Pergamon

Tetrahedron, Vol. 52, No. 9, pp. 3195-3222, 1996

0040-4020/96 $15.00 + 0.00

0040-4020(95)01105-6

SET-Photosensitized Reactions of α-Silylamino-Enones and Ynones Proceeding by 6-Endo α-Amino Radical Cyclization Pathways

Seock-Kyu Khim, Ericka Cederstrom, Dino C. Ferri and Patrick S. Mariano*

Department of Chemistry and Biochemistry
University of Maryland, College Park, MD 20742 USA

Key words: photochemistry; radical-cyclizations; single-electron-transfer; α-silylamines; hydropyridines

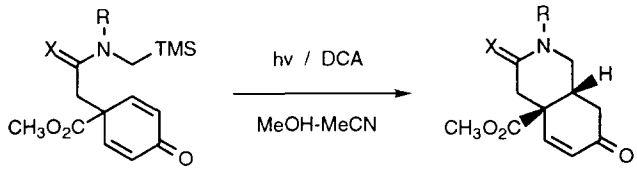
Abstract. *SET-photosensitized reactions of α,β-enones and -ynones containing tethered α-silylamine functions are described. The processes lead to hydropyridine ring construction via pathways involving 6-endo type α-amino radical cyclizations. High degrees of regio- and stereocontrol attend these reactions.*

INTRODUCTION

Methods for carbocyclic ring construction which rely on radical cyclization processes have gained wide attention in recent years.[1] The appeal of these methods has been fostered by the fact that mild conditions are required for radical generation and that the cyclization reactions are often accompanied by high degrees of regiocontrol offered by a combination of stereoelectronic and frontier molecular orbital (FMO) effects.[2] Over the same time period, single electron transfer (SET) promoted photochemical reactions have become the focus of increasing interest owing to the variety of new processes that this area has spawned and the fundamental mechanistic issues involved.[3] These types of photochemical reactions occur through pathways in which SET takes place within excited donor-acceptor pairs to produce charged radical intermediates. When designed properly, the ion radicals serve as precursors of neutral radical intermediates. As such, SET-

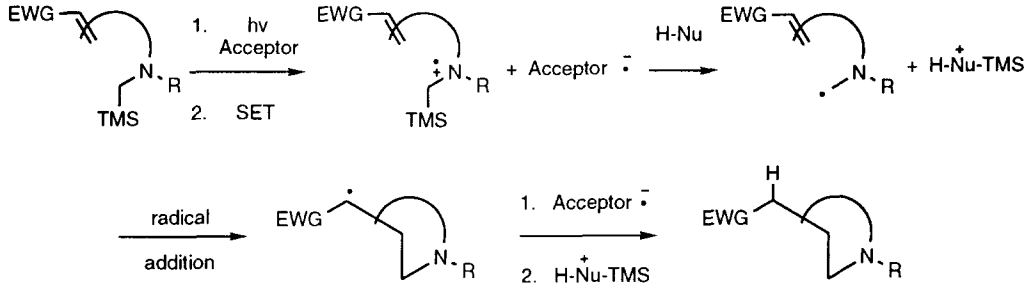
photochemical protocols relying of radical cyclization processes have been developed for the construction of carbocyclic and heterocyclic compounds.[4]

The recognition several years ago that SET-photosensitized reactions of α-silylamines and their amide analogs efficiently generate carbon centered α-amino and α-amido radicals[5] stimulated a number of studies in which this method was applied to the synthesis of N-heterocyclic compounds. In the course of these efforts, we demonstrated that SET-photosensitized reactions of enone-tethered α-silylamines and -amides (*e.g.* **1**) take place to efficiently produce N-heterocyclic products (*e.g.* **2**).[6] The mechanistic sequence responsible for these processes is shown schematically in Scheme 1. The key carbon-carbon bond forming step involves intramolecular addition of an α-amino radical to an electron withdrawing group substituted olefin.

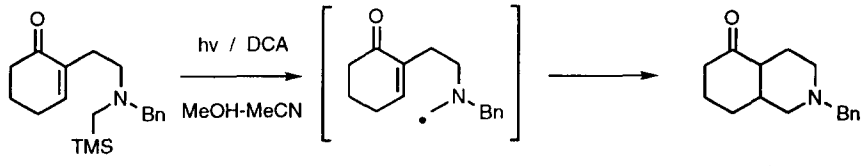


1 (X=O or H_2) 2

Scheme 1.

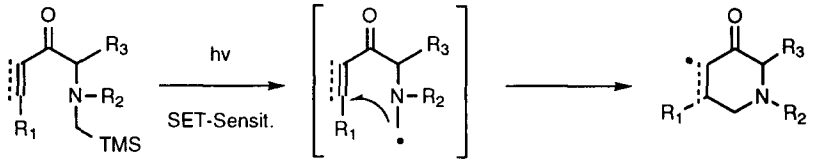


Nearly all of the photochemical reactions explored by us earlier proceed by 6-exo type α-amino and α-amido radical cyclization pathways (**1** → **2**). The regioselectivities in these cases are governed by a combination of stereoelectronic (6-exo >> 7-endo)[8] and FMO (β-addition) factors.[2] In one study of a 9,10-dicyanoanthracene (DCA) sensitized reaction we observed[6b] that the α-tethered amino-enone **3** reacts to yield the hydroisoquinoline **4** by an often less preferred (*vs.* 5-exo) 6-endo radical cyclization pathway. This regiochemical outcome was attributed to a dominance of FMO-effects in the case of highly electron rich α-amino radicals over stereoelectronic factors (5-exo > 6-endo) governing intramolecular cyclizations of simple alkyl radical-olefin systems.



3 4

Intrigued by this finding and its potential synthetic implications, we have designed systems to fully explore the α-amino radical cyclization regiochemistry issue. As part of our ensuing investigations, we have investigated the SET-sensitized photochemistry of a number of α-silylamino-enones and ynones of general structure **5**. Cyclizations of the intermediate α-amino radicals **6** derived from **5** can occur by the FMO-favored, but sterically and stereoelectronically disfavored, 6-endo routes. The results of this effort, detailed below, demonstrate the exceptionally strong influence of FMO-effects in governing the regiochemical course of α-amino radical cyclizations. In addition, this work has enabled us to simultaneously probe stereochemical questions associated with the application of this SET-photosensitization methodology to hydropyridine synthesis.[9]

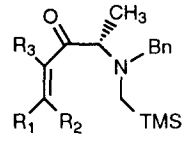


5 6

RESULTS AND DISCUSSION

Photosubstrate Synthesis. A wide variety of α-silylamino and α-silylamido conjugated enones and ynones were used in this study in order to probe several features

Scheme 2.

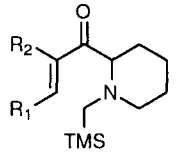


7 (R_1=CH_3, R_2=H, R_3=H)

8 (R_1=H, R_2=CH_3, R_3=H)

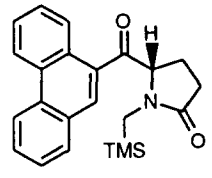
9 (R_1=R_2=CH_3, R_3=H)

10 (R_1,R_3=$(CH_2)_4$, R_2=H)

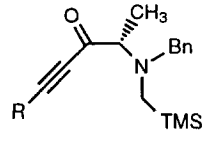


11 (R_1=CH_3, R_2=H)

12 (R_1,R_2=$(CH_2)_4$)



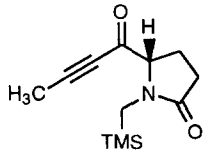
13



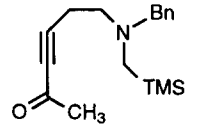
14 (R=CH_3)

15 (R=TMS)

16 (R=tBu)



17

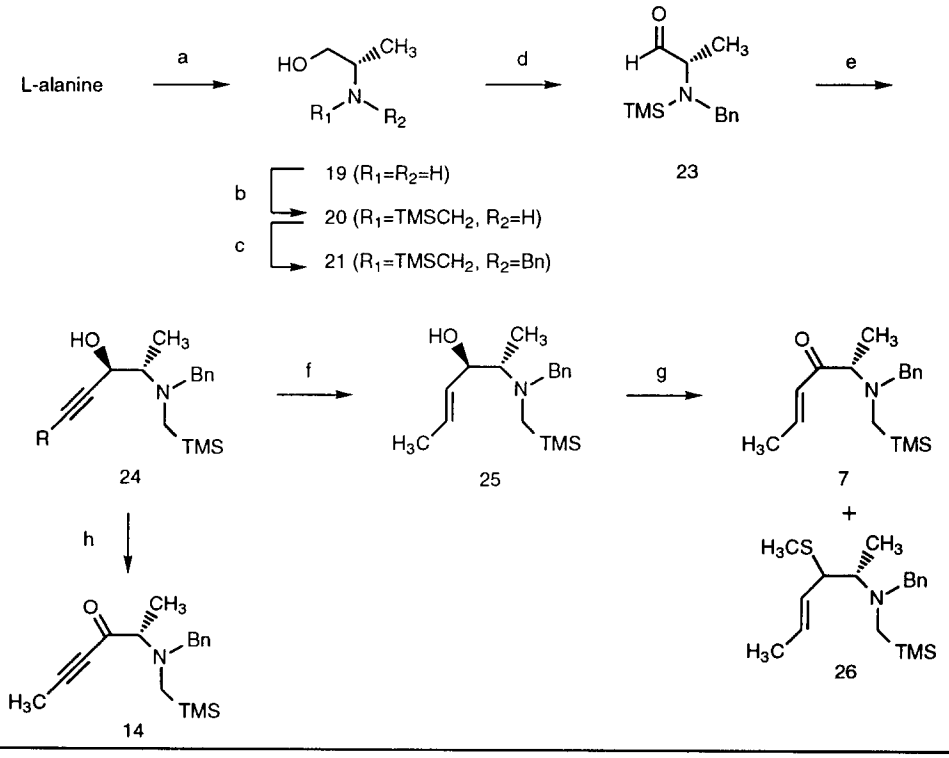


18

of SET-photoinduced methods for promoting 6-endo radical cyclization processes. These substances are depicted in Scheme 2. For the sake of brevity, only pathways employed to prepare representative members of this family of compounds will be discussed below and in the Experimental Section.

The α-silylamino-enones **7-10** and -ynones **14-16** were prepared by sequences starting with L-alanine and using the aldehyde **23** as a common synthetic intermediate (Scheme 3). Reduction of L-alanine followed by sequential N-TMS-methylation and benzylation provides the alanol derivative **21**. Aldehyde **23** is then produced by Swern oxidation of **21**. That enantiomeric integrity is preserved in this sequence was demonstrated by Mosher ester NMR analysis of the alcohol **21** produced by $NaBH_4$ reduction of aldehyde **23**. ^{1}H- ^{13}C- and ^{19}F-NMR analyses of the Mosher ester of **21** produced in this manner (from (R)-(+)-MPTA and **21**) showed that it has a >90% de. Treatment of aldehyde **23** with *in situ* generated (from 1-bromopropene and nBuLi) lithium propynylide yields the propargylic alcohol **24**, isolated as a single enantiomerically pure diastereomer in 90% yield. The high degree of stereoselectivity associated with this

Scheme 3.



(a) LAH, THF, 74%; (b) $TMSCH_2Cl$, K_2CO_3, MeCN, 67%; (c) BnBr, K_2CO_3, MeCN, 77%; (d) DMSO, $(COCl)_2$, TEA, CH_2Cl_2, 99%; (e) $CH_3CH{=}CHBr$, nBuLi, 90%; (f) Red-Al, THF, 90%; (g) (d) followed by Florosil chrom., 34% + 12%; (h) (d) 56%.

addition process is consistent with Felkin-Ahn[10] transition state considerations which predict a preference for re-face attack and, consequently, anti-amino alcohol production. This assignment was confirmed by use of the method developed by Ohtani and his coworkers[11] which relies on the relative chemical shifts of the propargylic alcohol methine protons in the Mosher esters of **24**.

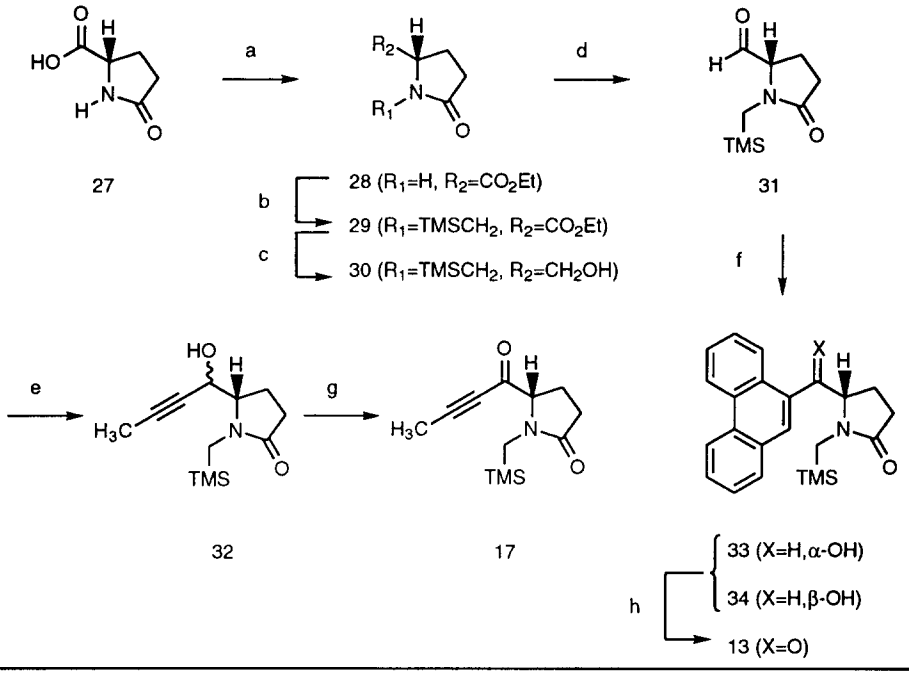
Stereoselective reduction of the ynol **24** with Red-Al[12] as expected provides the (E)-allylic alcohol **25**. Swern oxidation of this substance followed by Florosil chromatography gives the desired silylamino enone **7** (34%) along with the unexpected thioether **26** (12%). Several attempts to improve the efficiency in this oxidation (*e.g.*, PDC, PCC, Jones, NMO + TPAP) were unsuccessful. The enantiomeric purity of **7** was assessed by Mosher-ester analysis of the anti-allylic alcohol **25**, produced along with its syn-diastereomer in a 2:3 ratio by $NaBH_4$-$CeCl_3$ reduction of **7**. This analysis demonstrated that **7** is produced from enantiomerically pure alcohol **25** by the oxidation column chromatography sequence with only an *ca.* 16% ee. A more careful investigation seeking the cause of racemization has shown that it is a result of the required chromatographic step.

Swern oxidation of the propargylic alcohol **24** gives the ynone **14** (50% crude, > 80% purity). Attempts to purify this substance and its ynone relatives **15** and **16** by chromatographic procedures results in extremely low recovery of pure materials. Consequently, the ynones were used in their impurified (>80%) states in the photochemical studies described below.

The silylmethyl pyrrolidones **13** and **17** are synthesized starting with commercial (S)-(+)-pyroglutamic acid (**27**) by sequences using aldehyde **31** as a common intermediate (Scheme 4). Esterification of **27** followed by sequential N-silylmethylation (→**29**) and reduction provides the alcohol **30**. The enantiomeric purity of **30**, determined by Mosher ester analysis, varies considerably (40-80% ee) depending on the time used to prepare and handle the ester intermediates **28** and **29**. Conditions which lead to a maximized ee of 80% are outlined in the Experimental Section. Swern oxidation of **30** furnishes the aldehyde **31** with complete preservation of enantiomeric purity (assessed by conversion of **31** to **30** followed by Mosher ester analysis). Addition of lithium propynylide to aldehyde **31** gives a 4.5:1 mixture of the diastereomeric propargylic alcohols **32** which are transformed without separation to the ynone **17** by Swern oxidation.

Alternatively, addition of 9-phenanthrenyl Grignard to aldehyde **31** generates a 1:1 mixture of the diastereomeric alcohols **33** and **34**. Attempts to separate of these isomers on silica gel results in isolation of only one diastereomer of undetermined stereochemistry. Swern oxidation of the **33** + **34** mixture followed by silica-gel chromatography then gives the phenanthrenyl ketone **13**. Mosher analysis of the alcohols generated by reduction of **13** shows that the configurational integrity at the α-center is fully preserved in the sequence **31**→**13**.

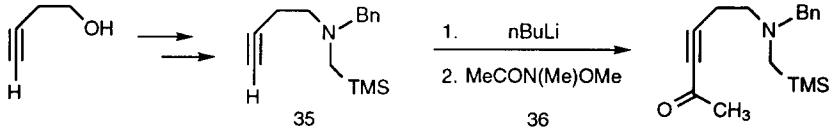
Scheme 4.



(a) $SOCl_2$, EtOH, 66%; (b) NaH, $TMSCH_2OTf$, DMF, 43%; (c) $NaBH_4$, EtOH, 74%; (d) DMSO, $(COCl)_2$, TEA, CH_2Cl_2, 70%, (e) $CH_3CH{=}CHBr$, nBuLi, THF, 63%; (f) 9-phenanthrenyl-MgBr, Et_2O, C_6H_6; (g) (d), 77%; (h) (d), 71%.

The third substrate type probed in this photochemical investigation is represented by the silylamino-ynone **18**. This material is prepared by a straight-forward, 4-step sequence beginning with conversion of 4-butynol to the tertiary amine derivative **35** (Scheme 5). Addition of the lithium acetylide of **35** to the Weinreb[13] amide **36** provides the amino-ynone **18**.

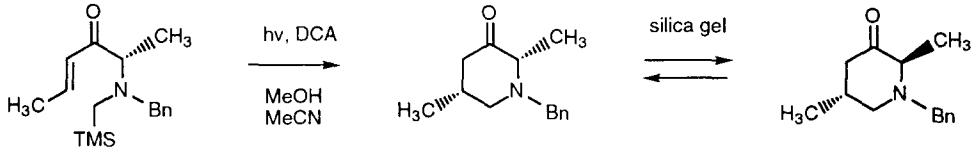
Scheme 5.



Silylamino-Enone SET-Photosensitized Reactions. Our earlier efforts in this area[6] have demonstrated that 9,10-dicyanoanthracene (DCA) serves as an excellent SET-photosensitizer for cyclization reactions of α-silylamines and -amides which contain tethered electron withdrawing group substituted olefins.[14] The general mechanistic sequence followed in these processes is outlined in Scheme 1. The key carbon-carbon

bond forming step involves the internal β-addition of the electron rich α-amino or -amido radical to the olefin moiety. As mentioned above, the major aim of the current investigation was to evaluate the efficiency, regiochemistry and stereochemistry of these SET-photocyclization reactions when the key radical cyclization process can occur by either a 5-exo or 6-endo mode.

Information about these issues derived initially from our studies of the silylamino-enones **7-10**. DCA sensitized irradiation of E-propenyl amino ketone **7** in 15% MeOH-MeCN followed by chromatographic separation on silica gel leads to isolation of the epimeric piperidinones **37** and **38** in equimolar amounts. ^{1}H NMR analysis of crude photolysates obtained by varying conversion irradiations reveals two interesting features of this process. Firstly, the cis-dimethyl isomer **37** is the exclusive kinetic (> *ca.* 9:1) product of this photoreaction. Thus, the trans isomer is formed by epimerization of **37** during the silica gel purification step. Secondly, the yield of **37** is highly dependent upon the percent-conversion of amino-enone **7** (*e.g.* 73% at 5%, 50% at 10%, 35% at 25%, 19% at 97%). This result suggests that the piperidinone **37** undergoes secondary SET-induced reaction under the conditions used for its formation. This latter finding explains why the yields of this and related photoreactions described below are at best only moderate if they are carried to completion (% conversion > 90%).



7 37 38

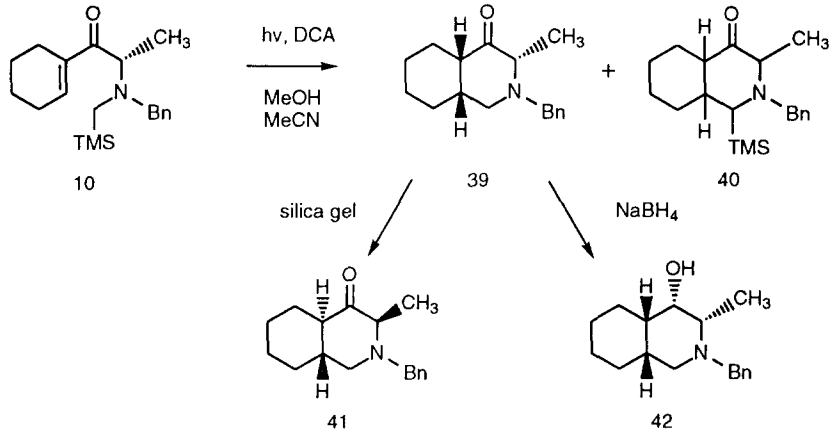
Assignments of stereochemistry to **37** and **38** turned out not to be simple task owing to the presence of complicated coupling patterns and fortuitous overlaps of key resonances. However, owing to the availability of ^{13}C NMR data for closely related model systems[15] (*e.g.* the epimeric 2,5-dimethylcyclohexanones and 1,2,5-trimethylpiperidines) and a reasonably simple analysis of conformational preferences and the γ-gauche effects of axial methyls on the methylene carbons in these systems, the relative stereochemistries of **37** and **38** could be assigned with a high degree of certainty. The ^{13}C resonance patterns which make this possible are summarized in Table 1.

In contrast to the reactivity of **7**, both the Z-propenyl and isobutenyl amino ketones **8** and **9** fail to yield detectable quantities of analogous piperidinone products when subjected to the SET-sensitized irradiation conditions.

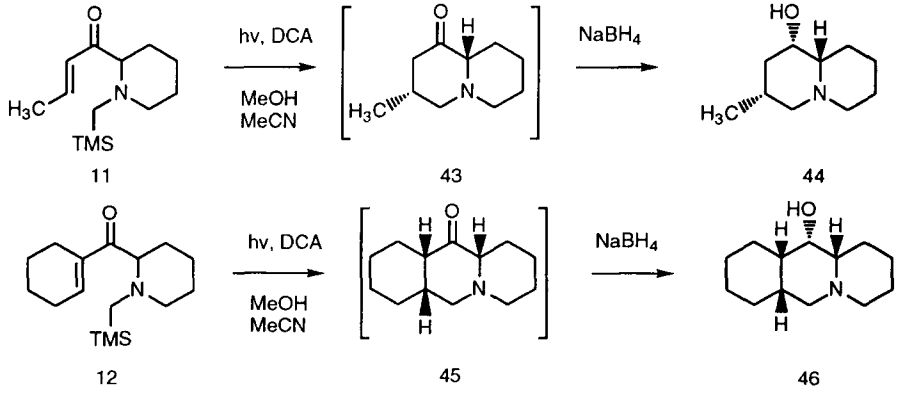
However, like **7** the cyclohexenyl amino-ketone **10** does produce a cyclization product when subjected to DCA-sensitized irradiation. ^{1}H NMR analysis of the crude photolysate indicates that a single major hydroisoquinolone **39** bearing the *trans, cis*-stereochemistry is produced in this process. Silica gel chromatographic separation, however, results in the isolation of the *trans, trans*-isomer **41** (20%) along with a minor amount (*ca.* 5%) of the silicon containing product **40**. The stereochemical assignments

to **39** and **41** are aided by ^{1}H NMR coupling data (*e.g.* in **39** $J_{H1\text{-}ax,H8a}$ = 3.7 Hz *vs.* in **41** $J_{H1\text{-}ax,H8a}$ = 10.8 Hz), ^{13}C-chemical shifts (*e.g.* for **39** C4a 47.9 ppm and C8a 37.6 ppm *vs.* for **41** C4a 49.3 ppm and C8a 42.1 ppm), and comparisons to data for the known desmethyl analogs studied earlier in our laboratory.[6b]

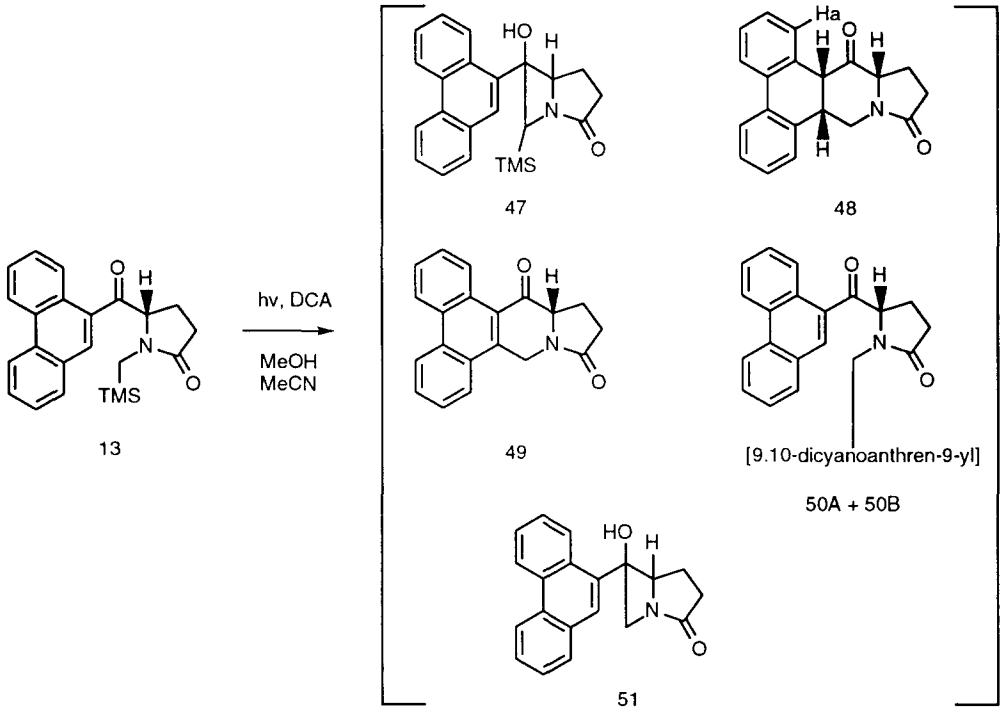
In order to gain supportive evidence for the assignment of **39** as the kinetic product of this photoreaction, the crude photolysate is directly treated with $NaBH_4$. Separation then yields a single alcohol **42** (32% for two steps) having the *trans*, *cis*-stereochemistry at the methyl and ring fusion centers and the α-configuration for the hydroxyl moiety. Accordingly, the carbonyl reduction, as anticipated occurs by hydride delivery from the less-sterically hindered face of **39**.



Similar patterns are observed for photoreactions of the piperidinyl-enones **11** and **12**. In each case, no attempt was made to isolate pure samples of the primary kinetic products (by ^{1}H NMR analyses of crude photolysates), **43** and **45**, respectively. Rather, the crude photolysates were directly treated with $NaBH_4$ followed by chromatographic separation. In each instance, only a single alcohol product, **44** and **46**, respectively, is isolated, but the yields of the two-step photochemical-reduction sequences are not high (*i.e.* 15% and 22%, respectively).



Studies of the SET-photosensitized reactions of the phenanthrenyl amino-ketone **13** enabled us to probe the nature of the intervening cyclization reaction when an α-amido radical is involved and where the competing 5-exo cyclization pathway would lead to a aryl stabilized radical center. Unlike that of the related amino-enones, DCA-sensitized irradiation of **13** is complicated by the competition between direct light absorption by the arylketone chromophore. Accordingly, when **13** is subjected to irradiation in the absence of DCA and under otherwise identical conditions, it is transformed to the silylazetidinol **47** by a route involving initial triplet arylketone γ-hydrogen abstraction.

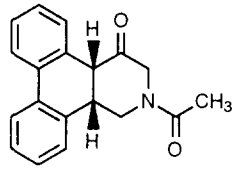


DCA-sensitized irradiation of **13** leads to a complex mixture of products which are separated only by repetitive reverse-phase HPLC. The major products formed in this process are the tricyclic ketone **48** and its aromatized analog **49**. ^{1}H NMR analysis of the crude photolysate showed that these substances are produced in respective yields of 30% and 22% at 65% conversion of **13**. In comparison, the DCA-adducts **50A** and **50B**, azetidinol **51** and direct irradiation product **47** are formed in only trace quantities (≤5%).

Characterizations of the major photoproducts are accomplished by spectroscopic methods (see Experimental Section). Specific features of the ^{1}H NMR spectrum of **48** which support both its structural and stereochemical assignment include the small 5.4 Hz coupling between the ring fusion hydrogens, the upfield shifted aryl hydrogen corresponding to H_a (see structure), resulting from ketone shielding effects, the large chemical shift difference (3.56 and 4.85 ppm) between the geminal α-N-methylene

hydrogens caused by the amide carbonyl deshielding of the equatorial-H, and the small coupling (<1 and 2 Hz) between these hydrogens and the vicinally disposed ring fusion hydrogen. Analysis of these data is aided by comparisons to those of a related hydrophenanthry ketone **52**, characterized in our earlier studies[6b] in this area.

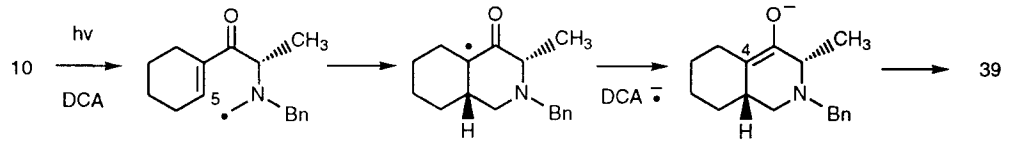
Mechanistic Issues. The results outlined above demonstrate that the SET-photosensitized reactions of properly structured silylamino-enones, although only modestly efficient, occur with high degrees of regiochemical and stereochemical control. Stereochemistry can be established at two steps in these processes, the first involving radical cyclization where the piperidinone ring C-



52

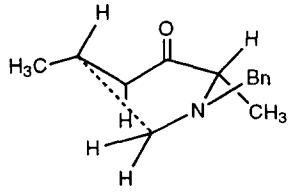
5 stereochemistry is introduced and the second enolate anion protonation creating C-4 stereochemistry. This is exemplified for photocyclization of the cyclohexenyl amino-ketone **10** in Scheme 6.

Scheme 6.

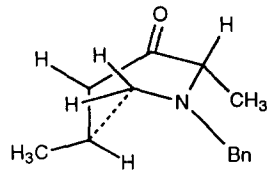


53

The selectivities associated with enolate protonation are well-known[16] and consequently it is not surprising that least hindered face protonation of **53** would yield the observed cis ring fused hydroisoquinolone **39**. In contrast, the high C-2, C-5 diastereoselectivities observed in these photoreactions are both unanticipated and at first difficult to understand. In order to gain information about the source of this control, modeling techniques were employed to analyze the radical cyclization transition states. For this purpose, molecular mechanics energy minimization routines were performed on transition states related to **54** and **55** which correspond to those involved in formation of the respective *cis*- and *trans*-2,5-dimethylpiperidinones **37** and **38**. The constraints imposed on the calculated transition states are the optimized approach angles and distances found in Houk's[17] *ab initio* calculations of transition states for radical additions to olefins and intuitively derived enone and α-amino radical geometries. Accordingly, the constraints incorporated in our energy minimizations include (1) 165° enone dihedral angle, (2) 2.3Å radical approach distance, (3) 102° radical approach angle, (4) 98° radical olefins CH angles, and (5) planar α-amino radical. Energy minimizations



54



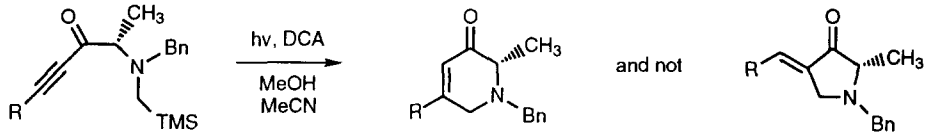
55

(Macromodel, MM2) show that transition states related to **54** are *ca.* 2 kcal/mol lower in energy than those related to **55**, a result consistent with the selective formation of the *cis*-dimethyl piperidinone **37** in the SET-phosensitized reactions. Two important factors appear to be responsible for the higher energy content of **55**. These include a repulsive $A^{1,2}$-type interaction between the N-benzyl group and adjacent C-2 methyl substituent and a transannular interaction between the C-2 methyl and the C-5 inside-hydrogen. If these models are truly reflective of the radical cyclization transition states, it would also be easy to explain why photoreactions of the Z-propenyl and isobutenyl amino ketones **8** and **9** are not successful. Radical cyclizations in reactions of these substances would require high energy *s-cis* enone conformations as well as highly crowded inside-methyl transition states.

Another and perhaps unexpected feature of these silylamino-enone SET-sensitized photocyclization processes is their high regioselectivities. In all of the cases probed, 6-endo type radical cyclizations predominate over the 5-exo mode even though the transition states for reactions by the former pathway appear to be more highly strained. It is noteworthy that this preference is also strongly adhered to in photoreaction of the phenanthrenyl amido ketone **13**, despite the fact that the 5-exo α-amido radical cyclization mode would lead to an aryl stabilized radical *via* a less strained transition state. Clearly, the regiochemical courses of α-amino (and amido) radical cyclizations involving additions to α,β-unsaturated ketones is strongly influenced by frontier orbital factors. Thus, the high nucleophilicity (high energy SOMO)[2] of these radicals not only controls their selective reactivity with EWG-substituted olefins[6a,14] but also it governs their cyclization regiochemical preferences.

Silylamino-Ynone SET-Photosensitized Reactions. Perhaps the most remarkable examples of the high degree of regiocontrol found in α-amino (or amido) radical cyclization reactions have been uncovered in our studies with the conjugated ynones **14-17**. DCA sensitized irradiation of the propynyl ketone **14** followed by chromatographic separation on silica gel leads to isolation of a single photoproduct characterized as the piperidenone **56** (21% based on 2-step conversion from ynol **24**, see above). In a similar manner, the TMS- and t-butyl-substituted amino-ynones **15** and **16** undergo DCA-sensitized photocyclization to produce the respective piperidenones **57** and **58** (20% and 26%, respectively, for 2-steps). It is important to note that although the isolated product yields in these amino-ynone photoreactions are low, ^{1}H NMR analysis of the crude

photolysates show that in no case is the photoproduct (*e.g.* **59**) of reaction by another regiochemical mode formed in detectable quantities.



14-16

56 (R=CH_3)

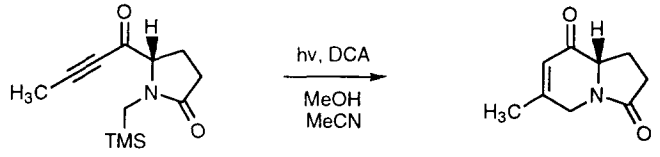
57 (R=TMS)

58 (R=tBu)

59

The structural assignments of these photoproducts as piperidenones **56-58** rather than as alkylidenepyrrolidinones **59** is aided by comparisons of their NMR-spectroscopic properties to those of simple cyclohexenone and 2-alkylidenecyclopentanone analogs. Characteristic in this regard are the consistent trends noted in the carbonyl, α- and β-carbon chemical shifts for **56-58** (*e.g.* for **56** 199.1, 133.7 and 158.9 ppm) which parallel those for 3-alkyl-substituted cyclohex-2-en-1-ones (*e.g.* 3-methyl 198.4, 126.5 and 162.3 ppm) and not for 2-alkylidenecyclopent-1-ones (*e.g.* neopentylidene 207.3, 137.1 and 136.4 ppm).

Even the presence of the constrained γ-lactam moiety in the amido-ynone **17** does not alter the regiochemical course of the photocyclization process. Thus, DCA-sensitized irradiation of **17** again leads to production of a single isolable photoproduct (19%) having the indolizidine structure **60**.

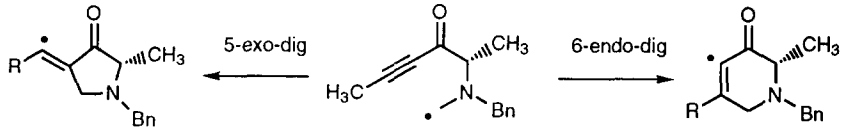


17

60

These results demonstrate that the key radical cyclization steps in these photoreaction pathways (Scheme 7) occur in a regioselective manner involving preferential

Scheme 7.

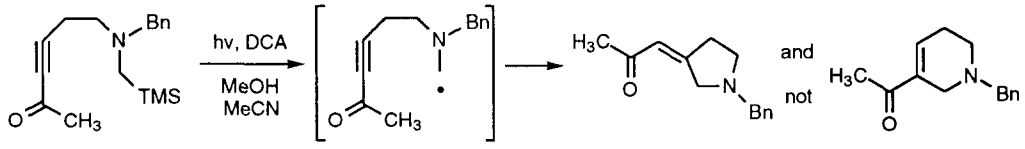


addition of the α-amino or α-amido radicals to sp-hybridized β-centers of the ynone moieties. The preference for reaction *via* the 6-endo-dig mode is retained even when the β-carbon bares a sterically bulky alkyl substituent.[7] It is reasonable to expect that the strong regiochemical driving force seen in these cases is not due to a through-pi-system

FMO effect since these intramoelecular α-amino radical additions almost certainly occur on the orthogonal π-moiety of the ynone chromophores. As such, the carbonyl grouping would only serve an inductive role in guiding approach of the α-amino radical.

In order to determine if the regioselectivities of the amino-ynone photocyclization processes might be associated with an indigenous stereoelectronic preference for 6-endo-dig over 5-exo-dig radical cyclization pathways, the SET-sensitized photochemistry of the reversed structured silylamino-ynone **18** was probed. In this case carbonyl guided internal addition of the radical center in intermediate **61** would result in production of the alkylidene-pyrrolidine product **62** while a 6-endo-dig preference would lead to formation of the acylpiperidene **63** (Scheme 8). That the former factor is more important in governing the regiochemical course of these radical cyclization processes is demonstrated by the exclusive production (56%) of **62** upon DCA-sensitized irradiation of **18**.

Scheme 8.



Summary. This investigation has shown that SET-photosensitized reactions of α-silylamino enones and ynones can serve as the key process in methods to construct piperidine ring containing products. The α-amino radical cyclization steps in these reactions occur with a high degree of stereochemical and regiochemical control. Thus, although the yields of these processes are at best only modest, the methodology holds synthetic potential in the area of N-heterocycle chemistry.

EXPERIMENTAL SECTION

General Procedures. All reported reactions were run under a dried nitrogen atmosphere; moisture sensitive reactions were run in oven dried glassware and transfers were performed by syringe or cannula. Unless otherwise noted, all reagents were obtained from commercial sources and used without further purification. Dimethyl sulfoxide and triethylamine were distilled from calcium hydride. Anhydrous solvents were obtained by distillation from the indicated reagents: ether (Na, benzophenone ketyl), tetrahydrofuran (Na, benzophenone ketyl), methylene chloride (P_2O_5). Column chromatography was performed with Silica gel 60 (SiO_2, 230-400 mesh), Florisil (100-200 mesh) or Alcoa Type F-20 Alumina (neutral, 80-120 mesh). All new compounds were judged to be >95% pure by ^1H NMR and ^{13}C NMR analysis and were isolated as oils unless otherwise specified.

Photochemical reactions were conducted by using an apparatus consisting of a 450-W medium-pressure mercury lamp surrounded by a Uranium filter (λ>320 nm) and within a quartz, water-cooled well that was purged with O_2-free N_2 both before and during irradiation. Photochemical reaction progress was monitored by gas chromatography and/or TLC. The solvents used in the photoreactions were spectrograde: MeCN(Baker) or MeOH (Baker). 9,10-Dicyanoanthracene (DCA) was purchased from Eastman Kodak and recrystallized ($CHCl_3$).

^1H NMR spectroscopic data are reported in ppm relative to $CHCl_3$ at 7.24 ppm, ^{13}C NMR chemical shifts are reported in ppm relative to the center peak of $CDCl_3$ at 77.0 ppm. Infrared (IR) spectroscopic samples are neat oils and bands are reported in units of cm^{-1}. Optical rotations were measured by using the 589 nm (sodium D) line in a 1.0 dm cell with a total volume of 2 mL. Specific rotations ([α]) are reported in degrees times 100 per decimeter at the specified temperature, and the concentration (c) is given in grams per 100 mL in $CHCl_3$. Mass spectra were recorded by using electron impact ionization unless specified as chemical ionization by CI.

(+)-(2S)-2-Amino-1-propanol (19). To a stirred suspension of LAH (40 g, 1.1 mol) in dry THF (1 L) was added L-alanine (50 g, 0.6 mol) portionwise over 2.5 h. The resulting suspension was stirred at reflux for 4 h and cooled to 25°C. The reaction mixture was quenched by addition of 30% aq. KOH solution. The resulting white suspension was filtered and washed with THF. The combined organic solutions were concentrated in vacuo at 25°C to give a colorless liquid which was distilled to provide 30.8 g (74%) of **19** : $[\alpha]^{27}$ +47.4° (c 0.48) (lit[18] $[\alpha]^{20}_D$ +18.0° (neat)); b.p. 35-38°C/0.025 mmHg (lit[18] 72-73 °C / mmHg); ^1H NMR 0.97(d, J = 6.5 Hz, 3H,CHC<u>H</u>$_3$), 2.56 (br s, 3H, NH_2 and OH), 2.93 (m, 1H, C<u>H</u>CH$_3$), 3.17 (dd, J = 10.6, 7.9 Hz, 1H, C<u>H</u>$_2$OH), 3.45 (dd, J = 10.6, 3.9 Hz, 1H, C<u>H</u>$_2$OH); ^{13}C NMR 19.9 (CH<u>C</u>H$_3$), 48.3 (<u>C</u>HCH$_3$), 68.2 (CH_2OH); IR 3303, 2888, 1596, 1458 ; LRMS m/z 75 (9), 74 (16), 58 (72); HRMS m/z 75.0689 (75.0684 calcd for C_3H_9NO).

(+)-(2S)-2-[N-(Trimethylsilylmethyl)]amino-1-propanol (20). A mixture of **19** (5.8 g, 76.9 mmol), K_2CO_3 (10.6g, 77 mmol), and $TMSCH_2Cl$ (10.7 mL, 77 mmol) in MeCN (60 mL) was stirred at reflux for 12 h, cooled to 25°C and filtered. The filtrate was concentrated under reduced pressure giving a residue which was distilled to provide 8.4 g (67%) of **20** : $[\alpha]^{27}$ +66.9° (c 0.67); b.p. 111-112°C/33.5 mmHg; ^1H NMR -0.02 (s, 9H, TMS), 0.96 (d, J = 6.5 Hz, 3H,CHC<u>H</u>$_3$), 1.86 and 2.07 (ABq, J = 13.5 Hz, 2H, C<u>H</u>$_2$TMS), 2.60 (m, 1H, CH), 3.18 (dd, J = 10.6, 7.2 Hz, 1H, C<u>H</u>$_2$OH), 3.50 (dd, J = 10.5, 4.1 Hz, 1H, C<u>H</u>$_2$OH); ^{13}C NMR -2.7 (TMS), 16.7 (CH<u>C</u>H$_3$), 36.4 (<u>C</u>H$_2$TMS), 57.6 (<u>C</u>HCH$_3$), 64.6 (CH_2OH); IR 3298, 2957, 1461; LRMS m/z 162 (M+1,100), 144 (52), 130 (79), 114 (10), 102 (14), 88 (13), 73 (22); HRMS m/z 162.1307 (162.1314 calcd for $C_7H_{20}NOSi$, M+1).

(+)-(2S)-2-[N-Benzyl-N-(trimethylsilyl)methyl]amino-1-propanol (21). A mixture of **20** (8.4 g, 52 mmol), K_2CO_3 (7.9 g, 57 mmol), and benzyl bromide (6.8 mL, 57 mmol) in MeCN (80 mL) was stirred at reflux for 5 h, cooled to room temperature and filtered. The filtrate was concentrated under reduced pressure to afford a residue which was

subjected to column chromatography (florisil, hexane:ether, 10:1) to give 9.9 g (77%) of product **21** : $[\alpha]^{26}$ +84.4° (c 0.03); ^{1}H NMR 0.05 (s, 9H, TMS), 0.84 (d, J = 6.6 Hz, 3H, CHC$\underline{H}_3$), 0.86 and 2.02 (ABq, J = 14.6 Hz, 2H, C$\underline{H}_2$TMS), 2.88 (h, J = 7.2Hz,1H, C$\underline{H}$CH$_3$), 3.30 (d, J = 8.1 Hz, 2H,C$\underline{H}_2$OH), 3.23 and 3.81 (ABq, J = 13.3 Hz, 2H, C$\underline{H}_2$Ph), 7.19-7.34 (m, 5H, aromatic); ^{13}C NMR -1.4 (TMS), 7.2 (CH$\underline{C}$H$_3$), 39.4 ($\underline{C}$H$_2$TMS), 56.2 ($\underline{C}$HCH$_3$), 56.4 ($\underline{C}$H$_2$Ph), 62.8(CH$_2$OH), 127.13, 128.5, and 128.9 (aromatic), 139.3 (ipso); IR 3439, 2958, 1494; LRMS m/z 251(10), 236 (9), 220 (99), 178 (87), 91 (100); HRMS m/z 251.1705 (251.1699 calcd for $C_{14}H_{25}NOSi$).

(+)-(2S)-2-[N-Benzyl-N-(trimethylsilyl)methyl]amino-propionaldehyde (23). To a solution of DMSO (0.80 mL, 12 mmol) in CH_2Cl_2 (10 mL) at -78°C was added oxalyl chloride (0.5 mL, 5.8 mmol) dropwise and the resulting solution was stirred at -78°C for 0.5 h. To this mixture was added dropwise alcohol **21** (0.73 g, 2.9 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred at -78°C for 1 h, triethylamine (2 mL, 15 mmol) was added, and stirring was continued for 2h at 25°C. The mixture was diluted with water and extracted with $CHCl_3$. The extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a **23** in 100% yield and >95% purity. This material was used directly in ensuing reactions: $[\alpha]^{26}$ +1.5° (c 0.47); ^{1}H NMR 0.07 (s, 9H, TMS), 1.04 (d, J = 6.7 Hz, 3H, CHC$\underline{H}_3$), 1.86 and 2.02 (ABq, J = 14.7 Hz, 2H, C$\underline{H}_2$TMS), 3.20 (q, J = 6.7 Hz, 1H, C$\underline{H}$CH3), 3.46 and 3.74 (ABq, J = 13.7 Hz, 2H, C$\underline{H}_2$Ph), 7.23-7.39 (m, 5H, aromatic), 9.67 (s, 1H); ^{13}C NMR -1.5 (TMS), 5.5 (CH$\underline{C}$H$_3$), 42.3 ($\underline{C}$H$_2$TMS), 58.2 ($\underline{C}$H$_2$Ph), 65.1 ($\underline{C}$HCH$_3$), 127.3, 128.4, and 128.7 (aromatic), 139.4 (ipso), 204.9 (CHO); IR 2955, 1729, 1675, 1248; LRMS m/z 249 (1), 224 (20), 182 (132), 154 (14), 91 (100); HRMS m/z 249.1571 (249.1549 calcd for $C_{14}H_{23}NOSi$).

(+)-(2S)-2-[N-Benzyl-N-(trimethylsilyl)methyl]amino-4-hexyn-3-ol (24). To a solution of an isomeric mixture (E:Z, 70:30) of 1-bromo-1-propene (Aldrich, 1.1 mL, 12 mmol) in THF (20 mL) at -78°C was added n-BuLi (1.6 M solution in hexane, 18 mL, 24 mmol) dropwise and stirred at -78°C for 2 h. To this mixture was added a solution of the crude aldehyde **23** (2.9 g, 12 mmol) in THF (5 mL) dropwise while maintaining the temperature at -78°C. The reaction mixture was warmed to 25°C slowly over 5 h, quenched with aq. NH_4Cl solution, and extracted with CH_2Cl_2. The extracts were washed with brine, dried over anhydrous Na_2SO_4, concentrated under reduced pressure to give residue which was subjected to flash chromatography (florisil, hexane:EtOAc, 15:1) to give 2.6 g (90%) of **24** : $[\alpha]^{27}$ +27.4° (c 4.11); 1H NMR 0.04 (s, 9H, TMS), 1.06 (d, J = 6.8 Hz, 3H, CHC$\underline{H}_3$), 1.79 (d, J = 2.3 Hz, 3H, CHC$\underline{H}_3$), 1.92 and 2.47 (ABq, J = 14.8 Hz, 2H, C$\underline{H}_2$TMS), 2.87 (p, J = 6.4 Hz, 1H, C$\underline{H}$CH3), 3.23 and 4.06 (ABq, J = 13.3 Hz, 2H, C$\underline{H}_2$Ph), 4.09 (m, 1H, C$\underline{H}$OH), 7.21-7.32 (m, 5H, aromatic); ^{13}C NMR -1.4 (TMS), 3.6 (CH$_3$), 8.0 (C≡C$\underline{C}$H$_3$), 41.8 ($\underline{C}$H$_2$TMS), 57.9 (CH), 58.5 ($\underline{C}$H$_2$Ph), 63.0 (CHOH), 79.5 (C≡$\underline{C}$CH$_3$), 82.1($\underline{C}$≡CCH$_3$), 127.2, 128.5, and 129.1 (aromatic), 139.5 (ipso); IR 3416, 3363, 2958, 1494; LRMS m/z 289 (2), 220 (99), 170 (11), 91 (100); HRMS m/z 289.1880 (289.1862 calcd for $C_{17}H_{17}NOSi$).

(+)-(2S,4E)-2-[N-Benzyl-N-(trimethylsilyl)methyl]amino-4-hexen-3-ol (25). To a solution of **24** (3.0 g, 11 mmol) in THF (30 mL) was added dropwise Red-Al (3.4 M in toluene, 12 mL, 42 mmol). The reaction mixture was stirred at 38°C overnight and quenched with aq. NH_4Cl solution. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by column chromatography (florisil, hexane:EtOAc, 15:1) yielded 2.7 g (90%) of **24** : $[\alpha]^{32}$ +30.9° (c 0.80); ^{1}H NMR 0.03 (s, 9H, TMS), 0.99 (d, J = 6.8 Hz, 3H, NCHC$\underline{H}_3$), 1.68 (d, J = 5.9 Hz, 3H, CH=CHC$\underline{H}_3$), 1.92 and 2.06 (ABq, J = 14.8 Hz, 2H, C$\underline{H}_2$TMS), 2.82 (q, J = 6.7 Hz, 1H, NCH), 3.26 and 3.77 (ABq, J = 13.5 Hz, 2H, C$\underline{H}_2$Ph), 3.88 (t, 1H, C$\underline{H}$OH), 5.61 (m, 2H, C$\underline{H}$=C$\underline{H}$CH$_3$), 7.21-7.71 (m, 5H, aromatic); ^{13}C NMR -1.2 (TMS), 7.9 (CH_3), 17.7 (C=C$\underline{C}$H$_3$), 42.3 ($\underline{C}$H$_2$TMS), 58.4 ($\underline{C}$H$_2$Ph), 59.7 (NCH), 73.5 (CHOH), 126.2 (C=$\underline{C}$CH$_3$), 126.9, 128.3, and 128.8 (aromatic), 132.3 ($\underline{C}$=CCH$_3$), 140.1 (ipso); IR 3408, 2958, 1451; LRMS *m/z* 291 (0.4), 221(24), 220 (100), 91 (99); HRMS *m/z* 291.2026 (291.2018 calcd for $C_{17}H_{29}NOSi$).

(-)-(2S,4E)-2-[N-Benzyl-N-(trimethylsilyl)methyl]amino-4-hexen-3-one (7). To a solution of DMSO (2.0 mL, 28 mmol) in CH_2Cl_2 (50 mL) at -78°C was added oxalyl chloride (1.2 mL, 14 mmol) dropwise. The resulting mixture was stirred at -78°C for 0.5 h andand mixed with a solution of **25** (2.7 g, 9.3 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred at -78°C for 2 h, triethylamine (6.5 mL, 47 mmol) was added and stirring was continued for 2h at 25°C. The reaction was diluted with water and extracted with $CHCl_3$. The extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a residue which was subjected to column chromatography (florisil, hexane:EtOAc, 30:1) to afford 0.9g (34%) of **7** and 0.35 (12%) of thioether **26.**

7: UV λ_{max} 224nm; $[\alpha]^{25}$ -6.5° (c 0.16); ^{1}H NMR 0.04 (s, 9H, TMS), 1.04 (d, J = 6.6 Hz, 3H, NCHC$\underline{H}_3$), 1.85 (dd, J = 1.6, 6.9 Hz, 3H, CH=CHC$\underline{H}_3$), 1.79 and 1.96 (ABq, J = 14.7 Hz, 2H, C$\underline{H}_2$TMS), 3.33 (q, J = 6.6 Hz, 1H, NCH), 3.35 and 3.70 (ABq, J = 13.4 Hz, 2H, C$\underline{H}_2$Ph), 6.58 (dq, J = 15.5, 1.5 Hz, 1H, C$\underline{H}$=CHCH$_3$), 6.82 (dq, J = 15.6, 6.8 Hz, 1H, CH=C$\underline{H}$CH$_3$), 7.22-7.36 (m, 5H, aromatic); ^{13}C NMR -1.3 (TMS), 5.3 (CH_3), 18.1 (C=C$\underline{C}$H$_3$), 41.2 ($\underline{C}$H$_2$TMS), 58.3 ($\underline{C}$H$_2$Ph), 63.4 (NCH), 127.1 ($\underline{C}$=CC=O), 128.3, 128.9, and 129.4 (aromatic), 139.7 (ipso), 141.4 (C=$\underline{C}$C=O), 200.9 (C=O); IR 2955, 1697, 1669, 1631, 1444; LRMS *m/z* 289(1), 220(100); HRMS *m/z* 289.1877 (289.1861 calcd for $C_{17}H_{27}NOSi$).

26: $[\alpha]^{28}$ +39.8° (c 0.43); ^{1}H NMR 0.01 (s, 9H, TMS), 1.08 (d, J = 6.4 Hz, 3H, NCHC$\underline{H}_3$), 1.74 (d, J = 4.8 Hz, 3H, CH=CHC$\underline{H}_3$), 1.89 (d, J = 2.4 Hz, 2H, C$\underline{H}_2$TMS), 1.92 (s, 3H, SCH$_3$), 2.62-2.76 (m, 1H, SCH), 3.20 and 3.73 (ABq, J = 13.7 Hz, 2H, C$\underline{H}_2$PH), 5.14-5.38 (m, 2H, C$\underline{H}$=C$\underline{H}$), 7.16-7.33 (m, 5H, aromatic); ^{13}C NMR -1.1 (TMS), 9.6 (CH_3), 14.0 (SCH$_3$), 17.6 (C=C$\underline{C}$H$_3$), 40.6 (CH$_2$TMS), 55.5 (SCH), 56.7 (CH$_2$Ph), 58.4 (NCH), 124.9 (C=$\underline{C}$CH$_3$), 126.6, 128.0, and 128.8 (aromatic), 131.9 ($\underline{C}$=CCH$_3$), 140.5 (ipso); IR 2959, 1452; LRMS *m/z* 321 (5), 274 (17), 220 (100), 129 (40); HRMS *m/z* 321.1871 (321.1847 calcd for $C_{24}H_{31}NS$).

Spectroscopic Data for Silylyamino-Enones 8-12.

8: ^{1}H NMR -0.03 (s, 9H, TMS), 0.97 (d, J = 6.5 Hz, 3H, NCHC$\underline{H}_3$), 1.73 and 1.89 (ABq, J = 14.7 Hz, 2H, C$\underline{H}_2$TMS), 2.01 (dd, J = 7.2, 1.7 Hz, 3H, CH=CHC$\underline{H}_3$), 3.23 (q, J = 6.6 Hz, 1H, NCH), 3.26 and 3.62 (ABq, J = 13.4 Hz, 2H, C$\underline{H}_2$Ph), 6.14 (dq, J = 11.4, 7.2 Hz, 1H, CH=C$\underline{H}$CH$_3$), 6.50 (dq, J = 11.6, 1.7 Hz, 1HC$\underline{H}$=CHCH$_3$), 7.14-7.29 (m, 5H, aromatic); ^{13}C NMR -1.3 (TMS), 5.0 (CH$_3$), 15.8 (C=C$\underline{C}$H$_3$), 41.4 ($\underline{C}$H$_2$TMS), 58.3 ($\underline{C}$H$_2$Ph), 64.7 (NCH), 126.9 (CH$_3\underline{C}$=C), 127.1, 128.3, and 128.9 (aromatic), 139.8 (ipso), 142.6 (CH$_3$C=$\underline{C}$), 202.9 (C=O); IR 34126, 2955, 1697, 1632, 1495, 1445, 1372, 1248.

9: ^{1}H NMR 0.03 (s, 9H, TMS), 1.02 (d, J = 6.6 Hz, 3H, CH$_3$), 1.81 and 1.96 (ABq, J = 14.7 Hz, 2H, C$\underline{H}_2$TMS), 1.88 (d, J = 1.0 Hz, 1H, CH), 3.34 and 3.68 (ABq, J = 13.5 Hz, 2H, C$\underline{H}_2$Ph), 6.47 (m, 1H, C=CH), 7.20-7.36 (m, 5H, aromatic).

10: $[\alpha]^{28}$ -25.7° (c 0.04); ^{1}H NMR 0.01 (s, 9H, TMS), 1.05 (d, J = 6.7 Hz, 3H, CH$_3$), 1.51-1.58 (m, 6H, (CH$_2$)3), 1.87 and 1.97 (ABq, J = 14.9 Hz, 2H, C$\underline{H}_2$TMS), 2.00-2.025 (m, 2H, (CH$_2$)), 3.46 and 3.65 (ABq, J = 13.6 Hz, 2H, C$\underline{H}_2$Ph), 3.89 (q, J = 6.6 Hz, 1H, NCH), 6.47 (t, J = 3.8 Hz, 1H, C=CH), 7.22-7.32 (m, 5H, aromatic); ^{13}C NMR -1.5 (TMS), 7.8 (CH$_3$), 21.6, 22.1, 23.3, 25.8 ((CH$_2$)4), 40.6 ($\underline{C}$H$_2$TMS), 57.0 (NCH), 58.5 ($\underline{C}$H$_2$Ph), 127.1, 128.1, and 129.3 (aromatic), 138.1 ($\underline{C}$=CC=O), 139.8 (C=$\underline{C}$C=O), 139.9 (ipso), 202.3 (CO); IR 3440, 2932, 1665; LRMS m/z 220 (100), 162 (13); HRMS m/z 329.2194 (329.2175 calcd for C$_{20}$H$_{31}$NOSi).

11: λ_{max} 227nm; ^{1}H NMR 0.01 (s, 9H, TMS), 1.14-1.30 (m, 1H), 1.36-1.94 (m, 6H), 1.56, and 1.83 (ABq, J = 14.3 Hz, 2H, C$\underline{H}_2$TMS), 1.87 (dd, J = 6.9 Hz, 3H, CH$_3$), 2.60 (dd, J = 10.7, 3.5 Hz, 1H), 2.94 (dt, J = 11.3, 3.0 Hz, 1H), 6.60 (dq, J = 15.6, 1.7 Hz, 1H, C$\underline{H}$=CHCO), 7.03 (dq, J = 15.6, 6.9 Hz, 1H, CH=C$\underline{H}$CO); ^{13}C NMR -1.1 (TMS), 18.2 (CH$_3$), 23.3, 25.8, and 29.2 (3CH$_2$), 49.3 ($\underline{C}$H$_2$TMS), 55.2 (NCH$_2$), 77.2 (NCH), 127.4 ($\underline{C}$H=CHO), 142.9 (CH=$\underline{C}$HC=O), 202.4 (C=O); LRMS 240 (M+1, 2), 170 (100), 91 (2); HRMS 240.1778 (240.1784 calcd for C$_{13}$H$_{26}$NOSi, M+1).

12: ^{1}H NMR 0.00 (s, 9H, TMS), 1.37-2.26 (m, 15H), 1.53 and 1.98 (ABq, J = 14.1 Hz, 2H, CH$_2$Ph), 3.00 (br dt, J = 11.3, 3.6 Hz, 1H), 3.15 (br d, J = 7.4 Hz, 1H), 7.49 (br s, 1H, C=CH); ^{13}C NMR -1.0 (TMS), 21.6, 22.1, 23.5, 23.7, 25.7, 26.0, and 30.6 (7CH$_2$), 48.6 (NCH$_2$), 55.8 ($\underline{C}$H$_2$TMS), 75.1 ($\underline{C}$HCH$_3$), 137.5 (HC=$\underline{C}$C=O), 140.9 ($\underline{C}$H=CC=O), 202.9 (C=O); IR 2934, 2854, 1633, 1437, 1248, 856 ; LRMS m/z 280 (M+1, 1), 264 (6), 190 (7), 170 (100), 96 (13), 73 (18); HRMS m/z 279.20187 (279.20184 calcd for C$_{16}$H$_{29}$NOSi, M+1).

(-)-(2S,3R)-2-[N-Benzyl-N-(trimethylsilyl)methyl]amino-4-hexyn-3-one (14). To a solution of DMSO (0.65 mL, 9.2 mmol) in CH_2Cl_2 (10 mL) at -78°C was added dropwise oxalyl chloride (0.4 mL, 4.6 mmol) and the resulting solution was stirred at -78°C for 0.5 h. To this solution was added **24** (663 mg, 2.3 mmol) in CH_2Cl_2 (3 mL) dropwise. The reaction mixture was stirred at -78°C for 1 h, triethylamine (1.6 mL, 12.0 mmol) was added and stirring was continued at room temperature for 3 h. The reaction mixture was diluted with water and extracted with CH_2Cl_2. The extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by

flash column chromatography (florisil, hexane: EtOAc, 20:1) gave 336 mg (51%) of **14** : $[\alpha]^{29}$ -48.9° (c 0.15); ^{1}H NMR 0.51 (s, 9H, TMS), 1.10 (d, *J* = 6.8Hz, 3H, CHC<u>H</u>$_3$), 2.01 (m, 2H, C<u>H</u>$_2$TMS), 2.04 (s, 3H, C≡CCH$_3$), 3.41 (q, *J* = 6.7Hz, 1H, C<u>H</u>CH$_3$), 3.49 and 3.76 (ABq, *J* = 13.9Hz, 2H, CH$_2$Ph), 7.20-7.43 (m, 5H, aromatic); ^{13}C NMR -1.5 (TMS), 4.2 (CH<u>C</u>H$_3$), 8.2 (C≡C<u>C</u>H$_3$), 41.5 (<u>C</u>H$_2$TMS), 58.0 (<u>C</u>H$_2$Ph), 65.9 (<u>C</u>HCH$_3$), 81.1 (CH$_3$<u>C</u>≡C), 90.7 (CH$_3$C≡<u>C</u>), 126.9 , 128.2, and 128.7 (aromatic), 139.9 (ipso), 190.1 (C=O); IR 2953, 2129, 1673.

Spectroscopic Data for Silylyamino-Ynones 15 and 16.

15: λ_{max} 192 nm; $[\alpha]^{27}$ -62.9° (c 0.28); ^{1}H NMR 0.06 (s, 9H, TMS), 0.26 (s, 9H, TMS), 1.09 (d, *J* = 6.7 Hz, 3H, CH$_3$), 1.94 and 2.02 (ABq, *J* = 14.8 Hz, 2H, C<u>H</u>$_2$TMS), 3.44 and 3.74 (ABq, *J* = 13.9 Hz, 2H, C<u>H</u>$_2$Ph), 3.47 (q, *J* = 6.7 Hz, 1H, C<u>H</u>CH$_3$), 7.21-7.45 (m, 5H, aromatic); ^{13}C NMR -1.4 (TMS), -0.7 (TMS), 7.2 (CH<u>C</u>H$_3$), 41.6 (<u>C</u>H$_2$TMS), 58.1 (<u>C</u>H$_2$Ph), 65.9 (<u>C</u>HCH$_3$), 127.0, 128.2, and 128.8 (aromatic), four quarternary carbons were not detected.; IR 2955, 1749, 1666, 1449, 1373, 1249, 1161, 1049.

16: λ_{max} 193nm; $[\alpha]^{18}$ -74.5° (c 0.15); ^{1}H NMR 0.07 (s, 9H, TMS), 1.10 (d, *J* = 6.7Hz, 3H, CHC<u>H</u>$_3$), 1.32 (s, 9H, C(CH$_3$)$_3$), 1.98 and 2.04 (ABq, *J* = 14.7Hz, 2H, C<u>H</u>$_2$TMS), 3.46 (q, *J* = 6.7Hz, 1H, CH), 3.48 and 3.76 (ABq, *J* = 14.0Hz, 2H, C<u>H</u>$_2$Ph), 7.22-7.47 (m, 5H, aromatic); ^{13}C NMR -1.4 (TMS), 7.8 (CH<u>C</u>H$_3$), 27.8 (<u>C</u>(CH$_3$)$_3$), 30.1, (C(<u>C</u>H$_3$)$_3$), 41.4 (<u>C</u>H$_2$TMS), 57.9 (<u>C</u>H$_2$Ph), 65.9 (<u>C</u>HCH$_3$), 80.5 (COC≡<u>C</u>), 101.5 (CO<u>C</u>≡C), 126.9, 128.1, and 128.7 (aromatic), 189.9 (C=O); IR 2966, 2202, 1666, 1449, 1361, 1261, 1611, 1061; LRMS *m/z* 330 (M+1, 1), 314 (6), 286 (6), 220 (100), 146 (3), 114 (6), 91 (91); HRMS *m/z* 330.2247 (330.2253 calcd for C$_{20}$H$_{32}$NOSi, M+1).

Ethyl (S)-(-)-2-Pyrrolidone-5-carboxylate (28). To a slurry of (S)-(+)-pyroglutamic acid **27** (5.31 g, 41.1 mmol) in absolute ethanol (70 mL) at 0 °C was added thionyl chloride (4.89 g, 41.1 mmol) via syringe. After stirring at 0°C for 10 min the solution was warmed to 25 °C and stirred for an additional 1 h. The reaction mixture was cooled (0°C), neutralized by addition of saturated NaHCO$_3$, and extracted with CHCl$_3$. The combined organic layers were dried and concentrated in vacuo to give 4.26 g (66%) of **28** as a crystalline solid (Et$_2$O, 54-55 °C); $[\alpha]^{25}$ -7.1° (c 0.06): ^{1}H NMR 1.26 (t, J = 7.1 Hz, 3H, CH$_3$), 2.16-2.23 (m, 1H, H-4), 2.26-2.37 (m, 2H, H-3 and H-4), 2.39-2.47 (m, 1H, H-3), 4.19 (q, J = 7.1 Hz, 2H, OC*H*$_2$), 4.19-4.21 (m, 1H, H-5), 6.54 (s, 1H, NH); ^{13}C NMR 14.1 (CH$_3$), 24.7 (C-4), 29.2 (C-3), 55.4 (C-5), 61.6 (CH$_2$O), 172.0 (NCO), 177.9 (OC(O)); IR 3384, 2984, 1737, 1698, 1204, 1098, 1029; LRMS *m/z* 157 (M, 4), 86 (13), 84 (100), 56 (15), 51 (40); HRMS m/z 157.0741 (157.0740 calcd for C$_7$H$_{11}$O$_3$N)

Ethyl (S)-(+)-1-Trimethylsilylmethyl-2-pyrrolidone-5-carboxylate (29). To a slurry of NaH (60% dispersion washed THF, 0.89 g, 22.2 mmol) in DMF (70 mL) at 0 °C was dropwise added a solution of ethyl ester **28** (3.17 g, 20.2 mmol) in DMF (5 mL). The reaction was stirred at 0 °C for 45 min and trimethylsilylmethyl triflate (5.20 g, 22.0 mmol) was added. The mixture was stirred at 25 °C for 1 h, diluted with water, and extracted with Et$_2$O. The combined extracts were washed with brine, dried, and concentrated in vacuo to give a residue which was subjected to column chromatography

(florisil, 2:3 EtOAc/hexane) to give 2.1 g (43%) of **29**: $[\alpha]^{24}$ +6.2° (c 0.08): ^{1}H NMR 0.04 (s, 9 H, SiMe3), 1.24 (t, J = 7.1 Hz, 3 H, C*H*3), 1.98-2.06 (m, 2 H, H-4), 2.22-2.35 (m, 2 H, H-4 and H-3), 2.39-47 (m, 1 H, H-3), 2.31 and 3.22 (ABq, J = 15.4 Hz, 2 H, NCH_2Si), 4.08 (dd, J = 8.8 and 3.0 Hz, 1 H, H-5), 4.19 (q, J = 7.1 Hz, 2 H, C*H*2O); ^{13}C NMR -1.6 (SiMe3), 14.2 (*C*H3), 22.9 (C-4), 29.0 (C-3), 33.4 (NCH_2Si), 61.4 (*C*H2O), 62.1 (C-5), 171.8 (OCO), 174.5 (NCO); IR 2955, 1742, 1694, 1250, 1198; LRMS *m/z* 243 (M, 13), 228 (22), 200 (14), 170 (100), 72 (27); HRMS m/z 243.1291 (243.1291 calcd for $C_{11}H_{21}NO_3Si$).

(S)-(+)-1-Trimethylsilylmethyl-2-pyrrolidone-5-methanol (30). To a solution of ester **29** (2.1 g, 8.6 mmol) in absolute ethanol (40 mL) at 0 °C was added $NaBH_4$ (0.656 g, 17.3 mmol). The mixture was stirred at 50 °C for 1.5 h, cooled to 0 °C, diluted with H_2O, and extracted with CH_2Cl_2. The combined extracts were washed with brine, dried and concentrated in vacuo to give 1.29 g (74%) of **30** (90%): $[\alpha]^{24}$ +31.0° (c 0.07) which was used in ensuing reactions without purification. Column chromatography (silica gel), followed by recrystallization (Et_2O) gave pure **30**: (Et_2O, 77-78°C): ^{1}H NMR 0.05 (s, 9H, SiMe3), 1.95-2.02 (m, 1H, H-4), 2.04-2.09 (m, 1 H, H-4), 2.23-2.32 (m, 1H, H-3), 2.39-2.48 (m, 1H, H-3), 2.34 and 3.24 (ABq, J = 15.4 Hz, 2H, NCH_2Si), 3.53-3.58 (m, 2H, -C*H*2 O), 3.83 (dd, J = 11.8 and 3.6 Hz, 1H, H-5); ^{13}C NMR -1.5 (SiMe3), 21.2 (C-4), 30.1 (C-3), 32.0 (NCH_2Si), 61.2 (C-5), 61.9 (CH_2O), 174.8 (CNO); IR 3849, 3293, 2908, 2359, 1650, 1462, 1248, 847; LRMS *m/z* 201 (M, 9), 186 (44), 170 (99), 73 (100); HRMS m/z 201.1184 (201.1185 calcd for $C_9H_{19}NO_2Si$)

1-Trimethylsilylmethyl-2-pyrrolidone-5-carboxaldehyde (31). To a solution of oxalyl chloride (1.09 g, 8.03 mmol) in CH_2Cl_2 (40 mL) at -78 °C was added DMSO (0.77 g, 9.9 mmol). The resulting mixture was stirred at - 78 °C for 40 min before adding a solution of alcohol **30** (0.79 g, 3.9 mmol) in CH_2Cl_2 (10 mL) at -78 °C. The mixture was stirred at -78 °C for 6 h before the addition of NEt_3 (1.2 g, 12.1 mmol). After the mixture was stirred at -78 °C for 3 h and at 25 °C for 10 h, H_2O was added. The resulting mixture was extracted with $CHCl_3$ and the combined extracts were washed with brine, dried and concentrated in vacuo to give 0.79 g of crude **31** which was used without purification. Aldehyde **31** can be purified by column chromatography (Florisil, 4:1 Et_2O/acetone): ^{1}H NMR 0.07 (s, 9H, SiMe3), 1.96-2.06 (m, 1H, H-4), 2.23-2.49 (m, 3H, H-4 and H-3), 2.39 and 3.27 (ABq, J = 15.3 Hz, 2H, NCH_2Si), 4.02 (ddd, J = 9.2, 4.2, and 3.0 Hz, 1H, H-5), 9.56 (d, J = 3.0 Hz, HCO); ^{13}C NMR -1.5 (SiMe3), 19.3 (C-4), 28.8 (C-3), 34.0 (NCH_2Si), 67.4 (C-5), 174.4 (NCO), 199.0 (CHO); IR 2953, 1660, 1651, 1463, 1423, 1249, 854; LRMS *m/z* 199 (M· 3), 184 (50), 170 (100); HRMS m/z 199.1030 (199.1029 calcd for $C_9H_{17S}NO_2Si$).

5-(1'-Hydroxy-2'-butynyl)-N-[(trimethylsilyl)methyl]pyrrolidin-2-one (32). To a solution of 1-bromo-1-propene (0.67 mL, 7.8 mmol) in THF (20 mL) at -78° C was added n-BuLi (9.4 mL, 15 mmol). The solution was stirred at -78° C for 2h. To the solution was added **31** (1.3 g, 6.5 mmol) in THF (5 mL) at -78°C. The solution was stirred for 4h at -78°C and at 25°C for 3h and diluted sequentially with ether and water. The organic layer

was separated, washed with brine, dried and concentrated in vacuo giving a residue which was subjected to column chromatography (silica gel, ether) to give 985 mg (63%) of **32** (diastereomeric ratio, 4.5:1 by ^{1}H NMR): $[\alpha]^{22}$ -2.3° (c 0.60); ^{1}H NMR 0.07 (s, 9H, TMS), 1.79 (d, J = 2.2Hz, 3H, CH_3), 2.02-2.21 (m, 2H, $COCH_2$), 2.26 (ddd, J = 16.8, 10.0, 4.5Hz, 1H, $COCH_2C\underline{H}_2$), 2.48 (m, 1H, C<u>H</u>OH), 2.51 and 3.25 (ABq, J = 15.2Hz, 1H, $C\underline{H}_2$TMS), 2.75 (br d, J = 4.9Hz, 1H, CHO<u>H</u>), 3.65 (m, 1H, CH), 4.53 (m, 1H, C<u>H</u>OH); ^{13}C NMR -1.3 (TMS), 3.6 ($CH\underline{C}H_3$), 20.5 ($\underline{C}H_2CH_2CO$), 29.7 ($\underline{C}H_2CO$), 33.2 ($\underline{C}H_2$TMS), 63.5 ($\underline{C}HCH_3$), 63.7 (CHOH), 83.6 (overlapped, <u>C</u>≡<u>C</u>), 174.8 (C=O); IR 3272, 2943, 2214, 1660, 1455, 1420, 1243, 1155; LRMS *m/z* 239 (2), 224 (14), 170 (100); HRMS *m/z* 239.1337 (239.1342 calcd for $C_{12}H_{21}NO_2Si$).

5-(2'-Butynoyl)-N-[(trimethylsilyl)methyl]pyrrolidin-2-one (17). The acetylenic alcohol **31** (550 mg, 2.3 mmol) was subjected to the Swern oxidation conditions to give 393 mg (72%) of ynone **17**: $[\alpha]^{25}_D$ +3.5° (c 0.51); ^{1}H NMR 0.05 (s, 9H, TMS), 2.02 (s, 3H, CH_3), 2.03-2.11 (m, 1H), 2.24-2.49 (m, 3H), 2.28 and 3.27 (ABq, J = 15.4Hz, 2H, $C\underline{H}_2$TMS), 4.11 (dd, J = 9.2, 2.3Hz, 1H, CH); ^{13}C NMR -1.5 (TMS), 4.3 ($CH\underline{C}H_3$), 21.9, 28.9, 33.7 ($(CH_2)_3$), 69.5 ($\underline{C}HCH_3$), 77.9 and 94.3 (<u>C</u>≡<u>C</u>), 174.6 (NC=O), 186.8 (CO); IR 3019, 2958, 2400, 2218, 1678, 1422, 1252, 1216; LRMS *m/z* 237(1), 221 (11), 208 (3), 170 (100), 156 (4); HRMS *m/z* 237.1176 (237.1185 calcd for $C_{12}H_{19}NO_2Si$).

1-Trimethylsilylmethyl-2-pyrrolidone-5-(9'-phenanthrenyl Methanol) (33 and 34). To a stirred solution of adehyde **31** (0.74 g, 2.9 mmol) in Et_2O (40 mL) was added dropwise a solution of 5.9 mmol of 9-phenanthrenyl magnesium bromide[19] in 8:3 Et_2O/benzene (55 mL) while simultaneously adding enough benzene (10 mL) to prevent precipitation. The mixture was stirred at 25 °C for 1 h, poured into saturated aqueous NH_4Cl at 0 °C, and extracted with Et_2O. The extracts were washed with saturated aqueous $NaHCO_3$, brine, dried and concentrated in vacuo to give 1.4 g of a residue which was subjected to flash chromatography (Florisil, 100% Et_2O) to give 0.25 g (25%) of a 1:1 mixture of diastereomers **33** and **34**: HPLC (reverse phase) separation provided each diastereomer.

33: ^{1}H NMR -0.04 (s, 9H, $SiMe_3$), 1.67-1.72 (m, 1H, H-4), 1.82-1.88 (m, 1H, H-4), 2.09-2.16 (m, 1H, H-3), 2.31-2.40 (m, 1H, H-3), 2.61 (broad s, 1H, OH), 2.66 and 3.32 (ABq, J = 15.2 Hz, 2H, NCH_2Si), 4.17 (t, J = 5.6 Hz, 1H, H-5), 5.36 (d, J = 6.3 Hz, 1H, C*H*OH), 7.58-7.69 (m. 4H, H-2', H-3', H-6', and H-7'), 7.83 (s, 1H, H-10'), 7.87 (d, 7.7 Hz, 1H, H-1' or H-8'), 8.17 (d, J = 7.9 Hz, 1H, H-1' of H-8'), 8.65 (d, J = 8.1 Hz, 1H, H-4' or H-5'), 8.74 (d, J = 8.2 Hz, 1H, H-4' or H-5'); ^{13}C NMR -1.3 ($SiMe_3$), 23.2 (C-4), 29.7 (C-3), 34.9 (NCH_2Si), 64.5 (C-5), 76.1 (CHOH), 122.5, 123.6, 123.9, 126.0, 126.6, 126.8, 127.0, 127.1, 128.8 (aromatic CH), 129.6, 130.2, 130.8, 131.0, 135.7, (aromatic C), 174.8 (NCO); IR 3353 (br), 2958, 1659, 1453, 1248, 852; EIMS *m/z* 377 (M· 0.3), 359 (0.3), 170 (100), 119 (17); HRMS m/z 377.1780 (377.1811 calcd for $C_{23}H_{27}NO_2Si$).

34: ^{1}H NMR 0.16 (s, 9H, $SiMe_3$), 1.51-1.56 (m, 1H, H-4), 2.11-2.27 (m, 2H, H-4, and H-3), 2.58-2.63 (m, 1H, H-3), 2.67 and 3.54 (ABq, J = 15.4 Hz, 2H, NCH_2Si), 3.95 (br d, J = 8.8 Hz, 1H, H-5), 5.87 (s, 1H, C*H*OH), 7.54-7.66 (m, 4H, aromatic), 7.81 (d, J = 7.9

Hz, 1H, aromatic), 7.94 (dd, J = 7.6 and 1.3 Hz, 1H, aromatic), 8.11 (s, 1H, aromatic), 8.63 (d, J = 7.9 Hz, 1H, aromatic), 8.72 (d, J = 7.8 Hz, 1H, aromatic); ^{13}C NMR -1.2 ($SiMe_3$), 18.2 (C-4), 30.5 (C-3), 30.6 (NCH_2Si), 63.9 (C-5), 67.5 (CHOH), 122.7, 123.6, 123.9, 125.2, 126.3, 126.6, 126.7, 126.9, and 128.9 (aromatic CH), 129.0, 129.9, 130.7, 131.4, and 133.8 (aromatic C), 175.4 (NCO); IR 3326 (br), 2952, 1652, 1472, 1248, 726; LRMS *m/z* 377 (M, 0.5), 170 (100); HRMS m/z 377.1811 (377.1811 calcd for $C_{23}H_{27}NO_2Si$).

1-Trimethylsilylmethyl-2-pyrrolidone-5-(9'-phenanthrenyl Methanone) (13). To a solution of oxalyl chloride (0.16 g, 1.3 mmol) in CH_2Cl_2 (3 mL) at -78 °C was added DMSO (0.22 g, 2.8 mmol). The resulting mixture stirred at -78 °C for 20 min before the addition of a solution of a 1:1 mixture of **33** and **34** (0.16 g, 0.41 mmol) in CH_2Cl_2 (3 mL) at -78 °C. The mixture was stirred at -78 °C for 5 h before NEt_3 (0.22 g, 2.1 mmol) was added. The resulting mixture was stirred at -78 °C for 1 h, at 25 °C for 6 h and diluted with H_2O. The resulting mixture was extracted with $CHCl_3$ and the extracts were washed with brine, dried, and concentrated in vacuo to give a residue which was subjected to flash column chromatography (silica, 100% Et_2O) to provide ketone **13** (0.11 g, 71%): $[\alpha]^{24} = -12.1^0$ (c 0.05): ^1H NMR 0.14 (s, 9H, $SiMe_3$), 2.03-2.06 (m, 1H, H-4), 2.27-2.58 (m, 3H, H-4 and H-3), 2.47 and 3.36 (ABq, J = 15.5 Hz, 2H, NCH_2Si), 5.20 (dd, J = 9.4 and 3.3 Hz, 1H, H-5), 7.61-7.81 (m, 4H, H-2', H-3', H-6', and H-7'), 7.96 (d, J = 7.9 Hz, 1H, H-8'), 8.06 (s, 1H, H-10'), 8.52 (dd, J = 8.3 and 1.3 Hz, 1H, H-1'), 8.71 (dd, J = 15.4 and 8.3 Hz, 2H, H-4' and H-5'); ^{13}C NMR -1.3 ($SiMe_3$), 22.9 (C-4), 28.9 (C-3), 34.0 (NCH_2Si), 66.5 (C-5), 122.8, 123.0, 126.1, 127.4, 127.6, 128.0, 129.5, 129.7, 129.8 (aromatic CH), 128.5, 129.6, 130.9, 132.1, 132.6 (aromatic), 174.6 (NCO), 200.5 (R_2CO); IR 2954, 1693, 1450, 1249, 1118, 854, 793; LRMS *m/z* 375 (M, 4), 177 (20), 176 (11), 170 (100); HRMS m/z 375.1669 (375.1655 calcd for $C_{23}H_{25}NO_2Si$)

6-(N-Benzyl-N-trimethylsilylmethyl)amino-3-hexyn-2-one (18). To a solution of acetylene **35** (1.0 g, 4.1 mmol) at -78 °C in THF (65 mL) was added to 3.8 mL (4.9 mmol) of a hexane solution of n-butyl lithium. After stirring at -78 °C for 1 h, amide **36** (0.55 g, 5.3 mmol) was added. After stirring this mixture at 25 °C for 10 h, water was added and the solution was extracted with ether. The extracts were dried and concentrated in vacuo. The residue was subjected to silica gel chromatography (5% ether/hexane) yielding 0.6 g (52%) of **18**. ^1H NMR 0.022 (s, 9H, $SiCH_3$), 1.95 (s, 2H, $SiCH_2$), 2.25 (s, 3H, H-1), 2.42 (t, *J* = 7.1 Hz, 2H, H-5), 2.59 (t, *J* = 7.2 Hz, 2H, H-6), 3.49 (s, 2H, benzylic), 7.18 - 7.30 (m, 5H, Ar-H); ^{13}C NMR -1.45 ($SiCH_3$), 17.0 ($SiCH_2$), 32.6 (C-1), 45.7 (C-5), 54.6 (C-6), 61.7 (benzylic), 81.9 (C-3), 92.7 (C-4) 127.0, 128.2, 128.6 and 139.6 (Aromatic); IR 2955, 2795, 1678, 1495, 1358, 856, 739 cm^{-1}; LRMS *m/z* 287 (M, 1), 206 (76), 177 (3), 105 (2), 91 (100), 73 (17), 59 (5); HRMS m/z 287.16971 (287.17053 calcd for $C_{17}H_{25}SiNO$).

DCA-Sensitized Irradiation of the Amino-Enone 7. A deoxygenated solution (100 mL) of 15% MeOH-MeCN in a quartz tube containing the amino-enone **7** (143 mg , 0.49 mmol) and DCA (23 mg, 0.10 mmol) was irradiated for 9 h. The photolysate was

concentrated in vacuo giving a residue which was subjected to preparative TLC (SiO_2, hexane: EtOAc, 4:1) to give **37** (7%), **38** (7%) and recovered **7** (19%).

37: $[\alpha]^{28}$ +1.8° (c 0.17); ^{1}H NMR 0.95 (d, J = 6.1 Hz, 3H, CHC$\underline{H}_3$), 1.21 (d, J = 6.7 Hz, 3H, NCHC$\underline{H}_3$), 2.09 -2.22 (m, 2H, H-4 and H-6), 2.38 (m, 1H, H-4), 2.58 (m, 2H, H-6), 3.22 (q, J = 6.8 Hz, 1H, NCH), 3.56 and 3.74 (ABq, J = 13.5 Hz, 2H, C$\underline{H}_2$Ph), 7.26-7.32 (m, 5H, aromatic); ^{13}C NMR 11.2 (NCH$\underline{C}H_3$), 19.3 ($\underline{C}H_3$), 30.9 (CH), 44.7 (CH_2N), 52.7 ($\underline{C}H_2$C=O), 57.9 ($\underline{C}H_2$Ph), 64.9 ($\underline{C}$HCH$_3$), 127.1, 128.3, and 128.5 (aromatic), 138.7 (ipso), 210.9 (C=O); IR 4213, 3431, 3019, 2962, 1716; LRMS m/z 217 (27), 189 (44), 174 (100), 91 (10); HRMS m/z 217.1452 (217.1466 calcd for $C_{14}H_{19}NO$).

38: $[\alpha]^{25}$ 0.00 (c 0.06); ^{1}H NMR 0.89 (d, J = 5.7 Hz, 3H, CHC$\underline{H}_3$), 1.29 (d, J = 6.5 Hz, 3H, NCHC$\underline{H}_3$), 1.96 - 2.01 (m, 1H), 2.06 -2.11 (m, 2H), 2.51 - 2.54 (m, 1H), 2.88 -2.89 (m, 1H), 2.97 (q, J = 6.5 Hz, 1H, NCH), 3.35 and 3.94 (ABq, J = 13.6 Hz, 2H, C$\underline{H}_2$Ph), 7.29-7.45 (m, 5H); ^{13}C NMR 12.9 (CH$\underline{C}$H$_3$), 19.5 (NC$\underline{C}$H$_3$), 30.5 ($\underline{C}$HCH$_3$), 47.0 (CH_2N), 57.6 ($\underline{C}H_2$C=O), 57.7 ($\underline{C}H_2$Ph), 65.6 (CHN), 127.1, 128.5, and 128.8 (aromatic), 138.5 (ipso), 208.7 (C=O); HRMS m/z 217.1447 (217.1466 calcd for $C_{14}H_{19}NO$).

DCA-Sensitized Irradiation of the Amino-Enone 10. A deoxygenated solution (500 mL) of 15% MeOH-MeCN in a quartz tube containing the amino ketone **10** (303 mg, 0.97 mmol) and DCA (100 mg, 0.44 mmol) was irradiated for 7h. The photolysate was concentrated in vacuo giving a residue which ^{1}H NMR analysis showed to contain **39** as a major product. Purification by preparative TLC (SiO_2, hexane: EtOAc, 1:1) gave 47 mg (20%) of **41** and 8 mg (5%) of the TMS-containing product **40**.

39: (Partial ^{1}H and ^{13}C NMR spectral data were obtained on the crude photolysate) ^{1}H NMR 1.29 (d, J = 6.4Hz, 3H, CHC$\underline{H}_3$), 2.51 (dd, J = 11.7, 3.7Hz, 1H, H-1ax), 2.73 (dd, J = 11.7, 2.6Hz, 1H, H-1eq), 2.85 (q, J = 6.4Hz, 1H, C$\underline{H}$CH$_3$), 3.20 and 4.04 (ABq, J = 13.5Hz, 2H, C$\underline{H}_2$Ph); ^{13}C NMR 12.9 (CH$\underline{C}$H$_3$), 21.8, 24.9, 25.6, and 28.6 ($4CH_2$), 37.6 ($\underline{C}$HCH_2N), 47.9 ($CH_2\underline{C}$HC=O), 56.7 (CH$\underline{C}H_2$N), 58.5 ($\underline{C}H_2$Ph), 66.3 ($\underline{C}$HCH$_3$), 139.1 (ipso), 208.9 (C=O).

40: ^{1}H NMR 0.10 (s, 9H, TMS), 1.26 (d, J = 7.2 Hz, 3H, CH_3), 1.11-1.30 (m, 4H), 1.75-1.81 (m, 3H), 1.99 (m, 1H), 2.09 (m, 1H, H-8a), 2.20 (m, 1H, H-4a), 2.77 (d, J = 11.1Hz, 1H, H-1ax), 3.01 (q, J = 7.2 Hz, 1H, C$\underline{H}$CH$_3$), 3.56 and 3.79 (ABq, J = 14.3 Hz, 2H, C$\underline{H}_2$Ph), 7.17-7.29 (m, 5H, aromatic); ^{13}C NMR -0.6 (TMS), 16.4 (CH$\underline{C}$H$_3$), 24.8, 25.6, 25.9, and 32.4 ($(CH_2)4$), 44.4 ($\underline{C}$HCH_2N), 51.9 ($CH_2\underline{C}$HC=O), 52.2 (N$\underline{C}$HTMS), 56.2 ($\underline{C}H_2$Ph), 62.8 (C=O$\underline{C}$HCH$_3$), 126.9, and 128.3 (overlapped) (aromatic), 139.3 (ipso), 215.6 (C=O).

41: $[\alpha]^{22}$ +2.4° (c 0.68); ^{1}H NMR 1.19 (d, J =7.0 Hz, 3H, CHC$\underline{H}_3$), 1.64 - 1.74 (m, 2H), 1.76 - 1.81 (m, 1H), 1.93 - 1.96 (m, 1H), 2.10 - 2.21 (m, 1H), 2.54 (dd, J = 12.3, 4.1 Hz, 1H, H-1eq), 2.67 (dd, J = 12.2 Hz, 10.8, 1H, H-1ax), 3.37 (q, J = 7.0 Hz, 1H, C$\underline{H}$CH$_3$), 3.63 (s, 2H, C$\underline{H}_2$Ph), 7.19 - 7.30 (m, 5H); ^{13}C NMR 10.8 (CH$\underline{C}$H$_3$), 24.4, 25.4, 25.5, and 30.8 ($(CH_2)4$), 42.1 ($\underline{C}$HCH_2N), 49.3 ($CH_2\underline{C}$HCO), 51.2 (CH_2N), 57.9 ($\underline{C}H_2$Ph), 65.2 ($\underline{C}$HCH$_3$), 127.1, 128.3, and 128.5 (aromatic), 138.7 (ipso), 211.9 (C=O); IR 2930,

2855, 1715, 1448, 1361, 1161; LRMS *m/z* 257 (6), 229 (18), 214 (100); HRMS *m/z* 257.1802 (257.1779 calcd for $C_{17}H_{23}NO$).

Direct Reduction of the Crude Photolysate from DCA-Sensitized Irradiation of 10. A deoxygenated solution (100 mL) of 15% MeOH-MeCN in quartz tube containing amino ketone **10** (150 mg, 0.46 mmol) and DCA (21 mg, 0.09 mmol) was irradiated for 7h. The photolysate was concentrated in vacuo giving a residue which was dissolved in MeOH and treated with $NaBH_4$ at -10°C. The reaction mixture was stirred for 1h, diluted with water, concentrated in vacuo, and extracted with $CHCl_3$. The extracts were washed with brine, separated, and dried over anhydrous Na_2SO_4. The residue obtained upon concentration was subjected to column chromatography (Florisil, hexanes: ethyl acetate, 20:1) to give 38 mg (36%) of the alcohol **42**, $[\alpha]^{22}$ +3.7° (c 0.61) ; ^{1}H NMR 1.10-1.29 (m, 2H), 1.15 (d, *J* = 6.4 Hz, 3H, CHC<u>H</u>$_3$), 1.32 (m, 1H), 1.45-1.54 (m, 4H), 1.63 (m, 1H), 1.72 (br d, *J* = 13.0 Hz, 1H), 1.87 (qt, *J* = 12.6, 4.0 Hz, 1H), 2.06 (dd, *J* = 11.5, 3.3 Hz, 1H, Hax), 2.36 (br q, *J* = 6.4 Hz, 1H, C<u>H</u>CH$_3$), 2.54 (br d, *J* = 11.5 Hz, 1H, Heq), 3.49 (br s, half width = 6.7Hz, 1H, C<u>H</u>OH), 3.02 and 3.96 (AB q, *J* = 13.5 Hz, 2H, C<u>H</u>$_2$Ph), 7.14-7.29 (m, 5H, aromatic); ^{13}C NMR 16.7 (CH<u>C</u>H$_3$), 22.9, 25.6, 29.6, and 30.1 ((CH$_2$)$_4$), 35.5 and 38.8 (<u>C</u>H<u>C</u>H), 57.0 (<u>C</u>H$_2$Ph), 58.0 (CH$_2$N), 62.3 (<u>C</u>HCH$_3$), 77.8 (<u>C</u>HOH), 126.7, 128.2, and 128.5 (aromatic), 140.0 (ipso); IR 3448, 2901, 1666, 1443, 1378, 1208, 1143; LRMS *m/z* 259 (3), 244 (39), 168 (17), 91 (100) ; HRMS *m/z* 259.1939 (259.1936 calcd for $C_{17}H_{25}NO$).

DCA-Sensitized Irradiation and Subsequent $NaBH_4$ Reduction of Amino-Enone 11. A deoxygenated solution (200 mL) of 15% MeOH-MeCN in a quartz tube containing amino ketone **11** (177 mg, 0.74 mmol) and DCA (45 mg, 0.18 mmol) was irradiated for 9h. The photolysate was concentrated in vacuo giving a residue from which DCA was removed by filtration of a cold methanolic suspension. Concentration of the filtrate gave a residue which was dissolved in MeOH and treated with $NaBH_4$ (30 mg, 0.79 mmol) at -10°C. The reaction mixture was stirred for 1h. The solution was diluted with water, concentrated in vacuo, and extracted with $CHCl_3$. The extracts were washed with brine, separated, and dried over anhydrous Na_2SO_4. The residue from cocentration was subjected to column chromatography (SiO_2, ether) to give 18mg (15%) of the alcohol **44**, ^{1}H NMR 1.14 (br d, *J* = 6.8Hz, 3H, CHC<u>H</u>$_3$), 1.29 (m, 1H), 1.43-1.72 (m, 8H), 1.79 (m, 1H), 1.85 (m, 1H), 2.25 (m, 1H), 2.56 (dd, *J* = 11.5, 4.6Hz, 1H), 2.82 (br d, *J* = 11.5Hz, 1H), 3.61 (br s, half width = ca. 7.6Hz); ^{13}C NMR 21.6, 24.4, 27.9, 32.9, 36.7, 38.3, 46.0, 59.1, 69.8, 70.0; LRMS *m/z* 169 (39), 154 (10), 140 (32), 125 (35), 98 (78), 83 (100); HRMS *m/z* 169.1465 (169.1467 calcd for $C_{10}H_{19}NO$).

DCA-Sensitized Irradiation and Subsequent $NaBH_4$ Reduction of Amino-Enone 12. A deoxygenated solution (200 mL) of 15% MeOH-MeCN in a quartz tube containing amino ketone **12** (270 mg, 0.97 mmol) and DCA (45 mg, 0.18 mmol) was irradiated 20h. The photolysate was concentrated in vacuo giving a residue from which DCA was removed by filtration of a cold methanolic suspension. Concentration of the filtrate gave a residue

which was dissolved in MeOH and treated with $NaBH_4$ (30 mg, 0.79 mmol) at -10°C. The reaction mixture was stirred for 1h. The resulting solution was diluted with water, concentrated in vacuo, and extracted with $CHCl_3$. The extracts were washed with brine, separated, and dried over anhydrous Na_2SO_4. The residue after concentration was subjected to column chromatography (Silica-gel, ether) to give 45mg (22%) of the alcohol **44**, ^1H NMR 0.79-1.99 (m, 18H), 2.22 (dd, J = 11.7, 4.3 Hz, 1H, $CH_2NC\underline{H}_2$), 2.60 (d, J = 11.7 Hz, 1H, $CH_2NC\underline{H}_2$), 2.83 (br d, J = 11.2 Hz, 1H, $C\underline{H}_2NCH_2$), 3.41 (br s, half width = ca. 5.5 Hz, 1H, C<u>H</u>OH); ^{13}C NMR 22.6, 24.0, 25.7, 26.1, 28.1, 30.6, and 30.7 ($7CH_2$), 35.5, and 38.1 (<u>C</u>H<u>C</u>HCHOH), 56.5 ($CH_2N\underline{C}H_2$), 63.3 ($\underline{C}H_2NCH_2$), 66.9 (NCH<u>C</u>HOH), 76.2 (N<u>C</u>HCHOH); IR 2923, 2861, 1444, 1127; LRMS *m/z* 209 (59), 192 (17), 178 (30), 166 (12), 138 (10), 124 (33), 110 (12), 97 (94), 84 (100); HRMS *m/z* 209.1789 (209.1779 calcd for $C_{13}H_{23}NO$).

Preparative DCA Sensitized Irradiation of Phenanthrenyl Ketone 13. A solution of 90 mg of the ketone **13** (0.24 mmol) in 100 mL of CH_3CN containing DCA (53 mg) was irradiated for 1.5 h. The photolysate was concentrated in vacuo to give a residue that was treated with cold (-78 °C) MeOH. The resulting heterogenous solution was filtered and the filtrate was concentrated in vacao. The residue was subjected to HPLC chromatographic separation (C-18 reverse phase; CH_3CN/H_2O). This gave photoproducts **48** (11%), **49** (8%), **50A** and **50B** (5%), and **47** (ca. 1%).

48: ^1H NMR 1.88-1.98 (m, 1H, H-13), 2.07-2.15 (m, 1H, H-13), 2.22 (ddd, J = 17.2, 10.5, and 2.7 Hz, 1H, H-12), 2.32-2.43 (m, 1H, H-12), 3.56 (dd, J = 14.1 and < 2 Hz, 1H, H-9), 3.67 (dd, J = 5.4 and < 2 Hz, 1H, H-8b), 3.96 (d, J = 5.4 Hz, 1H, H-14a), 4.16 (t, J = 8.0 Hz, 1H, H-13a), 4.85 (d, J = 14.1 Hz, 1H, H-9), 7.13 (d, J = 7.1 Hz, 1H, aromatic H-1), 7.26-7.34 (m, 3H, aromatic), 7.41 (t, J = 7.5 Hz, 2H, aromatic), 7.75 (d, J = 7.8 Hz, 1H, aromatic H-5 or H-4), 7.79 (d, J = 7.8 Hz, 1H, aromatic H-5 or H-4); ^{13}C NMR 18.9 (C-13), 29.7 (C-12), 39.5 (C-8b), 39.9 (C-9), 54.2 (C-14a), 63.9 (C-13a), 124.4, 124.7, 125.4, 127.9, 128.2, 128.4, 128.7, 128.8 (aromatic CH), 128.3, 128.9, 134.0, 134.6 (aromatic C), 173.5 (NCO), 204.2 (R_2CO); IR 3100, 2950, 1725, 1692, 1452; LRMS *m/z* 303 (M, 29), 275 (8), 228 (100), 203 (37), 178 (68); HRMS m/z 303.1259 (303.1259 calcd for $C_{20}H_{17}NO_2$)

49: ^1H NMR 2.05-2.66 (m, 4H, H-12 and H-13), 4.43-4.47 (m, 1H, H-13a), 4.77 and 5.84 (ABq, J = 18.2 Hz, 2H, H-9), 7.66-7.79 (m, 3H, aromatic), 7.82 (t, J = 7.1 Hz, 1H, aromatic), 8.14 (d, J = 8.5 Hz, 1H, aromatic), 8.67-8.70 (m, 1H, aromatic), 8.72 (d, J = 8.0 Hz, 1H, aromatic), 9.29-9.31 (m, 1H, aromatic); ^{13}C NMR 20.7 (C-13), 30.0 (C-12), 40.7 (C-9), 61.3 (C-13a), 122.6, 123.4, 124.9, 127.3, 127.4, 127.7, 128.2, 130.2 (aromatic CH), 125.2, 127.6,127.9, 132.7, 140.4, (aromatic C), 174.0 (NCO), 195.3 (R_2CO); IR 3100, 2925, 1681, 1448; LRMS *m/z* 301 (M, 59), 273 (18), 248 (21), 218 (100), 190 (87), 176 (43); HRMS m/z 301.1090 (301.1103 calcd for $C_{20}H_{15}NO_2$).

50A and 50B: ^1H NMR (mixture of diastereomers, A/B = 3.5:1) 1.60-2.39 (m, H-3 and H-4, A & B), 3.37 and 4.28 (ABq, J = 14.8 Hz, 2H, NCH_2, A), 3.51 and 4.87 (ABq, J = 14.5 Hz, 2H, NCH_2, B), 4.55-4.68 (m, 1H, H-5, B), 5.38 (s, 1H, CHCN, B), 5.65 (s,

1H, CHCN, A), 5.84-5.87 (m, 1H, H-5, A), 7.45-7.93 (m, 11H, aromatic, A & B), 7.99-8.18 (m, 1H, aromatic, A & B), 8.32-8.35 (m, 2H, aromatic, A & B), 8.47-8.74 (m, 3H, aromatic, A & B); ^{13}C NMR 22.1 (C-4, A & B), 27.4 (C-3, B), 27.9 (C-3, A), 34.3 (CHCN, B), 36.5 (CHCN, A), 49.8 (CH_2N, A), 54.6 (CH_2N, B), 63.7 (C-5, A), 64.3 (C-5, B), 117.5 (CHCN, A), 119.3 (CHCN, B), 121.1 (R_2CCN, B), 121.6 (R_2CCN, A), 122.7-130.0 (aromatic C and CH, A & B), 130.1, 131.5, 132.1, 132.2, 134.1, 134.2 (aromatic C, A & B), 175.8 (NCO, A & B), 199.6 (R_2CO, B, 199.9 (R_2CO, A); IR 3581, 2240, 1709, 1691,1641,1611,1548, 1529,673; LRMS(CI) *m/z* 532 (M+1, 1), 228 (100), 216 (30), 191 (18); HRMS(CI) m/z 532.2030 (532.2025 calcd for $C_{35}H_{23}N_3O_2$)

51: ^{1}H NMR 1.69-1.90 (broad s, 1H, OH), 2.05-2.13 (m, 1H, H-13), 2.28-2.42 (m, 2H, H-13 and H-12), 2.46-2.52 (m, 1H, H-12), 4.61 and 4.98 (ABq, J = 15.4 Hz, 2H, H-9), 4.81 (dd, J = 9.2 and 7.4 Hz, 1H, H-13a), 7.61-7.67 (m, 4H, aromatic), 7.75-7.77 (m, 1H, aromatic), 7.98-8.00 (m, 1H, aromatic), 8.30 (s, 1H, H-10), 8.67 (d, J = 8.3 Hz, H-4' or H-5'), 8.73 (dd, J = 8.0 and 1.5 Hz, 1H, H-4' or H-5').

Direct Irradiation of Phenanthrenyl Ketone 39. A 100 mL solution containing 49 mg (0.13 mmol) of ketone **13** in CH_3CN was irradiated for 8 h. The photosylate was concentrated in vacuo giving a residue that was shown by ^{1}H NMR spectroscopic analysis to consist of a mixture of **47** and unreacted ketone **13** in a 1:0.9 ratio. This photosylate was subjected to column chromatography (alumina, 9:1 hexane/Et_2O) to provide azetidine **47** (13 mg, 31%) and recovered **13** (10 mg, 0.03 mmol).

47: ^{1}H NMR -0.3 (s, 9H, $SiMe_3$), 2.36-2.40 (m, 1H, C-4), 2.45-2.58 (m, 3H, H-3, H-4, and OH), 2.76-2.81 (m, 1H, H-3), 4.44 (s, 1H, NCHSi), 5.25 (dd, J = 8.0 and 4.0 Hz, 1H, H-5), 7.46 (s, 1H, H-10'), 7.59-7.70 (m, 4H, H-2', H-3'', H-6', and H-7'), 7.86 (d, J = 7.6 Hz, 1H, aromatic), 8.12 (d, J = 8.1 Hz, 1H, aromatic), 8.66 (d, J = 8.2 Hz, 1H, H-4' or H-5'), 8.71 (d, J = 8.2 Hz, 1H, H-4' or H-5'); ^{13}C NMR -2.6 ($SiMe_3$), 18.9 (C-4), 31.9 (C-3), 68.6 (C-5), 71.7 (CHSi), 85.3 (C-OH), 122.6, 123.2, 125.1, 126.7, 127.0, 127.1, 127.5, 127.6, 128.9 (aromatic CH), 129.7, 130.6, 131.1, 135.0 (aromatic C), 185.9 (NCO); IR 3384 (br), 2966, 1682, 1450, 1362, 1250, 840; LRMS *m/z* 375 (M, 9), 218 (10), 202 (11), 170 (100); HRMS m/z 375.1626 (375.1655 calcd for $C_{23}H_{25}NO_2Si$).

DCA-Sensitized Irradiation of the Amino Ynone 14. A deoxygenated solution (150 mL) of 15% MeOH-MeCN in a quartz tube containing the amino ynone **14** (63 mg, 0.22 mmol) and DCA (10 mg, 0.04 mmol) was irradiated for 7.5 h. The photolysate was concentrated in vacuo giving a residue which was purified by preparative TLC (SiO_2, hexane: EtOAc, 3:1) to give 10 mg (21%) of **56** $[\alpha]^{22}$ +20.0° (c 0.16); ^{1}H NMR 1.15 (d, *J* = 6.9Hz, 3H, NCHC<u>H</u>3), 1.81 (s, 3H, C=CCH3), 3.04 and 3.24 (ABq, *J* = 18.8Hz, 2H, NCH_2), 3.25 (q, *J* = 6.9Hz, 1H, CH), 3.58 and 3.71 (ABq, *J* = 13.3Hz, 2H, C<u>H</u>2Ph), 5.82 (s, 1H, CH=C), 7.14-7.39 (m, 5H, aromatic); ^{13}C NMR 10.6 (CH<u>C</u>H3), 21.4 (C=C<u>C</u>H3), 51.7 (CH_2N), 57.6 (<u>C</u>H2Ph), 61.8 (<u>C</u>HCH3), 123.7 (<u>C</u>H=C), 127.3, 128.4, and 128.8 (aromatic), 137.8 (ipso), 158.9 (<u>C</u>=CH), 199.1 (CO); IR 3431, 2971, 2929, 1674 ; LRMS *m/z* 215 (5), 134 (35), 91 (100); HRMS *m/z* 215.319 (215.1310 calcd for $C_{14}H_{17}NO$).

DCA-Sensitized Irradiation of the Amino Ynone 15. A deoxygenated solution (500 mL) of 15% MeOH-MeCN in a quartz tube containing the amino ynone **15** (314 mg, 0.91 mmol) and DCA (45 mg, 0.20 mmol) was irradiated for 9 h. The photolysate was concentrated in vacuo giving a residue which was purified by column chromatography (florisil, hexane: EtOAc, 10:1) to give 49 mg (20%) of **57** $[\alpha]^{29}$ +1.9° (c 0.26); ^{1}H NMR 0.10 (s, 9H, TMS), 1.19 (d, *J* = 6.9Hz, 3H, CH_3), 3.27 (dd, *J* = 19.3, 1.9Hz, 1H, CH_2N), 3.34 (q, *J* = 6.9Hz, 1H, CH), 3.40 (br d, *J* = 19.3Hz, 1H, CH_2N), 3.65 and 3.79 (ABq, *J* = 13.3Hz, 2H, $C\underline{H}_2Ph$), 6.22 (dd, *J* = 1.9Hz, 1H, C=CH), 7.22-7.32 (m, 5H, aromatic); ^{13}C NMR -2.6 (TMS), 10.3 ($CH\underline{C}H_3$), 49.5 (NCH_2), 57.4 ($\underline{C}H_2Ph$), 62.2 ($\underline{C}HCH_3$), 127.3 , 128.4, and 128.7 (aromatic), 137.9 (ipso), 132.6 (C=$\underline{C}$H), 164.1 ($\underline{C}$=CH), 197.9 (C=O); IR 2254, 1673, 1460, 1381, 1252, 1097; LRMS *m/z* 271 (M-2, 3), 228 (54), 147 (15), 108 (18), 91 (100); HRMS *m/z* 271.1387 (271.1392 calcd for $C_{16}H_{23}NOSi$, M-2).

DCA-Sensitized Irradiation of the Amino Ynone 16. A deoxygenated solution (500 mL) of 15% MeOH-MeCN in a quartz tube containing the amino ynone **16** (208 mg, 0.63 mmol) and DCA (40 mg, 0.18 mmol) was irradiated for 9 h. The photolysate was concentrated in vacuo giving a residue which was purified by column chromatography (florisil, hexane: EtOAc, 20:1) to give 42 mg (26%) of **58** $[\alpha]^{24}$ +6.6° (c 0.86); ^{1}H NMR 1.06 (s, 9H, $C(CH_3)_3$), 1.24 (d, *J* = 7.0Hz, 3H, CH_3), 3.22 (d, *J* = 18.1Hz, 1H, CH_2N), 3.26 (q, J = 7.0Hz, 1H, CH), 3.42 (dd, *J* = 18.1, 1.5Hz, 1H, CH_2N), 3.62 and 3.78 (ABq, *J* = 13.4Hz, 2H, $C\underline{H}_2Ph$), 5.95 (brs, 1H, C=CH), 7.22-7.34 (m, 5H, aromatic); ^{13}C NMR 11.4 (CH_3), 28.3 ($C(\underline{C}H_3)_3$), 35.8 ($\underline{C}(CH_3)_3$), 47.3 (CH_2N), 57.4 ($\underline{C}H_2Ph$), 62.2 ($\underline{C}HCH_3$), 120.2 (C=$\underline{C}$CO), 127.3, 128.4, and 128.6 (aromatic), 169.8 (C=$\underline{C}$H), 200.0 (CO); IR 2967, 1676, 1454, 1365, 1302, 1252; LRMS *m/z* 257(2), 220(1), 200(4), 166 (46), 141 (4), 134 (36), 124 (11), 109 (43), 91 (100); HRMS *m/z* 257.1800 (257.1779 calcd for $C_{17}H_{23}NO$).

DCA-Sensitized Irradiation of the Amino Ynone 17. A deoxygenated solution (600 mL) of 15% MeOH-MeCN in a quartz tube containing the amino ynone **17** (162 mg, 0.68 mmol) and DCA (42 mg, 0.18 mmol) was irradiated for 14 h. The photolysate was concentrated in vacuo giving a residue which was purified by preparative TLC (SiO_2, EtOAc) to give 65mg (40%) of starting **17** and 13 mg (12%) of **60** $[\alpha]^{22}$ +10.6° (c 0.31); ^{1}H NMR 2.01 (s, 3H, CH_3), 2.20-2.48 (m, 4H, $(CH_2)_2$), 3.67 and 4.57 (br ABq, *J* = 19.7Hz, 2H, CH_2), 4.04 (m, 1H, CH), 5.99 (m, 1H, CH=C); ^{13}C NMR 20.4 ($CH\underline{C}H_2$), 21.2 ($\underline{C}H_3$), 29.9 ($CO\underline{C}H_2$), 43.7 (CH_2N), 60.1 ($N\underline{C}H$), 124.9 ($\underline{C}$H=C), 158.3 ($\underline{C}$=CH), 174.0 (NCO), 194.5 (CO); IR 1679, 1634, 1437, 1419, 1262; LRMS *m/z* 165 (27), 137 (15), 123 (38), 123 (38), 82 (100); HRMS *m/z* 165.0787 (165.0789 calcd for $C_9H_{11}NO_2$).

DCA-Sensitized Irradiation of the Amino Ynone 18. A deoxygenated solution (100 mL) of 15% MeOH-MeCN in a quartz tube containing the amino ynone **18** (50 mg, 0.17 mmol) and DCA (15 mg) was irradiated for 15 h. The photolysate was concentrated in vacuo giving a residue which was purified by chromatography (Silica-gel, Et_2O-hexane) to give 21 mg (56%) of **62**; ^{1}H NMR 2.16 (s, 3H, H1), 2.73 (t, J=6.6Hz, 2H, H6), 2.93 (m, 2H, H5), 3.25 (s, 2H, H8), 3.65 (s, 2H, $PhCH_2$), 6.15 (s, 1H, H3), 7.24-7.32 (m, 5H, aromatic); ^{13}C NMR 31.2 (C1), 32.5 (C6), 54.1 (benzylic), 60.3 (C5), 60.5 (C8), 98.6 (C3),

81.9 (C4), 119.0 (C3), 127.3, 128.4, 128.8 and 138.4 (aromatic); IR 2975, 1721, 1643, 1495, 1358, 856, 739; LRMS m/z 215 (M, 3), 172 (10), 159 (7), 120 (5), 91 (100), 69 (44); HRMS m/z 215.1303 (215.1310 calcd for $C_{14}H_{17}NO$).

REFERENCES

1. Ramaiah, M. *Tetrahedron, Report No. 233*, **1987**, *41*, 3541; Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.*, **1991**, *91*, 1237.
2. Giese, B. *Angew. Chem. Int. Ed. Engl.*, **1983**, *22*, 753.
3. Mariano, P. S.; Stavinoha, J. L. *Synthetic Organic Photochemistry*, Ed. Horspool W. M., Plenum Press, New York, **1984**, Chap. 3; Davidson, R. S. *Molecular Association*, Ed. Foster, R., Academic Press, New York, **1975**, Vol. 1, pp. 215-334; Mattes, S. L.; Farid, S. *Acc. Chem. Res.*, **1982**, *15*, 80.
4. (a) Mariano, P. S., *Acc. Chem. Res.*, **1983**, *16*, 130; (b) Mariano, P. S. *Photoinduced Electron Transfer, Part C*, Eds. Fox, M. A.; Channon, M. Elsevier, New York, **1988**, Chap. 4.6; Mariano, P. S. *Organic Photochemistry*, Ed. Padwa, A., Marcel-Dekker, New York, **1987**, Vol. 9, Chap. 1.
5. (a) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *J. Am. Chem. Soc.*, **1988**, *110*, 8099; (b) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.*, **1992**, *25*, 233; (c) Yoon, U. C.; Mariano, P. S.; Givens, R. S.; Atwater, B. W. *Advances in Electron Transfer Photochemistry*, Ed. Mariano, P. S., JAI Press, Greenwich, CT, **1994**, Vol. 4, pp. 117-206.
6. (a) Jeon, Y. T.; Lee, C. P.; Mariano, P. S. *J. Am. Chem. Soc.*, **1991**, *113*, 8847; (b) Xu, W.; Zhang, X. M.; Mariano, P. S. *J. Am. Chem. Soc.*, **1991**, *113*, 8863.
7. Choi, J-K.; Hart, D. J. *Tetrahedron*, **1985**, *41*, 3959.
8. Baldwin, J. E. *J. Chem. Soc. Chem. Commun.*, **1976**, 734.
9. For a communication outlining the preliminary findings of this investigation see Khim, S. K.; Mariano, P. S. *Tetrahedron Lett.*, **1994**, *35*, 999.
10. For a general review of this topic see Morrison, J. D.; Mosher, H. S. *Asymmetric Organic Reactions*, Prentice Hall, Englewood Cliffs, NJ, **1971**, Chaps. 3 and 4.
11. Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.*, **1991**, *113*, 4092; Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H.; *J. Org. Chem.*, **1991**, *56*, 1296; Kusumi, T.; Fukushima, T.; Ohtani, I.; Kakisawa, H. *Tetrahedron Lett.*, **1991**, *32*, 2939.
12. Chan, K. K.; Cohen, N.; De Noble, J. P.; Specian, A. C., Saucy, G. *J. Org. Chem.*,, **1976**, *41*, 3497; Denmark, S. E.; Jones, T. K. *J. Org. Chem.*, **1982**, *47*, 4595.
13. Nahm, S.; Weinreb, S. M. *Tetrahedron Lett.*, **1981**, *22*, 3815.
14. Hoegy, S. E.; Mariano, P. S. *Tetrahedron Lett.*, **1994**, *35*, 8319.
15. Stothers, J. B.; Tan, C. T. *Can. J. Chem.*, **1974**, *52*, 308; Eliel, E. L.; Kandasamy, D.; Yen, C.; Hargrave, K. D. *J. Am. Chem. Soc.*, **1980**, *102*, 3698; Aliev, A. E. *Zh. Org. Khim*, **1990**, *26*, 1595, 1393, 1201.

16. See Zimmerman,H. E.; Mariano,, P. S. *J. Am. Chem. Soc.*, **1968**, *90*, 6091 and references therein.
17. Houk, K. N.; Paddon-Row, M. N.; Spellmeyer, D. C.; Rondan, N. G.; Nagase, S. *J. Org. Chem.*, **1986**, *51*, 2874; Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.*, **1987**, *52*, 959.
18. Dickman, D. A.; Meyers, A. I. *Org. Syn., Coll. Vol. VII*, **1990**, *530*, 533.
19. Dornfield, C. A.; Coleman, G. H. *Org. Syn.*, **1955**, *3*, 701.

(*Received* 3 *October* 1995; *accepted* 4 *December* 1995)