Pentadienylnitrobenzyl and Pentadienylnitropiperonyl Photochemically Removable Protecting Groups

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New photochemically removable protecting groups have been developed based on classical nitrobenzyl compounds modified by the inclusion of a pentadienyl group. It serves to trap through an internal Diels−Alder reaction the nitroso group produced as part of the photochemical deprotection process, preventing its further photochemistry or chemical reactions with nucleophiles.

Introduction

Nitrobenzyl alcohol derivatives are among the best-known photochemically removable protecting groups.[1] They play an important role in a variety of technologies, including photolithography[2] and time-resolved studies in a variety of disciplines.[3,4] The kinetics and mechanism by which their photoremoval occurs have been extensively studied.[5] On UV irradiation, they undergo a net internal redox process, releasing the heteroatom and producing an intrinsically reactive *o*-nitrosocarbonyl compound, which has several drawbacks. The nitroso compound can act as an internal filter and has a photochemistry of its own[6] that can lead to other even more intensely absorbing materials, such as azo and azoxy compounds. It is often reactive with sensitive functionalities, particularly nucleophiles such as thiols[7] and amines, and can therefore be injurious[8] to the living systems in which nitrobenzyl groups are often used. Nitrobenzyl compounds have been used in the protection or "caging" of a variety of biomolecules despite these shortcomings,[1,9] but it is clear that wider application of the concept would be possible were superior photochemically removable groups available. We have developed novel groups for the protection of alcohols and phosphates[10] but have also aimed to develop more general photoremovable groups through improvements in the nitrobenzyl series. In short, a simple means to rapidly inactivate the nitroso group was needed. This report describes a solution to the problem of nitrobenzyl reactivity by trapping the product nitrosocompound as an internal hetero-Diels−Alder adduct.

The concept of trapping the nitroso compound is not new, and in many studies a high concentration of thiol has been included for this purpose, though some biological systems are incompatible with these conditions.[11] The hetero-Diels−Alder reaction of aryl nitroso compounds such as nitrosobenzene with butadienes is well-known,[12] but its bimolecular rate is far too slow to compete with the photochemical and polar reactions of the nitrosoarene.[13] The intramolecular hetero-Diels−Alder reaction was considered because this trapping reaction should be much faster, but a potential concern was interference by the diene with the photochemistry. Early mechanistic work on the nitrobenzyl deprotection reaction suggested that it is a singlet process and therefore would not be affected. Danishefsky's results[14] gave further encouragement to this thought. However, one study showed that deprotection of a nitrobenzyl ether includes a short-lived triplet biradical that can be quenched by a cyclohexadiene.[15]

Results

For initial evaluation of the approach, an unsubstituted aromatic ring was used because electron-donating groups

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(16) Compound **3a** was obtained as a mixture of diastereomers that apparently results from photochemical equilibration of the diene before deprotection. In one case, interruption of a reaction and reisolation of starting material showed it was an (*E*,*E*)/(*E*,*Z*) mixture.
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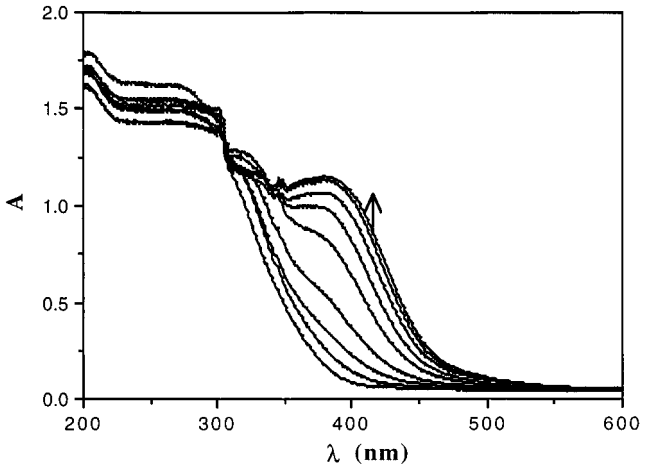
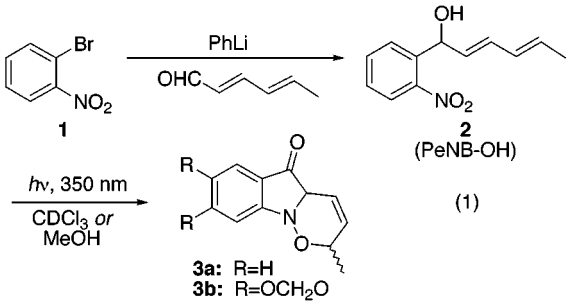
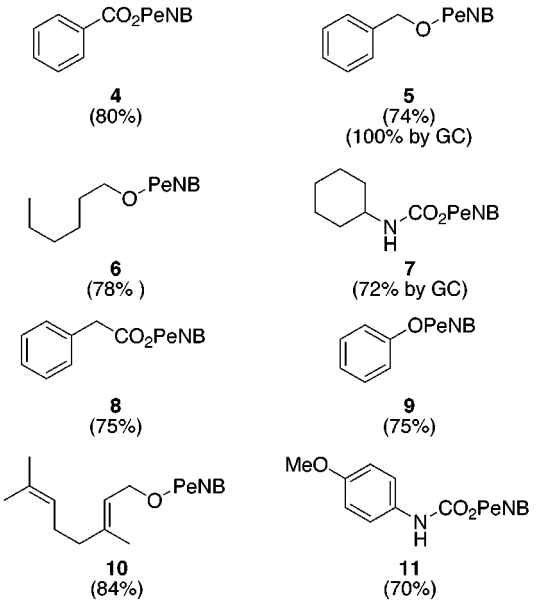


Figure 1. UV spectrum of the irradiation of **2** (1 mM, MeOH) with an Oriel arc lamp source delivered through a liquid light guide at times up to 6 min.

in the nitrosoarene slow cycloaddition.[12] The synthesis of pentadienylnitrobenzyl alcohol (PeNB-OH) was accomplished as shown in eq 1 (78%). To test the design,

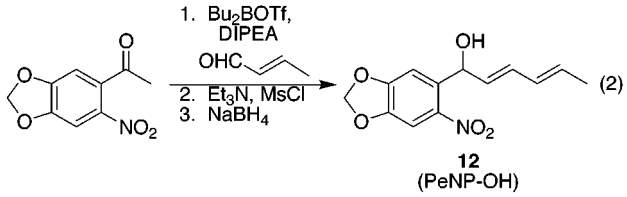


compound **2** was irradiated (10 mM in MeOH) with a 450 W Hanovia light source equipped with a water-cooled quartz immersion well to provide within 3 h the expected **3a**[16] as a barely separable mixture of diastereomers in 79% isolated yield, based on recovered starting material. These compounds were extensively characterized by spectroscopic means, including 2D NMR, to establish the regiochemistry as indicated, and hydrogenated (Pt/C) to a more readily separable mixture of dihydro derivatives. These compounds undergo interconversion in solution and deuterium exchange α to the ketone. The reaction to form **3a** gives an isosbestic point at 305 nm when followed by UV (Figure 1), showing that it is clean at low conversion. Eight derivatives **4**−**11**, encompassing some common functional groups (carboxylic acid, amine, alcohol, and phenol) that would be desirable to protect, were efficiently prepared from **2** by conventional routes (see the Experimental Section: esters from acid chlorides, aliphatic ethers from halides, aryl ethers via the Mitsunobu reaction under improved conditions,[17] carbamates from isocyanates). Protection reactions of **2** are limited to neutral or basic conditions because its benzylic/allylic character makes it somewhat acid-sensitive. Photochemical deprotection reactions (10 mM in MeOH) were conducted on a 0.2 mmol scale for 1.5−2 h at 254 nm for these PeNB derivatives, except for the phenyl ether, which required 4 h. Yields are given below each reactant. Compound **3a** was naturally also obtained in each of these reactions, though generally in somewhat lower yield (~60%) than in the irradiation of **2**.



Quantum yield studies were conducted with **2** using nitrobenzyl alcohol ($\Phi = 0.45$)[18] as an actinometer and following loss of starting material from 5 to 25% conversion by NMR with an internal standard. The measured quantum yield for **2** is 0.26. Quantum yields measured in the same way against nitrobenzyl cyclohexyl carbamate ($\Phi = 0.07$)[18] for the derivatives of **2** are as follows: **4**, 0.22; **5**, 0.41; **7**, 0.38. Rate studies of the benzyl and hexyl ethers were conducted using a 83 mW/cm^2 350 nm broad-band source, following the reaction by GC with internal standards. Both give 5 min half-lives.

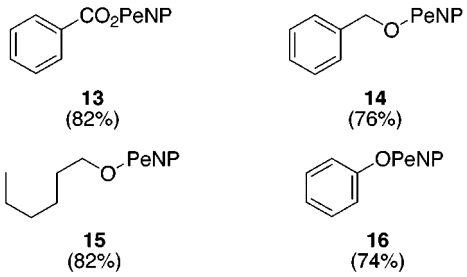
Success with this first group encouraged preparation and study of an analogue incorporating a red-shifting methylenedioxy group. An aldol approach (eq 2) was used in this case to produce pentadienylnitropiperonyl alcohol (**12**, PeNP-OH) (50%). It provides **3b** on Hanovia irradia-



tion in ~80% yield. Simultaneous irradiation of **2** and **12** in the Hanovia apparatus shows a half-time for the conversion of the former to **3a** of 30 min, while the conversion of the latter to **3b** has a half-time of 10 min, at least partially related to its greater absorption at 350 nm. The effectiveness of **12** as a protecting group was also demonstrated with ether and ester derivatives **13**−**16**. Deprotection reactions of these PeNP derivatives were performed at 350 nm for 3 h, except for the phenyl ether, which required 254 nm irradiation. The differing behavior of the phenyl derivatives may be related to energy transfer or competitive absorption. Again, the yields of deprotection reactions are given below each reactant.

Discussion and Conclusion

This work offers a novel strategy for the spatially and temporally controlled release of common functional groups



13 (82%) **14** (76%) **15** (82%) **16** (74%)

that does not produce a reactive byproduct or require additives. The reactions are clean and efficient in both the chemical and quantum sense, and they occur rapidly. The protected derivatives can be made through straightforward, traditional transformations, and in fact, the use of the Mitsunobu reaction should greatly expand the range of functional groups (imides, heterocycles, thiols) that can be readily protected. A disadvantage of these groups is their acid sensitivity, more so for **12**. The irradiation wavelengths are in open spectral windows (for biological systems). It is interesting that the intramolecular hetero-Diels−Alder cycloaddition process is so finely balanced, as analogues of **2** having zero or two terminal diene methyl groups do not undergo clean photochemical reaction to afford a cycloadduct, and Danishefsky obtained a cycloadduct in good yield from a dienone with an α-methoxy group but no terminal substitution.[14]

Experimental Section

All reagents were purchased from Aldrich unless otherwise indicated and were verified and/or titrated before use. 3,4-Methylenedioxyacetophenone was purchased from Lancaster Synthesis. Diethyl ether and THF were distilled from sodium/benzophenone immediately prior to use. Triethylamine and diisopropylamine were distilled from sodium and stored under argon. Acetonitrile, pyridine, benzene, and dichloromethane were freshly distilled from calcium hydride. Methanol was distilled from magnesium turnings immediately prior to use. All reactions were performed in oven-dried glassware under argon atmosphere unless otherwise noted. Flash column chromatography was carried out on EM Reagents silica gel 60 (230−400 mesh). Silica gel was deactivated by forming a slurry in 10% triethylamine in hexanes, filtering, and washing with copious amounts of hexanes. Capillary gas chromatography was performed with a 0.25 mm i.d. × 30 m DB-5.625 column. Melting points are uncorrected. ^{1}H NMR spectra were obtained on 300 or 400 MHz spectrometers. Broad-band irradiations were performed using a 450 W Hanovia light source equipped with a water-cooled quartz immersion well or a Rayonet photochemical reactor containing 16 phosphor-coated 350 nm lamps or 254 nm lamps. All single wavelength irradiations were performed using an Oriel light source. Elemental analyses were performed by Atlantic Microlabs.

1-(2-Nitrophenyl)-2,4-hexadien-1-ol (2). 2-Bromonitrobenzene (100 mg, 0.495 mmol) was dissolved in THF (5.5 mL), and the solution was cooled to −78 °C. A 1.8 M ether/hexane solution of phenyllithium (0.33 mL, 0.59 mmol) was added dropwise. This deep purple solution was stirred at −78 °C for 1.25 h, and then 2,4-hexadienal (82 μL, 0.74 mmol) was added dropwise. The reaction was stirred at −78 °C for 30 min and was allowed to warm to room temperature over another 15 min. Water was added carefully, and the mixture was extracted with ethyl acetate. The combined extracts were dried ($MgSO_4$) and evaporated; the residue was purified by flash chromatography using 5% ethyl acetate in hexanes as eluent to afford pure 1-(2-nitrophenyl)-2,4-hexadien-1-ol (84.4 mg, 78%) as a peach-colored solid. Mp: 70−71 °C. IR (CH_2Cl_2): 3587, 3440, 3057, 3022, 2924, 1658, 1609, 1529, 1356, 993, 857 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.92 (1H, d, J = 8 Hz), 7.78 (1H, d, J = 8 Hz), 7.63 (1H, t, J = 8 Hz), 7.43 (1H, t, J = 8 Hz), 6.35 (1H, dd, J = 10.0, 15.0 Hz), 6.04 (1H, m), 5.8 (3H, m), 2.45 (1H, d, J = 3.2 Hz), 1.75 (3H, d, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$): δ 138.0, 133.4, 132.1, 131.5, 130.3, 129.7, 128.6, 128.3, 128.2, 124.5, 69.7, 18.2. UV: λ_{max} 264 nm, ϵ = 5370 (CH_3CN). Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.46; H, 5.94; N, 6.35. HRMS (FAB, M^+): calcd for $C_{12}H_{13}NO_3$ 219.0895, found 219.0896.

Photocycloadduct 3a. Pentadienylnitrobenzyl alcohol (62.2 mg, 0.284 mmol) was dissolved in dry CH_3OH (28 mL) in a tightly capped Pyrex flask. The solution was irradiated while stirring without temperature control for 4 h using a 450 W Hanovia light source equipped with a water-cooled quartz immersion well. The CH_3OH was evaporated, and the residue was rotary chromatographed on a 1 mm silica plate utilizing 1:5 ethyl acetate/hexanes to elute **3a** (33.2 mg, 58%) as a 1:1 mixture of diastereomers. Some pentadienylnitrobenzyl alcohol (12.9 mg, 21%) was recovered as well. IR (KBr): 3343 (−OH, enol tautomer), 3071, 2975, 2926, 2873, 2245, 1713 (C═O, keto tautomer), 1613, 1485, 1469, 1320, 1155, 1102, 1050, 938, 901, 747, 687 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.53 (2H, d, J = 8 Hz), 7.42 (2H, t, J = 8 Hz), 6.79 (2H, t, J = 8 Hz), 6.73 (2H, d, J = 8 Hz), 6.29 (2H, t, J = 6.6 Hz), 5.53 (2H, dd, J = 5.6, 13.6 Hz), 5.14 (4H, m), 4.83 (2H, d, J = 5.6 Hz), 1.42 (3H, d, J = 6.5 Hz), 1.34 (3H, d, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$): δ 198.8, 198.6, 159.22, 159.17, 138.9, 138.7, 138.00, 137.97, 125.3 (two carbons), 124.7, 124.4, 119.87, 119.77, 118.9, 118.8, 112.05, 112.03, 101.1, 100.8, 82.8, 82.6, 22.3, 22.2. UV: λ_{max} 256 nm, ϵ = 5802 (CH_3CN). HRMS (FAB, M^+): calcd for $C_{12}H_{11}NO_2$ 201.0789, found 201.0782.

Hydrogenation of 3a. Five percent Pt on activated carbon (43 mg) was weighed into a flame-dried flask, and the photoadduct **3a** (25 mg, 0.124 mmol) was added as a solution in 0.5 mL of dry THF at room temperature. Triethylamine (2.5 mL, 0.018 mmol) was added, and the resulting mixture was subjected to 15 cycles of evacuating the flask enough to boil the THF and then releasing the vacuum to a H_2-filled balloon. The resulting H_2-saturated solution was stirred overnight at room temperature. The mixture was filtered through a pad of Celite, and the residue was purified by radial chromatography using 30% ethyl acetate in hexanes to afford the expected compounds as a 1:1 mixture of diastereomers (15.5 mg, 61%). The higher R_f (twice-developed 25% EtOAC in hexanes) compound gave the following data. ^{1}H NMR ($CDCl_3$): δ 7.53 (1H, d, J = 8 Hz), 7.42 (1H, t, J = 8 Hz), 6.82 (1H, t, J = 8 Hz), 6.75 (1H, d, J = 8 Hz), 4.75 (1H, bs), 4.41 (1H, m), 2.35 (2H, m), 2.04 (1H, m), 1.66 (1H, m), 1.34 (3H, d, J = 6.5 Hz). The lower R_f compound gave the following data. ^{1}H NMR ($CDCl_3$): δ 7.56 (1H, d, J = 8 Hz), 7.42 (1H, t, J = 8 Hz), 6.82 (1H, t, J = 8 Hz), 6.75 (1H, d, J = 8 Hz), 4.75 (1H, bs), 4.41 (1H, m), 2.36 (2H, m), 2.20 (1H, m), 2.00 (1H, m), 1.34 (3H, d, J = 6.5 Hz). The separated diastereomers were equilibrated to the original 1:1 diastereomeric mixture by allowing them to stand in CH_2Cl_2 solution overnight at room temperature. A 1:1 mixture of the diastereomers was stirred with D_2O, and the broad singlet at 4.75 disappeared from the ^{1}H NMR spectrum.

3b. Yield: 75% at 80% conversion. IR (CH_2Cl_2): 3358, 3080, 2976, 2905, 1697, 1618, 1485, 1302, 1063, 939, 910, 862, 833 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.91 (2H, s), 6.30 (2H, m), 6.27 (2H, s), 5.97 (4H, s), 5.56 (2H, ddd, J = 12.6, 5.8, 2.0 Hz), 5.17 (2H, m), 4.81 (2H, bd, J = 8.7 Hz), 1.45 (3H, d, J = 6.5 Hz), 1.37 (3H, d, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$): δ 196.3, 196.1, 158.7, 158.6, 157.03, 156.99, 144.2, 142.8, 142.7, 138.5, 138.4, 124.9, 124.6, 111.6, 111.5, 111.3, 102.6 (2 carbons), 101.99, 101.96, 93.30, 93.27, 82.9, 82.8, 22.24, 22.20. UV: λ_{max} 279 nm, ϵ 9638 (CH_3CN). HRMS (FAB, M^+): calcd for $C_{13}H_{11}NO_4$ 245.0688, found 245.0690.

1-(Benzoyloxy)-1-(2-nitrophenyl)-2,4-hexadiene (4). A mixture of 1-(2-nitrophenyl)-2,4-hexadien-1-ol (50.1 mg, 0.229 mmol) and 4-(dimethylamino)pyridine (4.2 mg, 0.034 mmol) was dissolved in dry CH_2Cl_2 (1.0 mL), and pyridine (50 μL, 0.62 mmol) was added in one portion. The solution was cooled to 0 °C, and benzoyl chloride (40 μL, 0.34 mmol) was added

dropwise. The reaction was allowed to warm to room temperature while being stirred overnight and then diluted with ethyl acetate (20 mL). The turbid mixture was washed with water and saturated aqueous $CuSO_4$ solution. The organic phase was dried ($MgSO_4$) and concentrated; the residue was purified by flash column chromatography using deactivated silica gel and 5% ethyl acetate in hexanes as eluent to afford pure 1-(benzoyloxy)-1-(2-nitrophenyl)-2,4-hexadiene (63.7 mg, 86%) as a yellow gum. IR (KBr): 3068, 3025, 2963, 2915, 2853, 1722, 1658, 1605, 1580, 1529, 1450, 1353, 1262, 1101, 1069, 990, 713 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.08 (2H, m), 7.97 (1H, m), 7.73 (1H, m), 7.60 (2H, m), 7.46 (2H, m), 7.08 (1H, d, J = 6.7 Hz), 6.39 (1H, dd, J = 10.5, 15.3 Hz), 6.08 (1H, m), 5.84 (3H, m), 1.77 (3H, d, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$): δ 165.1, 147.9, 135.2, 134.2, 133.5, 133.2, 132.5, 130.2, 129.7, 129.6, 128.6, 128.4, 128.12, 128.08, 124.6, 71.8, 18.2. Anal. Calcd for $C_{19}H_{17}NO_4$: C, 70.58; H, 5.30; N, 4.33. Found: C, 70.51; H, 5.33; N, 4.27.

1-Benzyloxy-1-(2-nitrophenyl)-2,4-hexadiene (5). 1-(2-Nitrophenyl)-2,4-hexadien-1-ol (50.2 mg, 0.229 mmol) and Ag_2O (123.8 mg, 0.534 mmol) were dissolved in dry DMF (1.0 mL). Benzyl bromide (82 μL, 0.69 mmol) was added in one portion, and the brown suspension was stirred at room temperature for 7 h. The mixture was vacuum filtered, and the cake was washed with ether (10 mL). The filtrate was combined with additional ether (40 mL), and the solution was washed with water, dried ($MgSO_4$), and evaporated; the residue was purified by preparative TLC using 5% ethyl acetate in hexanes to afford pure 1-benzyloxy-1-(2-nitrophenyl)-2,4-hexadiene (58.6 mg, 83%) as a pale oil. IR (KBr): 3065, 3026, 2914, 2862, 1659, 1607, 1528, 1452, 1353, 1070, 991, 742, 695 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.87 (1H, d, J = 8 Hz), 7.80 (1H, d, J = 8 Hz), 7.61 (1H, t, J = 8 Hz), 7.2−7.5 (6H, m), 6.33 (1H, dd, J = 10.4, 15.0 Hz), 6.05 (1H, m), 5.5−5.8 (3H, m), 4.54 (1H, d, J = 11.4 Hz), 4.44 (1H, d, J = 11.4 Hz), 1.75 (3H, d, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$): δ 148.5, 137.7, 136.7, 133.3, 133.2, 131.4, 130.5, 128.5, 128.3, 128.2, 128.10, 128.08, 127.6, 124.2, 76.6, 70.8, 18.1. Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.93; H, 6.24; N, 4.43.

1-(1-Hexyloxy)-1-(2-nitrophenyl)-2,4-hexadiene (6). A mixture of class IV KF/alumina reagent[19] (189 mg, 1.2 mmol) and 1-(2-nitrophenyl)-2,4-hexadien-1-ol (101.5 mg, 0.4630 mmol) was suspended in dry CH_3CN (0.65 mL). Hexyl iodide (104 μL, 0.705 mmol) was added in one portion, and the reaction was stirred vigorously at room temperature for 10 h. More hexyl iodide (104 μL, 0.705 mmol) and KF/alumina (195 mg, 1.3 mmol) were added, and the reaction was stirred overnight. More KF/alumina (230 mg, 1.5 mmol) was added, and the reaction was stirred for another 10 h. The mixture was filtered, and the residue was washed with ethyl acetate. The solvents were evaporated, and the residue was purified by radial chromatography on a 1 mm silica plate using 1% ether in hexanes to give pure 1-(1-hexyloxy)-1-(2-nitrophenyl)-2,4-hexadiene (75.7 mg, 54%) as a pale yellow oil. IR (KBr): 3020, 2932, 2861, 1659, 1608, 1529, 1467, 1450, 1354, 1303, 1090, 890, 856 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.86 (1H, d, J = 8 Hz), 7.73 (1H, d, J = 8 Hz), 7.60 (1H, t, J = 8 Hz), 7.40 (1H, t, J = 8 Hz), 6.28 (1H, dd, J = 10.4, 15.2 Hz), 6.03 (1H, m), 5.74 (1H, m), 5.61 (1H, m), 5.41 (1H, d, J = 7.0 Hz), 3.46 (1H, m), 3.31 (1H, m), 1.74 (3H, d, J = 6.8 Hz), 1.57 (2H, m), 1.2−1.4 (6H, m), 0.88 (3H, t, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$): δ 148.5, 137.2, 133.1, 132.8, 131.0, 130.6, 128.9, 128.4, 127.9, 124.1, 76.8, 69.3, 31.6, 29.7, 25.8, 22.6, 18.1, 14.0. HRMS (FAB, M^+): calcd for $C_{18}H_{25}NO_3$ 303.1834, found 303.1824.

Kinetics of Photodeprotection of PeNB Ethers. A 0.0125 M stock solution of **5** in CH_3OH (400 μL, 4.99×10^{-3} mmol) was placed in an oven-dried Pyrex vial, and a 0.0249 M solution of *n*-octanol in CH_3OH (100 μL, 2.49×10^{-3} mmol) was added as an internal GC standard. The solution was irradiated using a 350 nm Oriel light source equipped with an infrared filtering fiber optic cable, and 1 μL aliquots were removed and injected into a capillary GC at timed intervals to ascertain the concentration of $PhCH_2OH$ in solution and thus the percentage yield of deprotection (GC oven temperature = 100 °C, isothermal). Analogous response factor analyses were performed for **6** utilizing internal standards and GC conditions tailored for the substrate to be analyzed.

R	$t_{1/2}$ (min)	% yield	internal standard	GC oven temp (°C)
benzyl	5	100 ± 7	*n*-octanol	100
n-hexyl	5	79 ± 4	cyclohexanol	70

1-(Cyclohexylcarbamoyloxy)-1-(2-nitrophenyl)-2,4-hexadiene (7). 1-(2-Nitrophenyl)-2,4-hexadien-1-ol (51.2 mg, 0.234 mmol) was dissolved in THF (2.2 mL), and the solution was cooled to 0 °C. A 1.4 M solution of CH_3Li in ether (16 μL, 0.022 mmol) was quickly added, and this solution was stirred at 0 °C for 15 min. Cyclohexyl isocyanate (58 μL, 0.45 mmol) was added dropwise, and the reaction was stirred for 30 min. The reaction was quenched with the addition of water, and the mixture was extracted with ethyl acetate. The ethyl acetate was dried ($MgSO_4$) and evaporated, and the residue was purified by flash chromatography using deactivated silica gel and 5% ethyl acetate in hexanes as eluent to afford pure 1-(cyclohexylcarbamoyl)-1-(2-nitrophenyl)-2,4-hexadiene (67.9 mg, 84%) as an amber gum. IR (KBr): 3405, 3328, 3023, 2930, 2856, 2251, 1711 (C=O), 1522, 1449, 1352, 1313, 1252, 1225, 1031, 990, 735 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.91 (1H, d, J = 8.0 Hz), 7.62 (2H, m), 7.41 (1H, m), 6.73 (1H, d, J = 6.6 Hz), 6.28 (1H, dd, J = 10.4, 15.3 Hz), 6.02 (1H, m), 5.74 (2H, m), 4.75 (1H, d, J = 7.9 Hz), 3.43 (1H, m), 1.93 (2H, m), 1.74 (3H, d, J = 6.8 Hz), 1.65 (2H, m), 1.0−1.4 (6H, m). ^{13}C NMR ($CDCl_3$): δ 154.1, 147.8, 135.9, 133.5, 133.2, 131.9, 130.3, 128.2, 128.0, 126.7, 124.4, 71.4, 49.9, 33.2, 25.3, 24.7, 18.1. Anal. Calcd for $C_{19}H_{24}N_2O_4$: C, 66.26; H, 7.02; N, 8.13. Found: C, 66.19; H, 7.06; N, 8.03.

1-(2-Phenylacetoxy)-1-(2-nitrophenyl)-2,4-hexadiene (8). A mixture of 1-(2-nitrophenyl)-2,4-hexadien-1-ol (500 mg, 2.28 mmol) and 4-(dimethylamino)pyridine (28 mg, 0.228 mmol) was dissolved in dry CH_2Cl_2 (10 mL), and pyridine (0.55 mL, 6.84 mmol) was added. The solution was cooled to 0 °C, and phenylacetyl chloride (0.60 mL, 4.56 mmol) was added dropwise. The reaction was stirred for 20 min at 0 °C and then allowed to warm to room temperature while stirring overnight. The reaction mixture was diluted with water and extracted with CH_2Cl_2. The organic phase was washed with saturated aqueous $CuSO_4$ solution and brine, dried (Na_2SO_4), and concentrated. The residue was purified by flash column chromatography using deactivated silica gel and 5% ethyl acetate in hexanes (containing 2% NEt_3) as eluent to afford pure 1-(2-phenylacetoxy)-1-(2-nitrophenyl)-2,4-hexadiene (684 mg, 89%) as a pale orange oil. IR (neat): 3027, 2922, 1742 (C=O), 1530, 1352, 1245, 1139 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.91 (1H, ddd, J = 8.0, 1.6, 0.8 Hz), 7.50 (1H, m), 7.40 (2H, m), 7.28 (5H, m), 6.84 (1H, d, J = 6.4 Hz), 6.21 (1H, dd, J = 15.2, 10.4 Hz), 6.00 (1H, m), 5.74 (1H, dd, J = 14.8, 6.4 Hz), 5.68 (1H, dd, J = 15.2, 6.4 Hz), 3.66 (2H, s), 1.73 (3H, d, J = 6.4 Hz). ^{13}C NMR ($CDCl_3$): δ 169.8, 147.7, 134.9, 133.8, 133.4, 133.2, 132.1, 130.1, 129.1, 128.43, 128.41, 128.37, 128.3, 127.9, 127.0, 125.8, 124.3, 71.3, 41.2, 18.0. HRMS (FAB, $[M + H]^+$): calcd for $C_{20}H_{20}NO_4$ 338.1392, found 338.1382 (this compound contains an inseparable minor olefin stereoisomer (6%)).

1-Phenoxy-1-(2-nitrophenyl)-2,4-hexadiene (9). Tributylphosphine (0.85 mL, 3.42 mmol) was added to a solution of 1-(2-nitrophenyl)-2,4-hexadien-1-ol (500 mg, 2.28 mmol) and phenol (322 mg, 3.42 mmol) in dry benzene (15 mL) at 0 °C. 1,1′-(Azodicarbonyl)dipiperidine (863 mg, 3.42 mmol) was added to the solution with stirring. After 10 min, the reaction mixture was allowed to warm to room temperature and stirred for 20 h. Hexane was added, and the mixture was filtered through Celite. The solvent was evaporated, and the residue was purified by flash column chromatography using deactivated silica gel and 2% ethyl acetate in hexanes (containing 2% NEt_3) as eluent to afford 1-phenoxy-1-(2-nitrophenyl)-2,4-hexadiene (410 mg, 61%) as a yellow oil. IR (neat): 3033, 2915, 2854, 1596, 1523, 1492, 1345, 1233 cm^{-1}. ^1H NMR ($CDCl_3$): δ

(19) Ando, T.; Yamawaki, J.; Kawarte, T.; Sum, S.; Hanafusa, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2504−2507.

7.89 (1H, dd, J = 8.1, 0.9 Hz), 7.53 (2H, m), 7.38−7.23 (3H, m), 7.13 (1H, dd, J = 15.9, 1.2 Hz), 7.01−6.89 (3H, m), 6.23 (1H, dd, J = 15.9, 6.0 Hz), 5.88 (1H, dqd, J = 15.6, 6.6, 0.9 Hz), 5.65 (1H, ddd, J = 15.6, 6.6, 1.5 Hz), 5.28 (1H, td, J = 6.6, 1.2 Hz), 1.75 (3H, ddd, J = 6.6, 1.5, 0.9 Hz). ^{13}C NMR ($CDCl_3$): δ 157.4, 147.6, 133.9, 132.9, 132.2, 129.4, 129.2 (2 carbons), 128.9, 128.6, 128.1, 126.8, 124.4, 120.9, 116.1 (2 carbons), 78.6, 17.9. HRMS (FAB, $[M - H]^+$): calcd for $C_{18}H_{16}NO_3$ 294.1130, found 294.1118 (this compound contains an inseparable minor olefin stereoisomer (<8%)).

1-(1-Geranyloxy)-1-(2-nitrophenyl)-2,4-hexadiene (10). 1-(2-Nitrophenyl)-2,4-hexadien-1-ol (500 mg, 2.28 mmol) was dissolved in dry CH_3CN (10 mL) at room temperature. Geranyl bromide (0.54 mL, 2.74 mmol) and KF/alumina reagent (40%, 1.81 g, 11.4 mmol) were added in one portion. The reaction mixture was stirred vigorously for 10 h at room temperature. More geranyl bromide (0.54 mL, 2.74 mmol) and KF/alumina reagent (40%, 1.81 g, 11.4 mmol) were added, and the reaction was stirred overnight. The mixture was filtered through Celite, and the filter cake was washed with ethyl acetate (50 mL). The solvents were evaporated, and the residue was purified by flash column chromatography using deactivated silica gel and 2% ethyl acetate in hexanes (containing 2% NEt_3) as eluent to afford pure 1-(1-geranyloxy)-1-(2-nitrophenyl)-2,4-hexadiene (705 mg, 87%) as an orange oil. IR (neat): 2971, 2929, 2855, 1535, 1444, 1358, 1052 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.85 (1H, dd, J = 8.0, 1.2 Hz), 7.76 (1H, dd, J = 8.0, 1.2 Hz), 7.60 (1H, m), 7.39 (1H, m), 6.27 (1H, dd, J = 15.2, 10.8 Hz), 6.01 (1H, m), 5.74 (1H, dd, J = 14.8, 6.8 Hz), 5.62 (1H, dd, J = 15.2, 6.8 Hz), 5.48 (1H, d, J = 6.8 Hz), 5.34 (1H, m), 5.08 (1H, m), 4.01 (1H, dd, J = 11.6, 6.8 Hz), 3.92 (1H, dd, J = 11.6, 6.8 Hz), 2.05 (4H, m), 1.74 (3H, dd, J = 6.8, 1.2 Hz), 1.68 (3H, s), 1.59 (6H, d, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$): δ 148.4, 140.5, 136.9, 132.9, 132.7, 131.3, 130.7, 130.5, 128.8, 128.4, 127.8, 123.9, 123.8, 120.2, 75.4, 65.2, 39.4, 26.2, 25.5, 17.9, 17.5, 16.2. HRMS (FAB, $[M - H]^+$): calcd for $C_{22}H_{28}NO_3$ 354.2069, found 354.2061 (this compound contains an inseparable minor olefin stereoisomer (<13%)).

1-(Anisylcarbamoyloxy)-1-(2-nitrophenyl)-2,4-hexadiene (11). 1-(2-Nitrophenyl)-2,4-hexadien-1-ol (250 mg, 1.14 mmol) was dissolved in dry THF (5 mL), and the solution was cooled to 0 °C. A solution of CH_3Li (1.4 M in diethyl ether, 0.4 mL, 0.57 mmol) was added to the solution, and the reaction mixture was stirred for 15 min at 0 °C. 4-Methoxyphenyl isocyanate (0.23 mL, 1.59 mmol) was added dropwise to the mixture, and the reaction mixture was stirred for 30 min at 0 °C. The reaction was quenched with water, and the mixture was extracted with ethyl acetate. The organic phase was washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by flash column chromatography using deactivated silica gel and 10% ethyl acetate in hexanes (containing 2% NEt_3) as eluent to afford 1-(anisylcarbamoyloxy)-1-(2-nitrophenyl)-2,4-hexadiene (298 mg, 71%) as a brown oil. IR (neat): 3325 (N−H), 3020, 2916, 2834, 1730 (C═O), 1601, 1522, 1211, 1029 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.93 (1H, d, J = 9.0 Hz), 7.61 (2H, m), 7.42 (1H, m), 7.24 (2H, d, J = 7.5 Hz), 6.82 (3H, m), 6.66 (1H, bs), 6.31 (1H, dd, J = 15.0, 10.5 Hz), 6.02 (1H, m), 5.78 (1H, dd, J = 6.9, 3.3 Hz), 5.73 (1H, dd, J = 6.9, 3.6 Hz), 3.76 (3H, s), 1.74 (3H, d, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$): δ 155.8, 152.2, 147.6, 135.3, 133.9, 133.2, 132.1, 130.4, 130.1, 128.3, 128.0, 126.2, 124.4 (two carbons), 120.4, 114.0 (two carbons), 72.0, 55.4, 18.2. HRMS (FAB, $[M - CO_2]^+$): calcd for $C_{19}H_{20}N_2O_3$: 324.1473, found 324.1474.

3,4-Methylenedioxy-6-nitroacetophenone. 3,4-Methylenedioxyacetophenone (10 g, 61 mmol) was dissolved in CH_3NO_2 (78 mL) at room temperature; 90% HNO_3 (12.0 mL, 270 mmol) was added slowly with stirring and cooling with a 23 °C water bath. Stirring was continued for 3 h, at which time the reaction appeared complete, as evidenced by TLC analysis. The reaction mixture was carefully neutralized by the addition of saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried ($MgSO_4$), and the residue was purified by flash chromatography using 33% ethyl acetate in hexanes to afford 3,4-methylenedioxy-6-nitroacetophenone (9.43 g, 74%). Mp: 119−120 °C (lit.[20] mp 122−123 °C).

1-(3,4-Methylenedioxy-6-nitrophenyl)-3-hydroxy-4-hexen-1-one. 3,4-Methylenedioxy-6-nitroacetophenone (4.5 g, 21 mmol) was dissolved in dry CH_2Cl_2 (86 mL) cooled to 0 °C. A 1 M solution of dibutylboron triflate in CH_2Cl_2 (43.0 mL, 43.0 mmol) was added over 10 min, and the resulting orange/red solution was stirred at 0 °C for an additional 10 min. Diisopropylethylamine (8.20 mL, 47.07 mmol) was added over 3 min as a solution in 5 mL of CH_2Cl_2, and the resulting red/brown solution was stirred at 0 °C for 30 min. The reaction was allowed to warm to room temperature and was stirred an additional 30 min. It was cooled to −78 °C, and crotonaldehyde (4.22 mL, 50.9 mmol) was added over 10 min as a solution in 5 mL of CH_2Cl_2. This brown solution was stirred at −78 °C for 20 min, warmed to 0 °C, and stirred for 2 h. The reaction was quenched at 0 °C by the addition of pH 7 phosphate buffer (172 mL), CH_3OH (258 mL), and 30% H_2O_2 (172 mL), and this mixture was stirred vigorously at room temperature for a few min. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2. The combined extracts were washed successively with saturated aqueous NH_4Cl solution and saturated aqueous NaCl solution. The CH_2Cl_2 solution was dried ($MgSO_4$) and evaporated to give 1-(3,4-methylenedioxy-6-nitrophenyl)-3-hydroxy-4-hexen-1-one (6.97 g, 100%), which was used directly in the next step. ^{1}H NMR ($CDCl_3$): δ 7.56 (1H, s), 6.72 (1H, s), 6.20 (2H, s), 5.75 (1H, m), 5.50 (1H, m), 4.69 (1H, m), 2.90 (2H, m), 2.79 (1H, bs), 1.70 (3H, d, J = 6 Hz).

1-(3,4-Methylenedioxy-6-nitrophenyl)-2,4-hexadien-1-one. 1-(3,4-Methylenedioxy-6-nitrophenyl)-3-hydroxy-4-hexen-1-one (6.967 g, 21.5 mmol) was dissolved in dry CH_2Cl_2 (109 mL), and the solution was cooled to −78 °C. Triethylamine (6.0 mL, 43 mmol) was added quickly, and the reaction was stirred for 10 min. Methanesulfonyl chloride (3.33 mL, 43 mmol) was added dropwise, and the resulting solution was stirred at −78 °C for 30 min. The reaction was diluted with water, and the phases were separated. The aqueous phase was extracted with CH_2Cl_2. The combined CH_2Cl_2 extract was washed with 1 M HCl and saturated aqueous $NaHCO_3$ and dried ($MgSO_4$). The residue was purified by flash chromatography using 17% ethyl acetate in hexanes to afford mostly pure 1-(3,4-methylenedioxy-6-nitrophenyl)-2,4-hexadiene-1-one, which was obtained analytically pure by recrystallization from diisopropyl ether (3.14 g, 56%). Mp: 90−91 °C. IR (CH_2Cl_2): 3113, 3063, 3024, 2968, 2914, 2852, 1660 (C═O), 1630, 1610, 1589, 1520, 1483, 1425, 1395, 1345, 1157, 1036, 995, 931, 875 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.60 (1H, s), 6.76 (1H, s), 6.80 (1H, m), 6.08−6.30 (5H, m), 1.85 (3H, d, J = 6.3 Hz). ^{13}C NMR ($CDCl_3$): δ 192.5, 152.3, 148.7, 146.1, 141.8, 139.6, 133.0, 130.0, 127.4, 107.4, 104.8, 103.5, 18.8. Anal. Calcd for $C_{13}H_{11}NO_5$: C, 59.77; H, 4.24; N, 5.36. Found: C, 59.85; H, 4.31; N, 5.29.

1-(3,4-Methylenedioxy-6-nitrophenyl)-2,4-hexadien-1-o1 (12). 1-(3,4-Methylenedioxy-6-nitrophenyl)-2,4-hexadiene-1-one (3.66 g, 14.0 mmol) was dissolved in a mixture of THF (40 mL) and CH_3OH (73 mL), and the solution was cooled to 0 °C. Sodium borohydride (700 mg, 19 mmol) was added in small portions, and this turbid mixture was stirred at 0 °C for 30 min. The reaction mixture was diluted with water, and the mixture was extracted with ethyl acetate. The combined ethyl acetate was dried ($MgSO_4$) and evaporated to give fairly clean 1-(3,4-methylenedioxy-6-nitrophenyl)-2,4-hexadiene-1-o1 (3.90 g) as an orange, tacky oil. The oil was further purified by crystallization from ether/hexanes to afford light yellow crystals. Mp: 85−86 °C. IR (KBr): 3538, 3413, 3089, 3069, 3019, 2962, 2914, 2852, 1657, 1617, 1515, 1482, 1332, 1258, 1035, 991, 931, 878, 601 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.48 (1H, s), 7.21 (1H, s), 6.35 (1H, dd, J = 13, 8 Hz), 6.15 (2H, bs), 6.05 (1H, m), 5.79 (3H, m), 2.42 (1H, d, J = 3 Hz), 1.75 (3H, d, J = 6 Hz). ^{13}C NMR ($CDCl_3$): δ 152.2, 147.0, 141.7, 136.0, 131.7,

(20) Fetter, J.; Lempert, K.; Møller, J. *Tetrahedron* **1975**, *31*, 2559−2569.

131.3, 130.4, 129.8, 107.3, 105.2, 102.9, 69.3, 18.1. Anal. Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.23; H, 5.08; N, 5.40. UV: λ_{max} 350 nm, $\epsilon = 5659$ (CH_3CN). HRMS (FAB, $[M - H]^+$): calcd for $C_{13}H_{12}NO_5$ 262.0715, found 262.0721.

1-(Benzoyloxy)-1-(3,4-methylenedioxy-6-nitrophenyl)-2,4-hexadiene (13). A mixture of 1-(3,4-methylenedioxy-6-nitrophenyl)-2,4-hexadien-1-ol (500 mg, 1.90 mmol) and 4-(dimethylamino)pyridine (23 mg, 0.19 mmol) was dissolved in dry CH_2Cl_2 (10 mL), and pyridine (0.46 mL, 5.70 mmol) was added to this solution in one portion. The solution was cooled to 0 °C, and benzoyl chloride (0.33 mL, 2.85 mmol) was added dropwise. The reaction was stirred for 20 min at 0 °C and then allowed to warm to room temperature while stirring overnight. The reaction mixture was diluted with water and extracted with CH_2Cl_2. The organic phase was washed with saturated aqueous $CuSO_4$ solution and brine, dried (Na_2SO_4), and concentrated. The residue was purified by flash column chromatography using deactivated silica gel and 5% ethyl acetate in hexanes (containing 2% NEt_3) as eluent to afford pure 1-(benzoyloxy)-1-(3,4-methylenedioxy-6-nitrophenyl)-2,4-hexadiene (671 mg, 96%) as a yellow oil. IR (neat): 3056, 3008, 2912, 1720 (C═O), 1520, 1320, 1104, 1040 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.07 (2H, dd, $J = 8.6$, 1.1 Hz), 7.60−7.40 (4H, m), 7.11 (2H, m), 6.38 (1H, dd, $J = 15.3$, 10.3 Hz), 6.06 (3H, m), 5.84 (1H, dd, $J = 8.7$, 6.1 Hz), 5.80 (1H, dd, $J = 14.9$, 8.1 Hz), 1.75 (3H, d, $J = 6.4$ Hz). ^{13}C NMR ($CDCl_3$): δ 165.0, 152.2, 147.3, 141.9, 133.6, 133.3, 132.6, 132.3, 130.2, 129.64, 129.58, 128.4, 126.1, 106.6, 105.32, 105.29, 103.0, 77.0, 71.6, 18.2. HRMS (FAB, M^+): calcd for $C_{20}H_{17}NO_6$ 367.1056, found 367.1056.

1-(Benzyloxy)-1-(3,4-methylenedioxy-6-nitrophenyl)-2,4-hexadiene (14). NaH (137 mg, 5.70 mmol) was added to a solution of 1-(3,4-methylenedioxy-6-nitrophenyl)-2,4-hexadien-1-ol (500 mg, 1.90 mmol) in dry DMF (10 mL) at 0 °C. Benzyl bromide (0.29 mL, 2.47 mmol) was added dropwise to the mixture, and the reaction mixture was stirred for 5 h at room temperature. The reaction was quenched with water and extracted with diethyl ether. The organic phase was washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was purified by flash column chromatography using deactivated silica gel and 5% ethyl acetate in hexanes (containing 2% NEt_3) as eluent to afford pure 1-(benzyloxy)-1-(3,4-methylenedioxy-6-nitrophenyl)-2,4-hexadiene (369 mg, 55%) as an orange oil. IR (neat): 3008, 2928, 2864, 1680, 1632, 1520, 1480, 1344, 1056 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.32 (7H, m), 6.34 (1H, m), 6.10 (2H, dd, $J = 3.6$, 1.1 Hz), 6.02 (1H, m), 5.75 (1H, dd, $J = 15.0$, 6.7 Hz), 5.63 (2H, dd, 6.1, 3.0 Hz), 4.50 (1H, d, $J = 11.5$ Hz), 4.43 (1H, d, $J = 11.5$ Hz), 1.75 (3H, d, $J = 6.4$ Hz). ^{13}C NMR ($CDCl_3$): δ 152.2, 146.9, 142.1, 137.7, 134.7, 132.5, 131.1, 130.5, 128.6, 128.3, 127.63, 127.58, 107.0, 105.0, 102.8 (two carbons), 77.0, 76.1, 70.7, 18.1. HRMS (FAB, $[M - H]^+$): calcd for $C_{20}H_{18}NO_5$ 352.1185, found 352.1184. Anal. Calcd for $C_{20}H_{19}NO_5$: C, 67.98; H, 5.42; N, 3.96. Found: C, 67.91; H, 5.41; N, 3.90.

1-(Hexyloxy)-1-(3,4-methylenedioxy-6-nitrophenyl)-2,4-hexadiene (15). 1-(3,4-Methylenedioxy-6-nitrophenyl)-2,4-hexadien-1-ol (500 mg, 1.90 mmol) was dissolved in dry CH_3CN (10 mL) at room temperature, and hexyl iodide (0.42 mL, 2.85 mmol) and KF/alumina reagent (40 %, 690 mg, 4.75 mmol) were added in one portion. The reaction mixture was stirred vigorously for 10 h at room temperature. More hexyl iodide (0.42 mL, 2.85 mmol) and KF/alumina reagent (40%, 690 mg, 4.75 mmol) were added, and the reaction was stirred overnight. More KF/alumina reagent (40%, 690 mg, 4.75 mmol) was added, and the reaction was stirred for another 10 h. The mixture was filtered through Celite, and the filter cake was washed with ethyl acetate (50 mL). The solvents were evaporated, and the residue was purified by flash column chromatography using deactivated silica gel and 5% ethyl acetate in hexanes (containing 2% NEt_3) as eluent to afford pure 1-(hexyloxy)-1-(3,4-methylenedioxy-6-nitrophenyl)-2,4-hexadiene (434 mg, 66%) as an orange oil. IR (neat): 2954, 2930, 2859, 1519, 1484, 1254, 1037 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.44 (1H, s), 7.16 (1H, s), 6.27 (1H, dd, $J = 15.2$, 10.8 Hz), 6.10 (2H, m), 6.00 (1H, m), 5.73 (1H, dd, $J = 14.8$, 6.8 Hz), 5.59 (1H, dd, $J = 15.2$, 6.4 Hz), 5.48 (1H, d, $J = 6.8$ Hz), 4.43 (1H, m), 3.30 (1H, m), 1.73 (3H, d, $J = 6.8$ Hz), 1.58 (2H, m), 1.28 (6H, m), 0.88 (3H, t, $J = 6.4$ Hz). ^{13}C NMR ($CDCl_3$): δ 152.1, 146.8, 142.0, 135.2, 131.9, 130.6, 129.1, 106.9 (2 carbons), 104.9, 102.7, 76.5, 69.0, 31.5, 29.6, 25.7, 22.5, 18.0, 13.9. HRMS (FAB, $[M - H]^+$): calcd for $C_{19}H_{24}NO_5$ 346.1654, found 346.1640 (this compound contains an inseparable minor olefin stereoisomer (<15%)).

1-Phenoxy-1-(3,4-methylenedioxy-6-nitrophenyl)-2,4-hexadiene (16). Tributylphosphine (0.35 mL, 1.42 mmol) was added to a solution of 1-(3,4-methylenedioxy-6-nitrophenyl)-2,4-hexadien-1-ol (249 mg, 0.946 mmol) and phenol (134 mg, 1.42 mmol) in dry benzene (10 mL) at 0 °C. 1,1′-(Azodicarbonyl)dipiperidine (360 mg, 1.42 mmol) was added to the solution with stirring. After 10 min, the reaction mixture was allowed to warm to room temperature and stirred for 20 h. Hexane was added, and the mixture was filtered through Celite. The solvent was evaporated, and the residue was purified by flash column chromatography using deactivated silica gel and 5% ethyl acetate in hexanes (containing 2% NEt_3) as eluent to afford 1-phenoxy-1-(3,4-methylenedioxy-6-nitrophenyl)-2,4-hexadiene (211 mg, 66%) as a yellow oil. IR (neat): 3026, 2915, 1612, 1596, 1518, 1504, 1485, 1330, 1258, 1231, 1036 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.44 (1H, s), 7.26 (2H, m), 7.15 (1H, dd, $J = 15.9$, 1.2 Hz), 6.95 (4H, m), 6.10 (1H, dd, $J = 15.6$, 6.3 Hz), 6.06 (2H, s), 5.85 (1H, ddd, $J = 15.6$, 6.3, 1.2 Hz), 5.64 (1H, m), 5.26 (1H, td, $J = 6.3$, 0.6 Hz), 1.76 (3H, ddd, $J = 6.3$, 1.5, 0.6 Hz). ^{13}C NMR ($CDCl_3$): δ 157.4, 151.6, 147.2, 141.6, 132.8, 129.4, 129.2 (two carbons), 129.0, 127.7, 120.9, 116.1 (two carbons), 107.2, 105.1, 102.9, 78.7, 74.4, 17.9. HRMS (FAB, $[M - H]^+$): calcd for $C_{19}H_{16}NO_5$ 338.1028, found 338.1024 (this compound contains an inseparable minor olefin stereoisomer (<13%)).

Representative Photodeprotection of a PeNB Derivative (8). A 10 mM solution of 1-(2-phenylacetoxy)-1-(2-nitrophenyl)-2,4-hexadiene (56 mg, 0.166 mmol) in CH_3OH (16.6 mL) was prepared in an oven-dried quartz flask, and the flask was tightly capped under an argon atmosphere. The solution was irradiated for 90 min with vigorous stirring using a Rayonet photochemical reactor with 254 nm bulbs. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (3 mL). The solution was extracted with aqueous 1 N NaOH solution. The aqueous phase was washed with diethyl ether and acidified with concentrated HCl solution. The resulting aqueous solution was extracted with diethyl ether. The combined organic layers were dried (Na_2SO_4) and concentrated to give 17.0 mg of phenylacetic acid (75%).

Representative Photodeprotection of a PeNP Derivative (14). A 10.1 mM solution of 1-(benzyloxy)-1-(3,4-methylenedioxy-6-nitrophenyl)-2,4-hexadiene (50 mg, 0.141 mmol) in CH_3OH (14 mL) was prepared in an oven-dried Pyrex flask, and the flask was tightly capped under argon atmosphere. The solution was irradiated for 3 h with vigorous stirring using a Rayonet photochemical reactor with 350 nm bulbs. The solvent was evaporated, and the residue was purified by flash column chromatography using 20% ethyl acetate in hexanes as eluent to afford 11.6 mg of benzyl alcohol (76%).

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Supporting Information Available: Procedure for GC response factor analyses and ^1H NMR and ^{13}C NMR spectra of compounds characterized by HRMS (**3a**,**b**, **6**, **8**−**11**, **13**, **15**, and **16**) as evidence of their purity. This material is available free of charge via the Internet at http://pubs.acs.org.

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