Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Ketone Transformation as a Pathway to Inherently Chiral Rigidified Calix[4]arenes

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1. General Information

All chemicals were purchased from commercial sources and used without further purification. All samples were dried in the dessicator over P_2O_5 under vacuum (1 Torr) for 8 hours. Melting points were measured on Heiztisch Mikroskop Polytherm A (Wagner & Munz) and they are not corrected. ^{1}H and ^{13}C spectra were measured on Agilent 400-MR DDR2 (^{1}H: 400 MHz, ^{13}C: 100 MHz). Chemical shifts (δ) are given in parts per million (ppm) and are referenced to TMS as an internal standard, coupling constants (J) are in Hertz. IR spectra were measured on FTIR spectrometer Nicolet 740 in KBr transmission mode. The mass analyses were performed using ESI technique on a FT-MS (LTQ Orbitrap Velos) spectrometer. Purity of the substances and courses of the reactions were monitored by thin layer chromatography (TLC) using silica gel 60 F_{254} on aluminum-backed sheets (Merck) and analyzed at 254 and 365 nm. Column chromatography was performed on silica gel 60 with particle size 0.063-0.200 mm (Merck). Preparative thin-layer chromatography was performed on self-prepared glass plates (25×25 cm) covered by silica gel 60 PF_{254} containing $CaSO_4$ (Merck).

2. Experimental procedures and characterizations

Oxime-bridged- 25,26,27,28-tetrapropoxycalix[4]arene (6)

Calixarene **5** (0.078 g, 0.126 mmol) was dissolved in 5 ml of ethanol. Hydroxylamine hydrochloride (0.045 g, 0.648 mmol) was added followed by the addition of 1M HCl until pH of the reaction mixture reached 4. The reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC (eluent = cyclohexane:ethyl acetate 4:1, v/v). After the disappearance of the starting compound (7 days), 20 ml of dichloromethane were added. The mixture was washed with saturated solution of $NaHCO_3$ (10 ml) and water (10 ml) and dried over magnesium sulfate. The solvent was removed under reduced pressure to yield the title compound as a brown amorphous solid in 74% yield (0.060 g), m.p. 113-116 °C.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 8.59 (br s, 1H, C=N-*OH*), 7.31 (d, 1H, J = 7.8 Hz, Ar-*H*), 6.97-6.92 (m, 3H, Ar-*H*), 6.87-6.80 (m, 3H, Ar-*H*), 6.73-6.67 (m, 2H, Ar-*H*), 4.67 (d, 1H, J = 14.5 Hz, Ar-*CH*$_2$-Ar), 4.53 (d, 1H, J = 12.1 Hz, Ar-*CH*$_2$-Ar), 4.52 (d, 1H, J = 12.1 Hz, Ar-*CH*$_2$-Ar), 4.34 (d, 1H, J = 12.9 Hz, Ar-*CH*$_2$-Ar), 4.02-3.94 (m, 2H, O-*CH*$_2$), 3.89-3.77 (m, 4H, O-*CH*$_2$), 3.65-3.57 (m, 2H, O-*CH*$_2$), 3.32-3.26 (m, 3H, Ar-*CH*$_2$-Ar), 3.10 (d, 1H, J = 12.9 Hz, Ar-*CH*$_2$-Ar), 2.22-2.09 (m, 4H, O-CH$_2$-*CH*$_2$), 1.97-1.83 (m, 4H, O-CH$_2$-*CH*$_2$), 1.17 (t, 3H, J = 7.4 Hz, O-CH$_2$-CH$_2$-*CH*$_3$), 1.16 (t, 3H, J = 7.4 Hz, O-CH$_2$-CH$_2$-*CH*$_3$), 1.02 (t, 3H, J = 7.4 Hz, O-CH$_2$-CH$_2$-*CH*$_3$), 1.01 (t, 3H, J = 7.4 Hz, O-CH$_2$-CH$_2$-*CH*$_3$) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ 156.0, 155.9, 155.2, 155.0, 153.1, 136.0, 135.9, 134.7, 134.6 (2×), 134.5, 133.5, 133.3, 132.0, 131.2, 129.2, 129.1, 128.2, 128.1 (2×), 127.4, 127.1, 123.3, 122.9, 121.0, 77.2, 77.0, 76.8, 76.7, 32.0 (2×), 28.8, 23.5 (2×), 23.4 (2×), 23.0, 10.9 (2×), 10.1 (2×) ppm.

HRMS (ESI$^+$) calcd for $C_{41}H_{47}NO_5$ 656.33464 $[M+Na]^+$, 672.30858 $[M+K]^+$, found m/z 656.33464 $[M+Na]^+$ (100 %), 672.30817 $[M+K]^+$ (42 %)

IR (KBr) ν 3268.5, 2960.9, 2932.3, 2874.4, 1573.5, 1456.5, 1385.1, 1251.9, 1215.0 cm^{-1}

Amide-bridged- 25,26,27,28-tetrapropoxycalix[4]arene (7)

Calixarene **6** (0.038 g, 0.060 mmol) was dissolved in 10 ml of dry dichloromethane. The solution was cooled down to 0 °C followed by slow addition of $SOCl_2$ (0.170 ml, 2.343 mmol). The reaction mixture was stirred for 3 hours at 0 °C and then was allowed to reach the ambient temperature. The reaction mixture was washed with water (3×20 ml) and dried over magnesium sulfate. The solvent was removed under reduced pressure to yield crude product which was further purified by silica gel thin layer chromatography (eluent = cyclohexane:ethyl acetate 3:2, v/v). The title compound was obtained as a yellow amorphous solid in 59% yield (0.022 g), m.p. 290-293 °C.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 8.17 (s, 1H, Ar-*NH*-CO), 7.10 (d, 1H, *J* = 7.8 Hz, Ar-*H*), 7.05-6.98 (m, 2H, Ar-*H*), 6.94 (d, 1H, *J* = 8.2 Hz, Ar-*H*), 6.87 (d, 1H, *J* = 8.2 Hz, Ar-*H*), 6.83-6.75 (m, 2H, Ar-*H*), 6.74-6.69 (m, 1H, Ar-*H*), 6.60-6.50 (m, 2H, Ar-*H*), 4.71 (d, 1H, *J* = 12.5 Hz, Ar-*CH_2*-Ar), 4.53-4.45 (m, 2H, Ar-*CH_2*-Ar), 4.40 (d, 1H, *J* = 12.5 Hz, Ar-*CH_2*-Ar), 4.05-3.93 (m, 2H, O-*CH_2*), 3.86-3.66 (m, 6H, O-*CH_2*), 3.39 (d, 1H, *J* = 12.5 Hz, Ar-*CH_2*-Ar), 3.27 (d, 1H, *J* = 12.1 Hz, Ar-*CH_2*-Ar), 3.26 (d, 1H, *J* = 12.5 Hz, Ar-*CH_2*-Ar), 3.19 (d, 1H, *J* = 12.5 Hz, Ar-*CH_2*-Ar), 2.38-2.23 (m, 2H, O-CH_2-*CH_2*), 2.09-1.83 (m, 6H, O-CH_2-*CH_2*), 1.12 (t, 3H, *J* = 7.4 Hz, O-CH_2-CH_2-*CH_3*), 1.08 (t, 3H, *J* = 7.4 Hz, O-CH_2-CH_2-*CH_3*), 1.04 (t, 3H, *J* = 7.4 Hz, O-CH_2-CH_2-*CH_3*), 1.01 (t, 3H, *J* = 7.4 Hz, O-CH_2-CH_2-*CH_3*) ppm.
^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ 170.8, 156.2, 155.0 (2×), 152.9, 137.7, 135.7, 135.6, 135.5, 134.9, 134.2, 134.0, 132.5, 130.6, 129.3, 129.0, 128.5 (2×), 128.2, 127.9, 127.6, 124.3, 122.9, 122.8, 116.3, 78.0, 77.9, 77.4, 76.3, 31.3, 30.6, 30.4, 23.6, 23.5, 23.3, 23.1, 22.7, 10.7 (2×), 10.4, 9.9 ppm.
HRMS (ESI$^+$) calcd for $C_{41}H_{47}NO_5$ 656.33464 $[M+Na]^+$, 672.30858 $[M+K]^+$, found m/z 656.33509 $[M+Na]^+$ (100 %), 672.30809 $[M+K]^+$ (15 %)
IR (KBr) *v* 2960.4, 2931.9, 2874.3, 1652.6, 1587.5, 1458.5, 1384.7, 1215.5, 1006.2 cm^{-1}

Ester-bridged- 25,26,27,28-tetrapropoxycalix[4]arene (8)

Calixarene **5** (0.050 g, 0.081 mmol) was dissolved in dry toluene (5 ml). *m*-Chloroperbenzoic acid (0.028 g, 0.162 mmol) was added in small portions over 15 minutes. The reaction mixture was stirred overnight at ambient temperature. The solvent was removed under reduced pressure to yield crude product which was further purified by silica gel thin layer chromatography (eluent = cyclohexane:ethyl acetate 4:1, v/v). The title compound was obtained as a yellow amorphous solid in 58% yield (0.030 g), m.p. 149-152 °C.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 7.09-7.03 (m, 3H, Ar-*H*), 6.99 (d, 1H, *J* = 8.6 Hz, Ar-*H*), 6.86-6.80 (m, 3H, Ar-*H*), 6.72-6.67 (m, 2H, Ar-*H*), 6.56 (t, 1H, *J* = 7.4 Hz, Ar-*H*), 4.60 (d, 1H, *J* = 12.5 Hz, Ar-*CH_2*-Ar), 4.49 (d, 1H, *J* = 12.1 Hz, Ar-*CH_2*-Ar), 4.47 (d, 1H, *J* = 12.5 Hz, Ar-*CH_2*-Ar), 4.39 (d, 1H, *J* = 12.5 Hz, Ar-*CH_2*-Ar), 4.05-3.93 (m, 2H, O-*CH_2*), 3.88-3.65 (m, 6H, O-*CH_2*), 3.63 (d, 1H, *J* = 12.9 Hz, Ar-*CH_2*-Ar), 3.28 (d, 1H, *J* = 12.5 Hz, Ar-*CH_2*-Ar), 3.24 (d, 1H, *J* = 12.5 Hz, Ar-*CH_2*-Ar), 3.20 (d, 1H, *J* = 12.5 Hz, Ar-*CH_2*-Ar), 2.41-2.24 (m, 2H, O-CH_2-*CH_2*), 2.05-1.82 (m, 6H, O-CH_2-

CH₂), 1.14 (t, 3H, *J* = 7.4 Hz, O-CH_2-CH_2-*CH_3*), 1.11 (t, 3H, *J* = 7.4 Hz, O-CH_2-CH_2-*CH_3*), 1.04 (t, 3H, *J* = 7.4 Hz, O-CH_2-CH_2-*CH_3*), 1.00 (t, 3H, *J* = 7.4 Hz, O-CH_2-CH_2-*CH_3*) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ 167.4, 156.4, 155.0, 154.9, 152.9, 150.1, 138.8, 136.1, 136.0, 134.8, 134.1, 133.8, 133.0, 129.6, 128.7, 128.6, 128.5, 128.1, 127.9, 127.8, 126.7, 126.1, 123.1, 122.8, 115.4, 78.1, 78.0, 77.5, 76.3, 31.3, 30.4, 30.2, 23.5, 23.3, 23.2, 22.6, 22.5, 10.7 (2×), 10.4, 9.8 ppm.

HRMS (ESI$^+$) calcd for $C_{41}H_{46}O_6$ 657.31866 $[M+Na]^+$, 673.29260 $[M+K]^+$, found m/z 657.31897 $[M+Na]^+$ (100 %), 673.29297 $[M+K]^+$ (10 %)

IR (KBr) *v* 3342.0, 2960.5, 2927.8, 2874.1, 1735.5, 1590.4, 1458.4, 1262.7, 1093.3 cm^{-1}

3. Spectral characterization of compounds

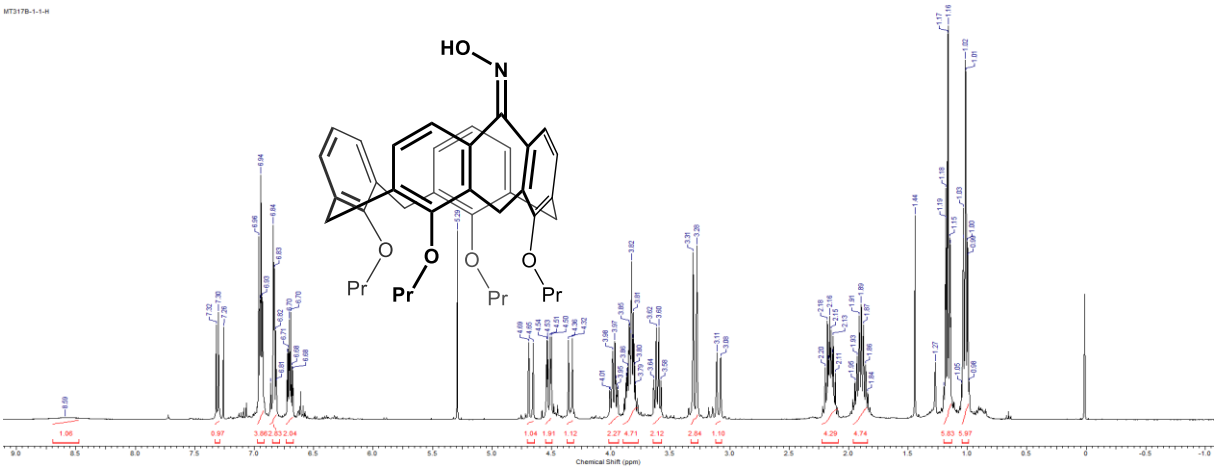

Figure 1. ^{1}H NMR of compound **6** ($CDCl_3$, 400 MHz).

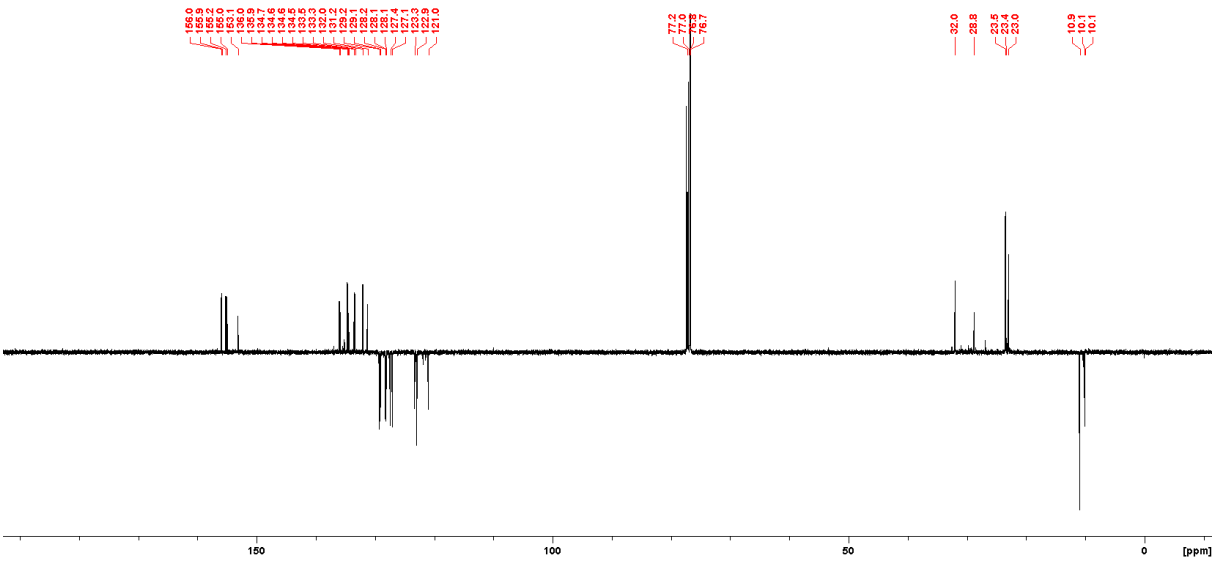

Figure 2. ^{13}C(APT) NMR of compound **6** ($CDCl_3$, 100 MHz).

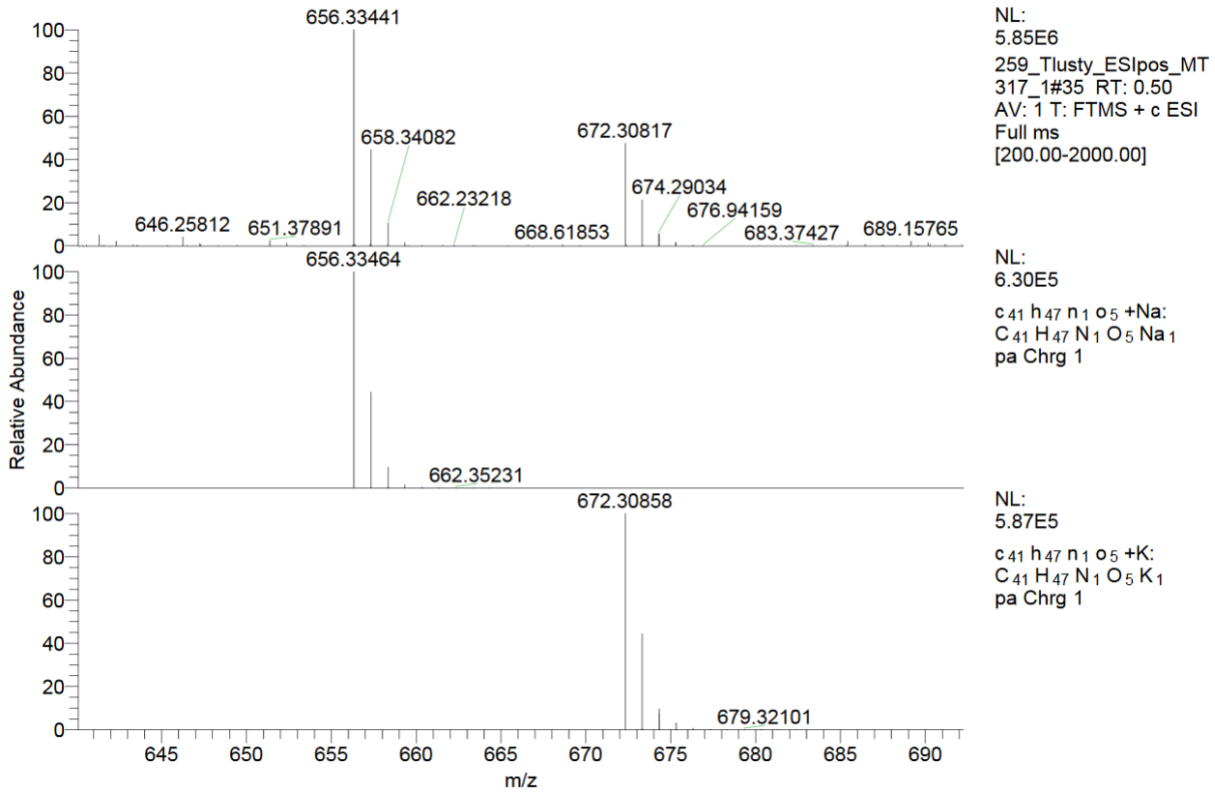

Figure 3. HRMS of compound **6** (ESI^+).

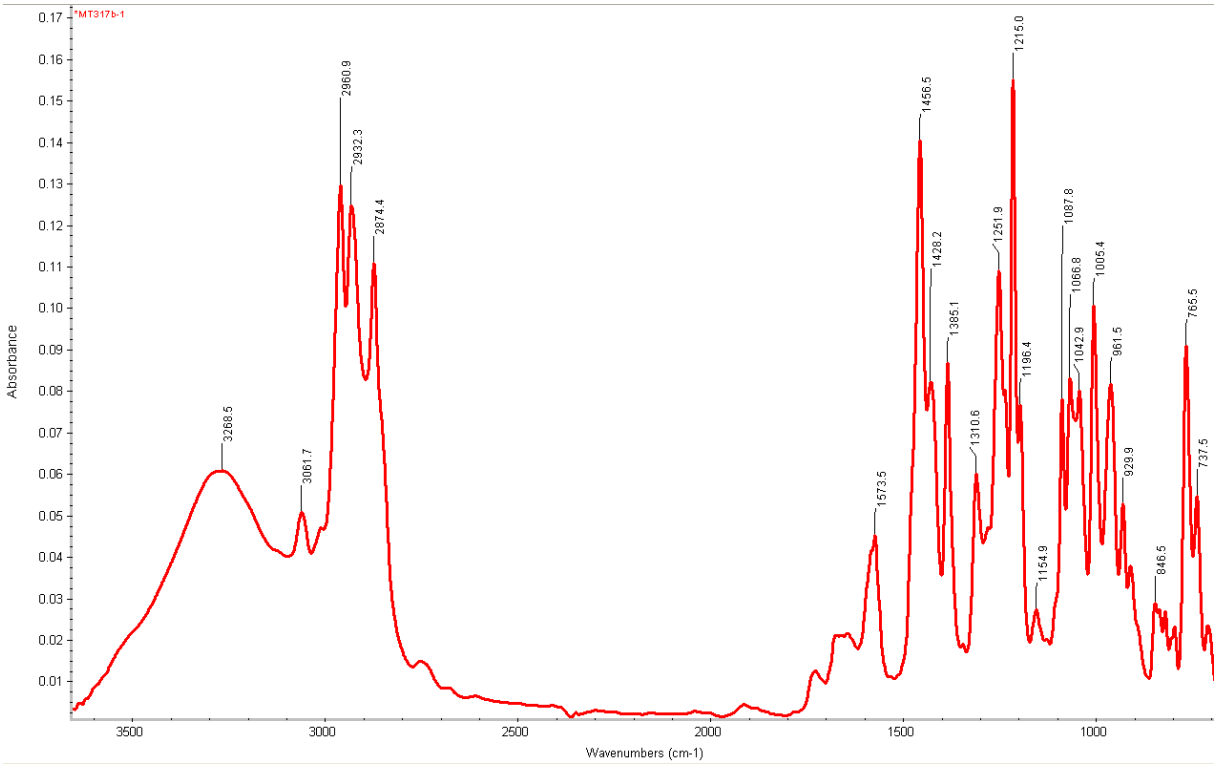

Figure 4. IR of compound **6** (KBr).

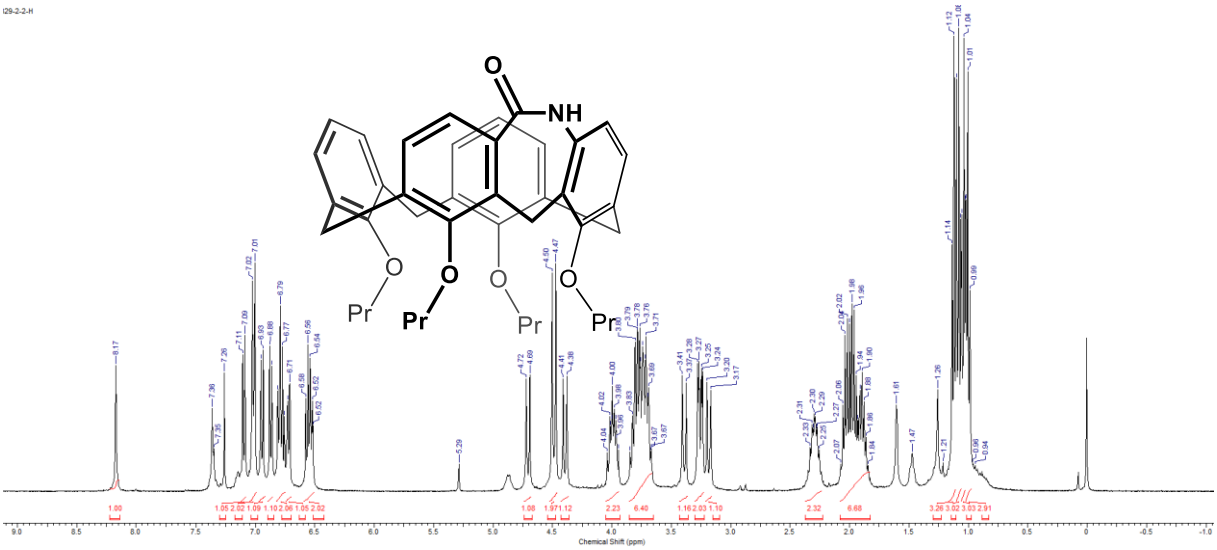

Figure 5. ^{1}H NMR of compound **7** ($CDCl_3$, 400 MHz).

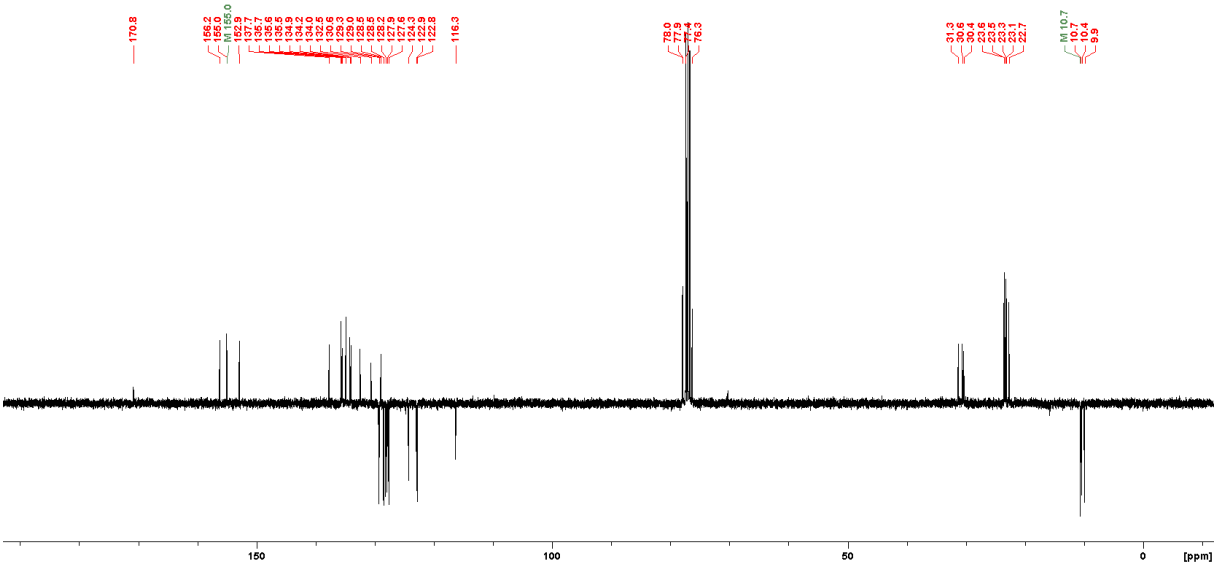

Figure 6. ^{13}C(APT) NMR of compound **7** ($CDCl_3$, 100 MHz).

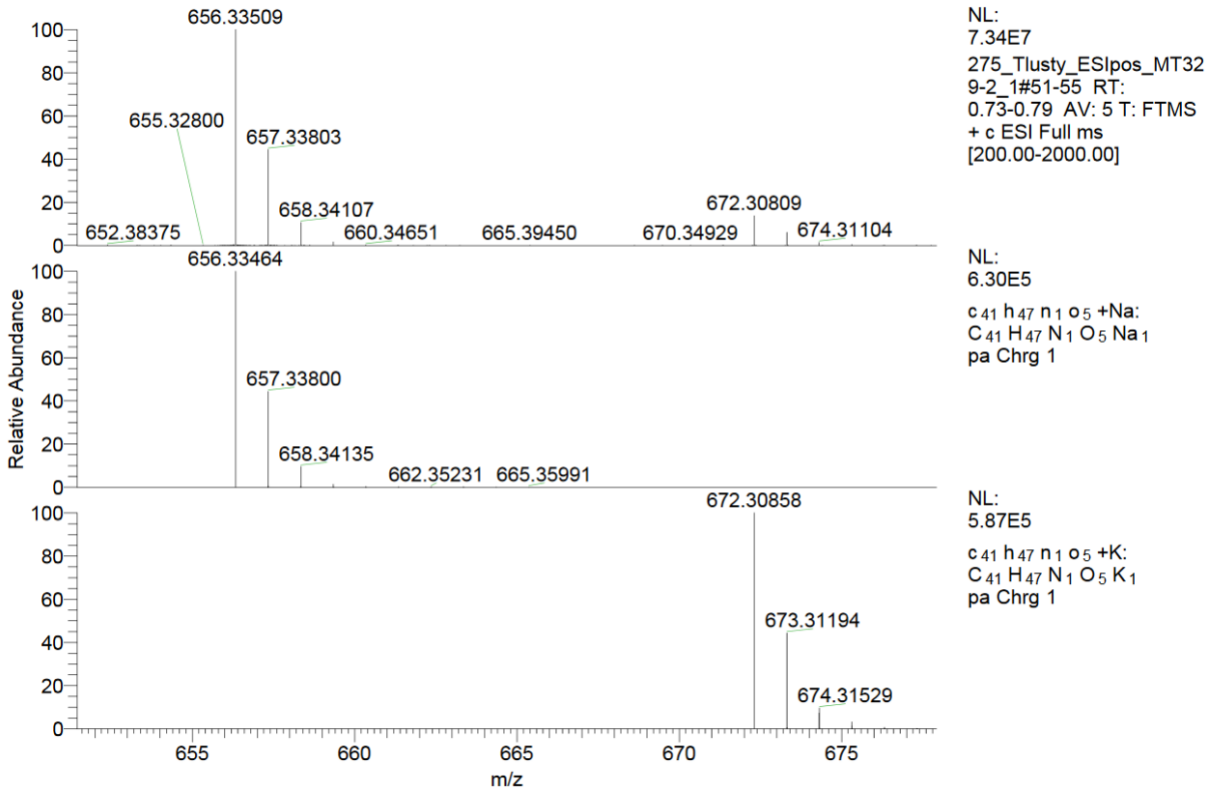

Figure 7. HRMS of compound **7** (ESI^+).

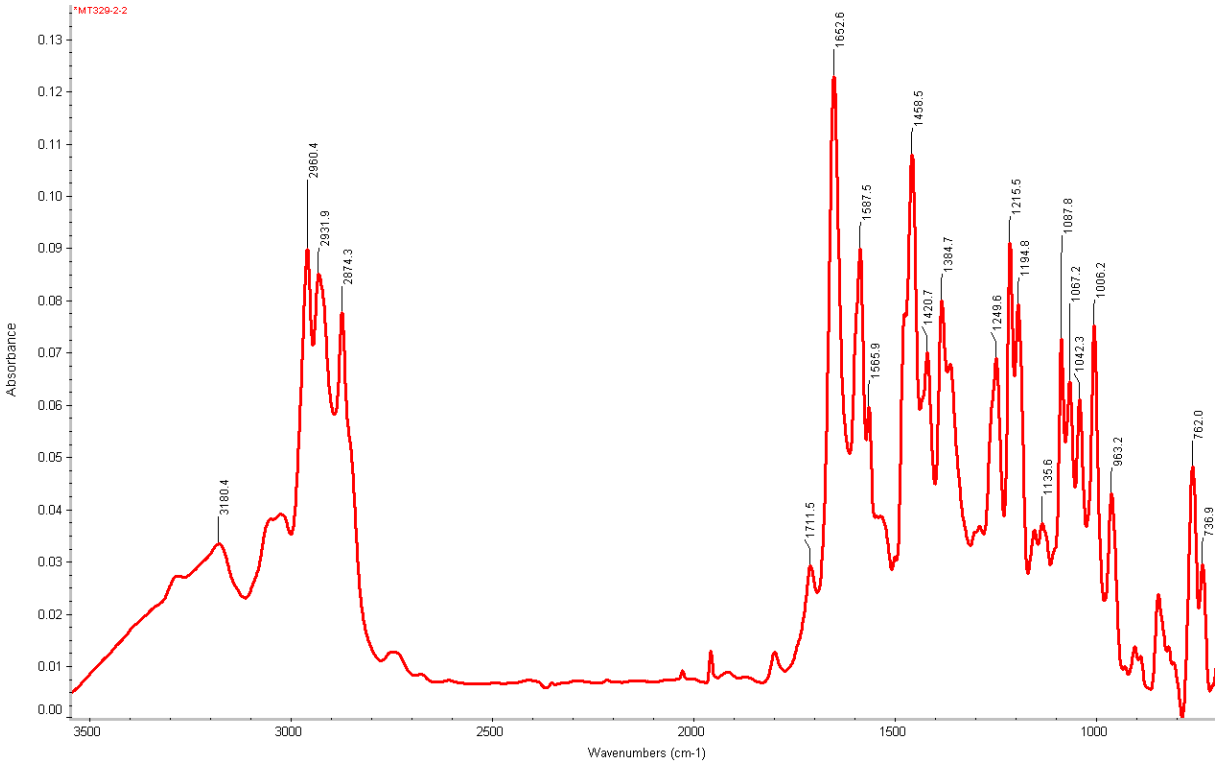

Figure 8. IR of compound **7** (KBr).

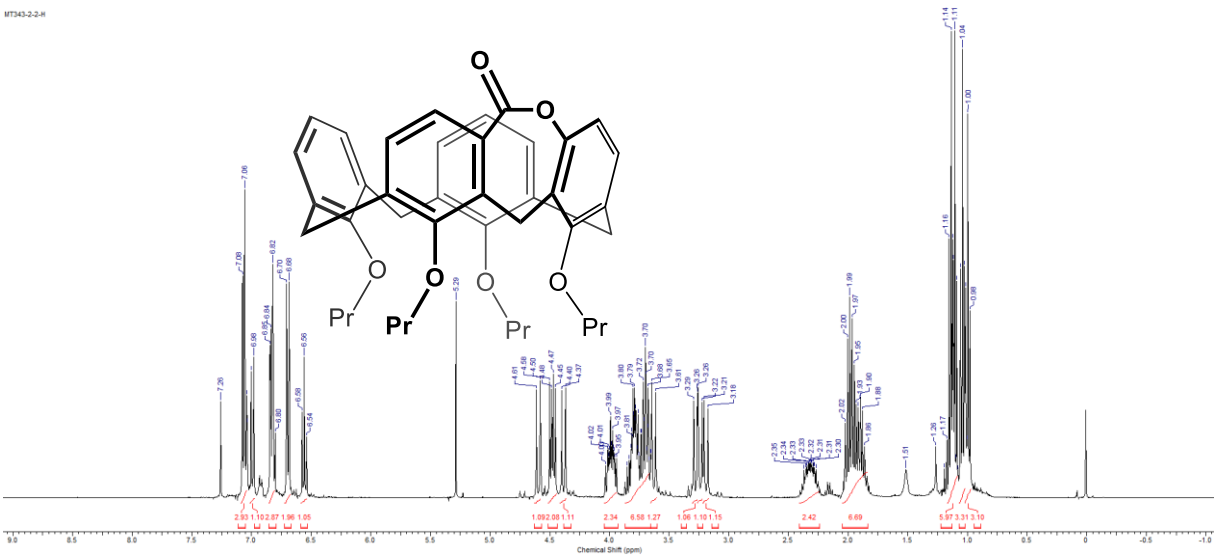

Figure 9. ^{1}H NMR of compound **8** ($CDCl_3$, 400 MHz).

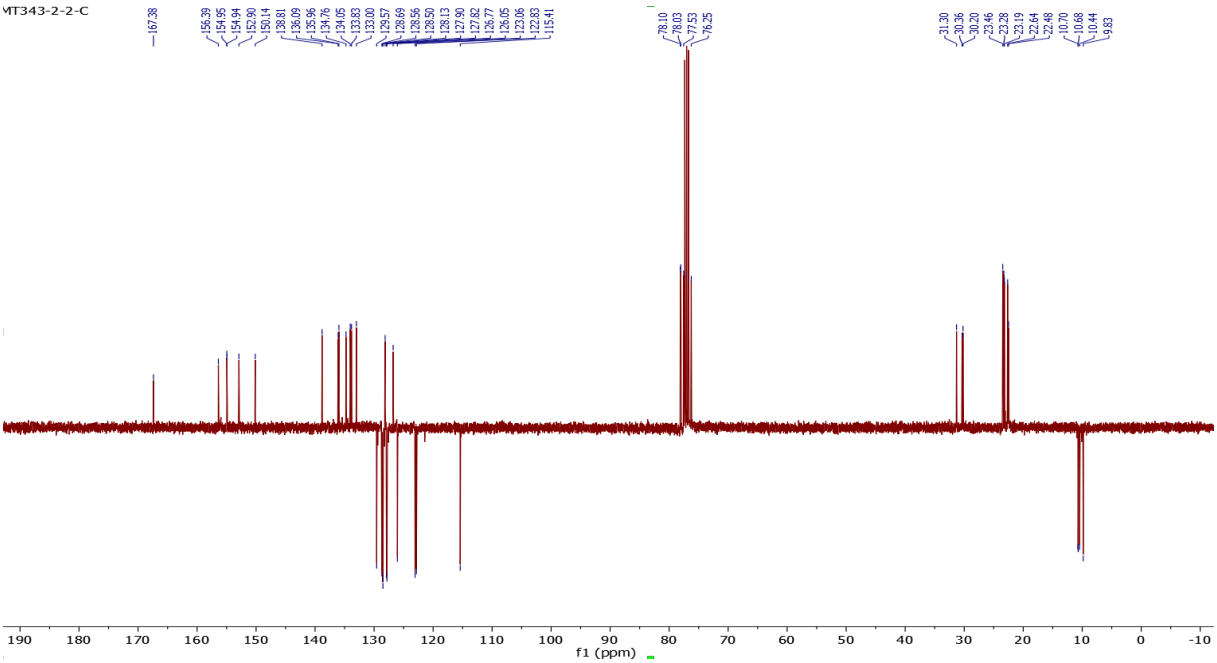

Figure 10. ^{13}C(APT) NMR of compound **8** ($CDCl_3$, 100 MHz).

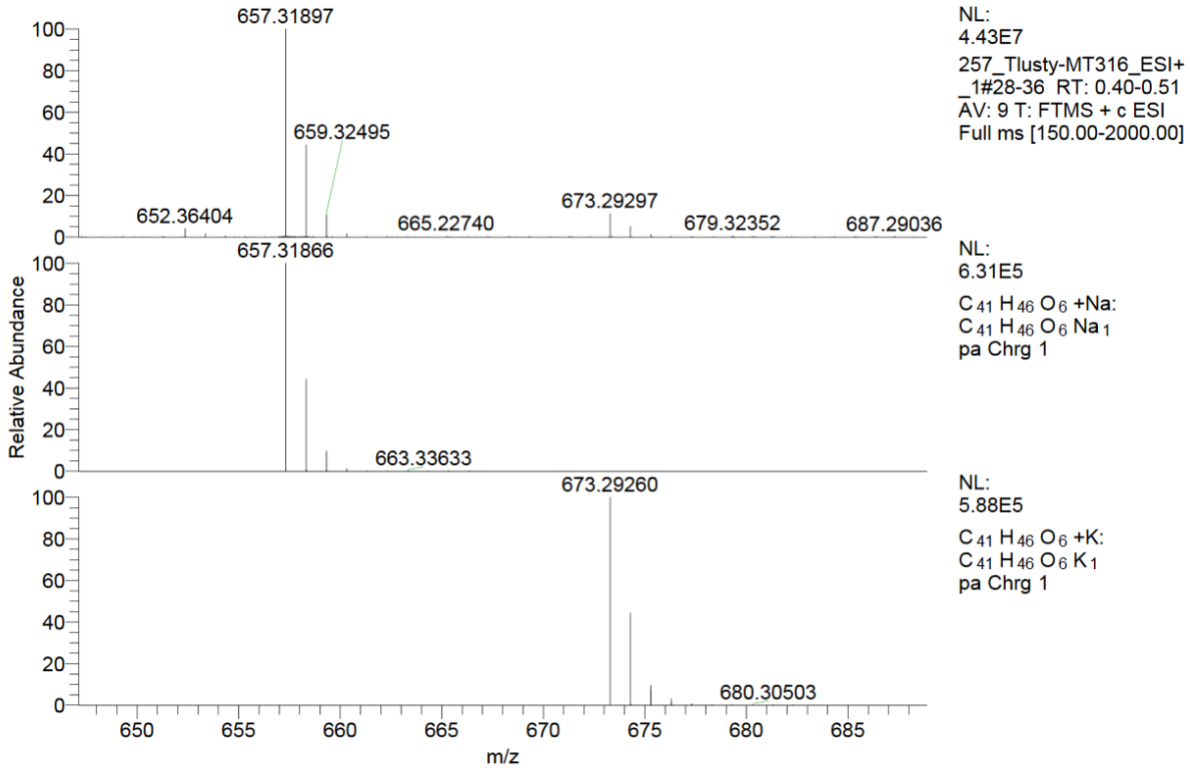

Figure 11. HRMS of compound **8** (ESI^+).

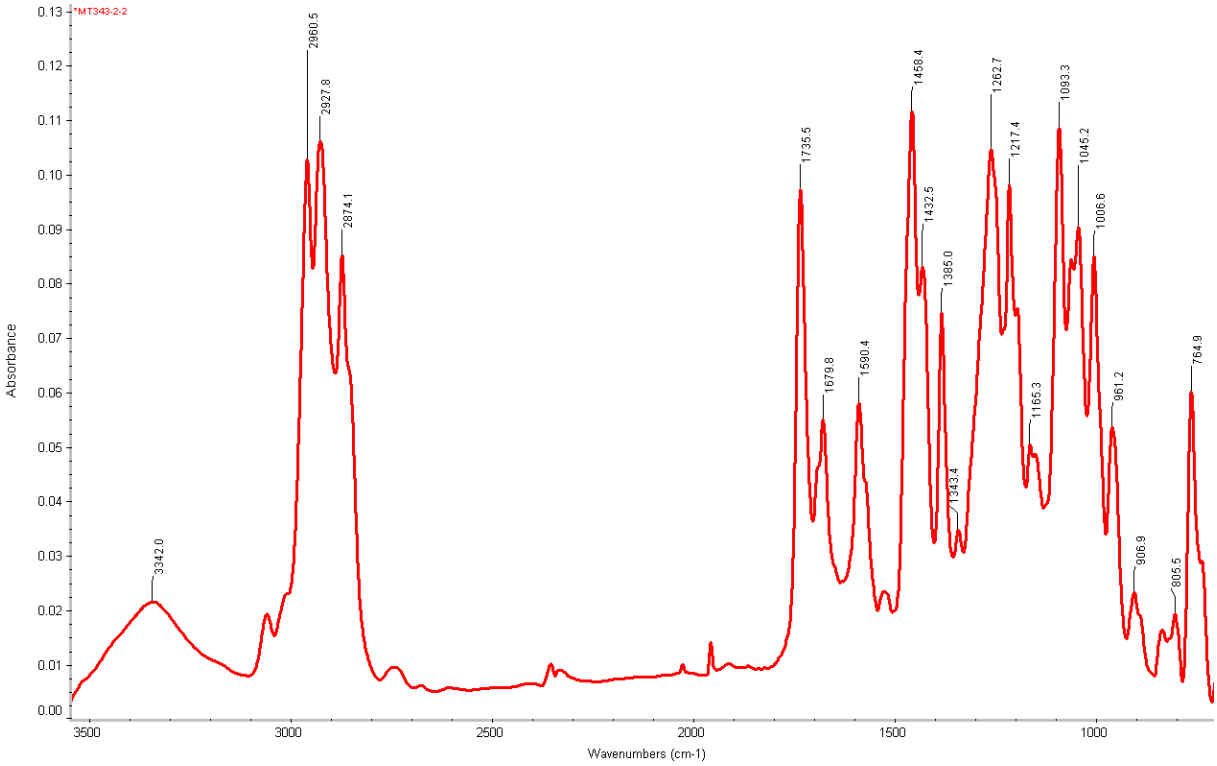

Figure 12. IR of compound **8** (KBr).

4. Chiral separation and ECD spectra

Chiral separation was performed using an automated preparative system AutoPurification (Waters, MA, USA) consisting of a binary pump module, PDA detector, column manager and fraction collector with separated fluidic ways for preparative and analytical mode. In the preparative mode, a polysaccharide column Chiralpak IA (250×20 mm ID, 5 µm) and in the analytical mode, a chiral polysaccharide column ChiralArt Amylose-SA (250×4.6 mm ID, 5 µm) were employed. The optimum mobile phase for both compounds **7** and **8** was heptane/propan-2-ol (96/4, v/v) with diethylamine (0.1 vol.%) as a basic additive. The flow rate was set to 15 mL/min, column temperature to 22 °C and detection wavelength to 254 nm. The sample concentration was 5 mg/mL, injection volume of 0.5 mL was employed. The samples were dissolved in a heptane/ethyl acetate/propan-2-ol /diethylamine (3/1/1/0.01, v/v/v/v) mixture and heptane/ethyl acetate (3/1, v/v) mixture for **7** and **8**, respectively. Fraction collection was set to ensure high purity of the collected enantiomers. Purity of enantiomers harvested in the collected fractions was verified by chiral separation in the analytical mode in heptane/propan-2-ol (9/1) with diethylamine (0.1 vol.%) and heptane/propan-2-ol (94/6) with diethylamine (0.1 vol.%) for **7** and **8**, respectively. For **7**, the optical purity of the first eluting enantiomer was >99.5%, the second enantiomer was 98.2% pure. In case of **8** the same optical purity, >99.5%, was found for both enantiomers.

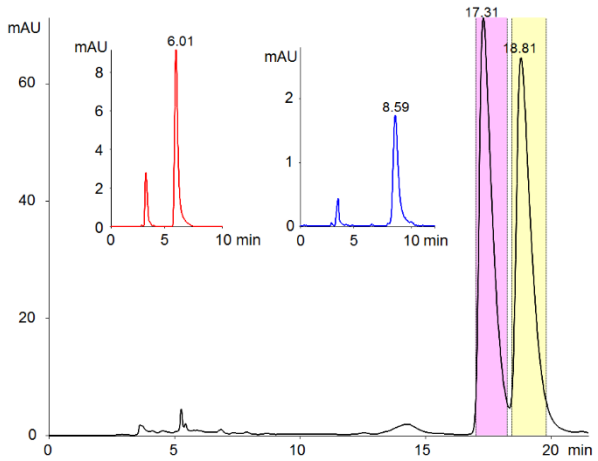

Figure 13. Preparative separation of **7**; the collected intervals of enantiomers are marked in colour. The analytical fraction purity control is depicted in the inset of the figure: the first eluting enantiomer at 6.01 min (red trace), the second eluting enantiomer at 8.59 min (blue trace). Colour version available on-line.

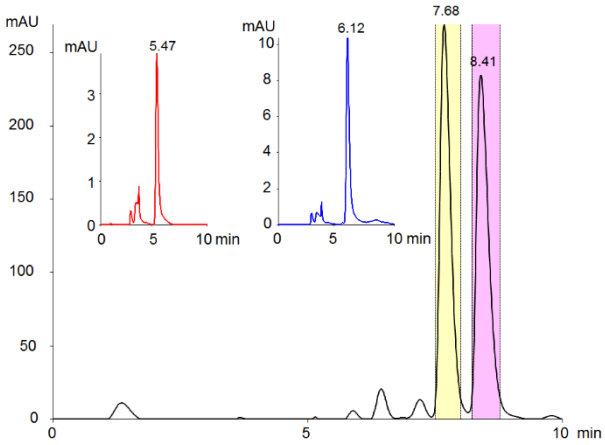

Figure 14. Preparative separation of **8**; the collected intervals of enantiomers are marked in colour. The analytical fraction purity control is depicted in the inset of the figure: the first eluting enantiomer at 5.47 min (red trace), the second eluting enantiomer at 6.12 min (blue trace). Colour version available on-line.

The enantiomeric nature of the separated substances was confirmed by ECD spectroscopy using Jasco J-810 (Jasco).

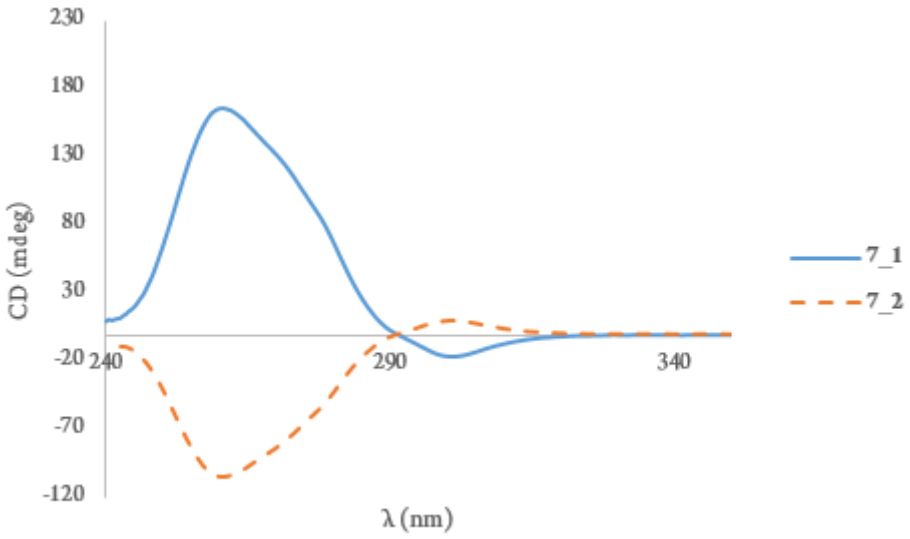

Figure 15. ECD spectra of both separated enantiomers of **7** in $CHCl_3$, the first eluting enantiomer **7_1** full (blue) line, the second eluting enantiomer **7_2** dashed (orange) line.

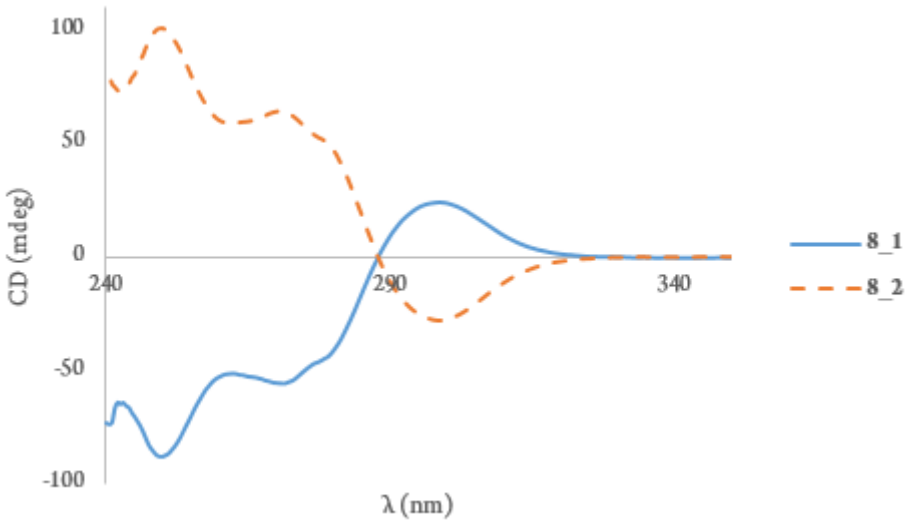

Figure 16. ECD spectra of both separated enantiomers of **8** in $CHCl_3$, the first eluting enantiomer **8_1** full (blue) line, the second eluting enantiomer **8_2** dashed (orange) line.

5. Crystalographic data

*Crystallographic data for **7**, 200 K*

M = 679.90 g.mol^{-1}, orthorhombic system, space group Pna21, a = 9.4753 (3) Å, b = 19.0877 (5) Å, c = 39.5036 (11) Å, Z = 8, V = 7144.7 (4) Å^3, D_c = 1.178 g.cm^{-3}, μ(Cu-Kα) = 0.61 mm^{-1}, crystal dimensions of 0.49 × 0.17 × 0.11 mm. Data were collected at 200 (2) K on a D8 Venture Photon CMOS diffractometer with Incoatec microfocus sealed tube Cu-Kα radiation. The structure was solved by charge flipping methods[x1] and anisotropically refined by full matrix least squares on F squared using the CRYSTALS suite of programs[x2] to final value R = 0.062 and wR = 0.156 using 12633 independent reflections (θ_{max} = 68.4°), 972 parameters and 183 restrains. The hydrogen atoms bonded to carbon atoms were placed in calculated positions refined with a riding constrains. The hydrogen atoms bonded to nitrogen atoms were placed from residual electron density maps and refined with soft restraints. The disordered functional group positions were found in difference electron density maps and refined with restrained geometry. MCE[x3] was used for visualization of electron density maps. The occupancy of disordered functional group was constrained to full. The structure crystallized in non-centrosymmetric space group, therefore the Flack parameter was refined to final value 0.27(7). The structure was deposited into Cambridge Structural Database under number CCDC 2017883.

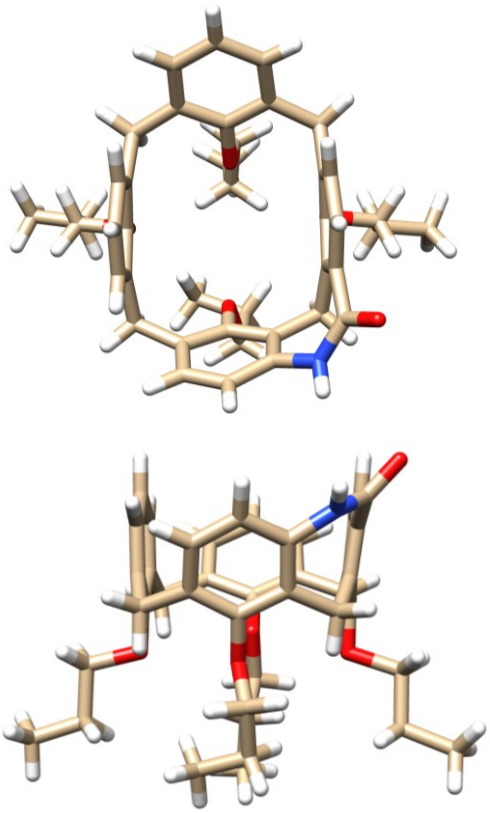

Figure 17. X-ray of compound **7** (200 K).

*Crystallographic data for **7et**, 200K*

M = 679.90 g.mol^{-1}, monoclinic system, space group $P2_1/n$, a = 12.9369 (5) Å, b = 17.1825 (6) Å, c = 17.9062 (6) Å, β = 102.0980 (16) °, Z = 4, V = 3891.9 (5) Å^3, D_c = 1.160 g.cm^{-3}, μ(Cu-Kα) = 0.61 mm^{-1}, crystal dimensions of 0.24 × 0.14 × 0.06 mm. Data were collected at 200 (2) K on a D8 Venture Photon CMOS diffractometer with Incoatec microfocus sealed tube Cu-Kα radiation. The structure was solved by charge flipping methods[x1] and anisotropically refined by full matrix least squares on F squared using the CRYSTALS suite of programs[x2] to final value R = 0.069 and wR = 0.108 using 7130 independent reflections (θ_{max} = 68.4°), 608 parameters and 142 restrains. The hydrogen atoms were placed in calculated positions and refined with a riding constrains. The disordered functional group positions were found in difference electron density maps and refined with restrained geometry. MCE[x3] was used for visualization of electron density maps. The occupancy of disordered functional group was constrained to full. The structure was deposited into Cambridge Structural Database under number CCDC 2017881.

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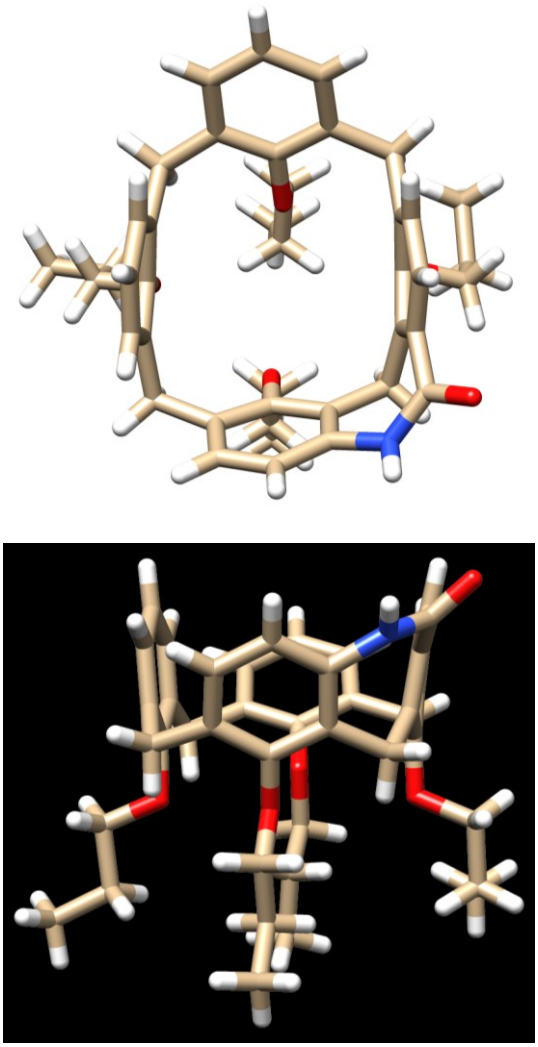


Figure 18. X-ray of compound **7et** (200 K).

*Crystallographic data for **7et**, 250K*

M = 679.90 g.mol^{-1}, monoclinic system, space group $P2_1/n$, a = 13.1917 (4) Å, b = 16.8403 (5) Å, c = 18.4369 (5) Å, β = 106.3131 (12) °, Z = 4, V = 3930.9 (2) Å^3, D_c = 1.149 g.cm^{-3}, μ(Cu-Kα) = 0.60 mm^{-1}, crystal dimensions of 0.38 × 0.29 × 0.25 mm. Data were collected at 250 (2) K on a D8 Venture Photon CMOS diffractometer with Incoatec microfocus sealed tube Cu-Kα radiation. The structure was solved by charge flipping methods[x1] and anisotropically refined by full matrix least squares on F squared using the CRYSTALS suite of programs[x2] to final value R = 0.066 and wR = 0.171 using 7199 independent reflections (ϑ_{max} = 68.4°), 538 parameters and 119 restrains. The hydrogen atoms were placed in calculated positions and refined with a riding constrains. The disordered functional group positions were found in difference electron density maps and refined with restrained geometry. MCE[x3] was used for visualization of electron density maps. The occupancy of disordered functional group was constrained to full. The structure was deposited into Cambridge Structural Database under number CCDC 2017882.

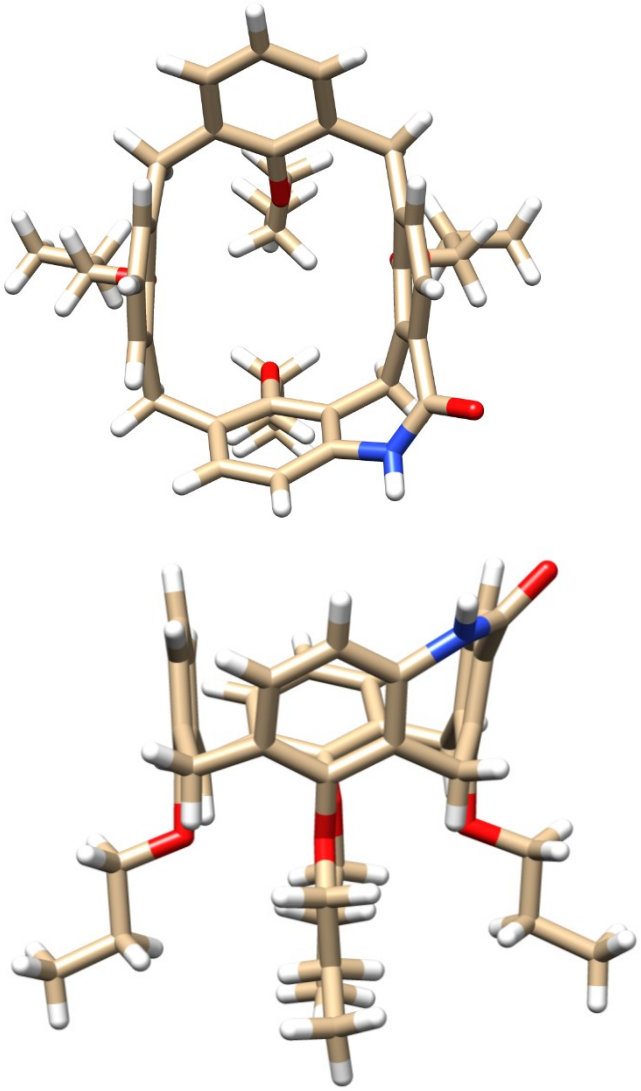


Figure 19. X-ray of compound **7et** (250K).

*The phase transition of **7et***

Upon cooling the ethanol solvate of **7** (**7et**) to 200 K the cracking of the crystals caused by phase transition occurred. The resulting crystal shards were large enough for the measurement, resulting in structure 7et_200K. Further experiments revealed the phase transition takes place in temperature range of 250 to 240 K with 250 K being still stable point, resulting in structure 7et_250K. Upon investigation of two temperature points the major difference between them is the appearance of disorder in low temperature phase. This disorder involves the amide group, resulting in partial presence of both enantiomers of inherently chiral substance in one crystallographic position. Such a disorder requires a rotation of 8.9 % of calixarene molecules and their associate solvent by 90 °. These changes are apparently large enough to break the crystal to pieces, but not large enough to pulverize the crystal, leading to creation of larger shards. The lattice parameters change during the phase transition as well, with *a* shortening by 0.255 Å, *c* shortening by 0.531 Å, *β* angle reduced by 4.21 ° and most notably *b* lengthening by 0.342 Å.

*Crystallographic data for **8***

M = 634.81 g.mol^{-1}, monoclinic system, space group $P2_1/c$, a = 18.1214 (9) Å, b = 12.6174 (7) Å, c = 16.088 (9) Å, β = 103.9902 (18) °, Z = 4, V = 3569.5 (3) Å^3, D_c = 1.181 g.cm^{-3}, μ(Mo-Kα) = 0.08 mm^{-1}, crystal dimensions of 0.67 × 0.42 × 0.39 mm. Data were collected at 200 (2) K on D8 Venture Photon CMOS diffractometer with Incoatec microfocus sealed tube Mo-Kα radiation. The structure was solved by charge flipping methods[x1] and anisotropically refined by full matrix least squares on F squared using the CRYSTALS suite of programs[x2] to final value R = 0.061 and wR = 0.165 using 7339 independent reflections (ϑ_{max} = 26.5°), 539 parameters and 128 restrains. The hydrogen atoms were placed in calculated positions and refined with a riding constrains. The disordered functional groups positions were found in difference electron density maps and refined with restrained geometry. MCE[x3] was used for visualization of electron density maps. The occupancy was constrained to full for each functional group. The structure was deposited into Cambridge Structural Database under number CCDC 2017884.

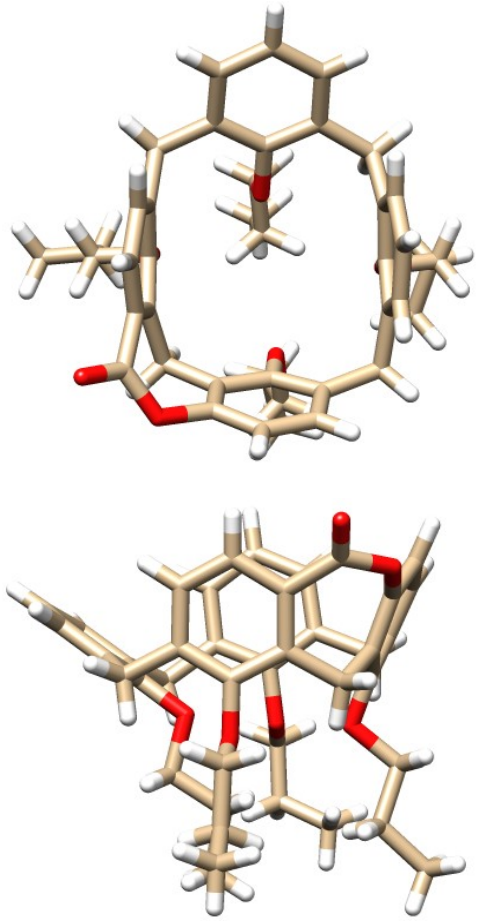


Figure 20. X-ray of compound **8**.

[x1] Palatinus, L., Chapuis, G. (2007). J. Appl. Cryst. 40, 786-790.

[x2] Betteridge, P.W., Carruthers, J.R., Cooper, R.I., Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.

[x3] Rohlicek J., Husak M.: J. Appl. Cryst. 40, 600 (2007)

6. Titration experiments

Calixarene **7** was dissolved in specified amount of $CDCl_3$. 0.5 ml of $CDCl_3$ was put in NMR tube. Solution of calixarene was gradually added to NMR tube to achieve different calixarene concentration (0.5 mM – 20.2 mM). The association constant was determined by analyzing CIS of protons of calixarene using nonlinear curve-fitting procedure (program BindFit).

M(calix)	633.829	g/mol
m(calix)	0.01534	g
c(calix)	0.0403	mol/l
V(CDCl3_ca	0.6	ml

	V (total) [m	V(addition, total) [n	V(addition) [ml]	c(calix) [mol/l]	shift [Hz]	shift 2 [Hz
1	0.506	0.006	0.006	0.00048	2969.48	2584.46
2	0.514	0.014	0.008	0.00110	2975.74	2585.25
3	0.524	0.024	0.010	0.00185	2982.78	2585.64
4	0.534	0.034	0.010	0.00257	2989.82	2586.03
5	0.544	0.044	0.010	0.00326	2996.48	2586.81
6	0.564	0.064	0.020	0.00458	3008.21	2587.59
7	0.584	0.084	0.020	0.00580	3018.39	2588.38
8	0.604	0.104	0.020	0.00695	3026.60	2589.16
9	0.634	0.134	0.030	0.00853	3037.56	2589.55
10	0.664	0.164	0.030	0.00996	3047.73	2590.33
11	0.714	0.214	0.050	0.01209	3061.04	2591.51
12	0.774	0.274	0.060	0.01428	3074.73	2592.68
13	0.844	0.344	0.070	0.01644	3087.25	2593.46
14	0.924	0.424	0.080	0.01851	3098.99	2594.64
15	1.004	0.504	0.080	0.02025	3108.77	2595.03

Kd	6.18	M^{-1}
Error	0.0127123	M^{-1}

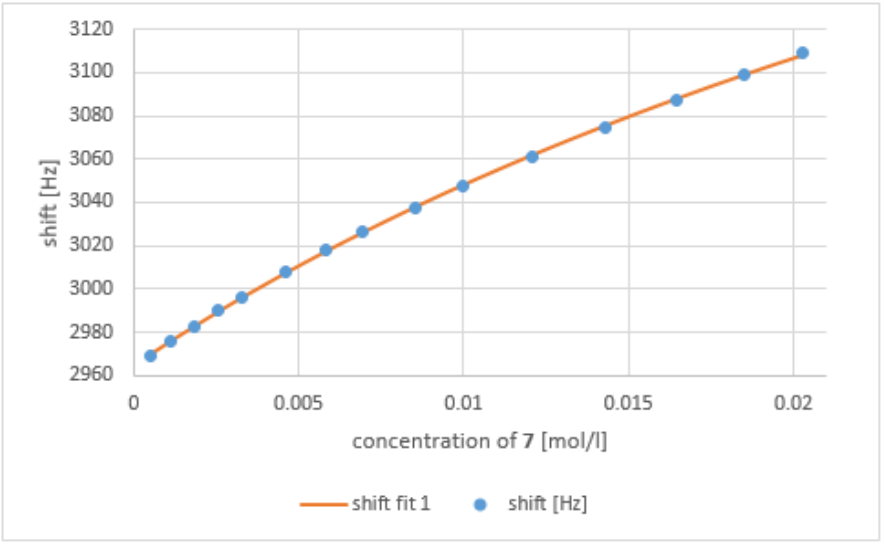


Figure 21. ^{1}H NMR concentration experiment of compound **7** ($CDCl_3$, 400 MHz).

Calixarene **7** was dissolved in specified amount of $C_2D_2Cl_4$. 0.5 ml of $C_2D_2Cl_4$ was put in NMR tube. Solution of calixarene was gradually added to NMR tube to achieve different calixarene concentration (0.2 mM – 10.2 mM). The association constant was determined by analyzing CIS of protons of calixarene using nonlinear curve-fitting procedure (program BindFit).

M(calix)	633.829	g/mol
m(calix)	0.00672	g
c(calix)	0.0204	mol/l
V(C2D2Cl4_	0.52	ml

	V (total) [m	V(addition, total) [n	V(addition) [ml]	c(calix) [mol/l]	shift [Hz]	shift 2 [Hz]
1	0.506	0.006	0.006	0.00024	3495.74	3095.08
2	0.514	0.014	0.008	0.00056	3505.92	3096.25
3	0.524	0.024	0.010	0.00093	3518.04	3097.03
4	0.534	0.034	0.010	0.00130	3528.61	3097.82
5	0.544	0.044	0.010	0.00165	3538.78	3098.21
6	0.564	0.064	0.020	0.00231	3556.78	3098.99
7	0.584	0.084	0.020	0.00293	3571.65	3100.16
8	0.604	0.104	0.020	0.00351	3584.95	3100.95
9	0.634	0.134	0.030	0.00431	3603.34	3102.12
10	0.664	0.164	0.030	0.00504	3619.78	3103.29
11	0.714	0.214	0.050	0.00611	3640.90	3104.86
12	0.774	0.274	0.060	0.00722	3662.03	3106.42
13	0.844	0.344	0.070	0.00831	3681.60	3107.60
14	0.914	0.414	0.070	0.00924	3698.03	3108.77
15	1.004	0.504	0.090	0.01024	3714.07	3109.94

Kd	12.3 M^{-1}
Error	0.0168879 M^{-1}

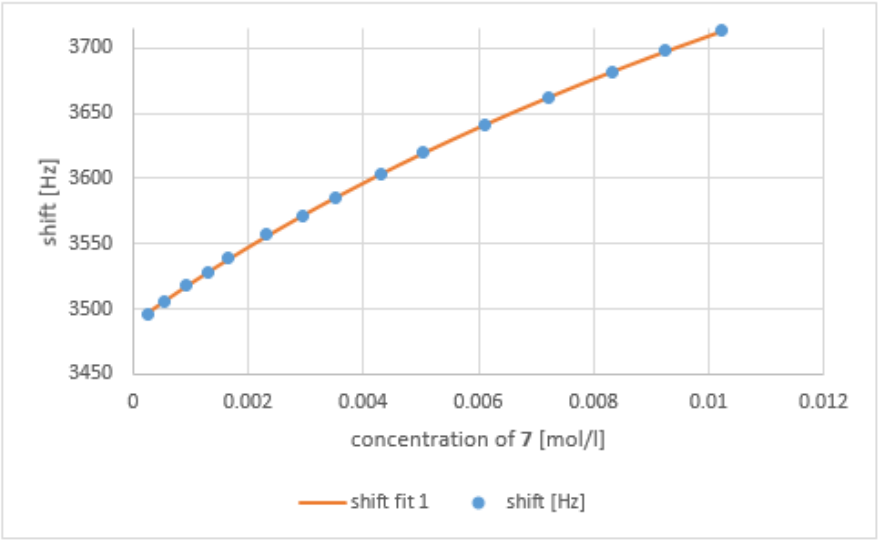


Figure 22. ^{1}H NMR concentration experiment of compound **7** ($C_2D_2Cl_4$, 400 MHz).

Calixarene **7_1** was dissolved in specified amount of $CDCl_3$. 0.5 ml of $CDCl_3$ was put in NMR tube. Solution of calixarene was gradually added to NMR tube to achieve different calixarene concentration (0.2 mM – 11.1 mM). The association constant was determined by analyzing CIS of protons of calixarene using nonlinear curve-fitting procedure (program BindFit).

M(calix)	633.829	g/mol
m(calix)	0.00525	g
c(calix)	0.0414	mol/l
V(CDCl3_ca	0.2	ml

	V (total) [m	V(addition, total) [n	V(addition) [ml]	c(calix) [mol/l]	shift [Hz]	shift 2 [Hz
1	0.502	0.002	0.002	0.00016	2974.17	2585.64
2	0.506	0.006	0.004	0.00049	2983.56	2586.81
3	0.514	0.014	0.008	0.00113	2995.30	2588.38
4	0.524	0.024	0.010	0.00190	3007.04	2589.55
5	0.534	0.034	0.010	0.00264	3017.21	2590.33
6	0.544	0.044	0.010	0.00335	3026.21	2591.51
7	0.554	0.054	0.010	0.00404	3034.04	2592.29
8	0.564	0.064	0.010	0.00470	3041.08	2592.68
9	0.574	0.074	0.010	0.00534	3047.73	2593.46
10	0.594	0.094	0.020	0.00655	3059.47	2594.64
11	0.614	0.114	0.020	0.00769	3069.64	2595.42
12	0.634	0.134	0.020	0.00875	3078.64	2596.59
13	0.654	0.154	0.020	0.00975	3087.25	2597.37
14	0.674	0.174	0.020	0.01069	3095.08	2597.77
15	0.684	0.184	0.010	0.01114	3098.99	2598.16

Kd	18.46 M^{-1}
Error	0.0899556 M^{-1}

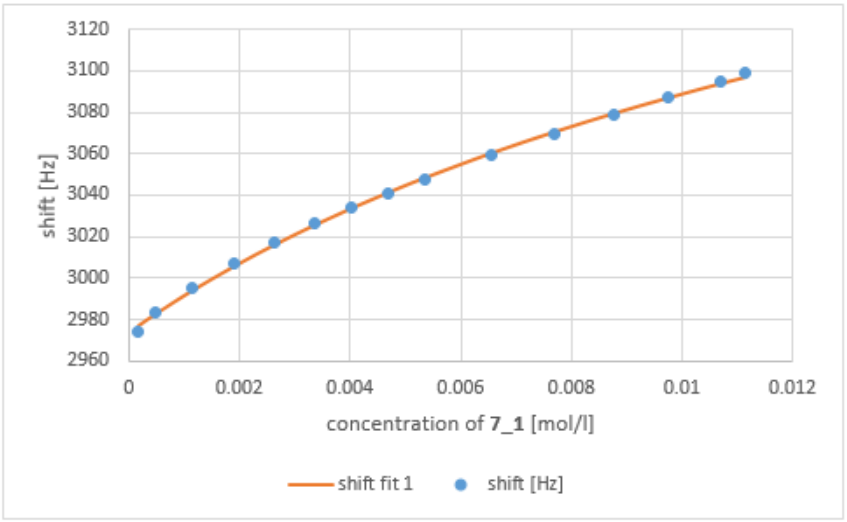


Figure 23. ^{1}H NMR concentration experiment of compound **7_1** ($CDCl_3$, 400 MHz).

Calixarene **7** was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of *N*-methylpyridinium iodide (NMPI) was added. The aliquots of NMPI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-49.551), ensuring constant host concentration during the experiment.

M(NMPI)	304.1755 g/mol	M(calix)	795.036 g/mol
m(NMPI)	0.00625 g	m(calix)	0.00140 g
c(NMPI)	0.0342 mol/l	c(calix)	0.0015 mol/l
V(C2D2Cl4	0.6 ml	V(C2D2Cl4	1.2 ml

	V (total) [ml]	V(additio	V(additio	c(NMPI) [	c(calix) [m	c(calix)/c(N	shift [Hz]	shift 2 [Hz	shift 3 [Hz	shift 4 [Hz]
1	0.5000	0.0000	0.0000	0.00000	0.00158	0.00000	3682.38	3133.81	3191.33	3103.29
2	0.5010	0.0010	0.0010	0.00029	0.00158	0.18494	3672.99	3132.64	3189.76	3104.08
3	0.5022	0.0022	0.0012	0.00064	0.00158	0.40589	3667.12	3131.46	3189.37	3104.86
4	0.5038	0.0038	0.0016	0.00111	0.00158	0.69886	3663.21	3129.90	3188.98	3106.42
5	0.5058	0.0058	0.0020	0.00168	0.00158	1.06246	3658.12	3127.16	3188.20	3107.99
6	0.5108	0.0108	0.0050	0.00310	0.00158	1.95901	3652.25	3120.51	3186.63	3112.29
7	0.5188	0.0188	0.0080	0.00532	0.00158	3.35755	3649.51	3116.21	3184.29	3119.73
8	0.5288	0.0288	0.0100	0.00799	0.00158	5.04621	3650.30	3108.77	3181.94	3128.73
9	0.5548	0.0548	0.0260	0.01449	0.00158	9.15184	3659.29	3096.25	3178.03	3147.51
10	0.5848	0.0848	0.0300	0.02128	0.00158	13.43547	3674.16	3086.08	3175.68	3164.33
11	0.6248	0.1248	0.0400	0.02931	0.00158	18.50708	3693.34	3077.08	3172.94	3179.98
12	0.6748	0.1748	0.0500	0.03801	0.00158	24.00108	3713.68	3069.64	3170.59	3193.68
13	0.7548	0.2548	0.0800	0.04953	0.00158	31.27749		3062.21	3167.86	3207.76
14	0.8548	0.3548	0.1000	0.06090	0.00158	38.45771	3760.24	3056.34	3165.51	3217.15
15	0.9548	0.4548	0.1000	0.06989	0.00158	44.13391	3775.50	3052.43	3164.33	3225.37
16	1.0748	0.5748	0.1200	0.07847	0.00158	49.55112	3787.63	3048.91	3163.55	3230.07

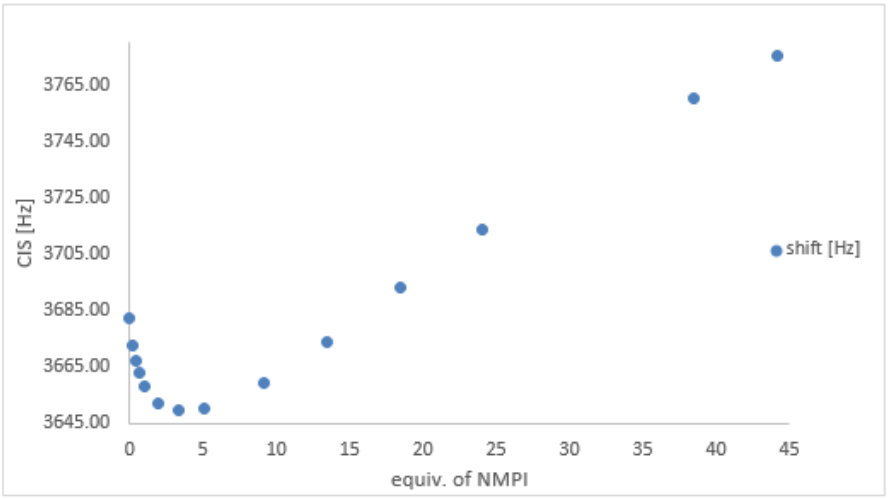


Figure 24. ^{1}H NMR titration of compound **7** with NMPI ($C_2D_2Cl_4$, 400 MHz).

Calixarene **7_2** was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.65 ml of the calixarene solution a specific amount of *N*-methylpyridinium iodide (NMPI) was added. The aliquots of NMPI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-52.382), ensuring constant host concentration during the experiment.

M(NMPI)	221.04147	g/mol	M(calix)	633.829 g/mol
m(NMPI)	0.01336	g	m(calix)	0.00080 g
c(NMPI)	0.1007	mol/l	c(calix)	0.0011 mol/l
V(C2D2Cl4_NMPI)	0.6	ml	V(C2D2Cl4_cali	1.2 ml

	V (total) [m	V(addition, total) [n	V(addition) [ml]	c(NMPI) [mol/l]	c(calix) [mol/l]	c(calix)/c(NM	shift [Hz]	shift 2 [Hz	shift 3 [Hz
1	0.5000	0.0000	0.0000	0.00000	0.00105	0.00000	3520.10	3125.30	3097.92
2	0.5006	0.0006	0.0006	0.00012	0.00105	0.11479	3522.06	3124.91	3099.09
3	0.5012	0.0012	0.0006	0.00024	0.00105	0.22931	3522.84	3124.13	3099.48
4	0.5020	0.0020	0.0008	0.00040	0.00105	0.38157	3525.19	3123.74	3100.26
5	0.5028	0.0028	0.0008	0.00056	0.00105	0.53334	3526.36	3122.96	3101.05
6	0.5042	0.0042	0.0014	0.00084	0.00105	0.79779	3529.49	3121.39	3102.22
7	0.5056	0.0056	0.0014	0.00112	0.00105	1.06078	3531.45	3120.61	3103.39
8	0.5136	0.0136	0.0080	0.00267	0.00105	2.53606	3543.97	3114.74	3109.65
9	0.5236	0.0236	0.0100	0.00454	0.00105	4.31675	3557.27	3108.09	3117.48
10	0.5536	0.0536	0.0300	0.00975	0.00105	9.27286	3589.75	3095.57	3135.48
11	0.5936	0.0936	0.0400	0.01588	0.00105	15.10173	3623.01	3083.83	3153.08
12	0.6436	0.1436	0.0500	0.02248	0.00105	21.36895	3653.92	3075.22	3169.13
13	0.7136	0.2136	0.0700	0.03015	0.00105	28.66759	3683.65	3067.00	3184.00
14	0.8036	0.3036	0.0900	0.03806	0.00105	36.18317	3708.70	3060.74	3195.73
15	0.9036	0.4036	0.1000	0.04499	0.00105	42.77793	3720.83	3056.05	3204.34
16	1.0036	0.5036	0.1000	0.05055	0.00105	48.05846	3732.49	3052.92	3209.82
17	1.1036	0.6036	0.1000	0.05510	0.00105	52.38203	3740.65	3050.96	3212.17

K	24.4 M^{-1}
Error	0.2906284 M^{-1}

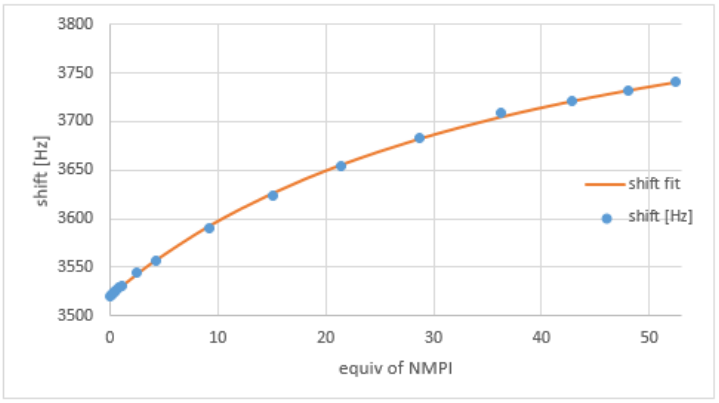


Figure 25. ^{1}H NMR titration of compound **7_2** with NMPI ($C_2D_2Cl_4$, 400 MHz).

Calixarene **7** was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of *N*-methylquinolinium iodide (NMQI) was added. The aliquots of NMQI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-47.870), ensuring constant host concentration during the experiment.

M(NMQI)	271.1015	g/mol	M(calix)	633.829 g/mol
m(NMQI)	0.02421	g	m(calix)	0.00119 g
c(NMQI)	0.14884	mol/l	c(calix)	0.00156 mol/l
V(C2D2Cl4	0.6	ml	V(C2D2Cl4	1.2 ml

	V (total) [ml]	V(additio	V(additio	c(NMQI) [	c(calix) [m	c(calix)/c(N	shift [Hz]	shift 2 [Hz	shift 3 [Hz	shift 4 [Hz	shift 5 [Hz	shift 6 [Hz]
1	0.5000	0.0000	0.0000	0.00000	0.00156	0.00000	3133.91	3675.05	3103.00	1772.28	2250.41	1842.31
2	0.5006	0.0006	0.0006	0.00018	0.00156	0.11434	3133.52	3668.79	3103.00	1773.06	2251.20	1843.10
3	0.5012	0.0012	0.0006	0.00036	0.00156	0.22841	3133.13	3666.05	3103.39	1773.06	2251.59	1843.49
4	0.5020	0.0020	0.0008	0.00059	0.00156	0.38007	3131.96	3662.52	3103.00	1773.45	2251.20	1843.88
5	0.5028	0.0028	0.0008	0.00083	0.00156	0.53125	3131.56	3659.39	3103.39	1773.84	2251.59	1844.27
6	0.5042	0.0042	0.0014	0.00124	0.00156	0.79466	3130.39	3654.70	3103.00	1774.23	2251.59	1844.27
7	0.5056	0.0056	0.0014	0.00165	0.00156	1.05662	3129.61	3650.40	3103.00	1773.84	2251.98	1844.66
8	0.5136	0.0136	0.0080	0.00394	0.00156	2.52610	3124.91	3640.22	3104.18	1775.80	2253.94	1846.62
9	0.5236	0.0236	0.0100	0.00671	0.00156	4.29980	3120.22	3633.57	3105.74	1776.97	2254.72	1847.40
10	0.5536	0.0536	0.0300	0.01441	0.00156	9.23645	3105.74	3634.74	3113.96	1781.28	2258.24	1850.53
11	0.5936	0.0936	0.0400	0.02347	0.00156	15.04244	3091.66	3648.05	3124.91	1784.80	2261.76	1852.49
12	0.6436	0.1436	0.0500	0.03321	0.00156	21.28505	3079.13	3666.44	3136.65	1787.93	2264.89	1854.05
13	0.7136	0.2136	0.0700	0.04455	0.00156	28.55503	3068.18	3689.91	3149.17	1791.06	2267.24	1855.23
14	0.8036	0.3036	0.0900	0.05623	0.00156	36.04111	3057.61	3708.69	3160.91	1792.62	2268.80	1855.23
15	1.0036	0.5036	0.2000	0.07469	0.00156	47.86977	3047.05	3736.33	3173.04	1794.58	2269.98	1854.84

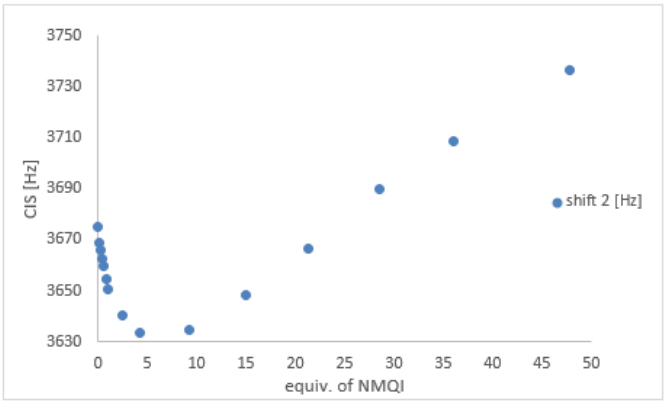


Figure 26. ^{1}H NMR titration of compound **7** with NMQI ($C_2D_2Cl_4$, 400 MHz).

Calixarene **7_2** was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of *N*-methylquinolinium iodide (NMQI) was added. The aliquots of NMQI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-45.104), ensuring constant host concentration during the experiment.

M(NMQI)	271.10147	g/mol	M(calix)	633.829 g/mol
m(NMQI)	0.02060	g	m(calix)	0.00105 g
c(NMQI)	0.12664	mol/l	c(calix)	0.00138 mol/l
V(C2D2Cl4_NMQI)	0.6	ml	V(C2D2Cl4_cali	1.2 ml

	V (total) [m	V(addition, total) [n	V(addition) [ml]	c(NMQI) [mol/l]	c(calix) [mol/l]	c(calix)/c(NM	shift [Hz]	shift 2 [Hz
1	0.5000	0.0000	0.0000	0.00000	0.00138	0.00000	3520.00	3125.20
2	0.5006	0.0006	0.0006	0.00015	0.00138	0.10995	3520.78	3125.20
3	0.5012	0.0012	0.0006	0.00030	0.00138	0.21964	3521.96	3125.20
4	0.5020	0.0020	0.0008	0.00050	0.00138	0.36549	3523.52	3124.81
5	0.5028	0.0028	0.0008	0.00071	0.00138	0.51087	3524.30	3124.03
6	0.5042	0.0042	0.0014	0.00105	0.00138	0.76418	3526.26	3123.25
7	0.5056	0.0056	0.0014	0.00140	0.00138	1.01608	3528.22	3122.07
8	0.5136	0.0136	0.0080	0.00335	0.00138	2.42919	3536.43	3117.38
9	0.5236	0.0236	0.0100	0.00571	0.00138	4.13486	3545.43	3112.29
10	0.5536	0.0536	0.0300	0.01226	0.00138	8.88212	3568.52	3100.55
11	0.5936	0.0936	0.0400	0.01997	0.00138	14.46539	3591.21	3090.77
12	0.6436	0.1436	0.0500	0.02826	0.00138	20.46853	3618.21	3079.43
13	0.8036	0.3036	0.1600	0.04785	0.00138	34.65852	3667.12	3060.25
14	0.9836	0.4836	0.1800	0.06227	0.00138	45.10409	3705.33	3046.95

K	7.51 M^{-1}
Error	0.13926544 M^{-1}

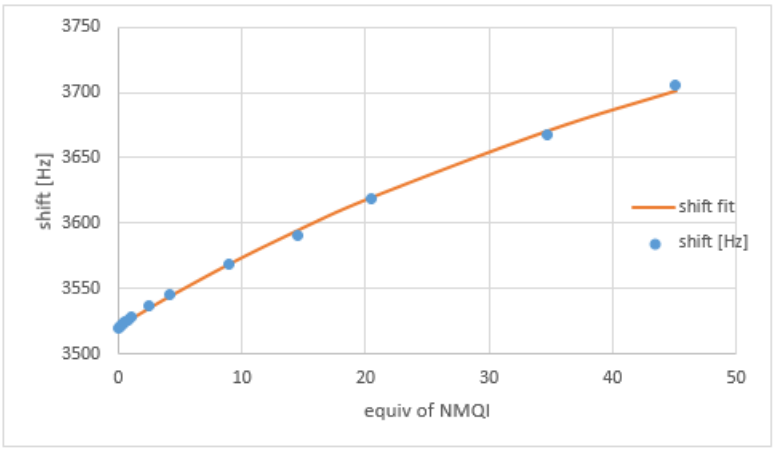


Figure 27. ^{1}H NMR titration of compound **7_2** with NMQI ($C_2D_2Cl_4$, 400 MHz).

Calixarene **7** was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of *N*-methylisoquinolinium iodide (NMII) was added. The aliquots of NMII were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-47.175), ensuring constant host concentration during the experiment.

M(NMII)	271.1015 g/mol	M(calix)	633.829 g/mol	
m(NMII)	0.02236 g	m(calix)	0.00120 g	
c(NMII)	0.13746 mol/l	c(calix)	0.00158 mol/l	
V(C2D2Cl4	0.6 ml	V(C2D2Cl4	1.2 ml	

	V (total) [ml]	V(additio	V(additio	c(NMII) [n	c(calix) [n	c(calix)/c(N	shift [Hz]	shift 2 [Hz	shift 3 [Hz	shift 4 [Hz	shift 5 [Hz	shift 6 [Hz]
1	0.5000	0.0000	0.0000	0.00000	0.00158	0.00000	3111.51	3681.99	3329.84	3133.81	3233.59	1842.31
2	0.5006	0.0006	0.0006	0.00016	0.00158	0.10417	3111.51	3675.34	3329.06	3133.81	3234.37	1843.10
3	0.5012	0.0012	0.0006	0.00033	0.00158	0.20809	3111.90	3670.25	3328.67	3133.81	3235.15	1843.49
4	0.5020	0.0020	0.0008	0.00055	0.00158	0.34626	3111.90	3667.12	3327.88	3133.42	3235.54	1843.88
5	0.5028	0.0028	0.0008	0.00077	0.00158	0.48399	3111.90	3664.77	3327.10	3132.64	3235.54	1844.27
6	0.5042	0.0042	0.0014	0.00115	0.00158	0.72397	3111.90	3661.25	3325.54	3131.46	3235.54	1844.27
7	0.5056	0.0056	0.0014	0.00152	0.00158	0.96263	3112.68	3657.73	3324.75	3131.46	3237.11	1844.66
8	0.5136	0.0136	0.0080	0.00364	0.00158	2.30139	3115.03	3646.38	3318.49	3127.55	3239.07	1846.62
9	0.5236	0.0236	0.0100	0.00620	0.00158	3.91732	3117.38	3638.56	3313.02	3124.42	3242.98	1847.40
10	0.5536	0.0536	0.0300	0.01331	0.00158	8.41483	3127.94	3633.47	3296.58	3115.42	3247.28	1850.53
11	0.5936	0.0936	0.0400	0.02168	0.00158	13.70435	3139.29	3637.77	3282.50	3106.81	3254.33	1852.49
12	0.6436	0.1436	0.0500	0.03067	0.00158	19.39165	3151.03	3648.34	3268.80	3098.60	3260.98	1854.05
13	0.7136	0.2136	0.0700	0.04115	0.00158	26.01494	3163.16	3662.42	3256.67	3091.16	3265.28	1855.23
14	0.8036	0.3036	0.0900	0.05193	0.00158	32.83509	3173.72	3678.47	3237.50	3084.51	3269.19	1855.23
15	1.0036	0.5036	0.2000	0.06898	0.00158	43.61154	3186.63	3694.68	3228.50	3076.30	3273.11	1854.84
16	1.0936	0.5936	0.0900	0.07461	0.00158	47.17499	3191.33	3700.51	3228.89	3073.56	3275.06	1856.06

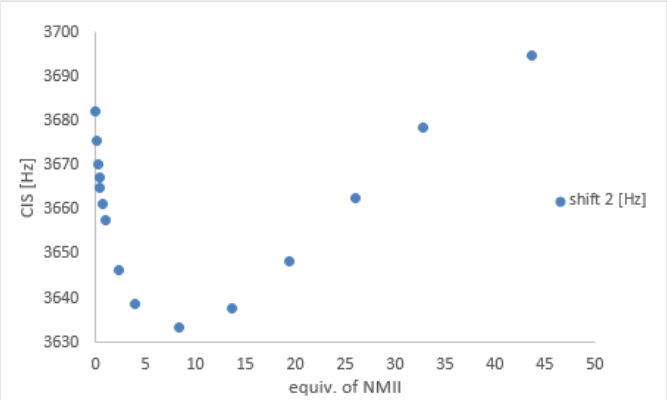


Figure 28. ^{1}H NMR titration of compound **7** with NMII ($C_2D_2Cl_4$, 400 MHz).

Calixarene **7_1** was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of *N*-methylisoquinolinium iodide (NMII) was added. The aliquots of NMII were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-47.752), ensuring constant host concentration during the experiment. The complexation constants were determined by analyzing CIS of protons of the host molecule using nonlinear curve-fitting procedure (program BindFit).

M(NMII)	271.10147	g/mol	M(calix)	633.829 g/mol
m(NMII)	0.01999	g	m(calix)	0.00106 g
c(NMII)	0.12289	mol/l	c(calix)	0.00140 mol/l
V(C2D2Cl4_NMII)	0.6	ml	V(C2D2Cl4_cali	1.2 ml

	V (total) [m	V(addition, total) [n	V(addition) [ml]	c(NMII) [mol/l]	c(calix) [mol/l]	c(calix)/c(NM	shift [Hz]	shift 2 [Hz	shift 3 [Hz]
1	0.5000	0.0000	0.0000	0.00000	0.00140	0.00000	3524.30	3125.60	3098.99
2	0.5006	0.0006	0.0006	0.00015	0.00140	0.10544	3526.26	3125.20	3099.77
3	0.5012	0.0012	0.0006	0.00029	0.00140	0.21063	3527.44	3125.20	3099.77
4	0.5020	0.0020	0.0008	0.00049	0.00140	0.35049	3529.39	3124.81	3100.55
5	0.5028	0.0028	0.0008	0.00068	0.00140	0.48991	3530.56	3124.42	3100.95
6	0.5042	0.0042	0.0014	0.00102	0.00140	0.73283	3532.91	3123.64	3101.73
7	0.5056	0.0056	0.0014	0.00136	0.00140	0.97439	3534.87	3122.86	3102.12
8	0.5136	0.0136	0.0080	0.00325	0.00140	2.32953	3543.87	3119.73	3105.25
9	0.5236	0.0236	0.0100	0.00554	0.00140	3.96521	3554.04	3116.60	3108.77
10	0.5536	0.0536	0.0300	0.01190	0.00140	8.51771	3577.91	3107.60	3118.94
11	0.5936	0.0936	0.0400	0.01938	0.00140	13.87190	3601.78	3099.77	3129.51
12	0.6436	0.1436	0.0500	0.02742	0.00140	19.62874	3625.25	3092.73	3140.46
13	0.7136	0.2136	0.0700	0.03679	0.00140	26.33301	3649.12	3085.29	3151.42
14	0.8036	0.3036	0.0900	0.04643	0.00140	33.23655	3670.25	3079.03	3161.59
15	1.0036	0.5036	0.2000	0.06167	0.00140	44.14476		3070.82	3175.29
16	1.0936	0.5936	0.0900	0.06671	0.00140	47.75177		3068.47	3179.20

K	13.38 M^{-1}
Error	0.1887249 M^{-1}

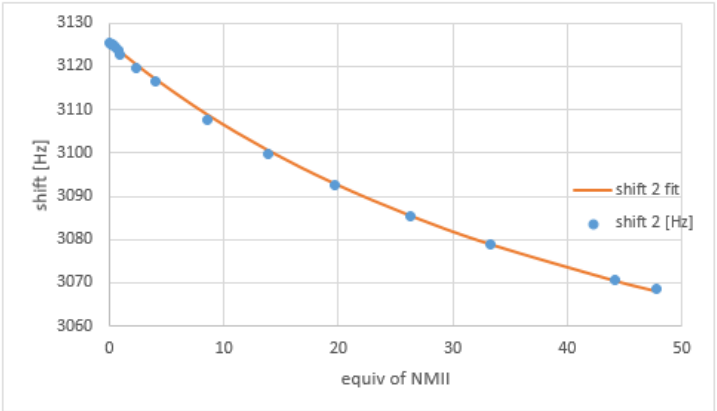


Figure 29. ^{1}H NMR titration of compound **7_1** with NMII ($C_2D_2Cl_4$, 400 MHz).

Calixarene **7_1** was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of (*S*)-1-Methyl-3-(1-methylpyrrolidin-2-yl)pyridinium iodide (NMNI) was added. The aliquots of NMNI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-50.445), ensuring constant host concentration during the experiment.

M(NMNI)	304.17547	g/mol	M(calix)	633.829 g/mol
m(NMNI)	0.02395	g	m(calix)	0.00107 g
c(NMNI)	0.13123	mol/l	c(calix)	0.00141 mol/l
V(C2D2Cl4_NM	0.6	ml	V(C2D2Cl4_cali	1.2 ml

	V (total) [m	V(addition, to	V(addition) [ml	c(NMNI) [mol/	c(calix) [mol/l]	c(calix)/c(NM	shift [Hz]	shift 2 [Hz	shift 3 [Hz
1	0.5000	0.0000	0.0000	0.00000	0.00141	0.00000	3523.52	3125.60	3098.99
2	0.5006	0.0006	0.0006	0.00016	0.00141	0.11139	3523.13	3125.20	3099.38
3	0.5012	0.0012	0.0006	0.00031	0.00141	0.22251	3523.91	3124.80	3099.77
4	0.5020	0.0020	0.0008	0.00052	0.00141	0.37026	3525.87	3124.03	3100.16
5	0.5028	0.0028	0.0008	0.00073	0.00141	0.51754	3524.70	3124.03	3100.55
6	0.5042	0.0042	0.0014	0.00109	0.00141	0.77415	3527.44	3123.25	3100.95
7	0.5056	0.0056	0.0014	0.00145	0.00141	1.02934	3529.00	3123.25	3102.12
8	0.5136	0.0136	0.0080	0.00347	0.00141	2.46089	3534.87	3118.55	3104.47
9	0.5236	0.0236	0.0100	0.00591	0.00141	4.18882	3542.30	3115.81	3107.60
10	0.5536	0.0536	0.0300	0.01271	0.00141	8.99804	3560.30	3107.21	3115.42
11	0.5936	0.0936	0.0400	0.02069	0.00141	14.65417	3583.39	3101.73	3125.99
12	0.6436	0.1436	0.0500	0.02928	0.00141	20.73565	3605.69	3092.73	3134.20
13	0.7136	0.2136	0.0700	0.03928	0.00141	27.81798	3628.38	3086.86	3143.59
14	0.8036	0.3036	0.0900	0.04958	0.00141	35.11082	3651.47	3079.03	3151.42
15	1.0036	0.5036	0.2000	0.06585	0.00141	46.63417	3680.03	3071.60	3161.20
16	1.0936	0.5936	0.0900	0.07123	0.00141	50.44458	3690.60	3068.86	3165.11

K	6.56 M^{-1}
Error	0.07847728 M^{-1}

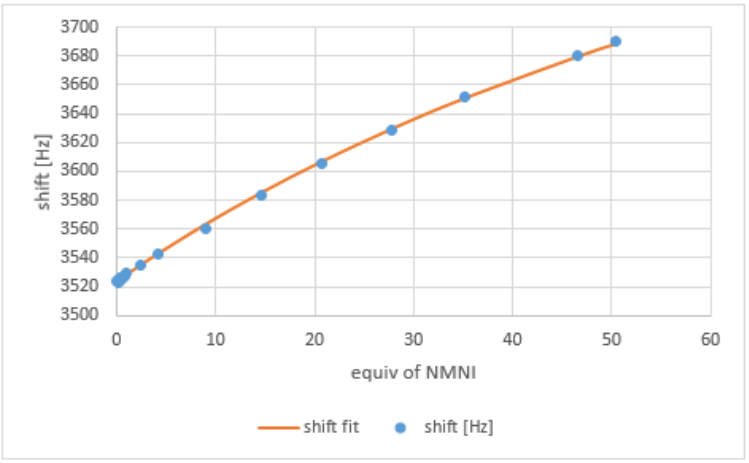


Figure 30. ^{1}H NMR titration of compound **7_1** with NMNI ($C_2D_2Cl_4$, 400 MHz).

Calixarene **7_2** was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of (*S*)-1-Methyl-3-(1-methylpyrrolidin-2-yl)pyridinium iodide (NMNI) was added. The aliquots of NMNI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-50.983), ensuring constant host concentration during the experiment.

M(NMNI)	304.17547 g/mol	M(calix)	633.829 g/mol	
m(NMNI)	0.02682 g	m(calix)	0.00119 g	
c(NMNI)	0.14695 mol/l	c(calix)	0.00156 mol/l	
V(C2D2Cl4_NM	0.6 ml	V(C2D2Cl4_cali	1.2 ml	

	V (total) [m	V(addition, to	V(addition) [ml	c(NMNI) [mol/	c(calix) [mol/l]	c(calix)/c(NM	shift [Hz]	shift 2 [Hz	shift 3 [Hz	shift 4 [Hz
1	0.5000	0.0000	0.0000	0.00000	0.00156	0.00000	3526.26	3107.60	3125.60	3316.93
2	0.5006	0.0006	0.0006	0.00018	0.00156	0.11258	3524.70	3107.60	3124.81	3316.15
3	0.5012	0.0012	0.0006	0.00035	0.00156	0.22488	3525.48	3107.99	3124.42	3315.76
4	0.5020	0.0020	0.0008	0.00059	0.00156	0.37421	3527.44	3109.16	3124.42	3315.76
5	0.5028	0.0028	0.0008	0.00082	0.00156	0.52306	3527.83	3108.77	3123.64	3314.58
6	0.5042	0.0042	0.0014	0.00122	0.00156	0.78241	3529.78	3109.94	3123.25	3313.80
7	0.5056	0.0056	0.0014	0.00163	0.00156	1.04033	3530.56	3109.94	3122.07	3312.63
8	0.5136	0.0136	0.0080	0.00389	0.00156	2.48716	3538.00	3113.47	3118.94	3308.32
9	0.5236	0.0236	0.0100	0.00662	0.00156	4.23352	3545.43	3116.60	3114.64	3302.45
10	0.5536	0.0536	0.0300	0.01423	0.00156	9.09407	3565.39	3125.60	3106.03	3291.11
11	0.5936	0.0936	0.0400	0.02317	0.00156	14.81057	3588.47	3135.38	3097.03	3279.37
12	0.6436	0.1436	0.0500	0.03279	0.00156	20.95695	3611.95	3145.16	3089.21	3268.80
13	0.7136	0.2136	0.0700	0.04399	0.00156	28.11487	3637.38	3154.94	3081.38	3259.02
14	0.8036	0.3036	0.0900	0.05552	0.00156	35.48555	3660.47	3163.55	3074.34	3250.41
15	1.0036	0.5036	0.2000	0.07374	0.00156	47.13188	3690.92	3174.51	3065.73	3235.54
16	1.0936	0.5936	0.0900	0.07977	0.00156	50.98297	3700.00	3177.64	3062.60	3233.59

K	6.96 M^{-1}
Error	0.09425232 M^{-1}

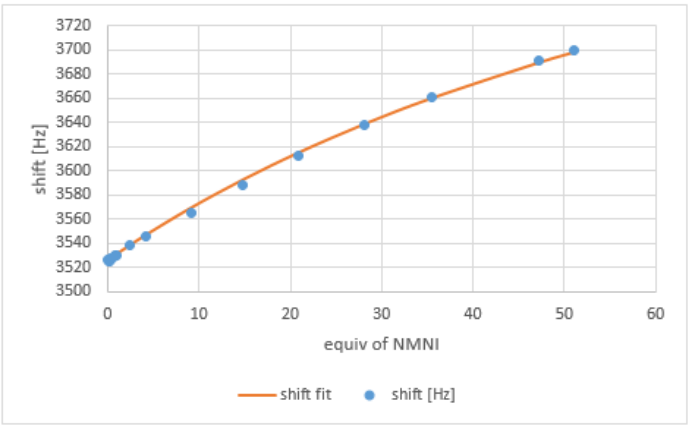


Figure 31. ^{1}H NMR titration of compound **7_2** with NMNI ($C_2D_2Cl_4$, 400 MHz).

Calixarene **7_1** was dissolved in specified amount of $CDCl_3$. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of (*S*)-1-Methyl-3-(1-methylpyrrolidin-2-yl)pyridinium iodide (NMNI) was added. The aliquots of NMNI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-65.671), ensuring constant host concentration during the experiment.

M(NMNI)	304.17547 g/mol	M(calix)	633.829 g/mol	
m(NMNI)	0.02682 g	m(calix)	0.00092 g	
c(NMNI)	0.14695 mol/l	c(calix)	0.00121 mol/l	
V(CDCl3_NMN	0.6 ml	V(CDCl3_calix)	1.2 ml	

	V (total) [m	V(addition, to	V(addition) [ml	c(NMNI) [mol/	c(calix) [mol/l]	c(calix)/c(NM	shift [Hz]	shift 2 [Hz	shift 3 [Hz	shift 4 [Hz	shift 5 [Hz
1	0.5000	0.0000	0.0000	0.00000	0.00121	0.00000	2998.04	2621.63	2587.98	2829.79	2750.36
2	0.5006	0.0006	0.0006	0.00018	0.00121	0.14615	2998.82	2621.63	2588.38	2829.79	2750.36
3	0.5012	0.0012	0.0006	0.00035	0.00121	0.29194	2998.82	2621.24	2588.38	2829.40	2750.36
4	0.5020	0.0020	0.0008	0.00059	0.00121	0.48579	2999.61	2621.24	2588.77	2829.01	2749.97
5	0.5028	0.0028	0.0008	0.00082	0.00121	0.67903	2999.61	2621.24	2589.16	2828.62	2749.97
6	0.5042	0.0042	0.0014	0.00122	0.00121	1.01571	3000.00	2620.85	2589.55	2828.23	2749.58
7	0.5056	0.0056	0.0014	0.00163	0.00121	1.35054	3000.78	2620.85	2589.94	2827.84	2749.58
8	0.5136	0.0136	0.0080	0.00389	0.00121	3.22879	3003.52	2619.29	2591.90	2825.10	2748.80
9	0.5236	0.0236	0.0100	0.00662	0.00121	5.49588	3007.43	2617.33	2594.64	2821.97	2748.02
10	0.5536	0.0536	0.0300	0.01423	0.00121	11.80576	3022.30	2613.42	2601.68	2815.31	2746.06
11	0.5936	0.0936	0.0400	0.02317	0.00121	19.22681	3039.52	2608.72	2608.72	2807.88	2744.49
12	0.6436	0.1436	0.0500	0.03279	0.00121	27.20593	3058.69	2604.03	2615.76	2800.84	2742.54
13	0.7136	0.2136	0.0700	0.04399	0.00121	36.49822	3079.03	2598.94	2623.59	2793.01	2740.58
14	0.8036	0.3036	0.0900	0.05552	0.00121	46.06670	3098.99	2593.85	2630.63	2785.97	2738.23
15	1.0036	0.5036	0.2000	0.07374	0.00121	61.18575	3131.07	2585.64	2641.20	2774.23	2735.10
16	1.0836	0.5836	0.0800	0.07915	0.00121	65.67068	3135.38	2583.68	2643.15	2771.88	2734.32

K	1.9 M^{-1}
Error	0.018126 M^{-1}

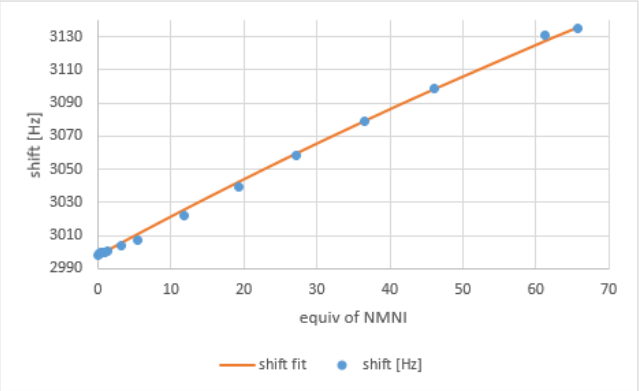


Figure 32. ^{1}H NMR titration of compound **7_1** with NMNI ($CDCl_3$, 400 MHz).

Calixarene **7_2** was dissolved in specified amount of $CDCl_3$. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of (*S*)-1-Methyl-3-(1-methylpyrrolidin-2-yl)pyridinium iodide (NMNI) was added. The aliquots of NMNI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-48.305), ensuring constant host concentration during the experiment.

M(NMNI)	304.17547 g/mol	M(calix)	633.829 g/mol	
m(NMNI)	0.02667 g	m(calix)	0.00123 g	
c(NMNI)	0.14613 mol/l	c(calix)	0.00162 mol/l	
V(CDCl3_NMN	0.6 ml	V(CDCl3_calix)	1.2 ml	

	V (total) [m	V(addition, to	V(addition) [ml	c(NMNI) [mol/	c(calix) [mol/l]	c(calix)/c(NM	shift [Hz]	shift 2 [Hz	shift 3 [Hz	shift 4 [Hz	shift 5 [Hz
1	0.5000	0.0000	0.0000	0.00000	0.00162	0.00000	3000.78	2621.63	2588.38	2829.79	2750.36
2	0.5006	0.0006	0.0006	0.00018	0.00162	0.10801	3001.56	2621.63	2588.77	2829.79	2750.36
3	0.5012	0.0012	0.0006	0.00035	0.00162	0.21577	3001.56	2621.24	2589.16	2829.40	2749.97
4	0.5020	0.0020	0.0008	0.00058	0.00162	0.35904	3001.95	2621.24	2589.55	2829.01	2749.97
5	0.5028	0.0028	0.0008	0.00081	0.00162	0.50186	3002.74	2620.85	2589.55	2828.62	2749.97
6	0.5042	0.0042	0.0014	0.00122	0.00162	0.75070	3003.52	2620.85	2590.33	2827.84	2749.97
7	0.5056	0.0056	0.0014	0.00162	0.00162	0.99816	3004.30	2620.46	2590.72	2827.84	2749.58
8	0.5136	0.0136	0.0080	0.00387	0.00162	2.38635	3007.04	2619.29	2592.68	2824.71	2748.80
9	0.5236	0.0236	0.0100	0.00659	0.00162	4.06193	3011.73	2617.33	2595.42	2821.58	2748.02
10	0.5536	0.0536	0.0300	0.01415	0.00162	8.72548	3026.60	2612.63	2602.46	2813.75	2746.45
11	0.5936	0.0936	0.0400	0.02304	0.00162	14.21027	3045.38	2608.33	2609.90	2805.92	2744.10
12	0.6436	0.1436	0.0500	0.03261	0.00162	20.10754	3064.95	2603.24	2617.33	2798.10	2742.15
13	0.7136	0.2136	0.0700	0.04374	0.00162	26.97534	3086.08	2597.77	2625.16	2789.88	2740.19
14	0.8036	0.3036	0.0900	0.05521	0.00162	34.04727	3106.03	2592.29	2632.20	2782.06	2738.23
15	1.0036	0.5036	0.2000	0.07333	0.00162	45.22156	3138.12	2584.07	2643.15	2769.54	2734.32
16	1.0776	0.5776	0.0740	0.07833	0.00162	48.30477	3142.03	2582.51	2644.33	2767.58	2733.54

K	2.56 M^{-1}
Error	0.02313728 M^{-1}

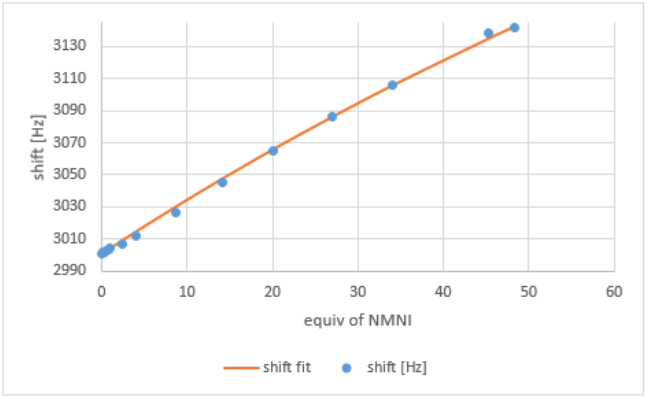


Figure 33. ^{1}H NMR titration of compound **7_2** with NMNI ($CDCl_3$, 400 MHz).

Calixarene **8** was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of *N*-methylquinolinium iodide (NMQI) was added. The aliquots of NMQI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-35.005), ensuring constant host concentration during the experiment. The complexation constant was determined by analyzing CIS of protons of the host molecule using nonlinear curve-fitting procedure (program BindFit).

M(NMQI)	271.10147 g/mol	M(calix)	634.813 g/mol
m(NMQI)	0.02387 g	m(calix)	0.00121 g
c(NMQI)	0.14675 mol/l	c(calix)	0.00158 mol/l
V(C2D2Cl4_NMQI)	0.6 ml	V(C2D2Cl4_cali	1.2 ml

	V (total) [m	V(addition, total) [n	V(addition) [ml]	c(NMQI) [mol/l]	c(calix) [mol/l]	c(calix)/c(NM	shift [Hz]	shift 2 [Hz]
1	0.5000	0.0000	0.0000	0.00000	0.00158	0.00000	3318.10	3120.12
2	0.5006	0.0006	0.0006	0.00018	0.00158	0.11105	3318.49	3120.12
3	0.5012	0.0012	0.0006	0.00035	0.00158	0.22184	3318.49	3120.51
4	0.5020	0.0020	0.0008	0.00058	0.00158	0.36914	3318.49	3120.51
5	0.5028	0.0028	0.0008	0.00082	0.00158	0.51598	3318.10	3120.12
6	0.5042	0.0042	0.0014	0.00122	0.00158	0.77182	3318.10	3120.12
7	0.5056	0.0056	0.0014	0.00163	0.00158	1.02624	3318.10	3120.12
8	0.5136	0.0136	0.0080	0.00389	0.00158	2.45348	3317.32	3119.73
9	0.5236	0.0236	0.0100	0.00661	0.00158	4.17620	3316.54	3118.94
10	0.5536	0.0536	0.0300	0.01421	0.00158	8.97094	3314.58	3118.16
11	0.5936	0.0936	0.0400	0.02314	0.00158	14.61003	3313.02	3116.99
12	0.6436	0.1436	0.0500	0.03274	0.00158	20.67319	3311.06	3115.81
13	0.7136	0.2136	0.0700	0.04393	0.00158	27.73419	3309.10	3114.64
14	0.8036	0.3036	0.0900	0.05544	0.00158	35.00506	3307.15	3113.47

K 4.13 M^{-1}

0.13309751 M^{-1}

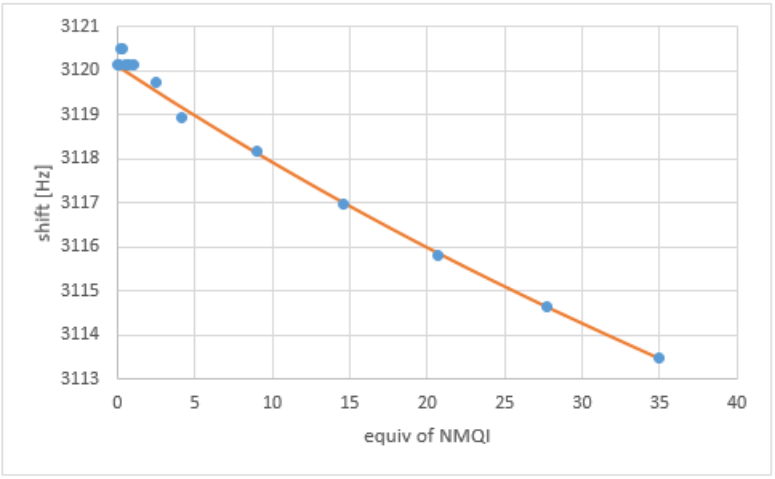


Figure 34. ^{1}H NMR titration of compound **8** with NMQI ($C_2D_2Cl_4$, 400 MHz).

Calixarene **8** was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of *N*-methylisoquinolinium iodide (NMII) was added. The aliquots of NMII were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-49.235), ensuring constant host concentration during the experiment. The complexation constant was determined by analyzing CIS of protons of the host molecule using nonlinear curve-fitting procedure (program BindFit).

M(NMII)	271.10147 g/mol	M(calix)	634.813 g/mol
m(NMII)	0.02734 g	m(calix)	0.00134 g
c(NMII)	0.16808 mol/l	c(calix)	0.00176 mol/l
V(C2D2Cl4_NMII)	0.6 ml	V(C2D2Cl4_cali	1.2 ml

	V (total) [m	V(addition, total) [n	V(addition) [ml]	c(NMII) [mol/l]	c(calix) [mol/l]	c(calix)/c(NM	shift [Hz]	shift 2 [Hz
1	0.5000	0.0000	0.0000	0.00000	0.00176	0.00000	3120.12	3310.28
2	0.5010	0.0010	0.0010	0.00034	0.00176	0.19015	3120.12	3310.28
3	0.5022	0.0022	0.0012	0.00074	0.00176	0.41734	3120.51	3310.28
4	0.5038	0.0038	0.0016	0.00127	0.00176	0.71857	3119.73	3309.49
5	0.5058	0.0058	0.0020	0.00193	0.00176	1.09243	3119.73	3309.49
6	0.5108	0.0108	0.0050	0.00355	0.00176	2.01426	3118.94	3308.32
7	0.5188	0.0188	0.0080	0.00609	0.00176	3.45224	3118.16	3307.15
8	0.5548	0.0548	0.0360	0.01660	0.00176	9.40995	3114.64	3302.45
9	0.5848	0.0848	0.0300	0.02437	0.00176	13.81439	3111.12	3299.71
10	0.6248	0.1248	0.0400	0.03357	0.00176	19.02903	3107.21	3293.45
11	0.6748	0.1748	0.0500	0.04354	0.00176	24.67798	3104.08	3289.15
12	0.7548	0.2548	0.0800	0.05674	0.00176	32.15961	3100.16	3284.45
13	0.8548	0.3548	0.1000	0.06976	0.00176	39.54233	3096.25	3280.15
14	0.9548	0.4548	0.1000	0.08006	0.00176	45.37861	3093.90	3277.02
15	1.0348	0.5348	0.0800	0.08687	0.00176	49.23548	3091.95	3275.06

K	3.33 M^{-1}
Error	0.05006655 M^{-1}

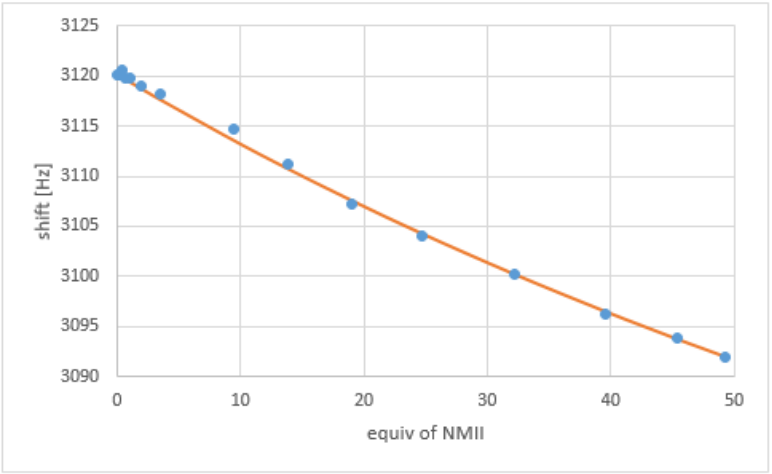


Figure 35. ^{1}H NMR titration of compound **8** with NMII ($C_2D_2Cl_4$, 400 MHz).

Calixarene **8_1** was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of (*S*)-1-Methyl-3-(1-methylpyrrolidin-2-yl)pyridinium iodide (NMNI) was added. The aliquots of NMNI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-51.635), ensuring constant host concentration during the experiment. The complexation constant was determined by analyzing CIS of protons of the host molecule using nonlinear curve-fitting procedure (program BindFit).

M(NMNI)	304.17547 g/mol	M(calix)	634.813 g/mol
m(NMNI)	0.02707 g	m(calix)	0.00119 g
c(NMNI)	0.14832 mol/l	c(calix)	0.00156 mol/l
V(C2D2Cl4_NM	0.6 ml	V(C2D2Cl4_cali	1.2 ml

	V (total) [m	V(addition, to	V(addition) [ml	c(NMNI) [mol/l]	c(calix) [mol/l]	c(calix)/c(NM	shift [Hz]	shift 2 [Hz
1	0.5000	0.0000	0.0000	0.00000	0.00156	0.00000	3309.89	3120.12
2	0.5006	0.0006	0.0006	0.00018	0.00156	0.11402	3310.28	3120.12
3	0.5012	0.0012	0.0006	0.00036	0.00156	0.22776	3309.89	3120.12
4	0.5020	0.0020	0.0008	0.00059	0.00156	0.37899	3309.89	3120.12
5	0.5028	0.0028	0.0008	0.00083	0.00156	0.52975	3309.89	3120.12
6	0.5042	0.0042	0.0014	0.00124	0.00156	0.79241	3309.49	3119.73
7	0.5056	0.0056	0.0014	0.00164	0.00156	1.05362	3309.49	3119.73
8	0.5136	0.0136	0.0080	0.00393	0.00156	2.51894	3308.32	3119.34
9	0.5236	0.0236	0.0100	0.00669	0.00156	4.28763	3306.74	3117.77
10	0.5536	0.0536	0.0300	0.01436	0.00156	9.21029	3302.84	3114.64
11	0.5936	0.0936	0.0400	0.02339	0.00156	14.99984	3298.54	3111.51
12	0.6436	0.1436	0.0500	0.03309	0.00156	21.22477	3295.02	3108.77
13	0.7136	0.2136	0.0700	0.04440	0.00156	28.47417	3291.11	3105.25
14	0.8036	0.3036	0.0900	0.05604	0.00156	35.93904	3287.19	3102.12
15	1.0036	0.5036	0.2000	0.07443	0.00156	47.73421	3282.11	3097.42
16	1.0936	0.5936	0.0900	0.08051	0.00156	51.63451	3280.54	3095.86

K	4.86 M^{-1}
Error	0.06144012 M^{-1}

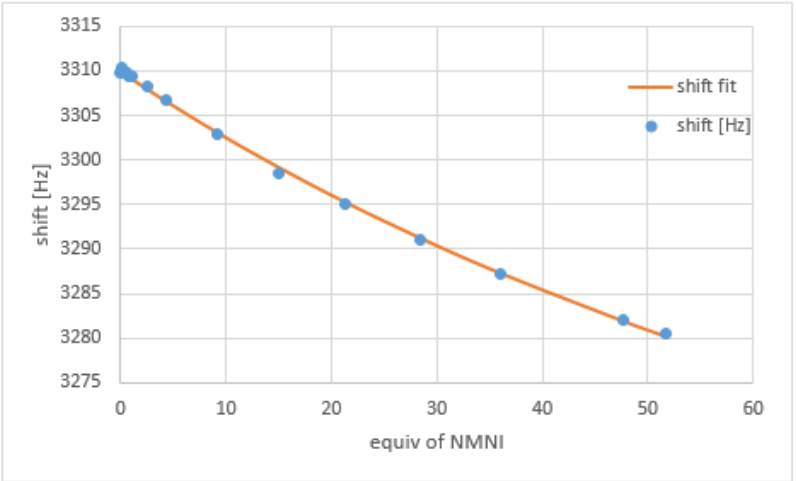


Figure 36. ^{1}H NMR titration of compound **8_1** with NMNI ($C_2D_2Cl_4$, 400 MHz).

Calixarene **8_2** was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of (*S*)-1-Methyl-3-(1-methylpyrrolidin-2-yl)pyridinium iodide (NMNI) was added. The aliquots of NMNI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-51.197), ensuring constant host concentration during the experiment. The complexation constant was determined by analyzing CIS of protons of the host molecule using nonlinear curve-fitting procedure (program BindFit).

M(NMNI)	304.17547	g/mol	M(calix)	634.813 g/mol
m(NMNI)	0.02658	g	m(calix)	0.00118 g
c(NMNI)	0.14564	mol/l	c(calix)	0.00154 mol/l
V(C2D2Cl4_NMNI)	0.6	ml	V(C2D2Cl4_cali	1.2 ml

	V (total) [m	V(addition, total) [n	V(addition) [ml]	c(NMNI) [mol/l]	c(calix) [mol/l]	c(calix)/c(NM	shift [Hz]	shift 2 [Hz
1	0.5000	0.0000	0.0000	0.00000	0.00154	0.00000	3120.12	3310.28
2	0.5006	0.0006	0.0006	0.00017	0.00154	0.11305	3120.12	3310.28
3	0.5012	0.0012	0.0006	0.00035	0.00154	0.22583	3120.90	3310.67
4	0.5020	0.0020	0.0008	0.00058	0.00154	0.37578	3120.51	3310.67
5	0.5028	0.0028	0.0008	0.00081	0.00154	0.52525	3120.12	3310.28
6	0.5042	0.0042	0.0014	0.00121	0.00154	0.78569	3119.73	3309.89
7	0.5056	0.0056	0.0014	0.00161	0.00154	1.04469	3119.73	3309.89
8	0.5136	0.0136	0.0080	0.00386	0.00154	2.49759	3118.94	3308.32
9	0.5236	0.0236	0.0100	0.00656	0.00154	4.25128	3117.77	3307.15
10	0.5536	0.0536	0.0300	0.01410	0.00154	9.13221	3115.03	3304.02
11	0.5936	0.0936	0.0400	0.02296	0.00154	14.87267	3112.29	3300.50
12	0.6436	0.1436	0.0500	0.03250	0.00154	21.04483	3109.55	3297.37
13	0.7136	0.2136	0.0700	0.04359	0.00154	28.23276	3106.03	3293.84
14	0.8036	0.3036	0.0900	0.05502	0.00154	35.63435	3102.90	3290.32
15	1.0036	0.5036	0.2000	0.07308	0.00154	47.32951	3098.21	3285.63
16	1.0936	0.5936	0.0900	0.07905	0.00154	51.19675	3097.03	3284.06

K	4.28 M^{-1}
Error	0.06182888 M^{-1}

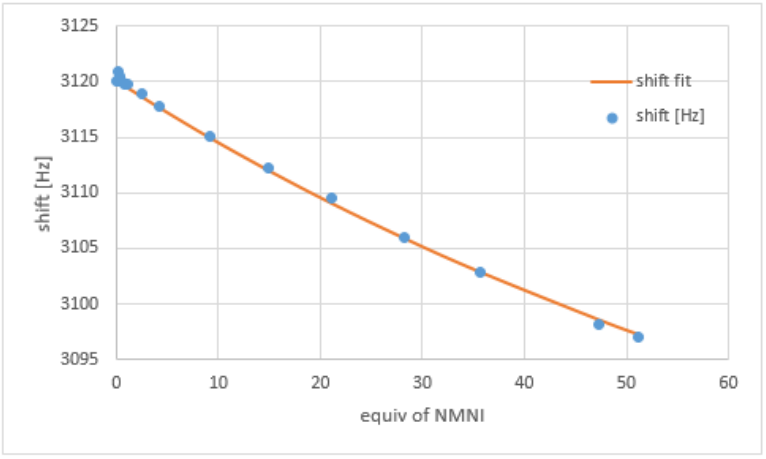


Figure 37. ^{1}H NMR titration of compound **8_2** with NMNI ($C_2D_2Cl_4$, 400 MHz).

Calixarene **5** was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of *N*-methylisoquinolinium iodide (NMII) was added. The aliquots of NMII were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-50.628), ensuring constant host concentration during the experiment. The complexation constant was determined by analyzing CIS of protons of the host molecule using nonlinear curve-fitting procedure (program BindFit).

M(NMII)	271.10147 g/mol	M(calix)	618.814 g/mol
m(NMII)	0.02227 g	m(calix)	0.00109 g
c(NMII)	0.13691 mol/l	c(calix)	0.00147 mol/l
V(C2D2Cl4_NMII)	0.6 ml	V(C2D2Cl4_cali	1.2 ml

	V (total) [m	V(addition, total) [n	V(addition) [ml]	c(NMII) [mol/l]	c(calix) [mol/l]	c(calix)/c(NM	shift [Hz]	shift 2 [Hz
1	0.5000	0.0000	0.0000	0.00000	0.00147	0.00000	3319.28	3177.24
2	0.5006	0.0006	0.0006	0.00016	0.00147	0.11179	3319.28	3177.24
3	0.5012	0.0012	0.0006	0.00033	0.00147	0.22332	3319.28	3177.24
4	0.5020	0.0020	0.0008	0.00055	0.00147	0.37160	3319.67	3177.64
5	0.5028	0.0028	0.0008	0.00076	0.00147	0.51942	3319.67	3177.64
6	0.5042	0.0042	0.0014	0.00114	0.00147	0.77696	3318.89	3177.24
7	0.5056	0.0056	0.0014	0.00152	0.00147	1.03308	3318.89	3177.24
8	0.5136	0.0136	0.0080	0.00363	0.00147	2.46982	3318.10	3176.85
9	0.5236	0.0236	0.0100	0.00617	0.00147	4.20402	3316.54	3176.46
10	0.5536	0.0536	0.0300	0.01326	0.00147	9.03068	3313.80	3175.29
11	0.5936	0.0936	0.0400	0.02159	0.00147	14.70733	3310.67	3174.11
12	0.6436	0.1436	0.0500	0.03055	0.00147	20.81088	3307.54	3172.94
13	0.7136	0.2136	0.0700	0.04098	0.00147	27.91890	3303.63	3171.38
14	0.8036	0.3036	0.0900	0.05172	0.00147	35.23821	3300.50	3169.81
15	1.0036	0.5036	0.2000	0.06870	0.00147	46.80336	3296.19	3167.46
16	1.0936	0.5936	0.0900	0.07431	0.00147	50.62760	3294.63	3167.07

K	3.87 M^{-1}
Error	0.06437745 M^{-1}

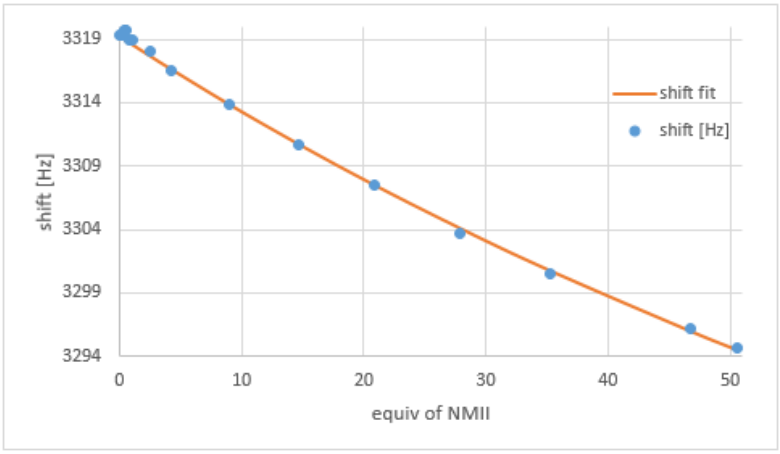
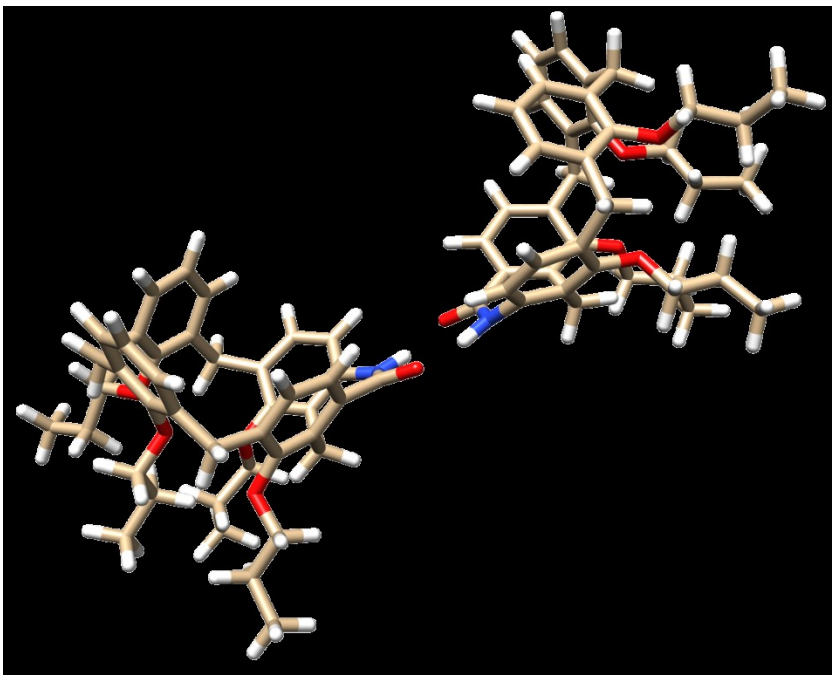


Figure 38. ^{1}H NMR titration of compound **5** with NMII ($C_2D_2Cl_4$, 400 MHz).

7. Theoretical calculations

Internal coordinates

Homodimer of **7** (DFT, B3LYP/6-31G)



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C	3.54253	2.457181	-1.12211
C	4.105109	2.960747	0.063115
C	3.311065	3.077436	1.222912
C	3.944555	3.441953	2.557133
C	4.956985	2.3633	2.903695
C	6.13687	2.265104	2.144816
C	7.102849	1.296859	2.452982
C	6.802959	0.306477	3.386955
C	5.568099	0.27752	4.0561
C	5.087478	-0.99577	4.749792
C	4.460095	-1.91988	3.693868
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C	3.287263	-3.2537	1.508104
C	2.462705	-2.77974	2.538664
C	0.943116	-2.86931	2.398467
C	0.439327	-2.12987	1.162792
C	0.130303	-2.81571	-0.02242

C	-0.24393	-2.12071	-1.17721
C	-0.29255	-0.72312	-1.16738
C	0.337885	-0.7247	1.159608
C	3.073564	-2.17373	3.656012
C	4.711262	1.38263	3.879858
C	1.946158	2.738651	1.136997
C	5.529598	3.397351	0.009166
N	6.378274	3.136632	1.048498
O	5.968511	3.977874	-1.03396
O	0.629527	-0.02831	2.340415
C	-0.51674	0.200194	3.241215
C	0.023114	0.798456	4.528459
C	-1.098	1.070449	5.54468
O	2.274582	-1.81033	4.767558
C	2.177033	-2.85746	5.799943
C	1.307857	-2.32645	6.931805
C	1.140368	-3.35391	8.063689
O	3.565288	1.511793	4.692276
C	3.855806	2.082046	6.021946
C	2.553689	2.165694	6.804535
C	2.7672	2.738681	8.215523
O	1.095571	3.047698	2.222317
C	0.60705	4.44032	2.218059
C	-0.2632	4.638437	3.451334
C	-0.83351	6.064249	3.533003
H	-0.53253	1.906874	0.873938
H	-0.53711	1.87102	-0.8927
H	1.838553	1.50773	-2.02287
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H	3.174051	3.482835	3.32489
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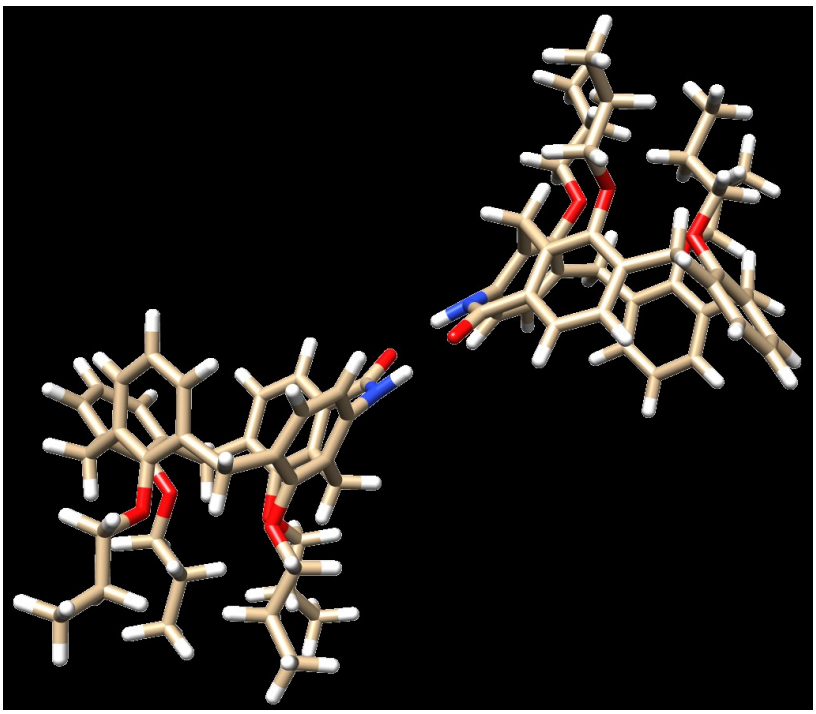
Heterodimer of **7** (DFT, B3LYP/6-31G)



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H	16.9718	3.251102	4.690852
H	16.92736	2.988004	2.94105
H	15.63946	2.336282	3.969039

The structure of (*cR*)-**7** was optimized using B3LYP DFT functional with 6-311++G(d,p) basis set. The ECD spectra were calculated on the B3LYP/6-311++G(dp) level.

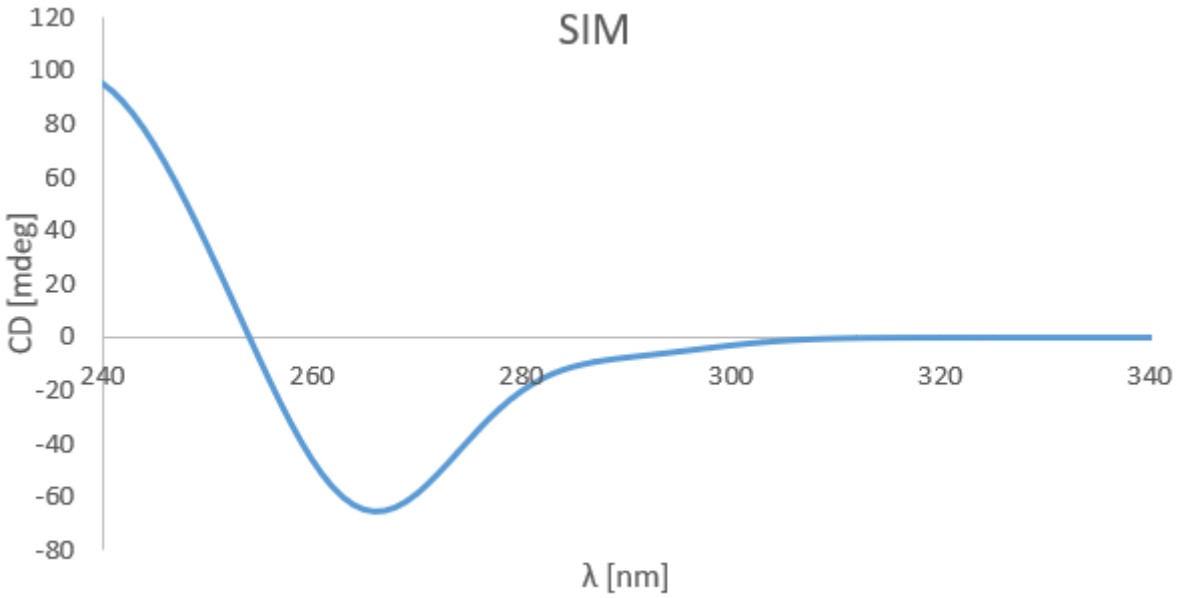

Figure 39. Simulated ECD spectra of (*cR*)-**7** (DFT, B3LYP/6-311++G(dp)).

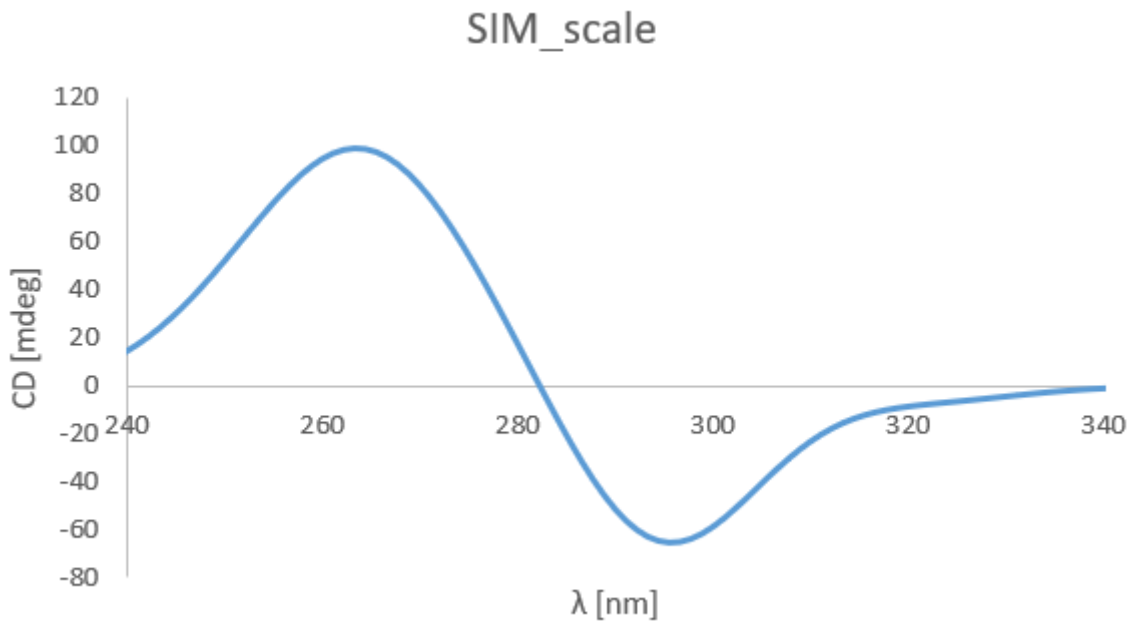

Figure 40. Simulated and scaled ECD spectra of (*cR*)-**7** (DFT, B3LYP/6-311++G(dp)).

The structure of (*cR*)-**8** was optimized using B3LYP DFT functional with 6-311++G(d,p) basis set. The ECD spectra were calculated on the B3LYP/6-311++G(dp) level.

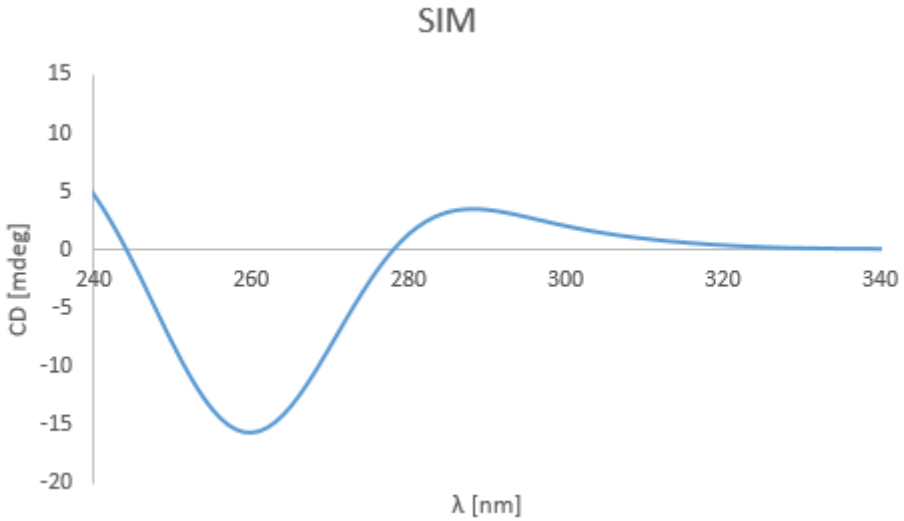

Figure 41. Simulated ECD spectra of (*cR*)-**8** (DFT, B3LYP/6-311++G(dp)).

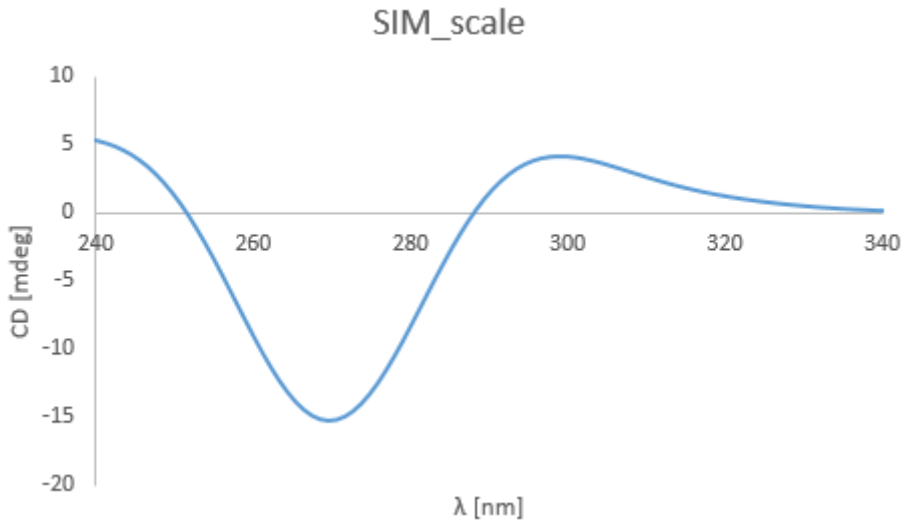

Figure 42. Simulated and scaled ECD spectra of (*cR*)-**8** (B3LYP/6-311++G(dp)).