

Supporting Information for

Unveiling the Electronic Structure Peculiarities of Phosphine Selenides as NMR Probes for Non-covalent Interactions: An Experimental and Theoretical Study

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Table S1. Geometry parameters of the considered crystalline phosphine selenides $R_3P=Se$ (R=Me, Et, *t*-Bu, Ph). All distances are given in Å, angles (\angle) – in degrees.

CCDC	R	r(P–Se), Å	r(P–C), Å	\angle (CPC), degree	\angle (CPSe), degree
MEPNSE01 [32]	Me	2.123	1.799	112.7	106.1
YOFTAR	Et	2.126	1.810	113.5	105.2
QIJFOE [26]	<i>t</i> -Bu	2.133	1.908	108.9	110.0
TPPHSE02 [33]	Ph	2.115	1.817	112.6	106.1
	Ph	2.113	1.818	112.9	106.0

Figure S1. The powder X-ray patterns for studied polymorph of trimethylphosphine selenide $\text{Me}_3\text{P}=\text{Se}$ (MEPNSE01). The space group $P2_1/m$, lattice parameters: $a = 6.4683(4) \text{ \AA}$, $b = 7.8246(8) \text{ \AA}$, $c = 6.6154(6) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 90.423(5)^\circ$.

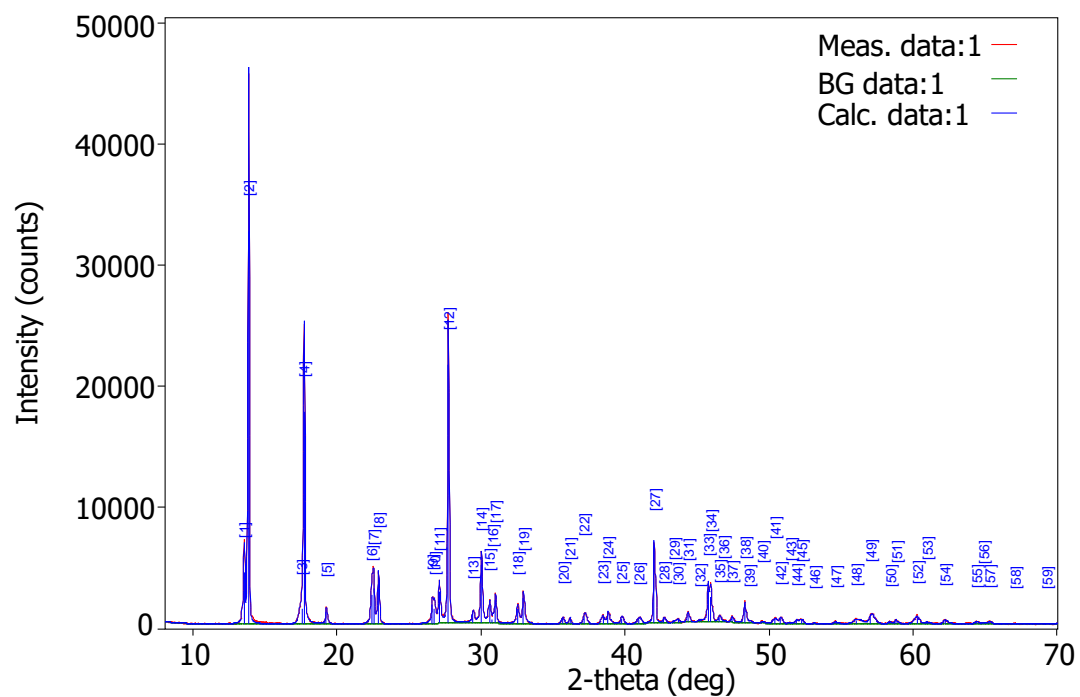


Figure S2. The powder X-ray patterns for studied polymorph of triethylphosphine selenide $\text{Et}_3\text{P}=\text{Se}(\text{YOFTAR})$. The space group $P31c$, lattice parameters: $a = b = 9.0487 \text{ \AA}$, $c = 6.5327 \text{ \AA}$, $\alpha = \beta = 90^\circ$.

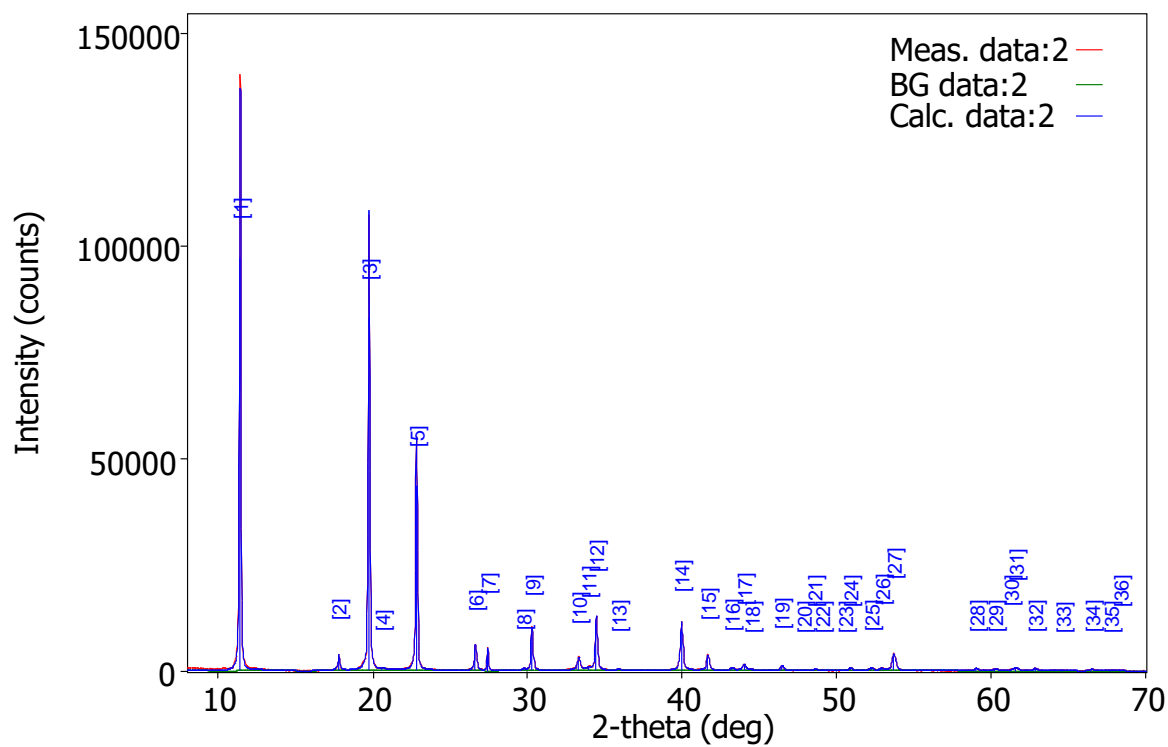


Figure S3. The powder X-ray patterns for studied polymorph of tris(*t*-butyl)phosphine selenide *t*-Bu₃P=Se (QIJFOE). The space group $Pa\bar{3}$, lattice parameters: $a = b = c = 14.5317(2)$ Å, $\alpha = \beta = \gamma = 90^\circ$.

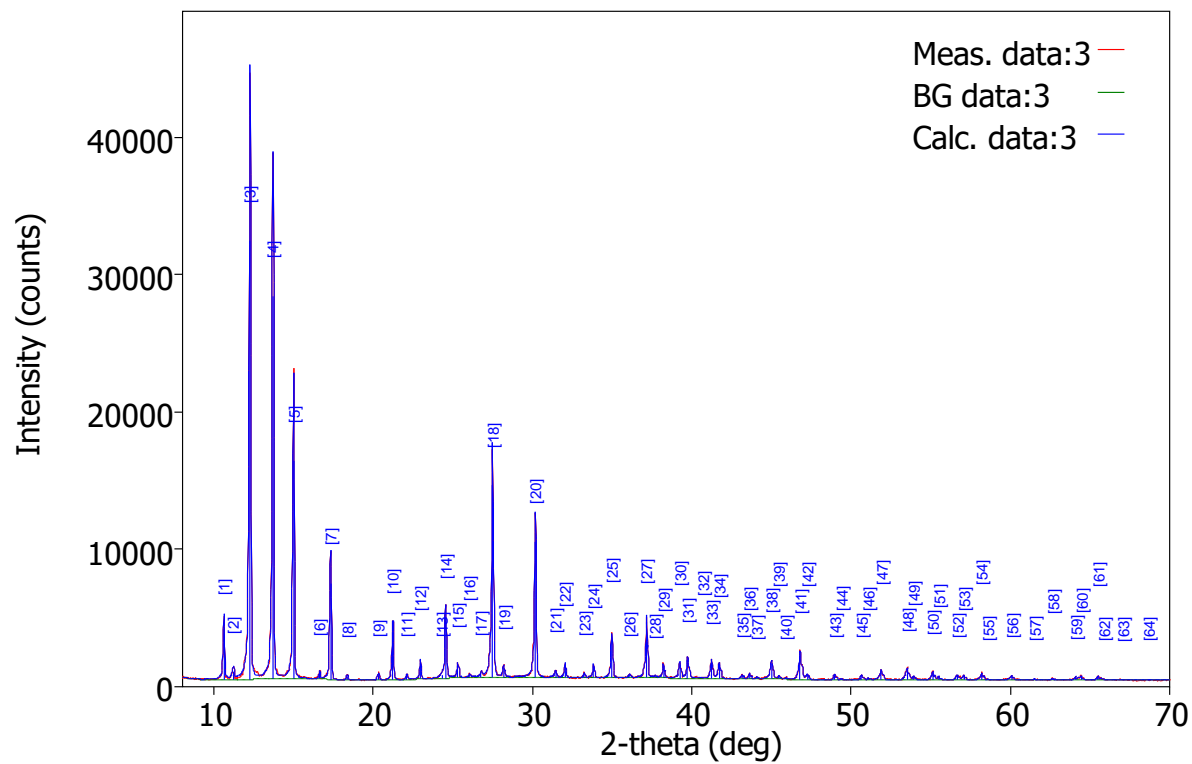


Figure S4. The powder X-ray patterns for studied polymorph of triphenylphosphine selenide $\text{Ph}_3\text{P}=\text{Se}$ (TPPHSE02). The space group $P2_1/c$, lattice parameters: $a = 18.451(3) \text{ \AA}$, $b = 9.6728(17) \text{ \AA}$, $c = 18.097(2) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 106.777(10)^\circ$.

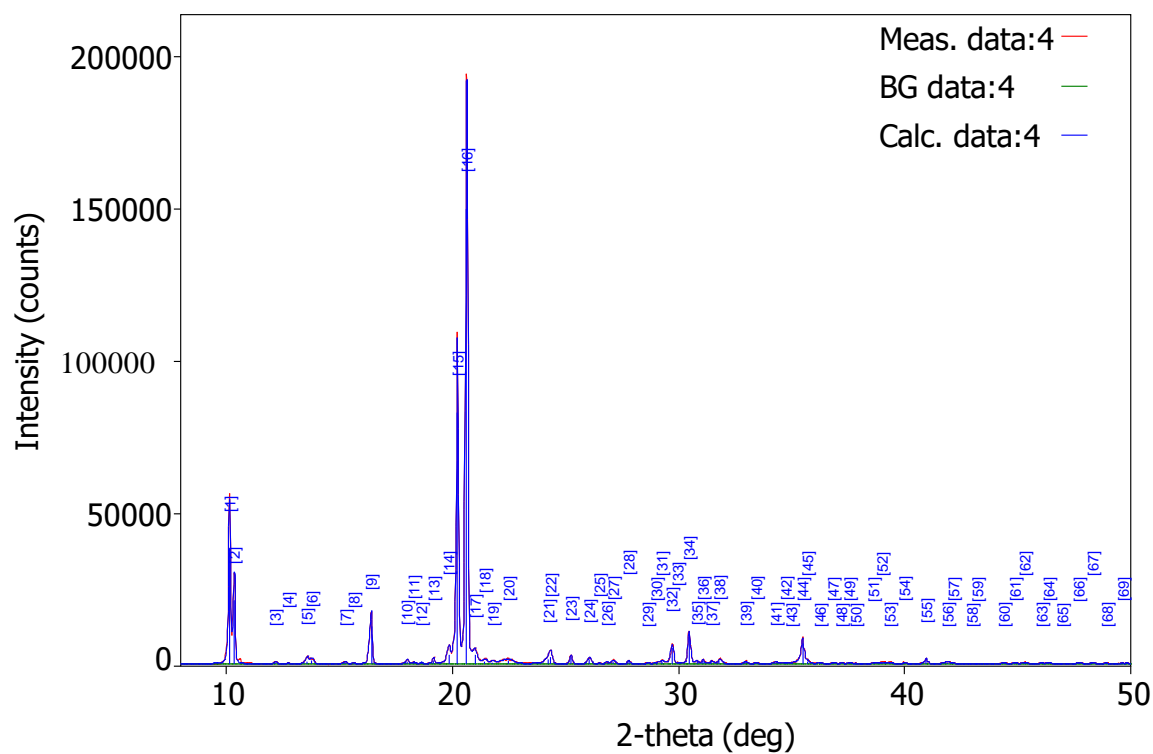


Figure S5. Dependence of the δ_{33} component of ^{31}P chemical shift anisotropy tensor with the P=Se bond length in studied phosphine selenides $\text{R}_3\text{P}=\text{Se}$ (where $\text{R}=\text{Me}$, Et , $t\text{-Bu}$ and Ph) in solid state. The spectral parameters were obtained by static NMR spectra, and the geometric parameters – by X-ray analysis.

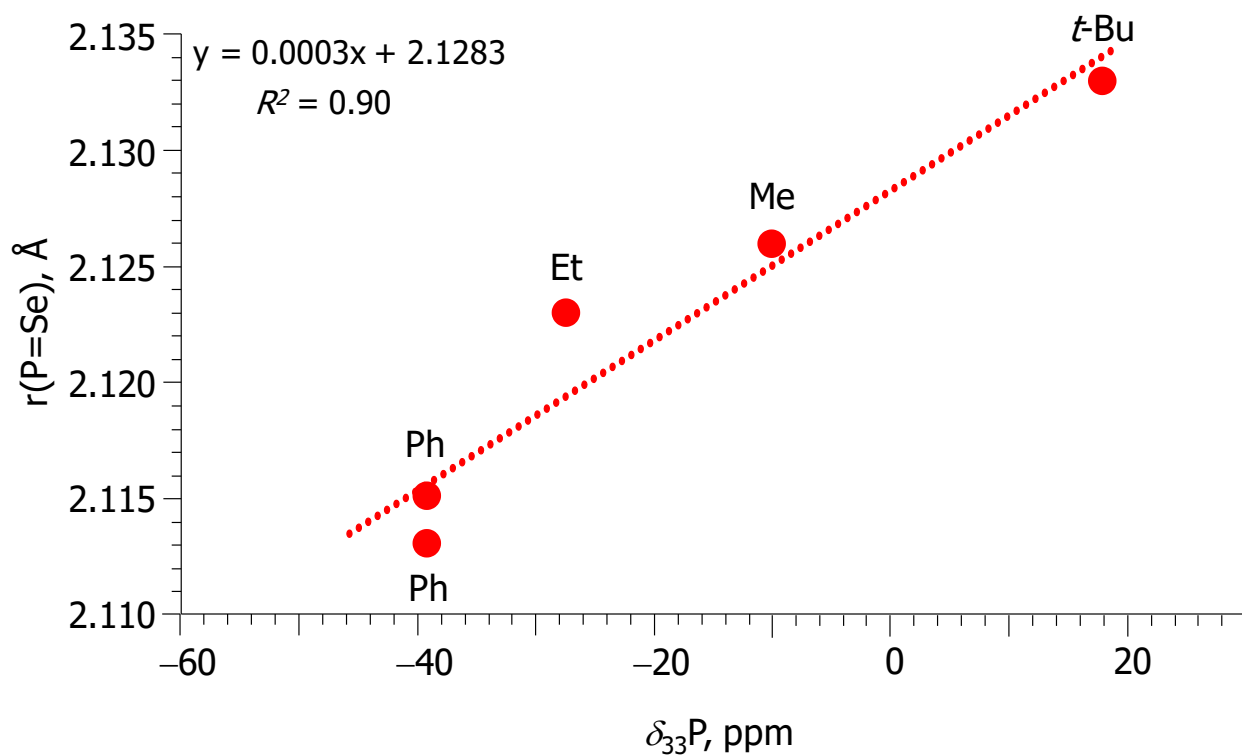


Figure S6. The ^{31}P and ^{77}Se NMR spectra of phosphine selenides $\text{R}_3\text{P}=\text{Se}$ (where $\text{R}=\text{Me}$, Et , $n\text{-Bu}$, $t\text{-Bu}$, Ph and MePh_2) in solution in $\text{CDF}_3/\text{CDClF}_2$ at 100 K. In red and blue colours the values of ^{31}P and ^{77}Se NMR chemical shifts are marked respectively. In black color the values of coupling constant $^1J_{\text{PSe}}$ are given.

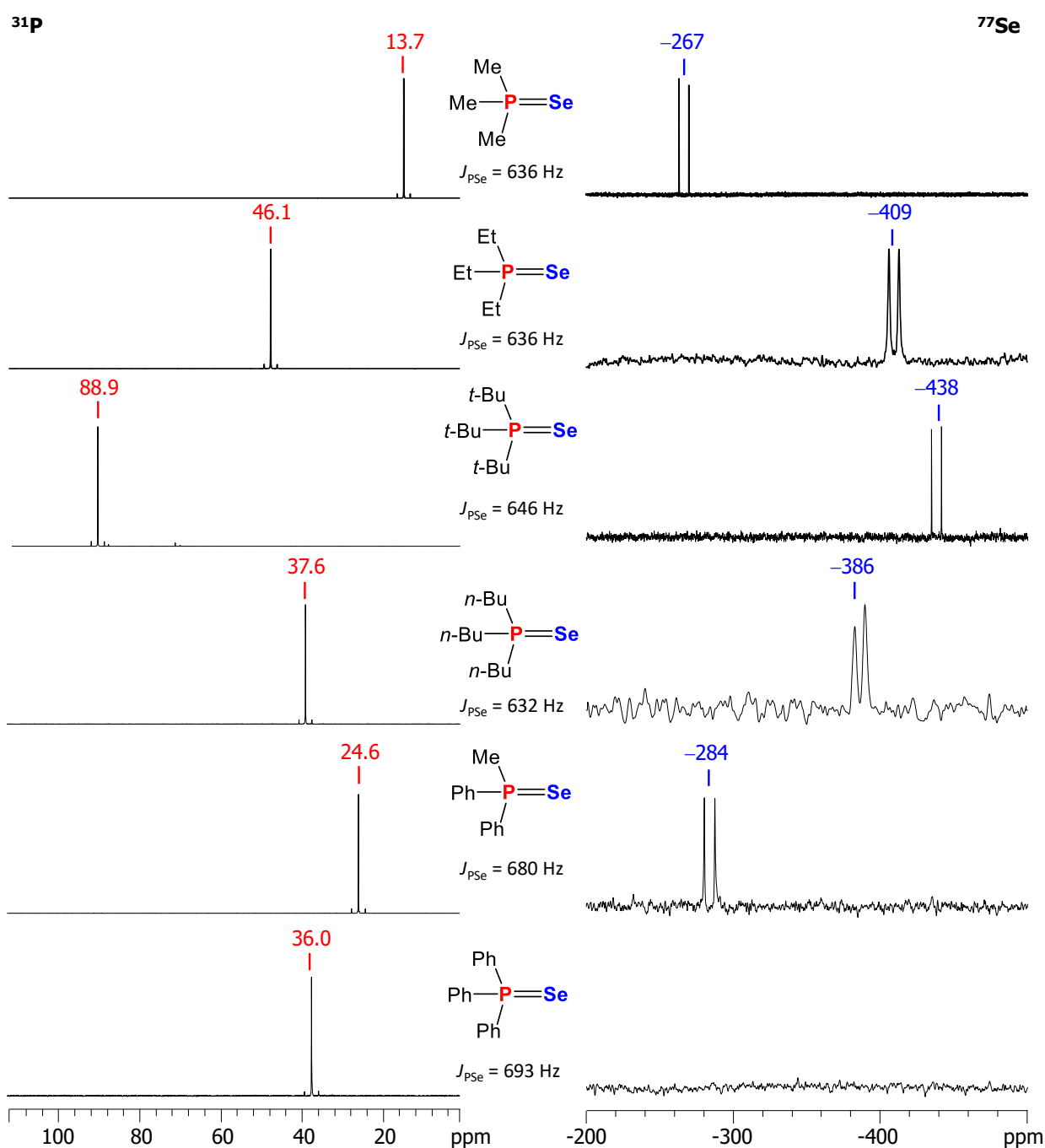


Table S2. Calculated (B3LYP/def2-TZVP) geometry and spectral NMR parameters of phosphine selenides $R_3P=Se$ in solution. The distances are given in Å, angles (\angle) – in degrees. The δP and δSe are presented in ppm and coupling constant values $^1J_{PSe}$ – in Hz.

R	r(P–Se), Å	r(P–C), Å	r(C–C), Å	\angle (CPC), degree	δP , ppm	δSe , ppm	$^1J_{PSe}$, Hz
Me	2.151	1.813	–	105.8	56.8	–289	680
Et	2.153	1.829	1.528	105.3	83.3	–491	680
<i>t</i> -Bu	2.174	1.929	1.540	108.9	132.6	–429	721
<i>n</i> -Bu	2.155	1.827	1.529	105.7	74.8	–439	674
Ph	2.149	1.820	1.397	106.5	75.5	–193	764
MePh ₂	2.147	1.819 1.816	1.397	105.9	65.5	–239	719

Table S3. Calculated geometry (PW6B95-GD3/def2-QZVP) and spectral (B97-2/pcsSeg-2) parameters of phosphine selenides $R_3P=Se$ in vacuum. The distances are given in Å, angles (\angle) – in degrees. The $\delta^{31}P$ and $\delta^{77}Se$ are presented in ppm and coupling constant values J_{P-Se} – in Hz.

R	r(P–Se), Å	r(P–C), Å	\angle (CPC), degree	\angle (CPSe), degree	$\delta^{31}P$, ppm	$\delta^{77}Se$, ppm	$^1J_{PSe}$, Hz
Me	2.090	1.809	104.1	114.5	32.0	–422	739
		1.809	104.1	114.5			
		1.809	104.0	114.5			
Et	2.096	1.821	104.9	113.0	57.1	–530	731
		1.821	104.4	114.3			
		1.820	105.2	114.1			
<i>n</i> -Bu	2.097	1.819	105.0	113.1	51.9	–509	729
		1.821	104.8	114.3			
		1.819	104.3	114.3			
<i>t</i> -Bu	2.117	1.901	109.3	109.6	100.5	–529	733
		1.900	109.3	109.7			
		1.901	109.3	109.7			
Ph	2.097	1.816	104.8	113.8	55.4	–434	779
		1.816	104.7	113.9			
		1.816	104.8	113.9			
MePh ₂	2.094	1.811 (Me)	103.5 (MPP)	113.8 (Me)	41.5	–491	777
		1.819 (Ph)	104.4 (PPP)	114.7 (Ph)			
		1.815 (Ph)	105.1 (PPM)	114.5 (Ph)			

Figure S7. Dependences of the δP NMR with the electron density values (ρ) at electron density critical points of type (3, -1) for P=Se and P-C bonds for $R_3P=Se$ (where R=Me, Et, *n*-Bu, *t*-Bu, Ph and MePh₂). The δP was obtained by quantum chemical calculation (B97-2/pcsSeg-2) and experimentally (NMR in solution in CDCl₃).

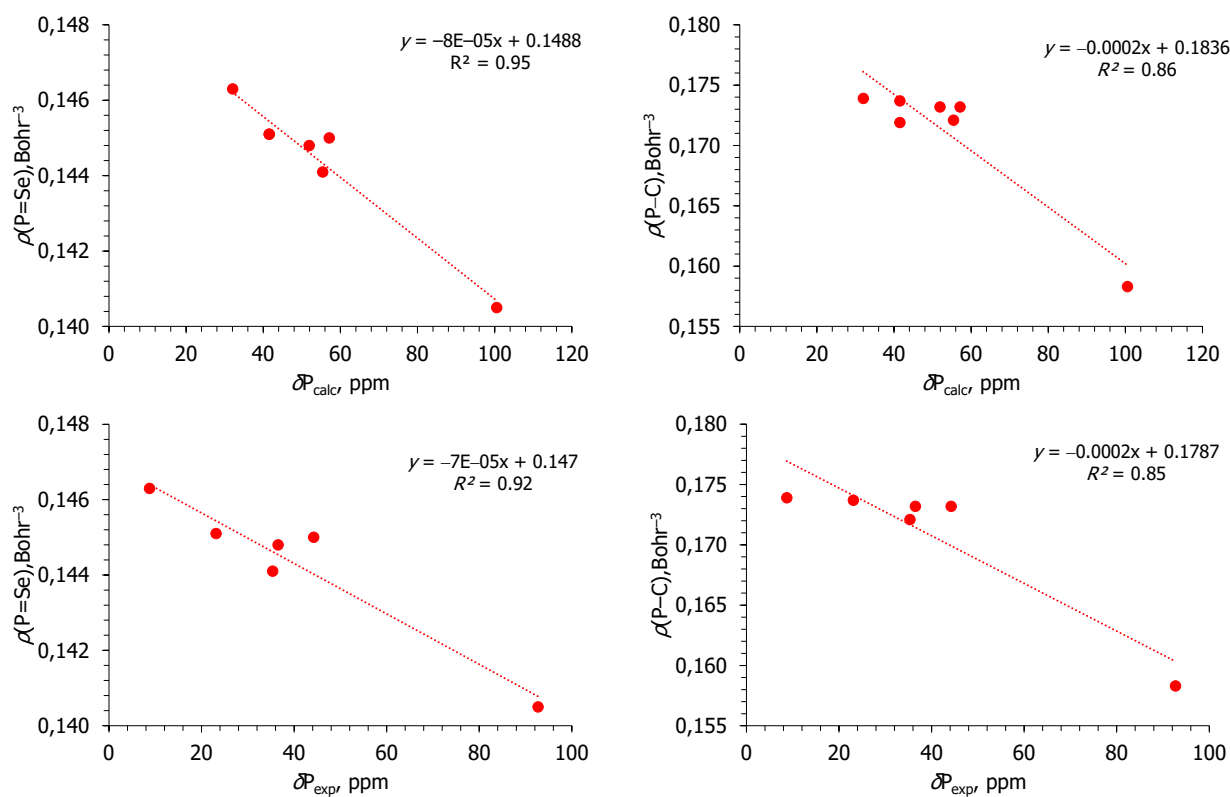


Figure S8. Dependences of the $\delta\mathcal{P}$ NMR with the kinetic (G) energy densities of electrons at electron density critical points of type (3, -1) for P=Se and P-C bonds for $R_3P=Se$ (where $R=Me, Et, n-Bu, t-Bu, Ph$ and $MePh_2$). The $\delta\mathcal{P}$ was obtained by quantum chemical calculation (B97-2/pcsSeg-2) and experimentally (NMR in solution in $CDCl_3$).

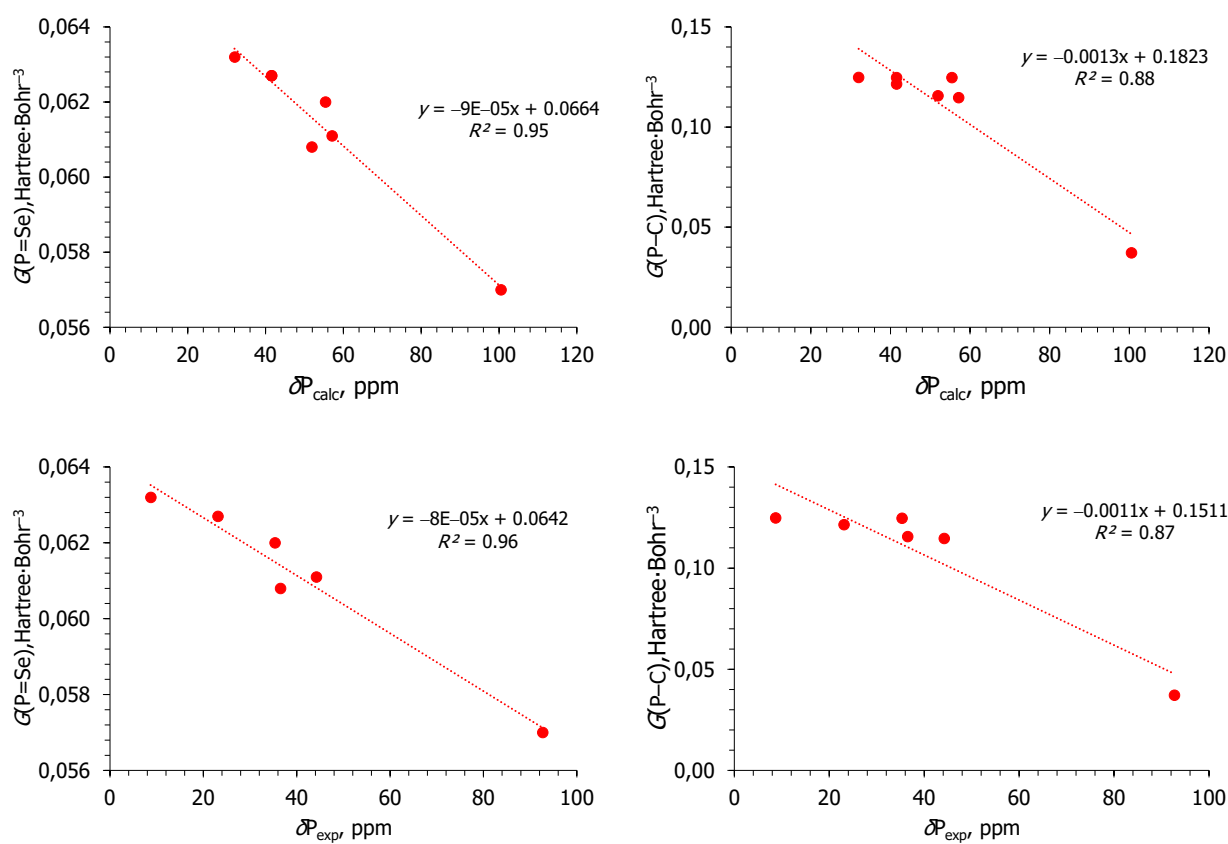


Figure S9. Dependences of the δSe NMR with the electron density values (ρ) at electron density critical points of type (3, -1) for P=Se and P-C bonds for $\text{R}_3\text{P}=\text{Se}$ (where R=Me, Et, *n*-Bu, *t*-Bu, Ph and MePh₂). The δP was obtained by quantum chemical calculation (B97-2/pcsSeg-2) and experimentally (NMR in solution in CDCl_3).

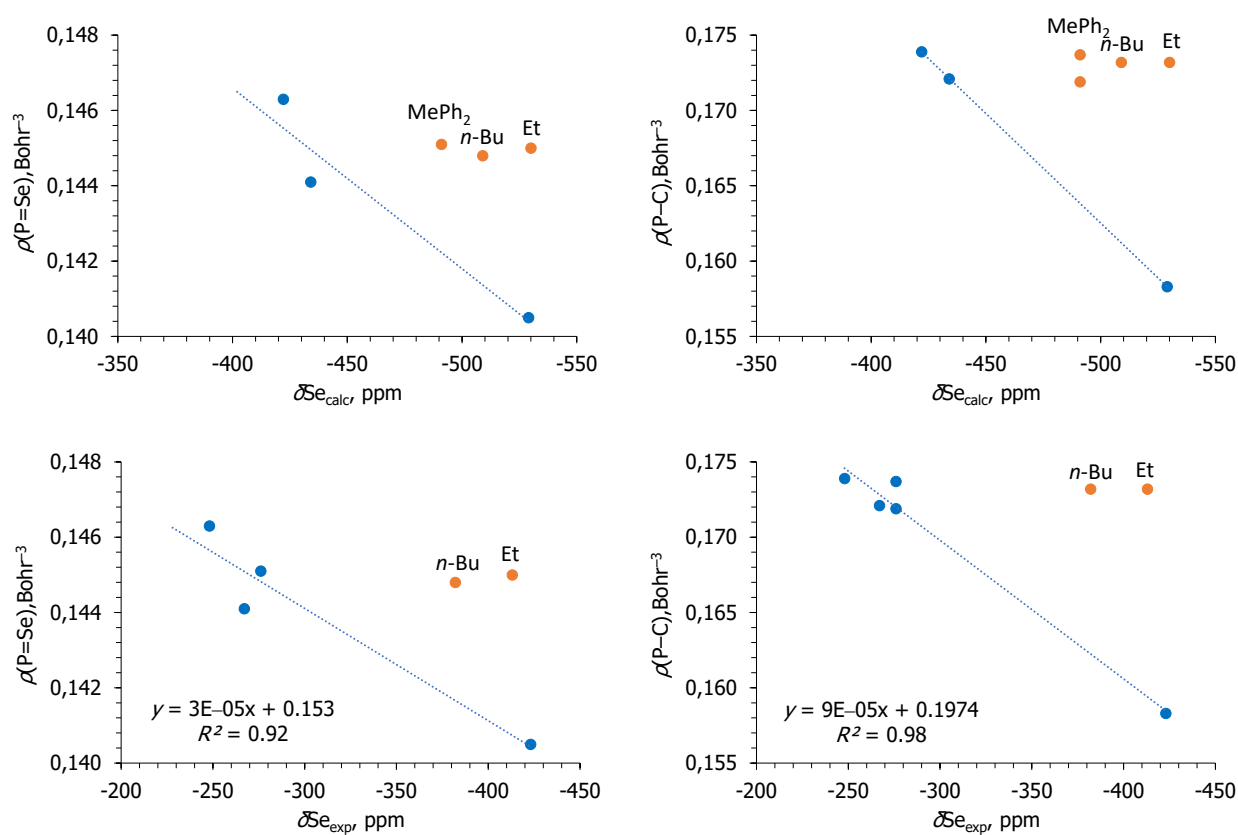


Figure S10. Dependences of the δSe NMR with the kinetic (G) energy densities of electrons at electron density critical points of type (3, -1) for P=Se and P-C bonds for $\text{R}_3\text{P}=\text{Se}$ (where R=Me, Et, *n*-Bu, *t*-Bu, Ph and MePh₂). The δP was obtained by quantum chemical calculation (B97-2/pcsSeg-2) and experimentally (NMR in solution in CDCl_3).

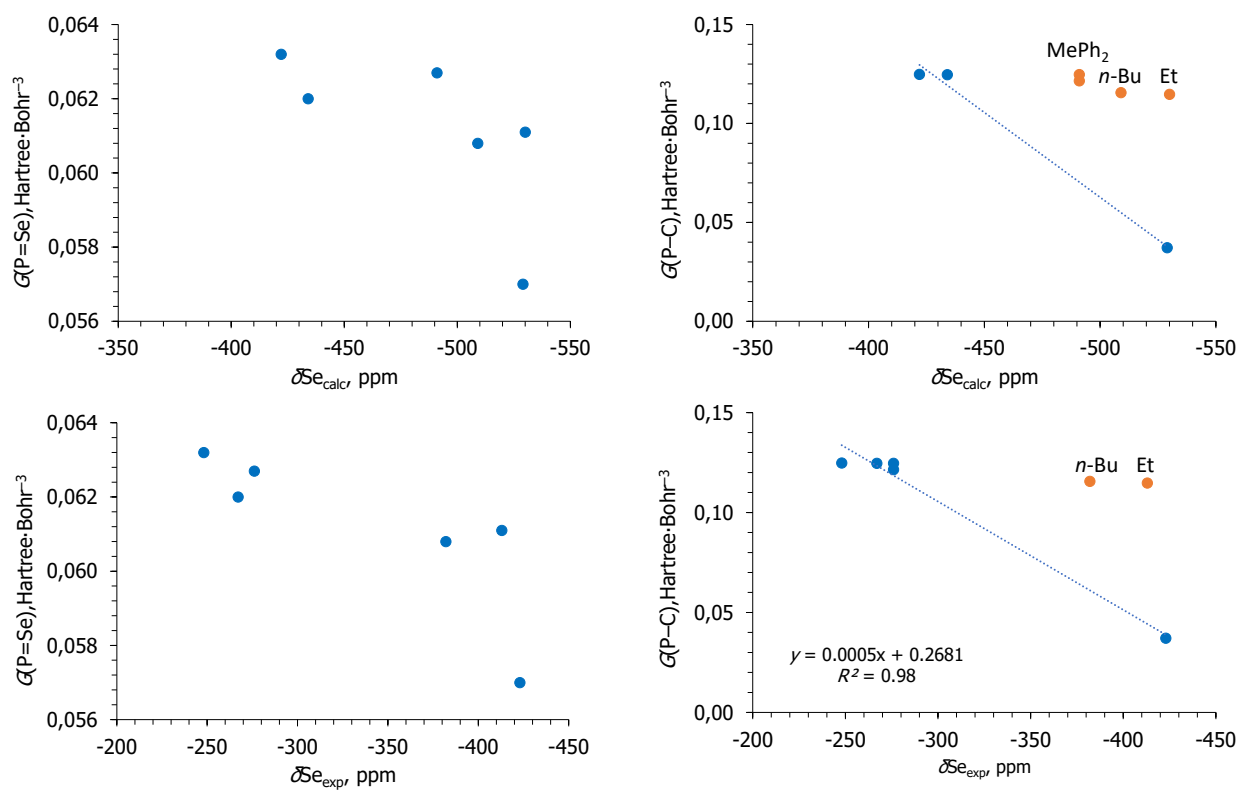


Figure S11. Dependences of the ${}^1J_{\text{PSe}}$ with the electron density Laplacian $\nabla^2\rho$ at electron density critical points of type (3, -1) for P=Se and P-C bonds for $\text{R}_3\text{P=Se}$ (where R=Me, Et, *n*-Bu, *t*-Bu, Ph and MePh₂). The J_{PSe} was obtained by quantum chemical calculation (B97-2/pcsSeg-2) and experimentally (NMR in solution in CDCl_3).

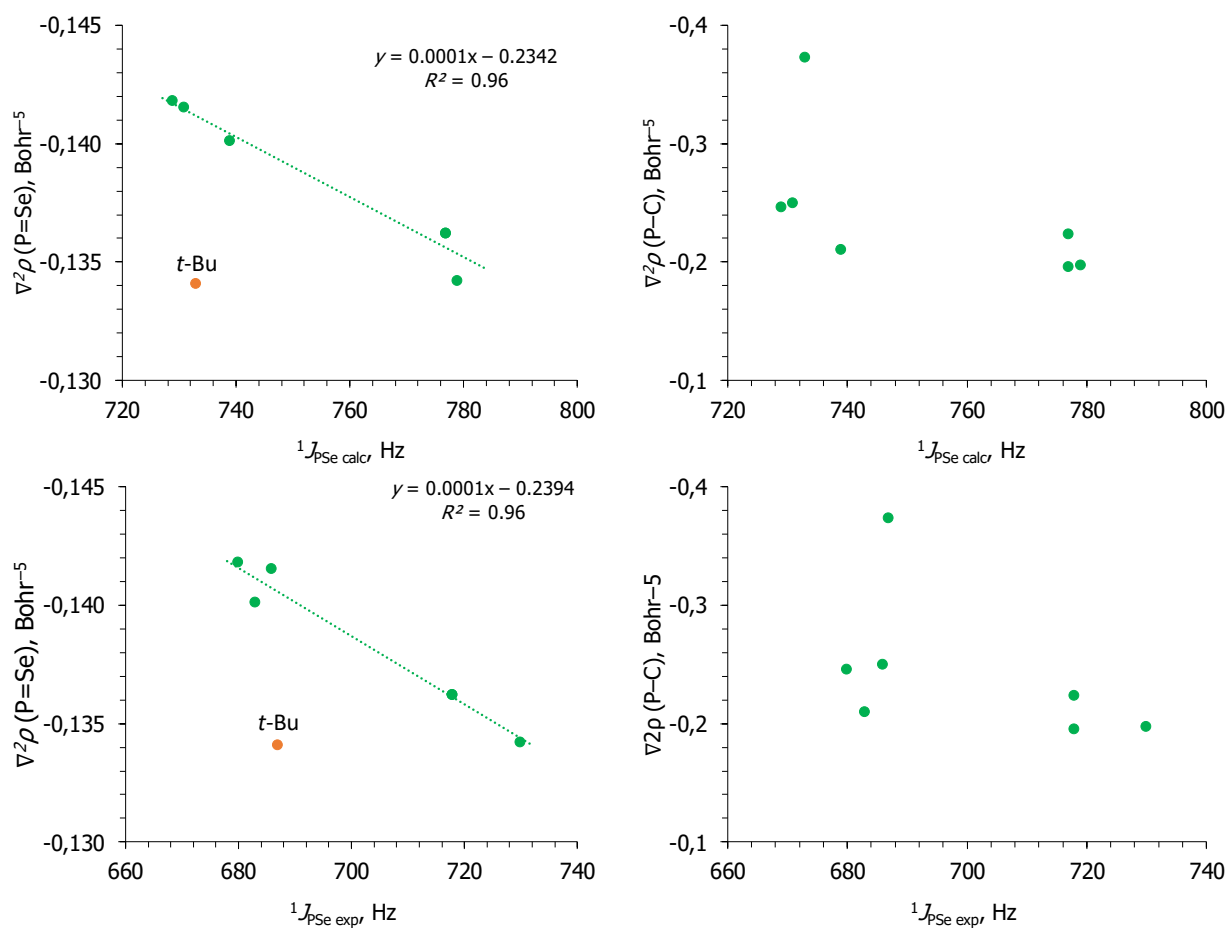


Figure S12. A graphical visualization of donor-acceptor (DA) interactions of natural bonding orbitals (NBOs) on an example of *n*-Bu₃PSe. The captions are made according to Table 3.

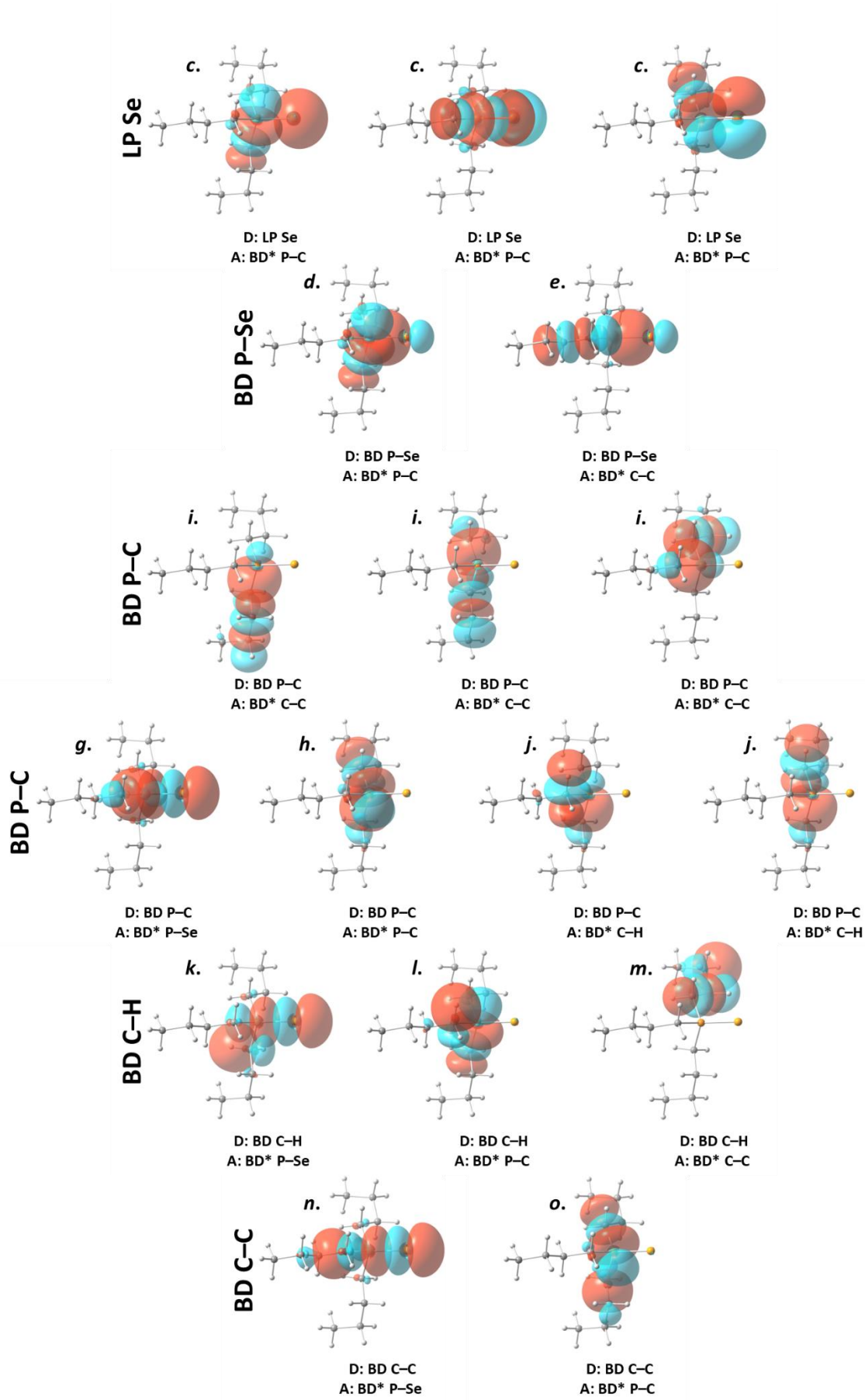


Figure S13. Dependences of the coupling constant $^1J_{\text{PSe}}$ with the energy of interaction between lone pairs (LP) of selenium atom and the BD* orbital of the P–C bond in studied phosphine selenides $\text{R}_3\text{P}=\text{Se}$ (where $\text{R}=\text{Me}$, Et , $n\text{-Bu}$, $t\text{-Bu}$ and Ph). NMR parameters were obtained by quantum chemical calculation in vacuum (B97-2/pcsSeg-2) and NMR spectroscopy in solution in CDCl_3 . NBO analysis was carried by quantum chemical calculation in vacuum (PW6B95-D3/def2-QZVP).

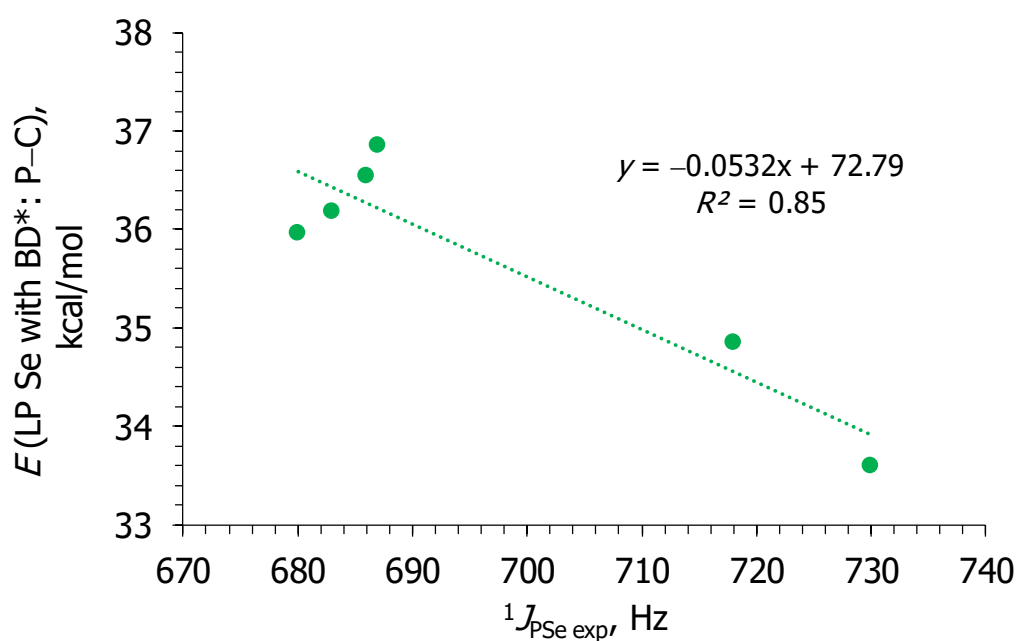
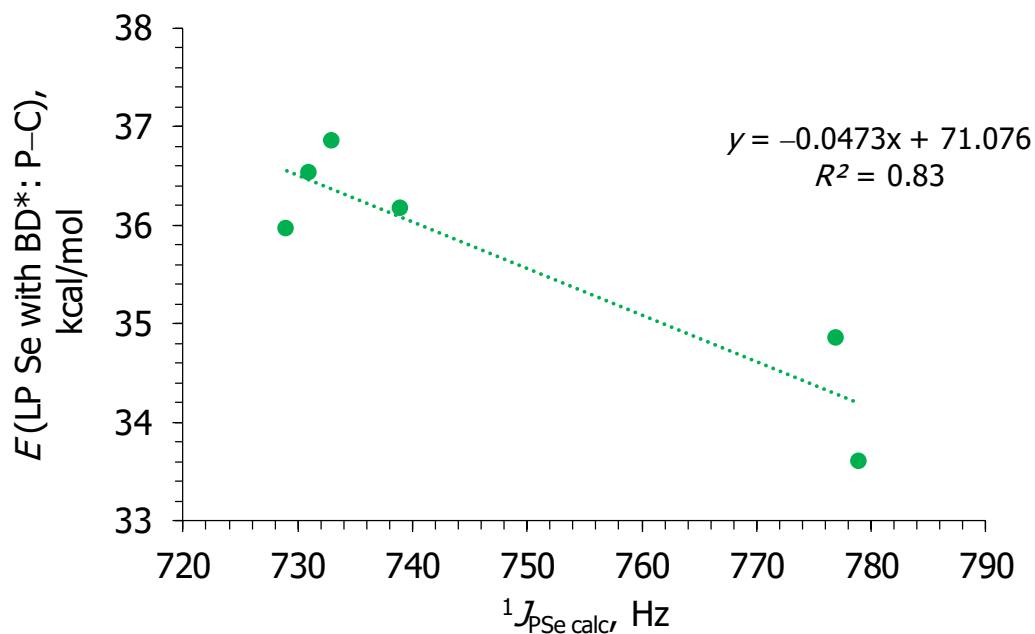
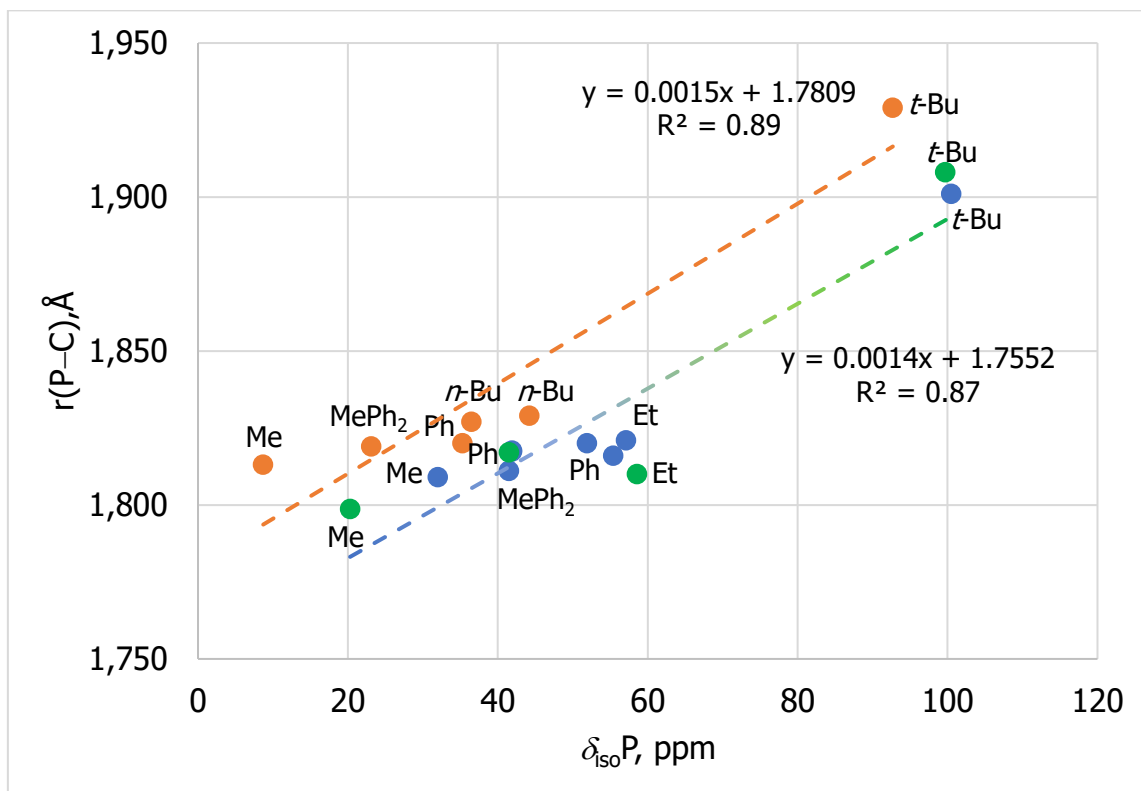
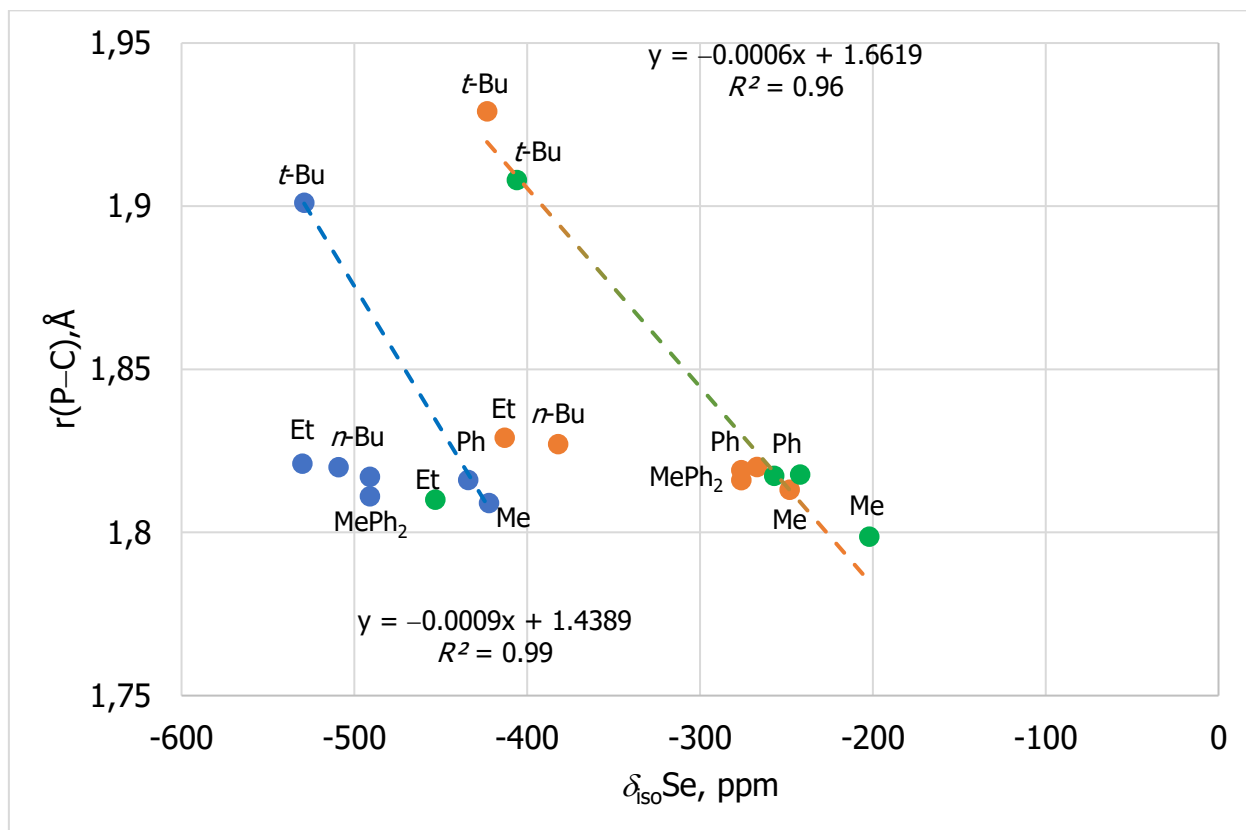


Figure S14. Dependence of the ^{31}P NMR isotropic chemical shift with the P–C bond length in studied phosphine selenides $\text{R}_3\text{P}=\text{Se}$ (where $\text{R}=\text{Me}$, Et , $n\text{-Bu}$, $t\text{-Bu}$, Ph and MePh_2) in solid state (green points), solution (orange points) and vacuum (blue points).



The data points obtained experimentally by MAS NMR and those calculated theoretically lie on the same correlation line (black). The points obtained for measurements in solution lie higher on their correlation line (orange), but at the same slope.

Figure S15. Dependence of the ^{77}Se NMR isotropic chemical shift with the P–C bond length in studied phosphine selenides $\text{R}_3\text{P}=\text{Se}$ (where $\text{R}=\text{Me}$, Et , $n\text{-Bu}$, $t\text{-Bu}$, Ph and MePh_2) in solid state (green points), solution (orange points) and vacuum (blue points).



The data points obtained for measurements in solid state and solution lie on the same correlation line (black). Only three points corresponding to $\text{Et}_3\text{P}=\text{Se}$ and $n\text{-Bu}_3\text{P}=\text{Se}$, in which the substituent is conjugated with the phosphorus atom, drop out from the general dependence. The points obtained for measurements in solution lie higher on their correlation line (orange), but at the same slope. For this dependence, only three points lie on the correlation line, corresponding to $\text{R}_3\text{P}=\text{Se}$, (where $\text{R}=\text{Me}$, Ph and $t\text{-Bu}$).