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SUPPORTING INFORMATION

DOI: 10.1002/ejoc.201400025
Title: Calixarene-Mediated Liquid-Membrane Transport of Choline Conjugates
Author(s): Birendra Babu Adhikari, Ayu Fujii, Michael P. Schramm*

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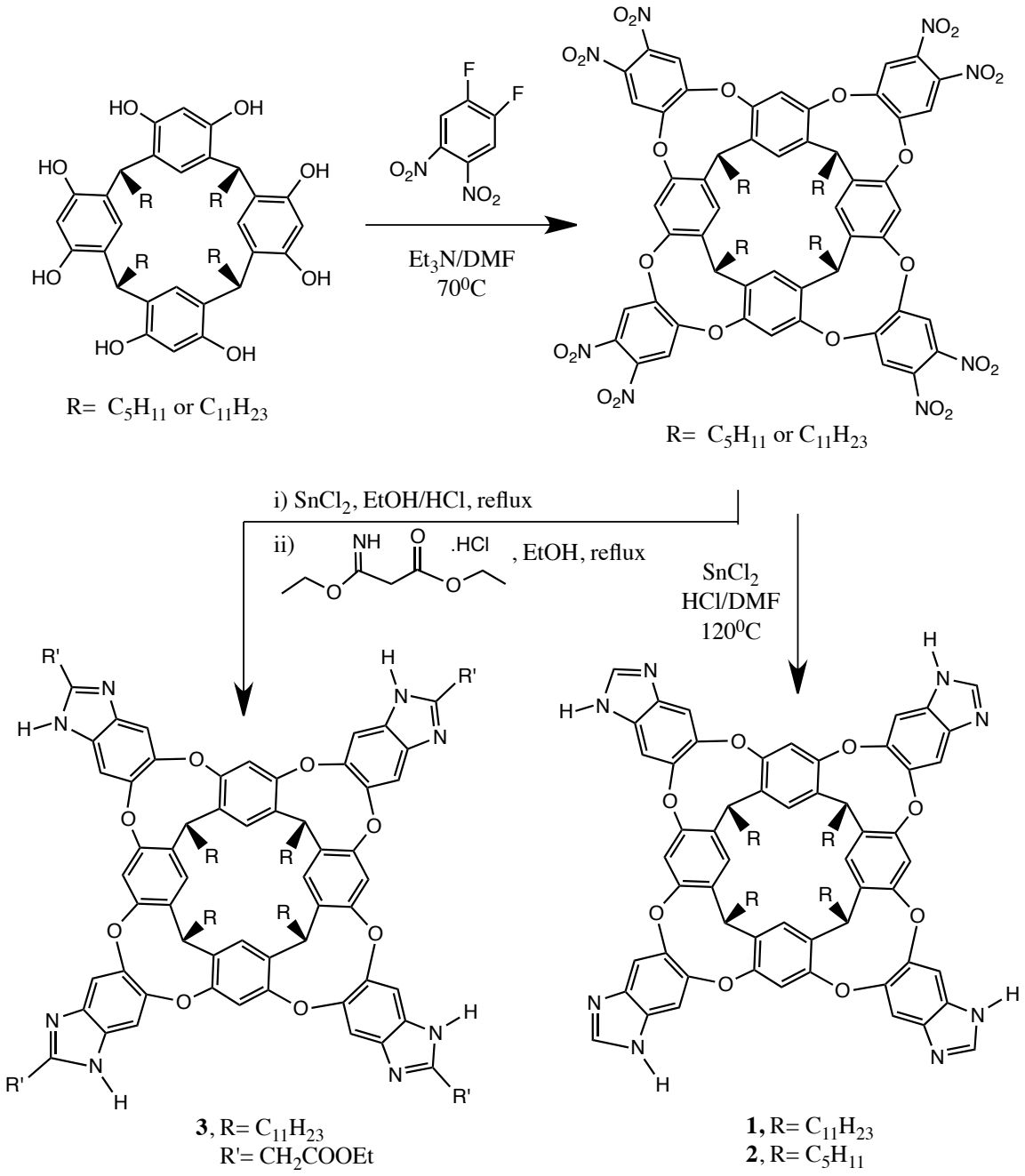
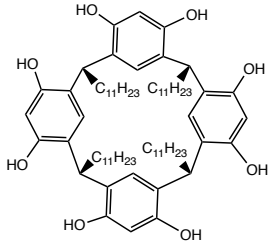
Scheme for synthesis of resorcinarene-based cavitands



Scheme 1. Synthesis of resorcinarene-based receptors

Synthesis of C_{11} footed resorcinarene[1]



To the mixture of 16.5 g (0.15 mmoles) resorcinol and 29.20 g (0.15 mmoles, 1 eq) dodecanal in 120 mL ethanol at 2 ^{0}C was added 24 mL conc. HCl over the period of 30 mins. The mixture was slowly heated to 75 ^{0}C and stirred overnight at that temperature. The resulting wine red colored solution was allowed to cool to room temperature and then slowly poured into water (400 mL). The resulting precipitate was collected by filtration and washed with water (2×100 mL). The precipitate was taken up in 200 mL chloroform and the solution was transferred to a separatory funnel. The separated organic layer was dried with anhy. $MgSO_4$, filtered and the solvent removed to dryness by rotary evaporation. The solid was dissolved in 80 mL hot methanol and the resulted orange colored solution was kept inside refrigerator overnight. The precipitate formed was collected by filtration and recrystallization of the material twice from methanol yielded 4.7 gram tan solid. The filtrate of the first crystallization was concentrated to dryness and pure product (3.7 g) was obtained after flash chromatography using DCM: Acetone = 1:1 as an eluting agent.[1] Total yield = 8.4 g (42%). ^{1}H NMR (400 MHz, Acetone-d_6, 25 ^{0}C) δ 0.88 (t, J= 6.8 Hz, 12 H), 1.29 (bm, 64 H), 1.36 (bm, 8 H), 2.29 (q, J= 6.8 Hz, 8 H), 4.29 (t, J= 7.6 Hz, 4 H), 6.23 (s, 4 H), 7.54 (s, 4 H), 8.49 (s, 6 H).

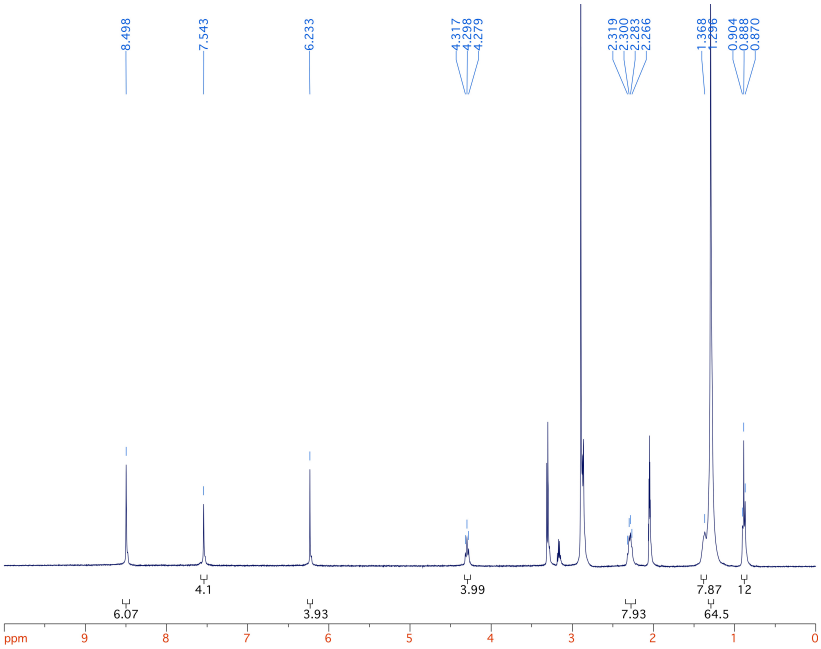
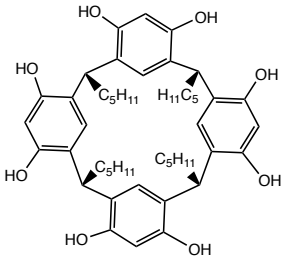


Figure 1. ^{1}H NMR (400 MHz) of C_{11} footed resorcinarene in acetone-d6.

1. L. M. Tunstad, J. A. Tucker, E. Dalcanale, J. Weiser, J. A. Bryant, J. C. Sherman, R. C. Helgeson, C. B. Knobler, D. J. Cram, *J. Org. Chem.*, **1989**, 54, 1305-1312.

Synthesis of C_5 footed resorcinarene[1]



To the mixture of 8.8 g (78 mmoles) resorcinol and 9.56 g (93.6 mmoles, 1.2 eq) hexanal in 120 mL ethanol at 2 ^{0}C was added 30 mL conc. HCl over the period of 30 mins. The mixture was slowly heated to 75 ^{0}C and stirred overnight at that temperature. The resulting wine red colored solution was allowed to cool to room temperature and then slowly poured into water (250 mL). The resulting precipitate was collected by filtration and washed with water (2×50 mL). The precipitate was suspended in 300 mL DCM and added acetone a little at a time till the suspension turned to solution. The solution was then transferred to a separatory funnel and the separated organic layer was dried with anhy. $MgSO_4$. The solvent was removed by rotary evaporation and the pure product was obtained after flash chromatography using DCM: Acetone = 2:1 as eluting agent (5.63 g, 35.8% yield). ^{1}H NMR (400 MHz, Acetone-d_6, 25 ^{0}C) δ 0.88 (t, J = 6.8 Hz, 12 H), 1.27-1.32 (m, 24 H), 2.29 (q, J = 6.8 Hz, 8 H), 4.29 (t, J = 7.6 Hz, 4 H), 6.12 (s, 4 H), 7.56 (s, 4 H), 8.45 (s, 4 H).

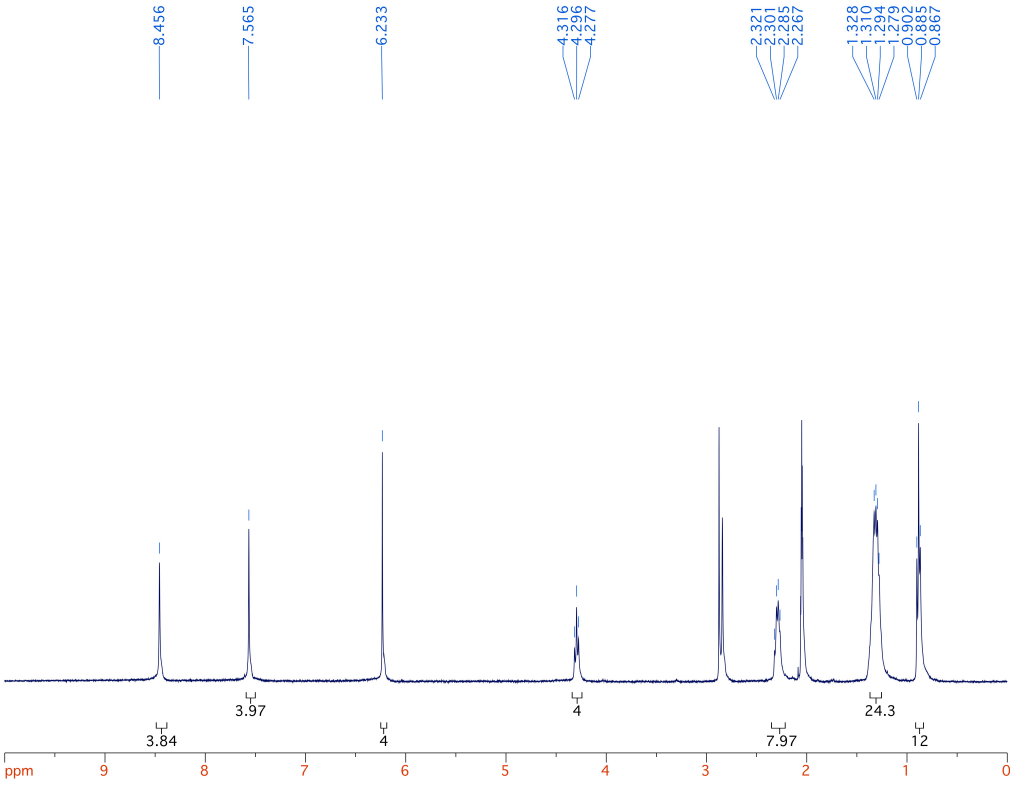
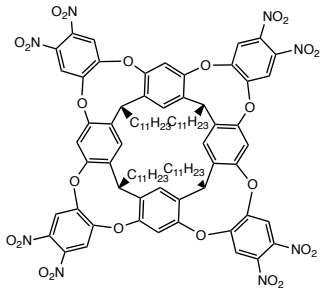


Figure 2. ^{1}H NMR (400 MHz) of C_5 footed resorcinarene in acetone-d6.

Synthesis of octanitro derivative of C_{11} footed resorcinarene[2]



To the mixture of 1.10 g (1.0 mmol) C_{11}-footed resorcinarene and 0.90 g (4.4 mmol, 4.4 eq) 1,2-difluoro-4,5-dinitrobenzene in 50 mL dry DMF was added 1.62 g (16.0 mmol, 16 eq) triethylamine dropwise. The resulting tan solution was slowly heated to 70 ^{0}C and stirred at that temperature for 16 h. The reaction mixture was cooled to room temperature and poured into 50 mL 0.1 M HCl solution. The resulting bright yellow precipitate was collected by filtration, washed with water and dried under high vacuum. Pure product was obtained after flash chromatography using 9:1 DCM: Hexane as eluting agent (1.03 g, 58.52%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{0}C) δ 0.87 (t, J = 6.8 Hz, 12 H), 1.23 (bs, 72 H), 1.97-2.06 (m, 8 H), 3.92 (t, J = 6.8 Hz, 4 H), 6.19 (s, 2 H), 7.00 (s, 4 H), 7.21 (s, 2 H), 7.63 and 7.65(2×s, 8 H).

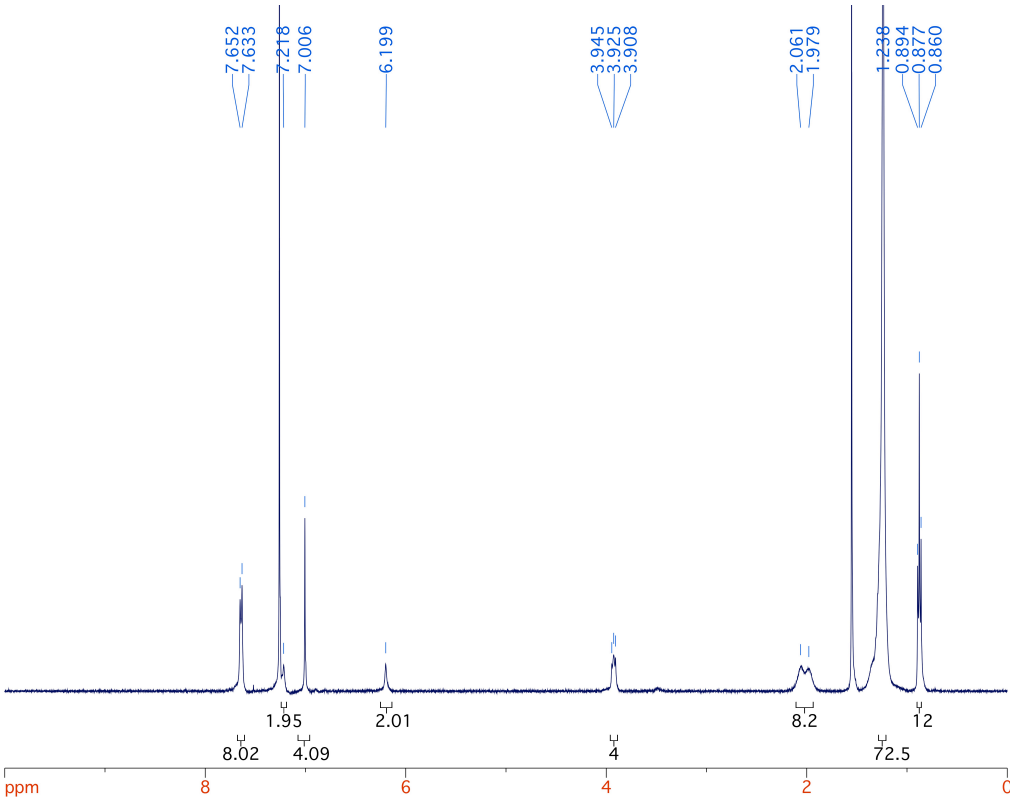


Figure 3. ^{1}H NMR (400 MHz) of octanitro derivative of C_{11} footed resorcinarene in $CDCl_3$.

2. F. C. Tucci, D. M. Rudkevich, J. Rebek, Jr., *J. Org. Chem.*, **1999**, 64, 4555-4559.

Synthesis of octanitro derivative of C_5 footed resorcinarene

The desired compound was synthesized by adopting the procedure reported for the synthesis of C_{11} footed analog.[2] To the mixture of 1.20 g (1.5 mmol) C_5 footed resorcinarene and 1.35 g (4.4 mmol, 4.4 eq) 1,2-difluoro-4,5-dinitrobenzene in 70 mL dry DMF was added 3.03 g (30.0 mmol, 20 eq) triethylamine dropwise. The resulting tan solution was slowly heated to 70 ^{0}C and stirred at that temperature for 16 h. The reaction mixture was cooled to room temperature and poured into 70 mL 0.1 M HCl solution. The resulting yellow precipitate was collected by filtration, washed with water and dried under high vacuum. The crude product was washed with DCM (3×20 mL) and the solid was collected by filtration. After vacuum drying, 0.8 g yellow solid was obtained. Rotary evaporation of the solvent from the filtrate followed by flash chromatography of the crude product using DCM as eluting agent afforded 0.3 g yellow solid as pure product (overall yield = 1.1 g, 49%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 ^{0}C) δ 0.83 (t, J = 6.8 Hz, 12 H), 1.23-1.33 (bm, 24 H), 2.33 (bs, 8 H), 5.49 (bs, 4 H), 7.78 (s, 4 H), 8.20 (s, 4 H) and 8.78 (s, 8 H).

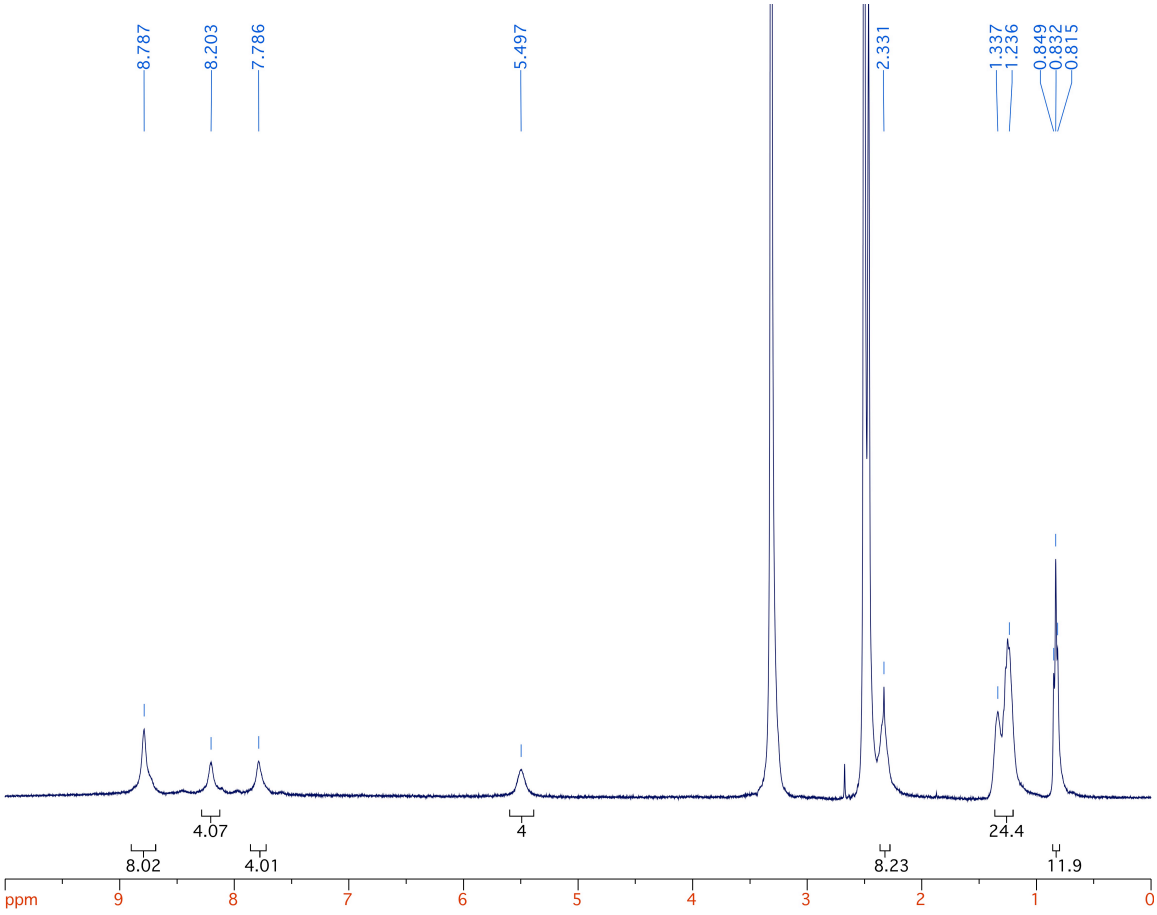


Figure 4. ^{1}H NMR (400 MHz) of octanitro derivative of C_5 footed resorcinarene in DMSO-d6.

Synthesis of C_{11} footed tetrabenzimidazole cavitand 1[3]

The mixture of 0.5 g (0.28 mmoles) octanitro derivative, 2.12 g (11.2 mmoles, 40 eq) $SnCl_2$ and 30 mL 2:1 mixture of DMF and conc. HCl was heated under argon at 120 ^{0}C for 24 hrs. Then, the reaction mixture was cooled to room temperature and poured into ice-water (100 mL). The precipitate formed was collected by filtration and washed with water. After drying under high vacuum overnight at 50 ^{0}C, 0.4 g off-white solid was obtained (90.23% yield). ^{1}H NMR (400 MHz, $CDCl_3$: MeOH-d_4= 4:1, 25 ^{0}C) δ 0.78 (t, J = 6.8 Hz, 12 H), 1.18 (bs, 64 H), 1.34-1.35 (bs, 8 H), 2.13 (q, J = 6.8 Hz, 8 H), 5.61 (t, J = 7.6 Hz, 4 H), 7.09 (s, 4 H), 7.45 (s, 4 H), 7.82 (bs, 8 H), 8.20 (bs, 4 H). M/Z, calculated for $C_{100}H_{120}O_8N_8$ 1562.07, found $[M+H]^+$ at 1563 and $[M+2H]^{2+}$ at 782.

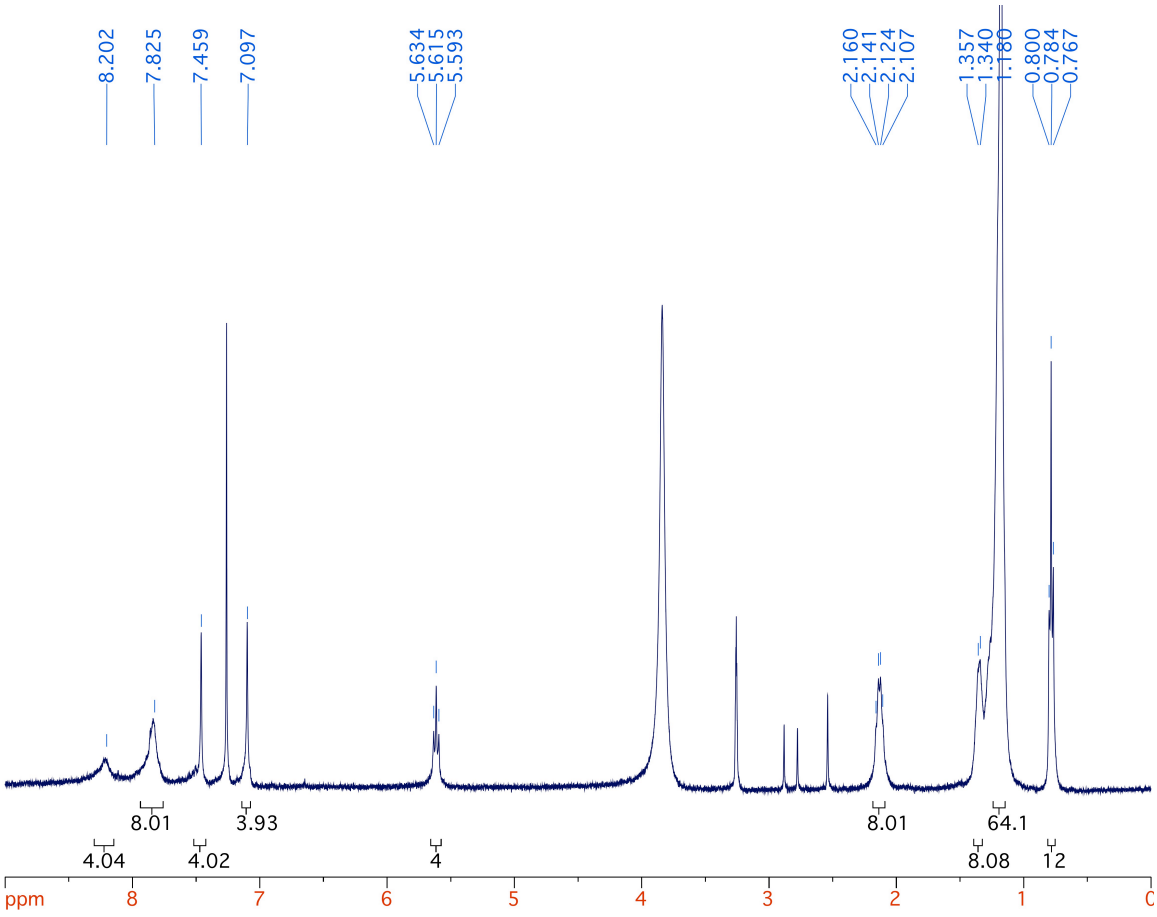


Figure 5. ^{1}H NMR (400 MHz) of 1 in $CDCl_3$: MeOH-d4 (4:1).

3. H.-J. Choi, Y. S. Park, J. Song, S. J. Youn, H.-S. Kim, S.-H. Kim, K. Koh, K. Paek, *J. Org. Chem.*, **2005**, 70, 5974-5981.

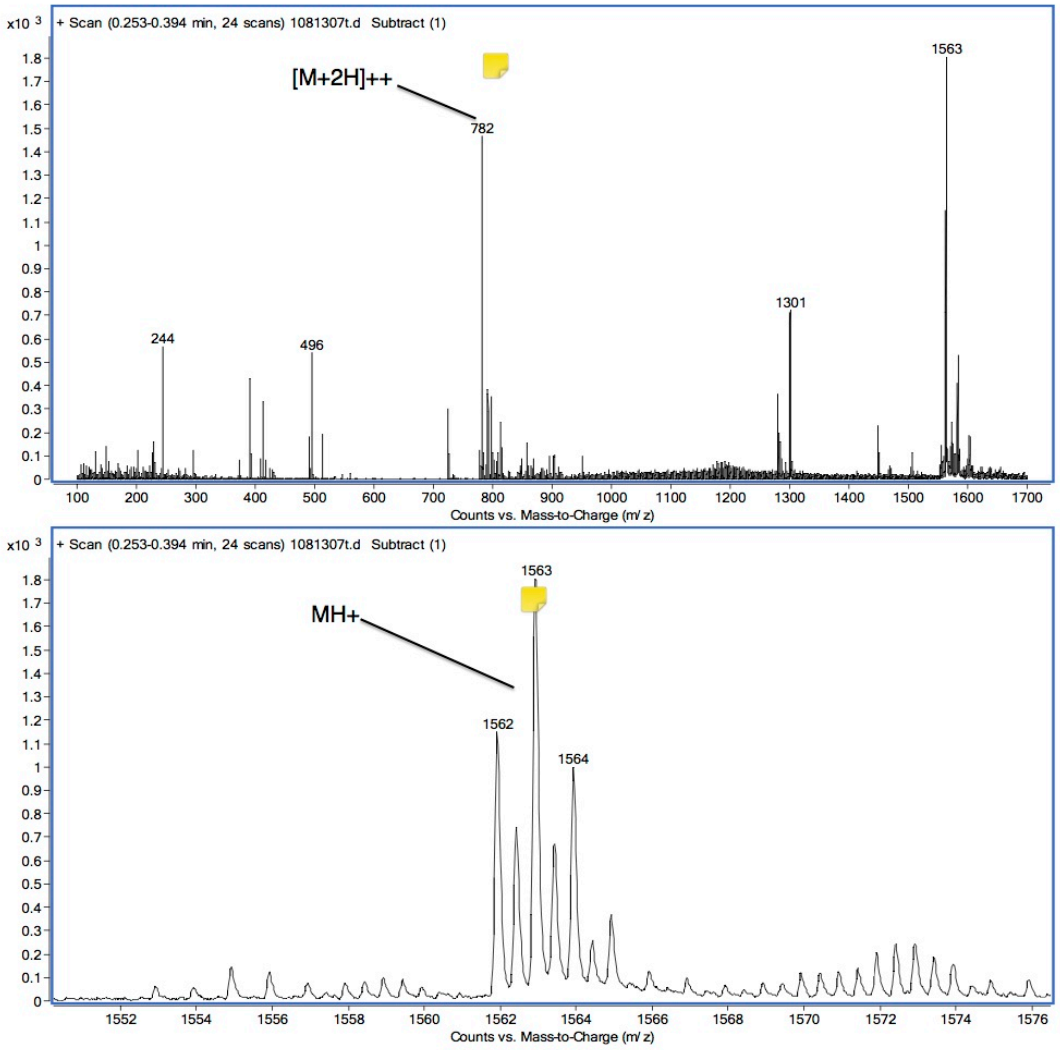


Figure 6. Mass spectrum of 1. $[M+H]^+$ at 1563 and $[M+2H]^{2+}$ at 782 amu.

Synthesis of C_5 footed tetrabenzimidazole cavitand 2

The desired product was also obtained by following the procedure adopted for the synthesis of **1** from C_{11} footed analog.[3] In a typical run, the mixture of 0.2 g (0.14 mmoles) octanitro cavitand, 1.08 g (5.6 mmoles, 40 eq) $SnCl_2$ and 15 mL 2:1 mixture of DMF and conc. HCl was heated under argon at 120 ^{0}C for 24 hrs. Then, the reaction mixture was cooled to room temperature and poured into ice-water (50 mL). The precipitate formed was collected by filtration and washed with water. The solid was taken up in DCM/MeOH 4:1 and the solvent was removed by rotary evaporation. After drying under high vacuum overnight at 50 ^{0}C, 0.17 g off-white solid was obtained (89.6% yield). ^{1}H NMR (400 MHz, $CDCl_3$: MeOH-d_4 = 4:1, 25 ^{0}C) δ 0.82 (t, J = 6.8 Hz, 12 H), 1.23-1.32 (bm, 24 H), 2.12 (bm, 8 H), 5.62 (t, J = 8.4 Hz, 4 H), 7.13 (s, 4 H), 7.54 (s, 4 H), 8.18 (s, 8 H), 8.77 (bs, 4 H). M/Z, calculated for $C_{76}H_{77}O_8N_8$ 1225.43, found $[M+H]^+$ at 1225.55.

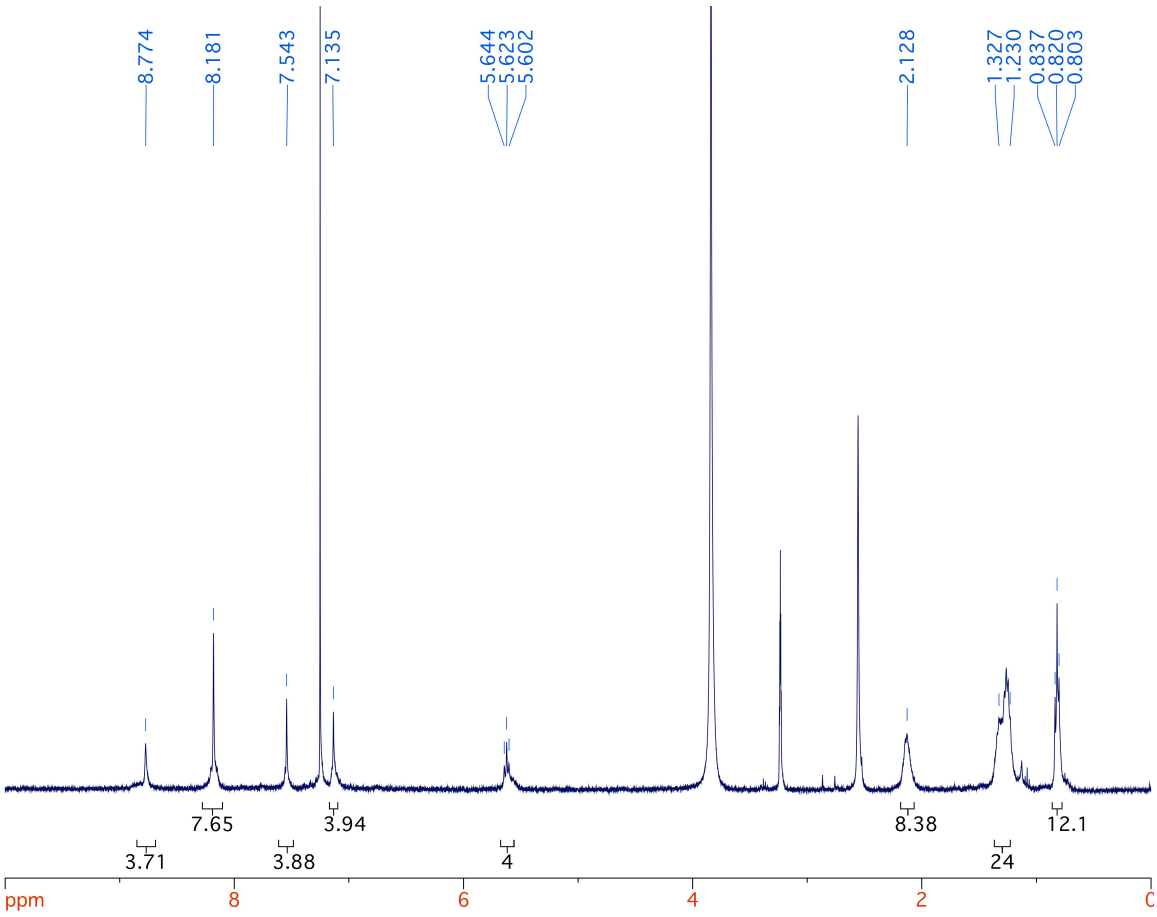


Figure 7. ^{1}H NMR (400 MHz) of 2 in $CDCl_3$: MeOH-d4 (4:1).

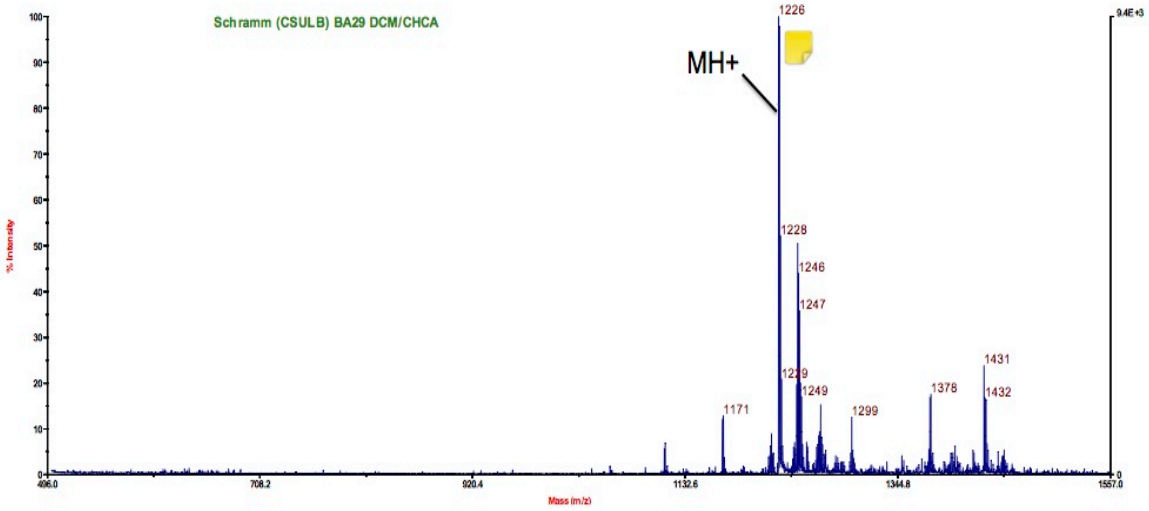


Figure 8. Mass spectrum of 2. $[M+H]^+$ at 1225.55 amu.

Synthesis of C_{11} footed immidate cavitand 3[4]

The mixture of 0.36 g (0.2 mmoles) C_{11} footed octanitro derivative, 1.51 g (8.0 mmoles, 40 eq) $SnCl_2$, 20 mL ethanol and 8 mL conc. HCl was stirred at refluxing condition under argon for 20 h. Then, the reaction mixture was cooled to room temperature and ethanol was removed by rotary evaporation. The resulting white solid was collected by filtration and washed with water (2×10 mL). After drying under high vacuum overnight, 0.32 g octaamine hydrochloride was obtained as off-white solid (86.5% yield), which was subjected to next step reaction without further purification. To the mixture of 0.32 g (0.176 mmoles) octaamine hydrochloride and 0.31 g (1.58 mmoles, 9 eq) ethyl 3-ethoxy-3-iminopropionate hydrochloride under argon was added 10 mL dry ethanol and the temperature was slowly raised to 80 ^{0}C and stirred for 24 h at that temperature. Then, the reaction mixture was allowed to cool to room temperature and the solvent was removed by rotary evaporation. The solid was taken up in dry methanol (20 mL), the suspension was filtered and the residue was washed with dry methanol (3×20 mL). After drying under high vacuum overnight, 0.31 g off-white solid was obtained in 92.26% yield. ^{1}H NMR (400 MHz, $CDCl_3$: MeOH-d_4 = 9:1, 25 ^{0}C) δ 0.85 (t, J= 6.8 Hz, 12 H), 1.24-1.28 (bm, 84 H), 1.41 (bm, 8 H), 2.20 (q, J= 6.8 Hz, 8 H), 4.19 (q, J= 7.6 Hz, 8 H), 5.69 (t, J= 7.6 Hz, 4 H), 7.20 (s, 4 H), 7.52 (s, 4 H), 8.12 (bs, 8 H).

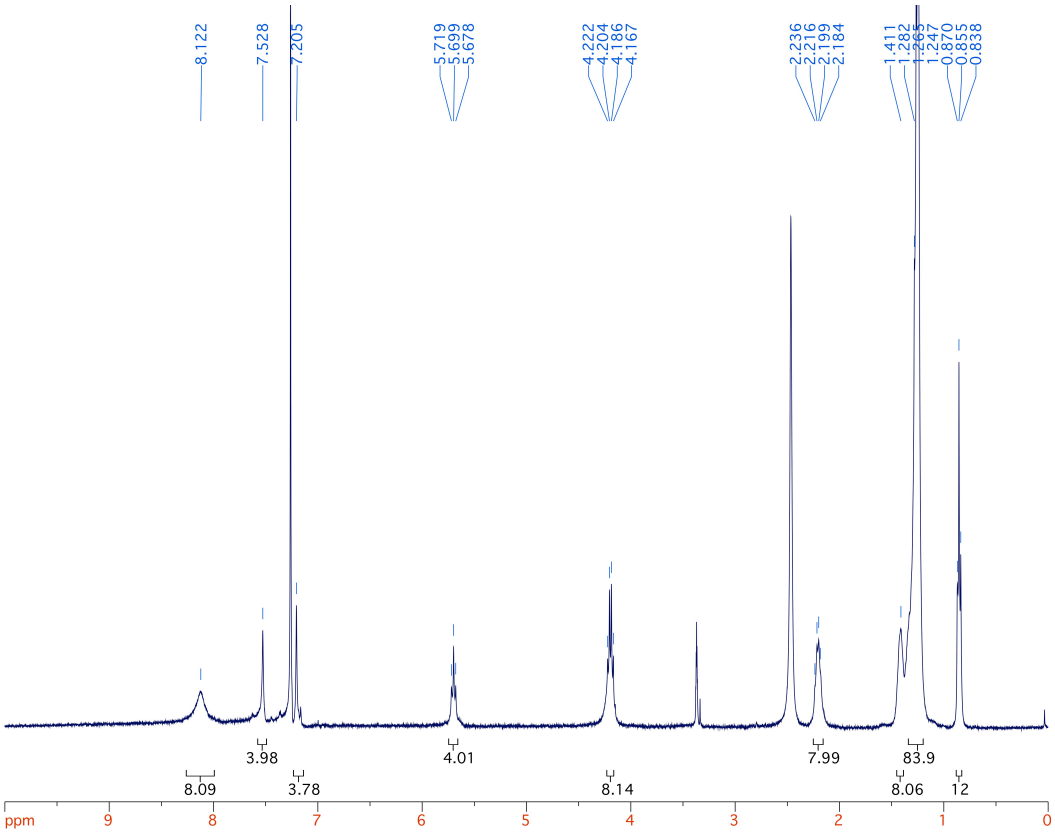
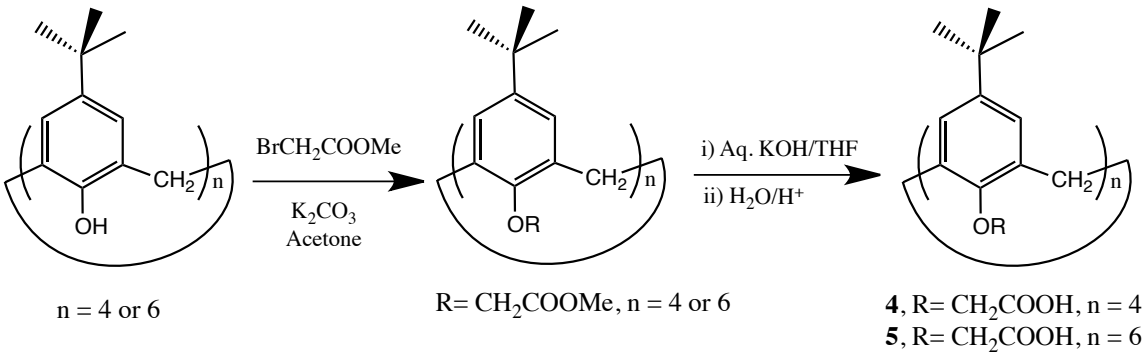


Figure 9. ^{1}H NMR (400 MHz) of 3 in $CDCl_3$: MeOH-d4 (9:1).

4. M. P. Schramm, R. J. Hooley, J. Rebek Jr., *J. Am. Chem. Soc.*, **2007**, 129, 9773-9779.

Scheme for synthesis of calixarene-based receptors



Scheme 2. Synthesis of calixarene-based receptors

The compounds 4-*tert*-butylcalix[4]arene (TBC[4]H) and 4-*tert*-butylcalix[6]arene (TBC[6]H) were purchased from Acros organics. Treatment of these compounds with methyl bromoacetate in presence of K_2CO_3 in dry acetone afforded the ester precursors of **4** and **5**, respectively in good yield following literature procedures cited in the main text.

Synthesis of *p-tert*-butylcalix[4]arene tetracarboxylic acid 4

To the solution of 0.1 g (0.106 mmoles) TBC[4]CH_2COOMe in 7 mL THF was added the solution of 0.15 g (2.66 mmoles, 25 eq) KOH in 3 mL water. The mixture was heated at refluxing condition overnight, cooled to room temperature and THF was removed by rotary evaporation. Then, the desired product was obtained as a while solid after addition of 5 mL 3 M HCl. The suspension was stirred overnight in order to ensure protonation of the carboxylate salt. The solid was separated by filtration and precipitated again from THF/H_2O. After filtration of the solid followed by vacuum drying overnight, 0.086 g product was obtained as a white solid (91.5 % yield). ^{1}H NMR (300 MHz, Acetone-d6, 25 ^{0}C) δ 1.12 (s, 36 H), 3.32 (d, J = 13.2 Hz, 4 H), 4.74 (s, 8 H), 4.94 (d, J = 12.6 Hz, 4 H), 7.07 (s, 8 H).

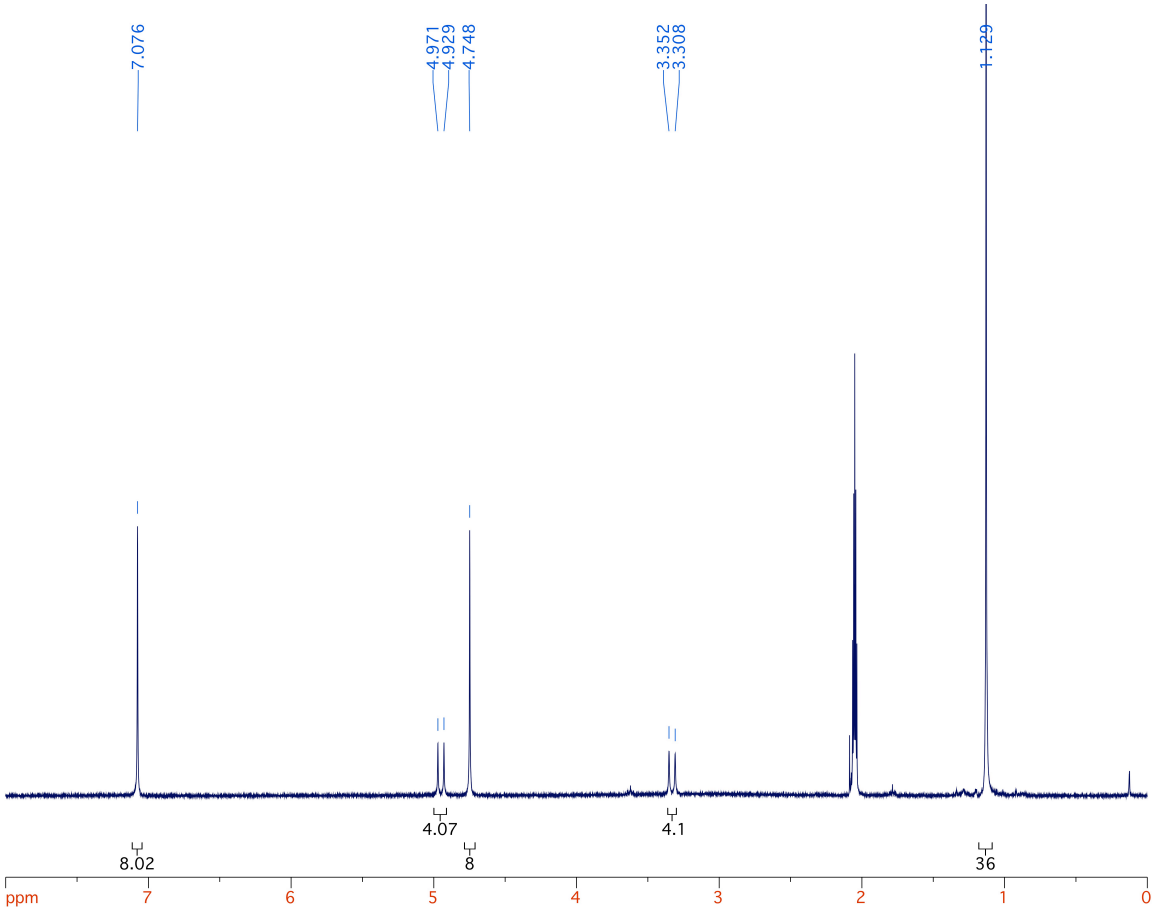


Figure 10. ^{1}H NMR (300 MHz) of 4 in acetone-d6.

Synthesis of *p-tert*-butylcalix[6]arene hexacarboxylic acid 5

To the solution of 0.35 g (0.25 mmoles) TBC[6]CH_2COOMe in 10 mL THF was added the solution of 0.35 g (6.25 mmoles, 25 eq) KOH in 5 mL water. The mixture was heated at refluxing condition overnight, cooled to room temperature and THF was removed by rotary evaporation. Then, the desired product was obtained as a while solid after addition of 10 mL 3 M HCl. The suspension was stirred overnight in order to ensure protonation of the carboxylate salt. The solid was separated by filtration and precipitated again from THF/H_2O. After filtration of the solid followed by vacuum drying overnight, 0.3 g product was obtained as a white solid (91.2 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{0}C) δ 1.08 (s, 54 H), 3.44 (d, J = 15.2 Hz, 6 H), 4.27 (bs, 12 H), 4.52 (d, J = 15.2 Hz, 6 H), 6.96 (s, 12 H), 9.37 (bs, 6 H).

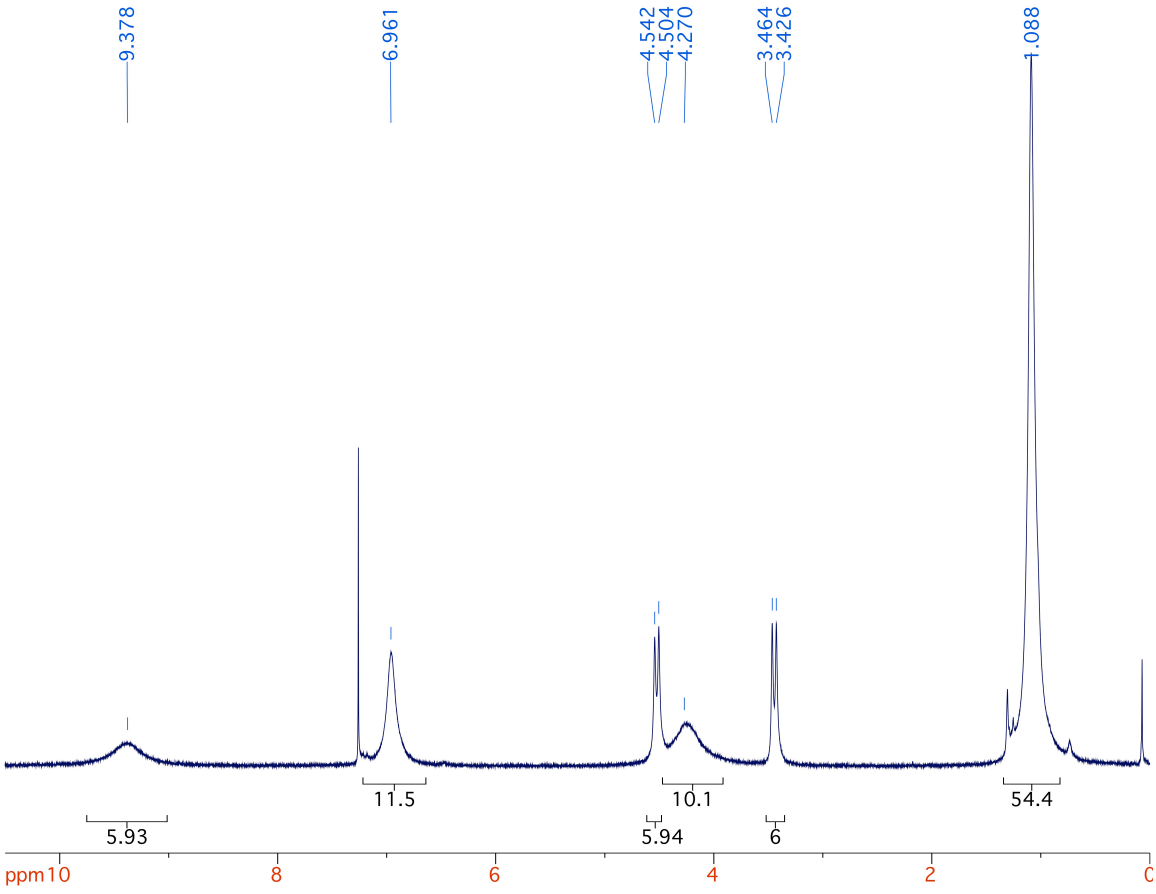
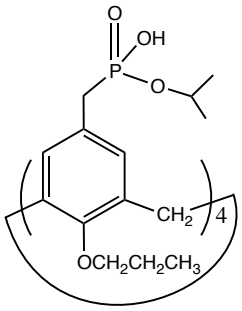


Figure 11. ^{1}H NMR (400 MHz) of 5 in $CDCl_3$.

Synthesis of tetrapropoxycalix[4]arene tetraphosphonic acid 6

The compound **6** was synthesized as described earlier[5]. ^{1}H NMR (300 MHz, MeOH-d4, 25 ^{0}C) δ 1.01 (t, J = 7.5 Hz, 12 H), 1.24 (d, J = 6.0 Hz, 24 H), 1.93 (m, 8 H), 2.80 (d, J = 21 Hz, 8 H), 3.10 (d, J = 13.5 Hz, 4 H), 3.83 (t, J = 7.2 Hz, 8 H), 4.43 (d, J = 13.2 Hz, 4 H), 4.53 (m, 4 H), 6.61 (d, J = 2.4 Hz, 8 H).



6

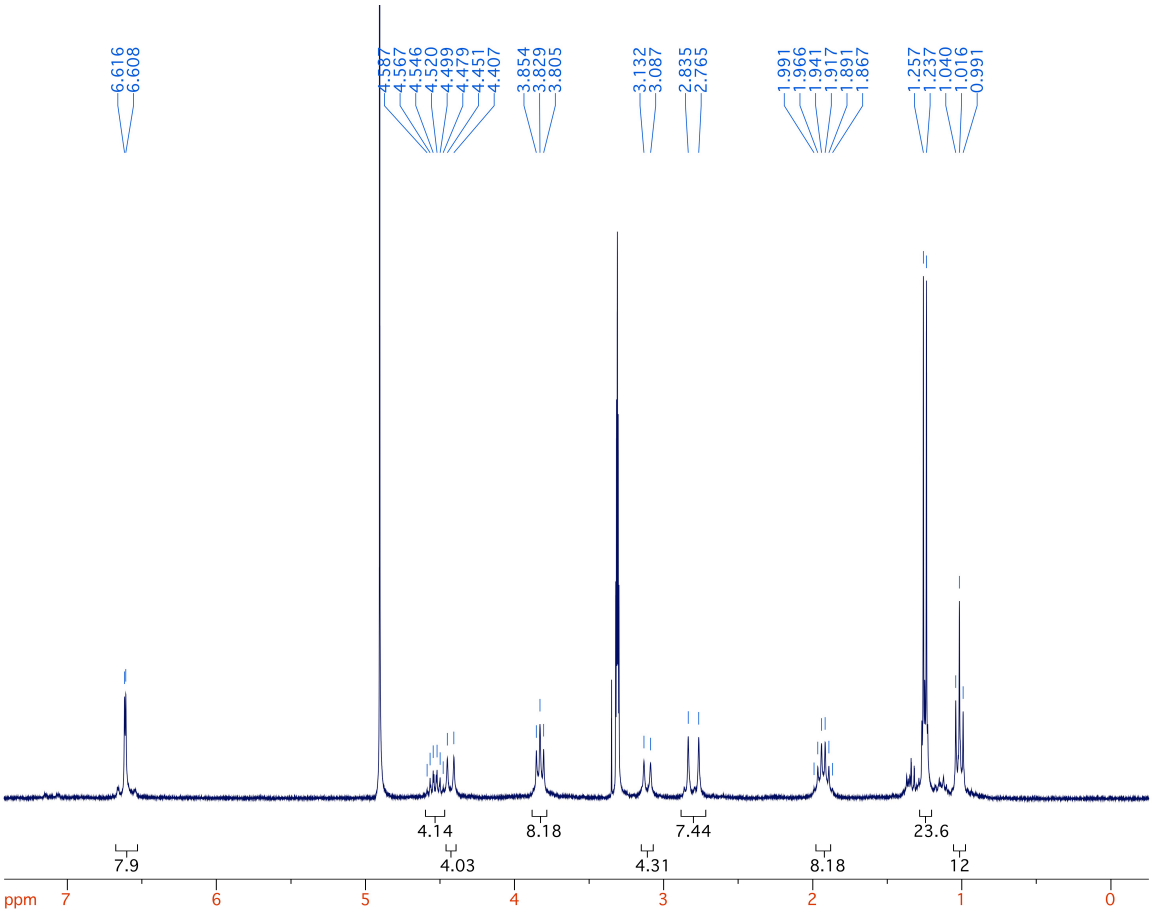


Figure 12. ^{1}H NMR (300 MHz) of tetrapropoxycalix[4]arene tetraphosphonic acid 6 in MeOH-d4.

5 K. Ohto, T. Yamasaki, K. Inoue, *Ars Separatoria Acta*, **2006**, 4, 96-106.

Synthesis of choline-handled substrates

Synthesis of FITC choline 9[6]

Fluorescein isothiocyanate (FITC) (79 mg, 0.20 mmol) was added to the solution of 38 mg (0.22 mmol, 1.1 eq) 2-aminoethyltrimethylammonium chloride hydrochloride and 58 mg (0.42 mmol, 2.1 eq) K_2CO_3 in 3 mL DI water. The mixture was then stirred at room temperature for 33 hrs. After vacuum filtration, the obtained residue was equally divided into four small test tubes, acetone (~ 5 mL) was added to each test tube and centrifugation was performed twice. The precipitate was collected in a 20 mL vial with the help of acetone. Rotary evaporation of acetone yielded an orange opaque solid (51 mg, 47% yield). ^{1}H NMR (300 MHz, D_2O, 25 ^{0}C) δ 3.21 (s, 9 H), 3.60 (t, J= 6.3 Hz, 2 H), 3.85 (bm, 2 H), 6.53 (d, J= 2.4 Hz, 2 H), 6.57 (d, J= 2.4 Hz, 1 H), 6.61 (d, J= 2.4 Hz, 1 H), 7.03 (d, J= 1.2 Hz, 2 H), 7.23 (t, J= 12 Hz, 1 H), 7.32 (s, 1 H), 7.35 (s, 1 H).

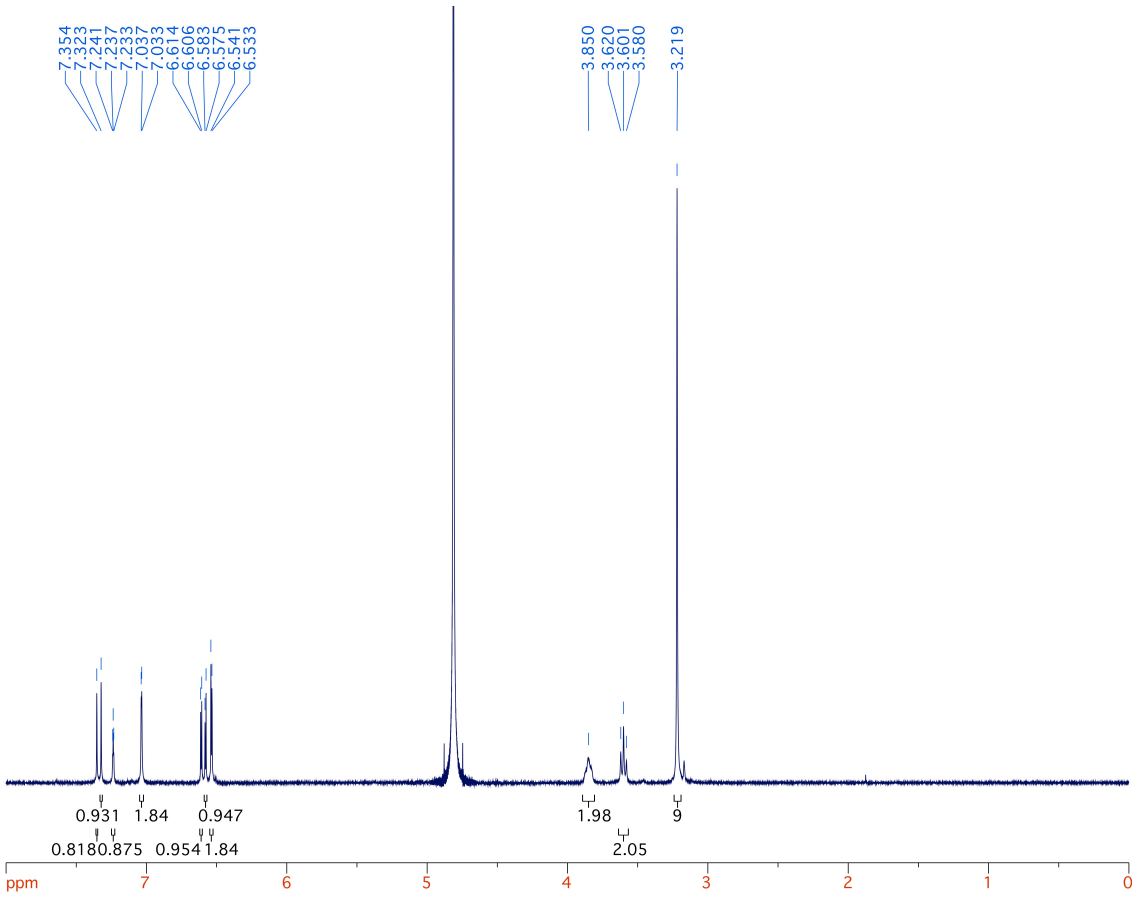


Figure 13. ^{1}H NMR (300 MHz) of 9 in D_2O (5 uL 40% NaOD in D_2O added).

6. Y. Liu, P. Liao, Q. Cheng, R. J. Hooley, *J. Am. Chem. Soc.*, **2010**, 132, 10383-10390.

Synthesis of FITC adamantane 10

FITC (101 mg, 0.26 mmol) was added to a mixture of 1-adamantanemethylamine (46 μL, 0.26 mmol, 1 eq) and K_2CO_3 (109 mg, 0.789 mmol, 3.0 eq) in 5 mL DI water. The mixture was stirred at room temperature for 19 hours and the solvent was removed by rotary evaporation. The resulted crude solid was subjected to flash chromatography using 4:1 DCM/MeOH as eluting agent to get pure product as an orange solid (53.8 mg, 38% yield). ^{1}H NMR (300 MHz, CD_3OD, 25 ^{0}C) δ 1.64 (d, J= 2.7 Hz, 6 H), 1.71–1.82 (m, 6 H), 2.02 (s, 3 H), 4.62 (s, 2 H), 6.56 (dd, J= 2.4 Hz, 5.8 Hz, 2 H), 6.68 (d, J= 2.1 Hz, 2 H), 6.76 (d, J= 8.4 Hz, 2 H), 7.16 (d, J= 8.4 Hz, 1 H), 7.82 (dd, J= 2.0 Hz, 8.2 Hz, 1 H), 8.20 (s, 1 H).

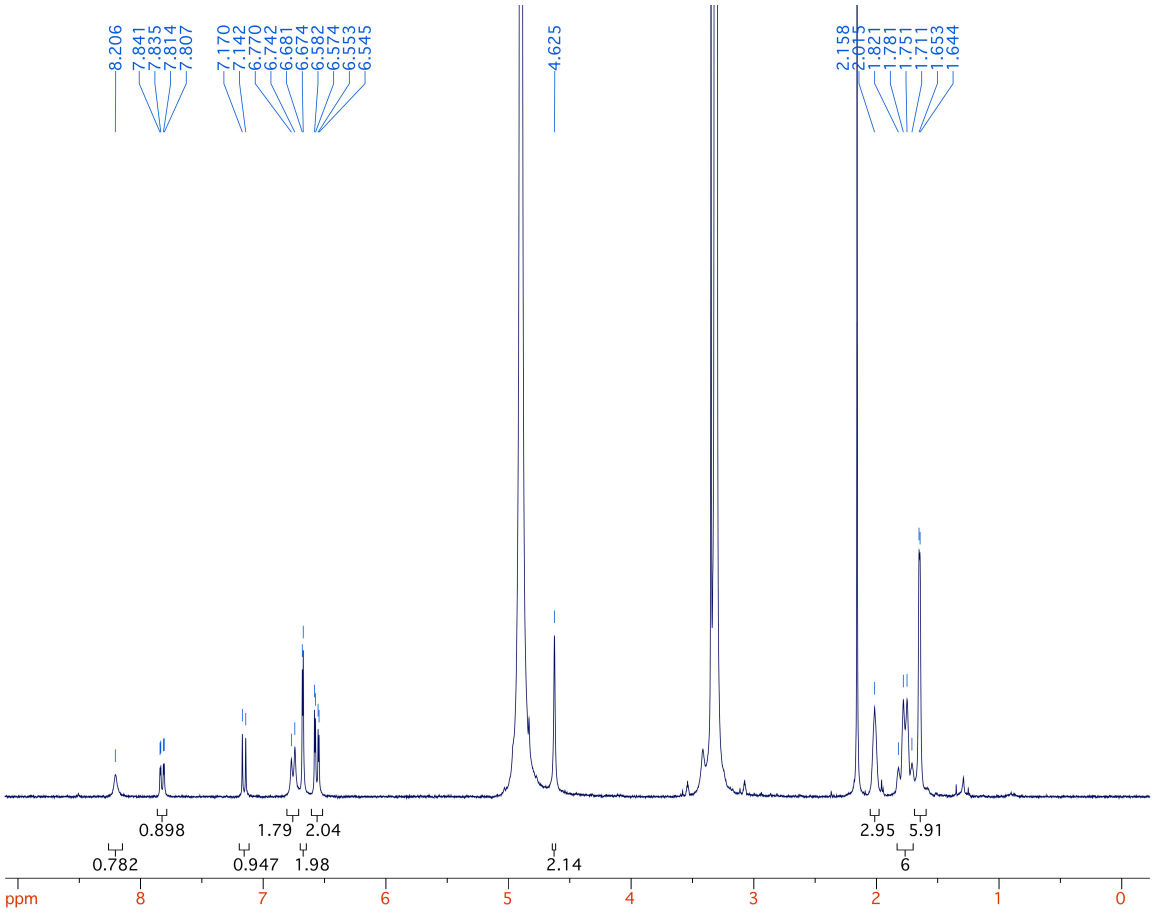
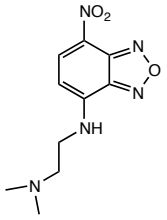


Figure 14. ^{1}H NMR (300 MHz) of FITC adamantane 10 in MeOH-d4.

Synthesis of NBD choline 11[7]

i) Synthesis of N,N-dimethylamine product



NBD-chloride (1.0 g, 5.0 mmol) dissolved in 55 mL ethanol was added to the mixture of 2.73 mL (25 mmol, 5 eq) N,N-dimethylethylenediamine and 1.02 g (10 mmol, 2 eq) $LiOAc.2H_2O$ in 18 mL ethanol. The mixture was stirred at 45 ^{0}C for 60 hours, completion of reaction being monitored by TLC. Rotary evaporation of the solvent yielded a thick paste to which 100 mL water was added and the desired product was extracted with ethyl acetate (3×20 mL). The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation and pure product was obtained after flash chromatography over silica gel using 6% MeOH in DCM as eluting agent (0.52 g, 41.5% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{0}C) δ 2.34 (s, 6 H), 2.72 (t, J= 6.0 Hz, 2 H), 3.49 (m, 2 H), 6.14 (d, J= 8.7 Hz, 1 H), 8.50 (d, J = 8.7 Hz, 1 H).

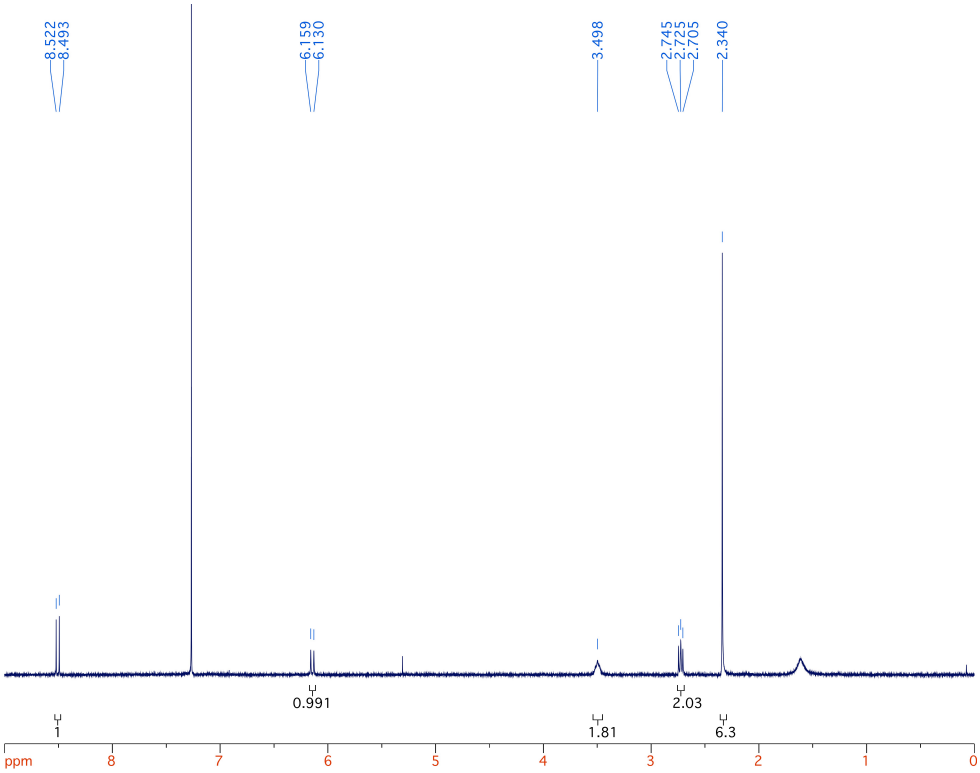


Figure 15. ^{1}H NMR (300 MHz) of N,N-dimethylethyl derivative of NBD in $CDCl_3$.

7. D. Bednarczyk, E. A. Mash, B. R. Aavula, S. H. Wright, *Pflügers Arch - Eur. J. Physiol.*, **2000**, 440, 184-192.

ii) Methylation of N,N-dimethylethyl derivative of NBD

To a solution of 0.3 g (1.19 mmol) N,N-dimethylamaine NBD product in 4 mL dry acetone was added 0.36 mL (5.78 mmol, 4.85 eq) methyl iodide and the reaction mixture was heated at refluxing condition for 68 hrs. When cooled to the room temperature, the resulting suspension was vacuum filtered and the solid was washed with dry acetone to yield an orange opaque solid (0.43 g, 93% yield). ^{1}H NMR (300 MHz, DMSO-d6, 25 ^{0}C) δ 3.18 (s, 9 H), 3.69 (t, J= 6.3 Hz, 2 H), 4.00 (m, 2 H), 6.57 (d, J= 9.0 Hz, 1 H), 8.57 (d, J= 8.7 Hz, 1 H). ^{13}C NMR (75 MHz, DMSO-d6, 25 ^{0}C) δ 37.69, 52.80, 62.38, 100.35, 121.89, 137.51, 144.07, 144.53.

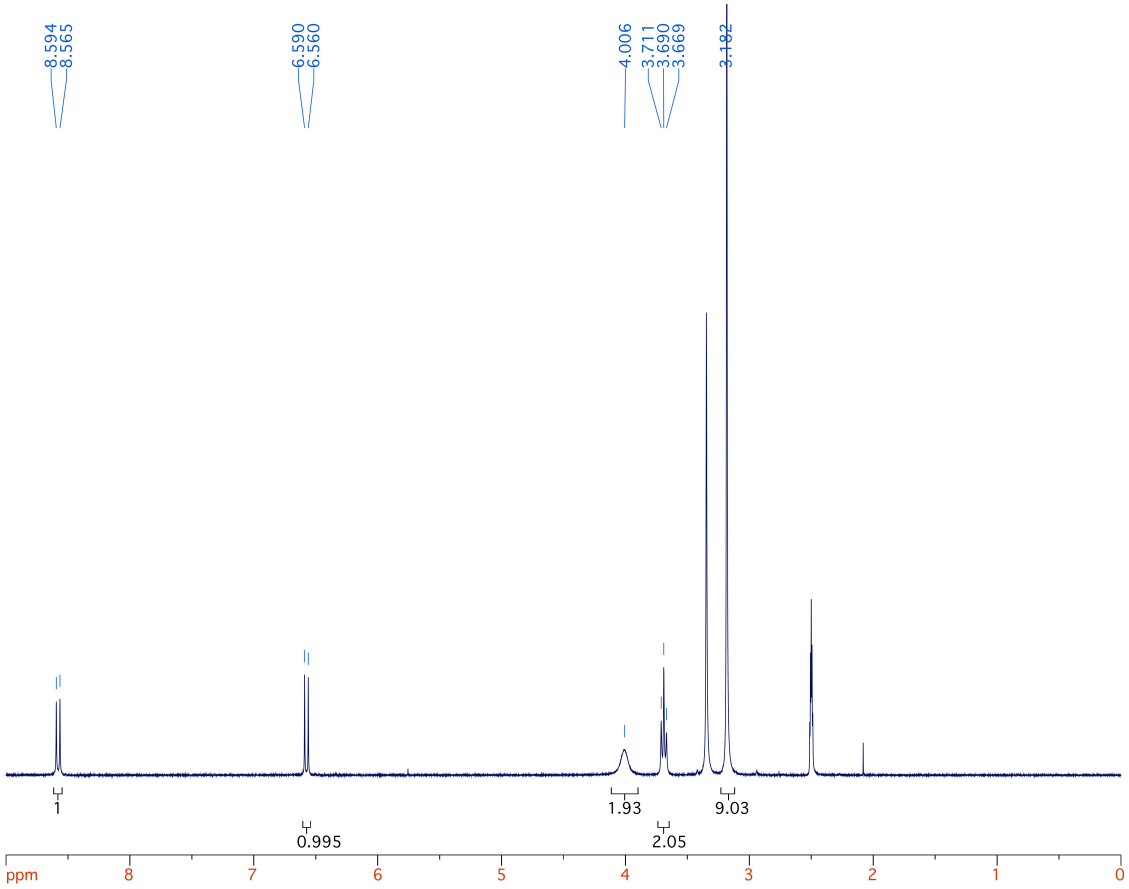


Figure 16. ^{1}H NMR (300 MHz) of 11 in DMSO-d6.

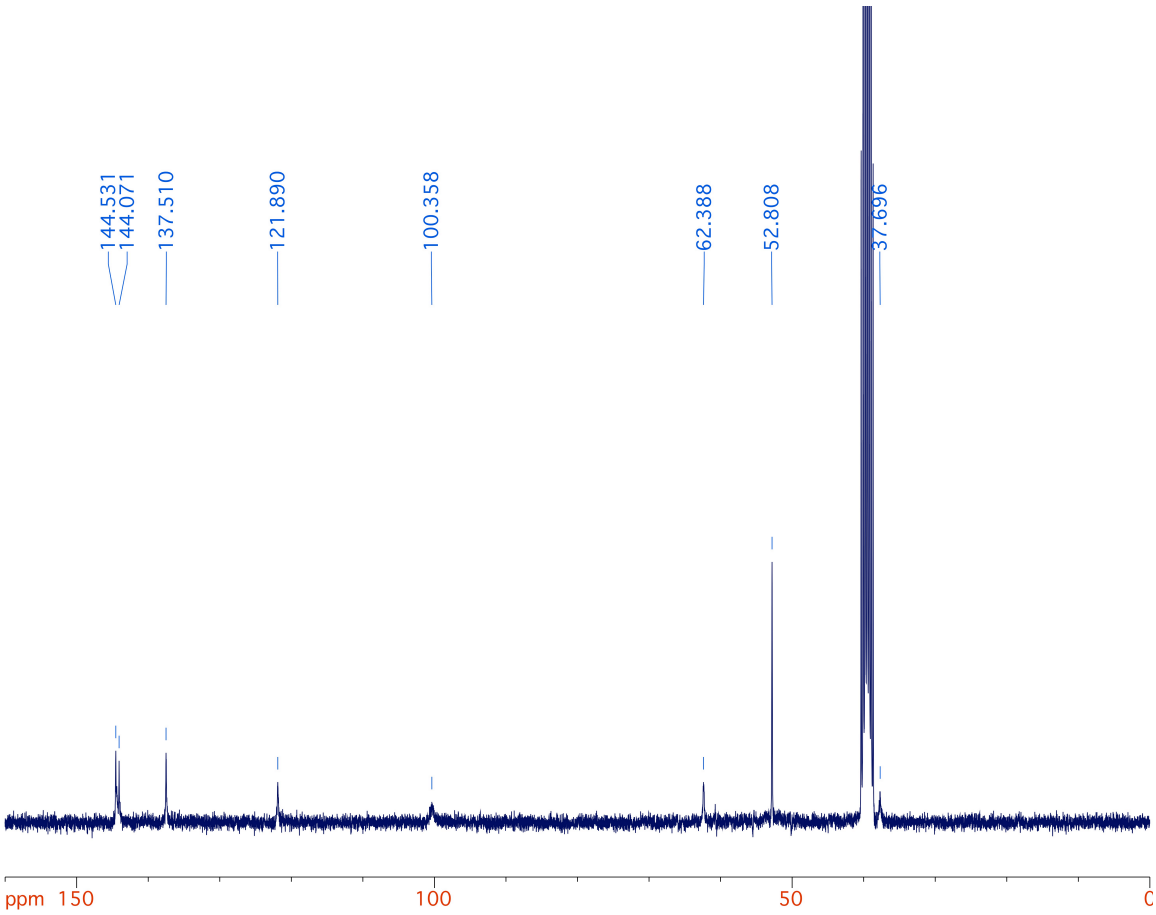


Figure 17. ^{13}C NMR of 11 in DMSO-d6.

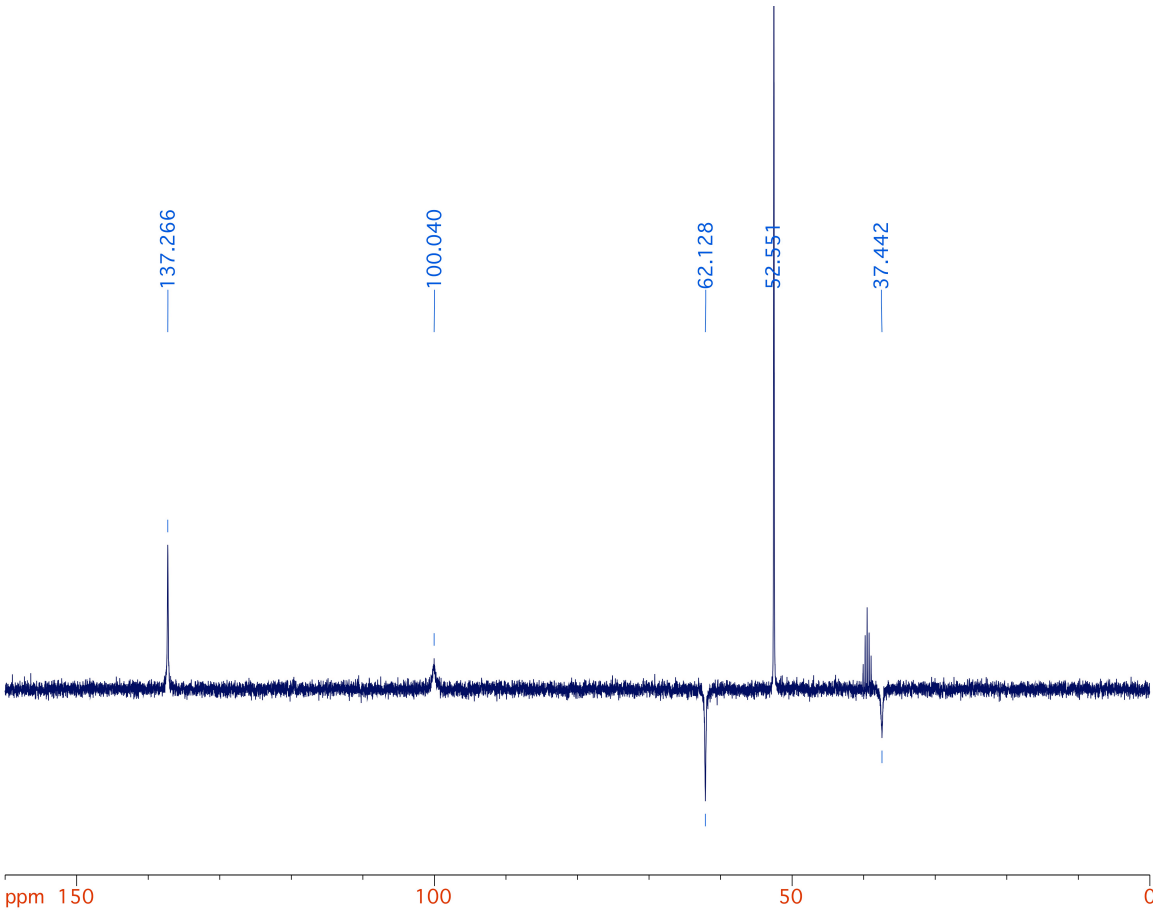


Figure 18. DEPT-135 of 11 in DMSO-d6.

Synthesis of 12[8]

The mixture of 0.2 g (0.74 mmoles) dansyl chloride and 120 µL (1.1 mmoles, 1.5 eq) N,N-dimethylethylenediamine in 7 mL dry acetone was heated at refluxing condition for 1 h. Then, 125 µL solution of K_2CO_3 containing 0.6 g K_2CO_3 in 1 mL water was added and the mixture was refluxed for 30 mins. This was followed by the addition of 184 µL (2.96 mmoles, 4 eq) methyl iodide and refluxing was continued for another 2 hrs. The white solid formed during refluxing was removed by filtration and water (20 mL) was added to the filtrate. However, no precipitation of the desired product occurred. Removal of acetone by rotary evaporation resulted to the formation of light green solid, which was then collected by filtration and washed with minimum amount of methanol. After vacuum drying, 0.17 g (49%) desired product was obtained. ^{1}H NMR (300 MHz, D_2O: Acetone-d6 = 4:1, 25 ^{0}C) δ 2.90 (s, 6 H), 3.26 (s, 9 H), 3.48 (t, J = 4.8 Hz, 2 H), 3.61 (t, J = 5.7 Hz, 2 H), 7.44 (d, J = 7.5 Hz, 1 H), 7.75 (2×t, J = 5.7 Hz, 2 H), 8.29 (d, J = 8.1 Hz, 2 H), 8.59 (d, J = 9 Hz, 1 H).

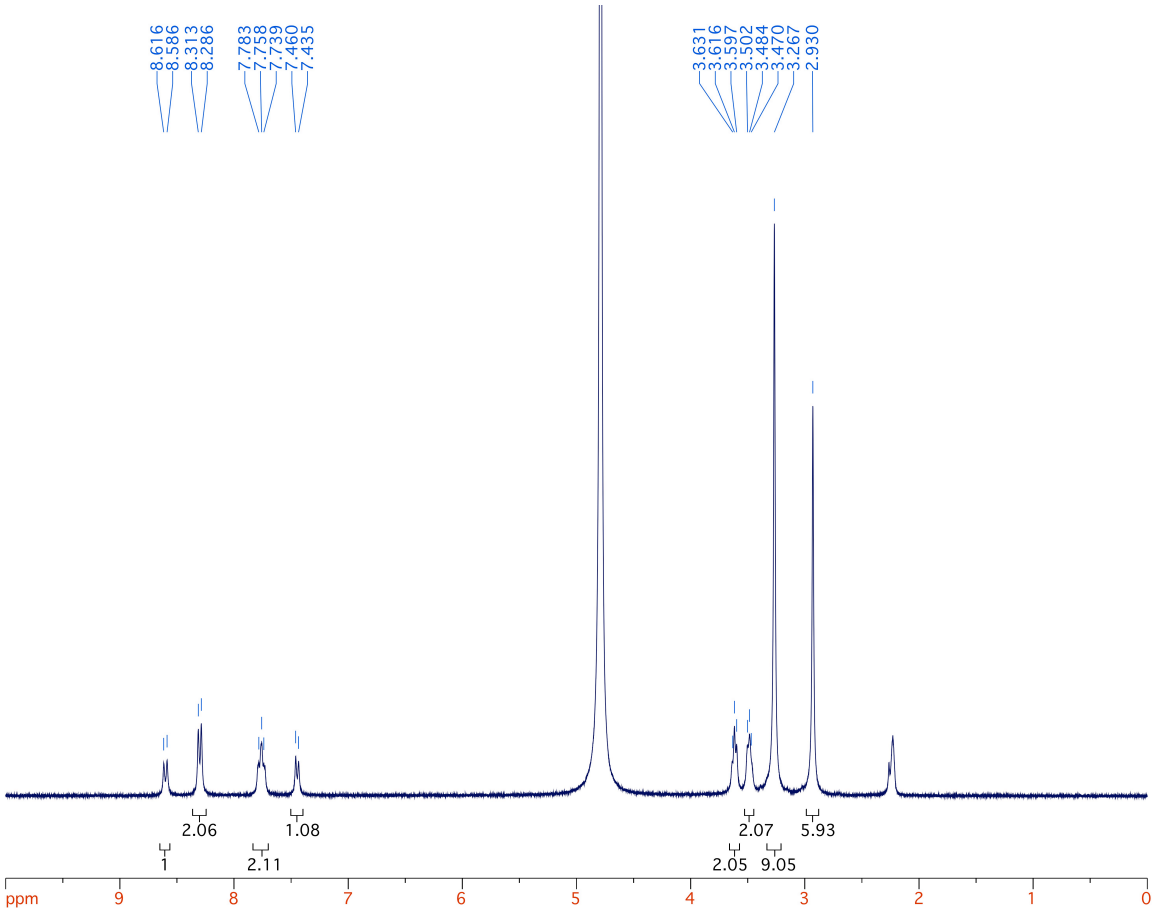


Figure 19. ^{1}H NMR (300 MHz) of 12 in D_2O:Acetone-d6 (4:1)

8. G. Weber, D. P. Borris, E. De Robertis, F. J. Barrantes, J. L. La Torre, M. C. L. De Carlin, *Mol. Pharmacol.*, **1971**, 7, 530-537.

^{1}H NMR spectra from binding studies

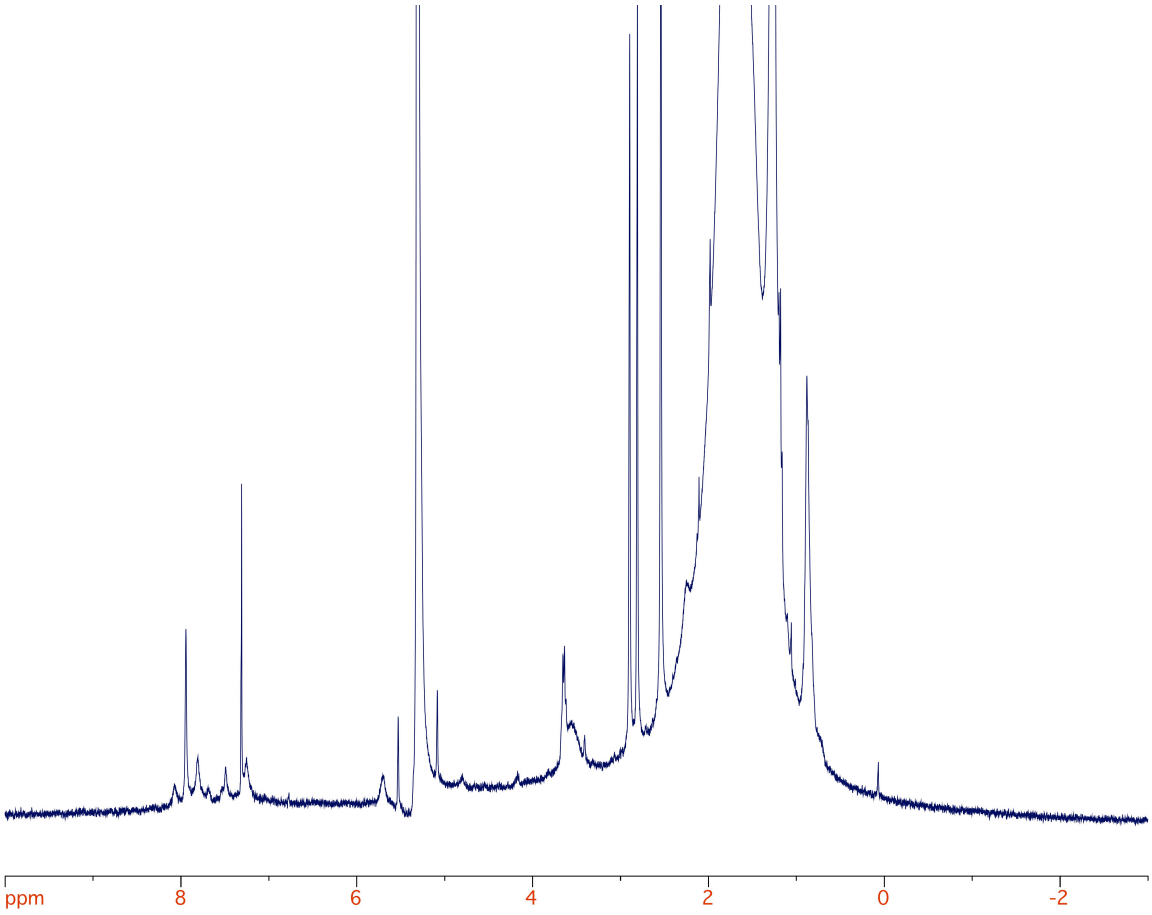


Figure 20. 400 MHz ^{1}H NMR of 1 (2 mg) in presence of 9 (4 mg) in 500 uL dichloromethane (DCM).

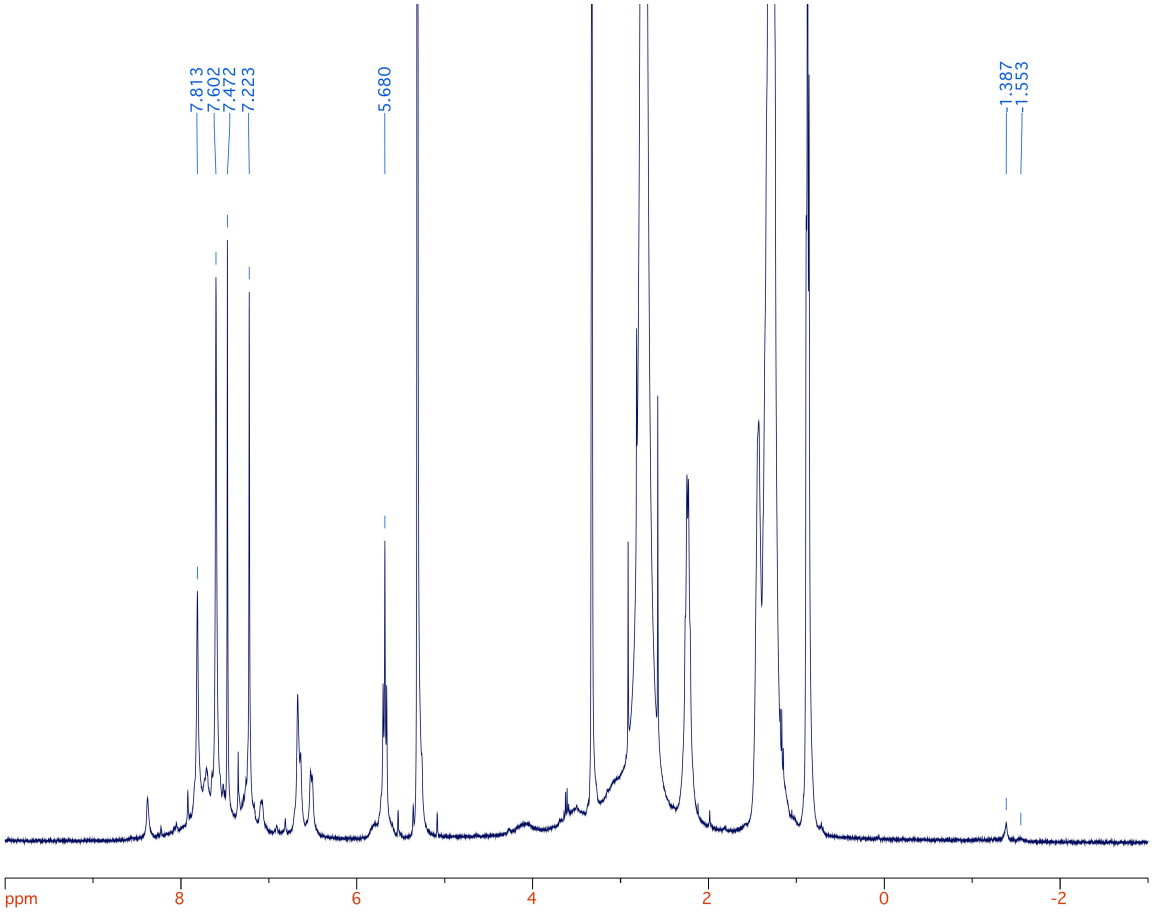
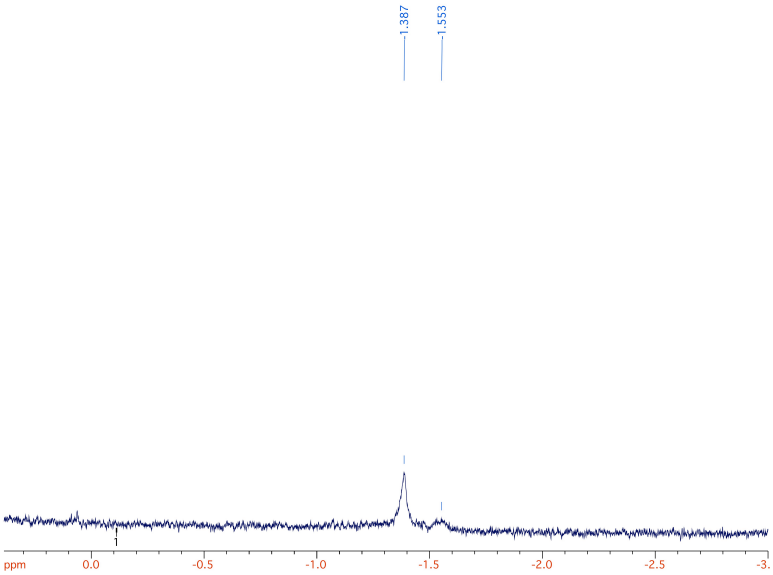


Figure 21. 400 MHz ^{1}H NMR of 1 in presence of 9 in DCM upon addition of 50 uL MeOH-d4



Shielded portion enlarged

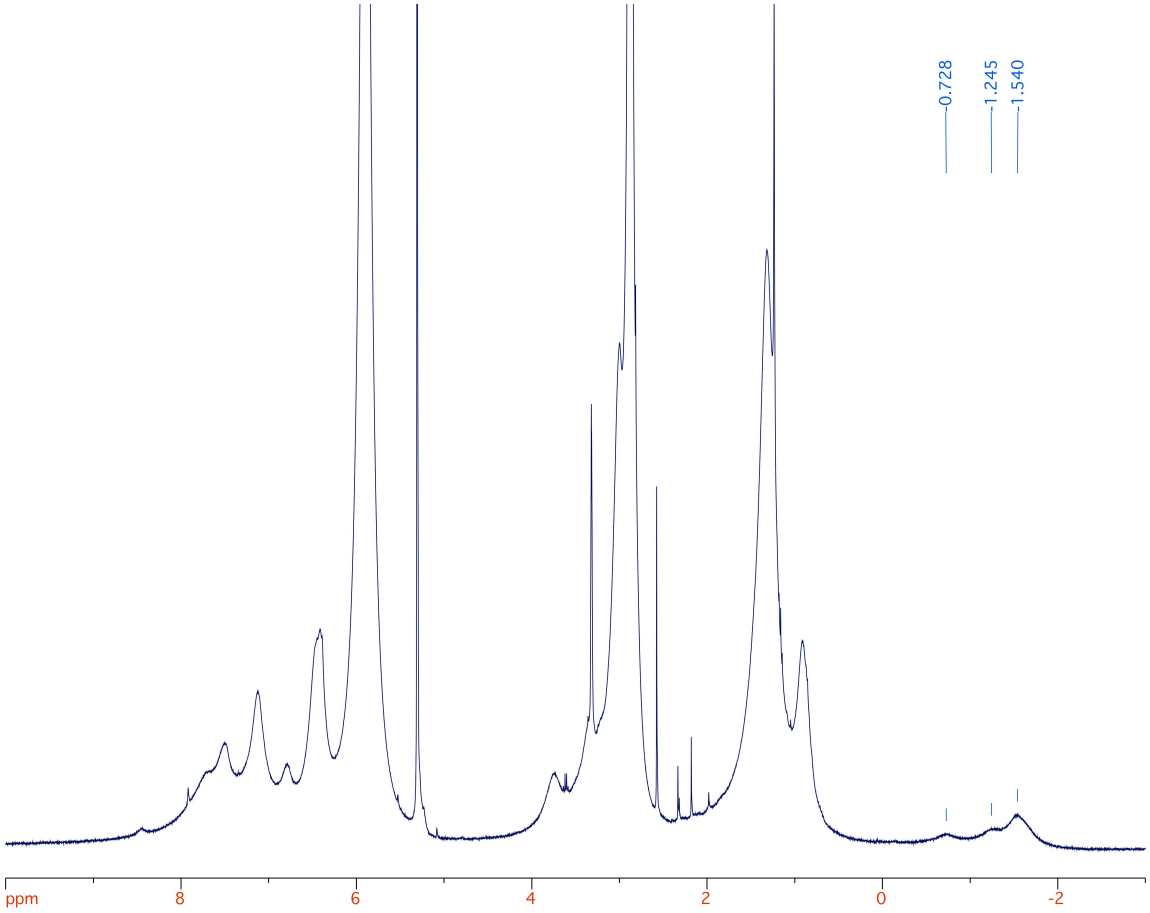
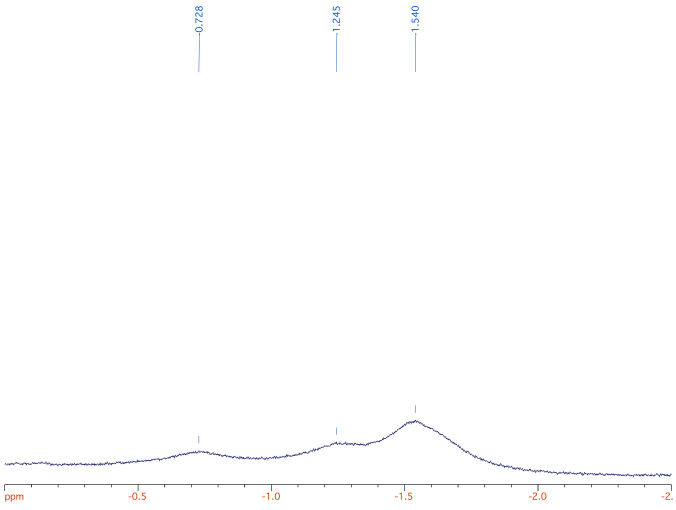


Figure 22. 400 MHz ^{1}H NMR of 1 in presence of 9 in DCM . Addition of 50 uL MeOH-d4 was followed by the addition of 5 uL NaOD (40% in D_2O)



Shielded portion enlarged

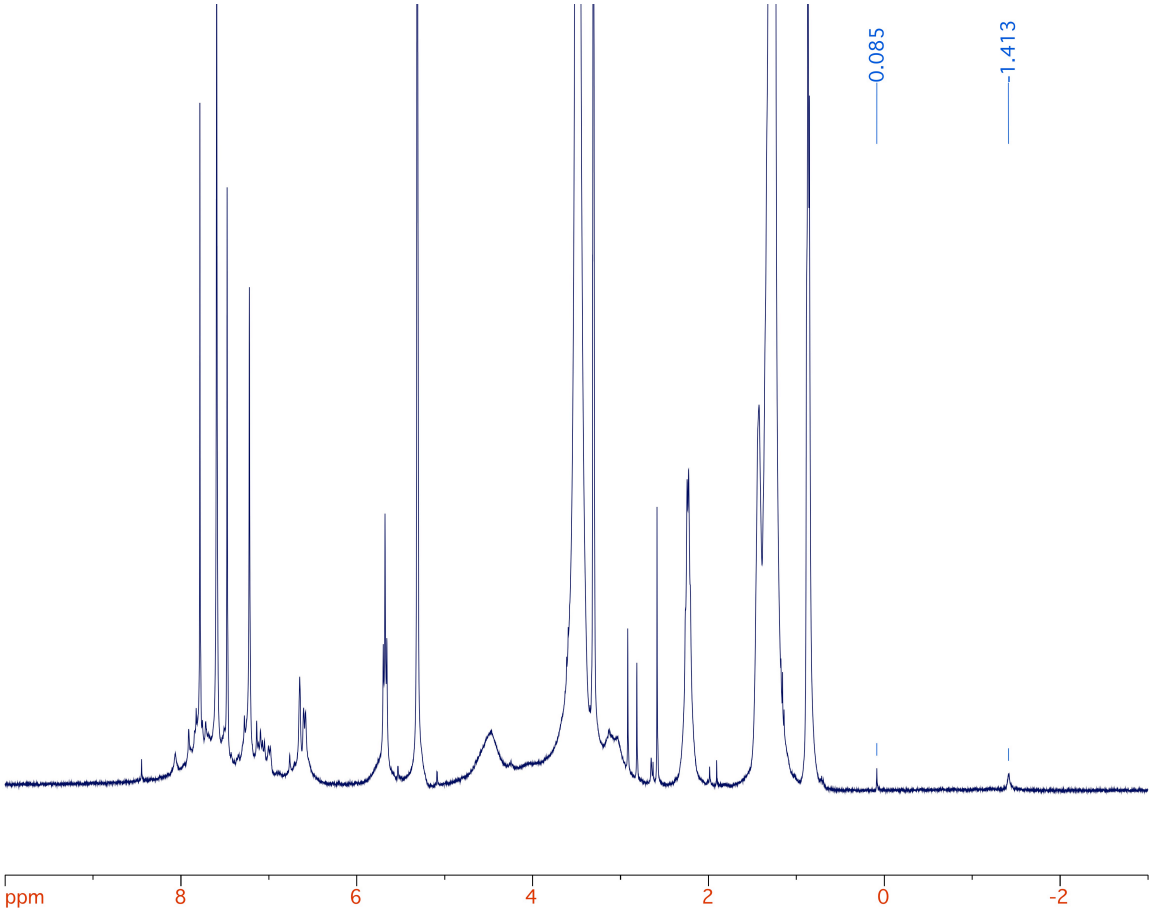
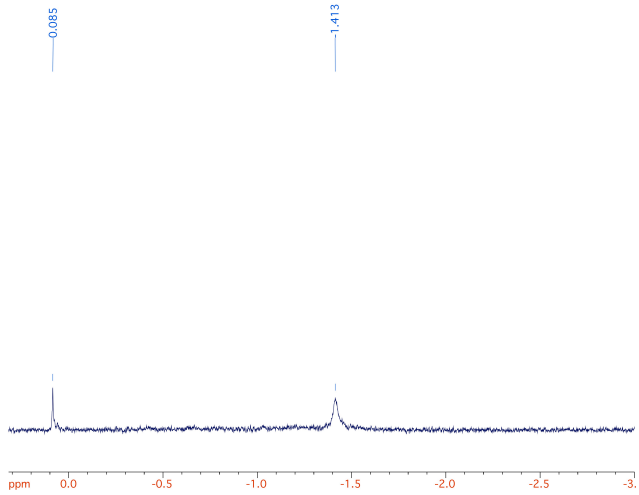


Figure 23. 400 MHz ^{1}H NMR of 1 in presence of 9 in DCM. Addition of 5 uL NaOD (40% in D_2O) was followed by the addition of 5.6 uL CF_3COOD to neutralize the added NaOD.



Shielded portion enlarged

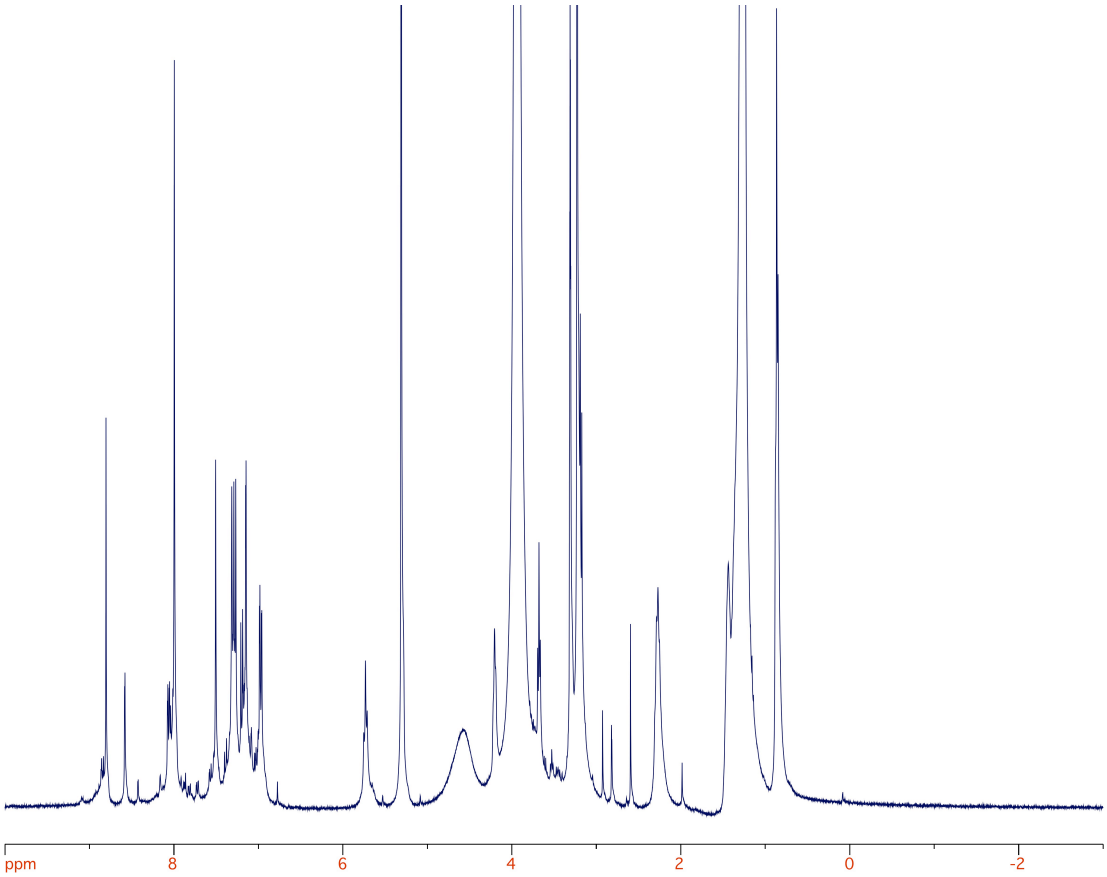
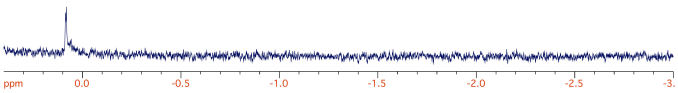
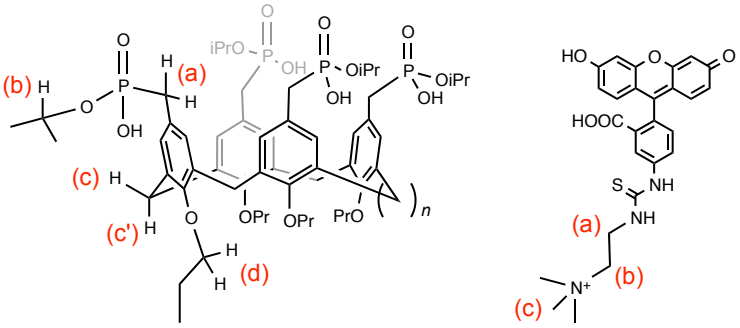


Figure 24. 400 MHz ^{1}H NMR of 1 in presence of 9 in DCM upon addition of another aliquot of 5.6 uL CF_3COOD after neutralization.



Shielded portion enlarged

^{1}H NMR experiment for binding of 9 by 6 in MeOH-d_4.



6: n = 4, R' = $CH_2PO_2OH(OiPr)$, R = nPr

9

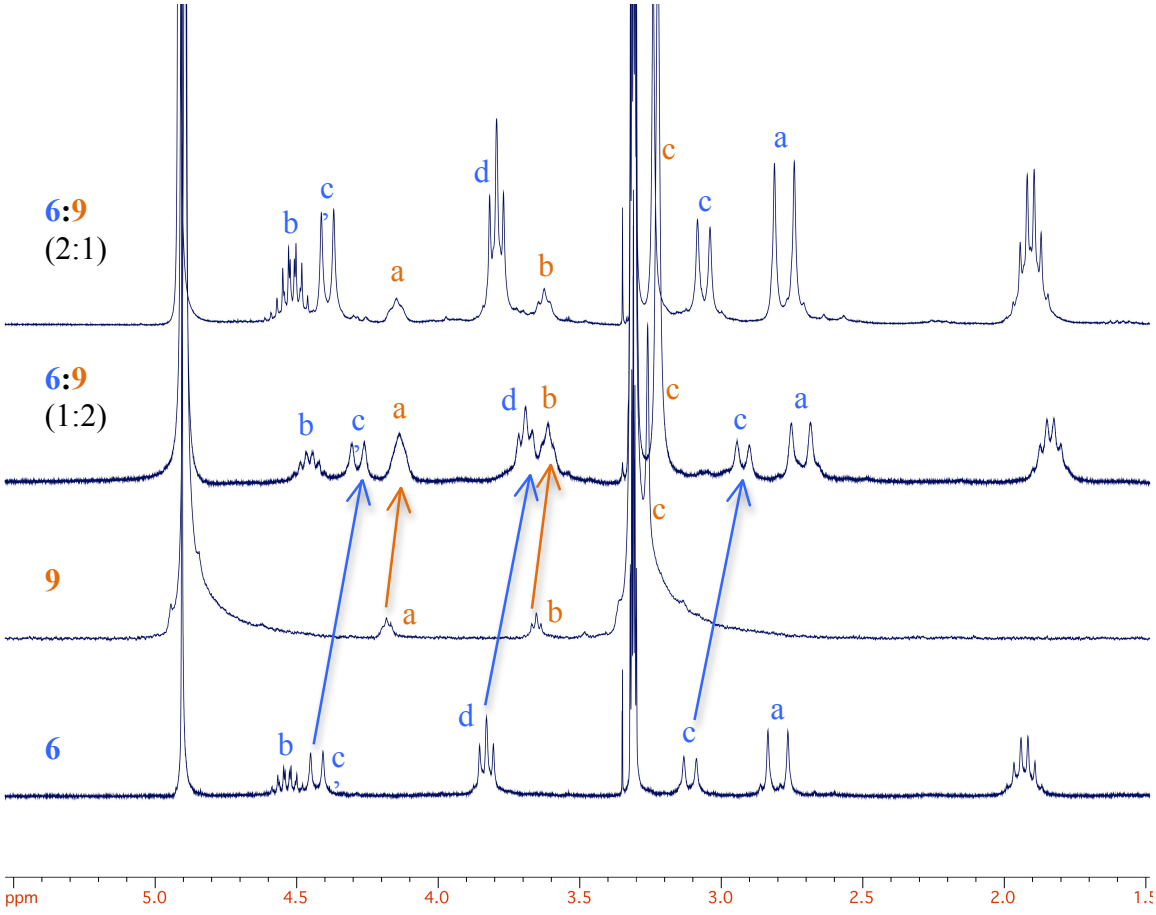


Figure 25. Partial ^{1}H NMR spectra (300 MHz) showing the chemical shift changes of the host 6 and guest 9 protons upon interaction in MeOH-d4.

Determination of concentration of absorbing species

Concentration of the absorbing species was computed from the relationship of measured absorbance and the values of slope and intercept of the equation of a straight line obtained from a calibration plot. A typical calibration plot of FITC Choline **9** is presented.

Concentration (uM)	Absorbance (at 493 nm)
0.05	0.006
0.25	0.022
0.5	0.041
1.0	0.079
2.5	0.201
5.0	0.413
7.5	0.596
10.0	0.738

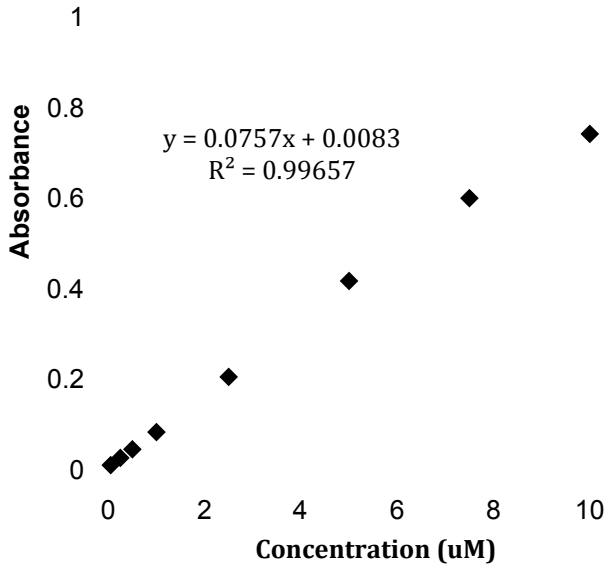


Figure 26. Calibration plot for determination of concentration of absorbing species.

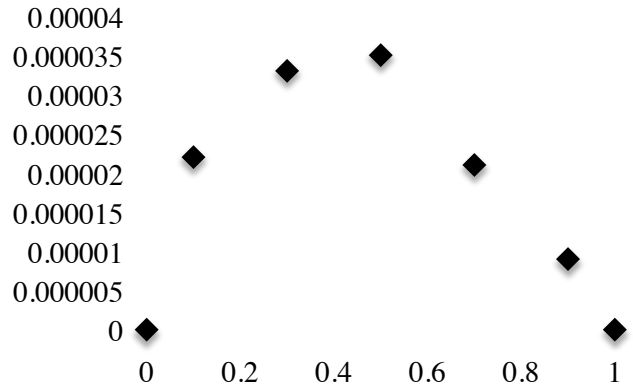
The absorption maxima (λ_{max}) of other fluorophore conjugates were at:

FITC Adamantane **10** 491 nm
NBD Choline **11** 460 nm
Dansyl Choline **12** 315 nm

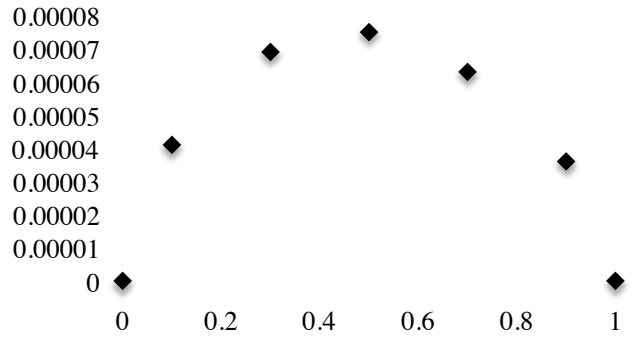
JOBS plot for binding of FITC choline 9 by calixarene 6 in MeOH-d4.

Guest Mol Fraction	[G]*∂ ammonium	[G]*∂ CH_2
0	0	0
0.1	2.2E-05	4.1E-05
0.3	3.3E-05	6.9E-05
0.5	3.5E-05	7.5E-05
0.7	2.1E-05	6.3E-05
0.9	9E-06	0.000036
1	0	0

Ammonium



CH_2



JOBS plot for binding of Dansyl choline 12 by pillar[6]arene 8 in $CDCl_3$/MeOH-d4 (1:4)

Guest Mol Fraction	[G]*∂ ammonium
0	0
0.2	0.000722
0.4	0.00096
0.5	0.00101
0.6	0.00084
0.8	0.000544
1	0