Electronic Supplementary Information (ESI)

Guest-mediated chirality transfer in host-guest complexes of an atropisomeric perylene bisimide cyclophane host

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1 Methods

UV-vis absorption spectra were recorded on a JASCO V670 or V770 spectrometer. Fluorescence spectra for titrations were recorded on a PTI QM4-2003 spectrometer. NMR spectra were recorded on a Bruker Avance III HD 400 or 600 MHz spectrometer. Chemical shifts (δ) are internally referenced to the residual proton solvent resonances or to natural abundance carbon resonances. The abbreviations for signal multiplicities are s = singlet, d = doublet, quint = quintet, m = multiplet. High resolution ESI-TOF mass spectrometry was performed on a Bruker Daltonic microTOF focus spectrometer. All solvents and reagents were purchased from commercial sources and used without further purification. Solvents for spectroscopic studies were of spectroscopic grade and used without further purification.

For the titration experiments, a solution of both PBI cyclophane **[2PBI]** ($c = 1.0 \cdot 10^{-5}$ mol L^{-1}) and the guest in excess in the corresponding solvent was titrated to a solution of pure **[2PBI]** of the same concentration in the same solvent keeping the host concentration constant during the experiment. The UV-vis and fluorescence titration data were fitted globally from $540 - 588$ nm and from $625 - 685$ nm, respectively, to equation (S1)[1] with ε_h, ε_{hg} and ε_{obs} as extinction coefficients at a given wavelength of the free host, the host-guest complex and the measured extinction coefficient, c_h^0 and c_g^0 as total concentrations of the host and the guest and K_a as binding constant. K_a was treated as shared variable.

$$\varepsilon_{obs} = \varepsilon_h + \frac{\varepsilon_{hg} - \varepsilon_h}{2c_h^0}\left(c_h^0 + c_g^0 + \frac{1}{K_a} \pm \sqrt{\left(c_h^0 + c_g^0 + \frac{1}{K_a}\right)^2 - 4c_h^0 c_g^0}\right) \quad \text{(S1)}$$

For the time-dependent NMR studies, an NMR tube with a solution of free **[2PBI]** in CDCl$_3$ (0.5 mL) with the integration standard dimethyl sulphone as well as a solution of (*S*)-**G4** of the desired concentration in CDCl$_3$ were cooled to 217 K in an acetone/dried ice bath. Directly before the measurement the guest solution (0.2 mL) was added to the NMR tube with the host, so that in the measured samples the concentrations were c_0 (**[2PBI]**) = $5 \cdot 10^{-4}$ mol L^{-1} and c_0 ((*S*)-**G4**) = $1.0 \cdot 10^{-3}$ mol L^{-1}, $2.5 \cdot 10^{-3}$ mol L^{-1} or $5.0 \cdot 10^{-3}$ mol L^{-1}, respectively. The sample was immediately placed in a cooled and shimmed NMR spectrometer where consecutive proton spectra were measured automatically (number of scans: 40, acquisition time: 2.5 s). Data treatment was carried out according to literature.[2]
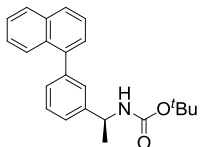
2 Synthesis of (*S*)-G3 and (*S*)-G4

Boc-protected (*S*)-1-(3-bromophenyl)ethylamine (**5**), which was used as precursor for the synthesis of (*S*)-**G3** was prepared according to literature.[3]
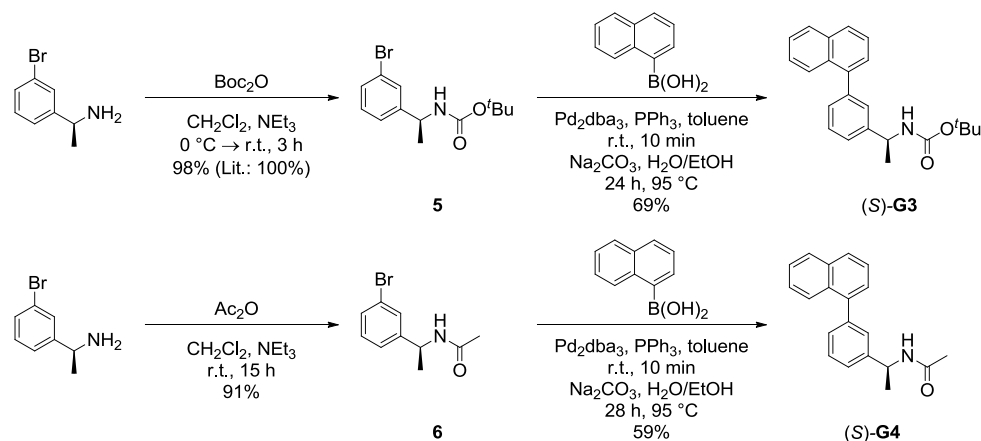
**Scheme S1.** Synthesis of the chiral guests (*S*)-**G3** and (*S*)-**G4**.

Synthesis of (*S*)-G3

The reaction conditions were adopted from literature.[4]

Under nitrogen atmosphere, **5**[3] (800 mg, 2.66 mmol, 1 eq.), 1-naphthylboronic acid (550 mg, 3.20 mmol, 1.2 eq.), Pd$_2$dba$_3$ (11.8 mg, 12.9 μmol, 0.5 mol%) and PPh$_3$ (140 mg, 532 μmol, 0.2 eq.) were dissolved in dry toluene (10.8 mL). The mixture was stirred at room temperature. After 10 min, Na$_2$CO$_3$ (1.13 g, 10.7 mmol, 4 eq.) and a mixture (1/1 vol%) of H$_2$O/EtOH (3 mL) were added and the reaction was heated to 95 °C for 24 h. After cooling down to room temperature, the mixture was extracted with CH$_2$Cl$_2$ (3x). The organic extracts were combined, washed with H$_2$O (1x) and dried over Na$_2$SO$_4$. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel, CH$_2$Cl$_2$) and flash chromatography (silica gel, CH$_2$Cl$_2$/pentane 80/20 → 100/0). The product (638 mg, 1.84 mmol, 69%) was obtained as a colorless, glassy solid. **Mp**: 44 – 45 °C. **^{1}H NMR** (CDCl$_3$, 400 MHz): δ = 7.93 – 7.86 (m, 3H, C*H*$_{aryl}$), 7.55 – 7.37 (m, 8H, C*H*$_{aryl}$), 5.06 – 4.56 (br m, 2H, N*H*, C*H*), 1.51 (d, ^3J = 6.2 Hz, 3H, C*H*$_3$), 1.44 (s, 9H, (C*H*$_3$)$_3$) ppm. **^{13}C NMR** (CDCl$_3$, 100 MHz): δ = 155.2, 144.2, 141.1, 140.3, 133.9, 131.7, 129.0, 128.6, 128.4, 127.8, 127.5, 127.1, 126.2, 126.1, 125.9, 125.5, 125.0, 79.6, 50.3, 28.5, 23.0 ppm. **HRMS** (ESI, pos. mode, CH$_3$CN/CH$_3$Cl): *m/z* 370.17736 [M+Na]$^+$, calculated for C$_{23}$H$_{25}$NNaO$_2$$^+$: 370.17775.

## Synthesis of acetyl-protected (*S*)-1-(3-bromophenyl)ethylamine (6)

The reaction conditions were adopted from literature.[5]
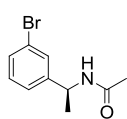
Under nitrogen atmosphere, (*S*)-1-(3-bromophenyl)ethylamine (714 μL, 1.00 g, 5.00 mmol, 1 eq.) was dissolved in dry CH_2Cl_2 (5 mL). After the addition of Ac_2O (708 μL, 765 mg, 7.50 mmol, 1.5 eq) and NEt_3 (1.04 mL, 759 mg, 7.50 mmol, 1.5 eq.) the reaction was stirred overnight at room temperature. Then it was successively washed with 2 N HCl (1x), saturated aqueous $NaHCO_3$ solution (1x) and brine (1x). The organic phase was dried over Na_2SO_4. After removal of the solvent the crude product was purified by column chromatography (silica gel, CH_2Cl_2/CH_3OH = 100/5) to give 1.10 g (453 mmol, 91%) of a colorless oil. **^{1}H NMR** (CD_2Cl_2, 400 MHz): δ = 7.46 − 7.35 (m, 1H, C*H*$_{aryl}$), 7.40 − 7.38 (m, 1H, C*H*$_{aryl}$), 7.27 − 7.20 (m, 2H, C*H*$_{aryl}$), 5.83 (br s, 1H, N*H*), 4.99 (quint, 1H, , ^3J = 7.1 Hz, C*H*), 1.94 (s, 3H, C*H*$_3$) 1.43 (d, ^3J = 7.0 Hz, 3H, C*H*$_3$) ppm. **^{13}C NMR** (CD_2Cl_2, 100 MHz): δ = 169.3, 146.8, 130.6, 130.5, 129.4, 125.3, 122.9, 48.8, 23.5, 22.2 ppm. **HRMS** (ESI, pos. mode, CH_3CN/CH_3Cl): *m/z* 264.00005 [M+Na]$^+$, calculated for $C_{10}H_{12}BrNNaO^+$: 263.99945.

Synthesis of (*S*)-G4

The reaction conditions were adopted from literature.[4]
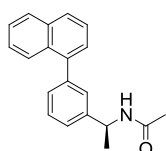
Under nitrogen atmosphere, **6** (1.00 g, 4.13 mmol, 1 eq.), 1-naphthylboronic acid (852 mg, 4.96 mmol, 1.2 eq.), Pd_2dba_3 (19 mg, 20.7 μmol, 0.5 mol%) and PPh_3 (21.7 mg, 82.6 μmol, 0.02 eq.) were dissolved in dry toluene (12.0 mL). The mixture was stirred at room temperature. After 10 min, Na_2CO_3 (876 g, 8.26 mmol, 2 eq.) and a mixture (1/1 vol%) of $H_2O/EtOH$ (4 mL) were added and the reaction was heated to 95 °C for 24 h. After cooling down to room temperature, the mixture was extracted with CH_2Cl_2 (3x). The organic extracts were combined, washed with H_2O (1x) and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel, CH_2Cl_2) and flash chromatography (silica gel, CH_2Cl_2/pentane 80/20 → 100/0). The product (705 mg, 2.44 mmol, 59%) was obtained as a colorless, glassy solid. **Mp**: 52 − 54 °C. **^{1}H NMR** (CDCl$_3$, 400 MHz): δ = 7.92 − 7.86 (m, 3H, C*H*$_{aryl}$), 7.55 − 7.36 (m, 8H, C*H*$_{aryl}$), 5.92 (d, 1H, ^3J = 7.3 Hz, N*H*), 5.22 (quint, 1H, , ^3J = 7.3 Hz, C*H*), 1.98 (s, 3H, C*H*$_3$) 1.53 (d, ^3J = 6.9 Hz, 3H, C*H*$_3$) ppm. **^{13}C NMR** (CDCl$_3$, 100 MHz): δ = 169.3, 143.4, 141.2, 140.1, 133.9, 131.6, 129.2, 128.7, 128.4, 127.9, 127.8, 127.1, 126.2, 126.0,

125.9, 125.5, 125.3, 48.9, 28.5, 23.6, 22.1 ppm. **HRMS** (ESI, pos. mode, CH_3CN/CH_3Cl): *m/z* 312.13575 $[M+Na]^+$, calculated for $C_{20}H_{19}NNaO^+$: 312.13588.
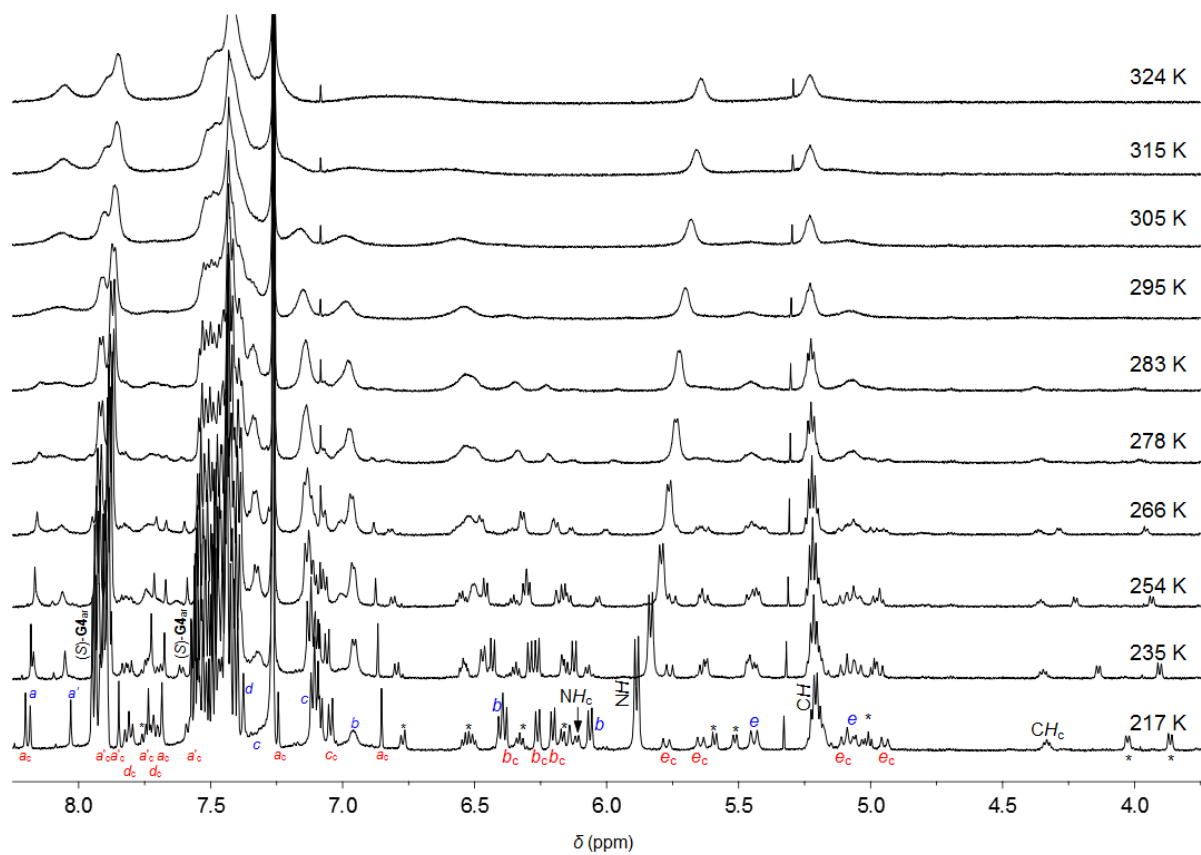
3   Temperature-dependent ^1H NMR spectra
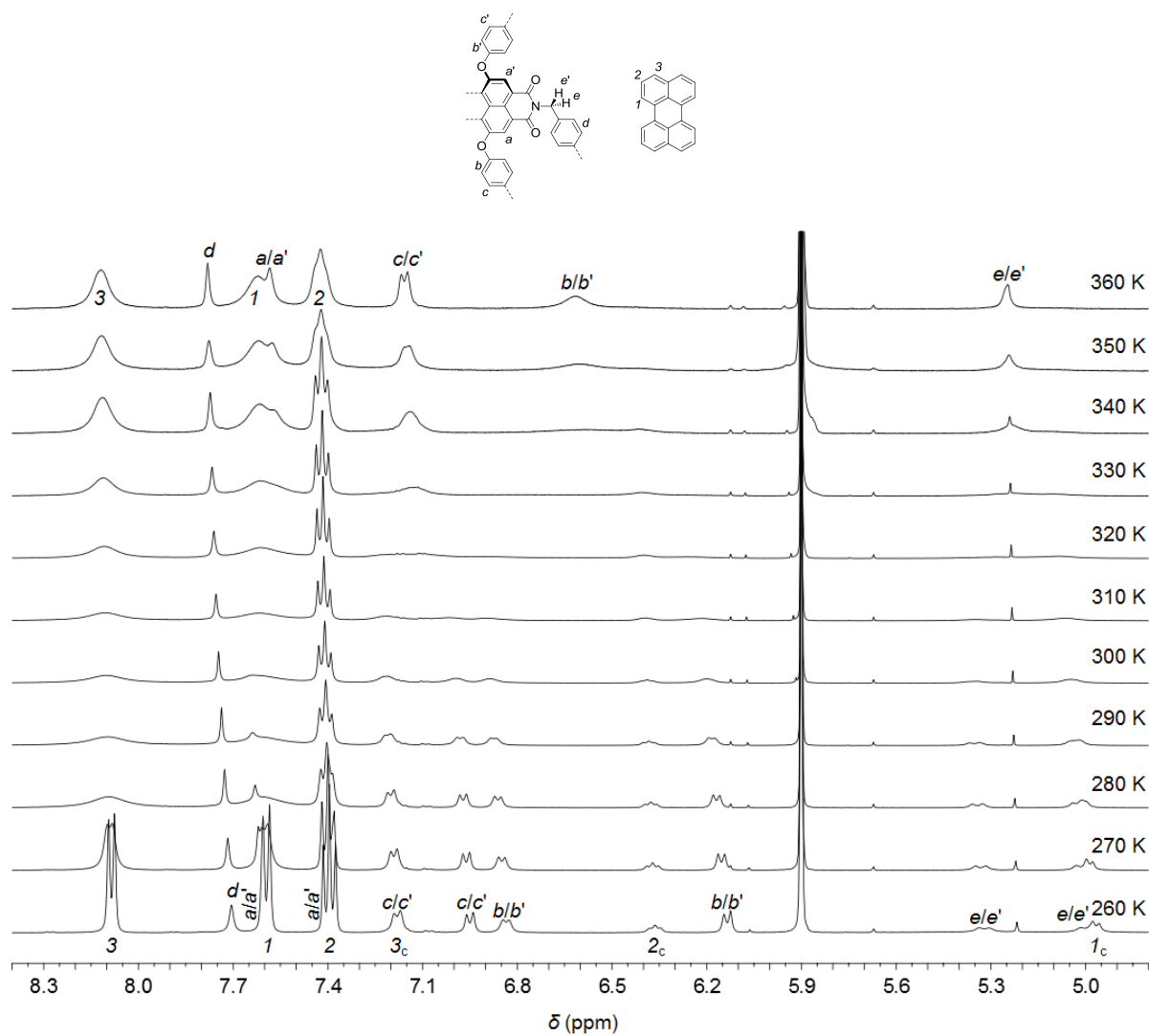
Fig. S1. Temperature-dependent ^1H NMR spectra ($C_2D_2Cl_4$, 400 MHz) of **[2PBI]** ($c = 1 \cdot 10^{-4}$ mol L^{-1}) in the presence of 8 equivalents of **G1** from 360 K to 260 K in steps of 10 K. Signals of the encapsulated guest **G1** are assigned as 1_c, 2_c and 3_c.
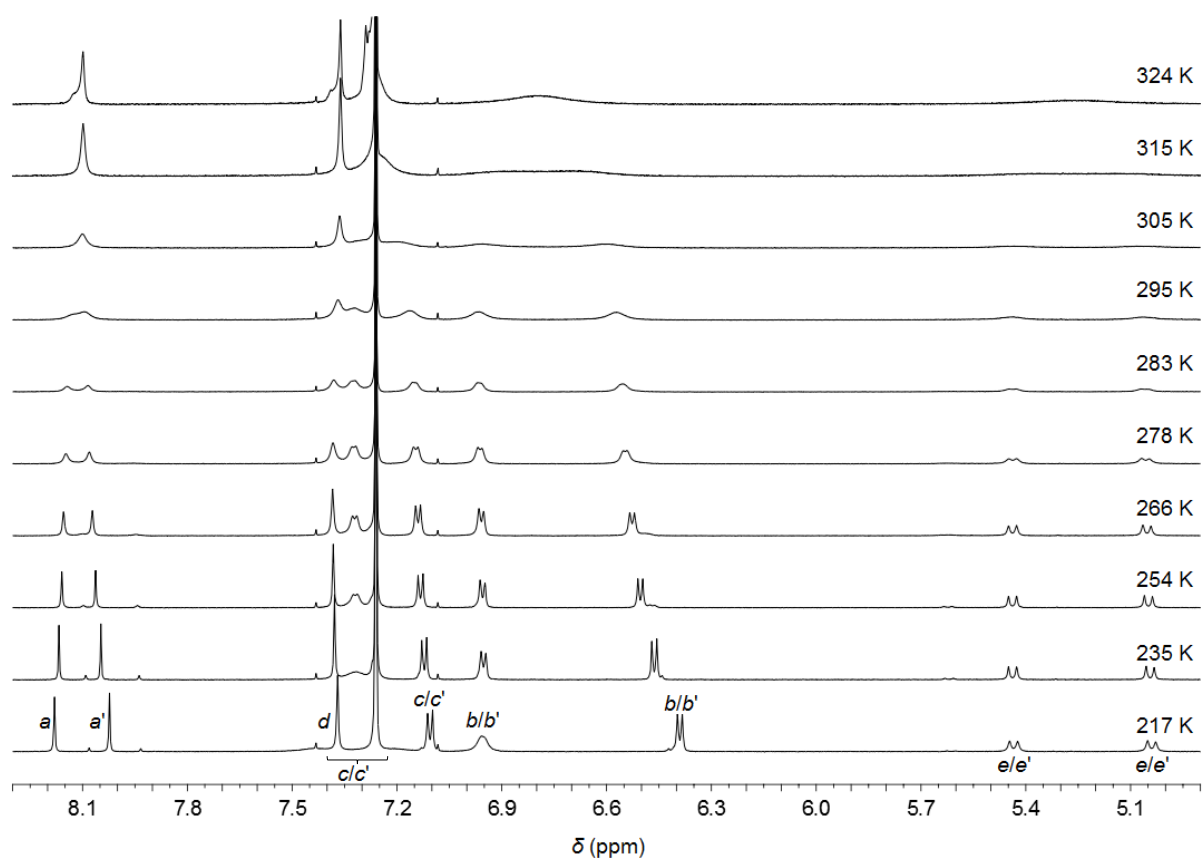
Fig. S2. Temperature-dependent ^{1}H NMR spectra (CDCl$_3$, 600 MHz) of **[2PBI]** ($c = 5 \cdot 10^{-4}$ mol L^{-1}) from 324 K to 217 K.

Fig. S3. Excerpt of the temperature-dependent ^{1}H NMR spectra (CDCl$_3$, 600 MHz) of **[2PBI]** ($c = 5 \cdot 10^{-4}$ mol L^{-1}) in the presence of 5 eq. of (*S*)-**G4** from 324 K to 217 K. Signals of the host in the host-guest complex (*S*)-**G4**⊂**[2PBI]** are assigned with $a_c - e_c$. Peaks assigned with a * correspond to aromatic signals of bound (*S*)-**G4**.
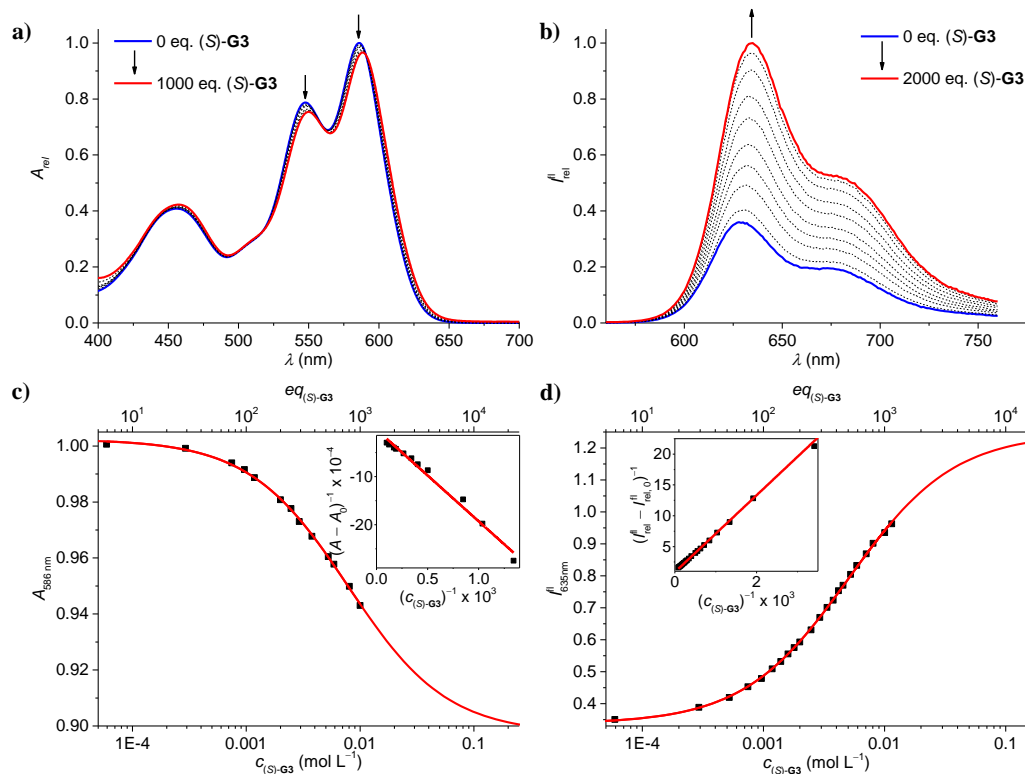
4 Host-guest titration experiments
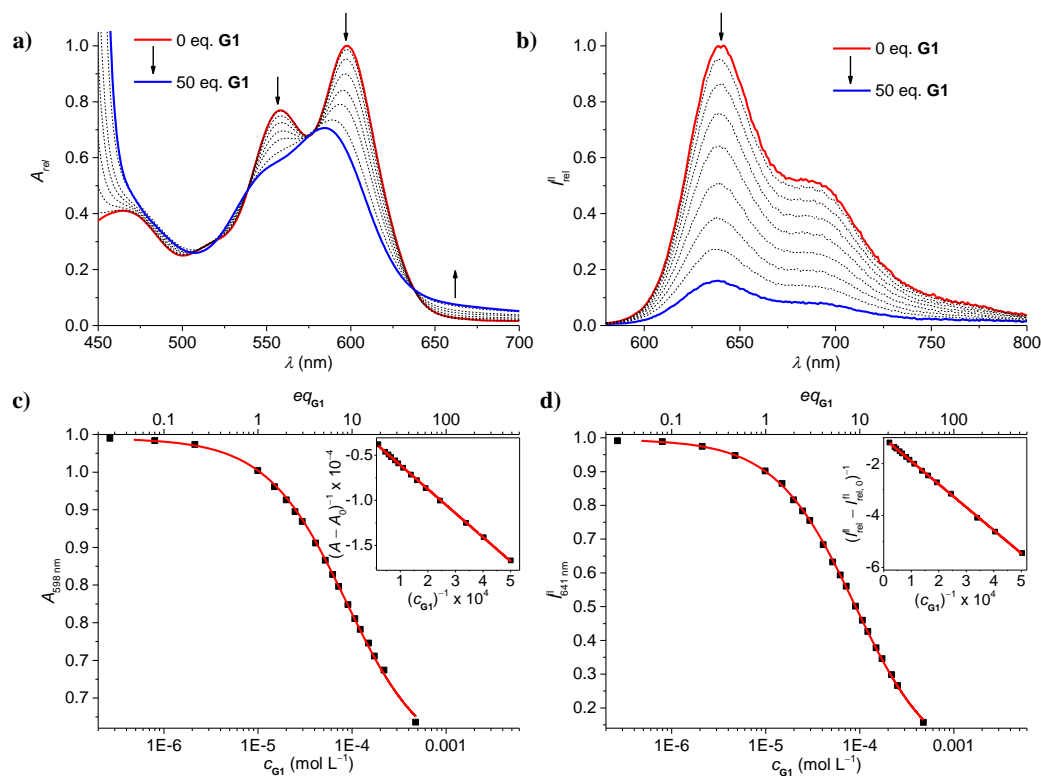
Fig. S4. (a) UV-vis and (b) fluorescence titration ($\lambda_{ex} = 530$ nm) of **[2PBI]** ($c_0 = 1 \cdot 10^{-5}$ mol L^{-1}) with **G1** in C$_2$H$_2$Cl$_4$ at 298 K. (c) Plots of UV-vis (598 nm) and (d) fluorescence (641 nm) titration data points as a function of guest concentration and fitting with a 1:1 binding model; insets: Benesi-Hildebrand plots showing a 1:1 stoichiometry of the host-guest complex.
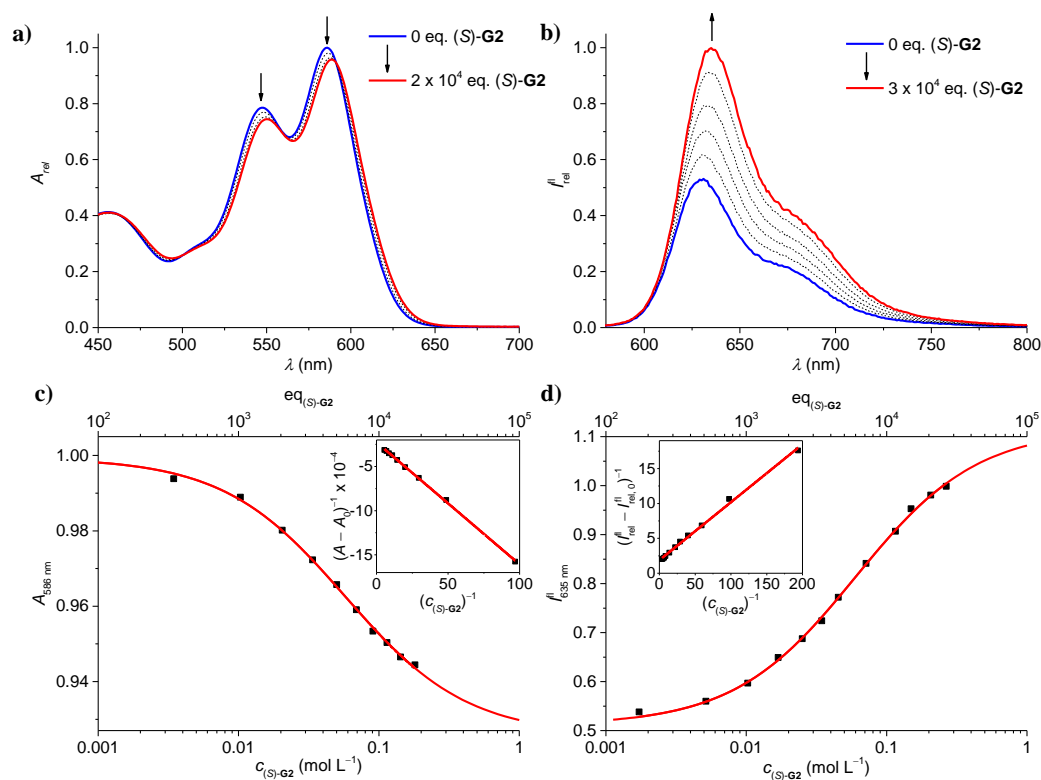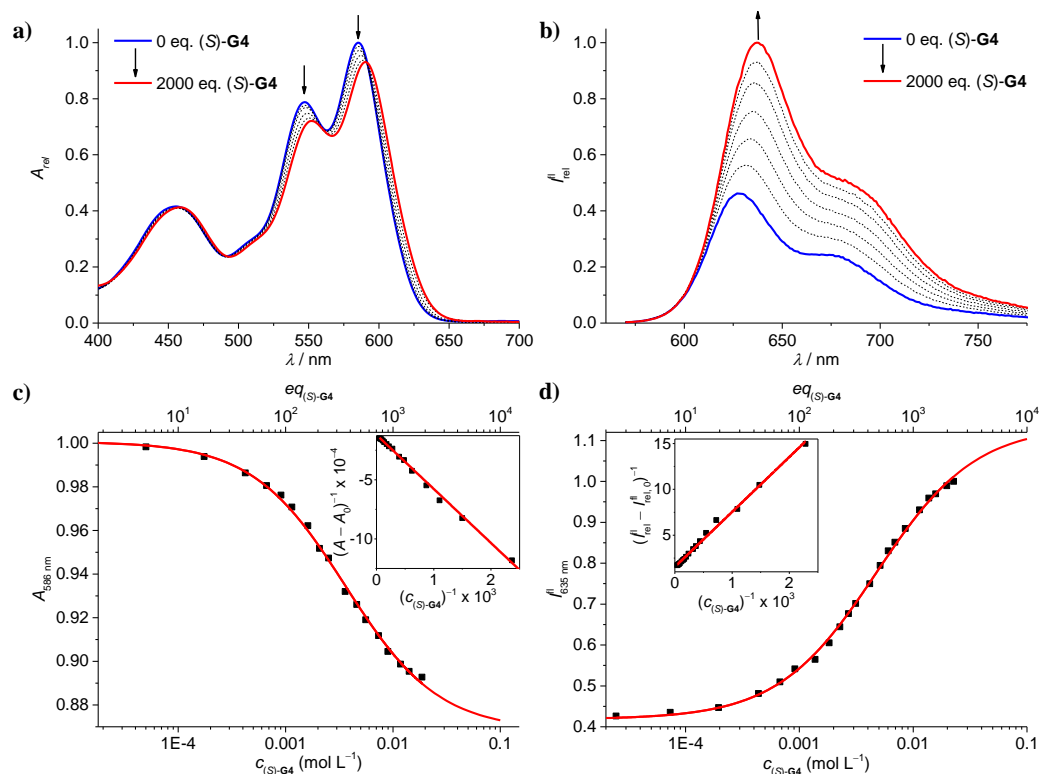

Fig. S5. (a) UV-vis and (b) fluorescence titration ($\lambda_{ex} = 530$ nm) of **[2PBI]** ($c_0 = 1 \cdot 10^{-5}$ mol L^{-1}) with (S)-**G2** in CHCl$_3$ at 298 K. (c) Plots of UV-vis (586 nm) and (d) fluorescence (635 nm) titration data points as a function of guest concentration and fitting with a 1:1 binding model; insets: Benesi-Hildebrand plots showing a 1:1 stoichiometry of the host-guest complex.
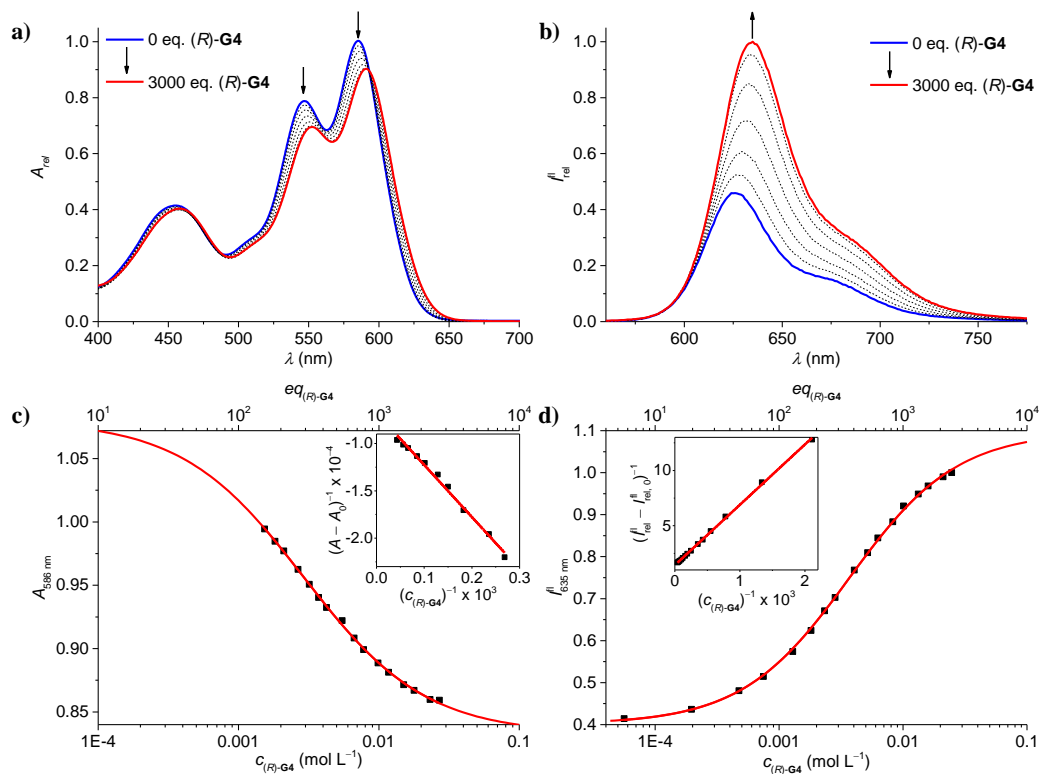
Fig. S6. (a) UV-vis and **(b)** fluorescence titration (λ_{ex} = 530 nm) of **[2PBI]** ($c_0 = 1 \cdot 10^{-5}$ mol L^{-1}) with (*S*)-**G3** in CHCl$_3$ at 298 K. **(c)** Plots of UV-vis (586 nm) and **(d)** fluorescence (635 nm) titration data points as a function of guest concentration and fitting with a 1:1 binding model; insets: Benesi-Hildebrand plots showing a 1:1 stoichiometry of the host-guest complex.

Fig. S7. (a) UV-vis and **(b)** fluorescence titration (λ_{ex} = 530 nm) of **[2PBI]** ($c_0 = 1 \cdot 10^{-5}$ mol L^{-1}) with (*S*)-**G4** in CHCl$_3$ at 298 K. **(c)** Plots of UV-vis (586 nm) and **(d)** fluorescence (635 nm) titration data points as a function of guest concentration and fitting with a 1:1 binding model; insets: Benesi-Hildebrand plots showing a 1:1 stoichiometry of the host-guest complex.

Fig. S8. (a) UV-vis and **(b)** fluorescence titration (λ_{ex} = 530 nm) of **[2PBI]** ($c_0 = 1 \cdot 10^{-5}$ mol L^{-1}) with (R)-**G4** in CHCl$_3$ at 298 K. **(c)** Plots of UV-vis (586 nm) and **(d)** fluorescence (635 nm) titration data points as a function of guest concentration and fitting with a 1:1 binding model; insets: Benesi-Hildebrand plots showing a 1:1 stoichiometry of the host-guest complex.

Table S1. Comparison of the binding constants K_a and the CD effects of the chiral guests (S)-**G2** − (S)-**G4** towards host **[2PBI]** in CHCl$_3$ at 298 K.

guest	K_a^{UV} (L mol^{-1})	K_a^{fl} (L mol^{-1})	$\varnothing\,K_a^{\,a}$ (L mol^{-1})	$\Delta\varepsilon$ (L mol^{-1} cm^{-1})	$g^{\,b}$
(S)-**G2**	14.7	15.4	15.1	+ 2 (580 nm)	+ 4.3 10^{-5}
(S)-**G3**	139	194	167	+ 27 (581 nm)	+ 3.7 10^{-4}
(S)-**G4**	285	208	247	+ 38 (585 nm)	+ 6.1 10^{-4}
(R)-**G4**	344	267	306	− 36 (585 nm)	− 5.7 10^{-4}

[a] Average from UV-vis and fluorescence titration experiments. [b] Dissymmetry factor g = $\Delta\varepsilon/\varepsilon$.
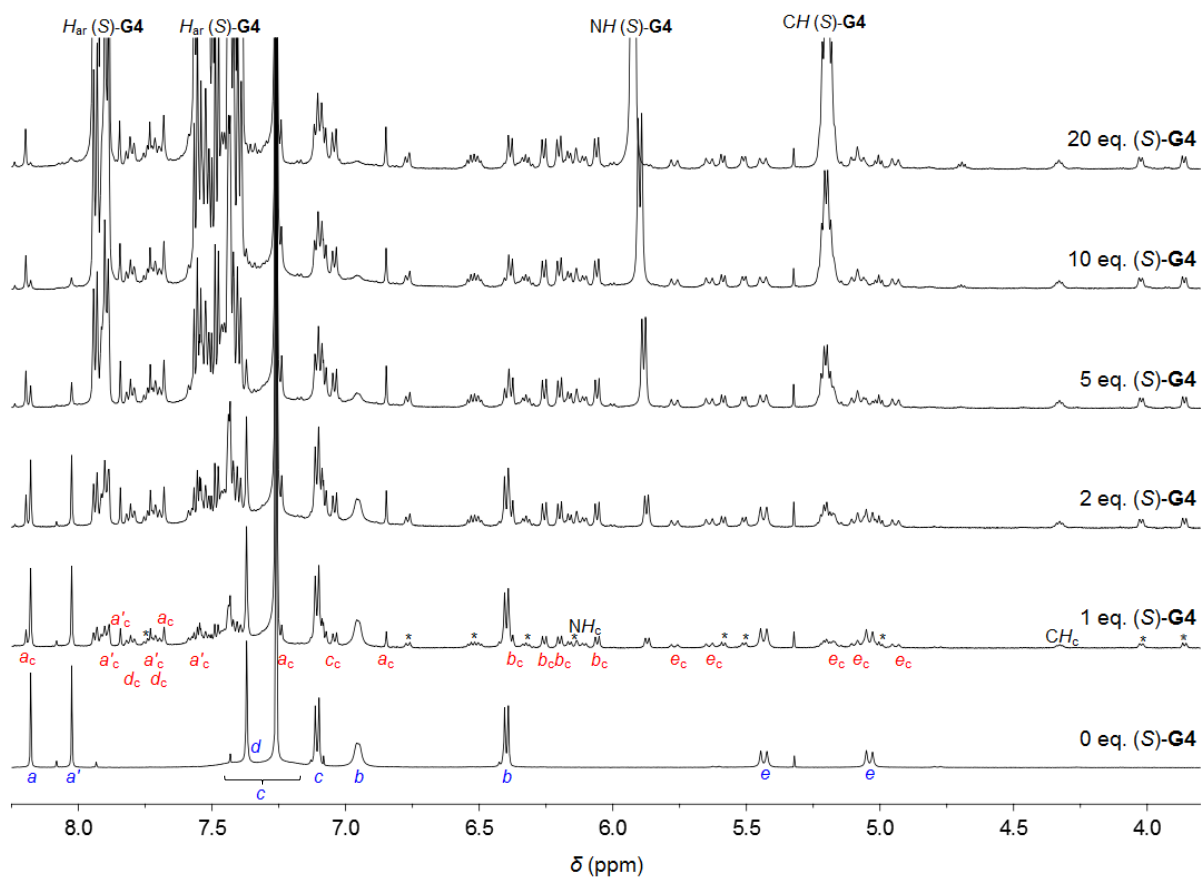
Fig. S9. ^{1}H NMR titration (CDCl$_3$, 600 MHz, 217 K,) of **[2PBI]** ($c_0 = 5 \cdot 10^{-4}$ mol L^{-1}) with (*S*)-**G4**. Signals of the host in the host-guest complex (*S*)-**G4**⊂**[2PBI]** are assigned with $a_c - e_c$. Peaks assigned with a red * correspond to aromatic signals of bound (*S*)-**G4**.
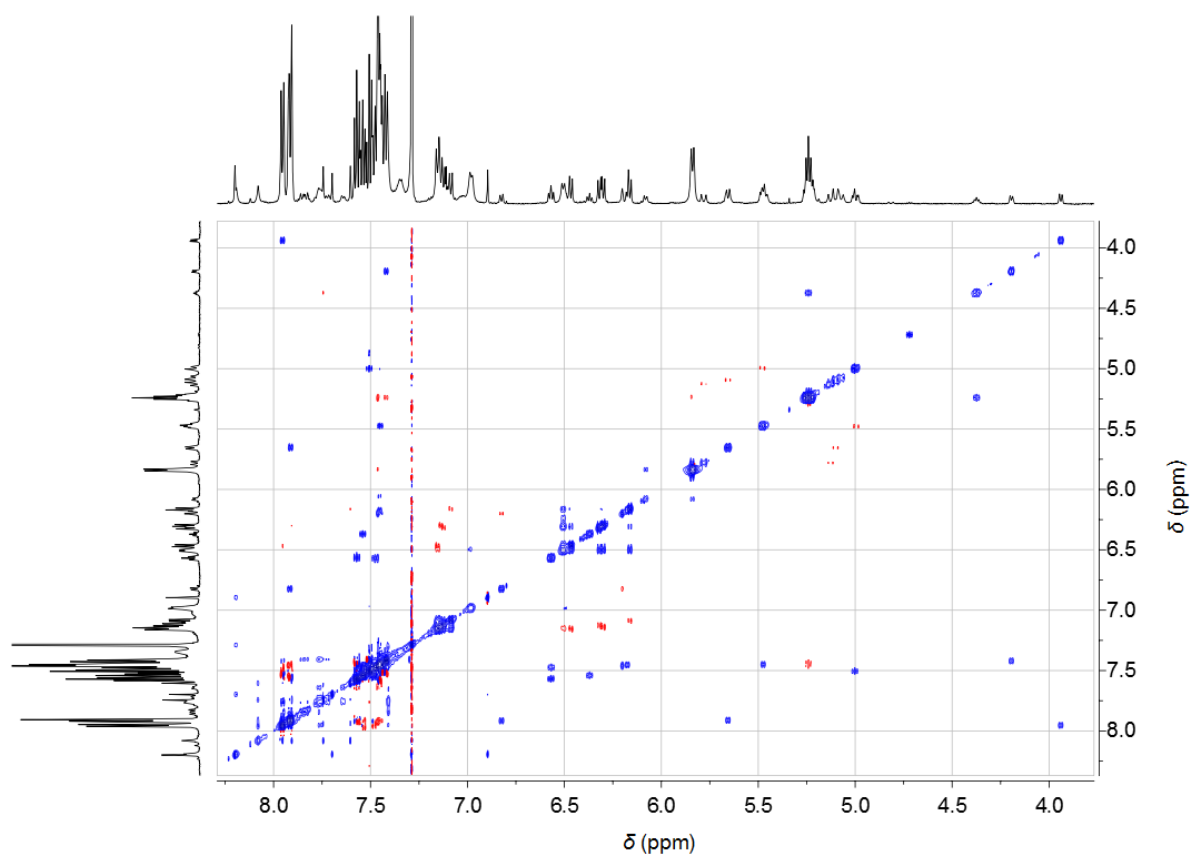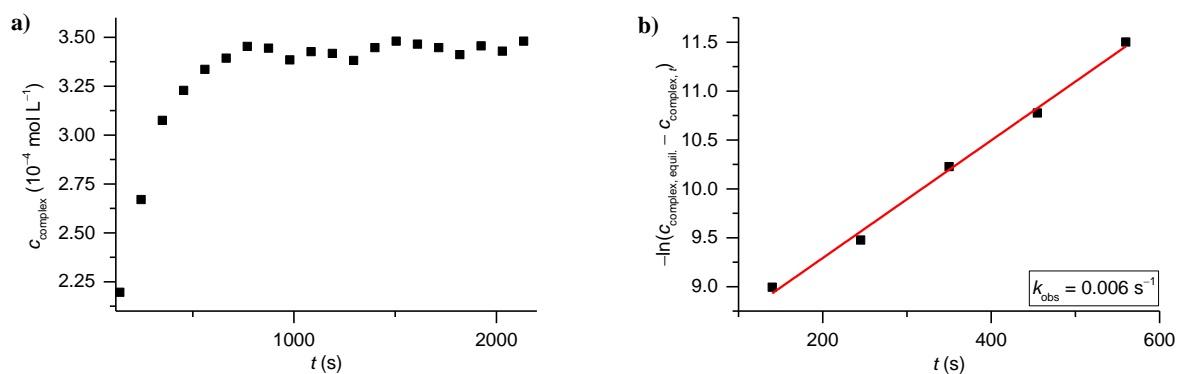
**Fig. S10.** ^{1}H-^{1}H ROESY (600 MHz, CDCl$_3$, 250 K) of **[2PBI]** ($c = 5 \cdot 10^{-4}$ L mol^{-1}) in the presence of 5 eq. of (*S*)-**G4**.
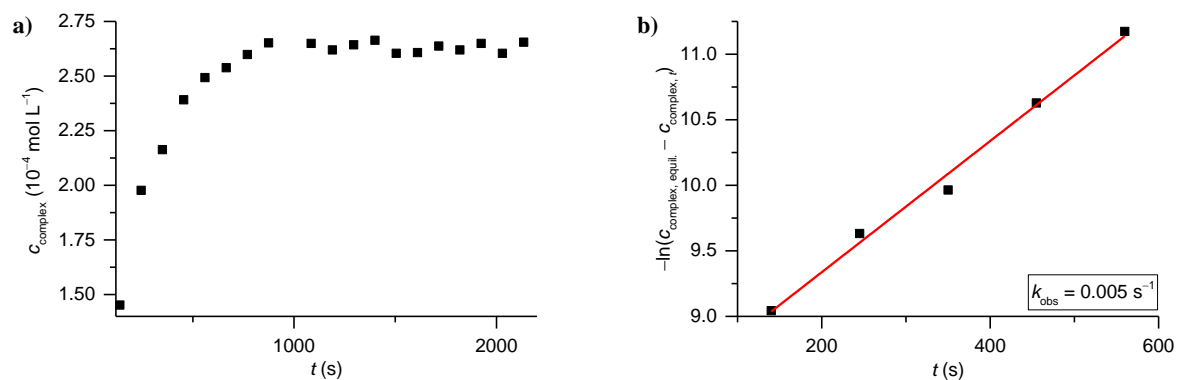
5 Kinetic ^{1}H NMR studies
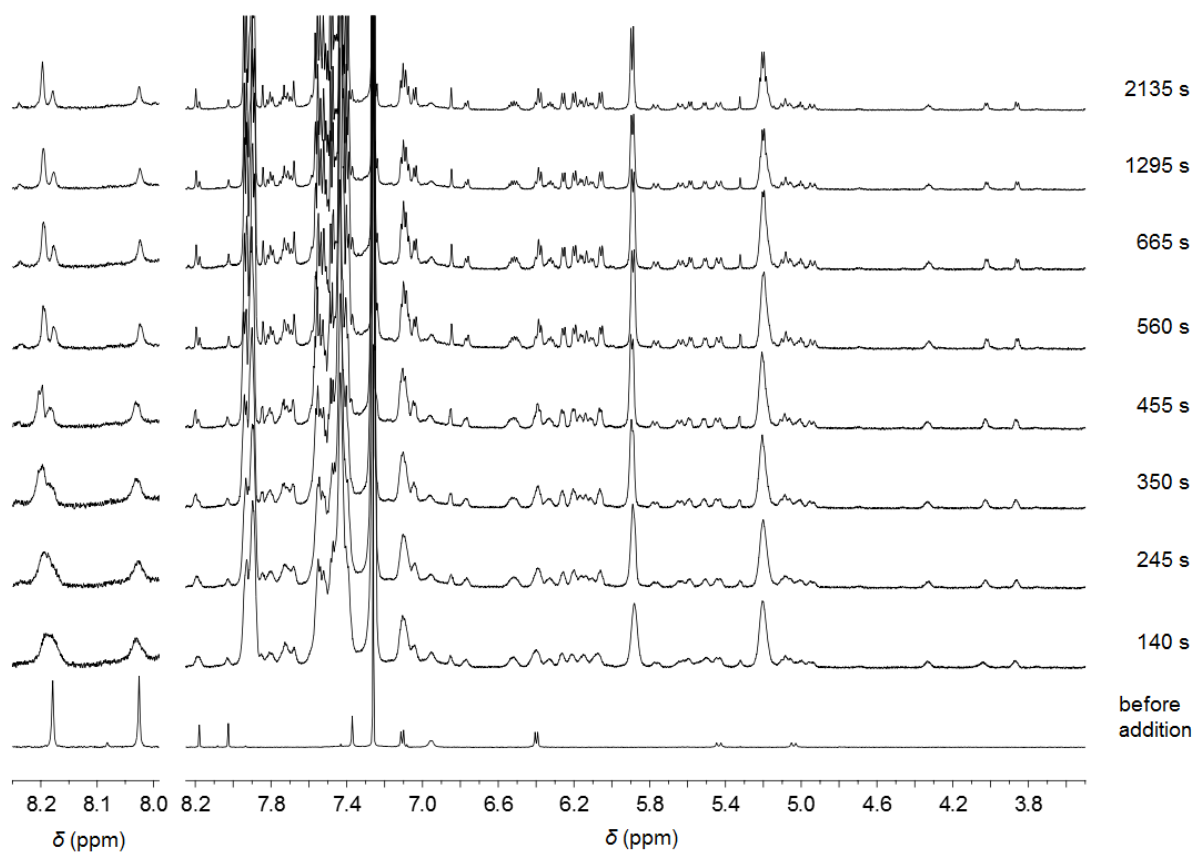
Fig. S11. Time-dependent ^{1}H NMR spectra (600 MHz, CDCl$_3$, 217 K, dimethyl sulphone as integration standard) of **[2PBI]** ($c_0 = 5 \cdot 10^{-4}$ mol L^{-1}) after the addition of 10 eq. of (*S*)-**G4** (right). Excerpt thereof showing the PBI core protons (left).
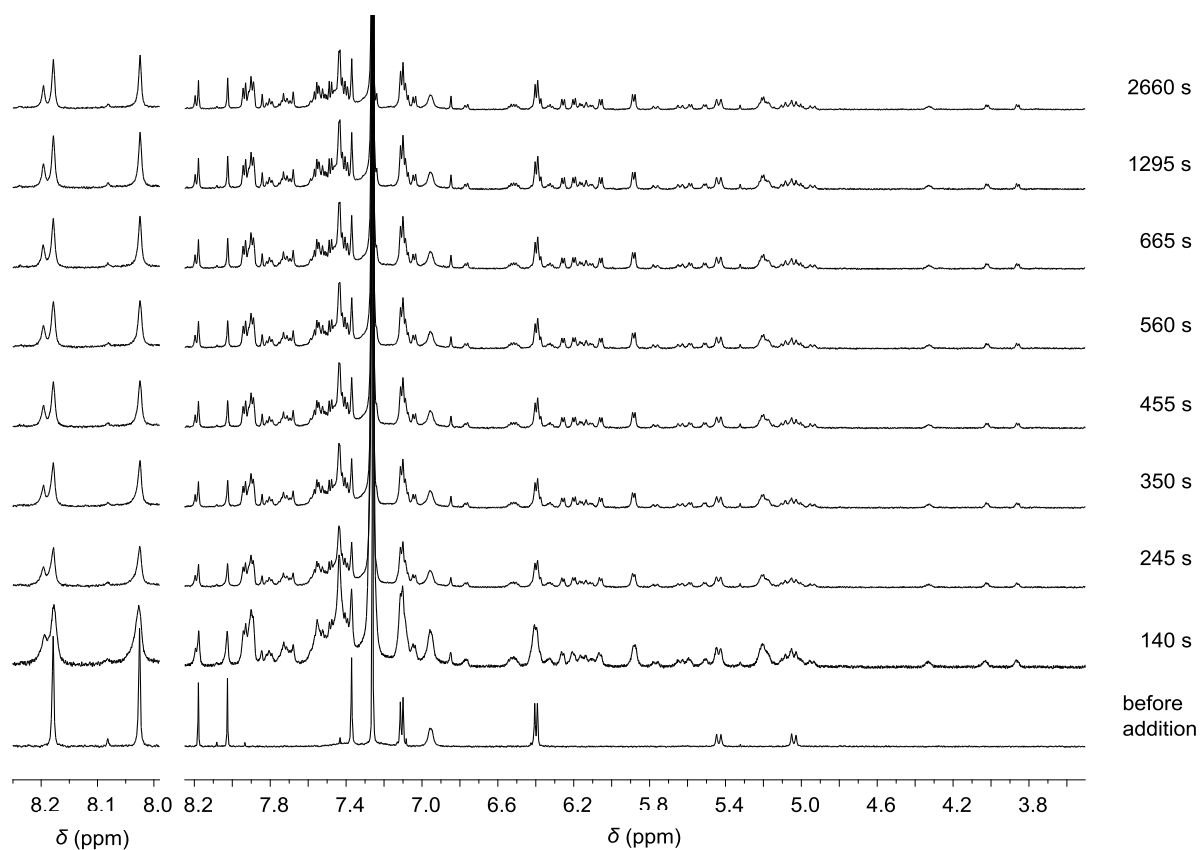

Fig. S12. (a) Plot of the complex concentration (*S*)-**G4**⊂**[2PBI]** as a function of time after the addition of 10 eq. of (*S*)-**G4**. **(b)** Plot showing the first order kinetics for the approach to the complexation equilibrium after the addition of 10 eq. of (*S*)-**G4**.
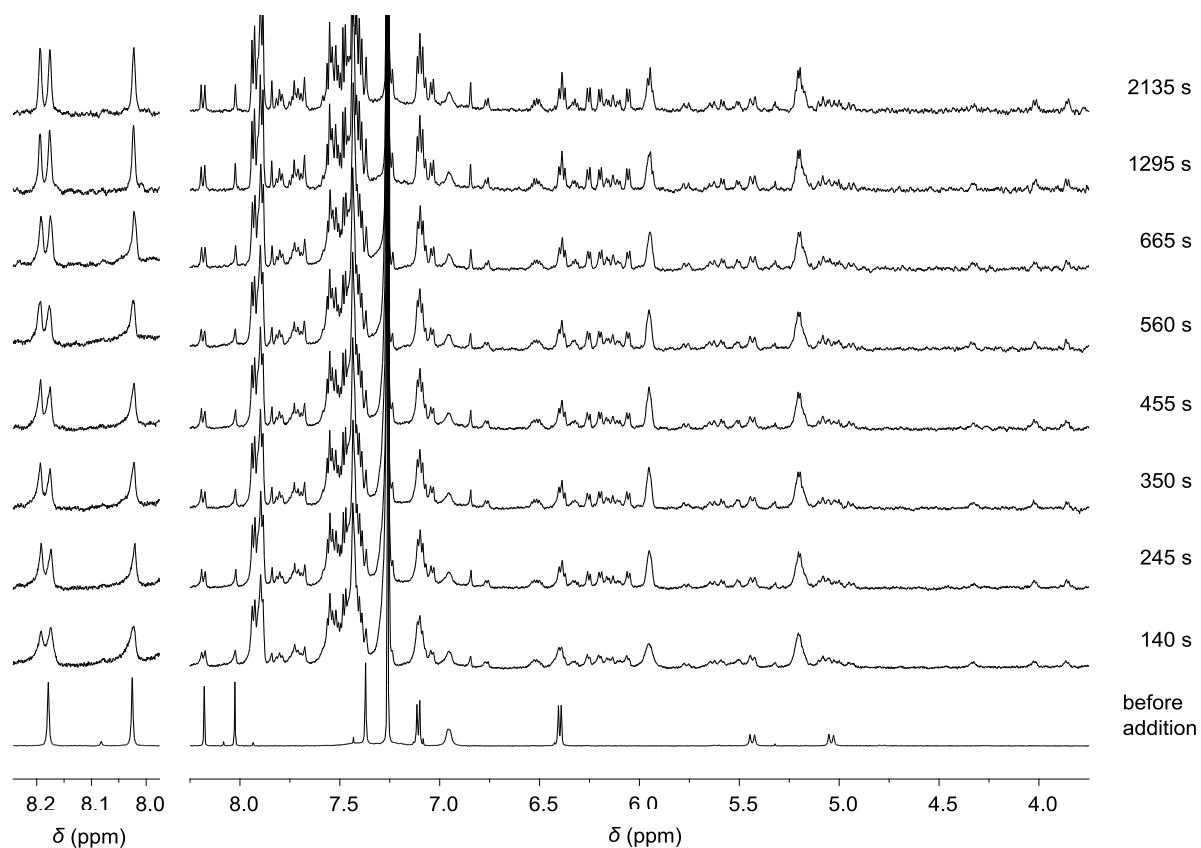
Fig. S13. Time-dependent ^{1}H NMR spectra (600 MHz, CDCl$_3$, 217 K, dimethyl sulphone as integration standard) of **[2PBI]** ($c_0 = 5 \cdot 10^{-4}$ mol L^{-1}) after the addition of 5 eq. of (*S*)-**G4** (right). Excerpt thereof showing the PBI core protons (left).

Fig. S14. (**a**) Plot of the complex concentration (*S*)-**G4**⊂**[2PBI]** as a function of time after the addition of 5 eq. of (*S*)-**G4**. (**b**) Plot showing the first order kinetics for the approach to the complexation equilibrium after the addition of 5 eq. of (*S*)-**G4**.
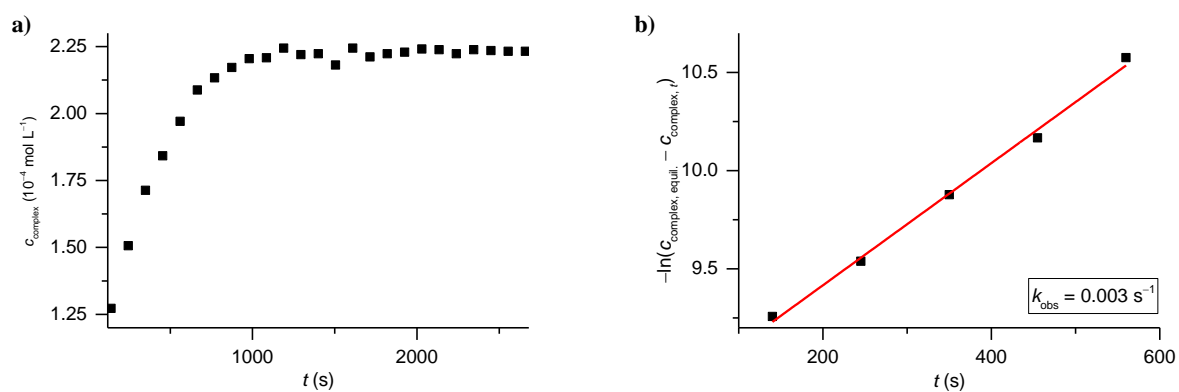
Fig. S15. Time-dependent ^{1}H NMR spectra (600 MHz, CDCl$_3$, 217 K, dimethyl sulphone as integration standard) of **[2PBI]** ($c_0 = 5 \cdot 10^{-4}$ mol L^{-1}) after the addition of 2 eq. of (*S*)-**G4** (right). Excerpt thereof showing the PBI core protons (left).

Fig. S16. (a) Plot of the complex concentration (*S*)-**G4**⊂**[2PBI]** as a function of time after the addition of 2 eq. of (*S*)-**G4**. **(b)** Plot showing the first order kinetics for the approach to the complexation equilibrium after the addition of 2 eq. of (*S*)-**G4**
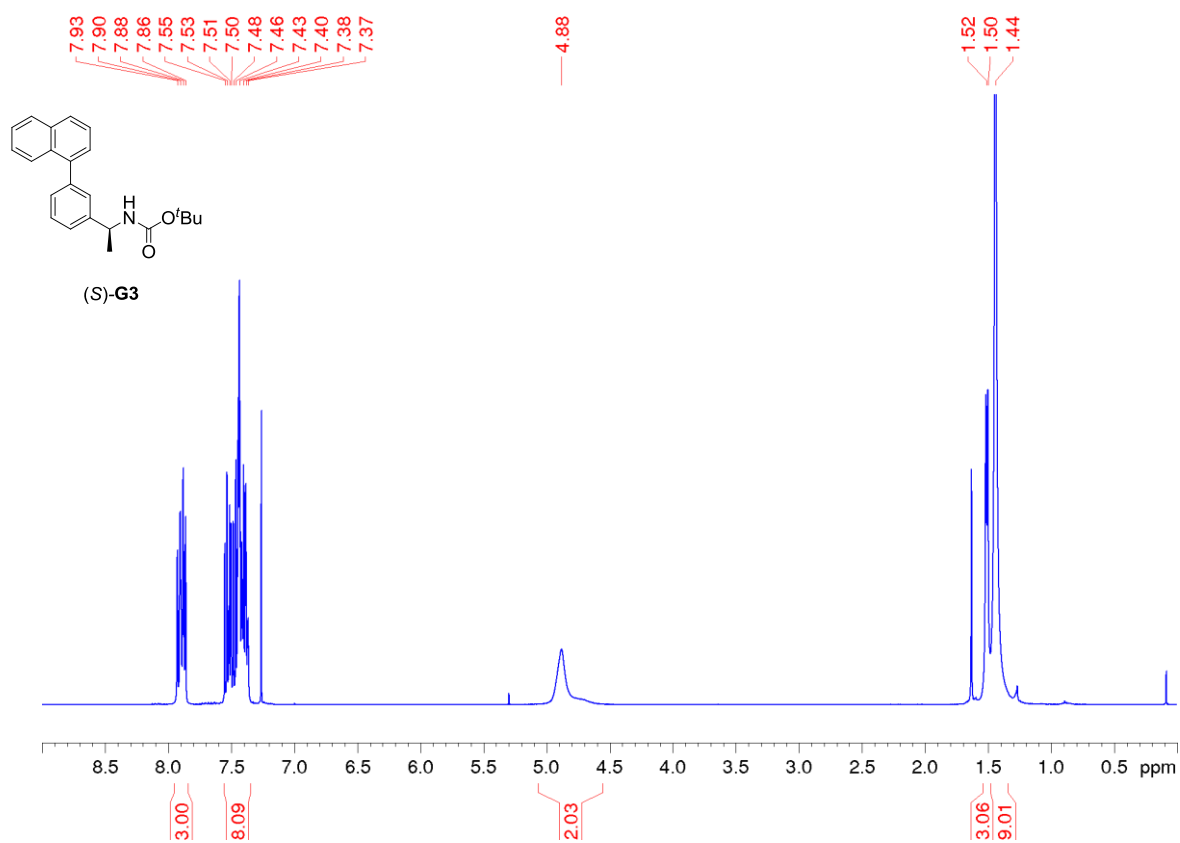
6 Characterization data

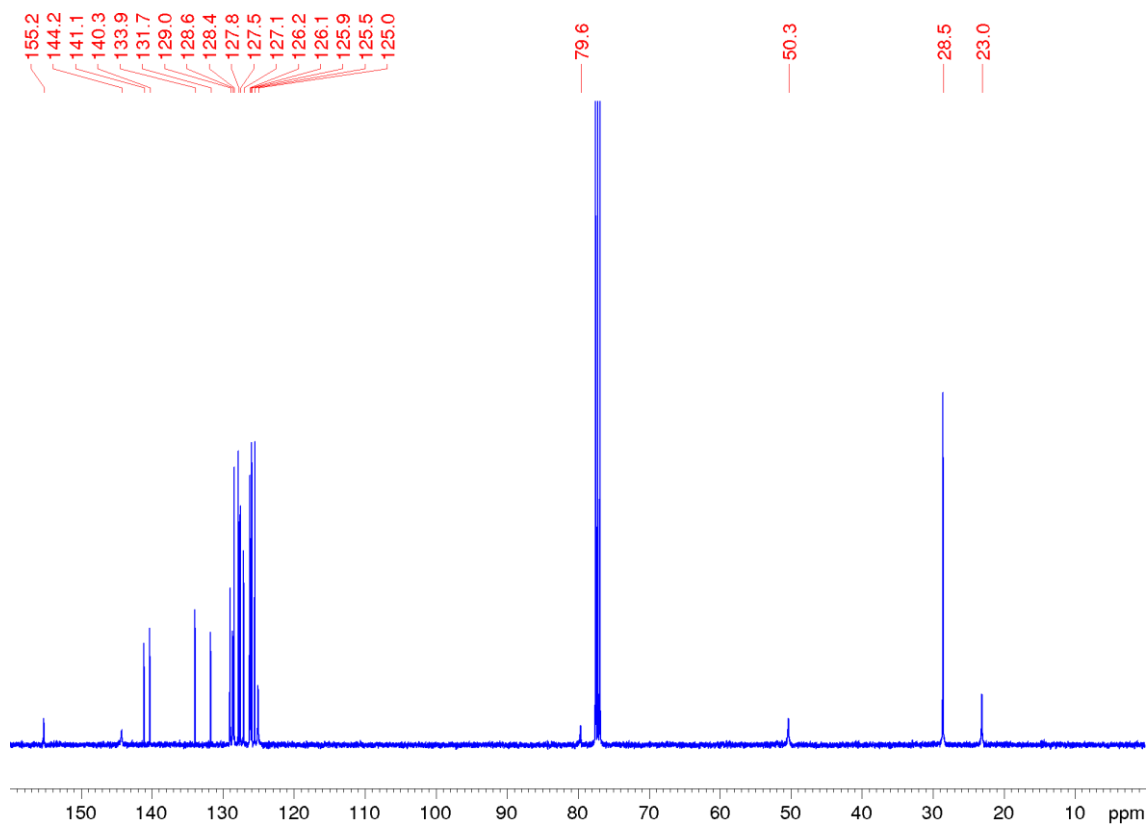**Fig. S17.** ^{1}H NMR (CDCl$_3$, 400 MHz, 295 K) of (*S*)-**G3**.

Fig. S18. ^{13}C NMR (CDCl$_3$, 100 MHz, 295 K) of (*S*)-**G3**

S16
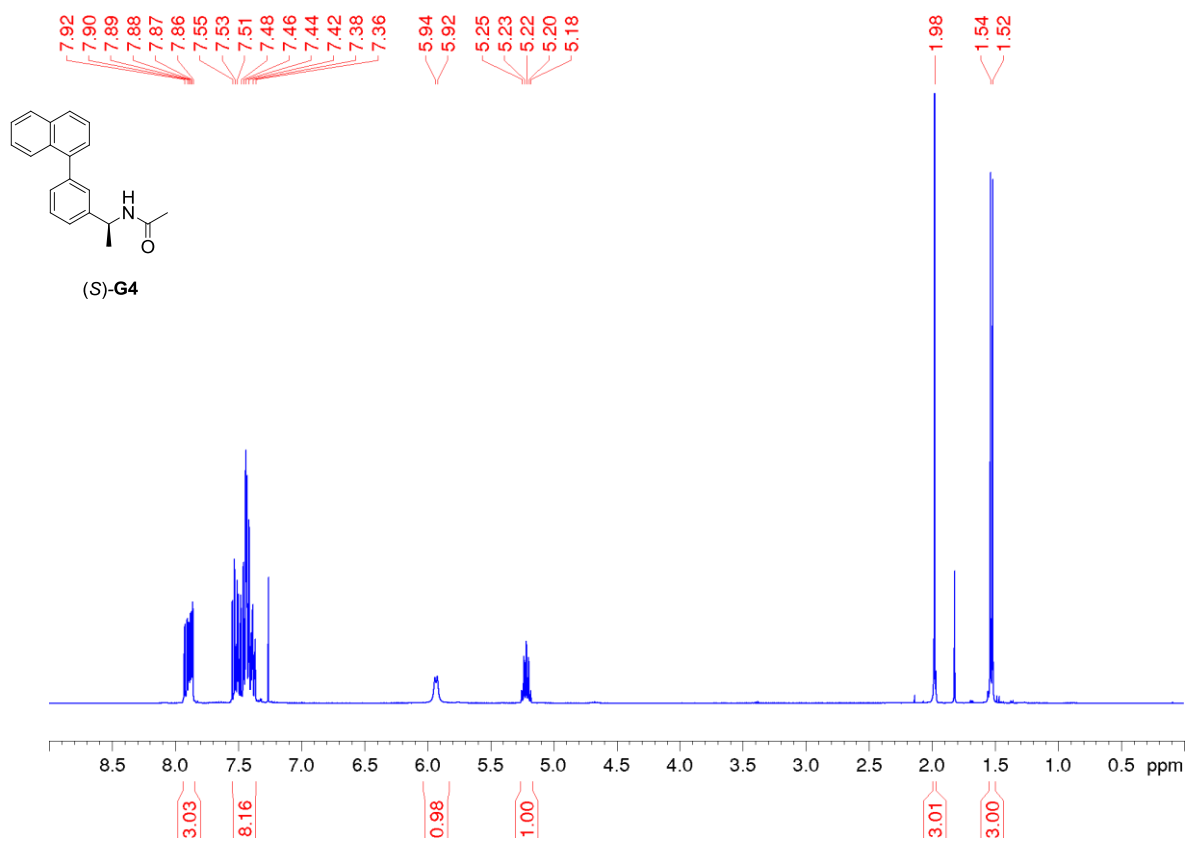
Fig. S19. ^{1}H NMR (CDCl$_3$, 400 MHz, 295 K) of (*S*)-**G4**.
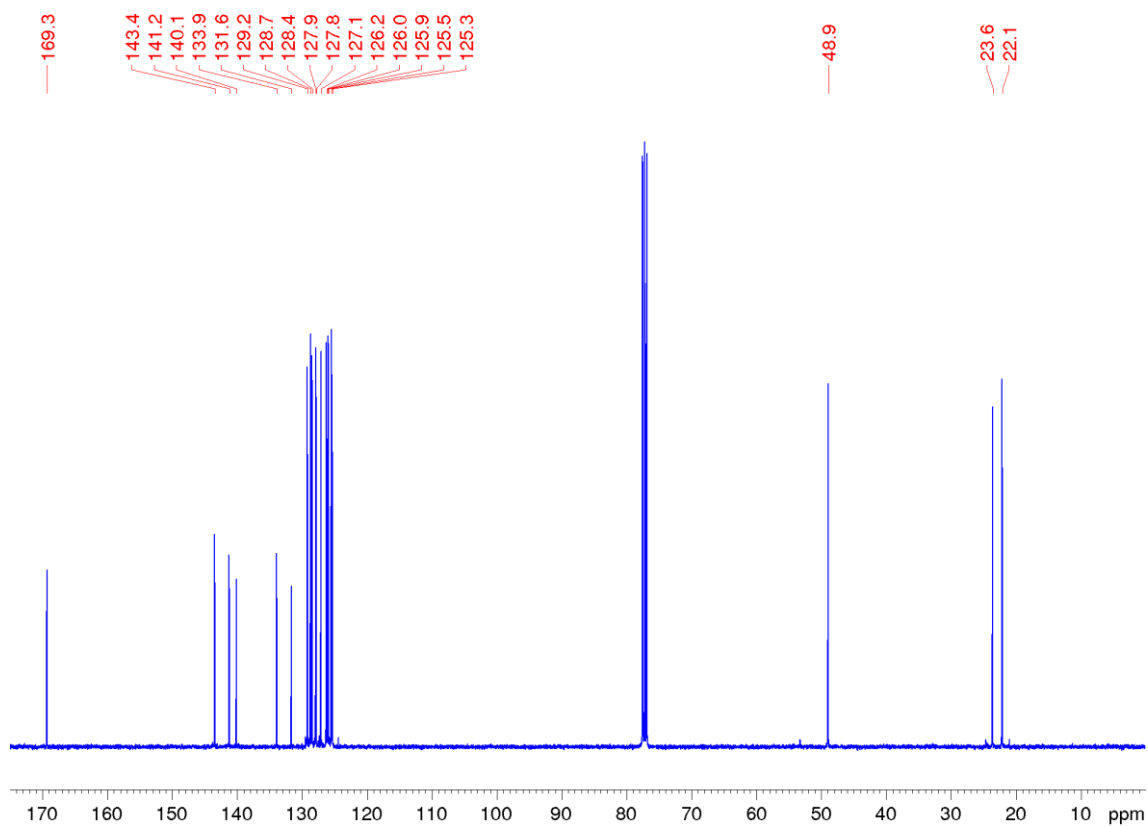
Fig. S20. ^{13}C NMR (CDCl$_3$, 100 MHz, 295 K) of (*S*)-**G4**.
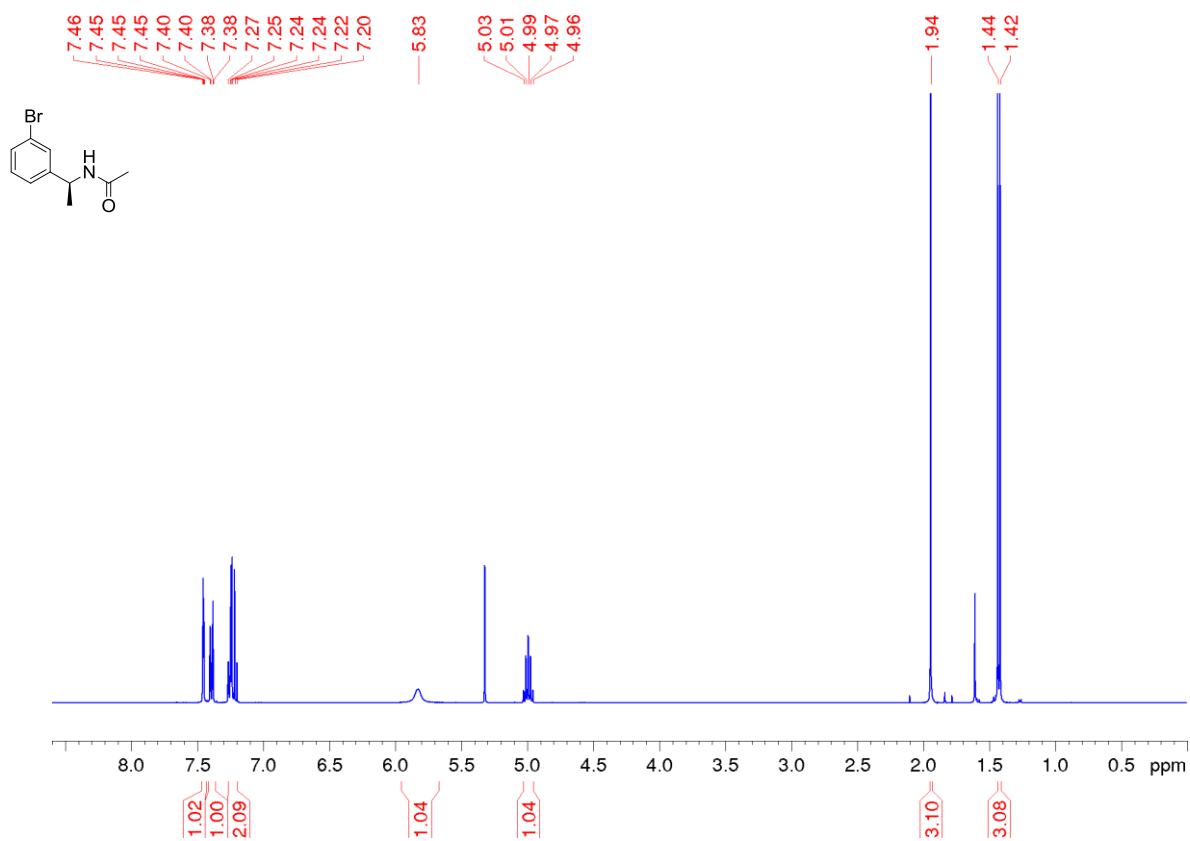
Fig. S21. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, 295 K) of **6**.
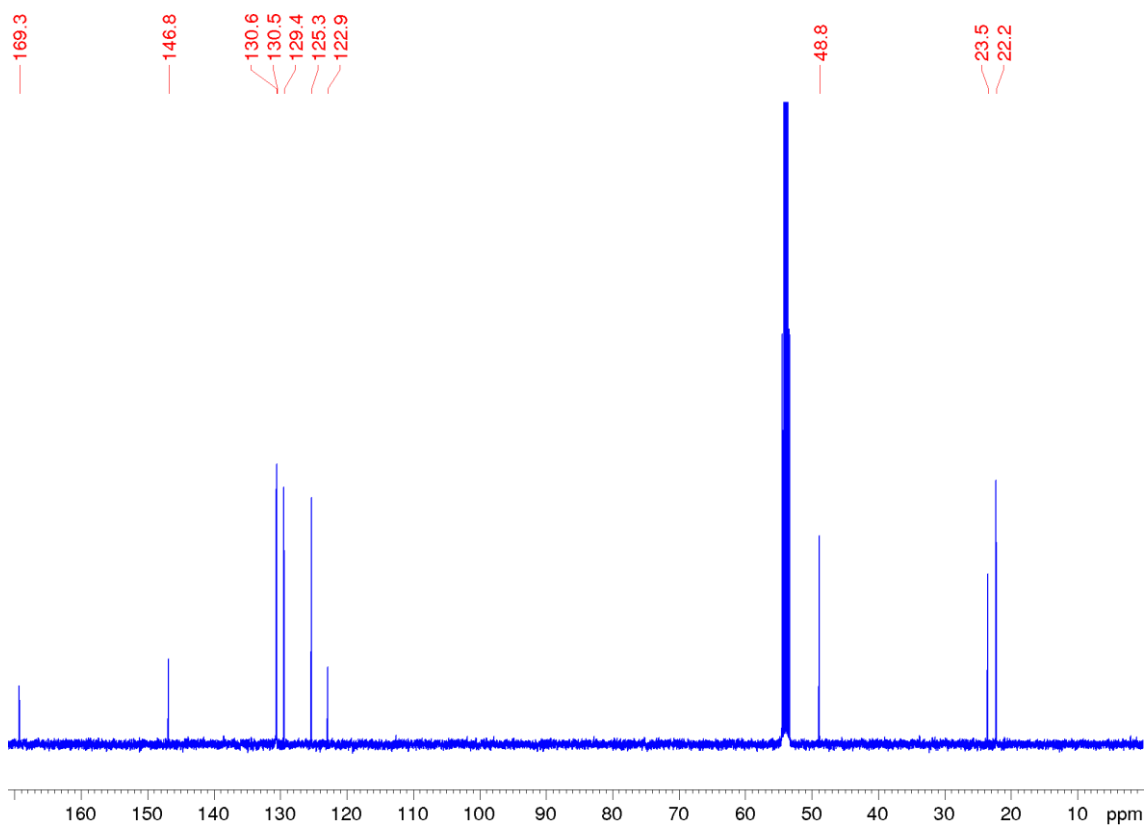
Fig. S22. ^{13}C NMR (CD$_2$Cl$_2$, 100 MHz, 295 K) of **6**.

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
370.17736	1	C23H25NNaO2	370.17775	1.04	51.1	1	100.00	11.5	even	ok
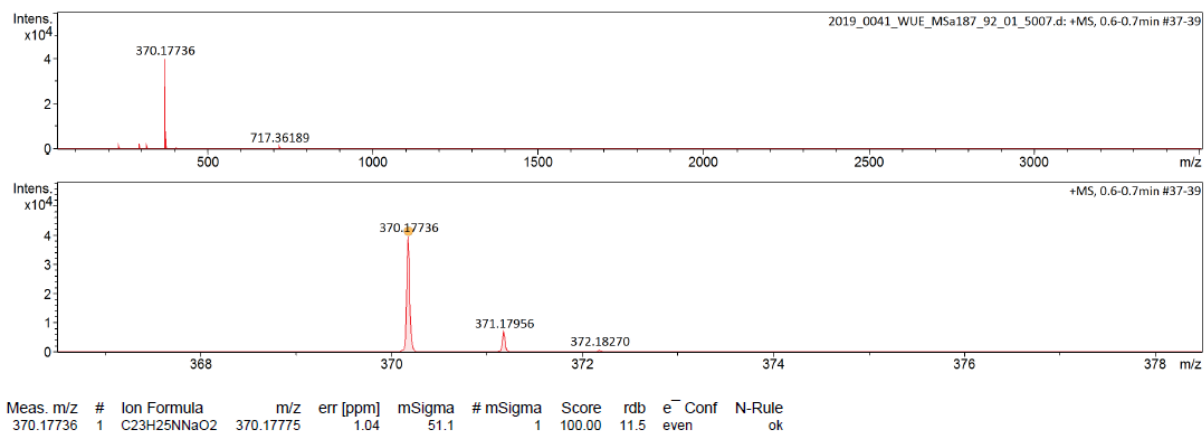
Fig. S23. High resolution mass spectrum (ESI, pos. mode, CH$_3$CN/CH$_3$Cl) of (*S*)-**G3**.

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
312.13575	1	C20H19NNaO	312.13588	0.44	9.8	1	100.00	11.5	even	ok
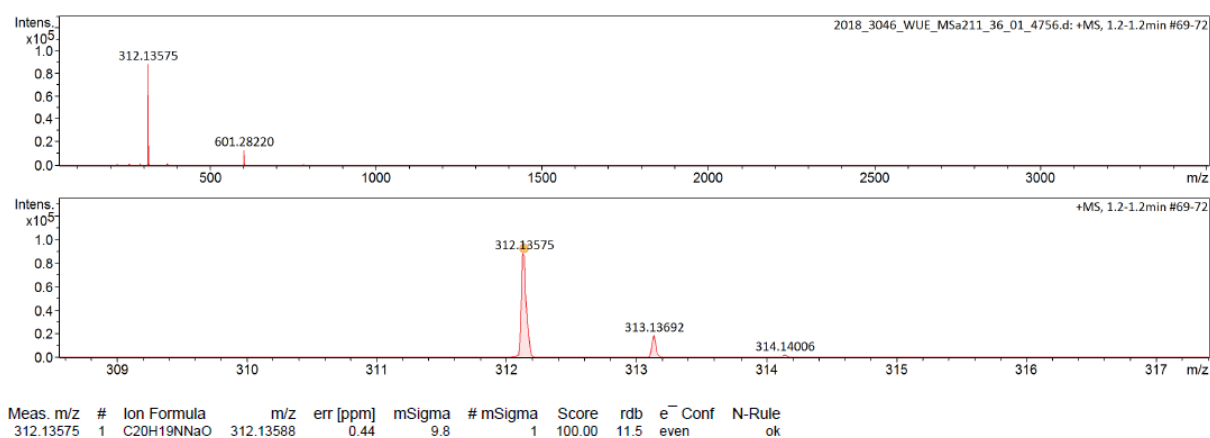
Fig. S 24. High resolution mass spectrum (ESI, pos. mode, CH$_3$CN/CH$_3$Cl) of (*S*)-**G4**.

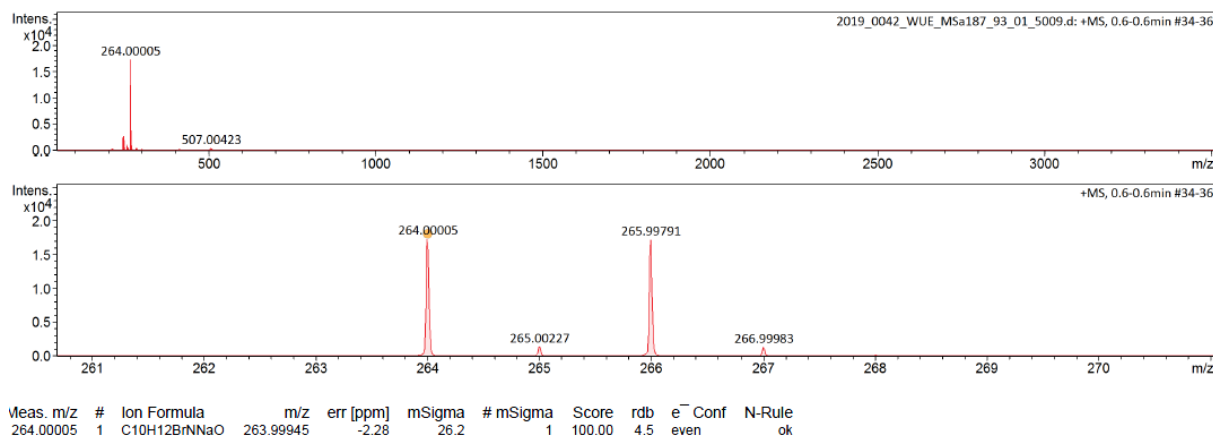| Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
264.00005	1	C10H12BrNNaO	263.99945	-2.28	26.2	1	100.00	4.5	even	ok

Fig. S25. High resolution mass spectrum (ESI, pos. mode, CH$_3$CN/CH$_3$Cl) of **6**.

7   Literature

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