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Photoacylation of Alcohols in Neutral Medium

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We report here conditions which allow the photoacylation of primary, secondary *and* tertiary alcohols with *N*-acetyl-5,7-dinitroindoline under exceptionally mild conditions, at wavelengths harmless to most functional groups, including otherwise photosensitive ones.

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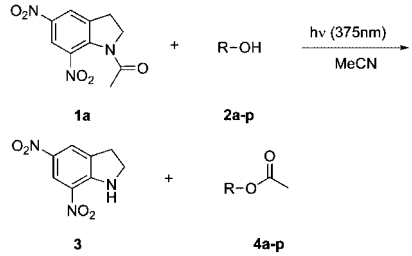
Introduction

The transformation of an alcohol into an ester is one of the most important reactions in organic synthesis, as attested by the countless preparative methods published to date.[1,2] However, in many instances, the existing methods require aggressive reagents (acid chlorides, strong bases or acids, activated alkylating agents) and are incompatible with sensitive functional groups. From this viewpoint, the photoinduced acylation of oxygen nucleophiles would represent an attractive alternative. While similar reactions have been successfully developed for the formation of amides and carbamates,[3–6] esters have proven to be more problematic targets, with the notable exception of methyl esters (when methanol is used as the solvent).[7] We report here conditions which allow the photoacylation of primary, secondary *and* tertiary alcohols with *N*-acetyl-5,7-dinitroindoline under exceptionally mild conditions, at wavelengths harmless to most functional groups, including otherwise photosensitive ones.

Results and Discussion

Our initial experiments, in which we used typical conditions that are suitable for the formation of amides (1 equiv. each of the nucleophile and acetyldinitroindoline in acetonitrile, irradiation at 350 nm), were unsuccessful and led only to deacetylated indoline, acetic acid and unreacted alcohol. Better conversion could only be obtained by using 3 equiv. of the acylating agent. These observations suggested that the photolysis irreversibly produced a species that rapidly decomposed to acetic acid and deacetylated indoline with trace amounts of moisture, if no powerful nucleophile (such as an amine) was available to react fast enough. A mechanistic study by time-resolved IR spectroscopy indeed showed a transient species with a lifetime of ca. 20 μs.[8,9]

We thus reasoned that anything capable of accelerating the bimolecular process required to form the desired ester would be beneficial. The addition of acyl transfer catalysts (such as *N*,*N*-4-dimethylaminopyridine) indeed increased the yields (from 22% to 56%). It was finally by increasing the concentration of the reactants, despite reaching saturation of the *N*-acetyl-5,7-dinitroindoline, that consistently good yields were obtained. Hence, irradiation of a 0.1 M solution of *N*-acetyl-5,7-dinitroindoline with 1 equiv. of an alcohol in strictly anhydrous acetonitrile at 375 nm for 16 h gave the corresponding acetate in good to excellent yields (Scheme 1, Table 1).



Scheme 1. Acetylation of alcohols with indoline **1a**.

The operating wavelength could be increased up to 405 nm, a wavelength where even very UV-photosensitive 3,5-dimethoxybenzoin ester **4p** is stable, without affecting the yields. This adds an interesting facet to our strategy of exploiting chromatic orthogonality[10] because both the esterification and the hydrolysis of **4p** can be carried out photochemically without the need for any external reagent.

The reaction is compatible with the presence of acetyl groups (Entry 13), conjugated and unconjugated alkenes alkynes (Entry 12), and functionalised phenols also react satisfactorily (Entry 7).

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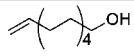
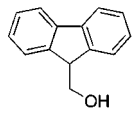
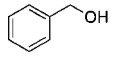
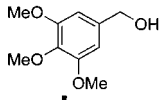
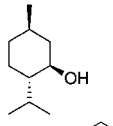
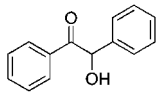
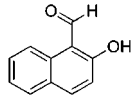
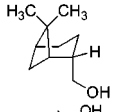
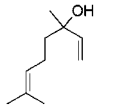
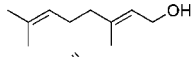
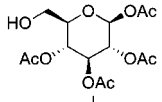
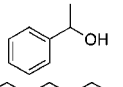
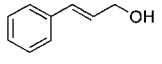
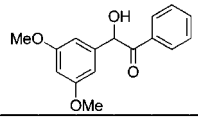
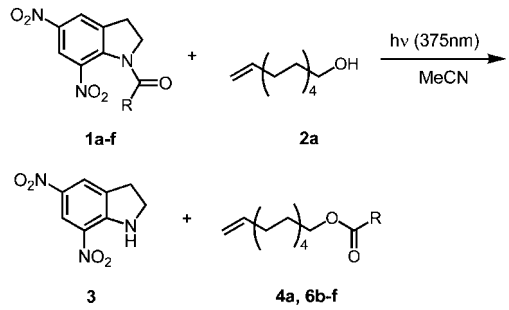
Table 1. Acetylation of alcohols with indoline **1a**.

Entry		Alcohol	Yield of **4**[a] [%]	Yield of **4**[b] [%]
1	**2a**		96	81
2	**2b**		76	63
3	**2c**		98	77
4	**2d**		95	83
5	**2e**		81	66
6	**2f**		76	67
7	**2g**		61	51
8	**2h**		90	72
9	**2i**		83	70
10	**2j**		57	47
11	**2k**		83	72
12	**2l**		70	64
13	**2m**		80	74
14	**2n**		77	69
15	**2o**		83	73
16	**2p**		76	68

[a] Determined in situ by ^{1}H NMR spectroscopy. [b] Isolated.

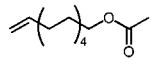
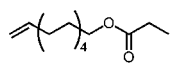
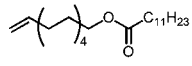
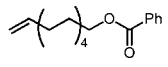
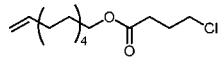
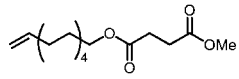
Other groups than simple acetyl can be transferred photochemically. To verify this, we successfully acylated 10-undecen-1-ol with a series of acylnitroindoles (**1a**–**f**), which were prepared in prior work[5] (Scheme 2, Table 2).

We emphasise the simplicity of the experiments, which can be carried out on a normal bench, without the need



Scheme 2. Acylation of alcohols with indolines **1a**–**f**.

Table 2. Acylation of alcohols with indolines **1a**–**f**.

Entry[a]	Indoline	R	Product	Yield[b] [%]	Yield[c] [%]
1	**1a**	CH_3	**4a** 	96	81
2	**1b**	CH_2CH_3	**6b** 	90	82
3	**1c**	$C_{11}H_{23}$	**6c** 	99	94
4	**1d**	C_6H_5	**6d** 	98	89
5	**1e**	$(CH_2)_3Cl$	**6e** 	80	74
6	**1f**	CH_2CH_2COOMe	**6f** 	83	78

[a] Conditions: 0.1 M solution in 1 mL of anhydrous acetonitrile for 16 h, mol ratio of *N*-acyl-5,7-dinitroindoline/alcohol is 1:1. [b] Determined by ^{1}H NMR spectroscopy. [c] Isolated yield.

of a mercury lamp, by using a small footprint LED-based photoreactor (Atlas Photonics Inc.) and quartz test tubes, under conventional magnetic stirring.

In conclusion, we extended the use of *N*-acyl-5,7-dinitrondoline for the photoacylation of alcohols with particularly mild conditions and a simple experimental protocol.

Experimental Section

General Methods: ^{1}H- and ^{13}C-NMR spectra were recorded with a Fourier transform Bruker-DRX-500 (500 MHz) or Bruker-DPX-360 (360 MHz) spectrometer with solvent used as a reference. For ^{13}C NMR, the number of hydrogen was determined by a DEPT sequence. IR spectra were recorded with a Fourier transform Mattson 5000 FTIR spectrometer, neat, in $CHCl_3$ (NaCl cell) or in KBr; absorption bands are in cm^{-1}. UV spectra were recorded with a Perkin Elmer Lambda 40 spectrometer; absorption bands are in nm. EI mass spectra were recorded with an HP 5988A Quadrupol spectrometer, with electron impact (70 eV) and ESI mass spectra with a Bruker FT/MS 4.7 T BioApex II spectrometer. Photochemical irradiations were carried out in a LUMOS 43 photoreactor (Atlas Photonics Inc.), in a quartz vessel, with 1 diode at 375, 385,

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405 or 430 nm, or in a Srinivasan-Griffin (Rayonet-RPR-100) photoreactor, in a quartz vessel, with 16 lamps at 254, 300, 350 or 420 nm. Unless otherwise indicated, all commercial reagents were used without further purification.

Typical Procedure for the Preparation of 1-Acyl-5,7-dinitroindolines: A solution of 5,7-dinitroindoline (43.0 mg, 0.21 mmol),[6] aluminium trichloride (68.5 mg, 0.51 mmol) and acid chloride (0.41 mmol) was heated at reflux in 1,2-dichloroethane (5 mL) for 2 to 6 h. Extraction, followed by trituration in cyclohexane to remove the remaining acid chloride (if not volatile), gave the desired 1-acyl-5,7-dinitroindoline pure or with remaining 5,7-dinitroindoline.

1-Propionyl-5,7-dinitroindoline (1b): Pale brown solid (m.p. 144–147 °C). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 8.26 (s, 1 H), 4.37 (t, J = 8.3 Hz, 2 H), 3.38 (t, J = 8.2 Hz, 2 H), 2.56 (q, J = 7.3 Hz, 2 H), 1.26 (t, J = 7.4 Hz, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 172.3 (C), 143.1 (C), 139.8 (C), 139.1 (C), 138.1 (C), 123.0 (CH), 119.8 (CH), 49.9 (CH_2), 29.0 (CH_2), 29.0 (CH_2), 8.7 (CH_3) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3024, 1697, 1608, 1548, 1462, 1382, 1342, 1280 cm^{-1}. UV/Vis (51 μM soln in MeCN) λ (ε, M^{-1}cm^{-1}): 204 (14310), 226 (13140), 353 (11180) nm. MS: m/z (%) = 265 (2) $[M]^+$, 209 (90), 163 (7), 117 (9), 89 (8), 57 (100). HRMS: calcd. for $C_{11}H_{11}N_3O_5$ 265.0699; found 265.0674.

1-Lauroyl-5,7-dinitroindoline (1c): Very pale brown solid, purified from remaining 5,7-dinitroindoline by chromatography (m.p. 105–108 °C). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 8.26 (s, 1 H), 4.37 (t, J = 8.3 Hz, 2 H), 3.37 (t, J = 8.2 Hz, 2 H), 2.51 (t, J = 7.4 Hz, 2 H), 1.74 (quint, J = 7.5 Hz, 2 H), 1.4–1.2 (m, 16 H), 0.88 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 171.8 (C), 143.2(C), 139.8 (C), 139.2 (C), 138.0 (C), 123.0 (CH), 119.9 (CH), 50.0 (CH_2), 35.7 (CH_2), 31.9(CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 28.5 (CH_2), 24.6 (CH_2), 22.6 (CH_2), 14.1 (CH_3) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2927, 2855, 1695, 1548, 1464, 1374, 1344, 1280 cm^{-1}. UV/Vis (51 μM soln in MeCN): λ (ε, M^{-1}cm^{-1}) = 226 (18240), 349 (13922) nm. MS: m/z (%) = 209 (96), 183 (18), 179 (18), 163 (5), 117 (8), 95 (13), 85 (23), 71 (38), 57 (100). HRMS: calcd. for $C_8H_7N_3O_4$, $C_{12}H_{23}O$ 209.0437, 183.1749; found 209.0437, 183.1749.

1-Benzoyl-5,7-dinitroindoline (1d): Yellow crystals, purified from remaining 5,7-dinitroindoline by recrystallisation (toluene/ethanol, 1:1) (m.p. 193–196 °C). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.69 (s, 1 H), 8.31 (s, 1 H), 7.76 (d, J = 7.4 Hz, 2 H), 7.61 (t, J = 7.6 Hz, 1 H), 7.51 (t, J = 7.7 Hz, 2 H), 4.39 (t, J = 8.2 Hz, 2 H), 3.33 (t, J = 8.2 Hz, 2 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 169.9 (C), 143.7 (C), 141.3 (C), 139.2 (C), 138.8 (C), 133.3 (C), 132.8 (CH), 128.8 (CH), 128.8 (CH), 123.5 (CH), 120.0 (CH), 53.7 (CH_2), 29.1 (CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 3100, 1661, 1600, 1545, 1528, 1439, 1372, 1338, 1306 cm^{-1}. UV (51 μM soln in MeCN): λ (ε, M^{-1}cm^{-1}) = 229 (19020), 353 (12550) nm. MS: m/z (%) = 313 (1) $[M]^+$, 105 (100), 77 (31). HRMS: calcd. for $C_{15}H_{11}N_3O_5$ 313.0699; found 313.0701.

1-(4-Chlorobutyryl)-5,7-dinitroindoline (1e): Yellow oil, purified from remaining 5,7-dinitroindoline by chromatography. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.59 (s, 1 H), 8.28 (s, 1 H), 4.42 (t, J = 8.4 Hz, 2 H), 3.69 (t, J = 6.0 Hz, 2 H), 3.40 (t, J = 8.4 Hz, 2 H), 2.75 (t, J = 6.8 Hz, 2 H), 2.32 (quint, J = 6.4 Hz, 2 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 170.7 (C), 143.5 (C), 139.6 (C), 139.3 (C), 138.1 (C), 123.2 (CH), 120.0 (CH), 50.0 (CH_2), 44.2 (CH_2), 32.1 (CH_2), 28.6 (CH_2), 27.3 (CH_2) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3022, 1694, 1609, 1548, 1438, 1391, 1344, 1280 cm^{-1}. UV/Vis (48 μM soln in MeCN): λ (ε, M^{-1}cm^{-1}) = 202 (17708), 225 (11250), 350 (8542) nm. MS: m/z (%) = 313 (1) $[M]^+$, 209 (100), 179 (10), 163 (9), 117 (16), 107 (19), 105 (60), 77 (36). HRMS: calcd. for $C_{12}H_{12}N_3O_5$ 313.0466; found 313.0480.

1-(3-Methoxycarbonylpropionyl)-5,7-dinitroindoline (1f): Yellow crystals, purified from remaining 5,7-dinitroindoline by recrystallisation (toluene/ethanol, 1:1) (m.p. 126–130 °C). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.53 (s, 1 H), 8.25 (s, 1 H), 4.49 (t, J = 8.2 Hz, 2 H), 3.68 (s, 3 H), 3.40 (t, J = 8.2 Hz, 2 H), 2.84–2.74 (m, 4 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 172.9 (C), 170.6 (C), 143.3 (C), 139.6 (C), 139.1 (C), 138.4 (C), 123.1 (CH), 119.8 (CH), 52.0 (CH_3), 50.1 (CH_2), 30.2 (CH_2), 28.7 (CH_2), 28.5 (CH_2) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3027, 1733, 1697, 1612, 1548, 1439, 1370, 1344, 1283, 1162 cm^{-1}. MS: m/z (%) = 323 (1) $[M]^+$, 292 (8), 209 (12), 163 (3), 115 (100), 87 (14), 59 (24), 55 (57). HRMS: calcd. for $C_{13}H_{13}N_3O_7$ 323.0754; found 323.0744.

Typical Procedure for the Photoacylation of Alcohols to Esters: All experiments were performed in anhydrous acetonitrile (dried by passing it, under an argon atmosphere, through a Grubbs purification system).[11] A mixture of 1-acyl-5,7-dinitroindoline (25.1 mg, 0.1 mmol), the alcohol (0.1 mmol, 1 equiv.) in dry MeCN (1 mL) was irradiated at 375 nm in a quartz tube for 16 h, under an argon atmosphere, with vigorous stirring. The reaction mixture was then concentrated under reduced pressure, and the yield of the ester was then estimated by ^{1}H NMR spectroscopy. 5,7-Dinitroindoline is insoluble in hexane and was removed by trituration and filtration, unless specified otherwise. Evaporation of the hexane filtrate gave the ester and (when applicable) some unreacted alcohol.

Undecen-10-enyl Acetate (4a): Purification by flash column chromatography [SiO_2, hexane/EtOAc (9:1)]. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 5.87–5.75 (m, 1 H), 5.01–4.91 (m, 2 H), 4.05 (t, J = 6.8 Hz, 2 H), 2.06–2.01 (m, 5 H), 1.64 (quint, J = 6.8 Hz, 2 H), 1.39–1.28 (m, 12 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 171.4 (C), 139.4 (CH), 114.3 (CH), 64.8 (CH_2) 34.0 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 28.7 (CH_2), 26.0 (CH_2), 21.2 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3078, 2928, 2856, 1743, 1641, 1464, 1441, 1388, 1366, 1240, 1039, 995, 910 cm^{-1}. MS (ESI): m/z (%) = 235.2 (100) $[M + Na]^+$. HRMS: calcd for $C_{13}H_{24}O_2$ 212.1776; found 212.1772.

9-Fluorenylmethyl Acetate (4b): Purification by flash column chromatography [SiO_2, hexane/EtOAc (9:1)]. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.78 (d, J = 7.2 Hz, 2 H), 7.61 (d, J = 7.2 Hz, 2 H), 7.42 (dd, J = 7.2 Hz, 2 H), 7.33 (dd, J = 7.2 Hz, 2 H), 4.37 (d, J = 7.2 Hz, 2 H), 4.22 (t, J = 7.3 Hz, 1 H), 2.16 (s, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 171.2 (C), 143.9 (C), 141.4 (C), 127.9 (CH), 127.2 (CH), 125.2 (CH), 120.2 (CH), 66.6 (CH_2), 46.9 (CH), 21.2 (CH_3) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3067, 3041, 3021, 2951, 1741, 1449, 1382, 1363, 1245, 1036, 759, 740 cm^{-1}. MS (ESI): m/z (%) = 261.1 (100) $[M + Na]^+$. HRMS: calcd. for $C_{16}H_{14}O_2$ 238.0994; found 238.0992.

Benzyl Acetate (4c): Purification by flash column chromatography [SiO_2, hexane/EtOAc (3:1)]. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.40–7.30 (m, 5 H), 5.11 (s, 2 H), 2.11 (s, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 171.1 (C), 136.1 (C), 128.7 (2 × CH), –128.4 (3 × CH), 66.5 (CH_2), 21.2 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3066, 3035, 2956, 1743, 1498, 1456, 1381, 1363, 1233, 1028, 966, 750, 699 cm^{-1}. MS (ESI): m/z (%) = 173.0 (100) $[M + Na]^+$. HRMS: calcd. for $C_9H_{10}O_2$ 150.0681; found 150.0673.

3,4,5-Trimethoxybenzyl Acetate (4d): Purification by flash column chromatography [SiO_2, hexane/EtOAc (3:1)]. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 6.59 (s, 2 H), 5.03 (s, 2 H), 3.87 (s, 6 H), 3.84 (s, 3 H), 2.11 (s, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 171.1 (C), 153.5 (2 × C), 138.1 (C), 131.6 (C), 105.7 (2 × CH), 66.8 (CH_2),

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61.0 (CH_3), 56.3 (2 × CH_3), 21.2 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2999, 2943, 1740, 1593, 1508, 1463, 1424, 1364, 1332, 1237, 1129, 1010 cm^{-1}. MS (ESI): *m/z* (%) = 263.1 (100) $[M + Na]^+$. HRMS: calcd. for $C_{12}H_{16}O_5$ 240.0998; found 240.0999.

(–)-Menthyl Acetate (4e): Purification by flash column chromatography [SiO_2, hexane/EtOAc (9:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 4.66 (td, *J* = 10.9, 4.1 Hz, 1 H), 2.03 (s, 3 H), 2.00–1.95 (m, 1 H), 1.92–1.79 (m, 1 H), 1.71–1.63 (m, 2 H), 1.55–1.41 (m, 1 H), 1.39–1.31 (m, 1 H), 1.11–0.94 (m, 2 H), 0.9–0.88 (m, 7 H), 0.77–0.75 (d, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 170.8 (C), 74.2 (CH), 47.0 (CH), 40.9 (CH_2), 34.2 (CH_2), 31.4 (CH), 26.3 (CH), 23.5 (CH_2), 22.0 (CH_3), 21.3 (CH_3), 20.7 (CH_3), 16.4 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2957, 2932, 2871, 1737, 1457, 1371, 1246, 1025 cm^{-1}. MS (ESI): *m/z* (%) = 221.1 (100) $[M + Na]^+$. HRMS: calcd. for $C_{12}H_{22}O_2$ 198.1620; found 198.1614.

2-Oxo-1,2-diphenylethyl Acetate (4f): The crude product was triturated with EtOAc. Evaporation of EtOAc gave the ester, the remaining alcohol and 5,7-dinitroindoline. Purification by flash column chromatography [SiO_2, hexane/EtOAc (6:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.2 Hz, 2 H), 7.53–7.32 (m, 8 H), 6.86 (s, 1 H), 2.21 (s, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 193.7 (C), 170.5 (C), 134.6 (C), 133.6 (C), 133.5 (CH), 129.3 (CH), 129.1 (2 × CH), 128.8 (2 × CH), 128.7 (2 × CH), 128.6 (2 × CH), 77.6 (CH), 20.8 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 1740, 1697, 1598, 1451, 1374, 1231, 1182, 1056, 1005, 973, 932, 758, 699, 526 cm^{-1}. MS (ESI): *m/z* (%) = 277.1 (100) $[M + Na]^+$. HRMS: calcd for $C_{16}H_{14}O_3$ 254.0943; found 254.0942.

1-Formylnaphthalen-2-yl Acetate (4 g): The crude product was triturated with EtOAc. Evaporation of EtOAc gave the ester, the remaining alcohol and 5,7-dinitroindoline. Purification by flash column chromatography [SiO_2, hexane/EtOAc (6:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 10.71 (s, 1 H), 9.14 (d, *J* = 8.6 Hz, 1 H), 8.10 (d, *J* = 9.1 Hz, 1 H), 7.88 (d, *J* = 8.2 Hz, 1 H), 7.68 (t, *J* = 7.3 Hz, 1 H), 7.56 (t, *J* = 7.5 Hz, 1 H), 7.28 (d, *J* = 9.6 Hz, 1 H), 2.44 (s, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 190.0 (C), 169.2 (C), 154.4 (C), 136.5 (CH), 131.8 (C), 131.1 (C), 129.6 (CH), 128.5 (CH), 126.7 (CH), 125.0 (CH), 121.6 (CH), 121.4 (C), 20.9 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 1767, 1688, 1617, 1576, 1511, 1434, 1372, 1342, 1189, 1161, 1061, 1036, 1017, 979, 893, 857, 826, 763, 743, 706, 675, 510 cm^{-1}. MS (ESI): *m/z* (%) = 237.0 (100) $[M + Na]^+$. HRMS: calcd for $C_{13}H_{10}O_3$ 214.0630; found 214.0625.

Cyclohexyl Acetate (4h): Purification by flash column chromatography [SiO_2, hexane/EtOAc (9:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 4.76–4.70 (m, 1 H), 2.03 (s, 3 H), 1.87–1.82 (m, 2 H), 1.74–1.70 (m, 2 H) 1.57–1.52 (m, 1 H), 1.44–1.20 (m, 5 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 170.6 (C), 72.7 (CH), 31.6 (2 × CH_2), 25.4 (CH_2), 23.8 (2 × CH_2), 21.5 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2940, 2861, 1737, 1452, 1379, 1364, 1241, 1126, 1046, 1023, 968, 907, 735 cm^{-1}. MS (ESI): *m/z* (%) = 286.3 {2 × $[M + H]^+$}, 165.1 (40) $[M + Na]^+$.

***trans*-(–)-Myrtyl Acetate (4i):** Purification by flash column chromatography [SiO_2, hexane/EtOAc (9:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 3.92–3.81 (m, 2 H), 2.34–2.25 (m, 1 H), 2.08–2.02 (m, 1 H), 2.03 (s, 3 H), 1.89–1.71 (m, 4 H), 1.67–1.59 (m, 1 H), 1.34–1.18 (m, 2 H), 1.21 (s, 3 H), 0.84 (s, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$) δ = 171.4 (C), 68.0 (CH_2), 42.3 (CH), 40.8 (CH), 39.1 (C), 34.1 (CH), 26.6 (CH_2), 23.9 (CH_3), 23.3 (CH_2), 21.0 (CH_3), 20.1 (CH_3), 18.1 (CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2979, 2945, 2917, 2870, 1743, 1463, 1386, 1367, 1236, 1031, 980 cm^{-1}. MS (ESI): *m/z* (%) = 219.1 (100) $[M + Na]^+$. HRMS: calcd. for $C_{12}H_{20}O_2$ 196.1463; found 196.1456.

(±)-Linaloyl Acetate (4j): Purification by flash column chromatography [SiO_2, hexane/EtOAc (9:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 6.01–5.93 (m, 1 H), 5.17,5.07 (m, 3 H), 2.01 (s, 3 H), 1.96 (t, *J* = 7.5 Hz, 2 H), 1.89–1.71 (m, 2 H), 1.67 (s, 3 H), 1.59 (s, 3 H), 1.53 (s, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$) δ = 170.0 (C), 141.8 (CH), 131.8 (C), 123.8 (CH), 113.1 (CH_2), 82.9 (C), 39.7 (CH_2), 25.7 (CH_3), 23.6 (CH_3), 22.3 (CH_2), 22.2 (CH_3), 17.6 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2973, 2930, 2861, 1740, 1450, 1370, 1248, 1173, 1093, 1019, 922 cm^{-1}. HRMS: calcd. for $C_{12}H_{20}O_2$ 196.1463; found 196.1458.

Geranyl Acetate (4k): Purification by flash column chromatography [SiO_2, hexane/EtOAc (9:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 5.34 (t, *J* = 7.2 Hz, 1 H), 5.08 (t, *J* = 6.8 Hz, 1 H), 4.58 (d, *J* = 7.3 Hz, 2 H), 2.14–2.00 (m, 4 H), 2.05 (s, 3 H), 1.70 (s, 3 H), 1.68 (s, 3 H), 1.60 (s, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 171.2 (C), 142.3 (C), 131.8 (C), 123.7 (CH), 118.2 (CH), 61.4 (CH_2), 39.5 (CH_2), 26.3 (CH_2), 25.7 (CH_3), 21.1 (CH_3), 17.7 (CH_3), 16.5 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2969, 2926, 2859, 1742, 1446, 1380, 1369, 1233, 1024, 982, 955 cm^{-1}. MS (ESI): *m/z* (%) = 219.1 (100) $[M + Na]^+$. HRMS: calcd. for $C_{12}H_{20}O_2$ 196.1463; found 196.1457.

1-Ethynylcyclohexyl Acetate (4l): Purification by flash column chromatography [SiO_2, hexane/EtOAc (9:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 2.60 (s, 1 H), 2.16–2.10 (m, 2 H), 2.05 (s, 3 H), 1.88–1.81 (m, 2 H), 1.65–1.59 (m, 4 H), 1.55–1.48 (m, 1 H), 1.38–1.27 (m, 1 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 169.3 (C), 83.7 (C), 75.1 (C), 74.2 (CH), 36.9 (2 × H_2), 25.1 (CH_2), 22.4 (2 × CH_2), 21.9 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3283, 2934, 2863, 2113, 1745, 1450, 1368, 1231, 1145, 1025, 957, 663 cm^{-1}. GC–MS: *m/z* (%) = 166.1 (2) $[M]^+$, 124.0 (58), 109 (40), 106 (50), 95 (74), 91 (10), 81 (92), 79 (68), 67 (52). HRMS: calcd. for $C_{10}H_{14}O_2$ 166.0994; found 160.0983.

1,2,3,4,6-Penta-*O*-acetyl-β-D-glucose (4m): The crude product was triturated with EtOAc. Evaporation of EtOAc gave the ester, the remaining alcohol and 5,7-dinitroindoline. Purification by flash column chromatography (SiO_2, CH_2Cl_2) to remove 5,7-dinitroindoline and [SiO_2, hexane/EtOAc (1:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 5.71 (d, *J* = 8.2 Hz, 1 H), 5.25 (dd, *J* = 9.3 Hz, 1 H), 5.15–5.10 (m, 2 H), 4.29 (dd, *J* = 12.5, 4.3 Hz, 1 H), 4.11 (dd, *J* = 12.5, 2.1 Hz, 1 H), 3.84 (dm, *J* = 10 Hz, 1 H), 2.11 (s, 3 H), 2.08 (s, 3 H), 2.03 (s, 6 H), 2.01 (s, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 170.6 (C), 170.1 (C), 169.4 (C), 169.2 (C), 169.0 (C), 91.7 (CH), 72.7 (2 × CH), 70.2 (CH), 67.7 (CH), 61.4 (CH_2), 20.8 (CH_3), 20.7 (CH_3), 20.6 (3 × CH_3) ppm. IR (neat/$CHCl_3$): $\tilde{\nu}$ = 3025, 1760, 1370, 1222, 1080, 1040, 758, 669 cm^{-1}. HRMS: calcd. for $C_{16}H_{22}O_{11}$ 390.1162; found 390.1156.

(±)-1-Phenylethyl Acetate (4n): Purification by flash column chromatography [SiO_2, hexane/EtOAc (9:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 7.36–7.28 (m, 5 H), 5.88 (q, *J* = 6.8 Hz, 1 H), 2.08 (s, 3 H), 1.54 (d, *J* = 6.8 Hz, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 170.3 (C), 141.7 (C), 128.5 (2 × CH), 127.9 (CH), 126.1 (2 × CH), 72.3 (CH), 22.2 (CH_3), 21.4 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3065, 3034, 2983, 2936, 1744, 1495, 1453, 1372, 1242, 1210, 1065, 1027, 945, 761, 700, 539 cm^{-1}. HRMS: calcd. for $C_{10}H_{12}O_2$ 164.0837; found 164.0831.

Cinnamyl Acetate (4o): Purification by flash column chromatography [SiO_2, hexane/EtOAc (9:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 7.3 Hz; 2 H), 7.33 (dd, *J* = 7.3 Hz, 2 H), 7.26 (dd, *J* = 7.1 Hz, 1 H), 6.66 (d, *J* = 15.9 Hz, 1 H), 6.29 (dt, *J* = 15.9, 6.6 Hz, 1 H), 4.73 (d, *J* = 6.4 Hz, 2 H), 2.10 (s, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 170.9 (C), 136.2 (C), 134.2 (CH), 128.6 (2 × CH), 128.1 (CH), 126.6 (2 × CH), 123.1 (CH), 65.1 (CH_2), 21.0 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3060, 3029, 2945, 1739,

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1495, 1490, 1455, 1381, 1363, 1233, 1027, 967, 747, 694 cm^{-1}. HRMS: calcd. for $C_{11}H_{12}O_2$ 176.0837; found 176.0832.

3′,5′-Dimethoxy-2-oxo-1,2-diphenyl Acetate (4p): For this photosensitive ester, the working wavelength was 405 nm. The crude product was triturated with EtOAc and evaporation of EtOAc gave the ester, the remaining alcohol and 5,7-dinitroindoline. Purification by flash column chromatography [SiO_2, hexane/EtOAc (3:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 7.94 (d, J = 7.8 Hz, 2 H), 7.52 (t, J = 7.3 Hz, 1 H), 7.41 (t, J = 7.8 Hz, 2 H), 6.75 (s, 1 H), 6.59 (d, J = 1.8 Hz, 2 H), 6.42 (t, J = 1.8 Hz, 1 H), 3.76 (s, 6 H), 2.21 (s, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 193.5 (C), 170.4 (C), 161.2 (2 × C), 135.5 (C), 134.5 (C), 133.5 (CH), 128.8 (2 × CH), 128.6 (2 × CH), 106.7 (2 × CH), 101.2 (CH), 77.6 (CH), 55.4 (2 × CH_3), 20.8 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3006, 2942, 2841, 1745, 1698, 1598, 1464, 1431, 1374, 1355, 1281, 1231, 1160, 1056, 1002, 839, 691 cm^{-1}. HRMS: calcd. for $C_{18}H_{18}O_5$ 314.1154; found 314.1147.

Undec-10-enyl Propionate (6b): Purification by flash column chromatography [SiO_2, hexane/EtOAc (9:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 5.85–5.77 (m, 1 H), 5.01–4.91 (m, 2 H), 4.05 (t, J = 6.8 Hz, 2 H), 2.32 (q, J = 7.7 Hz, 2 H), 2.06–2.00 (m, 2 H), 1.63–1.58 (m, 2 H), 1.37–1.28 (m, 12 H), 1.14 (t, J = 7.7 Hz, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 174.6 (C), 139.2 (CH), 114.3 (CH_2), 64.5 (CH_2) 33.8 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 28.6 (CH_2), 27.6 (CH_2), 25.9 (CH_2), 9.2 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2979, 2929, 2856, 1741, 1464, 1350, 1274, 1187, 1084, 995, 910 cm^{-1}. HRMS: calcd. for $C_{16}H_{26}O_2$ 226.1933; found 226.1929.

Undec-10-enyl Lauroate (6c): Purification by flash column chromatography [SiO_2, hexane/EtOAc (9:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 5.85–5.77 (m, 1 H), 5.01–4.91 (m, 2 H), 4.05 (t, J = 6.8 Hz, 2 H), 2.28 (t, J = 7.5 Hz, 2 H), 2.06–2.01 (m, 2 H), 1.63–1.57 (m, 4 H), 1.37–1.25 (m, 28 H), 0.88 (t, J = 6.5 Hz, 3 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 174.0 (C), 139.2 (CH), 114.1 (CH_2), 64.4 (CH_2), 34.4 (CH_2), 33.8 (CH_2), 31.9 (CH_2), 29.6 (2 × CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 28.6 (CH_2), 25.9 (CH_2), 25.0 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2929, 2856, 1739, 1467, 1173, 909 cm^{-1}. HRMS: calcd. for $C_{23}H_{44}O_2$ 352.3341; found 352.3334.

Undec-10-enyl Benzoate (6d): Purification by flash column chromatography [SiO_2, hexane/EtOAc (9:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 8.05 (d, J = 7.3 Hz, 2 H), 7.55 (dd, J = 7.7, 7.3 Hz 1 H), 7.44 (dd, J = 8.2, 7.3 Hz 1 H), 5.87–5.75 (m, 1 H), 5.01–4.92 (m, 2 H), 4.31 (t, J = 6.8 Hz, 2 H), 2.04 (q, J = 7.2 Hz, 2 H), 1.80–1.73 (m, 2 H), 1.46–1.30 (m, 12 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 166.7 (C), 139.2 (CH), 132.8 (CH), 130.5 (C), 129.5 (2 × CH), 128.3 (2 × CH), 114.1 (CH_2), 65.1 (CH_2) 33.8 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 28.7 (CH_2), 26.0 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2928, 2855, 1722, 1453, 1314, 1274, 1176, 1114, 1070, 1028, 910, 712 cm^{-1}. HRMS: calcd. for $C_{18}H_{26}O_2$ 274.1933; found 274.1929.

Undec-10-enyl 4-Chlorobutanoate (6e): Purification by flash column chromatography [SiO_2, hexane/EtOAc (9:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 5.85–5.77 (m, 1 H), 5.02–4.92 (m, 2 H), 4.07 (t, J = 6.8 Hz, 2 H), 3.60 (t, J = 6.4 Hz, 2 H), 2.50 (t, J = 7.2 Hz, 2 H), 2.13–2.01 (m, 4 H), 1.64–1.55 (m, 2 H), 1.42–1.29 (m, 12 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 172.8 (C), 139.2 (CH), 114.1 (CH_2), 64.8 (CH_2) 44.1 (CH_2), 33.8 (CH_2), 31.2 (CH_2), 29.4 (2 × CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 28.6 (CH_2), 27.7 (CH_2), 25.9 (CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2930, 2856, 1737, 1466, 1299, 1240, 1206, 1176, 1147, 911 cm^{-1}. HRMS: calcd. for $C_{18}H_{26}O_2$ 274.1700; 274.1697.

Methyl Undec-10-enylsuccinate (6f): Purification by flash column chromatography [SiO_2, hexane/EtOAc (4:1)]. ^1H NMR (360 MHz, $CDCl_3$): δ = 5.85–5.75 (m, 1 H), 5.01–4.91 (m, 2 H), 4.08 (t, J = 6.8 Hz, 2 H), 3.69 (s, 3 H), 2.63 (br. s, 4 H), 2.06–2.01 (m, 2 H), 1.65–1.58 (m, 2 H), 1.39–1.28 (m, 12 H) ppm. ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 172.8 (C), 172.4 (C), 139.2 (CH), 114.1 (CH_2), 64.9 (CH_2), 51.8 (CH_3), 33.8 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 28.6 (CH_2), 25.8(CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2927, 2856, 1739, 1438, 1357, 1214, 1162, 997 cm^{-1}. HRMS: calcd. for $C_{16}H_{28}O_4$ 284.1988; found 284.1983.

Supporting Information (see footnote on the first page of this article): ^1H- and ^{13}C-NMR spectra for **1a**–**f**, **4a**–**p** and **6b**–**f**.

Acknowledgments

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