

*Supporting information for*

## **Complexes of phosphine oxides with substituted phenols: hydrogen bond characterization based on shifts of P=O stretching bands**

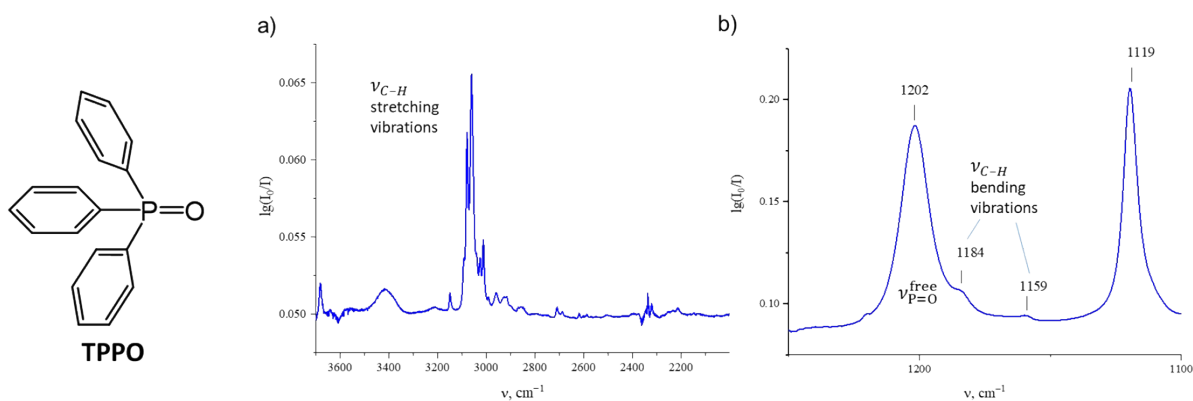
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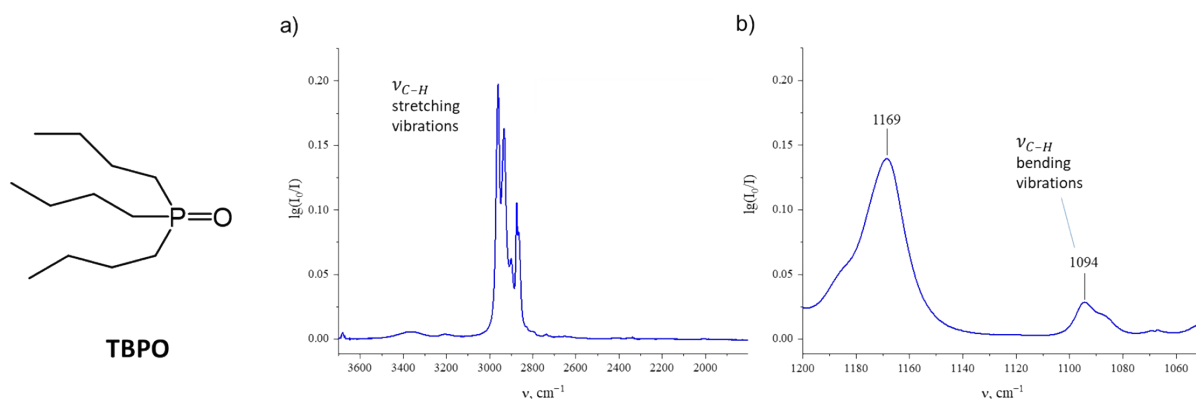
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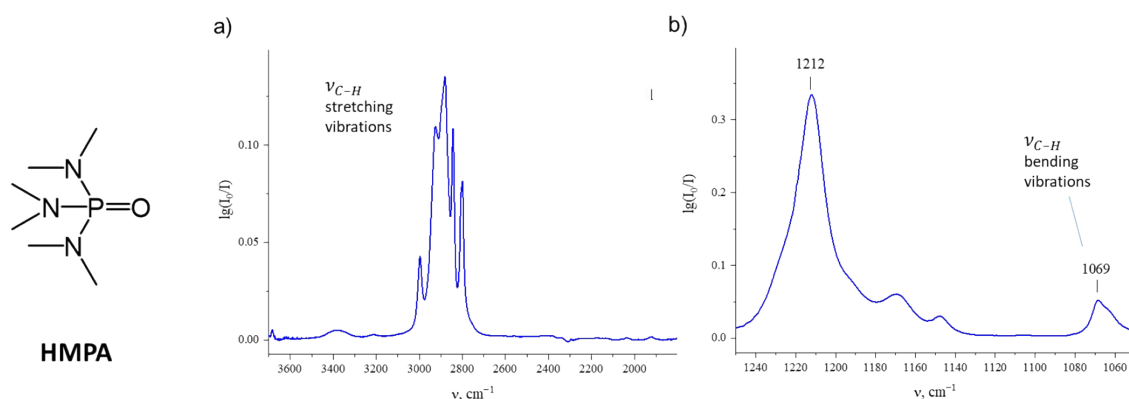
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**Fig. S1.** Parts of IR spectra of  $\sim 3.9 \text{ mmol L}^{-1}$  solution of triphenylphosphine oxide (TPPO) in  $\text{CCl}_4$  at room temperature. Spectral regions containing (a) O–H stretching band ( $2000\text{--}3700 \text{ cm}^{-1}$ ) and (b) P=O stretching band ( $1100\text{--}1250 \text{ cm}^{-1}$ ) are shown. The P=O band for free TPPO,  $\nu_{\text{P}=\text{O}}^{\text{free}}$ , is located at  $1202 \text{ cm}^{-1}$ .



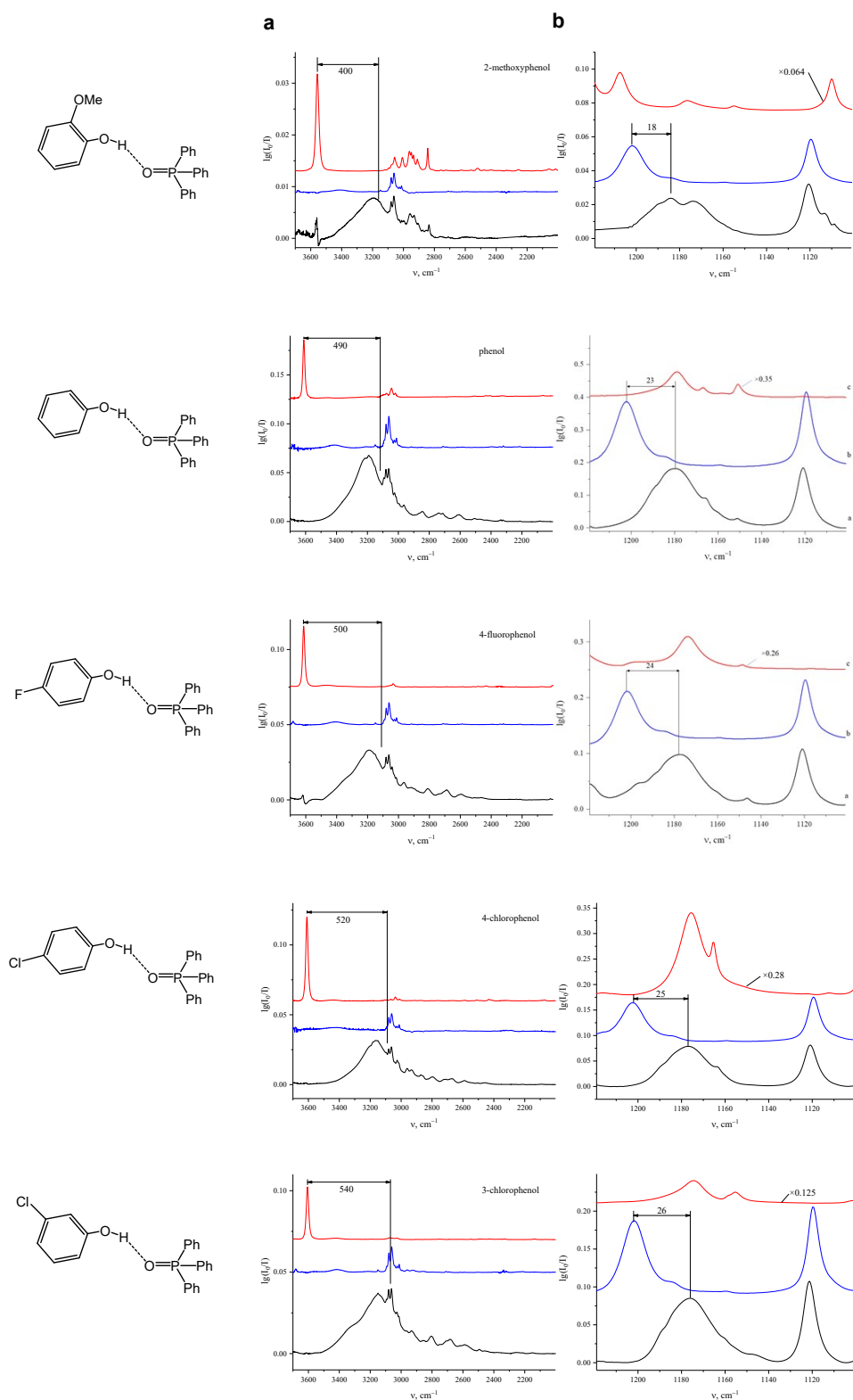
**Fig. S2.** Parts of IR spectra of  $\sim 4.7 \text{ mmol L}^{-1}$  solution of tributylphosphine oxide (TBPO) in  $\text{CCl}_4$  at room temperature. Spectral regions containing (a) O–H stretching band ( $2000\text{--}3700 \text{ cm}^{-1}$ ) and (b) P=O stretching band ( $1100\text{--}1250 \text{ cm}^{-1}$ ) are shown. The P=O band for free TBPO,  $\nu_{\text{P}=\text{O}}^{\text{free}}$ , is located at  $1169 \text{ cm}^{-1}$ .



**Fig. S3.** Parts of IR spectra of  $\sim 5.8 \text{ mmol L}^{-1}$  solution of hexamethylphosphoramide (HMPA) in  $\text{CCl}_4$  at room temperature. Spectral regions containing (a) O–H stretching band ( $2000\text{--}3700 \text{ cm}^{-1}$ ) and (b) P=O stretching band ( $1100\text{--}1250 \text{ cm}^{-1}$ ) are shown. The P=O band for free HMPA,  $\nu_{P=O}^{free}$ , is located at  $1212 \text{ cm}^{-1}$ .

**Table S1.** The wavenumbers of absorption bands corresponding to stretching vibration of OH group,  $\nu_{OH}^{free}$ , and P=O group,  $\nu_{P=O}^{free}$ , of TPPO, TBPO, HMPA and proton donors **1–10** in solutions in  $\text{CCl}_4$  at room temperature.

Compound	The type of vibration	The frequency of vibration, in $\text{cm}^{-1}$
<b>1</b>	$\nu_{OH}^{free}$ , stretching	3557
<b>2</b>		3611
<b>3</b>		3613
<b>4</b>		3609
<b>5</b>		3606
<b>6</b>		3594
<b>7</b>		3529
<b>8</b>		3516
<b>9</b>		3519
<b>10</b>		3619
<b>TPPO</b>	$\nu_{P=O}^{free}$ , stretching	1202
<b>TBPO</b>		1212
<b>HMPA</b>		1169



**Fig. S4.** Parts of IR spectra of complexes formed by TPPO and proton donors **1–10** in  $\text{CCl}_4$  solution at room temperature in the regions of (a) OH stretching vibrations (b) P=O stretching vibrations. The spectra of free proton donors (red) free TPPO (blue) and their complexes (black) are shown. Vertical bars indicate locations of OH and P=O vibrational bands for free species and the complexes.

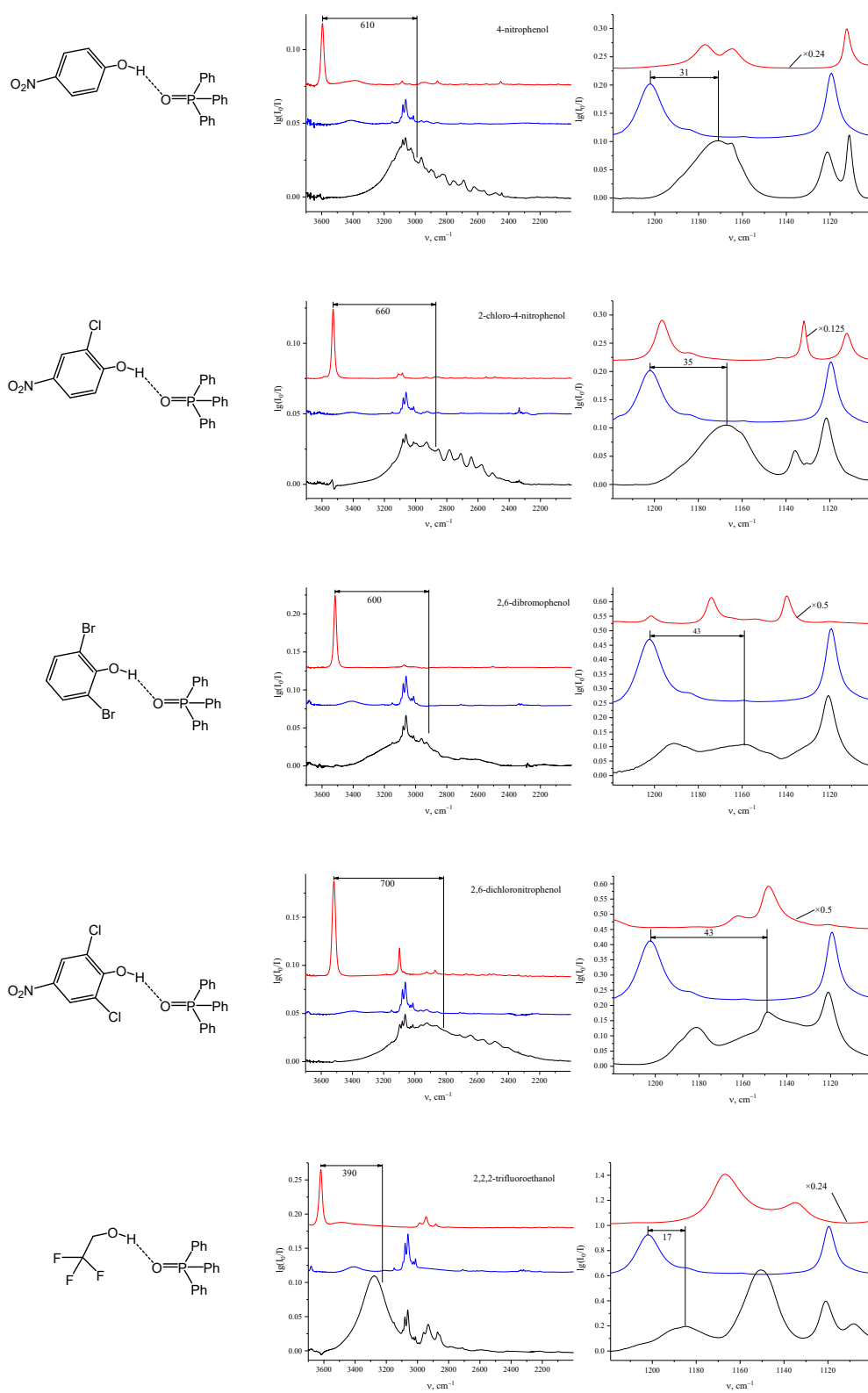
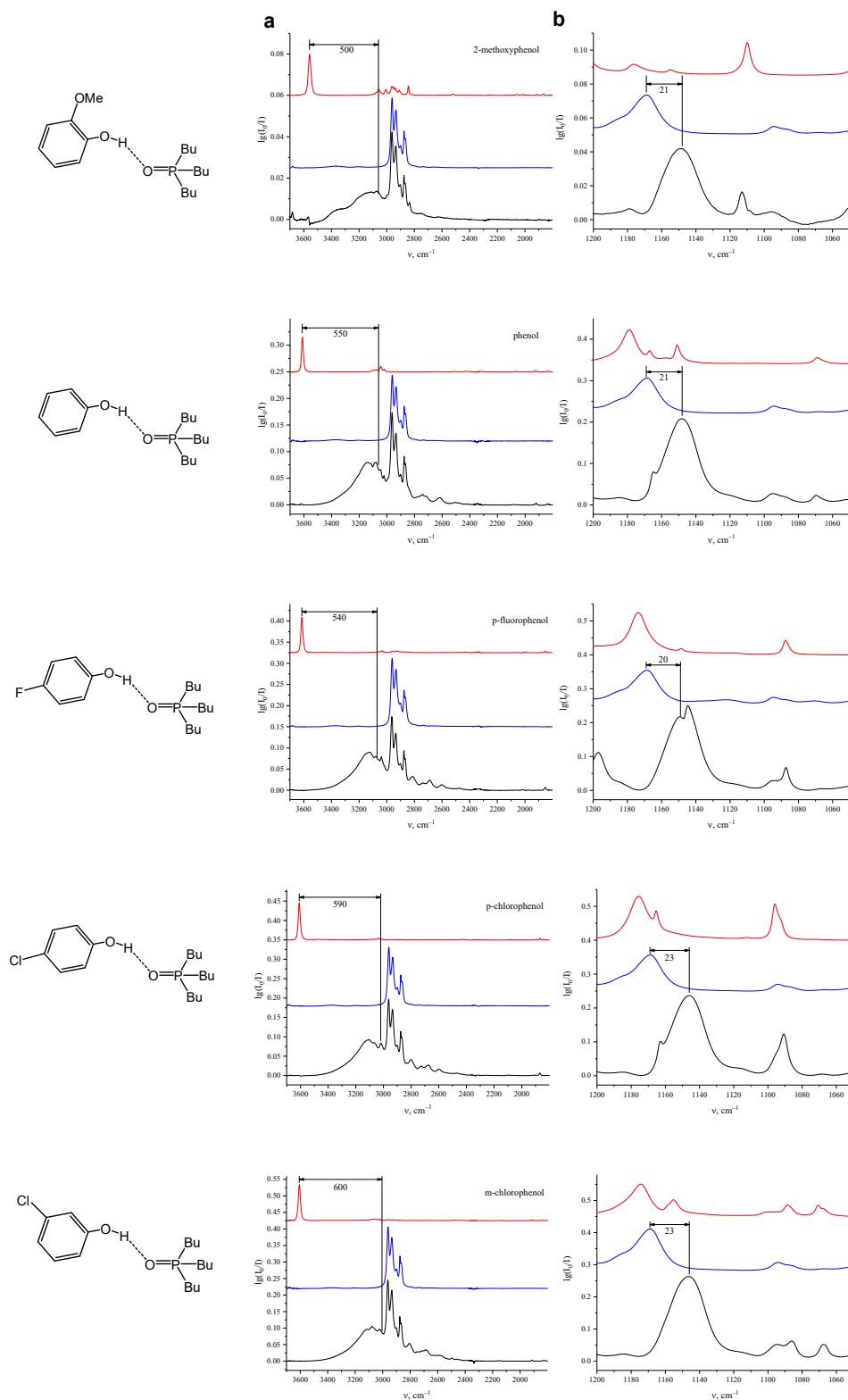


Fig. S4. (Continued)



**Fig. S5.** Parts of IR spectra of complexes formed by TBPO and proton donors 1–10 in  $\text{CCl}_4$  solution at room temperature in the regions of (a) OH stretching vibrations (b) P=O stretching vibrations. The spectra of free proton donors (red) free TBPO (blue) and their complexes (black) are shown. Vertical bars indicate locations of OH and P=O vibrational bands for free species and the complexes.

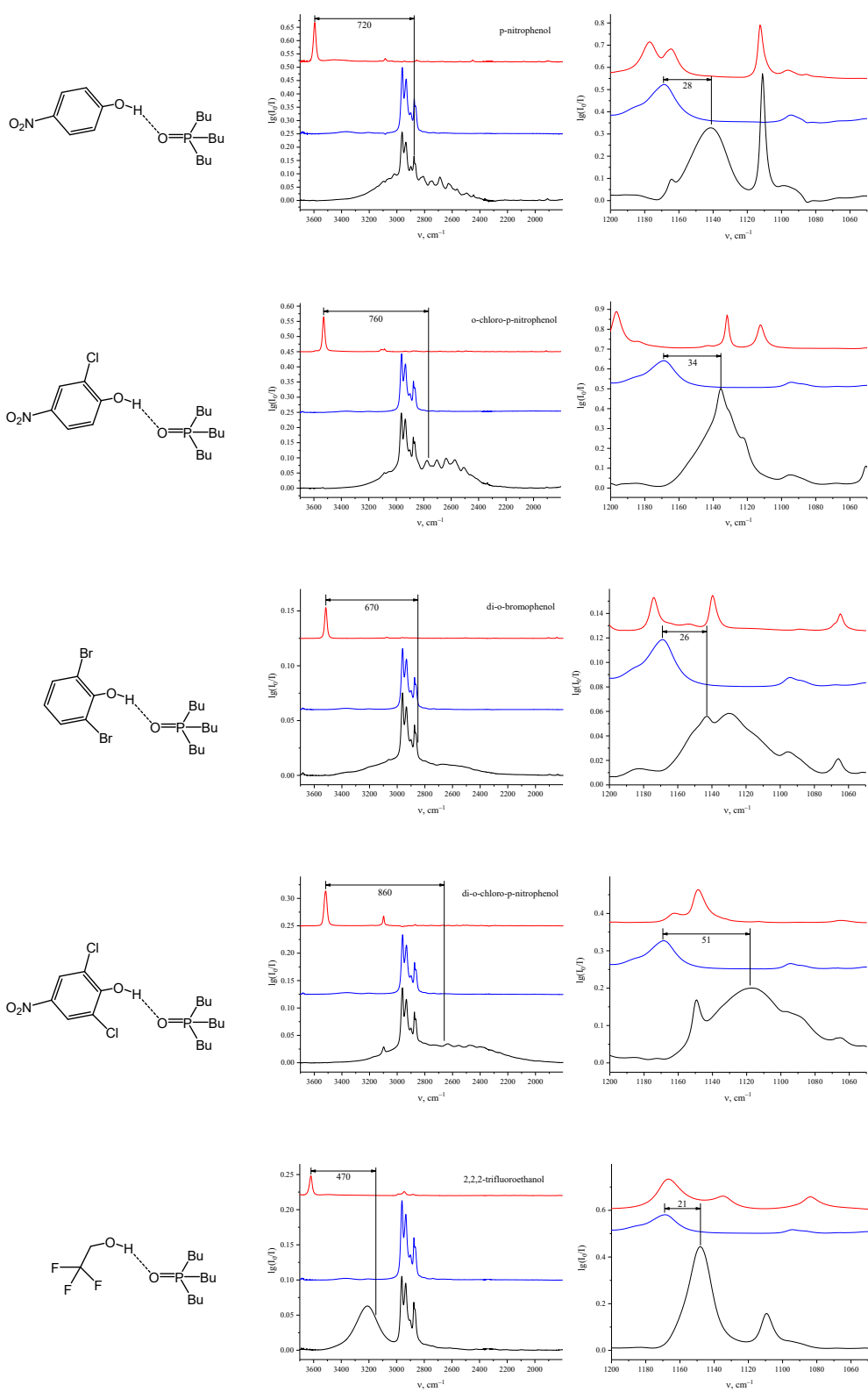
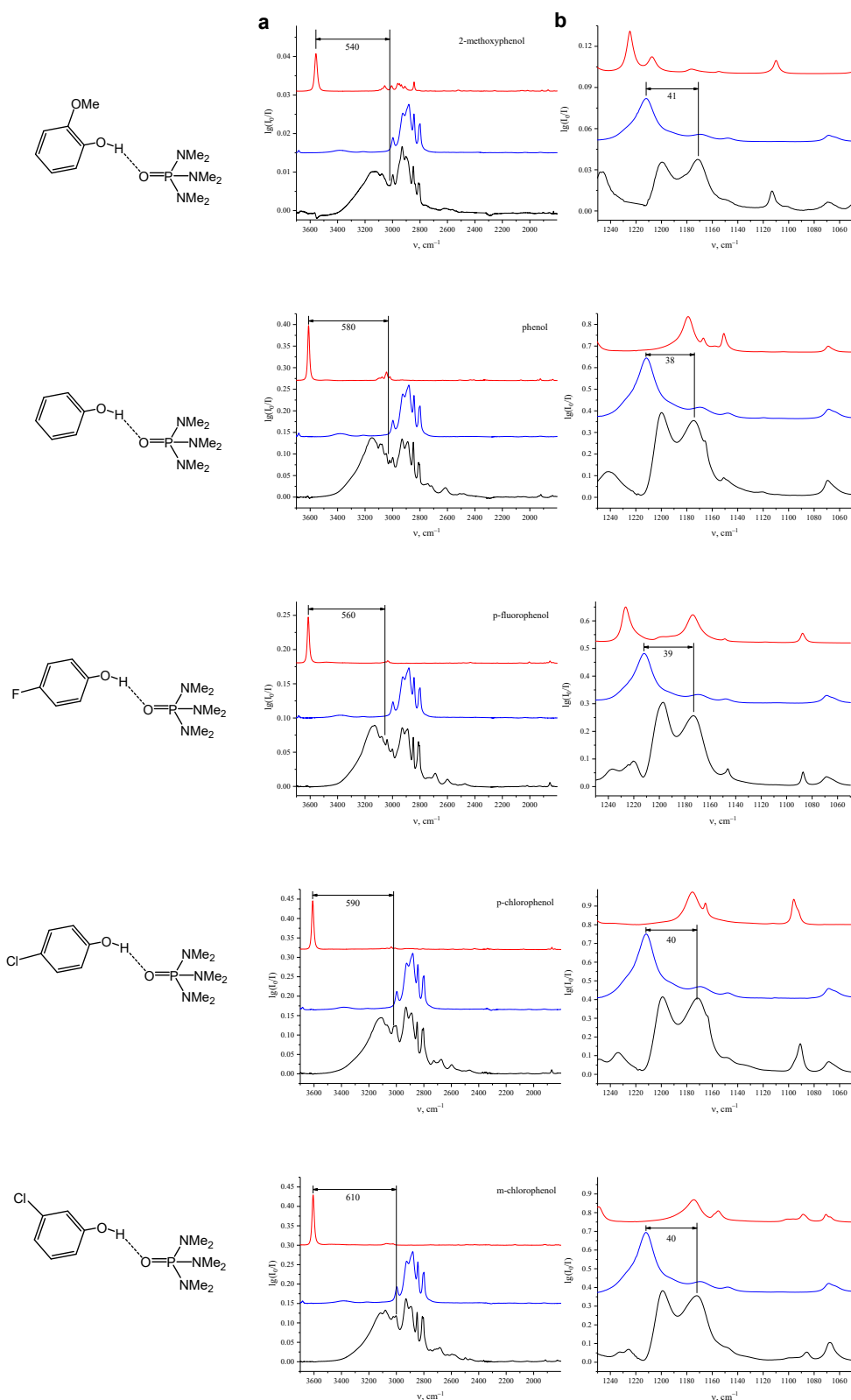


Fig. S5 (continued)



**Fig. S6.** Parts of IR spectra of complexes formed by HMPA and proton donors **1–10** in  $\text{CCl}_4$  solution at room temperature in the regions of (a) OH stretching vibrations (b) P=O stretching vibrations. The spectra of free proton donors (red) free HMPA (blue) and their complexes (black) are shown. Vertical bars indicate locations of OH and P=O vibrational bands for free species and the complexes.



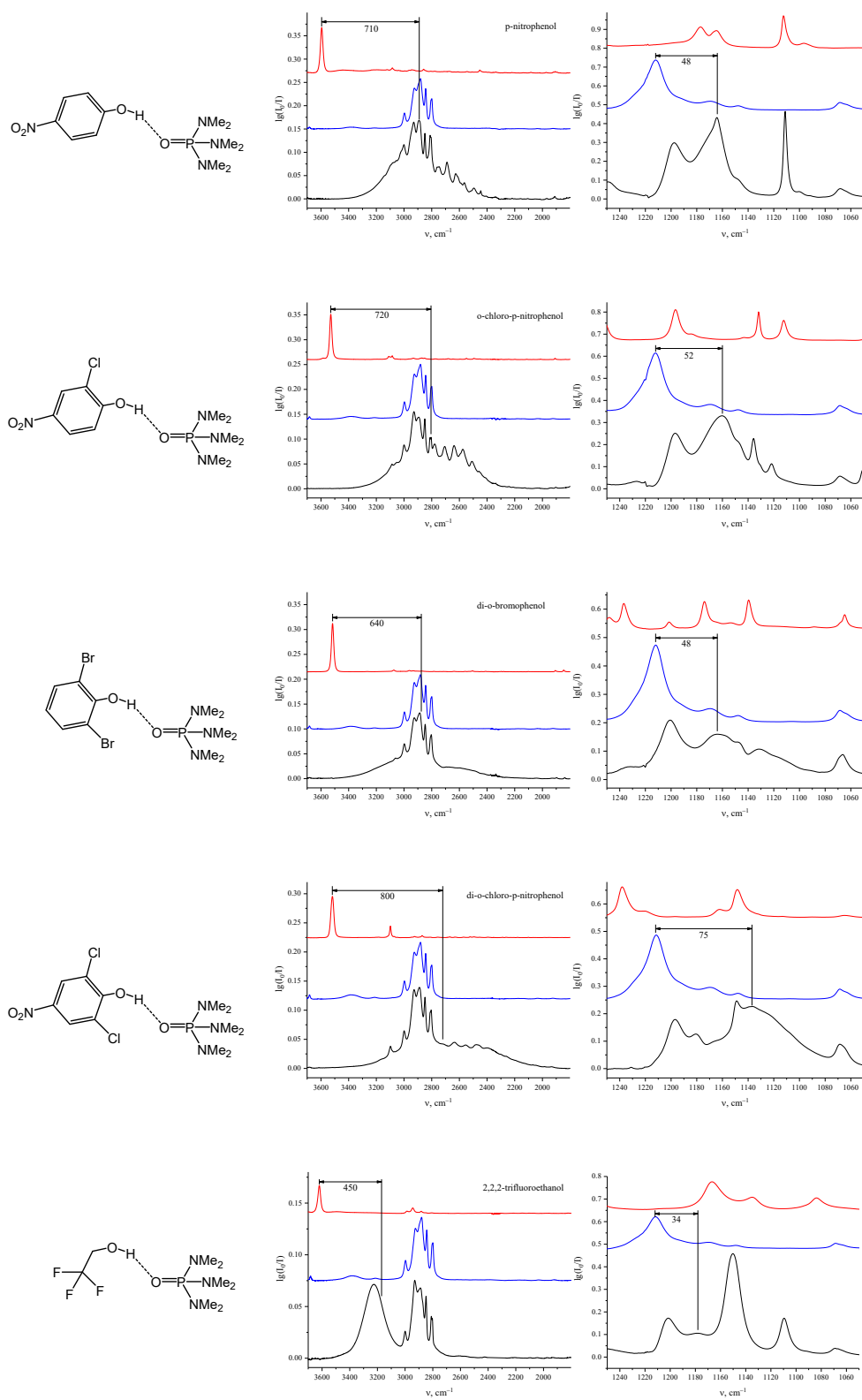
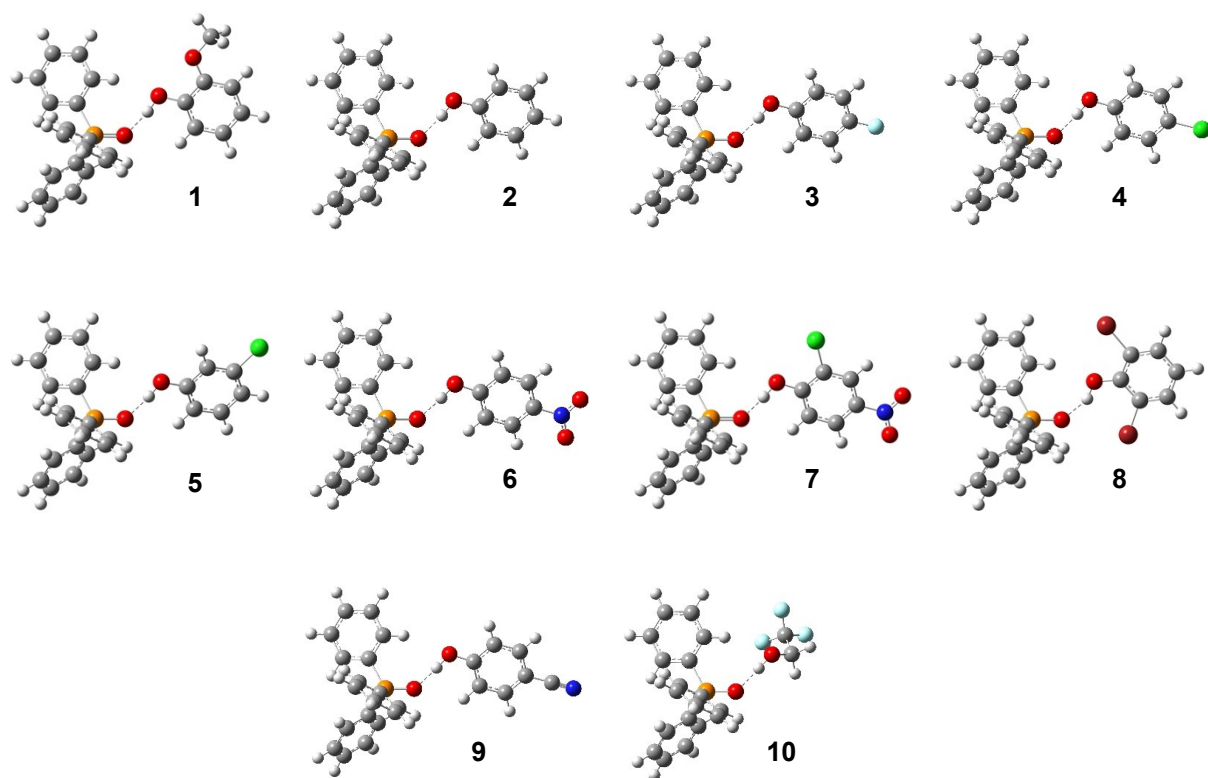


Fig. S6. (Continued)



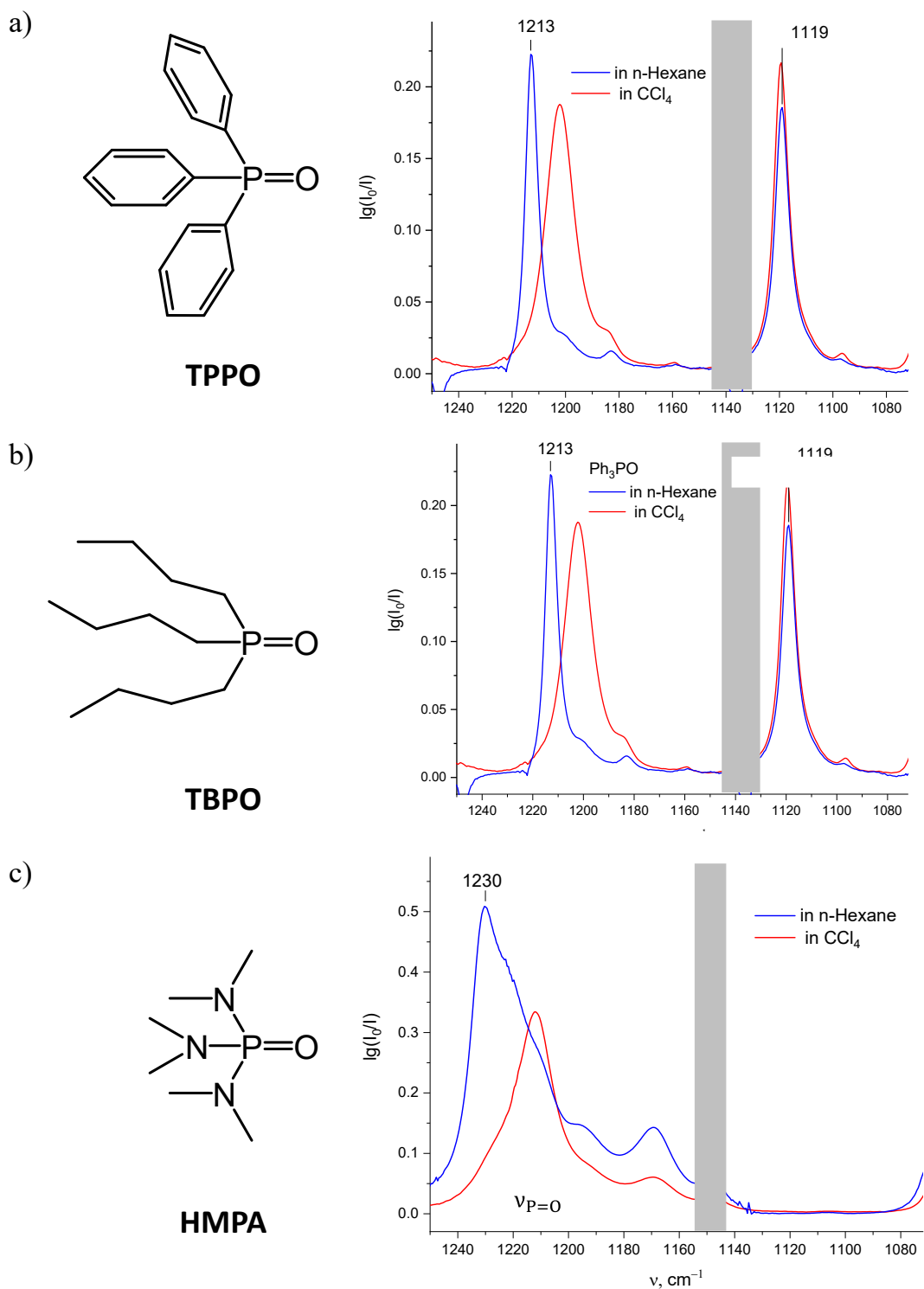
**Fig. S7.** Calculated (B3LYP/aug-cc-pVDZ) optimized geometries of hydrogen-bonded TPPO complexes with proton donors 1–10. Hydrogen bonds are shown in the plane of the figure.

**Table S2.** Calculated (B3LYP/aug-cc-pVDZ) parameters of hydrogen-bonded complexes of TPPO with proton donors 1–10: local electron kinetic,  $G$ , and potential,  $V$ , energy densities (in  $\text{kJ mol}^{-1} \text{Bohr}^{-3}$ ); interatomic distances within the hydrogen bridge,  $r_{\text{O}\cdots\text{O}}$ ,  $r_{\text{OH}}$  and  $r_{\text{H}\cdots\text{O}}$  (in  $\text{\AA}$ ); hydrogen bond angles  $\alpha$  and  $\beta$  (in degrees); the changes of  $^1\text{H}$  and  $^{31}\text{P}$  NMR chemical shifts,  $\Delta\delta\text{H}$  and  $\Delta\delta\text{P}$  (in ppm); the out-of-plane bending frequency,  $\gamma_{\text{O}\cdots\text{H}-\text{O}}$  (in  $\text{cm}^{-1}$ ).

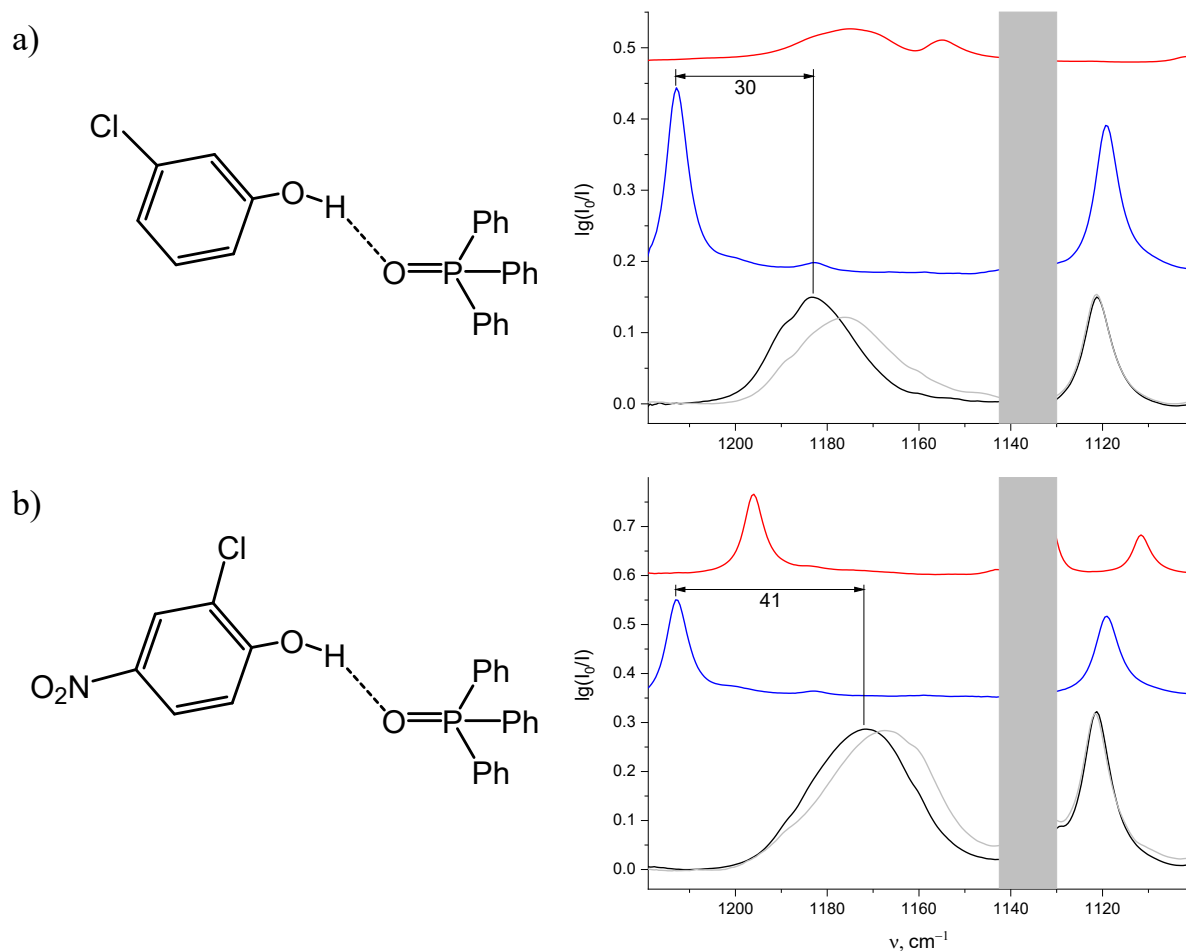
No.	Proton donor	$G$	$V$	$r_{\text{O}\cdots\text{O}}$	$r_{\text{OH}}$	$r_{\text{H}\cdots\text{O}}$	$\alpha^a$	$\beta^a$	$\Delta\delta\text{H}^b$	$\Delta\delta\text{P}^b$	$\gamma_{\text{O}\cdots\text{H}-\text{O}}$
1	2-methoxyphenol	95.5	91.7	2.680	0.989	1.698	125.4	171.4	7.09	8.99	825.5
2	phenol	94.5	90.3	2.685	0.989	1.701	126.3	173.1	6.88	8.64	814.3
3	4-fluorophenol	97.1	93.6	2.679	0.990	1.692	126.6	174.6	6.99	9.14	832.6
4	4-chlorophenol	100.3	97.8	2.668	0.991	1.680	127.3	174.9	7.15	9.45	842.4
5	3-chlorophenol	101.0	98.7	2.666	0.992	1.677	126.7	174.5	7.25	9.34	842.7
6	4-nitrophenol	113.6	116.8	2.631	0.998	1.634	129.0	176.9	7.87	10.63	905.1
7	2-chloro-4-nitrophenol	124.5	134.4	2.603	1.003	1.601	127.8	176.5	7.26	12.06	923.1
8	2,6-dibromophenol	89.7	85.3	2.641	0.994	1.717	129.5	153.0	5.98	8.04	814.3
9	2,6-dichloro-4-nitrophenol	116.2	123.2	2.581	1.007	1.619	129.9	158.1	7.63	10.04	901.0
10	2,2,2-trifluoroethanol	97.3	93.4	2.679	0.988	1.692	128.3	178.4	6.85	8.86	782.4

<sup>a</sup>  $\alpha$  – the angle POH,  $\beta$  – the angle OHO

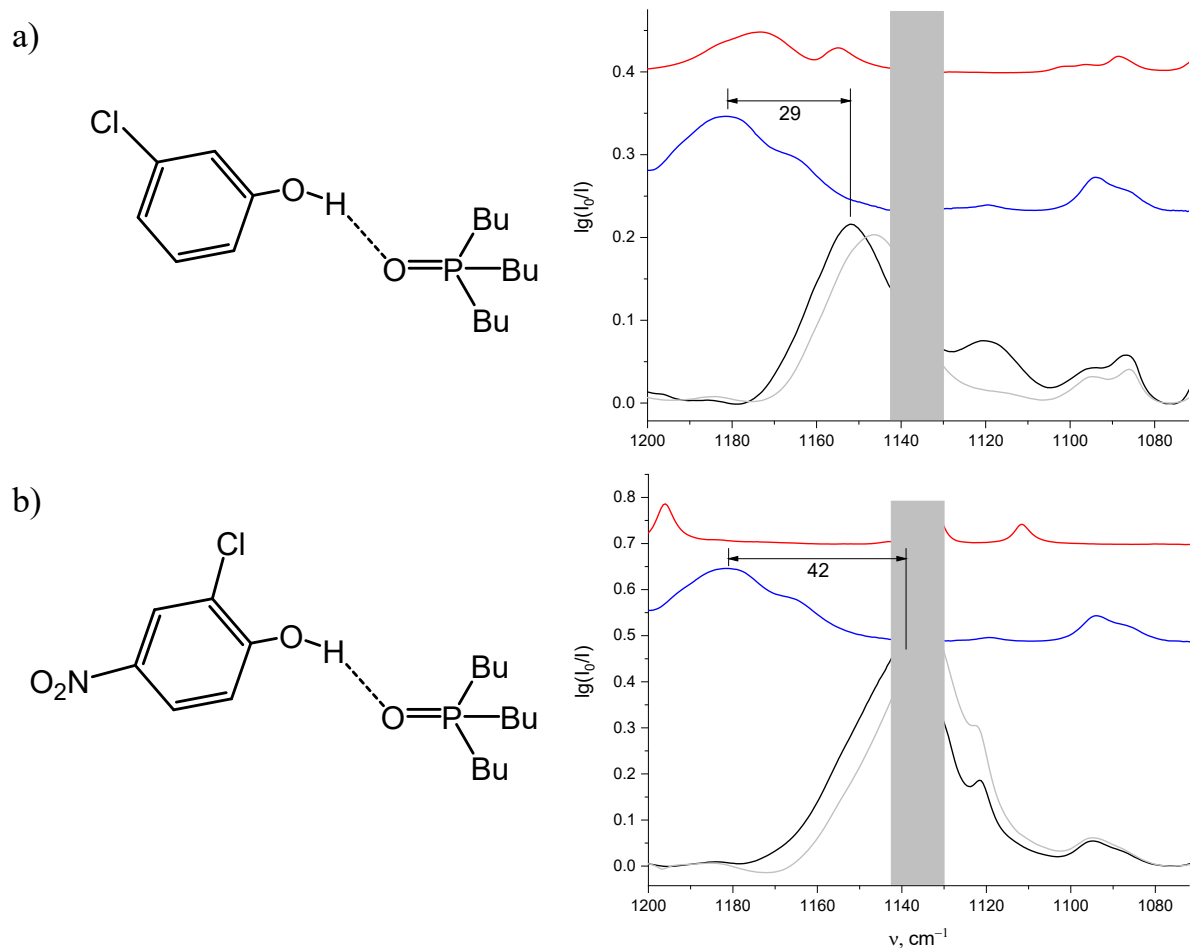
<sup>b</sup> Calculated by GIAO method at the same level of theory



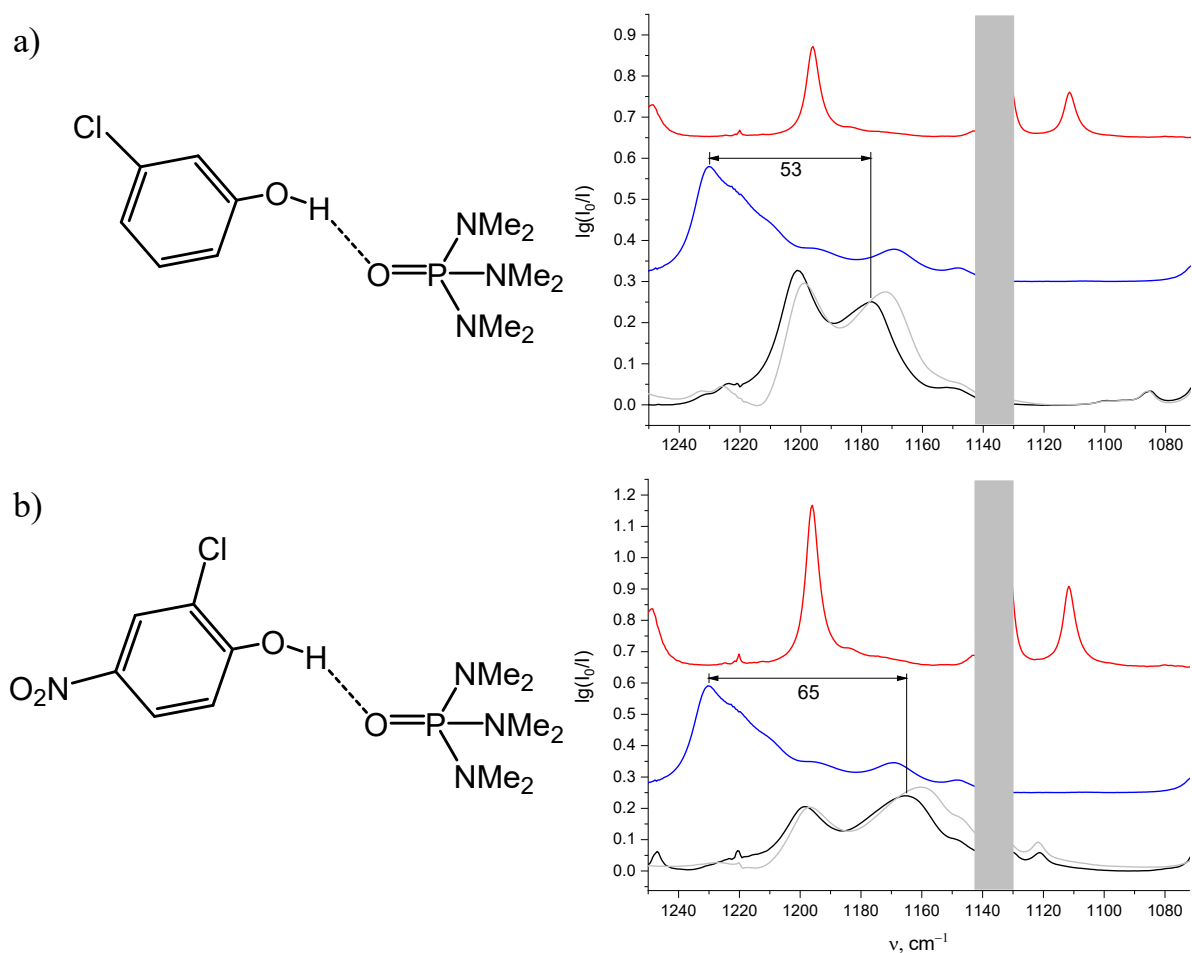
**Fig. S8.** Comparison of IR spectra of (a) TPPO, (b) TBPO and (c) HMPA in solutions in  $\text{CCl}_4$  (red) and *n*-hexane (blue) recorded at concentration values 5.9, 9.6 and 11.7  $\text{mmol L}^{-1}$ , respectively, at room temperature in the range of frequencies from  $1070 \text{ cm}^{-1}$  to  $1250 \text{ cm}^{-1}$ . Gray areas indicate ranges containing *n*-hexane absorption bands. For *n*-hexane solution the  $\text{P}=\text{O}$  vibration band,  $\nu_{\text{P}=\text{O}}$ , is located at  $\sim 1213 \text{ cm}^{-1}$  for free TPPO,  $\sim 1181 \text{ cm}^{-1}$  for free TBPO and  $\sim 1230 \text{ cm}^{-1}$  for free HMPA.



**Fig. S9.** Parts of IR spectra of TPPPO complexes with (a) 3-chlorophenol **5** (b) 2-chloro-4-nitrophenol **7** in *n*-hexane solution at room temperature in the range of frequencies from 1100  $\text{cm}^{-1}$  to 1220  $\text{cm}^{-1}$ . The spectra of free phenols **5** and **7** (red), free TPPPO (blue) and their complexes in *n*-hexane solution (black) are shown. IR spectra of the same complexes in  $\text{CCl}_4$  solution (gray) are shown for comparison. Gray areas indicate ranges containing *n*-hexane absorption bands. For *n*-hexane solution the shift of P=O vibration band upon complexation,  $\Delta\nu_{\text{P=O}}$ , equal to  $\sim 30 \text{ cm}^{-1}$  for complexes with 3-chlorophenol,  $\sim 41 \text{ cm}^{-1}$  for complexes with 2-chloro-4-nitrophenol.



**Fig. S10.** Parts of IR spectra of TBPO complexes with (a) 3-chlorophenol **5** (b) 2-chloro-4-nitrophenol **7** in *n*-hexane solution at room temperature in the range of frequencies from 1070  $\text{cm}^{-1}$  to 1200  $\text{cm}^{-1}$ . The spectra of free phenols **5** and **7** (red), free TBPO (blue) and their complexes in *n*-hexane solution (black) are shown. IR spectra of the same complexes in  $\text{CCl}_4$  solution (gray) are shown for comparison. Gray areas indicate ranges containing *n*-hexane absorption bands. For *n*-hexane solution the shift of P=O vibration band upon complexation,  $\Delta\nu_{\text{P=O}}$ , equal to  $\sim 29 \text{ cm}^{-1}$  for complexes with 3-chlorophenol,  $\sim 42 \text{ cm}^{-1}$  for complexes with 2-chloro-4-nitrophenol.



**Fig. S11.** Parts of IR spectra of HMPA complexes with (a) 3-chlorophenol **5** (b) 2-chloro-4-nitrophenol **7** in *n*-hexane solution at room temperature in the range of frequencies from 1070  $\text{cm}^{-1}$  to 1250  $\text{cm}^{-1}$ . The spectra of free phenols **5** and **7** (red), free HMPA (blue) and their complexes in *n*-hexane solution (black) are shown. IR spectra of the same complexes in  $\text{CCl}_4$  solution (gray) are shown for comparison. Gray areas indicate ranges containing *n*-hexane absorption bands. For *n*-hexane solution the shift of P=O vibration band upon complexation,  $\Delta\nu_{\text{P=O}}$ , equal to  $\sim 53 \text{ cm}^{-1}$  for complexes with 3-chlorophenol,  $\sim 65 \text{ cm}^{-1}$  for complexes with 2-chloro-4-nitrophenol.

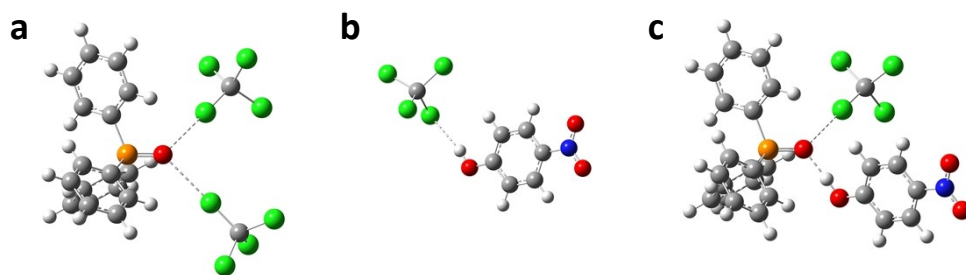
**Table S3.** The values of coefficients of determination ( $R^2$ ) calculated for fitting functions  $\Delta\nu_{\text{OH}}(\Delta\nu_{\text{P=O}})$  obtained using power functions given by Eqn (1) (without solvent correction) and Eqn (2) (with solvent correction).

Complexes with	$\Delta\nu_{\text{OH}}(\Delta\nu_{\text{P=O}})$	
	Without correction for solvent influence, Eqn (1)	With the correction for solvent influence, Eqn (2)
TPPO	0.91	0.90
TBPO	0.85	0.84
HMPA	0.82	0.81

**Table S4.** The wavenumbers of  $\nu_{OH}$  bands in IR spectra of free proton donors **1–10** in *n*-hexane solution at room temperature. The shifts of bands,  $\Delta\nu$ , upon the change of solvent from *n*-hexane to  $CCl_4$  are given in the last column.

No.	Proton donor	$\nu_{OH}^{in\ hexane}$ , $cm^{-1}$	$\Delta\nu$ , $cm^{-1}$
<b>1</b>	2-methoxyphenol	3566	9
<b>2</b>	phenol	3622	11
<b>3</b>	4-fluorophenol	3625	12
<b>4</b>	4-chlorophenol	3621	12
<b>5</b>	3-chlorophenol	3619	13
<b>6</b>	4-nitrophenol	3615	21
<b>7</b>	2-chloro-4-nitrophenol	3537	8
<b>8</b>	2,6-dibromophenol	3521	5
<b>9</b>	2,6-dichloro-4-nitrophenol	3529	10
<b>10</b>	2,2,2-trifluoroethanol	3629	10





**Fig. S12.** The optimized geometries (B3LYP/aug-cc-pVDZ, gas phase) of (a) isolated TPPO molecule solvated by two  $\text{CCl}_4$  molecules, (b) isolated 4-nitrophenol molecule solvated by one  $\text{CCl}_4$  molecule and (c) 1:1:1 complex formed by TPPO, 4-nitrophenol and  $\text{CCl}_4$ .

**Table S5.** The wavenumbers of OH and P=O stretching vibrations (in  $\text{cm}^{-1}$ ) for free TPPO, 4-nitrophenol and their complexes without or with additional  $\text{CCl}_4$  molecules. The wavenumbers for the complex without  $\text{CCl}_4$  molecules were taken from Table 2.

Complex	$\nu_{\text{OH}}$	$\nu_{\text{P=O}}$
4-nitrophenol free	3807	–
4-nitrophenol solvated by $\text{CCl}_4$	3765	–
TPPO free	–	1163.1
TPPO solvated by two $\text{CCl}_4$ molecule	–	1146.6
TPPO and 4-nitrophenol	3163	1135.8
TPPO and 4-nitrophenol solvated by $\text{CCl}_4$	3202	1131.8

An account for one or two explicit  $\text{CCl}_4$  molecules changes the complexation equilibrium reaction from the one shown in Fig. 7a to the one shown in Fig. 7b. As our calculations for TPPO complex with 4-nitrophenol **6** show, interaction with  $\text{CCl}_4$  expectedly decreases the  $\nu_{\text{P=O}}$  of “free” TPPO (from  $1163.1 \text{ cm}^{-1}$  to  $1146.6 \text{ cm}^{-1}$ ) and  $\nu_{\text{OH}}$  of “free” **6** (from  $3807 \text{ cm}^{-1}$  to  $3765 \text{ cm}^{-1}$ ). In the complex, the combined action of hydrogen bond with **6** and halogen bond with  $\text{CCl}_4$  decreases the  $\nu_{\text{P=O}}$  even further (to  $1131.8 \text{ cm}^{-1}$ ), and the  $|\Delta\nu_{\text{P=O}}|$  decreases ( $27.3 \text{ cm}^{-1}$  without  $\text{CCl}_4$ ,  $14.8 \text{ cm}^{-1}$  with  $\text{CCl}_4$ ). In a similar way, the anti-cooperative coupling between hydrogen and halogen bonds decreases  $\nu_{\text{OH}}$  less than if the solvent is absent, so that the resulting  $|\Delta\nu_{\text{OH}}|$  decreases ( $644 \text{ cm}^{-1}$  without  $\text{CCl}_4$ ,  $563 \text{ cm}^{-1}$  with  $\text{CCl}_4$ ).

Assuming that qualitatively similar shifts would be present for other complexes as well, one could expect that the account for explicit solvent molecule would shift all the datapoints in Figure 9 closer to the (0,0) point and the mismatch between the experiment and calculations would only increase. Thus, it seems that minimizing this mismatch is more sophisticated and laborious task than the current study could justify.