

Supporting Information for

Phosphide Selenides: Versatile NMR Probes for Analyzing Hydrogen and Halogen Bonds

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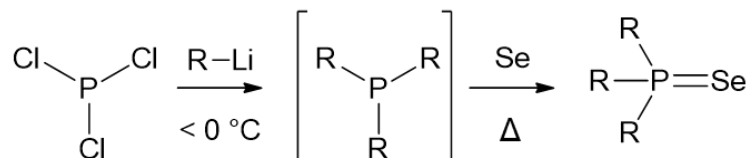
Table of contents

Scheme S1	Synthesis of phosphine selenides R ₃ PSe	3
Figure S1	¹ H and ¹³ C NMR spectra of Me ₃ PSe in CDCl ₃ at 298 K	4
Figure S2	¹ H and ¹³ C NMR spectra of Et ₃ PSe in CDCl ₃ at 298 K	5
Figure S3	¹ H and ¹³ C NMR spectra of <i>n</i> -Bu ₃ PSe in CDCl ₃ at 298 K	6
Figure S4	¹ H and ¹³ C NMR spectra of <i>t</i> -Bu ₃ PSe in CDCl ₃ at 298 K	7
Figure S5	¹ H and ¹³ C NMR spectra of Ph ₃ PSe in CDCl ₃ at 298 K	8
Figure S6	¹ H and ¹³ C NMR spectra of MePh ₂ PSe in CDCl ₃ at 298 K	9
Figure S7	¹ H NMR spectra of hydrogen-bonded complexes of Et ₃ PSe with various substituted phenols in solution in CD ₂ Cl ₂ at 180 K	10
Figure S8	¹ H and ³¹ P NMR spectra of hydrogen-bonded complex of Et ₃ PSe with 4-chlorophenol in solution in CDF ₃ /CDCIF ₂ at 100 K	11
Figure S9	¹ H NMR spectra of halogen-bonded complex of Et ₃ PSe with 4-fluoroiodobenzene in solution in CDF ₃ /CDCIF ₂ .	12
Table S1	Crystal data and structure refinement for halogen-bonded complex of Me ₃ PSe with C ₆ F ₅ I	13
Figure S10	³¹ P and ⁷⁷ Se MAS NMR spectra (12.5 kHz) of phosphine selenides Me ₃ PSe and <i>t</i> -Bu ₃ PSe and their complexes with C ₆ F ₅ I at 298 K.	14
Figure S11	³¹ P and ⁷⁷ Se NMR spectra of phosphine selenides R ₃ PSe (where R: Me, Et, <i>n</i> -Bu, <i>t</i> -Bu and Ph) in C ₆ F ₅ Br at 298 K.	15
Table S2	Experimental NMR parameters of the studied phosphine selenide R ₃ PSe (where R: Me, Et, <i>n</i> -Bu, <i>t</i> -Bu and Ph) in C ₆ F ₅ Br at 298 K.	16

Figure S12	Equilibrium structures of halogen-bonded complexes of phosphine selenides R ₃ PSe (R: Me, Et, <i>t</i> -Bu, <i>n</i> -Bu and Ph) with C ₆ F ₅ Br	17
Table S3	Calculated geometry of halogen-bonded complexes of phosphine selenides R ₃ PSe (R: Me, Et, <i>t</i> -Bu, <i>n</i> -Bu and Ph) in vacuum	18

Scheme S1. “One-pot” method of synthesis of phosphine selenides R_3PSe (where R: Me, Et and *n*-Bu).

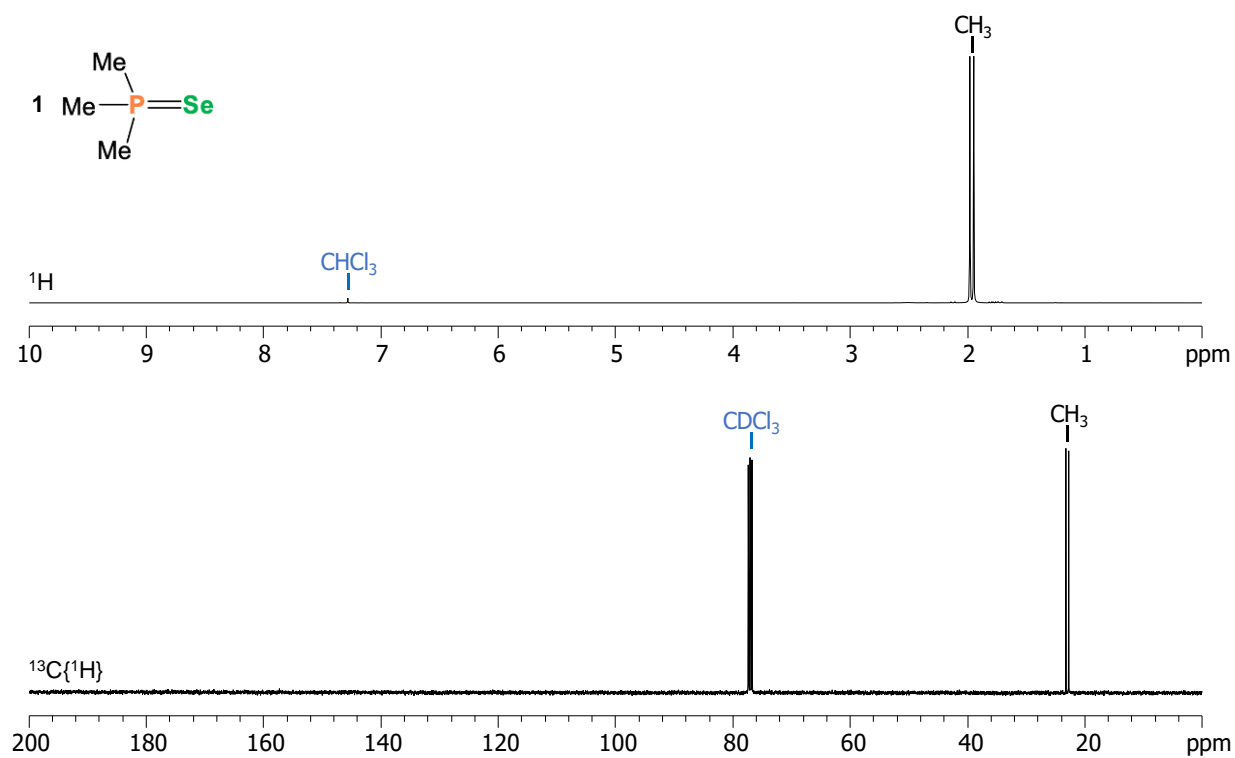
Trimethylphosphine selenide (Me_3PSe), triethylphosphine selenide (Et_3PSe) and tributylphosphine selenide ($n-Bu_3PSe$) were prepared by the «one-pot» method using phosphorus trichloride PCl_3 (NevaReaktiv) and organolithium reagents RLi (where R=Me, Et and *n*-Bu; purchased from Sigma Aldrich) according to the following scheme:



At the first stage a solution of 3 equivalents RLi was added to a solution of PCl_3 in freshly distilled anhydrous toluene while cooling. Next stage was carried out without phosphine isolation for 5 hours in the presence of 1.5 equivalents of metallic selenium in boiling solvent. The substances were then purified by recrystallization in toluene (in cases of Me_3PSe and Et_3PSe) or by chromatography (in case of $n-Bu_3PSe$, sorbent Al_2O_3 , eluent petroleum ether/benzene 1:1).

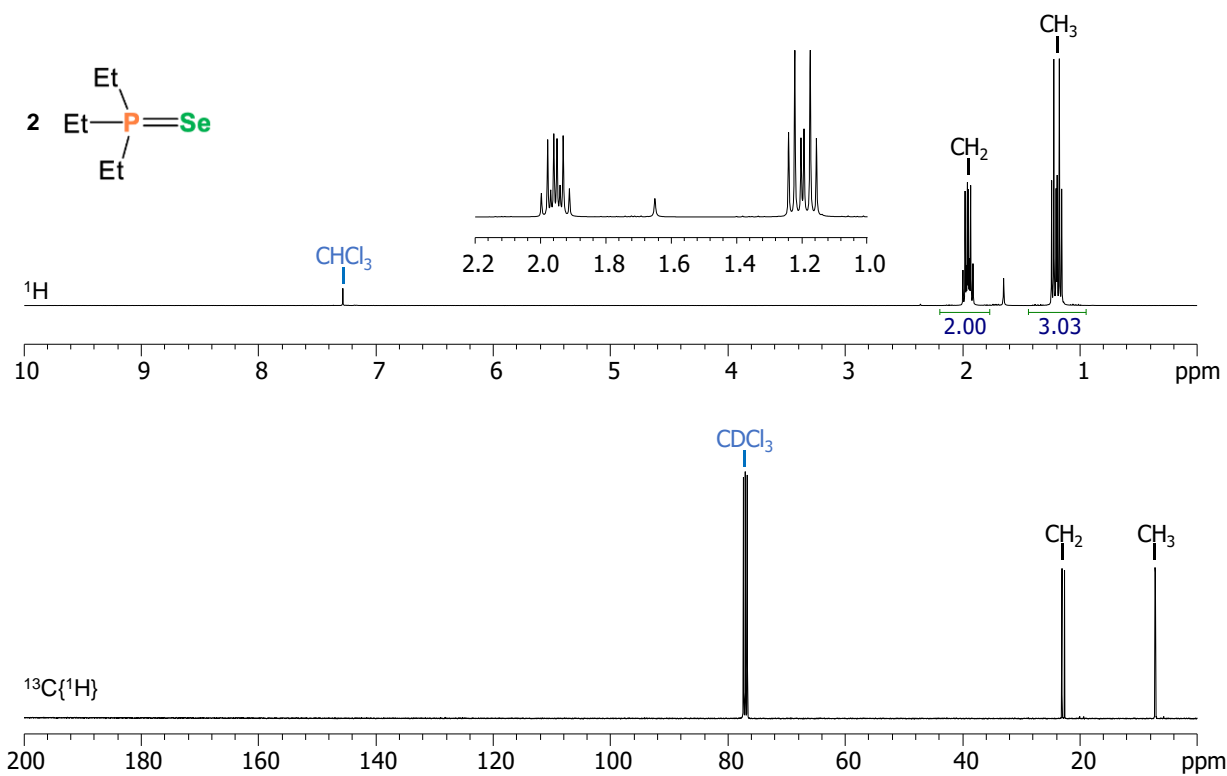
Tris(tert-butyl)phosphine selenide ($t-Bu_3PSe$), triphenylphosphine selenide (Ph_3PSe) and methyldiphenylphosphine selenide ($MePh_2PSe$) were synthesized according to standard methodology described in the literature from commercially available phosphines R_3P (where R = *t*-Bu, Ph and $R^1=Me$, $R^2=R^3=Ph$) (Sigma Aldrich) by oxidizing them with elemental selenium (Vekton). The reaction was carried out in boiling toluene for 5 hours in the presence of 1.5 equivalents of metallic selenium. The substances were then purified by recrystallization in toluene.

Figure S1. ^1H and ^{13}C NMR spectra of Me_3PSe in solution in CDCl_3 at 298 K.



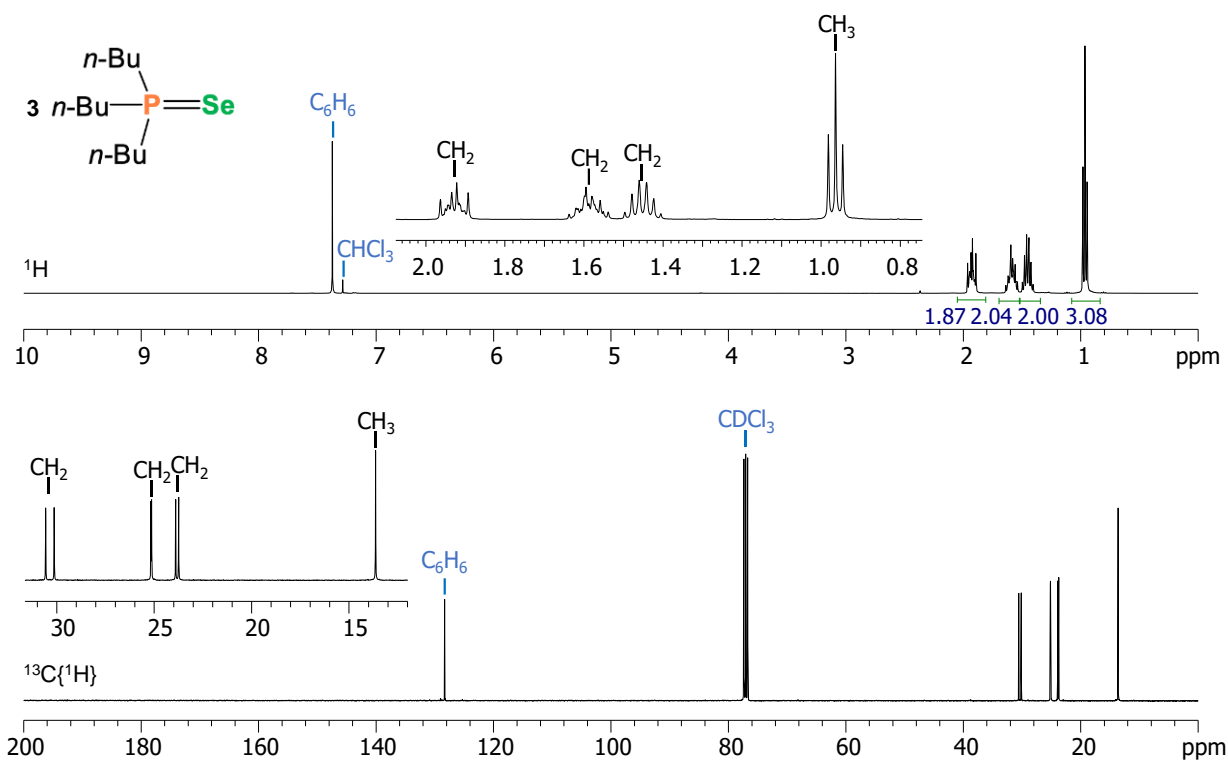
Trimethylphosphine selenide (**1**). ^1H NMR (CDCl_3 , 400 MHz): δ 1.96 (d, $^2J_{\text{HP}}=13.28$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz): δ 23.0 (d, $^1J_{\text{CP}}=49.0$ Hz).

Figure S2. ^1H and ^{13}C NMR spectra of Et_3PSe in solution in CDCl_3 at 298 K.



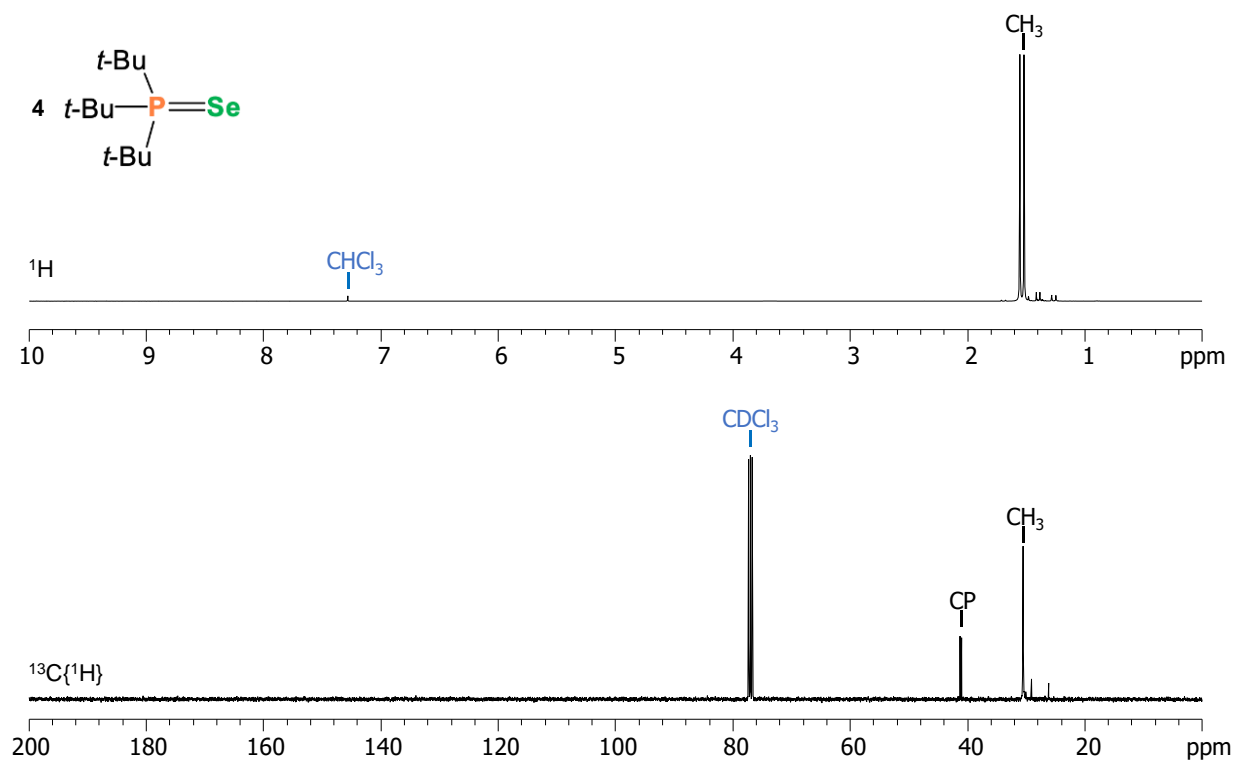
Triethylphosphine selenide (**2**). ^1H NMR (CDCl_3 , 400 MHz): δ 1.95 (dq, $^2J_{\text{HP}}=11.47$ Hz and $^3J_{\text{HH}}=7.61$ Hz), 1.20 (dt, $^2J_{\text{HP}}=18.86$ Hz and $^3J_{\text{HH}}=7.61$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz): δ 22.8 (d, $^1J_{\text{CP}}=45.0$ Hz), 7.2 (d, $^2J_{\text{CP}}=4.4$ Hz).

Figure S3. ^1H and ^{13}C NMR spectra of *n*-Bu₃PSe in solution in CDCl₃ at 298 K.



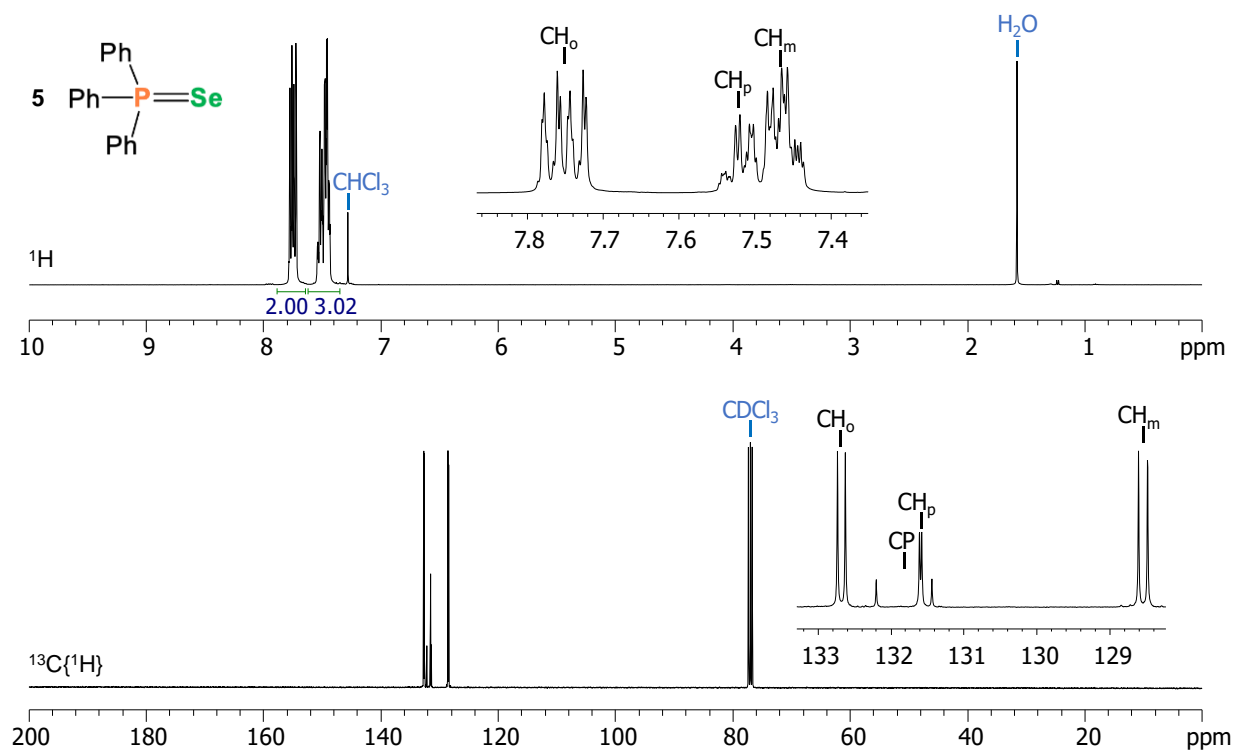
Tributhylphosphine selenide (**3**). ^1H NMR (CDCl_3 , 400 MHz): δ 1.98 – 1.88 (m), 1.67 – 1.52 (m), 1.45 (h, $^3J_{\text{HH}}=7.23$ Hz), 0.96 (t, $^3J_{\text{HH}}=7.23$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz): δ 30.4 (d, $^1J_{\text{CP}}=43.9$ Hz), 25.2 (d, $^2J_{\text{CP}}=3.8$ Hz), 23.8 (d, $^3J_{\text{CP}}=15.5$ Hz), 13.6 (s).

Figure S4. ^1H and ^{13}C NMR spectra of $t\text{-Bu}_3\text{PSe}$ in solution in CDCl_3 at 298 K.



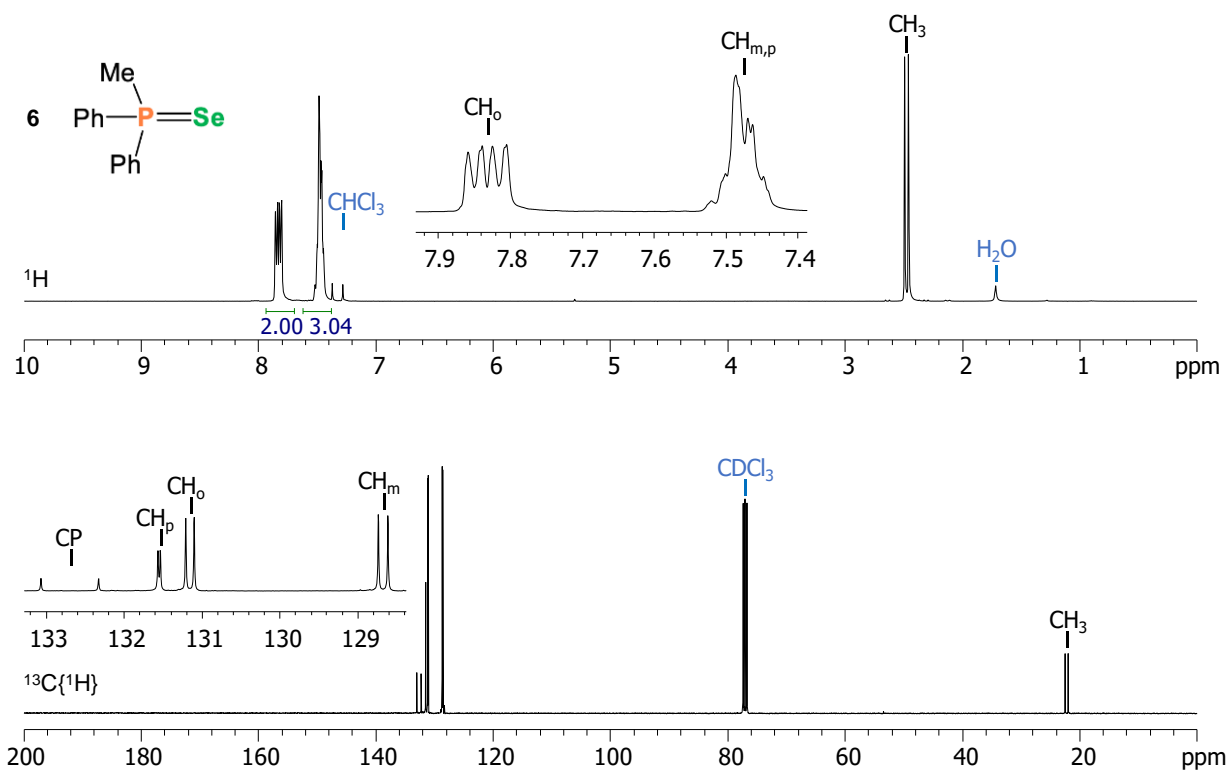
Tris(tert-butyl)phosphine selenide (**4**). ^1H NMR (CDCl_3 , 400 MHz): δ 1.54 (d, $^3J_{\text{HP}}=14.08$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz): δ 41.2 (d, $^1J_{\text{CP}}=26.1$ Hz), 30.5 (s).

Figure S5. ^1H and ^{13}C NMR spectra of Ph_3PSe in solution in CDCl_3 at 298 K.



Triphenylphosphine selenide (**5**). ^1H NMR (CDCl_3 , 400 MHz): δ 7.80 – 7.70 (m), 7.56 – 7.49 (m), 7.49 – 7.42 (m). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz): δ 132.7 (d, $^2J_{\text{CP}}=10.8$ Hz), 131.8 (d, $^1J_{\text{CP}}=76.7$ Hz), 131.6 (d, $^4J_{\text{CP}}=3.0$ Hz), 128.5 (d, $^3J_{\text{CP}}=12.4$ Hz).

Figure S6. ^1H and ^{13}C NMR spectra of MePh_2PSe in solution in CDCl_3 at 298 K.



Methyldiphenylphosphine selenide (**6**). ^1H NMR (CDCl_3 , 400 MHz): δ 7.83 (ddd, $^2J_{\text{HP}}=13.71$ Hz, $^3J_{\text{HH}}=7.82$ Hz and $^4J_{\text{HH}}=1.83$ Hz), 7.54 – 7.42 (m). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz): δ 132.7 (d, $^1J_{\text{CP}}=74.3$ Hz), 131.6 (d, $^4J_{\text{CP}}=3.1$ Hz), 131.2 (d, $^2J_{\text{CP}}=10.9$ Hz), 128.7 (d, $^3J_{\text{CP}}=12.3$ Hz).

Figure S7. ^1H NMR spectra of hydrogen-bonded complexes of Et_3PSe with various substituted phenols in solution in CD_2Cl_2 at 180 K.

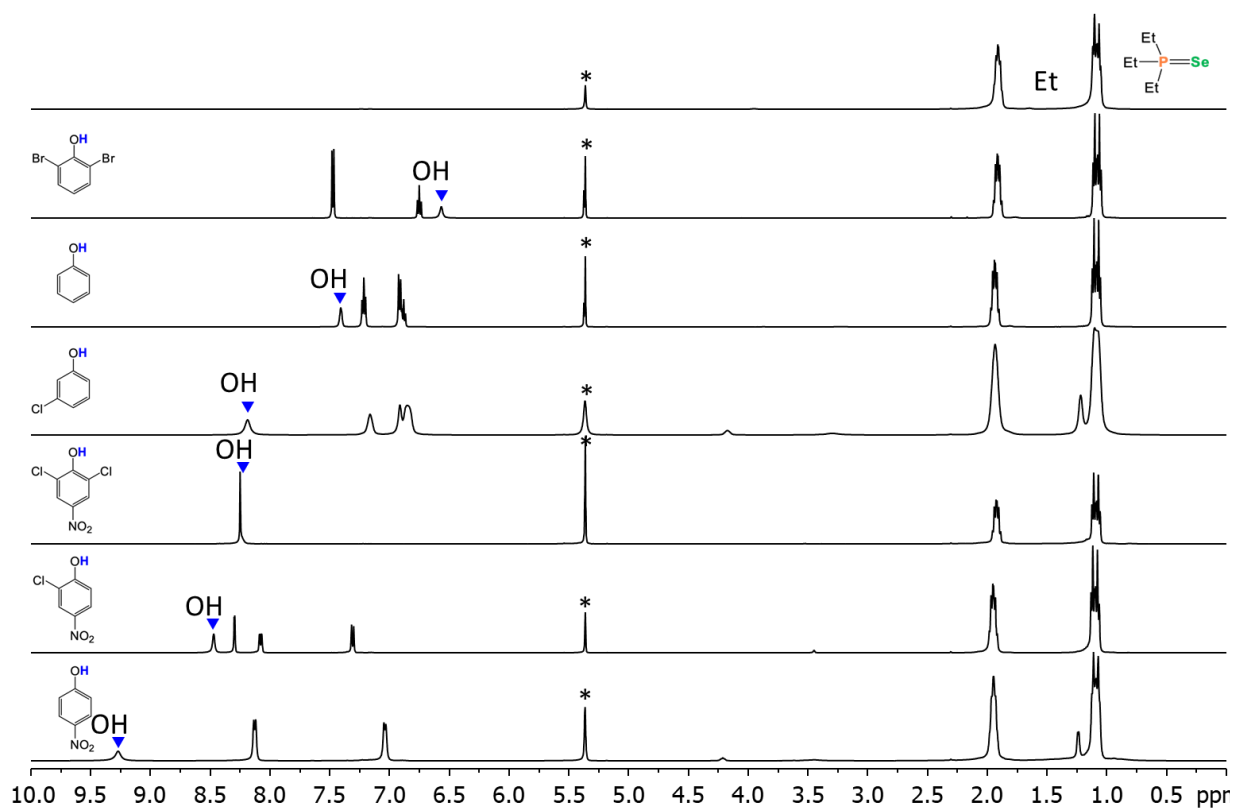


Figure S8. ^1H and ^{31}P NMR spectra of hydrogen-bonded complex of Et_3PSe with 4-chlorophenol in solution in $\text{CDF}_3/\text{CDClF}_2$ at 100 K.

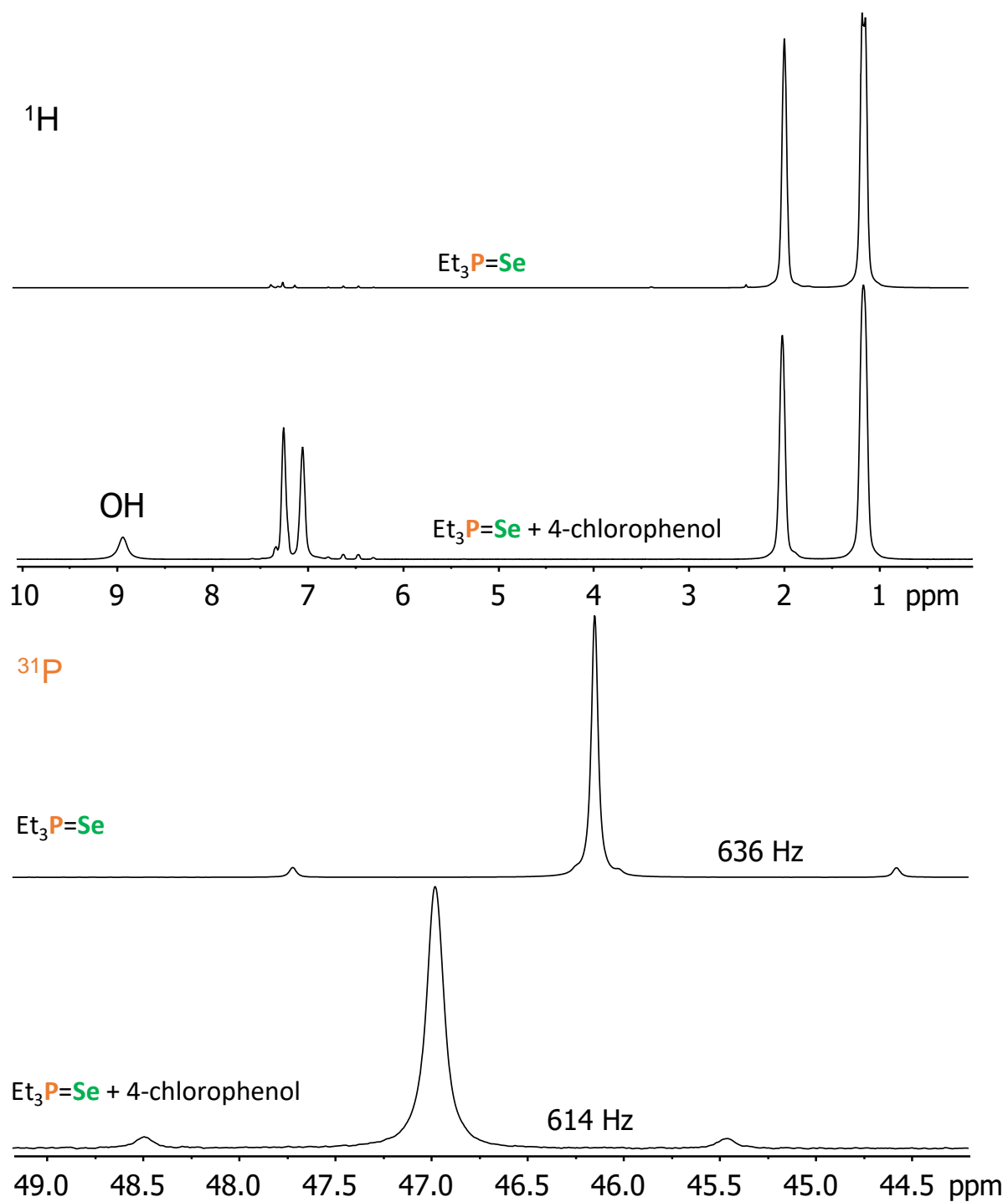


Figure S9. ^1H NMR spectra of halogen-bonded complex of Et_3PSe with 4-fluoriodobenzene in solution in $\text{CDF}_3/\text{CDClF}_2$ at various temperatures.

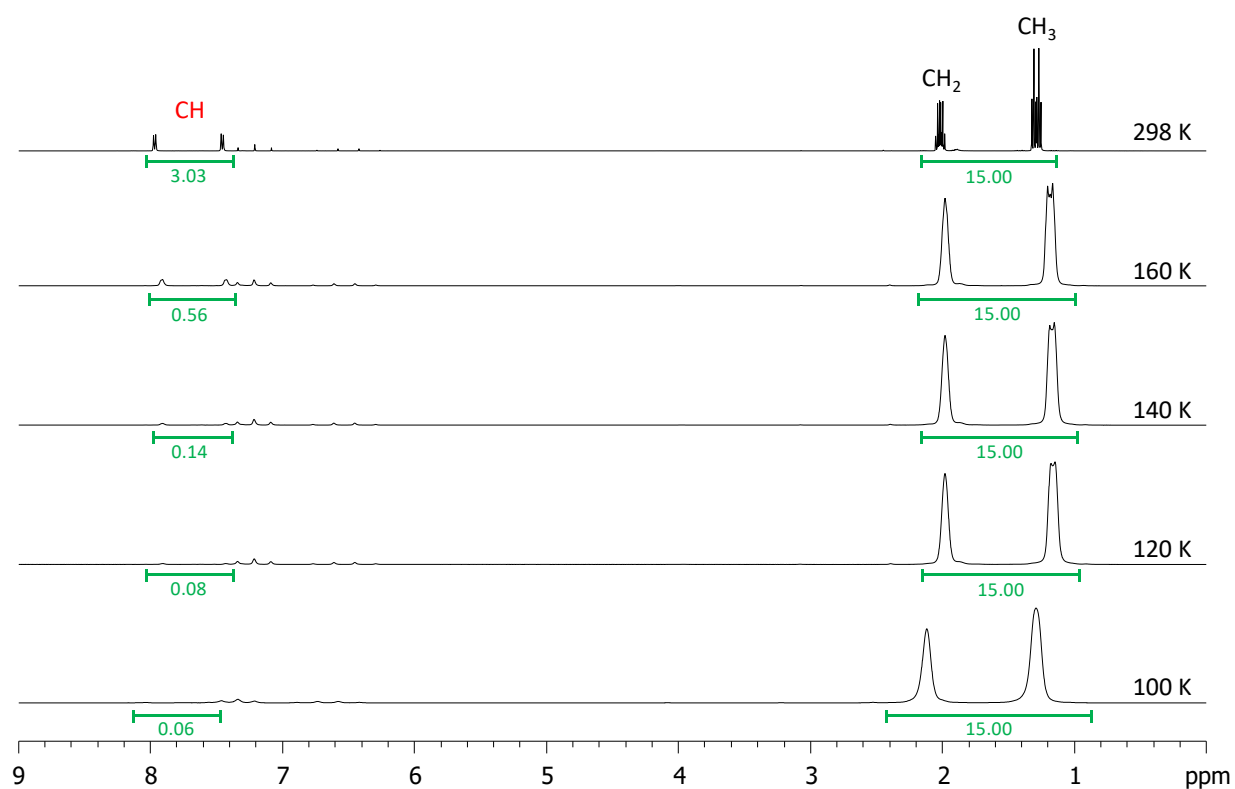


Table S1. Crystal data and structure refinement for halogen-bonded complex of Me₃PSe with C₆F₅I (CCDC: 2353352).

Identification code	Halogen-bonded complex of Me ₃ PSe and C ₆ F ₅ I
CSD code	2353352
Empirical formula	C ₉ H ₉ F ₅ IPSe
Formula weight	448.99
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	6.34130(10)
b/Å	27.4987(5)
c/Å	7.78480(10)
α/°	90
β/°	91.554(2)
γ/°	90
Volume/Å ³	1356.99(4)
Z	4
ρ _{calc} /cm ³	2.198
μ/mm ⁻¹	23.105
F(000)	840.0
Crystal size/mm ³	0.05 × 0.04 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.428 to 134.978
Index ranges	-7 ≤ h ≤ 7, -32 ≤ k ≤ 30, -9 ≤ l ≤ 9
Reflections collected	8395
Independent reflections	2432 [R _{int} = 0.0395, R _{sigma} = 0.0308]
Data/restraints/parameters	2432/0/157
Goodness-of-fit on F ²	1.048
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0244, wR ₂ = 0.0602
Final R indexes [all data]	R ₁ = 0.0257, wR ₂ = 0.0610
Largest diff. peak/hole / e Å ⁻³	0.76/-0.83

Figure S10. ^{31}P and ^{77}Se MAS NMR spectra (12.5 kHz) of phosphine selenides Me_3PSe and $t\text{-Bu}_3\text{PSe}$ and their complexes with $\text{C}_6\text{F}_5\text{I}$ at 298 K.

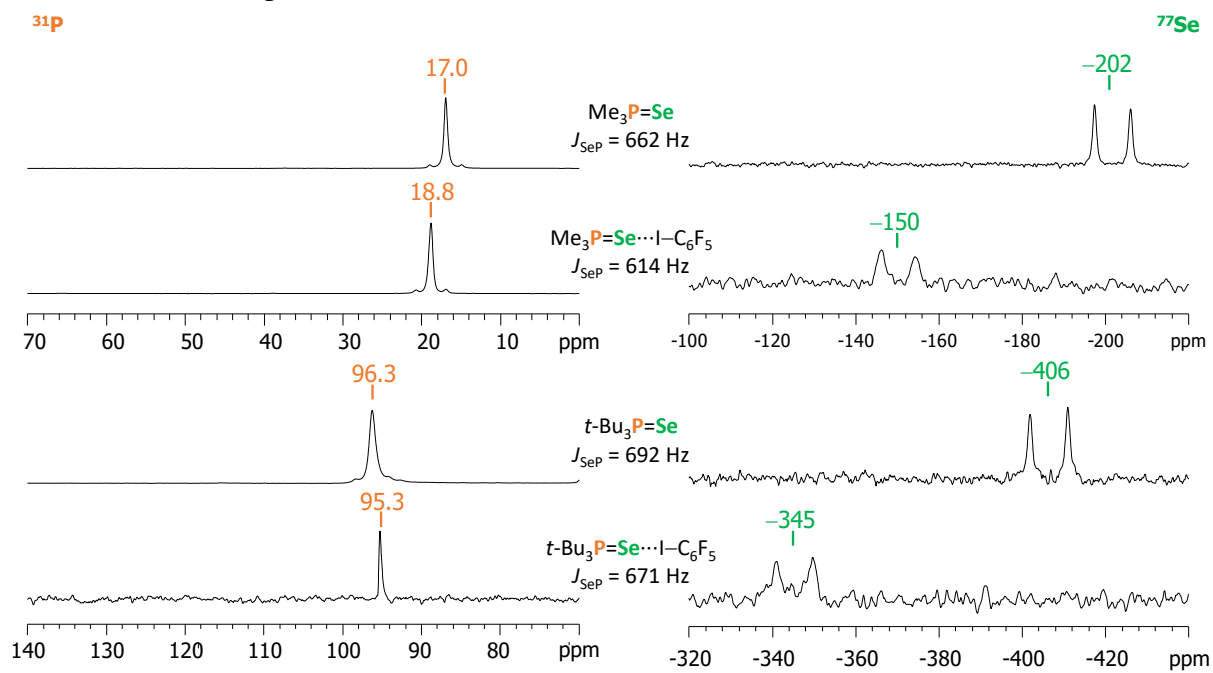


Figure S11. ^{31}P and ^{77}Se NMR spectra of phosphine selenides R_3PSe (where R: Me, Et, *n*-Bu, *t*-Bu and Ph) in $\text{C}_6\text{F}_5\text{Br}$ at 298 K.

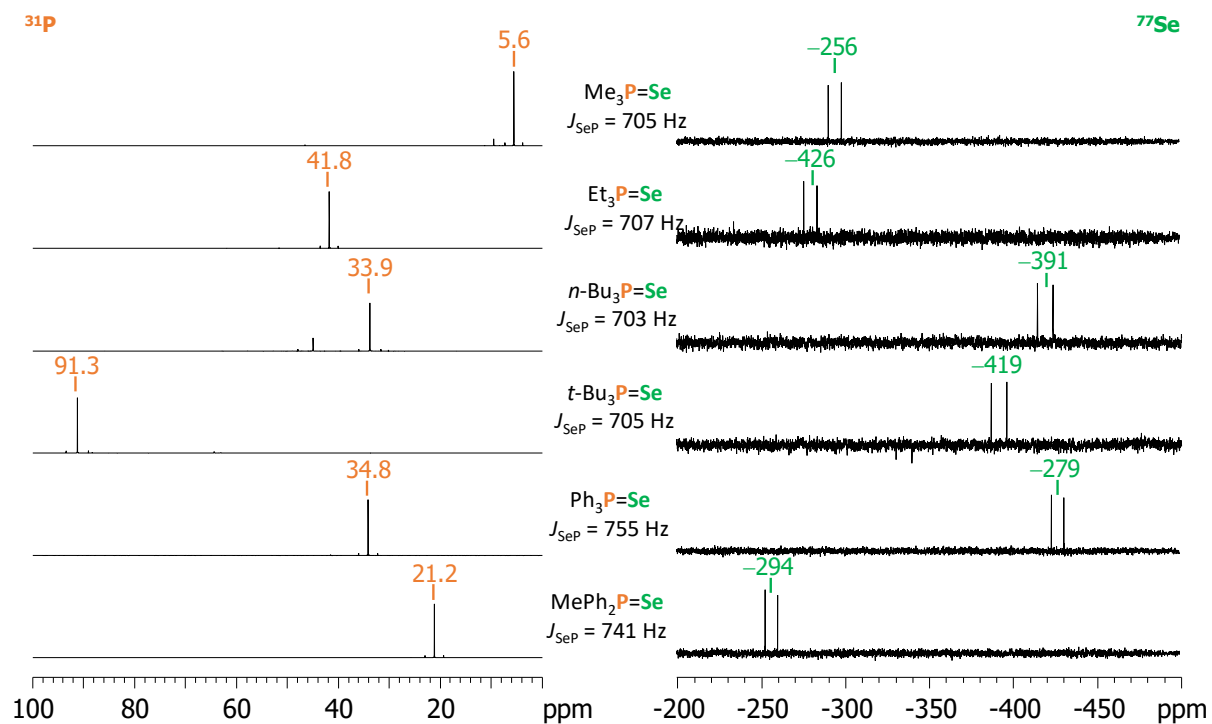


Table S2. Experimental NMR parameters of the studied phosphine selenide R₃PSe (where R: Me, Et, *n*-Bu, *t*-Bu and Ph) in C₆H₆ and C₆F₅Br at 298 K.

Acceptor	Solvent	δP	$\Delta\delta\text{P}$	δSe	$\Delta\delta\text{Se}$	J_{PSe}	ΔJ_{PSe}
Me ₃ PSe	C ₆ H ₆	5.9	–	–252	–	713	–
Me ₃ PSe	C ₆ F ₅ Br	5.6	–0.3	–256	–4	705	–8
Et ₃ PSe	C ₆ H ₆	42.6	–	–427	–	717	–
Et ₃ PSe	C ₆ F ₅ Br	41.8	–0.8	–426	+1	707	–10
<i>n</i> -Bu ₃ PSe	C ₆ H ₆	35.1	–	–393	–	713	–
<i>n</i> -Bu ₃ PSe	C ₆ F ₅ Br	33.9	–1.2	–391	+2	703	–10
<i>t</i> -Bu ₃ PSe	C ₆ H ₆	91.7	–	–423	–	711	–
<i>t</i> -Bu ₃ PSe	C ₆ F ₅ Br	91.3	–0.4	–419	+4	705	–6
Ph ₃ PSe	C ₆ H ₆	34.8	–	–278	–	757	–
Ph ₃ PSe	C ₆ F ₅ Br	34.2	–0.6	–279	–1	755	–2
MePh ₂ PSe	C ₆ H ₆	22.2	–	–291	–	746	–
MePh ₂ PSe	C ₆ F ₅ Br	21.2	–1.0	–294	–	741	–5

Figure S12. Equilibrium structures of halogen-bonded complexes of phosphine selenides R_3PSe (R: Me, Et, *t*-Bu, *n*-Bu and Ph) with C_6F_5Br . The values of $Se\cdots Br$ distance (in angstroms) are marketed in red color. The fractions of the $Se\cdots I$ distance from the sum of the van der Waals radii of selenium and iodine are shown in green in parentheses ($\omega_{vdW} = \frac{R_{Se\cdots I}}{R_{vdW}^{Se} + R_{vdW}^I}$).

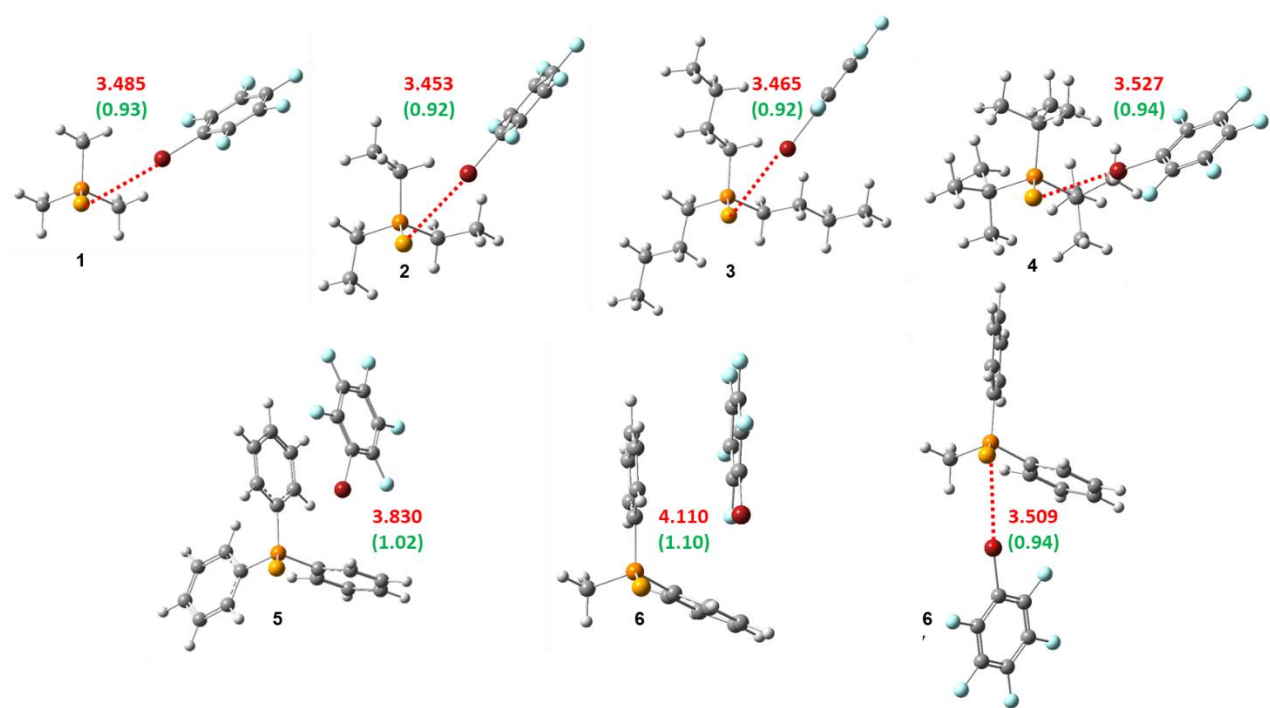


Table S3. Calculated geometry (PW6B95-GD3/def2-QZVP) of halogen-bonded complexes of phosphine selenides R₃PSe (R: Me, Et, *t*-Bu, *n*-Bu and Ph) in vacuum. The distances are given in Å, angles (∠) – in degrees.

R ₃ PSe	r(P=Se), Å	r(Se-I), Å	r(Se-C), Å	∠(PSeI),°	∠(SeIC),°
Halogen bond Se...I-C					
Me ₃ PSe	2.108	3.367	5.461	89.0	175.7
Et ₃ PSe	2.115	3.325	5.422	88.5	174.8
<i>n</i> -Bu ₃ PSe	2.117	3.350	5.442	92.1	174.1
<i>t</i> -Bu ₃ PSe	2.133	3.338	5.433	111.7	178.5
Ph ₃ PSe	2.112	3.461	5.547	89.8	177.5
MePh ₂ PSe (aryl)	2.112	3.424	5.511	86.9	174.8
MePh ₂ PSe (alkyl)	2.110	3.428	5.518	85.6	176.2
Halogen bond Se...Br-C					
Me ₃ PSe	2.101	3.485	5.344	84.3	170.1
Et ₃ PSe	2.107	3.453	5.304	88.2	168.1
<i>n</i> -Bu ₃ PSe	2.109	3.465	5.311	87.6	167.2
<i>t</i> -Bu ₃ PSe	2.125	3.527	5.402	108.3	178.8
Ph ₃ PSe	2.101	3.830	5.276	82.0	132.7
MePh ₂ PSe (aryl)	2.097	4.110	5.332	76.4	121.8
MePh ₂ PSe (alkyl)	2.103	3.509	5.380	82.2	174.9