Photocyclization Reactions of N-(Trimethylsilylmethoxyalkyl)-Phthalimides. Efficient and Regioselective Route to Heterocycles

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*Received July 24, 1991*

Studies have been conducted to explore single electron transfer (SET) induced photocyclization reactions of N-(trimethylsilylmethoxyalkyl)phthalimides(alkyl = Ethyl, n-propyl, n-butyl, n-pentyl, and n-octyl). Photocyclizations occur in methanol in high yields to produce cyclized products in which phthalimide carbonyl carbon is bonded to the carbon of side chain in place of the trimethylsilyl group. Mechanism for these photocyclizations involving intramolecular SET from oxygen in the α-silylmethoxy groups to the singlet excited state phthalimide moieties followed by desilylation of the intermediate α-silylmethoxy cation radicals and cyclization by radical coupling are proposed. In contrast, photoreaction of N-(trimethylsilylmethoxyethyl) phthalimide in acetone follows different reaction routes to produce two cyclized products in which carbon-carbon bond formation takes place between the phthalimide carbonyl carbon and the carbon α to silicon and oxygen atoms *via* triplet carbonyl hydrogen abstraction triplet carbonyl silyl group abstraction pathways. The normal singlet SET pathway dominates these triplet processes for photoreaction of this substance in methanol. The efficient and regioselective cyclization reactions observed for photolyses in methanol represent synthetically useful processes for construction of medium and large ring heterocyclic compounds.

Introduction

Our provious studies in the area electron transfor (SET) photochemistry using α-silyl electron donors led to observations that (1) photoinduced SET-desilylation sequences serve as the mechanistic basis for selective methods for carbon centered radical generation[1] and (2) sequential SET-desilylation and SET-deprotonation pathways compete in photoaddition reactions occurring between α-silylamine donors and cyclohexenone acceptors[2]. The competition between these pathways are known to be influenced by reaction conditions which control partitioning between the reactivity of contact and solvent separated ion radical pairs. In previous studies of photoinduced SET reaction of phthalimides 1 with α-silyl-n-electron donors 2-4[3], we observed that photoaddition reactions occur to yield photoadducts 5 *via* SET-desilylation mechanistic pathways exclusively (Scheme I).

In a continuation of these efforts, we have investigated SET-induced photocyclization reactions of phthalimides 6 which have intramolecularly linked α-silyl-n-electron donor groups. The design of this work was guided by earlier observations[4] of Kanaoka and Coyle made in their studies of photochemical reactions of N-substituted phthalimides *via* SET-deprotonation or hydrogen atom abstraction routes[5]. The photocyclization reactions of phthalimides of general structure 8 studied by Kanaoka and Coyle suffered from both low regioselectivities in the generation of intermediate carbon radicals and low product yields.

Based on our previous investigations of SET photochemistry using α-silyl-n-electron donors[1,3] we felt that photocyclizations of the silicone substituted phthalimides 6 could be highly efficient and regioselective and, as a result, might be useful for construction of medium and large ring heterocyclic compounds such as 7. In preliminary investigations we have explored photocyclization reactions of N-(trimethyl-
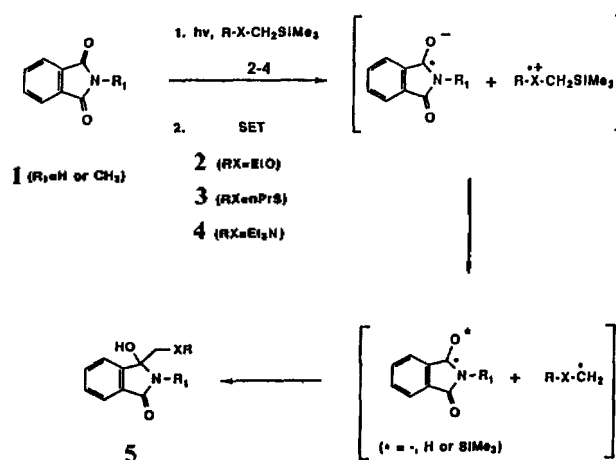
Scheme I

silylmethoxyalkyl) phthalimides (6, X=O) to test this proposal.
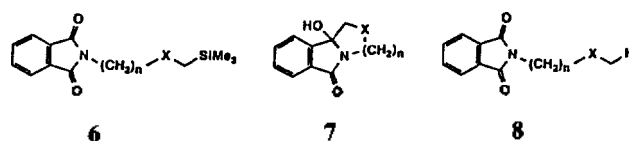
We now report preparative aspects of photocyclization reactions of N-(trimethylsilylmethoxyalkyl) phthalimides 6a-e (6 : X=O, n=2, 3, 4, 5 and 8) and new mechanistic observations in reactions involving singlet SET, triplet hydrogen atom abstraction and triplet silyl group abstraction processes.

Results

Preparation of N-(Trimethylsilylmethoxyalkyl) Ph-

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Table 1. Photochemical Reactions of N-(Trimethylsilylmethoxyalkyl) Phthalimides

Phthalimides	Concentration (mM)	Solvent	Reaction time(h)	% Conversion	Products (yields)[a]
6a	13.1	methanol	2	100	13a (98%)
6a	13.1	acetone	2	62	13a (32%), 14 (16%), 15 (19%)
6b	3.6	methanol	3	100	13b (99%)
6c	16.4	methanol	4	100	13c (83%), 16 (3%), 17 (2%)
6d	7.8	methanol	2	100	13d (83%), 19 (7%)
6e	8.3	methanol	4	45	21 (78%), 18 (16%), 20 (3%)

[a]Yields are based on consumed phthalimides 6a-e.
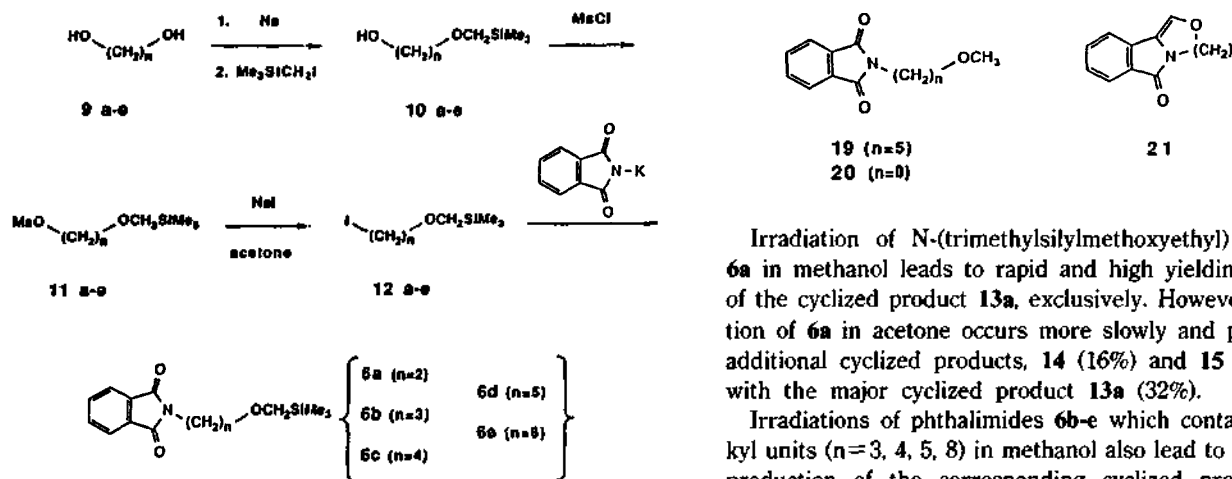
Scheme II

thalimides. For these photochemical studies five N-(tri-methylsilylmethoxyalkyl) phthalimide derivatives, 6a-e, were selected and prepared in modest to good yields starting with the corresponding alkanediols 9a-e by use of the reaction sequences outlined in Scheme II (see Experimental Section).

Photocyclizations of N-(Trimethylsilylmethoxyalkyl) Phthalimides. Phtocyclization reactions of N-(trimethylsilylmethoxyalkyl) phthalimides 6a-e were explored. Preparative photocyclization reactions were performed by irradiation of methanol or acetone solutions of phthalimides (7.8-18.1 mM) by using Pyrex glass filtered-light (λ>290 nm) and products were separated by silica gel chromatography (see Experimental Section). Product distributions and yields along with reaction conditions employed given in Table 1.
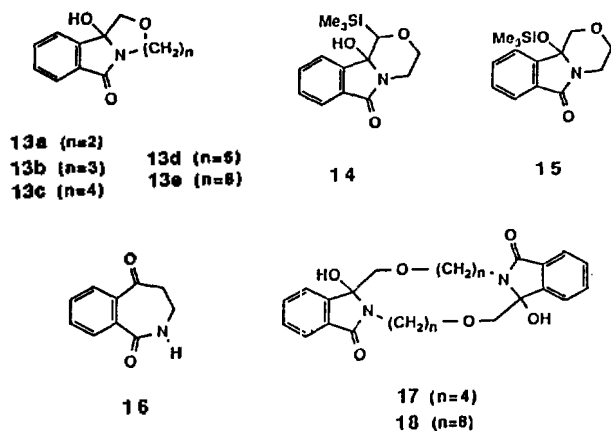
Irradiation of N-(trimethylsilylmethoxyethyl) phthalimide 6a in methanol leads to rapid and high yielding production of the cyclized product 13a, exclusively. However photoreaction of 6a in acetone occurs more slowly and produces two additional cyclized products, 14 (16%) and 15 (19%), along with the major cyclized product 13a (32%).

Irradiations of phthalimides 6b-e which contain longer alkyl units (n=3, 4, 5, 8) in methanol also lead to high yielding production of the corresponding cyclized products 13b-d. However in the case of phthalimide 6e, 21 is generated instead of the expected cyclized product 13e. The internal enol ether 21 is believed to be formed by dehydration of 13e. In photoreactions of 6c-e, the minor products 16, 17, 18, 19 and 20 are also observed.

Structural assignments to the photoproducts were made on the basis of spectroscopic data (see Experimental Section). IR spectra of major cyclized products 13a-d show characteristic absorption bands for the hydroxy groups at 3100-3600 cm^{-1} and imide carbonyl group at 1650-1700 cm^{-1}. Their ^{13}C-NMR spectra clearly show resonances which correspond to quarternary carbon C-3 at 84.3-90.3 ppm and methylene carbon α to oxygen atom at 72.5-76.9 ppm. Along with disappearance of resonances for trimethylsilyl group in the ^{1}H-NMR and ^{13}C-NMR spectra of the starting materials, the spectral features of the cyclization products are consistent with carbon-carbon bond formation between the phthalimide carbonyl carbons and carbons α to oxygen formerly occupied by the silicon substituents. In contrast, ^{13}C-NMR spectra of product 21 has resonances at 116.7 and 117.0 ppm for the corresponding olefinic carbons instead of resonances at ca. 84-91 ppm for quarternary carbon (C-3) and at ca. 72-77 ppm for methylene carbon α to oxygen which are observed in the spectra of 13a-d. The ^{1}H-NMR spectrum of 21 also contains a singlet for its olefinic hydrogen at 6.38 ppm. The ^{13}C-NMR spectrum of cyclized product 14 contains characteristic resonances at 1.08 ppm for the trimethylsilyl group, 81.7 ppm for the methine carbon with the α-silyl substituent and 88.6 ppm for the quarternary carbon C-3. These observations show that photocyclization has taken place between the phthalimide carbonyl and TMS substituted carbons. The ^{13}C-

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NMR spectrum of product **15** also contains resonance at 0.99 ppm for the trimethylsilyl group in addition to resonances at 76.0 ppm for the methylene carbon α to oxygen and resonance at 85.6 ppm for quarternary carbon C-3 all of which are consistent with the assigned structure. For structural assignments of dimeric cyclized products **17** and **18**, high resolution mass spectroscopic data are very informative; for example the m/z 466.2104 and 578.3408 molecular ions correspond to substances with molecular formulae of $C_{26}H_{30}N_2O_6$ and $C_{34}H_{46}N_2O_6$, respectively. In addition to data described above, all of the other spectroscopic properties (^1H-NMR, ^{13}C-NMR, IR and high resolution mass spectra) are in complete accord with the structures assigned.

Oxygen Quenching of Photoreaction of N-(Trimethylsilylmethoxyethyl) Phthalimide in Acetone. As described above, noticeable changes occur in the product distribution and reaction rate when acetone is used as solvent for photoreaction of N-(trimethylsilylmethoxyethyl) phthalimide **6a**. Compared with photoreaction of **6a** in methanol, two silicon containing cyclized products **14** and **15** are generated along with product **13a** and reaction rate become slower when irradiation is performed on solutions of **6a**. These observations suggest that excited state of phthalimide responsible for formation of products **14** and **15** is a triplet formed by energy transfer from triplet acetone while that for cyclized product **13a** is singlet arising by direct excitation. In order to obtain further information about the reactive excited states of **6a**, an oxygen quenching experiment was performed. Oxygen was found not to affect the efficiency of formation of **13a** and the conversion rate in reaction of **6a** in methanol while oxygen results in almost no quenching of the formation of **13a** and complete quenching of the production of **14** and **15** for photoreaction of **6a** in acetone. These results support the proposal made above about the phthalimide excited states responsible for formation of products **13a**, **14** and **15**.

Discussion

The observations presented above show that N-(trimethylsilylmethoxyalkyl) phthalimides undergo photocyclizations in methanol with high degrees of chemoselectivity and regioselectivity to generate cyclized products of various ring sizes (six to twelve-membered) in which the phthalimide carbonyl carbon is bonded to the α-oxygen carbon in place of the trimethylsilyl group. In the case of N-(trimethylsilylmethoxyoctyl) phthalimide (**6e**), the initially formed photocyclization product **13e** undergo water elimination to yield olefinic product **21** in a secondary ground state reaction.[3]

Results obtained in this study and those made in our earlier investigation of intermolecular photoinduced SET reactions of phthalimides **1** with the α-silyl-n-electron donors **2-4** in CH_3OH or CH_3CN suggest[3] that photocyclizations leading to **13a-d** and **21** follow the excited singlet state SET mechanisms (shown in Scheme III). Accordingly, intramolecular SET in singlet excited phthalimides results in generation of radical ion intermediates **22a-e** which undergo exclusive desilylation leading to biradicals **23a-e**. Unlike the case of cyclohexenone α-silylamine systems probed previously,[2] proton transfer between the two ion radical centers of **22a-e** is not favorable due to low basicity of the phthalimide radical
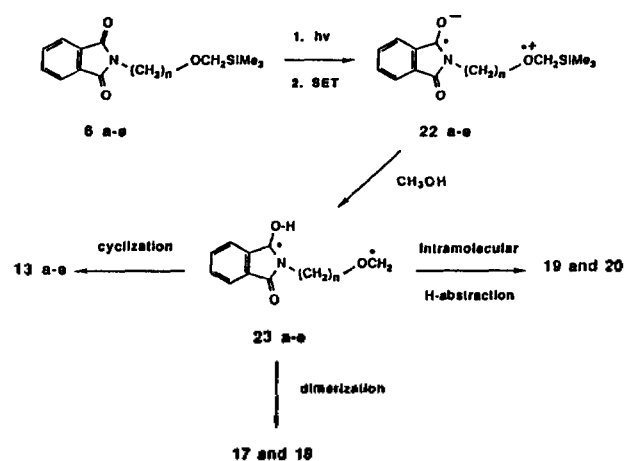
Scheme III
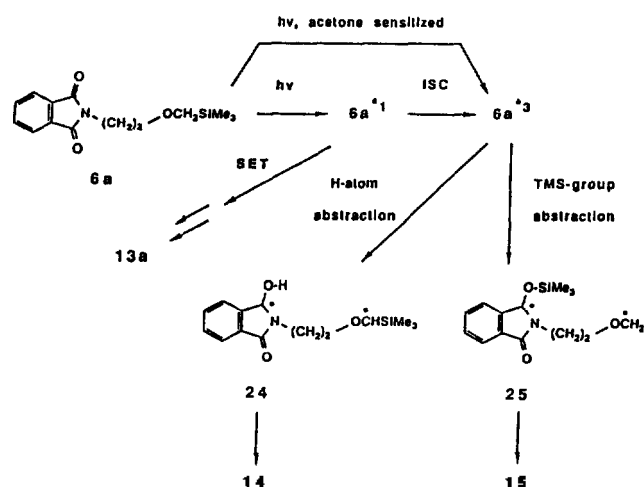
Scheme IV

anion.[6] Instead, preferential desilylation either with solvent methanol as a nucleophile or liberating a short-lived silenium ion dominates in the phthalimide systems.[7] Biradicals **24a-e** undergo cyclization to produce mainly cyclized products **13a-e** or dimerizations to give products **17** and **18**. The formation of open chain desilylated products **19** and **20** is interesting in that these are thought to be generated via intramolecular hydrogen atom abstraction of oxymethyl radical from hydroxy hydrogen in **23a-e**. The generation of benzazepinone lactam **16** in photoreactions of N-(trimethylsilylmethoxybutyl) phthalimide (**6c**) has a precedent in photocyclization of N-butylphthalimide and is believed occur via two-fold Norrish type II reactions (*i.e.*, sequential Type II cyclization and Type II elimination pathways).[8]

Further observations made in studies of the photoreaction of N-(trimethylsilylmethoxyethyl) phthalimide (**6a**) suggest that phthalimide singlet excited states follow SET-desilylation pathway to produce cyclized product whereas triplet reactions involve hydrogen atom or trimethylsilyl group abstraction routes to form products **14** and **15** (Scheme IV).

In theory, the triplet excited state of phthalimide **6a** can be generated by acetone sensitization or via intersystem crossing from an initially populated singlet excited state phthalimide. The carbonyl oxy-radical like triplet excited state

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of the phthalimide can undergo hydrogen atom abstraction to produce biradical **24** or trimethylsilyl group abstraction to form biradical **25** leading to the production of **14** or **15**, respectively. As the product yields demonstrate, trimethylsily group abstraction by triplet carbonyl predominates over hydrogen abstraction (*eg.*, **14** : **15** = 16% : 19%). Although greater steric interference is expected to be present in the transition state for abstraction of the more bulky trimethylsilyl group, a much more favorable combination of bond dissociation energies (C-Si, 318 KJ/mol; O-Si, 531 KJ/mol; C-H, 420 KJ/mol; and O-H, 462 KJ/mol)[9] could make this process competitive with hydrogen atom abstraction. Hydrogen abstraction leading to the production of product **14** follows an eightmembered transition state rather than the typically more favorable six-membered transition state perhaps owing to the oxygen[10] and silyl group[11] effect on weakening the C-H bonds.

Summary

This study demonstrates that photoreactions of N-(trimethylsilylmethoxyalkyl) phthalimides lead to high yielding productions of cyclized products with high degrees of chemoselectively and regioselectivity. Thus, the reactions appear to hold synthetic potential for the construction of medium and large ring heterocyclic compounds. We are continuing to explore the photocyclization reactions of phthalimides with α-silylaminoalkyl and α-silylthioalkyl chains in efforts to develop new methods for heterocycle synthesis and to probe interesting mechanistic issues associated with trimethylsilyl group abstraction in triplet carbonyl excited states.

Experimental Section

General Procedures. ¹H-NMR and ¹³C-NMR spectra were recorded by using Varian EM-360, Bruker WP-200 or AF-200 spectrometers. Chemical shifts are reported in parts per million relative to Me₄Si as an internal standard. For compounds containing Me₃Si groups, CHCl₃ was used as an internal standard. ¹³C-NMR resonances were assigned by use of the INEPT technique to determine the numbers of attached hydrogens. IR spectra were recorded on a Matton IR-10410E spectrometer. Preparative photochemical reactions were conducted with an apparatus consisting of a 450 W Hanovia medium pressure mercury vapor lamp (Ace) surrounded by a Pyrex filter in a water-cooled quartz immersion well surrounded by the solution being irradiated. The photolysis solutions were purged with nitrogen both before and during irradiations, and solvent used for photolysis was removed under reduced pressure after reactions. Preparative tlc was performed on 20×20 cm plate coated with E-Merck silica gel PF₂₅₄.

Low resolution mass spectral analyses were performed at 70 eV on Hitachi RMU-6 mass spectrometer and high resolution mass spectral analyses were performed at 70 eV on Hitachi VG-7070 mass spectrometer. Ammonia was used as the reagent gas for CI mass spectrometric measurements. Drying of organic layers obtained by work-up of reaction mixtures was performed by standing over anhydrous sodium sulfate. Molecular distillation was performed with a kugelrohr apparatus *in vacuo.*

Preparation of trimethylsilylmethoxyalcohols 10a·

e. To the corresponding diol such as ethylene glycol(12.4 g, 0.2 mol), 1,3-propanediol (19.0 g, 0.25 mol), 1,4-butanediol (12.6 g, 0.14 mol), 1,5-pentanediol (14.6 g, 0.14 mol) or 1,8-octanediol (13.7 g, 0.094 mol), was added Na metal (1.1 g, 0.048 mol) portionwise over a 20 min period with stirring. To this solution was added trimethylsilylmethyl iodide (10 g, 0.046 mol)dropwise and the resulting mixture was heated for 30 h at 80℃. The mixture was cooled to room temperature and extracted with n-pentane. The pentane solution was washed with water, dried and concentrated in vacuo to afford a residue. Moleular distillation (0.5 torr, 50-60℃) of the residue gave the corresponding trimethylsilylmethoxyalcohol. Yields of products **10a-e** and their spectral data are as follows. For trimethylsilylmethoxyethanol (**10a**)[12]; 6.28 g (91%). For 3-trimethylsilylmethoxy propanol (**10b**)[12]; 5.2 g (70%). For 4-trimethylsilylmethoxybutanol (**10c**); 5.58 g (68%); ¹H-NMR (CDCl₃) 0.00 (s, 9H, Si(CH₃)₃), 1.2-1.9 (m, 4H, -OCH₂-CH₂CH₂CH₂OH), 3.0 (s, 2H, -OCH₂Si), 3.2-3.8 (m, 5H, -OCH₂-CH₂CH₂CH₂OH); IR (KBr) 3200-3600 cm⁻¹ (OH stretching); mass spec (CI), m/z (rel, intensity) 177 (M+H⁺, 100), 159 (M⁺-OH, 4), 141 (M⁺-CH₂OH, 1), 130(1), 119(2), 105(1), 91(1); high resolution mass spec (CI), m/z 177.1308 (M+H⁻, C₈H₂₁O₂Si requires 177.1311). For 5-trimethylsilylmethoxypentanol (**10d**); 5.23 g (59%); ¹H-NMR(CDCl₃) 0.1 (s, 9H, Si(CH₃)₃), 1.0-2.0 (m, 6H, -OCH₂CH₂CH₂CH₂CH₂OH), 3.0 (s, 2H, -OCH₂Si), 3.1-3.8 (m, 5H, -OCH₂CH₂CH₂CH₂OH); IR (KBr) 3200-3600 cm⁻¹(OH stretching); mass spec (CI) m/z (rel. intensity) 191 (M+H⁺, 100), 173 (M⁺-OH, 5), 159 (M⁺-CH₂OH, 5), 159 (M⁺-CH₂CH₂OH, 2), 105 (54), 87 (12), 69(4); high resolution mass spec (CI) m/z 191.1451 (M+H⁺, C₉H₂₃O₂Si requires 191.1467). For 8-1150 (symmetric S=O stretching), 1100 cm⁻¹; mass spec(CI) m/z (rel. intensity) 269 (M+H⁺, 100), 183 (28), 168 (2), 166 (16), 153 (4); high resolution mass spec m/z 269.1245 (M+H⁺, C₁₀H₂₅O₄SiS requires 269.1243). For trimethylsilylmethoxyoctyl mesylate (**11e**); 4.8 g (56%); ¹H-NMR (CDCl₃) 0.01 (s, 9H, Si(CH₃)₃), 1.23-1.75 (m, 12H, -OCH₂(CH₂)₆CH₂O-), 2.97 (s, 3H, CH₃), 3.05 (s, 2H, -OCH₂Si), 3.34 (t, 2H, J=5.9 Hz, -OCH₂(CH₂)₆CH₂O-), 4.19 (t, 2H, J= 6.5 Hz, -OCH₂(CH₂)₆CH₂O-); IR (KBr) 2930, 2920, 1350 (asymmetric S=O stretchning), 1250, 1180 (symmetric S=O stretching), 1100 cm⁻¹; mass spec(CI) m/z (rel. intensity) 311 (M+H⁻, 100), 310 (M⁺, 3), 309 (M⁺), 241 (13), 240 (13), 239 (99), 237 (14); high resolution mass spec (CI) m/z 311.1712 (M+H⁺), C₁₃H₃₁O₄SiS requires 311.1712).

Preparation of Trimethylsilylmethoxyalkyl Iodides 12a-e. Solutions of trimethylsilylmethoxyalkyl mesylate (**11a**, 3.0 g, 13 mmol; **11b**, 3.1 g, 13 mmol; **11c**, 3.3 g, 13 mmol; **11d**, 3.5 g, 13 mmol; **11e**, 4.0 g, 13 mmol) in acetone (40 ml) were refluxed for 18h and cooled to room temperature. Each mixture was extracted with pentane (300 ml). The pentane solution was washed with water, dried, and concentrated to give a residue. Molecular distillation of each (0.4 torr 90-100℃) yielded the trimethylsilylmethoxyakyl iodide. Yields of products **11a-e** and their spectral data are as follows. For trimethylsilylmethoxyethyl iodide (**12a**);[12] 3.24 g (95%). For trimethylsilylmethoxypropyl iodide (**12b**);[12] 2.67 g (76%). For trimethylsilylmethoxybuthyl iodide (**12c**); 3.24 g (83%); ¹H-NMR (CDCl₃) 0.0 (s, 9H, Si(CH₃)₃), 1.3-2.2 (m, 4H, -OCH₂(CH₂)₂-CH₂-), 3.0 (s, 2H, -OCH₂Si), 3.2-3.8 (m, 4H, -OCH₂-(CH₂)₂-CH₂I); IR (KBr) 2950, 2850, 1250, 1100 cm⁻¹; mass spec (CI) m/z (rel intensity) 287 (M+H⁺, 100), 263 (4) 183 (81), 177

(88), 159 (34), 141 (5), 119 (8); high resolution mass spec (CI) m/z 287.0303 (M+H$^+$, $C_8H_{20}OISi$ requires 287.0328). For trimethylsilylmethoxypentyl iodide (12d); 2.54 g (65%); ^{1}H-NMR (CDCl$_3$) 0.02 (s, 9H, Si(CH$_3$)$_3$), 1.39-1.47 (m, 2H), 1.50-1.57 (m, 2H), 1.83 (quint, 2H), 3.05 (s, 2H, -OCH$_2$Si), 3.17 (t, 2H), 3.36 (t, 2H); IR (KBr) 2950, 2840, 1250, 1100 cm^{-1}; ^{13}C-NMR (CDCl$_3$)-3.0 (Si(CH$_3$)$_3$), 6.9 (CH$_2$I), 27.3 (CH$_2$), 28.4 (CH$_2$), 33.4 (CH$_2$), 64.8 (OCH$_2$Si), 74.9 (-CH$_2$OCH$_2$Si). For trimethylsilylmethoxyoctyl iodide (12e); 2.77 g (63%); ^{1}H-NMR (CDCl$_3$) 0.02 (s, 9H, Si(CH$_3$)$_3$), 1.23-1.86 (m, 12H, -OCH$_2$(CH$_2$)$_6$ CH$_2$I), 3.05 (s, 2H, CH$_2$Si), 3.17 (t, 2H, J=7.0 Hz, CH$_2$I), 3.35 (t, 2H, J=6.5 Hz, -CH$_2$O-CH$_2$Si); IR (KBr) 2950, 2850, 1250, 1100 cm^{-1}; mass spec(CI) m/z (rel. intensity) 343 (M$^+$, 14), 319 (3), 239 (11), 199 (3), 183 (15), 169 (11), 155 (5), 133 (5); high resolution mass spec (CI) m/z 343.0933 (M+H$^+$, $C_{12}H_{28}OSi$ requires 343.0954)

Preparation of N-(Trimethylsilylmethoxyalkyl) Phthalimides 6a-e. Solutions of the trimethylsilylmethoxyalkyl iodide (12a, 2.0 g, 7.2 mmol; 12b, 21.0 g, 7.2 mmol; 12c, 2.2 g, 7.2 mmol; 12d, 2.3 g, 7.2 mmol; 12e, 2.6 g, 7.2 mmol) and potassium phthalimide (1.4 g, 7.55 mmol) in DMF (20 m*l*) were heated for 2 h at 80-90℃. After removal of DMF under reduced pressure in each cace, the residue was dissolved in CH$_2$Cl$_2$ and the solution was filtered. Concentration of the solution *in vacuo* yielded N-(trimethylsilylmethoxyalkyl) phthalimide. Yields of products 6a-e and their spectral data are as follows. For N-(trimethylsilylmethoxyethyl) phthalimide (6a); 2.06 g (96%); ^{1}H-NMR (CDCl$_3$) −0.1 (s, 9H, Si(CH$_3$)$_3$), 3.0 (s, 2H, -CH$_2$Si), 3.4-3.9 (m, 4H, NCH$_2$CH$_2$O-), 7.4-7.8 (m, 4H, aromatic); IR (KBr) 1720 cm^{-1} (C=O stretching); ^{13}C-NMR (CDCl$_3$) −3.28 (Si(CH$_3$)$_3$), 37.0 (NCH$_2$CH$_2$O-), 64.8 (OCH$_2$Si), 71.5 (CH$_2$OCH$_2$Si), 123.1 (CH, aromatic), 132.2 (C, aromatic), 133.8 (CH, aromatic), 168.2 (C=O); mass spec m/z (rel intensity) 277 (M$^+$, 2), 262 (10), 246 (23), 218 (15), 175 (5), 174 (42), 130 (24), 103 (25), 73 (100); high resolution mass spec m/z 277.1157 ($C_{14}H_{19}O_3$NSi requires 277.1134). For N-(trimethylsilylmethoxypropyl) phthalimide (6b); 2.13 g (95 %); ^{1}H-NMR (CDCl$_3$) −0.05 (s, 9H, Si(CH$_3$)$_3$), 1.88 (quintet, 2H, -CH$_2$CH$_2$CH$_2$O-), 3.02 (s, 2H, -OCH$_2$Si), 3.41 (t, 2H, NCH$_2$ CH$_2$CH$_2$O-), 3.72 (t, 2H, NCH$_2$CH$_2$CH$_2$O), 7.63-7.76 (m, 2H, aromatic), 7.78-7.81 (m, 2H, aromatic); IR (KBr) 1710 cm^{-1} (C=O stretching); ^{13}C-NMR (CDCl$_3$) −3.22 (Si(CH$_3$)$_3$), 28.5 (NCH$_2$CH$_2$CH$_2$O) 35.6 (NCH$_2$CH$_2$CH$_2$O), 64.6 (-OCH$_2$Si), 72.7 (NCH$_2$), 123.0 (CH, aromatic), 132.2 (C, aromatic), 133.8 (CH, aromatic); mass spec m/z (rel. intensity) 291 (M$^+$, 4), 276 (M$^+$-CH$_3$, 25), 261 (5), 232 (13), 188 (100), 160 (11), 143 (2); high resolution mass spec m/z 291.1301 ($C_{15}H_{21}O_3$NSi requires 291.1291). For N-(trimethylsilylmethoxybutyl) phthalimide (6c); 2.22 g (95%); ^{1}H-NMR (CDCl$_3$) 0.02 (s, 9H, Si(CH$_3$)$_3$), 1.51-1.74 (m, 4H, NCH$_2$CH$_2$CH$_2$CH$_2$O-), 3.02 (s, 2H, OCH$_2$Si), 3.36 (t, 2H, -CH$_2$OCH$_2$Si), 3.66 (t, 2H, J=6.8 Hz, NCH$_2$-), 7.23-7.68 (m, 2H, aromatic), 7.77-7.81 (m, 2H, aromatic); IR (KBr) 1730 cm^{-1} (C=O stretching); ^{13}C-NMR (CDCl$_3$) −3.11 (Si(CH$_3$)$_3$), 25.4 (-CH$_2$(CH$_2$)$_2$CH$_2$-), 26.8 (-CH$_2$(CH$_2$)$_2$CH$_2$-), 37.8 (NCH$_2$(CH$_2$)$_2$CH$_2$O), 64.8 (OCH$_2$Si), 74.5 (NCH$_2$-), 123.1 (CH, aromatic), 132.1 (C, aromatic), 133.8 (CH, aromatic), 168.3 (C=O); mass spec (CI) m/z (rel. intensity) 307 (M+H$^+$, 4), 290 (29), 246 (14), 232 (100), 218 (71), 186 (5), 160 (43), 148 (7), 130 (13); high resolution mass spec (CI) m/z 306.1521 (M+H$^+$, $C_{16}H_{24}O_3$NSi, requires 306, 1525). For N-(trimethylsilylmethoxypentyl) phthalimide (6d); 2.29 g (94%); ^{1}H-NMR

(CDCl$_3$) 0.04 (s, 9H, Si(CH$_3$)$_3$), 1.20-1.72 (m, 6H, NCH$_2$(CH$_2$)$_3$ CH$_2$O-), 3.00 (s, 2H, -OCH$_2$Si), 3.32 (t, 2H, J=6.2 Hz, -CH$_2$ OCH$_2$Si), 3.63 (t, J=14.4 Hz, 2H, NCH$_2$-), 7.61-7.81 (m, 4H, aromatic); IR (KBr) 1720 cm^{-1} (C=O stretching); ^{13}C-NMR (CDCl$_3$) −3.1 (Si(CH$_3$)$_3$), 23.4 (CH$_2$), 28.3 (CH$_2$), 29.0 (CH$_2$), 37.9 (CH$_2$OCH$_2$Si), 64.6 (OCH$_2$Si), 74.8 (NCH$_2$-), 123.1 (CH, aromatic), 132.2 (C, aromatic), 133.7 (CH, aromatic), 168.3 (C=O); mass spec m/z (rel.intensity) 319 (M$^+$, 3), 305 (11), 304 (47), 232 (14), 218 (10), 216 (21), 215 (12), 186 (11), 161 (14), 160 (76), 151 (20), 148 (32); high resolution mass spec m/z 319.1624 ($C_{17}H_{25}O_3$NSi requires 319.1603). For N-(trimethylsilylmethoxyoctyl) phthalimide (6e); 2.60 g (95%); ^{1}H-NMR (CDCl$_3$) −0.01 (s, 9H, Si(CH$_3$)$_3$), 1.21-1.66 (m, 12H, NCH$_2$(CH$_2$)$_6$CH$_2$O-), 3.03 (s, 2H, OCH$_2$Si), 3.32 (t, 2H, J=6.4 Hz, -CH$_2$OCH$_2$Si), 3.63 (t, 2H, J=7.1 Hz, NCH$_2$-), 7.64-7.68 (m, 2H, aromatic); IR (KBr) 1720 cm^{-1} (C=O stretching); ^{13}C-NMR (CDCl$_3$) −3.1 (Si(CH$_3$)$_3$), 26.0 (CH$_2$), 26.8 (CH$_2$), 28.5 (CH$_2$), 29.1 (CH$_2$), 29.3 (CH$_2$), 29.4 (CH$_2$), 38.0 (-CH$_2$OCH$_2$Si), 64.6 (OCH$_2$Si), 75.2 (NCH$_2$-), 123.1 (CH, aromatic), 132.2 (C, aromatic), 133.7 (CH, aromatic), 168.3 (C=O); mass spec m/z (rel intenisty) 361 (M$^+$, 7), 331 (20), 302 (4), 298 (5), 260 (3), 232 (10), 206 (6), 160 (100), 148 (7); high resolution mass spec m/z 361.2094 ($C_{20}H_{31}O_3$NSi requires 361.2073).

Irradiation of N-(Trimethylsilylmethoxyethyl) Phthalimide (6a) in Methanol. A solution of N-(trimethylsilylmethoxyethyl) phthalimide (6a) (1.0 g, 6.61 mmol) in CH$_3$OH (200 m*l*) was irradiated for 2 h resulting in almost complete conversion. After removal of CH$_3$OH, the residue was subjected to preparative tlc (CH$_2$Cl$_2$: AcOEt=2 : 1) to yield 725 mg (98%) of cyclized product 13a.; mp 128-130℃. Spectral data for 13a: ^{1}H-NMR (CDCl$_3$) 3.0-4.4 (m, 7H, HOC-CH$_2$ OCH$_2$CH$_2$N), 7.4-7.6 (br.s, 4H, aromatic); IR (KBr) 3100-3600 (OH stretching), 1650 cm^{-1} (C=O stretching); ^{13}C-NMR (CDCl$_3$) 36.8 (NCH$_2$CH$_2$O), 66.3 (NCH$_2$CH$_2$O), 74.2 (HOCCH$_2$ O), 84.4 (quarternary C-3), 122.1 (CH, aromatic), 123.6 (CH, aromatic), 130.0 (CH, aromatic) 131.0 (C, aromatic), 132.3 (CH, aromatic), 144.4 (C, aromatic), 165.3 (C=O); mass spec., m/z 9rel intensity) 205 (M$^+$, 47) 187 (M$^+$-H$_2$O, 9), 175 (34), 173 (33), 160 (100), 146 (7), 130 (17), 105 (32); high resolution mass spec m/z 205.0735 ($C_{11}H_{11}O_3$N requires 205.0739).

Irradiation of N-(Trimethylsilylmethoxyethyl) Phthalimide (6a) in Acetone. A solution of N-(trimethylsilylmethoxyethyl) phthalimide (6a) (1.0 g, 3.61 mmol) in acetone (200 m*l*) was irradiated for 2h resulting in *ca.* 62% conversion. After similar work-up to the photolysis in methanol, 140 mg (32%) of product 13a, 100 mg (16%) of puoduct 14 (mp. 150-153℃) and 118 mg (19%) of product 15 were obtained. Spectral data for product 14: ^{1}H-NMR (CDCl$_3$) 0.20 (s, 9H, Si(CH$_3$)$_3$), 2.91 (s, 1H, OH), 3.21-3.51 (m, 2H, -OCH$_2$CH$_2$ N), 3.48 (s, 1H, methine), 3.97-4.17 (m, 2H, -OCH$_2$CH$_2$N), 7.44-7.78 (m, 4H, aromatic); IR (KBr) 3200-3600 (br. OH stretching), 1680 cm^{-1} (C=O stretching); ^{13}C-NMR (CDCl$_3$) −1.1 (Si(CH$_3$)$_3$), 37.4 (NCH$_2$CH$_2$O-), 68.5 (NCH$_2$CH$_2$O-), 81.7 (CHSi (CH$_3$)$_3$), 88.6 (quarternary C-3), 123.7 (CH, aromatic), 123.9 (CH, aromatic), 129.9 (CH, aromatic), 131.3 (CH, aromatic), 134.1 (C, aromatic), 144.5 (C, aromatic), 164.5 (C=O); mass spec m/z (rel. intensity) 277 (M$^-$, 26), 262 (M$^+$-CH3, 25), 247 (23), 246 (62), 218 (28), 187 (11), 175 (10), 174 (68), 173 (20), 161 (13), 160 (63), 151 (21), 130 (24), 105 (21), 103 (34); high resolution mass spec m/z 277.1134 ($C_{14}H_{19}O_3$NSi requires 277.1134). Spectral data for 15; ^{1}H-NMR (CDCl$_3$) −0.17

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(s, -Si(CH₃)₃), 3.08 (d, 1H, J = 11.3 Hz, diastereotopic SiOCC$\underline{H}_2$ O-), 3.26-3.41 (m, 2H, -OCH₂C$\underline{H}_2$N), 3.95-4.19 (m, 2H, -OC$\underline{H}_2$ CH₂N), 4.30 (d, 1H, J = 11.3 Hz, diastereotopic SiOCC$\underline{H}_2$O-); IR (KBr) 1710 cm⁻¹ (C=O stretching); ¹³C-NMR (CDCl₃) 0.99 (Si(CH₃)₃), 37.5 (N$\underline{C}$H₂CH₂O-), 66.8 (NCH₂$\underline{C}$H₂O-), 76.0 (C$\underline{C}$H₂ O-), 85.6 (C-3), 122.8 (CH, aromatic), 124.0 (CH, aromatic), 130.1 (CH, aromatic), 131.8 (C, aromatic), 132.0 (CH, aromatic), 145.0 (C, aromatic), 165.3 (C=O); mass spec m/z (rel. intensity) 277 (M⁺, 38), 262 (M⁺-CH₃, 11), 246 (100), 218 (41), 188 (13), 160 (12) 130 (42), 102 (31); high resolution mass spec m/z 277.1135 (C₁₄H₁₉O₃NSi requires 277.1134).

Oxygen Quenching of Photoreaction of N-(Trimethylsilylmethoxyethyl) Phthalimide (6a). Two solutions of N-(trimethylsilylmethoxyethyl) phthalimide (6a) (50 mg, 0.18 mmol) in CH₃OH (20 ml) were irradiated simultaneously in a Rayonet reactor with RUL-3000 lamps while purged with a stream of N₂ and the other with a stream of O₂. During irradiation, the two reaction mixtures were intermittently analyzed and compared by tlc (CH₂Cl₂ : AcOEt = 2 : 1) to examine their conversion rates and products formation. The photoreaction in methanol was observed not to be affected by O₂ and yielded proudct 13a with a similar rate to the photolysis under N₂ purging. O₂ and yielded proudct 13a with a similar rate to the photolysis under N₂ purging. Photolysis in acetone was affected by O₂ in which formation of products 14 and 15 was completely quenched while formation of 13a was not quenched.

Irradiation of N-(Trimethylsilylmethoxypropyl) Phthalimide (6b). A solution of N-(trimethylsilylmethoxypropyl) phthalimide (6b) (0.5 g, 1.72 mmol) in CH₃OH (200 ml) was irradiated for 3 h resulting almost complete conversion. After removal of CH₃OH, the residue was subjected to preparative tlc (CH₂Cl₂ : AcOEt = 2 : 1) to yield 370 mg (99%) of cyclized product 13b (mp 124-127°C). Spectral data for 13b: ¹H-NMR (CDCl₃) 1.72-1.93 (m, 2H, -OCH₂C$\underline{H}_2$CH₂N), 3.16-3.24 and 3.55-4.47 (m, 1H and m, 3H, -OC$\underline{H}_2$CH₂C$\underline{H}_2$N), 3.99 and 3.97 (two d, 2H, J = 13.0 Hz, diastereotopic -CC$\underline{H}_2$O), 4.47 (s, 1H, OH), 7.24-7.58 (m, 4H, aromatic); IR (KBr) 3100-3600 (br. OH stretching), 1700 cm⁻¹ (C=O stretching); ¹³C-NMR (CDCl₃) 29.0 (-OCH₂$\underline{C}$H₂CH₂N), 37.2 (NCH₂), 73.2 (-O$\underline{C}$H₂CH₂-), 76.5 (C-$\underline{C}$H₂O), 90.3 (C-3), 121.9 (CH, aromatic), 123.2 (CH, aromatic), 129.6 (CH, aromatic), 131.3 (C, aromatic), 132.5 (CH, aromatic), 145.4 (C, aromatic), 167.9 (C=O); mass spec (CI) m/z (rel. intensity) 220 (M+H⁺, 100), 202 (87), 187 (20), 161 (38), 148 (7), 133 (10), 117 (12), 102 (3); high resolution mass spec (CI) m/z 220.0979 (C₁₂H₁₄O₃N requires 220.0974).

Irradiation of N-(Trimethylsilylmethoxybutyl) Phthalimide (6c). A solution of N-(trimethylsilylmethoxypropyl) phthalimide (6c) (1.0 g, 3.28 mmol) in CH₃OH (200 ml) was irradiated for 4h resulting almost complete conversion. After removal of CH₃OH, the residue was subjected to preparative tlc (CH₂Cl₂ : AcOEt = 2 : 1) to yield 630 mg (83%) of 13c (mp. 122-125°C). 20 mg (3%) of 16⁸ and 35 mg (2%) of 17 (mp. 230-231°C). Spectral data for 13c: ¹H-NMR (CDCl₃) 1.46-1.87 (m, 4H, -OCH₂(C$\underline{H}_2$)₂CH₂N), 3.29-3.33 (m, 2H, NCH₂-), 3.43 and 4.04 (two d, 2H, J = 12.5 Hz, diastereotopic CC$\underline{H}_2$O-), 3.50-3.72 (m, 2H, -OC$\underline{H}_2$CH₂N), 4.92 (s, 1H, OH), 7.32-7.52 (m, 4H, aromatic); IR (KBr) 3100-3600 (OH stretching), 1670 cm⁻¹ (C=O stretching); ¹³C-NMR (CDCl₃) 25.3 (CH₂), 25.6 (CH₂), 37.7 (NCH₂), 72.3 (-O$\underline{C}$H₂CH₂N), 72.6 (C$\underline{C}$H₂O), 88.1

(C-3), 121.7 (CH, aromatic), 123.1 (CH, aromatic), 129.6 (CH, aromatic), 131.1 (C, aromatic), 132.1 (CH, aromatic), 145.1 (C, aromatic), 167.8 (C=O); mass spec m/z (rel. intensity) 233 (M⁺, 7), 216 (M⁺-OH, 7), 215 (M⁺-H₂O, 32), 201 (21), 187 (12), 186 (69), 174 (14), 173 (16), 161 (13), 160 (58), 130 (19), 117 (25), 113 (15), 105 (26); high resolution mass spec m/z 233.1052 (C₁₃H₁₅O₃N requires 233.1052). Spectral data for 17: ¹H-NMR (CD₃OD) 1.58-1.71 (m, 8H, 2-OCH₂(C$\underline{H}_2$)₂CH₂), 3.16-3.46 (m, 8H, 2-OC$\underline{H}_2$(CH₂)₂C$\underline{H}_2$N), 3.56-3.88 (m, 4H, 2 CC$\underline{H}_2$O-), 4.78 (s, 2H, 2OH), 7.38-7.61 (m, 8H, aromatic); IR (KBr) 3100-3600 (OH stretching), 1670 cm⁻¹ (C=O stretching); ¹³C-NMR (CD₃OD) 27.6 (CH₂), 27.9 (CH₂), 28.0 (CH₂), 28.8 (CH₂), 39.4 (NCH₂)-, 39.8 (NCH₂-), 72.7 (-O$\underline{C}$H₂CH₂-), 73.0 (-O$\underline{C}$H₂CH₂-), 73.2 (C$\underline{C}$H₂O), 73.5 (C$\underline{C}$H₂O), 90.6 (C-3), 90.8 (C-3'), 122.8 (CH, aromatic), 122.9 (CH, aromatic), 123.6 (CH, aromatic), 130.6 (CH, aromatic), 130.7 (CH, aromatic), 133.0 (C, aromatic), 133.4 (CH, aromatic), 148.0 (C, aromatic), 170.0 (C=O); mass spec m/z (rel. intensity) 467 (M+H⁺, 5), 449 (35), 430 (96), 234 (26), 216 (100), 200 (63), 186 (53), 174 (35), 160 (47), 146 (19), 132 (20), 117 (21); high resolution mass spec m/z 466.2104 (C₂₆H₃₀O₆N₂ requires 466.2104).

Irradiation of N-(Trimethylsilylmethoxypentyl) phthalimide (6d). A solution of N-(trimethylsilylmethoxypropyl) phthalimide (6d) (0.5 g, 1.57 mmol) in CH₃OH (200 ml) was irradiated for 2 h resulting almost complete conversion. After removal of CH₃OH, the residue was subjected to preparative tlc (CH₂Cl₂ : AcOEt = 2 : 1) to yield 320 mg (83%) of 13d and 30 mg (8%) of 19. Spectral data for 13d: ¹H-NMR (CDCl₃) 1.50-1.69 (br. s, 6H, -OCH₂(C$\underline{H}_2$)₃CH₂N), 3.35-3.53 (m, 2H, NCH₂-), 3.60 and 4.23 (two d, 2H, J = 11.1 Hz, diastereotopic CCH₂O), 3.75-3.88 (m, 2H, -OC$\underline{H}_2$CH₂), 7.40-7.69 (m, 4H, aromatic); IR (KBr) 3100-3500 (OH stretching), 1660 cm⁻¹ (C=O stretching); ¹³C-NMR (CDCl₃) 21.8 (CH₂), 27.1 (CH₂), 27.8 (CH₂), 38.5 (NCH₂-), 72.5 (O$\underline{C}$H₂CH₂-), 73.8 (C$\underline{C}$H₂O-), 89.3 (C-3), 121.8 (CH, aromatic), 123.2 (CH, aromatic), 129.9 (CH, aromatic), 131.8 (C, aromatic), 132.0 (CH, aromatic), 144.7 (C, aromatic), 168.6 (C=O); mass spec m/z (rel. intensity) 247 (M⁺, 25), 232 (M⁺-CH₃, 10), 215 (42), 200 (12), 175 (33), 160 (100), 148 (44), 130 (43), 105 (43), 102 (18); high resolution mass spec m/z 247.1219 (C₁₄H₁₇O₃N requires 247.1208). Spectral data for 19: ¹H-NMR (CDCl₃) 1.28-1.74 (m, 6H, -OCH₂(C$\underline{H}_2$)₃CH₂N), 3.28 (s, 3H, CH₃), 3.30 (t, 2H, J = 6.4 Hz, NCH₂-), 3.65 (t, 2H, J = 7.2 Hz, -OC$\underline{H}_2$CH₂-), 7.65-7.83 (m, 4H, aromatic); IR (KBr) 1710 cm⁻¹ (C=O stretching); ¹³C-NMR (CDCl₃) 23.3 (CH₂), 28.4 (CH₂), 29.1 (CH₂), 37.9 (NCH₂-), 58.5 (CH₃), 72.5 (-O$\underline{C}$H₂CH₂-), 123.1 (CH, aromatic), 132.2 (C, aromatic), 133.8 (CH, aromatic), 168.4 (C =O); mass spec m/z (rel. intensity) 247 (M⁺, 17), 232 (M⁺ -CH₃), 215 (52), 186 (22), 160 (100), 148 (23), 130 (12), 104 (4); high resolution mass spec m/z 247.1218 (C₁₄H₁₇O₃N requires 247.1208).

Irradiation of N-(Trimethylsilylmethoxybutyl) Phthalimide (6e). A solution of N-(trimethylsilylmethoxypropyl) phthalimide (6e) (0.6 g, 1.66 mmol) in CH₃OH (200 ml) was irradiated for 4 h resulting ca. 45% conversion. After removal of CH₃OH, the residue was subjected to preparative tlc (CH₂Cl₂ : AcOEt = 2 : 1) to yield 148 mg (78%) of 21 (mp. 134-136°C), 34 mg (16%) of 18 and 12 mg (3%) of 20. Spectral data for 21: ¹H-NMR (CDCl₃) 1.00-1.80 (m, 12H, -OCH₂(C$\underline{H}_2$)₆ CH₂N), 3.03-3.92 (m, 4H, -OCH₂(CH₂)₆C$\underline{H}_2$N), 6.38 (1H, vinylic H), 7.07-7.66 (m, 4H, aromatic); IR (KBr) 1690 cm⁻¹ (C=O

stretching); ^{13}C-NMR (CDCl$_3$) 21.4 (CH$_2$), 24.0 (CH$_2$-), 24.1 (CH$_2$), 24.8 (CH$_2$) 25.5 (CH$_2$), 26.6 (CH$_2$), 39.7 (NCH$_2$), 75.5 (-OCH$_2$CH$_2$-), 116.7 (vinylic C), 117.0 (vinylic CH), 123.2 (CH, aromatic), 126.8 (CH, aromatic), 127.9 (C, aromatic), 129.2 (CH, aromatic), 130.7 (CH, aromatic), 136.6 (C, aromatic), 166.3 (C=O); mass spec (CI) m/z (rel. intensity) 272 (M+ H$^+$, 51), 260 (4), 259 (2), 258 (6), 257 (3), 233 (6), 257 (3), 233 (3), 176 (51), 148 (15), 123 (8); high resolution mass spec m/z 271.1572 (C$_{17}$H$_{21}$O$_2$N requires 271.1572). Spectral data for **18**; ^{1}H-NMR (CD$_3$OD) 1.15-1.85 (m, 24H, 2-OCH$_2$- (CH$_2$)$_6$CH$_2$N), 3.20-3.83 (m, 12H, 2-CH$_2$OCH$_2$(CH$_2$)$_6$CH$_2$N), 7.38-7.84 (m, 8H, aromatic); IR (KBr) 3100-3600 (OH stretching), 1690 cm^{-1} (C=O stretching); ^{13}C-NMR (CD$_3$OD) 21.1 (CH$_2$), 21.3 (CH$_2$), 22.7 (CH$_2$), 22.9 (CH$_2$), 24.2 (CH$_2$), 25.6 (CH$_2$), 26.1 (CH$_2$), 26.7 (CH$_2$), 28.6 (CH$_2$), 29.1 (CH$_2$), 29.3 (CH$_2$), 29.7 (CH$_2$), 37.9 (NCH$_2$-), 38.1 (NCH$_2$-), 66.0 (CH$_2$), 67.9 (CH$_2$), 69.2 (-OCH$_2$CH$_2$), 73.5 (-OCH$_2$CH$_2$-), 93.5 (C-3), 96.4 (C-3'), 121.7 (CH, aromatic), 123.2 (CH, aromatic), 123.3 (CH, aromatic), 129.9 (CH, aromatic), 131.9 (CH, aromatic), 133.6 (CH, aromatic), 133.8 (CH, aromatic), 142.0 (C, aromatic), 168.8 (C=O); mass spec (CI) m/z (rel. intensity) 579 (M+H$^+$, 0.5), 413 (8), 395 (3), 344 (5), 304 (100), 288 (50), 276 (44), 258 (10), 233 (2); high resolution mass spec m/z 578.3408 (C$_{34}$H$_{46}$O$_6$N$_2$ requires 578.3356). Spectral data for **20**; ^{1}H-NMR (CDCl$_3$) 1.20-1.75 (m, 12H, -OCH$_2$(CH$_2$)$_6$CH$_2$N), 3.27 (s, 3H, CH$_3$), 3.30(t, 2H, J=6.5 Hz, NCH$_2$-), 3.62 (t, 2H, J=7.2 Hz, -OCH$_2$CH$_2$-), 7.63-7.82 (m, 4H, aromatic); IR (KBr) 1710 cm^{-1} (C=O stretching); ^{13}C-NMR (CDCl$_3$) 25.9 (CH$_2$), 26.7 (CH$_2$), 26.9 (CH$_2$), 28.5 (CH$_2$), 28.9 (CH$_2$), 29.0 (CH$_2$), 29.2 (CH$_2$), 29.5 (CH$_2$), 37.9 (NCH$_2$-), 58.4 (CH$_3$), 72.8 (-OCH$_2$ CH$_2$-), 123.0 (CH, aromatic), 132.1 (C, aromatic), 133.7 (CH, aromatic), 168.3 (C=O); mass spec m/z (rel. intensity) 289 (M$^+$, 81), 274 (M$^+$ -CH$_3$, 100) 257 (26), 240 (4), 160 (27), 148 (4), 130 (3); high resolution mass spec m/z 289.1685 (C$_{17}$H$_{23}$O$_3$N requires 289.1678).

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