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Supporting Information

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Supporting Information

A Polymer-bound Chiral Template for Enantioselective Photochemical Reactions

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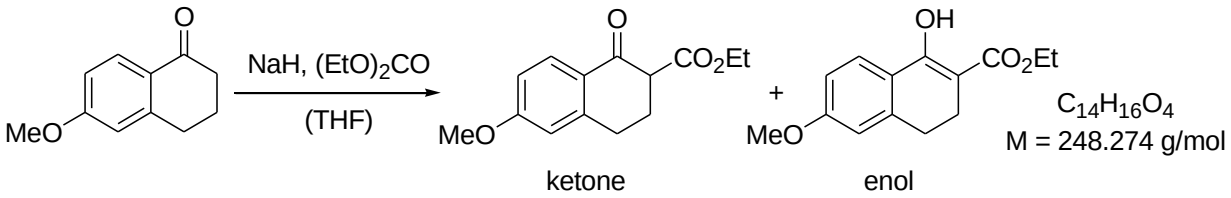
General Information. All reactions involving water-sensitive chemicals were carried out in flame-dried glassware with magnetic stirring under argon. Anhydrous *t*BuOH was distilled from CaH_2 prior to use. Common solvents [pentane (P), ethyl acetate (EtOAc), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), methanol (MeOH), ethanol (EtOH), tetrahydrofurane (THF), acetic acid (AcOH) and toluene] were distilled prior to use. All other reagents were used as received. Irradiation experiments were performed in toluene (Fluka) which was deaerated prior to use (60 minutes ultrasonification and Argon bubbling). TLC was performed on silica coated glass plates (0.25 mm silica gel 60, F_{254}) with detection by UV (254 nm). Flash column chromatography was performed as described by Still *et al.*[1] using silica gel 60 (Merck, 230-400 mesh) (ca 50 g for 1 g of material to be separated) with indicated solvents. HPLC analyses were performed with a HPLC system with diode-array-detector. The column used was a Daicel Chiralpak AD-H (250 × 4.6 mm) column for chiral separations. ^{1}H and ^{13}C-NMR spectra were recorded either on a Bruker AV-360 or on a Bruker AV-500 spectrometer at 298 K. Spectra were calibrated to their respective solvent residue signals ($CDCl_3$: ^{1}H 7.26 ppm, ^{13}C 77.16 ppm). Apparent multiplets which occur as a result of accidental equality of coupling constants to those of magnetically non-equivalent protons are marked as virtual (virt.). Multiplicities of ^{13}C-NMR signals were determined by DEPT and 2D HMQC experiments. IR spectra were recorded on a Perkin-Elmer 1600 FTIR. Mass spectra and high resolution mass spectra were performed on a Finnigan MAT 8200. Melting points are not corrected.

I. Synthesis and Characterization of 6-(11'-hydroxyundecyl)-substituted template 2

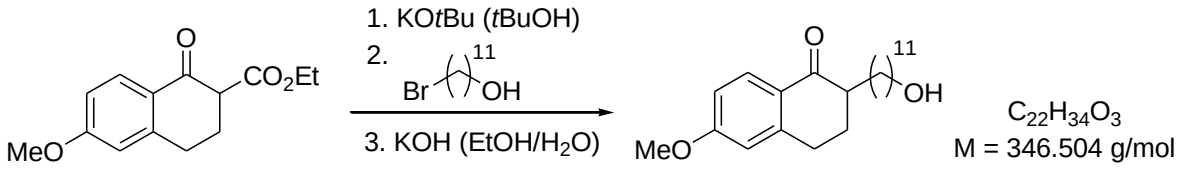
Ethyl 6-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate[2]



To a suspension of NaH (12.6 g, 525 mmol, 3.7 equiv, 100%) in 125 mL of THF were added 34.2 mL of diethyl carbonate (33.5 g, 284 mmol, 2.0 equiv) and refluxed. A solution of 6-methoxy-1-tetralone (25.0 g, 142 mmol) in 275 mL of THF was added dropwise over a period of 90 minutes and refluxing was continued for further 24 h. After cooling to room temperature, the reaction was quenched with 25 mL of AcOH and 400 mL of Et_2O were added. The suspension was washed with brine (5 × 150 mL). The organic layer was dried over Na_2SO_4, filtered and evaporated to dryness. The residue was purified by kugelrohr distillation (170 °C, 0.2 Torr) to provide 27.0 g (109 mmol, 77%) of ethyl 6-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (and its tautomeric enol form) as a colorless solid.

Ketone: **^{1}H-NMR** (360 MHz, $CDCl_3$): δ [ppm] = 1.26 (t, 3 H, ^{3}J = 7.1 Hz), 2.23-2.34 (m, 1 H), 2.85-3.04 (m, 2 H), 3.38-3.49 (m, 1 H), 3.52 (dd, 1 H, ^{3}J = 10.3 Hz, ^{3}J = 4.8 Hz), 3.82 (s, 3 H), 4.16-4.27 (m, 2 H), 6.66 (d, 1 H, ^{4}J = 2.5 Hz), 6.80 (dd, 1 H, ^{3}J = 8.8 Hz, ^{4}J = 2.5 Hz), 7.98 (d, 1 H, ^{3}J = 8.8 Hz); **^{13}C-NMR** (90.6 MHz, $CDCl_3$): δ [ppm] = 14.2 (q), 26.6 (t), 28.2 (t), 54.4 (d), 55.5 (q), 61.2 (t), 112.6 (d), 113.5 (d), 125.4 (s), 130.2 (d), 146.2 (s), 164.0 (s), 170.5 (s), 191.9 (s).
Enol: **^{1}H-NMR** (360 MHz, $CDCl_3$): δ [ppm] = 1.31 (t, 3 H, ^{3}J = 7.1 Hz), 2.53 (dd, 2 H, ^{3}J = 8.3 Hz, ^{3}J = 7.2 Hz), 2.75 (dd, 2 H, ^{3}J = 8.3 Hz, ^{3}J = 7.2 Hz), 3.80 (s, 3 H), 4.16-4.27 (m, 2 H), 6.67 (d, 1 H, ^{4}J = 2.6 Hz), 6.76 (dd, 1 H, ^{3}J = 8.6 Hz, ^{4}J = 2.6 Hz), 7.70 (d, 1 H, ^{3}J = 8.6 Hz), 12.53 (s, 1 H); **^{13}C-NMR** (90.6 MHz, $CDCl_3$): δ [ppm] = 14.4 (q), 20.6 (t), 28.3 (t), 55.3 (q), 60.4 (t), 95.0 (s), 111.7 (d), 113.2 (d), 122.9 (s), 126.1 (d), 141.8 (s), 161.5 (s), 165.5 (s), 172.8 (s).

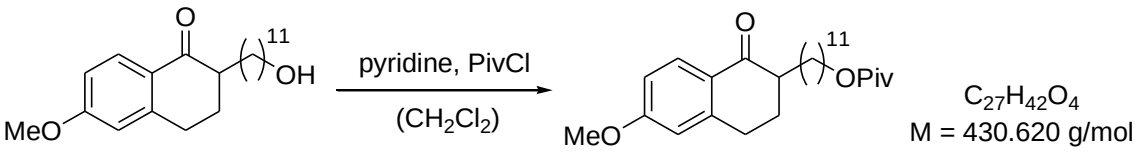
2-(11-Hydroxyundecyl)-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one



To a solution of KO*t*Bu (13.3 g, 119 mmol, 2.0 equiv) in 600 mL of *t*BuOH was added ethyl 6-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (14.8 g, 59.7 mmol) and refluxed for 30 minutes. After cooling to room temperature, 11-bromo-1-undecanol (60.0 g, 239 mmol, 4.0 equiv) was added and refluxed for further 2 h and then at 40 °C overnight. After cooling to room temperature, the reaction mixture was quenched with 50 mL of AcOH (colour change from purple to yellow) and most of the solvent was removed. The residue was taken in 600 mL of $CHCl_3$ and washed with brine (3 × 250 mL). The organic layer was dried over Na_2SO_4, filtered and evaporated to dryness. The crude product was dissolved in EtOH and KOH (15.1 g, 269 mmol, 4.5 equiv) in 22 mL of H_2O was added. The reaction mixture was refluxed for 6 h and after cooling to room temperature, the solution was taken in 600 mL of Et_2O and washed with brine (2 × 200 mL). The organic layer was dried over Na_2SO_4, filtered and evaporated to dryness. The residue was purified by column chromatography (9.0 × 20 cm, P/EtOAc = 90/10 → P/EtOAc = 70/30 as eluent) to give 9.67 g (27.9 mmol, 47%) of 2-(11-hydroxyundecyl)-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one as a colorless solid.

TLC R_f = 0.18 (P/EtOAc = 70/30); mp = 73 °C; **^{1}H-NMR** (360 MHz, $CDCl_3$): δ [ppm] = 1.20-1.41 (m, 17 H), 1.56 (virt. qu, 2 H, $^3J \cong 6.9$ Hz), 1.76-1.99 (m, 2 H), 2.20 (d virt. q, 1 H, ^2J = 13.3 Hz, $^3J \cong$ 4.9 Hz), 2.34-2.48 (m, 1 H), 2.89-2.97 (m, 2 H), 3.63 (t, 2 H, ^3J = 6.4 Hz), 3.84 (s, 3 H), 6.67 (d, 1 H, ^4J = 2.5 Hz), 6.81 (dd, 1 H, ^3J = 8.7 Hz, ^4J = 2.5 Hz), 7.99 (d, 1 H, ^3J = 8.7 Hz); **^{13}C-NMR** (90.6 MHz, $CDCl_3$): δ [ppm] = 25.9 (t), 27.2 (t), 28.3 (t), 28.8 (t), 29.5 (t), 29.6 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.9 (t), 32.9 (t), 47.3 (d), 55.5 (q), 63.2 (t), 112.5 (d), 113.2 (d), 126.4 (s), 130.0 (d), 146.5 (s), 163.4 (s), 199.5 (s); **IR** (KBr): $\tilde{\nu}$ = 3516 cm^{-1} (br), 3031 (w), 2914 (s), 2848 (s), 1734 (m), 1654 (m), 1602 (s), 1470 (m), 1280 (s), 1261 (s), 1138 (w), 1104 (w), 919 (w), 826 (w), 718 (w), 580 (w); **MS** (EI, 70 eV): *m/z* (%) = 346 (2) [M^+], 316 (1), 218 (1), 203 (1), 176 (100), 161 (6), 148 (4), 120 (2), 91 (2), 55 (5), 41 (4); **HRMS** (EI) calcd for $C_{23}H_{26}N_2O_3$ 346.25079, found 346.25102.

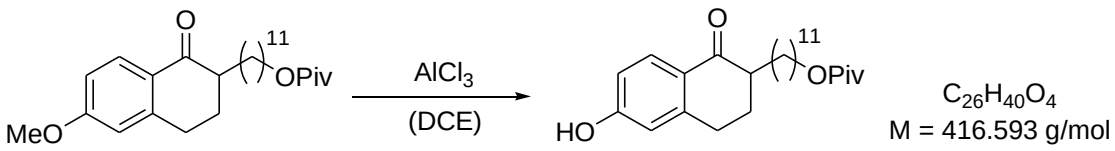
11-(6-Methoxy-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate



To a solution of 2-(11-hydroxyundecyl)-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (2.26 g, 6.52 mmol) in 19 mL of CH_2Cl_2 at 0 °C was added 790 µL of pyridine (774 mg, 9.78 mmol, 1.5 equiv) and then dropwise 1.23 mL of pivaloyl chloride (1.20 g, 9.78 mmol, 1.5 equiv). The reaction mixture was stirred at 0 °C for 3 h and then quenched with 100 mL of H_2O. The aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL), dried over Na_2SO_4, filtered and evaporated to dryness. The residue was purified by column chromatography (7.0 × 15 cm, P/EtOAc = 95/5 → P/EtOAc = 90/10 as eluent) to provide 2.84 g (6.60 mmol, 100%) of 11-(6-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate as a colorless oil.

TLC: R_f = 0.55 (P/EtOAc = 70/30); **^{1}H-NMR** (360 MHz, $CDCl_3$): δ [ppm] = 1.19 (s, 9 H), 1.23-1.51 (m, 17 H), 1.61 (virt. qu, 2 H, $^3J \cong$ 6.9 Hz), 1.80-1.97 (m, 2 H), 2.20 (d virt. q, 1 H, ^2J = 13.3 Hz, $^3J \cong$ 4.9 Hz), 2.36-2.47 (m, 1 H), 2.90-2.97 (m, 2 H), 3.84 (s, 3 H), 4.04 (t, 2 H, ^3J = 6.6 Hz), 6.67 (d, 1 H, ^4J = 2.5 Hz), 6.81 (dd, 1 H, ^3J = 8.7 Hz, ^4J = 2.5 Hz), 8.00 (d, 1 H, ^3J = 8.0 Hz); **^{13}C-NMR** (90.6 MHz, $CDCl_3$): δ [ppm] = 26.0 (t), 27.2 (t), 27.3 (q), 28.3 (t), 28.8 (t), 28.8 (t), 29.4 (t), 29.6 (t), 29.6 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.9 (t), 38.9 (s), 47.3 (d), 55.5 (q), 64.6 (t), 112.5 (d), 113.2 (d), 126.4 (s), 130.0 (d), 146.5 (s), 163.4 (s), 178.8 (s), 199.4 (s); **IR** (film): $\tilde{\nu}$ = 3061 cm^{-1} (w), 2926 (s), 2854 (s), 1727 (s), 1676 (s), 1601 (s), 1463 (m), 1362 (w), 1283 (s), 1251 (s), 1158 (s), 1031 (w); **MS** (EI, 70 eV): *m/z* (%) = 430 (4) [M^+], 329 (2), 189 (17), 176 (100), 148 (4), 120 (3), 103 (2), 85 (3), 69 (3), 57 (14); **HRMS** (EI) calcd for $C_{27}H_{42}NO_4$ 430.30831, found 430.30787.

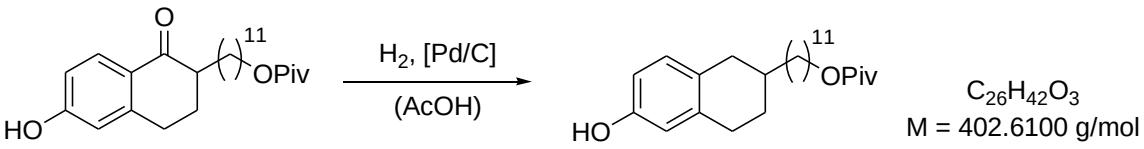
11-(6-Hydroxy-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate



To a solution of 11-(6-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate (100 mg, 232 μmol) in 9 mL of 1,2-dichloroethane (DCE) was added $AlCl_3$ (155 mg, 1.16 mmol, 5.0 equiv) and refluxed for 3 h. After cooling to room temperature, the reaction mixture was quenched with 15 mL of 20% aqueous K/Na tartrate. The aqueous layer was extracted with EtOAc (3 × 25 mL), dried over Na_2SO_4, filtered and evaporated to dryness. The residue was purified by column chromatography (1.0 × 10 cm, P/EtOAc = 95/5 as eluent) to provide 75.7 mg (176 μmol, 76%) of 11-(6-hydroxy-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate as a colorless oil.

TLC R_f = 0.61 (P/EtOAc = 50/50); **^{1}H-NMR** (360 MHz, $CDCl_3$): δ [ppm] = 1.20 (s, 9 H), 1.22-1.54 (m, 17 H), 1.61 (virt. qu, 2 H, $^3J \cong$ 6.9 Hz), 1.80-1.96 (m, 2 H), 2.14-2.24 (m, 1 H), 2.39-2.49 (m, 1 H), 2.81-2.99 (m, 2 H), 4.05 (t, 2 H, ^3J = 6.6 Hz), 6.69 (d, 1 H, ^4J = 2.5 Hz), 6.79 (dd, 1 H, ^3J = 8.6 Hz, ^4J = 2.5 Hz), 7.55 (s, 1 H), 7.95 (d, 1 H, ^3J = 8.6 Hz); **^{13}C-NMR** (90.6 MHz, $CDCl_3$): δ [ppm] = 26.0 (t), 27.2 (t), 27.3 (q), 28.2 (t), 28.4 (t), 28.7 (t), 29.3 (t), 29.6 (t), 29.6 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.9 (t), 38.9 (s), 47.2 (d), 64.9 (t), 114.5 (d), 114.7 (d), 125.7 (s), 130.4 (d), 147.1 (s), 161.2 (s), 179.4 (s), 200.5 (s); **IR** (film): $\tilde{\nu}$ = 3321 cm^{-1} (br), 2925 (s), 2854 (s), 1726 (m), 1699 (w), 1653 (m), 1596 (s), 1577 (s), 1465 (m), 1357 (m), 1283 (s), 1228 (s), 1156 (s), 910 (m), 732 (m); **MS** (EI, 70 eV): *m/z* (%) = 416 (2) [M^+], 331 (1), 315 (1), 202 (1), 175 (11), 162 (100), 147 (5), 69 (2), 57 (10), 41 (5); **HRMS** (EI) calcd for $C_{26}H_{40}O_4$ 416.29266, found 416.29372.

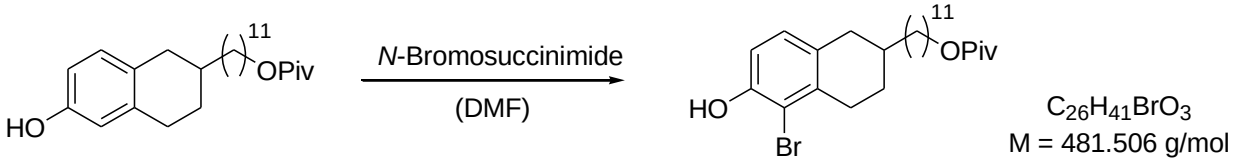
11-(6-Hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate



In an autoclave 10% Pd/C (2.12 g, 1.99 mmol, 5.4 mol%) was added to a solution of 11-(6-hydroxy-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate (15.4 g, 36.8 mmol) in 400 mL of AcOH. Under hydrogen atmosphere the suspension was stirred vigorously for 3 h at 6 bar. The reaction mixture was filtered, washed several times with EtOAc and the filtrate was evaporated to dryness. The residue was purified by column chromatography (7.0 × 15 cm, P/EtOAc = 95/5 → P/EtOAc = 90/10 as eluent) to provide 14.4 g (35.8 mmol, 97%) of 11-(6-hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate as a colorless oil.

TLC R_f = 0.59 (P/EtOAc = 50/50); **^{1}H-NMR** (360 MHz, $CDCl_3$): δ [ppm] = 1.20 (s, 9 H), 1.24-1.42 (m, 19 H), 1.57-1.73 (m, 3 H), 1.84-1.94 (m, 1 H), 2.30 (dd, 1 H, ^2J = 16.1 Hz, ^3J = 10.0 Hz), 2.71-2.81 (m, 3 H), 4.05 (t, 2 H, ^3J = 6.6 Hz), 4.87 (s, 1 H), 6.55 (d, 1 H, ^4J = 2.7 Hz), 6.59 (dd, 1 H, ^3J = 8.1 Hz, ^4J = 2.7 Hz), 6.92 (d, 1 H, ^3J = 8.1 Hz); **^{13}C-NMR** (90.6 MHz, $CDCl_3$): δ [ppm] = 26.1 (t), 27.1 (t), 27.4 (q), 28.8 (t), 29.4 (t), 29.5 (t), 29.6 (t), 29.7 (t), 29.7 (t), 29.8 (t), 29.8 (t), 30.0 (t), 34.6 (d), 35.6 (t), 36.6 (t), 38.9 (s), 64.7 (t), 113.0 (d), 115.1 (d), 129.2 (s), 130.2 (d), 138.5 (s), 153.4 (s), 179.0 (s); **IR** (film): $\tilde{\nu}$ = 3195 cm^{-1} (br), 2920 (s), 2851 (m), 1728 (s), 1634 (w), 1503 (m), 1284 (m), 1155 (s), 1096 (w), 858 (w); **MS** (EI, 70 eV): *m/z* (%) = 402 (100) [M^+], 318 (44), 300 (50), 159 (55), 145 (27), 133 (36), 120 (45), 107 (11), 85 (13), 57 (75); **HRMS** (EI) calcd for $C_{26}H_{41}O_3$ 402.31339, found 402.31293.

11-(5-Bromo-6-hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate

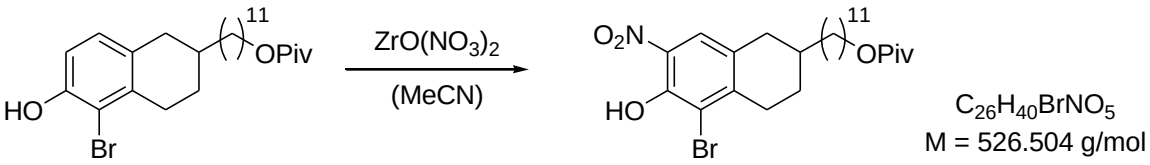


To a solution of 11-(6-hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate (56.5 mg, 140 μmol) in 1 mL of *N*,*N*-Dimethylformamide (DMF) at 0 °C was added *N*-bromosuccinimide (24.9 mg, 140 μmol, 1.0 equiv) and stirred for 8 h. The reaction mixture was quenched with 20 mL of H_2O and the aqueous layer was extracted with CH_2Cl_2 (6 × 25 mL), dried over Na_2SO_4, filtered and evaporated to dryness. The residue was purified by column chromatography (1.0 × 20 cm, P → P/Et_2O = 95/5 as eluent) to provide 47.8 mg (99.3 μmol, 71%) as a mixture of the 5-/7-bromosubstituted isomers in a ratio of 16/1 as a yellow oil.

TLC R_f = 0.67 (P/EtOAc = 70/30); **^{1}H-NMR** (360 MHz, $CDCl_3$): δ [ppm] = 1.20 (s, 9 H), 1.23-1.43 (m, 19 H), 1.52-1.70 (m, 3 H), 1.92-2.01 (m, 1 H), 2.34 (dd, 1 H, ^2J = 15.9 Hz, ^3J = 10.5 Hz), 2.62 (ddd, 1 H, ^2J = 17.5 Hz, ^3J = 10.9 Hz, ^3J = 6.3 Hz), 2.77 (dd, 1 H, ^2J = 15.9 Hz, ^3J = 3.8 Hz), 2.87 (ddd, 1 H, ^2J = 17.5 Hz, ^3J = 5.7 Hz, ^3J = 3.3 Hz), 4.05 (t, 2 H, ^3J = 6.6 Hz), 5.51 (s, 1 H), 6.73 (s, 1 H), 6.81 (d, 1 H, ^3J = 8.3 Hz), 6.93 (d, 1 H, ^3J = 8.3 Hz), 7.14 (s, 1 H); **^{13}C-NMR** (90.6 MHz, $CDCl_3$): δ [ppm] = 26.1 (t), 27.1 (t), 27.4 (q), 28.8 (t), 29.4 (t), 29.5 (t), 29.7 (t), 29.7 (t), 29.8 (t), 29.8 (t), 30.0 (t), 30.1 (t), 33.8 (d), 36.1 (t), 36.1 (t), 38.9 (s), 64.6 (t), 113.0 (d), 113.4 (s), 129.2 (d), 130.9 (s), 136.7 (s), 150.2 (s), 178.8 (s); **IR** (film): $\tilde{\nu}$ = 3423 cm^{-1} (br), 2923 (s), 2852 (m), 1728 (s), 1704 (m), 1602 (w), 1479 (s), 1284 (s), 1158 (s), 1038 (w), 806 (w); **MS** (EI, 70 eV): *m/z* (%) = 482 (14) [M^+], 401 (100), 378 (24), 317 (34), 299 (44),

239 (21), 213 (13), 159 (13), 133 (25), 103 (17), 85 (33), 57 (96), 41 (13); **HRMS** (EI) calcd for $C_{26}H_{41}O_3{}^{79}Br$ 480.22391, found 480.22200.

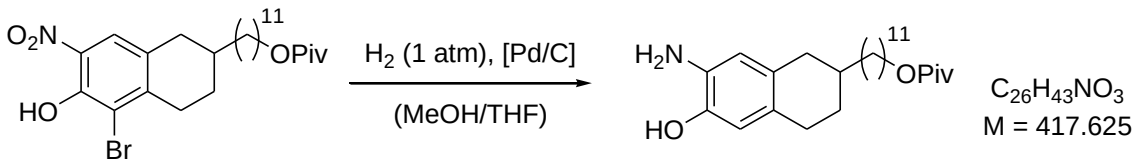
11-(5-Bromo-6-hydroxy-7-nitro-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate



To a solution of a mixture of the 5-/7-bromosubstituted isomers (48.4 mg, 101 μmol; 5-Br/7-Br = 16/1) in 2 mL of MeCN was added $ZrO(NO_3)_2$ (23.4 mg, 101 μmol, 1.0 equiv) and stirred for 10 h at 50 °C. The reaction mixture was quenched with 20 mL of H_2O and the aqueous layer was extracted with EtOAc (3 × 25 mL), dried over Na_2SO_4, filtered and evaporated to dryness. The residue was purified by column chromatography (1.0 × 10 cm, P/Et_2O = 95/5 as eluent) to provide 33.9 mg (64.4 μmol, 64%) of 11-(5-bromo-6-hydroxy-7-nitro-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate as a yellow oil.

TLC R_f = 0.34 (P/EtOAc = 9/1); **^{1}H-NMR** (360 MHz, $CDCl_3$): δ [ppm] = 1.19 (s, 9 H), 1.21-1.46 (m, 19 H), 1.54-1.74 (m, 3 H), 1.94-2.07 (m, 1 H), 2.40 (dd, 1 H, ^2J = 16.0 Hz, ^3J = 10.3 Hz), 2.59-2.77 (m, 1 H), 2.85 (dd, 1 H, ^2J = 16.0 Hz, ^3J = 3.9 Hz), 3.00 (ddd, 1 H, ^2J = 19.0 Hz, ^3J = 5.7 Hz, ^3J = 3.3 Hz), 4.04 (t, 2 H, ^3J = 6.6 Hz), 7.82 (s, 1 H), 11.06 (s, 1 H); **^{13}C-NMR** (90.6 MHz, $CDCl_3$): δ [ppm] = 26.0 (t), 27.0 (t), 27.3 (q), 28.7 (t), 28.8 (t), 29.3 (t), 29.6 (t), 29.7 (t), 29.7 (t), 29.8 (t), 29.9 (t), 31.6 (t), 33.4 (d), 35.7 (t), 36.0 (t), 38.9 (s), 64.6 (t), 115.3 (s), 123.5 (d), 130.8 (s), 132.0 (s), 148.6 (s), 150.0 (s), 178.8 (s); **IR** (film): $\tilde{\nu}$ = 3171 cm^{-1} (br), 2924 (s), 2853 (m), 1726 (s), 1617 (m), 1530 (s), 1453 (s), 1313 (m), 1283 (m), 1254 (m), 1232 (w), 1155 (s), 761 (w); **MS** (EI, 70 eV): *m/z* (%) = 526 (1) [M^+], 509 (2), 492 (9), 405 (7), 390 (7), 326 (25), 298 (16), 249 (17), 85 (29), 57 (100), 41 (23); **HRMS** (EI) calcd for $C_{26}H_{38}NO_4{}^{79}Br$ [M-H_2O]$^+$ 507.19843, found 507.19809.

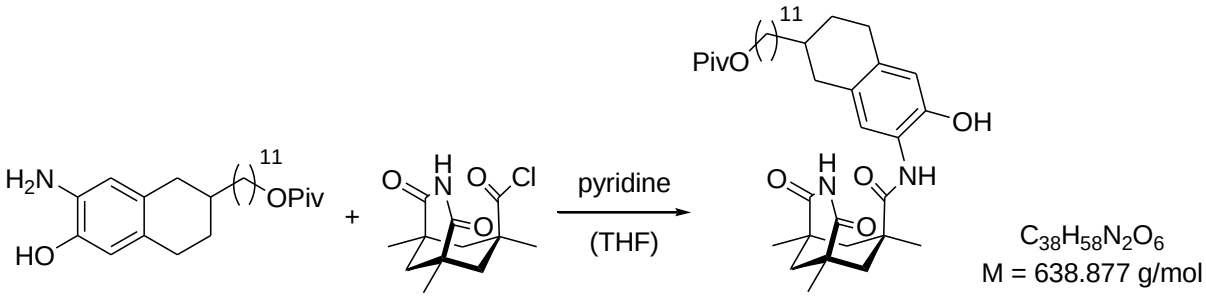
11-(7-Amino-6-hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate



To a solution of 11-(5-bromo-6-hydroxy-7-nitro-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate (4.50 g, 8.56 mmol) in 34 mL of MeOH/THF (v/v = 1/1) was added 10% Pd/C (477 mg, 447 μmol, 5.22 mol%) and stirred under hydrogen atmosphere vigorously for 5 h. The reaction mixture was filtered, washed several times with EtOAc and the filtrate was evaporated to dryness. The residue was purified by column chromatography (3.0 × 10 cm, 1. P/EtOAc = 70/30 → EtOAc; 2. CH_2Cl_2/MeOH = 90/10 as eluent) to provide 4.09 g (8.20 mmol, 98%; [M+HBr]) of 11-(7-amino-6-hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate as a pale yellow solid.

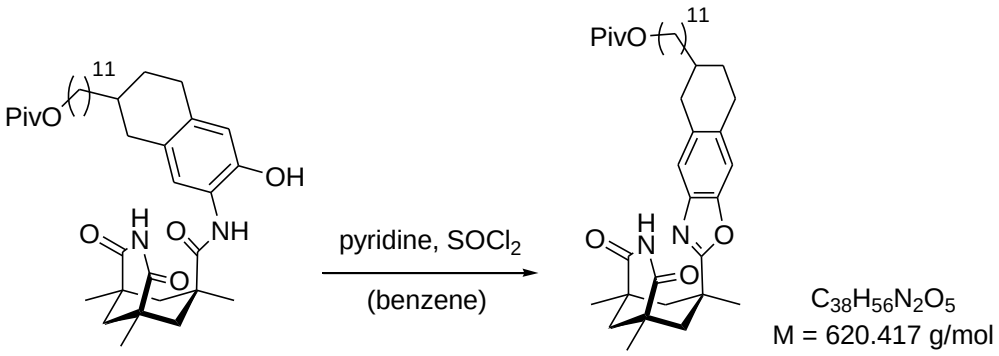
TLC R_f = 0.43 (P/EtOAc = 5/5); mp = 71 °C; **^{1}H-NMR** (360 MHz, $CDCl_3$): δ [ppm] = 1.20 (s, 9 H), 1.26-1.42 (m, 19 H), 1.61-1.68 (m, 3 H), 1.82-1.94 (m, 1 H), 2.27 (dd, 1 H, ^3J = 16.0 Hz, ^3J = 10.4 Hz), 2.62-2.75 (m, 3 H), 3.94 (br, 2 H), 4.07 (t, 2 H, ^3J = 6.6 Hz), 6.46 (s, 1 H), 6.48 (s, 1 H); **^{13}C-NMR** (90.6 MHz, $CDCl_3$): δ [ppm] = 26.1 (t), 27.1 (t), 27.4 (q), 28.7 (t), 28.8 (t), 29.4 (t), 29.7 (t), 29.7 (t), 29.8 (t), 29.8 (t), 29.9 (t), 30.1 (t), 34.6 (d), 35.7 (t), 36.6 (t), 38.9 (s), 64.7 (t), 115.3 (d), 118.0 (d), 128.5 (s), 129.6 (s), 132.0 (s), 142.8 (s), 178.9 (s); **IR** (film): $\tilde{\nu}$ = 3366 cm^{-1} (m), 3283 (m), 3060 (w), 2919 (s), 2850 (m), 1728 (s), 1523 (m), 1480 (w), 1461 (m), 1438 (w), 1283 (m), 1268 (w), 1234 (w), 1152 (s), 872 (w); **MS** (EI, 70 eV): *m/z* (%) = 417 (7) [M$^+$], 333 (2), 315 (1), 279 (2), 202 (1), 167 (6), 149 (11), 80 (100), 71 (6), 57 (11); **HRMS** (EI) calcd for $C_{26}H_{43}NO_3$ 417.32428, found 417.32265.

11-(7-Hydroxy-6-(1,5,7-trimethyl-2,4-dioxo-3-aza-bicyclo[3.3.1]nonane-7-carboxamido)-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate



To a solution of 11-(7-amino-6-hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate (111 mg, 266 μmol) in 3 mL of THF was added 1,5,7-trimethyl-2,4-dioxo-3-aza-bicyclo[3.3.1]nonan-7-carbonylchlorid[3] (68.6 mg, 266 μmol, 1.0 equiv) and 34 μL of pyridine (33.7 mg, 426 μmol, 1.6 equiv). The reaction mixture was refluxed for 16 h. After cooling to room temperature, the solution was quenched with 30 mL of H_2O and the aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL), dried over Na_2SO_4, filtered and evaporated to dryness. The crude product was used in the next step without further purification.

11-(2-(1,5,7-Trimethyl-2,4-dioxo-3-aza-bicyclo[3.3.1]nonan-7-yl)-5,6,7,8-tetrahydronaphtho[2,3-*d*]oxazol-6-yl)undecyl pivalate

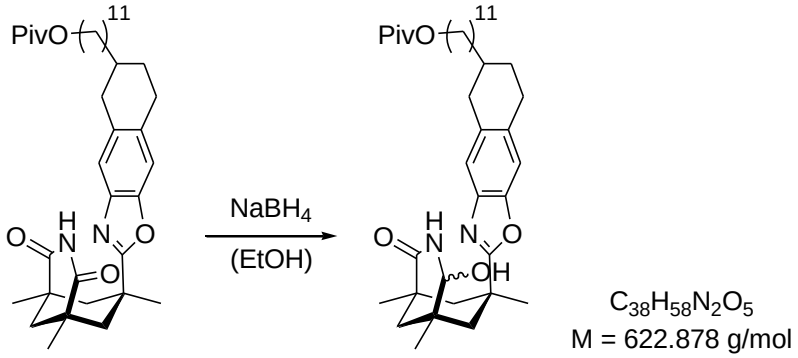


To a solution of the crude product of 11-(7-hydroxy-6-(1,5,7-trimethyl-2,4-dioxo-3-aza-bicyclo[3.3.1]nonane-7-carboxamido)-1,2,3,4-tetrahydronaphthalen-2-yl)undecyl pivalate (266 μmol) in 5 mL of benzene was added 96 μL of $SOCl_2$ (158 mg, 1.33 mmol, 5.0 equiv) and 140 μL of pyridine (137 mg, 1.73 mmol, 6.5 equiv) and refluxed for 3 h. After cooling to room temperature, the reaction mixture was concentrated and taken in 50 mL of CH_2Cl_2. After addition of 25 mL of 1 N HCl, the aqueous layer was extracted with CH_2Cl_2 (5 × 50 mL), dried over Na_2SO_4, filtered and evaporated to dryness. The residue was purified by column chromatography (2.0 × 10 cm, P/EtOAc = 90/10 as eluent) to provide 142 mg (229 μmol, 86% over two steps) of 11-(2-(1,5,7-trimethyl-2,4-dioxo-3-aza-bicyclo[3.3.1]nonan-7-yl)-5,6,7,8-tetrahydronaphtho[2,3-*d*]oxazol-6-yl)undecyl pivalate as a colorless solid.

TLC R_f = 0.69 (P/EtOAc = 30/70); **^{1}H-NMR** (360 MHz, $CDCl_3$): δ [ppm] = 1.19 (s, 9 H), 1.26-1.40 (m, 28 H), 1.44-1.51 (m, 3 H), 1.57-1.66 (m, 2 H), 1.66-1.76 (m, 1 H), 1.89-1.96 (m, 1 H), 2.00 (d, 1 H, ^2J =

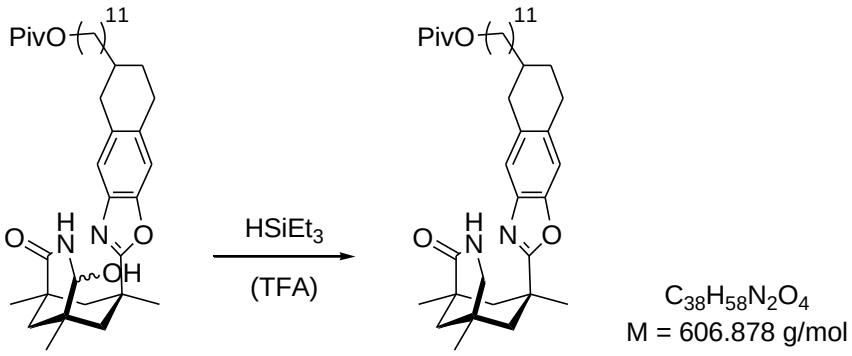
13.3 Hz), 2.47 (dd, 1 H, ^{2}J = 16.1 Hz, ^{3}J = 10.5 Hz), 2.84-2.97 (m, 3 H), 3.04-3.11 (m, 2 H), 4.04 (t, 2 H, ^{3}J = 6.6 Hz), 6.88 (s, 1 H), 7.15 (s, 1 H), 7.31 (s, 1 H); **^{13}C-NMR** (90.6 MHz, $CDCl_3$): δ [ppm] = 24.8 (q), 26.1 (t), 27.1 (t), 27.4 (q), 28.8 (t), 29.4 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.8 (t), 29.8 (t), 30.0 (t), 30.1 (t), 32.7 (q), 34.4 (d), 36.6 (t), 36.8 (t), 37.3 (s), 38.9 (s), 40.3 (s), 44.8 (t), 44.9 (t), 45.0 (t), 64.6 (t), 110.0 (d), 119.6 (d), 133.7 (s), 134.7 (s), 139.1 (s), 148.8 (s), 168.7 (s), 175.9 (s), 178.8 (s); **IR** (film): $\tilde{\nu}$ = 3186 cm^{-1} (br), 3137 (w), 3084 (m), 2966 (w), 2923 (s), 2853 (m), 1726 (s), 1697 (s), 1461 (s), 1383 (m), 1364 (m), 1284 (m), 1256 (w), 1220 (m), 1209 (m), 1153 (s), 1085 (m), 846 (m); **MS** (EI, 70 eV): *m/z* (%) = 620 (99) [M^+], 519 (15), 407 (7), 365 (100), 351 (6) , 212 (6), 172 (8), 121 (8), 85 (7), 57 (36); **HRMS** (EI) calcd for $C_{38}H_{56}N_2O_5$ 620.41895, found 620.41680.

11-(2-(2-Hydroxy-1,5,7-trimethyl-4-oxo-3-aza-bicyclo[3.3.1]nonan-7-yl)-5,6,7,8-tetrahydronaphtho[2,3-*d*]oxazol-6-yl)undecyl pivalate



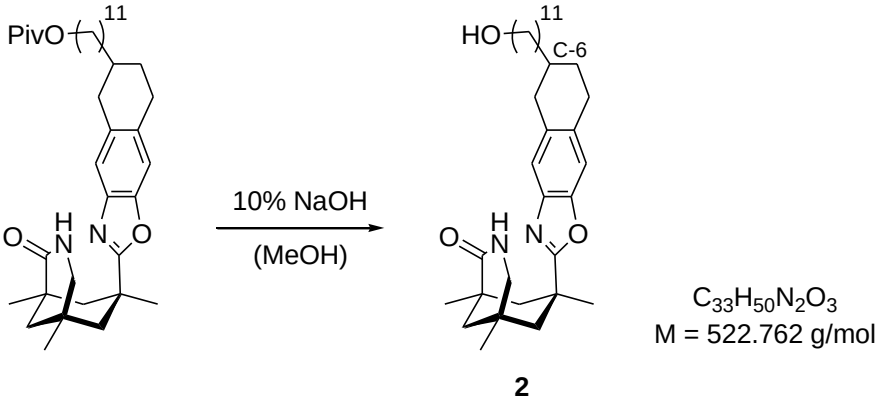
To a solution of 11-(2-(1,5,7-trimethyl-2,4-dioxo-3-aza-bicyclo[3.3.1]nonan-7-yl)-5,6,7,8-tetrahydronaphtho[2,3-*d*]oxazol-6-yl)undecyl pivalate (132 mg, 213 μmol) in 7 mL of EtOH at 0 °C was added $NaBH_4$ (322 mg, 8.52 mmol, 40 equiv) over a period of 30 minutes. It was stirred for 1 h at 0 °C and then 3 h at room temperature. The reaction mixture was quenched with 50 mL of H_2O and the aqueous layer was extracted with CH_2Cl_2 (3 × 70 mL), dried over Na_2SO_4, filtered and evaporated to dryness. The crude product was used in the next step without further purification.

11-(2-(1,5,7-Trimethyl-2-oxo-3-aza-bicyclo[3.3.1]nonan-7-yl)-5,6,7,8-tetrahydronaphtho[2,3-*d*]oxazol-6-yl)undecyl pivalate



To a solution of the crude product of 11-(2-(2-hydroxy-1,5,7-trimethyl-4-oxo-3-aza-bicyclo[3.3.1]nonan-7-yl)-5,6,7,8-tetrahydronaphtho[2,3-*d*]oxazol-6-yl)undecyl pivalate (213 μmol) in 2 mL of trifluoroacetic acid (TFA) was added 288 μL of $HSiEt_3$ (210 mg, 1.81 mmol, 8.5 equiv) and stirred for 16 h at room temperature. The reaction mixture was quenched with 40 mL of aqueous saturated $NaHCO_3$ and the aqueous layer was extracted with CH_2Cl_2 (4 × 50 mL), dried over Na_2SO_4, filtered and evaporated to dryness. The crude product was used in the next step without further purification.

7-(6-(11-Hydroxyundecyl)-5,6,7,8-tetrahydronaphtho[2,3-*d*]oxazol-2-yl)-1,5,7-trimethyl-3-aza-bicyclo[3.3.1]nonan-2-one 2



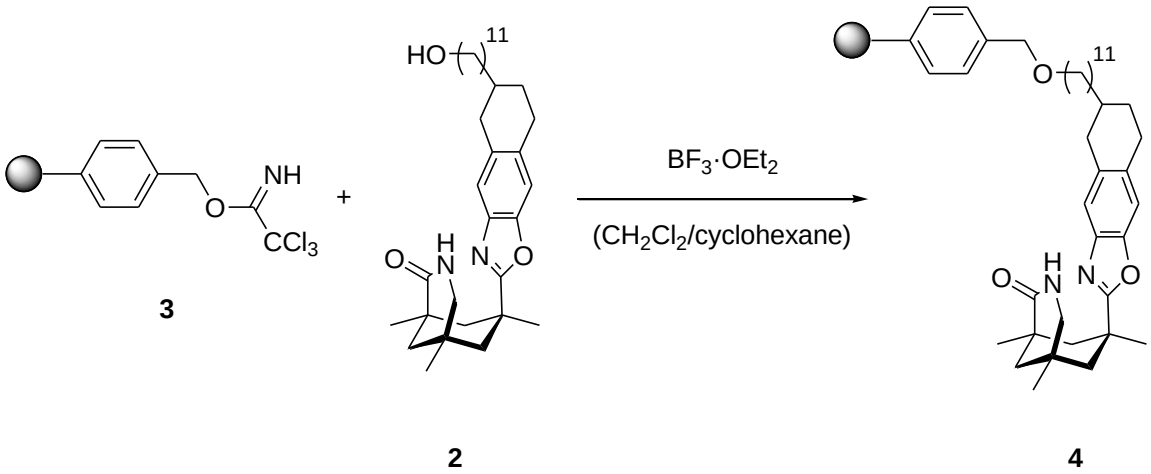
A solution of 11-(2-(1,5,7-trimethyl-2-oxo-3-aza-bicyclo[3.3.1]nonan-7-yl)-5,6,7,8-tetrahydronaphtho[2,3-*d*]oxazol-6-yl)undecyl pivalate (213 μmol) in 3.5 mL of 10% methanolic NaOH was stirred for 16 h at room temperature. The reaction mixture was quenched with 40 mL of H_2O and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), dried over Na_2SO_4, filtered and evaporated to

dryness. The residue was purified by column chromatography (2.0 × 10 cm, P/EtOAc = 50/50 as eluent) to provide 103 mg (197 μmol, 92%) of **2** as a colorless solid. Purification of **2** was achieved by semi-preparative HPLC (Daicel Chiralpak AD, 250 × 20.0 mm, Hexane/*i*PrOH = 70/30) to obtain a pair of enantiomerically pure diastereoisomers resulting from the stereogenic center at C-6.

TLC R_f = 0.24 (P/EtOAc = 30/70); mp = 79 °C; **^{1}H-NMR** (360 MHz, $CDCl_3$): δ [ppm] = 1.05 (s, 3 H), 1.21 (s, 3 H), 1.24-1.43 (m, 25 H), 1.48-1.60 (m, 2 H), 1.63-1.79 (m, 2 H), 1.87-1.98 (m, 1 H), 2.40-2.53 (m, 1 H), 2.79-3.01 (m, 6 H), 3.20-3.28 (m, 1 H), 3.61 (td, ^3J = 6.6 Hz, ^3J = 2.3 Hz), 4.69 (s, 1 H), 7.18 (s, 1 H), 7.27 (s, 1 H); **^{13}C-NMR** (90.6 MHz, $CDCl_3$): δ [ppm] = 25.3 (q), 25.9 (t), 27.0 (t), 27.1 (t), 29.3 (q), 29.6 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.9 (t), 29.9 (t), 30.0 (t), 30.0 (t), 30.9 (s), 32.9 (t), 33.4 (q), 34.4 (d), 34.4 (d), 36.5 (t), 36.6 (t), 36.8 (t), 36.8 (t), 37.7 (s), 38.6 (s), 45.3 (t), 46.1 (t), 46.1 (t), 47.3 (t), 47.3 (t), 52.8 (t), 63.1 (t), 110.2 (d), 118.9 (d), 133.2 (s), 133.2 (s), 134.0 (s), 134.1 (s), 139.4 (s), 148.9 (s), 148.9 (s), 170.7 (s), 175.1 (s); **IR** (film): $\tilde{\nu}$ = 3365 cm^{-1} (br), 2923 (s), 2851 (s), 1655 (s), 1557 (m), 1490 (w), 1463 (s), 1383 (w), 1291 (m), 1260 (m), 1084 (m), 847 (w); **MS** (EI, 70 eV): *m/z* (%) = 523 (100) [M^+], 495 (6), 467 (6), 426 (), 398 (11), 384 (23), 351 (9), 111 (19), 96 (8), 55 (8), 43 (8); **HRMS** (EI) calcd for $C_{33}H_{50}N_2O_3$ 522.38214, found 522.38338.

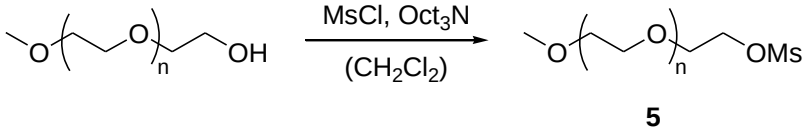
II. Grafting template 2 on Polymeric Supports

Wang resin bound template 4



Commercially available (Aldrich) Wang trichloroacetimidate **3** (100 mg, 74 μmol, loading 0.74 mmol g^{-1}, 200-400 mesh) was washed four times with 4 mL of THF and then suspended in 1.5 mL of cyclohexane. A solution of 7-(6-(11-hydroxyundecyl)-5,6,7,8-tetrahydronaphtho[2,3-*d*]oxazol-2-yl)-1,5,7-trimethyl-3-aza-bicyclo[3.3.1]nonan-2-one **2** (77.4 mg, 148 μmol, 2.0 equiv) in 1.5 mL of CH_2Cl_2 was added, stirred for 5 minutes and then 10 μL $BF_3{\cdot}OEt_2$ (11.6 mg, 81.4 μmol, 1.1. equiv) was added. After stirring for 16 h, the reaction mixture was quenched with 5 mL of MeOH, stirred for additional 15 minutes and filtered. The filter residue was washed intensively with H_2O, MeOH, Et_2O, DCM, Et_2O, MeOH, DCM, Et_2O and P. Completion of the reaction and product formation was detected by IR (disappearance of the absorption bands at 1662 and 3336 cm^{-1} and appearance of the carbonyl stretching band at 1707 cm^{-1}). Loading of template **4** on Wang resin was determined by elemental analysis (N, 0.48 → 0.17 mmol g^{-1}).

MPEG 2000 mesylate 5[4]

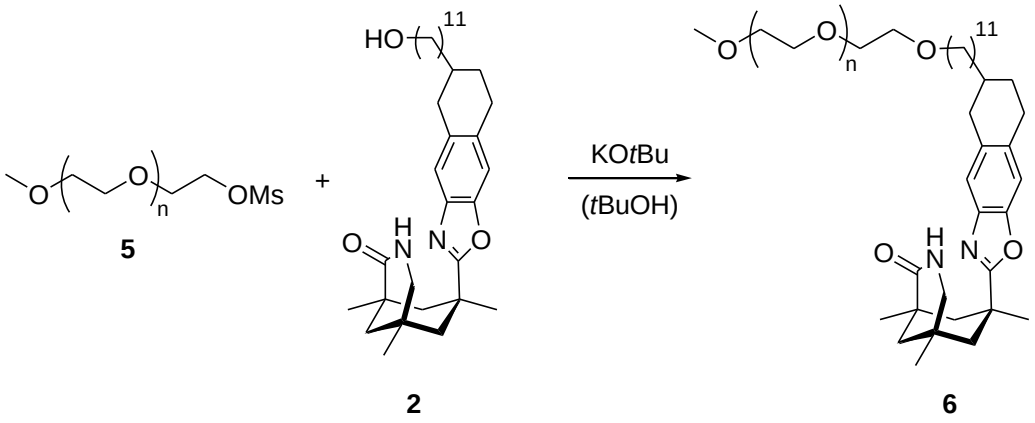


To a solution of commercially available (Aldrich) methoxy polyethylene glycol (1.00 g, 500 μmol, M_w = 2000; MPEG 2000) in 10 mL of CH_2Cl_2 at 0 °C was added 193 μL of MsCl (286 mg, 2.50 mmol,

5.0 equiv) and 437 μL of Oct_3N (354 mg, 1.00 mmol, 2.0 equiv). After stirring for 2 h at 0 °C, the reaction mixture was warmed to room temperature and stirred for further 1 h. The solvent was concentrated and taken in 20 mL of Et_2O. The solution was stored at 3 °C for 8 h. The precipitate was filtered, washed with Et_2O (2 × 20 mL) and evaporated to dryness to provide 820 mg (280 μmol, 0.341 mmol g^{-1} OMs) of **5** as a colorless solid.

^{1}H-NMR (360 MHz, $CDCl_3$): δ [ppm] = 3.07 (s, 3 H), 3.36 (s, 3 H), 3.40-3.85 (m, 232 H), 4.34-4.38 (m, 2 H); **^{13}C-NMR** (90.6 MHz, $CDCl_3$): δ [ppm] = 37.9 (q), 59.1 (q), 69.2 (t), 69.2 (t), 70.7 (t), 72.1 (t).

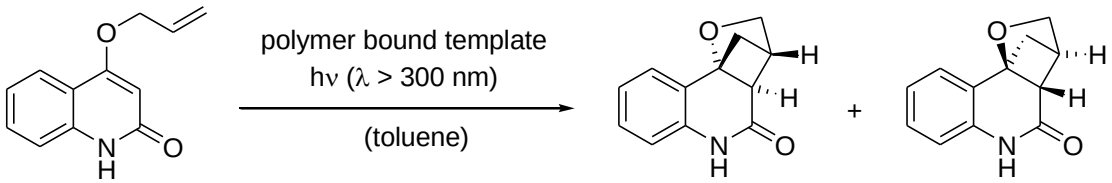
MPEG 2000 bound template 6



To a solution of 7-(6-(11-hydroxyundecyl)-5,6,7,8-tetrahydronaphtho[2,3-*d*]oxazol-2-yl)-1,5,7-trimethyl-3-aza-bicyclo[3.3.1]nonan-2-one **2** (157 mg, 300 μmol, 4.4 equiv) in 1.5 mL of *t*BuOH was added KO*t*Bu (33.7 mg, 300 μmol, 4.4 equiv) and refluxed for 1.5 h. After cooling to room temperature, MPEG 2000 mesylate **5** (200 mg, 68.2 μmol, 0.341 mmol/g) was added and refluxed for 72 h. The solvent was evaporated to dryness and the residue dissolved again in a few drops of CH_2Cl_2. The solution was taken in 80 mL of Et_2O and stored at 3 °C for 8 h. The precipitate was filtered, washed with Et_2O (2 × 20 mL) and evaporated to dryness. This procedure was repeated to provide 192 mg of **6** (47.2 μmol, 0.20 mmol g^{-1}) as a colorless solid.

III. Enantioselective Photocycloaddition Reactions

3,3a,4,5-Tetrahydro-3,9b-methanofuro[3,2-*c*]quinolin-4(2*H*)-one 7



7 **8** *ent*-**8**

General Procedure for [2+2]-Photocycloaddition of Wang resin bound templates

2 mL of a 1.5 mM solution of 4-(allyloxy)quinolin-2(1*H*)-one **7** in deaerated toluene were added to the Wang resin bound polymer **4** (200 mg, 34.0 μmol, 0.17 mmol g^{-1}) and swollen for 30 minutes at room temperature. The supernatant solution (ca. 1.5 mL) was removed via syringe and the residual suspension of polymer **4** in toluene irradiated for 4 h (light source: RPR 3000 Å, −74 °C, Duran filter). The suspension was filtered through a sintered glass frit and washed intensively with MeOH, CH_2Cl_2, Et_2O and P. The filter residue was dried under high vacuum and reused in the next run. The filtrate was evaporated to dryness and the residue analyzed by chiral HPLC (Daicel Chiralpak AD-H (250 × 4.6 mm), Hexane/*i*PrOH = 95/5, 1 mL/min) t_R = 22.9 min (**8**), t_R = 26.3 min (*ent*-**8**), t_R = 30.7 min (**7**).

Run[a]	e.r.[b]	Recovery (%)[c]	Conversion (%)
1	93/7	99	31
2	93/7	91	25
3	93/7	96	27
4	92/8	96	24
5	93/7	96	27

[a] The irradiation was conducted at a concentration of 1.5 mM at −74 °C in toluene as the solvent. [b] The enantiomeric ratio (**8**/*ent*-**8**) was determined by HPLC (Daicel Chiralpak AD-H, 250×4.6, Hexane/*i*PrOH = 95/5). [c] The recovery yield of **4** was determined after filtration and evaporation to dryness relative to the previous run.

(Table 1 reproduced above)

General Procedure for [2+2]-Photocycloaddition of MPEG bound templates

To a solution of 4-(allyloxy)quinolin-2(1*H*)-one **7** (0.207 mg, 1.03 μmol) in 2.1 mL of deaerated toluene was added MPEG 2000 bound template **6** (138 mg, 27.6 μmol, 0.20 mmol g^{-1}) and irradiated for 4 h (light source: RPR 3000 Å, −74 °C, Duran filter). The solvent was evaporated and the residue dissolved again in a few drops of CH_2Cl_2. The solution was taken in 80 mL of Et_2O and stored at 3 °C for 8 h. The precipitate was filtered through a sintered glass frit, washed with Et_2O (2 × 20 mL) and evaporated to dryness. The filter residue was once again diluted in a few drops of CH_2Cl_2 and 80 mL of Et_2O were added and stored at 3 °C for 8 h. The precipitate was filtered through a sintered glass frit, washed with Et_2O (2 × 20 mL) and evaporated to dryness for the use in the next run. The filtrate of the first precipitation was also evaporated to dryness and the residue analyzed by chiral HPLC (Daicel Chiralpak AD-H (250 × 4.6 mm), Hexane/*i*PrOH = 95/5, 1 mL/min) t_R = 22.9 min (**8**), t_R = 26.3 min (*ent*-**8**), t_R = 30.7 min (**7**).

Run[a]	e.r.[b]	Recovery (%)[c]	Conversion (%)
1	95/5	99	96
2	95/5	99	98
3	96/4	97	97
4	96/4	98	99
5	96/4	97	96

[a] The irradiation was conducted at a concentration of 0.5 mM at −74 °C in toluene as the solvent. [b] The enantiomeric ratio (**8**/*ent*-**8**) was determined by HPLC (Daicel Chiralpak AD-H, 250×4.6, Hexane/^{i}PrOH = 95/5). [c] The recovery yield of **6** was determined after precipitation in ether, filtration and evaporation to dryness relative to the previous run.

(Table 2 reproduced above)

References

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(2) H. Immer, J. F. Bagli, *J. Org. Chem.* **1968**, *33*, 2457-2462.

(3) J. Rebek, Jr., B. Askew, M. Killoran, D. Nemeth, F. T. Lin, *J. Am. Chem. Soc.* **1987**, *109*, 2426-2431.

(4) M. Bengaglia, M. Cinquini, F. Cozzi, *Tetrahedron Lett.* **1999**, *40*, 2019-2020.