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PAPER

Exploration of photochemical reactions of *N*-trimethylsilylmethyl-substituted uracil, pyridone, and pyrrolidone derivatives†

Dae Won Cho,[a,d] Chan Woo Lee,[b] Jong Gu Park,[a] Sun Wha Oh,[c] Nam Kyoung Sung,[a] Hea Jung Park,[a] Kyung Mok Kim,[a] Patrick S. Mariano*[d] and Ung Chan Yoon*[a]

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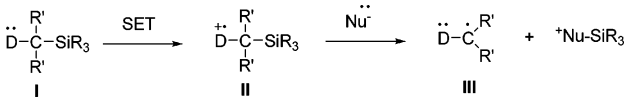
Photochemical reactions of *N*-trimethylsilylmethyl-substituted uracil, pyridone and pyrrolidone derivatives were carried out to determine if silicone containing substituents have an impact on excited state reaction profiles. The results show that ultraviolet irradiation of *N*-trimethylsilylmethyl substituted uracils in the presence of substituted alkenes leads to efficient formation of both dimeric and cross [2+2]-cycloaddition products. Qualitatively similar observations were made in a study of the photochemistry of *N*-trimethylsilylmethyl-2-pyridone. The combined results demonstrate that [2+2]-photocycloaddition is a more efficient excited state reaction pathway for the uracil and pyridone substrates as compared to other processes, such as ylide-forming trimethylsilyl group C-to-O migration. Finally, photoreactions of *N*-trimethylsilylmethyl-2-pyrrolidone in solutions containing dipolarophiles, such as methyl acrylate, lead to the formation of the desilylation product, *N*-methyl-2-pyrrolidone by way of a simple, non-ylide generating, protodesilylation process. In addition, observations were made which show that orbital symmetry allowed photocycloreversion reactions of dimeric uracil derivatives, involving cyclobutane ring splitting, to take place. These processes, which lead to the formation of monomeric uracils, appear to be stimulated by the presence of electron donor groups on the cyclobutane ring, a likely result of a new SET promoted cyclobutane ring cleavage pathway. In the cases of *N*-trimethylsilylmethyl-substituted cyclobutane derivatives that possess phthalimide groups, highly efficient excited state cleavage of the cyclobutane moiety occurs to produce uracil derivatives and corresponding vinyl phthalimide.

1. Introduction

Silicon containing organic compounds serve as key substrates in synthetically useful chemical reactions.[1] In addition, substances that possess trialkylsilyl substitution at sites adjacent to electron donor centers undergo ready oxidation to generate silicon stabilized cation radical intermediates **II** (Scheme 1), which participate in fast nucleophile-assisted desilylation reactions that produce neutral, carbon-centered radicals **III**.[2–7]

From the time of the early pioneering studies by Kanaoka[8–10] and Coyle[11,12] of the single electron transfer (SET) photochemistry of *N*-alkylphthalimides, efforts in our laboratories have focused on developing the preparative potential of inter- and intra-molecular



Scheme 1

reactions of phthalimide acceptor- α-trimethylsilyl electron donor systems.[13–15] In this work,[2–7] we have shown that phthalimides (**1**, Scheme 2) containing tethered α-silyl electron donors undergo intramolecular, photoinduced SET to form zwitterionic biradicals **2** that, through intrachain SET, generate silicon-stabilized 1,ω-zwitterionic biradicals **3**. Silophile induced α-desilylation at the cation radical centers in **3** results in the production of 1,ω-biradicals **4** that undergo C–C bond formation to form cyclic products **5**. By using this mechanistic analysis as a guide, SET promoted photoreactions of diverse types of phthalimide substrates have been devised for the preparation of a variety of *N*-heterocyclic and macrocyclic systems.

In these investigations, we observed that irradiation of *N*-trimethylsilylmethylphthalimide **6** (Y = $SiMe_3$) promotes an excited state reaction involving sequential intramolecular SET-C-to-O trimethylsilyl group migration to form the azomethine

[a]*Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan, 609-735, Korea*
[b]*Department of Chemistry, Hanyang University, Seoul, 133-791, Korea*
[c]*Basic Science Research Institute, Pukyong National University, Busan, 608-735, Korea*
[d]*Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico, 87131, USA. E-mail: ucyoon@pusan.ac.kr, mariano@unm.edu*

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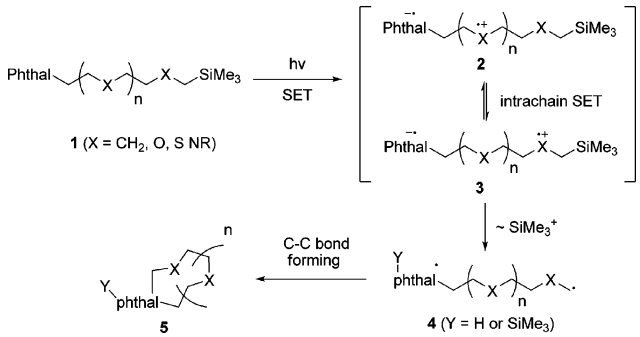


Scheme 2

ylide **7** (Scheme 3). Interestingly, this type of process, involving an analogous C-to-O hydrogen migration, does not take place with *N*-alkylphthalimide analogs **6** (Y = H).[13–15]

Scheme 3

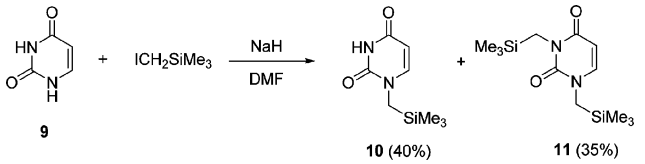
Since other conjugated imides and amides that contain *N*-silylmethyl substitution are transformed to their corresponding azomethine ylides by photoinduced C-to-O silyl migration,[13–17] it is possible that this novel reaction is a general excited state process. Another general excited state process involves excited state [2+2] cycloaddition.[14,18–21] An interesting feature related to [2+2]-cycloaddition reactions, which generate strained cyclobutane ring systems, is the orbital topology allowed,[22–23] and the photoinduced cycloreversion reaction, which cleaves the four-membered ring to produce a pair of olefins. The importance of this reaction is exemplified by the biologically interesting cleavage of photogenerated pyrimidine dimers in DNA.[24–30] It is known that UV induced damage of DNA is caused, in part, by cyclobutane formation through [2+2]-cycloaddition between proximal pyrimidine chromophores. To reverse this damage, enzymes, dubbed photolyases,[28–31] have evolved to promote electron transfer processes to generate cyclobutane radical cation or anion intermediates, which undergo cyclobutane ring splitting.[24–27,32–35]

Our continuing interest in this area stimulated an exploration for photoreactions of substrates that contain structures and substitution patterns that enable the operation of SET promoted, ylide forming silyl migration and other general excited state processes. Below, we describe the results of a photochemical investigation of *N*-trimethylsilylmethyl-uracils and *N*-trimethylsilylmethyl-2-pyridone substances that are capable of participating in a competitive excited state [2+2]-cycloaddition and SET promoted C-to-O silyl migration reactions.

2. Results and discussion

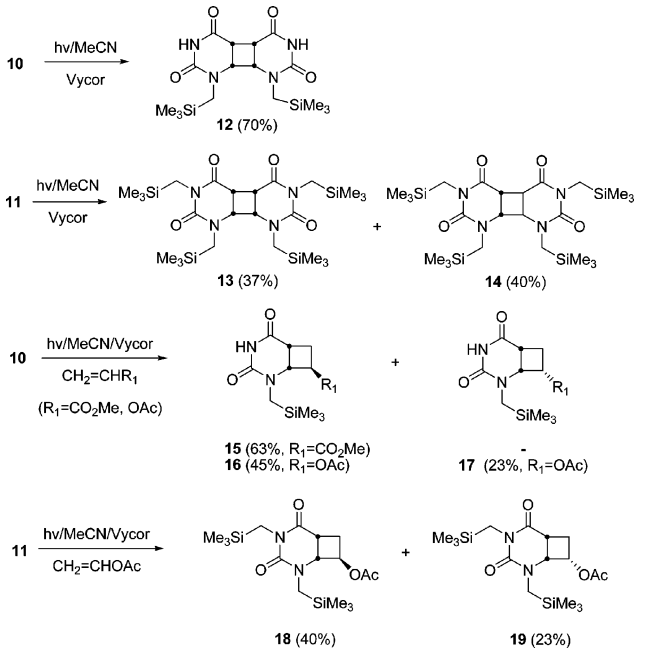
Photoreaction of the *N*-trimethylsilylmethyl-uracils 10 and 11

These studies began with the preparation of the *N*-trimethylsilylmethyl-uracils **10** and **11** *via* reaction of uracil (**9**) with trimethylsilylmethyl iodide promoted by NaH in anhydrous DMF. This process gives both the mono- and bis-trimethylsilylmethyl- substituted uracils **10** (40%) and **11** (35%), respectively (Scheme 4).

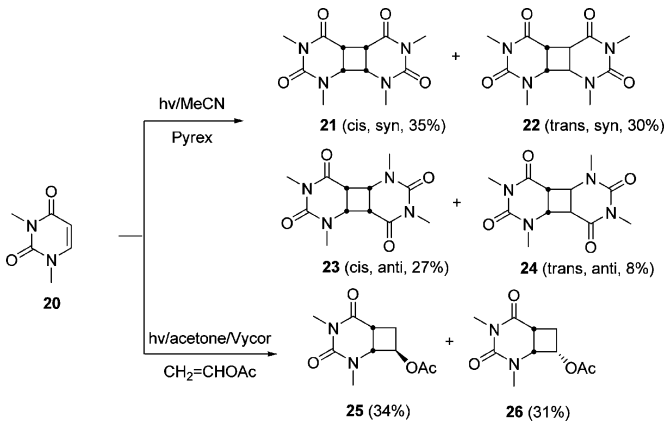


Scheme 4

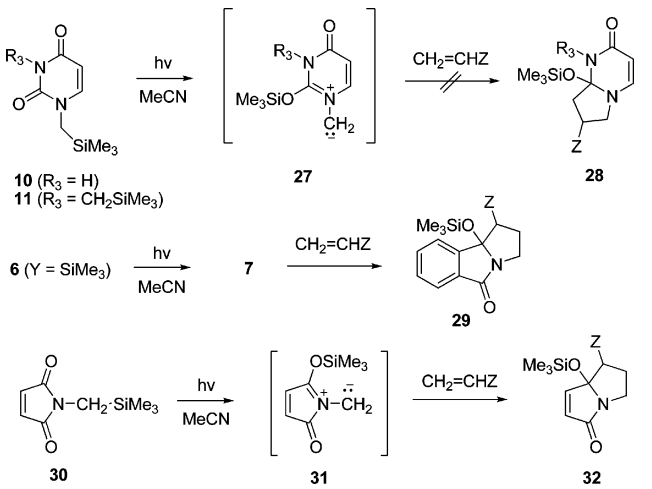
Direct irradiation (Vycor, $\lambda > 220$ nm) of **10** in deoxygenated MeCN leads to efficient production of the *syn*-[2+2] dimer **12** (70%) as the major product (Scheme 5 and 6). Similarly, irradiation of **11** under the same conditions gives rise to a mixture of the *syn*- and *anti*-diastereomeric cycloadducts **13** and **14** (77%). Photoreactions of **10** in MeCN containing methyl acrylate (0.1 M) and vinyl acetate (10–20 mM) produce the respective crossed [2+2] cycloaddition products **15** (63%), and **16** and **17** (68%). The photoreaction of bis-trimethylsilylmethyl uracil **11** in MeCN in the presence of vinyl acetate also generates the corresponding cycloadducts **18** and **19** (63%). Assignment of regiochemistry and stereochemistry to cycloadducts **12–19** was made on the basis of their characteristic ^{1}H- and ^{13}C-NMR properties and comparisons with those of closely related 1,3-dimethyluracil derived photocycloadducts **21–26** (Scheme 6).[36–37] Interestingly, the ^{1}H-NMR spectrum of the symmetric dimer **12** contains an AB quartet (3.45 and 4.06 ppm) that corresponds to CH_2SiMe_3 protons, which are apparently rendered non-equivalent as a consequence of restricted rotation about the N–C bond This phenomenon is a likely result of steric effects caused by the location of the



Scheme 5



Scheme 6



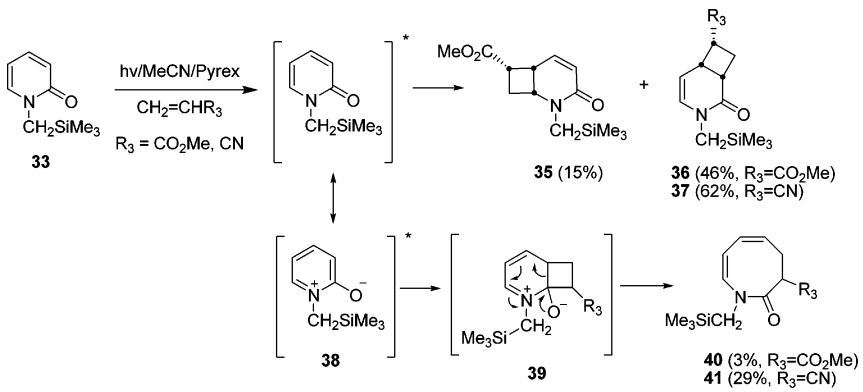
Scheme 7

CH_2SiMe_3 groups in the crowded environment of the *syn*-tricyclic ring system. This behavior is also seen in the ^{1}H-NMR spectra of structurally similar substances (see supporting information†). For instance, dimer **13** which has two different kinds of methylene protons associated with the two sets of CH_2SiMe_3 groups, has a spectrum in which one set of methylene protons appear as a singlet at 3.28 ppm as a consequence of their chemical equivalence and another set of CH_2SiMe_3 protons that resonate as an AB quartet.

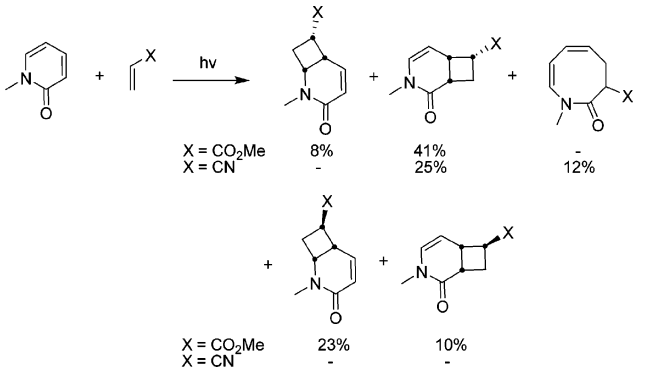
At the outset of this effort, we anticipated that incorporation of *N*-silylmethyl moieties in place of *N*-methyl groups on the uracil ring system would enable the operation of excited state SET-promoted C-to-O silyl migration leading to the formation of transient azomethine ylides **27** (Scheme 7), as occurs in the case with other conjugated imides (*e.g.*, *N*-trimethylsilylmethylphthalimide **6** (Y = $SiMe_3$)[13,15] and *N*-trimethylsilylmethylmaleimide **30**[16]). However, as is demonstrated by the results outlined above, irradiation of the *N*-trimethylsilylmethyl substituted uracils **10** and **11** fails to produce ylide intermediate **27**, which would have participated in ready dipolar cycloaddition reactions with the olefinic dipolarophiles to form pyrrolizidines **28**. Instead, [2+2]-cycloaddition occurs selectively in the excited states of these substrates to produce photodimers **12–14** and **15–19**.

Photoreactions of *N*-trimethylsilylmethyl-2-pyridone (33) and *N*-trimethylsilylmethy-2-pyrrolidinone (34)

Photochemical reactions of *N*-trimethylsilylmethyl-2-pyridione (**33**),[17] prepared by reaction of trimethylsilymethyl iodide with 2-hydroxypyridine, in MeCN solutions containing either methyl acrylate or acrylonitrile take place in a qualitatively similar manner to those of the *N*-trimethylsilylmethyl uracils **10** and **11**. In contrast to the results of its thermal reaction,[17] irradiation of an MeCN solution of **33** containing methyl acrylate induces production of the crossed [2+2] cycloadducts **35** (15%) and **36** (46%), along with eight-member ring dienamide **40** (3%) (Scheme 8). The latter substance arises by way of cyclobutane ring formation through [2+2]-cycloaddition of the acrylate ester across the C_1–C_2 positions of the 2-pyridone ring system followed by cyclohexadiene-to-hexatriene like electrocyclic ring opening. In addition, irradiation of **33** in MeCN solutions containing acrylonitrile leads to the formation of a similar product spectrum including **37** (62%) and **41** (29%). Assignments of photoproduct structures and stereochemistry of **35–37** and **40–41** are mainly based upon comparisons of their spectroscopic data with those of previously characterized photoproducts previously generated in



Scheme 8



Scheme 9

closely related reactions of *N*-methyl-2-pyridone with alkenes[38–40] (Scheme 9).

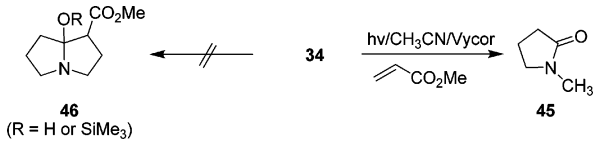
As part of an investigation exploring novel routes for the synthesis of retronecine derivatives (**42**, Scheme 10), Vedejs and his co-workers observed that azomethine ylide **44** formation takes place when *N*-[(trimethylsilyl)methyl] pyrrolidinone **34** is sequentially treated with methyl triflate and CsF.[41–42] The ylide **44**, formed in this manner, was trapped with methyl acrylate to generate the pyrrolizidine product **42** (Scheme 10).

In contrast to this chemistry, the photoreaction of **34**, induced by irradiation of a MeCN solution containing methyl acrylate (0.1 M) and LiCl, does not form a dipolar cycloadduct **46** (Scheme 11) *via* an intermediate ylide. Instead, this process only generates the desilylation product *N*-methylpyrrolidinone (**45**) in a 77% yield (Scheme 11). Although the desilylation process observed to place in this reaction is reminiscent of other photoreactions in which azomethine ylides serve as intermediates,[13] the absence of a dipolarophile-trapping product, such as **46**, suggests that C-to-O silyl migration does not occur in the excited state of **34**.

The results described above show that excited state photochemical processes involving C-to-O silyl migration, which are observed in diverse *N*-trimethylsilylmethyl substituted conjugated imides and amides,[13,15,16] do not compete with [2+2] photocycloaddition processes in similarly substituted uracils and 2-pyridones and with desilylation of 2-pyrrolidinones.

Photocycloreversion reactions of the [2+2] cycloadducts

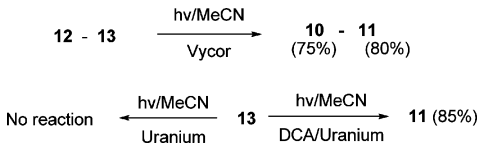
As described above, photochemically induced cycloreversion of cyclobutane ring containing dimeric uracil derivatives is a biologically relevant process, owing to its relationship to the action of photolyases that catalyze the cleavage of cyclobutane pyrimidine dimers formed by the photoinduced [2+2]-cycloaddition between adjacent pyrimidine bases within DNA sequences. The excited state processes that repair photodamaged DNA are believed to proceed through SET pathways.[24–35] Thus, we believed that an



Scheme 11

investigation of factors governing the efficiencies of electron transfer promoted cycloreversion reactions of cyclobutane containing dimers of uracil and related substances could provide interesting information about DNA photorepair.

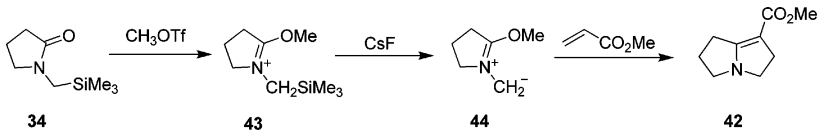
To evaluate the role, if any, played by the *N*-trimethylsilylmethyl group in photochemical cycloreversion reactions of the [2+2]-cycloadducts, photoreactions of the *syn*-uracil dimers **12** and **13** in MeCN were carried out. Irradiation (Vycor) of the photodimer **12** and **13** gives rise to cycloreversion to produce the respective uracils **10** and **11** in high yields (Scheme 12). When uranium grass filtered light ($\lambda > 330$ nm) is used along with the SET-photosensitizer 9,10-dicyanoanthracene (the light absorbing species), the tetra-trimethylsilylmethyl substituted uracil dimer **13** reacts to generate uracil **11**. On the other hand, as expected uranium glass filtered light irradiation of **13** without the SET-photosensitizer induces no cycloreversion reaction to give **11**.



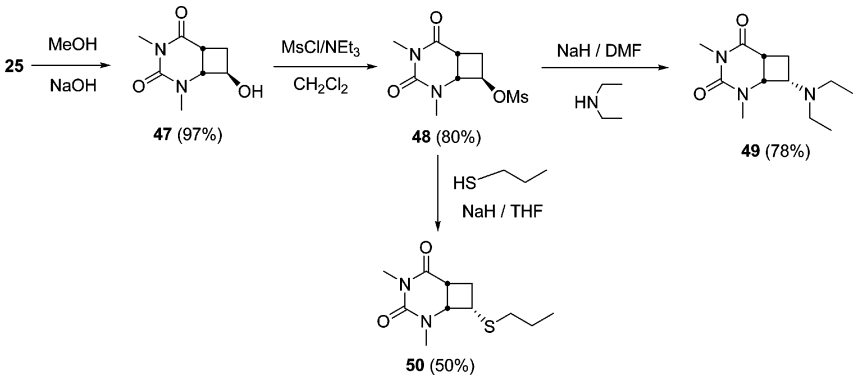
Scheme 12

Another set of substrates explored in this effort contain the diverse heteroatom substituted, 1,3-dimethyluracil based-cyclobutanes **25**,[36–37] **49** and **50**. As shown in Scheme 6, acetoxy-substituted dimethyluracil [2+2]-cycloadduct **25** can be prepared by using a well known procedure.[17] Hydrolysis of the acetate ester moiety in **25** using methanolic sodium hydroxide forms the alcohol **47**, which undergoes a reaction with methanesulfonyl chloride in the presence of triethylamine to form the mesylate **48** (Scheme 13). The mesylate can be used to introduce various heteroatom containing side chains to the uracil [2+2]-adduct, as exemplified by the amine group in **49** and thioether in **50**.

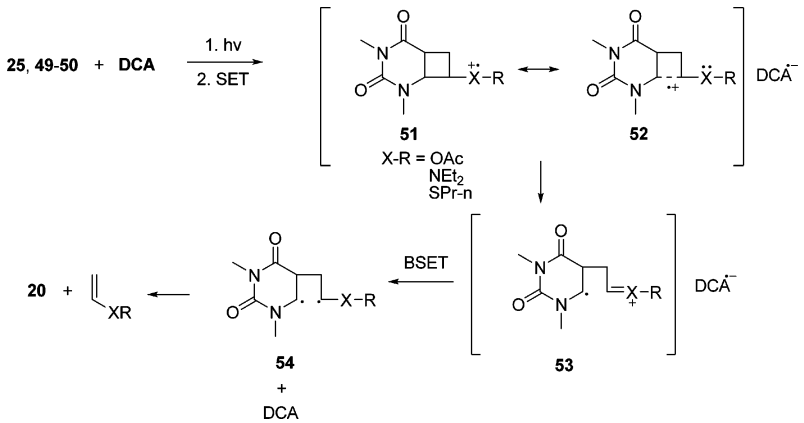
Irradiation (uranium) of cyclobutanes **25**, **49** and **50** in MeCN solutions containing DCA were carried out, while monitoring the formation of 1,3-dimethyl-uracil **20** as a function of irradiation time. The results arising from monitoring these reactions are compiled in Table 1. Irradiation of solutions containing DCA and cyclobutanes **25**, **49** and **50** promotes efficient formation



Scheme 10



Scheme 13



Scheme 14

Table 1 Photocycloreversion reactions of cyclobutane derivatives **25**, **49** and **50** to form **20**[a]

	Yields of **20** (presence of DCA)		
Irradiation time (h)	**25**	**49**	**50**
1	—	70	60
3	5	90	80
4	10	100	90
6	30	—	100
10	50	—	—

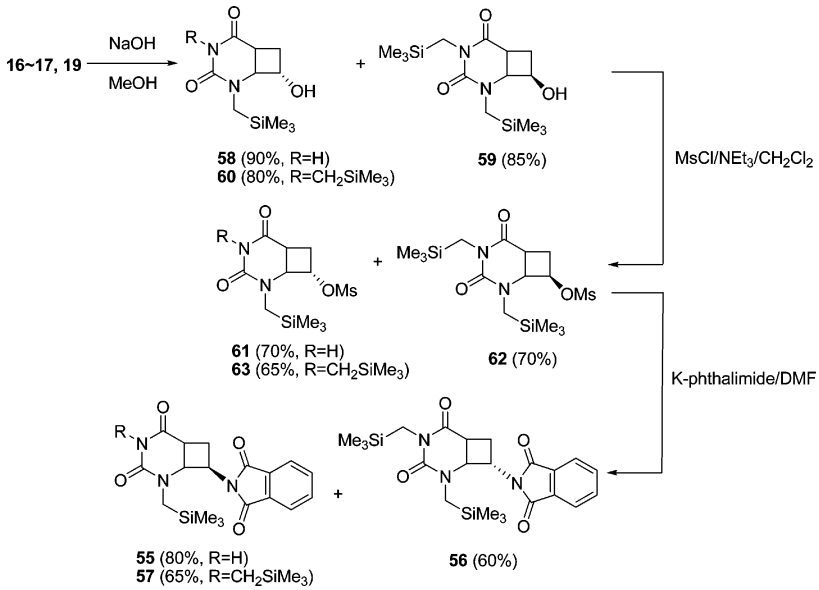
[a] Irradiation of photoreactant (2 mM) containing DCA (4 mM) was carried out.

of **20**. While amine and thioether substituted substrates **49** and **50** are completely converted to **20** during a 4–6 h, irradiation period, only 50% of the acetoxy derivative **25** is transformed to **20** after 10 h of irradiation. The different photoreversion reaction efficiencies reflected by the percent conversion *vs.* irradiation time data correlates with oxidation potentials of pendent heteroatom electron donor groups that are linked to the cyclobutane rings in **25**, **49** and **50**. Based on the inverse relationship that exists between the rates of excited state electron transfer and oxidation potentials of donors,[43–48] it appears that the mechanistic pathways followed in cycloreversion of the amine ($E_{1/2}(+)$ *ca.* 0.6 V *vs.* SCE) and thioether ($E_{1/2}(+)$ *ca.* 1.4 V *vs.* SCE) substrates begin with SET from the heteroatom centers in **49** and **50** to the DCA singlet excited state ($E_{1/2}^{S1}(-)$ *ca.* 2.8 V *vs.* SCE) (Scheme 14). This is followed by cyclobutane ring cleavage, back electron transfer to the DCA anion radical and 1,4-biradical fragmentation. Owing to the excessively large oxidation potential of the acetoxy moiety ($E_{1/2}(+) > 2.5$ V *vs.* SCE), either a different, less efficient, non-SET mechanistic route operates in the cycloreversion reaction of **25** or the initial rate of SET from **25** to DCA is slow compared with the decay of the DCA singlet excited state.

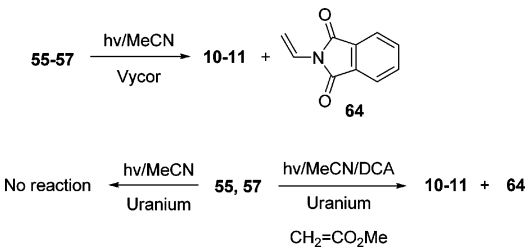
Photochemistry of phthalimide substituted cyclobutanes

The *N*-trimethylsilylmethyl-substituted cyclobutane tethered phthalimides **55–57** were synthesized *via* routes starting with the cyclobutanes **16** and **18–19**. Treatment of these substances with methanolic sodium hydroxide affords the corresponding alcohols **58–60**, which undergo sequential *O*-mesylation and *N*-alkylation with potassium phthalimide to produce the respective cyclobutyl ring linked phthalimides **55–57** (Scheme 15).

Reactions of **55–57** in MeCN solutions induced by 1 h irradiation with Vycor filtered light (100% reactant conversions) yield the trimethylsilylmethyl group containing uracils **10** and **11** along with *N*-vinylphthalimide **64** (Scheme 16). In addition, 15 h irradiation (uranium) of MeCN solutions of **55** and **57**, containing DCA



Scheme 15



Scheme 16

(0.5 mM) and methyl acrylate (20 mM) DCA, brings about clean formation of **10**, **11** and **64**.

3. Conclusions

In this investigation, the photochemical reactivity of a diverse variety of *N*-trimethylsilylmethyl substituted uracil, 2-pyridone and 2-pyrrolidone derivatives has been explored. Although the excited states of the *N*-trimethylsilylmethyl containing substrates do not undergo sequential SET - C-to-O silyl migration processes, they do participate in efficient [2+2]-cycloaddition leading to cyclobutane containing products. Orbital topology allowed photocycloreversion reactions of uracil derived cyclobutanes, promoted by direct irradiation, resulted in efficient formation of the corresponding uracils. A novel finding in this effort is that the DCA-photosensitized SET reactions of amine and thioether containing uracil [2+2] cycloadducts take place efficiently by way of an interesting SET promoted pathway to form uracil and alkenes. Finally, in the cases of *N*-trimethylsilylmethyl substituted uracil cyclobutylphthalimides, highly efficient excited state cycloreversion takes place to generate uracil and *N*-vinylphthalimide upon either direct or SET photosensitized irradiation.

4. Experimental

General Procedure

^{1}H- and ^{13}C-NMR spectra were recorded using $CDCl_3$ solutions unless otherwise noted and chemical shifts are reported in parts per million relative to $CHCl_3$ (^{1}H-NMR 7.24 ppm and ^{13}C-NMR 77.0 ppm) as an internal standard. IR spectral bands are reported in cm^{-1}. Preparative photochemical reactions were conducted with an apparatus consisting of a 450 W Hanovia medium pressure mercury lamp surrounded by a Vycor, Pyrex or Uranium glass filter in a water-cooled quartz immersion well immersed in the solution being irradiated. Photolysis solutions were purged with nitrogen before and during irradiation. The photolysates were concentrated *in vacuo* giving residues which were subjected to silica gel column chromatography. High resolution (HRMS) mass spectra were obtained by using electron impact ionization unless otherwise noted. All new compounds described are isolated as oils in >90% purity (by NMR analysis) unless noted otherwise.

Preparation of *N*-trimethylsilylmethyl substituted uracils 10 and 11

A solution of uracil (**9**) (4.7 g, 42 mmol) in anhydrous DMF (50 mL) containing NaH (2 g, 83 mmol) was stirred at 0 °C for 2 h. Trimethylsilylmethyl iodide (10 g, 47 mmol) was added dropwise and the resulting solution was stirred for 10 h at 110 °C. Concentration of solution *in vacuo* gave a residue which was diluted with $CHCl_3$ and washed with water. The organic layer was dried, filtered and concentrated *in vacuo* to afford a residue which was subjected to silica gel chromatography (1 : 4 EtOAc–hexane) to afford **10** (3.3 g, 40%) and **11** (4.1 g, 35%).

10: ^{1}H-NMR 0.12 (s, 9H, $SiMe_3$), 3.32 (s, 2H, CH_2SiMe_3), 5.67 (d, 1H, J = 7.8 Hz, COCH), 7.08 (d, 1H, J = 7.8 Hz, NCH); ^{13}C-NMR –2.3 ($SiMe_3$), 40.3 (CH_2SiMe_3), 101.6 (COCH), 145.0 (NCH), 151.0 and 164.2 (CO); IR (KBr) 1690 (amide), 1450

(C═C); LRMS (EI) *m/z* (rel. intensity) 198 (M^+, 36), 183 (100), 73 (11); HRMS (EI) *m/z* 198.0761 ($C_8H_{14}N_2O_2Si_1$ requires 198.0825).

11: ^{1}H-NMR 0.04 (s, 9H, $SiMe_3$), 0.08 (s, 9H, $SiMe_3$), 3.33 (s, 2H, CH_2SiMe_3), 3.50 (s, 2H, CH_2SiMe_3), 5.67 (d, 1H, J = 7.8 Hz, COCH), 7.02 (d, 1H, J = 7.8 Hz, NCH); ^{13}C-NMR −2.2 and −1.6 ($SiMe_3$), 32.4 (s, 2H, CH_2SiMe_3), 41.3 (CH_2SiMe_3), 100.5 (COCH), 141.6 (NCH), 151.2 and 162.8 (CO); IR (KBr) 1690 (amide), 1450 (C═C); LRMS (EI) *m/z* (rel. intensity) 284 (M^+, 32), 269 (100), 243 (8), 183 (7), 167 (6), 99 (5); HRMS (EI) *m/z* 284.1379 ($C_{12}H_{24}N_2O_2Si_2$ requires 284.1376).

Irradiation of *N*-trimethylsilylmethyl uracil derivatives 10 and 11; formation of photodimers 12 and 13–14

Independent solutions of uracils **10** (300 mg, 1.5 mmol), **11** (300 mg, 1.0 mmol) in MeCN (200 mL) were irradiated by using Vycor glass filtered light for 1 h (100% conversion). The photolysates were concentrated *in vacuo* to give residues which were subjected to silica gel chromatography (1 : 1 EtOAc–hexane) to afford **12** (415 mg, 70%) from **10**, and **13** (210 mg, 37%) and **14** (227 mg, 40%) from **11**.

12: ^{1}H-NMR 0.07 (s, 18H, $SiMe_3$), 2.37 and 3.16 (two d, 2H, J = 15.1 Hz, two diastereotopic CH_2TMS), 2.52 (s, 2H, NH), 3.45 (d, 4H, J = 8.4 Hz, COCH), 4.06 (d, 4H, J = 8.4 Hz, NCH); ^{13}C-NMR (DMSO) −0.9 ($SiMe_3$), 38.4 (*C*HCO), 40.4 (CH_2SiMe_3), 60.5 (NCH), 151.3 and 169.9 (amide, NCO); IR (KBr) 1694 (amide, NCO); LRMS (EI) *m/z* (rel. intensity) 396 (M^+, 5), 381 (52), 271 (550), 183 (100), 73 (32); HRMS (EI) *m/z* 396.1644 ($C_{16}H_{28}N_4O_4Si_2$ requires 396.1649).

13: ^{1}H-NMR 0.02 (s, 18H, $SiMe_3$), 0.09 (S, 18H, $SiMe_3$), 2.16 and 3.34 (two d, 4H, J = 15.1 Hz, two diastereotopic CH_2TMS), 3.28 (s, 4H, CH_2SiMe_3), 3.69–3.73 (m, 2H, COCH), 3.92–3.97 (m, 2H, NCH); ^{13}C-NMR −2.0 ($SiMe_3$), 1.1 ($SiMe_3$), 33.6 (*C*HCO), 40.0 (CH_2SiMe_3), 40.6 (CH_2SiMe_3), 55.7 (NCH), 152.9 and 165.5 (amide, NCO); IR (KBr) 1694 (amide, NCO); LRMS (EI) *m/z* (rel. intensity) 568 (M^+, 0.2), 553 (16), 357 (42), 283 (37), 269 (99), 73 (100); HRMS (EI) *m/z* 568.2751 ($C_{24}H_{48}N_4O_4Si_4$ requires 568.2753).

14: ^{1}H-NMR ($CDCl_3$) 0.05 (s, 9H, $SiMe_3$), 0.07 (s, 9H, $SiMe_3$), 0.08 (s, 9H, $SiMe_3$), 0.10 (s, 9H, $SiMe_3$), 2.26 and 3.48 (two d, 2H, J = 15.2 Hz, two diastereotopic CH_2TMS), 3.36 and 3.49 (two d, 2H, J = 15.2 Hz, two diastereotopic CH_2TMS), 3.54 (d, 2H, J = 8.2 Hz, COCH), 3.75 (d, 2H, J = 8.2 Hz, NCH); ^{13}C-NMR −1.0 ($SiMe_3$), −1.1 ($SiMe_3$), 33.2 *C*HCO), 40.0 (CH_2SiMe_3), 40.9 (CH_2SiMe_3), 60.5 (NCH), 151.8, and 168.0 (amide, NCO); LRMS *m/z* (rel, intensity) 568 (M^+,0.8), 553 (14), 551 (30), 355 (56), 283 (47), 269 (100), 73(34); HRMS *m/z* 568.2781 ($C_{24}H_{48}N_4O_4Si_4$ requires 568.2753).

Irradiation of trimetylsilylmethyl uracil 10 in the presence of methyl acrylate; formation of [2+2] photoadduct 15

A solution of uracil **10** (300 mg, 1.5 mmol) in MeCN (150 mL) containing methyl acrylate (1.4 g, 15 mmol) was irradiated by using Vycor glass filtered light for 1 h (100% conversion). The photolysate was concentrated *in vacuo* to give a residue which was subjected to silica gel chromatography (1 : 1 EtOAc–hexane) to afford **15** (268 mg, 63%).

15: ^{1}H-NMR 0.09 (s, 9H, $SiMe_3$), 2.44 and 3.27 (two d, 2H, J = 15.5 Hz, two diastereotopic CH_2TMS), 2.40–2.48 (m, 2H, $CHCH_2$), 3.24–3.32 (m, 2H, $COCHCH_2$ and $CHCO_2CH_3$), 3.72 (s, 3H, CO_2CH_3), 4.12 (t, 1H, J = 8.5 Hz, NCH), 8.55 (s, 1H, NH); ^{13}C-NMR −1.1 ($SiMe_3$), 24.9 ($CHCH_2$), 36.3 (*C*HCO), 37.8 ($CHCO_2CH_3$), 46.2 (CH_2SiMe_3), 52.7 (CO_2CH_3), 55.8 (NCH), 152.6 ($CONCH_2SiMe_3$), and 172. 1 (CO_2CH_3), 173.1 (NHCO); IR (KBr) 1690 (amide); LRMS (EI) *m/z* (rel. intensity) 284 (M^+, 19), 269 (85), 225 (42), 198 (29), 183 (100), 73 (56), 55 (29); HRMS (EI) *m/z* 284.1187 ($C_{12}H_{20}N_2O_4Si$ requires 284.1192).

Irradiation of trimethylsilylmethyl uracil derivatives (10–11) in the presence of vinyl acetate; formation of [2+2] photoadducts 16–19

Independent solutions of the uracils **10** (300 mg, 1.5 mmol) and **11** (300 mg, 1.5 mmol) in MeCN (150 mL) containing vinyl acetate (260 mg, 3 mmol for **10**, 170 mg, 2 mmol for **11**) were irradiated by using Vycor filtered light for 1 h (93% conversion of **10**) and 100% conversion of **11**). The photolysates were concentrated *in vacuo* to give residues which were subjected to silica gel chromatography (1 : 1 EtOAc–hexane) to afford **16** (180 mg, 45%) and **17** (90 mg, 23%) from **10**, and **18** (150 mg, 40%) and **19** (85 mg, 23%) from **11**.

16: ^{1}H-NMR 0.04 (s, 9H, $SiMe_3$), 2.01 (s, 3H, CH_3CO), 2.43 and 3.21 (two d, 2H, J = 15.0 Hz, two diastereotopic CH_2TMS), 2.55–2.67 (m, 2H, $CHCH_2$), 3.18– 3.30 (m, 1H, COCH), 3.78–3.86 (m, 1H, NCH), 4.95–5.08 (m, 1H, $CHOCOCH_3$), 9.01 (s, 1H, NH); ^{13}C-NMR −1.7 ($SiMe_3$), 20.5 (CH_3CO), 29.4 ($CHCH_2$), 31.8 (CH_2SiMe_3), 38.1 (*C*HCO), 59.1 (NCH), 73.3 ($CHOCOCH_3$), 151.3 ($CONCH_2SiMe_3$), 169.3 ($COCH_3$), 171.2 (NHCO); IR (KBr) 1690 (amide); LRMS (EI) *m/z* (rel. intensity) 284 (M^+, 1.3), 269 (40), 198 (50), 183 (100), 169 (15), 74 (89), 62 (25); HRMS (EI) *m/z* 284.1195 ($C_{12}H_{20}N_2O_4Si$ requires 284.1192).

17: ^{1}H-NMR 0.02 (s, 9H, $SiMe_3$), 1.99 (s, 3H, $OCOCH_3$), 2.20 and 3.23 (two d, 2H, J = 15.4 Hz, two diastereotopic CH_2TMS), 2.65–2.75 (m, 2H, $CHCH_2$), 3.25–3.31 (m, 1H, COCH), 3.96–4.04 (m, 1H, NCH), 5.15–5.25 (m, 1H, $CHOCOCH_3$), 8.83 (s, 1H, NH); ^{13}C-NMR −1.7 ($SiMe_3$), 20.5 (CH_3CO), 29.8 ($CHCH_2$), 36.8 (CH_2SiMe_3), 37.9 (*C*HCO), 55.0 (NCH), 72.0 ($CHOCOCH_3$), 151.3 ($CONCH_2SiMe_3$), 171.7 ($COCH_3$), 171.6 (NHCO); IR (KBr) 1690 (amide); LRMS (EI) *m/z* (rel. intensity) 284 (M^+, 1.3), 269 (40), 198 (50), 183 (100), 169 (15), 74 (89), 62 (25); HRMS (EI) *m/z* 284.1195 ($C_{12}H_{20}N_2O_4Si$ requires 284.1192).

18: H-NMR 0.04 (s, 9H, $SiMe_3$), 0.08 (s, 9H, $SiMe_3$), 2.06 (s, 3H, $COCH_3$), 2.14–2.30 (m, 2H, $CHCH_2$), 2.57–2.69 (m, 1H, $CHOCOCH_3$), 2.51 and 3.26 (two d, 2H, J = 15.3 Hz, two diastereotopic CH_2TMS), 3.33 and 3.44 (two d, 2H, J = 15.3 Hz, two diastereotopic CH_2TMS), 3.75–3.83 (m, 1H, COCH), 4.95–5.05 (m, 1H, NCH); ^{13}C-NMR −1.6 ($SiMe_3$), 20.8 ($COCH_3$), 29.2 ($CHCH_2$), 30.0 (CH_2SiMe_3), 32.0 (CH_2SiMe_3), 40.2 (*C*HCO), 59.1 (NCH), 74.2 ($CHOCOCH_3$), 151.8 ($CONCH_2SiMe_3$), 169.2 ($COCH_3$), 169.5 (NHCO); IR (KBr) 1690 (amide); IR (KBr) 1690 (amide); LRMS (EI) *m/z* (rel. intensity) 370 (M^+, 3.6), 355 (51), 327 (5), 283 (67), 269 (100), 210 (11), 183 (8), 73 (18); HRMS (EI) *m/z* 370.1732 ($C_{16}H_{32}N_2O_4Si_2$ requires 370.1744).

19: ^{1}H-NMR 0.08 (s, 9H, $SiMe_3$), 0.09 (s, 9H, $SiMe_3$), 1.94 (s, 3H, $COCH_3$), 2.25 and 3.24 (two d, 2H, J = 15.3 Hz, two

diastereotopic CH_2TMS), 2.46–2.59 (m, 2H, CHCH_2), 2.68–2.85 (m, 1H, CHOCOCH$_3$), 3.33 and 3.46 (two d, 2H, J = 15.3 Hz, two diastereotopic CH_2TMS), 3.95–4.02 (m, 1H, COCH), 5.20–5.30 (m, 1H, NCH); ^{13}C-NMR –1.6 (SiMe$_3$), 20.8 (*C*OCH$_3$), 30.3 (CH*C*H$_2$), 32.0 (CH$_2$SiMe$_3$), 32.4 (CH$_2$SiMe$_3$), 39.7 (*C*HCO), 57.8 (NCH), 73.7 (*C*HOCOCH$_3$), 151.9 (*C*ONCH$_2$SiMe$_3$), 169.5 (COCH$_3$), 169.9 (NHCO); IR (KBr) 1690 (amide); LRMS (EI) m/z (rel. intensity) 370 (M$^+$, 2), 355 (47), 327 (3), 283 (66), 269 (100), 210 (7), 183 (4), 73 (11); HRMS (EI) m/z 370.1732 ($C_{16}H_{32}N_2O_4Si_2$ requires 370.1744).

Irradiation of *N*-trimethylsilylmethyl-2-pyridone 33 in the presence of methyl acrylate; formation of 35, 36 and 40

A solution of pyridone **33** (500 mg, 3 mmol) in MeCN (200 mL) containing methyl acrylate (2.5 mL, 28 mmol) was irradiated by using Pyrex filtered light for 11 h (86% conversion). The photolysate was concentrated *in vacuo* to give a residue which was subjected to silica gel chromatography (ether) to afford **35** (90 mg, 15%), **36** (270 mg, 46%) and **40** (20 mg, 3%).

35: ^{1}H-NMR –0.01 (s, 9H, SiMe$_3$), 2.40–2.49 (m, 1H, CHCH_2), 2.59–2.67 (m, 1H, CHCH_2), 2.72 (q, 2H, J = 7.5 Hz, CH_2SiMe$_3$), 3.13–3.20 (m, 1H, CH(CO$_2$CH$_3$)), 3.49–3.60 (m, 1H, CHCH(CO$_2$CH$_3$)), 3.61 (s, 3H, CH$_3$), 3.77–3.83 (m, 1H, CHNCO), 5.83–5.86 (m, 1H, COCH=CH), 6.17–6.28 (m, 1H, COCH=CH); ^{13}C-NMR –1.6 (SiMe$_3$), 32.4 (CH$_2$), 37.3 (SiCH$_3$), 37.4 (CH$_3$), 39.1, 51.6 and 51.7 (CH), 125.7 and 135.5 (CH, alkenyl), 161.2 and 171.3 (C=O).

36: ^{1}H-NMR –0.07 (s, 9H), 2.34–2.41 (m, 1H, CHCH_2), 2.61–2.74 (m, 1H, CHCH_2), 2.86 (AB q, 2H, J = 7.6 Hz, CH_2SiMe$_3$), 3.03–3.12 (m, 1H, CHCO$_2$CH$_3$), 3.27–3.37 (m, 1H, COCH), 3.54 (s, 3H, CH$_3$), 4.61–4.65 (m, 1H, CHCH(CO$_2$CH$_3$)), 5.79–5.81 (m, 1H, CH=CHN), 7.12 (m, 1H, CH=CHN); ^{13}C-NMR –2.1 (SiMe$_3$), 28.3 and 38.2 (CH$_2$), 34.4 (CH), 37.5 (CH$_3$), 41.8 and 51.2 (CH), 102.0 and 131.6 (CH, alkenyl), 166.9 and 171.9 (C=O).

40: ^{1}H-NMR –0.01 (s, 9H, SiMe$_3$), 2.80–2.82 (m, 2H, CH$_2$), 3.13 (AB q, 2H, J = 7.4 Hz, CH_2SiMe$_3$), 3.65 (s, 3H, CH$_3$), 4.33 and 4.35 (dd, 1H, J = 3.0 Hz, J = 4.8 *Hz*, CHCO$_2$CH$_3$), 5.54–5.58 (m, 1H, CH$_2$CH=CH), 5.64–5.69 (m, 1H, CH$_2$CH=CH), 5.73–5.78 (m, 1H, NCH=CH), 5.85 (d, 1H, J = 4.6 Hz, NCH=CH); ^{13}C-NMR –1.8 (SiMe$_3$), 31.0 and 39.6 (CH$_2$), 45.2 and 52.2 (CH), 118.9, 121.5, 128.9 and 135.5 (CH, alkenyl), 169.4 and 170.2 (C=O).

Irradiation of *N*-trimethylsilylmethyl-2-pyridone 33 in the presence of methyl acrylate and LiCl

A solution of pyridone **33** (400 mg, 2 mmol) in acetone (100 mL) containing methyl acrylate (950 mg, 11 mmol) and LiCl (0.2 g, 0.4 mmol) was irradiated by using Pyrex filtered light for 16 h (75% conversion). The photolysate was concentrated *in vacuo* to give a residue which was subjected to silica gel chromatography (ether) to afford **35** (86 mg, 20%), **36** (70 mg, 16%) and **40** (33 mg, 8%).

Irradiation of *N*-trimethylsilylmethyl-2-pyridone 33 in the presence of acrylonitrile; formation of 37 and 41

A solution of pyridone **33** (500 mg, 3 mmol) in MeCN (200 mL) containing acrylonitrile (2 mL, 30 mmol) was irradiated by using Pyrex filtered light for 17 h (80% conversion). The photolysate was concentrated *in vacuo* to give a residue which was subjected to silica gel chromatography (ether) to afford **37** (320 mg, 62%) and **41** (150 mg, 29%).

37: ^{1}H-NMR 0.00 (s, 9H), 2.63–2.73 (m, 2H, CH$_2$), 2.96 (AB q, 2H, J = 15.0 Hz, CH_2SiMe$_3$), 3.21–3.27 (m, 1H, CHCN), 3.33–3.43 (m, 2H, CH_2CHCN), 4.93–4.96 (m, 1H, CHCO), 6.04–6.07 (m, 1H, CH=CHN), 7.10 (m, 1H, CH=CHN); ^{13}C-NNR –2.1 (SiMe$_3$), 27.2, 35.7 and 36.9 (CH), 30.7 and 38.4 (CH$_2$), 101.3 and 132.6 (CH, alkenyl), 118.8 (CN), 165.5 (C=O); IR (KBr) 3050 and 2235 (CN stretching), 1640 (C=O stretching).

41: ^{1}H-NMR 0.07 (s, 9H, SiMe$_3$), 2.87–2.90 (m, 2H, CH$_2$), 2.99 (AB q, 2H, J = 15.0 Hz, CH_2SiMe$_3$), 4.50 (t, 1H, J = 4.8 Hz, CHCN), 5.57–5.70 (m, 3H), 5.82 (d, 1H, J = 4.6 Hz, NCH=CH); ^{13}C-NMR –2.0 (SiMe$_3$), 32.7 (CH), 33.4 and 39.9 (CH$_2$), 117.5 (CN), 111.9, 122.1, 128.1 and 128.8 (CH, alkenyl), 164.8 (C=O); IR (KBr) 3050 and 2250 (CN stretching), 1660 (C=O stretching).

Irradiation of *N*-trimethylsilylmethyl-2-pyrrolidone 34

A solution of pyrrolidone **34** (200 mg, 1 mmol) in MeCN (100 mL) containing methyl acrylate (1 g, 12 mmol) was irradiated by using Vycor filtered light for 17 h (70% conversion). The photolysate was concentrated *in vacuo* to give a residue which was subjected to silica gel chromatography (1 : 5 EtOAc–hexane) to afford **45** (62 mg, 77%).

Irradiation of uracil photodimers 12 and 13; formation of uracil monomer 10 and 11

Independent solutions of uracil dimers **12** (100 mg, 0.3 mmol) and **13** (100 mg, 0.2 mmol) in MeCN (200 mL) were irradiated by using Vycor filtered light for 1 h (100% conversion). The photolysates were concentrated *in vacuo* to give residues which were subjected to silica gel chromatography (1 : 1 EtOAc–hexane) to afford **10** (74 mg, 75%) and **11** (77 mg, 80%) respectively.

Irradiation of photodimer 13 in the presence of DCA

A solution of dimer **13** (100 mg, 0.2 mmol) in MeCN (200 mL) containing DCA (15 mg, 0.1 mmol) was irradiated by using uranium glass filtered light for 15 h (60% conversion). The photolysate was concentrated *in vacuo* to give a residue which was subjected to silica gel chromatography (1 : 1 EtOAc–hexane) to afford **11** (49 mg, 85%).

Preparation of uracil based cyclobutylalcohol 47

A solution of **25** (0.5 g, 2 mmol) in MeOH (20 mL) containing 0.1 M methanolic sodium hydroxide (0.9 mL) was stirred at room temperature for 20 min. Concentration of solution *in vacuo* gave a residue which was subjected to silica gel column chromatography (EtOAc) to afford **47** (0.4 g, 97%).

47: ^{1}H-NMR 2.01–2.21 and 2.44–2.56 (m, 2H, CH$_2$), 3.03 (s, 3H, CHNCH_3), 3.14 (s, 3H, CON(CH$_3$)CO), 3.20–3.38 (m, 1H, COCHCH$_2$), 3.60–3.70 (m, 1H, CHNCH$_3$), 4.19–4.31 (m, 1H, CHOH); ^{13}C-NMR 27.9 (CON(*C*H$_3$)CO), 30.5 (CH$_2$), 32.6 (CO*C*), 34.6 (CHN*C*H$_3$), 59.9 (NCH), 73.2 (*C*HOH), 152.5

($NCH_3C(=O)NCH_3$), 171.7 ($N(CH_3)COCH$); IR (KBr) 3200–3600 cm^{-1} (br, OH stretching).

Preparation of uracil based cyclobutyl mesylate 48

A solution of alcohol **47** (1 g, 5.5 mmol) in CH_2Cl_2 (30 mL) containing triethylamine (0.8 g, 8 mmol) was stirred for 30 min at 0 °C. MsCl (0.7 g, 6 mmol) was added dropwise and the resulting solution was stirred for 1 h at 0 °C. Concentration of solution *in vacuo* gave a residue which was diluted with CH_2Cl_2 and washed with water. The organic layer was dried, filtered and concentrated *in vacuo* to afford **48** (1.2 g, 80%).

48: mp 112–113 °C; ^{1}H-NMR: 2.41–2.48 and 2.64–2.68 (m, 2H, $CHCH_2$), 3.00 (s, 3H, OMs), 3.05 (s, 3H, $CHNCH_3$), 3.06 (s, 3H, $CON(CH_3)CO$), 3.32–3.35 (m, 1H, $COCHCH_2$), 3.97–1.02 (m, 1H, $CHNCH_3$), 4.89–4.95 (m, 1H, -CHOMs); ^{13}C-NMR: 28.0 ($CON(CH_3)CO$), 30.2 (CH_2CHOMs), 31.3 ($CHCH_2$), 34.9 ($CHNCH_3$), 38.3 (SO_2CH_3), 58.1 ($N(CH_3)CHCHOMs$), 77.2 (CHOMs), 152.1 (NCON), 169.9 ($CON(CH_3)CH$); IR (KBr) 1700 (C=O stretching), 1375 (S=O asymetric), 1175 (S=O symmetric); LRMS (EI) *m/z* (rel. intensity) 262 (M^+, 1), 183 (12), 162 (6), 141 (17), 140 (100); HRMS (EI) *m/z* 262.0622 ($C_9H_{14}N_2O_5S$ requires 262.0623).

Preperation of uracil based cyclobutyl amine 49

A solution of NaH (0.1 g, 5 mmol) in dry DMF (15 mL) containing diethylamine (1.5 g, 21 mmol) was stirred at 0 °C for 30 min. Mesylate **48** (1.1 g, 4 mmol) in dry DMF (10 mL) was added dropwise and the resulting solution was stirred for 24 h at 60 °C. Concentration of the solution *in vacuo* gave a residue which was subjected to silica gel column chromatography (EtOAc) to afford **49** (0.8 g, 78%).

49: mp 53–54 °C; ^{1}H-NMR: 1.00 (t, 6H, J = 7.1 Hz, CH_2CH_3), 2.12–2.19 and 2.27–2.34 (m, 2H, $CH_2CHN(CH_2CH_3)_2$), 2.59 (q, 4H, J = 7.4 Hz, CH_2CH_3), 3.06 (s, 3H, $CHNCH_3$), 3.14–3.21 (m, 1H, $COCHCH_2$), 3.23 (s, 3H, $CON(CH_3)CH$), 3.28–3.37 (m, 1H, $CHN(CH_2CH_3)_2$), 3.65 (t, 1H, J = 7.6 Hz, $CHNCH_3$); ^{13}C-NMR: 11.1, 27.9, 33.1, 35.9, 42.6, 57.1, 65.1, 152.8, 172.2

Preparation of uracil based cyclobutyl thioether 50

A solution of NaH (10 mg, 0.4 mmol) in THF (10 mL) containing 1-propanethiol (0.2 mL, 2 mmol) was stirred at 0 °C for 30 min. Mesylate **48** (94 mg, 0.4 mmol) in dry THF (10 mL) was added dropwise and the resulting solution was stirred for 24 h at 60 °C. Concentration of the solution *in vacuo* gave a residue which was diluted with ether and washed with water. The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo* to afford a residue which was subjected to silica gel column chromatography (ether) to afford **50** (43 mg, 50%).

50: ^{1}H-NMR: 0.98 (t, 3H, J = 7.4 *Hz*, $SCH_2CH_2CH_3$), 1.52–1.62 (m, 2H, J = 7.2 Hz, $SCH_2CH_2CH_3$), 2.15–2.22 and 2.56–2.63 (m, 2H, CH_2CHS), 2.51 (t, 2H, J = 7.2 Hz, $SCH_2CH_2CH_3$), 3.05 (s, 3H, $CHNCH_3$), 3.23 (s, 3H, $CON(CH_3)CO$), 3.34–3.39 (m, 2H, COCH and CHS), 3.66–3.72 (m, 1H, $N(CH_3)CH$); ^{13}C-NMR: 13.3 (CH_2CH_3), 23.8 (CH_2CH_3), 27.5 ($CON(CH_3)CO$), 30.5 ($CHCH_2$), 35.1 (COCH), 34.2 (COCH), 34.7 ($CHNCH_3$), 35.0 (SCH_2CH_2), 40.0 ($CHSCH_2$), 61.2 (NCH), 152.5 (NCH_3CO), 172.0 ($N(CH_3)COCH$).

Irradiation of uracil based cyclobutyl acetate 25 in the presence of DCA

A solution of **25** (80 mg, 0.4 mmol) in MeCN (200 mL) containing DCA (15 mg, 0.1 mmol) was irradiated by using uranium filtered light for 10 h (50% conversion). The photolysate was concentrated *in vacuo* to give a residue which was subjected to silica gel column chromatography (EtOAc) to yield **20** (22 mg, 91%).

Irradiation of uracil based cyclobutyl amine 49 in the presence of DCA

A solution of **49** (80 mg, 0.4 mmol) in MeCN (200 mL) containing DCA (15 mg, 0.1 mmol) was irradiated by using uranium filtered light for 4 h (100% conversion). The photolysate was concentrated *in vacuo* to give a residue which was subjected to silica gel column chromatography (EtOAc) to afford **20** (29 mg, 90%).

Irradiation of uracil based cyclobutyl thioether 50 in the presence of DCA

A solution of **50** (100 mg, 0.4 mmol) in MeCN (200 mL) containing DCA (15 mg, 0.1 mmol) was irradiated by using uranium filtered light for 6 h (100% conversion). The photolysate was concentrated *in vacuo* to give a residue which was subjected to silica gel column chromatography (EtOAc) to afford **20** (52 mg, 91%).

Preparation of uracil based cyclobutyl alcohols 58–60

A 5% methanolic NaOH 20 mL was added dropwise to respective MeOH (30 mL) solutions of **16** (200 mg, 0.7 mmol), **18** (200 mg, 0.5 mmol) and **19** (200 mg, 0.5 mmol). These solutions were stirred at 0 °C for 30 min and concentrated *in vacuo* to give residues which were diluted with CH_3Cl and washed with water. The organic layers were dried, filtered and concentrated *in vacuo* to afford residues which were subjected to silica gel column chromatography (1 : 2 EtOAc–hexane) to afford **58** (150 mg, 90%), **59** (150 mg, 85%) and **60** (140 mg, 80%) respectively.

58: ^{1}H-NMR: 0.11 (s, 9H, $SiMe_3$), 1.90 (br s, 1H, OH), 2.40 and 3.35 (two d, 2H, J = 15.2 Hz, two diastereotopic CH_2TMS), 2.16–2.29 and 2.65–2.89 (m, 2H, $CHCH_2$), 3.18–3.29 (m, 1H, CHCO), 3.86–3.93 (m, 1H, NCH), 4.43–4.51 (br s, 1H, CHOH), 8.14 (br s, 1H, NH); ^{13}C-NMR: –1.8 ($SiMe_3$), 33.6 ($CHCH_2$), 35.5 (CH_2SiMe_3), 38.4 (CHCO), 56.3 (NCH), 69.8 (CHOH), 152.7 (CHNCO), 172.0 (COCH); IR (KBr) 1690 (amide).

59: ^{1}H-NMR: 0.02 (s, 9H, $SiMe_3$), 0.09 (s, 9H, $SiMe_3$), 1.90 (s, 1H, OH), 2.04–2.19 and 2.44–2.54 (m, 2H, $CHCH_2$), 2.62 and 3.28 (two d, 2H, J = 15.2 Hz, two diastereotopic CH_2TMS), 3.29 and 3.42 (two d, 2H, J = 15.2 Hz, two diastereotopic CH_2TMS), 3.57–3.66 (m, 2H, CHCO and NCH), 4.22–4.35 (m, 1H, CHOH); ^{13}C-NMR: –1.7 ($SiMe_3$), 31.2 ($CHCH_2$), 32.7 (CH_2SiMe_3), 33.3 (CH_2SiMe_3), 40.2 (CHCO), 60.9 (NCH), 74.0 (CHOH), 152.3 ($CONCH_2SiMe_3$), 171.7 ($COCH_3$); LRMS (EI) *m/z* (rel. intensity) 328 (M^+, 5), 311 (51), 284 (54), 269 (70), 256 (70), 195 (14), 73 (48); HRMS (EI) *m/z* 328.1630 ($C_{14}H_{28}N_2O_5Si_2$ requires 328.1639).

60: ^{1}H-NMR: 0.08 (s, 9H, $SiMe_3$), 0.09 (s, 9H, $SiMe_3$), 1.99–2.14 and 2.80–2.92 (m, 2H, $CHCH_2$), 2.44 and 3.26 (two d, 2H, J = 15.2 Hz, two diastereotopic CH_2TMS), 3.33 and 3.48 (two d, 2H, J = 15.2 Hz, two diastereotopic CH_2TMS), 3.78–3.83 (m,

2H, C*H*CO and C*H*N), 4.39–4.47 (m, 1H, C*H*OH); ^{13}C-NMR: –1.7 ($SiMe_3$), –1.6 ($SiMe_3$), 31.2 ($CHCH_2$), 30.7 ($CHCH_2$), 34.5 (CH_2SiMe_3), 35.1 (CH_2SiMe_3), 39.4 (*C*HCO), 54.6 (NCH), 69.4 (CHOH), 154.0 ($CONCH_2SiMe_3$), 171.2 ($COCH_3$); IR (KBr) 1690 (amide).

Preparation of uracil based cyclobutyl mesylates 61–63

Independent solutions of **58** (200 mg, 0.8 mmol), **59** (200 mg, 0.6 mmol) and **60** (100 mg, 0.3 mmol) in CH_2Cl_2 (50 mL) containing triethylamine (2 g, 0.2 mmol) were stirred at 0 °C for 1 h. MsCl (131 mg, 0.9 mmol for **58–60**) was added dropwise to each and the resulting solutions were stirred at room temperature for 5 h and concentrated *in vacuo* to give residues which were diluted with ether and washed with water. The organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo* to afford residues which were subjected to silica gel column chromatography (1 : 3 EtOAc–hexane) to afford **61** (183 mg, 70%), **62** (194 mg, 70%) and **63** (80 mg, 65%) respectively.

61: ^{1}H-NMR: 0.11 (s, 9H, $SiMe_3$), 2.36 and 3.37 (two d, 2H, J = 15.4 Hz, two diastereotopic C*H*$_2$TMS), 2.46–2.55 and 2.76–2.80 (m, 2H, CHC*H*$_2$), 3.05 (s, 3H, OMs), 3.30–3.39 (m, 1H, C*H*CO) 4.11–4.18 (m, 1H, NC*H*), 5.23–5.29 (m, 1H, C*H*OMs), 8.02 (br s, 1H, NH); ^{13}C-NMR: –1.7 ($SiMe_3$), 31.1 (OMs), 36.4 ($CHCH_2$), 37.9 (CO*C*H), 39.0 (CH_2SiMe_3), 55.3 (NCH), 76.1 (*C*HOMs), 152.0 (CHN*C*O), 170.7 (*C*OCH); IR (KBr) 1700(C═O), 1180 and 1361 (OMs, stretching); LRMS (EI) m/z (rel. intensity) 320 (4), 241 (28), 189 (51), 183 (100), 73 (41); HRMS (EI) m/z 320.0867 ($C_{11}H_{20}N_2O_5SiS$ requires 320.0862).

62: ^{1}H-NMR: 0.04 (s, 9H, $SiMe_3$), 0.10 (s, 9H, $SiMe_3$), 2.41–2.50 and 2.63–2.74 (m, 2H, $CHCH_2$) 2.58 and 3.34 (two d, 2H, J = 15.4 Hz, two diastereotopic C*H*$_2$TMS), 3.02 (s, 3H, OMs), 3.24–3.38 (m, 1H, COCH) 3.32 and 3.44 (two d, 2H, J = 15.4 Hz, two diastereotopic C*H*$_2$TMS), 3.92–4.00 (m, 1H, NCH), 4.85–4.96 (m, 1H, C*H*OMs); ^{13}C-NMR: –1.7 ($SiMe_3$), –1.6 ($SiMe_3$), 30.5 (OMs), 31.5 ($CHCH_2$), 32.5 (CO*C*H), 38.5 (CH_2SiMe_3), 39.7 (CH_2SiMe_3), 58.2 (NCH), 77.6 (*C*HOMs), 151.7 (CHN*C*O), 169.1 (*C*OCH); IR (KBr) 1690 and 1660 (NCO); LRMS (EI) m/z (rel. intensity) 406 (6), 390 (94), 311 (69), 284 (80), 269 (95), 195 (27), 152 (11); HRMS (EI) m/z 406.1417 ($C_{15}H_{30}N_2O_5Si_2S$ requires 406.1414).

63: ^{1}H-NMR: 0.04 (s, 9H, $SiMe_3$), 0.07 (s, 9H, $SiMe_3$), 2.34 and 3.32 (two d, 2H, J = 15.4 Hz, two diastereotopic C*H*$_2$TMS), 2.42–2.49 and 2.77–2.92 (m, 2H, CHC*H*$_2$), 2.98 (s, 3H, OMs), 3.35 and 3.43 (two d, 2H, J = 15.4 Hz, two diastereotopic C*H*$_2$TMS), 3.27–3.33 (m, 1H, CHCO), 4.05–4.12 (m, 1H, NCH), 5.15–5.21 (m, 1H, C*H*OMs); ^{13}C-NMR: –1.6 ($SiMe_3$), 31.4 (OMs), 32.3 ($CHCH_2$), 35.6 (CO*C*H), 38.7 (CH_2SiMe_3), 39.2 (CH_2SiMe_3), 53.9 (NCH), 75.9 (*C*HOMs), 152.6 (CHN*C*O), 169.2 (*C*OCH); IR (KBr) 1700 and 1660 (NCO); LRMS (EI) m/z (rel. intensity) 406 (6), 390 (94), 311 (69), 284 (80), 269 (95), 195 (27), 152 (11); HRMS (EI) m/z 406.1417 ($C_{15}H_{30}N_2O_5Si_2S$ requires 406.1414).

Preparation of *N*-uracil based cyclobutyl phthalimides 55–57

Independent solutions of **61** (200 mg, 0.6 mmol), **62** (100 mg, 0.2 mmol) and **63** (100 mg, 0.2 mmol) in DMF (50 mL) containing potassium phthalimde (11 g, 0.6 mmol) were stirred at 110 °C for 20 h and concentrated *in vacuo* giving residues which were diluted with CH_2Cl_2 and washed with water. The organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo* to afford residues which were subjected to silica gel column chromatography (1 : 3 EtOAc–hexane) to yield **55** (186 mg, 80%), **56** (71 mg, 65%) and **57** (65 mg, 60%) respectively.

55: ^{1}H-NMR: 0.03 (s, 9H, $SiMe_3$), 1.53 (s, 1H, NH), 2.23 and 3.26 (two d, 2H, J = 15.0 Hz, two diastereotopic C*H*$_2$TMS), 2.48–2.59 and 3.39–3.49 (m, 2H, CHC*H*$_2$), 2.93–3.09 (m, 1H, COC*H*), 4.78–5.00 (m, 2H, NC*H* and $CH_2CHN(CO)_2$), 7.75–7.90 (m, 4H, aromatic); ^{13}C-NMR: –1.8 ($SiMe_3$), 26.7 ($CHCH_2$), 33.2 (CO*C*H), 37.9 (CH_2SiMe_3), 51.2 (NCH), 56.3 ($CH_2CHN(CO)_2$), 123.6, 131.3, and 134.5 (CH, aromatic), 151.6 (CHN*C*O), 167.7 (*C*OCH), 171.3 (CO); IR (KBr) 1720 and 1690 (NCO); LRMS (EI) m/z (rel. intensity) 371 (1.4), 356 (27), 246 (26), 198 (60), 183 (100), 173 (15), 73 (56); HRMS (EI) m/z 371.1299 ($C_{22}H_{32}N_3O_4Si_2$ requires 371.1301).

56: ^{1}H-NMR: 0.02 (s, 9H, $SiMe_3$), 0.09 (s, 9H, $SiMe_3$), 2.27 and 3.27 (two d, 2H, J = 15.2 Hz, two diastereotopic C*H*$_2$TMS), 2.42–2.53 and 3.36–3.45 (m, 2H, CHC*H*$_2$), 2.93–3.09 (m, 1H, COC*H*), 3.40 and 3.52 (two d, 2H, J = 15.2 Hz, two diastereotopic C*H*$_2$TMS), 4.73–4.90 (m, 2H, NC*H* and $CH_2CHN(CO)_2$), 7.74–7.80 (m, 4H, aromatic); ^{13}C-NMR: –1.6 ($SiMe_3$), –1.7 ($SiMe_3$), –1.6 ($SiMe_3$), 27.6 ($CHCH_2$), 32.4 (CO*C*H), 33.3 (CH_2SiMe_3), 39.4 (CH_2SiMe_3), 51.3 (NCH), 54.7 ($CH_2CHN(CO)_2$), 151.8 (CHN*C*O), 167.8 (*C*OCH), 170.3 (CO), 123.6, 131.5, and 134.5 (CH, aromatic); IR (KBr) 1780 and 1700 (NCO); LRMS (EI) m/z (rel. intensity) 457 (M^+, 1), 442 (40), 284 (100), 267 (35), 246 (1), 210 (11); HRMS (EI) m/z 457.1851 ($C_{22}H_{31}N_3O_4Si_2$ requires 457.1853).

57: ^{1}H-NMR: 0.07 (s, 9H, $SiMe_3$), 0.08 (s, 9H, $SiMe_3$), 2.26 and 3.35 (two d, 2H, J = 15.3 Hz, two diastereotopic C*H*$_2$TMS), 2.41–2.52 and 3.38–3.47 (m, 2H, CHC*H*$_2$), 2.92–3.08 (m, 1H, COC*H*), 3.38 and 3.51 (two d, 2H, J = 15.3 Hz, two diastereotopic C*H*$_2$TMS), 4.71–4.88 (m, 2H, NC*H* and $CH_2CHN(CO)_2$), 7.73–7.88 (m, 4H, aromatic); ^{13}C-NMR: –1.7 ($SiMe_3$), –1.6 ($SiMe_3$), 27.5 ($CHCH_2$), 32.4 (CO*C*H), 33.3 (CH_2SiMe_3), 39.4 (CH_2SiMe_3), 51.3 (NCH), 54.7 ($CH_2CHN(CO)_2$), 151.8 (CHN*C*O), 167.7 (*C*OCH), 170.1 (CO), 123.6 and 134.4 (CH, aromatic); IR (KBr) 1780 and 1700 (C═O stretching); LRMS (EI) m/z (rel. intensity) 457 (1.5), 442 (52), 284 (100), 267 (29), 246 (30), 210 (16); HRMS (EI) m/z 457.1834 ($C_{22}H_{31}N_3O_4Si_2$ requires 457.1853).

Irradiation of phthalimides 55–57

Independent solutions of **55** (100 mg, 0.3 mmol), **56** (100 mg, 0.2 mmol) and **57** (100 mg, 0.2 mmol) in MeCN (200 mL) containing methyl acrylate (230 mL, 2.6 mmol) were irradiated by using Vycor filtered light for 1 h (100% conversion in each case). The photolysates were concentrated *in vacuo* to give residues which were subjected to silica gel column chromatography (1 : 2 EtOAc–hexane) to afford **10** (46 mg, 77%) and **64** (40 mg, 77%) from **55**, **11** (48 mg, 85%) and **64** (30 mg, 85%) from **56**, and **11** (51 mg, 90%) and **64** (29 mg, 85%) from **57**.

Irradiation of phthalimides 55 and 57 in the presence of methyl acrylate and DCA

Independent solutions of **55** (100 mg, 0.3 mmol) and **57** (100 mg, 0.2 mmol) in MeCN (150 mL) containing methyl acrylate (230 mL, 3 mmol) and DCA (15 mg, 0.1 mmol) were irradiated by using

uranium filtered light for 15 h (20% conversion of **55** and 55% conversion of **57**). The photolysates were concentrated *in vacuo* to give residues which were subjected to silica gel column chromatography (1 : 2 EtOAc–hexane) to afford **10** (11 mg, 90%) and **64** (9 mg, 85%) from **55**, and **11** (25 mg, 80%) and **64** (15 mg, 81%) from **57**.

Irradiation of MeCN (150 mL) solutions of **55** and **57** without DCA did not give any products.

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