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# Supramolecular double-helices based on complementary phosphate-guanidinium pairing

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# 1 General information

## 1.1 Analytical methods

The NMR spectra were recorded on a Bruker DMX 300 spectrometer (1H: 300 MHz), a Bruker Avance NEO 400 spectrometer ($^{1}$H: 400 MHz, $^{13}$C: 101 MHz, $^{19}$F: 376 MHz, $^{31}$P: 162 MHz), DMX 500 spectrometer ($^{1}$H: 500 MHz) and DRX 600 spectrometer ($^{1}$H: 600 MHz, $^{13}$C: 151 MHz, $^{31}$P: 243 MHz) All NMR experiments were performed at room temperature except otherwise stated. The residual proton signals of the deuterated solvents were used to reference the spectra. The chemical shifts of the residual proton signals of the solvents in the $^{1}$H NMR are: [$D_1$]-chloroform: $\delta$ = 7.26 ppm, [$D_6$]-dimethylsulfoxid: $\delta$ = 2.50 ppm, [$D_4$]-methanol: 3.31 ppm. The apparent coupling constants are given in Hertz. The description of the fine structure means: s = singlet, br s = broad singlet, d = doublet, ps d = pseudo doublet, br d = broad doublet, t = triplet, m = multiplet.

All IR spectra were measured on a Jasco FT/IR-430 spectrometer

High resolution ESI mass spectra were recorded on a Bruker Maxis 4G spectrometer or a Thermo Scientific Orbitrap LTQ-XL mass spectrometer.

Reversed phase medium performance liquid chromatography (MPLC) was performed with the following setup: Armen Instrument Spot Liquid Chromatography Flash system (detection wavelength: 263 nm), YMC GEL ODS-AQ 12 nm, S-50 µm in Kronlab glass columns with 10 mm diameter and 500 mm length. Methanol for MPLC was used analytically pure (VWR). Water for MPLC was purified with a TKA MicroPure ultrapure water system.

Reversed phase analytical high performance liquid chromatography (HPLC) was performed with the following setup: Dionex HPLC system: P680 pump, ASI-100 automated sample injector, UVD-340U UV detector (detection wavelength: 263 nm), UltiMate 3000 Column Compartment; YMC-Pack ODS-A column (3.0 x 150 mm, 5 µm, 12 nm; type: AA12S05-1503QT).

Chiral normal phase analytical high-performance liquid chromatography (HPLC) was used for determination of the enantiomeric purity and it was performed on a chiral CEL OD-H column (0.46 × 25 cm). An Erma Degasser ERC-3512, a Merck Hitachi Intelligent Pump L-6200A and a Knauer Smartline UV Detector 2600 (wavelength: 254 nm) were set up for the performance. The HPLC experiments were carried out in hexane: 2-propanol (25 : 75) at a flow of 0.3 mL/min.

Elemental analyses were performed on Euro EA – CHNSO Elemental Analyser from HEKAtech GmbH.

CD absorption spectra were recorded on a JASCO J-815 spectrophotometer. The quartz cuvettes were from Hellma®Analytics type 100-QS (10 mm light path). All solvents were spectrometric grade.

## 1.2 Material and Methods

POLYGRAM® SIL G / UV254 TLC plates (silica gel 0.2 mm, 40 × 80 mm) were used for thin-layer chromatography, and a UV Hand Lamp (Herolab GmbH) with the wavelengths 254 nm and 366 nm was used for the evaluation. Purifications were carried out by column chromatography with silica gel of the type MN 60 M (Machery-Nagel) with a particle size of 0.04-0.063 mm.

All reactions that needed exclusion of residual air or humidity were performed under an argon inert gas atmosphere using common Schlenk-techniques. Unless otherwise stated, all commercially purchased chemicals were not purified before use. Solvents for synthetic procedures were used analytically pure, solvents for aqueous extraction processes or flash column chromatographies were of technical grade.

Technical grade ethyl acetate and cyclohexane were always distilled before being used for work-ups or columns. Anhydrous dichloromethane was dried over calcium hydride, whilst anhydrous tetrahydrofuran was dried over sodium, both solvents being freshly distilled prior to use. *N*,*N*-diisopropylethylamine (DIPEA) and 2,2,6,6-Tetramethylpiperidine (TMP) were dried over calcium hydride, distilled and stored over molecular sieves under argon.

Sodium hydride (60% dispersion in mineral oil), 1,4-diethynylbenzene, trimethylsilyl chloride, *tert*-butyl carbamate and 1,3-bis(diphenylphosphino)propane were purchased from TCI and used without further purification. (*R*)-1,1′-Binaphthyl-2,2′-diol (>99.9% *ee*) and (*S*)-1,1′-binaphthyl-2,2′-diol (>99.9% *ee*) were purchased from RCA Separations and used without further purification. Phosphourus tribromide (1.0 M in dichlormethane), *n*-butyllithium (2.7 M in toluene), borane-tetrahydrofuran complex (1.0 M in tetrahydrofuran), and tetrabutylammonium fluoride (1.0 M in tetrahydrofuran), were purchased from ACROS Organics and were used without further purification. Sodium chloride and sodium sulfate were purchased from VWR. Hydrochloric acid (12 M) was purchased from Bernd Kraft GmbH and used without further purification. Trifluoromethanesulfonic anhydride (>98%), palladium(II) acetate, *N*,*N*'-diisopropylcarbodiimide and trifluoroacetic acid were purchased from Fluorochem. Palladiumtetrakistriphenylphosphine(0) and tetrabutylammonium hydroxide 30-hydrate were purchased from Sigma-Aldrich. Iodine monochloride was purchased from Alfa Aesar.

Phosphoric acid (*rac*)-**1** was purchased from Alfa Aesar and used without further purification. Guanidine (*rac*)-**2** was prepared according to literature procedures.[7-8] The diiodide (*S*)-**3** was synthesized according to literature procedure.[9-12]. Bisphosphoric acids (*S*,*S*)-**9** and (*R*,*R*)-**9** were synthesized according to literature procedure. [13]

# 2 Synthetic procedures

## 2.1 Overview

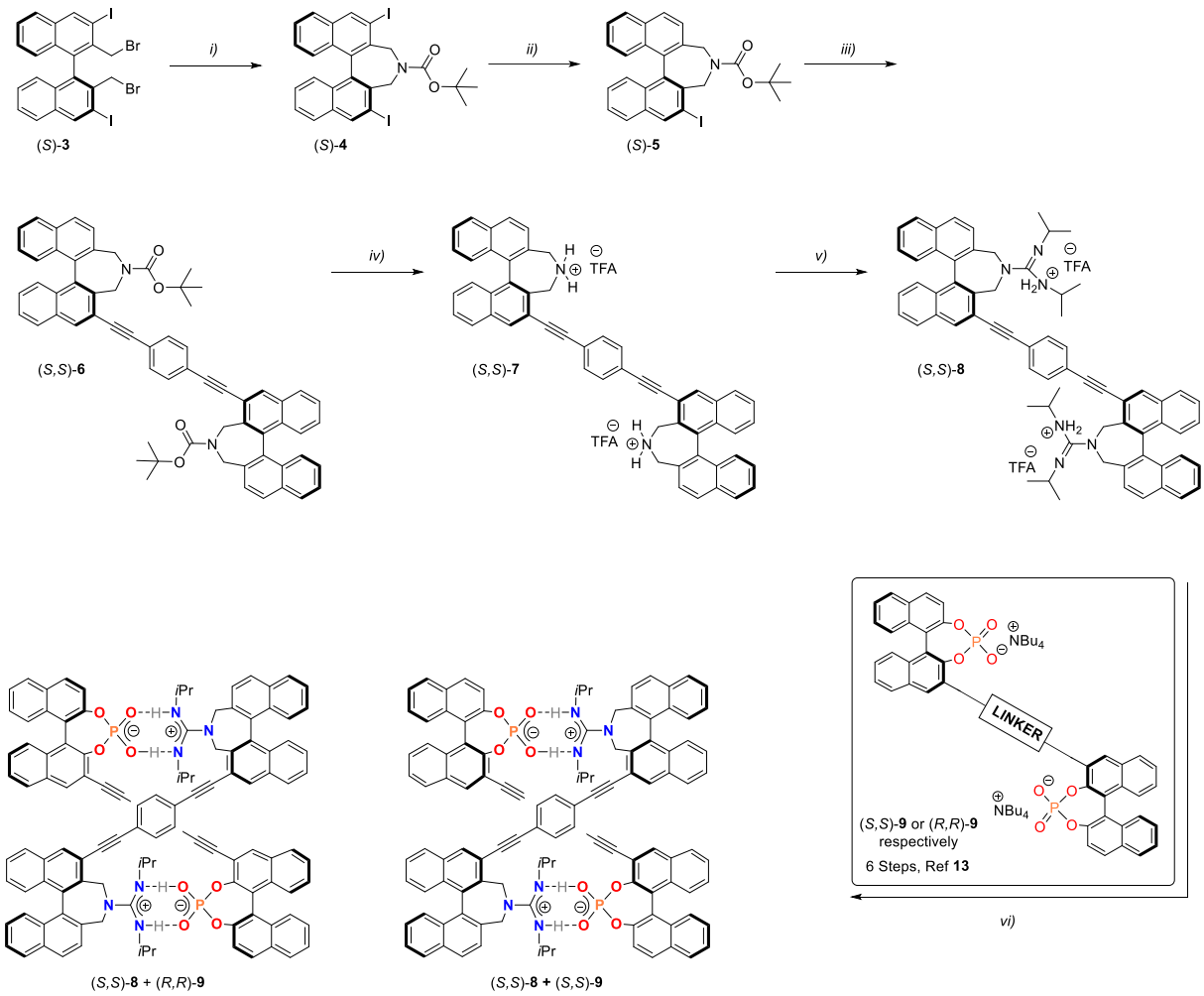
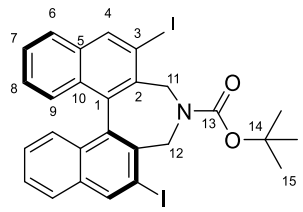



**Figure S1:** Synthesis of the bis-guanidine (*S*,*S*)-**8.** Reagents and conditions: *i)* NaH, *tert*-butyl carbamate, 0°C, THF/DMF, 77%; *ii*) *n*-BuLi, 0 °C, toluene, then MeOH, 63%; *iii*) 1,4-diethynylbenzene, CuI, $Pd(PPh_3)_4$, 80°C, ACN:$NEt_3$, 86%. *iv*) TFA, RT, DCM, 76%; *v*) NaOH, then *n*-BuLi, diisopropylcarbodiimide, RT, toluene, 33%, *vi*) (*S*,*S*)-**9**, respectively (*R*,*R*)-**9**, DMSO, RT.

## 2.2 Synthesis of compound (*S*)-**4**[1,2]



Compound (*S*)-**3** (1.81 g, 2.61 mmol, 1 eq) and *tert*-butyl carbamate (0.458 g, 3.91 mmol, 1.5 eq) were dissolved in dry tetrahydrofuran (40 ml). Sodium hydride (60% in petroleum ether, 0.510 g, 13.1 mmol, 5 eq) was suspended in dry dimethylformamide (40 mL). At 0 °C, the solution of compound (*S*)-**3** and *tert*-butyl carbamate was slowly added to the sodium hydride suspension. The reaction mixture was stirred for 24 hours. After complete conversion a saturated solution of sodium chloride (50 ml) was added and the organic layer was separated. The aqueous phase was extracted with ethyl acetate (5x50 ml). The combined organic layer was dried over anhydrous sodium sulfate and was concentrated in *vacuo.* The crude product was purified by column chromatography (20x4 cm, cyclohexane:ethyl acetate 20:1) and afforded the product (*S*)-**4** as a white crystalline solid (1.30 g, 2.01 mmol, 77.4%).

Same procedure was applied to synthesize (*rac*)-**4:** (*rac*)-**4** (340 mg, 0.985 mmol, 1 eq.) gave the desired product (*rac*)-**4** (415 mg, 0.640 mmol, 65.1 %).

$C_{27}H_{23}NO_2I_2$, MW = 646.98 g/mol.

**NMR:** For compound **4**, we observe separate signals for the methylene-groups 11 and 12, probably due to slow rotation around the N-C amide bond. However, for the binaphthyl-backbone only one set of signals was observed.

**$^1$H-NMR (600 MHz, [D$_1$]-chloroform, 298 K) δ [in ppm]** = 8.60 (s, 2 H, H-4), 7.81 (d, $^3J$ = 8.5 Hz, 2 H, H-6), 7.48 (t, $^3J$ = 7.4 Hz, 2 H, H-7), 7.27-7.24 (m, 4 H, H-8/9), 5.64 (d, $^2J$ = 12.4 Hz, 1 H, H-11/12), 5.49 (d, $^2J$ = 12.4 Hz, 1 H, H-11/12), 3.59 (d, $^2J$ = 12.9 Hz, 1 H, H-11/12), 3.50 (d, $^2J$ = 12.9 Hz, 1 H, H-11/12), 1.51 (s, 9 H, H-25).

**$^{13}$C-NMR (151 MHz, [D$_1$]-chloroform, 298 K) δ [in ppm]** = 153.3 (C-13), 140.2 (C-4), 136.2 (C-1), 134.5 (C-10), 130.9 (C-5), 127.5 (C-9), 127.3 (C-6), 126.9 (C-7/8), 98.0 (C-3), 97.8 (C-2), 80.4 (C-14), 51.8 (C-11/12), 51.1 (C-11/12), 28.6 (C-15).

**$^1$H,$^1$H-COSY (600 MHz / 600 MHz, [D$_1$]-chloroform, 298 K) δ [in ppm]** = 7.81 / 7.48 (H-6 / H-7), 7.48 / 7.81, 7.27-7.24 (H-7 / H-6, H-8/9), 7.27-7.24 / 7.48 (H-8/9 / H-7), 5.64 / 3.50 (H-11 / H-12), 5.49 / 3.60 (H-11 / H-12), 3.60 / 5.49 (H-12 / H-11), 3.50 / 5.64 (H-12 / H-11).

**$^1$H,$^{13}$C-GHSQC (600 MHz / 151 MHz, [D$_1$]-chloroform, 298 K) δ ($^1$H) / δ ($^{13}$C) [in ppm]** = 8.60 / 140.2 (H-4 / C-4), 7.81 / 127.3 (H-6 / C-6), 7.48 / 126.9 (H-7 / C-7/8), 7.27-7.24 / 126.9 (H-8/9 / C-7/8), 7.27-7.24 / 127.5 (H-8/9 / C-9), 5.64 / 51.1 (H-11/12 / C-11/12), 5.49 / 51.8 (H-11/12 / C-11/12), 3.59 / 51.8 (H-11/12 / C-11/12), 3.50 / 51.1 (H-11/12 / C-11/12), 1.57 / 28.6 (H-15 / C-15).

**$^1$H,$^{13}$C-GHMBC (600 MHz / 151 MHz, [D$_1$]-chloroform, 298 K) δ ($^1$H) / δ ($^{13}$C) [in ppm]** = 8.60 / 134.5, 130.9, 127.3, 98,0/97.8 (H-4 / C-10, C-5, C-6, C-3/2), 7.81 / 140.2, 130.5, 126,9 (H-6 / C-4, C-5,C-7/8), 7.48 / 134.5, 127.5, (H-7 / C-10, C-9), 7.27-7.24 / 136.2, 130.9, 127.3, 126.9, 134.5 (H-8/9 / C-1, C-5, C-6, C-7/8, C-10), 5.64 / 136.2, 98.0, 97.8 (H-11/12 / C-1, C-3, C-2), 5.63 / 136.2, 98.0, 97.8 (H-11/12 / C-1, C-3, C-2), 3.59 / 136.2, 98.0, 97.8 (H-11/12 / C-1, C-3, C-2), 3.50 / 136.2, 98.0, 97.8 (H-11/12 / C-1, C-3, C-2).

**Elemental analysis =** calcd (%) for $C_{27}H_{23}NO_2I_2$ : C: 50.10, H: 3.58, I: 39.21. N: 2.16, O: 4.94; found: C: 50.05, H: 3.48, I: 37.10 N: 2.17, O: 4.77.

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[1] The synthesis of compound (*S*)-**4** was developed at the same time by Widhalm et al.[1]

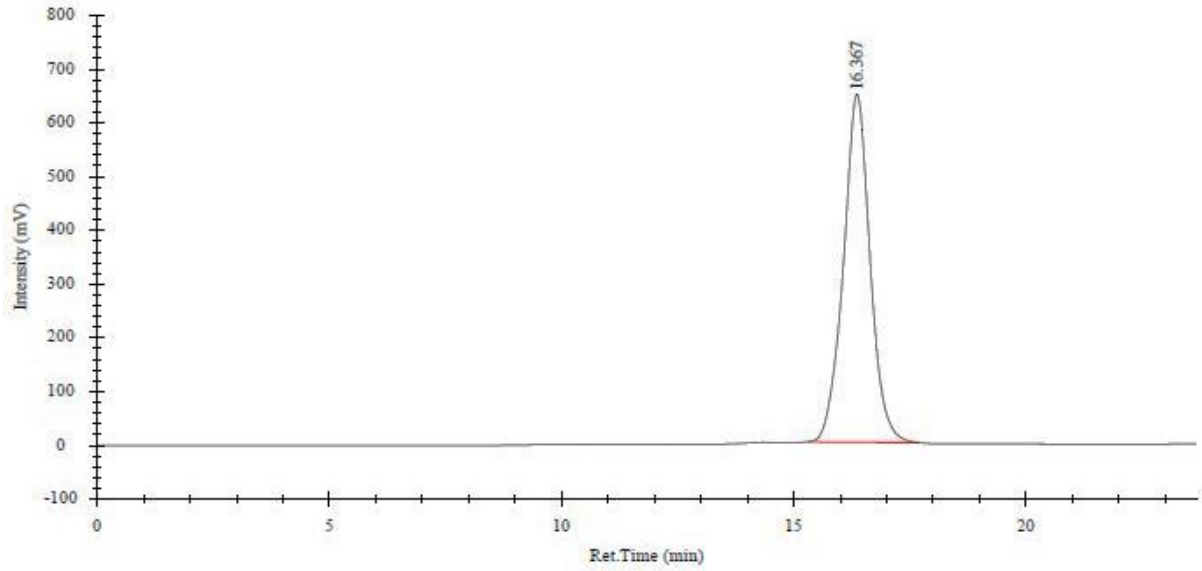
[2] Compound (*S*)-**4** was synthesized following a procedure of Maruoka et al.[2]

**MS (**ESI-pos, MeOH**)**: *m/z* = 647.9892 for ([M + H]$^+$), 591.9265 ([M + H – *tert*-butyl]$^+$), 1294.9709 ([2M + H]$^+$), calcd for $C_{27}H_{23}NO_2I_2$ = 647.9891.

**IR (ATR-FT):** $\tilde{\nu}$ (cm$^{-1}$) = 3054, 2969, 2923, 2877, 2360, 2113, 1689, 1550, 1457, 1396, 1241, 1157, 1110, 1025, 964, 925, 871, 817, 740.

**Chiral HPLC** of (*S*)-**4** and (*rac*)-**4:**

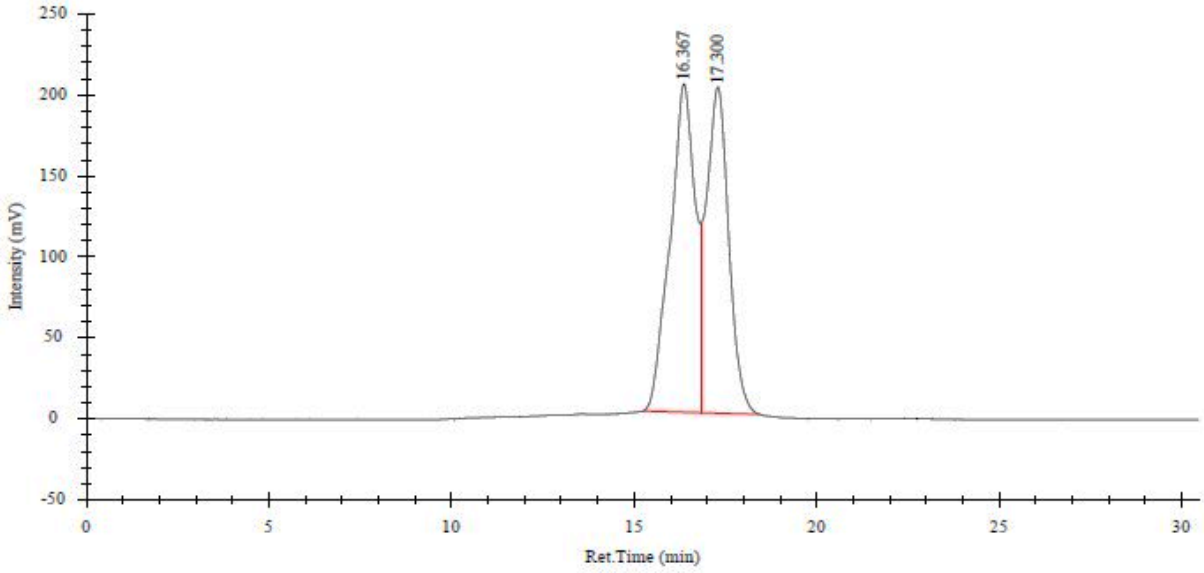
Because the X-ray analysis of (*S*)-**4** showed a small amount of co-crystallized (*R*)-**4**, we checked the enantiopurity by chiral HPLC. Although no baseline-separation for the racemate could be achieved, HPLC proves high stereopurity for (*S*)-**4**.




Calculation Method: Percent

| Peak-No. | Window-No. | Ret. Time (min) | Area | Response-Factor | Percent | Name |
|---|---|---|---|---|---|---|
| 1 | 0 | 16.367 | 25942520.00 | | 100.000 | |

**Figure S2:** Chiral HPLC chromatogram and integration table of (*S*)-**4** (hexane : isopropanol 25 : 75, 0.3 ml/min); $t_R$ (area): 16.36 min (100%).




Calculation Method: Percent

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|---|---|---|---|---|---|---|
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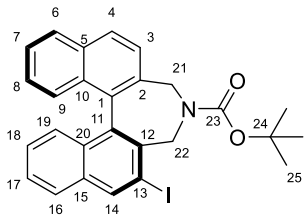
| 2 | 0 | 17.300 | 8665431.00 | | 47.496 | |

**Figure S3:** Chiral HPLC chromatogram and integration table of (*rac*)-**4** (hexane : isopropanol 25 : 75, 0.3 ml/min); $t_R$ (area): 16.36 min (52.5%), 17.3 min (47.5%).

## 2.3 Synthesis of compound (*S*)-**5**



Compound (*S*)-**4** (601 mg, 0.927 mmol, 1 eq) was dissolved in dry toluene (36 ml) and *n*-butyl lithium (0.377 mL, 2.7 M solution in toluene, 1.02 mmol, 1.1 eq.) in toluene was added at 0 °C. The reaction mixture was stirred for 5 minutes. Then methanol (5 ml) was added and the mixture was stirred for additional 10 minutes. Removal of the solvent was followed by purification of the crude product by column chromatography (20x4 cm, cyclohexane:acetone 30:1) and afforded the product (*S*)-**5**[3] as a white crystalline solid (0.304 g, 5.83 mmol, 63.1%).

$C_{27}H_{24}INO_2$, MW = 521.08 g/mol.

**$^1$H-NMR (400 MHz, [D$_1$]-chloroform, 298 K) δ [in ppm]** = 8.59 (s, 1 H, H-14), 7.98 (d, $^3J$ = 8.4 Hz, 1 H, H-4), 7.95 (d, $^3J$ = 8.2 Hz, 1 H, H-6), 7.81 (d, $^3J$ = 8.5 Hz, 1 H, H-16), 7.63 (br d, $^3J$ = 7.9 Hz, 1 H, H-3), 7.48 (dt, $^3J$ = 6.9 Hz, $^4J$ = 1.2 Hz 1 H, H-7), 7.45 (dt, $^3J$ = 7.0 Hz, $^4J$ = 1.2 Hz 1 H, H-17), 7.35 (d, $^3J$ = 8.5 Hz, 1 H, H-9), 7.30 (d, $^3J$ = 8.5 Hz, 1 H, H-19), 7.29-7.26 (m, 2 H, merged with chloroform, H-8+H-18), 5.64-5.45 (m, 1 H, H-21/22), 5.06-4.86 (m, 1 H, H-21/22), 3.67 (d, $^2J$ = 13.3 Hz 1 H, H-21/22), 3.53 (d, $^2J$ = 13.3 Hz 1 H, H-21/22), 1.55 (s, 9 H, merged with water signal, H-25).

**$^{13}$C-NMR (100.61 MHz, [D$_1$]-chloroform, 298 K) δ [in ppm]** = 153.9 (C-23), 139.8 (C-14), 136.6 (C-2), 135.1 (C-12), 134.6 (C-15), 133.29 (C-5), 133.22 (C-13), 131.30 (C-10/20), 131.23 (C-10/20),

129.8 (C-4), 128.5 (C-6), 127.83 (C-8), 127.74 (C-3), 127.31 (C-9), 127.24 (C-16), 126.89 (C-17), 126.77 (C-18), 126.4 (C-8), 126.0 (C-7), 116.7 (C-11), 98.1 (C-1), 80.32 (C-24) 52.00 (C-21/22), 47.2 (C-21/22), 28.7 (C-25).

**$^{1}$H,$^{1}$H-COSY (400 MHz / 600 MHz, [D$_1$]-chloroform, 298 K) δ [in ppm]** = 7.98 / 7.63 (H-4 / H-3), 7.95 / 7.48 (H-6 / H-7), 7.81 / 7.45 (H-16 / H-17), 7.63 / 7.98 (H-3 / H-4), 7.48 / 7.27 (H-7 / H-8+H-18), 7.45 / 7.81, 7.27 (H-17 / H-16, H-8+H-18), 7.35 / 7.27 (H-9 / H-8+H-18), 7.27 / 7.48, 7.45, 7.35 (H-8+H-18 / H-7, H-17, H-9), 5.48 / 3.67 (H-21/22/ H-21/22), 5.03 / 3.53 (H-21/22/ H-21/22), 3.67 / 5.48 (H-21/22 / H-21/22), 3.53 /5.03 (H-21/22 / H-21/22).

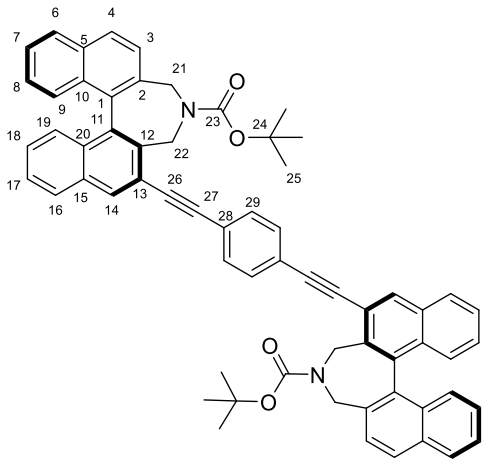
**$^{1}$H,$^{13}$C-GHSQC (400 MHz / 100.61 MHz, [D$_1$]-chloroform, 298 K) δ ($^{1}$H) / δ ($^{13}$C) [in ppm]** = 8.59 / 139.78 (H-14 / C-14), 7.98 / 129.8 (H-4 / C-4), 7.95 / 128.5 (H-6 / C-6), 7.81 / 127.24 (H-16 / C-16), 7.63 / 127.74 (H-3 / C-3), 7.48 / 126.0 (H-7 / C-7), 7.45 / 126.89 (H-17 / C-17), 7.35 / 127.31/127.24 (H-9 / C-9/16), 7.30 / 127.83 (H-19 / C-19), 7.29-7.25 / 126.4/126.77 (H-8/18 / C-8+C-18), 5.46 / 52.0 (H-21/22 / C-21/22), 5.02 / 47.2 (H-21/22 / C-21/22), 3.67 / 52.0 (H-21/22 / C-21/22), 3.53 / 47.2 (H-21/22 / C-21/22), 1.55 / 28.7 (H-25 / C25).

**$^{1}$H,$^{13}$C-GHMBC (400 MHz / 100.61 MHz, [D$_1$]-chloroform, 298 K) δ ($^{1}$H) / δ ($^{13}$C) [in ppm]** = 8.59 / 135.1, 131.30/131.23, 127.31/127.24 (H-14 / C-12, C-10/20, C-9/16), 7.98 / 136.6, 133.29, 131.30, 128.5 (H-4 / C-2, C-5, C-10, C-6), 7.95 / 131.30/131.23, 129.8, 126.4 (H-6 / C-10/20, C-4, C8), 7.81 / 139.8, 131.3/131.21, 126.77 (H-16 / C-14, C-10/20, C-18), 7.48 / 133.31, 127.31/127.24 (H-7 / C-5, C-9/16), 7.45 / 134.6, 127.83 (H-17 / C-15, C-19), 7.35 / 133.29, 126.0 (H-9 / C-5, C-7), 7.30 / 134.6, 126.89 (H-19 / C-15, C-17), 7.29-7.26 / 131.30/131.23, 128.5, 126.89 (H-8+H18 / C-10/20, C-6, C-17), 1.55 / 80.1 (H-25 / C-24).

**MS (**ESI-pos, MeOH**)**: *m/z* = 522.0927 ([M + H]$^{+}$), 466.0302 ([M + H – *tert*-butyl]$^{+}$), 1065.1588 ([2M + Na]$^{+}$), calcd for $C_{27}H_{24}INO_2$ = 522.0925.

**IR (ATR-FT):** $\tilde{\nu}$ (cm$^{-1}$) = 2975, 1687, 1552, 1402, 1365, 1272, 1245, 1155, 1105, 960, 910, 869, 823, 750, 732, 626.

## 2.4 Synthesis of compound (*S*,*S*)-**6**



Compound (*S*,*S*)-**5** (570 mg, 1.10 mmol, 2.1 eq), 1,4-diethynylbenzene (65.1 mg, 0.516 mmol, 1 eq), copper iodide (8.58 mg, 45.1 µmol, 0.1 eq) and palladiumtetrakistriphenylphosphine(0) (52.1 mg, 45.1 µmol, 0.1 eq) were dissolved in a dry and degassed mixture of acetonitrile:triethylamine (1:1 ratio, 30 ml total). The reaction mixture was stirred at 80 C for 18 hours. After cooling to room temperature all volatiles were evaporated and the crude product was purified by column chromatography (20x4 cm, cyclohexane:ethyl acetate 10:1) and afforded the product (*S*,*S*)-**6**[4] as a yellow solid (0.401 g, 0.505 mmol, 86%).

$C_{64}H_{52}N_2O_4$, MW = 912.13 g/mol.

**$^1$H-NMR (600 MHz, [D$_1$]-chloroform, 323 K) δ [in ppm]** = 8.28 (s, 2 H, H-14), 7.99 (d, $^3J$ = 8.4 Hz, 2 H, H-4), 7.96 (d, $^3J$ = 8.1 Hz, 2 H, H-6), 7.92 (d, $^3J$ = 8.2 Hz, 2 H, H-16), 7.69 (br s, 4 H, H-29), 7.63 (d, $^3J$ = 7.5 Hz, 2 H, H-3), 7.49 (t, $^3J$ = 7.4 Hz, 2 H, H-17), 7.48 (t, $^3J$ = 7.4 Hz, 2 H, H-7), 7.42 (d, $^3J$ = 8.4 Hz, 2 H, H-9), 7.36 (d, $^3J$ = 8.7 Hz, 2 H, H-19), 7.29 (t, $^3J$ = 7.6 Hz, 2 H, H-8), 7.27 (t, $^3J$ = 7.4 Hz, 2 H, H-18), 5.76 (br s, 2 H, H-21/22), 5.06 (br s, 2 H, H-21/22), 3.64 (d, $^2J$ = 13.5 Hz, 2 H, H-21/22), 3.53 (d, $^2J$ = 12.4 Hz, 2 H, H-21/22), 1.46 (br s, 18 H, H-25).

**$^{13}$C-NMR (151 MHz, [D$_1$]-chloroform, 323 K) δ [in ppm]** = 154.4 (C-23), 136.6 (C-11), 134.72 (C-1), 133.69 (C-2), 133.5 (C-5+C-12), 133.3 (C-14), 133.0 (C-15), 132.0 (C-29), 131.6 (C-10), 131.5 (C-20), 129.7 (C-4), 128.5 (C-6), 128.3 (C-16), 127.8 (C-19), 127.59 (C-3/9), 127.53 (C-3/9), 127.1 (C-18), 126.7 (C-17), 126.3 (C-8), 126.0 (C-7), 123.6 (C-13/18), 121.2 (C-13/18), 93.3 (C-27), 90.2 (C-26), 80.1 (C-24), 47.7 (C-21/22), 45.2 (C-21/22), 28.70 (C-25).

**$^1$H,$^1$H-COSY (600 MHz / 600 MHz, [D$_1$]-chloroform, 323 K) δ [in ppm]** = 7.99 / 7.63 (H-4 / H-3), 7.63 / 7.99 (H-3 / H-4) 7.96 / 7.48 (H-6 / H-7), 7.92 / 7.49 (H-16 / H-17), 7.48 / 7.96 (H-7 / H-6), 7.49 / 7.92 (H-17 / H-16), 7.42 / 7.29 (H-9 / H-8), 7.29 / 7.42 (H-8 / H-9), 7.36 / 7.27 (H-19 / H-18), 7.27 / 7.36 (H-18 / H-19).

**$^1$H,$^{13}$C-GHSQC (600 MHz / 151 MHz, [D$_1$]-chloroform, 323 K) δ ($^1$H) / δ ($^{13}$C) [in ppm]** = 8.28 / 133.3 (H-14 / C-14), 7.99 / 129.7 (H-4 / C-4), 7.96 / 128.5 (H-6 / C-6), 7.92 / 128.3 (H-16 / C-16), 7.69 / 132.0 (H-29 / C-29), 7.63 / 127.59/127.53 (H-3 / C-3/9), 7.49 / 126.7 (H-17 / C-17), 7.48 / 126.0 (H-7 / C-7), 7.42 / 127.59/127.53 (H-9 / C-3/9), 7.36 / 127.8 (H-19 / C-19), 7.29 / 126.3 (H-8 / C-8), 7.27 / 127.1 (H-18 / C-18), 3.53 / 45.2 (H-21/22 / C-21/22), 1.46 / 28.7 (H-25 / C25).

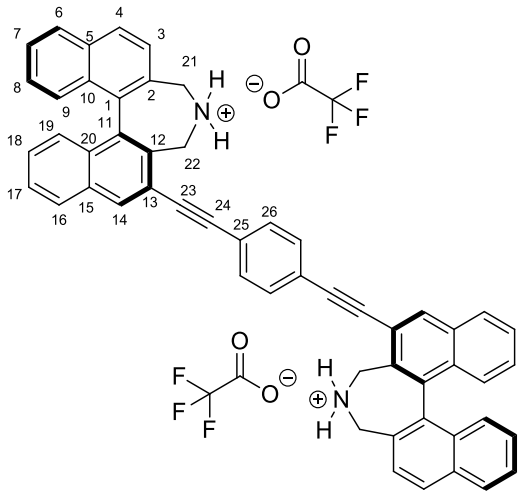
**$^1$H,$^{13}$C-GHMBC (600 MHz / 151 MHz, [D$_1$]-chloroform, 323 K) δ ($^1$H) / δ ($^{13}$C) [in ppm]** = 8.28 / 133.5, 131.5, 128.3, 90.17 (H-14 / C-5+C12, C-20, C-16, C-26), 7.99 / 133.69, 131.6, 128.5 (H-4 / C-2, C-10, C-6), 7.96 / 131.6, 129.7, 126.3 (H-6 / C-10, C-4, C8), 7.92 / 133.3, 131.5, 127.1 (H-16 / C-14, C-20, C-18), 7.63 / 134.7, 133.5 (H-3 / C-1, C-5), 7.49 / 133.0, 131.5, 127.8 (H-17 / C-15, C-20, C-19), 7.48 / 131.63 (H-7 / C-10), 7.42 / 134.7, 133.5, 126.0 (H-9 / C-1, C-5, C-7), 7.36 / 136.6, 133.0, 131.5, 126.7 (H-19 / C-11, C-15, C-20, C-17), 7.29 / 131.6, 128.5 (H-8 / C-10, C-6), 7.27 / 131.5, 128.3 (H-18 / C-20, C-16).

**Elemental analysis =** calcd (%) for $C_{64}H_{52}N_2O_4$ : C: 84.18, H: 5.75 N: 3.07, O: 7.01; found: C: 83.9, H: 5.62, N: 3.25, O: 6.98.

**MS (**ESI-pos, MeOH**)**: *m/z* = 935.3817 for ([M+Na]$^+$), 935.3819 calcd for $C_{64}H_{52}N_2O_4$

**IR (ATR-FT):** $\tilde{\nu}$ (cm$^{-1}$) = 3054, 2977, 2923, 2869, 2360, 1920, 1689, 1504., 1457.92, 1396, 1249, 1157, 1103, 871, 825, 748.

## 2.5 Synthesis of compound **7**



Compound (*S,S*)-**6** (18.5 mg, 0.0203 mmol, 1 eq), was dissolved in a dry and degassed dichloromethane (3 ml), then trifluoric acetic acid (63.6 mg, 0.557 mmol, 27.5 eq) was added and the mixture was stirred at room temperature for 18 hours. The organic layer was washed with water (5 ml), dried over sodium sulfate and concentrated in *vacuo* to give the product (*S,S*)-**7**[2,5] as a yellow solid (11.0 mg, 0.0154 mmol, 76.1%).

$C_{58}H_{38}F_6N_2O_4$, MW = 940.94 g/mol.

**$^1$H-NMR (600 MHz, [D$_1$]-chloroform, 298 K) δ [in ppm]** = 8.27 (s, 2 H, H-14), 7.99 (d, $^3J$ = 7.5 Hz, 2 H, H-4), 7.96 (d, $^3J$ = 7.5 Hz, 2 H, H-6), 7.92 (d, $^3J$ = 7.9 Hz, 2 H, H-16), 7.62 (d, $^3J$ = 8.4 Hz, 2 H, H-3), 7.58 (s, 4 H, H-26), 7.48 (t, $^3J$ = 7.3 Hz, 2 H, H-17), 7.47 (t, $^3J$ = 7.8 Hz, 2 H, H-7), 7.41 (d, $^3J$ = 8.5 Hz, 2 H, H-9), 7.38 (d, $^3J$ = 8.6 Hz, 2 H, H-19), 7.30-7.27 (m, 2 H, H-8), 7.27-7.25 (m, 2 H, H-18), 4.62 (d, $^2J$ = 13.3 Hz, 2 H, H-21), 3.92 (d, $^2J$ = 13.3 Hz, 2 H, H-22), 3.53 (d, $^2J$ = 11.8 Hz, 2 H, H-22), 3.40 (d, $^2J$ = 11.8 Hz, 2 H, H-21).

**$^1$H-NMR (400 MHz, [D$_6$]-dimethylsulfoxid, 298 K) δ [in ppm]** = 8.44 (s, 2 H, H-14), 8.09 (d, $^3J$ = 8.69 Hz, 4 H, H-4+H-16), 8.06 (d, $^3J$ = 8.19 Hz, 2 H, H-6), 7.72 (s, 4 H, H-26), 7.66 (d, $^3J$ = 8.46 Hz, 2 H, H-3), 7.54 (dt, $^3J$ = 7.48 Hz, $^4J$ = 1.05 Hz, 2 H, H-17), 7.50 (d, $^3J$ = 7.48 Hz, $^4J$ = 1.21 Hz, 2 H, H-7), 7.35 (dt, $^3J$ = 8.82 Hz, $^4J$ = 1.21 Hz, 2 H, H-18), 7.33 (dt, $^3J$ = 8.54 Hz, $^4J$ = 1.29 Hz, 2 H, H-8), 7.24 (d, $^3J$ = 8.33 Hz, 2 H, H-9), 7.20 (d, $^3J$ = 8.54 Hz, 2 H, H-19), 4.41 (d, $^2J$ = 12.09 Hz, 2 H, H-22$_{1/2}$), 3.79 (d, $^2J$ = 12.09 Hz, 2 H, H-21$_{1/2}$), 3.20 (d, $^2J$ = 12.09 Hz, 2 H, H-22$_{1/2}$), 3.12 (d, $^2J$ = 12.09 Hz, 2 H, H-21$_{1/2}$).

**$^{13}$C-NMR (100.61 MHz, [D$_6$]-dimethylsulfoxid, 298 K) δ [in ppm]** = 135.6 (C-2), 135.20 (C-11/12), 135.11 (C-11/12), 133.4 (C-1), 132.9 (C-14), 132.5 (C-5), 131.97 (C-15), 131.82 (C-26), 130.6 (C-10+C-20), 129.0 (C-4), 128.47 (C-6), 128.42 (C-16), 127.4 (C-3), 127.2 (C-18), 126.6 (C-19), 126.33 (C-9/17), 126.28 (C-9/17), 126.1 (C-8), 125.4 (C-7), 122.7 (C-25), 119.6 (C-13) 92.1 (C-24), 90.5 (C-23), 47.9 (C-21), 45.0 (C-22).

**$^1$H,$^1$H-COSY (400 MHz / 400 MHz, [D$_6$]-dimethylsulfoxid, 298 K) δ [in ppm]** = 8.09 / 7.66, 7.54 (H-4+H-16 / H-3, H-17), 8.06 / 7.50 (H-6 / H-7), 7.66/7.54 / 8.09 (H-3, H-17 / H-4+H-16), 7.50 / 8.06 (H-7 / H-6), 7.54/7.50 / 7.35/7.33 (H-17/7 / H-18/8), 7.35/7.33 / 7.54/7.50, 7.24/7.20 (H-18/8 / H-17/7, H-9/19), 7.24/7.20 / 7.35/7.33 (H-9/19 / H-18/8), 4.41 / 3.12 (H-22$_{1/2}$ / H-22$_{1/2}$), 3.79 / 3.20 (H-21$_{1/2}$ / H-21$_{1/2}$), 3.12 / 4.41 (H-22$_{1/2}$ / H-22$_{1/2}$), 3.20 / 3.79 (H-21$_{1/2}$ / H-21$_{1/2}$).

**$^1$H,$^{13}$C-GHSQC (400 MHz / 100.61 MHz, [D$_6$]-dimethylsulfoxid, 298 K) δ ($^1$H) / δ ($^{13}$C) [in ppm]** = 8.44 / 132.9 (H-14 / C-14), 8.09 / 129.0, 128.42 (H-4/16 / C-4/16), 8.06 / 128.47 (H-6 / C-6), 7.72 / 131.82 (H-26 / C-26), 7.66 / 127.4 (H-3 / C-3), 7.54 / 126.33, 126.28 (H-17 / C-9/17), 7.50 / 125.4 (H-7 / C-7), 7.35 / 127.2 (H-18 / C-18), 7.33 / 126.1 (H-8 / C-8), 7.24 / 126.33, 126.28 (H-9 / C-9/17), 7.20 /

126.6 (H-19 / C-19), 4.41 / 45.0 (H-22$_{1/2}$ / C-22), 3.79 / 47.9 (H-21$_{1/2}$ / C-21), 3.20 / 47.9 (H21$_{1/2}$ / C-21), 3.12 / 45.0 (H-22$_{1/2}$ / C22).

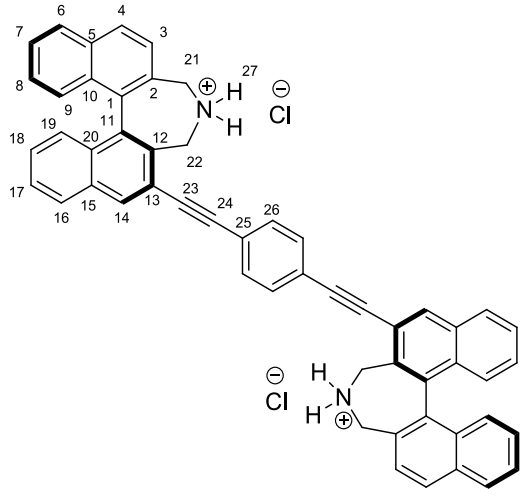
**$^{1}$H,$^{13}$C-GHMBC (400 MHz / 100.61 MHz, [D$_6$]-dimethylsulfoxid, 298 K) δ ($^{1}$H) / δ ($^{13}$C) [in ppm]** = 8.44 / 135.20/135.11, 130.6, 128.42, 90.5 (H-14 / C-11/12, C-10/20, C-16, C-23), 8.09 / 135.6, 130.6, 128.47, 127.2 (H-4+H-16 / C-2, C-10+C-20, C-6, C-18), 8.06 / 130.6, 129.0, 126.1 (H-6 / C-10+C-20, C-4, C-8), 7.72 / 122.7, 92.1 (H-26 / C-25, C-24), 7.66 / 133.4, 132.5, 47.9 (H-3 / C-1, C-5, C-21), 7.54 / 131.82, 126.6 (H-17 / C-15, C-19), 7.50 / 132.5, 126.33/126.28 (H-7 / C-5, C-9/17), 7.35 / 130.6, 128.42 (H-18 / C-10+C-20, C-16), 7.33 / 130.6, 128.47/128.42 (H-8 / C-10+C-20, C-6/16), 7.24 / 132.5, 125.4 (H-9 / C-5, C-7), 7.20 / 135.20/135.11, 131.97, 126.33/126.28 (H-19 / C-11/12, C-15, C-9/17), 4.41 / 135.20/135.11, 119.6 (H-22$_{1/2}$ / C-11/12, C-13), 3.79 / 135.6, 133.4, 127.4 (H21$_{1/2}$ / C-2, C-1, C-3), 3.20 / 135.6 (H21$_{1/2}$ / C-2), 3.12 / 135.20/135.11, 119.6 (H22$_{1/2}$ / C-11/12, C-13).

**$^{19}$F-NMR (376.5 MHz, [D$_6$]-Dimethylsulfoxid, 298 K) δ [in ppm]** -73.41

**MS (**ESI-pos, MeOH**)**: *m/z* = 713.2954 for ([M+H]$^{+}$), 357.1513 for ([M+2H]$^{2+}$), 713.2951, 375.1512 calcd for $C_{54}H_{36}N_2$,

**IR (ATR-FT):** $\tilde{\nu}$ (cm$^{-1}$) = 3744, 3045, 2952, 2923, 2848, 2673, 2489, 2360, 2331, 2206, 1733, 1699, 1683, 1652, 1575, 1558, 1538, 1506, 1423, 1209, 1184, 1105, 1029, 880, 827, 806, 748, 649, 609.

## 2.6 Synthesis of compound (*S*,*S*)-**10**

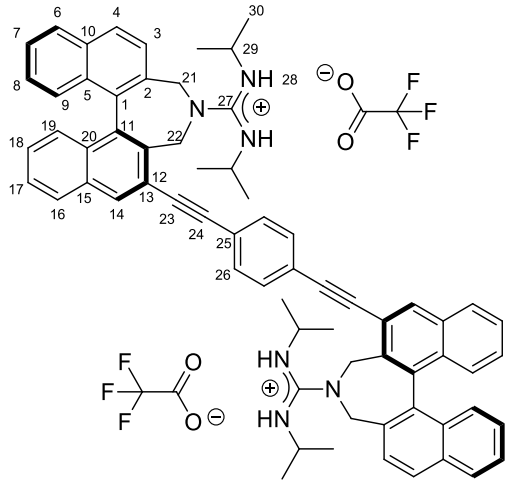


Compound (*S*,*S*)-**6** (39.5 mg, 43.3 µmol, 1 eq), was dissolved in degassed methanol (3 ml), then concentrated hydrochloric acid (10.39 ml, 0.866 mmol, 10 eq) was added and the mixture was stirred at room temperature for 18 hours. Then dichloromethane 10 ml was added and the organic layer was washed with water (15 ml), dried over sodium sulfate and concentrated in *vacuo* to give the product (*S*,*S*)-**10**[5] as a yellow solid (31.7 mg, 40.3 µmol, 93.2%).

$C_{54}H_{38}N_2Cl_2$, MW = 785.81 g/mol

**$^{1}$H-NMR (600 MHz, [D$_6$]-dimethylsulfoxid, 298 K) δ [in ppm]** = 9.94 (br s, 4H, H-27), 8.58 (s, 2 H, H-14), 8.25-8.23 (m, 2 H, H-4), 8.18 (d, $^{3}J$ = 8.1 Hz, 2 H, H-16), 8.15 (d, $^{3}J$ = 8.8 Hz, 2 H, H-6), 7.85 (s, 4 H, H-26), 7.82 (d, $^{3}J$ = 8.2 Hz, 2 H, H-3), 7.66 (t, $^{3}J$ = 7.5 Hz, 2 H, H-17), 7.62 (t, $^{3}J$ = 7.5 Hz, 2 H, H-7), 7.44 (t, $^{3}J$ = 7.4 Hz, 2 H, H-18), 7.41 (t, $^{3}J$ = 7.9 Hz, 2 H, H-8), 7.24 (d, $^{3}J$ = 8.6 Hz, 2 H, H-9), 7.21 (d, $^{3}J$ = 8.6 Hz, 2 H, H-19), 4.84 (d, $^{2}J$ = 14.4 Hz, 2 H, H-22$_{1/2}$), 4.40 (d, $^{2}J$ = 12.3 Hz, 2 H, H-21$_{1/2}$), 3.61 (d, $^{2}J$ = 12.6 Hz, 2 H, H-22$_{1/2}$), 3.56 (d, $^{2}J$ = 13.7 Hz, 2 H, H-21$_{1/2}$).

## 2.7 Synthesis of compound **8**



First, compound (*S*,*S*)-**7** (33.1 mg, 46.5 µmol, 1 eq), was dissolved in dichloromethane (10 ml), then sodium hydroxide solution (1 M, 2.00 ml, 2.00 mmol, 16 eq), was added and the organic layer was separated, dried over sodium sulfate and concentrated in *vacuo*. It was then dissolved in dry toluene (2 ml), *n*-butyl lithium (51.1 µL, 2.7 M in toluene, 0.138 mmol, 3 eq.) was added and the solution immediately turned dark red. Then *N*,*N*'-diisopropylcarbodiimide (14.9 µl, 12.2 mg, 96.1 µmol, 2.1 eq) was added and the mixture was stirred at room temperature for one hour, leading to formation of a brown mixture. Methanol (5 ml) was added and all volatiles were removed to give the crude product as a yellow solid. The crude product was purified by HPLC (methanol/water, 15ml/min) and was obtained as the TFA salt (*S*,*S*)-**8**. (10.5 mg, 8.79 µmol, 32.5%).

$C_{72}H_{66}F_6N_6O_4$, MW = 1193.35 g/mol.

**$^1$H-NMR**[3] **(400 MHz, [D$_4$]-methanol, 298 K) δ [in ppm]** = 8.44 (s, 2 H, $H_{Aryl}$), 8.16 (d, $^3J$ = 8.4 Hz, 2 H, $H_{Aryl}$), 8.08 (d, $^3J$ = 8.1 Hz, 4 H, $H_{Aryl}$), 7.71 (d, $^3J$ = 8.4 Hz, 2 H, $H_{Aryl}$), 7.67 (s, 4 H, $H_{Aryl}$), 7.65-7.56 (m, 4 H, $H_{Aryl}$), 7.47-7.36 (m, 8 H, $H_{Aryl}$), 5.22 (d, $^2J$ = 12.8 Hz, 2 H, $H_{Methylen}$), 4.51 (d, $^2J$ = 11.9 Hz, 2 H, $H_{Methylen}$), 4.08 (d, $^2J$ = 12.4 Hz, 2 H, $H_{Methylen}$), 3.99 (d, $^2J$ = 12.1 Hz, 2 H, $H_{Methylen}$), 3.80 (s br, 4 H, $H_{Isopropyl}$), 1.31 (d, $^2J$ = 6.5 Hz, 12 H, $H_{Isopropyl}$), 1.22 (d, $^2J$ = 6.4 Hz, 12 H, $H_{Isopropyl}$).

**$^1$H-NMR (400 MHz, [D$_1$]-chloroform, 298 K) δ [in ppm]** = 9.32 (s, 2 H, N-H), 9.08 (s, 2 H, NH), 8.34 (s, 2 H, $H_{Aryl}$), 8.09 (d, $^3J$ = 7.9 Hz, 2 H, $H_{Aryl}$), 8.04 – 7.99 (m, 4 H, $H_{Aryl}$), 7.67 (s, 4 H, $H_{Aryl}$), 7.61 – 7.52 (m, 8 H, $H_{Aryl}$), 7.45 (d, $^3J$ = 8.4 Hz, 2 H, $H_{Aryl}$), 7.42-7.34 (m, 4 H, $H_{Aryl}$), 5.12 (d, $^2J$ = 12.2 Hz, 2 H, $H_{Methylen}$), 4.33 (d, $^2J$ = 12.2 Hz, 2 H, $H_{Methylen}$), 4.03 (d, $^2J$ = 12.5 Hz, 2 H, $H_{Methylen}$), 3.87 (d, $^2J$ = 12.2 Hz, 2 H, $H_{Methylen}$), 3.36 (s br, 4 H, $H_{Isopropyl}$), 1.31 – 1.22 (m, 12 H, $H_{Isopropyl}$), 1.08 (d, $^2J$ = 10.3 Hz, 12 H, $H_{Isopropyl}$).

**$^1$H-NMR (600 MHz, [D$_6$]-dimethylsulfoxid, 298 K) δ [in ppm]** = 8.56 (s, 2 H, H-14), 8.21 (d, $^3J$ = 8.3 Hz, 2 H, H-4), 8.17 (d, $^3J$ = 8.3 Hz, 2 H, H-6), 8.14 (d, $^3J$ = 8.3 Hz, 2 H, H-16), 7.83 (d, $^3J$ = 8.4 Hz, 2 H, H-3), 7.70 (br s, 2 H, H-28),7.68 (s, 4 H, H-26 merged with $NH_2$ signal), 7.66 (t, $^3J$ = 7.5 Hz, 2 H, H-17), 7.61 (t, $^3J$ = 7.5 Hz, 2 H, H-7), 7.47 (t, $^3J$ = 7.7 Hz, 2 H, H-8), 7.44 (t, $^3J$ = 7.6 Hz, 2 H, H-18), 7.36 (d, $^3J$ = 8.5 Hz, 2 H, H-9), 7.31 (d, $^3J$ = 8.5 Hz, 2 H, H-19), 4.97 (d, $^2J$ = 13.2 Hz, 2 H, H-22$_{1/2}$), 4.46 (d, $^2J$ = 12.3 Hz, 2 H, H-21$_{1/2}$), 4.00 (d, $^2J$ = 12.8 Hz, 2 H, H-21$_{1/2}$), 3.94 (d, $^2J$ = 12.7 Hz, 2 H, H-22$_{1/2}$), 3.75 (br s, 4 H, H-29 merged with water signal), 1.20 (d, $^2J$ = 5.70 Hz, 12 H, H-30$_{1/2}$), 1.10 (br s, 12 H, H-30$_{1/2}$).

**$^{13}$C-NMR (151 MHz, [D$_6$]-dimethylsulfoxid, 298 K) δ [in ppm]** = 157.7 (q, $^2J$ = 30.6 Hz, TFA-Carbon), 155.7 (C-27), 135.6 (C-11), 133.85 (C-1/14), 133.82 (C-1/14), 133.2 (C-5), 132.7 (C-15), 131.8 (C-26), 131.4 (C-2), 130.7 (C-12), 130.4 (C-10/20), 130.0 (C-4), 128.6 (C-6/16), 128.1 (C-8), 127.54 (C-3), 127.47 (C-17), 126.9 (C-18), 126.7 (C-19), 126.6 (C-7), 126.5 (C-9), 122.4 (C-25), 119.2 (C-13), 92.5 (C-24) 89.3 (C-23), 51.3 (C-21), 48.8 (C-22), 46.4 (C-29), 23.2 (C-30$_{1/2}$), 21.9 (C-30$_{1/2}$).

[3] Analysis of the complexes **8**+**9** was conducted in $CDCl_3$ due to the higher association contansts in this solvent. Spectra of the individual compounds **8** and **9** in $CDCl_3$ are shown in the appendix. Due to better spectral resolution and less signal overlap, full NMR-characterization of the individual compounds **9** was carried out in DMSO-$d_6$.

**$^{1}$H,$^{1}$H-COSY (600 MHz / 600 MHz, [D$_6$]-dimethylsulfoxid, 298 K) δ [in ppm]** = 8.21 / 7.83 (H-4 / H-3), 8.17 / 7.61 (H-6 / H-7), 8.14 / 7.66 (H-16 / H-17), 7.83 / 8.21 (H-3 / H-4), 7.66 / 8.14, 7.44 (H-17 / H-16, H-18), 7.61 / 8.17, 7.47 (H-7 / H-6, H-8), 7.47 / 7.61 (H-8 / H-7), 7.44 / 7.66 (H-18 / H-17), 4.97 / 3.94 (H-22$_{1/2}$ / H-22$_{1/2}$), 4.46 / 4.00 (H-21$_{1/2}$ / H-21$_{1/2}$), 4.00 / 4.46 (H-21$_{1/2}$ / H-21$_{1/2}$),3.94 / 4.97 (H-22$_{1/2}$ / H-22$_{1/2}$).

**$^{1}$H,$^{13}$C-GHSQC (600 MHz / 151 MHz, [D$_6$]-dimethylsulfoxid, 298 K) δ ($^{1}$H) / δ ($^{13}$C) [in ppm]** = 8.56 / 133.85/133.82 (H-14 / C-1/14), 8.21 / 130.0 (H-4 / C-4), 8.17 / 128.6 (H-6 / C-6/16), 8.14 / 128.6 (H-16 / C-6/16), 7.83 / 127.54 (H-3 / C-3), 7.68 / 131.8 (H-26 / C26), 7.66 / 127.47 (H-17 / C-17), 7.61 / 126.6 (H-7 / C-7), 7.47 / 128.1 (H-8 / C-8), 7.44 / 126.9 (H-18 / C-18), 7.36 / 126.5 (H-9 / C-9), 7.31 / 126.7 (H-19 / C-19), 4.97 / 48.8 (H-22$_{1/2}$ / C-22), 4.46 / 51.3 (H-21$_{1/2}$ / C-21), 4.00 / 51.3 (H21$_{1/2}$ / C-21) 3.94 / 48.8 (H-22$_{1/2}$ / C22), 1.20 / 21.9 (H-30$_{1/2}$ / C-30$_{1/2}$), 1.10 / 23.2 (H-30$_{1/2}$ / C-30$_{1/2}$).

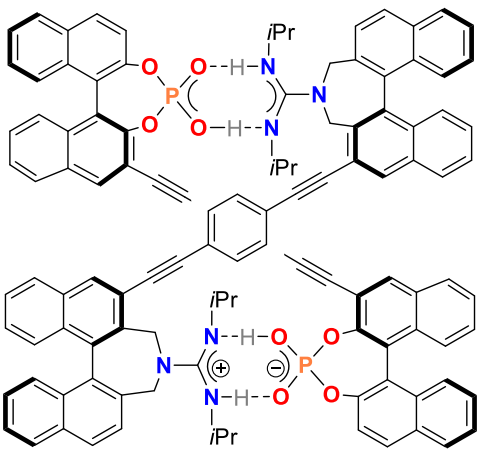
**$^{1}$H,$^{13}$C-GHMBC (600 MHz / 151 MHz, [D$_6$]-dimethylsulfoxid, 298 K) δ ($^{1}$H) / δ ($^{13}$C) [in ppm]** = 8.56 / 130.7, 130.4, 128.6, 89.3 (H-14 / C-12, C-10/20, C-6/16, C-23), 8.21 / 131.4, 130.4, 128.6 (H-4 / C-2, C-10/20, C-6/16), 8.17 / 133.85/133.82, 130.4, 128.1 (H-6 / C-1/14, C-10/20, C-8), 8.14 / 130.4, 126.9 (H-16 / C-10/20, C-18), 7.83 / 133.85/133.82, 133.2, 51.3 (H-3 / C-1/14, C-5, C-21), 7.68 / 122.4, 92.5 (H-26 / C-25, C-24), 7.66 / 132.7, 126.7 (H-17 / C-15, C-19), 7.61 / 133.2, 126.5 (H-7 / C-5, C-9), 7.47 / 130.4, 128.6 (H-8 / C-10/20, C-6/16), 7.44 / 130.4, 128.56 (H-18 / C-10/20, C-6/16), 7.36 / 133.85/133.82, 133.2, 126.6 (H-9 / C-1/14, C-5, C-7), 7.31 / 135.7, 132.7, 127.47 (H-19 / C-11, C-15, C-17), 4.97 / 135.6, 130.7, 119.2 (H-22$_{1/2}$ / C-11, C-12, C-13), 4.46 / 133.85/133.82, 131.4, 127.54 (H21$_{1/2}$ / C-1/14, C-2, C-3), 4.00 / 133.85/133.82, 131.4, 127.54 (H21$_{1/2}$ / C-1/14, C-2, C-3), 3.94 / 135.6, 130,7, 119.2 (H22$_{1/2}$ / C-11, C-12, C-13), 1.20 / 46.4, 23.2 (H-30$_{1/2}$ / C-29, C-30$_{1/2}$), 1.10 / 21.9 (H-30$_{1/2}$ / C-30$_{1/2}$).

**$^{19}$F-NMR (376.5 MHz, [D$_6$]-dimethylsulfoxid, 298 K) δ [in ppm]** -73.61

**MS (**ESI-pos, MeOH**)**: *m/z* = 965.5266 for ([M+H]$^{+}$), 483.2669 for ([M+2H]$^{2+}$) calcd for $C_{68}H_{64}N_6$ = 965.5265, 483.2669.

**IR (ATR-FT):** $\tilde{\nu}$ (cm$^{-1}$) = 3240, 3061, 2973, 2927, 2878, 2853, 1683, 1606, 1455, 1267, 1250, 1200, 1128, 834, 799, 751, 718.

## 2.8 Synthesis of compound (*S*,*S*)-**8** + (*S*,*S*)-**9**




(*S*,*S*)-**8**x(*S*,*S*)-**9**

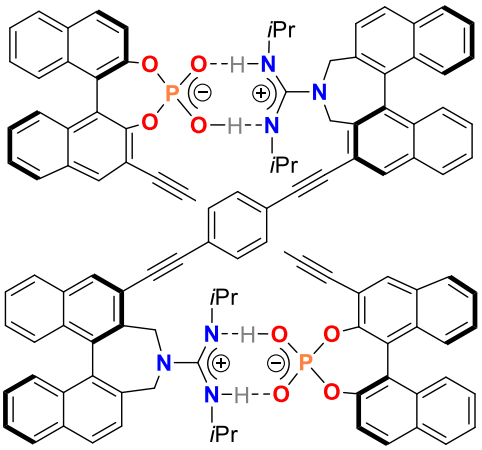
First, compound (*S*,*S*)-**8** (2.61 mg, 2.19 µmol, 1 eq), was dissolved in dimethylsulfoxid (0.729 ml), and directly added into a NMR-tube. Then compound (*S*,*S*)-**9** in dimethylsulfoxid (75 mM, 7.8 µl, 2.19 µmol, 1 eq), was added and the resulting solution was analyzed by NMR-spectroscopy.

Compound (*S*,*S*)-**8** (5.31 mg, 5.11 µmol, 1 eq), was dissolved in chloroform (0.852 ml), and 0.250 ml were transferred into a NMR-tube, Compound (*S*,*S*)-**9** (5.62 mg, 4.32 µmol, 1 eq), was dissolved in chloroform (0.721 ml), and 0.250 ml were transferred into the same NMR tube to give an overall concentration of 3 mM of the helix. The solution was analyzed by NMR-spectroscopy.

**$^1$H-NMR (500 MHz, [D$_6$]-dimethylsulfoxid, 298 K) δ [in ppm]** = 8.51 (s, 3 H, $H_{Aryl}$), 8.32 (s, 6 H, $H_{Aryl}$), 8.16-8.09 (m, 12 H, $H_{Aryl}$), 8.04-7.99 (m, 21 H, $H_{Aryl}$), 7.80-7.75 (m, 10 H, $H_{Aryl}$), 7.59 (s, 18 H, $H_{Aryl}$), 7.46-7.39 (m, 27 H, $H_{Aryl}$), 7.34-7.26 (m, 21 H, $H_{Aryl}$), 7.16-7.13 (m, 14 H, $H_{Aryl}$), 5.02 (d, $^2J$ = 13.2 Hz, 2 H, $H_{methylene}$), 4.37 (d, $^2J$ = 12.4 Hz, 2 H, $H_{methylene}$), 3.96 (d, $^2J$ = 12.8 Hz, 2 H, $H_{methylene}$), 3.88 (d, $^2J$ = 12.7 Hz, 2 H, $H_{methylene}$), 3.74 (br s, 4 H, $H_{isoprppyl}$), 1.22-1.01 (m, 24 H, $H_{isoprppyl}$, merged with tetrabutylammonium signals).

**$^1$H-NMR (400 MHz, [D$_1$]-chloroform, 298 K) δ [in ppm]** = 9.78 (s, 2 H, $H_{Aryl}$), 8.35 (s, 2 H, $H_{Aryl}$), 8.25 (s, 2 H, $H_{Aryl}$), 8.11 (d, $^3J$ = 8.9 Hz, 2 H, $H_{Aryl}$), 8.07-8-02 (m, 4 H, $H_{Aryl}$), 7.99-7.97 (m, 2 H, $H_{Aryl}$), 7.93-7.89 (m, 14 H, $H_{Aryl}$), 7.71 (s, 4 H, $H_{Aryl}$), 7.66-7.63 (m, 4 H, $H_{Aryl}$), 7.59-7.55 (m, 4 H, $H_{Aryl}$), 7.51-7.46 (m, 6 H, $H_{Aryl}$), 7.41-7.34 (m, 10 H, $H_{Aryl}$), 7.29-7.26 (m, 2 H, merged with chlorform signal, $H_{Aryl}$), 7.26-7.21 (m, 4 H, merged with chlorform signal $H_{Aryl}$), 5.29 (d, $^2J$ = 10.6 Hz, 2 H, $H_{methylene}$), 4.41 (d, $^2J$ = 12.4 Hz, 2 H, $H_{methylene}$), 4.05 (d, $^2J$ = 12.8 Hz, 2 H, $H_{methylene}$), 3.88 (d, $^2J$ = 12.7 Hz, 2 H, $H_{methylene}$), 3.36 (br s, 4 H, $H_{isoprppyl}$), 1.28-1.26 (m, 16 H, $H_{isoprppyl}$,), 1.16-1.12 (m, 8 H, $H_{isoprppyl}$).

## 2.9 Synthesis of compound (*S*,*S*)-**8** + (*R*,*R*)-**9**




(*S*,*S*)-**8**x(*R*,*R*)-**9**

First, compound (*S*,*S*)-**8** (2.61 mg, 2.19 µmol, 1 eq), was dissolved in dimethylsulfoxid (0.729 ml), and directly added into a NMR tube. Then compound (*R*,*R*)-**9** in dimethylsulfoxid (75 mM, 7.8 µl, 2.19 µmol, 1 eq), was added and the resulting solution was analyzed by NMR spectroscopy.

Compound (*S*,*S*)-**8** (5.31 mg, 5.11 µmol, 1 eq), was dissolved in chloroform (0.852 ml), and 0.250 ml were transferred into a NMR tube. Compound (*R*,*R*)-**9** (5.71 mg, 4.39 µmol, 1 eq), was dissolved in chloroform (0.732 ml), and 0.250 ml were transferred into the same NMR tube to give an overall concentration of 3 mM of the helix. The solution was analyzed by NMR spectroscopy.

**$^1$H-NMR (500 MHz, [D$_6$]-dimethylsulfoxid, 298 K) δ [in ppm]** = 8.51 (s, 3 H, $H_{Aryl}$), 8.34 (s, 4 H, $H_{Aryl}$), 8.31 (s, 3 H, $H_{Aryl}$), 8.16-8.08 (m, 11 H, $H_{Aryl}$), 8.05-7.98 (m, 23 H, $H_{Aryl}$), 7.81-7.76 (m, 10 H, $H_{Aryl}$), 7.58 (s, 21 H, $H_{Aryl}$), 7.46-7.38 (m, 29 H, $H_{Aryl}$), 7.32-7.26 (m, 24 H, $H_{Aryl}$), 7.17-7.13 (m, 17 H, $H_{Aryl}$), 4.99 (d, $^2J$ = 13.2 Hz, 2 H, $H_{methylene}$), 4.37 (d, $^2J$ = 12.4 Hz, 2 H, $H_{methylene}$), 3.96 (d, $^2J$ = 12.8 Hz, 2 H, $H_{methylene}$), 3.88 (d, $^2J$ = 12.7 Hz, 2 H, $H_{methylene}$), 3.74 (br s, 4 H, $H_{isoprppyl}$), 1.22-1.13 (m, 40 H, $H_{isoprppyl}$, merged with tetrabutylammonium signals), 1.02-1.01 (m, 18 H, $H_{isoprppyl}$).

**$^1$H-NMR (400 MHz, [D$_1$]-chloroform, 298 K) δ [in ppm]** = 9.76 (s, 2 H, $H_{Aryl}$), 8.26 (s, 2 H, $H_{Aryl}$), 8.18 (s, 2 H, $H_{Aryl}$), 8.06-8-7.74 (m, 22 H, $H_{Aryl}$), 7.61-7.48 (m,14 H, $H_{Aryl}$), 7.46-7.33 (m, 17 H, $H_{Aryl}$), 7.32-7.23 (m, 21 H, merged with chlorform signal, $H_{Aryl}$), 5.15 (d, $^2J$ = 10.6 Hz, 2 H, $H_{methylene}$), 4.33-4.10 (m, 4 H, $H_{methylene}$), 3.96-3.78 (m, 6 H, $H_{methylene}$), 3.36 (br s, 4 H, $H_{isoprppyl}$), 1.25-1.00 (m, 24 H, $H_{isoprppyl}$).

# 3 X-Ray crystal structure analyses

The crystals were mounted on nylon loops in inert oil. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated $Mo_{K\alpha}$ radiation, $\lambda$ = 0.71073 Å) at 100(2) K. Data of mt_383m_sq were collected on a Bruker AXS D8 Venture diffractometer with Photon II detector (mono-chromated $Cu_{K\alpha}$ radiation, $\lambda$ = 1.54178 Å, mirco-focus source).The structures were solved by Direct Methods (SHELXS-97)[14] and refined anisotropically by full-matrix least-squares on $F^2$ (SHELXL-2014)[15,16]. Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2/3). Hydrogen atoms were refined using a riding model or rigid methyl groups. The OH hydrogen atoms of fos016_4 and mt_317_2 were refined freely. In fos016_27 the hydrogen atoms of NH groups were refined freely. Those of the methanol molecule were refined using AFIX 147 i.e. rotating refinement with a bond angle fixed to the tetrahedral angle. In case of the disordered molecules they were restraint to point towards the most reasonable H bond acceptor employing a FLAT restraint. This was not possible for H95K. Since its position did not converge properly the refinement was damped to settle its position. In st010_4 the NH hydrogen atoms were refined freely with its NH bond length restraint to 0.87 Å and its displacement parameter constrained to 1.2 times the U eq of the connecting N atom.

In fos016_27 the atoms of the disordered solvent molecules could only be refined isotropically. The phenyl ring of the toluene molecule was constraint to a regular hexagon. Despite the use of distance restraints (SADI, DFIX) in some cases the bond length are not very realistic and should be ignored. The residual electron density suggests further disorder components of methanol 95 which could not be modeled properly. Mt_240_23 and mt_317_2 were refined as an inversion twin. Thus, the enantiopurity of Mt_240_23 cannot be confirmed. In mt_383m_sq the central phenyl ring is disordered over the two-fold axis. Two alternate positions were used in the refinement and the local symmetry was ignored in the refinement (negative PART). The bond lengths were restrained to be equal to 1.39 Å (DFIX, σ = 0.001) and the angle were restrained to be equal (SADI, σ = 0.001). The ring was restrained to planarity (FLAT, σ = 0.001). All atoms of both positions were refined with common displacement parameters (EADP) and the connecting atoms (C30, C30’ and C36, C36’) were constrained to equal positions (EXYZ). In addition, the structure contains highly disordered solvent – possibly methanol. The final refinement was done with a solvent free dataset from a PLATON/SQUEEZE[17] run. Since the nature and amount of the solvent is not clear it was not included in the sum formula. The Flack parameter suggests twinning by inversion, however refining so yields a very high standard uncertainty for the BASF rendering it meaningless. Thus, the twinning model was discarded. The chosen chirality resembles chemical expectation but should not be considered reliable. St_010 contains highly disordered solvent – possibly chloroform. The final refinement was done with a solvent free dataset from a PLATON/SQUEEZE[17] run. Since the nature and amount of the solvent is not clear it was not included in the sum formula.

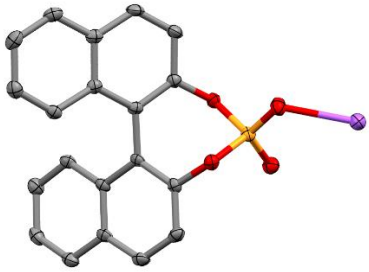


**Figure S4:** Molecular structure of (*rac*)-**1** in the solid state. Only (*S*)-isomer shown, solvent molecules and hydrogen atoms omitted for clarity and thermal ellipsoids set at the 60% probability level.

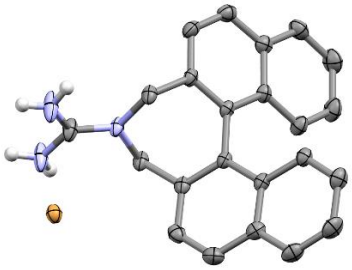


**Figure S5:** Molecular structure of (*rac*)-**2** in the solid state. Only (*S*)-isomer shown, hydrogen atoms omitted for clarity and thermal ellipsoids set at the 60% probability level.

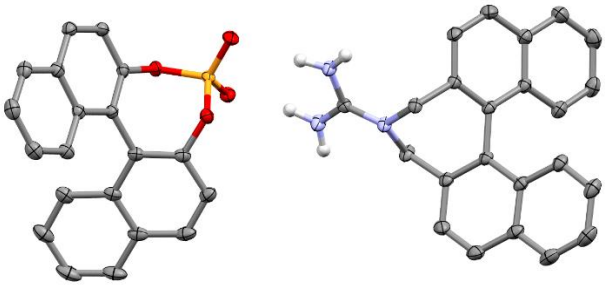


**Figure S6:** Molecular structure of complex (*rac*)-**1** + (*rac*)-**2** in the solid state. Only (*S*,*S*)-isomer shown, solvent molecules and hydrogen atoms omitted for clarity and thermal ellipsoids set at the 60% probability level.

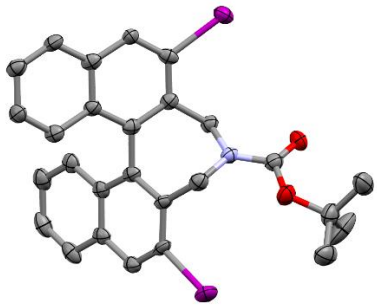


**Figure S7:** Molecular structure of (*S*)-**4** in the solid state. Solvent molecules and hydrogen atoms omitted for clarity and thermal ellipsoids set at the 50% probability level.

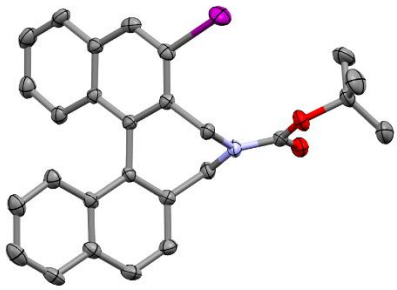


**Figure S8:** Molecular structure of (*R*)-**5** in the solid state. Hydrogen atoms omitted for clarity and thermal ellipsoids set at the 50% probability level. Monoiodide **5** was analyzed as the (*R*)-isomer because suitable crystals could only be obtained in this case.

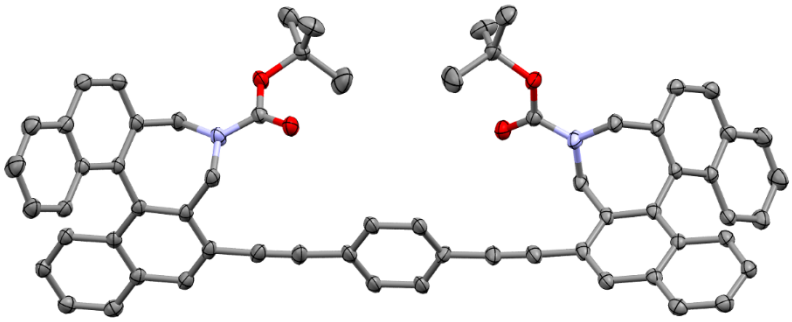


**Figure S9:** Molecular structure of (*S*,*S*)-**6** in the solid state. Hydrogen atoms omitted for clarity and thermal ellipsoids set at the 50% probability level. Only one orientation of the disorder is displayed for clarity.

**Table S1:** Details of the X-ray crystal structure analyses of (*rac*)-**1**, (*rac*)-**2** and (*S*)-**5**.

| **Compound** | (*rac*)-**1** | (*rac*)-**1** + (*rac*)-**2** | (*S*)-**5** |
|---|---|---|---|
| **Identification code** | **fos016_4m** | **fos016_27m** | **mt_240_23_mom** |
| **CCDC-Number** | 2078130 | 2078131 | 2078132 |
| Empirical formula | $C_{22}H_{20}NaO_6P$ | $C_{44.92}H_{38.29}N_3O_{5.43}P$ | $C_{27}H_{24}I\ NO_2$ |
| *M* | 434.34 | 738 | 521.37 |
| Crystal size [mm] | 0.325 × 0.189 × 0.076 | 0.259 × 0.258 × 0.201 | 0.378 × 0.246 × 0.192 |
| *T* [K] | 100(1) | 100(1) | 100(2) |
| Crystal system | monoclinic | triclinic | monoclinic |
| Space group | $P2_1/c$ | $P\ \bar{1}$ | $P2_1$ |
| *a* [Å] | 19.211(2) | 18.1178(12) | 10.158(5) |
| *b* [Å] | 8.5749(9) | 19.5762(12) | 9.420(4) |
| *c* [Å] | 12.3647(13) | 22.3911(12) | 12.633(5) |
| *α* [°] | 90 | 80.708(3) | 90 |
| *β* [°] | 97.328(7) | 72.212(2) | 108.94(2) |
| *γ* [°] | 90 | 86.459(3) | 90 |
| *V* [Å$^3$] | 2020.2(4) | 7462.1(8) | 1143.4(8) |
| *Z* | 4 | 8 | 2 |
| $D_{calc}$ [g·cm$^{-1}$] | 1.428 | 1.314 | 1.514 |
| $\mu$(Mo$K\alpha$ [mm$^{-1}$]) | 0.195 | 0.127 | 1.424 |
| Transmissions | 1/0.77 | 0.75/0.68 | 0.75/0.51 |
| *F*(000) | 904 | 3098 | 524 |
| Index ranges | $-28 \le h \le 27$ | $-27 \le h \le 27$ | $-15 \le h \le 15$ |
| | $-12 \le k \le 9$ | $-27 \le k \le 27$ | $-14 \le k \le 13$ |
| | $-17 \le l \le 18$ | $-32 \le l \le 33$ | $-19 \le l \le 19$ |
| $\vartheta_{max}$ [°] | 33.235 | 33.203 | 33.14 |
| Reflections collected | 20004 | 153929 | 40148 |
| Independent reflections | 6780 | 50065 | 8111 |
| $R_{int}$ | 0.0491 | 0.0315 | 0.0541 |
| Refined parameters | 281 | 2038 | 284 |
| $R_1$ [$I > 2\sigma(I)$] | 0.049 | 0.0545 | 0.0544 |
| $wR_2$ [all data] | 0.1348 | 0.1584 | 0.1386 |
| *x*(Flack) | | | 0.22(3) |
| GooF | 1.011 | 1.032 | 1.052 |
| $\Delta\rho_{final}$ (max/min) [e·Å$^{-3}$] | 0.454/-0.618 | 1.466/-0.801 | 2.000/-1.129 |

**Table S2:** Details of the X-ray crystal structure analyses of (*S*,*S*)-**6**, (*S*)-**4** and (*rac*)-**2**.

| **Compound** | (*S,S*)-**6** | (*S*)-**4** | (*rac*)-**2** |
|---|---|---|---|
| **Identification code** | **mt_317_2m** | **mt_383m_sq** | **st010_4m** |
| **CCDC-Number** | 2078133 | 2078134 | 2078135 |
| Empirical formula | $C_{28}H_{27}I_2NO_3$ | $C_{64}H_{52}N_2O_4$ | $C_{23}H_{20}BrN_3$ |
| *M* | 679.3 | 913.07 | 418.33 |
| Crystal size [mm] | 0.261 × 0.173 × 0.011 | 0.101 × 0.079 × 0.052 | 0.173 × 0.125 × 0.095 |
| *T* [K] | 100(2) | 104(2) | 100(1) |
| Crystal system | monoclinic | tetragonal | triclinic |
| Space group | $P2_1$ | $P4_32_12$ | *P* -1 |
| *a* [Å] | 11.8508(16) | 10.0422(3) | 8.8577(2) |
| *b* [Å] | 9.1039(12) | 10.0422(3) | 8.9307(2) |
| *c* [Å] | 13.2298(17) | 53.3248(16) | 18.7699(4) |
| *α* [°] | 90 | 90 | 91.7000(10) |
| *β* [°] | 115.219(6) | 90 | 93.9750(10) |
| *γ* [°] | 90 | 90 | 108.2000(10) |
| *V* [Å$_3$] | 1291.3(3) | 5377.6(4) | 1405.06(5) |
| *Z* | 2 | 4 | 2 |
| $D_{calc}$ [g·cm$^{-3}$] | 1.747 | 1.128 | 0.989 |
| $\mu$(Cu$K\alpha$ [mm$^{-1}$]) | 19.363 | 0.547 | 1.471 |
| Transmissions | 0.75/0.44 | 0.75/0.68 | 0.75/0.61 |
| *F*(000) | 664 | 1928 | 428 |
| Index ranges | -15 ≤ *h* ≤ 15 | -12 ≤ *h* ≤ 12 | -10 ≤ *h* ≤ 13 |
| | -11 ≤ *k* ≤ 10 | -11 ≤ *k* ≤ 12 | -13 ≤ *k* ≤ 9 |
| | -16 ≤ *l* ≤ 16 | -68 ≤ *l* ≤ 66 | -28 ≤ *l* ≤ 27 |
| $\vartheta_{max}$ [°] | 81.331 | 79.876 | 32.575 |
| Reflections collected | 49382 | 84164 | 38397 |
| Independent reflections | 5431 | 5790 | 9887 |
| $R_{int}$ | 0.0778 | 0.0412 | 0.033 |
| Refined parameters | 316 | 328 | 260 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0427 | 0.0453 | 0.0464 |
| $wR_2$ [all data] | 0.1088 | 0.1217 | 0.1212 |
| *x*(Flack) | 0.163(12) | 0.24(5) | |
| GooF | 1.064 | 1.028 | 1.052 |
| $\Delta\rho_{final}$ (max/min) [e·Å$^{-3}$] | 2.152/-0.577 | 0.521/-0.574 | 0.851/-0.381 |

# 4 NMR-Titrations

## 4.1 Titration experiments

### 4.1.1 Titration of (S)-**8**

To perform the $^{1}$H NMR titration, stock solutions of compounds (*S*,*S*)-**8** - (*S*,*S*)-**9**, the guanidine bis-tetrafluoric acid salt [(*S*,*S*)-$\mathbf{8}^{2+}(TFA^{-})_2$, host] (3 mM) and the ammoniumphosphates [(*R*,*R*)-$\mathbf{9}^{2-}(Bu_4N^{+})_2$] and [(*S*,*S*)-$\mathbf{9}^{2-}(Bu_4N^{+})_2$, guest] (75 mM) were prepared in [$D_1$]-chloroform. [$D_1$]-chloroform was treated with basic Alox before use. The titration was performed as detailed below. All samples were prepared by subsequent addition of the guest stock solution (samples 1-13).

**Table S3:** Titration protocol.

| Sample No | Eq Guest to Host | V (Guest) added [µl] | V (Host) [ml] | V (Solvent) [ml] | V (total) [ml] |
|---|---|---|---|---|---|
| 1 | 0 | 0.00 | 0.2 | 0.4 | 0.600 |
| 2 | 0.1 | 0.80 | | | 0.601 |
| 3 | 0.2 | 0.80 | | | 0.602 |
| 4 | 0.35 | 1.20 | | | 0.603 |
| 5 | 0.5 | 1.20 | | | 0.604 |
| 6 | 0.65 | 1.20 | | | 0.605 |
| 7 | 0.8 | 1.20 | | | 0.606 |
| 8 | 1 | 1.60 | | | 0.608 |
| 9 | 1.15 | 1.20 | | | 0.609 |
| 10 | 1.3 | 1.20 | | | 0.610 |
| 11 | 1.5 | 1.60 | | | 0.612 |
| 12 | 1.8 | 2.40 | | | 0.614 |
| 13 | 2 | 1.60 | | | 0.616 |

## 4.1.2 NMR stacked plots

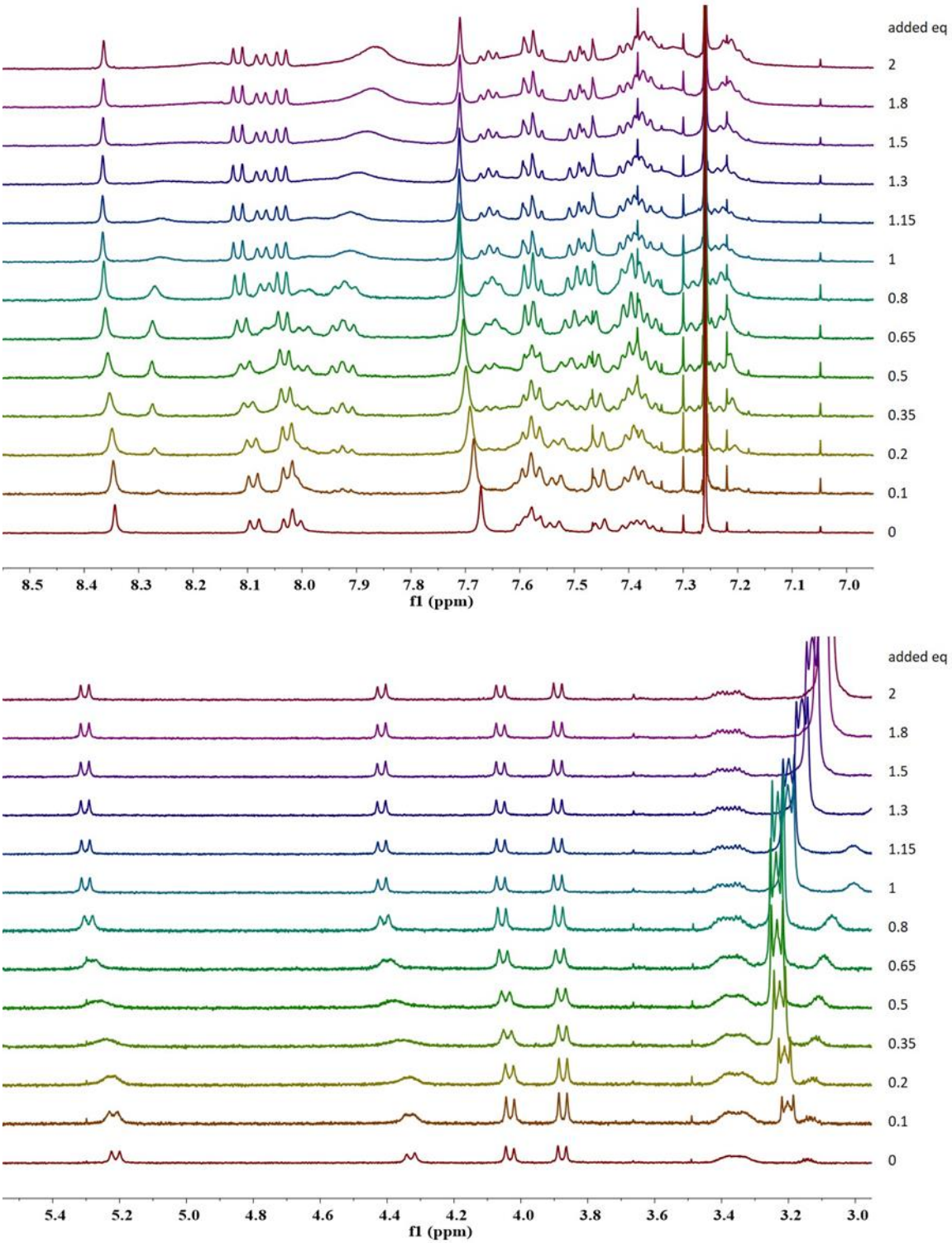



**Figure S10:** Stacked NMR spectra (top: aromatic region, bottom: aliphatic region) for the binding of [(*S*,*S*)-**9**$^{2-}$($Bu_4N^+$)$_2$] (0.10 to 2 equivalents) to [(*S*,*S*)-**8**$^{2+}$($TFA^-$)$_2$] [all: 500 MHz, [$D_1$]-chloroform, 298K, initial concentration of [(*S*,*S*)-**8**$^{2+}$($TFA^-$)$_2$]: 1 mM].

The chemical shift of H-22$_{1/2}$ was used for the construction of the binding isotherms.

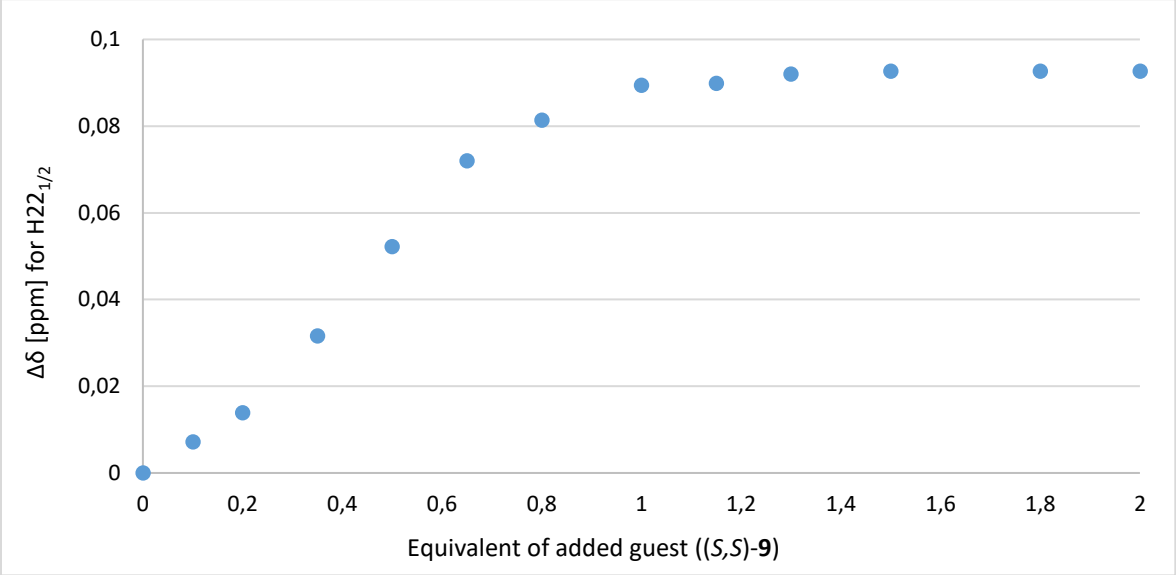



**Figure S11:** Binding isotherm for the binding of (*S,S*)-**9** (as $(Bu_4N^+)_2$ -salt) to (*S,S*)-**8** (as $(TFA^-)_2$ salt) in [$D_1$]-chloroform [initial concentration of host: 1 mM, plotted for H-22.

**Table S4:** The added equivalents of (*S,S*)-**9**$^{2-}$(Bu4N$^+$)$_2$], the measured chemical shifts are given, and the change in chemical shift (Δδ) of the titration of [(*S,S*)-**9**$^{2-}$(Bu4N$^+$)$_2$]) to [(*S,S*)-**8**$^{2+}$(TFA$^-$)$_2$] are given.

| equivalents of (*S,S*)-**9** to (*S,S*)-**8** | δ H22$_{1/2}$ (ppm) | Δδ H22$_{1/2}$ (ppm) |
|---|---|---|
| 0 | 5.2115 | 0 |
| 0.1 | 5.2187 | 0.0072 |
| 0.2 | 5.2254 | 0.0139 |
| 0.35 | 5.2431 | 0.0316 |
| 0.5 | 5.2637 | 0.0522 |
| 0.65 | 5.2835 | 0.072 |
| 0.8 | 5.2929 | 0.0814 |
| 1 | 5.3009 | 0.0894 |
| 1.15 | 5.3014 | 0.0899 |
| 1.3 | 5.3035 | 0.092 |
| 1.5 | 5.3042 | 0.0927 |
| 1.8 | 5.3042 | 0.0927 |
| 2 | 5.3042 | 0.0927 |

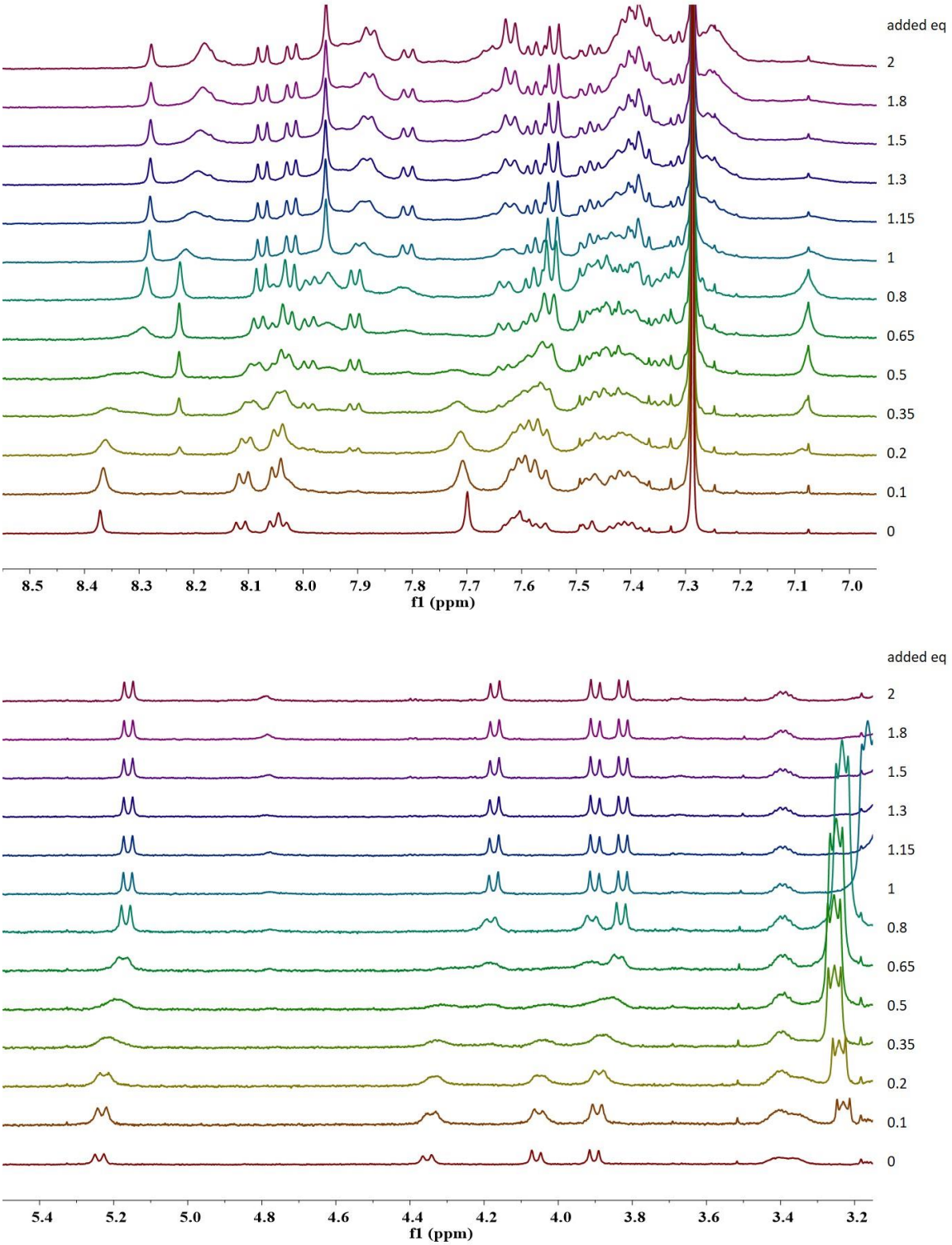



**Figure S12:** Stacked NMR spectra (top: aromatic region, bottom: aliphatic region) for the binding of [(*R*,*R*)-**9**$^{2-}$($Bu_4N^+$)$_2$](0.10 to 2 equivalents) to [(*S*,*S*)-**8**$^{2+}$($TFA^-$)$_2$] [all: 500 MHz, [$D_1$]-chloroform, 298K, initial concentration of [(*S*,*S*)-**8**$^{2+}$($TFA^-$)$_2$]: 1 mM].

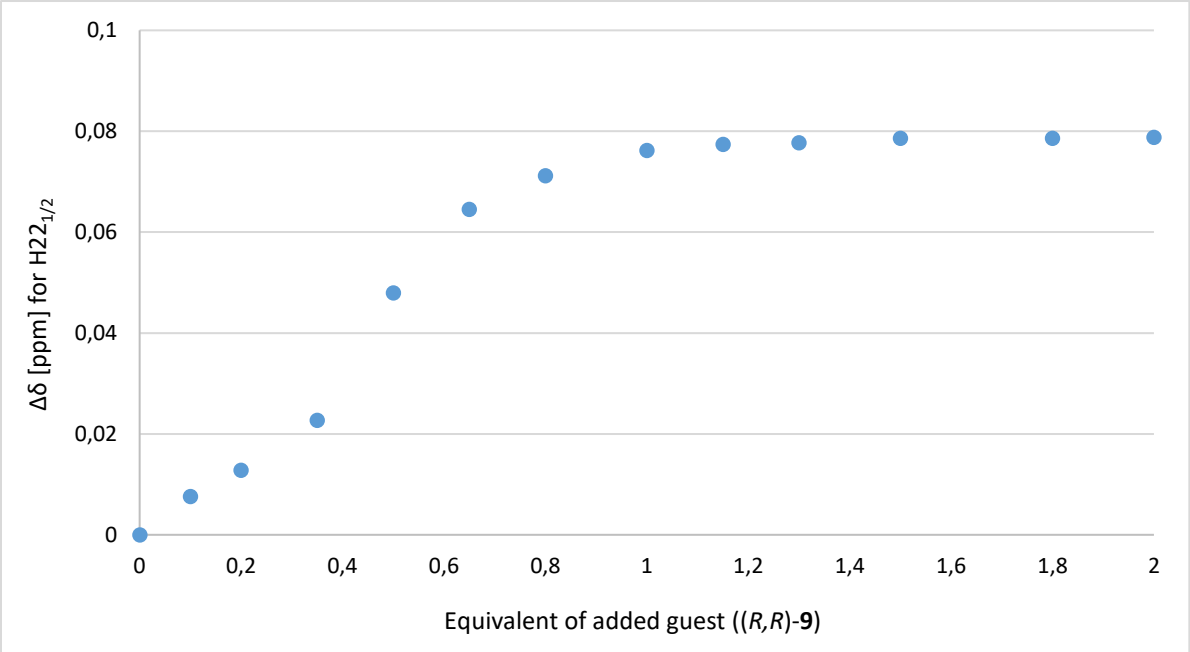



**Figure S13:** Binding isotherm for the binding of (*R*,*R*)-**9** (as $(Bu_4N^+)_2$ -salt) to (*S*,*S*)-**8** (as $(TFA^-)_2$ salt) in [$D_1$]-chloroform [initial concentration of host: 1 mM, plotted for H-22.

**Table S5:** The added equivalents of (*R*,*R*)-$\mathbf{9}^{2-}(Bu4N^+)_2$], the measured chemical shifts are given, and the change in chemical shift (Δδ) of the titration of [(*R*,*R*)-$\mathbf{9}^{2-}(Bu4N^+)_2$]) to [(*S*,*S*)-$\mathbf{8}^{2+}(TFA^-)_2$] are given.

| equivalents of (*R*,*R*)-**9** to (*S*,*S*)-**8** | δ H22$_{1/2}$ (ppm) | Δδ H22$_{1/2}$ (ppm) |
|---|---|---|
| 0 | 5.2389 | 0 |
| 0.1 | 5.2313 | 0.0076 |
| 0.2 | 5.2261 | 0.0128 |
| 0.35 | 5.2162 | 0.0227 |
| 0.5 | 5.1909 | 0.048 |
| 0.65 | 5.1744 | 0.0645 |
| 0.8 | 5.1677 | 0.0712 |
| 1 | 5.1627 | 0.0762 |
| 1.15 | 5.1615 | 0.0774 |
| 1.3 | 5.1612 | 0.0777 |
| 1.5 | 5.1603 | 0.0786 |
| 1.8 | 5.1603 | 0.0786 |
| 2 | 5.1601 | 0.0788 |

## 4.2 Data analysis

The sigmoidal binding isotherms indicate competitive displacement of the triflate counterions from the bisguanidinium-salt (*S*,*S*)-**8** upon addition of the bisphosphates (*S*,*S*)-**9** / (*R*,*R*)-**9**. Thus, we did not determine absolute association constants of the bisphosphate-guests to the bisguanidinium-host, but used Leito´s method for relative binding constant determination.[18] This is based on determination of the relative molar fraction of complex (*S*,*S*)-**8** + (*S*,*S*)-**9** and (*S*,*S*)-**8** + (*R*,*R*)-**9** at identical stoichiometries of the components, determined from the chemical shift Δδ in relation to the maximum chemical shift Δδmax observed at the end of the titration.

**Table S6:** Determination of the relative binding constants of the complexes (*S*,*S*)-**8**+(*S*,*S*)-**9** and (*S*,*S*)-**8**+(*R*,*R*)-**9**

| titration No | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| equivalents of **9** | 0 | 0.1 | 0.2 | 0.35 | 0.5 | 0.65 | 0.8 | 1 | 1.15 | 1.3 | 1.5 | 1.8 | 2 | |
| δ ($^1$H) for (*S*,*S*)-**9** | 5.212 | 5.219 | 5.225 | 5.243 | 5.264 | 5.284 | 5.293 | 5.301 | 5.301 | 5.304 | 5.304 | 5.304 | 5.304 | |
| Δδ ($^1$H) for (*S*,*S*)-**9** | 0 | 0.007 | 0.014 | 0.032 | 0.052 | 0.072 | 0.081 | 0.089 | 0.090 | 0.092 | 0.093 | 0.093 | 0.093 | = Δδmax |
| δ ($^1$H) for (*R*,*R*)-**9** | 5.239 | 5.231 | 5.226 | 5.216 | 5.191 | 5.174 | 5.168 | 5.163 | 5.162 | 5.161 | 5.160 | 5.160 | 5.160 | |
| Δδ ($^1$H) for (*R*,*R*)-**9** | 0 | -0.008 | -0.013 | -0.023 | -0.048 | -0.064 | -0.071 | -0.076 | -0.077 | -0.078 | -0.079 | -0.079 | -0.079 | = Δδmax |
| α = Δδ / Δδmax for (*S*,*S*)-**9** | 0 | 0.078 | 0.150 | 0.341 | 0.563 | 0.777 | 0.878 | 0.964 | 0.970 | 0.992 | 1 | 1 | 1 | |
| α = Δδ / Δδmax for (*R*,*R*)-**9** | 0 | 0.096 | 0.162 | 0.288 | 0.609 | 0.819 | 0.904 | 0.967 | 0.982 | 0.986 | 0.997 | 0.997 | 1 | |
| K(A)/K(B) | - | 0.7889 | 0.9095 | 1.2782 | 0.827 | 0.7711 | 0.7689 | 0.9244 | 0.5807 | 1.8606 | - | - | - | |

Mean: 0.90 +- 0.1803

# 5 DOSY NMR

## 5.1 Experimenal data

The $^{1}$H DOSY NMR experiments were run on a Bruker Avance Neo II 500 MHz spectrometer (Bruker BioSpin, Rheinstetten, Germany) at a hydrogen resonance frequency of 500 MHz. Simple single-pulse excitation was used to obtain hydrogen line spectra. An external standard was used for a reliable determination of the chemical shifts. Spin-lattice relaxation times were determined in a conventional inversion recovery experiment.

$^{1}$H NMR diffusion experiments were run with a Bruker DIFBBI probe head. All measurements were performed at 298 K. For all measurements, the stimulated echo pulse sequence with two gradient pulses was used. 64 scans were accumulated for each setting. The time between two gradient pulses Δ was 25 ms. The gradients were adjusted to strengths G between 1 and 150 G/cm with a duration δ of 1.0 ms. All measurements (the full set of gradient strengths under the variation from 1 to 150 G/cm) were repeated two times.

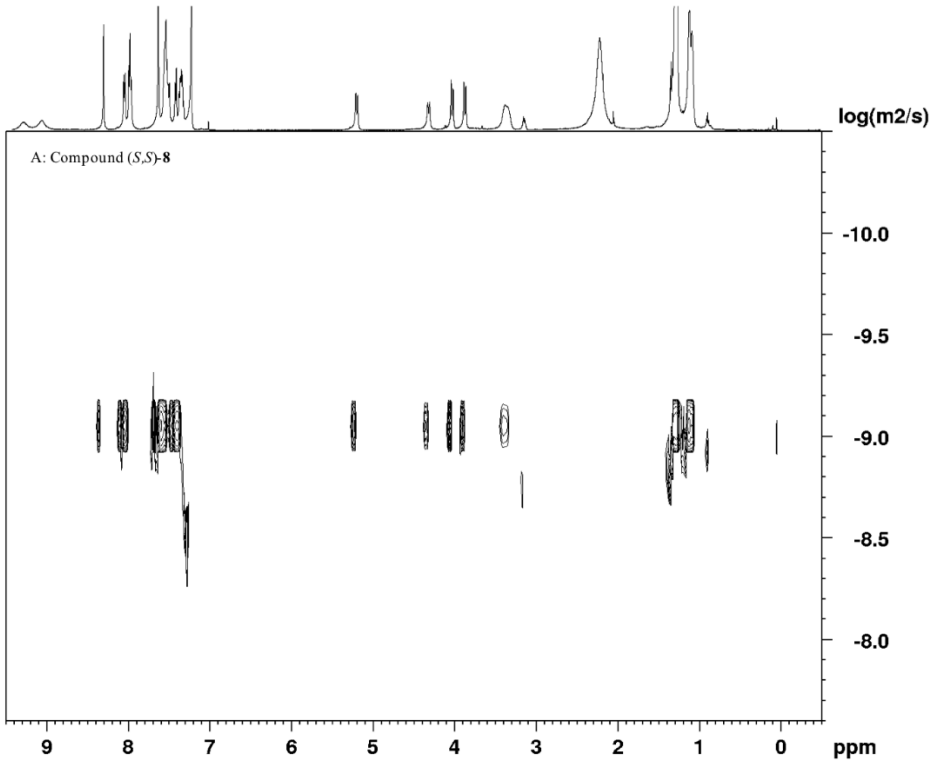



**Figure S14:** DOSY plot of compound (*S*,*S*)-**8** (3 mM, $CDCl_3$, 500 MHz, 298K).

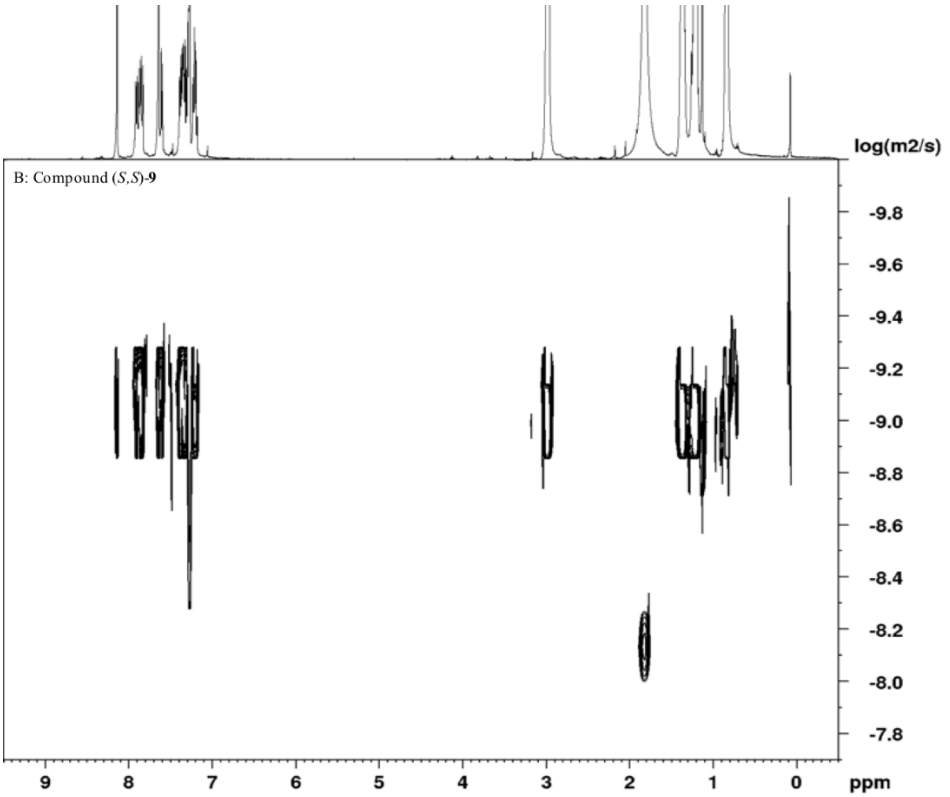



**Figure S15:** DOSY plot of compound (*S*,*S*)-**9** (3 mM, $CDCl_3$, 500 MHz, 298K).

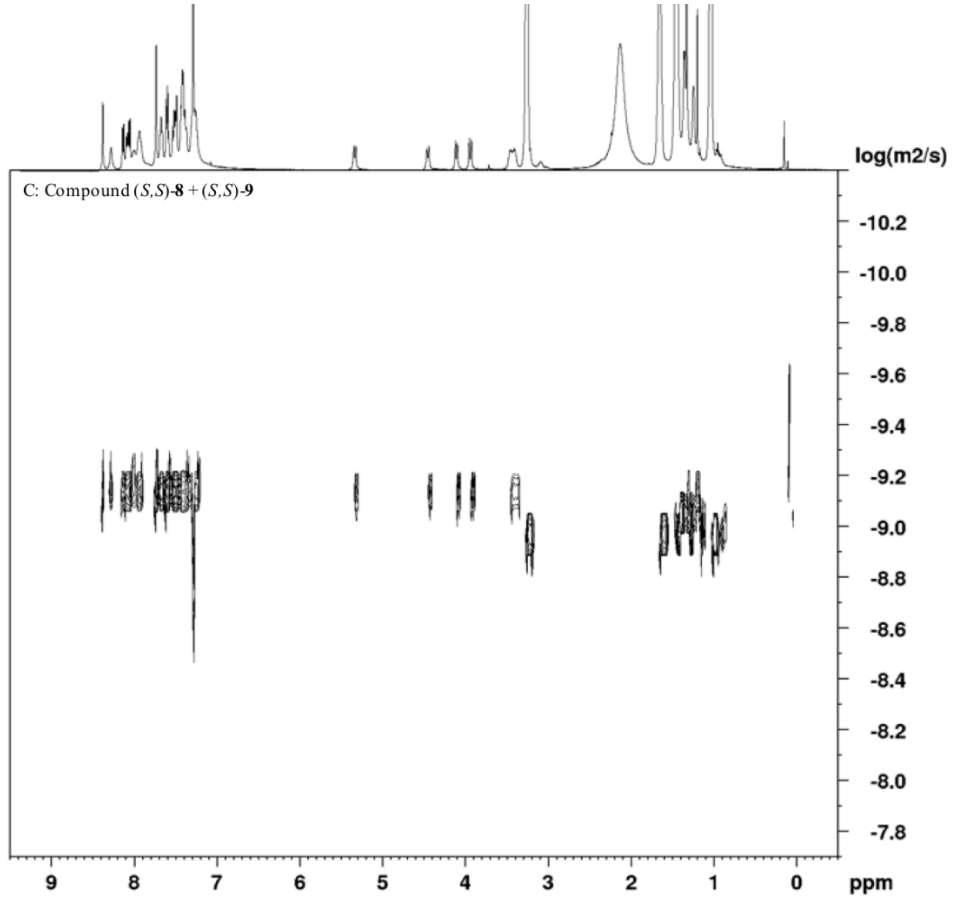



**Figure S16:** DOSY plot of complex (*S*,*S*)-**8** + (*S*,*S*)-**9** (each 3 mM, $CDCl_3$, 500 MHz, 298K).

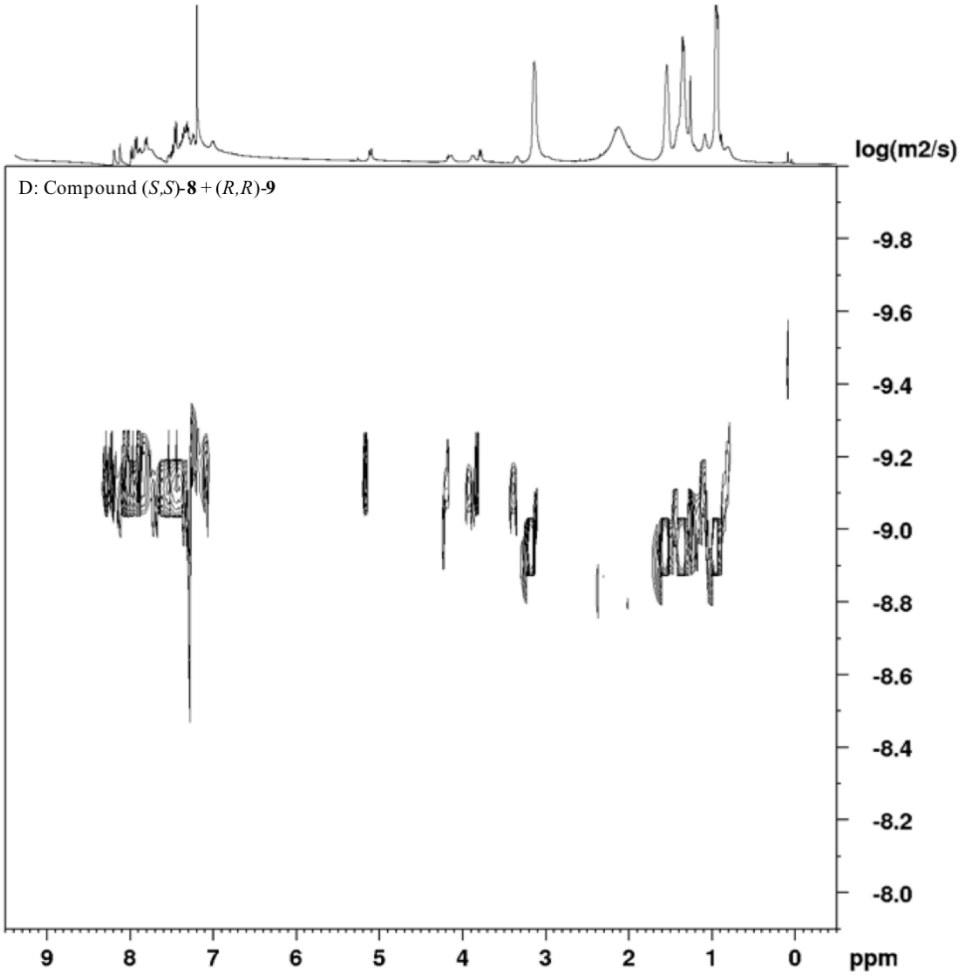



**Figure S17:** DOSY plot of complex (*S*,*S*)-**8** + (*R*,*R*)-**9** (each 3 mM, $CDCl_3$, 500 MHz, 298K).

**Table S7:** Diffusion coefficients as determined per DOSY NMR. All measurements were performed in [$D_1$]-chloroform at 298 K.

| Compound | | (*S*,*S*)-**8** | | (*S*,*S*)-**9** | | (*S*,*S*)-**8** + (*S*,*S*)-**9** | | (*S*,*S*)-**8** + (*R*,*R*)-**9** | |
|---|---|---|---|---|---|---|---|---|---|
| **Assignment** | **Integral region** | **Diffusion coefficient** | **Mean diffusion coefficient** | **Diffusion coefficient** | **Mean diffusion coefficient** | **Diffusion coefficient** | **Mean diffusion coefficient** | **Diffusion coefficient** | **Mean diffusion coefficient** |
| | **[ppm]** | **[$10^{-10}$ $m^2s^{-1}$]** | **[$10^{-10}$ $m^2s^{-1}$]** | **[$10^{-10}$ $m^2s^{-1}$]** | **[$10^{-10}$ $m^2s^{-1}$]** | **[$10^{-10}$ $m^2s^{-1}$]** | **[$10^{-10}$ $m^2s^{-1}$]** | **[$10^{-10}$ $m^2s^{-1}$]** | **[$10^{-10}$ $m^2s^{-1}$]** |
| Aromatic signals | 8.4 | 6.78 | 6.79 ± 0.32 | - | 6.27 ± 0.05 | 6.01 | 6.00 ± 0.14 | - | 6.05 ± 0.23 |
| | 8.3 | - | | - | | 5.77 | | 6.03 | |
| | 8.2 | - | | - | | 6.02 | | 5.76 | |
| | 8.1 | 7.00 | | 6.25 | | 5.99 | | 6.09 | |
| | 8.0 | 6.96 | | 6.23 | | 5.78 | | 6.04 | |
| | 7.9 | - | | 6.33 | | - | | 5.79 | |
| | 7.7 | 6.91 | | - | | 6.00 | | - | |
| | 7.6 | - | | - | | 5.95 | | 6.17 | |
| Benzylic signals | 5.2-5.3 | 6.93 | | - | | 6.06 | | 6.07 | |
| | 4.2-4.4 | 6.09 | | - | | 6.11 | | - | |
| | 3.8-3.9 | - | | - | | 6.06 | | 6.00 | |
| | 3.4 | 6.87 | | - | | 6.28 | | 6.54 | |
| Tetrabutyl-ammonium signals | 1.4 | - | - | - | 6.89 ± 0.09 | 8.33 | 8.77 ± 0.60 | 8.71 | 8.69 ± 0.35 |
| | 1.2 | - | | 6.95 | | 8.53 | | 8.33 | |
| | 1.0 | - | | 6.82 | | 9.46 | | 9.03 | |

## 5.2 Calculated hydrodynamic radii

The dimensions of the resulting structures were estimated by determining the widths and heights of the structures (see figure S37 to S41), based on the DFT-calculated structures (see chapter 7). The resulting average value was used to calculate the hydrodynamic radii based on the Stokes-Einstein equation for spherical particles (see table S2).

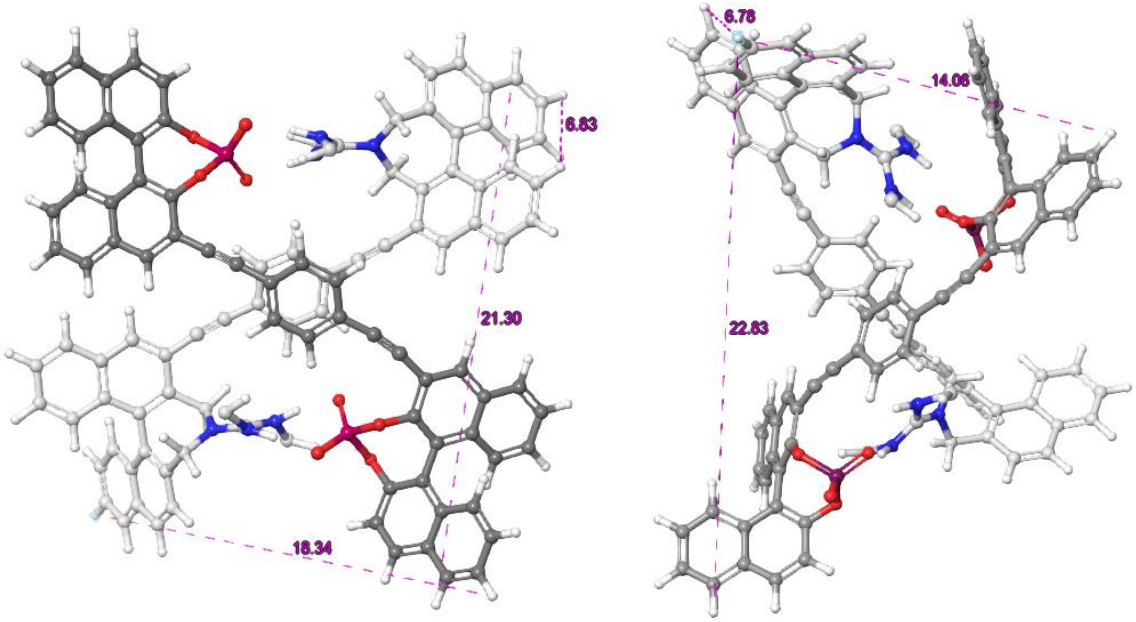



**Figure S 18**: Left: Dimensions of the complex (*S*,*S*)-**8** + (*S*,*S*)-**9** (calculated average diameter for both structures: $r_{mean}$ = 15.5 Å). Right: Dimensions of the complex (*S*,*S*)-**8** + (*R*,*R*)-**9** (calculated average diameter for both structures: $r_{mean}$ = 14.5 Å).

**Table S 8:** Diffusion coefficients as determined per DOSY-NMR and calculated using the Stokes-Einstein-equation a) determined by NMR ($CDCl_3$, 500 MHz, 298 K) b) Calculated using the Stokes-Einstein-equation based on the dimensions of the DFT-calculated molecular structures.

| Complex | DOSY[(a)] D [$10^{-10}$ $m^2$ $s^{-1}$] | Calculated[(b)] D [$10^{-10}$ $m^2$ $s^{-1}$] |
|---|---|---|
| (*S*,*S*)-**8** + (*S*,*S*)-**9** | 5.2[(d)] | 6.0 |
| (*S*,*S*)-**8** + (*R*,*R*)-**9** | 5.5 | 6.1 |

# 6 Circular dichroism

## 6.1 CD measurements

In order to further characterize the structures of (*S*,*S*)-**8**+(*S*,*S*)-**9** and (*S*,*S*)-**8**+(*R*,*R*)-**9**, we carried out ECD measurements. To perform ECD measurements stock solutions of (*S*,*S*)-**8**, (*S*,*S*)-**9** and (*R*,*R*)-**9** (1 mM each) were prepared. Stock solutions were used to prepare the samples with concentrations of 10 µM in chloroform. The samples were measured at 25 °C.

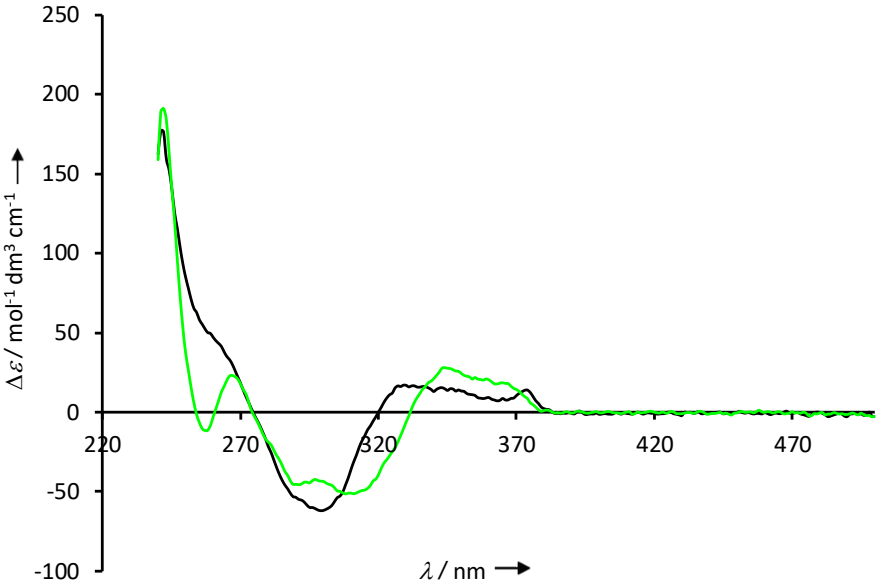



**Figure S19:** CD spectra of the monomers (*S*,*S*)-**8** (green) and (*S*,*S*)-**9** (black) in $CHCl_3$ (c = $10^{-5}$ M).

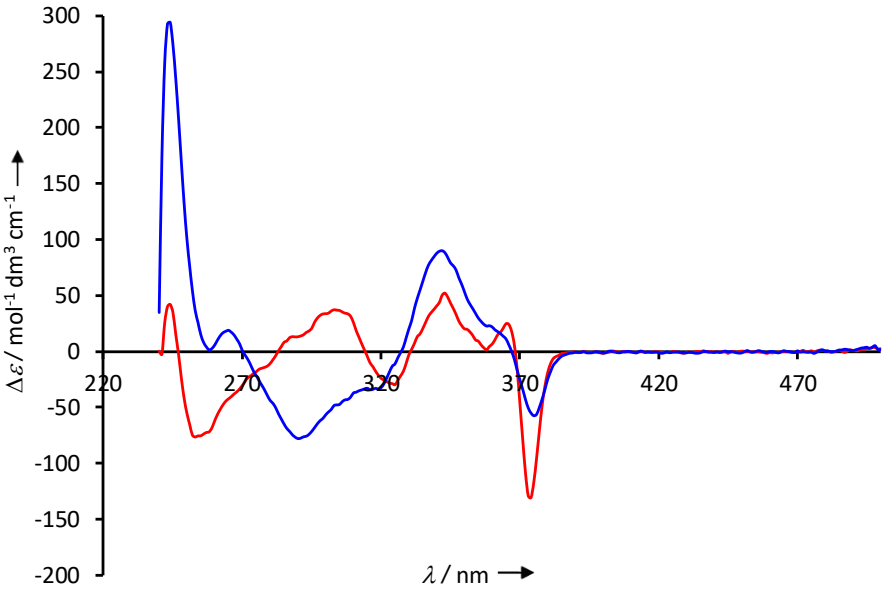



**Figure S20:** CD spectra of the homochiral complex (*S*,*S*)-**8**+(*S*,*S*)-**9** (blue) and the heterochiral complex (*S*,*S*)-**8**+(*R*,*R*)-**9** (red) in $CHCl_3$ (c = $10^{-5}$ M).

# 7 Calculated structures and CD spectra

## 7.1 Computational details

All calculations were performed by using the program package Gaussian 16[19]. The geometrical parameters of all stationary points were optimized by means of the density functional B3LYP[20-22] together with the dispersion correction with Becke-Johnson damping[23] (D3BJ). As basis set 6-31G(d) was applied. In order to take solvent effects into account, chloroform was considered as solvent by using the SMD[24] model. For all structures C1 symmetry was applied. Frequency calculations were carried out at each of the stationary points to verify the nature of the stationary point. It turned out that all stationary states have no imaginary frequency. The CD spectra were simulated with time-dependent density functional theory (TD-DFT), using the functional cam-B3LYP[25], the basis set 6-31G* and the SMD model (chloroform as solvent). The energy, oscillator strength, and rotatory strength were calculated for each of the 150 lowest singlet excitations

## 7.2 Structures of the monomers and dimers

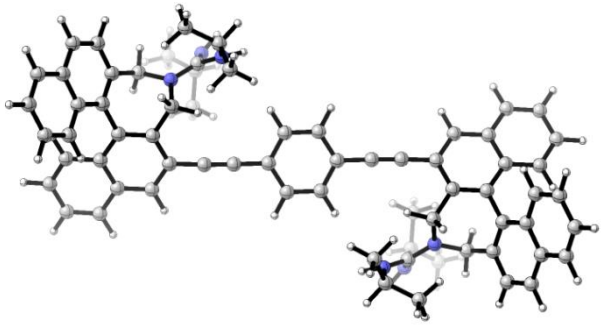


**Figure S21:** Molecular structures (CYLview20) of the cationic part of (S,S)-8 calculated by means of B3LYP-D3BJ(SMD)/6-31G*. Color codes: grey, carbon; white, hydrogen; blue, nitrogen.

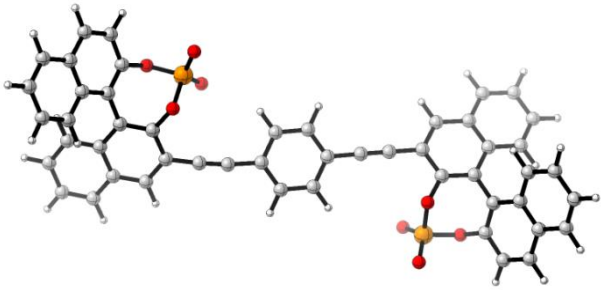


**Figure S22:** Molecular structures (CYLview20) of the anionic part of (S,S)-9 calculated by means of B3LYP-D3BJ(SMD)/6-31G*. Color codes: grey, carbon; white, hydrogen; brown, phosphorus; red, oxygen.

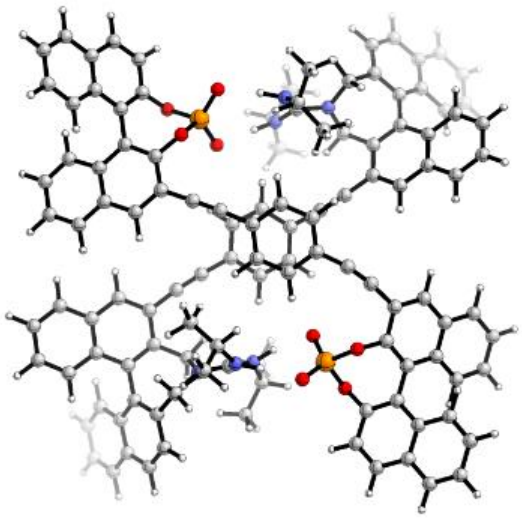


**Figure S23:** Molecular structure (CYLview20) of the homochiral complex (*S*,*S*)-**8**+(*S*,*S*)-**9** calculated by means of B3LYP-D3BJ(SMD)/6-31G*. Color codes: grey, carbon; white, hydrogen; brown, phosphorus; blue, nitrogen; red, oxygen.

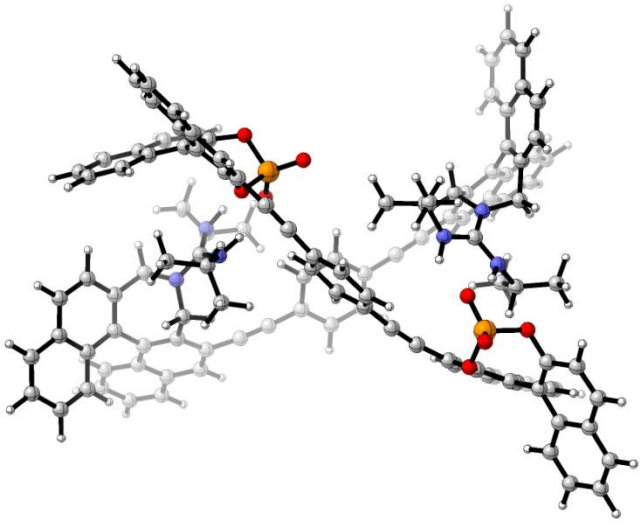


**Figure S24:** Molecular structure (CYLview20) of the heterochiral complex (*S*,*S*)-**8**+(*R*,*R*)-**9** calculated by means of B3LYP-D3BJ(SMD)/6-31G*. Color codes: grey, carbon; white, hydrogen; brown, phosphorus; blue, nitrogen; red, oxygen.

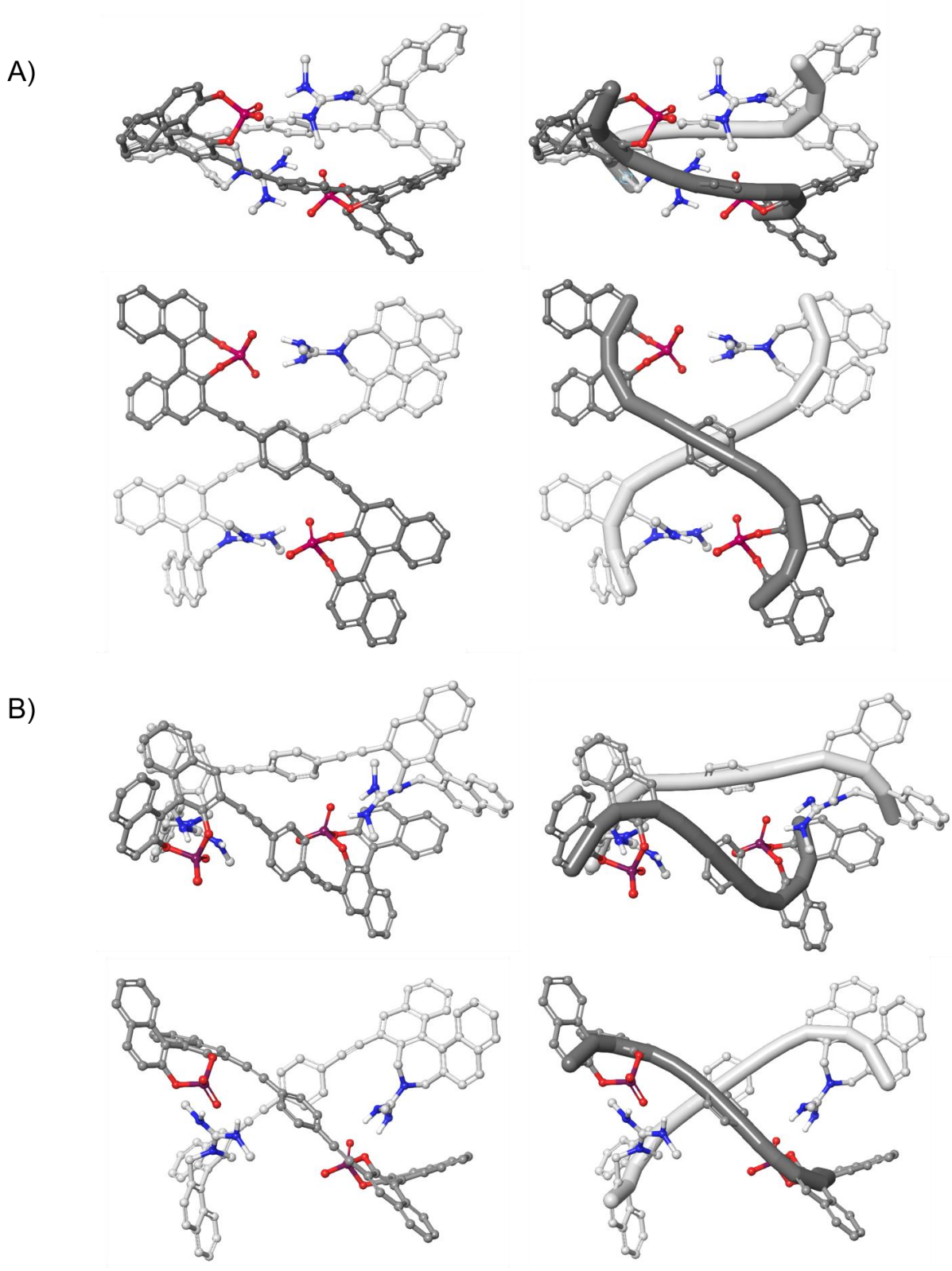



**Figure S25:** Molecular structures of the dimeric complexes as calculated by means of B3LYP-D3BJ(SMD)/6-31G* (C atoms: light grey for (*S*,*S*)-**8**, dark grey for (*S*,*S*)/(*R*,*R*)-**9**, N atoms: blue, O atoms: red, P-atoms: orange, nonpolar hydrogen-atoms and Me-groups omitted for clarity. A) Top-view and side-view of the double-helical homochiral complex (*S*,*S*)-**8**+(*S*,*S*)-**9**. B) Top-view and side-view of the on-helical heterochiral complex (*S*,*S*)-**8**+(*R*,*R*)-**9**. The structures on the right show the C3´ C1´ C1-C3-C11-C12-C13-C13-C12-C11-C3-C1-C1´-C3´ trajectory highlighted for each subunit, for numbering see figure 3 in the main paper).

## 7.3 Calculated transition orbitals

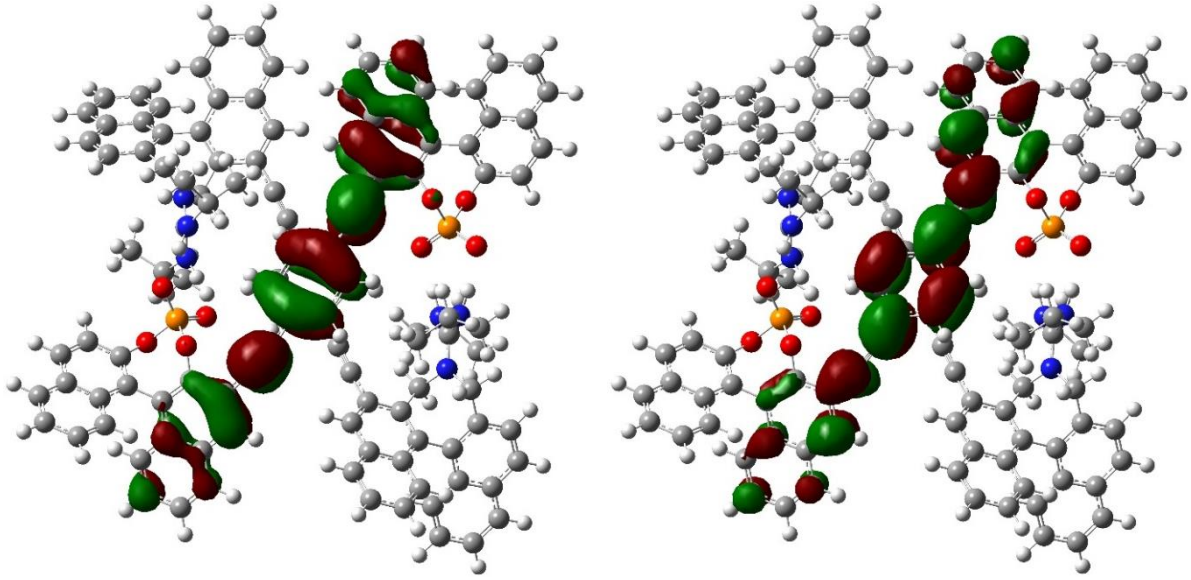


**Figure S26:** Occupied (left) and virtual (right) natural transition orbitals of the π-π* band at 355 nm of the homochiral complex (*S*,*S*)-**8**+(*S*,*S*)-**9** calculated by means of TD-cam-B3LYP(SMD)/6-31G*.

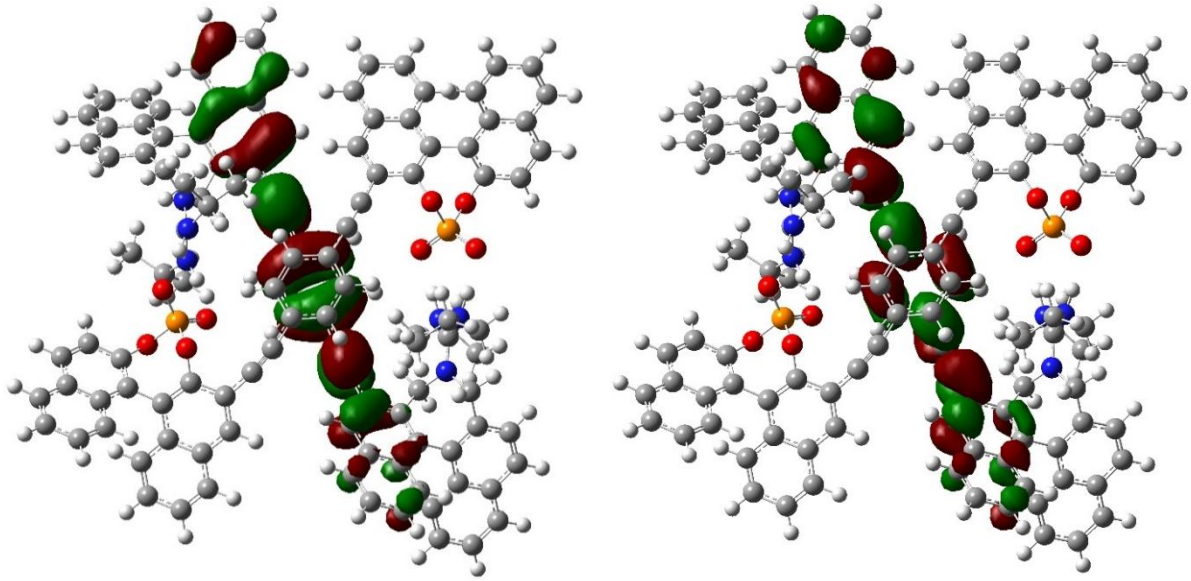


**Figure S27:** Occupied (left) and virtual (right) natural transition orbitals of the π-π* band at 343 nm of the homochiral complex (*S*,*S*)-**8**+(*S*,*S*)-**9** calculated by means of TD-cam-B3LYP(SMD)/6-31G*.

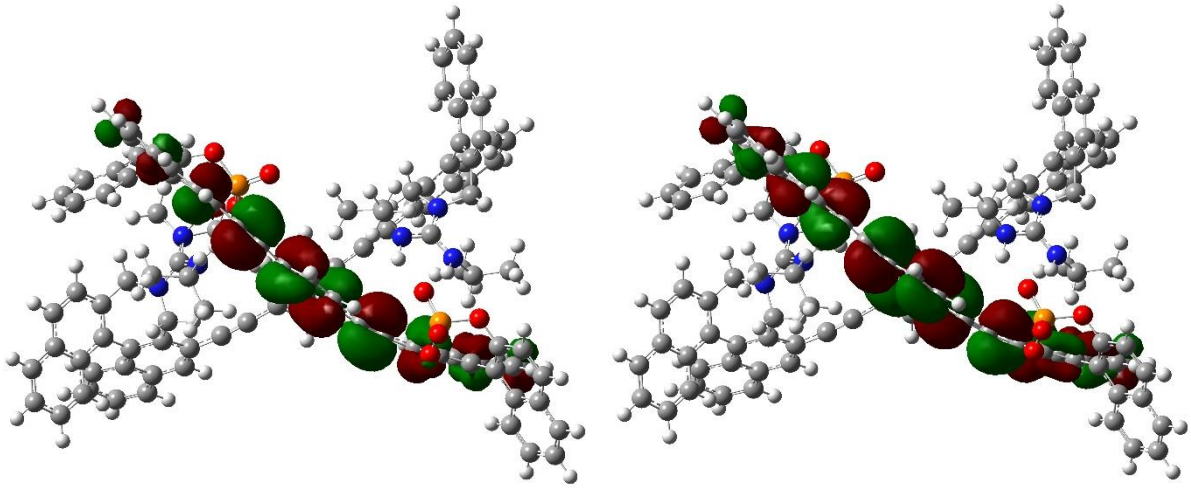


**Figure S28:** Occupied (left) and virtual (right) natural transition orbitals of the π-π* band at 357 nm of the heterochiral complex (*S*,*S*)-**8**+(*R*,*R*)-**9** calculated by means of TD-cam-B3LYP(SMD)/6-31G*.

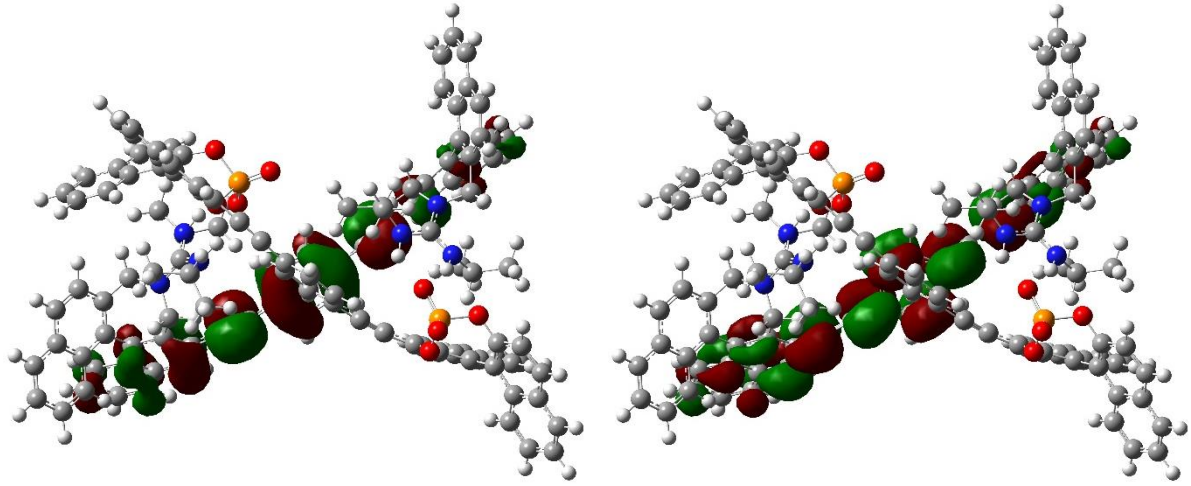


**Figure S29:** Occupied (left) and virtual (right) natural transition orbitals of the π-π* band at 335 nm of the heterochiral complex (*S*,*S*)-**8**+(*R*,*R*)-**9** calculated by means of TD-cam-B3LYP(SMD)/6-31G*.

## 7.4 Calculated CD spectra

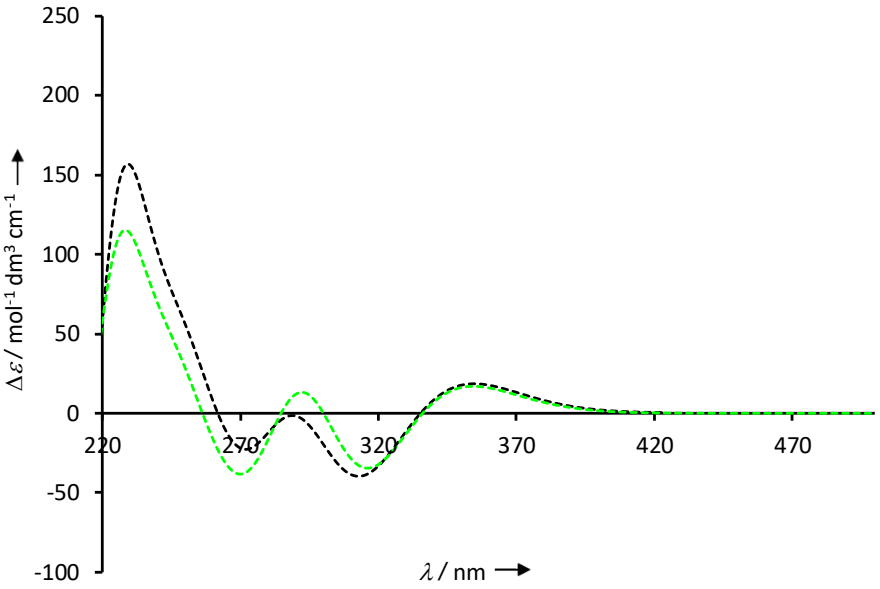



**Figure S30:** TD-cam-B3LYP(SMD)/6-31G*-calculated CD spectra of the monomers (*S*,*S*)-**8** (green) and (*S*,*S*)-**9** (black).

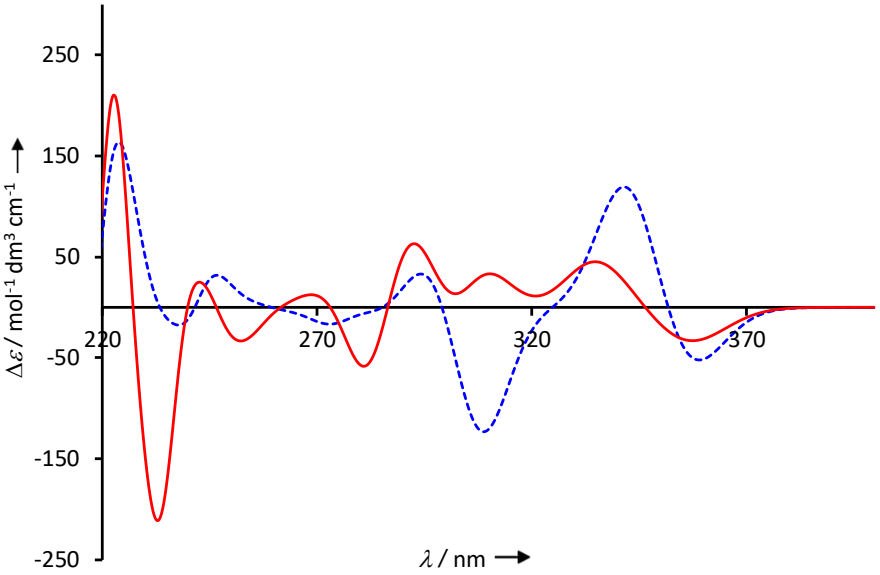



**Figure S31:** TD-cam-B3LYP(SMD)/6-31G*-calculated CD spectra of the homochiral complex (*S*,*S*)-**8**+(*S*,*S*)-**9** (blue, dashed line) and the heterochiral complex *S*,*S*)-**8**+(*R*,*R*)-**9** (red, solid line).

# 8 Calculated structure of hypothetical longer double-helix

The structure of a possible longer double-helical structure was calculated (Schroedinger Suite, MacroModel 11.8, OPLS force field, solvent: chloroform). Here, a hypothetical extension of the subunits in the 3´-positions is used, using the same 1,4-bisethynyl-linker and an additional 1,1´-binaphthyl phosphate or 1,1´-binaphthyl guanidinium species. As can be seen from figure S31, this indeed results in an extended double-helical structure with two crossing points, which might in principle even be further extended.

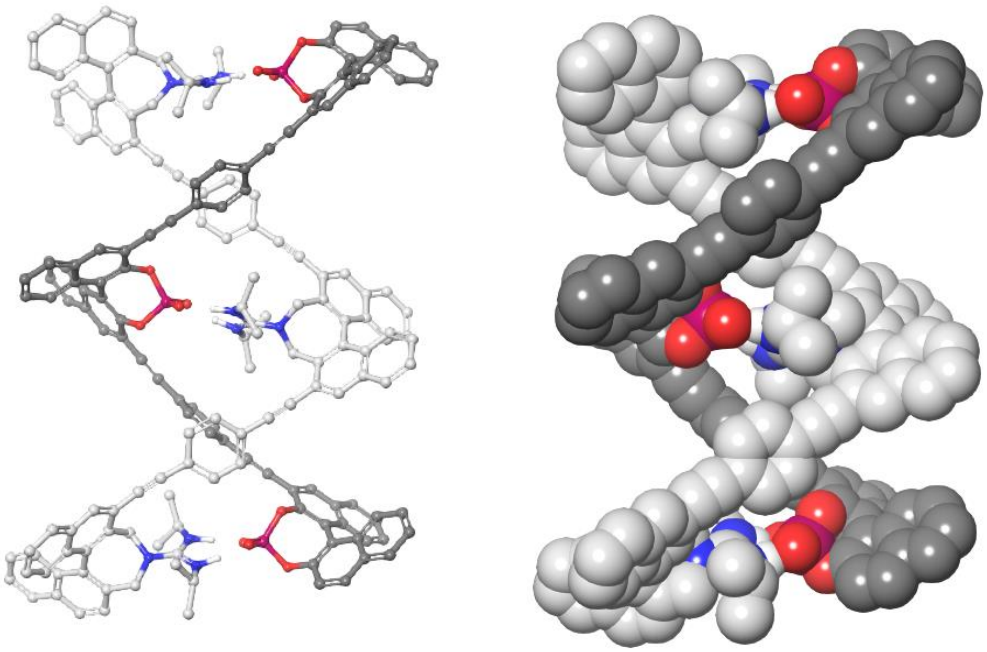


**Figure S32**: Molecular structures of a hypothetical extended double-helix based on an (S,S,S)-trisphosphate and an (S,S,S)-trisguanidinium species (Schroedinger Suite, MacroModel 11.8, OPLS force field, solvent: chloroform, C atoms: light grey for trisguanidinium species, dark grey for trisphosphate, N atoms: blue, O atoms: red, P-atoms: purple, nonpolar hydrogen-atoms omitted for clarity).

# 9 Appendix

## 9.1 NMR-spectra

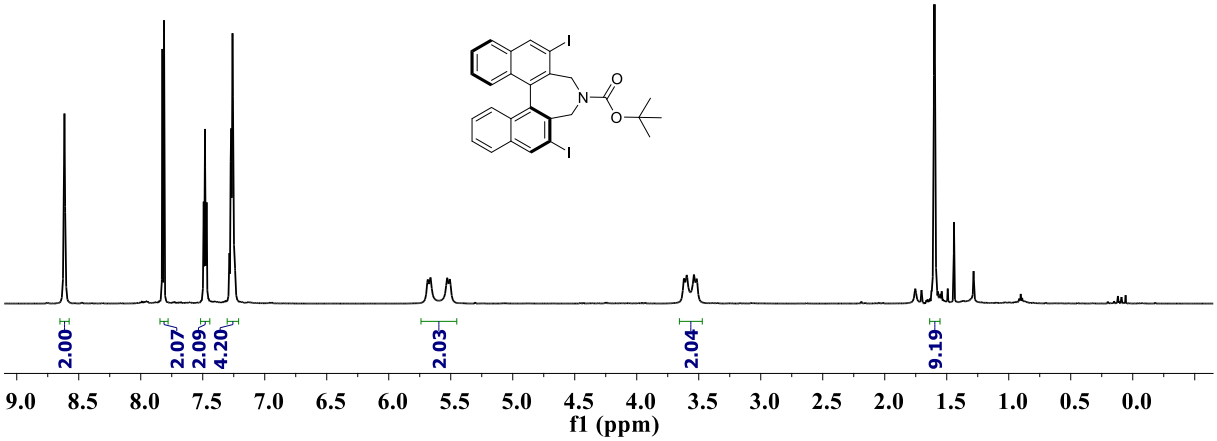



**Figure S33:** $^{1}$H NMR spectrum of (*S*)-**4** ($CDCl_3$, 600 MHz, 298 K).

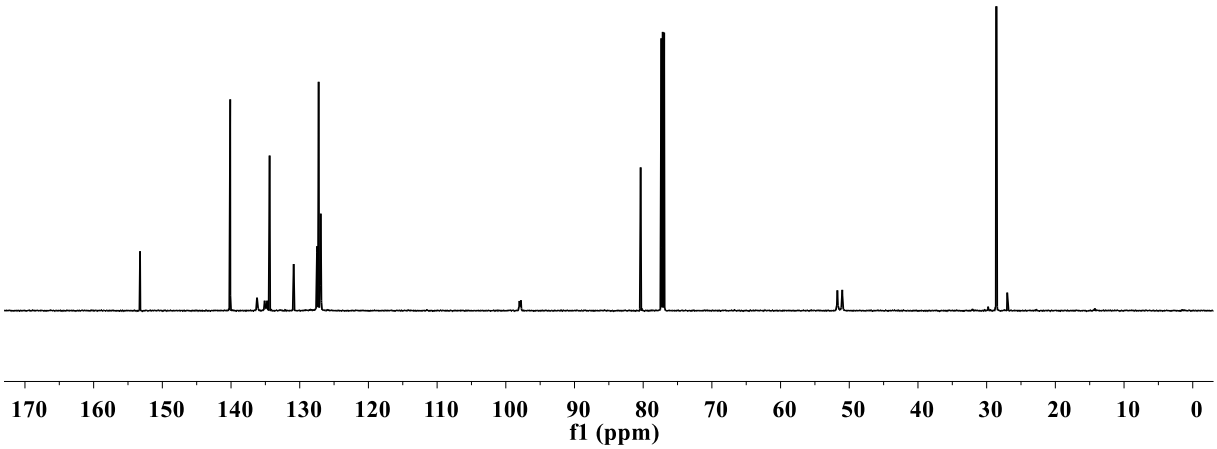



**Figure S34:** $^{13}$C NMR spectrum of (*S*)-**4** ($CDCl_3$, 150 MHz, 298 K).

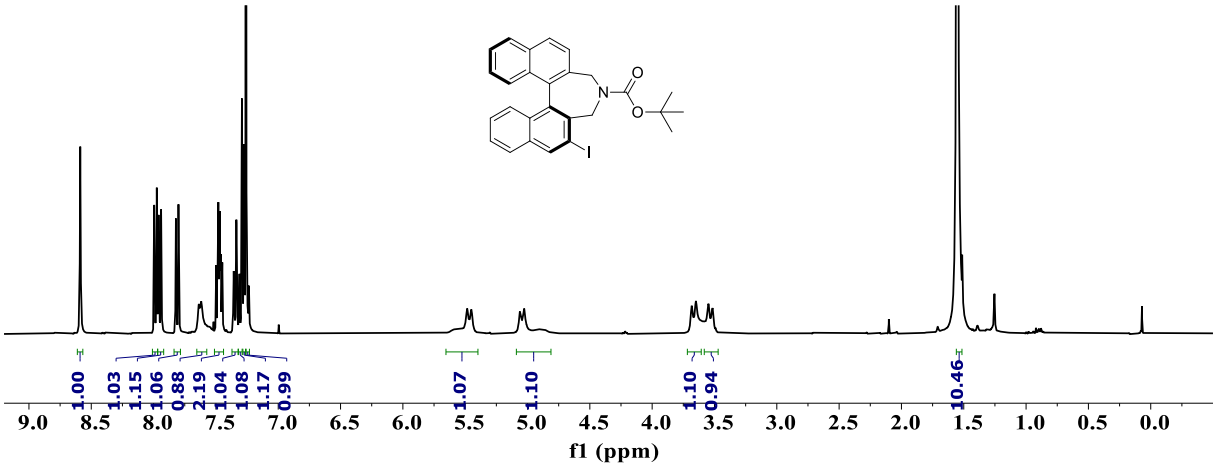



**Figure S35:** $^{1}$H NMR spectrum of (*S*)-**5** ($CDCl_3$, 400 MHz, 298 K).

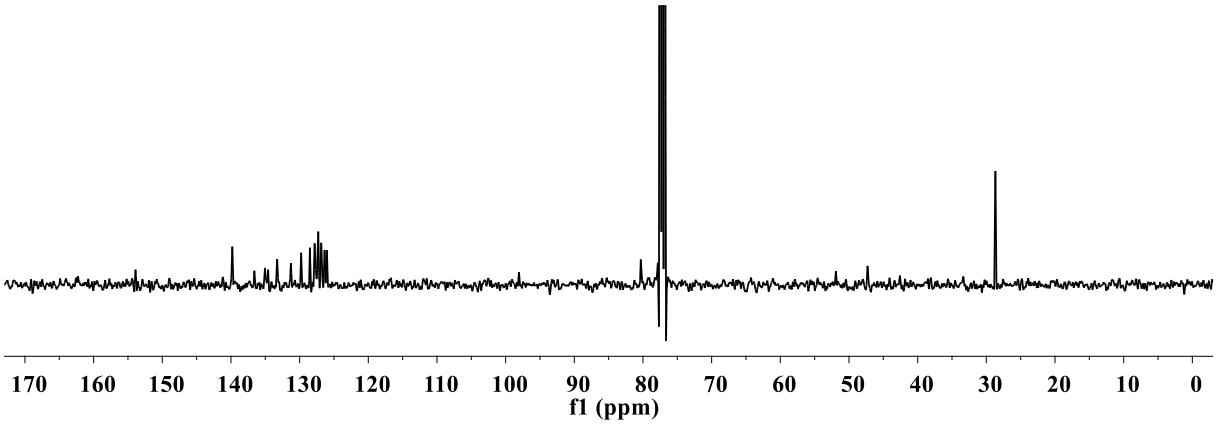



**Figure S36:** $^{13}$C NMR spectrum of (*S*,*S*)-**5** ($CDCl_3$, 100.62 MHz, 298 K).

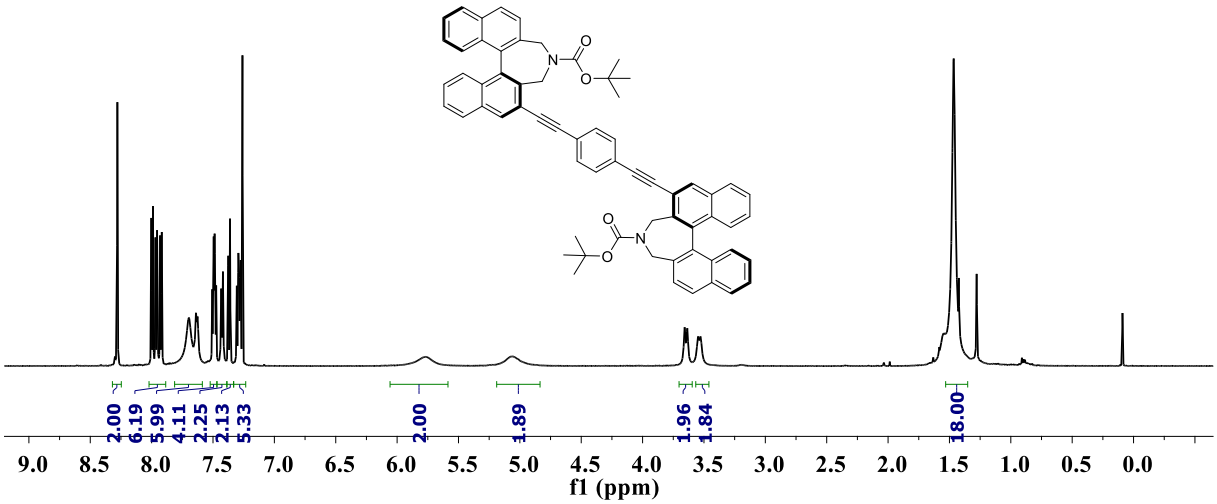



**Figure S37:** $^{1}$H NMR spectrum of (*S*,*S*)-**6** ($CDCl_3$, 600 MHz, 323 K).

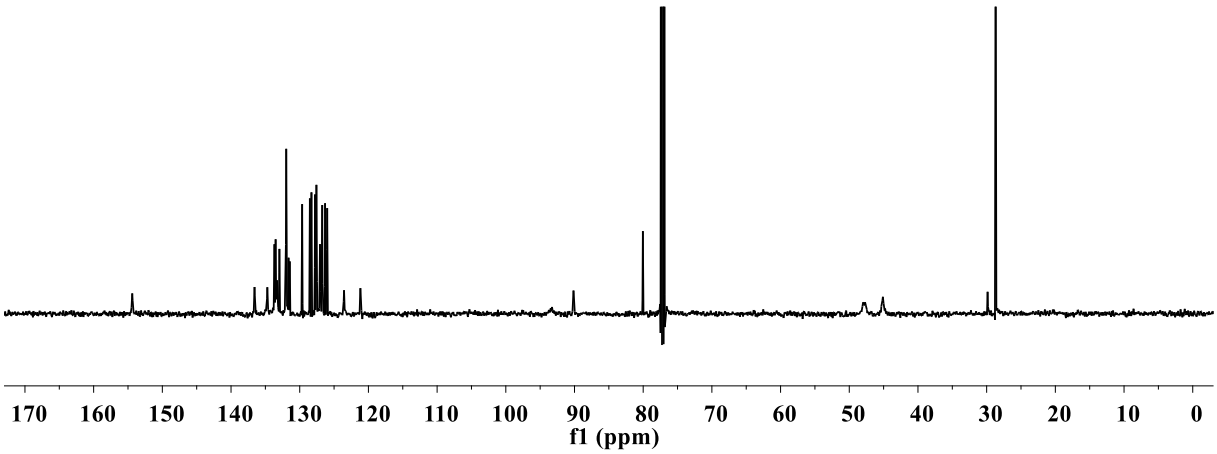



**Figure S38:** $^{13}$C NMR spectrum of (*S*,*S*)-**6** ($CDCl_3$, 150 MHz, 323 K).

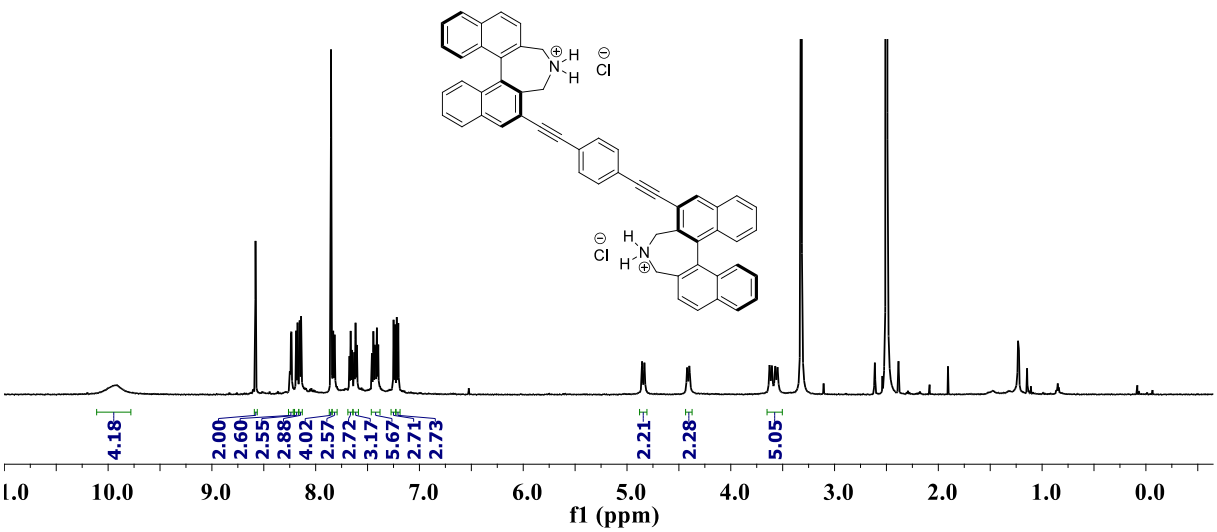



**Figure S39:** $^{1}$H NMR spectrum of (*S*,*S*)-**10** (DMSO-$d_6$, 600 MHz, 298 K).

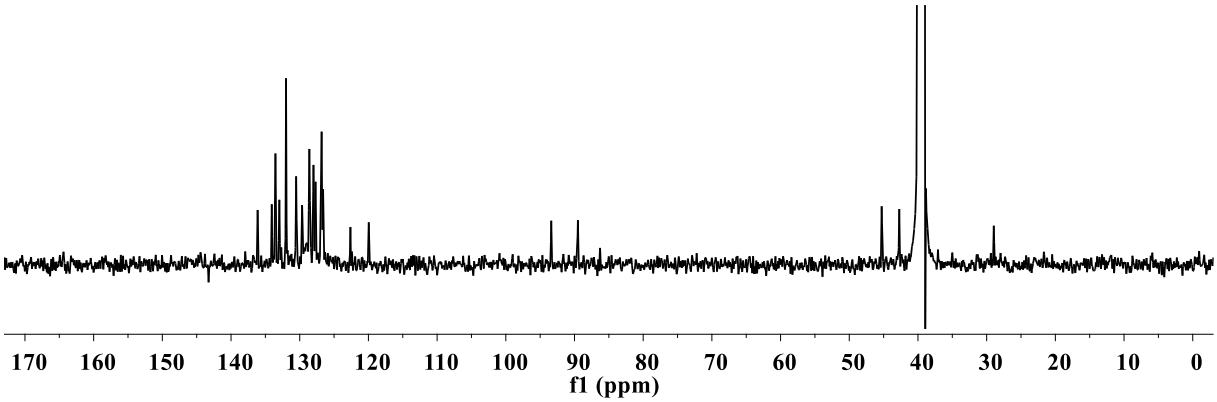



**Figure S40:** $^{13}$C NMR spectrum of (*S*,*S*)-**10** (DMSO-$d_6$, 150 MHz, 298 K).

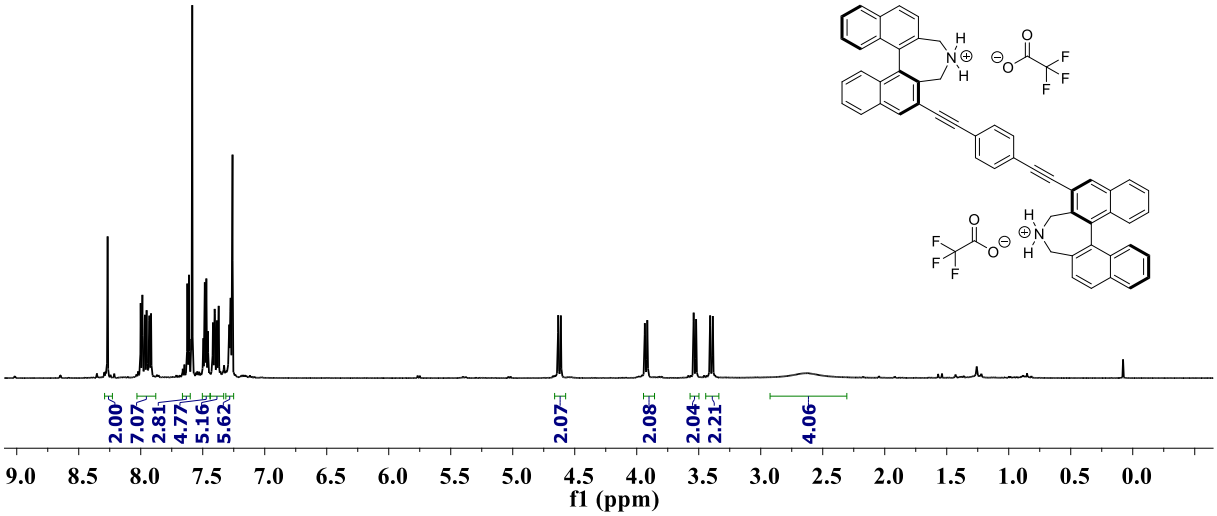



**Figure S41:** $^{1}$H NMR spectrum of (*S*,*S*)-**7** ($CDCl_3$, 600 MHz, 298 K).

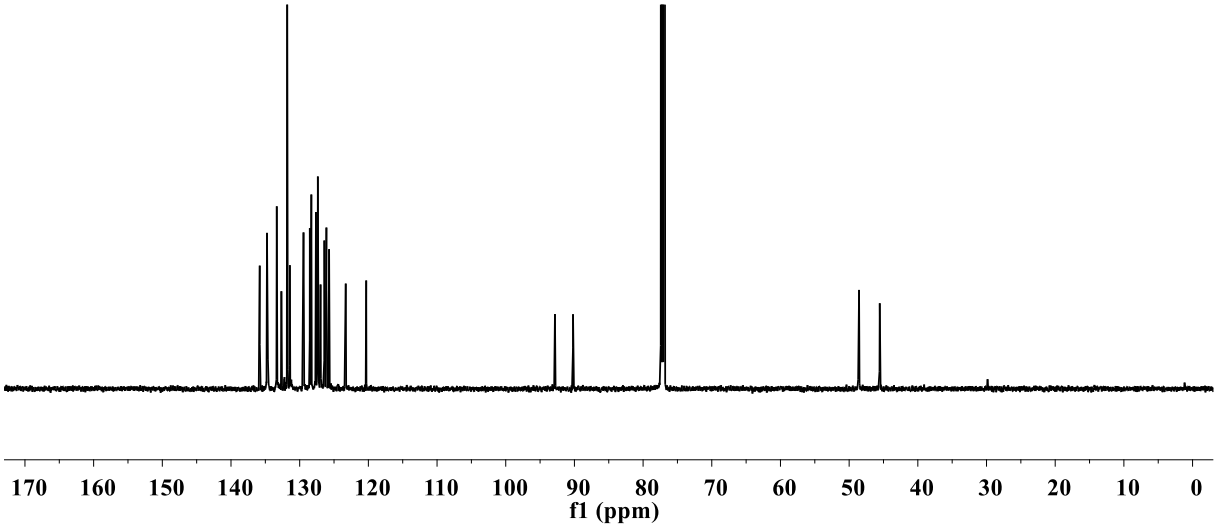



**Figure S42:** $^{13}$C NMR spectrum of (*S*,*S*)-**7** ($CDCl_3$, 150 MHz, 298 K).

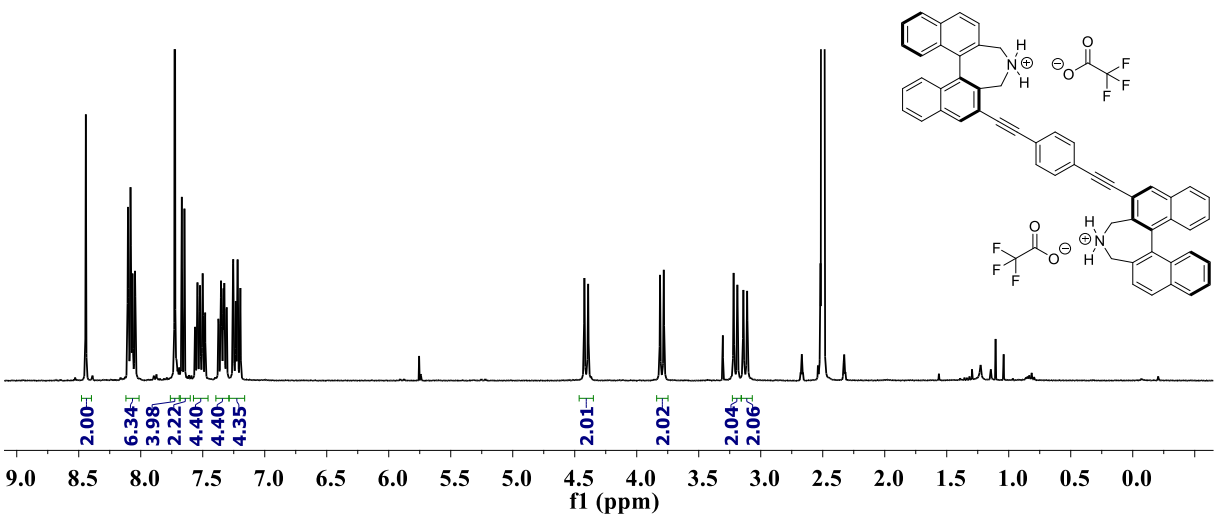



**Figure S43:** $^{1}$H NMR spectrum of (*S*,*S*)-**7** (DMSO-$d_6$, 400 MHz, 298 K).

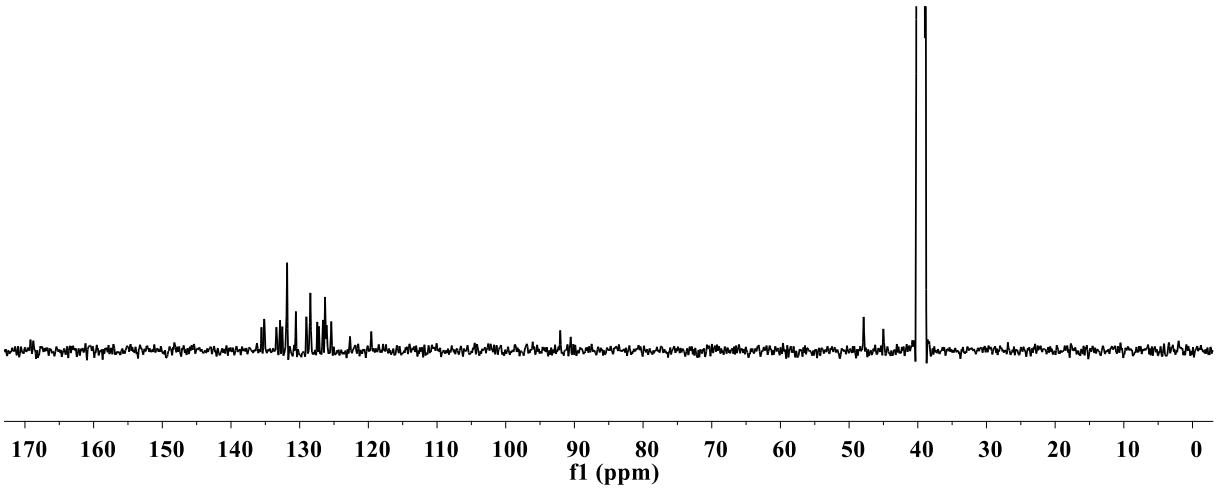



**Figure S44:** $^{13}$C NMR spectrum of (*S*,*S*)-**7** (DMSO-$d_6$, 100.62 MHz, 298 K).

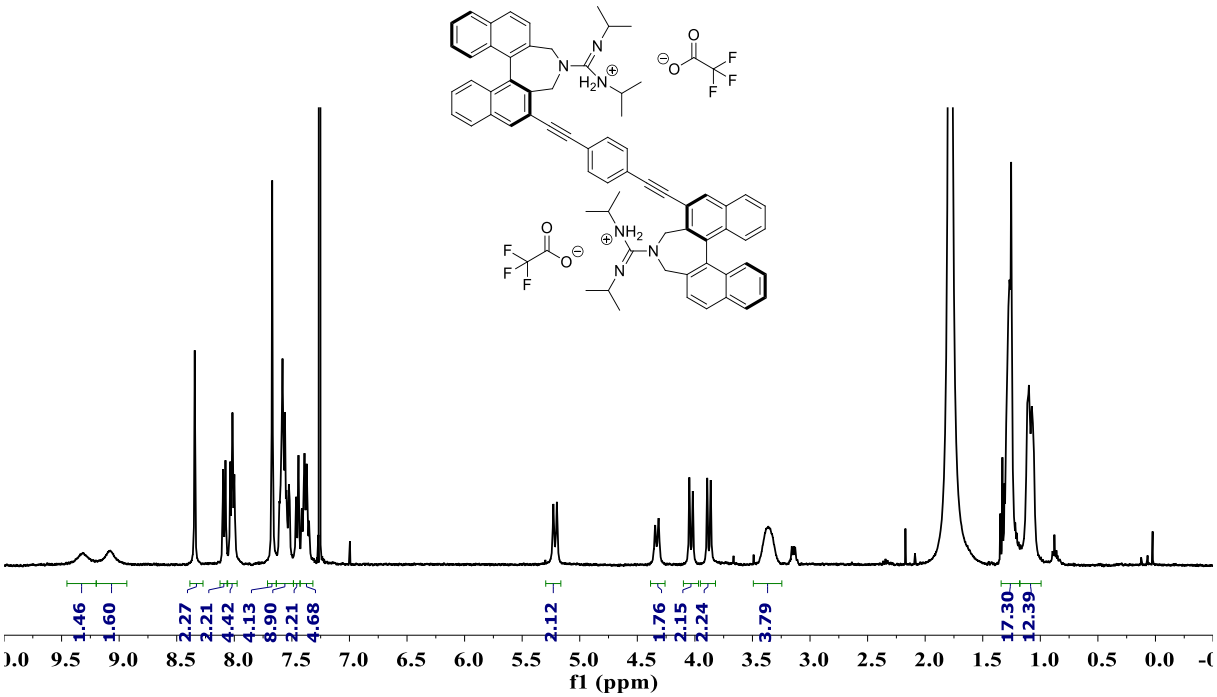



**Figure S45:** $^{1}$H NMR spectrum of (*S*,*S*)-**8** ($CDCl_3$, 400 MHz, 298 K).

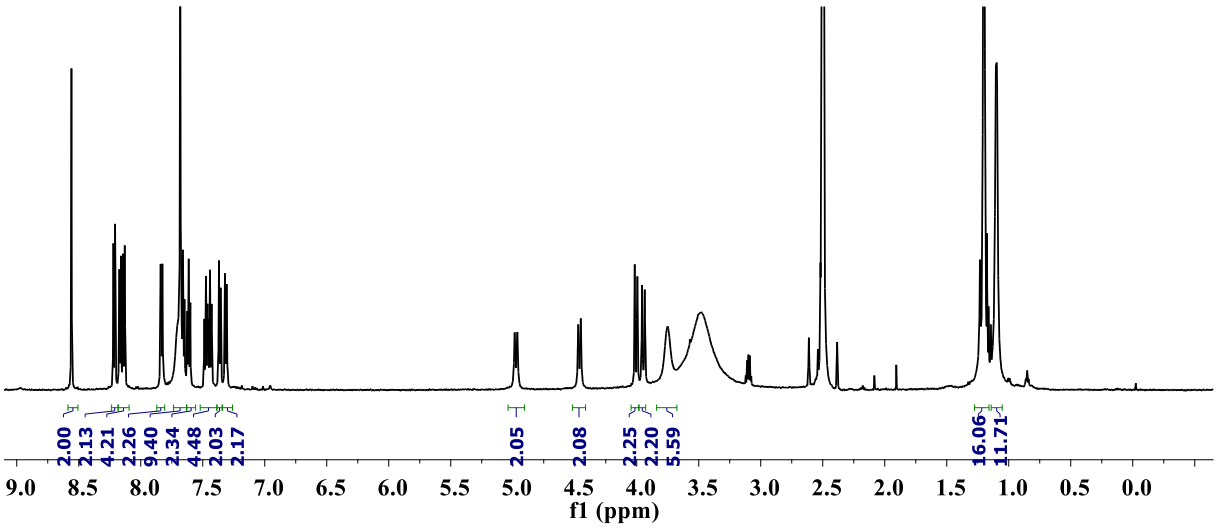



**Figure S46:** $^{1}$H NMR spectrum of (*S*,*S*)-**8** (DMSO-$d_6$, 600 MHz, 298 K).

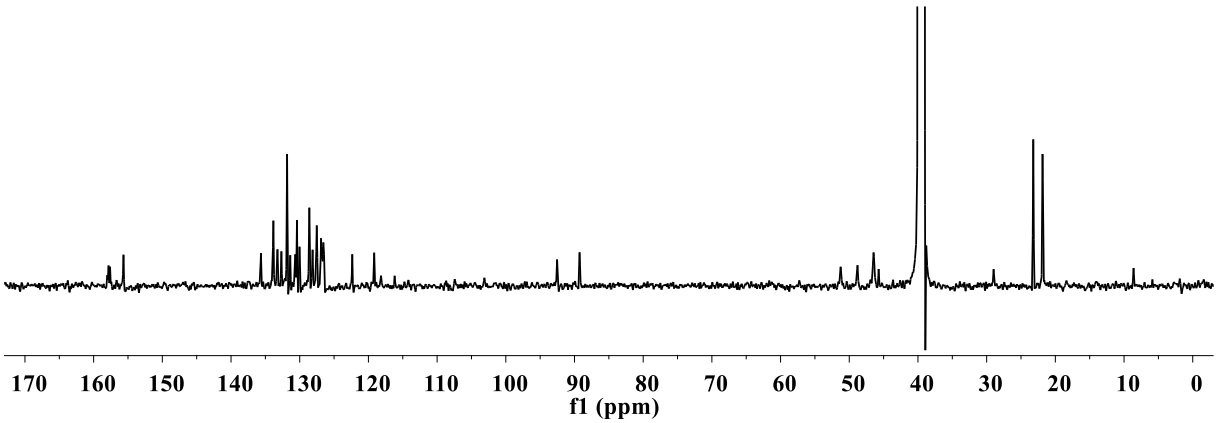



**Figure S47:** $^{13}$C NMR spectrum of (*S*,*S*)-**8** (DMSO-$d_6$, 151 MHz, 298 K).

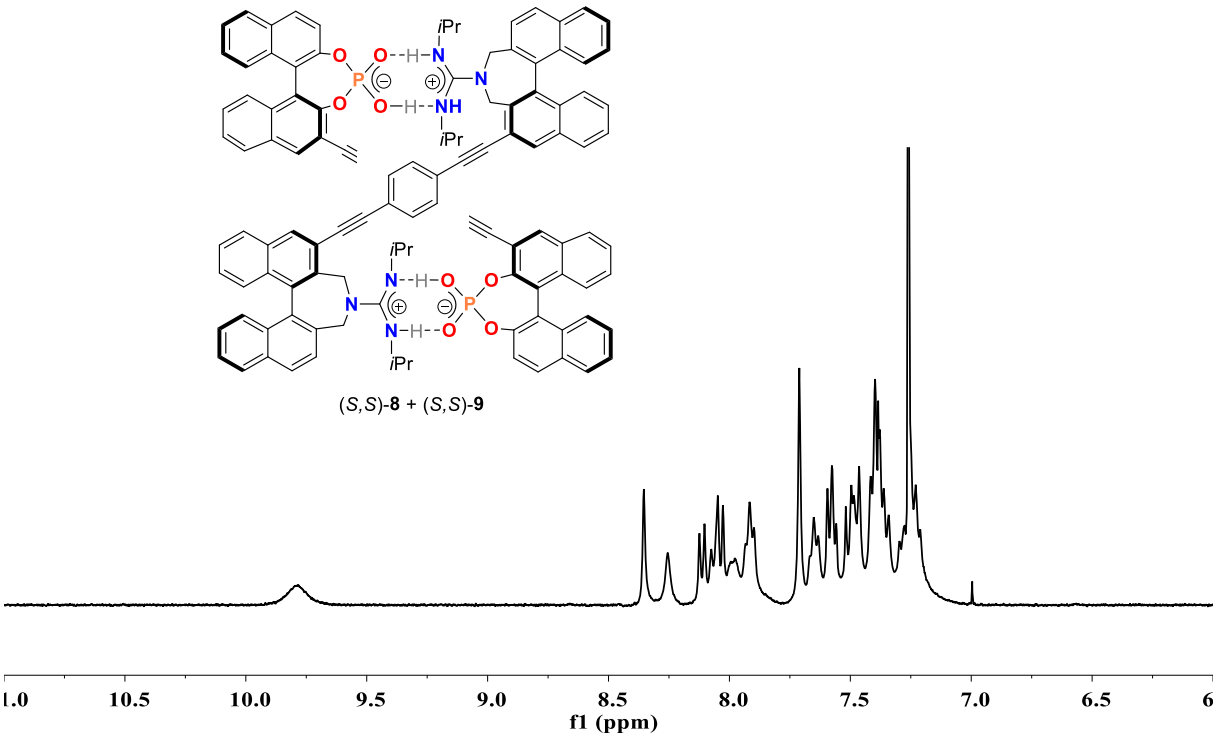



**Figure S48:** $^{1}$H NMR spectrum (aromatic region) of (*S*,*S*)-**8** (3 mM) + (*S*,*S*)-**9** (3 mM) ($CDCl_3$, 400 MHz, 298 K).

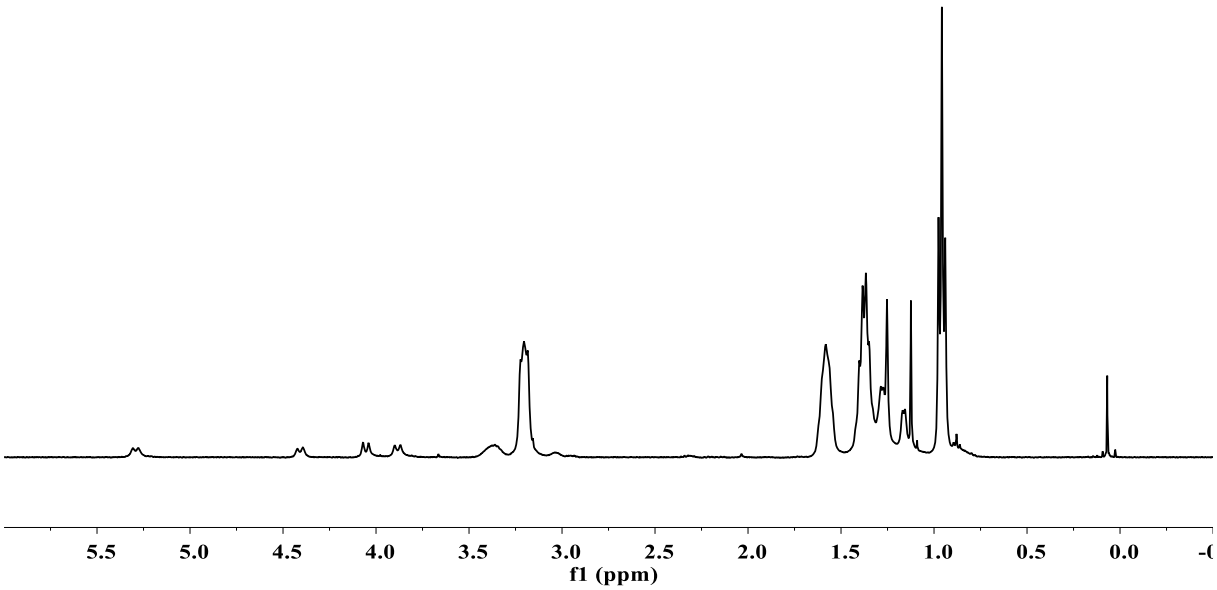



**Figure S49:** $^{1}$H NMR spectrum (aliphatic region) of (*S*,*S*)-**8** (3 mM) + (*S*,*S*)-**9** (3 mM) ($CDCl_3$, 400 MHz, 298 K).

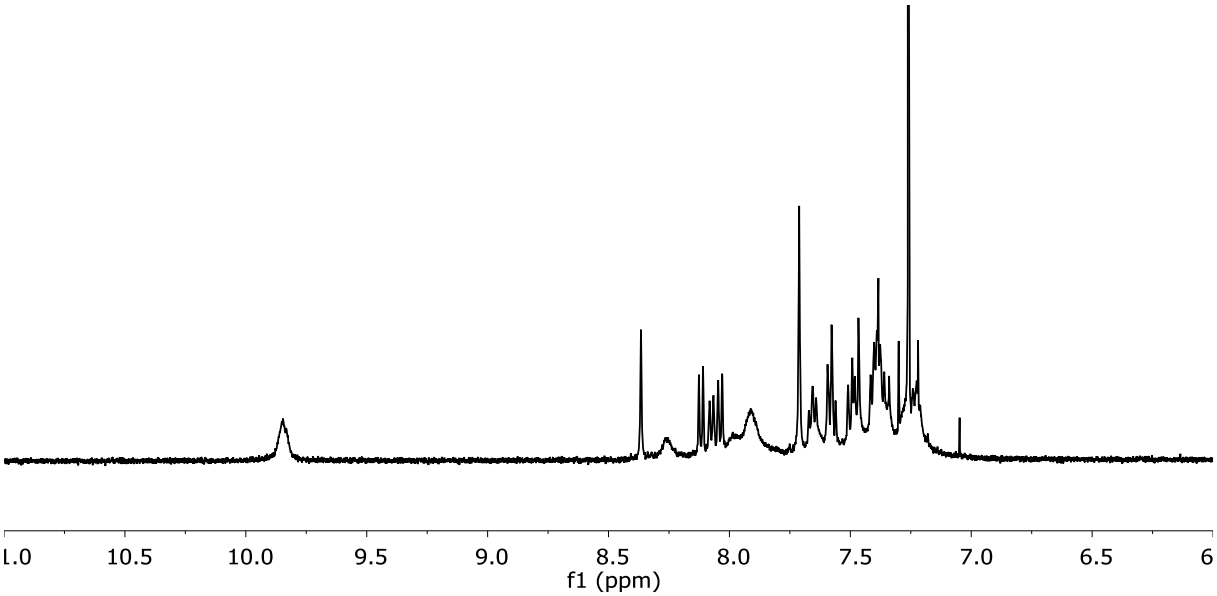



**Figure S50:** $^{1}$H NMR spectrum (aromatic region) of (*S*,*S*)-**8** (1 mM) + (*S*,*S*)-**9** (1 mM) ($CDCl_3$, 500 MHz, 298 K).

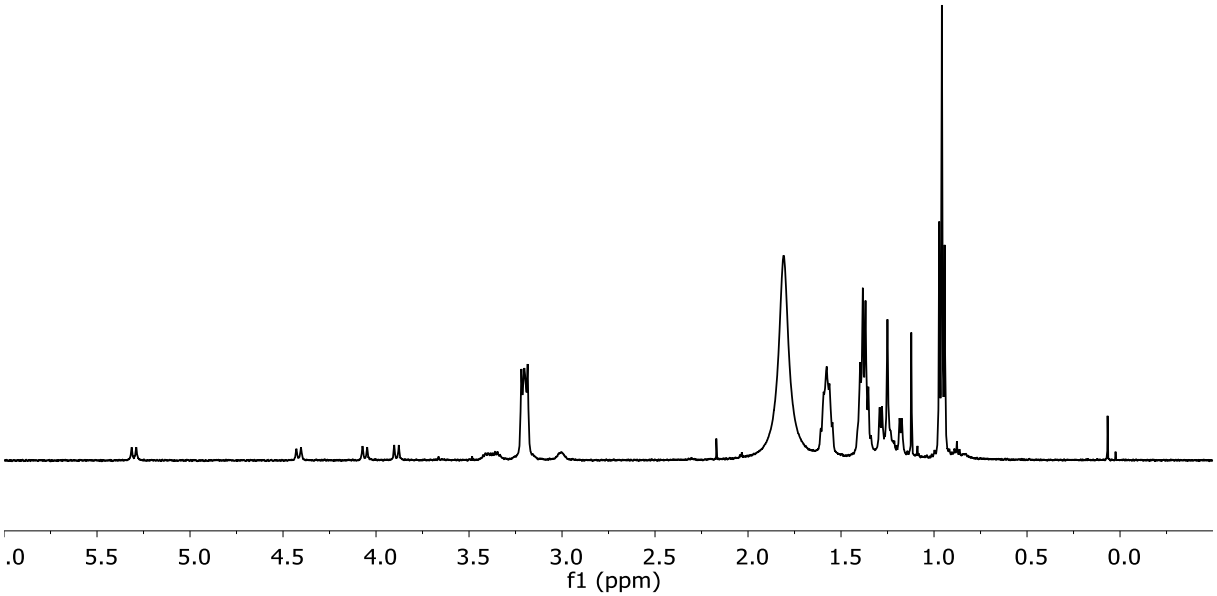



**Figure S51:** $^{1}$H NMR spectrum (aliphatic region) of (*S*,*S*)-**8** (1 mM) + (*S*,*S*)-**9** (1 mM) ($CDCl_3$, 500 MHz, 298 K).

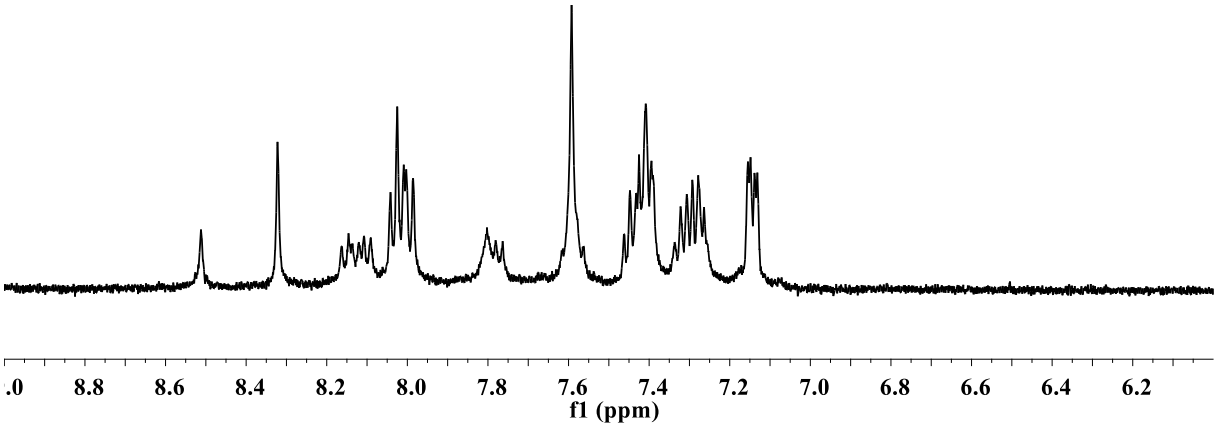



**Figure S52:** $^{1}$H NMR spectrum (aromatic region) of (*S*,*S*)-**8** (1 mM) + (*S*,*S*)-**9** (1 mM) (DMSO-$d_6$, 500 MHz, 298 K).

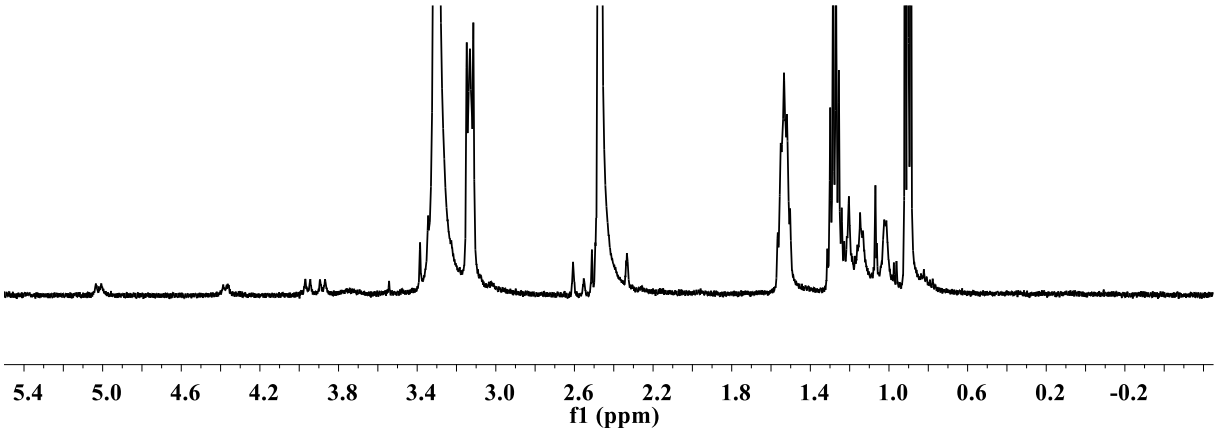



**Figure S53:** $^{1}$H NMR spectrum (aliphatic region) of (*S*,*S*)-**8** (1 mM) + (*S*,*S*)-**9** (1 mM) (DMSO-$d_6$, 500 MHz, 298 K).

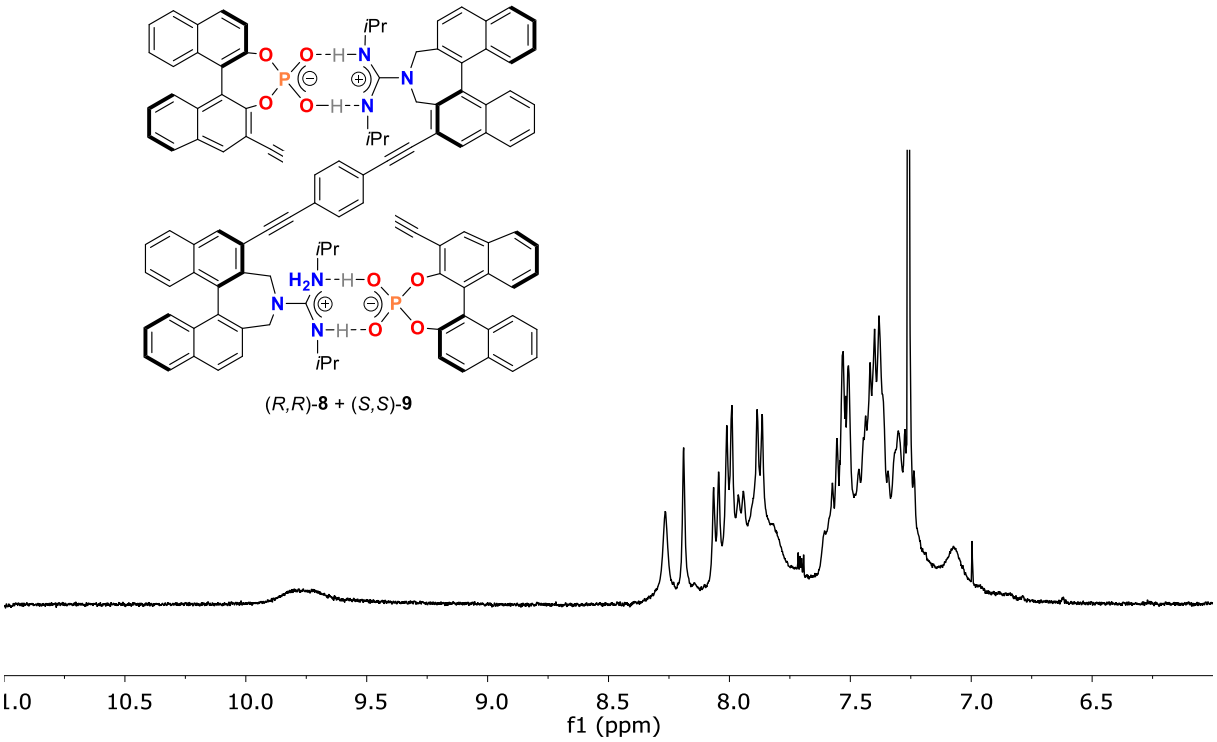



**Figure S54:** $^{1}$H NMR spectrum (aromatic region) of (*S*,*S*)-**8** (3 mM) + (*R*,*R*)-**9** (3 mM) ($CDCl_3$, 400 MHz, 298 K).

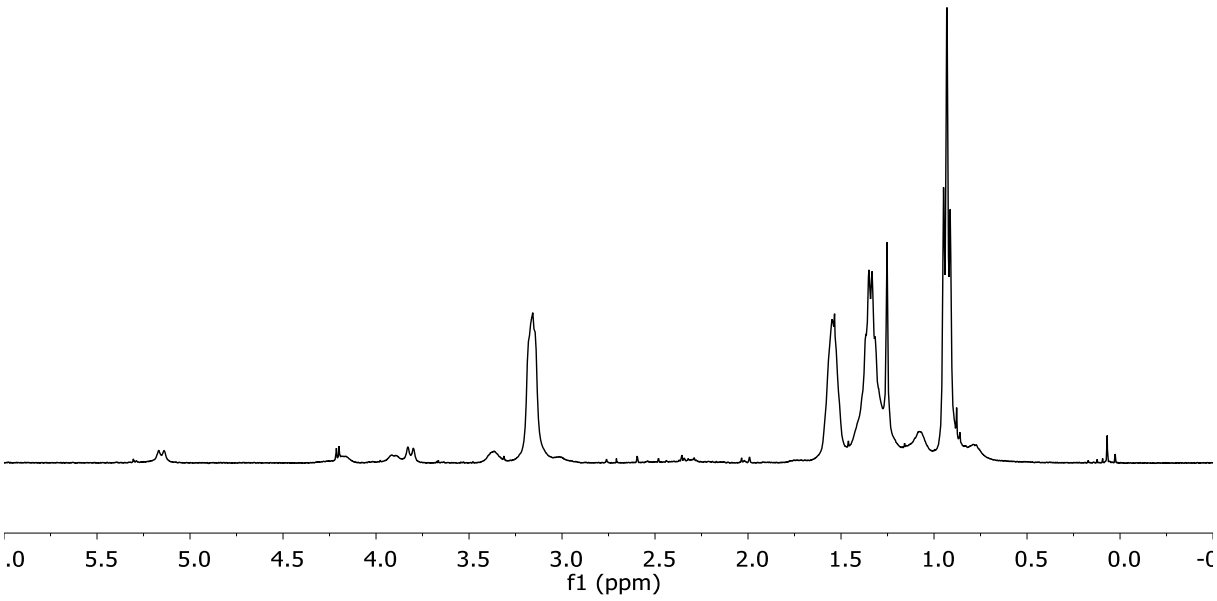



**Figure S55:** $^{1}$H NMR spectrum (aliphatic region) of (*S*,*S*)-**8** (3 mM) + (*R*,*R*)-**9** (3 mM) ($CDCl_3$, 400 MHz, 298 K).

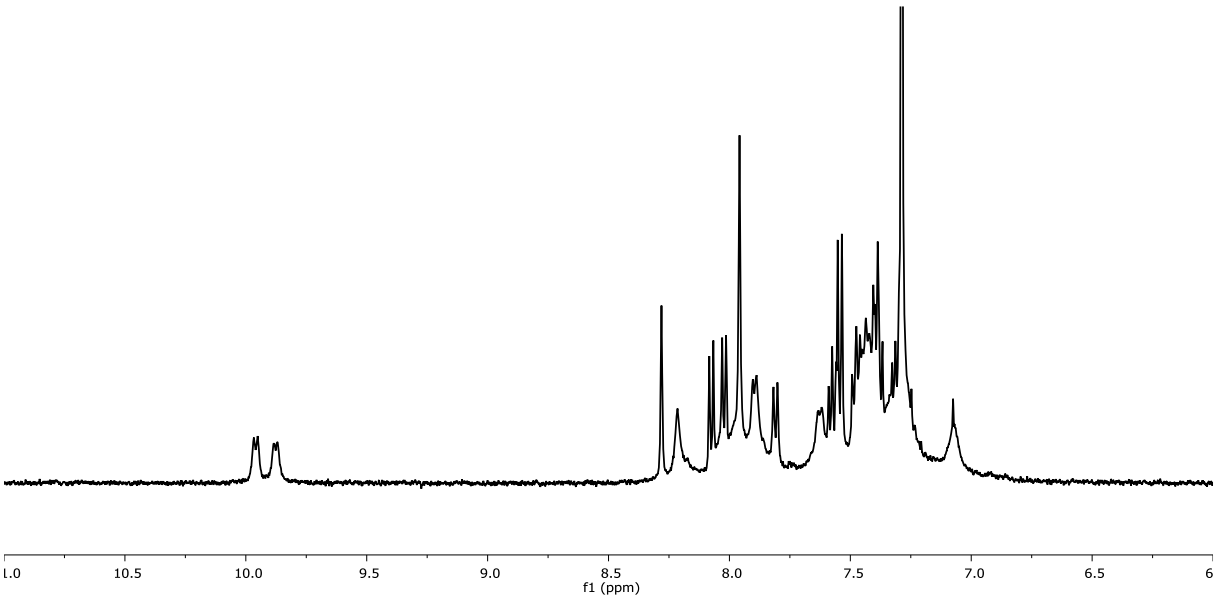



**Figure S56:** $^{1}$H NMR spectrum (aromatic region) of (*S*,*S*)-**8** (1 mM) + (*R*,*R*)-**9** (1 mM) ($CDCl_3$, 500 MHz, 298 K).

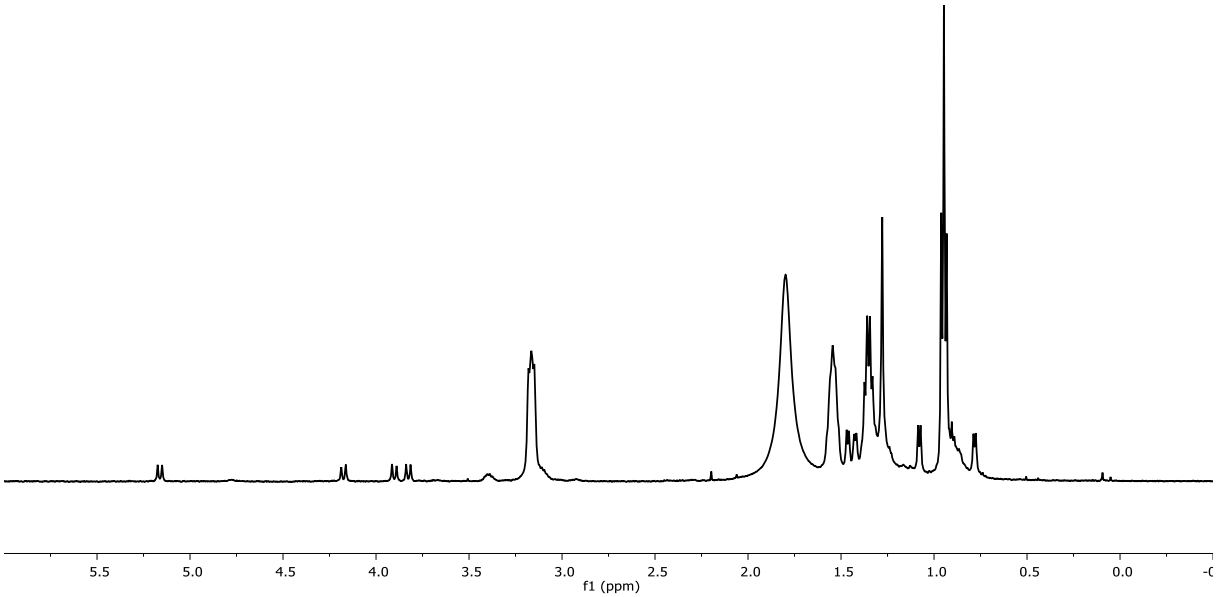



**Figure S57:** $^{1}$H NMR spectrum (aliphatic region) of (*S*,*S*)-**8** (1 mM) + (*R*,*R*)-**9** (1 mM) ($CDCl_3$, 500 MHz, 298 K).

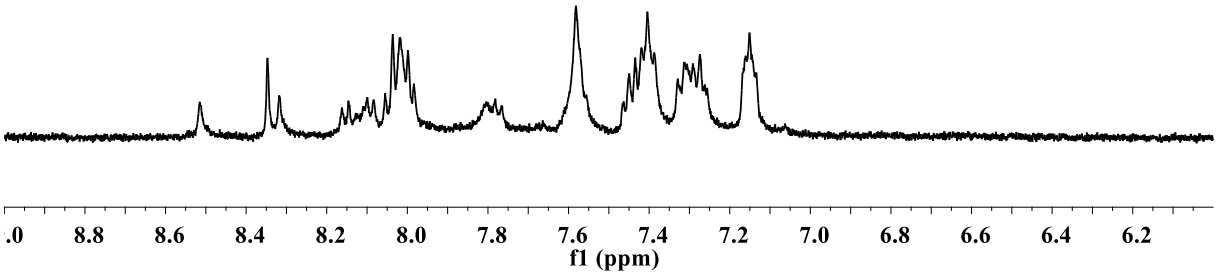



**Figure S58:** $^{1}$H NMR spectrum (aromatic region) of (*S*,*S*)-**8** (1 mM) + (*R*,*R*)-**9** (1 mM) (DMSO-$d_6$, 500 MHz, 298 K).

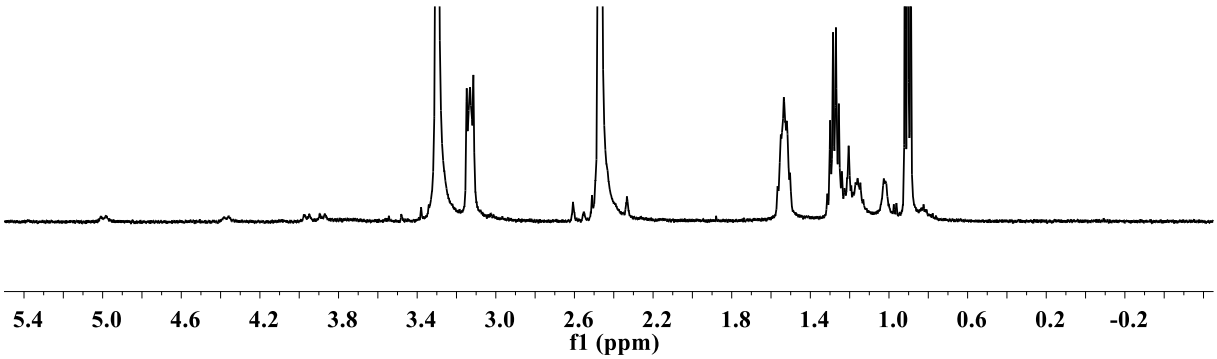



**Figure S59:** $^{1}$H NMR spectrum (aliphatic region) of (*S*,*S*)-**8** (1 mM) + (*R*,*R*)-**9** (1 mM) (DMSO-$d_6$, 500 MHz, 298 K).

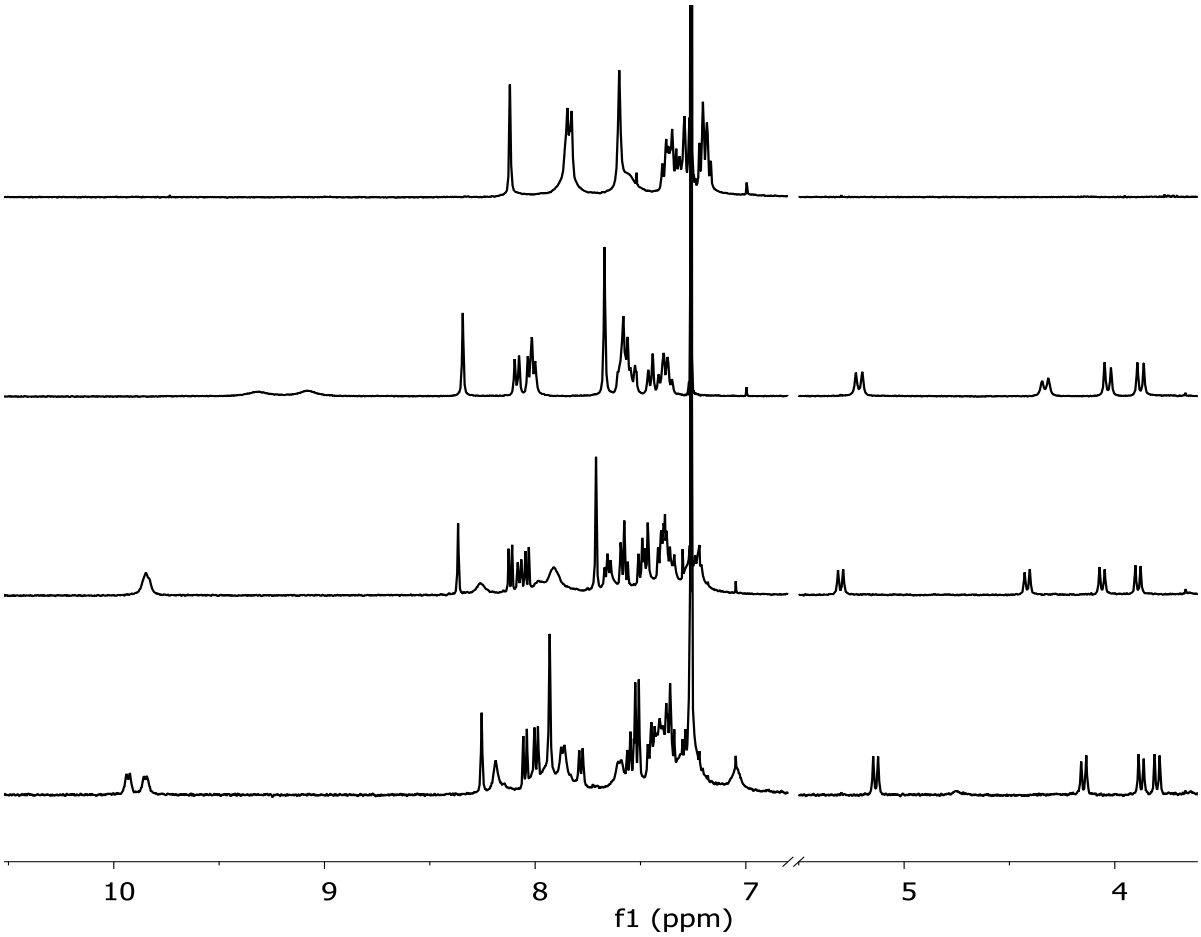



**Figure S60:** Stacked $^{1}$H NMR spectra of compound (*S*,*S*)-**9**, compound (*S*,*S*)-**8**, complex (*S*,*S*)-**8** + (*S*,*S*)-**9** and complex (*S*,*S*)-**8** + (*R*,*R*)-**9** ($CDCl_3$, 400 MHz (components), 500 MHz (complexes, 1 mM of each component), 298 K).

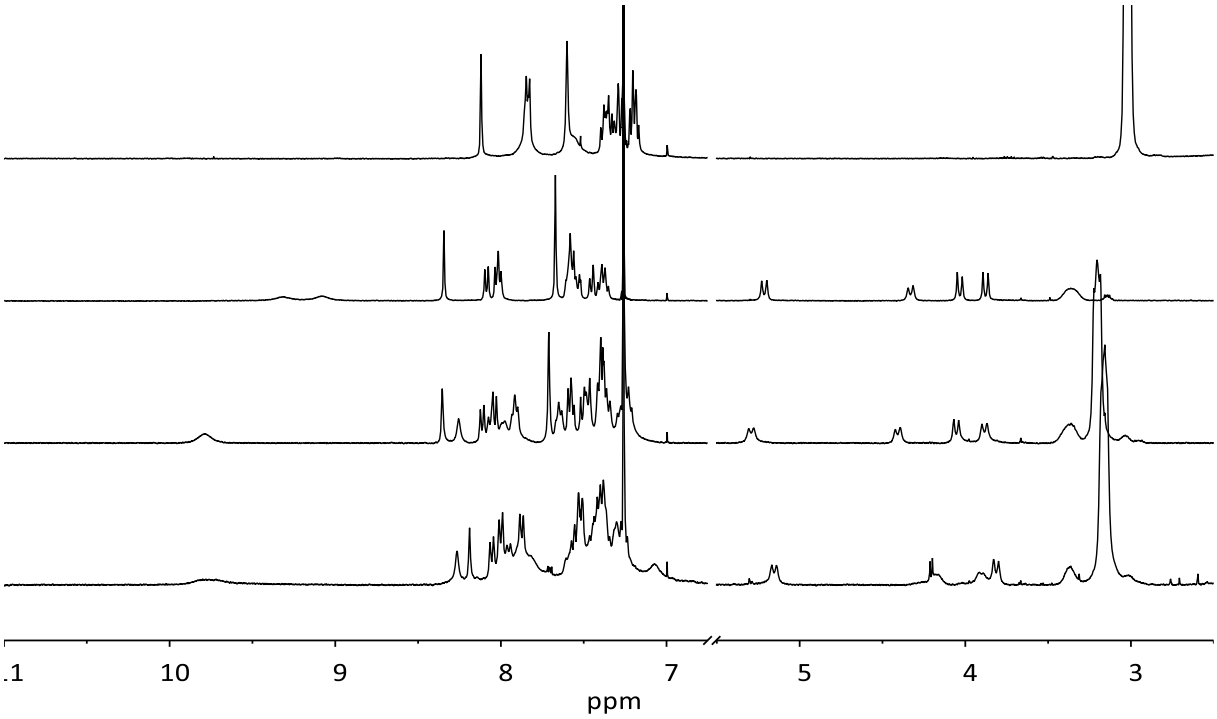



**Figure S61:** Stacked $^{1}$H NMR spectra of compound (*S*,*S*)-**9**, compound (*S*,*S*)-**8**, complex (*S*,*S*)-**8** + (*S*,*S*)-**9** and complex (*S*,*S*)-**8** + (*R*,*R*)-**9** ($CDCl_3$, all 400 MHz, 3 mM of each component for the complexes, 298 K).

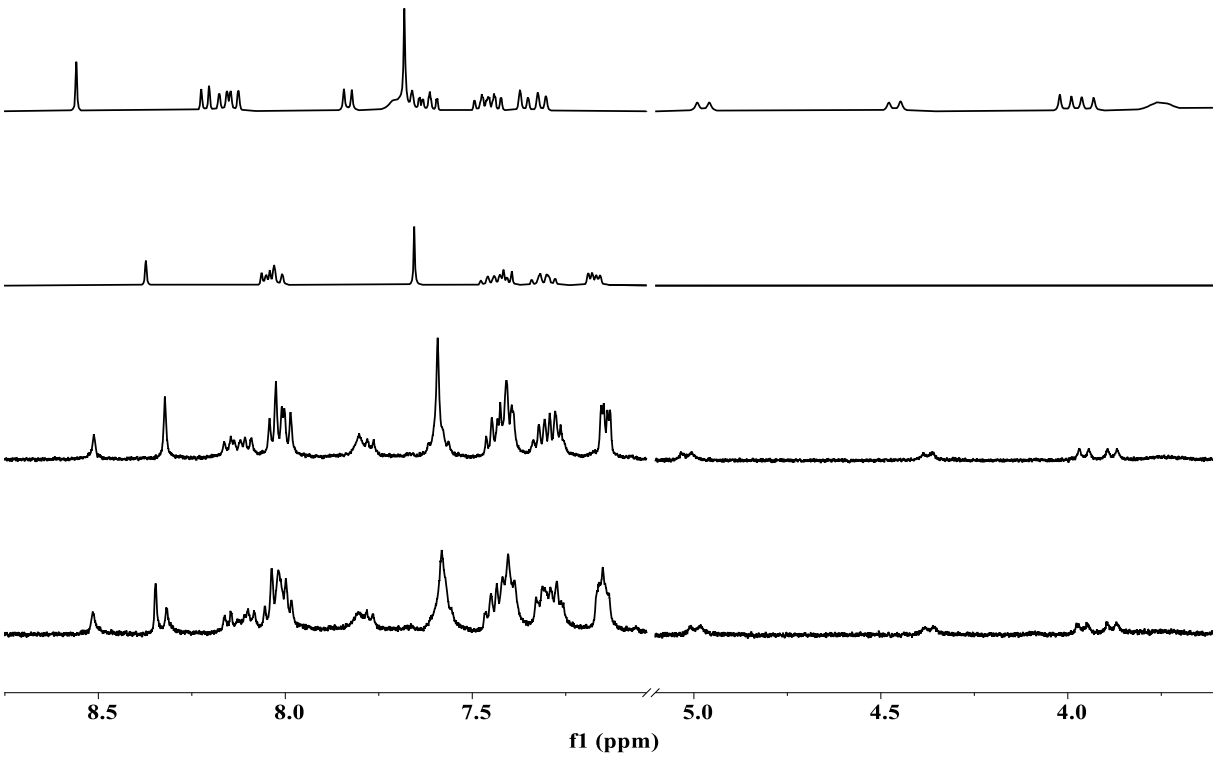



**Figure S62:** Stacked $^{1}$H NMR spectra of compound (*S*,*S*)-**8**, compound (*S*,*S*)-**9**, complex (*S*,*S*)-**8** + (*S*,*S*)-**9** and complex (*S*,*S*)-**8** + (*R*,*R*)-**9** (all: 1 mM, DMSO-$d_6$, 500 MHz, 298 K).

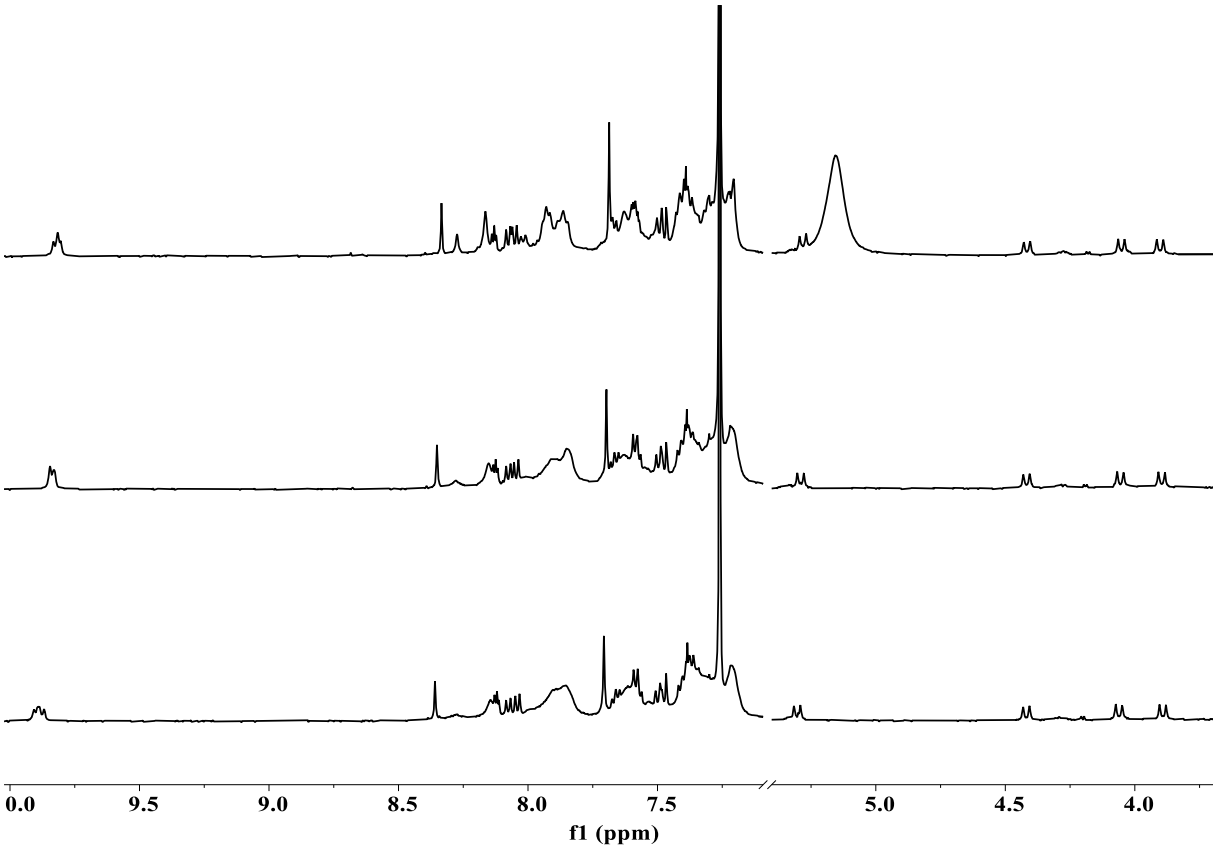



**Figure S63:** Stacked VT-$^{1}$H NMR spectra of complex (*S*,*S*)-**8** + (*S*,*S*)-**9** (all: 1 mM, $CDCl_3$, 500 MHz, 253, 273, 293 K).

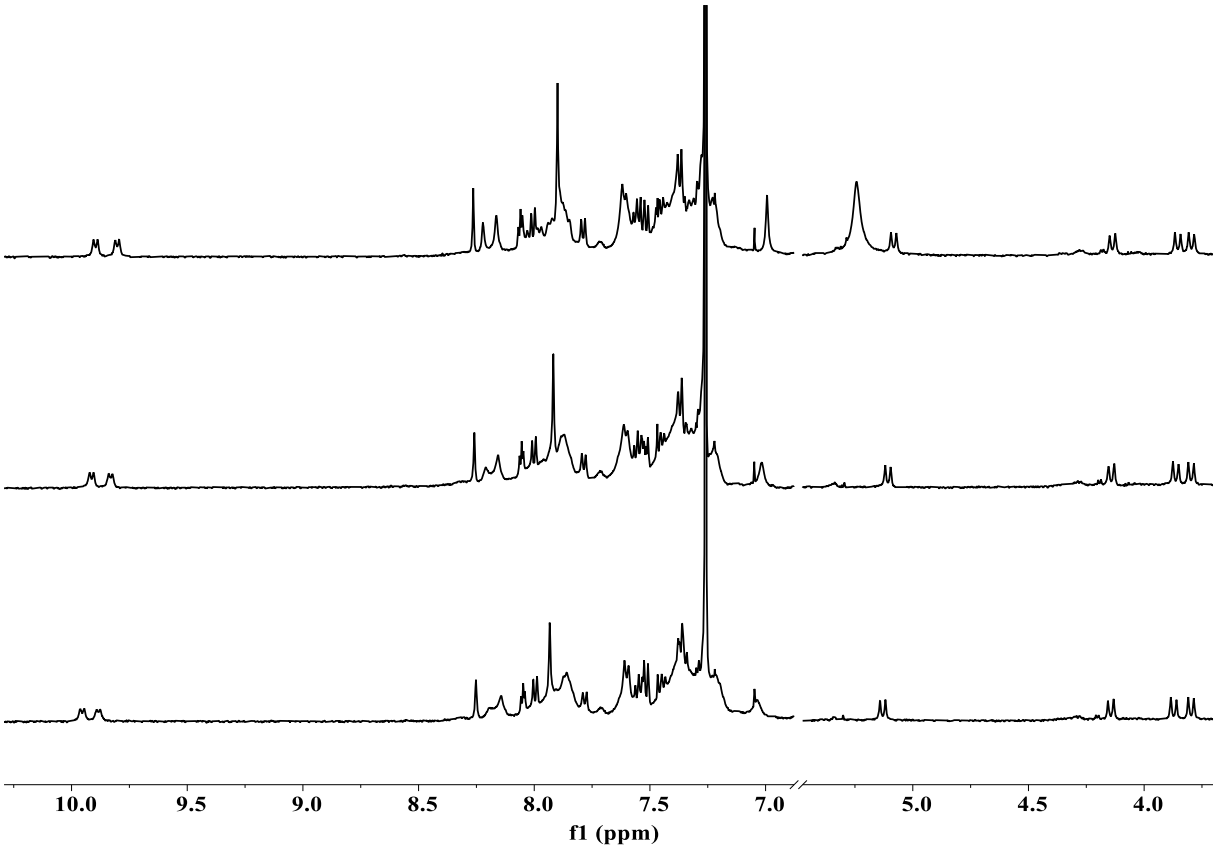



**Figure S64:** Stacked VT-$^{1}$H NMR spectra of complex (*S*,*S*)-**8** + (*R*,*R*)-**9** (all: 1 mM, $CDCl_3$, 500 MHz, 253, 273, 293 K).

## 9.2 Cartesian Coordinates and Absolute Energies for all calculated compounds

**Table S9:** Absolute energies [au] calculated by B3LYP-D3BJ(SMD)/6-31G*.

| Compound | *E* |
|---|---|
| cationic part of (*S*,*S*)-**8** | -2959.617658 |
| anionic part of (*S*,*S*)-**9** | -3206.161525 |
| (*S*,*S*)-**8**+(*S*,*S*)-**9** | -6165.939758 |
| (*S*,*S*)-**8**+(*R*,*R*)-**9** | -6165.942056 |

Cartesian coordinates of the optimized geometry for the cationic part of (*S*,*S*)-**8** at B3LYP-D3BJ(SMD)/6-31G* level of theory (number of imaginary frequencies = 0):

| | | | |
|---|---|---|---|
| C | 10.94082500 | -0.63788700 | -4.09456100 |
| C | 10.05211100 | -1.64442800 | -3.64628900 |
| C | 9.24590700 | -1.43188000 | -2.55111800 |
| C | 9.28634400 | -0.20008800 | -1.84087300 |
| C | 10.16002400 | 0.83121400 | -2.32112900 |
| C | 10.98749200 | 0.57445100 | -3.44711300 |
| C | 8.46510100 | 0.06513000 | -0.69615300 |
| C | 8.46501200 | 1.33498200 | -0.12803900 |
| C | 9.31859100 | 2.34820200 | -0.62621200 |
| C | 10.16225400 | 2.09699000 | -1.68094400 |
| C | 5.67281600 | -2.80928200 | 0.90535000 |
| C | 5.23686200 | -1.56911400 | 0.46516800 |
| C | 6.18468200 | -0.63633300 | -0.07114400 |
| C | 7.53140700 | -0.95754200 | -0.14038800 |
| C | 8.00165800 | -2.20680600 | 0.38529900 |
| C | 7.04486600 | -3.14767300 | 0.88997600 |
| C | 9.37990200 | -2.53867100 | 0.46323600 |
| C | 9.78687900 | -3.75156300 | 0.97401800 |
| C | 8.83833000 | -4.69522300 | 1.43526100 |
| C | 7.49656600 | -4.39606000 | 1.39785400 |
| C | 5.72847500 | 0.73161600 | -0.51590500 |
| C | 3.85960200 | -1.21924100 | 0.53792000 |
| C | 2.69436400 | -0.87043900 | 0.57844800 |
| C | 1.34074100 | -0.43885400 | 0.60578800 |
| C | 1.03453200 | 0.93834100 | 0.61046500 |
| C | -0.28265600 | 1.37055000 | 0.61299300 |
| C | -1.34106000 | 0.43889300 | 0.60586900 |
| C | -1.03486200 | -0.93831200 | 0.60973500 |
| C | 0.28233400 | -1.37051200 | 0.61218000 |
| C | -2.69462800 | 0.87059800 | 0.57853300 |
| C | -3.85974800 | 1.21971500 | 0.53790600 |
| C | -8.83876300 | 4.69532000 | 1.43507600 |
| C | -9.78723800 | 3.75147000 | 0.97407600 |
| C | -9.38016000 | 2.53857700 | 0.46337900 |
| C | -8.00187900 | 2.20689700 | 0.38529200 |
| C | -7.04515400 | 3.14794900 | 0.88976200 |
| C | -7.49696200 | 4.39633900 | 1.39753600 |
| C | -7.53151700 | 0.95763100 | -0.14030900 |
| C | -6.18476300 | 0.63658900 | -0.07109600 |
| C | -5.23700100 | 1.56954000 | 0.46504400 |
| C | -5.67306000 | 2.80972300 | 0.90509400 |
| C | -10.16197700 | -2.09733800 | -1.68065200 |
| C | -9.31825600 | -2.34838500 | -0.62592800 |
| C | -8.46479400 | -1.33502800 | -0.12782900 |
| C | -8.46507800 | -0.06519600 | -0.69599100 |
| C | -9.28636300 | 0.19984200 | -1.84072900 |
| C | -10.15992000 | -0.83159600 | -2.32090700 |
| C | -9.24607400 | 1.43158200 | -2.55106900 |
| C | -10.05233100 | 1.64396300 | -3.64623400 |
| C | -10.94094900 | 0.63729700 | -4.09441300 |
| C | -10.98745300 | -0.57500500 | -3.44688500 |

| | | | |
|---|---|---|---|
| C | -7.51552500 | -1.65131700 | 1.00472200 |
| C | -5.72838600 | -0.73130100 | -0.51579900 |
| H | 11.57499400 | -0.82367800 | -4.95643800 |
| H | 10.00364500 | -2.59187800 | -4.17517100 |
| H | 8.56473900 | -2.20955500 | -2.22696600 |
| H | 11.65195100 | 1.36240900 | -3.79179600 |
| H | 9.30460300 | 3.32715000 | -0.15546000 |
| H | 10.82910700 | 2.87056600 | -2.05190700 |
| H | 4.95542200 | -3.52530200 | 1.29455100 |
| H | 10.11732100 | -1.82315700 | 0.11986600 |
| H | 10.84618900 | -3.98508100 | 1.02657200 |
| H | 9.17507300 | -5.64966700 | 1.82873000 |
| H | 6.75910200 | -5.10358700 | 1.76704100 |
| H | 1.84480300 | 1.66062800 | 0.60516700 |
| H | -0.50940100 | 2.43176000 | 0.61121800 |
| H | -1.84514400 | -1.66059800 | 0.60397000 |
| H | 0.50908100 | -2.43172100 | 0.60982900 |
| H | -9.17559000 | 5.64976200 | 1.82847700 |
| H | -10.84657600 | 3.98484000 | 1.02675400 |
| H | -10.11752800 | 1.82292500 | 0.12019300 |
| H | -6.75955300 | 5.10401100 | 1.76655400 |
| H | -4.95572500 | 3.52586600 | 1.29418000 |
| H | -10.82873800 | -2.87101800 | -2.05156500 |
| H | -9.30415500 | -3.32729600 | -0.15510600 |
| H | -8.56499200 | 2.20936200 | -2.22699300 |
| H | -10.00397900 | 2.59138100 | -4.17518400 |
| H | -11.57517100 | 0.82296900 | -4.95627700 |
| H | -11.65182100 | -1.36306900 | -3.79149900 |
| N | -6.12594500 | -1.73696700 | 0.49409000 |
| H | -7.58115000 | -0.88839100 | 1.78428100 |
| H | -7.75831600 | -2.61548800 | 1.45007900 |
| H | -6.16314300 | -0.98099100 | -1.48566700 |
| H | -4.64622000 | -0.76749000 | -0.60549700 |
| N | 6.12621400 | 1.73727000 | 0.49393900 |
| H | 6.16331600 | 0.98112500 | -1.48578100 |
| H | 4.64631300 | 0.76799100 | -0.60560000 |
| C | 5.26938100 | 2.67732300 | 0.92337300 |
| N | 4.35510700 | 3.21216600 | 0.08663000 |
| C | 4.54234200 | 3.70125900 | -1.31443800 |
| C | 6.00753800 | 3.94487300 | -1.67129800 |
| H | 6.04377300 | 4.43205800 | -2.65079800 |
| H | 6.59360500 | 3.02626300 | -1.73792800 |
| H | 6.48718100 | 4.61203700 | -0.94770900 |
| C | 3.80797700 | 2.83321300 | -2.33863900 |
| H | 4.04657100 | 4.67784500 | -1.29815600 |
| H | 3.76067000 | 3.36908000 | -3.29266700 |
| H | 2.78243500 | 2.62685500 | -2.01505400 |
| H | 4.31467000 | 1.88162500 | -2.51522900 |
| C | -4.54252700 | -3.70071900 | -1.31478700 |
| C | -6.00785800 | -3.94409300 | -1.67124400 |
| H | -6.04437700 | -4.43188400 | -2.65042800 |
| H | -6.59368100 | -3.02536200 | -1.73835700 |
| H | -6.48758600 | -4.61069200 | -0.94717800 |
| C | -3.80830700 | -2.83283700 | -2.33920200 |
| H | -3.76191900 | -3.36846300 | -3.29340900 |
| H | -2.78243000 | -2.62716500 | -2.01623000 |
| H | -4.31454400 | -1.88088500 | -2.51517200 |
| C | -5.26897500 | -2.67701600 | 0.92322800 |
| N | -4.35478600 | -3.21156500 | 0.08616700 |
| H | -4.04699900 | -4.67743800 | -1.29862000 |
| N | -5.29108100 | -3.11901200 | 2.19568400 |
| C | 5.40243600 | 2.34405000 | 3.46975600 |
| C | 5.08350100 | 0.86035800 | 3.30281000 |
| H | 5.01579900 | 0.41398500 | 4.30014300 |
| H | 5.85345300 | 0.31645600 | 2.75238800 |
| H | 4.12405400 | 0.70677200 | 2.80090400 |
| C | 6.72725900 | 2.59949400 | 4.19054000 |
| H | 6.93848100 | 3.67242800 | 4.25038500 |
| H | 7.56802100 | 2.10619400 | 3.69703300 |

| | | | |
|---|---|---|---|
| H | 6.66140100 | 2.20973100 | 5.21190900 |
| N | 5.29175800 | 3.11891300 | 2.19597100 |
| C | -5.40193200 | -2.34481000 | 3.46982900 |
| C | -5.08251100 | -0.86114400 | 3.30367000 |
| H | -5.85181700 | -0.31701500 | 2.75255300 |
| H | -4.12252500 | -0.70761100 | 2.80274600 |
| H | -5.01579400 | -0.41500400 | 4.30117100 |
| C | -6.72697600 | -2.60021900 | 4.19023200 |
| H | -4.60693100 | -2.78124400 | 4.08420700 |
| H | -6.66098700 | -2.21140600 | 5.21195300 |
| H | -6.93871500 | -3.67310400 | 4.24909900 |
| H | -7.56747200 | -2.10604600 | 3.69716100 |
| H | -3.56701100 | -3.63900800 | 0.56035500 |
| H | -4.87729900 | -4.03667400 | 2.31872200 |
| H | 4.60712800 | 2.77989600 | 4.08415800 |
| H | 4.87813700 | 4.03658500 | 2.31945600 |
| H | 3.56753500 | 3.63969300 | 0.56108100 |
| C | 7.51582300 | 1.65143300 | 1.00451000 |
| H | 7.58135800 | 0.88853800 | 1.78410700 |
| H | 7.75873900 | 2.61558800 | 1.44982200 |

Cartesian coordinates of the optimized geometry for the anionic part of (*S*,*S*)-**9** at B3LYP-D3BJ(SMD)/6-31G* level of theory (number of imaginary frequencies = 0):

| | | | |
|---|---|---|---|
| C | 11.26397600 | -0.73419600 | -3.40480100 |
| C | 10.30569000 | -1.64934500 | -2.90867000 |
| C | 9.40229300 | -1.26522500 | -1.94259200 |
| C | 9.40426000 | 0.05534300 | -1.41328700 |
| C | 10.34896800 | 0.99189600 | -1.95116200 |
| C | 11.27561600 | 0.55997500 | -2.93701800 |
| C | 8.48096200 | 0.48715300 | -0.40177000 |
| C | 8.45783000 | 1.83353300 | -0.05667900 |
| C | 9.37858600 | 2.75871100 | -0.60171700 |
| C | 10.31871600 | 2.34158000 | -1.51006800 |
| C | 5.57353900 | -2.17987900 | 1.35760800 |
| C | 5.17316300 | -0.98827800 | 0.77422200 |
| C | 6.16615900 | -0.11604900 | 0.22266000 |
| C | 7.51532000 | -0.43863600 | 0.24620300 |
| C | 7.93414700 | -1.62846500 | 0.93284700 |
| C | 6.94177200 | -2.51669100 | 1.46635500 |
| C | 9.30114100 | -1.95620300 | 1.14122600 |
| C | 9.66646200 | -3.11306300 | 1.79456200 |
| C | 8.68456200 | -4.00915500 | 2.28000700 |
| C | 7.35133500 | -3.70941400 | 2.12286300 |
| O | 5.74166500 | 1.02513900 | -0.39190000 |
| C | 3.80444300 | -0.61894700 | 0.71215300 |
| C | 2.63271800 | -0.29616800 | 0.67312800 |
| C | 1.26944200 | 0.09844300 | 0.62309700 |
| C | 0.92735100 | 1.43686500 | 0.33776100 |
| C | -0.40352200 | 1.82433800 | 0.27862000 |
| C | -1.43150500 | 0.88695400 | 0.50281300 |
| C | -1.09079100 | -0.45040000 | 0.79958500 |
| C | 0.23892300 | -0.83650200 | 0.85845000 |
| C | -2.80568100 | 1.24203400 | 0.43862600 |
| C | -4.00741400 | 1.42430400 | 0.41894500 |
| C | -9.48892800 | 3.97490400 | 1.53858300 |
| C | -10.25680100 | 2.81590700 | 1.27532700 |
| C | -9.65592400 | 1.66299200 | 0.81872100 |
| C | -8.25373900 | 1.60148700 | 0.59544200 |
| C | -7.47292800 | 2.76338600 | 0.90989900 |
| C | -8.12481400 | 3.94207500 | 1.36466400 |
| C | -7.59385300 | 0.42280500 | 0.10580900 |
| C | -6.20752900 | 0.39686100 | 0.06874400 |
| C | -5.42164100 | 1.54077900 | 0.42636700 |
| C | -6.06425300 | 2.70799300 | 0.80347100 |
| C | -9.74681000 | -3.17364100 | -0.94539400 |
| C | -8.71130400 | -3.20236500 | -0.04559700 |
| C | -8.00710100 | -2.01606300 | 0.26552000 |

| | | | |
|---|---|---|---|
| C | -8.33992300 | -0.79392300 | -0.30855400 |
| C | -9.36525600 | -0.76728200 | -1.31385400 |
| C | -10.09277000 | -1.96779100 | -1.61105400 |
| C | -9.67382400 | 0.39999900 | -2.06646200 |
| C | -10.67447300 | 0.39624500 | -3.01272500 |
| C | -11.42207100 | -0.77759600 | -3.26787000 |
| C | -11.12690900 | -1.93475500 | -2.58399800 |
| O | -6.99947900 | -2.09082200 | 1.19275600 |
| O | -5.55175700 | -0.71547700 | -0.37258500 |
| H | 11.97459100 | -1.05061600 | -4.16346500 |
| H | 10.27615400 | -2.66303300 | -3.29916800 |
| H | 8.66517700 | -1.97416400 | -1.58511700 |
| H | 11.98974400 | 1.28236100 | -3.32537400 |
| H | 9.31311800 | 3.79277900 | -0.27969200 |
| H | 11.03493900 | 3.04597600 | -1.92535800 |
| H | 4.82564700 | -2.85298700 | 1.76566200 |
| H | 10.06516400 | -1.27460400 | 0.78739200 |
| H | 10.71947600 | -3.33577600 | 1.94417300 |
| H | 8.98592700 | -4.92123900 | 2.78761100 |
| H | 6.58359900 | -4.37465700 | 2.51000600 |
| H | 1.72024500 | 2.15886600 | 0.17081300 |
| H | -0.66125300 | 2.85484100 | 0.05538000 |
| H | -1.88816200 | -1.16224000 | 0.99134200 |
| H | 0.49761400 | -1.86561400 | 1.08674600 |
| H | -9.97549800 | 4.87953400 | 1.89255400 |
| H | -11.33047000 | 2.83210000 | 1.44196600 |
| H | -10.25736400 | 0.78100200 | 0.63494200 |
| H | -7.51593800 | 4.81494500 | 1.58667500 |
| H | -5.47631000 | 3.58338600 | 1.06230300 |
| H | -10.29931300 | -4.08002800 | -1.17933900 |
| H | -8.40711300 | -4.11972900 | 0.44743600 |
| H | -9.10070900 | 1.30321100 | -1.89502400 |
| H | -10.88489500 | 1.30183600 | -3.57539100 |
| H | -12.21283400 | -0.76597100 | -4.01300300 |
| H | -11.67459100 | -2.85221000 | -2.78620200 |
| O | 7.55463200 | 2.28958800 | 0.86774200 |
| P | 5.95072200 | 2.51834600 | 0.38058900 |
| O | 5.15681700 | 2.57039100 | 1.64311600 |
| O | 5.88206100 | 3.53577800 | -0.71060100 |
| P | -5.40124200 | -2.06399700 | 0.63967300 |
| O | -5.14822400 | -3.21745500 | -0.27434900 |
| O | -4.57006400 | -1.73618800 | 1.83734200 |

Cartesian coordinates of the optimized geometry for (*S*,*S*)-**8**+(*S*,*S*)-**9** at B3LYP-D3BJ(SMD)/6-31G* level of theory (number of imaginary frequencies = 0):

| | | | |
|---|---|---|---|
| C | 2.68823400 | 11.72784200 | 3.05651500 |
| C | 1.36298500 | 11.23324700 | 3.03774900 |
| C | 1.06198400 | 10.05316600 | 2.39483000 |
| C | 2.06882400 | 9.29894000 | 1.73155500 |
| C | 3.41877800 | 9.78077100 | 1.79218200 |
| C | 3.69266800 | 11.00912300 | 2.45066500 |
| C | 1.79036400 | 8.06581300 | 1.04742700 |
| C | 2.86456700 | 7.32652100 | 0.57163100 |
| C | 4.19550000 | 7.79090200 | 0.64382900 |
| C | 4.46314600 | 9.00689900 | 1.22076900 |
| C | -2.22030400 | 6.47069700 | 0.72979100 |
| C | -1.19440600 | 5.69713100 | 1.24418200 |
| C | 0.12138900 | 6.25802100 | 1.31419200 |
| C | 0.40754500 | 7.54119800 | 0.88582000 |
| C | -0.64016300 | 8.30431200 | 0.26213800 |
| C | -1.96961300 | 7.76576200 | 0.21954100 |
| C | -0.41082500 | 9.56482000 | -0.35010500 |
| C | -1.44107700 | 10.27305200 | -0.92973500 |
| C | -2.75916800 | 9.75945100 | -0.93127800 |
| C | -3.01273500 | 8.52819800 | -0.37322100 |
| O | 1.10749100 | 5.48460700 | 1.88520800 |
| C | -1.35791400 | 4.35224000 | 1.66232000 |

| | | | |
|---|---|---|---|
| C | -1.32035600 | 3.18323200 | 1.99589900 |
| C | -1.03456900 | 1.81454000 | 2.24006900 |
| C | -2.01747600 | 0.86294900 | 2.56880600 |
| C | -1.68952900 | -0.48381500 | 2.64049600 |
| C | -0.37157700 | -0.91029500 | 2.38726300 |
| C | 0.62312600 | 0.05242800 | 2.12654100 |
| C | 0.29850500 | 1.39330800 | 2.04820200 |
| C | -0.04029000 | -2.28373500 | 2.27108800 |
| C | 0.29829200 | -3.42372400 | 2.01997800 |
| C | 4.22892000 | -7.87757600 | 0.47107000 |
| C | 3.25592400 | -8.87467300 | 0.22266600 |
| C | 1.91900500 | -8.62272900 | 0.44119800 |
| C | 1.47808300 | -7.36028100 | 0.92065600 |
| C | 2.46222900 | -6.33543100 | 1.12036700 |
| C | 3.83604800 | -6.63226100 | 0.90314700 |
| C | 0.09429200 | -7.06698900 | 1.17902100 |
| C | -0.25773300 | -5.76648500 | 1.49744200 |
| C | 0.71384100 | -4.73648500 | 1.68622700 |
| C | 2.05496400 | -5.04114800 | 1.51291100 |
| C | -3.02976600 | -10.02966000 | 0.77848900 |
| C | -3.10167000 | -8.83101200 | 0.11412900 |
| C | -2.07636500 | -7.87557500 | 0.28138000 |
| C | -0.96983300 | -8.10221500 | 1.08663600 |
| C | -0.92665800 | -9.31840300 | 1.85145900 |
| C | -1.95821100 | -10.29895800 | 1.67037200 |
| C | 0.08078300 | -9.58241000 | 2.81989600 |
| C | 0.09439800 | -10.76205800 | 3.53048600 |
| C | -0.89966700 | -11.74558500 | 3.31667000 |
| C | -1.90688900 | -11.51073600 | 2.40949200 |
| O | -2.18328800 | -6.69117500 | -0.42476800 |
| O | -1.57782300 | -5.43199100 | 1.69737900 |
| H | 2.91044000 | 12.66329700 | 3.56208700 |
| H | 0.57504500 | 11.78602000 | 3.54170700 |
| H | 0.04412200 | 9.68296900 | 2.40333500 |
| H | 4.72022200 | 11.36307700 | 2.47637900 |
| H | 4.98125100 | 7.16512800 | 0.23370700 |
| H | 5.48237400 | 9.37999400 | 1.27291900 |
| H | -3.22604000 | 6.06496900 | 0.67655800 |
| H | 0.59447900 | 9.96761200 | -0.36758400 |
| H | -1.23708400 | 11.23278100 | -1.39609100 |
| H | -3.56273700 | 10.33108100 | -1.38662200 |
| H | -4.01507500 | 8.10795300 | -0.38773300 |
| H | -3.04256400 | 1.18373500 | 2.71931300 |
| H | -2.45285900 | -1.22463500 | 2.84977500 |
| H | 1.63334600 | -0.27772100 | 1.92390300 |
| H | 1.04313600 | 2.12505800 | 1.75744700 |
| H | 5.28124900 | -8.09536100 | 0.31191200 |
| H | 3.56553200 | -9.84822900 | -0.14660100 |
| H | 1.18702200 | -9.39512700 | 0.23895600 |
| H | 4.56841300 | -5.84931300 | 1.07962700 |
| H | 2.80160400 | -4.26570000 | 1.65447200 |
| H | -3.80722400 | -10.77798600 | 0.65035600 |
| H | -3.92892900 | -8.58864900 | -0.54448400 |
| H | 0.84205700 | -8.83521100 | 3.00789800 |
| H | 0.87291700 | -10.93523100 | 4.26828100 |
| H | -0.87354200 | -12.67400900 | 3.88001800 |
| H | -2.69195100 | -12.24579400 | 2.25058600 |
| O | 2.64880200 | 6.10041400 | -0.03187400 |
| P | 2.27661300 | 4.79562000 | 0.93192800 |
| O | 1.71477900 | 3.75851500 | -0.00276300 |
| O | 3.41027700 | 4.44379000 | 1.85492900 |
| P | -2.60707100 | -5.31202600 | 0.39550300 |
| O | -3.99452300 | -5.41105800 | 0.96532100 |
| O | -2.23419700 | -4.17105300 | -0.51189300 |
| C | 11.44378700 | -0.56705700 | -4.31665600 |
| C | 10.49206900 | -1.61481300 | -4.30571500 |
| C | 9.47256800 | -1.62676100 | -3.38093800 |
| C | 9.34923100 | -0.59294100 | -2.41134700 |
| C | 10.29075300 | 0.48841200 | -2.45302900 |

| | | | |
|---|---|---|---|
| C | 11.33874800 | 0.46366600 | -3.41228800 |
| C | 8.30259600 | -0.56767300 | -1.43032800 |
| C | 8.16242200 | 0.54512100 | -0.60525200 |
| C | 9.08861800 | 1.61321600 | -0.67363600 |
| C | 10.14072900 | 1.57666100 | -1.55604700 |
| C | 5.29006000 | -3.65322900 | -1.17165600 |
| C | 4.93200600 | -2.32610800 | -1.34908200 |
| C | 5.95485900 | -1.32493700 | -1.45477800 |
| C | 7.29332100 | -1.66373600 | -1.32910000 |
| C | 7.66732300 | -3.02129200 | -1.04805700 |
| C | 6.64432700 | -4.02556500 | -1.01284800 |
| C | 9.00415400 | -3.41421000 | -0.77382800 |
| C | 9.31978000 | -4.73293400 | -0.52921700 |
| C | 8.31567500 | -5.73017200 | -0.54922300 |
| C | 7.00594200 | -5.38134500 | -0.78223400 |
| C | 5.57664700 | 0.12275600 | -1.65996400 |
| C | 3.56653400 | -1.93568500 | -1.39584000 |
| C | 2.42973200 | -1.50186400 | -1.38111300 |
| C | 1.13771200 | -0.91850800 | -1.29991100 |
| C | 1.01000600 | 0.48644700 | -1.34233400 |
| C | -0.22522400 | 1.09003900 | -1.17237100 |
| C | -1.37182800 | 0.29724400 | -0.97104600 |
| C | -1.24688900 | -1.10663300 | -0.94484000 |
| C | -0.01053800 | -1.71000800 | -1.10605200 |
| C | -2.64809600 | 0.88522600 | -0.76556600 |
| C | -3.76286700 | 1.33167800 | -0.57419100 |
| C | -8.27601700 | 4.85831800 | 1.63758300 |
| C | -9.35129100 | 4.09459200 | 1.12401100 |
| C | -9.11391700 | 2.98702400 | 0.33971800 |
| C | -7.78878300 | 2.58499700 | 0.02520900 |
| C | -6.70070100 | 3.33984000 | 0.57608400 |
| C | -6.97934800 | 4.48424700 | 1.37199900 |
| C | -7.49490800 | 1.43592300 | -0.78367700 |
| C | -6.18261500 | 1.01882000 | -0.94419400 |
| C | -5.10035900 | 1.77476900 | -0.38319400 |
| C | -5.37007200 | 2.92411300 | 0.34122500 |
| C | -10.50745400 | -1.02665700 | -2.65819700 |
| C | -9.60003900 | -1.55983500 | -1.77517000 |
| C | -8.62707700 | -0.74066400 | -1.15506600 |
| C | -8.56697900 | 0.62206800 | -1.43113000 |
| C | -9.45837000 | 1.18735200 | -2.40225500 |
| C | -10.45562800 | 0.34838300 | -3.00191800 |
| C | -9.37349600 | 2.54081400 | -2.83271100 |
| C | -10.25069200 | 3.04518900 | -3.76589900 |
| C | -11.26004200 | 2.22482300 | -4.32455800 |
| C | -11.35350600 | 0.90411700 | -3.95280800 |
| C | -7.63060800 | -1.35653600 | -0.20065900 |
| C | -5.89793700 | -0.27704600 | -1.66637700 |
| H | 12.24632500 | -0.57400000 | -5.04864500 |
| H | 10.56362100 | -2.41374600 | -5.03824800 |
| H | 8.74555700 | -2.42970400 | -3.39437000 |
| H | 12.05023000 | 1.28536500 | -3.42297200 |
| H | 8.95849700 | 2.46307300 | -0.00960900 |
| H | 10.85840100 | 2.39167800 | -1.59401700 |
| H | 4.51989900 | -4.41638400 | -1.11962900 |
| H | 9.78349400 | -2.66168200 | -0.75398100 |
| H | 10.34881100 | -5.00998000 | -0.31916100 |
| H | 8.58156900 | -6.76789400 | -0.36940300 |
| H | 6.22161800 | -6.13214900 | -0.78966700 |
| H | 1.89432200 | 1.09789200 | -1.47686700 |
| H | -0.30050300 | 2.17167500 | -1.15745000 |
| H | -2.11332600 | -1.72769800 | -0.76227000 |
| H | 0.06653200 | -2.78961700 | -1.05412100 |
| H | -8.47893800 | 5.73173000 | 2.25052300 |
| H | -10.37304600 | 4.38205900 | 1.35464700 |
| H | -9.94670300 | 2.40673900 | -0.03980100 |
| H | -6.14370800 | 5.04986300 | 1.77585500 |
| H | -4.54822400 | 3.49526600 | 0.76260600 |
| H | -11.26367800 | -1.65506500 | -3.12091800 |

| | | | |
|---|---|---|---|
| H | -9.62380900 | -2.61920100 | -1.53517500 |
| H | -8.59976700 | 3.17929500 | -2.42382500 |
| H | -10.16432300 | 4.08108400 | -4.08127000 |
| H | -11.94900900 | 2.63832800 | -5.05547900 |
| H | -12.11035700 | 0.25745300 | -4.38918800 |
| N | -6.28982100 | -1.41696000 | -0.81631100 |
| H | -7.60647700 | -0.77051800 | 0.72125400 |
| H | -7.92069400 | -2.37559100 | 0.05629400 |
| H | -6.43701500 | -0.31003800 | -2.61652900 |
| H | -4.83621200 | -0.37215300 | -1.87045600 |
| N | 5.73919500 | 0.87005300 | -0.40016900 |
| H | 6.19722000 | 0.55989400 | -2.44634800 |
| H | 4.53606900 | 0.21007800 | -1.95857600 |
| C | 4.78687600 | 1.73103200 | 0.03127700 |
| N | 4.05453400 | 2.43944600 | -0.84792700 |
| C | 4.51375700 | 3.23775500 | -2.01558500 |
| C | 6.01706100 | 3.50654900 | -2.02066900 |
| H | 6.23799500 | 4.22920100 | -2.81323900 |
| H | 6.61273800 | 2.61176900 | -2.21521700 |
| H | 6.34240300 | 3.94202100 | -1.07001200 |
| C | 3.99635000 | 2.67049000 | -3.33926800 |
| H | 4.01259400 | 4.20005400 | -1.85945200 |
| H | 4.17120600 | 3.39621100 | -4.14136700 |
| H | 2.91899200 | 2.48385700 | -3.28254100 |
| H | 4.49652200 | 1.73789700 | -3.61426100 |
| C | -4.72805100 | -3.12070500 | -2.89379600 |
| C | -6.19249800 | -3.22571200 | -3.31479200 |
| H | -6.23058400 | -3.59980000 | -4.34335100 |
| H | -6.71422900 | -2.26658500 | -3.29398300 |
| H | -6.73823900 | -3.93204700 | -2.68050600 |
| C | -3.91458300 | -2.16472400 | -3.77114900 |
| H | -3.88602900 | -2.54593700 | -4.79808300 |
| H | -2.88482600 | -2.09079700 | -3.40700300 |
| H | -4.34507500 | -1.15988900 | -3.79835100 |
| C | -5.42067200 | -2.41775500 | -0.53177000 |
| N | -4.53755700 | -2.84811600 | -1.44773100 |
| H | -4.28588800 | -4.11702000 | -3.01199400 |
| N | -5.41115100 | -3.01938400 | 0.66836600 |
| C | 4.39662600 | 0.89812500 | 2.41976500 |
| C | 4.28258700 | -0.54498600 | 1.92983000 |
| H | 3.91847800 | -1.16093000 | 2.75893900 |
| H | 5.23790500 | -0.96462700 | 1.60940800 |
| H | 3.57424300 | -0.64250100 | 1.10399300 |
| C | 5.47506700 | 1.08174100 | 3.48956600 |
| H | 5.52355300 | 2.12722400 | 3.81186000 |
| H | 6.46321300 | 0.78361300 | 3.12636000 |
| H | 5.23538600 | 0.46671200 | 4.36412900 |
| N | 4.52670700 | 1.90330200 | 1.33520300 |
| C | -5.43916700 | -2.41345600 | 2.02513400 |
| C | -5.16127700 | -0.91171900 | 2.04626000 |
| H | -6.00452800 | -0.31116100 | 1.70197000 |
| H | -4.28851100 | -0.65907400 | 1.44092600 |
| H | -4.95409300 | -0.61534100 | 3.07995100 |
| C | -6.69969200 | -2.80767000 | 2.79802800 |
| H | -4.59230000 | -2.90465700 | 2.51892600 |
| H | -6.59392900 | -2.51395900 | 3.84842500 |
| H | -6.84719600 | -3.89217200 | 2.76220100 |
| H | -7.59544400 | -2.32238000 | 2.40021300 |
| H | -3.71465800 | -3.33450100 | -1.05821000 |
| H | -4.94757100 | -3.94266800 | 0.67856400 |
| H | 3.43546300 | 1.15829200 | 2.87919600 |
| H | 4.08978500 | 2.81336400 | 1.55848500 |
| H | 3.16139600 | 2.79387200 | -0.47423200 |
| C | 6.99180700 | 0.63987900 | 0.34775600 |
| H | 6.92061700 | -0.27550000 | 0.94075900 |
| H | 7.12375000 | 1.47715700 | 1.03255500 |

Cartesian coordinates of the optimized geometry for (*S*,*S*)-**8**+(*R*,*R*)-**9** at B3LYP-D3BJ(SMD)/6-31G* level of theory (number of imaginary frequencies = 0):

| | | | |
|---|---|---|---|
| C | -10.38084100 | -7.65377300 | -2.48337500 |
| C | -9.29540900 | -7.64158000 | -1.57595300 |
| C | -8.49156100 | -6.52966000 | -1.45725600 |
| C | -8.72835000 | -5.36461500 | -2.23747700 |
| C | -9.80326100 | -5.39644900 | -3.18656500 |
| C | -10.62130500 | -6.55411700 | -3.27458000 |
| C | -7.91477700 | -4.18586900 | -2.13490900 |
| C | -8.12986000 | -3.15607600 | -3.04230400 |
| C | -9.17878000 | -3.19267500 | -3.98692100 |
| C | -10.01247500 | -4.28162400 | -4.04083700 |
| C | -4.71752500 | -3.66168900 | 0.73102300 |
| C | -4.49695000 | -3.45473800 | -0.62052700 |
| C | -5.56948300 | -3.67838000 | -1.54188800 |
| C | -6.83856900 | -4.03941700 | -1.12090400 |
| C | -7.09143600 | -4.14987300 | 0.29108500 |
| C | -6.00169000 | -4.00280500 | 1.21339800 |
| C | -8.39470600 | -4.33528300 | 0.82557200 |
| C | -8.60233300 | -4.42031200 | 2.18548900 |
| C | -7.51781100 | -4.32719400 | 3.08952000 |
| C | -6.24609400 | -4.11757400 | 2.60927600 |
| O | -5.29971900 | -3.53646200 | -2.87868200 |
| C | -3.28025700 | -2.92810400 | -1.11917600 |
| C | -2.32770100 | -2.35878400 | -1.61385100 |
| C | -1.30049200 | -1.59161800 | -2.21711400 |
| C | -0.19203000 | -1.15940300 | -1.46305300 |
| C | 0.74271900 | -0.30634300 | -2.02280700 |
| C | 0.61220600 | 0.12215900 | -3.36272500 |
| C | -0.47622600 | -0.33916400 | -4.12769400 |
| C | -1.42525700 | -1.17875800 | -3.56100300 |
| C | 1.56522600 | 1.05129000 | -3.85152700 |
| C | 2.43266500 | 1.86699900 | -4.09924100 |
| C | 6.73305000 | 5.84763600 | -6.06303800 |
| C | 7.30833300 | 6.07908700 | -4.79173500 |
| C | 6.83473700 | 5.42285600 | -3.67613300 |
| C | 5.76087100 | 4.49980500 | -3.77088700 |
| C | 5.15771900 | 4.28860200 | -5.05670300 |
| C | 5.67754400 | 4.97404700 | -6.18801100 |
| C | 5.24387000 | 3.79373100 | -2.63143500 |
| C | 4.11230600 | 3.02050200 | -2.79469100 |
| C | 3.51694500 | 2.78101400 | -4.07536700 |
| C | 4.05466000 | 3.40967600 | -5.18400800 |
| C | 6.98668300 | 4.13592100 | 1.30886400 |
| C | 5.65665200 | 4.40302700 | 1.10103100 |
| C | 5.09784800 | 4.23734100 | -0.18584200 |
| C | 5.86586900 | 3.86994800 | -1.28279000 |
| C | 7.23279900 | 3.48941000 | -1.05552200 |
| C | 7.79512300 | 3.63234800 | 0.25625800 |
| C | 8.04459600 | 2.91040700 | -2.07028000 |
| C | 9.33774600 | 2.51322700 | -1.80831300 |
| C | 9.89802900 | 2.68212700 | -0.51974000 |
| C | 9.13792900 | 3.23160100 | 0.48831300 |
| O | 3.74562300 | 4.47639500 | -0.33119200 |
| O | 3.57841900 | 2.36119200 | -1.71937400 |
| H | -11.01020200 | -8.53560200 | -2.56311900 |
| H | -9.08873100 | -8.52095300 | -0.97223900 |
| H | -7.65541900 | -6.54207600 | -0.76815000 |
| H | -11.43727900 | -6.55640000 | -3.99296400 |
| H | -9.29693800 | -2.34710200 | -4.65619500 |
| H | -10.82787500 | -4.31549900 | -4.75836300 |
| H | -3.90780500 | -3.50002900 | 1.43612500 |
| H | -9.23820800 | -4.39878400 | 0.14957800 |
| H | -9.61050800 | -4.55525900 | 2.56680300 |
| H | -7.69533100 | -4.40400300 | 4.15832300 |
| H | -5.40549300 | -4.01315500 | 3.29041500 |
| H | -0.09800800 | -1.46984300 | -0.42974100 |
| H | 1.56513800 | 0.07121100 | -1.42629700 |
| H | -0.58493800 | -0.01002600 | -5.15598200 |

| | | | |
|---|---|---|---|
| H | -2.28794800 | -1.50048900 | -4.13437900 |
| H | 7.11852300 | 6.36885000 | -6.93453700 |
| H | 8.12728200 | 6.78594400 | -4.69246200 |
| H | 7.27755900 | 5.61851100 | -2.70660800 |
| H | 5.21466500 | 4.79878300 | -7.15568200 |
| H | 3.62236000 | 3.23609100 | -6.16455400 |
| H | 7.42801500 | 4.26801900 | 2.29208100 |
| H | 5.00734300 | 4.73844500 | 1.90301200 |
| H | 7.62883300 | 2.76325100 | -3.05956600 |
| H | 9.93118100 | 2.06203300 | -2.59847000 |
| H | 10.92190200 | 2.37332000 | -0.32916800 |
| H | 9.54923600 | 3.35686200 | 1.48683700 |
| O | -7.32756500 | -2.03148700 | -3.01662600 |
| P | -5.78921700 | -2.15118600 | -3.68227300 |
| O | -5.07116900 | -0.94226700 | -3.13513200 |
| O | -5.82084300 | -2.48208300 | -5.13194500 |
| P | 2.73751400 | 3.15667200 | -0.50918500 |
| O | 2.90079900 | 2.20092300 | 0.65482900 |
| O | 1.41556800 | 3.66446600 | -0.96129900 |
| C | -5.89109200 | 8.97186100 | 2.23972400 |
| C | -5.33554100 | 8.12992500 | 3.23304100 |
| C | -5.41680400 | 6.76077800 | 3.11709800 |
| C | -6.06197000 | 6.15749300 | 2.00213400 |
| C | -6.59086000 | 7.01264600 | 0.97925000 |
| C | -6.49978000 | 8.42200200 | 1.13576200 |
| C | -6.17205500 | 4.73778600 | 1.84247200 |
| C | -6.71146700 | 4.21457800 | 0.67283700 |
| C | -7.20756600 | 5.07124800 | -0.33809700 |
| C | -7.16980300 | 6.43566000 | -0.18033600 |
| C | -4.58088100 | 1.92723900 | 4.70079500 |
| C | -4.11875500 | 1.94321400 | 3.39393300 |
| C | -4.67425800 | 2.87553700 | 2.45922500 |
| C | -5.64199400 | 3.78445500 | 2.86131800 |
| C | -6.16340500 | 3.74090100 | 4.19689600 |
| C | -5.61006300 | 2.79822600 | 5.12356600 |
| C | -7.23931600 | 4.56016700 | 4.63151500 |
| C | -7.71639100 | 4.47681500 | 5.92101900 |
| C | -7.14498800 | 3.56887600 | 6.84448900 |
| C | -6.11668900 | 2.74499500 | 6.45081700 |
| C | -4.27384600 | 2.81446000 | 1.00392100 |
| C | -3.06675300 | 1.06063800 | 3.01063100 |
| C | -2.12663200 | 0.33813800 | 2.73638600 |
| C | -0.97992700 | -0.47736500 | 2.52079800 |
| C | 0.15863600 | 0.03446200 | 1.86584800 |
| C | 1.31544500 | -0.72630400 | 1.77231000 |
| C | 1.37556400 | -2.01870800 | 2.33603300 |
| C | 0.21919000 | -2.54873300 | 2.94464000 |
| C | -0.93887900 | -1.79078100 | 3.03377700 |
| C | 2.60425300 | -2.73727700 | 2.36581000 |
| C | 3.68233200 | -3.29483000 | 2.46856200 |
| C | 8.23305400 | -6.20503300 | 5.37710500 |
| C | 9.28636600 | -5.71180100 | 4.57068400 |
| C | 9.01941400 | -4.93236800 | 3.46662000 |
| C | 7.68443400 | -4.60910000 | 3.10613400 |
| C | 6.62137600 | -5.07251500 | 3.95053400 |
| C | 6.92991900 | -5.88564600 | 5.07536900 |
| C | 7.35545200 | -3.81201800 | 1.95910300 |
| C | 6.03989800 | -3.43934300 | 1.73039700 |
| C | 4.99342700 | -3.83141700 | 2.62755900 |
| C | 5.29085300 | -4.67096800 | 3.68969300 |
| C | 10.30535300 | -2.11645100 | -0.70315800 |
| C | 9.41102100 | -1.32069900 | -0.02900400 |
| C | 8.45390100 | -1.88983600 | 0.84464300 |
| C | 8.39842600 | -3.26879700 | 1.03704800 |
| C | 9.27448700 | -4.12190600 | 0.28862900 |
| C | 10.25440000 | -3.52821900 | -0.57464400 |
| C | 9.18566900 | -5.54117900 | 0.32811200 |
| C | 10.04455100 | -6.32642900 | -0.40699300 |
| C | 11.03790100 | -5.73727300 | -1.22561900 |

| | | | |
|---|---|---|---|
| C | 11.13401300 | -4.36793400 | -1.30967700 |
| C | 7.44784900 | -0.98832600 | 1.52557500 |
| C | 5.72619200 | -2.53880400 | 0.56402400 |
| H | -5.82281400 | 10.05061700 | 2.34702200 |
| H | -4.83507900 | 8.56927800 | 4.09124500 |
| H | -4.97670500 | 6.12909000 | 3.87969400 |
| H | -6.91299800 | 9.05718100 | 0.35646600 |
| H | -7.62744700 | 4.63337800 | -1.23942400 |
| H | -7.56496100 | 7.09219100 | -0.95089200 |
| H | -4.15260300 | 1.22896500 | 5.41323600 |
| H | -7.69212400 | 5.25359800 | 3.93302300 |
| H | -8.54201700 | 5.11063900 | 6.23153200 |
| H | -7.52835100 | 3.51858100 | 7.85946400 |
| H | -5.67902900 | 2.03214900 | 7.14455700 |
| H | 0.14491700 | 1.03757600 | 1.45320500 |
| H | 2.18632700 | -0.30350300 | 1.28753100 |
| H | 0.25031500 | -3.54785000 | 3.36689300 |
| H | -1.81688700 | -2.19526500 | 3.52721200 |
| H | 8.45895700 | -6.82345900 | 6.24090900 |
| H | 10.31522200 | -5.94683400 | 4.82751800 |
| H | 9.83633000 | -4.55644100 | 2.86251100 |
| H | 6.11265800 | -6.23808700 | 5.69901900 |
| H | 4.50048100 | -4.99127300 | 4.36151300 |
| H | 11.04765200 | -1.67600400 | -1.36345200 |
| H | 9.42821600 | -0.24197800 | -0.15743200 |
| H | 8.42271800 | -6.00680900 | 0.94066700 |
| H | 9.95562700 | -7.40815500 | -0.36388100 |
| H | 11.71203400 | -6.36974200 | -1.79602700 |
| H | 11.87825600 | -3.90288600 | -1.95101200 |
| N | 6.12407000 | -1.15995500 | 0.89304800 |
| H | 7.40067200 | -1.21761200 | 2.59498800 |
| H | 7.73401900 | 0.05710500 | 1.41269600 |
| H | 6.24937400 | -2.88499800 | -0.33018700 |
| H | 4.65910500 | -2.53491600 | 0.36178500 |
| N | -5.37279500 | 2.20907800 | 0.22559800 |
| H | -4.04063700 | 3.81346300 | 0.62591600 |
| H | -3.39541300 | 2.18717200 | 0.87729700 |
| C | -5.16225600 | 1.20623900 | -0.66120700 |
| N | -6.08180000 | 0.25231000 | -0.86337600 |
| C | -6.82006100 | -0.55052600 | 0.14749800 |
| C | -8.32997100 | -0.32280600 | 0.06990900 |
| H | -8.84245700 | -1.08872100 | 0.66252800 |
| H | -8.62525200 | 0.65820700 | 0.45343700 |
| H | -8.67142300 | -0.41117900 | -0.96635100 |
| C | -6.25751900 | -0.44784200 | 1.56298000 |
| H | -6.64228000 | -1.57339000 | -0.18749600 |
| H | -6.74433100 | -1.20895300 | 2.18030400 |
| H | -5.18169800 | -0.64573000 | 1.57649900 |
| H | -6.43681700 | 0.52117500 | 2.03227300 |
| C | 5.31575000 | 0.67997700 | 3.08580100 |
| C | 3.95546600 | 0.93367600 | 3.74066900 |
| H | 4.04705100 | 0.85497000 | 4.82939800 |
| H | 3.58709500 | 1.93640100 | 3.49761900 |
| H | 3.21095500 | 0.20810300 | 3.40508900 |
| C | 6.39225100 | 1.59499600 | 3.66802200 |
| H | 6.52536700 | 1.37918400 | 4.73378700 |
| H | 7.35382900 | 1.46050200 | 3.16498200 |
| H | 6.09803400 | 2.64392100 | 3.56783800 |
| C | 5.25526700 | -0.13582700 | 0.72599700 |
| N | 5.18888600 | 0.86204800 | 1.62199000 |
| H | 5.59224000 | -0.36238500 | 3.25363800 |
| N | 4.41527200 | -0.11497500 | -0.32185100 |
| C | -3.29196700 | 2.32495100 | -1.91930700 |
| C | -3.46134000 | 2.35976500 | -3.44054900 |
| H | -2.93538100 | 3.22659000 | -3.85478600 |
| H | -3.04066500 | 1.45713800 | -3.89681600 |
| H | -4.51779300 | 2.42385400 | -3.72105200 |
| C | -1.82065300 | 2.25773400 | -1.51402300 |
| H | -1.69661000 | 2.24769900 | -0.42723900 |

| | | | |
|---|---|---|---|
| H | -1.35834500 | 1.35302300 | -1.91299200 |
| H | -1.26940400 | 3.11685500 | -1.90735400 |
| N | -4.03249500 | 1.15975900 | -1.38640500 |
| C | 4.68212100 | -0.50361100 | -1.73695200 |
| C | 4.02468600 | -1.82691600 | -2.14523400 |
| H | 4.60635400 | -2.70215600 | -1.84731100 |
| H | 3.02004600 | -1.91391300 | -1.72217100 |
| H | 3.92896000 | -1.84911000 | -3.23633900 |
| C | 6.16006800 | -0.43136200 | -2.11659900 |
| H | 4.16629300 | 0.28285600 | -2.28677400 |
| H | 6.24408800 | -0.54614700 | -3.20273300 |
| H | 6.59168200 | 0.53683200 | -1.84700700 |
| H | 6.75942500 | -1.21886900 | -1.65331300 |
| H | 4.56265700 | 1.62552900 | 1.33626700 |
| H | 3.70109400 | 0.61091700 | -0.22420100 |
| H | -3.75741500 | 3.21597900 | -1.49221900 |
| H | -3.92853000 | 0.29785000 | -1.92404100 |
| H | -5.91738900 | -0.25802000 | -1.74376100 |
| C | -6.73723500 | 2.71756000 | 0.47542600 |
| H | -7.17100500 | 2.23664800 | 1.35663800 |
| H | -7.34815700 | 2.45186700 | -0.38672900 |

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