Supplementary Information for:

Optically active distorted cyclic triptycenes: chiral stationary phases for HPLC

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1. Materials

Anhydrous solvents (acetone, tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF)), common organic solvents and potassium carbonate were purchased from Kanto Kagaku (Tokyo, Japan). Copper (I) iodide (CuI), triethylamine, diisopropylamine (DIPA) and tetra-*n*-butylammonium fluoride (TBAF) (1.0 M in THF, 0.32 mL, 0.32 mmol) were from Sigma-Aldrich (St. Louis, MO, USA). 2-[2-(2-Chloroethoxy)ethoxy]ethanol and 4-methylphenol were from Tokyo Kasei Kogyo (TCI) (Tokyo, Japan). 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl), *N*,*N*-dimethyl-4-aminopyridine (DMAP), chloromethyl methyl ether (MOMCl), 4-bromocatechol and (triisopropylsilyl)acetylene (TIPSA) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) was purchased from Nacalai (Kyoto, Japan). Porous spherical silica gel with a mean particle size of 5 μm and a mean pore diameter of 30 nm (Daiso gel SP-300-5) was purchased from OSAKA SODA (Osaka, Japan) and was silanized using (3-azidopropyl)triethoxysilane[S1] in toluene/pyridine (8/1, v/v) at 100 °C to prepare an azide-functionalized silica gel (A-silica). All starting materials for the synthesis of axially chiral biaryl compounds were purchased from Nacalai, Wako Pure Chemical Industries and TCI. Chiralpak IG columns (column dimensions: 25 × 2.0 cm (i.d.) and 25 × 0.46 cm (i.d.)) were purchased from Daicel (Tokyo, Japan). *rac*-2,6-Diaminotriptycene (*rac*-**1**),[S2] 4-[(triisopropylsilyl)ethynyl]phenol,[S3] 2-(methoxymethoxy)phenol,[S4] **10**,[S5] **11a**[S5] and **11d**[S5] were prepared according to a literature procedure.

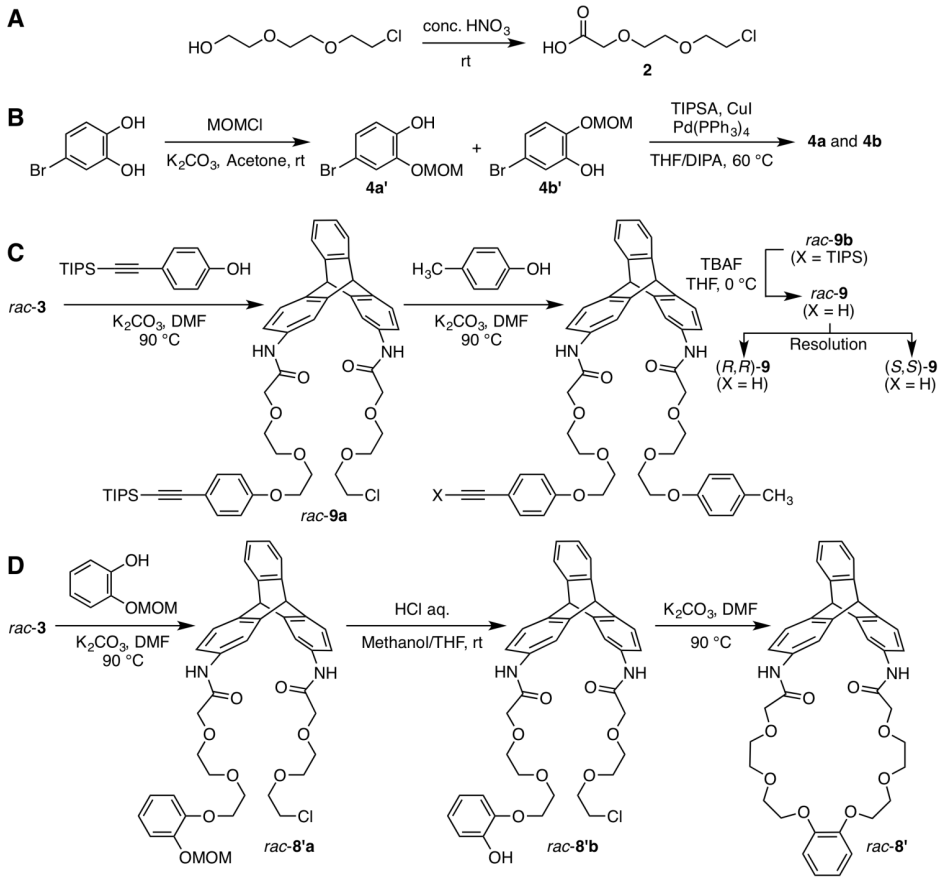
2. Instruments

NMR spectra were taken on a JNM-ECA 500 (JEOL) (500 MHz for ^{1}H, 125 MHz for ^{13}C) spectrometer in $CDCl_3$ using tetramethylsilane as the internal standard. Melting points were measured on a Yanako melting point apparatus and were uncorrected. Thermogravimetric analysis (TGA) was conducted with a TG/DTA6200 (SII NanoTechnology, Chiba, Japan) at a heating rate of 10 °C min^{-1} under an air flow. IR spectra were obtained using a JASCO (Hachioji, Japan) Fourier Transform IR-4700 spectrophotometer with a KBr pellet. Absorption and circular dichroism (CD) spectra were measured using a JASCO V-570 (a scanning rate of 200 nm min^{-1} and a bandwidth of 1.0 nm) and a JASCO J-725 (a scanning rate of 100 nm min^{-1} and a bandwidth of 1.0 nm) spectrometers, respectively, with a quartz cell of 1.0 mm path length (UV-grade) (GL Sciences, Tokyo, Japan). The temperature was controlled using a JASCO ETC-505T (absorption spectroscopy) and a JASCO PTC-348WI apparatus (CD spectroscopy).

The optical rotation was measured at 25 °C with a JASCO P-1030 polarimeter. Chromatographic separations of enantiomers were performed using a JASCO PU-2080 Intelligent HPLC pump equipped with a column oven (JASCO CO-1560), a multi-wavelength detector (JASCO MD-2018) and a CD detector (JASCO CD-2095). A solution of a chiral compound was injected into the chromatographic system by a Rheodyne Model 7125 injector (Rheodyne, Rohnert Park, CA, USA). The single crystal X-ray diffraction measurement was performed on a Bruker Venture D8 diffractometer with Cu Kα radiation (λ = 1.54178 Å). High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 spectrometer with fast atom bombardment (FAB) as the ionization technique.

3. Synthesis

2-[2-(2-Chloroethoxy)ethoxy]acetic acid (**2**), catechol derivatives (a mixture of **4a** and **4b**) and triptycene derivatives ((*R*,*R*)- and (*S*,*S*)-**9** and *rac*-**8'**) were prepared according to Scheme S1. Axially chiral biaryl compounds were synthesized thorough common condensation reactions using the corresponding alcohols and carboxylic acids as starting materials.



Scheme S1 Synthesis of 2-[2-(2-chloroethoxy)ethoxy]acetic acid (**2**) (A), catechol derivatives (a mixture of **4a** and **4b**) (B) and triptycene derivatives ((*R*,*R*)- and (*S*,*S*)-**9** (C) and *rac*-**8'** (D)).

2-[2-(2-Chloroethoxy)ethoxy]acetic acid (**2**). 2-[2-(2-Chloroethoxy)ethoxy]ethanol (7.77 g, 46.1 mmol) was slowly added to 60% HNO_3 aqueous solution (20 mL) and the mixture was stirred at room temperature for 48 h. After quenching the reaction with ice-cold water, the mixture was extracted with dichloromethane, and the organic layer was dried over anhydrous Na_2SO_4 and concentrated. The target compound (6.8 g, 80% yield) was obtained as a pale yellow oil and was used for the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 4.19 (s, 2H, CH_2), 3.82-3.64 (m, 8H, CH_2).

4a/**4b** mixture. To a solution of 4-bromocatechol (5.16 g, 27.3 mmol) and potassium carbonate (5.66 g, 40.9 mmol) in anhydrous acetone (82 mL) was added MOMCl (2.19 g, 27.2 mmol). After stirring at room temperature for 12 h, the mixture was diluted with ethyl acetate, washed with 1 N HCl aqueous solution and water, and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was passed through a short pad of silica gel using hexane/ethyl acetate (4/1, v/v) as the eluent and the solvent was removed under a reduced pressure. The residue (4.57 g) was dissolved in degassed THF/DIPA (3/1, v/v) (65 mL). To this solution was added $Pd(PPh_3)_4$ (1.08 g, 0.93 mmol), CuI (358 mg, 1.88 mmol) and TIPSA (6.85 g, 37.6 mmol). The solution was stirred at 60 °C for 48 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, washed with 1 N HCl aqueous solution and water, and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography using hexane/ethyl acetate (4/1, v/v) as the eluent to give the desired **4a**/**4b** mixture (72/28, mol/mol) as a pale yellow oil (4.94 g, 54%). ^{1}H NMR (500 MHz, $CDCl_3$, rt): **4a**: δ 7.18 (d, J = 2.3 Hz, 1H, ArH), 7.10 (dd, J = 8.0, 1.7 Hz, 1H, ArH), 6.86 (d, J = 8.6 Hz, 1H, ArH), 6.08 (s, 1H, OH), 5.20 (s, 2H, CH_2), 3.52 (s, 3H, CH_3), 1.12 (s, 21H, TIPS); **4b**: δ 7.07 (d, J = 1.7 Hz, 1H, ArH), 7.00-6.96 (m, 2H, ArH), 5.87 (s, 1H, OH), 5.20 (s, 2H, CH_2), 3.50 (s, 3H, CH_3), 1.12 (s, 21H, TIPS).

rac-**3**. 2-[2-(2-Chloroethoxy)ethoxy]acetic acid (4.63 g, 25.3 mmol), *rac*-**1** (3.26 g, 11.4 mmol) and DMAP (3.08 g, 25.1 mmol) were dissolved in anhydrous DMF (41 mL), and the solution was cooled to 0 °C. To this solution was added EDC-HCl (4.83 g, 25.1 mmol) and the mixture was stirred at room temperature for 12 h. The mixture was diluted with hexane/ethyl acetate (1/3, v/v), washed with 1 N HCl aqueous solution and water, and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography using dichloromethane/ethyl acetate (1/1, v/v) as the eluent to give the desired product as a viscous orange oil (5.37 g, 77% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.53 (s, 2H, NH), 7.81 (s, 2H, ArH), 7.35 (dd, J = 5.5, 3.0 Hz, 2H, ArH), 7.30 (d, J = 8.0 Hz, 2H, ArH), 7.07

(dd, J = 7.7, 2.0 Hz, 2H, ArH), 6.98 (dd, J = 6.0, 4.0 Hz, 2H, ArH), 5.38 (s, 2H, CH), 4.06 (s, 4H, CH_2), 3.78 (t, J = 5.4 Hz, 4H, CH_2), 3.73-3.67 (m, 8H, CH_2), 3.64 (t, J = 5.7 Hz, 4H, CH_2).

rac-**6**. To a solution of *rac*-**3** (5.46 g, 8.90 mmol) and potassium carbonate (1.84 g, 13.3 mmol) in anhydrous DMF (24 mL) was added the **4a**/**4b** mixture (72/28, mol/mol) (3.42 g, 14.7 mmol). The solution was stirred at 90 °C for 72 h. After cooling to room temperature, the reaction mixture was diluted with hexane/ethyl acetate (1/2, v/v), washed with water, and then dried over Na_2SO_4. After removing the solvent by evaporation, the crude product was passed through a short pad of silica gel using hexane/acetone (1/1, v/v) as the eluent and the solvent was removed under a reduced pressure. The residue containing *rac*-**5** (2.47 g) was dissolved in THF/methanol (1/1, v/v) (81 mL). To this solution was slowly added conc. HCl (8.1 mL). After stirring at room temperature for 6 h. The mixture was diluted with hexane/ethyl acetate (1/4, v/v) and the solution was washed with water, and then dried over Na_2SO_4. After filtration, the solvent was removed by evaporation and the crude product was purified by silica gel chromatography using hexane/acetone (1/1, v/v) as the eluent to give *rac*-**6** as a viscous yellow oil (1.43 g, 18% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.58 (s, 1H, NH), δ 8.50 (s, 1H, NH), 7.79-7.78 (m, 2H, ArH) 7.34-7.32 (m, 2H, ArH), 7.28 (d, J = 8.0 Hz, 1H, ArH), 7.20 (d, J = 8.0 Hz, 1H, ArH), 7.10-6.96 (m, 6H, ArH), 6.82 (d, J = 8.0 Hz, 1H, ArH), 5.34 (s, 1H, CH), 5.30 (s, 1H, CH), 4.17-4.15 (m, 2H, CH_2), 4.10 (s, 2H, CH_2), 4.07 (s, 2H, CH_2), 3.80-3.72 (m, 12H, CH_2), 3.65 (t, J = 5.4 Hz, 2H, CH_2), 1.11 (s, 21H, TIPS).

rac-**7**. Potassium carbonate (7.13 g, 51.6 mmol) and *rac*-**6** (1.42 g, 1.64 mmol) were dispersed in anhydrous DMF (1600 mL) and the solution was stirred at 90 °C for 72 h. After cooling to room temperature, the reaction mixture was diluted with hexane/ethyl acetate (1/4, v/v), washed with water, and then dried over Na_2SO_4. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane/acetone (1/1, v/v) as the eluent to give the desired product as a viscous orange oil (1.06 g, 78% yield). The enantiomers were resolved by chiral high-performance liquid chromatography (HPLC) on Chiralpak IG (column dimensions: 25 cm × 2.0 cm (i.d.); eluent: hexane/ethyl acetate (3/2, v/v); flow rate 10 mL min^{-1}; temperature *ca.* 20 °C) to give (*R*,*R*)-**7** (246 mg, 0.296 mmol) and (*S*,*S*)-**7** (246 mg, 0.296 mmol) as a pale yellow solid. The enantiomeric excess of the resulting (*R*,*R*)- and (*S*,*S*)-**7** were confirmed to be 99% and 96%, respectively, by chiral HPLC using a Chiralpak IG (column dimensions: 25 cm × 0.46 cm (i.d.); eluent: hexane/ethyl acetate (3/2, v/v); flow rate 0.4 mL min^{-1}; temperature *ca.* 20 °C; $t_{(R,R)\text{-}7}$ = 53.2 min, $t_{(S,S)\text{-}7}$ = 58.7 min). *rac*-**7**: ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.76 (s, 1H, NH), 8.74 (s, 1H, NH), 7.78 (s, 1H, ArH), 7.64 (s, 1H, ArH), 7.36-7.30 (m, 2H,

ArH), 7.15 (d, J = 8.0 Hz, 1H, ArH), 7.09 (s, 1H, ArH), 7.00-6.97 (m, 2H, ArH), 6.94 (d, J = 8.0 Hz, 1H, ArH), 6.91 (d, J = 8.0 Hz, 1H, ArH), 6.73 (d, J = 8.6 Hz, 1H, ArH), 6.67 (d, J = 8.0 Hz, 1H, ArH), 6.52 (d, J = 8.0 Hz, 1H, ArH), 5.26 (s, 1H, CH), 5.21 (s, 1H, CH), 4.10-3.51 (m, 20H, CH_2), 1.22 (s, 21H, TIPS). (*R*,*R*)-**7**: ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.76 (s, 1H, NH), 8.74 (s, 1H, NH), 7.78 (s, 1H, ArH), 7.64 (s, 1H, ArH), 7.36-7.30 (m, 2H, ArH), 7.16 (d, J = 8.0 Hz, 1H, ArH), 7.09 (s, 1H, ArH), 7.00-6.97 (m, 2H, ArH), 6.95 (d, J = 8.0 Hz, 1H, ArH), 6.91 (d, J = 8.0 Hz, 1H, ArH), 6.73 (d, J = 8.6 Hz, 1H, ArH), 6.66 (d, J = 8.0 Hz, 1H, ArH), 6.51 (d, J = 8.0 Hz, 1H, ArH), 5.26 (s, 1H, CH), 5.21 (s, 1H, CH), 4.10-3.51 (m, 20H, CH_2), 1.22 (s, 21H, TIPS). (*S*,*S*)-**7**: ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.76 (s, 1H, NH), 8.74 (s, 1H, NH), 7.78 (s, 1H, ArH), 7.63 (s, 1H, ArH), 7.36-7.30 (m, 2H, ArH), 7.15 (d, J = 8.6 Hz, 1H, ArH), 7.09 (s, 1H, ArH), 7.00-6.97 (m, 2H, ArH), 6.94 (d, J = 8.0 Hz, 1H, ArH), 6.91 (d, J = 8.0 Hz, 1H, ArH), 6.73 (d, J = 8.6 Hz, 1H, ArH), 6.66 (d, J = 7.4 Hz, 1H, ArH), 6.50 (d, J = 8.0 Hz, 1H, ArH), 5.25 (s, 1H, CH), 5.21 (s, 1H, CH), 4.10-3.50 (m, 20H, CH_2), 1.22 (s, 21H, TIPS).

(*R*,*R*)-**8**. To a solution of (*R*,*R*)-**7** (224 mg, 0.269 mmol) in THF (11 mL) was added TBAF (1.0 M in THF, 0.32 mL, 0.32 mmol). The mixture was stirred at 0 °C for 1 h and was diluted with dichloromethane. The solution was washed with 1 N HCl aqueous solution and water, and then dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the crude product was then purified by silica gel chromatography using hexane/acetone (1/1, v/v) as the eluent to give the desired product as a pale yellow solid (180 mg, 99% yield). Mp: 126.6–127.1 °C. $[\alpha]^{25}_D$ +75.0 (*c* 0.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.73 (s, 1H, NH), 8.72 (s, 1H, NH), 7.74 (d, J = 1.7 Hz, 1H, ArH), 7.67 (d, J = 1.7 Hz, 1H, ArH), 7.37-7.32 (m, 2H, ArH), 7.06-7.02 (m, 2H, ArH), 7.01-6.97 (m, 2H, ArH), 6.85-6.81 (m, 2H, ArH), 6.76-6.72 (m, 2H, ArH), 6.56 (d, J = 8.6 Hz, 1H, ArH), 5.25 (s, 1H, CH), 5.24 (s, 1H, CH), 4.05 (d, J = 3.4 Hz, 2H, CH_2), 4.04 (d, J = 1.7 Hz, 2H, CH_2), 3.89-3.56 (m, 16H, CH_2), 3.15 (s, 1H, C≡CH). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 168.33, 149.58, 148.34, 146.63, 146.51, 144.17, 144.12, 141.74, 141.63, 134.08, 134.00, 126.23, 125.37, 123.86, 123.78, 123.61, 123.53, 118.08, 116.65, 116.61, 116.29, 116.02, 114.89, 113.41, 83.76, 76.41, 71.69, 71.65, 70.59, 70.56, 70.44, 70.33, 69.81, 68.32, 67.86, 53.62, 53.57. IR (KBr, cm^{-1}): 2101 (C≡C), 1680 (C=O). HRMS (FAB): *m*/*z* calcd for $C_{40}H_{39}N_2O_8$ ($M+H^+$), 675.2701; found 675.2717.

(*S*,*S*)-**8**. The title compound was prepared from (*S*,*S*)-**7** in the same way as (*R*,*R*)-**8** and obtained in 99% yield as a pale yellow solid. Mp: 124.8–125.3 °C. $[\alpha]^{25}_D$ –75.0 (*c* 0.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.73 (s, 1H, NH), 8.72 (s, 1H, NH), 7.74 (d, J = 1.7 Hz, 1H, ArH), 7.67 (d, J = 1.7 Hz, 1H, ArH), 7.37-7.32 (m, 2H, ArH), 7.06-7.02 (m, 2H, ArH), 7.01-6.97

(m, 2H, ArH), 6.85-6.81 (m, 2H, ArH), 6.76-6.72 (m, 2H, ArH), 6.56 (d, J = 8.0 Hz, 1H, ArH), 5.25 (s, 1H, CH), 5.24 (s, 1H, CH), 4.05 (d, J = 3.4 Hz, 2H, CH_2), 4.04 (d, J = 1.1 Hz, 2H, CH_2), 3.89-3.57 (m, 16H, CH_2), 3.15 (s, 1H, C≡CH). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 168.33, 149.58, 148.34, 146.63, 146.51, 144.17, 144.11, 141.74, 141.63, 134.08, 134.00, 126.23, 125.37, 123.86, 123.78, 123.62, 123.53, 118.06, 116.65, 116.61, 116.29, 116.02, 114.89, 113.40, 83.76, 76.41, 71.69, 71.64, 70.59, 70.56, 70.44, 70.32, 69.81, 68.32, 67.86, 53.62, 53.57. IR (KBr, cm^{-1}): 2101 (C≡C), 1682 (C=O). HRMS (FAB): m/z calcd for $C_{40}H_{39}N_2O_8$ ($M+H^+$), 675.2701; found 675.2713.

rac-**9a**. To a solution of *rac*-**3** (3.80 g, 6.20 mmol) and potassium carbonate (1.28 g, 9.26 mmol) in anhydrous DMF (19 mL) was added 4-[(triisopropylsilyl)ethynyl]phenol (1.70 g, 6.20 mmol). The solution was stirred at 90 °C for 72 h. After cooling to room temperature, the reaction mixture was diluted with hexane/ethyl acetate (1/4, v/v), washed with water, and then dried over Na_2SO_4. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane/acetone (3/2, v/v) as the eluent to give the desired product as a viscous brown oil (2.58 g, 49% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.61 (s, 1H, NH), 8.51 (s, 1H, NH), 7.84 (d, J = 1.7 Hz, 1H, ArH), 7.79 (d, J = 1.7 Hz, 1H, ArH), 7.39 (d, J = 8.6 Hz, 2H, ArH), 7.36-7.33 (m, 1H, ArH), 7.32-7.29 (m, 1H, ArH), 7.27 (d, J = 8.0 Hz, 1H, ArH), 7.10 (d, J = 8.0 Hz, 1H, ArH), 7.05 (dd, J = 8.0, 2.3 Hz, 1H, ArH), 6.99-6.94 (m, 3H, ArH), 6.78 (d, J = 8.6 Hz, 2H, ArH), 5.33 (s, 1H, CH), 5.30 (s, 1H, CH), 4.12 (t, J = 4.6 Hz, 2H, CH_2), 4.07 (s, 2H, CH_2), 4.06 (s, 2H, CH_2), 3.88 (t, J = 4.3 Hz, 2H, CH_2), 3.79 (t, J = 5.7 Hz, 2H, CH_2), 3.74-3.71 (m, 8H, CH_2), 3.65 (t, J = 5.7 Hz, 2H, CH_2), 1.14 (s, 21H, TIPS).

rac-**9b**. To a solution of *rac*-**9a** (2.57 g, 3.01 mmol) and potassium carbonate (624 mg, 4.52 mmol) in anhydrous DMF (9 mL) was added 4-methylphenol (0.49 g, 4.5 mmol). The solution was stirred at 90 °C for 72 h. After cooling to room temperature, the reaction mixture was diluted with hexane/ethyl acetate (1/4, v/v), washed with water, and then dried over Na_2SO_4. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane/acetone (3/2, v/v) as the eluent to give the desired product as a viscous brown oil (1.59 g, 57% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.68 (s, 1H, NH), 8.66 (s, 1H, NH), 7.82 (d, J = 13.2 Hz, 2H, ArH), 7.39 (d, J = 7.4 Hz, 2H, ArH), 7.30-7.28 (m, 2H, ArH), 7.10-7.01 (m, 5H, ArH), 6.97-6.95 (m, 3H, ArH), 6.79 (d, J = 7.4 Hz, 2H, ArH), 6.77 (d, J = 2.3 Hz, 2H, ArH), 5.25 (s, 1H, CH), 5.23 (s, 1H, CH), 4.13-4.10 (m, 4H, CH_2), 4.06 (s, 4H, CH_2), 3.90-3.87 (m, 4H, CH_2), 3.75 (s, 8H, CH_2), 1.14 (s, 21H, TIPS).

rac-**9**. To a solution of *rac*-**9b** (1.73 g, 1.88 mmol) in THF (75 mL) was added tetra-*n*-butylammonium fluoride (1.0 M in THF, 2.3 mL, 2.3 mmol). The mixture was stirred at 0 °C for 1 h and was diluted with dichloromethane. The solution was washed with 1 N HCl aqueous solution and water, and then dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the crude product was then purified by silica gel chromatography using hexane/acetone (1/1, v/v) as the eluent to give the desired product as a pale yellow solid (1.37 g, 95% yield). The enantiomers were resolved by chiral high-performance liquid chromatography (HPLC) on Chiralpak IG (column dimensions: 25 cm × 2.0 cm (i.d.); eluent: hexane/ethyl acetate (3/7, v/v); flow rate 10 mL min^{-1}; temperature *ca.* 20 °C) to give (*R*,*R*)-**9** (346 mg, 0.451 mmol) and (*S*,*S*)-**9** (457 mg, 0.596 mmol) as a pale yellow solid. The enantiomeric excess of the resulting (*R*,*R*)- and (*S*,*S*)-**9** were confirmed to be 99% by chiral HPLC using a Chiralpak IG (column dimensions: 25 cm × 0.46 cm (i.d.); eluent: hexane/ethyl acetate (3/7, v/v); flow rate 0.4 mL min^{-1}; temperature *ca.* 20 °C; $t_{(R,R)\text{-}\mathbf{9}}$ = 19.7 min, $t_{(S,S)\text{-}\mathbf{9}}$ = 23.7 min). (*R*,*R*)-**9**: Mp: 59.2–59.7 °C. $[\alpha]^{25}_{D}$ +68.0 (*c* 0.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.64 (s, 1H, NH), 8.61 (s, 1H, NH), 7.83 (d, *J* = 1.7 Hz, 1H, ArH), 7.82 (d, *J* = 1.7 Hz, 1H, ArH), 7.37 (d, *J* = 8.6 Hz, 2H, ArH), 7.30-7.28 (m, 2H, ArH), 7.09-6.90 (m, 8H, ArH), 6.79-6.76 (m, 4H, ArH), 5.25 (s, 1H, CH), 5.22 (s, 1H, CH), 4.11 (t, *J* = 4.6 Hz, 4H, CH_2), 4.06 (s, 4H, CH_2), 3.89-3.87 (m, 4H, CH_2), 3.74 (s, 8H, CH_2), 3.04 (s, 1H, C≡CH), 2.30 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 168.01, 167.96, 158.97, 156.55, 146.30, 146.21, 145.07, 141.36, 141.21, 134.56, 134.45, 133.76, 130.40, 130.09, 125.24, 123.90, 123.86, 123.65, 123.61, 116.27, 116.23, 116.03, 116.00, 114.68, 114.57, 114.54, 83.66, 76.20, 71.20, 71.17, 70.50, 70.41, 70.35, 70.14, 69.89, 67.33, 67.27, 53.62, 53.53, 20.59. IR (KBr, cm^{-1}): 2103 (C≡C), 1678 (C=O). HRMS (FAB): *m*/*z* calcd for $C_{47}H_{47}N_2O_8$ ($M+H^+$), 767.3327; found 767.3340. (*S*,*S*)-**9**: Mp: 58.8–59.3 °C. $[\alpha]^{25}_{D}$ –67.5 (*c* 0.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.64 (s, 1H, NH), 8.61 (s, 1H, NH), 7.83 (d, *J* = 1.7 Hz, 1H, ArH), 7.82 (d, *J* = 1.7 Hz, 1H, ArH), 7.36 (d, *J* = 8.6 Hz, 2H, ArH), 7.30-7.28 (m, 2H, ArH), 7.09-6.90 (m, 8H, ArH), 6.79-6.75 (m, 4H, ArH), 5.24 (s, 1H, CH), 5.22 (s, 1H, CH), 4.11-4.09 (m, 4H, CH_2), 4.05 (s, 4H, CH_2), 3.89-3.87 (m, 4H, CH_2), 3.73 (s, 8H, CH_2), 3.04 (s, 1H, C≡CH), 2.29 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 168.03, 167.99, 158.98, 156.57, 146.31, 146.23, 145.10, 145.08, 141.36, 141.21, 134.58, 134.48, 133.77, 130.39, 130.11, 125.25, 123.91, 123.88, 123.66, 123.62, 116.29, 116.25, 116.04, 116.00, 114.68, 114.59, 114.55, 83.68, 76.24, 71.21, 71.17, 70.50, 70.41, 70.34, 70.14, 69.88, 67.34, 67.28, 53.62, 53.54, 20.62. IR (KBr, cm^{-1}): 2103 (C≡C), 1680 (C=O). HRMS (FAB): *m*/*z* calcd for $C_{47}H_{47}N_2O_8$ ($M+H^+$), 767.3327; found 767.3340.

rac-**8'a**. To a solution of *rac*-**3** (0.60 g, 0.98 mmol) and potassium carbonate (0.21 g, 1.5 mmol) in anhydrous DMF (3 mL) was added 2-(methoxymethoxy)phenol (0.16 g, 1.0 mmol). The solution was stirred at 90 °C for 72 h. After cooling to room temperature, the reaction mixture was diluted with hexane/ethyl acetate (1/4, v/v), washed with water, and then dried over Na_2SO_4. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane/acetone (1/1, v/v) as the eluent to give the desired product as a viscous yellow oil (0.30 g, 42% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.66 (s, 1H, NH), 8.52 (s, 1H, NH), 7.85 (d, J = 2.3 Hz, 1H, ArH), 7.81 (d, J = 2.3 Hz, 1H, ArH), 7.35-7.28 (m, 2H, ArH), 7.25 (d, J = 6.5 Hz, 1H, ArH), 7.12-7.10 (m, 2H, ArH), 7.04 (dd, J = 8.0, 2.3 Hz, 1H, ArH), 6.99-6.88 (m, 6H, ArH), 5.33 (s, 1H, CH), 5.30 (s, 1H, CH), 5.08 (s, 1H, CH_2), 4.19 (t, J = 4.9 Hz, 2H, CH_2), 4.07 (s, 2H, CH_2), 4.06 (s, 2H, CH_2), 3.91 (t, J = 4.6 Hz, 2H, CH_2), 3.80-3.70 (m, 10H, CH_2), 3.66 (t, J = 5.7 Hz, 2H, CH_2), 3.39 (s, 3H, CH_3).

rac-**8'b**. To a solution of *rac*-**8'a** (0.29 g, 0.40 mmol) in THF/methanol (1/1, v/v) (12 mL) was slowly added conc. HCl (1.2 mL). After stirring at room temperature for 6 h. The mixture was diluted with hexane/ethyl acetate (1/4, v/v) and the solution was washed with water, and then dried over Na_2SO_4. After filtration, the solvent was removed by evaporation and the crude product was purified by silica gel chromatography using hexane/acetone (1/1, v/v) as the eluent to give *rac*-**8'b** as a yellow solid (0.20 g, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.74 (s, 1H, NH), 8.52 (s, 1H, NH), 7.80 (s, 1H, ArH), 7.74 (s, 1H, ArH), 7.33-7.29 (m, 2H, ArH), 7.25 (s, 1H, OH), 7.20 (d, J = 7.4 Hz, 1H, ArH), 7.12-7.05 (m, 3H, ArH), 6.98-6.94 (m, 4H, ArH), 6.87-6.83 (m, 2H, ArH), 5.35 (s, 1H, CH), 5.26 (s, 1H, CH), 4.18 (t, J = 4.0 Hz, 2H, CH_2), 4.10 (s, 2H, CH_2), 4.07 (s, 2H, CH_2), 3.79-3.70 (m, 12H, CH_2), 3.66 (t, J = 5.7 Hz, 2H, CH_2).

rac-**8'**. Potassium carbonate (1.27 g, 9.20 mmol) and *rac*-**8'b** (0.19 g, 0.28 mmol) were dispersed in anhydrous DMF (270 mL) and the solution was stirred at 90 °C for 72 h. After cooling to room temperature, the reaction mixture was diluted with hexane/ethyl acetate (1/4, v/v), washed with water, and then dried over Na_2SO_4. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane/acetone (1/2, v/v) as the eluent to give the desired product as a white solid (71 mg, 40% yield). Mp: 177.2–177.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.76 (s, 2H, NH), 7.70 (d, J = 1.7 Hz, 2H, ArH), 7.33 (q, J = 2.9 Hz, 2H, ArH), 6.99 (q, J = 2.9 Hz, 4H, ArH), 6.88 (q, J = 3.2 Hz, 2H, ArH), 6.81 (dd, J = 8.0, 1.7 Hz, 2H, ArH), 6.70 (d, J = 7.4 Hz, 2H, ArH), 5.21 (s, 2H, CH), 4.05 (d, J = 1.7 Hz, 4H, CH_2), 3.92-3.88 (m, 2H, CH_2), 3.83-3.71 (m, 8H, CH_2), 3.68-3.57 (m, 6H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 168.39, 148.94, 146.56, 144.20, 141.64, 134.13, 125.40, 123.81, 123.65, 121.89,

116.49, 116.06, 114.46, 71.74, 70.65, 70.43, 70.12, 68.18, 53.66. IR (KBr, cm^{-1}): 1677 (C=O). HRMS (FAB): *m*/*z* calcd for $C_{38}H_{39}N_2O_8$ ($M+H^+$), 651.2701; found 651.2710.

rac-1,1'-Binaphthyl-2,2'-diyl bis(4-cyanobenzoate) (*rac*-**11b**). *rac*-1,1'-Bi-2-naphthol (500 mg, 1.75 mmol), 4-cyanobenzoic acid (0.77 g, 5.2 mmol), DMAP (0.64 g, 5.2 mmol) were dissolved in anhydrous dichloromethane (9 mL) and the solution was cooled to 0 °C. To this solution was added EDC-HCl (1.0 g, 5.2 mmol) and the mixture was stirred at rt for 12 h. The mixture was diluted with dichloromethane, washed with 1 N HCl aqueous solution and water, and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography using hexane/dichloromethane (1/4, v/v) as the eluent to give the desired product as a white solid (0.87 g, 91% yield). Mp: 194.5–195.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.01 (d, J = 9.2 Hz, 2H, ArH), 7.94 (d, J = 8.0 Hz, 2H, ArH), 7.62 (d, J = 8.6 Hz, 4H, ArH), 7.54-7.48 (m, 8H, ArH), 7.41-7.36 (m, 4H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 163.30, 146.63, 133.26, 133.00, 132.20, 131.80, 130.27, 130.11, 128.34, 127.37, 126.30, 126.02, 123.53, 121.42, 117.92, 116.77. IR (KBr, cm^{-1}): 2231 (C≡N), 1741 (C=O). HRMS (FAB): *m*/*z* calcd for $C_{36}H_{21}N_2O_4$ ($M+H^+$), 545.1496; found 545.1506.

(*R*)-(+)-1,1'-Binaphthyl-2,2'-diyl bis(4-cyanobenzoate) ((*R*)-**11b**). The title compound was prepared from (*R*)-1,1'-bi-2-naphthol and 4-cyanobenzoic acid in the same way as *rac*-**11b** and obtained in 99% yield as a white solid. Mp: 122.3–122.8 °C. $[\alpha]^{25}_D$ +86.0 (*c* 0.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.01 (d, J = 8.6 Hz, 2H, ArH), 7.93 (d, J = 8.0 Hz, 2H, ArH), 7.63 (d, J = 8.6 Hz, 4H, ArH), 7.54-7.48 (m, 8H, ArH), 7.41-7.36 (m, 4H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 163.26, 146.60, 133.23, 132.96, 132.17, 131.76, 130.24, 130.08, 128.30, 127.33, 126.26, 125.99, 123.50, 121.39, 117.88, 116.72. IR (KBr, cm^{-1}): 2232 (C≡N), 1742 (C=O). HRMS (FAB): *m*/*z* calcd for $C_{36}H_{21}N_2O_4$ ($M+H^+$), 545.1496; found 545.1497.

rac-1,1'-Binaphthyl-2,2'-diyl bis(4-nitrophenylacetate) (*rac*-**11c**). The title compound was prepared from *rac*-1,1'-bi-2-naphthol and 4-nitrophenylacetic acid in the same way as *rac*-**11b** and obtained in 66% yield as a yellow solid. Mp: 177.3–177.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.89 (d, J = 9.2 Hz, 2H, ArH), 7.80 (d, J = 8.6 Hz, 2H, ArH), 7.68 (d, J = 8.6 Hz, 4H, ArH), 7.39 (t, J = 7.4 Hz, 2H, ArH), 7.33 (d, J = 9.2 Hz, 2H, ArH), 7.16 (t, J = 7.7 Hz, 2H, ArH), 6.92 (d, J = 8.0 Hz, 2H, ArH), 6.84 (d, J = 8.6 Hz, 4H, ArH), 3.55 (s, 4H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 168.17, 146.66, 146.20, 139.89, 132.99, 131.63, 129.77, 129.72, 128.01, 127.00, 126.19, 125.55, 123.32, 123.09, 121.40, 41.22. IR (KBr, cm^{-1}): 1752 (C=O). HRMS (FAB): *m*/*z* calcd for $C_{36}H_{25}N_2O_8$ ($M+H^+$), 613.1605; found 613.1618.

rac-1,1'-Binaphthyl-2,2'-diyl bis(3-nitrobenzoate) (*rac*-**11e**). The title compound was prepared from *rac*-1,1'-bi-2-naphthol and 3-nitrobenzoic acid in the same way as *rac*-**11b** and obtained in 89% yield as a white solid. Mp: 178.8–179.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.32-8.29 (m, 4H, ArH), 8.02 (d, J = 8.6 Hz, 2H, ArH), 7.94 (d, J = 4.6 Hz, 2H, ArH), 7.93 (d, J = 3.4 Hz, 2H, ArH), 7.56 (d, J = 9.2 Hz, 2H, ArH), 7.53-7.39 (m, 8H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 162.81, 148.19, 146.61, 135.49, 133.25, 131.87, 130.99, 130.28, 129.68, 128.38, 127.82, 127.47, 126.38, 126.02, 124.87, 123.54, 121.32. IR (KBr, cm^{-1}): 1746 (C=O). HRMS (FAB): m/z calcd for $C_{36}H_{21}N_2O_8$ ($M+H^+$), 585.1292; found 585.1304.

4. Determination of absolute configuration

According to Fig. S1A, (*R*,*R*)-**1** was prepared from a previously reported (*R*,*R*)-**1a**, whose absolute configuration had been determined by the single crystal X-ray structure analysis.[S6] Because the CD spectrum of the resulting (*R*,*R*)-**1** was totally overlapped with that of the optically active **1** prepared from the first-eluted component in Fig. 1A (Fig. S1B), the absolute configurations of the first- and second-eluted components in Fig. 1A were assigned to be 9*R*,10*R* and 9*S*,10*S*, respectively. The absolute configuration of the optically active **9** was also determined in the same way as **7**. A representative synthetic procedure for (*R*,*R*)-**1** through hydrolysis is described below.

To a solution of (*R*,*R*)-**1a** (38 mg, 0.070 mmol) in ethanol (4 mL) was added sodium hydroxide (30 mg, 0.75 mmol) and the mixture was stirred at 90 °C for 24 h. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using dichloromethane/ethyl acetate (4/1, v/v) as the eluent to give (*R*,*R*)-**1** as a pale yellow solid (4 mg, 21% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.30-7.28 (m, 2H, ArH), 7.09 (d, J = 8.0 Hz, 2H, ArH), 6.95-6.93 (m, 2H, ArH), 6.74 (s, 2H, ArH), 6.24 (d, J = 8.0 Hz, 2H, ArH), 5.15 (s, 2H, CH).

5. Preparation of HPLC columns

Preparation of chiral packing materials (CPMs). Immobilization of optically active triptycene derivatives (**8** and **9**) bearing an ethynyl group onto A-silica by the Huisgen 1,3-dipolar cycloaddition reaction was carried out using CuI as a catalyst in a dry Schlenk flask under nitrogen atmosphere according to a method reported previously (Scheme 2).[S7]

(*R*,*R*)-**8**-based CPM**.** A-silica (500 mg) was dispersed in a solution of (*R*,*R*)-**8** (80 mg, 0.118 mmol) and CuI (22 mg, 0.11 mmol) in DMF/triethylamine (12/1, v/v) (1.1 mL). After stirring at room temperature for 72 h, the resulting (*R*,*R*)-**8**-bound silica gel was collected by filtration, washed with dichloromethane, methanol, DMF, chloroform and acetonitrile, and dried *in vacuo* at room temperature overnight. The content of (*R*,*R*)-**8** chemically bonded to silica gel was estimated to be 7 wt% by TGA.

(*S*,*S*)-**8**- and (*R*,*R*)-**9**-based CPMs were prepared from (*S*,*S*)-**8** and (*R*,*R*)-**9** in the same way as (*R*,*R*)-**8**-based CPM, respectively, and the contents of (*S*,*S*)-**8** and (*R*,*R*)-**9** chemically bonded to silica gel were estimated to be 7 wt% by TGA.

Preparation of chiral columns. After fractionating with sieves, each packing material was packed into a stainless-steel column (25 × 0.20 cm (i.d.)) by a slurry packing technique using a Chemco ECONO-PACKER MODEL CPP-085 (Chemco, Osaka, Japan).[S8] The number of theoretical plates per column was estimated to be approximately 2000 for benzene using a hexane/2-propanol (97 : 3, v/v) mixture as the eluent at a flow rate of 0.2 mL min^{-1}, respectively. 1,3,5-Tri-*t*-butylbenzene was used as a non-retained compound to estimate the hold-up time (t_0).[S9]

Supporting data

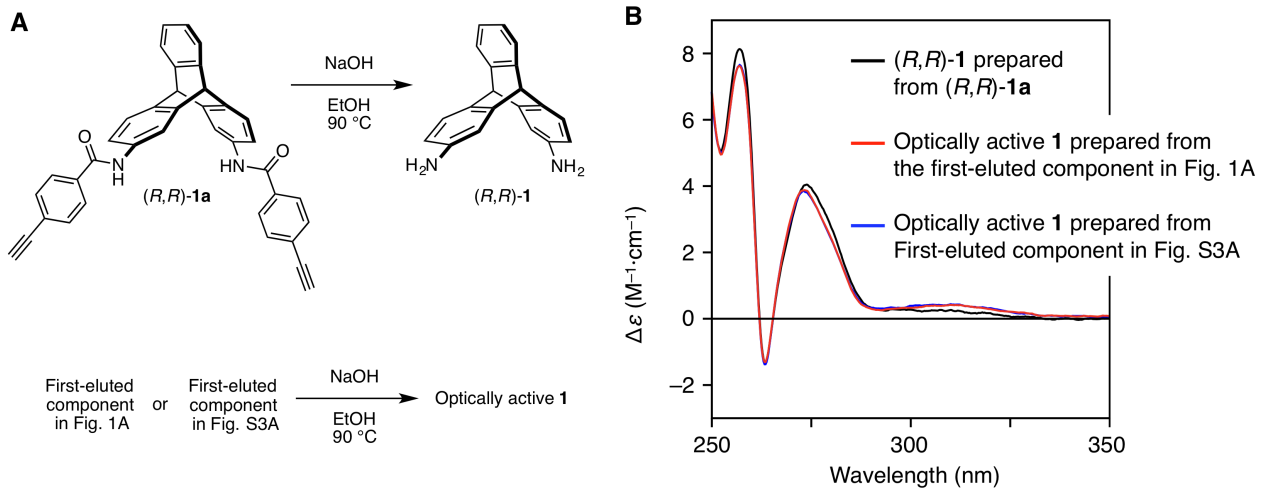


Fig. S1 (A) Synthesis of optically active **1**. (B) CD and absorption spectra of optically active **1** in chloroform at 25 °C. [**1**] = 1.0×10^{-3} M.

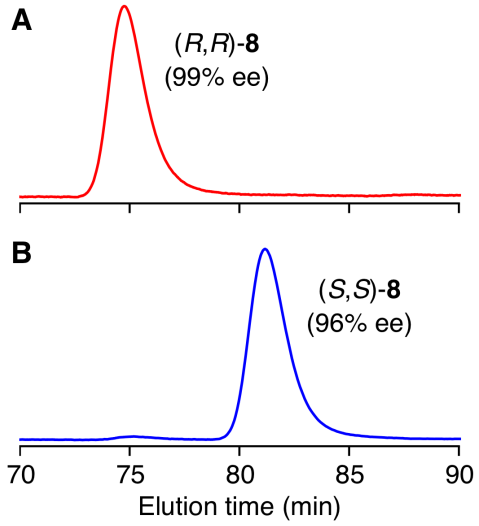


Fig. S2 Elution profiles of (*R*,*R*)-**8** (A) and (*S*,*S*)-**8** (B) on Chiralpak IG (column, 25 cm × 0.46 cm (i.d.); eluent, hexane/ethyl acetate (1/1, v/v); flow rate, 0.4 mL min^{-1}; temperature, *ca.* 20 °C). The chromatograms depict UV traces recorded at 254 nm.

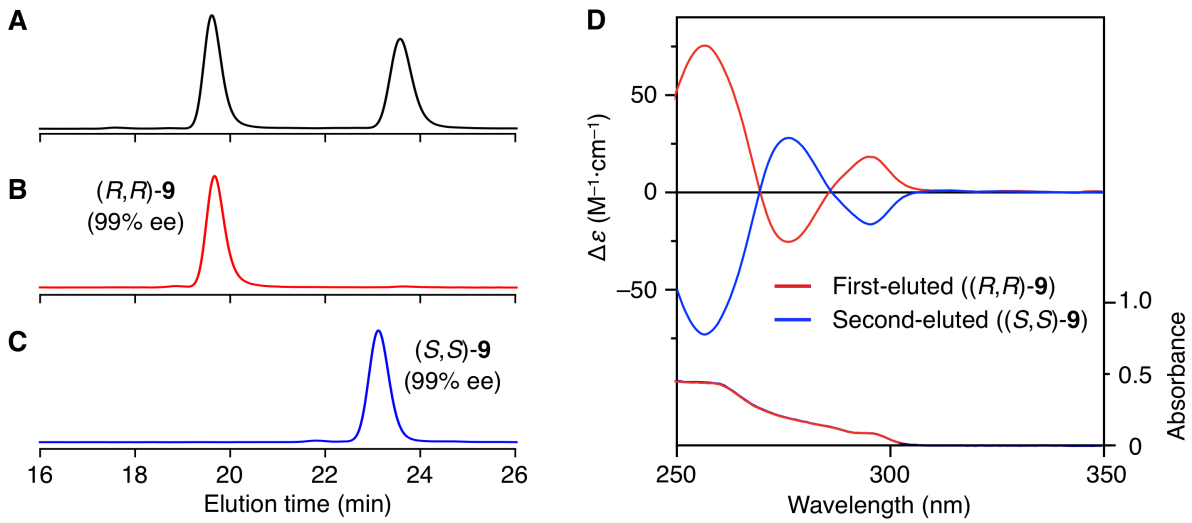


Fig. S3 Elution profiles of *rac*-**9** (A), (*R*,*R*)-**9** (B) and (*S*,*S*)-**9** (C) on Chiralpak IG (column, 25 cm × 0.46 cm (i.d.); eluent, hexane/ethyl acetate (3/2, v/v); flow rate, 0.4 mL min^{-1}; temperature, *ca.* 20 °C). The chromatograms depict UV traces recorded at 254 nm. (D) CD and absorption spectra of the first- (red line) and second-eluted (blue line) components in chloroform at 25 °C. [**9**] = 1.0 × 10^{-4} M.

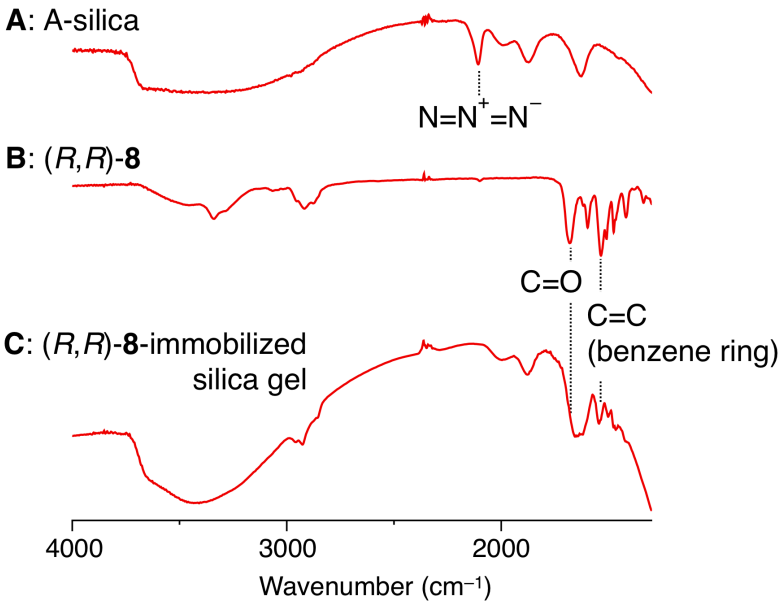


Fig. S4 IR spectra of A-silica (A), (*R*,*R*)-**8** (B) and (*R*,*R*)-**8**-immobilized silica gel (C) in KBr pellets.

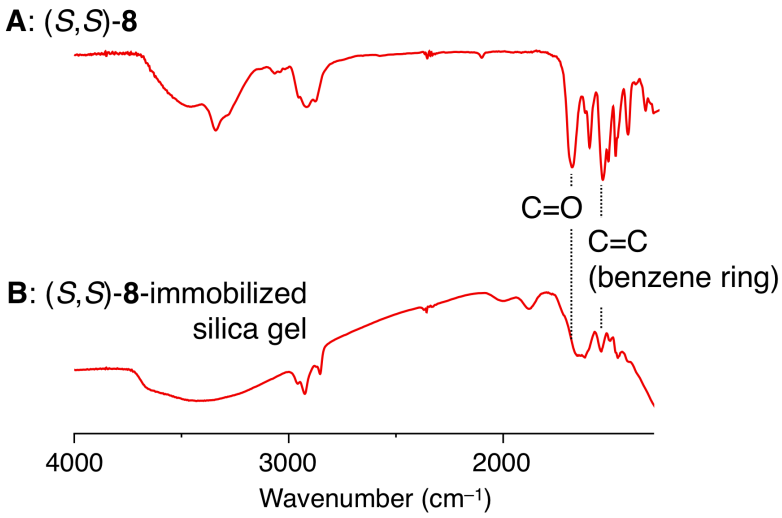


Fig. S5 IR spectra of (*S*,*S*)-**8** (A) and (*S*,*S*)-**8**-immobilized silica gel (B) in KBr pellets.

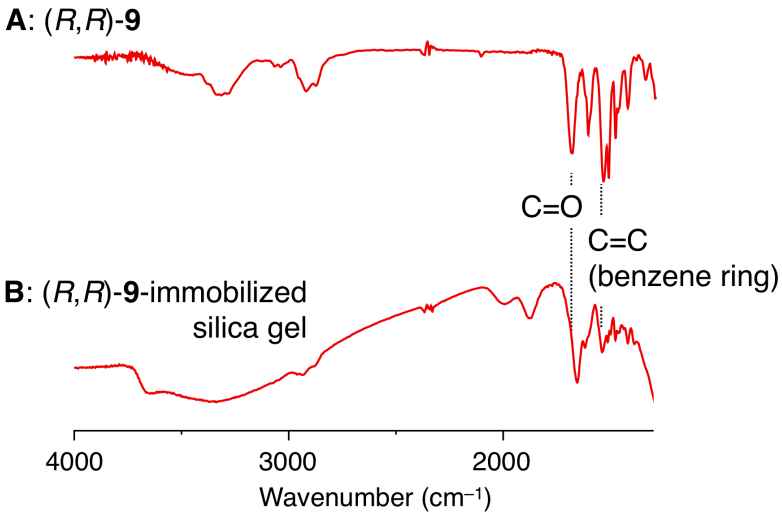


Fig. S6 IR spectra of (*R*,*R*)-**9** (A) and (*R*,*R*)-**9**-immobilized silica gel (B) in KBr pellets.

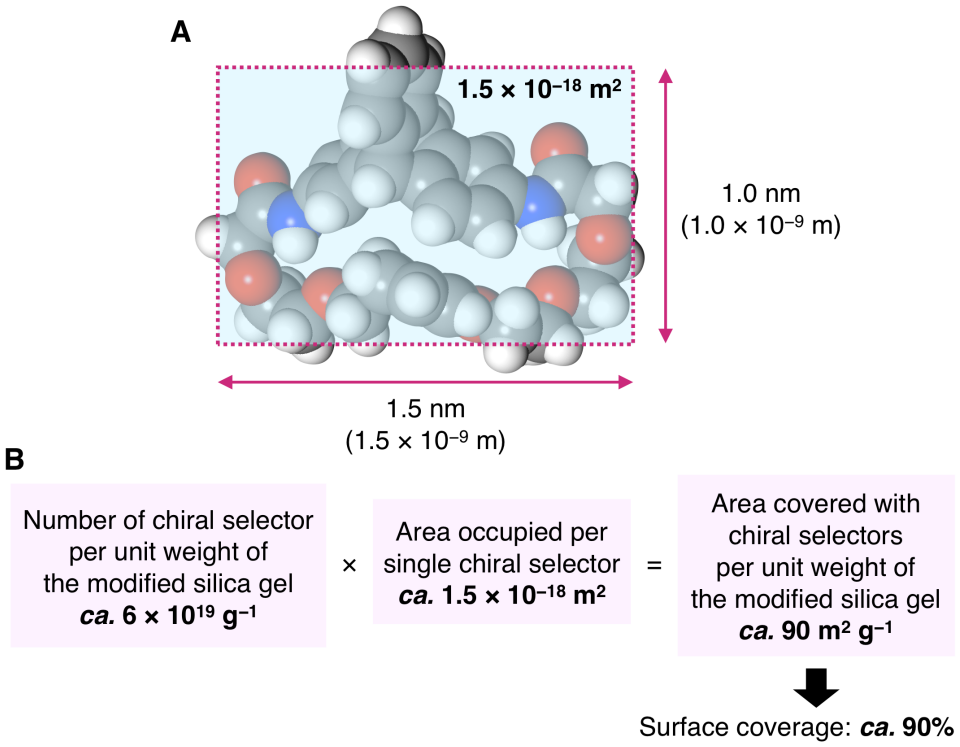


Fig. S7 (A) X-ray crystal structure of **8'** represented by a space-filling model. (B) Derivation of the area covered with chiral selectors per unit weight of the modified silica.

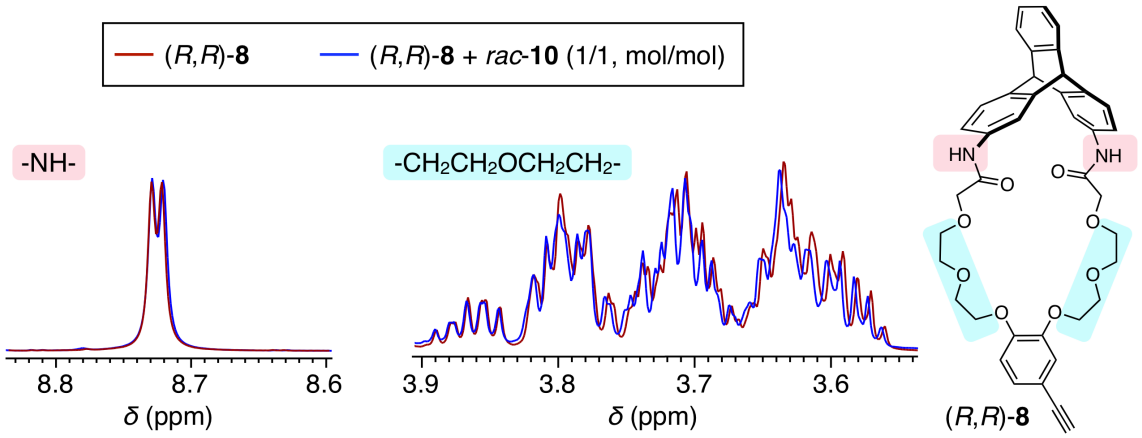


Fig. S8 ^{1}H NMR spectra of (*R*,*R*)-**8** in the absence (red lines) and presence (blue lines) of *rac*-**10** in $CDCl_3$ at room temperature. [(*R*,*R*)-**8**] = [*rac*-**10**] = 30 mM.

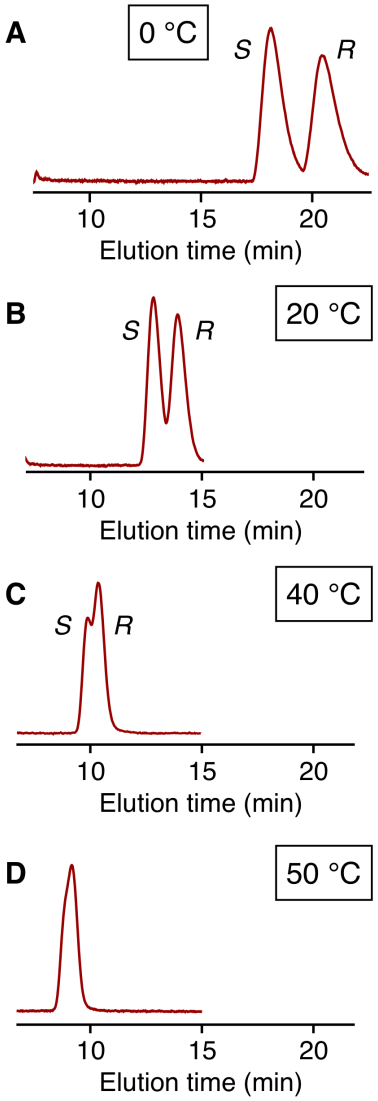


Fig. S9 Elution profiles of **10** on the (*R*,*R*)-**8**-based CSP at various column temperatures (column dimensions, 25 × 0.20 cm (i.d.); eluent, hexane/2-propanol (97/3, v/v); flow rate, 0.2 mL min^{-1}; temperature, 0 (A), 20 (B), 40 (C) and 50 (D) °C). The chromatograms depict UV traces recorded at 254 nm.

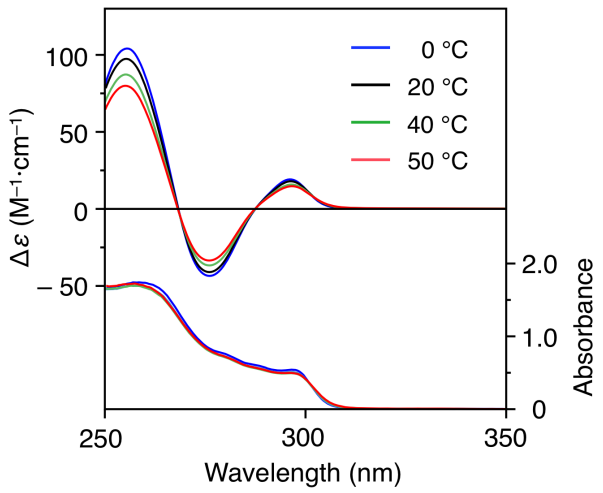


Fig. S10 CD and absorption spectra of (*R*,*R*)-**8** in chloroform at various temperatures. [(*R*,*R*)-**8**] = 5.0×10^{-4} M.

Table S1 Resolutions of racemates on the (*R*,*R*)-**8**-based CSP

H/E (v/v)[a]	97/3		90/10		85/15	
Racemate	k_1	α	k_1	α	k_1	α
10	1.54 (*S*)	1.14	0.52 (*S*)	1.13	0.43 (*S*)	1.09
11a	5.82 (*S*)	1.09	2.43 (*S*)	1.10	1.92 (*S*)	1.10
11b	7.49 (*S*)	1.14	3.53 (*S*)	1.10	2.52 (*S*)	1.10
11c	8.09	1.00	3.40	1.00	2.53	1.00
11d	1.27	1.00	0.52	1.00	0.44	1.00
11e	9.66	1.00	4.34	1.00	3.28	1.00

[a] Eluent: H = hexane; E = ethanol. Column: 25 cm × 0.20 cm (i.d.). Flow rate: 0.20 mL min^{-1}. Temperature: 20 °C. The characters in parentheses represent the absolute configuration of the first-eluted enantiomer.

Table S2 Resolutions of racemates on the (*R*,*R*)-**8**-based CSP at different temperatures

Temperature (°C)	0		20		40		50	
Racemate	k_1	α	k_1	α	k_1	α	k_1	α
10	2.45 (*S*)	1.17	1.54 (*S*)	1.14	0.93 (*S*)	1.10	0.83 (*S*)	*ca.* 1
11a	10.9 (*S*)	1.12	5.82 (*S*)	1.09	3.06 (*S*)	1.08	2.32 (*S*)	1.07
11b	18.0 (*S*)	1.15	7.49 (*S*)	1.14	4.52 (*S*)	1.06	3.49 (*S*)	1.06

Column: 25 cm × 0.20 cm (i.d.). Eluent: hexane/ethanol (97/3, v/v). Flow rate: 0.20 mL min^{-1}. Temperature: 20 °C. The characters in parentheses represent the absolute configuration of the first-eluted enantiomer.

Table S3 Resolutions of racemates on the (*S*,*S*)-**8**-based CSP at different temperatures

Temperature (°C)	0		40		50	
Racemate	k_1	α	k_1	α	k_1	α
10	2.33 (*R*)	1.17	0.88 (*R*)	1.09	0.74 (*R*)	*ca.* 1
11a	10.5 (*R*)	1.11	2.92 (*R*)	1.07	2.22 (*R*)	1.06
11b	18.5 (*R*)	1.11	4.42 (*R*)	1.07	3.31 (*R*)	1.06

Column: 25 cm × 0.20 cm (i.d.). Eluent: hexane/ethanol (97/3, v/v). Flow rate: 0.20 mL min^{-1}. The characters in parentheses represent the absolute configuration of the first-eluted enantiomer.

Table S4 Resolutions of racemates on the (*R*,*R*)-**9**-based CSP

Temperature (°C)	0	
Racemate	k_1	α
10	1.84	1.0
11a	7.29	1.0
11b	14.3	1.0
11c	11.3	1.0
11d	1.08	1.0
11e	14.5	1.0

Column: 25 cm × 0.20 cm (i.d.). Eluent: hexane/ethanol (97/3, v/v). Flow rate: 0.20 mL min^{-1}. The characters in parentheses represent the absolute configuration of the first-eluted enantiomer.

NMR spectral data

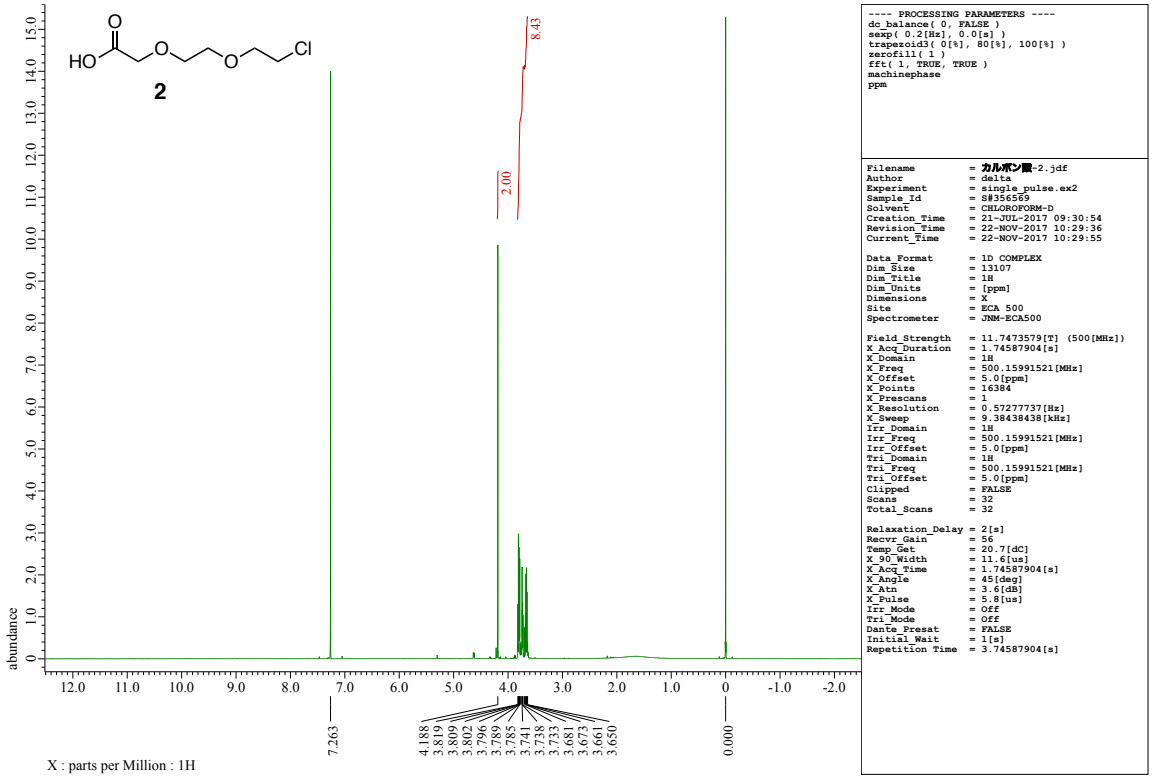


Fig. S11 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of **2**.

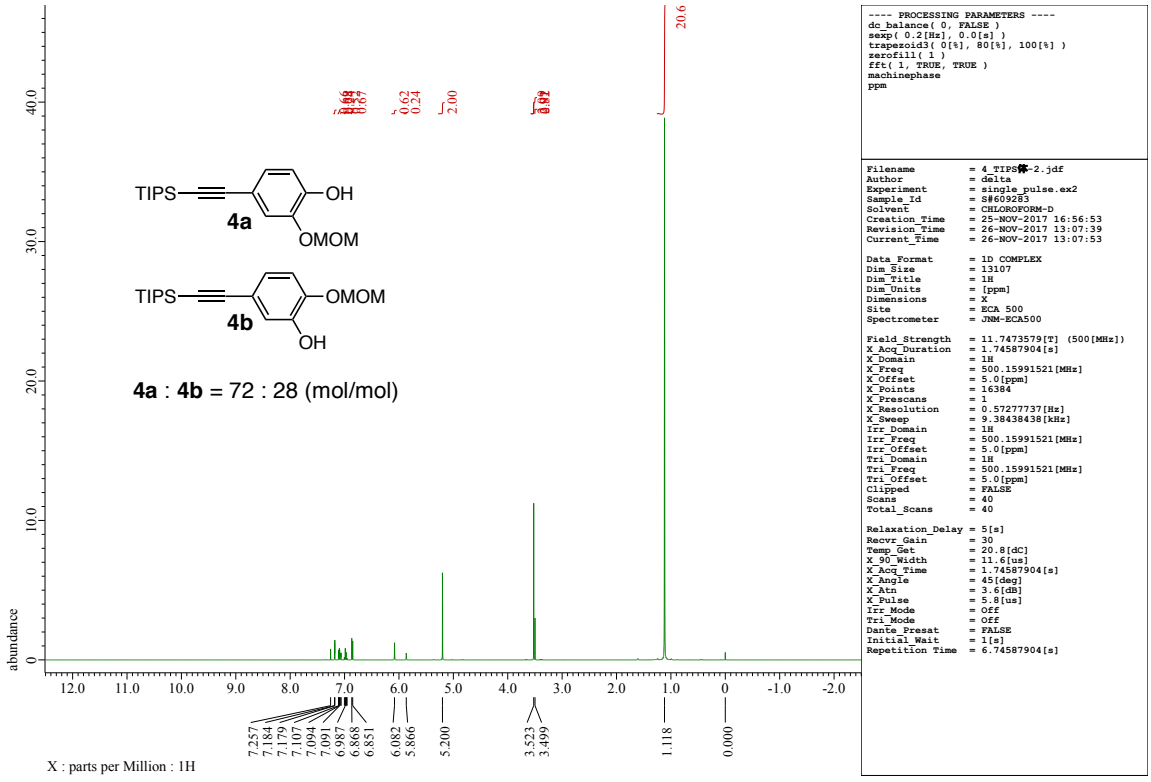


Fig. S12 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of the **4a** and **4b** mixture.

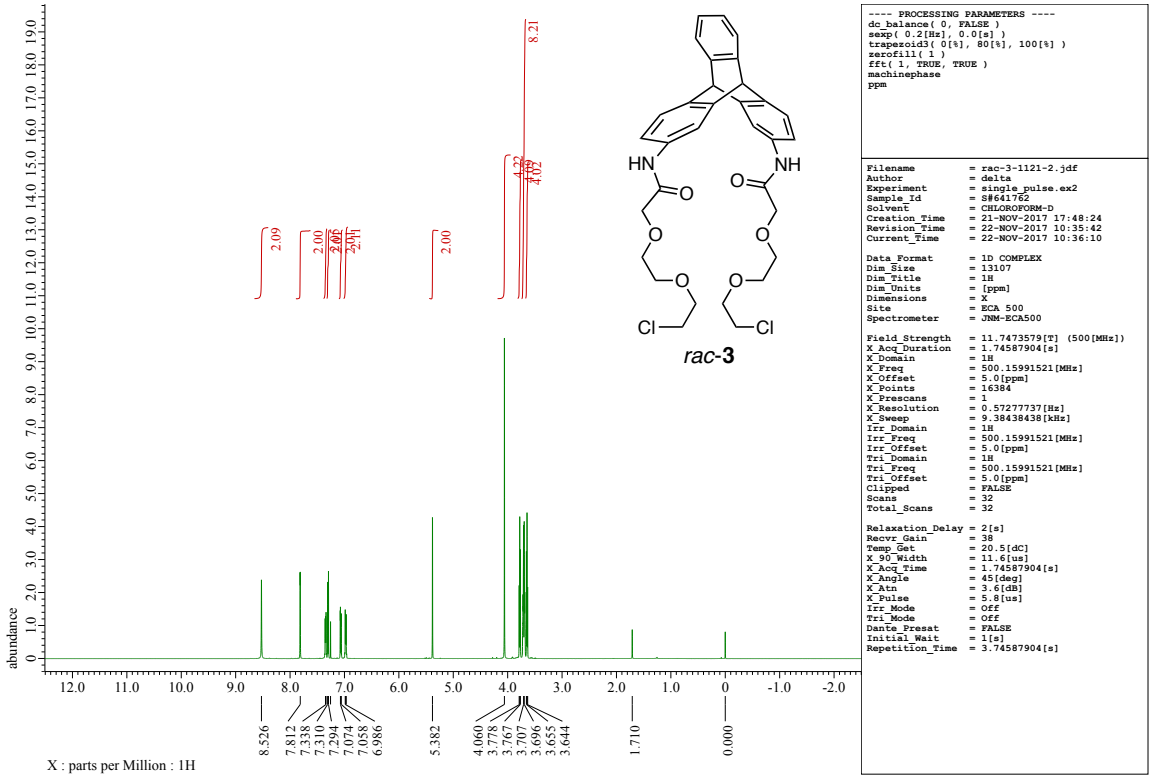


Fig. S13 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of *rac*-**3**.

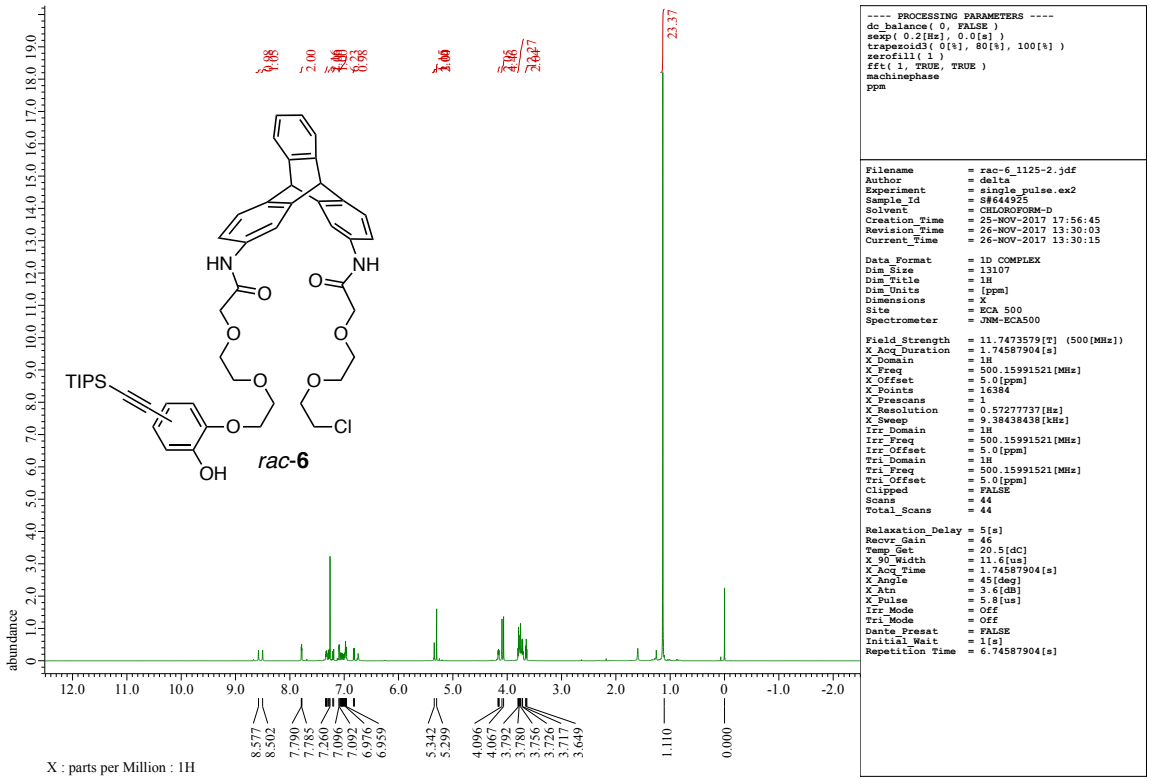


Fig. S14 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of *rac*-**6**.

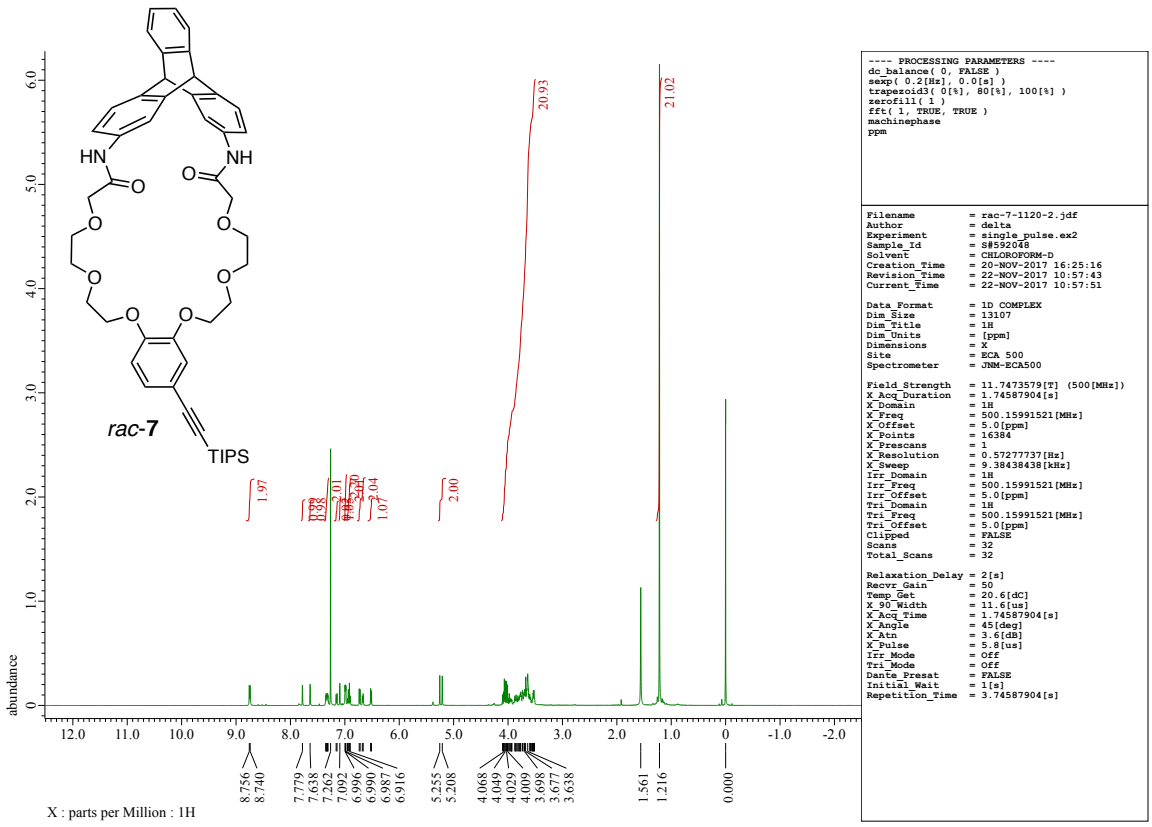


Fig. S15 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of *rac*-**7**.

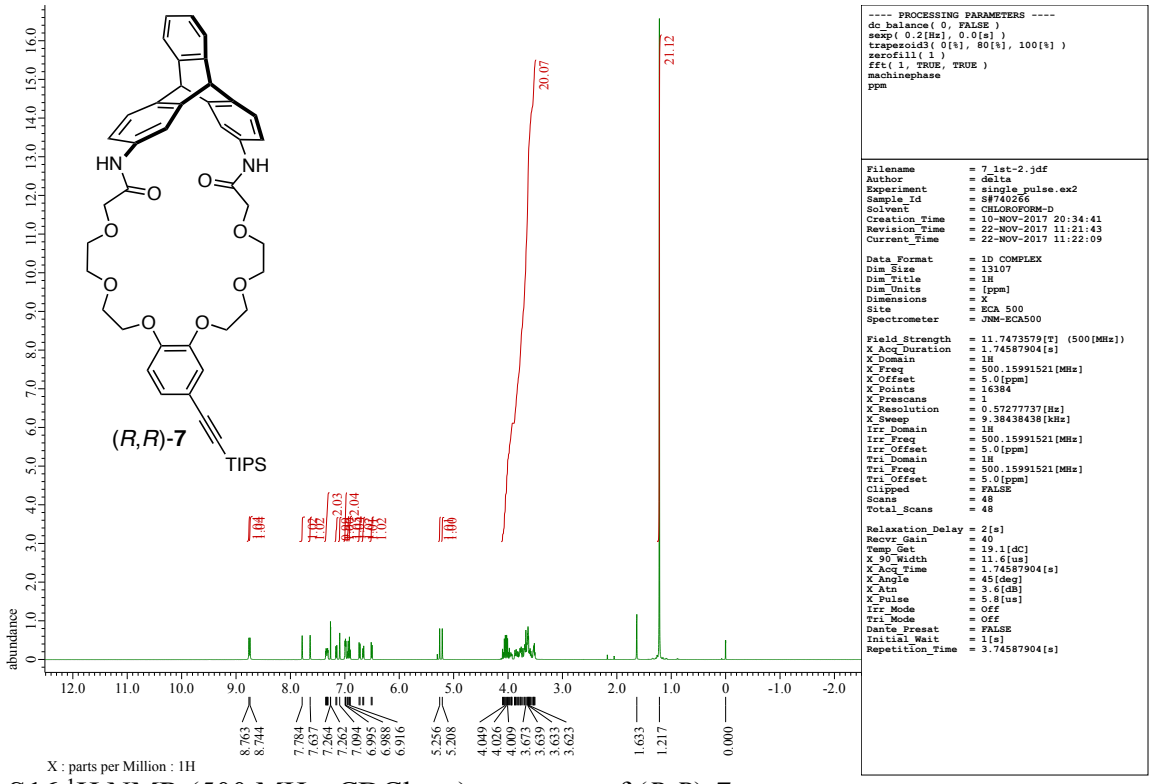


Fig. S16 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of (*R*,*R*)-**7**.

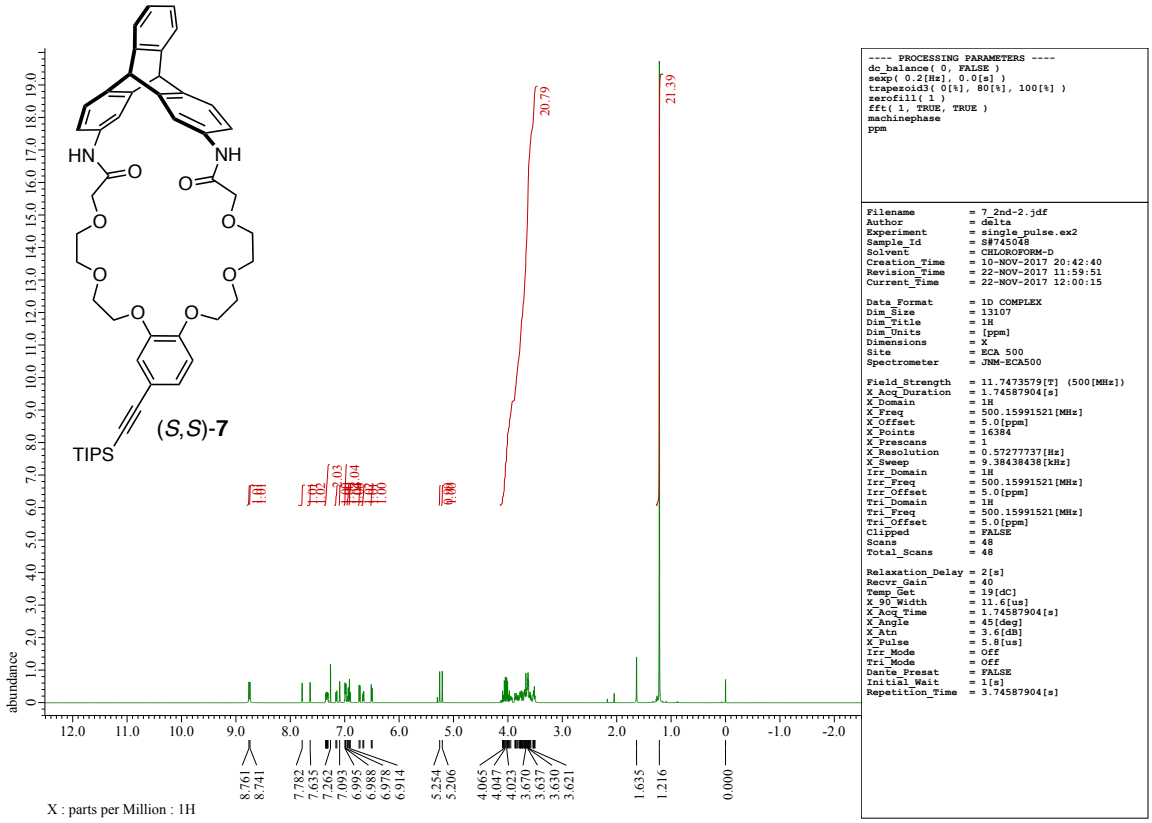


Fig. S17 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of (*S*,*S*)-**7**.

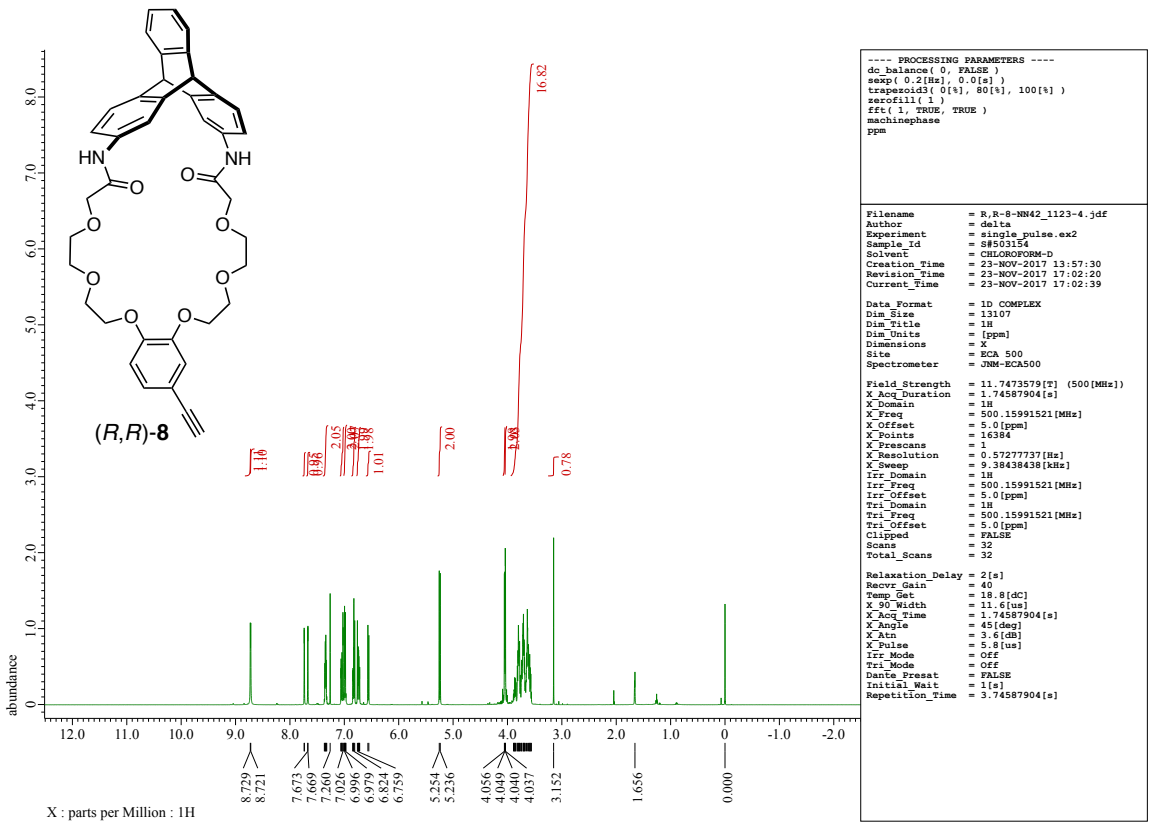


Fig. S18 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of (*R*,*R*)-**8**.

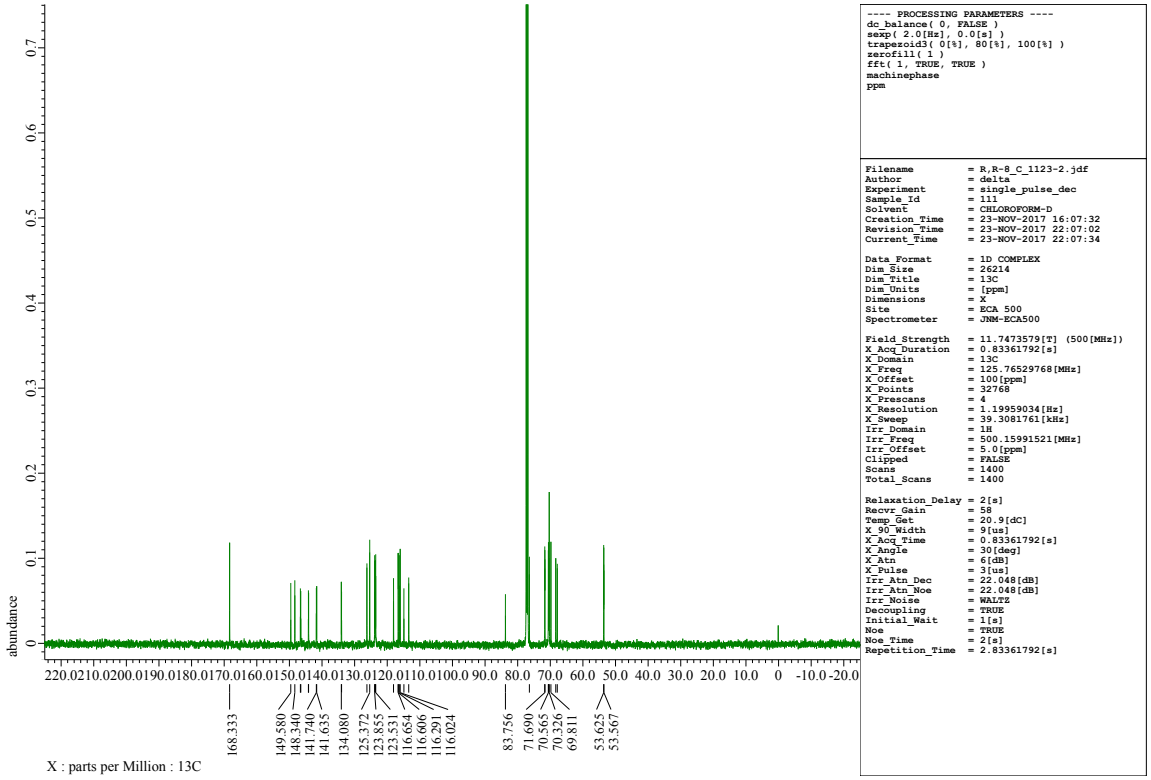


Fig. S19 ^{13}C NMR (125 MHz, $CDCl_3$, rt) spectrum of (*R*,*R*)-**8**.

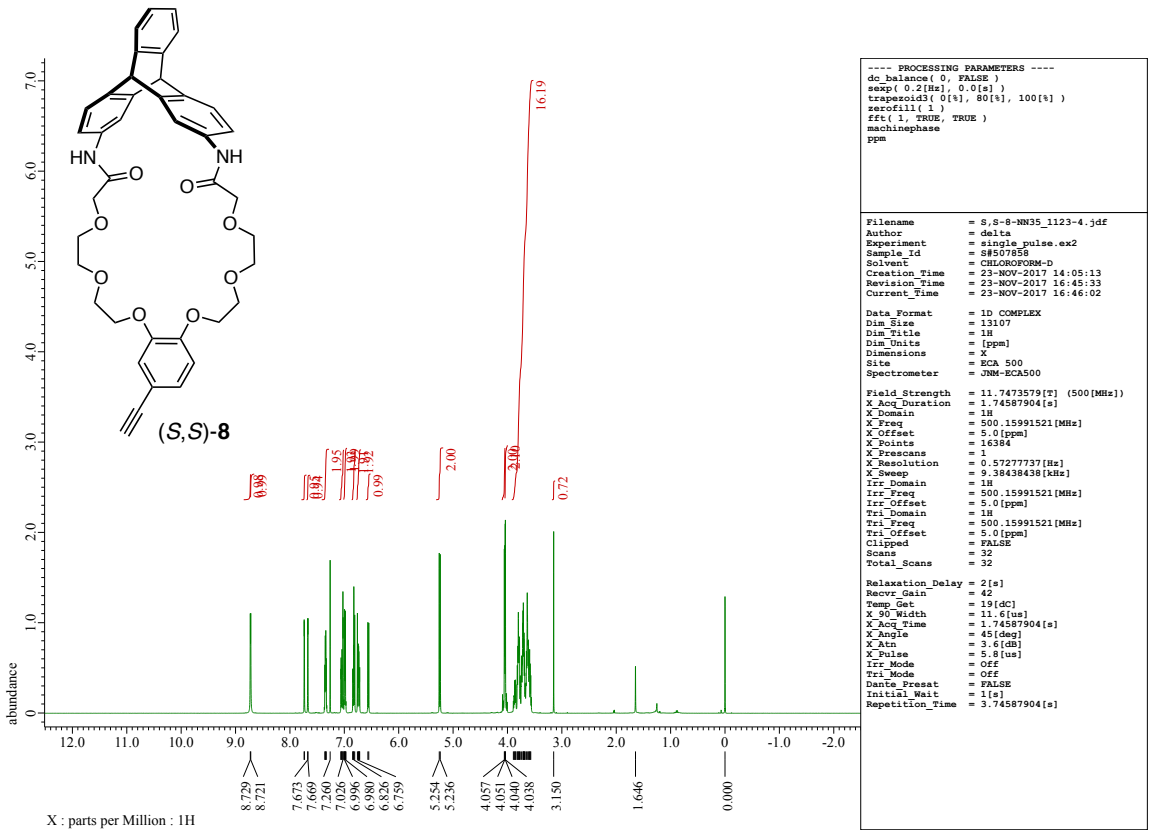


Fig. S20 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of (*S*,*S*)-**8**.

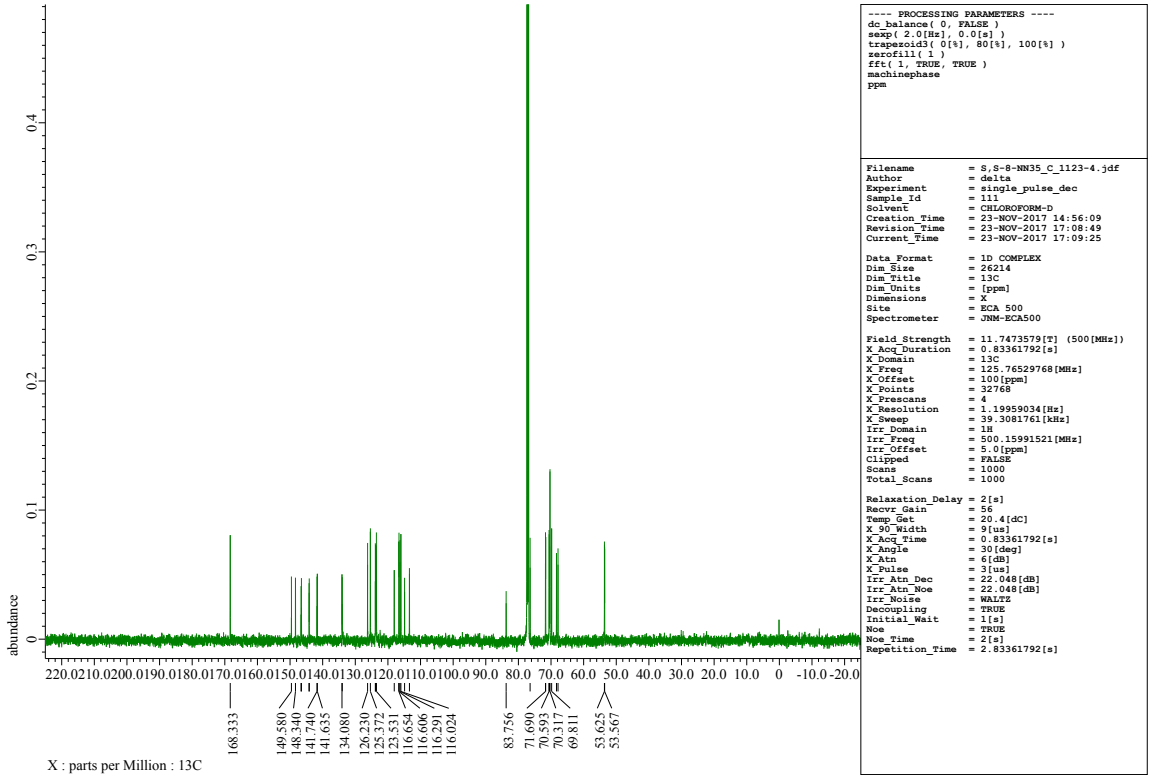


Fig. S21 ^{13}C NMR (125 MHz, $CDCl_3$, rt) spectrum of (*S*,*S*)-**8**.

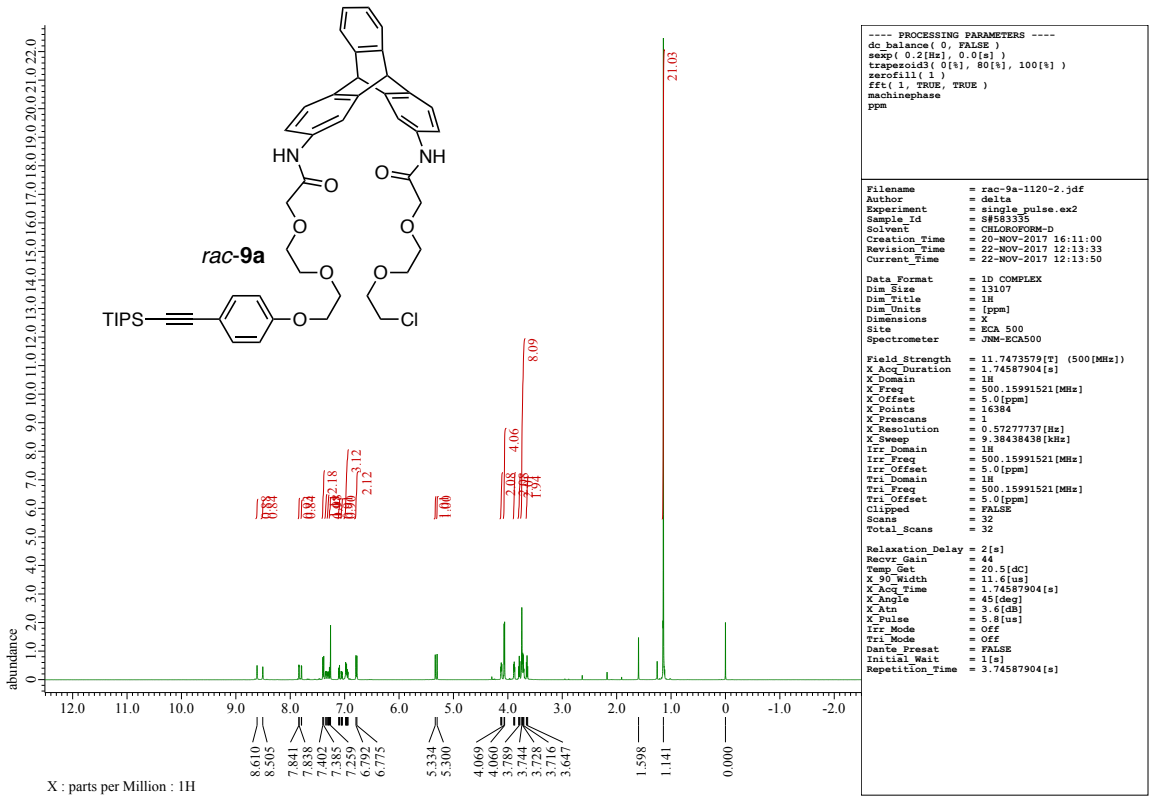


Fig. S22 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of *rac*-**9a**.

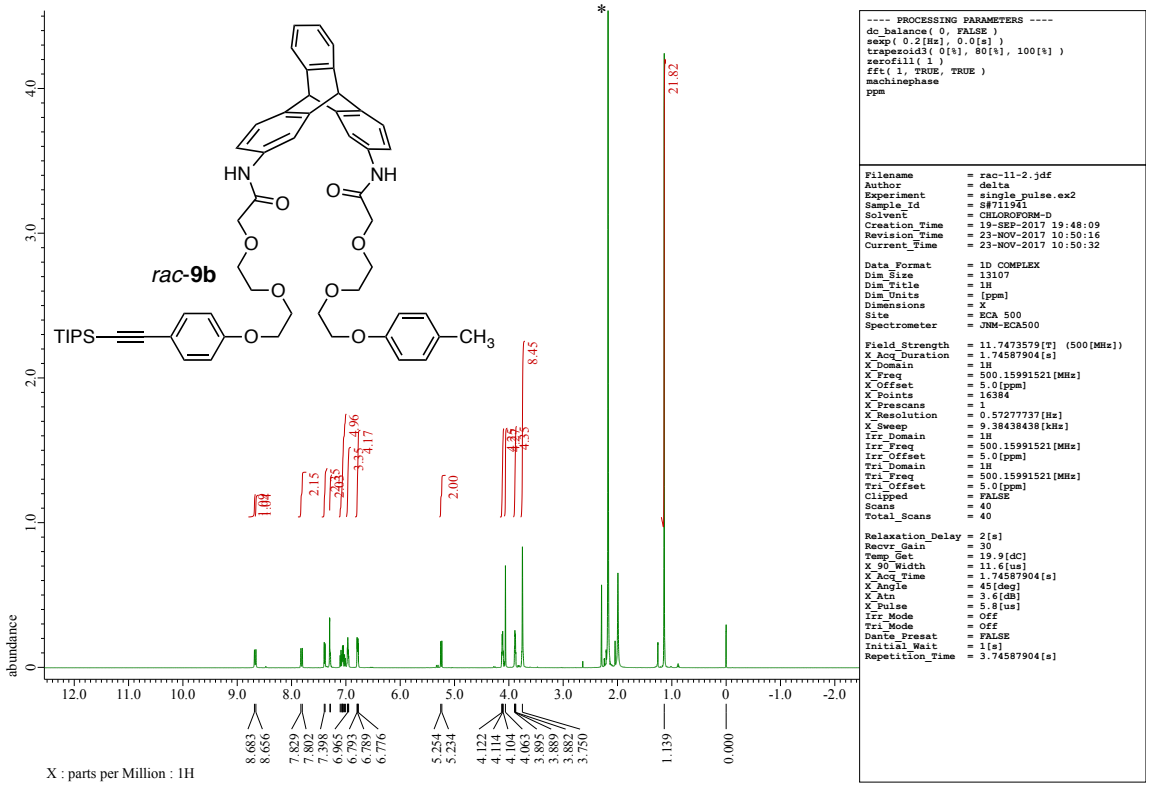


Fig. S23 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of *rac*-**9b**. Asterisk denotes a residual solvent peak.

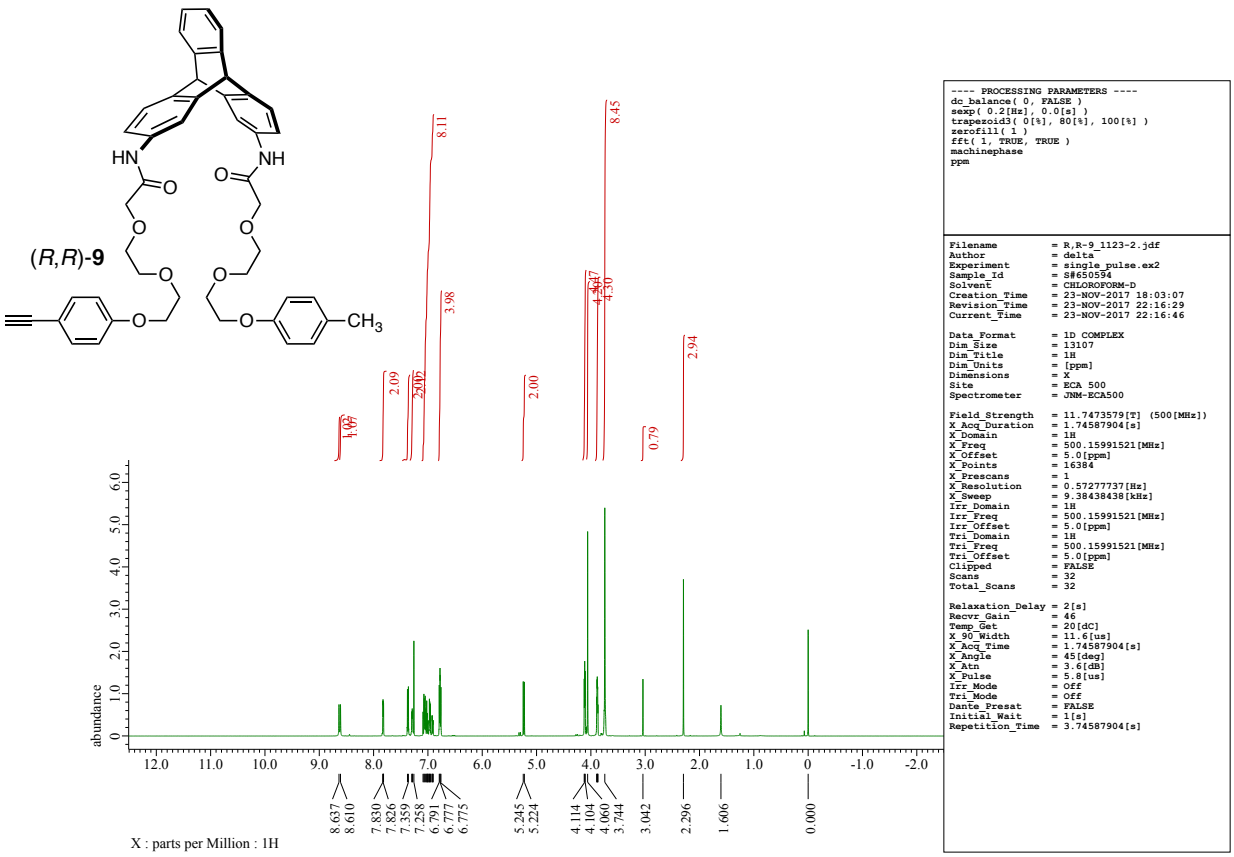


Fig. S24 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of (*R*,*R*)-**9**.

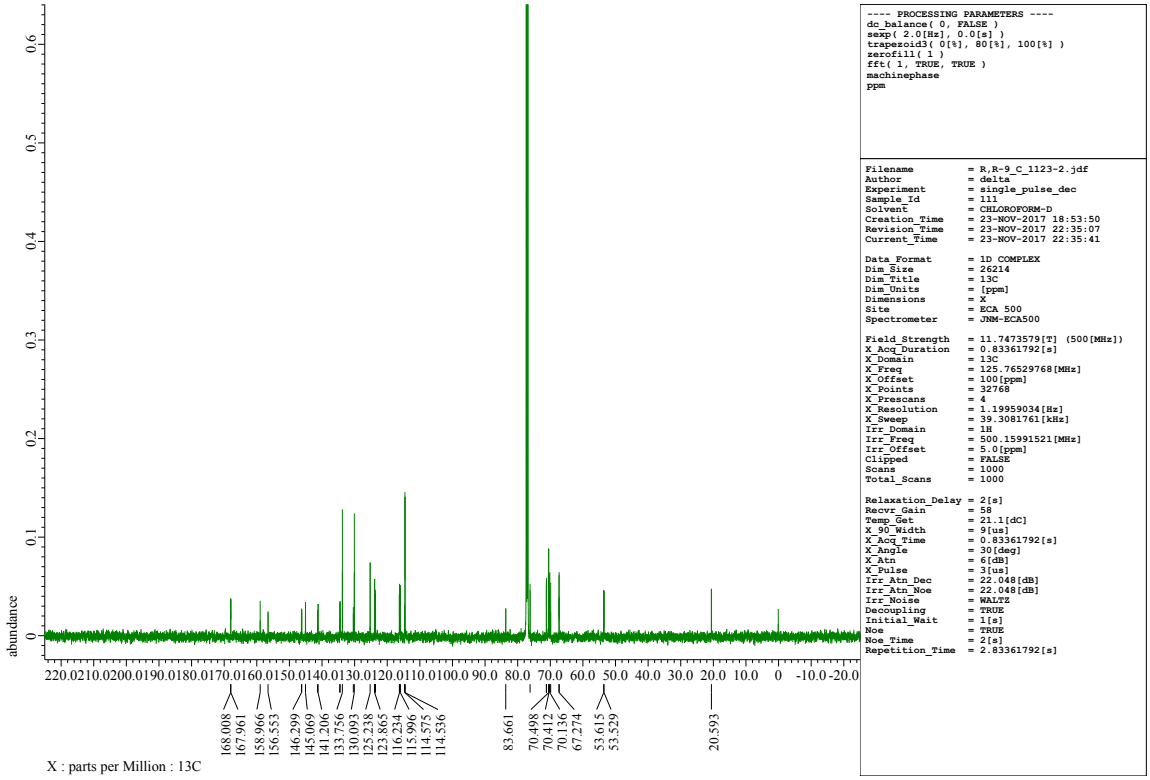


Fig. S25 ^{13}C NMR (125 MHz, $CDCl_3$, rt) spectrum of (*R*,*R*)-**9**.

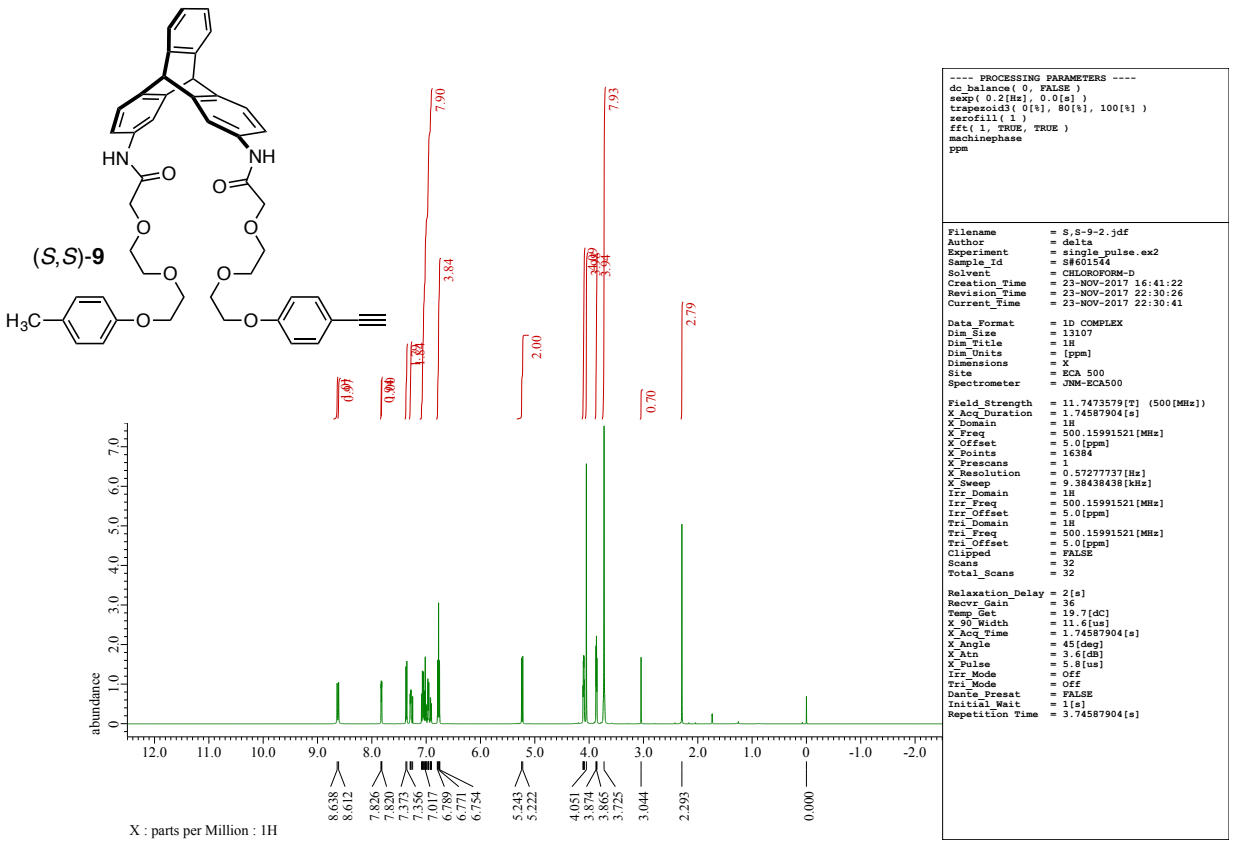


Fig. S26 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of (*S*,*S*)-**9**.

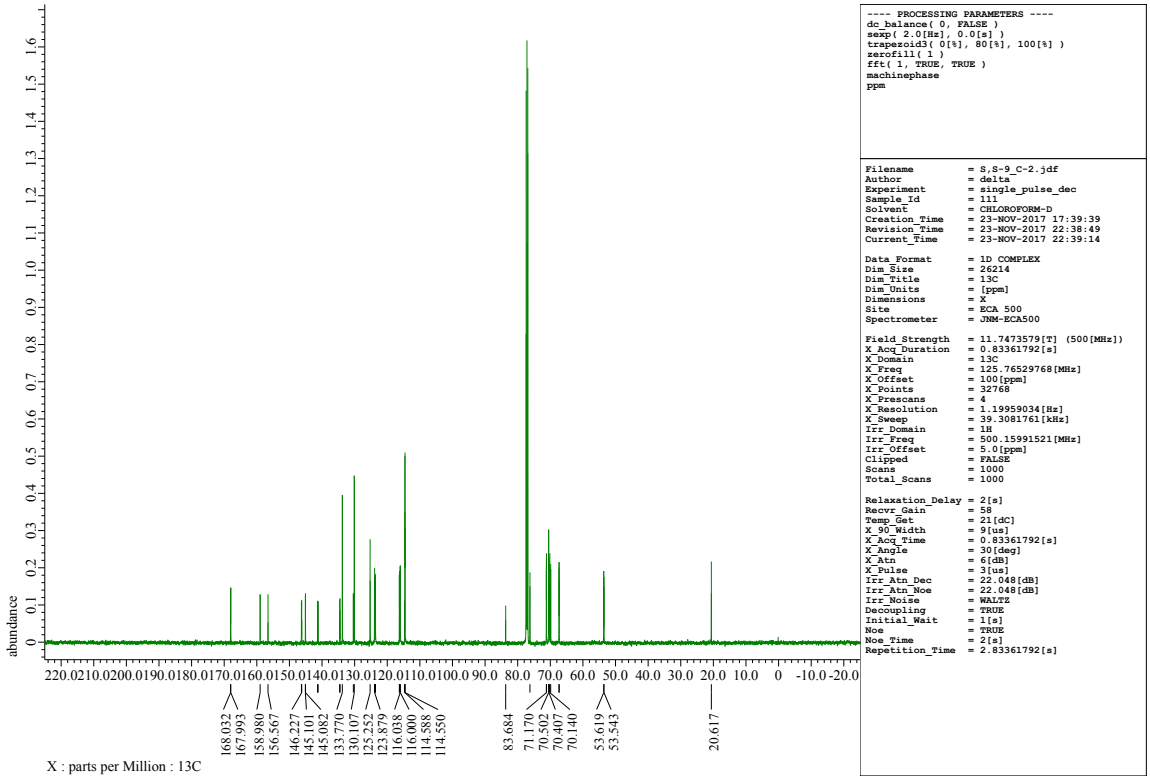


Fig. S27 ^{13}C NMR (125 MHz, $CDCl_3$, rt) spectrum of (*S*,*S*)-**9**.

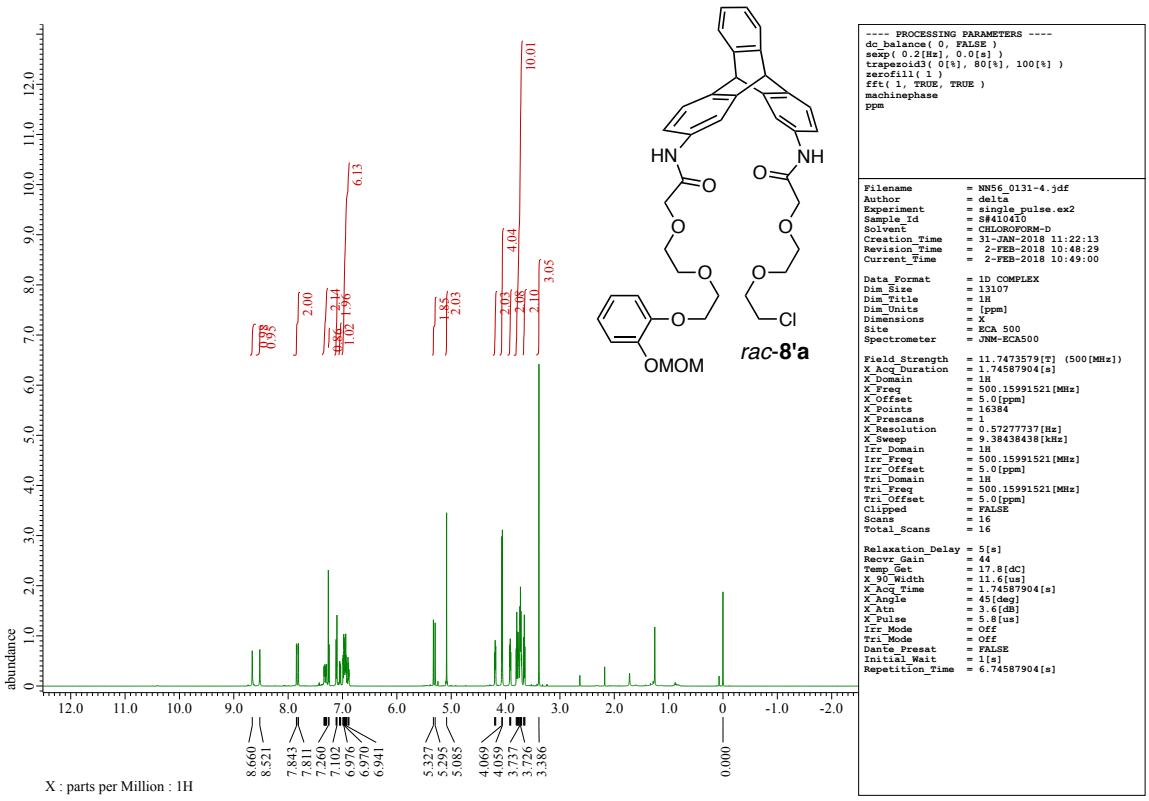


Fig. S28 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of *rac*-**8'a**.

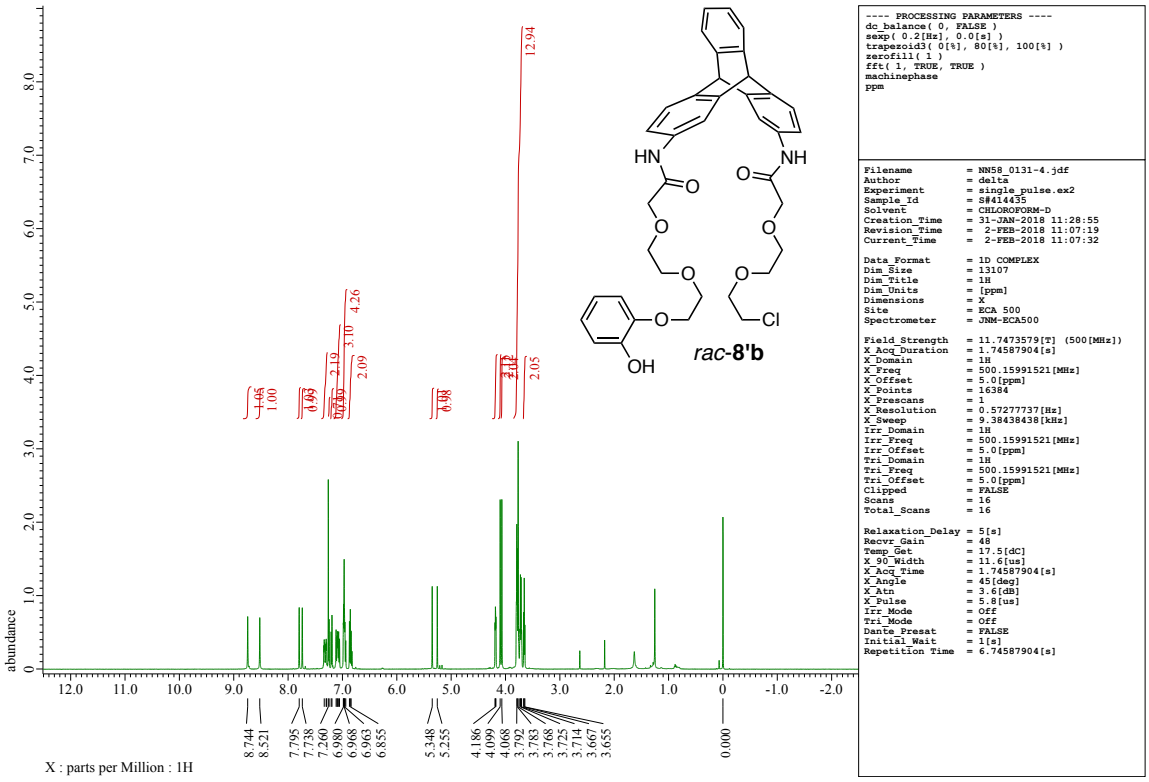


Fig. S29 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of *rac*-**8'b**.

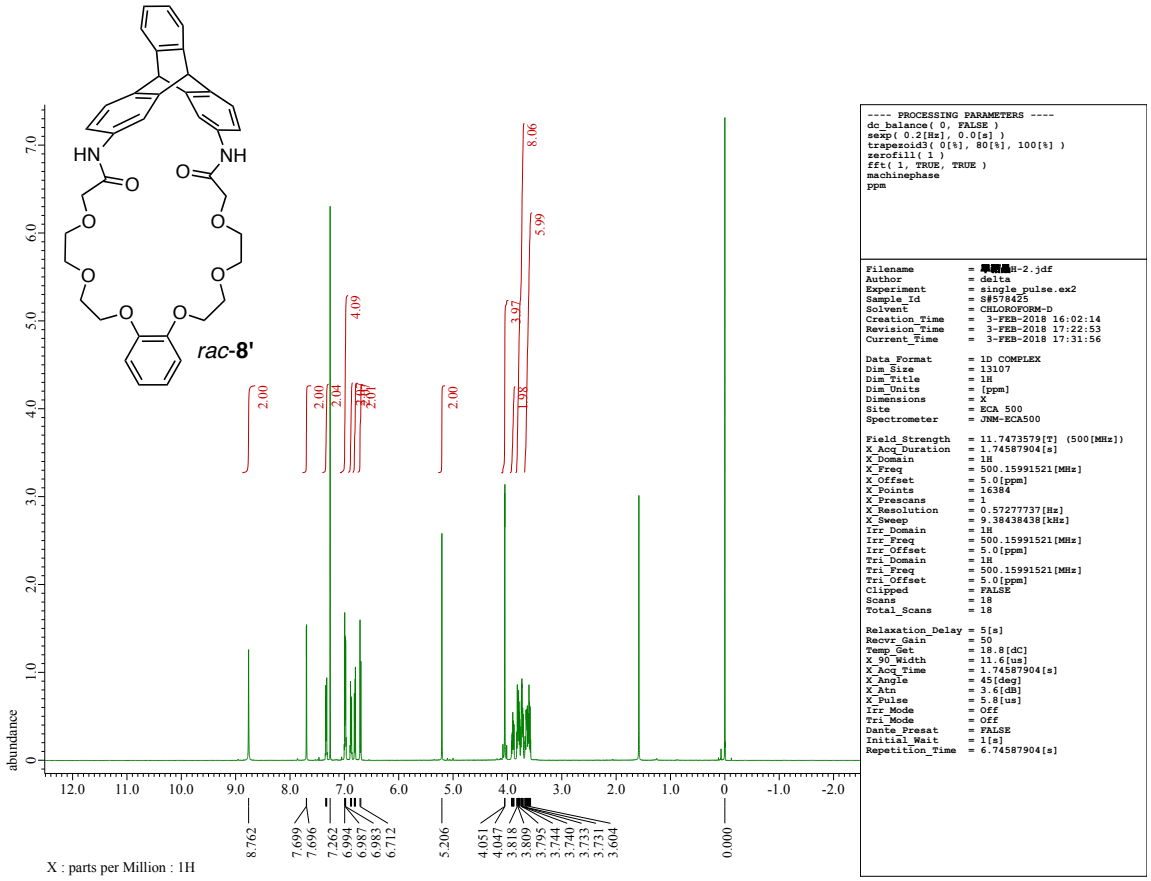


Fig. S30 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of *rac*-**8'**.

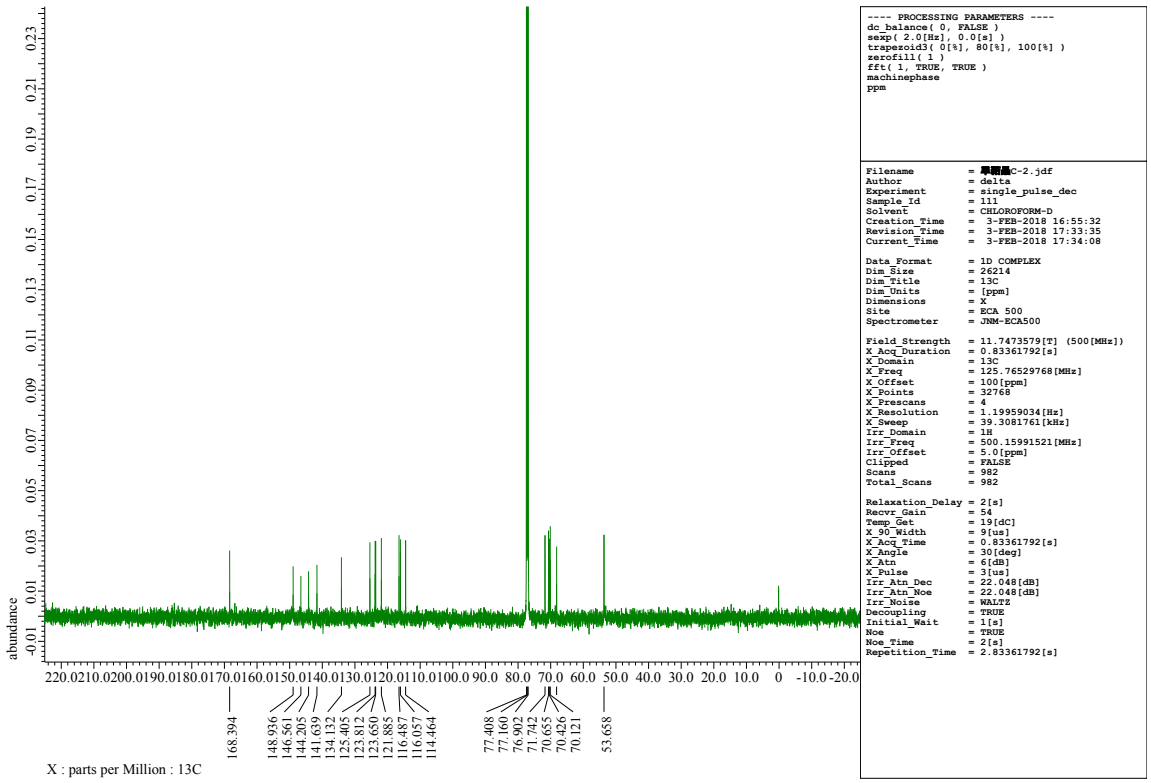


Fig. S31 ^{13}C NMR (125 MHz, $CDCl_3$, rt) spectrum of *rac*-**8'**.

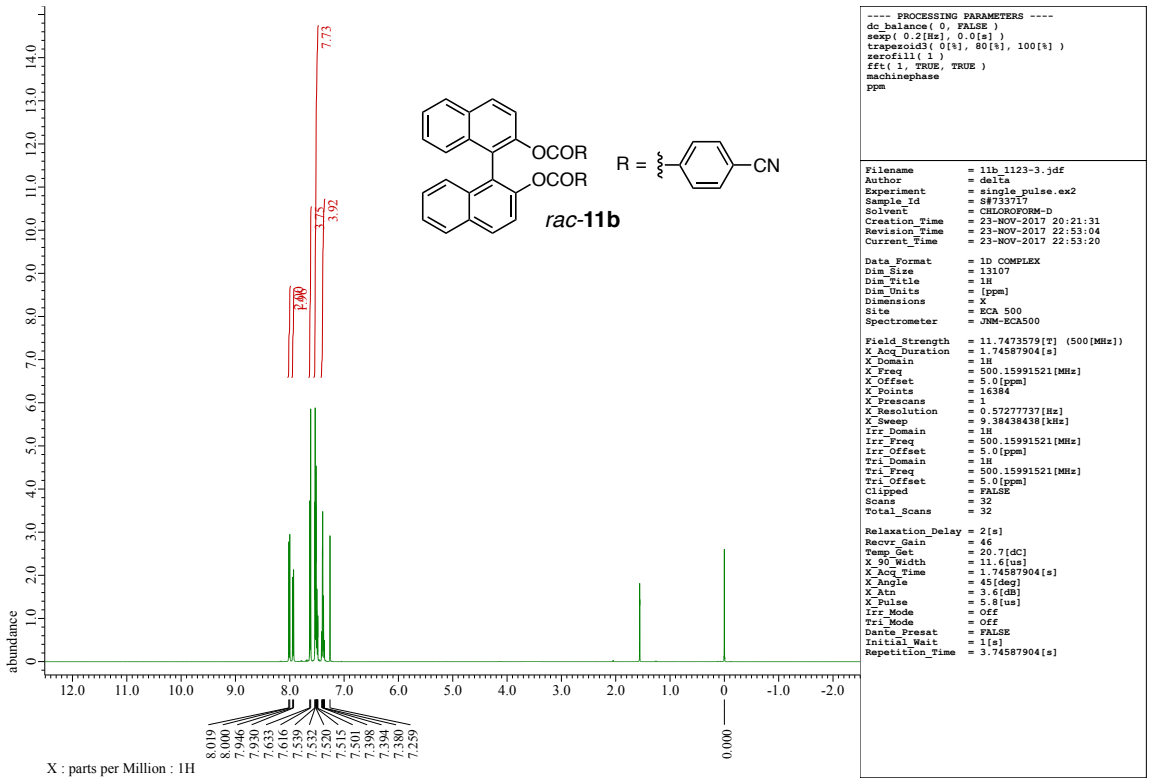


Fig. S32 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of *rac*-**11b**.

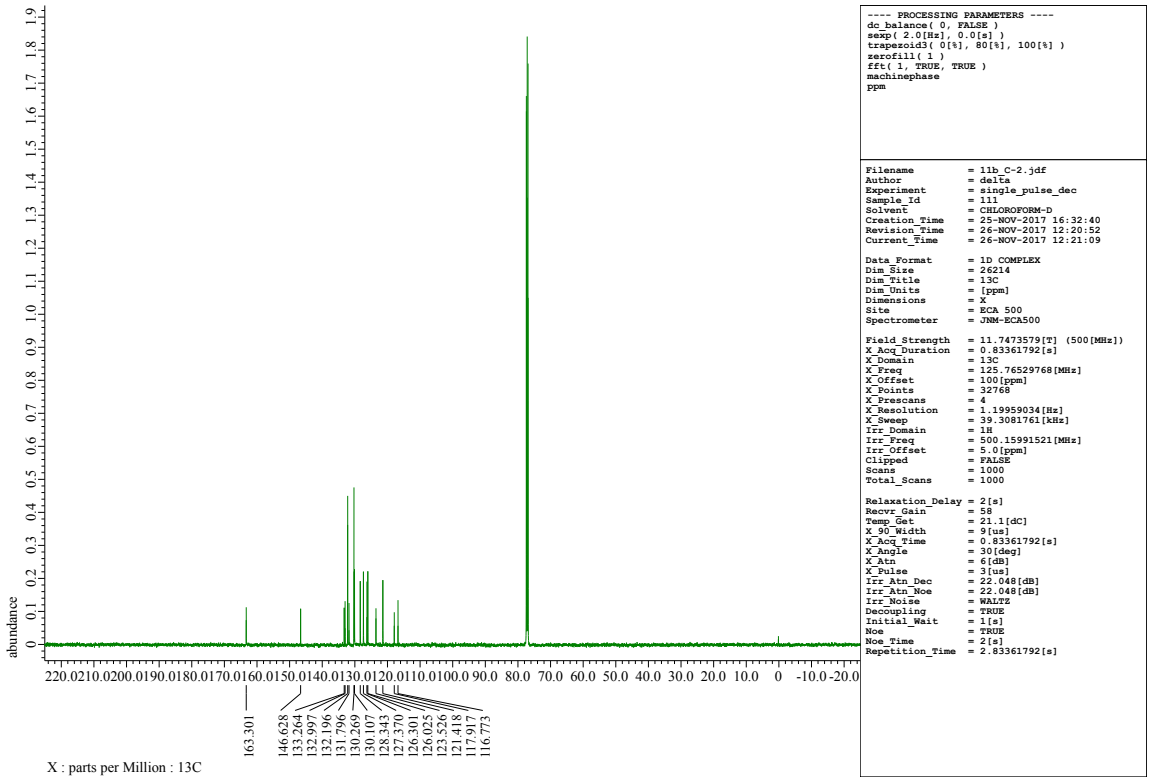


Fig. S33 ^{13}C NMR (125 MHz, $CDCl_3$, rt) spectrum of *rac*-**11b**.

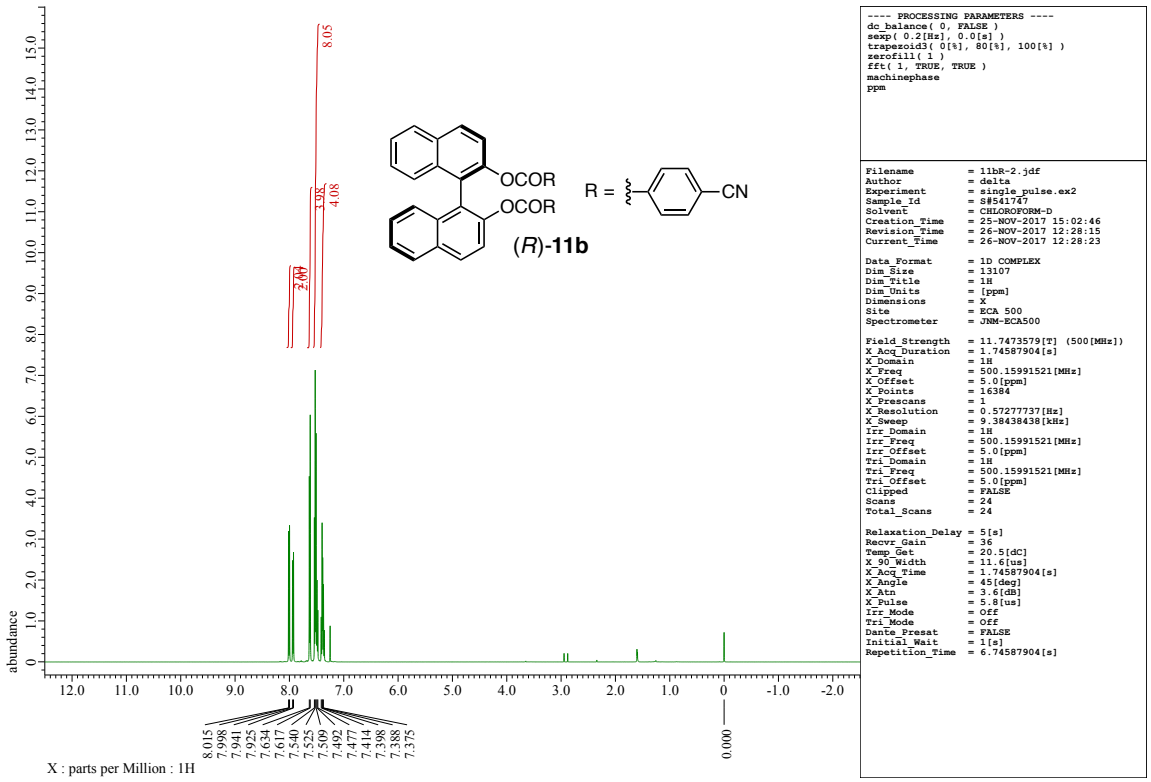


Fig. S34 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of (*R*)-**11b**.

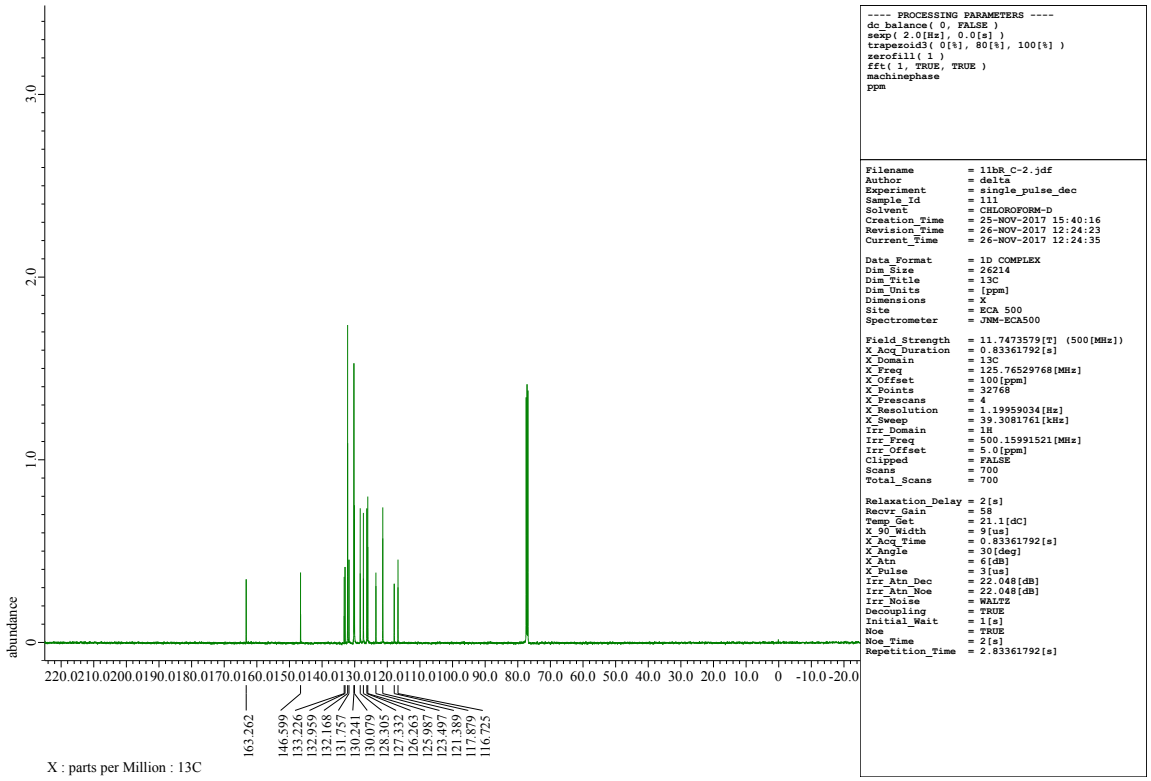


Fig. S35 ^{13}C NMR (125 MHz, $CDCl_3$, rt) spectrum of (*R*)-**11b**.

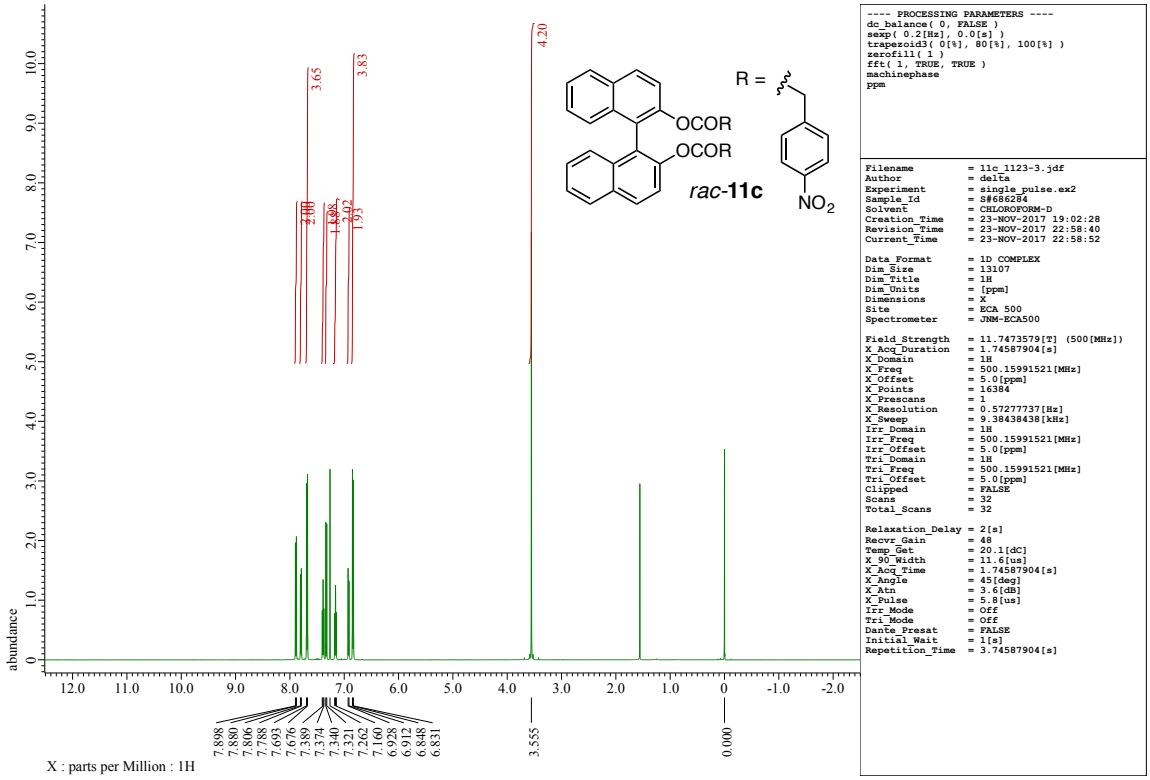


Fig. S36 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of *rac*-**11c**.

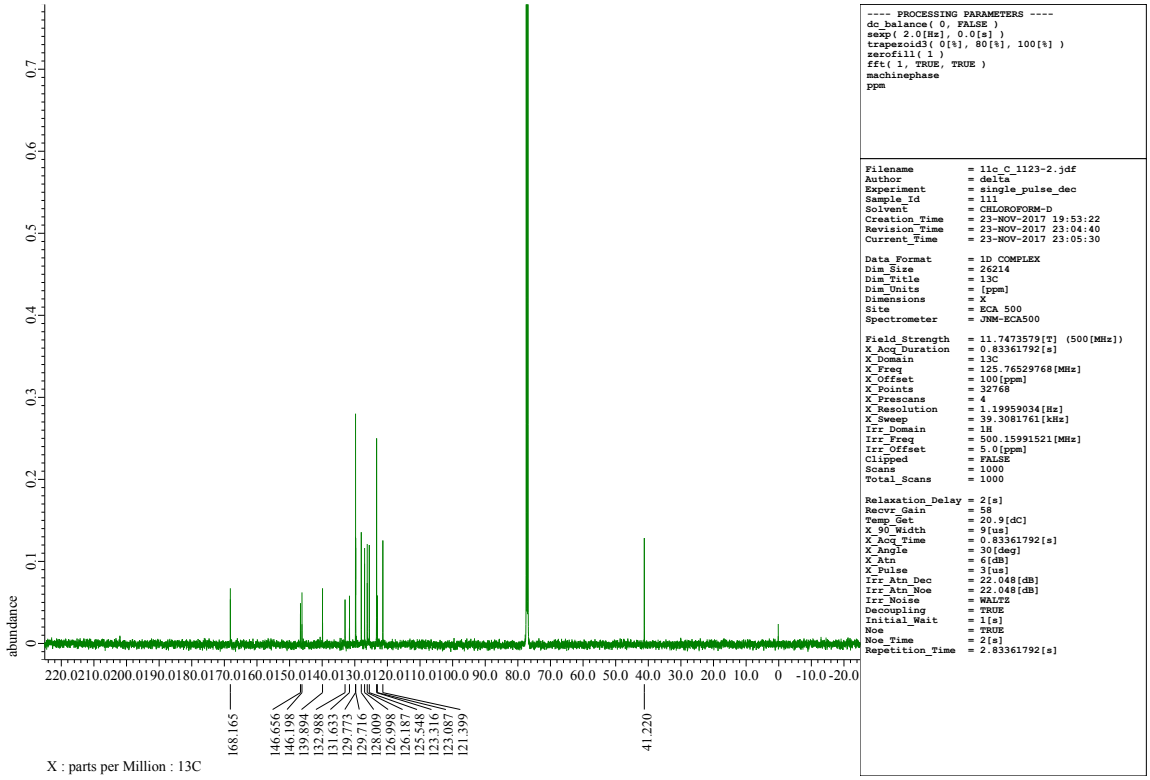


Fig. S37 ^{13}C NMR (125 MHz, $CDCl_3$, rt) spectrum of *rac*-**11c**.

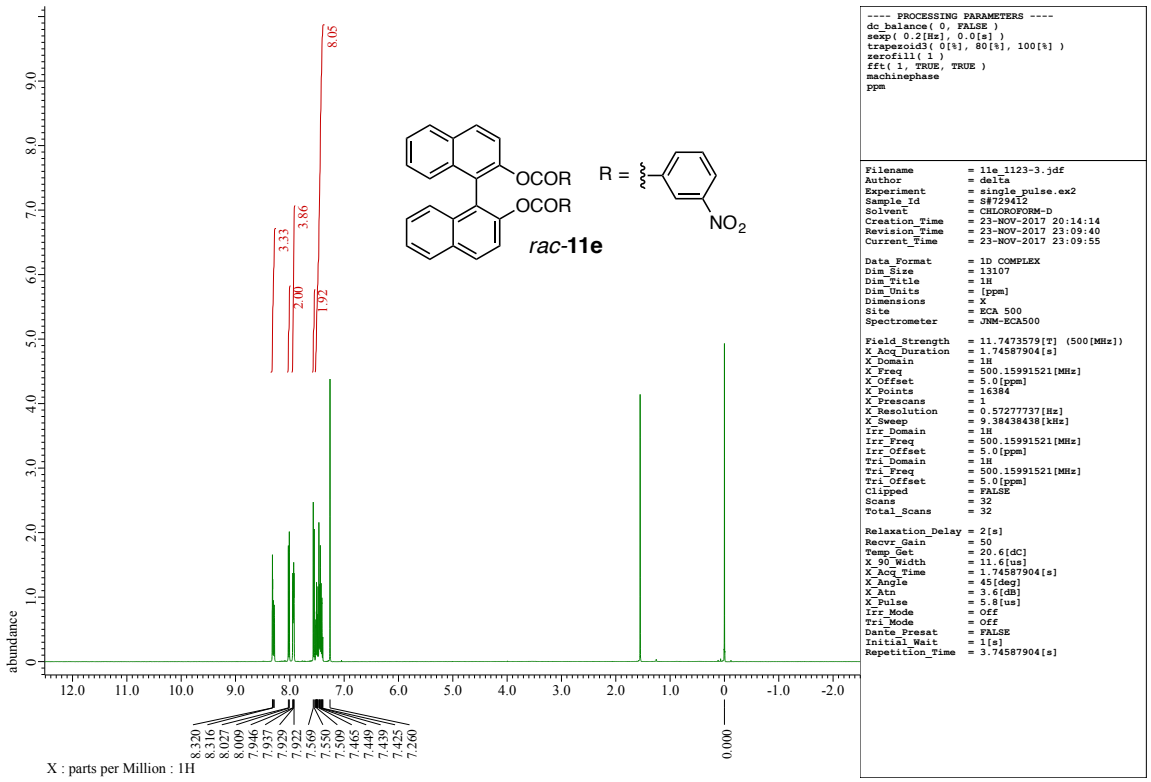


Fig. S38 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of *rac*-**11e**.

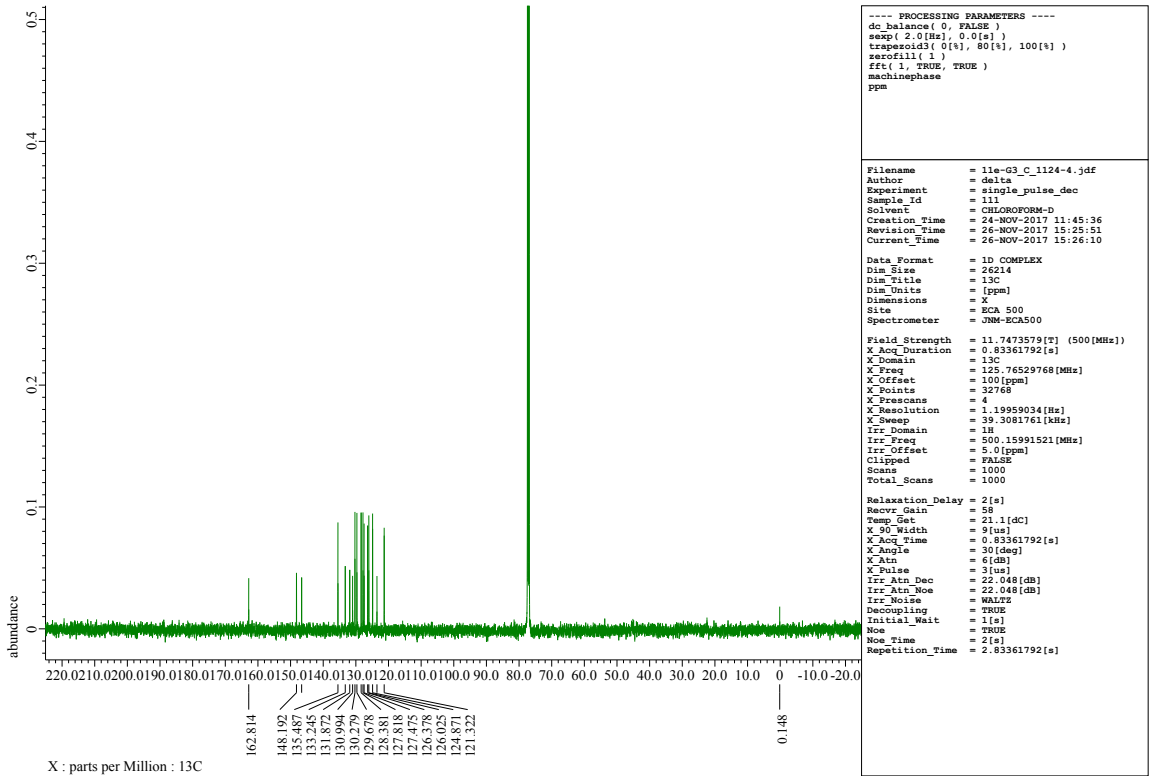


Fig. S39 ^{13}C NMR (125 MHz, $CDCl_3$, rt) spectrum of *rac*-**11e**.

Caption for supporting movie

Movie S1. X-ray crystal structure of **8'** represented by a space-filling model (Animated version of Fig. S7A).

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