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Wavelength-Controlled Orthogonal Photolysis of Protecting Groups

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The selective control of a chemical process by the use of an electromagnetic wave has been a challenging goal for several decades. In this article, we describe for the first time the use of a monochromatic light beam to differentiate two different reactive centers. A direct application of this concept is found in the chemistry of protecting groups. Two different photolabile protecting groups were tuned to be responsive to a specific wavelength (e.g., 254 or 420 nm). Using derivatives of the 2-nitroveratryl fragment (such as **10**, sensitive at 420 nm) and 3′,5′-dimethoxybenzoin fragment (such as **4**, sensitive at 254 nm), it was shown that energy transfer phenomena did not erode the selectivity. Both the inter- and the intramolecular cases were studied and showed selectivities within the synthetically useful range. Hence, we could replace the traditional *chemical* orthogonality by a *chromatic* orthogonality.

Introduction

The selective control of a chemical process by the use of an electromagnetic wave has been a challenging goal for several decades.[1] Most of the physical properties of a wave have been exploited in this context. Light pulses were shown to initiate different types of reactions depending on their duration and sequences, for example on acetophenone.[2] Polarization has been used to induce asymmetry in organic reactions by using circularly polarized light (cpl).[3] The wavelength has also been used as a tunable parameter.[4] The dissociation of one among several ligands around chromium complexes was performed by using monochromatic light beams, sometimes with high selectivity.[5] In organic synthesis, it was found that the photolysis of bicyclo[3.1.0]hexenones gave different products when performed at 313 nm or at 366 nm.[6] Despite these significant studies, the scarcity of examples misrepresents the importance of such control.

However, serious difficulties have to be overcome to achieve this goal. Central to organic photochemistry is the so-called *Kasha rule*, stating that fluorescence always occurs from the lowest singlet excited state, regardless of the initial excitation. This is the consequence of a fast and efficient nonradiative internal conversion (IC).[7] One should, therefore, not expect to be able to carry out different chemical reactions at different wavelengths; this is, however, contradicted by multiple counter-examples.[5,6] On a polychromophoric molecule, careful control of all forms of energy transfer (e.g., through dipolar[8] or exchange[9] mechanisms) has to be considered in order to allow isolation of the sites.

The ability to absorb energy at a specific site, and *keep it localized* until the suitable chemical reaction is finished, is an important goal in chemistry, and this work aims at addressing this issue. We decided to illustrate the concept by the design of an orthogonal protecting group scheme.[10] This is, however, only one of the many aspects of the field.

Photolabile protecting groups have been known since the early 1960s.[11] They react through different types of mechanisms, with the excitation of a diverse variety of chromophores (carbonyl, nitro, aryl groups, etc.).[12] This mechanistic diversity opens the door for an individual control by the wavelength.

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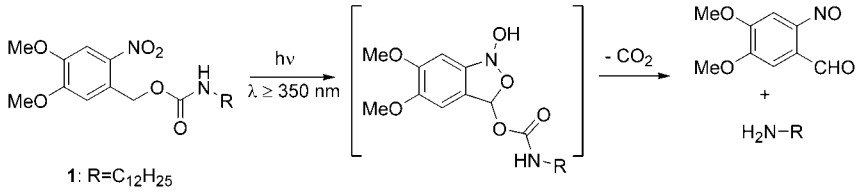
SCHEME 1



1: R=$C_{12}H_{25}$

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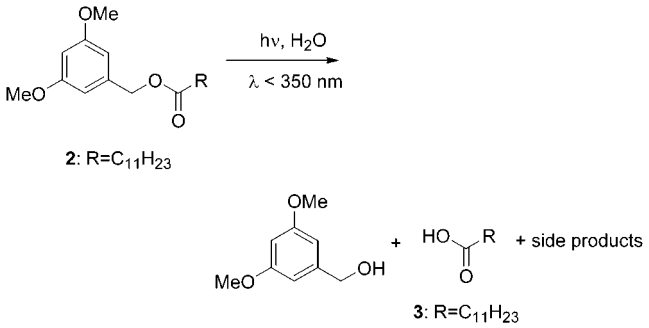
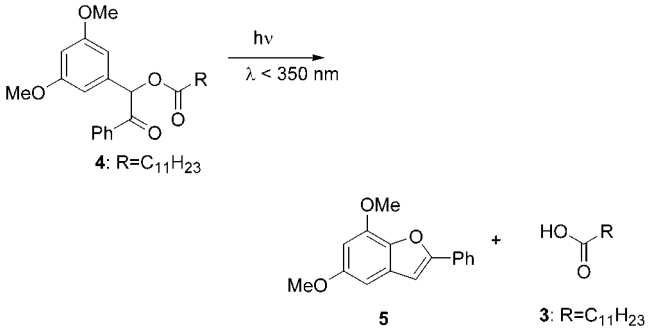


2: R=$C_{11}H_{23}$

3: R=$C_{11}H_{23}$

SCHEME 3

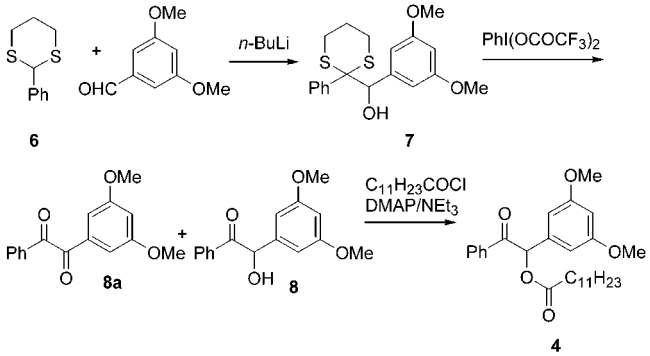


4: R=$C_{11}H_{23}$

5

3: R=$C_{11}H_{23}$

SCHEME 4



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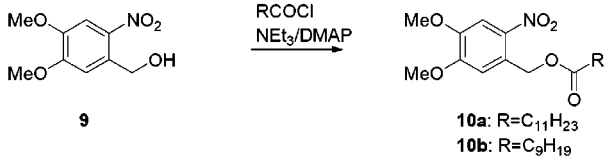

9

10a: R=$C_{11}H_{23}$

10b: R=C_9H_{19}

The 2-nitroveratryl group was introduced in 1970 by Patchornik and Woodward as a nitrogen protecting group (Scheme 1).[13]

The substituents around the aromatic ring were optimized to show a maximal reactivity at a wavelength of 350 nm. This relatively long wavelength was attractive because of its harmless energy content for sensitive amino acids such as tryptophan or tyrosine. To date, it is still one of the only photolabile protecting groups working at low energy (up to 420 nm), and we selected it for this property. At the other end of the UV spectrum, arylmethyl groups were known to be highly reactive, such as the 3,5-dimethoxybenzyl alcohol derivatives.[14] These ester derivatives were shown to be inert at 350 nm and above,[15] making them an attractive complement to the 2-nitroveratryl system (Scheme 2).

At 254 nm, the lauroyl ester **2** was photolyzed 27 times faster than the carbamate **1**. However, when a 1:1 mixture of **1** and **2** was photolyzed, almost no selectivity was obtained.[15] This observation suggested an intermolecular energy transfer. We reasoned that by shortening the lifetime of the excited state of an analogue of **2**, the chemical reaction (i.e., the rupture of the benzylic C−O bond) would favorably compete with the energy transfer. The substitution of the benzylic methylene group with a benzoyl moiety, as in benzoin **4**, indeed maintained the high reactivity at 254 nm, while suppressing the energy transfer. Such esters were shown by Sheehan to be unaffected in their photochemical reactivity by naphthalene or even neat piperilene.[16] The side product is a substituted benzofuran **5**, inert both chemically and photochemically under the reaction conditions (Scheme 3).

Results and Discussion

Preparation of the Substrates. The benzoin ester **4** was prepared by acylation of benzoin **8**, itself prepared by the protocol of Chan.[17] The condensation of the lithiated thioacetal **6** with 3,5-dimethoxybenzaldehyde proceeded quantitatively and was followed by the oxidative deprotection of the thioacetal **7** with $PhI(OCOCF_3)_2$ in variable yields;[18] great care in the stoichiometry (1.5 equiv) and following the reaction by TLC had to be taken to minimize the formation of diketone **8a** (Scheme 4).

(13) Patchornik A.; Amit, B.; Woodward, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 6333−6335.

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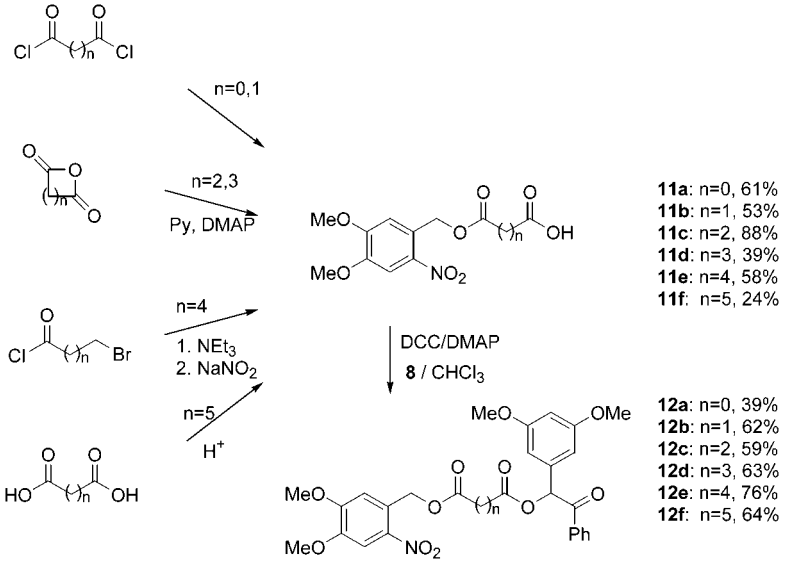
SCHEME 6



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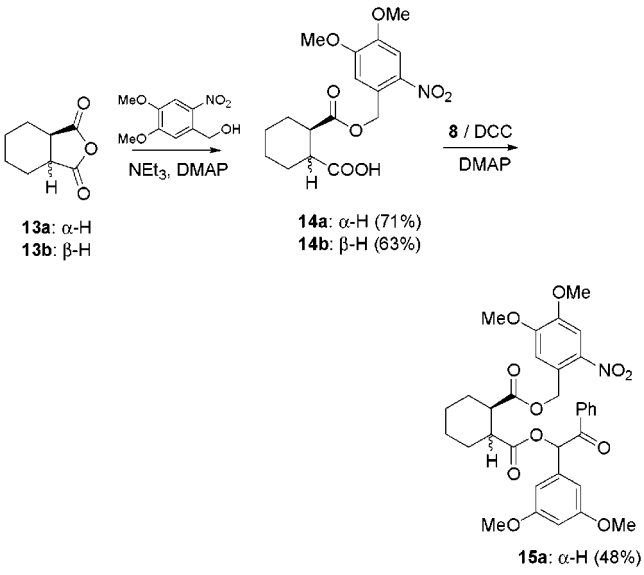

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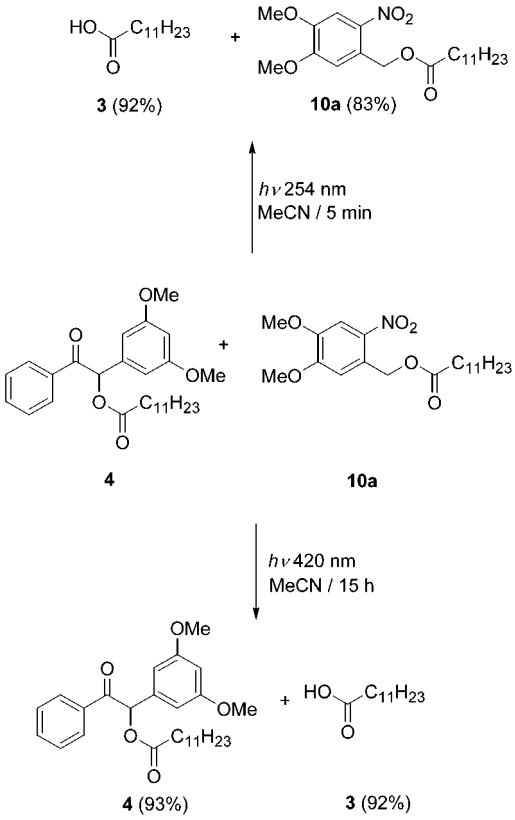

Despite these measures, we could not avoid its presence, together with unreacted **7**.

The esters **10a**,**b** were prepared by classical acylation of the 2-nitroveratryl alcohol with the corresponding acid chlorides (Scheme 5). The esters **11a**−**f** were synthesized following different routes, depending on intrinsic reactivity and starting materials availability. Hence, the monoesters **11a**,**b** were prepared by acylation of 2-nitroveratryl alcohol with oxalyl chloride (1.0 equiv, 61%) or malonyl chloride (1.0 equiv, 53%) (Scheme 6). The esters **11c**,**d** were prepared by the opening of succinic or glutaric anhydrides in the presence of pyridine and DMAP (**11c**: 88%, **11d**: 39%). The ester **11e** was prepared in a two-step procedure, in an overall yield of 58%. First acylating the alcohol **9** with 6-bromohexanoyl chloride in the presence of triethylamine and DMAP, and then the primary bromide was converted into a carboxylic acid by oxidation with sodium nitrite in the presence of DMSO and acetic acid.[19] Finally, the diester **11f** was prepared in modest yield by acid-catalyzed esterification of pimelic acid (24%). All these monoesters were converted into diesters **12a**−**f** by a DCC-mediated esterification with the benzoin **8** (39% to 76%).

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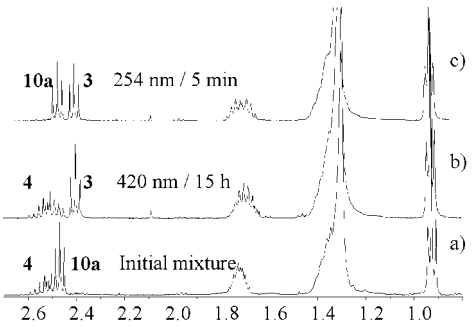
SCHEME 9



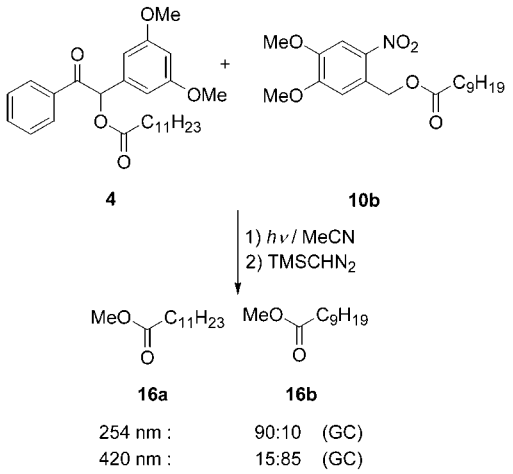
We also prepared 1,2-disubstituted cyclohexane derivatives, to force the proximity between the two chromophores. The *cis*-diester **15a** was prepared by the opening of the *cis* anhydride **13a** with 2-nitroveratrol in the presence of triethylamine and DMAP (71%), followed by a DCC-mediated esterification with benzoin **8** (48%). Unfortunately, the all equatorial *trans*-monoester **14b** failed to undergo further esterification.

Intermolecular Discrimination in the Photolysis. To assess the relative reactivity of the esters **4** and **10a**, we subjected a 1:1 mixture to a 254 nm irradiation during 5 min in acetonitrile.[20] ^{1}H NMR analysis showed that formation of acid **3** occurred in a 92% yield, while the ester **10a** was kept virtually intact (83%) as shown below (Scheme 8). On the other hand, the same experiment at 420 nm reversed the trend, keeping intact the ester **4** (93%) with the release of acid **3** (92%).

This experiment clearly showed that it was possible to select individuals from a mixture by an influence that is external to the reaction mixture, thus achieving control of a chemical process by means of an electromagnetic wave. Further illustration is shown in the Scheme 9 with the ^{1}H NMR spectra of the mixtures before (trace a) and after both irradiations (traces b and c). It is worth mentioning the complex multiplicity of the Cα-methylene group in ester **4**, due to the presence of a chiral center in the protecting group. This is potentially a drawback, but the practical enantioselective preparation of benzoin **8** has been previously published.[21]

We decided to exploit differential chromatic properties to selectively release one or another compound in solution by the choice of the wavelength (Scheme 10). Thus, we prepared a 1:1 mixture of esters **10b** and **4**. The difference in the length of the hydrocarbon chain should have a negligible effect on the reactivity but should allow a convenient quantification by GC analysis after suitable derivatization. The crude mixture resulting from the photolysis at 254 nm for 5 min was esterified by the addition of $TMSCHN_2$.[22] GC analysis showed a 90:10 ratio of C_{11}/C_9 esters **16a** and **16b**, confirming the much higher reactivity of the benzoin at this wavelength. On the other hand, the 420 nm irradiation for 16 h yielded a 15:85 ratio, favoring the C_9 ester, again confirming the higher reactivity of the 2-nitroveratryl ester at long wavelength.[20] This C_{11}/C_9 ratio is in fact a measurement of the combination of nonspecific absorption and energy transfer.[23] The values obtained, although with room for improvement, enter the synthetically useful range. In particular, they show that the energy transfer influence is minimal.

SCHEME 10



Intramolecular Discrimination in the Photolysis. The benefits of wavelength-controlled external group discrimination would be more apparent in the orthogonal cleavage of protecting groups. The term orthogonality was introduced a few decades ago to designate groups that can be cleaved in the presence of each other by specific reagents and conditions, irrespective of the sequence.[10] In the case we describe here, we would observe a *chromatic* orthogonality instead of *chemical* orthogonality. Energy transfer is again central to this issue, since both chromophores would be located on the same substrate. The energy transfer rate is distance dependent.[7,8,9] The absence of mutual interference, at least at the ground state, was confirmed by UV spectroscopy. The spectrum of diester **12c** (alternate line) was almost exactly the sum (full line) of the spectra of **11c** and **18c** (dashed and dotted lines) (Scheme 11).

Thus, we first investigated the photolysis of diester **12f** ($n = 5$), with both photosensitive groups quite distant (but with a flexible spacer). Irradiation at 254 nm followed by esterification with $TMSCHN_2$ gave 70% of methyl ester **19f** (isolated yield), with no ester **18f** detected by ^{1}H NMR analysis of the crude mixture. On the other hand, irradiation at 420 nm and esterification yielded 70% of methyl ester **18f**, with no ester **19f** detected (Scheme 12).

To investigate the distance dependence, we gradually shortened the length of the tether from $n = 5$ to $n = 0$. The same range of selectivity was observed, regardless of the tether length. Even the oxalate ($n = 0$) gave satisfactory results. The instability of the oxalic acid monoester toward $TMSCHN_2$ prevented, however, the esterification and purification.[24] These results are summarized in Table 1. The total orthogonality was further checked by the photolysis of the methyl ester **18e** at 254

(20) By reactivity, we imply the net reaction rate under specific conditions; it includes the quantum yield, the absorbance at the wavelength, and all the experimental parameters.

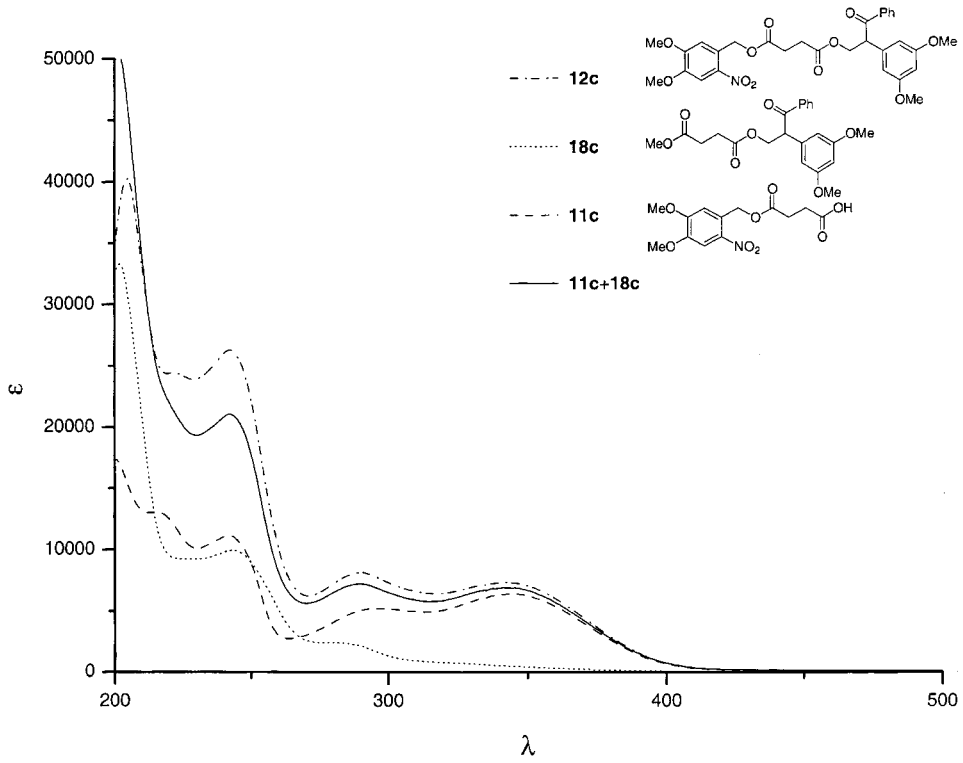
(21) Pirrung, M. C.; Shuey, S. W. *J. Org. Chem.* **1994**, *59*, 3890−3897.

(22) (a) Shiori, T.; Aoyama, T.; Mori, S. *Org. Synth.* **1990**, *68*, 1−7. (b) Hashimoto, N.; Aoyama, T.; Shiori, T. *Chem. Pharm. Bull.* **1981**, *29*, 1475−1478.

(23) The width at half-height of the emission spectrum of a Rayonet bulb was estimated as 35 nm.

(24) Wragg, R. T. *J. Chem. Soc.* **1965**, 7162−7165.

SCHEME 11



SCHEME 12

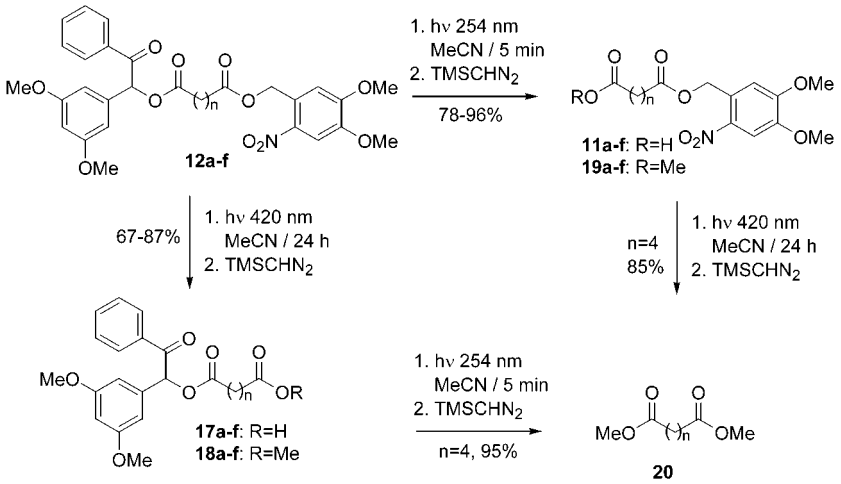


TABLE 1

entry	diester	*n*	254 nm[a]	420 nm[b]
1	**12f**	5	92 (70)	70 (70)
2	**12e**	4	78 (69)	87 (68)
3	**12d**	3	96 (79)	85 (81)
4	**12c**	2	94 (81)	85 (72)
5	**12b**	1	94 (85)	83 (70)
6	**12a**	0	86 (27)	67

[a] Yield of **11a**−**f** determined by ^{1}H NMR; in parentheses, yield of **19a**−**f** isolated. [b] Yield of **17a**−**f** determined by ^{1}H NMR; in parentheses, yield of **18a**−**f** isolated.

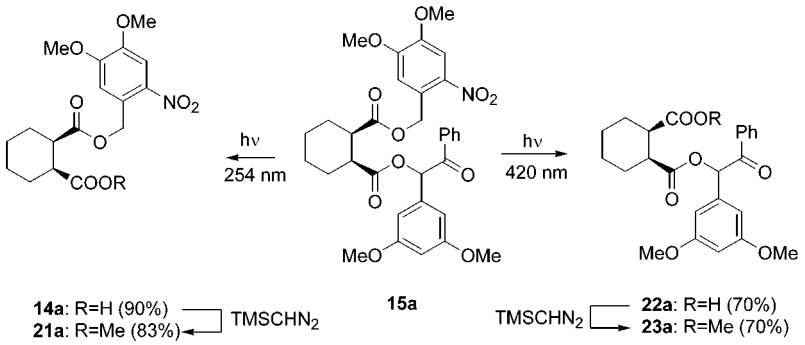
nm, indeed yielding dimethyl adipate **20** (95%), and by the photolysis at 420 nm of the methyl ester **19e** (85%) (Scheme 12).

Conformationally constrained systems also allowed a wavelength-based discrimination, and the diester **15a** smoothly underwent the photolysis at 254 nm yielding 90% of monoacid **14a**, as well as at 420 nm yielding monoacid **22a** (70%) (Scheme 13).

Conclusion

Our goal was to determine the outcome of a chemical reaction by an influence external to the reaction medium. Despite many pitfalls, the selective absorption of light at a specific site and the possibility of keeping the energy localized at this site were possible. An illustration of this concept in the orthogonal removal of protecting groups by using monochromatic light was achieved. This is the first time that such approach was used in a preparatively useful scheme. We are currently expanding the range of functional groups to be protected. This article dealt with only one specific illustration, and we are now exploring

SCHEME 13



other applications, such as color-sensitive photoresponsive materials and solid-phase organic synthesis.

Experimental Section

All reactions were carried out under argon, with magnetic stirring, unless otherwise specified. Purchased chemicals were used without further purification, unless otherwise specified. Solvents were dried by distillation from drying agents as follows: Et_2O and THF (Na/benzophenone), toluene and benzene (Na); MeCN and CH_2Cl_2 (CaH_2); MeOH ($Mg(OMe)_2$). Flash column chromatography (FC): SiO_2. Melting points uncorrected.

Dodecanoic Acid 1-(3,5-Dimethoxyphenyl)-2-oxo-2-phenylethyl Ester (4). The dimethoxybenzoin **8** (67 mg, 0.245 mmol), triethylamine (50 mg, 0.49 mmol), and *N*,*N*-(dimethylamino)pyridine (3 mg, 0.0245 mmol) were dissolved in anhydrous dichloromethane (2 mL). Lauroyl chloride (64 mg, 0.294 mmol) was then added, and the mixture was stirred at 25 °C for 12 h. Ethyl acetate was added, and the mixture was washed with 10% HCl and aq bicarbonate. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by FC (cyclohexane/AcOEt 10/1) to give 80 mg of **4**, as a colorless oil (72%): TLC R_f 0.53 (cyclohexane/AcOEt 4/1); IR ($CHCl_3$) ν_{max} 2925, 2853, 1739, 1698, 1597, 1463, 1430, 1351, 1281, 1206, 1159, 1114, 1068 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 6.8 Hz, 3 H), 1.3−1.5 (16 H), 1.69 (m, 2 H), 2.50 (m, 2 H), 3.78 (s, 6 H), 6.43 (t, J = 2.3, 1 H), 6.61 (d, J = 2.3, 2 H), 6.77 (s, 1 H), 7.42 (t, J = 7.5, 2 H), 7.54 (t, J = 7.5, 1 H), 7.95 (d, J = 7.3, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1, 22.7, 24.8, 29.1, 29.2, 29.24, 29.3, 29.4, 29.6, 31.9, 34.0, 55.4, 101.1, 106.6, 128.6, 128.8, 133.4, 134.7, 135.7, 161.2, 173.2, 193.8; MS (EI) *m*/*z* (%) 454 (7, $M^{+\bullet}$), 349 (10), 255 (13), 254 (21), 183 (100), 105 (78); HR-MS 454.2792 ($C_{28}H_{38}O_5$ calcd 454.2719).

2-Phenyl-[1,3]-dithiane (6). 1,3-Propanedithiol (10.8 g, 0.1 mol) was added to a solution of benzaldehyde (10.6 g, 0.1 mol) in dichloromethane (200 mL). A mixture prepared by the slow addition at 0 °C of acetyl chloride (10 mL) to methanol (20 mL) in dichloromethane (20 mL. *Caution: exothermic reaction!*) was slowly added, and the mixture was stirred at RT for 3 h. Sodium hydroxide (1 N) was added, and the phases were separated. The organic phase was washed with brine and dried over $MgSO_4$, and the solvent was evaporated. The resulting solid was recrystallized twice from methanol, to give the pure expected thioacetal **6** as white crystals (12.1 g, 62%): mp 74 °C; IR ($CHCl_3$) ν_{max} 3000, 2902, 1496, 1452, 1424, 1277, 1228, 1173, 1073, 911, 698, 470 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.0−1.8 (1 H), 2.2−2.1 (1 H), 3.0−2.8 (2 H), 3.1−3.0 (2 H), 5.2 (s, 1 H), 7.4−7.2 (3 H), 7.48 (d, J = 6 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) 25.1, 32.1, 51.5, 127.7, 128.4, 128.7, 139.1.

(3,5-Dimethoxyphenyl)(2-phenyl-[1,3]-dithian-2-yl)-methanol (7). The dithiane **6** (1 g, 5.1 mmol) was dissolved in 20 mL of dry THF and cooled to 0 °C. *n*-BuLi (1.1 equiv) was added dropwise under argon, and the mixture was stirred at 0 °C for 30 min. A solution of 3,5-dimethoxybenzaldehyde (845 mg, 5.1 mmol) in THF was added, and the mixture was stirred for 30 min at 0 °C, warmed to room temperature over 1 h, and quenched with a satd NH_4Cl solution. The organic phase was washed with brine and dried over $MgSO_4$. After evaporation, **7** (1.85 g, quant.) was obtained as a thick yellow oil: TLC R_f 0.34 (cyclohexane/AcOEt 3/1); IR ($CHCl_3$) ν_{max} 3590, 3015, 2960, 2910, 2840, 1730, 1600, 1520, 1465, 1430, 1330, 1200, 1160, 1060 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.92 (m, 2 H), 2.70 (m, 4 H), 3.56 (s, 6 H), 4.93 (s, 1 H), 5.99 (s, 2 H), 6.29 (s, 1 H), 7.30 (m, 3 H), 7.73 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 24.8, 27.1, 27.3, 55.1, 66.3, 81.0, 100.8, 106.0, 127.5, 128.1, 130.7, 137.5, 139.4, 159.4; MS (EI) *m*/*z* (%) 362 (1, $M^{+\bullet}$), 195 (100), 169 (68), 121 (26), 77 (5); HR-MS 344.0904 ($C_{19}H_{20}O_2S_2$ calcd 344.0905).

3′,5′-Dimethoxybenzoin (8). The dithiane **7** (3.63 g, 10 mmol) was dissolved in 15 mL of acetonitrile and 2.5 mL of water. Bis(trifluoroacetoxy)iodobenzene (6.45 g, 15 mmol) in 10 mL of acetonitrile was slowly added at room temperature to the vigorously stirred solution. After 1 h, AcOEt was added. The organic phase was washed with a satd $NaHCO_3$ solution and brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by FC (silica gel). Recrystallization (cyclohexane/AcOEt) gave **8** (1.53 g, 56%) as a white solid: TLC R_f 0.19 (cyclohexane/AcOEt 3/1); mp 113 °C; IR ($CHCl_3$) ν_{max} 3460, 3015, 2940, 2840, 1680, 1600, 1460, 1450, 1330, 1270, 1160, 1060 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.73 (s, 6 H), 5.85 (s, 1 H), 6.35 (s, 1 H), 6.47 (s, 2 H), 7.40 (t, J = 7.5 Hz, 2 H), 7.54 (t, J = 7.5 Hz, 1 H), 7.94 (d, J = 8.3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) 55.4, 76.2, 100.5, 105.8, 128.7, 129.1, 133.5, 134.0, 141.0, 161.3, 198.7; MS (EI) *m*/*z* (%) 272 (18, $M^{+\bullet}$), 167 (100), 139 (59), 124 (12), 105 (62), 77 (47), 51 (12); HR-MS 272.1039 ($C_{16}H_{16}O_4$ calcd 272.1048). Small amounts of diketone **8a** were also isolated.

(3,5-Dimethoxyphenyl)phenylethane-1,2-dione (8a). Yellow oil; TLC R_f 0.31 (cyclohexane/AcOEt 3/1); IR ($CHCl_3$) ν_{max} 3015, 2940, 2840, 1675, 1595, 1460, 1445, 1355, 1160, 1065 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 6 H), 6.73 (s, 1 H), 7.09 (s, 2 H), 7.50 (t, J = 7.7 Hz, 2 H), 7.65 (t, J = 7.6 Hz, 1 H), 7.95 (d, J = 8.3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) 55.7, 107.4, 107.5, 129.0, 129.9, 132.9, 134.7, 134.9, 161.1, 194.3, 194.4; MS (EI) *m*/*z* (%) 270 (7, $M^{+\bullet}$), 165 (100), 137 (26), 122 (17), 105 (29), 84 (12), 77 (28), 51 (10). HR-MS 270.0896 ($C_{16}H_{14}O_4N$ calcd 270.0892).

2-Nitroveratrol (9). To a solution of 6-nitroveratraldehyde (10 g, 47.4 mmol) in 200 mL of methanol was slowly added $NaBH_4$ (0.9 g, 23.8 mmol). The mixture was stirred at room temperature for 1 h. The solvent was then evaporated, and the residue was partitioned between AcOEt and water. After extraction with AcOEt, the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and evaporated. Recrystallization from AcOEt gave **9** (8,3 g, 82%) as a yellow solid: TLC R_f 0.13 (cyclohexane/AcOEt 7/3); mp 155 °C; IR ($CHCl_3$) ν_{max} 3020, 2940, 2850, 1520, 1330, 1275, 1080 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 1 drop of DMSO) δ 3.94 (s, 3 H), 3.99 (s, 3 H), 4.96 (s, 2 H), 7.23 (s, 1 H), 7.69 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 1 drop of DMSO) 56.3, 56.4, 62.4, 108.0,

110.6, 132.8, 139.5, 147.7, 153.8; MS (EI) *m*/*z* (%) 213 (49, $M^{+\bullet}$), 196 (18), 180 (17), 168 (23), 151 (15), 136 (100); HR-MS 213.0664 ($C_9H_{11}O_5N$ calcd 213.0637).

Dodecanoic Acid 4,5-Dimethoxy-2-nitrobenzyl Ester (10a). The nitroveratrol **9** (54 mg, 0.253 mmol), triethylamine (51 mg, 0.506 mmol), and *N*,*N*-(dimethylamino)pyridine (3 mg, 0.0253 mmol) were dissolved in anhydrous dichloromethane (1 mL). Lauroyl chloride (61 mg, 0.279 mmol) was then added, and the mixture was stirred at 25 °C for 12 h. Ethyl acetate was added, and the mixture was washed with 10% HCl and aq bicarbonate. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was recrystallized from cyclohexane/ethyl acetate to give 80 mg of **10a**, as yellow crystals (80%): TLC R_f 0.67 (cyclohexane/AcOEt 2/1); mp 74−75 °C; IR ($CHCl_3$) ν_{max} 2929, 2850, 1736, 1587, 1523, 1464, 1334, 1278, 1171, 1068, 792 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3 H), 1.2−1.4 (16 H), 1.69 (m, 2 H), 2.43 (t, J = 7.3, 2 H), 3.97 (s, 3 H), 3.99 (s, 3 H), 5.52 (s, 2 H), 7.01 (s, 1 H), 7.73 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1, 22.7, 25.0, 29.2, 29.26, 29.3, 29.4, 29.6, 31.9, 34.3, 56.36, 56.4, 63.0, 108.3, 110.5, 127.2, 140.1, 148.3, 153.5, 173.1; MS (EI) *m*/*z* (%) 395 (5, $M^{+\bullet}$), 200 (4), 197 (11), 196 (46), 181 (10), 180 (41), 168 (17), 167 (100), 152 (14), 151 (70), 137 (11), 136 (100), 95 (13), 85 (17), 83 (12), 73 (34), 71 (29), 69 (24), 67 (10), 60 (33), 57 (74), 55 (60); HR-MS 395.2304 ($C_{21}H_{33}O_6N$ calcd 395.2304).

Decanoic Acid 4,5-Dimethoxy-2-nitrobenzyl Ester (10b). The nitroveratrol **9** (215 mg, 1 mmol), triethylamine (202 mg, 2 mmol), and *N*,*N*-(dimethylamino)pyridine (12 mg, 0.1 mmol) were dissolved in anhydrous dichloromethane (10 mL). Decanoyl chloride (229 mg, 1.2 mmol) was then added, and the mixture was stirred at 25 °C for 2 h. Ethyl acetate was added, and the mixture was washed with 10% HCl and aq bicarbonate. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was recrystallized from cyclohexane to give 258 mg of **10b**, as a yellow solid (70%): TLC R_f 0.5 (cyclohexane/AcOEt 4/1); mp 69−70 °C; IR ($CHCl_3$) ν_{max} 2916, 2849, 1735, 1578, 1526, 1509, 1459, 1437, 1387, 1318, 1273, 1226, 1171, 1066, 978, 870, 796 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.9 Hz, 3 H), 1.1−1.4 (12 H), 1.69 (q, J = 7.6 Hz, 2 H), 2.42 (t, J = 7.6, 2 H), 3.97 (s, 3 H), 3.99 (s, 3 H), 5.52 (s, 2 H), 7.01 (s, 1 H), 7.73 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1, 22.6, 25.0, 29.15, 29.21, 29.24, 29.4, 29.4, 31.8, 34.3, 56.3, 56.4, 63.0, 108.3, 110.4, 127.2, 140.0, 148.2, 153.4, 173.1; MS (EI) *m*/*z* (%) 367 (3, $M^{+\bullet}$), 321 (2), 196 (33), 180 (28), 167 (77), 136 (100); HR-MS 367.1984 ($C_{19}H_{29}O_6N$ calcd 367.1995).

Oxalic Acid Mono(4,5-dimethoxy-2-nitrobenzyl) Ester (11a). To a stirred solution of oxalyl chloride (127 mg, 1 mmol) at 0 °C in 1 mL of dichloromethane was added dropwise a solution of 2-nitroveratrol **9** (213 mg, 1 mmol) in 20 mL of CH_2Cl_2 (2 h). After the addition was completed, the mixture was stirred overnight at room temperature. The mixture was basified with a satd $NaHCO_3$ solution, and the aqueous layer was acidified and extracted with AcOEt. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and evaporated. Recrystallization (cyclohexane/AcOEt) gave **11a** (174 mg, 61%) as a yellow solid: mp 189−190 °C; IR ($CHCl_3$) ν_{max} 3020, 2940, 1740, 1585, 1525, 1465, 1330, 1280, 1170, 1070 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 197 (20000), 243 (10900), 345 (6500); ^1H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 3 H), 3.91 (s, 3 H), 5.62 (s, 2 H), 7.08 (s, 1 H), 7.67 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 56.2, 56.3, 64.4, 108.0, 109.8, 125.8, 139.3, 148.2, 153.6, 158.3, 158.9; MS (EI) *m*/*z* (%) 285 (17, $M^{+\bullet}$), 213 (26), 181 (34), 136 (100); HR-MS 285.0484 ($C_{11}H_{11}O_8N$ calcd 285.0484).

Malonic Acid Mono(4,5-dimethoxy-2-nitrobenzyl) Ester (11b). To a stirred solution of malonyl dichloride (141 mg, 1 mmol) at 0 °C in 1 mL of dichloromethane was added dropwise a solution of 2-nitroveratrol (213 mg, 1 mmol) in 20 mL of CH_2Cl_2 (2 h). After the addition was completed, the mixture was stirred overnight at room temperature. The mixture was basified with a satd $NaHCO_3$ solution, and the aqueous layer was acidified and extracted with AcOEt. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and evaporated. Recrystallization (cyclohexane/AcOEt) gave **11b** (160 mg, 53%) as a yellow solid: mp 160−161 °C; IR ($CHCl_3$) ν_{max} 3025, 2940, 1730, 1585, 1525, 1460, 1380, 1330 1280, 1070 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 197 (17200), 242 (10600), 345 (6800); ^1H NMR (500 MHz, $CDCl_3$) δ 3.58 (s, 2 H), 3.96 (s, 3 H), 3.99 (s, 3 H), 5.64 (s, 2 H), 7.09 (s, 1 H), 7.74 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 41.6, 56.3, 56.7, 63.8, 108.0, 109.6, 127.4, 139.2, 147.9, 153.9, 166.3, 168.4; MS (EI) *m*/*z* (%) 299 (4, $M^{+\bullet}$), 255 (12), 213 (9), 167 (32), 136 (100); HR-MS 299.0628 ($C_{12}H_{13}O_8N$ calcd 299.0641).

Succinic Acid Mono(4,5-dimethoxy-2-nitrobenzyl) Ester (11c). 2-Nitroveratrol **9** (426 mg, 2 mmol), succinic anhydride (201 mg, 2 mmol), and *N*,*N*-(dimethylamino)-pyridine (24 mg, 0.2 mmol) were dissolved in 2 mL of pyridine and 2 mL of chloroform (ethanol-free, stabilized on amylene). The mixture was stirred at 50 °C for 24 h. Ethyl acetate was added, and the solution was washed twice with 10% HCl and extracted with satd $NaHCO_3$ solution. The basic aqueous phase was washed with ether, acidified with 10% HCl, and extracted with AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and evaporated. Recrystallization (cyclohexane/AcOEt) gave **11c** (550 mg, 88%) as a white solid: mp 138 °C; IR ($CHCl_3$) ν_{max} 3020, 2940, 1740, 1720, 1585, 1525, 1465, 1380, 1280, 1170, 1070 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 200 (17400), 242 (11100), 345 (6400); ^1H NMR (500 MHz, $CDCl_3$) δ 2.74 (s, 4 H), 3.95 (s, 3 H), 3.98 (s, 3 H), 5.55 (s, 2 H), 7.00 (s, 1 H), 7.71 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 28.6, 28.7, 56.4, 56.4, 63.6, 108.2, 110.2, 126.9, 139.8, 148.2, 153.6, 171.5, 177.6; MS (EI) *m*/*z* (%) 313 (9, $M^{+\bullet}$), 286 (9), 213 (3), 196 (11), 167 (37), 136 (100); HR-MS 313.0803 ($C_{13}H_{15}O_8N$ calcd 313.0798).

Glutaric Acid Mono(4,5-dimethoxy-2-nitrobenzyl) Ester (11d). 2-Nitroveratrol **9** (426 mg, 2 mmol), glutaric anhydride (228 mg, 2 mmol), and *N*,*N*-(dimethylamino)-pyridine (24 mg, 0.2 mmol) were dissolved in 2 mL of pyridine and 2 mL of chloroform (ethanol-free, stabilized on amylene). The mixture was stirred at 50 °C for 24 h. Ethyl acetate was added, and the solution was washed twice with 10% HCl and extracted with satd $NaHCO_3$ solution (3 × 50 mL). The basic aqueous phase was washed with ether, acidified with 10% HCl, and extracted with AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and evaporated. Recrystallization (cyclohexane/AcOEt) gave **11d** (255 mg, 39%) as an orange solid: mp 110−111 °C; IR ($CHCl_3$) ν_{max} 3020, 2980, 1740, 1710, 1580, 1525, 1465, 1330, 1280, 1070 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 198 (21100), 242 (11200), 345 (6300); ^1H NMR (500 MHz, $CDCl_3$) δ 2.00 (m, 2 H), 2.43 (t, J = 7.3 Hz, 2 H), 2.50 (t, J = 7.3 Hz, 2 H), 3.93 (s, 3 H), 3.96 (s, 3 H), 5.48 (s, 2 H), 6.98 (s, 1 H), 7.69 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 19.8, 32.9, 33.0, 56.4, 63.3, 108.2, 110.5, 126.8, 140.0, 148.3, 153.5, 172.2, 179.0; MS (EI) *m*/*z* (%) 327 (11, $M^{+\bullet}$), 286 (3), 196 (21), 167 (53), 151 (38), 136 (100); HR-MS 327.0949 ($C_{14}H_{17}O_8N$ calcd 327.0954).

6-Bromohexanoic Acid 4,5-Dimethoxy-2-nitrobenzyl Ester. 2-Nitroveratrol **9** (213 mg, 1 mmol), triethylamine (278 μL, 2 mmol), and *N*,*N*-(dimethylamino)pyridine (24 mg, 0.2 mmol) were mixed in 5 mL of CH_3Cl (ethanol-free, stabilized on amylene) at room temperature. To the mixture was slowly added 6-bromohexanoyl chloride (153 μL, 1 mmol). The mixture was stirred at room temperature for 1 h. Ethyl acetate was added, and the solution was washed with 10% HCl, with satd $NaHCO_3$ solution, and with brine. The organic phase was dried over $MgSO_4$, filtered, and evaporated to give the title compound (390 mg, quant.) as a pure pale yellow solid: TLC R_f 0.22 (cyclohexane/AcOEt 3/1); mp 64−65 °C; IR ($CHCl_3$) ν_{max} 3030, 2940, 1740, 1710, 1580, 1525, 1330, 1280, 1180, 1070, 873 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.49 (m, 2 H), 1.70 (m, 2 H), 1.87 (m, 2 H), 2.43 (t, J = 7.4 Hz, 2 H), 3.40 (t, J = 6.8 Hz, 2 H), 3.95 (s, 3 H), 3.98 (s, 3 H), 5.49 (s, 2 H), 6.98 (s, 1 H), 7.71 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 24.0, 27.6, 32.3, 33.9, 56.4, 63.2, 108.2, 110.6, 126.8, 140.0, 148.2, 153.3, 172.7;

MS (EI) *m*/*z* (%) 391 (3, $M^{+\bullet}$), 389 (3), 213 (1), 196 (22), 167 (59), 151 (42), 136 (100); HR-MS 389.0468 ($C_{15}H_{20}O_6NBr$ calcd 389.0474).

Adipic Acid Mono(4,5-dimethoxy-2-nitrobenzyl) Ester (11e). A mixture of 6-Bromohexanoic acid 4,5-dimethoxy-2-nitrobenzyl ester (390 mg, 1 mmol), sodium nitrite (207 mg, 3 mmol), and acetic acid (580 μL, 10 mmol) in DMSO was stirred at 45 °C for 24 h. Ethyl acetate was added, and the organic phase was washed several times with water. The solution was extracted with satd $NaHCO_3$ solution. The basic aqueous phase was acidified with 10% HCl and extracted with AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and evaporated. The recrystallization (cyclohexane/AcOEt) gave **11e** (200 mg, 58%) as a yellow solid: mp 113−114 °C; IR ($CHCl_3$) ν_{max} 3030, 2940, 1740, 1710, 1580, 1525, 1460, 1330, 1280, 1180, 1070 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 197 (16600), 242 (10600), 343 (6100); ^1H NMR (500 MHz, $CDCl_3$) δ 1.71 (m, 4 H), 2.45 (t, J = 7.1 Hz, 2 H), 2.38 (t, J = 7.1 Hz, 2 H), 3.95 (s, 3 H), 3.97 (s, 3 H), 5.50 (s, 2 H), 6.98 (s, 1 H), 7.70 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 24.1, 24.3, 33.5, 33.8, 56.4, 63.3, 108.3, 110.6, 126.9, 140.1, 148.3, 153.4, 172.6, 178.7; MS (EI) *m*/*z* (%) 341 (6, $M^{+\bullet}$), 286 (3), 213 (1), 196 (18), 167 (51), 151 (37), 136 (100); HR-MS 341.1113 ($C_{15}H_{19}O_8N$ calcd 341.1110).

Pimelic Acid Mono(4,5-dimethoxy-2-nitrobenzyl) Ester (11f). Pimelic acid (470 mg, 2.94 mol), 2-nitroveratrol **9** (939 mg, 4.4 mmol), and *p*-toluenesulfonic acid monohydrate (6 mg, 0.029 mmol) were dissolved in toluene (50 mL) and the mixture was refluxed for 3 h with removal of the water using a Dean−Stark apparatus. The toluene was distilled, and the residue was diluted in ethyl acetate. The mixture was extracted with half-saturated sodium bicarbonate. The basic aqueous phases were combined, acidified with 10% HCl, and reextracted with ethyl acetate. A microcrystalline solid was obtained (254 mg, 24%): mp 113−114 °C; IR ($CHCl_3$) ν_{max} 3030, 2940, 1740, 1715, 1580, 1520, 1460, 1330, 1280, 1180, 1070 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 198 (24800), 242 (11800), 342 (6800); ^1H NMR (500 MHz, $CDCl_3$) δ 1.41 (m, 4 H), 1.69 (m, 4 H), 2.37 (t, J = 7.4 Hz, 2 H), 2.43 (t, J = 7.1 Hz, 2 H), 3.96 (s, 3 H), 3.98 (s, 3 H), 5.50 (s, 2 H), 6.99 (s, 1 H), 7.71 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 24.3, 24.6, 28.5, 33.3, 33.9, 56.4, 63.2, 108.3, 110.6, 127.0, 140.1, 148.3, 153.4, 172.8, 177.3; MS (EI) *m*/*z* 355 (7, $M^{+\bullet}$), 286 (1), 196 (28), 167 (69), 151 (40), 136 (100); HR-MS 196.0614 ($C_9H_{10}O_4N^+$ calcd 196.0610).

General Procedure for the Coupling Reaction. The alcohol (220 μmol), the acid (220 μmol), and *N*,*N*-(dimethylamino)pyridine (2.7 mg, 22 μmol) were dissolved in 5 mL of chloroform (ethanol-free, stabilized on amylene). *N*,*N*′-Dicyclohexylcarbodiimide (DCC, 68 mg, 330 μmol) was then added, and the mixture was stirred at 60 °C for 24 h. The mixture was filtered and washed with 10% HCl, with satd $NaHCO_3$ solution, and with brine. The organic phase was dried over $MgSO_4$, filtered, and evaporated. The residue was purified by FC (silica gel, cyclohexane/AcOEt).

Oxalic Acid (4,5-Dimethoxy-2-nitrobenzyl) Ester (3′,5′-Dimethoxybenzoin) Ester (12a). Following the general procedure, the monoester **11a** (63 mg, 220 μmol) and 3′,5′-dimethoxybenzoin **8** (60 mg, 220 μmol) in the presence of DCC (68 mg, 330 μmol) gave **12a** (43 mg, 36%) as a pale red solid: TLC R_f 0.09 (cyclohexane/AcOEt 3/1); mp 168 °C; IR ($CHCl_3$) ν_{max} 3030, 2940, 2840, 1775, 1750, 1700, 1600, 1525, 1460, 1330, 1280, 1180, 1070 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 198 (24700), 242 (12300), 286 (6500), 344 (7000); ^1H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 6 H), 3.89 (s, 3 H), 3.96 (s, 3 H), 5.78 (s, 2 H), 6.43 (s, 1 H), 6.60 (s, 2 H), 6.89 (s, 1 H), 7.20 (s, 1 H), 7.42 (t, J = 7.5 Hz, 2 H), 7.55 (t, J = 7.5 Hz, 1 H), 7.76 (s, 1 H), 7.92 (d, J = 7.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 55.4, 56.4, 65.1, 80.0, 101.4, 107.1, 108.1, 109.3, 125.9, 128.7, 128.8, 133.8, 133.9, 134.1, 139.2, 148.3, 153.9, 156.2, 156.5, 161.4, 191.2; MS (EI) *m*/*z* (%) 539 (1, $M^{+\bullet}$), 256 (3), 196 (16), 165 (35), 136 (8), 105 (100); HR-MS 539.1405 ($C_{27}H_{25}O_{11}N$ calcd 539.1423).

Malonic Acid (4,5-Dimethoxy-2-nitrobenzyl) Ester (3′,5′-Dimethoxybenzoin) Ester (12b). Following the general procedure, the monoester **11b** (66 mg, 220 μmol) and 3′,5′-dimethoxybenzoin **8** (60 mg, 220 μmol) in the presence of DCC (68 mg, 330 μmol) gave **12b** (76 mg, 62%) as a pale yellow solid: TLC R_f 0.10 (cyclohexane/AcOEt 3/1); mp 159 °C; IR ($CHCl_3$) ν_{max} 3025, 2940, 2840, 1740, 1700, 1600, 1525, 1465, 1330, 1280, 1160, 1070 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 202 (57100), 243 (22400), 287 (7400), 346 (7600); ^1H NMR (400 MHz, $CDCl_3$) δ 3.69 (m, 2 H), 3.74 (s, 6 H), 3.78 (s, 3 H), 3.94 (s, 3 H), 5.63 (ab, J_{ab} = 19.8 Hz, 2 H), 6.40 (s, 1 H), 6.56 (s, 2 H), 6.78 (s, 1 H), 7.13 (s, 1 H), 7.41 (t, J = 9.2 Hz, 2 H), 7.54 (t, J = 9.0 Hz, 1 H), 7.72 (s, 1 H), 7.90 (d, J = 9.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 41.2, 55.3, 56.5, 64.0, 78.7, 101.3, 106.7, 107.9, 109.7, 127.2, 128.7, 128.8, 133.8, 134.2, 134.5, 139.2, 147.9, 153.9, 161.3, 165.3, 166.3, 192.6; MS (EI) *m*/*z* (%) 553 (2, $M^{+\bullet}$), 296 (6), 272 (7), 196 (62), 167 (58), 139 (33), 105 (100); HR-MS 553.1576 ($C_{28}H_{27}O_{11}N$ calcd 553.1584).

Succinic Acid (4,5-Dimethoxy-2-nitrobenzyl) Ester (3′,5′-Dimethoxybenzoin) Ester (12c). Following the general procedure, the monoester **11c** (69 mg, 220 μmol) and 3′,5′-dimethoxybenzoin **8** (60 mg, 220 μmol) in the presence of DCC (68 mg, 330 μmol) gave **12c** (74 mg, 59%) as a white solid: TLC R_f 0.09 (cyclohexane/AcOEt 3/1); mp 131 °C; IR ($CHCl_3$) ν_{max} 3030, 2940, 2840, 1740, 1700, 1600, 1525, 1465, 1330, 1280, 1160, 1070 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 202 (57100), 243 (22400), 287 (7400), 346 (7600); ^1H NMR (500 MHz, $CDCl_3$) δ 2.82 (m, 4 H), 3.73 (s, 6 H), 3.83 (s, 3 H), 3.93 (s, 3 H), 5.54 (ab, J_{ab} = 15.1 Hz, 2 H), 6.38 (s, 1 H), 6.55 (s, 2 H), 6.71 (s, 1 H), 7.00 (s, 1 H), 7.39 (t, J = 7.4 Hz, 2 H), 7.52 (t, J = 7.4 Hz, 1 H), 7.7 (s, 1 H), 7.90 (d, J = 7.3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) 29.0, 29.1, 55.3, 55.4, 56.4, 63.5, 78.0, 101.2, 106.7, 108.1, 109.6, 127.6, 128.7, 128.7, 133.7, 134.4, 135.1, 139.5, 148.0, 153.8, 161.2, 171.6, 171.9, 193.1; MS (EI) *m*/*z* (%) 567 (1, $M^{+\bullet}$), 316 (9), 270 (4), 255 (4), 196 (76), 165 (63), 137 (11), 105 (100); HR-MS 316.1294 ($C_{18}H_{20}O_5$ calcd 316.1311).

Glutaric Acid (4,5-Dimethoxy-2-nitrobenzyl) Ester (3′,5′-Dimethoxybenzoin) Ester (12d). Following the general procedure, the monoester **11d** (72 mg, 220 μmol) and 3′,5′-dimethoxybenzoin **8** (60 mg, 220 μmol) in the presence of DCC (68 mg, 330 μmol) gave **12d** (80 mg, 63%) as a yellow oil: TLC R_f 0.07 (cyclohexane/AcOEt 3/1); IR ($CHCl_3$) ν_{max} 3025, 2940, 2840, 1740, 1700, 1600, 1520, 1465, 1330, 1280, 1160, 1070 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 203 (56400), 244 (24400), 288 (7800), 345 (6500); ^1H NMR (500 MHz, $CDCl_3$) δ 2.06 (m, 2 H), 2.57 (m, 4 H), 3.72 (s, 6 H), 3.91 (s, 3 H), 3.92 (s, 3 H), 5.50 (s, 2 H), 6.38 (s, 1 H), 6.55 (s, 2 H), 6.72 (s, 1 H), 7.00 (s, 1 H), 7.38 (t, J = 7.0 Hz, 2 H), 7.49 (t, J = 7.0 Hz, 1 H), 7.69 (s, 1 H), 7.90 (d, J = 7.2 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) 20.0, 32.8, 32.9, 55.3, 56.2, 56.3, 63.1, 77.6, 100.9, 106.7, 108.1, 109.9, 127.2, 128.6, 133.5, 134.4, 135.1, 139.7, 148.0, 153.5, 161.1, 172.1, 172.2, 193.4; MS (EI) *m*/*z* (%) 581 (1, $M^{+\bullet}$), 316 (9), 255 (5), 196 (100), 167 (27), 136 (14), 105 (84); HR-MS 581.1874 ($C_{30}H_{31}O_{11}N$ calcd 581.1897).

Adipic Acid (4,5-Dimethoxy-2-nitrobenzyl) Ester (3′,5′-Dimethoxybenzoin) Ester (12e). Following the general procedure, the monoester **11e** (76.2 mg, 220 μmol) and 3′,5′-dimethoxybenzoin **8** (60 mg, 220 μmol) in the presence of DCC (68 mg, 330 μmol) gave **12e** (100 mg, 76%) as a yellow oil: TLC R_f 0.12 (cyclohexane/AcOEt 3/1); IR ($CHCl_3$) ν_{max} 3025, 2940, 2840, 1740, 1700, 1600, 1525, 1465, 1330, 1280, 1160, 1070 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 202 (48900), 243 (21200), 287 (6700), 345 (5600); ^1H NMR (500 MHz, $CDCl_3$) δ 1.75 (m, 4 H), 2.50 (m, 4 H), 3.74 (s, 6 H), 3.94 (s, 3 H), 3.95 (s, 3 H), 5.50 (s, 2 H), 6.39 (s, 1 H), 6.56 (s, 2 H), 6.73 (s, 1 H), 6.99 (s, 1 H), 7.39 (t, J = 7.8 Hz, 2 H), 7.50 (t, J = 7.4 Hz, 1 H), 7.70 (s, 1 H), 7.91 (d, J = 8.2 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) 24.3, 26.9, 33.5, 33.8, 55.4, 56.4, 56.4, 63.2, 77.6, 101.1, 106.7, 108.2, 110.3, 127.2, 128.6, 128.7, 133.5, 134.6, 135.4, 139.9, 148.2, 153.5, 161.2, 172.6, 172.7, 193.6; MS (EI) *m*/*z* (%) 595 (1, $M^{+\bullet}$), 316 (3), 255 (3), 196 (100), 165 (17), 136 (4), 105 (32); HR-MS 595.2036 ($C_{31}H_{33}O_{11}N$ calcd 595.2054).

Pimelic Acid (4,5-Dimethoxy-2-nitrobenzyl) Ester (3′,5′-Dimethoxybenzoin) Ester (12f). Following the general procedure, the monoester **11f** (38 mg, 110 μmol) and 3′,5′-dimethoxybenzoin **8** (30 mg, 110 μmol) in the presence of DCC (35 mg, 165 μmol) gave **12f** (42 mg, 64%) as a pale yellow solid: TLC R_f 0.15 (cyclohexane/AcOEt 7/3); mp 101−102 °C; IR ($CHCl_3$) ν_{max} 3025, 2940, 2840, 1740, 1700, 1600, 1525, 1465, 1330, 1280, 1160, 1070 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 202 (50000), 243 (20200), 286 (6200), 340 (5200); ^1H NMR (500 MHz, $CDCl_3$) δ 1.41 (m, 2 H), 1.70 (m, 4 H), 2.45 (m, 4 H), 3.74 (s, 6 H), 3.94 (s, 3 H), 3.97 (s, 3 H), 5.50 (s, 2 H), 6.39 (s, 1 H), 6.57 (s, 2 H), 6.73 (s, 1 H), 7.00 (s, 1 H), 7.39 (t, J = 7.7 Hz, 2 H), 7.50 (t, J = 7.4 Hz, 1 H), 7.70 (s, 1 H), 7.92 (d, J = 7.2 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) 24.4, 24.5, 28.4, 33.7, 33.9, 55.4, 56.4, 63.1, 77.5, 101.0, 106.6, 108.2, 110.4, 127.1, 128.6, 128.7, 133.5, 134.6, 135.5, 139.9, 148.2, 153.4, 161.2, 172.8, 172.9, 193.6; MS (EI) m/z (%) 609 (1, $M^{+\bullet}$), 414 (1), 328 (2), 255 (5), 196 (100), 165 (63), 136 (19), 105 (73); HR-MS 609.2241 ($C_{32}H_{35}O_{11}N$ calcd 609.2210).

***cis*-Cyclohexane-1,2-dicarboxylic Acid Mono(4,5-dimethoxy-2-nitrobenzyl) Ester (14a).** 2-Nitroveratrol **9** (426 mg, 2 mmol), *cis*-cyclohexane-1,2-dicarboxylic anhydride (308 mg, 2 mmol), and *N*,*N*-(dimethylamino)pyridine (24.4 mg, 0.2 mmol) were dissolved in 2 mL of pyridine and 2 mL of chloroform (ethanol-free, stabilized on amylene). The mixture was stirred at 50 °C for 24 h. Ethyl acetate was added, and the solution was washed with 10% HCl and extracted with satd $NaHCO_3$ solution. The basic aqueous phase was washed with ether, acidified with 10% HCl, and extracted with AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and evaporated. Recrystallization (toluene) gave **14a** (520 mg, 71%) as a yellow solid: mp 162 °C; IR ($CHCl_3$) ν_{max} 3030, 2940, 2860, 1735, 1710, 1580, 1525, 1460, 1330, 1280, 1180, 1070, 910 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 197 (20000), 243 (10900), 344 (6500); ^1H NMR (400 MHz, $CDCl_3$) δ 1.50 (m, 4 H), 1.83 (m, 2 H), 2.05 (m, 2 H), 2.85 (m, 1 H), 2.98(m, 1 H), 3.94 (s, 3 H), 3.97 (s, 3 H), 5.51 (ab, J_{ab} = 15.1 Hz, 2 H), 7.00 (s, 1 H), 7.69 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 23.5, 23.8, 25.8, 26.5, 42.4, 56.3, 56.4, 63.3, 108.1, 110.2, 127.3, 139.8, 148.1, 153.5, 172.9, 179.3; MS (EI) m/z (%) 367 (11, $M^{+\bullet}$), 213 (5), 196 (23), 180 (17), 167 (62), 151 (69), 136 (100); HR-MS 213.0653 ($C_9H_{11}O_5N$ calcd 213.0637).

***trans*-Cyclohexane-1,2-dicarboxylic Acid Mono(4,5-dimethoxy-2-nitrobenzyl) Ester (14b).** 2-Nitroveratrol **9** (426 mg, 2 mmol), *trans*-cyclohexane-1,2-dicarboxylic anhydride (308 mg, 2 mmol), and *N*,*N*-(dimethylamino)pyridine (24 mg, 0.2 mmol) were dissolved in 2 mL of pyridine and 2 mL of chloroform (ethanol-free, stabilized on amylene). The mixture was stirred at 50 °C for 24 h. Ethyl acetate was added, and the solution was washed with 10% HCl and extracted with satd $NaHCO_3$ solution. The basic aqueous phase was washed with ether, acidified with 10% HCl, and extracted with AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and evaporated. Recrystallization (toluene) gave **14b** (460 mg, 63%) as a yellow solid: mp 152 °C; IR ($CHCl_3$) ν_{max} 3020, 2940, 2860, 1735, 1710, 1580, 1525, 1465, 1330, 1280, 1220, 1070 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 197 (20000), 243 (10900), 344 (6500); ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (m, 4 H), 1.83 (m, 2 H), 2.15 (m, 2 H), 2.70 (m, 2 H), 3.95 (s, 3 H), 3.98 (s, 3 H), 5.52 (ab, J_{ab} = 14.9 Hz, 2 H), 6.99 (s, 1 H), 7.71 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 25.1, 28.8, 28.9, 44.2, 44.5, 56.4, 56.5, 63.4, 108.2, 110.1, 127.4, 139.7, 148.1, 153.6, 174.4, 179.7; MS (EI) m/z (%) 367 (5, $M^{+\bullet}$), 213 (3), 196 (17), 180 (12), 167 (49), 151 (49), 136 (88), 109 (29), 81(100); HR-MS 367.1302 ($C_{17}H_{21}O_8N$ calcd 367.1267).

***cis*-Cyclohexane-1,2-dicarboxylic Acid (4,5-Dimethoxy-2-nitrobenzyl) Ester (3′,5′-Dimethoxybenzoin) Ester (15a).** Following the general procedure, the monoester **14a** (80 mg, 220 μmol) and 3′,5′-dimethoxybenzoin **8** (60 mg, 220 μmol) in the presence of DCC (68 mg, 330 μmol) gave **15a** (66 mg, 48%, mixture of two diastereoisomers, ratio 55/45) as a yellow oil: TLC R_f 0.10 (cyclohexane/AcOEt 3/1); IR ($CHCl_3$) ν_{max} 3020, 2940, 2840, 1730, 1700, 1600, 1525, 1465, 1330, 1280, 1160, 1070, 910 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 202 (62100), 243 (26000), 289 (6900), 343 (6900); ^1H NMR (500 MHz, $CDCl_3$) major diastereoisomer: δ 1.3−2.3 (m, 8 H), 2.8−3.2 (m, 2 H), 3.70 (s, 6 H), 3.80 (s, 3 H), 3.93 (s, 3 H), 5.38 (ab, J_{ab} = 19.6 Hz, 2 H), 6.33 (s, 1 H), 6.50 (s, 2 H), 6.67 (s, 1 H), 7.01 (s, 1 H), 7.38 (t, 2 H), 7.50 (t, 1 H), 7.69 (s, 1 H), 7.88 (d, 2 H); minor diastereoisomer: δ 1.3−2.3 (m, 8 H), 2.8−3.2 (m, 2 H), 3.69 (s, 6 H), 3.84 (s, 3 H), 3.93 (s, 3 H), 5.47 (ab, J_{ab} = 19.2 Hz, 2 H), 6.29 (s, 1 H), 6.48 (s, 2 H), 6.70 (s, 1 H), 6.99 (s, 1 H), 7.37 (t, 2 H), 7.50 (t, 1 H), 7.67 (s, 1 H), 7.86 (d, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$), mixture of both diastereoisomers: 23.0, 23.6, 24.4, 25.4, 26.3, 27.1, 55.2, 56.3, 63.2, 77.4, 100.7, 106.5, 107.9, 109.8, 127.9, 128.6, 128.7, 133.5, 134.4, 135.2, 139.2, 147.8, 153.6, 161.0, 172.9, 173.0, 193.3; MS (EI) m/z (%) 621 (1, $M^{+\bullet}$), 316 (10), 255 (6), 196 (96), 180 (18), 165 (80), 137 (15), 122 (12), 105 (100), 82 (25), 77 (43); HR-MS 621.2233 ($C_{33}H_{35}O_{11}N$ calcd 621.2210).

General Procedure for the Selective Cleavage of Photolabile Protecting Groups. In a quartz vessel, the diester (20 μmol) was dissolved in 10 mL of acetonitrile. The mixture was degassed by bubbling argon and stirred under irradiation at 254 nm for 10 min or 419 nm for 24 h. The solvent was evaporated, and the yield was determined by NMR. The crude product was methylated with (trimethylsilyl)-diazomethane (200 μmol) in 2 mL of a benzene/ethanol mixture (1/1) for 1 h. The solvent was evaporated, and the residue was purified by FC (silica gel, cyclohexane/AcOEt).

Oxalic Acid (4,5-Dimethoxy-2-nitrobenzyl) Ester Methyl Ester (19a). The diester **12a** (10.8 mg, 20 μmol) was stirred under irradiation at 254 nm for 10 min (NMR yield of **11a**: 86%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2 M in hexane), and the purification gave **19a** (1.7 mg, 28%) as a yellow solid: TLC R_f 0.10 (cyclohexane/AcOEt 3/1); mp 112−113 °C; IR ($CHCl_3$) ν_{max} 3020, 2940, 2855, 1775, 1750, 1585, 1525, 1465, 1335, 1280, 1170, 1070 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.95 (s, 3 H), 3.97 (s, 3 H), 4.00 (s, 3 H), 5.73 (s, 2 H), 7.12 (s, 1 H), 7.76 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 53.8, 56.4, 56.5, 65.3, 108.3, 110.3, 125.3, 139.8, 148.6, 153.7, 156.9, 157.8; MS (EI) m/z (%) 299 (44, $M^{+\bullet}$), 196 (100), 165 (18), 151 (22), 136 (47); HR-MS 299.0639 ($C_{12}H_{13}O_8N$ calcd 299.0641).

Oxalic Acid (3′,5′-Dimethoxybenzoin) Ester Methyl Ester (18a). The diester **12a** (10.8 mg, 20 μmol) was stirred under irradiation at 419 nm for 24 h (NMR yield of **17a**: 67%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2 M in hexane). The ^1H NMR spectrum of the crude product showed only decomposition products.

Malonic Acid (4,5-Dimethoxy-2-nitrobenzyl) Ester Methyl Ester (19b). The diester **12b** (11.1 mg, 20 μmol) was stirred under irradiation at 254 nm for 10 min (NMR yield of **11b**: 94%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2M in hexane), and the purification gave **19b** (5.3 mg, 85%) as a yellow solid: TLC R_f 0.18 (cyclohexane/AcOEt 7/3); mp 103 °C; IR ($CHCl_3$) ν_{max} 3025, 2930, 2855, 1740, 1585, 1525, 1465, 1330, 1280, 1150, 1070 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.54 (s, 2 H), 3.77 (s, 3 H), 3.97 (s, 3 H), 4.04 (s, 3 H), 5.64 (s, 2 H), 7.16 (s, 1 H), 7.75 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 41.3, 52.6, 56.4, 56.7, 64.1, 108.1, 110.0, 126.9, 139.5, 148.2, 153.8, 165.8, 167.0; MS (EI) m/z (%) 313 (17, $M^{+\bullet}$), 224 (9), 196 (30), 167 (33), 151 (35), 136 (92), 57 (100); HR-MS 313.0776 ($C_{13}H_{15}O_8N$ calcd 313.0798).

Malonic Acid (3′,5′-Dimethoxybenzoin) Ester Methyl Ester (18b). The diester **12b** (11.1 mg, 20 μmol) was stirred under irradiation at 419 nm for 24 h (NMR yield of **17b**: 83%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2 M in hexane), and the purification gave **18b** (5.2 mg, 70%) as a yellow oil: TLC R_f 0.11 (cyclohexane/AcOEt 3/1); IR ($CHCl_3$) ν_{max} 3025, 2930, 2855, 1740, 1600, 1460, 1330, 1280, 1070, 910 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 201 (21300), 243 (6000); ^1H NMR (500 MHz, $CDCl_3$) δ 3.56 (s, 2 H), 3.74 (s, 3 H), 3.75 (s, 6 H), 6.41 (s, 1 H), 6.58 (s, 2 H), 6.80 (s, 1 H), 7.40 (t, J = 7.8 Hz, 2

H), 7.52 (t, $J = 7$ Hz, 1 H), 7.92 (d, $J = 7.3$ Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) 41.0, 52.6, 55.4, 78.4, 101.3, 106.7, 128.7, 128.8, 133.6, 134.4, 134.9, 161.2, 165.9, 166.5, 192.6; MS (EI) *m*/*z* (%) 372 (4, $M^{+\bullet}$), 241 (12), 196 (9), 167 (32), 105 (57), 57 (100); HR-MS 372.1187 ($C_{20}H_{20}O_7$ calcd 372.1209).

Succinic Acid (4,5-Dimethoxy-2-nitrobenzyl) Ester Methyl Ester (19c). The diester **12c** (11.4 mg, 20 μmol) was stirred under irradiation at 254 nm for 10 min (NMR yield of **11a**: 94%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2 M in hexane), and the purification gave **19c** (5.3 mg, 81%) as a yellow solid: TLC R_f 0.13 (cyclohexane/AcOEt 3/1); mp 67−68 °C; IR ($CHCl_3$) ν_{max} 3020, 2940, 2855, 1740, 1585, 1525, 1465, 1330, 1280, 1160, 1070 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.72 (m, 4 H), 3.68 (s, 3 H), 3.96 (s, 3 H), 4.03 (s, 3 H), 5.57 (s, 2 H), 7.05 (s, 1 H), 7.73 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 28.7, 29.0, 51.9, 56.4, 56.5, 63.5, 108.1, 110.1, 127.3, 139.7, 148.1, 153.7, 171.8, 172.7; MS (EI) *m*/*z* (%) 327 (2, $M^{+\bullet}$), 224 (8), 196 (12), 167 (16), 151 (16), 136 (29), 55 (100); HR-MS 327.0949 ($C_{14}H_{17}O_8N$ calcd 327.0954).

Succinic Acid (3′,5′-Dimethoxybenzoin) Ester Methyl Ester (18c). The diester **12c** (11.4 mg, 20 μmol) was stirred under irradiation at 419 nm for 24 h (NMR yield of **17c**: 85%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2 M in hexane), and the purification gave **18c** (5.6 mg, 72%) as a yellow oil: TLC R_f 0.15 (cyclohexane/AcOEt 7/3); IR ($CHCl_3$) ν_{max} 3020, 2930, 2840, 1740, 1700, 1600, 1460, 1350, 1280, 1150, 1070, 910 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 201 (33300), 243 (9900); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.68 (m, 2 H), 2.82 (t, $J = 7$ Hz, 2 H), 3.68 (s, 3 H), 3.76 (s, 6 H), 6.41 (s, 1 H), 6.58 (s, 2 H), 6.76 (s, 1 H), 7.40 (t, $J = 7.7$ Hz, 2 H), 7.52 (t, $J = 7.6$ Hz, 1 H), 7.93 (d, $J = 8.4$ Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) 28.8, 29.0, 51.9, 55.4, 78.8, 101.2, 106.6, 128.6, 128.8, 133.5, 134.5, 135.3, 161.2, 171.8, 172.5, 193.3; MS (EI) *m*/*z* (%) 386 (1, $M^{+\bullet}$), 255 (8), 166 (5), 115 (100), 105 (25); HR-MS 386.1337 ($C_{21}H_{22}O_7$ calcd 386.1366).

Glutaric Acid (4,5-Dimethoxy-2-nitrobenzyl) Ester Methyl Ester (19d). The diester **12d** (11.6 mg, 20 μmol) was stirred under irradiation at 254 nm for 10 min (NMR yield of **11d**: 96%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2 M in hexane), and the purification gave **19d** (4.8 mg, 70%) as a yellow solid: TLC R_f 0.07 (cyclohexane/AcOEt 3/1); mp 74 °C; IR ($CHCl_3$) ν_{max} 3020, 2940, 2855, 1740, 1585, 1525, 1465, 1330, 1280, 1175, 1070 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.01 (qt, $J = 7.3$ Hz, 2 H), 2.41 (t, $J = 7.3$ Hz, 2 H), 2.50 (t, $J = 7.4$ Hz, 2 H), 3.67 (s, 3 H), 3.96 (s, 3 H), 3.99 (s, 3 H), 5.52 (s, 2 H), 7.00 (s, 1 H), 7.72 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 20.1, 32.9, 33.2, 51.6, 56.4, 63.5, 108.2, 110.5, 126.9, 140.0, 148.3, 153.5, 172.2, 173.3; MS (EI) *m*/*z* (%) 341 (9, $M^{+\bullet}$), 196 (66), 167 (52), 151 (44), 136 (91), 59 (100); HR-MS 341.1097 ($C_{15}H_{19}O_8N$ calcd 341.1110).

Glutaric Acid (3′,5′-Dimethoxybenzoin) Ester Methyl Ester (18d). The diester **12d** (11.6 mg, 20 μmol) was stirred under irradiation at 419 nm for 24 h (NMR yield of **17d**: 85%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2 M in hexane), and the purification gave **18d** (6.5 mg, 81%) as a yellow oil: TLC R_f 0.09 (cyclohexane/AcOEt 3/1); IR ($CHCl_3$) ν_{max} 3020, 2955, 2840, 1740, 1700, 1600, 1460, 1350, 1280, 1150, 1070 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 205 (44500), 243 (11700); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.01 (m, 2 H), 2.55 (m, 4 H), 3.67 (s, 3 H), 3.76 (s, 6 H), 6.41 (s, 1 H), 6.58 (s, 2 H), 6.75 (s, 1 H), 7.40 (t, $J = 7.9$ Hz, 2 H), 7.52 (t, $J = 7.8$ Hz, 1 H), 7.93 (d, $J = 7.9$ Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) 20.0, 32.9, 33.0, 51.6, 55.4, 77.6, 101.1, 106.6, 128.6, 128.8, 133.5, 134.5, 135.4, 161.2, 172.4, 173.4, 193.5; MS (EI) *m*/*z* (%) 400 (3, $M^{+\bullet}$), 255 (7), 165 (8), 129 (100), 105 (31); HR-MS 400.1512 ($C_{22}H_{24}O_7$ calcd 400.1522).

Adipic Acid (4,5-Dimethoxy-2-nitrobenzyl) Ester Methyl Ester (19e). The diester **12e** (11.9 mg, 20 μmol) was stirred under irradiation at 254 nm for 10 min (NMR yield of **11e**: 78%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2 M in hexane), and the purification gave **19e** (4.9 mg, 69%) as a yellow solid: TLC R_f 0.13 (cyclohexane/AcOEt 7/3); mp 50−51 °C; IR ($CHCl_3$) ν_{max} 3020, 2935, 2855, 1740, 1585, 1525, 1465, 1330, 1280, 1160, 1070 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70 (m, 4 H), 2.34 (t, $J = 7.1$ Hz, 2 H), 2.44 (t, $J = 7.3$ Hz, 2 H), 3.66 (s, 3 H), 3.96 (s, 3 H), 3.99 (s, 3 H), 5.50 (s, 2 H), 6.99 (s, 1 H), 7.72 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 24.4, 26.9, 33.6, 33.9, 51.6, 56.4, 63.2, 108.3, 110.5, 127.0, 140.1, 148.3, 153.4, 172.6, 173.7; MS (EI) *m*/*z* (%) 355 (4, $M^{+\bullet}$), 224 (5), 196 (38), 167 (35), 151 (27), 136 (49), 55 (100); HR-MS 355.1277 ($C_{16}H_{21}O_8N$ calcd 355.1267).

Adipic Acid (3′,5′-Dimethoxybenzoin) Ester Methyl Ester (18e). The diester **12e** (11.9 mg, 20 μmol) was stirred under irradiation at 419 nm for 24 h (NMR yield of **17e**: 87%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2 M in hexane), and the purification gave **18e** (5.6 mg, 68%) as a yellow oil: TLC R_f 0.25 (cyclohexane/AcOEt 7/3); IR ($CHCl_3$) ν_{max} 3030, 2960, 2840, 1730, 1700, 1600, 1460, 1350, 1280, 1150, 1070, 910 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70 (m, 4 H), 2.33 (m, 2 H), 2.50 (m, 2 H), 3.66 (s, 3 H), 3.76 (s, 6 H), 6.41 (s, 1 H), 6.58 (s, 2 H), 6.74 (s, 1 H), 7.40 (t, $J = 7.7$ Hz, 2 H), 7.52 (t, $J = 7.4$ Hz, 1 H), 7.93 (d, $J = 7.4$ Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) 24.2, 24.3, 33.5, 33.6, 51.5, 55.4, 77.5, 101.1, 106.6, 128.6, 128.7, 133.5, 134.6, 135.5, 161.2, 172.7, 173.7, 193.6; MS (EI) *m*/*z* (%) 414 (5, $M^{+\bullet}$), 255 (11), 165 (17), 143 (100), 111 (49), 105 (57); HR-MS 414.1668 ($C_{23}H_{26}O_7$ calcd 414.1678).

Pimelic Acid (4,5-Dimethoxy-2-nitrobenzyl) Ester Methyl Ester (19f). The diester **12f** (11 mg, 18.4 μmol) was stirred under irradiation at 254 nm for 10 min (NMR yield of **11f**: 90%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2 M in hexane), and the purification gave **19f** (4.8 mg, 71%) as a yellow solid: TLC R_f 0.15 (cyclohexane/AcOEt 7/3); mp 79−80 °C; IR ($CHCl_3$) ν_{max} 2980, 2930, 2870, 1735, 1585, 1525, 1465, 1330, 1280, 1160, 1110, 1070 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.40 (m, 2 H), 1.70 (m, 4 H), 2.32 (t, $J = 7.6$ Hz, 2 H), 2.43 (t, $J = 7.4$ Hz, 2 H), 3.67 (s, 3 H), 3.97 (s, 3 H), 4.00 (s, 3 H), 5.51 (s, 2 H), 7.00 (s, 1 H), 7.73 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 24.5, 24.6, 28.6, 33.8, 34.0, 51.5, 56.4, 63.2, 108.3, 110.6, 127.0, 140.1, 148.3, 153.4, 172.8, 174.0; MS (EI) *m*/*z* (%) 369 (5, $M^{+\bullet}$), 196 (72), 180 (18), 167 (67), 151 (50), 136 (100); HR-MS 369.1385 ($C_{17}H_{23}O_8N$ calcd 369.1423).

Pimelic Acid (3′,5′-Dimethoxybenzoin) Ester Methyl Ester (18f). The diester **12f** (11 mg, 18.4 μmol) was stirred under irradiation at 419 nm for 24 h (NMR yield of **17f**: 70%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2 M in hexane), and the purification gave **18f** (5.4 mg, 69%) as a yellow oil: TLC R_f 0.10 (cyclohexane/AcOEt 4/1); IR ($CHCl_3$) ν_{max} 2980, 2930, 2870, 1730, 1700, 1600, 1460, 1380, 1350, 1260, 1150, 1070 cm^{-1}; UV (MeCN) λ_{max} (ϵ) 201 (20900), 243 (5700); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.40 (m, 2 H), 1.68 (m, 4 H), 2.32 (t, $J = 7.4$ Hz, 2 H), 2.50 (m, 2 H), 3.67 (s, 3 H), 3.77 (s, 6 H), 6.42 (s, 1 H), 6.59 (s, 2 H), 6.75 (s, 1 H), 7.41 (t, $J = 8.2$ Hz, 2 H), 7.53 (t, $J = 8.2$ Hz, 1 H), 7.94 (d, $J = 8.2$ Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) 24.4, 24.6, 28.5, 33.7, 33.8, 51.5, 55.4, 77.5, 101.1, 106.6, 128.6, 128.8, 133.5, 134.6, 135.6, 161.2, 172.3, 174.0, 193.6; MS (EI) *m*/*z* (%) 428 (3, $M^{+\bullet}$), 255 (10), 166 (15), 157 (100), 125 (39), 111 (15), 105 (47); HR-MS 428.1854 ($C_{24}H_{28}O_7$ calcd 428.1835).

***cis*-Cyclohexane-1,2-dicarboxylic Acid (4,5-Dimethoxy-2-nitrobenzyl) Ester Methyl Ester (21a).** The diester **15a** (12.5 mg, 20 μmol) was stirred under irradiation at 254 nm for 10 min (NMR yield of **14a**: 90%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2 M in hexane), and the purification gave **21a** (6.3 mg, 83%) as a yellow solid: TLC R_f 0.24 (cyclohexane/AcOEt 3/1); mp 50−51 °C; IR ($CHCl_3$) ν_{max} 3020, 2940, 2860, 1730, 1600, 1520, 1460, 1330, 1280, 1170, 1070 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60 (m, 4 H), 1.80 (m, 2 H), 2.08 (m, 2 H), 2.91 (m, 2 H), 3.62 (s, 3 H), 3.95 (s, 3 H), 4.04 (s, 3 H), 5.55 (ab, $J_{ab} = 14.7$ Hz, 2 H), 7.09 (s, 1 H), 7.72 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 23.7, 26.2, 26.3, 42.6, 42.7, 51.7, 56.4, 56.7, 63.3, 108.1, 110.3, 127.7, 139.7, 148.0, 153.7, 173.2, 174.2; MS (EI) *m*/*z* (%) 381 (3, $M^{+\bullet}$), 196 (25),

169 (68), 151 (21), 109 (56), 81 (100); HR-MS 381.1388 ($C_{18}H_{23}O_8N$ calcd 381.1423).

***cis*-Cyclohexane-1,2-dicarboxylic Acid (3′,5′-Dimethoxybenzoin) Ester Methyl Ester (23a).** The diester **15a** (12.5 mg, 20 μmol) was stirred under irradiation at 419 nm for 24 h (NMR yield of **22a**: 70%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2 M in hexane), and the purification gave **23a** (6.2 mg, 70%, mixture of two diastereoisomers, ratio 55/45) as a yellow oil: TLC R_f 0.53 (cyclohexane/AcOEt 7/3); IR ($CHCl_3$) ν_{max} 3030, 2930, 2860, 1730, 1640, 1600, 1460, 1350, 1280, 1220, 1170 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) major diastereoisomer: δ 1.2−2.2 (m, 8 H), 2.82 (m, 1 H), 3.06 (m, 1 H), 3.60 (s, 3 H), 3.75 (s, 6 H), 6.39 (s, 1 H), 6.57 (s, 2 H), 6.75 (s, 1 H), 7.40 (t, J = 7.6 Hz, 2 H), 7.51 (t, J = 7.6 Hz, 1 H), 7.93 (d, J = 7.2 Hz, 2 H); minor diastereoisomer: δ 1.2−2.2 (m, 8 H), 2.80 (m, 1 H), 3.06 (m, 1 H), 3.52 (s, 3 H), 3.76 (s, 6 H), 6.39 (s, 1 H), 6.58 (s, 2 H), 6.77 (s, 1 H), 7.40 (t, J = 7.6 Hz, 2 H), 7.51 (t, J = 7.6 Hz, 1 H), 7.93 (d, J = 7.2 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) mixture of both diastereoisomers 23.2, 23.5, 23.9, 24.1, 42.0, 42.6, 51.5, 55.4, 77.3, 101.0, 106.5, 128.6, 128.8, 133.4, 133.7, 135.6, 161.0, 173.1, 174.0, 193.6; MS (EI) m/z (%) 440 (2, $M^{+\bullet}$), 288 (43), 254 (38), 245 (16), 169 (100), 139 (16), 109 (35), 97 (13), 81 (67), 57 (25); HR-MS 440.1840 ($C_{25}H_{28}O_7$ calcd 440.1835).

Adipic Acid Dimethyl Ester (20). The diester **18e** (5.6 mg, 13.5 μmol) was stirred under irradiation at 254 nm for 10 min (NMR yield of adipic acid monomethyl ester: 95%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2 M in hexane), and the purification gave **20** (1.5 mg, 66%) as a colorless oil: TLC R_f 0.47 (cyclohexane/AcOEt 3/1); IR ($CHCl_3$) ν_{max} 3030, 2955, 2870, 1730, 1585, 1438, 1370, 1230, 1160, 1075, 1150 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.63 (m, 4 H), 2.31 (m, 4 H), 3.65 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) 24.3, 33.6, 51.4, 173.7; MS (EI) m/z (%) 143 (28), 114 (54), 111 (38), 101 (45), 83 (28), 74 (38), 59 (100), 55 (78).

The diester **19e** (4.9 mg, 13.8 μmol) was stirred under irradiation at 419 nm for 24 h (NMR yield of adipic acid monomethyl ester: 85%). The residue was then methylated with $TMSCHN_2$ (100 μL, 2 M in hexane), and the purification gave **20** (1.9 mg, 79%).

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Supporting Information Available: Proton and carbon NMR spectra for all cited compounds. These materials are available free of charge via the Internet at http://pubs.acs.org.

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