Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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A Fluorescent Cyclotriveratrylene : Synthesis, Emission properties and Acetylcholine recognition in water

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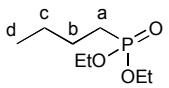
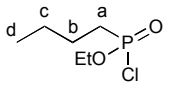
1/ Synthesis of Ethyl *n*-Butylphosphonochloridoate 2

Diethyl *n*-Butylphosphonate [i] :



A mixture of triethylphosphite (19.1 mL, 110 mmol) and *n*-butyl bromide (10.8 mL, 100 mmol) were heated at 120 °C for 72 h. After cooling at room temperature, water (50 mL) was added to the reaction mixture which was then extracted with diethyl ether (2 × 50 mL), washed with water (4 × 100 mL), dried over magnesium sulphate, filtered and concentrated *in vacuo*. Diethyl *n*-butylphosphonate **5** (6.077 g, 31%) was isolated as a colourless oil; ν_{max}(NaCl)/cm^{-1}(2988, 2875, 2352, 1469, 1390, 1024, 963); δ_H(300.13 MHz; $CDCl_3$) 0.89 (3H, t, *J* 7.2, H_d), 1.30 (6H, t, *J* 7.2, $OCH_2C\underline{H_3}$), 1.39 (2H, m, *J* 7.2, H_c), 1.49-1.74 (4H, m, *J* 7.2, $H_{a,b}$), 4.06 (2H, m, *J* 7.2, $OC\underline{H_2}CH_3$); δ_C(62.9 MHz; $CDCl_3$) 13.51 (s, C_d), 16.43 (d, *J* 7.3, $OCH_2\underline{C}H_3$), 23.62 (d, *J* 21, C_c), 24.43 (d, *J* 6, C_b), 26.31 (s, C_a), 61.31 (d, *J* 8, $O\underline{C}H_2CH_3$); δ_P(120.1 MHz; $CDCl_3$) 32.43 (s).

Ethyl *n*-Butylphosphonochloridoate 2:



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To a solution of **3** (3.884 g, 20 mmol) in dry dichloromethane (100 mL) at 0 °C was added dropwise oxalyl chloride (4.4 mL, 50 mmol) under inert conditions. The mixture was stirred for 20 minutes at 0 °C and 16 h at room temperature. The crude liquid was concentrated under reduced pressure. Dry dichloromethane (50 mL) was added and evaporated *in vacuo* to remove the oxalyl chloride excess (repeated twice). The residual yellow oil **2** (3.602 g, 98%) was used without further purification; δ_H(300.13 MHz; $CDCl_3$) 0.93 (3H, t, *J* 7.2, H_d), 1.38

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(3H, t, *J* 7.2, OCH_2CH_3), 1.46 (2H, m, *J* 7.2, H_c), 1.70 (2H, m, *J* 7.2, H_b), 2.16 (2H, m, J 7.2, H_a), 4.24 (2H, m, *J* 7.2, OCH_2CH_3); δ_C(75.5 MHz; $CDCl_3$) 13.42 (s, *J* 1.1, C_d), 15.88 (d, *J* 7.3, $OCH_2\underline{C}H_3$), 23.19 (d, *J* 20, C_c), 24.35 (d, *J* 6.1, C_b), 33.33 (d, *J* 123, C_a), 62.97 (d, *J* 8.2, $O\underline{C}H_2CH_3$); δ_P(120.1 MHz; $CDCl_3$) 45.19.

2/ **UV-Vis absorption and fluorescence emission of Probe 1**

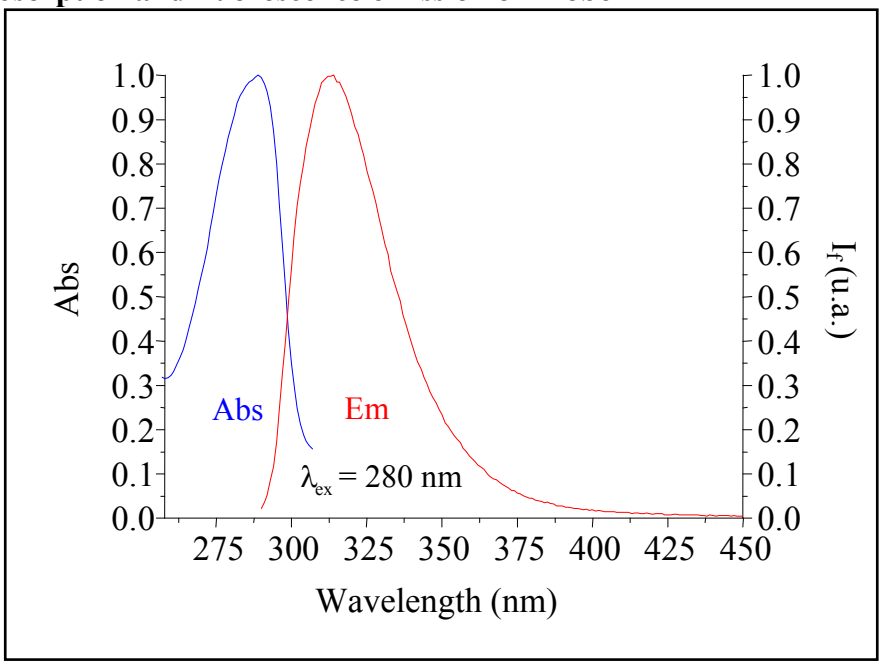

Figure S1 : Normalized UV-Vis absorption and fluorescence emission of Probe 1

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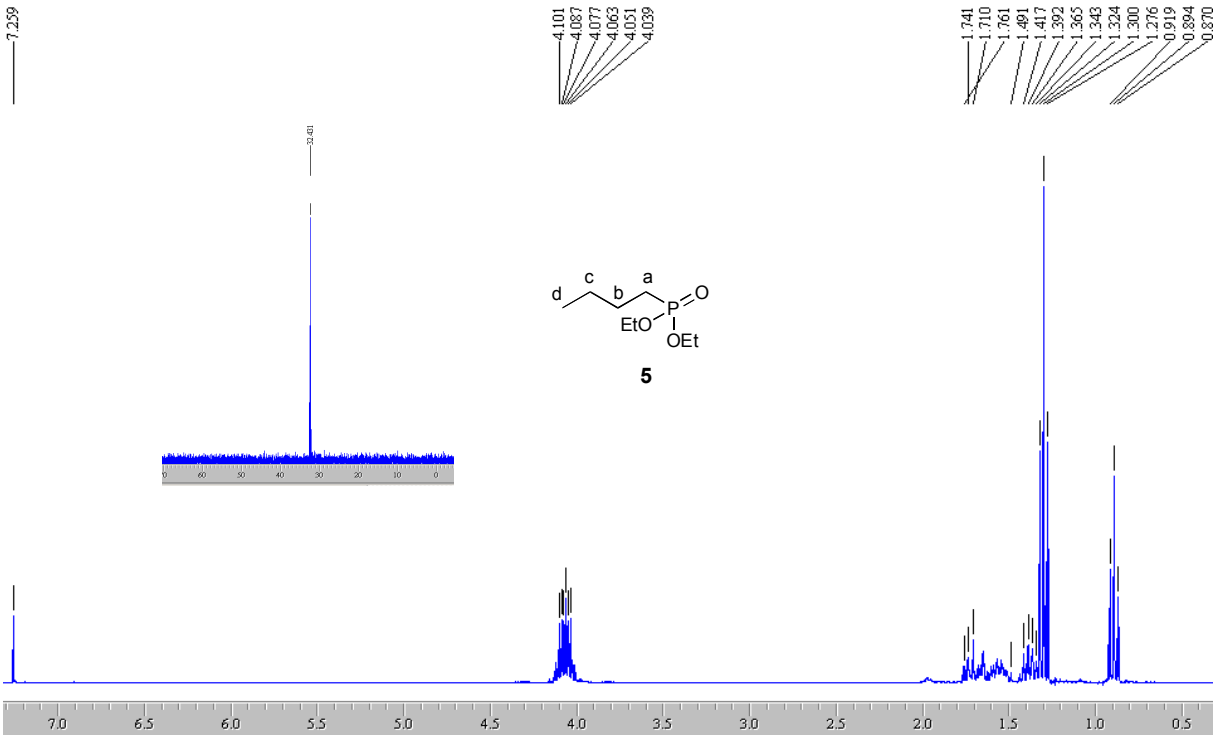
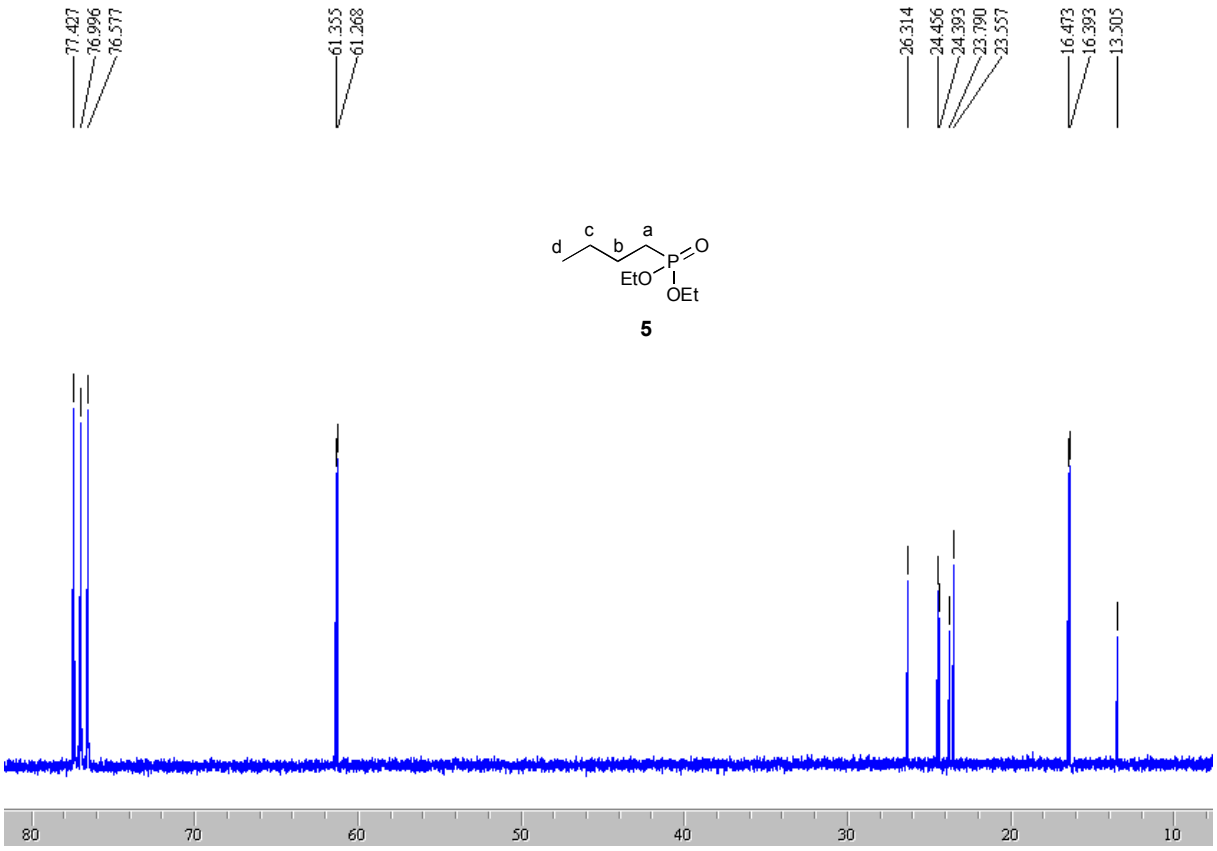
3/ NMR Spectra:

^{1}H and ^{31}P NMR of compound **5** ($CDCl_3$)



^{13}C NMR of compound **5** ($CDCl_3$)



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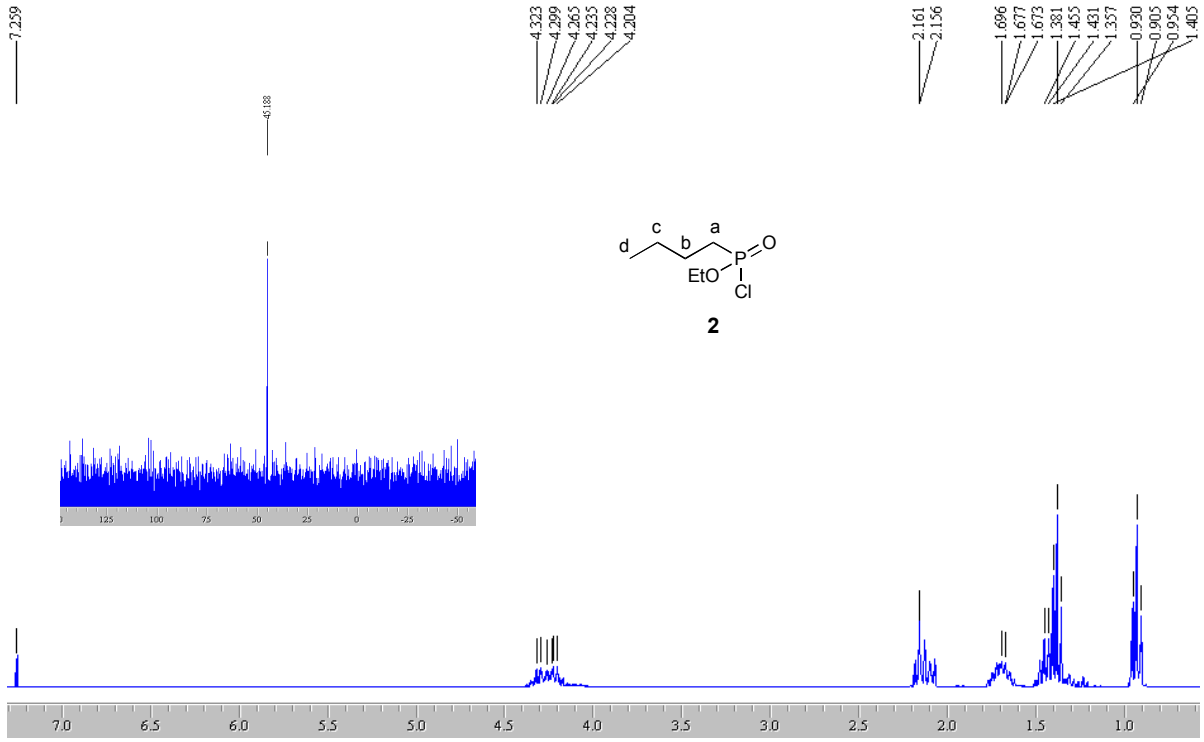
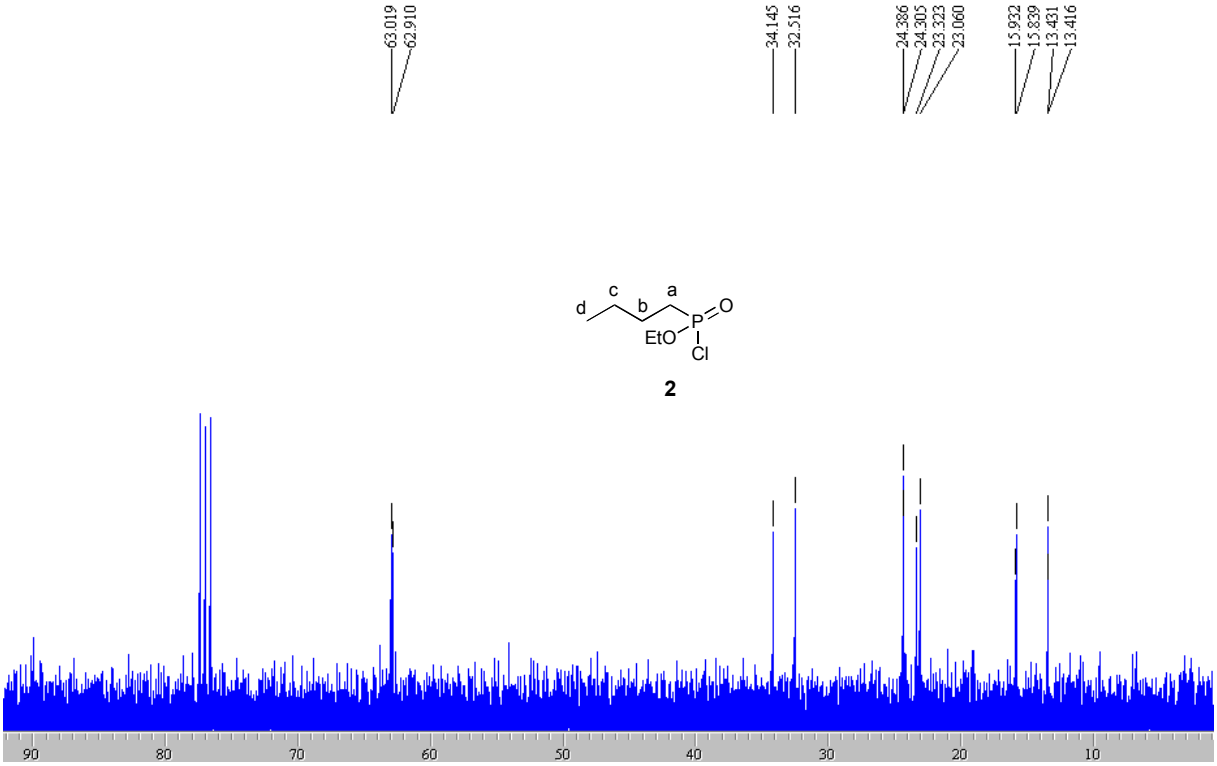
^{1}H and ^{31}P NMR of compound **2** ($CDCl_3$)



^{13}C NMR of compound **2** ($CDCl_3$)



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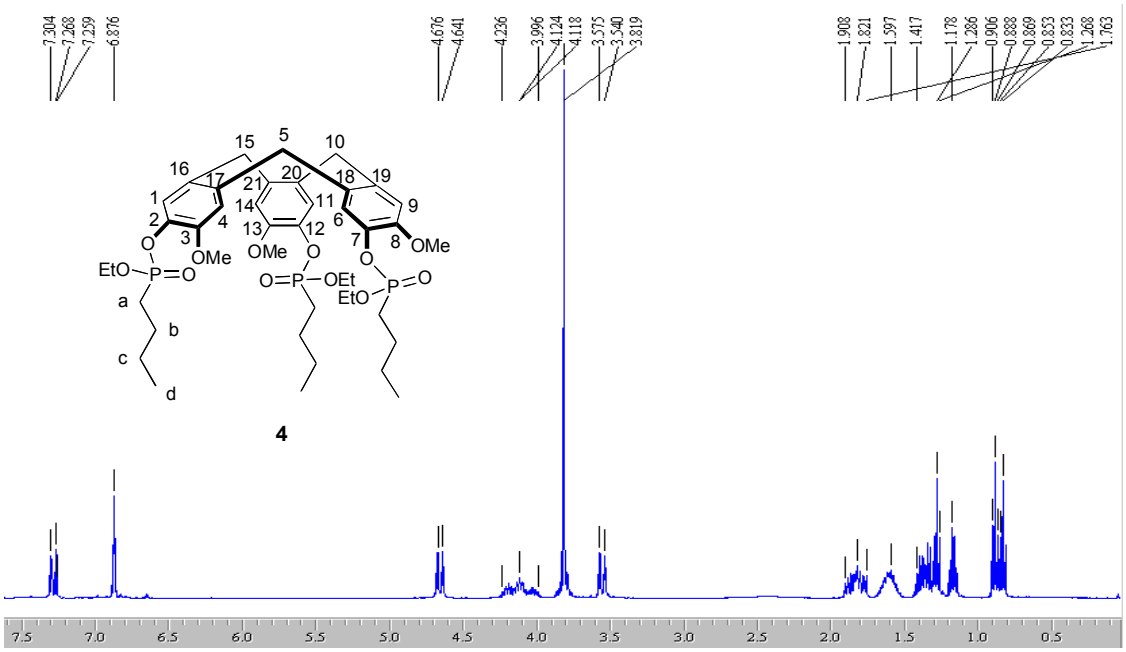
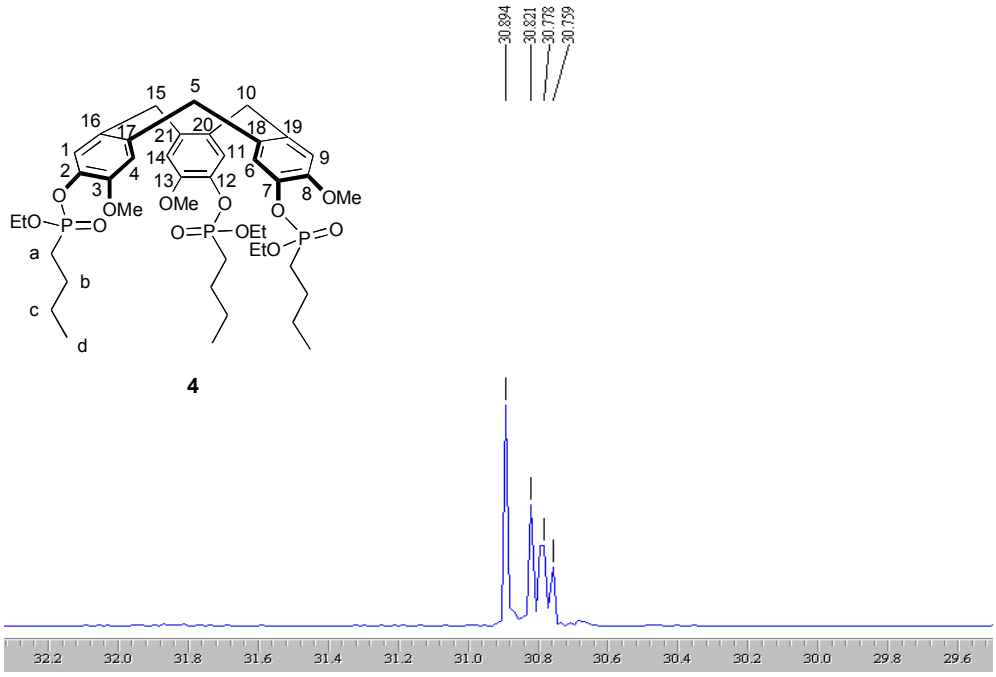
^{1}H NMR of CTV **4** ($CDCl_3$)



^{31}P NMR of CTV **4** ($CDCl_3$)



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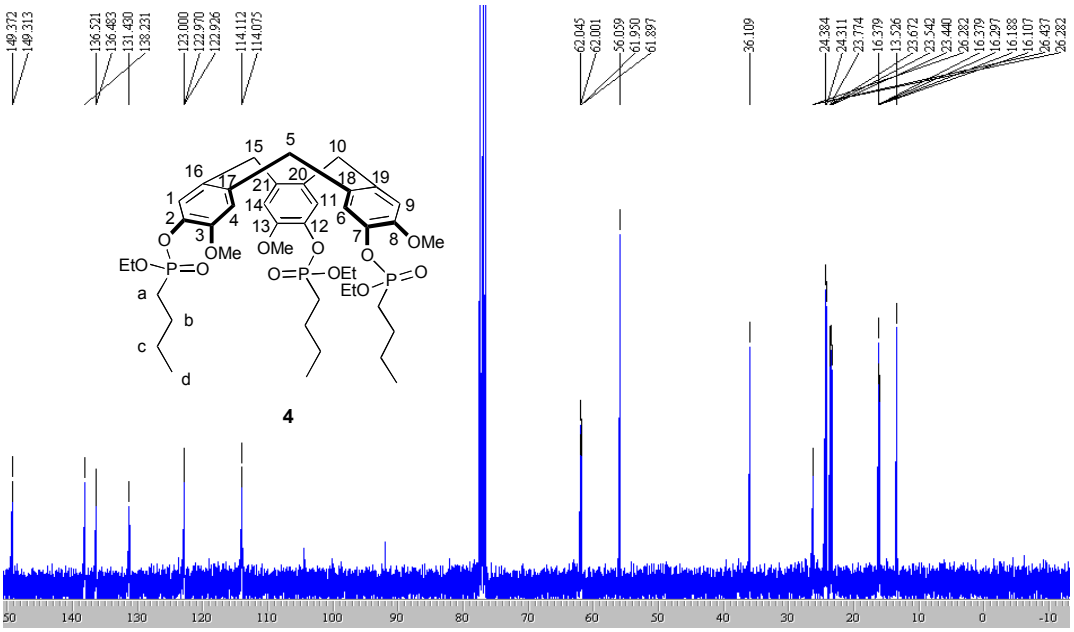
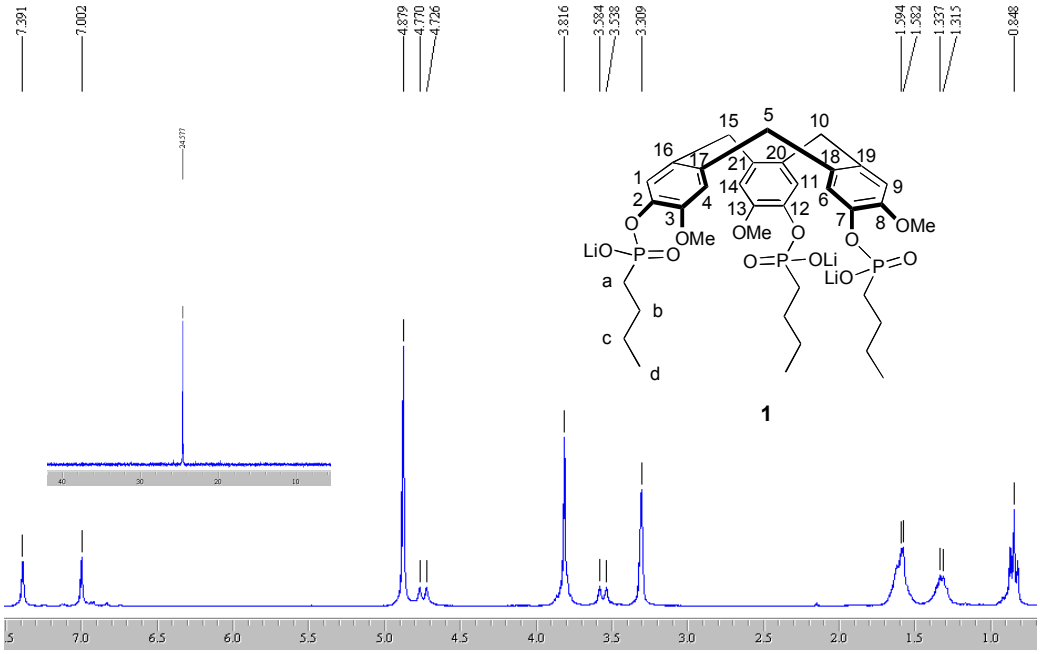
^{13}C NMR of CTV **4** ($CDCl_3$)



^{1}H and ^{31}P NMR of Probe **1** (CD_3OD)



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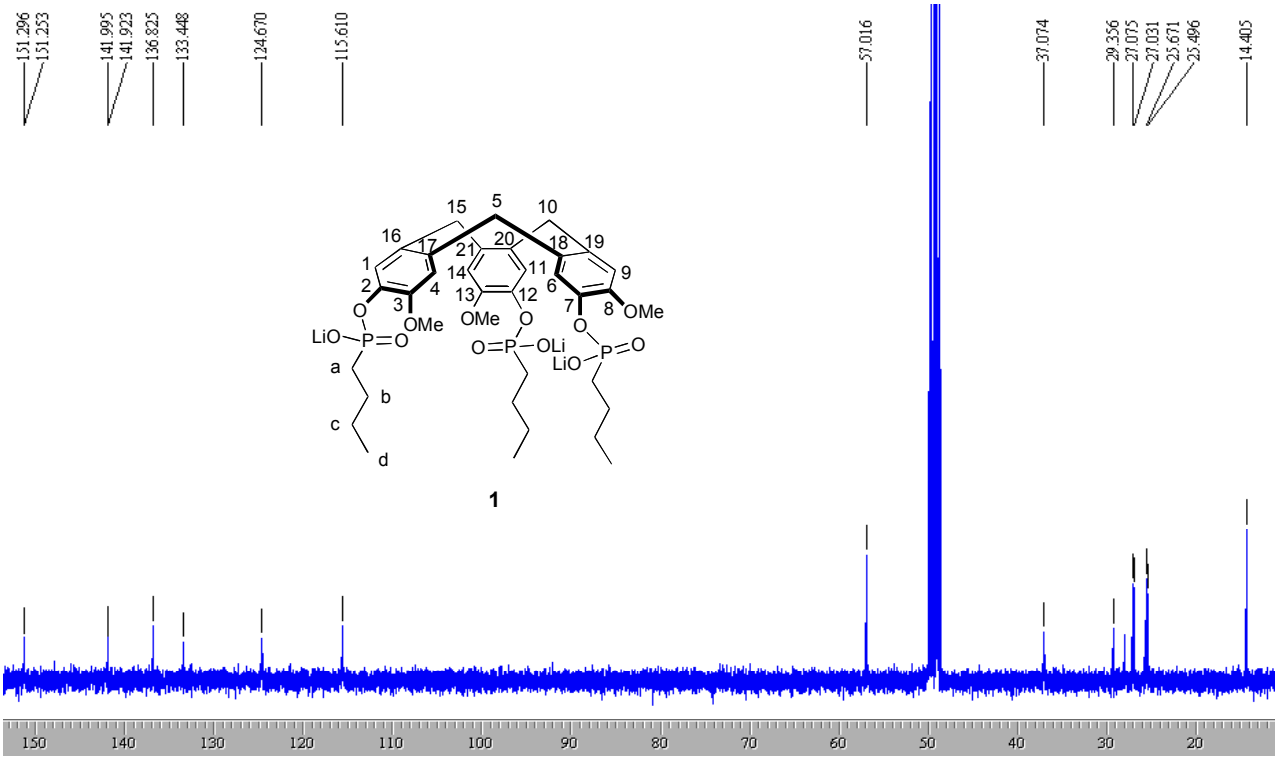
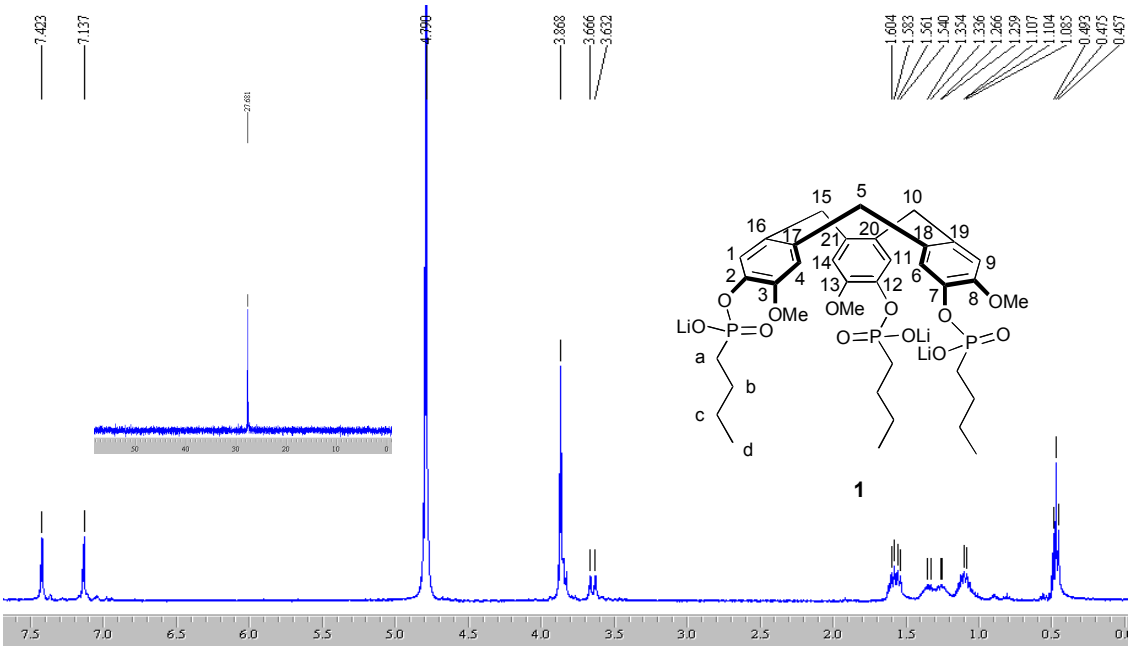
^{13}C NMR of Probe **1** (CD_3OD)



^{1}H and ^{31}P NMR of Probe **1** (D_2O)



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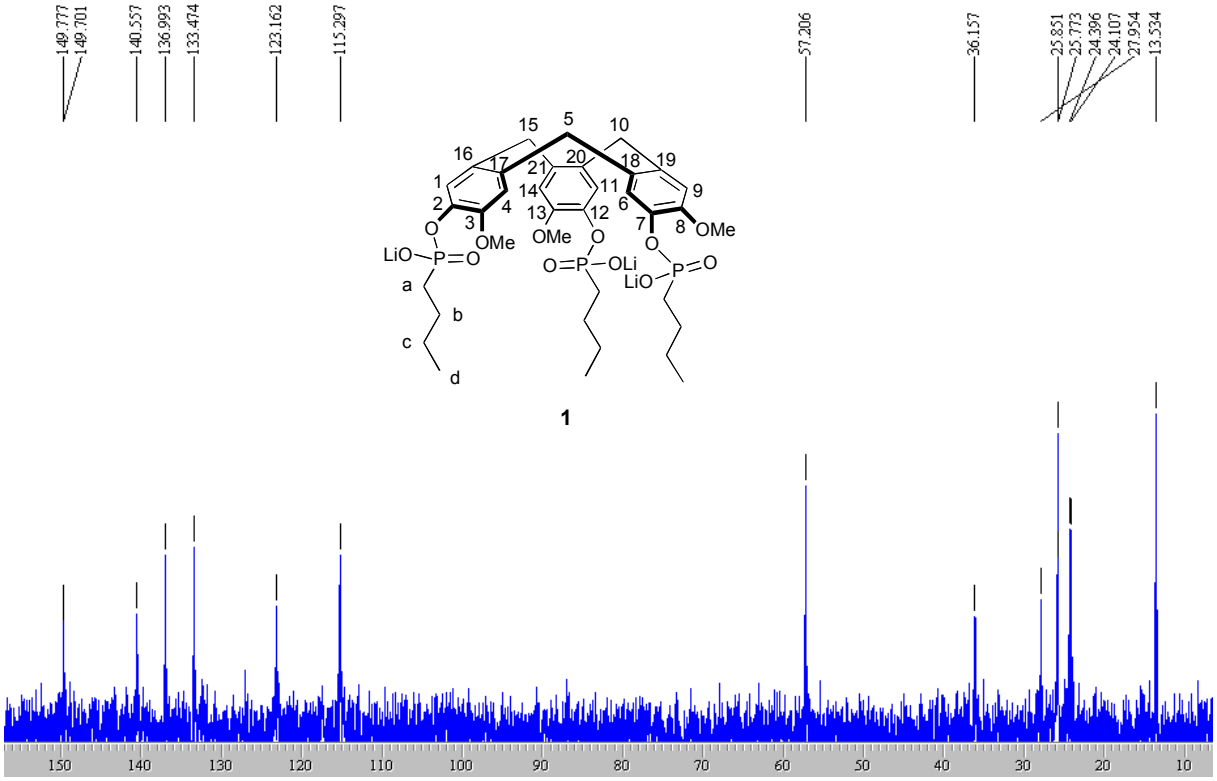
^{13}C NMR of Probe **1** (D_2O)



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4/ ^{1}H NMR Titration of ACh

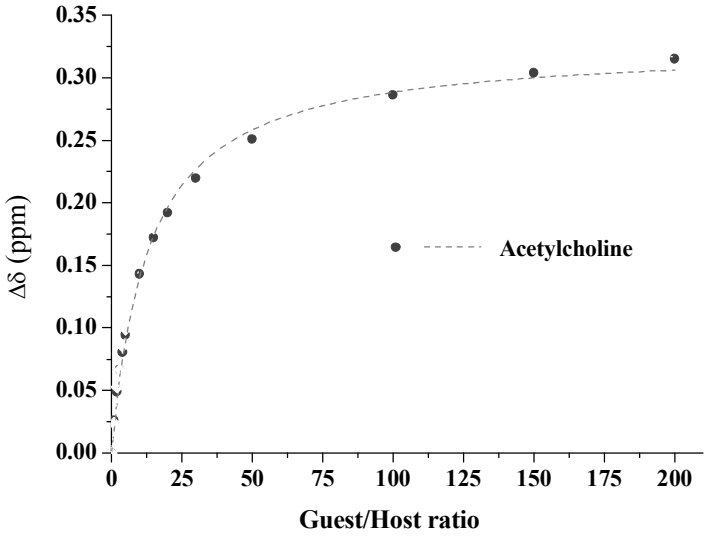

Figure S2: ^{1}H NMR chemical shift variation of probe **1** (10^{-3} M) upon titration with ACh (●). Data fitting with a 1:1 binding model is shown as dotted lines.

References

[i] (a) G. M. Kosolapoff, *J. Am. Chem. Soc.,* 1945, **67**, 1180-1182. (b) S. Gobec, I. Plantan, J. Mravljak, R. A. Wilson, G. S. Besra and D. Kikelj, *Bio. Med. Chem. Lett.*, 2004, **14**, 3559-3562.

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