Supporting Information

for

Supramolecular polymers with reversed viscosity/temperature profile for application in motor oils

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Experimental part
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1. General

1.1 Synthesis

Each chemical mentioned is commercially available and was used without purification unless specified. All reactions were carried out under an atmosphere of argon in a pre-heated flask and all chemicals were added in argon flow. THF (Tetrahydrofuran) was freshly distilled from sodium/benzophenone. DCM (dichloromethane) and DMF (N,N-dimethylformamide) were freshly distilled from CaH₂. Diisopropylethylamine was dried over CaH₂ by refluxing for 72 h after which it was distilled under an atmosphere of argon and stored over molecular sieve under an atmosphere of argon.

¹H- and ¹³C NMR spectra were recorded in CDCl₃ and DMSO-d₆ on Bruker DMX 300, AV Neo 400 NMR and Bruker DMX 600 spectrometers.

IR spectra were measured on a Jasco FT/IR-430 with ATR attachment spectrometer.

Low and High resolution ESI mass spectra were recorded with a Bruker amaZon SL and a Bruker maXis 4G spectrometer, respectively.

For each chiral compound, the (S)-enantiomer, e.g., (S)-BINAM and L-Glutamic acid, was used.

For Flash chromatography columns were packed with Silica gel 60 M (40–63 µm) from Macherey-Nagel.

Medium performance liquid chromatography (MPLC) was carried out using Armen Instrument Liquid Chromatography Flash Apparatus. Packed columns of Kronlab were used with RP18 from YMC. (YMC-ODS-AQ: 60 cm length, 3 cm diameter, 5 µm particle size, 12 nm pore size)

1.2 Viscosity measurements

The viscosity measurements were carried out in a “Rolling-ball viscometer Lovis 2000 M” by Anton Paar with a sample amount of 100 µL to 200 µL and a temperature range of −30 °C to 100 °C. All viscosity measurements were carried out at neutral pH, which was adjusted if necessary, by adding aqueous 0.1 N NaOH or 0.1 N HCl, monitored by pH-Meter 766 from Knickarray.

For each sample (compound and concentration) three different solutions were prepared and filtered through syringe filters (0.4 µm). Each solution was measured heating up at 25 °C, 35 °C, 45 °C, 55 °C, 65 °C, 75 °C, 85 °C, 95 °C and 100 °C and cooling down at the same temperatures except for chloroform solutions, where the maximum temperature was 50 °C. Each data point was measured by the viscometer in a sequence of six times while varying the drop angle of the sphere and each sequence was done three times. After every measurement session, the sample holder was completely cooled down to room temperature and washed with acetone and cyclohexane, after which it was dried with compressed air. With this method, falling time, kinematic viscosity and dynamic viscosity were measured.
The specific viscosity was calculated with the kinematic viscosity of each solution and the pure solvent. Therefore, the viscosity of the pure solvent was measured the same way as described before. By the formula of the specific viscosity the percentage behaviour was obtained.

$$
\eta_{sp} = \frac{\eta_C - \eta_0}{\eta_0}
$$

The specific viscosity ($\eta_{sp}$) results out of the dynamic viscosity of each concentration ($\eta_C$) and the equivalent dynamic viscosity of the solvent ($\eta_0$) at each temperature.
### 1.3 Abbreviations

| Symbol | Description | Abbreviation | Full Form |
|--------|-------------|--------------|-----------|
| δ      | chemical shift | h            | hour (s)  |
| °C     | degree celsius | HCTU         | 1-H-Benzotriazolium 1-[
|        |              |              | [bis(dimethylamino)-methylene]-5chloro-|
|        |              |              | hexafluorophosphate |
| ACP    | aminopyridine carbonyl | pyrrole carboxylic acid | |
| BINAM  | 1,1′-binaphthyl-2,2′-diamine | | |
| BINOL  | 1,1′-binaphthyl-2,2′-diol | | |
| Boc    | tert-butyloxy carbonyl | | |
| tBu    | tert-butyl | Hz | Hertz |
| br     | broad | m | milli / multiplett / meter |
| c      | concentration | M | mol/L |
| calcd. | calculated | m/z | mass per charge |
| CDCl₃  | deuterated chloroform | Me | methyl |
| d      | doublet / diameter / day | MeOH | methanol |
| DCM    | dichloromethane | MHz | megahertz |
| DIPEA  | N,N’-diisopropylethyl amine | min | minute (s) |
| DLS    | dynamic light scattering | μM | micromolar |
| DMSO   | dimethyl sulfoxide | MPLC | medium performance liquid chromatography |
| DMSO- d₆ | deuterated dimethyl sulfoxide | MS | mass spectrometry |
| Glu    | glutamic acid | p | para |
| e.g.   | for example | Pd/C | palladium on charcoal |
| equiv  | equivalent | ppm | parts per million |
| ESI-MS | electrospray ionization mass spectrometry | q | quadruplet |
|        |               | r | radius |
| Et₃N   | triethylamine | rt | room temperature |
| FT-IR  | fourier transform infrared spectroscopy | s | singlet / second(s) |
| g      | gram | t | time |
| GCP    | guanidinio carbonyl | TFA | trifluoroacetic acid |
|        | pyrrole | THF | tetrahydrofuran |
|        | | VI | viscosity index |
2. Synthesis of the BINAM-GCP motif 1

![Synthetic scheme of BINAM-GCP motif](image)

Scheme S1: Synthetic scheme of BINAM-GCP motif.

2.1 Synthesis of the protected GCP-BINAM motif 9

In a dried Schlenk tube the deprotected GCP building block 5\(^1\) (0.10 g, 0.228 mmol, 2.5 equiv) was dissolved in dry DCM (20 mL). DMF (0.5 mL) was added and the solution was cooled to 0 °C. At this temperature oxalyl chloride (24 µL, 34.7 mg, 0.273 mmol, 3 equiv) was added to give a red solution. The solution was stirred for three hours over which it was allowed to reach room temperature. Subsequently the solvents were removed in vacuo to give a light red foam, which was dissolved in dry THF (20 mL). This solution was added to a solution of (S)-1,1'-binaphthalene-2,2'-diamine (26.0 mg, 0.09 mmol, 1 equiv) and Diisopropylethylamine (76.6 µL, 58.2 mg, 0.450 mmol, 5 equiv) in THF (20 mL) at room temperature. The reaction mixture was stirred for 16 hours until a yellow suspension formed.

\(^1\) C. Schmuck, D. Rupprecht, C. Urban and N. Walden, *Synthesis* **2006**, 89-96.
The solvent was removed in vacuo and the residue was dissolved in DCM (20 mL). The organic layer was washed with water (3 × 10 mL) and brine (3 × 10 mL) and dried over MgSO₄. Solvents were removed in vacuo. The product was purified by flash chromatography (φ = 3 cm, h = 30 cm, CyHex:EtOAc = 2:1) to give the pure 9 (51.2 mg, 0.0455 mmol, 50%) as a white solid.

Re: 0.34 (CyHex:EtOAc = 2:1). ¹H-NMR: (400 MHz, CDCl₃) δ [ppm] = 1.52 (s, 18 H, 2 x C-(CH₃)), 1.57 (s, 18 H, 2 x C-(CH₃)), 2.03 - 2.04 (m, 6 H, 2 x CH₃), 2.19 - 2.27 (m, 4 H, 2 x CH₂), 7.10 (d, 3 J = 8.5 Hz, 2 H, 2 x BINOL-H), 7.27 - 7.30 (m, 2 H, 2 x BINOL-H), 7.39 - 7.46 (m, 2 H, 2 x BINOL-H), 7.91 (d, 3 J = 8.1 Hz, 2 H, 2 x BINOL-H), 7.98 (d, 3 J = 9.00 Hz, 2 H, 2 x BINOL-H), 8.36 (d, 3 J = 8.9 Hz, 2 H, 2 x BINOL-H). ¹³C-NMR: (151 MHz, CDCl₃) δ [ppm] = 9.7, 21.4, 28.0, 28.4, 38.4, 81.3, 83.2, 121.5, 121.9, 122.5, 125.2, 125.6, 126.0, 127.2, 127.7, 127.9, 128.3, 129.5, 131.3, 132.3, 134.9, 153.0, 158.0, 160.4, 171.3, 172.9. HR-MS: (ESI, MeOH): m/z = 1125.5397 ([M+H]+), calcd. 1125.5404 (for [C₆₀H₄8N₁₀O₁]⁺).

FT-IR: (ATR): ʋ [cm⁻¹] = 3508, 3267, 3062, 2925, 2630, 1845, 1771, 1675, 1621, 1141, 1130, 1141, 1078, 895, 830, 681, 524. Melting point: 138 °C.

2.2 Deprotection of the BINAM-GCP-Motif 1

The (S)-BINAM-GCP-motif 9 (100 mg, 0.0889 mmol) was dissolved in DCM (5 mL) and cooled to 0 °C. Trifluoroacetic acid (2.5 mL) was added slowly and the mixture was allowed to warm up to room temperature over the course of one hour. The mixture was stirred at room temperature for an additional four hours and the solvent was removed in vacuo. Hydrochloric acid (1 M in H₂O, 10 mL) was added and the resulting solution was dried in vacuo. Product 1 (63.3 mg, 0.0715 mmol, 80%) was obtained as a white solid after purification by MPLC (φ = 3 cm, h = 60 cm, RP18, methanol:water = 1:10 to pure methanol).

Re: 0.08 (CyHex:EtOAc = 1:1). ¹H-NMR: (300 MHz, DMSO-d6) δ [ppm] = 1.89 - 1.94 (m, 6 H, 2 x CH₃), 2.15 - 2.17 (m, 4 H, 2 x CH₂), 2.35 - 2.43 (m, 4 H, 2 x CH₂), 7.03 (d, 3 J = 9.07 Hz, 2 H, 2 x BINOL-H), 7.29 (d, 3 J = 7.82 Hz, 1 H, 2 x BINOL-H), 7.49 (t, 3 J = 6.57 Hz, 2 H, 2 x BINOL-H), 7.82 (d, 3 J = 9.38 Hz, 2 H, 2 x BINOL-H), 8.03 (d, 3 J = 8.44 Hz, 1 H, 2 x BINOL-H), 8.09 (d, 3 J = 9.07 Hz, 2 H, 2 x BINOL-H), 8.24 - 8.33 (br m, 6 H), 11.02 (br s, 2 H), 11.85 (br s, 2 H), 13.18 (br s, 2 H). ¹³C-NMR: (151 MHz, DMSO-d6) δ [ppm] = 13.9, 22.1, 28.7, 120.4, 122.8, 123.5, 124.4, 124.7, 125.2, 126.5, 127.1, 127.7, 130.0, 130.4, 133.0, 134.2, 136.7, 154.3, 158.6, 161.7, 166.8. HR-MS: (ESI, MeOH): m/z = 813.3115 ([M+H⁺-2HCl]+), calcd. 813.3103 (for [C₄₂H₄₁N₁₀O₁]⁺).

FT-IR: (ATR): ʋ [cm⁻¹] = 3531, 3054, 2867, 2627, 1773, 1691, 1660, 1120,1066, 1074,1070, 815, 777. Elemental analysis: calcd. (%) for C₄₂H₄₂Cl₂N₁₀O₁: C 56.95, H 4.78, N 15.81; found: C 52.80, H 3.91, N 11.20. Melting point: 166 °C.
3. Synthesis of the BINAM-GCP motif 2

Scheme S2: Synthetic scheme of BINAM-ACP motif.

3.1 Synthesis of the ACP binding motif 11

Pyrrole 10 (1.00 g, 3.21 mmol, 1 equiv), HCTU (1.59 g, 3.85 mmol, 1.2 equiv) and DMAP (1.17 g, 9.63 mmol, 3 equiv) were dissolved in DCM (50 mL) and DMF (2 mL). After stirring for 30 minutes, 6-methylpyridine-2-amine (0.52 g, 4.81 mmol, 1.5 equiv) was added and the mixture was stirred for another 16 h at room temperature. The solvents were removed under reduced pressure and the residue was resolved in DCM (20 mL).

After washing with water (3 × 10 mL) and brine (3 × 10 mL) the combined organic layers were evaporated and the residue was purified by flash chromatography (φ = 5 cm, h = 40 cm, CyHex:EtOAc = 5:1). Product 11 (0.630 g, 1.57 mmol, 49%) was obtained as a white solid.

Rf: 0.61 (CyHex:EtOAc = 5:1). $^1$H-NMR: (400 MHz, CDCl$_3$) δ [ppm] = 1.55 (s, 9 H, (C-CH$_3$)$_3$), 2.30 (s, 3 H, CH$_3$), 2.47 (s, 3 H, CH$_3$), 2.73 (t, $^3$J = 7.0 Hz, 2 H, CH$_2$), 3.09 (t, $^3$J = 7.0 Hz, 2 H, CH$_2$), 3.70 (s, 3 H, CH$_3$), 6.91 (d, $^3$J = 7.5 Hz, 1 H, pyr-CH$_2$), 7.63 (dd, $^3$J = 7.5, 8.2 Hz, 1 H, pyr-CH$_1$), 8.10 (d, $^3$J = 8.2 Hz, 1 H, pyr-CH$_2$), 10.04 (s, 1 H, NH), 10.21 (br s, 1 H, NH). $^{13}$C-NMR: (151 MHz, CDCl$_3$) δ [ppm] = 10.4, 20.3, 23.8, 28.5, 33.9, 52.1, 81.8, 112.1, 119.3, 123.4, 124.8, 125.8, 126.5, 139.4, 151.2, 156.1,
159.9, 160.3, 174.2. **HR-MS**: (ESI, MeOH): m/z = 402.2036 ([M+H]+), calcd. 402.2023 (for [C21H28N3O5]+). **FT-IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3332, 3301, 2923, 1695, 1664, 1604, 1569, 1542, 1438, 1365, 1336, 1278, 1249, 1155, 1135, 1078, 983, 842, 779, 709, 609. **Melting Point**: 101 °C.

### 3.2 Deprotection of the ACP building block 6

To a solution of the protected ACP building block **11** (1.00 g, 2.49 mmol, 1 equiv) in THF (50 mL) LiOH·H$_2$O (0.418 g, 9.96 mmol, 4 equiv) in water (20 mL) was added. The reaction mixture was stirred for 1 h at 0 °C and 8 h at room temperature. The mixture was diluted with water (10 mL) and washed with Et$_2$O (3 × 30 mL). The solution was acidified by 0.5 M NaHSO$_4$ (10 mL) and directly extracted with EtOAc (3 × 30 mL). All organic layers were collected, washed with brine (3 × 30 mL) and dried with MgSO$_4$. Solvents were removed in vacuo. The product **6** (0.860 g, 2.22 mmol, 89%) was obtained as a white powder.

**Rf**: 0.22 (CyHex:EtOAc = 3:1). **$^1$H-NMR**: (400 MHz, DMSO-d$_6$) $\delta$ [ppm] = 1.55 (s, 9 H, C-(CH$_3$)$_9$), 2.20 (s, 3 H, CH$_3$), 2.40 (t, $^3$J = 7.7 Hz, 2 H, CH$_2$), 2.43 (s, 3 H, CH$_3$), 2.97 (t, $^3$J = 7.7 Hz, 2 H, CH$_2$), 6.98 (d, $^3$J = 7.3 Hz, 1 H, pyr-CH$_2$), 7.66 (dd, $^3$J = 7.3, 8.4 Hz, 1 H, pyr-CH$_2$), 8.01 (d, $^3$J = 8.4 Hz, 1 H, pyr-CH$_2$), 10.71 (s, 1 H, NH), 12.04 (br s, 1 H), 12.07 (s, 1 H). **$^{13}$C-NMR**: (151 MHz, DMSO-d$_6$) $\delta$ [ppm] = 9.8, 20.2, 23.6, 28.1, 34.3, 80.8, 111.3, 118.7, 122.1, 123.7, 124.9, 130.3, 138.4, 151.6, 156.5, 158.9, 160.4, 174.2. **HR-MS**: (ESI, MeOH): m/z = 410.1680 ([M+Na]+), calcd. 410.1686 (for [C$_{20}$H$_{25}$N$_3$O$_5$Na]+). **FT-IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3311, 2919, 1704, 1670, 1612, 1571, 1450, 1367, 1319, 1272, 1218, 1159, 1128, 1089, 1000, 923, 890, 844, 800, 779, 730, 659, 628, 611. **Melting point**: 195 °C.
3.3 Synthesis of the protected BINAM-ACP Motif 12

![Synthesis of the protected BINAM-ACP Motif 12](image)

The deprotected ACP building block 6 (100 mg, 0.258 mmol, 3 equiv) was dissolved in dry DCM (20 mL) and DMF (0.5 mL). The solution was cooled to 0 °C. At this temperature oxalyl chloride (22.0 µL, 32.7 mg, 0.258 mmol, 3 equiv) was added to give a red solution. The solution was stirred for three hours over which the ice bath was allowed to reach room temperature. Subsequently the solvent was removed in vacuo to give a light red foam, which was dissolved in dry THF (20 mL). This solution was added to a solution of (S)-1,1’-binaphthalene-2,2’-diamine (24.5 mg, 0.09 mmol, 1 equiv) and diisopropylethylamine (72.3 µL, 54.9 mg, 0.425 mmol, 5 equiv) in THF (20 mL) at room temperature and was stirred for 16 hours until a yellow suspension formed. The solvent was removed in vacuo and the residue was dissolved in DCM (20 mL). The organic layer was washed with water (3 × 15 mL) and brine (3 × 15 mL), dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography (ϕ = 3 cm, h = 30 cm, CyHex:EtOAc = 2:1) to give 12 (59.2 mg, 58.0 mmol, 67%) as a white solid.

**Re:** 0.25 (CyHex:EtOAc = 2:1). ¹H-NMR: (300 MHz, DMSO-d₆) δ [ppm] = 1.55 (s, 18 H, 2 x C-(CH₃)), 2.00 (s, 6 H, 2 x CH₃), 2.14 - 2.27 (m, 4 H, 2 x CH₂), 2.43 (s, 6 H, 2 x CH₃), 2.65 - 2.84 (m, 4 H, 2 x CH₂), 6.98 (d, ³J = 7.5 Hz, 2 H, 2 x pyr-CH), 7.04 (d, ³J = 8.8 Hz, 2 H, 2 x pyr-CH), 7.19 (d, ³J = 8.8 Hz, 2 H, 2 x BINOL-H), 7.27 (dd, ³J = 7.5, 8.7 Hz, 2 H, 2 x pyr-CH), 7.43 (t, ³J = 7.5 Hz, 2 H, 2 x BINOL-H), 7.67 (t, ³J = 7.8 Hz, 2 H, 2 x BINOL-H), 7.91 (d, ³J = 8.1 Hz, 2 H, 2 x BINOL-H), 8.0 (d, ³J = 9.4 Hz, 2 H, 2 x BINOL-H), 8.2 (d, ³J = 8.44 Hz, 2 H, 2 x BINOL-H), 8.23 (br s, 2 H, 2 x NH), 10.63 (br s, 2 H, 2 x NH), 11.97 (br s, 2 H, 2 x NH). ¹³C-NMR: (75 MHz, DMSO-d₆) δ [ppm] = 10.2, 20.8, 23.0, 31.7, 35.2, 87.3, 108.3, 120.5, 122.8, 125.2, 126.8, 127.1, 127.9, 129.1, 130.6, 131.1, 131.9, 132.6, 133.7, 135.9, 137.1, 138.2, 142.1, 156.5, 157.9, 158.7, 161.1, 181.5. HR-MS: (ESI, MeOH): m/z = 1023.4752 ([M+H]+), calcld. 1023.4763 (for [CoH₁₀₂N₂Os]⁺). FT-IR: (ATR): ν [cm⁻¹] = 3452, 3446, 3087, 2866, 2642, 1778 1649, 1646, 1200, 1071, 1057, 868, 795, 624, 531. **Melting point:** 210 °C.
3.4 Deprotection of the BINAM-ACP Motif 2

(S)-BINAM ACP motif 12 (100 mg, 0.0977 mmol) was dissolved in DCM (5 mL) under ice bath cooling (0 °C). TFA (1 mL) was added and the mixture was stirred for one hour over which the ice bath was allowed to thaw. Subsequently the mixture was stirred for additional four hours at room temperature. The reaction was monitored by TLC. After completion the solvent was removed in vacuo and the residue was resolved in 1 M aqueous hydrochloric acid (10 mL). The resulting solution was dried in vacuo and the crude product was purified by MPLC ($\phi = 3$ cm, $h = 60$ cm, RP18, MeOH:H$_2$O = 1:10 to pure MeOH). The pure product 2 (79.0 mg, 0.0867 mmol, 89%) was obtained as a white solid.

$R_f$: 0.11 (CyHex:EtOAc = 2:1). $^1$H-NMR: (300 MHz, DMSO-$d_6$) $\delta$ [ppm] = 1.95 (s, 6 H, 2 x CH$_3$), 2.09 - 2.13 (m, 4 H, 2 x CH$_2$), 2.41 (s, 6 H, 2 x CH$_3$), 2.53 - 2.66 (m, 4 H, 2 x CH$_2$), 6.90 (d, $^3J = 9.1$ Hz, 2 H, 2 x pyr-CH), 6.96 (d, $^3J = 7.2$ Hz, 2 H, 2 x pyr-CH), 7.23 (dd, $^3J = 9.1$, 7.2, 2 H, 2 x pyr-CH), 7.41 (t, $^3J = 8.1$, 2 H, 2 x BINOL-H), 7.63 (t, $^3J = 8.1$, 2 H, 2 x BINOL-H), 7.81 (d, $^3J = 9.1$ Hz, 2 H, 2 x BINOL-H), 7.87 (d, $^3J = 8.1$ Hz, 2 H, 2 x BINOL-H), 7.95 (d, $^3J = 8.8$ Hz, 2 H, 2 x BINOL-H), 8.01 (d, $^3J = 8.8$ Hz, 2 H, 2 x BINOL-H), 8.78 (br s, 2 H, 2 x NH), 10.66 (br s, 2 H, 2 x OH), 12.09 (br s, 2 H, 2 x NH). $^{13}$C-NMR: (75 MHz, DMSO-$d_6$) $\delta$ [ppm] = 10.3, 22.0, 22.5, 37.2, 89.5, 111.2, 123.2, 124.1, 125.6, 126.3, 126.9, 127.4, 127.9, 128.8, 129.4, 131.8, 133.2, 135.1, 137.6, 139.7, 141.1, 154.6, 157.2, 159.5, 162.4, 182.5. HR-MS: (ESI, MeOH): m/z = 933.3354 ([M+Na]$^+$), calcd. 933.3331 (for [C$_{52}$H$_{46}$N$_8$O$_8$Na]$^+$). FT-IR: (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3551, 3522, 3023, 2866, 2474, 1729, 1645, 1635, 1604, 1085, 1052, 1050, 896, 757, 676, 648. Elemental analysis: calcd. (%) for C$_{52}$H$_{46}$N$_8$O$_8$: C 68.56, H 5.09, N 12.30; found: C 68.40, H 4.77, N 8.55. Melting point: Decomposition at 265 °C.
4. Synthesis of the amino acid extended BINAM-ACP 3

Scheme S3: Synthetic scheme of amino acid extended BINAM-ACP (3).
4.1 Synthesis of BINAM-glutamic acid 13

L-Boc-glutamic acid benzyl ester (7.11 g, 21.1 mmol, 3 equiv), HCTU (8.71 g, 21.1 mmol, 3 equiv) and DMAP (4.30 g, 35.1 mmol, 5 equiv) were dissolved in DCM (100 mL) and DMF (1 mL) and stirred for one hour. Subsequently (S)-BINAM (2.00 g, 7.02 mmol, 1 equiv) was added and the reaction mixture was stirred for 16 hours at room temperature.

The solvent was evaporated in vacuo and the residue was redissolved in EtOAc. The organic layer was washed with water (3 x 50 mL) and brine (3 x 50 mL) and dried over MgSO₄. The solvent was evaporated and the crude product purified by flash chromatography (φ = 6 cm, h = 50 cm, CyHex:EtOAc = 5:1) to obtain the product 13 (4.35 g, 4.71 mmol, 67%) as a white foam.

Rt: 0.52 (CyHex:EtOAc = 5:1). ¹H-NMR: (300 MHz, DMSO-d₆) δ [ppm] = 1.27 - 1.37 (m, 22 H, 2 x C-(CH₃)₃ + 2 x CH₂), 1.85 - 1.92 (m, 4 H, 2 x CH₂), 3.76 - 3.84 (m, 2 H, 2 x CH), 5.01 (s, 4 H, 2 x CH₂), 6.75 (d, 3J = 7.82 Hz, 2 H, 2 x BINOL-H), 6.85 (d, 3J = 8.44 Hz, 2 H, 2 x BINOL-H), 7.20 (d, 3J = 7.50 Hz, 2 H, 2 x BINOL-H), 7.32 - 7.38 (m, 12 H, 2 x BINOL-H + 2 x CdH), 7.89 (d, 3J = 7.82 Hz, 2 H, 2 x BINOL-H), 7.92 (br s, 2 H, 2 x NH), 7.99 (d, 3J = 9.07 Hz, 2 H, 2 x BINOL-H), 8.90 (br s, 2 H, 2 x NH). ¹³C-NMR: (75 MHz, DMSO-d₆) δ [ppm] = 17.8, 30.3, 34.3, 54.8, 64.1, 81.5, 120.5, 122.5, 125.0, 125.8, 127.2, 128.9, 129.2, 132.3, 133.5, 136.9, 138.9, 140.7, 142.5, 149.3, 160.7, 176.0, 180.9. HRMS: (ESI, MeOH): m/z = 923.4187 ([M+H]+), calc'd. 923.4226 (for [C₈H₁₆O₈N₄O₁₀][⁺]). FT-IR: (ATR): ν [cm⁻¹] = 2979, 1675, 1596, 1496, 1452, 1365, 1247, 1160, 1052, 865, 811, 746, 696. Melting point: 67 °C.

4.2 Deprotection of BINAM-Glutamic acid 7

The (S)-BINAM glutamic acid 13 (200 mg, 0.217 mmol) was dissolved in DCM (6 mL) and TFA (3 mL) was added to initiate deprotection. The mixture was stirred for three hours at room temperature and the reaction progress was monitored by TLC. The solvent was removed in vacuo and the residue was dissolved in 1 M aqueous hydrochloric acid (10 mL) and dried in vacuo again. The crude product was purified by MPLC (φ = 2 cm, h = 30 cm, RP18, MeOH:HO = 1:10 to pure MeOH). Hydrochloric acid (1 M in H₂O, 10 mL) was added and the resulting solution was dried in vacuo. The hydrochloride 7 (145 mg, 0.182 mmol, 84%) was obtained as a white solid.
R: 0.05 (CyHex:EtOAc = 4:1). 1H-NMR: (300 MHz, DMSO-d6) δ [ppm] = 1.25 - 1.32 (m, 4 H, 2 x CH3), 1.42 - 1.70 (m, 4 H, 2 x CH3), 3.77 - 3.82 (m, 2 H, 2 x CH2), 5.05 (s, 4 H, 2 x CH2), 6.94 (d, 3J = 8.44 Hz, 2 H, 2 x BINOL-H), 7.19 (t, 3J = 7.19 Hz, 2 H, 2 x BINOL-H), 7.31 - 7.48 (m, 12 H, 2 x BINOL-H + 2 x CdHs), 7.68 (d, 3J = 9.07 Hz, 2 H, 2 x BINOL-H), 7.86 (d, 3J = 8.13 Hz, 2 H, 2 x BINOL-H), 7.96 (d, 3J = 9.07 Hz, 2 H, 2 x BINOL-H), 8.14 (br s, 4 H, 2 x NH2), 9.63 (s, 2 H, 2 x NH). 13C-NMR: (75 MHz, DMSO-d6) δ [ppm] = 18.5, 36.7, 56.3, 66.7, 120.1, 121.6, 122.7, 123.2, 125.6, 126.7, 128.2, 132.4, 134.0, 135.4, 137.9, 140.5, 142.4, 145.9, 165.8, 169.3. HR-MS: (ESI, MeOH): m/z = 723.3168 ([M+H+-2HCl]+), calcd. 723.3177 (for [C18H14N4O6]+). FT-IR: (ATR): v [cm⁻¹] = 2983, 1775, 1664, 1597, 1489, 1484, synthe1451, 1356, 1277, 1155, 1048, 852, 801, 702, 680. Melting point: 98 °C.

4.3 Synthesis of the BINAM-glutamic acid-ACP motif 14

A solution of building block 6 (100 mg, 0.258 mmol, 3 equiv) in dry DCM (20 mL) and DMF (0.5 mL) was cooled to 0 °C. At this temperature oxalyl chloride (22.0 µL, 32.7 mg, 0.258 mmol, 3 equiv) was added, which resulted in a yellow solution. The solution was stirred for 16 hours over which the ice bath was allowed to reach room temperature. Subsequently the solvents were removed in vacuo, yielding a yellow foam which was dissolved in dry THF (20 mL). This solution was added to a solution of the deprotected (S)-BINAM glutamic acid 7 (62.2 mg, 0.0860 mmol, 1 equiv) and diisopropylethylamine (72.0 µL, 54.7 mg, 0.423 mmol, 5 equiv) in THF (20 mL) at room temperature. The reaction mixture was stirred for 16 hours until a suspension had formed. The solvent was removed in vacuo and the residue was dissolved in DCM (20 mL). The organic layer was washed with water (3 × 15 mL) and brine (3 × 15 mL) and dried over MgSO4. The solvents were removed in vacuo and the residue was purified by column chromatography (φ = 3 cm, h = 30 cm, CyHex:EtOAc = 4:1) to give pure 14 (102 mg, 0.0698 mmol, 81%) as a white solid.

R: 0.46 (CyHex:EtOAc = 2:1). 1H-NMR: (300 MHz, CDCl3) δ [ppm] = 1.56 (s, 18 H, 2 x C-(CH3)5), 2.24 (s, 6 H, 2 x CH3), 2.52 (s, 6 H, 2 x CH3), 2.67 - 2.78, (m, 8 H, 4 x CH2), 3.15 (t, 3J = 7.3 Hz, 4 H, 2 x CH2), 3.27 (t, 3J = 7.2 Hz, 4 H, 2 x CH2), 3.80 - 3.81 (m, 2 H, 2 x CH2), 5.08 (s, 4 H, 2 x CH2), 6.86 (d, 3J = 7.5 Hz, 2 H, 2 x pyr-CH), 6.96 (d, 3J = 2.8 Hz, 2 H, 2 x pyr-CH), 7.07 (d, 3J = 3.8 Hz, 2 H, 2 x BINOL-H), 7.27 - 7.30 (m, 14 H, 2 x BINOL-H + 2 x CdHs + 2 x pyr-CH), 7.43 (d, 3J = 3.5 Hz, 2 H, 2 x BINOL-H), 7.53 (t, 3J = 6.3 Hz, 2 H, 2 x BINOL-H), 7.69 (d, 3J = 3.3, 2 H, 2 x BINOL-H), 8.07 (d, 3J = 8.1 Hz, 2 H, 2 x BINOL-H). 13C-NMR: (75 MHz, CDCl3) δ [ppm] = 26.2, 27.2, 30.3, 30.8, 31.3, 36.8, 43.1, 62.7, 66.9, 70.7, 94.6, 104.9, 109.8, 112.7, 113.8, 119.4, 121.3, 123.8, 127.0, 131.0, 131.8,
132.7, 134.7, 137.0, 138.0, 138.7, 140.7, 141.7, 142.1, 142.8, 147.2, 149.8, 152.5, 156.1, 157.1, 167.8, 171.4, 174.1. **HR-MS:** (ESI, DCM): m/z = 1461.6493 ([M+H]+), calcd. 1461.6554 (for [C_{81}H_{89}N_{10}O_{14}]^+). **FT-IR:** (ATR): ν [cm⁻¹] = 3437, 3266, 3058, 2925, 2710, 1798, 1675, 1666, 1634, 1581, 1058, 1030, 1012, 821, 801, 765, 653, 641. **Melting point:** Decomposition at 254 °C.

4.4 Deprotection of the BINAM-glutamic acid-ACP motif 3

The (S)-BINAM glutamic acid ACP motif 14 (100 mg, 0.0684 mmol) was dissolved in DCM (5 mL) and TFA (1 mL) was added to initiate deprotection. The mixture was stirred for 16 hours and the reaction progress was monitored by TLC. The solvent was removed in vacuo, and the residue was taken up in 1 M aqueous hydrochloric acid (10 mL), dried in vacuo and the crude product was purified by MPLC (φ = 2 cm, h = 30 cm, RP18, MeOH:H₂O = 1:10 to pure MeOH). The deprotected product 3 (88.5 mg, 65.6 µmol, 96%) was obtained as a white solid.

**Rf:** 0.21 (CyHex:EtOAc = 4:1). **¹H-NMR:** (300 MHz, CDCl₃) δ [ppm] = 2.04 (s, 6 H, 2 x CH₃), 2.27, (s, 4 H, 2 x CH₂), 2.30 - 2.33 (m, 4 H, 2 x CH₂), 2.36 - 2.38 (m, 4 H, 2 x CH₂), 2.69 - 2.71 (m, 4 H, 2 x CH₂), 2.85 - 2.88 (m, 4 H, 2 x CH₂), 4.27 - 4.29 (m, 2 H, 2 x CH₂), 4.97 (s, 4 H, 2 x CH₂), 6.98 (d, J = 4.97 Hz, 2 H, pyr-CH), 7.12 (d, J = 2.8 Hz, 2 H, pyr-CH), 7.17 (d, J = 5.6 Hz, 2 H, 2 x BINOL-H), 7.32 (m, 14 H, 2 x BINOL-H + 2 x C₆H₅ + 2 x pyr-CH), 7.45 (d, J = 4.7 Hz, 2 H, 2 x BINOL-H), 7.55 (t, J = 3.1 Hz, 2 H, 2 x BINOL-H), 7.66 (d, J = 5.6 Hz, 2 H, 2 x BINOL-H), 7.87 (d, J = 3.1 Hz, 2 H, 2 x BINOL-H). **¹³C-NMR:** (75 MHz, CDCl₃) δ [ppm] = 25.9, 29.4, 30.0, 30.5, 36.6, 42.8, 62.4, 66.6, 72.2, 94.9, 104.6, 109.5, 110.2, 113.5, 119.2, 121.1, 130.2, 130.7, 131.5, 132.4, 134.4, 136.7, 137.7, 138.4, 140.4, 141.4, 141.8, 142.5, 149.5, 150.8, 152.3, 154.0, 156.8, 167.6, 168.8, 173.8. **HR-MS:** (ESI, MeOH): m/z = 1371.5078 ([M+Na]+), calcd. 1371.5122 (for [C_{81}H_{89}N_{10}O_{14}Na]^+). **FT-IR:** (ATR): ν [cm⁻¹] = 3415, 3030, 2901, 2891, 1847, 1672, 1621, 1071, 1100, 922, 859, 821, 794, 633. **Elemental analysis:** calcd. (%) for C_{81}H_{89}N_{10}O_{14}S: C 67.64, H 5.38, N 10.38; found: C 67.2, H 4.60, N 8.76. **Melting point:** Decomposition at 219 °C.

S14
5. Synthesis of the substituted BINAM-GCP motif 4

Scheme S4: Synthetic scheme of 4

5.1 Synthesis of BINAM-Br-ACP 15

A dry schlenk tube was filled with a solution of the deprotected ACP building block 6 (26.0 mg, 0.0671 mmol, 3 equiv) in dry DCM (10 mL). DMF (0.1 mL) was added and the solution was cooled to 0 °C. At this temperature oxalyl chloride (6.0 µL, 8.52 mg, 0.0671 mmol, 3 equiv) was added yielding a yellow solution. The solution was stirred for 16 hours over which the ice bath was allowed to thaw. Subsequently the solvents were removed in vacuo yielding a yellow foam, which was dissolved in dry THF (10 mL). At room temperature this solution was added to a solution of

S15
the brominated (S)-BINAM \(^8\), (9.89 mg, 0.0224 mmol, 1 equiv) and diisopropylethylamine (18.8 \(\mu\)L, 14.3 mg, 0.111 mmol, 5 equiv) in THF (20 mL). After stirring for 16 hours at the same temperature a suspension had formed. The solvents were removed under reduced pressure and the residue was dissolved in DCM (20 mL). The organic layer was washed with water (3 \(\times\) 15 mL) and brine (3 \(\times\) 15 mL) and dried over MgSO\(_4\). The product was purified by flash chromatography (\(\phi = 3\) cm, \(h = 30\) cm, CyHex:EtOAc = 10:1) yielding 15 (13.8 mg, 0.0117 mmol, 52\%) as a white solid.

Re: 0.56 (CyHex:EtOAc = 3:1). \(^1\)H-NMR: (300 MHz, DMSO-\(d_6\)) \(\delta\) [ppm] = 1.56 (s, 18 H, 2 x C-(CH\(_3\))), 1.98 (s, 6 H, 2 x CH\(_3\)), 2.22 (t, \(\^3J = 6.7\) Hz, 4 H, 2 x CH\(_2\)), 2.41 (s, 6 H, 2 x CH\(_3\)), 2.76 (t, \(\^3J = 6.6\) Hz, 4 H, 2 x CH\(_2\)), 6.7 (d, \(\^3J = 9.1\) Hz, 2 H, 2 x pyr-CH), 6.99 (d, \(\^3J = 8.4\) Hz, 2 H, 2 x pyr-CH), 7.22 (dd, \(\^3J = 8.4\) Hz, 9.2 Hz, 2 H, 2 x pyr-CH), 7.23 (d, \(\^3J = 8.8\) Hz, 2 H, 2 x BINOL-\(H\)), 7.66 (t, \(\^3J = 6.0\) Hz, 2 H, 2 x BINOL-\(H\)), 7.74 (d, \(\^3J = 9.1\) Hz, 2 H, 2 x BINOL-\(H\)), 7.98 (d, \(\^3J = 1.9\) Hz, 2 H, 2 x BINOL-\(H\)), 8.02 (d, \(\^3J = 6.0\) Hz, 2 H, 2 x BINOL-\(H\)), 8.20 (br s, 2 H, 2 x NH), 10.59 (br s, 2 H, 2 x NH), 11.93 (br s, 2 H, 2 x NH). \(^{13}\)C-NMR: (151 MHz, CDCl\(_3\)) \(\delta\) [ppm] =12.2, 19.3, 21.1, 30.3, 35.2, 88.1, 114.5, 118.6, 120.2, 121.6, 123.3, 123.8, 125.4, 126.8, 127.1, 128.2, 128.7, 129.7, 129.9, 130.7, 132.3, 133.2, 133.9, 135.9, 149.3, 153.5, 162.8, 175.9. HR-MS: (ESI, MeOH): \(m/z = 1181.2826\) ([M+H\(^+\)], calcd. 1181.2953 (for [C\(_{108}\)H\(_{102}\)Br\(_2\)N\(_2\)O\(_4\)I\(^-\)])). FT-IR: (ATR): \(\tilde{\nu}\) [cm\(^{-1}\)] = 3403, 3321, 3061, 2876, 2464, 1843, 1796, 1663, 1629, 1130, 1108, 1034, 864, 753, 585, 572. Melting point: 204 °C.

5.2 Synthesis of Hexyl-BINAM-ACP 16

The brominated product 15 (20.0 mg, 0.0169 mmol, 1 equiv) and 1,3-bis(diphenyl phosphino)propane nickel(II) chloride (0.220 mg, 0.406 \(\mu\)mol, 2.4 mol \%) were dissolved in dry Et\(_2\)O (20 mL). The mixture was cooled to \(-10\) °C in an ice/NaCl bath. Then a 0.8 M solution of hexyl magnesium bromide in Et\(_2\)O (40.0 \(\mu\)L, 0.034 mmol, 2 equiv) was added at this temperature. The cooling bath was allowed to thaw while stirring was continued for 16 hours. The catalyst was filtered of and the organic layer was washed with 0.5 M HCl (2 \(\times\) 10 mL), water (3 \(\times\) 15 mL) and brine (3 \(\times\) 15 mL). After the removal of the solvents under reduced pressure, the crude product was purified by flash chromatography (\(\phi = 3\) cm, \(h = 30\) cm, CyHex:EtOAc = 7:1). The pure product 16 (15.8 mg, 0.0133 mmol, 78\%) was obtained as a white solid.

Re: 0.68 (CyHex:EtOAc = 4:1). \(^1\)H-NMR: (400 MHz, CDCl\(_3\)) \(\delta\) [ppm] = 0.91 (t, \(\^3J = 6.88\) Hz, 6 H, 2 x CH\(_3\)), 1.24 - 1.46 (m, 12 H, 2 x CH\(_2\)-CH\(_2\)-CH\(_2\)-), 1.28 - 1.56 (m, 24 H, 2 x C-(CH\(_3\))- + 2 x CH\(_3\)), 2.30 (s, 6 H, 2 x CH\(_3\)), 2.56 (s, 4 H, 2 x CH\(_2\)), 3.05 (br s, 8 H, 2 x CH\(_3\)), 2.61 - 2.67 (m, 8 H, 4 x CH\(_2\)), 2.71 (t, \(\^3J = 7.5\) Hz, 4 H, 2 x CH\(_2\)), 6.89 (d, \(\^3J = 9.1\) Hz, 2 H, pyr-CH), 7.02 (d, \(\^3J = 6.0\) Hz, 2 H, 2 x pyr-CH), 7.15 (d, \(\^3J = 8.8\) Hz, 2 H, 2 x

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\(^2\) A. Sakakura, K. Suzuki and K. Ishihara, *Adv. Synth. Catal.* **2006**, *348*, 2457-2465.
BINOL-H), 7.26 (dd, \(^3J = 6.1\) Hz, 9.1 Hz, 2 H, 2 x pyr-CH), 7.64 (t, \(^3J = 7.8\) Hz, 2 H, 2 x BINOL-H), 7.7 (d, \(^3J = 8.76\) Hz, 2 H, 2 x BINOL-H), 7.9 (d, \(^3J = 2.19\) Hz, 2 H, 2 x BINOL-H), 8.1 (d, \(^3J = 6.88\) Hz, 2 H, 2 x BINOL-H). \(^{13}\)C-NMR: (151 MHz, CDCl\(_3\)) \(\delta\) [ppm] = 12.5, 13.9, 22.5, 22.9, 29.2, 30.2, 30.7, 30.8, 31.7, 35.2, 36.1, 81.4, 104.2, 115.5, 117.8, 119.6, 124.1, 125.7, 127.4, 128.5, 129.3, 130.2, 132.1, 132.9, 134.3, 135.3, 137.1, 137.5, 141.4, 149.7, 155.5, 160.0, 160.7, 174.5. HR-MS: (ESI, DCM): m/z = 1191.6701 ([M+H]+), calcd. 1191.6641 (for [C\(_{72}H_{39}N_{9}O_{5}\])]. FT-IR: (ATR): \(\tilde{\nu}\) [cm\(^{-1}\)] = 3462, 3358, 3070, 2872, 2684, 1821, 1742, 1633, 1630, 1172, 1134, 1040, 944, 765, 748, 550. Melting point: 255 °C.

5.3 Deprotection of hexyl-BINAM-ACP 4

The (S)-BINAM hexyl ACP motif 16 (12 mg, 0.00101 mmol) was dissolved in DCM (5 mL) and TFA (1 mL) was added to initiate deprotection. The mixture was stirred for 16 hours and the reaction progress was monitored by TLC. The solvent was removed \(\textit{in vacuo}\) and the crude product was purified by MPLC (\(\phi = 2\) cm, h = 30 cm, RP18, MeOH:H\(_2\)O = 1:10 to pure MeOH). The deprotected product 4 (9.80 mg, 0.00908 mmol, 90%) was obtained as a white solid.

\(\text{Rf: } 0.33\) (CyHex:EtOAc = 4:1). \(^1\)H-NMR: (400 MHz, CDCl\(_3\)) \(\delta\) [ppm] = 0.88 (t, \(^3J = 7.97\) Hz, 6 H, 2 x CH\(_3\)), 1.18 - 1.36 (m, 12 H, 2 x CH\(_2\)-CH\(_2\)-CH\(_2\)), 1.52 (m, 4 H, 2 x CH\(_2\)), 1.55 (m, 4 H, 2 x CH\(_2\)), 2.05 (s, 6 H, 2 x CH\(_3\)), 2.16 (m, 4 H, 2 x CH\(_2\)), 2.46 (s, 6 H, 2 x CH\(_3\)), 2.78 (m, 4 H, 2 x CH\(_2\)), 6.87 (m, 4 H, 2 x CH\(_2\)), 6.90 (m, 2 H, 2 x BINOL-H + 2 x pyr-CH), 7.15 (d, \(^3J = 9.1\) Hz, 2 H, 2 x pyr-CH), 7.23 (d, \(^3J = 6.7\) Hz, 2 H, 2 x BINOL-H), 7.28 (d, \(^3J = 2.2\) Hz, 2 H, 2 x BINOL-H), 7.62 (dd, \(^3J = 7.5\) Hz, 9.0 Hz, 2 H, pyr-CH), 7.71 (d, \(^3J = 8.8\) Hz, 2 H, 2 x BINOL-H), 7.93 (d, \(^3J = 2.2\) Hz, 2 H, 2 x BINOL-H). \(^{13}\)C-NMR: (151 MHz, CDCl\(_3\)) \(\delta\) [ppm] = 12.0, 14.1, 21.4, 21.9, 28.6, 28.9, 29.3, 30.2, 32.7, 34.6, 37.2, 109.6, 114.5, 117.2, 119.7, 123.5, 126.1, 126.8, 127.2, 128.7, 130.4, 131.6, 132.9, 133.7, 135.3, 136.5, 138.4, 140.8, 146.5, 154.9, 164.4, 166.0, 173.2. HR-MS: (ESI, DCM): m/z = 1101.5299 ([M+Na]+), calcd. 1101.5209 (for [C\(_{64}H_{59}N_{9}O_{5}\)]). FT-IR: (ATR): \(\tilde{\nu}\) [cm\(^{-1}\)] = 3456, 3121, 3021, 2925, 1756, 1658, 1655, 1635, 1143, 1058, 1066, 955, 791, 764. Elemental analysis: calcd. (%) for C\(_{64}H_{59}N_{9}O_{5}\): C 71.22, H 6.54, N 10.38; found: C 69.40, H 6.02, N 10.60. Melting point: Decomposition at 278 °C.
6. Viscosity measurements

Figure S1: Kinematic viscosity of pure chloroform.

Figure S2: Kinematic viscosity of pure DMSO.

Figure S3: Kinematic viscosity of pure toluene.

Figure S4: Kinematic viscosity of pure Nynas NS8.

Figure S5: Kinematic viscosity of Nexbase 3020.

Figure S6: Kinematic viscosity of Nexbase 3043.
6.1 Viscosity measurements of 1 in DMSO

Figure S7: Kinematic (left) and specific (right) viscosity for 1 in DMSO at 200 mM.

Figure S8: Kinematic (left) and specific (right) viscosity for 1 in DMSO at 180 mM.

Figure S9: Kinematic (left) and specific (right) viscosity for 1 in DMSO at 160 mM.
Figure S10: Kinematic (left) and specific (right) viscosity for 1 in DMSO at 140 mM.

Figure S11: Kinematic (left) and specific (right) viscosity for 1 in DMSO at 120 mM.

Figure S12: Kinematic (left) and specific (right) viscosity for 1 in DMSO at 100 mM.
Figure S13: Kinematic (left) and specific (right) viscosity for 1 in DMSO at 80 mM.

Figure S14: Kinematic (left) and specific (right) viscosity for 1 in DMSO at 60 mM.

Figure S15: Kinematic (left) and specific (right) viscosity for 1 in DMSO at 50 mM.
Figure S16: Kinematic (left) and specific (right) viscosity for 1 in DMSO at 40 mM.

Figure S17: Kinematic (left) and specific (right) viscosity for 1 in DMSO at 30 mM.

Figure S18: Specific viscosity for 1 in DMSO at 55 °C.
Figure S19: Kinematic viscosity of all measurements of 1 in DMSO.

Figure S20: Specific viscosity of all measurements of 1 in DMSO.
6.2 Viscosity measurements of 2

6.2.1 Measurement of 2 in DMSO

Figure S21: Kinematic (left) and specific (right) viscosity for 2 in DMSO at 200 mM

Figure S22: Kinematic (left) and specific (right) viscosity for 2 in DMSO at 180 mM.

Figure S23: Kinematic (left) and specific (right) viscosity for 2 in DMSO at 160 mM.
Figure S24: Kinematic (left) and specific (right) viscosity for 2 in DMSO at 140 mM.

Figure S25: Kinematic (left) and specific (right) viscosity for 2 in DMSO at 120 mM.

Figure S26: Kinematic (left) and specific (right) viscosity for 2 in DMSO at 100 mM.
Figure S27: Kinematic (left) and specific (right) viscosity for 2 in DMSO at 80 mM.

Figure S28: Kinematic (left) and specific (right) viscosity for 2 in DMSO at 60 mM.

Figure S29: Kinematic (left) and specific (right) viscosity for 2 in DMSO at 50 mM.
Figure S30: Kinematic (left) and specific (right) viscosity for \(2\) in DMSO at 40 mM.

Figure S31: Kinematic (left) and specific (right) viscosity for \(2\) in DMSO at 30 mM.

Figure S32: Specific viscosity for \(2\) in DMSO at 55 °C.
Figure S33: Kinematic viscosity of all measurements of 2 in DMSO.

Figure S34: Specific viscosity of all measurements of 2 in DMSO.
6.2.2 Measurement of 2 in chloroform

Figure S35: Kinematic (left) and specific (right) viscosity for 2 in chloroform at 100 mM.

Figure S36: Kinematic (left) and specific (right) viscosity for 2 in chloroform at 80 mM.

Figure S37: Kinematic (left) and specific (right) viscosity for 2 in chloroform at 60 mM.
Figure S38: Kinematic (left) and specific (right) viscosity for 2 in chloroform at 40 mM.

Figure S39: Kinematic viscosity of all measurements of 2 in chloroform.

Figure S40: Specific viscosity of all measurements of 2 in chloroform.
6.2.3 Measurement of 2 in toluene

Figure S41: Kinematic (left) and specific (right) viscosity for 2 in toluene at 100 mM.

Figure S42: Kinematic (left) and specific (right) viscosity for 2 in toluene at 80 mM.

Figure S43: Kinematic (left) and specific (right) viscosity for 2 in toluene at 60 mM.
Figure S44: Kinematic (left) and specific (right) viscosity for 2 in toluene at 40 mM.

Figure S45: Kinematic viscosity of all measurements of 2 in toluene.

Figure S46: Specific viscosity of all measurements of 2 in toluene.
6.2.4 Measurement of 2 in Nynas NS8

Figure S47: Kinematic (left) and specific (right) viscosity for 2 in Nynas NS8 at 60 mM.

6.3 Viscosity measurements of 3

6.3.1 Measurement of 3 in Nynas NS8

Figure S48: Kinematic (left) and specific (right) viscosity for 3 in Nynas NS8 at 100 mM.

Figure S49: Kinematic (left) and specific (right) viscosity for 3 in Nynas NS8 at 80 mM.
Figure S50: Kinematic (left) and specific (right) viscosity for 3 in Nynas NS8 at 60 mM.

Figure S51: Kinematic (left) and specific (right) viscosity for 3 in Nynas NS8 at 40 mM.

Figure S52: Kinematic (left) and specific (right) viscosity for 3 in Nynas NS8 at 20 mM.
Figure S53: Kinematic viscosity of all measurements of 3 in Nynas NS8.

Figure S54: Specific viscosity of all measurements of 3 in Nynas NS8.
6.3.2 Measurement of 3 in Nexbase 3020

Figure S55: Kinematic (left) and specific (right) viscosity for 3 in Nexbase 3020 at 40 mM.

6.3.2 Measurement of 3 in Toluene

Figure S56: Kinematic (left) and specific (right) viscosity for 3 in toluene at 100 mM.

Figure S57: Kinematic (left) and specific (right) viscosity for 3 in toluene at 80 mM.
Figure S58: Kinematic (left) and specific (right) viscosity for 3 in toluene at 60 mM.

Figure S59: Kinematic (left) and specific (right) viscosity for 3 in toluene at 40 mM.

Figure S60: Kinematic (left) and specific (right) viscosity for 3 in toluene at 30 mM.
Figure S61: Kinematic viscosity of all measurements of 3 in toluene.

Figure S62: Specific viscosity of all measurements of 3 in toluene.
6.4 Viscosity measurement of 4

6.4.1 Measurement of 4 in DMSO

Figure S63: Kinematic (left) and specific (right) viscosity for 4 in DMSO at 60 mM.

6.4.2 Measurement of 4 in chloroform

Figure S64: Kinematic (left) and specific (right) viscosity for 4 in DMSO at 60 mM.

6.4.3 Measurement of 4 in toluene

Figure S65: Kinematic (left) and specific (right) viscosity for 4 in toluene at 60 mM.
6.4.4 Measurement of 4 in Nynas NS8

Figure S66: Kinematic (left) and specific (right) viscosity for 4 in Nynas NS8 at 100 mM.

Figure S67: Kinematic (left) and specific (right) viscosity for 4 in Nynas NS8 at 80 mM.

Figure S68: Kinematic (left) and specific (right) viscosity for 4 in Nynas NS8 at 60 mM.
Figure S69: Kinematic (left) and specific (right) viscosity for 4 in Nynas NS8 at 40 mM.

Figure S70: Kinematic (left) and specific (right) viscosity for 4 in Nynas NS8 at 20 mM.

Figure S71: Kinematic viscosity of all measurements of 4 in Nynas NS8.
Figure S72: Specific viscosity of all measurements of 4 in Nynas NS8.

6.4.5 Measurement of 4 in Nexbase 3020

Figure S73: Kinematic (left) and specific (right) viscosity for 4 in Nexbase 3020 at 60 mM.
Table S1: Viscosity measurements of I in DMSO.

| Temp (°C) | 200 mM Kin. V. (mm²/s) | 180 mM Kin. V. (mm²/s) | 160 mM Kin. V. (mm²/s) | 140 mM Kin. V. (mm²/s) | 120 mM Kin. V. (mm²/s) | 100 mM Kin. V. (mm²/s) | 80 mM Kin. V. (mm²/s) | 60 mM Kin. V. (mm²/s) | 50 mM Kin. V. (mm²/s) | 40 mM Kin. V. (mm²/s) | 30 mM Kin. V. (mm²/s) |
|-----------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
|           | 4.891 3.945 3.184 2.666 2.274 1.944 1.711 1.500 1.409 | 4.443 3.486 2.776 2.296 1.952 1.689 1.484 1.314 1.252 | 4.071 3.265 2.688 2.251 1.927 1.680 1.466 1.300 1.234 | 3.883 3.104 2.554 2.125 1.847 1.575 1.370 1.224 1.157 | 3.544 2.868 2.316 1.972 1.688 1.476 1.299 1.144 1.086 | 3.408 2.651 2.160 1.788 1.522 1.312 1.165 1.025 0.969 | 3.408 2.651 2.160 1.788 1.522 1.312 1.165 1.025 0.969 | 3.141 2.487 2.020 1.719 1.420 1.225 1.103 0.979 0.929 | 3.141 2.487 2.020 1.719 1.420 1.225 1.103 0.979 0.929 | 2.945 2.361 2.115 1.806 1.546 1.193 1.066 0.963 0.903 | 2.945 2.361 2.115 1.806 1.546 1.193 1.066 0.963 0.903 | 2.752 2.195 1.821 1.513 1.283 1.095 0.988 0.864 0.821 |
|           | Specific V. | Specific V. | Specific V. | Specific V. | Specific V. | Specific V. | Specific V. | Specific V. | Specific V. | Specific V. | Specific V. |
|           | 1.441 1.398 1.302 1.273 1.205 1.152 1.133 1.101 1.077 | 1.218 1.116 1.030 1.052 0.910 0.880 0.859 0.842 0.830 | 1.032 0.982 0.944 0.902 0.868 0.850 0.833 0.822 0.819 | 0.938 0.884 0.847 0.811 0.783 0.750 0.730 0.715 0.705 | 0.769 0.735 0.690 0.663 0.637 0.630 0.620 0.603 0.601 | 0.715 0.654 0.595 0.547 0.544 0.531 0.527 0.517 0.513 | 0.675 0.609 0.562 0.511 0.475 0.453 0.446 0.436 0.429 | 0.568 0.510 0.461 0.419 0.377 0.356 0.366 0.369 0.369 | 0.508 0.450 0.401 0.362 0.329 0.322 0.326 0.330 0.330 | 0.470 0.433 0.352 0.327 0.299 0.277 0.266 0.250 0.244 | 0.374 0.332 0.295 0.285 0.288 0.279 0.276 0.270 0.268 | 0.290 0.259 0.244 0.225 0.202 0.192 0.182 0.182 0.177 |
Table S2: Viscosity measurement of 2 in DMSO.

| Temp (°C) | 25  | 35  | 45  | 55  | 65  | 75  | 85  | 95  | 100 |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| **200 mM**      |     |     |     |     |     |     |     |     |     |
| Kin. V. (mm²/s) | 4.891 | 3.950 | 3.184 | 2.666 | 2.274 | 1.944 | 1.712 | 1.500 | 1.409 |
| Specific V. (mm²/s) | 1.441 | 1.398 | 1.302 | 1.253 | 1.205 | 1.152 | 1.143 | 1.101 | 1.077 |
| **180 mM**      |     |     |     |     |     |     |     |     |     |
| Kin. V. (mm²/s) | 4.443 | 3.412 | 2.752 | 2.296 | 1.952 | 1.689 | 1.485 | 1.314 | 1.246 |
| Specific V. (mm²/s) | 1.218 | 1.071 | 0.990 | 0.940 | 0.893 | 0.870 | 0.859 | 0.842 | 0.836 |
| **160 mM**      |     |     |     |     |     |     |     |     |     |
| Kin. V. (mm²/s) | 4.071 | 3.265 | 2.681 | 2.251 | 1.927 | 1.672 | 1.465 | 1.300 | 1.234 |
| Specific V. (mm²/s) | 1.032 | 0.982 | 0.939 | 0.902 | 0.868 | 0.851 | 0.833 | 0.822 | 0.819 |
| **140 mM**      |     |     |     |     |     |     |     |     |     |
| Kin. V. (mm²/s) | 3.883 | 3.104 | 2.554 | 2.125 | 1.820 | 1.575 | 1.373 | 1.224 | 1.157 |
| Specific V. (mm²/s) | 0.938 | 0.884 | 0.847 | 0.796 | 0.765 | 0.744 | 0.719 | 0.715 | 0.705 |
| **120 mM**      |     |     |     |     |     |     |     |     |     |
| Kin. V. (mm²/s) | 3.544 | 2.868 | 2.366 | 1.972 | 1.696 | 1.476 | 1.299 | 1.144 | 1.083 |
| Specific V. (mm²/s) | 0.769 | 0.741 | 0.711 | 0.667 | 0.644 | 0.635 | 0.626 | 0.603 | 0.597 |
| **100 mM**      |     |     |     |     |     |     |     |     |     |
| Kin. V. (mm²/s) | 3.437 | 2.689 | 2.178 | 1.843 | 1.592 | 1.395 | 1.230 | 1.091 | 1.039 |
| Specific V. (mm²/s) | 0.715 | 0.632 | 0.575 | 0.557 | 0.544 | 0.539 | 0.529 | 0.529 | 0.531 |
| **80 mM**       |     |     |     |     |     |     |     |     |     |
| Kin. V. (mm²/s) | 3.408 | 2.651 | 2.160 | 1.788 | 1.522 | 1.312 | 1.165 | 1.025 | 0.969 |
| Specific V. (mm²/s) | 0.701 | 0.609 | 0.562 | 0.509 | 0.475 | 0.453 | 0.458 | 0.436 | 0.429 |
| **60 mM**       |     |     |     |     |     |     |     |     |     |
| Kin. V. (mm²/s) | 3.137 | 2.581 | 2.168 | 1.855 | 1.617 | 1.416 | 1.248 | 1.089 | 1.015 |
| Specific V. (mm²/s) | 0.565 | 0.566 | 0.567 | 0.568 | 0.568 | 0.568 | 0.562 | 0.526 | 0.497 |
| **50 mM**       |     |     |     |     |     |     |     |     |     |
| Kin. V. (mm²/s) | 2.856 | 2.324 | 1.941 | 1.650 | 1.429 | 1.247 | 1.097 | 0.965 | 0.905 |
| Specific V. (mm²/s) | 0.425 | 0.411 | 0.403 | 0.394 | 0.386 | 0.381 | 0.373 | 0.352 | 0.335 |
| **40 mM**       |     |     |     |     |     |     |     |     |     |
| Kin. V. (mm²/s) | 2.578 | 2.070 | 1.715 | 1.446 | 1.243 | 1.079 | 0.948 | 0.841 | 0.796 |
| Specific V. (mm²/s) | 0.287 | 0.256 | 0.240 | 0.222 | 0.205 | 0.195 | 0.186 | 0.179 | 0.174 |
| **30 mM**       |     |     |     |     |     |     |     |     |     |
| Kin. V. (mm²/s) | 2.626 | 2.099 | 1.718 | 1.438 | 1.244 | 1.084 | 0.953 | 0.848 | 0.808 |
| Specific V. (mm²/s) | 0.310 | 0.274 | 0.243 | 0.215 | 0.206 | 0.200 | 0.192 | 0.189 | 0.191 |
Table S3: Viscosity measurement of 2 in chloroform.

| Temp (°C) | 25   | 30   | 35   | 40   | 45   | 50   |
|----------|------|------|------|------|------|------|
| 100 mM   | Kin. V. (mm²/s) | 0.718 | 0.689 | 0.662 | 0.635 | 0.611 | 0.590 |
|          | Specific V. | 0.879 | 0.881 | 0.882 | 0.879 | 0.864 | 0.856 |
| 80 mM    | Kin. V. (mm²/s) | 0.628 | 0.613 | 0.593 | 0.572 | 0.557 | 0.542 |
|          | Specific V. | 0.643 | 0.674 | 0.684 | 0.693 | 0.698 | 0.705 |
| 60 mM    | Kin. V. (mm²/s) | 0.537 | 0.537 | 0.522 | 0.509 | 0.502 | 0.493 |
|          | Specific V. | 0.407 | 0.465 | 0.485 | 0.506 | 0.532 | 0.553 |
| 40 mM    | Kin. V. (mm²/s) | 0.455 | 0.437 | 0.420 | 0.403 | 0.388 | 0.376 |
|          | Specific V. | 0.195 | 0.196 | 0.196 | 0.195 | 0.188 | 0.185 |

Table S4: Viscosity measurement of 2 in toluene.

| Temp (°C) | 25   | 35   | 45   | 55   | 65   | 75   | 85   | 95   | 100  |
|----------|------|------|------|------|------|------|------|------|------|
| 100 mM   | Kin. V. (mm²/s) | 1.231 | 1.173 | 1.100 | 1.018 | 0.920 | 0.823 | 0.737 | 0.663 | 0.631 |
|          | Specific V. | 0.784 | 0.768 | 0.752 | 0.736 | 0.720 | 0.712 | 0.704 | 0.696 | 0.688 |
| 80 mM    | Kin. V. (mm²/s) | 1.111 | 1.069 | 1.025 | 0.972 | 0.899 | 0.814 | 0.735 | 0.665 | 0.636 |
|          | Specific V. | 0.610 | 0.612 | 0.632 | 0.657 | 0.681 | 0.692 | 0.700 | 0.702 | 0.706 |
| 60 mM    | Kin. V. (mm²/s) | 0.886 | 0.864 | 0.852 | 0.833 | 0.792 | 0.727 | 0.663 | 0.604 | 0.580 |
|          | Specific V. | 0.283 | 0.303 | 0.356 | 0.421 | 0.481 | 0.512 | 0.533 | 0.547 | 0.551 |
| 40 mM    | Kin. V. (mm²/s) | 0.849 | 0.803 | 0.747 | 0.686 | 0.615 | 0.548 | 0.489 | 0.438 | 0.415 |
|          | Specific V. | 0.228 | 0.206 | 0.188 | 0.168 | 0.151 | 0.139 | 0.126 | 0.118 | 0.108 |

Table S5: Viscosity measurement of 3 in Nynas NS8.

| Temp (°C) | 25   | 35   | 45   | 55   | 65   | 75   | 85   | 95   | 100  |
|----------|------|------|------|------|------|------|------|------|------|
| 60 mM    | Kin. V. (mm²/s) | 17.348 | 12.045 | 8.921 | 6.802 | 5.311 | 4.256 | 3.486 | 2.930 | 2.714 |
|          | Specific V. | 0.335 | 0.355 | 0.371 | 0.388 | 0.403 | 0.415 | 0.425 | 0.430 | 0.432 |

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Table S6: Viscosity measurement of 3 in Nynas NS8.

| Temp (°C) | 25      | 35      | 45      | 55      | 65      | 75      | 85      | 95      | 100     |
|----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 100 mM   | 15.059  | 10.125  | 7.312   | 5.440   | 4.159   | 3.272   | 2.640   | 2.194   | 2.024   |
| Specific V. | 0.159   | 0.139   | 0.124   | 0.110   | 0.098   | 0.088   | 0.079   | 0.071   | 0.068   |
| 80 mM    | 14.322  | 9.704   | 7.053   | 5.278   | 4.056   | 3.206   | 2.598   | 2.167   | 2.002   |
| Specific V. | 0.102   | 0.092   | 0.084   | 0.077   | 0.071   | 0.066   | 0.062   | 0.058   | 0.056   |
| 60 mM    | 13.751  | 9.371   | 6.843   | 5.143   | 3.968   | 3.147   | 2.558   | 2.139   | 1.979   |
| Specific V. | 0.060   | 0.056   | 0.053   | 0.051   | 0.049   | 0.048   | 0.047   | 0.046   | 0.046   |
| 40 mM    | 13.161  | 8.996   | 6.583   | 4.955   | 3.827   | 3.040   | 2.473   | 2.070   | 1.914   |
| Specific V. | 0.013   | 0.012   | 0.012   | 0.011   | 0.011   | 0.010   | 0.010   | 0.010   | 0.010   |

Table S7: Viscosity measurement of 3 in Nexbase 3020.

| Temp (°C) | 25      | 35      | 45      | 55      | 65      | 75      | 85      | 95      | 100     |
|----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 40 mM    | 14.356  | 9.586   | 6.639   | 4.781   | 3.625   | 2.868   | 2.349   | 1.976   | 1.771   |
| Specific V. | 13.297  | 2.876   | -2.042  | -5.988  | -8.650  | -11.124 | -12.504 | -12.713 | -12.875 |

Table S8. Viscosity measurement of 3 in toluene.

| Temp (°C) | 25      | 35      | 45      | 55      | 65      | 75      | 85      | 95      | 100     |
|----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 100 mM   | 1.690   | 1.341   | 1.121   | 0.955   | 0.818   | 0.705   | 0.614   | 0.542   | 0.514   |
| Specific V. | 1.474   | 1.042   | 0.803   | 0.645   | 0.545   | 0.481   | 0.434   | 0.402   | 0.388   |
| 80 mM    | 1.606   | 1.274   | 1.065   | 0.907   | 0.777   | 0.669   | 0.583   | 0.515   | 0.488   |
| Specific V. | 1.351   | 0.940   | 0.713   | 0.563   | 0.468   | 0.407   | 0.362   | 0.331   | 0.319   |
| 60 mM    | 1.477   | 1.172   | 0.979   | 0.835   | 0.715   | 0.616   | 0.537   | 0.474   | 0.449   |
| Specific V. | 1.140   | 0.767   | 0.559   | 0.423   | 0.337   | 0.281   | 0.241   | 0.212   | 0.201   |
| 40 mM    | 1.374   | 1.090   | 0.911   | 0.776   | 0.665   | 0.573   | 0.499   | 0.441   | 0.417   |
| Specific V. | 1.011   | 0.660   | 0.465   | 0.337   | 0.256   | 0.204   | 0.166   | 0.139   | 0.128   |
| 20 mM    | 1.305   | 1.035   | 0.865   | 0.738   | 0.632   | 0.544   | 0.474   | 0.419   | 0.397   |
| Specific V. | 0.911   | 0.577   | 0.392   | 0.270   | 0.193   | 0.143   | 0.107   | 0.082   | 0.072   |
### Table S9: Viscosity measurement of 4 in DMSO.

| Temp (°C) | 25  | 35  | 45  | 55  | 65  | 75  | 85  | 95  | 100 |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 60 mM     |     |     |     |     |     |     |     |     |     |
| Kin. V.  (mm²/s) | 2.760 | 2.245 | 1.864 | 1.576 | 1.358 | 1.176 | 1.023 | 0.915 | 0.863 |
| Specific V. | 0.498 | 0.493 | 0.488 | 0.482 | 0.477 | 0.471 | 0.461 | 0.442 | 0.422 |

### Table S10: Viscosity measurement of 4 in chloroform.

| Temp (°C) | 25  | 30  | 35  | 40  | 45  | 50  |
|-----------|-----|-----|-----|-----|-----|-----|
| 60 mM     |     |     |     |     |     |     |
| Kin. V.  (mm²/s) | 0.484 | 0.467 | 0.460 | 0.448 | 0.432 | 0.419 |
| Specific V. | 0.366 | 0.405 | 0.427 | 0.445 | 0.457 | 0.470 |

### Table S11: Viscosity measurement of 4 in toluene.

| Temp (°C) | 25  | 35  | 45  | 55  | 65  | 75  | 85  | 95  | 100 |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 60 mM     |     |     |     |     |     |     |     |     |     |
| Kin. V.  (mm²/s) | 0.753 | 0.726 | 0.707 | 0.683 | 0.642 | 0.581 | 0.524 | 0.471 | 0.447 |
| Specific V. | 0.241 | 0.254 | 0.295 | 0.345 | 0.390 | 0.409 | 0.421 | 0.426 | 0.425 |

### Table S12: Viscosity measurement of 4 in Nynas NS8.

| Temp (°C) | 25  | 35  | 45  | 55  | 65  | 75  | 85  | 95  | 100 |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 100 mM    |     |     |     |     |     |     |     |     |     |
| Kin. V.  (mm²/s) | 25.371 | 16.173 | 11.218 | 8.064 | 5.977 | 4.583 | 3.610 | 2.939 | 2.682 |
| Specific V. | 0.700 | 0.631 | 0.584 | 0.548 | 0.517 | 0.493 | 0.471 | 0.452 | 0.441 |
| 80 mM     |     |     |     |     |     |     |     |     |     |
| Kin. V.  (mm²/s) | 19.183 | 12.739 | 9.135 | 6.767 | 5.153 | 4.048 | 3.259 | 2.703 | 2.488 |
| Specific V. | 0.476 | 0.433 | 0.404 | 0.381 | 0.361 | 0.346 | 0.332 | 0.319 | 0.313 |
| 60 mM     |     |     |     |     |     |     |     |     |     |
| Kin. V.  (mm²/s) | 17.085 | 11.719 | 8.641 | 6.570 | 5.125 | 4.115 | 3.377 | 2.848 | 2.640 |
| Specific V. | 0.315 | 0.318 | 0.328 | 0.341 | 0.354 | 0.368 | 0.380 | 0.390 | 0.393 |
| 40 mM     |     |     |     |     |     |     |     |     |     |
| Kin. V.  (mm²/s) | 15.289 | 10.328 | 7.496 | 5.606 | 4.306 | 3.404 | 2.758 | 2.300 | 2.123 |
| Specific V. | 0.176 | 0.162 | 0.152 | 0.144 | 0.137 | 0.132 | 0.127 | 0.123 | 0.120 |
| 20 mM     |     |     |     |     |     |     |     |     |     |
| Kin. V.  (mm²/s) | 13.963 | 9.518 | 6.956 | 5.232 | 4.039 | 3.208 | 2.609 | 2.183 | 2.019 |
| Specific V. | 0.074 | 0.071 | 0.069 | 0.068 | 0.067 | 0.067 | 0.066 | 0.066 | 0.065 |

### Table S13: Viscosity measurement of 4 in Nexbase 3020.

| Temp (°C) | 25  | 35  | 45  | 55  | 65  | 75  | 85  | 95  | 100 |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 60 mM     |     |     |     |     |     |     |     |     |     |
| Kin. V.  (mm²/s) | 17.576 | 12.792 | 9.717 | 7.507 | 5.964 | 4.891 | 4.103 | 3.510 | 3.153 |
| Specific V. | 0.387 | 0.407 | 0.434 | 0.461 | 0.485 | 0.508 | 0.528 | 0.551 | 0.562 |
7. DLS Measurements

7.1 DLS Measurement of the 1 in 60 mM DMSO

Figure S74: DLS measurement of 1 in 60 mM DMSO at 25 °C. Signal number peak: 100%.

Figure S75: DLS measurement of 1 in 60 mM DMSO at 60 °C. Signal number peak left: 93.7% peak right 6.3%.

Figure S76: DLS measurement of 1 in 60 mM DMSO at 100 °C. Signal number peak left: 94.5% peak right 5.5%.
7.2 DLS Measurement of 2 in 60 mM DMSO

Figure S77: DLS measurement of 2 in 60 mM DMSO at 25 °C. Signal number peak left: 95.1% peak right 4.9%.

Figure S78: DLS measurement of 2 in 60 mM DMSO at 60 °C. Signal number peak left: 94.1% peak right 4.9%.

Figure S79: DLS measurement of 2 in 60 mM DMSO at 100 °C. Signal number peak left: 86.4% peak right 13.6%.
7.3 DLS Measurement of the 2 in 60 mM Chloroform

Figure S80: DLS measurement of 2 generation in 60 mM chloroform at 25 °C. Signal number peak left: 98.0% peak right 2.0%.

Figure S81: DLS measurement of 2 in 60 mM chloroform at 37 °C. Signal number peak left: 90.5% peak right 9.5%.

Figure S82: DLS measurement of 2 in 60 mM chloroform at 50 °C. Signal number peak left: 79.2% peak right 20.8%.
7.4 DLS Measurement of the 2 in toluene

Figure S83: DLS measurement of 2 in 60 mM toluene at 25 °C. Signal number peak left: 98.9% peak right 1.1%.

Figure S84: DLS measurement of 2 in 60 mM toluene at 60 °C. Signal number peak left: 81.3% peak right 18.7%.

Figure S85: DLS measurement of 2 in 60 mM toluene at 100 °C. Signal number peak left: 65.4% peak right 34.6%.
8. Force field calculations

For molecular modelling studies, the Schrödinger Maestro Suite (11.8) was used. The structures were calculated using MacroModel and OPLS 2005 force field choosing chloroform as the solvent. Energy minimization was performing using the PCRG-method (maximum 50000 steps, convergence threshold 0.01).

8.1 Force field calculation of 1

![Diagram of BINAM GCP system 1]

Figure S86: Force field calculation of the BINAM GCP system 1 to form cyclic structures (OPLS force field). Left: Front view. Right: Side view.
8.2 Force field calculation of 2

Figure S87: Force field calculation of the BINAM ACP system 2 to form cyclic structures (OPLS force field). Left: Front view. Right: Side view.
9. NMR-Spectra

Figure S88: $^1$H-NMR of 9. 400 MHz, Solvent: CDCl$_3$, 27 °C.

Figure S89: $^{13}$C-NMR of 9. 151 MHz, Solvent: CDCl$_3$, 27 °C.
Figure S90: $^1$H-NMR of 1. 300 MHz, Solvent: DMSO-d$_6$, 27 °C.

Figure S91: $^{13}$C-NMR of 1. 151 MHz, Solvent: DMSO-d$_6$, 27 °C.
Figure S92: $^1$H-NMR of 11. 400 MHz, Solvent: CDCl$_3$, 27 °C.

Figure S93: $^{13}$C-NMR of 11. 151 MHz, Solvent: CDCl$_3$, 27 °C.
Figure S94: $^1$H-NMR of 6. 400 MHz, Solvent: DMSO-d$_6$, 27 °C.

Figure S95: $^{13}$C-NMR of 6. 151 MHz, Solvent: DMSO-d$_6$, 27 °C.
Figure S96: $^1$H-NMR of 12. 300 MHz, Solvent: DMSO-d$_6$, 27 °C.

Figure S97: $^{13}$C-NMR of 12. 75 MHz, Solvent: DMSO-d$_6$, 27 °C.
Figure S98: $^1$H-NMR of 2. 300 MHz, Solvent: DMSO-d$_6$, 27 °C.

Figure S99: $^{13}$C-NMR of 2. 75 MHz, Solvent: DMSO-d$_6$, 27 °C.
Figure S100: $^1$H-NMR of 13. 300 MHz, Solvent: DMSO-$d_6$, 27 °C.

Figure S101: $^{13}$C-NMR of 13. 75 MHz, Solvent: DMSO-$d_6$, 27 °C.
Figure S102: $^1$H-NMR of 7. 300 MHz, Solvent: DMSO-d$_6$, 27 °C.

Figure S103: $^{13}$C-NMR of 7. 75 MHz, Solvent: DMSO-d$_6$, 27 °C.
Figure S104: $^1$H-NMR of 14, 300 MHz, Solvent: CDCl₃, 27 °C.

Figure S105: $^{13}$C-NMR of 14, 75 MHz, Solvent: CDCl₃, 27 °C.
Figure S106: $^1$H-NMR of 3. 300 MHz, Solvent: CDCl$_3$, 27 °C.

Figure S107: $^{13}$C-NMR of 3. 75 MHz, Solvent: CDCl$_3$, 27 °C.
Figure S108: $^1$H-NMR of 15. 400 MHz, Solvent: DMSO-$d_6$, 27 °C.

Figure S109: $^{13}$C-NMR of 15. 151 MHz, Solvent: DMSO-$d_6$, 27 °C.
Figure S110: $^1$H-NMR of 16. 400 MHz, Solvent: CDCl$_3$, 27 °C.

Figure S111: $^{13}$C-NMR of 16. 151 MHz, Solvent: CDCl$_3$, 27 °C.
Figure S112: $^1$H-NMR of 4. 400 MHz, Solvent: CDCl$_3$, 27 °C.

Figure S113: $^{13}$C-NMR of 4. 151 MHz, Solvent: CDCl$_3$, 27 °C.