Supporting information for

Fully reversible guest exchange in tetraphosphonate cavitand complexes probed by fluorescence spectroscopy

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Experimental part

General Method

^{1}H NMR spectra were obtained using a Bruker AC-300 (300 MHz) or a Bruker AVANCE 300 (300 MHz) spectrometer. All chemical shifts (δ) were reported in ppm relative to the proton resonances resulting from incomplete deuteration of the NMR solvents. ^{31}P NMR spectra were obtained using a Bruker AMX-400 (162 MHz) spectrometer. All chemical shifts (δ) were recorded in ppm relative to external 85% H_3PO_4 at 0.00 ppm. Electrospray ionization ESI-MS experiments were performed on a Waters ZMD spectrometer equipped with an electrospray interface. Column chromatography was performed using silica gel 60 (MERCK 70-230 mesh). All solvents were dried and distilled using standard procedures. All commercial reagents were ACS reagent grade and used as received.

Photophysical Experiments

The solvent used for photophysical measurements was dichloromethane from Merck (UVASOL) without further purification. Absorption spectra in solution were recorded on a Perkin–Elmer Lambda 40 spectrophotometer. The fluorescence spectra were recorded with an Edinburgh FLS920 equipped with a Hamamatsu R928P photomultiplier. The same instrument equipped with a PCS900 PC card was used for the Time Correlated Single Photon Counting experiments. All the photophysical measurements were performed in aerated solutions.

Spectrofluorimetric Titration

Stability constants were determined by fitting the fluorescence spectra recorded during the titration of the hosts and the tetrabutyl ammonium salts of the different anions; a solution of the host species of known concentration typically 4 - 12 μM was used. The data were fitted with the global analysis program SPECFIT.

Electrochemical Experiments

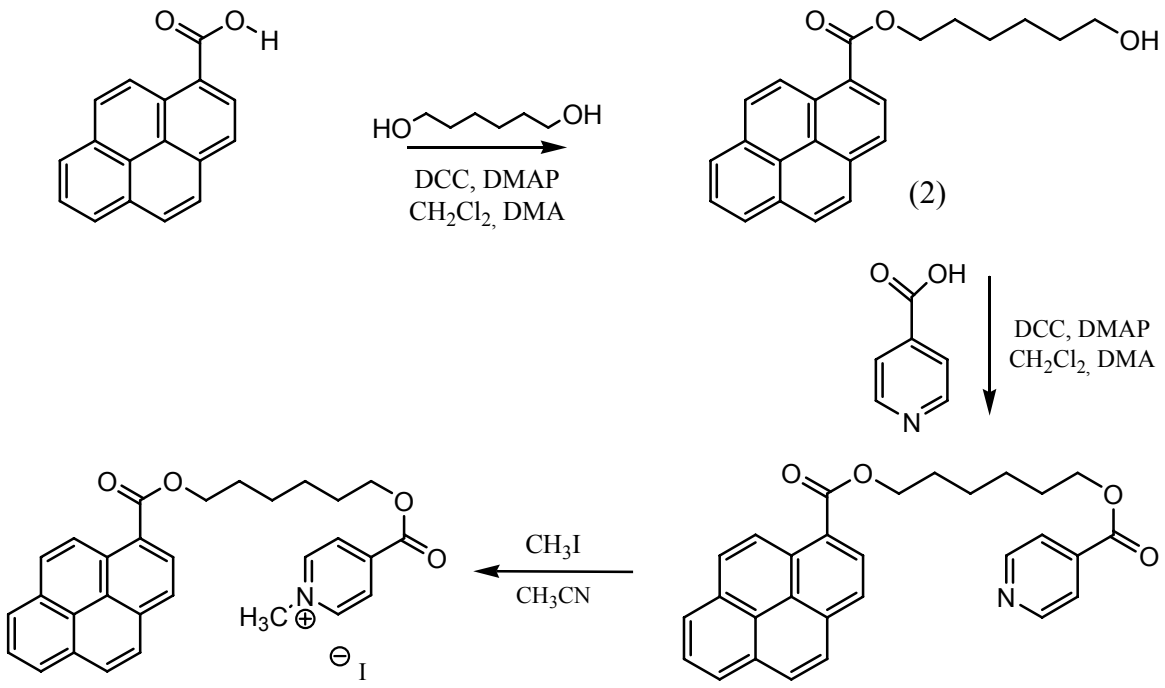
Cyclic voltammetric (CV) experiments were carried out at room temperature, in argon-purged CH_2Cl_2 (Romil Hi-Dry) solutions containing 0.1 M Bu_4NPF_6 as supporting electrolyte, with an Autolab 30 multipurpose instrument interfaced to a personal computer. The working electrode was a glassy carbon electrode (0.08 cm^2, Amel); its surface was routinely polished with 0.3 micron alumina-water slurry on a felt surface, immediately prior to use. In all cases, the counter electrode was a Pt spiral, separated from the bulk solution with a fine glass frit, and an Ag wire was used as

a quasi-reference electrode. Ferrocene ($E_{1/2}$ = +0.51 V vs SCE in CH_2Cl_2) was present as an internal standard.

ITC Titration

ITC titrations were performed using an isothermal titration microcalorimeter Microcal VP-ITC. All measurements were performed at (298 ±0,02) K. The host solution was filled into the cell of the ITC instrument and guest solutions were added with the syringe. In each case control experiments with dilution of guest in the solvent were performed and were found to be negligible. Concentration of cavitand **Tiiii [C_3H_7, CH_3, Ph]** 0.25 mM in dichloromethane; concentration of the guest **3b** 2.5 mM in dichloromethane. The volume of injection was 10 µL and the stirring speed was 300 rpm. Samples were weight with a microbalance Mettler Toledo MX5. The solvent was previously degassed by sonication during 15 min. Titrations were made 3 times in order to be reproducible. Analysis and curve fitting were done using the software MCS Origin-ITC 7.0 program.

Synthesis of the guests



Synthesis of the 6-hydroxyhexyl pyrene-1-carboxylate (2): To a solution of 1-pyrene carboxylic acid (200 mg, 0.812 mmol) dissolved in 15 mL of CH_2Cl_2 and 1 mL of DMA, DCC (168 mg, 0.812 mmol) and DMAP (33 mg, 0.268 mmol) were added. The solution was stirred at room temperature for 4 hours, then hexane-1,6-diol (115 mg, 0.974 mmol) was added and the resulting mixture was stirred at room temperature for three days. The crude was purified by column chromatography on silica gel by using CH_2Cl_2 as eluant to give compound (1) as brown powder in 42% yield (117 mg, 0.338 mmol).

^{1}H NMR ($CDCl_3$, 300 MHz) δ = 9.25 (d, 1H, J=9.3 Hz, Pyrene*H*), 8.61 (d, 1H, J=8.1 Hz, Pyrene*H*), 8.27-8.02 (m, 7H, Pyrene*H*), 4.50 (t, 2H, J=6.6 Hz, PyreneCOOCH_2R), 3.67 (t, 2H, J=6.3 Hz, RCH_2CH_2OH), 1.91 (m, 2H, $PyreneCOOCH_2CH_2R$), 1.68-1.48 (m, 6H, $RCH_2(CH_2)_3CH_2OH$); **MS** [ESI, m/z] = 381.1 $[M+Cl]^-$.

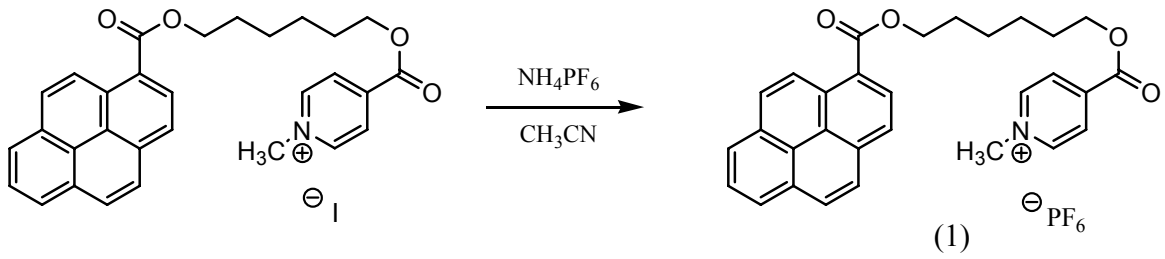
Synthesis of the 6-(pyrene-1-carbonyloxy)hexyl isonicotinate: To a solution of (2) (117 mg, 0.338 mmol) dissolved in 10 mL of CH_2Cl_2 and 1 mL of DMA, DCC (139 mg, 0.676 mmol) and DMAP (50 mg, 0.446 mmol) were added. The solution was stirred at room temperature for 4 hours, then isonicotinic acid (83 mg, 0.676 mmol) was added and the resulting mixture was stirred

at room temperature for three days. The crude was purified by column chromatography on silica gel by using CH_2Cl_2/ethylacetate (90/10 v/v) as eluant to give the desired compound as brown powder in 79% yield (121 mg, 0.268 mmol).

^{1}H NMR ($CDCl_3$, 300 MHz) δ = 9.21 (d, 1H, J=9.6 Hz, Pyrene*H*), 8.71 (d, 2H, J=5.6 Hz, PyH_o), 8.53 (d, 1H, J=8.1 Hz, Pyrene*H*), 8.13-7.88 (m, 7H, Pyrene*H*), 7.76 (d, 2H, J=5.6 Hz, PyH_m), 4.47 (t, 2H, J=6.6 Hz, PyreneCOOCH_2R), 4.29 (t, 2H, J=6.3 Hz, RCH_2OCOPy), 1.86 (m, 2H, PyreneCOOCH$_2$CH_2R), 1.74 (m, 2H, CH_2CH$_2$OCOPy), 1.51 (m, 4H, PyreneCOO(CH$_2$)$_2$(CH_2)$_2$R; **MS** [ESI, m/z] =452.4 $[M+H]^+$.

Synthesis of 1-methyl-4-((6-(pyrene-1-carbonyloxy)hexyloxy)carbonyl)pyridinium iodide: CH_3I (83 ul, 1.34 mmol) was added to a solution of 6-(pyrene-1-carbonyloxy)hexyl isonicotinate (121 mg, 0.268 mmol) dissolved in 10 mL of CH_3CN. The solution was refluxed for two days and the precipitate formed was filtered to give the desired salt as yellow powder in 50% yield (80 mg, 0.135 mmol).

^{1}H NMR ($CDCl_3$, 300 MHz) δ = 9.20 (d, 1H, J=9.3 Hz, Pyrene*H*), 8.96 (d, 2H, J=6.3 Hz, PyH_o), 8.59 (d, 1H, J=8.1 Hz, Pyrene*H*), 8.30-8.07 (m, 9H, Pyrene*H* e PyH_m), 4.55 (t, 2H, J=6.3 Hz, PyreneCOOCH_2R), 4.47 (t, 2H, J=6.3 Hz, RCH_2OCOPy), 4.41 (s, PyCH_3), 1.99 (m, 2H, PyreneCOOCH$_2$CH_2R), 1.89 (m, 2H, RCH_2CH$_2$OCOPy), 1.64 (m, 4H, PyreneCOO(CH$_2$)$_2$(CH_2)$_2$R; **MS** [ESI, m/z] = 466.4 $[M-I]^+$.



(1)

Synthesis of 1-methyl-4-((6-(pyrene-1-carbonyloxy)hexyloxy)carbonyl)pyridinium hexafluorophosphate (1): To a solution of 1-methyl-4-((6-(pyrene-1-carbonyloxy)hexyloxy) carbonyl)pyridinium iodide (50 mg, 0.084 mmol) dissolved in 2 mL of CH_3CN and 1 mL of water, NH_4PF_6 (27 mg, 0.168 mmol) was added. The solution was stirred at room temperature for three

hours, then the solvent was removed and the crude was extracted with water and CH_2Cl_2. The organic phase was dried over sodium sulphate and evaporated to give compound (1) as white powder in quantitative yield (51.4 mg, 0080 mmol).

^{1}H NMR (CD_3CN, 300 MHz) δ = 9.04 (d, 1H, J=9.3 Hz, Pyrene*H*), 8.50 (d, 2H, J=5.7 Hz, PyH_o), 8.25-8.05 (m, 10H, Pyrene*H* e PyH_m), 4.45 (t, 2H, J=6.3 Hz, PyreneCOOCH_2R), 4.33 (t, 2H, J=6.6 Hz, RCH_2OCOPy), 4.16 (s, PyCH_3), 1.87 (m, 2H, PyreneCOOCH$_2$CH_2R), 1.78 (m, 2H, RCH_2CH$_2$OCOPy), 1.55 (m, 4H, PyreneCOO(CH$_2$)$_2$(CH_2)$_2$R; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ = -141.1 (m, J_{P-F}=706 Hz, PF_6); **MS** [ESI, m/z] = 466.4 $[M\text{-}PF_6]^+$.

The preparation of guests **3a,b** followed the same procedure of the one reported above for guest **1**, starting from the corresponding isonicotinate esters.

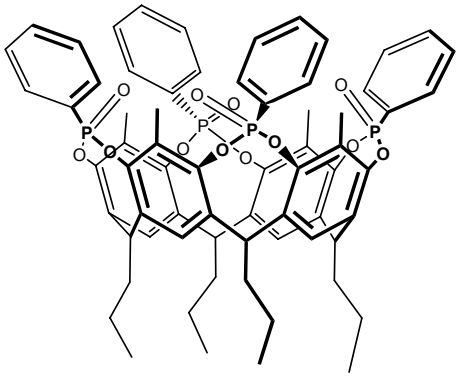
3a: ^{1}H NMR: (300 MHz, DMSO-d_6) δ(ppm): 3.98 (s, 3H, O**CH$_3$**), 4.41 (s, 3H, N**CH$_3$**), 8.48 (d, 2H, **H$_{mPy}$**, J=6.3 Hz), 9.14 (d, 2H, **H$_{oPy}$**, J=6.3 Hz). **^{31}P NMR** (162 MHz, DMSO-d_6) δ(ppm): -141.3 (m, **P**F_6^- , J_{P-F}=715 Hz). **MS** [ESI, m/z] = 152.5 $[M - PF_6]^+$.

3b: ^{1}H NMR: (300 MHz, $CDCl_3$) δ(ppm): 0.96 (t, 3H, **CH$_3$,** J=7.3 Hz), 1.43 (m, 2H, OCH$_2$CH$_2$**CH$_2$**CH$_3$), 1.76 (m, 2H, OCH$_2$**CH$_2$**CH$_2$CH$_3$), 4.41 (t, 2H, O**CH$_2$**CH$_2$CH$_2$CH$_3$, J=6.7 Hz), 4.47 (s, 3H, N**CH$_3$**), 8.40 (d, 2H, **H$_{mPy}$**, J=5.6 Hz), 8.84 (d, 2H, **H$_{oPy}$**, J=5.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ(ppm): -146.5 (m, **P**F_6^- , J_{P-F}=713 Hz). **MS** [ESI, m/z] = 195.0 $[M - PF_6]^+$.

Synthesis of the hosts

Cavitand **Tiiii[$C_{11}H_{23}$, H, Ph]** was prepared following a published procedure (see J.-P. Dutasta, B. Bibal, P. Delangle, I. Gosse and J.-C. Mulatier, *Phosphorus, Sulfur and Silicon*, 1999, **144-146**, 337-341 for the specific cavitand and B. Bibal, B. Tinant, J.-P. Declercq and J.-P. Dutasta, *Supramol. Chem.* 2003, **15**, 25-32 for the general procedure).

Synthesis of Tiiii[C_3H_7, CH_3, Ph]



To a solution of resorcinarene (0.60 g, 0.80 mmol) in freshly distilled pyridine (20 mL) dichlorophenylphosphine (0.447 mL, 3.39 mmol) was added slowly, at room temperature. After 3 hours of stirring at 80 °C, the solution was allowed to cool at room temperature and 8 mL of a mixture of 35% H_2O_2 and $CHCl_3$ (1:1) was added. The resulting mixture was stirred for 30 minutes at room temperature, then the solvent was removed under reduced pressure and water added. The precipitate obtained in this way was collected by vacuum filtration, and purified by re-crystallization (H_2O:CH_3CN 8:2). The product is a fine white powder (0.91 g, 0.76 mmol, 94%)

^{1}H NMR (300 MHz, 298 K,$CDCl_3$) δ (ppm): 8.09 (m, 8H, P(O)Ar**H**$_o$); 7.61 (m, 4H, P(O)Ar**H**$_p$); 7.52 (m, 8H, P(O)Ar**H**$_m$); 7.13 (s, 4H, Ar**H**); 4.81 (t, 4H, ArC**H**, J = 7.4 Hz); 2.34-2.20 (m, 8H + 12H, C**H$_2$**CH_2CH_3 + ArC**H$_3$**); 1.41 (m, 8H, CH_2C**H$_2$**CH_3); 1.04 (t, 12H, CH_2CH_2C**H$_3$**, J = 7.4 Hz). **^{31}P NMR** (162 MHz, 298 K, $CDCl_3$) δ (ppm): 4.02 (s, P=O). **ESI-MS**: *m/z* calcd for $C_{68}H_{68}O_{12}P_4$ (1201.2 Da) $[M+H]^+$: 1202.2; found 1201.6. Anal. Calc. for $C_{68}H_{68}O_{12}P_4$: C, 68.00; H, 5.71; P, 10.31. Found: C, 68.32; H, 5.97; P 10.03.

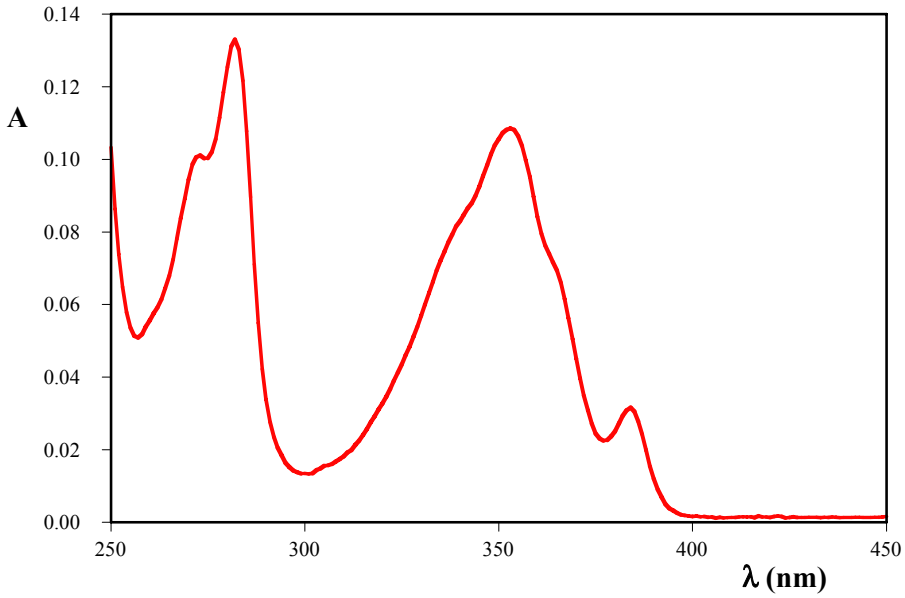


Figure S1: Absorption spectrum of a 4.2 x 10^{-6} M dichloromethane solution of **1**.

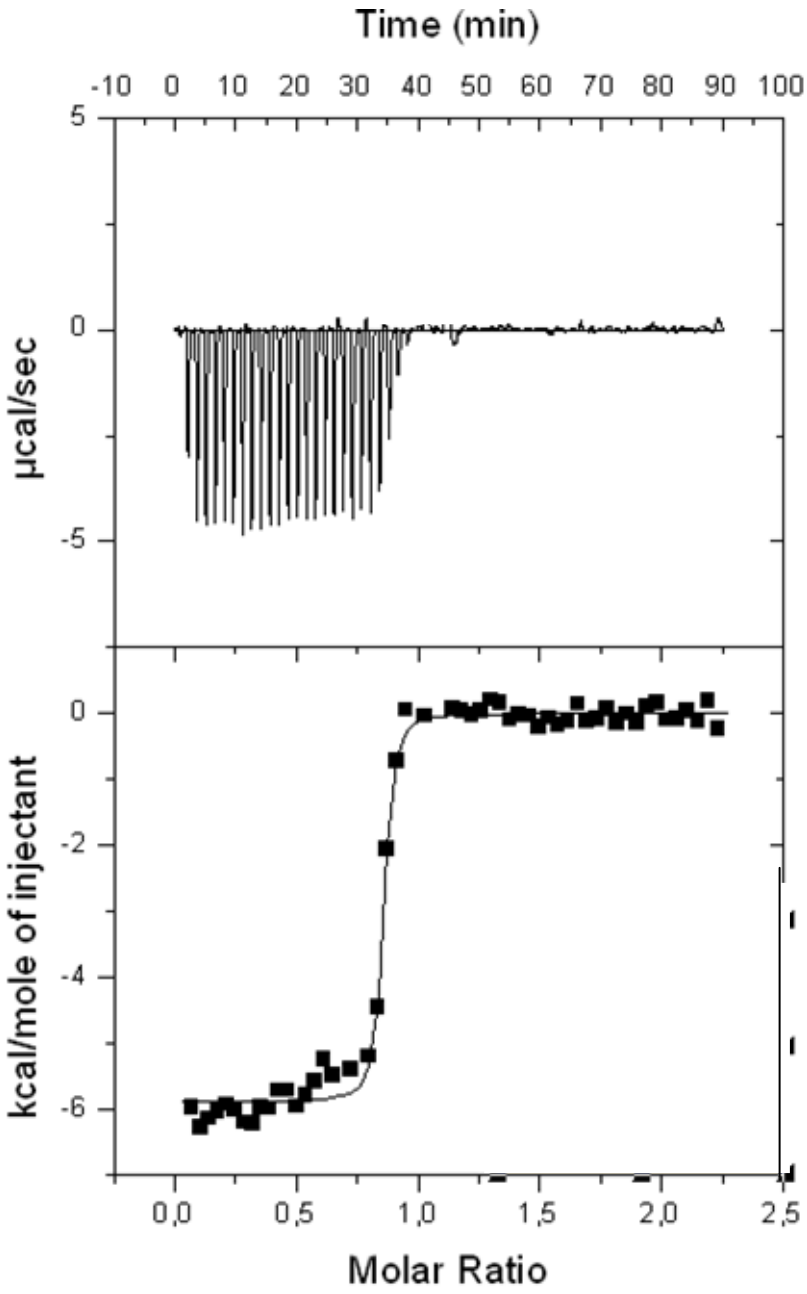


Figure S2: ITC trace of the titration of cavitand **Tiiii[C_3H_7, CH_3, Ph]** with **3b** in CH_2Cl_2. Titration mode: guest (**3b**) into host (**Tiiii[C_3H_7, CH_3, Ph]**) solution; one-site model.

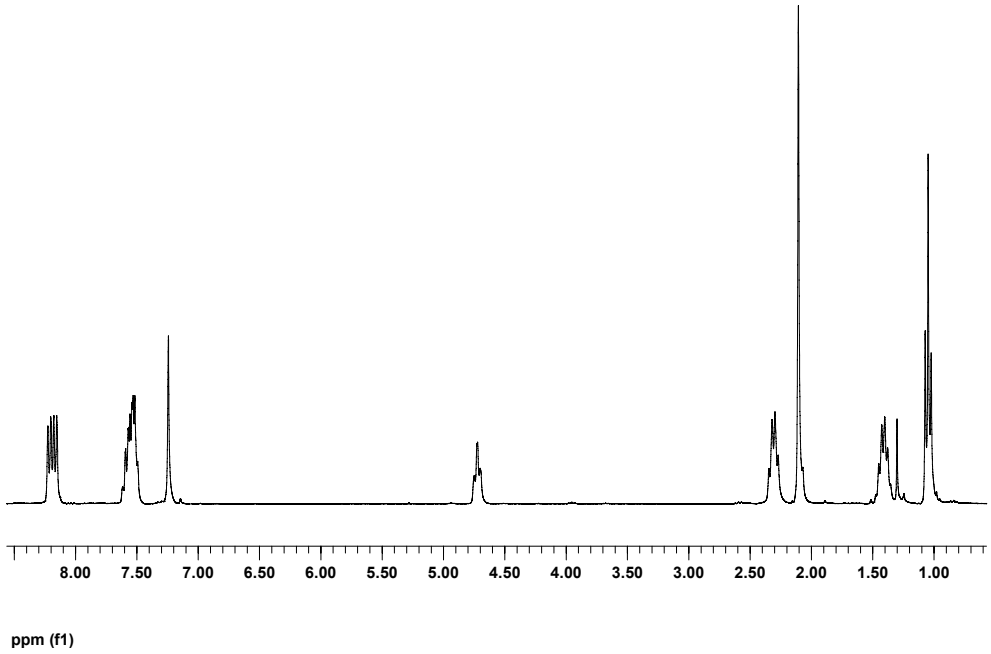


Figure S3. ^{1}H NMR spectrum of **Tiiii[C_3H_7, CH_3, Ph]** in $CDCl_3$.

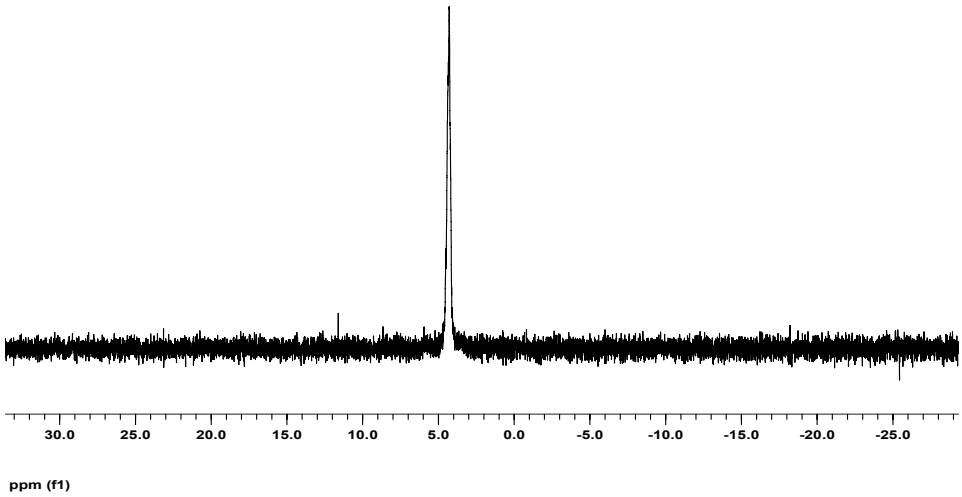


Figure S4. ^{31}P NMR spectrum of **Tiiii[C_3H_7, CH_3, Ph]** in $CDCl_3$.