 Hz), 3.64 (t, 2H, *J*=5.7 Hz), 3.84 (t, 2H, *J*=5.7 Hz), 7.67 (q, 2H, *J*=2.4 Hz), 7.80 (q, 2H, *J*=2.4 Hz); ^{13}C NMR ($CDCl_3$) δ −3.2, 37.3, 53.7, 53.9, 56.4, 59.1, 65.2, 67.6, 69.4, 74.0, 123.1, 132.0, 133.8, 133.9, 168.1; HRMS (FAB) *m*/*z* 409.2162 (M+1, $C_{20}H_{33}N_2O_5Si$ requires 409.2159).

Compound **85**: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9H), 1.24–1.43 (m, 4H), 1.49–1.59 (m, 2H), 2.47 (t, 2H, *J*=7.5 Hz), 2.60–2.67 (m, 4H), 3.04 (s, 2H), 3.41 (t, 2H, *J*=6.0 Hz), 3.52 (t, 2H, *J*=6.3 Hz), 3.61 (t, 2H, *J*=6.6 Hz), 3.67 (t, 2H, *J*=6.0 Hz), 3.88 (t, 2H, *J*=5.7 Hz), 7.70 (q, 2H, *J*=2.4 Hz), 7.84 (q, 2H, *J*=2.4 Hz); ^{13}C NMR ($CDCl_3$) δ −3.1, 23.3, 26.8, 32.5, 37.4, 53.5, 53.8, 55.2, 62.6, 65.2, 67.6, 69.3, 74.0, 123.2, 132.0, 133.8, 168.2; HRMS (FAB) *m*/*z* 451.2624 (M+1, $C_{23}H_{39}N_2O_5Si$ requires 451.2628).

5.3.17. Preparation of ***86*** *and* ***87****.* Solutions of aminoalcohols **84** (1.7 g, 4 mmol) and **85** (1.6 g, 4 mmol) in anhydrous THF 60 mL containing phthalimide (0.8 g, 5 mmol for **84**, 0.7 g, 5 mmol for **85**) and PPh_3 (1.4 g, 5 mmol for **84**, 1.2 g, 5 mmol for **85**) were stirred at room temperature for 30 min. DIAD (1.1 g, 5 mmol for **84**, 1.0 g, 5 mmol for **85**) was added dropwise in the dark, respectively and the resulting solutions were stirred at room temperature for 12 h. Concentration of the solutions in vacuo gave residues, which were triturated with hexane. The solutions were filtered and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (1:1 EtOAc/*n*-hexane for **86** and 5:2 EtOAc/*n*-hexane for **87**) to afford **86** (1.1 g, 65%) and **87** (1.3 g, 64%), respectively.

Compound **86**: ^{1}H NMR ($CDCl_3$) δ −0.03 (s, 9H), 2.68–2.81 (m, 6H), 3.00 (s, 2H), 3.36 (t, 2H, *J*=5.7 Hz), 3.46 (t, 2H, *J*=6.0 Hz), 3.60 (t, 2H, *J*=6.0 Hz), 3.69 (t, 2H, *J*=6.6 Hz), 3.83 (t, 2H, *J*=5.7 Hz), 7.68 (q, 4H, *J*=2.4 Hz), 7.80–7.84 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −3.2, 36.3, 37.2, 52.5, 53.7, 53.8, 65.0, 67.5, 69.4, 74.1, 122.9, 123.1, 132.0, 132.1, 133.6, 133.7, 168.0, 168.1; HRMS (EI) *m*/*z* 537.2291 (M^+, $C_{28}H_{35}N_3O_6Si$ requires 537.2295).

Compound **87**: ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 9H), 1.22–1.30, 1.36–1.45, and 1.59–1.69 (m, 6H), 2.44 (t, 2H, *J*=7.5 Hz), 2.59–2.65 (m, 4H), 3.03 (s, 2H), 3.39 (t, 2H, *J*=5.7 Hz), 3.50 (t, 2H, *J*=6.3 Hz), 3.62–

3.69 (m, 4H), 3.87 (t, 2H, *J*=5.4 Hz), 7.68–7.72 (m, 4H), 7.82–7.85 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −3.2, 24.5, 26.6, 28.4, 37.2, 37.8, 53.4, 53.8, 54.9, 65.0, 67.5, 69.2, 74.1, 122.9, 123.0, 131.9, 133.6, 133.7, 168.0, 168.2; HRMS (FAB) *m*/*z* 580.2841 (M+1, $C_{31}H_{42}N_3O_6Si$ requires 580.2843).

*5.3.18. Preparation of **94**–**96**.* Solutions of known aminoalcohols **37**[2] (1.0 g, 5 mmol), **38** (1.0 g, 4 mmol), and **92**[2] (1.5 g, 5 mmol) in CH_3CN 70 mL each containing K_2CO_3 (0.9 g, 6 mmol for **37** and **38**, 1.1 g, 8 mmol for **92**) were stirred at 80 °C for 1 h. The known trimethylsilylmethylthioethyl iodide **93**[16] (1.6 g, 6 mmol for **37**, 1.2 g, 4 mmol for **38**, 1.6 g, 6 mmol for **92**) was added dropwise and the resulting solutions were stirred at 120 °C for 12 h. Concentration of solutions in vacuo gave residues, which were diluted with CH_2Cl_2 and extracted with water, respectively. The extracts were dried with Na_2SO_4, filtered and concentrated in vacuo to yield **94** (0.8 g, 47%), **95** (0.5 g, 49%), and **96** (0.8 g, 51%).

Compound **94**: ^{1}H NMR ($CDCl_3$) δ 0.02 and 0.07 (s, 18H), 1.77 (s, 2H), 2.57–2.80 (m, 8H), 3.09 (s, 2H), 3.45 (t, 2H, *J*=5.4 Hz), 3.52 (t, 2H, *J*=5.1 Hz); ^{13}C NMR ($CDCl_3$) δ −3.1, −1.8, 18.5, 34.3, 53.2, 53.7, 55.9, 59.1, 65.4, 74.0; HRMS (FAB) *m*/*z* 338.2002 (M+1, $C_{14}H_{36}NO_2Si_2S$ requires 338.2005).

Compound **95**: ^{1}H NMR ($CDCl_3$) δ 0.04 and 0.09 (s, 18H), 1.78 (s, 2H), 2.59–2.82 (m, 8H), 3.14 (s, 2H), 3.52–3.60 (m, 8H); ^{13}C NMR ($CDCl_3$) δ −3.5, −2.2, 18.0, 33.7, 53.0, 53.4, 55.8, 58.8, 64.9, 69.4, 69.7, 74.2; HRMS (FAB) *m*/*z* 382.2264 (M+1, $C_{16}H_{40}NO_3Si_2S$ requires 382.2267).

Compound **96**: ^{1}H NMR ($CDCl_3$) δ 0.02 and 0.07 (s, 18H), 1.76 (s, 2H), 2.56–2.79 (m, 8H), 3.12 (s, 2H), 3.50–3.60 (m, 8H); ^{13}C NMR ($CDCl_3$) δ −3.3, −2.0, 18.3, 33.9, 53.1, 53.5, 55.9, 59.0, 65.1, 69.5, 70.1, 70.2, 70.3, 74.5; HRMS (FAB) *m*/*z* 426.2528 (M+1, $C_{18}H_{44}NO_4Si_2S$ requires 426.2530).

*5.3.19. Preparation of **97**–**99**.* Solutions of aminoalcohols **94** (2.9 g, 9 mmol), **95** (0.9 g, 2 mmol), and **96** (1.3 g, 3 mmol) in anhydrous THF (40 mL) containing phthalimide (1.6 g, 11 mmol for **94**, 0.4 g, 3 mmol for **95**, 0.5 g, 3 mmol for **96**) and PPh_3 (2.9 g, 11 mmol for **94**, 0.7 g, 3 mmol for **95**, 0.9 g, 3 mmol for **96**) were stirred at room temperature for 30 min. DIAD (2.2 g, 11 mmol for **94**, 0.5 g, 3 mmol for **95**, 0.7 g, 3 mmol for **96**) was added dropwise in the dark and the resulting solutions were stirred at room temperature for 12 h. Concentration in vacuo gave residues, which were triturated with hexane. The solutions were filtered and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (1:8 EtOAc/*n*-hexane for **97**, 1:3 EtOAc/*n*-hexane for **98**, and 1:5 EtOAc/*n*-hexane for **99**) to yield **97** (2.4 g, 62%), **98** (0.5 g, 44%), and **99** (0.8 g, 50%).

Compound **97**: ^{1}H NMR ($CDCl_3$) δ −0.04, 0.00 (two s, 18H), 1.17 (s, 2H), 2.46–2.51 (m, 2H), 2.71–2.82 (m, 4H), 3.04 (s, 2H), 3.42 (t, 2H, *J*=5.8 Hz), 3.74 (t, 2H, *J*=6.6 Hz), 7.66–7.72 (m, 2H), 7.79–7.85 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −3.1, −1.8, 18.3, 33.7, 36.2, 51.8, 53.0, 54.1, 65.1, 74.0, 123.0, 132.0, 133.6, 168.2; HRMS (EI) *m*/*z* 466.2137 (M^+, $C_{22}H_{38}N_2O_3Si_2S$ requires 466.2142).

Compound **98**: ^{1}H NMR ($CDCl_3$) δ 0.02, 0.05 (two s, 18H), 1.75 (s, 2H), 2.48–2.53 (m, 2H), 2.73–2.83 (m, 6H), 3.12 (s, 2H), 3.47–3.52 (m, 6H), 3.75 (t, 2H, *J*=6.6 Hz), 7.70 and 7.83 (two q, 4H, *J*=3.0 Hz); ^{13}C NMR ($CDCl_3$) δ −3.2, −1.9, 18.3, 33.5, 36.0, 51.7, 53.2, 54.3, 65.2, 69.7, 70.0, 74.3, 122.9, 132.0, 133.6, 168.1; HRMS (FAB) *m*/*z* 511.2485 (M+1, $C_{24}H_{43}N_2O_4Si_2S$ requires 511.2482).

Compound **99**: ^{1}H NMR ($CDCl_3$) δ 0.03, 0.05 (two s, 18H), 1.70 and 1.75 (rotameric s, 2H), 2.48–2.53 (m, 2H), 2.73–2.82 (m, 6H), 3.13 (s, 2H), 3.47–3.62 (m, 10H), 3.75 (t, 2H, *J*=6.6 Hz), 7.70 and 7.83 (two q, 4H, *J*=3.0 Hz); ^{13}C NMR ($CDCl_3$) δ −3.2, −1.9, 18.2, 33.4, 36.0, 51.7, 53.1, 54.0, 65.1, 69.6, 70.1, 70.3, 74.5, 122.9, 132.0, 133.6, 168.1; HRMS (FAB) *m*/*z* 555.2742 (M+1, $C_{26}H_{47}N_2O_5Si_2S$ requires 555.2744).

5.4. Photochemical reactions

*5.4.1. Photoreactions of **30** and **31** to give **36** and **61**.* Nitrogen purged solutions of phthalimide **30** (0.3 g, 0.6 mmol) and **31** (0.3 g, 0.6 mmol) in MeOH 150 mL containing 7 mM $HClO_4$ (1 mmol) were irradiated by using Pyrex glass filtered light for 1 h to give almost 100% conversion. Concentration of the photolysates in vacuo gave residues, which were diluted with CH_2Cl_2 and extracted with 5% $NaHCO_3$. The extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (1:5 EtOAc/*n*-hexane) to afford **36** (190 mg, 76%) and **61** (190 mg, 73%).

Compound **36**: ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9H), 1.22–1.41 (m, 4H), 1.64 (br s, 2H), 2.72 (t, 4H, *J*=6.0 Hz), 2.83 (t, 2H, *J*=6.9 *Hz*), 3.06 (s, 2H), 3.47 (t, 2H, *J*=6 Hz), 4.05–4.18 (m, 4H), 6.58 (s, 1H), 7.31–7.37 (m, 1H), 7.45 (d, 2H, *J*=3.6 Hz), 7.80 (d, 1H, *J*=7.8 Hz); ^{13}C NMR ($CDCl_3$) δ −3.1, 21.8, 23.2, 25.9, 38.4, 48.9, 50.0, 54.5, 65.3, 74.2, 74.6, 117.1, 123.3, 126.9, 127.7, 129.1, 130.9, 136.6, 166.4; HRMS (FAB) is not measured due to the decomposition.

Compound **61**: ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 9H), 1.22–1.36 (m, 2H), 1.46–1.60 (m, 4H), 1.96–2.06 (m, 2H), 2.44–2.62 (m, 4H), 2.74 (s, 3H), 2.90–3.02 (m, 6H), 3.06 (s, 3H), 3.36 (t, 2H, *J*=6.3 Hz), 3.67 (two d, 2H, *J*=13.2 Hz), 7.34 (d, 1H, *J*=6.6 Hz), 7.49, 7.58 (two t, 2H, *J*=7.2 Hz), 7.83 (d, 1H, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ −3.1, 24.0, 27.8, 29.3, 41.7, 50.4, 52.8, 58.3, 60.5, 64.6, 75.1, 95.6, 122.0, 123.0, 129.7, 132.2, 132.8, 143.3, 168.8; HRMS (EI) *m*/*z* 450.2376 (M^+, $C_{23}H_{38}N_2O_3SiS$ requires 450.2372).

*5.4.2. Photoreactions of **46** and **47** to give **57** and **58**.* The nitrogen purged solutions of **46** (0.40 g, 0.8 mmol) and **47** (0.4 g, 0.8 mmol) in MeOH 170 mL containing 6.6 mM $HClO_4$ (1 mmol for **46** and **47**) were irradiated by using Pyrex glass filtered light for 1.5 h, respectively. Concentration of the photolysate in vacuo gave residues, which were diluted with CH_2Cl_2 and extracted with 5% $NaHCO_3$. The extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to give residue, which were subjected to silica gel column chromatography (20:1 EtOAc/MeOH for **57** and 8: 1 EtOAc/*n*-hexane for **58**) to afford **57** (170 mg, 48%) and **58** (210 mg, 52%), respectively.

Compound **57**: ^{1}H NMR ($CDCl_3$) δ 1.19 (t, 3H, *J*=7.2 Hz), 2.62–2.94 (m, 9H), 3.99–3.71 (m, 14H), 3.78–3.92 (m, 2H), 4.23–4.26 (d, 1H), 7.38–7.58 (m, 3H), 7.72–7.79 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 15.1, 38.8, 49.6, 51.3, 55.6, 66.4, 68.0, 69.5, 69.7, 70.3, 70.4, 71.0, 74.1, 93.2, 121.9, 123.1, 130.0, 131.9, 133.0, 141.5, 168.0; HRMS (FAB) *m*/*z* 423.2494 (M+1, $C_{22}H_{35}N_2O_6$ requires 423.2495).

Compound **58**: ^{1}H NMR ($CDCl_3$) δ 1.19 (t, 3H, *J*=7.9 Hz), 1.23–1.31 (b, 6H), 1.54–1.56 (b, 2H), 2.52–2.59 (m, 4H), 2.73–2.84 (m, 5H), 3.08–3.29 (m, 2H), 3.37–3.71 (m, 10H), 3.79–3.85 (m, 1H), 4.23–4.27 (d, 1H), 7.39–7.42 (d, 1H), 7.48–7.58 (m, 2H) 7.78–7.81 (d, 1H); ^{13}C NMR ($CDCl_3$) δ 15.2, 26.1, 27.4, 29.7, 49.9, 50.8, 52.9, 65.9, 69.7, 70.7, 71.0, 72.5, 74.3, 93.2, 121.9, 123.2, 130.1, 131.9, 133.0, 141.5, 168.3; HRMS (EI) *m*/*z* 420.2625 (M+1, $C_{23}H_{36}N_2O_5$ requires 420.2624).

*5.4.3. Photoreactions of **54** and **55** to give **59** and **60**.* Nitrogen purged solutions of **54** (0.4 g, 0.9 mmol) and **55** (0.3 g, 0.7 mmol) in 170 mL MeOH containing each 10 mM $HClO_4$ (2 mmol for **54**) and 6 mM $HClO_4$ (1.0 mmol for **55**) were irradiated by using Pyrex glass filtered light for 30 min for **54** and 1.5 h for **55**. Concentration of the photolysates in vacuo gave residues, which were diluted with CH_2Cl_2 and extracted with 5% $NaHCO_3$. The extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to give residues, which were subjected to silica gel column chromatography (1:5 EtOAc/*n*-hexane for **59** and 5:2 EtOAc/*n*-hexane for **60**) to afford **59** (192 mg, 62%) and **60** (190 mg, 47%).

Compound **59**: ^{1}H NMR ($CDCl_3$) δ 0.76 (t, 3H, *J*=7.2 Hz), 1.11–1.27 (m, 4H), 1.33–1.42 (m, 2H), 2.46–2.58 (m, 4H), 2.75 (t, 2H, *J*=8.1 Hz),

2.82 (s, 3H), 3.31–3.41 (m, 2H), 3.52–3.69 (m, 4H), 3.99, 4.59 (two d, 2H, J=10.8 Hz), 7.40 (d, 1H, J=7.8 Hz) 7.47–7.58 (m, 2H), 7.81 (d, 1H, J=6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 13.8 22.3, 27.6, 29.4, 40.7, 49.8, 54.1, 58.1, 58.5, 71.6, 75.9, 93.8, 122.0, 123.0, 129.8, 131.7, 133.2, 141.7, 168.1; HRMS (FAB) m/z 333.2182 (M+1, $C_{19}H_{29}N_2O_3$ requires 333.2178).

Compound **60**: ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3H, J=7.1 Hz), 1.17–1.30 (m, 12H), 1.49–1.56 (m, 2H), 2.52–2.86 (m, 9H), 3.12–3.27 (m, 2H), 3.41–3.71 (m, 6H), 3.76–3.85 (m, 1H), 4.23–4.26 (d, 1H), 7.40–7.42 (m, 1H), 7.48–7.58 (m, 2H) 7.78–7.81 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 27.4, 29.2 29.4, 31.7, 38.2, 49.9, 51.0, 52.9, 56.6, 61.7, 69.6, 70.9, 72.3, 74.1, 93.2, 121.9, 123.2, 130.0, 131.9, 132.9, 141.5, 168.4; HRMS (FAB) m/z 419.2914 (M+1, $C_{24}H_{39}N_2O_4$ requires 419.2910).

5.4.4. Photoreactions of ***75–77*** *to give* ***78–80***. Solutions of **75** (230 mg, 0.6 mmol), **76** (270 mg, 0.7 mmol), and **77** (140 mg, 0.4 mmol) in 170 mL methanol were irradiated by using Pyrex glass filtered light for 50 min. The photolysates were concentrated in vacuo to give residues, which were subjected to silica gel column chromatography (2:1 EtOAc/*n*-hexane for **78** and **80**, 1:2 EtOAc/*n*-hexane for **79**) to afford **78** (120 mg, 63%), **79** (150 mg, 68%), and **80** (60 mg, 52%).

Compound **78**: ^{1}H NMR (Acetone-d_6) δ 1.28–1.56, 1.67–1.74 (m, 12H), 3.23–3.57 (m, 8H), 3.87, 3.98 (two d, 2H, J=9.9 Hz), 5.44 (s, 1H), 7.45–7.63 (m, 4H); ^{13}C NMR (Acetone-d_6) δ 0.2, 25.1, 26.3, 27.6, 27.8, 39.7, 70.3, 71.2, 72.1, 74.3, 89.8, 123.2, 123.3, 130.2, 132.6, 133.6, 147.7, 168.0; HRMS (FAB) m/z 334.2024 (M+1, $C_{19}H_{28}NO_4$ requires 334.2018).

Compound **79**: ^{1}H NMR ($CDCl_3$) δ 1.35–1.74(m, 12H), 3.28–3.58 (m, 8H), 3.62, 3.89 (two d, 2H, J=9.3 Hz), 4.25 (s, 1H), 7.43–7.56, 7.71–7.74 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 22.4, 23.5, 27.7, 28.7, 28.8, 40.3, 67.7, 69.4, 71.2, 75.1, 88.3, 122.0, 123.3, 130.0, 131.9, 132.2, 167.5; HRMS (FAB) m/z 334.2016 (M+1, $C_{19}H_{28}NO_4$ requires 334.2018).

Compound **80**: ^{1}H NMR ($CDCl_3$) δ 1.22–1.70 (m, 12H), 3.38 (t, 2H, J=9.0 Hz), 3.51–3.72 (m, 4H), 3.68, 3.84 (two d, 2H, J=10.5 Hz), 4.18 (m, 2H), 6.10 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 23.9, 25.0, 25.1, 25.9, 26.6, 26.9, 28.2, 40.6, 70.5, 71.6, 72.2, 76.4, 88.2, 122.2, 123.5, 129.7, 131.3, 132.2, 144.6, 167.4; HRMS (FAB) m/z 334.2022 (M+1, $C_{19}H_{28}NO_4$ requires 334.2018).

5.4.5. Photoreactions of ***86*** *and* ***87*** *to* ***88*** *and* ***89***. Nitrogen purged solutions of **86** (0.4 g, 0.7 mmol) and **87** (0.3 g, 0.5 mmol) in MeOH 150 mL each containing 10 mM $HClO_4$ (2 mmol) were irradiated by using Pyrex glass filtered light for 30 min. Concentration of the photolysates in vacuo gave residues, which were diluted with CH_2Cl_2 and extracted with 5% $NaHCO_3$. The respective extracts were dried with Na_2SO_4, filtered and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (3:2 EtOAc/*n*-hexane for **88** and 5:2 EtOAc/*n*-hexane for **89**) to afford **88** (210 mg, 61%) and **89** (190 mg, 68%).

Compound **88**: ^{1}H NMR ($CDCl_3$) δ 2.59–2.76 (m, 6H), 2.79 (s, 3H), 3.28–3.40 (m, 4H), 3.44–3.62 (m, 4H), 4.05 and 4.51 (two d, 2H, J=10.8 Hz), 7.35–7.55 and 7.68–7.83 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 29.6, 37.3, 40.8, 50.0, 54.2, 56.9, 58.9, 67.6, 69.8, 71.1, 94.0, 122.2, 122.9, 123.0, 123.1, 129.9, 131.9, 132.0, 133.2, 133.6, 133.9, 141.9, 168.0, 168.1; HRMS (EI) m/z 479.2056 (M^+, $C_{26}H_{29}N_3O_6$ requires 479.2055).

Compound **89**: ^{1}H NMR ($CDCl_3$) δ 1.22–1.30 (m, 2H), 1.37–1.47 (m, 2H), 1.57–1.66 (m, 2H), 2.38 (t, 2H, J=7.5 Hz), 2.49–2.66 (m, 4H), 2.71 (s, 3H), 3.27–3.47 (m, 4H), 3.59–3.81 (m, 6H), 3.97 and 4.32 (two d, 2H, J=9.6 Hz), 7.38–7.56 (m, 4H), 7.65–7.68 (m, 2H), 7.75–7.80 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 24.4, 26.8, 28.3, 37.8, 39.3, 49.7, 53.9, 54.9, 56.5, 68.9, 69.2, 70.1, 72.5, 94.1, 121.9, 123.1, 129.6, 131.9, 132.1, 133.1, 133.8, 142.5, 168.4, 169.0; HRMS (EI) m/z 521.2526 (M^+, $C_{29}H_{35}N_3O_6$ requires 521.2530).

5.4.6. Photoreactions ***97–99*** *to give* ***100–103***. Nitrogen purged solutions of **97** (0.3 g, 0.6 mmol), **98** (0.4 g, 0.7 mmol), and **99** (0.4 g, 0.8 mmol) in 150 mL of MeOH each containing 7.0 mM $HClO_4$ (1 mmol) were irradiated by using Pyrex glass filtered light for 1.5 h (for **97**) and 2 h (for **98** and **99**) to give almost 100% conversions, respectively. Concentration of the photolysate in vacuo gave residues, which were diluted with CH_2Cl_2 and extracted with 5% $NaHCO_3$. The extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (1:4 EtOAc/*n*-hexane for **97**, 1:3 EtOAc/*n*-hexane for **98** and **99**) to yield **100** (200 mg, 85%), **101** (270 mg, 85%), **102** (143 mg, 36%), and **103** (193 mg, 52%).

Compound **100**: ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 9H), 2.08 (br d, 2H, J=14.4 Hz), 2.45–2.53 (m, 2H), 2.70–2.85 (m, 4H), 2.75 (s, 3H), 2.93–3.10 (m, 4H), 3.49, 3.65 (two d, 2H, J=14.1 Hz), 7.36 (d, 1H, J=7.5 Hz), 7.51, 7.59 (two t, 2H, J=7.2 Hz), 7.83 (d, 1H, J=7.5 Hz); ^{13}C NMR ($CDCl_3$) δ −3.0, 41.5, 50.2, 53.5, 57.3, 61.1, 65.2, 74.5, 95.5, 122.0, 122.9, 129.5, 132.0, 143.3, 168.8; HRMS (FAB) m/z 409.1985 (M+1, $C_{20}H_{32}N_2O_3Si_2S$ requires 409.1981).

Compound **101**: ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9H), 2.09 (br d, 2H, J=14.7 Hz), 2.44–2.54 (m, 2H), 2.69–3.16 (m, 4H), 2.75 (s, 3H), 3.13 (s, 2H), 3.42–3.67 (m, 8H), 7.35 (d, 1H, J=7.2 Hz), 7.45 (t, 1H, J=7.5 Hz), 7.58 (t, 1H, J=7.5 Hz), 7.82 (d, 1H, J=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ −3.1, 24.0, 41.4, 50.3, 53.4, 57.3, 61.0, 65.3, 69.8, 70.0, 74.5, 122.0, 122.9, 129.5, 132.0, 132.8, 143.4, 168.7; HRMS (FAB) m/z 453.2248 (M+1, $C_{22}H_{37}N_2O_4SiS$ requires 453.2243).

Compound **102**: ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 9H), 2.08 (br d, 2H, J=14.7 Hz), 2.45–2.54 (m, 2H), 2.69–2.98 (m, 4H), 2.75 (s, 3H), 3.13 (s, 2H), 3.50–3.70 (m, 12H), 7.34 (d, 1H, J=7.5 Hz), 7.47–7.61 (m, 2H), 7.81 (d, 1H, J=7.5 Hz); ^{13}C NMR ($CDCl_3$) δ −3.1, 29.6, 41.5, 49.4, 50.4, 53.5, 57.3, 61.1, 61.9, 65.4, 69.8, 70.4, 70.5, 74.6, 122.1, 123.0, 129.6, 132.1, 132.9, 143.5, 168.8; HRMS (FAB) m/z 497.2507 (M+1, $C_{24}H_{41}N_2O_5SiS$ requires 497.2505).

Compound **103**: ^{1}H NMR δ 0.02 (s, 9H), 2.62–2.72 (br s, 2H), 2.89 (t, 2H, J=4.8 Hz), 3.12 (s, 2H), 3.17–3.40 (m, 4H), 3.42 (t, 2H, J=5.1 Hz), 3.48–3.74 (m, 10H), 6.37 (s, 1H), 7.45–7.58 (m, 2H), 7.64 (d, 1H, J=7.8 Hz), 7.81 (d, 1H, J=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ −3.1, 29.6, 37.3, 41.8, 57.0, 57.3, 59.6, 65.3, 70.1, 70.2, 70.3, 74.6, 96.9, 119.4, 122.8, 129.3, 131.7, 137.3, 145.6, 168.1; HRMS (FAB) m/z 465.2249 (M+1, $C_{23}H_{37}N_2O_4SiS$ requires 465.2243).

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Supplementary data

NMR spectra are included. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2010.02.074.

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