Electronic Supplementary Information

Resorcin[4]arene cavitand with 1,3,2-benzodiazaborolyl walls as a fluorescence receptor for ammonium cations

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1. General

NMR spectra were taken a JEOL Lambda 500 (^{1}H: 500 MHz) or JEOL JNM-AL400, (^{1}H: 400 MHz) spectrometers. Chemical shifts (δ) are reported downfield from the initial standard Me_4Si. MALDI-TOF-MS was recorded on a BRUKER AUTOFLEX III where dithranol and distilled THF was used as a matrix and solvent, respectively. In addition, fast atom bombardment (FAB) mass spectra were obtained on a JEOL JMS-700 spectrometer where *m*-nitrobenzyl alcohol was used as a matrix. The absorption spectra and fluorescence spectra were measured using a Shimadzu UV-3100PC spectrophotometer and a JASCO FP-6300 spectrophotometer, respectively. Elemental analyses were obtained on a Yanaco CHN CORDER MT-5.

2. Material

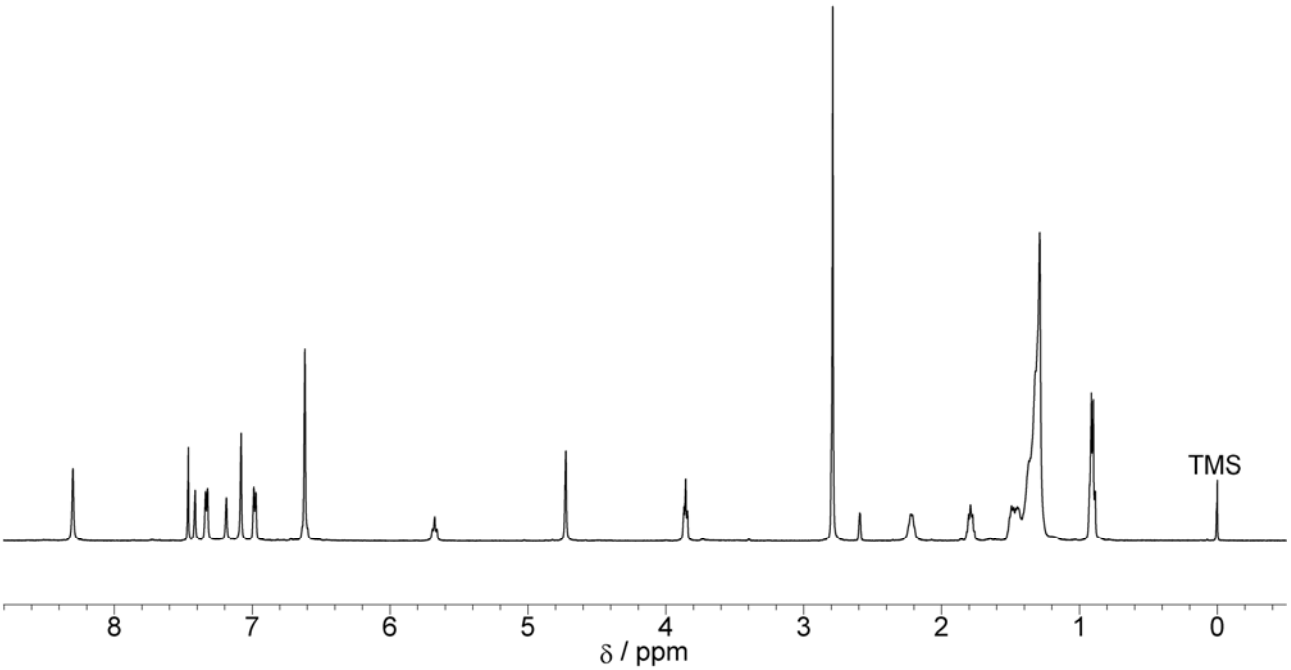
Reagents used for the synthesis were commercially available and used as supplied. Guest species were purchased from chemical suppliers among which quaternary ammonium ions as bromide or iodide salts were exchanged to the corresponding hexafluorophosphate salts using KPF_6. In addition, hexamethylethylenediammonium $2PF_6$ was prepared from tetramethylenediamine *via* methylation with an excess amount of MeI and anion exchange with KPF_6.

3. Synthesis of tetra(benzodiazaborole)-appended cavitand 1

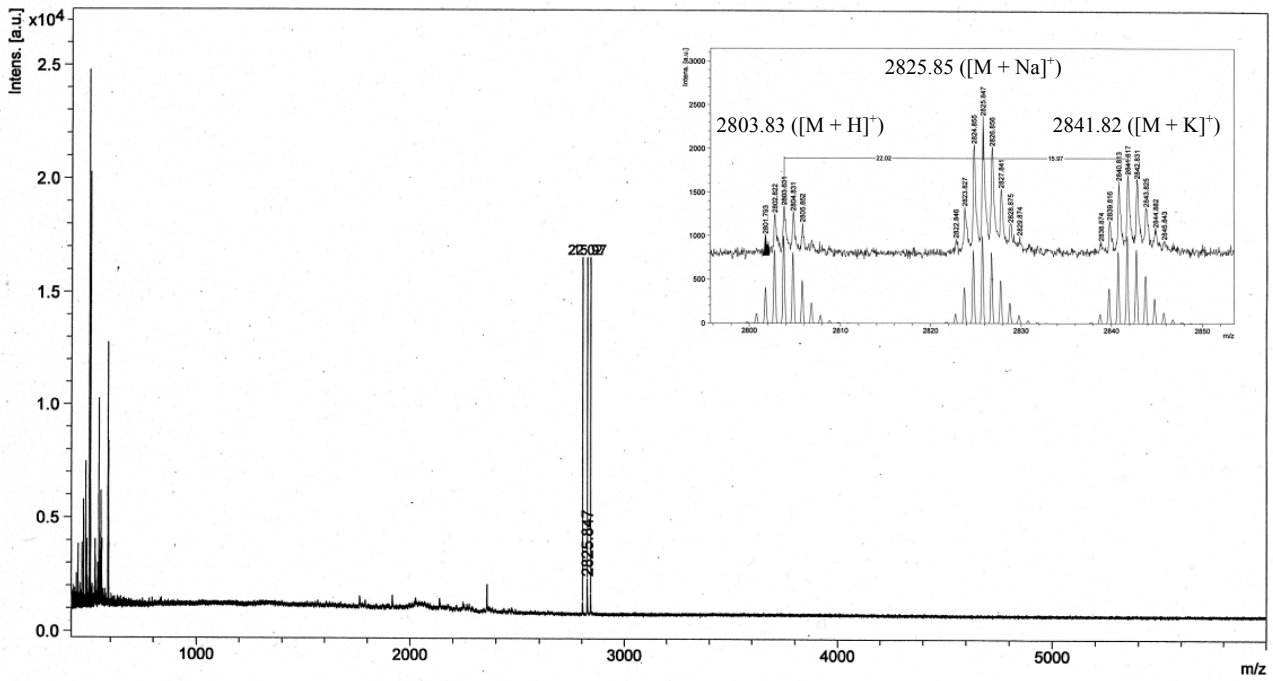
Octaaminocavitand (**2**·nHCl) (1.01 g, 0.557 mmol),[1] dissolved in EtOH-H_2O (1:1 v/v) (20 mL), was basified with 1N NaOH aqueous solution. The product was extracted with CH_2Cl_2 (50 mL × 3), the organic phase being washed with EtOH-H_2O (1:1 v/v) (50 mL), dried with Na_2SO_4, and evaporated under reduced pressure. After the dryness *in vacuo* for 1 h, a brown solid was obtained. This solid and 4-dihydroxyborylbenzyloxy-(4-octyloxy)benzene[2] (784.8 mg, 2.20 mmol) were dissolved in dry toluene (50 mL) under a N_2 atmosphere. The mixture was refluxed for 36 h at 70 °C using a Dean-Stark trap, and evaporated up to 1/3 volume. The addition of MeCN into the solution allows the detection of target as a precipitate, being followed by recrystallization with acetone to give **1** as a yellow solid (474 mg, 30 % yield): ^{1}H NMR (500 MHz, $CDCl_3$–DMSO-d_6 (9:1 v/v), 21 °C) δ 8.29 (s, 8H), 7. 41 (s, 4H), 7.32 (d, J = 7.6 Hz, 8H), 7.18 (s, 4H), 7.07 (s, 8H), 6.97 (d, J = 7.8 Hz, 8H), 6.61 (s, 16H), 5.67 (t, J = 8.3 Hz), 4.72 (s, 8H), 3.85 (t, J = 6.6 Hz, 8H), 2.22 (quart, J = 7.1 Hz, 8H), 1.79 (quint, J = 7.2 Hz, 8H), 1.52 – 1.46 (m, 8H), 1.45 – 1.42 (m, 8H), 1.41 – 1.29 (m, 96H), 0.927–0.885 (m, 24H); MALDI-TOF-MS m/z = 2803.83

$[M + H]^+$, 2825.85 $[M + Na]^+$, 2841.82 $[M + K]^+$; Anal. calcd. for $C_{180}H_{228}B_4N_8O_{16}$: C 77.18; H 8.27; N 4.00; Found: C 77.18; H 8.27; N 3.95 %.

<^{1}H NMR (500 MHz, $CDCl_3$–DMSO-d_6 (9:1 v/v), 21 °C) >



<MALDI-TOF-MS>



4. Synthesis of 4-(4-octyloxybenzeneoxymethyl)phenyl-1,3,2-benzodiazaborole 3

Under a N_2 atmosphere, phenylenediamine (501 mg, 4.63 mmol) and 4-dihydroxyborylbenzyloxy-(4-octyloxy)benzene (1.65 g, 4.62 mmol) were dissolved in dry toluene (150 mL). The mixture was stirred under reflux for 14 h. The resulting solid was collected and reprecipitated with THF–*n*-hexane. In this way, 1.17 g of **3** was obtained as a white solid in 59 % yield: ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.13 (s, 2H), 7.90 (d, J = 7.7 Hz, 2H), 7.47 (d, J = 7.7 Hz, 2H), 7.05 (dd, J = 5.6, 3.2 Hz, 2H), 6.94 (d, J = 9.1 Hz, 2H), 6.85 (d, J = 9.1 Hz, 2H), 6.81 (dd, J = 5.7, 3.2 Hz, 2H), 5.06 (s, 2H), 3.87 (t, J = 6.5 Hz, 2H), 1.66 (quart, J = 7.1 Hz, 2H), 1.38 (quint, J = 7.1 Hz, 2H), 1.31 – 1.26 (m, 8H), 0.86 (t, J = 6.8 Hz, 3H); FAB-MS m/z = 428 $[M]^+$; Anal. calcd. for $C_{27}H_{33}BN_2O_2$: C 75.70; H 7.76; N 6.54; Found: C 75.42; H 7.84; N 6.53 %.

Reference

1. A. R. Far, A. Shivanyuk and J. Rebek, Jr., *J. Am. Chem. Soc.*, 2002, **124**, 2854.
2. Y. Kubo, W. Yoshizumi and T. Minami, *Chem. Lett.*, 2008, **37**, 1238.

5. The determination of fluorescence quantum yield

The fluorescence quantum yield (Φ_{exp}) of **1** was calculated from eq. (1) (J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, 991).

$$\phi = \phi_R \times \frac{\int_0^\infty F(\lambda)\mathrm{d}\lambda}{\int_0^\infty F_R(\lambda)\mathrm{d}\lambda} \times \frac{A_R}{A} \times \frac{n^2}{{n_R}^2} \quad (1)$$

where $F(\lambda)$ and $F_R(\lambda)$ describe the corrected fluorescence intensities of the compound and the reference, respectively, and A and A_R describe the corresponding absorbance at the excitation wavelength (λ = 303 nm). The reference used was *p*-terphenyl (Φ_R = 0.92) (S. Maruyama and Y. Kawanishi, *J. Mater. Chem.*, 2002, **12**, 2245). The refractive indexes are n = 1.4246 for CH_2Cl_2 (solvent) and n_R = 1.4262 for cyclohexane, respectively. Although fluorescence spectrum of compound **1** was measured in CH_2Cl_2–DMSO (9:1 v/v), for the estimation of quantum yield in this study the refractive value of CH_2Cl_2 was employed.

6. 2D NOESY spectrum of 1 with hexyltrimethylammonium hexafluorophosphate 4

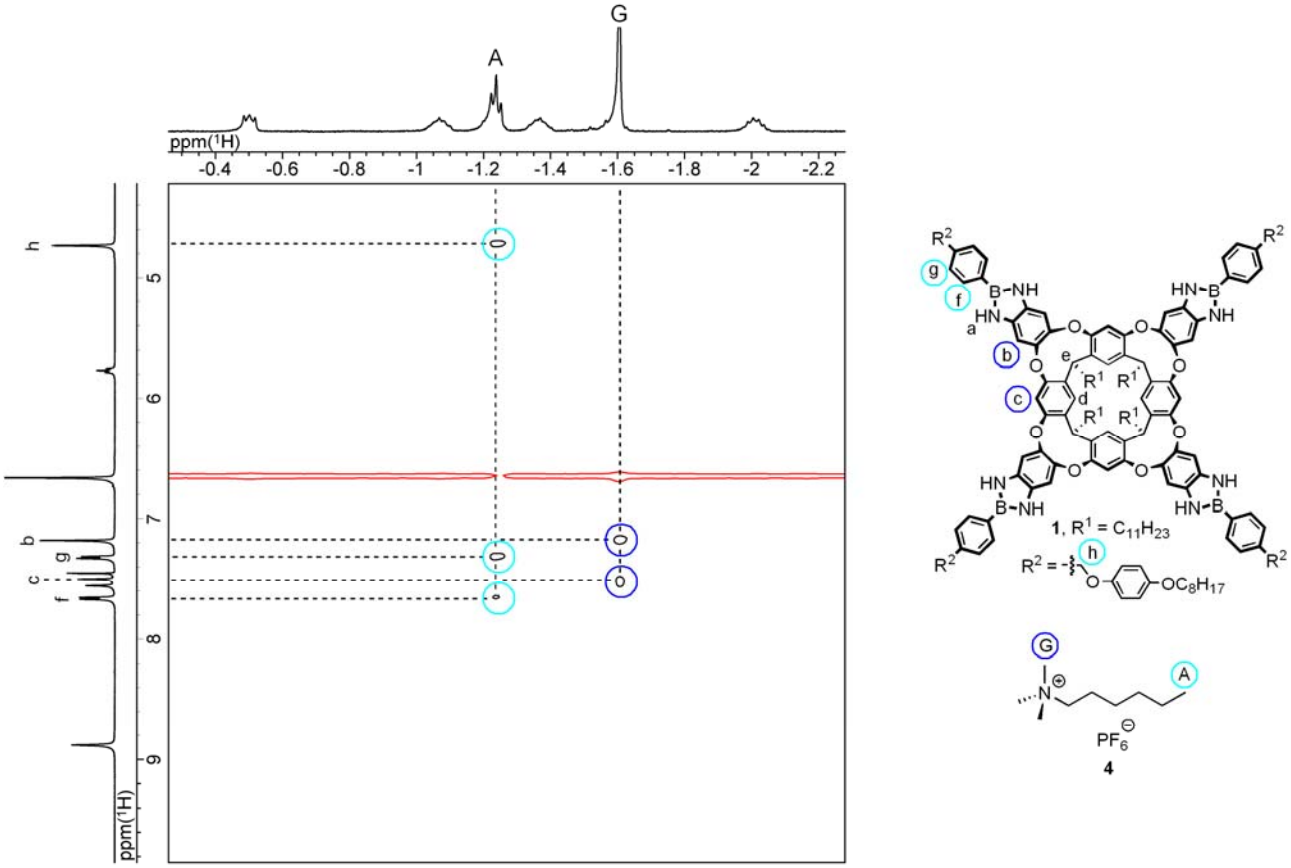
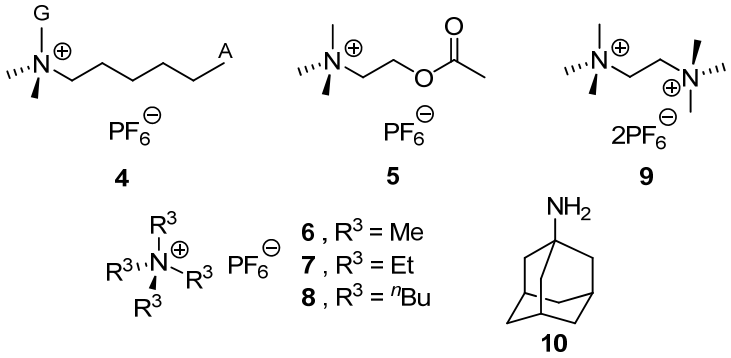


Figure S1. 2D NOESY spectrum of **1** (5 mM) and **4** (5 mM) in $CDCl_3$–DMSO-d_6 (9:1 v/v) at 25 °C, 500 MHz.

7. Fluorescence titrations of 1 with several guests



The emission scan parameters used are as follows: excitation at λ = 335 nm, excitation slit = 5 nm, emission slit = 10 nm, scanning rate = 500 nm min^{-1}. The scan range is from 310 nm to 500 nm. Figures S2 ~ S7 show fluorescence titrations of **1** with several guests. Among them the experimental data of Figures S2 and S3 could be approximately reproduced in terms of eq. (2) assuming the following equation to estimate the association constants K:

$$\frac{I}{I_0}-1=\frac{\left(\frac{I_{\lim}-I_0}{I_0}\right)}{2H_0K}[1+KH_0+KG_0-\{(1+KH_0+KG_0)^2-4K^2H_0G_0\}^{1/2}] \quad (2)$$

where H_0 and G_0 are concentrations of receptor **1** and guest, respectively. On another front I is the guest (**G**) concentration-dependent fluorescence intensity at 357 nm, with I_0 and I_{lim} denoting intensity at zero and infinite salt concentrations, respectively. The K values ($(1.6 \pm 0.71) \times 10^7$ M^{-1} for **1** with **5** and $(3.8 \pm 4.9) \times 10^8$ M^{-1} for **1** with **6**) were evaluated by three individual measurements.

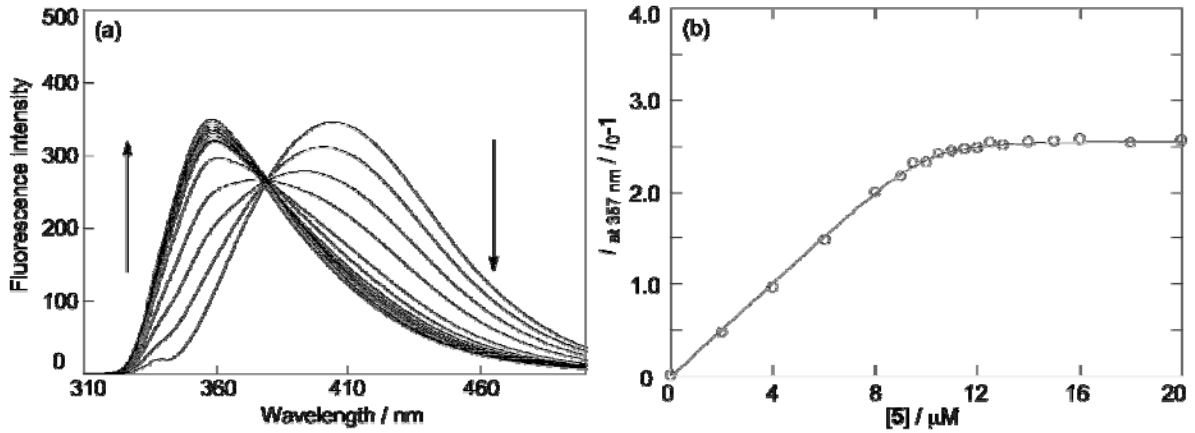


Figure S2. (a) Fluorescence spectra of **1** upon the addition of **5**, (b) plots of fluorescence intensity (I/I_0–1) at 357 nm upon the addition of incremental amounts of **5**. The data were collected in CH_2Cl_2–DMSO (9:1 v/v) at 25 °C, [**1**] = 10 μM, [**5**] = 0, 2, 4, 6, 8, 9, 9.5, 10, 10.5, 11, 11.5, 12, 12.5, 13, 14, 15, 16, 18, 20 μM.

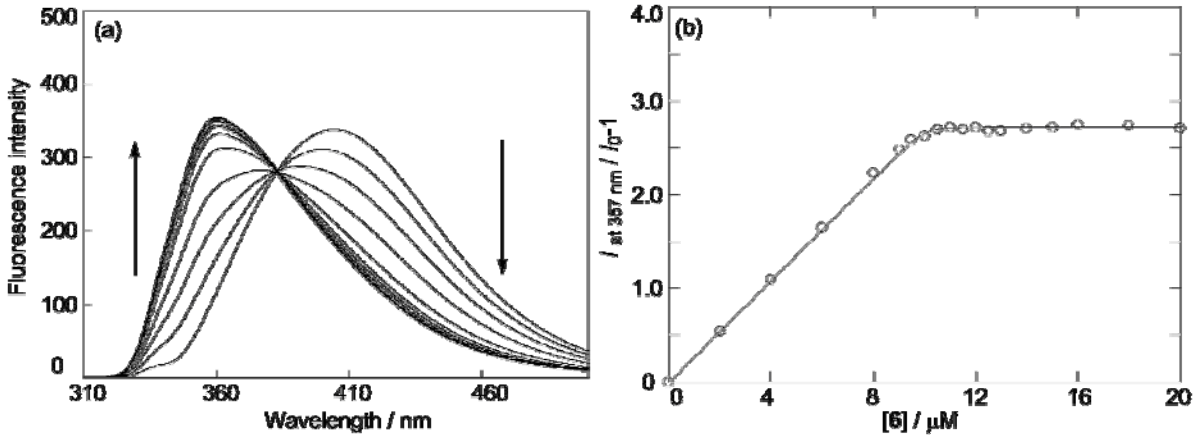


Figure S3. (a) Fluorescence spectra of **1** upon the addition of **6**, (b) plots of fluorescence intensity (I/I_0–1) at 357 nm upon incremental amounts of **6**. The data were collected in CH_2Cl_2–DMSO (9: 1 v/v) at 25 °C, [**1**] = 10 μM, [**6**] = 0, 2, 4, 6, 8, 9, 9.5, 10, 10.5, 11, 11.5, 12, 12.5, 13, 14, 15, 16, 18, 20 μM.

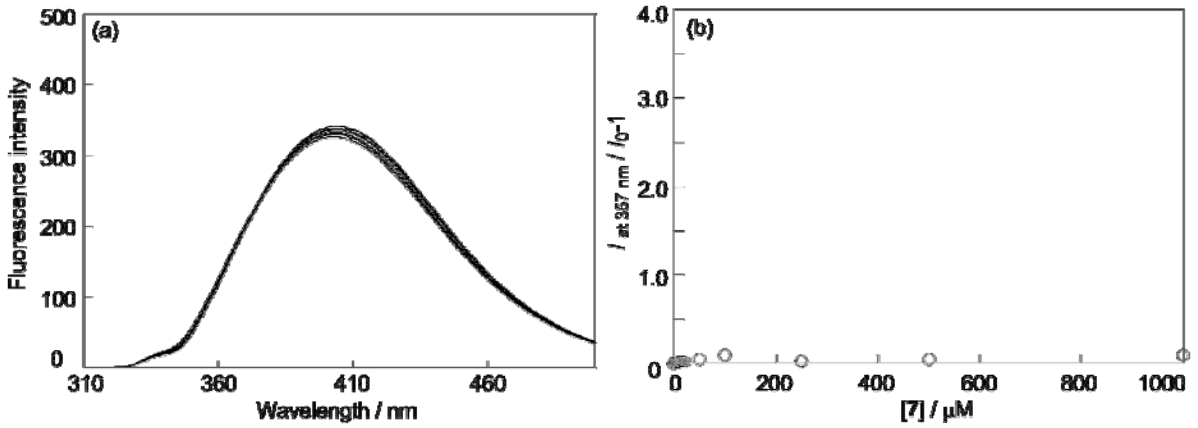


Figure S4. (a) Fluorescence spectra of **1** upon the addition of **7**, (b) plots of fluorescence intensity (I/I_0–1) at 357 nm upon the addition of incremental amounts of **7**. The data were collected in CH_2Cl_2–DMSO (9:1 v/v) at 25 °C, [**1**] = 10 μM, [**7**] = 0, 4, 8, 10, 15, 20, 50, 100, 250, 500, 1000 μM.

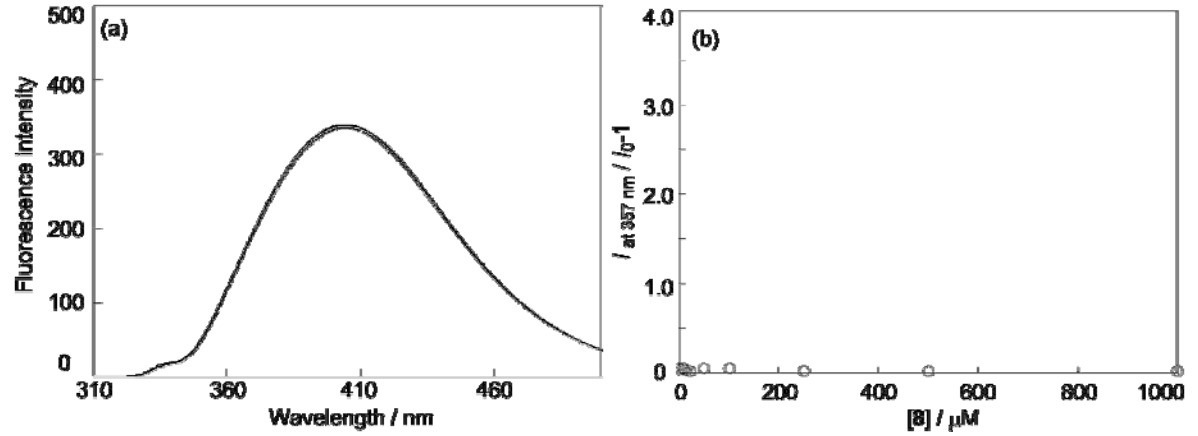


Figure S5. (a) Fluorescence spectra of **1** upon the addition of **8**, (b) plots of fluorescence intensity (I/I_0–1) at 357 nm upon the addition of incremental amounts of **8**. The data were collected in CH_2Cl_2–DMSO (9:1 v/v) at 25 °C, [**1**] = 10 μM, [**8**] = 0, 4, 8, 10, 15, 20, 50, 100, 250, 500, 1000 μM

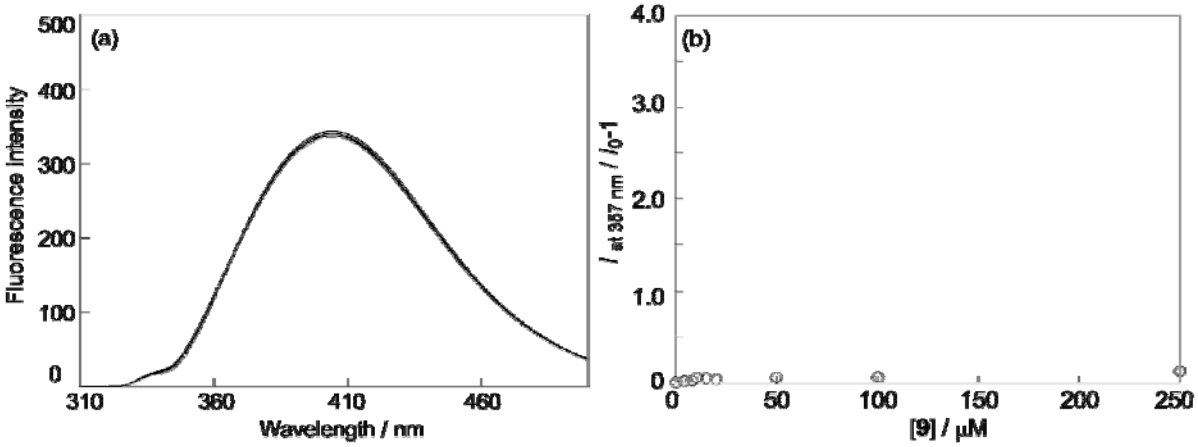


Figure S6. (a) Fluorescence spectra of **1** upon the addition of **9**, (b) plots of fluorescence intensity (I/I_0–1) at 357 nm upon the addition of incremental amounts of **9**. The data were collected in CH_2Cl_2–DMSO (9:1 v/v) at 25 °C, [**1**] = 10 μM, [**9**] = 0, 4, 8, 10, 15, 20, 50, 100, 250 μM.

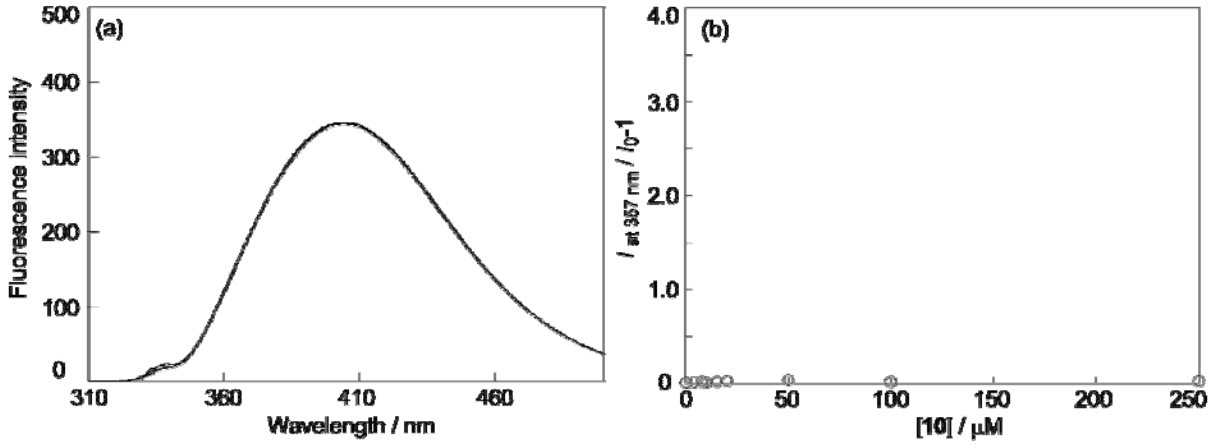


Figure S7. (a) Fluorescence spectra of **1** upon the addition of **10**, (b) plots of fluorescence intensity (I/I_0–1) at 357 nm upon the addition of incremental amounts of **10**. The data were collected in CH_2Cl_2–DMSO (9:1 v/v) at 25 °C, [**1**] = 10 μM, [**10**] = 0, 4, 8, 10, 15, 20, 50, 100, 250 μM.

8. Fluorescence titrations of control 3 with hexyltrimethylammonium hexafluorophosphate 4

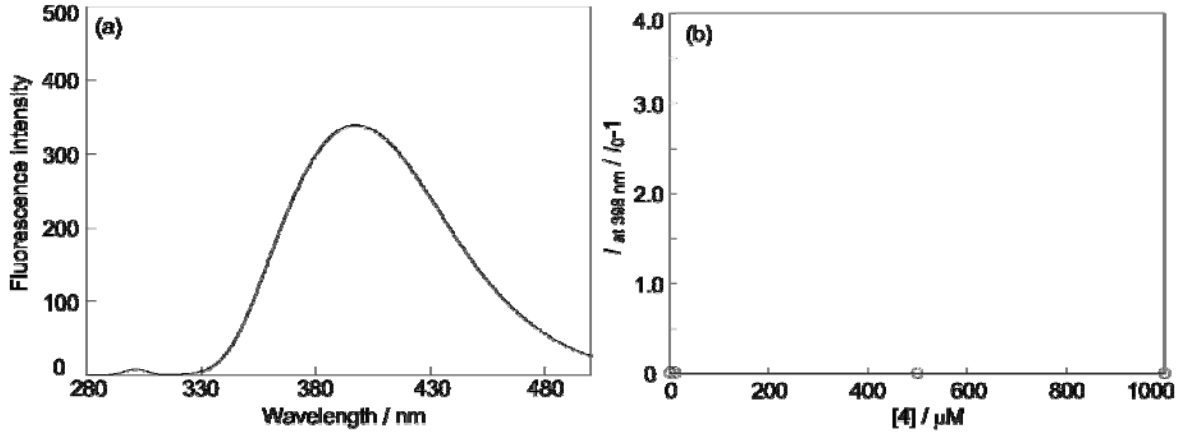


Figure S8. (a) Fluorescence spectra of **3** upon the addition of **4**, (b) plots of fluorescence intensity (I/I_0–1) at 398 nm upon the addition of incremental amounts of **4**. The data were collected in CH_2Cl_2–DMSO (9:1 v/v) at 25 °C, [**3**] = 10 μM, [**4**] = 0, 5, 10, 500, 1000 μM.

9. ^{1}H NMR spectra

The determination of binding constants by means of ^{1}H NMR was carried out as follows: a $CDCl_3$–DMSO-d_6 (9:1 v/v) solution of **1** and 1 equiv. of guests were allowed to equilibrate at room temperature in an NMR tube, and then ^{1}H NMR spectrum was acquired. Integration of the bound and free peaks corresponding to suitable host protons gave the equilibrium concentrations of bound and free host, from which the binding constant K could be determined. In this way the K values of **1** with **4** and **1** with **6** were estimated to be 9×10^5 M^{-1} and 2000 M^{-1}, respectively.

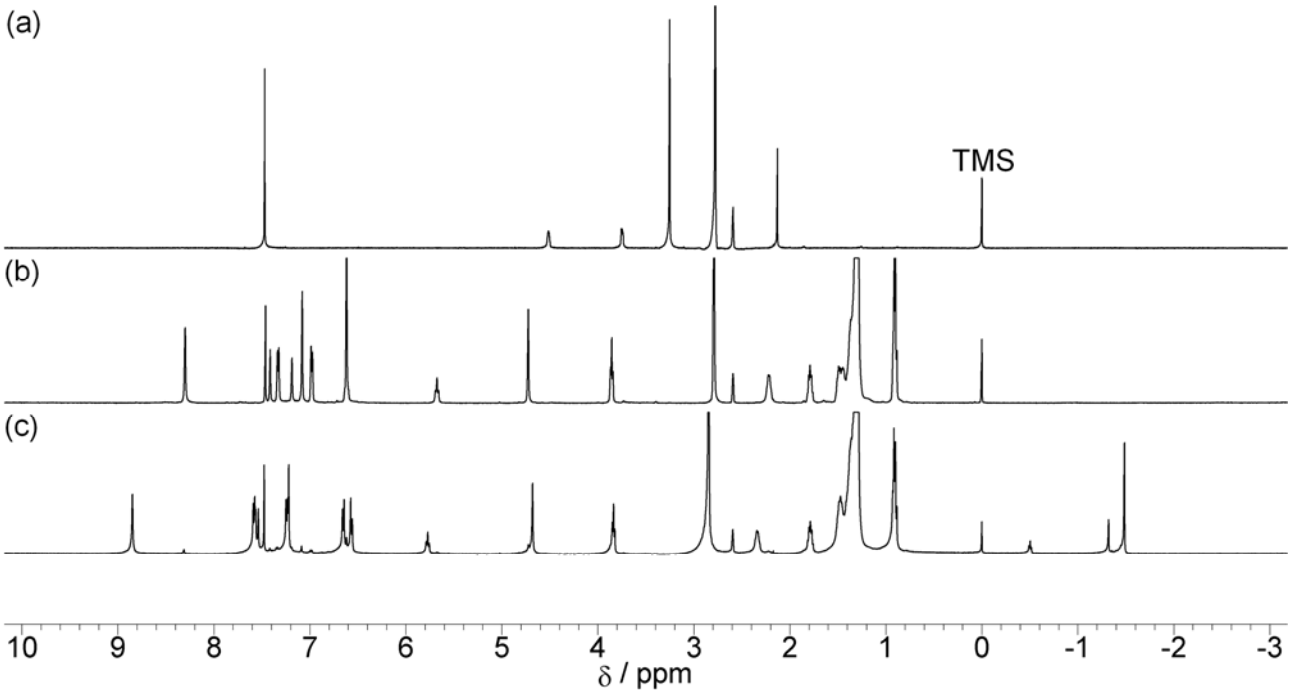


Figure S9. ^{1}H NMR (500 MHz) in $CDCl_3$–DMSO-d_6 (9:1 v/v) at 21 ºC: (a) acetylcholine PF_6^- **5** (2.5 mM), (b) **1** (2.5 mM), (c) **1** (2.5 mM) plus **5** (2.5 mM).

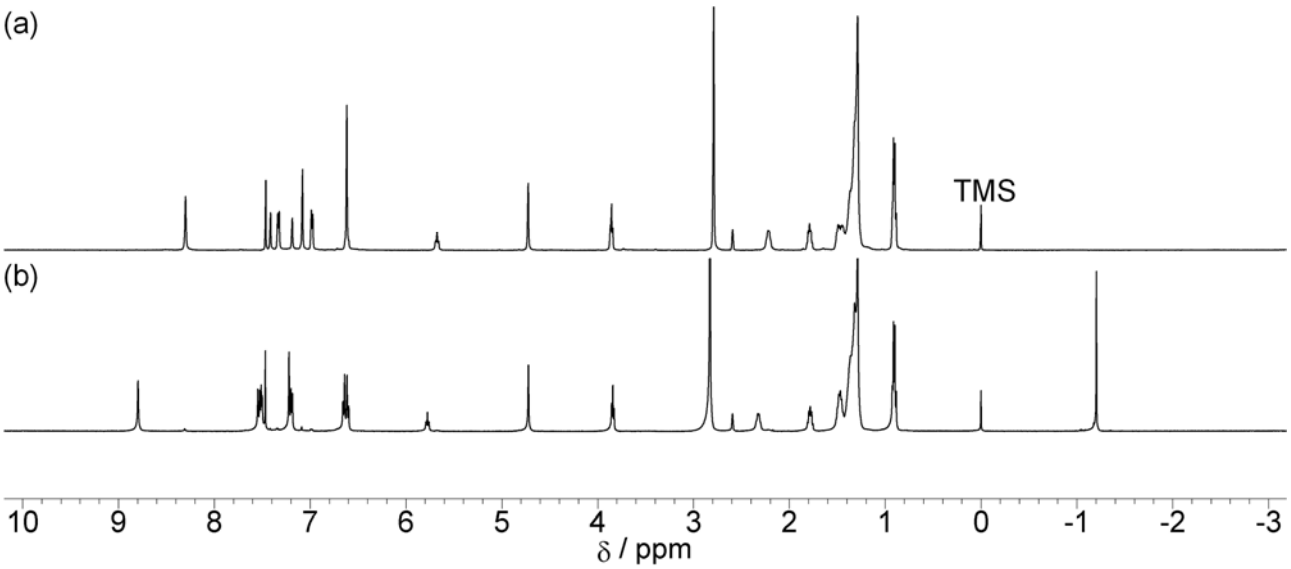


Figure S10. ^{1}H NMR (500 MHz) in $CDCl_3$–DMSO-d_6 (9:1 v/v) at 21 ºC: (a) **1** (2.5 mM), (b) **1** (2.5 mM) plus **6** (2.5 mM).

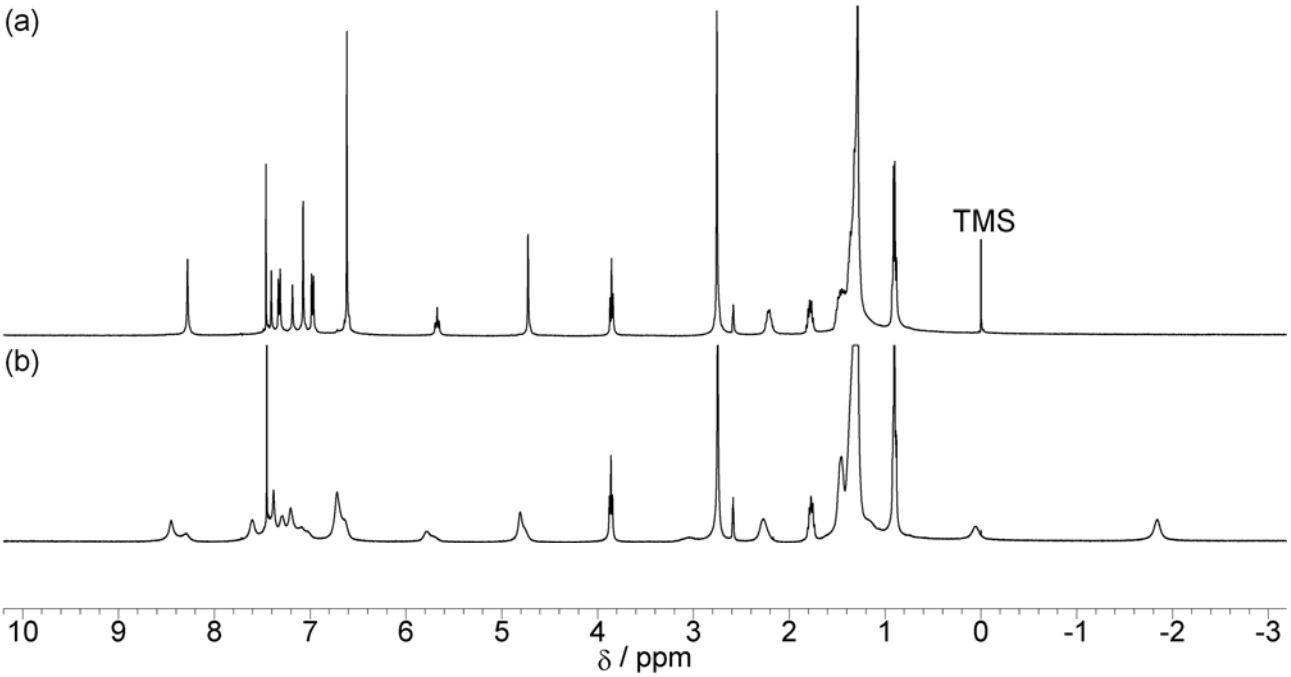


Figure S11. ^{1}H NMR (400 MHz) in $CDCl_3$–DMSO-d_6 (9:1 v/v) at 25 ºC: (a) **1** (2.5 mM), (b) **1** (2.5 mM) plus **7** (2.5 mM).

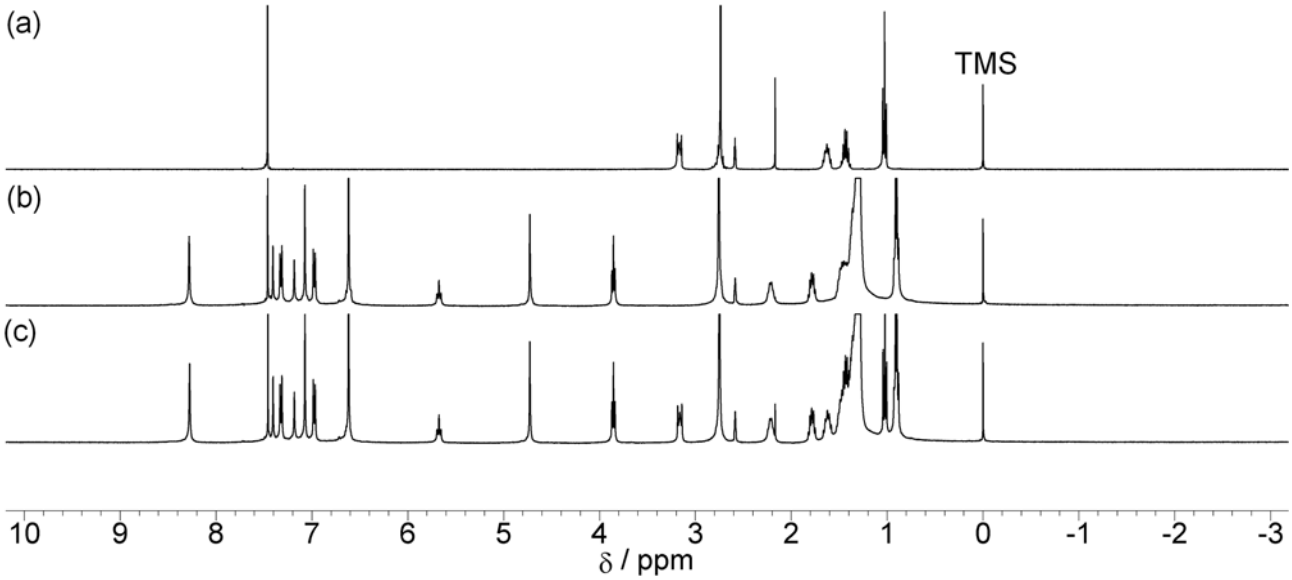


Figure S12. ^{1}H NMR (400 MHz) in $CDCl_3$–DMSO-d_6 (9:1 v/v) at 25 ºC: (a) **8** (2.5 mM), (b) **1** (2.5 mM), (c) **1** (2.5 mM) plus **8** (2.5 mM).

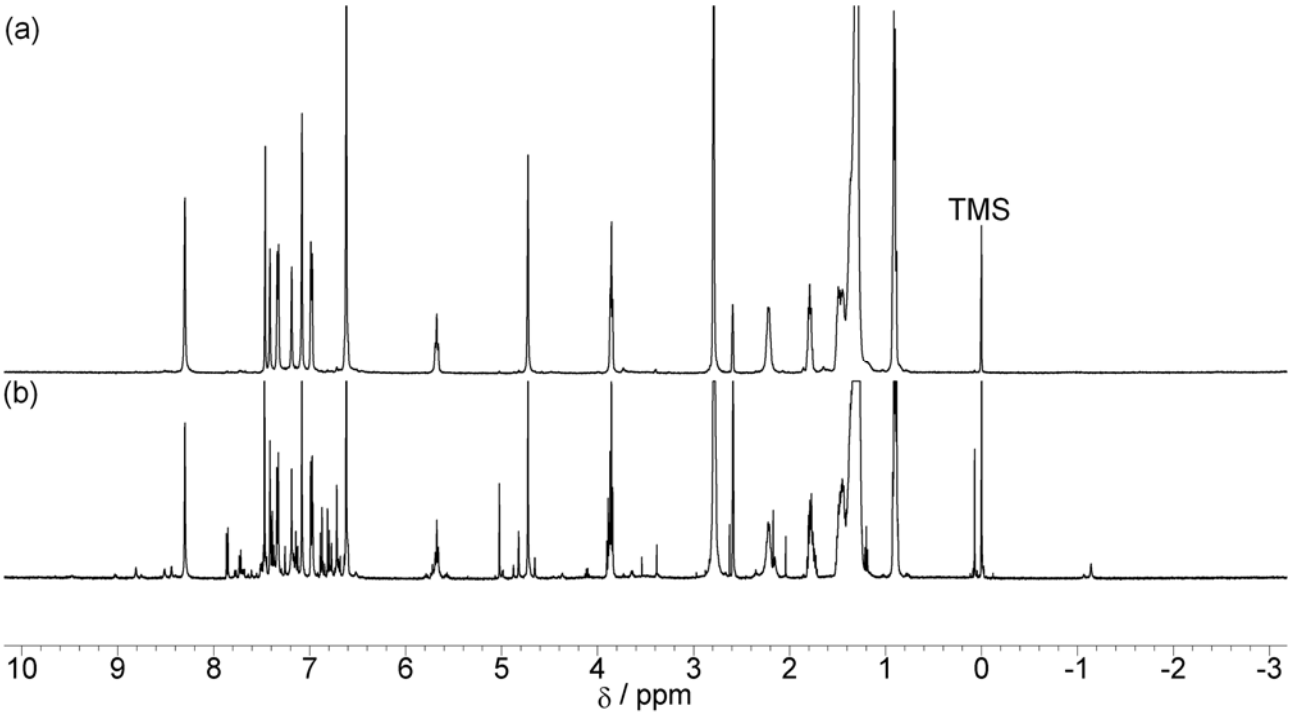


Figure S13. ^{1}H NMR (500 MHz) in $CDCl_3$–DMSO-d_6 (9:1 v/v) at 23 ºC: (a) **1** (2.5 mM), (b) The measurement was carried out after (solid (**9**)–liquid (2.5 mM of **1** in $CDCl_3$–DMSO-d_6 (9:1 v/v)) two-phase extraction.

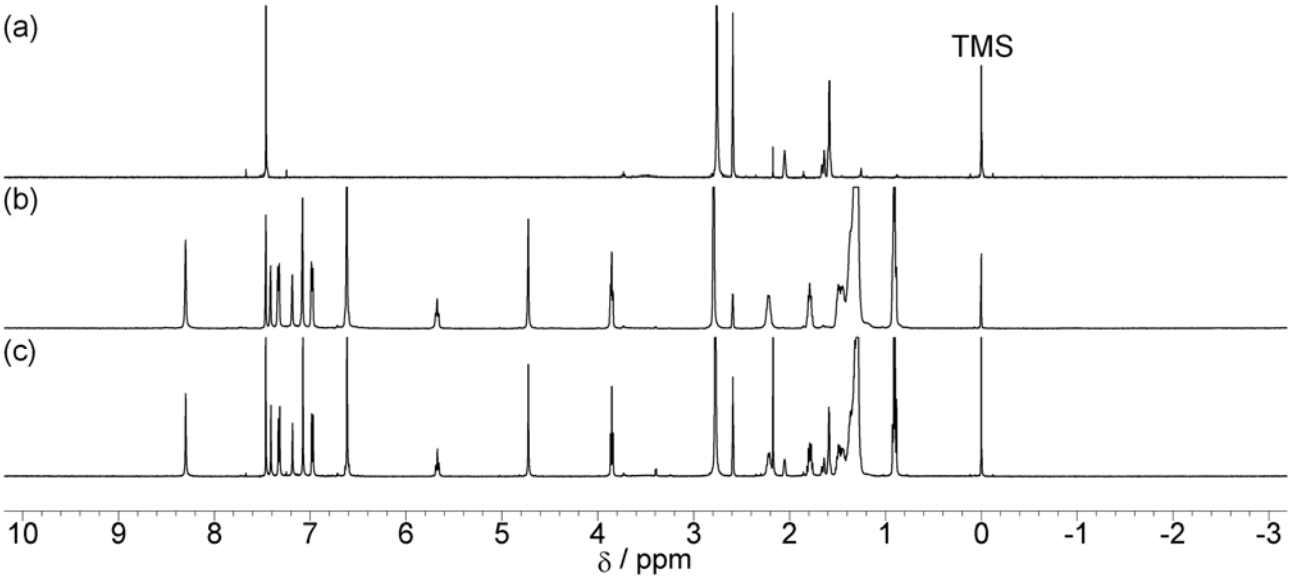


Figure S14. ^{1}H NMR (500 MHz) in $CDCl_3$–DMSO-d_6 (9:1 v/v) at 21 ºC: (a) 1-aminoadamantane **10** (1 mM), (b) **1** (2.5 mM), (c) **1** (1 mM) plus **10** (1 mM). Because 1-aminoadamantane **10** has a low solubility in $CDCl_3$–DMSO-d_6 (9:1 v/v), concentration of 1 mM was employed for the measurements of (a) and (c).

10. ^{1}H NMR spectra for the control experiment using 3

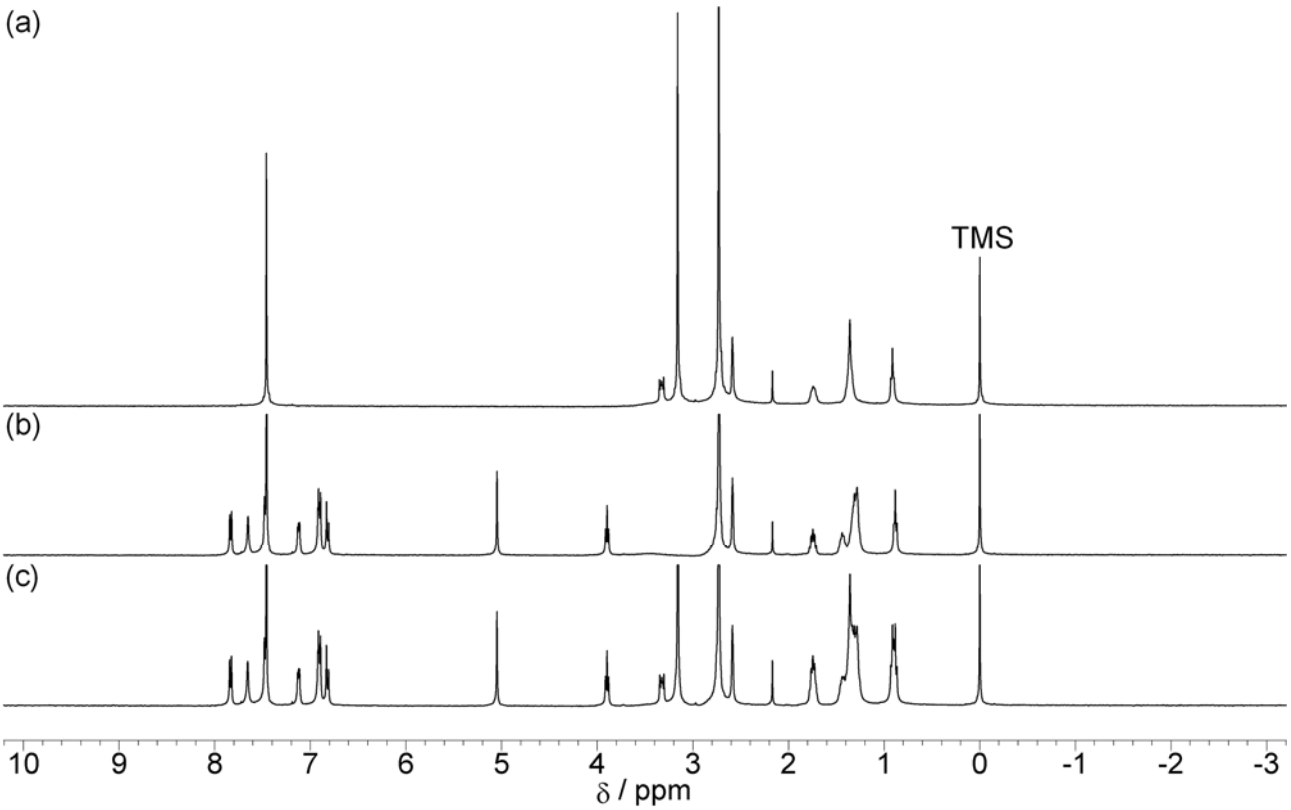


Figure S15. ^{1}H NMR (400 MHz) in $CDCl_3$-DMSO-d_6 (9:1 v/v) at 25 ºC: (a) **4** (2.5 mM), (b) **3** (2.5 mM), (c) **3** (2.5 mM) plus **4** (2.5 mM).