

## Supplementary Information

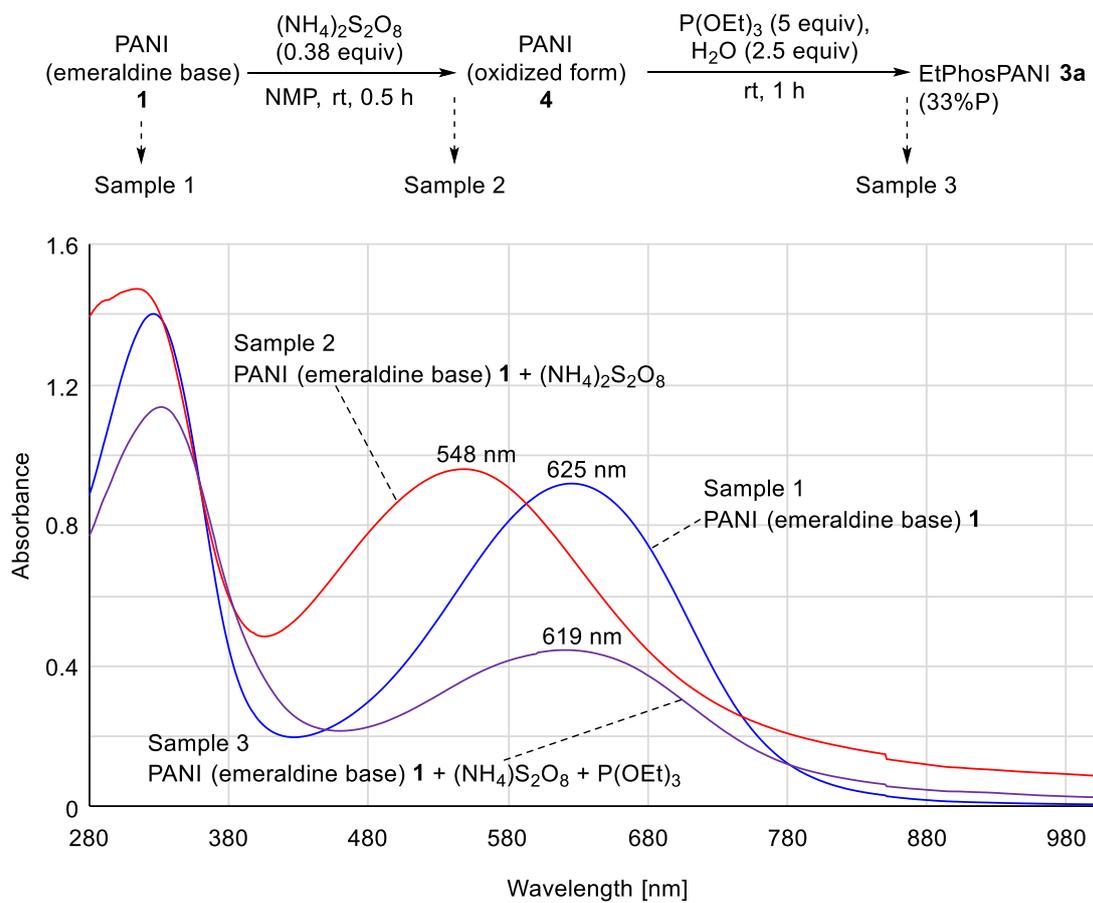
### **Synthesis of Phosphonic Acid Ring-Substituted Polyanilines via Direct Phosphonation to Polymer Main Chains**

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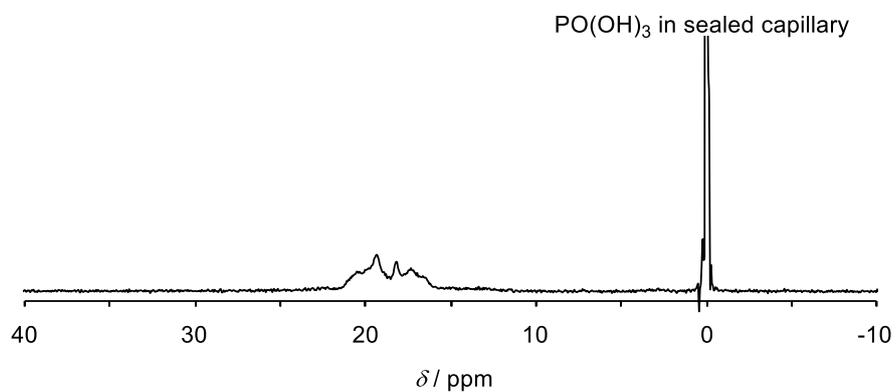
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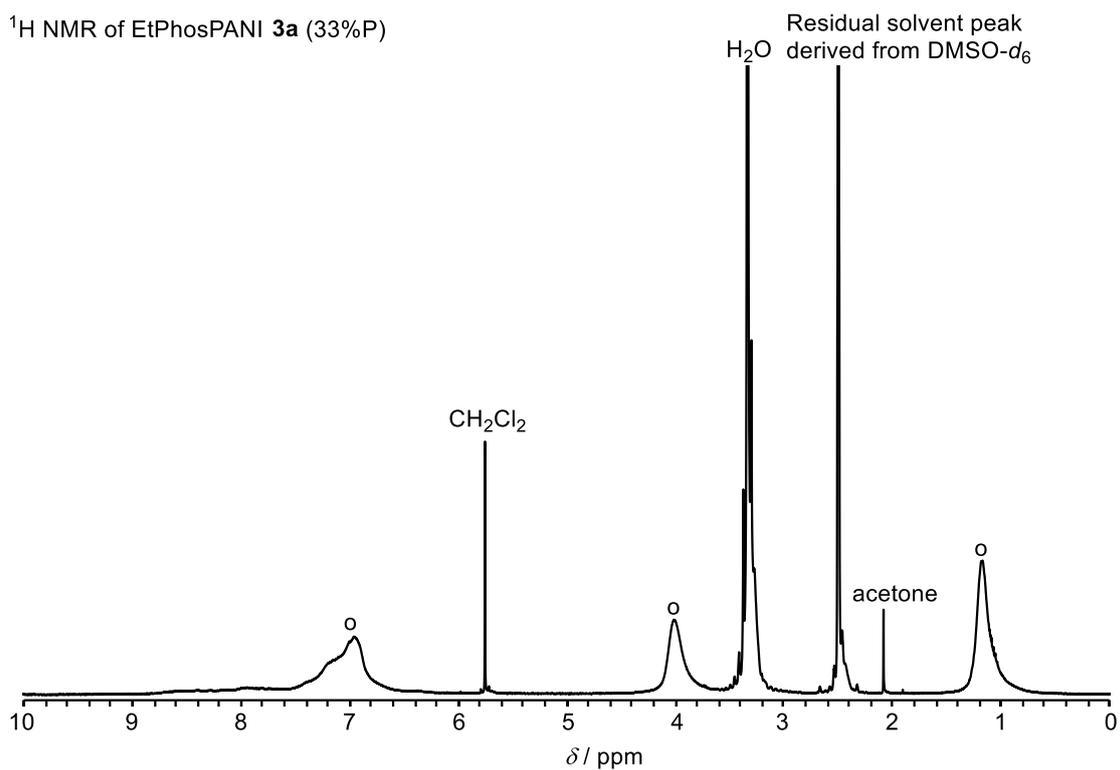
**Fig. S1.** UV-vis-NIR absorption spectra for the diluted samples 1-3 in NMP (the concentration for samples 1-3 is 0.22, 1.1, and 2.2 mM based on an aniline unit of PANI, respectively).

$^{31}\text{P}$  NMR of EtPhosPANI **3a** (33%P)

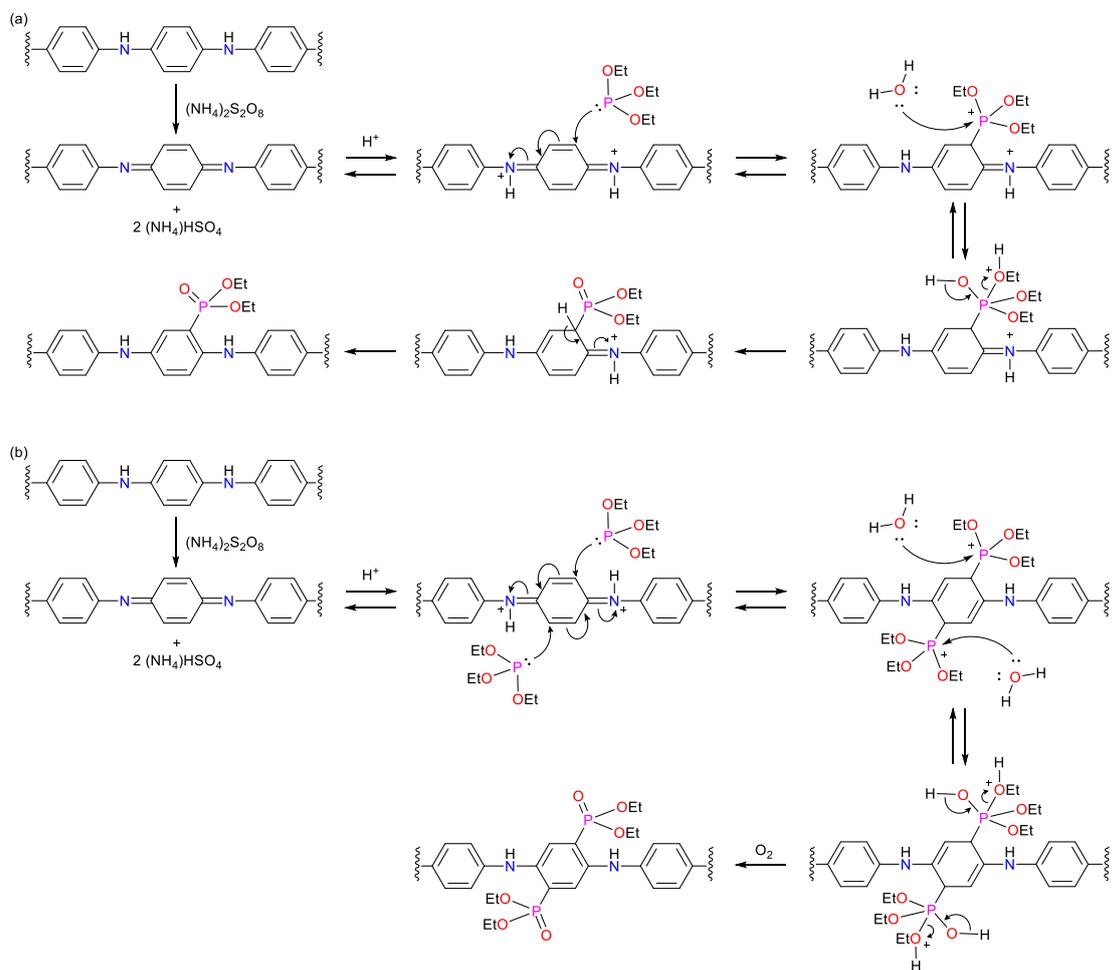


**Fig. S2.**  $^{31}\text{P}$  NMR spectrum for EtPhosPANI **3a** (33%P) in DMSO-*d*<sub>6</sub> (162 MHz).

$^1\text{H}$  NMR of EtPhosPANI **3a** (33%P)

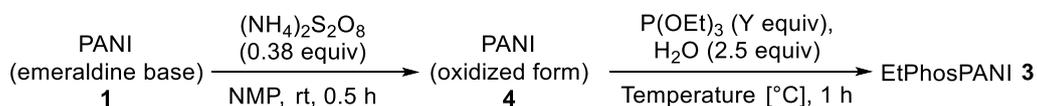


**Fig. S3.**  $^1\text{H}$  NMR spectrum for EtPhosPANI **3a** (33%P) (the peaks are marked as o) in DMSO-*d*<sub>6</sub> (400 MHz).



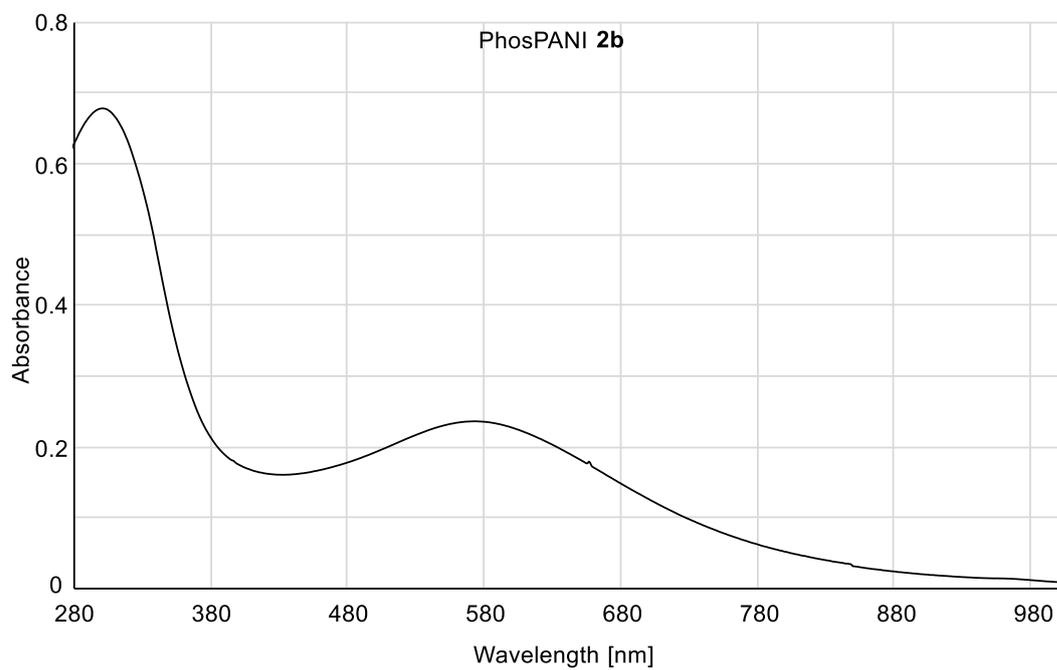
**Scheme S1.** Proposed mechanistic pathway of (a) mono-phosphonation and (b) di-phosphonation.

**Table S1.** Investigation of substitution ratio of phosphonate toward the reaction temperature and equivalents of P(OEt)<sub>3</sub><sup>a</sup>



Entry	P(OEt) <sub>3</sub> Y [equiv] <sup>a</sup>	Temperature [°C]	Substitution ratio of phosphonate [%] <sup>b</sup>	Yield [%] <sup>c</sup>
1 <sup>d,g</sup>	0.75	rt	9	56
2 <sup>d</sup>	2.5	rt	24	54
3 <sup>e</sup>	7.8	rt	37	63
4 <sup>e</sup>	15	rt	42	63
5 <sup>e</sup>	7.8	60	46	65
6 <sup>f</sup>	7.8	60	52	77
7 <sup>e</sup>	7.8	120	49	25
8 <sup>e</sup>	15	60	37	50

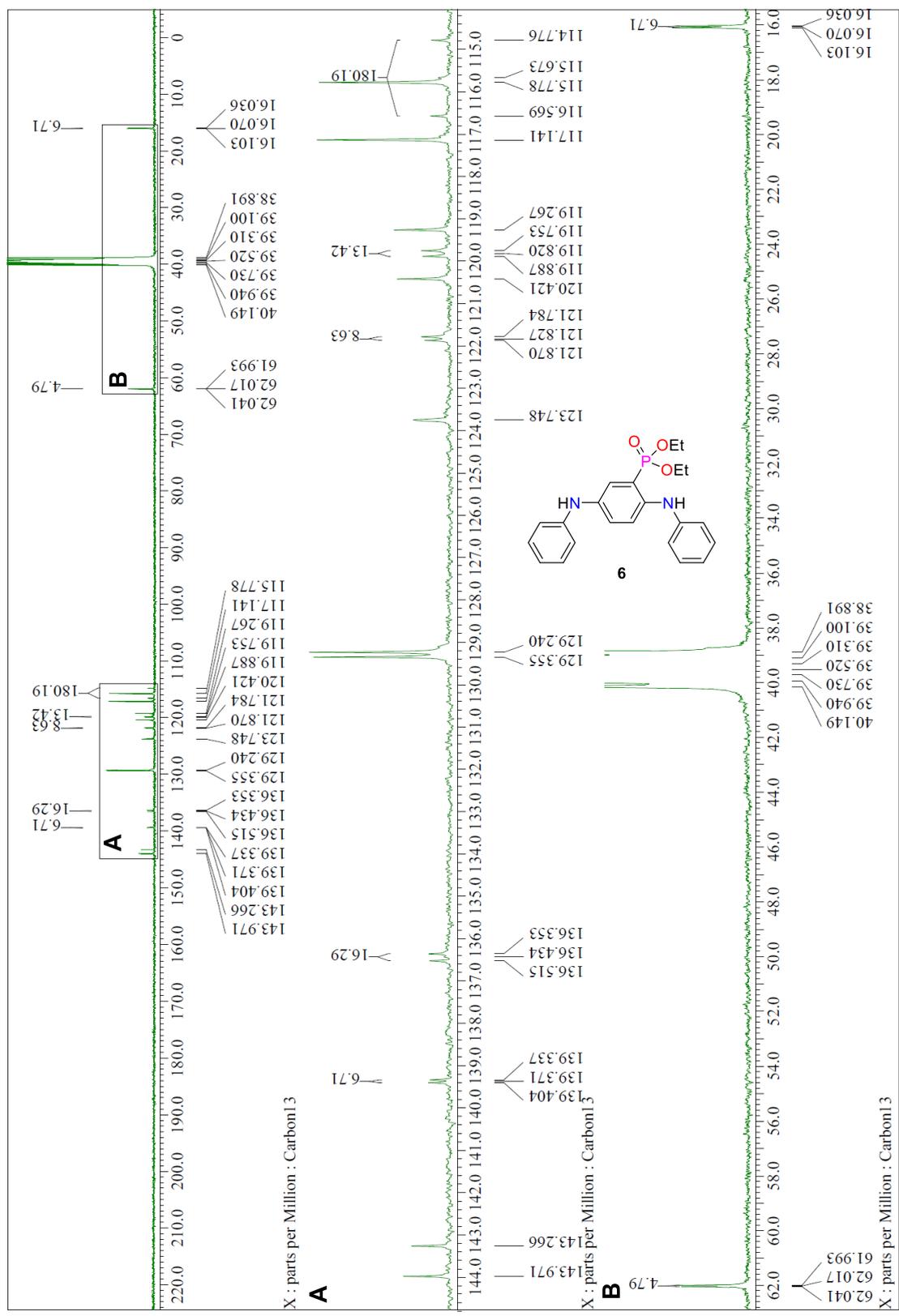
<sup>a</sup>Equivalents were calculated based on an aniline unit of PANI **1**. Amounts of the reagents were calculated based on the mole number of **1**. <sup>b</sup>Substitution ratio of phosphonate was calculated similarly to those for EtPhosPANIs **3a-c** based on ICP-AES analysis although TGA analysis was not conducted for these entries in this Table except entry 6. <sup>c</sup>Yield [%] = (mole of product)/(mole of substrate)\*100, where mole of **3** is calculated using the molecular weight of **3** estimated from the structure given in Fig. 1 in the main text. <sup>d</sup>The reactions were carried out using 101 mg of **1** (1.12 mmol) and 5.0 mL of NMP. <sup>e</sup>The reactions were carried out using 362 mg of **1** (4.00 mmol) and 20.0 mL of NMP. <sup>f</sup>This entry is described for EtPhosPANI **3b**. The reactions were carried out using 1.81 g of **1** (20.00 mmol) and 100.0 mL of NMP. <sup>g</sup>Reaction time for phosphonation step was 1.5 h.



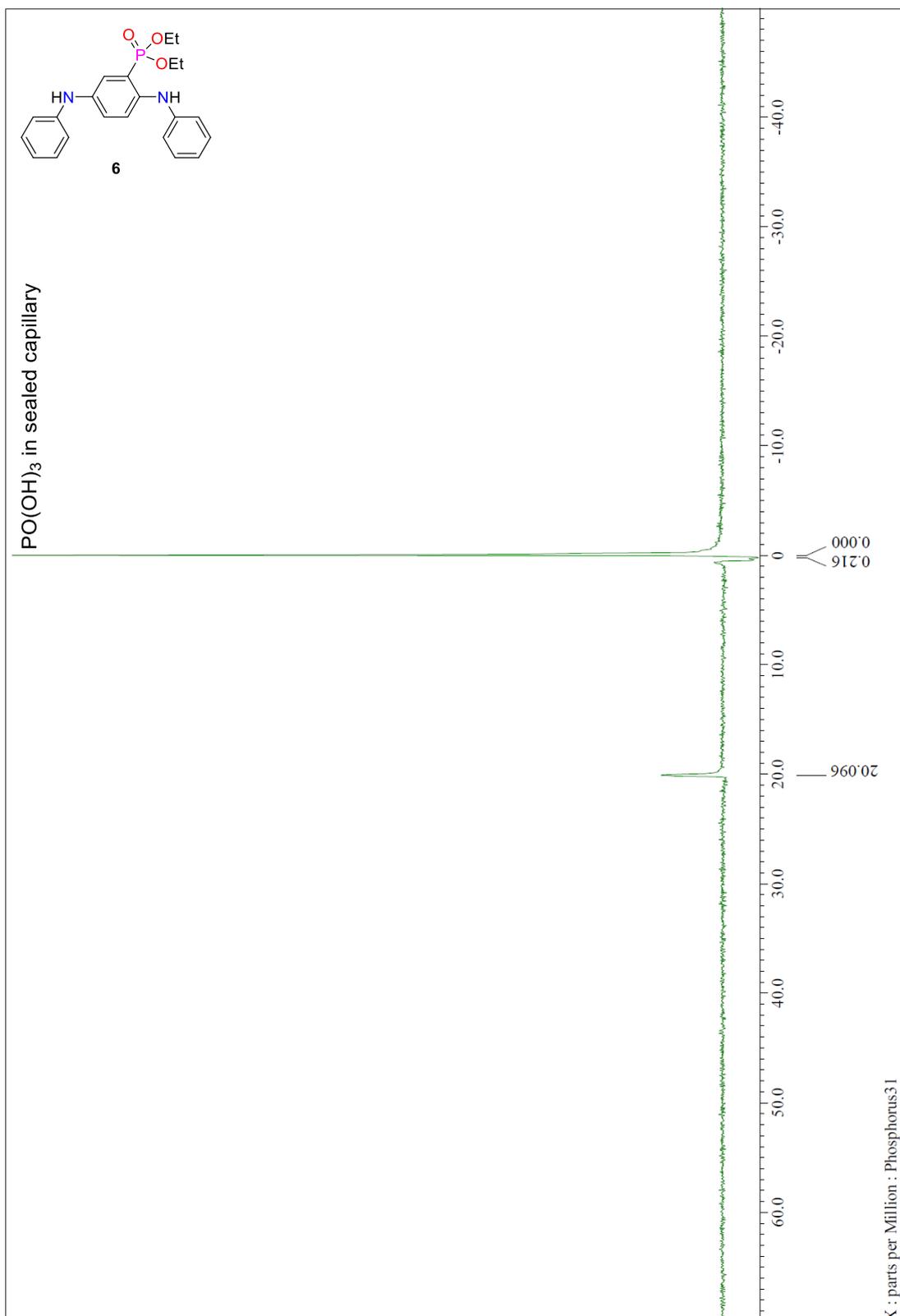
**Fig. S4.** UV-vis-NIR absorption spectrum for ca.  $5.4 \times 10^{-2}$  g/L of PhosPANI **2b** in  $\text{H}_2\text{O}/\text{MeOH}/0.15 \text{ M NH}_3 \text{ aq.} = 1/1/1$  (v/v).



<sup>13</sup>C NMR spectrum in DMSO-d<sub>6</sub> (100 MHz)

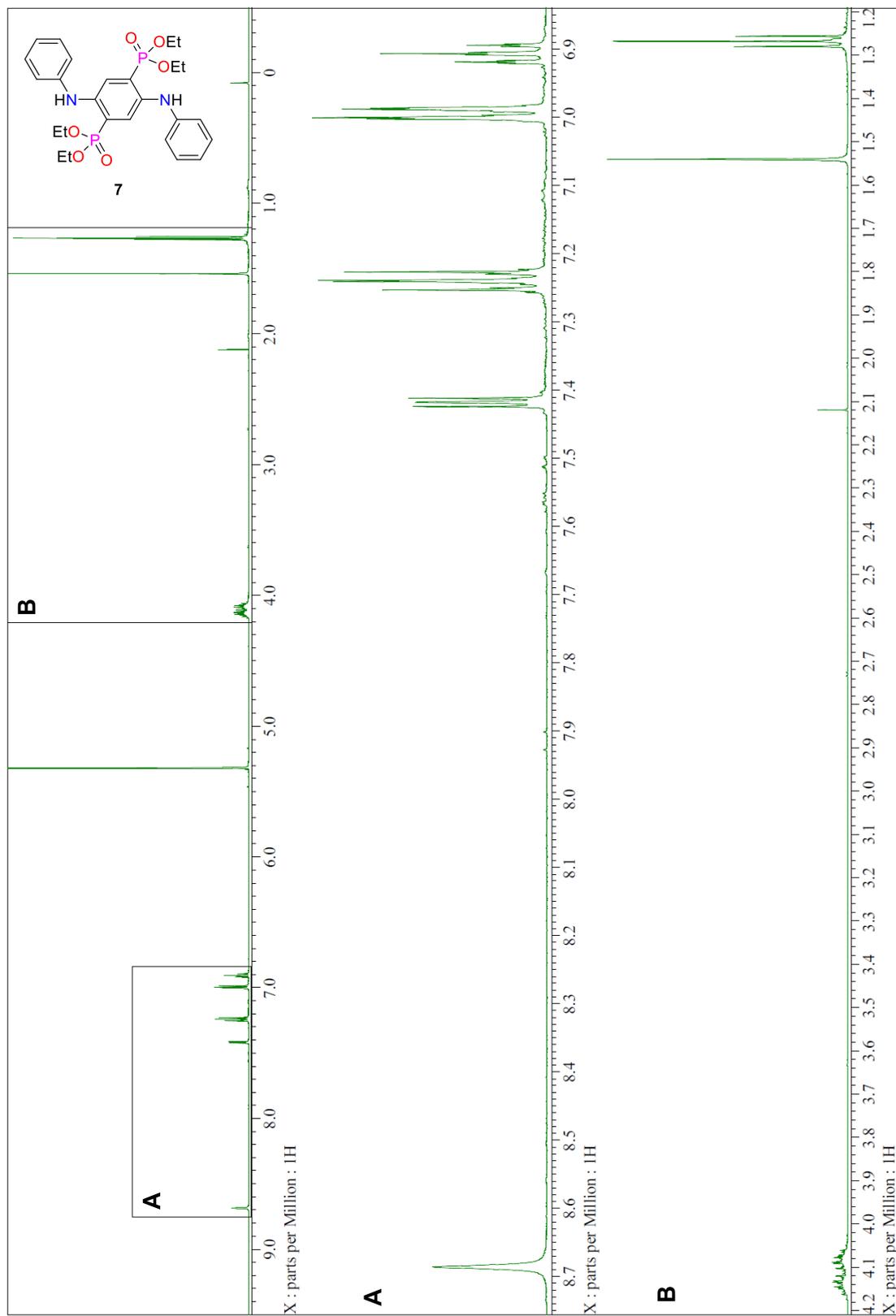


$^{31}\text{P}$  NMR spectrum in  $\text{DMSO-}d_6$  (162 MHz)

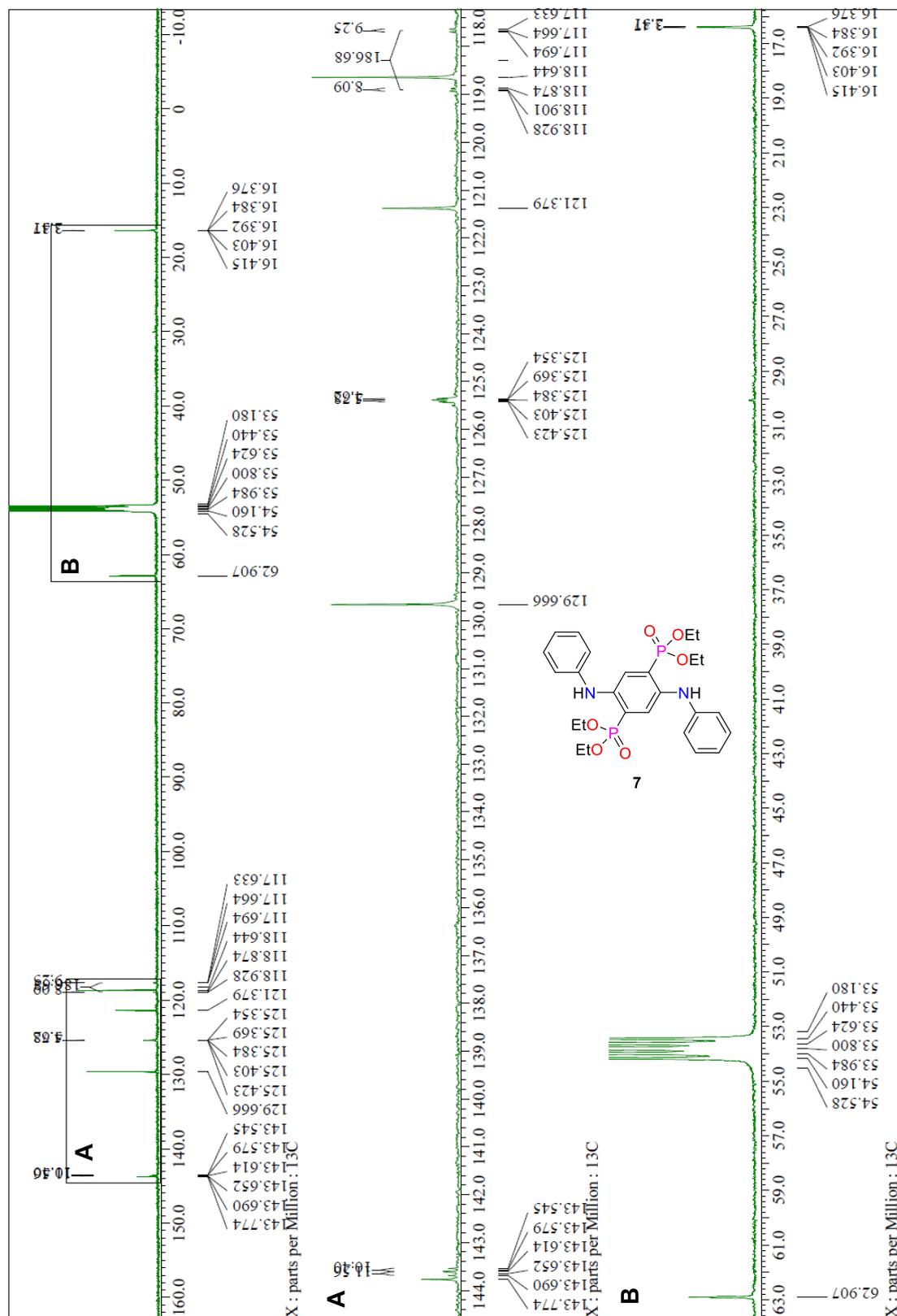


# NMR spectra for 7

<sup>1</sup>H NMR spectrum in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz)



<sup>13</sup>C NMR spectrum in CD<sub>2</sub>Cl<sub>2</sub> (150 MHz)



$^{31}\text{P}$  NMR spectrum in  $\text{CD}_2\text{Cl}_2$  (162 MHz)

