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1. General information

**NMR Spectroscopy.** 1H NMR spectra were recorded on a high-field spectrometer (1H 600.15 MHz and 500 MHz, 13C 150 MHz and 125.75 MHz), equipped with a broadband inverse gradient probehead. Spectra were referenced to the residual solvent signal (chloroform-d, 7.24 ppm or acetone-d6 2.05 ppm). Two dimensional NMR spectra were recorded with 2048 data points in the t2 domain and up to 1024 points in the t1 domain, with a 1s recovery delay.

**Mass Spectrometry.** High resolution and Accurate Mass spectra were recorded on a Bruker apex ultra Apex-Qe 7T instrument (Bruker) spectrometer using the electrospray technique. The acetonitrile, dichloromethane or methanol were used as solvents for recording the mass spectra. The potential between the spray needle and the orifice was set to 4.5 kV.

**LC-MS analysis.** The LC-MS analysis was performed on Shimadzu LC IT-TOF. Separation was carried out on an RP-Zorbax (50x2.1 mm, 3.5 μm) column with a gradient elution of 0-80% B in A (A = 0.1% HCOOH in water; B = 0.1% HCOOH in MeCN) at room temperature over a period of 20 min (flow rate: 0.1 mL/min).

**UV-Vis Spectroscopy.** Electronic spectra were recorded on a Varian Carry-50 Bio spectrophotometer.

**Fluorescence.** Steady state fluorescence spectra were recorded with a JASCO FP-8600 Spectrofluorometer apparatus.

**X-ray Analysis.** X-Ray quality crystals were prepared by precipitation from DCM/MeOH (3), CDCl3 (4a, 6) and (CD3)2CO (5-Ac, 4-Ac, 8). Diffraction data were collected on a Rigaku Oxford Diffraction XtalLAB Synergy-R D diffractometer equipped with a HyPix ARC 150° Hybrid Photon Counting (HPC) detector using CuKα (λ = 1.54184 Å) for 4-Ac, 5-Ac and 8 at 80, 100 and 100 K, respectively. Diffraction data for 3 were collected on a Kuma KM4 diffractometer equipped with Sapphire CCD detector at 100 K using MoKα (λ = 0.71073 Å). Diffraction data for 4a and 6 were collected on a Xcalibur Gemini Ultra diffractometer equipped with Ruby CCD detector at 100 K using CuKα (λ = 1.54184 Å). Data were processed using the CrystAlisPro software. The structures were solved by intrinsic phasing with SHELXT (2015 release) and refined by full-matrix least-squares methods based F² using SHELXL. For all structures, H atoms bound to C atoms were placed in the geometrically idealized positions and treated in riding mode, with C-H = 0.95Å and Uiso(H) = 1.2Ueq(C) for C-H groups, and C-H = 0.98Å and Uiso(H) = 1.5Ueq(C) for CH₃ groups, while the O- and N-bound H atoms were refined freely.

The diffraction data for crystal of 5-Ac was insufficient for publication therefore only a model of structure is presented.

**Theoretical calculations.** Geometry optimization for 6 was carried out with the Gaussian 09¹ software package within unconstrained C1 symmetry, with starting coordinates derived from X-ray analysis. Becke’s three-parameter exchange functional with the gradient-corrected correlation formula of Lee, Yang and Parr (DFT-B3LYP)² were used with the 6-31G(d,p) basis set. The polarizable continuum model of solvation was used (PCM, standard dichloromethane/chloroform/acetone parametrization) for all optimizations. Harmonic vibrational frequencies were calculated using analytical second derivatives as a verification of local minimum achievement with no negative frequencies observed. Wiberg indices were calculated with application of NBO analysis implemented into Gaussian package.

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¹ Gaussian 09, Revision E.01; M. J. Frisch et al., Gaussian, Inc.: Wallingford CT, 2009.
² a) C. T. Lee, W. T. Yang, R. G. Parr, Phys. Rev. B, 1988, 37, 785-789. b) A. D. Becke, Phys. Rev. A, 1988, 38, 3098-3100.

**Supporting Information**
2. Experimental section

All solvents (MeOH, Ethyl Acetate, CHCl₃, n-hexane, toluene, acetone, water) if not indicated differently were used without purification. CH₂Cl₂ was distilled over CaH₂. Chloroform-d was prepared directly before using by passing through a basic alumina column. All reactions were performed under inert atmosphere.

2.1 Experimental procedures

Scheme S1. Synthetic approach. Conditions: **a)** I: 1 (1 eq.), 2 (1eq.), Pd(PPh₃)₄ (0.1 eq.), K₂CO₃ (3 eq.), KF (4 eq.), Toluene/DMF, 110 °C, 72 h; **b)** BBr₃ (10eq.), EtN₃ (13 eq.), Toluene, reflux, Ar, 2 h; **c)** BBr₃ (10eq.), Toluene, reflux, Ar, 2 h; **d)** MeOH (or CD₃OD), 4 days; **e)** Zn(Hg), CDCl₃, Ar, 24 h (incubation 12h, 60°C); **f)** Acetone, CF₃COOH (0.1 %); **g)** BBr₃ (10 eq.), o-dichlorobenzene, reflux, Ar, 2 h; **h)** O₂, 24 h.
Compound 1 was prepared according to previously described procedure.\(^3\)

**Compound 2**\(^4\). In a two-necked round bottom flask 5 g (21 mmol) of 2,6-dibromopyridine was dissolved in 150 mL of THF. The mixture was degassed by pump-thaw method and then the resulting solution cooled to -78°C. A solution of nBuLi in hexanes (23 mmol, 9.2 mL of a 2.5 M solution) was added dropwise to the cooled solution. After a period of 5 min, a solution of diethyl carbonate (9.5 mmol, 1.15 mL in 20 mL THF) was slowly added to the solution of the lithiate. After stirring for 2 h at -78°C, the reaction was allowed to warm to ca. 0°C and quenched by adding 10% solution of HCl to reach slightly acidic pH. The resulting mixture was basified with 10% aqueous K₂CO₃, and the crude product partitioned between CHCl₃ and water. The aqueous layer was washed twice with CHCl₃, and the organic layers combined and dried with anhydrous MgSO₄. The resulting brown solution was decolorized with activated carbon, and the solvent removed under reduced pressure. The crude products were purified on Flash chromatography using hexane/DMC (2:8, v:v) eventually giving compound 2 as white needles in 45% yield. Mp. 155-156°C (lit. 155-156.5°C).\(^1\) \(^1\)H NMR (500 MHz, 300K, CDCl₃) δ = 8.09 (dd, \(\delta J = 8.0\) Hz, \(\delta J = 0.8\) Hz, 2H), 7.76 (pseudo t, \(\delta = 8.0\) Hz, 2H), 7.70 (dd, \(\delta J = 8.0\), \(\delta J = 0.8\), 2H), \(^{13}\)C NMR (150 MHz, 300K, CDCl₃) δ = 189.2, 154.1, 141.6, 139, 131.5, 124.3, 120.5, 119.6, 118.2, 25.3 ppm. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₃H₆Br₂N₂O₃Na 364.8719; Found 364.8702.

**Compound 3.** In 100 mL two-necked round bottom flask, was charged with 1 (0.16 g, 0.3 mmol), tetrakis(triphenylphosphine)palladium(0) (0.034 g, 0.3 mmol, 0.1 eq.), potassium fluoride (0.068 g, 1.18 mmol, 4 eq.), potassium carbonate (0.12 g, 0.88 mmol, 3 eq.) and 2 (0.1 g, 0.3 mmol, 1 eq.). The mixture was dried under vacuum overnight. Then 20 mL of dry toluene and 20 mL of dry DMF were added via syringe. The mixture was then degassed by pump-thaw method (or bubble the solution with Ar) and stirred in 110°C on heating mantle for 96 h under Ar. After cooling to room temperature, the solution was diluted with ethyl acetate and passed through pad silica gel. The solution of the lithiate in 150 mL of THF was slowly added to the cooled solution. After that time 1.15 mL in 20 mL THF was slowly added to the solution of the lithiate. After stirring for 2 h at -78°C, the reaction was allowed to warm to ca. 0°C and quenched by adding 10% solution of HCl to reach slightly acidic pH. The resulting mixture was basified with 10% aqueous K₂CO₃, and the crude product partitioned between CHCl₃ and water. The aqueous layer was washed twice with CHCl₃, and the organic layers combined and dried with anhydrous MgSO₄. The resulting brown solution was decolorized with activated carbon, and the solvent removed under reduced pressure. The crude products were purified on Flash chromatography using hexane/DMC (2:8, v:v) eventually giving compound 2 as white needles in 45% yield. Mp. 155-156°C (lit. 155-156.5°C).\(^1\) \(^1\)H NMR (500 MHz, 300K, CDCl₃) δ = 8.09 (dd, \(\delta J = 8.0\) Hz, \(\delta J = 0.8\) Hz, 2H), 7.76 (pseudo t, \(\delta = 8.0\) Hz, 2H), 7.70 (dd, \(\delta J = 8.0\), \(\delta J = 0.8\), 2H), \(^{13}\)C NMR (150 MHz, 300K, CDCl₃) δ = 189.2, 154.1, 141.6, 139, 131.5, 124.3, 120.5, 119.6, 118.2, 25.3 ppm. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₃H₆Br₂N₂O₃Na 364.8719; Found 364.8702.

**Procedures for boron insertion:**

**Procedure 1 (see Fig. S79):** 15 mL of solution of 3 in toluene (10 mg, 0.022 mmol, 1 eq.) was placed in a 25 mL two-necked round-bottom flask and argon was bubbled through the solution for 15 min. Next, the mixture was refluxed for 15 min using heating mantle and then BB₃ was added (21 µl, 0.21 mmol, 10 eq.) and refluxed for 15 min with the same source of heating. After that time Et₃N (30 µl, 0.21 mmol, 10 eq.) was added and the reflux condition was continued for 2 h using heating mantle. After completion, the brown solid was separated, extracted with chloroform, washed with water, dried over Na₂SO₄ and evaporated. The crude product was purified by a preparative reversed-phase HPLC on a Vydac C18 column (22 mm × 250 mm), using solvent systems: S1: 0.1% aqueous TFA, S2: acetonitrile + 0.1% TFA, linear gradient was individually set for compound, flow rate 7.0 mL/min, UV detection at 280 nm. The fractions of compounds 4a and 5 and were collected and evaporated.

**Procedure 2 (see Fig. S80):** 15 mL of solution of 3 in toluene (10 mg, 0.022 mmol, 1 eq.) was placed in a 25 mL two-necked round-bottom flask and argon was bubbled through the solution for 15 min. Next, the mixture was refluxed using heating mantle for 15 min and then BB₃ was added (21 µl, 0.21 mmol, 10 eq.) and refluxed using heating mantle for 2 h. After completion, the brown solid was separated,

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\(^3\) Arnold, L et. al. Chem. Commun. 2011, 47, 970-972; (b) Maeda, Ch.; et al. Angew. Chem. Int. Ed. 2011, 50, 5691-5694.

\(^4\) Tetrahedron, 2001, 57, 1175-1182

\(^5\) J. Am. Chem. Soc., 1996, 118, 5783-5790.
extracted with chloroform, washed with water, dried over Na₂SO₄ and evaporated. The crude product was purified by a preparative reversed-phase HPLC on a Vydac C18 column (22 mm × 250 mm), using solvent systems: S1: 0.1% aqueous TFA, S2: acetonitrile + 0.1% TFA, linear gradient was individually set for compound, flow rate 7.0 mL/min, UV detection at 280 nm. The fractions of compounds 4a, 6 and 8 were collected and evaporated.

**Procedure 2a (see Fig. S95):** 15 mL of solution of 3 in toluene (10 mg, 0.022 mmol, 1 eq.) was placed in a 25 mL two-necked round-bottom flask and argon was bubbled through the solution for 15 min. Next, the mixture was refluxed using heating mantle for 15 min and then BBr₃ was added (21 µL, 0.21 mmol, 10 eq.) and refluxed using heating mantle for 12 h. After completion, the brown solid was separated, extracted with chloroform, washed with water, dried over Na₂SO₄ and evaporated. The crude product was analyzed by LC-MS t on an RP-Zorbax (50×2.1 mm, 3.5 µm) column with a gradient elution of 0-80% B in A (A = 0.1% HCOOH in water; B = 0.1% HCOOH in MeCN) at room temperature over a period of 20 min (flow rate: 0.1 mL/min). LC-MS analysis revealed compounds 6 (62%), 4a (13%), 7 (18%) and 8 (7%). The composition of obtained compounds was calculated based on LC-MS spectrum.

**Procedure 3 (see Fig. S96-97):** 15 mL of solution of 3 in o-dichlorobenzene (10 mg, 0.022 mmol, 1 eq.) was placed in a 25 mL two-necked round-bottom flask and argon was bubbled through the solution for 15 min. Next, the mixture was refluxed using heating mantle for 15 min and then BBr₃ was added (21 µL, 0.21 mmol, 10 eq.) and refluxed using heating mantle for 2 h. After completion, the brown solid was separated, extracted with chloroform, washed with water, dried over Na₂SO₄ and evaporated. The crude product (monomer monoisotopic mass 472.253) was purified by a preparative reversed-phase HPLC on a Vydac C18 column (22 mm × 250 mm), using solvent systems: S1: 0.1% aqueous TFA, S2: acetonitrile + 0.1% TFA, linear gradient was individually set for compound, flow rate 7.0 mL/min, UV detection at 280 nm. The fraction of unstable product 7 was collected and evaporated. Then the product 7 was analyzed by LC-MS t on an RP-Zorbax (50×2.1 mm, 3.5 µm) column with a gradient elution of 0-80% B in A (A = 0.1% HCOOH in water; B = 0.1% HCOOH in MeCN) at room temperature over a period of 20 min (flow rate: 0.1 mL/min). LC-MS analysis revealed compounds 4a (41%) and 8 (59%).

![Scheme S2. Potential mechanism for C=O reduction observed for 3 and activated by BBr₃.](image)

**General procedure of reduction:** 2 mg of compound 4a was dissolved in 500 µL of CDCl₃ in a glove-box conditions. To this solution 50 eq. (w/w) of zinc amalgam was added and the reaction was controlled by LC-MS analysis and NMR spectroscopy.

**Compound 4a. Procedure 1.** Yield of isolated product: 28% (2.9 mg). **1H NMR** (600 MHz, 300K, (CD₃)₂CO) δ = 9.53 (dd, 3J = 8.5 Hz, 4J = 0.9 Hz, 2H), 8.97 - 8.93 (m, 2H), 8.88 (d, 4J = 1.2 Hz, 2H), 8.81 (dd, 3J = 1.2 Hz, 2H), 8.82 (dd, 3J = 7.64 Hz, 4J = 0.9 Hz, 2H), 1.60 (s, 18H), **13C NMR** (150 MHz, 300K, (CD₃)₂CO) partial signals obtained by correlation experiments HMBC, HSQC, δ = 177.0, 148.6, 146.1, 143.7, 143.5, 138.3, 127.6, 126.3, 125.4, 125.1, 121.7, 112, 35.7, 31.6; **HRMS (ESI) m/z:** [M]+ Calcd for
Compounds 1-3 were synthesized by the reaction of the appropriate reagents in the presence of 

\[ \text{compound 1} \rightarrow \text{compound 2} \rightarrow \text{compound 3} \]

Diffuse reflectance FTIR spectroscopy (DRIFT) was used to analyze the organic compounds. The spectra showed characteristic absorptions for the functional groups present in each compound, confirming their identities.

**Structure of Compound 1**

[Structure image]

**Structure of Compound 2**

[Structure image]

**Structure of Compound 3**

[Structure image]

**NMR Data**

- **1H NMR**
- **13C NMR**
- **HRMS**

**UV-Vis Spectra**

- Maxima at 313, 342, 438 nm

**Mass Spectra**

- [M]+ calcd for C3H3O3 469.2329; Found 469.2329; UV-Vis: 313, 342, 438 nm

**Supporting Information**

- For 0.5 mg of compound 6 dissolved in 0.5 ml of MeOH in a glove-box conditions, the product 4c was monitored using LC-MS equipment.

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6 For 0.5 mg of compound 6 dissolved in 0.5 ml of MeOH in a glove-box conditions, the product 4c was monitored using LC-MS equipment.
3. NMR spectra

3.1 NMR spectra of 2

Figure S1. $^1$H NMR spectrum of 2 (CDCl$_3$, 300K, 500 MHz)

Figure S2. $^1$H NMR spectrum (zoom, aromatic region) of 2 (CDCl$_3$, 300K, 500 MHz).
Figure S3. $^{13}$C NMR spectrum of 2 (CDCl$_3$, 300K, 150 MHz)

Figure S4. HSQC NMR spectrum of 2 (CDCl$_3$, 300K, 500 MHz)
Figure S5. HMBC NMR spectrum of 2 (CDCl$_3$, 300K, 500 MHz)
3.2 NMR spectra of 3

**Figure S6.** $^1$H NMR spectrum of 3 (CDCl$_3$, 300K, 500 MHz)

**Figure S7.** $^1$H NMR spectrum (zoom, aromatic region) of 3 (CDCl$_3$, 300K, 500 MHz).
Figure S8. $^{13}$C NMR spectrum of 3 (CDCl$_3$, 300K, 150 MHz).

Figure S9. HSQC NMR spectrum of 3 (CDCl$_3$, 300K, 500 MHz).

Supporting Information
Reductive Dimerization of Macrocycles Activated by BBr₃
Monika Kijewska, Miłosz Siczek, Miłosz Pawlicki*

Supporting Information

Figure S10. HSQC NMR spectrum (zoom, aromatic region) of 3 (CDCl₃, 300K, 500 MHz).

Figure S11. HMBC NMR spectrum of 3 (CDCl₃, 300K, 500 MHz).
Figure S12. HMBC NMR spectrum (zoom, aromatic region) of 3 (CDCl₃, 300K, 500 MHz).

Figure S13. NOESY NMR spectrum of 3 (CDCl₃, 300K, 500 MHz).
Figure S14. NOESY NMR spectrum (zoom, aromatic region) of 3 (CDCl₃, 300K, 500 MHz).
3.3 NMR spectra of 4a

Figure S15. $^1$H NMR spectrum of 4a ((CD$_3$)CO, 300K, 500 MHz)

Figure S16. $^1$H NMR spectrum (zoom, aromatic region) of 4a ((CD$_3$)CO, 300K, 500 MHz).
Figure S17. $^{13}$C NMR spectrum of 4a ((CD$_3$)CO, 300K, 150 MHz).

Figure S18. COSY spectrum of 4a ((CD$_3$)CO, 300K, 500 MHz).
Figure S19. COSY spectrum (zoom, aromatic region) of 4a ([CD$_3$]CO, 300K, 500 MHz).

Figure S20. HMBC spectrum of 4a ([CD$_3$]CO, 300K, 500 MHz).
Figure S21. HMBC spectrum (zoom, aromatic region) of 4a ((CD$_3$)CO, 300K, 500 MHz).

Figure S22. HMBC spectrum (zoom, aromatic region) of 4a ((CD$_3$)CO, 300K, 500 MHz).
Figure S23. HSQC spectrum (zoom, aromatic region) of 4a ((CD$_3$)$_2$CO, 300K, 500 MHz).

Figure S24. NOESY spectrum of 4a ((CD$_3$)$_2$CO, 300K, 500 MHz).
Figure S25. NOESY spectrum (zoom, aromatic region) of 4a ([CD$_3$]CO, 300K, 500 MHz).
3.4 NMR spectra of 4b

Figure S26. $^1$H NMR spectrum of 4b (CD$_3$OD, 300K, 500 MHz).

Figure S27. $^1$H NMR spectrum (zoom, aromatic region) of 4b (CD$_3$OD, 300K, 600 MHz).
Figure S28. $^{13}$C spectrum of 4b (CD$_3$OD, 300K, 150 MHz).

Figure S29. HSQC spectrum of 4b (CD$_3$OD, 300K, 600 MHz).
Figure S30. HSQC spectrum (zoom, aromatic region) of 4b (CD$_3$OD, 300K, 600 MHz).

Figure S31. HMBC spectrum of 4b (CD$_3$OD, 300K, 600 MHz).
Figure S32. HMBC spectrum (zoom, aromatic region) of 4b (CD$_3$OD, 300K, 600 MHz).

Figure S33. NOESY spectrum of 4b (CD$_3$OD, 300K, 600 MHz).
Figure S34. NOESY spectrum (zoom, aromatic region) of 4b (CD$_3$OD, 300K, 600 MHz).
3.5 NMR spectra of 4-Ac

Figure S35. Comparison of $^1$H NMR spectra of 4a (panel A) and 4-Ac (panel B) ((CD$_3$)$_2$CO, 300K, 500 MHz).
**Figure S36.** $^1$H NMR spectrum of 4-Ac ((CD$_3$)CO, 300K, 500 MHz).

**Figure S37.** $^1$H NMR spectrum (zoom, aromatic region) of 4-Ac ((CD$_3$)CO, 300K, 500 MHz).
3.6 NMR spectra of 5 and 5-Ac

Figure S38. $^1$H spectrum of 5 ((CD$_3$)$_2$CO, 300K, 600 MHz).

Figure S39. $^1$H spectrum of 5 (zoom, aromatic region) ((CD$_3$)$_2$CO, 300K, 600 MHz).
Figure S40. Stability of compound 5 (zoom, aromatic region) ((CD$_3$)$_2$CO, 300K, 600 MHz).

Figure S41. Stability of compound 5 (zoom, aliphatic region) ((CD$_3$)$_2$CO, 300K, 600 MHz).
Figure S42. $^1$H spectrum of 5-Ac ((CD$_3$)$_2$CO, 300K, 600 MHz).

Figure S43. $^1$H spectrum (zoom, aromatic region) of 5-Ac ((CD$_3$)$_2$CO, 300K, 600 MHz).
Figure S44. $\text{C}^{13}$ spectrum of 5-Ac ((CD$_3$)$_2$CO, 300K, 150 MHz).

Figure S45. HMBC spectrum of 5-Ac ((CD$_3$)$_2$CO, 300K, 600 MHz).
Reductive Dimerization of Macrocycles Activated by BBr$_3$
Monika Kijewska, Miłosz Siczek, Miłosz Pawlicki*

Figure S46. HMBC spectrum (zoom, aromatic region) of 5-Ac ((CD$_3$)$_2$CO, 300K, 600 MHz).

Figure S47. NOESY spectrum of 5-Ac ((CD$_3$)$_2$CO, 300K, 600 MHz).
Figure S48. NOESY spectrum (zoom, aromatic region) of 5-Ac (CD$_3$OD, 300K, 600 MHz).
3.7 NMR spectra of 6

**Figure S49.** $^1$H NMR spectrum of 6 ((CD$_3$)CO, 300K, 500 MHz)

**Figure S50.** $^1$H NMR spectrum (zoom, aromatic region) of 6 ((CD$_3$)CO, 300K, 500 MHz).
Reductive Dimerization of Macrocycles Activated by BBr$_3$
Monika Kijewska, Miłosz Siczek, Miłosz Pawlicki*

Figure S51. $^{13}$C NMR spectrum of 6 ((CD$_3$)$_2$CO, 300K, 150 MHz)

Figure S52. DEPT135 NMR spectrum of 6 ((CD$_3$)$_2$CO, 300K, 150 MHz)

Supporting Information
Figure S53. COSY NMR spectrum of 6 ((CD₃)CO, 300K, 500 MHz).

Figure S54. COSY NMR spectrum (zoom, aromatic region) of 6 ((CD₃)CO, 300K, 500 MHz).
Figure S55. HMBC NMR spectrum of 6 ((CD$_3$)CO, 300K, 500 MHz).

Figure S56. HMBC NMR spectrum (zoom, aromatic region) of 6 ((CD$_3$)CO, 300K, 500 MHz).
Figure S57. NOESY NMR spectrum of 6 ((CD3)CO, 300K, 500 MHz).

Figure S58. NOESY NMR spectrum (zoom, aromatic region) of 6 ((CD3)CO, 300K, 500 MHz).
3.8 NMR spectra of 8

Figure S59. $^1$H NMR spectrum of 8 ((CD$_3$)$_2$CO, 300K, 500 MHz).

Figure S60. $^1$H NMR spectrum (zoom, aromatic region) of 8 ((CD$_3$)$_2$CO, 300K, 500 MHz).
3.9 NMR spectra of incubation of 6 in MeOD

Figure S61. $^1$H NMR spectra of 6 incubated in CD$_3$OD (A - start; B - 12 h; C - 24 h; D - 10 days; E - 19 days; F – 25 days; G – 36 days) (A - D – inert atmosphere, after 14 days the sample was exposed on air).
Figure S62. $^1$H NMR spectra (zoom, aromatic region) of 6 incubated in CD$_3$OD (A - start; B - 12 h; C - 24 h; D - 10 days; E - 19 days; F - 25 days; G - 36 days) (A - D – inert atmosphere, after 14 days the sample was exposed on air).
4. LC-MS and MS spectra

4.1 ESI-MS spectrum of 2

Figure S63. ESI-MS spectrum of 2 performed in 10 mM of NaCl in methanol (M*, M** - ions formed in the ion source).

Figure S64. ESI-MS spectrum of 2 (zoom) with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).
4.2 ESI-MS spectrum of 3

![ESI-MS spectrum of 3](image1)

**Figure S65.** ESI-MS spectrum of 3.

![ESI-MS spectrum of 3 (zoom) with simulated spectrum](image2)

**Figure S66.** ESI-MS spectrum of 3 (zoom) with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).
4.3 ESI-MS spectrum of 4a

Figure S67. ESI-MS spectrum of 4a.

Figure S68. ESI-MS spectrum of 4a (zoom) with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).
4.4 ESI-MS spectra of 4b

Figure S69. ESI-MS spectrum of 4b.

Figure S70. ESI-MS spectrum of 4b (zoom) with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).
4.5 ESI-MS spectra of 4c

**Figure S71.** ESI-MS spectrum of 4c

**Figure S72.** ESI-MS spectrum of 4c (zoom) with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).
4.6 ESI-MS spectrum of 4-Ac

Figure S73. ESI-MS spectrum of 4-Ac (zoom) with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).

4.7 ESI-MS spectrum of 5

Figure S74. ESI-MS spectrum of 5 (zoom) with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).

Supporting Information
4.8 ESI-MS spectrum of 5-Ac

![ESI-MS spectrum of 5-Ac](image)

Figure S75. ESI-MS spectrum of 5-Ac (zoom) with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).
4.9 ESI-MS spectrum of 6

**Figure S76.** ESI-MS spectrum of 6.

**Figure S77** ESI-MS spectrum of 6 (zoom) with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).
4.10 ESI-MS spectrum of 8

![ESI-MS spectrum of 8](image)

**Figure S78** ESI-MS spectrum of 8 (zoom) with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).
4.11 LC-MS of crude mixture (Procedure 1)

Figure S79 LC-MS analysis of crude mixture (MS value m/z = 469.223; m/z=477.225; m/z=486.229) (A); ESI-MS spectrum (B-D).
4.12 LC-MS of crude mixture (Procedure 2)

Figure S80 LC-MS analysis of crude mixture (MS value m/z=469.227; m/z=486.230; m/z=470.235) (A); ESI-MS spectrum (B-D).
4.13 LC-MS of 4a

![LC-MS Analysis of 4a](image)

**Figure S81** LC-MS analysis of 4a (MS value m/z = 486.234) (A); ESI-MS spectrum (B).

4.14 LC-MS of 4b

![LC-MS Analysis of 4b](image)

**Figure S82** LC-MS analysis of 4b (MS value m/z = 503.270) (A); ESI-MS spectrum (B).
4.15 LC-MS of 4c

Figure S83 LC-MS analysis of 4c (MS value m/z = 500.250) (A); ESI-MS spectrum (B).

4.16 LC-MS of 5

Figure S84 LC-MS analysis of 5 (MS value m/z = 477.227) (A); ESI-MS spectrum (B).
4.17 LC-MS of 6

Figure S85 LC-MS analysis of 6 (MS value m/z = 469.232) (A); ESI-MS spectrum (B).

4.18 LC-MS of 8

Figure S86 LC-MS analysis of 8 (MS value m/z = 477.238) (A); ESI-MS spectrum (B).
4.19 LC-MS of incubation of 6 in water-acetonitrile (v:v, 1:1) in 60°C for 12 h

**Figure S87** LC-MS analysis before (A) and after (B) incubation of 6 in water-acetonitrile (1:1, v:v) in 60°C for 12 h (MS value m/z = 469.233; m/z = 486.234); ESI-MS spectra (C,D).
4.20 LC-MS of incubation of 4a in water-acetonitrile (v:v, 1:1) in 60°C for 12h

**Figure S88** LC-MS analysis before (A) and after (B) incubation of 4a in water-acetonitrile (1:1, v:v) in 60°C for 12 h (MS value m/z = 486.234); ESI-MS spectrum (C).
4.21 LC-MS of incubation of 6 in CD$_3$OD in 60°C for 12 h

**Figure S89** LC-MS analysis before (A) and after (B) incubation of 6 in CD$_3$OD in 60°C for 12 h (MS value $m/z = 469.231$; $m/z = 503.269$); ESI-MS spectra (C,D).
4.22 LC-MS of incubation of 6 in MeOH in 60°C for 2 h

Figure S90 LC-MS analysis before (A) and after (B) incubation of 6 in MeOH in 60°C for 2 h (MS value m/z = 469.231; m/z = 500.248); ESI-MS spectra (C,D).
4.23 LC-MS of incubation of mixture of 4a and 6 in CD$_3$OD in 60°C for 2 h

**Figure S91** LC-MS analysis before (A) and after (B) incubation of mixture of 6 and 4a in CD$_3$OD in 60°C for 2 h (MS value $m/z = 486.234$; $m/z = 469.231$; $m/z = 503.269$); ESI-MS spectra (C-E).
4.24 LC-MS of incubation of pure 5 in acetone-d6

Figure S92 LC-MS analysis of incubation of pure 5 in acetone-d₆ for 4 days (MS value m/z = 508.759; m/z = 477.235) (A) and the same mixture diluted with water for 10 days (MS value m/z = 506.246; m/z = 477.235) (B); ESI-MS spectra (C, D);
4.25 LC-MS of products after reduction of 4a

Figure S93 LC-MS analysis of mixture after reduction of 4a using amalgamate (MS value $m/z = 486.235$; $m/z = 477.231$) (A); ESI-MS spectra (B,C).
4.26 LC-MS of products after incubation of 4a and 4b

Figure S94 LC-MS analysis of mixture after incubation of 4a and 4b in CDCl₃ in 60°C for 12 h (MS value m/z = 486.236; m/z = 503.270; m/z = 477.231) (A); ESI-MS spectra (B-D).
4.27 LC-MS of crude products (Procedure 2a)

**Figure S95** LC-MS analysis of crude mixture after the reaction with BBr₃ (MS value \( m/z = 486.236; m/z = 472.253; m/z = 469.230; m/z = 470.238 \)) (A); after 5 days (B); ESI-MS spectra (C-F).
4.28 LC-MS of products before and after purification (Procedure 3)

**Figure S96** LC-MS analysis of crude product (MS value $m/z = 472.2553$) (A); ESI-MS spectra (B).

**Figure S97** LC-MS analysis of products after purification (MS value $m/z = 486.231$, $m/z = 470.237$) (A); ESI-MS spectra (B,C).
5. UV-Vis spectra

Figure S98. UV-Vis spectrum of 3 (DCM, 298K)

Figure S99. UV-Vis spectra (MeCN, 298K)
Reductive Dimerization of Macrocycles Activated by BBr$_3$
Monika Kijewska, Miłosz Siczek, Miłosz Pawlicki*

**Figure S100.** Extinction spectra (MeCN, 298K)

**Figure S101.** UV-Vis spectra of 4a and 4b (MeCN, 298K)
Figure S102. UV-VIS spectra of 6 under UV radiation (MeCN, 298K)

6. Emission spectra

Figure S103. Emission spectra of 6 (blue), 4a (green), 8 (grey) (MeCN, 298 K)
Figure S104. Excitation spectra of 6 (blue; emission detection 510 nm), 4a (green; emission detection 506 nm) and 8 (grey; emission detection 511 nm) (MeCN, 298 K)
## 7. Crystal Data

| Identification code | 3 kijba | 4a mkij01a | 4a-Ac mkij8pa | 6 mkijdibra | 8 mkij5a |
|---------------------|---------|------------|---------------|-------------|---------|
| CCDC number         |         |            |               |             |         |
| Empirical formula   | C_{35}H_{35}N_{15}O_{12}[C_{35}H_{35}BN_{3}O_{2}Cl] | [C_{35}H_{35}N_{15}O_{12}][C_{1}F][C_{35}H_{35}BN_{3}O_{2}Cl] | [C_{35}H_{35}N_{15}O_{12}][C_{1}F][C_{35}H_{35}BN_{3}O_{2}Cl] | [C_{35}H_{35}N_{15}O_{12}][C_{1}F][C_{35}H_{35}BN_{3}O_{2}Cl] | [C_{35}H_{35}N_{15}O_{12}][C_{1}F][C_{35}H_{35}BN_{3}O_{2}Cl] |
| Formula weight      | 570.49  | 760.57     | 715.56        | 1814.77     | 1344.53 |
| Temperature/K       | 100     | 100        | 80            | 100         | 100     |
| Crystal system      | monoclinic | monoclinic | triclinic     | monoclinic  | triclinic |
| Space group         | P2_{1}/c | P2_{1}/c   | P-1           | C2/c        | P-1     |
| a/Å                 | 16.088(5) | 15.180(8)  | 15.015(3)     | 23.9735(6)  | 12.012(3) |
| b/Å                 | 15.757(4) | 14.412(8)  | 16.747(3)     | 13.8399(3)  | 13.164(2) |
| c/Å                 | 11.772(3) | 15.751(9)  | 16.884(3)     | 24.1518(9)  | 21.540(4) |
| α°                  | 109.16(3) | 102.04(4)  | 106.23(3)     | 104.620(3)  | 89.74(3) |
| β°                  | 91.96(2)  | 91.96(2)   | 91.96(2)      | 91.96(2)    | 86.42(3) |
| γ°                  | 102.34(3) | 102.34(3)  | 102.34(3)     | 102.34(3)   | 91.96(2) |
| Volume/Å³            | 2818.9(14) | 3370(3)   | 3548.7(15)    | 7753.9(4)   | 3315.8(12) |
| Temperature/K        | 100(2)   | 100(2)     | 80(2)         | 100(2)      | 100(2)  |
| Z                    | 4        | 4          | 4             | 4           | 2       |
| ρ_{calc}/g/cm³       | 1.344    | 1.499      | 1.339         | 1.555       | 1.347   |
| μ/mm⁻¹               | 0.30     | 5.68       | 0.84          | 7.42        | 0.83    |
| F(000)               | 1198     | 1560       | 1504          | 3656        | 1412    |
| Crystal size/mm²     | 0.45×0.31×0.1 | 0.07×0.06×0.03 | 0.36×0.22×0.05 | 0.16×0.03×0.02 | 0.10×0.05×0.01 |
| Radiation type       | MoKα(λ = 0.71073) | CuKα(λ = 1.54184) | CuKα(λ = 1.54184) | CuKα(λ = 1.54184) | CuKα(λ = 1.54184) |
| 2θ range for data collection/° | 2.9 to 27.5 | 4.2 to 68.0 | 3.0 to 75.8 | 3.7 to 68.0 | 2.1 to 67.5 |
| Index ranges         | −20 ≤ h ≤ 20 | −14 ≤ h ≤ 18 | −18 ≤ h ≤ 17 | −28 ≤ h ≤ 28 | −14 ≤ h ≤ 14 |
| Reflections collected | 22853 | 14997 | 68131 | 12449 | 55770 |
| Independent reflections | 6415 | 6014 | 14546 | 12449 | 11842 |
| R_{int}              | 0.0672   | 0.0851     | 0.0277        | 0.0504      | 0.0821  |
| Final R_{I} values  | 0.0676   | 0.0779     | 0.0444        | 0.0504      | 0.0821  |
| Final wR(F²) values | 0.1649   | 0.1683     | 0.1219        | 0.1045      | 0.2231  |
| Final R_{I} values  | 0.0965   | 0.1169     | 0.0491        | 0.0967      | 0.0956  |
| Final wR(F²) values | 0.1901   | 0.1889     | 0.1256        | 0.1155      | 0.2331  |
| Goodness of fit on F² | 1.038  | 1.062      | 1.071         | 0.818       | 1.067   |
| Largest diff. peak/hole /eÅ⁻³ | 0.37, −0.55 | 0.48, −0.49 | 0.56, −0.38 | 0.74, −0.65 | 0.87, −0.53 |
Figure S105. Crystal structure of 3. Thermal ellipsoids present 50% probability
Figure S106. Crystal structure of 4a. Thermal ellipsoids present 50% probability.
Figure S107. Crystal structure of 4a_Ac. Thermal ellipsoids present 50% probability.
Figure S108. Model of 5-Ac. Thermal ellipsoids present 50% probability.
Figure S109. Crystal structure of 6. Thermal ellipsoids present 50% probability
**Figure S110.** Crystal structure of 8. Thermal ellipsoids show 50% probability.