

## Table of contents

|  |            |
|--|------------|
| <b>1. Synthesis and Materials .....</b>            | <b>S2</b>  |
| 1.1. Chemicals and Materials .....                 | S2         |
| 1.2. CTV-Br derivative <b>4</b> .....              | S2         |
| 1.3. CTV-NH <sub>2</sub> derivative <b>5</b> ..... | S2         |
| 1.4. Compound <b>6</b> .....                       | S2         |
| 1.5. Hemicryptophane <b>3</b> .....                | S2         |
| <b>2. NMR and mass spectra .....</b>               | <b>S4</b>  |
| <b>3. Photophysic studies .....</b>                | <b>S11</b> |
| 3.1. Spectra and properties .....                  | S11        |
| 3.2. Fluorescence titration.....                   | S11        |
| <b>4. <sup>1</sup>H NMR Titrations .....</b>       | <b>S13</b> |
| 4.1. General procedure .....                       | S13        |
| 4.2. Titration curve for acetylcholine.....        | S13        |
| <b>5. Computational method .....</b>               | <b>S15</b> |
| <b>References .....</b>                            | <b>S19</b> |

## 1. Synthesis and Materials

### 1.1. Chemicals and Materials

Starting material and solvents were of commercial grade and were used without further purification. Chromatography was carried out with Merck 60 A (0.040 - 0.063 mm) silica gel. TLC was performed with Merck silica gel 60 F<sub>254</sub> plates. Melting points were determined with a Büchi Melting Point B-545. IR spectra were obtained using a Bruker Alpha Platinum ATR. <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded at 298 K on a Bruker Avance III HD 300 MHz spectrometer and a Bruker Avance III HD 400 MHz. <sup>1</sup>H NMR and <sup>13</sup>C NMR chemical shifts  $\delta$  are reported in ppm referenced to the protonated residual solvent signal. Coupling constants *J* are given in Hz. HRMS were performed on a SYNAPT G2 HDMS (Waters) mass spectrometer with API and spectra were obtained with TOF analysis. Measurements were realized with two internal standards. UV spectra were recorded on a Agilent Cary 60 UV-Vis spectrophotometer and fluorescence spectra on a Jasco FP-8600 spectrofluorometer.

### 1.2. CTV-Br derivative 4

CTV-Br derivative **4** was prepared according to the common published procedure.<sup>1</sup>

### 1.3. CTV-NH<sub>2</sub> derivative 5

The two-step synthesis of CTV-NH<sub>2</sub> derivative **5** was done according to the previously published procedure.<sup>2</sup>

### 1.4. Compound 6

NaOH (80 mg, 2.00 mmol) was added to a solution of 1-hydroxy-2-naphtaldehyde (262 mg, 1.52 mmol) in absolute ethanol (15 mL). The mixture was stirred at r.t. for 30 minutes and 1,3,5-tris(bromomethyl)benzene (155 mg, 0.434 mmol) was added. The reaction mixture was refluxed for 20 h and cooled to 4 °C overnight. The solid obtained was filtered off and wash with cold ethanol and cold water to afford trialdehyde **6** as a slightly brown solid (138 mg, 51 %).

*R*<sub>f</sub> = 0.52 (CH<sub>2</sub>Cl<sub>2</sub>); mp 141–142 °C; IR  $\nu_{\text{max}}/\text{cm}^{-1}$  3050, 2852, 1671, 1612, 1398, 1266; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  10.48 (s, 1H), 8.28 (d, *J* = 8.1 Hz, 1H), 7.95–7.88 (m, 2H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.70–7.61 (m, 3H), 5.34 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  189.4, 160.5, 138.2, 137.5, 129.5, 128.5, 127.9, 127.5, 127.1, 125.5, 125.1, 123.3, 122.8, 79.1; HRMS (ESI-TOF) *m/z*: found 631.2115 [M + NH<sub>4</sub>]<sup>+</sup>, calcd for C<sub>42</sub>H<sub>34</sub>NO<sub>6</sub>: 631.2115.

### 1.5. Hemicryptophane 3

In a 250 mL round bottom flask was added CTV-NH<sub>2</sub> derivative **5** (106 mg, 0.197 mmol) dissolved in a 1/1 mixture of CHCl<sub>3</sub>/MeOH (90 mL). A solution of **6** (113 mg, 0.179 mmol) in the same mixture of solvent (60 mL) was added dropwise under stirring at r.t. and the reaction mixture was stirred at r.t. for 48 h. It was cooled to 0 °C and NaBH<sub>4</sub> (245 mg, 6.48 mmol) was added portionwise. The mixture was stirred at r.t. during 4 h and solvents were evaporated. The crude residue was dissolved in CHCl<sub>3</sub> (30 mL) and washed with a 10 % NaOH solution (30 mL). Aqueous phase was extracted with CHCl<sub>3</sub> (30 mL) and combined organic layers were washed with a 10 % NaOH solution (3 x 25 mL), dried over MgSO<sub>4</sub>. Organic solvent was removed under reduced pressure to afford a yellowish solid purified by silica gel column chromatography (CHCl<sub>3</sub>/MeOH/Et<sub>3</sub>N, gradient from 97/1/2 to 90/8/2). Hemicryptophane **3** was obtained as a white solid (71 mg, 35 %).

*R*<sub>f</sub> = 0.33 (CHCl<sub>3</sub>/MeOH/Et<sub>3</sub>N: 94/4/2); mp 250 °C (decomposition);  $\lambda_{\text{max}}$  (DMSO + 2% H<sub>2</sub>O)/nm 288 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  20 000); IR  $\nu_{\text{max}}/\text{cm}^{-1}$  2968, 2901, 1607, 1572, 1508, 1452, 1259; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  8.06–8.01 (m, 1H), 7.86–7.81 (m, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H),

7.48–7.42 (m, 3H), 6.93 (s, 1H), 6.79 (s, 1H), 4.87 (d,  $J = 14.9$  Hz, 1H), 4.79 (d,  $J = 16.5$  Hz, 1H), 4.75 (d,  $J = 13.9$  Hz, 1H), 4.22–4.15 (m, 2H), 4.05 (q,  $J = 13.6$  Hz, 2H), 3.67 (s, 3H), 3.53 (d,  $J = 13.7$  Hz, 1H), 3.07–3.00 (m, 1H), 2.98–2.89 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  152.6, 148.9, 146.7, 137.8, 134.4, 133.1, 131.8, 128.2, 127.9, 127.2, 126.3, 126.0, 125.9, 125.8, 124.3, 122.2, 117.2, 113.6, 75.9, 69.0, 55.9, 47.6, 47.4, 36.5; HRMS (ESI-TOF)  $m/z$ : found 560.7591  $[\text{M} + 2\text{H}]^{2+}$ , calcd for  $\text{C}_{72}\text{H}_{71}\text{N}_3\text{O}_9$ : 560.7590.

## 2. NMR and mass spectra

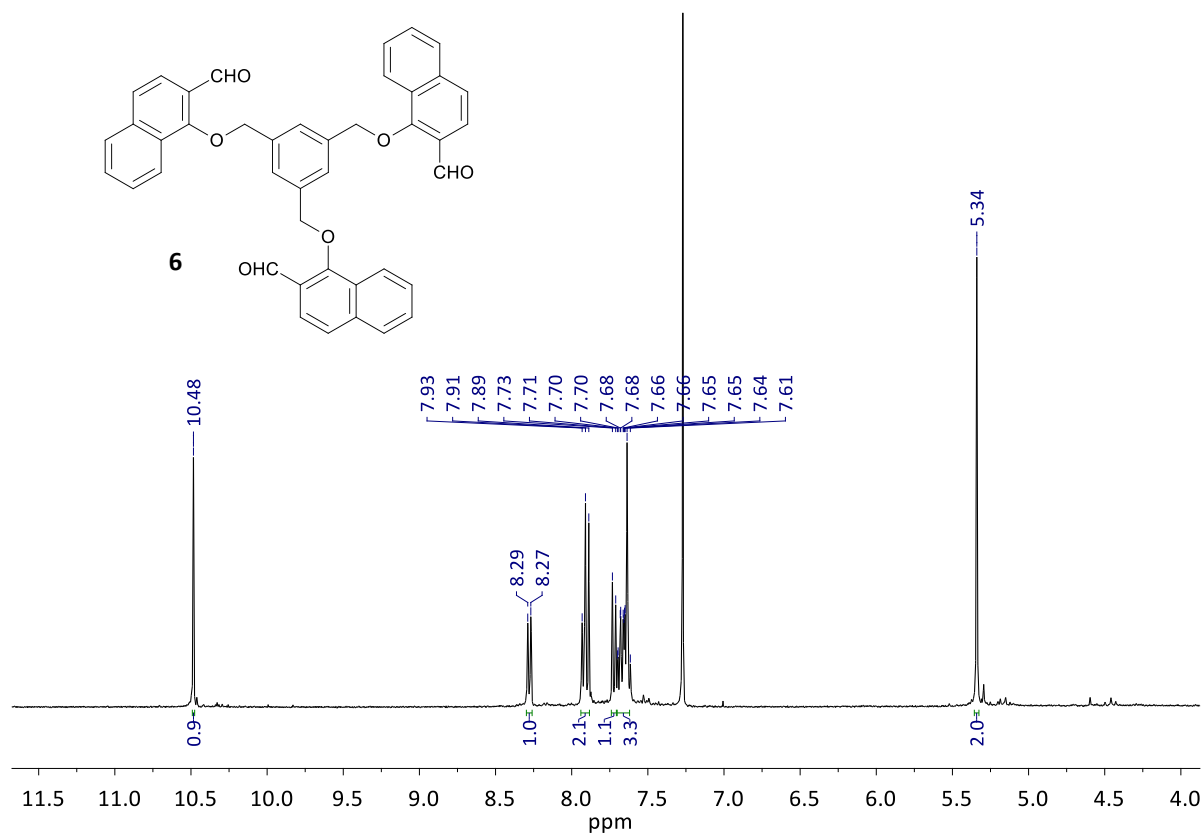


Figure S1. <sup>1</sup>H NMR Spectrum of **6** (CDCl<sub>3</sub>, 400 MHz, 298 K).

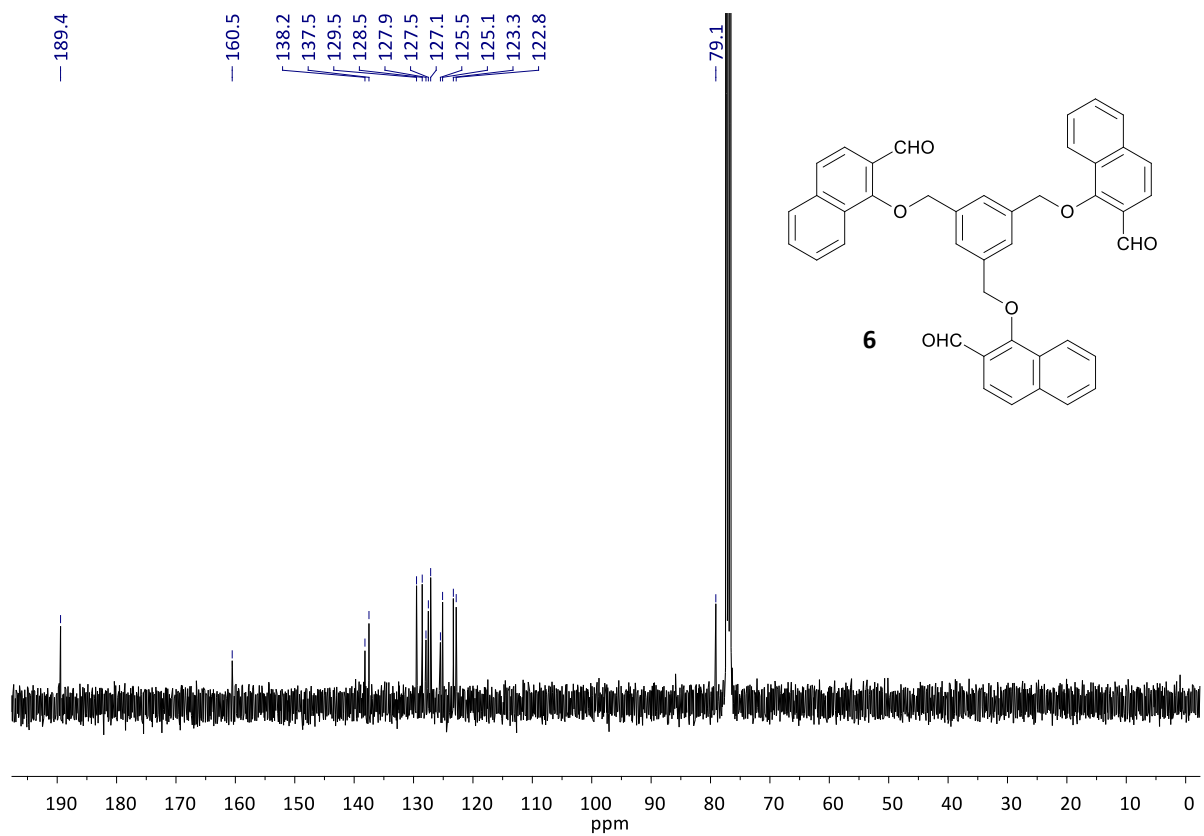


Figure S2. <sup>13</sup>C NMR Spectrum of **6** (CDCl<sub>3</sub>, 100 MHz, 298 K).

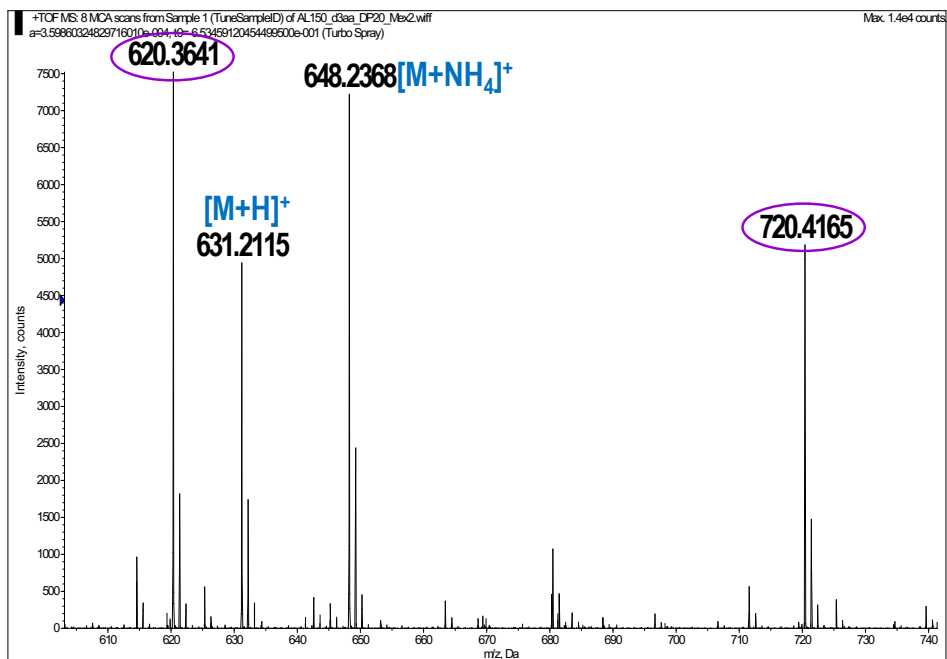


Figure S3. HRMS Spectrum of  $6+H^+$  and  $6+NH_4^+$ . Expected peaks are observed at 631.2115 and 648.2368 and internal standards  $NH_4^+$  adducts with two oligomers of PMMA600 chosen for analysis at 620.3641 and 720.4165.

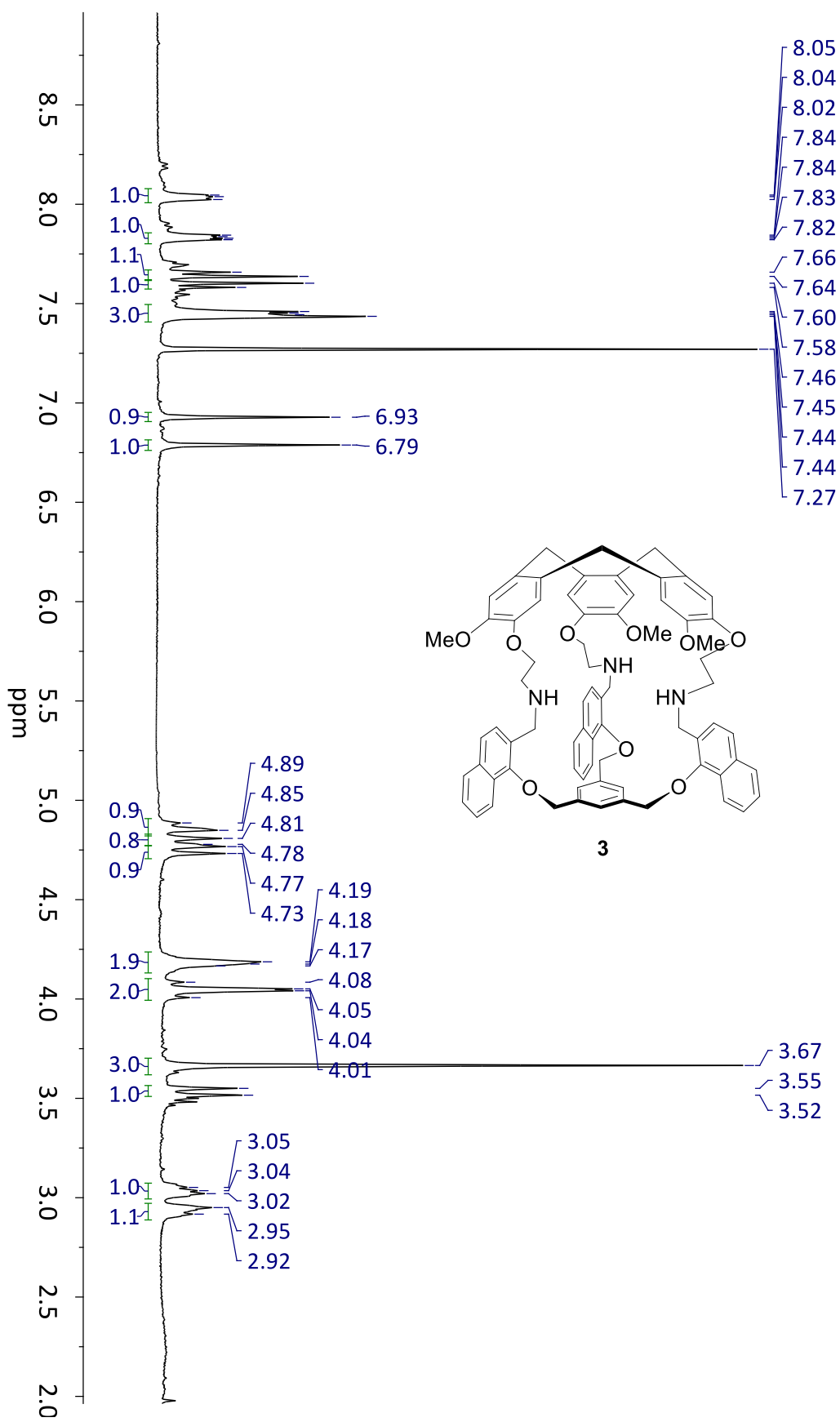


Figure S4. <sup>1</sup>H NMR Spectrum of **3** (CDCl<sub>3</sub>, 400 MHz, 298 K).

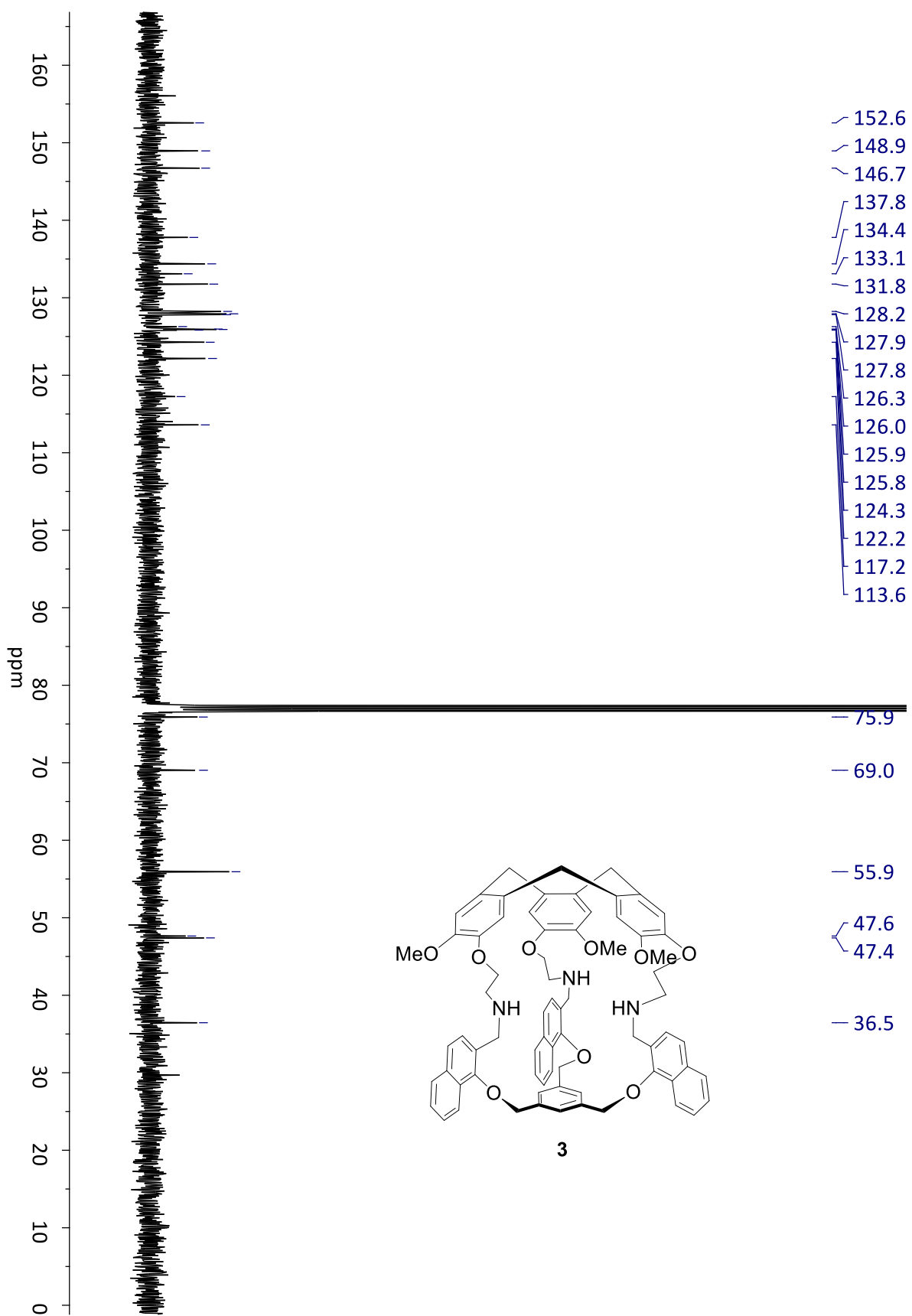


Figure S5. <sup>13</sup>C NMR Spectrum of **3** (CDCl<sub>3</sub>, 100 MHz, 298 K).

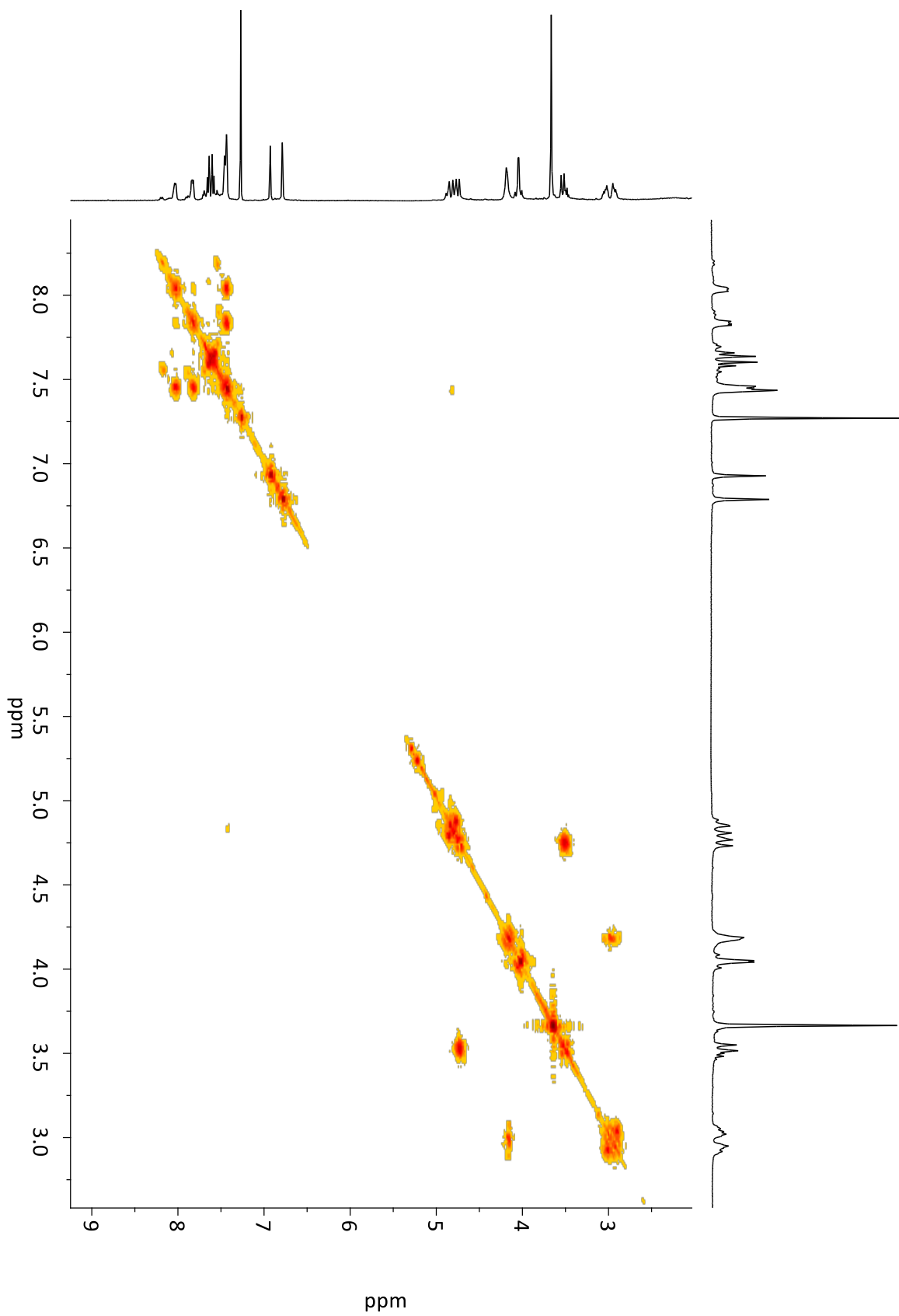


Figure S6. COSY Spectrum of **3** (CDCl<sub>3</sub>, 400 MHz, 298 K).



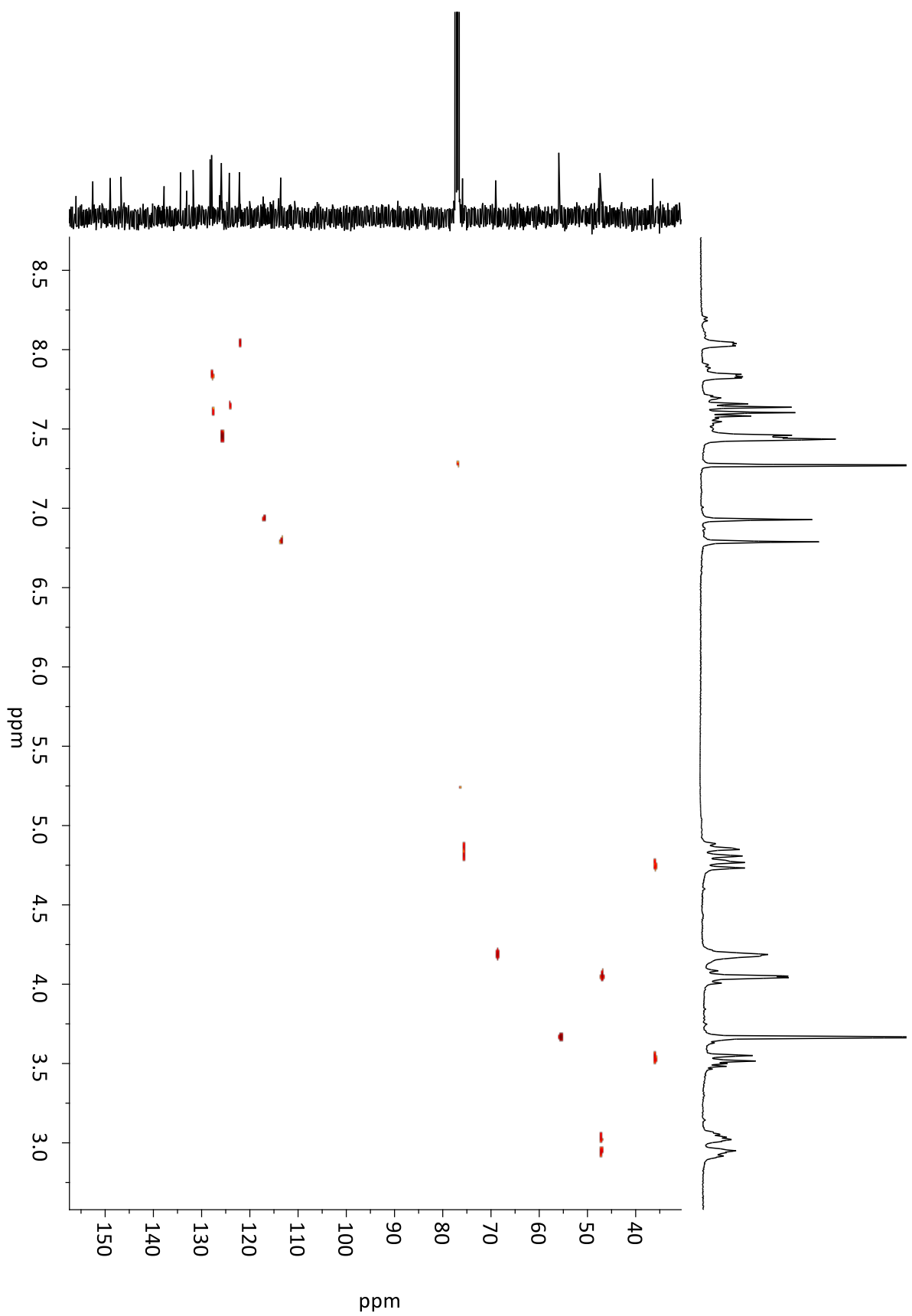


Figure S7. HSQC Spectrum of **3** ( $\text{CDCl}_3$ , 400 MHz, 298 K).

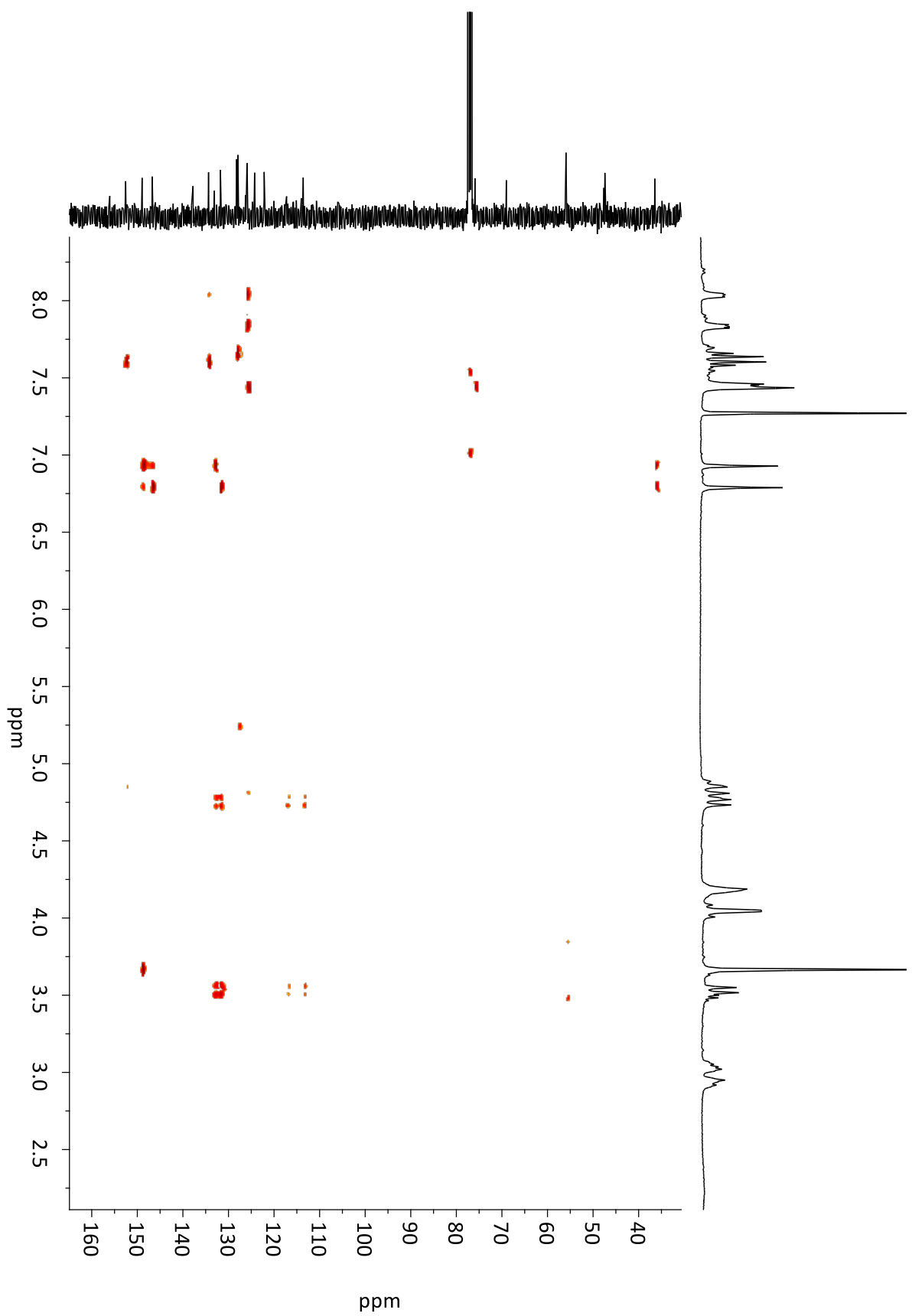


Figure S8. HMBC Spectrum of **3** (CDCl<sub>3</sub>, 400 MHz, 298 K).

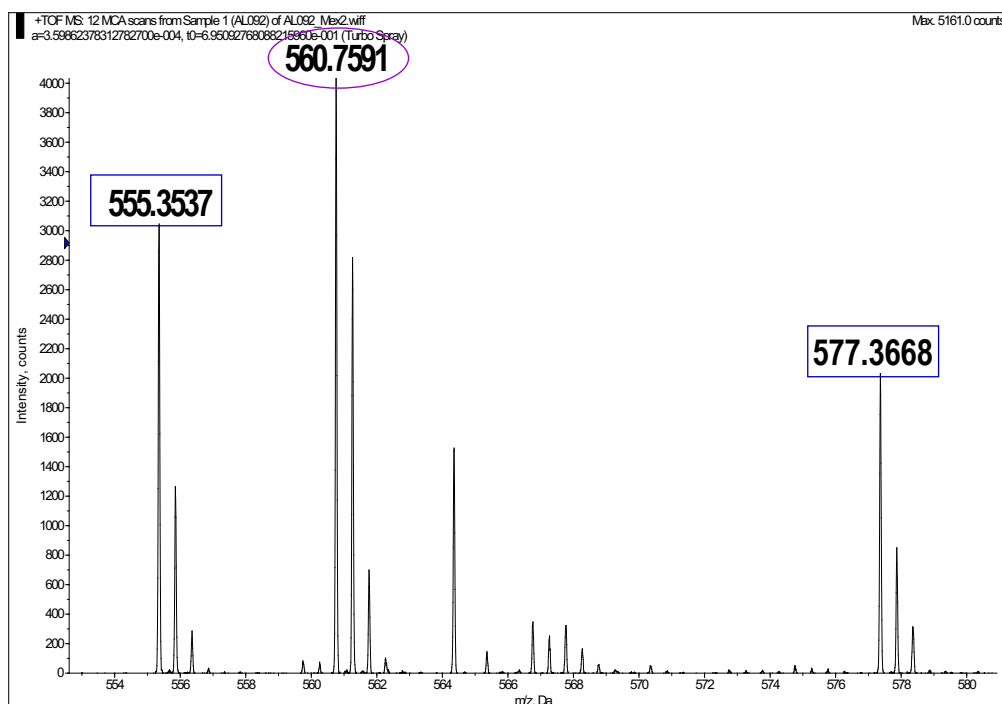


Figure S9. HRMS Spectrum of **3**+2H<sup>+</sup>. Expected peak is observed at 560.7591 and internal standards NH<sub>4</sub><sup>+</sup> adducts with two oligomers of PEG1000 chosen for analysis at 555.3537 and 577.3668.

### 3. Photophysical studies

#### 3.1. Spectra and properties

2.90 mg of hemicryptophane **3** were dissolved in 10.0 mL of DMSO containing 2% H<sub>2</sub>O and diluted by a factor 10. The absorption spectrum of the 25.9 μM solution in DMSO + 2% H<sub>2</sub>O was recorded between 265 nm and 500 nm using a quartz cuvette (1 cm x 1 cm x 4.5 cm). A maximum at 288 nm was observed with an extinction coefficient  $\epsilon = 2.0 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ .

The emission spectrum ( $\lambda_{\text{exc}} = 290 \text{ nm}$ ) was recorded between 300 nm and 550 nm with a maximum at 326 nm. Emission spectra of 4 solutions of hemicryptophane **3** in DMSO containing 2% H<sub>2</sub>O, with absorbance lower than 0.1, were recorded, and the average quantum yield was calculated with quinine bisulfate in H<sub>2</sub>SO<sub>4</sub> (0.5 M). All these solutions afforded the same results.

Absorption:  $\lambda_{\text{max}} = 288 \text{ nm}$ ,  $\epsilon = 2.0 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ .

Emission:  $\lambda_{\text{exc}} = 290 \text{ nm}$ ,  $\lambda_{\text{max}} = 326 \text{ nm}$ , quantum yield: 1.8%.

#### 3.2. Fluorescence titration

##### 3.2.1. General procedure

2.5 mL of a solution of hemicryptophane **3** (5.0 μM) in DMSO + 2% H<sub>2</sub>O was taken into the quartz cuvette, and then certain equivalents of a concentrated guest solution (5.0 mM) in the same solvents were added stepwise with a microsyringe. The final volume of the solution was almost unchanged (2.5 mL) since very small volume of guest solution was added. The solution was mixed and incubated for 30 s before irradiation at 290 nm at 25 °C. The corresponding emission values at 362 nm during titration were then recorded.

### 3.2.2. Titration curves

#### 3.2.2.1 Acetylcholine

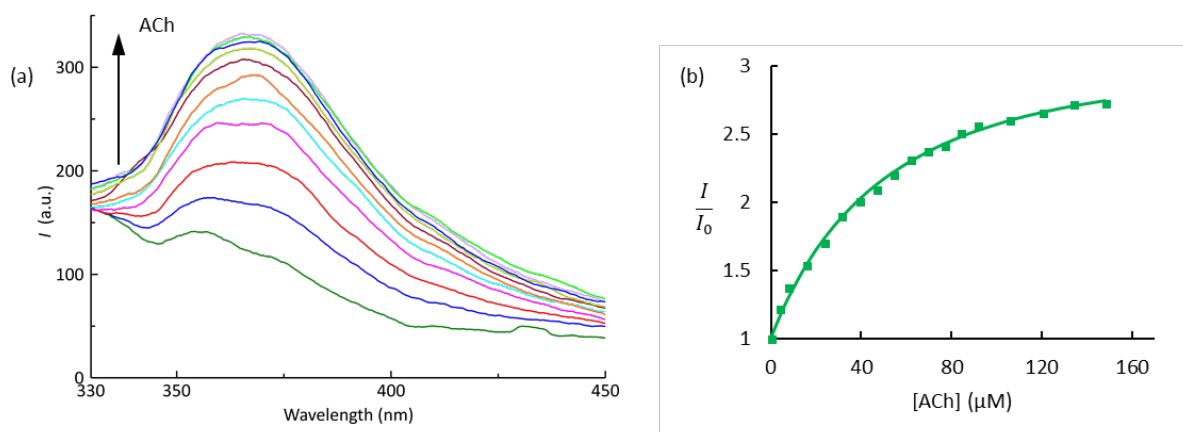


Figure S10. (a) Fluorescence titration of 5.0  $\mu\text{M}$  of hemicryptophane **3** with acetylcholine (counterion  $\text{Cl}^-$ ) excited at 290 nm in DMSO + 2%  $\text{H}_2\text{O}$ . (b) Relative fluorescence intensity as a function of the concentration of acetylcholine.

#### 3.2.2.2 Choline

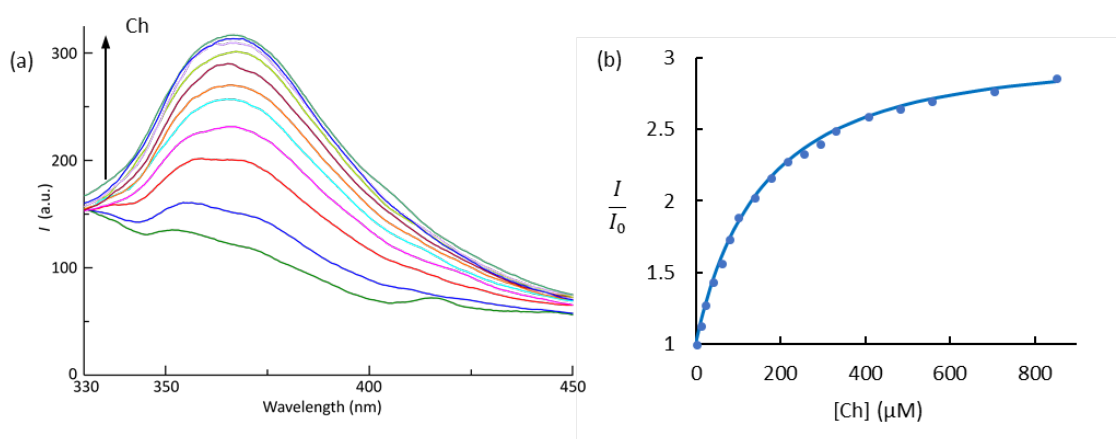


Figure S11. (a) Fluorescence titration of 5.0  $\mu\text{M}$  of hemicryptophane **3** with choline (counterion  $\text{Cl}^-$ ) excited at 290 nm in DMSO + 2%  $\text{H}_2\text{O}$ . (b) Relative fluorescence intensity as a function of the concentration of choline.

#### 3.2.2.3 Choline phosphate

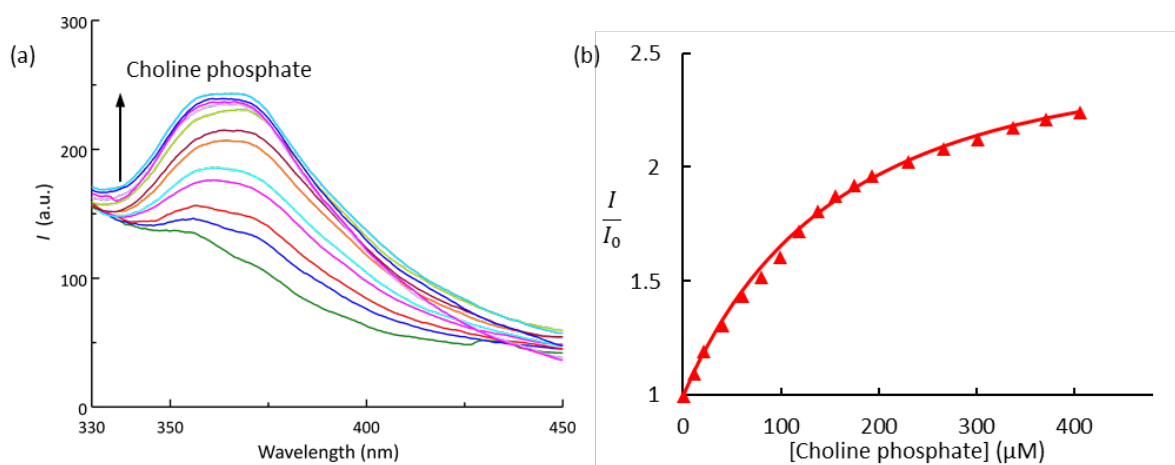


Figure S12. (a) Fluorescence titration of 5.0  $\mu\text{M}$  of **3** with choline phosphate (counterions  $\text{Cl}^-$  and  $\text{Ca}^{2+}$ ) excited at 290 nm in DMSO + 2%  $\text{H}_2\text{O}$ . (b) Relative fluorescence intensity as a function of the concentration of choline phosphate.

## 4. <sup>1</sup>H NMR Titrations

### 4.1. General procedure

A solution of hemicryptophane host **3** ( $1.0 \times 10^{-3}$  M in CDCl<sub>3</sub>/MeOD 95/5, 500  $\mu$ L) was titrated in NMR tubes with aliquots of a concentrated solution ( $5.0 \times 10^{-3}$  M in the same solvent) of picrate salts of neurotransmitters. The shifts  $\Delta\delta$  of the host's protons signals at 7.61 and 7.55 ppm were measured after each addition and plotted as a function of the guest/host ratio ( $[G]/[H]$ ). Association constant  $K_a$  was obtained by nonlinear least-squares fitting of these plots using bindfit program from Thordarson's group.<sup>3</sup>  $K_a$ , covariance and RMS of the fit are reported.

### 4.2. Titration curve for acetylcholine

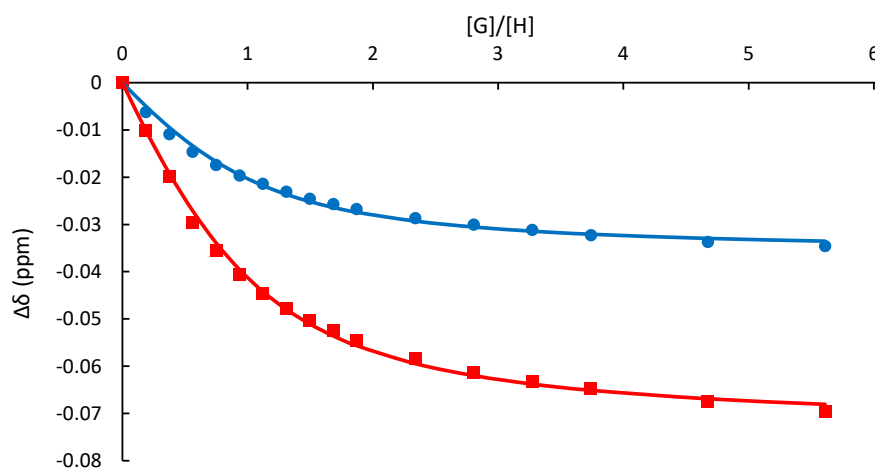


Figure S13. Titration curve of host **3** with acetylcholine. The chemical induced shifts  $\Delta\delta$  of host's protons at 7.61 ppm (●) and 7.55 ppm (■) were measured and plotted as a function of the ratio  $[G]/[H]$  (dots). Curves were fitted with the bindfit program (lines).

| Guest | $K_a$ (L.mol <sup>-1</sup> ) | cov                   | RMS (ppm)             |
|-------|------------------------------|-----------------------|-----------------------|
| ACh   | $5.5 \times 10^3 \pm 4.2\%$  | $2.13 \times 10^{-3}$ | $9.05 \times 10^{-4}$ |

Table S1.  $K_a$ , covariance and RMS obtained from fits of the titration curves.

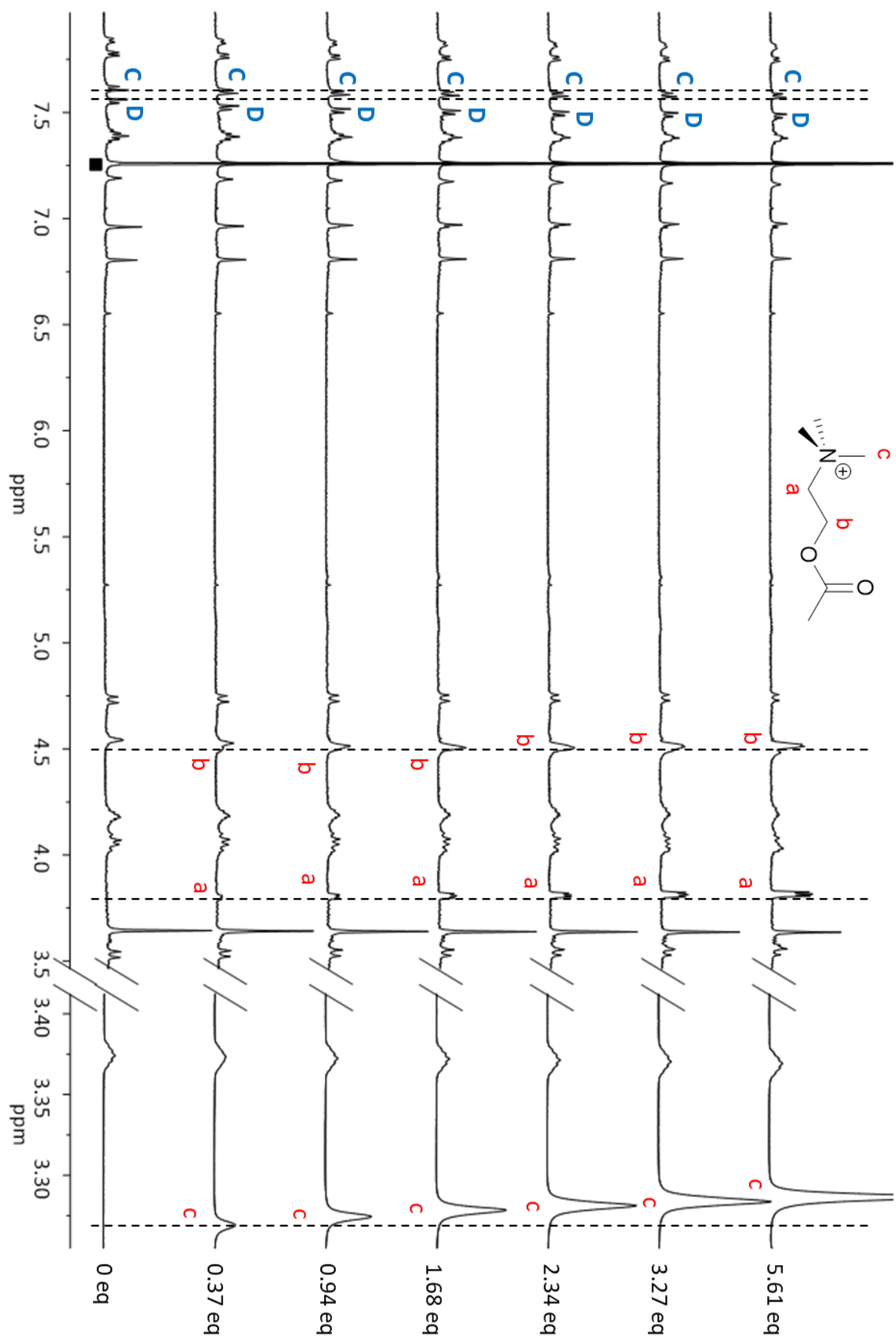


Figure S14.  $^1\text{H}$  NMR Spectra of **3** (1 mM in  $\text{CDCl}_3/\text{MeOD}$  95/5) for several additions of a concentrated solution of acetylcholine picrate (5 mM in the same solvents), with protons C and D used to give the binding constant.

## 5. Computational method

In order to access geometrical information upon the host–guest species, full geometry optimizations were performed using restricted Density Functional Theory (DFT) calculations. A combination of BP86 functional and an all electron 6-31G\* basis set including polarization functions has proven to be very satisfactory for similar issues.<sup>4</sup> However, we checked using the hybrid B3LYP functional that our results do not suffer from the arbitrariness of the exchange correlation functional. All calculations were carried out using the Gaussian 03 suite of program.<sup>5</sup>

ACh@3

Cartesian coordinates :

179

optimized

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | -7.563560 | 4.672452  | -0.507059 |
| C | -8.607617 | 3.282253  | -1.764735 |
| H | -9.384676 | 1.809892  | -3.154890 |
| H | -7.168996 | 1.211885  | -4.069530 |
| C | -8.491428 | 2.299987  | -2.778117 |
| H | 4.478785  | -8.408406 | -2.287054 |
| H | -9.587838 | 3.537770  | -1.373131 |
| H | 0.378977  | -8.526333 | -0.982628 |
| C | 2.442604  | -8.603573 | -1.565455 |
| H | 4.123607  | -6.175010 | -3.284013 |
| C | 3.504122  | -7.933198 | -2.222533 |
| H | 6.567650  | 6.007854  | -2.993690 |
| H | 2.612451  | -9.585944 | -1.134695 |
| H | 8.177063  | 4.038201  | 1.288244  |
| C | 8.520214  | 5.506008  | -0.238214 |
| C | 8.060305  | 6.063571  | -1.455256 |
| H | 9.421467  | 5.895874  | 0.226052  |
| H | 8.612837  | 6.877972  | -1.915320 |
| N | -0.552603 | -0.235175 | 0.080919  |
| C | -0.437049 | -1.594954 | -0.578390 |
| C | 0.769389  | -2.440669 | -0.196405 |
| O | 1.900058  | -1.948539 | -0.918941 |
| C | 0.624819  | 0.637504  | -0.269244 |
| C | -1.800892 | 0.443422  | -0.429699 |
| C | -0.657508 | -0.402078 | 1.572560  |
| C | 3.103499  | -2.610580 | -0.913923 |
| O | 3.978892  | -2.148311 | -1.607815 |
| C | -0.326017 | -0.207887 | -4.131636 |
| C | 1.005861  | -0.612828 | -3.971437 |
| C | 1.982696  | 0.347540  | -3.704974 |
| C | 1.646979  | 1.706844  | -3.622101 |
| C | 0.315856  | 2.094782  | -3.780105 |
| C | -0.680466 | 1.138357  | -4.024748 |
| C | -2.132602 | 1.544064  | -4.119040 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 2.723361  | 2.707576  | -3.273883 |
| C | 1.394589  | -2.068416 | -4.049029 |
| O | 0.324634  | -2.856134 | -3.507395 |
| O | 3.161069  | 2.397704  | -1.949626 |
| O | -2.370073 | 2.505945  | -3.092550 |
| C | -1.873583 | -4.168771 | -2.331615 |
| N | -2.429295 | -4.437439 | -0.998930 |
| C | -2.505390 | 4.535559  | -1.238375 |
| N | -2.714219 | 5.105496  | 0.093003  |
| C | 3.933008  | 1.280441  | 0.333817  |
| N | 4.492940  | 0.599841  | 1.506428  |
| C | -0.241575 | 4.951178  | 0.628105  |
| C | -4.020075 | -3.973631 | 0.789442  |
| C | -3.564774 | -3.606155 | -0.627391 |
| C | -1.546950 | 5.766037  | 0.671562  |
| C | 4.076474  | -1.292078 | 3.082149  |
| C | 3.534977  | -0.396597 | 1.970555  |
| C | 2.039734  | -6.053847 | -2.703133 |
| C | 0.968130  | -6.730518 | -2.040034 |
| C | 1.813021  | -4.755902 | -3.235460 |
| C | 0.583047  | -4.141498 | -3.107938 |
| C | -0.512185 | -4.822500 | -2.478722 |
| C | -0.293789 | -6.084231 | -1.965277 |
| C | -6.077229 | 2.592391  | -2.805327 |
| C | -6.194732 | 3.585514  | -1.782367 |
| C | -4.783276 | 2.239066  | -3.278429 |
| C | -3.658639 | 2.834817  | -2.749334 |
| C | -3.760331 | 3.856596  | -1.750320 |
| C | -5.011906 | 4.205236  | -1.295243 |
| C | 6.650044  | 3.951071  | -0.241881 |
| C | 6.184935  | 4.514724  | -1.472827 |
| C | 5.908868  | 2.887366  | 0.346314  |
| C | 4.772784  | 2.389029  | -0.242100 |
| C | 4.316506  | 2.965840  | -1.470604 |
| C | 4.999414  | 3.998609  | -2.069994 |
| C | -1.505573 | 1.873120  | 4.034367  |
| C | -1.557745 | 2.654489  | 2.866757  |
| C | -0.419587 | 3.114526  | 2.222299  |
| C | 0.843175  | 2.924485  | 2.825226  |
| C | 0.902366  | 2.182899  | 4.003583  |
| C | -0.242344 | 1.599619  | 4.583329  |
| O | -0.522822 | 3.567294  | 0.930619  |
| C | -3.047705 | -1.224985 | 4.058312  |
| C | -3.572295 | -2.239682 | 3.239302  |
| C | -4.289219 | -1.971481 | 2.077932  |
| C | -4.512711 | -0.626325 | 1.708213  |
| C | -4.062229 | 0.384661  | 2.559966  |
| C | -3.322056 | 0.111714  | 3.725665  |



|   |           |           |           |
|---|-----------|-----------|-----------|
| O | -4.869006 | -2.960922 | 1.326797  |
| C | -2.819674 | 1.295412  | 4.549355  |
| C | -0.697554 | -1.767468 | 4.794516  |
| C | -0.340752 | -2.913288 | 4.055293  |
| C | 0.935395  | -3.094756 | 3.535122  |
| C | 1.932789  | -2.129153 | 3.812482  |
| C | 1.586712  | -1.014445 | 4.566393  |
| C | 0.278108  | -0.792679 | 5.037991  |
| O | 3.179222  | -2.386049 | 3.309949  |
| C | -0.013364 | 0.563476  | 5.678923  |
| C | -2.156953 | -1.639217 | 5.221313  |
| O | -5.146709 | -0.428223 | 0.521510  |
| C | -5.577676 | 0.890500  | 0.187275  |
| O | 1.909984  | 3.441104  | 2.159799  |
| C | 3.181157  | 3.467737  | 2.820194  |
| O | 1.318051  | -4.132857 | 2.729967  |
| C | 0.344830  | -5.101242 | 2.369819  |
| H | -1.089735 | -0.960052 | -4.309736 |
| H | 3.004816  | 0.035081  | -3.506750 |
| H | 0.035514  | 3.138587  | -3.673520 |
| H | -2.383016 | 1.983796  | -5.095411 |
| H | -2.768943 | 0.660213  | -3.978334 |
| H | 3.570558  | 2.625998  | -3.968858 |
| H | 2.341637  | 3.736467  | -3.320304 |
| H | 1.573747  | -2.384070 | -5.086758 |
| H | 2.314572  | -2.218081 | -3.479224 |
| H | -1.796481 | -3.092793 | -2.547051 |
| H | -2.571470 | -4.577036 | -3.075783 |
| H | -1.689027 | -4.352817 | -0.304274 |
| H | -1.675083 | 3.816525  | -1.277653 |
| H | -2.231198 | 5.356140  | -1.918430 |
| H | -2.994427 | 4.349254  | 0.713960  |
| H | 2.977846  | 1.723258  | 0.640784  |
| H | 3.695437  | 0.564841  | -0.471270 |
| H | 5.357574  | 0.134857  | 1.226921  |
| H | 0.188170  | 4.934440  | -0.376888 |
| H | 0.512894  | 5.349707  | 1.311991  |
| H | -4.591067 | -4.905015 | 0.787155  |
| H | -3.141048 | -4.122058 | 1.434712  |
| H | -4.380917 | -3.772884 | -1.338988 |
| H | -3.356678 | -2.518025 | -0.655664 |
| H | -1.374806 | 6.719441  | 0.153960  |
| H | -1.796087 | 6.007139  | 1.711251  |
| H | 4.276307  | -0.730393 | 4.002315  |
| H | 5.010730  | -1.770657 | 2.774896  |
| H | 3.190448  | -1.064328 | 1.162238  |
| H | 2.647146  | 0.135378  | 2.334645  |
| C | 3.308207  | -6.688376 | -2.780481 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 1.200355  | -8.014138 | -1.478160 |
| H | 2.639837  | -4.255623 | -3.725424 |
| H | -1.119378 | -6.594741 | -1.476364 |
| C | -7.255378 | 1.965364  | -3.290181 |
| C | -7.481693 | 3.913268  | -1.281164 |
| H | -4.709942 | 1.488441  | -4.057417 |
| H | -5.089270 | 4.983120  | -0.541160 |
| C | 7.827686  | 4.471596  | 0.353925  |
| C | 6.919151  | 5.578932  | -2.058254 |
| H | 6.248123  | 2.462409  | 1.287299  |
| H | 4.648227  | 4.444258  | -2.994936 |
| H | -2.511840 | 2.839366  | 2.383044  |
| H | 1.867720  | 1.998657  | 4.460940  |
| H | -3.445667 | -3.278618 | 3.530497  |
| H | -4.284137 | 1.416750  | 2.313652  |
| H | -2.736404 | 1.022587  | 5.602715  |
| H | -3.577840 | 2.086282  | 4.509586  |
| H | -1.101813 | -3.661624 | 3.867849  |
| H | 2.345992  | -0.271040 | 4.779560  |
| H | -0.862677 | 0.508067  | 6.360694  |
| H | 0.845649  | 0.864206  | 6.289006  |
| H | -2.257661 | -0.949781 | 6.060964  |
| H | -2.496451 | -2.611981 | 5.595465  |
| H | -6.141557 | 0.795057  | -0.739284 |
| H | -6.226722 | 1.307374  | 0.966696  |
| H | -4.729916 | 1.567765  | 0.018717  |
| H | 3.103218  | 3.978883  | 3.787345  |
| H | 3.589617  | 2.459385  | 2.950330  |
| H | 3.842648  | 4.021295  | 2.153636  |
| H | 0.845388  | -5.794046 | 1.690899  |
| H | -0.025497 | -5.648224 | 3.245646  |
| H | -0.510048 | -4.639652 | 1.851282  |
| C | 3.235214  | -3.838229 | -0.049068 |
| H | -0.823737 | 0.572897  | 2.014843  |
| H | 2.538361  | -4.614783 | -0.382200 |
| H | 3.024011  | -3.621217 | 1.003952  |
| H | 4.251820  | -4.217365 | -0.153676 |
| H | 0.264205  | -0.825324 | 1.965260  |
| H | -1.498893 | -1.057359 | 1.796373  |
| H | -1.880841 | 1.413562  | 0.062061  |
| H | -2.672139 | -0.170983 | -0.202002 |
| H | -1.698454 | 0.596675  | -1.503255 |
| H | 0.463196  | 1.630914  | 0.147826  |
| H | 0.710837  | 0.692252  | -1.352045 |
| H | 1.518423  | 0.181121  | 0.135674  |
| H | 0.543529  | -3.464712 | -0.507632 |
| H | 0.966978  | -2.454362 | 0.878202  |
| H | -0.427545 | -1.436830 | -1.656820 |

H -1.345830 -2.130186 -0.305176

## **References**

- 1 B. Chatelet, E. Payet, O. Perraud, P. Dimitrov-Raytchev, L.-L. Chapellet, V. Dufaud, A. Martinez and J.-P. Dutasta, *Org. Lett.*, 2011, **13**, 3706–3709.
- 2 A. Long, O. Perraud, M. Albalat, V. Robert, J.-P. Dutasta and A. Martinez, *J. Org. Chem.*, 2018, **83**, 6301–6306.
- 3 D. B. Hibbert and P. Thordarson, *Chem. Commun.*, 2016, **52**, 12792–12805.
- 4 O. Perraud, V. Robert, A. Martinez and J.-P. Dutasta, *Chem. – Eur. J.*, 2011, **17**, 13405–13408.
- 5 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al., *Gaussian Inc Wallingford CT*, 2009.