Supporting Information

For

Synthesis and complexing properties of cyclic benzylopeptoids – a new family of extended macrocyclic peptoids

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List of abbreviations

ACN: acetonitrile

DCM:dichloromethane

DCC*: N,N'*-dicyclohexylcarbodiimide

DIPEA: *N,N*-diisopropylethylamine

DMAP: 4-dimethylaminopyridine

DMF: dimethylformamide

ESI: electrospray ionisation

Fmoc: 9-fluorenylmethoxycarbonyl

HATU: *O*-(7-azabenzotriazol-1-yl)-*N*,*N*,*N*',*N*'-tetramethyluronium hexafluorophosphate

HFIP: hexafluoroisopropanol

RP HPLC: reversed-phase high-performance liquid chromatography

TCDE: tetrachlorodideuteroethane

TFA: trifluoroacetic acid

TFPB: tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

TCE: 1,1,2,2-tetrachloroethane

TLC: thin layer chromatography

1.0 Synthesis

1.1 General procedures

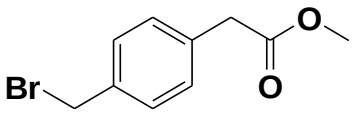
Starting materials and reagents purchased from commercial suppliers were generally used without purification unless otherwise mentioned. Reaction temperatures were measured externally; reactions were monitored by TLC on Merck silica gel plates (0.25 mm) and visualized by UV light or by spraying with ninhydrin solution. Flash chromatography was performed on Merck silica gel 60 (particle size: 0.040-0.063 mm) and the solvents employed were of analytical grade. HPLC analysis were performed on a JASCO LC-NET II/ADC and a Thermo Scientific instruments. The first one comprises a JASCO Model PU-2089 Plus Pump and a JASCO MD-2010 Plus UV-vis multiple wavelength detector set at 220 nm, the second one a Finnigan Surveyor LC Pump Plus and a Finnigan Surveyor UV/Vis Plus Detector set at 220 nm. The column used was a C_{18} reversed-phase analytical column (Waters, Bondapak, 10 μ m, 125 Å, 3.9 mm × 300 mm) run with linear gradients of ACN (0.1% TFA) into H_2O (0.1% TFA) over 30 min, at a flow rate of 1.0 mL/min for the analytical runs. High resolution mass spectra were acquired using a Bruker solariX XR Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 T refrigerated actively-shielded superconducting magnet (Bruker Biospin, Wissembourg, France). The samples were ionized in positive ion mode using the ESI ion source. The mass range was set to *m/z* 200 – 1500. The mass spectra were calibrated externally using a NaTFA solution ionization positive ion mode. A linear calibration was applied. Low resolution ESI-MS analysis in positive ion mode was performed using a Finnigan LCQ Deca ion trap mass spectrometer (ThermoFinnigan, San Josè, CA, USA) and the mass spectra were acquired and processed using the Xcalibur software provided by Thermo Finnigan. Samples were dissolved in 1:1 CH_3OH/H_2O, 0.1 % formic acid, and infused in the ESI source by using a syringe pump; the flow rate was 5 μl/min. The capillary voltage was set at 4.0 V, the spray voltage at 5 kV, and the tube lens offset at -40 V. The capillary temperature was 220 °C. Data were acquired in MS^1 and MS^n scanning modes. Zoom scan was used in these experiments. High-resolution ESI-MS spectra were recorded on a Q-Star Applied Biosystem mass spectrometer.

NMR spectra were recorded on a Bruker DRX 600 (^1H at 600.13 MHz, ^{13}C at 150.90 MHz), Bruker DRX 400 (^1H at 400.13 MHz, ^{13}C at 100.03 MHz), Bruker DRX 300 (^1H at 300.1 MHz, ^{13}C at 75.5 MHz) and Bruker DRX 250 (^1H at 250.0 MHz, ^{13}C at 62.5

MHz). Chemical shifts (δ) are reported in ppm relative to the residual solvent peak ($CHCl_3$, δ = 7.26; $^{13}CDCl_3$, δ = 77.0; CD_2HCN, δ = 1.94; $^{13}CD_3CN$, δ = 1.32; C_2DHCl_4, δ = 6.0; $^{13}CCD_2Cl_4$, δ = 73.8) and the multiplicity of each signal is designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; bs, broad singlet. Coupling constants (J) are quoted in Hertz. DEPT, COSY, HMBC, HSQC and ROESY experiments completed the full assignment of each signal. Purity of all products described in the present paper has been determined by HPLC analysis at 220 nm.

1.2 Synthetic procedures

Compound 10



10

To a solution of 4-(bromomethyl)phenylacetic acid (1.80 g, 7.86 mmol) in MeOH (20 mL) was added trimethylsilyl chloride (1.58 mmol, 0.200 mL), and the mixture was stirred for 5 h. The solvent was removed in vacuo. In order to remove traces of HCl, the residue was dissolved in MeOH (20 mL) and concentrated in vacuo and again dissolved in MeOH (20 mL) and again concentrated to give **10** as an oil (1.85 g, 97%). The crude material was used in the next step without further purification.

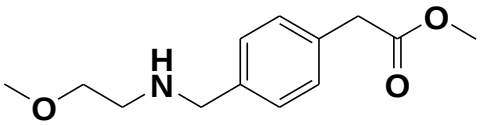
TLC (SiO_2): R_f = 0.92 (DCM:MeOH 95:5).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (2H, d, *J* 8.0 Hz, -Ar), 7.23 (2H, d, *J* 8.0 Hz, -Ar), 4.45 (2H, s, C*H*$_2$-Br), 3.66 (3H, s, COOC*H*$_3$), 3.60 (2H, s, C*H*$_2$-$COOCH_3$).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6 (*C*$OOCH_3$), 136.5 (-*C*CH_2Br), 134.1 (-*C*CH_2CO), 129.6, (-*C*H x 2) 129.2 (-*C*H x 2), 52.0 (-COO*C*H_3), 40.7 (-*C*H_2CO), 33.1 (-*C*H_2Br).

ESI-MS: 243.2 m/z (100, $[M + H]^+$), 245.0 m/z (98, $[M + H]^+$).

Compound 14



14

To a solution of methoxyethyl amine (3.30 mL, 38.3 mmol) in dry DMF (4 mL) was slowly added (20 minutes) a solution of 4-(bromomethyl)phenyl acetate **10** (1.87 g, 7.69 mmol) in dry DMF (40 mL). After the addition the mixture was stirred for 1 h. The solvent was removed in vacuo and left overnight under high vacuum (to remove the excess of the low volatile amine) to give a crude material (2.85 g, pale yellow oil). The residue was purified by flash chromatography (silica gel, DCM/CH_3OH, from: 100/0 to 95/05, 1% triethylamine in both eluents) to give the free amine **14** as an oil (1.28 g, 70%).

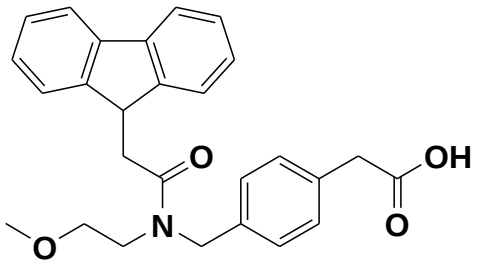
TLC (SiO_2): R_f = 0.30 (DCM:MeOH 95:5, 1% triethylamine).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (2H, d, *J* 8.0 Hz, -Ar), 7.26 (2H, d, *J* 8.0 Hz, -Ar), 3.80 (2H, s, Ar-C$\underline{H}_2$-NH), 3.69 (3H, s, COOC$\underline{H}_3$), 3.62 (2H, s, C$\underline{H}_2$-COOH), 3.52 (2H, t, *J* 6.0 Hz, C$\underline{H}_2$-OCH_3), 3.36 (3H, s, CH_2O-C$\underline{H}_3$), 2.80 (2H, t, *J* 6.0 Hz, C$\underline{H}_2$-CH_2-OCH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0 ($\underline{C}OOCH_3$), 139.0 (-$\underline{C}CH_2NH$), 132.4 (-$\underline{C}CH_2CO$), 129.1 (-$\underline{C}$H x 2), 128.3 (-$\underline{C}$H x 2), 71.8 (-$\underline{C}H_2OCH_3$), 58.7 (-$CH_2O\underline{C}H_3$), 53.4 (Ar-$\underline{C}H_2NH$), 51.9 (-COO$\underline{C}H_3$), 48.6 (Ar-$CH_2NH\underline{C}H_2$), 40.7 (-C$\underline{C}H_2CO$).

ESI-MS: 238.5 m/z $[M + H]^+$.

Compound 16



16

To a stirred solution of **14** (2.21 g, 9.30 mmol) in 1,4-dioxane (28 mL), $LiOH•H_2O$ (0.468 g, 11.2 mmol) in H_2O (28 mL) was added. After 3 hours, $NaHCO_3$ (0.937 g, 11.2 mmol), DMAP (57 mg, 0.46 mmol), and Fmoc-Cl (3.12 g, 12.1 mmol) were added. The reaction mixture was stirred overnight. Subsequently, $KHSO_4$ was added (until pH=3) and the mixture was concentrated in vacuo to remove the excess of 1,4-dioxane. After checking again the pH of the remaining water (and, eventually, adjusting it to pH=3), ethyl acetate (100 mL) was added to the mixture. The aqueous layer was extracted three times with ethyl acetate and the combined organic phases were dried over $MgSO_4$, filtered and

the solvent evaporated in vacuo to give a crude material (4.34 g). The residue was purified by flash chromatography (silica gel, hexanes/ethyl acetate, from: 80/20 to 40/60, 1% AcOH) to give **16** as a viscous oil (1.90 g, 46%).

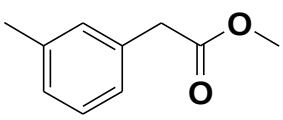
TLC (SiO_2): R_f = 0.44 (hexanes:ethyl acetate 1:1, 1% AcOH)

^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ 9.60 (1H, bs, COOH), 7.78 (1H, d, *J* 7.4 Hz, –Ar[Fmoc]), 7.73 (1H, d, *J* 7.4 Hz, –Ar[Fmoc]), 7.62 (1H, d, *J* 7.4 Hz, –Ar[Fmoc]), 7.50-7.20 (7H, m, –Ar[Fmoc] and –Ar, overlapped), 7.16 (1H, d, *J* 7.4 Hz, –Ar[Fmoc]), 7.03 (1H, d, *J* 7.4 Hz, –Ar[Fmoc]), 4.63 (1H, d, *J* 6.6 Hz, -C*H*$_2$-[Fmoc] rot. a), 4.54 (2H, m, -C*H*$_2$-[Fmoc] rot. b, -CC*H*$_2$N rot. a, overlapped), 4.47 (1H, s, -CC*H*$_2$N rot. b), 4.26 (0.5H, t, *J* 6.6 Hz,-C*H*[Fmoc] rot. a), 4.21 (0.5H, t, *J* 6.6 Hz,-C*H*[Fmoc] rot. b), 3.65 (1H, s, C*H*$_2$-COOH rot. a), 3.63 (1H, s, C*H*$_2$-COOH rot. b), 3.52 (1 H, t, *J* 5.3 Hz, -C*H*$_2$OCH$_3$ rot. a), 3.45 (1H, t, *J* 5.3 Hz, -NC*H*$_2$-CH$_2$OCH$_3$ $_2$ rot. a), 3.32 (1.5 H, s, -OC*H*$_3$ rot. a), 3.20 (2H -NCH$_2$-C*H*$_2$OCH$_3$ rot. b and -NC*H*$_2$-CH$_2$OCH$_3$ rot. b), 3.17 (1.5 H, s, -OC*H*$_3$ rot. b).

^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers) δ 176.7 (-*C*OOH), 156.5 (-*C*O[Fmoc] rot. a), 156.3 (-*C*O[Fmoc] rot. b), 143.9 (-*C*[Fmoc] rot. a), 143.8 (-*C*[Fmoc] rot. b), 141.3 (-*C*[Fmoc] rot. a), 141.2 (-*C*[Fmoc] rot. b), 136.6, (-*C*[Ar]), 132.4 (-*C*[Ar] rot. a), 132.3 (-*C*[Ar] rot. b), 130.0 (-*C*H[Ar] rot. a), 129.9 (-*C*H[Ar] rot. b), 129.5, (-*C*H[Ar]), 129.3, (-*C*H[Ar]), 127.9 (-*C*H[Fmoc] rot. a), 127.5 (-*C*H[Fmoc] rot. a), 127.3 (-*C*H[Fmoc] rot. b), 127.0 (-*C*H[Fmoc] rot. a), 126.9 (-*C*H[Fmoc] rot. b), 124.7 (-*C*H[Fmoc]), 124.6 (-*C*H[Fmoc] rot. b), 119.8 (-*C*H[Fmoc] rot. b), 70.8 (-*C*H$_2$[Fmoc] rot. a), 70.6 (-*C*H$_2$[Fmoc] rot. b), 67.3 (-*C*H$_2$OCH$_3$ rot. a), 66.9 (-*C*H$_2$OCH$_3$ rot. b), 58.6 (-CH$_2$O*C*H$_3$ rot. a), 58.5 (-CH$_2$O*C*H$_3$ rot. b), 51.0 (-Ar-*C*H$_2$N- rot. a), 50.8 (-Ar-*C*H$_2$N- rot. b), 47.3 (-*C*H[Fmoc] rot. a), 47.1 (-*C*H[Fmoc] rot. b), 46.5 (-N*C*H$_2$CH$_2$OCH$_3$ rot. a), 45.7 (-N*C*H$_2$CH$_2$OCH$_3$ rot. b), 40.6 (-*C*H$_2$COOH).

ESI-MS: 446.3 m/z (100, $[M + H]^+$), 468.4 m/z (71, $[M + Na]^+$).

Compound 12



12

To a solution of 3-(methyl)phenyl acetic acid (1.00 g, 6.67 mmol) in MeOH (16 mL) was added trimethylsilyl chloride (0.67 mmol, 0.084 mL), and the mixture was stirred for 18 h. The solvent was removed in vacuo and the residue was dissolved in MeOH (20 mL) and concentrated in vacuo and again dissolved in MeOH (20 mL) and again concentrated to give **12** as an oil (1.07 g, 98%). The crude material was used in the next step without further purification.

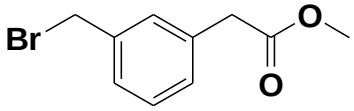
TLC (SiO_2): R_f = 0.70 (hexanes:ethyl acetate 95:5).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (1H, t, *J* 8.0 Hz, -Ar), 7.11 (1H, s, -Ar), 7.10 (2H, d, *J* 8.0 Hz, -Ar), 3.71 (3H, s, COOC$\underline{H}_3$), 3.61 (2H, s, C$\underline{H}_2$-COOCH$_3$), 2.36 (3H, s, Ar-C$\underline{H}_3$).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8 ($\underline{C}$OOCH$_3$), 137.9 (-$\underline{C}$CH$_3$), 133.7 (-$\underline{C}$CH$_2$CO), 129.8, (-$\underline{C}$H) 128.2, (-$\underline{C}$H), 127.6, (-$\underline{C}$H) 126.0 (-$\underline{C}$H), 51.7 (-COO$\underline{C}$H$_3$), 40.3 (-$\underline{C}$H$_2$CO), 21.1 (-$\underline{C}$H$_3$).

ESI-MS: 165.1 m/z $[M + H]^+$.

Compound 13



13

Compound **12** (3.00 g, 20.0 mmol), N-bromosuccinimide (4.25 g, 24.0 mmol) and benzoylperoxide (0.05 g, 1.0 mmol) were dissolved in 240 ml of ethyl acetate. The mixture was refluxed for 15 h and concentrated. The crude **13**, containing the insoluble succinimide, was purified by flash chromatography (silica gel, hexanes/ethyl acetate, from: 95/5 to 80/20) to give **13** as a yellow oil (2.67 g, 55%).

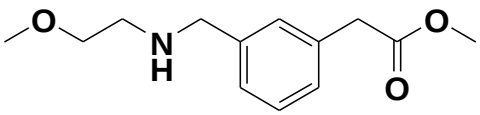
TLC (SiO_2): R_f = 0.40 (hexanes:ethyl acetate 95:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (3H, m, -Ar), 7.25 (1H, m, -Ar), 4.50 (2H, s, C$\underline{H}_2$-Br), 3.72 (3H, s, COOC$\underline{H}_3$), 3.65 (2H, s, C$\underline{H}_2$-COOCH$_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6 ($\underline{C}$OOCH$_3$), 138.0 (-$\underline{C}$CH$_2$Br), 134.4 (-$\underline{C}$CH$_2$CO), 129.8, (-$\underline{C}$H), 129.3 (-$\underline{C}$H), 128.9, (-$\underline{C}$H) 127.8 (-$\underline{C}$H), 52.0 (-COO$\underline{C}$H$_3$), 40.8 (-$\underline{C}$H$_2$CO), 33.2 (-$\underline{C}$H$_2$Br).

ESI-MS: 243.3 m/z (100, $[M + H]^+$), 245.1 m/z (100, $[M + H]^+$).

Compound 15



15

To a solution of methoxyethyl amine (5.30 mL, 61.7 mmol) in dry DMF (6 mL) was slowly added (20 minutes) a solution of 3-(bromomethyl)phenyl acetate **13** (3.00 g, 12.3 mmol) in dry DMF (65 mL). After the addition the mixture was stirred for 1 h. The solvent was removed in vacuo and the crude material left overnight under high vacuum to give a 4.5 g of pale yellow oil. The residue was purified by flash chromatography (silica gel, DCM/CH_3OH, from: 100/0 to 95/05, 1% triethylamine in both eluents) to give the free amine **15** as an oil (2.20 g, 76%).

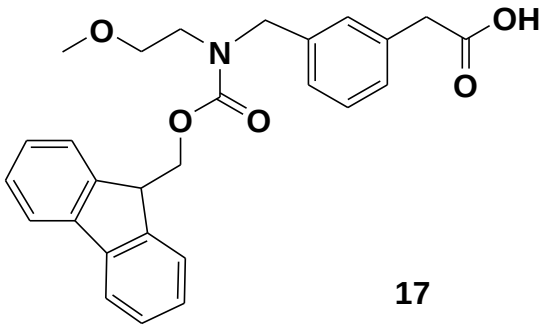
TLC (SiO_2): R_f = 0.35 (DCM:MeOH 95:5,1% triethylamine).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (3H, m, -Ar), 7.17 (1H, m, -Ar), 3.81 (2H, s, Ar-C*H*$_2$-NH), 3.67 (3H, s, COOC*H*$_3$), 3.61 (2H, s, C*H*$_2$-COOH), 3.53 (2H, t, *J* 6.0 Hz, C*H*$_2$-OCH_3), 3.34 (3H, s, CH_2O-C*H*$_3$), 3.29 (1H, bs, N*H*), 2.81 (2H, t, *J* 6.0 Hz, C*H*$_2$-CH_2-OCH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9 (*C*$OOCH_3$), 139.2 (-*C*CH_2NH), 134.0 (-*C*CH_2CO), 129.2 (-*C*H), 128.6 (-*C*H), 128.0 (-*C*H), 127.1 (-*C*H), 71.2 (-*C*H_2OCH_3), 58.7 (-CH_2O*C*H_3), 53.2 (Ar-*C*H_2NH), 51.9 (-COO*C*H_3), 48.2 (Ar-CH_2NH*C*H_2), 40.9 (-C*C*H_2CO).

ESI-MS: 238.2 m/z $[M + H]^+$.

Compound 17



17

To a stirred solution of **15** (3.10 g, 13.1 mmol) in 1,4-dioxane (40 mL), $LiOH•H_2O$ (0.659 g, 15.7 mmol) in H_2O (40 mL) was added. After 3 hours, $NaHCO_3$ (1.32 g, 15.7 mmol), DMAP (80 mg, 0. 65 mmol), and Fmoc-Cl (4.40 g, 17.0 mmol) were added. The reaction mixture was stirred overnight. Subsequently, $KHSO_4$ was added (until pH=3) and the mixture was concentrated in vacuo to remove the excess of 1,4-dioxane. After checking again the pH of the remaining water (and, eventually, adjusting it to pH=3), ethyl acetate (100 mL) was added to the mixture. The aqueous layer was extracted three times with ethyl acetate and the combined organic phases were dried over $MgSO_4$, filtered and the solvent evaporated in vacuo to give a crude material (5.50 g). The residue was purified by flash chromatography (silica gel, hexanes/ethyl acetate, from: 80/20 to 40/60, 1% AcOH) to give **17** as an oil (2.56 g, 44%).

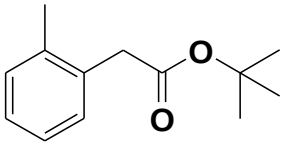
TLC (SiO_2): R_f = 0.48 (hexanes:ethyl acetate 1:1, 1% AcOH).

^{1}H NMR (600 MHz, $CDCl_3$, mixture of rotamers) δ 7.78 (1H, d, *J* 7.4 Hz, –Ar[Fmoc]), 7.73 (1H, d, *J* 7.4 Hz, –Ar[Fmoc]), 7.62 (1H, d, *J* 7.4 Hz, –Ar[Fmoc]), 7.44 (1H, d, *J* 7.4 Hz, –Ar[Fmoc]), 7.41-6.99 (8H, m, –Ar[Fmoc] and –Ar, overlapped), 4.62 (1H, d, *J* 6.6 Hz, -C*H*$_2$-[Fmoc] rot. a), 4.53 (2H, m, -C*H*$_2$-[Fmoc] rot. b, -CC*H*$_2$N rot. a, overlapped), 4.51 (1H, s, -CC*H*$_2$N rot. b), 4.28 (0.5H, t, *J* 6.6 Hz, -C*H*[Fmoc] rot. a), 4.21 (0.5H, t, *J* 6.6 Hz,-C*H*[Fmoc] rot. b), 3.62 (1H, s, C*H*$_2$-COOH rot. b), 3.52 (1 H, t, *J* 5.3 Hz, -NCH$_2$-C*H*$_2$OCH$_3$ rot. a), 3.47 (1H, t, *J* 5.3 Hz, -NC*H*$_2$-CH$_2$OCH$_3$ rot. a), 3.33 (1.5 H, s, -OC*H*$_3$ rot. a), 3.20 (3.5 H, m, -OC*H*$_3$ rot. b, -NCH$_2$-C*H*$_2$OCH$_3$ rot. b and -NC*H*$_2$-CH$_2$OCH$_3$ rot. b).

^{13}C NMR (150 MHz, $CDCl_3$, mixture of rotamers) δ 176.8 (-*C*OOH), 156.5 (-*C*O [Fmoc]), 156.3 (Ar), 143.9 (Ar), 143.8 (Ar), 141.3 (Ar), 141.2 (Ar), 138.1 (Ar), 128.9 (Ar), 128.8 (Ar), 128.7 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 127.5 (Ar), 127.0 (Ar), 126.9 (Ar), 125.9 (Ar), 124.8 (Ar), 124.7 (Ar), 119.8 (Ar), 70.8 (-*C*H$_2$[Fmoc] rot. a), 70.6 (-*C*H$_2$[Fmoc] rot. b), 67.4 (-*C*H$_2$OCH$_3$ rot. a), 67.0 (-*C*H$_2$OCH$_3$ rot. b), 58.7 (-CH$_2$O*C*H$_3$ rot. a), 58.6 (-CH$_2$O*C*H$_3$ rot. b), 51.3 (-Ar-*C*H$_2$N- rot. a), 51.0 (-Ar-*C*H$_2$N- rot. b), 47.3 (-*C*H[Fmoc] rot. a), 47.2 (-*C*H[Fmoc] rot. b), 46.7 (-N*C*H$_2$-CH$_2$O rot. a), 45.7 (-N*C*H$_2$-CH$_2$O rot. b), 40.8 (-*C*H$_2$COOH).

ESI-MS: 446.3 m/z $[M + H]^+$.

Compound 21



21

To a solution of 2-(methyl)phenyl acetic acid (3.00 g, 20.0 mmol) in dry DCM (15 mL), DMAP (0.244 g, 0.200 mmol), *t*-BuOH (2.22 g, 30.0 mmol) and DCC (5.36 g, 26.0 mmol) were sequentially added. The mixture was stirred overnight, filtered (to remove the *N,N'*-dicyclohexyl urea), and the filtrate was concentrated in vacuo to give a crude material (4.40 g). The residue was purified by flash chromatography (silica gel, hexanes/ethyl acetate, from: 100% hexanes to 94/6) to give **21** as an oil (2.80 g, 68%).

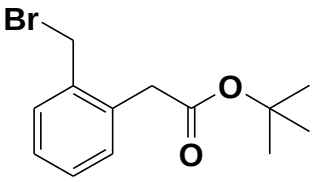
TLC (SiO_2): R_f = 0.68 (hexanes:ethyl acetate 95:5).

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.197 (4H, bs, -Ar), 3.57 (2H, s, -C$\underline{H_2}$-COO), 2.34 (3H, s, Ar-C$\underline{H_3}$), 1.47 (9H, s, *t*-Bu).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 170.8 ($\underline{C}$OO-*t*-Bu), 136.6 (-$\underline{C}CH_3$), 133.4 (-$\underline{C}CH_2COO$), 130.1, (-$\underline{C}$H) 130.0, (-$\underline{C}$H), 127.1, (-$\underline{C}$H) 126.0 (-$\underline{C}$H), 80.7 ($\underline{C}$-O-*t*Bu), 40.4 (-$\underline{C}H_2$-COO), 28.0 (-C($\underline{C}H_3)_3$, x 3), 19.5 (-$\underline{C}H_3$).

ESI-MS: 207.1 m/z $[M + H]^+$.

Compound 22



22

Compound **21** (1.40 g, 6.79 mmol), N-bromosuccinimide (1.93 g, 10.8 mmol) and benzoyl peroxide (0.082 g, 0.34 mmol) were dissolved in 70 mL of ethyl acetate. The mixture was heated at 85°C for 30 minutes and concentrated. The crude **22** (3.3 g), containing the insoluble succinimide, was immediately purified by flash chromatography (silica gel, hexanes/ethyl acetate, from: 100% hexanes to 98/2) to give **22** as an oil (1.30 g, 67%).[1]

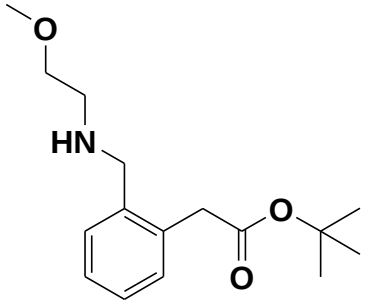
TLC (SiO_2): R_f = 0.54 (hexanes:ethyl acetate 95:5).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.25 (4H, m, -Ar), 4.59 (2H, s, C$\underline{H_2}$-Br), 3.71 (2H, s, C$\underline{H_2}$-COO*t*-Bu), 1.44 (9H, s, *t*-Bu).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3 (<u>C</u>OO-*t*-Bu), 136.2 (-<u>C</u>CH_2Br), 133.9 (-<u>C</u>CH_2CO), 131.1, (-<u>C</u>H) 130.6 (-<u>C</u>H), 129.1, (-<u>C</u>H) 127.7 (-<u>C</u>H), 81.2 (<u>C</u>-O-*t*Bu), 39.6 (-<u>C</u>H_2CO), 31.8 (-<u>C</u>H_2Br), 28.0 (-C(<u>C</u>H_3)$_3$, x 3).

ESI-MS: 285.0 m/z (100, $[M + H]^+$), 287.0 m/z (97, $[M + H]^+$).

Compound 23



23

To a solution of methoxyethyl amine (1.95 mL, 22.8 mmol) in dry DCM (6 mL) was slowly added (15 minutes) a solution of the compound **22** (1.30 g, 4.56 mmol) in dry DCM (65 mL). After the addition the mixture was stirred for 45 minutes. The solvent was removed in vacuo and the crude was left overnight under high vacuum to give 1.6 g of pale yellow oil. The residue was purified by flash chromatography (silica gel, DCM/CH_3OH, from: 100/0 to 98/03, 1% triethylamine in both eluents) to give the free amine **23** as an oil (1.00 g, 78%).

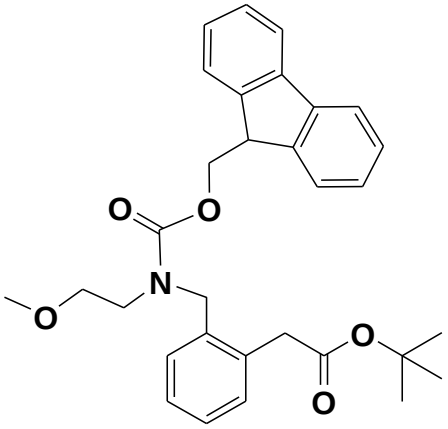
TLC (SiO_2): R_f = 0.37 (DCM:MeOH 95:5,1% triethylamine).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (1H, m, -Ar), 7.21 (3H, m, -Ar), 3.81 (2H, s, Ar-C$\underline{H_2}$-NH), 3.65 (2H, s, C$\underline{H_2}$-COO*t*-Bu), 3.50 (2H, t, *J* 6.0 Hz, C$\underline{H_2}$-OCH_3), 3.33 (3H, s, CH_2O-C$\underline{H_3}$), 2.81 (2H, t, *J* 6.0 Hz, C$\underline{H_2}$-CH_2-OCH_3), 2.17 (1H, bs, -N$\underline{H}$), 1.41 (9H, s, *t*-Bu).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1 (<u>C</u>OO-*t*-Bu), 138.2 (-<u>C</u>CH_2NH), 133.5 (-<u>C</u>CH_2CO), 130.5 (-<u>C</u>H), 129.3 (-<u>C</u>H), 127.2 (-<u>C</u>H), 127.1 (-<u>C</u>H), 80.7 (<u>C</u>-O-*t*Bu), 71.8 (-<u>C</u>H_2OCH_3), 58.6 (-CH_2O<u>C</u>H_3), 51.4 (Ar-<u>C</u>H_2NH), 48.8 (Ar-CH_2NH<u>C</u>H_2), 39.5 (-C<u>C</u>H_2CO), 27.9 (-C(<u>C</u>H_3)$_3$, x 3).

ESI-MS: 280.2 m/z $[M + H]^+$.

Compound 24



24

To a stirred solution of **23** (1.90 g, 6.81 mmol) in 1,4-dioxane (35 mL), a water solution (21 mL) containing $NaHCO_3$ (1.14 g, 13.6 mmol) and DMAP (42 mg, 0.34 mmol) were added. To this solution Fmoc-Cl (2.29 g, 8.85 mmol) was added in two portions (in five minutes). The reaction mixture was stirred overnight. Ethyl acetate (100 mL) and water (40 mL) were added to the solution. The aqueous layer was extracted two times with ethyl acetate (80 mL) and the combined organic phases were washed with brine and dried over $MgSO_4$, filtered and evaporated in vacuo to give a crude material (3.40 g). A small portion of this residue was purified by flash chromatography on silica gel for analytical purposes (silica gel, hexanes/ethyl acetate, from: 100% hexanes to 80/20) to give **24** as an viscous oil. The remaining crude material was used in the next step without further purification.

TLC (SiO_2): R_f = 0.39 (hexanes:ethyl acetate 85:15).

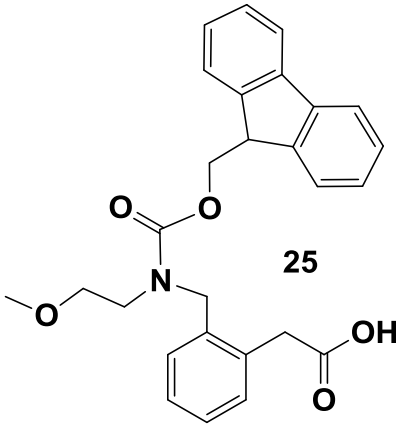
^{1}H NMR (300 MHz, TCDE, 373 K) δ 7.78 (2H, d, *J* 7.4 Hz, –Ar[Fmoc]), 7.57 (2H, d, *J* 7.4 Hz, –Ar[Fmoc]), 7.44 (2H, t, *J* 7.4 Hz, –Ar[Fmoc]), 7.32 (2H, t, *J* 7.4 Hz, –Ar[Fmoc]), 7.28 (3H, m, –Ar), 7.18 (1H, m, –Ar), 4.65 (2H, s, Ar-C$\underline{H_2}$-NH), 4.59 (2H, d, *J* 6.6 Hz, -C$\underline{H_2}$-[Fmoc]), 4.29 (2H, t, *J* 6.6 Hz, -C$\underline{H}$-[Fmoc]), 3.60 (2H, s, C$\underline{H_2}$-COO*t*-Bu), 3.41 (4H, m, -C$\underline{H_2}$-C$\underline{H_2}$-OCH_3, overlapping), 3.31 (3H, s, CH_2O-C$\underline{H_3}$), 1.49 (9H, s, *t*-Bu).

^{13}C NMR (75 MHz, TCDE, 373 K) δ 170.1 (-$\underline{C}$OO-*t*-Bu), 156.2 (-$\underline{C}$O-[Fmoc]), 144.0 (-$\underline{C}$-[Fmoc], x 2), 141.2 (-$\underline{C}$-[Fmoc], x 2), 136.1 (-$\underline{C}$-[Ar]), 133.0 (-$\underline{C}$-[Ar]), 130.5 (-$\underline{C}$H-[Ar]), 127.4 (-$\underline{C}$H-[Ar] and -$\underline{C}$H-[Fmoc], x 2), 127.1 (-$\underline{C}$H-[Ar] x 2), 126.9 (-$\underline{C}$H-[Fmoc], x 2), 124.7

(-<u>C</u>H-[Fmoc], x 2), 119.7 (-<u>C</u>H-[Fmoc], x 2), 80.7 (<u>C</u>-O-*t*Bu), 70.7 (-<u>C</u>H_2OCH_3), 67.2 (-<u>C</u>H_2[Fmoc]), 58.4 (-CH_2O<u>C</u>H_3), 48.7 (-Ar-<u>C</u>H_2N-), 47.6 (-N<u>C</u>H_2-CH_2O), 46.3 (-<u>C</u>H[Fmoc]), 39.5 (-<u>C</u>H_2COO-*t*-Bu), 28.0 (-C(<u>C</u>H_3)$_3$, x 3).

ESI-MS: 502.2 m/z $[M + H]^+$.

Compound 25



25

To a stirred solution of crude **24** (3.39 g) in DCM (40 mL), trifluoroacetic acid (8 mL) was slowly added. After 2 hours the mixture was concentrated in vacuo and the residue (4.4 g) was purified by flash chromatography (silica gel, hexanes/ethyl acetate, from: 80/20 to 50/50, 1% AcOH) to give **25** as a viscous yellow oil (2.16 g, 71%, two steps).

TLC (SiO_2): R_f = 0.55 (hexanes:ethyl acetate 1:1, 1% AcOH).

^{1}H NMR (300 MHz, TCDE, 353 K) δ 7.77 (2H, d, *J* 7.4 Hz, –Ar[Fmoc]), 7.55 (2H, d, *J* 7.4 Hz, –Ar[Fmoc]), 7.42 (2H, t, *J* 7.4 Hz, –Ar[Fmoc]), 7.31 (2H, t, *J* 7.4 Hz, –Ar[Fmoc]), 7.28 (3H, m, –Ar), 7.16 (1H, m, –Ar), 4.62 (2H, s, Ar-C<u>*H*$_2$</u>-NH), 4.58 (2H, d, *J* 6.6 Hz, -C<u>*H*$_2$</u>-[Fmoc]), 4.25 (2H, t, *J* 6.6 Hz, -C<u>*H*</u>-[Fmoc]), 3.68 (2H, s, C<u>*H*$_2$</u>-COOH), 3.35 (2H, m, -C<u>*H*$_2$</u>-CH_2-OCH_3), 3.33 (2H, m, -CH_2-C<u>*H*$_2$</u>-OCH_3), 3.26 (3H, s, CH_2O-C<u>*H*$_3$</u>).

^{13}C NMR (75 MHz, TCDE, 353 K) δ 173.9 (-<u>C</u>OO-*t*-Bu), 156.2 (-<u>C</u>O-[Fmoc]), 143.9 (-<u>C</u>-[Fmoc], x 2), 141.2 (-<u>C</u>-[Fmoc], x 2), 136.0 (-<u>C</u>-[Ar]), 132.0 (-<u>C</u>-[Ar]), 130.7 (-<u>C</u>H-[Ar]), 128.1 (-<u>C</u>H-[Ar]), 127.5 (-<u>C</u>H-[Ar] and -<u>C</u>H-[Fmoc], x 2), 127.4 (-<u>C</u>H-[Ar]), 126.9 (-<u>C</u>H-[Fmoc], x 2), 124.7 (-<u>C</u>H-[Fmoc], x 2), 119.7 (-<u>C</u>H-[Fmoc], x 2), 70.6 (-<u>C</u>H_2OCH_3), 67.2 (-<u>C</u>H_2[Fmoc]), 58.4 (-CH_2O<u>C</u>H_3), 48.8 (-Ar-<u>C</u>H_2N-), 47.5 (-N<u>C</u>H_2-CH_2O), 46.0 (-<u>C</u>H[Fmoc]), 37.6 (-<u>C</u>H_2COOH).

ESI-MS: 446.2 m/z $[M + H]^+$,

1.3 General Information for solid-phase synthesis of linear precursors 26-31

The linear oligomers **26**-**31** were synthesized on solid phase using the monomeric approach.[2] Solid phase syntheses were undertaken manually in polypropylene syringes fitted with two polyethylene filter discs. All solvents and soluble reagents were removed by suction. Washings between deprotection and coupling steps were carried out with DMF (3 × 1 min) and DCM (3 × 1 min) using 1 mL of solvent solvent for every 100 mg of resin for each single wash. The coupling efficiency was followed by chloranil colorimetric test. Each treatment was carried out in orbital shakers.

1.4 Solid-phase synthesis of linear precursors 26-31

In a typical synthesis 2-chlorotrityl chloride resin (α-dichlorobenzhydryl-polystyrene cross-linked with 1% DVB; 100 – 200 mesh; 1.63 mmol g^{-1}, 0.400 g, 0.652 mmol)[3] was swollen in dry DCM (4 mL) for 30 min and washed twice with dry DMF (4 mL) and dry DCM (4 mL). The first monomer (*i.e.* **16**) was loaded on the resin with the following protocol; 0.67 equiv. of **16** (290 mg, 0.652 mmol) and 4.0 equiv. of DIPEA (454 µL, 2.61 mmol) were dissolved in dry DCM (4 mL) and the solution was added onto the resin. The resulting mixture was shaken on a shaker platform for 90 min at room temperature, and then rinsed with 4 mL aliquots of dry DCM (3 × 1 min). To terminate the excess of reactive positions, the resin was incubated with 4 mL of a capping solution; DCM/MeOH/DIPEA (17:2:1) and the reaction was shaken for 15 min. The “capping” mixture was removed by suction and the resin was again treated with 4 mL of the capping solution (DCM/MeOH/DIPEA - 17:2:1) for 15 min. The “capping” mixture was removed by suction and the resin was washed three times with 4 mL aliquots of dry DMF.

The oligomer elongation was realized alternating deprotection and coupling steps, until the desired length was accomplished. The Fmoc-deprotection treatment was carried out with 4 mL aliquots of piperidine/DMF (1:4) (1 x 3 min, 1 x 5 min). The resin was washed with 4 mL aliquots of DMF (3 × 1 min), DCM (3 × 1 min) and DMF (3 × 1 min). The amide coupling was performed with 3.0 equiv of **16** (870 mg, 1.96 mmol), 3.0 equiv of HATU (745 mg, 1.96 mmol) and 6.0 equiv of DIPEA (683 µL, 3.92 mmol) in 4 mL of dry DMF (1 h). After that, the resin was washed with 4 mL aliquots of DMF (3 × 1 min), DCM (3 × 1 min) and DMF (3 × 1 min) and the solid-phase was ready for further

deprotection/coupling cycles. After every step, before the Fmoc deprotection, few beads of resin were subjected to the chloranil test (3 drops of acetone plus 3 drops of a saturated solution of chloranil in toluene were mixed with a small portion of resin beads and left standing for five minutes in a microcentrifuge tube: the results were invariably negative).

Once the desired length was accomplished, the resulting deprotected linear oligomer was washed with 4 mL aliquots of DMF (3 × 1 min), DCM (3 × 1 min) and cleaved using 4 mL of a hexafluoroisopropanol (HFIP)/DCM (1:4) solution (2 x 30 min). The filtrate, containing the desired linear oligomer, was concentrated in vacuo.

1 mg of the final product was dissolved in 100 μl in a 50% acetonitrile solution in water and analyzed by RP-HPLC [oligomers purity: >95%; conditions: 5 → 100% A in 30 min for the all oligomers (A, 0.1% TFA in acetonitrile, B, 0.1% TFA in water); flow: 1 mL min^{-1},λ = 220 nm]. The linear oligomers were subjected to the cyclization reaction without further purification.

Table S1 reports important data for the linear oligomers **26-31**.

Table S1. Relevant data for linear benzylopeptoids **26-31**

	26	**27**	**28**	**29**	**30**	**31**
Yield*	60%	84%	75%	60%	67%	80%
Physical state	Viscous oil	Viscous oil	Viscous oil	Viscous oil	Viscous oil	Viscous oil
HPLC-retention time (t_R)**	11.9 min	9.0 min	10.4 min	13.6 min	10.5 min	11.2 min
Mass, m/z (ESI)	634.3 $[M+H]^+$	634.4 $[M+H]^+$	634.3 $[M+H]^+$	839.4 $[M+H]^+$	839.5 $[M+H]^+$	839.5 $[M+H]^+$

* Yields calculated on the basis of the amount of used resin and the resin loading (1.63 mmol g^{-1}).

** See the HPLC chromatograms in the proper section.

1.5 General procedure for the cyclization reactions: synthesis of 3-8

A solution of the linear precursors **26**-**31** (0.20 mmol), previously co-evaporated three times with toluene, was prepared under nitrogen in dry DMF (17 mL). The mixture was added dropwise to a stirred solution of HATU (304 mg, 0.80 mmol) and DIPEA (209 µL, 1.2 mmol) in dry DMF (50 mL) by a syringe pump in 6 h, at room temperature in anhydrous atmosphere. After 18 h the resulting mixture was concentrated in vacuo and the dark brown oil was dissolved in ethyl acetate (50 mL) and washed with a solution of HCl (1.0 M, 25 mL). The water layer was extracted with ethyl acetate (2 × 50 mL) and the combined organic phase was washed with a half-saturated solution of $NaHCO_3$ (25 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. A small sample of cyclic products (~1 mg) was dissolved in 100 µl in a 50% acetonitrile solution in water and analyzed by RP-HPLC [purity >95% for oligomers **3**-**8**, conditions: 5% – 100% A in 30 min (A, 0.1% TFA in acetonitrile, B, 0.1% TFA in water); flow: 1 mL min^{-1},λ = 220 nm]. The crude residue was purified on a C18 silica gel, (water/acetonitrile, from: 8/2 to 4/6) to give the cyclic oligomers **3**-**8**. An alternative (or further) purification can be performed on silica gel (hexanes/ethyl acetate, from: 80/20 to 100% ethyl acetate and then ethyl acetate/MeOH, from: 100% ethyl acetate to 5% MeOH). The silica gel purification is not compatible with benzylopeptoid **8** (its complexing abilities hampers the column elution).

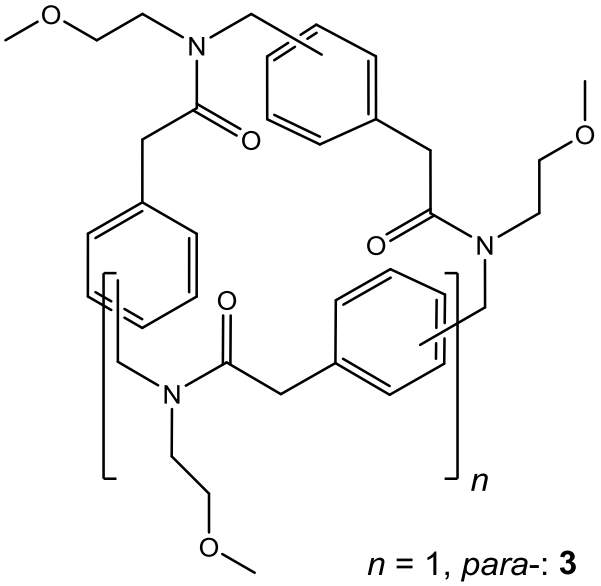
Table S2 reports selected data for the cyclic benzylopeptoids **3-8**.

Table S2. Relevant data for cyclic benzylopeptoids **3-8**

	3	**4**	**5**	**6**	**7**	**8**
Yield	65%	53%	32%	57%	72%	26%
Physical state	Viscous oil	Viscous oil	White solid	Viscous oil	Viscous oil	Viscous oil
HPLC-retention time (t_R)	13.3 min.	13.0 min.	10.4 min.	14.7 min.	12.5 min.	12.0 min.
Mass, m/z (ESI)	616.6 (100, $[M+H]^+$), 638.7 (90, $[M+Na]^+$), 654.6 (20, $[M+K]^+$)	616.6 (100, $[M+H]^+$), 638.7 (10, $[M+Na]^+$), 327.6 (40, $[M+H+K]^{2+}$)	638.3 (70, $[M+Na]^+$), 327.6 (100, $[M+H+K]^{2+}$)	821.4 (100, $[M+H]^+$), 843.4 (70, $[M+Na]^+$), 430.3 (30, $[M+H+K]^{2+}$)	821.4 (100, $[M+H]^+$), 843.4 (20, $[M+Na]^+$), 430.3 (10, $[M+H+K]^{2+}$)	821.4 (100, $[M+H]^+$), 843.4 (40, $[M+Na]^+$), 430.3 (30, $[M+H+K]^{2+}$)
HR-Mass, m/z (ESI)* $[M + H]^+$	616.338880 (calcd for $C_{36}H_{46}N_3O_6^+$ 616.338113)	616.340004 (calcd for $C_{36}H_{46}N_3O_6^+$ 616.338113)	616.339887 (calcd for $C_{36}H_{46}N_3O_6^+$ 616.338113)	843.434320 (calcd for $C_{48}H_{60}N_4NaO_8^+$ 843.430336)	821.443023 (calcd for $C_{48}H_{61}N_4O_8^+$ 821.448391)	821.446777 (calcd for $C_{48}H_{61}N_4O_8^+$ 821.448391)

* The possible formation of higher order oligomers (cyclic hexamers or octamers) was excluded thanks to the zoom-scan technique (HR-ESI of the pseudomolecular parent peaks).

Compound 3

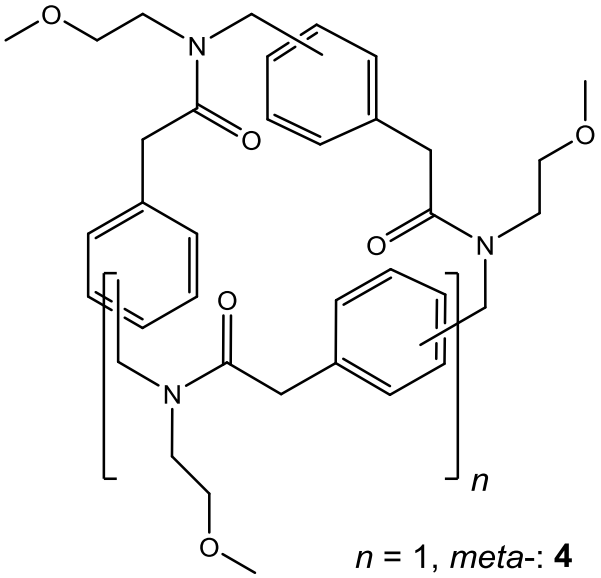


n = 1, *para*-: **3**

^{1}H-NMR: (600 MHz, CD_3CN, mixture of rotamers)[4] δ: 7.31 (1 H, d, *J* 7.4 Hz, Ar-*H*), 7.20 (9 H, m, Ar-*H*), 6.92 (2 H, m, Ar-*H*), 4.76–4.53 (6 H, m, Ar-CH_2-N), 3.85–3.32 (18 H, m, COCH_2Ar, NC$H_2$$CH_2OCH_3$, NCH_2CH_2OCH_3), 3.29 - 3.18 (9 H, m, NCH_2CH_2OCH_3).

^{13}C-NMR: (150 MHz, CD_3CN, mixture of rotamers, broad signals) δ: 172.7, 172.5, 137.7, 137.5, 135.9, 135.6, 129.8, 129.5, 129.2, 128.9, 127.6, 127.5, 71.3, 71.0, 59.2, 58.9, 53.0, 49.3, 48.8, 48.5, 48.5, 48.3, 48.2, 47.4, 41.3, 41.0, 39.1.

Compound 4

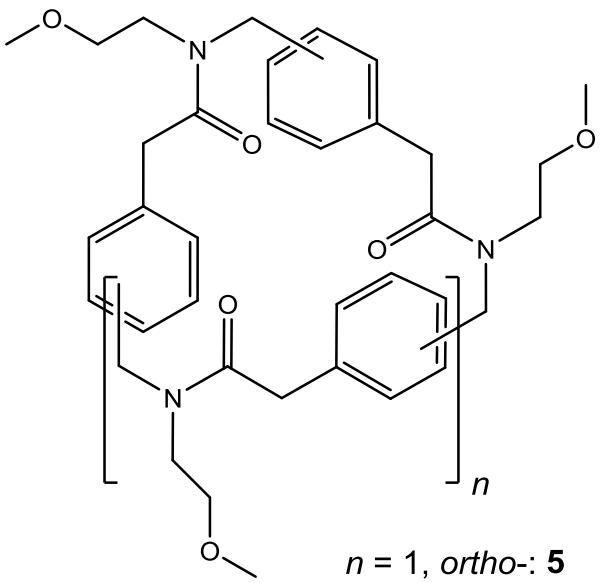


n = 1, *meta*-: **4**

^{1}H-NMR: (600 MHz, CD_3CN, mixture of rotamers) δ: 7.33-6.79 (12 H, m, Ar-*H*), 4.60–4.51 (6 H, m, Ar-C*H*$_2$-N), 3.82–3.55 (6 H, m, COC*H*$_2$Ar), 3.52-3.35 (12 H, m, NC*H*$_2$CH$_2$OCH$_3$, NCH$_2$C*H*$_2$OCH$_3$), 3.29 - 3.20 (9 H, m, NCH$_2$CH$_2$OC*H*$_3$).

^{13}C-NMR: (150 MHz, CD_3CN, mixture of rotamers, broad signals) δ: 172.4, 139.5, 139.3, 137.2, 129.8, 129.6, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 127.4, 127.1, 126.0, 125.8, 71.2, 71.0, 59.3, 58.9, 53.1, 53.0, 52.9, 49.8, 49.0, 48.9, 48.0, 47.9, 47.6, 46.6, 46.4, 41.5, 41.2, 41.1, 40.7, 40.6.

Compound 5



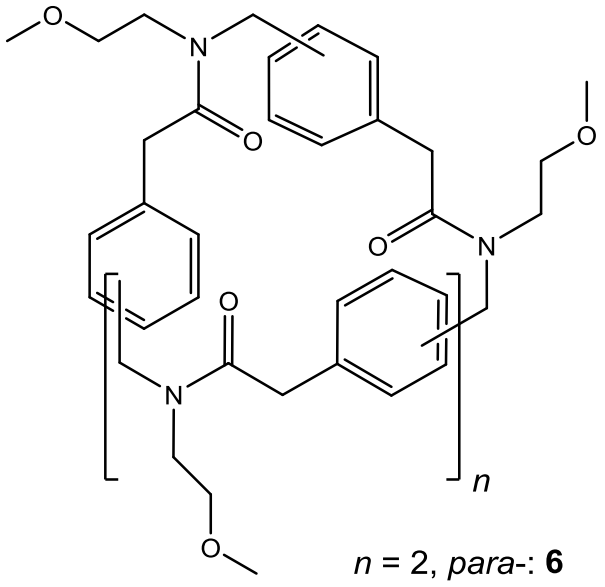
n = 1, *ortho*-: **5**

^{1}H-NMR: (600 MHz, CD_3CN, mixture of rotamers) δ: 7.29-7.05 (12 H, m, Ar-*H*), 4.57 (2 H, bs, Ar-C*H*$_2$-N), 4.43 (2 H, bs, Ar-C*H*$_2$-N), 4.13 (2 H, bs, Ar-C*H*$_2$-N), 3.75–3.40 (18 H, m, COC*H*$_2$Ar, NC*H*$_2$CH$_2$OCH$_3$, NCH$_2$C*H*$_2$OCH$_3$), 3.32 (3 H, s, NCH$_2$CH$_2$OC*H*$_3$), 3.31 (3 H, s, NCH$_2$CH$_2$OC*H*$_3$), 3.22 (3 H, s, NCH$_2$CH$_2$OC*H*$_3$).

^{1}H-NMR: (600 MHz, TCDE, 373 K) δ: 7.30 (9 H, bs, Ar-*H*), 7.19 (3 H, bs, Ar-*H*), 4.61 (6 H, bs, Ar-C*H*$_2$-N), 3.74 (6 H, bs, NC*H*$_2$CH$_2$OCH$_3$), 3.63 (6 H, bs, COC*H*$_2$Ar, NCH$_2$C*H*$_2$OCH$_3$), 3.54 (6 H, bs, NCH$_2$C*H*$_2$OCH$_3$), 3.33 (9 H, s, NCH$_2$CH$_2$OC*H*$_3$).

^{13}C-NMR: (150 MHz, CD_3CN, mixture of rotamers, broad signals) δ: 173.1, 172.9, 171.9, 138.6, 138.1, 136.7, 135.7, 135.2, 134.5, 131.6, 129.3, 129.1, 128.3, 128.1, 127.9, 127.6, 125.5, 125.3, 71.3, 71.1, 71.0, 59.2, 59.0, 58.9, 51.6, 50.6, 50.2, 48.3, 47.2, 46.6, 37.8, 37.7, 36.9.

Compound 6

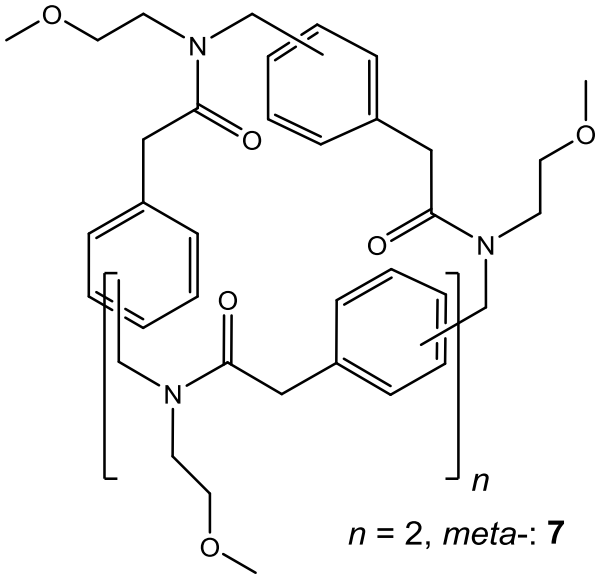


n = 2, *para*-: **6**

^{1}H-NMR: (600 MHz, CD_3CN, mixture of rotamers) δ: 7.33-6.70 (16 H, m, Ar-*H*), 4.63–4.57 (8 H, m, Ar-C*H*$_2$-N), 3.80–3.55 (8 H, m, COC*H*$_2$Ar), 3.50–3.38 (16 H, m, NC*H*$_2$CH$_2$OCH$_3$, NCH$_2$C*H*$_2$OCH$_3$), 3.37–3.20 (12 H, m, NCH$_2$CH$_2$OC*H*$_3$).

^{13}C-NMR: (150 MHz, CD_3CN, mixture of rotamers, broad signals) δ: 172.4, 172.3, 172.2, 137.6, 136.9, 136.0, 130.7, 130.6, 130.5, 130.4, 130.3, 130.2, 130.1, 130.0, 128.8, 128.7, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 127.5, 71.2, 71.0, 59.2, 58.9, 52.7, 48.9, 48.8, 48.6, 48.1, 48.0, 47.9, 47.8, 46.4, 46.3, 46.2, 41.1, 40.5, 40.3.

Compound 7

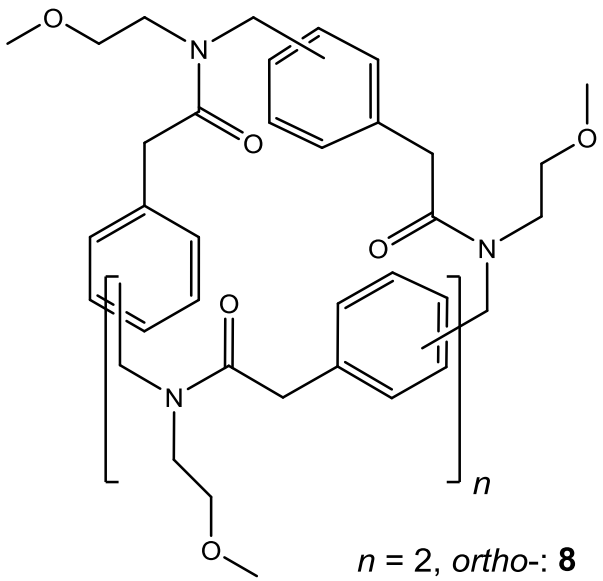


n = 2, *meta*-: **7**

^{1}H-NMR: (600 MHz, CD_3CN, mixture of rotamers) δ: 7.33-6.70 (16 H, m, Ar-*H*), 4.63–4.50 (8 H, m, Ar-C*H*$_2$-N), 3.80–3.52 (8 H, m, COC*H*$_2$Ar), 3.51–3.35 (16 H, m, NC*H*$_2$CH$_2$OCH$_3$, NCH$_2$C*H*$_2$OCH$_3$), 3.37–3.20 (12 H, m, NCH$_2$CH$_2$OC*H*$_3$).

^{13}C-NMR: (150 MHz, CD_3CN, mixture of rotamers, broad signals) δ: 172.2, 172.1, 139.5, 139.0, 138.8, 137.8, 137.4, 137.1, 129.7, 129.6, 129.5, 129.4, 129.2, 129.1, 129.0, 128.8, 128.7, 128.4, 128.2, 127.0, 126.9, 126.8, 125.8, 125.7, 71.2, 71.0, 59.2, 58.9, 53.0, 49.1, 48.1, 48.0, 46.7, 41.2, 41.1, 40.9, 40.7.

Compound 8



n = 2, *ortho*-: **8**

^{1}H-NMR: (600 MHz, CD_3CN, mixture of rotamers) δ: 7.20-6.85 (16 H, m, Ar-*H*), 4.77–3.90 (8 H, m, Ar-C*H*$_2$-N), 3.90–3.52 (8 H, m, COC*H*$_2$Ar), 3.51–3.35 (16 H, m, NC*H*$_2$CH$_2$OCH$_3$, NCH$_2$C*H*$_2$OCH$_3$), 3.34–3.13 (12 H, m, NCH$_2$CH$_2$OC*H*$_3$).

^{13}C-NMR: (75 MHz, CD_3CN, mixture of rotamers, broad signals) δ: 173.7, 173.1, 171.6, 138.4, 136.6, 135.6, 132.3, 132.1, 132.0, 130,6, 129,3, 129.2, 128.6, 128.3, 128.1, 127.9, 127.7, 127.6, 127.4, 126.2, 125.6, 71.2, 71.0, 70.8, 59.4, 58.9, 59.3, 59.0, 58.9, 51.6, 51.3, 51.0, 48.1, 48.0, 47.7, 47.6, 47.1, 46.9, 46.7, 38.1, 38.0, 37.9, 37.7, 37.5.

1.6 Attempted complexation with sodium picrate

To a 4.0 mM solution of **3-8** in CD_3CN:$CDCl_3$ 9:1 (0.5 mL), were added increasing amounts of Na^+ picrate. After any addition the mixture was stirred vigorously for 3 minutes and the spectrum was acquired. No hint of signals' coalescence was observed in any of the ^{1}H NMR spectra.

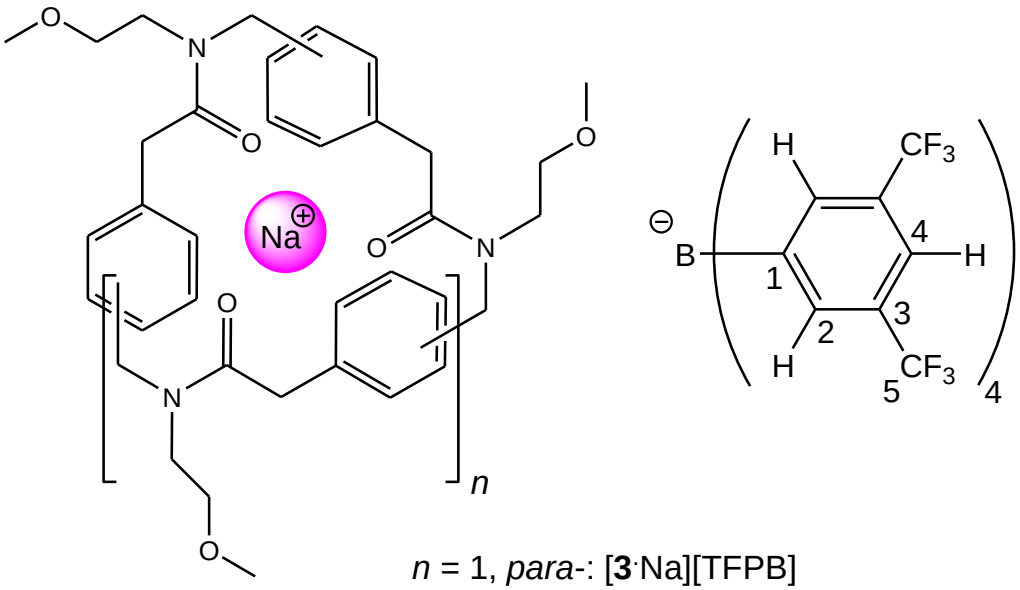
The sodium picrate was prepared according to literature procedures,[5] and dried under high vacuum before use.

1.7 Complexation with NaTFPB

To 4.0 mM solutions of **3-8** in $CDCl_3$ (0.5 mL) were added increasing amounts of NaTFPB (usually, 0.5 equivalents, see ^{1}H NMR spectra in the next section). After every addition the mixture was sonicated for 5 minutes and the ^{1}H NMR spectra were recorded. The addition was stopped when the NaTFPB could not be further dissolved in the sample. Integration of the hosts/guests resonances gave the final complex stoichiometry.

The NaTFPB salt was prepared according to literature procedures,[6] and dried overnight, under high vacuum, before use.[7]

[**3**·Na][TFPB] **complex**

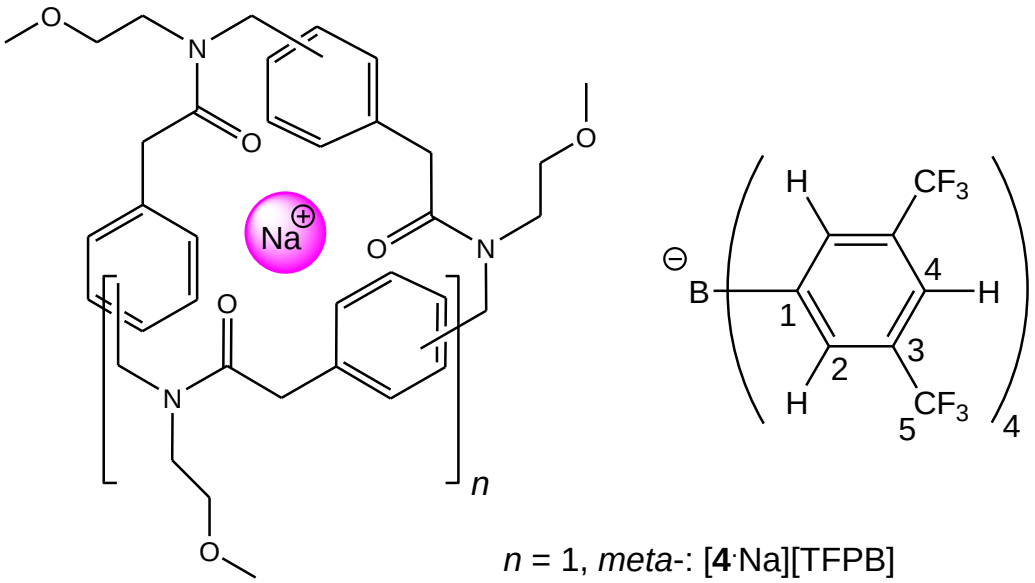


n = 1, *para*-: [**3**·Na][TFPB]

^{1}H-NMR: (600 MHz, $CDCl_3$) δ: 7.70 (8H, s, TFPB-*o*-*H*), 7.51 (4H, s, TFPB-*p*-*H*), 6.92 (6H, d, *J* 7.8 Hz, Ar-*H*), 6.89 (6H, d, *J* 7.8 Hz, Ar-*H*), 4.39 (6H, bs, Ar-C*H*$_2$-N), 3.74 (12H, bs, COC*H*$_2$Ar, NC*H*$_2$CH$_2$OCH$_3$,), 3.58 (6H, t, *J* 4.2 Hz, NCH$_2$C*H*$_2$OCH$_3$), 3.41 (9H, s, NCH$_2$CH$_2$OC*H*$_3$).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ: 173.7 (*C*=O), 161.6 (q, *J* 52 Hz, C-1), 136.4 (*C*-CH$_2$N), 134.8 (C-2), 134.0 (*C*-CH$_2$C=O), 129.8 (*C*H-Ar), 128.9 (C-3, q, *J* 33 Hz), 124.9 (*C*H-Ar), 124.5 (q, *J* 271 Hz, C-5), 117.5 (C-4), 69.7 (-*C*H$_2$-OCH$_3$), 58.9 (-CH$_2$-O*C*H$_3$), 52.4 (Ar-*C*H$_2$N), 51.0 (N-*C*H$_2$-CH$_2$-OCH$_3$), 39.1 (Ar-*C*H$_2$C=O).

[**4**·Na][TFPB] **complex**

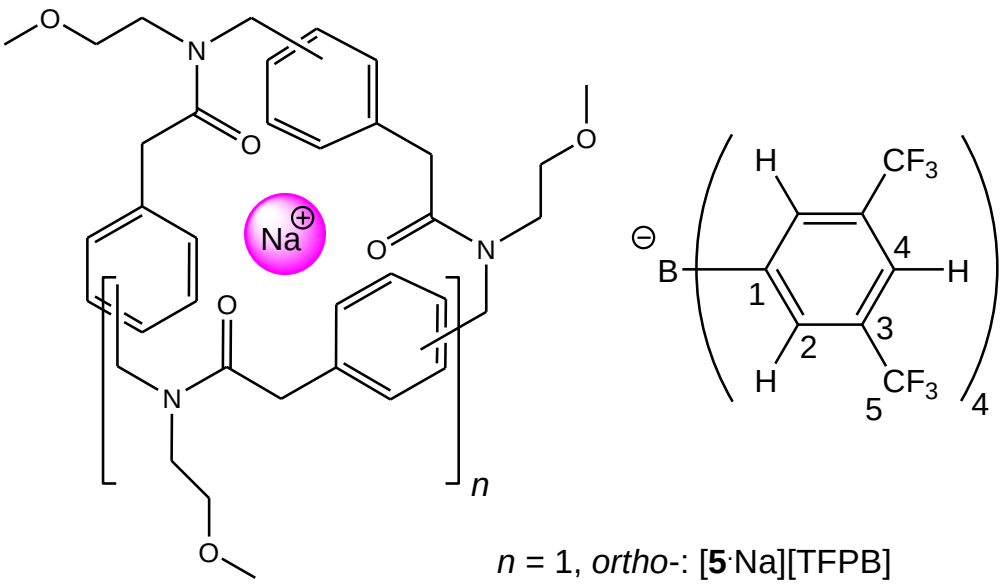


n = 1, *meta*-: [**4**·Na][TFPB]

^{1}H-NMR: (600 MHz, $CDCl_3$) δ: 7.71 (8H, s, TFPB-*o*-*H*), 7.51 (4H, s, TFPB-*p*-*H*), 7.17 (3H, t, *J* 7.8 Hz, Ar-*H*), 7.08 (3H, d, *J* 7.8 Hz, Ar-*H*), 6.93 (3H, bs, Ar-*H*), 6.88 (3H, d, *J* 7.8 Hz, Ar-*H*), 4.27 (6H, bs, Ar-CH_2-N), 3.83 (6H, t, *J* 5.4 Hz, NC$H_2$$CH_2OCH_3$), 3.69 (6H, bs, COC$H_2$Ar), 3.66 (6H, t, *J* 5.4 Hz, $NCH_2CH_2$$OCH_3$), 3.41 (9H, s, $NCH_2CH_2OCH_3$).

^{13}C-NMR: (150 MHz, $CDCl_3$) δ: 173.0 (*C*=O), 161.7 (q, *J* 52 Hz, C-1), 137.9 (*C*-CH_2N), 134.8 (C-2), 134.3 (*C*-CH_2C=O), 131.5 (*C*H-Ar), 128.8 (q, *J* 33 Hz C-3, and *C*H-Ar), 128.2 (*C*H-Ar), 124.5 (q, *J* 271 Hz, C-5 and *C*H-Ar), 117.5 (C-4), 70.2 (-*C*H_2-OCH_3), 59.1 (-CH_2-O*C*H_3), 53.5 (Ar-*C*H_2N), 51.0 (N-*C*H_2-CH_2-OCH_3), 39.1 (Ar-*C*H_2C=O).

[**5**·Na][TFPB] **complex**

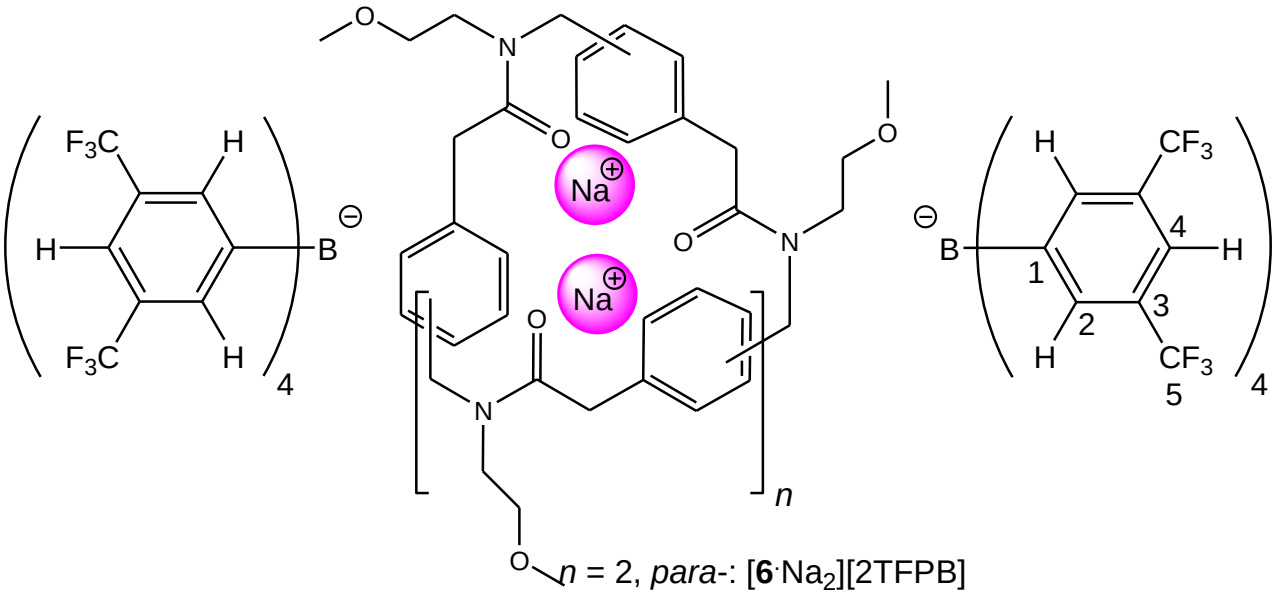


n = 1, *ortho*-: [**5**·Na][TFPB]

^{1}H-NMR: (600 MHz, TCDE, 373 K) δ: 7.76 (8H, s, TFPB-*o*-*H*), 7.57 (4H, s, TFPB-*p*-*H*), 7.33 (6 H, bs, Ar-*H*), 7.26 (3 H, d, *J* 6.6 Hz, Ar-*H*), 7.21 (3 H, d, *J* 6.6 Hz,, Ar-*H*), 4.60 (6 H, bs, Ar-C*H*$_2$-N), 3.90 (6 H, bs, COC*H*$_2$Ar), 3.64 (12 H, bs, NC*H*$_2$CH$_2$OCH$_3$, NCH$_2$C*H*$_2$OCH$_3$), 3.33 (9 H, s, NCH$_2$CH$_2$OC*H*$_3$).

^{13}C-NMR: (150 MHz, TCDE, 373 K) δ: 172.3 (*C*=O), 161.8 (q, *J* 52 Hz, C-1), 135.1 (*C*-CH$_2$N), 134.7 (C-2), 133.5 (*C*-CH$_2$C=O), 130.7 (*C*H-Ar), 128.8 (C-3, q, *J* 33 Hz), 128.7 (*C*H-Ar), 128.3 (*C*H-Ar), 127.6 (*C*H-Ar), 124.5 (q, *J* 271 Hz, C-5), 117.2 (C-4), 70.9 (-*C*H$_2$-OCH$_3$), 58.3 (-CH$_2$-O*C*H$_3$), 50.3 (Ar-*C*H$_2$N), 48.8 (N-*C*H$_2$-CH$_2$-OCH$_3$), 38.6 (Ar-*C*H$_2$C=O).

[**6**·Na$_2$][2TFPB] **complex**

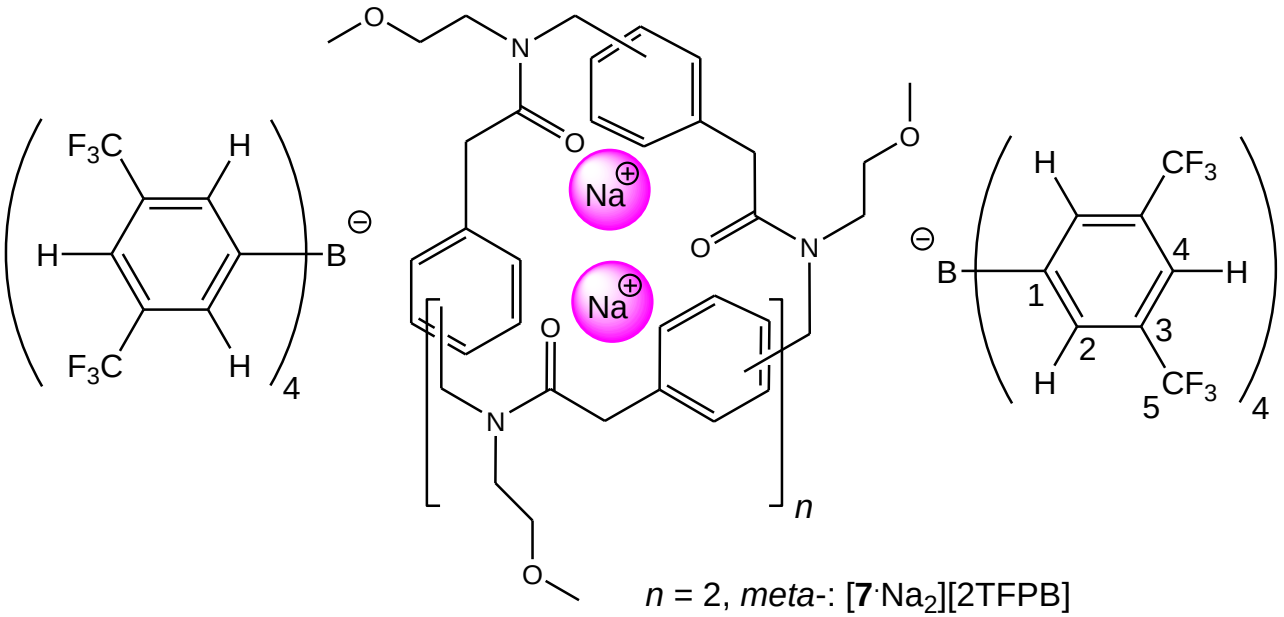


n = 2, *para*-: [**6**·Na$_2$][2TFPB]

^{1}H-NMR: (400 MHz, CDCl$_3$) δ: 7.72 (16H, s, TFPB-*o*-*H*), 7.53 (8H, s, TFPB-*p*-*H*), 6.95 (16H, m, Ar-*H*), 4.26 (6H, bs, Ar-C*H*$_2$-N), 3.75 (6H, broad signal, NC*H*$_2$CH$_2$OCH$_3$), 3.76 (6H, bs, COC*H*$_2$Ar), 3.59 (6H, broad signal, NCH$_2$C*H*$_2$OCH$_3$), 3.43 (9H, s, NCH$_2$CH$_2$OC*H*$_3$).

^{13}C-NMR: (150 MHz, CDCl$_3$) δ: 174.1 (*C*=O), 161.7 (q, *J* 52 Hz, C-1), 136.8 (*C*-CH$_2$N), 134.8 (C-2), 134.1 (*C*-CH$_2$C=O), 130.2 (*C*H-Ar), 128.9 (q, *J* 33 Hz, C-3), 124.9 (*C*H-Ar), 124.5 (q, *J* 271 Hz, C-5), 117.5 (C-4), 69.6 (-*C*H$_2$-OCH$_3$), 59.0 (-CH$_2$-O*C*H$_3$), 52.5 (Ar-*C*H$_2$N), 51.3 (N-*C*H$_2$-CH$_2$-OCH$_3$), 39.1 (Ar-*C*H$_2$C=O).

[**7**·Na$_2$][2TFPB] **complex**

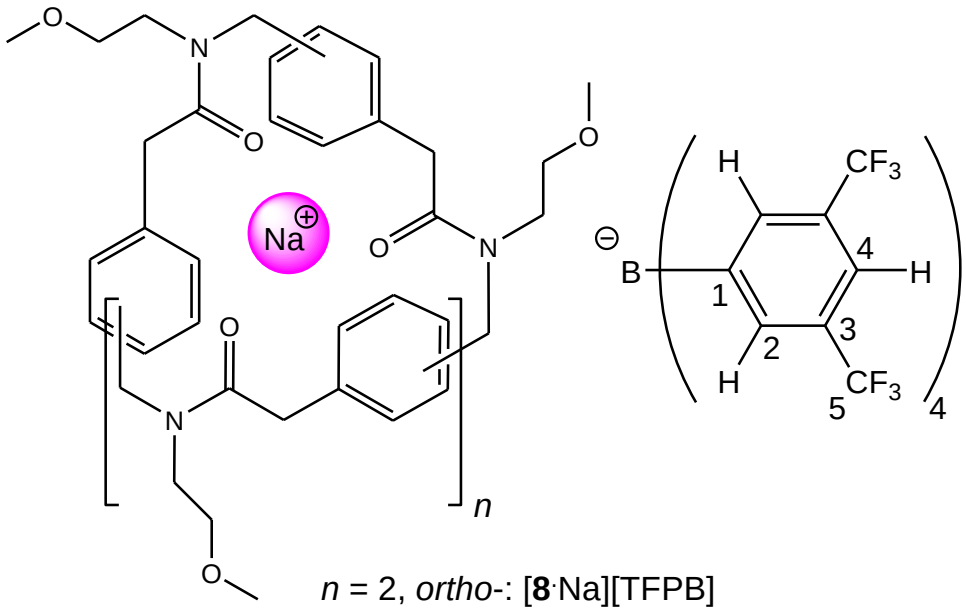


n = 2, *meta*-: [**7**·Na_2][2TFPB]

^{1}H-NMR: (600 MHz, $CDCl_3$, mixture of conformers: in this spectrum the major species – ~55% of the total - is described) δ: 7.69 (16H, s, TFPB-*o*-*H*), 7.51 (8H, s, TFPB-*p*-*H*), 7.12 (3H, t, *J* 7.8 Hz, Ar-*H*), 6.94 (3H, d, *J* 7.8 Hz, Ar-*H*), 6.90 (3H, d, *J* 7.8 Hz, Ar-*H*), 6.78 (3H, bs, Ar-*H*), 4.33 (6H, bs, Ar-CH_2-N), 3.76 (6H, t, *J* 5.4 Hz, NC$H_2$$CH_2OCH_3$), 3.71 (6H, bs, COC$H_2$Ar), 3.56 (6H, bs, $NCH_2CH_2OCH_3$), 3.36 (9H, s, $NCH_2CH_2OCH_3$).

^{13}C-NMR: (150 MHz, $CDCl_3$ mixture of conformers: in this spectrum the major species – ~55% of the total - is described) δ: 174.3 (*C*=O), 161.8 (q, *J* 52 Hz, C-1), 137.8 (*C*-CH_2N), 135.5 (*C*-CH_2C=O), 134.8 (C-2), 129.2 (*C*H-Ar), 128.9 (q, *J* 33 Hz C-3), 128.4 (*C*H-Ar), 127.7 (x 2, *C*H-Ar), 124.6 (q, *J* 271 Hz, C-5), 117.5 (C-4), 69.6 (-*C*H_2-OCH_3), 59.0 (-CH_2-O*C*H_3), 51.7 (Ar-*C*H_2N), 50.6 (N-*C*H_2-CH_2-OCH_3), 39.6 (Ar-*C*H_2C=O).

[**8**·Na][TFPB] **complex**

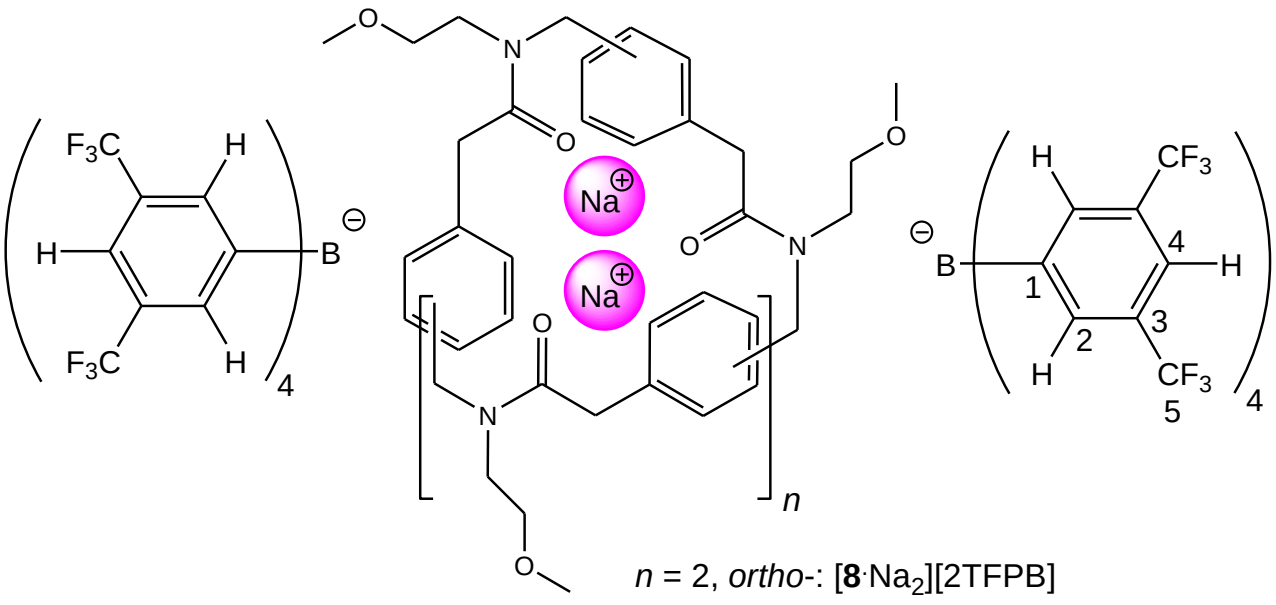


n = 2, *ortho*-: [**8**·Na][TFPB]

^{1}H-NMR: (600 MHz, $CDCl_3$, very broad signals) δ: 7.71 (8H, s, TFPB-*o*-*H*), 7.52 (4H, s, TFPB-*p*-*H*), 7.12 (8H, m, Ar-*H*), 7.09 (4H, m, Ar-*H*), 6.90 (4H, d, *J* 7.8 Hz, Ar-*H*), 4.53 (8H, very broad signal, Ar-CH_2-N), 3.82 (16H, bs, COCH_2Ar and NC$H_2$$CH_2OCH_3$), 3.57 (8H, bs, $NCH_2CH_2OCH_3$), 3.39 (9H, s, $NCH_2CH_2OCH_3$).

^{13}C-NMR: (150 MHz, $CDCl_3$) δ: 171.6 (*C*=O), 161.7 (q, *J* 52 Hz, C-1), 136.1 (*C*-CH_2N), 134.8 (C-2), 132.8 (*C*-CH_2C=O), 130.5 (*C*H-Ar), 128.8 (q, *J* 33 Hz C-3), 127.7 (*C*H-Ar), 127.3 (*C*H-Ar), 124.8 (q, *J* 271 Hz, C-5), 123.3 (*C*H-Ar), 117.4 (C-4), 70.2 (-*C*H_2-OCH_3), 59.0 (-CH_2-O*C*H_3), 50.0 (Ar-*C*H_2N), 48.7 (N-*C*H_2-CH_2-OCH_3), 36.2 (Ar-*C*H_2C=O).

[**8**·Na_2][2TFPB] **complex**



n = 2, *ortho*-: [**8**·Na_2][2TFPB]

^{1}H-NMR: (600 MHz, $CDCl_3$, very broad signals) δ: 7.69 (16H, s, TFPB-*o*-*H*), 7.50 (8H, s, TFPB-*p*-*H*), 7.12 (4H, m, Ar-*H*), 7.06 (8H, m, Ar-*H*), 6.95 (4H, d, *J* 7.2 Hz, Ar-*H*), 4.89 (8H, very broad signal, Ar-C*H*$_2$-N), 3.91 (8H, bs, COC*H*$_2$Ar), 3.73 (8H, bs, NC*H*$_2$CH$_2$OCH$_3$), 3.50 (8H, bs, NCH$_2$C*H*$_2$OCH$_3$), 3.30 (9H, s, NCH$_2$CH$_2$OC*H*$_3$).

^{13}C-NMR: (150 MHz, $CDCl_3$) δ: 172.8 (*C*=O), 161.7 (q, *J* 52 Hz, C-1), 135.6 (*C*-CH$_2$N), 134.8 (C-2), 132.3 (*C*-CH$_2$C=O), 131.1 (*C*H-Ar), 128.9 (q, *J* 33 Hz C-3), 127.8 (*C*H-Ar), 128.3 (*C*H-Ar), 124.8 (q, *J* 271 Hz, C-5), 123.3 (*C*H-Ar), 117.5 (C-4), 69.6 (-*C*H$_2$-OCH$_3$), 58.9 (-CH$_2$-O*C*H$_3$), 50.5 (Ar-*C*H$_2$N), 49.4 (N-*C*H$_2$-CH$_2$-OCH$_3$), 37.0 (Ar-*C*H$_2$C=O).

1.8 Evaluation of the K_a for the [3-8·Na$_x$][XTFPB] complexes

To 0.67 mM solutions of **3-8** in $CDCl_3$ (0.5 mL containing 1.0 μL of 1,1,2,2-tetrachloroethane -TCE - as internal standard), were added proper amounts of NaTFPB (one equivalent for benzylopeptoids **3**-**5** and two equivalents for benzylopeptoids **6**-**7**). After the addition the mixture was sonicated for 5 minutes in a heated bath (60 °C). The H·G complex concentration, at the equilibrium – $[H{\cdot}G]_{eq}$ – was evaluated by integration of the ^{1}H NMR signal of TCE versus the chosen values (see Table S3) of the guest molecules. On the basis of the stoichiometry of the complex, two equilibria are possible (equilibrium (1) and (2)).

$$H + G \rightleftharpoons H{\cdot}G \qquad (1)$$

$$H + 2\,G \rightleftharpoons H{\cdot}G_2 \qquad (2)$$

Equation (3) was used to obtain the concentration of the $[H{\cdot}G]_{eq}$ or $[H{\cdot}G_2]_{eq}$ species in both the cases.

$$[H{\cdot}G]_{eq} \text{ or } [H{\cdot}G_2]_{eq} = \frac{F_b}{F_a} \times [TCE] \times \frac{N_a}{N_b} \qquad (3)$$

where F_a and F_b are the areas of the signals of TCE and the guest, respectively; N_a and N_b are the numbers of the nuclei which cause the signals (N_a for TCE and N_b are the guest). [TCE] is the concentration in the NMR sample (the addition of 1.0 μL in 0.5 mL $CDCl_3$ gives a 0.0189 M solution).

In the case of a complex with a single sodium ion, the evaluation of the species at the equilibrium follows the relation (4) :

$$[H]_{eq} = [G]_{eq} = [H]_i - [H{\cdot}G]_{eq} \qquad (4)$$

In the case of a complex with two sodium ions, the evaluation of the species at the equilibrium, follows the relation (5) and (6):

$$[H]_{eq} = [H]_i - [H{\cdot}G_2]_{eq} \qquad (5)$$

$$[G]_{eq} = [G]_i - 2[H{\cdot}G_2]_{eq} \qquad (6)$$

(where $[G]_i = 2[H]_I$).

The *K*a, were calculated as follows:

$$K_a = \frac{[H{\cdot}G]_{eq}}{[H]_{eq} \times [G]_{eq}} \qquad (7)$$

for the equilibrium (1), and

$$K_a = \frac{[H{\cdot}G]_{eq}}{[H]_{eq} \times [G]^2_{eq}} \qquad (8)$$

for the equilibrium (2). Table S3 reports important data for the K_a evaluation of the cyclic oligomers **3**-**8**.

Table S3. Relevant data for the K_a evaluation for the sodium complexes of the cyclic benzylopeptoids **3**-**8**.

	3	**4**	**5**	**6**	**7**	**8**
Host concentration*	0.67 mM	0.67 mM	0.67 mM	0.67 mM	0.67 mM	0.67 mM
Guest concentration	0.67 mM	0.67 mM	0.67 mM	1.34 mM	1.34 mM	0.67 mM and 1.34 mM
δ integrated peak (ppm)**	4.41	4.27	4.10	4.21	6.68	4.88
K_a value*** (25 °C)	$1.7 \cdot 10^3$ M^{-1}	$15.1 \cdot 10^3$ M^{-1}	$0.4 \cdot 10^3$ M^{-1}	$76.3 \cdot 10^3$ M^{-2}	$47.0 \cdot 10^3$ M^{-2}	$301 \cdot 10^3$ M^{-2}
ΔG° (kcal/mol)	4.4	5.7	3.5	6.6	6.4	7.5
ESI-Mass, *m/z*	638.5 ($[M+Na]^+$	638.6 ($[M+Na]^+$	638.5 ($[M+Na]^+$	839.5**** $[M+Na]^+$	839.5**** $[M+Na]^+$	839.5**** $[M+Na]^+$

* Because of aggregation/precititation of the H·G complexes, the concentration can have a profound effect on the K_a. A comparison of the K_a can be properly done at the same concentration (0.67 mM).

** The ^{1}H NMR spectra are reported in Figures S1-S6.

*** Figures within ±10% in multiple experiments.

**** No double charged peak ($[M+2Na]^{++}$ was observed in the cyclic tetramers mass spectra (probably for the relatively low K_2).

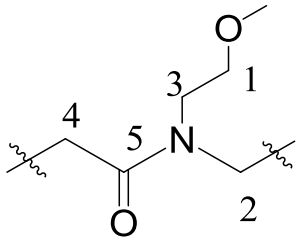


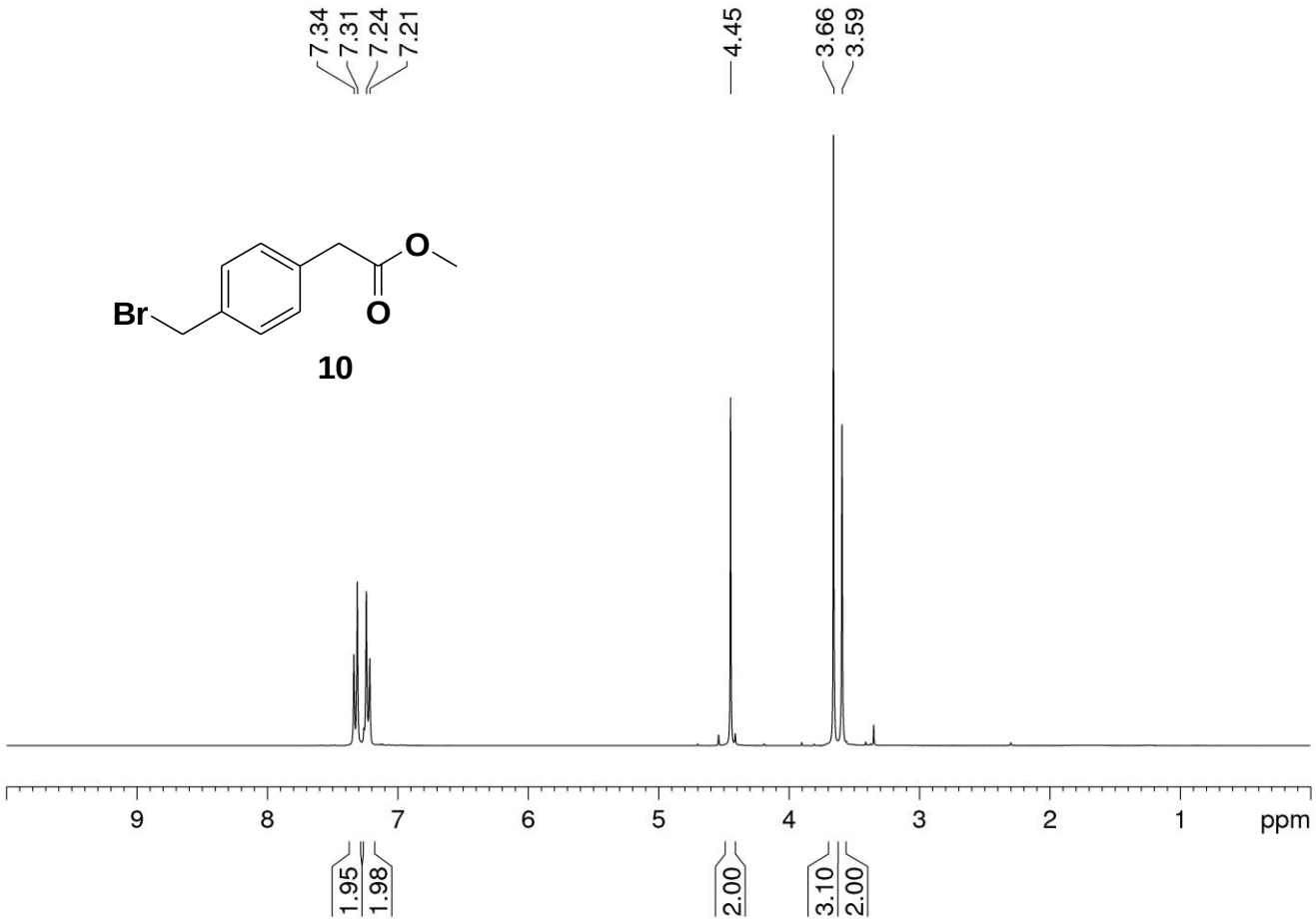
Table S4. Selected ^{13}C NMR data for the complexes of benzylopeptoids **3**-**8**.

	$[\mathbf{3}\cdot Na]^+$	$[\mathbf{4}\cdot Na]^+$	$[\mathbf{5}\cdot Na]^+$	$[\mathbf{6}\cdot 2Na]^{2+}$	$[\mathbf{7}\cdot 2Na]^{2+}$	$[\mathbf{8}\cdot 2Na]^{2+}$
1	69.7	70.1	70.9	69.6	69.6	69.6
2	52.4	53.5	50.3	52.5	51.7	50.5
3	51.0	51.0	48.8	51.3	51.6	49.4
4	39.1	39.1	38.6	39.1	39.6	37.0
5	173.7	173.0	172.3	174.1	174.3	172.8

2.0 ^{1}H-NMR and ^{13}C-NMR spectra

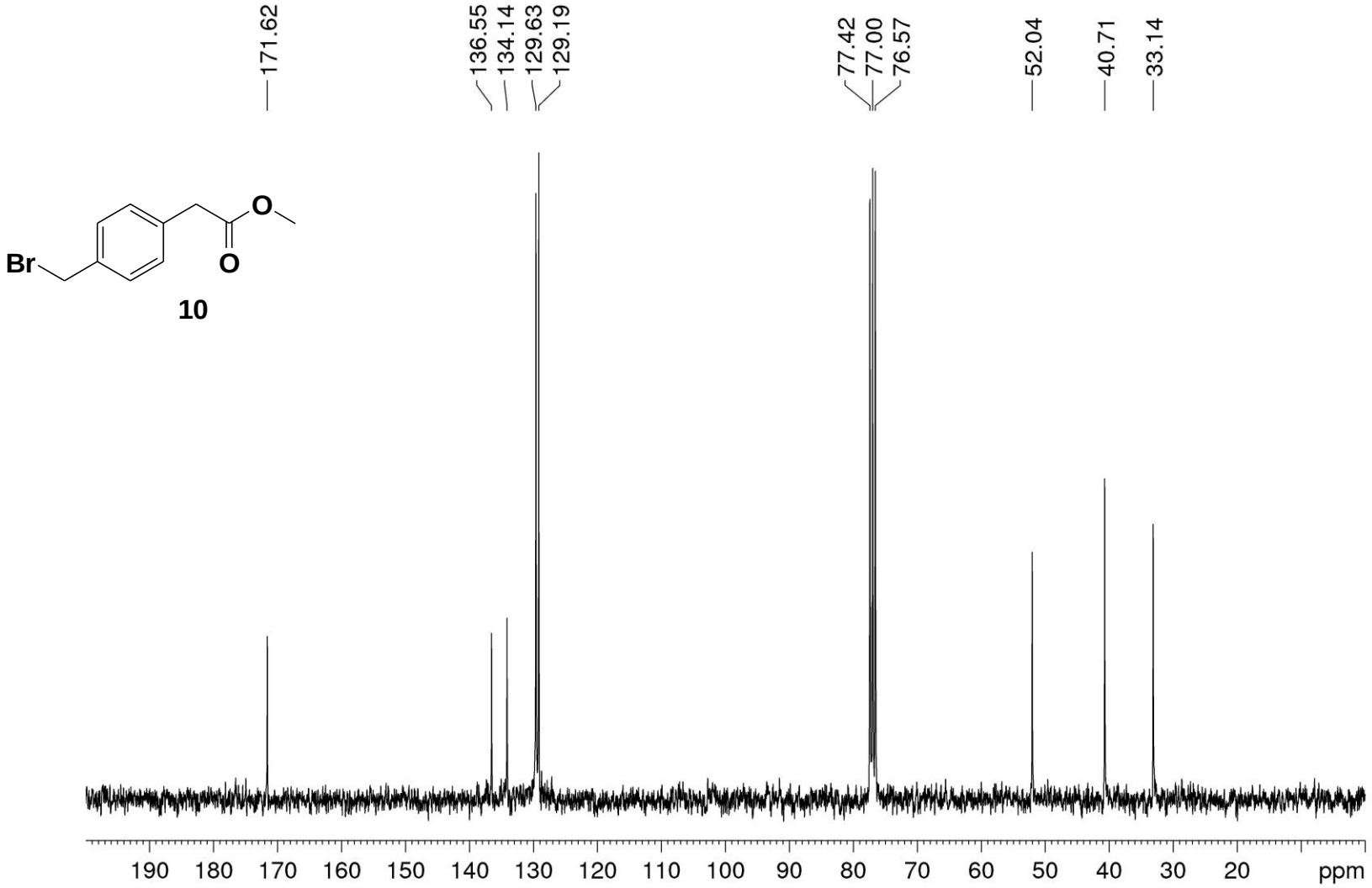
2.1 Spectra of the synthetic precursors 10-25

^{1}H NMR (300 MHz, $CDCl_3$)

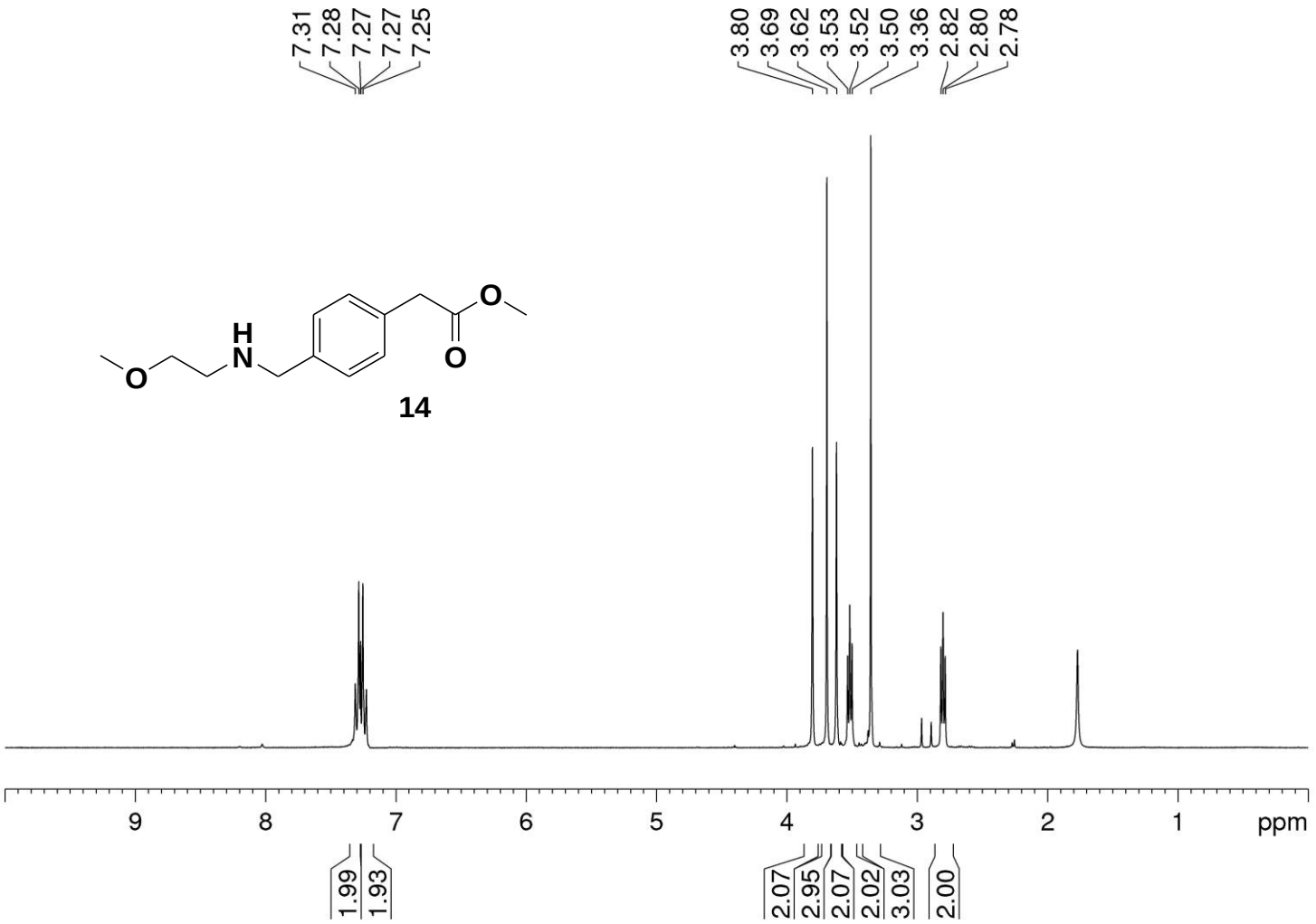


10

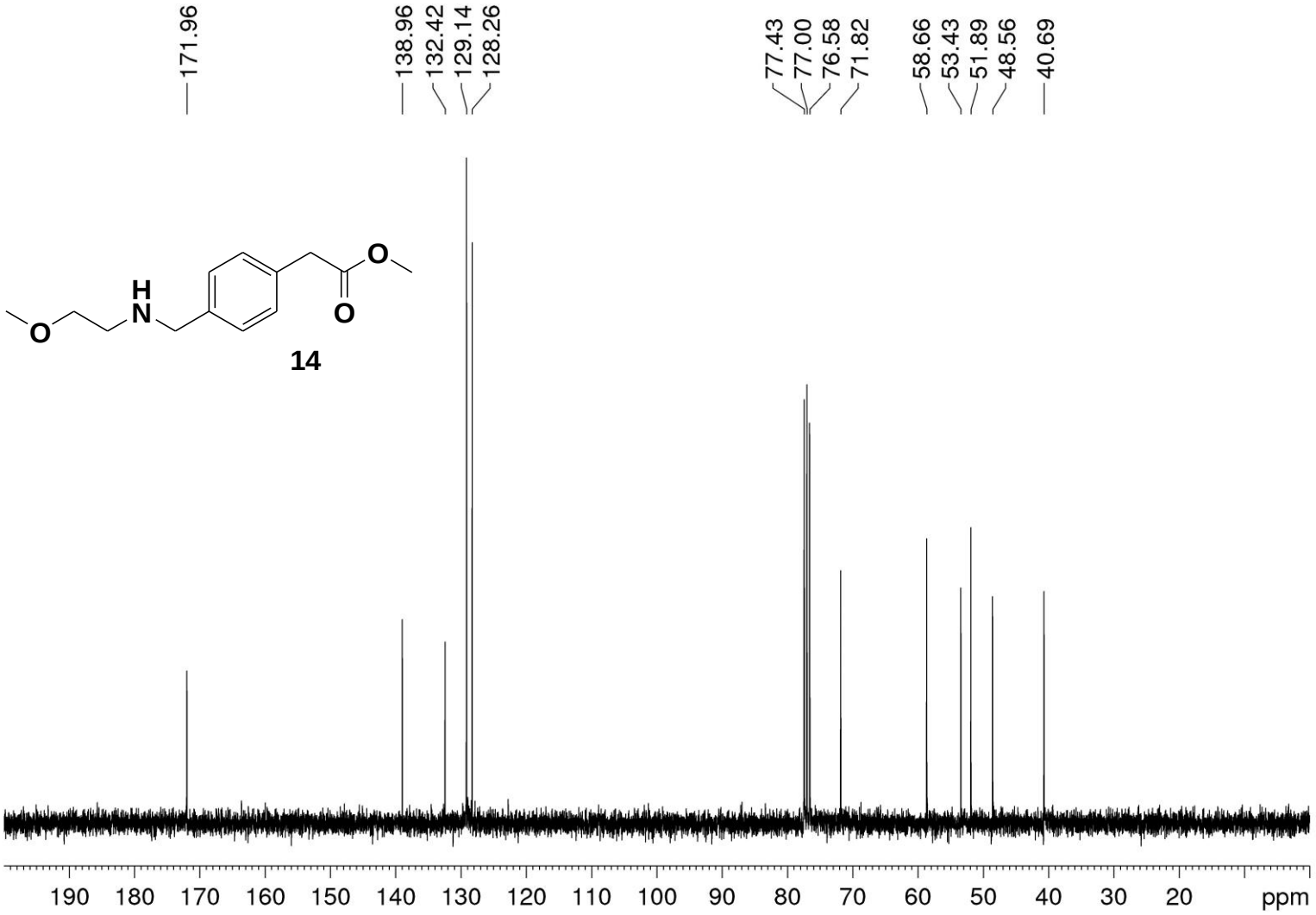
^{13}C NMR (75 MHz, $CDCl_3$)



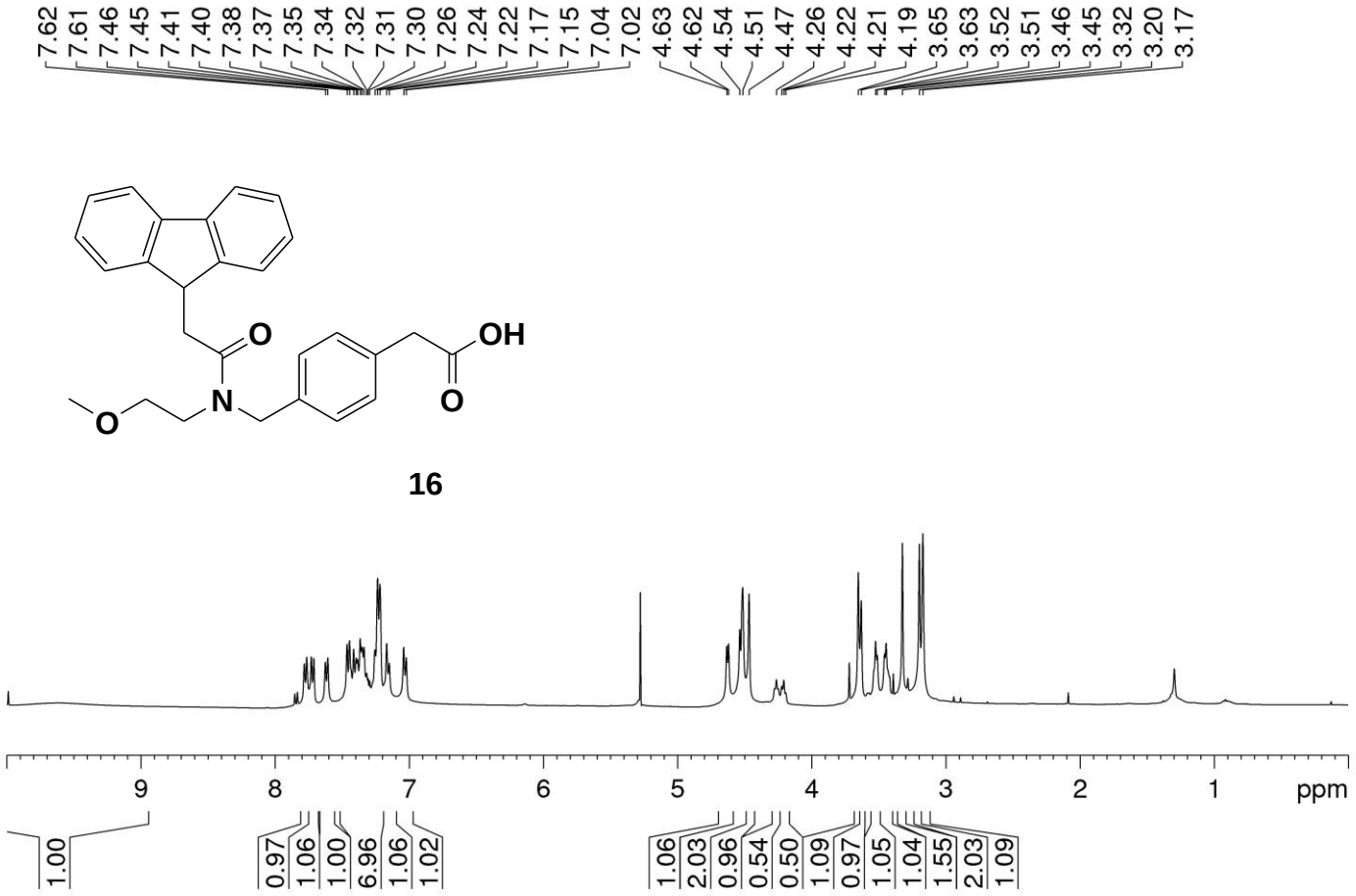
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

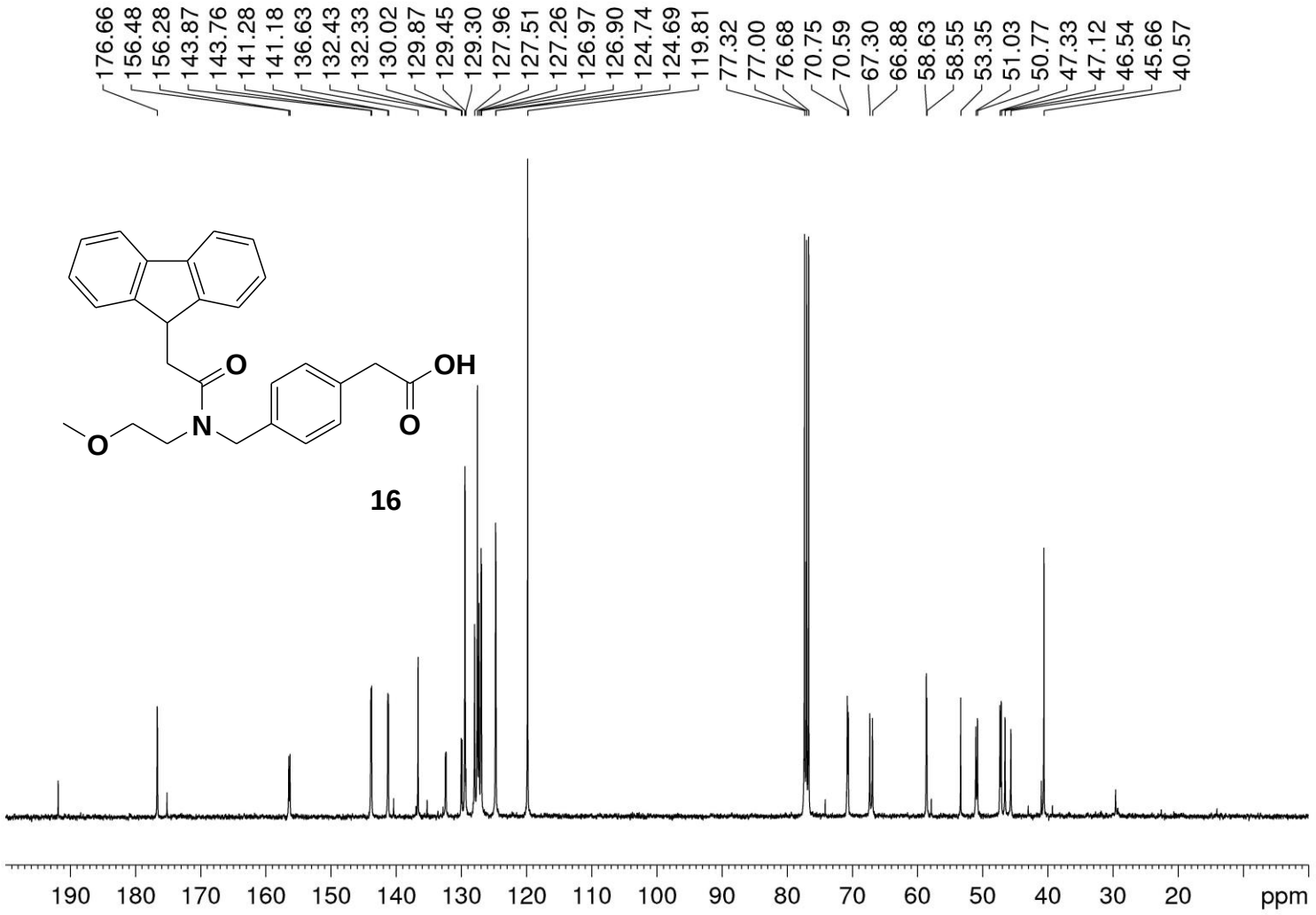


^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers)

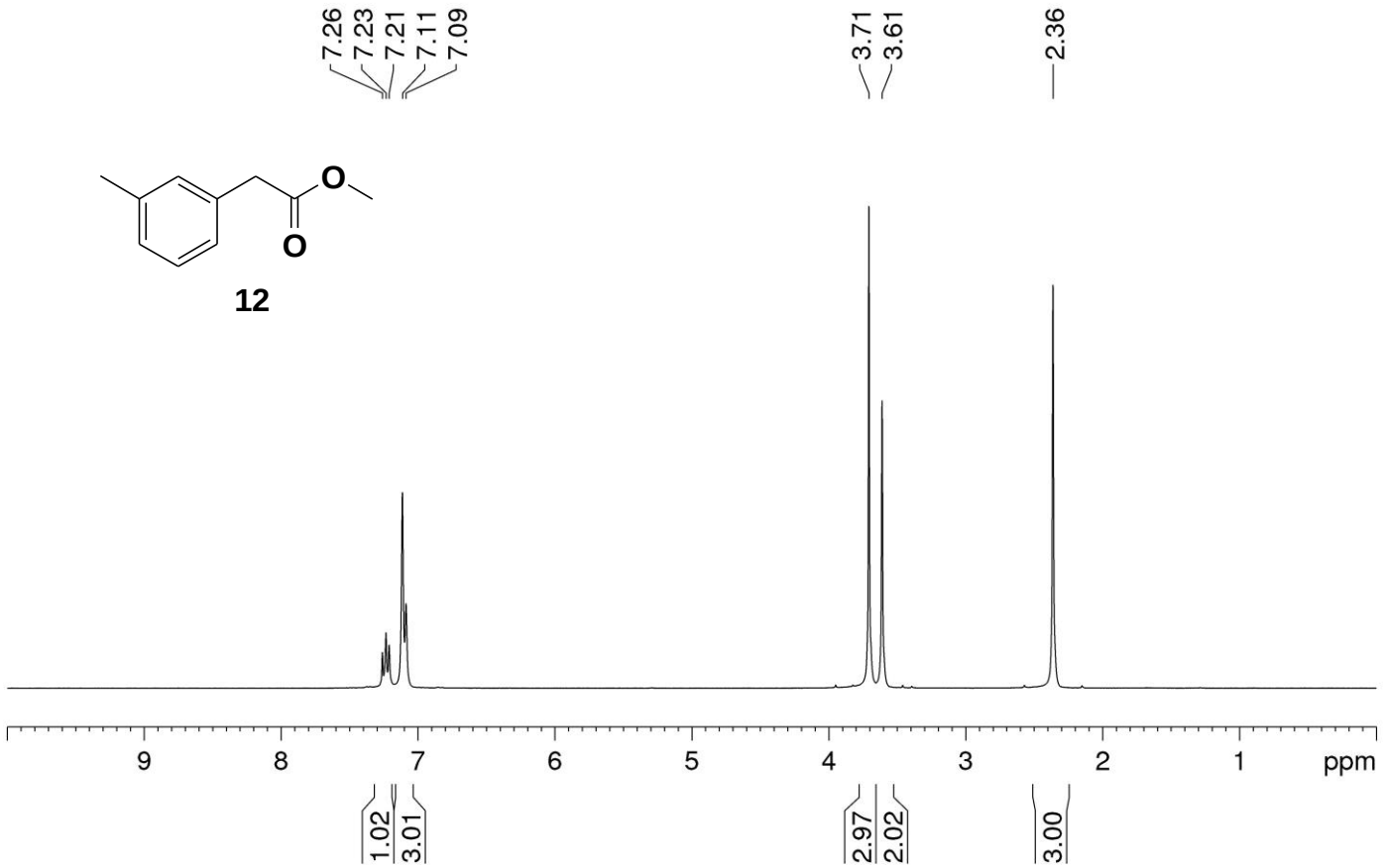


16

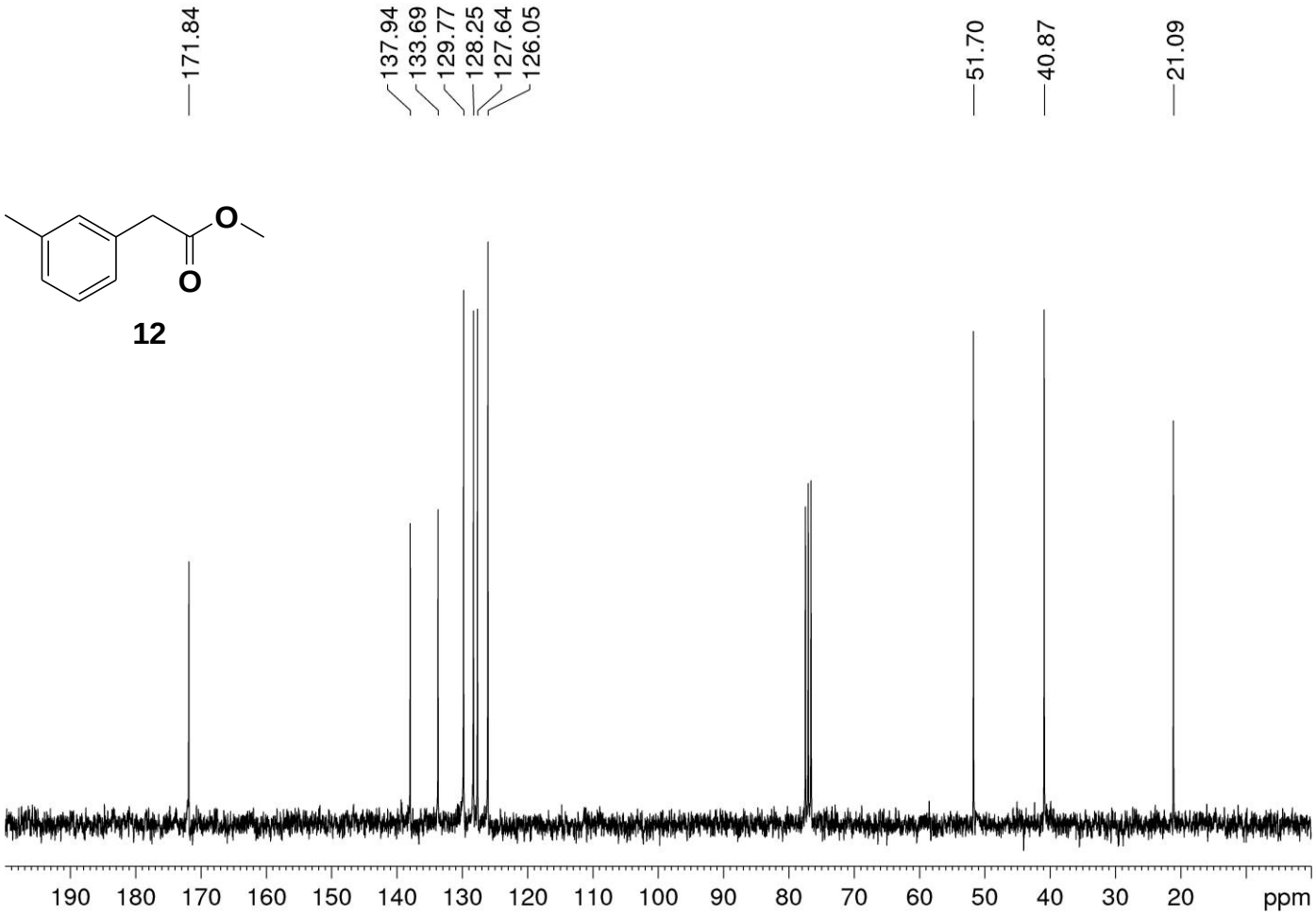
^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers)



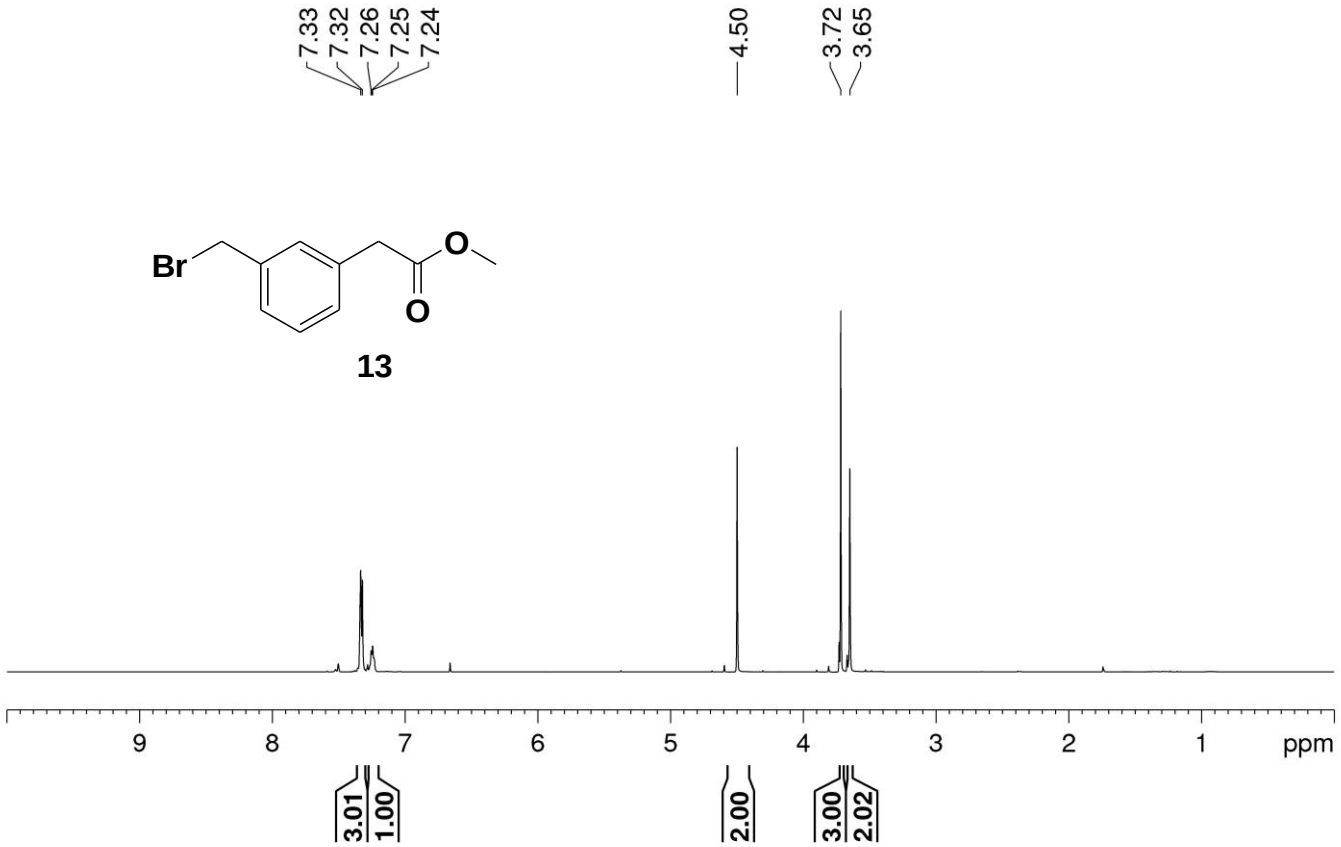
^{1}H NMR (300 MHz, $CDCl_3$)



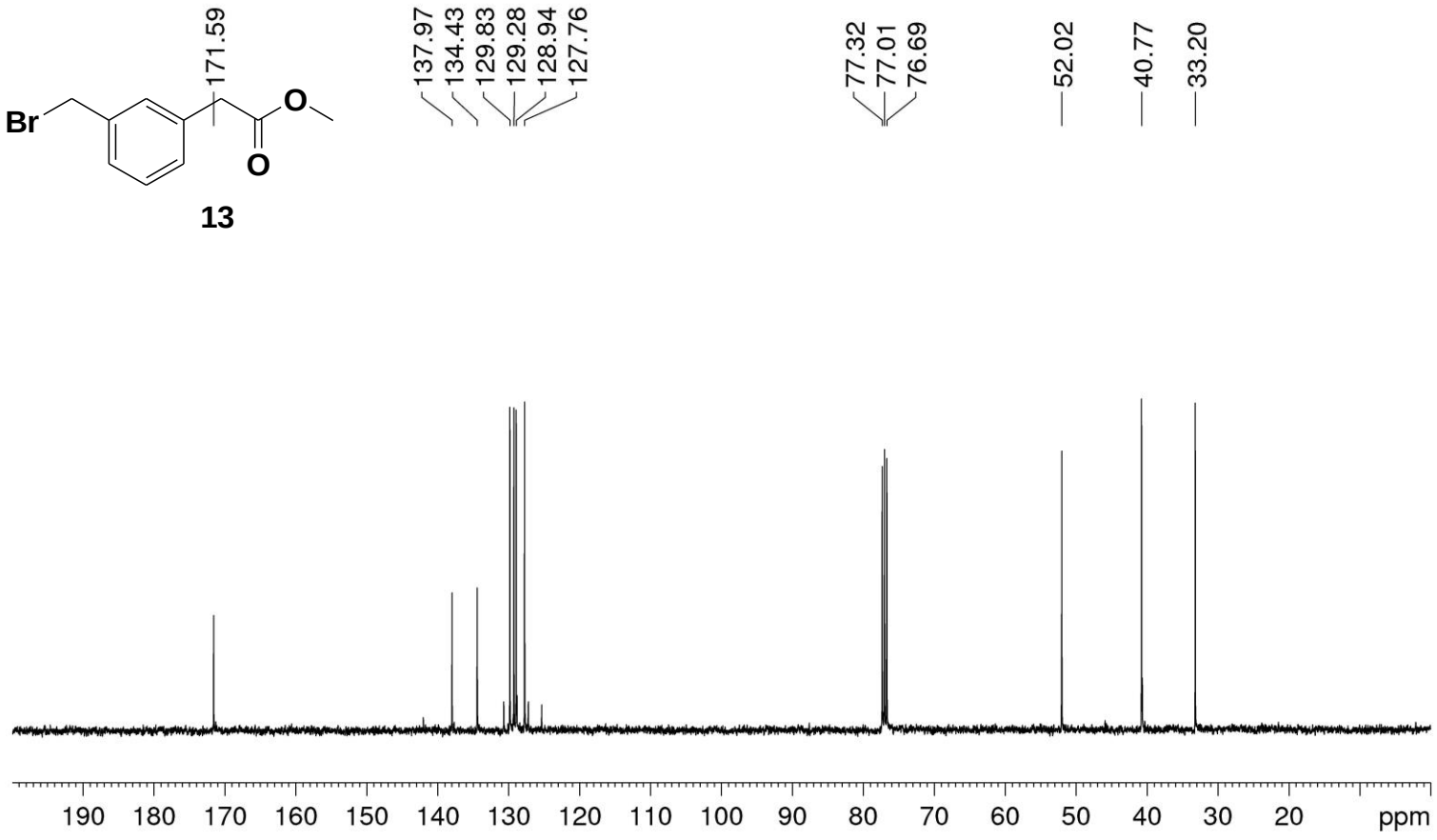
^{13}C NMR (75 MHz, $CDCl_3$)



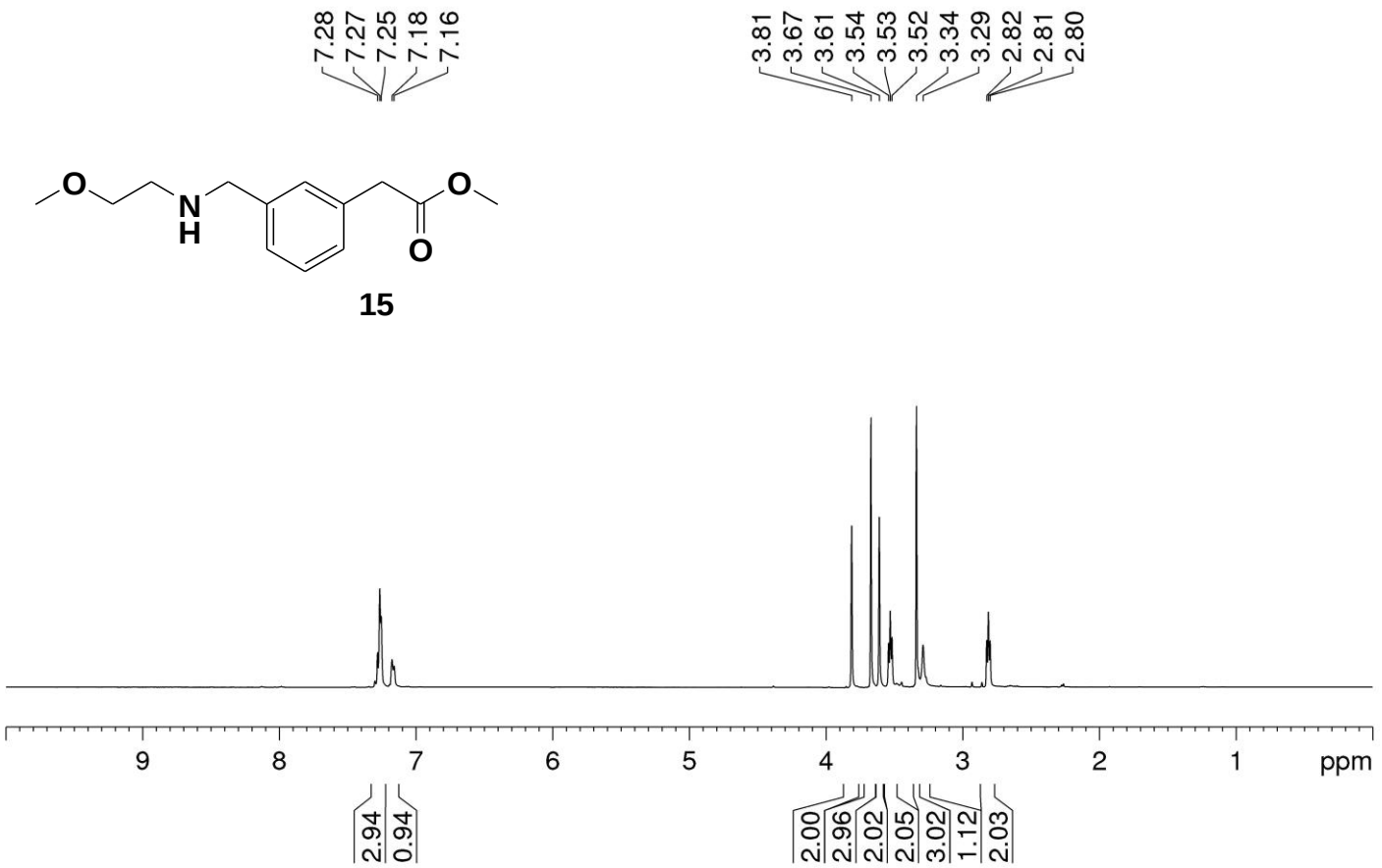
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

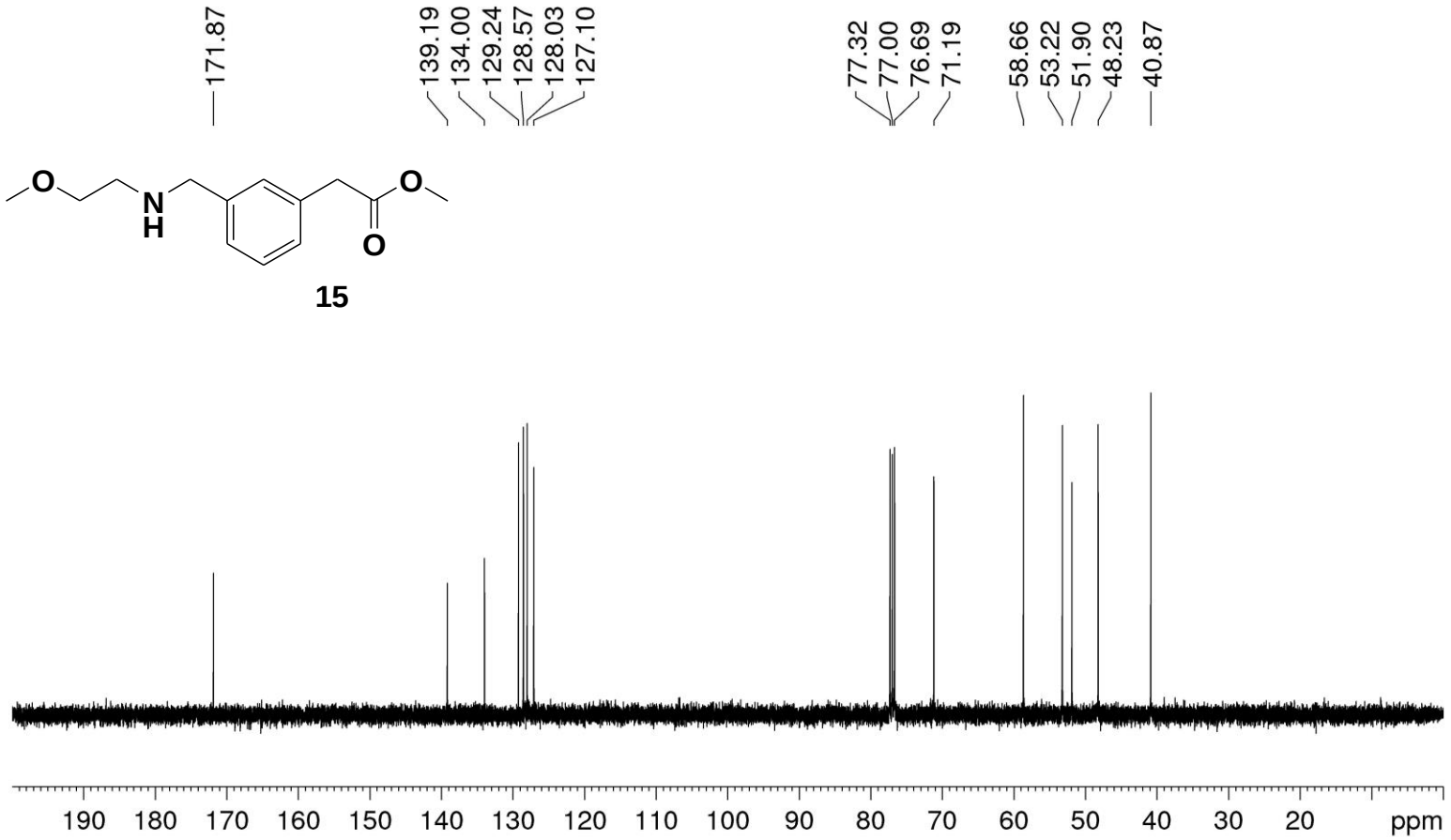


^{1}H NMR (400 MHz, $CDCl_3$)



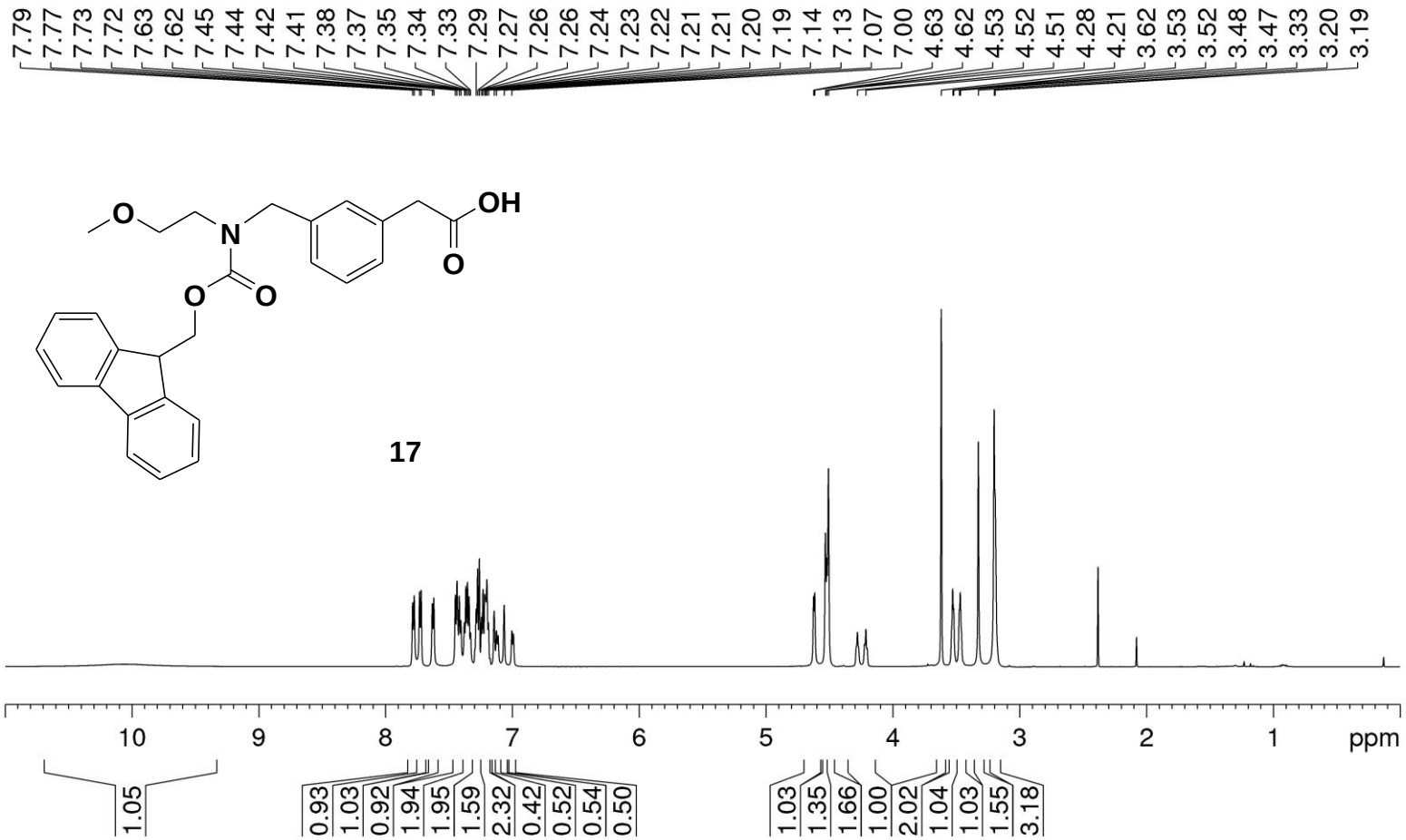
15

^{13}C NMR (100 MHz, $CDCl_3$)

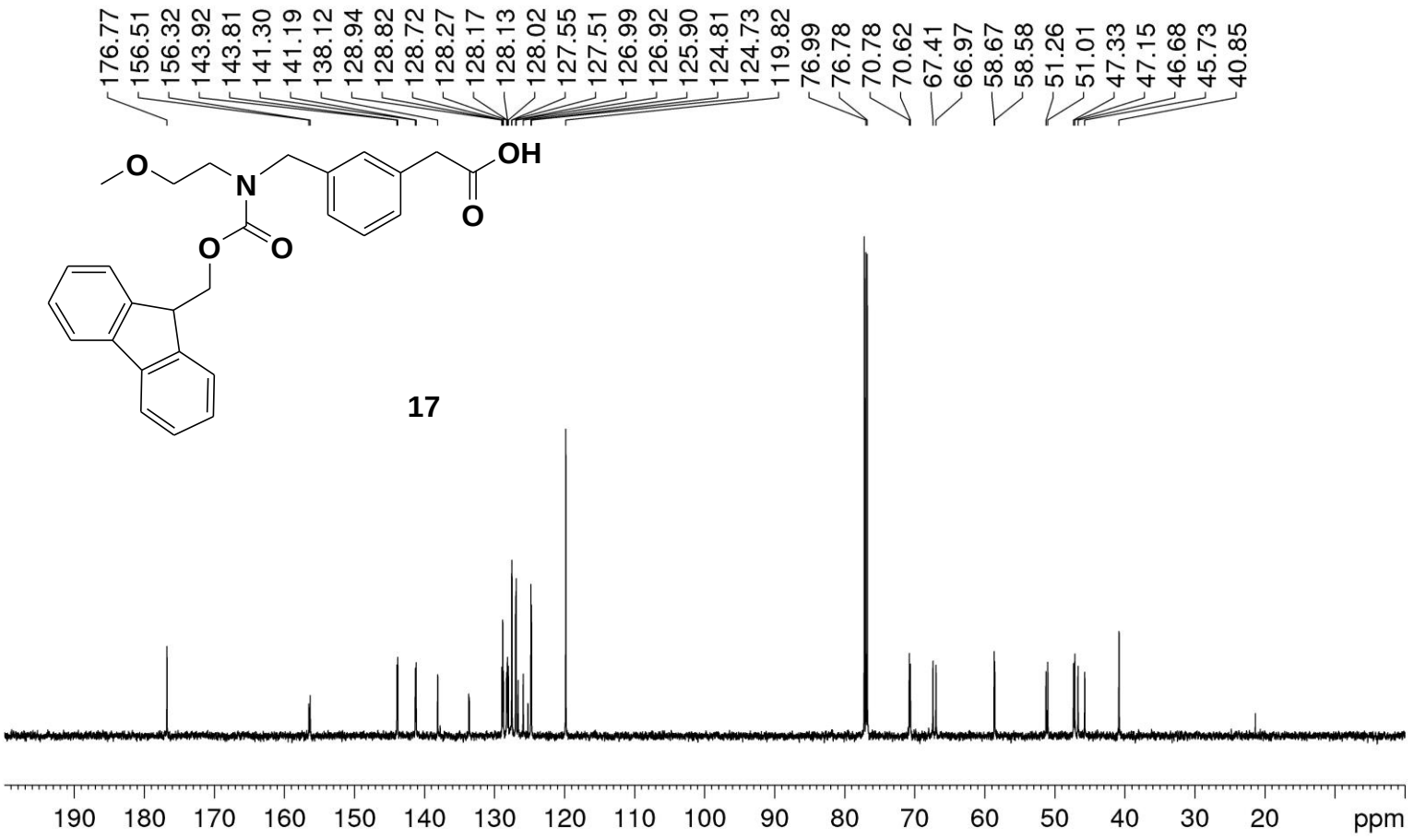


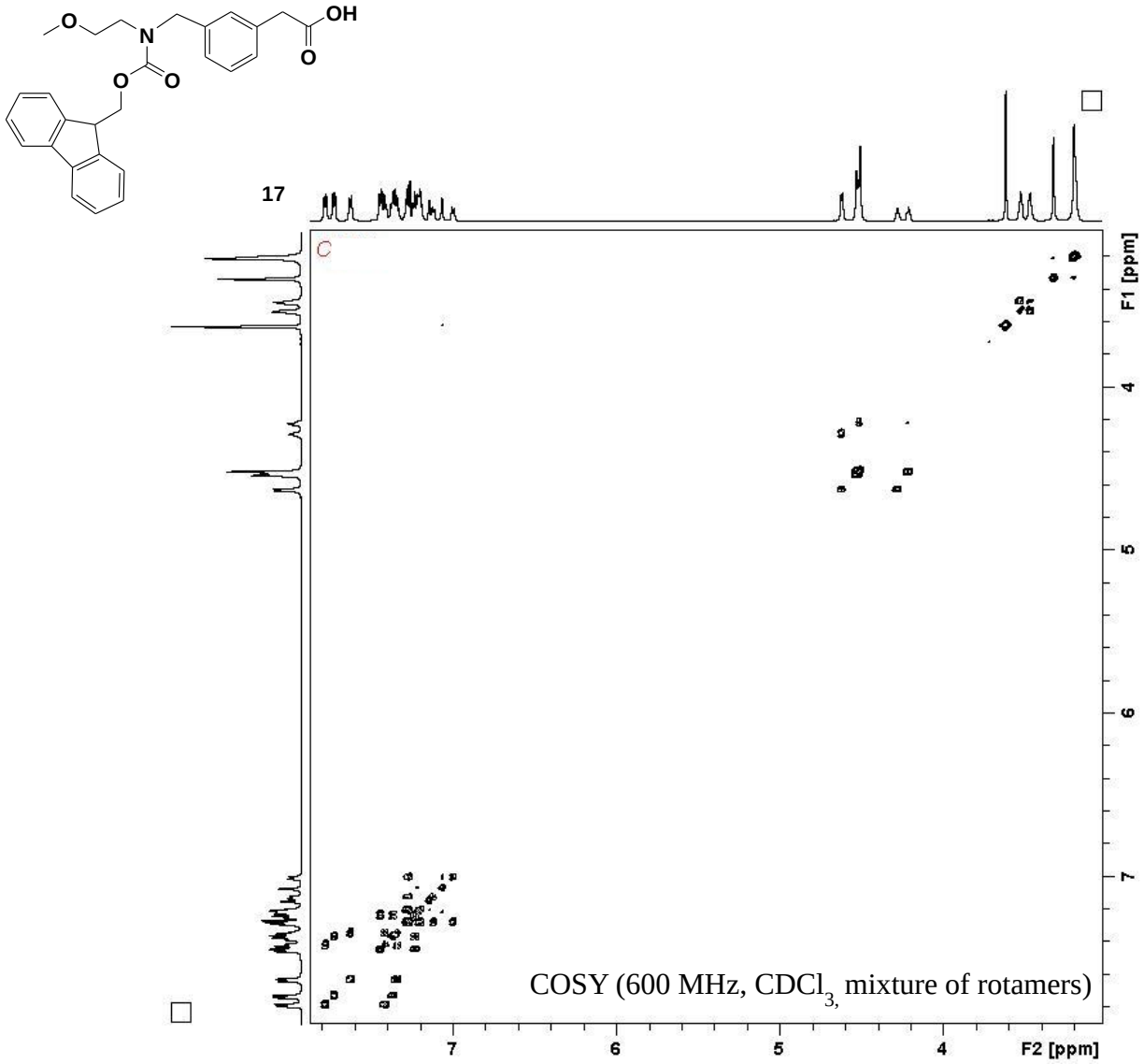
15

^{1}H NMR (600 MHz, $CDCl_3$, mixture of rotamers)

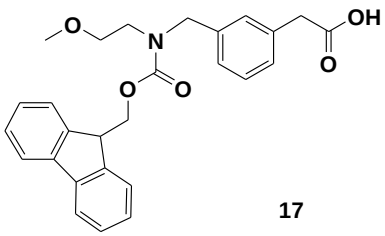


^{13}C NMR (150 MHz, $CDCl_{3,}$ mixture of rotamers)



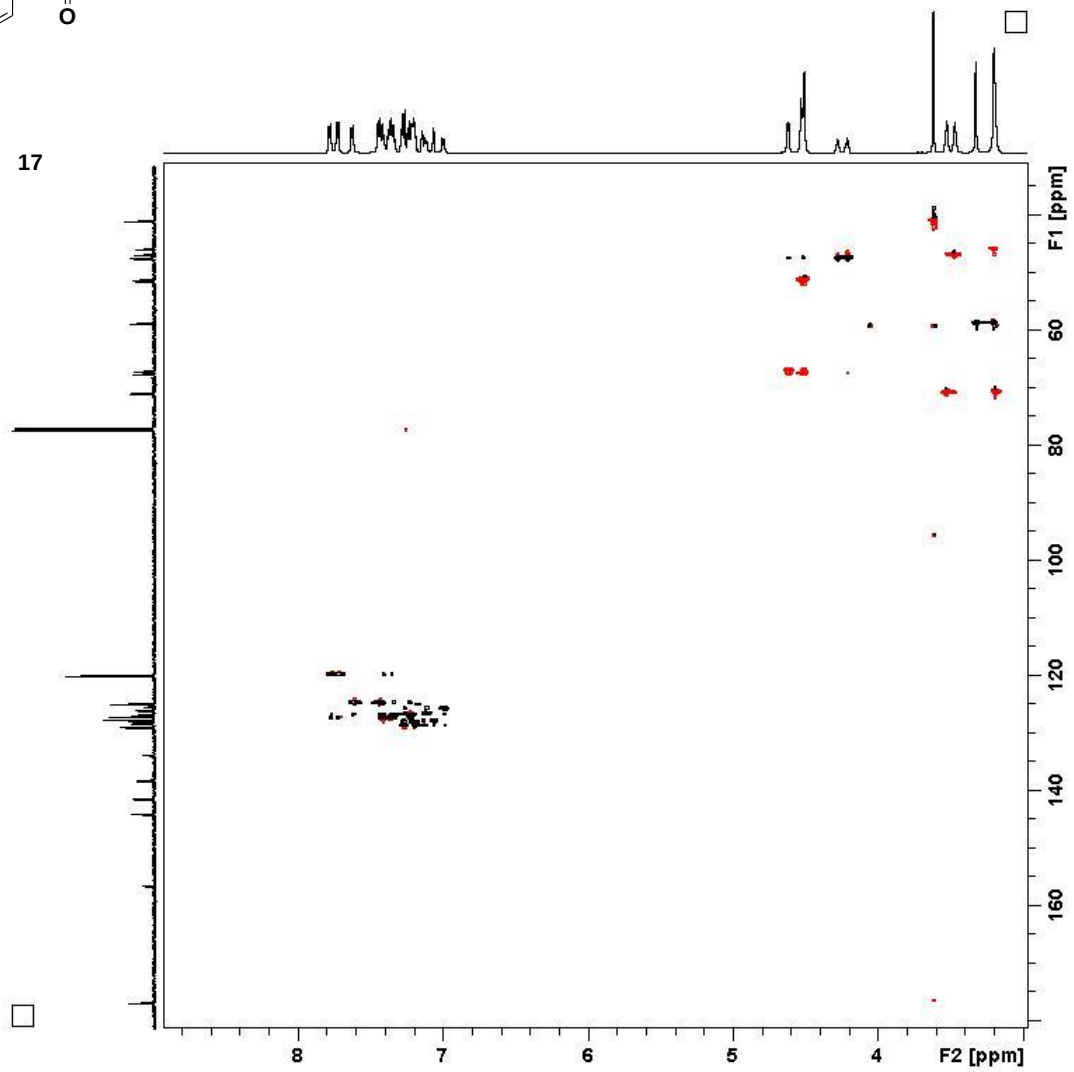


COSY (600 MHz, $CDCl_{3,}$ mixture of rotamers)

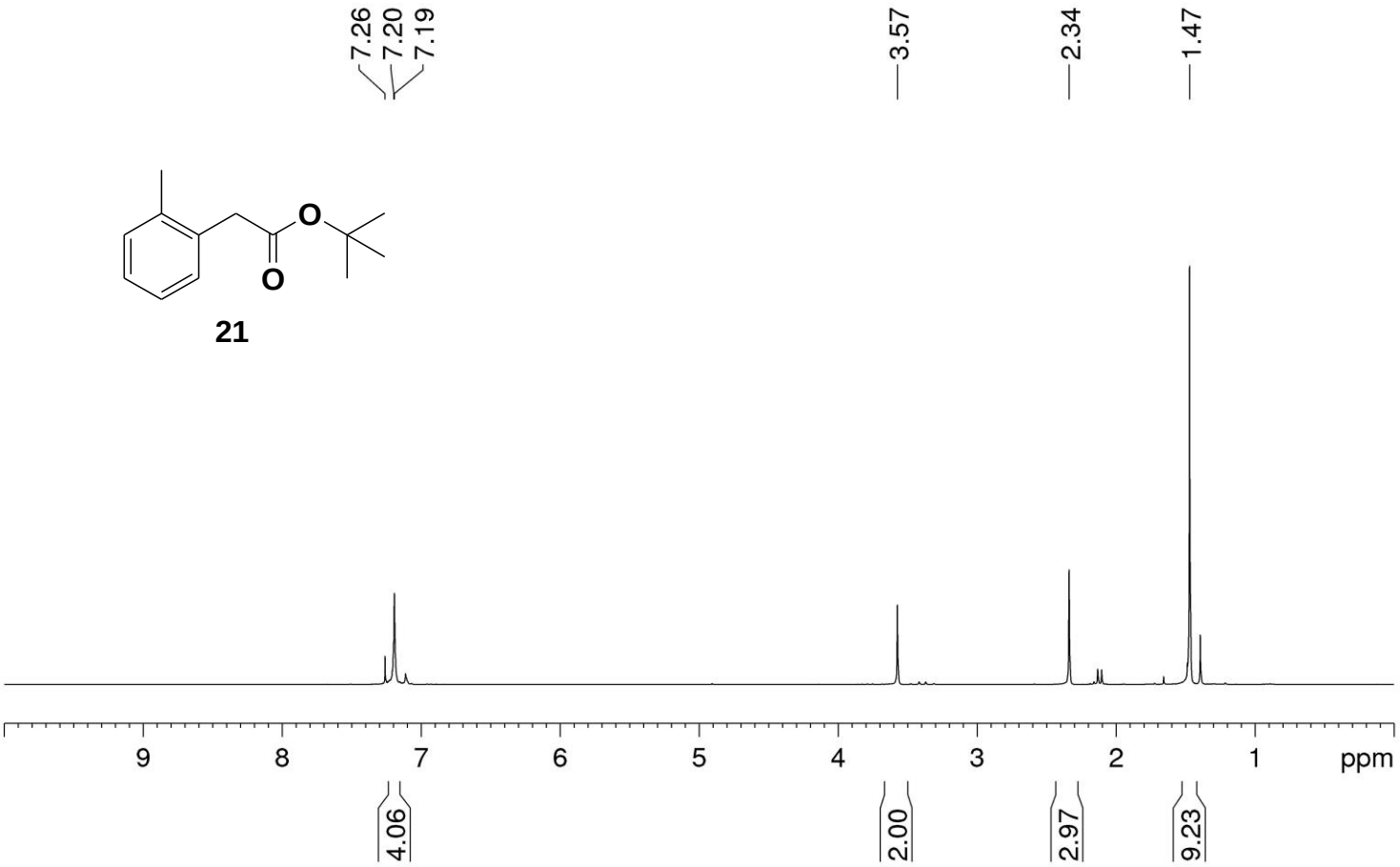


HSQC (600 MHz, $CDCl_3$, mixture of rotamers)

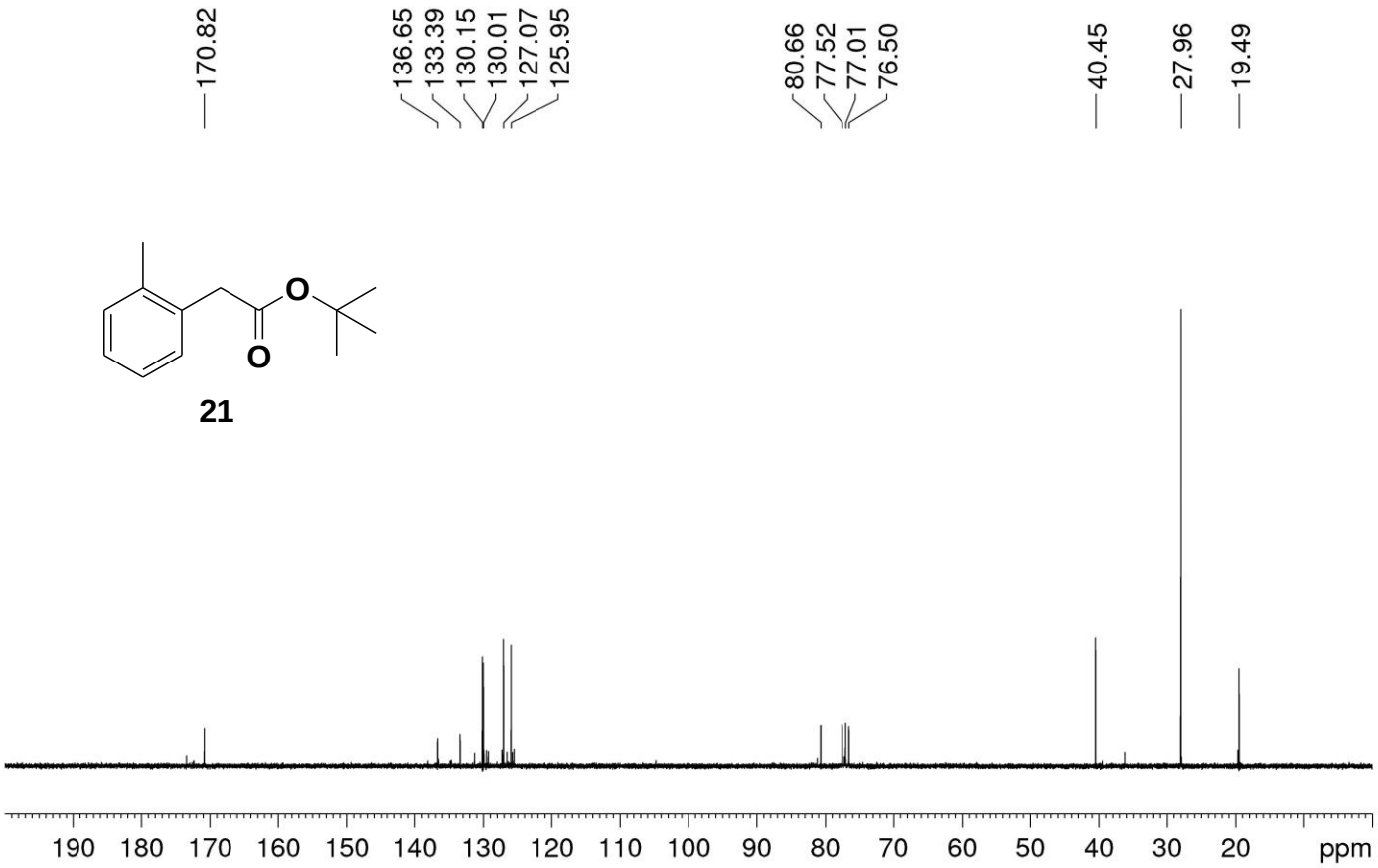
17



^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR (62.5 MHz, $CDCl_3$)



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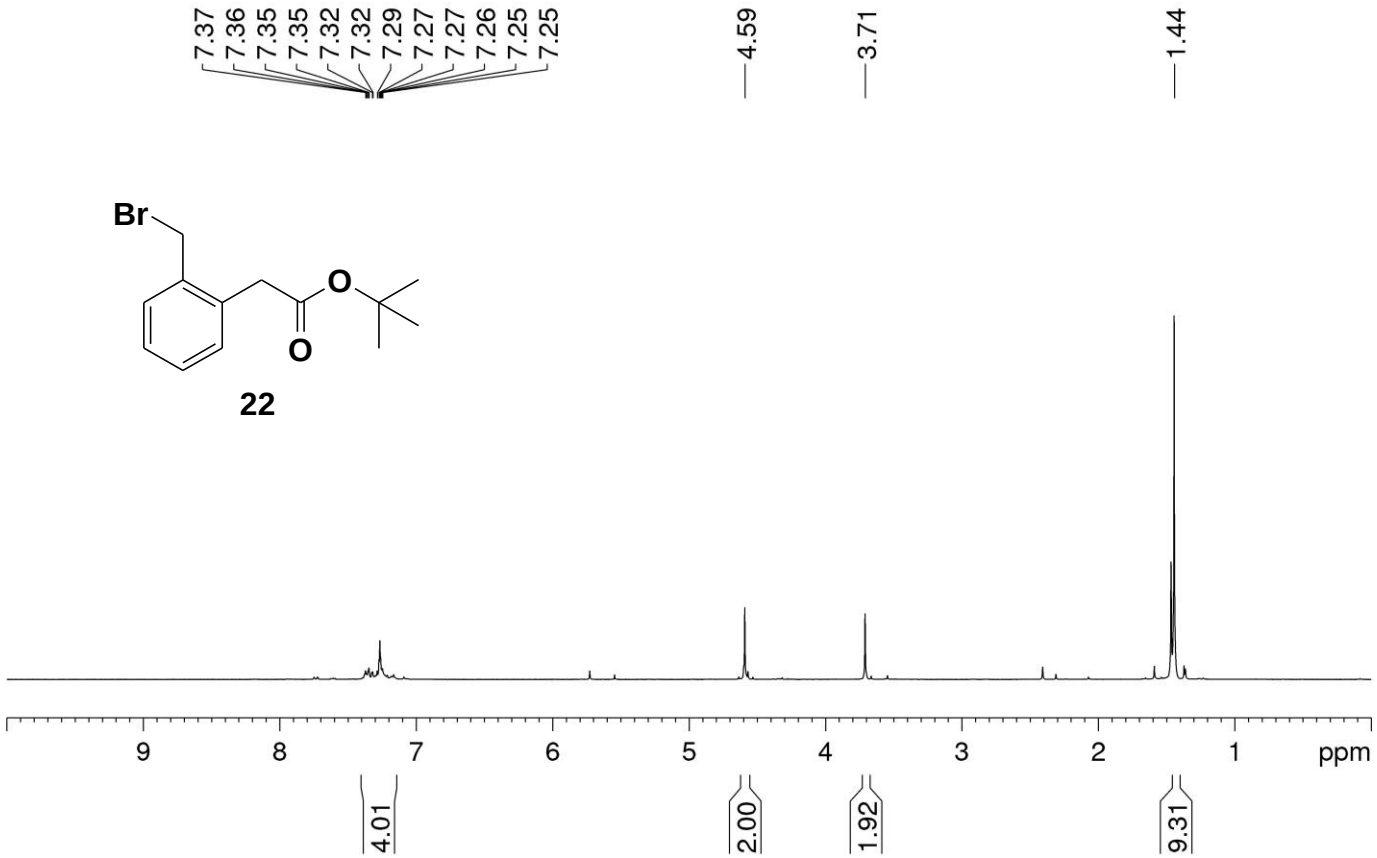
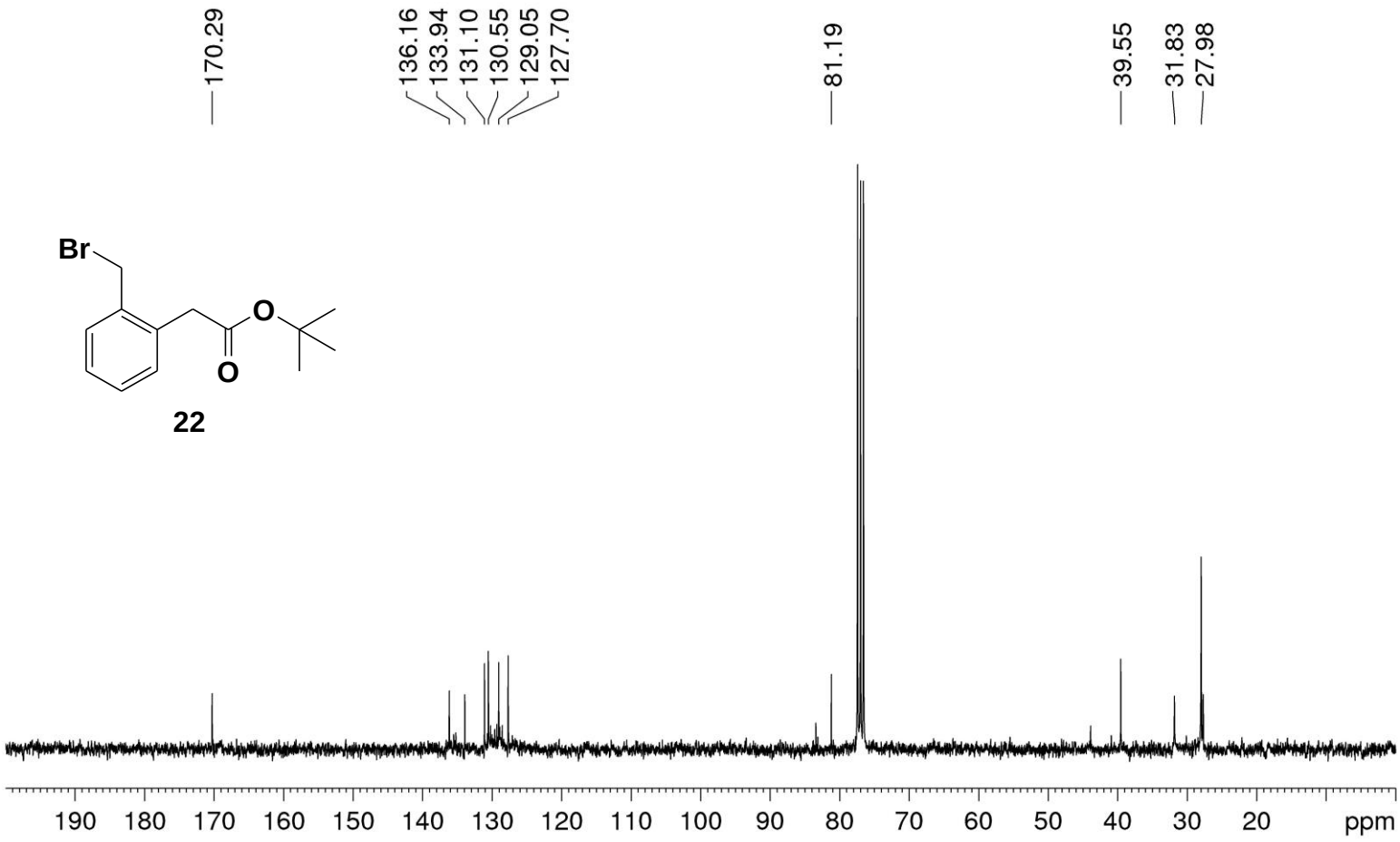
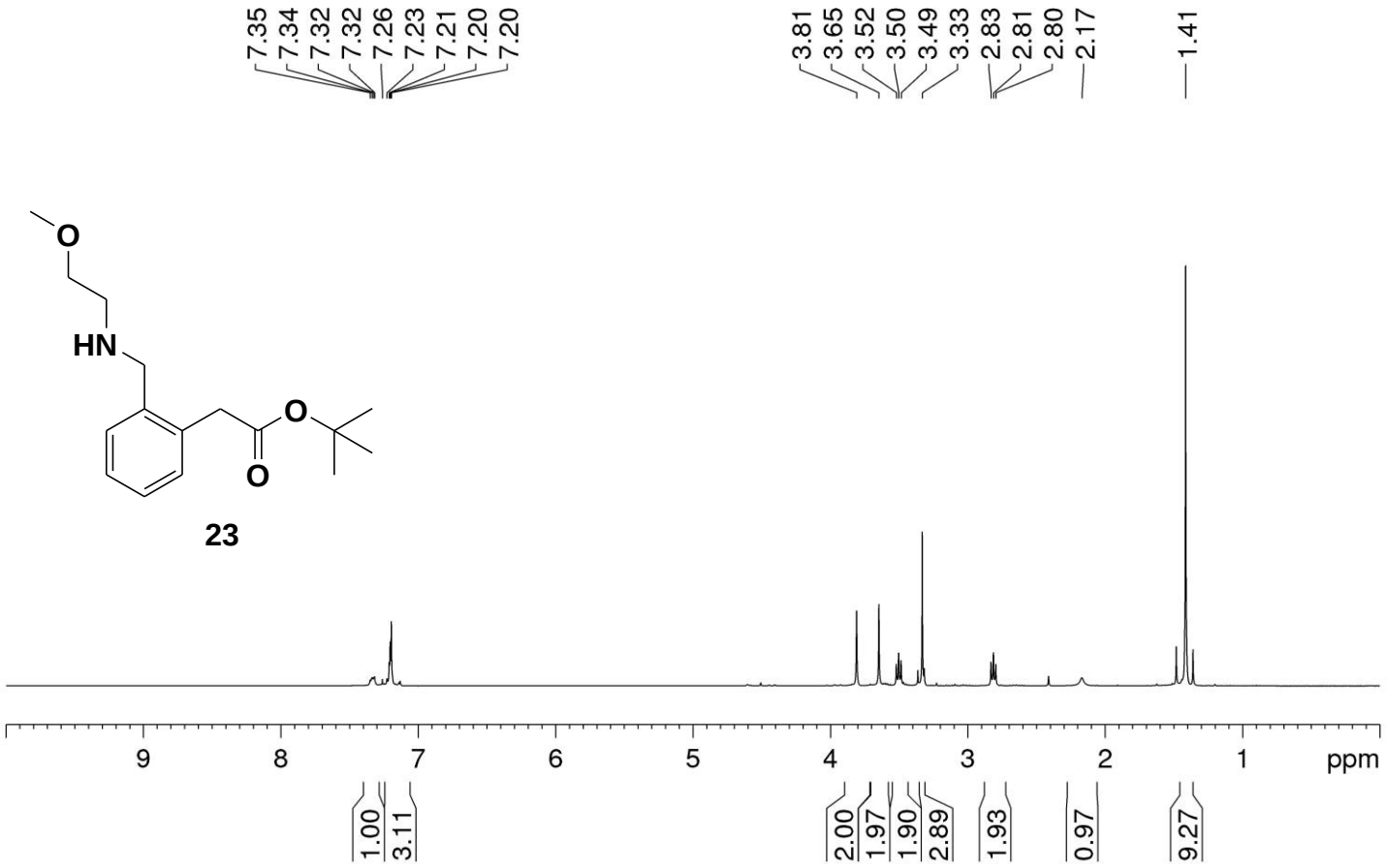
^{1}H NMR (300 MHz, $CDCl_3$)



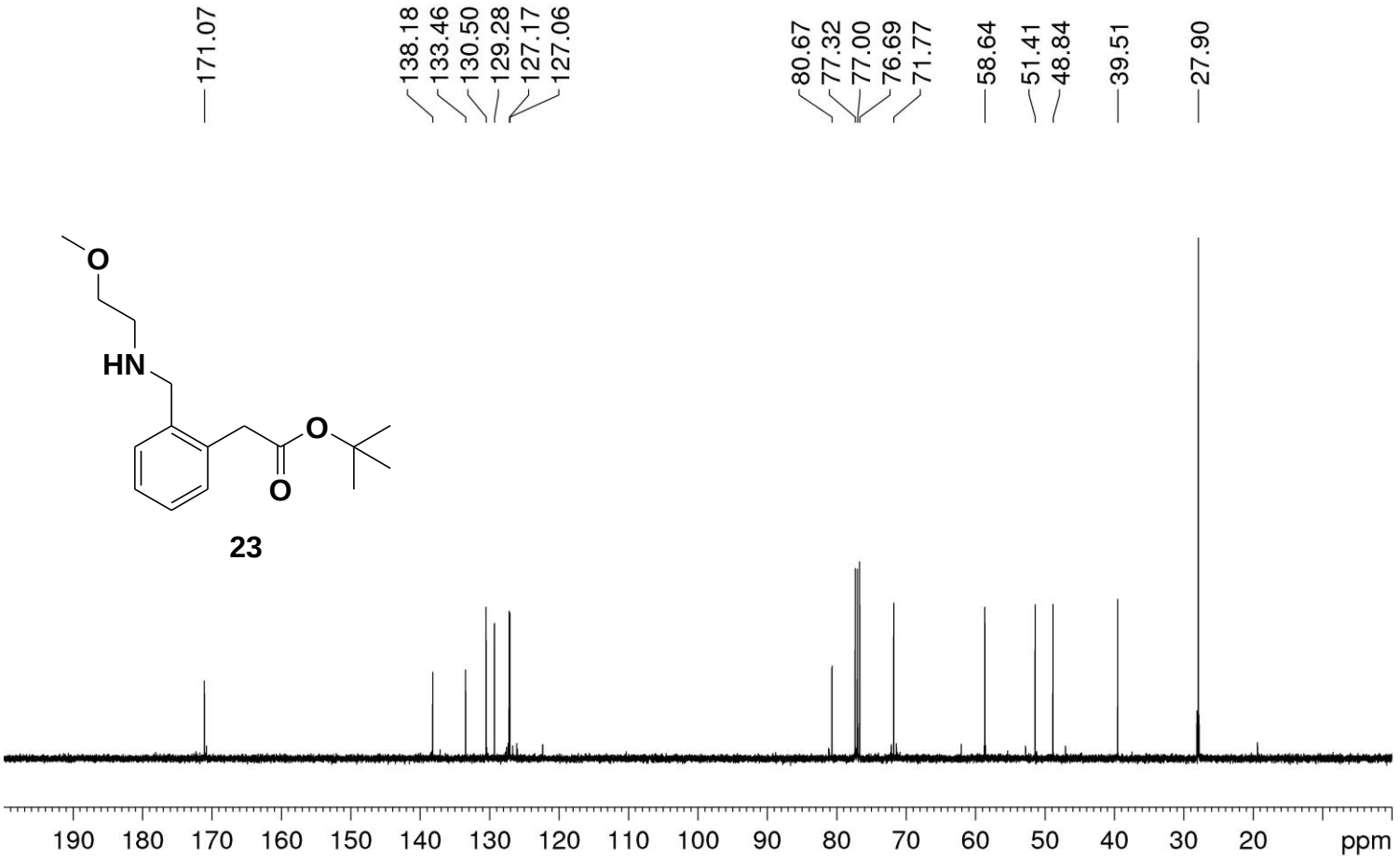
^{13}C NMR (75 MHz, $CDCl_3$)



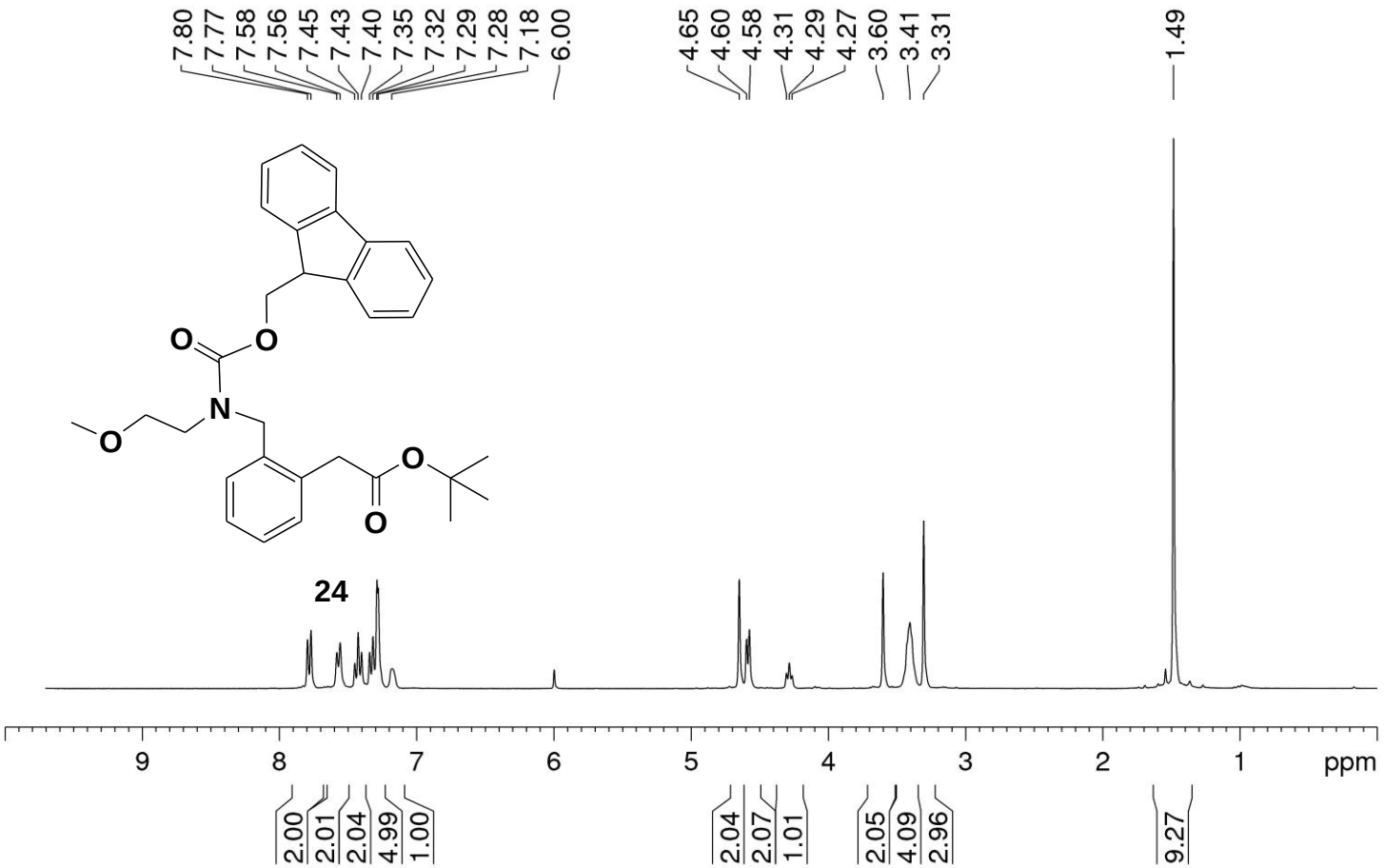
^{1}H NMR (300 MHz, $CDCl_3$)



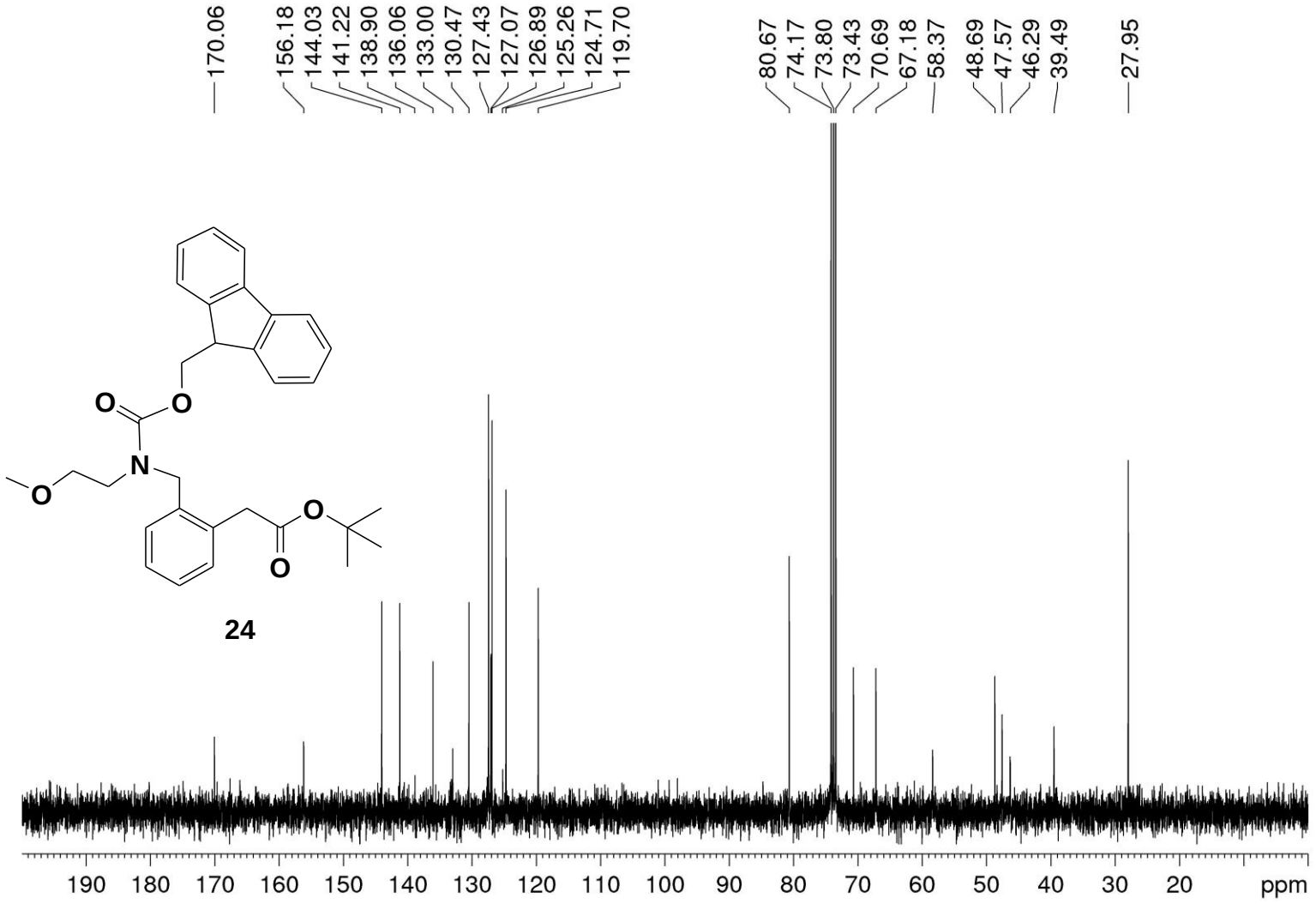
^{13}C NMR (100 MHz, $CDCl_3$)



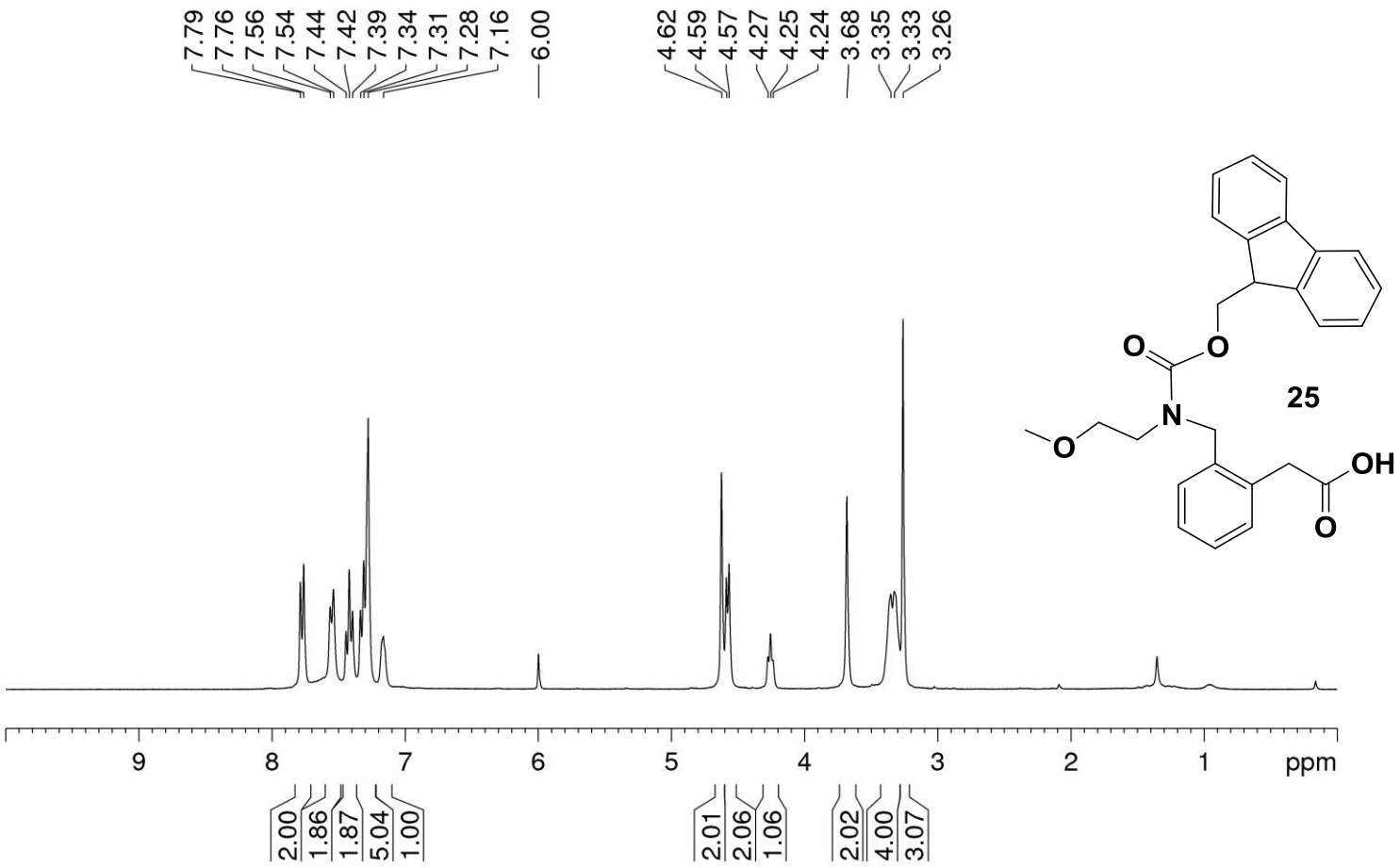
^{1}H NMR (300 MHz, TCDE, 373 K)



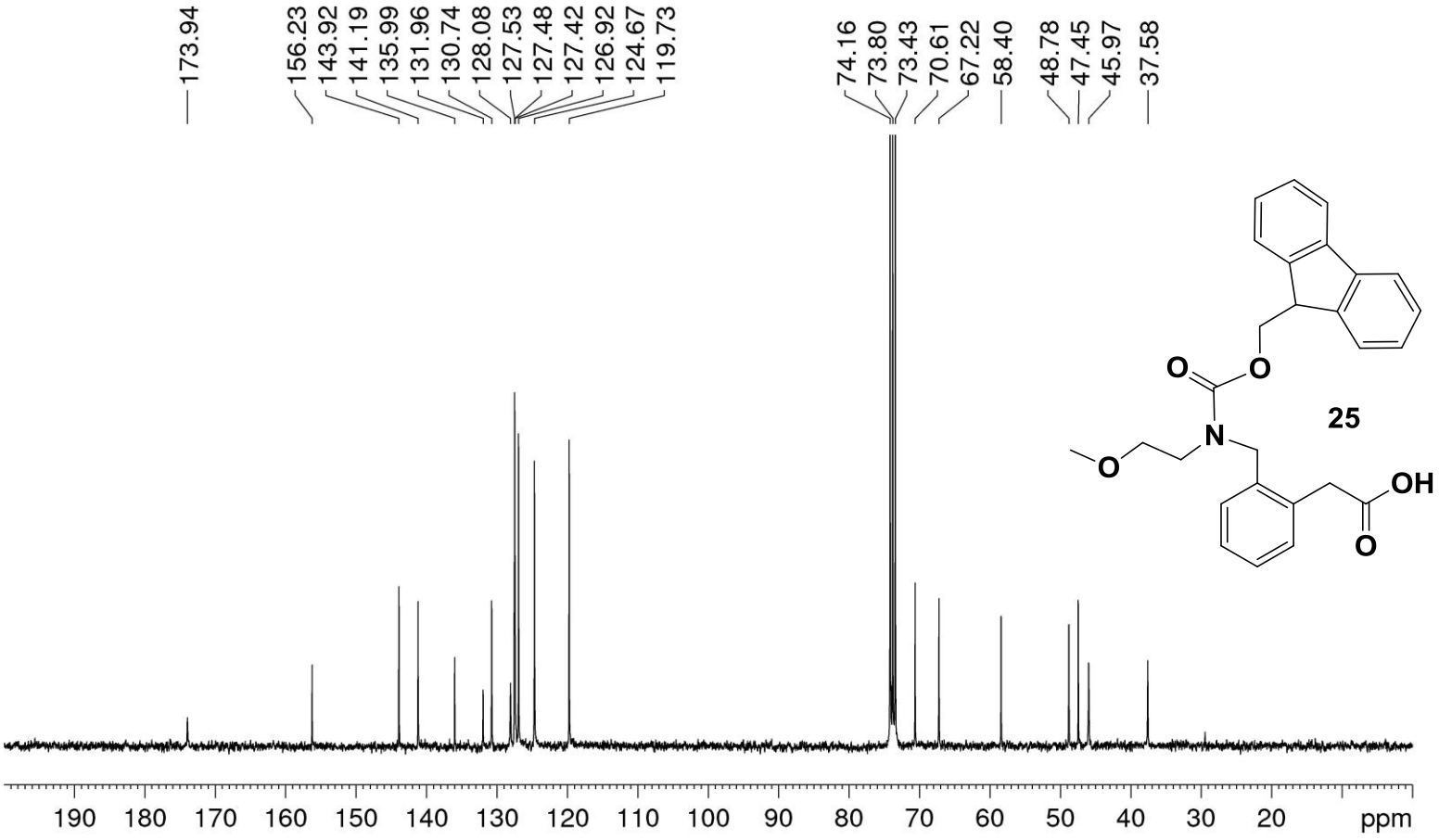
^{13}C NMR (75 MHz, TCDE, 373 K)



^{1}H NMR (300 MHz, TCDE, 353 K)

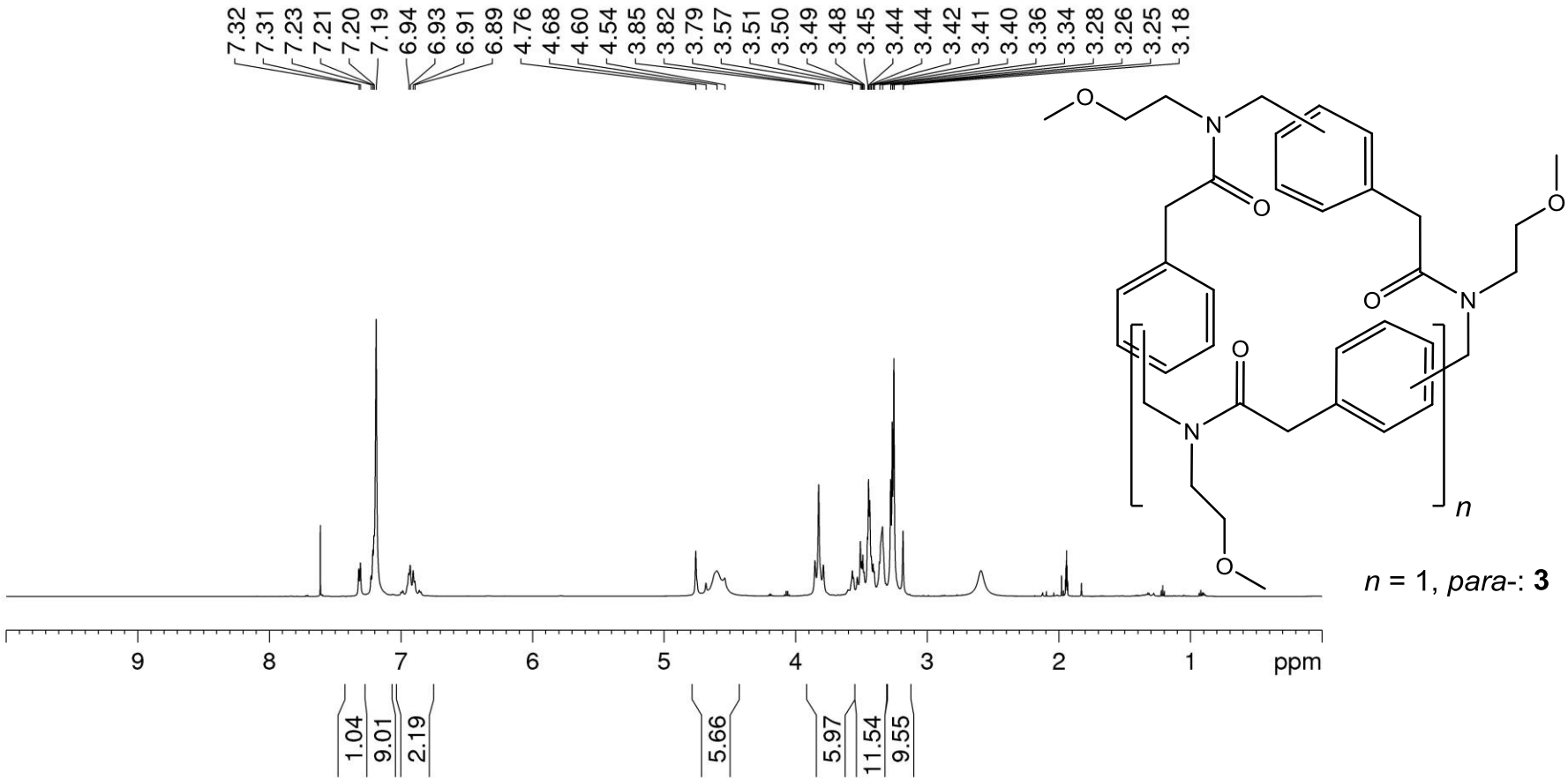


^{13}C NMR (75 MHz, TCDE, 353 K)

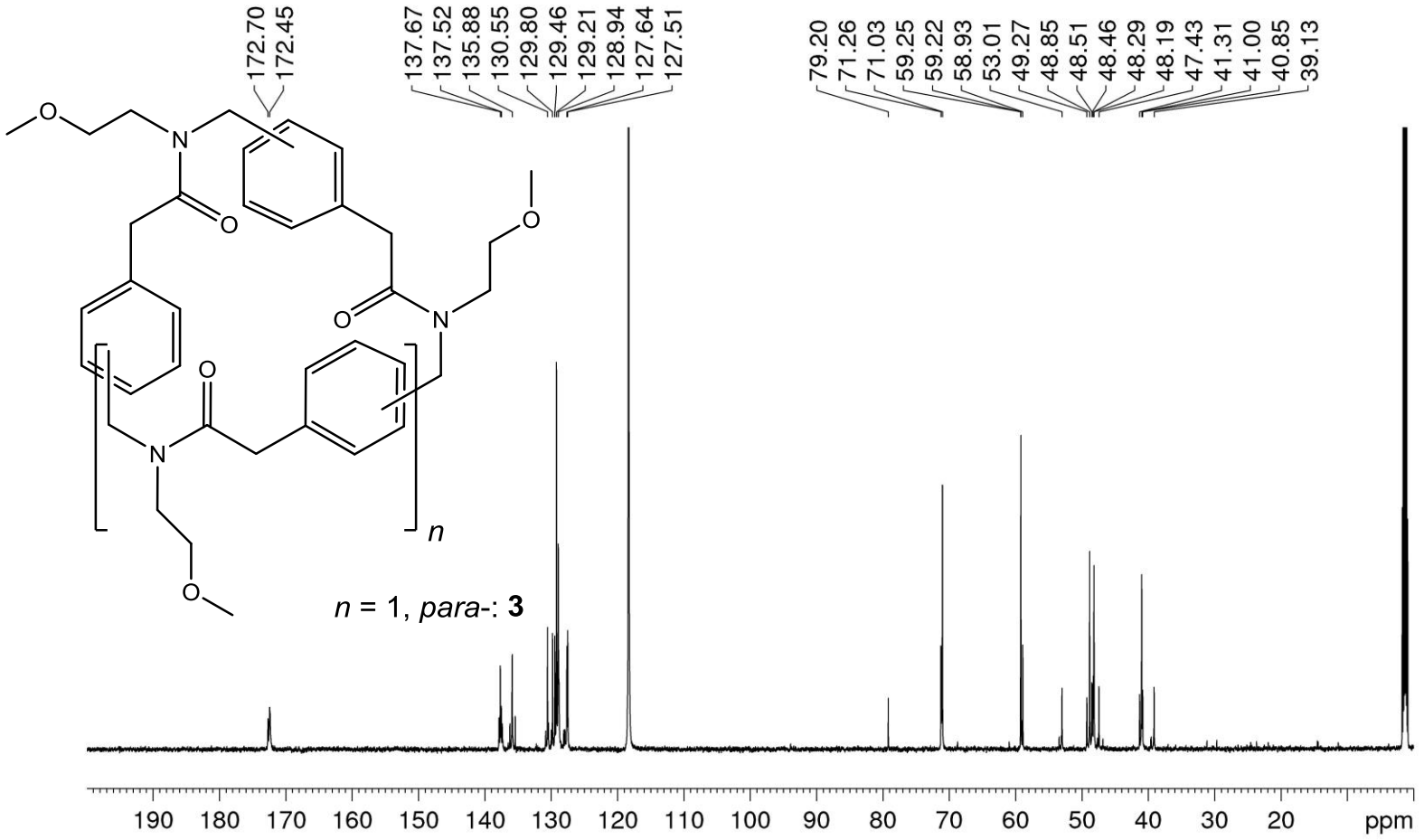


2.2 Spectra of the cyclic benzylopeptoids 3-8

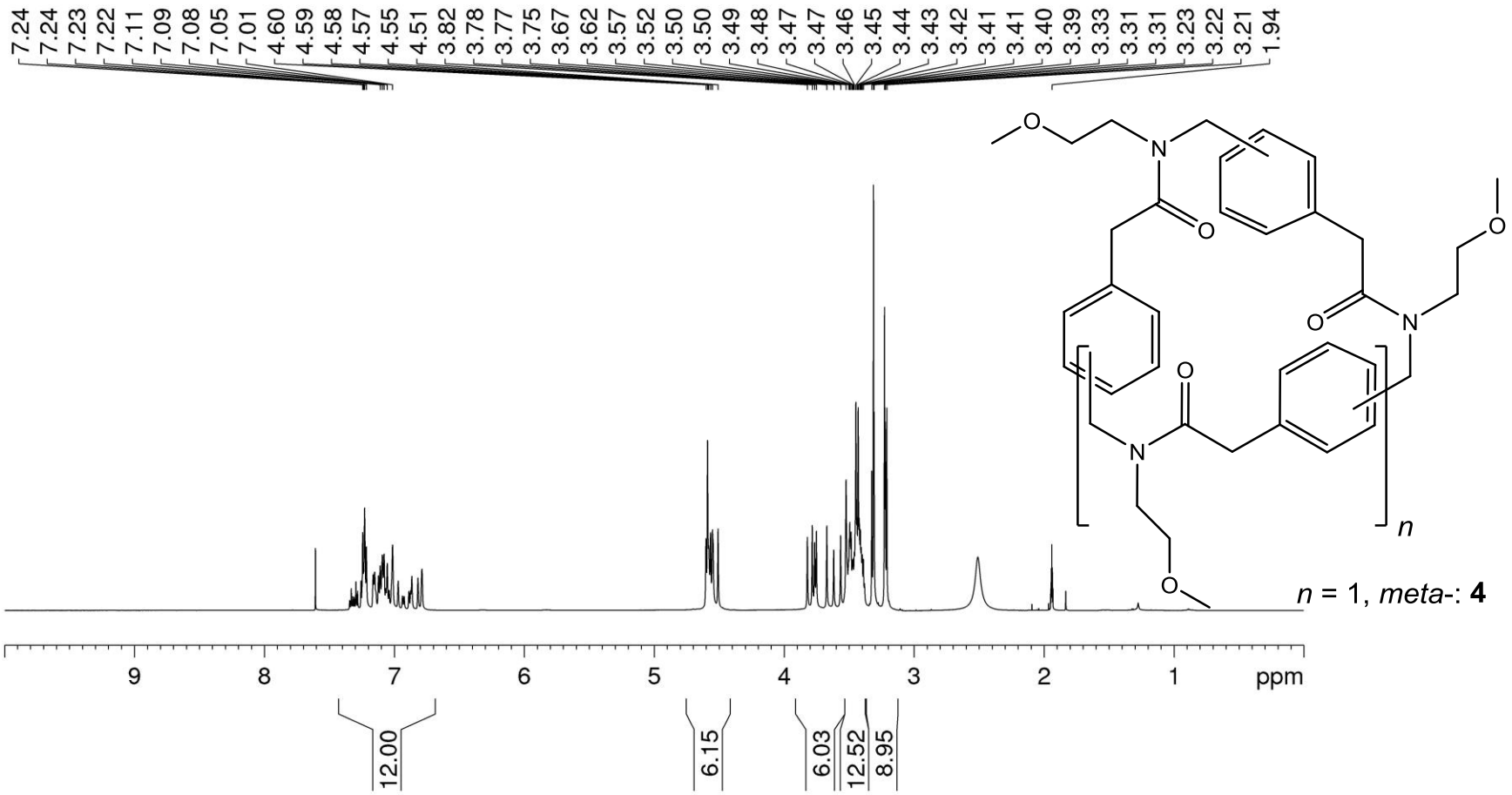
^{1}H-NMR: (600 MHz, CD_3CN, mixture of rotamers)



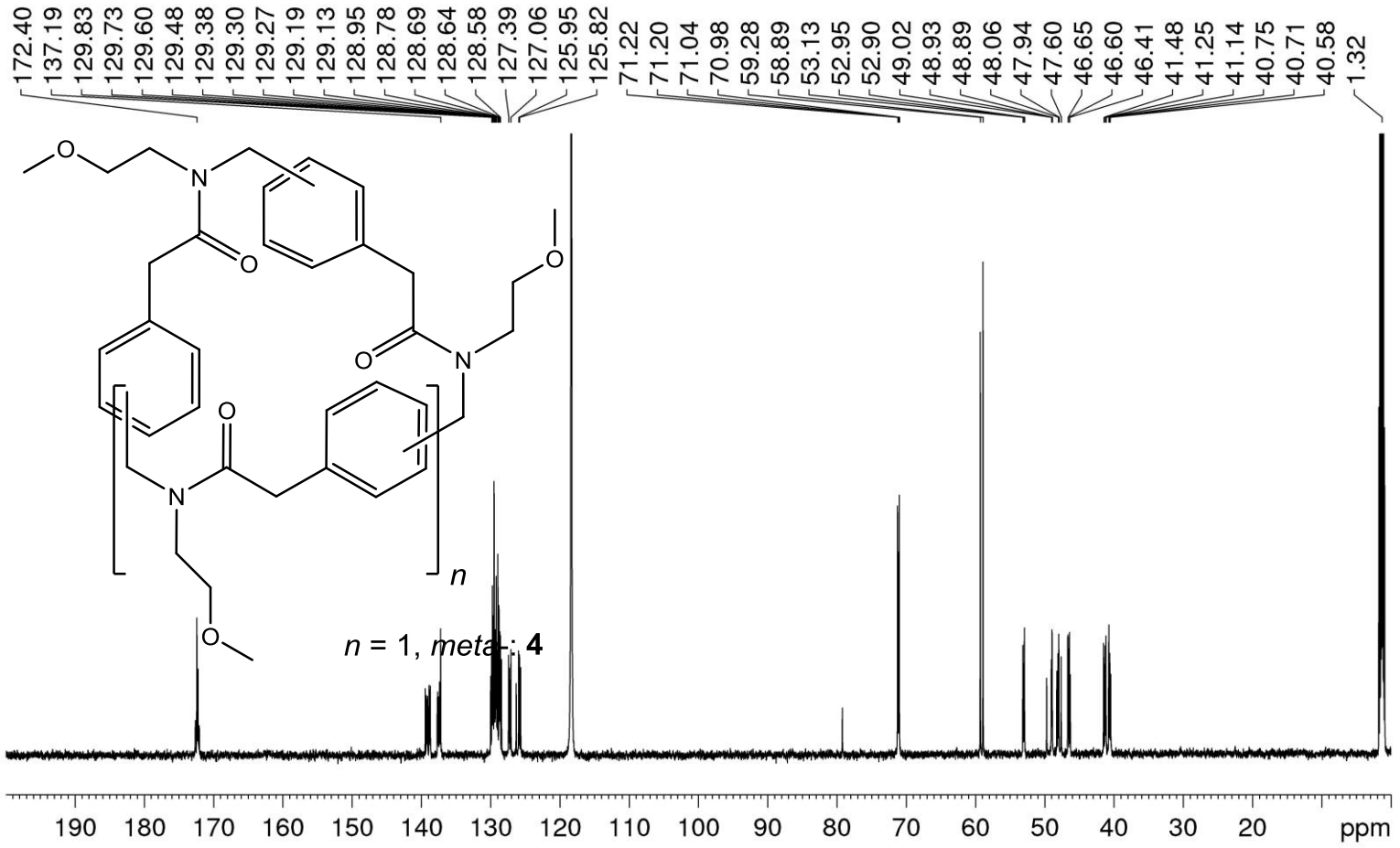
^{13}C-NMR: (150 MHz, CD_3CN, mixture of rotamers)



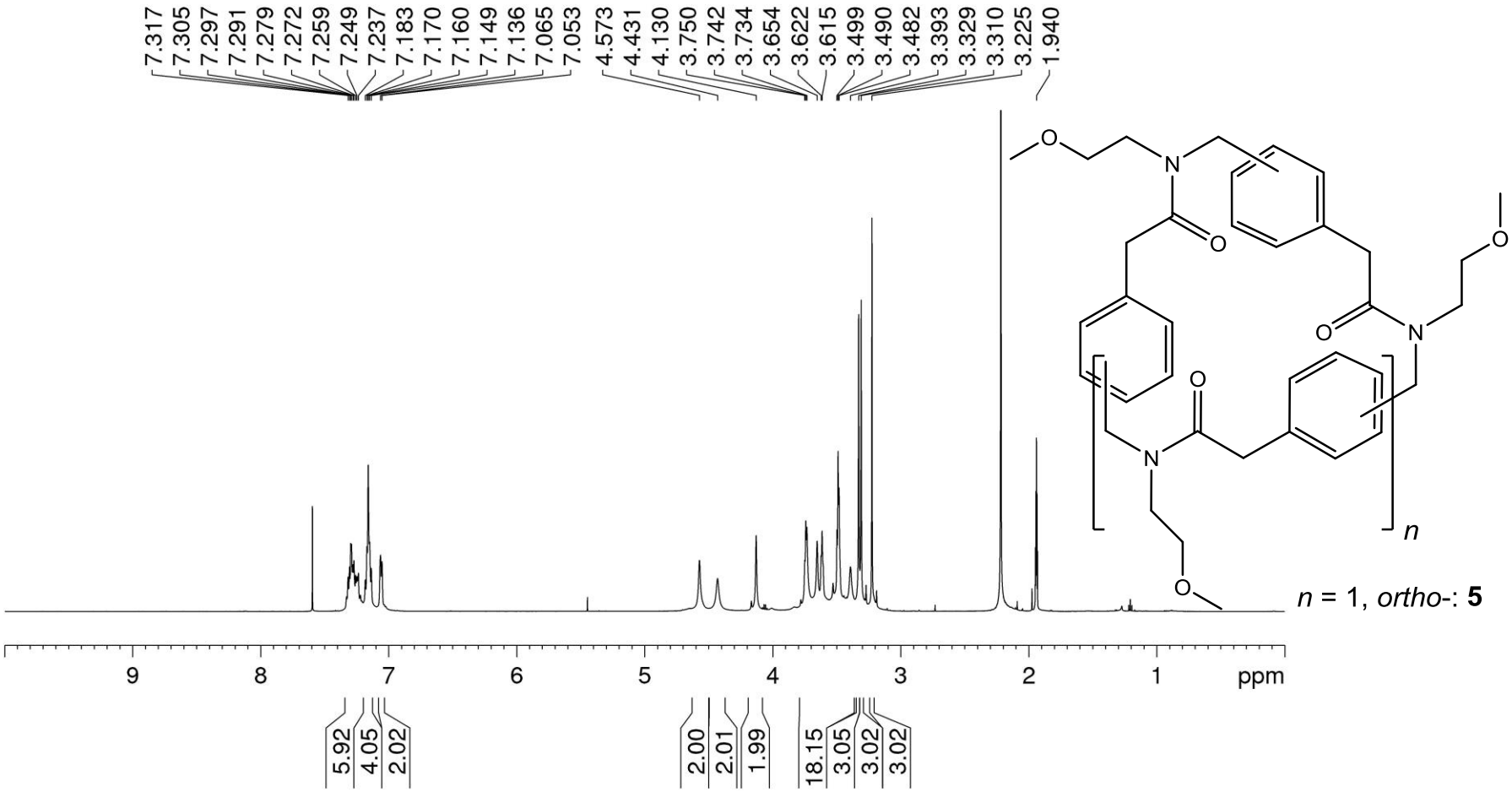
^{1}H-NMR: (600 MHz, CD_3CN, mixture of rotamers)



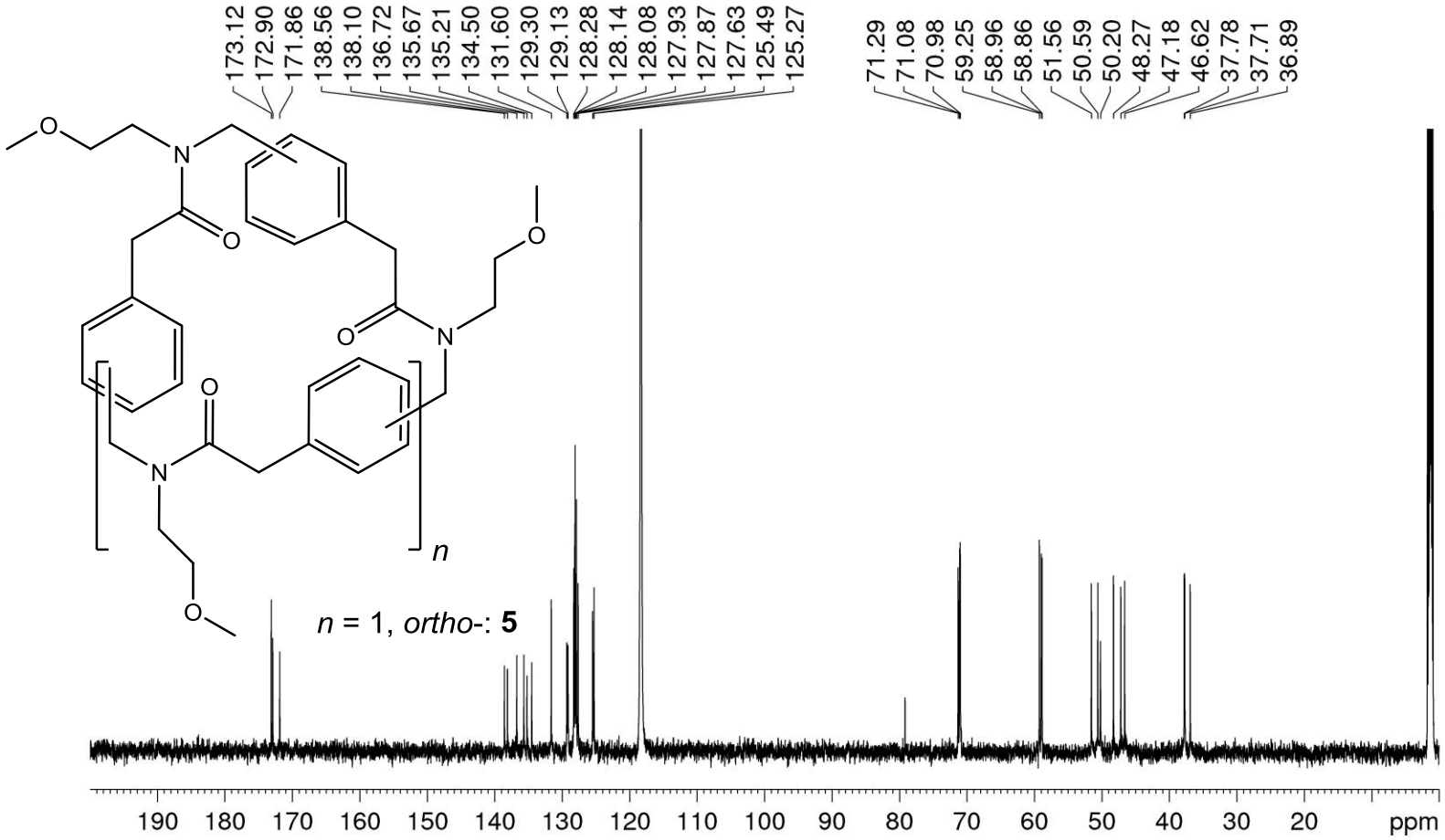
^{13}C-NMR: (150 MHz, CD_3CN, mixture of rotamers)



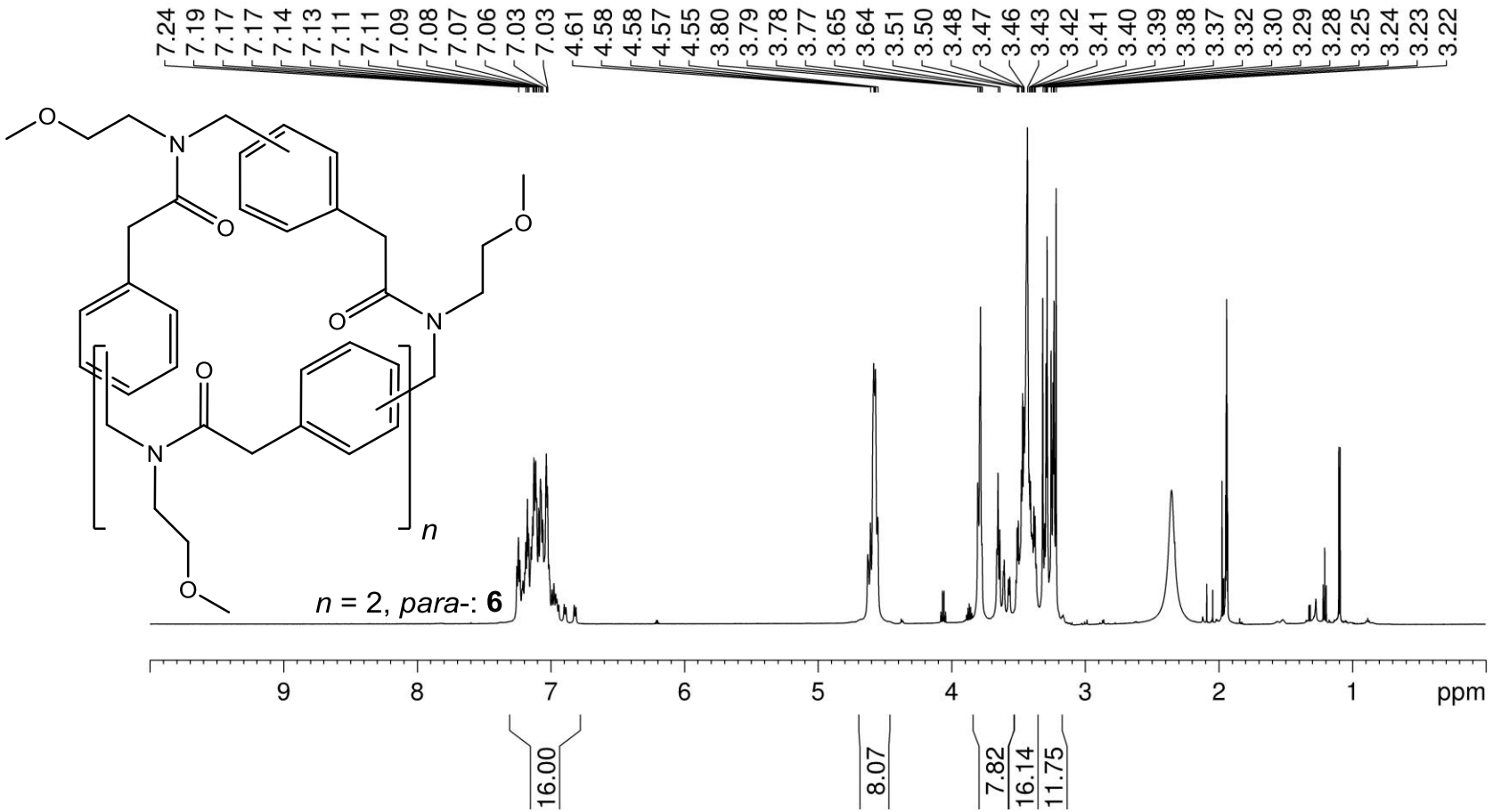
^{1}H-NMR: (600 MHz, CD_3CN, mixture of rotamers)



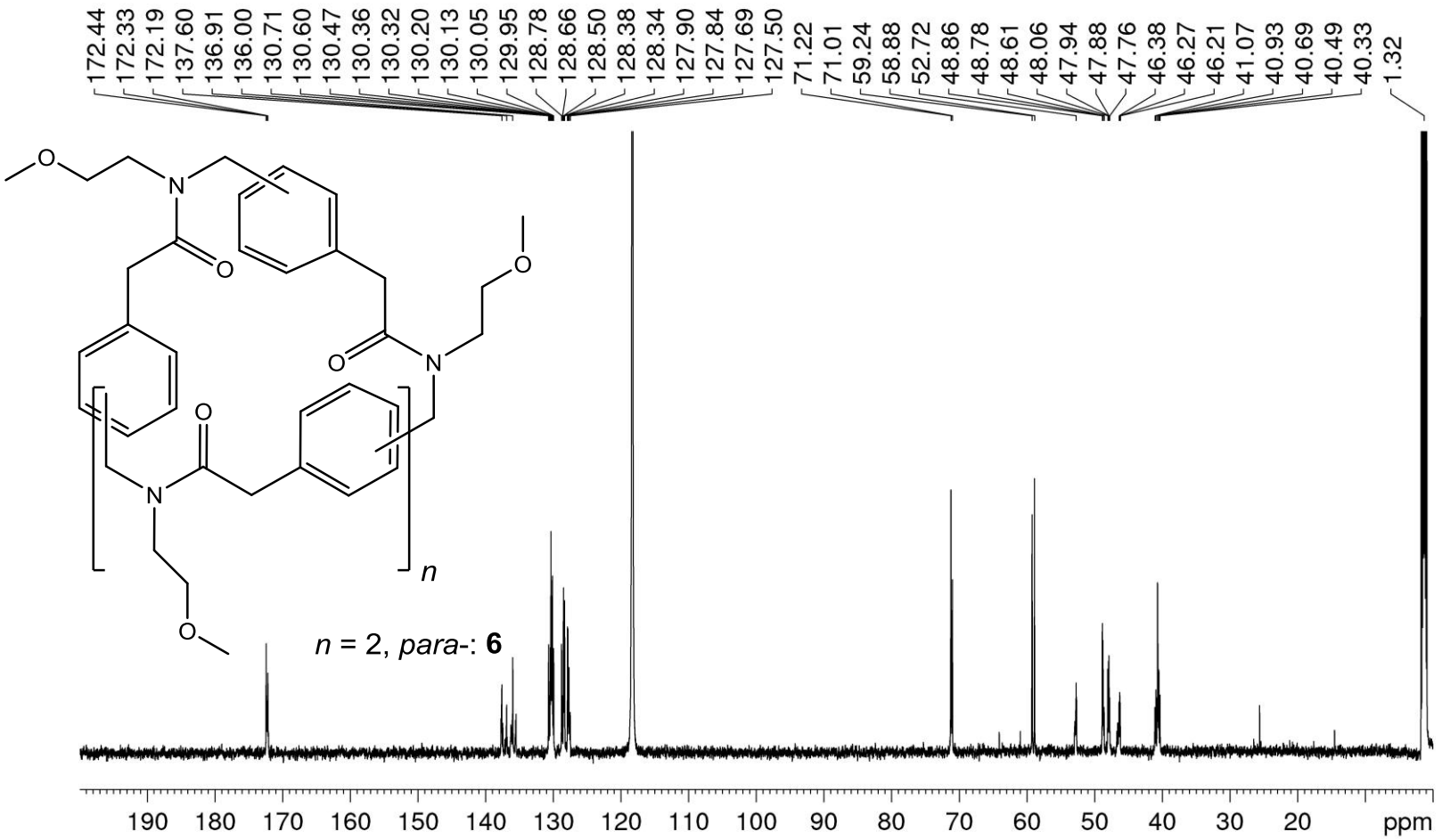
^{13}C-NMR: (150 MHz, CD_3CN, mixture of rotamers)



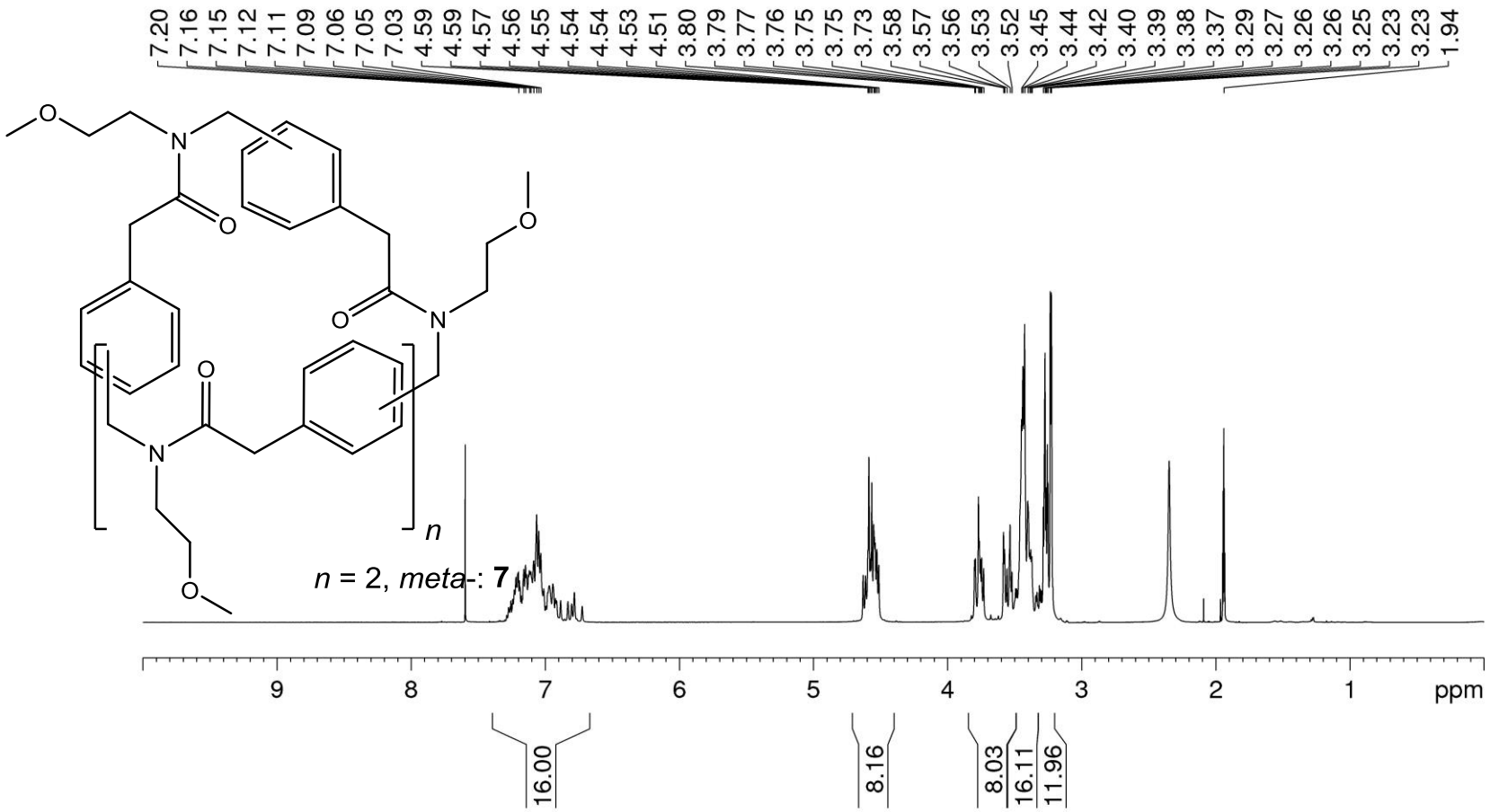
^{1}H-NMR: (600 MHz, CD_3CN, mixture of rotamers)



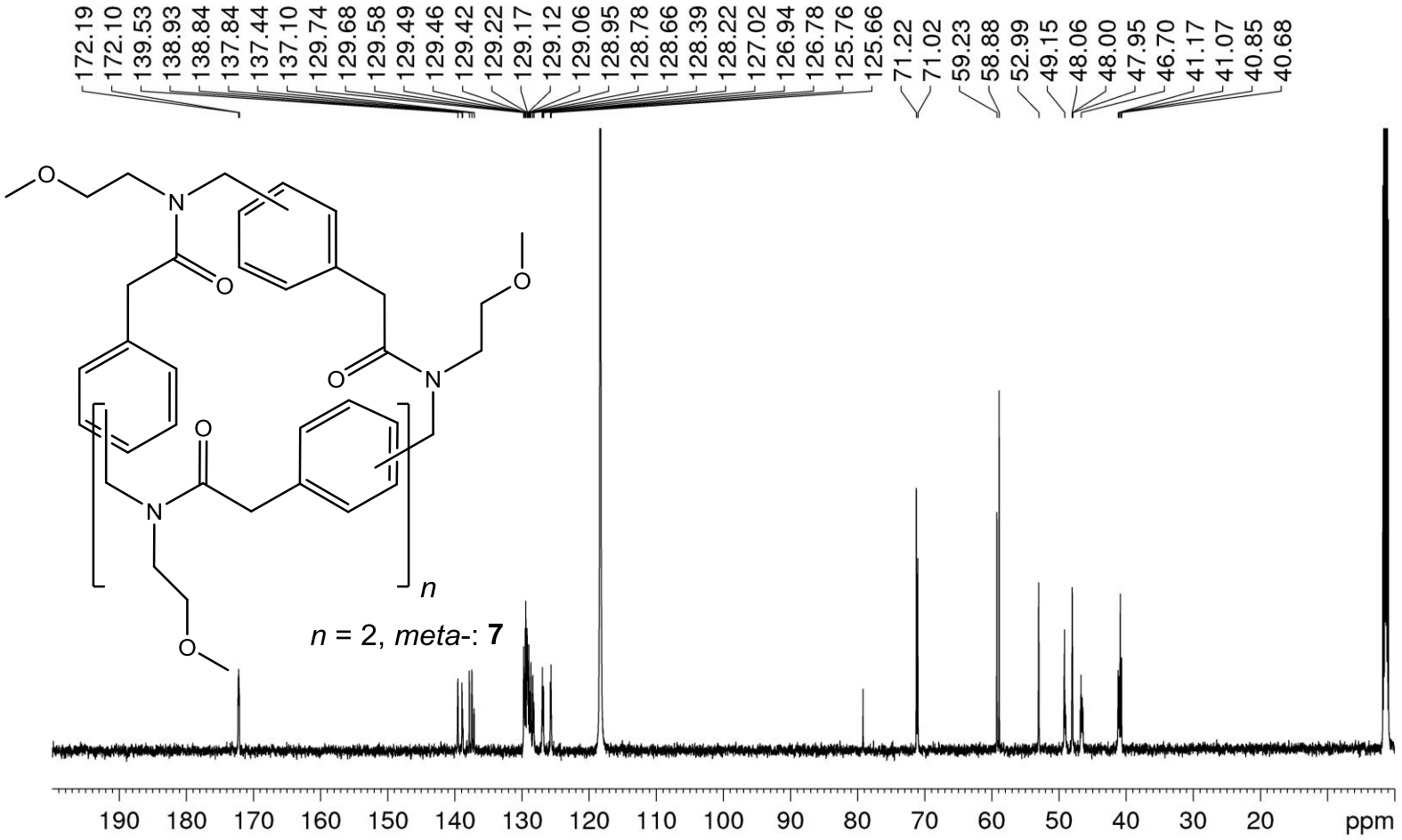
^{13}C-NMR: (150 MHz, CD_3CN, mixture of rotamers)



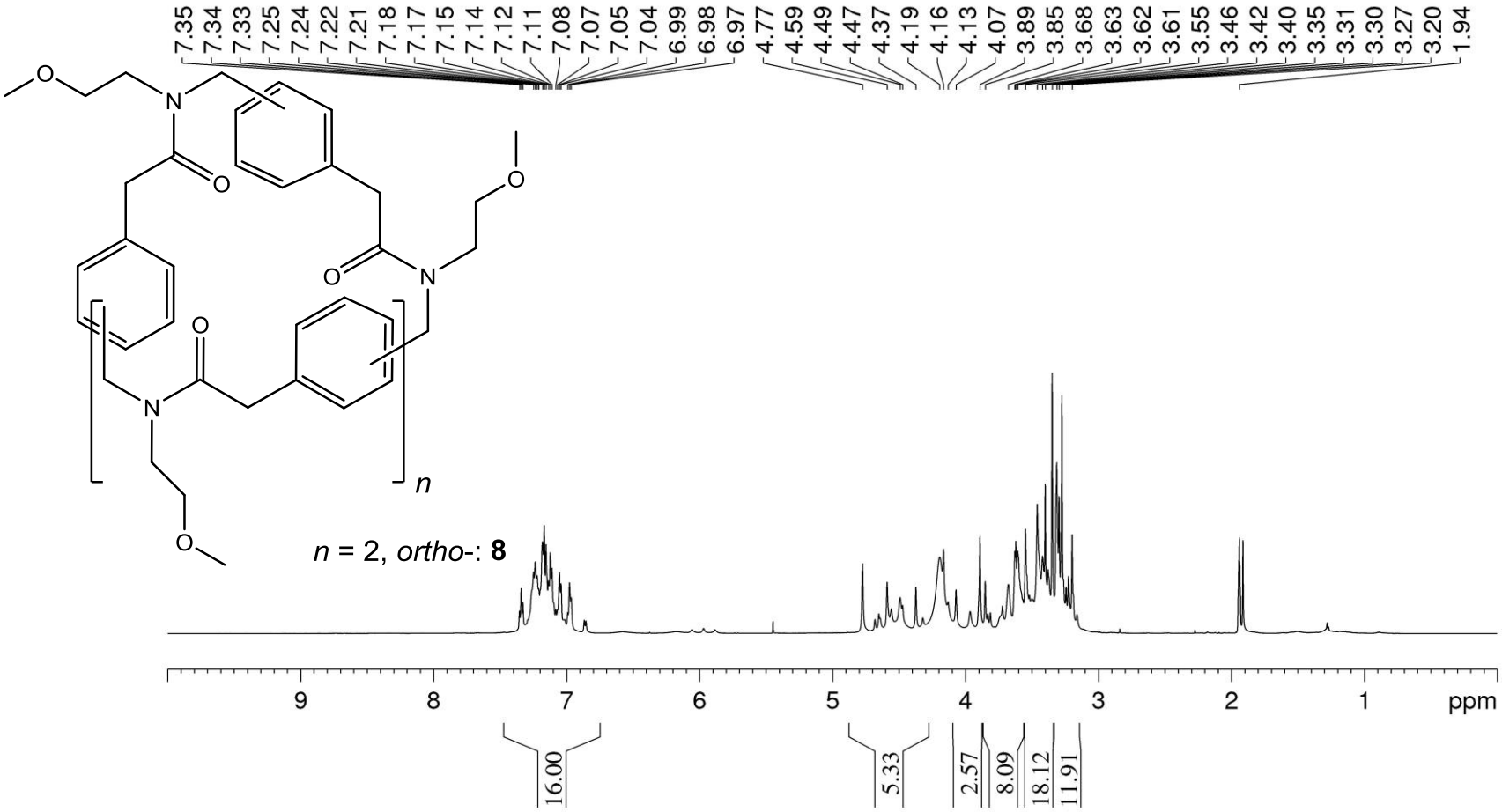
^{1}H-NMR: (600 MHz, CD_3CN, mixture of rotamers)



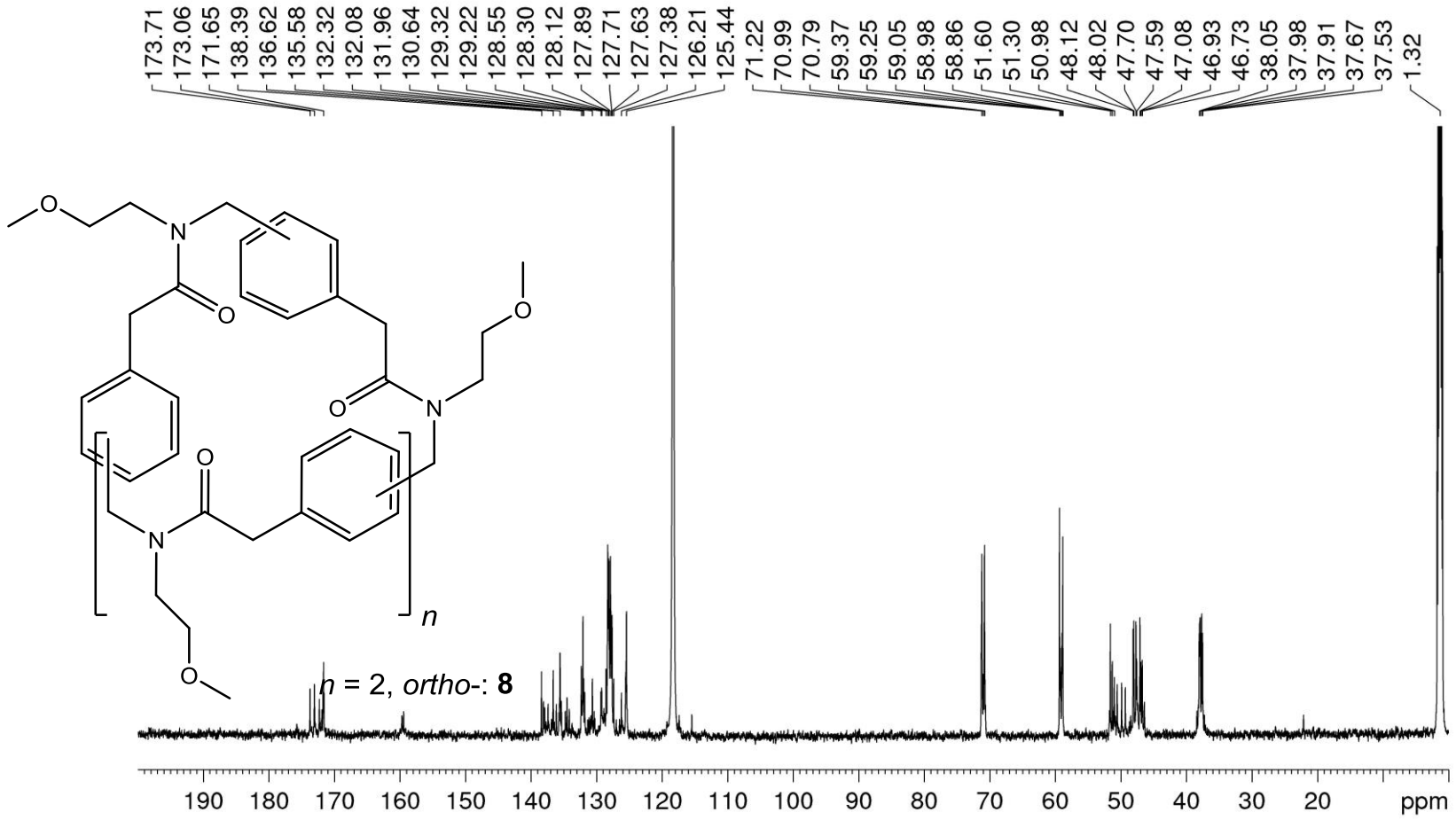
^{13}C-NMR: (150 MHz, CD_3CN, mixture of rotamers)



^{1}H-NMR: (600 MHz, CD_3CN, mixture of rotamers)

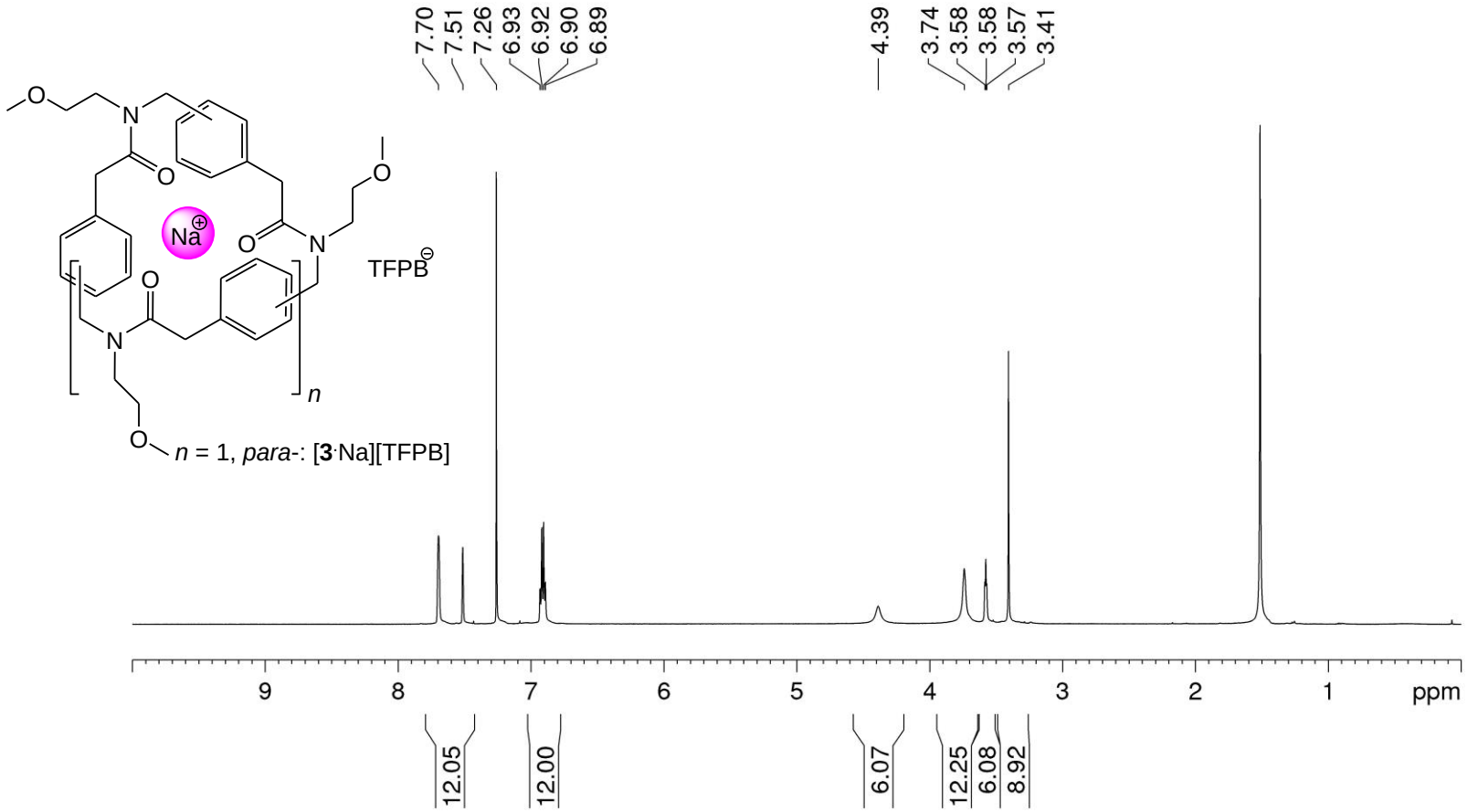


^{13}C-NMR: (150 MHz, CD_3CN, mixture of rotamers)

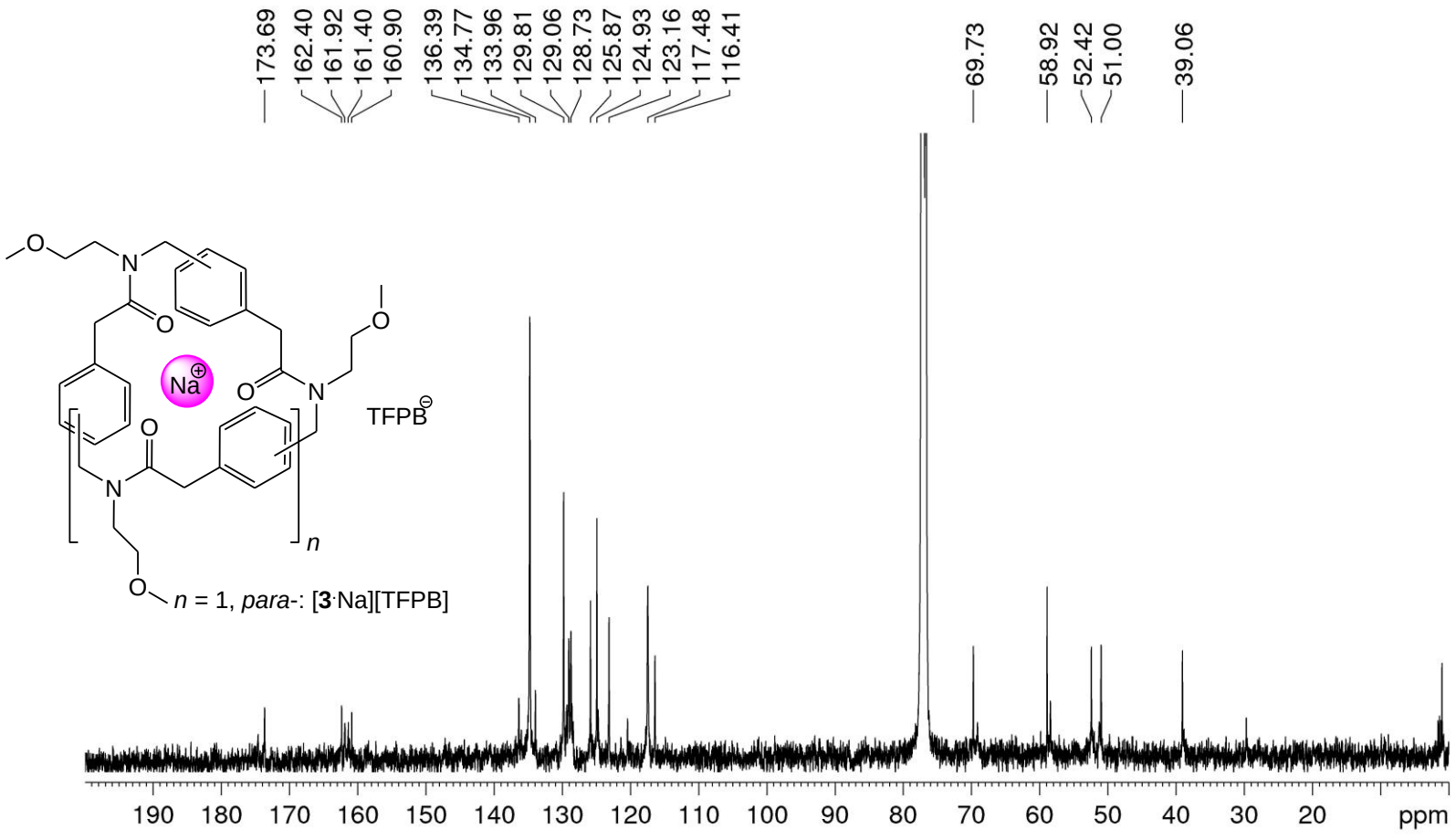


2.3 Spectra of the complexed benzylopeptoids 3-8

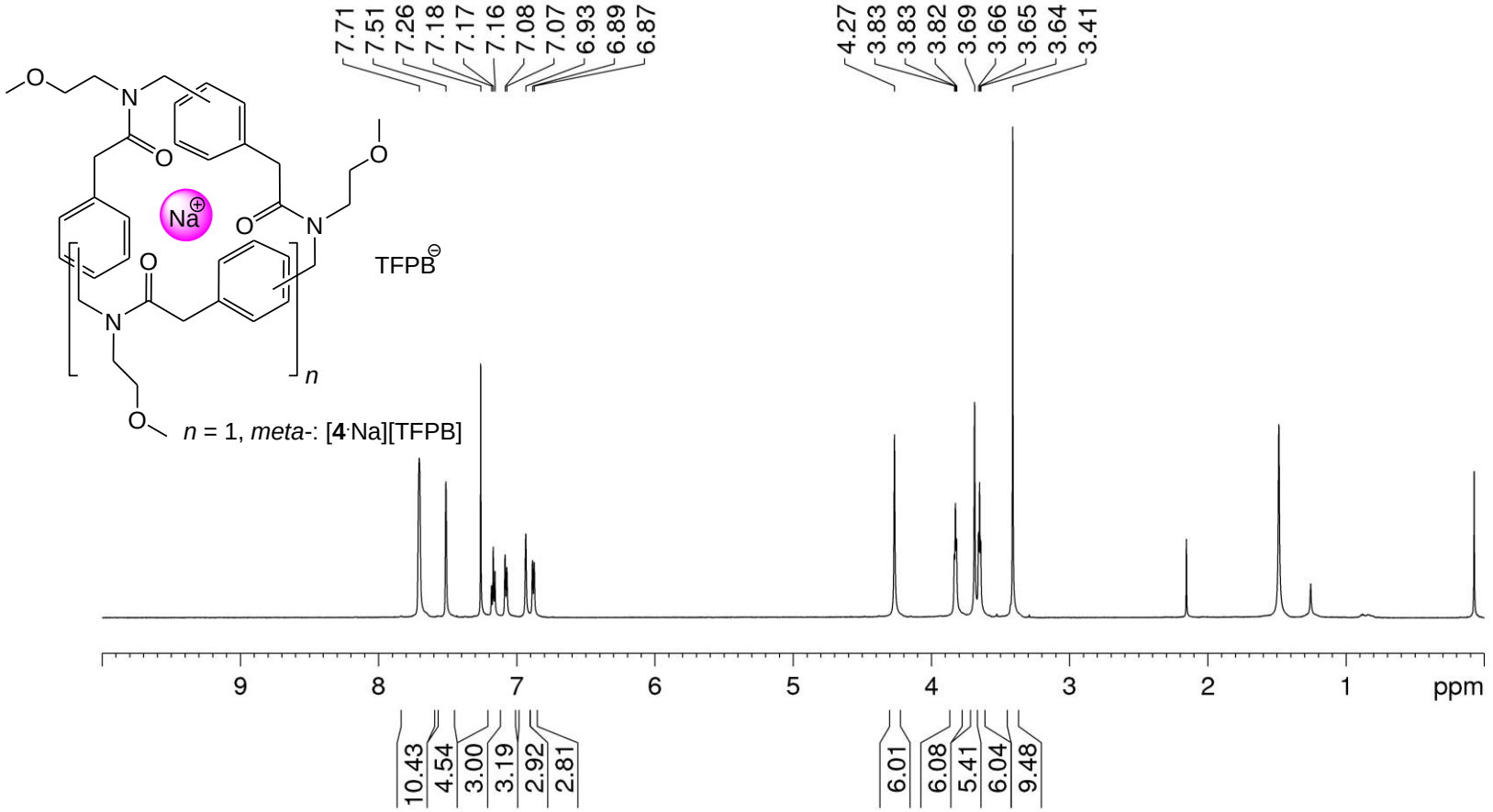
^{1}H-NMR: (600 MHz, $CDCl_3$)



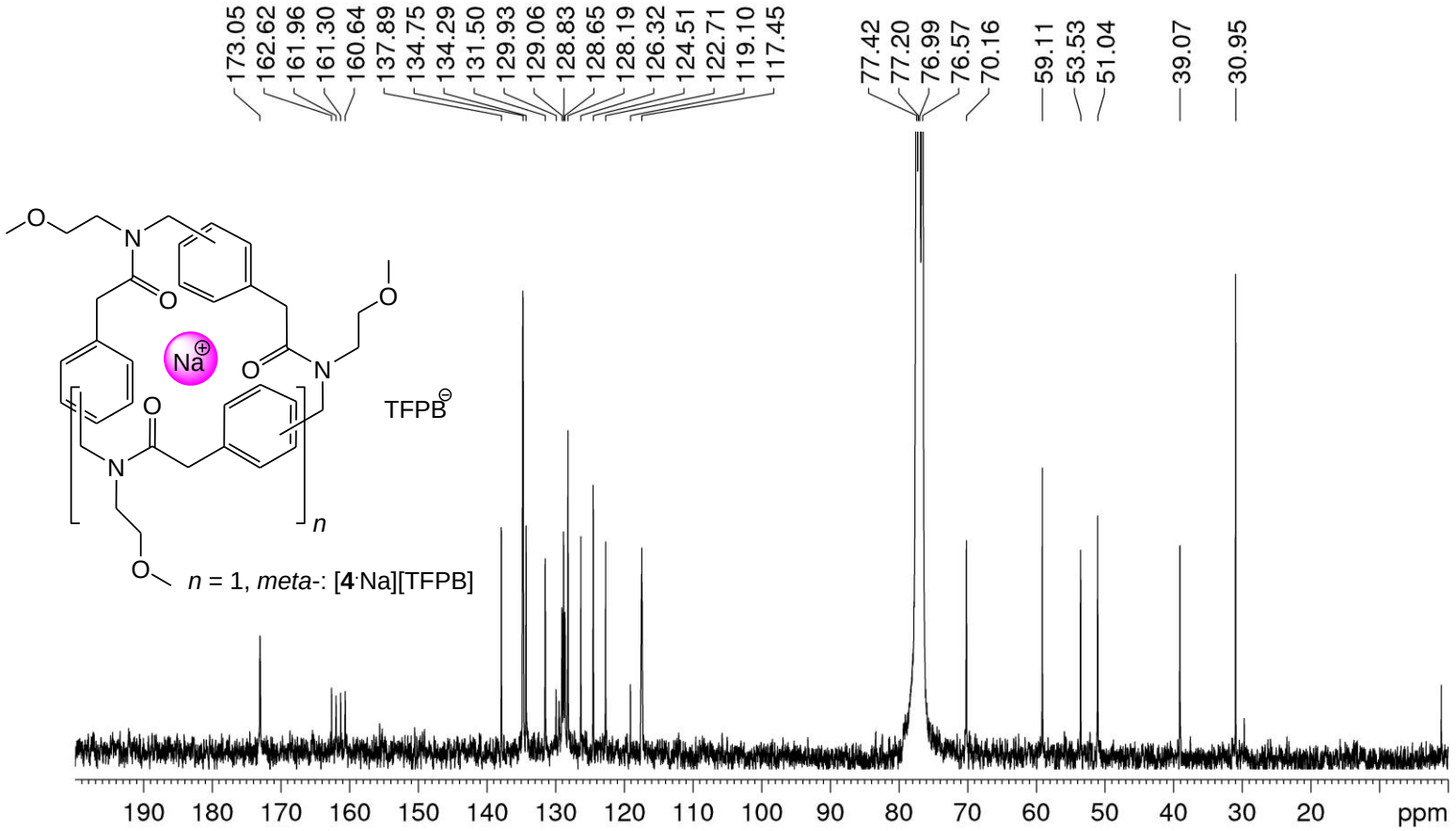
^{13}C-NMR: (100 MHz, $CDCl_3$)



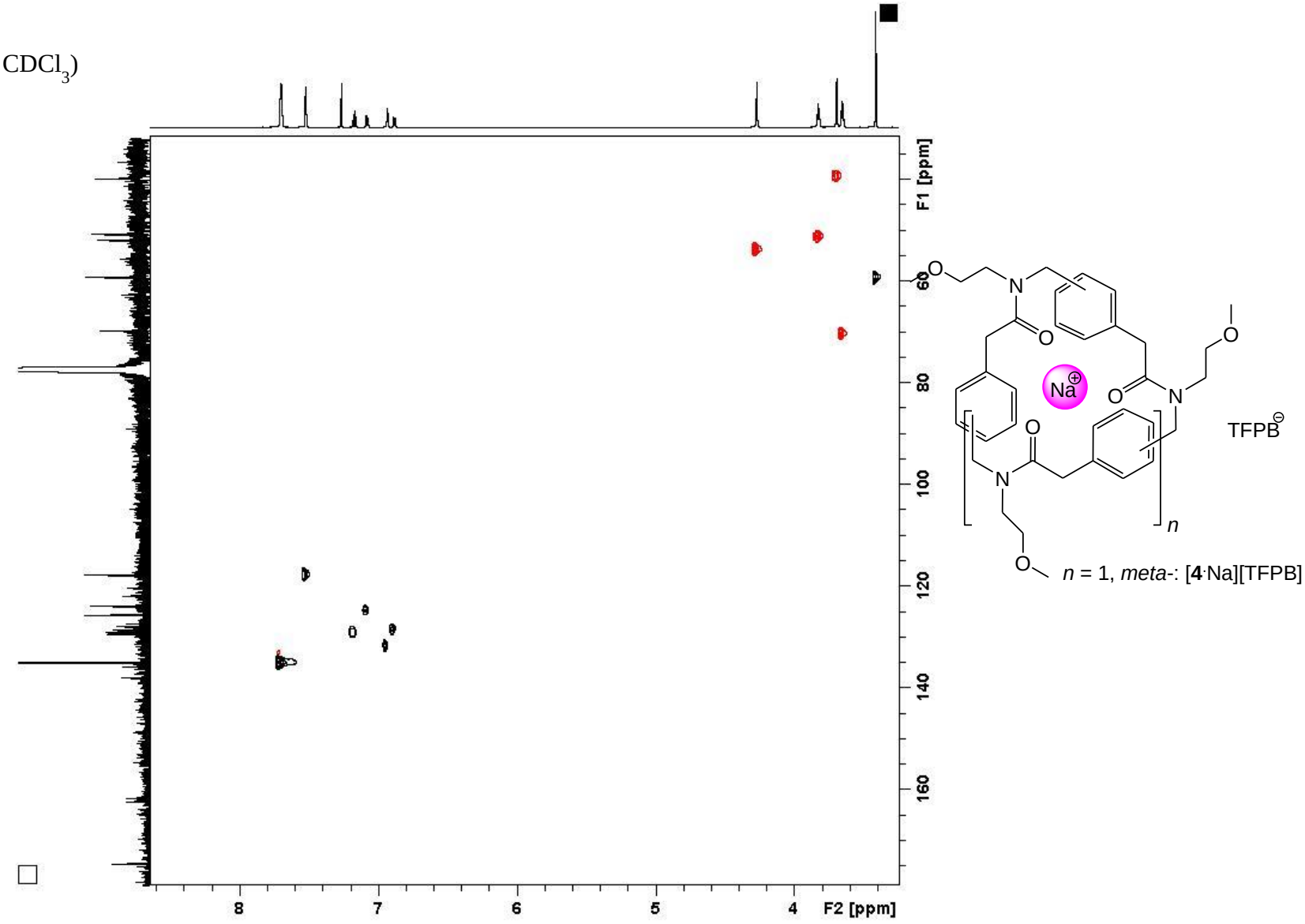
^{1}H-NMR: (600 MHz, $CDCl_3$)



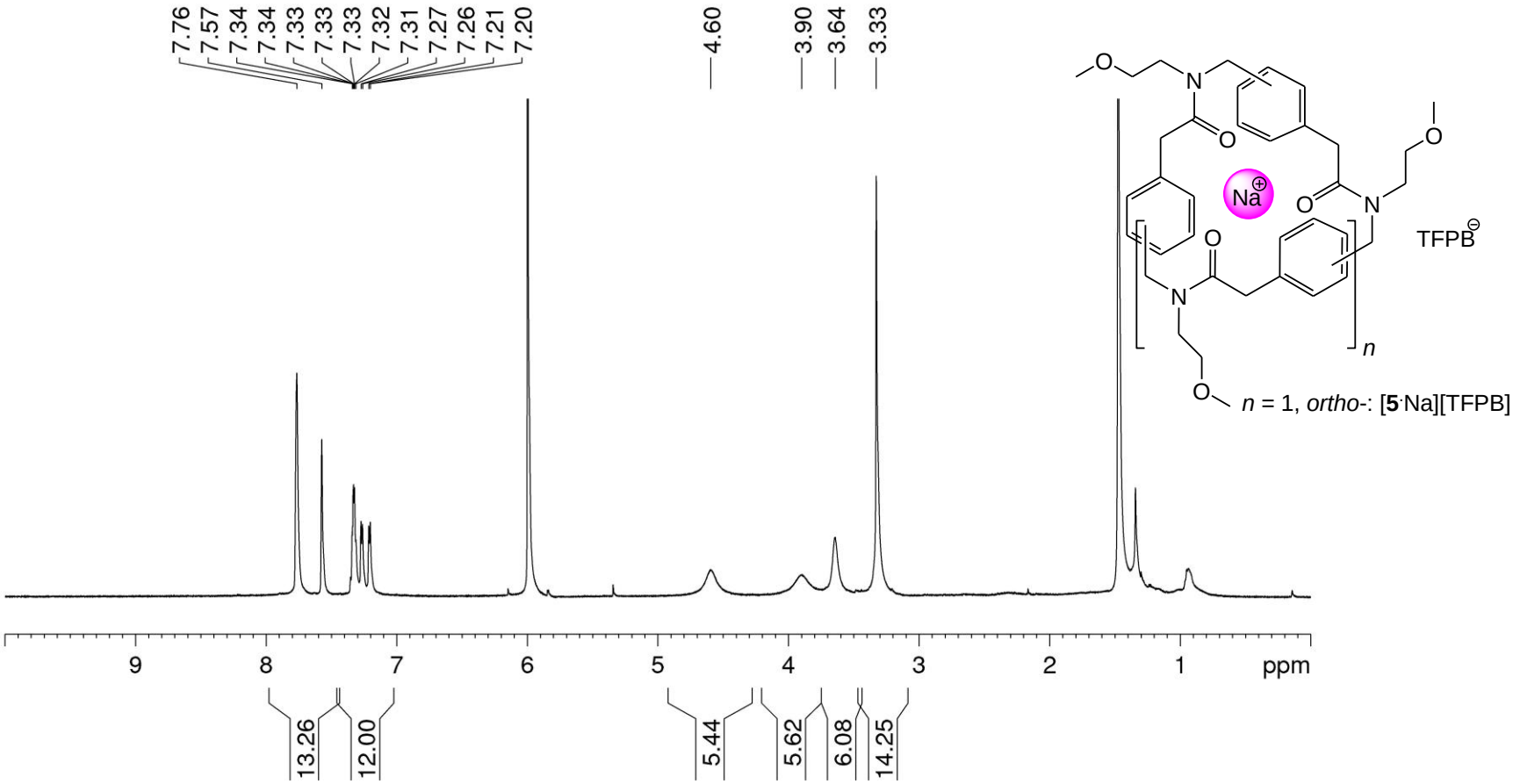
^{13}C-NMR: (150 MHz, $CDCl_3$)



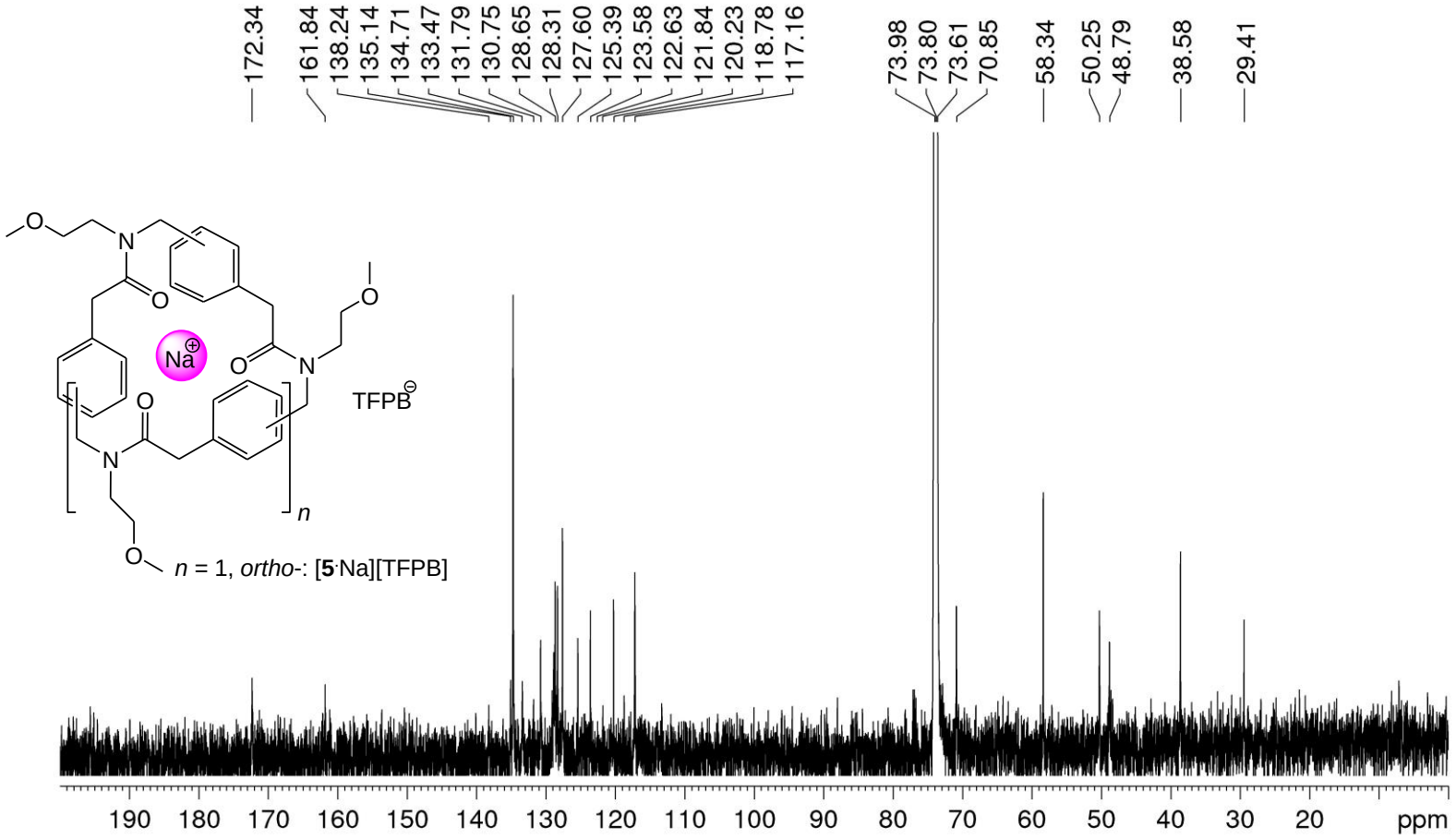
HSQC: (600 MHz, $CDCl_3$)



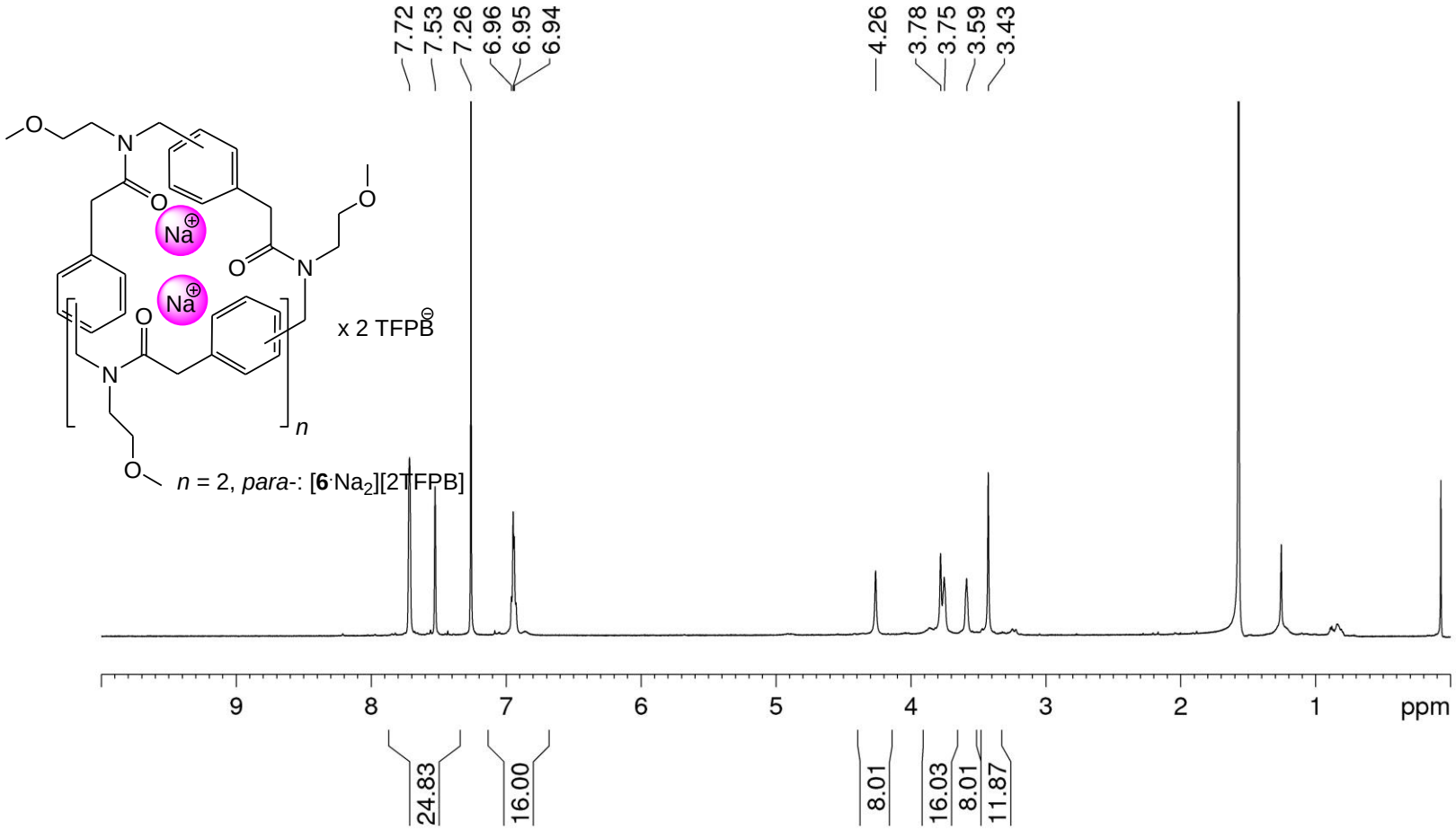
^{1}H-NMR: (600 MHz, TCDE, 373 K)



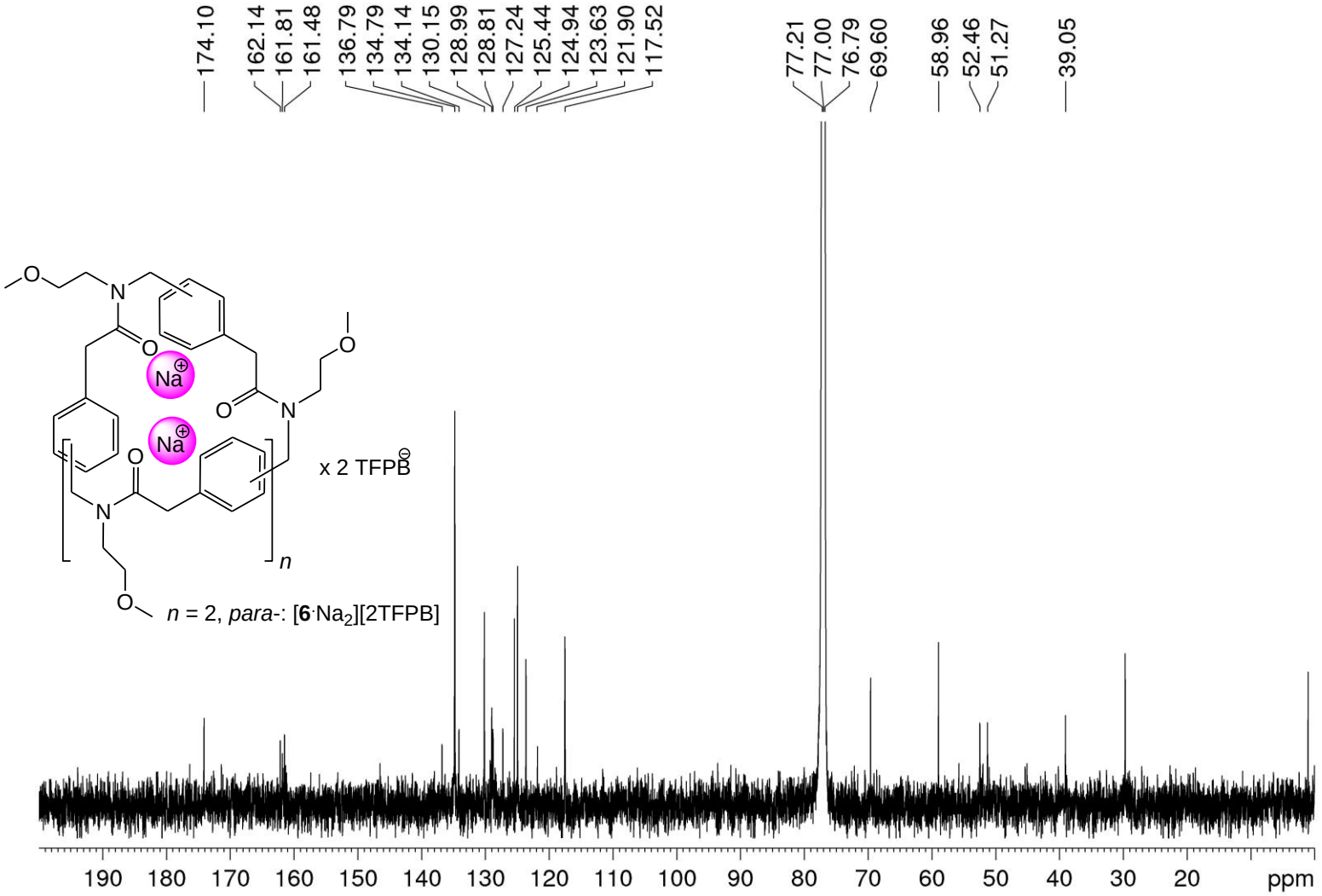
^{13}C-NMR: (150 MHz, TCDE, 373 K)



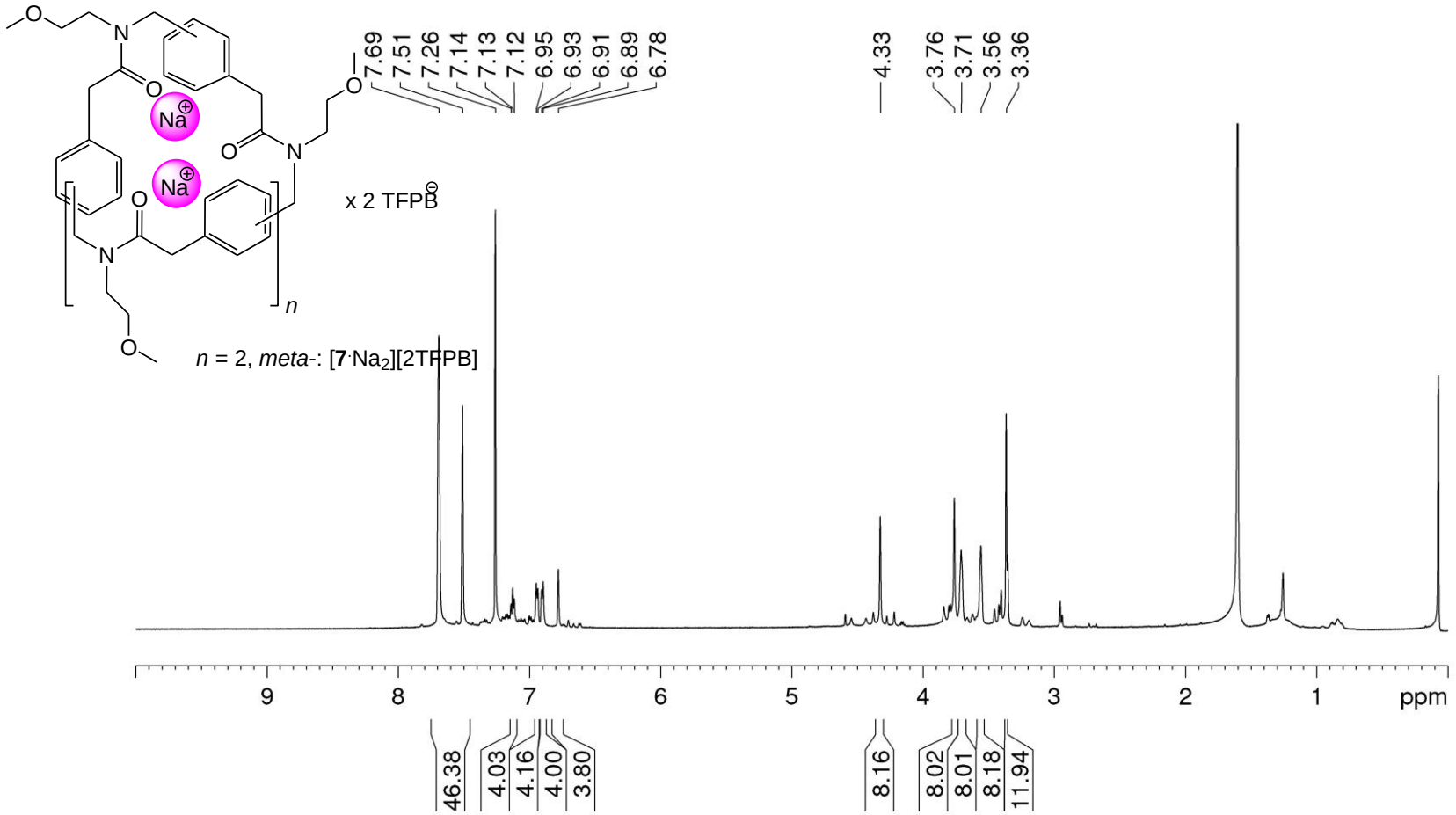
^{1}H-NMR: (600 MHz, $CDCl_3$)



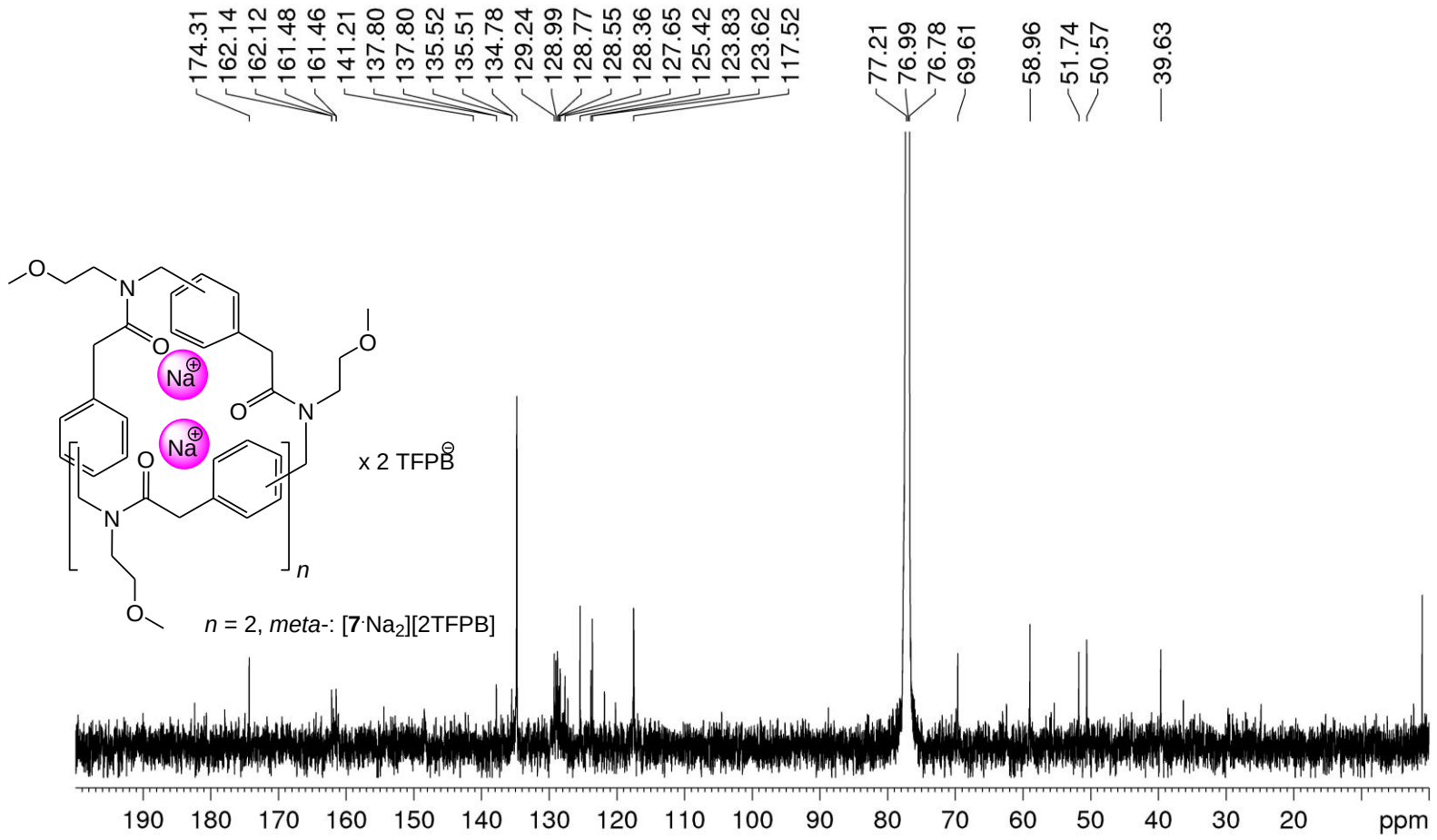
^{13}C-NMR: (150 MHz, $CDCl_3$)



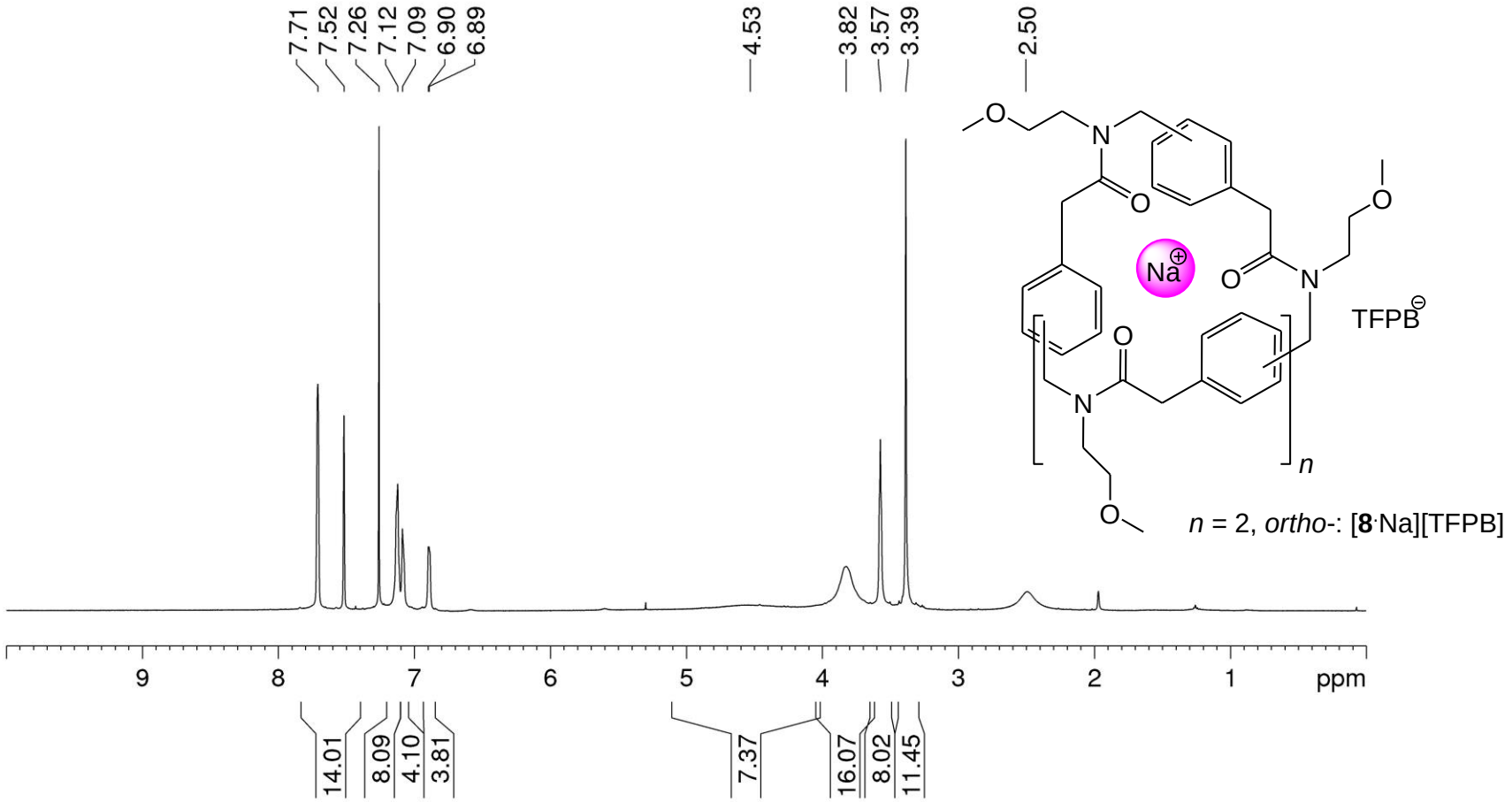
^{1}H-NMR: (600 MHz, $CDCl_3$)



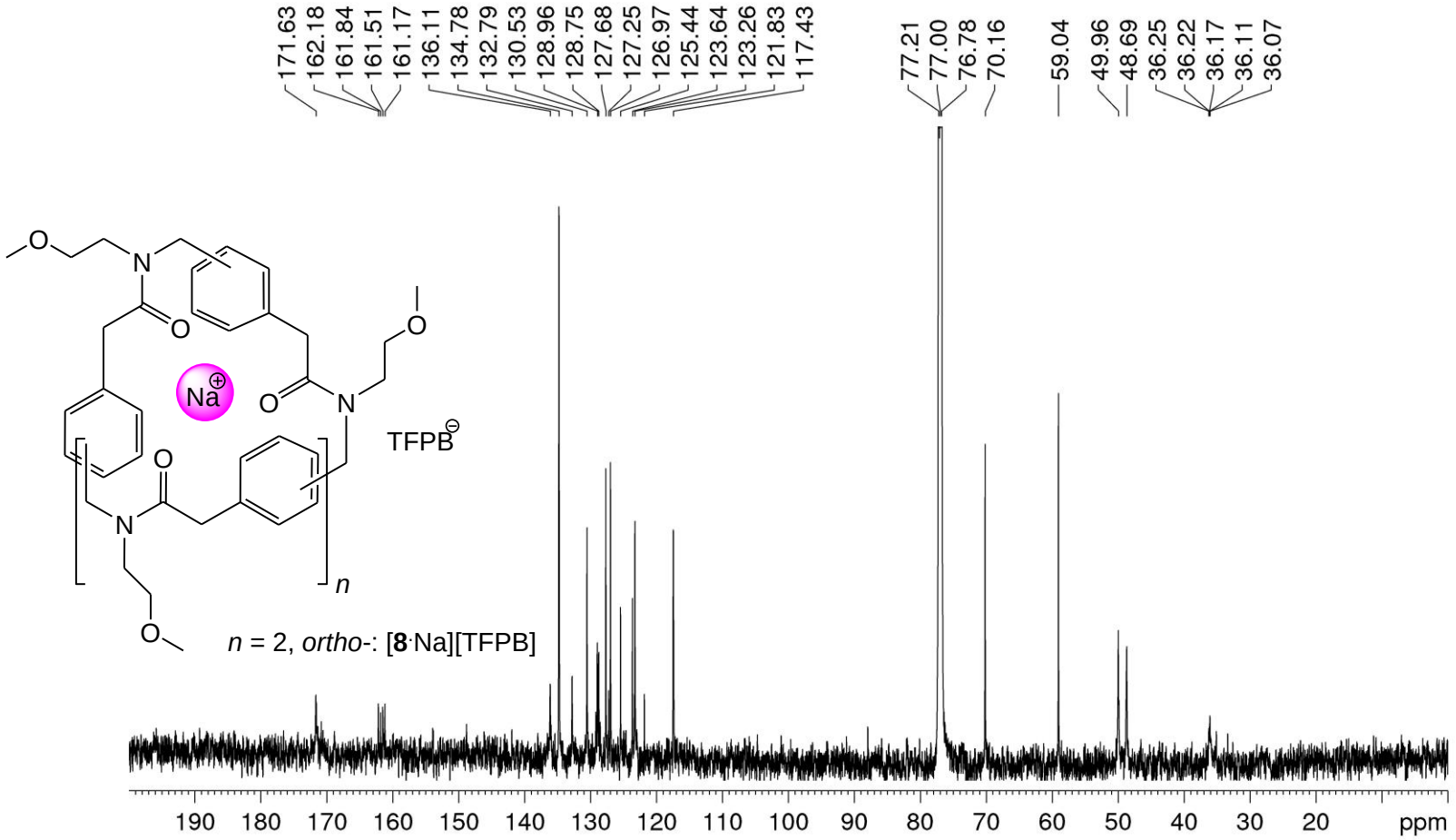
^{13}C-NMR: (150 MHz, $CDCl_3$)



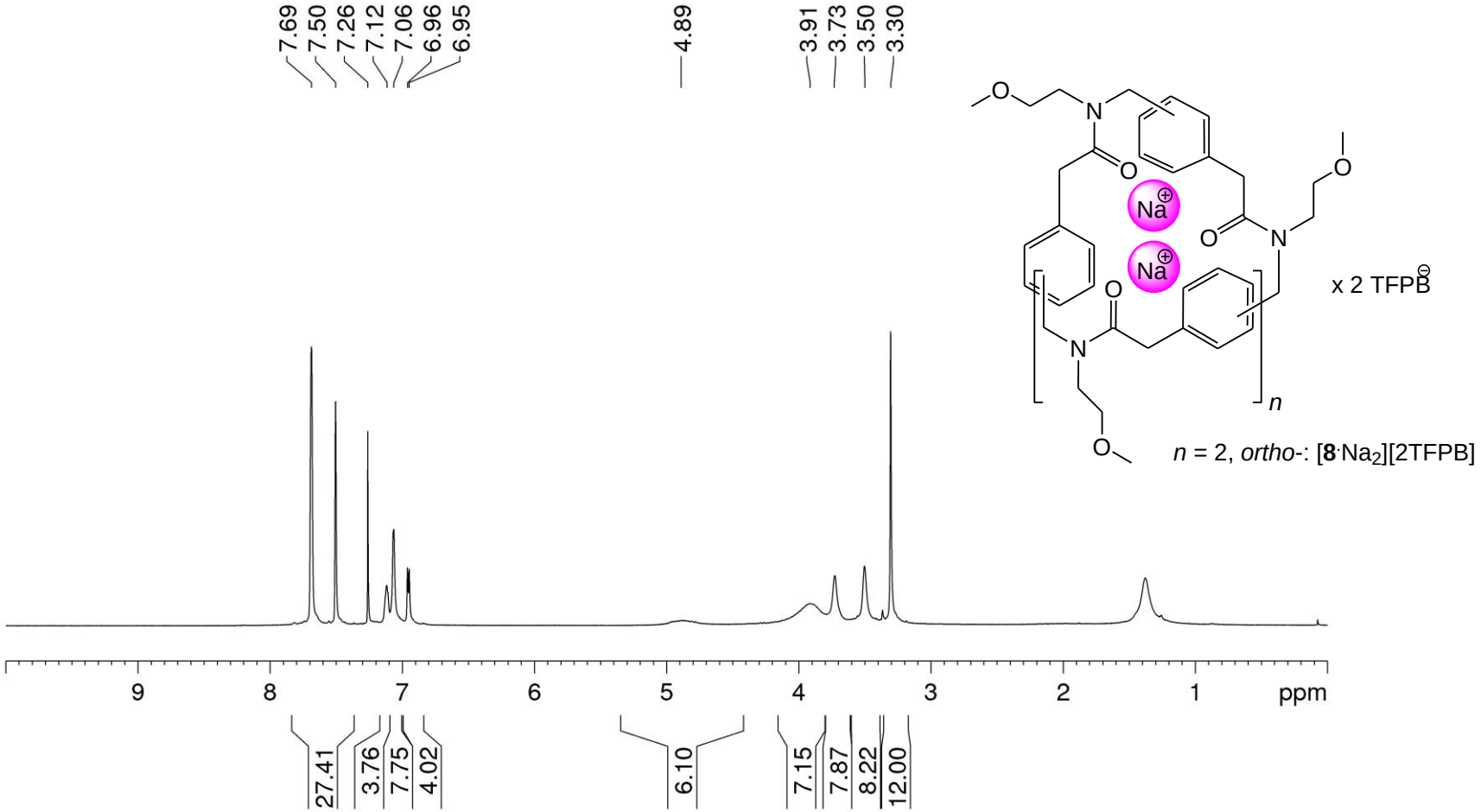
^{1}H-NMR: (600 MHz, $CDCl_3$)



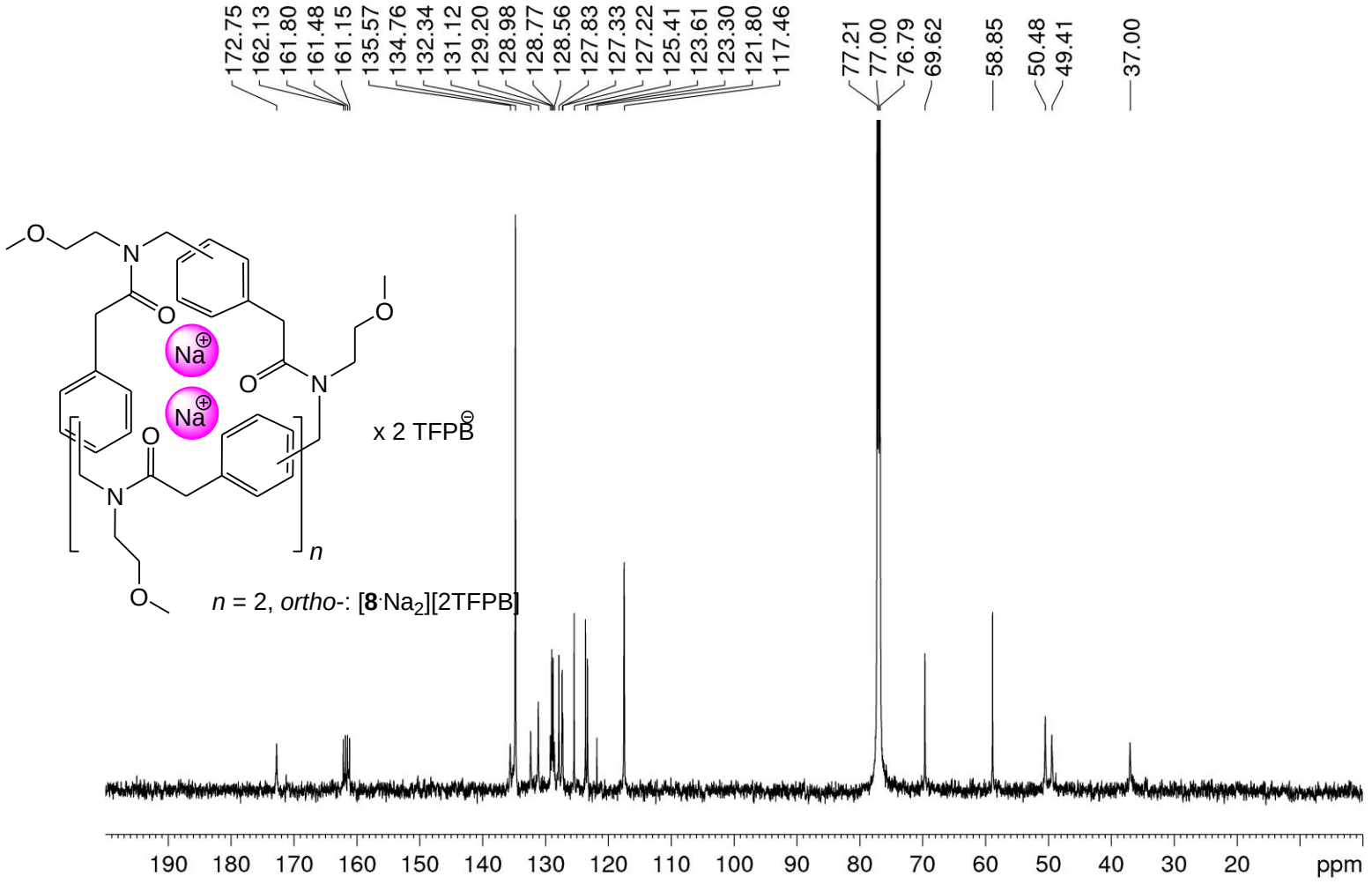
^{13}C-NMR: (150 MHz, $CDCl_3$)



^{1}H-NMR: (600 MHz, $CDCl_3$)



^{13}C-NMR: (150 MHz, $CDCl_3$)



2.4 K_a evaluation for the complexed benzylopeptoids 3-8

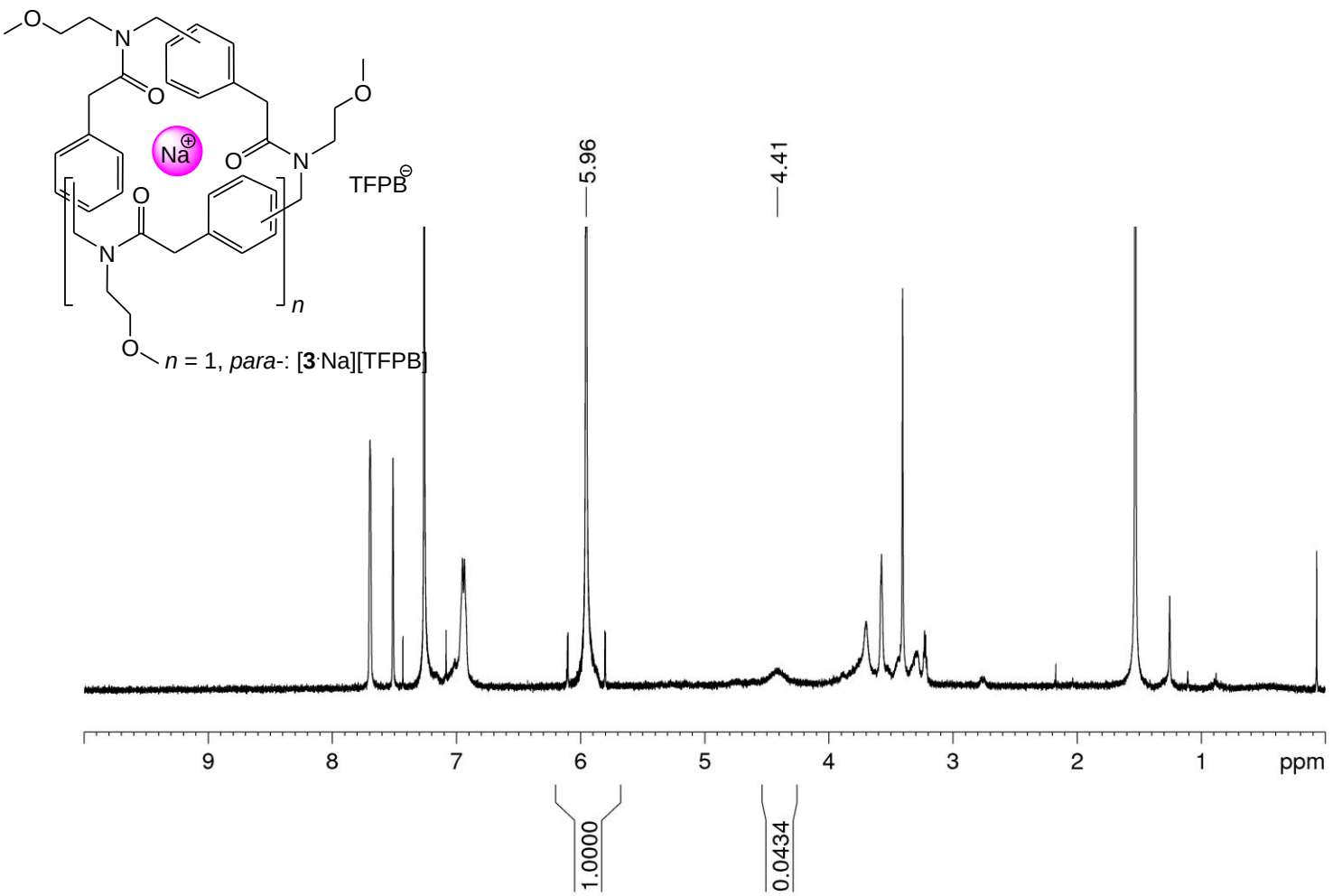


Figure S1. K_a evaluation for the complexed benzylopeptoid $[\mathbf{3}\cdot Na]^+$. ^{1}H-NMR: (600 MHz, $CDCl_3$).

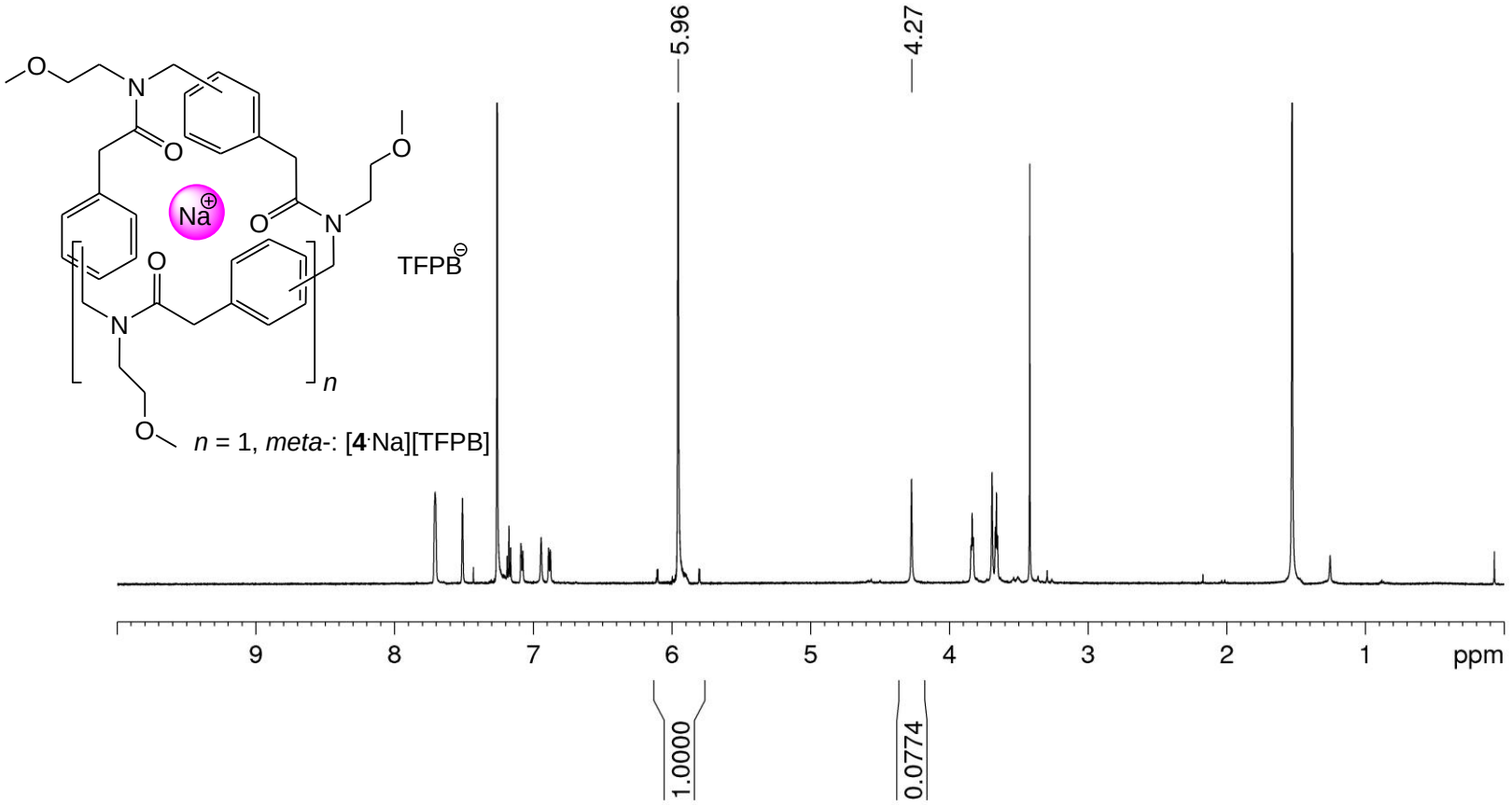


Figure S2. K_a evaluation for the complexed benzylopeptoid $[\mathbf{4}\cdot Na]^+$. $^{-}$H-NMR: (600 MHz, $CDCl_3$).

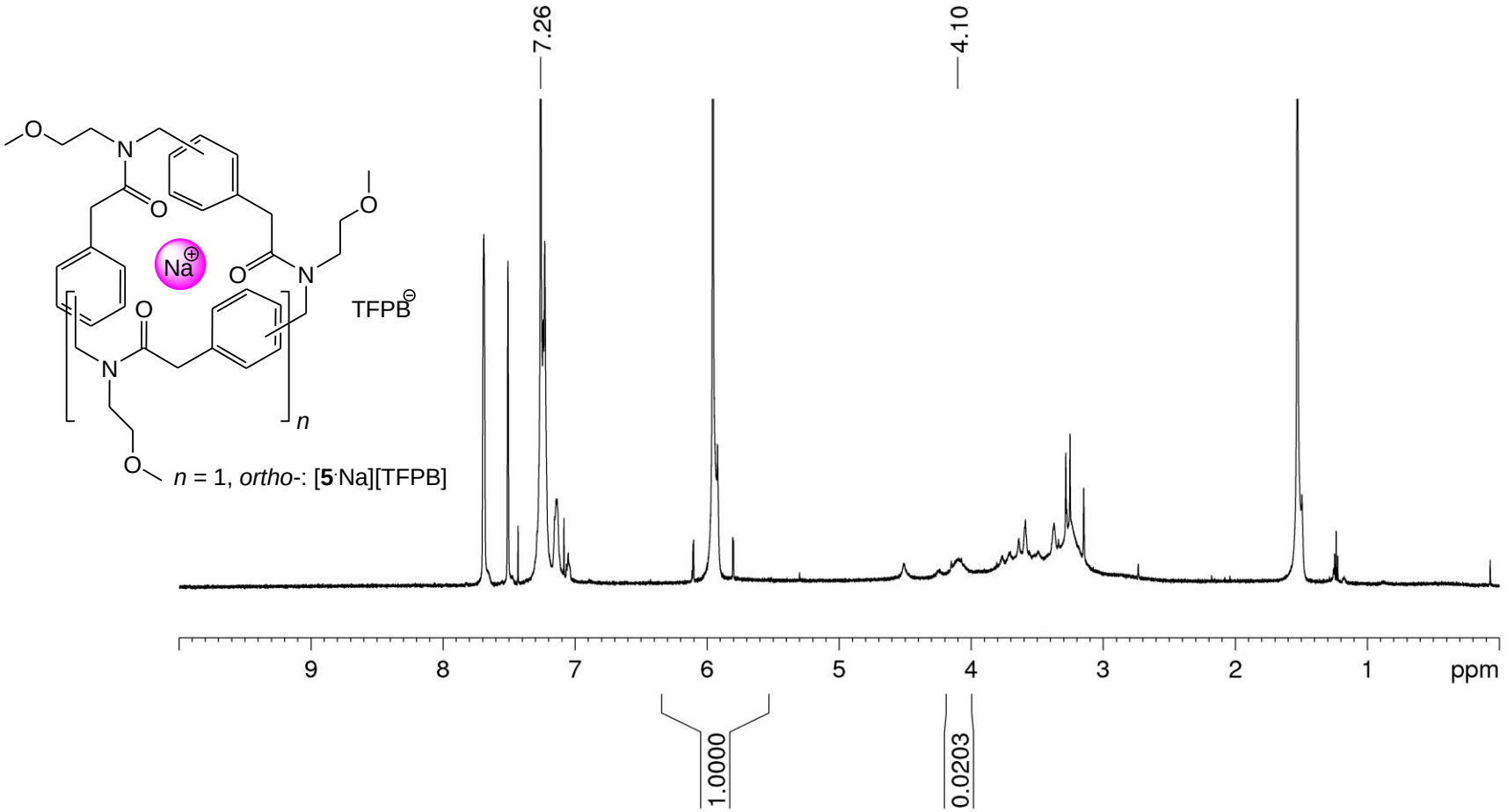


Figure S3. K_a evaluation for the complexed benzylopeptoid $[\mathbf{5}\cdot Na]^+$. ^{1}H-NMR: (600 MHz, $CDCl_3$).

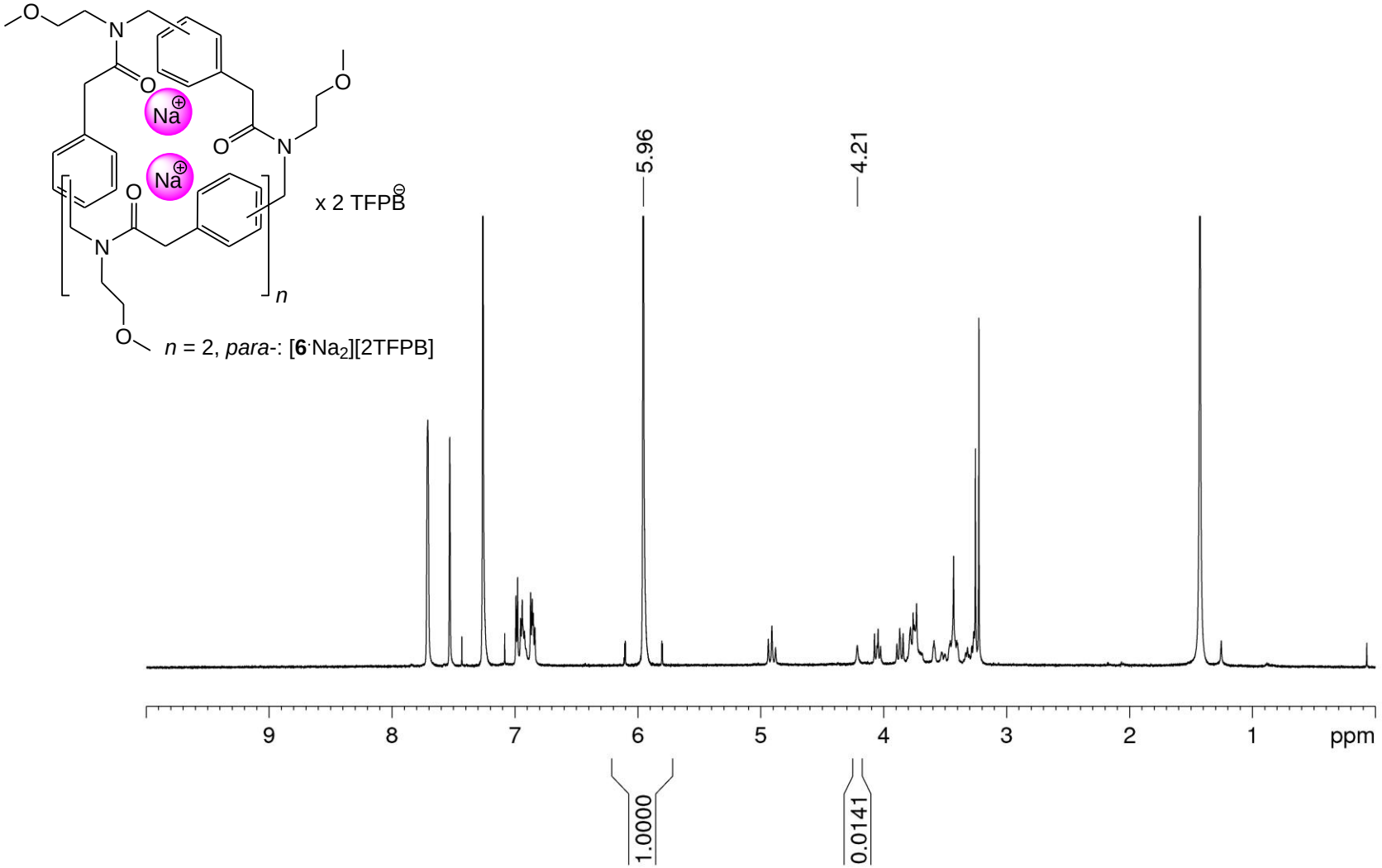


Figure S4. K_a evaluation for the complexed benzylopeptoid $[\mathbf{6}\cdot 2Na]^{2+}$. ^{1}H-NMR: (600 MHz, $CDCl_3$).

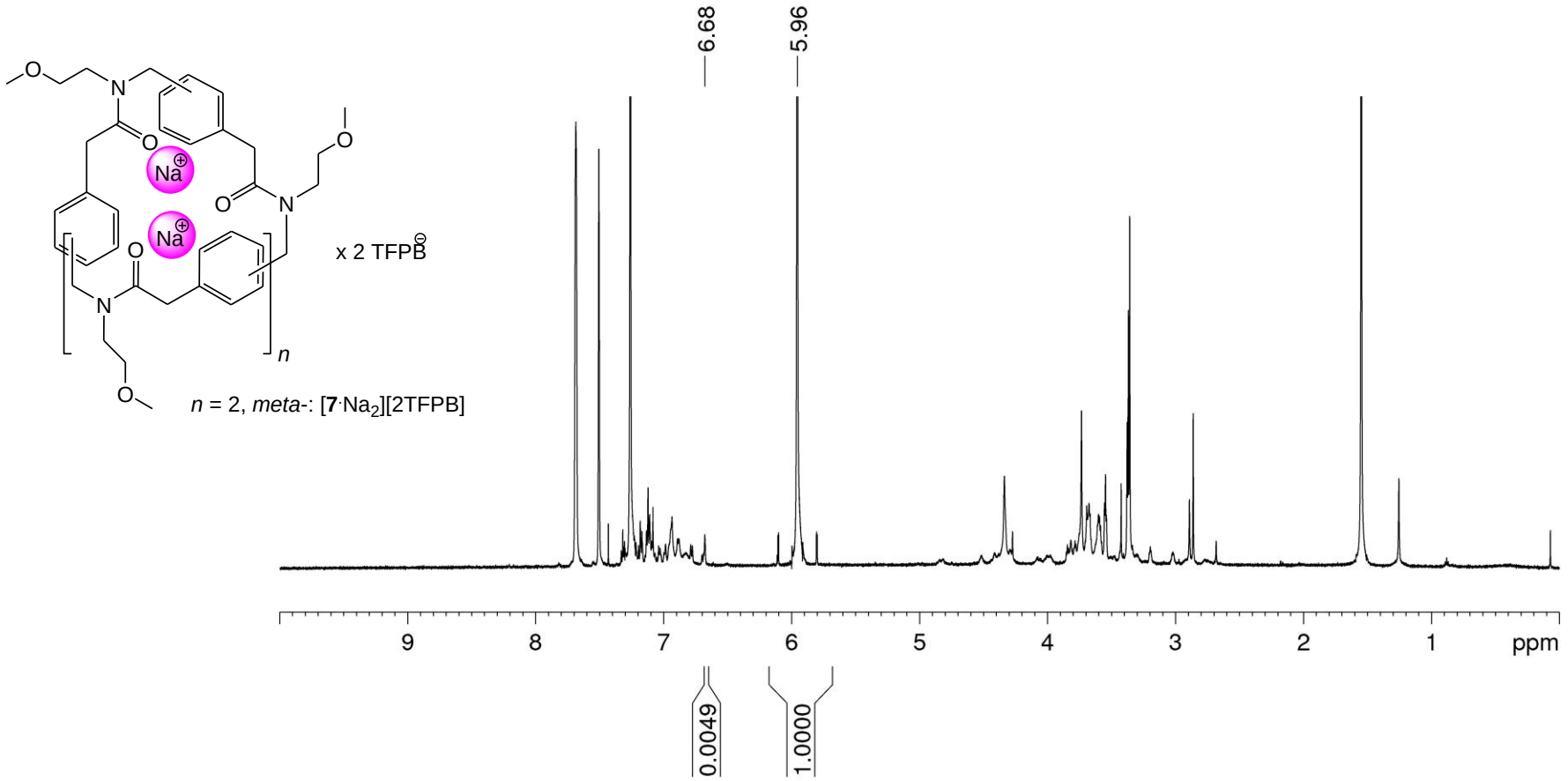


Figure S5. K_a evaluation for the complexed benzylopeptoid $[\mathbf{7}\cdot 2Na]^{2+}$. ^{1}H-NMR: (600 MHz, $CDCl_3$).

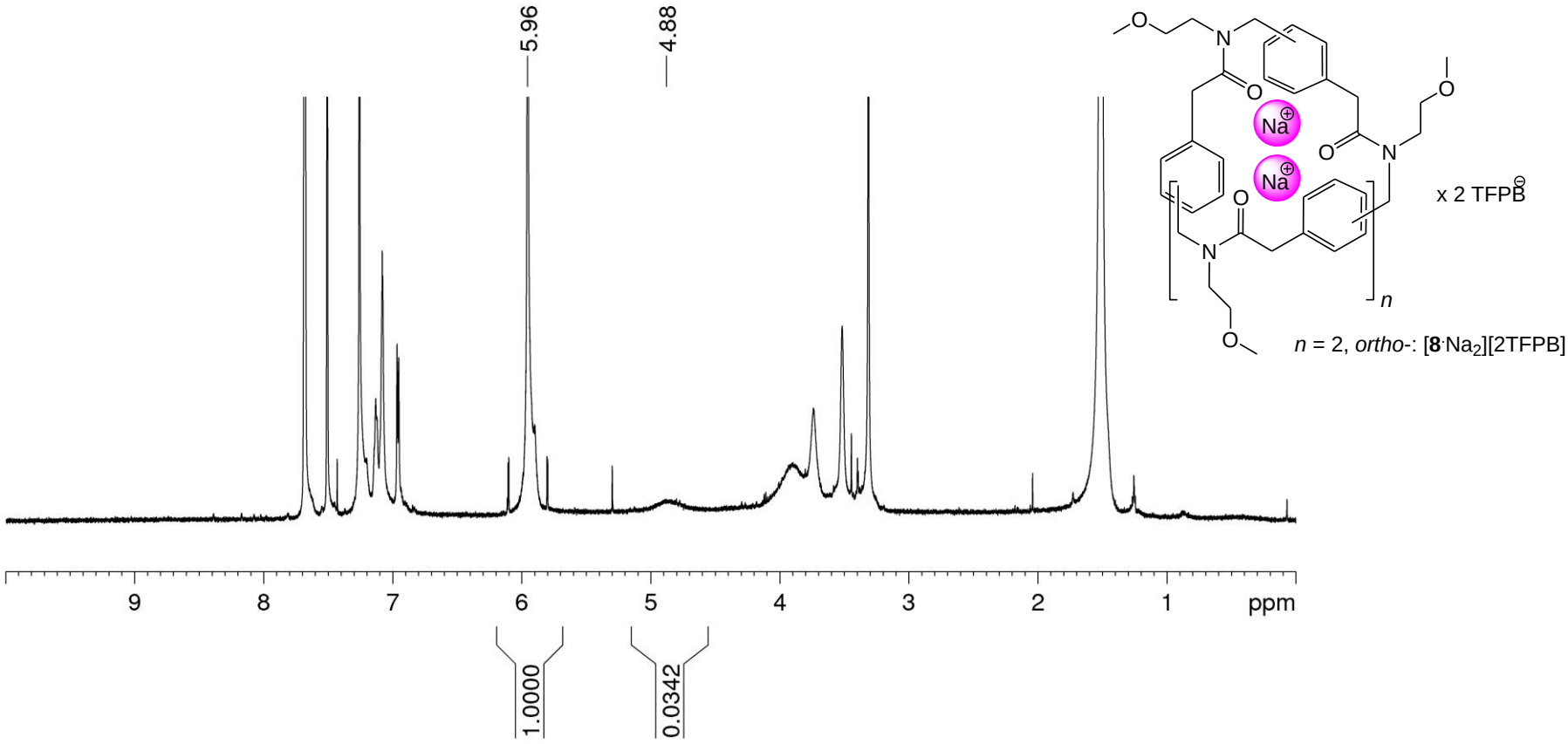


Figure S6. K_a evaluation for the complexed benzylopeptoid $[\mathbf{8}\cdot 2Na]^{2+}$. ^{1}H-NMR: (600 MHz, $CDCl_3$).

2.5 ROESY experiment for the complexed benzylopeptoid $[4{\cdot}Na]^+$

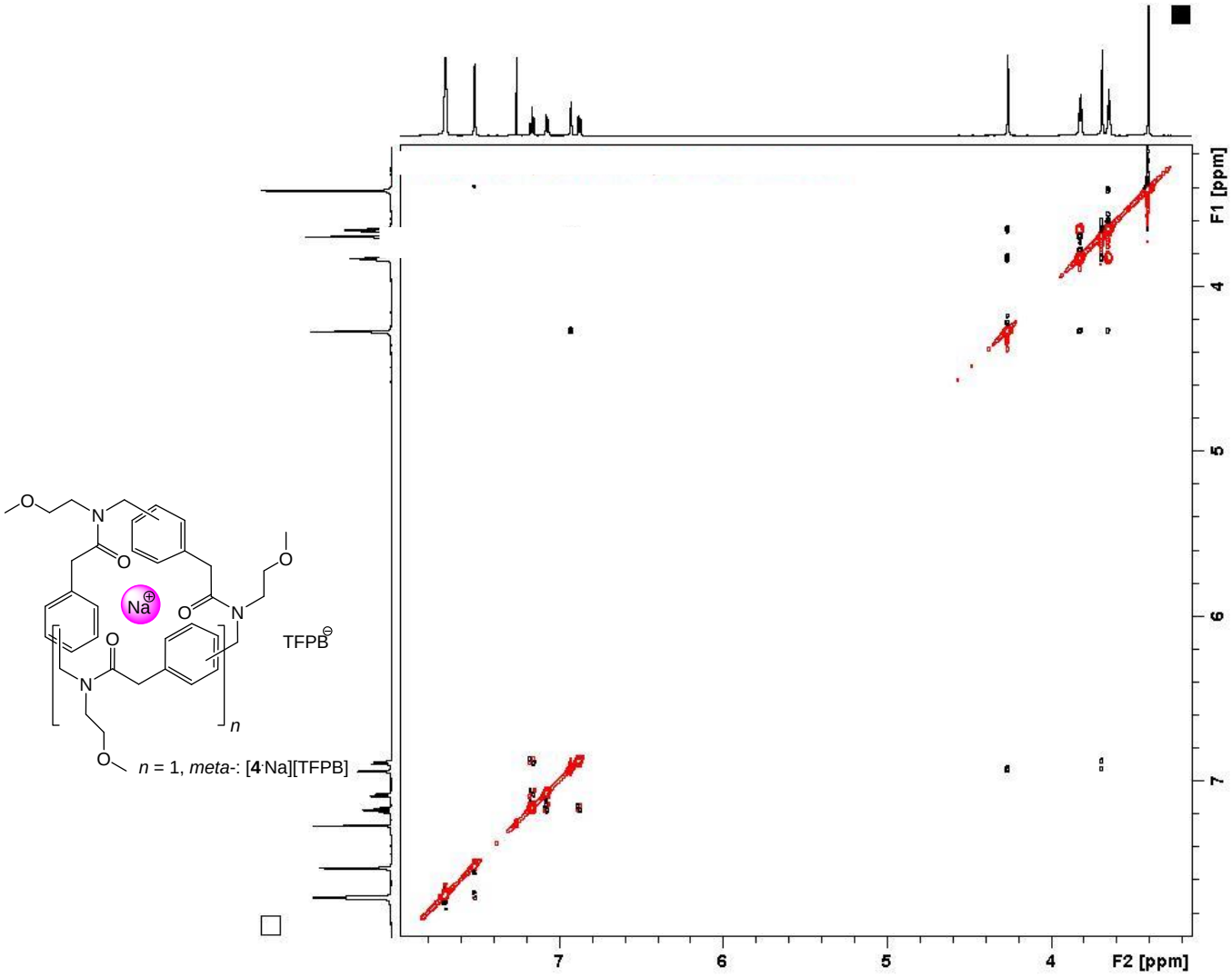


Figure S7. *ROESY* experiment for the complexed benzylopeptoid $[\mathbf{4}{\cdot}Na]^+$ (600 MHz, $CDCl_3$). Note: dipolar coupling in black and scalar coupling in red.

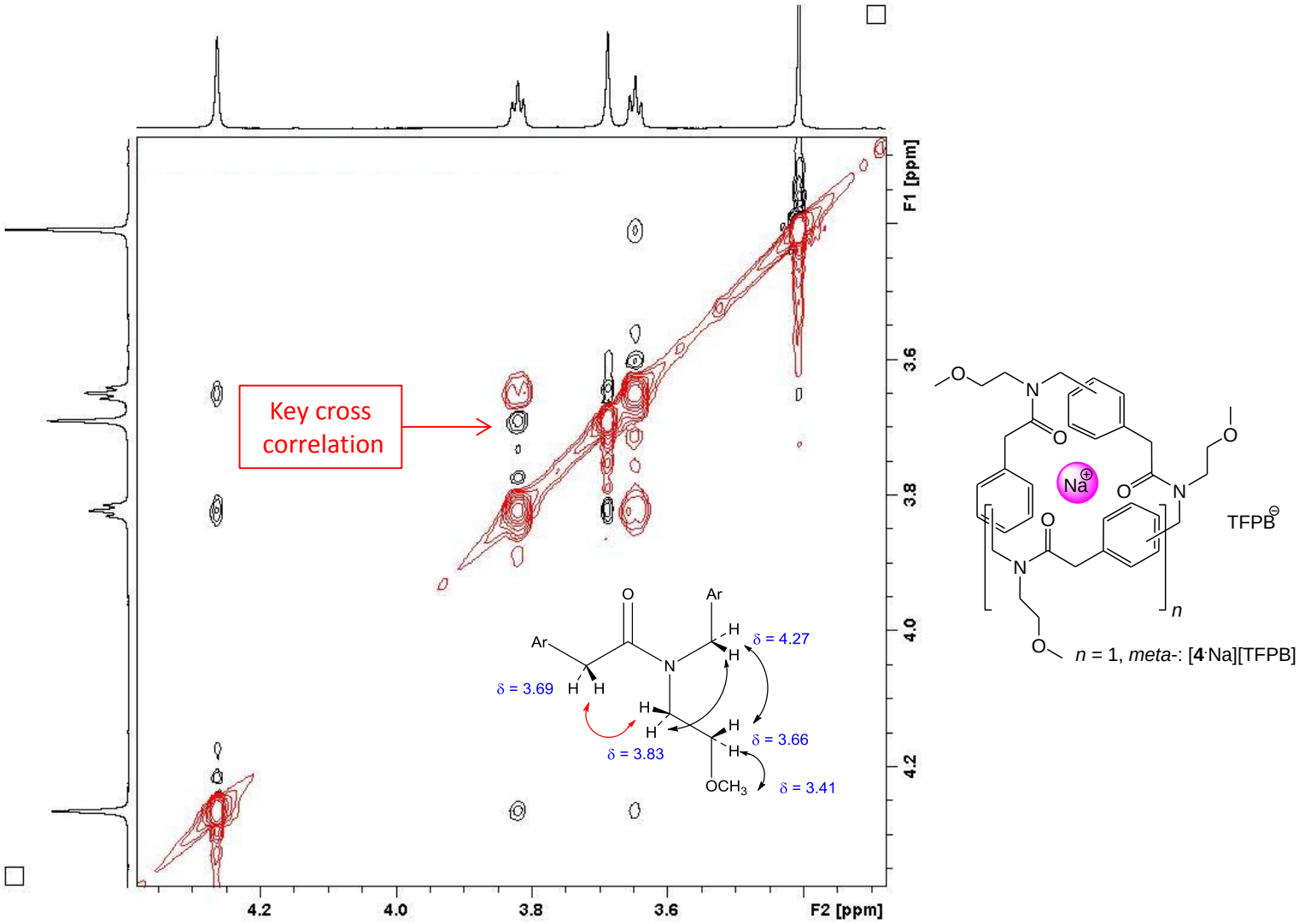


Figure S8. Enlargment of the *ROESY* experiment for the complexed benzylopeptoid $[\mathbf{4}\cdot Na]^+$ (600 MHz, $CDCl_3$).
Note: dipolar coupling in black and scalar coupling in red.

2.6 Variable temperature experiment on compound 5 and $[5{\cdot}Na]^+$

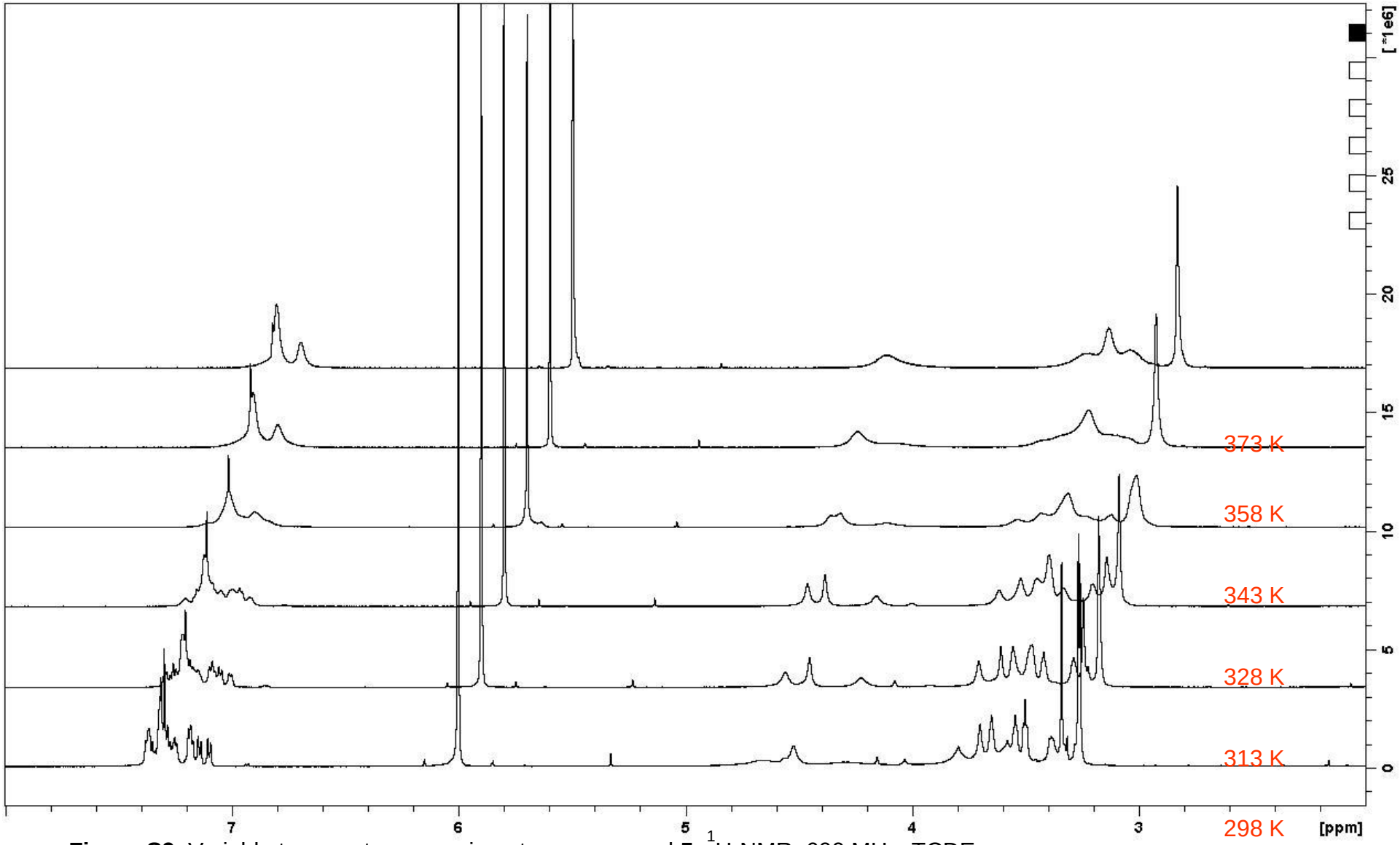


Figure S9. Variable temperature experiment on compound **5**. ^{1}H-NMR: 600 MHz, TCDE.

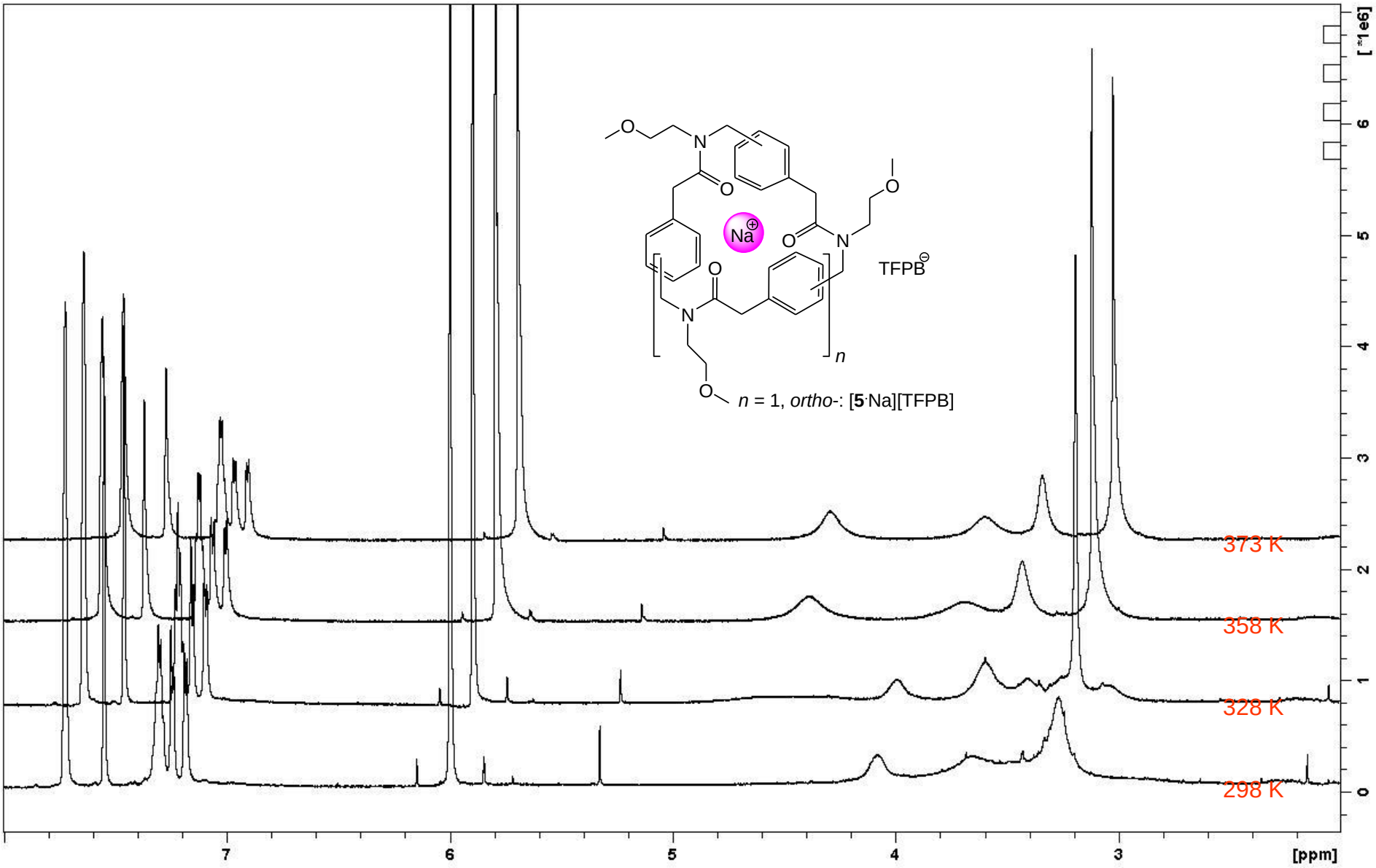


Figure S10. Variable temperature experiment on compound $[\mathbf{5}\cdot Na]^{+}$. ^{1}H-NMR: 600 MHz, TCDE.

2.7 Titration of 3-8 with NaTFPB

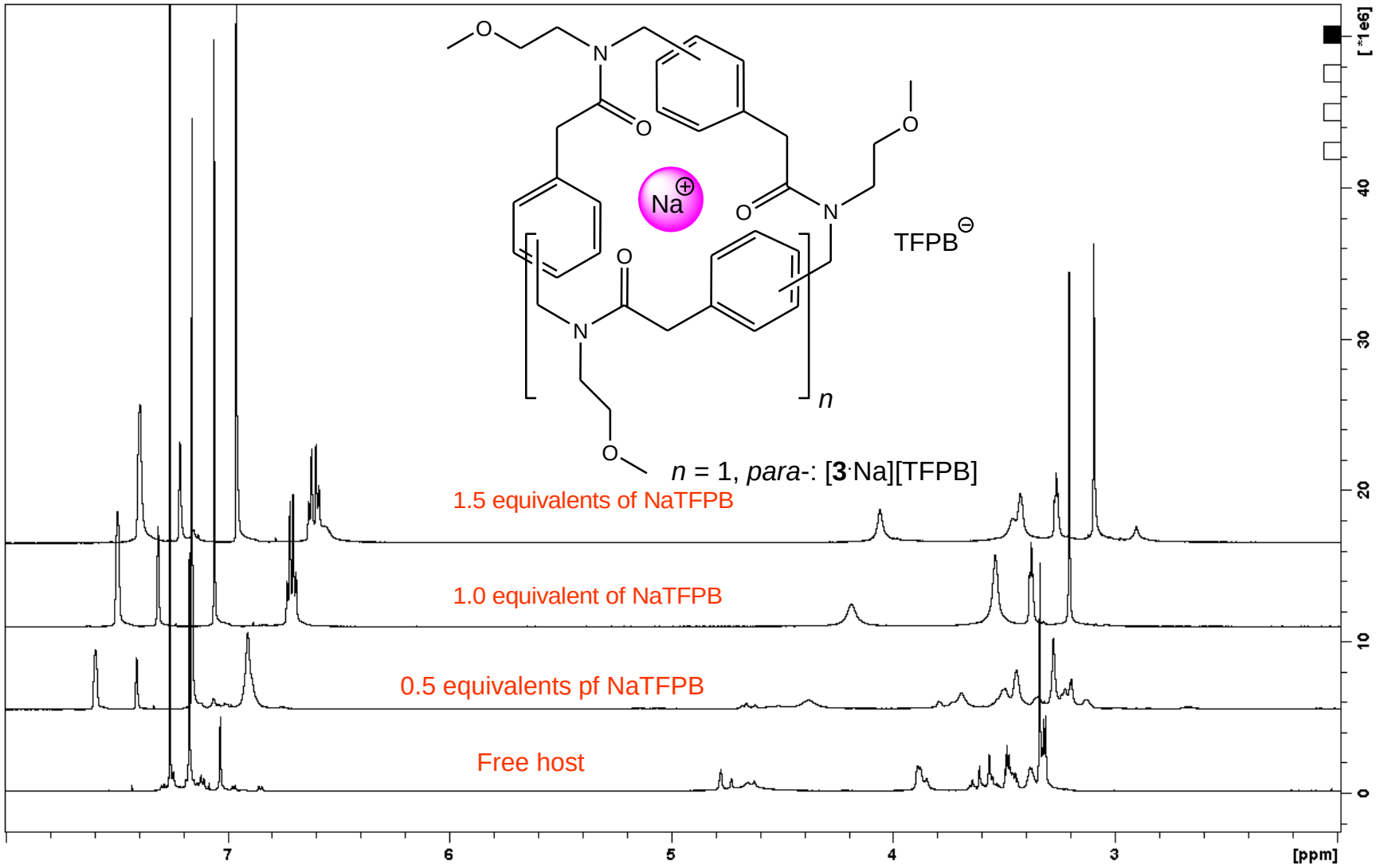


Figure S11. Titration experiment on compound **3** to give complex $[\mathbf{3}\cdot Na]^{+}$. ^{1}H-NMR: 600 MHz, $CDCl_3$. Offset: 0.1 ppm.

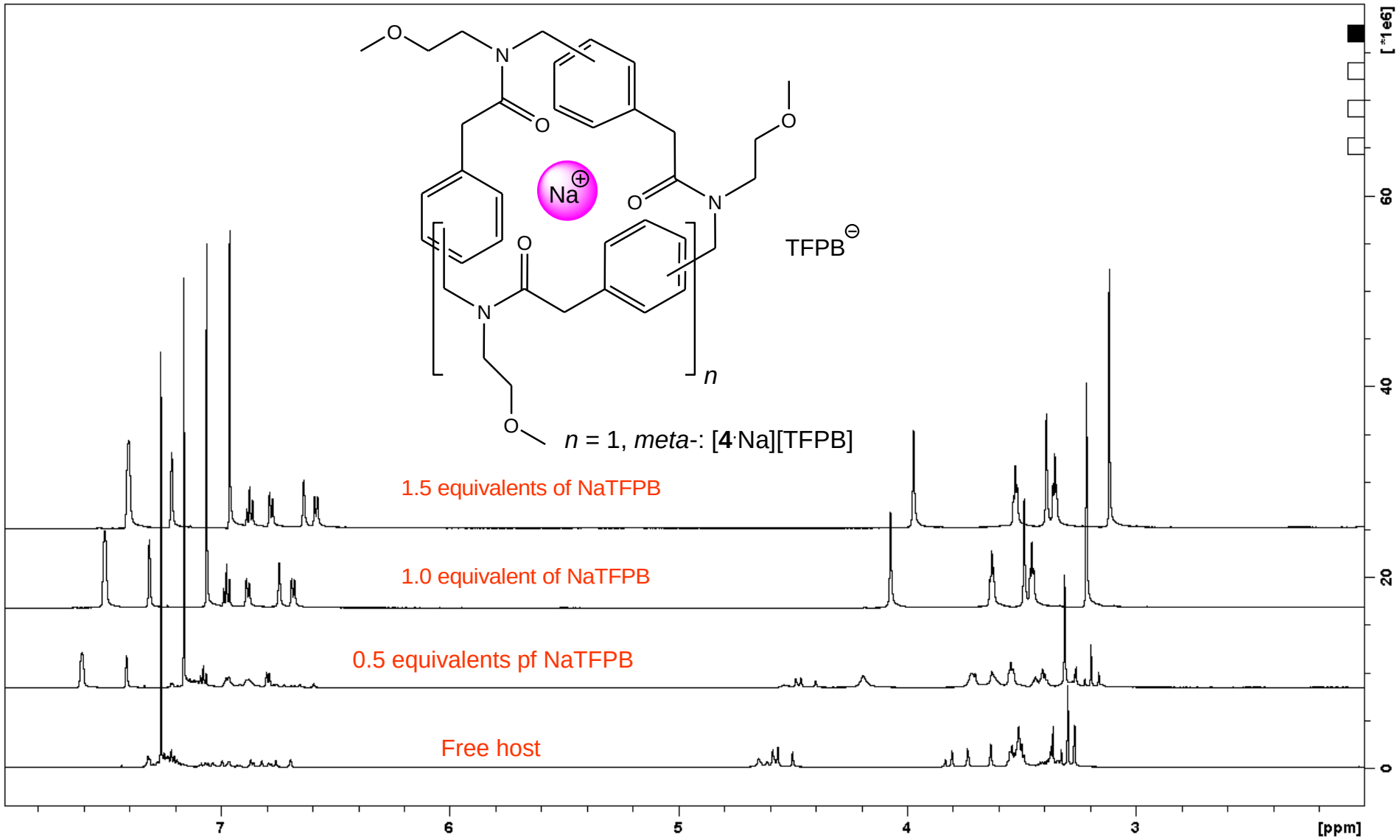


Figure S12. Titration experiment on compound **4** to give complex $[\mathbf{4}\cdot Na]^+$. ^{1}H-NMR: 600 MHz, $CDCl_3$. Offset: 0.1 ppm.

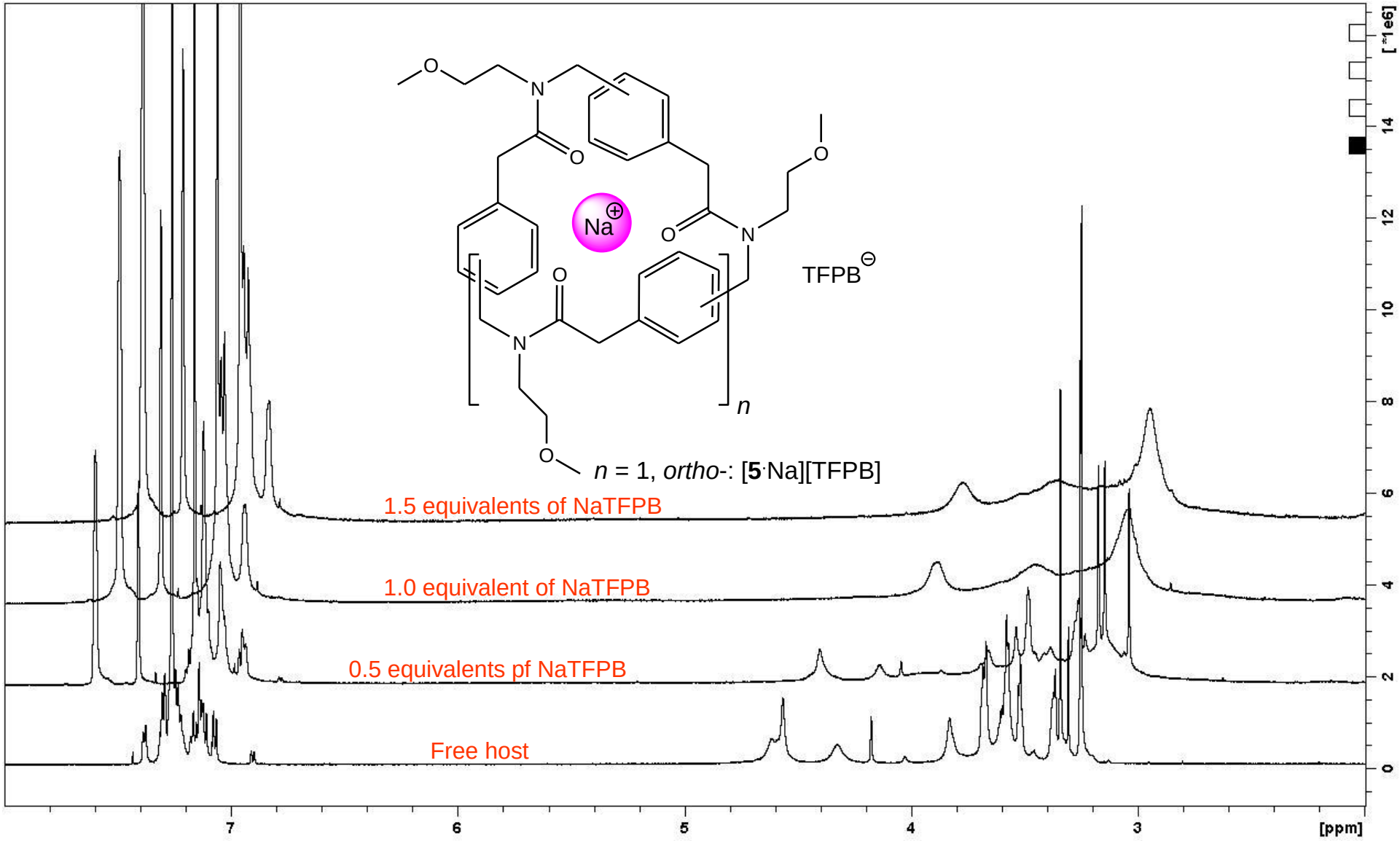


Figure S13. Titration experiment on compound **5** to give complex $[\mathbf{5}\cdot Na]^+$. ^{1}H-NMR: 600 MHz, $CDCl_3$. Offset: 0.1 ppm.

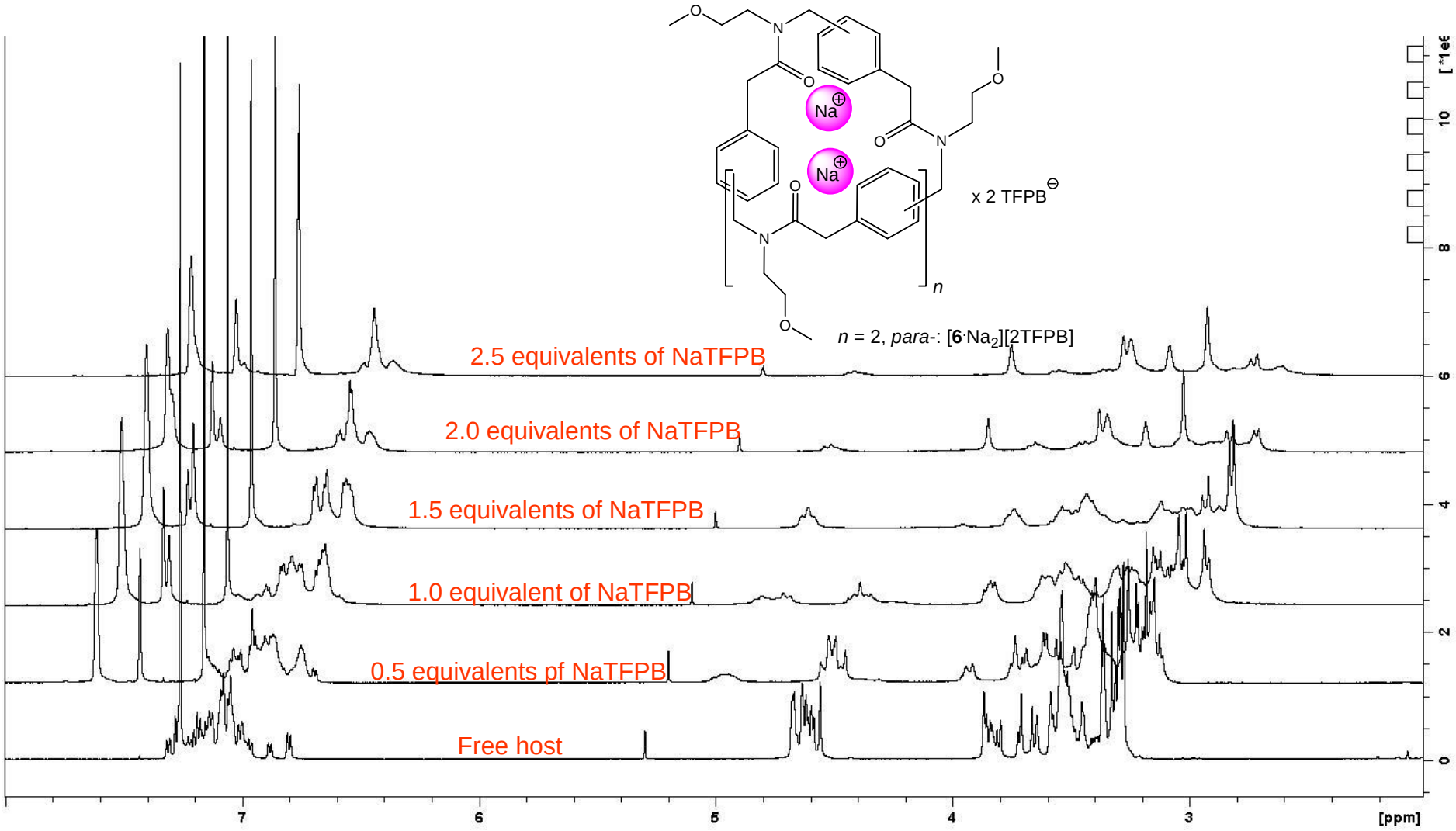


Figure S14. Titration experiment on compound **6** to give complex $[\mathbf{6}\cdot 2Na]^{2+}$. ^{1}H-NMR: 600 MHz, $CDCl_3$. Offset: 0.1 ppm.

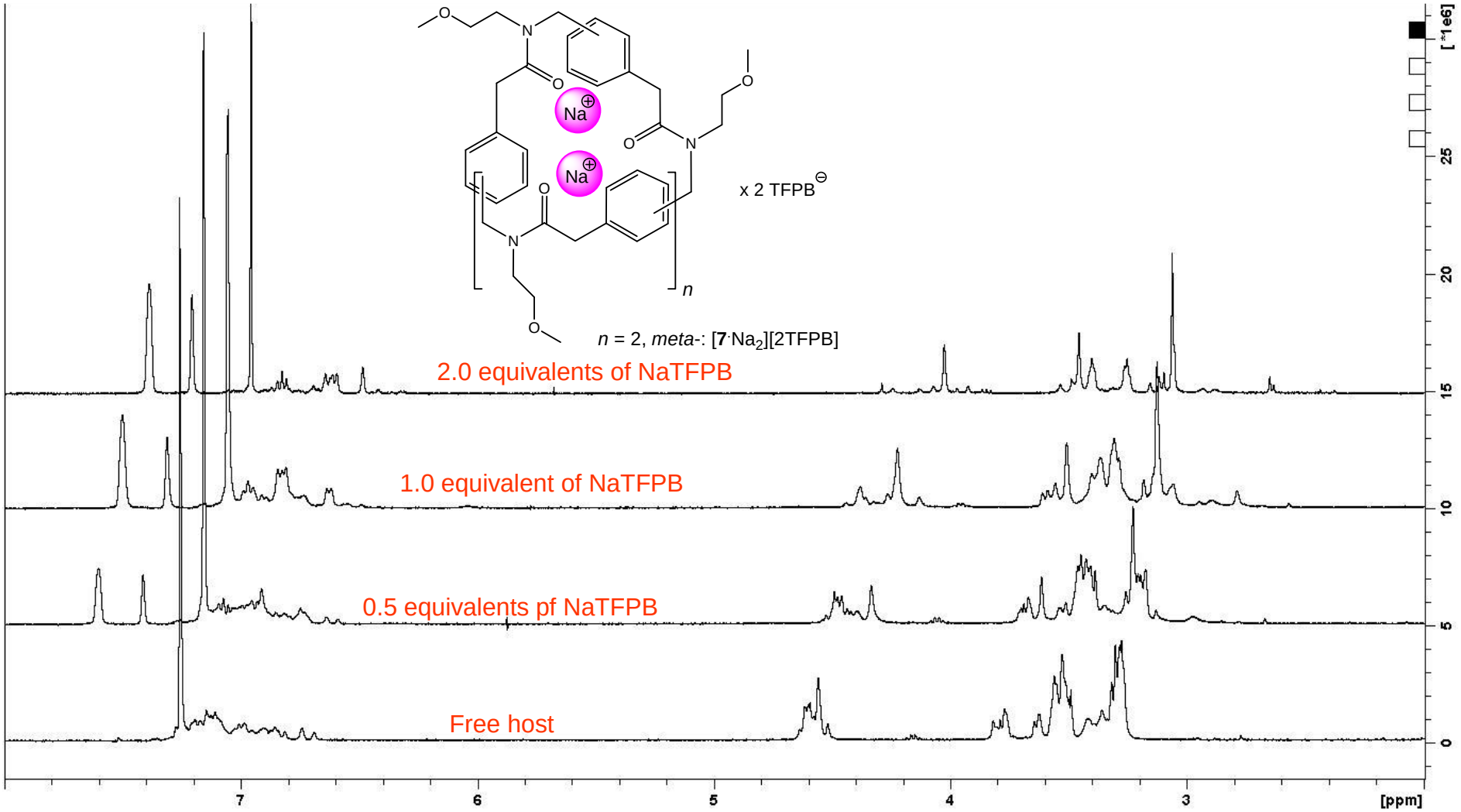


Figure S15. Titration experiment on compound **7** to give complex $[\mathbf{7}\cdot 2Na]^{2+}$. ^{1}H-NMR: 600 MHz, $CDCl_3$. Offset: 0.1 ppm.

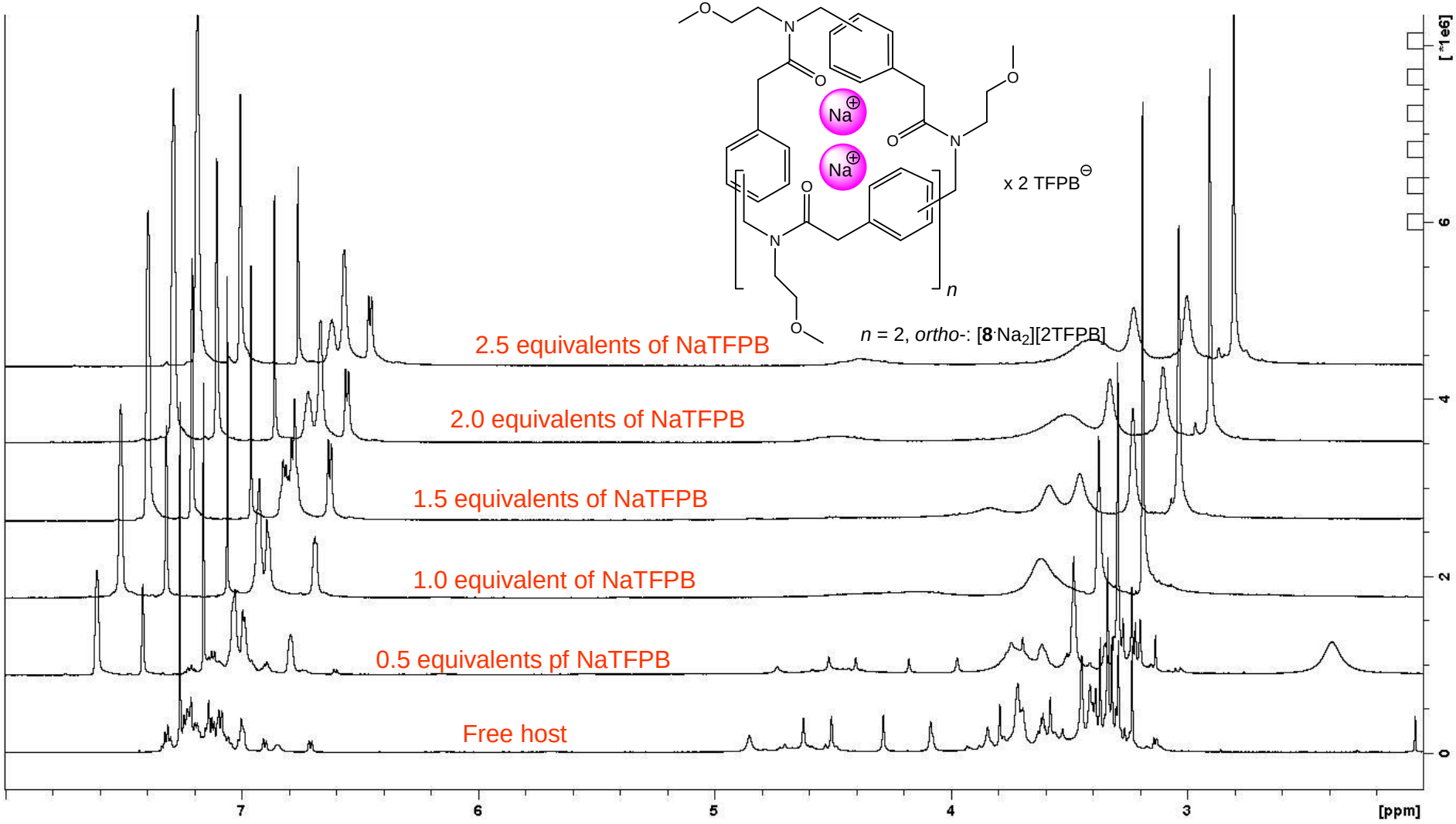


Figure S16. Titration experiment on compound **8** to give complexes $[\mathbf{8}\cdot Na]^{+}$ and $[\mathbf{8}\cdot 2Na]^{2+}$. ^{1}H-NMR: 600 MHz, $CDCl_3$. Offset: 0.1 ppm.

3.0 HPLC analysis

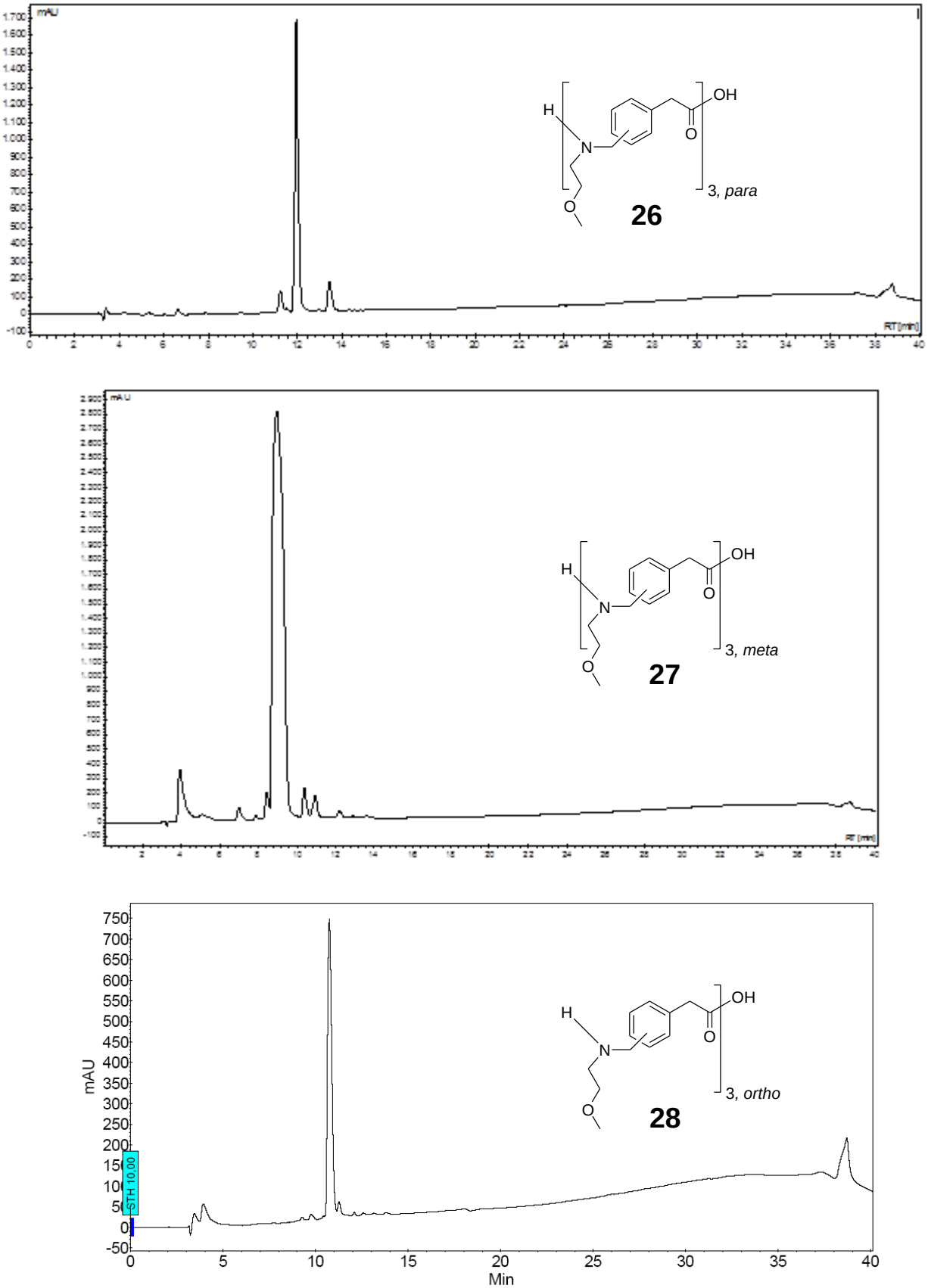


Figure S17: HPLC chromatograms of trimeric linear **26**-**28** as crude mixture. Conditions: 5 → 100% A in 30 min (A, 0.1% TFA in acetonitrile, B, 0.1% TFA in water); flow: 1 mL min^{-1}, 220 nm.

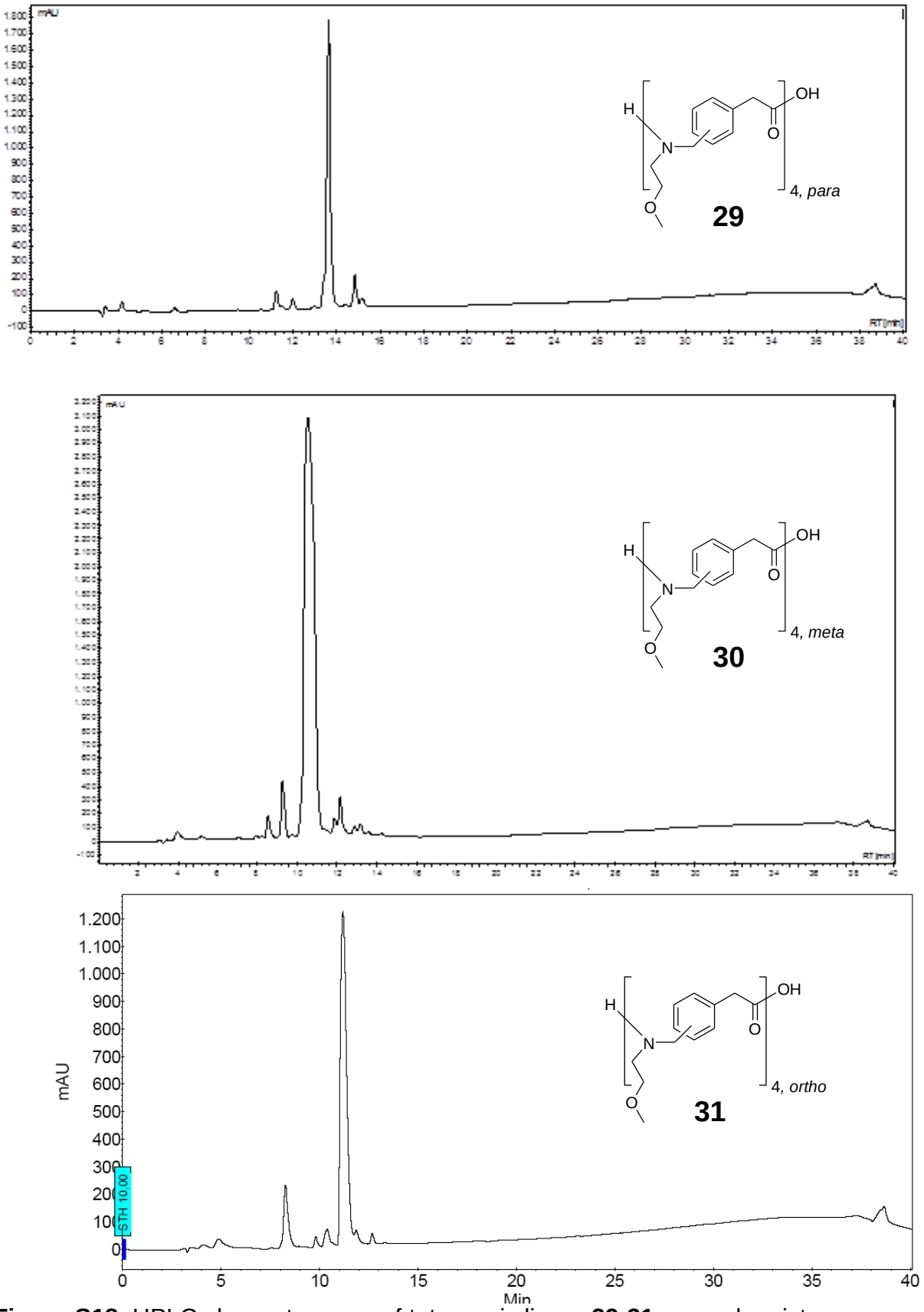
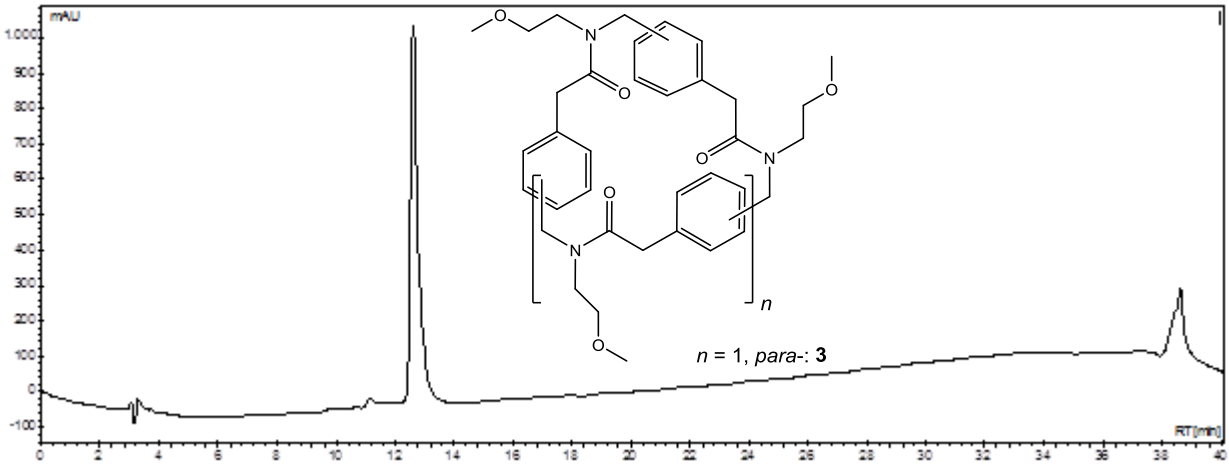
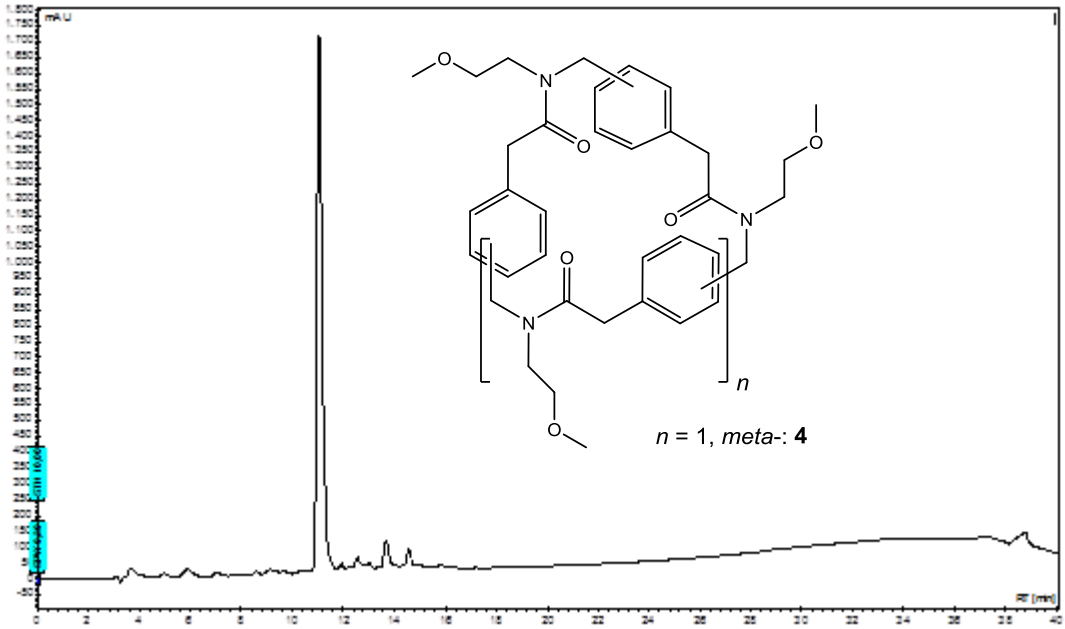


Figure S18: HPLC chromatograms of tetrameric linear **29**-**31** as crude mixture. Conditions: 5 → 100% A in 30 min (A, 0.1% TFA in acetonitrile, B, 0.1% TFA in water); flow: 1 mL min^{-1}, 220 nm.





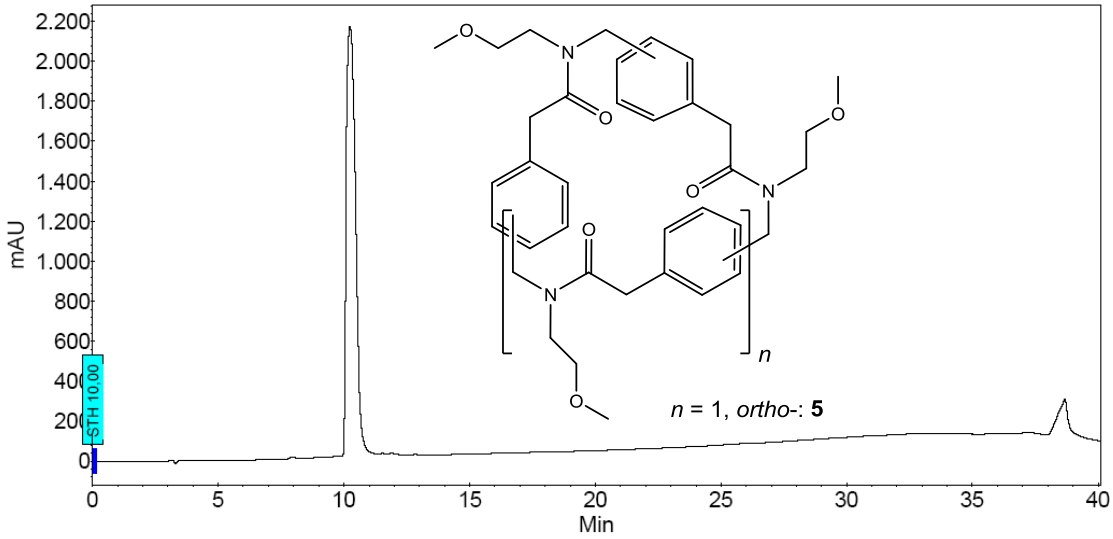


Figure S19: HPLC chromatogram of trimeric cyclic **3**-**5** as crude mixture Conditions: 5 → 100% A in 30 min (A, 0.1% TFA in acetonitrile, B, 0.1% TFA in water); flow: 1 mL min^{-1}, 220 nm

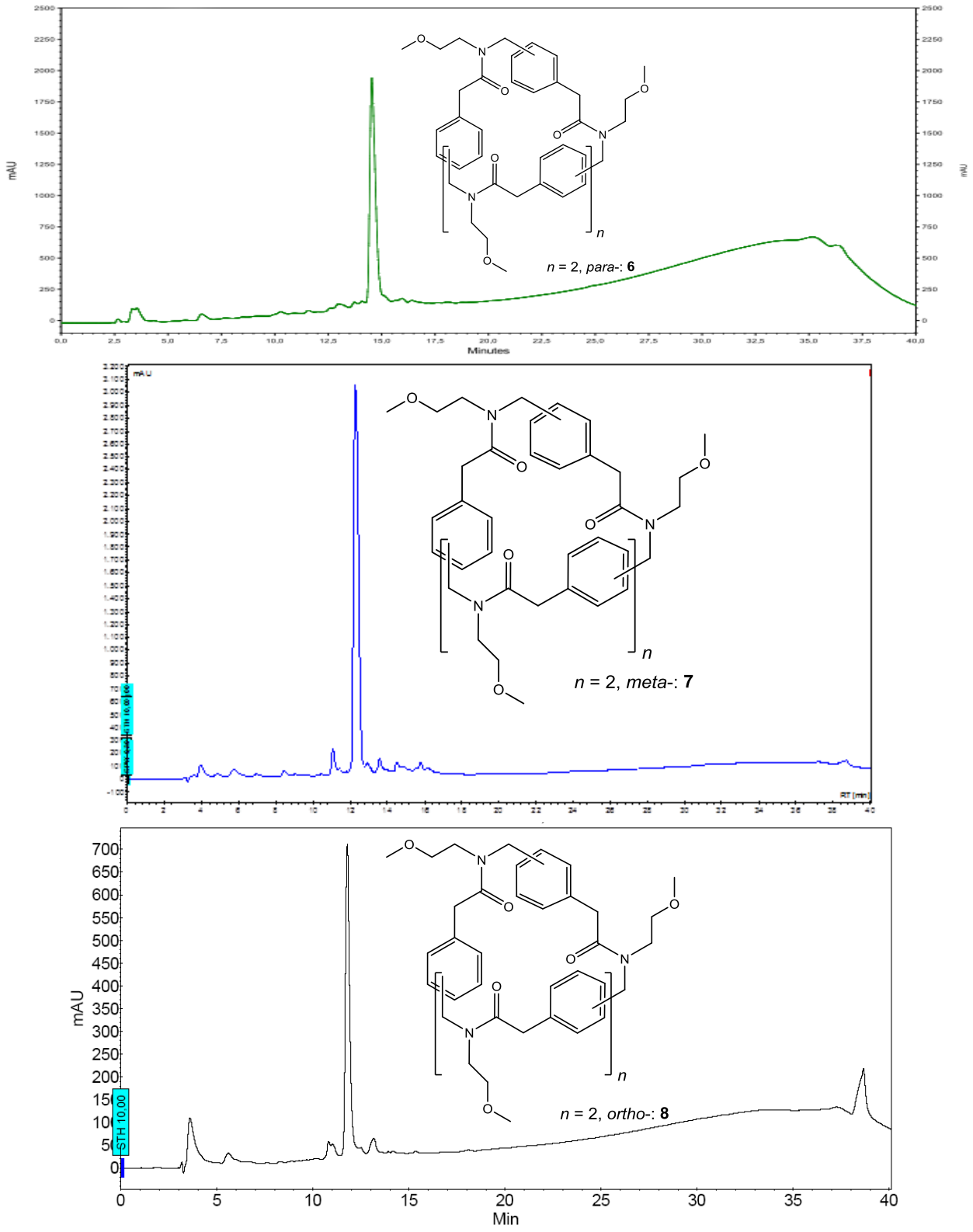


Figure S20: HPLC chromatogram of tetrameric cyclic **6**-**8** as crude mixture Conditions: 5 → 100% A in 30 min (A, 0.1% TFA in acetonitrile, B, 0.1% TFA in water); flow: 1 mL min^{-1}, 220 nm

4.0 Computational studies

4.1 Computational details

The DFT calculations were performed with the Gaussian09 set of programs,[8] using the BP86 functional of Becke and Perdew.[9] The electronic configuration of the molecular systems was described with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for H, C, N, O (SVP keyword in Gaussian).[10] The geometry optimizations were performed without symmetry constraints, and the characterization of the located stationary points was performed by analytical frequency calculations. Solvent effects including contributions of non electrostatic terms have been estimated in single-point calculations on the gas phase optimized structures, based on the polarizable continuous solvation model PCM using $CHCl_3$ as a solvent.[11,12]

4.2 Cartesian coordinates of calculated structures

1
Na SCF Done: -162.156233146 A.U.

Na	0.000000	0.000000	0.000000

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Compound **3** SCF Done: -1551.93832616 A.U.

C	1.888839	2.715498	-1.028680
C	2.852177	1.700648	-1.108428
C	3.848999	1.566660	-0.113695
C	3.842977	2.474193	0.964906
C	2.879075	3.495874	1.041733
C	1.891709	3.634359	0.046766
C	4.930974	0.502243	-0.233833
C	4.413003	-0.899122	-0.604840
N	3.990722	-1.723420	0.420009
C	3.838161	-1.322804	1.810496
C	0.865085	4.752589	0.103363
N	-0.501718	4.312315	0.422181
C	-0.772680	3.974802	1.811479
C	3.685583	-3.126426	0.100696
C	2.202895	-3.453299	0.047217
C	1.407054	-2.988880	-1.025882
C	0.045985	-3.314184	-1.103680
C	-0.567155	-4.111533	-0.108966
C	0.223191	-4.560983	0.967994
C	1.590180	-4.238355	1.042988
C	-2.028986	-4.519495	-0.227363
C	-2.985219	-3.374405	-0.603798
N	-3.487504	-2.591563	0.418109
C	-3.065159	-2.656868	1.809044
C	-4.551582	-1.628433	0.096766

C	-4.095351	-0.180095	0.042255
C	-4.473465	0.743333	1.036079
C	-4.069250	2.088577	0.962726
C	-3.280405	2.548355	-0.110927
C	-2.892919	1.618632	-1.104068
C	-3.291247	0.276969	-1.027334
C	-2.900808	4.017774	-0.227495
C	-1.429356	4.272085	-0.600880
H	-0.230898	-5.190563	1.751905
H	-0.557778	-2.964068	-1.956618
H	1.879043	-2.380521	-1.814394
H	2.193484	-4.620224	1.884279
H	4.147646	-3.322116	-0.887310
H	4.184179	-3.770165	0.859086
O	4.398441	-1.265596	-1.785554
H	4.669329	-1.702060	2.450382
H	2.885343	-1.731108	2.210349
H	3.783494	-0.223389	1.906002
H	5.610043	0.765448	-1.071487
H	5.543977	0.480430	0.690321
H	-2.285178	1.966685	-1.954933
H	-4.392110	2.796905	1.744642
H	-5.109926	0.412672	1.874505
H	-2.998507	-0.436000	-1.814926
H	-4.950360	-1.933337	-0.891087
H	-5.358476	-1.738896	0.855198
O	-3.294579	-3.184583	-1.785568
H	-3.805175	-3.192546	2.449156
H	-2.081880	-3.151461	1.904167
H	-2.949353	-1.626976	2.209700
H	-2.138296	-5.243096	-1.061790
H	-2.354018	-5.037078	0.698470
H	2.851551	1.003971	-1.962239
H	4.616376	2.394994	1.747830
H	2.908610	4.207536	1.884313
H	1.126811	2.821921	-1.817691
H	1.171310	5.505363	0.863500
H	0.801634	5.252857	-0.883361
O	-1.107524	4.448230	-1.781495
H	-0.879175	4.881357	2.452651
H	-1.686078	3.359699	1.901073
H	0.066780	3.368237	2.213386
H	-3.187021	4.557295	0.698456
H	-3.470441	4.476247	-1.062520

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Compound **3**+Na SCF Done: -1714.12033944 A.U.

C	2.468535	-2.955626	1.083649
C	1.127039	-3.352177	1.208435
C	0.377225	-3.735013	0.076742
C	1.008161	-3.706955	-1.184963
C	2.344604	-3.301699	-1.308676

C	3.095492	-2.922954	-0.177889
C	-1.059058	-4.188910	0.219500
C	-2.103007	-3.146148	-0.214990
N	-3.421680	-3.412228	0.053988
C	-3.920195	-4.683380	0.586162
C	4.553510	-2.510778	-0.319991
N	4.877313	-1.235829	0.342442
C	5.991293	-1.229519	1.285107
C	-4.448675	-2.480458	-0.445433
C	-4.244391	-1.030258	-0.044148
C	-4.559441	-0.004722	-0.960612
C	-4.287909	1.337449	-0.656664
C	-3.682624	1.692415	0.568528
C	-3.443978	0.674098	1.516054
C	-3.733104	-0.669077	1.219282
C	-3.166546	3.095374	0.777737
C	-1.845689	3.294620	-0.004758
N	-1.229647	4.506660	0.057681
C	-1.740360	5.665311	0.790820
C	-0.033709	4.715257	-0.781944
C	1.173090	3.866763	-0.412310
C	2.073355	3.481827	-1.426715
C	3.185851	2.682200	-1.135622
C	3.428019	2.235097	0.180940
C	2.547709	2.651523	1.199443
C	1.437684	3.464134	0.910262
C	4.545169	1.257264	0.465838
C	4.247681	-0.121246	-0.173719
Na	-1.301074	0.108098	-0.818286
H	-3.001348	0.930736	2.492868
H	-4.507793	2.116863	-1.404149
H	-4.988358	-0.263432	-1.942858
H	-3.509073	-1.450743	1.962702
H	-4.509992	-2.544872	-1.554760
H	-5.422821	-2.843293	-0.054684
O	-1.771028	-2.090739	-0.793055
H	-3.110435	-5.268969	1.052190
H	-4.379496	-5.304117	-0.214928
H	-4.691198	-4.492325	1.360327
H	-1.230917	-5.107315	-0.386644
H	-1.253598	-4.483460	1.272443
H	2.723287	2.323791	2.237724
H	3.858455	2.369750	-1.948205
H	1.888235	3.794077	-2.468105
H	0.758693	3.763592	1.725475
H	-0.300823	4.516587	-1.841873
H	0.216462	5.794913	-0.710920
O	-1.363337	2.366532	-0.689585
H	-2.172197	6.423846	0.101005
H	-2.520196	5.371574	1.514600
H	-0.916509	6.144652	1.357940

H	-3.907979	3.846961	0.429138
H	-2.998215	3.297337	1.857003
H	0.661154	-3.381329	2.208064
H	0.445862	-4.003660	-2.085376
H	2.814761	-3.266887	-2.304472
H	3.032755	-2.663868	1.984339
H	5.207127	-3.285748	0.132657
H	4.809330	-2.449616	-1.399794
O	3.462102	-0.230563	-1.119635
H	6.944508	-1.522891	0.789977
H	6.136420	-0.224225	1.717282
H	5.809409	-1.937563	2.121907
H	4.701356	1.168013	1.559831
H	5.506773	1.624005	0.039503

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Compound **4** SCF Done: -1551.92860586 A.U.

C	3.207317	3.895154	-0.158745
C	4.218136	3.018472	-0.592818
C	3.914550	1.671073	-0.882819
C	2.580782	1.240965	-0.740913
C	1.568813	2.092794	-0.256677
C	1.891404	3.436008	0.026494
C	0.213098	1.479483	0.035176
N	-0.958286	2.337597	-0.158879
C	-1.827705	2.468361	0.916905
C	-1.222639	2.715310	-1.543563
C	-3.271058	2.929436	0.653146
C	0.678044	-1.899461	2.510270
C	-0.175569	-2.204144	1.437485
C	0.355549	-2.601536	0.190165
C	1.757858	-2.648178	0.038781
C	2.629758	-2.341007	1.107377
C	2.072390	-1.980160	2.352648
C	4.139444	-2.351943	0.892474
N	4.668975	-1.040864	0.473709
C	4.673933	-0.762763	-0.882581
C	4.937909	-0.075263	1.528981
C	4.986149	0.679559	-1.322277
C	-6.292269	0.544262	0.798645
C	-5.459770	1.653077	1.023520
C	-4.181801	1.724799	0.426084
C	-3.766245	0.653279	-0.388521
C	-4.588246	-0.468774	-0.621005
C	-5.862422	-0.515913	-0.020691
C	-4.078657	-1.578144	-1.529758
N	-2.979222	-2.389258	-0.970762
C	-1.682828	-2.054738	-1.312748
C	-3.382286	-3.482972	-0.096725
O	-1.428406	-1.016558	-1.939440
C	-0.544068	-3.028344	-0.963187
O	-1.503601	2.137859	2.060235

O	4.384168	-1.625441	-1.718556
H	3.455658	4.946351	0.060534
H	5.252740	3.384552	-0.703205
H	2.318270	0.198261	-0.985366
H	1.110843	4.115271	0.405878
H	0.178844	1.165949	1.100113
H	0.086012	0.566230	-0.590091
H	-1.407923	1.819662	-2.178630
H	-0.339140	3.246429	-1.958176
H	-2.090149	3.394071	-1.618247
H	-3.359752	3.637994	-0.197573
H	-3.593992	3.470188	1.563667
H	0.249754	-1.594244	3.478040
H	-1.265437	-2.119449	1.575688
H	2.195154	-2.920734	-0.935594
H	2.732795	-1.758480	3.207437
H	4.406079	-3.076509	0.099478
H	4.658544	-2.641564	1.830709
H	5.592743	-0.534335	2.302072
H	4.004522	0.274102	2.024779
H	5.454663	0.814181	1.128791
H	5.043107	0.626490	-2.428998
H	5.984898	1.011457	-0.965038
H	-7.286833	0.503576	1.271284
H	-5.803604	2.473568	1.674714
H	-2.774429	0.661186	-0.862320
H	-6.525401	-1.379285	-0.199227
H	-4.908592	-2.272070	-1.784739
H	-3.692509	-1.135350	-2.469430
H	-3.883948	-4.301244	-0.663254
H	-2.517351	-3.906724	0.443031
H	-4.096900	-3.107984	0.667601
H	-0.919447	-4.058024	-0.783479
H	0.065802	-3.074879	-1.887551

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Compound **4**+Na SCF Done: -1714.13765823 A.U.

C	-3.598134	2.435527	2.094852
C	-2.555999	3.288067	1.688906
C	-2.100702	3.274858	0.354977
C	-2.707837	2.386617	-0.557054
C	-3.734558	1.511702	-0.159278
C	-4.183922	1.549155	1.178025
C	-4.335448	0.546587	-1.170707
N	-4.340650	-0.863369	-0.729295
C	-3.129019	-1.477148	-0.578860
C	-5.614989	-1.541889	-0.474246
C	-3.141072	-2.939852	-0.100072
C	3.920487	1.898285	2.084938
C	4.137340	0.569074	1.681219
C	3.894176	0.178307	0.349178
C	3.424641	1.145641	-0.563553

C	3.179234	2.472369	-0.167539
C	3.441820	2.846268	1.167607
C	2.636598	3.472730	-1.177967
N	1.420361	4.182026	-0.729273
C	0.284720	3.438499	-0.570093
C	1.468247	5.625343	-0.477675
C	-0.973951	4.181738	-0.088871
C	-0.313289	-4.302479	2.102686
C	-1.574855	-3.837715	1.690390
C	-1.791851	-3.453380	0.351786
C	-0.718344	-3.540553	-0.558949
C	0.554769	-3.980370	-0.155098
C	0.748297	-4.370796	1.187232
C	1.692226	-4.024625	-1.165757
N	2.917480	-3.326507	-0.725391
C	2.843656	-1.970604	-0.572106
C	4.140020	-4.093579	-0.469505
O	1.790611	-1.356164	-0.833036
C	4.116658	-1.251768	-0.091579
O	-2.070416	-0.873590	-0.843038
O	0.279206	2.218550	-0.828082
H	-3.954472	2.464727	3.136480
H	-2.095313	3.973952	2.418741
H	-2.357994	2.361571	-1.601725
H	-4.996005	0.881474	1.509064
H	-3.772579	0.621662	-2.124664
H	-5.388795	0.818861	-1.385088
H	-5.658950	-2.531340	-0.972227
H	-6.437004	-0.927967	-0.886319
H	-5.809048	-1.687183	0.611312
H	-3.524740	-3.557364	-0.946011
H	-3.883836	-3.061899	0.714655
H	4.128451	2.195461	3.124736
H	4.502234	-0.171952	2.411366
H	3.225477	0.852881	-1.607004
H	3.269212	3.883950	1.496694
H	2.413405	2.944990	-2.128842
H	3.396777	4.248756	-1.401149
H	2.416271	6.027776	-0.879211
H	1.426549	5.868674	0.606656
H	0.639377	6.157585	-0.986650
H	-1.312316	4.831672	-0.929869
H	-0.705706	4.878660	0.731408
H	-0.159389	-4.613837	3.147748
H	-2.400095	-3.777576	2.418767
H	-0.873252	-3.239269	-1.607619
H	1.734369	-4.730321	1.523296
H	1.979781	-5.074389	-1.378899
H	1.347248	-3.575829	-2.120676
H	5.022875	-3.630021	-0.953624
H	4.353956	-4.203782	0.616468

H	4.023223	-5.106519	-0.896800
H	4.583802	-1.830948	0.731103
H	4.850130	-1.285865	-0.931271
Na	-0.001155	-0.007097	-0.648836

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Compound **5** SCF Done: -1551.91257424 A.U.

C	-5.657147	-2.933142	-0.743962
C	-4.433279	-3.469001	-0.311894
C	-3.341834	-2.644026	0.027679
C	-3.492774	-1.230257	-0.083222
C	-4.722892	-0.704006	-0.525460
C	-5.802551	-1.541521	-0.850022
C	-2.316525	-0.302024	0.166707
N	-2.619637	1.067451	0.591385
C	-2.063781	2.102991	-0.159177
C	-3.136548	1.227754	1.943434
C	-1.818266	3.446457	0.558418
C	5.361478	-3.443329	-0.748418
C	5.220485	-2.111271	-0.327418
C	3.964454	-1.569585	0.015474
C	2.814479	-2.403828	-0.086412
C	2.965272	-3.736607	-0.517727
C	4.225985	-4.262495	-0.842354
C	1.424608	-1.846223	0.172748
N	0.387260	-2.786402	0.598407
C	-0.784010	-2.825497	-0.155773
C	0.506092	-3.316297	1.950503
O	-0.816426	-2.440590	-1.323296
C	-2.068894	-3.287261	0.564382
C	0.307257	6.358766	-0.753640
C	-0.777613	5.575198	-0.325183
C	-0.619875	4.218896	0.024787
C	0.678113	3.636129	-0.075492
C	1.757770	4.429701	-0.508699
C	1.583607	5.783190	-0.841133
C	0.885285	2.153505	0.184117
N	2.218029	1.721590	0.608559
C	2.844732	0.738099	-0.156872
C	2.618271	2.077277	1.962778
O	2.528670	0.529415	-1.327133
C	3.891720	-0.144557	0.551834
O	-1.711599	1.935488	-1.325512
H	-6.491999	-3.604550	-0.999159
H	-4.319198	-4.563010	-0.232171
H	-4.822217	0.388785	-0.626558
H	-6.752539	-1.104430	-1.196388
H	-1.733327	-0.219111	-0.774539
H	-1.642557	-0.749695	0.933970
H	-2.350114	1.110419	2.728055
H	-3.911657	0.454211	2.121377
H	-3.622874	2.212524	2.075942

H	-1.681677	3.273737	1.648320
H	-2.728500	4.077582	0.463843
H	6.357993	-3.836183	-1.004580
H	6.113466	-1.467788	-0.258646
H	2.064514	-4.365372	-0.604623
H	4.317303	-5.307289	-1.179046
H	1.062757	-1.375185	-0.764021
H	1.481254	-1.039810	0.942210
H	1.560830	-3.611902	2.129362
H	-0.113013	-4.223328	2.082570
H	0.223204	-2.575319	2.737259
H	-1.989516	-3.088884	1.656058
H	-2.158428	-4.390462	0.463537
H	0.150989	7.416261	-1.018817
H	-1.780704	6.028270	-0.256528
H	2.751737	3.962022	-0.597021
H	2.444681	6.382601	-1.176826
H	0.154624	1.797352	0.948353
H	0.666132	1.603832	-0.754633
H	2.129580	1.445496	2.744953
H	3.715142	2.010403	2.088627
H	2.332989	3.132151	2.153516
H	4.891362	0.330168	0.439567
H	3.693297	-0.178690	1.645088

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Compound **5**+Na SCF Done: -1714.12012968 A.U.

C	-5.236341	-1.222035	-1.930134
C	-4.413389	-2.079918	-1.182395
C	-3.581661	-1.595538	-0.152049
C	-3.583874	-0.198189	0.126431
C	-4.411778	0.652889	-0.628031
C	-5.234946	0.152959	-1.650686
C	-2.718888	0.356339	1.253689
N	-2.453955	1.806327	1.254995
C	-1.490459	2.264656	0.393153
C	-3.068890	2.617846	2.305729
C	-0.872987	3.655280	0.633063
C	3.678946	-3.907936	-1.936101
C	4.010375	-2.770972	-1.180740
C	3.174836	-2.299868	-0.147305
C	1.965025	-3.000645	0.125125
C	1.641850	-4.138437	-0.637543
C	2.487954	-4.596370	-1.661069
C	1.047583	-2.532094	1.250747
N	-0.338777	-3.031554	1.248914
C	-1.219966	-2.424061	0.391140
C	-0.730042	-3.969789	2.300511
O	-0.798146	-1.706573	-0.530650
C	-2.731997	-2.584029	0.634700
C	1.555630	5.132150	-1.940428
C	0.402357	4.852145	-1.189283

C	0.407850	3.894210	-0.154877
C	1.618727	3.197434	0.124549
C	2.768285	3.484868	-0.633889
C	2.745904	4.444244	-1.659750
C	1.668593	2.176424	1.256501
N	2.791642	1.221902	1.260532
C	2.711801	0.158464	0.398089
C	3.797208	1.351358	2.315105
O	1.883770	0.167471	-0.527737
C	3.603456	-1.072355	0.644270
O	-1.082965	1.538631	-0.528491
H	-5.876964	-1.630229	-2.726975
H	-4.416937	-3.160246	-1.402877
H	-4.403320	1.733350	-0.414870
H	-5.875675	0.839392	-2.225769
H	-1.734426	-0.153388	1.229275
H	-3.181974	0.116876	2.236149
H	-2.562193	2.495742	3.290116
H	-4.130330	2.322757	2.425565
H	-3.056466	3.688746	2.033947
H	-0.702420	3.792267	1.724031
H	-1.618672	4.431589	0.353733
H	4.352226	-4.252667	-2.736034
H	4.946095	-2.229881	-1.398469
H	0.701296	-4.673044	-0.429827
H	2.213737	-5.490427	-2.242358
H	0.992783	-1.424592	1.230398
H	1.484240	-2.815740	2.233496
H	0.049431	-4.751004	2.405999
H	-1.673263	-4.483219	2.039982
H	-0.857393	-3.471859	3.288771
H	-2.932429	-2.503042	1.726232
H	-3.030926	-3.618624	0.357990
H	1.522043	5.888592	-2.739557
H	-0.531765	5.395329	-1.408514
H	3.699609	2.936405	-0.422079
H	3.659937	4.651859	-2.237598
H	1.694875	2.702123	2.236347
H	0.734142	1.579071	1.238789
H	3.423085	1.001597	3.304228
H	4.710234	0.781543	2.062994
H	4.090915	2.415403	2.415973
H	4.650768	-0.813916	0.373613
H	3.627751	-1.288317	1.735477
Na	0.006489	0.001856	-1.638670

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Compound **6** SCF Done: -2069.24269162 A.U.

C	-2.655495	3.891495	0.269725
C	-1.323322	4.616686	0.212487
C	-2.777254	2.497558	0.076358
C	-4.013337	1.854006	0.242914

C	-5.166202	2.569295	0.630651
C	-5.047689	3.960905	0.819003
C	-3.816751	4.609760	0.627789
H	-1.897914	1.913530	-0.227256
H	-4.081108	0.765938	0.081585
C	-6.507062	1.873014	0.820273
H	-5.930825	4.549312	1.121029
H	-3.753991	5.700573	0.781901
H	-7.050681	1.788819	-0.144900
N	-6.387372	0.500064	1.320537
H	-7.145544	2.474088	1.508520
C	-5.820622	0.356436	2.654828
C	-6.911666	-0.520181	0.543087
O	-7.504632	-0.295040	-0.516475
C	-6.648391	-1.982945	0.956851
H	-6.565545	-2.136136	2.049719
H	-7.538539	-2.543617	0.607741
C	-5.397297	-2.485814	0.248115
C	-5.372595	-2.559465	-1.163110
C	-4.208237	-2.946139	-1.839944
C	-3.022696	-3.252872	-1.137224
C	-3.052297	-3.202075	0.270326
C	-4.224785	-2.829577	0.952135
H	-6.276817	-2.281248	-1.726785
H	-4.212202	-2.989253	-2.942292
C	-1.742586	-3.527225	-1.910631
H	-2.140119	-3.444224	0.839165
H	-4.219572	-2.797502	2.054834
N	-0.772008	-4.390371	-1.237218
H	-1.995090	-3.959289	-2.906571
H	-1.210957	-2.567766	-2.089073
C	0.466184	-3.843758	-0.923495
C	-1.106618	-5.806214	-1.167594
H	-5.541206	-0.689525	2.866119
H	-4.900376	0.971289	2.740217
H	-6.535431	0.697141	3.439911
O	0.701491	-2.645908	-1.084548
C	1.541353	-4.816730	-0.390145
H	-0.497458	-6.330972	-0.409687
H	-2.171678	-5.918154	-0.875357
H	-0.965600	-6.320776	-2.147450
C	2.834730	-4.137246	0.007582
H	1.139672	-5.387118	0.474362
H	1.734188	-5.575191	-1.184047
C	3.364413	-4.299148	1.302684
C	4.568319	-3.674615	1.675776
C	5.271887	-2.863230	0.763830
C	4.745953	-2.706149	-0.539440
C	3.550400	-3.335147	-0.910556
H	2.827222	-4.924295	2.036010
H	4.966641	-3.826540	2.693497

C	6.542207	-2.131406	1.167144
H	5.286455	-2.069170	-1.257669
H	3.153884	-3.187983	-1.926175
N	6.317483	-0.714233	1.513354
H	7.004350	-2.626392	2.049113
H	7.267534	-2.133504	0.331127
C	6.555014	0.226974	0.519482
C	5.668825	-0.482103	2.796097
O	6.948661	-0.104095	-0.609017
C	6.368515	1.719628	0.844323
H	6.231836	1.914027	1.927949
H	7.325649	2.201106	0.557416
C	5.230591	2.372823	0.074077
C	3.940581	1.794997	0.039448
C	2.877340	2.436753	-0.611271
C	3.063997	3.687358	-1.243280
C	4.352700	4.255591	-1.223726
C	5.421050	3.605323	-0.581129
H	3.765039	0.816229	0.515265
H	1.884615	1.958860	-0.639504
C	1.889783	4.398276	-1.899026
H	4.528096	5.222882	-1.724700
H	6.421100	4.069643	-0.583235
H	1.357653	3.718857	-2.594161
N	0.879880	4.848335	-0.927732
H	2.253251	5.279040	-2.473901
C	-0.335828	4.180172	-0.889535
C	1.294461	5.923859	-0.040298
H	5.672999	0.588225	3.065383
H	4.612393	-0.834842	2.794186
H	6.205788	-1.035693	3.597591
O	-0.594200	3.271255	-1.682052
H	0.487527	6.209185	0.655373
H	2.181523	5.625751	0.562397
H	1.576161	6.828047	-0.626880
H	-1.510925	5.708626	0.124798
H	-0.803867	4.488557	1.191101

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Compound **6**+Na SCF Done: -2231.43679165 A.U.

C	-2.553851	3.145633	1.058334
C	-1.254223	3.869437	0.777397
C	-2.677603	2.235951	2.133455
C	-3.897279	1.573804	2.381447
C	-5.026738	1.800564	1.562111
C	-4.896766	2.702347	0.480851
C	-3.682612	3.362890	0.237188
H	-1.822148	2.069957	2.810348
H	-3.977021	0.903575	3.253642
C	-6.355249	1.100618	1.819197
H	-5.766694	2.874961	-0.170330
H	-3.615526	4.074734	-0.602124

H	-7.183292	1.730748	1.440328
N	-6.453442	-0.216111	1.160686
H	-6.503774	0.944161	2.906890
C	-6.085714	-1.385324	1.947345
C	-6.770299	-0.211923	-0.185090
O	-7.025410	0.839479	-0.780950
C	-6.698602	-1.539165	-0.961474
H	-7.170273	-2.386877	-0.426092
H	-7.283293	-1.360890	-1.885578
C	-5.250047	-1.857709	-1.298058
C	-4.462426	-0.916915	-2.002868
C	-3.102911	-1.167132	-2.261275
C	-2.484953	-2.358130	-1.815967
C	-3.279779	-3.310316	-1.148490
C	-4.638021	-3.062129	-0.892705
H	-4.928370	0.020713	-2.347602
H	-2.514639	-0.427889	-2.834789
C	-1.009046	-2.608839	-2.088127
H	-2.828465	-4.254467	-0.803802
H	-5.233710	-3.825039	-0.364929
N	-0.289841	-3.281470	-0.992410
H	-0.899778	-3.253704	-2.985131
H	-0.505275	-1.646278	-2.328088
C	-0.208863	-2.633751	0.208369
C	0.449022	-4.497092	-1.338998
H	-6.394229	-2.315722	1.440010
H	-4.988280	-1.446819	2.130866
H	-6.597347	-1.356344	2.932861
O	-0.781649	-1.532934	0.374989
C	0.624556	-3.234607	1.339530
H	-0.235033	-5.250309	-1.782451
H	1.252908	-4.275336	-2.073790
H	0.924529	-4.937964	-0.447247
C	2.119114	-2.986328	1.152516
H	0.266650	-2.731902	2.261816
H	0.425428	-4.318427	1.466286
C	3.074750	-3.974892	1.466295
C	4.450314	-3.716753	1.328758
C	4.910776	-2.471306	0.855156
C	3.951389	-1.487963	0.532642
C	2.581086	-1.736408	0.687111
H	2.744859	-4.958384	1.841310
H	5.176172	-4.502897	1.595526
C	6.397615	-2.194767	0.659900
H	4.280748	-0.503883	0.165221
H	1.859441	-0.939777	0.444199
N	6.751924	-0.794246	0.899588
H	7.000691	-2.855751	1.319967
H	6.686639	-2.406899	-0.391816
C	6.988854	0.000740	-0.212846
C	6.720480	-0.361418	2.290799

O	7.070446	-0.476643	-1.346157
C	7.012638	1.535802	-0.044422
H	7.273549	1.880337	0.973165
H	7.790474	1.905854	-0.740561
C	5.642735	2.058378	-0.449053
C	4.659907	2.375070	0.511342
C	3.355679	2.732251	0.123307
C	3.003167	2.802167	-1.238265
C	3.996239	2.518018	-2.201588
C	5.288902	2.139004	-1.815286
H	4.908890	2.332535	1.584251
H	2.603287	2.954426	0.897046
C	1.585972	3.108467	-1.706177
H	3.750135	2.578473	-3.275101
H	6.037510	1.881374	-2.580014
H	1.068226	2.168594	-1.984940
N	0.733990	3.767333	-0.707758
H	1.620824	3.746537	-2.617581
C	-0.355493	3.109504	-0.216812
C	1.047474	5.165162	-0.396967
H	7.166561	0.640568	2.411523
H	5.684275	-0.339077	2.697936
H	7.312407	-1.065574	2.914723
O	-0.623521	1.933511	-0.546538
H	0.833132	5.410241	0.660058
H	2.130367	5.327761	-0.558474
H	0.486582	5.869512	-1.050653
H	-1.466431	4.886230	0.386021
H	-0.681984	4.019213	1.719907
Na	-2.002474	0.269654	0.017655

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Compound **6**+2Na SCF Done: -2393.61630227 A.U.

C	4.658179	-3.175817	0.473000
C	3.539195	-4.163371	0.233606
C	4.629401	-2.305753	1.586159
C	5.550370	-1.251069	1.704348
C	6.518985	-1.023628	0.702548
C	6.608232	-1.946800	-0.362055
C	5.692476	-3.008423	-0.474883
H	3.859232	-2.440431	2.363434
H	5.485367	-0.570509	2.568574
C	7.438278	0.186625	0.742449
H	7.381589	-1.814328	-1.136466
H	5.767033	-3.696590	-1.333015
H	7.926298	0.310599	-0.249050
N	6.774762	1.448050	1.134981
H	8.251624	0.015294	1.478266
C	7.505354	2.289074	2.088836
C	5.660723	1.840150	0.448048
O	5.180514	1.121906	-0.454804
C	4.990618	3.177325	0.814067

H	4.889638	3.255104	1.917437
H	5.670048	4.003267	0.509038
C	3.636504	3.343624	0.154476
C	3.498858	4.041177	-1.061458
C	2.240952	4.184530	-1.672092
C	1.085160	3.624806	-1.090848
C	1.221304	2.923322	0.127816
C	2.476116	2.790812	0.742334
H	4.384536	4.491376	-1.538163
H	2.160431	4.745119	-2.618074
C	-0.268085	3.753734	-1.774022
H	0.330792	2.485740	0.608050
H	2.553454	2.257048	1.704808
N	-1.326993	4.294847	-0.901466
H	-0.177346	4.410723	-2.665830
H	-0.626408	2.763744	-2.118723
C	-2.400048	3.517578	-0.588391
C	-1.205137	5.709907	-0.540721
H	6.922747	3.185582	2.359450
H	7.716429	1.721228	3.018190
H	8.474030	2.624681	1.658836
O	-2.474543	2.320340	-0.954028
C	-3.538901	4.163273	0.233933
H	-1.701742	5.932096	0.420842
H	-0.131588	5.956088	-0.423737
H	-1.632131	6.370877	-1.326706
C	-4.657948	3.175768	0.473242
H	-3.128345	4.530248	1.199268
H	-3.909239	5.062161	-0.304091
C	-4.629051	2.305433	1.586181
C	-5.550080	1.250790	1.704273
C	-6.518869	1.023663	0.702576
C	-6.608209	1.947089	-0.361797
C	-5.692413	3.008691	-0.474512
H	-3.858724	2.439827	2.363348
H	-5.485004	0.570046	2.568348
C	-7.438268	-0.186515	0.742423
H	-7.381648	1.814799	-1.136158
H	-5.767086	3.697103	-1.332437
N	-6.774850	-1.447961	1.134956
H	-8.251597	-0.015088	1.478242
H	-7.926319	-0.310417	-0.249075
C	-5.660897	-1.840175	0.447925
C	-7.505744	-2.289202	2.088415
O	-5.180669	-1.121972	-0.454949
C	-4.990914	-3.177443	0.813826
H	-4.890201	-3.255496	1.917196
H	-5.670298	-4.003280	0.508407
C	-3.636688	-3.343657	0.154443
C	-2.476360	-2.790947	0.742488
C	-1.221473	-2.923408	0.128085

C	-1.085211	-3.624732	-1.090643
C	-2.240960	-4.184377	-1.672076
C	-3.498921	-4.041072	-1.061570
H	-2.553774	-2.257293	1.705016
H	-0.331019	-2.485905	0.608500
C	0.268057	-3.753645	-1.773794
H	-2.160336	-4.744853	-2.618116
H	-4.384560	-4.491191	-1.538421
H	0.626352	-2.763662	-2.118546
N	1.326988	-4.294723	-0.901256
H	0.177291	-4.410664	-2.665576
C	2.400190	-3.517544	-0.588483
C	1.205109	-5.709764	-0.540426
H	-6.922901	-3.185387	2.359589
H	-7.717694	-1.721286	3.017517
H	-8.473977	-2.625308	1.657803
O	2.474852	-2.320407	-0.954351
H	1.701742	-5.931903	0.421134
H	0.131559	-5.955905	-0.423403
H	1.632077	-6.370780	-1.326387
H	3.909528	-5.062016	-0.304837
H	3.128851	-4.530727	1.198876
Na	3.961554	-0.652113	-0.907075
Na	-3.961426	0.652083	-0.907028

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Compound **7** SCF Done: -2069.25206694 A.U.

C	-3.217087	2.257386	-0.192856
C	-2.029274	2.622369	0.473682
C	-1.934889	3.905071	1.057864
C	-3.019919	4.792302	0.981937
C	-4.201780	4.414279	0.319894
C	-4.313007	3.142559	-0.282439
C	-0.858216	1.654413	0.535186
N	0.187549	1.939522	-0.468460
C	-0.192355	1.689827	-1.854988
C	1.324553	2.601054	-0.044189
O	1.470487	2.964112	1.127442
C	2.429419	2.872805	-1.092418
C	3.810994	2.946275	-0.476946
C	4.187369	4.029051	0.349746
C	5.468522	4.075067	0.917855
C	6.388412	3.036449	0.681277
C	6.032746	1.944197	-0.133672
C	4.742513	1.916903	-0.708344
H	3.463977	4.833058	0.552201
H	5.754191	4.925401	1.557754
H	7.395776	3.078864	1.129308
C	6.996900	0.797705	-0.390458
H	4.470662	1.067763	-1.357965
H	2.174152	3.838780	-1.585433
H	2.428363	2.106942	-1.891876

H	-0.910936	2.454458	-2.229023
H	0.687127	1.692019	-2.523101
H	-0.687043	0.698429	-1.924505
H	-1.214565	0.618786	0.359996
H	-0.361961	1.715664	1.522080
H	-1.004560	4.191696	1.573934
H	-2.949869	5.788682	1.447808
H	-5.049372	5.118388	0.266702
H	-3.285990	1.252834	-0.643508
H	8.003338	1.053128	0.010003
N	6.565587	-0.477003	0.208365
H	7.088484	0.603728	-1.477549
C	6.133555	-1.483172	-0.629992
C	6.622443	-0.563134	1.661418
O	6.006218	-1.318414	-1.850078
C	5.786454	-2.848021	-0.004689
H	5.930450	-1.333474	2.045979
H	7.651867	-0.780493	2.030799
H	6.298721	0.406296	2.094825
C	4.321526	-2.954978	0.398207
H	6.003050	-3.578540	-0.811350
H	6.438643	-3.102523	0.854424
C	3.306623	-2.618915	-0.525435
C	1.943926	-2.702778	-0.182923
C	1.589707	-3.144806	1.110875
C	2.586549	-3.495034	2.033470
C	3.945326	-3.398854	1.682274
H	3.603343	-2.277001	-1.531530
C	0.880655	-2.269238	-1.181972
H	0.526535	-3.210288	1.393341
H	2.305369	-3.841238	3.040988
H	4.721372	-3.681658	2.413137
N	-0.301481	-3.135290	-1.209326
H	0.509953	-1.255557	-0.924919
H	1.328060	-2.210538	-2.199916
C	-1.534971	-2.593350	-0.898230
C	-0.091916	-4.532220	-1.586756
O	-1.687869	-1.387004	-0.677101
C	-2.730547	-3.567808	-0.856637
C	-3.852951	-3.110392	0.054049
H	-3.104843	-3.662683	-1.901680
H	-2.400602	-4.580873	-0.552213
H	0.036491	-5.203856	-0.708682
H	-0.923249	-4.913027	-2.210642
H	0.833876	-4.601597	-2.191766
C	-4.782529	-2.137407	-0.363561
C	-5.851474	-1.741794	0.471170
C	-5.970283	-2.323598	1.750589
C	-5.038649	-3.280702	2.187044
C	-3.989134	-3.673435	1.341884
H	-4.696169	-1.678976	-1.361910

C	-6.861999	-0.714540	-0.017988
H	-6.811907	-2.038734	2.404303
H	-5.139209	-3.733601	3.186383
H	-3.270378	-4.438298	1.680969
H	-7.797469	-0.797532	0.577500
N	-6.402830	0.681047	0.061100
H	-7.100945	-0.903052	-1.083071
C	-6.511752	1.329533	1.358770
C	-5.917140	1.265680	-1.092962
O	-5.784696	0.619699	-2.139335
C	-5.571347	2.763622	-1.052986
H	-5.979986	2.297274	1.365867
H	-7.576370	1.499371	1.643465
H	-6.044345	0.695230	2.143248
H	-6.434890	3.350926	-0.672475
H	-5.445871	3.036526	-2.121576

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Compound **7**+Na SCF Done: -2231.45925707 A.U.

C	0.589377	-3.380866	0.103885
C	1.868661	-3.267342	0.677654
C	2.998904	-3.322100	-0.166019
C	2.841109	-3.484422	-1.550971
C	1.555666	-3.587506	-2.111309
C	0.414383	-3.537047	-1.287590
C	2.014610	-3.114484	2.186920
N	3.019893	-2.115787	2.584734
C	4.294409	-2.550009	3.165308
C	2.702726	-0.802581	2.369527
O	1.606536	-0.480403	1.867416
C	3.762508	0.260341	2.681375
C	4.608983	0.533849	1.438686
C	6.017463	0.619550	1.471847
C	6.736150	0.867677	0.287737
C	6.066490	1.026366	-0.940475
C	4.659986	0.941296	-0.989078
C	3.956573	0.699212	0.205062
H	6.558494	0.498622	2.424972
H	7.835030	0.934131	0.322712
H	6.645256	1.205988	-1.861660
C	3.853362	1.095655	-2.270662
H	2.862725	0.627900	0.161125
H	4.405031	-0.008803	3.541853
H	3.200253	1.174690	2.963244
H	4.385428	-3.645927	3.051270
H	5.157722	-2.087710	2.645267
H	4.362714	-2.316600	4.250421
H	2.311892	-4.080940	2.644503
H	1.033957	-2.832654	2.622789
H	4.011133	-3.232034	0.258786
H	3.728410	-3.533895	-2.201581
H	1.439321	-3.710434	-3.200445

H	-0.297758	-3.339044	0.759323
H	3.148700	0.246772	-2.373935
N	3.048392	2.335691	-2.303938
H	4.519488	1.104128	-3.157723
C	1.771734	2.321407	-1.808272
C	3.750381	3.516282	-2.800664
O	1.268041	1.287743	-1.325262
C	0.977400	3.643122	-1.867915
H	3.138549	4.428264	-2.702548
H	4.688956	3.671058	-2.225703
H	4.018800	3.391659	-3.872625
C	-0.414317	3.537940	-1.286675
H	1.551313	4.421528	-1.318012
H	0.926660	3.988581	-2.922367
C	-0.589577	3.381357	0.104722
C	-1.868960	3.267587	0.678216
C	-2.999044	3.322503	-0.165662
C	-2.840984	3.485232	-1.550537
C	-1.555438	3.588564	-2.110602
H	0.297435	3.339391	0.760315
C	-2.015155	3.114261	2.187408
H	-4.011353	3.232227	0.258912
H	-3.728160	3.534836	-2.201308
H	-1.438897	3.711803	-3.199682
N	-3.020286	2.115219	2.584761
H	-1.034523	2.832507	2.623364
H	-2.312734	4.080509	2.645239
C	-2.702702	0.802124	2.369541
C	-4.294991	2.549074	3.165176
O	-1.606380	0.480285	1.867491
C	-3.762168	-0.261131	2.681321
C	-4.608745	-0.534715	1.438709
H	-3.199625	-1.175372	2.962965
H	-4.404639	0.007690	3.541944
H	-4.362856	2.316867	4.250583
H	-4.386981	3.644783	3.049862
H	-5.158008	2.085463	2.645842
C	-3.956515	-0.699094	0.204858
C	-4.660018	-0.941426	-0.989181
C	-6.066440	-1.027673	-0.940256
C	-6.735923	-0.869906	0.288171
C	-6.017145	-0.621587	1.472187
H	-2.862736	-0.626908	0.160647
C	-3.853552	-1.094895	-2.270970
H	-6.645290	-1.207494	-1.861350
H	-7.834741	-0.937252	0.323401
H	-6.558044	-0.501414	2.425483
H	-3.149113	-0.245788	-2.373904
N	-3.048285	-2.334731	-2.304996
H	-4.519802	-1.103093	-3.157937
C	-3.750058	-3.515247	-2.802208

C	-1.771690	-2.320481	-1.809161
O	-1.268176	-1.286927	-1.325720
C	-0.977205	-3.642087	-1.869171
H	-3.137517	-4.426927	-2.705748
H	-4.687986	-3.671264	-2.226513
H	-4.019596	-3.389612	-3.873764
H	-0.926155	-3.987063	-2.923768
H	-1.551155	-4.420801	-1.319751
Na	0.000070	0.000048	0.204052

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Compound **7**+2Na SCF Done: -2393.61596301 A.U.

C	2.749765	-3.549088	-0.775151
C	1.467372	-3.868414	-0.280430
C	1.309131	-4.099801	1.100067
C	2.414793	-4.013938	1.964400
C	3.683173	-3.680864	1.461753
C	3.863230	-3.440740	0.082222
C	0.297726	-3.903584	-1.260312
N	-0.948048	-4.482090	-0.741749
C	-1.063121	-5.941980	-0.808083
C	-1.946410	-3.641636	-0.349592
O	-1.772823	-2.400638	-0.332134
C	-3.302843	-4.260638	0.048764
C	-4.307898	-3.220464	0.502124
C	-4.525348	-2.974682	1.875469
C	-5.412090	-1.961503	2.285833
C	-6.073610	-1.167156	1.333647
C	-5.865399	-1.386005	-0.046113
C	-5.002631	-2.431055	-0.443835
H	-4.005266	-3.584801	2.631669
H	-5.590613	-1.792827	3.359390
H	-6.753478	-0.367438	1.667914
C	-6.559759	-0.526927	-1.096336
H	-4.843238	-2.612993	-1.520807
H	-3.144508	-5.008645	0.854163
H	-3.697110	-4.831639	-0.820474
H	-0.091014	-6.394222	-0.528091
H	-1.823186	-6.322753	-0.103354
H	-1.325320	-6.282820	-1.833658
H	0.586565	-4.475900	-2.168382
H	0.061777	-2.869985	-1.584927
H	0.318259	-4.360472	1.503922
H	2.287260	-4.216373	3.039387
H	4.544533	-3.621600	2.147148
H	2.884373	-3.374202	-1.856027
H	-7.627241	-0.821041	-1.168236
N	-6.537301	0.924189	-0.814898
H	-6.103028	-0.719490	-2.090948
C	-5.316547	1.525648	-0.717909
C	-7.824969	1.624349	-0.858347
O	-4.273376	0.845934	-0.840303

C	-5.223177	3.039131	-0.457470
H	-7.699027	2.700975	-0.654530
H	-8.292553	1.520072	-1.860960
H	-8.522204	1.205722	-0.103402
C	-3.863073	3.440446	0.082407
H	-5.429401	3.558075	-1.421022
H	-6.017962	3.364143	0.243438
C	-2.749698	3.549228	-0.775024
C	-1.467313	3.868621	-0.280330
C	-1.308989	4.099602	1.100227
C	-2.414561	4.013287	1.964631
C	-3.682939	3.680179	1.461993
H	-2.884373	3.374628	-1.855940
C	-0.297795	3.904332	-1.260338
H	-0.318124	4.360301	1.504078
H	-2.286970	4.215417	3.039669
H	-4.544230	3.620602	2.147449
N	0.948034	4.482614	-0.741631
H	-0.061862	2.870910	-1.585523
H	-0.586755	4.477125	-2.168068
C	1.946428	3.642000	-0.349930
C	1.063045	5.942545	-0.807271
O	1.772851	2.400986	-0.333087
C	3.302872	4.260800	0.048690
C	4.307761	3.220511	0.502162
H	3.697308	4.831750	-0.820504
H	3.144515	5.008785	0.854095
H	1.823263	6.322994	-0.102534
H	1.325028	6.283879	-1.832736
H	0.090982	6.394631	-0.526873
C	5.002473	2.430966	-0.443719
C	5.865140	1.385865	-0.045886
C	6.073204	1.167068	1.333908
C	5.411754	1.961577	2.285995
C	4.525177	2.974847	1.875520
H	4.843152	2.612870	-1.520714
C	6.559705	0.526761	-1.095977
H	6.752953	0.367287	1.668265
H	5.590194	1.792952	3.359573
H	4.005159	3.585094	2.631660
H	7.627144	0.821044	-1.167829
N	6.537433	-0.924317	-0.814325
H	6.103015	0.719115	-2.090645
C	7.825302	-1.624173	-0.856780
C	5.316719	-1.526021	-0.718261
O	4.273538	-0.846518	-0.841729
C	5.223363	-3.039468	-0.457617
H	7.699571	-2.700685	-0.652222
H	8.293276	-1.520490	-1.859275
H	8.522100	-1.204813	-0.101846
H	6.018096	-3.364429	0.243362

H	5.429661	-3.558483	-1.421120
Na	-2.980553	-0.613084	0.107799
Na	2.980294	0.613002	0.105029

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Compound **8** SCF Done: -2069.23669559 A.U.

C	-0.870633	-3.430347	0.039419
C	-0.388583	-2.736612	1.310532
C	0.945895	-2.920406	1.773002
C	1.351307	-2.283897	2.965328
C	0.481684	-1.454644	3.692325
C	-0.819691	-1.240595	3.213946
C	-1.242541	-1.881064	2.037204
H	2.380809	-2.440186	3.329951
H	0.825276	-0.970928	4.620328
H	-1.510809	-0.571266	3.749544
H	-2.260217	-1.698801	1.659405
C	1.982232	-3.720063	0.994086
H	1.514217	-4.582686	0.472811
C	2.620258	-2.870789	-0.125431
H	2.727960	-4.143255	1.692019
O	1.883983	-2.328010	-0.961458
N	3.992394	-2.724923	-0.173424
C	4.572294	-2.044581	-1.352920
C	4.944755	-3.352179	0.736684
H	5.872299	-2.745195	0.749310
H	4.562724	-3.383469	1.773582
H	5.214732	-4.387540	0.423858
C	5.464051	-0.849073	-1.045095
H	5.167981	-2.791946	-1.924711
H	3.709477	-1.756084	-1.984384
C	4.953582	0.379967	-0.538483
C	5.853524	1.446640	-0.320855
C	7.225661	1.317259	-0.586398
C	7.730643	0.104851	-1.082707
C	6.848548	-0.963531	-1.306183
C	3.491247	0.544441	-0.184157
H	5.458189	2.405280	0.044997
H	7.900471	2.170243	-0.410020
H	8.804707	-0.009132	-1.299754
H	7.236453	-1.915218	-1.708184
C	2.806399	1.829288	-0.692328
H	2.887235	-0.308093	-0.557628
H	3.378530	0.503993	0.922960
O	3.379186	2.666909	-1.397466
N	1.482928	1.953631	-0.310871
C	0.683596	3.037826	-0.889875
C	0.792473	0.963843	0.519841
H	0.672858	-0.009415	-0.003824
H	1.333084	0.778788	1.470085
H	-0.211423	1.349432	0.777334
H	1.365136	3.558501	-1.596063

H	-0.143460	2.594949	-1.485038
C	0.148455	4.032245	0.136154
C	-1.215841	4.427752	0.197779
C	-1.608178	5.369388	1.174073
C	-0.688555	5.923090	2.077055
C	0.660661	5.537505	2.009727
C	1.065227	4.602181	1.046140
C	-2.268902	3.880012	-0.750906
H	-2.667895	5.671226	1.225378
H	-1.025192	6.654797	2.828666
H	1.399142	5.967815	2.705120
H	2.123096	4.299521	0.983888
C	-2.655175	2.416980	-0.445026
H	-3.182495	4.510511	-0.677842
H	-1.937395	3.961657	-1.808566
O	-2.270122	1.850288	0.581617
N	-3.421006	1.748281	-1.384402
C	-3.487211	0.289044	-1.286429
C	-3.966246	2.350458	-2.594681
H	-4.945365	1.882294	-2.827195
H	-4.144186	3.433068	-2.458276
H	-3.300175	2.208185	-3.477493
H	-3.250862	-0.143248	-2.282091
H	-2.654767	-0.013973	-0.618429
C	-4.780964	-0.295379	-0.735965
C	-5.077847	-1.680337	-0.901555
C	-6.264176	-2.189360	-0.327345
C	-7.147829	-1.372103	0.396381
C	-6.849622	-0.010498	0.557568
C	-5.674471	0.513193	-0.005649
C	-4.200838	-2.614874	-1.730113
H	-6.507759	-3.256212	-0.469008
H	-8.066904	-1.800044	0.827099
H	-7.528618	0.646434	1.124129
H	-5.431016	1.579524	0.122370
C	-2.692189	-2.681747	-1.395261
H	-4.642785	-3.633187	-1.702823
H	-4.214523	-2.297035	-2.793501
O	-1.871438	-2.173155	-2.163338
N	-2.306016	-3.317382	-0.225778
C	-3.201686	-4.128072	0.592659
H	-2.829644	-4.143742	1.636733
H	-4.221320	-3.701283	0.616231
H	-3.257829	-5.182519	0.232526
H	-0.598885	-4.512261	0.082313
H	-0.339716	-2.999880	-0.834580

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Compound **8**+Na SCF Done: -2231.43132108 A.U.

C	-0.590366	-3.970848	-0.146418
C	-0.343832	-3.338145	1.222540
C	0.985972	-3.164347	1.698376

C	1.185284	-2.579409	2.967647
C	0.106310	-2.166399	3.766066
C	-1.204516	-2.339638	3.294608
C	-1.419488	-2.922710	2.034010
H	2.215350	-2.442802	3.336009
H	0.291942	-1.712919	4.751847
H	-2.064006	-2.022645	3.905580
H	-2.449479	-3.045891	1.664619
C	2.207320	-3.568748	0.889407
H	2.061055	-4.556402	0.396018
C	2.576243	-2.541143	-0.201125
H	3.063969	-3.705161	1.579733
O	1.745480	-1.685143	-0.562066
N	3.816707	-2.609430	-0.768766
C	4.202169	-1.566686	-1.751840
C	4.835392	-3.581830	-0.374926
H	5.510613	-3.188425	0.416607
H	4.375925	-4.519997	-0.014582
H	5.454828	-3.837314	-1.257999
C	4.918720	-0.369266	-1.130781
H	4.871672	-2.054771	-2.489925
H	3.281831	-1.266746	-2.283856
C	4.282714	0.876842	-0.863892
C	5.035294	1.890192	-0.226582
C	6.379992	1.709858	0.127051
C	7.017050	0.495030	-0.171259
C	6.284854	-0.524189	-0.795831
C	2.848517	1.179539	-1.302890
H	4.550333	2.851804	0.005627
H	6.932033	2.522919	0.623927
H	8.079288	0.343315	0.075396
H	6.792991	-1.469811	-1.046660
C	2.060884	1.955005	-0.237681
H	2.869876	1.701889	-2.281019
H	2.302197	0.229089	-1.444791
O	1.639889	1.366849	0.773362
N	1.862254	3.304399	-0.410639
C	1.374233	4.088768	0.745978
C	2.349516	4.032496	-1.590042
H	2.000652	5.080407	-1.531836
H	3.459019	4.053762	-1.658767
H	1.950618	3.601469	-2.530576
H	2.131931	4.020614	1.556589
H	1.369485	5.148185	0.414463
C	0.019632	3.779166	1.381570
C	-1.219208	3.735461	0.690676
C	-2.414507	3.623135	1.436577
C	-2.413055	3.547855	2.836102
C	-1.187275	3.572263	3.520835
C	0.004625	3.686841	2.792759
C	-1.346377	3.731981	-0.830588

H	-3.376676	3.595715	0.898681
H	-3.363152	3.469343	3.387134
H	-1.157570	3.507577	4.619720
H	0.965592	3.710684	3.332113
C	-1.717888	2.309471	-1.275952
H	-2.082304	4.492492	-1.154027
H	-0.381500	3.976485	-1.314334
O	-0.959598	1.371322	-0.975512
N	-2.898467	2.089019	-1.941724
C	-3.270619	0.690803	-2.209902
C	-3.730025	3.165118	-2.495083
H	-4.614106	2.714615	-2.982653
H	-4.103711	3.860870	-1.715384
H	-3.185088	3.756701	-3.261639
H	-3.673999	0.632524	-3.246298
H	-2.338724	0.096046	-2.169115
C	-4.284905	0.092905	-1.229026
C	-4.459132	-1.316967	-1.132270
C	-5.447155	-1.828661	-0.263532
C	-6.255815	-0.986357	0.515473
C	-6.073689	0.401498	0.433967
C	-5.099958	0.924414	-0.433059
C	-3.593116	-2.314497	-1.899961
H	-5.592422	-2.920196	-0.201022
H	-7.022649	-1.414557	1.179410
H	-6.692905	1.082390	1.038606
H	-4.969777	2.015068	-0.485824
C	-2.259232	-2.579780	-1.187012
H	-4.172305	-3.237482	-2.086174
H	-3.312703	-1.919105	-2.898142
O	-1.437905	-1.650394	-1.080043
N	-1.953409	-3.816623	-0.677821
C	-2.810708	-5.000226	-0.656748
H	-2.831916	-5.435476	0.364272
H	-3.848287	-4.746142	-0.932215
H	-2.442989	-5.780478	-1.359168
H	-0.375704	-5.060807	-0.105459
H	0.109979	-3.515183	-0.875136
Na	0.046831	-0.325188	0.131230

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Compound **8**+2Na SCF Done: -2393.59695073 A.U.

C	-2.407777	2.200458	-1.508375
C	-3.759465	1.989751	-0.826336
C	-4.631660	0.956601	-1.275453
C	-5.895822	0.818113	-0.664068
C	-6.307091	1.665838	0.377872
C	-5.441126	2.672519	0.829591
C	-4.181548	2.828968	0.224840
H	-6.583040	0.034266	-1.022799
H	-7.303936	1.542453	0.828240
H	-5.747622	3.347991	1.643149

H	-3.514832	3.632930	0.574473
C	-4.239623	-0.039504	-2.369215
H	-3.593401	0.430607	-3.139236
C	-3.425135	-1.184448	-1.759160
H	-5.150023	-0.384375	-2.891024
O	-2.324722	-0.915708	-1.217124
N	-3.885817	-2.464529	-1.716965
C	-3.044048	-3.422716	-0.965780
C	-5.050648	-3.008324	-2.420644
H	-5.762422	-3.472438	-1.706673
H	-5.582436	-2.219471	-2.978126
H	-4.732805	-3.784695	-3.148407
C	-2.940105	-3.098669	0.524585
H	-3.502300	-4.424577	-1.094827
H	-2.043785	-3.459301	-1.440513
C	-1.720690	-3.143739	1.258466
C	-1.754653	-2.870936	2.649909
C	-2.946073	-2.544941	3.313888
C	-4.149168	-2.496836	2.586371
C	-4.135673	-2.778234	1.212954
C	-0.376514	-3.505234	0.646199
H	-0.817386	-2.925098	3.226627
H	-2.939665	-2.350528	4.397607
H	-5.098214	-2.259194	3.091146
H	-5.083880	-2.750146	0.653493
C	0.718624	-2.436991	0.816295
H	-0.018298	-4.452246	1.106131
H	-0.460149	-3.732563	-0.436688
O	0.432769	-1.282707	1.241947
N	1.991235	-2.797633	0.495548
C	3.091951	-1.830775	0.785121
C	2.333938	-4.168428	0.092323
H	3.357299	-4.169971	-0.324099
H	2.306829	-4.875674	0.949446
H	1.652349	-4.535809	-0.698020
H	2.653090	-0.837373	0.615805
H	3.355031	-1.918552	1.863376
C	4.359199	-1.971525	-0.040655
C	4.515171	-1.390123	-1.334716
C	5.739223	-1.584725	-2.013011
C	6.800764	-2.305870	-1.441777
C	6.655846	-2.852842	-0.158214
C	5.442167	-2.682078	0.525547
C	3.408219	-0.610956	-2.050164
H	5.860287	-1.174534	-3.029538
H	7.738380	-2.438764	-2.003237
H	7.480369	-3.412613	0.308993
H	5.326783	-3.112128	1.534514
C	2.910527	0.689802	-1.398706
H	3.737960	-0.405658	-3.088928
H	2.493281	-1.232423	-2.124171

O	1.822417	0.689055	-0.777635
N	3.613145	1.854756	-1.501721
C	2.942711	3.062276	-0.975336
C	4.862533	2.022429	-2.249476
H	5.541495	2.703193	-1.698556
H	5.381381	1.054145	-2.355317
H	4.681938	2.452293	-3.259043
H	3.562340	3.932943	-1.275691
H	1.963190	3.166273	-1.483724
C	2.755383	3.073225	0.542551
C	1.566596	3.553574	1.169851
C	1.490359	3.540192	2.584822
C	2.546859	3.064317	3.380534
C	3.720497	2.598359	2.759914
C	3.816376	2.613427	1.357953
C	0.361663	4.059338	0.391855
H	0.580217	3.925729	3.072916
H	2.461700	3.078837	4.478134
H	4.568067	2.241880	3.365737
H	4.740395	2.251539	0.879816
C	-0.674583	2.974181	0.028891
H	-0.162587	4.821748	1.010437
H	0.674623	4.596889	-0.524436
O	-0.691034	1.861801	0.622969
N	-1.564983	3.269140	-0.952173
C	-1.691885	4.596224	-1.571652
H	-2.746365	4.746781	-1.873706
H	-1.437199	5.403861	-0.862147
H	-1.053750	4.691458	-2.477353
H	-2.569598	2.452554	-2.579659
H	-1.829359	1.256061	-1.499174
Na	1.230324	0.864043	1.389995
Na	-1.681814	-0.282059	0.787768

5.0 Ionophoric Activity

5.1 General procedures

L-α-phosphatidyl-DL-glycerol sodium salt (EYPG, 20 mg/mL chloroform solution) was purchased from Avanti Polar Lipids; egg yolk phosphatidylcholine (EYPC, 100 mg/mL chloroform solution) and 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS) were from Sigma; Triton® X-100 and HEPES buffer were from Fluka; all salts were of the best grade available from Aldrich and were used without further purification. Liposomes were prepared by extrusion using a 10 mL LipexTM Thermobarrel EXTRUDER (Northern Lipids Inc.) connected to a thermostatic bath kept at 25°C. The 100 nm polycarbonate membranes were Nucleopore Track-Etch Membranes from Whatman. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. All fluorimetric measurements were performed at 25 °C. The ionophores concentration is given in percent with respect to the total concentration of lipids. Mother solutions of ionophores were prepared in DMSO. Control experiments showed that the amount of DMSO added to the vesicular suspension in the different experiments (maximum amount 2 % in volume) did not affect the permeability of the membrane.

5.2 HPTS assay

A mixture of 150 µL of EYPC chloroform solution (100 mg/mL, 20 µmol) and 40 µL of EYPG chloroform solution (20 mg/mL, 1 µmol) was first evaporated under Ar-flux to form a thin film and then dried under high vacuum for 3 h. The lipid cake was hydrated in 1.5 mL of 0.1 mM HPTS solution (HEPES 25 mM, 100 mM NaCl, pH 7) for 30 min at 40°C. The lipid suspension was submitted to 5 freeze-thaw cycles (-196°C/40°C) using liquid nitrogen and a thermostatic bath, and then extruded under nitrogen pressure (15 bar) at room temperature (10 extrusions through a 0.1 µm polycarbonate membrane). The LUV suspension was separated from extravesicular dye by size exclusion chromatography (SEC) (stationary phase: pre-packed column Sephadex™ G-25, mobile phase: HEPES buffer 25 mM, 100 mM NaCl, pH 7) and diluted with HEPES buffer (HEPES 25 mM, 100 mM NaCl, pH 7) to give a stock solution with a lipid concentration of 5 mM (assuming 100% of lipids were incorporated into liposomes). 104 µL of the lipid suspension were placed in a fluorimetric cell and diluted to 3040 µL with the appropriate buffer solution (25 mM HEPES pH 7) containing 100 mM of the salt under investigation (MCl with M = Li^+, Na^+, K^+, Rb^+, Cs^+). The total lipid concentration in the fluorimetric cell was 0.17 mM. An

aliquot of solution of the ionophore in DMSO (10-50 µL of the appropriate mother solution in order to obtain the desired molcompound/mollipid ratio) was then added to the lipid suspension and the cell was incubated at 25°C for 10 min. After incubation, the time course of fluorescence was recorded for 50 s monitoring the HPTS emission at 510 nm with excitation wavelengths set alternatively at 403 and 460 nm on a 0.5+0.5 s cycle. Then 50 µL of 0.5 M MOH (with M = Li^+, Na^+, K^+, Rb^+, Cs^+) were rapidly added through an injector port and the fluorescence emission was recorded for 300 s. Maximal changes in dye emission were obtained by final lysis of the liposomes with a detergent (40 µL of 5% aqueous Triton® X-100). The data set consists of emission intensities at 510 nm modulated by alternating excitation at 403 nm and 460 nm on a 0.5+0.5 s cycle. The concentration of the conjugate base form of HPTS is related to the emission intensity at 510 nm during the period in which the dye is excited at 460 nm (E_{460}) while the concentration of the protonated form is related to the emission intensity at 510 nm during the period in which the dye is excited at 403 nm (E_{403}). Fluorescence time courses were normalized using the following equation, where the subscripts 0, ∞ and t denote the emission ratio before the base pulse, after detergent lysis, and at an intermediate time, respectively.

$$FI = \frac{\left(\frac{E_{403}}{E_{460}}\right)_t - \left(\frac{E_{403}}{E_{460}}\right)_0}{\left(\frac{E_{403}}{E_{460}}\right)_\infty - \left(\frac{E_{403}}{E_{460}}\right)_0} \times 100$$

The results obtained with compounds **3**-**8** are reported in Figure S21.

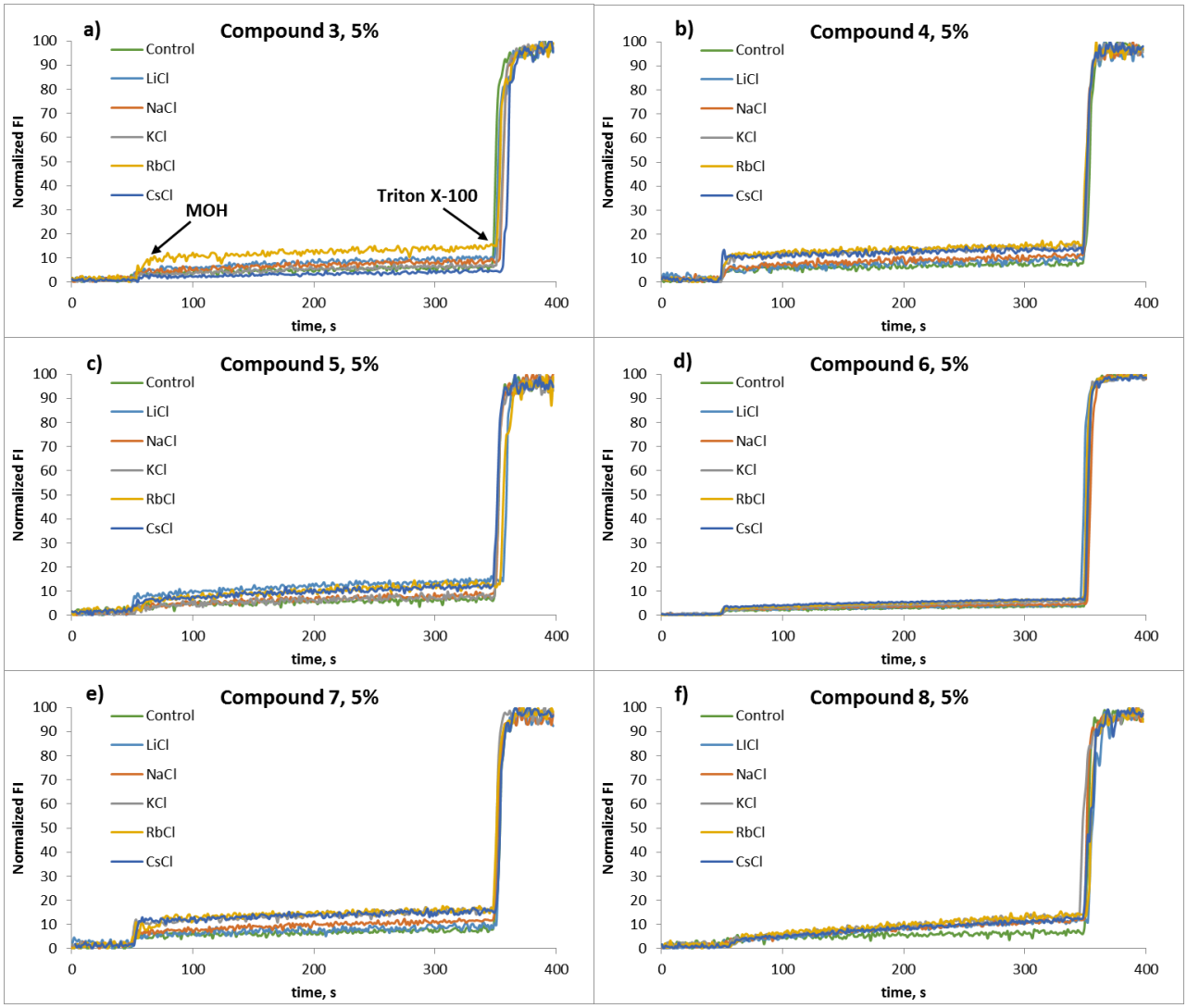

Figure S21: Normalized fluorescence change in HPTS emission as a function of time after addition of the base (50 μL of 0.5 M MOH, with M = Li^+, Na^+, K^+, Rb^+, Cs^+, depending on the cation present in the extravesicular buffer solution) to 95:5 EYPC/EYPG LUVs (100 nm diameter) loaded with HPTS (0.1 mM HPTS, 0.17 mM total lipid concentration, 25 mM HEPES pH 7.0) and 100 mM MCl (with M = Li^+, Na^+, K^+, Rb^+, Cs^+), in the presence of a 5% concentration of compounds **3-8**. The concentration of the ionophore is given in percent with respect to the total lipid concentration. The control trace has been recorded in the absence of ionophore. The arrows indicate the time of MOH and Triton X-100 addition.

6.0 References and notes

1. The anchimeric assistance of the carbonyl group increases the reactivity of the bromine (as leaving group in the substitution reaction) in compound **22**. The presence of traces of water in the crude compound can promote the formation of the corresponding benzyl alcohol and hydrobromic acid. The acid sensitivity of the *t*-butyl ester can decompose the batch. It is, therefore, suggested immediate reaction of the substrate **22** with the methoxyethylamine.
2. Preliminary attempts made on the *para*-isomers to construct the oligomers in the classic "submonomeric" accretion conditions were disappointing (low amounts, <5%, of desired compound were invariably observed after detachment from the 2-chlorotrityl resin, even doubling the reaction times and promoting the amine substitution of the resin-bound 4-(bromomethyl)phenylacetic acid in the presence of KI. It must be noted that a factor facilitating the solid-phase synthesis of the arylopeptoids is the fact that the bromotoluic acid derivatives are formal arylogues of the α-bromoacetic acid. In those acid derivatives the electron withdrawing effect of the carbonyl group propagates on the bromomethyl moiety and promotes the secondary amines nucleophilic substitutions. In the case of the benzylopeptoids, there is no conjugation between the carbonyl group and the phenyl ring (the substrates are bromomethyl*phenylacetate* derivatives).
3. The steric congestion of this resin hampers the feared intramolecular cyclization (and detachment) of the first *ortho*-isomer unit (once freed by the Fmoc group).
4. Lower temperature ^{1}H NMR spectra taken at 268 and 253 K (using CD_3CN as solvent) did not simplify the overall appearance of the spectra.
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7. It is worth noting that the low coordinating TFPB anion in a poorly coordinating solvent ($CDCl_3$) facilitates the sodium cation complexation (respect to the sodium picrate complex formation).
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12. It must be noted that in all the studied complexed peptoids a *trans*-junction has been always found (see, for example, ref. 27, 29 and 34 of the paper). The reason is that *trans*-peptoid junctions can efficiently expose the coordinating carbonyl group to the cations (avoiding the interference of the side chain).