Optochemical Control of Bacterial Gene Expression: Novel Photocaged Compounds for Different Promoter Systems

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**Bacterial strains and plasmids**

All bacterial strains, plasmids and oligonucleotides used in this study are listed in Table S1.

| Table S1: Bacterial strains, plasmids and oligonucleotides used in this study. |
| --- |
| **Strains, plasmids, oligonucleotides** | **Relevant features, description or sequences a,b** | **References** |
| **Strains** |  |  |
| *E. coli* DH5α | F- φ80lacZΔM15 Δ(lacZYA-argF) U169 recA1 endA1 hsdR17 phoA supE44 thi-1 gyrA96 relA1 deoR | [1] |
| *E. coli* Tuner (DE3) | F ompT hsdS (r− m−) gal dcm lacY1(Δ3757) | Novagen, Merck KGaA |
| *E. coli* LMG194 | F− ΔlacX74 galE galK thi rpsL ΔphoA Δara714 leu::Tn10 | [2] |
| **Plasmids** |  |  |
| pRhotHi-2-lacI-eYFP | pBBR1-MCS-derivative, KmR, CmR, pBBR22b-lacI, Pγ7-lacO-MCS with NdeI XhoI inserted eyfp | [3] |
| pM117-R45T-GFPmut3 | pMB1 replicon, *xylS* with R45T mutation, *Pm_m17* with inserted gfpmut3 | [4] |
| pM-R45T-GFPmut3 | pMB1 replicon, *xylS* with R45T mutation, *Pm* with inserted gfpmut3 | [5] and this work |
| pBNTmcs(t)-Km | KmR, nagR, vector for *PnagAa* and tac RBS controlled expression | [6] |
| pBNTmcs-mCherry-Km | pBNTmcs(t)-Km derivative with *EcoRI/XbaI* inserted mcherry | This work |
| pBTBX-2 | pBBR1 replicon, KmR, *araC*, araBAD promoter | [7] |
| pBTBX-2-mCherry | pBBR1 replicon, KmR, *araC*, araBAD promoter with tac RBS and inserted mcherry | This work |
| **Oligonucleotides** |  |  |
| 1) XylS_SalI_fw | Binds upstream of SalI-site after *xylS*. Sequence: 5’-GAGACACACGTGGCTTTCC-3’ | [4] |
| 2) XylS_SacI_rev | Binds upstream of SacI-site in front of *xylS*. Sequence: 5’-ATCGACTTGGCGCCTTTCTAC-3’ | [4] |
| 3) XylS_R45T_rev | Binds within *xylS* and inserts R45T point mutation. Sequence: 5’-CAGGCAACGCTGCACCACAGAATC-3’ | [4] |
| 4) XlyS_R45T-fw | Binds within *xylS* and inserts R45T point mutation. Sequence: 5’-GATTCTGTGGTGCAGCGTGCCCTG-3’ | [4] |
| 5) pBTBX_for | Binds at the 3’ end of the pBTBX-2 plasmid. 5’-GTTCTAGAAAAATTCCGTCACAGC-3’ | This work |
| 6) pBTBX_rev | Binds at the 5’ end of the araBAD promoter on the pBTBX-2 plasmid. 5’-CATACCCGTTTTTTTGGGCTAG-3’ | This work |
| 7) mCherry_for | Binds at the 5’ end of the *mcherry* gene, inserts overhangs for In-Fusion® cloning. Sequence: 5’-GTTTTTGGGCTAGCAGGAAACAGGAGGTACC-3’ | This work |
| 8) mCherry_rev | Binds at the 3’ end of *mcherry* gene, inserts overhangs for In-Fusion® cloning. Sequence: 5’-GTTGACGAATTTTCTAGAACTTCTTGTACAGC-3’ | This work |

a Underlined nucleotides indicate the point mutation used for XylS mutagenesis (AGG → ACG).
b Bold nucleotides indicate the inserted overhangs for In-Fusion® cloning.
S2  General methods for chemical synthesis procedures

All chemicals for synthesis were obtained from commercial suppliers and used without further purification unless stated otherwise. Solvents were reagent grade and were dried as well as purified by common methods. Thin-layer chromatography (TLC) was performed using pre-coated silica gel plates (Polygram® SIL G/UV, Macherey-Nagel) and components were visualized via oxidative staining or UV-light. Flash chromatography was performed on silica gel (Merck silica gel 60 (0.063–0.200 µm) and solvents for flash chromatography (petroleum ether/ethyl acetate/dichloromethane/n-pentane) were distilled prior to use. Optical rotation was determined at 20 °C on a Perkin Elmer Polarimeter 241 MC against sodium D-line and melting points were recorded using a Büchi melting point B-545 apparatus.

The NMR spectra ($^1$H and $^{13}$C) were measured at 20 °C on a Bruker Avance/DRX 600 spectrometer in deuterated solvents (CDCl$_3$, DMSO-$d_6$, acetone-$d_6$, D$_2$O). The chemical shifts are given in ppm relative to the solvent ($^1$H: CDCl$_3$ = 7.26 ppm, $^1$H: DMSO-$d_6$ = 3.31 ppm, $^1$H: acetone-$d_6$ = 2.05 ppm, $^1$H: D$_2$O = 4.79 ppm / $^{13}$C: CDCl$_3$ = 77.16 ppm, $^{13}$C: DMSO-$d_6$ = 39.52 ppm, $^{13}$C: acetone-$d_6$ = 29.84 ppm). Signals were assigned by means of H-COSY-, HSQC- and HMBC-experiments and splitting patterns are reported as singlet (s), doublet (d), triplet (t), multiplet (m), and broad singlet (brs). The IR spectra were recorded with a Perkin Elmer SpectrumOne IR-spectrometer ATR (Waltham, USA). HRMS (ESI) spectra were recorded by the centrum of analytics of the Heinrich Heine University. UV-Vis absorption spectra were recorded on a Genesys 10S UV/VIS Spectrophotometer (Thermo Scientific) and uncaging experiments were performed in a quartz cuvette with the LUMOS 43® from Atlas Photonics at 375 nm, 405 nm and 430 nm. Light intensity was quantified using a Thermal Power Sensor (S302C, Thorlabs Inc, USA) and the decay was detected by a Jasco HPLC system [column: Hyperclone 5 µ ODS (C18) 120 (Phenomenex)] combined with an UV/Vis-detector.
S3  Experimental procedures for the preparation of compounds

S3.1  Synthetic scheme for preparation of coumarin 7

![Synthetic scheme for preparation of coumarin 7](image)

Scheme S1: Synthetic scheme for preparation of coumarin 7. Reagents and conditions: i) DMF-DMA, DMF, reflux, 23 h; ii) NaIO₄, THF/H₂O (1:1), RT, 2 h; iii) NaBH₄, EtOH, 0 °C → RT, 4 h; iv) 4-nitrophenyl chloroformate, DIPEA, CH₂Cl₂, RT, 19 h; v) N,N'-dimethylethylenediamine, CH₂Cl₂, 0 °C, 30 min.

Synthesis of (E)-7-(Diethylamino)-4-[2-(dimethylamino)vinyl]-2H-chromen-2-one (S2)

Coumarin S2 was synthesized using a procedure of Weinrich et al.⁸ Coumarin S1 (15.0 g, 64.9 mmol) was dissolved in DMF (150 mL). After the addition of DMF-DMA (17.2 mL, 130 mmol) the reaction mixture was heated to reflux for 23 h. The reaction mixture was cooled to room temperature, diluted with CH₂Cl₂ and saturated NaHCO₃ solution was added. The organic phase was separated, and the aqueous phase was extracted with CH₂Cl₂. The combined organic phase was dried with anhydrous MgSO₄ and concentrated under reduced pressure to yield a brown solid (18.4 g, 64.3 mmol, 99%). The compound S2 was used in the following reactions without further purification. The spectroscopic data are consistent with previously reported literature values.⁹ ¹H-NMR (600 MHz, CDCl₃): δ [ppm] = 1.18 (t, 3J₁₀,₁₀ = 7.2 Hz, 6 H, 10-H), 2.98 (s, 6 H, 6'-H), 3.38 (q, 3J₉,₁₀ = 7.2 Hz, 4 H, 9-H), 5.21 (d, 3J₄',₅' = 13 Hz, 1 H, 4'-H), 5.84 (s, 1 H, 3-H), 6.47 (d, 3J₉,₅ = 2.6 Hz, 1 H, 8-H), 6.54 (dd, 3J₆,₅ = 9.0 Hz, 4J₆,₈ = 2.6 Hz, 1 H, 6-H), 7.20 (d, 3J₅,₅' = 13.0 Hz, 1 H, 5'-H), 7.51 (d, 3J₅,₆ = 9.0 Hz, 1 H, 5-H); ¹³C-NMR (151 MHz, CDCl₃): δ [ppm] = 12.6 (C-10), 41.0 (C-6'), 44.7 (C-9), 87.5 (C-4'), 93.5 (C-3), 98.2 (C-8), 108.0 (C-6), 108.2 (C-4a), 124.9 (C-5), 146.7 (C-5'), 150.2 (C-7), 152.4 (C-4), 156.5 (C-8a), 163.5
Synthesis of 7-(Diethylamino)-2-oxo-2H-chromene-4-carbaldehyde (S3)

Coumarin S3 was synthesized using a procedure of Weinrich et al.\textsuperscript{[8]} Coumarin S2 (18.4 g, 64.3 mmol) was dissolved in THF/H\textsubscript{2}O (1:1, 110 mL). After the addition of NaIO\textsubscript{4} (41.3 g, 193 mmol) the reaction mixture was stirred for 2 h at room temperature. The precipitate was filtered off, washed with ethyl acetate and volatile solvents were removed under reduced pressure and washed with saturated NaHCO\textsubscript{3} solution. The organic phase was separated and the aqueous layer was extracted with CH\textsubscript{2}Cl\textsubscript{2}. The combined organic phase was dried with anhydrous MgSO\textsubscript{4} and concentrated under reduced pressure to yield a brown solid (15.7 g, 64.1 mmol, quant.). The compound S3 was used in the following reactions without further purification. The spectroscopic data are consistent with previously reported literature values.\textsuperscript{[8]} \textsuperscript{1}H-NMR (600 MHz, CDCl\textsubscript{3}): δ [ppm] = 1.22 (t, J\textsubscript{10,9} = 7.1 Hz, 6 H, 10-H), 3.43 (q, J\textsubscript{9,10} = 7.1 Hz, 4 H, 9-H), 6.45 (s, 1 H, 3-H), 6.53 (d, J\textsubscript{8,6} = 2.6 Hz, 1 H, 8-H), 6.63 (dd, J\textsubscript{6,5} = 9.2 Hz, J\textsubscript{6,8} = 2.6 Hz, 1 H, 6-H), 8.31 (d, J\textsubscript{5,6} = 9.2 Hz, 1 H, 5-H), 10.03 (s, 1 H, 4′-H); \textsuperscript{13}C-NMR (151 MHz, CDCl\textsubscript{3}): δ [ppm] = 12.5 (C-10), 45.0 (C-9), 97.9 (C-8), 104.0 (C-4a), 109.8 (C-6), 117.6 (C-3), 127.2 (C-5), 144.0 (C-8a), 151.0 (C-7), 157.5 (C-4), 162.0 (C-2), 192.6 (C-4′); R\textsubscript{f} = 0.29 (PE/EtOAc 50:50); IR (atr-film): ʋ [cm\textsuperscript{-1}] = 2972, 1703, 1607, 1582, 1518, 1424, 1376, 1354, 1267, 1228, 1196, 1142, 1111, 1077, 1053, 901, 822, 780, 732, 640, 475; MS (ESI, positive ion): m/z (%) = 278.3 (100) [M+CH\textsubscript{3}OH+H]\textsuperscript{+}; m.p.: 77.7 °C.
Synthesis of 7-(Diethylamino)-4-(hydroxymethyl)-2H-chromen-2-one (3)

Coumarin 3 was synthesized using a modified procedure of Weinrich et al.\textsuperscript{[8]} Coumarin S3 (5.00 g, 20.4 mmol) was dissolved in ethanol (405 mL) and cooled to 0 °C. After the addition of NaBH\textsubscript{4} at 0 °C the reaction mixture was stirred at room temperature for 4 h. The reaction was quenched by addition of 1 M HCl (150 mL) and diluted with H\textsubscript{2}O (90.0 mL). The solution was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3×100 mL) and the combined organic phase was washed with H\textsubscript{2}O (90 mL). Subsequently it was dried with anhydrous MgSO\textsubscript{4} and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO\textsubscript{2} (petroleum ether/ethyl acetate 50:50) to yield a yellow solid (2.07 g, 8.37 mmol, 41%). The spectroscopic data are consistent with previously reported literature values.\textsuperscript{[8]}

\textsuperscript{1}H-NMR (600 MHz, CDCl\textsubscript{3}): δ [ppm] = 1.20 (t, \textsuperscript{3}J\textsubscript{10,9} = 7.1 Hz, 6 H, 10-H), 1.93 (t, \textsuperscript{3}J\textsubscript{OH,4′} = 5.8 Hz, 1 H, 4′-OH), 3.41 (q, \textsuperscript{3}J\textsubscript{9,10} = 7.1 Hz, 4 H, 9-H), 4.83 (dd, \textsuperscript{3}J\textsubscript{4′,OH} = 5.8 Hz, \textsuperscript{4}J\textsubscript{4,3} = 1.3 Hz, 2 H, 4′-H), 6.25 (t, \textsuperscript{4}J\textsubscript{3,4′} = 1.3 Hz, 1 H, 3-H), 6.51 (d, \textsuperscript{4}J\textsubscript{6,6} = 2.6 Hz, 1 H, 8-H), 6.56 (dd, \textsuperscript{4}J\textsubscript{6,5} = 9.0 Hz, \textsuperscript{4}J\textsubscript{6,8} = 2.6 Hz, 1 H, 6-H), 7.32 (d, \textsuperscript{3}J\textsubscript{5,6} = 9.0 Hz, 1 H, 5-H); \textsuperscript{13}C-NMR (151 MHz, CDCl\textsubscript{3}): δ [ppm] = 12.5 (C-10), 44.8 (C-9), 60.8 (C-4′), 97.7 (C-8), 105.2 (C-3), 106.4 (C-4a), 108.7 (C-6), 124.5 (C-5), 150.6 (C-7), 155.6 (C-4), 156.1 (C-8a), 163.2 (C-2); R\textsubscript{f} = 0.36 (PE/EtOAc 50:50); IR (atr-film): \textbar\nu [cm\textsuperscript{-1}]\textbar = 2013, 2001, 1000; MS (ESI, positive ion): m/z (%) = 254.3 (100) [M+Li]\textsuperscript{+}; m.p.: 139.9 °C.
Synthesis of \(\text{[7-(Diethylamino)-2-oxo-2H-chromen-4-yl]methyl (4-nitrophenyl) carbonate (5)}\)

Coumarin 5 was synthesized using modified procedures of Gao et al.\(^9\) and Fomina et al.\(^10\) Coumarin 3 (2.00 g, 8.09 mmol) was dissolved in dry CH\(_2\)Cl\(_2\) (10.0 mL) under nitrogen atmosphere. \(N,N\)-Diisopropylethylamine (DIPEA) (2.82 mL, 16.2 mmol) was added and the reaction mixture was stirred for 15 min before 4-nitrophenyl chloroformate (3.26 g, 16.2 mmol) dissolved in dry CH\(_2\)Cl\(_2\) (10 mL) was added over 2 h via a syringe pump. The reaction mixture was stirred for 19 h and diluted with CH\(_2\)Cl\(_2\). It was washed with 1 M HCl (20 mL) and saturated NaHCO\(_3\) solution (3×20 mL). The organic phase was dried with anhydrous MgSO\(_4\) and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO\(_2\) (CH\(_2\)Cl\(_2\)/n-pentane 98:2) to yield a yellow solid (1.48 g, 3.60 mmol, 44%). The spectroscopic data are consistent with previously reported literature values.\(^9\) \(^1H\)-NMR (600 MHz, CDCl\(_3\)): \(\delta \text{ [ppm]} = 1.22 \text{ (t, } 3\text{ }J_{10,9} = 7.1 \text{ Hz, 6 H, 10-H)}, \) 3.43 (q, \(3\text{ }J_{9,10} = 7.1 \text{ Hz, 4 H, 9-H}), \) 5.40 (s, 2 H, 1′-H) 6.22 (s, 1 H, 3-H), 6.54 (d, \(4\text{ }J_{8,6} = 2.6 \text{ Hz, 1 H, 8-H}), \) 6.61 (dd, \(3\text{ }J_{6,5} = 9.0 \text{ Hz, 4 }J_{6,8} = 2.6 \text{ Hz, 1 H, 6-H}), \) 7.31 (d, \(3\text{ }J_{5,6} = 9.0 \text{ Hz, 1 H, 5-H}), \) 7.42 (d, \(3\text{ }J_{2′,3′} = 8.6 \text{ Hz, 2 H, 2″-H}), \) 8.30 (d, \(3\text{ }J_{3′,2′} = 8.6 \text{ Hz, 2 H, 3″-H}); \) \(^13\text{C-NMR (151 MHz, CDCl}_3\): \(\delta \text{ [ppm]} = 12.5 \text{ (C-10), 44.9 \text{ (C-9), 65.9 \text{ (C-1′), 98.0 \text{ (C-8), 105.7 \text{ (C-4a), 107.0 \text{ (C-3), 108.9 \text{ (C-6), 121.8 \text{ (C-2″), 124.4 \text{ (C-5), 125.5 \text{ (C-3″), 145.7 \text{ (C-4″), 147.9 \text{ (C-4), 151.0 \text{ (C-7), 152.3 \text{ (C-2′), 155.3 \text{ (C-1″), 165.6 \text{ (C-8a), 161.7 \text{ (C-2), Rf = 0.10 \text{(CH}_2\text{Cl}_2/n-pentane 98:2); IR (atr-film): } \tilde{\nu} \text{ [cm}^{-1}] = 2968, 1772, 1708, 1591, 1520, 1489, 1446, 1423, 1335, 1268, 1218, 1194, 1142, 1109, 1090, 1040, 986, 956, 856, 838, 816, 792, 750, 704, 679, 567, 528, 493, 467; HRMS (ESI): m/z calculated for C\(_{21}\)H\(_{21}\)N\(_2\)O\(_7\): [M+H\(^+\): 413.1343; found: 413.1340; m.p.: 159.9 °C.}

Synthesis of \(\text{[7-(Diethylamino)-2-oxo-2H-chromen-4-yl]methyl methyl[2-(methylamino)ethyl]carbamate (7)}\)

Coumarin 7 was synthesized using a modified procedure of Fomina et al.\(^10\) Coumarin 5 (50.0 mg, 0.12 mmol) was dissolved in CH\(_2\)Cl\(_2\) (1.30 mL). It was added dropwise over 30 min to a solution of \(N,N\)-dimethylethlenediamine (0.14 mL, 1.21 mmol) in CH\(_2\)Cl\(_2\) (2.6 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C. The solvent was removed under reduced pressure, the residue was
dissolved in ethyl acetate and washed subsequently with saturated NaHCO$_3$ and saturated NaCl solution. The organic phase was dried with anhydrous MgSO$_4$ and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO$_2$ (ethyl acetate/methanol/triethylamine 87:10:3) to yield a viscous dark yellow oil (27.0 mg, 74.7 µmol, 62%). $^1$H-NMR (600 MHz, CDCl$_3$): δ [ppm] = 1.19 (t, $^3$J$_{10,9}$ = 7.1 Hz, 6 H, 10-H), 2.42–2.51 (m, 4 H, 5'-H, NH), 2.80 (m, 2 H, 4'-H), 2.95–3.04 (m, 3 H, 2''-H), 3.39 (q, $^3$J$_{9,10}$ = 7.1 Hz, 4 H, 9-H), 3.44–3.49 (m, 2 H, 3'-H), 5.23 (s, 2 H, 1'-H), 6.10 (s, 1 H, 3-H), 6.49 (d, $^4$J$_{8,6}$ = 2.6 Hz, 1 H, 8-H), 6.55 (d, $^3$J$_{6,5}$ = 9.0 Hz, $^4$J$_{6,8}$ = 2.6 Hz, 1 H, 6-H), 7.27–7.31 (m, 1 H, 5-H); $^{13}$C-NMR (151 MHz, CDCl$_3$): δ [ppm] = 12.5 (C-10), 34.8, 35.5 (C-2''), 36.1, 36.4 (C-5''), 44.8 (C-9), 48.6, 48.9 (C-3'), 49.3, 49.7 (C-4''), 62.5, 62.6 (C-1''), 97.9 (C-8), 105.8 (C-4a), 106.1, 106.2 (C-3), 108.7 (C-6), 124.4, 124.5 (C-5), 150.6, 150.7 (C-4, C-7), 155.6, 155.9 (C-2''), 156.3 (C-8a), 162.2 (C-2); R$_f$ = 0.15 (EtOAc/MeOH/NEt$_3$ 87:10:3); IR (atr-film): $\tilde{\nu}$ [cm$^{-1}$] = 2960, 2926, 2859, 1709, 1605, 1526, 1422, 1358, 1275, 1197, 1143, 1078, 821, 767; HRMS (ESI): m/z calculated for C$_{19}$H$_{28}$N$_3$O$_4$ [M+H]$^+$: 362.2074; found: 362.2077.
S3.2  Synthetic scheme for preparation of carbohydrates 8 and 11

Scheme S2: Synthetic scheme for preparation of carbohydrates 8 and 11. Reagents and conditions: i) Ac₂O, DMAP, pyridine, 0 °C → RT, 18 h; ii) AcOH, ethylenediamine, THF, RT, 24 h; iii) 4-nitrophenyl chloroformate, 2,6-lutidine, MeCN, RT, 18 h; iv) Ac₂O, HBr (33 wt%) in AcOH, RT, 3 h.

Synthesis of L-Arabino-pyranose tetraacetate (S4)

α-L-Arabino-pyranose tetraacetate (S4) was synthesized using a procedure of Wahler et al. α-L-Arabino-pyranose (2a) (1.00 g, 6.66 mmol) was dissolved in dry pyridine (5.00 mL) and cooled to 0 °C. After the addition of acetic anhydride (5.04 mL, 53.3 mmol) and 4-dimethylaminopyridine (DMAP) (325 mg, 2.66 mmol) the reaction mixture was stirred for 18 h with the temperature slowly rising to room temperature. The reaction was quenched and diluted by addition of water and ethyl acetate. The organic phase was separated and washed with water as well as saturated NaCl solution. Subsequently it was dried with anhydrous MgSO₄ and concentrated under reduced pressure. Repeated coevaporation with toluene under reduced pressure yielded a colourless solid (1.77 g, 5.58 mmol, 84%). The spectroscopic data are consistent with previously reported literature values. [11] 1H-NMR (600 MHz, CDCl₃): δ [ppm] = 2.01, 2.01, 2.13, 2.14 (s, 12 H, 1″-H, 2″-H, 3″-H, 4″-H), 3.81 (dd, 2 J₅₅₅ = 13.2 Hz, 3 J₅₄ = 2.0 Hz, 1 H, 5-Hₐ), 4.05 (dd, 2 J₅₅₅ = 13.2 Hz, 3 J₅₄ = 1.5 Hz, 1 H, 5-Hₐ), 5.28–5.39 (m, 3 H, 2-H, 3-H, 4-H), 6.33 (d, 3 J₅₂ = 3.1 Hz, 1 H, 1-H); 13C-NMR (151 MHz, CDCl₃): δ [ppm] = 19.7, 19.8, 21.0, 21.0 (C-1″, C-2″, C-3″, C-4″), 62.9 (C-3 or C-4), 66.8 (C-3 or C-4), 67.1 (C-2), 68.5 (C-3 or C-4), 90.3 (C-1), 169.2 (C-1′), 170.0, 170.2, 170.4 (C-2′, C-3′, C-4′); Rf = 0.63 (PE/EtOAc 1:1); IR (atr-film): v [cm⁻¹] = 1736, 1372, 1212, 1113, 1065, 1010, 942, 894, 755, 602, 552, 471; MS (ESI, positive ion): m/z (%) = 341.0 (100) [M+Na]+, 357.0 (15) [M+K]+; m.p.: 94.4 °C; [α]D²⁰ = 151.8 (c = 0.5, CHCl₃).
Synthesis of 2,3,4-Tri-O-acetyl-α,β-L-arabinopyranose (S5)

(2,3,4-tri-O-acetyl)-α,β-L-arabinopyranose (S5) was synthesized using a procedure of Duléry et al.\textsuperscript{[12]} Glacial acetic acid (1.01 mL, 17.6 mmol) was added dropwise to a solution of ethylenediamine (1.01 mL, 15.1 mmol) in THF (250 mL), which immediately lead to the formation of a precipitate. L-arabinopyranose tetraacetate (S4) (4.00 g, 12.6 mmol) was added and the reaction mixture was stirred at room temperature for 24 h. After the addition of water, the reaction mixture was extracted with CH₂Cl₂. The organic phase was subsequently washed with 1 M HCl, saturated NaHCO₃ solution and water. Following this, the organic phase was dried with anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO₂ (petroleum ether/ethyl acetate 55:45) to yield (2,3,4-tri-O-acetyl)-α,β-L-arabinopyranose (S5) as a colorless oil (2.28 g, 8.26 mmol, 66%) in α:β ratio of 1:3. The spectroscopic data are consistent with previously reported literature values.\textsuperscript{[13]} α/β-Anomers: R<sub>f</sub> = 0.18 (PE/EtOAc 1:1); IR (atr-film): ν [cm⁻¹] = 3455, 1739, 1371, 1216, 1139, 1057, 1007, 936, 889, 765, 736, 603, 465; MS (ESI, positive ion): m/z (%) = 299.0 (100) [M+Na]<sup>+</sup>; α-Anomer: <sup>1</sup>H-NMR (600 MHz, CDCl₃): δ [ppm] = 2.00 (s, 3 H, CH₃), 2.08 (s, 3 H, CH₃), 2.13 (s, 3 H, CH₃), 3.66 (dd, <sup>3</sup>J<sub>5a,5b</sub> = 13.4 Hz, <sup>3</sup>J<sub>5a,4</sub> = 1.1 Hz, 1 H, 5-Hₐ), 4.01 (dd, <sup>3</sup>J<sub>5b,5a</sub> = 13.4 Hz, <sup>3</sup>J<sub>5a,4</sub> = 2.5 Hz, 1 H, 5-Hₐ), 4.60 (d, <sup>3</sup>J<sub>1,2</sub> = 6.7 Hz, 1 H, 1-H), 5.03–5.09 (m, 2 H, 2-H and 3-H), 5.24–5.27 (m, 1 H, 4-H); <sup>13</sup>C-NMR (151 MHz, CDCl₃): δ [ppm] = 20.7, 20.9, 21.0 (C-2", C-3", C-4"), 64.2 (C-5), 68.1 (C-4), 70.2 (C-2), 71.3 (C-3), 96.2 (C-1), 170.2, 170.5, 171.2 (C-2’, C-3’, C-4’); β-Anomer: <sup>1</sup>H-NMR (600 MHz, CDCl₃): δ [ppm] = 2.00 (s, 3 H, 4"-H), 2.08 (s, 3 H, 2"-H or 3"-H), 2.12 (s, 3 H, 2"-H or 3"-H), 3.59 (brs, 1 H, 1-OH), 3.68 (dd, <sup>3</sup>J<sub>5a,5b</sub> = 13.1 Hz, <sup>3</sup>J<sub>5a,4</sub> = 2.3 Hz, 1 H, 5-Hₐ), 4.18 (dd, <sup>3</sup>J<sub>5b,5a</sub> = 13.1 Hz, <sup>3</sup>J<sub>5a,4</sub> = 1.5 Hz, 1 H, 5-Hₐ), 5.16 (dd, <sup>3</sup>J<sub>1,2</sub> = 10.5 Hz, <sup>3</sup>J<sub>1,4</sub> = 3.4 Hz, 1 H, 3-H), 5.33–5.36 (m, 1 H, 4-H), 5.38 (dd, <sup>3</sup>J<sub>2,3</sub> = 10.5 Hz, <sup>3</sup>J<sub>2,1</sub> = 3.5 Hz, 1 H, 2-H), 5.45 (d, <sup>3</sup>J<sub>1,2</sub> = 3.5 Hz, 1 H, 1-H); <sup>13</sup>C-NMR (151 MHz, CDCl₃): δ [ppm] = 20.8 (C-4"), 20.9 (C-2" or C-3"), 21.0 (C-2" or C-3"), 60.4 (C-5), 67.0 (C-2), 68.8 (C-3), 69.2 (C-4), 91.0 (C-1), 170.3 (C-4"), 170.6 (C-2’), 170.6 (C-3’).
Synthesis of 2,3,4-Tri-O-acetyl-1-O-(4-nitrophenyloxycarbonyl)-α-L-arabinopyranoside (11)

Carbohydrate 11 was synthesized using a modified procedure of André et al. The anomeric mixture of carbohydrate S5 (408 mg, 1.48 mmol) was dissolved in MeCN (49.0 mL) and cooled to 0 °C. After the addition of 4-nitrophenyl chloroformate (316 mg, 1.57 mmol) and 2,6-lutidine (0.18 mL, 1.57 mmol) the reaction mixture was stirred for 18 h at room temperature. The reaction mixture was quenched by addition of water and diluted with CH₂Cl₂. The organic phase was washed with water and saturated NaCl solution. Following this, the organic phase was dried with anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO₂ (petroleum ether/ethyl acetate 60:40) to mainly yield the α-anomer as a colorless solid (133 mg, 302 µmol, 20%). Unreacted substrate was reisolated as an anomeric mixture with α:β ratio of 1:1.8. ¹H-NMR (600 MHz, CDCl₃): δ [ppm] = 2.10 (s, 3 H, 3″-H), 2.14 (s, 3 H, 4″-H), 2.14 (s, 3 H, 2″-H), 3.83 (dd, 3J₅a,5b = 12.5 Hz, 3J₅a,4 = 2.8 Hz, 1 H, 5-Hₐ), 4.18 (dd, 3J₅b,5a = 12.5 Hz, 3J₅a,4 = 5.1 Hz, 1 H, 5-Hₐ), 5.19 (dd, 3J₅a = 7.8 Hz, 3J₅b,4 = 3.4 Hz, 1 H, 3-H), 5.31–5.36 (m, 2 H, 2-H, 4-H), 5.69 (d, 3J₁,₂ = 5.6 Hz, 1 H, 1-H), 7.41 (d, 3J₈₉ = 9.1 Hz, 2 H, 8-H), 8.29 (d, 3J₉₈ = 9.1 Hz, 2 H, 9-H); ¹³C-NMR (151 MHz, CDCl₃): δ [ppm] = 20.8, 20.9, 21.0 (C-2″, C-3″, C-4″), 62.8 (C-5), 66.3 (C-4), 67.9 (C-2), 69.0 (C-3), 96.1 (C-1), 121.8 (C-8), 125.5 (C-9), 145.8 (C-10), 151.1 (C-6), 155.1 (C-7), 169.3 (C-2′), 170.0 (C-3′), 170.1 (C-4′); Rₛ = 0.28 (PE/EtOAc 70:30); IR (atr-film): ν [cm⁻¹] = 1746, 1594, 1527, 1492, 1370, 1346, 1217, 1173, 1087, 1055, 965, 913, 860, 729, 599, 504; HRMS (ESI): m/z calculated for C₁₈H₂₁N₂O₁₂⁺ [M+NH₄]⁺: 459.1246; found: 459.1247; m.p.: 52–58 °C; [α]D²⁰ = -3 (c = 1.0, CHCl₃).
Synthesis of 2,3,4-Tri-O-acetyl-β-L-arabinopyranosyl bromide (8)

The carbohydrate 8 was synthesized using a procedure of Kartha et al.\textsuperscript{[15]} α-L-Arabinopyranose (2a) (1.00 g, 6.66 mmol) was dissolved in acetic anhydride (5.04 mL, 53.3 mmol) and stirred at room temperature. HBr solution 33 wt% in AcOH (1.50 mL, 8.57 mmol) was added to the suspension. After the solid was completely dissolved (1 h) additional HBr solution 33 wt% in AcOH (7.5 mL, 42.9 mmol) was added and the reaction mixture was stirred for additional 2 h. Subsequently the reaction mixture was concentrated under reduced pressure. Toluene (3×20 ml) was added and removed under reduced pressure. The crude product was recrystallized from Et\textsubscript{2}O to yield a colorless solid (926 mg, 2.73 mmol, 41%). The spectroscopic data are consistent with previously reported literature values.\textsuperscript{[16]} \textsuperscript{1}H-NMR (600 MHz, CDCl\textsubscript{3}): δ [ppm] = 2.03 (s, 3 H, CH\textsubscript{3}), 2.11 (s, 3 H, CH\textsubscript{3}), 2.15 (s, 3 H, CH\textsubscript{3}), 3.93 (dd, \textsuperscript{2}J\textsubscript{5a,5b} = 13.3 Hz, \textsuperscript{3}J\textsubscript{5a,4} = 1.7 Hz, 1 H, 5-H\textsubscript{a}), 4.21 (d, \textsuperscript{2}J\textsubscript{5b,5a} = 13.3 Hz, 1 H, 5-H\textsubscript{b}), 5.09 (ddd, \textsuperscript{3}J\textsubscript{2,3} = 11.8 Hz, \textsuperscript{3}J\textsubscript{2,1} = 3.9 Hz, \textsuperscript{3}J\textsubscript{2,4} = 1.6 Hz, 1 H, 2-H), 5.37–5.43 (m, 2 H, 3-H, 4-H), 6.70 (d, \textsuperscript{3}J\textsubscript{1,2} = 3.9 Hz, 1 H, 1-H); \textsuperscript{13}C-NMR (151 MHz, CDCl\textsubscript{3}): δ [ppm] = 20.8, 20.9, 21.0 (C-2", C-3", C-4"), 64.9 (C-5), 67.8, 68.0 (C-3, C-4), 68.1 (C-2), 89.8 (C-1), 169.9, 170.2, 170.2 (C-2', C-3', C-4'); R\textsubscript{f} = 0.70 (PE/EtOAc 1:1); IR (atr-film): ν [cm\textsuperscript{-1}] = 1734, 1375, 1211, 1098, 1069, 1043, 992, 929, 891, 685, 577, 601, 539, 473; m.p.: 115.6 °C; [α]\textsubscript{D}\textsuperscript{20} = 153.3 (c = 1.0, CHCl\textsubscript{3})
**S3.3 Synthetic scheme for preparation of carbohydrates 10 and 12**

Scheme S3: Synthetic scheme for preparation of carbohydrates 10 and 12. Reagents and conditions: i) 2,2-dimethoxypropane, CSA, acetone, RT, 8 h; ii) TBS-Cl, pyridine, RT, 20 h; iii) 4-nitrophenyl chloroformate, pyridine, RT, 20 h; iv) TrCl, DMAP, pyridine, RT, 18 h; v) PMB-Cl, NaH, DMF, RT, 18 h; vi) CSA, MeOH, CH₂Cl₂, 0 °C → RT, 48 h.

**Synthesis of Isopropyl 3,4-O-(1-methylethylidene)-1-thio-β-D-galactopyranoside (S6)**

Carbohydrate S6 was synthesized using a modified procedure of Du et al. Isopropyl β-D-1-thiogalactopyranoside (1a) (5.00 g, 19.9 mmol) was dissolved in acetone (147 mL). After the addition of camphorsulfonic acid (CSA) (945 mg, 3.99 mmol) and 2,2-dimethoxypropane (3.66 mL, 29.9 mmol) the reaction mixture was stirred for 8 h at room temperature. The reaction mixture was quenched by addition of NaHCO₃ and the solvent was removed under reduced pressure. The residue was dissolved in CH₂Cl₂ and subsequently washed with NaHCO₃ solution. The aqueous phase was extracted with CH₂Cl₂ (3×) and the combined organic phases were washed with saturated NaCl solution. Following this, the organic phase was dried with anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO₂ (petroleum ether/ethyl acetate 50:50) to yield a white solid (3.90 g, 14.0 mmol, 70%). ¹H-NMR (600 MHz, DMSO-d₆): δ [ppm] = 1.22 (d, JCH₂CH₃ = 6.9 Hz, 3 H, CH₃), 1.23 (d, JCH₂CH₃ = 6.9 Hz, 3 H, CH₃), 1.25 (s, 3 H, 7-H or 8-H), 1.38 (s, 3 H, 7-H or 8-H), 3.14 (septet, JCH₂CH₃ = 6.9 Hz, 1 H, S-CH), 3.23 (ddd, J₂,1 = 9.9 Hz, J₂,3 = 6.6 Hz, J₂,2-OH = 6.1 Hz, 1 H, 2-H), 3.51 (m, 2 H, 6-H), 3.73 (td, J₅,₆ = 6.3 Hz, J₅,₄ = 2.0 Hz, 1 H, 5-H), 3.92 (dd, J₃,₂ = 6.6 Hz, J₃,₄ = 5.6 Hz, 1 H, 3-H), 4.14 (dd, J₄,₃ = 5.6 Hz, J₄,₅ = 2.0 Hz, 1 H, 4-H), 4.35 (d, J₁,₂ = 9.9 Hz, 1 H, 1-H), 4.73 (t, J₆,OH₆ = 5.6 Hz, 1 H, 6-OH), 5.29 (d, J₂-OH₂ = 6.1 Hz, 1 H, 2-OH);
13C-NMR (151 MHz, DMSO-d6): δ [ppm] = 23.7 (CH₃), 23.8 (CH₃), 26.4, 28.2 (C-7, C-8), 33.4 (SCH), 60.6 (C-6), 71.8 (C-2), 73.4 (C-4), 76.5 (C-5), 79.5 (C-3), 83.9 (C-1), 108.4 (C-7); Rₜ = 0.23 (PE/EtOAc 50:50); IR (atr-film): ν [cm⁻¹] = 3301, 2990, 2924, 2864, 1460, 1369, 1239, 1215, 1141, 1073, 1025, 962, 872, 840, 725, 641, 570, 536, 504; HRMS (ESI): m/z calculated for C₁₂H₂₀NO₂S⁺ [M+NH₄]⁺: 296.1526; found: 296.1527; m.p.: 89.8 °C; [α]D²⁰ = 3.4 (c = 1.0, CHCl₃)

Synthesis of Isopropyl 6-O-(tert-butyldimethylsilyl)-3,4-O-(1-methylethylidene)-1-thio-β-D-galactopyranoside (9)

Carbohydrate 9 was synthesized using a modified procedure of Du et al.¹¹ Carbohydrate S6 (1.00 g, 3.59 mmol) was dissolved in dry pyridine (20.0 mL) under nitrogen atmosphere. Tert-butyldimethylsilyl chloride (TBS-Cl) (1.14 g, 7.54 mmol) was added portion wise and the reaction mixture was stirred for 20 h at room temperature. After completion, the solvent was removed under reduced pressure. The residue was dissolved in CH₂Cl₂ and subsequently washed with water. The organic phase was dried with anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO₂ (petroleum ether/ethyl acetate 85:15) to yield a white solid (1.05 g, 2.67 mmol, 74%). ¹H-NMR (600 MHz, DMSO-d6): δ [ppm] = 0.04 (s, 3 H, 7-H), 0.05 (s, 3 H, 7-H), 0.86 (s, 9 H, 9-H), 1.22 (d, 3JCH,SCH = 6.8 Hz, 3 H, CH₃), 1.23 (d, 3JCH,SCH = 6.8 Hz, 3 H, CH₃), 1.24 (s, 3 H, 11-H or 12-H), 1.38 (s, 3 H, 11-H or 12-H), 3.13 (septet, 3JSCH₂ = 6.8 Hz, 1 H, SCH), 3.23 (dd, 3J₂,₁ = 9.9 Hz, 3J₂,₃ = 7.0 Hz, 1 H, 2-H), 3.66 (dd, 3J₆a,₆b = 10.4 Hz, 3J₆a,₅ = 7.2 Hz, 1 H, 6-H), 3.71 (dd, 3J₆b,₆a = 10.4 Hz, 3J₆b,₅ = 5.4 Hz, 1 H, 6-H), 3.81 (ddd, 3J₅,₆a = 7.2 Hz, 3J₅,₆b = 5.4 Hz, 3J₅,₄ = 2.0 Hz, 1 H, 5-H), 3.93 (dd, 3J₃,₁ = 7.0 Hz, 3J₃,₄ = 5.4 Hz, 1 H, 3-H), 4.14 (dd, 3J₄,₃ = 5.4 Hz, 3J₄,₅ = 2.0 Hz, 1 H, 4-H), 4.37 (dd, 3J₁,₂ = 9.9 Hz, 1 H, 1-H), 5.28 (brs, 1 H, 2-OH); ¹³C-NMR (151 MHz, DMSO-d6): δ [ppm] = -5.6 (C-7), -5.4 (C-7), 17.9 (C-8), 23.7 (CH₃), 23.8 (CH₃), 25.6 (C-9), 26.3, 28.1 (C-11, C-12), 33.5 (SCH), 62.3 (C-6), 71.7 (C-2), 73.2 (C-4), 76.0 (C-5), 79.5 (C-3), 83.8 (C-1), 108.5 (C-10); Rₜ = 0.62 (PE/EtOAc 60:40); IR (atr-film): ν [cm⁻¹] = 3407, 2945, 2927, 2857, 1472, 1385, 1358, 1223, 1241, 1141, 1110, 1075, 1025, 962, 876, 836, 772, 714, 582, 532, 477; HRMS (ESI): m/z calculated for C₁₈H₃₀O₅S₂⁺ [M+H⁺]: 393.2125; found: 393.2121; m.p.: 45.3 °C; [α]D²⁰ = -15.5 (c = 1.0, CHCl₃)
Synthesis of Isopropyl 6-O-(tert-butyltrimethylsilyl)-3,4-O-(1-methylethylidene)-2-O-(4-nitrophenyloxy carbonyl)-1-thio-β-D-galactopyranoside (12)

Carbohydrate 9 (1.00 g, 2.55 mmol) was dissolved in dry pyridine (20.0 mL) under nitrogen atmosphere. 4-nitrophenyl chloroformate (2.26 g, 11.2 mmol) was added portion wise and the reaction mixture was stirred for 20 h. The reaction mixture was diluted with CH$_2$Cl$_2$ and washed with water. The organic phase was dried with anhydrous MgSO$_4$ and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO$_2$ (petroleum ether/ethyl acetate 85:15) to yield a white solid (1.23 g, 2.21 mmol, 87%).

$^1$H-NMR (600 MHz, CDCl$_3$): δ [ppm] = 0.08 (s, 6 H, 7-H), 0.89 (s, 9 H, 9-H), 1.33 (d, $^3$J$_{CH,SH}$ = 6.8 Hz, 3 H, CH$_3$), 1.33 (d, $^3$J$_{CH,SH}$ = 6.8 Hz, 3 H, CH$_3$), 1.36 (s, 3 H, 11-H or 12-H), 1.56 (s, 3 H, 11-H or 12-H), 3.21 (septet, $^3$J$_{CH,SH}$ = 6.8 Hz, 1 H, SCH), 3.81–3.93 (m, 3 H, 5-H, 6-H), 4.27 (dd, $^3$J$_{3,2}$ = 7.3 Hz, $^3$J$_{3,4}$ = 5.2 Hz, 1 H, 3-H), 4.32 (dd, $^3$J$_{1,3}$ = 5.2 Hz, $^3$J$_{4,5}$ = 1.4 Hz, 1 H, 4-H), 4.53 (d, $^3$J$_{1,2}$ = 10.4 Hz, 1 H, 1-H), 4.85 (dd, $^3$J$_{2,1}$ = 10.4 Hz, $^3$J$_{2,3}$ = 7.3 Hz, 1 H, 2-H), 7.37–7.45 (m, 2 H, 2′-H), 8.21–8.31 (m, 2 H, 3′-H); $^{13}$C-NMR (151 MHz, CDCl$_3$): δ [ppm] = −5.4 (C-7), −5.2 (C-7), 18.4 (C-8), 24.1 (CH$_3$), 24.2 (CH$_3$), 25.9 (C-9), 26.5, 28.0 (C-11, C-12), 35.8 (SCH), 62.1 (C-6), 73.6 (C-4), 76.8 (C-3), 77.3 (C-5), 77.8 (C-2), 82.4 (C-1), 110.8 (C-10), 122.0 (C-2′), 125.4 (C-3′), 145.6 (C-4′), 152.1 (C-2′), 155.7 (C-1′); $R_f$ = 0.73 (PE/EtOAc 70:30); IR (atir-film): $\tilde{\nu}$ [cm$^{-1}$] = 2954, 2929, 2853, 1768, 1617, 1594, 1519, 1492, 1464, 1374, 1345, 1307, 1247, 1215, 1164, 1117, 1072, 989, 957, 878, 836, 774, 751, 707, 674, 641, 573, 536, 499; HRMS (ESI): m/z calculated for C$_{25}$H$_{36}$NO$_5$SSi$^+$ [M+H]$^+$: 558.2188; found: 558.2186; m.p.: 135.0 °C; [α]$_D^{20}$ = 48.8 (c = 1.0, CHCl$_3$)
Synthesis of Isopropyl 6-Ω-trityl-1-thio-β-D-galactopyranoside (S7)

Carbohydrate S7 was synthesized using a modified procedure of Du et al. Isopropyl β-D-1-thiogalactopyranoside (1a) (5.00 g, 21.0 mmol) was dissolved in dry pyridine (5 mL) under nitrogen atmosphere. Trityl chloride (TrCl) (1.17 g, 42.0 mmol) and 4-dimethylaminopyridine (DMAP) (256 mg, 2.10 mmol) were added and the reaction mixture was stirred for 18 h at room temperature. The reaction mixture was diluted with ethyl acetate and subsequently washed with water (3×), saturated NaHCO₃ solution (1×) and saturated NaCl solution (1×). The organic phase was dried with anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO₂ (petroleum ether/ethyl acetate 50:50) to yield a white solid (7.68 g, 16.0 mmol, 76%). ⁱH-NMR (600 MHz, DMSO-d₆): δ [ppm] = 1.28 (d, 3JCH₃,SCH = 6.8 Hz, 3 H, CH₃), 1.31 (d, 3JCH₃,SCH = 6.8 Hz, 3 H, CH₃), 2.93 (dd, 2J₆a,₆b = 9.7 Hz, 3J₆a,₅ = 3.7 Hz, 1 H, 6-Hₐ), 3.20–3.28 (m, 2 H, SCH, 6-Hₐ), 3.28–3.32 (m, 2 H, 2-H, 3-H), 3.56 (brs, 1 H, 6-Hₐ), 3.61 (dd, 3J₅,₆a = 7.7 Hz, 3J₅,₆b = 3.7 Hz, 1 H, 5-H), 4.36–4.39 (m, 1 H, 1-H), 4.42 (d, 3J₄-OH,₄ = 4.5 Hz, 1 H, 4-OH), 4.82 (d, 3J₃-ΟΗ,₃ = 4.6 Hz, 1 H, 3-OH), 4.92 (d, 3J₂-ΟΗ,₂ = 5.2 Hz, 1 H, 2-OH), 7.25 (t, 3J₅,₆ = 7.2 Hz, 3 H, 5'-H), 7.32 (t, 3J₄,₅ = 7.6 Hz, 6 H, 4'-H), 7.41 (d, 3J₃,₄ = 7.4 Hz, 6 H, 3'-H); ¹³C-NMR (151 MHz, DMSO-d₆): δ [ppm] = 23.7 (CH₃), 23.8 (CH₃), 33.6 (SCH), 64.0 (C-6), 69.3 (C-4), 69.8 (C-2), 74.5 (C-3), 77.6 (C-5), 84.8 (C-1), 85.7 (C-1'), 126.9 (C-5'), 127.8 (C-4'), 128.3 (C-3'), 143.9 (C-2'), Rₐ = 0.11 (PE/EtOAc 50:50); IR (atr-film): ν [cm⁻¹] = 3400, 3062, 2925, 2870, 1736, 1594, 1490, 1448, 1368, 1240, 1152, 1060, 1030, 899, 872, 833, 766, 746, 701, 650, 632, 584; HRMS (ESI): m/z calculated for C₂₈H₄₆NO₅S⁺ [M+NH₄]⁺: 498.2309; found: 498.2311; m.p.: 68.8 °C; [α]D²₀ = −23.5 (c = 1.0, CHCl₃)
Synthesis of Isopropyl 2,3,4-tri-O-(4-methoxybenzyl)-6-O-trityl-1-thio-β-D-galactopyranoside (S8)

Carbohydrate S8 was synthesized using modified procedures of Ruda et al.\textsuperscript{[19]} Carbohydrate S7 (100 mg, 208 µmol) and 4-methoxybenzyl chloride (PMB-Cl) (126 µL, 936 mmol) was dissolved in dry DMF (2.00 mL) under nitrogen atmosphere. The mixture was added dropwise over 30 min via a syringe pump to NaH (60%, 37.5 mg, 936 µmol) in dry DMF (2.00 mL) and was stirred for 18 h at room temperature. After completion, the reaction mixture was cooled to 0 °C and quenched by the addition of MeOH. Ethyl acetate was added, and the mixture was washed with water (3×) and saturated NaCl solution. The organic phase was dried with anhydrous MgSO\(_4\) and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO\(_2\) (petroleum ether/ethyl acetate 90:10 to ethyl acetate/methanol 90:10) to yield a white solid (129 mg, 153 µmol, 74%). \(^1\)H-NMR (600 MHz, DMSO-d\(_6\)): δ [ppm] = 1.27 (d, \(^3\)J\(_{\text{CH3,SCH}}\) = 6.8 Hz, 3 H, CH\(_3\)), 1.30 (d, \(^3\)J\(_{\text{CH3,SCH}}\) = 6.8 Hz, 3 H, CH\(_3\)), 2.82 (dd, \(^2\)J\(_{\text{6a,6b}}\) = 9.5 Hz, \(^2\)J\(_{\text{6a,5}}\) = 4.5 Hz, 1 H, 6-H\(_a\)), 3.17–3.28 (m, 2 H, 6-H\(_b\), SCH), 3.40 (t, \(^3\)J\(_{\text{2,3}}\) = 9.4 Hz, 1 H, 2-H), 3.70–3.74 (m, 1 H, 5-H), 3.72 (s, 3 H, OCH\(_3\)), 3.73 (s, 3 H, OCH\(_3\)), 3.74 (s, 3 H, OCH\(_3\)), 3.88 (d, \(^2\)J\(_{\text{4′a,4′b}}\) = 11.0 Hz, 1 H, 4-H\(_a\)), 4.53–4.62 (m, 5 H, 1-H, 2′-H, 3′-H\(_a\), 4′-H\(_b\)), 4.67 (d, \(^2\)J\(_{\text{3′b,3′a}}\) = 11.4 Hz, 1 H, 3′-H\(_b\)), 6.72–6.79 (m, 2 H, arom. H), 6.85–6.92 (m, 6 H, arom. H), 7.20–7.25 (m, 2 H, arom. H), 7.25–7.41 (m, 17 H, arom. H); \(^1\)C-NMR (151 MHz, DMSO-d\(_6\)): δ [ppm] = 23.7 (CH\(_3\)), 23.7 (CH\(_3\)), 34.3 (SCH), 55.0 (OCH\(_3\)), 63.6 (C-6), 71.2 (C-3′), 73.3 (C-4′), 73.9 (C-4), 74.1 (C-2′), 76.7 (C-5), 77.8 (C-2), 82.8 (C-3), 83.3 (C-1), 85.9 (C-1′), 113.4 (arom. C), 113.6 (arom. C), 127.0 (arom. C), 127.9 (arom. C), 128.2 (arom. C), 129.3 (arom. C), 129.9 (arom. C), 130.4 (arom. C), 130.5 (arom. C), 130.6 (arom. C), 134.7 (arom. C), 158.6 (arom. C), 158.7 (arom. C), 158.7 (arom. C); R\(_f\) = 0.05 (PE/EtOAc 90:10); IR (atr-film): \(\tilde{\nu}\) [cm\(^{-1}\)] = 3038, 2931, 2835, 1612, 1586, 1512, 1449, 1360, 1245, 1173, 1152, 1078, 1031, 899, 820, 747, 705, 650, 632, 600, 515; HRMS (ESI): m/z calculated for C\(_{52}\)H\(_{60}\)NO\(_8\)S\(_2\)+ [M+NH\(_4\)]+: 858.4034; found: 858.4031; m.p.: 53.4 °C; [\(\alpha\)]\(_D\)^20 = 6.4 (c = 1.0, CHCl\(_3\))
Synthesis of Isopropyl 2,3,4-tri-O-(4-methoxybenzyl)-1-thio-β-D-galactopyranoside (10)

Carbohydrate 10 was synthesized using modified procedures of Ruda et al.\textsuperscript{19} Carbohydrate S8 (1.28 g, 1.52 mmol) was dissolved in dry CH$_2$Cl$_2$ (63 mL) under nitrogen atmosphere and cooled to 0 °C. Camphorsulfonic acid (CSA) (37.6 mg, 167 μmol) in methanol (6.3 mL) was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was stirred for 48 h. After completion, the solvent was evaporated under reduced pressure. The residue was purified by flash-column chromatography on SiO$_2$ (petroleum ether/ethyl acetate 70:30 to petroleum ether/ethyl acetate 30:70) to yield a white solid (662 mg, 1.11 mmol, 73%). The spectroscopic data are consistent with previously reported literature values.\textsuperscript{20} $^1$H-NMR (600 MHz, CDCl$_3$): δ [ppm] = 1.32 (d, $^3$J$_{CH3,SCH}$ = 6.8 Hz, 3 H, CH$_3$), 1.33 (d, $^3$J$_{CH3,SCH}$ = 6.8 Hz, 3 H, CH$_3$), 3.21 (septet, $^3$J$_{CH,CH}$ = 6.8 Hz, 1 H, SCH), 3.34–3.38 (m, 1 H, 5-H), 3.40 (dd, $^3$J$_{CH,CH}$ = 11.1 Hz, $^3$J$_{CH,5-H}$ = 5.1 Hz, 1 H, 6-H$_a$), 3.53 (dd, $^3$J$_{CH,CH}$ = 9.3 Hz, $^3$J$_{CH,CH}$ = 2.8 Hz, 1 H, 3-H), 3.70–3.79 (m, 3 H, 2-H, 4-H, 6-H$_b$), 3.80 (s, 6 H, OCH$_3$), 3.82 (s, 3 H, OCH$_3$), 4.46 (d, $^3$J$_{CH,CH}$ = 9.7 Hz, 1 H, 1-H), 4.59 (d, $^3$J$_{CH,CH}$ = 11.7 Hz, 1 H, 1″-H$_a$), 4.68 (d, $^3$J$_{CH,CH}$ = 11.4 Hz, 1 H, 1″-H$_b$), 4.71 (d, $^3$J$_{CH,CH}$ = 9.8 Hz, 1 H, 1′-H$_a$), 4.72 (d, $^3$J$_{CH,CH}$ = 11.4 Hz, 1 H, 1″-H$_b$), 4.82 (d, $^3$J$_{CH,CH}$ = 9.8 Hz, 1 H, 1′-H$_b$), 4.87 (d, $^3$J$_{CH,CH}$ = 11.7 Hz, 1 H, 1″-H$_b$), 6.86 (d, $^3$J$_{CH,CH}$ = 8.5 Hz, 2 H, 4″-H), 6.86 (d, $^3$J$_{CH,CH}$ = 8.5 Hz, 2 H, 4‴-H), 6.89 (d, $^3$J$_{CH,CH}$ = 8.5 Hz, 2 H, 4‴-H), 7.25 (d, $^3$J$_{CH,CH}$ = 8.5 Hz, 2 H, 3″-H), 7.31 (d, $^3$J$_{CH,CH}$ = 8.5 Hz, 2 H, 3‴-H), 7.33 (d, $^3$J$_{CH,CH}$ = 8.5 Hz, 2 H, 3‴-H); $^{13}$C-NMR (151 MHz, CDCl$_3$): δ [ppm] = 24.1 (CH$_3$), 35.4 (CH$_3$), 55.4 (SCH), 55.4, 55.4 (C-6′, C-6″, C-6‴), 62.4 (C-6), 72.6 (C-4), 73.0 (C-1″), 73.6 (C-1‴), 75.6 (C-1′), 78.6 (C-2), 78.7 (C-5), 84.1 (C-3), 85.2 (C-1), 113.8, 113.9, 114.0 (C-4′, C-4″, C-4‴), 129.4 (C-3″), 130.1 (C-3″), 130.2 (C-3″), 130.5, 130.6, 130.7 (C-2′, C-2″, C-2‴), 159.4, 159.4, 159.5 (C-5′, C-5″, C-5‴); $R_f$ = 0.09 (PE/EtOAc 70:30); IR (atm-film): $\tilde{\nu}$ [cm$^{-1}$] = 3355, 2948, 2910, 2864, 2841, 1614, 1585, 1513, 1462, 1360, 1302, 1249, 1169, 1136, 1097, 1081, 1050, 1028, 996, 875, 819, 776, 700, 636, 603, 568, 515; HRMS (ESI): m/z calculated for C$_{38}$H$_{46}$NO$_6$S$^+$ [M+NH$_4$]$^+$: 616.2939; found: 616.2945; m.p.: 137.2 °C; [$\alpha$]$^D_{20}$ = −12.7 (c = 1.0, CHCl$_3$).
S3.4 Synthetic scheme for preparation of photocaged arabinose 2b

Scheme S4: Synthetic scheme for preparation of photocaged arabinose 2b. Reagents and conditions: i) AgOTf, CH2Cl2, RT, 22 h; ii) NH3 in MeOH (7 m), MeOH, RT.

Synthesis of 2,3,4-Tri-O-acetyl-1-O-[(7-(diethylamino)-2-oxo-2H-chromen-4-yl)methyl]-α-L-arabinopyranose (13)

Coumarin 13 was synthesized using a modified procedure of Binder et al. [16] A Schlenk tube was charged with 500 mg molecular sieve (5 Å) and carbohydrate 8 (200 mg, 0.59 mmol) dissolved in dry CH2Cl2 (10 mL) under nitrogen atmosphere. A second Schlenk tube was charged with 500 mg molecular sieve (5 Å) and coumarin 3 (438 mg, 1.77 mmol) dissolved in dry CH2Cl2 (10 mL) under nitrogen atmosphere. After stirring for 1 h the dissolved carbohydrate 8 was added to the coumarin solution. Silver triflate (182 mg, 708 µmol) was added and the reaction was stirred for 21 h at room temperature in the dark. The reaction mixture was filtered over celite to remove the molecular sieve. The solvent was removed under reduced pressure and the residue was purified by flash-column chromatography on aluminium oxide (neutral) (petroleum ether/ethyl acetate 50:50) to yield a yellow solid (176 mg, 348 µmol, 59%).

$^1$H-NMR (600 MHz, CDCl3): δ [ppm] = 1.18 (t, $^3J_{9,10} = 7.1$ Hz, 6 H, 10-H), 2.00 (s, 3 H, CH3), 2.04 (s, 3 H, CH3), 2.13 (s, 3 H, CH3), 3.39 (q, $^3J_{9,10} = 7.1$ Hz, 4 H, 9-H), 3.65 (dd, $^3J_{5a,5b} = 12.8$ Hz, $^3J_{5a,4'} = 2.1$ Hz, 1 H, 5″-Ha), 4.04 (dd, $^3J_{5b,5a} = 12.8$ Hz, $^3J_{5b,4'} = 4.0$ Hz, 1 H, 5″-Hb), 4.58 (d, $^3J_{1',2'} = 6.4$ Hz, 1 H, 1″-H), 4.67 (dd, $^3J_{4a,4b} = 14.7$ Hz, $^3J_{4a,3} = 1.3$ Hz, 1 H, 4″-Hb), 4.93 (dd, $^3J_{4b,4a} = 14.7$ Hz, $^3J_{4b,3} = 1.3$ Hz, 1 H, 4″-Hb), 5.07 (dd, $^3J_{3',2'} = 8.8$ Hz, $^3J_{3',4'} = 3.5$ Hz, 1 H, 3″-Hb), 5.24 (dd, $^3J_{2',3'} = 8.8$ Hz, $^3J_{2',1'} = 6.4$ Hz, 1 H, 2″-H), 5.27 (dd, $^3J_{1',5b} = 4.0$ Hz, $^3J_{1',3'} = 3.5$ Hz, $^3J_{1',5a} = 2.1$ Hz, 1 H, 4″-H), 6.17 (t, $^3J_{3',1'} = 1.3$ Hz, 1 H, 3-H), 6.51 (d, $^3J_{6,5} = 2.6$ Hz, 1 H, 8-H), 6.56 (dd, $^3J_{6,6} = 8.9$ Hz, $^3J_{6,8} = 2.6$ Hz, 1 H, 6-H), 7.27 (d, $^3J_{5,6} = 8.9$ Hz, 1 H, 5-H); $^{13}$C-NMR (151 MHz, CDCl3): δ [ppm] = 12.5 (C-10), 20.8, 20.8, 21.0 (CH3), 45.0 (C-9), 62.8 (C-5″), 65.9 (C-4″), 67.3 (C-4′), 69.1 (C-2″), 69.8 (C-3″), 98.1 (C-8), 99.6 (C-1″), 106.5 (C-4a), 107.1 (C-3), 108.8 (C-6), 124.8 (C-5), 150.5 (C-4), 150.6 (C-7), 156.4 (C-8a), 162.0 (C-2), 169.5 (C-2″), 170.2 (C-3″), 170.4 (C-4″); $R_f = 0.51$ (PE/EtOAc 50:50); IR (atr-film): $\tilde{\nu}$ [cm$^{-1}$]
Photocaged arabinose 2b was synthesized using modified procedures of Bier et al.\textsuperscript{[21]} Coumarin 13 (135 mg, 267 μmol) was dissolved in MeOH (0.60 mL) and stirred at room temperature in the dark. Ammonia in MeOH (7 M, 230 μL, 1.61 mmol) was added and the reaction mixture was stirred until complete conversion. The solvent was evaporated under reduced pressure to yield a yellow solid (100 mg, 264 μmol, quant.).\textsuperscript{1}H-NMR (600 MHz, Aceton-\textit{d}_6): δ [ppm] = 1.20 (t, 3\textsubscript{J}10,9 = 7.1 Hz, 6 H, 10-H), 3.50 (q, 3\textsubscript{J}9,10 = 7.1 Hz, 4 H, 9-H), 3.59 (dd, 3\textsubscript{J}5\textsubscript{a},5\textsubscript{b} = 12.4 Hz, 3\textsubscript{J}5\textsubscript{a},4\textsubscript{r} = 1.9 Hz, 1 H, 5\textsuperscript{a}-H\textsubscript{a}), 3.59–3.64 (m, 1 H, 3\textsuperscript{″}-H), 3.68 (d, 3\textsubscript{J}4\textsubscript{a}-OH,4\textsubscript{r} = 4.3 Hz, 1 H, 4\textsuperscript{″}-OH), 3.71 (ddd, 3\textsubscript{J}2\textsuperscript{″},3\textsuperscript{″}r = 8.4 Hz, 3\textsubscript{J}2\textsuperscript{″},1\textsuperscript{″} = 6.7 Hz, 3\textsubscript{J}2\textsuperscript{″},2\textsuperscript{″}-OH = 4.1 Hz, 1 H, 2\textsuperscript{″}-H), 3.82–3.86 (m, 1 H, 4\textsuperscript{″}-H), 3.91 (dd, 2\textsubscript{J}5\textsubscript{b},5\textsubscript{a} = 12.4 Hz, 3\textsubscript{J}5\textsubscript{b},4\textsubscript{r} = 3.3 Hz, 1 H, 5\textsuperscript{a}-H\textsubscript{b}), 3.98 (d, 3\textsubscript{J}3\textsuperscript{″}-OH,3\textsuperscript{″}r = 5.5 Hz, 1 H, 3\textsuperscript{″}-OH), 4.41 (d, 3\textsubscript{J}1\textsuperscript{″},2\textsuperscript{″} = 6.7 Hz, 1 H, 1\textsuperscript{″}-H), 4.47 (d, 3\textsubscript{J}2\textsuperscript{″},OH2\textsuperscript{″} = 4.1 Hz, 1 H, 2\textsuperscript{″}-OH), 4.76 (dd, 2\textsubscript{J}4\textsubscript{a},4b = 15.2 Hz, 4\textsubscript{J}4\textsubscript{a},3 = 1.4 Hz, 1 H, 4\textsuperscript{″}-H\textsubscript{b}), 4.98 (dd, 2\textsubscript{J}4\textsubscript{b},4\textsubscript{a} = 15.2 Hz, 4\textsubscript{J}4\textsubscript{b},3 = 1.4 Hz, 1 H, 4\textsuperscript{″}-H\textsubscript{b}), 6.26 (t, 4\textsubscript{J}3\textsubscript{a},4 = 1.4 Hz, 1 H, 3-H), 6.49 (d, 4\textsubscript{J}8,6 = 2.6 Hz, 1 H, 8-H), 6.69 (dd, 3\textsubscript{J}6,5 = 9.0 Hz, 4\textsubscript{J}6,8 = 2.6 Hz, 1 H, 6-H), 7.47 (d, 3\textsubscript{J}5,6 = 9.0 Hz, 1 H, 5-H); \textsuperscript{13}C-NMR (151 MHz, Aceton-\textit{d}_6): δ [ppm] = 12.7 (C-10), 45.1 (C-9), 66.3 (C-5\textsuperscript{″}), 66.4 (C-4\textsuperscript{″}), 68.9 (C-4\textsuperscript{″}), 72.3 (C-2\textsuperscript{″}), 73.9 (C-3\textsuperscript{″}), 98.0 (C-8), 104.1 (C-1\textsuperscript{″}), 106.9 (C-3), 107.1 (C-4\textsuperscript{a}), 109.4 (C-6), 126.0 (C-5), 151.5 (C-7), 152.9 (C-4), 157.2 (C-8a), 161.8 (C-2); R\textsubscript{f} = 0.33 (PE/EtOAc 50:50); IR (atrt-film): ν [cm\textsuperscript{-1}] = 3443, 2954, 2921, 2847, 1706, 1623, 1527, 1441, 1360, 1328, 1138, 1088, 1011, 855, 824, 794, 763, 610, 511; HRMS (ESI): m/z calculated for C\textsubscript{19}H\textsubscript{26}NO\textsubscript{10}\textsuperscript{+} [M+H]\textsuperscript{+}: 380.1704; found: 380.1697; m.p.: 129–130 °C; [α]\textsubscript{D} 19 = −18.6 (c = 0.5, MeOH); UV-Vis (MeOH): λ\textsubscript{max} (ε) = 272 nm (60914 dm\textsuperscript{3} mol\textsuperscript{-1} cm\textsuperscript{-1}), 388 (17236).
S3.5 Synthetic scheme for preparation of photocaged IPTG 1c

Scheme S5: Synthetic scheme for preparation of photocaged IPTG 1c. Reagents and conditions: i) AcOH, DCC, DMAP, 0 °C → RT, 20 h; ii) Lawesson’s reagent, toluene, reflux, 12 h; iii) malononitrile, NEt₃, AgNO₃, RT, 4 h; iv) HCl in EtOH (1.25 M), EtOH, reflux, 15 h; v) 4-nitrophenyl chloroformate, DIPEA, CH₂Cl₂, 22 h; vi) 9, DMAP, CH₂Cl₂, RT, 20 h; vii) TFA, H₂O, CH₂Cl₂, 0 °C, 10 min.
Synthesis of [7-(Diethylamino)-2-oxo-2H-chromen-4-yl]methyl acetate (S9)

Coumarin S9 was synthesized using a modified procedure of Gandioso et al.\textsuperscript{[22]} Coumarin 3 (500 mg, 2.02 mmol) was dissolved in dry CH$_2$Cl$_2$ (35 mL) under nitrogen atmosphere. 4-Dimethylaminopyridine (DMAP) (299 mg, 2.43 mmol) and acetic acid (139 µL, 2.43 mmol) were added, and the reaction mixture was cooled to 0 °C. N,N'-Dicyclohexylcarbodiimide (DCC) (501 mg, 2.43 mmol) was added at 0 °C and the reaction mixture was stirred for 20 h in the dark. After filtration, the organic filtrate was washed with 1 M HCl and saturated NaHCO$_3$ solution. The organic phase was dried with anhydrous MgSO$_4$ and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO$_2$ (CH$_2$Cl$_2$) to yield a red solid (518 mg, 1.79 mmol, 89%). The spectroscopic data are consistent with previously reported literature values.\textsuperscript{[22]} $^1$H-NMR (600 MHz, CDCl$_3$): δ [ppm] = 1.19 (t, $^3$J$_{10,9}$ = 7.1 Hz, 6 H, 10-H), 2.18 (s, 3 H, 2″-H), 3.40 (q, $^3$J$_{9,10}$ = 7.1 Hz, 4 H, 9-H), 5.20 (d, $^4$J$_{3,4}$ = 1.3 Hz, 2 H, 4′-H) 6.11 (t, $^4$J$_{3,4'}$ = 1.3 Hz, 1 H, 3-H), 6.50 (d, $^4$J$_{6,8}$ = 2.6 Hz, 1 H, 8-H), 6.56 (dd, $^3$J$_{6,5}$ = 9.0 Hz, $^4$J$_{6,8}$ = 2.6 Hz, 1 H, 6-H), 7.27 (d, $^3$J$_{5,6}$ = 9.0 Hz, 1 H, 5-H); $^{13}$C-NMR (151 MHz, CDCl$_3$): δ [ppm] = 12.5 (C-10), 20.9 (C-2″), 44.9 (C-9), 61.4 (C-4′), 97.9 (C-8), 106.1 (C-4a), 106.5 (C-3), 108.8 (C-6), 124.5 (C-5), 149.5 (C-4), 150.8 (C-7), 156.4 (C-8a), 162.0 (C-2), 170.3 (C-1″); R$_f$ = 0.57 (PE/EtOAc 50:50); IR (atr-film): $\tilde{\nu}$ [cm$^{-1}$] = 2974, 1748, 1706, 1597, 1527, 1440, 1415, 1376, 1272, 1240, 1196, 1140, 1074, 1013, 933, 841, 823, 811, 666, 598, 560; HRMS (ESI): m/z calculated for C$_{16}$H$_{20}$NO$_4$ $^\ast$ [M+H]$^+$: 290.1387; found: 290.1389; m.p.: 108.3 °C.
Synthesis of [7-(Diethylamino)-2-thioxo-2H-chromen-4-yl]methyl acetate (S10)

Coumarin S10 was synthesized using a modified procedure of Gandioso et al.\textsuperscript{[22]} Coumarin S9 (2.00 g, 6.91 mmol) was dissolved in dry toluene (237 mL) under nitrogen atmosphere. Lawesson’s reagent (1.82 g, 4.49 mmol) was added, and the reaction mixture was heated to reflux for 12 h in the dark. The solution was concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO\textsubscript{2} (CH\textsubscript{2}Cl\textsubscript{2}) to yield an orange solid (1.78 g, 5.83 mmol, 84%). The spectroscopic data are consistent with previously reported literature values.\textsuperscript{[22]} \textsuperscript{1}H-NMR (600 MHz, CDCl\textsubscript{3}): \( \delta \) [ppm] = 1.22 (t, \( ^3J_{10,9} = 7.1 \) Hz, 6 H, 10-H), 2.19 (s, 3 H, 2″-H), 3.43 (q, \( ^3J_{9,10} = 7.1 \) Hz, 4 H, 9-H), 5.18 (d, \( ^4J_{4',3} = 1.3 \) Hz, 2 H, 4'-H), 6.66 (d, \( ^3J_{6,5} = 9.0 \) Hz, 4 H, 6-H); 6.68 (d, \( ^3J_{8,6} = 2.6 \) Hz, 1 H, 8-H); 7.06 (t, \( ^4J_{3,4} = 1.3 \) Hz, 1 H, 3-H); 7.34 (d, \( ^3J_{5,6} = 9.0 \) Hz, 1 H, 5-H); \textsuperscript{13}C-NMR (151 MHz, CDCl\textsubscript{3}): \( \delta \) [ppm] = 12.5 (C-10), 20.9 (C-2″) 45.1 (C-9), 61.1 (C-4′), 97.6 (C-8), 108.3 (C-4a), 110.4 (C-6), 120.7 (C-3), 124.6 (C-5), 142.0 (C-4), 151.2 (C-7), 159.1 (C-8a), 170.4 (C-1″), 197.3 (C-2); \( R_f = 0.60 \) (CH\textsubscript{2}Cl\textsubscript{2}); IR (atr-film): \( \tilde{\nu} \) [cm\textsuperscript{-1}] = 2971, 1743, 1625, 1574, 1516, 1432, 1399, 1376, 1354, 1290, 1250, 1217, 1197, 1180, 1147, 1071, 1029, 967, 855, 822, 795, 652; HRMS (ESI): m/z calculated for C\textsubscript{16}H\textsubscript{20}NO\textsubscript{3}S\textsuperscript{+} [M+H]\textsuperscript{+}: 306.1158; found: 306.1160; m.p.: 137.9 °C
Synthesis of \([2\text{-}(\text{Dicyanomethylene})\text{-}7\text{-}(\text{diethylamino})\text{-}2\text{H}-\text{chromen-4-yl}]\text{methyl acetate (S11)}\)

Coumarin S11 was synthesized using a procedure of Gandioso et al.\(^{[22]}\) Coumarin S10 (1.00 g, 3.27 mmol) was dissolved in dry MeCN (100 mL) under nitrogen atmosphere. After addition of malononitrile (1.09 g, 16.5 mmol) and triethylamine (NEt\(_3\)) (9.13 mL, 65.5 mmol), the reaction mixture was stirred for 20 min at room temperature in the dark. The reaction mixture became intensely red. Silver nitrate (1.12 g, 6.58 mmol) was added and the reaction mixture was stirred for additional 4 h at room temperature in the dark. The reaction mixture was filtered and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO\(_2\) (CH\(_2\)Cl\(_2\)) to yield an orange-red solid (616 mg, 1.83 mmol, 56%). The spectroscopic data are consistent with previously reported literature values.\(^{[22]}\)\(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta\) [ppm] = 1.24 (t, \(\text{J}_{10,9} = 7.1\text{ Hz}, 6\text{ H}, 10\text{-H})\), 2.21 (s, 3 H, \(2\text{″-H}\)), 3.45 (q, \(\text{J}_{9,10} = 7.1\text{ Hz}, 4\text{ H}, 9\text{-H})\), 5.24 (d, \(\text{J}_{4,3} = 1.2\text{ Hz}, 2\text{ H}, 4\text{′-H})\), 6.62 (d, \(\text{J}_{8,6} = 2.6\text{ Hz}, 1\text{ H}, 8\text{-H})\), 6.70 (dd, \(\text{J}_{6,5} = 9.0\text{ Hz}, \text{J}_{6,8} = 2.6\text{ Hz}, 1\text{ H}, 6\text{-H})\), 6.75 (t, \(\text{J}_{3,4} = 1.2\text{ Hz}, 1\text{ H}, 3\text{-H})\), 7.34 (d, \(\text{J}_{5,6} = 9.0\text{ Hz}, 1\text{ H}, 5\text{-H})\); \(^{13}\)C-NMR (151 MHz, CDCl\(_3\)): \(\delta\) [ppm] = 12.5 (C-10), 20.9 (C-2″), 45.3 (C-9), 55.9 (C-2′), 61.2 (C-4″), 97.9 (C-8), 106.2 (C-3), 107.4 (C-4a), 111.1 (C-6), 113.9 (CN), 114.6 (CN), 125.0 (C-5), 146.1 (C-4), 151.6 (C-7), 155.1 (C-8a), 170.3 (C-1″), 171.9 (C-2); \(R_f = 0.48\) (PE/EtOAc 70:30); IR (atr-film): \(\nu [\text{cm}^{-1}] = 2969, 2924, 2215, 1750, 1638, 1586, 1524, 1430, 1358, 1320, 1259, 1224, 1148, 1079, 816, 687\); HRMS (ESI): m/z calculated for C\(_{19}\)H\(_{20}\)N\(_3\)O\(_3^+\) [M+H]\(^+\): 338.1499; found: 338.1495; m.p.: 202–203 °C.
Synthesis of 2-(Dicyanomethylene)-7-(diethylamino)-4-(hydroxymethyl)-2H-chromen (4)

Coumarin 4 was synthesized using a procedure of Fournier et al.\textsuperscript{[23]} Coumarin S11 (500 mg, 1.48 mmol) was dissolved in dry EtOH (316 mL) under nitrogen atmosphere. After addition of HCl in EtOH (1.25 M, 2.96 mL, 3.71 mmol), the reaction mixture was heated to reflux for 15 h in the dark. Then, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO\textsubscript{2} (dichloromethane/acetone 95:5) to yield an orange-red solid (403 mg, 1.36 mmol, 92%). The spectroscopic data are consistent with previously reported literature values.\textsuperscript{[23]}

\textsuperscript{1}H-NMR (600 MHz, CDCl\textsubscript{3}): \( \delta \) [ppm] = 1.24 (t, \( ^3J_{10,9} = 7.1 \text{ Hz}, 6 \text{ H}, 10\text{-H}), 3.45 (q, \( ^3J_{9,10} = 7.1 \text{ Hz}, 4 \text{ H}, 9\text{-H}), 4.89 (s, 2 \text{ H}, 4'\text{-H}), 6.63 (d, \( ^3J_{8,6} = 2.6 \text{ Hz}, 1 \text{ H}, 8\text{-H}), 6.71 (dd, \( ^3J_{6,5} = 9.0 \text{ Hz}, ^4J_{6,8} = 2.6 \text{ Hz}, 1 \text{ H}, 6\text{-H}), 6.98 (s, 1 \text{ H}, 3\text{-H}), 7.36 (d, \( ^3J_{5,6} = 9.0 \text{ Hz}, 1 \text{ H}, 5\text{-H}); \textsuperscript{13}C-NMR (151 MHz, CDCl\textsubscript{3}): \( \delta \) [ppm] = 12.6 (C-10), 45.4 (C-9), 54.9 (C-2'), 60.8 (C-4'), 97.8 (C-8), 105.4 (C-3), 107.7 (C-4a), 111.2 (C-6), 114.2 (CN), 115.0 (CN), 125.0 (C-5), 151.4 (C-4), 151.6 (C-7), 154.9 (C-8a), 172.3 (C-2); \( R_f = 0.44 \) (CH\textsubscript{2}Cl\textsubscript{2}/acetone 95:5); IR (atr-film): \( \tilde{\nu} \) [cm\textsuperscript{-1}] = 3431, 2972, 2918, 2199, 1741, 1634, 1575, 1504, 1418, 1355, 1319, 1254, 1189, 1144, 1085, 821, 686, 508; MS (ESI, positive ion): m/z (%) = 296.3 (100) [M+H]\textsuperscript{+}; m.p.: 179–180 °C
Synthesis of [2-(Dicyanomethylene)-7-(diethylamino)-2H-chromen-4-yl]methyl (4-nitrophenyl) carbonate (6)

Coumarin 6 was synthesized using modified procedures of Gao et al.\textsuperscript{[9]} and Fomina et al.\textsuperscript{[10]} Coumarin 4 (250 mg, 846 μmol) was dissolved in dry CH$_2$Cl$_2$ (15.0 mL) under nitrogen atmosphere. N,N-Diisopropylethylamine (DIPEA) (295 μL, 1.69 mmol) was added and the reaction mixture was stirred for 15 min before 4-nitrophenyl chloroformate (341 mg, 1.69 mmol) was added portion wise. The reaction mixture was stirred for 22 h and diluted with CH$_2$Cl$_2$. It was washed with 1 M HCl (1×) and saturated NaHCO$_3$ solution (3×). The organic phase was dried with anhydrous MgSO$_4$ and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO$_2$ (petroleum ether/ethyl acetate 70:30) to yield a red solid (179 mg, 389 μmol, 46%). $^1$H-NMR (600 MHz, CDCl$_3$): δ [ppm] = 1.25 (t, $^3$J$_{10,9} = 7.1$ Hz, 6 H, 10-H), 3.46 (q, $^3$J$_{9,10} = 7.1$ Hz, 4 H, 9-H), 5.42 (s, 2 H, 4′-H), 6.61 (d, $^3$J$_{8,6} = 2.5$ Hz, 1 H, 8-H), 6.69 (dd, $^3$J$_{6,5} = 9.0$ Hz, $^4$J$_{6,8} = 2.5$ Hz, 1 H, 6-H), 6.80 (s, 1 H, 3-H), 7.35 (d, $^3$J$_{5,6} = 9.0$ Hz, 1 H, 5-H), 7.43 (m, 2 H, 2″-H), 8.31 (m, 2 H, 3″-H); $^{13}$C-NMR (151 MHz, CDCl$_3$): δ [ppm] = 12.6 (C-10), 45.2 (C-9), 56.5 (C-2′), 65.5 (C-4′), 97.6 (C-8), 106.3 (C-3), 106.7 (C-4a), 110.9 (C-6), 113.7 (CN), 114.5 (CN), 121.9 (C-2″), 124.9 (C-5), 125.6 (C-3″), 144.2 (C-4), 145.9 (C-4″), 152.0 (C-7), 152.2 (C-5′), 155.2, 155.2 (C-8a, C-1″), 171.7 (C-2); R$_f$ = 0.28 (PE/EtOAc 60:40); IR (atr-film): $\tilde{\nu}$ [cm$^{-1}$] = 2215, 1774, 1638, 1584, 1548, 1523, 1489, 1432, 1350, 1321, 1259, 1216, 1148, 1083, 860; HRMS (ESI): m/z calculated for C$_{24}$H$_{21}$N$_4$O$_6^+$ [M+H]$^+$: 461.1456; found: 461.1457; m.p.: 209–211 °C
Synthesis of Isopropyl 6-O-(tert-butyldimethylsilyl)-2-O-[[dicyanomethylene]-7-(diethylamino)-2H-chromen-4-yl]methylxycarbonyl]-3,4-O-(1-methylethylidene)-1-thio-β-D-galactopyranoside (13)

Coumarin 13 was synthesized using modified procedures of Suzuki et al.[24] Coumarin 6 (0.12 g, 0.25 mmol) was dissolved in dry CH2Cl2 (4.0 mL) under nitrogen atmosphere. After the addition of 4-dimethylaminopyridine (DMAP) (31 mg, 0.26 mmol) and carbohydrate 9 (90 mg, 0.23 mmol) the reaction mixture was stirred for 20 h at room temperature in the dark. Then, it was diluted with CH2Cl2, washed with saturated NaHCO3 and saturated NaCl solution. The organic phase was dried with anhydrous MgSO4 and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO2 (petroleum ether/ethyl acetate 80:20) to yield a red solid (0.15 g, 0.22 mmol, 96%). 1H-NMR (600 MHz, CDCl3): δ [ppm] = 0.07 (s, 3 H, 7″-H), 0.07 (s, 3 H, 7″-H), 0.89 (s, 9 H, 9″-H), 1.23 (t, 3J10,9 = 7.1 Hz, 6 H, 10-H), 1.29 (d, 3JCH3,SCH = 6.8 Hz, 3 H, CH3), 1.30 (d, 3JCH3,SCH = 6.8 Hz, 3 H, CH3), 1.35 (s, 3 H, 11″-H or 12″-H), 1.55 (s, 3 H, 11″-H or 12″-H), 3.19 (septet, 3JCH3,CH3 = 6.8 Hz, 1 H, SCH), 3.44 (q, 3J9,10 = 7.1 Hz, 4 H, 9-H), 3.80–3.89 (m, 3J7r,4r = 5.6 Hz, 3 H, 5″-H, 6″-H), 4.23 (dd, 3J9r,2r = 7.3 Hz, 3J9r,4r = 5.3 Hz, 1 H, 3″-H), 4.29 (dd, 3J4r,3r = 5.3 Hz, 3J4r,5r = 1.9 Hz, 1 H, 4″-H), 4.49 (d, 3J2r,1r = 10.4 Hz, 1 H, 1″-H), 4.79 (dd, 3J2r,3r = 10.4 Hz, 3J2r,5r = 7.3 Hz, 1 H, 2″-H), 5.25 (dd, 3J4a,4b = 15.5 Hz, 4J4a,4b = 1.2 Hz, 1 H, 4′-HΔ), 5.39 (dd, 3J4b,4a = 15.5 Hz, 4J4b,4a = 1.2 Hz, 1 H, 4′-Hδ), 6.58 (d, 4J6,6 = 2.6 Hz, 1 H, 8-H), 6.64 (dd, 3J6,5 = 9.1 Hz, 4J6,8 = 2.6 Hz, 1 H, 6-H), 6.81 (m, 1 H, 3-H), 7.29 (d, 3J6,6 = 9.1 Hz, 1 H, 5-H); 13C-NMR (151 MHz, CDCl3): δ [ppm] = −5.4 (C-7″), −5.3 (C-7″), 12.6 (C-10), 18.3 (C-8″), 24.0 (CH3), 24.1 (CH3), 25.9 (C-9″), 26.5, 28.0 (C-11″, C-12″), 35.8 (SCH), 45.1 (C-9), 55.9 (C-2′), 62.1 (C-6′), 64.7 (C-4′), 73.6 (C-4″), 77.0 (C-3′), 77.2 (C-5′), 77.3 (C-2′), 82.4 (C-1′), 97.5 (C-8), 106.0 (C-3), 106.8 (C-4a), 110.6 (C-10″), 110.8 (C-6), 114.0 (CN), 114.5 (CN), 124.9 (C-5), 145.4 (C-4), 151.8 (C-7), 154.2 (C-5′), 155.0 (C-8a), 171.9 (C-2); Rf = 0.24 (PE/EtOAc 80:20); IR (atrazine): ν [cm⁻¹] = 2955, 2929, 2859, 2216, 1756, 1639, 1586, 1548, 1525, 1432, 1383, 1356, 1319, 1257, 1223, 1196, 1148, 1111, 1078, 1047, 983, 871, 839, 760; HRMS (ESI): m/z calculated for C38H32N2O8SSi+ [M+H]⁺: 714.3239; found: 714.3237; m.p.: 79–81 °C; [α]D²⁰ = −18.0 (c = 0.1, CHCl₃).
Synthesis of Isopropyl 2-O-{[[dicyanomethylene]-7-(diethylamino)-2H-chromen-4-yl]methylxycarbonyl}-1-thio-β-D-galactopyranoside (1c)

Photocaged IPTG 1c was synthesized using modified procedures of Suzuki et al.\[24\] Coumarin 13 (0.10 g, 0.14 mmol) was dissolved in CH₂Cl₂ (1.0 mL) and cooled to 0 °C. After the addition of trifluoroacetic acid (TFA) (1.0 mL, 13 mmol) and water (40 µL, 2.2 mmol), the reaction mixture was stirred for 10 min at 0 °C in the dark. Then the reaction mixture was concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO₂ (ethyl acetate) to yield a red solid (72 mg, 0.13 mmol, 92%). ¹H-NMR (600 MHz, Aceton-d₆): δ [ppm] = 1.18–1.28 (m, 12 H, 10-H, CH₃), 3.20 (septet, 3J_{CH,CH₃} = 6.8 Hz, 1 H, SCH), 3.59 (q, 3J_{δ,δ,10} = 7.1 Hz, 4 H, 9-H), 3.67 (t, 3J_{δ,δ,4′} = 5.6 Hz, 1 H, 5″-H), 3.77 (m, 2 H, 6″-H), 3.86 (dd, 3J_{δ,δ,2″} = 9.3 Hz, 3J_{δ,δ,3″} = 3.4 Hz, 1 H, 3″-H), 4.10 (d, 3J_{δ,δ,3′} = 3.4 Hz, 1 H, 4″-H), 4.65 (d, 3J_{δ,δ,1″} = 10.1 Hz, 1 H, 1″-H), 4.88 (dd, 3J_{δ,δ,1‴} = 10.1 Hz, 3J_{δ,δ,3‴} = 9.3 Hz, 1 H, 2″-H), 5.43 (d, 3J_{δ,δ,4‴} = 15.5 Hz, 1 H, 4′-H), 5.53 (d, 3J_{δ,δ,4‴} = 15.5 Hz, 1 H, 4′-H), 6.74–6.79 (m, 2 H, 3-H, 8-H), 6.91 (dd, 3J_{δ,δ,5} = 9.1 Hz, 4J_{δ,δ,8} = 2.6 Hz, 1 H, 6-H), 7.63 (d, 3J_{δ,δ,6} = 9.1 Hz, 1 H, 5-H), ¹³C-NMR (151 MHz, Aceton-d₆): δ [ppm] = 12.7 (C-10), 24.2 (CH₃), 24.6 (CH₃), 35.5 (SCH), 45.5 (C-9), 55.1 (C-2′), 62.3 (C-6″), 65.4 (C-4′), 70.4 (C-4″), 73.4 (C-3′), 77.3 (C-2″), 79.8 (C-5″), 83.5 (C-1″), 97.6 (C-8), 106.0 (C-3), 107.7 (C-4a), 111.9 (C-6), 114.3 (CN), 115.2 (CN), 126.8 (C-5), 147.9 (C-4), 153.0 (C-7), 155.1 (C-5″), 155.9 (C-8a), 172.6 (C-2); R₇ = 0.23 (EtOAc); IR (atr-film): v [cm⁻¹] = 3359, 2954, 2924, 2855, 2216, 1748, 1672, 1638, 1584, 1522, 1433, 1381, 1320, 1258, 1193, 1139, 1076, 1053, 984, 800, 725; HRMS (ESI): m/z calculated for C₂₇H₃₅N₂O₇S⁺ [M+NH₄]⁺: 560.2061; found: 560.2055; m.p.: 153.8 °C; [α]₀²⁰ = 74 (c = 0.1, CHCl₃); UV-Vis [Tris buffer (20 mM, pH 7.5)/MeCN 1:1]: λ_{max} (ε) = 252 nm (18618 dm³ mol⁻¹ cm⁻¹), 276 (14338), 488 (18938).

reversed-phase HPLC: tᵣ = 14.6 min; column: HyperClone 5 µ ODS (C18) 120 (Phenomenex); detection (UV): 488 nm; eluent: H₂O/MeOH 40:60; flow rate: 0.5 mL/min; column temperature: 25 °C; sample sol vent: Tris buffer (20 mM, pH 7.5)/MeCN 1:1.
S3.6 Synthetic scheme for preparation of photocaged IPTG 1b and 1d

Scheme S6: Synthetic scheme for preparation of photocaged IPTG 1b and 1d. Reagents and conditions: i) 9, DMAP, CH₂Cl₂, RT, 20 h; ii) TFA, H₂O, CH₂Cl₂, 0 °C, 10 min; iii) 10, DMAP, CH₂Cl₂, RT, 20 h; iv) TFA, H₂O, CH₂Cl₂, 0 °C → RT, 1 h.

Synthesis of Isopropyl 6-O-(tert-butyldimethylsilyl)-2-O-[[7-(diethylamino)-2-oxo-2H-chromen-4-yl]methyl]oxycarbonyl]-3,4-O-(1-methylethylidene)-1-thio-β-D-galactopyranoside (14)

Coumarin 14 was synthesized using modified procedures of Suzuki et al. Coumarin 5 (98 mg, 0.24 mmol) was dissolved in dry CH₂Cl₂ (2 mL) under nitrogen atmosphere. After the addition of 4-dimethylaminopyridine (DMAP) (30 mg, 0.24 mmol) and carbohydrate 9 (85 mg, 0.22 mmol) the reaction mixture was stirred for 20 h at room temperature in the dark. Then, it was diluted with CH₂Cl₂, washed with saturated NaHCO₃ and saturated NaCl solution. The organic phase was dried with anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash-column
chromatography on SiO₂ (petroleum ether/ethyl acetate 80:20) to yield a yellow solid (0.11 g, 0.17 mmol, 77%). ³H-NMR (600 MHz, CDCl₃): δ [ppm] = 0.06 (s, 3 H, 7°-H), 0.07 (s, 3 H, 7°-H), 0.89 (s, 9 H, 9°-H), 1.19 (t, ³J₁₀,₉ = 7.1 Hz, 6 H, 10-H), 1.29 (d, ³J₁₃,₁₂,SCH = 6.8 Hz, 3 H, CH₃), 1.30 (d, ³J₁₃,₁₂,SCH = 6.8 Hz, 3 H, CH₃), 1.35 (s, 3 H, 11°-H or 12°-H), 1.56 (s, 3 H, 11°-H or 12°-H), 3.17 (septet, ³J₁₂,₁₁,SCH = 6.8 Hz, 1 H, SCH), 3.40 (q, ³J₆,₁₀ = 7.1 Hz, 4 H, 9-H), 3.79–3.91 (m, 3 H, 5°-H, 6°-H), 4.22 (dd, ³J₉,₂ = 7.3 Hz, ³J₃,₄ = 5.3 Hz, 1 H, 3°-H), 4.29 (d, ³J₄,₃ = 5.2 Hz, ³J₄,₅ = 1.9 Hz, 1 H, 4°-H), 4.48 (d, ³J₉,₂ = 10.4 Hz, 1 H, 1°-H), 4.80 (dd, ³J₉,₁ = 10.4 Hz, ³J₉,₂ = 7.3 Hz, 1 H, 2°-H), 5.23 (d, ³J₁₄,₁₅ = 14.9 Hz, 1 H, 4°-H), 5.38 (d, ³J₁₅,₁₆ = 14.9 Hz, 1 H, 4°-H), 6.21 (s, 1 H, 3-H), 6.50 (d, ³J₆,₅ = 2.6 Hz, 1 H, 8-H), 6.56 (dd, ³J₆,₅ = 9.0 Hz, ³J₆,₅ = 2.6 Hz, 1 H, 6-H), 7.25 (d, ³J₅,₆ = 9.0 Hz, 1 H, 5-H); ¹³C-NMR (151 MHz, CDCl₃): δ [ppm] = –5.4 (C-7°), –5.3 (C-7°), 12.5 (C-10), 18.3 (C-8°), 24.0 (CH₃), 24.1 (CH₃), 25.9 (C-9°), 26.5, 28.0 (C-11°, C-12°), 35.7 (SCH), 44.9 (C-9), 62.1 (C-6°), 65.0 (C-4°), 73.5 (C-4°), 76.9 (C-3°), 77.1 (C-5°), 77.1 (C-2°), 82.5 (C-1°), 98.0 (C-8), 106.0 (C-4a), 106.7 (C-3), 108.8 (C-6), 110.6 (C-10°), 124.4 (C-5), 148.7 (C-4), 150.7 (C-7), 154.3 (C-5°), 156.4 (C-8a), 162.0 (C-2); Rf = 0.24 (PE/EtOAc 80:20); IR (atr-film): ν [cm⁻¹] = 2969, 2931, 2870, 1745, 1713, 1603, 1527, 1420, 1356, 1336, 1217, 1139, 1094, 1064, 1023, 841, 751, 667, 601, 510; HRMS (ESI): m/z calculated for C₃₀H₅₂O₈SSi⁺ [M+H]⁺: 666.3127; found: 666.3124; m.p.: 69 °C; [α]₉⁰° = 16 (c = 0.1, CHCl₃).

Synthesis of Isopropyl 2-O-[[7-(diethylamino)-2-oxo-2H-chromen-4-yl]methyloxycarbonyl]-1-thio-β-D-galactopyranoside (1b)

Photocaged IPTG 1b was synthesized using modified procedures of Suzuki et al. Coumarin 14 (159 mg, 238 µmol) was dissolved in CH₂Cl₂ (1 mL) and cooled to 0 °C. After the addition of trifluoroacetic acid (TFA) (1.70 mL, 22.2 mmol) and water (68.8 µL, 3.82 mmol), the reaction mixture was stirred for 10 min at 0 °C in the dark. Then the reaction mixture was concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO₂ (ethyl acetate) to yield a yellow solid (117 mg, 229 µmol, 96%). ¹H-NMR (600 MHz, Aceton-d₆): δ [ppm] = 1.21 (t, ³J₁₀,₉ = 7.1 Hz, 6 H, 10-H), 1.25 (d, ³J₁₃,₁₂,SCH = 6.7 Hz, 3 H, CH₃), 1.29 (d, ³J₁₃,₁₂,SCH = 6.7 Hz, 3 H, CH₃), 3.21 (septet, ³J₁₂,₁₁,SCH = 6.7 Hz, 1 H, SCH), 3.51 (q, ³J₉,₁₀ = 7.1 Hz, 4 H, 9-H), 3.67 (t, ³J₉,₂ = 5.6 Hz, 1 H, 5°-H), 3.77 (m, 2 H, 6°-H), 3.84 (dd, ³J₉,₂ = 9.3 Hz, ³J₉,₂ = 3.4 Hz, 1 H, 3°-H), 4.08 (d, ³J₁₃,₁₂,SCH = 3.4 Hz,
1 H, 4″-H), 4.65 (d, 3J1″,2″ = 10.1 Hz, 1 H, 1″-H), 4.87 (dd, 3J2″,1″ = 10.1 Hz, 3J2″,3″ = 9.3 Hz, 1 H, 2″-H), 5.33 (d, 3J4a,4b = 15.2 Hz, 1 H, 4″-H), 5.45 (d, 3J9b,4a = 15.2 Hz, 1 H, 4′-H), 6.09 (s, 1 H, 3-H), 6.52 (d, 4J9,6 = 2.6 Hz, 1 H, 8-H), 6.72 (dd, 3J6,5 = 9.0 Hz, 4J8,6 = 2.6 Hz, 1 H, 6-H), 7.48 (d, 3J5,6 = 9.0 Hz, 1 H, 5-H), 71C-NMR (151 MHz, Aceton-d6): δ [ppm] = 12.7 (C-10), 24.2 (CH3), 24.6 (CH3), 35.6 (SCH), 45.2 (C-9), 62.3 (C-6″), 65.4 (C-4′), 70.4 (C-4″), 73.5 (C-3″), 77.0 (C-2″), 79.9 (C-5″), 83.8 (C-1″), 98.1 (C-8), 106.5 (C-4a), 106.7 (C-3), 109.5 (C-6), 125.9 (C-5), 150.5 (C-4), 151.8 (C-7), 155.4 (C-5′), 157.3 (C-8a), 161.4 (C-2); Rf = 0.24 (EtOAc); IR (atr-film): v [cm⁻¹] = 3405, 2962, 2925, 2862, 1755, 1679, 1603, 1528, 1424, 1357, 1255, 1200, 1139, 1054, 984, 800, 725; HRMS (ESI): m/z calculated for C24H34NO9S+ [M+H]+: 512.1949; found: 512.1952; m.p.: 96.0 °C; [α]D20 = 28 (c = 0.1, CHCl3); UV-Vis [Tris buffer (20 mM, pH 7.5)/MeCN 1:1]: λmax (ε) = 246 nm (21496 dm³ mol⁻¹ cm⁻¹), 386 (24984).

reversed-phase HPLC: tR = 9.8 min; column: HyperClone 5 μ ODS (C18) 120 (Phenomenex); detection (UV): 392 nm; eluent: H2O/MeOH 40:60; flowrate: 0.5 mL/min; column temperature: 25 °C; sample solvent: Tris buffer (20 mM, pH 7.5)/MeCN 1:1.

Synthesis of Isopropyl 6-O-{[7-(diethylamo)-2-oxo-2H-chromen-4-yl]methoxy carbonyl}-2,3,4-tri-O-(4-methoxybenzyl)-1-thio-β-D-galactopyranoside (16)

Coumarin 16 was synthesized using modified procedures of Suzuki et al.[24] Coumarin 5 (60 mg, 0.15 mmol) was dissolved in dry CH2Cl2 (2.0 mL) under nitrogen atmosphere. After the addition of 4-dimethylaminopyridine (DMAP) (20 mg, 0.16 mmol) and carbohydrate 10 (96 mg, 0.16 mmol) the reaction mixture was stirred for 20 h at room temperature in the dark. Then, it was diluted with CH2Cl2, washed with saturated NaHCO3 and saturated NaCl solution. The organic phase was dried with anhydrous MgSO4 and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO2 (petroleum ether/ethyl acetate 60:40) to yield a yellow solid (84 mg, 0.10 mmol, 66%). 1H-NMR (600 MHz, CDCl3): δ [ppm] = 1.20 (t, 3J10,9 = 7.1 Hz, 6 H, 10-H), 1.31 (d, 3JCH3,SCH = 6.8 Hz, 6 H, CH3), 3.20 (septet, 3JSCH,CH3 = 6.8 Hz, 1 H, SCH), 3.41 (q, 3J9,10 = 7.1 Hz, 4 H, 1H, 5-H), 5.33 (d, 3J4a,4b = 15.2 Hz, 1 H, 4″-H), 5.45 (d, 3J9b,4a = 15.2 Hz, 1 H, 4′-H), 6.09 (s, 1 H, 3-H), 6.52 (d, 4J9,6 = 2.6 Hz, 1 H, 8-H), 6.72 (dd, 3J6,5 = 9.0 Hz, 4J8,6 = 2.6 Hz, 1 H, 6-H), 7.48 (d, 3J5,6 = 9.0 Hz, 1 H, 5-H), 71C-NMR (151 MHz, Aceton-d6): δ [ppm] = 12.7 (C-10), 24.2 (CH3), 24.6 (CH3), 35.6 (SCH), 45.2 (C-9), 62.3 (C-6″), 65.4 (C-4′), 70.4 (C-4″), 73.5 (C-3″), 77.0 (C-2″), 79.9 (C-5″), 83.8 (C-1″), 98.1 (C-8), 106.5 (C-4a), 106.7 (C-3), 109.5 (C-6), 125.9 (C-5), 150.5 (C-4), 151.8 (C-7), 155.4 (C-5′), 157.3 (C-8a), 161.4 (C-2); Rf = 0.24 (EtOAc); IR (atr-film): v [cm⁻¹] = 3405, 2962, 2925, 2862, 1755, 1679, 1603, 1528, 1424, 1357, 1255, 1200, 1139, 1054, 984, 800, 725; HRMS (ESI): m/z calculated for C24H34NO9S [M+H]+: 512.1949; found: 512.1952; m.p.: 96.0 °C; [α]D20 = 28 (c = 0.1, CHCl3); UV-Vis [Tris buffer (20 mM, pH 7.5)/MeCN 1:1]: λmax (ε) = 246 nm (21496 dm³ mol⁻¹ cm⁻¹), 386 (24984).

reversed-phase HPLC: tR = 9.8 min; column: HyperClone 5 μ ODS (C18) 120 (Phenomenex); detection (UV): 392 nm; eluent: H2O/MeOH 40:60; flowrate: 0.5 mL/min; column temperature: 25 °C; sample solvent: Tris buffer (20 mM, pH 7.5)/MeCN 1:1.

Synthesis of Isopropyl 6-O-{[7-(diethylamo)-2-oxo-2H-chromen-4-yl]methoxy carbonyl}-2,3,4-tri-O-(4-methoxybenzyl)-1-thio-β-D-galactopyranoside (16)
Synthesis of Isopropyl 6-O-[[7-(diethylamino)-2-oxo-2H-chromen-4-yl]methyloxy carbonyl]-1-thio-β-D-galactopyranoside (1d)

Photocaged IPTG 1d was synthesized using modified procedures of Suzuki et al.\textsuperscript{[24]} Coumarin 16 (40 mg, 46 µmol) was dissolved in CH2Cl2 (1.0 mL) and cooled to 0 °C. After the addition of trifluoroacetic acid (TFA) (0.33 mL, 4.3 mmol) and water (13 µL, 0.73 mmol), the reaction mixture was stirred in the dark for 10 min at 0 °C and 1 h at room temperature. Then the reaction mixture was concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO2 (petroleum ether/ethyl acetate 50:50 to 10:90) to yield a yellow solid (20 mg, 39 µmol, 78%). 1H-NMR (600 MHz, CDCl3): δ [ppm] = 1.19 (t, 3J10,9 = 7.1 Hz, 6 H, 10-H), 1.31 (d, 3J13,SC6H = 6.7 Hz, 3 H, CH3), 1.32 (d, 3J13,SC6H = 6.7 Hz, 3 H, CH3), 3.15–3.25 (m, 2 H, SCH, 2″-OH), 3.31 (s, 1 H, 4″-OH), 3.53–3.58 (m, 2 H, 3″-H, 5″-H), 3.74–3.84 (m, 11 H, 2″-H, 4″-H, OCH3), 4.03 (dd, 2J6‴-6‴ = 10.9 Hz, 3J6‴-5‴ = 9.9 Hz, 1 H, 6‴-H3), 4.29 (dd, 2J6‴-6‴ = 10.9 Hz, 3J6‴-5‴ = 6.6 Hz, 1 H, 6‴-H3), 4.47 (dd, 3J1,2 = 9.7 Hz, 1 H, 1-H), 4.58 (d, 2J11‴-11‴ = 11.5 Hz, 1 H, 11‴-H), 4.67–4.74 (m, 3 H, 1‴-H6‴, 6‴-H), 4.81 (d, 2J7‴,1‴ = 9.8 Hz, 1 H, 1‴-H6‴), 4.90 (d, 2J11‴,11‴ = 11.5 Hz, 1 H, 11‴-H3), 5.21 (m, 2 H, 4″-H), 6.12 (t, 4J3,4 = 1.3 Hz, 1 H, 3-H), 6.51 (d, 4J6‴,6‴ = 2.6 Hz, 1 H, 8-H), 6.57 (dd, 4J6‴,6‴ = 9.0 Hz, 4J6‴,8‴ = 2.6 Hz, 1 H, 6-H), 6.84 (d, 3J1‴,1‴ = 8.5 Hz, 2 H, 14‴-H), 6.86 (d, 3J4‴,1‴ = 8.5 Hz, 2 H, 4‴-H), 6.89 (d, 3J9‴,9‴ = 8.5 Hz, 2 H, 9‴-H), 7.24 (d, 3J13‴,1‴ = 8.5 Hz, 2 H, 13‴-H), 7.26 (d, 3J5‴,6‴ = 9.0 Hz, 1 H, 5‴-H), 7.31 (d, 3J6‴,9‴ = 8.5 Hz, 2 H, 8‴-H), 7.32 (d, 3J9‴,4‴ = 8.5 Hz, 2 H, 3‴-H); 13C-NMR (151 MHz, CDCl3): δ [ppm] = 12.6 (C-10), 24.0 (CH3), 35.6 (SCH), 44.9 (C-9), 55.4, 55.4, 55.4 (OCH3), 64.8 (C-4‴), 67.2 (C-6‴), 72.3 (C-4‴), 73.0 (C-6‴), 73.8 (C-11‴), 75.4 (C-1‴), 75.6 (C-5‴), 78.3 (C-2‴), 83.9 (C-3‴), 85.2 (C-1‴), 98.0 (C-8), 105.9 (C-4‴a), 106.7 (C-3), 108.8 (C-6), 113.8, 113.9, 114.0 (C-4‴, C-9‴, C-14‴), 124.4 (C-5), 129.4 (C-8‴), 130.1 (C-3‴), 130.2 (C-13‴), 130.4, 130.5, 130.7 (C-2‴, C-7‴, C-12‴), 148.7 (C-4), 150.9 (C-7), 154.3 (C-5‴), 156.4 (C-8a), 159.4, 159.4, 159.4 (C-5‴, C-10‴, C-15‴), 161.8 (C-2); Rf = 0.31 (PE/EtOAc 60:40); IR (atrr-film): ν [cm⁻¹] = 2966, 2930, 2906, 2864, 2835, 1753, 1715, 1604, 1513, 1422, 1357, 1244, 1173, 1078, 1032, 822, 570, 519; HRMS (ESI): m/z calculated for C46H61N3O12S+ [M+NH4]+: 889.3940; found: 889.3929; m.p.: 93.6 °C; [α]D²⁰ = −18.8 (c = 1.0, CHCl₃).
3.40 (q, \(^3J_{9,10} = 7.1\) Hz, 4 H, 9-H), 3.62–3.71 (m, 2 H, 2″-H, 3″-H), 3.74 (s, 1 H, 3″-OH), 3.80 (m, 1 H, 5″-H), 4.04 (brs, 1 H, 4″-H), 4.40 (dd, \(^3J_{6a^*,6b^*} = 11.4\) Hz, \(^3J_{5a^*,5b^*} = 5.0\) Hz, 1 H, 6″-H), 4.42 (m, 1 H, 1″-H), 4.48 (dd, \(^3J_{6b^*,6a^*} = 11.4\) Hz, \(^3J_{6b^*,5b^*} = 7.2\) Hz, 1 H, 6″-H), 5.23 (dd, \(^3J_{4a,4b} = 15.2\) Hz, \(^4J_{6a,6b} = 1.3\) Hz, 1 H, 4′-H), 5.27 (dd, \(^3J_{4b,4a} = 15.2\) Hz, \(^4J_{4b,5b} = 1.3\) Hz, 1 H, 4′-H), 6.12 (dd, \(^3J_{3,4a} = 1.3\) Hz, \(^4J_{3,4b} = 1.3\) Hz, 1 H, 4″-H), 6.49 (d, \(^4J_{8,6} = 2.6\) Hz, 1 H, 8-H), 6.56 (dd, \(^3J_{6,5} = 9.0\) Hz, \(^4J_{6,8} = 2.6\) Hz, 1 H, 6-H), 7.26 (d, \(^3J_{5,6} = 9.0\) Hz, 1 H, 5-H); \(^1^3^C-NMR (151 MHz, CDCl₃): \(δ \) [ppm] = 12.6 (C-10), 24.1 (CH₃), 24.3 (CH₃), 36.1 (SCH), 44.9 (C-9), 64.9 (C-4′), 67.4 (C-6′), 68.8 (C-4″), 70.4 (C-2″), 74.6 (C-3″), 75.9 (C-5″), 86.1 (C-1″), 97.9 (C-8), 105.9 (C-4a), 106.5 (C-3), 108.9 (C-6), 124.5 (C-5), 148.9 (C-4), 150.9 (C-7), 154.7 (C-5′), 156.4 (C-8a), 162.0 (C-2); \(R_f = 0.35\) (EtOAc); IR (atr-film): \(\tilde{ν} \) [cm⁻¹] = 3424, 2971, 2923, 2870, 1751, 1720, 1605, 1528, 1423, 1356, 1266, 1196, 1143, 1100, 1080, 1052, 1031, 967, 871, 828, 791, 743; HRMS (ESI): m/z calculated for \(C_{24}H_{34}NO_9S^+ [M+H]^+\): 512.1949; found: 512.1953; m.p.: 85–87 °C; \([α]_D^{20} = 22.0\) (c = 0.1, CHCl₃); UV-Vis [Tris buffer (20 mM, pH 7.5)/MeCN 1:1]: \(λ_{\text{max}} \) (ε) = 273 nm (28210 dm³ mol⁻¹ cm⁻¹), 386 (12004).

reversed-phase HPLC: \(t_R = 8.0\) min; column: HyperClone 5 µ ODS (C18) 120 (Phenomenex); detection (UV): 386 nm; eluent: H₂O/MeOH 40:60; flowrate: 0.5 mL/min; column temperature: 25 °C; sample solvent: Tris buffer (20 mM, pH 7.5)/MeCN 1:1.

S32
S3.7 Synthetic scheme for preparation of photocaged IPTG 1e and photocaged arabinose 2c

Scheme S7: Synthetic scheme for preparation of photocaged IPTG 1e and photocaged arabinose 2c. Reagents and conditions: i) 12, DIPEA, DMAP, CH₂Cl₂, RT, 24 h; ii) TFA, H₂O, 0 °C, 10 min; iii) 11, DIPEA, DMAP, CH₂Cl₂, RT, 24 h; iv) NH₃ in MeOH (7 M), MeOH, RT.
Synthesis of Isopropyl-6-O-( tert-butylidimethylsilyl)-2-O-[[2-(((7-diethylamino)-2-oxo-2H-chromen-4-yl)methoxycarbonyl)(methyl)amino)ethyl](methyl)carbamoyl]-3,4-O(1-methylethylidene)-1-thio-β-D-galactopyranoside (18)

Coumarin 18 was synthesized using modified procedures of Wang et al.[25] Coumarin 7 (227 mg, 628 µmol) was dissolved in dry CH₂Cl₂ (11 mL) under nitrogen atmosphere. After the addition of 4-dimethylaminopyridine (DMAP) (6 mg, 0.06 mmol), carbohydrate 12 (200 mg, 359 µmol) and N,N-diisopropylethylamine (DIPEA) (1.10 mL, 6.29 mmol) the reaction mixture was stirred for 24 h at room temperature in the dark. Then, it was diluted with CH₂Cl₂, washed with saturated NaHCO₃ and saturated NaCl solution. The organic phase was dried with anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO₂ (petroleum ether/ethyl acetate 50:50) to yield a slightly yellow foam (270 mg, 346 µmol, 97%). ¹H-NMR (600 MHz, CDCl₃): δ [ppm] = 0.06 (s, 6 H, 7″-H), 0.88 (s, 9 H, 9″-H), 1.20 (t, ³J₁₀,₉ = 7.1 Hz, 6 H, 10-H), 1.23–1.33 (m, 9 H, CH₃, 11-H or 12-H), 1.55 (s, 3 H, 11-H or 12-H), 2.86–3.07 (m, 6 H, CH₃a, CH₃b), 3.17 (septet, ³Jₛ(CH₃) = 6.8 Hz, 1 H, SCH), 3.28–3.62 (m, 4 H, 6′-H, 7″-H), 3.41 (q, ³J₉,₁₀ = 7.1 Hz, 4 H, 9-H), 3.75–3.90 (m, 3 H, 5″-H, 6″-H), 4.13–4.22 (m, 1 H, 3″-H), 4.22–4.28 (m, 1 H, 4″-H), 4.44–4.55 (m, 1 H, 1″-H), 4.79–4.91 (m, 1 H, 2″-H), 5.20–5.30 (m, 2 H, 4′-H), 6.03–6.13 (m, 1 H, 3-H), 6.50 (d, ³J₈,₆ = 2.6 Hz, 1 H, 8-H), 6.57 (d, ³J₆,₅ = 9.0 Hz, 1 H, 6-H), 7.27–7.36 (m, 1 H, 5-H); ¹³C-NMR (151 MHz, CDCl₃): δ [ppm] = −5.4 (C-7″), −5.3 (C-7″), 12.6 (C-10), 18.4 (C-8″), 23.9 (CH₃), 24.0 (CH₃), 25.9 (C-9″), 26.5, 28.0 (C-11″, C-12″), 34.9 (SCH), 35.0 (CH₃a/b), 35.3 (CH₃a/b), 35.6 (CH₃a/b), 35.9 (CH₃a/b), 36.0 (CH₃a/b), 36.1 (CH₃a/b), 44.9 (C-9), 46.7, 46.8, 47.2, 47.3, 47.5, 48.0, 48.1 (C-6′, C-7″), 62.2 (C-4′), 62.5 (C-6″), 62.7 (C-6″), 73.6, 73.6, 73.7 (C-2″, C-4″), 77.1 (C-5″), 77.5 (C-3″), 77.6 (C-3″), 77.6 (C-3″), 82.6 (C-1″), 82.7 (C-1″), 82.8 (C-1″), 82.9 (C-1″), 97.9 (C-8), 105.9, 106.1, 106.4 (C-3, C-4a), 108.8 (C-6), 110.4 (C-10″), 124.4 (C-5), 124.5 (C-5), 124.6 (C-5), 124.7 (C-5), 150.5, 150.6, 150.8 (C-4, C-7), 155.1, 155.3, 155.5, 155.6 (C-5″, C-8″), 156.3 (C-8a), 156.4 (C-8a), 162.1 (C-2); Rf = 0.31 (PE/ EtOAc 50:50); IR (atr-film): ʋ [cm⁻¹] = 2960, 2930, 2859, 1710, 1606, 1529, 1466, 1422, 1358, 1219, 1125, 1081, 874, 839, 779; HRMS (ESI): m/z calculated for C₁₉H₂₉N₂O₁₀SSI⁺ [M+H]⁺: 780.3920; found: 780.3935; m.p.: 68.0 °C; [α]D²₀ = 0.4 (c = 1.0, CHCl₃).
Synthesis of Isopropyl 2-O-[[2-(((7-(diethylamino)-2-oxo-2H-chromen-4-yl) methoxycarbonyl)(methyl)amino)ethyl][methyl]carbamoyl]-1-thio-β-D-galactopyranoside (1e)

Photocaged IPTG 1e was synthesized using modified procedures of Suzuki et al.\textsuperscript{[24]} Coumarin 18 (0.11 mg, 0.14 mmol) was dissolved in trifluoroacetic acid (TFA) (1.0 mL) and cooled to 0 °C. After the addition of water (41 µL, 2.3 mmol) the reaction mixture was stirred for 10 min at 0 °C in the dark. Then the reaction mixture was concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO\textsubscript{2} (ethyl acetate/methanol 95:5) to yield a yellow solid (89 mg, 0.14 mmol, quant.). The product was a mixture of cis and trans isomers on carbamate bonds. \textsuperscript{1}H-NMR (600 MHz, DMSO-\textit{d}_6, 60 °C): \(\delta\) [ppm] = 1.15 (t, \(\text{J}_{10,9} = 7.0\) Hz, 6 H, 10-H), 1.19 (d, \(\text{J}_{\text{CH,CH}_3} = 6.8\) Hz, 3 H, \(\text{CH}_3\)), 1.22 (d, \(\text{J}_{\text{CH,CH}_3} = 6.8\) Hz, 3 H, \(\text{CH}_3\)), 2.85 (s, 3 H, \(\text{CH}_3\)a or \(\text{CH}_3\)b), 2.95 (brs, 3 H, \(\text{CH}_3\)a or \(\text{CH}_3\)b), 3.07-3.12 (m, 1 H, SCH), 3.34-3.47 (m, 9 H, 9-H, 6′-H, 7′-H, 5″-H), 3.50 (dd, \(\text{J}_{6″a,6″b} = 10.9\) Hz, \(\text{J}_{6″a,5″} = 6.0\) Hz, 1 H, 6″-H), 3.54 (dd, \(\text{J}_{6″b,6″a} = 10.9\) Hz, \(\text{J}_{6″b,5″} = 6.0\) Hz, 1 H, 6″-H), 3.56 (brs, 1 H, 3″-H), 3.78 (d, \(\text{J}_{4″-a} = 3.3\) Hz, 1 H, 4″-H), 4.48 (brs, 1 H, 1″-H), 4.72 (dd, \(\text{J}_{2″-a,1″} = 10.1\) Hz, \(\text{J}_{2″-a,3″} = 9.3\) Hz, 1 H, 2″-H), 5.25 (s, 2 H, 4′-H), 5.95 (s, 1 H, 3-H), 6.53 (d, \(\text{J}_{8,6} = 2.6\) Hz, 1 H, 8-H), 6.71 (dd, \(\text{J}_{6,5} = 9.0\) Hz, \(\text{J}_{6,8} = 2.6\) Hz, 1 H, 6-H), 7.48 (d, \(\text{J}_{5,6} = 9.0\) Hz, 1 H, 5-H); \textsuperscript{13}C-NMR (151 MHz, DMSO-\textit{d}_6, 60 °C): \(\delta\) [ppm] = 12.0 (C-10), 23.4 (CH\textsubscript{3}), 23.8 (CH\textsubscript{3}), 33.7 (SCH), 34.7, 34.9 (CH\textsubscript{3a/b}), 43.7 (C-9), 45.9, 46.1 (C-6′, C-7′), 60.3 (C-6″), 61.9 (C-4′), 68.4 (C-4″), 72.1 (C-2″), 72.6 (C-3″), 78.9 (C-5″), 82.7 (C-1″), 96.8 (C-8), 104.6 (C-3), 105.3 (C-4a), 108.7 (C-6), 125.0 (C-5), 150.4 (C-7), 151.0 (C-4), 154.5 (C-5′), 155.1 (C-8′), 160.3 (C-2); IR (atrazfilm): \(\nu\) [cm\textsuperscript{-1}] = 3406, 2966, 2928, 2870, 1697, 1603, 1526, 1484, 1423, 1357, 1274, 1200, 1133, 1078, 862, 825, 803, 759; HRMS (ESI): m/z calculated for C\textsubscript{35}H\textsubscript{44}N\textsubscript{3}O\textsubscript{10}S\textsubscript{5} [M+H\textsuperscript{+}]: 626.2742; found: 626.2753; m.p.: 95.5 °C; [\(\alpha\)\textsubscript{D}]	extsuperscript{20} = −22.6 (c = 1.0, CHCl\textsubscript{3}); UV-Vis [Tris buffer (20 mM, pH 7.5)/MeCN 1:1]: \(\lambda_{\text{max}}\) (\(\epsilon\)) = 272 nm (17662 dm\textsuperscript{3} mol\textsuperscript{-1} cm\textsuperscript{-1}), 305 (4142), 386 (17184).

reversed-phase HPLC: \(t_R = 8.2\) min; column: HyperClone 5 µ ODS (C18) 120 (Phenomenex); detection (UV): 386 nm; eluent: H\textsubscript{2}O/MeOH 40:60; flowrate: 0.5 mL/min; column temperature: 25 °C; sample solvent: Tris buffer (20 mM, pH 7.5)/MeCN 1:1.
Synthesis of 2,3,4-Tri-O-acetyl-1-O-[[2-[[7-(diethylamino)-2-oxo-2H-chromen-4-yl]methoxycarbonyl]{{methyl}amino}ethyl]{{methyl}carbamoyl}-α-L-arabinopyranoside (17)

Coumarin 17 was synthesized using modified procedures of Wang et al.[25] Coumarin 7 (57 mg, 0.16 mmol) was dissolved in dry CH₂Cl₂ (2.9 mL) under nitrogen atmosphere. After the addition of 4-dimethylaminopyridine (DMAP) (2.0 mg, 16 µmol), carbohydrate 11 (40 mg, 91 µmol) and N,N-diisopropylethylamine (DIPEA) (0.28 mL, 1.6 mmol) the reaction mixture was stirred for 24 h at room temperature in the dark. Then, it was diluted with CH₂Cl₂, washed with saturated NaHCO₃ and saturated NaCl solution. The organic phase was dried with anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO₂ (petroleum ether/ethyl acetate 30:70) to yield a slightly yellow foam (51 mg, 77 µmol, 85%). The product was a mixture of cis and trans isomers on carbamate bonds. ¹H-NMR (600 MHz, CDCl₃): δ [ppm] = 1.19 (t, 3J₁₀,₉ = 7.1 Hz, 6 H, 10-H), 1.99–2.07 (m, 6 H, CH₃), 2.09–2.16 (m, 3 H, CH₃), 2.88–2.98 (m, 3 H, CH₂b), 2.98–3.07 (m, 3 H, CH₃a), 3.18–3.68 (m, 4 H, 6’-H, 7’-H), 3.40 (q, 3J₉,₁₀ = 7.1 Hz, 4 H, 9-H), 3.77 (m, 1 H, 5”-Hₐ), 3.98 (dd, 3J₉₈,₅ₐ = 12.9 Hz, 3J₉₈,₅ₕ = 3.7 Hz, 1 H, 5”-Hₕ), 5.06–5.33 (m, 5 H, 2”-H, 3”-H, 4”-H, 4’-H), 5.52–5.61 (m, 1 H, 1”-H), 6.01–6.13 (m, 1 H, 3-H), 6.50 (s, 1 H, 8-H), 6.57 (d, 3J₆₅,₆ₕ = 9.0 Hz, 1 H, 6-H), 7.26–7.34 (m, 1 H, 5-H); ¹³C-NMR (151 MHz, CDCl₃): δ [ppm] = 12.5 (C-10), 20.7 (CH₃), 20.7 (CH₃), 20.8 (CH₃), 20.9 (CH₃), 21.0 (CH₃), 34.7, 34.7, 34.8, 35.2, 35.5, 35.5, 35.6, 35.8 (CH₃a, CH₃b), 44.9 (C-9), 46.3, 46.4, 46.9, 47.1, 47.3, 47.6 (C-6’, C-7’), 62.4 (C-4’), 62.5 (C-4’), 62.7 (C-4’), 63.5 (C-5’), 63.6 (C-5’), 64.4 (C-5’), 64.5 (C-5’), 67.2, 67.6, 67.7, 68.2, 68.3 (C-2”, C-4”), 69.7 (C-3’), 69.8 (C-3”), 70.3 (C-3”), 70.4 (C-3”), 93.5 (C-1”), 93.6 (C-1”), 93.9 (C-1”), 94.1 (C-1”), 98.0 (C-8), 105.8, 105.9, 106.2, 106.4 (C-3, C-4a), 108.8 (C-6), 124.4 (C-5), 124.5 (C-5), 124.6 (C-5), 150.3, 150.4, 150.5, 150.7 (C-4, C-7), 153.9 (C-8’), 154.1 (C-8’), 154.4 (C-8’), 155.2 (C-5’), 155.3 (C-5’), 155.6 (C-5’), 155.7 (C-5’), 156.3 (C-8a), 162.0 (C-2), 162.1 (C-2), 169.5, 169.7, 169.8, 169.9, 169.9, 169.9, 170.0, 170.2, 170.3, 170.3 (C-2”, C-3”, C-4”); R₂ = 0.25 (PE/EtOAc 30:70); IR (atr-film): ν [cm⁻¹] = 2972, 2930, 1746, 1713, 1605, 1528, 1422, 1371, 1221, 1137, 1088, 1055, 760; m.p.: 82.7 °C; [α]D²⁰ = 10.6 (c = 1.0, CHCl₃)
Synthesis of $1-O$-[[2-((7-(diethylamino)-2-oxo-2H-chromen-4-yl) methoxycarbonyl)(methyl)amino)ethyl][methyl]carbamoyl]-α-L-arabinopyranoside (2c)

Photocaged arabinose 2c was synthesized using modified procedures of Binder et al.\cite{16} Coumarin 17 (40 mg, 60 µmol) was dissolved in MeOH (0.20 mL) and stirred at room temperature in the dark. Ammonia in MeOH (7 M, 54 µL, 0.38 mmol) was added and the reaction mixture was stirred until complete conversion. The solvent was evaporated under reduced pressure to yield a yellow solid (28 mg, 52 µmol, 86%). The product was a mixture of cis and trans isomers on carbamate bonds. $^1$H-NMR (600 MHz, CDCl$_3$): δ [ppm] = 1.20 (t, $^3$J$_{10,9} = 7.1$ Hz, 6 H, 10″-H), 2.92–2.98 (m, 3 H, CH$_3$b), 2.99–3.05 (m, 1 H, 5″-H), 3.70–3.78 (m, 1 H, 3″-H), 3.78–3.92 (m, 1 H, 2″-H), 3.92–3.99 (m, 1 H, 4″-H), 3.99–4.09 (m, 1 H, 5″-Hb), 5.14–5.32 (m, 2 H, 4′-H), 5.32–5.46 (m, 1 H, 1″-H), 6.03–6.17 (m, 1 H, 3-H), 6.52 (s, 1 H, 8-H), 6.57–6.68 (m, 1 H, 6-H), 7.27–7.36 (m, 1 H, 5-H); $^{13}$C-NMR (151 MHz, CDCl$_3$): δ [ppm] = 12.5 (C-10), 34.5, 34.6, 34.9, 35.4, 35.8, 36.2 (CH$_3$a, CH$_3$b), 45.0 (C-9), 46.5, 46.7, 47.1, 47.4, 47.5, 47.5 (C-6′, C-7′), 62.4 (C-4′), 62.5 (C-4′), 62.9 (C-4′), 63.1 (C-4′), 66.6 (C-5″), 66.8 (C-5″), 68.2 (C-4″), 70.6 (C-2″), 70.8 (C-2″), 71.0 (C-2″), 73.3 (C-3″), 73.4 (C-3″), 73.6 (C-3″), 96.4 (C-1″), 96.5 (C-1″), 96.6 (C-1″), 96.6 (C-1″), 98.0 (C-8), 105.9, 106.0 (C-3, C-4a), 109.1 (C-6), 124.5 (C-5), 124.6 (C-5), 150.4, 150.5, 151.4 (C-4, C-7), 154.6 (C-8′), 154.7 (C-8′), 156.0, 156.0, 156.2, 156.3, 156.6 (C-5′, C-8a), 162.6 (C-2), 162.7 (C-2); R$_f$ = 0.08 (EtOAc/MeOH 95:5); IR (atr-film): $\tilde{\nu}$ [cm$^{-1}$] = 3423, 2966, 2927, 1703, 1603, 1528, 1490, 1423, 1357, 1275, 1216, 1131, 1080, 827, 761; HRMS (ESI): m/z calculated for C$_{25}$H$_{36}$N$_3$O$_{10}$+ [M+H]$^+$: 538.2395; found: 538.2397; m.p.: 67–73 °C; [α]$_D^{20}$ = 5.0 (c = 1.0, CHCl$_3$); UV-Vis [Tris buffer (20 mM, pH 7.5)/MeCN 1:1]: $\lambda_{max}$ ($e$) = 273 nm (28656 dm$^3$ mol$^{-1}$ cm$^{-1}$), 385 (14070).

reversed-phase HPLC: $t_R$ = 18.3 min; column: HyperClone 5 µ ODS (C18) 120 (Phenomenex); detection (UV): 385 nm; eluent: H$_2$O/MeOH 55:45; flowrate: 0.5 mL/min; column temperature: 25 °C; sample solvent: Tris buffer (20 mM, pH 7.5)/MeCN 1:1.
S3.8 Synthetic scheme for preparation of photocaged salicylic acid 22a and the corresponding sodium form 22b

Scheme S8: Synthetic scheme for preparation of photocaged salicylic acid 22a and the corresponding sodium form 22b.
Reagents and conditions: i) NaBH₄, CH₂Cl₂, EtOH, AcOH, 0 °C, 3 h; ii) CBr₄, PPh₃, CH₂Cl₂, 0 °C → RT, 6 h; iii) ethyl salicylate, K₂CO₃, acetone, RT, 2 d; iv) KOH (0.2 M), MeOH, 60 °C, 4 h; v) NaOH (0.2 M), MeOH, RT, 5 min.

Synthesis of 4,5-Bis(ethoxycarbonylmethoxy)-2-nitrobenzalcohol (24)

Alcohol 24 was synthesized using a procedure of Ni et al.⁴¹ 4,5-Bis(ethoxycarbonylmethoxy)-2-nitrobenzaldehyde (23) (881 mg, 2.48 mmol) was dissolved in a mixture of CH₂Cl₂, EtOH and acetic acid (35:5:1, 10.0 mL). After the solution was cooled to 0 °C NaBH₄ (188 mg, 4.96 mmol, 2.00 Äq.) was added and the reaction mixture was stirred for 3 h at 0 °C. The reaction was quenched by addition of 1 M HCl (2 mL), diluted with ethyl acetate and washed with saturated NaCl solution. The organic phase was dried with anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO₂ (toluene/ethyl acetate 80:20) to yield a yellow solid (649 mg, 1.82 mmol, 73%). The spectroscopic data are consistent with previously reported literature values.⁴¹ ¹H-NMR (600 MHz, CDCl₃): δ [ppm] = 1.30 (t, ³J₁₁,₁₀ or ₁₁′,₁₀′ = 7.2 Hz, 3 H, 11-H or 11′-H), 1.31 (t, ³J₁₁,₁₀ or ₁₁′,₁₀′ = 7.2 Hz, 3 H, 11-H or 11′-H), 2.13 (br, 1 H, OH), 4.28 (q, ³J₁₀,₁₁ or ₁₀′,₁₁′ = 7.2 Hz, 2 H, 10-H or 10′-H), 4.28 (q, ³J₁₀,₁₁ or ₁₀′,₁₁′ = 7.2 Hz, 2 H, 10-H or 10′-H), 4.77 (s, 2 H, 8-H or 8′-H), 4.83 (s, 2 H, 8-H or 8′-H), 4.94 (s, 2 H, 7-H), 7.17 (s, 1 H, 3-H or 6-H), 7.70 (s, 1 H, 3-H or 6-H); ¹³C-NMR (151 MHz, CDCl₃): δ [ppm] = 14.3, 14.3 (C-11, C-11′), 61.8, 61.9 (C-10, C-10′), 62.5 (C-7), 66.2 (C-8′), 66.6 (C-8), 112.0, 113.5 (C-3, C-6), 133.6, 140.4 (C-1, C-2), 146.5 (C-5), 152.7 (C-4), 167.8 (C-9′), 168.1 (C-9); Rₚ = 0.32 (Toluol/EtOAc 80:20); IR (atr-film): ν [cm⁻¹] = 2992, 1742, 1580, 1507, 1282,
1193, 1072, 1019, 792; MS (ESI, positive ion): m/z (%) = 380.2 (100) [M+Na]^+, 737.3 (5) [2M+Na]^+; m.p.: 76 °C.

**Synthesis of 4,5-Bis(ethoxycarbonylmethoxy)-2-nitrobenzyl bromide (25)**

Bromide 25 was synthesized using a procedure of Tietze et al.[27] A Schlenk tube was charged with Alcohol 24 (1.00 g, 2.80 mmol) and tetrabromomethane (CBr₄) (1.16 g, 3.50 mmol) dissolved in dry CH₂Cl₂ (14.0 mL) under nitrogen atmosphere in the dark. A second Schlenk tube was charged with triphenylphosphane (PPh₃) (918 mg, 3.50 mmol) dissolved in dry CH₂Cl₂ under nitrogen atmosphere. Both solutions were cooled to 0 °C and the cooled PPh₃ solution was added dropwise to the dissolved alcohol 24. The reaction mixture was stirred for 10 min at 0 °C and 6 h at room temperature. SiO₂ was added to the reaction mixture and the solvent was removed under reduced pressure. The residue was purified by flash-column chromatography on SiO₂ (petroleum ether/ethyl acetate 65:35) to yield a white solid (1.13 g, 2.69 mmol, 96%). ¹H-NMR (600 MHz, CDCl₃): δ [ppm] = 1.31 (t, ³J₁₁,₁₀ = 7.1 Hz, 3 H, 11-H), 1.31 (t, ³J₁₁’,₁₀’ = 7.1 Hz, 3 H, 11’-H), 4.29 (q, ³J₁₀,₁₁;₁₀’,₁₁’ = 7.1 Hz, 4 H, 10-H, 10’-H), 4.78 (2, 2 H, 8’-H), 4.81 (s, 2 H, 7-H), 4.83 (s, 2 H, 8-H), 6.94 (s, 1 H, 6-H), 7.65 (s, 1 H, 3-H); ¹³C-NMR (151 MHz, CDCl₃): δ [ppm] = 14.3 (C-11), 14.3 (C-11’), 29.7 (C-7), 61.9 (C-10), 62.0 (C-10’), 66.5 (C-8), 66.5 (C-8’), 112.1 (C-3), 117.2 (C-6), 128.5 (C-2), 141.2 (C-1), 147.6 (C-5), 151.9 (C-4), 167.7 (C-9), 167.8 (C-9’); Rf = 0.62 (PE/EtOAc 60:40); IR (atir-film): ν [cm⁻¹] = 2992, 1739, 1616, 1581, 1522, 1479, 1449, 1409, 1380, 1356, 1339, 1289, 1264, 1202, 1184, 1120, 1080, 1043, 1025, 930, 881, 798, 758, 732, 672; HRMS (ESI): m/z calculated for C₁₅H₁₅O₈NBrNa⁺ [M+Na]^+: 442.0108; found: 442.0108; m.p.: 118°C.
Synthesis of Ethyl 2-O-[4,5-bis(ethoxycarbonylmethoxy)-2-nitrobenzyl]salicylate (26)

Ethyl salicylate (0.11 mL, 0.71 mmol) was dissolved in dry acetone (1.0 mL) and dry K₂CO₃ (56 mg, 0.40 mmol) was added. After stirring for 10 min bromide 25 (0.10 g, 0.24 mmol) was added and the reaction mixture was stirred for 2 d at room temperature in the dark. After completion, the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate and subsequently washed with water and saturated NaHCO₃ solution. The organic phase was dried with anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash-column chromatography on SiO₂ (petroleum ether/ethyl acetate 80:20) to yield a white solid (0.11 g, 0.22 mmol, 92%).

**1H-NMR (600 MHz, CDCl₃):** δ [ppm] = 1.25 (t, 3J₁₁,₁₀ = 7.1 Hz, 3 H, 11-H), 1.31 (t, 3J₁₁′,₁₀′ = 7.1 Hz, 3 H, 11′-H), 1.40 (t, 3J₉₈,₉₉ = 7.1 Hz, 3 H, 9″-H), 4.23 (q, 3J₁₀,₁₁ = 7.1 Hz, 2 H, 10-H), 4.29 (q, 3J₁₀′,₁₁′ = 7.1 Hz, 2 H, 10′-H), 4.38 (q, 3J₉₈,₉₉ = 7.1 Hz, 2 H, 8″-H), 4.81 (s, 2 H, 8′-H), 5.05 (s, 2 H, 8-H), 5.52 (s, 2 H, 7-H), 5.73 (dd, 3J₅₄,₅₅ = 8.4 Hz, 3 H, 4″-H), 7.03 (dd, 3J₅₄,₅₅ = 7.5 Hz, 1 H, 5″-H), 7.14 (d, 3J₅₄,₅₅ = 8.4 Hz, 1 H, 3″-H), 7.53 (dd, 3J₅₄,₅₅ = 8.4 Hz, 1 H, 6″-H), 7.82 (s, 1 H, 3-H), 7.93 (d, 3J₆₇,₆₈ = 7.5 Hz, 1 H, 6″-H), 8.23 (s, 1 H, 6-H);

**13C-NMR (151 MHz, CDCl₃):** δ [ppm] = 14.2 (C-11), 14.3 (C-11′), 14.5 (C-9″), 60.7 (C-8″), 61.6 (C-10), 61.7 (C-10′), 65.8 (C-8), 66.8 (C-8′), 67.3 (C-7), 111.9 (C-3), 112.8 (C-6), 113.2 (C-3″), 119.8 (C-1″), 120.8 (C-5″), 130.8 (C-1), 132.1 (C-6″), 134.2 (C-4″), 138.9 (C-2), 146.1 (C-4), 153.4 (C-5), 158.0 (C-2″), 165.2 (C-7″), 168.0 (C-9), 168.3 (C-9″); Rᵣ = 0.23 (PE/EtOAc 70:30); IR (atrr-film): ν [cm⁻¹] = 3104, 2992, 1771, 1743, 1713, 1582, 1524, 1488, 1449, 1425, 1377, 1329, 1291, 1242, 1195, 1112, 1080, 1020, 895, 859, 826, 803, 753, 700, 683, 661; HRMS (ESI): m/z calculated for C₂₂H₂₇O₁₁NNa⁺ [M+Na⁺]: 528.1476; found: 528.1476; m.p.: 133°C
Synthesis of 2-O-[4,5-Bis(carboxymethoxy)-2-nitrobenzyl]salicylic acid (BC-cSal) (22a)

To a solution of salicylate 26 (200 mg, 396 µmol) in MeOH (11.9 mL) a 0.2 M solution of KOH (11.9 mL, 2.37 mmol) was added. The reaction mixture was heated to 60 °C and stirred until complete conversion (4 h). After the reaction was completed as indicated by TLC, 1 M HCl was added and the precipitate was filtered off and washed. The precipitate was dried to yield a white solid (153 mg, 363 µmol, 92%).

$^1$H-NMR (600 MHz, DMSO-$d_6$): δ [ppm] = 4.89 (s, 2 H, 8′-H), 4.91 (s, 2 H, 8-H), 5.49 (s, 2 H, 7-H), 7.06 (dd, $^3J_{5′,6′}$ = 7.0 Hz, $^3J_{5′,4′}$ = 6.9 Hz 1 H, 5′-H), 7.22 (d, $^3J_{3′,4′}$ = 7.9 Hz, 1 H, 3′-H), 7.56 (dd, $^3J_{4′,3′}$ = 7.9 Hz, $^3J_{4′,5′}$ = 6.9 Hz, 1 H, 4″-H), 7.72 (s, 1 H, 3-H), 7.79 (d, $^3J_{6′,5′}$ = 7.0 Hz, 1 H, 6″-H), 7.80 (s, 1 H, 6-H); $^{13}$C-NMR (151 MHz, DMSO-$d_6$): δ [ppm] = 65.0 (C-8), 65.5 (C-8′), 66.7 (C-7), 110.4 (C-3), 112.2 (C-6), 113.7 (C-3″), 120.7 (C-1″), 120.7 (C-5″), 128.7 (C-1), 131.6 (C-6″), 133.7 (C-4″), 139.0 (C-2), 145.9 (C-4), 152.2 (C-5), 157.1 (C-2″), 166.9 (C-7″), 169.1 (C-9), 169.8 (C-9″); IR (atr-film): $\tilde{\nu}$ [cm$^{-1}$] = 2923, 1708, 1801, 1585, 1525, 1490, 1428, 1380, 1311, 1285, 1245, 1214, 1079, 1027, 900, 849, 821, 750, 698, 671; HRMS (ESI): m/z calculated for C$_{18}$H$_{15}$O$_{11}$NK$^+$ [M+K]$^+$: 460.0276; found: 460.0276; m.p.: 264 °C (decay); UV-Vis [sodium phosphate buffer (100 mM, pH 7.4)]: $\lambda_{max}$ ($\varepsilon$) = 290 nm (5027 dm$^3$ mol$^{-1}$ cm$^{-1}$), 346 (5852).

reversed-phase HPLC: $t_R$ = 9.6 min; column: HyperClone 5 µ ODS (C18) 120 (Phenomenex); detection (UV): 346 nm; eluent: sodium phosphate buffer (100 mM, pH 7.4)/MeOH 15:85; flowrate: 0.5 mL/min; column temperature: 25 °C; sample solvent: sodium phosphate buffer (100 mM, pH 7.4).
Synthesis of Trisodium 2-O-[4,5-bis(carboxymethoxy)-2-nitrobenzyl]salicylate (22b)

To a solution of salicylic acid 22a (60 mg, 0.14 mmol) in MeOH (2.5 mL) a 0.2 M solution of NaOH (2.1 mL, 0.43 mmol) was added. The reaction mixture was stirred for 5 min before it was lyophilised overnight to yield a solid (69 mg, 0.14 mmol, quant.). $^1$H-NMR (600 MHz, D$_2$O): $\delta$ [ppm] = 4.56 (s, 2 H, 8$′$-H), 4.62 (s, 2 H, 8-H), 5.43 (s, 2 H, 7-H), 7.03 (d, $^3$J$_{3″,4″}$ = 8.2 Hz, 1 H, 3″-H), 7.06 (ddd, $^3$J$_{5″,6″}$ = 7.5 Hz, $^3$J$_{5″,5′}$ = 7.4 Hz, $^4$J$_{5″,3″}$ = 1.0 Hz, 1 H, 5″-H), 7.36 (ddd, $^3$J$_{4″,3″}$ = 8.2 Hz, $^3$J$_{4″,5″}$ = 7.4 Hz, $^4$J$_{4″,6″}$ = 1.8 Hz, 1 H, 4″-H), 7.41 (s, 1 H, 3-H), 7.46 (dd, $^3$J$_{6″,5″}$ = 7.5 Hz, $^3$J$_{6″,4″}$ = 1.8 Hz, 1 H, 6″-H), 7.74 (s, 1 H, 6-H), $^{13}$C-NMR (151 MHz, D$_2$O): $\delta$ [ppm] = 67.3, 67.3 (C-8, C-8$′$), 67.6 (C-7), 109.4 (C-3), 111.4 (C-6), 113.8 (C-3″), 121.4 (C-5″), 128.3 (C-6″), 129.5 (C-1), 129.7 (C-4″), 130.2 (C-1″), 139.0 (C-2), 145.7 (C-4), 152.1 (C-5), 154.1 (C-2″), 174.9 (C-9), 175.4 (C-9$′$), 176.0 (C-7″); IR (atr-film): $\tilde{\nu}$ [cm$^{-1}$] = 3216, 1603, 1553, 1521, 1425, 1382, 1329, 1273, 1214, 1100, 1070, 1020, 855, 818, 753, 695, 663; m.p.: 245 °C (decay).
S4 Supporting data

S4.1 UV-Vis spectra of compounds

Figure S1: UV-Vis spectrum of compound 2b (0.10 mM in MeOH, 25 °C).

Figure S2: UV-Vis spectrum of compound 1c [0.05 mM in Tris buffer (20 mM, pH 7.5)/MeCN 50:50, 25 °C].
Figure S3: UV-Vis spectrum of compound 1b [25.0 µM in Tris buffer (20 mM, pH 7.5)/MeCN 50:50, 25 °C].

Figure S4: UV-Vis spectrum of compound 1d [0.05 mM in Tris buffer (20 mM, pH 7.5)/MeCN 50:50, 25 °C].
Figure S5: UV-Vis spectrum of compound 1e [0.05 mM in Tris buffer (20 mM, pH 7.5)/MeCN 50:50, 25 °C].

Figure S6: UV-Vis spectrum of compound 2c [0.05 mM in Tris buffer (20 mM, pH 7.5)/MeCN 50:50, 25 °C].
Figure S7: UV-Vis spectrum of compound 22a [125 μM in sodium phosphate buffer (100 mM, pH 7.4), 25 °C].
### S4.2 Photon flux densities of light sources

Table S3: Determined photon flux densities ($q_{n,p}$)

| wavelength | $q_{n,p}$ (mol s$^{-1}$) |
|------------|--------------------------|
| 365 nm     | $6.49 \times 10^{-8}$    |
| 405 nm     | $1.91 \times 10^{-7}$    |
| 430 nm     | $1.22 \times 10^{-7}$    |
S4.3 Irradiation experiments

Figure S8: *In vitro* decay of 2b (1 mM in H$_2$O/DMSO 99:1) via reversed-phase HPLC after irradiation with 405 nm (44.6 mW cm$^{-2}$, room temperature).

Figure S9: *In vitro* decay of 1c [0.5 mM in Tris buffer (20 mM, pH 7.5)/MeCN 1:1] via reversed-phase HPLC after irradiation with 375 nm (6.4 mW cm$^{-2}$, room temperature) and 430 nm (45.6 mW cm$^{-2}$, room temperature).
Figure S10: *In vitro* decay of 1b [0.5 mM in Tris buffer (20 mM, pH 7.5)/MeCN 1:1] via reversed-phase HPLC after irradiation with 375 nm (6.4 mW cm$^{-2}$, room temperature), 405 nm (44.6 mW cm$^{-2}$, room temperature) and 430 nm (45.6 mW cm$^{-2}$, room temperature).

Figure S11: *In vitro* decay of 1d [0.5 mM in Tris buffer (20 mM, pH 7.5)/MeCN 1:1] via reversed-phase HPLC after irradiation with 375 nm (6.4 mW cm$^{-2}$, room temperature).
**Figure S12:** *In vitro* decay of 1e [0.5 mM in Tris buffer (20 mM, pH 7.5)/MeCN 1:1] via reversed-phase HPLC after irradiation with 375 nm (6.4 mW cm$^{-2}$, room temperature), 405 nm (44.6 mW cm$^{-2}$, room temperature) and 430 nm (45.6 mW cm$^{-2}$, room temperature).

**Figure S13:** *In vitro* decay of 2c [0.5 mM in Tris buffer (20 mM, pH 7.5)/MeCN 1:1] via reversed-phase HPLC after irradiation with 430 nm (45.6 mW cm$^{-2}$, room temperature).
Figure S14: In vitro decay of 22a [0.5 mM in sodium phosphate buffer (100 mM, pH 7.4)] via reversed-phase HPLC after irradiation with 375 nm (6.4 mW cm⁻², room temperature).
Table S3: Fitting parameters for 1b–e, 2b–c and 22a at different wavelength.

| photocaged inducer | λ [nm] | $y_0$   | $A_i$  | $t_1$  | $k$    | $r$       |
|--------------------|--------|---------|--------|--------|--------|-----------|
| 2b                 | 375    | -0.19104| 1.18966| 230.51535| 0.00434| 159.78106 |
| 1c                 | 430    | -0.01254| 0.97483| 2.83993 | 0.35212| 1.96849   |
| 1b                 | 375    | 0.0004873| 1.02624| 246.92187| 0.00405| 171.1532  |
| 1b                 | 405    | -0.02632| 1.03705| 33.42057 | 0.02992| 23.16538  |
| 1b                 | 430    | -0.01504| 1.05356| 40.75615 | 0.02454| 28.25001  |
| 1d                 | 375    | 0.01084 | 1.00002| 3.7118  | 0.26941| 2.57283   |
| 1e                 | 375    | -0.09535| 1.06979| 46.27316| 0.02161| 32.07411  |
| 1e                 | 405    | -0.06395| 1.09129| 5.79684 | 0.17251| 4.01806   |
| 1e                 | 430    | -0.02656| 1.03055| 7.48242 | 0.13365| 5.18642   |
| 2c                 | 430    | 0.00417 | 0.96575| 5.79819 | 0.17247| 4.019     |
| 22a                | 375    | -0.00435| 0.9935 | 3.52342 | 0.28382| 2.44225   |
S4.4 HPLC-Traces

**Figure S15**: UV traces at 388 nm of the reversed-phase HPLC analysis of 2b (1 mM in H$_2$O/DMSO 99:1) before irradiation and after 240 min of irradiation at 405 nm (44.6 mW cm$^{-2}$, room temperature).

**Figure S16**: UV traces at 488 nm of the reversed-phase HPLC analysis of 1c [0.5 mM in Tris buffer (20 mM, pH 7.5)/MeCN 50:50] before irradiation and after 20 min of irradiation at 430 nm (45.6 mW cm$^{-2}$, room temperature).
Figure S17: A) UV traces at 392 nm of the reversed-phase HPLC analysis of 1b [0.5 mM in Tris buffer (20 mM, pH 7.5)/MeCN 50:50] before irradiation and after 10 min of irradiation at 375 nm (6.4 mW cm$^{-2}$, room temperature); B) UV traces at 392 nm of the reversed-phase HPLC analysis of 1b [0.5 mM in Tris buffer (20 mM, pH 7.5)/MeCN 50:50] before irradiation and after 5 min of irradiation at 405 nm (44.6 mW cm$^{-2}$, room temperature); C) UV traces at 392 nm of the reversed-phase HPLC analysis of 1b [0.5 mM in Tris buffer (20 mM, pH 7.5)/MeCN 50:50] before irradiation and after 10 min of irradiation at 430 nm (45.6 mW cm$^{-2}$, room temperature).

Figure S18: UV traces at 386 nm of the reversed-phase HPLC analysis of 1d [0.5 mM in Tris buffer (20 mM, pH 7.5)/MeCN 50:50] before irradiation and after 15 min of irradiation at 375 nm (6.4 mW cm$^{-2}$, room temperature).
Figure S19: A) UV traces at 386 nm of the reversed-phase HPLC analysis of 1e [0.5 mM in Tris buffer (20 mM, pH 7.5)/MeCN 50:50] before irradiation and after 10 min of irradiation at 375 nm (6.4 mW cm⁻², room temperature); B) UV traces at 386 nm of the reversed-phase HPLC analysis of 1e [0.5 mM in Tris buffer (20 mM, pH 7.5)/MeCN 50:50] before irradiation and after 5 min of irradiation at 405 nm (44.6 mW cm⁻², room temperature); C) UV traces at 386 nm of the reversed-phase HPLC analysis of 1e [0.5 mM in Tris buffer (20 mM, pH 7.5)/MeCN 50:50] before irradiation and after 10 min of irradiation at 430 nm (45.6 mW cm⁻², room temperature).

Figure S20: UV traces at 385 nm of the reversed-phase HPLC analysis of 2c [0.5 mM in Tris buffer (20 mM, pH 7.5)/MeCN 50:50] before irradiation and after 10 min of irradiation at 430 nm (45.6 mW cm⁻², room temperature).
Figure S21: UV traces at 346 nm of the reversed-phase HPLC analysis of 22a [0.5 mM in sodium phosphate buffer (100 mM, pH 7.4)] before irradiation and after 15 min of irradiation at 375 nm (6.4 mW cm$^{-2}$, room temperature).
S4.5 Stability measurements

Figure S22: UV traces at absorption maxima of the reversed-phase HPLC analysis of 2b (A), 1c (B), 1b (C), 1d (D), 1e (E) and 2c (F) for determination of stability. The reported values in Table 1 are means of triplicate measurements.
Figure S23: UV traces at absorption maxima of the reversed-phase HPLC analysis of 22a for determination of stability. The reported value is the mean of triplicate measurements.
S4.6 ESI measurements

Figure S24: ESI-MS measurements of 1e (1 mM in MeOH/H₂O 1:1) for detection of the intermediate S14 after irradiation with 430 nm (45.6 mW cm⁻², room temperature) for A) 0 min; B) 10 min; C) 20 min; D) 20 min plus allowing it to stand for 19 h at room temperature.
Figure S25: ESI-MS measurements of 2c (1 mM in MeOH/H$_2$O 1:1) for monitoring of the intermediate 19 after irradiation with 430 nm (45.6 mW cm$^{-2}$, room temperature) for A) 0 min; B) 3 min; C) 10 min; D) 10 min plus allowing it to stand for 3 h at room temperature.
S4.7 Toxicity of both the novel photocaged inducer variants and the light exposure

**Figure S26:** A–C: Growth of *E. coli* Tuner (DE3)/pRhotHi-2-lacl-eYFP expression cultures in the presence of the novel photocaged IPTG variants 1b (A), 1d (B) or 1c (C) compared to uninduced (0 µM) and induced (50 or 125 µM IPTG) cultures. Cells were grown in LB medium at 30 °C and 1200 rpm over 20 h using a ThermoMixer C (Eppendorf, Germany). Cell growth was analysed by determining the optical density at 580 nm. After 2.5 h, formation of photoproducts was induced in cultures via blue light exposure at 447 nm for 10 min (BL; ~10 mW cm⁻²) and conventional IPTG (1a) was added manually. D: Growth of *E. coli* LMG194/pBTBX-2-mCherry expression cultures in the presence of the novel photocaged arabinose variant 2c (50 µM) compared to uninduced (-Ara; 0 µM) and induced (+Ara; 50 µM) cultures. Cells were grown in LB medium at 37 °C and 1200 rpm over 20 h using a ThermoMixer C (Eppendorf, Germany). Cell growth was analysed by determining the optical density at 580 nm. After 2.5 h, formation of photoproducts was induced in cultures via blue light exposure at 447 nm for 10 min or 30 min (BL; ~10 mW cm⁻²) and conventional arabinose (2a) was added manually. E: Growth of *E. coli* Tuner(DE3)/pBNTmcs-mCherry expression cultures in the presence of the novel photocaged salicylic acid (Sal) variants BC-cSal (22a) and BC-cSal*Na (22b) compared to uninduced (-Sal; 0 µM) and induced (+Sal; 1000 µM Sal) cultures. Cells were grown in LB medium at 30 °C and 1200 rpm over 20 h using a ThermoMixer C (Eppendorf, Germany). Cell growth was analysed by determining the optical density at 580 nm. After 2.5 h formation of photoproducts was induced in cultures via light exposure at 365 nm for 30 min (~1 mW cm⁻²) and conventional Sal was added manually. Values are means of biological triplicate measurements and error bars indicate the respective standard deviation.
S4.8  

*In vivo* results of photocaged IPTG 1e

![Graph showing normalized in vivo eYFP fluorescence intensity](image)

**Figure S27:** Normalized *in vivo* eYFP fluorescence intensity of *E. coli* Tuner (DE3)/pRhotHi-2-lacI-eYFP expression cultures supplemented with 500 µM or 1000 µM of the photocaged compound 1e. All cultures were incubated in the dark for 20 h in LB medium at 30 °C and light-mediated induction of reporter gene expression was performed after 2.5 h by blue light exposure at 447 nm (BL; ~90 mW cm²) for 10 min or the addition of respective amounts of conventional IPTG (1a). *In vivo* fluorescence intensities were determined by using a BioLector system (λ<sub>ex</sub> = 508 nm, λ<sub>em</sub> = 532 nm), normalized to cell densities and are shown in relation to the respective fluorescence intensities of a culture induced with conventional IPTG (1a). Values are means of triplicate measurements. Error bars indicate the respective standard deviations.
S4.9  NMR spectra of compounds

Figure S29: $^1$H- and $^{13}$C-NMR spectra of S2 in CDCl$_3$ (600 MHz/151 MHz).
Figure S30: $^1$H- and $^{13}$C-NMR spectra of S3 in CDCl$_3$ (600 MHz/151 MHz).
Figure S31: $^1$H- and $^{13}$C-NMR spectra of 3 in CDCl$_3$ (600 MHz/151 MHz).
Figure S32: $^1$H- and $^{13}$C-NMR spectra of 5 in CDCl$_3$ (600 MHz/151 MHz).
Figure S33: $^1$H- and $^{13}$C-NMR spectra of 7 in CDCl$_3$ (600 MHz/151 MHz).
Figure S34: $^1$H- and $^{13}$C-NMR spectra of S4 in CDCl$_3$ (600 MHz/151 MHz).
Figure S35: $^1$H- and $^{13}$C-NMR spectra of S5 in CDCl$_3$ (600 MHz/151 MHz).
Figure S36: $^1$H- and $^{13}$C-NMR spectra of 11 in CDCl$_3$ (600 MHz/151 MHz).
Figure S37: $^1$H- and $^{13}$C-NMR spectra of 8 in CDCl$_3$ (600 MHz/151 MHz).
Figure S38: $^1$H- and $^{13}$C-NMR spectra of S6 in DMSO-$d_6$ (600 MHz/151 MHz).
Figure S39: $^1$H- and $^{13}$C-NMR spectra of 9 in DMSO-$d_6$ (600 MHz/151 MHz).
Figure S40: $^1$H- and $^{13}$C-NMR spectra of 12 in CDCl$_3$ (600 MHz/151 MHz).
Figure S41: \(^1\text{H}\)- and \(^{13}\text{C}\)-NMR spectra of S7 in DMSO-\(d_6\) (600 MHz/151 MHz).
Figure S42: $^1$H- and $^{13}$C-NMR spectra of S8 in DMSO-$d_6$ (600 MHz/151 MHz).
**Figure S43**: $^1$H- and $^{13}$C-NMR spectra of 10 in CDCl$_3$ (600 MHz/151 MHz).
Figure S44: $^1$H- and $^{13}$C-NMR spectra of 13 in CDCl$_3$ (600 MHz/151 MHz).
Figure S45: $^1$H- and $^{13}$C-NMR spectra of 2b in acetone-$d_6$ (600 MHz/151 MHz).
Figure S46: $^1$H- and $^{13}$C-NMR spectra of S9 in CDCl$_3$ (600 MHz/151 MHz).
Figure S47: $^1$H- and $^{13}$C-NMR spectra of S10 in CDCl$_3$ (600 MHz/151 MHz).
Figure S48: $^1$H- and $^{13}$C-NMR spectra of S11 in CDCl$_3$ (600 MHz/151 MHz).
Figure S49: $^1$H- and $^{13}$C-NMR spectra of 4 in CDCl$_3$ (600 MHz/151 MHz).
Figure S50: $^1$H- and $^{13}$C-NMR spectra of 6 in CDCl$_3$ (600 MHz/151 MHz).
Figure S51: $^1$H- and $^{13}$C-NMR spectra of 13 in CDCl$_3$ (600 MHz/151 MHz).
Figure S52: $^1$H- and $^{13}$C-NMR spectra of 1c in acetone-$d_6$ (600 MHz/151 MHz).
Figure S53: $^1$H- and $^{13}$C-NMR spectra of 14 in CDCl$_3$ (600 MHz/151 MHz).
Figure S54: $^1$H- and $^{13}$C-NMR spectra of 1b in acetone-$d_6$ (600 MHz/151 MHz).
Figure S55: $^1$H- and $^{13}$C-NMR spectra of 16 in CDCl$_3$ (600 MHz/151 MHz).
Figure S56: $^1$H- and $^{13}$C-NMR spectra of 1d in CDCl$_3$ (600 MHz/151 MHz).
Figure S57: $^1$H- and $^{13}$C-NMR spectra of 18 in CDCl$_3$ (600 MHz/151 MHz).
Figure S58: $^1$H- and $^{13}$C-NMR spectra of 1e in DMSO-$d_6$ (600 MHz/151 MHz) at 60 °C.
Figure S59: $^1$H- and $^{13}$C-NMR spectra of 17 in CDCl$_3$ (600 MHz/151 MHz).
Figure S60: $^1$H- and $^{13}$C-NMR spectra of 2c in CDCl$_3$ (600 MHz/151 MHz).
Figure S61: $^1$H- and $^{13}$C-NMR spectra of 22 in CDCl$_3$ (600 MHz/151 MHz).
Figure 62: $^1$H- and $^{13}$C-NMR spectra of 23 in CDCl$_3$ (600 MHz/151 MHz).
Figure S63: $^1$H- and $^{13}$C-NMR spectra of 24 in CDCl$_3$ (600 MHz/151 MHz).
Figure S64: $^1$H- and $^{13}$C-NMR spectra of 22a in DMSO-$d_6$ (600 MHz/151 MHz).
Figure S65: $^1$H- and $^{13}$C-NMR spectra of 22b in D$_2$O (600 MHz/151 MHz).
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