

A Bis(Acridino)-Crown Ether for Recognizing Oligoamines in Spermine Biosynthesis

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1. ^1H -NMR and ^{13}C -NMR spectra of the new compounds and the previously reported, but not characterized compound **17**

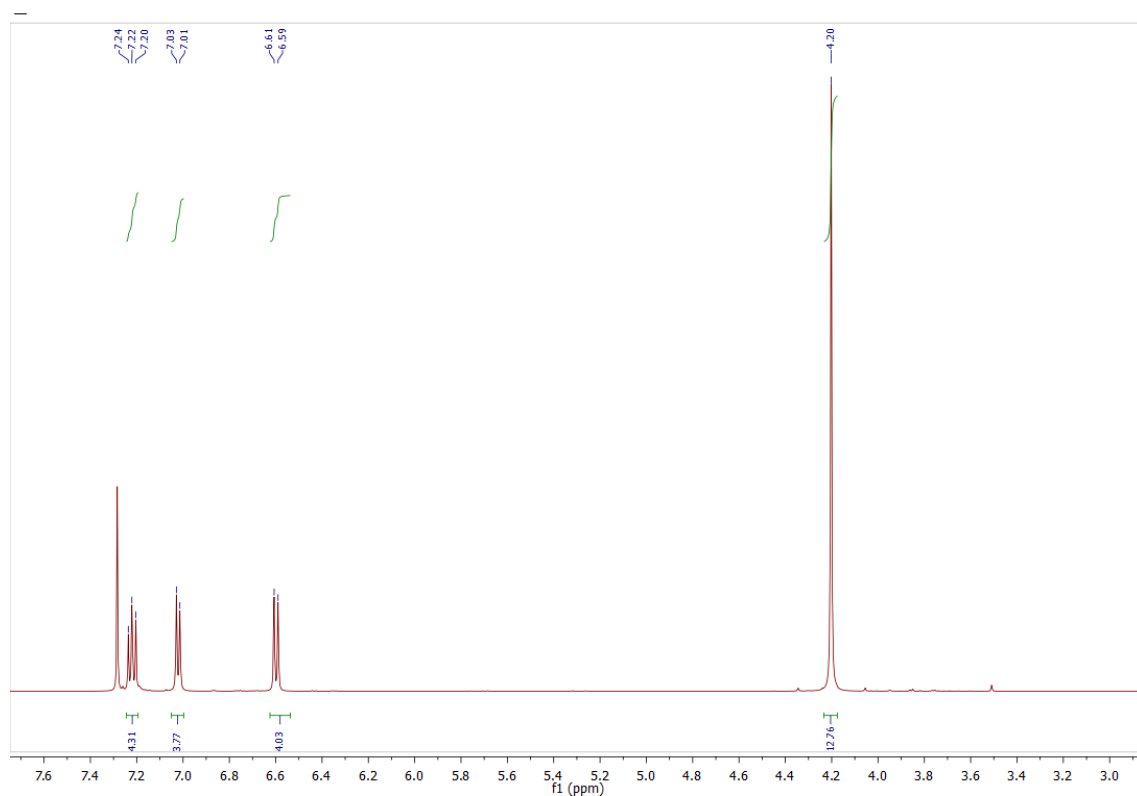


Figure S1: ^1H -NMR spectrum of **14** (CDCl_3)

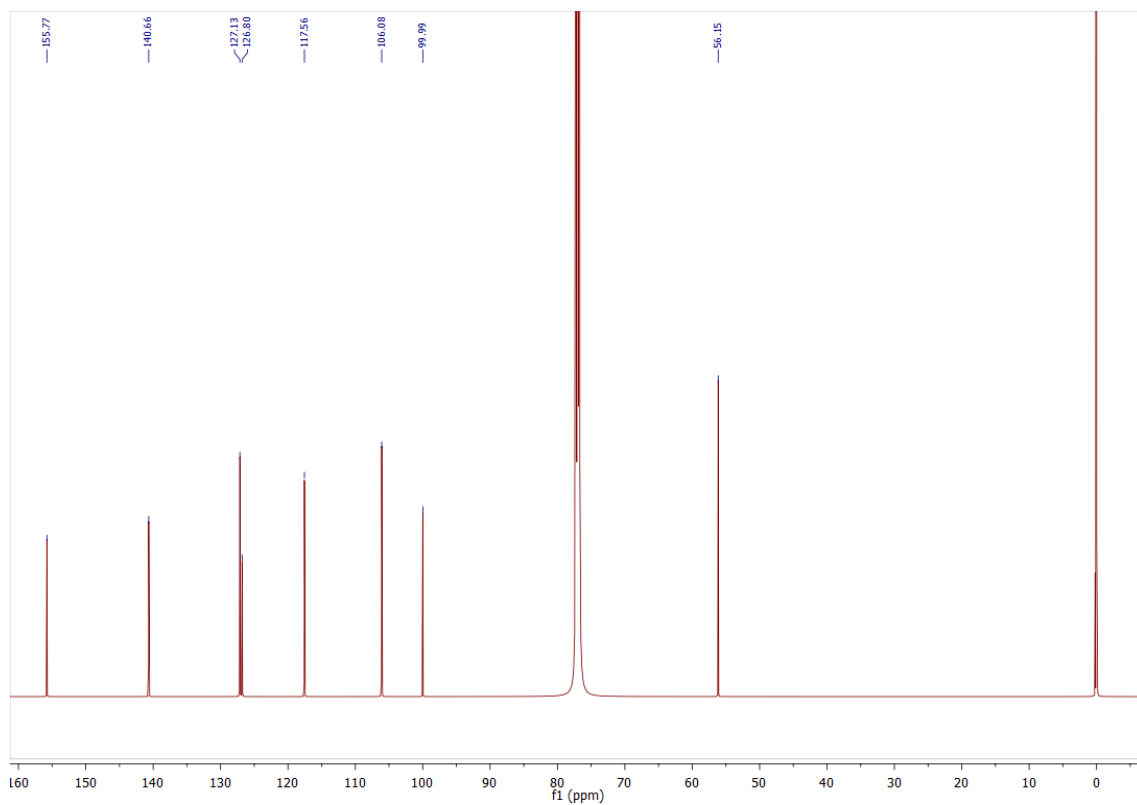


Figure S2: ^{13}C -NMR spectrum of **14** (CDCl_3)

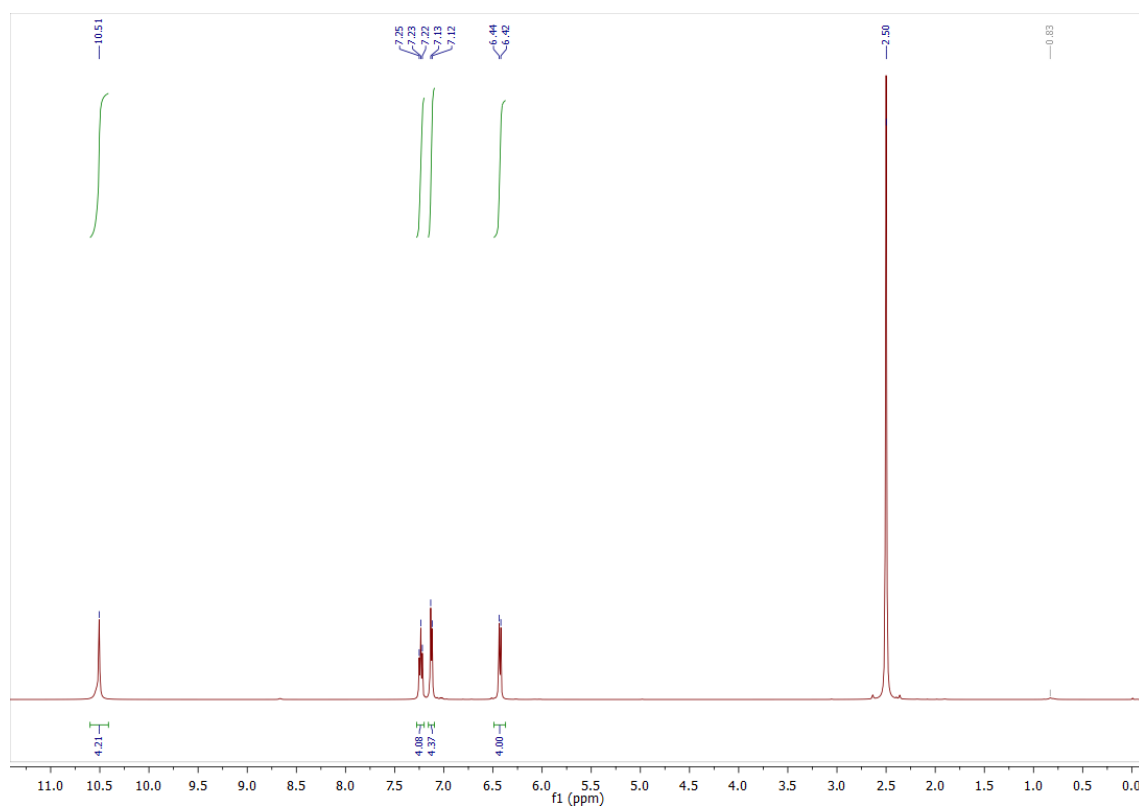


Figure S3: ¹H-NMR spectrum of **15** (DMSO-*d*₆)

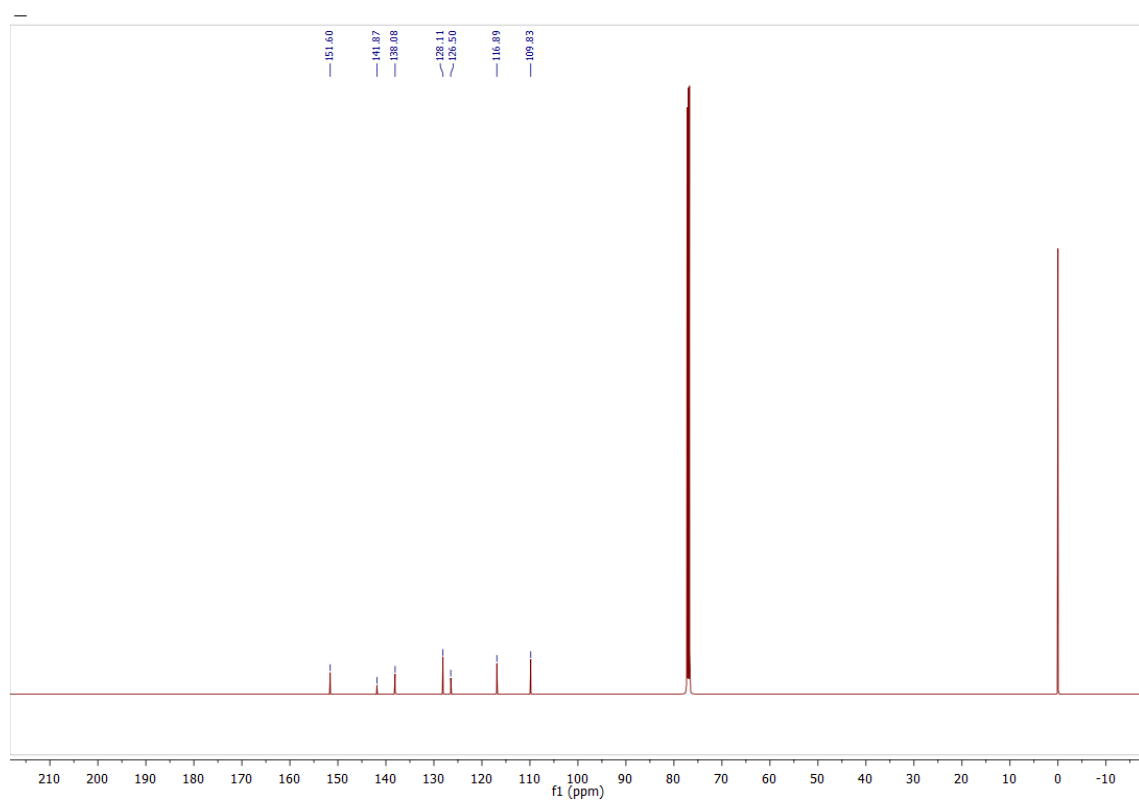


Figure S4: ¹³C-NMR spectrum of **15** (DMSO-*d*₆)

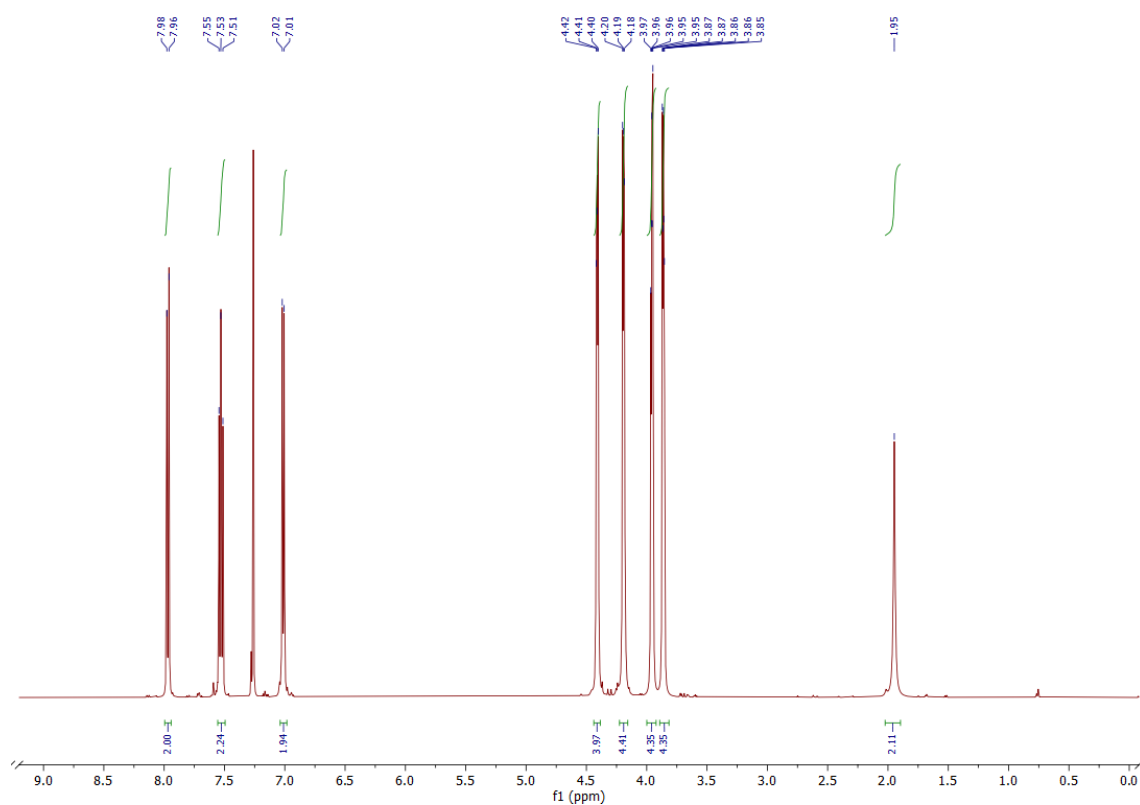


Figure S5: ¹H-NMR spectrum of **17** (CDCl₃)

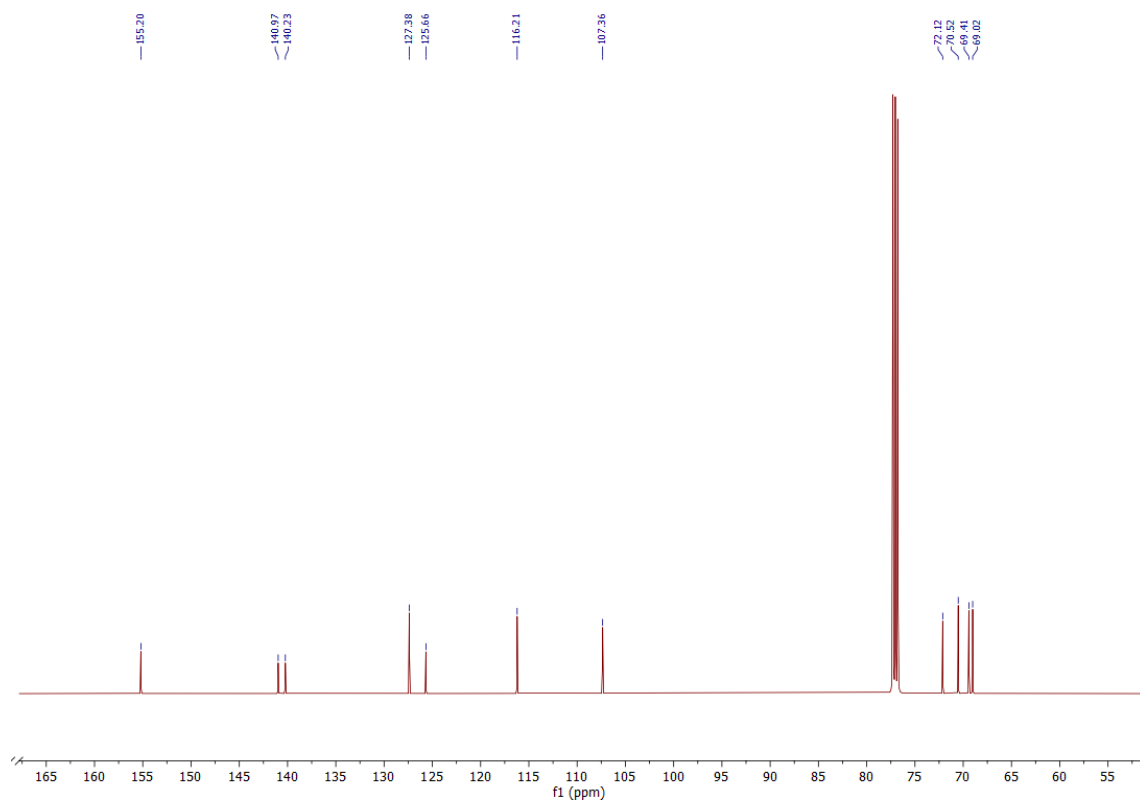


Figure S6: ¹³C-NMR spectrum of **17** (CDCl₃)

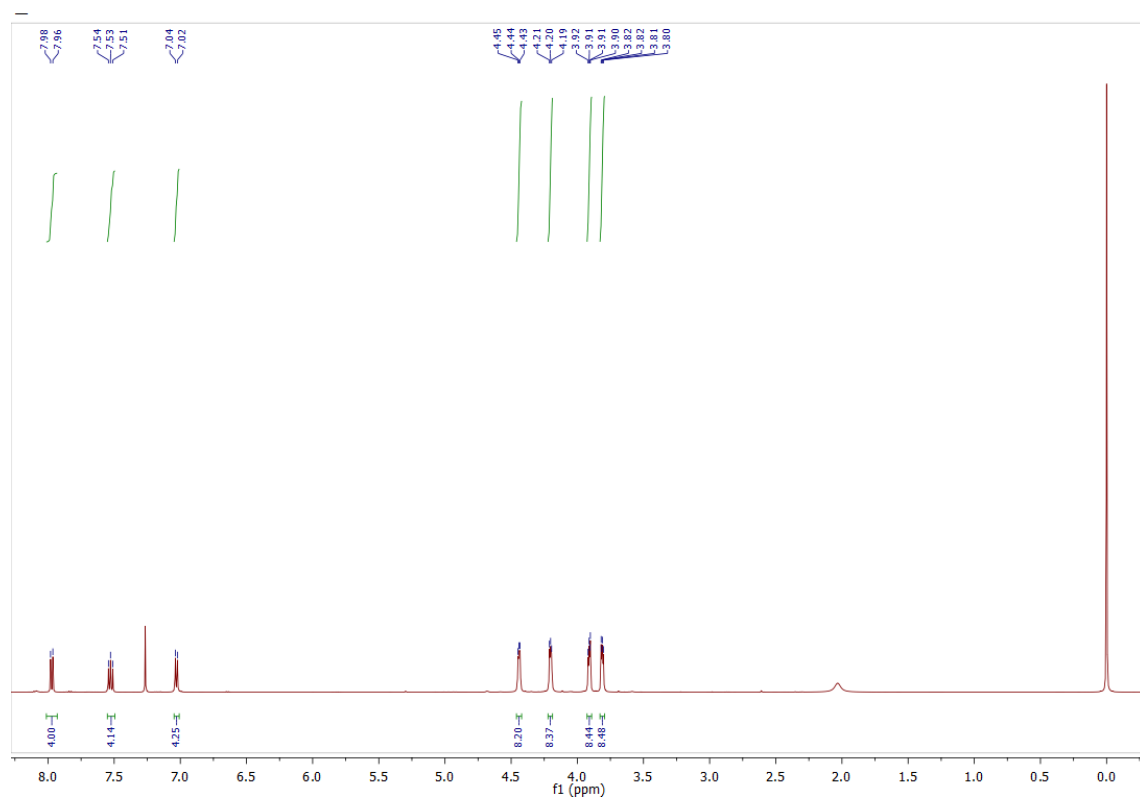


Figure S7: ^1H -NMR spectrum of **10** (CDCl_3)

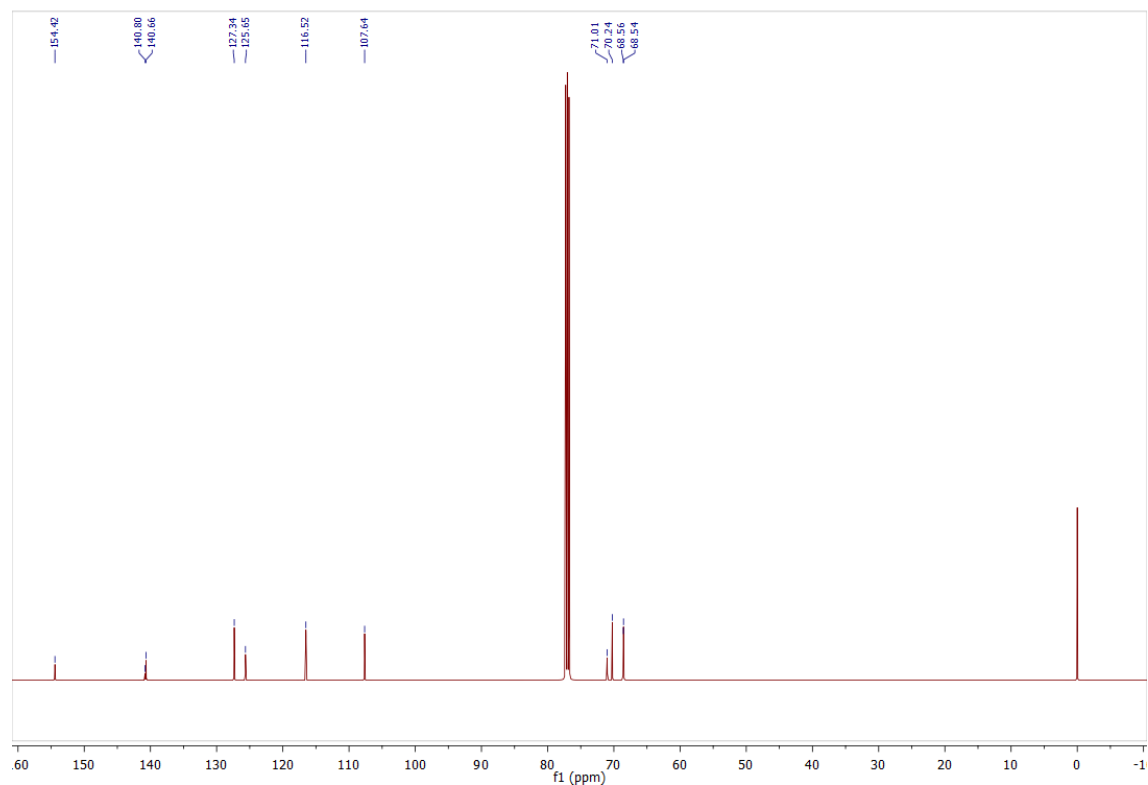


Figure S8: ^{13}C -NMR spectrum of **10** (CDCl_3)

2. UV-spectroscopic investigation of the new crown ether (**10**)

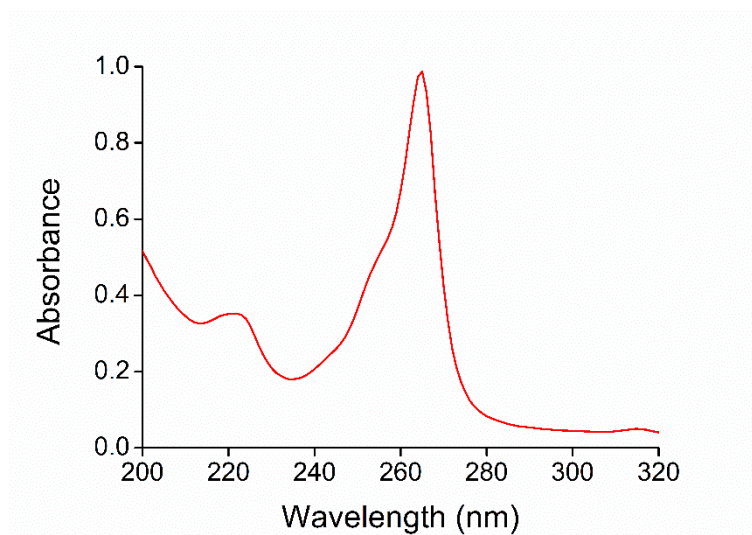


Figure S9: UV spectrum of **10** in acetonitrile

3. Results for neutral oligoamines

It is important to note, that the presence of water traces could not be fully excluded and the titration experiments were not carried out under an inert atmosphere. Although a partial protonation of the neutral guest molecules could take place, these experiments can serve as an estimation on the effects of replacing water with other solvents. It can be concluded, that the values of the stability constants for neutral amin analogues decreased at least one order of magnitude. However, investigating of these bioactive molecules in non-aqueous media is rarely relevant in practice.

Table S1. Calculated stability constants and cooperativity in binding for the determined consecutive 1:1 and 1:2 (host:guest) amine-coordination of the host molecule

guest amine ¹	logK ₁ ²	logK ₂ ³	binding cooperativity effects ⁴
n-butylamine	1.5±0.2	<<1.5	non-cooperative
putrescine	1.7±0.2	<<1.7	non-cooperative
<i>N,N'</i> -bis(2-aminoethyl)-1,3-propanediamine	2.0±0.2	<<2.0	non-cooperative
norspermidine	2.8±0.2	<<2.0	non-cooperative
spermine	4.4±0.1	3.6±0.1	negative cooperativity ($\alpha=0.6$)
spermidine	4.8±0.1	4.2±0.2	non-cooperative

¹ Added in acetonitrile solution in a neutral, free-amine form.

² Complex stability constant for 1:1 (host:guest) complexes as the first step of coordination.

³ Complex stability constant for 1:2 (host:guest) complexes as the second step of coordination

⁴ Calculated according to [54], where $K_1=4K_2$ refers to a non-cooperative stepwise binding, while α expresses the extent of cooperativity.

4. Reported data for the characterization of 9-chloro-4,5-dimethoxyacridine (**12**) [52,53]

$R_f = 0.82$ (silica gel TLC, dichloromethane:methanol = 10:1)

M.p.: 220–225°C (decomposition)

IR (KBr) $\nu_{\max} = 3438, 3343, 3084, 3067, 3036, 3004, 2968, 2838, 1626, 1607, 1595, 1534, 1487, 1456, 1448, 1410, 1331, 1270, 1224, 1077, 971, 810, 746, 575 \text{ cm}^{-1}$

$^1\text{H-NMR}$ (300 MHz, CDCl_3) $\delta = 4.14$ (s, 6H, OCH_3), 7.06 (d, $J = 8 \text{ Hz}$, 2H, Ar-H), 7.58 (t, $J = 8 \text{ Hz}$, 2H, Ar-H), 7.99 (d, $J = 8 \text{ Hz}$, 2H, Ar-H) ppm

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) $\delta = 56.42, 106.84, 116.16, 125.86, 127.83, 140.67, 140.69, 155.66 \text{ ppm}$

HRMS $m/z = 274.06292$ ($\text{M}+\text{H}$) $^+$ (calculated for $\text{C}_{15}\text{H}_{12}\text{ClNO}_2$, 273.05566).