Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Rotaxanes comprising cyclic phenylenedioxydiacetamides and secondary mono- and bis-dialkylammonium ions: Effect of macrocyclic ring size on pseudorotaxane formation

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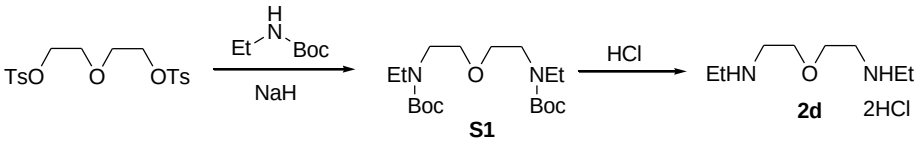
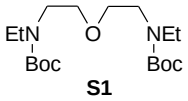
TOC

Experimental

Synthesis of the diamine **2d**.

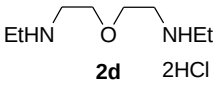


Compound S1



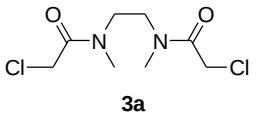
A solution of *N*-Boc-ethylamine (7.00 g, 48.3 mmol) in dry THF (60 mL) and di(ethylene glycol) ditosylate (9.10 g, 24.0 mmol) were added to a suspension of NaH (1.16 g, 48.3 mmol) in dry THF (100 mL) and then the mixture was stirred for 2 days at 40 °C. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2. The solution was washed with 5% $NaHSO_4$ (aq.) and sat. NaCl (aq.), dried ($MgSO_4$), and concentrated. The residue was chromatographed (SiO_2; hexane/EtOAc, 6:1) to give the carbamate **S1** (6.65 g, 77%) as a colorless oil. IR (NaCl, ν_{max}, cm^{-1}): 2974, 2933, 2874, 1685, 1412, 1364, 1284, 1165. ^1H NMR (500 MHz, $CDCl_3$) δ: 1.09 (br t, *J* = 6.5 Hz, 6H), 1.45 (s, 18H), 3.19–3.43 (m, 8H), 3.46–3.62 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: [13.1 and 13.5 (major)], [28.2], [42.4 and 43.0 (major)], [46.4], [69.6], [78.9], [154.9 and 155.3 (major)]. HRMS (FAB) calcd for $C_{18}H_{37}N_2O_5^+$ $[M + H]^+$ *m/z* 361.2702, found: 361.2696.

Compound 2d



A solution of hydrogen chloride in 1,4-dioxane (4 M, 50 mL, 200 mmol) was added to a solution of **S1** (7.30 g, 20.3 mmol) in diethyl ether (100 mL) at room temperature. After stirring overnight, the precipitate was collected by filtration, giving **2d** (3.60 g, 76%) as a white powder. IR (KBr, ν_{max}, cm^{-1}): 3447, 2973, 2809, 1576, 1452, 1112, 801. ^1H NMR (500 MHz, DMSO-d_6) δ: 1.25 (t, *J* = 7.5 Hz, 6H), 2.95 (sex, *J* = 7.5 Hz, 4H), 3.04–3.12 (m, 4H), 3.69 (t, *J* = 5.3 Hz, 4H), 9.11 (br s, 4H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 10.8, 41.9, 45.8, 65.3. HRMS (FAB) calcd for $C_8H_{21}N_2O^+$ $[M – HCl – Cl]^+$ *m/z* 161.1654, found 161.1659.

Compound 3a

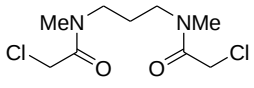


A solution of chloroacetyl chloride (3.8 mL, 48 mmol) in CH_2Cl_2 (100 mL) was added to a solution of *N*,*N*′-dimethylethylenediamine (2.4 mL, 22 mmol) in 10% $NaHCO_3$ (aq.)

(120 mL, 0.11 mol) in an ice bath and then the mixture was stirred for 2 h at room temperature. The organic layer was separated, dried (Na_2SO_4), and concentrated. The residual solid was washed with hexane to afford the amide **3a** (4.50 g, 82%) as a white powder. IR (KBr, ν_{max}, cm^{-1}): 2996, 2953, 1654, 1651, 1486, 1420, 1278, 1180, 1106, 795. ^1H NMR (500 MHz, $CDCl_3$) δ: 3.02, 3.12 (major), and 3.15 (each s, 6H), 3.56 and 3.61 (major) (each s, 4H), 4.05 (major), 4.08, and 4.14 (each s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: [34.1, 35.9 (major) and 37.3], [40.6, 41.0 and 41.4 (major)], [45.1 (major), 47.1, 47.6], [166.9, 167.1 (major)].

The ^1H and ^{13}C NMR spectra ($CDCl_3$) of **3a** were identical to those reported previously.[S1]

Compound 3b

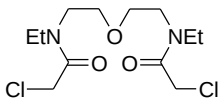


3b

3b (1.83 g) was synthesized from *N*,*N*´-dimethyl-1,3-propanediamine (2.00 g, 19.6 mmol), using the procedure described above, as a white powder (93% yield). IR (KBr, ν_{max}, cm^{-1}): 2997, 2955, 2877, 1662, 1481, 1410, 1282, 1143, 1058, 790. ^1H NMR (500 MHz, $CDCl_3$) δ: 1.80–1.88 (major), 1.88–1.96, and 2.00–2.08 (each m, 2H), 2.96, 2.99, 3.09 (major) and 3.12 (each s, 6H), 3.34–3.49 (m, 4H), 4.08 (major) and 4.09 (each s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: [24.3 (major) and 26.1], [33.5, 35.6 (major), and 35.7], [40.8, 41.2, and 41.5 (major)], [45.6, 45.7 (major), and 47.9], [166.3, 166.4 (major), 166.8]. HRMS (FAB) calcd for $C_9H_{17}Cl_2N_2O_2^+$ $[M + H]^+$ *m*/*z* 255.0662, found: 255.0666.

The ^{13}C NMR spectrum of **3b** was identical to that reported previously.[S2]

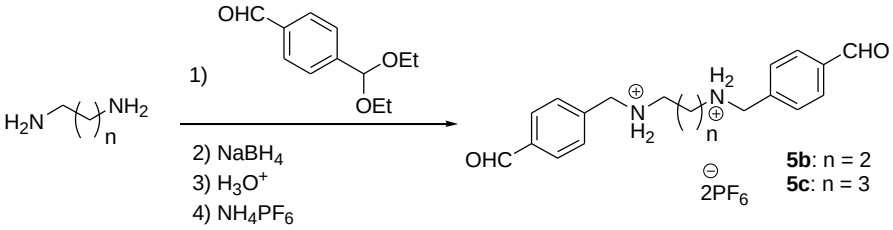
Compound 3d



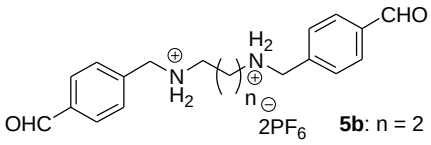
3d

3d (1.86 g) was synthesized from **2d** (1.50 g, 6.43 mmol), using the procedure described above, as a white powder (93% yield). IR (KBr, ν_{max}, cm^{-1}): 2976, 2936, 2874, 1654, 1648, 1459, 1119, 1090, 788. ^1H NMR (500 MHz, $CDCl_3$) δ: 1.14 (major), 1.22, and 1.23 (each t, *J* = 7.3 Hz, 6H), 3.37–3.65 (m, 12H), 4.09 (major), 4.11, and 4.18 (each s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: [11.0, 11.1, and 12.7 (major)], 39.8, 39.9, 40.3, 40.4, 40.6, 40.8, 42.2, 42.4, 43.8, 44.1, 46.0, [67.2, 67.3 (major), and 67.9], [164.6, 164.69 (major), 164.72, and 164.9]. HRMS (FAB) calcd for $C_{12}H_{23}Cl_2N_2O_3^+$ $[M + H]^+$ *m*/*z* 313.1086, found: 313.1078.

Synthesis of bis-dialkylammonium salts **5b** and **5c**.

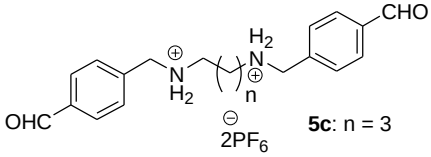


Compound 5b



A solution of trimethylenediamine (0.40 mL, 4.3 mmol) and terephthalaldehyde mono(diethylacetal) (1.9 mL, 9.6 mmol) in toluene (40 mL) was heated under reflux for 2 h using a Dean–Stark apparatus. After evaporation of the solvent, the residue was dissolved in EtOH (30 mL). $NaBH_4$ (0.33 g, 8.7 mmol) was added and then the mixture was stirred at 60 °C for 6 h. After evaporation of the solvent, the residue was treated 10% Na_2CO_3 (aq.). The aqueous phase was extracted with CH_2Cl_2. The combined organic phases were washed with sat. NaCl, then dried (Na_2SO_4) and concentrated. The residue was dissolved in THF (20 mL) and treated with 10% HCl (aq.) (27 mL, 87 mmol) and then left at room temperature for 6 h. After evaporation of the THF, the precipitate was collected by filtration to afford the crude ammonium chloride as a solid. NH_4PF_6 (3.6 g, 22 mmol) was added to a suspension of the crude ammonium chloride in water (30 mL) and acetone (30 mL), and then the mixture was stirred at room temperature for 2 days. After evaporation of the acetone, the precipitate was collected by filtration to afford the ammonium hexafluorophosphate **5b** (0.61 g, 24%) as a white powder. IR (KBr): ν_{max}, cm^{-1}: 2980, 2940, 2797, 1700, 830, 560. ^1H NMR (500 MHz, CD_3CN) δ: 2.07 (quin, J = 7.9 Hz, 2H), 3.23 (t, J = 7.9 Hz, 4H), 4.28 (s, 4H), 7.08 (br s, 4H), 7.63–7.70 (m, 4H), 7.95–8.02 (m, 4H), 10.05 (s, 2H). ^{13}C NMR (125 MHz, CD_3CN) δ: 23.3, 45.9, 52.2, 131.0, 131.8, 137.2, 138.3, 193.3. HRMS (FAB) calcd for $C_{19}H_{23}N_2O_2^+$ $[M - HPF_6 - PF_6]^+$ m/z 311.1749, found, 311.1765.

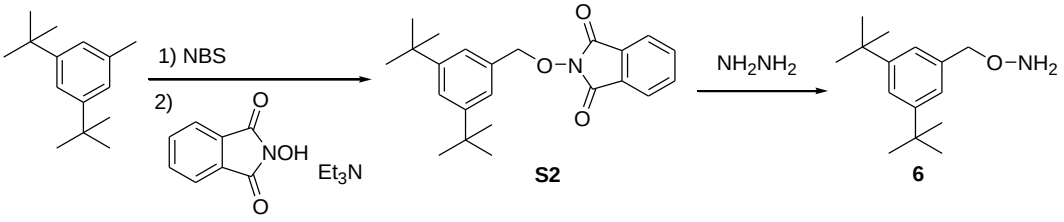
Compound 5c



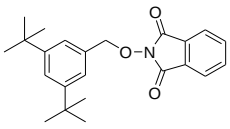
5c (6.2 g) was synthesized from 1,4-diaminobutane (1.2 g, 11 mmol) and terephthalaldehyde mono(diethylacetal) (5.0 g, 24 mmol), using the procedure described above, as a white solid (89% yield). IR (KBr, ν_{max}, cm^{-1}): 2981, 2943, 2796, 1700, 833,

560. ^{1}H NMR (500 MHz, CD_3CN) δ: 1.65–1.74 (m, 4H), 3.01–3.12 (m, 4H), 4.24 (s, 4H), 6.88 (br s, 4H), 7.62–7.68 (m, 4H), 7.74–8.01 (m, 4H), 10.04 (s, 2H). ^{13}C NMR (125 MHz, CD_3CN) δ: 23.5, 48.3, 52.1, 130.9, 131.8, 137.4, 138.3, 193.2. HRMS (FAB) calcd for $C_{20}H_{25}N_2O_2^+$ $[M - HPF_6 - PF_6]^+$ *m*/*z* 325.1911, found: 325.1919.

Synthesis of the *O*-benzylhydroxylamine **6**.

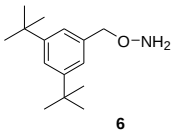


Compound S2



A solution of 3,5-di-*tert*-butyltoluene (5.00 g, 24.5 mmol), NBS (4.35 g, 24.5 mmol), and AIBN (catalytic) in benzene (80 mL) was heated under reflux overnight. After cooling, the precipitate was removed by filtration. The filtrate was washed with 10% Na_2SO_3 (aq.) and sat NaCl (aq.) and dried (Na_2SO_4). Evaporation of the solvent gave the crude bromide. A solution of the crude product, *N*-hydroxyphthalimide (4.40 g, 27.0 mmol), and triethylamine (2.73 g, 27.0 mmol) in dry DMF (70 mL) was stirred at 45 °C overnight. After evaporation of the solvent, the residue was purified through column chromatography (SiO_2; hexane/AcOEt, 20:1) to afford **S2** (5.20 g, 57%) as a white solid. IR (KBr, ν_{max}, cm^{-1}): 2962, 2903, 1737, 1717, 1464, 1367, 1183, 1134, 966, 879. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.29 (s, 18H), 5.22 (s, 2H), 7.35 (d, *J* = 2.0 Hz), 7.41 (t, *J* = 2.0 Hz, 1H), 7.70–7.74 (m, 2H), 7.77–7.82 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 31.3, 34.8, 80.5, 123.3, 124.3, 128.9, 132.6, 134.3, 151.0, 163.4. HRMS (FAB) calcd for $C_{23}H_{27}NO_3^+$ $[M + H]^+$ *m*/*z* 366.2069, found, 366.2061.

Compound 6



A solution of *N*-(3,5-di-*tert*-butylbenzyloxy)phthalimide (**S2**, 870 mg, 2.38 mmol) and hydrazine monohydrate (2.98 g, 59.5 mmol) in EtOH (25 mL) was stirred at 60 °C overnight. The precipitate filtered off and the filtrate concentrated. $CHCl_3$ was added to the residue and the insoluble solid was filtered off. The filtrate was washed with sat. NaCl (aq.), dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2;

hexane/EtOAc, 20:1) to give **6** (460 mg, 82%) as a colorless oil. IR (NaCl, ν_{max}, cm^{-1}): 3315, 3242, 3154, 2963, 2905, 2867, 1600, 1478, 1363, 1249, 998, 895, 865, 714. ^1H NMR (500 MHz, $CDCl_3$) δ: 1.33 (s, 18H), 4.69 (s, 2H), 5.38 (br s, 2H), 7.29 (d, *J* = 2.0 Hz, 2H), 7.39 (t, *J* = 2.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 31.4, 34.7, 78.8, 122.1, 122.5, 136.2, 150.8. HRMS (FAB) calcd for $C_{15}H_{26}NO^+$ $[M + H]^+$ *m*/*z* 236.2014, found, 236.2021.

Axle molecule 8a

A solution of mono-ammonium salt **5a** (126 mg, 210 μmol) and **6** (122 mg, 518 μmol) in acetonitrile (2 mL) was stirred at room temperature overnight. After evaporation of the solvent, the residue was washed with hexane to give **8a** as a white powder (150 mg, 70%). IR (KBr, ν_{max}, cm^{-1}): 3644, 3579, 3233, 2964, 1601, 1464, 1423, 1363, 1249, 1203, 1015, 996, 841, 558. ^1H NMR (600 MHz, DMSO-d_6) for major isomer δ: 1.28 (s, 36H), 3.24 (br s, 4H), 4.24 (br s, 4H), 5.16 (s, 4H), 7.24 (br s, 4H), 7.35 (br s, 2H), 7.49–7.55 (m, 4H), 7.69–7.75 (m, 4H), 8.35 (s, 2H), 8.86 (br s, 4H). ^{13}C NMR (150 MHz, DMSO-d_6) for major isomer δ: 31.3, 34.5, 42.5, 50.1, 76.4, 121.5, 122.6, 127.2, 130.3, 132.9, 133.2, 136.4, 148.5, 150.3. HRMS (FAB) calcd for $C_{48}H_{67}N_4O_2^+$ $[M – HPF_6 – PF_6]^+$ *m*/*z* 731.5259, found: 731.5255.

Axle molecule 8b

8b (80.0 mg, 70%) was synthesized from mono-ammonium salt **5d** (50.5 mg, 126 μmol) and **6** (113 mg, 480 μmol), using the procedure described above, as a white powder. IR (KBr, ν_{max}, cm^{-1}): 3649, 3257, 3229, 2964, 1601, 1476, 1465, 1419, 1411, 1363, 1249, 1203, 1016, 997, 847, 558. ^1H NMR (600 MHz, $CDCl_3$) for major isomer δ: 1.32 (s, 36H), 4.13–4.19 (m, 4H), 5.18 (s, 4H), 6.75 (br s, 2H), 7.26 (br s, 4H), 7.34–7.42 (m, 6H), 7.61–7.65 (m, 4H), 8.07 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) for major isomer δ: 31.4, 34.8, 51.1, 77.6, 122.3, 123.0, 128.0, 129.8, 130.2, 134.4, 135.8, 147.5, 150.9. HRMS (FAB) calcd for $C_{46}H_{62}N_3O_2^+$ $[M – PF_6]^+$ *m*/*z* 688.4837, found: 688.4841.

References

S1. T. C. Pickel, G. J. Karahalis, C. T. Buru, J. Bacsa and C. C. Scarborough, *Eur. J. Org. Chem.*, 2018, 6876–6889.

S2. T. Rodopoulos, K. Ishihara, M. Rodopoulos, M. J. Zaworotko, M. Maeder and A. McAuley, *Can. J. Chem.*, 2005, **83**, 894–902.

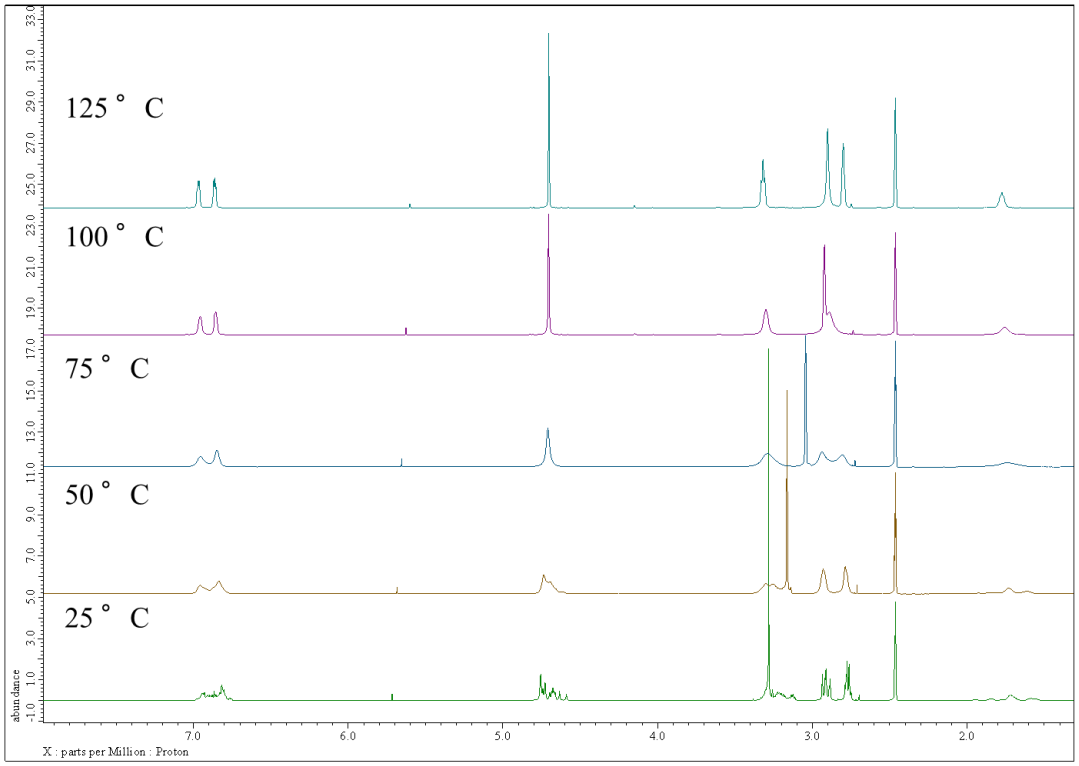


Figure S1. ^{1}H NMR spectra (600 MHz, DMSO-d_6) of the lactam **1b**, recorded at 25–125 °C.

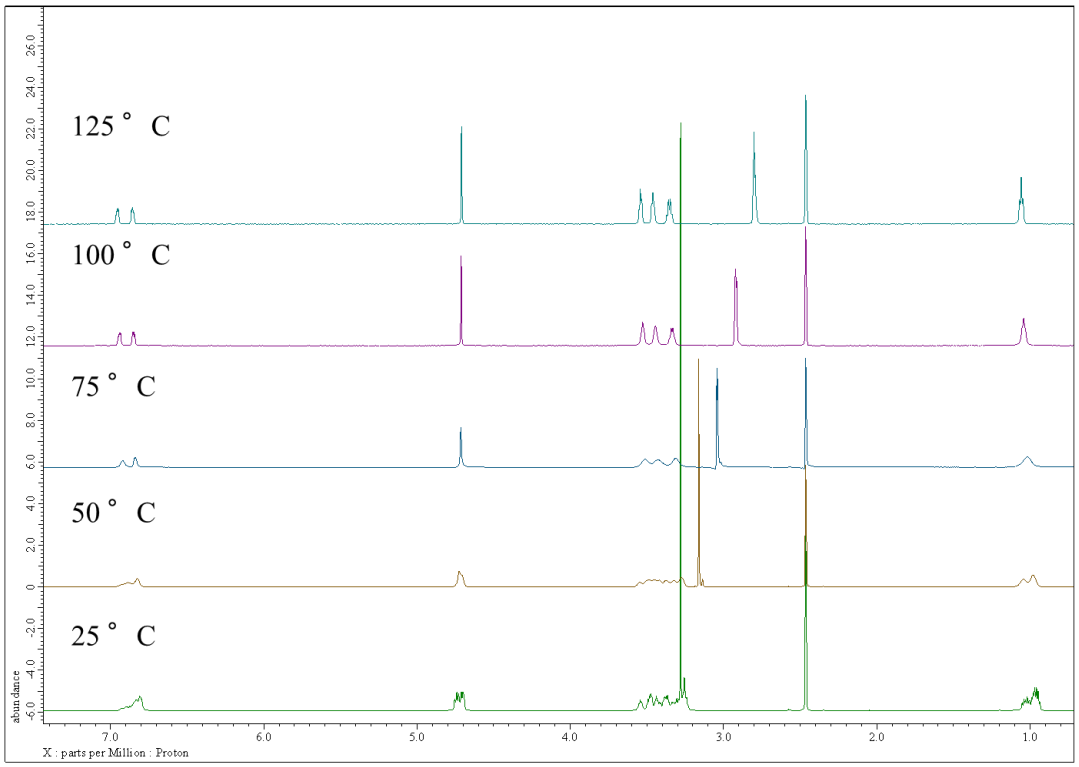


Figure S2. ^{1}H NMR spectra (600 MHz, DMSO-d_6) of the lactam **1d**, recorded at 25–125 °C.

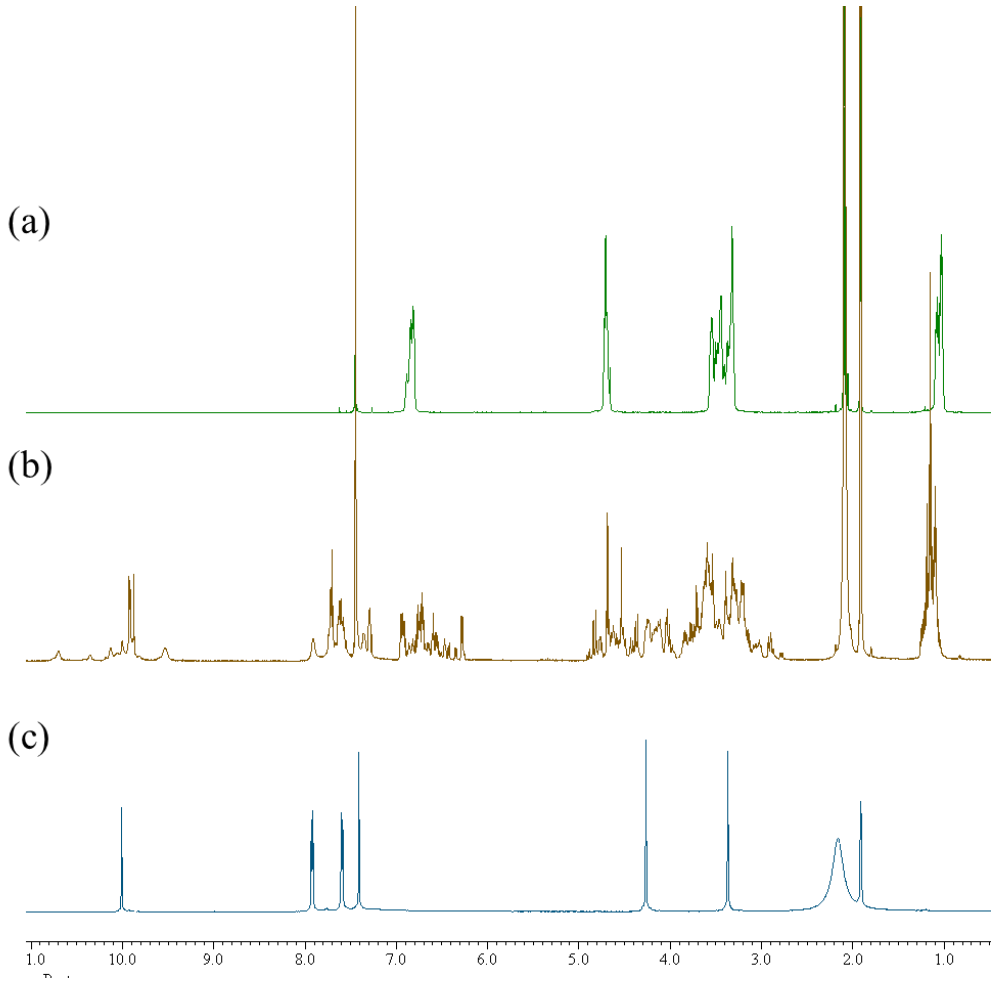


Figure S3. ^{1}H NMR spectra [600 MHz, $CDCl_3/CD_3CN$ (1:1), 25 °C] of (a) the lactam **1d**, (b) a mixture of **1d** (3 mM) and **5a** (3 mM), and (c) **5a**.

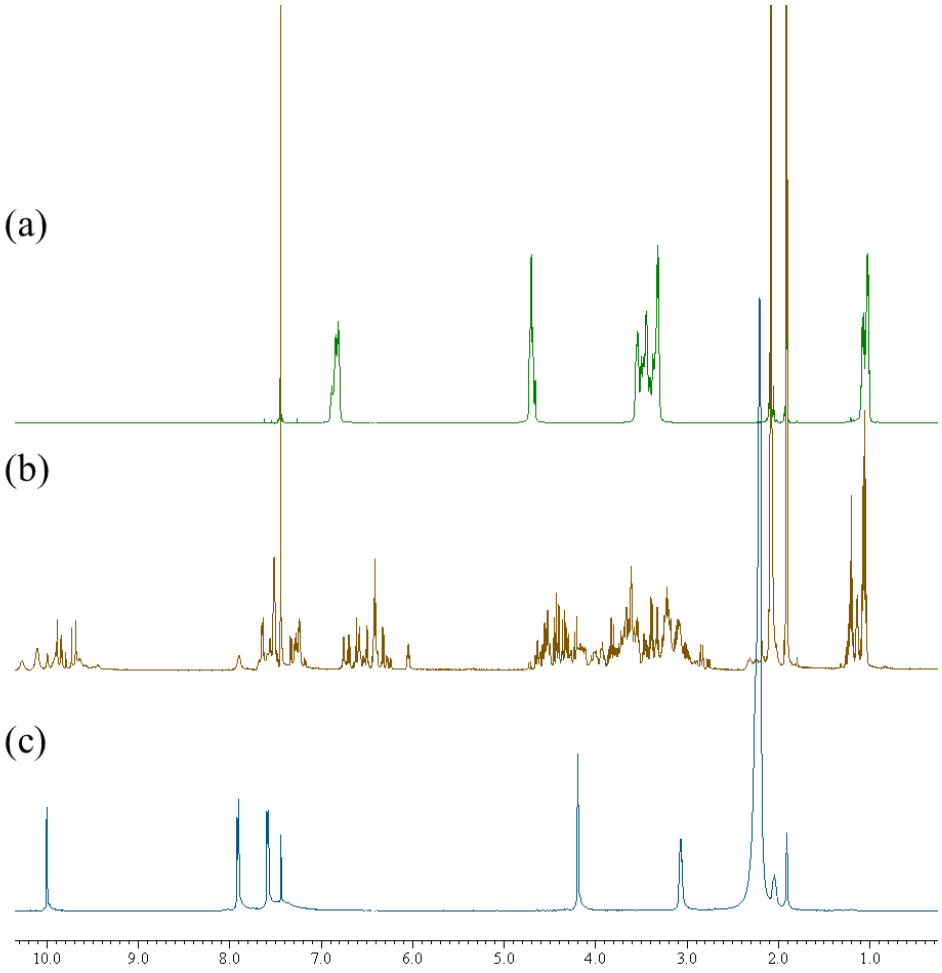


Figure S4. ^{1}H NMR spectra [600 MHz, $CDCl_3/CD_3CN$ (1:1), 25 °C] of (a) the lactam **1d**, (b) a mixture of **1d** (3 mM) and **5b** (3 mM), and (c) **5b**.

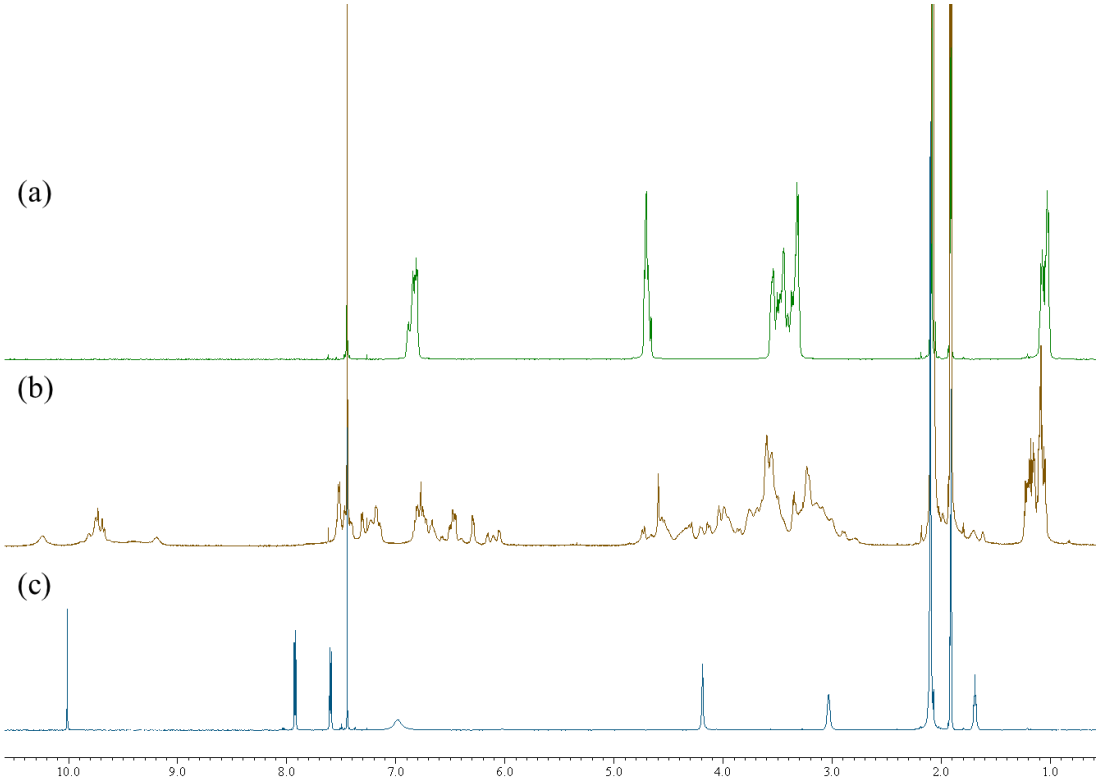


Figure S5. ^{1}H NMR spectra [600 MHz, $CDCl_3/CD_3CN$ (1:1), 25 °C] of (a) the lactam **1d**, (b) a mixture of **1d** (3 mM) and **5c** (3 mM), and (c) **5c**.

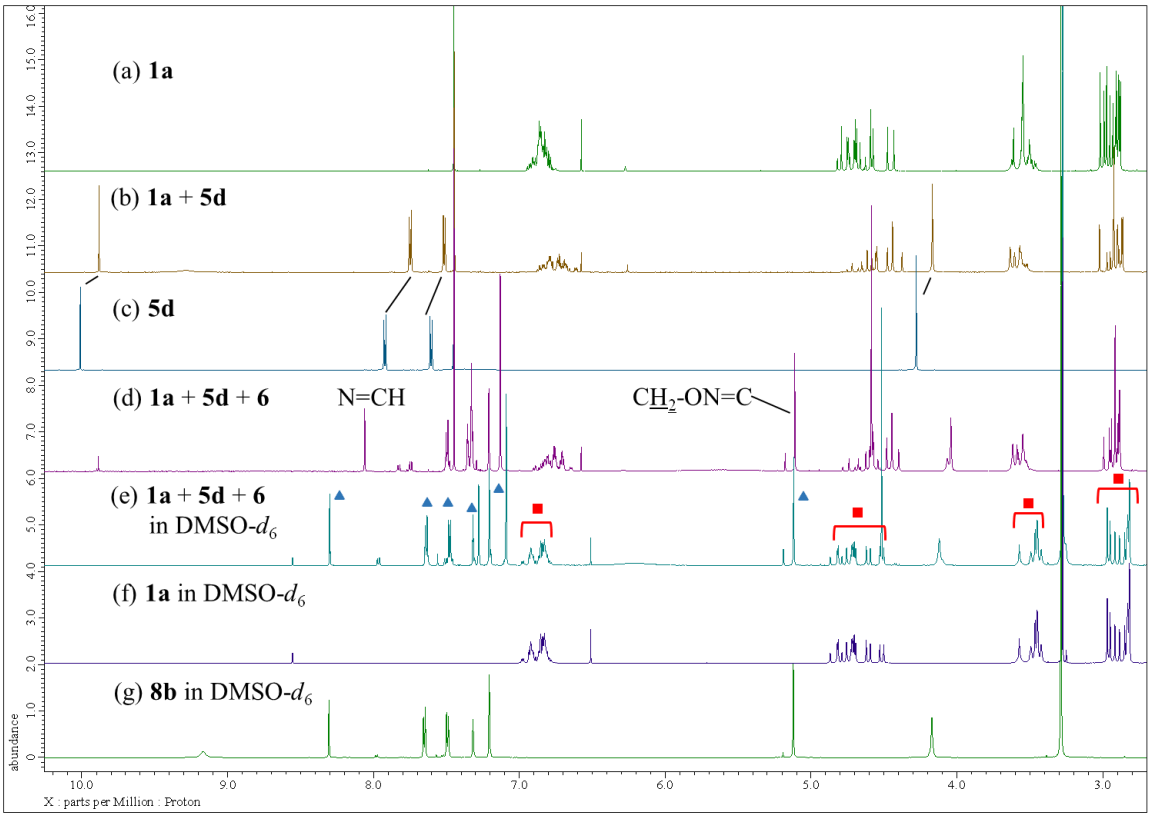


Figure S6. (a–d) ^{1}H NMR spectra [600 MHz, $CDCl_3/CD_3CN$ (1:1), 25 °C] of (a) **1a**, (b) a mixture of **1a** (3 mM) and **5d** (3 mM), (c) **5d**, and (d) the sample in (b) plus **6** (4 eq). (e–g) ^{1}H NMR spectra (600 MHz, DMSO-d_6, 25 °C) of (e) the sample in (d) after exchange of the mixed solvent for DMSO-d_6, (f) **1a**, and (g) the axle molecule **8b**. ▲: **8b**; ■: **1a**.

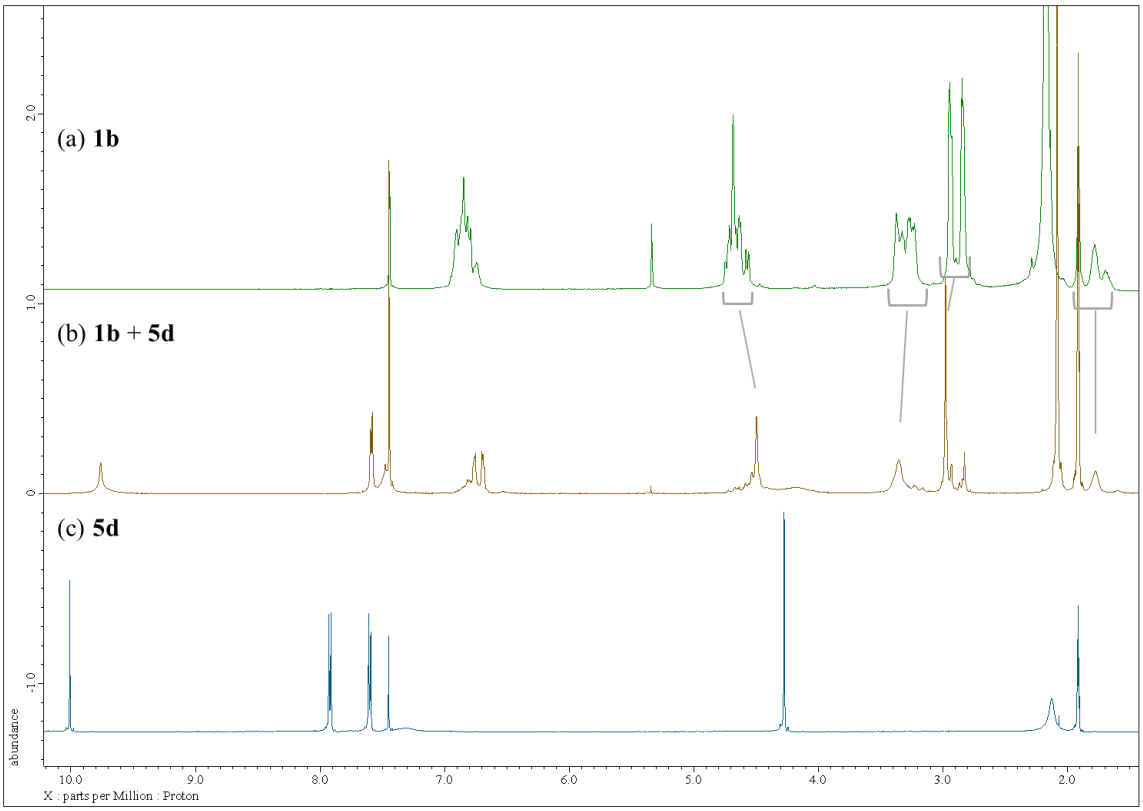


Figure S7. ^{1}H NMR spectra [500 MHz, $CDCl_3/CD_3CN$ (1:1), 25 °C] of (a) **1b**, (b) a mixture of **1b** (3 mM), **5d** (3 mM), and (c) **5d**.

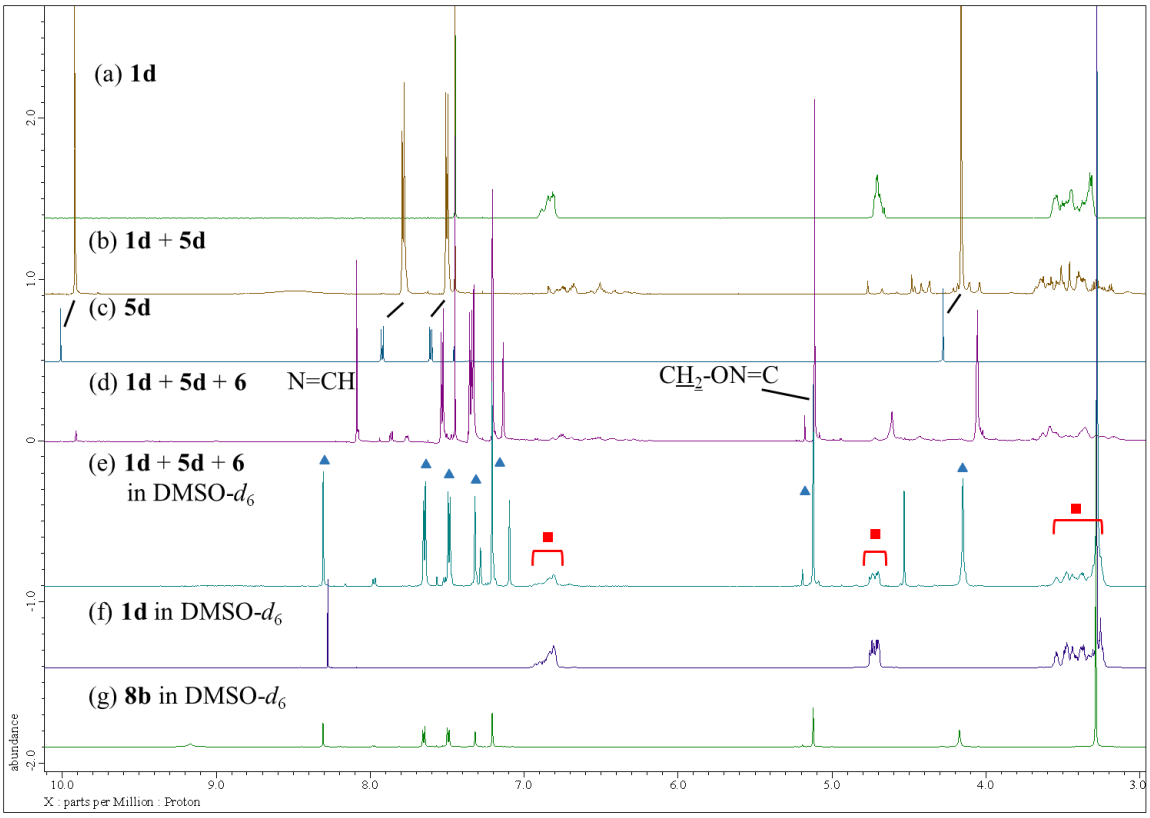
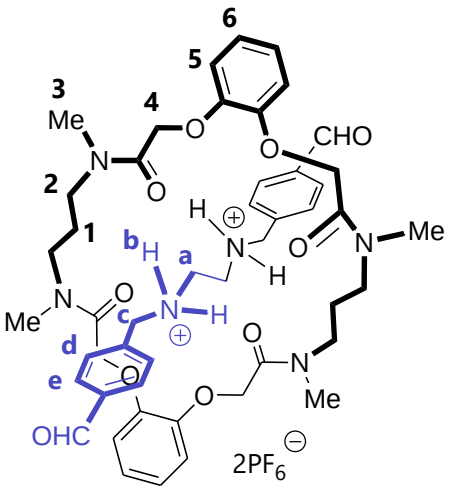


Figure S8. (a–d) ^{1}H NMR spectra [600 MHz, $CDCl_3/CD_3CN$ (1:1), 25 °C] of (a) **1d**, (b) a mixture of **1d** (3 mM) and **5d** (9 mM), (c) **5d**, and (d) the sample in (b) plus **6** (3 eq for **5d**). (e–g) ^{1}H NMR spectra (600 MHz, DMSO-d_6, 25 °C) of (e) the sample in (d) after exchange of the mixed solvent for DMSO-d_6, (f) **1d**, and (g) the axle molecule **8b**. ▲: **8b**; ■: **1d**.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5
3
Me
4
O
CHO
2
N
O
1
b
H
a
H
N
O
N
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N
H
d
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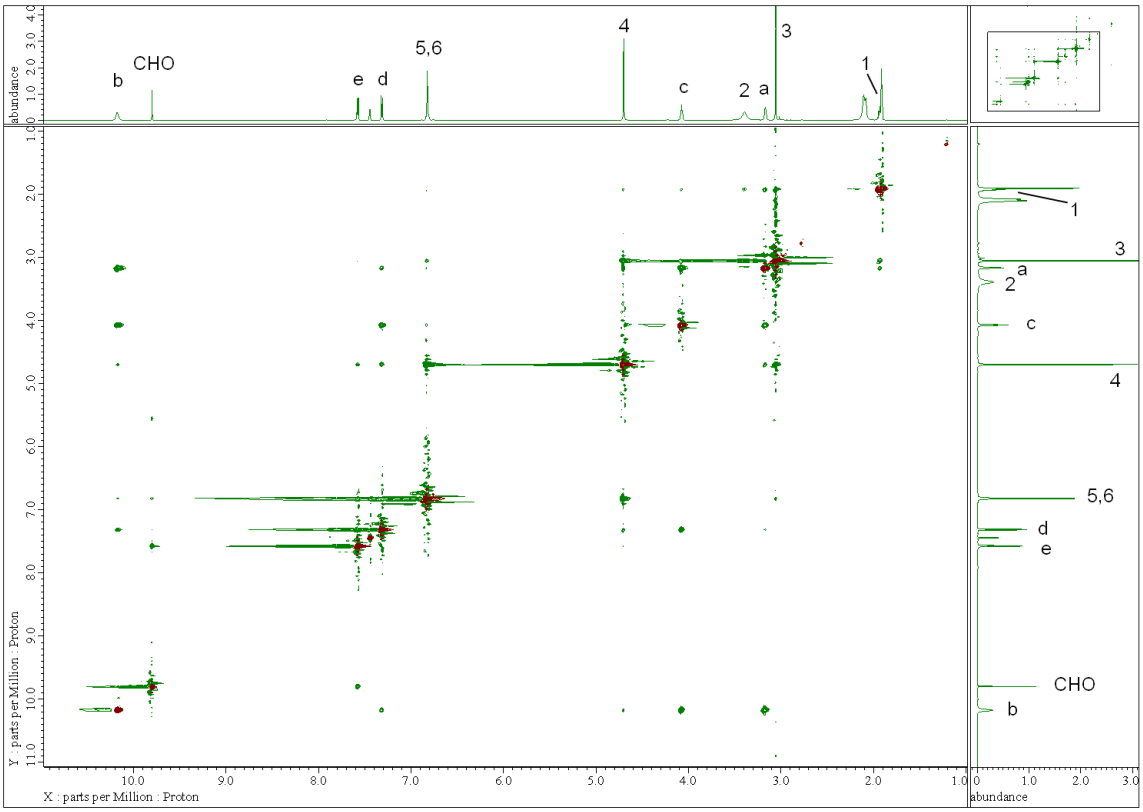
e
O
O
N
Me
OHC
2PF6


abundance
b
CHO
e
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5,6
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c
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Y : parts per Million : Proton
X : parts per Million : Proton
abundance
CHO

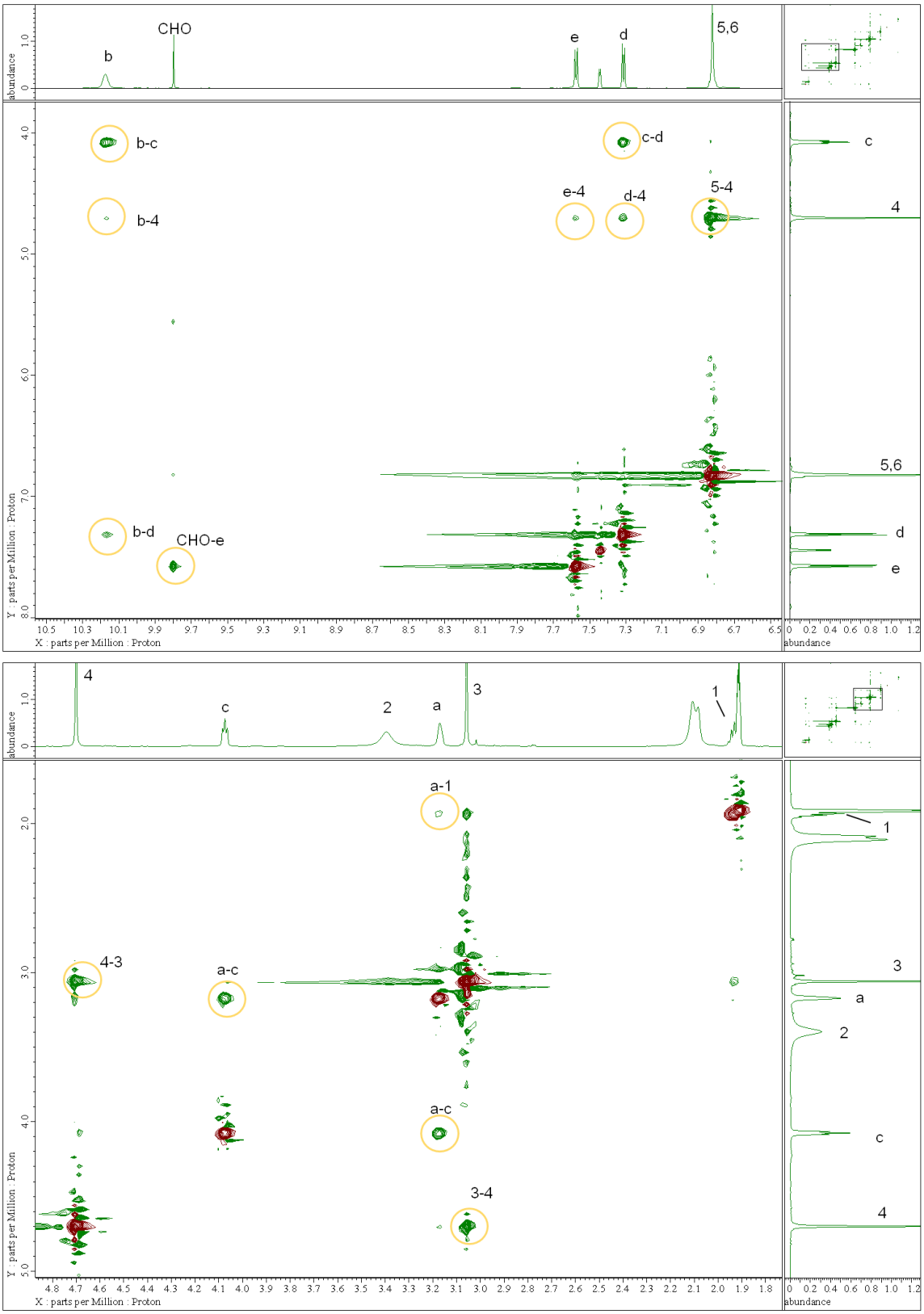
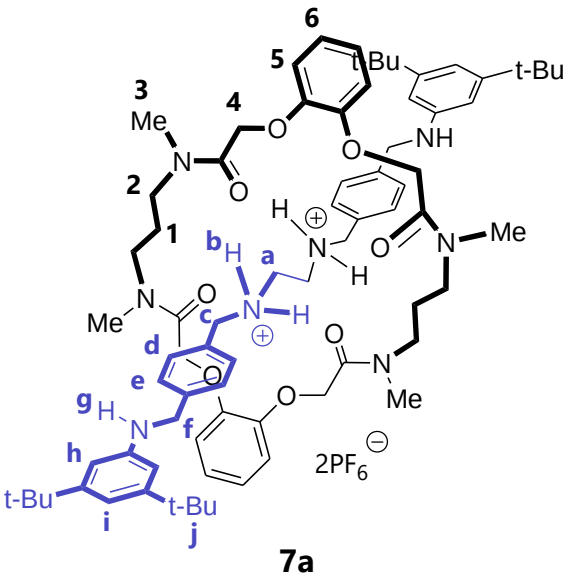


Figure S9. ROESY [600 MHz, $CDCl_3/CD_3CN$ (1:1)] spectrum of a mixture of the lactam **1b** (5 mM) and the bis-dialkylammonium salt **5a** (5 mM).



7a

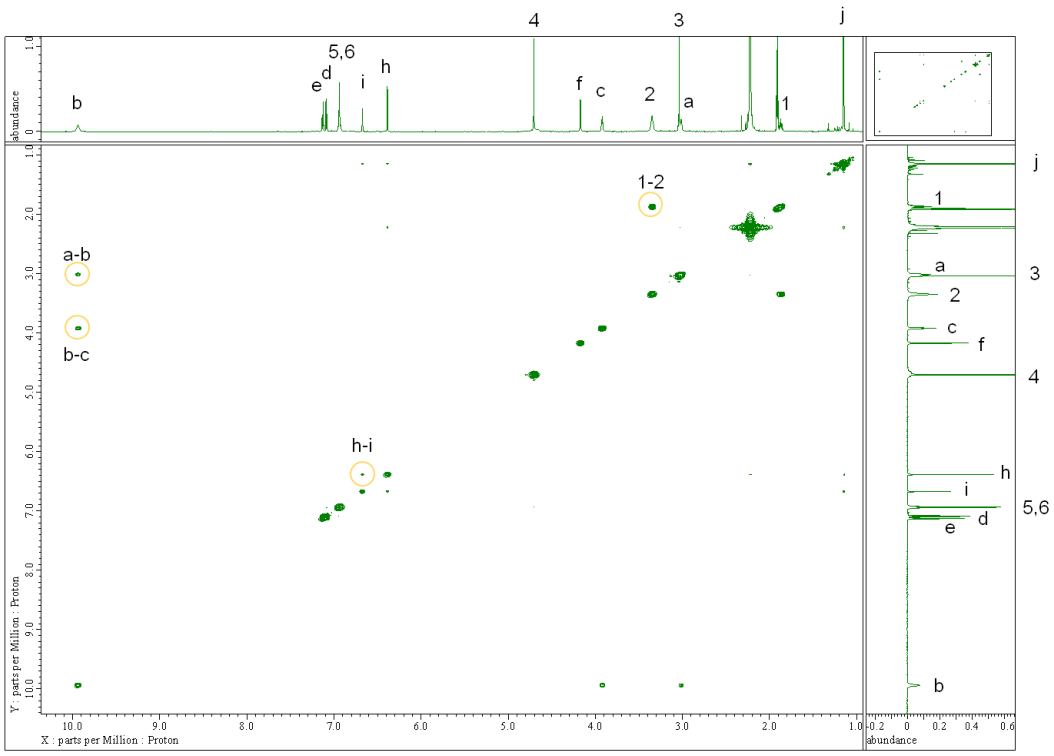
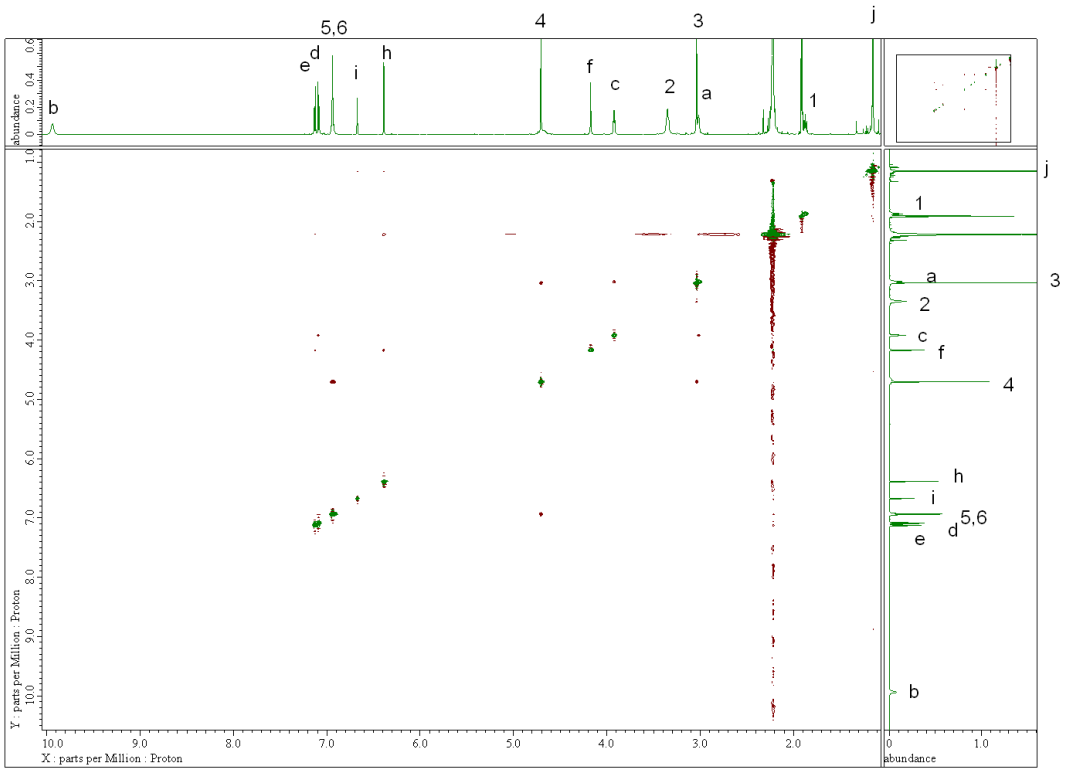


Figure S10a. COSY (600 MHz, CD_3CN) spectrum of the [2]rotaxane **7a**.


5,6
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3
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e
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i
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c
2
a
1
b
abundance
Y : parts per Million : Proton
X : parts per Million : Proton
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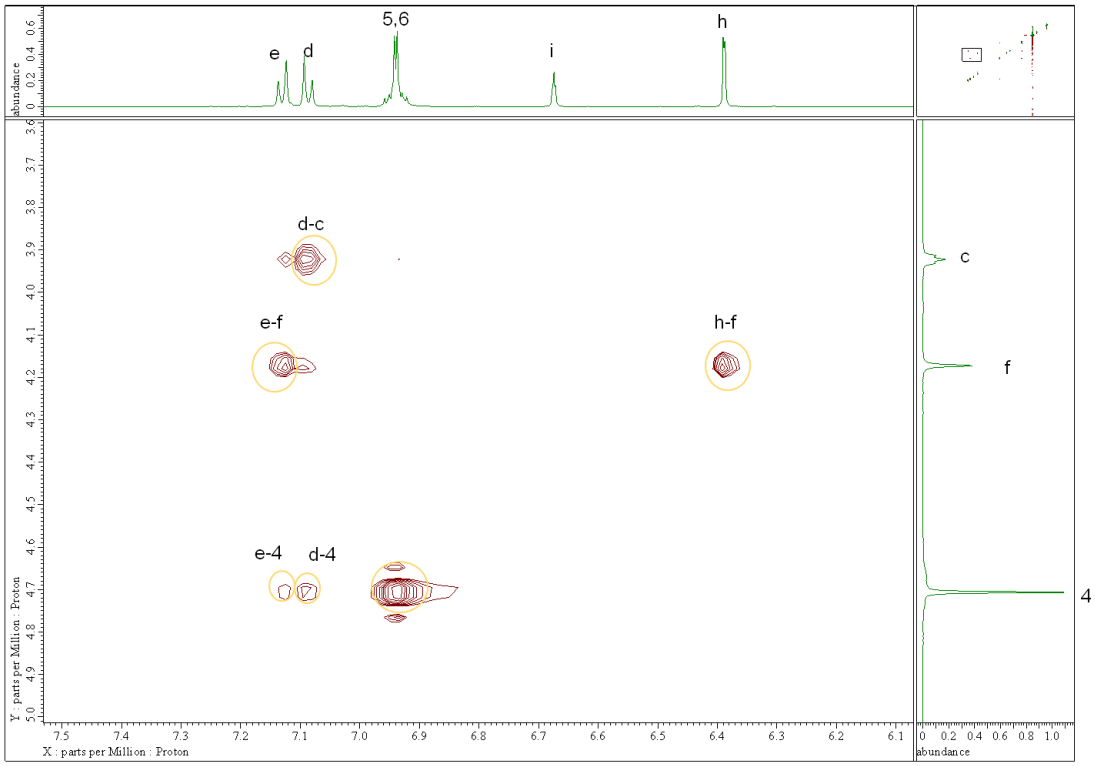
5,6
e
d
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h-f
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d-4
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f
4
abundance
Y : parts per Million : Proton
X : parts per Million : Proton
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
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6.3
6.2
6.1
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0.2
0.4
0.6
0.8
1.0

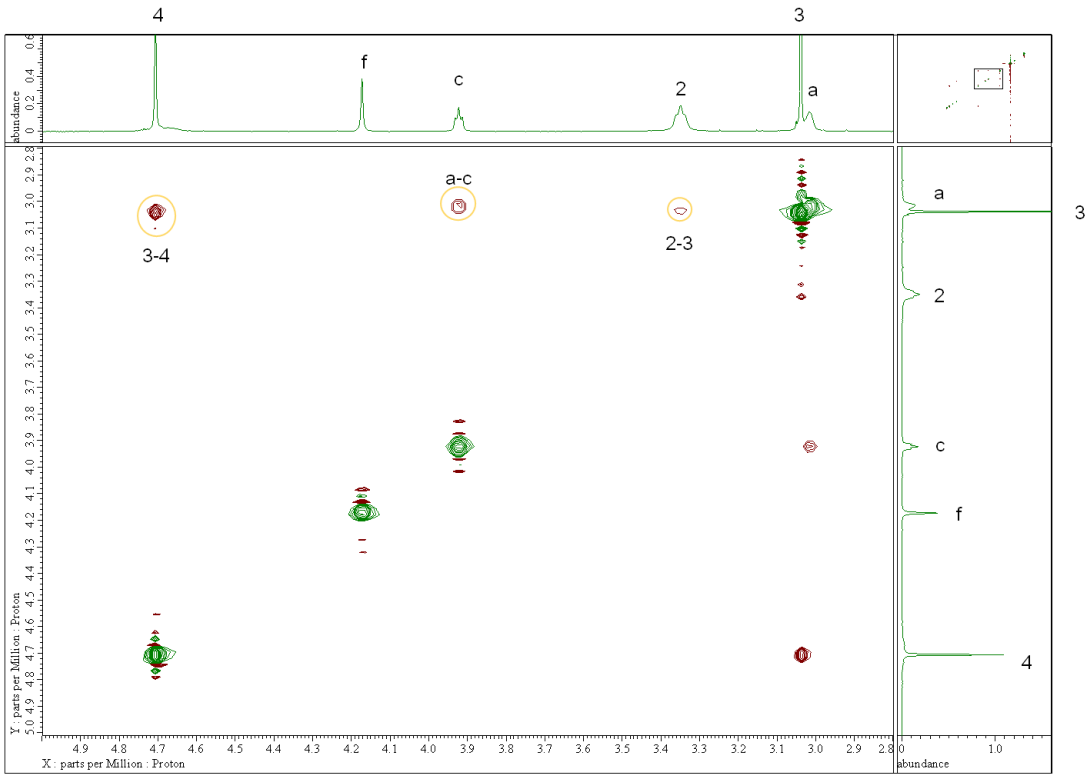
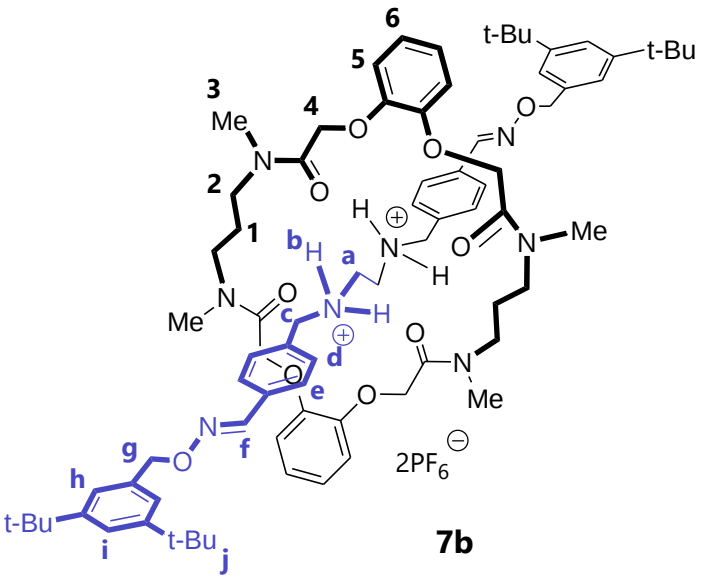


Figure S10b. ROESY (600 MHz, CD_3CN) spectrum of the [2]rotaxane **7a**.



7b

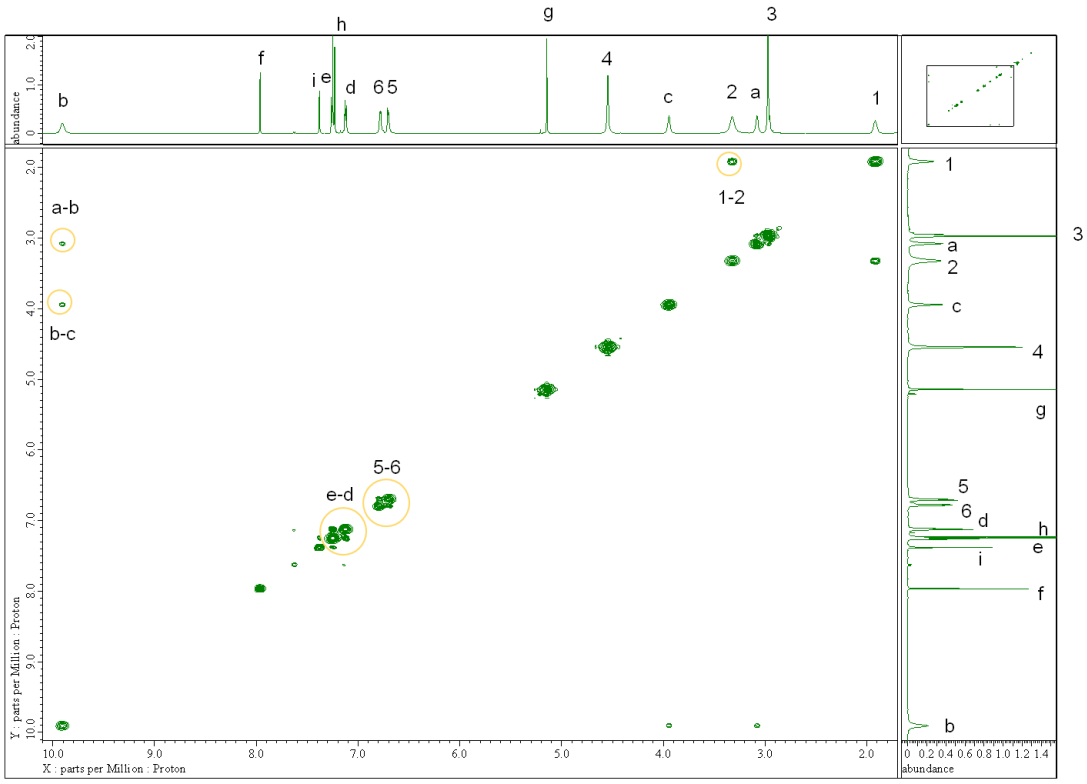
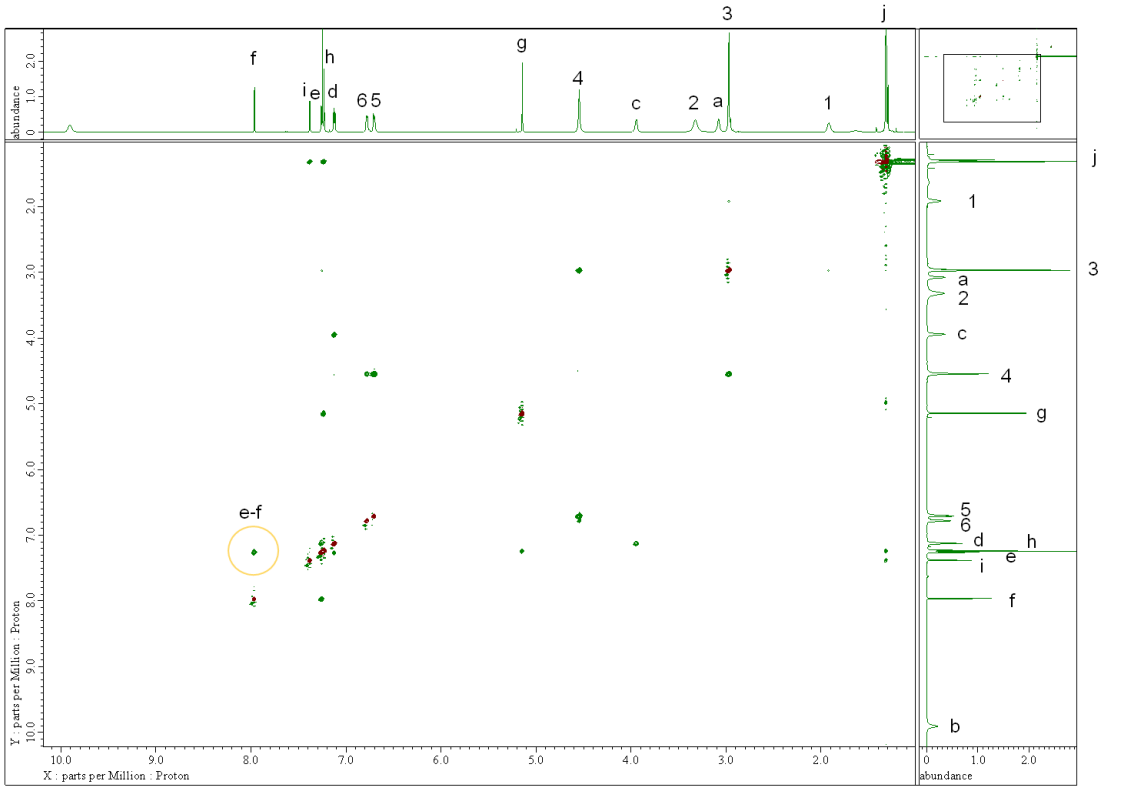


Figure S11a. COSY (600 MHz, $CDCl_3$) spectrum of the [2]rotaxane **7b**.


f
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abundance
Y : parts per Million : Proton
X : parts per Million : Proton
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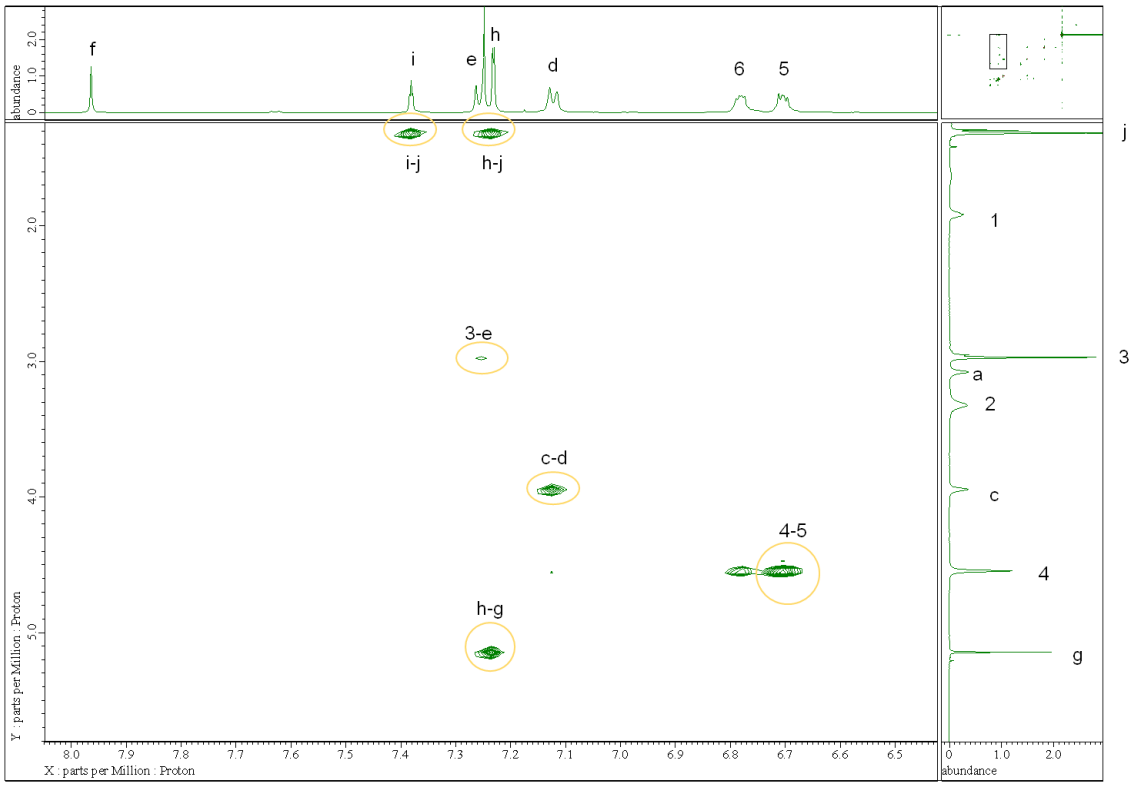
f
i
e
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abundance
i-j
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j
1
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c-d
c
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4
h-g
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Y : parts per Million : Proton
X : parts per Million : Proton
abundance

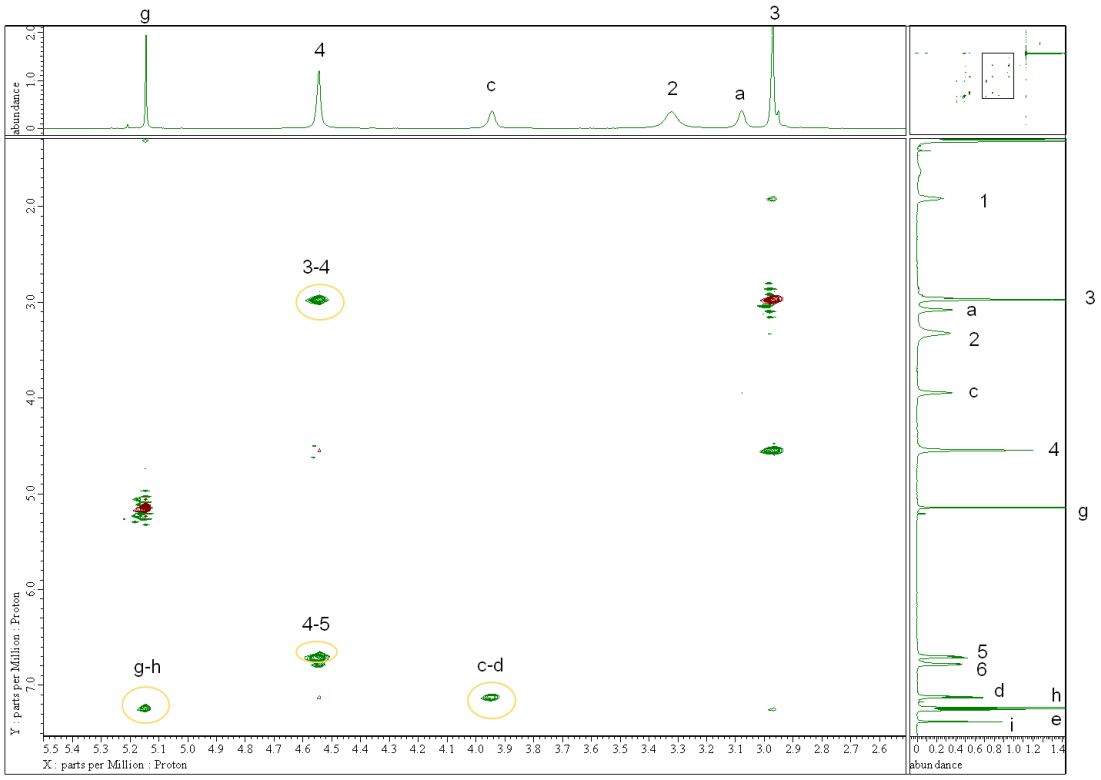
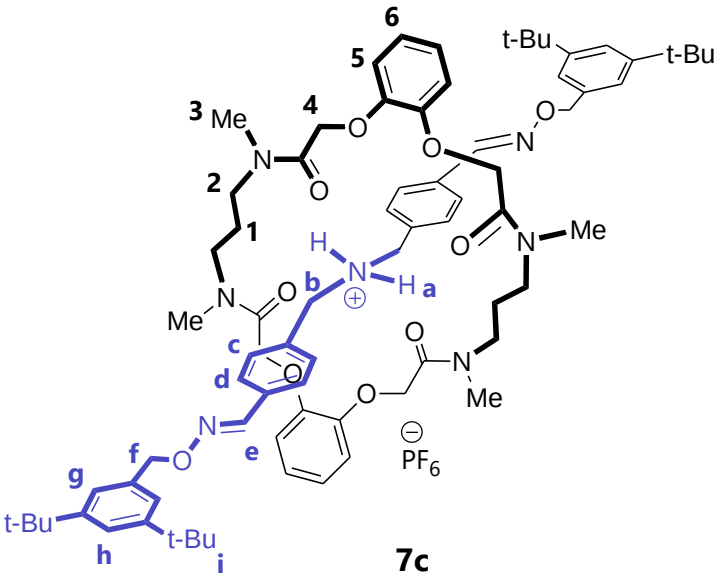


Figure S11b. ROESY (600 MHz, $CDCl_3$) spectrum of the [2]rotaxane **7b**.



7c

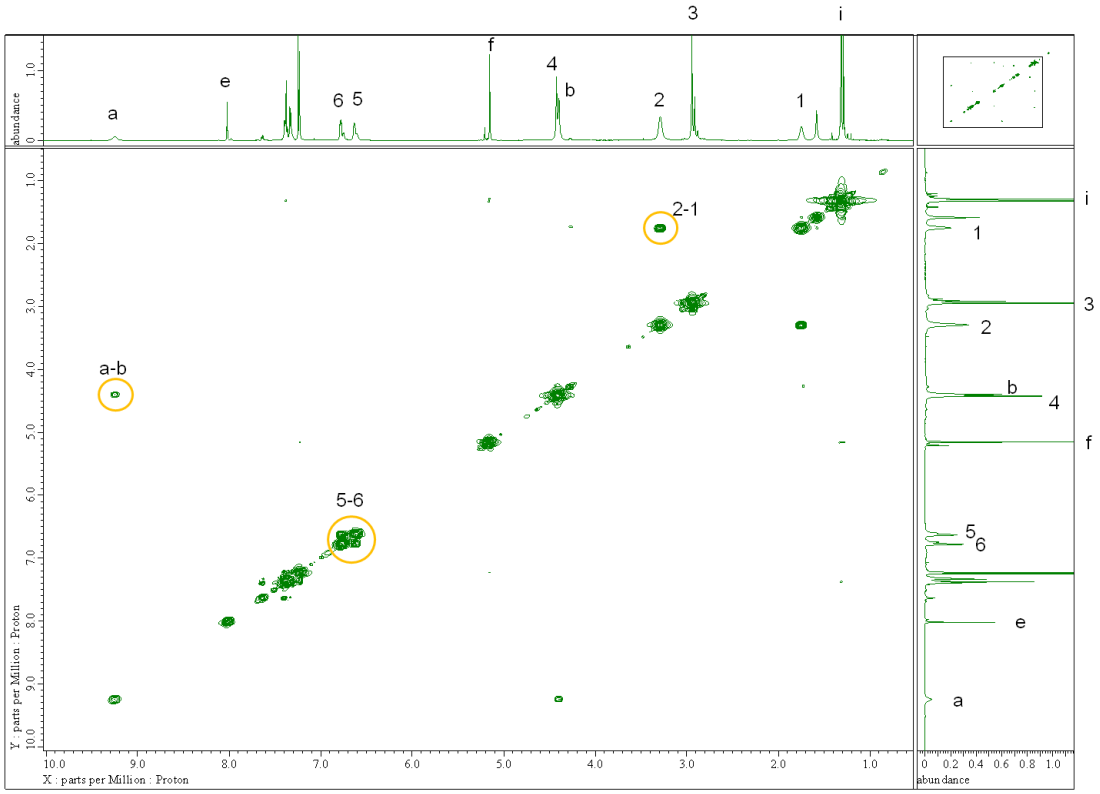
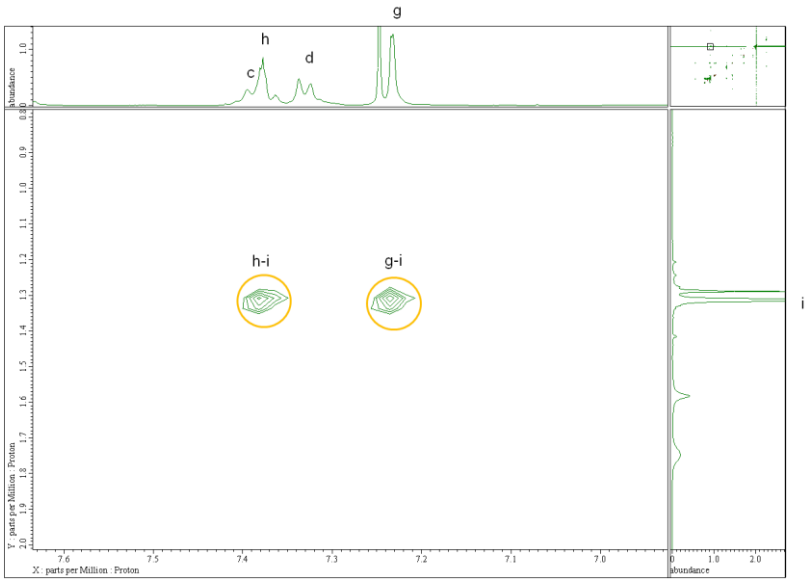


Figure S12a. COSY (600 MHz, $CDCl_3$) spectrum of the [2]rotaxane **7c**.


g
h
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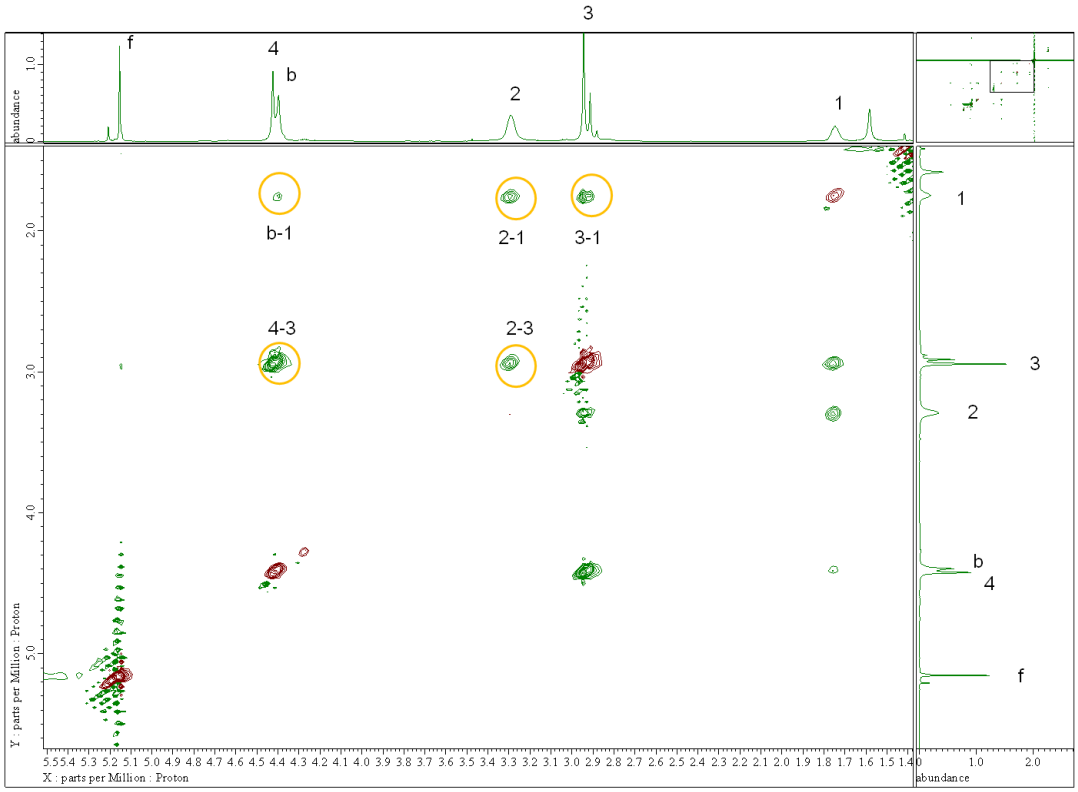
abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance


3
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4
b
2
1
b-1
2-1
3-1
4-3
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1
3
2
b
4
f
abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

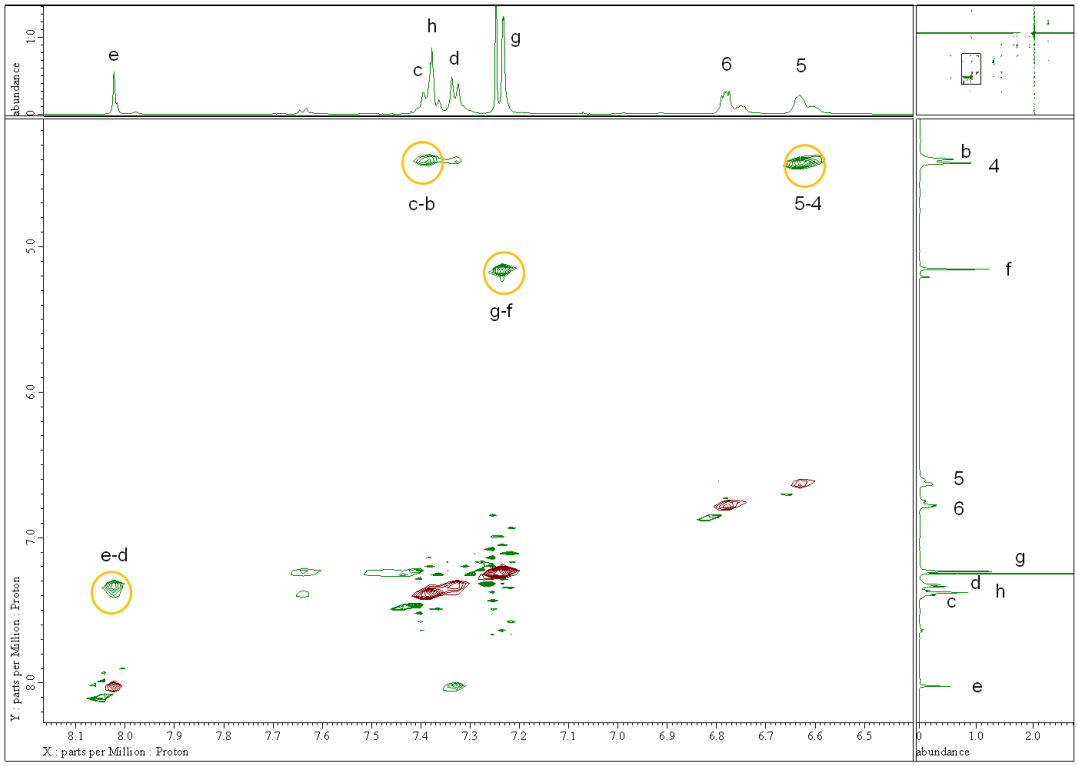

Figure S12b. ROESY (600 MHz, $CDCl_3$) spectrum of the [2]rotaxane **7c**.

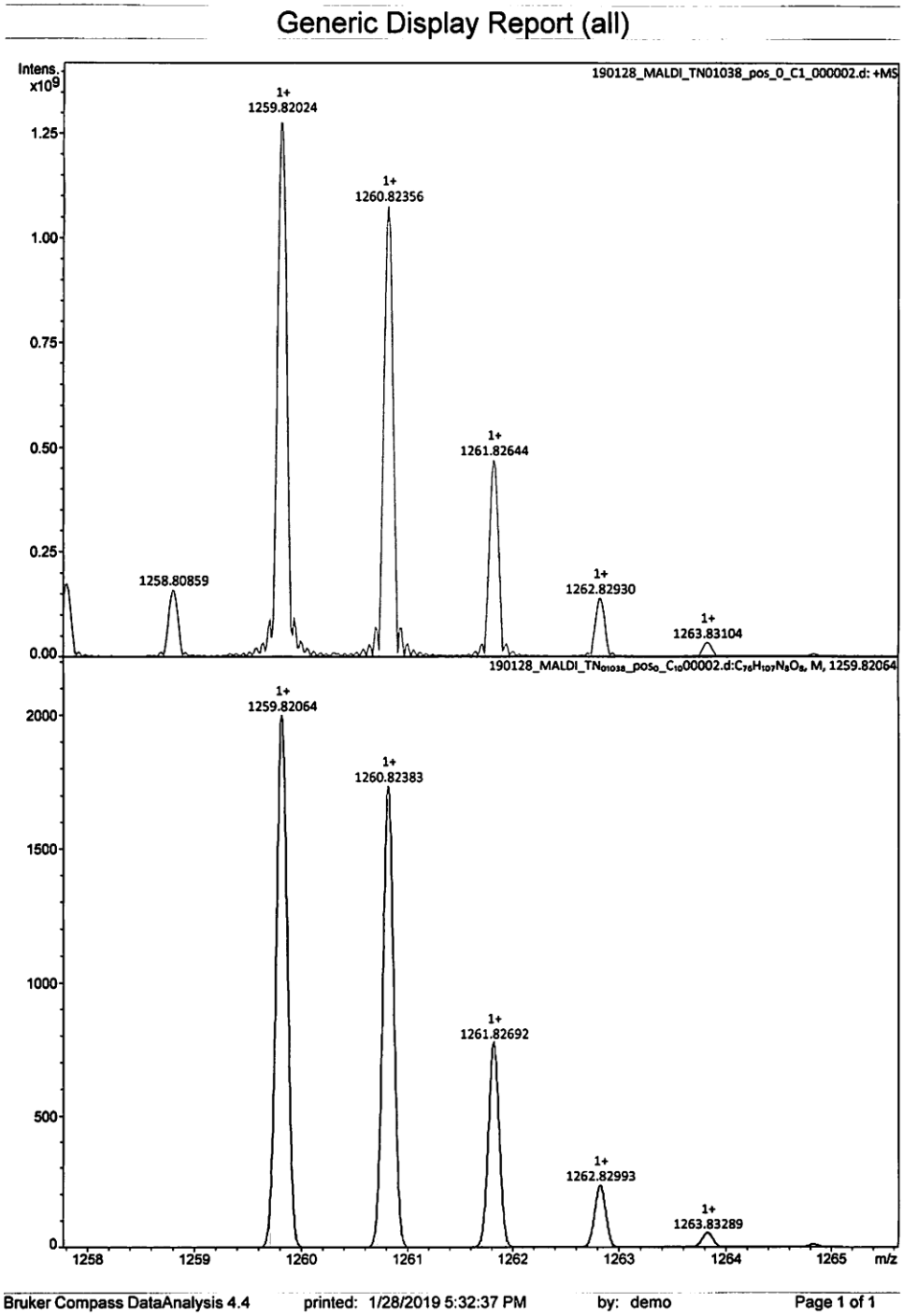

Figure S13. MALDI-TOF mass spectrum of the [2]rotaxane **7a**.

Upper: experimental isotopic pattern; lower: calculated isotopic pattern.

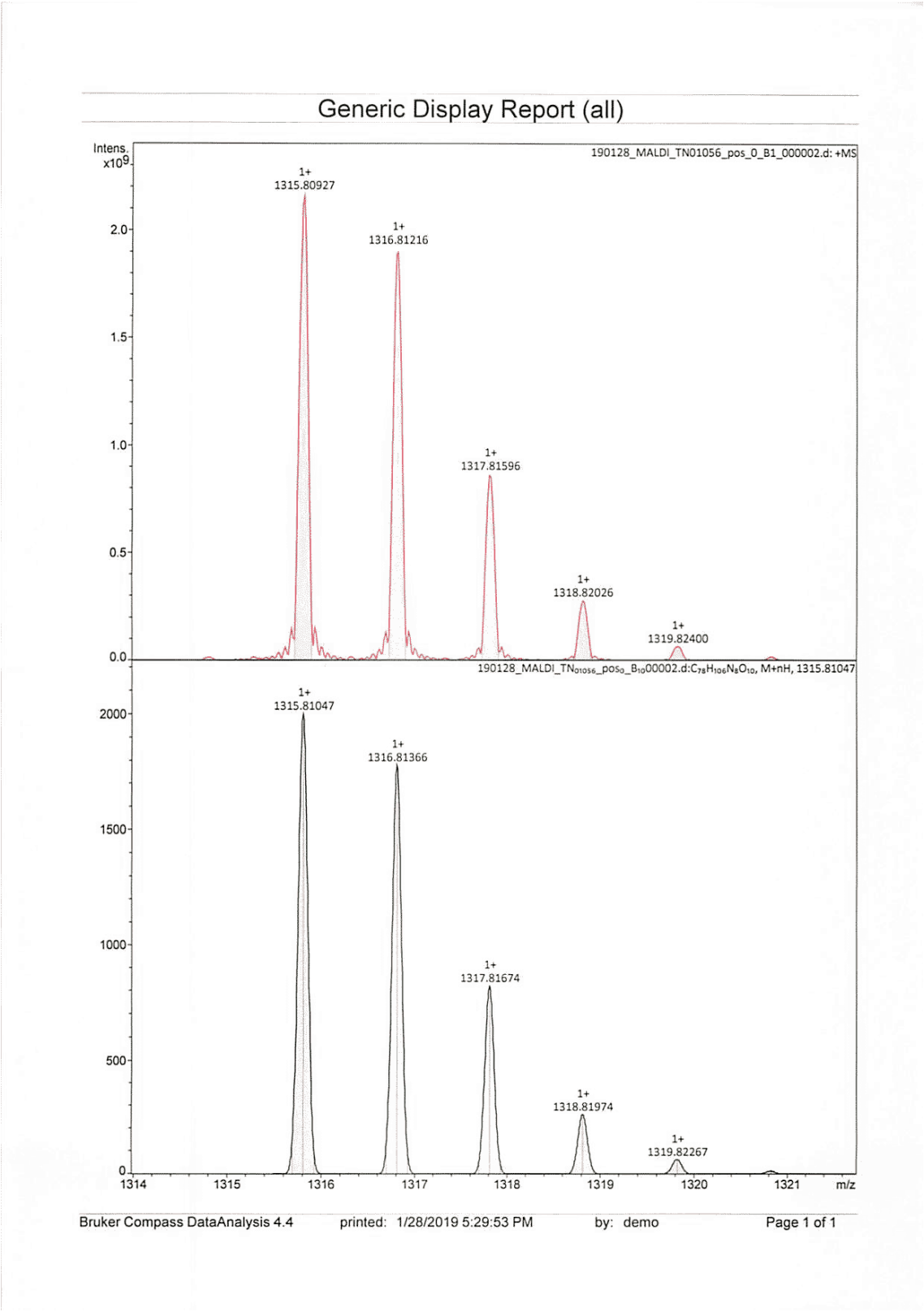

Figure S14. MALDI-TOF mass spectrum of the [2]rotaxane **7b**.

Upper: experimental isotopic pattern; lower: calculated isotopic pattern.

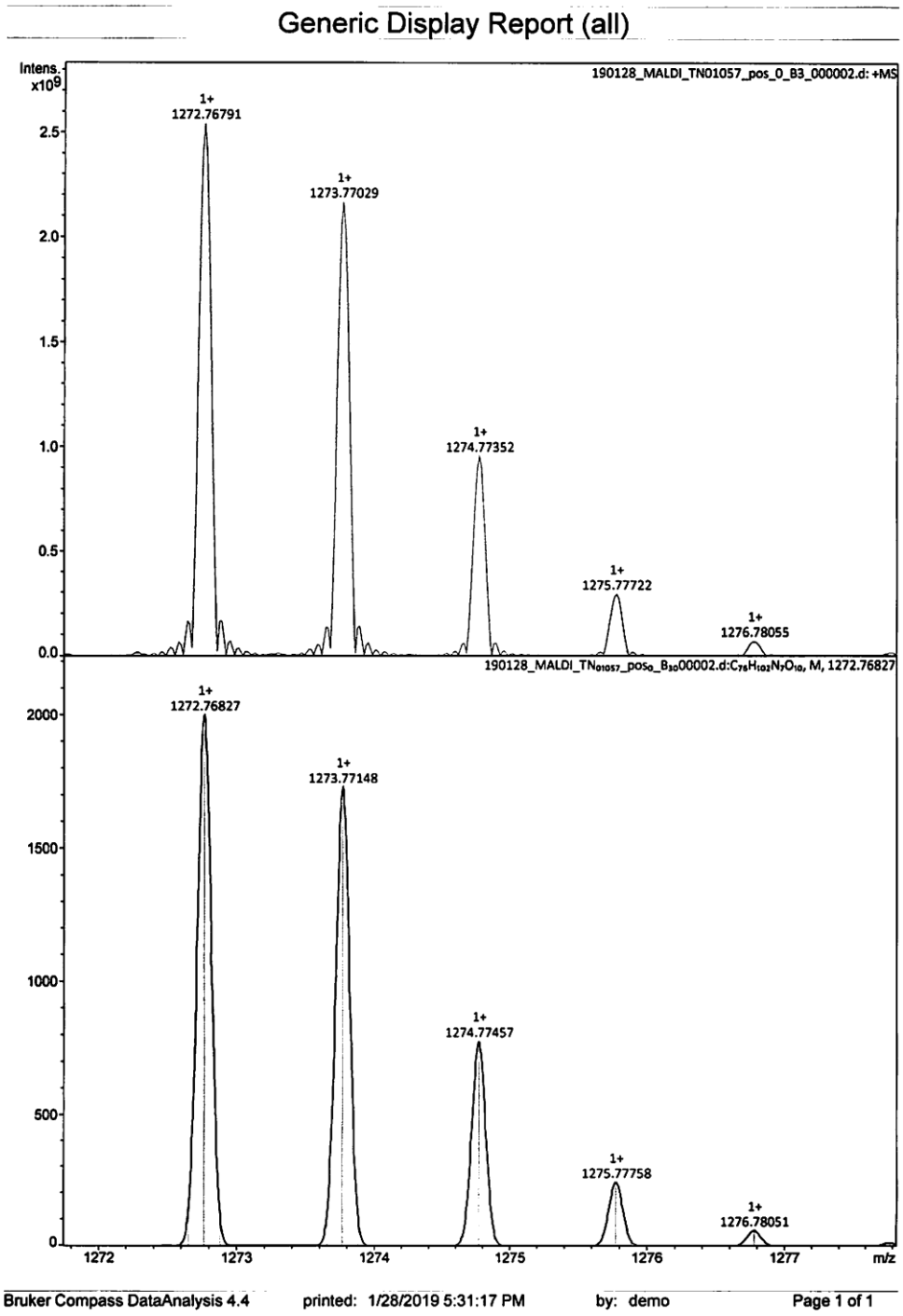

Figure S15. MALDI-TOF spectrum of the [2]rotaxane **7c**.

Upper: experimental isotopic pattern; lower: calculated isotopic pattern.

Table S1. Crystal data and structure refinement parameters for the lactam **1b**.

Empirical Formula	$C_{34}H_{44}Cl_{12}N_4O_8$
Formula Weight	1062.18
Temperature	–100.0 °C
Crystal System	triclinic
Space Group	P-1 (#2)
Lattice Parameters	a = 10.0502(3) Å
	b = 10.8877(4) Å
	c = 11.4091(4) Å
	α = 84.205(6)°
	β = 74.087(5)°
	γ = 78.083(6)°
Volume	1173.39(8) Å^3
Z value	1
ρ_{calc}	1.503 g/cm^3
F (000)	544.00
Crystal Color	colorless
Crystal Size	0.540 × 0.300 × 0.120 mm
Radiation	Mo Kα (λ = 0.71075 Å)
$2\theta_{max}$	54.9°
Number of Reflections Measured	Total: 23419
	Unique: 5354 (R_{int} = 0.0244)
Goodness-of-Fit on F^2	1.047
Residuals: R_1 [$I > 2.00\sigma$ (I)]	0.0836
Residuals: wR_2 (All reflections)	0.2322

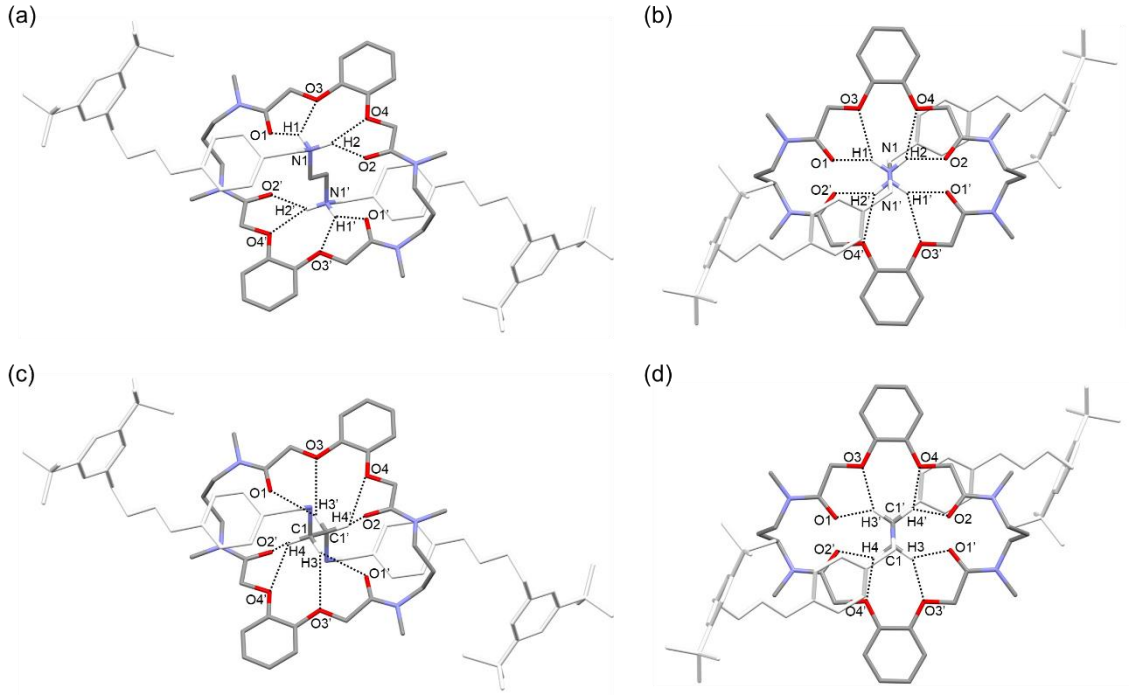

Figure S16. Crystal structure of the [2]rotaxane **7b**. The major (a, b) NH···O and (c, d) CH···O interactions are highlighted with dotted lines. Hydrogen bond distances (Å): (a, b) 2.73 [N(1)$^{+}$···O(1)], 2.65 [N(1)$^{+}$···O(2)], 1.96 [H(1)···O(1)], 1.89 [H(2)···O(2)], 2.54 [H(1)···O(3)], 2.51 [H(2)···O(4)]; (c, d) 2.53 [H(3)´···O(1)], 2.72 [H(4)´···O(2)], 2.70 [H(3)´···O(3)], 2.50 [H(4)´···O(4)]. Hydrogen bond angles (deg): N(1)$^{+}$–H(1)···O(1) and N(1)$^{+}$–H(2)···O(2), 141 and 140, respectively. Hydrogen atoms, PF_6^- ions, and ^{t}Bu disorder have been omitted for clarity.

Table S2. Crystal data and structure refinement parameters for the [2]rotaxane **7b**.

Empirical Formula	$C_{78}H_{108}F_{12}N_8O_{10}P_2$
Formula Weight	1607.69
Temperature	–100.0 °C
Crystal System	triclinic
Space Group	P-1 (#2)
Lattice Parameters	a = 8.69360 Å
	b = 11.55039 Å
	c = 22.97133 Å
	α = 79.01400°
	β = 79.44700°
	γ = 65.70200°
Volume	2049.61022 Å^3
Z value	1
ρ_{calc}	1.302 g/cm^3
F (000)	850.00
Crystal Color	colorless
Crystal Size	0.010 × 0.010 × 0.010 mm
Radiation	Synchrotron (λ = 0.81078 Å)
$2\theta_{max}$	58.5°
Number of Reflections Measured	Total: 21074
	Unique: 7442 (R_{int} = 0.1011)
Goodness-of-Fit on F^2	1.131
Residuals: R_1 [$I > 2.00\sigma(I)$]	0.1434
Residuals: wR_2 (All reflections)	0.4088

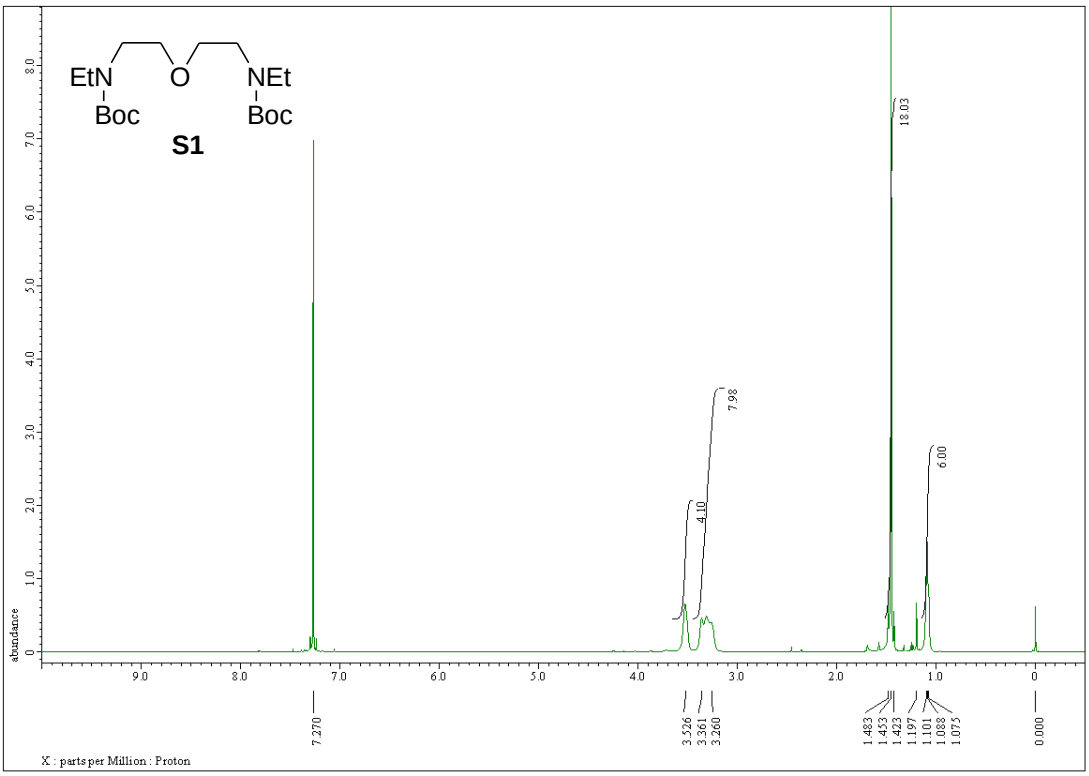

Figure S17a. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the carbamate **S1**.

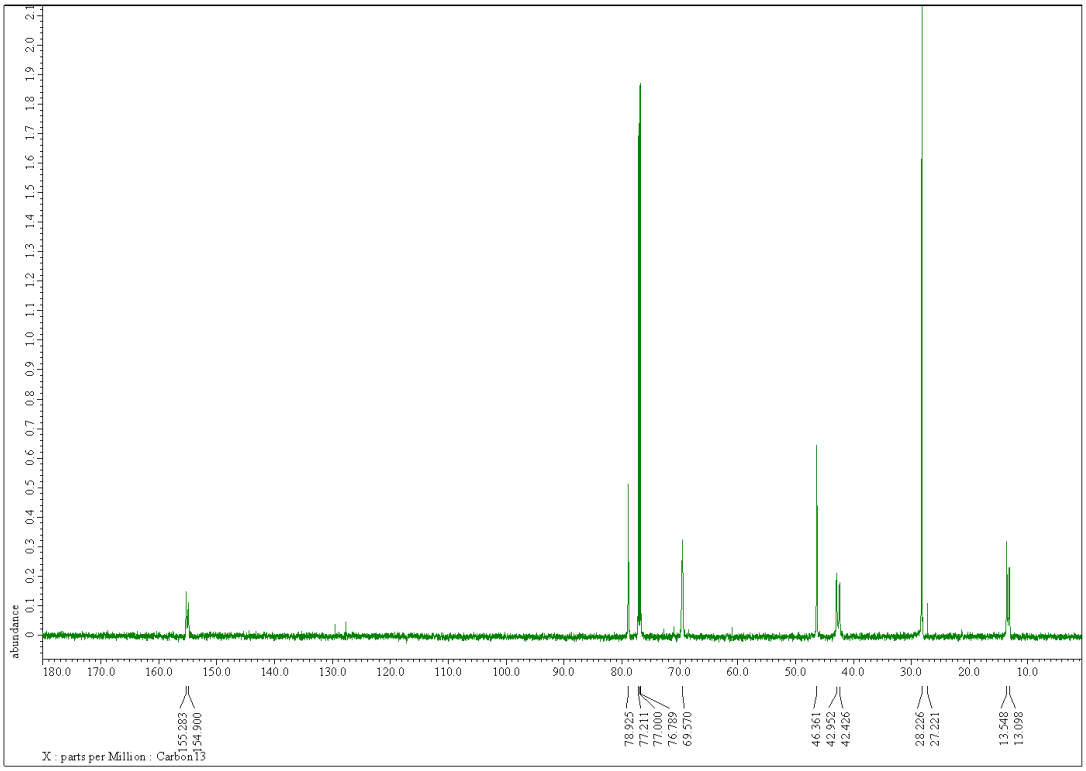

Figure S17b. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of the carbamate **S1**.

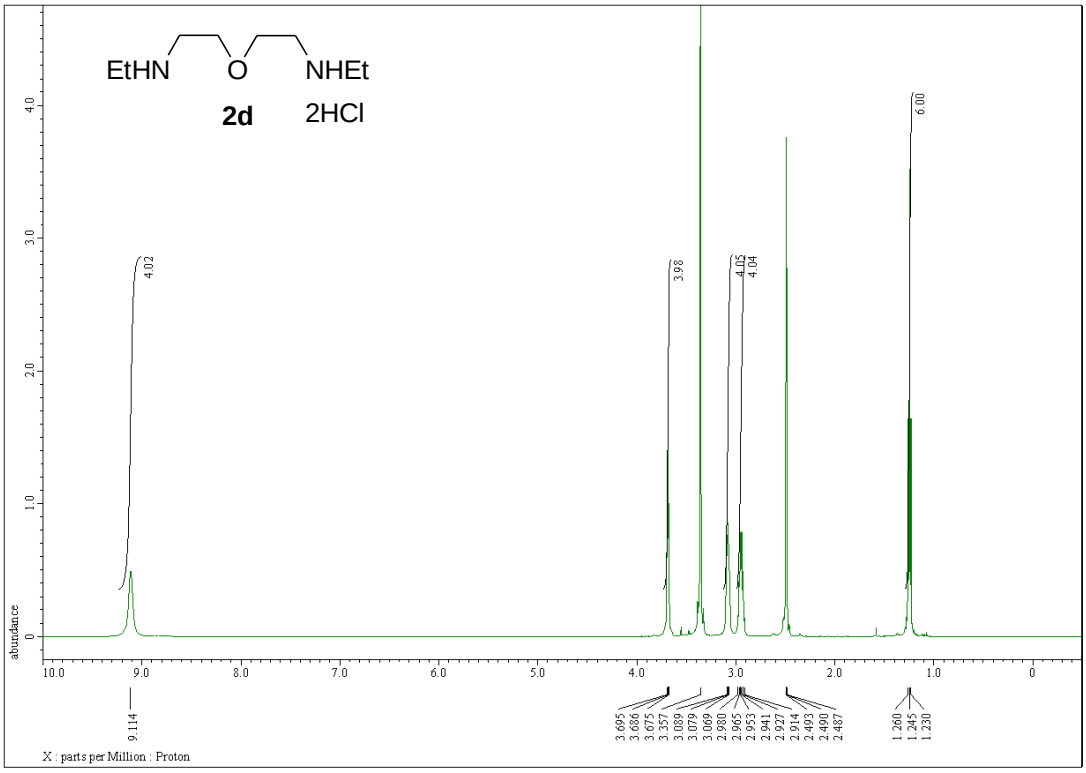

Figure S18a. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the dialkylammonium salt **2d**.

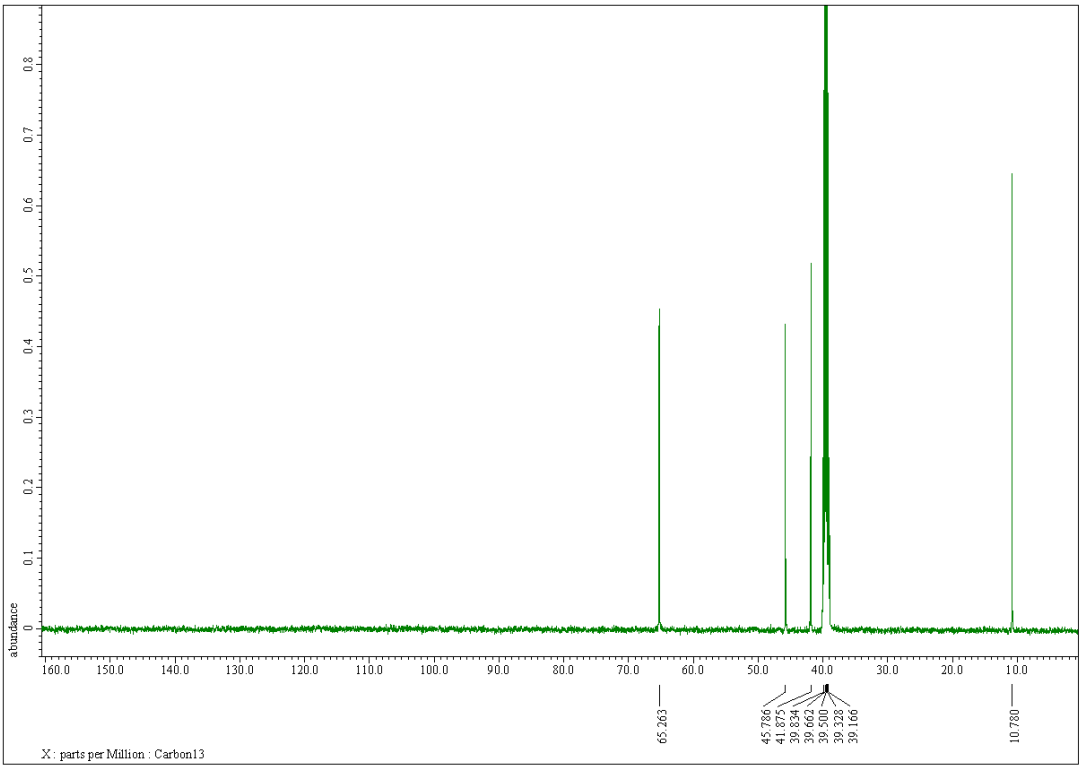

Figure S18b. ^{13}C NMR spectrum (125 MHz, DMSO-d_6) of the dialkylammonium salt **2d**.

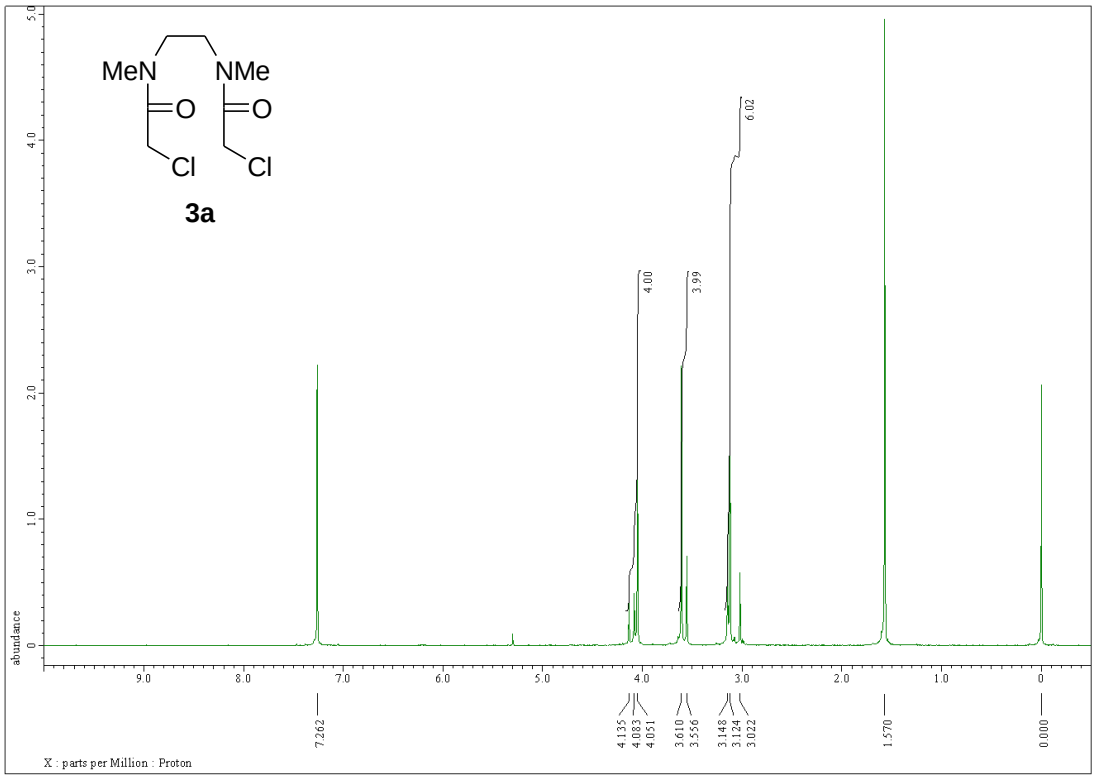

Figure S19a. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the chloride **3a**.

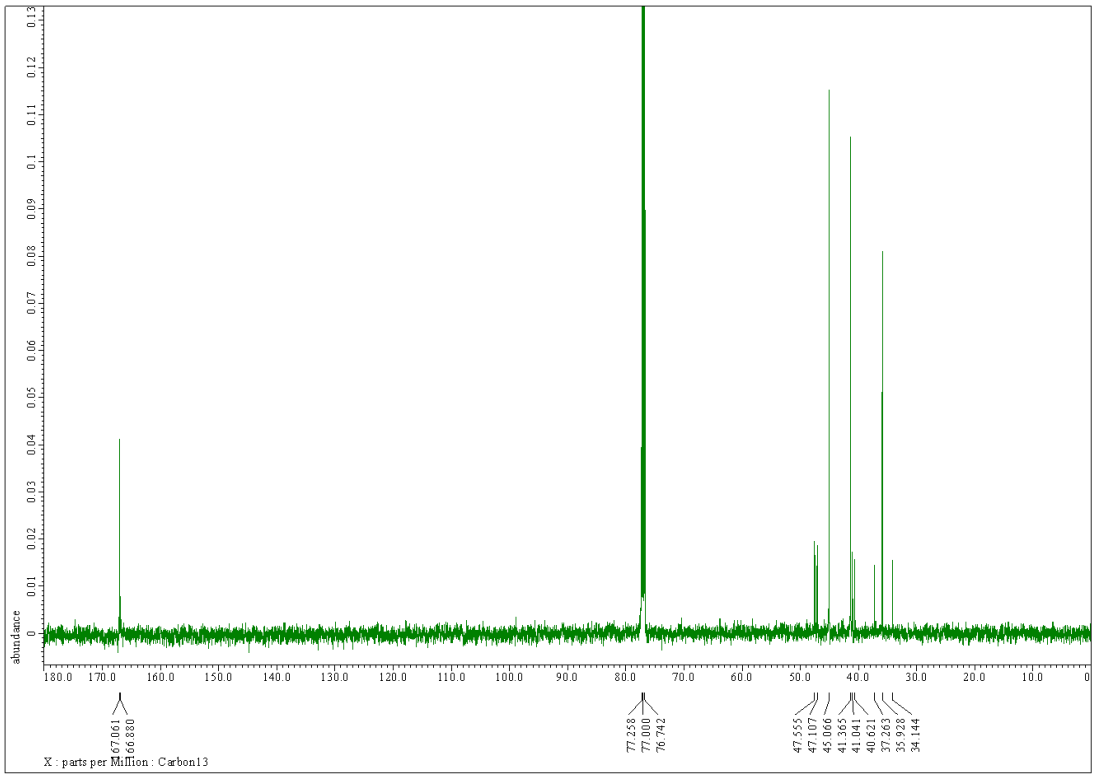

Figure S19b. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the chloride **3a**.

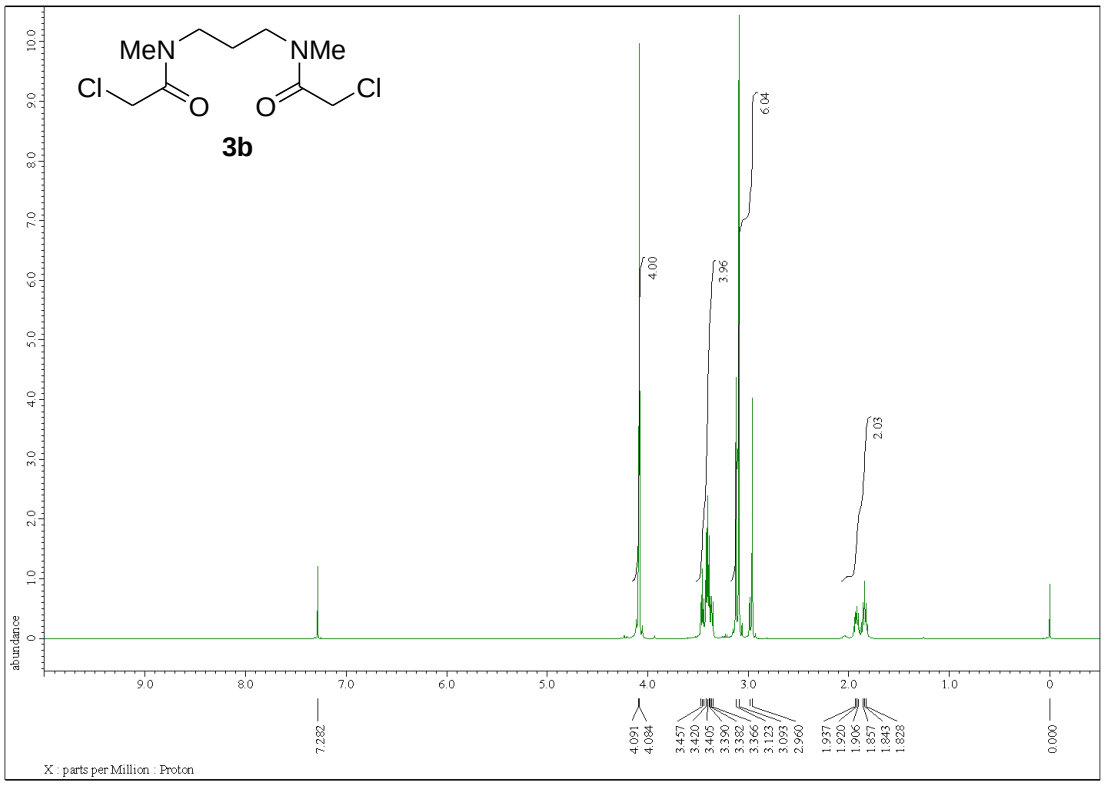

Figure S20a. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the chloride **3b**.

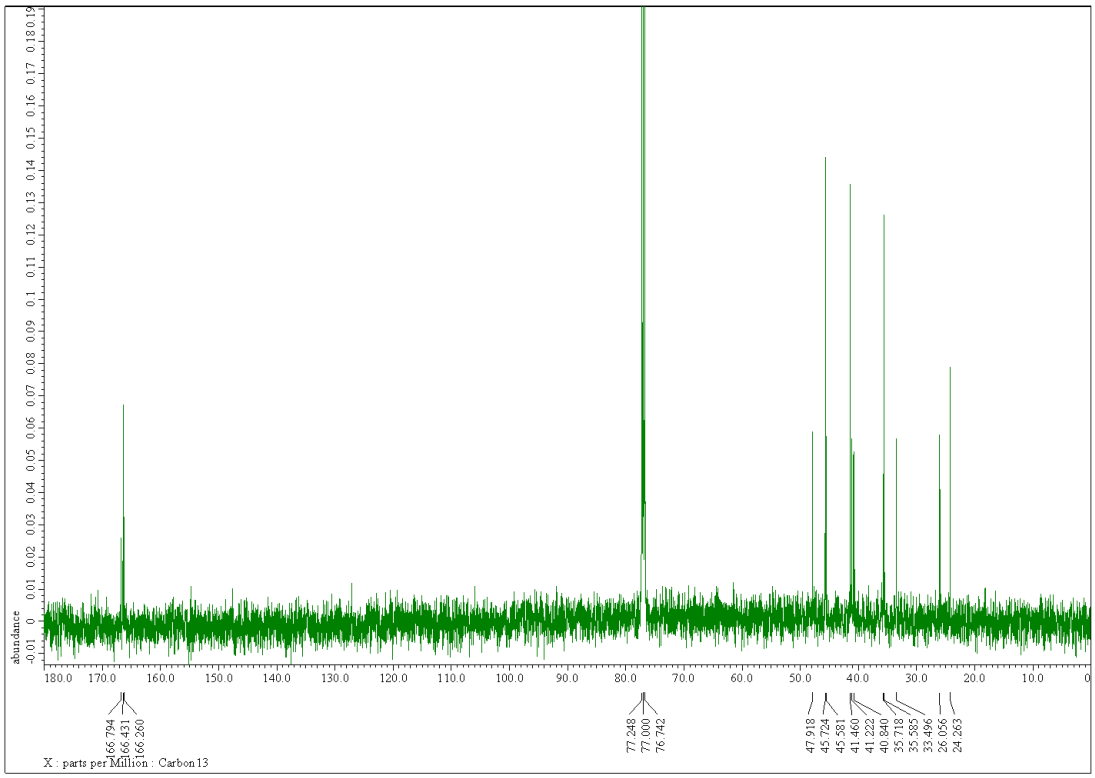

Figure S20b. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the chloride **3b**.

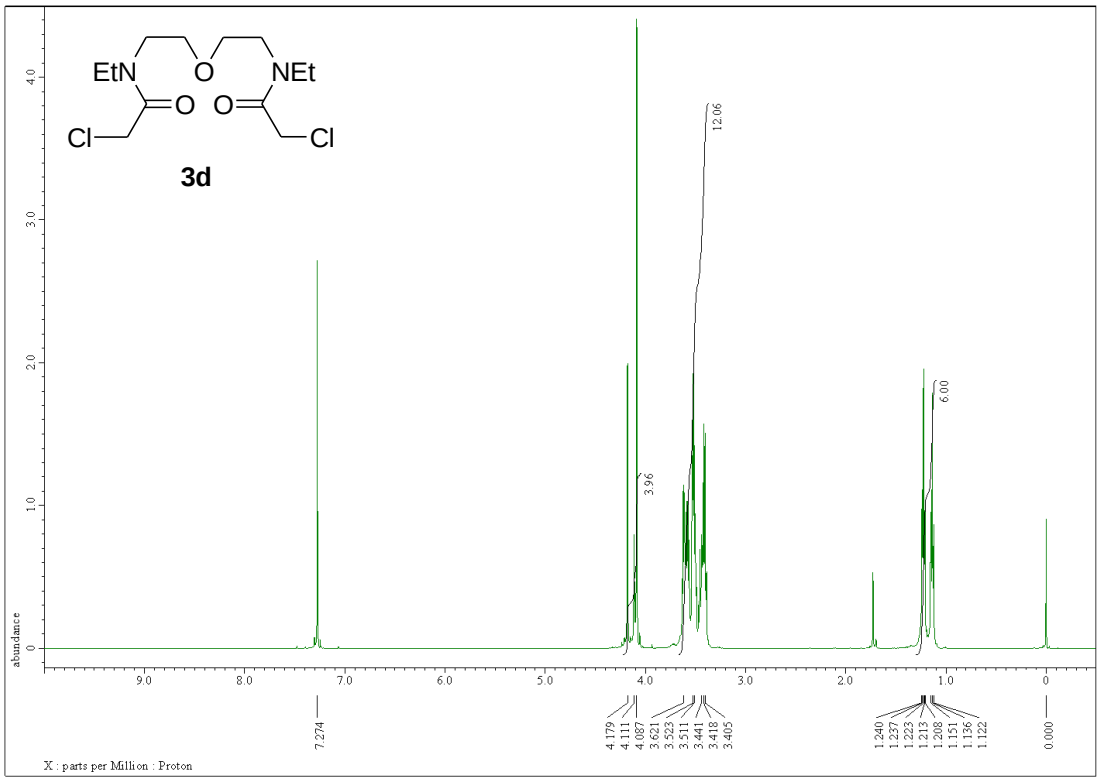

Figure S21a. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the chloride **3d**.

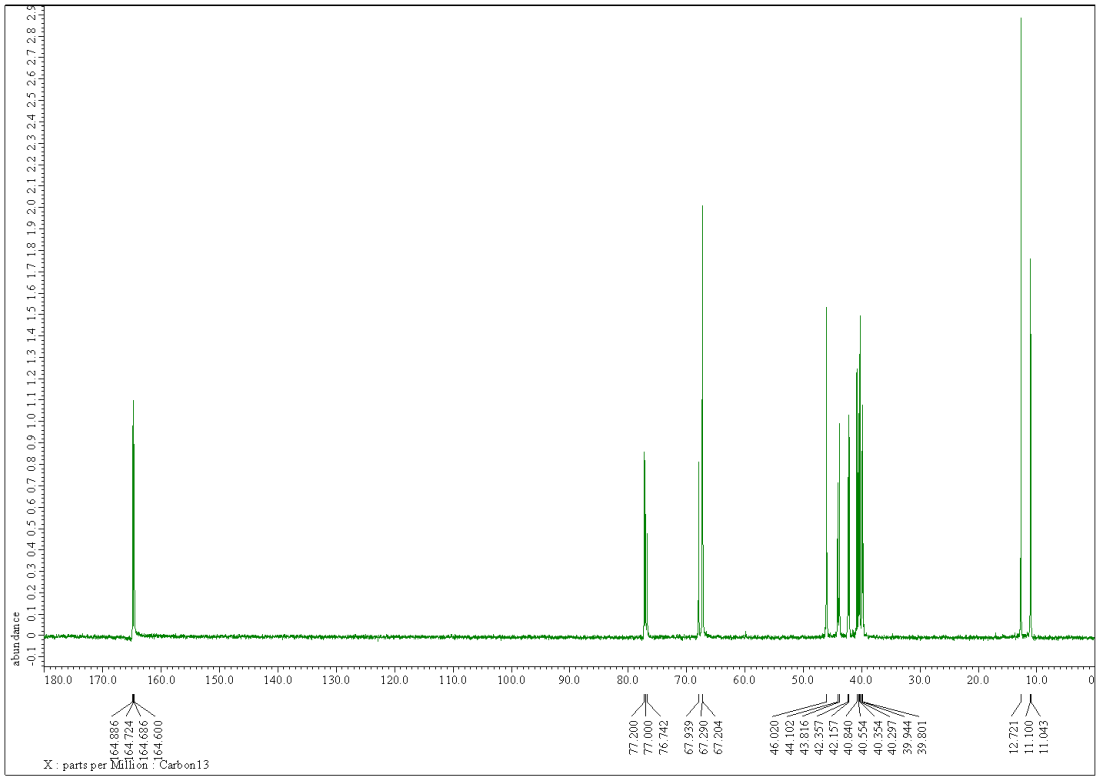

Figure S21b. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the chloride **3d**.

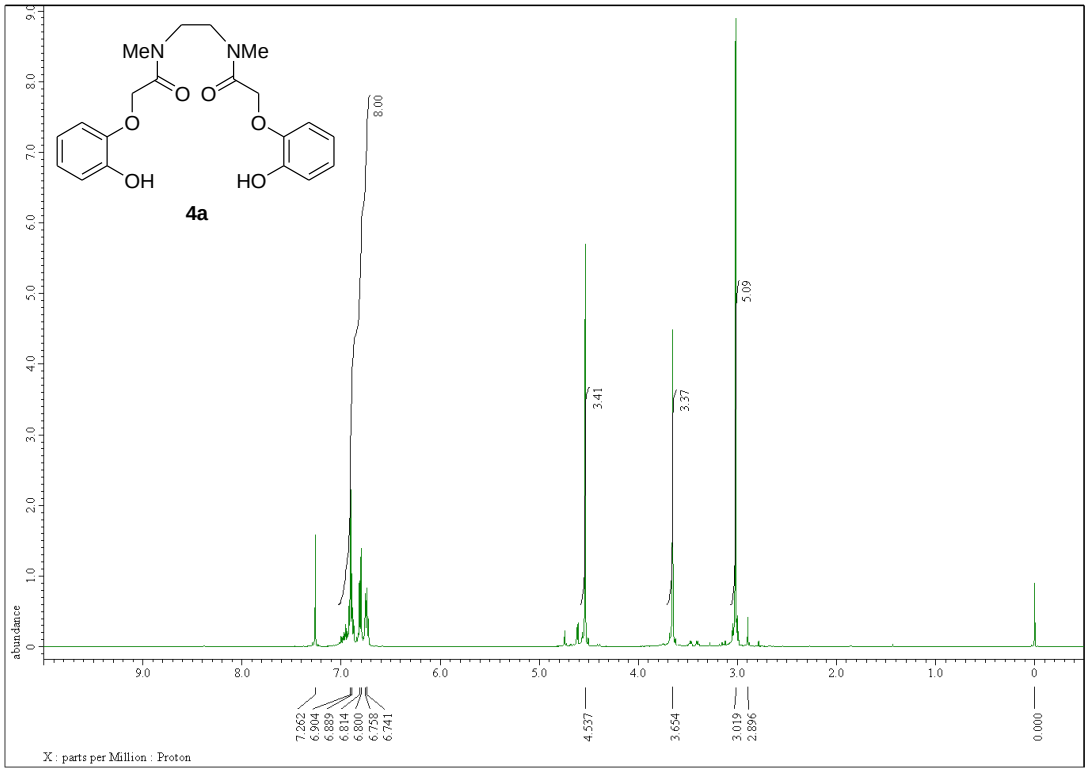

Figure S22a. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the amide **4a**.

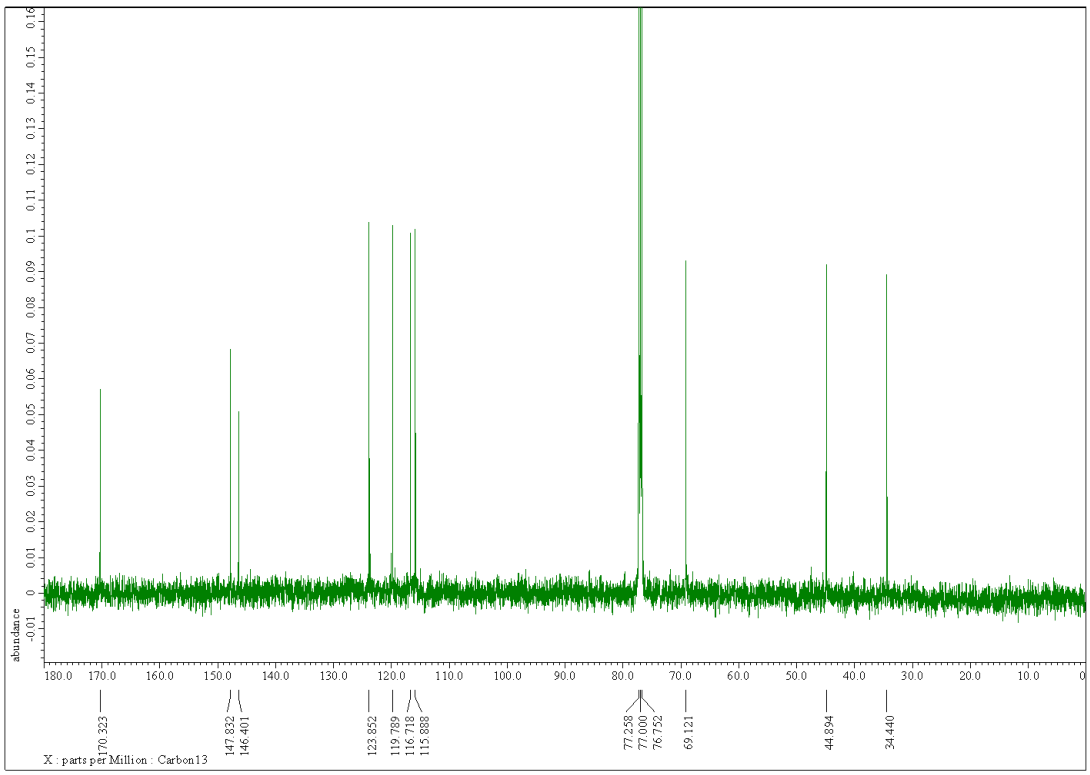

Figure S22b. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the amide **4a**.

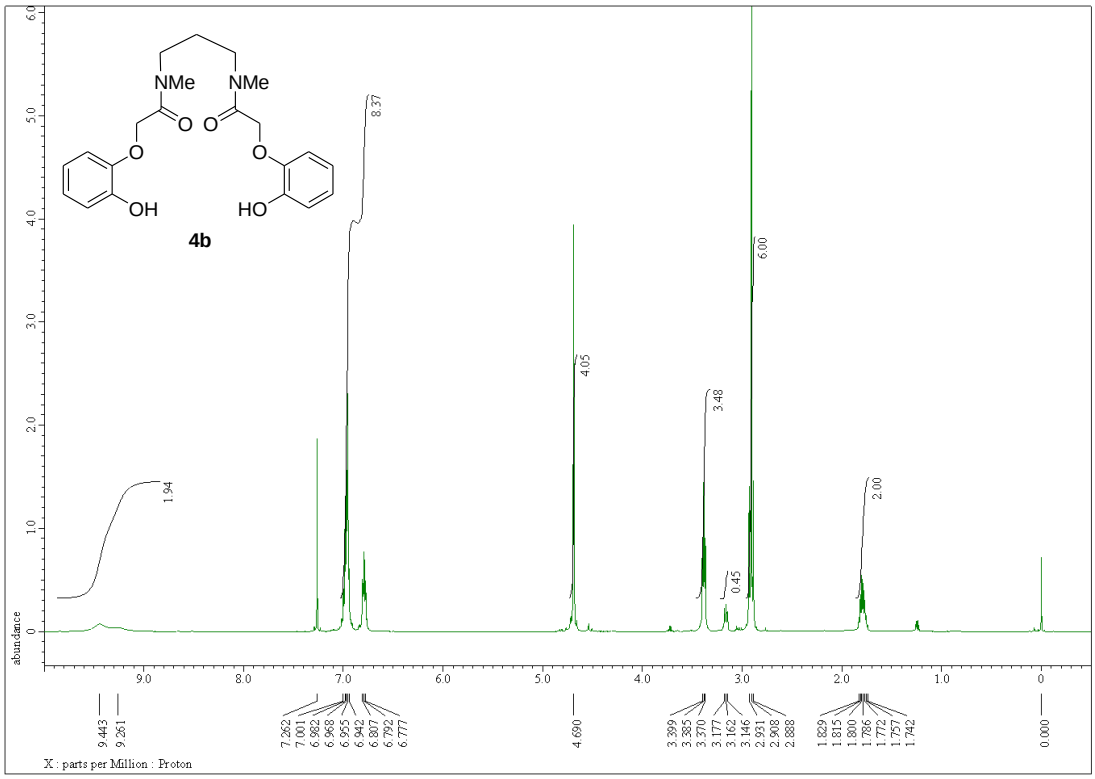

Figure S23a. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the amide **4b**.

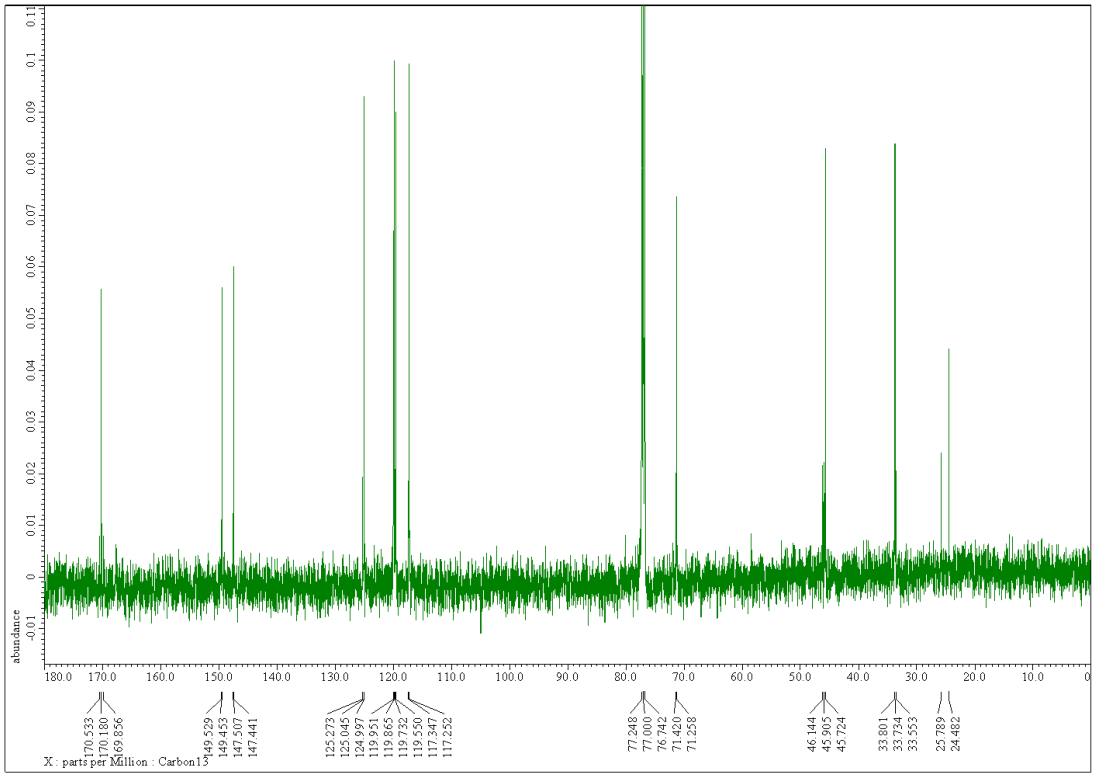

Figure S23b. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the amide **4b**.

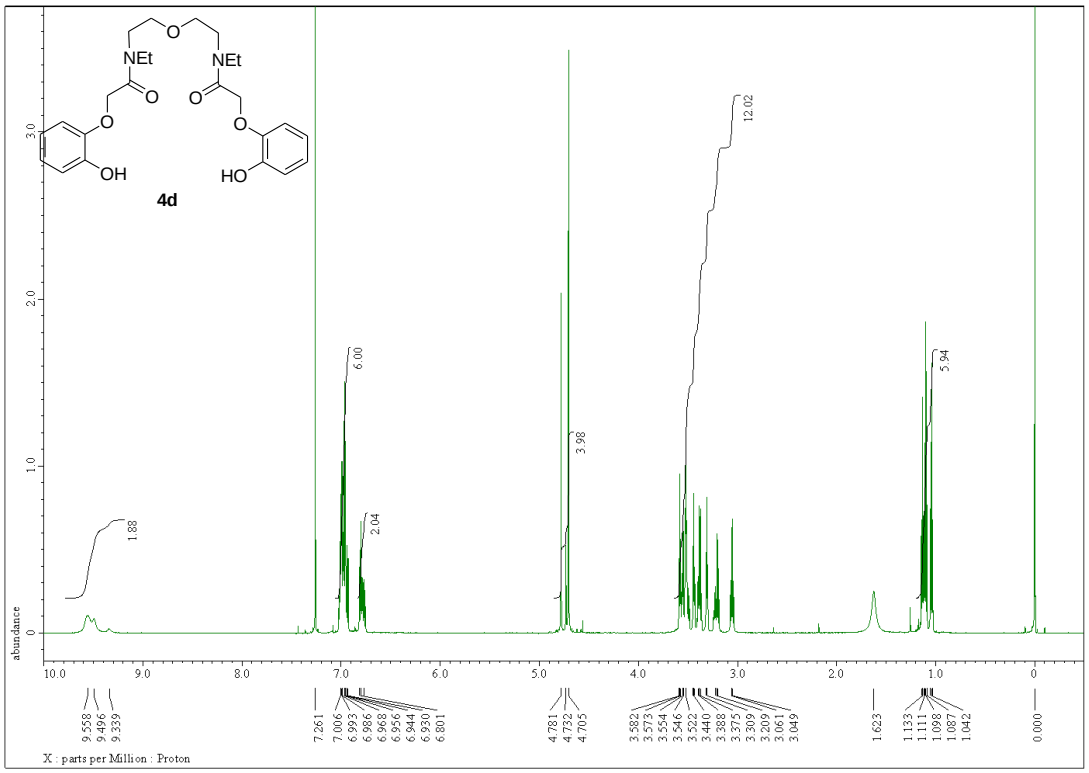

Figure S24a. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of the amide **4d**.

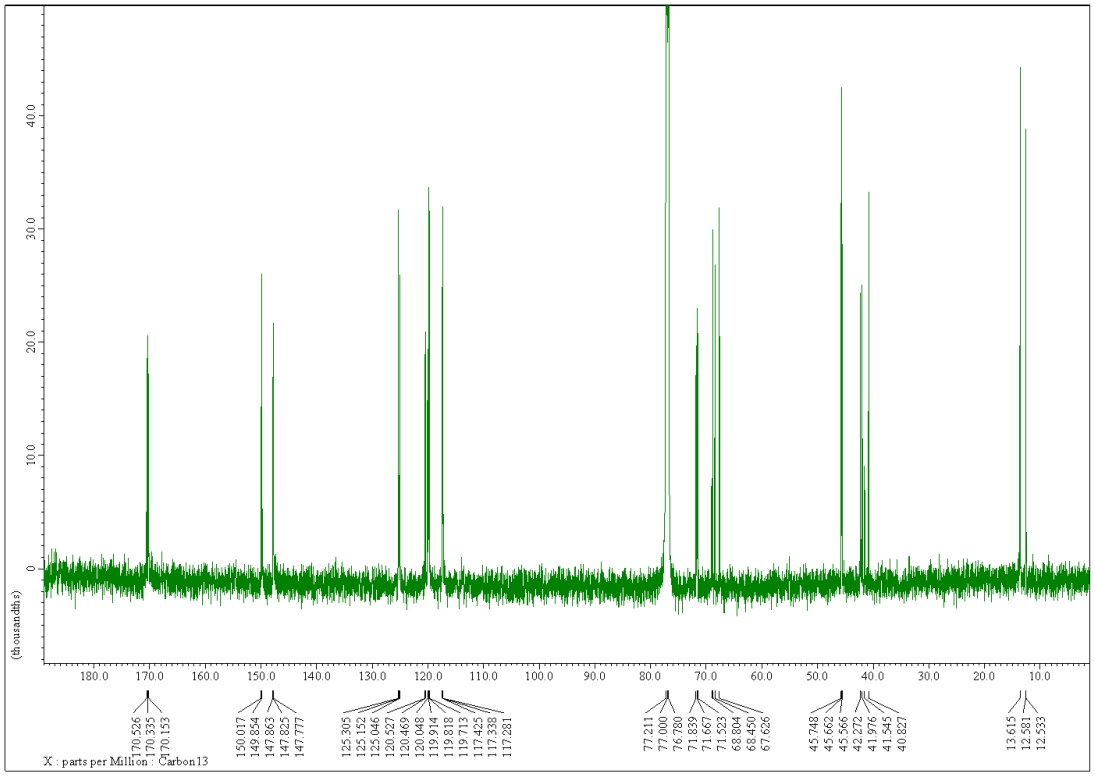

Figure S24b. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the amide **4d**.

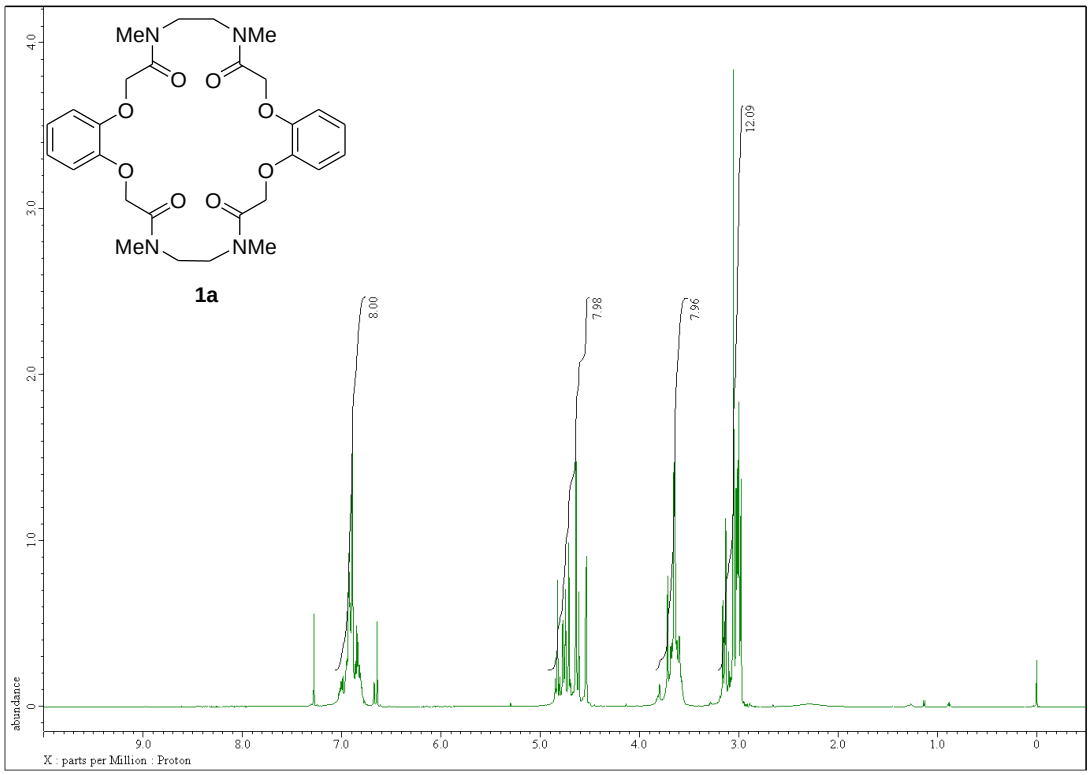

Figure S25a. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the cyclic tetraamide **1a**.

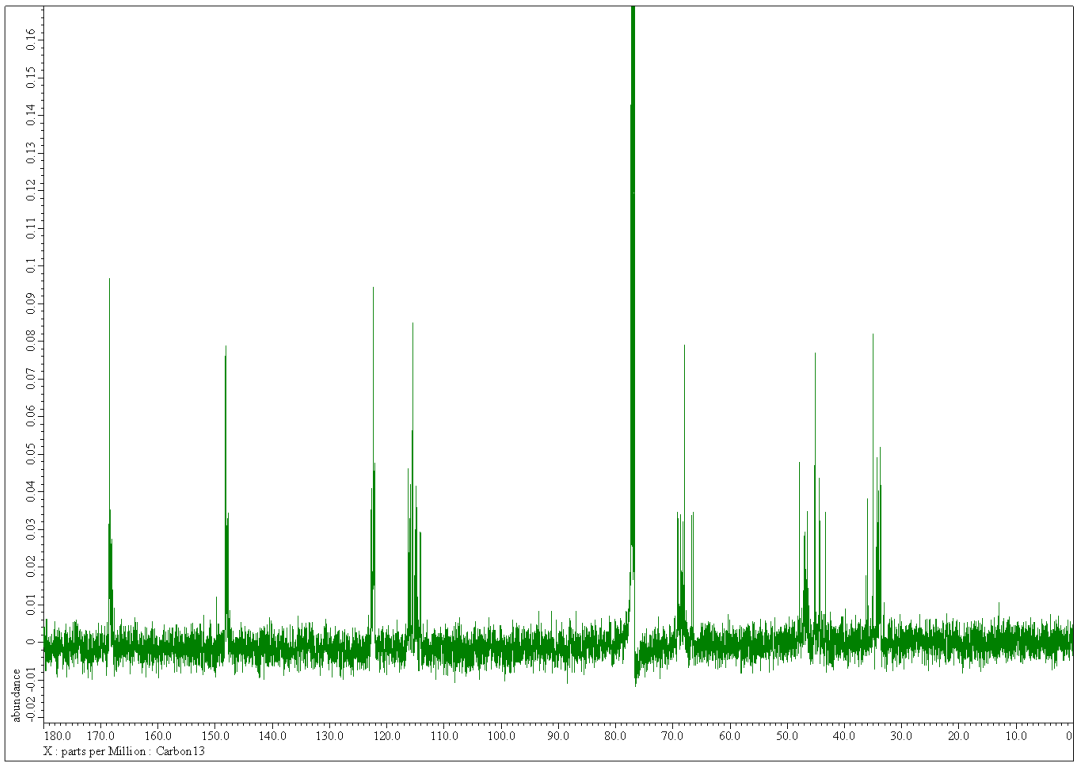

Figure S25b. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the cyclic tetraamide **1a**.

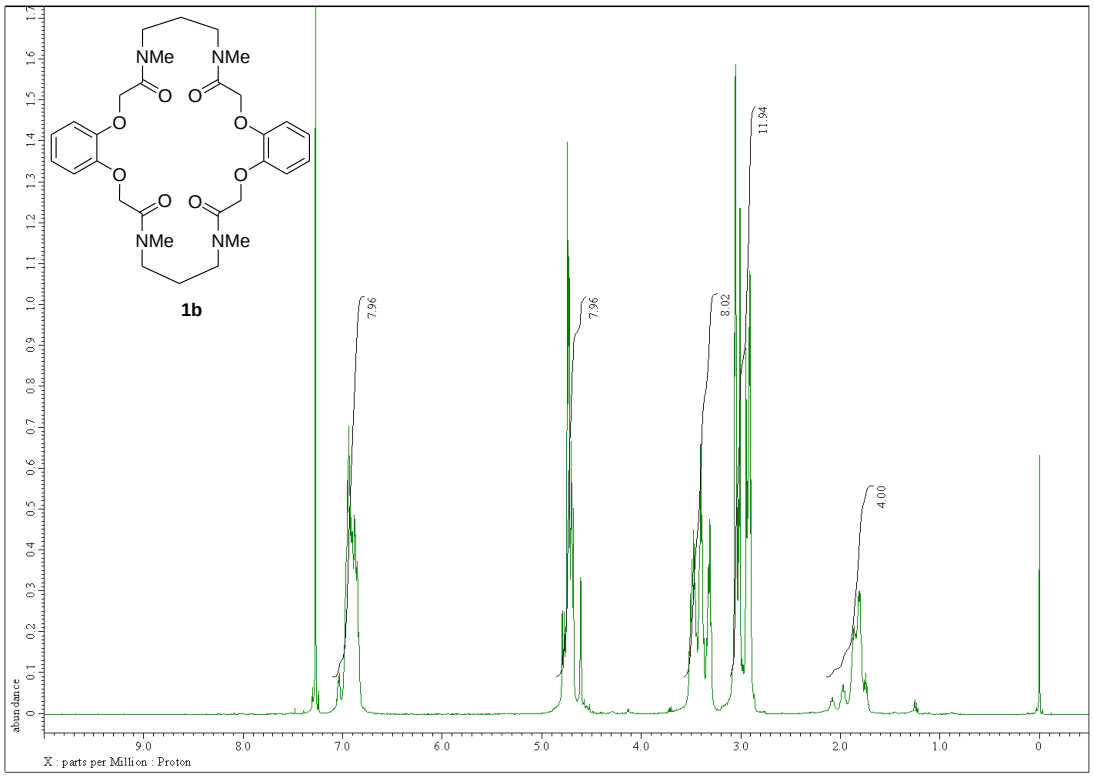

Figure S26a. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the cyclic tetraamide **1b**.

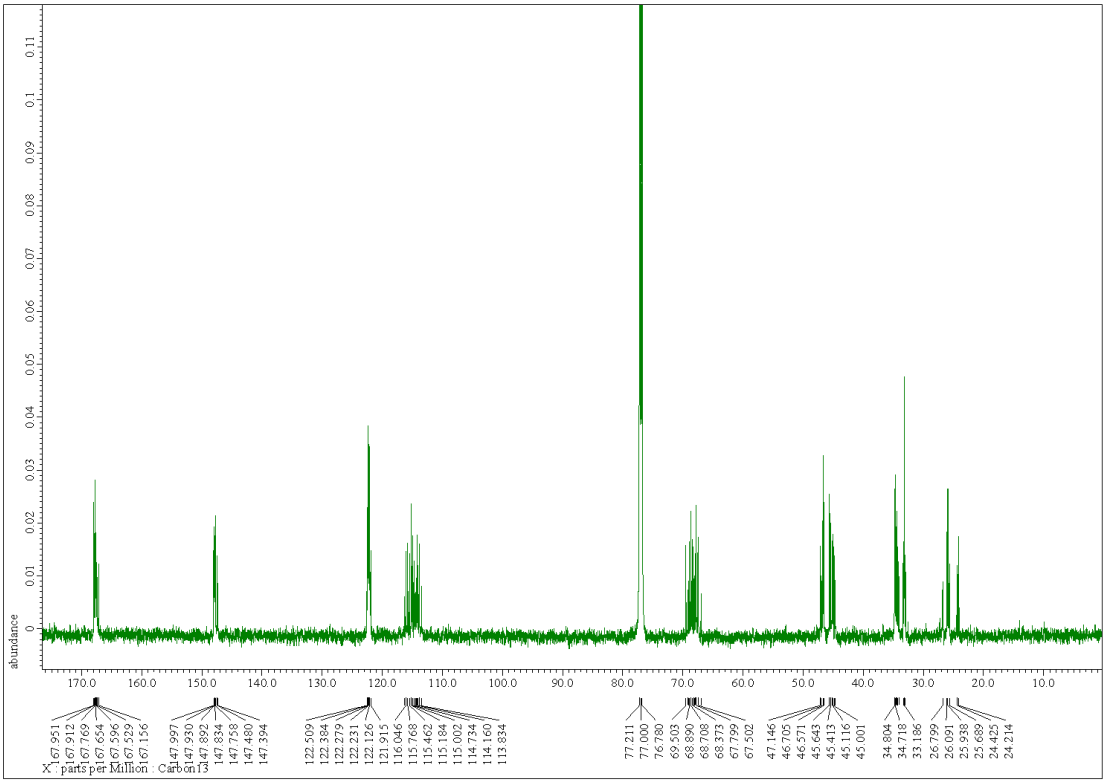

Figure S26b. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the cyclic tetraamide **1b**.

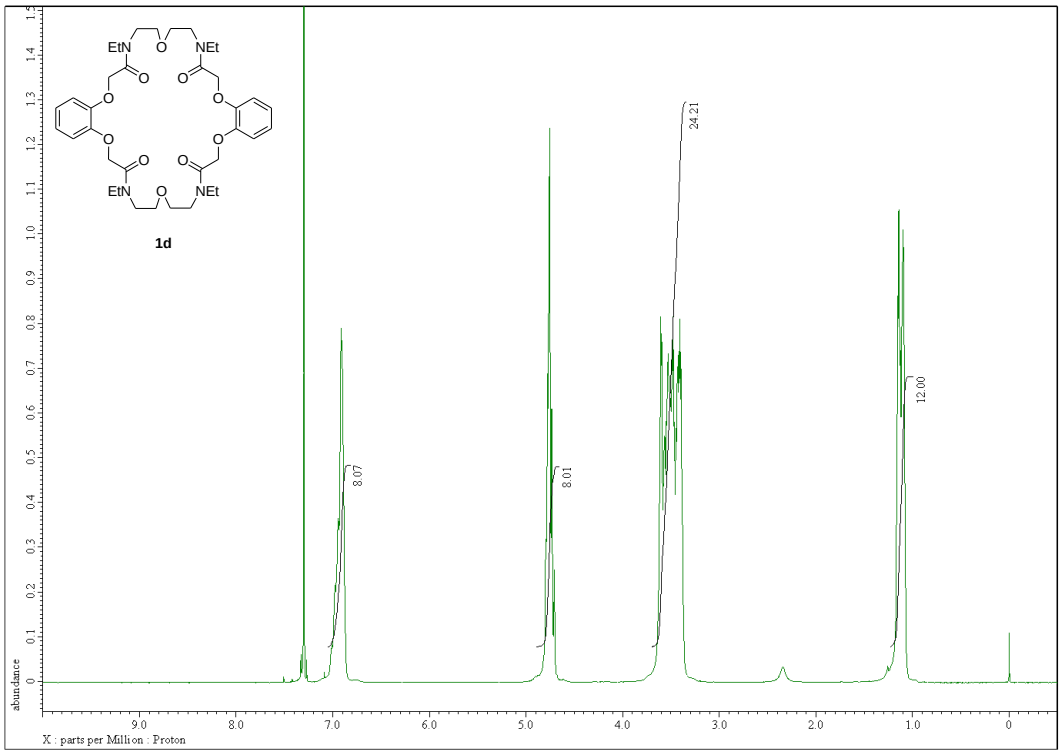

Figure S27a. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the cyclic tetraamide **1d**.

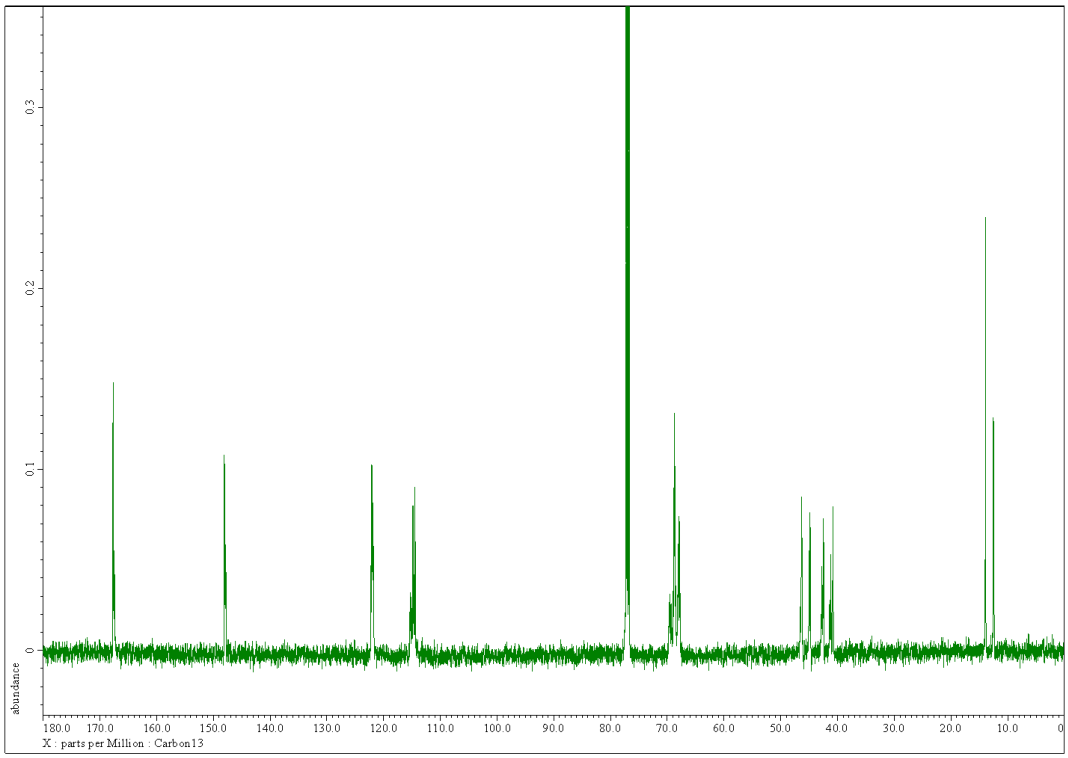

Figure S27b. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the cyclic tetraamide **1d**.

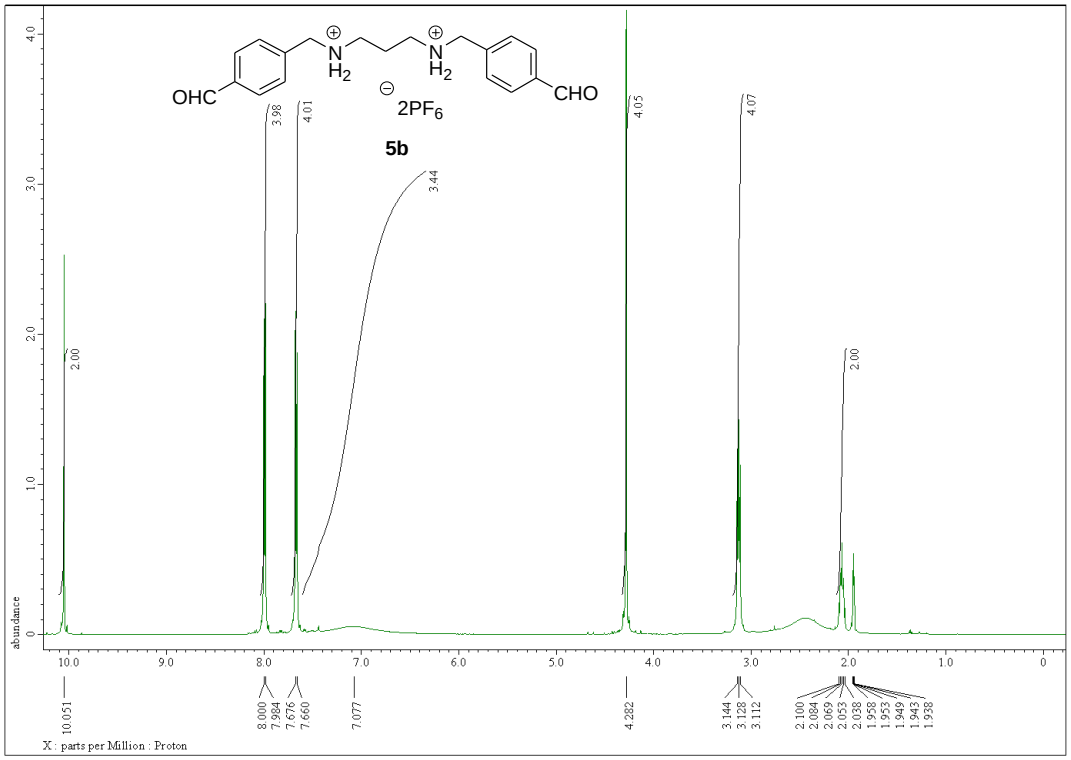

Figure S28a. ^{1}H NMR spectrum (500 MHz, CD_3CN) of the ammonium salt **5b**.

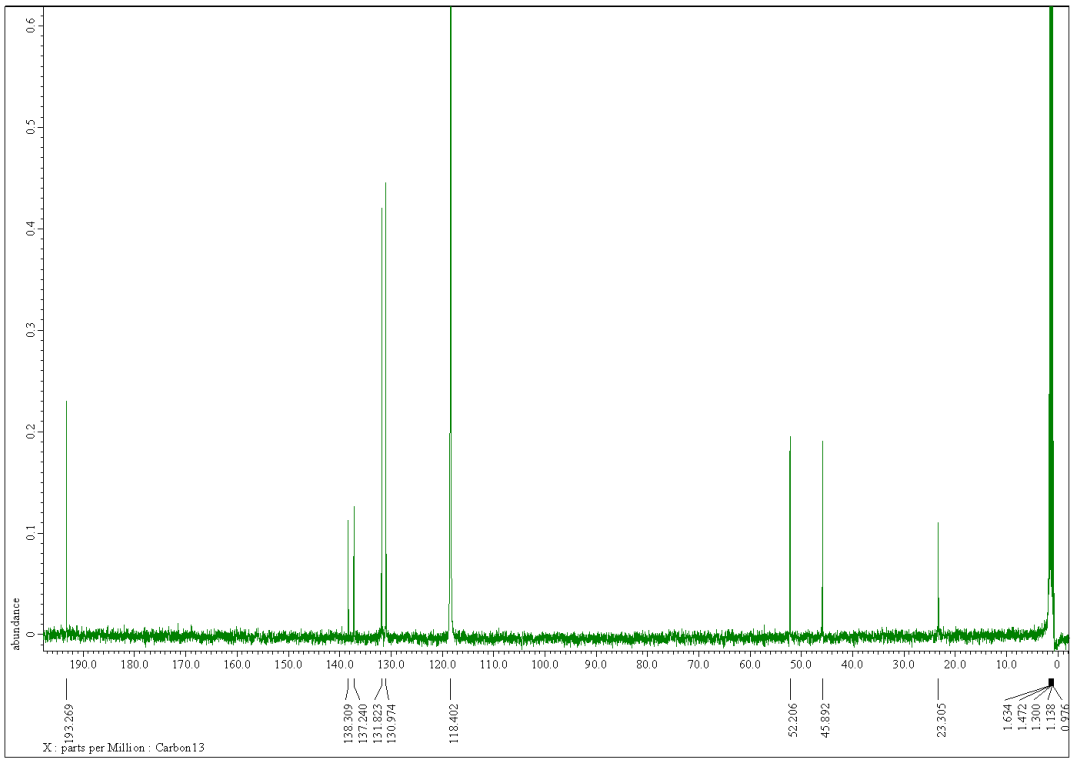

Figure S28b. ^{13}C NMR spectrum (125 MHz, CD_3CN) of the ammonium salt **5b**.

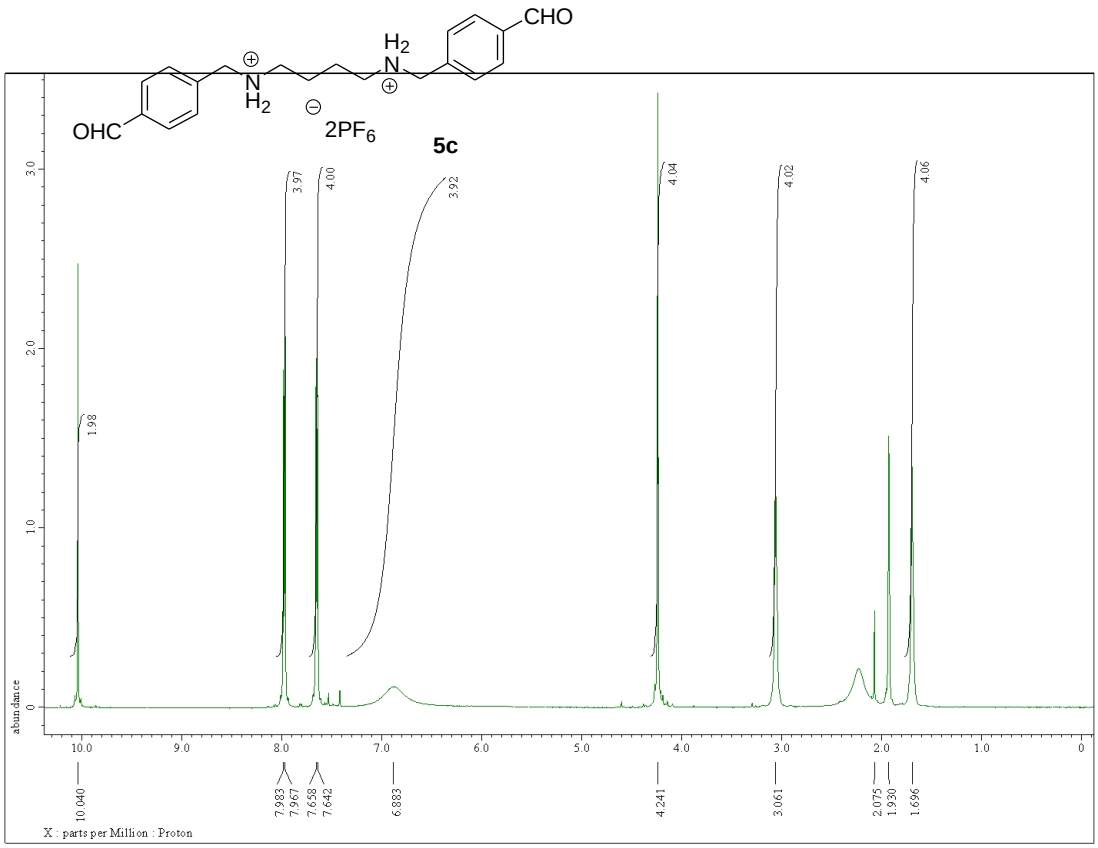

Figure S29a. ^{1}H NMR spectrum (500 MHz, CD_3CN) of the dialkylammonium salt **5c**.

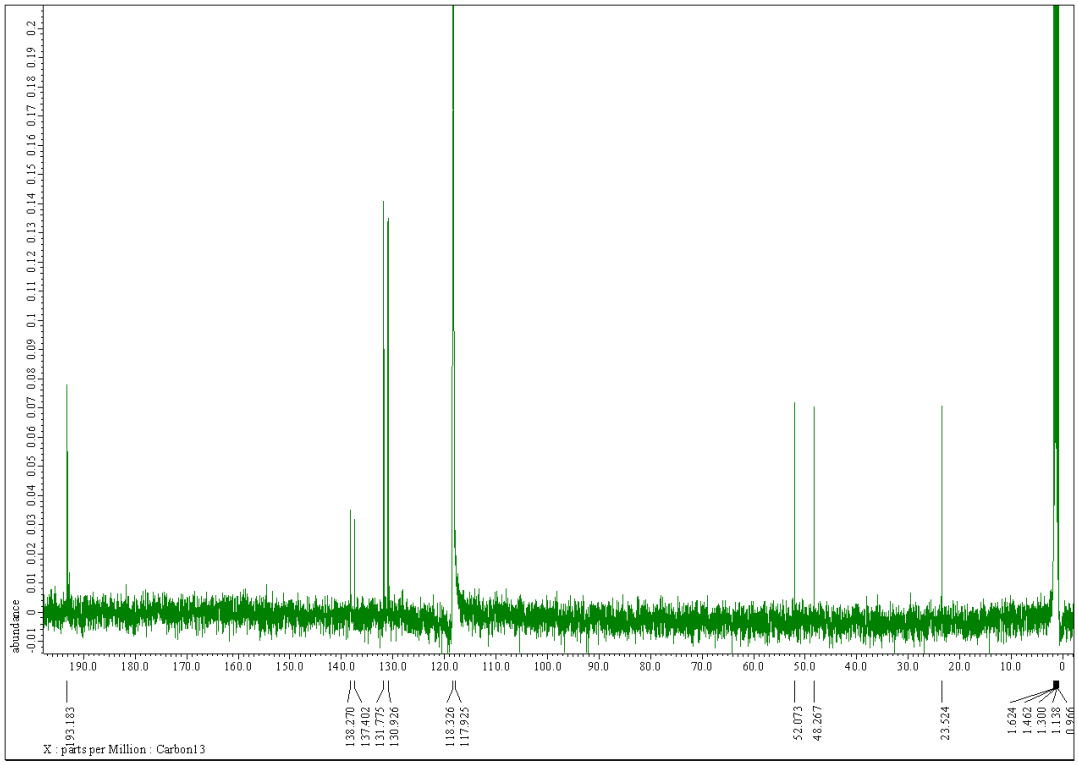

Figure S29b. ^{13}C NMR spectrum (125 MHz, CD_3CN) of the dialkylammonium salt **5c**.

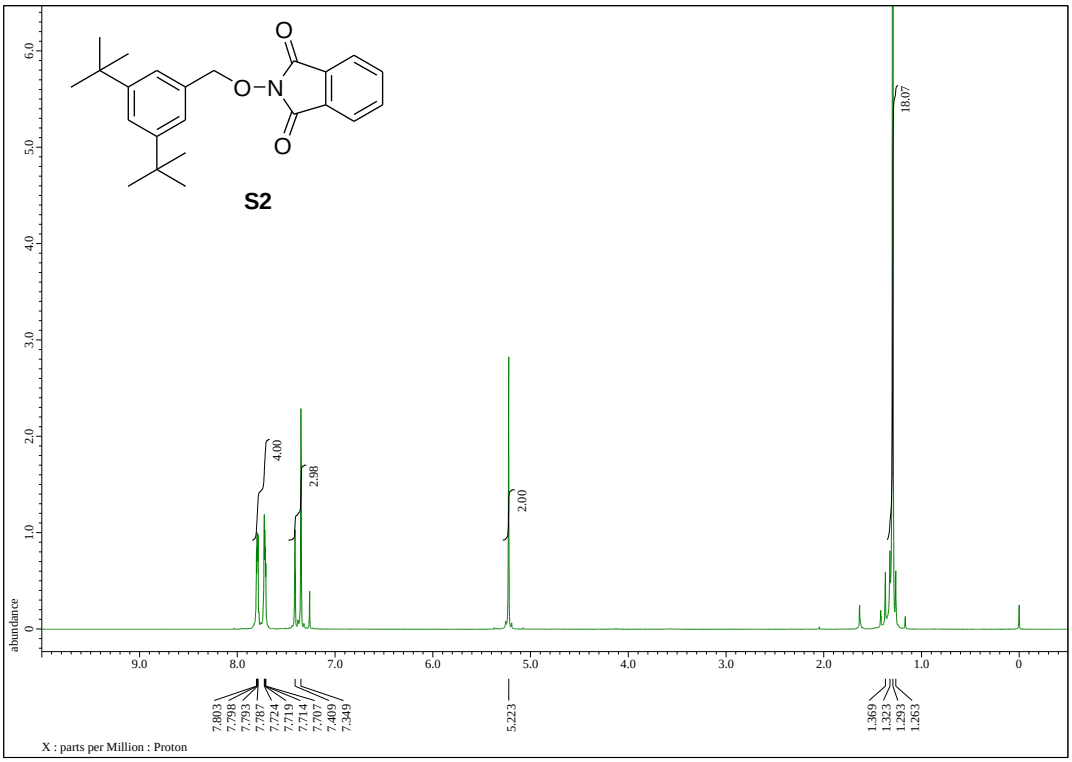

Figure S30a. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the phthalimide **S2**.

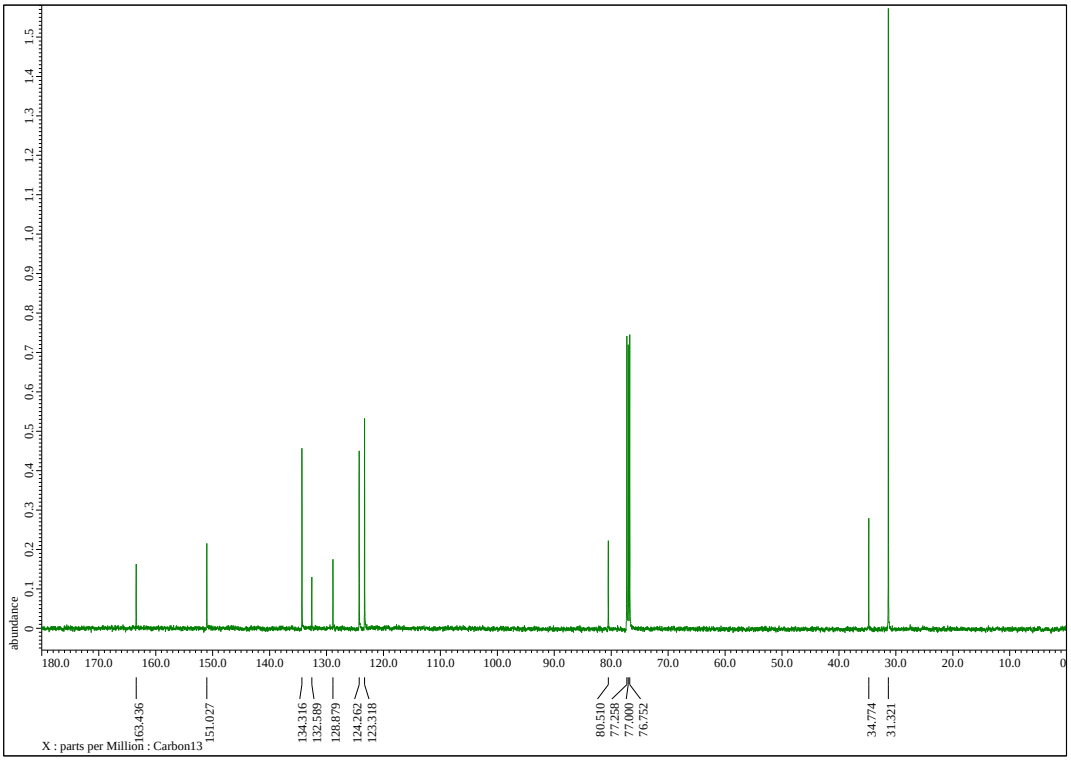

Figure S30b. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the phthalimide **S2**.

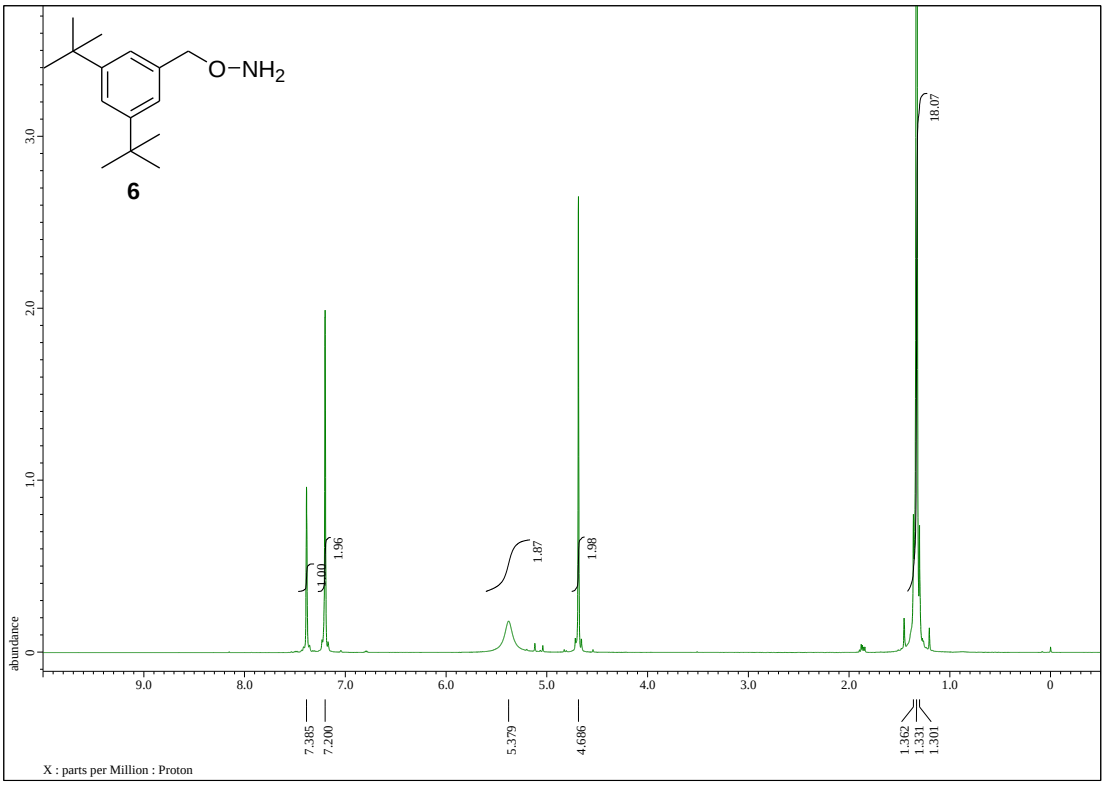

Figure S31a. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the *O*-benzylhydroxylamine **6**.

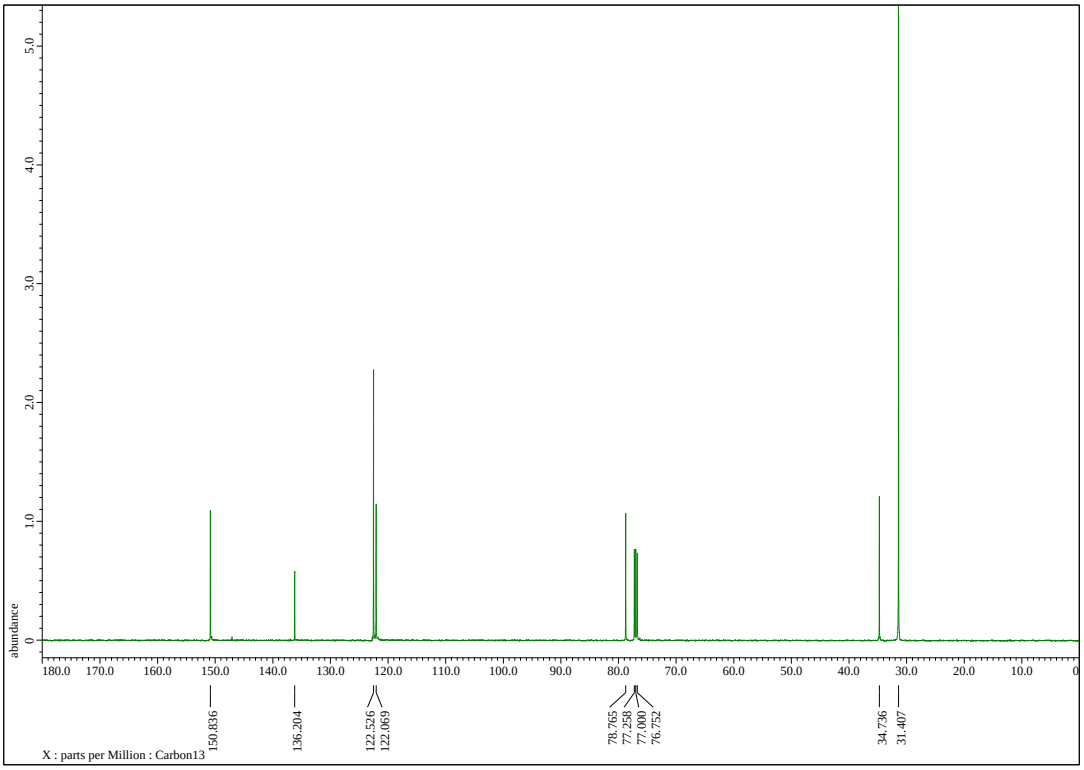

Figure S31b. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the *O*-benzylhydroxylamine **6**.

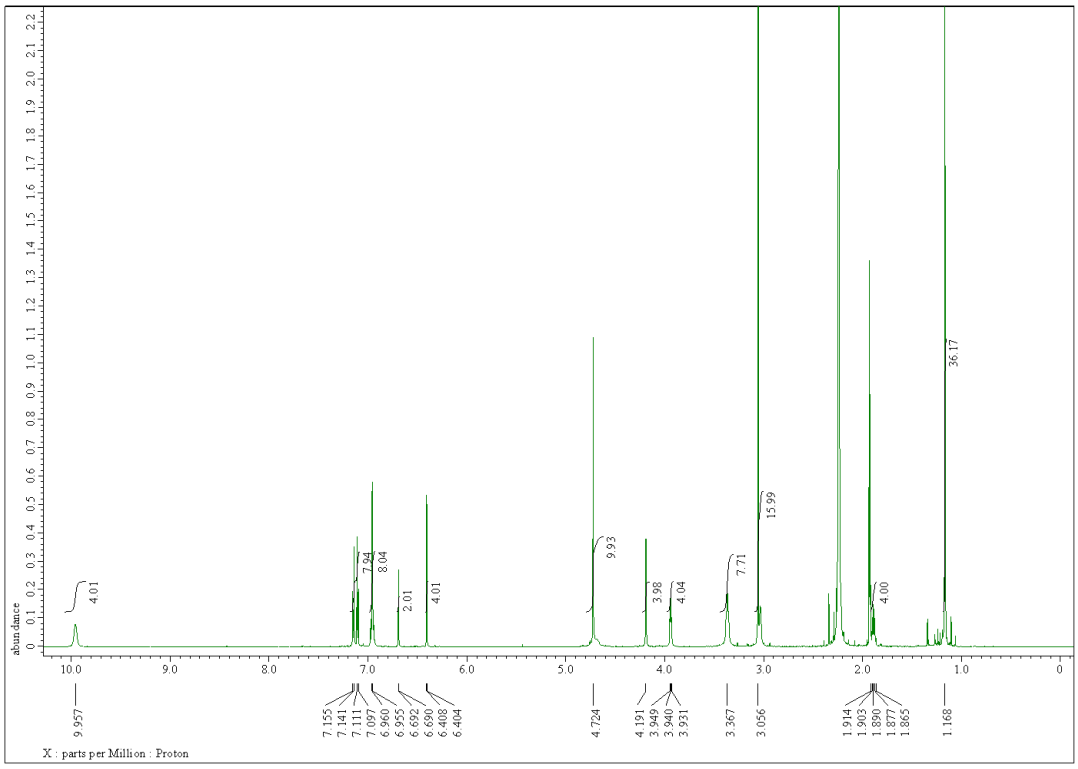

Figure S32a. ^{1}H NMR spectrum (600 MHz, CD_3CN) of the [2]rotaxane **7a**.

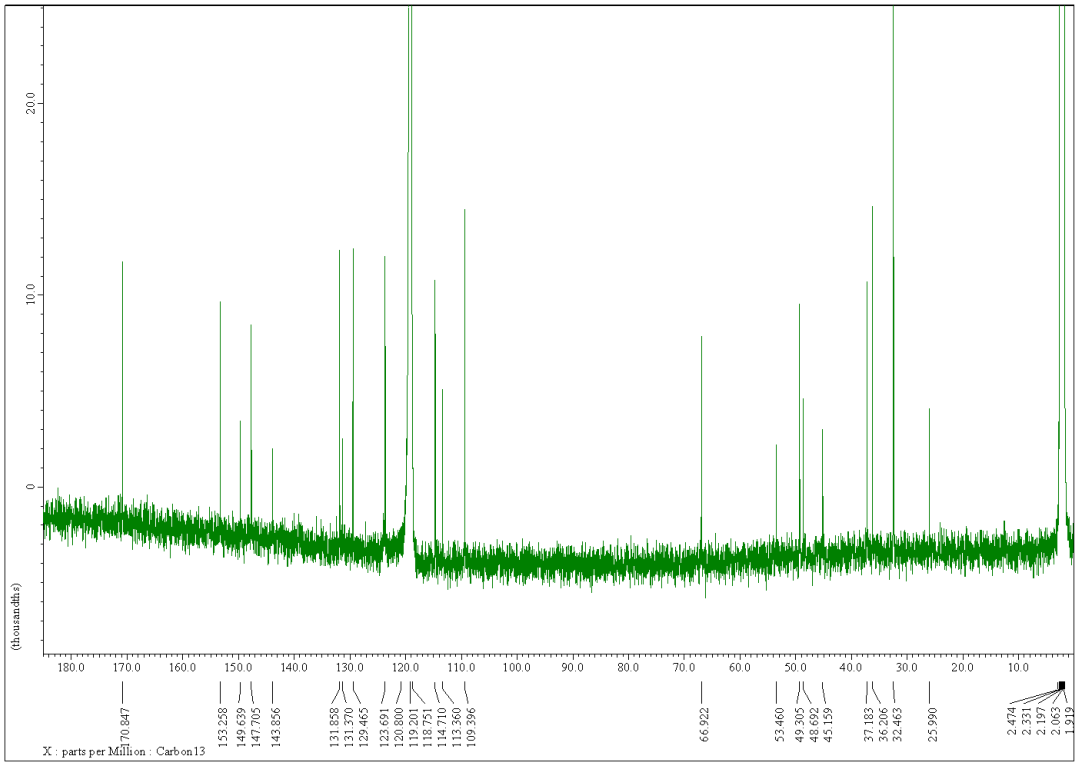

Figure S32b. ^{13}C NMR spectrum (150 MHz, CD_3CN) of the [2]rotaxane **7a**.

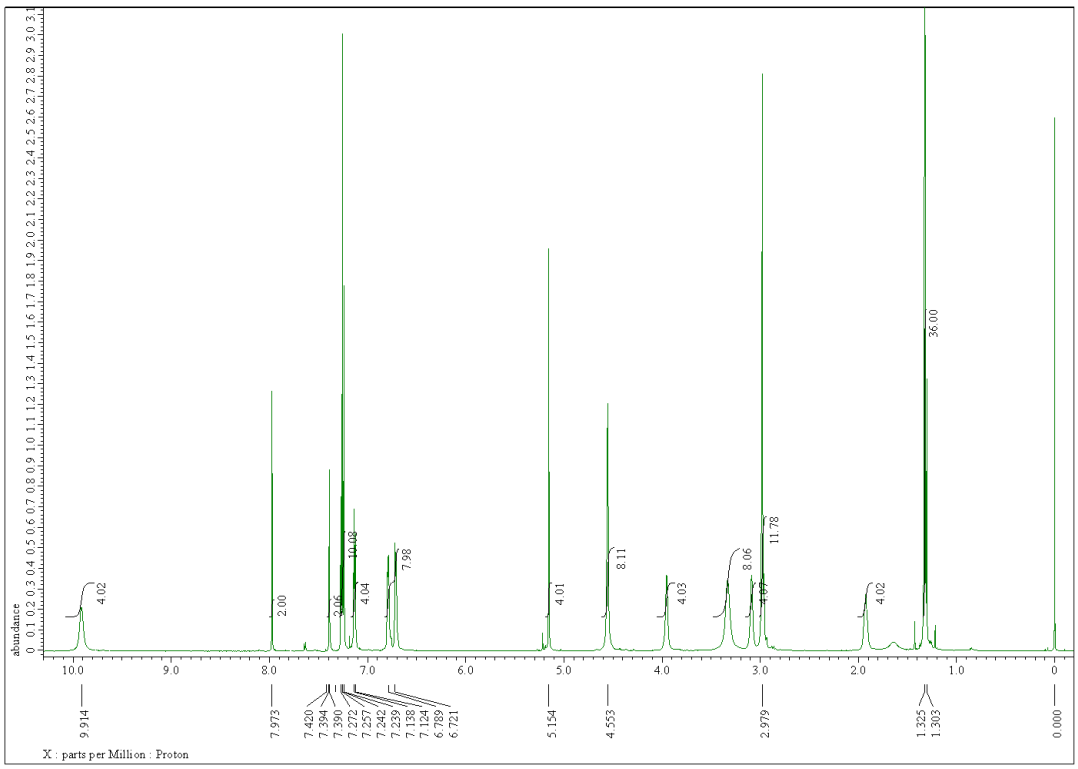

Figure S33a. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of the [2]rotaxane **7b**.

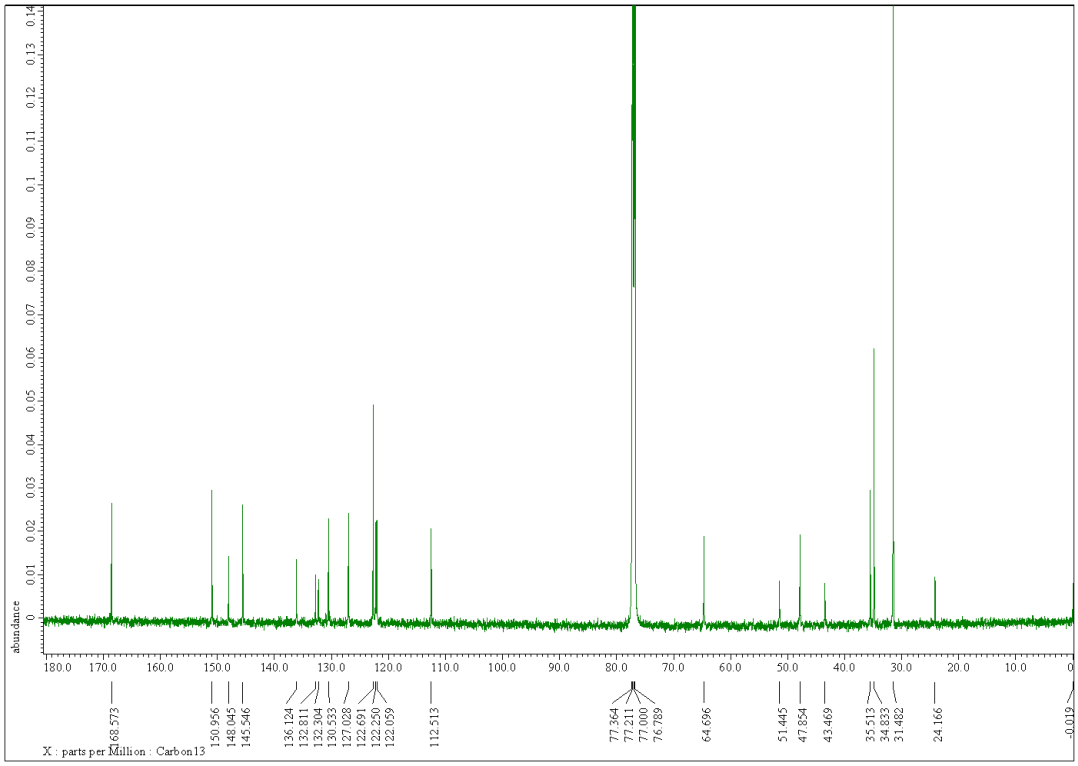

Figure S33b. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of the [2]rotaxane **7b**.

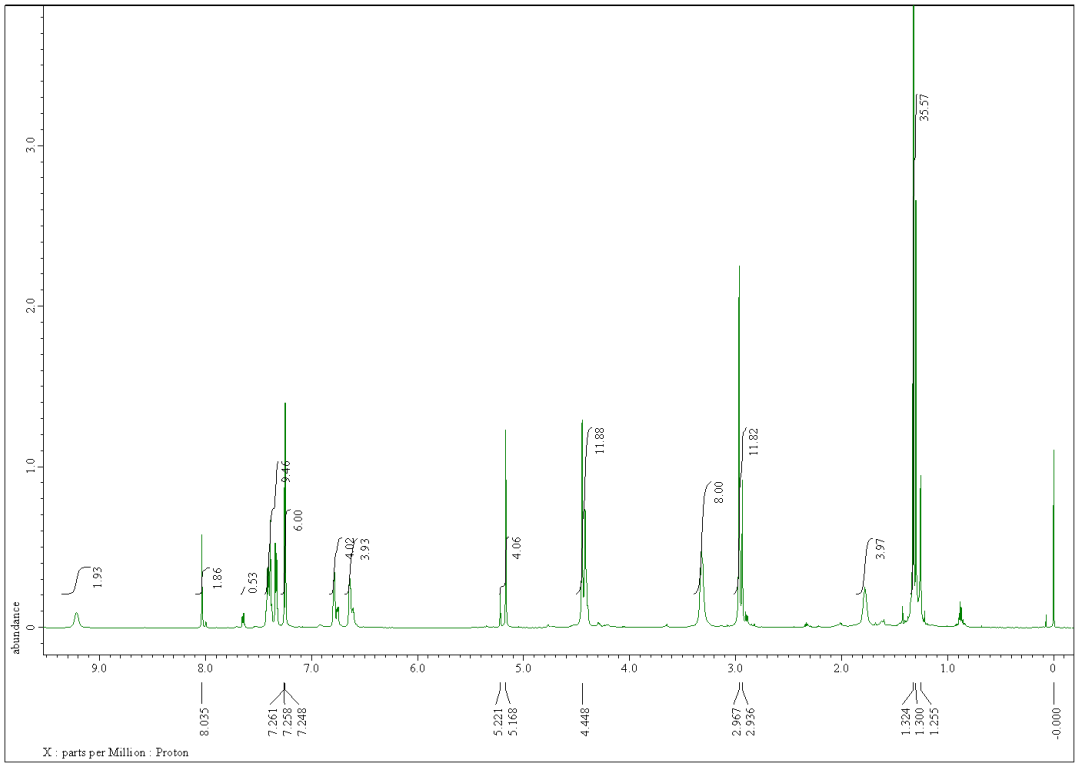

Figure S34a. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of the [2]rotaxane **7c**.

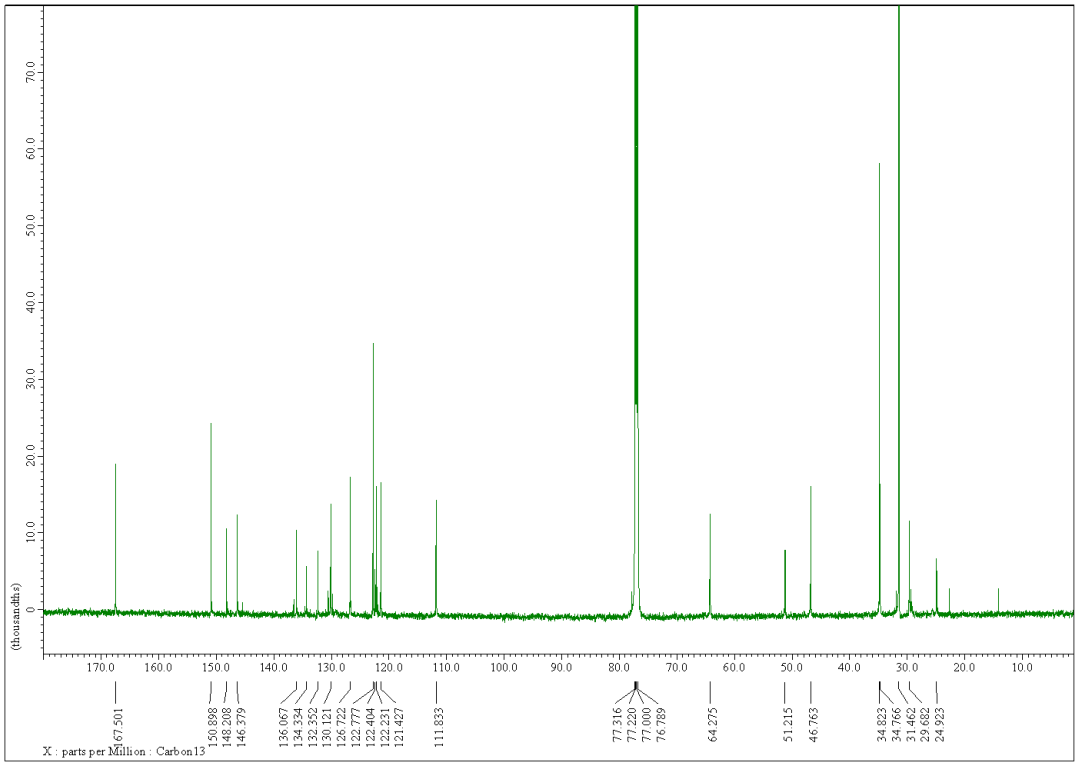

Figure S34b. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of the [2]rotaxane **7c**.

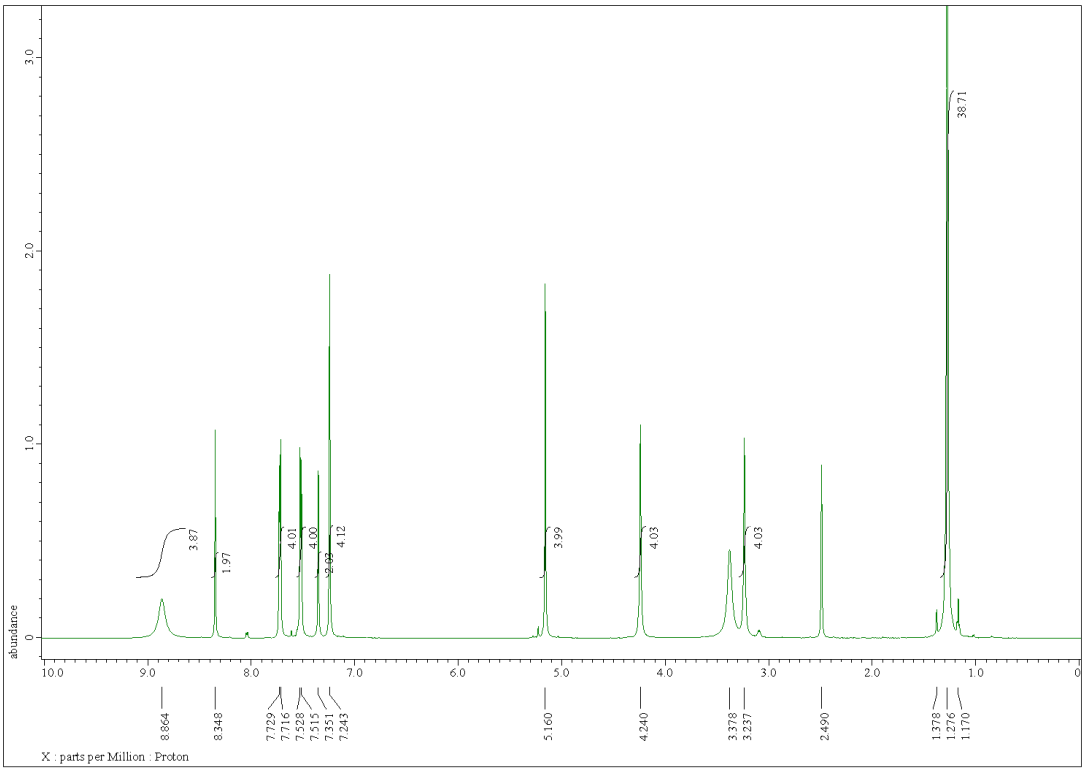

Figure S35a. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of the axle molecule **8a**.

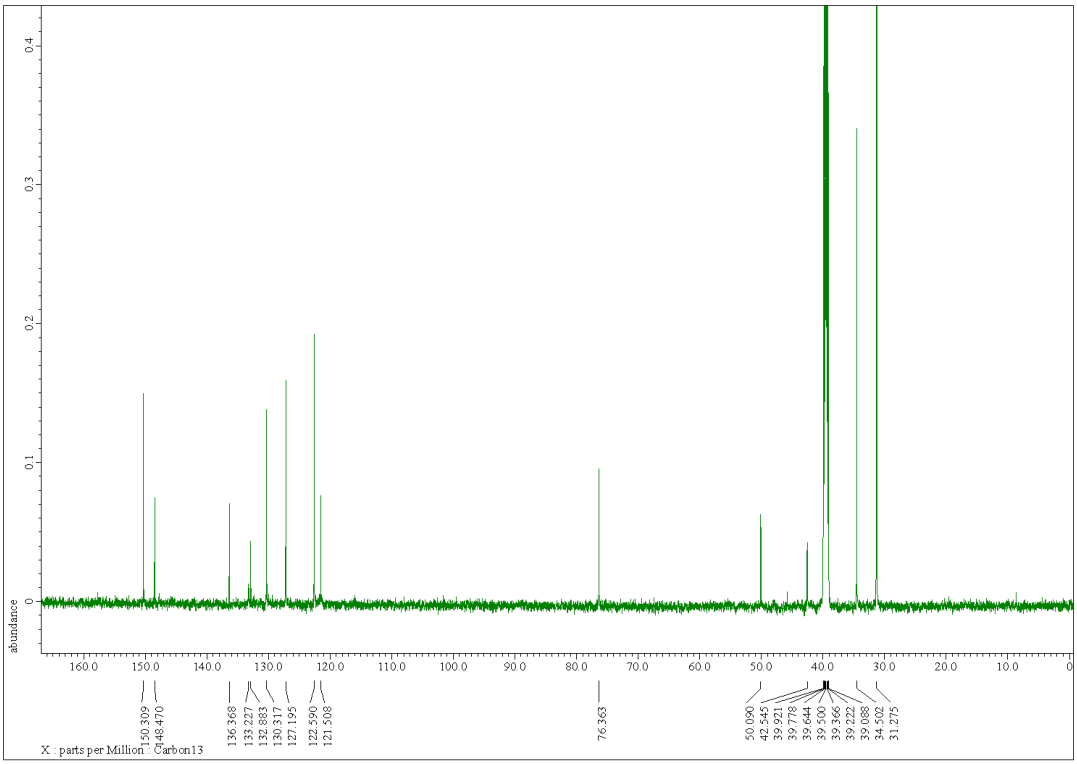

Figure S35b. ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of the axle molecule **8a**.

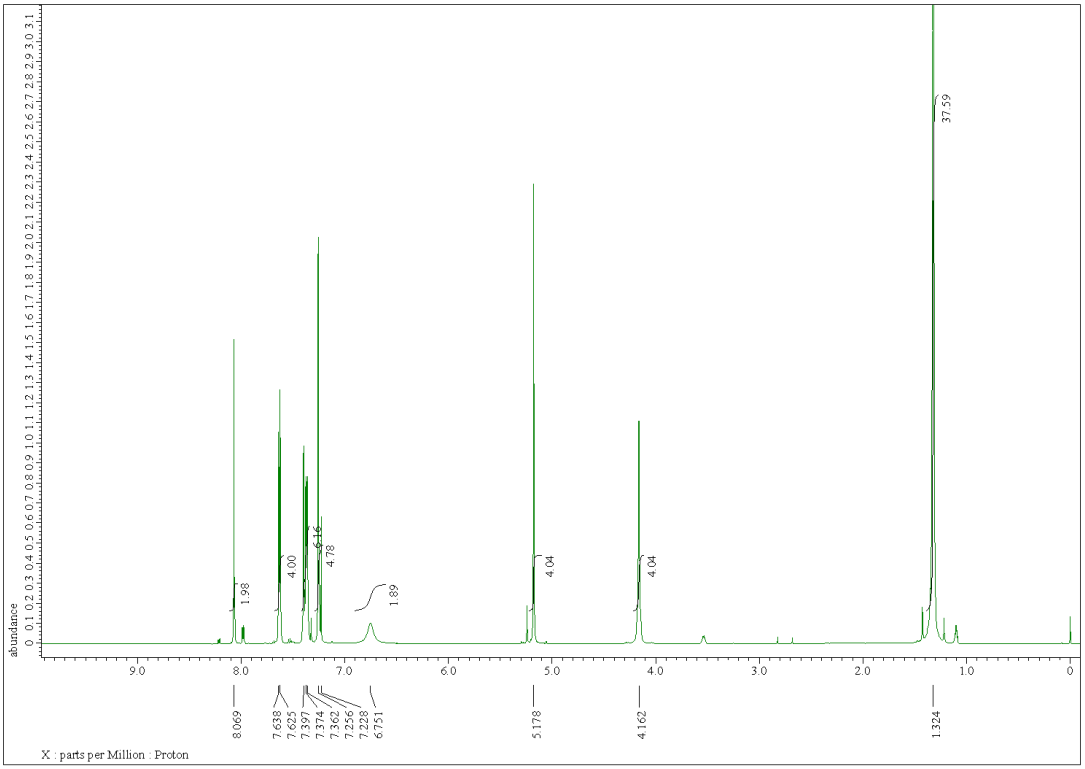

Figure S36a. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of the axle molecule **8b**.

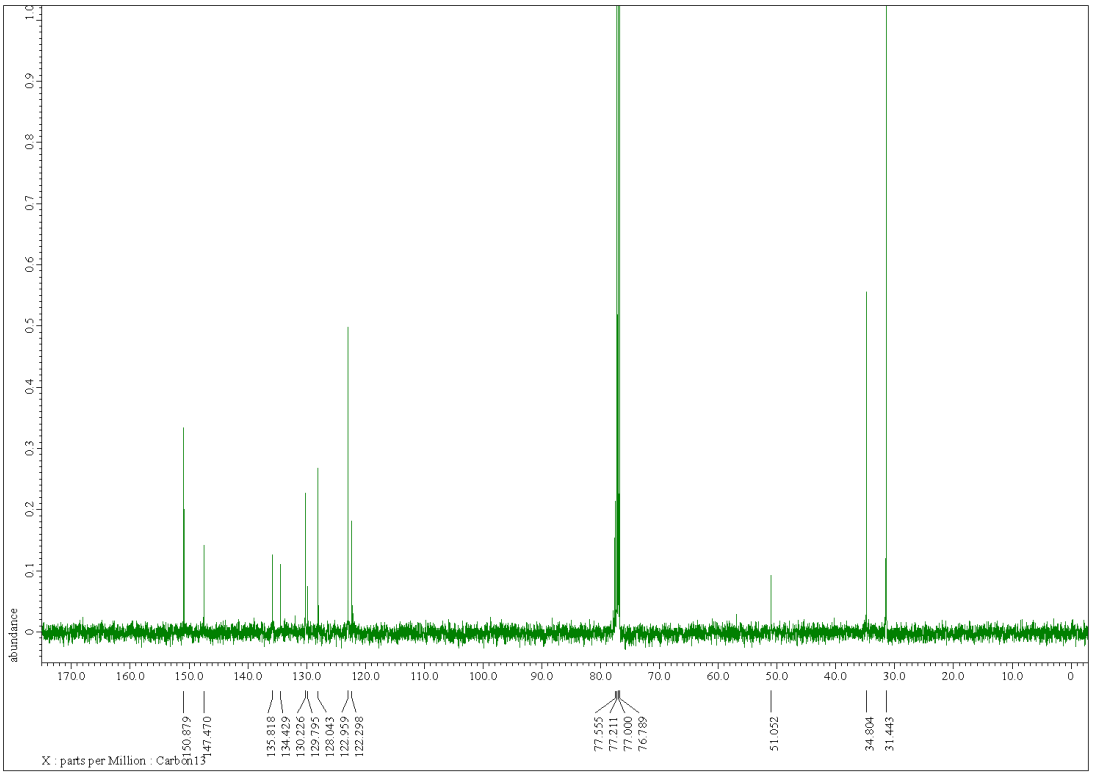

Figure S36b. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of the axle molecule **8b**.