state required for abstraction of this hydrogen will be highly strained, favoring the alternative hydrogen abstraction from the acyl radical center to yield aldehyde 4 (transition state 11 in Scheme IV). In the 1,6-biradical derived from 2, the chain bearing the radical center and the hydrogen at the α-carbon of the four-membered ring have a cis relationship, favoring transition state 12 (Scheme IV) which results in formation of ketene 6.

Experimental Section

Reagents and solvents were obtained commercially and used as received. The testosterone acetate–cyclopentene adducts 1 and 2 were prepared according to ref 8. The mass spectra were taken on a HP 5988 mass spectrometer coupled to a HP 5890 GC, interfaced to a HP 9216 data processor. The GC was equipped with a 25 m × 0.25 mm dimethylsilicone capillary column and operated in the temperature-programmed mode (150–290 °C, heating rate: 32 °C/min). FTIR spectra were recorded on a Nicolet DX (10 scans, resolution: 4 cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a General Electric QE-300 spectrometer, using TMS as the internal standard.

Irradiation of 1 and 2. Argon-purged solutions of 1 (0.012 M) in ethyl acetate and of 2 (0.012 M) in methanol were irradiated with a Hanovia 450-W high-pressure mercury lamp until conversion of the starting material was complete (GC–MS analysis). After irradiation, in each case, the solvent was removed under reduced pressure. The products 4 and 10, respectively, were purified by preparative TLC on Baker Si500F silica gel TLC plates, with hexane–ether (3:2 v/v) as the eluent.

4: ^1H NMR (300 MHz, $CDCl_3$) δ 9.93 (d, J = 3.6 Hz, 1 H, CHO), 6.20 (dd, J_{ab} = 11 Hz, J_{ac} = 17.7 Hz, 1 H, H_a) 5.19 (d, 1 H, H_b), 4.99 (1 H, d, H_c), 4.52 (t, 1 H, CHOAc), 2.1 (s, 3 H, AcO), 1.2 (s, 3 H, CH_3) 0.8 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.65, 171.10, 145.26, 115.12, 82.64, 60.58, 54.53, 50.97, 45.38, 44.96, 42.79, 40.10, 36.90, 35.20, 33.87, 30.98, 30.82, 28.37, 27.66, 27.52, 27.04, 23.29, 22.80, 21.50, 14.30, 12.16. IR ($CDCl_3$, cm^{-1}): 2930, 2830, 1735, 1725, 1400, 1350, 1250, 1000; MS m/z (rel intensity) 398 (M^+, 9), 355 (4), 331 (32), 330 (M^+ – 68 (cyclopentene), 27), 271 (18), 253 (26), 219 (19), 175 (22), 173 (23), 147 (52), 133 (43), 107 (61), 105 (72), 97 (67), 95 (48), 93 (85), 91 (89), 81 (81), 79 (96), 67 (100); HRMS calcd for $C_{26}H_{38}O_3$ 398.2821, found 398.2843.

10: ^1H NMR (300 MHz, $CDCl_3$) δ 4.60 (t, 1 H, C*H*OAc), 3.57 (s, 3 H, CH_3O), 2.2 (s, 3 H, CH_3), 0.84 (t, 3 H, CH_3CH_2), 0.77 (s, 3 H, CH_3), 0.76 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.00, 171.12, 82.84, 55.38, 51.62, 51.39, 50.68, 50.41, 47.28, 42.83, 42.50, 40.27, 37.66, 36.51, 35.05, 29.36, 29.13, 28.53, 28.23, 27.62, 27.51, 23.50, 21.51, 21.17, 12.29, 12.06, 11.88; IR (KBr, cm^{-1}) 2920, 1737, 1430, 1360, 1210, 913; MS m/z (rel intensity) 430 (M^+, 6), 362 (M^+ – 68 (cyclopentene), 32), 341 (31), 302 (18), 289 (19), 167 (52), 147 (41), 105 (49), 100 (51), 95 (51), 93 (78), 91 (68), 81 (89), 79 (78), 67 (100); HRMS calcd for $C_{27}H_{42}O_4$ 430.3083, found 430.3087.

Detection of Ketene 6. Ketene 6 was generated by irradiating an argon-purged solution of 2 (0.012 M) in ethyl acetate at ambient temperature for 45 min. GC–MS analysis of the reaction mixture showed the presence of ketene 6 (ca. 20%) along with unreacted starting material (ca. 54%) and traces of 8, 9, and an isomeric aldehyde analogous to 4. A few drops of the reaction mixture containing 6 were dispersed on a ZnSe plate. The solvent was allowed to evaporate and the FTIR spectrum shown in Figure 1 was acquired. The mass spectrum of 6 was obtained by GC–MS: MS m/z (rel intensity) 399 (6), 398 (M^+, 17), 302 (12), 175 (11), 164 (11), 161 (13) 159 (14), 147 (38), 105 (47), 91 (100), 79 (65), 67 (59). At this point, ketene 6 was trapped as ester 10 by adding 0.5 mL of methanol to the mixture. The trapping of the ketene by methanol was inferred from the disappearance of its GC peak (retention time: ca. 10 min), IR absorption at 2096 cm^{-1}, and concomitant appearance of the GC peak (rt ca. 11.3 min) due to 10.

Photolysis of 2 in Ethyl Acetate. Upon prolonged irradiation (2–5 h) of 2 in ethyl acetate, the intermediate ketene 6 extrudes CO, yielding compounds 8 and 9. The structures were assigned, assuming that the products are formed by intramolecular insertion of carbene 7. A mixture of the insertion products was separated from unreacted starting material by preparative TLC on Baker Si500F silica gel TLC plates, with hexane–ether (3:2 v/v) as the eluent. Attempts to separate 8 and 9 were unsuccessful, and therefore the ^1H and ^{13}C NMR data could not be unambiguously assigned. However, the presence of a triplet at δ 4.52 (1 H, CHOAc) and singlets at δ 2.2 (3 H, AcO), 0.98 (3 H, CH_3), and 0.84 (3 H, CH_3) in the ^1H NMR spectrum acquired from a 4:1 mixture of these products, indicated that both compounds retained the steroid carbon skeleton of the starting material 2. The presence of 9 in the mixture was supported by additional resonances (multiplet) observed in the region 0.72–0.77 ppm attributable to the newly formed methyl group (3 H, CH_3CH) in 9. The absence of the carbonyl moiety at the A ring is indicated by the absence of signals in the region 190–220 ppm of the ^{13}C NMR spectrum. The mass spectra of 8 and 9 were obtained by GC–MS analysis: MS m/z (rel intensity) for 8 371 (4), 370 (M^+, 14), 355 (5), 341 (26), 281 (14), 187 (17), 175 (18), 161 (20), 159 (39), 147 (36), 146 (23), 145 (39), 136 (69), 131 (47), 121 (43), 119 (55), 107 (77), 105 (82), 93 (77), 91 (100), 81 (70), 79 (90), 77 (48), 67 (62); for 9 371 (3), 370 (M^+, 10), 355 (5), 341 (22), 282 (9), 281 (10), 187 (21), 175 (22), 163 (15), 161 (18), 159 (33), 147 (46), 146 (27), 145 (32), 137 (34), 136 (67), 135 (58), 133 (35), 121 (38), 119 (44), 107 (73), 105 (71), 95 (42), 93 (77), 91 (90), 81 (67), 79 (100), 77 (43), 67 (66).

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Registry No. 1, 131105-30-1; 2, 131176-85-7; 4, 137648-21-6; 6, 137648-22-7; 8, 137648-23-8; 9, 137648-24-9; 10, 137648-25-0.

Supplementary Material Available: ^1H NMR spectra of 4 and the mixture of 8 and 9 and the ^{13}C NMR spectrum of 10 (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Stereoselective Synthesis and Peptide Incorporation of (*S*)-α-Amino-(2,2′-bipyridine)-6-propanoic Acid†

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Recent approaches in the area of de novo protein synthesis have centered on the incorporation of metal cation binding sites within polypeptides as the basis for the assembly of new three-dimensional structures with defined structural, and potentially functional, properties.[1] A problem encountered in this quest, however, is that the number and diversity of *naturally* occurring metal-binding amino acids is limited, particularly when compared to the wide variety of synthetic ligands which are available for selective complexation of metal ions in aqueous media.[2] Thus, current objectives[3] involve an expansion of the repertoire of protein building blocks through the design and synthesis of *unnatural* metal-binding amino acids that would enhance metal cation selectivities as well as widen the range of metal coordination geometries beyond that which is currently available. We report herein the stereoselective synthesis of (*S*)-α-amino-(2,2′-bipyridine)-6-

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Scheme I

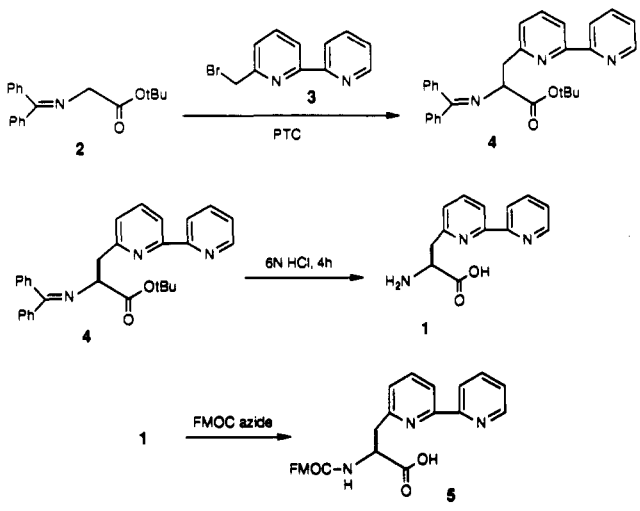

Chart I

Ac-Bpa-Thr-Pro-D-Ala-Val-Xaa-NH_2

6: Xaa=Bpa

7: Xaa=Phe

propanoic acid (1), Bpa, and its incorporation into two model peptides.

The stereoselective synthesis of 1 was accomplished through the asymmetric alkylation of commercially available *N*-(diphenylmethylene)glycine *tert*-butyl ester (2) with 6-(bromomethyl)-2,2′-bipyridine (3)[4] using the phase-transfer catalyst (8*S*,9*R*)-(−)-*N*-benzylchinchonidinium chloride (Scheme I) according to the method of O'Donnell et al.[5] The alkylation proceeds with modest asymmetric induction, 53% ee[6] in favor of the *S* enantiomer,[7] and affords an 83% chemical yield of pure product, 4. Enantiomerically pure material (>99% ee)[7] is obtained, as reported for several other derivatives,[5] after removing the racemate through crystallization from a hexane solution of enantiomerically enriched 4 at 4° C. Hydrolysis of 4 was then effected by refluxing in 6 N hydrochloric acid for 4 h to provide (*S*)-1 in 40% overall yield from 2.

Peptides 6 and 7 which incorporate 1 as an integral component of the polypeptide backbone were obtained by solid-phase synthesis methodology.[8,9] Toward this end, 1 was converted to the corresponding 9-fluorenylmethyl carbamate (FMOC) derivative 5 through treatment with FMOC azide in 50% aqueous dioxane containing 5% sodium carbonate (90% yield).[10] These peptides were synthesized using (benzotriazol-1-yloxy)tris(dimethylamino)phosphonium hexafluorophosphate/1-hydroxybenzotriazole (BOP/HOBT)[11] mediated amide couplings of FMOC-protected amino acids on PAL resin.[12] The completed peptides were N-terminus acetylated on the resin, cleaved by standard procedures, and purified by gel filtration on Biorad P2 gel filtration medium. The metal binding properties of peptides 6 and 7 (Chart I) have been studied using circular dichroism and ultraviolet/visible spectroscopy.[13]

In conclusion, this note illustrates the stereoselective synthesis and peptide incorporation of an amino acid possessing a bidentate unsaturated nitrogen-containing ligand. The long term advantage of making this moiety an integral component of an α-amino acid is that it allows for incorporation of the ligand anywhere within the primary sequence of a synthetic peptide. Incorporation of the bipyridyl moiety into the polyamide framework should prove to be useful in de novo design of metalloproteins for both structural and functional roles, since it combines the wide scope of coordination chemistry available to this ligand with the versatility of protein biopolymers as templates for the assembly of organized three-dimensional structures.

Experimental Section

^1H and ^{13}C NMR spectra were recorded at 500 MHz and 126 MHz, respectively, using TMS or DMSO-d_6 as internal standards.[14] Optical rotations were recorded at room temperature in a microcell, 1-dm path length. Mass spectra were taken on a ZAB mass spectrometer in fast atom bombardment (FAB) mode at the University of California Riverside Regional Mass Spec. Facility. Thin layer chromatography (TLC) was carried out using EM Reagents hard TLC plates with fluorescence indicator (SiO_2 60, F-254). Flash column chromatography was carried out according to the procedure of Still[15] using J. T. Baker (~40 μm) flash silica gel.

The asymmetric induction in the phase-transfer-catalyzed reaction was determined by HPLC analysis of the corresponding Mosher's amide[6] prepared from the amino acid methyl ester by reaction with excess (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride. Purification of the final product was achieved by PTLC (eluent chloroform/methanol, 10:1). HPLC analysis was carried out on a DNBPG covalent column, 5 μm (4.6 × 250 mm), eluent 3% i-PrOH/hexanes, 1.2 mL/min.[14]

Peptide Synthesis. All peptides were synthesized on a 0.1–0.2-mmol scale using solid-phase FMOC-amino protection and BOP/HOBT activated-ester chemistry on an automated peptide synthesizer. PAL resin was used to afford amides at the carboxy terminus. For the commercially available residues, 4.0 amino acid

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(6) The enantiomeric excesses can be evaluated either by ^1H NMR or HPLC analysis of the (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid amide (Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512) prepared from the methyl ester of 1. HPLC provides a more accurate analysis due to complicating resonances in the ^1H NMR spectrum. Chromatography was carried out on a DNBPG covalent column (5 μm, 4.6 × 250 mm), solvent 3% i-PrOH/hexanes, 1.2 mL/min (retention times: *S* derivative 19.8 min, *R* derivative 18.4 min). In addition, the optical purity of the underivatized amino acid can be determined directly on a CROWNPAK CR(−) column (Daicel).

(7) The absolute stereochemical outcome of the asymmetric alkylation has been demonstrated to be quite predictable with a wide variety of electrophiles.[5] In addition, the change in the direction of the optical rotation of 1 in going to an acidic aqueous solution $[[\alpha]^{25}_D$ −18.6° (*c* 1, H_2O); $[\alpha]^{25}_D$ −12.9° (*c* 1, 5 N HCl)] is in keeping with the Clough–Lutz–Jirgenson rule (see Greenstein, J. P.; Winitz, M. *Chemistry of the Amino Acids*, Vol. 1; John Wiley and Sons: New York, 1961; p 85). Finally, the order of elution from the CROWNPAK CR(−) column is also consistent with this assignment.

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equiv were used per coupling; however, for Bpa only 2.5 equiv were employed. Activated esters were formed in situ using BOP, HOBT, and 0.451 M *N*-methylmorpholine in *N*,*N*-dimethylformamide (DMF). Coupling times varied from 1 to 2 h depending upon coupling efficiency of the particular amino acid. Deprotection of FMOC-protected amine groups was performed using a 7-min 20% piperidine/DMF wash. All peptides were acetyl capped on the resin using 21 equiv of acetic anhydride and 5 equiv of triethylamine in 3 mL of DMF. After shaking for 2 h with the acyl capping reagents, the resin was washed with dichloromethane and briefly air dried. The peptide was then cleaved from the resin using Reagent R as described by Milligen[12] and lyophilized from water. Purity was assessed by reverse-phase HPLC (H_2O/CH_3CN mixtures; UV 256, 228 nm detection) and 1D NMR. Impure peptides were purified using P2 gel filtration chromatography with 50 mM acetic acid as eluent. Fractions containing pure peptide were identified by HPLC and concentrated by lyophilization. Pure peptides were stored at −20 °C.

***N*-(Diphenylmethylene)-α-amino-(2,2′-bipyridine)-6-propanoic Acid *tert*-Butyl Ester (4).** *N*-(Diphenylmethylene)glycine *tert*-butyl ester (**2**) (1.3 g, 4.4 mmol), *N*-benzylcinchonidinum chloride (0.31 g, 0.736 mmol), and **3** (0.95 g, 3.68 mmol) were added to a suspension of 20 mL of dichloromethane (CH_2Cl_2) and 7.04 mL of 50% aqueous sodium hydroxide and stirred vigorously for 1 h at room temperature, at which time it was complete as evaluated by TLC. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (20 mL). The combined organic phases were concentrated in vacuo. The residue was redissolved in CH_2Cl_2 (40 mL) and water (20 mL). The organic phase was separated, washed with water (2 × 10 mL), dried (Na_2SO_4), and concentrated to afford the crude product. The product was purified by flash chromatography (eluent hexane/ethyl acetate, 7:1). Prior to loading the compound, the silica column was pretreated with several volumes of the eluent which also contained 0.5% triethylamine.[16] The pure yield was 1.37 g (83%). At this stage, 65 mg of material was removed for stereochemical analysis. The product was crystallized from hexane at 4 °C. The solid product (0.69 g) was removed and the filtrate concentrated to afford an oil (0.58 g). The chemical yield of optically pure material is approximately 40%, mp (DL) 90–91 °C, (L) oil; $[\alpha]^{25}_D$ −327° (*c* 1, EtOAc); ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 9 H), 3.40 (dd, 1 H, *J* = 9.2 and 13.4 Hz), 3.52 (dd, 1 H, *J* = 4.3 and 13.4 Hz), 4.63 (dd, 1 H, *J* = 4.3 and 9.2 Hz), 7.16 (m, 4 H), 7.27 (m, 5 H), 7.32 (t, 1 H, *J* = 6.1 Hz), 7.52 (d, 1 H, *J* = 8.1 Hz), 7.65 (t, 1 H, *J* = 7.9 Hz), 7.69 (dd, 1 H, *J* = 1.5 and 7.6 Hz), 8.09 (d, 1 H, *J* = 7.9 Hz), 8.18 (d, 1 H, *J* = 7.9 Hz), 8.64 (dd, 1 H, *J* = 1.5 and 3.5 Hz); ^{13}C NMR ($CDCl_3$) δ 28.0, 41.8, 66.5, 81.1, 118.4, 121.4, 123.4, 124.4, 127.8, 128.0, 128.1, 128.7, 130.0, 136.3, 136.5, 136.9, 139.6, 148.9, 155.4, 156.2, 158.0, 170.6, 170.9, 203.3. Anal. Calcd for $C_{30}H_{29}N_3O_2$: C, 77.72; H, 6.30; N, 9.06. Found: C, 78.08; H, 6.15; N, 9.09.

(*S*)-α-Amino-(2,2′-bipyridine)-6-propanoic Acid (1). A suspension of optically pure **4** (0.5 g) was refluxed in 6 N hydrochloric acid (10 mL) for 4 h. The hydrolyzed reaction mixture was then cooled, extracted with ether (3 × 5 mL), and concentrated to dryness. The residual material was lyophilized several times from water to afford 0.3 g (100%) of the amino acid hydrochloride: mp 220 °C dec; $[\alpha]^{25}_D$ −18.6° (*c* 1, H_2O; pH 7.0) −12.9° (*c* 1, 5 N HCl); MS (M^+) 244; ^{1}H NMR (D_2O) δ 3.30 (dd, 1 H, *J* = 6.6 and 12.5 Hz), 3.35 (dd, 1 H, *J* = 5.0 and 12.5 Hz), 4.09 (dd, 1 H, *J* = 5.0 and 6.6 Hz), 7.29 (d, 1 H, *J* = 7.4 Hz), 7.49 (t, 1 H, *J* = 6.1 Hz), 7.79 (t, 1 H, *J* = 7.6 Hz), 7.82 (t, 1 H, *J* = 7.7 Hz), 7.98 (t, 1 H, *J* = 7.7 Hz), 8.07 (d, 1 H, *J* = 7.9 Hz), 8.50 (d, 1 H, *J* = 4.1 Hz); ^{13}C NMR (D_2O) δ 37.8, 54.9, 121.7, 123.9, 126.1, 140.2, 141.5, 148.2, 154.0, 154.6, 157.2, 174.1; UV (H_2O, free zwitterion) λ_{max} 238 (ϵ = 8.95 × 10^3), 284 (ϵ = 13.42 × 10^3).

***N*-[(9*H*-Fluoren-9-ylmethoxy)carbonyl]-α-amino-(2,2′-bipyridine)-6-propanoic Acid (5).** A solution of FMOC azide (0.81 g, 3.1 mmol) in 10 mL of 1,4-dioxane was added dropwise with stirring to a solution of **1** (0.75 g, 3.0 mmol) in 10 mL of 10% aqueous sodium carbonate at 0 °C, over 2 h. The reaction was then allowed to warm to room temperature and stirred for 36 h. The mixture was diluted with 100 mL of distilled water and extracted 3 times with 50 mL of ether. The aqueous phase was cooled in an ice bath and brought to pH 2 with concentrated hydrochloric acid. The suspension was then centrifuged (5000 rpm) for 10 min. The aqueous phase was decanted and the solid washed with water (2 × 50 mL), centrifuged, and decanted. The solid was taken up in methanol and concentrated in vacuo to yield 1.36 g (90%) of white powder: $[\alpha]^{25}_D$ −61.3° (*c* 1, MeOH); ^{1}H NMR (CD_3OD) δ 3.34 (m, 1 H), 3.62 (m, 1 H), 4.02 (t, 1 H, *J* = 7.2 Hz), 4.28 (m, 2 H), 5.13 (m, 1 H), 7.07 (m, 1 H), 7.20 (t, 1 H, *J* = 7.4 Hz), 7.26 (m, 1 H), 7.32 (t, 1 H, *J* = 7.3 Hz), 7.44 (d, 1 H, *J* = 7.4 Hz), 7.46 (d, 1 H, *J* = 7.4 Hz), 7.59 (t, 1 H, *J* = 7.9 Hz), 7.65 (d, 1 H, *J* = 7.4 Hz), 7.69 (d, 1 H, *J* = 7.5 Hz), 8.00 (t, 1 H, *J* = 5.2 Hz), 8.05 (t, 1 H, *J* = 7.8 Hz), 8.28 (d, 1 H, *J* = 7.8 Hz), 8.65 (d, 1 H, *J* = 7.5 Hz), 8.69 (d, 1 H, *J* = 8.0 Hz), 8.78 (d, 1 H, *J* = 4.9 Hz); ^{13}C NMR (CD_3OD) δ 39.7, 39.8, 48.2, 54.0, 67.8, 120.9, 122.1, 125.4, 126.0, 128.0, 128.1, 128.3, 128.7, 128.8, 128.9, 140.7, 142.4, 143.4, 144.8, 145.0, 145.1, 146.8, 148.3, 148.4, 149.3, 158.8, 158.9, 160.0, 160.1, 173.8, 175.1; high res MS [M^+], calcd for $C_{28}H_{24}N_3O_4$ 466.1767, obsd 466.1781.

Ac-Bpa-Thr-Pro-D-Ala-Val-Bpa-NH$_2$ (6): ^{1}H NMR (D_2O) δ 8.29 (s, 2 H), 7.63 (m, 8 H), 7.21 (m, 2 H), 7.10 (m, 2 H), 4.30 (d, 1 H, *J* = 5.8 Hz), 3.99 (d, 1 H, *J* = 7.14 Hz), 3.86 (t, 1 H, *J* = 7.52 Hz), 3.77 (t, 1 H, *J* = 6.1 Hz), 3.66 (d, 1 H, *J* = 7.23 Hz), 3.36 (m, 2 H), 3.16 (m, 1 H), 2.93 (m, 4 H), 1.64 (m, 13 H), 0.99 (d, 3 H, *J* = 7.2 Hz), 0.90 (d, 3 H, *J* = 6.4 Hz), 0.39 (d, 3 H, *J* = 6.8 Hz), 0.36 (d, 3 H, *J* = 6.8 Hz); high res MS [M^+], calcd for $C_{45}H_{56}N_{11}O_8$ 878.4313, obsd 878.4285.

Ac-Bpa-Thr-Pro-D-Ala-Val-Phe-NH$_2$ (7): ^{1}H NMR (DMSO-d_6) δ 8.75 (d, 1 H, *J* = 4.4 Hz), 8.52 (d, 1 H, *J* = 7.9 Hz), 8.30 (m, 2 H), 8.09 (t, 1 H, *J* = 7.1 Hz), 7.91 (m, 5 H), 7.58 (t, 1 H, *J* = 6.6 Hz), 7.40 (d, 1 H, *J* = 7.6 Hz), 7.24 (m, 7 H), 4.98 (m, 1 H), 4.58 (t, 1 H, *J* = 6.3 Hz), 4.40 (m, 1 H), 4.32 (m, 2 H), 4.40 (m, 2 H), 3.73 (m, 1 H), 3.63 (m, 1 H), 3.32 (m, 1 H), 3.11 (m, 2 H), 2.86 (m, 1 H), 2.04 (m, 2 H), 1.81 (m, 6 H), 1.20 (d, 3 H, *J* = 7.0 Hz), 1.11 (d, 3 H, *J* = 6.2 Hz), 0.77 (d, 3 H, *J* = 6.8 Hz), 0.70 (d, 3 H, *J* = 6.8 Hz); high res MS [M^+], calcd for $C_{41}H_{54}N_9O_8$ 800.4095, obsd 800.4135.

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Registry No. **1**·HCl, 137495-60-4; **2**, 81477-94-3; **3**, 83478-63-1; **4**, 137495-61-5; **5**, 137495-62-6; **6**, 136391-83-8; **7**, 136391-83-8; (8*S*,9*R*)-(−)-*N*-benzylcinchonidinium chloride, 69257-04-1.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of compounds 1–7 and HPLC traces of amino acid derivatives and peptides (13 pages). Ordering information is given on any current masthead page.

(16) This treatment was found necessary to avoid decomposition of the acid-labile imine product.

Wavelength Dependence of the Photolysis of Some Anthracene-Containing Sulfonium Salts

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Considerable interest is currently focused on photoacid generating systems.[1,2] Sulfonium salts are among the most

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