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# α-Carboxy-6-nitroveratryl: A Photolabile Protecting Group for Carboxylic Acids

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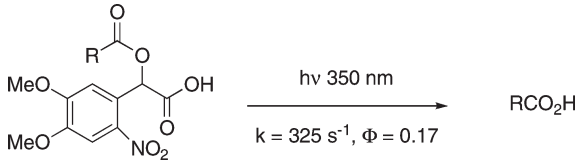


The synthesis of a new photolabile protecting group for carboxylic acids, α-carboxy-6-nitroveratryl (αCNV), is described. Bromide **3**, prepared in four steps from 3,4-dimethoxyphenylacetic acid, was used to alkylate carboxylic acids under mild conditions in good yield. Palladium-catalyzed deallylation afforded the acids **4a**−**h**, which underwent rapid and quantitative photolysis at wavelengths longer than 300 nm to liberate the carboxylic acid in good to quantitative yield. The rate of photolysis and quantum yield were determined to be 325 $s^{-1}$ and 0.17.

The photoprotection ("caging") of biologically important molecules is an area of considerable interest and has found widespread application in the biological field in recent years.[1] Photorelease of bioactive molecules is particularly valuable when conducting time-resolved studies of rapid biological processes, since photoliberation of the bioactive molecule can occur on the millisecond to microsecond time scale, beyond the limit of flow techniques.

Photolabile protecting groups have been developed for a number of biologically relevant functional groups, including carboxylates,[2] phosphates,[3] alcohols,[2c,4] phenols,[2c,g,5] thiols,[4b] amines,[6] and carbonyls.[7] To be useful in biological experiments, the protecting group should display rapid photolysis kinetics, high aqueous solubility and dark stability, good biocompatibility (including the photolysis products), high quantum yield, and long-wavelength excitation.[3]

In particular, the low wavelength, high energy light required for deprotection of certain protecting groups may result in cell damage or protein modification, and accordingly, there has been interest in protecting groups that will release acids upon irradiation at longer wavelengths.[2b,8] Given the broad applicability of photolabile caging, it is desirable to have at our disposal a number of photolabile protecting groups offering a range of photolysis characteristics.

The 2-nitrobenzyl group and its derivatives are the most widely studied photolabile protecting groups. The 2-nitrobenzyl group, discovered by Barltrop and Schofield in 1966, shows millisecond kinetics for acid release at relatively low wavelength excitation.[9] The α-carboxy-2-nitrobenzyl (αCNB) protecting group shows much faster photolysis kinetics, releasing acids on the microsecond time scale, but still has a low excitation wavelength.[10] By contrast, the 6-nitroveratryl protecting group may be removed by photolysis at longer wavelengths up to 420 nm, but the time scale for acid release is of the order of seconds.[11]

Herein, we present the results of our studies into a new photolabile protecting group, the α-carboxy-6-nitroveratryl (αCNV) group. Our aim was to produce a photolabile protecting group with long wavelength absorption and improved kinetics for acid release compared with the 6-nitroveratryl group.

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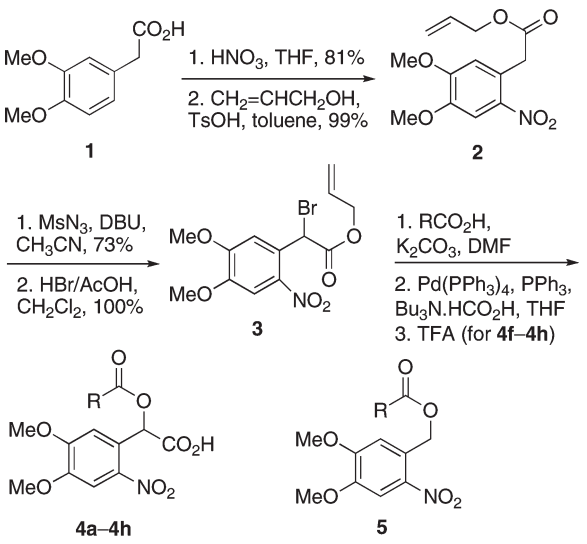
**SCHEME 1. Formation of Esters 4a−h**




The αCNV protecting group was synthesized from the commercially available 3,4-dimethoxyphenylacetic acid **1**, which was nitrated and esterified with allyl alcohol to give **2** in an overall yield of 80%. The allyl ester was chosen for its ability to be removed under essentially neutral conditions, compatible with acid-sensitive substrates such as β-lactams (vide infra).[12] Direct reaction between an alkyl halide and a carboxylate salt provides a very mild and clean method for ester formation, and so **2** was transformed into bromide **3** by a two-step procedure. Diazo transfer using methansulfonyl azide and DBU smoothly afforded the diazo ester, which was quantitatively converted into the bromide **3** by treatment with HBr/AcOH, Scheme 1.

The bromide **3** was reacted with a range of acids in DMF with potassium carbonate as base, affording the corresponding esters in good to excellent yields. Allyl ester cleavage was accomplished by stirring with $Pd(PPh_3)_4$ and tributylammonium formate in THF, affording the deprotected esters **4a−h**, Table 1. The allyl cleavage was normally complete within 15 min; excessively long reaction times (several hours) led to decarboxylation, affording the corresponding 6-nitroveratryl derivatives **5**. In the case of the amino acid derivatives **4f−h**, TFA treatment effected Boc group removal, yielding the amino acid esters as the TFA salts; the ester showed no signs of instability toward TFA.

The photolability of the compounds was determined by irradiation with a 400 W medium-pressure mercury lamp, filtered through Pyrex to cut off wavelengths below 300 nm. Photolyses were carried out on solutions prepared either in deuterated water, methanol or acetone; released product and remaining starting material was determined by integration of the relevant resonances in the $^1$H NMR spectrum in comparison to an internal standard (for a typical spectrum see Supporting Information, Figure S4). Conversion of the starting material was quantitative, while control solutions kept in the dark showed no evidence of degradation even after several days. Darkening of the solution occurred as the photolysis proceeded, possibly as a result of the formation of diazo compounds which are known by products from the photolysis of some nitrobenzyl derivatives.[13]

**TABLE 1. Preparation and Photolysis of Esters 4a−h**

| entry | ester | acid | esterification (%) | deallylation (%) | photolysis yield[c] (%) |
|---|---|---|---|---|---|
| 1 | **4a** | acetic[a] | 68[a] | 79 | 90 |
| 2 | **4b** | propanoic | 71 | 80 | quant |
| 3 | **4c** | hexanoic | 90 | 75 | quant |
| 4 | **4d** | benzoic | 73 | 71 | quant |
| 5 | **4e** | Penicillin G[a] | 84[a] | 80 | 72 |
| 6 | **4f** | Gly | 82 | 60[b] | 92 |
| 7 | **4g** | GABA | 76 | 64[b] | quant |
| 8 | **4h** | Phe | 78 | 54[b] | quant |

[a]Esterification employed the sodium salt rather than the free acid and $K_2CO_3$. [b]Overall yield for deallylation and Boc cleavage. [c]Photolysis was performed in deuterated water, methanol, or acetone. Photolysis yield was measured by integration of resonances in the $^1$H NMR spectrum in comparison to an internal standard (DMSO or $Me_6Si_2$); conversion was quantitative in all cases.

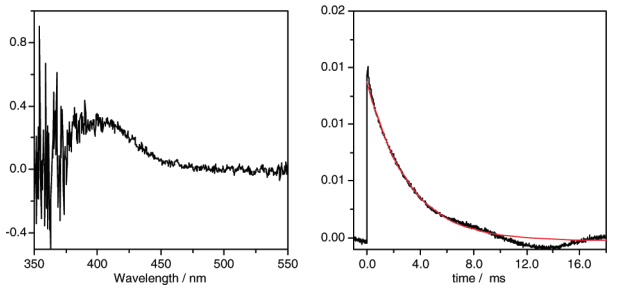



**FIGURE 1.** Transient absorption spectrum of **4d** in ethanol/water (1:1) 10 μs after pulsed excitation at 355 nm and decay of the transient absorption monitored at 390 nm. The red line represents the best fit according to a monoexponential decay with $k = 325\ s^{-1}$. The feature at 14 ms is an experimental artifact.

The quantum yield of the photorelease reaction in ethanol/water (1:1) solutions was determined by ferrioxalate actinometry to be 0.17 ± 0.03 upon irradiation at 365 nm. Laser flash photolysis ($\lambda_{ex} = 355$ nm) of solutions of **4d** in ethanol/water (1:1) revealed the rapid formation of a transient absorption with a maximum at 410 nm (Figure 1). The latter is assigned to the *aci*-nitro intermediate based on its similarity with previously reported absorption spectra of analogous intermediates. The photolysis kinetics were determined by monitoring the transient absorption at 390 nm, which decayed monoexponentially on the millisecond time scale ($k = 325\ s^{-1}$) toward the initial absorbance level. The decay of the *aci*-nitro signal has previously been correlated with product release, although detailed investigations by Wirz and co-workers[14] and by Corrie and co-workers[15] showed that the hydrolysis of the hemiacetal can be rate-limiting, with the rate-limiting step being dependent on solvent, pH, and the nature of the leaving group.

To provide a simple comparison between the αCNB and αCNV protecting groups, the acetates of both were photolyzed side-by-side in deuterated acetone with a 400 W Pyrex-jacketed, medium-pressure mercury lamp. As evident from Figure 2, under these conditions release of acetic acid from

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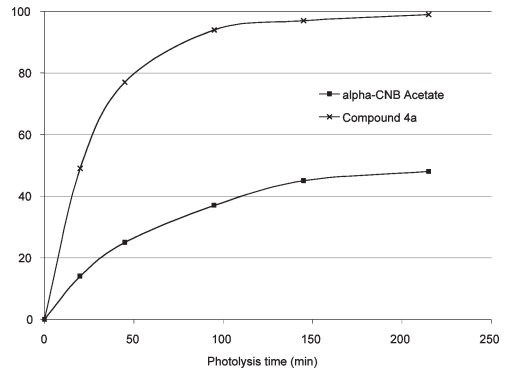


**FIGURE 2.** Comparative photolysis of αCNB acetate and **4a** in acetone through Pyrex.

the αCNV ester is significantly faster than from the αCNB ester.

In conclusion, we have developed a short, high-yielding route to αCNV esters, applicable to a range of carboxylic acid derivatives. The αCNV protecting group has the desirable absorption characteristics of the 6-nitroveratryl group, but αCNV esters photolyze some 2−3 orders of magnitude faster than 6-nitroveratryl esters. The chemistry is applicable to the protection and release of neurotransmitters (e.g., glycine and GABA) and $\beta$-lactam antibiotics (e.g., penicillin), as well as simple carboxylic acids and should be readily extendable to the caging of peptides and other biomolecules.

## Experimental Section

**General Esterification Procedure.** The acid (2.08 mmol, 1.5 equiv) was dissolved in DMF (20 mL), and $K_2CO_3$ (2.08 mmol, 1.5 equiv) was added. The suspension was stirred for 30 min at room temperature before a solution of bromide **3** (1.39 mmol, 1 equiv) in DMF (5 mL) was added. Alternatively, if the carboxylate salt of the acid was available, this (2.08 mmol, 1.5 equiv) was suspended in DMF and a solution of the bromide (1.39 mmol, 1.0 equiv) added. The solution was stirred at room temperature until no bromide remained (1 h to overnight). The reaction mixture was poured into water and extracted with $Et_2O$. The combined organic extracts were washed with 50% saturated $NaHCO_3$ and water, dried over $MgSO_4$, and concentrated. The esters did not usually contain significant impurities, but column chromatography (100% hexane to 7:3 hexane/EtOAc) was necessary to remove residual DMF.

**Deallylation Procedure.** $Pd(PPh_3)_4$ and $PPh_3$ were dissolved in degassed THF (5 mL) and stirred at rt for 5 min in the dark. A 1.2 M solution of $Bu_3NHCOOH$ (made by mixing a 1:1 molar ratio of $Bu_3N$ and HCOOH in dry, degassed THF) was added followed by a solution of the ester in THF (5 mL). When all of the ester had been consumed (TLC), the THF was evaporated and the residue was partitioned between 50% saturated aqueous $NaHCO_3$ and $Et_2O$. The organic layer was extracted with 50% saturated $NaHCO_3$, and the combined aqueous layers were washed with $Et_2O$. The aqueous phase was acidified to pH 1−2 with 2 M HCl and extracted with EtOAc. The combined EtOAc layers were dried over $MgSO_4$ and concentrated to give the acid.

**Acetic Acid α-Carboxy-4,5-dimethoxy-2-nitrobenzyl Ester (4a).** Acetic acid α-allyloxycarbonyl-4,5-dimethoxy-2-nitrobenzyl ester (428 mg, 1.26 mmol) was treated with $Pd(PPh_3)_4$ (50 mg, 0.043 mmol), $PPh_3$ (330 mg, 1.26 mmol), and $Bu_3NHCO_2H$ (1.2 M solution in THF, 4.2 mL, 5.04 mmol) according to the general procedure to give acetic acid α-carboxy-4,5-dimethoxy-2-nitrobenzyl ester (**4a**) as a colorless solid (298 mg, 79%): mp 148−151 °C (from EtOAc); IR (film) 3417 (br), 2942, 1743, 1618, 1584, 1526 $cm^{-1}$; UV (MeOH) $\lambda_{max}$ (log $\varepsilon$) 338 (3.89), 243 (4.28), 222 (4.23), 204 (4.35); $^1H$ NMR (300 MHz, acetone-$d_6$) $\delta$ 2.17 (s, 3H), 3.97 (s, 6H), 6.88 (s, 1H), 7.19 (s, 1H), 7.70 (s, 1H); $^{13}C$ NMR (75 MHz, acetone-$d_6$) $\delta$ 20.5, 56.7, 56.8, 70.3, 109.2, 111.6, 124.8, 141.8, 150.2, 154.4, 169.0, 170.0; MS (electrospray) $m/z$ 344 (35, $[M - H + 2Na]^+$), 322 (100, $[M + Na]^+$); HRMS (electrospray) calcd for $C_{12}H_{13}NO_8Na$ 322.0539, found 322.0543.

**Propanoic Acid α-Carboxy-4,5-dimethoxy-2-nitrobenzyl Ester (4b).** Propanoic acid α-allyloxycarbonyl-4,5-dimethoxy-2-nitrobenzyl ester (445 mg, 1.26 mmol) was treated with $Pd(PPh_3)_4$ (50 mg, 0.043 mmol), $PPh_3$ (330 mg, 1.26 mmol), and $Bu_3NHCO_2H$ (1.2 M solution in THF, 4.2 mL, 5.04 mmol) according to the general procedure to give propanoic acid α-carboxy-4,5-dimethoxy-2-nitrobenzyl ester (**4b**) (316 mg, 80%) as a colorless oil: IR (film) 3520 (br), 3310 (br), 2942, 1742, 1618, 1584, 1525 $cm^{-1}$; UV (MeOH) $\lambda_{max}$ (log $\varepsilon$) 338 (4.01), 243 (4.38), 206 (4.41); $^1H$ NMR (300 MHz, acetone-$d_6$) $\delta$ 1.14 (t, $J$ = 7.5 Hz, 3H), 2.50 (q, $J$ = 7.5 Hz, 2H), 3.95 (s, 3H), 3.96 (s, 3H), 6.90 (s, 1H), 7.19 (s, 1H), 7.69 (s, 1H); $^{13}C$ NMR (75 MHz, acetone-$d_6$) $\delta$ 10.2, 28.6, 57.6, 57.7, 71.2, 110.1, 112.5, 125.9, 142.7, 151.1, 155.3, 170.1, 174.4; MS (electrospray) $m/z$ 336 (22, $[M + Na]^+$), 240 (100); HRMS (electrospray) calcd for $C_{13}H_{15}NO_8Na$ 336.0695, found 336.0685.

**Hexanoic Acid α-Carboxy-4,5-dimethoxy-2-nitrobenzyl Ester (4c).** Hexanoic acid α-allyloxycarbonyl-4,5-dimethoxy-2-nitrobenzyl ester (267 mg, 0.68 mmol) was treated with $Pd(PPh_3)_4$ (30 mg, 0.026 mmol), $PPh_3$ (177 mg, 0.68 mmol), and $Bu_3NHCO_2H$ (1.2 M solution in THF, 2.27 mL, 2.72 mmol) according to the general procedure to give hexanoic acid α-carboxy-4,5-dimethoxy-2-nitrobenzyl ester (**4c**) (180 mg, 75%) as a colorless oil: IR (film) 3530 (br), 2932, 2858, 1745, 1616, 1584, 1526 $cm^{-1}$; UV (MeOH) $\lambda_{max}$ (log $\varepsilon$) 337 (4.08), 241 (4.46), 221 (4.46), 208 (4.47); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 0.83−0.88 (m, 2H), 1.24−1.31 (m, 4H), 1.60−1.67 (m, 2H), 2.37−2.46 (m, 2H), 3.95 (s, 3H), 3.97 (s, 3H), 6.92 (s, 1H), 7.02 (s, 1H), 7.66 (s, 1H), 10.32 (br s, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 22.2, 24.4, 31.1, 33.8, 56.4, 56.5, 69.6, 108.3, 110.9, 123.6, 140.5, 149.1, 153.2, 172.3; MS (electrospray) $m/z$ 378 (100, $[M + Na]^+$); HRMS (electrospray) calcd for $C_{16}H_{21}NO_8Na$ 378.1165, found 378.1159.

**Benzoic Acid α-Carboxy-4,5-dimethoxy-2-nitrobenzyl Ester (4d).** Benzoic acid α-allyloxycarbonyl-4,5-dimethoxy-2-nitrobenzyl ester (408 mg, 1.02 mmol) was treated with $Pd(PPh_3)_4$ (40 mg, 0.035 mmol), $PPh_3$ (270 mg, 1.03 mmol), and $Bu_3NHCO_2H$ (1.2 M solution in THF, 3.4 mL, 4.08 mmol) according to the general procedure to give benzoic acid α-carboxy-4,5-dimethoxy-2-nitrobenzyl ester (**4d**) (261 mg, 71%) as a colorless solid: mp 53−56 °C; IR (film) 3520 (br), 3280 (br), 2940, 1727, 1584, 1526 $cm^{-1}$; UV (MeOH) $\lambda_{max}$ (log $\varepsilon$) 324 (3.75), 283 (3.77), 230 (4.38), 206 (4.31); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.95 (s, 3H), 3.96 (s, 3H), 7.12 (broad s, 2H), 7.44 (t, $J$ = 7.4 Hz, 2H), 7.58 (t, $J$ = 7.4 Hz, 1H), 7.69 (s, 1H), 8.06 (d, $J$ = 7.4 Hz, 2H), 9.69 (broad s, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 56.6, 56.7, 70.6, 108.6, 111.5, 123.7, 128.7, 128.8, 130.1, 133.9, 140.6, 149.4, 153.5, 165.2, 172.7; MS (electrospray) $m/z$ 400 (10, $[M + K]^+$), 384 (100, $[M + Na]^+$); HRMS (electrospray) calcd for $C_{17}H_{15}NO_8Na$ 384.0695, found 384.0706.

**Penicillin G α-Carboxy-4,5-dimethoxy-2-nitrobenzyl Ester (4e).** Penicillin G α-allyloxycarbonyl-4,5-dimethoxy-2-nitrobenzyl ester (112 mg, 0.18 mmol) was treated with $Pd(PPh_3)_4$ (9 mg, 0.008 mmol), $PPh_3$ (48 mg, 0.18 mmol), and $Bu_3NHCO_2H$ (1.2 M solution in THF, 0.61 mL, 0.73 mmol) according to the general procedure. Following removal of the solvent, the residue was subjected to purification by HPLC to afford the tributylammonium salt ($t_R$ 34.57 min, 100:0 to 0:100 water/acetonitrile over 40 min). This was dissolved in water (5 mL), acidified to pH 3 with HCl, and immediately extracted with ethyl

acetate. Drying over $MgSO_4$ and removal of the solvent gave penicillin G α-carboxy-4,5-dimethoxy-2-nitrobenzyl ester (**4e**) (83 mg, 80%) as a colorless gum: IR (film) 3406 (br), 2963, 2874, 1784, 1748, 1667, 1632, 1583, 1524 $cm^{-1}$; UV ($H_2O$) $\lambda_{max}$ (log $\varepsilon$) 339 (3.70), 297 (3.65), 244 (4.13), 209 (4.40); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.37, 1.42, 1.44, 1.48 (4*s*, 6H), 3.63 (s, 2H), 3.93, 3.95, 3.96, 3.98 (4*s*, 6H), 4.39, 4.48 (2s, 1H), 5.47, 5.52 (2d, $J$ = 4.1 Hz, 1H), 5.59−5.65 (m, 1H), 6.15, 6.21 (2d, $J$ = 8.0 Hz, 1H), 6.82, 6.84 (2s, 1H), 6.97, 7.00 (2*s*, 1H), 7.24−7.36 (m, 5H), 7.65, 7.69 (2*s*, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 26.4, 31.6, 31.9, 43.2, 56.5, 56.65, 56.71, 58.9, 64.7, 67.9, 68.0, 70.2, 70.3, 71.0, 71.3, 108.4, 108.6, 111.5, 112.0, 127.8, 128.9, 129.0, 129.2, 129.6, 133.5, 140.3, 140.6, 149.4, 153.4, 166.2, 166.3, 169.4, 169.5, 171.1, 171.2, 173.2, 173.4; MS (electrospray) $m/z$ 596 (100, $[M + Na]^+$); HRMS (electrospray) calcd for $C_{26}H_{27}N_3O_{10}NaS$ 596.1315, found 596.1332.

***N*-(*tert*-Butoxycarbonyl)glycine α-Carboxy-4,5-dimethoxy-2-nitrobenzyl Ester Trifluoroacetate Salt (4f).** *N*-(*tert*-Butoxycarbonyl)glycine α-allyloxycarbonyl-4,5-dimethoxy-2-nitrobenzyl ester (250 mg, 0.55 mmol) was treated with $Pd(PPh_3)_4$ (30 mg, 0.026 mmol), $PPh_3$ (144 mg, 0.55 mmol), and $Bu_3NHCO_2H$ (1.2 M solution in THF, 1.83 mL, 2.2 mmol) according to the general procedure to give a colorless solid which was stirred for 1 h in trifluoroacetic acid (1 mL). Removal of the trifluoroacetic acid in vacuo and trituration of the residue with diethyl ether afforded *N*-(*tert*-butoxycarbonyl)glycine α-carboxy-4,5-dimethoxy-2-nitrobenzyl ester trifluoroacetate salt (**4f**) (142 mg, 60%) as a colorless solid: mp 166−169 °C; IR (solid) 3070 (br), 2969, 2938, 2906, 2844, 1758, 1727, 1686, 1578, 1513 $cm^{-1}$; UV ($D_2O$) $\lambda_{max}$ (log $\varepsilon$) 355 (3.78), 223 (4.23), 208 (3.98); $^1H$ NMR (300 MHz, $D_2O$ + NaOD) $\delta$ 3.03 (s, 2H), 3.78 (s, 3H), 3.82 (s, 3H), 5.36 (s, 1H), 7.08 (s, 1H), 7.54 (s, 1H); $^{13}C$ NMR (125 MHz, $D_2O$ + NaOD) $\delta$ 46.8, 58.28, 58.34, 74.6, 110.6, 113.7, 134.5, 142.1, 149.4, 155.0, 180.7, 183.8; MS (electrospray) $m/z$ 337 (100, $[M + Na]^+$); HRMS (electrospray) calcd for $C_{12}H_{14}N_2O_8Na$ 337.0648, found 337.0639.

**4-(*tert*-Butoxycarbonylamino)butyric Acid α-Carboxy-4,5-dimethoxy-2-nitrobenzyl Ester Trifluoroacetate Salt (4g).** 4-(*tert*-Butoxycarbonylamino)butyric acid α-allyloxycarbonyl-4,5-dimethoxy-2-nitrobenzyl ester (489 mg, 1.01 mmol) was treated with $Pd(PPh_3)_4$ (40 mg, 0.035 mmol), $PPh_3$ (266 mg, 1.01 mmol), and $Bu_3NHCO_2H$ (1.2 M solution in THF, 3.4 mL, 4.08 mmol) according to the general procedure to give a colorless solid which was stirred for 1 h in trifluoroacetic acid (1 mL). Removal of the trifluoroacetic acid in vacuo and trituration of the residue with diethyl ether afforded 4-(*tert*-butoxycarbonylamino-)butyric acid α-carboxy-4,5-dimethoxy-2-nitrobenzyl ester trifluoroacetate salt (**4g**) (294 mg, 64%) as a colorless solid: mp 164−167 °C; IR (solid) 3100, 2945, 1714, 1701, 1617, 1578, 1532 $cm^{-1}$; UV ($D_2O$) $\lambda_{max}$ (log $\varepsilon$) 354 (3.63), 313 (3.69), 244 (4.07), 206 (3.91); $^1H$ NMR (300 MHz, $D_2O$) $\delta$ 1.89−1.98 (m, 2H), 2.50−2.68 (m, 2H), 3.00 (t, $J$ = 7.5 Hz, 2H), 3.80 (s, 3H), 3.87 (s, 3H), 6.63 (s, 1H), 7.04 (s, 1H), 7.54 (s, 1H); $^{13}C$ NMR (75 MHz, $D_2O$) $\delta$ 22.2, 30.7, 38.8, 56.5, 56.6, 71.6, 109.0, 112.7, 123.6, 140.4, 149.0, 153.3, 171.8, 173.5; MS (electrospray) $m/z$ 365 (100, $[M + Na]^+$); HRMS (electrospray) calcd for $C_{14}H_{18}N_2O_8Na$ 365.0961, found 365.0963.

***N*-(*tert*-Butoxycarbonyl)phenylalanine α-Carboxy-4,5-dimethoxy-2-nitrobenzyl Ester Trifluoroacetate Salt (4h).** *N*-(*tert*-Butoxycarbonyl)phenylalanine α-allyloxycarbonyl-4,5-dimethoxy-2-nitrobenzyl ester (140 mg, 0.26 mmol) was treated with $Pd(PPh_3)_4$ (12 mg, 0.01 mmol), $PPh_3$ (67 mg, 0.26 mmol), and $Bu_3NHCO_2H$ (1.2 M solution in THF, 0.9 mL, 1.08 mmol) according to the general procedure to give a colorless solid which was stirred for 1 h in trifluoroacetic acid (1 mL). The trifluoroacetic acid was removed in vacuo and the residue purified by HPLC to afford *N*-(*tert*-butoxycarbonyl)phenylalanine α-carboxy-4,5-dimethoxy-2-nitrobenzyl ester trifluoroacetate salt (**4h**) (73 mg, 54%) as a colorless gum: $t_R$ 20.79 min (100:0 to 0:100 water/acetonitrile over 40 min); IR (film) 3425 (br), 2942, 1757, 1674, 1585, 1526 $cm^{-1}$; UV ($H_2O$) $\lambda_{max}$ (log $\varepsilon$) 348 (3.56), 312 (3.51), 247 (3.90); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 3.07−3.34 (m, 2H), 3.79, 3.80, 3.90, 3.94 (4s, 6H), 4.32−4.37 and 4.55−4.60 (2m, 1H), 6.74−6.84 (m, 2H), 6.98−7.05 and 7.08−7.16 (2m, 5H), 7.55 (s, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 35.9, 36.2, 54.5, 54.8, 56.41, 56.47, 56.55, 72.2, 72.7, 108.2, 108.4, 112.2, 116.0 (q, $J$ = 289 Hz), 122.1, 122.2, 127.6, 127.8, 128.7, 129.0, 129.1, 129.2, 133.0, 133.2, 140.4, 140.5, 149.4, 149.5, 153.47, 153.50, 162.1 (q, $J$ = 37 Hz), 168.0, 169.0, 170.1, 170.3; MS (electrospray) $m/z$ 427 (100, $[M + Na]^+$), 405 (20, $[M + H]^+$); HRMS (electrospray) calcd for $C_{19}H_{21}N_2O_8$ 405.1298, found 405.1305.

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**Supporting Information Available:** Experimental procedures for all compounds not detailed in the Experimental Section. $^1H$ and $^{13}C$ NMR spectra for all compounds. Details of photolysis kinetics and quantum yield determinations. This material is available free of charge via the Internet at http://pubs.acs.org.