Supplementary Information

for:

An abiotic, tetrameric, eight-helix bundle

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1 List of Abbreviations

CD → circular dichroism

DCM → dichloromethane

DIPEA → *N*,*N*-diisopropylethylamine

DMF → *N*,*N*-dimethylformamide

DOSY → diffusion-ordered spectroscopy

ESI → electrospray ionization

EtOAc → ethylacetate

eq → equivalent

Fmoc → fluorenylmethoxycarbonyl

HBTU → Hexafluorophosphate Benzotriazole Tetramethyl Uronium

Hex → Hexane

HFIP → hexafluroisopropanol

HR-ESI → high-resolution electrospray ionization

HRMS → high-resolution mass spectrometry

HSQC → heteronuclear single quantum correlation

MeOH → methanol

min → minutes

MS → mass spectrometry

MW → microwave

NMR → nuclear magnetic resonance

r. t. → room temperature

SPS → solid phase synthesis

TFA → trifluoroacetic acid

THF → tetrahydrofuran

UV/Vis → ultraviolet–visible

2 Supplementary Figures

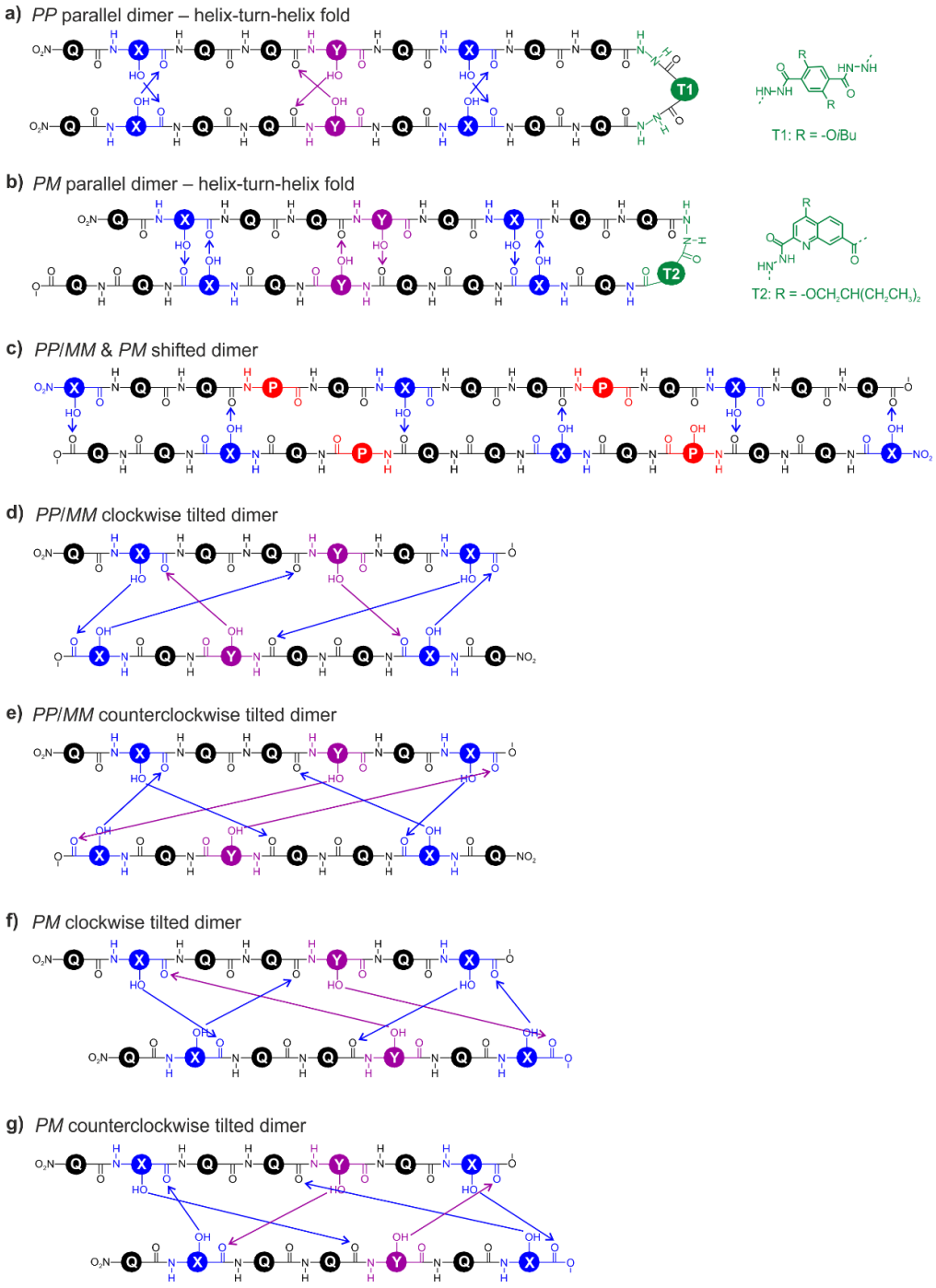


Figure S1. Schematic representation of hydrogen-bonding interfaces of previously described and hypothetical self-organizations. a) and b) Hydrogen bonding interfaces as characterized in a *PP*/*MM* (a) and *PM* (b) parallel dimer, as observed in helix-turn-helix tertiary structures stabilized by a T1 or T2 turn unit, respectively.[1-3] c) Hydrogen bonding interface as observed in *PP*/*MM* and *PM* shifted dimers.[4] d) and e) Hydrogen bonding interfaces observed in *PP*/*MM* clockwise (d) and counterclockwise (e) tilted dimers.[1] f) and g) Hypothetical hydrogen bonding interfaces in *PM* clockwise (f) and counterclockwise (g) tilted dimers.

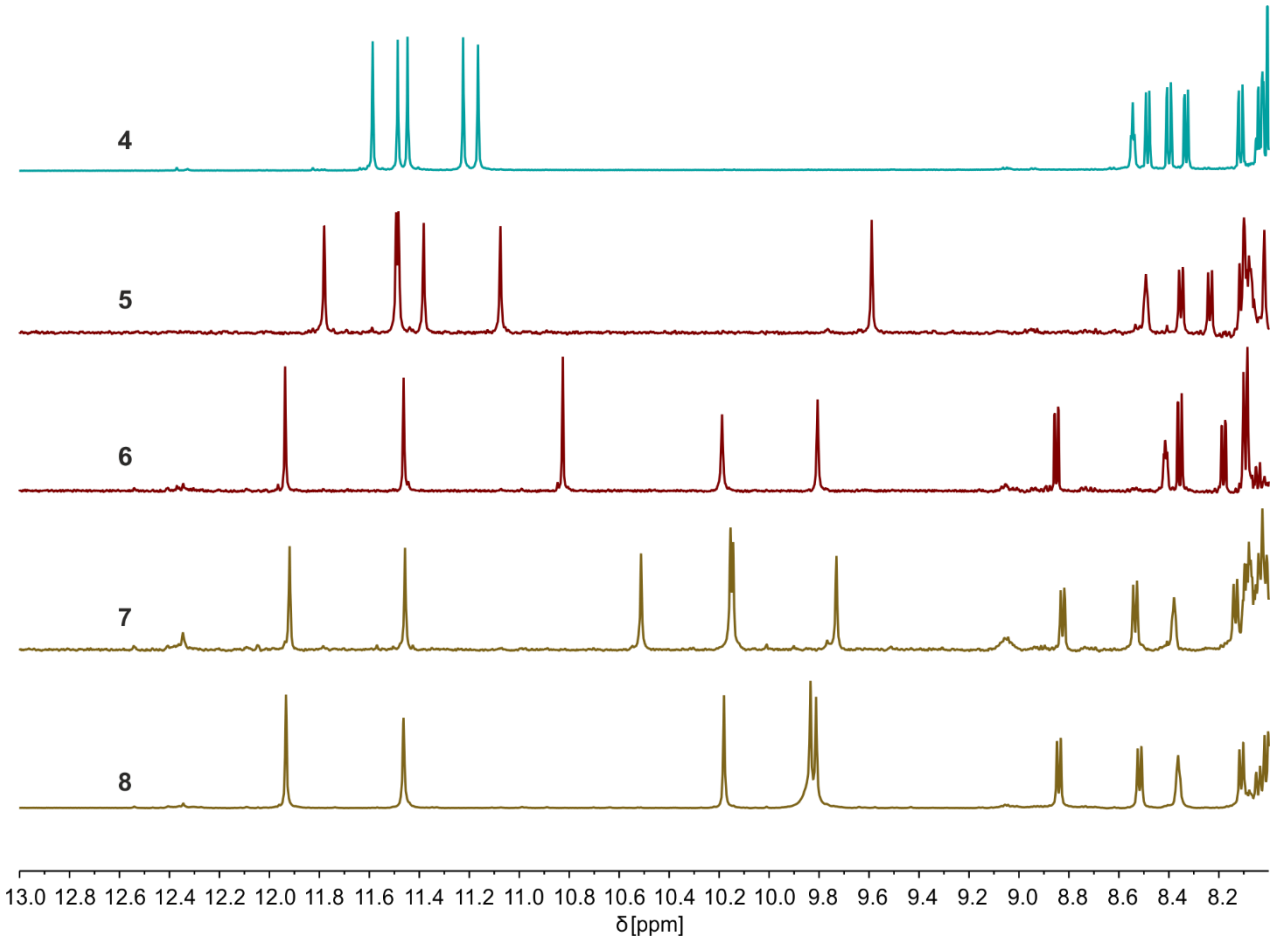


Figure S2. Sequences 4-8 show one set of ^{1}H NMR signals in $CDCl_3$. Extracts of ^{1}H NMR spectra (500 MHz, 25 °C) of **4-8** in $CDCl_3$ at 2.4 mM showing the amide region. Different color of the ^{1}H NMR signals indicate the presence of a different level of handedness-control: Achiral sequences are marked in turquoise, sequences at which one unit controls handedness are marked in brown and sequences at which two units are inducing handedness control are marked in gold.

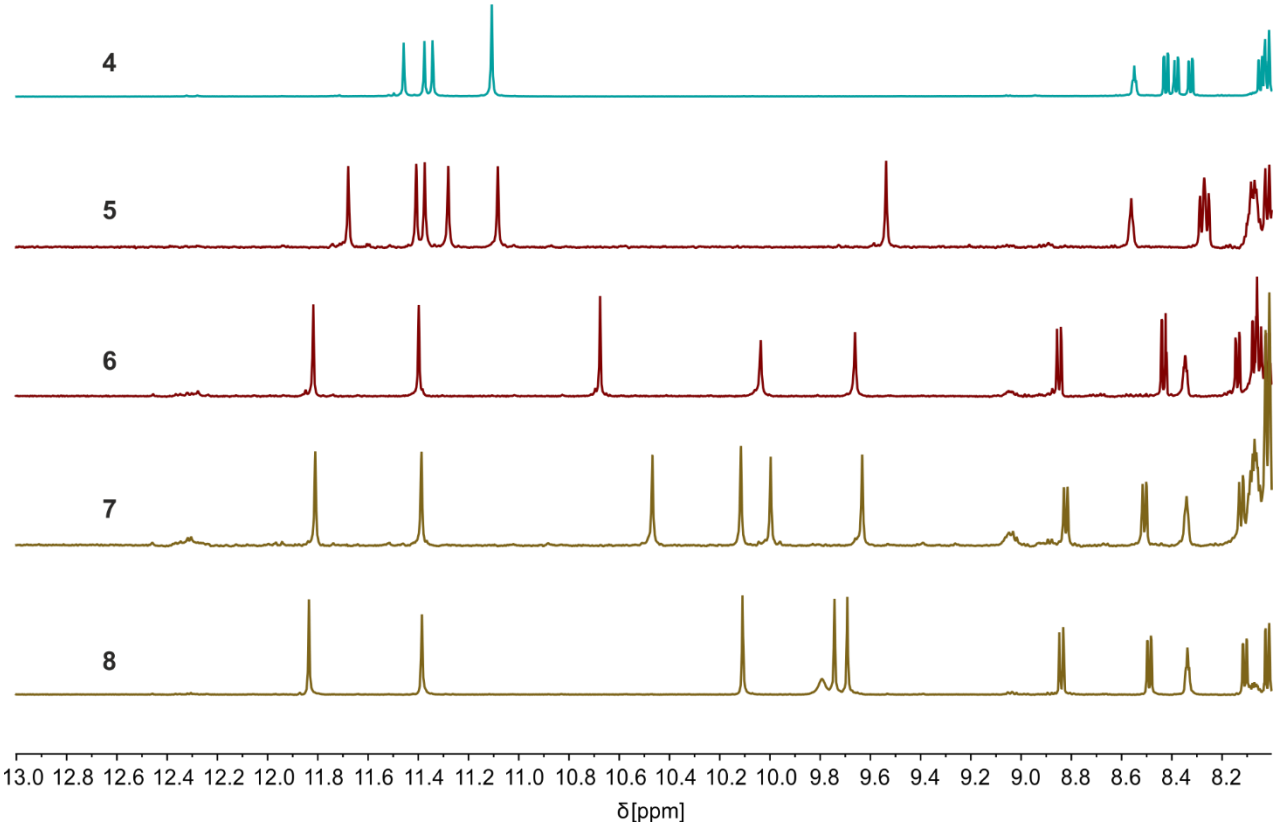


Figure S3. Sequences 4-8 show one set of ^{1}H NMR signals in CD_2Cl_2. Extracts of ^{1}H NMR spectra (500 MHz, 25 °C) of **4-8** in CD_2Cl_2 at 2.4 mM showing the amide region. Different color of the ^{1}H NMR signals indicate the presence of a different level of handedness-control: Achiral sequences are marked in turquoise, sequences at which one unit controls handedness are marked in brown and sequences at which two units are inducing handedness control are marked in gold.

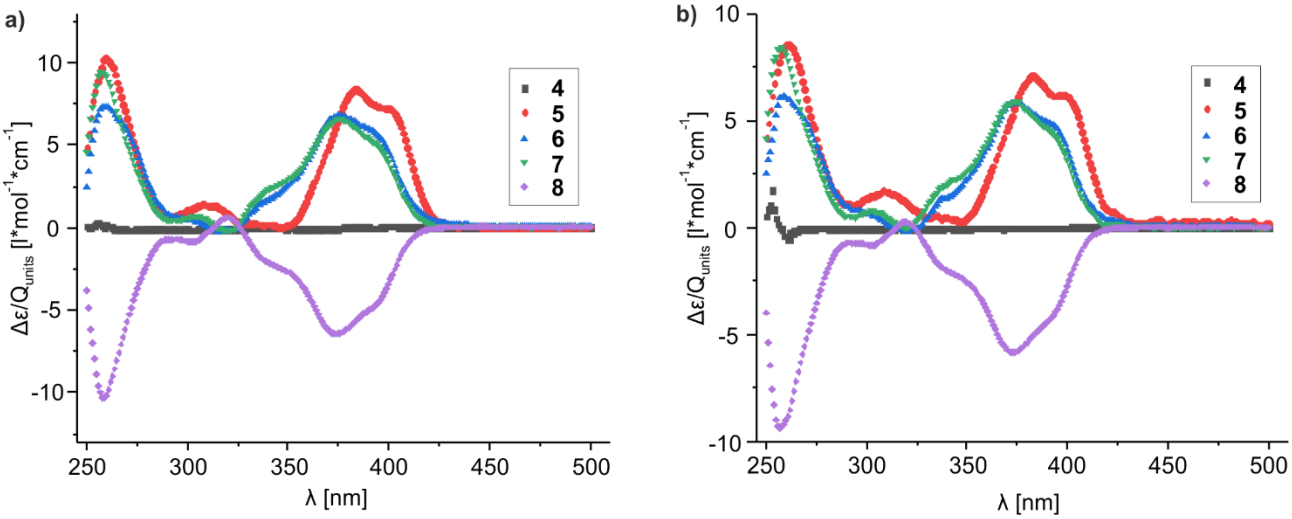


Figure S4. **The chiral B unit biases helix handedness quantitatively and overcomes the opposing effect of a camphanyl group.** CD spectra of **4-8** in $CHCl_3$ (a) and CH_2Cl_2 (b) between 250 and 500 nm at 25 °C. The molar extinction (Δε) is normalized for the number of Q units for better comparability.

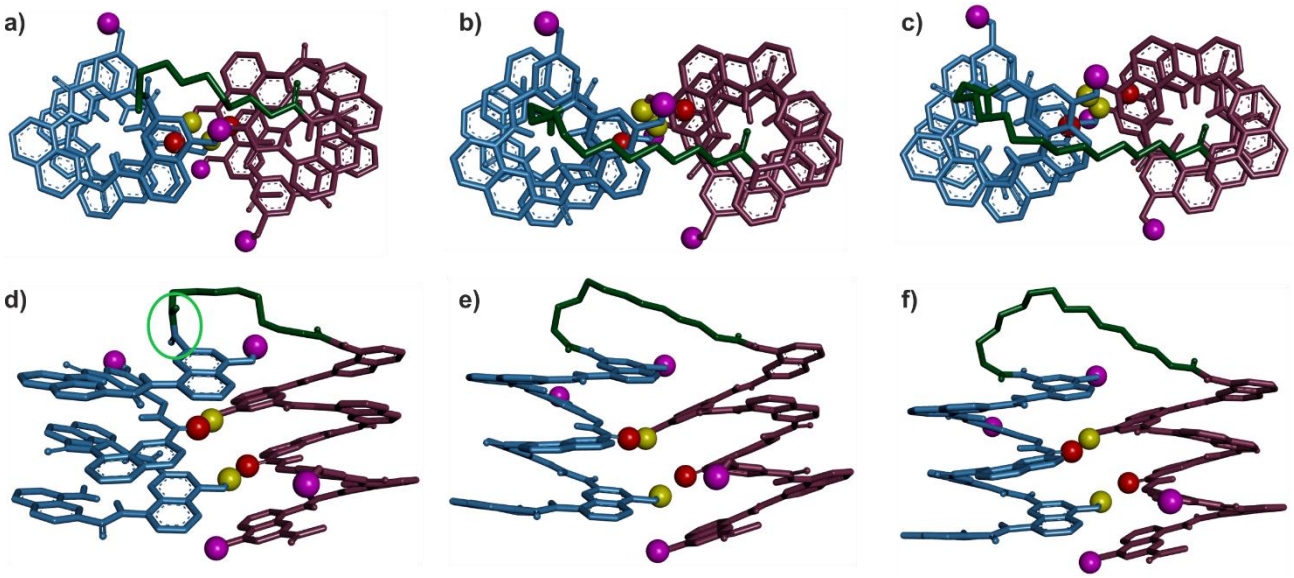


Figure S5. Energy minimized models[5] of *PM* shifted dimers[4] connected by flexible linkers of different lengths, showing hydroxy groups not involved in hydrogen bonding. Top view of a computational model[5] of a *PM* shifted dimer[4] containing a flexible linker unit with a flexible peg2 (a), peg3 (b) and peg4 (c) backbone, respectively. Side view of a computational model[5] of a *PM* shifted dimer[4] containing a flexible linker unit with a flexible peg2 (d), peg3 (e) and peg4 (f) backbone, respectively. Purple and blue helices represent *M*- and *P*-handedness, respectively. The hydroxyl protons and carbonyl oxygen atoms of the hydrogen-bonding arrays are shown as yellow and red balls. The flexible linker is shown in green. Hydrogen and other side-chains are omitted for clarity. The linker amide bond is turned out of the plane (marked in light green) in (d).

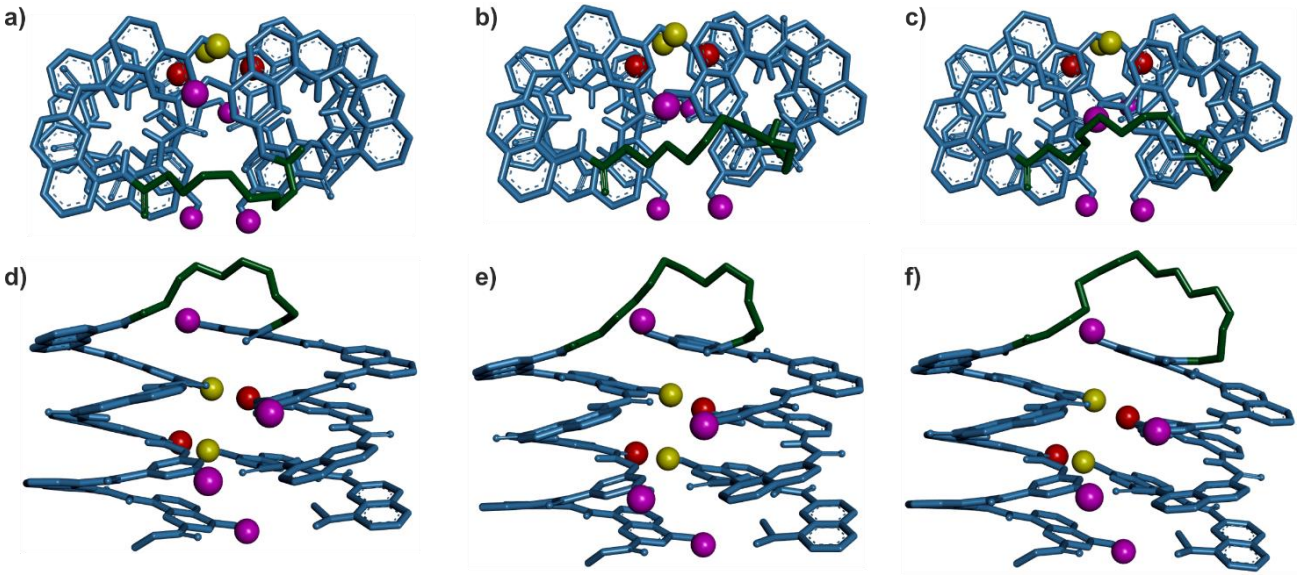


Figure S6. Energy minimized models[5] of *PP* shifted dimers[4] connected by flexible linkers of different lengths, showing hydroxy groups not involved in hydrogen bonding. Top view of a computational model[5] of a *PP* shifted dimer[4] containing a flexible linker unit with a flexible peg2 (a), peg3 (b) and peg4 (c) backbone, respectively. Side view of a computational model[5] of a *PP* shifted dimer[4] containing a flexible linker unit with a flexible peg2 (d), peg3 (e) and peg4 (f) backbone, respectively. The hydroxyl protons and carbonyl oxygen atoms of the hydrogen-bonding arrays are shown as yellow and red balls. Non-hydrogen-bonded hydroxyl groups are marked in brown. Blue helices represent *P*-handedness. The flexible linker is shown in dark green. Hydrogen and other side-chains are omitted for clarity.

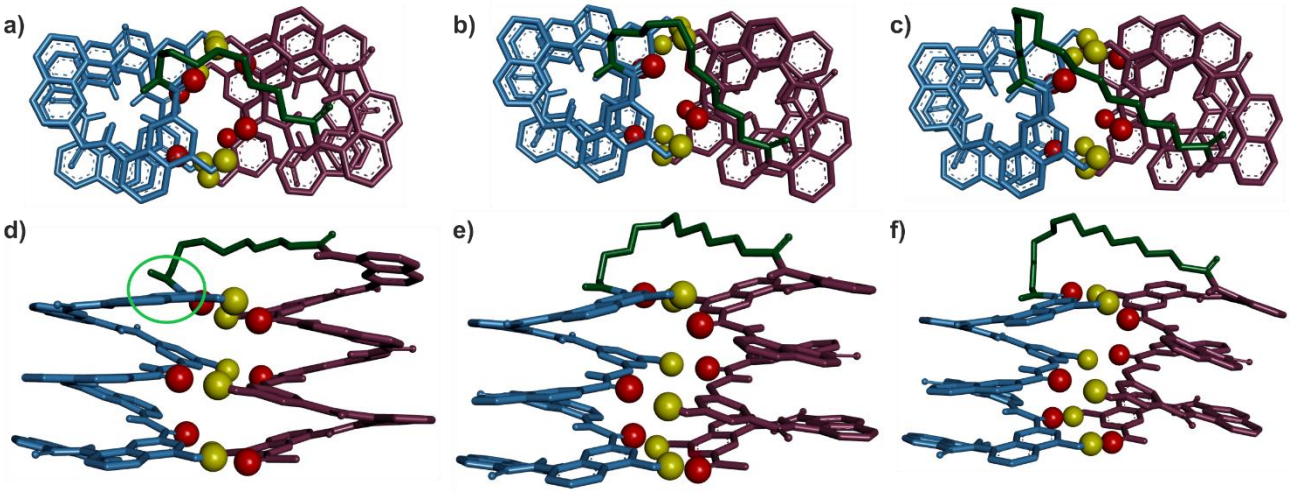


Figure S7. Energy minimized models[5] of *PM* parallel dimers[2] connected by flexible linkers of different lengths. Only minor perturbations are observed.[1, 4] Top view of a computational model[5] of a *PM* parallel dimer[2] containing a flexible linker unit with a flexible peg2 (a), peg3 (b) and peg4 (c) backbone, respectively. Side view of a computational model[5] of a *PM* parallel dimer[2] containing a flexible linker unit with a flexible peg2 (d), peg3 (e) and peg4 (f) backbone, respectively. Purple and blue helices represent *M*- and *P*-handedness, respectively. The hydroxyl protons and carbonyl oxygen atoms of the hydrogen-bonding arrays are shown as yellow and red balls. The flexible linker is shown in green. Hydrogen and other side-chains are omitted for clarity. The linker amide bond is turned out of the plane (marked in light green) in (d).

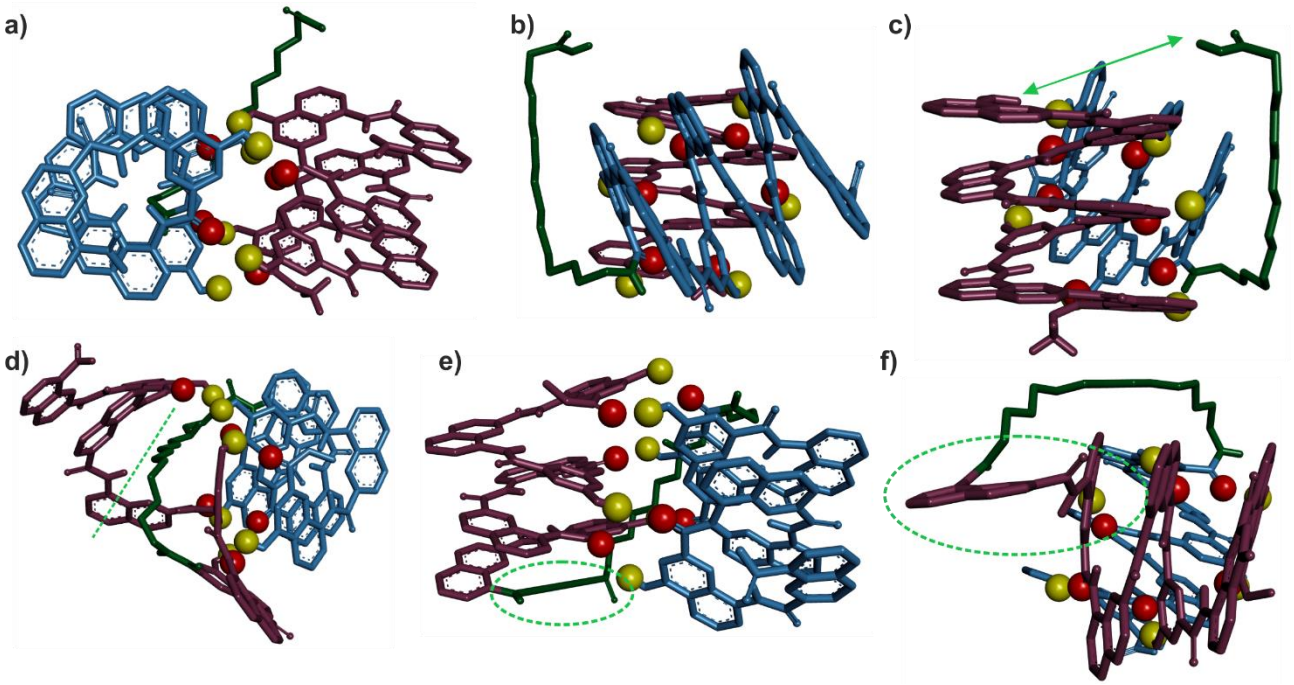


Figure S8. Energy minimized models[5] of *PM* clockwise tilted dimers emphasizing the insufficient length of even the longest linker. Top- (a), side- (b) and front-view (c) of a computational model[5] of a *PM* clockwise tilted dimer in respect to head-to-tail arrangement containing a flexible linker unit with a peg4-backbone. Here the flexible linker is only linked to one helix and not to the other. The great distance between the linker and the N-Terminus of the other not connected helix is marked by a green arrow in (c). This amplifies the unlikelihood of the formation of a *PM*-clockwise tilted dimer (with respect to head-to-head arrangement). Computational model[5] of a *PM*-clockwise tilted dimer (with respect to head-to-head arrangement) stabilized by a flexible linker with a peg4-backbone. Here the linker goes through the helix (d), part of the linker is stretched (e) or the helix-partially unfolds (f). The unlikely conformations are marked in green. The hydroxyl protons and carbonyl oxygen atoms of the hydrogen-bonding arrays are shown as yellow and red balls. Blue and purple helices represent *P*- and *M*-handedness, respectively. The flexible linker is shown in dark green. Hydrogens and other side-chains are omitted for clarity. This model has only been modelled in the case of a peg4-based linker.

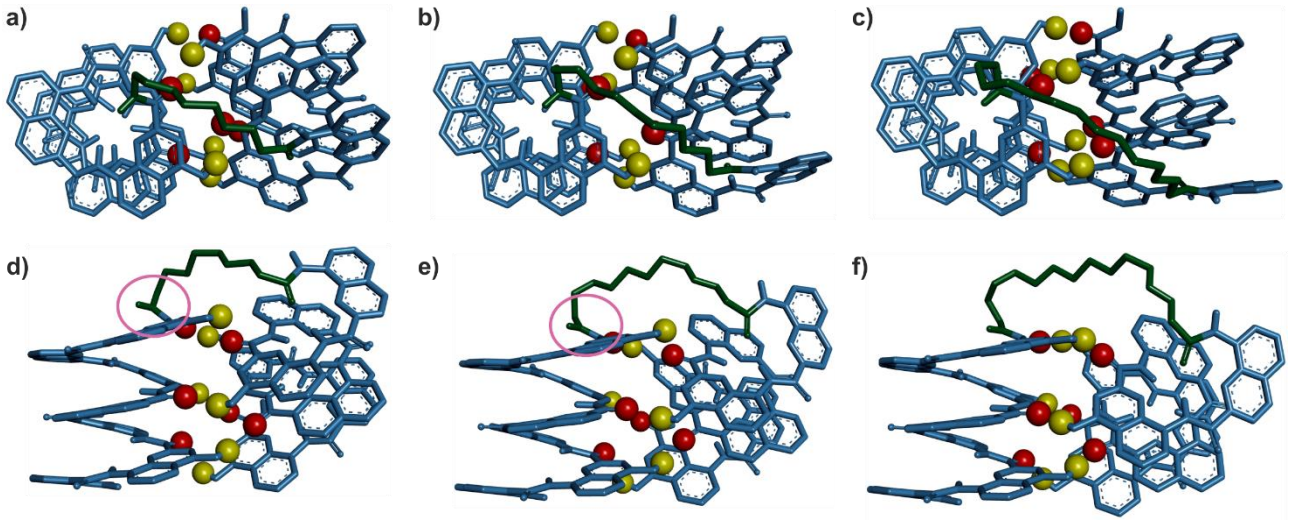


Figure S9. Energy minimized models[5] of *PP* counterclockwise tilted dimers connected by flexible linkers of different lengths. T3-2eg and T3-3eg linkers perturb the conformation. Top view of a computational model[5] of a *PP* counterclockwise tilted dimer with respect to head-to-head arrangement containing a flexible linker unit with a flexible peg2 (a), peg3 (b) and peg4 (c) backbone, respectively. Side view of a computational model[5] of a *PP* counterclockwise tilted dimer with respect to head-to-head containing a flexible linker unit with a flexible peg2 (d), peg3 (e) and peg4 (f) backbone, respectively. The hydroxyl protons and carbonyl oxygen atoms of the hydrogen-bonding arrays are shown as yellow and red balls. Blue helices represent *P*-handedness, respectively. The flexible linker is shown in dark green. Hydrogens and other side-chains are omitted for clarity. The linker amide bond is turned out of the plane (marked in pink) in (d) and (e).

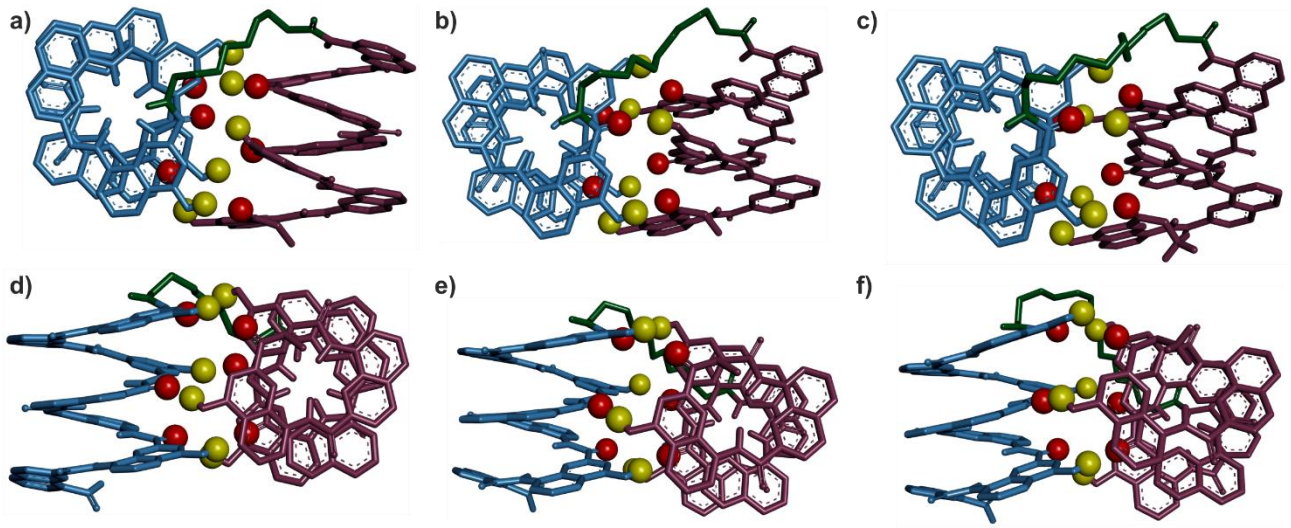


Figure S10. Energy minimized models[5] of *PM* counterclockwise tilted dimer connected by flexible linkers of different lengths.[6] Top view of a computational model[5] of a *PM* counterclockwise tilted dimer with respect to head-to-tail arrangement containing a flexible linker unit with a flexible peg2 (a), peg3 (b) and peg4 (c) backbone, respectively. Side view of a computational model[5] of a *PM* counterclockwise tilted dimer with respect to head-to-tail arrangement containing a flexible linker unit with a flexible peg2 (d), peg3 (e) and peg4 (f) backbone, respectively. The hydroxyl protons and carbonyl oxygen atoms of the hydrogen-bonding arrays are shown as yellow and red balls. Blue and purple helices represent *P*- and *M*-handedness, respectively. The flexible linker is shown in dark green. Hydrogens and other side-chains are omitted for clarity.

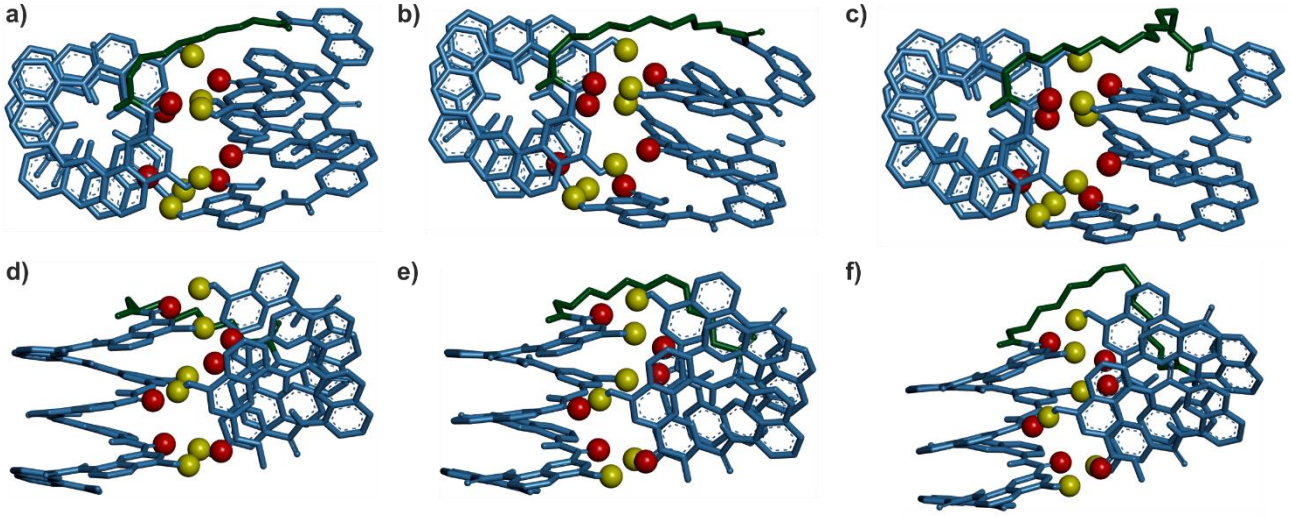


Figure S11. Energy minimized models[5] of *PP* clockwise tilted dimer connected by flexible linkers of different lengths. All linkers seem compatible witht the helix-helix arrangement.Top view of a computational model[5] of a *PP* clockwise tilted dimer with respect to head to head containing a flexible linker unit with a flexible peg2 (a), peg3 (b) and peg4 (c) backbone, respectively. Side view of a computational model[5] of a *PP* clockwise tilted dimer with respect to head to head containing a flexible linker unit with a flexible peg2 (d), peg3 (e) and peg4 (f) backbone, respectively. The hydroxyl protons and carbonyl oxygen atoms of the hydrogen-bonding arrays are shown as yellow and red balls. Blue helices represent *P*-handedness, respectively. The flexible linker is shown in dark green. Hydrogens and other side-chains are omitted for clarity. Blue helices represent *P*-handedness, respectively.

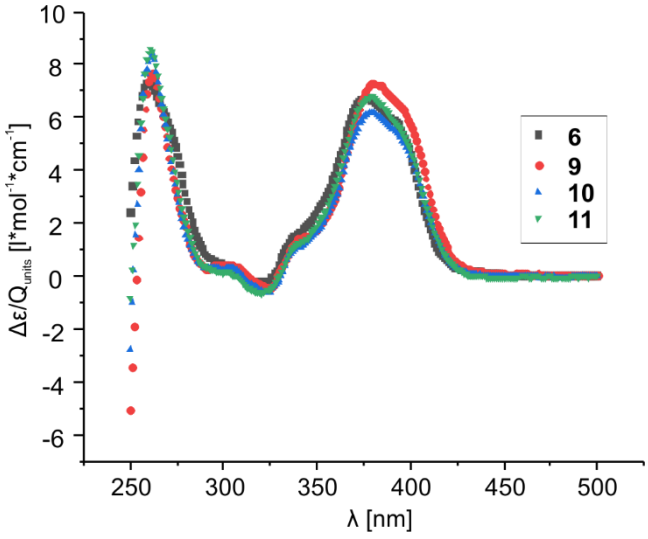


Figure S12. Confirmation of the formation of a *P*-homochiral species in 9-11. CD spectra of **6**, **9**, **10** and **11** in chloroform between 250 and 500 nm at 25 °C. The molar extinction (Δε) is normalized for the number of Q units for better comparability.

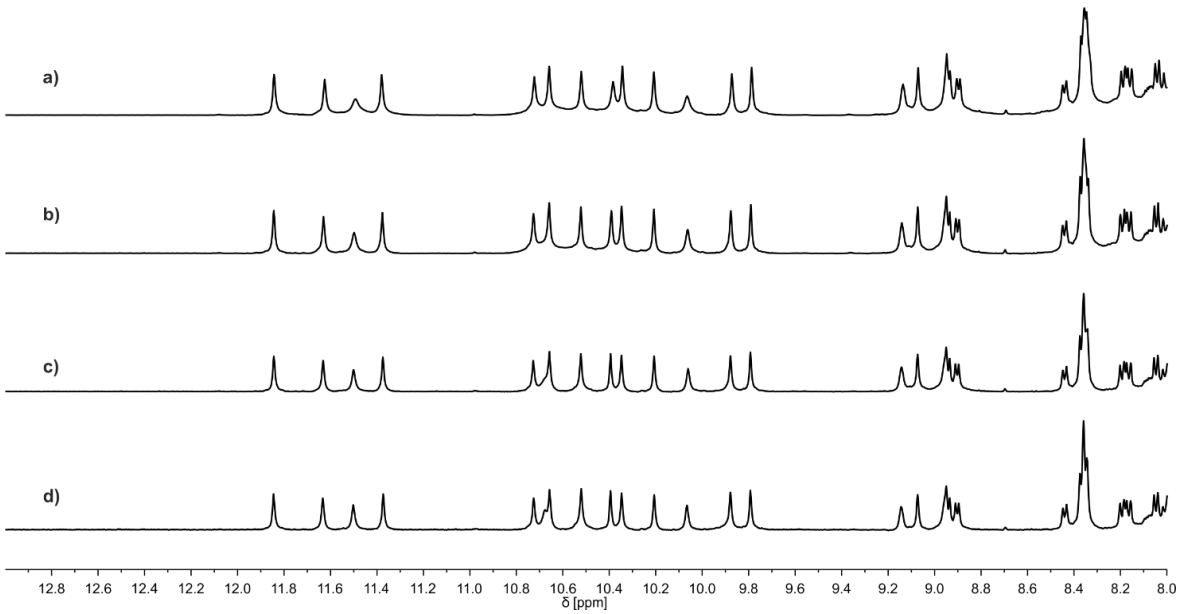


Figure S13. A single species of 9 prevails over a range of concentrations. Part of the ^{1}H NMR spectra (500 MHz, 25 °C) in $CDCl_3$ after 2 weeks showing amide resonances of **9** at 6.28 mM (a), 3.14 mM (b), 1.57 mM (c), and 0.79 mM (d), respectively.

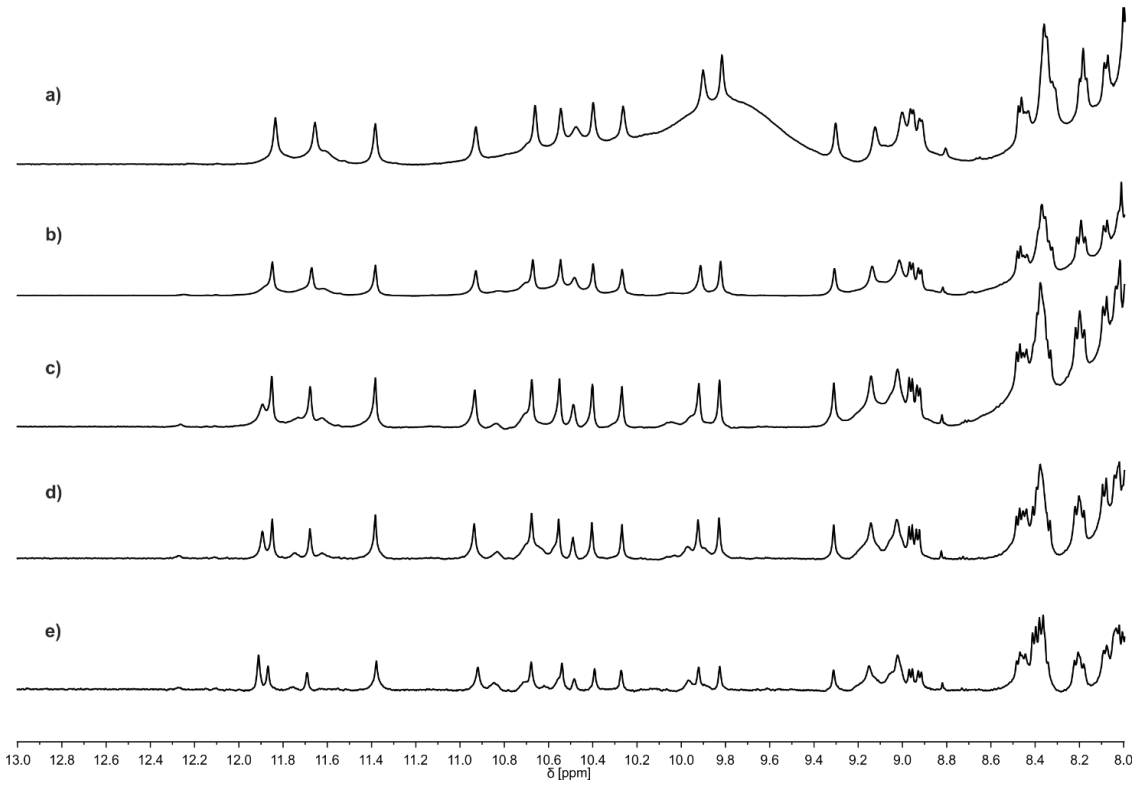


Figure S14. A single species of 10 prevails over a range of concentrations. Part of the ^{1}H NMR spectra (500 MHz, 25 °C) in $CDCl_3$ after 2 weeks showing amide resonances of **10** at 13.90 mM (a), 6.95 mM (b), 3.48 mM (c), 1.74 mM (d), and 0.87 mM (e), respectively.

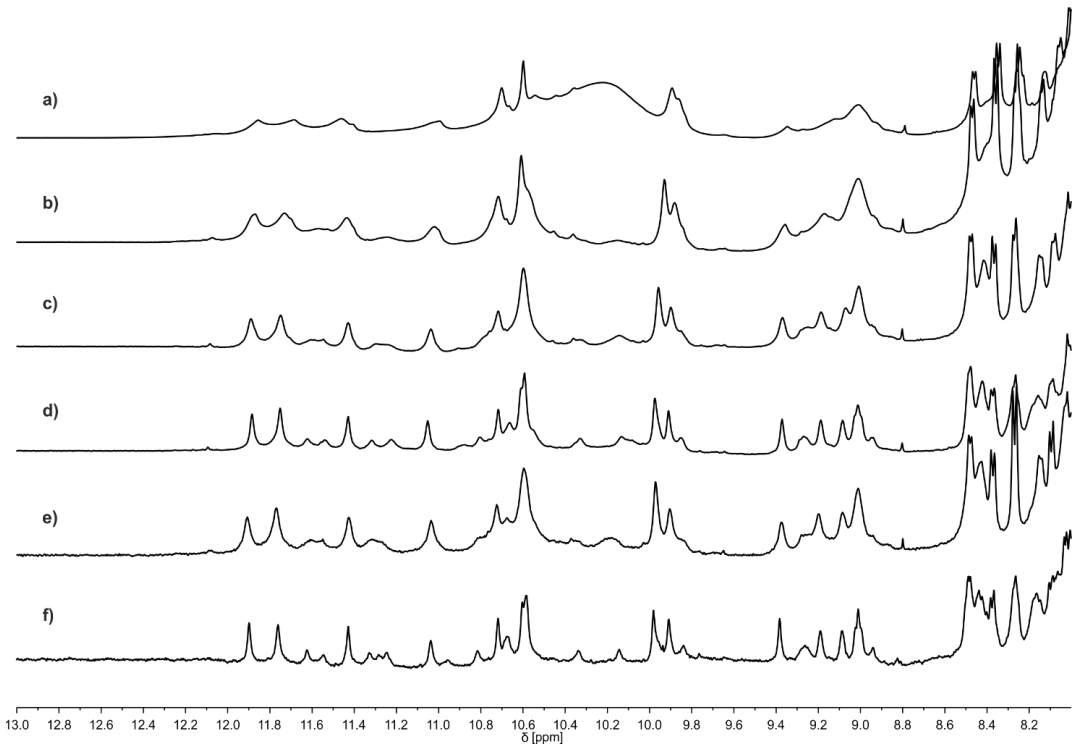


Figure S15. A single species of 11 prevails over a range of concentrations. Part of the ^{1}H NMR spectra (500 MHz, 25 °C) in $CDCl_3$ after 2 weeks showing amide resonances of **11** at 18.49 mM (a), 9.24 mM (b), 4.62 mM (c), 2.31 mM (d), 1.16 mM (e) and 0.58 mM (f), respectively.

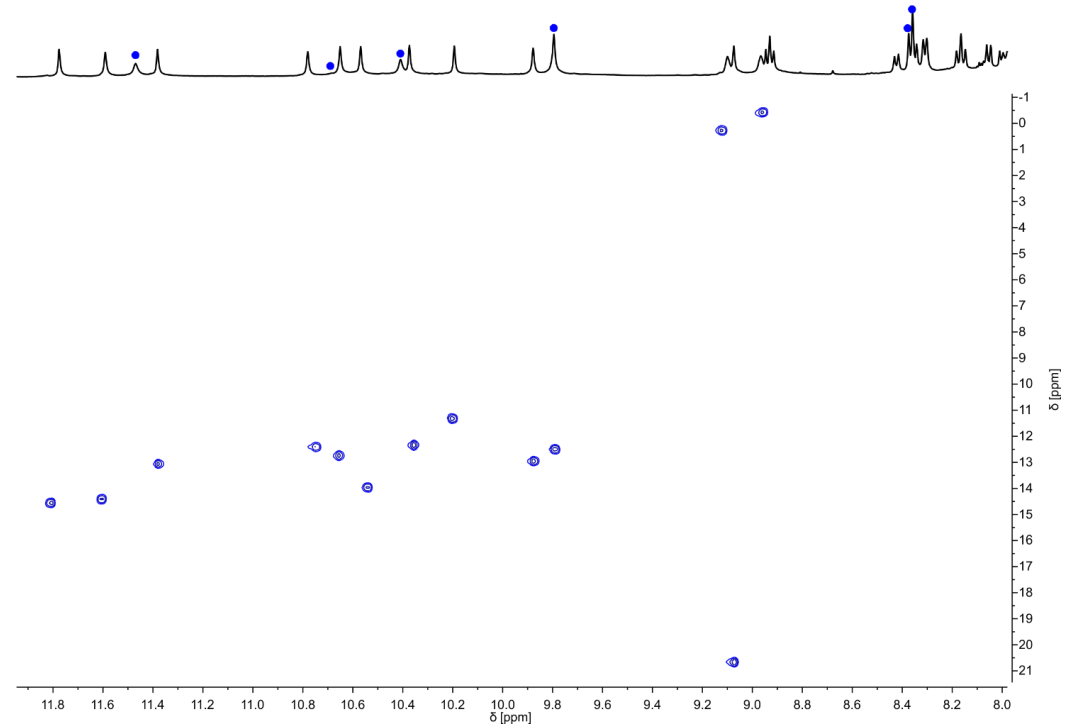


Figure S16. Identification of hydrogen bonded OH signals of 9 in $CDCl_3$. Part of the ^{1}H,^{15}N-HSQC NMR spectra (500 MHz, $CDCl_3$) at 25 °C showing amide resonances of **9** at 6.28 mM and 2 weeks after pyridine-treatment. Only NH resonances correlate, blue dots indicate the signals of OH protons.

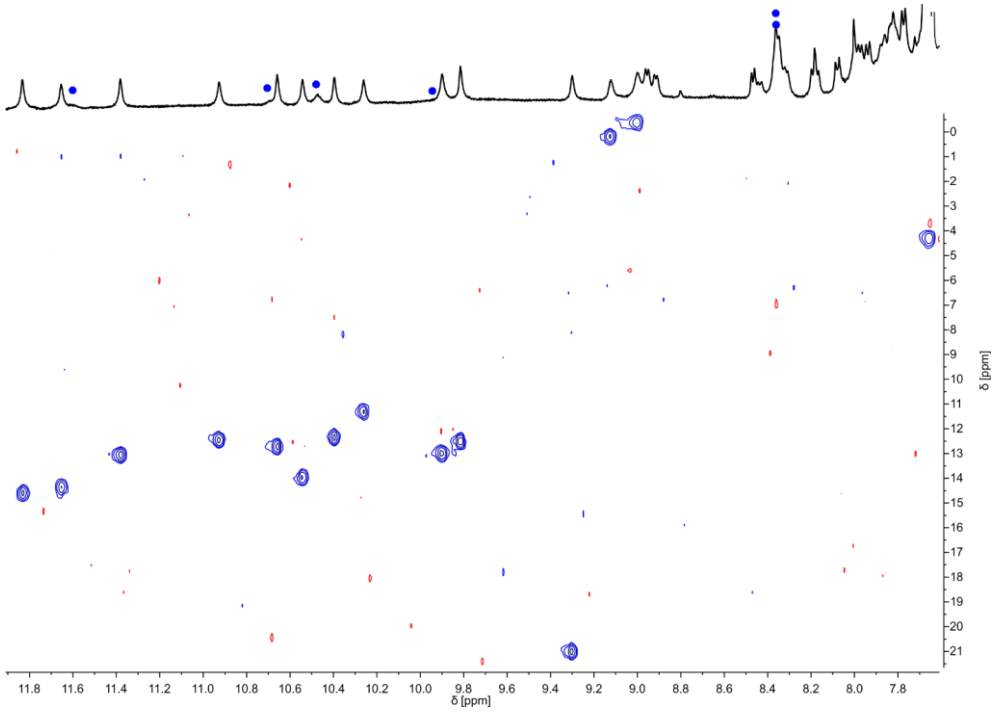


Figure S17. Identification of hydrogen bonded OH signals of 10 in $CDCl_3$. Part of the $^{1}H,^{15}N$-HSQC NMR spectra (500 MHz, $CDCl_3$) at 25 °C showing amide resonances of **10** at 13.90 mM and 2 weeks after pyridine-treatment. Only NH resonances correlate, blue dots indicate the signals of OH protons.

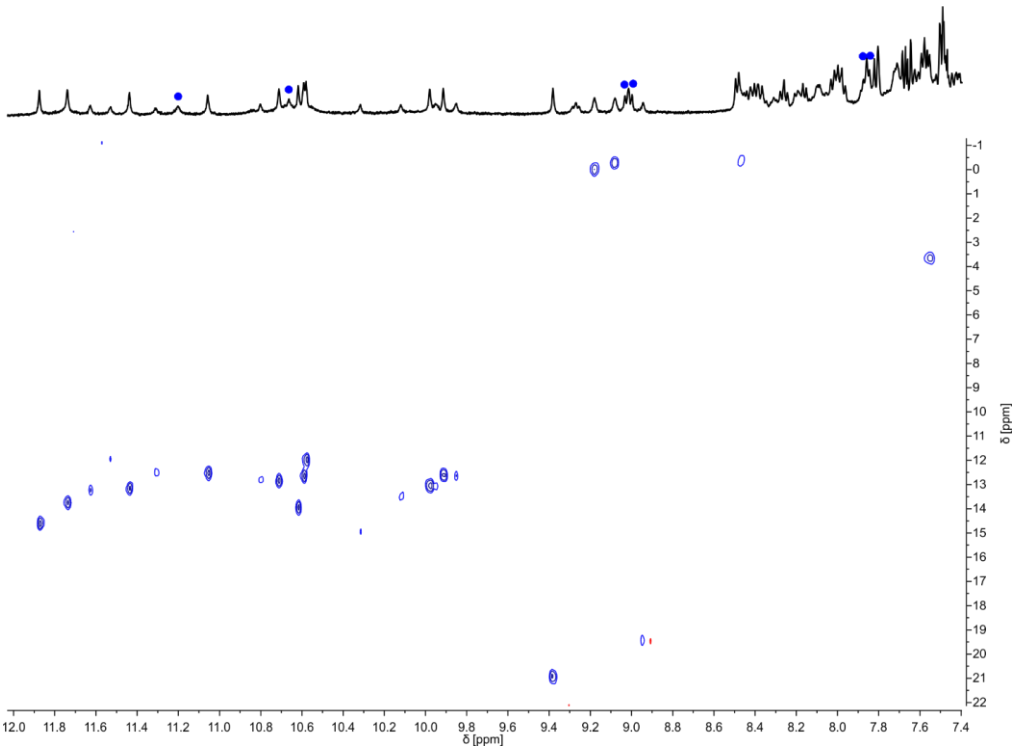


Figure S18. **Identification of hydrogen bonded OH signals of 11 in $CDCl_3$.** Part of the $^{1}H,^{15}N$-HSQC NMR spectra (500 MHz, $CDCl_3$) at 25 °C showing amide resonances of **11** at 2.31 mM and 2 weeks after pyridine-treatment. Only NH resonances correlate, blue dots indicate the signals of OH protons.

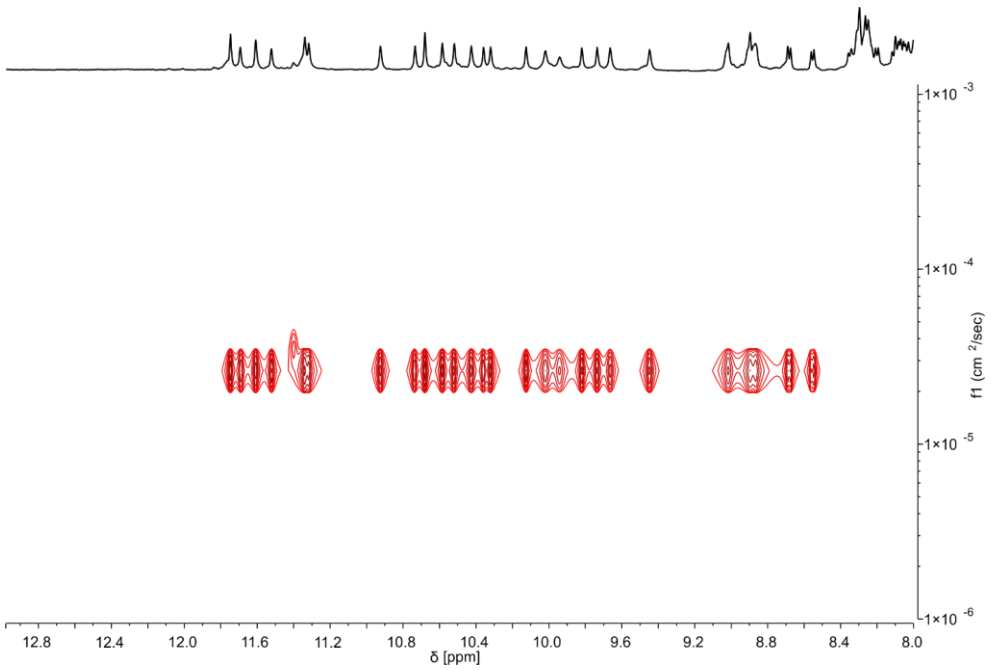


Figure S19. Compound 9 has the same hydrodynamic radius as its protected precursor, and is thus monomeric. Extract of ^{1}H DOSY (500 MHz, $CDCl_3$) at 25 °C of a 1 to 1 mixture of **9** and its protected precursor **24** each at 1.62 mM, and after 3 weeks showing amide resonances and hydrogen-bonded hydroxyl groups, respectively. Δ = 115 ms, δ = 0.6 ms. The extracted value of the diffusion coefficient of **9** and **24** is 2.67×10^{-5}, each.

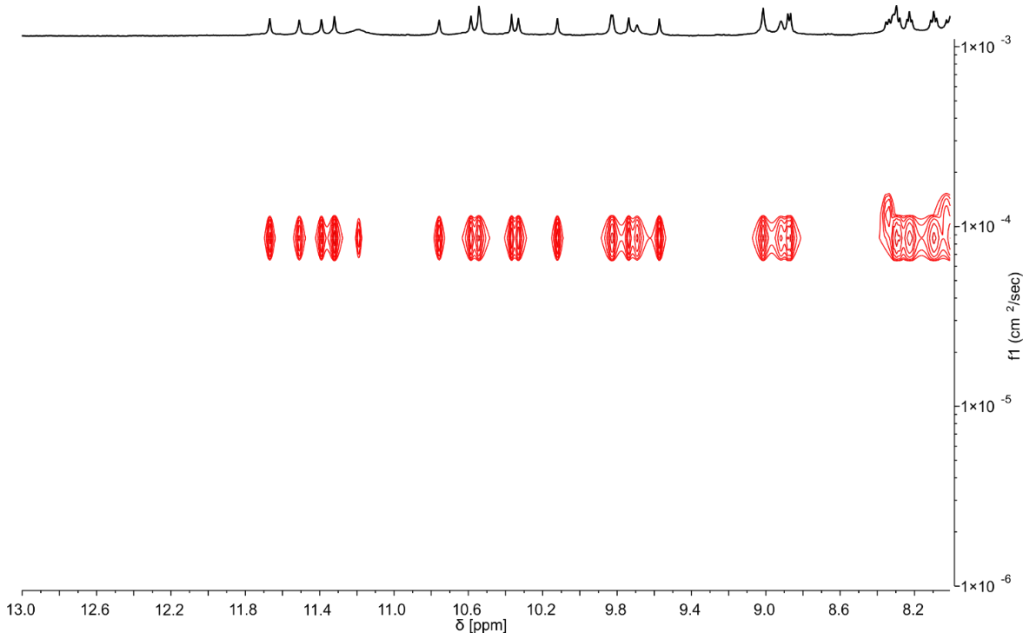


Figure S20. Compound 9 has a similiar hydrodynamic radius to 10, 11, 13, 15 and 17. Extract of ^{1}H DOSY (500 MHz, $CDCl_3$) at 25 °C of **9** at 1.62 mM and after 2 weeks showing amide resonances and hydrogen-bonded hydroxyl groups, respectively. Δ = 75 ms, δ = 0.6 ms. The extracted value of the diffusion coefficient of **9** is 8.62×10^{-5}.

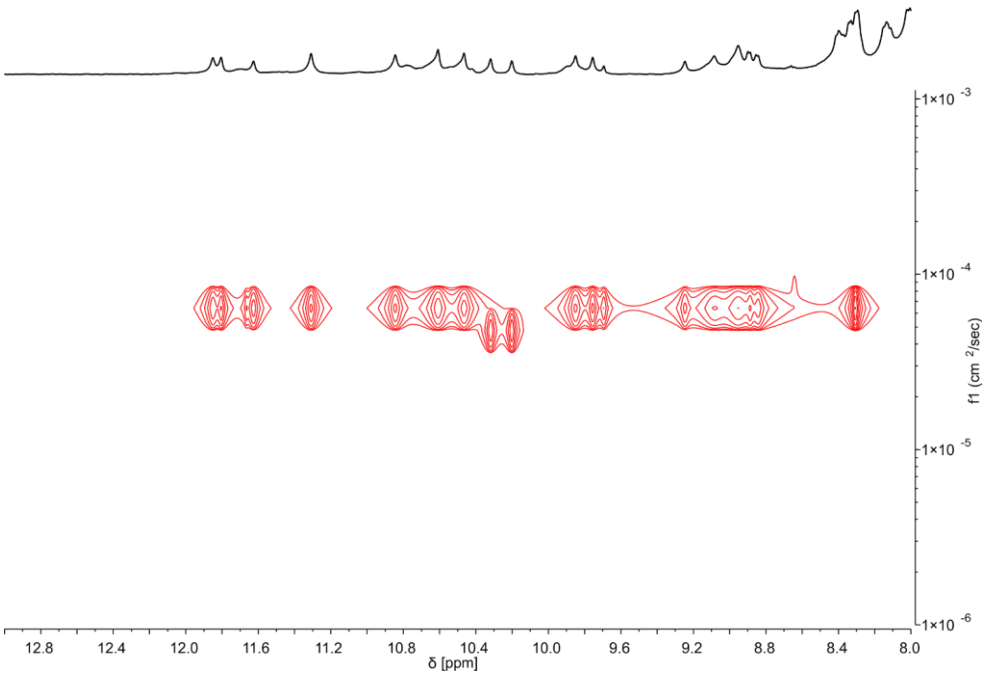


Figure S21. Compound 10 has a similiar hydrodynamic radius to 9, 11, 13, 15 and 17. Extract of ^{1}H DOSY (500 MHz, $CDCl_3$) at 25 °C of **10** at 1.62 mM and after 2 weeks showing amide resonances and hydrogen-bonded hydroxyl groups, respectively. Δ = 250 ms, δ = 0.6 ms. The extracted value of the diffusion coefficient of **10** is 6.40 × 10^{-5}.

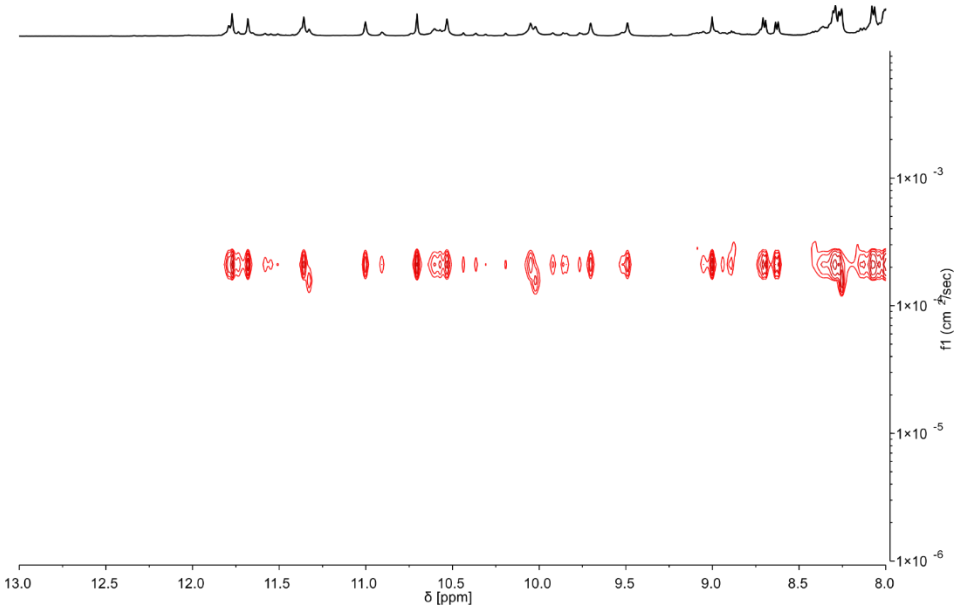


Figure S22. Compound 10 has the same hydrodynamic radius as its protected precursor, and is thus monomeric. Extract of ^{1}H DOSY (500 MHz, $CDCl_3$) at 25 °C of a 1 to 1 mixture of **10** and its protected precursor **26** at 1.39 mM, each and after 2 days showing amide resonances and hydrogen-bonded hydroxyl groups, respectively. Here signals corresponding to **10** are more broad. Δ = 250 ms, δ = 0.6 ms. The extracted value of the diffusion coefficient of **10** and **26** is 2.10 × 10^{-4}, each.

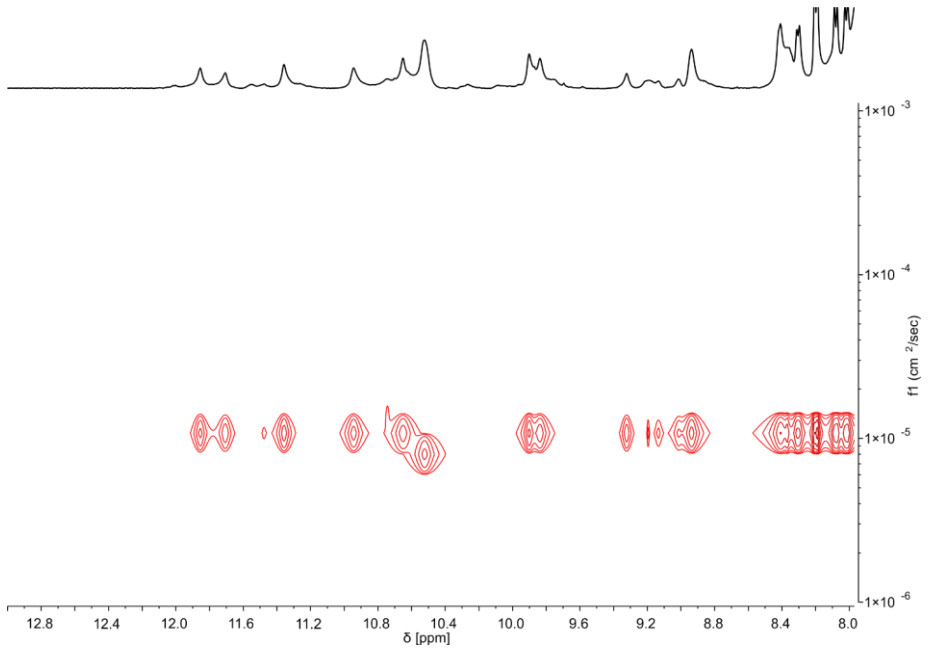


Figure S23. Compound 11 has a similiar hydrodynamic radius to 9, 10, 13, 15 and 17, and is thus monomeric. Extract of ^{1}H DOSY (400 MHz, $CDCl_3$) at 25 °C of **11** at 1.39 mM and after 2 weeks showing amide resonances and hydrogen-bonded hydroxyl groups, respectively. Δ = 200 ms, δ = 0.6 ms. The extracted value of the diffusion coefficient of **11** is 1.08×10^{-5}.

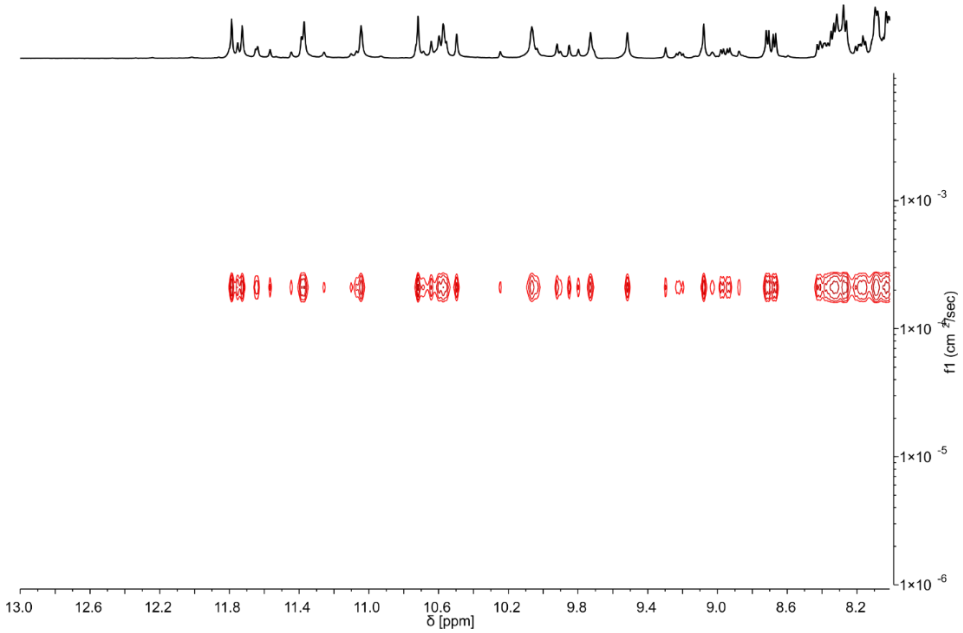


Figure S24. Compound 11 has the same hydrodynamic radius as its protected precursor, and is thus monomeric. Extract of ^{1}H DOSY (500 MHz, $CDCl_3$) at 25 °C of a 1 to 1 mixture of **11** and its protected precursor **28** at 1.39 mM, each and after 12 hours showing amide resonances and hydrogen-bonded hydroxyl groups, respectively. Here signals corresponding to **11** are more broad and a 2nd species is formed. Δ = 200 ms, δ = 0.6 ms. The extracted value of the diffusion coefficient of **11** and **28** is 2.10×10^{-4}, each.

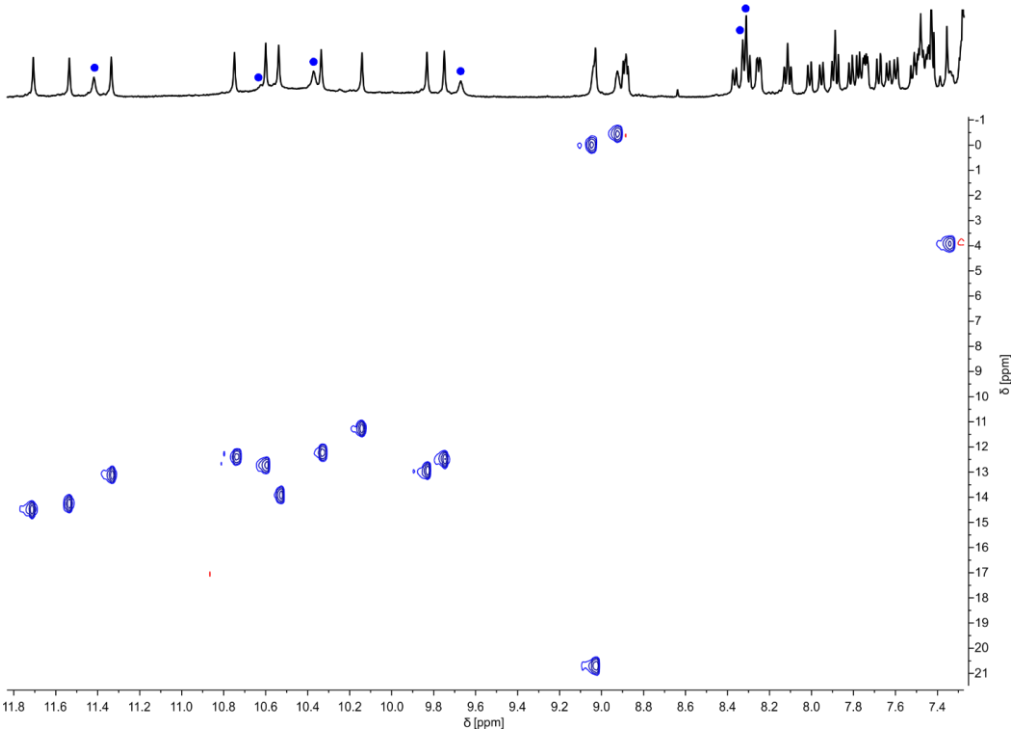


Figure S25. **Identification of hydrogen bonded OH signals of 12 in $CDCl_3$.** Part of the $^{1}H,^{15}N$-HSQC NMR spectra (500 MHz, $CDCl_3$) at 25 °C showing amide resonances of **12** at 15.04 mM and 2 weeks after pyridine-treatment. Only NH resonances correlate, blue dots indicate the signals of OH protons.

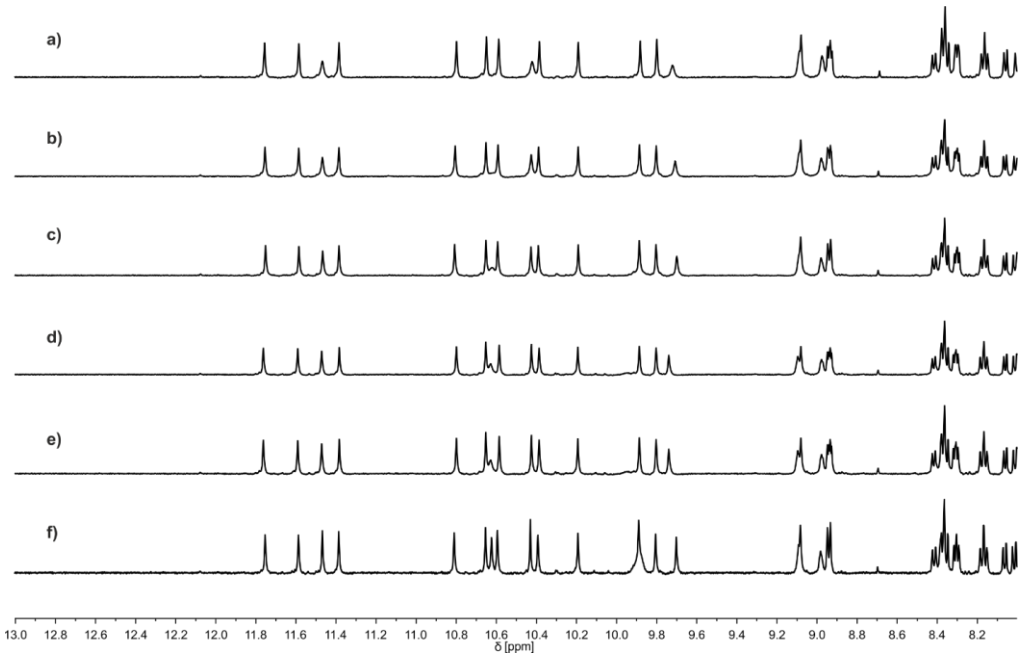


Figure S26. The spectrum of 12 does not depend on concentration. Part of the ^{1}H NMR spectra (500 MHz, 25 °C) in $CDCl_3$ after 2 weeks showing amide resonances of **12** at 15.04 mM (a), 7.52 mM (b), 3.76 mM (c), 1.88 mM (d), 0.94 mM (e) and 0.47 mM (f), respectively.

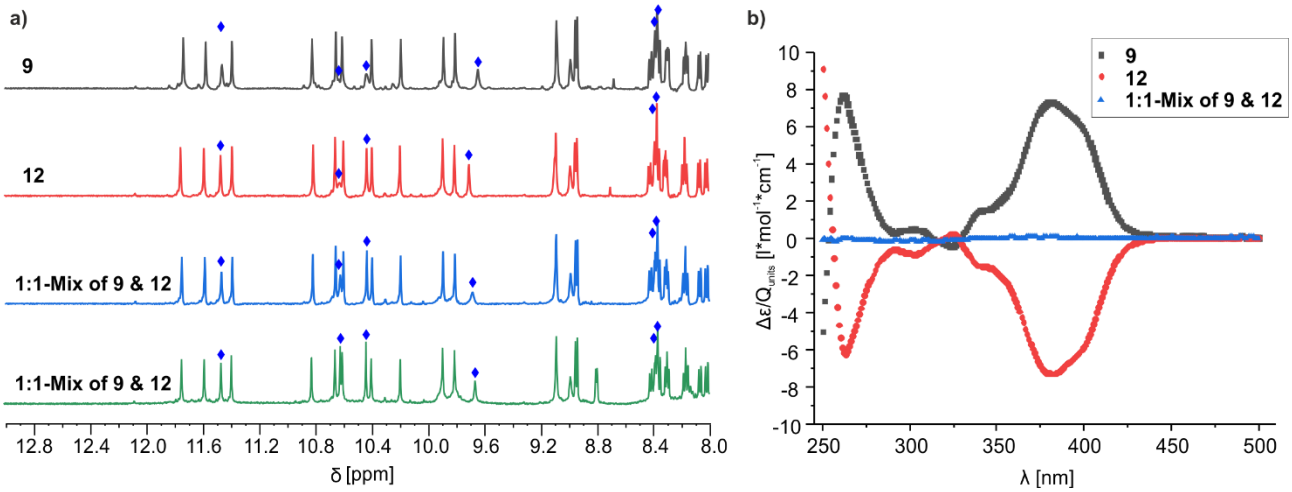


Figure S27. Compound 9 and 12 form the enantiomeric species and fold without interfering with one another. Extracts of ^{1}H NMR spectra (500 MHz, 25 °C) of **9**, **12** and a 1:1-mixture of **9** and **12** in $CDCl_3$ at 2.3 mM (in total) each before (blue) and after disruption by pyridine (green) showing the amide region and hydrogen-bonded hydroxyl groups (a). CD spectra of **9**, **12** and a 1:1-mixture of **9** and **12** in $CHCl_3$ before disruption by pyridine between 250 and 500 nm (b). The molar extinction (Δε) is normalized for the number of Q units for better comparability.

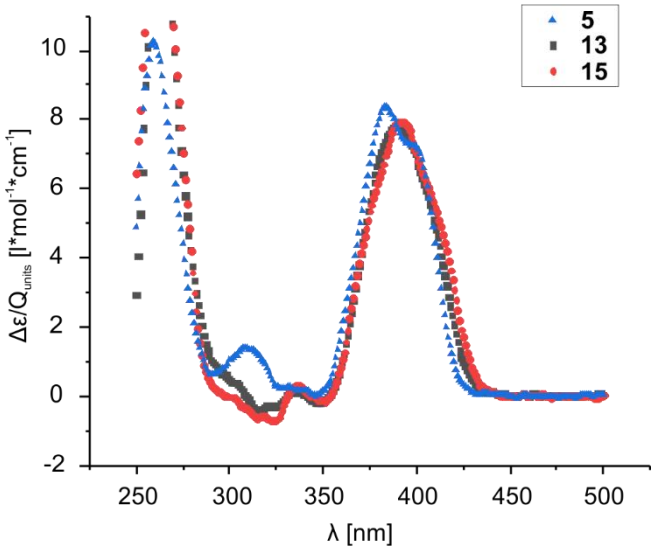


Figure S28. **Assignment of *P*-helicity in 13 and 15.** CD spectra of **5**, **13** and **15** in chloroform between 250 and 500 nm at 25 °C. The molar extinction (Δε) is normalized for the number of Q units for better comparability.

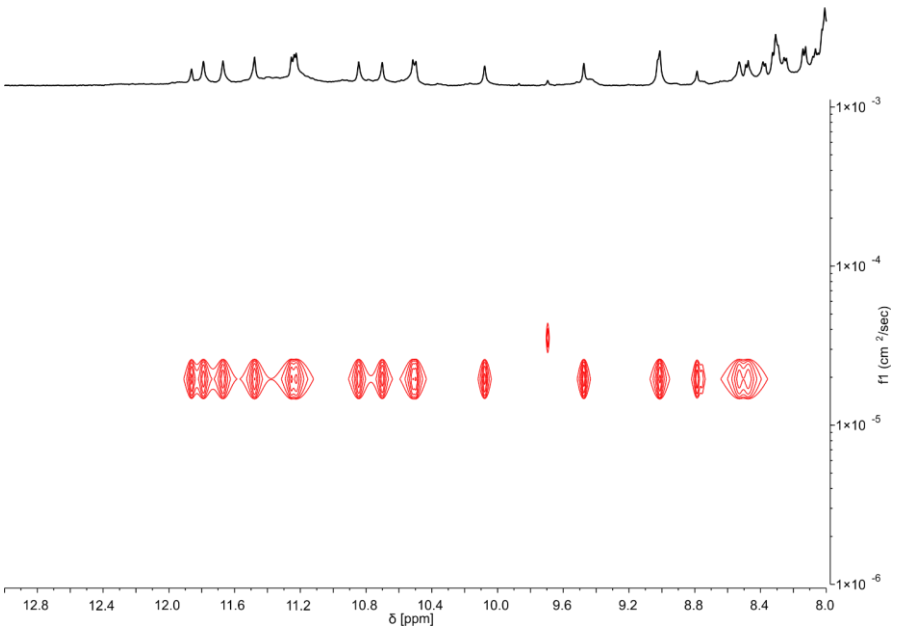


Figure S29. Compound 13 has a similiar hydrodynamic radius to 9, 10, 11, 15 and 17, and is thus monomeric. Extract of ^{1}H DOSY (400 MHz, $CDCl_3$) at 25 °C of **13** at 1.62 mM and after 2 weeks showing amide resonances and hydrogen-bonded hydroxyl groups, respectively. Δ = 275 ms, δ = 0.6 ms. The extracted value of the diffusion coefficient of **13** is 1.95×10^{-5}.

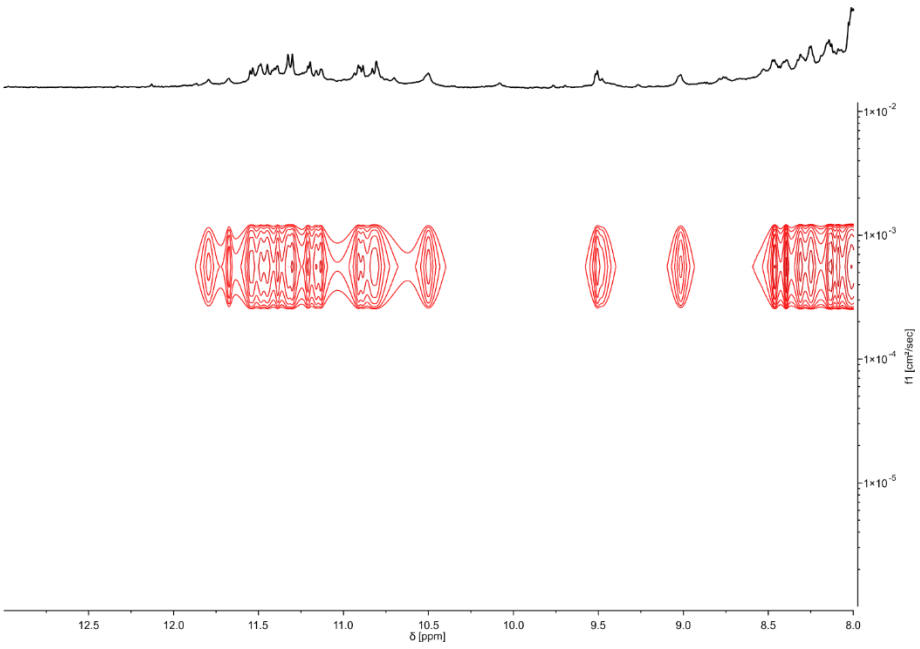


Figure S30. Compound 13 has the same hydrodynamic radius as its protected precursor, and is thus monomeric. Extract of ^{1}H DOSY (500 MHz, $CDCl_3$) at 25 °C of a 1 to 1 mixture of **13** and its protected precursor **32** at 0.74 mM, each and after 4 days showing amide resonances and hydrogen-bonded hydroxyl groups, respectively. Here some signals corresponding to **13** appear more broad. Δ = 275 ms, δ = 0.6 ms. The extracted value of the diffusion coefficient of **13** and **32** is 5.56×10^{-4}, each.

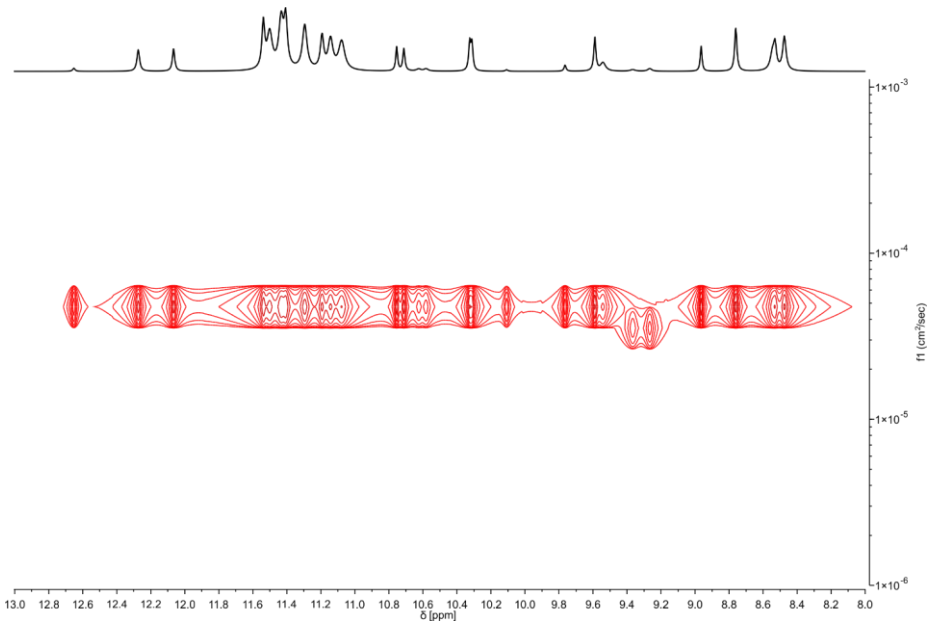


Figure S31. Compound 15 has a similiar hydrodynamic radius to 9, 10, 11, 13 and 17, and is thus monomeric. Extract of ^{1}H DOSY (500 MHz, $CDCl_3$) at 25 °C of **15** at 1.62 mM and after 2 weeks showing amide resonances and hydrogen-bonded hydroxyl groups, respectively. Δ = 100 ms, δ = 0.6 ms. The extracted value of the diffusion coefficient of **15** is 4.76 × 10^{-5}.

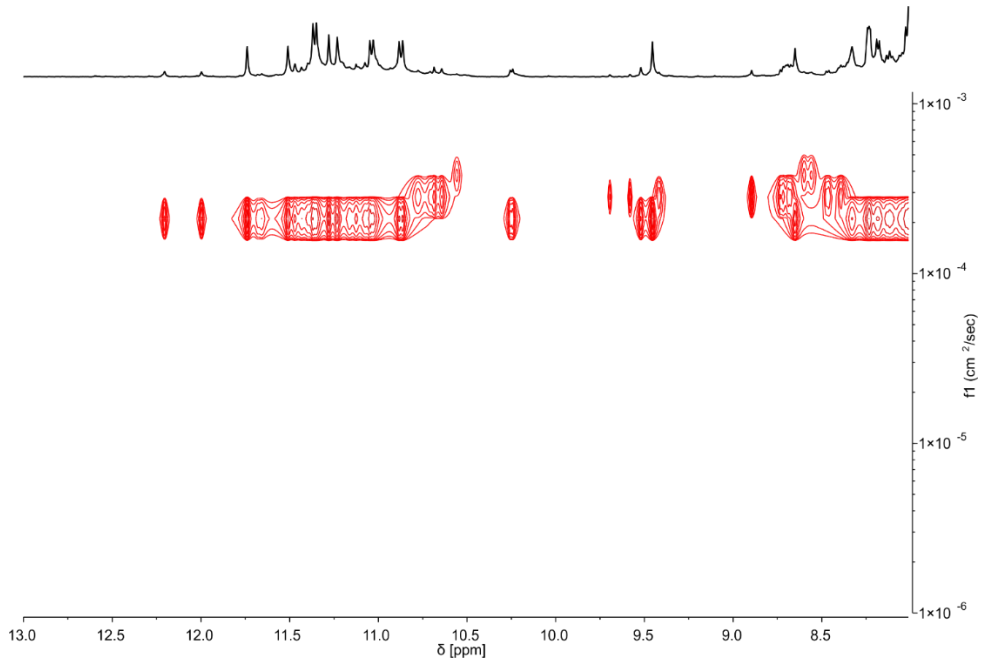


Figure S32. Compound 15 has the same hydrodynamic radius as its protected precursor, and is thus monomeric. Extract of ^{1}H DOSY (500 MHz, $CDCl_3$) at 25 °C of a 1 to 1 mixture of **15** and its protected precursor **36** at 0.4 mM and 1.39 mM, respectively and after 1 week showing amide resonances and hydrogen-bonded hydroxyl groups, respectively. Δ = 275 ms, δ = 0.6 ms. The extracted value of the diffusion coefficient of **15** and **36** is 2.11 × 10^{-4}, each.

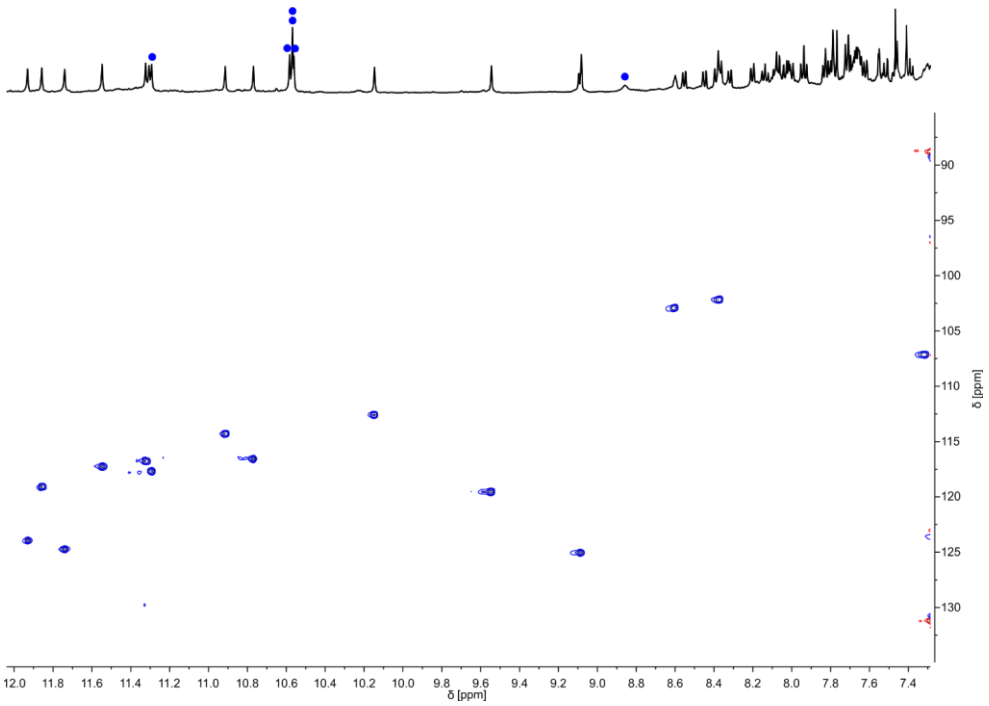


Figure S33. Identification of hydrogen bonded OH signals of 13 in $CDCl_3$. Part of the $^{1}H,^{15}N$-HSQC NMR spectra (500 MHz, $CDCl_3$) at 25 °C showing amide resonances of **13** at 7.73 mM and 2 weeks after pyridine-treatment. Only NH resonances correlate, blue dots indicate the signals of OH protons.

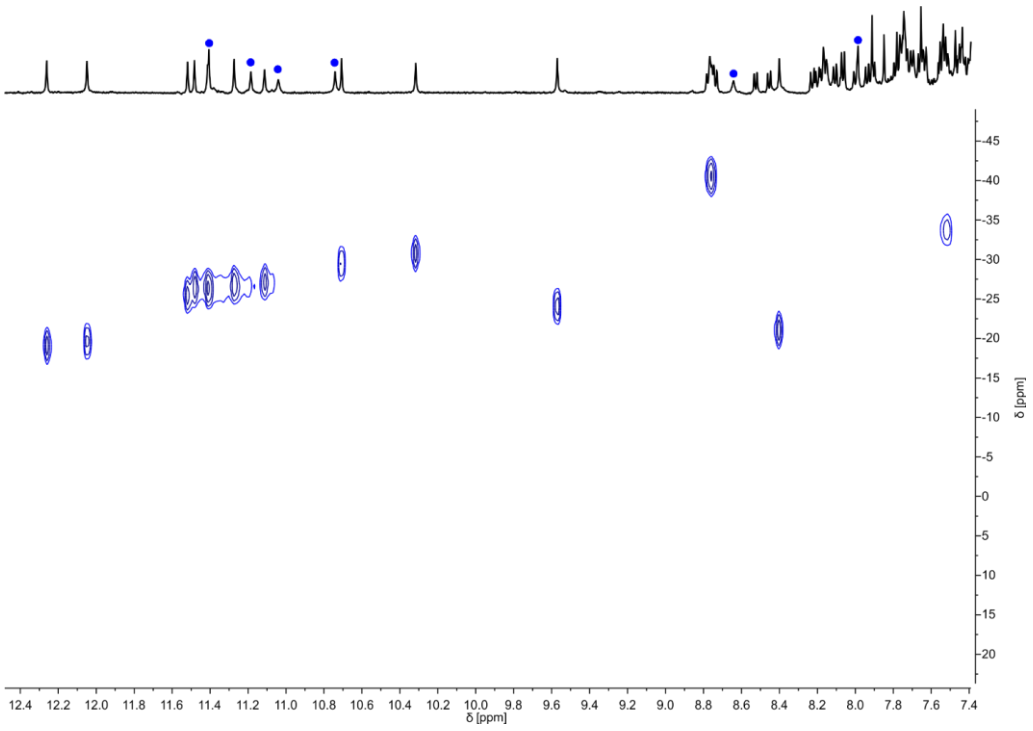


Figure S34. **Identification of hydrogen bonded OH signals of 15 in $CDCl_3$.** Part of the $^{1}H,^{15}N$-HSQC NMR spectra (500 MHz, $CDCl_3$) at 25 °C showing amide resonances of **15** at 9.0 mM and 2 weeks after pyridine-treatment. Only NH resonances correlate, blue dots indicate the signals of OH protons.

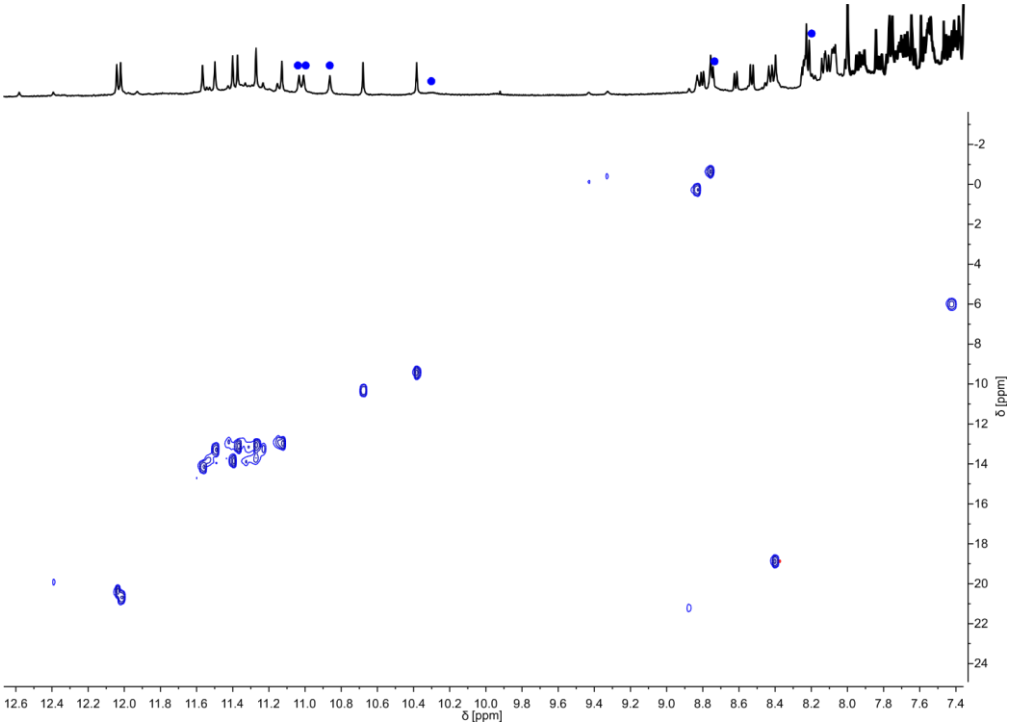


Figure S35. Identification of hydrogen bonded OH signals of 17 in $CDCl_3$. Part of the $^{1}H,^{15}N$-HSQC NMR spectra (500 MHz, $CDCl_3$) at 25 °C showing amide resonances of **17** at 7.73 mM and 2 weeks after pyridine-treatment. Only NH resonances correlate, blue dots indicate the signals of OH protons.

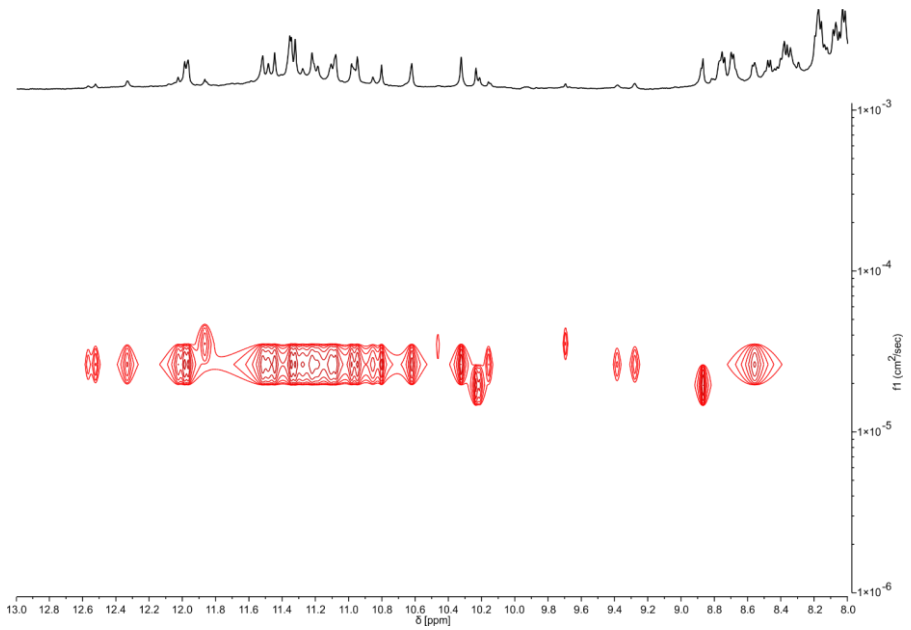


Figure S36. Compound 17 has a similiar hydrodynamic radius to 9-11, 13 & 15, and is thus monomeric. Extract of ^{1}H DOSY (500 MHz, CDCl3) at 25 °C of **17** at 1.62 mM and after 2 weeks showing amide resonances and hydrogen-bonded hydroxyl groups, respectively. Δ = 100 ms, δ = 1.0 ms. The extracted value of the diffusion coefficient of **17** is 2.63 × 10^{-5}.

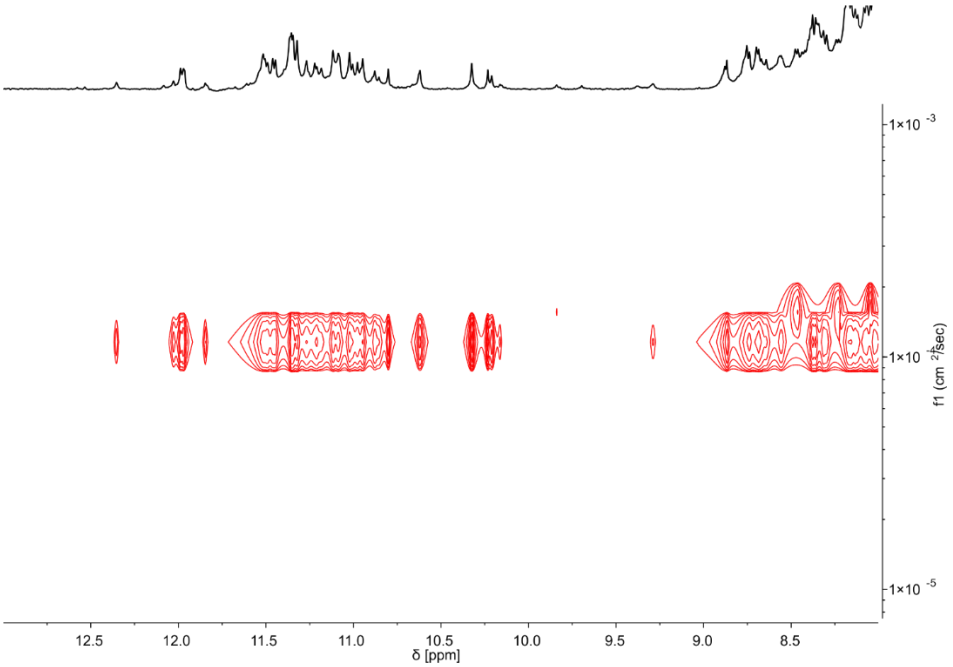


Figure S37. Compound 17 has the same hydrodynamic radius as its protected precursor, and is thus monomeric. Extract of ^{1}H DOSY (500 MHz, $CDCl_3$) at 25 °C of a 1 to 1 mixture of **17** and its protected precursor **40** at 0.45 mM, each and after 1 week showing amide resonances and hydrogen-bonded hydroxyl groups, respectively. Δ = 110 ms, δ = 1.0 ms. The extracted value of the diffusion coefficient of **17** and **40** is 1.16 × 10^{-4}, each.

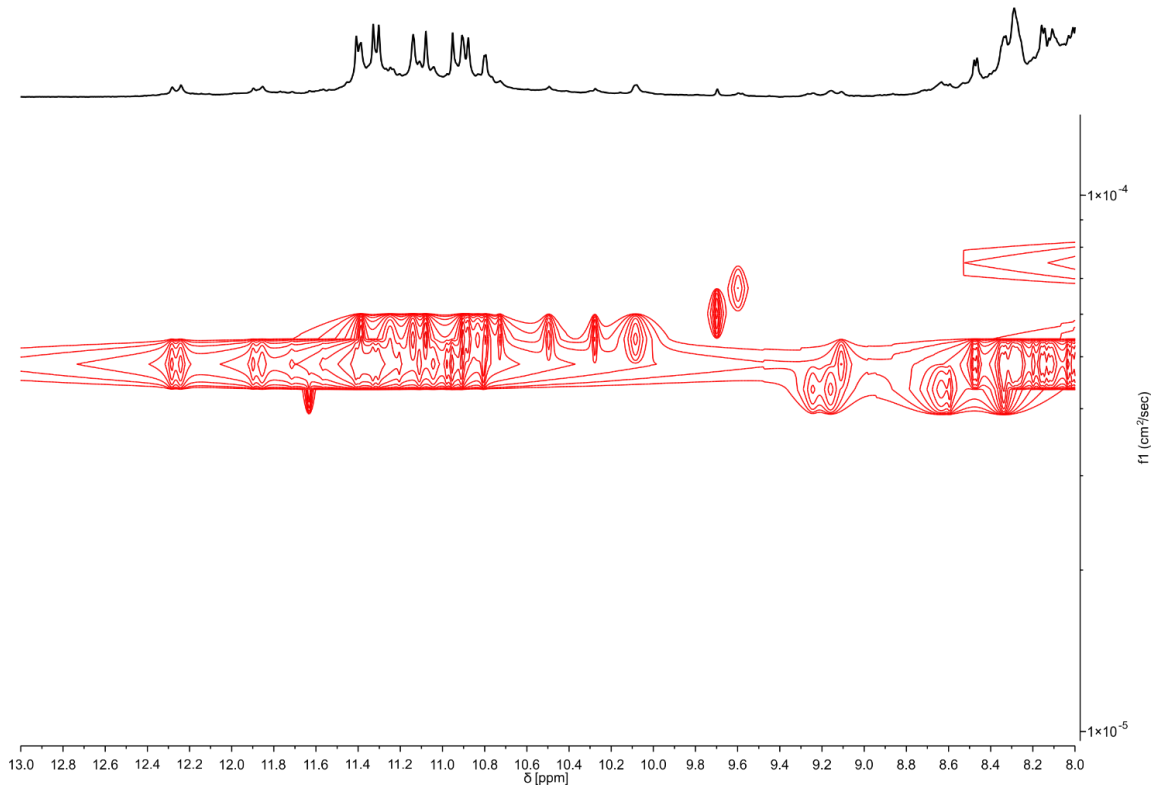


Figure S38. Compound 16 has a different hydrodynamic radius from its protected precursor. Extract of ^{1}H DOSY (500 MHz, $CDCl_3$) at 25 °C of a 1 to 1 mixture of **16** and its protected precursor **38** at 3.24 mM, respectively and after 3 weeks showing amide resonances and hydrogen-bonded hydroxyl groups, respectively. Δ = 110 ms, δ = 1.0 ms. The extracted value of the diffusion coefficient of **16** and **38** is 4.81×10^{-5} and 5.32×10^{-5}, respectively.

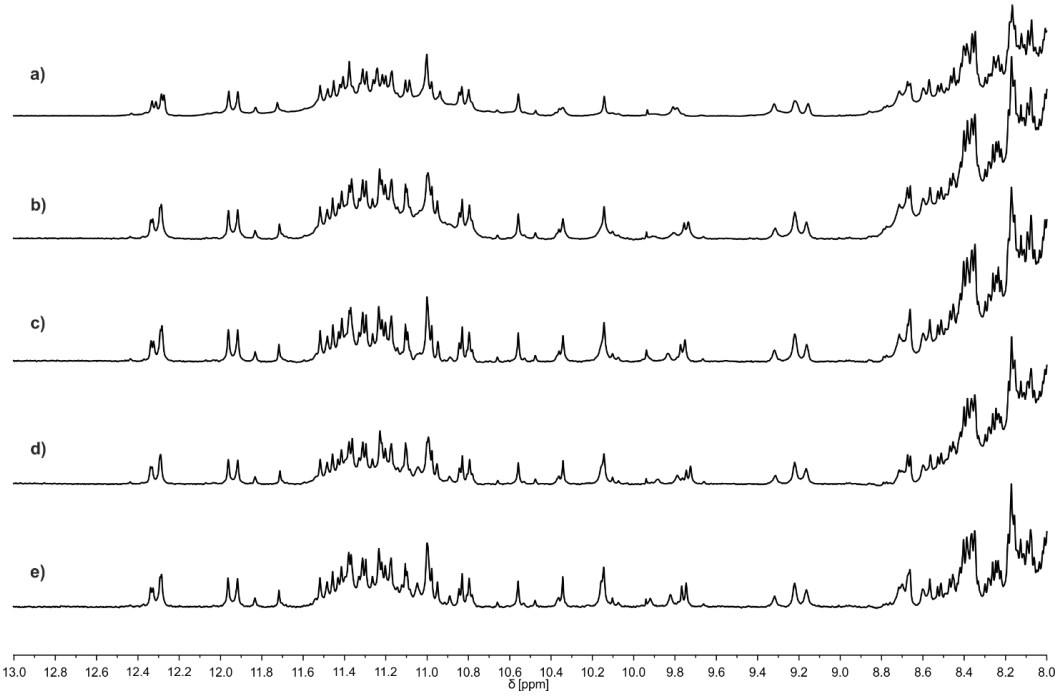


Figure S39. The spectrum of 16 does not depend on concentration. Part of the ^{1}H NMR spectra (500 MHz, 25 °C) in $CDCl_3$ after 2 weeks showing amide resonances of **16** at 7.41 mM (a), 3.70 mM (b), 1.85 mM (c), 0.93 mM (d) and 0.46 mM (e), respectively.

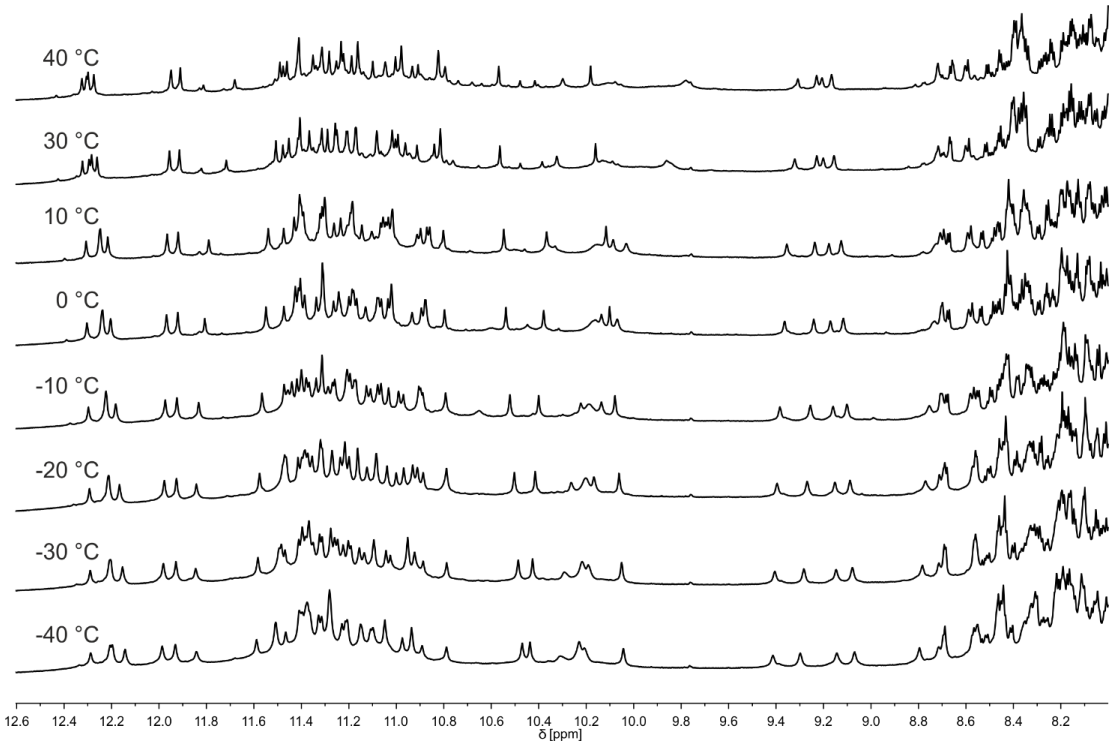


Figure S40. The aggregate formed by 16 is stable over a wide range of temperature. Part of the 800 MHz ^{1}H NMR spectra of **16** (6.90 mM in $CDCl_3$) showing the amide and hydroxy proton resonances at different temperatures. The corresponding temperatures are indicated at left.

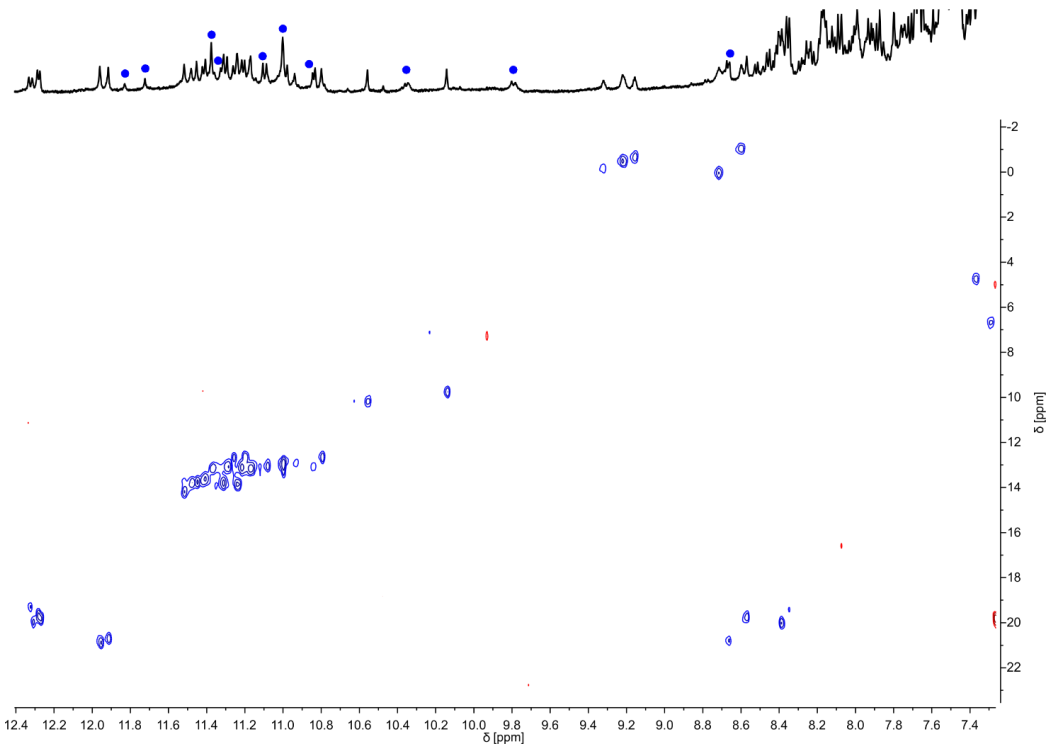


Figure S41. Identification of hydrogen bonded OH signals of 16 in $CDCl_3$. Part of the $^{1}H,^{15}N$-HSQC NMR spectra (500 MHz, $CDCl_3$) at 25 °C showing amide resonances of **16** at 7.73 mM after a two-week incubation. Only NH resonances correlate, blue dots indicate the signals of OH protons.

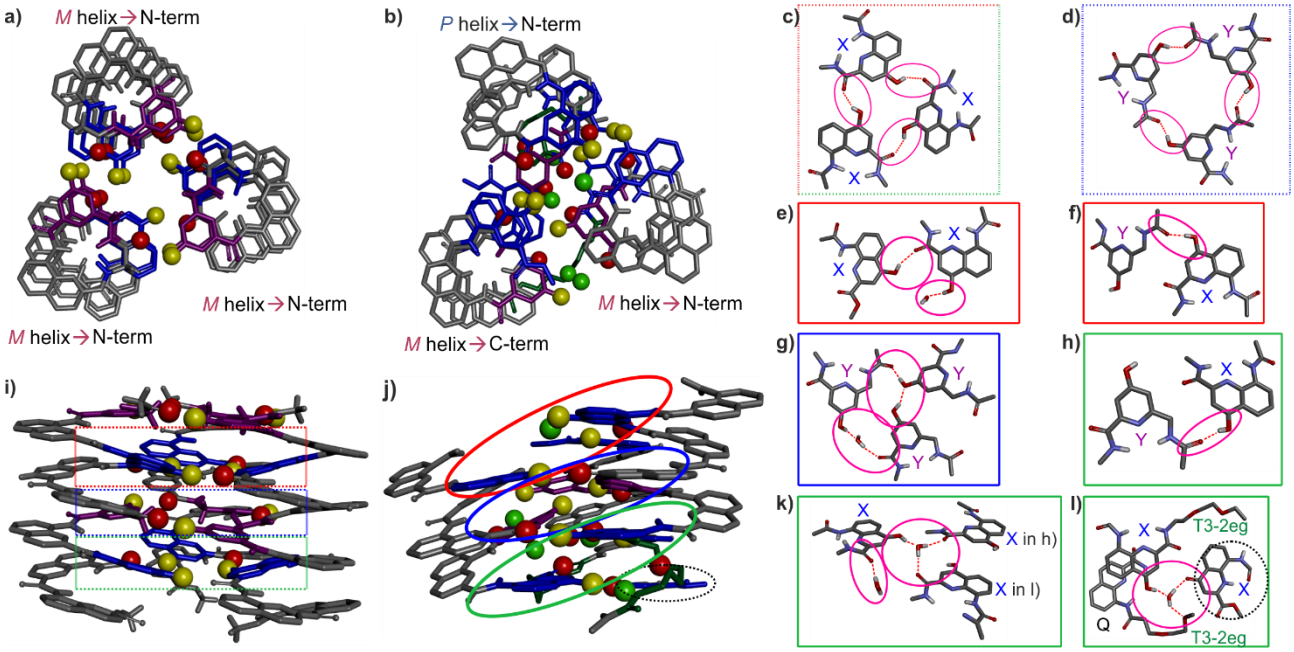


Figure S42. Comparison of the previously described trimeric bundle[1] and the one found in the crystal structure of 16. Top- (a) and side-view (i) of crystal structure and hydrogen-bonding patterns (c & d) of a trimer of **2**.[1] Top- (b) and side-view (j) of crystal structure and hydrogen-bonding patterns (e-h, k, l) of the distorted trimeric hydrogen bonding interface of **16**. Hydrogen bonds found in the distorted trimer in **16** are marked with boxes in the corresponding color in j. Here hydrogen bonds at the same level as in the trimer of **2** are marked in the same color. Hydrogen bonds belonging to **2** are marked with boxes using dashed lines in the same colors. The X-unit belonging to helices of the dimeric hydrogen bonding interface is marked with a black circle in j & l. The hydroxy groups and carbonyl groups of the hydrogen-bonding arrays are shown as yellow and red balls, respectively. Water molecules are shown as green balls. X-units, Y-units and linker units are shown in blue, violet and green tubes, respectively. Included solvent molecules, hydrogens and other side-chains are omitted for clarity.

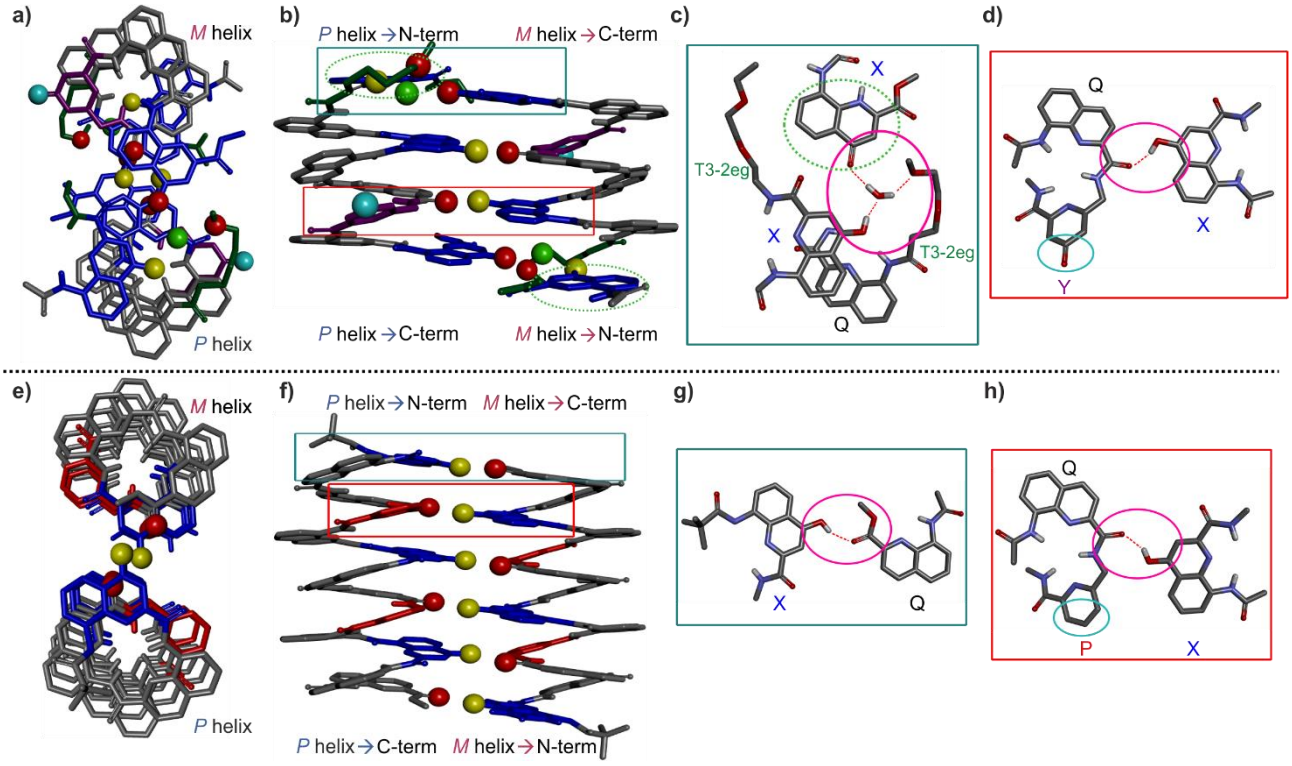


Figure S43. Comparison of the previously described dimeric bundle[4] and the one found in the crystal structure of 16. Top- (a) and side-view (b) of crystal structure and hydrogen-bonding patterns (c & d) of the shifted head-to-tail PM dimeric hydrogen bonding interface of **16**. Top- (e) and side-view (f) of crystal structure and hydrogen-bonding patterns (g & h) of a shifted head-to-tail PM dimer of **3**.[4] The hydroxyl protons and carbonyl oxygen atoms of the hydrogen-bonding arrays are shown as yellow and red balls, respectively. Water molecules are shown as green balls. The X-units are shown in blue and the Y units in violet tubes. Included solvent molecules, hydrogens and other side-chains are omitted for clarity.

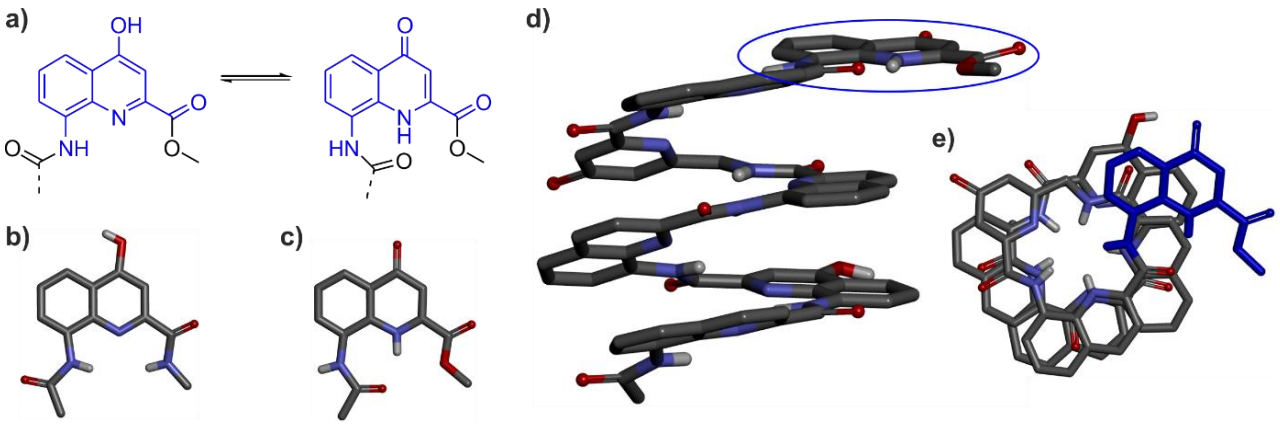


Figure S44. A flipped X unit in its quinolinone tautomeric form was found in the structure of 16. Quinoline-quinolinone-equilibrium of a C-terminal X-unit belonging to a B and B´-domain (a). Part of the crystal structure of 16 showing a X-quinoline unit (b) and a X-quinolinone unit (c). Side- (d) and top- (e) view of the C-terminal helix of a B and B´-domain. The flipped X-quinolinone unit is marked with a blue circle in (d) and shown in blue in (e). Side chains, hydrogen atoms and included solvent molecules are omitted for clarity.

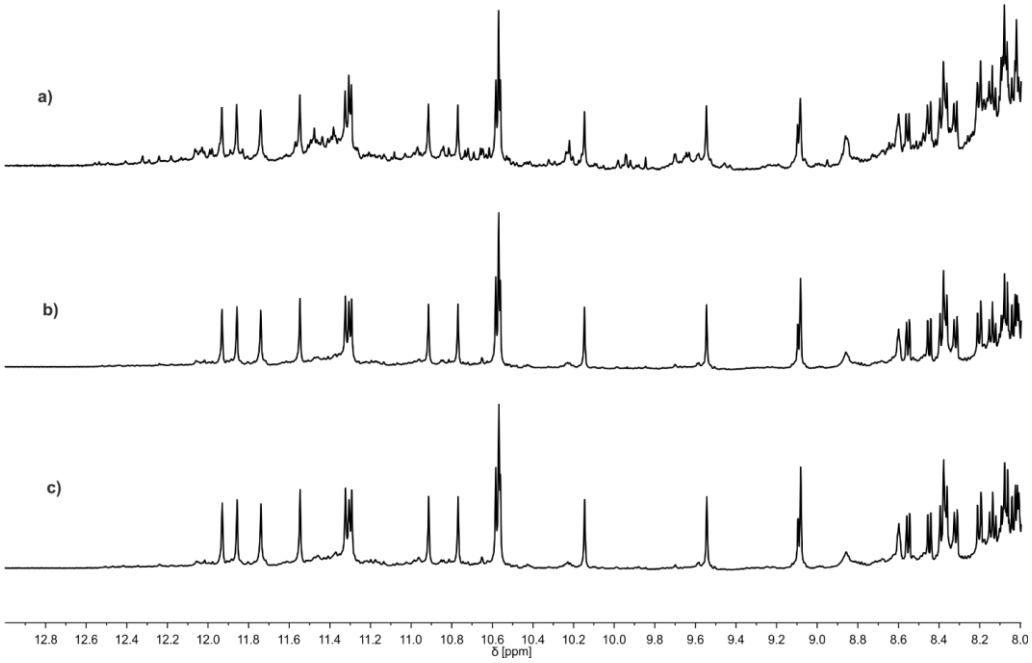


Figure S45. **Control experiment to verify that thermodynamic equilibrium is reached in spectra of 13.** Part of the ^{1}H NMR spectra (500 MHz, 25 °C) in $CDCl_3$ at 5.8 mM showing amide resonances of **13** after 24 hours (a), 1 week (b) and 2 weeks (c), respectively.

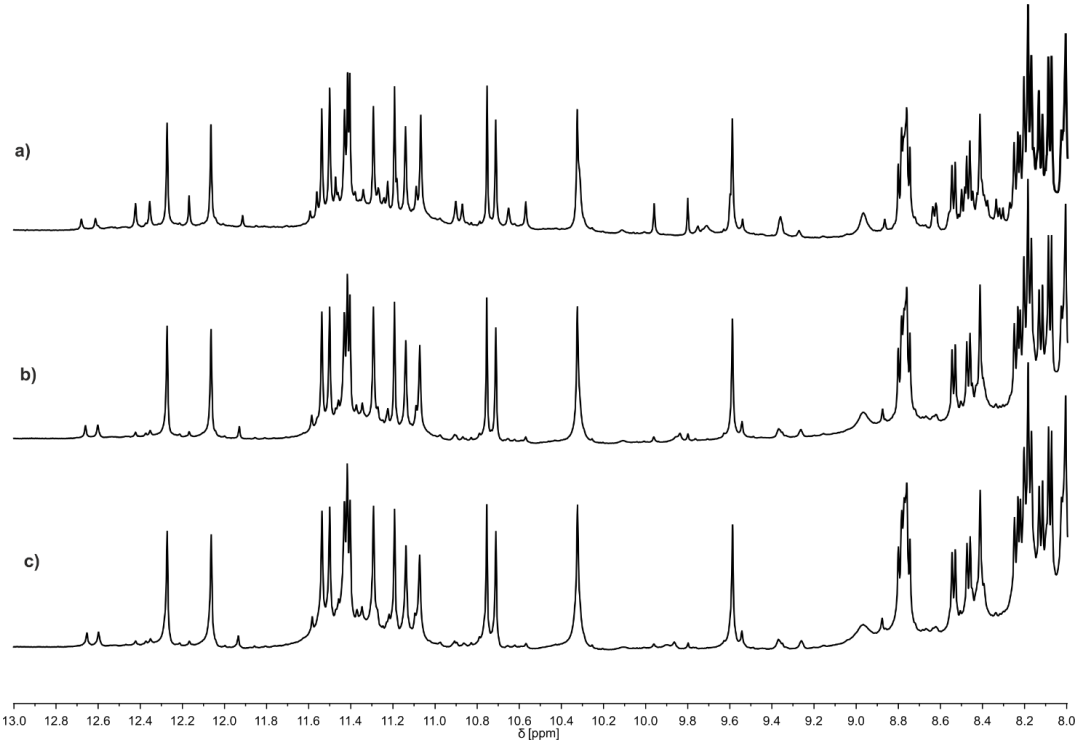


Figure S46. Control experiment to verify that thermodynamic equilibrium is reached in spectra of 15. Part of the ^{1}H NMR spectra (500 MHz, 25 °C) in $CDCl_3$ at 7.5 mM showing amide resonances of **15** after 24 hours (a), 1 week (b) and 2 weeks (c), respectively.

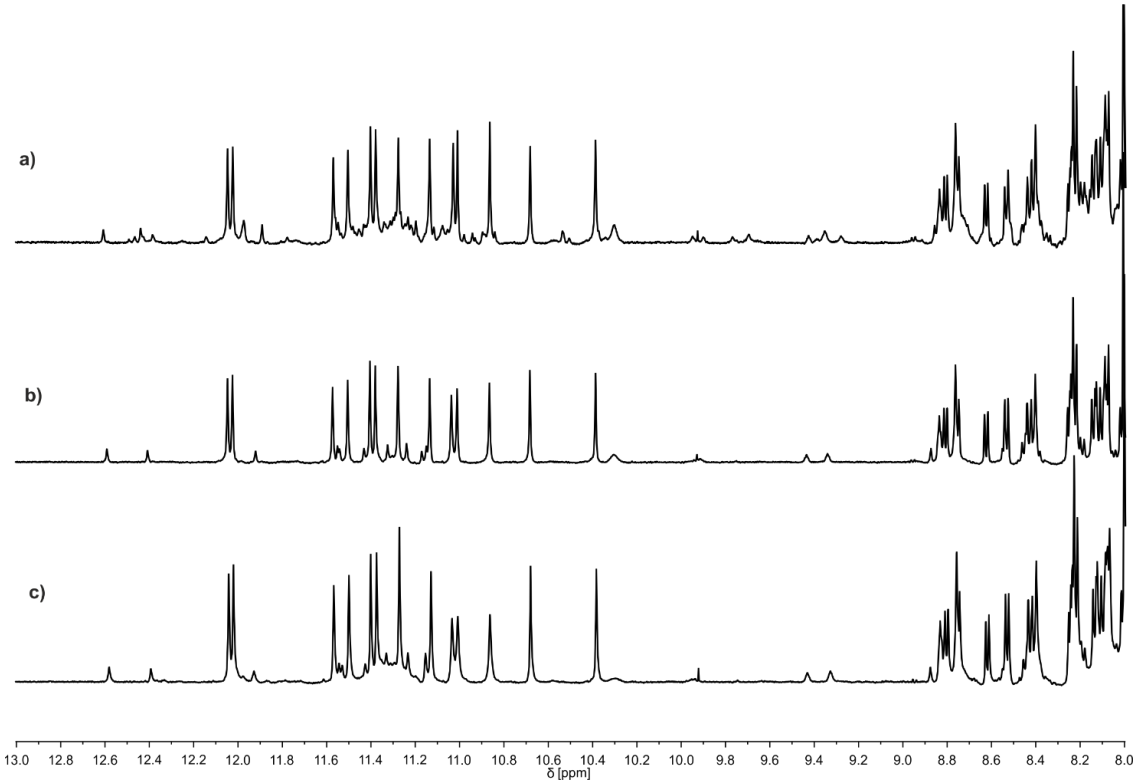


Figure S47. **Control experiment to verify that thermodynamic equilibrium is reached in spectra of 17.** Part of the ^{1}H NMR spectra (500 MHz, 25 °C) in $CDCl_3$ at 7.5 mM showing amide resonances of **17** after 24 hours (a), 3 weeks (b) and 6 weeks (c), respectively.

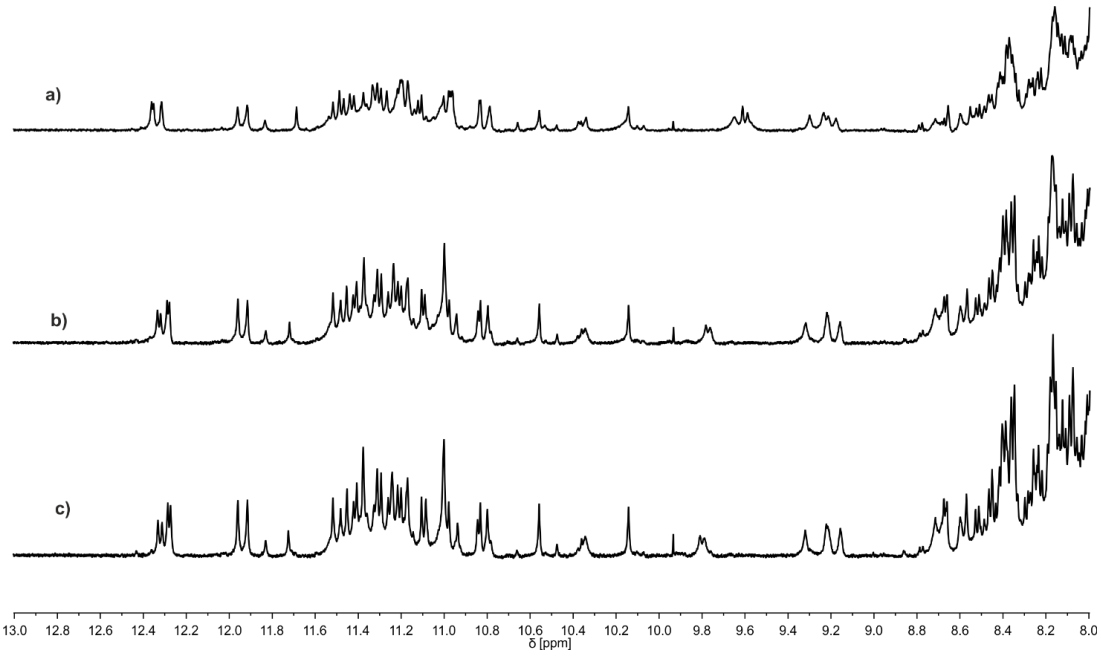


Figure S48. Control experiment to verify that thermodynamic equilibrium is reached in spectra of 16. Part of the ^{1}H NMR spectra (500 MHz, 25 °C) in $CDCl_3$ at 7.5 mM showing amide resonances of **16** after 24 hours (a), 3 weeks (b) and 6 weeks (c), respectively.

3 Supplementary methods

3.1 HRMS analyses

HR-MS spectra were recorded on a Bruker microTOF II by direct infusion from acetonitrile in positive ionization mode. The instrument was calibrated in positive mode by direct infusion of a calibration solution (Agilent Technologies ESI-L Low Concentration Tuning Mix). The mass sample was prepared by adding 10 µL of a solution of the sample in DCM (0.1 mg/mL) to 1 mL of a solution of 0.1% formic acid in acetonitrile.

3.2 Molecular modelling

Models were simulated by using Maestro version 11.5 (Schrödinger Inc.). Energy minimized structures were obtained using MacroModel energy minimization with the following parameters: force field: MMFFs; solvent: none; electrostatic treatment: constant dielectric; dielectric constant: 1.0; charges from: force field; cutoff: normal; Van der Waals: 7.0; electrostatic: 12.0; H-bond: 4.0; mini method: TNCG; maximum iterations: 2500; converge on: gradient; convergence threshold: 0.05; constraints: distances. As a starting point, the coordinates of previously described crystal structures CCDC entry # 1451494 (*PP* clockwise and counterclockwise tilted dimer),[1] CCDC entry # 2209187 (for models of *PP* shifted head-to-tail dimer),[4] CCDC entry # 1955168 (for models of *PM* parallel head-to-tail dimer),[2] CCDC entry # 2209189 (for models of *PM* shifted head-to-tail dimer),[4] were used. For models of the *PM* clockwise and counterclockwise tilted dimer the crystal structures CCDC entry # 1451494[1] and CCDC entry # 2209189[4] were combined. A single helix was first energy-minimized. In a second round, two helices were placed in a plausible arrangement, and distance constraints between plausible hydrogen-bonding partners were set on purpose to 2.5. While setting the constraints, it was important to match the hydroxy group to their correct hydrogen-bonding carbonyl partner. The energy-minimized model was fixed regarding possible unlikely conformations and energy-minimized again. Then all constraints were removed, and energy minimization was repeated. Typically, only minimal changes occurred at this stage. Then the connecting T3-linker was introduced, and the model again energy minimized without fixed distances. If no changes were observed another energy minimization with fixed distances has been run. If afterwards no changes were observed the structure was exported as a mol2-file.

3.3 Nuclear magnetic resonance spectroscopy

NMR spectra were recorded on different NMR spectrometers: (I) an Avance III HD NMR spectrometer 500 MHz (Bruker BioSpin) with CryoProbe™ Prodigy for ^{1}H NMR, ^{1}H,^{15}N-HSQC, and DOSY spectra of foldamers. (II) an Avance III HD NMR spectromter 800 MHz with cryoprobe (Bruker BioSpin) for variable temperature measurements. Chemical shifts are described in part per million (ppm, δ) relative to the ^{1}H residual signal of the deuterated solvent used. Meaning DMSO-d_6 (δ 2.50 ppm), pyridine-d_5 (δ 8.74 ppm), CD_2Cl_2 (δ 5.32 ppm) and $CDCl_3$ (δ 7.16 ppm). ^{1}H NMR splitting patterns with observed first-order coupling are entitled as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) or broad singlet (bs). Coupling constants (*J*) are ported in Hertz.

Sample preparation and incubation times to reach equilibrium required attention. The required equilibration times of sequences **9**-**17** were estimated by equilibrating each sample in $CDCl_3$ after complete disruption of the aggregates. Complete disruption was achieved by dissolving the sample in pyridine and then evaporating the solvent. Spectra were measured at different time intervals from 2h to 6 weeks until no further change was observed.
In the case of sequences **9**-**12** and **14**, equilibration times were generally fast (around 5 min). Samples were typically incubated for 2h, which gave a large margin. In the case of **13**, **15** and **17**, equilibration times are considerably longer, and incubation of two to three weeks is indicated (Figures S45-47). In the case of **16**, slight changes in regard to signal sharpening are observed over time (Figure S48).

^{1}H,^{15}N-HSQC spectra were recorded with a phase-sensitive pulse sequence with sensitivity enhancement using trim pulses in inept transfer (hsqcetgpsi2) from the Bruker pulse program library. Data acquisition was performed utilizing non-uniform sampling (NUS; NUS amount: 50% with an automatically created NUSList) yielding 1024 (F2) x 128 (F1) data points in Echo/Antiecho gradient selection mode. The recycling delay was 2.0 s and 64 transients per increment were applied at a sweep width of 2.5 kHz in F2 and 7 kHz in F1 resulting in an acquisition time of 0.1462 s. NUS processing was performed using the fully automated NUS processing tool provided by MestReNova. Zero filling in F1 has been used to yield a final matrix of 1K x 1K real points.
The DOSY spectra were recorded by applying a pulse sequence with stimulated echo using bipolar gradient pulses for diffusion from the Bruker pulse program library (stebpgp1s). The diffusion delay Δ (big delta) and the diffusion gradient pulse length δ (little delta) was set to values specified in the respective capture. The number of gradient steps were set to 32 with linear spacing starting from 2% reaching 95% of the full gradient strength in the final step. For each of the 32 gradient amplitudes, 256 transients of 65k complex data points were acquired. DOSY processing was performed with the DOSY processing tool from MestReNova (v.12.x64) employing the Peak Heights Fit algorithm including the

autocorrect peak position with 32 points in diffusion dimension and a window of $1.00*10^{-6}$ to $1.00*10^{-2}$ cm^2 s^{-1}.

3.4 CD studies

All CD spectra were recorded on a Jasco J-810 spectrometer with 10 mm quartz cuvette. The following parameters were used: wavelength range from 500 to 250 nm. Scan speed: 200 nm/min; accumulation: 3; response time: 1.0 s; bandwidth: 2; temperature: 25 °C; sensitivity: standard (100 mdeg); data pitch: 1 nm; nitrogen gas flow rate: 500 L/h. The sample solution was prepared in distilled chloroform or DCM filtered over alumina before use. Δε values (in $cm^2.mmol^{-1}$) were obtained by using the formula: Δε = m°/(C.l.32980) where m°= CD value in millidegrees; l = cuvette pathlength in cm; C = sample concentration in mol/L. The CD spectra of all samples were carried out at 0.01 mM in chloroform and DCM. Thus, a solution of each in pyridine was prepared, and the same volume was taken, respectively. After the removal of the solvent, the samples were dissolved and incubated in chloroform or DCM.

3.5 X-ray crystallography

Single crystal weres obtained from an acetonitrile, chloroform and toluene mixture. Solvents were not dried. X-ray diffraction experiments for **16** were performed at the IECB x-ray facility (CNRS UMS 3033, University of Bordeaux) with a Rigaku FRX rotating anode (2.9 kW) diffractometer. CuKα radiation was monochromated with high flux Osmic Varimax HF mirrors for data collection. The x-ray source is equipped with a Pixel Hybrid Dectris Eiger 1M detector and partial chi goniometer (AFC11). The data were processed with CrysAlis PRO software[7] with a multiscan absorption correction. Crystal was kept at 100(2) K during data collection. The structure was solved with the ShelXT[8] structure solution program using a dual-space algorithm. Crystal model refinement was performed with ShelXL [9] package using Least Squares minimization implemented in Olex2[10].

During refinement, anisotropic displacement parameters were used only for backbones. For two isobutoxy side chains, not all C atoms were found (in total three carbon atoms are missing from the model). Also, the H atom of one hydroxyl group that do not form hydrogen bonds, the hydrogen atoms of isobutyl side chains, of the methyl groups of terminal esters and Se-CH3 substituent and of acetonitrile molecules were not localized. However, these atoms must belong to the structure and be involved in X-ray diffraction. They were thefore included in SFAC calculations. The difference between the formula unit and and the refined atoms is C3, H151. The foldamer molecules' C-and N-bound hydrogen atoms were placed in an idealized position. H atoms of side chains were not localized.

Hydrogen atoms of water molecules and OH groups of foldamer molecules were identified based on possible hydrogen bond interactions. All H atoms were refined in the riding-model approximation, with $U_{iso}(H)=1.2U_{eq}$(CH, CH_2, NH), $U_{iso}(H)=1.5U_{eq}$(OH, CH_3). EADP and DELU instructions were employed to model temperature parameters. The geometry of the molecules was improved with DFIX and AFIX commands.

Wide channels occupying about 35% of the unit cell volume are formed in the structure. These channels are filled with severely disordered solvent molecules that were removed using the solvent masking procedure implemented in Olex29. The solvent radius was set to 1.2 Å, and the calculated total potential solvent-accessible void volume and electron counts per unit cell were 7644 $Å^3$ and 1939. Considering the high number of electrons calculated for the channels and the variety of solvents used for crystallization, it is impossible to determine the solvent composition reliably. However, structure factors include contributions from the .fab file.

The final cif files were checked using IUCR's checkcif algorithm. Due to the characteristics of the crystal, i.e. large volume fractions of disordered solvent molecules, weak diffraction intensity, incompleteness of the data and moderate resolution, A - level and B - level alerts remain in the check cif file. These alerts are inherent to the data and refinement procedures and do not reflect errors. They are explicitly listed below and have been divided into two groups. The first group illustrates the poor quality of the data and refinement statistics compared to that expected for small molecule structures from highly diffracting crystals. The second group is connected to decisions made during refinement and explained below.

Group 1:

THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.4762
PLAT023_ALERT_3_A Resolution (too) Low [sin(theta)/Lambda < 0.6].. 0.48 Ang-1
PLAT084_ALERT_3_A High wR2 Value (i.e. > 0.25) ..... 0.48 Report
PLAT934_ALERT_3_A Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers .. 77 CheckPLAT082_ALERT_2_B High R1 Value ..... 0.16 Report
PLAT241_ALERT_2_B High' MainMol' Ueq as Compared to Neighbors
PLAT242_ALERT_2_B Low 'MainMol' Ueq as Compared to Neighbors

Group 2:

PLAT201_ALERT_2_A Isotropic non-H Atoms in Main Residue(s)
Not all atoms were refined with ADPs
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing)
Not all H-atoms were localized, but they were used in SFAC calculation

Table S1 Crystal data and refinement details

Identification code	**16**
Chemical formula	2(C171H157N29O33Se)·5(H2O)·4(C2 H3N)·[+solvents]*
Formula weight	6704.71
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions (Å, °)	a=27.1355 (6) α=67.428 (2)
	b=29.0697 (6) β=80.522 (2)
	c=33.4936 (7) γ=62.942 (2)
Volume ($Å^3$)	21724.7 (9)
Z	2
Density (calculated) ($Mg\ m^{-3}$)	1.02
Absorption coefficient (mm^{-1})	0.78
Crystal size (mm)	0.60 × 0.40 × 0.07
Completeness	99.5 (up to 47.24°)
Reflections collected	132507
Reflections observed [I > 2σ(I)]	29171
R_{int}	0.028
Data/parameters/restraints	39094/3273/179
Goodness-of-fit on F^2	2.09
Final R indices [I > 2σ(I)]	0.1553, 0.4558
R indices (all data)	0.1722, 0.4739
Largest diff. peak and hole	0.99, -0.82
CCDC #	2216678

Experiments were carried out at 100 K with Cu Ka radiation. Absorption was corrected by multi-scan

* Solvent mask was used to remove severely disordered solvent molecules

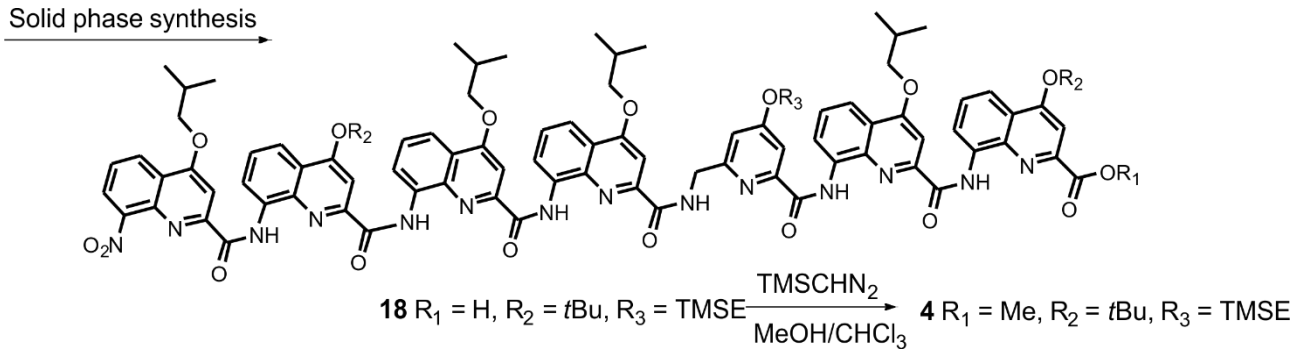
Table S2. Intermolecular hydrogen bonds geometry in the crystal structure. Atom numbers are those of the cif file.

D—H···A	D—H	H···A	D···A	D—H···A
O1B-H1B···O4W	0.84	1.75	2.579 (7)	168
O5A-H5A···O1W^{i}	0.84	1.77	2.587 (7)	160
O1W-H1WB···O3E	0.84	1.83	2.653 (7)	166
O1W-H1WA···O8F^{i}	0.84	2.12	2.797 (7)	137
O1E-H1E···O14F	0.84	1.89	2.638 (9)	148
O4D-H4D···O14C	0.84	1.77	2.604 (9)	173
O4A-H4A···O4D	0.84	2.03	2.814 (8)	155
O4W-H4WA···O7F	0.84	1.92	2.740 (8)	164
O4W-H4WB···O7C	0.84	1.88	2.712 (8)	172
O5D-H5D···O4C	0.84	1.80	2.596 (11)	157
O3A-H3A···O4F	0.84	1.82	2.622 (9)	158
O2B-H2B···O3W	0.84	1.73	2.541 (13)	162
O2W-H2WA···O12C	0.84	1.90	2.743 (10)	178
O2W-H2WB···O8C	0.84	1.96	2.798 (10)	178
O3W-H3WA···O5C	0.84	2.04	2.864 (10)	165
O3W-H3WB···O2W	0.84	1.88	2.711 (11)	170
O3D-H3D···O5W	0.84	1.75	2.564 (16)	163
O5W-H5WB···O2C	0.84	1.94	2.773 (11)	174
O5W-H5WA···O2D^{ii}	0.84	2.06	2.863 (14)	156

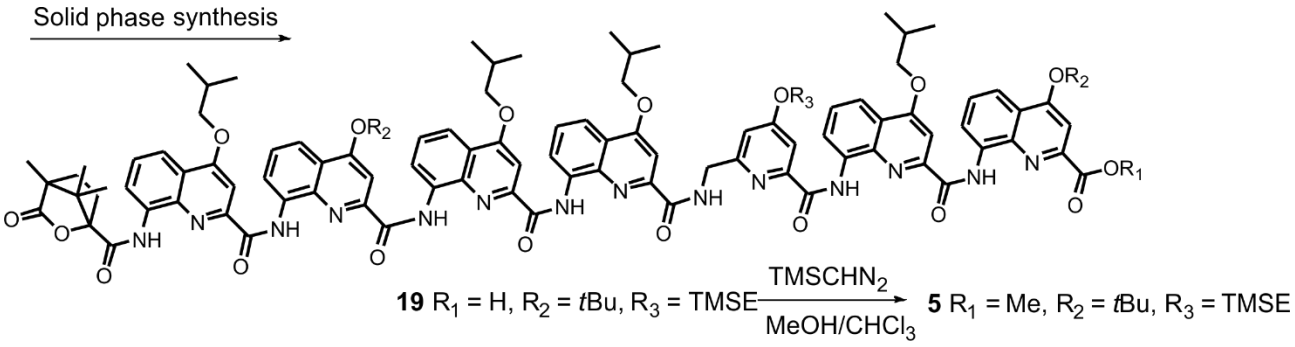
(i) 1-x, 2-y, 1-z; (ii) 1-x, 1-y, 2-z

4 Synthetic Schemes

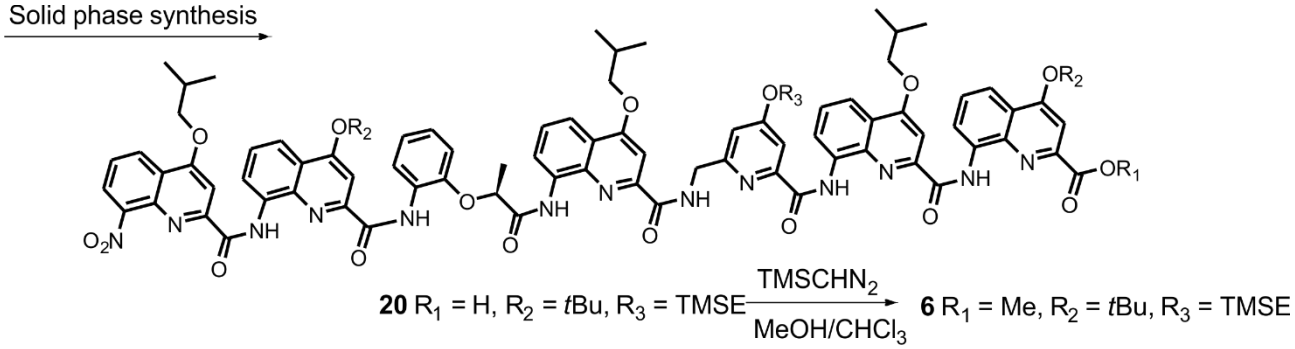
4.1 Synthesis of sequences to test handedness-induction via chiral B-unit



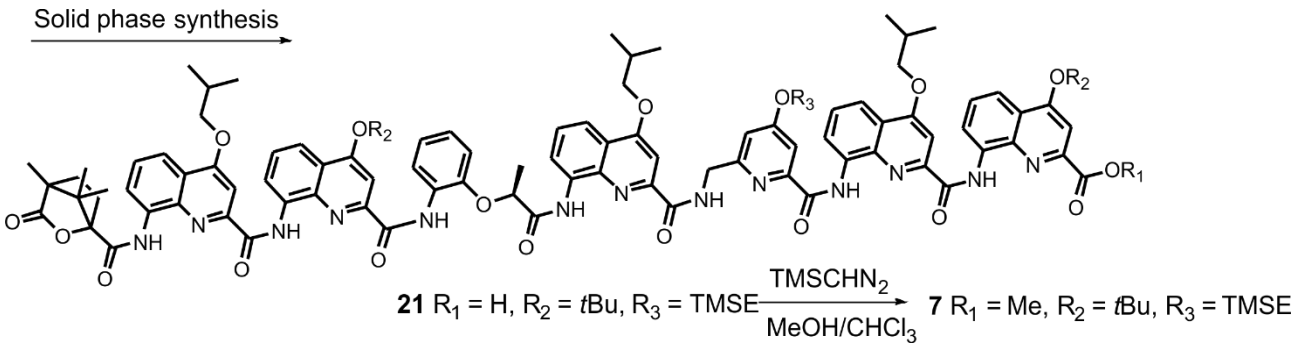
Scheme 1. Synthesis of **4**.



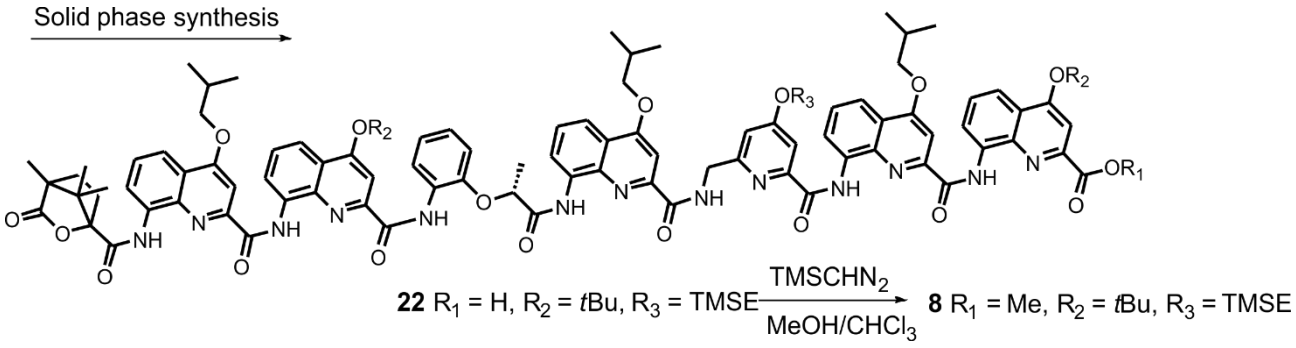
Scheme 2. Synthesis of **5**.



Scheme 3. Synthesis of **6**.

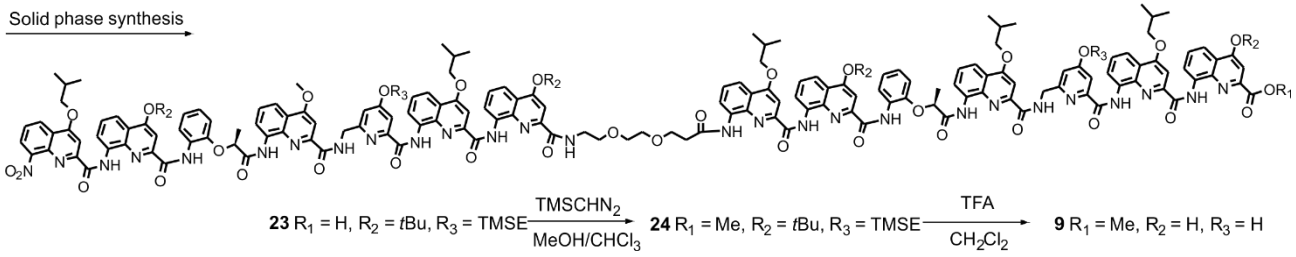


Scheme 4. Synthesis of **7**.

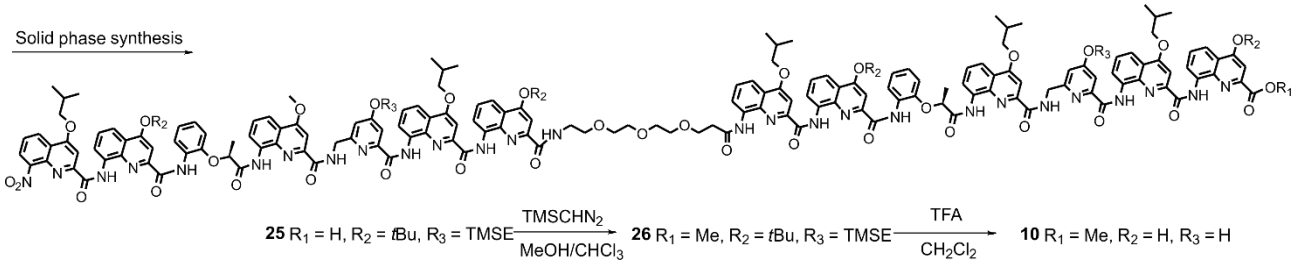


Scheme 5. Synthesis of **8**.

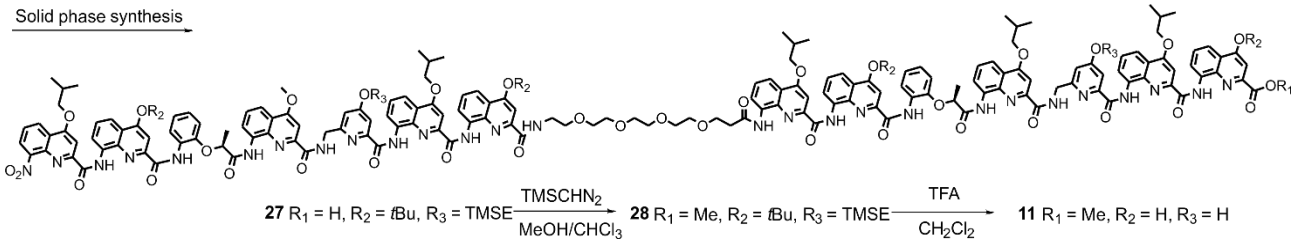
4.2 Synthesis of helix-turn-helix-motif with a flexible linker and handedness-control in both helices via a chiral B-unit



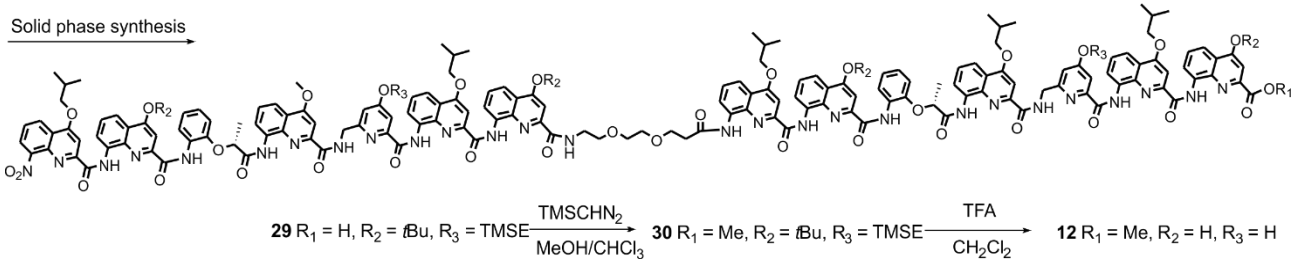
Scheme 6. Synthesis of **9**.



Scheme 7. Synthesis of **10**.

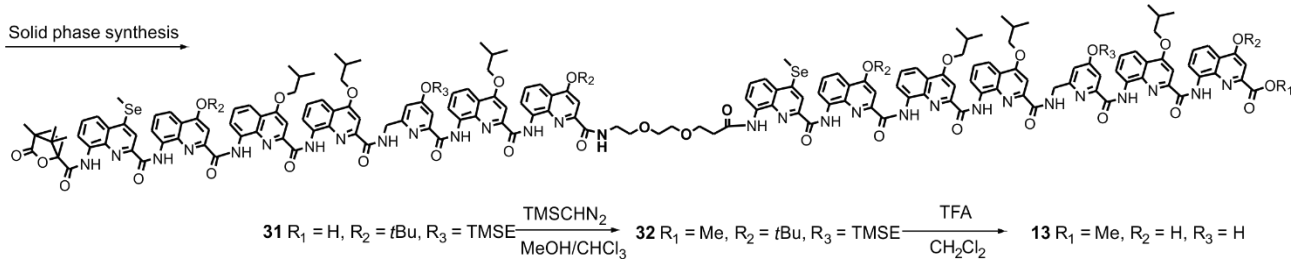


Scheme 8. Synthesis of **11**.

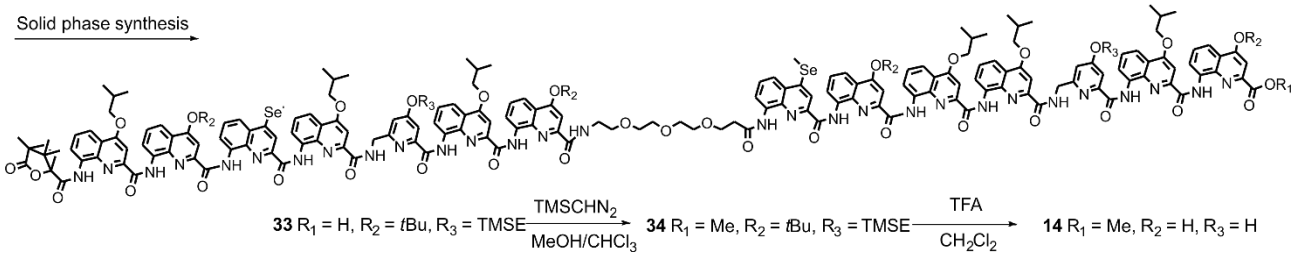


Scheme 9. Synthesis of **12**.

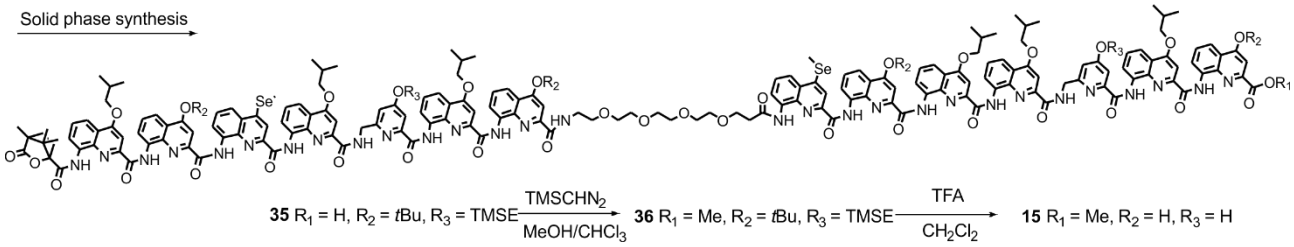
4.3 Synthesis of helix-turn-helix-motif with a flexible linker and handedness-control in one helix



Scheme 10. Synthesis of **13**.

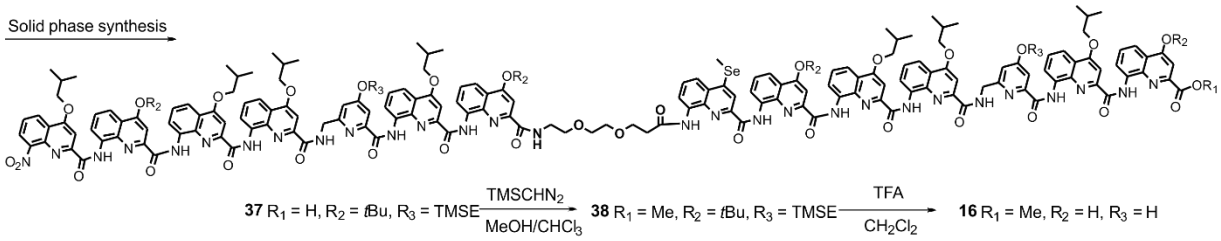


Scheme 11. Synthesis of **14**.

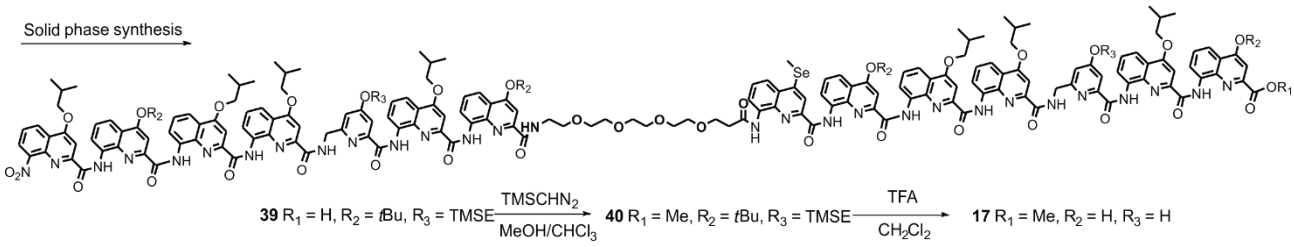


Scheme 12. Synthesis of **15**.

4.4 Synthesis of helix-turn-helix-motif with a flexible linker and without any handedness-control



Scheme 13. Synthesis of **16**.



Scheme 14. Synthesis of **17**.

5 Experimental Procedures

5.1 General methods

Commercially available reagents were purchased from Sigma-Aldrich, Alfa-Aesar or TCI and were used without further purification unless otherwise specified. SASRIN resin (100-200 mesh, loading 0.7-1.0 mmol/g) was purchased from Bachem. Tetrahydrofuran (THF), dichloromethane (DCM) and toluene were dried over alumina columns (MBRAUN SPS-800 solvent purification system); diisopropylethylamine (DIPEA) was distilled over ninhydrin and then over potassium hydroxide (KOH); chloroform was distilled over calcium hydride (CaH_2) prior to use. Solid phase synthesis (SPS) was performed manually under MW-irradiation on a CEM Discover (Liberty Bio) microwave oven using an open reaction vessel and an internal fibre optic probe for temperature control. High-resolution electrospray mass spectra were recorded on a Thermo Exactive orbitrap instrument.

5.2 Solid phase synthesis general methods

The monomers Fmoc-Q^B-OH,[11] Fmoc-Q^M-OH[12], Fmoc-B^R-OH[13], Fmoc-<u>X</u>-OH[4] (<u>X</u> denotes tBu-protected X), and Fmoc-<u>Y</u>-OH[3] (<u>Y</u> denotes TMSE-protected Y) have been synthesized according to literature. The synthesis of Fmoc-Q^S-OH and Fmoc-B^S-OH will be published elsewhere.

6.3.1 Loading of the resin via HBTU-coupling

SASRIN resin (800 mg, 100-200 mesh, loading 0.7-1.0 mmol/g) was swollen in DMF for 1 h, transferred to the microwave vessel and washed three times with dry DMF (purchased as 'extra-dry' solvent from Acros Organics). DIPEA (272 µL, 2 eq.) was added to a mixture of <u>X</u> (471 mg; 0.7 eq.) and HBTU (456 mg, 1.5 eq.) in dry DMF (5 mL), then the mixture was added to the resin. The reaction mixture was subjected to treatment in the microwave (50 °C, 20 min, 25 W), then the resin was washed five times with DMF until the washing solution was colourless, then it was washed ten times with DCM. If the loading was sufficient, a capping was performed, otherwise, the resin re-loaded. Capping was performed by adding a mixture of DCM/pyridine/benzoyl chloride (v/v/v, 3:1:1), and the resin was left for 30 min, then it was rinsed 20x times with DCM.

6.3.2 Estimation of the loading

After drying a small part of the resin under vacuum for 5 h, the loading of the resin was determined. To a small amount of resin (1-2 mg), a freshly prepared mixture of DMF/piperidine (v/v, 8:2, 3 mL) was added. The mixture was shaken and incubated for 5 min. Then the absorption was measured at 290 nm using a NanoDrop One Microvolume UV-Vis Spectrophotometer and a Hellma quartz glass cuvette 104 (path length 10 mm). Three replicates were measured, then the loading was calculated with the following equation:

$$\text{loading}\left(\text{in }\frac{\text{mmol}}{\text{g}}\right) = \frac{A_{290\text{ nm}}}{1.65 * m_{\text{resin}}(\text{in mg})} \quad (1)$$

6.3.3 Solid Phase Synthesis via in-situ-activation

After swelling of the SASRIN resin (800 mg, 100-200 mesh, loading 0.388 mmol/g, 0.310 µmol) in DMF for 1 h, the resin was transferred into the microwave vessel and washed three times with DMF. For deprotection, an 8:2 mixture of DMF/piperidine (6 mL) was added to the resin and nitrogen was bubbled through the suspension for 3 min. The solution was removed, the resin was washed five times with DMF, and an 8:2 mixture of DMF/piperidine (6 mL) was added again. After bubbling nitrogen through the suspension for 7 min, the resin was washed five times with DMF and five times with THF. For coupling, dry THF (4 mL) and 2,3,5-collidine (5 eq. with regards to the resin-loading) were added to the resin. A mixture of the monomer (2 eq. with regards to the resin-loading) and PPh_3 (4 eq. with regards to the resin-loading) in dest. chloroform (4 mL) or dry NMP (4 mL) was prepared. All monomers except for Fmoc-P-OH were dissolved in dest. chloroform. Fmoc-P-OH was dissolved in dry NMP. After the addition of trichloroacetonitrile (4 eq. with regards to the resin-loading), this mixture was added to the resin. Then the reaction mixture was subjected to treatment in the microwave (50 °C, 5 min, 50 W) Then the resin was washed five times with dry THF, then dry THF (4 mL) and 2,3,5-collidine (5 eq. with regards to the resin-loading) were added to the resin. Again, a mixture of monomer (2 eq. with regards to the resin-loading) and PPh_3 (4 eq. with regards to the resin-loading) in dest. chloroform (4 mL) or dry NMP (4 mL) with trichloroacetonitrile was prepared and added to the resin. The reaction mixture was again subjected to microwave vessel treatment (50 °C, 5 min, 25 W). After washing with DCM, THF, DMF and DCM, in that order, the resin was kept in a swollen state at 10 °C.

The sequence Fmoc-NH-Y-Q-X-OH needed to be deprotected by adding an 8:2 mixture of DMF/piperidine (6 mL) to the resin and subjecting it to MW treatment (50 °C, 5 min, 25 W). This step was repeated twice, and the in-situ coupling was then proceeded.

For installation of (1S)-camphanic amide, the resin (0.030 mmol) was Fmoc deprotected (20% piperidine in DMF, 1 x 3 min and 1 x 7 min), washed with DMF and dry THF, then a solution of DIPEA (31.1 µL, 10 eq.) in dry THF (0.5 mL) was added to the resin. To this suspension a solution of (1S)-camphanic acid chloride (3 eq.) in dry THF (0.5 mL) was added, and rests on the reaction vessel was rinsed down with dry THF (0.5 mL). The reaction was carried out under MW irradiation (25 W) at 50°C for 5 min. The resin was washed briefly with dry THF, and the process was repeated. Successively the resin was washed with DMF and DCM.

6.3.4 Mini Cleavage

To perform a mini cleavage, SASRIN resin (~5 mg) was swelled in DCM for 15 min, then HFIP [DCM (2.8 mL) and HFIP (1.2 mL)] were added, and the mixture was stirred at r. t. for 1 h. Then the solvent was evaporated.

6.2.3 Full Cleavage

To perform the full cleavage, SASRIN resin (~50 mg) was swelled in DCM for 15 min, HFIP [DCM/HFIP, v/v, 1:1 (6 mL in total)] was added, and the mixture was stirred at r. t. for 12 h. Then the solvent was evaporated. The process was repeated until no more foldamer is left on the resin (up to three times).

5.3 Synthesis of oligomers

6.3.1 Synthesis of sequences to test handedness-induction via chiral B-unit

O_2N-Q^B<u>X</u>$Q^B$$Q^B$<u>Y</u>$Q^B$<u>X</u>-OH (**18**) Compound **18** was synthesized using the SPS procedures reported in 5.2 on SASRIN resin loaded via HBTU-coupling described in 5.2 (scale: 78 µmol). After full cleavage and precipitation in ethyl acetate/n-Hex, the product was obtained as a yellow solid (61.13 mg, 45 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.61 (s, 1H), 11.26 (d, J = 4.0 Hz, 2H), 11.18 (s, 1H), 10.96 (s, 1H), 8.70 (d, J = 3.9 Hz, 1H), 8.50 – 8.47 (m, 1H), 8.40 (dd, J = 8.2, 1.5 Hz, 1H), 8.32 (dd, J = 7.5, 1.4 Hz, 1H), 8.12 (d, J = 1.3 Hz, 1H), 8.05 (dd, J = 10.1, 1.3 Hz, 2H), 8.03 – 7.97 (m, 3H), 7.86 – 7.82 (m, 1H), 7.77 (dd, J = 8.3, 1.3 Hz, 1H), 7.62 – 7.58 (m, 3H), 7.43 – 7.38 (m, 3H), 7.37 – 7.32 (m, 2H), 7.21 – 7.16 (m, 2H), 6.97 (d, J = 2.2 Hz, 1H), 6.73 (s, 1H), 6.60 (d, J = 2.2 Hz, 1H), 6.35 (s, 1H), 6.26 (s, 1H), 4.00 – 3.98 (m, 2H), 3.90 – 3.87 (m, 1H), 3.83 – 3.81 (m, 1H), 3.79 – 3.75 (m, 1H), 2.51 – 2.42 (m, 1H), 2.34 – 2.21 (m, 2H), 1.78 – 1.66 (m, 4H), 1.61 – 1.54 (m, 7H), 1.53 – 1.44 (m, 9H), 1.38 – 1.28 (m, 12H), 1.23 – 1.13 (m, 6H), 1.10 – 0.99 (m, 3H), 0.90 – 0.80 (m, 12H), 0.24 (s, 9H). **MS** calcd for $C_{96}H_{102}N_{14}NaO_{17}Si$ $[M+Na]^+$ 1773.7209, found (HR-ESI) 1774.5839.

O_2N-Q^B<u>X</u>$Q^B$$Q^B$<u>Y</u>$Q^B$<u>X</u>-OMe (**4**) Compound **18** (61.13 mg, 35 µmol, 1 eq.) was dissolved in a mixture of dry Chloroform/MeOH 3:2 (5 mL) under N_2. $TMSCHN_2$ (solut. 2 M in Hex, 42 µL, 0.07 mmol, 2 eq.) was added dropwise, and the solution was stirred at r.t. for 2 h. A few drops of acetic acid were added, and the solution was stirred for 5 min at r.t. Then the solution was diluted with DCM, washed with $NaHCO_3$, dried $MgSO_4$, filtered and concentrated. The product was obtained as a yellow solid (47.56 mg, 77 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.59 (s, 1H), 11.49 (s, 1H), 11.45 (s, 1H), 11.22 (s, 1H), 11.16 (s, 1H), 8.54 (t, *J* = 3.7 Hz, 1H), 8.49 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.40 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.33 (dd, *J* = 7.6, 1.4 Hz, 1H), 8.11 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.05 – 7.99 (m, 3H), 7.84 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.81 (s, 1H), 7.77 (ddd, *J* = 8.4, 2.3, 1.3 Hz, 2H), 7.64 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.41 – 7.36 (m, 3H), 7.35 – 7.30 (m, 1H), 7.23 (dd, *J* = 8.2, 7.5 Hz, 1H), 7.19 – 7.14 (m, 2H), 6.89 (d, *J* = 2.3 Hz, 1H), 6.70 (s, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 6.38 (s, 1H), 6.27 (s, 1H), 4.29 – 4.20 (m, 2H), 4.16 (dd, *J* = 8.8, 6.2 Hz, 1H), 4.06 (ddd, *J* = 8.7, 6.4, 4.9 Hz, 2H), 4.00 (dd, *J* = 8.7, 7.3 Hz, 1H), 3.91 – 3.77 (m, 5H), 3.39 – 3.36 (m, 1H), 3.15 (s, 3H), 2.51 – 2.35 (m, 4H), 2.33 – 2.25 (m, 2H), 2.19 – 2.14 (m, 1H), 2.05 – 1.98 (m, 1H), 1.72 (s, 6H), 1.61 (s, 8H), 1.35 – 1.24 (m, 10H), 1.23 – 1.16 (m, 12H), 0.90 – 0.80 (m, 3H), 0.23 (s, 9H). **MS** calcd for $C_{97}H_{104}N_{14}NaO_{17}Si$ $[M+Na]^+$ 1787.7365 found (HR-ESI) 1788.6438.

(1*S*)-Camph-Q^{B}XQ^{B}Q^{B}YQ^{B}X-OH (**19**) Compound **19** was synthesized using the SPS procedures reported in 5.2 on SASRIN resin loaded via HBTU-coupling described in 5.2 (scale: 78 µmol). After full cleavage and precipitation in EtOAc/n-Hex, the product was obtained as a yellow solid (60.79 mg, 41 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.81 (s, 1H), 11.41 (s, 1H), 11.25 (s, 1H), 11.09 (s, 1H), 10.99 (s, 1H), 9.57 (s, 1H), 8.57 (d, *J* = 3.8 Hz, 1H), 8.36 (d, *J* = 7.4 Hz, 1H), 8.24 (d, *J* = 7.4 Hz, 1H), 8.13 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.01 – 7.92 (m, 2H), 7.87 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.83 – 7.77 (m, 3H), 7.74 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.69 – 7.66 (m, 1H), 7.62 – 7.58 (m, 2H), 7.48-7.44 (m, 4H), 7.40 – 7.33 (m, 2H), 7.16 – 7.11 (m, 2H), 7.10 – 7.03 (m, 2H), 6.81 (s, 1H), 6.61 (s, 1H), 6.10 (s, 1H), 4.29 – 4.11 (m, 3H), 4.03 – 3.93 (m, 4H), 3.90 – 3.81 (m, 3H), 3.77 – 3.71 (m, 2H), 2.48 – 2.41 (m, 3H), 2.36 – 2.30 (m, 3H), 2.27 – 2.24 (m, 3H), 1.74 – 1.67 (m, 9H), 1.62 – 1.55 (m, 10H), 1.38 – 1.28 (m, 10H), 1.11 – 0.99 (m, 12H), 0.91 – 0.79 (m, 3H), 0.66 (s, 3H), 0.61 (s, 3H), 0.23 (s, 9H), 0.16 (s, 3H). **MS** calcd for $C_{106}H_{116}N_{14}NaO_{18}Si$ $[M+Na]^+$ 1923.8254, found (HR-ESI) 1924.6668.

(1*S*)-Camph-Q^{B}XQ^{B}Q^{B}YQ^{B}X-OMe (**5**) Compound **19** (60.79 mg, 32 µmol, 1 eq.) was dissolved in a mixture of dry Chloroform/MeOH 3:2 (5 mL) under N_2. $TMSCHN_2$ (solut. 2 M in Hex, 39 µL, 0.064 mmol, 2 eq.) was added dropwise, and the solution was stirred at r.t. for 2 h. A few drops of acetic acid were added, and the solution was stirred for 5 min at r.t. Then the solution was diluted with DCM, washed with $NaHCO_3$, dried $MgSO_4$, filtered and concentrated. The product was obtained as a yellow solid (77.55 mg, 70 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.78 (s, 1H), 11.49 (s, 1H), 11.48 (s, 1), 11.38 (s, 1H), 11.08 (s, 1H), 9.59 (s, 1H), 8.49 (s, 1H), 8.35 (d, *J* = 7.3 Hz, 1H), 8.24 (d, *J* = 7.3 Hz, 1H), 8.11 – 8.06 (m, 2H), 8.02 (s, 1H), 7.97 – 7.92 (m, 2H), 7.89 – 7.83 (m, 2H), 7.83 – 7.72 (m, 2H), 7.70 – 7.61 (m, 1H), 7.45 – 7.37 (m, 7H), 7.07 (d, *J* = 4.1 Hz, 1H), 6.94 (d, *J* = 2.3 Hz, 1H), 6.76 (s, 1H), 6.56 (s, 1H), 6.39 (s, 1H), 6.12 (s, 1H), 5.58 (s, 1H), 5.35 (s, 1H), 5.31 – 5.28 (m, 1H), 4.69 (s, 1H), 4.40 – 4.37 (m, 1H), 4.25-4.19 (m, 3H), 4.19 – 4.09 (m, 4H), 4.09 – 4.01 (m, 3H), 4.01 – 3.96 (m, 3H), 3.94 – 3.80 (m, 3H), 3.79 – 3.72 (m, 1H), 3.71 – 3.58 (m, 9H), 3.47 – 3.35 (m, 3H), 3.13 (s, 3H), 2.96 (s, 3H), 2.88 (s, 3H), 2.49 – 2.39 (m, 3H), 2.36 – 2.18 (m, 11H), 2.09-2.00 (m, 4H), 1.35 – 1.27 (m, 2H), 1.24 – 1.17 (m, 2H), 0.90 – 0.79 (m, 3H), 0.66 (s, 3H), 0.61 (s, 3H), 0.23 (s, 9H), -0.05 (s, 3H). **MS** calcd for $C_{107}H_{118}N_{14}NaO_{18}Si$ $[M+Na]^+$ 1937.8410 found (HR-ESI) 1938.7302.

O$_2$N-Q^{B}XB^{S}Q^{B}YQ^{B}X-OH (**20**) Compound **20** was synthesized using the SPS procedures reported in 5.2 on SASRIN resin loaded via HBTU-coupling described in 5.2 (scale: 53 µmol). After full cleavage and precipitation in EtOAc/*n*-Hex, the product was obtained as a yellow solid (46.96 mg, 53 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.72 (s, 1H), 10.98 (s, 1H), 10.85 (s, 1H), 10.23 (s, 1H), 9.82 (s, 1H), 8.86 (dd, *J* = 7.7, 1.3 Hz, 1H), 8.57 (s, 1H), 8.37 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.26 – 8.23 (m, 1H), 8.08 – 8.01 (m, 1H), 7.91 – 7.84 (m, 2H), 7.82 – 7.73 (m, 2H), 7.63 – 7.56 (m, 2H), 7.57 – 7.51 (m, 3H), 7.51 – 7.43 (m, 3H), 7.37 – 7.27 (m, 2H), 7.14 – 7.10 (m, 2H), 6.87 – 6.84 (m, 1H), 6.66 – 6.60 (m, 2H), 6.52 (d, *J* = 7.9 Hz, 1H), 6.48 (s, 1H), 6.44 (s, 1H), 5.58 (s, 1H), 4.29 – 4.16 (m, 5H), 4.16 – 4.10 (m, 3H), 4.09 – 4.03 (m, 3H), 4.00 – 3.98 (m, 1H), 3.90 – 3.78 (m, 5H), 2.37 – 2.31 (m, 3H), 2.28 – 2.25 (m, 2H), 1.73 – 1.63 (m, 3H), 1.62 – 1.54 (m, 3H), 1.53 – 1.45 (m, 3H), 1.42 – 1.30 (m, 8H),

1.22-1.10 (m, 5H), 1.10 – 1.02 (m, 5H), 0.96 – 0.91 (m, 3H), 0.91 – 0.76 (m, 3H), 0.21 (s, 9H). **MS** calcd for $C_{91}H_{97}N_{13}NaO_{17}Si$ $[M+Na]^+$ 1694.6787, found (HR-ESI) 1695.5758.

O_2N-Q^{B}XB^{S}Q^{B}YQ^{B}X-OMe (**6**) Compound **20** (46.96 mg, 28 µmol, 1 eq.) was dissolved in a mixture of dry Chloroform/MeOH 3:2 (5 mL) under N_2. $TMSCHN_2$ (solut. 2 M in Hex, 34 µL, 0.056 mmol, 2 eq.) was added dropwise, and the solution was stirred at r.t. for 2 h. A few drops of acetic acid were added, and the solution was stirred for 5 min at r.t. Then the solution was diluted with DCM, washed with $NaHCO_3$, dried $MgSO_4$, filtered and concentrated. The product was obtained as a yellow solid (38.23 mg, 81 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.94 (s, 1H), 11.46 (s, 1H), 10.83 (s, 1H), 10.19 (s, 1H), 9.81 (s, 1H), 8.85 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.44 – 8.40 (m, 1H), 8.36 (dd, *J* = 8.4, 1.5 Hz, 1H), 8.18 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.09 (dt, *J* = 7.6, 1.6 Hz, 2H), 7.84 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.80 – 7.72 (m, 3H), 7.70 – 7.63 (m, 4H), 7.58 – 7.39 (m, 5H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.83 (td, *J* = 7.6, 1.7 Hz, 1H), 6.62 (s, 1H), 6.58 (t, *J* = 7.2 Hz, 1H), 6.52 (d, *J* = 6.4 Hz, 2H), 6.39 (d, *J* = 2.4 Hz, 1H), 4.26 – 4.18 (m, 4H), 4.11 – 3.99 (m, 4H), 3.92 (s, 1H), 3.87 (t, *J* = 7.9 Hz, 1H), 3.83 – 3.76 (m, 2H), 3.75 – 3.64 (m, 1H), 3.50 (dd, *J* = 15.9, 8.3 Hz, 2H), 3.39 (s, 3H), 2.51 – 2.42 (m, 1H), 2.40 – 2.20 (m, 2H), 2.05 – 1.99 (m, 1H), 1.75 – 1.67 (m, 4H), 1.39 – 1.27 (m, 8H), 1.21 – 1.15 (m, 12H), 0.90 – 0.78 (m, 3H), 0.22 (s, 9H), 0.19 (d, *J* = 6.6 Hz, 3H), 0.12 (q, *J* = 3.4 Hz, 3H), 0.07 (s, 3H). **MS** calcd for $C_{92}H_{99}N_{13}NaO_{17}Si$ $[M+Na]^+$ 1708.6943 found (HR-ESI) 1709.5631.

(1*S*)-Camph-Q^{B}XB^{S}Q^{B}YQ^{B}X-OH (**21**) Compound **21** was synthesized using the SPS procedures reported in 5.2 on SASRIN resin loaded via HBTU-coupling described in 5.2 (scale: 53 µmol). After full cleavage and precipitation in EtOAc/*n*-Hex, the product was obtained as a yellow solid (42.48 mg, 44 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.67 (s, 1H), 10.95 (s, 1H), 10.53 (s, 1H), 10.16 (s, 1H), 10.14 (s, 1H), 9.74 (s, 1H), 8.86 (dd, *J* = 7.5, 1.2 Hz, 1H), 8.54 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.46 (s, 1H), 8.23 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.02 (td, *J* = 8.0, 1.5 Hz, 3H), 7.89 – 7.84 (m, 3H), 7.66 – 7.59 (m, 3H), 7.58 – 7.52 (m, 3H), 7.40 – 7.29 (m, 4H), 7.14 – 7.10 (m, 2H), 6.70 (s, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 6.50 (s, 1H), 6.43 (d, *J* = 2.3 Hz, 1H), 6.40 (s, 1H), 4.27 – 4.16 (m, 4H), 4.08 – 4.01 (m, 2H), 3.91 – 3.80 (m, 6H), 3.71 – 3.62 (m, 2H), 3.10 (tt, *J* = 7.4, 3.7 Hz, 2H), 2.74 – 2.68 (m, 1H), 2.51 – 2.44 (m, 1H), 2.38 – 2.21 (m, 10H), 2.03 – 1.98 (m, 2H), 1.73 – 1.52 (m, 5H), 1.50 – 1.37 (m, 4H), 1.37 – 1.26 (m, 8H), 1.22 – 1.12 (m, 8H), 1.09 – 0.99 (m, 8H), 0.67 (s, 3H), 0.46 (s, 3H), 0.21 (s, 9H). **MS** calcd for $C_{101}H_{111}N_{13}NaO_{18}Si$ $[M+Na]^+$ 1844.7832, found (HR-ESI) 1845.6781.

(1*S*)-Camph-Q^{B}XB^{S}Q^{B}YQ^{B}X-OMe (**7**) Compound **21** (42.48 mg, 23 µmol, 1 eq.) was dissolved in a mixture of dry Chloroform/MeOH 3:2 (5 mL) under N_2. $TMSCHN_2$ (solut. 2 M in Hex, 28 µL, 0.046 mmol, 2 eq.) was added dropwise, and the solution was stirred at r.t. for 2 h. A few drops of acetic acid were added, and the solution was stirred for 5 min at r.t. Then the solution was diluted with DCM, washed with $NaHCO_3$, dried $MgSO_4$, filtered and concentrated. The product was obtained as a yellow solid (35.05 mg, 83 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.92 (s, 1H), 11.46 (s, 1H), 10.51 (s, 1H), 10.15 (s, 1H), 10.14 (s, 1H), 9.73 (s, 1H), 8.84 – 8.81 (m, 1H), 8.54 (d, *J* = 7.6 Hz, 1H), 8.38 (s, 1H), 8.13 (d, *J* = 6.3 Hz, 1H), 8.09 – 7.93 (m, 2H), 7.90 – 7.80

(m, 2H), 7.79 – 7.71 (m, 2H), 7.71 – 7.61 (m, 3H), 7.61 – 7.52 (m, 1H), 7.52 – 7.42 (m, 1H), 7.35 (d, *J* = 26.7 Hz, 3H), 7.24 – 7.10 (m, 2H), 6.85 (t, *J* = 7.0 Hz, 1H), 6.64 (s, 1H), 6.52 (dd, *J* = 18.2, 8.2 Hz, 2H), 6.44 (s, 1H), 6.37 (s, 1H), 5.58 (s, 1H), 4.69 (s, 2H), 4.39 – 4.36 (m, 2H), 4.23 – 3.97 (m, 5H), 3.92 (s, 1H), 3.90 – 3.78 (m, 3H), 3.68 – 3.62 (m, 2H), 3.56 – 3.47 (m, 2H), 3.36 (s, 3H), 2.96 (s, 1H), 2.88 (s, 1H), 2.57 – 2.42 (m, 2H), 2.42 – 2.29 (m, 3H), 2.10 – 1.98 (m, 3H), 1.73 – 1.63 (m, 8H), 1.39 – 1.27 (m, 8H), 1.24 – 1.16 (m, 7H), 1.12 (s, 3H), 1.06 (s, 3H), 0.96 (s, 3H), 0.91 – 0.80 (m, 3H), 0.67 (s, 3H), 0.46 (s, 3H), 0.21 (s, 9H). **MS** calcd for $C_{102}H_{113}N_{13}NaO_{18}Si$ $[M+Na]^+$ 1858.7988 found (HR-ESI) 1859.7043.

(1*S*)-Camph-Q^{B}XB^{R}Q^{B}YQ^{B}X-OH (**22**) Compound **22** was synthesized using the SPS procedures reported in 5.2 on SASRIN resin loaded via HBTU-coupling described in 5.2 (scale: 53 µmol). After full cleavage and precipitation in EtOAc/*n*-Hex, the product was obtained as a yellow solid (43.00 mg, 44 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.99 (s, 1H), 11.30 (s, 1H), 10.30 (s, 1H), 9.12 (s, 1H), 9.06 (d, *J* = 7.6 Hz, 1H), 8.48 (d, *J* = 7.5 Hz, 1H), 8.13 (s, 1H), 8.05 – 8.01 (m, 2H), 7.98 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.63 – 7.54 (m, 5H), 7.49 – 7.46 (m, 3H), 7.36 (dd, *J* = 16.6, 8.6 Hz, 2H), 7.18 – 7.11 (m, 3H), 7.03 (s, 1H), 6.91 (d, *J* = 12.7 Hz, 1H), 6.88 (d, *J* = 6.9 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.69 (s, 1H), 6.62 – 6.58 (m, 1H), 6.39 (s, 1H), 4.72 (s, 1H), 4.64 (s, 1H), 4.53 – 4.48 (m, 1H), 4.28 – 4.09 (m, 4H), 3.99 – 3.87 (m, 3H), 3.84 – 3.72 (m, 4H), 2.41 – 2.30 (m, 9H), 2.30 – 2.24 (m, 4H), 2.06 – 1.98 (m, 11H), 1.61 – 1.52 (m, 6H), 1.50 – 1.44 (m, 6H), 1.44 – 1.32 (m, 7H), 1.19 – 0.98 (m, 6H), 0.98 – 0.76 (m, 6H), 0.19 (s, 9H). **MS** calcd for $C_{101}H_{111}N_{13}NaO_{18}Si$ $[M+Na]^+$ 1844.7832, found (HR-ESI) 1845.6798.

(1*S*)-Camph-Q^{B}XB^{R}Q^{B}YQ^{B}X-OMe (**8**) Compound **22** (43.00 mg, 23 µmol, 1 eq.) was dissolved in a mixture of dry Chloroform/MeOH 3:2 (5 mL) under N_2. $TMSCHN_2$ (solut. 2 M in Hex, 28 µL, 0.046 mmol, 2 eq.) was added dropwise, and the solution was stirred at r.t. for 2 h. A few drops of acetic acid were added, and the solution was stirred for 5 min at r.t. Then the solution was diluted with DCM, washed with $NaHCO_3$, dried $MgSO_4$, filtered and concentrated. The product was obtained as a yellow solid (35.55 mg, 84 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.93 (s, 1H), 11.46 (s, 1H), 10.18 (s, 1H), 9.83 (s, 1H), 9.81 (s, 2H), 8.84 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.55 – 8.49 (m, 1H), 8.36 (t, *J* = 3.7 Hz, 1H), 8.11 (d, *J* = 6.4 Hz, 1H), 8.05 – 7.88 (m, 3H), 7.85 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.81 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.70 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.66 (s, 1H), 7.56 (t, *J* = 7.9 Hz, 2H), 7.44 (td, *J* = 8.1, 4.2 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.22 (s, 1H), 7.16 – 7.10 (m, 2H), 6.89 (td, *J* = 7.8, 1.7 Hz, 1H), 6.70 (s, 1H), 6.59 (t, *J* = 7.8 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.40 (d, *J* = 2.7 Hz, 2H), 4.30 – 3.96 (m, 5H), 3.94 – 3.79 (m, 2H), 3.59 – 3.48 (m, 1H), 3.38 (t, *J* = 7.1 Hz, 1H), 3.34 (s, 3H), 2.52 – 2.19 (m, 6H), 1.61 – 1.55 (m, 11H), 1.36 – 1.31 (m, 6H), 1.28 – 1.19 (m, 19H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.73 (s, 3H), 0.43 (s, 3H), 0.21 (s, 9H), 0.07 (s, 3H), -0.06 – -0.12 (m, 3H). **MS** calcd for $C_{102}H_{113}N_{13}NaO_{18}Si$ $[M+Na]^+$ 1858.7988 found (HR-ESI) 1859.6670.

5.3.2 Synthesis of sequences with a helix-turn-helix-motif and handedness-control in both helices

O_2N-Q^B<u>X</u>$B^S$$Q^M$<u>Y</u>$Q^B$<u>X</u>-T3-2eg-$Q^B$<u>X</u>$B^S$$Q^B$<u>Y</u>$Q^B$<u>X</u>-OH (**23**) Compound **23** was synthesized using the SPS procedures reported in 5.2 on SASRIN resin loaded via HBTU-coupling described in 5.2 (scale: 93 µmol). The product was obtained after full cleavage and precipitation in EtOAc/*n*-Hex as a yellow solid (162.34 mg, 49 %). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C) δ [ppm] 11.57 (s, 1H), 11.46 (s, 1H), 10.88 (s, 1H), 10.84 (s, 1H), 10.62 (s, 1H), 10.31 (s, 1H), 9.98 (s, 1H), 9.83 (s, 1H), 9.59 (s, 1H), 9.32 (s, 1H), 8.97 (s, 1H), 8.63 (s, 1H), 8.59 – 8.54 (m, 1H), 8.39 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.31 – 8.19 (m, 1H), 8.12 – 7.92 (m, 5H), 7.92 – 7.73 (m, 7H), 7.71 – 7.49 (m, 6H), 7.48 – 7.32 (m, 13H), 7.32 – 7.20 (m, 6H), 7.15 (dq, *J* = 14.4, 6.7 Hz, 3H), 7.03 – 6.99 (m, 2H), 6.96 (dd, *J* = 7.6, 3.5 Hz, 1H), 6.75 (tt, *J* = 9.7, 4.7 Hz, 2H), 6.54 (t, *J* = 7.2 Hz, 1H), 6.46 (t, *J* = 7.6 Hz, 1H), 6.41 (d, *J* = 4.4 Hz, 2H), 6.36 – 6.33 (m, 1H), 6.25 (s, 1H), 4.27 – 4.17 (m, 6H), 4.14 (dd, *J* = 9.0, 7.2 Hz, 4H), 3.96 – 3.91 (m, 2H), 3.72 – 3.62 (m, 6H), 3.50 – 3.42 (s, 2H), 2.71 – 2.65 (m, 1H), 2.65 – 2.55 (m, 2H), 2.45 – 2.29 (m, 7H), 1.66 (s, 9H), 1.61 (d, *J* = 3.27 Hz, 18H), 1.52 (s, 9H), 1.34 – 1.22 (m, overlap with solvent residue of ethyl acetate), 1.21 – 1.11 (m, 39H), 0.21 (s, 9H), 0.19 (s, 9H) 0.04 (d, *J* = 5.9 Hz, 3H), -0.25 (s, 3H). **MS** calcd for $C_{186}H_{201}N_{27}NaO_{34}Si_2$ $[M+Na]^+$ 3435.4260, found (HR-ESI) 3437.2217.

O_2N-Q^B<u>X</u>$B^S$$Q^M$<u>Y</u>$Q^B$<u>X</u>-T3-2eg-$Q^B$<u>X</u>$B^S$$Q^B$<u>Y</u>$Q^B$<u>X</u>-OMe (**24**) Compound **23** (162.34 mg, 45.57 µmol, 1 eq.) was dissolved in a mixture of dry Chloroform/MeOH 3:2 (5 mL) under N_2. $TMSCHN_2$ (solut. 2 M in Hex, 26 µL, 0.091 mmol, 2 eq.) was added dropwise, and the solution was stirred at r.t. for 2 h. A few drops of acetic acid were added, and the solution was stirred for 5 min at r.t. Then the solution was diluted with DCM, washed with $NaHCO_3$, dried $MgSO_4$, filtered and concentrated. The product was obtained as a yellow solid (151.57 mg, 93 %). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C) δ [ppm] 11.71 (s, 1H), 11.59 (s, 1H), 11.36 (s, 1H), 10.92 (s, 1H), 10.60 (s, 1H), 10.39 (s, 1H), 9.94 (s, 1H), 9.86 (s, 1H), 9.60 (s, 1H), 9.39 (s, 1H), 8.95 (s, 1H), 8.77 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.59 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.40 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.25 (q, *J* = 3.9 Hz, 2H), 8.20 – 8.17 (m, 1H), 8.08 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.05 – 8.01 (m, 2H), 8.00 – 7.96 (m, 2H), 7.89 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.85 – 7.72 (m, 4H), 7.67 – 7.58 (m, 8H), 7.50 – 7.43 (m, 4H), 7.43 – 7.37 (m, 4H), 7.34 – 7.27 (m, 4H), 7.27 – 7.11 (m, 5H), 7.08 – 7.04 (m, 1H), 7.01 (d, *J* = 2.2 Hz, 1H), 6.94 – 6.90 (m, 1H), 6.76 (qd, *J* = 7.8, 1.7 Hz, 3H), 6.60 – 6.51 (m, 2H), 6.48 – 6.35 (m, 3H), 6.33 (dd, *J* = 6.3, 2.6 Hz, 2H), 6.26 (d, *J* = 2.2 Hz, 1H), 4.24 – 4.18 (m, 4H), 4.18 – 4.08 (m, 6H), 4.04 (s, 3H), 4.02 (d, *J* = 8.0 Hz, 3H), 3.92 (d, *J* = 6.5 Hz, 1H), 3.80 – 3.77 (m, 3H), 3.70 (dd, *J* = 6.6, 4.5 Hz, 2H), 3.36 – 3.33 (m, 2H), 2.70 (dd, *J* = 7.1, 5.0 Hz, 2H), 2.62 (dt, *J* = 9.9, 4.9 Hz, 1H), 2.50 – 2.31 (m, 7H), 2.31 – 2.24 (m, 3H), 2.24 – 2.15 (m, 4H), 2.02 – 1.98 (m, 2H), 1.86 – 1.80 (m, 2H), 1.67 – 1.64 (m, 7H), 1.63 (s, 9H), 1.63 (s, 9H), 1.35 – 1.29 (m, 10H), 1.22 – 1.17 (m, 21H), 1.16 – 1.13 (m, 8H), 1.09 (d, *J* = 6.7 Hz, 4H), 0.21 (s, 9H), 0.19 (s, 9H), 0.06 (d, *J* = 2.3 Hz, 3H), -0.18 (d, *J* = 6.3 Hz, 3H). **MS** calcd for $C_{187}H_{203}N_{27}NaO_{34}Si_2$ $[M+Na]^+$ 3449.4417 found (HR-ESI) 3451.1943.

O_2N-Q^BXB^SQ^MYQ^{B}X-T3-2eg-Q^BXB^SQ^BYQ^{B}X-OMe (**9**) Compound **24** (24.25 mg, 6.78 µmol) was treated with a 50 % solution of TFA in DCM (4 mL) at r.t. for 48 h. Then the solvent was removed under vacuum, obtaining

the product as a yellow solid (21.37 mg, quant.). **^{1}H NMR** (500 MHz, Pyridine-d_5, 25 °C) δ [ppm] 12.41 (s, 1H), 12.31 (s, 1H), 12.08 (s, 1H), 11.52 (s, 1H), 11.20 (s, 1H), 11.03 (s, 1H), 10.64 (s, 1H), 10.52 (s, 1H), 10.20 (s, 1H), 10.00 (s, 1H), 9.72 (s, 1H), 9.26 (dd, *J* = 7.6, 1.3 Hz, 1H), 9.16 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.99 (t, *J* = 3.6 Hz, 1H), 8.87 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.80 – 8.76 (m, 2H), 8.63 – 8.57 (m, 2H), 8.52 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.45 – 8.37 (m, 5H), 8.30 (ddd, *J* = 7.5, 3.0, 1.3 Hz, 2H), 8.16 (ddd, *J* = 17.0, 8.0, 2.4 Hz, 2H), 8.08 – 8.04 (m, 2H), 8.00 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.95 – 7.88 (m, 5H), 7.84 (d, *J* = 2.7 Hz, 2H), 7.80 – 7.72 (m, 7H), 7.69 – 7.65 (m, 2H), 7.57 – 7.51 (m, 5H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.34 (dt, *J* = 22.5, 7.9 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.13 (s, 1H), 7.07 – 7.02 (m, 2H), 6.98 – 6.76 (m, 4H), 6.75 (d, *J* = 2.2 Hz, 1H), 6.70 (d, *J* = 2.1 Hz, 1H), 4.40 (q, *J* = 6.4 Hz, 1H), 4.26 (dd, *J* = 8.4, 6.0 Hz, 1H), 4.20 (s, 1H), 4.10 (s, 3H), 4.02 (dd, *J* = 8.9, 6.3 Hz, 4H), 3.98 – 3.90 (m, 4H), 3.88 – 3.83 (m, 1H), 3.70 – 3.61 (m, 4H), 3.52 – 3.49 (m, 1H), 3.24 (ddd, *J* = 16.7, 11.4, 7.0 Hz, 1H), 3.15 (dt, *J* = 9.6, 5.8 Hz, 2H), 2.99 (td, *J* = 10.1, 9.5, 6.0 Hz, 3H), 2.95 – 2.88 (m, 1H), 2.71 (dt, *J* = 10.3, 5.6 Hz, 1H), 2.63 (dt, *J* = 10.4, 5.3 Hz, 1H), 2.53 (dt, *J* = 13.5, 6.7 Hz, 3H), 2.38 (dt, *J* = 15.6, 6.1 Hz, 2H), 2.19 – 2.00 (m, 5H), 1.29 (d, *J* = 6.6 Hz, 4H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.07 – 0.95 (m, 23H), 0.45 (d, *J* = 6.5 Hz, 3H), 0.29 – 0.24 (m, 3H). **MS** calcd for $C_{161}H_{147}N_{27}Na_2O_{34}$ $[M+2Na]^{2+}$ 1524.0194, found (HR-ESI) 1524.3674.

O_2N-Q^{B}XB^{S}Q^{M}YQ^{B}X-T3-3eg-Q^{B}XB^{S}Q^{B}YQ^{B}X-OH (**25**) Compound **25** was synthesized using the SPS procedures reported in 5.2 on SASRIN resin loaded via HBTU-coupling described in 5.2 (scale: 93 µmol). The product was obtained after full cleavage and precipitation in EtOAc/*n*-Hex as a yellow solid (154.29 mg, 46 %). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C) δ [ppm] 11.67 (s, 1H), 11.57 (d, *J* = 8.6 Hz, 1H), 11.03 (s, 1H), 10.91 (s, 1H), 10.63 (s, 1H), 10.51 (s, 1H), 9.97 (s, 1H), 9.64 (s, 1H), 9.46 (s, 1H), 9.09 (s, 1H), 8.77 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.68 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.41 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.33 – 8.24 (m, 3H), 8.19 – 8.15 (m, 1H), 8.10 – 8.03 (m, 3H), 8.03 – 7.95 (m, 3H), 7.93 – 7.90 (m, 1H), 7.87 – 7.75 (m, 3H), 7.72 – 7.61 (m, 9H), 7.52 – 7.35 (m, 10H), 7.34 – 7.26 (m, 3H), 7.25 – 7.13 (m, 3H), 7.12 – 7.08 (m, 2H), 6.80 (td, *J* = 7.8, 1.7 Hz, 2H), 6.62 – 6.55 (m, 2H), 6.51 (q, *J* = 8.8, 8.2 Hz, 3H), 6.46 – 6.41 (m, 2H), 6.40 – 6.31 (m, 3H), 4.28 – 4.16 (m, 9H), 4.14 – 3.98 (m, 16H), 3.98 – 3.90 (m, 2H), 3.84 – 3.78 (m, 4H), 3.77 – 3.68 (m, 3H), 3.56 – 3.45 (m, 2H), 3.17 – 3.04 (m, 2H), 2.71 – 2.57 (m, 4H), 2.51 – 2.42 (m, 3H), 2.41 – 2.31 (m, 2H), 2.31 – 2.24 (m, 3H), 2.20 – 2.16 (m, 3H), 1.67 (s, 9H), 1.64 (s, 9H), 1.63 (s, 9H), 1.55 (s, 9H), 1.38 – 1.24 (m, 10H), 1.24 – 1.14 (m, 10H), 1.13 (d, *J* = 6.7 Hz, 2H), 1.08 (d, *J* = 6.7 Hz, 2H), 0.90 – 0.87 (m, 2H), 0.21 (s, 18H), 0.07 (t, *J* = 2.2 Hz, 3H), -0.12 (d, *J* = 6.6 Hz, 3H). **MS** calcd for $C_{188}H_{205}N_{27}NaO_{35}Si_2$ $[M+Na]^+$ 3479.4522, found (HR-ESI) 3479.1593.

O_2N-Q^{B}XB^{S}Q^{M}YQ^{B}X-T3-3eg-Q^{B}XB^{S}Q^{B}YQ^{B}X-OMe (**26**) Compound **25** (154.29 mg, 42.78 µmol, 1 eq.) was dissolved in a mixture of dry Chloroform/MeOH 3:2 (5 mL) under N_2. $TMSCHN_2$ (solut. 2 M in Hex, 24.5 µL, 0.086 mmol, 2 eq.) was added dropwise, and the solution was stirred at r.t. for 2 h. A few drops of acetic acid were added, and the solution was stirred for 5 min at r.t. Then the solution was diluted with DCM, washed with $NaHCO_3$, dried $MgSO_4$, filtered and concentrated. The product was obtained as a yellow solid (148.69 mg, 96 %). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C) δ [ppm] 11.74 (s, 1H), 11.68 (s, 1H), 11.38 (s, 1H), 11.03

(s, 1H), 10.62 (s, 1H), 10.51 (s, 1H), 9.97 (s, 1H), 9.94 (s, 1H), 9.65 (s, 1H), 9.44 (s, 1H), 9.08 (s, 1H), 8.82 – 8.78 (m, 1H), 8.68 (dd, *J* = 7.5, 1.2 Hz, 1H), 8.41 (dd, *J* = 8.3, 1.4 Hz, 2H), 8.34 – 8.28 (m, 3H), 8.12 – 7.94 (m, 10H), 7.89 – 7.75 (m, 4H), 7.72 – 7.61 (m, 6H), 7.59 – 7.29 (m, 9H), 7.27 – 7.05 (m, 7H), 6.81 – 6.76 (m, 3H), 6.58 (d, *J* = 8.0 Hz, 3H), 6.51 – 6.41 (m, 3H), 6.40 – 6.33 (m, 2H), 6.32 (d, *J* = 2.2 Hz, 1H), 4.23-4.17 (m, 4H), 4.14 – 4.02 (m, 3H), 3.98-3.94 (m, 1H), 3.82-3.78 (m, 3H), 3.75-3.68 (m, 3H), 3.36 – 3.34 (m, 2H), 3.34 (s, 3H), 3.16-3.08 (m, 2H), 3.06-3.02 (m, 1H), 2.98 (s, 1H), 2.89-2.85 (m, 1H), 2.84 – 2.78 (m, 2H), 2.71 – 2.60 (m, 2H), 2.51 – 2.33 (m, 4H), 2.32 – 2.22 (m, 3H), 2.18 – 2.15 (m, 2H), 2.04 – 1.97 (m, 1H), 1.90 – 1.84 (m, 1H), 1.64 (s, 18H), 1.63 (s, 9H), 1.58 (s, 9H), 1.36 – 1.31 (m, 4H), 1.23 – 1.15 (m, 24H), 1.13 (d, *J* = 6.8 Hz, 4H), 1.09 – 1.07 (m, 4H), 0.90 – 0.81 (m, 2H), 0.24 – 0.22 (m, 4H), 0.21 (d, *J* = 1.2 Hz, 18H), 0.09 – 0.06 (m, 3H), -0.12 (d, *J* = 6.6 Hz, 3H). **MS** calcd for $C_{189}H_{207}N_{27}NaO_{35}Si_2$ $[M+Na]^+$ 3493.4679 found (HR-ESI) 3495.1820.

O_2N-Q^{B}XB^{S}Q^{M}YQ^{B}X-T3-3eg-Q^{B}XB^{S}Q^{B}YQ^{B}X-OMe (**10**) Compound **26** (25.54 mg, 7.05 µmol) was treated with a 50 % solution of TFA in DCM (3 mL) at r.t. for 48 h. Then the solvent was removed under vacuum, obtaining the product as a yellow solid (22.55 mg, quant.).**^{1}H NMR** (500 MHz, Pyridine-d_5, 25 °C) δ [ppm] 12.43 (s, 1H), 12.36 (s, 1H), 12.09 (s, 1H), 11.60 (s, 1H), 11.21 (s, 1H), 11.12 (s, 1H), 10.66 (s, 1H), 10.59 (s, 1H), 10.23 (s, 1H), 10.03 (s, 1H), 9.86 (s, 1H), 9.30 – 9.26 (m, 1H), 9.23 – 9.20 (m, 1H), 9.02 (t, *J* = 3.7 Hz, 1H), 8.96 (t, *J* = 3.8 Hz, 1H), 8.88 (d, *J* = 7.4 Hz, 1H), 8.82 (t, *J* = 6.8 Hz, 1H), 8.63 – 8.55 (m, 3H), 8.50 – 8.41 (m, 3H), 8.35-8.29 (m, 3H), 8.16 (td, *J* = 8.5, 2.0 Hz, 1H), 8.07 (dd, *J* = 8.5, 3.5 Hz, 4H), 8.01 – 7.95 (m, 2H), 7.96 – 7.87 (m, 3H), 7.87 – 7.82 (m, 3H), 7.81 – 7.67 (m, 3H), 7.58 – 7.50 (m, 3H), 7.49 – 7.38 (m, 3H), 7.32 (td, *J* = 7.9, 3.6 Hz, 3H), 7.08 – 7.04 (m, 3H), 7.03 – 6.93 (m, 3H), 6.92 – 6.84 (m, 3H), 6.84 – 6.77 (m, 3H), 6.75 (dd, *J* = 5.6, 2.1 Hz, 3H), 4.44 – 4.40 (m, 1H), 4.30 – 4.26 (m, 1H), 4.25 – 4.20 (m, 1H), 4.12 (s, 3H), 4.09 – 4.00 (m, 3H), 3.99 – 3.95 (m, 3H), 3.95 – 3.85 (m, 3H), 3.84 – 3.80 (m, 1H), 3.75 – 3.62 (m, 2H), 3.54 – 3.49 (m, 5H), 3.43 – 3.38 (m, 1H), 3.33 – 3.27 (m, 1H), 3.19 – 3.15 (m, 2H), 3.15 – 3.09 (m, 3H), 2.98 – 2.95 (m, 2H), 2.83 – 2.67 (m, 2H), 2.62 – 2.56 (m, 2H), 2.55 – 2.53 (m, 1H), 2.50 (d, *J* = 5.9 Hz, 1H), 2.44 – 2.36 (m, 2H), 2.17 – 2.02 (m, 6H), 1.31 (d, *J* = 6.5 Hz, 4H), 1.23 (dd, *J* = 7.0, 4.2 Hz, 4H), 1.16 (t, *J* = 7.3 Hz, 1H), 1.09 – 0.94 (m, 18H), 0.46 (d, *J* = 6.4 Hz, 3H), 0.31 (d, *J* = 7.3 Hz, 3H). **MS** calcd for $C_{163}H_{151}N_{27}NaO_{35}$ $[M+Na]^+$ 3069.0758, found (HR-ESI) 3070.8337, calcd for $C_{163}H_{151}N_{27}Na_2O_{35}$ $[M+2Na]^{2+}$ 1546.0325, found (HR-ESI) 1546.4091.

O_2N-Q^B<u>X</u>B^{S}Q^M<u>Y</u>Q^B<u>X</u>-T3-4eg-Q^B<u>X</u>B^{S}Q^B<u>Y</u>Q^B<u>X</u>-OH (**27**) Compound **27** was synthesized using the SPS procedures reported in 5.2 on SASRIN resin loaded via HBTU-coupling described in 5.2 (scale: 93 µmol). The product was obtained after full cleavage and precipitation in EtOAc/*n*-Hex as a yellow solid (125.62 mg, 37%). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C) δ [ppm] 11.73 (s, 1H), 11.53 (s, 1H), 11.09 (s, 1H), 10.92 (s, 1H), 10.68 (s, 1H), 10.56 (s, 1H), 10.05 (s, 2H), 10.00 (s, 1H), 9.68 (s, 1H), 9.43 (s, 2H), 9.18 (s, 1H), 8.77 – 8.69 (m, 1H), 8.41 (td, *J* = 8.6, 2.7 Hz, 1H), 8.38 – 8.30 (m, 2H), 8.12 – 7.97 (m, 6H), 7.94 (s, 1H), 7.89 – 7.73 (m, 7H), 7.69 – 7.55 (m, 6H), 7.53 – 7.38 (m, 9H), 7.34 (dd, *J* = 17.9, 9.9 Hz, 3H), 7.29 – 7.13 (m, 4H), 7.10 (t, *J* = 7.9 Hz, 1H), 6.84 – 6.77 (m, 2H), 6.60 (t, *J* = 7.7 Hz, 2H), 6.54 – 6.46 (m, 3H), 6.45 – 6.36 (m, 3H), 6.34 (dd, *J* = 6.6, 1.8 Hz, 2H), 4.28 – 4.18

(m, 8H), 4.00 (t, *J* = 6.8 Hz, 1H), 3.81 (t, *J* = 7.6 Hz, 1H), 3.77 – 3.69 (m, 5H), 3.29 – 3.24 (m, 1H), 3.20 – 3.13 (m, 1H), 3.03 – 2.95 (m, 1H), 2.70 – 2.65 (m, 1H), 2.62 – 2.53 (m, 2H), 2.45 – 2.32 (m, 4H), 2.28 – 2.18 (m, 1H), 1.78 – 1.71 (m, 1H), 1.69 (s, 9H), 1.64 (d, *J* = 3.2 Hz, 18H), 1.60 (s, 9H), 1.53 – 1.50 (m, 1H), 1.46 – 1.33 (m, 4H), 1.23 – 1.09 (m, overlap with signals corresponding to ethyl acetate), 0.92 – 0.85 (m, overlap with signals correspondiing to *n*-Hex.), 0.78 – 0.75 (m, 1H), 0.22 (s, 18H), 0.12 – 0.10 (m, 3H), -0.08 – -0.15 (m, 3H). **MS** calcd for $C_{190}H_{209}N_{27}Na_2O_{36}Si_2$ $[M+2Na]^{2+}$ 1773.2338, found (HR-ESI) 1774.1275.

O_2N-Q^{B}XB^{S}Q^{M}YQ^{B}X-T3-4eg-Q^{B}XB^{S}Q^{B}YQ^{B}X-OMe (**28**) Compound **27** (125.62 mg, 34.41 µmol, 1 eq.) was dissolved in a mixture of dry Chloroform/MeOH 3:2 (5 mL) under N_2. $TMSCHN_2$ (solut. 2 M in Hex, 20 µL, 0.069 mmol, 2 eq.) was added dropwise, and the solution was stirred at r.t. for 2 h. A few drops of acetic acid were added, and the solution was stirred for 5 min at r.t. Then the solution was diluted with DCM, washed with $NaHCO_3$, dried $MgSO_4$, filtered and concentrated. The product was obtained as a yellow solid (113.49 mg, 90 %). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C) δ [ppm] 11.76 (s, 1H), 11.72 (s, 1H), 11.39 (s, 1H), 11.08 (s, 1H), 10.64 (s, 1H), 10.56 (s, 1H), 9.99 (s, 1H), 9.69 – 9.65 (m, 1H), 9.46 (s, 1H), 8.81 (dd, *J* = 7.5, 1.2 Hz, 1H), 8.73 (dd, *J* = 7.5, 1.2 Hz, 1H), 8.42 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.37 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.31 (dt, *J* = 7.8, 3.7 Hz, 2H), 8.13 – 8.11 (m, 2H), 8.07 (ddd, *J* = 7.6, 5.1, 1.5 Hz, 2H), 8.04 – 7.98 (m, 3H), 7.86 (dt, *J* = 8.3, 1.1 Hz, 2H), 7.85 – 7.81 (m, 2H), 7.79 – 7.74 (m, 2H), 7.71 – 7.63 (m, 5H), 7.60 – 7.52 (m, 2H), 7.51 – 7.40 (m, 12H), 7.32 (s, 3H), 7.26 – 7.11 (m, 6H), 6.81 (dtd, *J* = 9.7, 7.7, 1.6 Hz, 2H), 6.59 (d, *J* = 4.2 Hz, 2H), 6.54 (s, 1H), 6.53 – 6.44 (m, 2H), 6.37 (t, *J* = 1.8 Hz, 2H), 6.34 (d, *J* = 2.2 Hz, 1H), 4.25 – 4.18 (m, 6H), 4.13 – 4.08 (m, 2H), 4.08 – 4.04 (m, 4H), 4.06 – 4.01 (m, 1H), 3.99 (q, *J* = 6.4 Hz, 1H), 3.85 – 3.77 (m, 4H), 3.77 – 3.71 (m, 2H), 3.34 (s, 3H), 3.30 – 3.25 (m, 2H), 3.18 – 3.13 (m, 2H), 3.01 – 2.92 (m, 3H), 2.88 – 2.83 (m, 2H), 2.75 – 2.66 (m, 5H), 2.61 – 2.54 (m, 3H), 2.48 – 2.42 (m, 1H), 2.42 – 2.25 (m, 7H), 2.23-2.19 (m, 1H), 2.09 – 2.05 (m, 1H), 1.96 (dt, *J* = 15.1, 5.0 Hz, 1H), 1.65 – 1.63 (m, 24H), 1.37 – 1.26 (m, 14H), 1.24 – 1.13 (m, 28H), 1.10 (d, *J* = 6.7 Hz, 2H), 0.23 – 0.22 (m, 1H), 0.22 (s, 18H), 0.14 – 0.11 (m, 1H), 0.10 – 0.08 (m, 3H), -0.09 (d, *J* = 6.5 Hz, 3H). **MS** calcd for $C_{191}H_{211}N_{27}NaO_{36}Si_2$ $[M+Na]^+$ 3537.4941 found (HR-ESI) 3539.2315, calcd for $C_{191}H_{211}N_{27}Na_2O_{36}Si_2$ $[M+2Na]^{2+}$ 1780.2417 found (HR-ESI) 1781.0692.

O_2N-Q^{B}XB^{S}Q^{M}YQ^{B}X-T3-4eg-Q^{B}XB^{S}Q^{B}YQ^{B}X-OMe (**11**) Compound **28** (34.30 mg, 9.36 µmol) was treated with a 50 solution of TFA in DCM (2 mL) at r.t. for 48 h. Then the solvent was removed under vacuum, obtaining the product as a yellow solid (30.33 mg, quant.).**^{1}H NMR** (500 MHz, Pyridine-d_5, 25 °C) δ [ppm] 12.44 (s, 1H), 12.39 (s, 1H), 12.11 (s, 1H), 11.63 (s, 1H), 11.22 (s, 1H), 11.16 (s, 1H), 10.67 (s, 1H), 10.62 (s, 1H), 10.25 (s, 1H), 10.05 (s, 1H), 9.90 (s, 1H), 9.31 – 9.23 (m, 2H), 9.04 (t, *J* = 3.8 Hz, 1H), 8.98 (t, *J* = 3.7 Hz, 1H), 8.91 – 8.88 (m, 1H), 8.85 (dt, *J* = 7.6, 1.6 Hz, 2H), 8.61 (ddt, *J* = 7.7, 3.8, 2.0 Hz, 3H), 8.52 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.46 – 8.41 (m, 3H), 8.36 – 8.32 (m, 3H), 8.17 – 8.15 (m, 1H), 8.12 – 8.06 (m, 3H), 8.00 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.95 – 7.89 (m, 5H), 7.89 – 7.83 (m, 3H), 7.80 – 7.69 (m, 7H), 7.57 – 7.50 (m, 2H), 7.50 – 7.41 (m, 4H), 7.35 (dd, *J* = 15.1, 7.7 Hz, 3H), 7.19 (d, *J* = 9.5 Hz, 2H), 7.08 (d, *J* = 7.1 Hz, 2H), 7.01 – 6.79 (m, 3H), 6.79 – 6.76 (m, 2H), 4.46-4.42

(m, 1H), 4.31-4.28 (m, 1H), 4.25-4.22 (m, 1H), 4.13 (s, 3H), 4.10 – 4.01 (m, 3H), 4.00-3.96 (m, 1H), 3.95 – 3.87 (m, 3H), 3.77 – 3.72 (m, 2H), 3.68-3.64 (m, 3H), 3.56 (s, 3H), 3.55 – 3.46 (m, 3H), 3.29 – 3.16 (m, 4H), 3.16 – 3.09 (m, 3H), 3.07 – 3.02 (m, 2H), 3.02 – 2.89 (m, 3H), 2.89 – 2.83 (m, 2H), 2.76 – 2.71 (m, 2H), 2.63 – 2.55 (m, 1H), 2.43-2.38 (m, 1H), 2.19 – 2.01 (m, 2H), 1.31 (d, *J* = 6.7 Hz, 4H), 1.23 (d, *J* = 6.8 Hz, 4H), 1.16 (t, *J* = 7.3 Hz, 1H), 1.09 – 0.97 (m, 30H), 0.48 (d, *J* = 6.1 Hz, 3H), 0.33 (d, *J* = 6.6 Hz, 3H). **MS** calcd for $C_{165}H_{155}N_{27}NaO_{36}$ $[M+Na]^+$ 3113.1020 found (HR-ESI) 3113.8610, calcd for $C_{165}H_{155}N_{27}Na_2O_{36}$ $[M+2Na]^{2+}$ 1568.0456 found (HR-ESI) 1568.4159.

O_2N-Q^{B}XB^{R}Q^{M}YQ^{B}X-T3-2eg-Q^{B}XB^{R}Q^{B}YQ^{B}X-OH (**29**) Compound **29** was synthesized using the SPS procedures reported in 5.2 on SASRIN resin loaded via HBTU-coupling described in 5.2 (scale: 55 µmol). After full cleavage, the product was obtained as a yellow solid (97.97 mg, 50 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.68 (s, 1H), 11.58 (s, 1H), 10.99 (s, 1H), 10.89 (s, 1H), 10.75 (s, 1H), 10.52 (s, 1H), 10.09 (s, 1H), 10.05 (s, 1H), 9.73 (s, 1H), 9.53 (s, 1H), 9.40 (s, 3H), 8.98 (s, 1H), 8.77 (d, *J* = 7.6 Hz, 1H), 8.62 (dd, *J* = 7.4, 1.2 Hz, 1H), 8.36 – 8.21 (m, 6H), 8.13 – 7.98 (m, 6H), 7.93 – 7.84 (m, 2H), 7.84 – 7.72 (m, 3H), 7.72 – 7.58 (m, 7H), 7.58 – 7.51 (m, 4H), 7.50 – 7.40 (m, 6H), 7.40 – 7.31 (m, 4H), 7.19 (q, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.09 – 7.00 (m, 3H), 6.73 (q, *J* = 7.0 Hz, 2H), 6.56 – 6.34 (m, 4H), 6.27 (s, 1H), 4.26 – 4.09 (m, 6H), 4.04 – 3.92 (m, 2H), 3.84 – 3.74 (m, 3H), 3.69 – 3.64 (m, 3H), 3.15-3.10 (m, 7H), 2.83-2.81 (m, 2H), 2.70 – 2.64 (m, 1H), 2.61-2.56 (m, 1H), 2.46 – 2.41 (m, 1H), 2.41 – 2.32 (m, 10H), 2.32 – 2.21 (m, 8H), 2.05 – 1.99 (m, 5H), 1.92-1.88 (m, 14H), 1.73 – 1.65 (m, 14H), 1.66 – 1.55 (m, overlap with solvent residue of water), 1.20 – 1.09 (m, overlap with signals corresponding to HFIP), 1.07-1.06 (m, 4H), 0.19 (s, 9H), 0.17 (s, 9H), 0.14 (d, *J* = 5.3 Hz, 3H), -0.09 (s, 3H). **MS** calcd for $C_{186}H_{201}N_{27}NaO_{34}Si_2$ $[M+Na]^+$ 3435.4260, found (HR-ESI) 3437.2217.

O_2N-Q^{B}XB^{R}Q^{M}YQ^{B}X-T3-2eg-Q^{B}XB^{R}Q^{B}YQ^{B}X-OMe (**30**) Compound **29** (31.03 mg, 8.71 µmol, 1 eq.) was dissolved in a mixture of dry Chloroform/MeOH 3:2 (5 mL) under N_2. $TMSCHN_2$ (solut. 2 M in Hex, 5 µL, 0.017 mmol, 2 eq.) was added dropwise, and the solution was stirred at r.t. for 2 h. A few drops of acetic acid were added, and the solution was stirred for 5 min at r.t. Then the solution was diluted with DCM, washed with $NaHCO_3$, dried $MgSO_4$, filtered and concentrated. The product was obtained as a yellow solid (31.16 mg, quant.). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.82 (s, 1H), 11.68 (s, 1H), 11.41 (s, 1H), 10.99 (s, 1H), 10.75 (s, 1H), 10.50 (s, 1H), 10.09 (s, 1H), 10.02 (s, 1H), 9.74 (s, 1H), 9.52 (s, 1H), 8.96 (s, 1H), 8.75 (dd, *J* = 7.5, 1.2 Hz, 1H), 8.62 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.34 – 8.26 (m, 4H), 8.13 – 8.08 (m, 2H), 8.06 – 7.99 (m, 3H), 7.90 – 7.86 (m, 1H), 7.82 – 7.72 (m, 5H), 7.70 – 7.59 (m, 6H), 7.55 (d, *J* = 1.3 Hz, 1H), 7.46 – 7.39 (m, 5H), 7.39 – 7.29 (m, 5H), 7.24 – 7.13 (m, 4H), 7.11 (t, *J* = 8.0 Hz, 2H), 7.03 (td, *J* = 12.5, 4.4 Hz, 4H), 6.75 – 6.69 (m, 2H), 6.54 (d, *J* = 7.1 Hz, 2H), 6.49 – 6.35 (m, 5H), 6.27 (dd, *J* = 12.2, 2.2 Hz, 2H), 4.19 – 4.15 (m, 3H), 4.07 – 4.00 (m, 3H), 3.99 – 3.93 (m, 2H), 3.84 – 3.77 (m, 1H), 3.75 – 3.72 (m, 2H), 3.67 – 3.65 (m, 2H), 3.34 (s, 3H), 3.05 – 2.97 (m, 1H), 2.82 – 2.80 (m, 2H), 2.68 – 2.64 (m, 1H), 2.60 – 2.54 (m, 1H), 2.47 – 2.40 (m, 3H), 2.36 – 2.18 (m, 4H), 2.18 – 2.12 (m, 3H), 2.11 – 2.07 (m, 2H), 1.90 – 1.85 (m, 1H), 1.80 – 1.77 (m, 1H), 1.58 – 1.56 (m, 22H), 1.35 – 1.22

(m, overlap with solvent residue of ethyl acetate), 1.19 – 1.09 (m, 22H), 1.06 (d, *J* = 6.7 Hz, 4H), 0.20 (s, 9H), 0.17 (s, 9H), 0.13 (d, *J* = 5.9 Hz 3H), -0.10 (d, *J* = 5.3 Hz, 3H). **MS** calcd for $C_{187}H_{203}N_{27}NaO_{34}Si_2$ $[M+Na]^+$ 3449.4417 found (HR-ESI) 3451.1943.

O_2N-$Q^BXB^RQ^MYQ^BX$-T3-2eg-$Q^BXB^RQ^BYQ^BX$-OMe (**12**) Compound **30** (31.16 mg, 8.71 µmol) was treated with a 50 % solution of TFA in DCM (4 mL) at r.t. for 48 h. Then the solvent was removed under vacuum, obtaining the product as a yellow solid (27.46 mg, quant.). **^{1}H NMR** (500 MHz, Pyridine-d_5, 25 °C) δ [ppm] 12.41 (s, 1H), 12.31 (s, 1H), 12.08 (s, 1H), 11.52 (s, 1H), 11.20 (s, 1H), 11.03 (s, 1H), 10.64 (s, 1H), 10.52 (s, 1H), 10.20 (s, 1H), 10.00 (s, 1H), 9.72 (s, 1H), 9.26 (dd, *J* = 7.6, 1.3 Hz, 1H), 9.16 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.99 (t, *J* = 3.6 Hz, 1H), 8.87 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.80 – 8.76 (m, 2H), 8.63 – 8.57 (m, 2H), 8.52 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.45 – 8.37 (m, 5H), 8.30 (ddd, *J* = 7.5, 3.0, 1.3 Hz, 2H), 8.16 (ddd, *J* = 17.0, 8.0, 2.4 Hz, 2H), 8.08 – 8.04 (m, 2H), 8.00 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.95 – 7.88 (m, 5H), 7.84 (d, *J* = 2.7 Hz, 2H), 7.80 – 7.72 (m, 7H), 7.69 – 7.65 (m, 2H), 7.57 – 7.51 (m, 5H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.34 (dt, *J* = 22.5, 7.9 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.13 (s, 1H), 7.07 – 7.02 (m, 2H), 6.98 – 6.76 (m, 4H), 6.75 (d, *J* = 2.2 Hz, 1H), 6.70 (d, *J* = 2.1 Hz, 1H), 4.40 (q, *J* = 6.4 Hz, 1H), 4.26 (dd, *J* = 8.4, 6.0 Hz, 1H), 4.20 (s, 1H), 4.10 (s, 3H), 4.02 (dd, *J* = 8.9, 6.3 Hz, 4H), 3.98 – 3.90 (m, 4H), 3.88 – 3.83 (m, 1H), 3.70 – 3.61 (m, 4H), 3.52 – 3.49 (m, 1H), 3.24 (ddd, *J* = 16.7, 11.4, 7.0 Hz, 1H), 3.15 (dt, *J* = 9.6, 5.8 Hz, 2H), 2.99 (td, *J* = 10.1, 9.5, 6.0 Hz, 3H), 2.95 – 2.88 (m, 1H), 2.71 (dt, *J* = 10.3, 5.6 Hz, 1H), 2.63 (dt, *J* = 10.4, 5.3 Hz, 1H), 2.53 (dt, *J* = 13.5, 6.7 Hz, 3H), 2.38 (dt, *J* = 15.6, 6.1 Hz, 2H), 2.19 – 2.00 (m, 5H), 1.29 (d, *J* = 6.6 Hz, 4H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.07 – 0.95 (m, 23H), 0.45 (d, *J* = 6.5 Hz, 3H), 0.29 – 0.24 (m, 3H). **MS** calcd for $C_{161}H_{147}N_{27}Na_2O_{34}$ $[M+2Na]^{2+}$ 1524.0194, found (HR-ESI) 1524.3674.

5.3.3 Synthesis of sequences with a helix-turn-helix-motif and handedness-control in one helix

(1*S*)-Camph-$Q^S\underline{X}Q^BQ^B\underline{Y}Q^B\underline{X}$-T3-2eg-$Q^S\underline{X}Q^BQ^B\underline{Y}Q^B\underline{X}$-OH (**31**) Compound **31** was synthesized using the SPS procedures reported in 5.2 on SASRIN resin loaded via HBTU-coupling described in 5.2 (scale: 60 µmol). After full cleavage and precipitation in EtOAc/*n*-Hex, the product was obtained as a yellow solid (112.00 mg, 49 %). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C) δ [ppm] 11.55 (dd, *J* = 8.3, 3.8 Hz, 2H), 11.44 – 11.41 (m, 3H), 11.33 (s, 1H), 11.28 (s, 1H), 11.23 (s, 1H), 11.19 (d, *J* = 4.6 Hz, 3H), 11.16 (d, *J* = 5.1 Hz, 1H), 11.12 (d, *J* = 6.2 Hz, 1H), 10.96 (dd, *J* = 10.8, 4.7 Hz, 4H), 10.92 (s, 2H), 10.90 (d, *J* = 3.4 Hz, 1H), 10.88 – 10.85 (m, 2H), 9.55 (s, 1H), 9.54 (s, 1H), 8.56 – 8.37 (m, 6H), 8.28 – 8.17 (m, 4H), 8.17 – 8.10 (m, 2H), 7.99 – 7.94 (m, 8H), 7.92 – 7.80 (m, 10H), 7.76 – 7.70 (m, 9H), 7.63 – 7.52 (m, 12H), 7.51 – 7.37 (m, 13H), 7.36 – 7.20 (m, 12H), 7.18 – 7.01 (m, 9H), 7.00 – 6.95 (m, 1H), 6.86 – 6.82 (m, 1H), 6.78 – 6.74 (m, 2H), 6.71 – 6.69 (m, 1H), 6.65 – 6.59 (m, 3H), 6.57 – 6.48 (m, 4H), 6.45 – 6.39 (m, 2H), 6.22 – 6.07 (m, 9H), 4.52 (p, *J* = 6.2 Hz, 1H), 4.29 – 3.92 (m, overlap with signals corresponding to ethyl acetate), 3.90 – 3.66 (m, 24H), 3.29 (d, *J* = 16.1 Hz, 4H), 2.64 – 2.59 (m, 10H), 2.49 – 2.37 (m, 15H), 1.68 – 1.54 (m, 128H), 1.34 – 1.20 (m, overlap with signal corresponding to ethyl acetate), 1.20 – 1.13 (m, 30H), 1.12 – 1.05 (m, 21H), 0.61 (d, *J* = 3.2 Hz, 5H), 0.58 (d, *J* = 3.0 Hz, 5H), 0.26 – 0.19 (m, 56H),

0.12 (d, *J* = 3.5 Hz, 5H), 0.03 (s, 1H), 0.01 (s, 1H), (mixture of two diastereomers *PP* & *PM* and their ratio is 1:1, both are reported). **MS** calcd for $C_{203}H_{219}N_{29}O_{33}Se_2Si_2$ $[M+Na]^+$ 3829.4113 found (HR-ESI) 15360.

(1*S*)-Camph-Q^{S}XQ^{B}Q^{B}YQ^{B}X-T3-2eg-Q^{S}XQ^{B}Q^{B}YQ^{B}X-OMe (**32**) Compound **31** (112.00 mg, 29 µmol, 1 eq.) was dissolved in a mixture of dry Chloroform/MeOH 3:2 (5 mL) under N_2. $TMSCHN_2$ (solut. 2 M in Hex, 17 µL, 0.058 mmol, 2 eq.) was added dropwise, and the solution was stirred at r.t. for 2 h. A few drops of acetic acid were added, and the solution was stirred for 5 min at r.t. Then the solution was diluted with DCM, washed with $NaHCO_3$, dried $MgSO_4$, filtered and concentrated. The product was obtained as a yellow solid (77.55 mg, 70 %). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C) δ [ppm] 11.55 (dd, *J* = 8.5, 3.3 Hz, 2H), 11.51 (s, 1H), 11.43 (s, 1H), 11.42 – 11.39 (m, 2H), 11.31 – 11.29 (m, 4H), 11.26 (s, 1H), 11.20 (t, *J* = 5.4 Hz, 3H), 11.16 (d, *J* = 4.0 Hz, 1H), 10.98 (d, *J* = 4.8 Hz, 1H), 10.95 (d, *J* = 3.2 Hz, 1H), 10.92 (s, 1H), 10.91-10.89 (m, 2H), 10.85 (s, 1H), 10.83 (s, 1H), 9.55 (s, 1H), 9.54 (s, 1H), 8.56 – 8.36 (m, 10H), 8.27 – 8.22 (m, 3H), 8.14 – 8.06 (m, 4H), 8.06 – 8.03 (m, 2H), 8.00 – 7.92 (m, 7H), 7.90 – 7.78 (m, 7H), 7.76 – 7.71 (m, 7H), 7.67 – 7.54 (m, 9H), 7.54 – 7.48 (m, 2H), 7.48 – 7.39 (m, 7H), 7.39 – 7.34 (m, 5H), 7.31 – 7.21 (m, 7H), 7.19 – 7.08 (m, 7H), 7.08 – 7.00 (m, 4H), 7.00 – 6.90 (m, 3H), 6.79 – 6.78 (m, 1H), 6.71 – 6.67 (m, 3H), 6.63 – 6.58 (m, 3H), 6.55 – 6.50 (m, 3H), 6.50 – 6.44 (m, 3H), 6.44 – 6.39 (m, 2H), 6.22 – 6.06 (m, 9H), 4.22 – 4.09 (m, 4H), 4.08 – 3.92 (m, 4H), 3.88 – 3.72 (m, 9H), 3.31 – 3.23 (m, 2H), 3.15 (s, 3H), 3.07 (s, 3H), 2.63 – 2.60 (m, 6H), 2.55 (s, 1H), 2.49 – 2.35 (m, 3H), 2.36 – 2.13 (m, 16H), 2.09 – 1.88 (m, 18H), 1.68 – 1.62 (m, 31H), 1.62 – 1.56 (m, 56H), 1.35 – 1.34 (m, 68H), 1.23 – 1.06 (m, 27H), 0.62 – 0.61 (m, 5H), 0.58 – 0.57 (m, 5H), 0.24 – 0.22 (m, 17H), 0.22 – 0.20 (m, 27H), 0.13 – 0.11 (m, 5H), (mixture of two diastereomers *PP* & *PM* and their ratio is 1:1, both are reported). **MS** calcd for $C_{204}H_{221}N_{29}NaO_{33}Se_2Si_2$ $[M+Na]^+$ 3843.4268 found (HR-ESI) 3844.1257.

(1*S*)-Camph-Q^{S}XQ^{B}Q^{B}YQ^{B}X-T3-2eg-Q^{S}XQ^{B}Q^{B}YQ^{B}X-OMe (**13**) Compound **32** (15.76 mg, 4.13 µmol) was treated with a 50 % solution of TFA in DCM (4 mL) at r.t. for 48 h. Then the solvent was removed under vacuum, obtaining the product as a yellow solid (14.03 mg, quant.). **^{1}H NMR** (500 MHz, Pyridine-d_5, 25 °C) δ [ppm] 12.27 (s, 1H), 12.23 (s, 1H), 12.17 (s, 1H), 12.12 – 12.10 (m, 1H), 12.04 (d, *J* = 22.2 Hz, 1H), 11.91 (s, 1H), 11.88 (d, *J* = 11.5 Hz, 1H), 11.83 (s, 1H), 11.67 (d, *J* = 2.3 Hz, 1H), 11.55 – 11.49 (m, 1H), 11.48 – 11.42 (m, 1H), 10.10 (s, 1H), 9.18 (d, *J* = 11.3 Hz, 2H), 9.11 (dd, *J* = 11.7, 7.3 Hz, 1H), 9.03 (s, 1H), 8.68 – 8.61 (m, 3H), 8.60 – 8.53 (m, 1H), 8.49 (dd, *J* = 23.1, 7.4 Hz, 1H), 8.42 – 8.31 (m, 5H), 8.26 – 8.14 (m, 6H), 8.05 – 7.91 (m, 3H), 7.87 – 7.80 (m, 4H), 7.79 – 7.73 (m, 3H), 7.70 – 7.61 (m, 3H), 7.57 – 7.48 (m, 4H), 7.48 – 7.40 (m, 4H), 7.39 – 7.29 (m, 4H), 7.07 – 6.97 (m, 3H), 6.89 – 6.74 (m, 5H), 6.52 – 6.44 (m, 1H), 4.43 – 4.32 (m, 1H), 4.08 – 3.96 (m, 3H), 3.94 – 3.75 (m, 6H), 3.67 – 3.60 (m, 2H), 3.15 – 3.06 (m, 1H), 3.06 – 2.95 (m, 1H), 2.81 – 2.74 (m, 1H), 2.72 – 2.63 (m, 1H), 2.43 – 2.21 (m, 6H), 2.21 – 2.05 (m, 4H), 1.88 – 1.70 (m, 1H), 1.70 – 1.63 (m, 1H), 1.59 – 1.51 (m, 2H), 1.49 – 1.42 (m, 2H), 1.35 – 1.13 (m, 34H), 1.13 – 1.00 (m, 18H), 0.66 (s, 3H), 0.58 (s, 3H), 0.23 (s, 3H). **MS** calcd for $C_{178}H_{165}N_{29}NaO_{33}Se_2$ $[M+Na]^+$ 3419.0347, found (HR-ESI) 3419.7741.

(1*S*)-Camph-Q^{B}XQ^{S}Q^{B}YQ^{B}X-T3-3eg-Q^{S}XQ^{B}Q^{B}YQ^{B}X-OH (**33**) Compound **33** was synthesized using the SPS procedures reported in 5.2 on SASRIN resin loaded via HBTU-coupling described in 5.2 (scale: 32 µmol). After full cleavage and precipitation in DCM/MeOH, the product was obtained as a yellow solid (56.00 mg, 45 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.76 (s, 1H), 11.54 (s, 1H), 11.28 (s, 1H), 11.27 (s, 1H), 11.19 (d, *J* = 1.9 Hz, 1H), 11.15 (d, *J* = 3.3 Hz, 1H), 11.03 (t, *J* = 3.4 Hz, 2H), 10.91 – 10.88 (m, 2H), 9.46 (s, 1H), 8.63 (s, 1H), 8.41 (t, *J* = 3.7 Hz, 1H), 8.30 (q, *J* = 3.6 Hz, 1H), 8.23 – 8.19 (m, 2H), 8.14 – 8.09 (m, 1H), 8.03 – 7.95 (m, 4H), 7.91 (dp, *J* = 8.3, 1.3 Hz, 1H), 7.86 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.79 – 7.72 (m, 3H), 7.71 – 7.64 (m, 7H), 7.60 – 7.49 (m, 6H), 7.44 – 7.28 (m, 8H), 7.21 – 7.16 (m, 2H), 7.11 – 6.99 (m, 5H), 6.86 – 6.78 (m, 2H), 6.68 – 6.61 (m, 2H), 6.50 – 6.40 (m, 3H), 6.30 – 6.26 (m, 2H), 6.05 (d, *J* = 3.7 Hz, 1H), 4.20 – 4.08 (m, 5H), 3.98 – 3.93 (m, 3H), 3.92 – 3.87 (m, 1H), 3.84 – 3.74 (m, 5H), 3.70 – 3.66 (m, 2H), 2.58 – 2.53 (m, 6H), 2.42 – 2.38 (m, 4H), 2.38 – 2.30 (m, 6H), 2.27 – 2.21 (m, 2H), 2.17 – 2.11 (m, 4H), 2.04 – 1.96 (m, 4H), 1.75 – 1.67 (m, 2H), 1.64 – 1.62 (m, 18H), 1.56 – 1.53 (m, 22H), 1.29 – 1.18 (m, 26H), 1.19 – 1.10 (m, 14H), 1.08 (dd, *J* = 6.7, 1.8 Hz, 3H), 1.04 (dd, *J* = 6.7, 1.5 Hz, 3H) 0.59 (s, 3H), 0.54 (s, 3H), 0.18 – 0.15 (m, 18H), 0.09 (s, 3H). **MS** calcd for $C_{205}H_{223}N_{29}NaO_{34}Se_2Si_2$ $[M+Na]^+$ 3873.4373, found (HR-ESI) 3874.2232, calcd for $C_{205}H_{223}KN_{29}NaO_{34}Se_2Si_2$ $[M+Na+K]^{2+}$ 1959.7003, found (HR-ESI) 1959.0897.

(1*S*)-Camph-Q^{B}XQ^{S}Q^{B}YQ^{B}X-T3-3eg-Q^{S}XQ^{B}Q^{B}YQ^{B}X-OMe (**34**) Compound **33** (56.00 mg, 14.5 µmol, 1 eq.) was dissolved in a mixture of dry Chloroform/MeOH 3:2 (5 mL) under N_2. $TMSCHN_2$ (solut. 2 M in Hex, 8.5 µL, 0.029 mmol, 2 eq.) was added dropwise, and the solution was stirred at r.t. for 2 h. A few drops of acetic acid were added, and the solution was stirred for 5 min at r.t. Then the solution was diluted with DCM, washed with $NaHCO_3$, dried $MgSO_4$, filtered and concentrated. The product was obtained as a yellow solid (52 mg, 87 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.79 (s, 1H), 11.54 (s, 1H), 11.42 (s, 1H), 11.40 (s, 1H), 11.33 (s, 1H), 11.25 (s, 1H), 11.07 (d, *J* = 4.7 Hz, 1H), 11.05 (s, 1H), 10.93 (d, *J* = 1.9 Hz, 1H), 10.90 (d, *J* = 1.6 Hz, 1H), 9.51 (d, *J* = 1.6 Hz, 1H), 8.65 (d, *J* = 1.8 Hz, 1H), 8.38 (t, *J* = 3.7 Hz, 1H), 8.27 (dtd, *J* = 8.7, 4.5, 1.6 Hz, 3H), 8.24 (dt, *J* = 7.6, 1.2 Hz, 1H), 8.09 – 8.04 (m, 2H), 8.04 – 7.99 (m, 1H), 7.97 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.92 (ddd, *J* = 7.6, 3.4, 1.3 Hz, 1H), 7.85 (td, *J* = 7.8, 1.3 Hz, 2H), 7.79 (ddt, *J* = 7.8, 5.1, 1.5 Hz, 2H), 7.76 – 7.66 (m, 6H), 7.65 – 7.60 (m, 3H), 7.59 – 7.53 (m, 2H), 7.47 – 7.42 (m, 2H), 7.40 (dt, *J* = 5.9, 2.5 Hz, 2H), 7.39 – 7.34 (m, 4H), 7.33 – 7.29 (m, 2H), 7.23 – 7.18 (m, 2H), 7.13 – 7.07 (m, 4H), 7.06 – 6.99 (m, 3H), 6.90 (t, *J* = 2.2 Hz, 1H), 6.88 (dd, *J* = 3.6, 2.2 Hz, 1H), 6.74 (s, 1H), 6.69 (d, *J* = 4.4 Hz, 1H), 6.50 (t, *J* = 2.7 Hz, 1H), 6.48 (d, *J* = 2.2 Hz, 1H), 6.44 (d, *J* = 10.0 Hz, 1H), 6.34 (s, 1H), 6.32 (s, 1H), 6.10 (d, *J* = 3.4 Hz, 1H), 4.23 – 4.13 (m, 4H), 4.03 – 3.94 (m, 3H), 3.94 – 3.87 (m, 2H), 3.86 – 3.78 (m, 3H), 3.74 – 3.69 (m, 3H), 3.46 – 3.39 (m, 1H), 3.35 (dt, *J* = 16.8, 3.9 Hz, 1H), 3.10 (s, 3H), 3.08 – 2.96 (m, 4H), 2.72 – 2.65 (m, 2H), 2.63 – 2.60 (m, 2H), 2.58 (s, 3H), 2.46 – 2.27 (m, 13H), 2.22 – 2.18 (m, 3H), 2.10 – 1.98 (m, 6H), 1.83 – 1.72 (m, 5H), 1.72 – 1.69 (m, 3H), 1.69 – 1.64 (m, 13H), 1.60 – 1.55 (m, 20H), 1.33 – 1.21 (m, 16H), 1.21 – 1.15 (m, 14H), 1.12 (dd, *J* = 6.7, 1.5 Hz, 4H), 1.07 (d, *J* = 6.7 Hz, 4H), 0.63 (s, 3H), 0.59 (s, 3H), 0.23 – 0.19 (m, 18H), 0.13 (s, 3H). **MS** calcd for $C_{206}H_{225}N_{29}NaO_{34}Se_2Si_2$

$[M+Na]^+$ 3887.4530 found (HR-ESI) 3888.1566, calcd for $C_{206}H_{225}N_{29}Na_2O_{34}Se_2Si_2$ $[M+2Na]^{2+}$ 1955.2211 found (HR-ESI) 1955.5673.

(1*S*)-Camph-Q^{B}XQ^{S}Q^{B}YQ^{B}X-T3-3eg-Q^{S}XQ^{B}Q^{B}YQ^{B}X-OMe (**14**) Compound **34** (5.66 mg, 1.46 µmol) was treated with a 50 % solution of TFA in DCM (4 mL) at r.t. for 48 h. Then the solvent was removed under vacuum, obtaining the product as a yellow solid (5.04 mg, quant.). **^{1}H NMR** (500 MHz, Pyridine-d_5, 25 °C) δ [ppm] 12.39 (s, 1H), 12.20 (s, 1H), 12.10 (s, 1H), 12.06 (s, 1H), 12.00 (s, 1H), 11.87 (d, *J* = 2.3 Hz, 1H), 11.65 (d, *J* = 2.7 Hz, 1H), 11.62 (s, 1H), 11.59 (d, *J* = 5.7 Hz, 1H), 11.53 (d, *J* = 5.1 Hz, 1H), 10.05 (s, 1H), 9.28 (d, *J* = 4.4 Hz, 1H), 9.15 (d, *J* = 4.6 Hz, 1H), 9.03 (s, 1H), 8.92 – 8.77 (m, 2H), 8.70 (s, 2H), 8.59 (ddd, *J* = 12.6, 8.4, 6.6 Hz, 2H), 8.44 – 8.37 (m, 7H), 8.35 – 8.28 (m, 4H), 8.24 (ddd, *J* = 7.6, 3.2, 1.3 Hz, 1H), 8.17 (ddd, *J* = 9.6, 6.9, 5.5 Hz, 4H), 8.11 (s, 1H), 8.09 – 8.03 (m, 3H), 8.00 (dt, *J* = 8.2, 1.4 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 2.2 Hz, 1H), 7.80 (ddd, *J* = 12.2, 6.6, 3.7 Hz, 2H), 7.77 – 7.72 (m, 3H), 7.72 – 7.67 (m, 2H), 7.56 – 7.50 (m, 3H), 7.46 (td, *J* = 7.9, 3.7 Hz, 1H), 7.40 – 7.31 (m, 2H), 7.31 – 7.25 (m, 2H), 7.02 (s, 1H), 6.97 (d, *J* = 5.4 Hz, 1H), 6.91 – 6.84 (m, 2H), 6.82 (d, *J* = 5.0 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.54 (d, *J* = 3.0 Hz, 1H), 4.31 – 4.26 (m, 1H), 4.16 (s, 1H), 3.93 – 3.77 (m, 6H), 3.67 – 3.58 (m, 3H), 3.39 – 3.33 (m, 2H), 3.32 (s, 3H), 3.25 – 3.20 (m, 2H), 3.00 (t, *J* = 6.1 Hz, 1H), 2.95 (t, *J* = 6.1 Hz, 1H), 2.88 – 2.84 (m, 2H), 2.72 – 2.65 (m, 4H), 2.62 – 2.57 (m, 4H), 2.55 – 2.52 (m, 3H), 2.46 – 2.27 (m, 3H), 2.24 – 2.15 (m, 4H), 2.11 – 2.06 (m, 2H), 1.90 – 1.69 (m, 2H), 1.16 – 1.01 (m, 44H), 0.68 (s, 3H), 0.59 (s, 3H), 0.24 (s, 3H). **MS** calcd for $C_{180}H_{169}N_{29}NaO_{34}Se_2$ $[M+Na]^+$ 3463.0609, found (HR-ESI) 3463.9677, calcd for $C_{180}H_{169}N_{29}Na_2O_{34}Se_2$ $[M+2Na]^{2+}$ 1743.0251, found (HR-ESI) 1743.5069.

(1*S*)-Camph-Q^{B}<u>X</u>Q^{S}Q^{B}<u>Y</u>Q^{B}<u>X</u>-T3-4eg-Q^{S}<u>X</u>Q^{B}Q^{B}<u>Y</u>Q^{B}<u>X</u>-OH (**35**) Compound **35** was synthesized using the SPS procedures reported in 5.2 on SASRIN resin loaded via HBTU-coupling described in 5.2 (scale: 32 µmol). After full cleavage and precipitation in DCM/MeOH, the product was obtained as a yellow solid (53.00 mg, 42 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.81 (s, 1H), 11.59 (s, 1H), 11.35 (s, 1H), 11.30 (s, 1H), 11.17 (s, 1H), 11.11 (s, 2H), 10.96 – 10.91 (m, 3H), 9.52 (s, 1H), 8.72 (s, 1H), 8.42 (s, 1H), 8.37 (s, 1H), 8.33 – 8.29 (m, 2H), 8.29 – 8.25 (m, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 8.00 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 2H), 7.92 – 7.87 (m, 3H), 7.84 – 7.79 (m, 4H), 7.77 – 7.69 (m, 4H), 7.67 – 7.61 (m, 4H), 7.61 – 7.54 (m, 4H), 7.44 – 7.38 (m, 4H), 7.36 – 7.32 (m, 3H), 7.30 (d, *J* = 3.3 Hz, 3H), 7.24 – 7.22 (m, 2H), 7.16 – 7.05 (m, 2H), 7.04 (d, *J* = 6.0 Hz, 3H), 6.90 (s, 1H), 6.81 (s, 1H), 6.72 (s, 1H), 6.57 (d, *J* = 2.2 Hz, 1H), 6.50 (d, *J* = 2.1 Hz, 1H), 6.48 (d, *J* = 2.5 Hz, 1H), 6.35 (s, 1H), 6.31 (s, 1H), 6.08 (d, *J* = 1.2 Hz, 1H), 4.27 – 4.14 (m, 3H), 4.01 – 3.97 (m, 2H), 3.94 – 3.91 (m, 2H), 3.90 – 3.81 (m, 2H), 3.78 – 3.73 (m, 2H), 3.73 – 3.64 (m, 2H), 3.45 – 3.40 (m, 2H), 3.18 – 3.03 (m, 2H), 2.86 – 2.77 (m, 2H), 2.72 – 2.65 (m, 2H), 2.64 – 2.56 (m, 2H), 2.54 – 2.51 (m, 2H), 2.47 – 2.34 (m, 6H), 2.32 – 2.20 (m, 2H), 2.04 – 1.99 (m, 4H), 1.87 – 1.81 (m, 2H), 1.81 – 1.73 (m, 4H), 1.70 – 1.56 (m, 8H), 1.65 (s, 8H), 1.63 (s, 8H), 1.59 – 1.57 (m, 8H), 1.52 – 1.45 (m, 10H), 1.20 – 1.13 (m, 34H), 1.12 – 1.03 (m, 11H), 0.64 (s, 3H), 0.59 (s, 3H), 0.23 – 0.17 (m, 19H), 0.19 (s, 3H), 0.14 (s, 3H). **MS** calcd for $C_{207}H_{227}N_{29}NaO_{35}Se_2Si_2$ $[M+Na]^+$ 3917.4636, found (HR-ESI) 3918.1596.

(1*S*)-Camph-Q^{B}XQ^{S}Q^{B}YQ^{B}X-T3-4eg-Q^{S}XQ^{B}Q^{B}YQ^{B}X-OMe (**36**) Compound **35** (53.00 mg, 13.6 µmol, 1 eq.) was dissolved in a mixture of dry Chloroform/MeOH 3:2 (5 mL) under N_2. $TMSCHN_2$ (solut. 2 M in Hex, 16.5 µL, 0.027 mmol, 2 eq.) was added dropwise, and the solution was stirred at r.t. for 2 h. A few drops of acetic acid were added, and the solution was stirred for 5 min at r.t. Then the solution was diluted with DCM, washed with $NaHCO_3$, dried $MgSO_4$, filtered and concentrated. The product was obtained as a yellow solid (77.55 mg, 70 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.82 (s, 1H), 11.59 (s, 1H), 11.45 (s, 1H), 11.43 (s, 1H), 11.36 (s, 1H), 11.31 (s, 1H), 11.12 (s, 1H), 11.10 (s, 1H), 10.97 (s, 1H), 10.95 (s, 1H), 9.53 (s, 1H), 8.73 (s, 1H), 8.43 (s, 1H), 8.35 – 8.29 (m, 3H), 8.26 (d, *J* = 7.6 Hz, 1H), 8.10 – 8.05 (m, 4H), 8.00 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.95 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.87 (ddt, *J* = 9.9, 7.5, 1.5 Hz, 2H), 7.80 (ddd, *J* = 7.0, 5.6, 1.5 Hz, 2H), 7.77 – 7.70 (m, 8H), 7.69 – 7.61 (m, 2H), 7.58 – 7.53 (m, 2H), 7.48 – 7.38 (m, 2H), 7.37 (d, *J* = 5.0 Hz, 1H), 7.34 – 7.30 (m, 3H), 7.30 – 7.27 (m, 2H), 7.22 (td, *J* = 7.8, 2.4 Hz, 2H), 7.15 – 7.08 (m, 3H), 7.08 – 7.05 (m, 3H), 6.91 (t, *J* = 2.1 Hz, 2H), 6.75 (s, 1H), 6.73 (s, 1H), 6.61 (s, 1H), 6.52 (d, *J* = 7.9, 2.3 Hz, 2H), 6.47 (d, *J* = 2.3 Hz, 1H), 6.36 (s, 1H), 6.35 (s, 1H), 6.13 (d, *J* = 1.8 Hz, 1H), 4.25 – 4.09 (m, 7H), 4.06 – 3.93 (m, 6H), 3.91 – 3.83 (m, 5H), 3.82 – 3.71 (m, 4H), 3.11 (s, 3H), 2.71 – 2.59 (m, 6H), 2.54 – 2.50 (m, 2H), 2.44 – 2.35 (m, 7H), 2.26 – 2.19 (m, 5H), 2.09 – 1.95 (m, 7H), 1.69 (d, *J* = 1.8 Hz, 8H), 1.65 (s, 8H), 1.59 (s, 8H), 1.58 (d, *J* = 2.0 Hz, 8H), 1.36 – 1.28 (m, 31H), 1.23 – 1.04 (m, 24H), 0.64 (s, 3H), 0.59 (s, 3H), 0.23 (d, *J* = 1.2 Hz, 7H), 0.21 (s, 8H), 0.14 (s, 3H). **MS** calcd for $C_{208}H_{229}N_{29}NaO_{35}Se_2Si_2$ $[M+Na]^+$ 3931.4792 found (HR-ESI) 3932.1708.

(1*S*)-Camph-Q^{B}XQ^{S}Q^{B}YQ^{B}X-T3-4eg-Q^{S}XQ^{B}Q^{B}YQ^{B}X-OMe (**15**) Compound **36** (5.88 mg, 1.50 µmol) was treated with a 50 % solution of TFA in DCM (4 mL) at r.t. for 48 h. Then the solvent was removed under vacuum, obtaining the product as a yellow solid (5.24 mg, quant.). **^{1}H NMR** (500 MHz, Pyridine-d_5, 25 °C) δ [ppm] 12.16 (s, 1H), 11.99 (s, 1H), 11.86 (s, 1H), 11.83 (s, 1H), 11.77 (s, 1H), 11.66 (s, 1H), 11.42 (s, 1H), 11.40 (s, 1H), 11.38 (s, 1H), 11.33 (s, 1H), 9.81 (s, 1H), 9.09 (s, 1H), 8.92 (s, 1H), 8.80 (s, 1H), 8.64 – 8.58 (m, 2H), 8.38 (dd, *J* = 22.5, 7.5 Hz, 2H), 8.21 – 8.14 (m, 5H), 8.10 (td, *J* = 7.8, 1.6 Hz, 2H), 8.05 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.02 – 7.99 (m, 1H), 7.95 (d, *J* = 8.1 Hz, 3H), 7.86 – 7.79 (m, 3H), 7.71 – 7.66 (m, 3H), 7.63 (d, *J* = 2.9 Hz, 1H), 7.61 – 7.54 (m, 3H), 7.55 – 7.49 (m, 3H), 7.49 – 7.45 (m, 1H), 7.45 (s, 1H), 7.37 (s, 2H), 7.32 – 7.25 (m, 3H), 7.24 – 7.19 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.15 – 7.10 (m, 3H), 7.06 (t, *J* = 7.7 Hz, 3H), 6.82 – 6.76 (m, 3H), 6.69 – 6.57 (m, 3H), 6.31 (s, 1H), 4.08 – 4.02 (m, 1H), 3.92 (t, *J* = 7.4 Hz, 1H), 3.88 – 3.81 (m, 3H), 3.68 – 3.61 (m, 7H), 3.61 – 3.54 (m, 4H), 3.48 – 3.41 (m, 2H), 3.39 – 3.33 (m, 3H), 3.09 (s, 3H), 2.87 – 2.82 (m, 1H), 2.78 – 2.75 (m, 2H), 2.69 – 2.59 (m, 5H), 2.58 – 2.55 (m, 3H), 2.55 – 2.45 (m, 6H), 2.42 – 2.35 (m, 2H), 2.31 – 2.25 (m, 3H), 2.26 – 2.20 (m, 3H), 2.19 (d, *J* = 3.6 Hz, 4H), 2.17 – 2.10 (m, 2H), 2.10 – 2.02 (m, 2H), 1.95 (dd, *J* = 13.5, 7.0 Hz, 4H), 1.89 – 1.82 (m, 1H), 1.63 – 1.55 (m, 1H), 1.36 – 1.30 (m, 3H), 1.13 – 0.96 (m, 18H), 0.96 – 0.85 (m, 8H), 0.44 (s, 3H), 0.35 (s, 3H), 0.00 (s, 3H). **MS** calcd for $C_{182}H_{173}N_{29}NaO_{35}Se_2$ $[M+Na]^+$ 3507.0872, found (HR-ESI) 3506.9803, calcd for $C_{182}H_{173}KN_{29}NaO_{35}Se_2$ $[M+Na+K]^{2+}$ 1773.0252, found (HR-ESI) 1773.5141.

5.3.4 Synthesis of achiral sequences with a helix-turn-helix-motif

O_2N-Q^BX$Q^B$$Q^BYQ^B$X-T3-2eg-$Q^SXQ^B$$Q^BYQ^B$X-OH (**37**) Compound **37** was synthesized using the SPS procedures reported in 5.2 on SASRIN resin loaded via HBTU-coupling described in 5.2 (scale: 31 µmol). After full cleavage, the product was obtained as a yellow solid (96.00 mg, 85 %). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C) δ [ppm] 11.42 (d, *J* = 5.2 Hz, 2H), 11.35 (d, *J* = 4.2 Hz, 2H), 11.13 – 11.11 (m, 4H), 11.04 (s, 1H), 11.03 (s, 1H), 11.00 (s, 1H), 10.99 (s, 1H), 10.93 (s, 1H), 10.91 (s, 1H), 10.88 (d, *J* = 2.3 Hz, 3H), 10.87 (s, 2H), 10.86 (s, 1H), 10.85 (s, 1H), 10.80 (s, 1H), 8.53 (s, 1H), 8.46 (s, 1H), 8.43 (d, *J* = 3.7 Hz, 2H), 8.37 (ddd, *J* = 8.2, 4.0, 1.7 Hz, 5H), 8.31 (d, *J* = 7.7 Hz, 2H), 8.22 (dd, *J* = 8.2, 6.9 Hz, 3H), 8.14 (dd, *J* = 11.3, 7.3 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.98 – 7.85 (m, 7H), 7.79 (d, *J* = 1.3 Hz, 1H), 7.74 (dd, *J* = 12.3, 7.3 Hz, 7H), 7.70 – 7.67 (m, 2H), 7.65 – 7.58 (m, 11H), 7.47 – 7.39 (m, 12H), 7.39 – 7.27 (m, 8H), 7.27 – 7.22 (m, 6H), 7.19 – 7.12 (m, 6H), 7.09 – 7.01 (m, 4H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.76 – 6.74 (m, 3H), 6.67 – 6.63 (m, 4H), 6.61 (dd, *J* = 4.8, 2.2 Hz, 3H), 6.49 (d, *J* = 13.7 Hz, 4H), 6.41 (d, *J* = 9.2 Hz, 2H), 6.18 – 6.12 (m, 8H), 6.08 (s, 1H), 4.23 – 4.09 (m, 10H), 4.03 – 3.98 (m, 10H), 3.87 – 3.79 (m, 9H), 3.80 – 3.71 (m, 7H), 2.61 – 2.54 (m, 14H), 2.41 – 2.36 (m, 11H), 2.37 – 2.29 (m, 6H), 2.29 – 2.25 (m, 3H), 2.21 – 2.16 (m, 5H), 2.05 – 1.98 (m, 13H), 1.73 – 1.68 (m, 44H), 1.67 – 1.62 (m, 31H), 1.59 – 1.54 (m, 41H), 1.40 – 1.35 (m, 23H), 1.15 – 1.04 (m, 13H), 0.22 (d, *J* = 1.6 Hz, 37H), 0.20 (s, 19H), (mixture of two diastereomers *PP* and *PM* and their ratio is 1:1, both are reported). **MS** calcd for $C_{196}H_{211}N_{29}NaO_{33}SeSi_2$ $[M+Na]^+$ 3657.4320, found (HR-ESI) 3659.2401.

O_2N-Q^BX$Q^B$$Q^BYQ^B$X-T3-2eg-$Q^SXQ^B$$Q^BYQ^B$X-OMe (**38**) Compound **37** (96.00 mg, 26 µmol, 1 eq.) was dissolved in a mixture of dry Chloroform/MeOH 3:2 (5 mL) under N_2. $TMSCHN_2$ (solut. 2 M in Hex, 15 µL, 0.052 mmol, 2 eq.) was added dropwise, and the solution was stirred at r.t. for 2 h. A few drops of acetic acid were added, and the solution was stirred for 5 min at r.t. Then the solution was diluted with DCM, washed with $NaHCO_3$, dried $MgSO_4$, filtered and concentrated. The product was obtained after precipitation in EtOAc/*n*-Hex as a yellow solid (38.89 mg, 41 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.48 (s, 1H), 11.47 (s, 1H), 11.46 (s, 1H), 11.40 (s, 2H), 11.37 (s, 2H), 11.21 (s, 1H), 11.20 (s, 1H), 11.15 (d, *J* = 1.6 Hz, 2H), 11.02 (s, 2H), 10.98 (s, 1H), 10.97 (s, 1H), 10.95 (s, 2H), 10.88 (s, 1H), 10.87 (s, 1H), 8.54 (d, *J* = 7.5 Hz, 2H), 8.41 (ddd, *J* = 7.6, 4.3, 1.3 Hz, 2H), 8.38 – 8.33 (m, 6H), 8.22 (dt, *J* = 7.7, 1.3 Hz, 3H), 8.18 (dd, *J* = 7.5, 1.3 Hz, 2H), 7.98 (ddd, *J* = 7.5, 2.9, 1.3 Hz, 5H), 7.95 – 7.89 (m, 4H), 7.91 – 7.87 (m, 4H), 7.86 – 7.80 (m, 4H), 7.78 (ddt, *J* = 8.1, 2.9, 1.3 Hz, 4H), 7.76 – 7.64 (m, 4H), 7.64 – 7.58 (m, 4H), 7.38 (dd, *J* = 8.1, 2.2 Hz, 7H), 7.34 (ddd, *J* = 7.6, 6.3, 2.3 Hz, 5H), 7.32 – 7.27 (m, 5H), 7.22 – 7.15 (m, 7H), 7.15 – 7.09 (m, 4H), 7.07 – 7.01 (m, 4H), 7.00 – 6.95 (m, 5H), 6.92 – 6.89 (m, 2H), 6.87 (dd, *J* = 6.8, 2.3 Hz, 4H), 6.84 (d, *J* = 3.5 Hz, 2H), 6.73 – 6.69 (m, 5H), 6.58 (t, *J* = 9.2 Hz, 3H), 6.48 – 6.43 (m, 4H), 6.33 – 6.28 (m, 4H), 6.14 (d, *J* = 13.2 Hz, 3H), 6.07 (d, *J* = 9.0 Hz, 2H), 4.23 – 4.06 (m, 10H), 4.06 – 3.94 (m, 8H), 3.91 – 3.75 (m, 12H), 3.76 – 3.64 (m, 10H), 3.35 – 3.25 (m, 6H), 3.13 – 3.08 (m, 4H), 3.09 (s, 3H), 3.08 (s, 3H), 2.86 – 2.81 (m, 2H), 2.65 – 2.60 (m, 4H), 2.59 – 2.55 (m, 6H), 2.53 (s, 3H), 2.44 – 2.28 (m, 26H), 2.27 (s, 9H), 2.09 – 1.98 (m, 2H), 1.85 – 1.70 (m, 18H), 1.69 – 1.67 (m, 18H), 1.65 (s, 9H), 1.57 (s, 9H), 1.56 – 1.55 (m, 18H), 1.54 (s, 9H), 1.22 – 1.13 (m, 47H), 1.13 – 1.04 (m, 24H), 0.22 (s, 9H), 0.20 – 0.19 (m,

27H), (mixture of two diastereomers *PP* and *PM* and their ratio is 1:1, both are reported).**MS** calcd for $C_{197}H_{213}N_{29}Na_2O_{33}SeSi_2$ $[M+2Na]^{2+}$ 1847.2184 found (HR-ESI) 1847.5735.

O_2N-Q^BX$Q^B$$Q^BYQ^B$X-T3-2eg-$Q^SXQ^B$$Q^BYQ^B$X-OMe (**16**) Compound **16** (16.22 mg, 4.45 µmol) was treated with a 50 % solution of TFA in DCM (4 mL) at r.t. for 48 h. Then the solvent was removed under vacuum, obtaining the product as a yellow solid (14.58 mg, quant.). **^{1}H NMR** (500 MHz, Pyridine-d_5, 25 °C) δ [ppm] 12.23 (s, 3H), 12.12 (d, *J* = 4.0 Hz, 2H), 12.07 (s, 3H), 12.02 (s, 2H), 11.85 (s, 2H), 11.75 (s, 1H), 11.74 (s, 1H), 11.71 (s, 1H), 11.70 (s, 1H), 11.60 (s, 1H), 11.58 (s, 1H), 11.52 (s, 1H), 11.47 (s, 1H), 11.45 (s, 1H), 11.42 (s, 1H), 9.13 (d, *J* = 16.5 Hz, 3H), 9.09 (s, 2H), 9.08 – 9.05 (m, 2H), 8.92 – 8.88 (m, 4H), 8.83 (d, *J* = 7.5 Hz, 4H), 8.71 – 8.65 (m, 4H), 8.65 – 8.59 (m, 4H), 8.54 – 8.50 (m, 2H), 8.43 – 8.30 (m, 10H), 8.17 – 8.09 (m, 7H), 8.07 – 8.01 (m, 7H), 7.99 – 7.90 (m, 8H), 7.84 – 7.76 (m, 8H), 7.76 – 7.64 (m, 9H), 7.48 – 7.42 (m, 8H), 7.39 – 7.35 (m, 4H), 7.33 – 7.29 (m, 4H), 7.05 (s, 1H), 7.00 (d, *J* = 4.1 Hz, 3H), 6.94 (s, 1H), 6.89 (s, 1H), 6.87 (s, 1H), 6.85 – 6.83 (m, 3H), 6.79 (d, *J* = 2.2 Hz, 1H), 6.77 – 6.74 (m, 3H), 6.53 – 6.49 (m, 4H), 4.27 – 4.22 (m, 2H), 4.18 – 4.10 (m, 8H), 4.08 – 4.00 (m, 7H), 3.96 – 3.72 (m, 11H), 3.66 – 3.56 (m, 5H), 3.33 – 3.29 (m, 3H), 3.31 (s, 3H), 3.30 (s, 3H), 3.11 – 3.00 (m, 1H), 2.99 – 2.92 (m, 1H), 2.80 – 2.72 (m, 2H), 2.71 – 2.63 (m, 5H), 2.55 – 2.44 (m, 6H), 2.43 – 2.31 (m, 10H), 2.31 – 2.17 (m, 8H), 2.13 – 2.05 (m, 6H), 1.30 – 1.14 (m, 53H), 1.14 – 0.99 (m, 38H), (mixture of two diastereomers *PP* and *PM* and their ratio is 1:1, both are reported). **MS** calcd for $C_{171}H_{157}N_{29}NaO_{33}Se$ $[M+Na]^+$ 3247.0556, found (HR-ESI) 3247.9970, calcd for $C_{171}H_{158}N_{29}NaO_{33}Se$ $[M+H+Na]^{2+}$ 1624.0314, found (HR-ESI) 1624.4006.

O_2N-Q^B<u>X</u>$Q^B$$Q^B$<u>Y</u>$Q^B$<u>X</u>-T3-4eg-$Q^S$<u>X</u>$Q^B$$Q^B$<u>Y</u>$Q^B$<u>X</u>-OH (**39**) Compound **39** was synthesized using the SPS procedures reported in 5.2 on SASRIN resin loaded via HBTU-coupling described in 5.2 (scale: 21 µmol). After full cleavage, the product was obtained as a yellow solid (32.05 mg, 41 %). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.59 (s, 1H), 11.53 (s, 1H), 11.34 (s, 1H), 11.19 (s, 1H), 11.16 (s, 1H), 11.10 (s, 1H), 11.09 (s, 1H), 11.07 (s, 1H), 10.96 (s, 1H), 10.94 (s, 1H), 8.71 (s, 1H), 8.47 – 8.43 (m, 2H), 8.40 (d, *J* = 4.1 Hz, 1H), 8.37 (d, *J* = 1.5 Hz, 1H), 8.32 (d, *J* = 7.4 Hz, 1H), 8.26 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.19 (dd, *J* = 7.7, 1.3 Hz, 1H), 8.01 – 95 (m, 3H), 7.91 – 7.85 (m, 2H), 7.83 – 7.72 (m, 3H), 7.72 – 7.62 (m, 4H), 7.62 – 7.54 (m, 5H), 7.49 – 7.36 (m, 8H), 7.36 – 7.28 (m, 5H), 7.23 – 7.15 (m, 4H), 7.15 – 7.02 (m, 4H), 6.81 (s, 2H), 6.66 (s, 1H), 6.57 (d, *J* = 2.3 Hz, 1H), 6.51 (d, *J* = 2.2 Hz, 1H), 6.35 (s, 1H), 6.30 (s, 1H), 6.21 (s, 1H), 6.07 (s, 1H), 4.27 – 4.10 (m, 4H), 4.06 – 3.96 (m, 4H), 3.94 – 3.90 (m, 1H), 3.86 – 3.78 (m, 4H), 3.77 – 3.66 (m, 2H), 3.46 – 3.36 (m, 1H), 3.34 – 3.30 (m, 1H), 3.17 – 3.05 (m, 3H), 2.86 – 2.83 (m, 3H), 2.83 – 2.79 (m, 2H), 2.66 – 2.63 (m, 1H), 2.63 – 2.56 (m, 3H), 2.55 – 2.50 (m, 2H), 2.45 – 2.40 (m, 3H), 2.41 – 2.34 (m, 3H), 2.33 – 2.29 (m, 1H), 2.27 – 2.25 (m, 3H), 2.25 – 2.19 (m, 1H), 2.05 – 1.98 (m, 2H), 1.91 – 1.86 (m, 3H), 1.78 – 1.67 (m, 18H), 1.65 – 1.61 (m, 15H), 1.59 – 1.57 (m, 18H), 1.54 – 1.44 (m, 10H), 1.21 – 1.03 (m, 20H), 0.24 – 0.22 (m, 26H). **MS** calcd for $C_{200}H_{219}N_{29}NaO_{35}SeSi_2$ $[M+Na]^+$ 3745.4844, found (HR-ESI) 3747.2139.

O_2N-Q^B<u>X</u>$Q^B$$Q^B$<u>Y</u>$Q^B$<u>X</u>-T3-4eg-$Q^5$<u>X</u>$Q^B$$Q^B$<u>Y</u>$Q^B$<u>X</u>-OMe (**40**) Compound **39** (32.00 mg, 8.61 µmol, 1 eq.) was dissolved in a mixture of dry Chloroform/MeOH 3:2 (5 mL) under N_2. $TMSCHN_2$ (solut. 2 M in Hex, 5 µL, 0.017 mmol, 2 eq.) was added dropwise, and the solution was stirred at r.t. for 2 h. A few drops of acetic acid were added, and the solution was stirred for 5 min at r.t. Then the solution was diluted with DCM, washed with $NaHCO_3$, dried $MgSO_4$, filtered and concentrated. The product was obtained as a yellow solid (32.17 mg, quant.). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ [ppm] 11.57 (s, 1H), 11.53 (s, 1H), 11.43 (s, 1H), 11.41 (s, 1H), 11.34 (s, 1H), 11.18 (s, 1H), 11.09 (s, 2H), 11.07 (s, 1H), 10.94 (s, 1H), 8.71 (s, 1H), 8.45 (d, *J* = 7.4 Hz, 1H), 8.42 (s, 1H), 8.38 (d, *J* = 8.5 Hz, 2H), 8.30 (d, *J* = 7.2 Hz, 1H), 8.27 – 8.18 (m, 2H), 8.19 (d, *J* = 7.4 Hz, 2H), 8.10 – 7.94 (m, 5H), 7.91 – 7.87 (m, 2H), 7.81 – 7.71 (m, 5H), 7.71 – 7.62 (m, 2H), 7.57 – 7.46 (m, 6H), 7.47 – 7.30 (m, 5H), 7.17 – 7.11 (m, 4H), 7.09 – 7.06 (m, 2H), 6.92 (s, 2H), 6.82 (s, 2H), 6.74 (s, 2H), 6.67 (s, 2H), 6.51 (s, 1H), 6.34 (s, 2H), 6.33 (s, 1H), 6.19 (s, 1H), 6.11 (s, 1H), 4.24 – 4.16 (m, 4H), 4.16 – 4.10 (m, 4H), 4.08 – 3.97 (m, 5H), 4.06 – 3.96 (m, 9H), 3.55 – 3.47 (m, 8H), 3.40 – 3.37 (m, 8H), 3.10 (s, 3H), 2.64 – 2.51 (m, 14H), 2.39 – 2.25 (m, 19H), 2.05 – 1.98 (m, 9H), 1.72 – 1.54 (m, 21H), 1.20 – 1.02 (m, 34H), 0.24 – 0.22 (m, 18). **MS** calcd for $C_{201}H_{221}N_{29}NaO_{35}SeSi_2$ $[M+Na]^+$ 3759.5001 found (HR-ESI) 3759.2182.

O_2N-Q^BX$Q^B$$Q^BYQ^B$X-T3-4eg-$Q^5XQ^B$$Q^BYQ^B$X-OMe (**17**) Compound **40** (30.00 mg, 8.03 µmol) was treated with a 50 % solution of TFA in DCM (4 mL) at r.t. for 48 h. Then the solvent was removed under vacuum, obtaining the product as a yellow solid (26.59 mg, quant.). **^{1}H NMR** (500 MHz, Pyridine-d_5, 25 °C) δ [ppm]
12.27 (s, 1H), 12.23 (s, 1H), 12.10 (s, 1H), 12.06 (s, 1H), 11.96 (s, 1H), 11.77 (s, 1H), 11.75 (s, 1H), 11.66 (s, 1H), 11.60 (s, 1H), 11.56 (s, 1H), 9.31 (s, 1H), 9.18 – 9.14 (m, 1H), 9.13 (t, *J* = 3.4 Hz, 1H), 8.95 – 8.91 (m, 1H), 8.87 – 8.82 (m, 2H), 8.71 – 8.68 (m, 2H), 8.62 (d, *J* = 8.2 Hz, 1H), 8.54 (dd, *J* = 7.5, 1.4 Hz, 1H), 8.44 (s, 1H), 8.43 – 8.37 (m, 3H), 8.37 – 8.32 (m, 2H), 8.20 – 8.16 (m, 4H), 8.14 (d, *J* = 7.4 Hz, 1H), 8.07 – 8.01 (m, 3H), 7.98 (s, 1H), 7.93 – 7.90 (m, 1H), 7.85 (d, *J* = 3.0 Hz, 2H), 7.79 – 7.72 (m, 4H), 7.71 (d, *J* = 6.0 Hz, 2H), 7.49 – 7.37 (m, 8H), 7.37 – 7.31 (m, 3H), 7.31 – 7.26 (m, 2H), 7.09 – 7.05 (m, 1H), 7.02 (s, 1H), 6.97 (s, 1H), 6.89 (s, 1H), 6.84 – 6.80 (m, 2H), 6.57 (s, 1H), 6.55 (s, 1H), 4.27 – 4.25 (m, 1H), 4.18 – 4.15 (m, 1H), 4.11 – 4.07 (m, 2H), 3.98 – 3.90 (m, 2H), 3.90 – 3.83 (m, 3H), 3.79 – 3.76 (m, 3H), 3.64 – 3.58 (m, 3H), 3.49 – 3.42 (m, 3H), 3.33 (s, 3H), 3.07 – 3.04 (m, 3H), 3.03 – 2.98 (m, 2H), 2.90 – 2.83 (m, 3H), 2.80 – 2.79 (m, 3H), 2.75 – 2.69 (m, 3H), 2.63 – 2.57 (m, 2H), 2.52 (d, *J* = 6.8 Hz, 4H), 2.41 – 2.36 (m, 3H), 2.35 – 2.27 (m, 3H), 2.23 – 2.19 (m, 2H), 2.18 – 2.07 (m, 3H), 1.67 – 1.61 (m, 2H), 1.69 – 1.62 (m, 2H), 1.14 – 1.10 (m, 16H), 1.09 – 1.02 (m, 22H), **MS** calcd for $C_{175}H_{165}N_{29}NaO_{35}Se$ $[M+Na]^+$ 3335.1080, found (HR-ESI) 3334.8369.

6 References

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7 NMR spectra of new compounds

7.1 Sequences to test handedness-induction via chiral B-unit

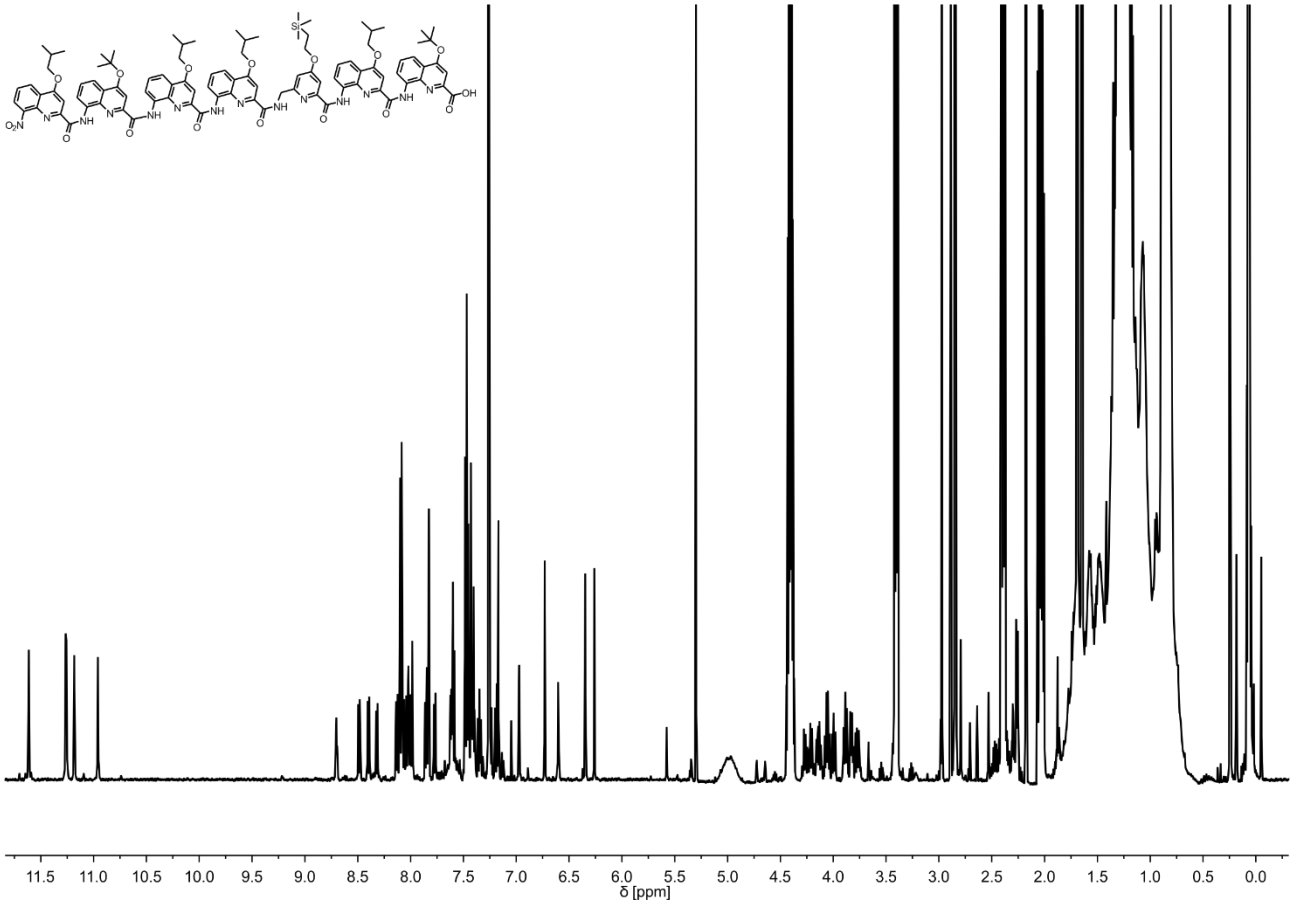

Figure S49. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **18**.

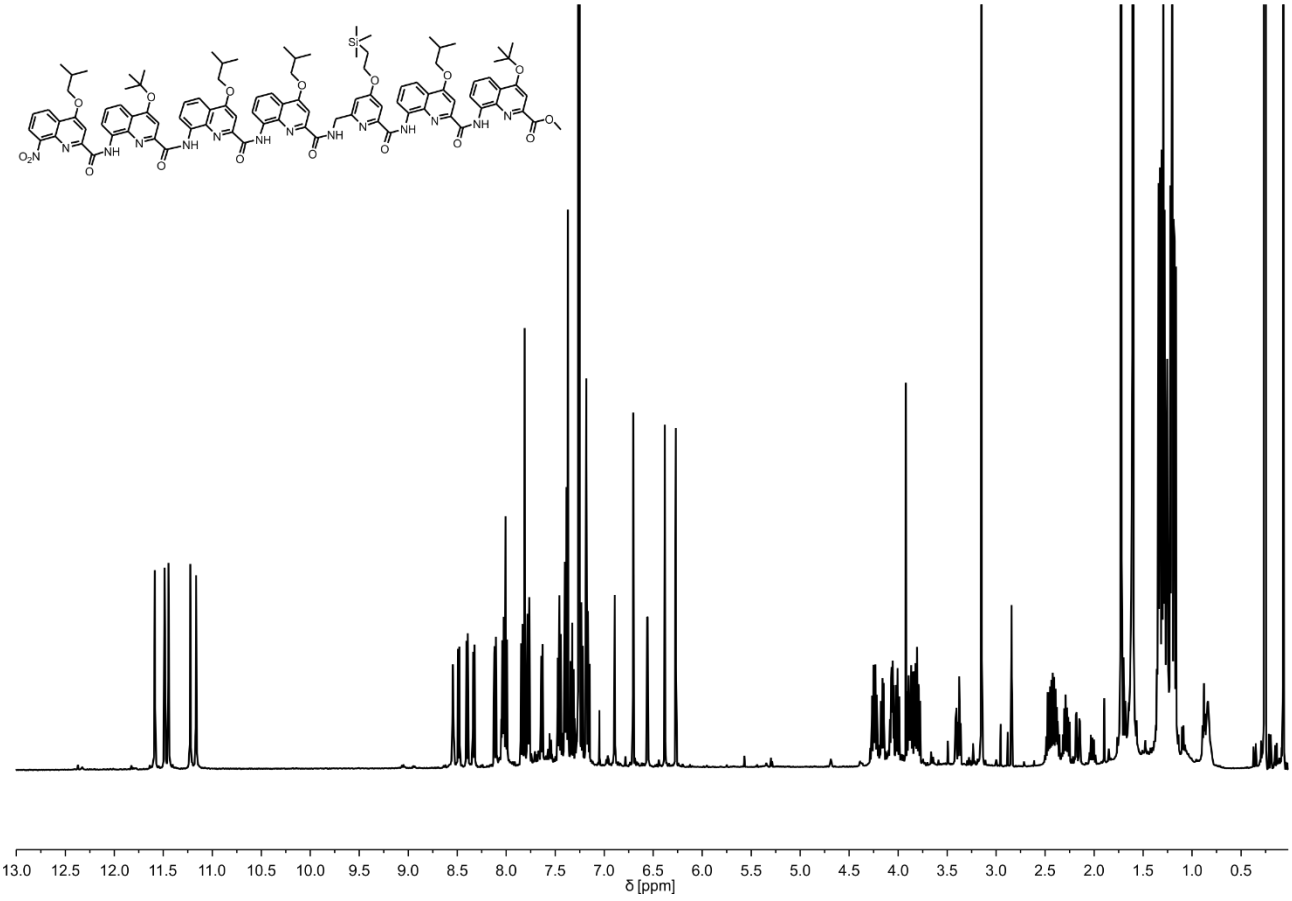

Figure S50. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4**.

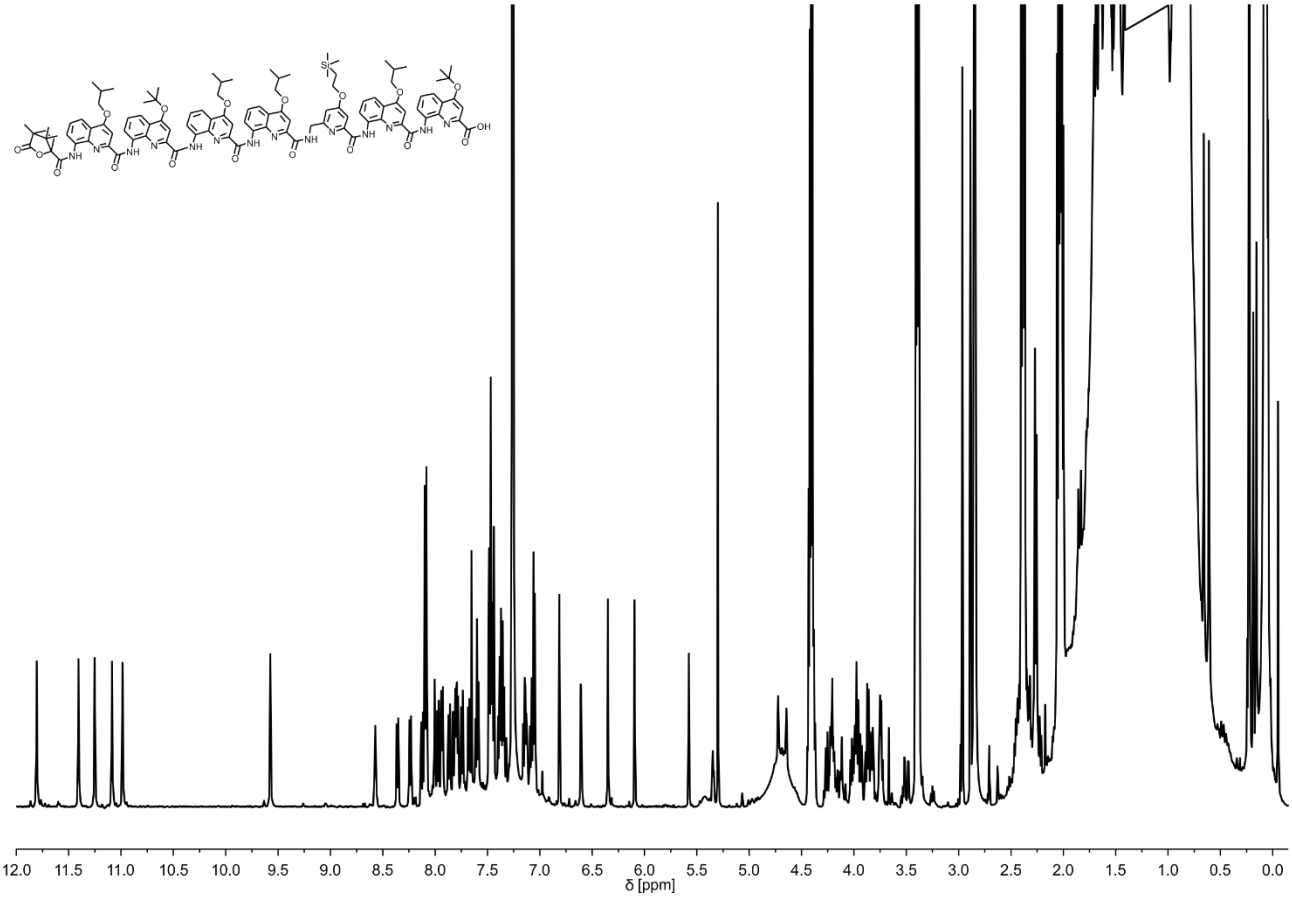

Figure S51. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **19**.

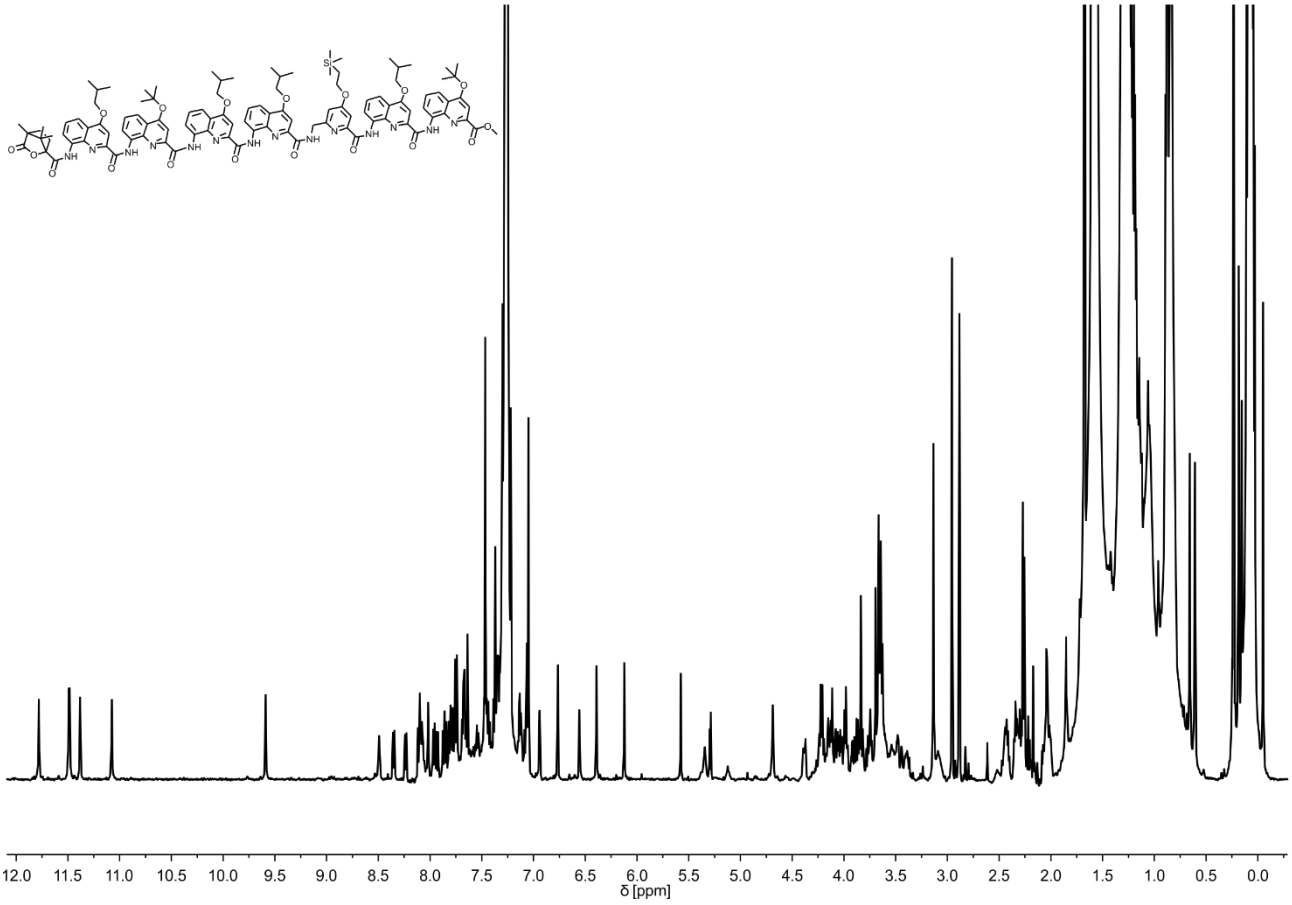

Figure S52. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5**.

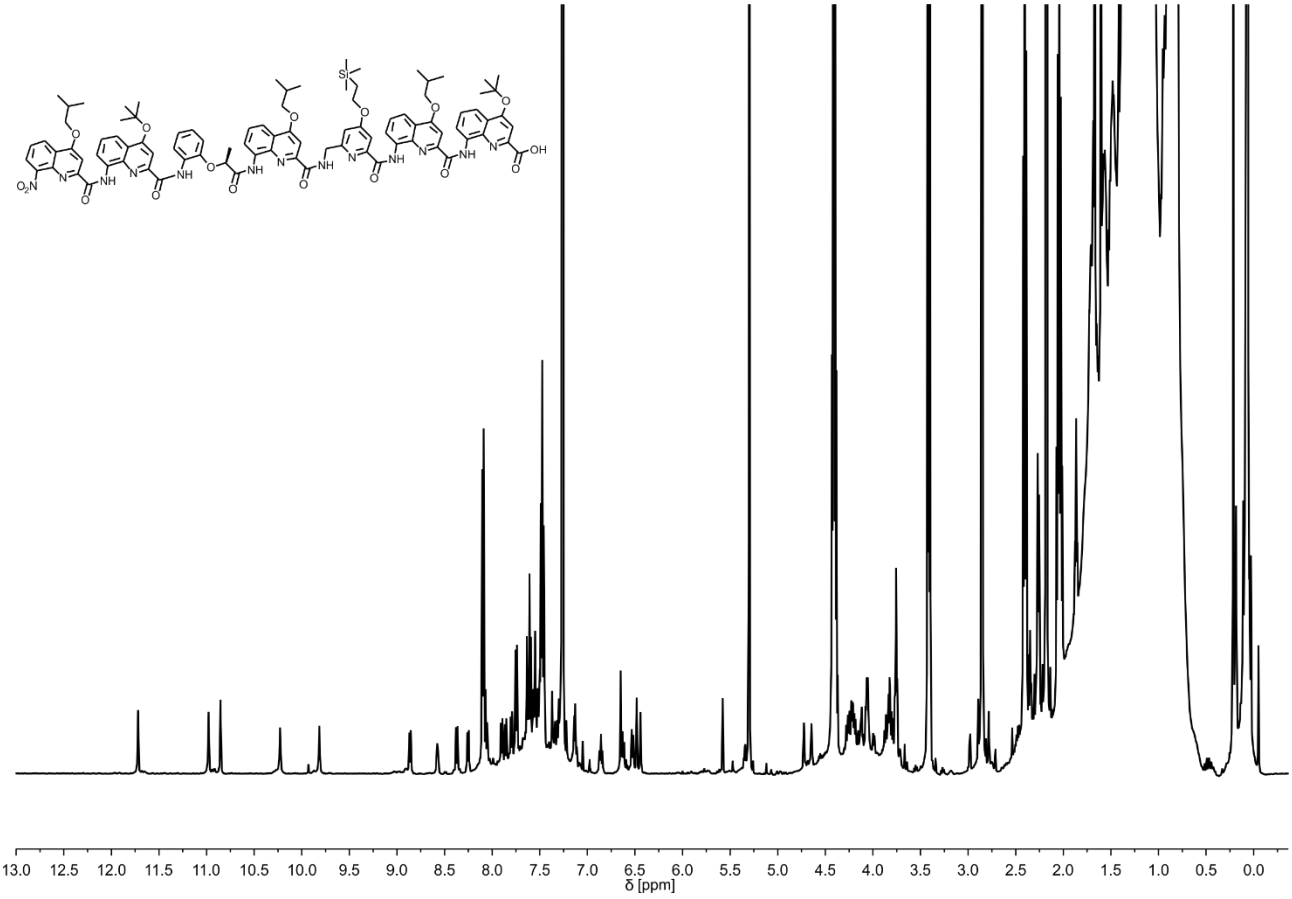

Figure S53. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **20**.

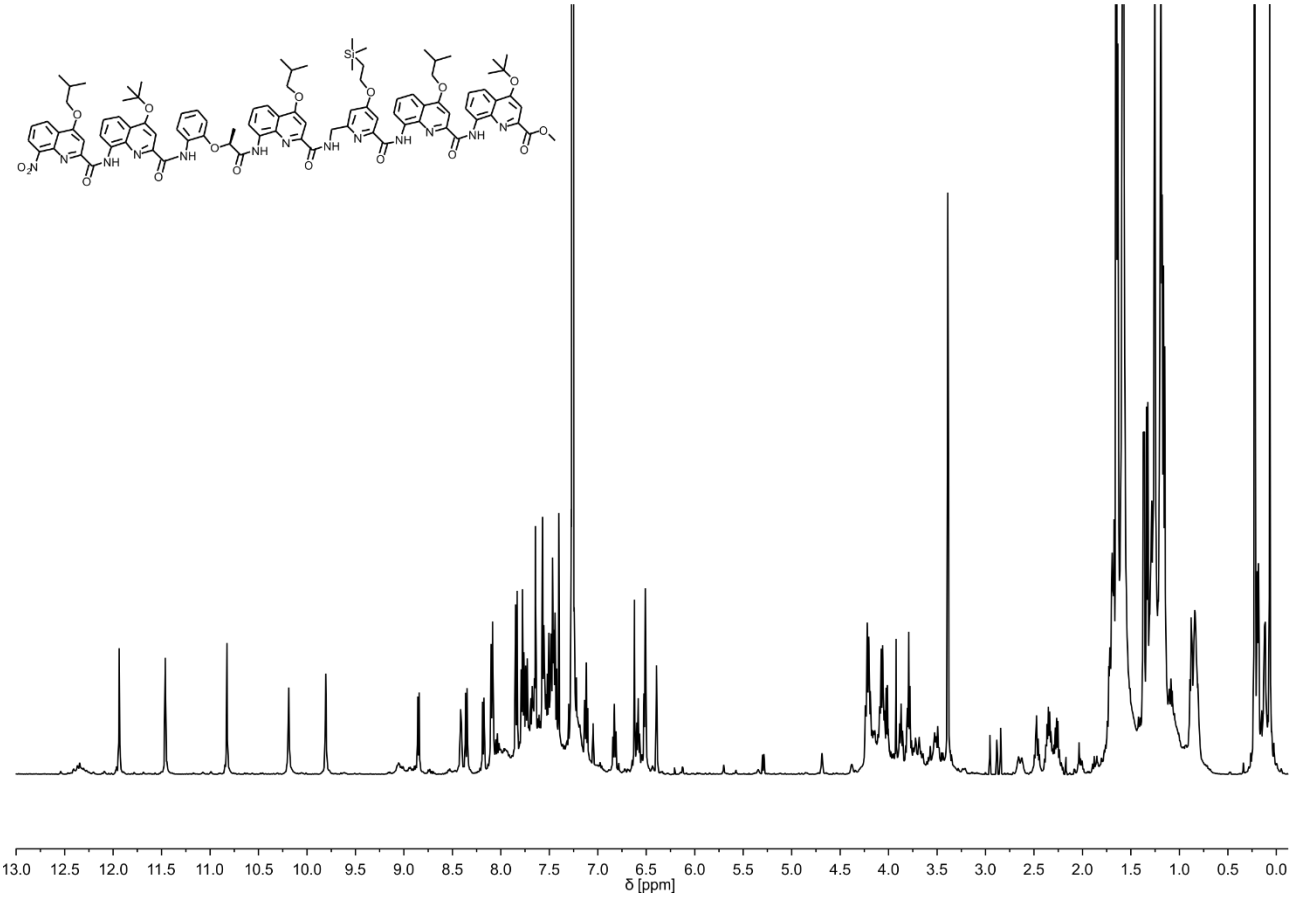

Figure S54. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **6**.

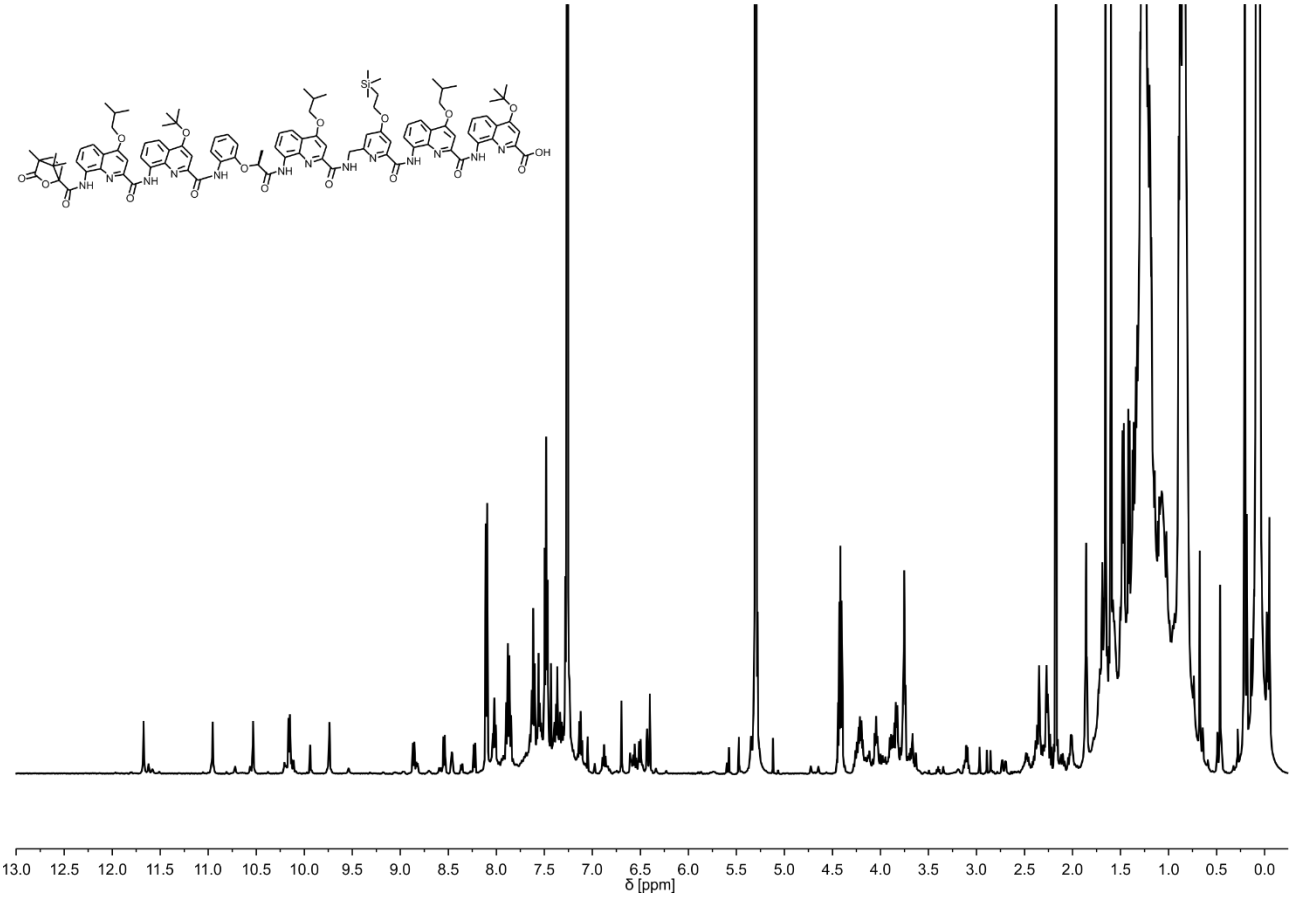

Figure S55. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **21**.

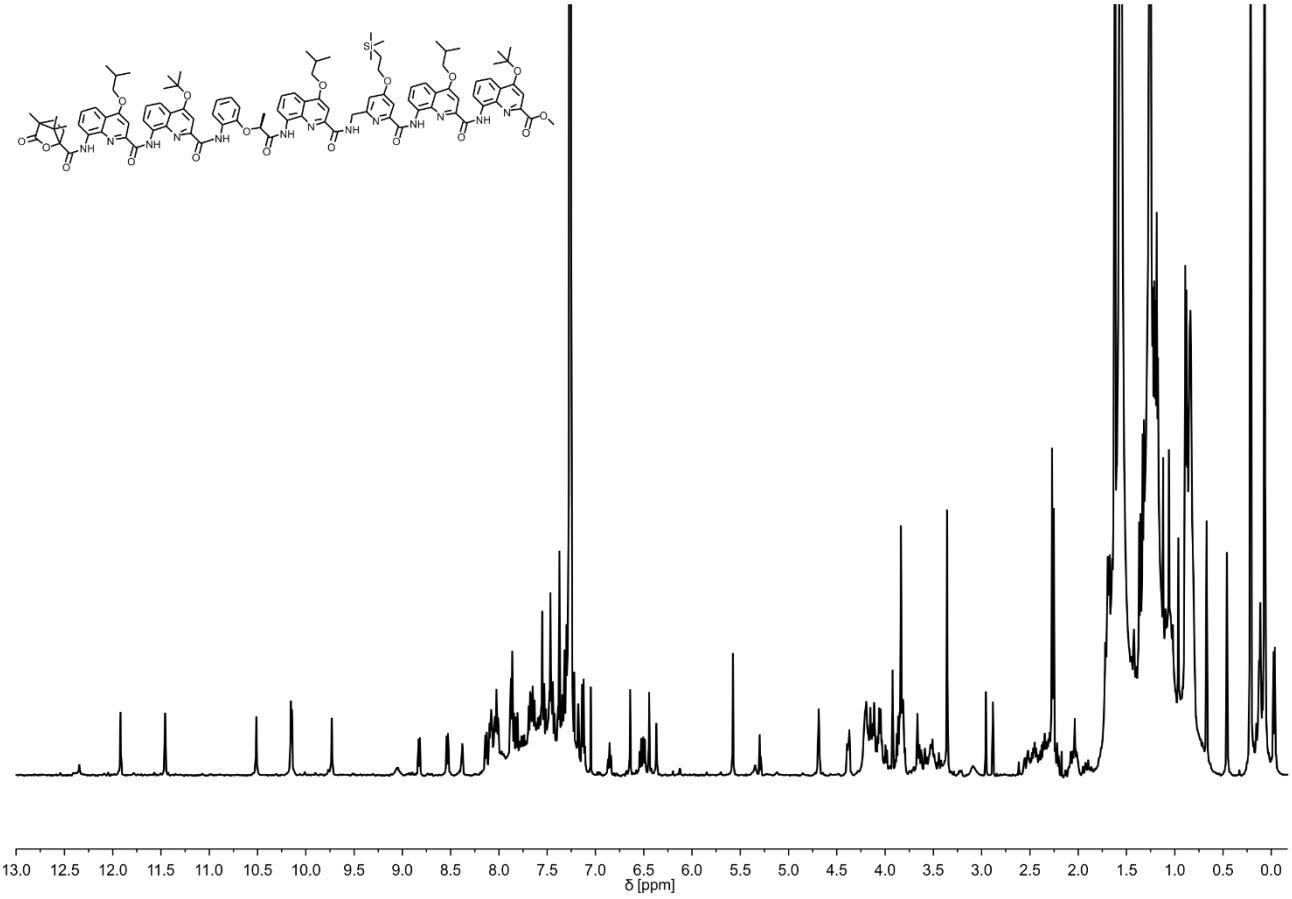

Figure S56. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **7**.

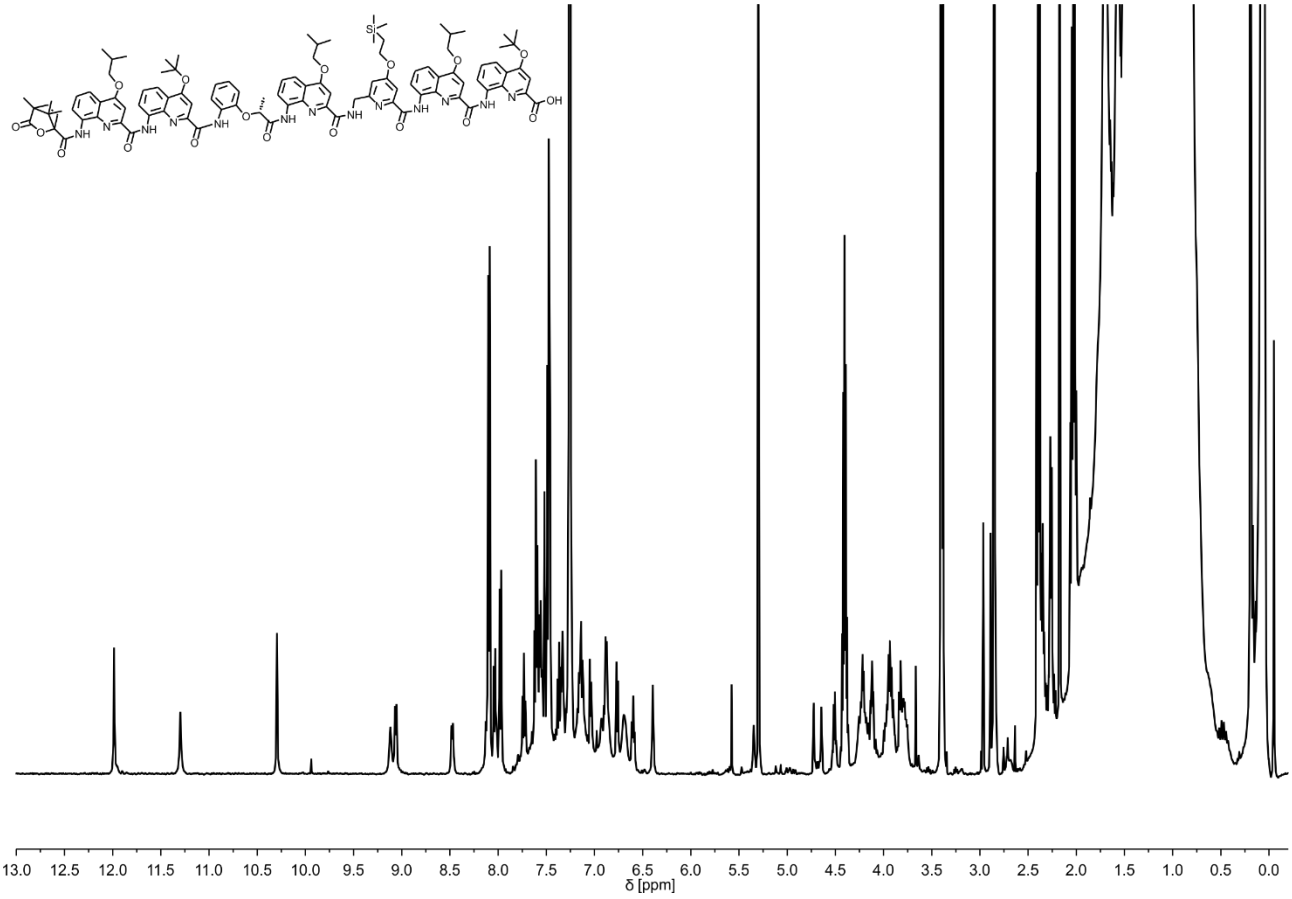

Figure S57. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **22**.

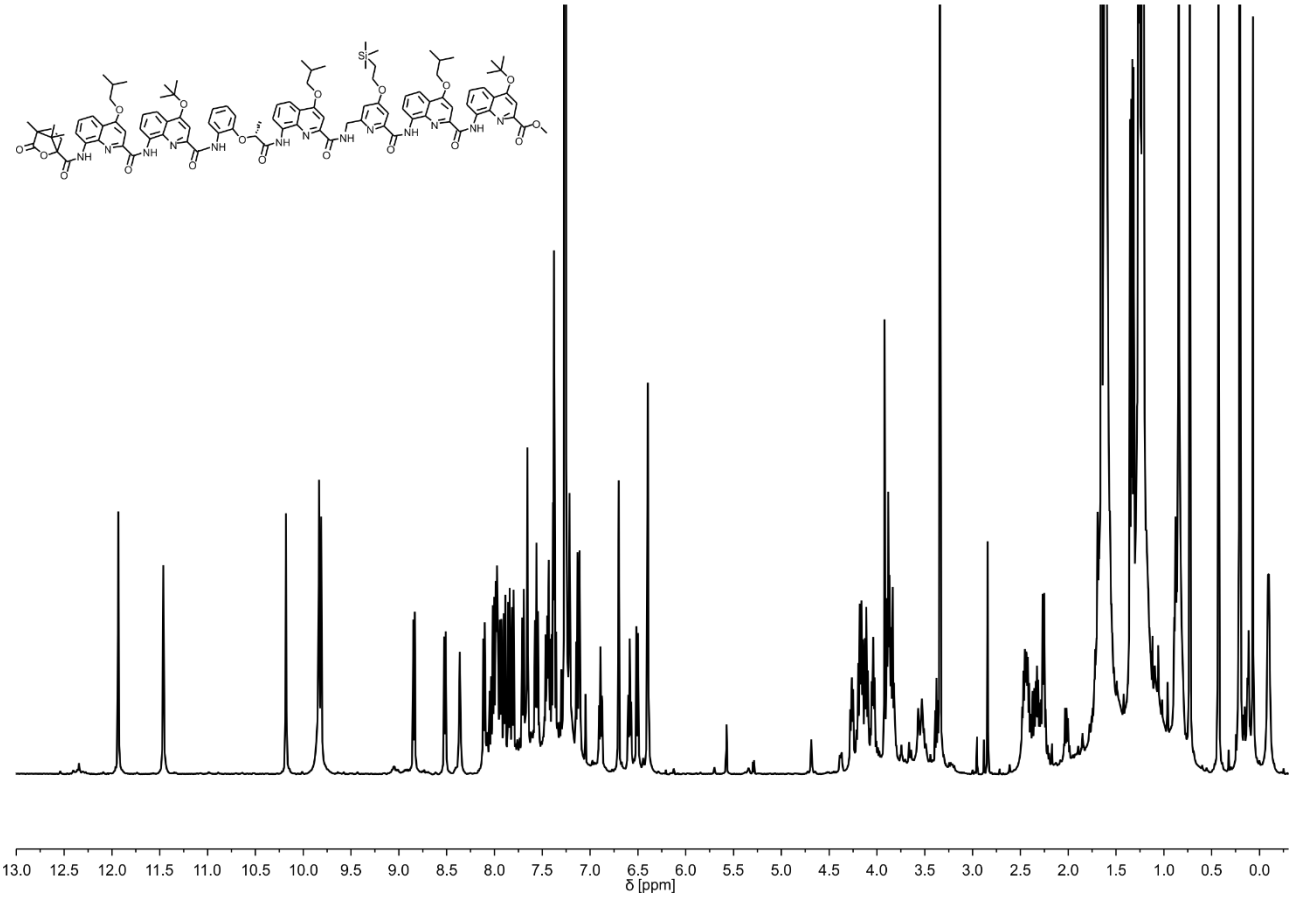

Figure S58. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **8**.

7.2 Sequences with a helix-turn-helix-motif and handedness-control in both helices

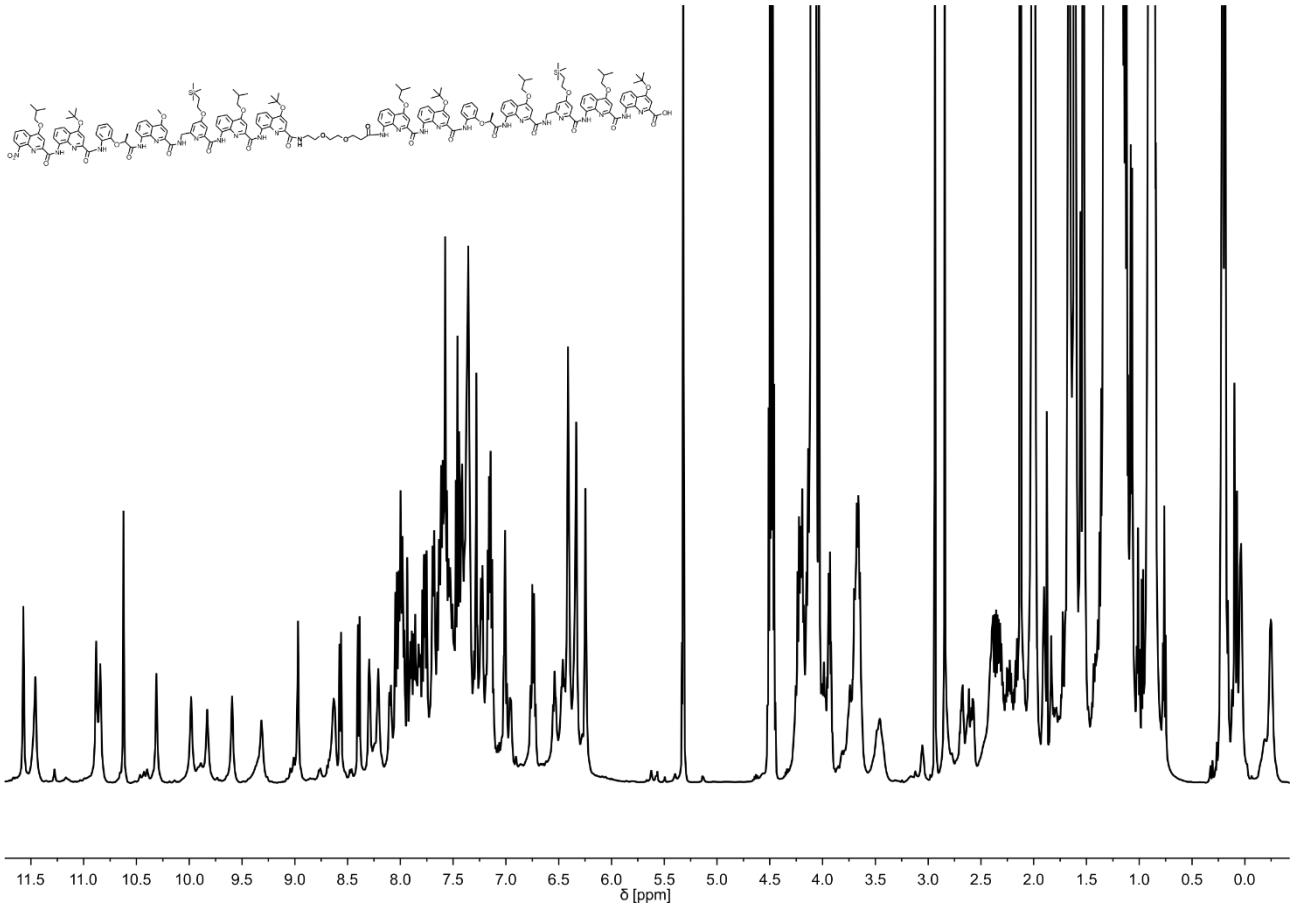

Figure S59. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of **23**.

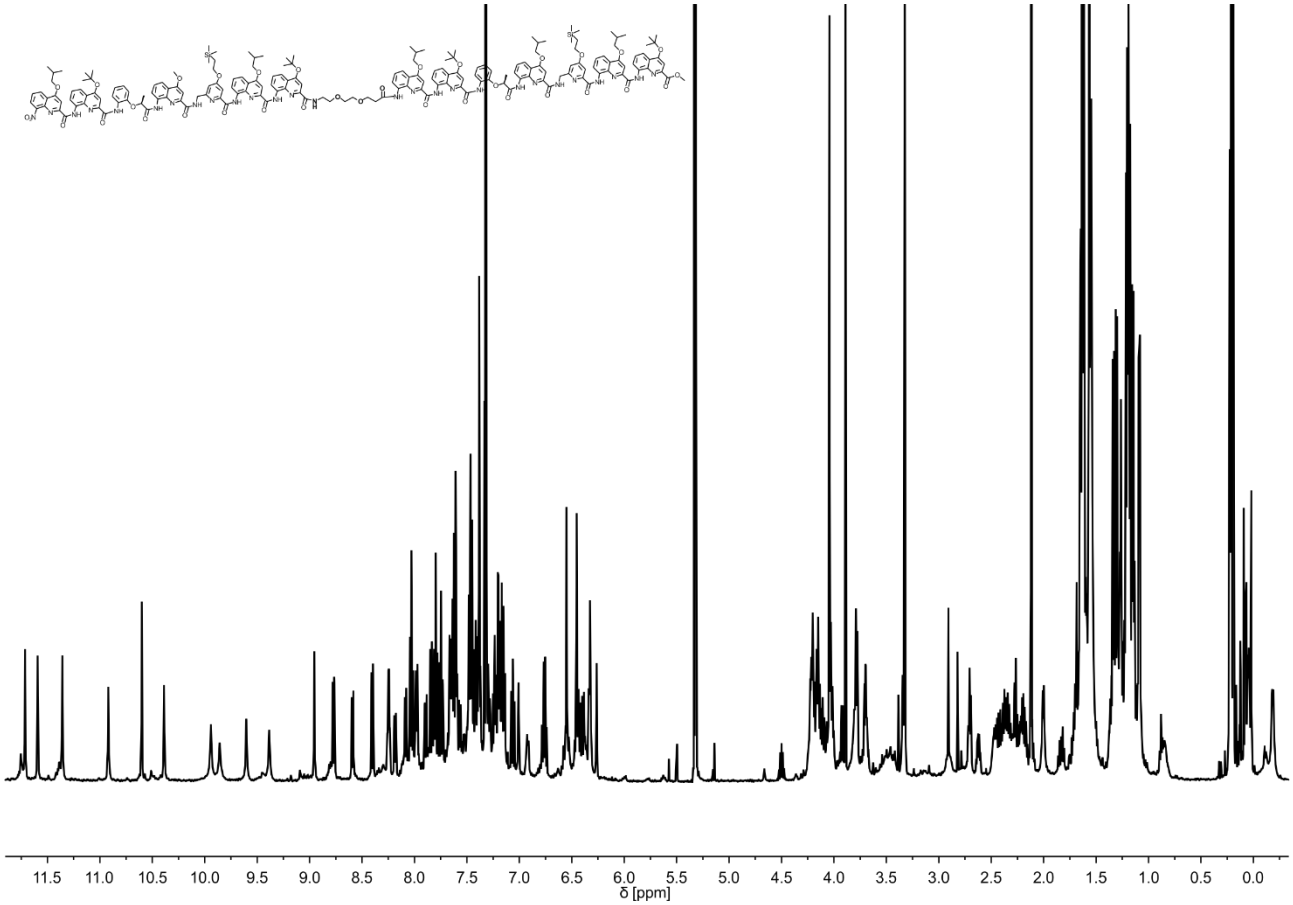

Figure S60. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of **24**.

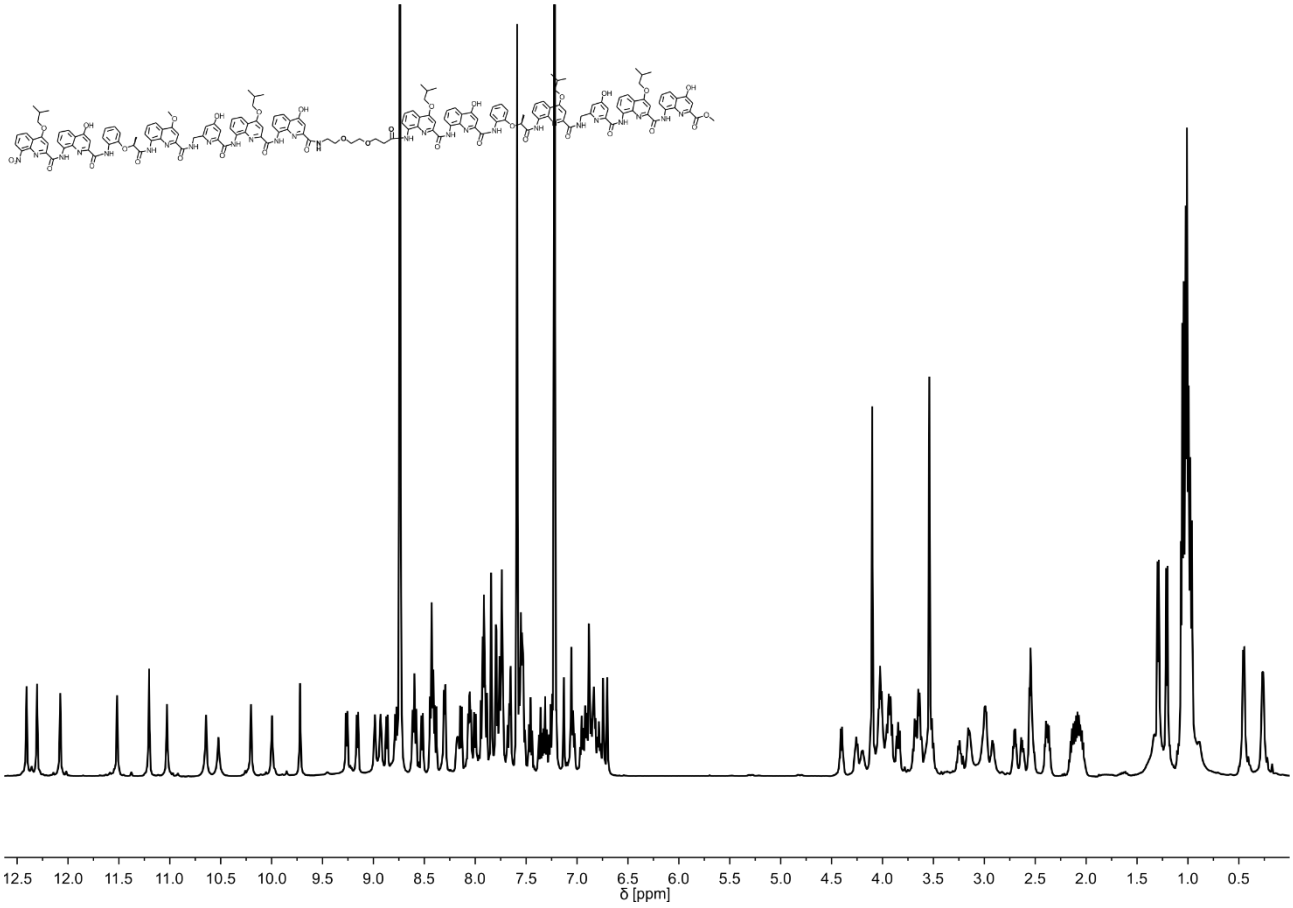

Figure S61. ^{1}H NMR spectrum (500 MHz, Pyridine-d_5) of **9**.

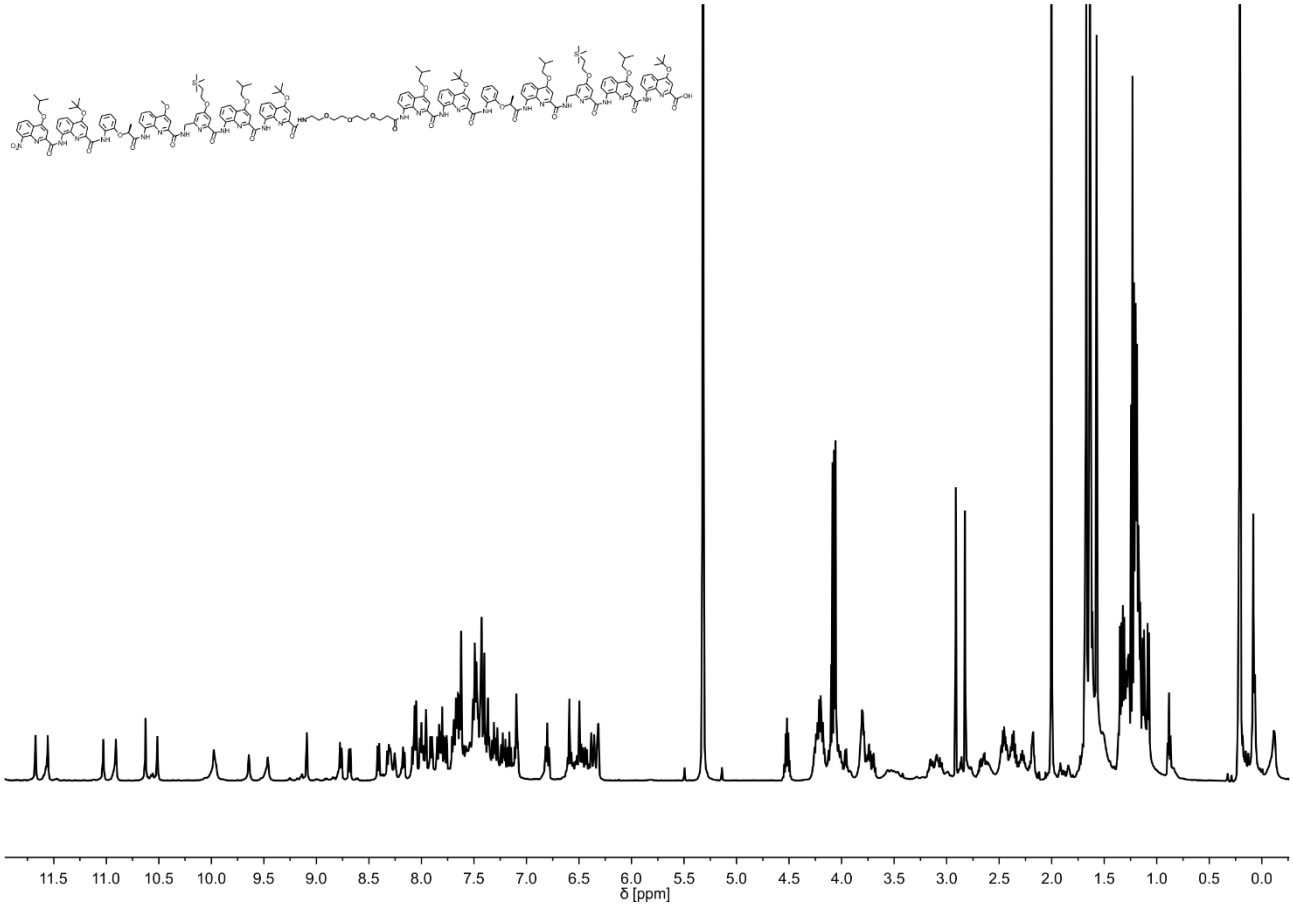

Figure S62. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of **25**.

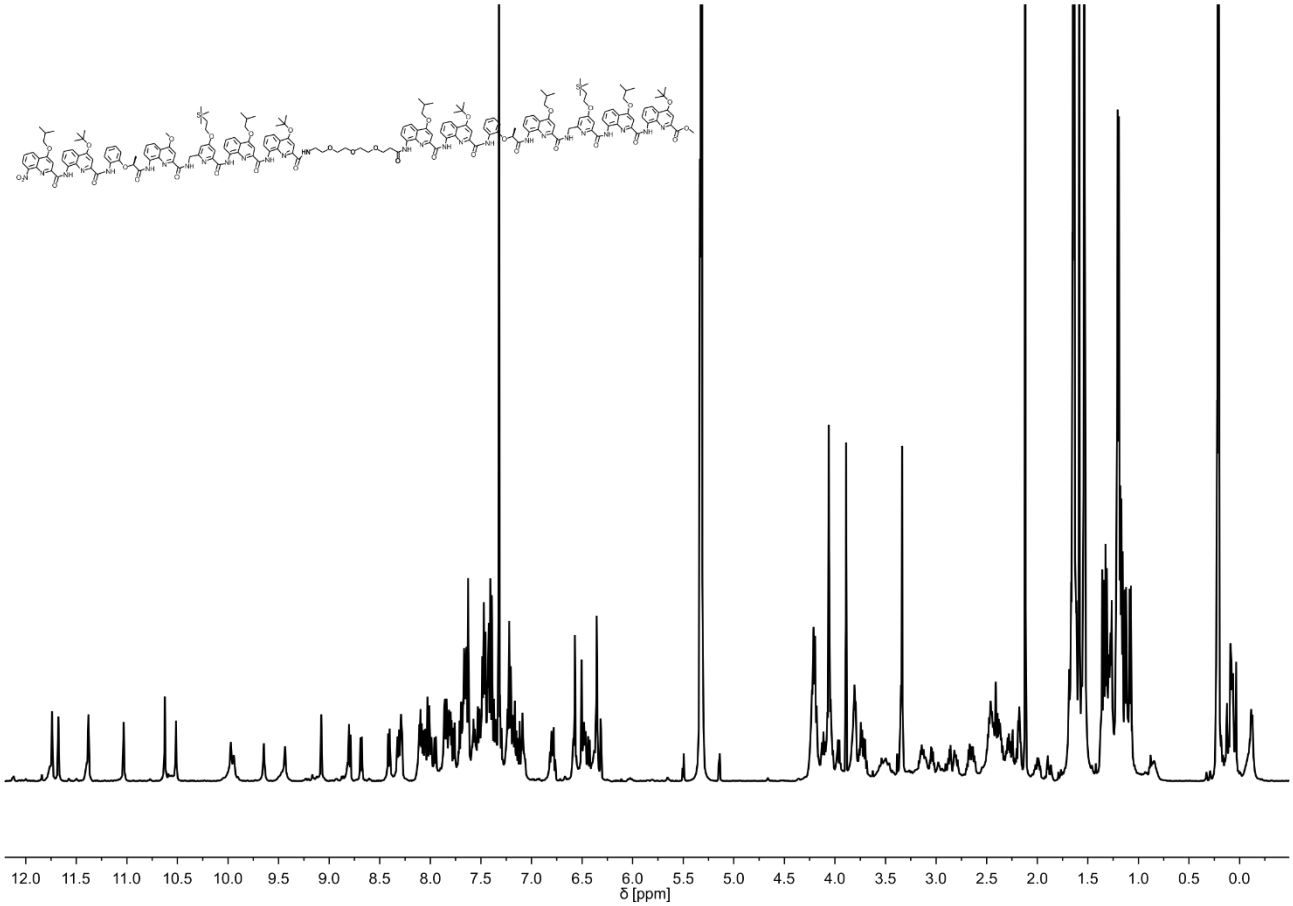

Figure S63. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of **26**.

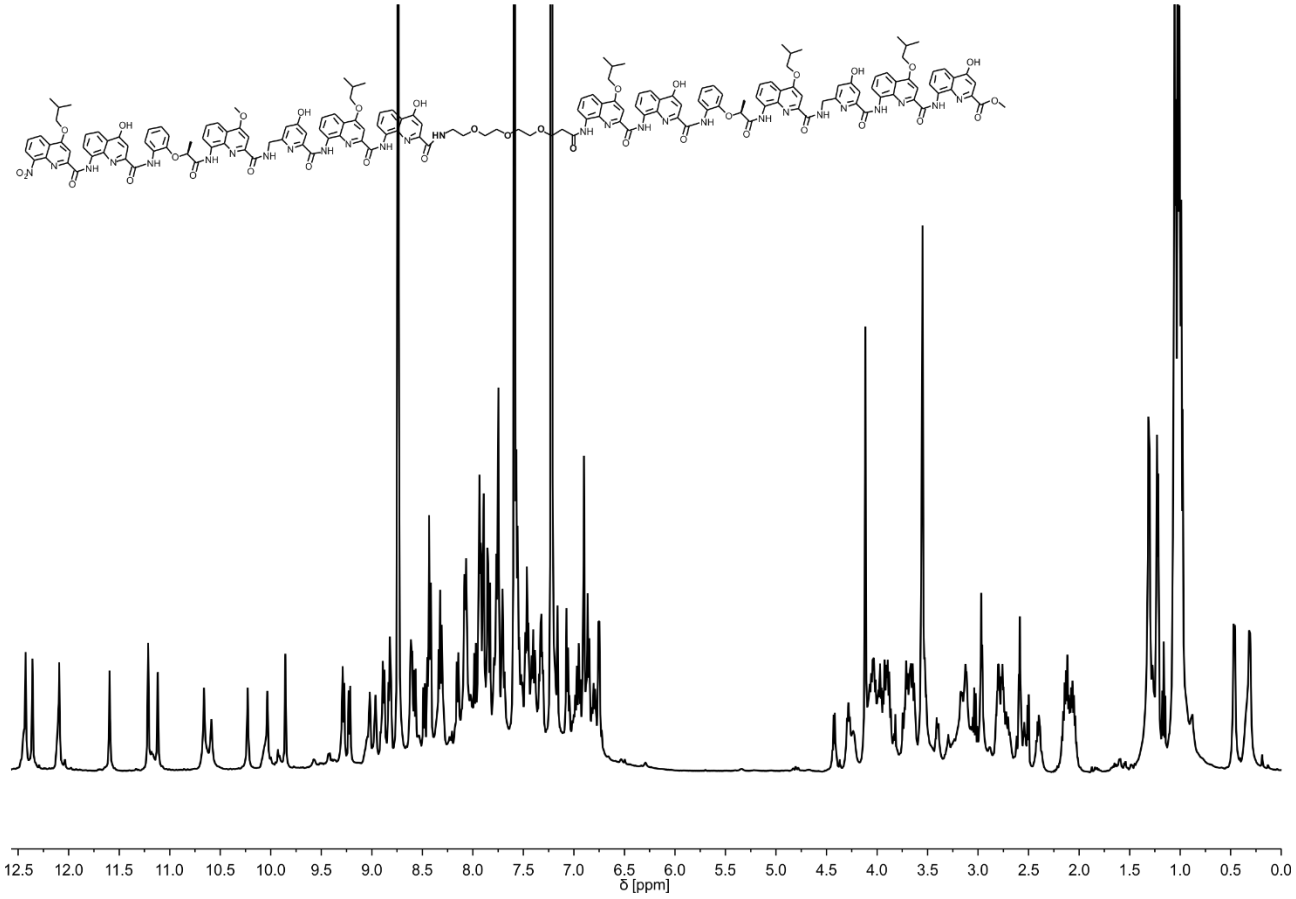

Figure S64. ^{1}H NMR spectrum (500 MHz, Pyridine-d_5) of **10**.

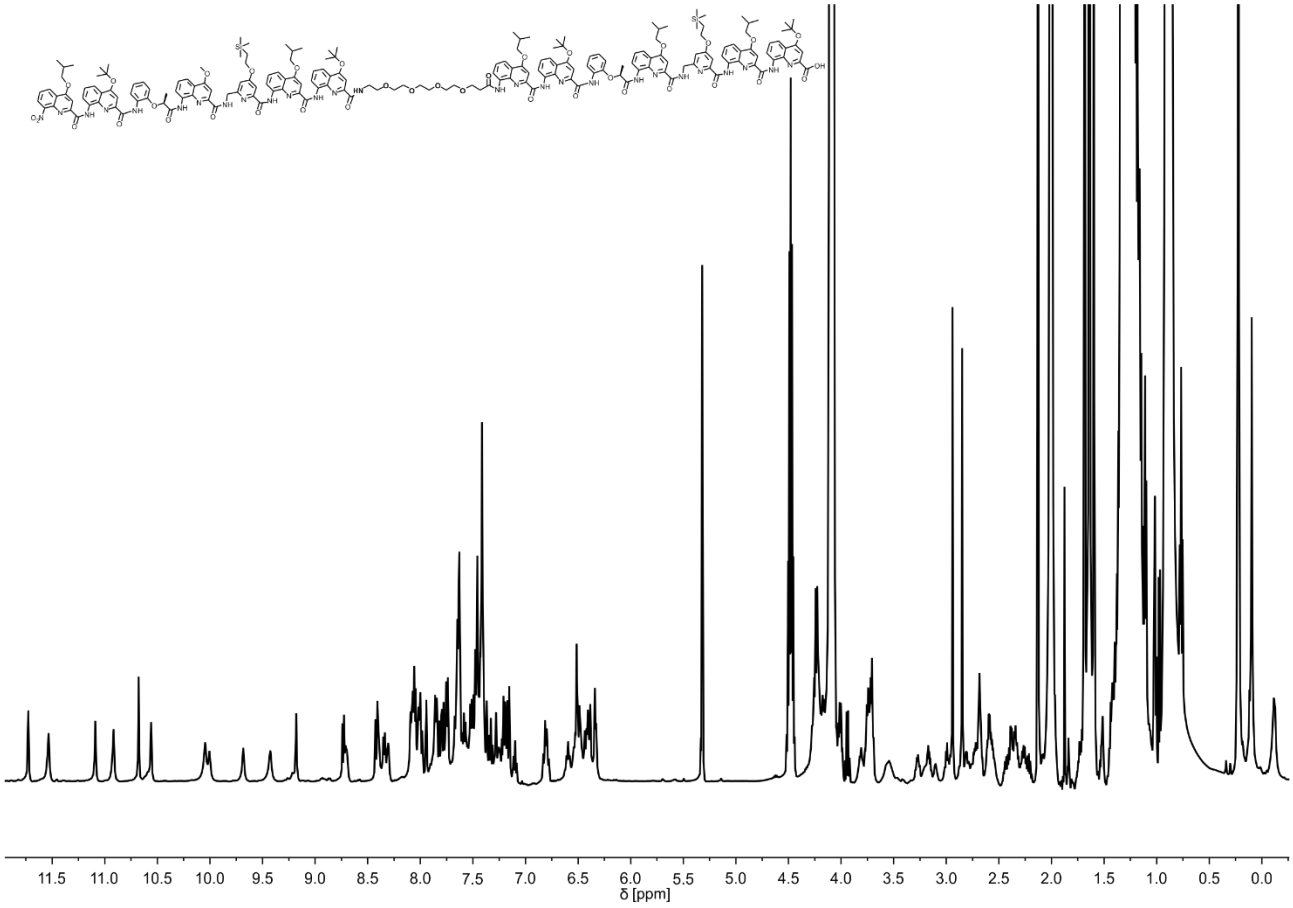

Figure S65. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of **27**.

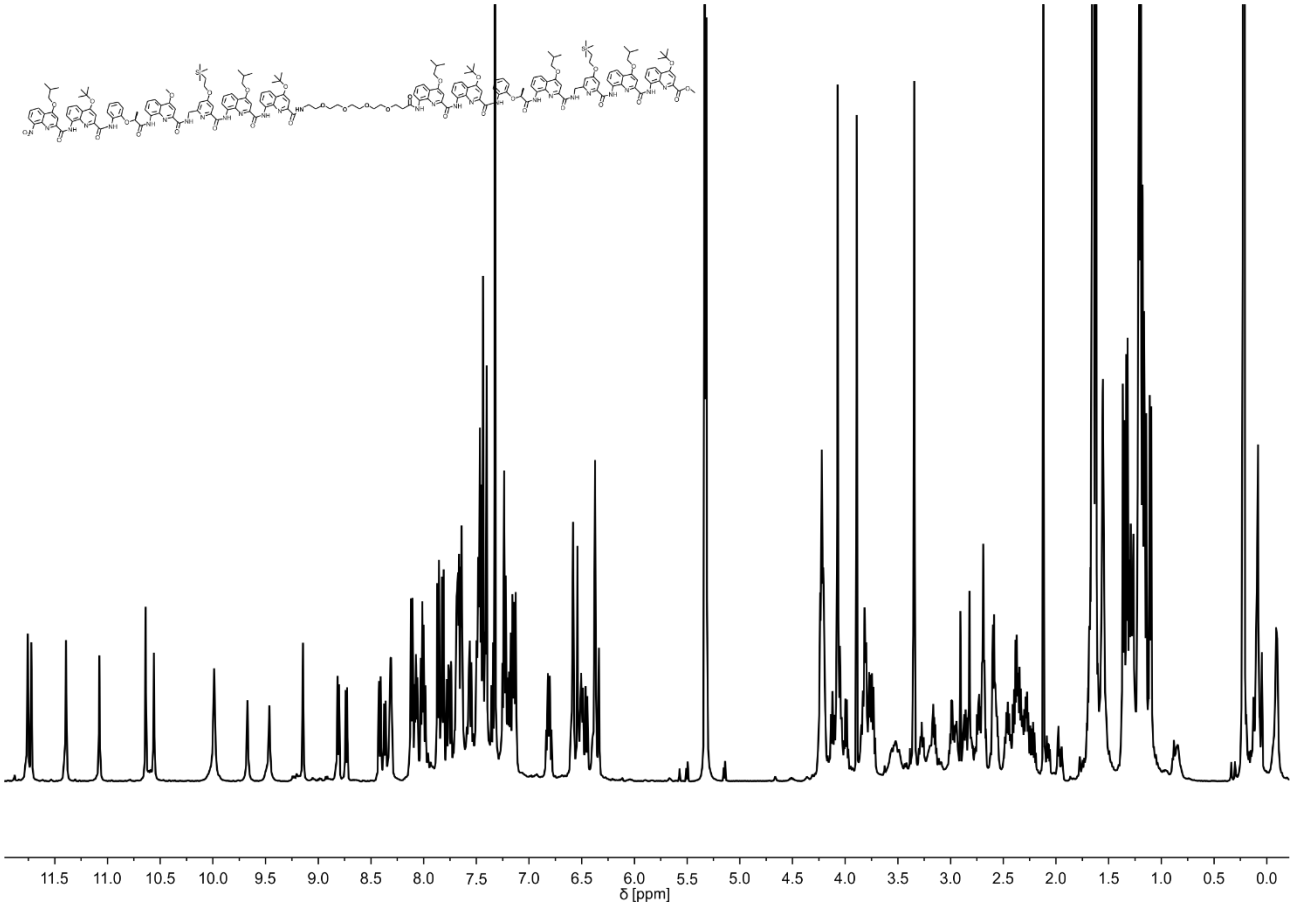

Figure S66. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of **28**.

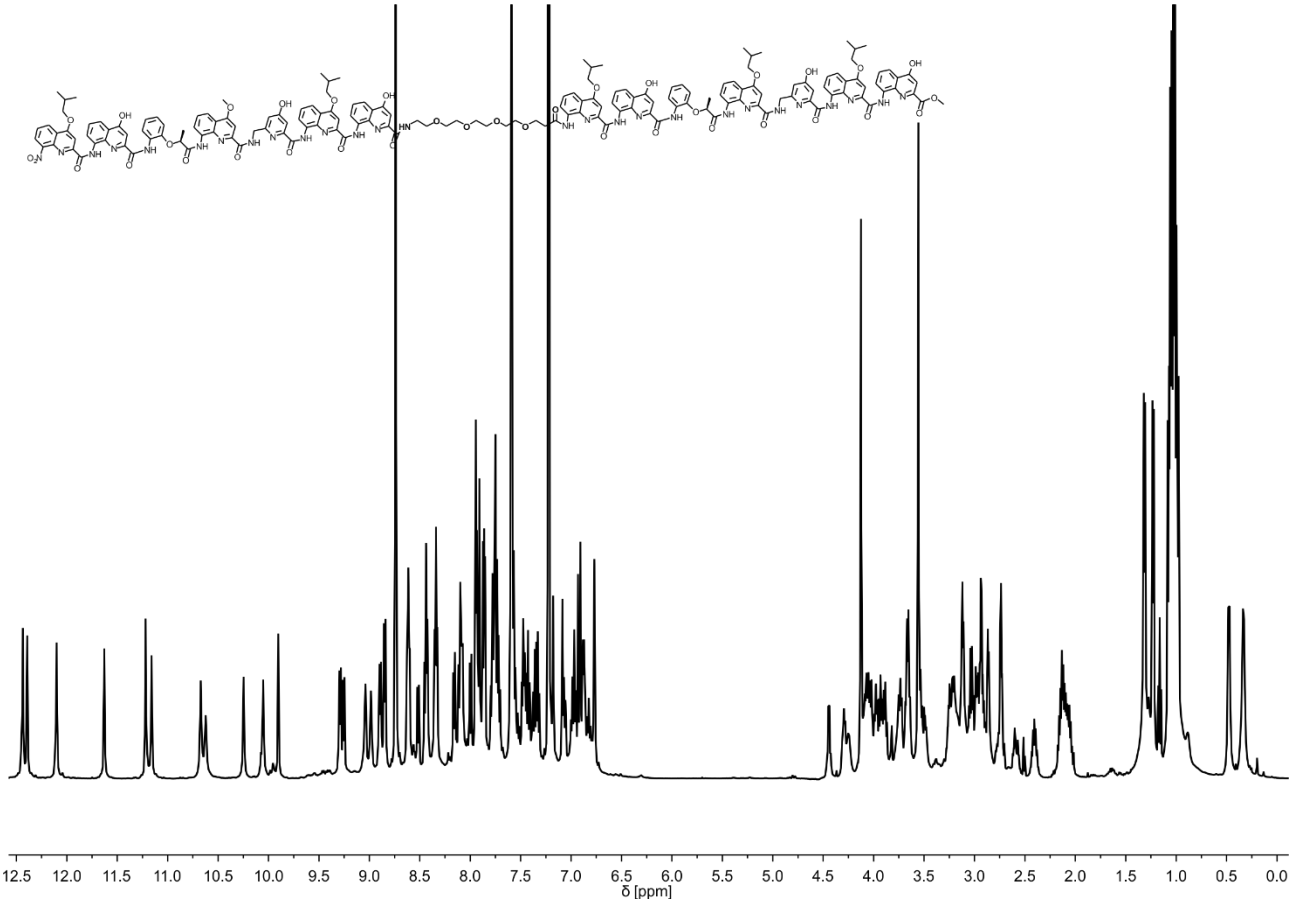

Figure S67. ^{1}H NMR spectrum (500 MHz, Pyridine-d_5) of **11**.

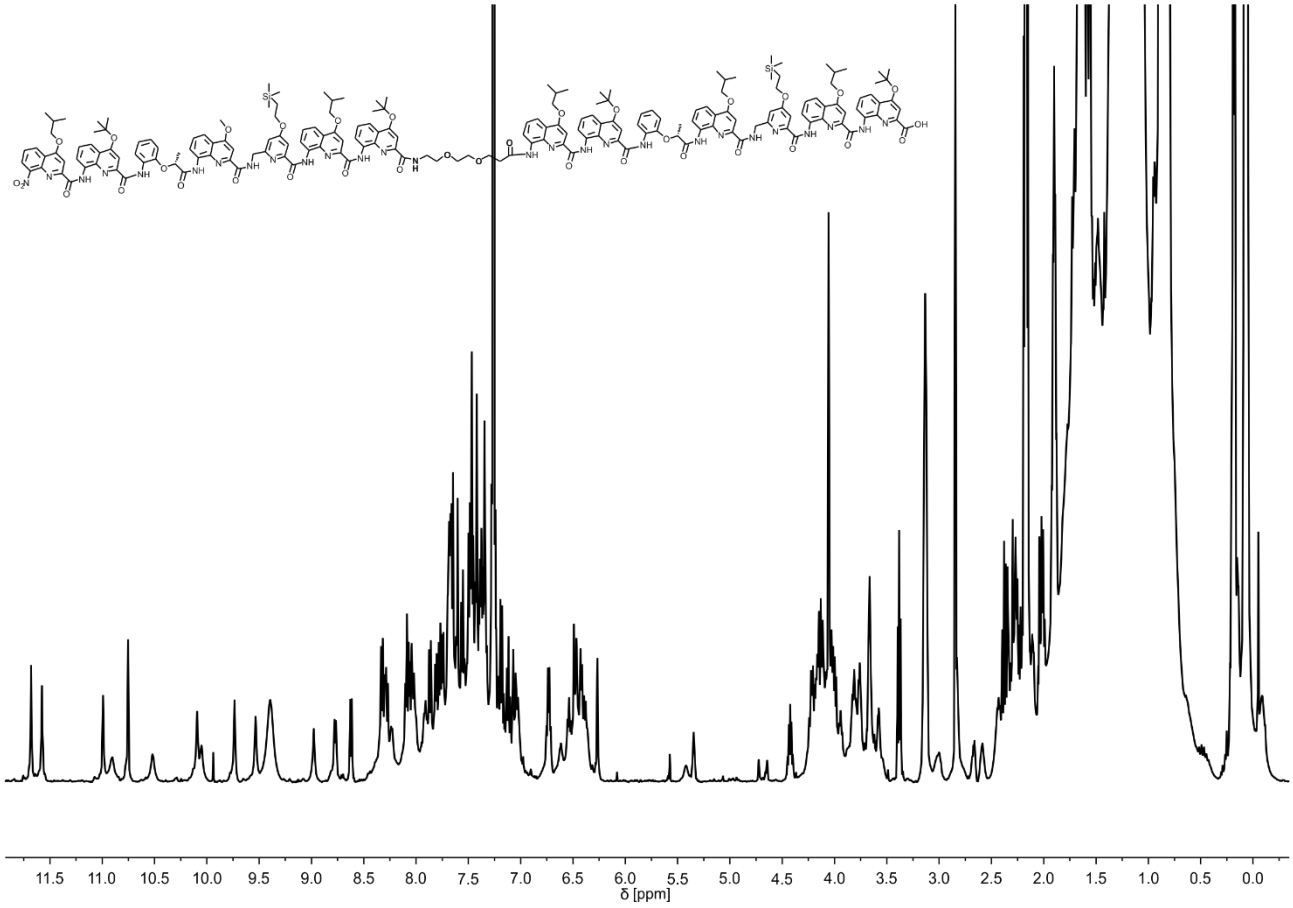

Figure S68. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **29**.

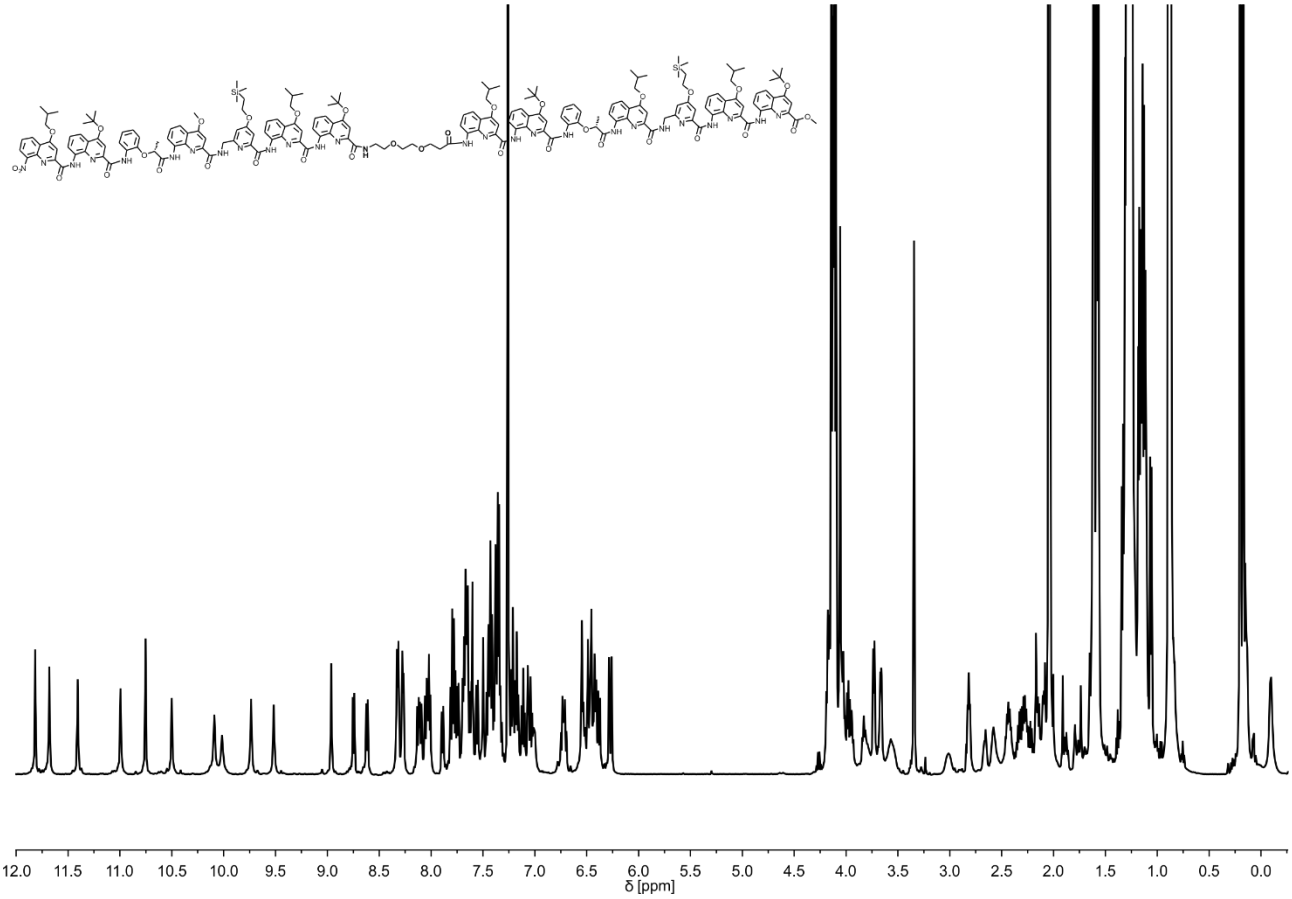

Figure S69. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **30**.

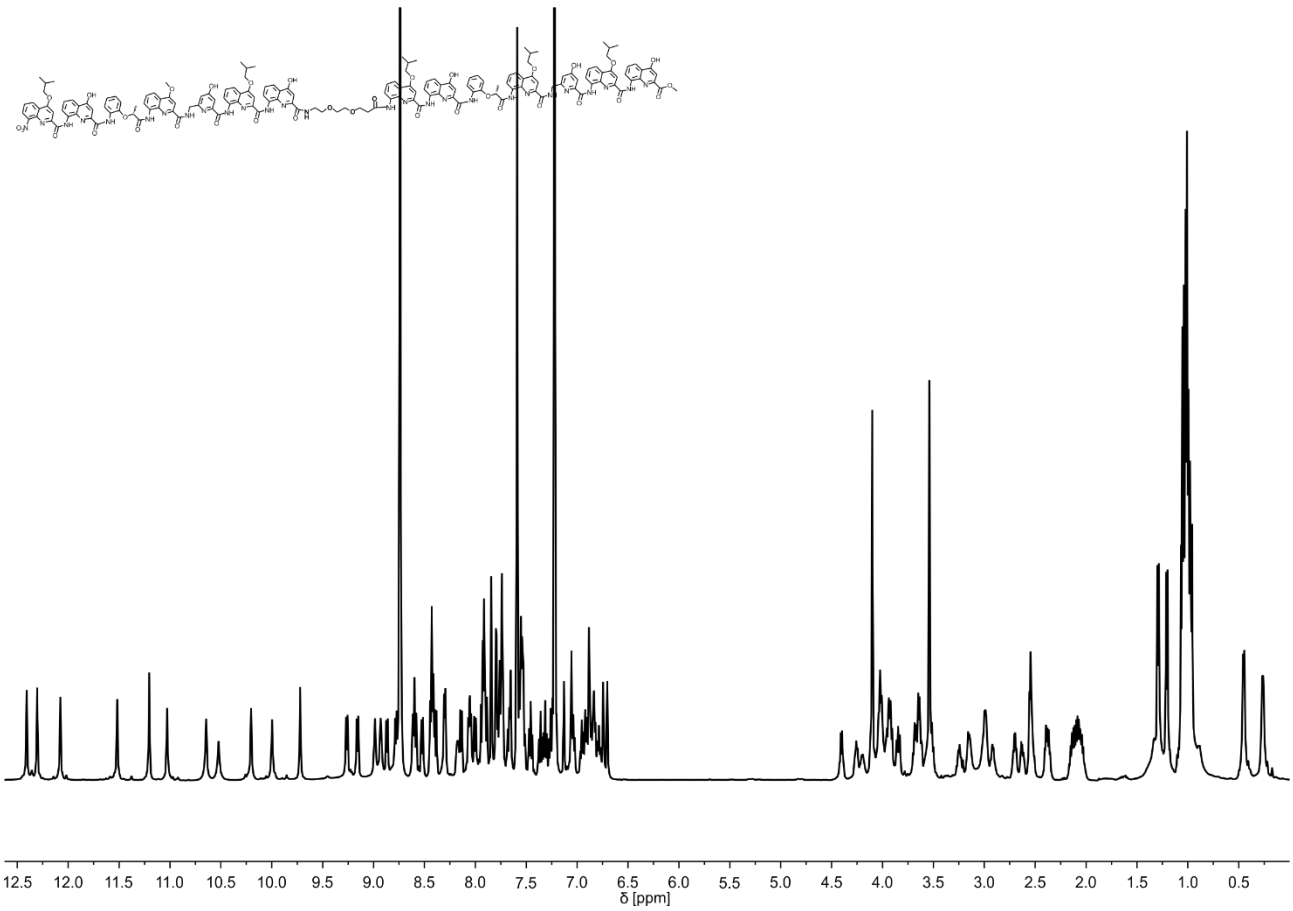

Figure S70. ^{1}H NMR spectrum (500 MHz, Pyridine-d_5) of **12**.

7.3 Sequences with a helix-turn-helix-motif and handedness-control in one helix

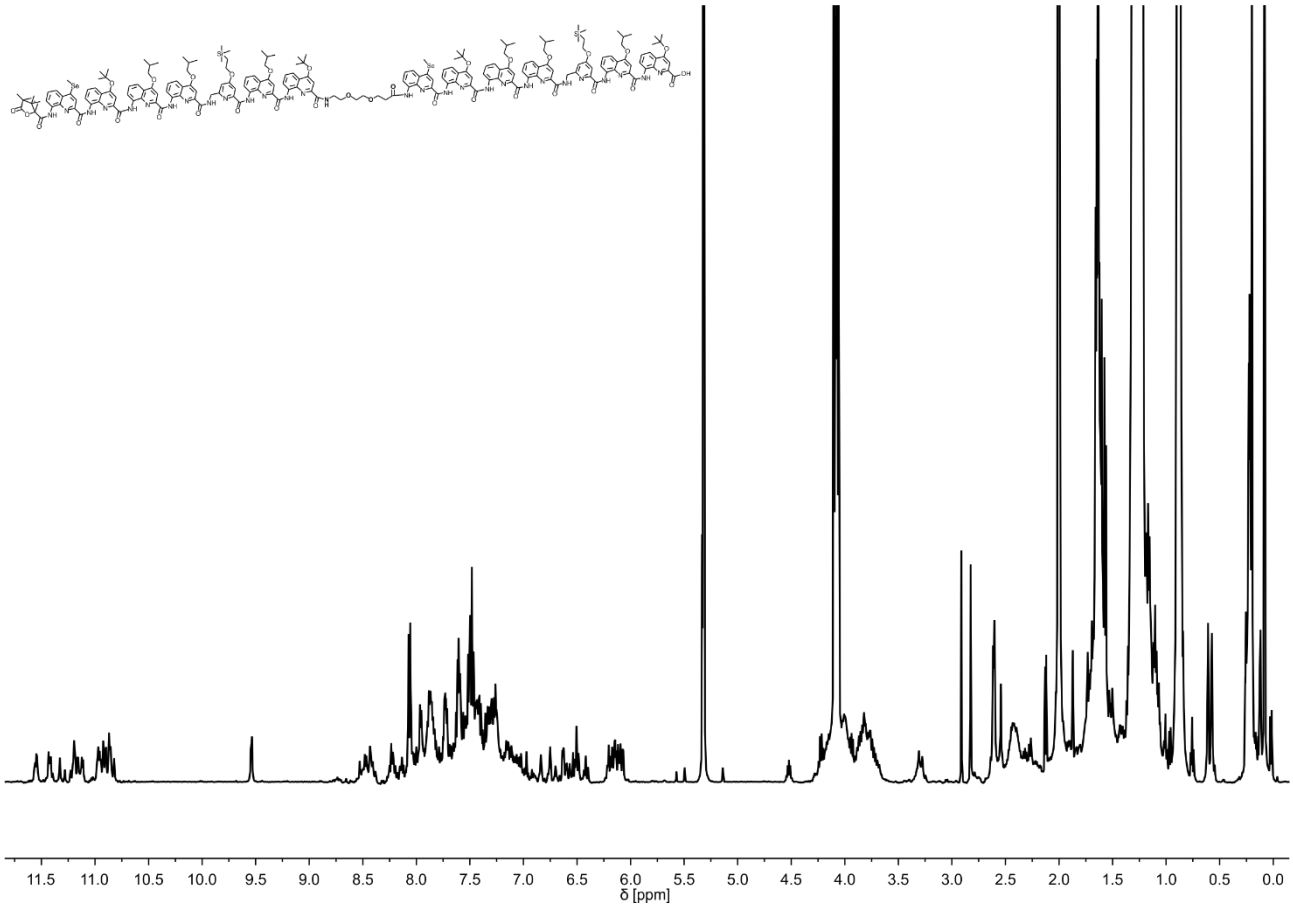

Figure S71. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of **31**.

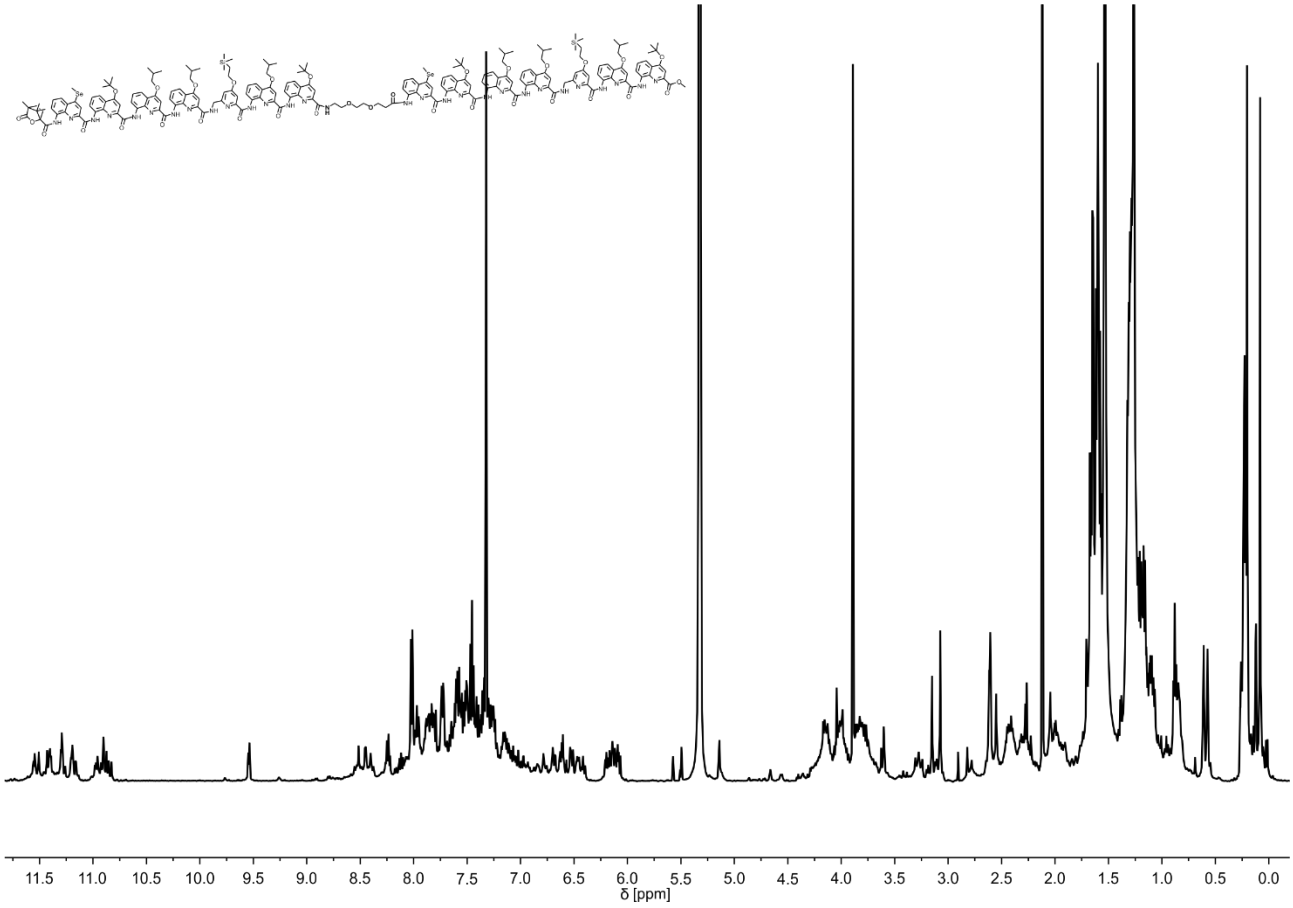

Figure S72. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of **32**.

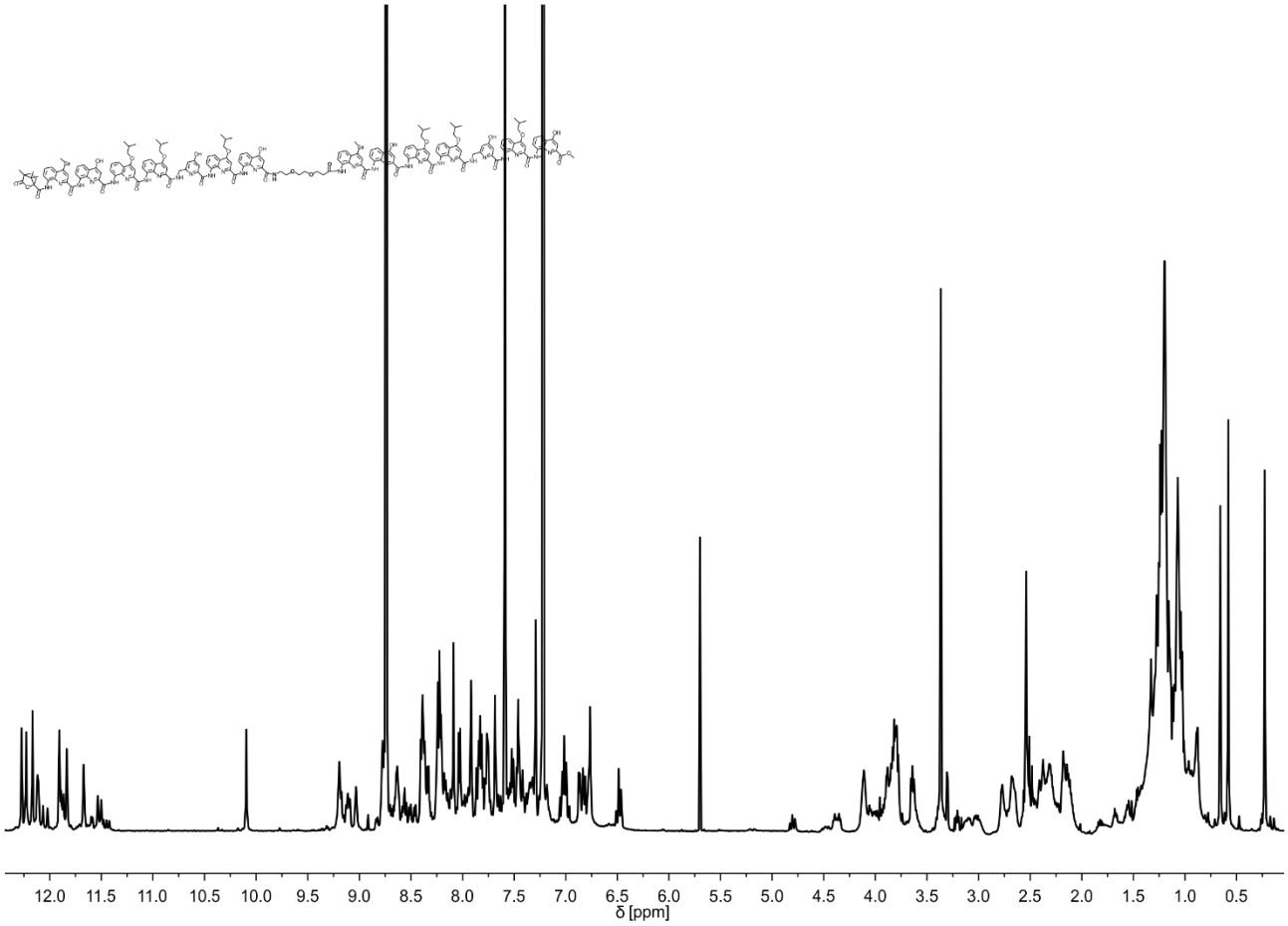

Figure S73. ^{1}H NMR spectrum (500 MHz, Pyridine-d_5) of **13**.

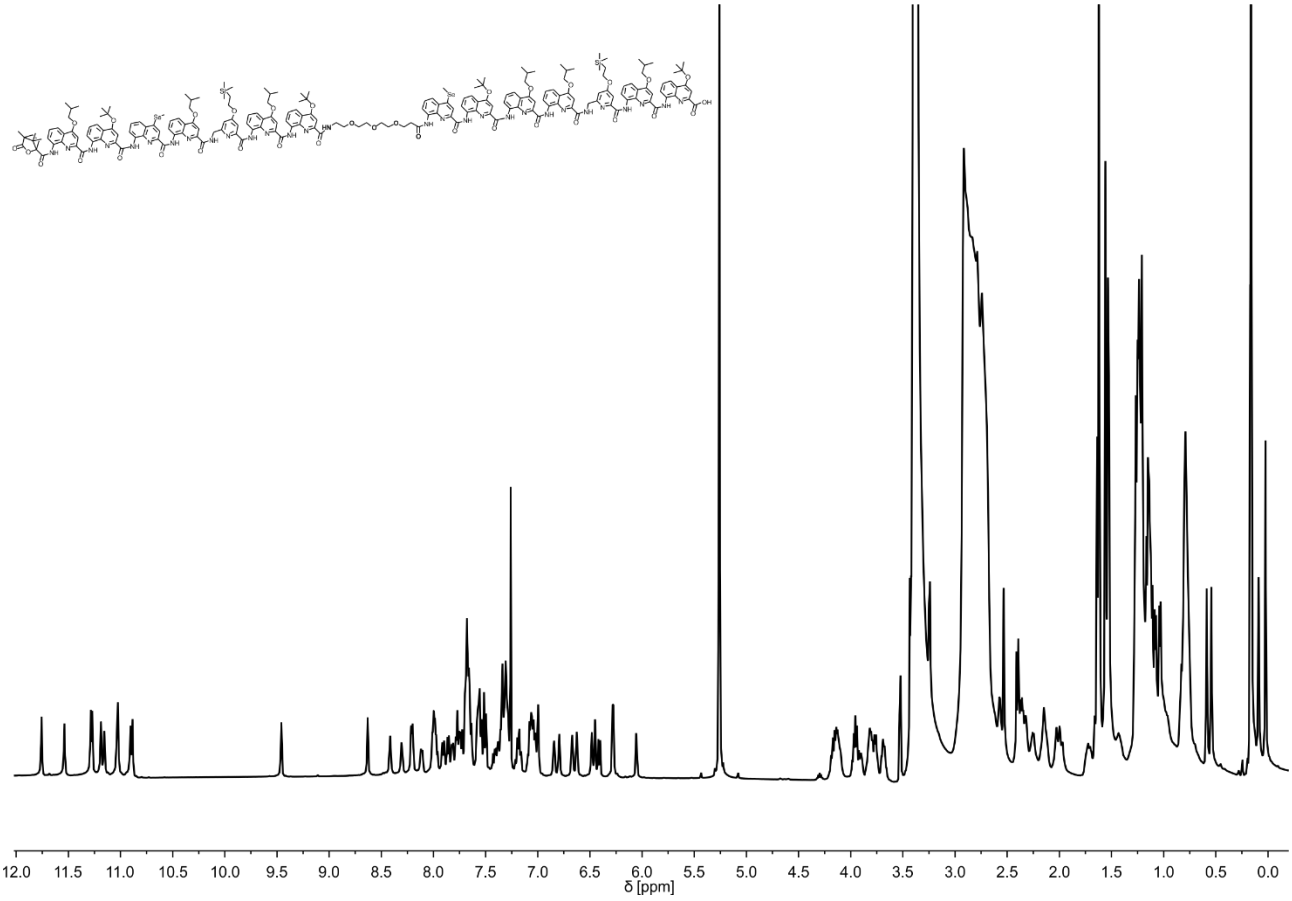

Figure S74. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **33**.

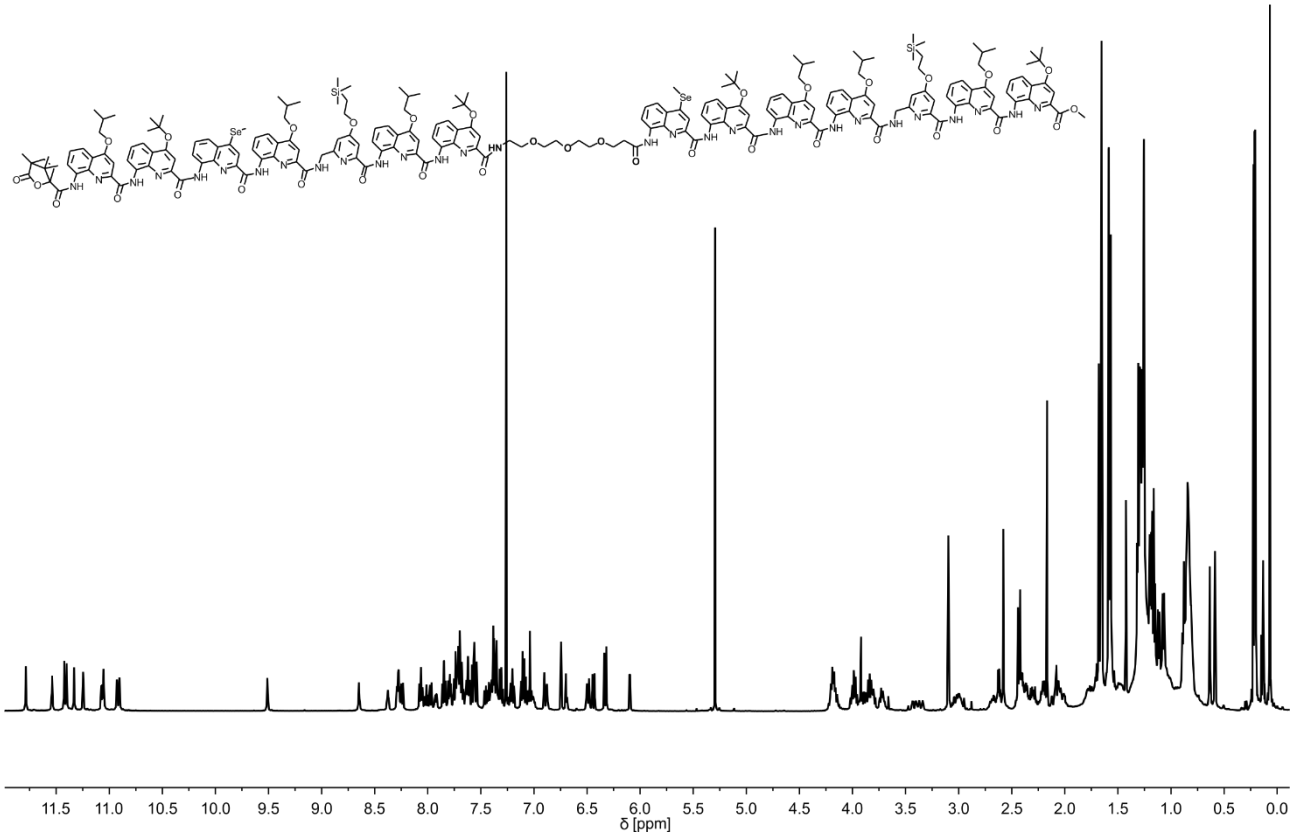

Figure S75. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **34**.

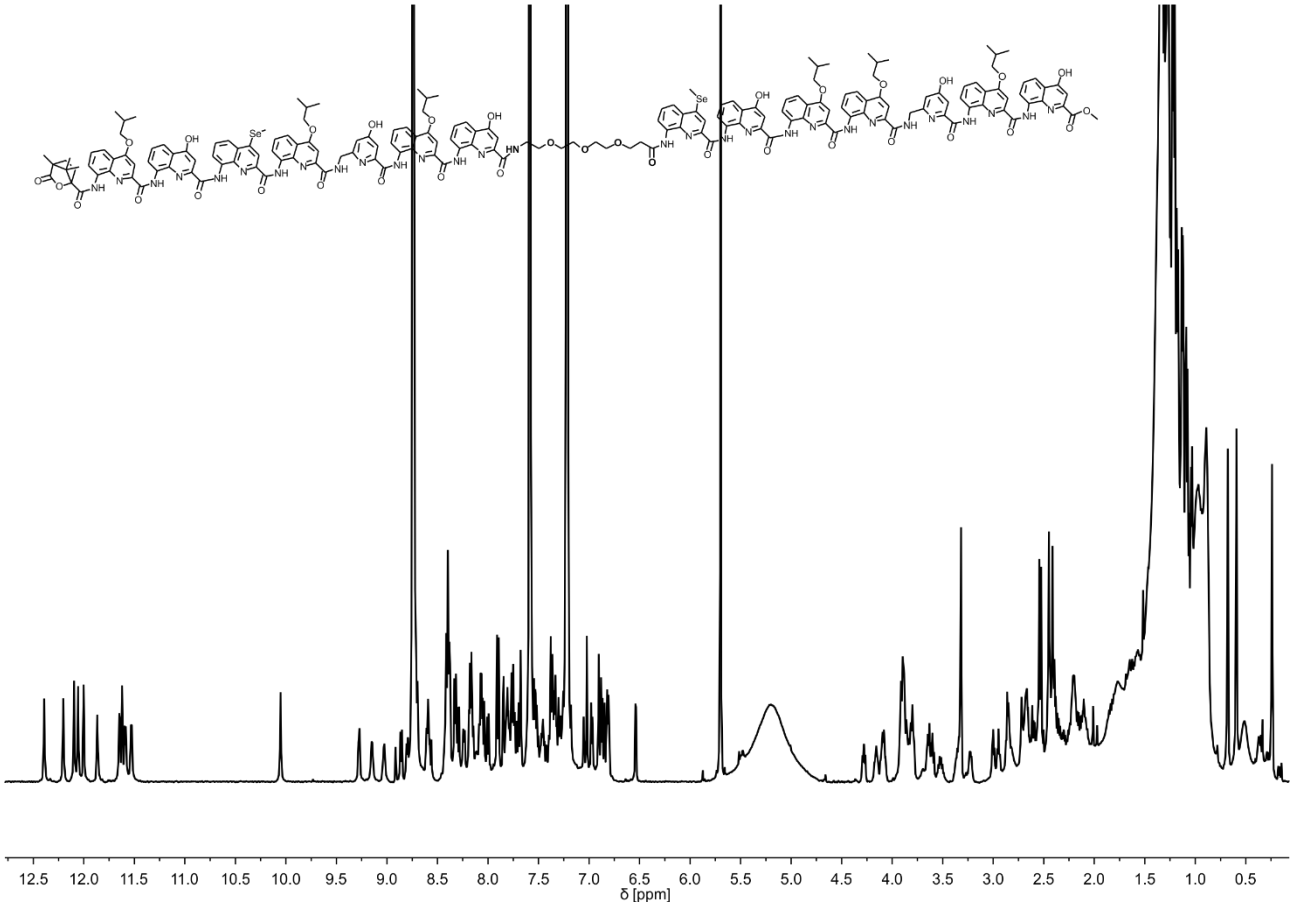

Figure S76. ^{1}H NMR spectrum (500 MHz, Pyridine-d_5) of **14**.

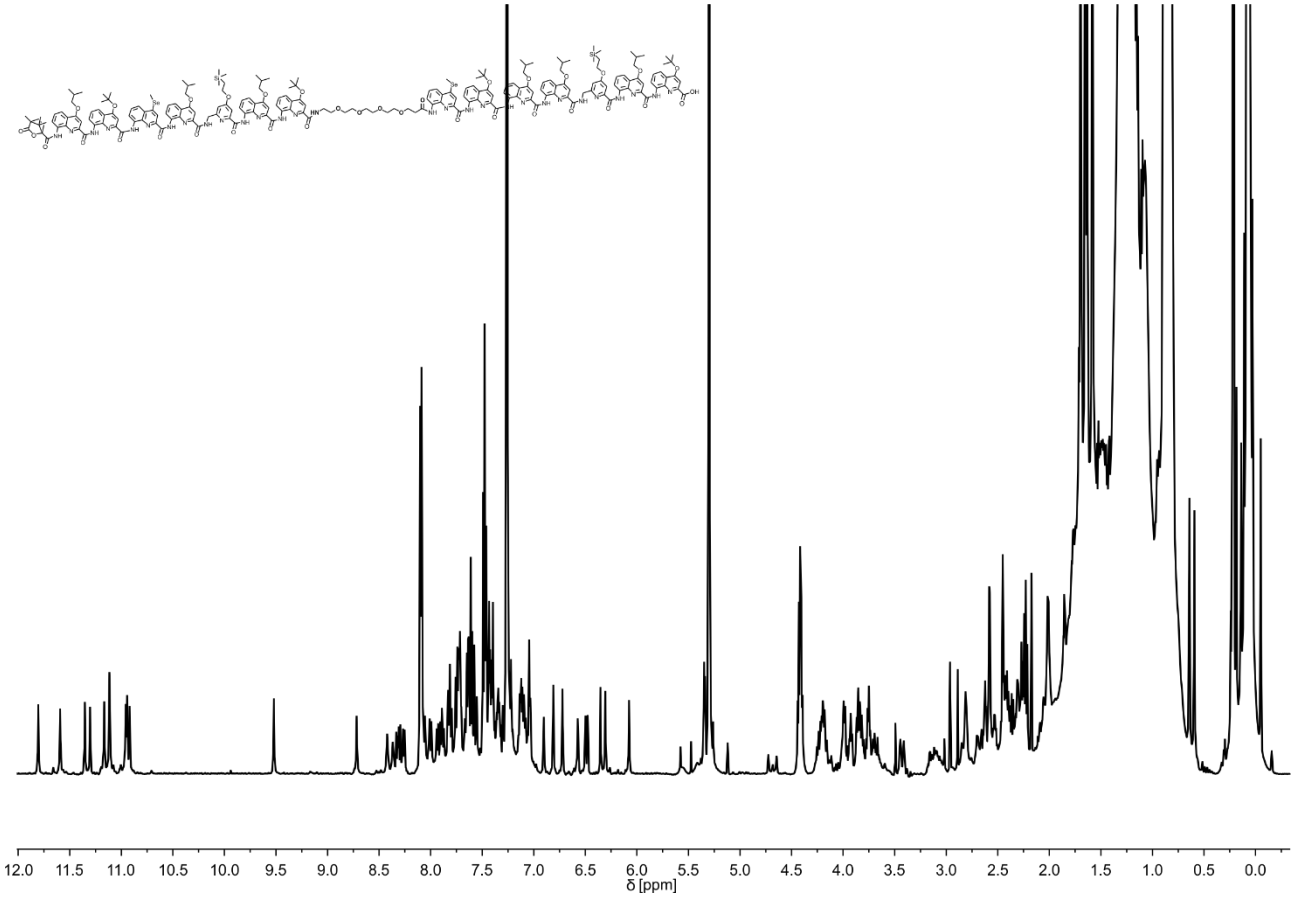

Figure S77. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **35**.

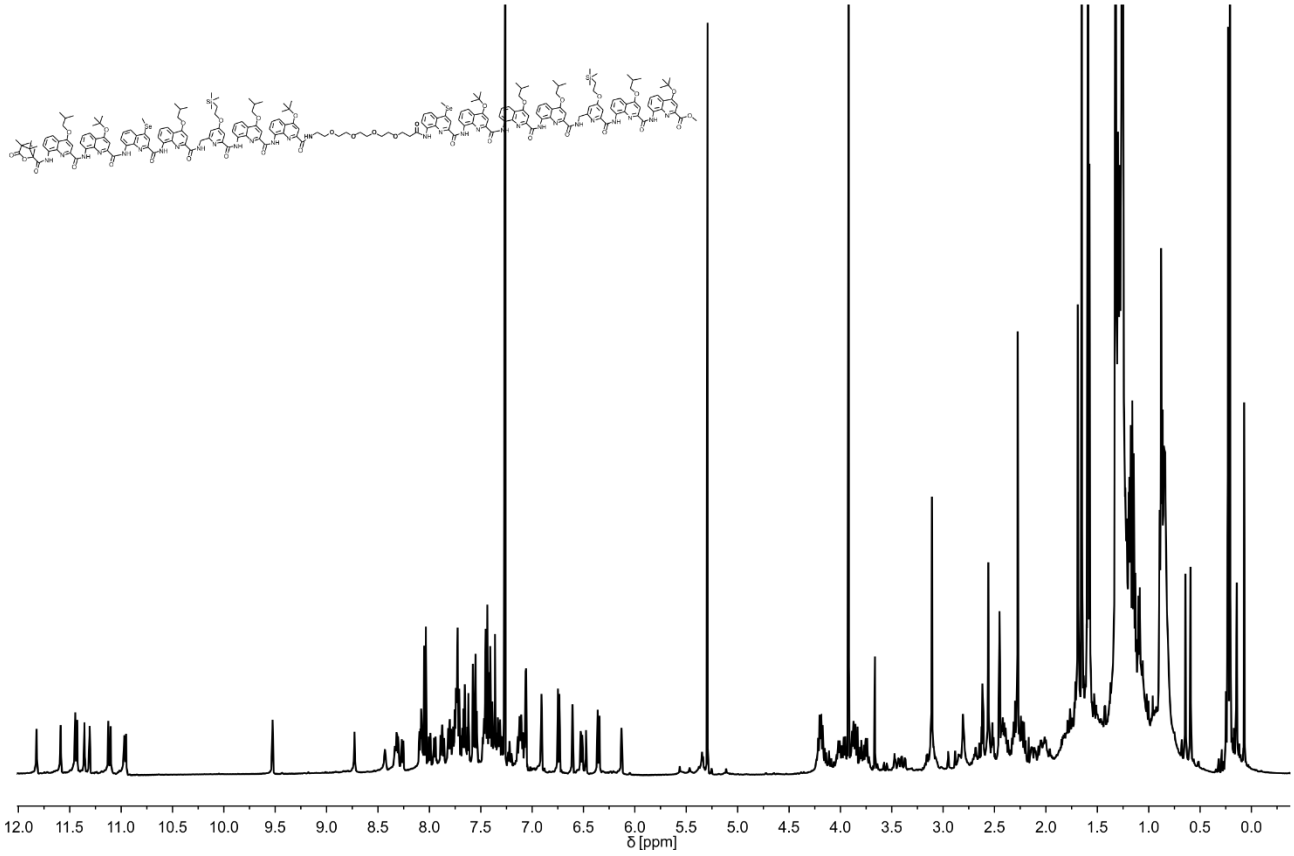

Figure S78. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **36**.

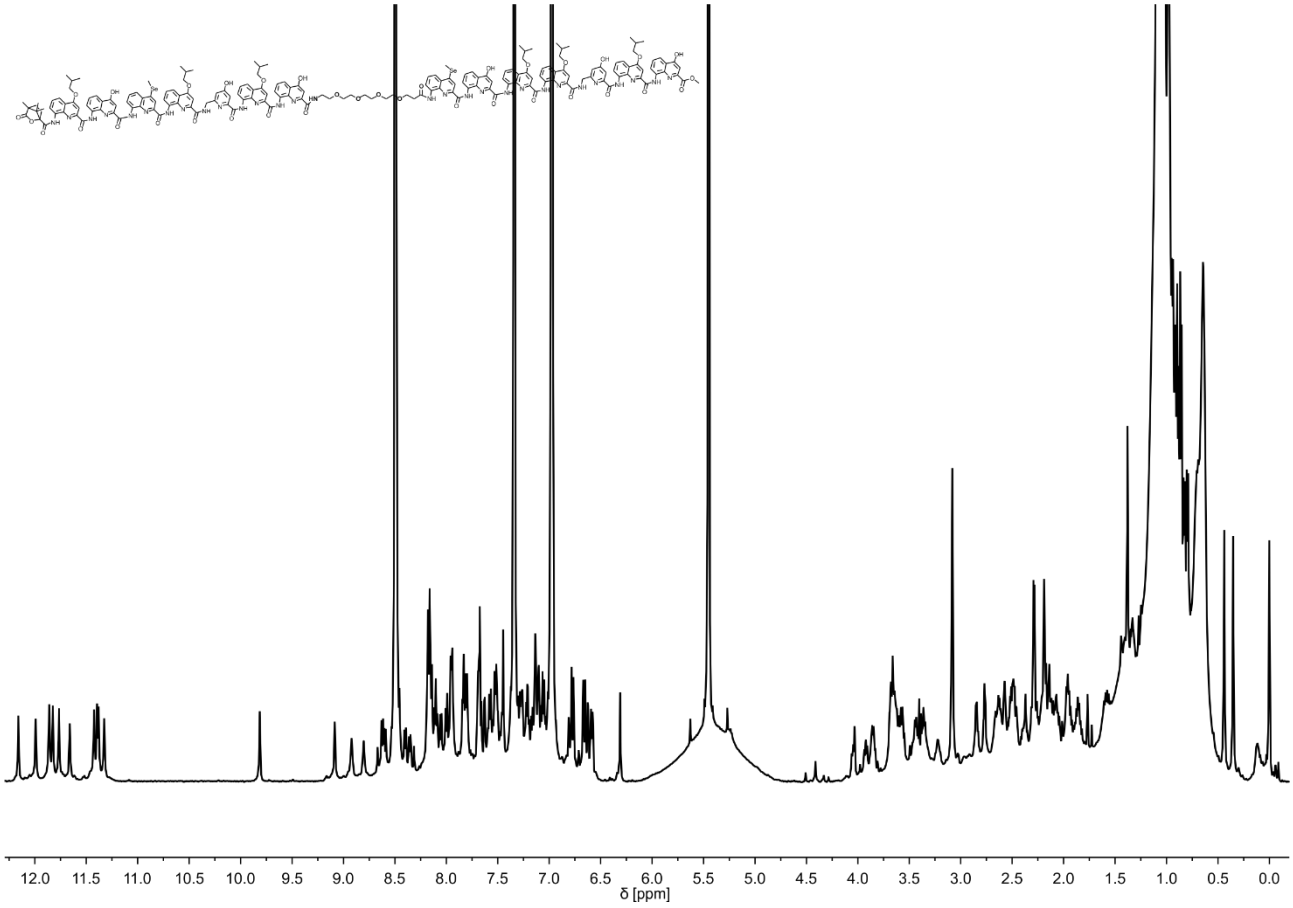

Figure S79. ^{1}H NMR spectrum (500 MHz, Pyridine-d_5) of **15**.

7.4 Achiral sequences with a helix-turn-helix-motif

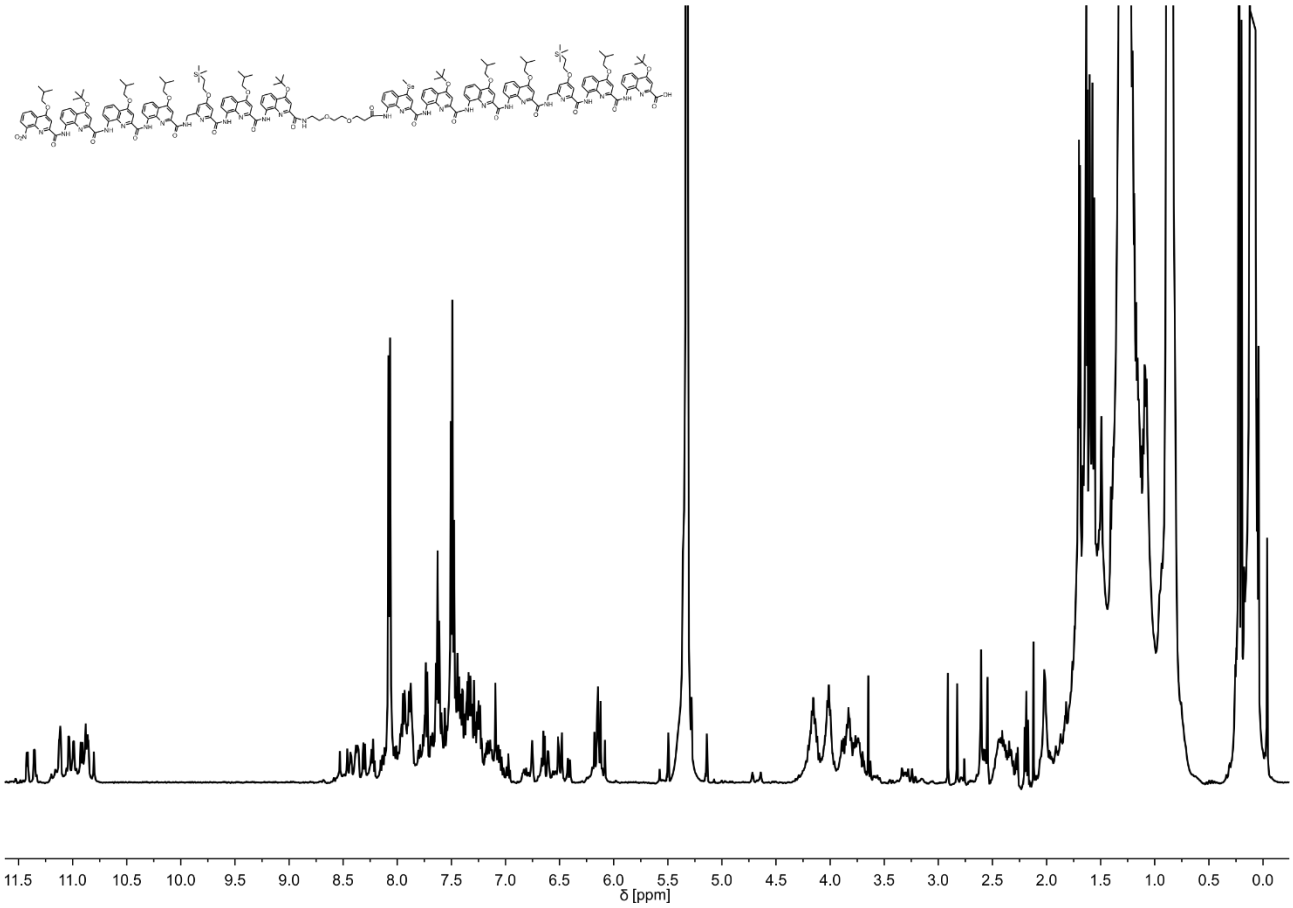

Figure S80. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of **37**.

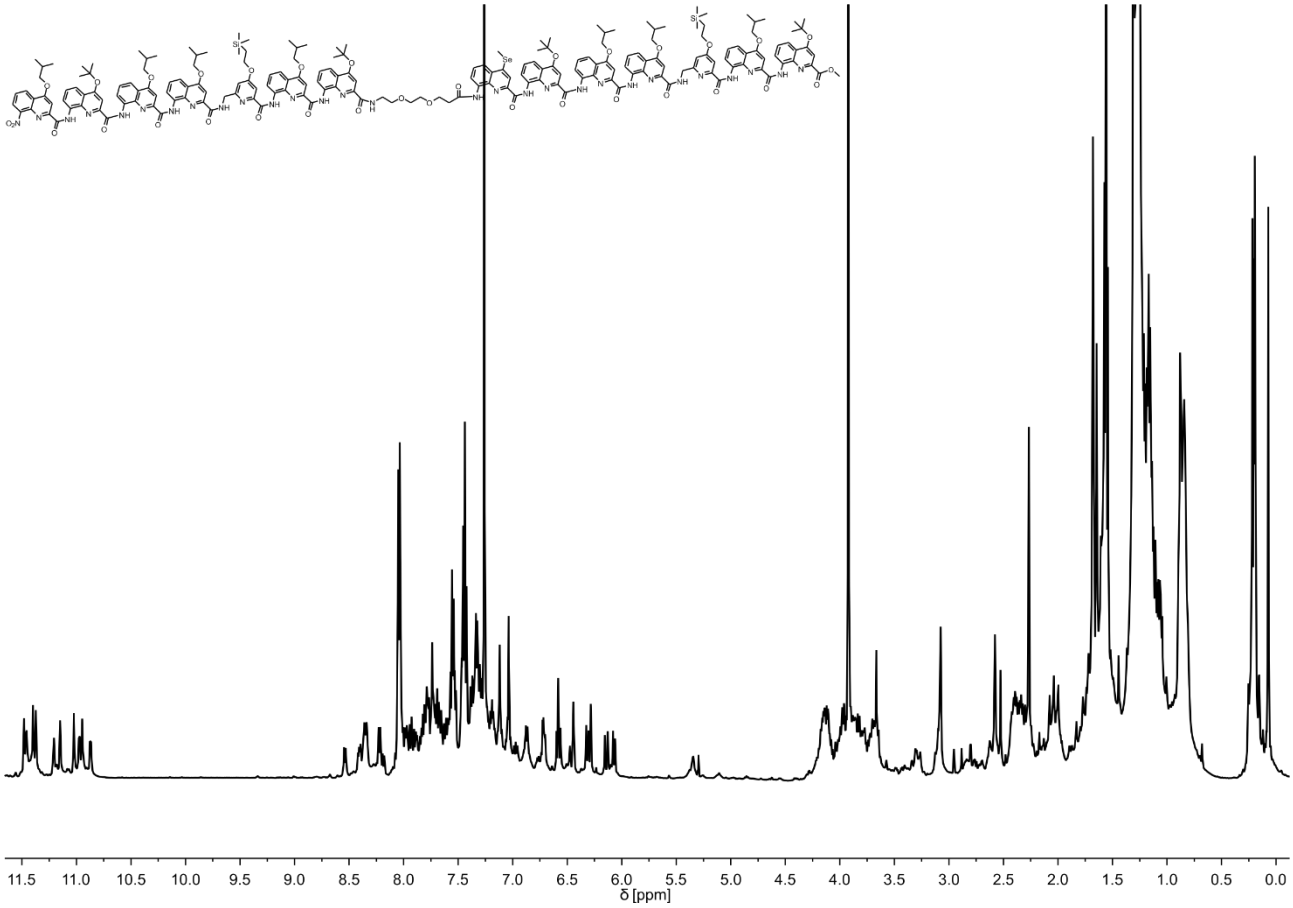

Figure S81. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **38**.

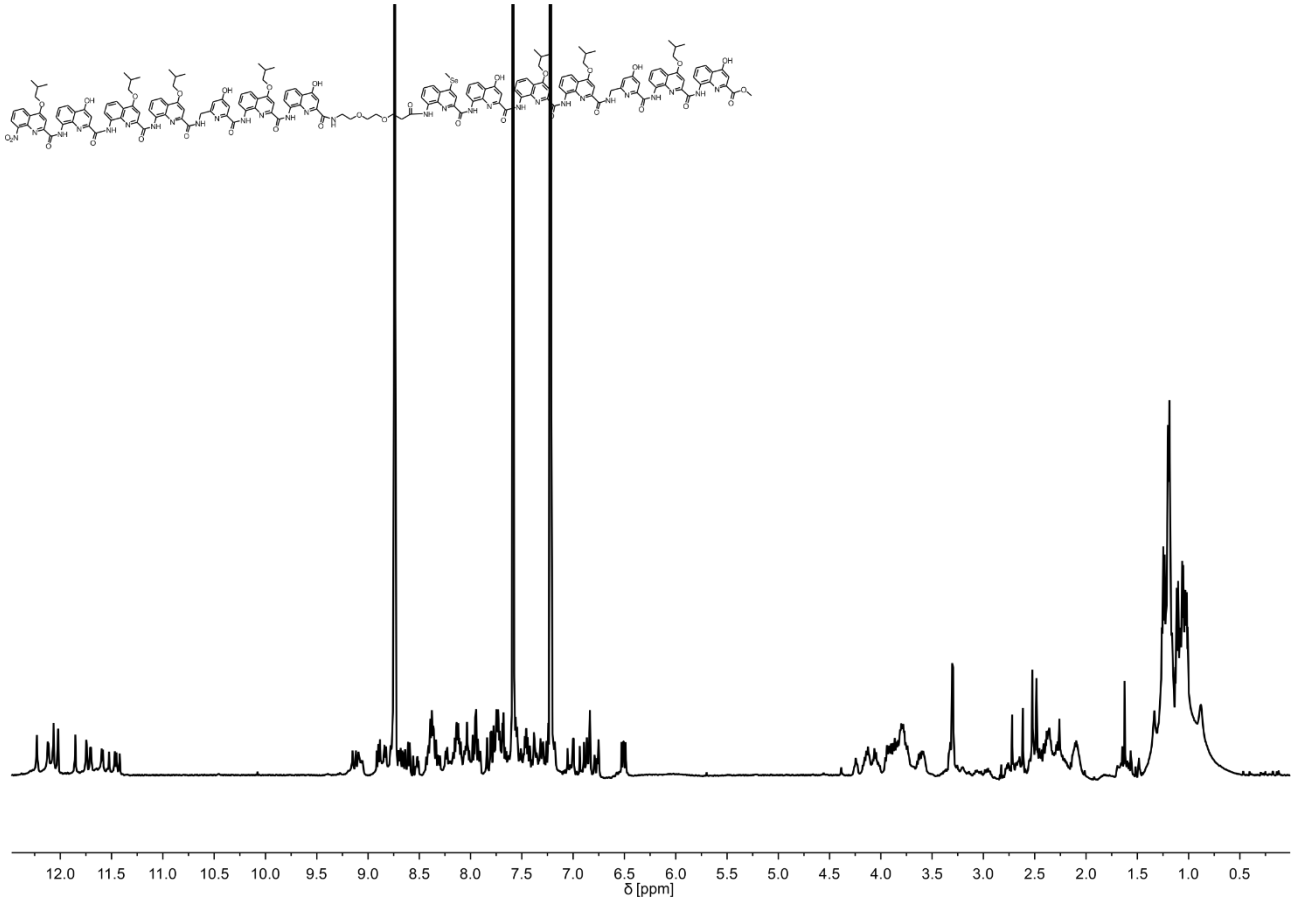

Figure S82. ^{1}H NMR spectrum (500 MHz, Pyridine-d_5) of **16**.

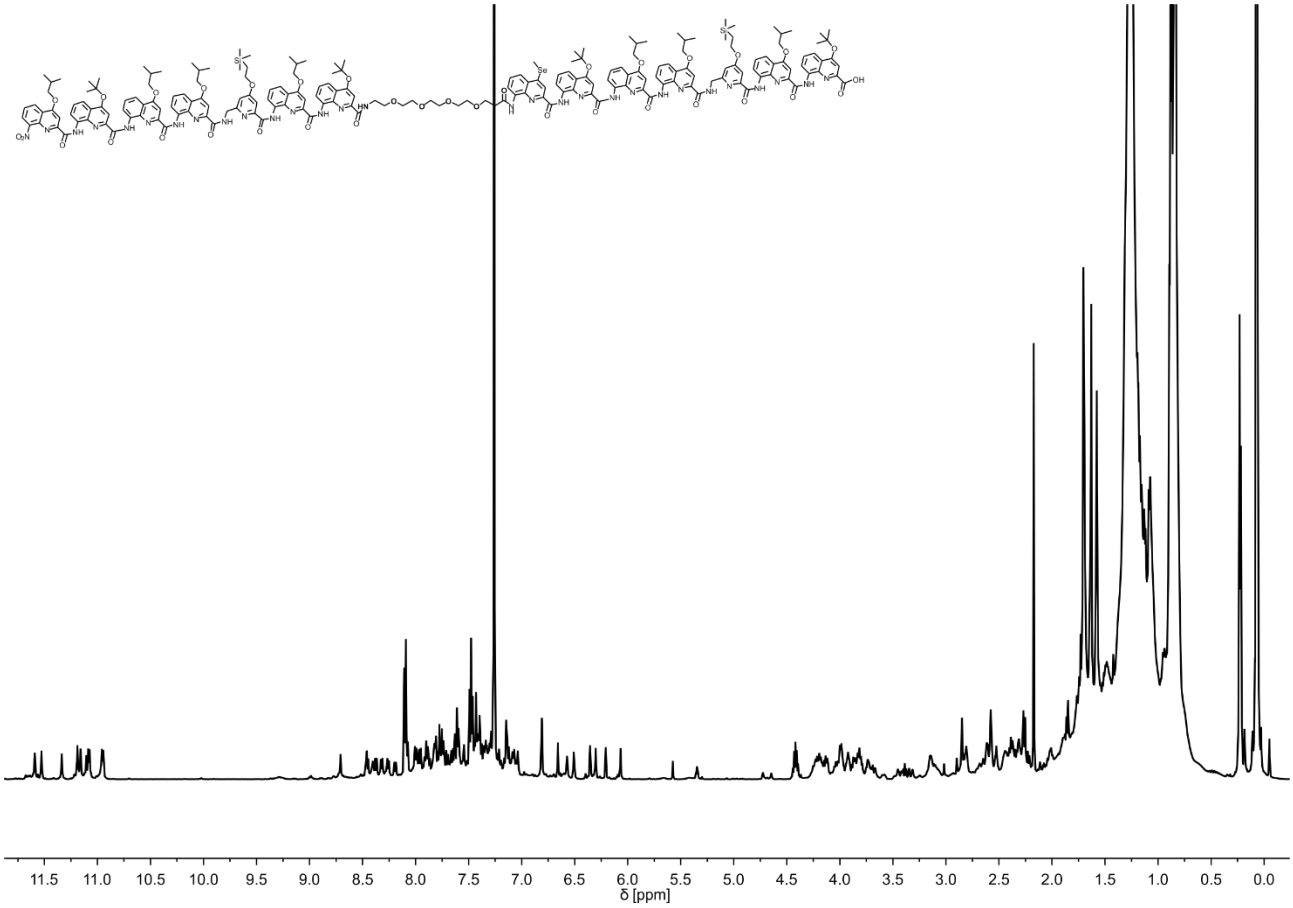

Figure S83. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **39**.

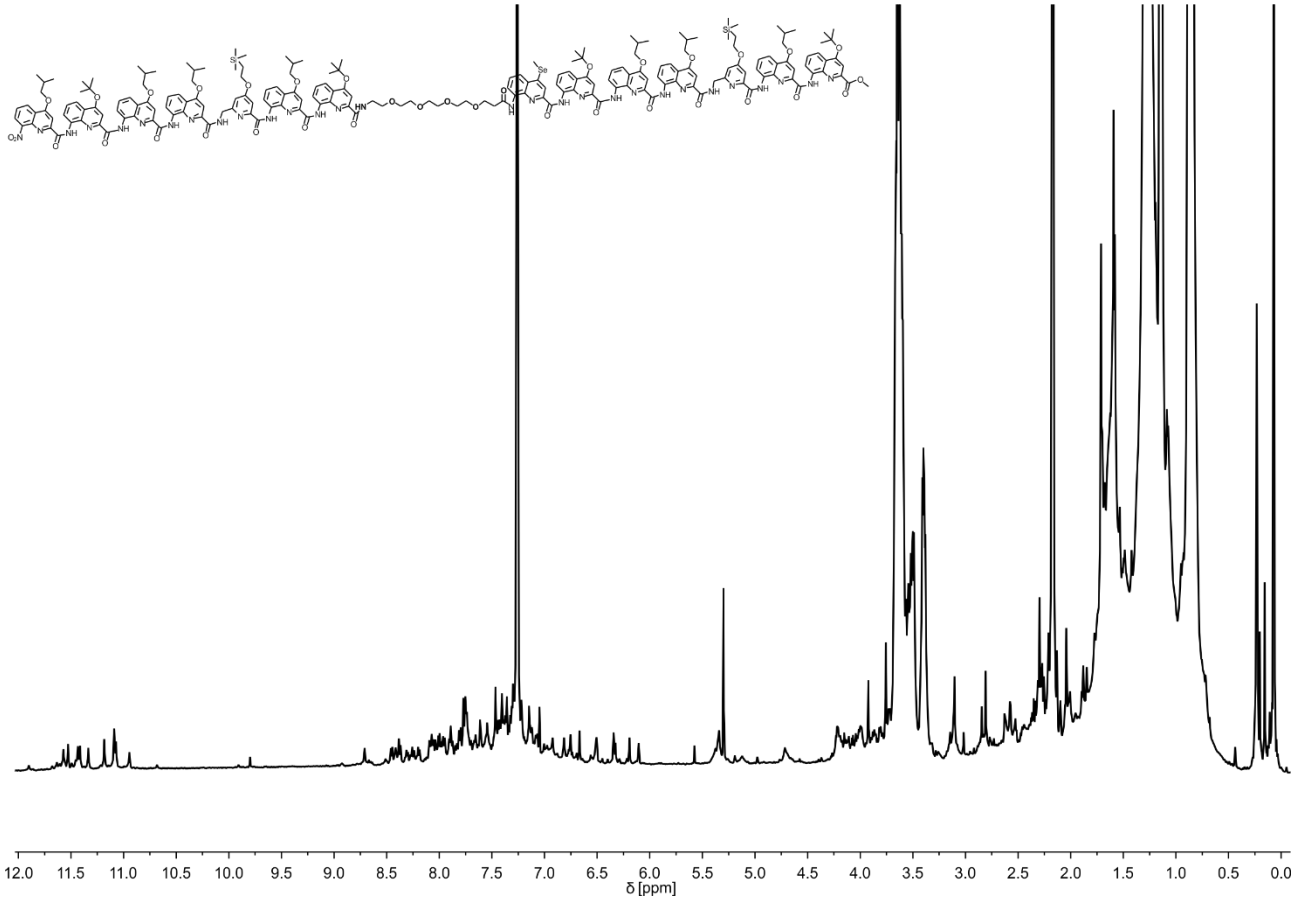

Figure S84. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **40**.

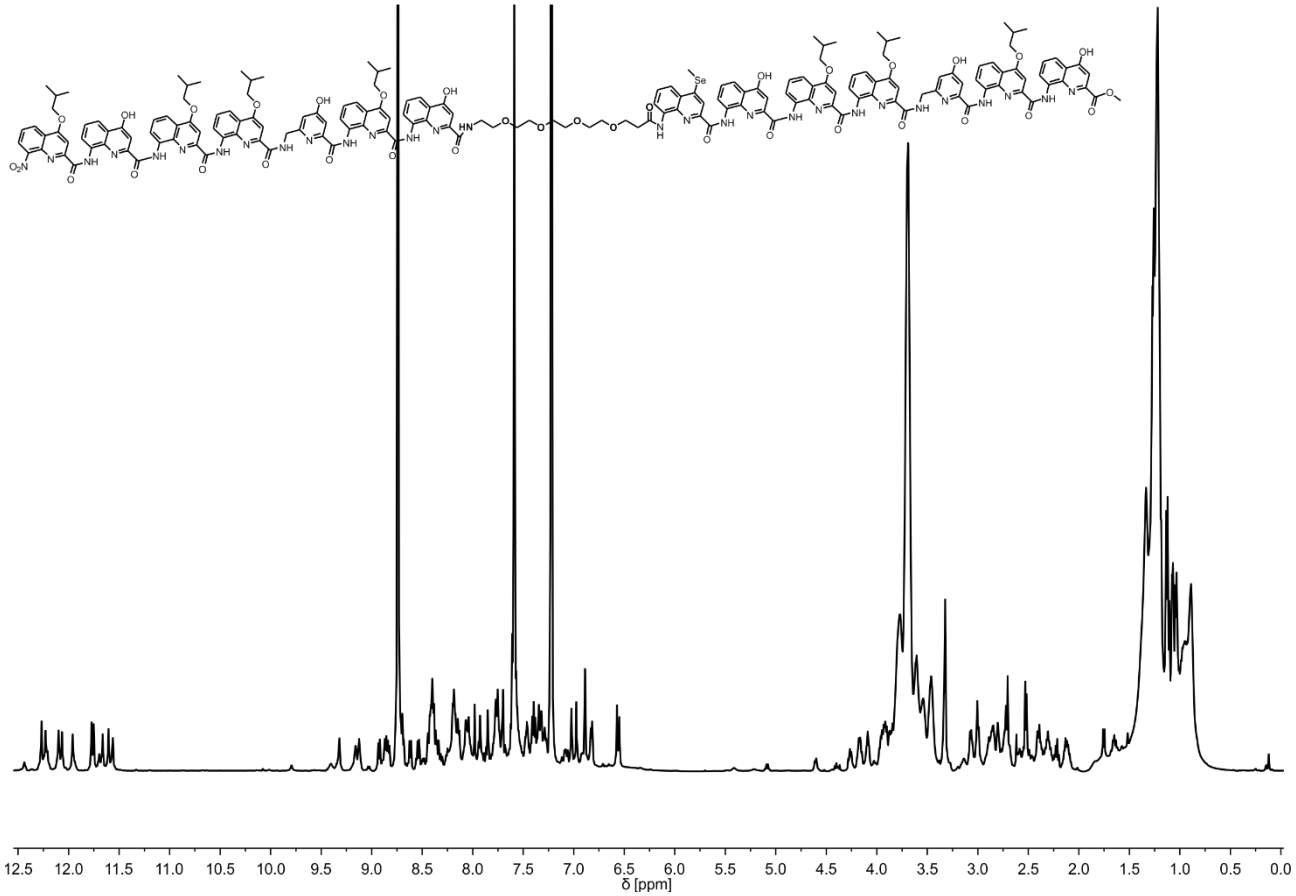

Figure S85. ^{1}H NMR spectrum (500 MHz, Pyridine-d_5) of **17**.