

EFFICIENT AND REGIOSELECTIVE PHOTOCYCLIZATION REACTIONS  
OF *N*-[( $\omega$ -TRIMETHYLSILYLMETHOXY)POLYOXALKYL]PHTHALIMIDES  
TO AZACROWN ETHERS

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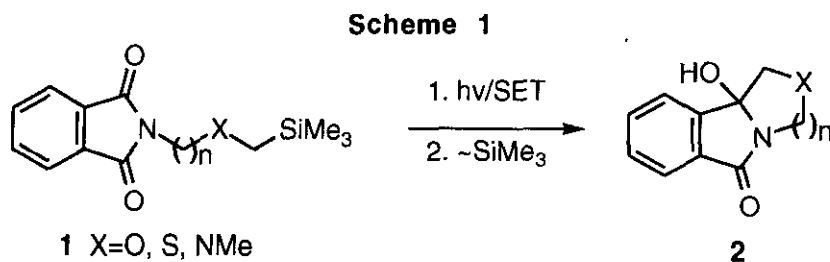
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**Abstract**—Single electron transfer induced photocyclization reactions of *N*-[( $\omega$ -trimethylsilylmethoxy)polyoxalkyl]phthalimides have been explored. Photocyclizations occur in methanol in modest to high yield to produce cyclized products in which phthalimide carbonyl carbon is bonded to the  $\omega$ -carbon of side chain in place of the trimethylsilyl group. The efficient, chemoselective, and regioselective cyclization reactions represent synthetically useful processes for construction of azacrown ethers of various sizes.

## INTRODUCTION

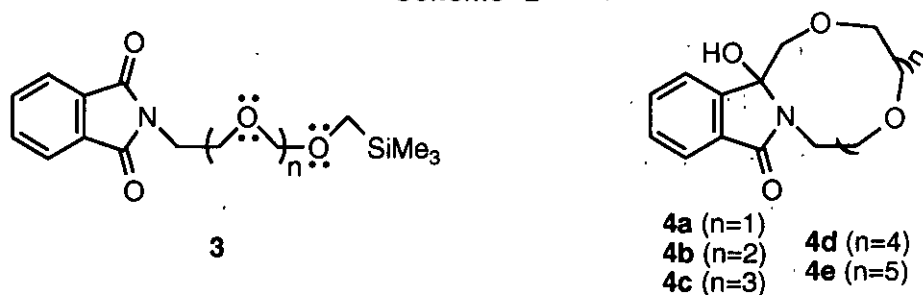
There have been recently a number of reports for photochemical cyclizations of *N*-substituted phthalimides leading to new heterocycles with either nitrogen and oxygen, nitrogen and sulfur or nitrogen and nitrogen atoms in the newly formed rings.<sup>1</sup> However the photochemical cyclization reactions utilized a mechanistic route involving intramolecular hydrogen abstraction by excited phthalimide carbonyls or sequential single electron transfer (SET)-deprotonation and suffered from both low regioselectivities in generation of the intermediate carbon radicals and low product yields. Our recent studies in the area of SET photochemistry using  $\alpha$ -silyl electron donors have shown that photoinduced sequential SET-desilylation

pathways are predominant over SET-deprotonation pathways and serve as the basis for efficient and highly regioselective methods for carbon centered radical generation.<sup>2-4</sup> For example, phthalimide- $\alpha$ -silyl-n-electron donor systems have been found to undergo photoaddition<sup>3</sup> and photocyclization reactions<sup>4</sup> via sequential SET-desilylation pathways exclusively. These efforts have shown that photocyclization reactions of phthalimides (**1**) are useful for construction of medium and large ring heterocyclic compounds (**2**) (Scheme 1).



The phthaloyl chromophore in excited phthalimides has a modestly high reduction potential and as a result, phthalimides participate in SET-promoted photoreactions with arene, thioether, ether and amine donors. Yoshida<sup>5</sup> and Owen<sup>6</sup> have demonstrated that  $\alpha$ -trialkylsilyl substituted arenes, alkenes, ethers, thioethers, and amines are more easily oxidized than their non-silicon analogues. Based on our previous investigations of SET-promoted photoreactions of phthalimide- $\alpha$ -silyl-n-electron donor systems<sup>3,4</sup> and  $\alpha$ -trialkylsilyl substituent effects on oxidation potentials of electron donors, we felt that SET from  $\alpha$ -silyl ether oxygens to the phthaloyl chromophore of excited phthalimides (**3**) would be more efficient than those from other ether oxygen(s). Thus, we proposed that SET-promoted photocyclization reactions might be useful for efficient and regioselective route to azacrown ethers<sup>7</sup> such as **4** (Scheme 2). In investigations of this proposal, we have explored photocyclization reactions of *N*-[( $\omega$ -trimethylsilylmethoxy)polyoxalkyl]phthalimides (**3**) to determine if SET-promoted photocyclization reactions occur in high yields to produce cyclized products (**4**). We now report preparative aspects of photocyclization reactions of *N*-[( $\omega$ -trimethylsilylmethoxy)polyoxalkyl]phthalimide (**3a-e**) leading to azacrown ethers (**4a-e**).

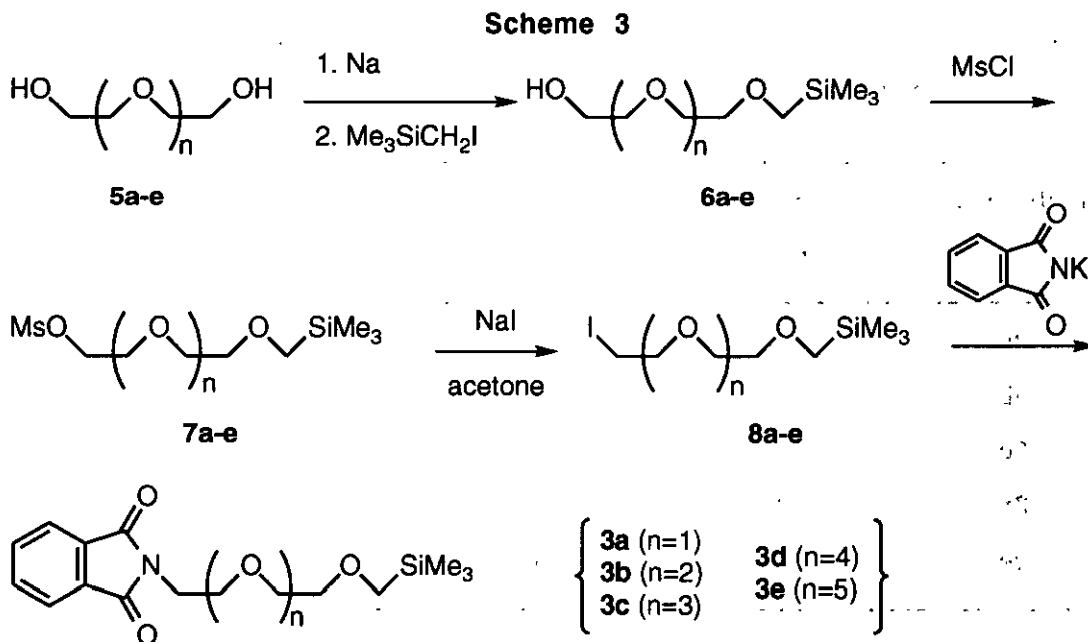
## Scheme 2



## RESULTS

Preparation of *N*-[( $\omega$ -trimethylsilylmethoxy)polyoxalkyl]phthalimides

For these photochemical studies, five *N*-[( $\omega$ -trimethylsilylmethoxy)polyoxalkyl]phthalimide derivatives (**3a-e**) were prepared in modest to good yields starting from the corresponding polyethylene glycols (**5a-e**) by use of the reaction sequences outlined in Scheme 3.

Photocyclizations of *N*-[( $\omega$ -trimethylsilylmethoxy)polyoxalkyl]phthalimides

Photocyclization reactions of *N*-[( $\omega$ -trimethylsilylmethoxy)polyoxalkyl]phthalimides (**3a-e**) were explored. These reactions were performed by irradiation of methanol solution of the phthalimides (5.5-8.8 mM) by using Pyrex glass filtered-light ( $\lambda > 290\text{nm}$ ) and products were separated by silica gel chromatography. Product yields along with reaction conditions employed are given in Table 1. Irradiation of *N*-[( $\omega$ -trimethylsilylmethoxy)polyoxalkyl]phthalimides (**3a-e**) in methanol leads to modest to high yielding production of the cyclized products (**4a-e**).<sup>8</sup> Structural assignments of the photoproducts were made on the basis of their characteristic spectroscopic data. Ir spectra of the cyclized products (**4a-e**) show characteristic absorption bands for the hydroxy group at  $3100\text{-}3600\text{ cm}^{-1}$  and amide carbonyl group at  $1660\text{-}1700\text{ cm}^{-1}$ . Their <sup>13</sup>C-nmr spectra clearly show resonances which correspond to quaternary carbon C-3 at  $88.5\text{-}89.6\text{ ppm}$  and methylene carbon  $\alpha$  to the quaternary carbon at  $73.6\text{-}76.5\text{ ppm}$ . Further their <sup>1</sup>H-nmr spectra characteristically show a pair of doublets ( $J=10.1\text{-}11.3\text{ Hz}$ ) in the region of  $3.81\text{-}4.11\text{ ppm}$  for two diastereotopic methylene hydrogens  $\alpha$  to the quaternary carbon and oxygen atoms.

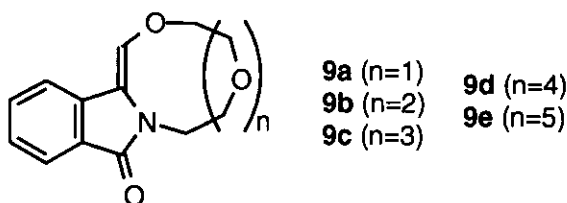
Table 1. Photocyclization Reactions of *N*-[( $\omega$ -Trimethylsilylmethoxy)polyoxalkyl]phthalimides (**3**) in Methanol.

| Phthalimide | Concentration<br>(mM) | Reaction Time<br>(h) | % Conversion | Product <sup>a</sup> |
|-------------|-----------------------|----------------------|--------------|----------------------|
| <b>3a</b>   | 6.2                   | 4                    | 100          | <b>4a</b> (99%)      |
| <b>3b</b>   | 5.5                   | 5                    | 100          | <b>4b</b> (60%)      |
| <b>3c</b>   | 6.1                   | 6                    | 64           | <b>4c</b> (64%)      |
| <b>3d</b>   | 8.8                   | 5                    | 66           | <b>4d</b> (50%)      |
| <b>3e</b>   | 3.0                   | 4                    | 87           | <b>4e</b> (53%)      |

a. Yields are based on consumed phthalimides (**3a-e**).

Along with the disappearance of resonances for the trimethylsilyl group present in the <sup>1</sup>H-nmr and <sup>13</sup>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  $\omega$ -carbons formerly occupied by the silicon substituents. In addition, all of the other spectroscopic properties ( $^1\text{H}$ -nmr,  $^{13}\text{C}$ -nmr, ir and high resolution mass spectra) are in complete accord with the structures assigned. Finally, the cyclized products (**4a-e**) were observed to undergo slow dehydration in solution to generate unsaturated azacrown ethers (**9a-e**).<sup>9</sup>



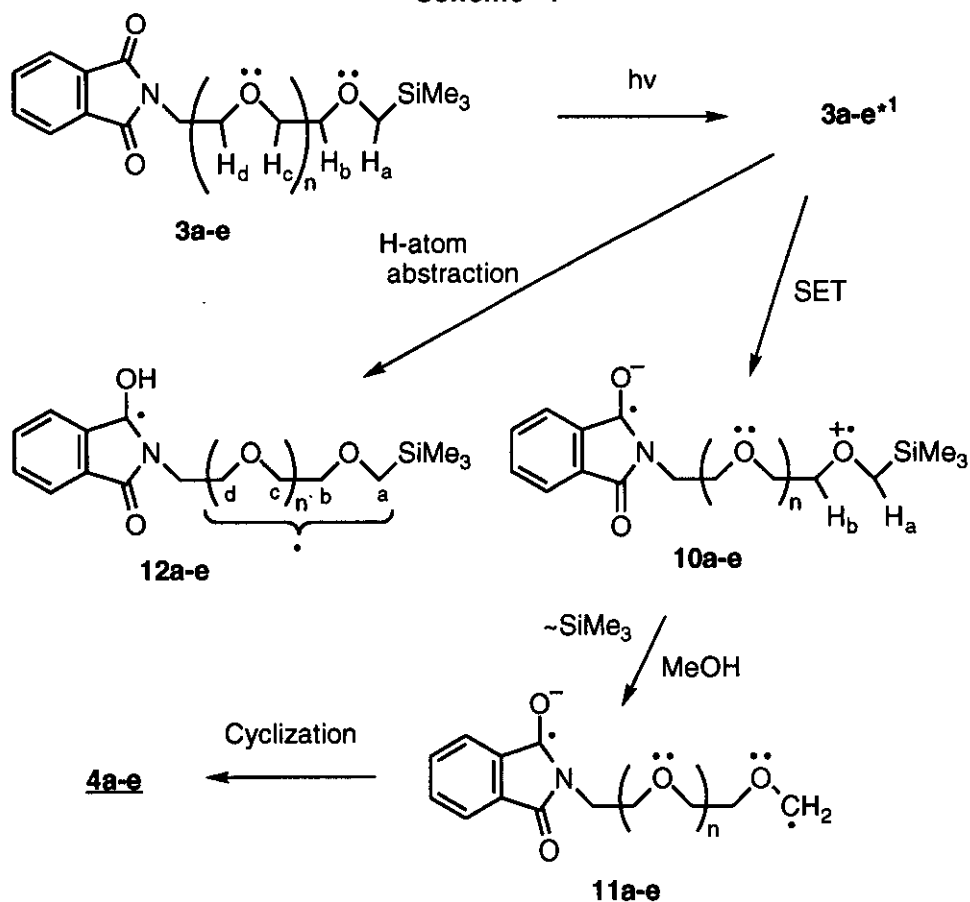
## DISCUSSION

The observations presented above show that *N*-[( $\omega$ -trimethylsilylmethoxy)polyoxalkyl]phthalimides (**3**) undergo photocyclizations in methanol with high degrees of chemoselectivity and regioselectivity to generate azacrown ethers of various sizes (aza-9-crown-3 to aza-21-crown-7). In the products, the phthalimide carbonyl carbon is bonded to  $\omega$ -methylene carbon in place of the trimethylsilyl group. As noted above, photoreactions of **3a-e** are much more sluggish in acetone or acetone-methanol than in methanol and this solvent effect is also noticed in photocyclizations of *N*-(trimethylsilylmethoxyalkyl)- and *N*-(trimethylsilylmethylthioalkyl)phthalimides.<sup>4</sup> Results obtained in this study and observations made in our earlier investigations<sup>4</sup> suggest that photocyclizations leading to azacrown ethers (**4a-e**) follow excited singlet state SET mechanisms<sup>10</sup> (Scheme 4).

Accordingly, intramolecular SET in singlet excited phthalimides (**3a-e**<sup>\*1</sup>) results in generation of radical ion intermediates (**10a-e**) which undergo exclusive desilylation leading to biradicals (**11a-e**). Proton transfer between either one of the two protons ( $\text{H}_a$  and  $\text{H}_b$ ) and ion radical centers of **10a-e** is not favorable due to low basicity of phthalimide radical anion<sup>3</sup> and instead preferential desilylation by solvent, methanol occurs predominantly.

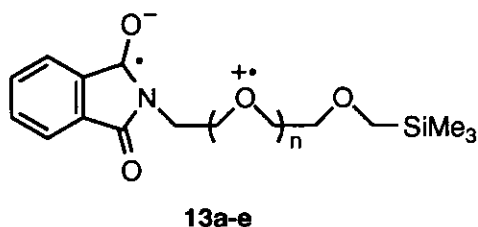
Biradicals (**11a-e**) undergo cyclizations to produce exclusively cyclized products (**4a-e**). The intramolecular SET-induced processes appear to occur from the phthalimide singlet excited state produced by direct irradiation in the methanol. In contrast, photoreactions in acetone are promoted in part by triplet sensitization. The triplet phthalimides formed in this manner, react by H-atom abstraction mechanisms (Norrish Type II pathways).<sup>4</sup> Excited states of phthalimides are known to participate in efficient intramolecular hydrogen atom abstraction reactions.<sup>1</sup> Like their ketone counterparts, *N*-alkylphthalimides display a distinct preference for  $\gamma$ -hydrogen by their excited states.<sup>11</sup>

Scheme 4



However, as seen in the photochemistry of alkoxy,<sup>12</sup> thioalkyl,<sup>13</sup> and arylalkyl<sup>14</sup> substituted systems, apparent hydrogen abstractions at sites adjacent to electron donor moieties, even

when they are remote, can often overwhelm that at the  $\gamma$ -position. These observations have led Kanaoka<sup>12-14</sup> to the reasonable suggestion that charge transfer interactions between donor groups and the phthalimide excited acceptor occur, to activate reaction at sites adjacent to the donor centers. Considering the observations and suggestions made by Kanaoka, we see that *N*-[( $\omega$ -trimethylsilylmethoxy)polyoxalkyl]phthalimides (**3a-e**) contain more than four potential hydrogens ( $H_a$ - $H_d$ ) which the excited phthalimide carbonyl can abstract. Thus, the intramolecular hydrogen abstraction can result in generation of regioisomeric mixtures of biradical intermediates (**12a-e**) in which the carbon radical centers are adjacent to oxygens (Scheme 4). These intermediates can then produce several possible regioisomeric products. Furthermore, intramolecular SET to the excited phthalimide can occur from several possible oxygen *n*-electron donating sites in the polyoxalkyl chain. This would lead to several different radical cations, *e.g.* **10a-e** and **13a-e**. Proton transfers in **13a-e** would yield the same regioisomeric biradical (thus products) that are derived by hydrogen abstraction.



In the light of these possible chemical reactivities, the high degree of chemo- and regioselectivities observed in photocyclization reactions of *N*-[( $\omega$ -trimethylsilylmethoxy)polyoxalkyl]phthalimides are remarkable and suggest a great synthetic potential.

## SUMMARY

The study demonstrates that photoreactions of *N*-[( $\omega$ -trimethylsilylmethoxy)polyoxalkyl]phthalimides lead to modest to high yielding production of cyclized products with high degrees of chemoselectivity and regioselectivity.

## EXPERIMENTAL

### General Procedures.

$^1\text{H}$ -Nmr and  $^{13}\text{C}$ -nmr spectra were recorded by using 200 MHz and 400 MHz spectrometer and chemical shifts are reported in values in part per million downfield from tetramethylsilane employed as internal standards; abbreviations used are s (singlet), d (doublet), t (triplet) and m (multiplet).  $^{13}\text{C}$ -Nmr resonances were assigned by use of the DEPT technique to determine the number of attached hydrogens. All compounds were obtained as oils (unless specified otherwise by giving recorded melting point) and in purities of >90 % as judged by  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr. Microanalyses were performed by the Korea Basic Science Center.

Preparative photolyses were conducted with an apparatus consisting of 450 W Hanovia medium mercury vapor lamp surrounded by a Pyrex filter in a quartz immersion well under inert atmospheres. Low resolution mass spectral analyses were performed at 70 eV on Hitachi RMU-6 mass spectrometer. High resolution mass spectral analyses were performed at 70 eV on Hitachi VG-7070 mass spectrometer.

### Preparations of $\omega$ -(trimethylsilylmethyl)polyethylene glycols (**6a-e**).

To excess polyethylene glycol (**5a**; 16.1 ml, 0.17 mol; **5b**, 22.6 ml, 0.17 mol; **5c**, 17.6 ml, 0.10 mol in 50 ml of THF; **5d**, 25.0 g, 0.10 mol in 100 ml of THF; **5e**, 28.0 g, 0.10 mol in 100 ml of THF) was added Na metal (0.8 g, 35 mmol) portionwise over a 2 h period with stirring. To this solution was added trimethylsilylmethyl iodide (5.2 ml, 35 mmol) dropwise and the resulting mixture was heated for 2 days at 80 °C. The mixture was cooled to room temperature and extracted with *n*-pentane. The pentane solution was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo* to afford a residue. From the residue, 4.17 g (62%) of **6a** and 4.13 g (50%) of **6b** were obtained respectively by vacuum distillation (**6a**, 78-80 °C/0.5 torr; **6b** 134-136 °C/3 torr). The residues for **6c-e** were subjected to column chromatographic separation (for **6c** and **6e**, silica, ethyl acetate:*n*-hexane=1:1; for **6d**, Florisil, chloroform) to yield 1.76 g (18%) of **6c**, 2.27 g (20%) of **6d** and 1.29 g (10%) of **6e**. Spectral data for **6a**:  $^1\text{H}$ -Nmr ( $\text{CDCl}_3$ ) -0.03 (s, 9H,  $\text{SiMe}_3$ ), 3.09 (s, 2H,  $\text{OCH}_2\text{SiMe}_3$ ), 3.46-3.62 (m,



9H,  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_2\text{OCH}_2$ );  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) -3.2 ( $\text{SiMe}_3$ ), 61.7 ( $\text{OCH}_2\text{SiMe}_3$ ), 65.5 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 70.1 ( $\text{HOCH}_2\text{CH}_2\text{OCH}_2$ ), 72.4 ( $\text{HOCH}_2\text{CH}_2$ ), 74.9 ( $\text{HOCH}_2$ ); ir (KBr), 3250-3500, 1250, 1100  $\text{cm}^{-1}$ ; ms (CI), m/z (rel. intensity) 193 ( $\text{M}^++1$ , 9), 132 (9), 117 ( $\text{CH}_2\text{CH}_2\text{SiMe}_3$ , 14), 103 ( $\text{OCH}_2\text{SiMe}_3$ , 83), 87 ( $\text{CH}_2\text{SiMe}_3$ , 23), 73 ( $\text{SiMe}_3$ , 100), 61 (46); high resolution ms (CI), m/z 193.1248 ( $\text{M}^++\text{H}^+$ ,  $\text{C}_8\text{H}_{21}\text{O}_3\text{Si}$  requires 193.1260). Spectral data for **6b**:  $^1\text{H}$ -Nmr ( $\text{CDCl}_3$ ) -0.01 (s, 9H,  $\text{SiMe}_3$ ), 3.09 (s, 2H,  $\text{OCH}_2\text{SiMe}_3$ ), 3.50-3.66 (m, 13H,  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2$ );  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) -3.2 ( $\text{SiMe}_3$ ), 61.6 ( $\text{CH}_2\text{SiMe}_3$ ), 65.4 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 70.2 ( $\text{CH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 70.3 ( $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$ ), 70.6 ( $\text{HOCH}_2\text{CH}_2\text{OCH}_2$ ), 72.5 ( $\text{HOCH}_2\text{CH}_2$ ), 74.6 ( $\text{HOCH}_2$ ); ir (KBr), 3200-3600, 1280, 1100  $\text{cm}^{-1}$ ; ms (CI), m/z (rel. intensity) 237 ( $\text{M}^++1$ , 7), 175 (5), 154 (8), 147 ( $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 15), 133 ( $\text{M}^+-\text{OCH}_2\text{SiMe}_3$ , 35), 117 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 41), 103 ( $\text{OCH}_2\text{SiMe}_3$ , 100); high resolution ms (CI), m/z 237.1501 ( $\text{M}^++\text{H}^+$ ,  $\text{C}_{10}\text{H}_{25}\text{O}_4\text{Si}$  requires 237.1522). Spectral data for **6c**:  $^1\text{H}$ -Nmr ( $\text{CDCl}_3$ ) -0.02 (s, 9H,  $\text{SiMe}_3$ ), 3.09 (s, 2H,  $\text{OCH}_2\text{SiMe}_3$ ), 3.50-3.65 (m, 17H,  $\text{HOCH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2$ );  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) -3.2 ( $\text{SiMe}_3$ ), 61.6 ( $\text{CH}_2\text{SiMe}_3$ ), 65.4 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 70.2-70.5 ( $\text{HOCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OCH}_2$ ), 72.5 ( $\text{HOCH}_2\text{CH}_2$ ), 74.6 ( $\text{HOCH}_2$ ); ir (KBr), 3200-3600, 1270, 1100  $\text{cm}^{-1}$ ; ms (CI), m/z (rel. intensity) 281 ( $\text{M}^++1$ , 6), 207 ( $\text{M}^+-\text{SiMe}_3$ , 3), 177 ( $\text{M}^+-\text{OCH}_2\text{SiMe}_3$ , 26), 161 ( $(\text{CH}_2\text{OCH}_2)_2\text{SiMe}_3$ , 33), 147 ( $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 74), 133 (100); high resolution ms (CI), m/z 281.1788 ( $\text{M}^++\text{H}^+$ ,  $\text{C}_{12}\text{H}_{29}\text{O}_5\text{Si}$  requires 281.1784). Spectral data for **6d**:  $^1\text{H}$ -Nmr ( $\text{CDCl}_3$ ) 0.02 (s, 9H,  $\text{SiMe}_3$ ), 3.13 (s, 2H,  $\text{OCH}_2\text{SiMe}_3$ ), 3.53-3.73 (m, 21H,  $\text{HOCH}_2(\text{CH}_2\text{OCH}_2)_4\text{CH}_2$ );  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) -2.9 ( $\text{SiMe}_3$ ), 61.8 ( $\text{OCH}_2\text{SiMe}_3$ ), 65.5 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 70.5-70.7 ( $\text{HOCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_3\text{OCH}_2$ ), 72.6 ( $\text{HOCH}_2\text{CH}_2$ ), 74.8 ( $\text{HOCH}_2$ ); ir (KBr), 3200-3600, 1250, 1100  $\text{cm}^{-1}$ ; ms (CI), m/z (rel. intensity) 325 ( $\text{M}^++1$ , 17), 219 (4), 160 (17), 132 (44), 117 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 54), 103 ( $\text{OCH}_2\text{SiMe}_3$ , 74), 87 ( $\text{CH}_2\text{SiMe}_3$ , 86), 73 ( $\text{SiMe}_3$ , 100); high resolution ms (CI), m/z 325.2049 ( $\text{M}^++\text{H}^+$ ,  $\text{C}_{14}\text{H}_{33}\text{O}_6\text{Si}$  requires 325.2046). Spectral data for **6e**:  $^1\text{H}$ -Nmr ( $\text{CDCl}_3$ ) -0.02 (s, 9H,  $\text{SiMe}_3$ ), 3.09 (s, 2H,  $\text{OCH}_2\text{SiMe}_3$ ), 3.16-3.64 (m, 25H,  $\text{HOCH}_2(\text{CH}_2\text{OCH}_2)_5\text{CH}_2$ );  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) -2.9 ( $\text{SiMe}_3$ ), 61.8 ( $\text{OCH}_2\text{SiMe}_3$ ), 65.5 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 70.4-70.7 ( $\text{HOCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_4\text{OCH}_2$ ), 72.7 ( $\text{HOCH}_2\text{CH}_2$ ), 74.7 ( $\text{HOCH}_2$ ); ir (KBr), 3350-3600, 1250, 1100  $\text{cm}^{-1}$ ; ms (CI), m/z (rel. intensity) 369 ( $\text{M}^++1$ , 5), 219 (4), 175 ( $\text{CH}_2(\text{CH}_2\text{OCH}_2)_2\text{SiMe}_3$ , 10), 161 ( $(\text{CH}_2\text{OCH}_2)_2\text{SiMe}_3$ ,

17); 133 (26), 117 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 75), 103 ( $\text{OCH}_2\text{SiMe}_3$ , 100); high resolution ms (CI),  $m/z$  369.2301 ( $\text{M}^++\text{H}^+$ ;  $\text{C}_{16}\text{H}_{37}\text{O}_7\text{Si}$  requires 369.2309).

#### Preparations of $\omega$ -(trimethylsilylmethoxy)polyoxalkyl mesylates (**7a-e**).

To a solution of  $\omega$ -(trimethylsilylmethyl)polyethylene glycol (8.55 mmol, **6a**; 1.64 g; **6b**, 2.02 g; **6c**, 2.40 g; **6d**, 2.77 g; **6e**; 3.14 g) and triethylamine (2.4 ml, 17.1 mmol) in 60 ml of ether was added methanesulfonyl chloride (1.3 ml, 17.1 mmol) dropwise in 20 ml of ether for 1 h at 0 °C. The solution was stirred for 25 h at 25 °C and was extracted with ether. The ether solution was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated to afford a residue. From the residue, 2.08 g (90%) of **7a** and 2.28 g (85%) of **7b** were respectively obtained by vacuum distillation (**7a**, 140-142 °C/1 torr; **7b**, 160-162 °C/0.8 torr), and 2.03 g (75%) of **7c**, 2.89 g (84%) of **7d** and 2.98 g (78%) of **7e** were respectively obtained by column chromatography (silica; ethyl acetate:n-hexane=1:1). Spectral data for **7a**:  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) -0.04 (s, 9H,  $\text{SiMe}_3$ ), 3.00 (s, 3H,  $\text{CH}_3$ ), 3.06 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 3.47-3.49 (m, 2H,  $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 3.56-3.58 (m, 2H,  $\text{CH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 3.68-3.70 (m, 2H,  $\text{MsOCH}_2\text{CH}_2$ ), 4.28-4.31 (m, 2H,  $\text{MsOCH}_2$ );  $^{13}\text{C-nmr}$  ( $\text{CDCl}_3$ ) -3.2 ( $\text{SiMe}_3$ ), 37.5 ( $\text{CH}_3$ ), 65.3 ( $\text{CH}_2\text{SiMe}_3$ ), 68.9 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 69.4 ( $\text{CH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 70.3 ( $\text{MsOCH}_2\text{CH}_2$ ), 74.6 ( $\text{MsOCH}_2$ ); ir (KBr), 1350, 1180  $\text{cm}^{-1}$ ; ms (CI),  $m/z$  (rel. intensity) 271 ( $\text{M}^++1$ , 47), 241 (11), 196 (7), 175 (54), 153 (79), 131 ( $\text{CH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 57), 123 ( $\text{MsOCH}_2\text{CH}_2$ , 67), 103 ( $\text{OCH}_2\text{SiMe}_3$ , 68), 87 ( $\text{CH}_2\text{SiMe}_3$ , 80), 73 ( $\text{SiMe}_3$ , 100); high resolution ms (CI),  $m/z$  271.1040 ( $\text{M}^++\text{H}^+$ ,  $\text{C}_9\text{H}_{23}\text{O}_5\text{SSi}$  requires 271.1036). Spectral data for **7b**:  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) -0.02 (s, 9H,  $\text{SiMe}_3$ ), 3.01 (s, 3H,  $\text{CH}_3$ ), 3.08 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 3.47-3.49 (m, 2H,  $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 3.54-3.56 (m, 2H,  $\text{CH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 3.60 (s, 4H,  $\text{MsOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$ ), 3.70-3.72 (m, 2H,  $\text{MsOCH}_2\text{CH}_2$ ), 4.31-4.32 (m, 2H,  $\text{MsOCH}_2$ );  $^{13}\text{C-nmr}$  ( $\text{CDCl}_3$ ) -3.2 ( $\text{SiMe}_3$ ), 37.5 ( $\text{CH}_3$ ), 65.3 ( $\text{CH}_2\text{SiMe}_3$ ), 68.8-70.6 ( $\text{MsOCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2$ ), 74.6 ( $\text{MsOCH}_2$ ); ir (KBr), 1350, 1180  $\text{cm}^{-1}$ ; ms (CI),  $m/z$  (rel. intensity) 315 ( $\text{M}^++1$ , 14), 241 ( $\text{M}^+-\text{SiMe}_3$ , 7), 219 (21), 211 ( $\text{M}^+-\text{OCH}_2\text{SiMe}_3$ , 13), 175 (56), 153 (76), 131 ( $\text{CH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 84), 123 ( $\text{MsOCH}_2\text{CH}_2$ , 94), 103 ( $\text{OCH}_2\text{SiMe}_3$ , 100); high resolution ms (CI),  $m/z$  315.1277 ( $\text{M}^++\text{H}^+$ ,  $\text{C}_{11}\text{H}_{27}\text{O}_6\text{SSi}$  requires 315.1298). Spectral data for **7c**:  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) 0.00 (s, 9H,  $\text{SiMe}_3$ ), 3.04 (s, 3H,  $\text{CH}_3$ ), 3.10

(s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 3.50-3.53 (m, 2H,  $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 3.56-3.62 (m, 10H,  $\text{MsOCH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2$ ), 3.71-3.74 (m, 2H,  $\text{MsOCH}_2\text{CH}_2$ ), 4.34-4.35 (m, 2H,  $\text{MsOCH}_2$ );  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) -3.1 ( $\text{SiMe}_3$ ), 37.6 ( $\text{CH}_3$ ), 65.4 ( $\text{CH}_2\text{SiMe}_3$ ), 68.9-70.6 ( $\text{MsOCH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2$ ), 74.6 ( $\text{MsOCH}_2$ ); ir (KBr), 1350, 1180  $\text{cm}^{-1}$ ; ms (CI), m/z (rel. intensity) 359 ( $\text{M}^++1$ , 53), 241 ( $\text{M}^+-\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 10), 211 (16), 175 (66), 167 ( $\text{Ms}(\text{OCH}_2\text{CH}_2)_2$ , 100), 154 (35), 152 (96), 139 (60), 131 ( $\text{CH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 91); high resolution ms (CI), m/z 359.1570 ( $\text{M}^++\text{H}^+$ ,  $\text{C}_{13}\text{H}_{31}\text{O}_7\text{SSi}$  requires 359.1560). Spectral data for **7d**:  $^1\text{H}$ -Nmr ( $\text{CDCl}_3$ ) 0.03 (s, 9H,  $\text{SiMe}_3$ ), 3.08 (s, 3H,  $\text{CH}_3$ ), 3.14 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 3.53-3.78 (m, 18H,  $\text{MsOCH}_2(\text{CH}_2\text{OCH}_2)_4\text{CH}_2$ ), 4.35-4.39 (m, 2H,  $\text{MsOCH}_2$ );  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) -2.9 ( $\text{SiMe}_3$ ), 37.8 ( $\text{CH}_3$ ), 65.5 ( $\text{CH}_2\text{SiMe}_3$ ), 69.1-70.8 ( $\text{MsOCH}_2(\text{CH}_2\text{OCH}_2)_4\text{CH}_2$ ), 74.8 ( $\text{MsOCH}_2$ ); ir (KBr), 1350, 1170  $\text{cm}^{-1}$ ; ms (CI), m/z (rel. intensity) 403 ( $\text{M}^++1$ , 1), 167 ( $\text{Ms}(\text{OCH}_2\text{CH}_2)_2$ , 26), 153 ( $\text{MsOCH}_2\text{CH}_2\text{OCH}_2$ , 16), 131 ( $\text{CH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 15), 123 ( $\text{MsOCH}_2\text{CH}_2$ , 100), 117 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 10), 103 ( $\text{OCH}_2\text{SiMe}_3$ , 36), 101 (13); high resolution ms (CI), m/z 403.1847 ( $\text{M}^++\text{H}^+$ ,  $\text{C}_{15}\text{H}_{35}\text{O}_8\text{SSi}$  requires 403.1822). Spectral data for **7e**:  $^1\text{H}$ -Nmr ( $\text{CDCl}_3$ ) 0.02 (s, 9H,  $\text{SiMe}_3$ ), 3.07 (s, 3H,  $\text{CH}_3$ ), 3.13 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 3.54-3.78 (m, 22H,  $\text{MsOCH}_2(\text{CH}_2\text{OCH}_2)_5\text{CH}_2$ ), 4.35-4.39 (m, 2H,  $\text{MsOCH}_2$ );  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) -2.9 ( $\text{SiMe}_3$ ), 37.8 ( $\text{CH}_3$ ), 65.3 ( $\text{CH}_2\text{SiMe}_3$ ), 69.1-70.1 ( $\text{MsOCH}_2(\text{CH}_2\text{OCH}_2)_5\text{CH}_2$ ), 74.8 ( $\text{MsOCH}_2$ ); ir (KBr), 1350, 1170  $\text{cm}^{-1}$ ; ms (CI), m/z (rel. intensity) 447 ( $\text{M}^++1$ , 7), 175 (20), 167 ( $\text{Ms}(\text{OCH}_2\text{CH}_2)_2$ , 58), 156 (31), 153 (29), 133 (28), 123 ( $\text{MsOCH}_2\text{CH}_2$ , 100), 115 (21), 103 ( $\text{OCH}_2\text{SiMe}_3$ , 86); high resolution ms (CI), m/z 447.2087 ( $\text{M}^++\text{H}^+$ ,  $\text{C}_{17}\text{H}_{39}\text{O}_9\text{SSi}$  requires 447.2084).

#### Preparations of $\omega$ -(trimethylsilylmethoxy)polyoxalkyl iodides (**8a-e**).

To a solution of sodium iodide (4.65 g, 31.0 mmol) in 100 ml of acetone was added  $\omega$ -(trimethylsilylmethoxy)polyoxalkyl mesylates (6.2 mmol, **7a**, 1.67 g; **7b**, 1.95 g; **7c**, 2.22 g; **7d**, 2.49 g; **7e**, 2.77 g) and the resulting mixture was stirred for 20 h at 40-50  $^\circ\text{C}$ . The mixture was cooled to room temperature and extracted with n-pentane. The pentane solution was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated to afford a residue. From the residue, 1.40 g (75%) of **8a** and 1.72 g (80%) of **8b** were respectively obtained by vacuum distillation (**8a**, 105-108  $^\circ\text{C}/1.8$  torr, **8b** 118-120  $^\circ\text{C}/1$  torr), and 2.32 g (96%) of **8c**, 2.36 g

(88%) of **8d** and 2.08 g (70%) of **8e** were respectively obtained by column chromatography (silica, ethyl acetate:n-hexane=1:3). Spectral data for **8a**:  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) 0.02 (s, 9H,  $\text{SiMe}_3$ ), 3.13 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 3.22 (t, 2H,  $J=6.9\text{Hz}$ ,  $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 3.53-3.55 (m, 2H,  $\text{ICH}_2\text{CH}_2$ ), 3.60-3.63 (m, 2H,  $\text{ICH}_2\text{CH}_2\text{OCH}_2$ ), 3.74 (t, 2H,  $J=7.0\text{Hz}$ ,  $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ );  $^{13}\text{C-nmr}$  ( $\text{CDCl}_3$ ) -3.0 ( $\text{SiMe}_3$ ), 3.2 ( $\text{ICH}_2$ ), 65.5 ( $\text{CH}_2\text{SiMe}_3$ ), 70.1 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 72.0 ( $\text{ICH}_2\text{CH}_2\text{OCH}_2$ ), 74.8 ( $\text{ICH}_2\text{CH}_2$ ); ir (KBr), 1250, 1110  $\text{cm}^{-1}$ ; ms (EI), m/z (rel. intensity) 301 ( $\text{M}^+-1$ , 1), 229 ( $\text{M}^+-\text{SiMe}_3$ , 4), 198 (43), 175 (8), 131 ( $\text{CH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 10), 117 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 15), 103 ( $\text{OCH}_2\text{SiMe}_3$ , 86), 87 ( $\text{CH}_2\text{SiMe}_3$ , 12), 73 ( $\text{SiMe}_3$ , 100); high resolution ms (EI), m/z 302.0261 ( $\text{C}_8\text{H}_{19}\text{O}_2\text{Si}$  requires 302.0919). Spectral data for **8b**:  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) 0.00 (s, 9H,  $\text{SiMe}_3$ ), 3.11 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 3.22 (t, 2H,  $J=6.9\text{Hz}$ ,  $\text{ICH}_2$ ), 3.52-3.54 (m, 2H,  $\text{ICH}_2\text{CH}_2$ ), 3.59-3.64 (m, 6H,  $\text{ICH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ), 3.72 (t, 2H,  $J=7.0\text{Hz}$ ,  $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ );  $^{13}\text{C-nmr}$  ( $\text{CDCl}_3$ ) -3.1 ( $\text{SiMe}_3$ ), 29.6 ( $\text{ICH}_2$ ), 65.3 ( $\text{CH}_2\text{SiMe}_3$ ), 70.2-70.6 ( $\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 71.9 ( $\text{ICH}_2\text{CH}_2\text{OCH}_2$ ), 74.7 ( $\text{ICH}_2\text{CH}_2$ ); ir (KBr) 1250, 1100  $\text{cm}^{-1}$ ; ms (EI), m/z (rel. intensity) 346 ( $\text{M}^+$ , 6), 273 ( $\text{M}^+-\text{SiMe}_3$ , 11), 229 ( $\text{M}^+-\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 5), 198 (40), 175 (22), 171 ( $\text{ICH}_2\text{CH}_2$ , 13), 155 ( $\text{ICH}_2\text{CH}_2$ , 100), 130 (29), 117 (11), 103 ( $\text{OCH}_2\text{SiMe}_3$ , 98); high resolution ms (EI), m/z 346.0490 ( $\text{C}_{10}\text{H}_{23}\text{O}_3\text{Si}$  requires 346.0561). Spectral data for **8c**:  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) 0.01 (s, 9H,  $\text{SiMe}_3$ ), 3.12 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 3.24 (t, 2H,  $J=6.9\text{Hz}$ ,  $\text{ICH}_2$ ), 3.52-3.55 (m, 2H,  $\text{ICH}_2\text{CH}_2$ ), 3.59-3.64 (m, 10H,  $\text{ICH}_2\text{CH}_2\text{OCH}_2(\text{CH}_2-\text{OCH}_2)_2$ ), 3.73 (t, 2H,  $J=6.9\text{Hz}$ ,  $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ );  $^{13}\text{C-nmr}$  ( $\text{CDCl}_3$ ) -3.0 ( $\text{SiMe}_3$ ), 2.9 ( $\text{ICH}_2$ ), 65.4 ( $\text{CH}_2\text{SiMe}_3$ ), 70.2-70.7 ( $\text{ICH}_2\text{CH}_2\text{OCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2$ ), 72.0 ( $\text{ICH}_2\text{CH}_2\text{OCH}_2$ ), 74.7 ( $\text{ICH}_2\text{CH}_2$ ); ir (KBr), 1230, 1100  $\text{cm}^{-1}$ ; ms (CI), m/z (rel. intensity) 391 ( $\text{M}^++1$ , 3), 317 ( $\text{M}^+-\text{SiMe}_3$ , 8), 287 ( $\text{M}^+-\text{OCH}_2\text{SiMe}_3$ , 14), 254 (52), 198 (41), 161 (42), 131 ( $\text{CH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 60), 126 (58), 117 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 84), 103 ( $\text{OCH}_2\text{SiMe}_3$ , 98); high resolution ms (CI), m/z 391.0792 ( $\text{M}^++\text{H}^+$ ,  $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Si}$  requires 391.0802). Spectral data for **8d**:  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) 0.03 (s, 9H,  $\text{SiMe}_3$ ), 3.14 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 3.27 (t, 2H,  $J=6.9\text{Hz}$ ,  $\text{ICH}_2$ ), 3.55-3.78 (m, 20H,  $\text{ICH}_2(\text{CH}_2\text{OCH}_2)_5$ );  $^{13}\text{C-nmr}$  ( $\text{CDCl}_3$ ) -2.9 ( $\text{SiMe}_3$ ), 3.0 ( $\text{ICH}_2$ ), 65.5 ( $\text{CH}_2\text{SiMe}_3$ ), 70.3-70.8 ( $\text{ICH}_2\text{CH}_2\text{OCH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2$ ), 72.1 ( $\text{ICH}_2\text{CH}_2\text{OCH}_2$ ), 74.8 ( $\text{ICH}_2\text{CH}_2$ ); ir (KBr), 1250, 1100  $\text{cm}^{-1}$ ; ms (CI), m/z (rel. intensity) 435 ( $\text{M}^++1$ , 2), 287 ( $\text{M}^+-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 4), 198 (12), 175 (10), 161 (19), 147 ( $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 10), 131 ( $\text{CH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 28), 117 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 66), 103 ( $\text{OCH}_2\text{SiMe}_3$ , 100); high resolution ms (CI), m/z 435.1068 ( $\text{M}^++\text{H}^+$ ,  $\text{C}_{14}\text{H}_{32}\text{O}_5\text{Si}$

requires 435.1064). Spectral data for **8e**:  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) 0.02 (s, 9H,  $\text{SiMe}_3$ ), 3.13 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 3.25 (t, 2H,  $J=7.1\text{Hz}$ ,  $\text{ICH}_2$ ), 3.56-3.65 (m, 20H,  $\text{ICH}_2(\text{CH}_2\text{OCH}_2)_5$ ), 3.74 (t, 2H,  $J=6.9\text{Hz}$ ,  $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ );  $^{13}\text{C-nmr}$  ( $\text{CDCl}_3$ ) -2.9 ( $\text{SiMe}_3$ ), 3.0 ( $\text{ICH}_2$ ), 65.5 ( $\text{CH}_2\text{SiMe}_3$ ), 70.3-70.8 ( $\text{ICH}_2\text{CH}_2\text{OCH}_2(\text{CH}_2\text{OCH}_2)_4\text{CH}_2$ ), 72.1 ( $\text{ICH}_2\text{CH}_2\text{OCH}_2$ ), 74.8 ( $\text{ICH}_2\text{CH}_2$ ); ir (KBr), 1240, 1100  $\text{cm}^{-1}$ ; ms (CI),  $m/z$  (rel. intensity) 479 ( $\text{M}^++1$ , 1), 287 ( $\text{M}^+-\text{OCH}_2(\text{CH}_2\text{OCH}_2)_2\text{SiMe}_3$ , 7), 198 (10), 161 (22), 147 (11), 131 ( $\text{CH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 24), 128 (10), 117 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 62), 103 ( $\text{OCH}_2\text{SiMe}_3$ , 100); high resolution ms (CI),  $m/z$  479.1319 ( $\text{M}^++\text{H}^+$ ,  $\text{C}_{16}\text{H}_{38}\text{O}_6\text{Si}$  requires 479.1326).

Preparations of *N*-[( $\omega$ -trimethylsilylmethoxy)polyoxalkyl]phthalimides (**3a-e**).

To a solution of  $\omega$ -(trimethylsilylmethoxy)polyoxalkyl iodides (4.5 mmol, **8a**, 1.36 g; **8b**, 1.55 g; **8c**, 1.76g; **8d**, 1.95 g; **8e**, 2.15 g) in DMF (15ml) was added potassium phthalimide (1.24 g, 6.8 mmol) and the reaction mixture was stirred for 4 h at 40-50 °C. After removal of DMF *in vacuo*, the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered. Concentration of the filtrate and column chromatography (silica, ethyl acetate:n-hexane=1:2) gave *N*-[( $\omega$ -trimethylsilylmethoxy)polyoxalkyl]phthalimides (**3a-e**) respectively (**3a**, 1.39 g, 96%; **3b**, 1.61 g, 98%; **3c**, 1.66 g, 90%; **3d**, 2.00 g, 98%; **3e**, 1.88 g, 84%). Spectral data for **3a**:  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) -0.05 (s, 9H,  $\text{SiMe}_3$ ), 3.06 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 3.46-3.48 (m, 2H,  $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 3.56-3.58 (m, 2H,  $\text{NCH}_2\text{CH}_2\text{OCH}_2$ ), 3.70 (t, 2H,  $J=5.8\text{Hz}$ ,  $\text{NCH}_2\text{CH}_2$ ), 3.85 (t, 2H,  $J=5.8\text{Hz}$ ,  $\text{NCH}_2$ ), 7.65-72.67 (m, 2H, aromatic), 7.78-7.80 (m, 2H, aromatic);  $^{13}\text{C-nmr}$  ( $\text{CDCl}_3$ ) -3.2 ( $\text{SiMe}_3$ ), 37.3 ( $\text{NCH}_2$ ), 65.4 ( $\text{CH}_2\text{SiMe}_3$ ), 67.9 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 69.9 ( $\text{NCH}_2\text{CH}_2\text{OCH}_2$ ), 74.5 ( $\text{NCH}_2\text{CH}_2$ ), 132.2 and 133.8 (CH, aromatic), 132.1 (C, aromatic), 168.2 (C=O); ir (KBr), 3500, 1780, 1720  $\text{cm}^{-1}$ ; ms (CI),  $m/z$  (rel. intensity) 322 ( $\text{M}^++1$ , 2), 321 ( $\text{M}^+$ , 5), 248 ( $\text{M}^+-\text{SiMe}_3$ , 12), 232 (55), 218 ( $\text{M}^+-\text{OCH}_2\text{SiMe}_3$ , 11), 174 ( $\text{M}^+-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 100), 160 ( $\text{M}^+-\text{(CH}_2\text{OCH}_2)_2\text{SiMe}_3$ , 17), 147 (32), 130 (27), 103 ( $\text{OCH}_2\text{SiMe}_3$ , 52), 73 ( $\text{SiMe}_3$ , 94); high resolution ms (CI),  $m/z$  322.1485 ( $\text{M}^++\text{H}^+$ ,  $\text{C}_{16}\text{H}_{24}\text{NO}_4\text{Si}$  requires 322.1475); Anal. Calcd for  $\text{C}_{16}\text{H}_{23}\text{NO}_4\text{Si}$ ; C, 59.78; H, 7.21; N, 4.36. Found: C, 60.03; H, 7.28; N, 4.24. Spectral data for **3b**:  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) -0.05 (s, 9H,  $\text{SiMe}_3$ ), 3.04 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 3.41-3.43 (m, 2H,  $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 3.48-3.50 (m, 2H,  $\text{CH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 3.53-3.57 (m, 4H,  $\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$ ), 3.67 (t, 2H,

$J=5.8\text{Hz}$ ,  $\text{NCH}_2\text{CH}_2$ ), 3.82 (t, 2H,  $J=5.9\text{Hz}$ ,  $\text{NCH}_2$ ), 7.63-7.64 (m, 2H, aromatic), 7.75-7.77 (m, 2H, aromatic);  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) -3.2 ( $\text{SiMe}_3$ ), 37.1 ( $\text{NCH}_2$ ), 65.2 ( $\text{CH}_2\text{SiMe}_3$ ), 67.7 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 70.0-70.4 ( $\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ), 74.5 ( $\text{NCH}_2\text{CH}_2$ ), 123.0 and 133.7 (CH, aromatic), 132.0 (C, aromatic), 168.0 (C=O); ir (KBr), 1770 and 1710  $\text{cm}^{-1}$ ; ms (EI),  $m/z$  (rel. intensity) 365 ( $\text{M}^+$ , 7), 336 (16), 277 (35), 262 ( $\text{M}^+-\text{OCH}_2\text{SiMe}_3$ , 10), 246 (35), 233 (43), 174 ( $\text{M}^+-\text{OCH}_2(\text{CH}_2\text{OCH}_2)\text{SiMe}_3$ , 100), 160 ( $\text{M}^+(\text{CH}_2\text{OCH}_2)_3\text{SiMe}_3$ , 73), 147 (57), 130 (78), 117 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 28); high resolution ms (EI),  $m/z$  365.1655 ( $\text{C}_{18}\text{H}_{27}\text{NO}_5\text{Si}$  requires 365.1659); Anal. Calcd for  $\text{C}_{18}\text{H}_{27}\text{NO}_5\text{Si}$ ; C, 59.15; H, 7.45; N, 3.83. Found: C, 59.46; H, 7.53; N, 3.92. Spectral data for **3c**:  $^1\text{H}$ -Nmr ( $\text{CDCl}_3$ ) -0.02 (s, 9H,  $\text{SiMe}_3$ ), 3.08 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 3.48-3.61 (m, 12H,  $\text{NCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_3$ ), 3.68 (t, 2H,  $J=5.8\text{Hz}$ ,  $\text{NCH}_2\text{CH}_2$ ), 3.84 (t, 2H,  $J=5.9\text{Hz}$ ,  $\text{NCH}_2$ ), 7.65-7.67 (m, 2H, aromatic), 7.77-7.79 (m, 2H, aromatic);  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) -3.1 ( $\text{SiMe}_3$ ), 37.2 ( $\text{NCH}_2$ ), 65.3 ( $\text{CH}_2\text{SiMe}_3$ ), 67.8 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 70.0-70.6 ( $\text{NCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OCH}_2$ ), 74.6 ( $\text{NCH}_2\text{CH}_2$ ), 123.1 and 133.8 (CH, aromatic), 132.0 (C, aromatic), 168.1 (C=O); ir (KBr), 1720  $\text{cm}^{-1}$ ; ms (EI),  $m/z$  (rel. intensity) 409 ( $\text{M}^+$ , 3), 379 (10), 321 (16), 277 (21), 262 (14), 233 (53), 174 ( $\text{M}^+-\text{OCH}_2(\text{CH}_2\text{OCH}_2)_3\text{SiMe}_3$ , 100), 147 (80), 130 (67), 117 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 65); high resolution ms (EI),  $m/z$  409.1918 ( $\text{C}_{20}\text{H}_{31}\text{NO}_6\text{Si}$  requires 409.1921); Anal. Calcd. for  $\text{C}_{20}\text{H}_{31}\text{NO}_6\text{Si}$ ; C, 58.65; H, 7.63; N, 3.42. Found: C, 58.42; H, 7.56; N, 3.36. Spectral data for **3d**:  $^1\text{H}$ -Nmr ( $\text{CDCl}_3$ ) 0.02 (s, 9H,  $\text{SiMe}_3$ ), 3.15 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 3.56-3.68 (m, 16H,  $\text{NCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_4$ ), 3.70-3.76 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ), 3.88-3.94 (m, 2H,  $\text{NCH}_2$ ), 7.68-7.73 (m, 2H, aromatic), 7.81-7.86 (m, 2H, aromatic);  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) -2.9 ( $\text{SiMe}_3$ ), 37.4 ( $\text{NCH}_2$ ), 65.5 ( $\text{CH}_2\text{SiMe}_3$ ), 68.1 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ ), 70.1-70.6 ( $\text{NCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_3\text{OCH}_2$ ), 74.7 ( $\text{NCH}_2\text{CH}_2$ ), 123.2 and 134.0 (CH, aromatic), 132.2 (C, aromatic), 168.4 (C=O); ir (KBr), 1720  $\text{cm}^{-1}$ ; ms (EI),  $m/z$  (rel. intensity) 453 ( $\text{M}^+$ , 1), 366 ( $\text{M}^+-\text{CH}_2\text{SiMe}_3$ , 1), 277 (6), 246 (5), 187 (17), 174 (100), 131 ( $\text{CH}_2\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 7), 117 ( $\text{CH}_2\text{OCH}_2\text{SiMe}_3$ , 19), 103 ( $\text{OCH}_2\text{SiMe}_3$ , 24); high resolution ms (EI),  $m/z$  453.2157 ( $\text{C}_{22}\text{H}_{35}\text{NO}_7\text{Si}$  requires 453.2183); Anal. Calcd for  $\text{C}_{22}\text{H}_{35}\text{NO}_7\text{Si}$ ; C, 58.25; H, 7.78; N, 3.09. Found: C, 57.98; H, 7.63; N, 2.96. Spectral data for **3e**:  $^1\text{H}$ -Nmr ( $\text{CDCl}_3$ ) 0.03 (s, 9H,  $\text{SiMe}_3$ ), 3.14 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 3.53-3.64 (m, 20H,  $\text{NCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_5$ ), 3.70-3.76 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ), 3.89 (t, 2H,  $J=5.6\text{Hz}$ ,  $\text{NCH}_2$ ), 7.69-7.73 (m, 2H, aromatic), 7.82-7.86 (m, 2H, aromatic);  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) -2.9 ( $\text{SiMe}_3$ ), 37.4

(NCH<sub>2</sub>), 65.5 (CH<sub>2</sub>SiMe<sub>3</sub>), 68.0 (CH<sub>2</sub>OCH<sub>2</sub>SiMe<sub>3</sub>), 70.2-70.8 (NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>OCH<sub>2</sub>)<sub>4</sub>), 74.8 (NCH<sub>2</sub>CH<sub>2</sub>), 123.3 and 134.0 (CH, aromatic), 132.0 (C, aromatic), 168.3 (C=O); ir (KBr), 1720 cm<sup>-1</sup>; ms (CI), m/z (rel. intensity) 498 (M<sup>+</sup>+1, 4), 350 (M<sup>+</sup>-OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>SiMe<sub>3</sub>, 2), 262 (M<sup>+</sup>-OCH<sub>2</sub>(CH<sub>2</sub>OCH<sub>2</sub>)<sub>3</sub>SiMe<sub>3</sub>, 9), 217 (19), 187 (48), 174 (M<sup>+</sup>-OCH<sub>2</sub>(CH<sub>2</sub>OCH<sub>2</sub>)<sub>5</sub>SiMe<sub>3</sub>, 100), 147 (OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>SiMe<sub>3</sub>, 26), 131 (CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>SiMe<sub>3</sub>, 3), 116 (26), 103 (OCH<sub>2</sub>SiMe<sub>3</sub>, 59); high resolution ms (CI), m/z 498.2528 (M<sup>+</sup>+H<sup>+</sup>, C<sub>24</sub>H<sub>40</sub>NO<sub>8</sub>Si requires 498.2523); Anal. Calcd for C<sub>24</sub>H<sub>39</sub>NO<sub>8</sub>Si; C, 57.92; H, 7.90; N, 2.81. Found: C, 58.13; H, 8.12; N, 2.74.

#### Irradiations of *N*-[(ω-trimethylsilylmethoxy)polyoxalkyl]phthalimides (**3a-e**).

A solution of *N*-[(ω-trimethylsilylmethoxy)polyoxalkyl]phthalimides (**3a**, 400 mg, 1.25 mmol; **3b**, 400 mg, 1.10 mmol; **3c**, 500 mg, 1.22 mmol; **3d**, 400 mg, 0.88 mmol; **3e**, 300 mg, 0.60 mmol) in 200 ml of methanol was irradiated with Pyrex-filtered light under N<sub>2</sub>. Concentration of the photolyzate gave a residue which was subjected to column chromatography (silica, ethyl acetate:n-hexane=3:1) yielding cyclized product (**4a-e**). The reaction conditions and products yields are given in Table 1. Spectral data for **4a**: mp 130-132 °C (acetone); <sup>1</sup>H-nmr (DMSO-d<sub>6</sub>) 3.20-3.25 (m, 1H, NCH<sub>2</sub>), 3.34-3.40 (m, 3H, C(OH)NCH<sub>2</sub>CH<sub>2</sub>), 3.44-3.53 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>), 3.73-3.79 (m, 1H, NCH<sub>2</sub>), 3.83-3.91 (m, 2H, C(HO)CH<sub>2</sub>OCH<sub>2</sub>), 4.05 and 4.09 (two d, 2H, J=11.0Hz, C(HO)CH<sub>2</sub>), 6.58 (s, 1H, C=CH), 7.47-7.51 (m, 1H, aromatic), 7.56-7.64 (m, 3H, aromatic); <sup>13</sup>C-nmr (DMSO-d<sub>6</sub>) 40.9 (NCH<sub>2</sub>), 70.5 (NCH<sub>2</sub>CH<sub>2</sub>), 70.8 (NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>), 73.6 (NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>), 76.5 (C(OH)CH<sub>2</sub>), 89.6 (COH), 122.2, 122.5, 129.3 and 132.1 (CH, aromatic), 131.9 and 147.0 (C, aromatic), 167.6 (C=O); ir (KBr), 3200-3600, 3100, 1660 cm<sup>-1</sup>; ms (CI), m/z (rel. intensity) 248 (M<sup>+</sup>-1, 4), 231 (M<sup>+</sup>-H<sub>2</sub>O, 100), 202 (42), 172 (74), 160 (53), 145 (47), 130 (74), 117 (89), 103 (69); high resolution ms (CI), m/z 249.1000 (C<sub>13</sub>H<sub>15</sub>NO<sub>4</sub> requires 249.1001); Anal. Calcd for C<sub>13</sub>H<sub>15</sub>NO<sub>4</sub>; C, 62.64; H, 6.07; N, 5.62. Found: C, 62.41; H, 5.86; N, 5.44. Spectral data for **4b**: mp 127-128 °C (acetone); <sup>1</sup>H-nmr (CDCl<sub>3</sub>) 2.12 (s, 1H, OH), 3.40-3.43 (m, 1H, NCH<sub>2</sub>), 3.48-3.56 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 3.58-3.63 (m, 1H, NCH<sub>2</sub>), 3.66-3.80 (m, 8H, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>), 3.83 and 3.92 (two d, 2H, J=11.3Hz, C(OH)CH<sub>2</sub>), 6.03 (s, 1H, C=CH), 7.38-7.49 (m, 3H, aromatic), 7.63-7.65 (m, 1H,

aromatic);  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) 39.0 ( $\text{NCH}_2$ ), 68.0 ( $\text{NCH}_2\text{CH}_2$ ), 69.6 ( $\text{NCH}_2\text{CH}_2\text{OCH}_2$ ), 70.3 ( $\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$ ), 70.6 ( $\text{C(OH)CH}_2\text{OCH}_2\text{CH}_2$ ), 73.2 ( $\text{C(OH)CH}_2\text{OCH}_2$ ), 76.0 ( $\text{C(OH)CH}_2$ ), 89.3 ( $\text{COH}$ ), 122.0, 123.2, 129.5 and 132.0 (CH, aromatic), 131.4 and 144.5 (C, aromatic), 167.6 ( $\text{C=O}$ ); ir (KBr), 3200-3600, 1670  $\text{cm}^{-1}$ ; ms (EI), m/z (rel. intensity) 293 ( $\text{M}^+$ , 22), 276 ( $\text{M}^+-\text{OH}$ , 65), 275 ( $\text{M}^+-\text{H}_2\text{O}$ , 57), 234 (8), 218 (13), 205 (24), 174 ( $\text{M}^+(\text{OCH}_2\text{CH}_2)_2\text{CH}_2\text{C(OH)}$ , 100), 160 (40), 130 (16), 103 (12), 83 (24); high resolution ms (EI), m/z 293.1260 ( $\text{C}_{15}\text{H}_{19}\text{NO}_5$  requires 293.1263); Anal. Calcd for  $\text{C}_{15}\text{H}_{19}\text{NO}_5$ ; C, 61.42; H, 6.53; N, 4.78. Found: C, 61.18; H, 6.29; N, 5.07. Spectral data for **4c**: mp 98-99 °C (acetone);  $^1\text{H}$ -nmr ( $\text{CDCl}_3$ ) 1.87 (s, 1H, OH), 3.56-3.78 (m, 16H,  $\text{NCH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2$ ), 3.83 and 4.09 (two d, 2H,  $J=10.1\text{Hz}$ ,  $\text{C(OH)CH}_2$ ), 5.31 (s, 1H,  $\text{C=CH}$ ), 7.39-7.74 (m, 4H, aromatic);  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) 39.9 ( $\text{NCH}_2$ ), 70.1-71.4 ( $\text{NCH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2$ ), 75.5 ( $\text{C(OH)CH}_2$ ), 88.5 ( $\text{COH}$ ), 123.0, 123.1, 129.4 and 132.0 (CH, aromatic), 131.2 and 145.6 (C, aromatic), 167.8 ( $\text{C=O}$ ); ir (KBr), 3100-3600, 1680  $\text{cm}^{-1}$ ; ms (CI), m/z (rel. intensity) 337 ( $\text{M}^+$ , 2), 319 ( $\text{M}^+-\text{H}_2\text{O}$ , 89), 290 (18), 232 (25), 218 (14), 202 (61), 187 (83), 172 (100), 161 (70); high resolution ms (CI), m/z 319.1425 ( $\text{M}^+-\text{H}_2\text{O}$ ,  $\text{C}_{17}\text{H}_{21}\text{NO}_5$  requires 319.1420); Anal. Calcd for  $\text{C}_{17}\text{H}_{23}\text{NO}_6$ ; C, 60.52; H, 6.87; N, 4.15. Found: C, 60.63; H, 6.63; N, 4.26. Spectral data for **4d**: mp 92-94 °C (acetone);  $^1\text{H}$ -nmr ( $\text{DMSO}-d_6$ ) 3.28-3.60 (m, 21H,  $\text{C(OH)NCH}_2(\text{CH}_2\text{OCH}_2)_4\text{CH}_2$ ), 3.81 and 3.89 (two d, 2H,  $J=11.0\text{Hz}$ ,  $\text{C(OH)CH}_2$ ), 6.55 (s, 1H,  $\text{C=CH}$ ), 7.49-7.63 (m, 4H, aromatic);  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) 39.7 ( $\text{NCH}_2$ ), 69.9 ( $\text{NCH}_2\text{CH}_2$ ), 70.3-71.0 ( $\text{NCH}_2\text{CH}_2\text{OCH}_2(\text{CH}_2\text{OCH}_2)_3$ ), 71.8 ( $\text{C(OH)CH}_2\text{OCH}_2$ ), 74.3 ( $\text{C(OH)CH}_2$ ), 88.8 ( $\text{COH}$ ), 122.4, 123.3, 129.5 and 132.2 (CH, aromatic), 131.5 and 145.6 (C, aromatic), 168.1 ( $\text{C=O}$ ); ir (KBr), 3100-3600, 1700  $\text{cm}^{-1}$ ; ms spec.(EI), m/z (rel. intensity), 363( $\text{M}^+-\text{H}_2\text{O}$ , 72), 202 (13), 187 (100), 172 (54), 158 (17), 145 (12), 131 (45), 117 (17), 103 (36); high resolution ms spec.(EI), m/z 363.1668 ( $\text{M}^+-\text{H}_2\text{O}$ ,  $\text{C}_{19}\text{H}_{25}\text{NO}_6$  requires 363.1682); Anal. Calcd for  $\text{C}_{19}\text{H}_{27}\text{NO}_7$ ; C, 59.83; H, 7.13; N, 3.67. Found: C, 59.65; H, 7.34; N, 3.71. Spectral data for **4e**:  $^1\text{H}$ -Nmr ( $\text{CDCl}_3$ ) 2.52 (s, 1H, OH), 3.46-3.71 (m, 24H,  $\text{N}(\text{CH}_2\text{CH}_2\text{O})_6$ ), 3.97 and 4.11 (two d, 2H,  $J=10.5\text{Hz}$ ,  $\text{C(OH)CH}_2$ ), 5.85 (s, 1H,  $\text{C=CH}$ ), 7.45-7.77 (m, 4H, aromatic);  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ) 39.5 ( $\text{NCH}_2$ ), 70.1-71.0 ( $\text{NCH}_2(\text{CH}_2\text{OCH}_2)_5$ ), 71.7 ( $\text{C(OH)CH}_2\text{OCH}_2$ ), 73.6 ( $\text{C(OH)CH}_2$ ), 88.8 ( $\text{COH}$ ), 122.7, 123.2, 129.4 and 132.1 (CH, aromatic), 131.5 and 146.2 (C, aromatic), 168.2( $\text{C=O}$ ); ir (KBr), 3100-3600, 1670  $\text{cm}^{-1}$ ; ms (EI), m/z (rel. intensity), 408 ( $\text{M}^+-\text{OH}$ , 11), 407 ( $\text{M}^+-\text{H}_2\text{O}$ , 36), 207 (14),



187 (100), 172 (42), 149 (14), 131 (49), 117 (17), 103 (27); high resolution ms (EI),  $m/z$  407.1926 ( $M^+ - H_2O$ ,  $C_{21}H_{29}NO_7$  requires 407.1944); Anal. Calcd for  $C_{21}H_{31}NO_8$ ; C, 59.28; H, 7.34; N, 3.29. Found: C, 59.63; H, 7.62; N, 3.48.

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7. (a) Synthetic approach to crown ether analogs by photocyclizations of *N*-[ $\omega$ -(methylthio)polyoxalkyl]phthalimides has been reported.<sup>7(b)</sup> The photocyclizations utilized a mechanistic pathway involving SET-deprotonation and lower oxidation potential of thioether sulfur than those of ether oxygen(s). (b) M. Wada, H. Nakai, Y. Sato, Y. Hatanaka and Y. Kanaoka, *Chem. Pharm. Bull.*, 1983, **31**, 429.
8. Photoreactions of **3a-e** in acetone or acetone-methanol (1:1) occur much more sluggishly (at least 5 times) than in methanol and prolonged irradiations lead to complex and inseparable mixtures.
9. The dehydration has many precedents in the photochemistry of phthalimides<sup>1,3-4</sup> and <sup>1</sup>H-nmr spectra of the isolated azacrown ether (**4a-e**) revealed tiny appearance of resonances for olefinic hydrogens of dehydrated product (**9a-e**) (**9a**, 6.55; **9b**, 6.03; **9c**, 5.31; **9d**, 6.55; **9e**, 5.85 ppm) and their increases on standing.
10. (a) Triplet state SET mechanism has been proposed for photocyclizations of *N*-(methylthioalkyl)phthalimides.<sup>10(b)</sup> (b) Y. Hatanaka, Y. Sato, H. Nakai, M. Wada, T. Mizoguchi and Y. Kanaoka, *Liebigs Ann. Chem.*, 1992, 1113.
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