

Supplementary information

**Solvent Effect on the ^{77}Se NMR Chemical Shift of Diphenyl
Diselenides**

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General Information

Proton nuclear magnetic resonance spectra (^1H NMR) were recorded at 400 MHz on a Bruker Avance III HD spectrometer. Chemical shifts (δ) are reported in ppm, and the abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), td (triple doublet) and m (multiplet). NMR data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz and integrated intensity. ^1H NMR chemical shifts were referenced to the tetramethylsilane (TMS; 0.0 ppm) internal standard. ^{77}Se NMR spectra were obtained at 76.3 MHz and referenced to the diphenyl diselenide ($\text{C}_6\text{H}_5\text{SeSeC}_6\text{H}_5$; 463.0 ppm) external standard employing the substitution method (IUPAC). Spectra were recorded in either CDCl_3 , D_3CCN , $\text{Py-}d_5$, C_6D_6 , D_3COD , $\text{D}_3\text{CCO}_2\text{H}$, $\text{THF-}d_8$ or $\text{DMSO-}d_6$ solutions. The NMR analyses of chalcogenide nuclides were carried out in a ^1H -decoupled pulse sequence, *zgpg* for ^{77}Se and coupled pulse sequence, *zg* for ^{77}Se (Bruker Pulse Sequences). The CDCl_3 , D_3CCN , $\text{Py-}d_5$, C_6D_6 , D_3COD , $\text{D}_3\text{CCO}_2\text{D}$, $\text{THF-}d_8$ or $\text{DMSO-}d_6$ deuterated solvents were purchased from Sigma-Aldrich (Merck). The diaryl diselenides and diphenyl ditelluride were prepared according to the literature.¹

^{77}Se NMR analyses in distinct deuterated solvents

Diphenyl diphenyl diselenide (5.0 mg) was added in a vial followed by addition of the respective deuterated solvent (700 μL). The vial was then mixed and put into an NMR tube (5 mm) and the NMR analyses were carried at 25°C. The chemical shifts were referenced by substitution method,^{2,3} derived from the standard chemical shift of diphenyl ditelluride or diphenyl diselenide in CDCl_3 recorded individually for each sample before the NMR analysis into specific deuterated solvent.

$^{77}\text{Se}\{^1\text{H}\}$ and ^{77}Se NMR chemical shifts recorded in different concentrations

¹ N. Petragani, H. A. Stefani, *Tetrahedron*, **2005**, *61*, 1613.

² R. K. Harris, E. D. Becker, S. M. C. De Menezes, R. Goodfellow, P. Granger, *Pure and Applied Chemistry*, **2001**, *73*(11), 1795.

³ R. K. Harris, E. D. Becker, S. M. C. De Menezes, P. Granger, R. E. Hoffman, K. W. Zilm, *Pure and Applied Chemistry*, **2008**, *80*(1), 59.

Diphenyl diselenide (mg - amount was varied according to the concentration) was added in a vial followed by addition of the respective deuterated solvent (700 μL). The vial was then mixed and put into an NMR tube (5 mm) alongside with a coaxial tube (external reference) containing diphenyl diselenide in the concentration used in the analyses of deuterated solvent (5.0 mg in 700 μL). Three aliquots were added into the deuterated solvent media to evaluate the ^{77}Se NMR chemical shift sensitivity. The NMR analyses were carried at 25°C in a decoupled ($^{77}\text{Se}\{^1\text{H}\}$) and coupled (^{77}Se) NMR pulse sequences.

Table S1: Effect on the ^{77}Se NMR chemical shifts of diphenyl diselenide in distinct concentrations.^{a,b,c}

Entry	(PhSe) ₂ in CDCl ₃ [mg/700 μL] ^a	^{77}Se Chemical Shift (ppm)	^{77}Se $\Delta\delta$ (ppm)
1	10.0	463.0	0
2	50.0	463.0	0
3	100.0	463.0	0
4 ^d	10.0	463.0	0
5 ^d	50.0	463.0	0
6 ^d	100.0	463.0	0

^a It was used the 5.0 mg of diphenyl diselenid in CDCl₃ as external standard in the substitution method (IUPAC); ^b NMR analyses were performed at 25°C; ^c Spectra are contained in the Figures S9, S10, S11, S12, S13 and S14; ^d ^{77}Se NMR analyses were recorded employing the coupled NMR pulse sequence.

Table S2: Effect on the ^{77}Se NMR chemical shifts of diphenyl diselenide in distinct concentrations and temperatures.^a

Entry	(PhSe) ₂ in DMSO- <i>d</i> ₆ [mg/700μL]	Temperature (°C)	^{77}Se Chemical Shift (ppm)	^{77}Se $\Delta\delta$ (ppm)
1	10.0	25	448.0	0
2	10.0	35	450.0	+2
3	10.0	45	453.0	+5
4	10.0	55	455.0	+7
5	100.0	25	448.0	0
6	100.0	35	450.0	+2
7	100.0	45	453.0	+5
8	100.0	55	455.0	+7

^a It was used the 5.0 mg of diphenyl diselenide in CDCl_3 as external standard in the substitution method (IUPAC);

Additional Computational Material

Ab initio molecular dynamics was carried out employing the ADMP method as implemented in Gaussian 16.[1–3] The OPBE density functional[4] combined with the large cc-pVTZ basis set was employed. ADMP was run with velocity scaling all the way through the simulation and checking the temperature (300 K) every five steps with a maximum allowed variation of 1 K. The simulation was carried out for 11000 steps of 0.1 fs each, i.e. for 1.1 ps total time. The first 100 fs were discarded, and the subsequent 1 ps of dynamics was considered for the calculation of the NMR shielding. Implicit solvent was employed in ADMP via the SMD solvation method[5], using either benzene or dimethylsulfoxide as solvent. To compute the ^{77}Se shielding constant, 51 structures were generated taking snapshots from the AIMD trajectory every 20 fs. Chemical shifts were computed for both Se nuclei on each snapshot, employing the B3LYP density functional combined with cc-pVTZ basis set. Solvation was treated according to the continuum solvation model PCM,[6] using either benzene or dimethylsulfoxide as solvents. Shielding constants were averaged for the two Se nuclei, and also along the overall trajectory. Chemical shifts were computed using dimethylselenide as standard, for which the shielding constant was computed on the fully optimized geometry of the minimum employing the same level of theory above described. For diphenyldiselenide in benzene and dimethylsulfoxide, a chemical shift of 574 ppm and 585 was computed, respectively, in qualitative agreement with the discussion provided in the main text.

1. Schlegel, H.B.; Millam, J.M.; Iyengar, S.S.; Voth, G.A.; Daniels, A.D.; Scuseria, G.E.; Frisch, M.J. Ab Initio Molecular Dynamics: Propagating the Density Matrix with Gaussian Orbitals. *J. Chem. Phys.* **2001**, *114*, 9758–9763, doi:10.1063/1.1372182.
2. Iyengar, S.S.; Schlegel, H.B.; Millam, J.M.; A. Voth, G.; Scuseria, G.E.; Frisch, M.J. Ab Initio Molecular Dynamics: Propagating the Density Matrix with Gaussian Orbitals. II. Generalizations Based on Mass-Weighting, Idempotency, Energy Conservation and Choice of Initial Conditions. *J. Chem. Phys.* **2001**, *115*, 10291–10302, doi:10.1063/1.1416876.
3. Gaussian 16, Revision B.01.
4. Swart, M.; Ehlers, A.W.; Lammertsma *, K. Performance of the OPBE Exchange-Correlation Functional. *Mol. Phys.* **2004**, *102*, 2467–2474, doi:10.1080/0026897042000275017.
5. Marenich, A. V.; Cramer, C.J.; Truhlar, D.G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378–6396, doi:10.1021/jp810292n.
6. Scalmani, G.; Frisch, M.J. Continuous Surface Charge Polarizable Continuum Models of Solvation. I. General Formalism. *J. Chem. Phys.* **2010**, *132*, doi:10.1063/1.3359469.

Selected ^{77}Se NMR Spectra

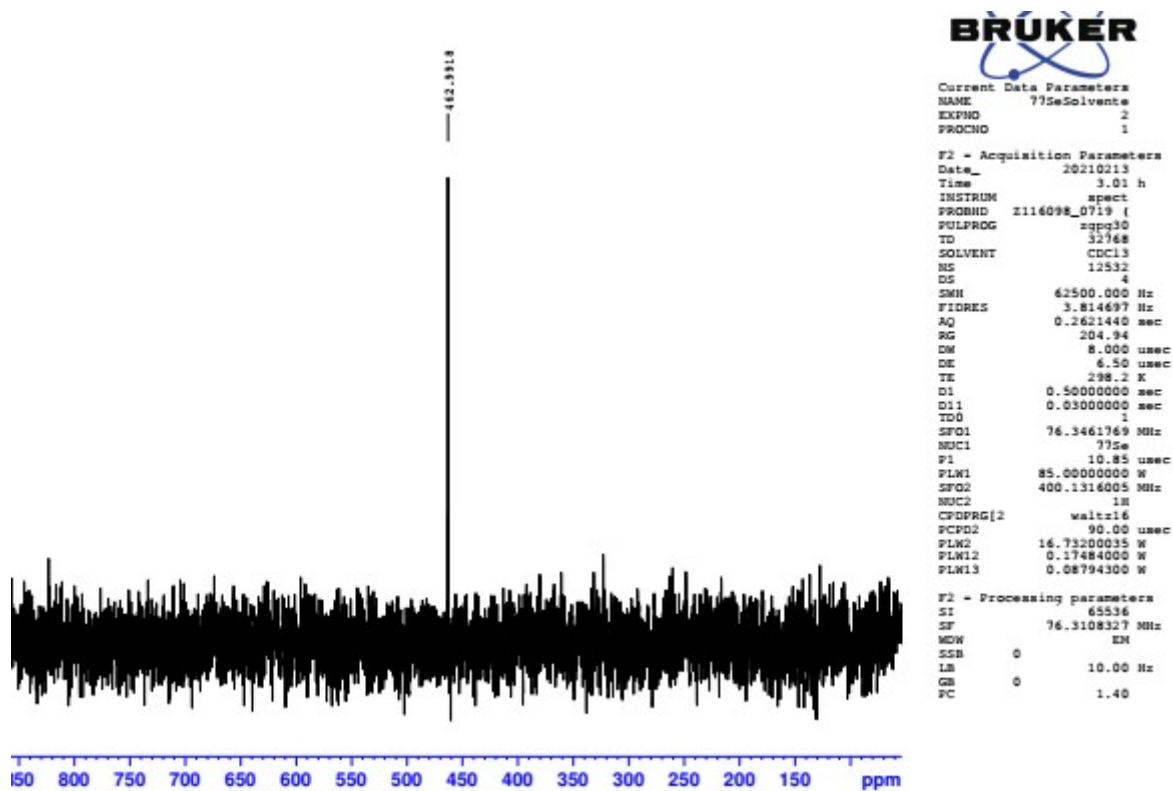


Figure S1: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum (76.3 MHz, CDCl_3) of diphenyl diselenide.

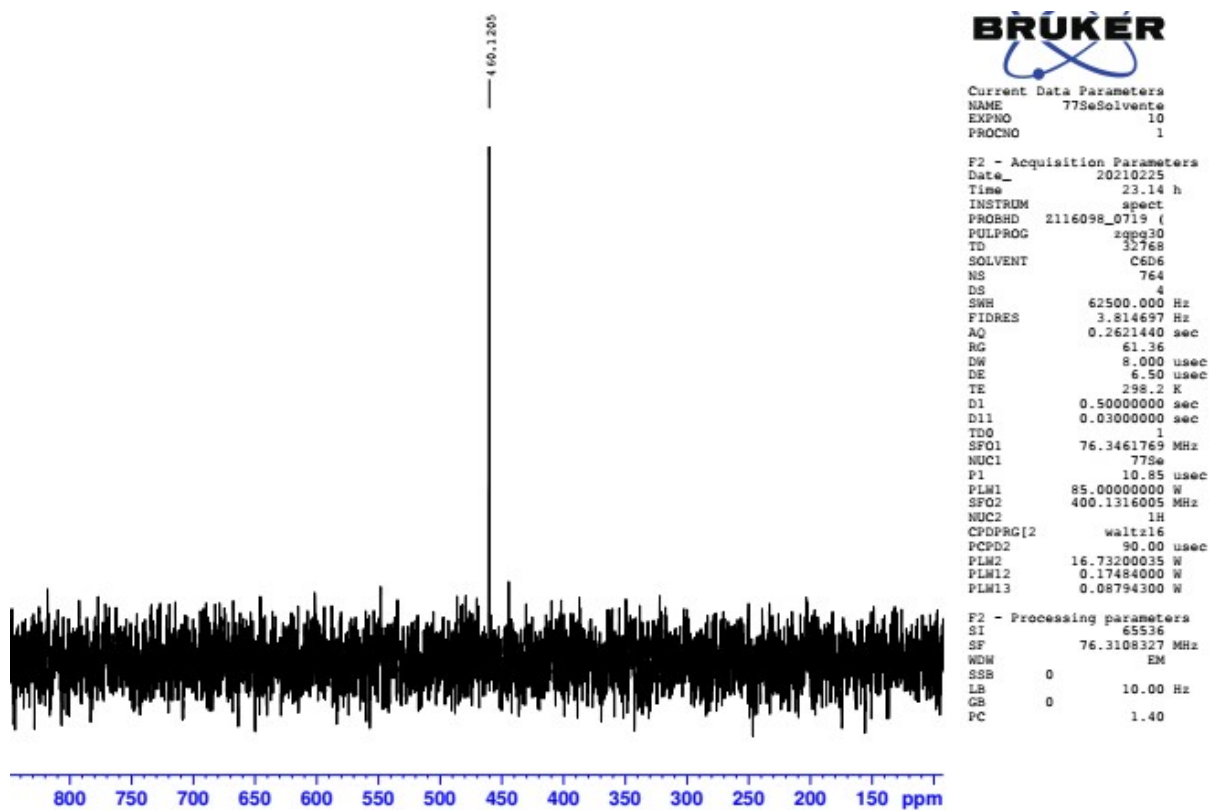


Figure S2: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum (76.3 MHz, C_6D_6) of diphenyl diselenide.

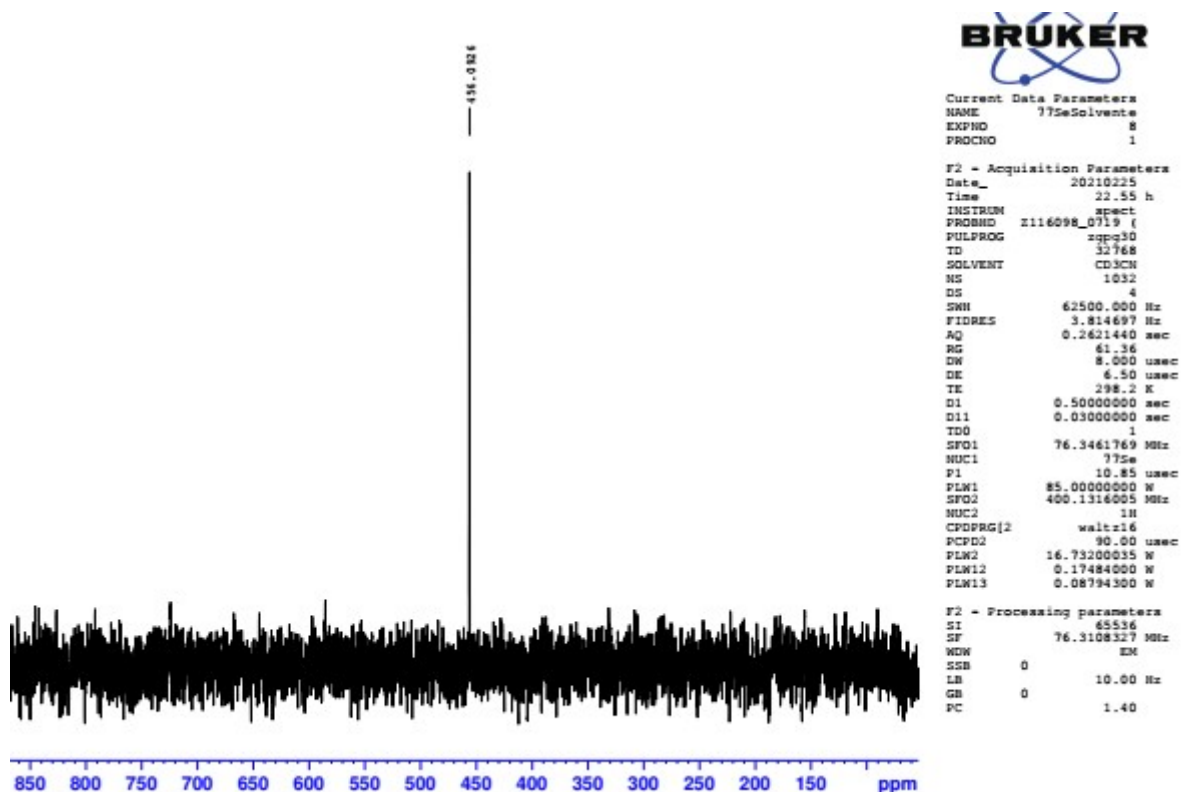


Figure S3: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum (76.3 MHz, D_3CCN) of diphenyl diselenide.

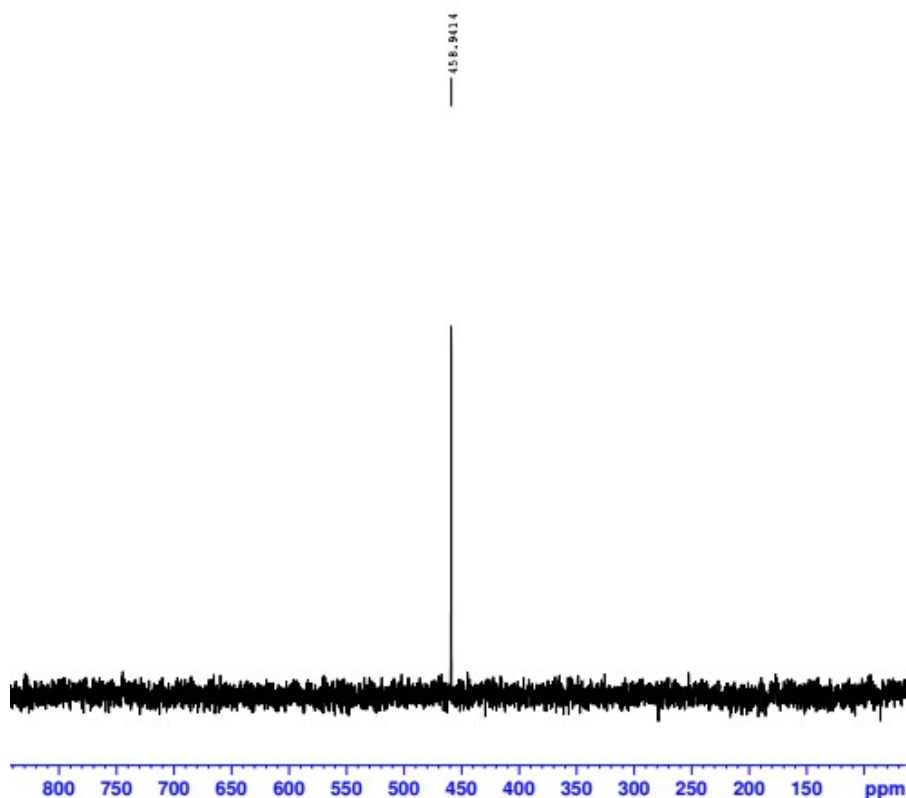


Figure S4: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum (76.3 MHz, D_3COD) of diphenyl diselenide.

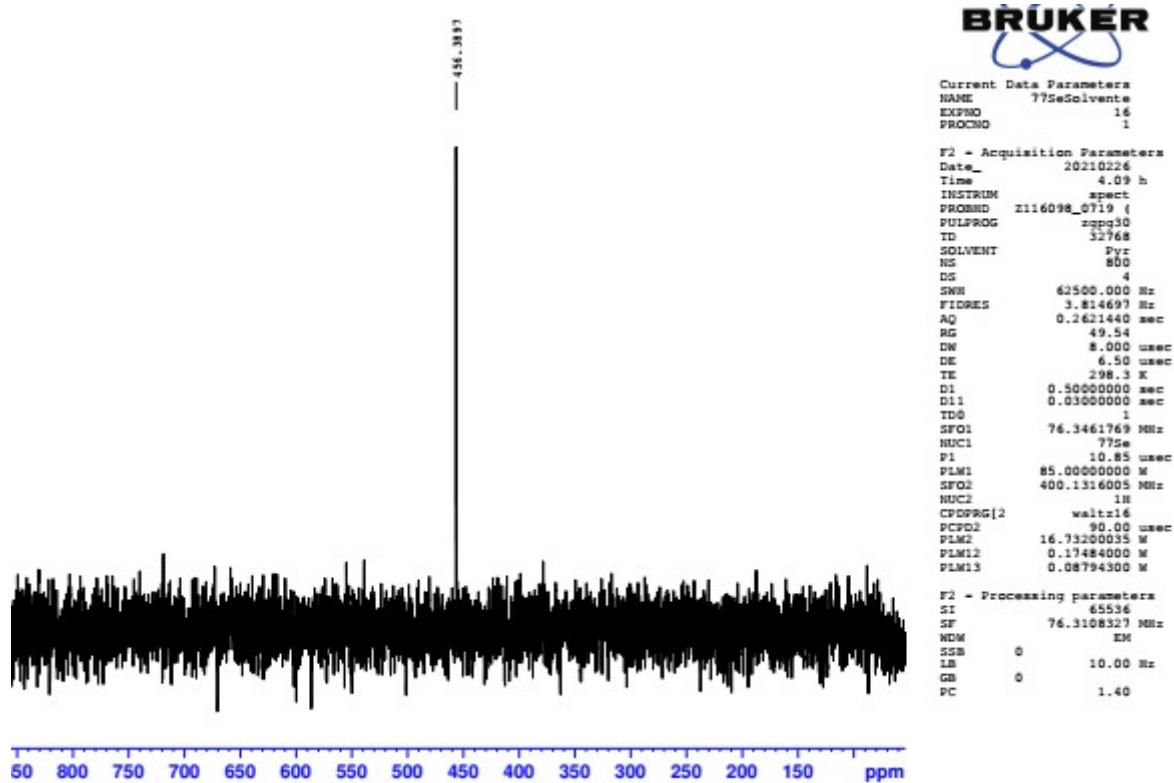


Figure S5: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum (76.3 MHz, Py-d_5) of diphenyl diselenide.

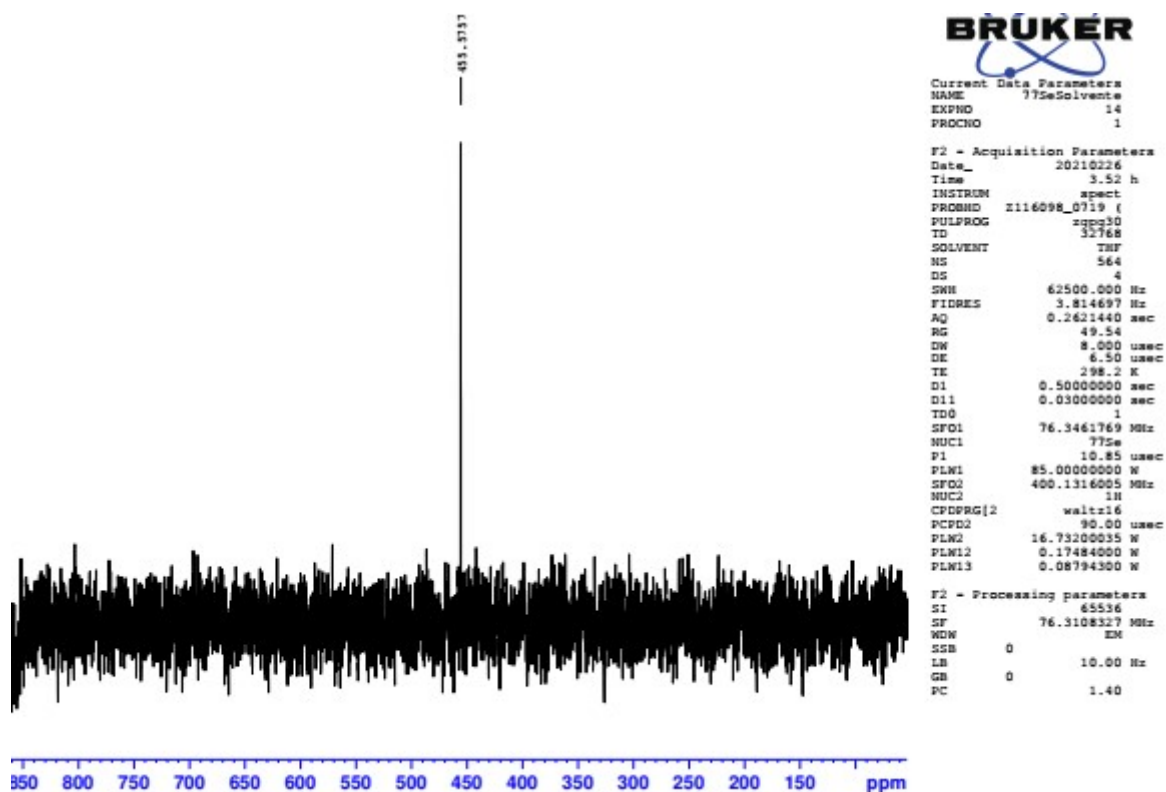


Figure S6: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum (76.3 MHz, $\text{THF-}d_8$) of diphenyl diselenide.

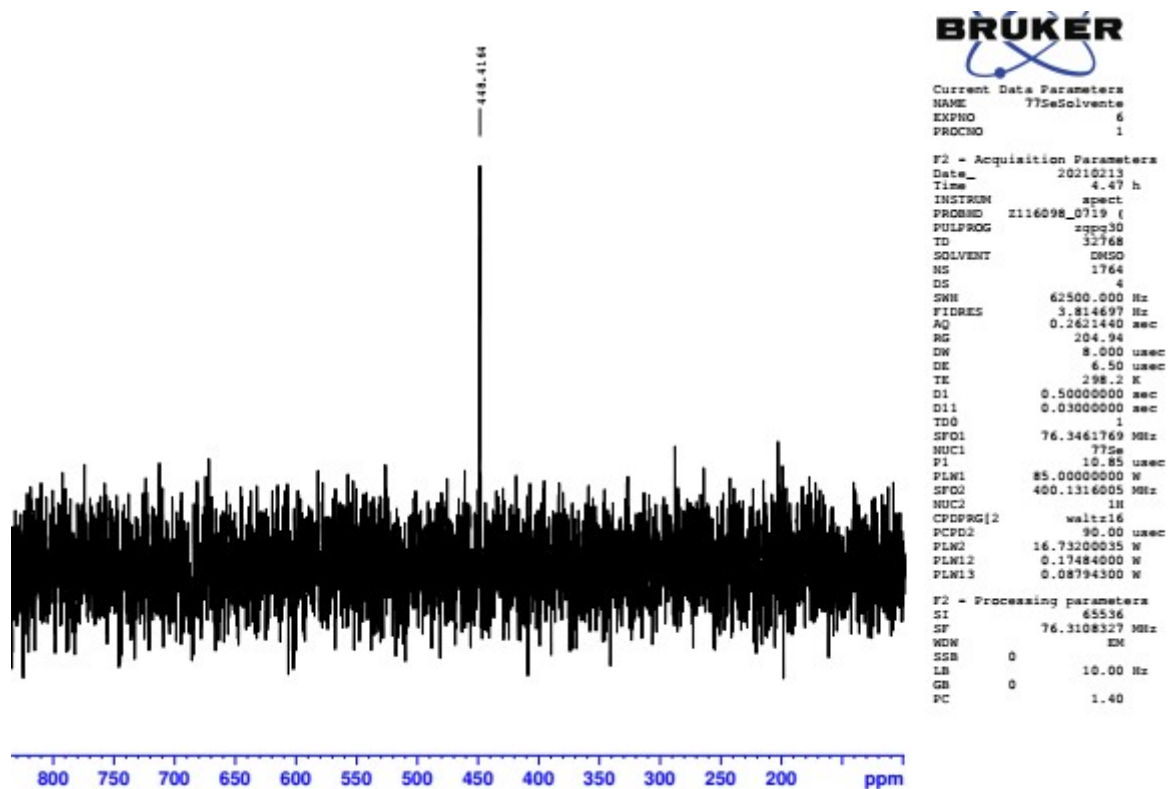


Figure S7: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum (76.3 MHz, $\text{DMSO-}d_6$) of diphenyl diselenide.

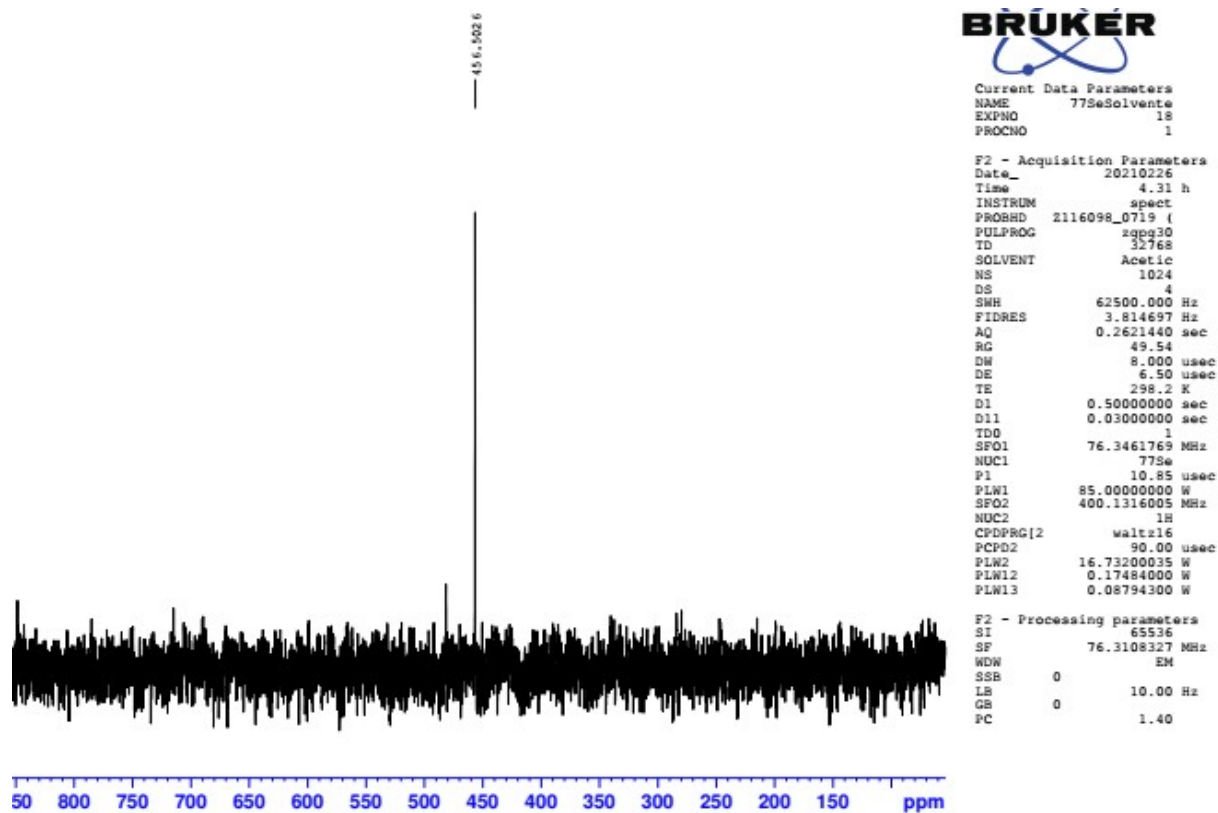


Figure S8: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum (76.3 MHz, $\text{D}_3\text{CCO}_2\text{D}$) of diphenyl diselenide.

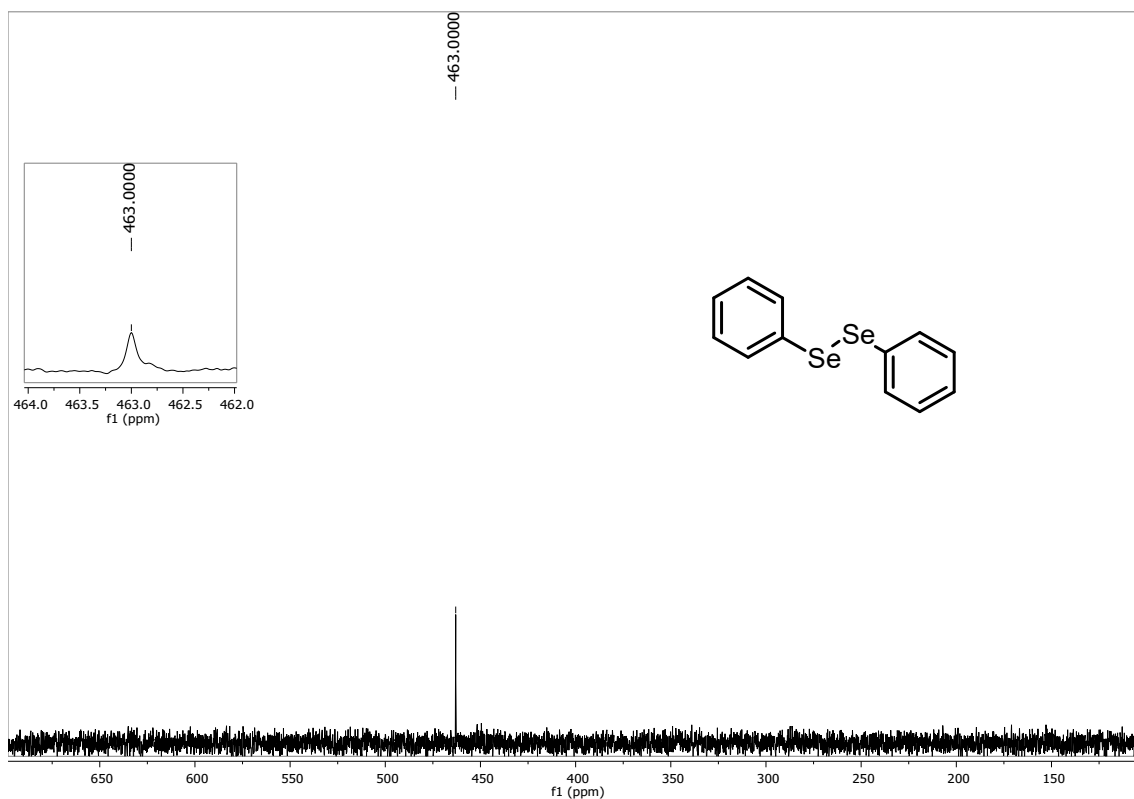


Figure S9: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum (76.3 MHz, CDCl_3) of diphenyl diselenide (10.0 mg / 700 μL) referenced by an external standard of diphenyl diselenide (5.0 mg / 700 μL).

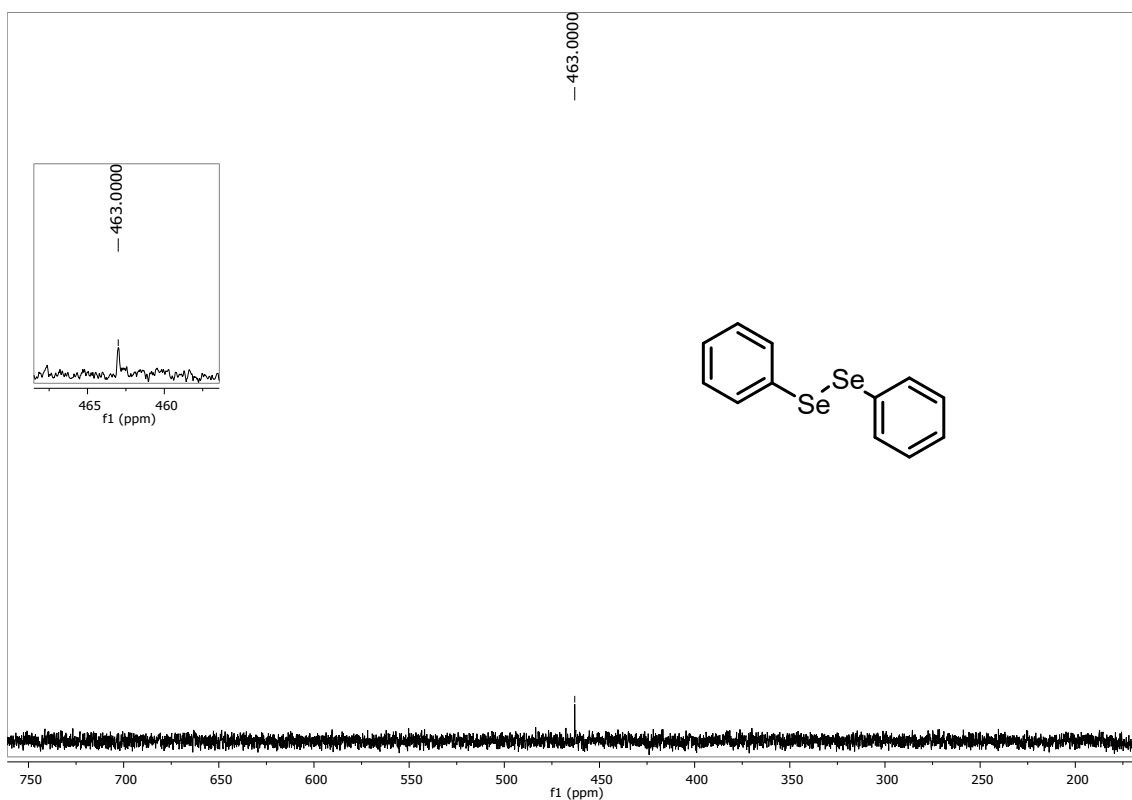


Figure S10: ^{77}Se NMR spectrum (76.3 MHz, CDCl_3) of diphenyl diselenide (10.0 mg / 700 μL) referenced by an external standard of diphenyl diselenide (5.0 mg / 700 μL).

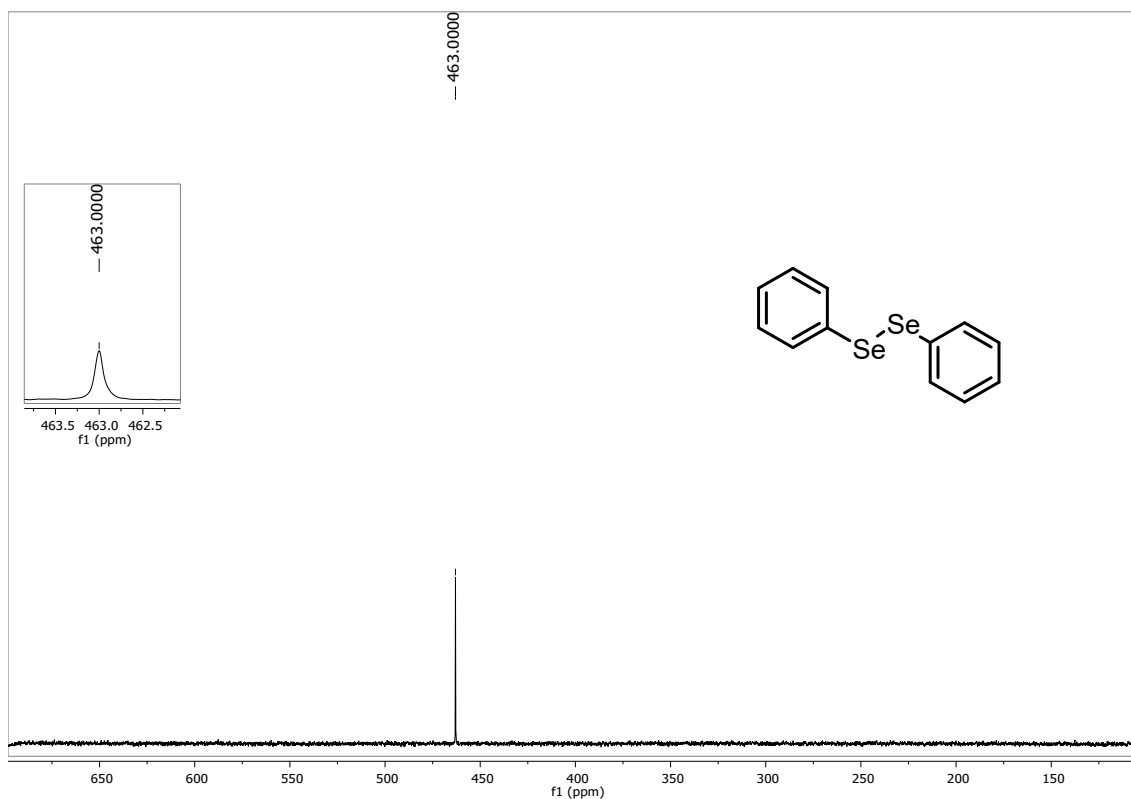


Figure S11: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum (76.3 MHz, CDCl_3) of diphenyl diselenide (50.0 mg / 700 μL) referenced by an external standard of diphenyl diselenide (5.0 mg / 700 μL).

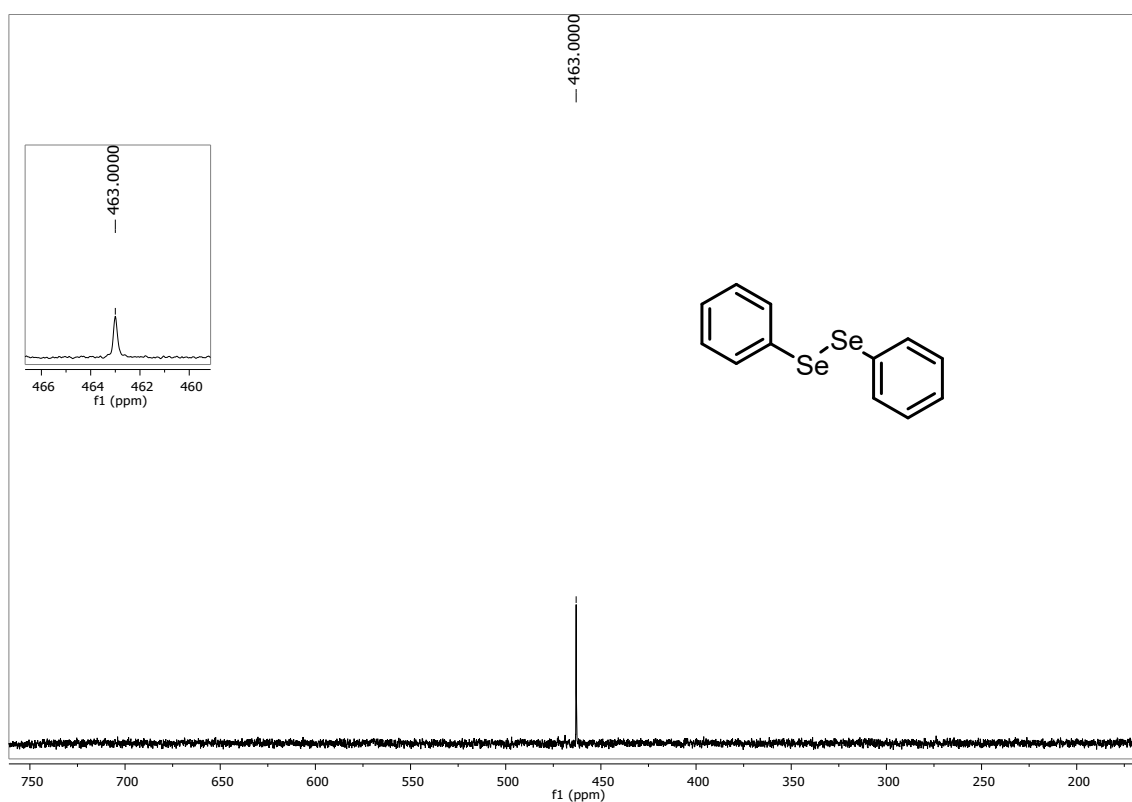


Figure S12: ^{77}Se NMR spectrum (76.3 MHz, CDCl_3) of diphenyl diselenide (50.0 mg / 700 μL) referenced by an external standard of diphenyl diselenide (5.0 mg / 700 μL).

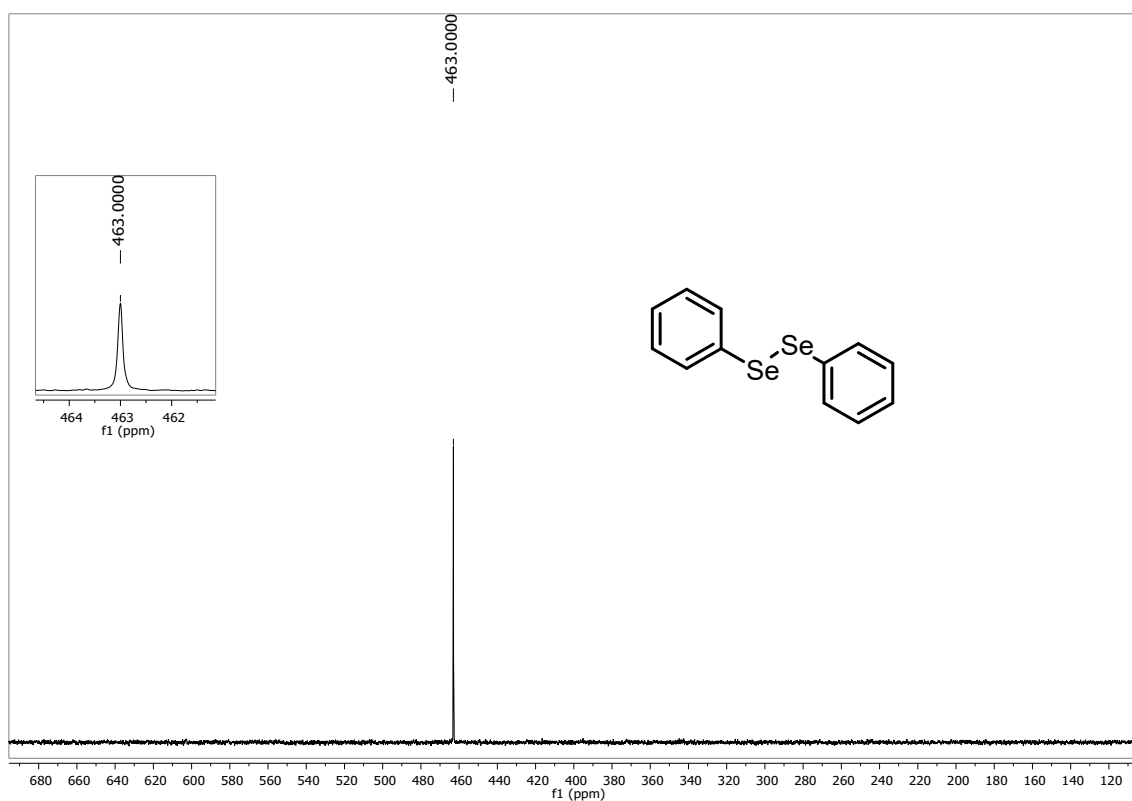


Figure S13: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum (76.3 MHz, CDCl_3) of diphenyl diselenide (100.0 mg / 700 μL) referenced by an external standard of diphenyl diselenide (5.0 mg / 700 μL).

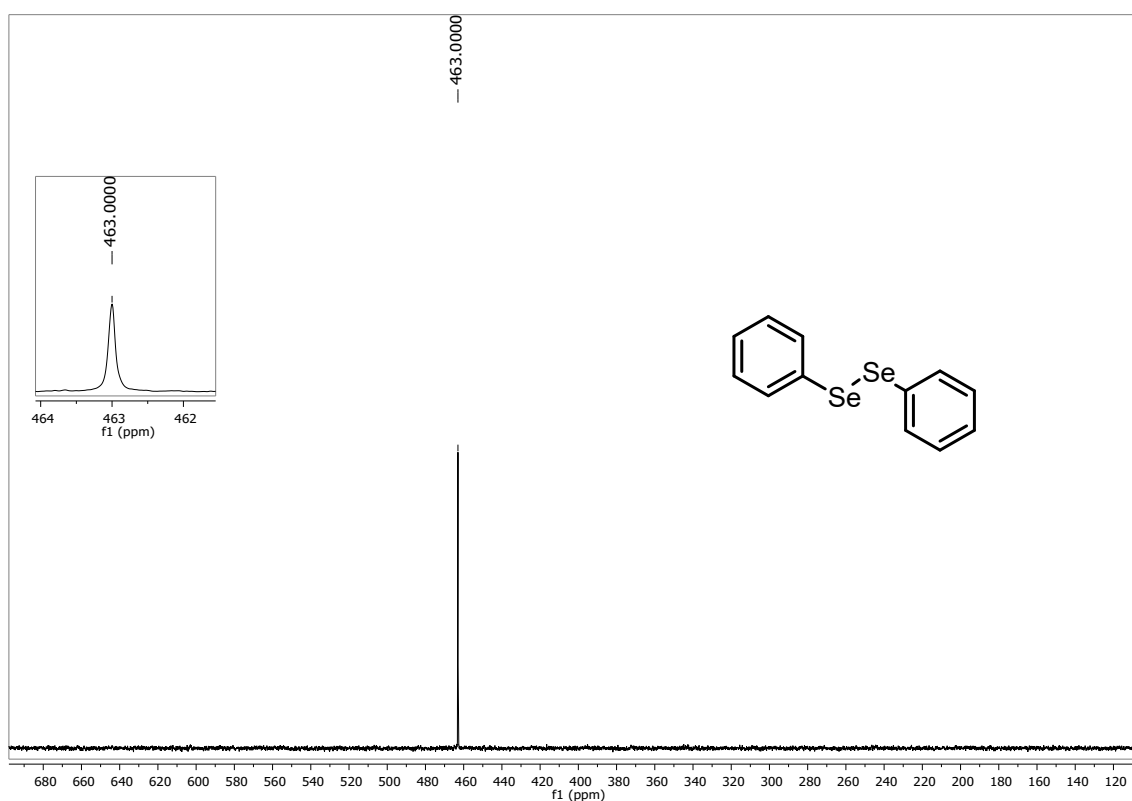


Figure S14: ^{77}Se NMR spectrum (76.3 MHz, CDCl_3) of diphenyl diselenide (100.0 mg / 700 μL) referenced by an external standard of diphenyl diselenide (5.0 mg / 700 μL).

¹H, ¹³C and ⁷⁷Se NMR Spectra of (*p*-CH₃OPhSe)₂

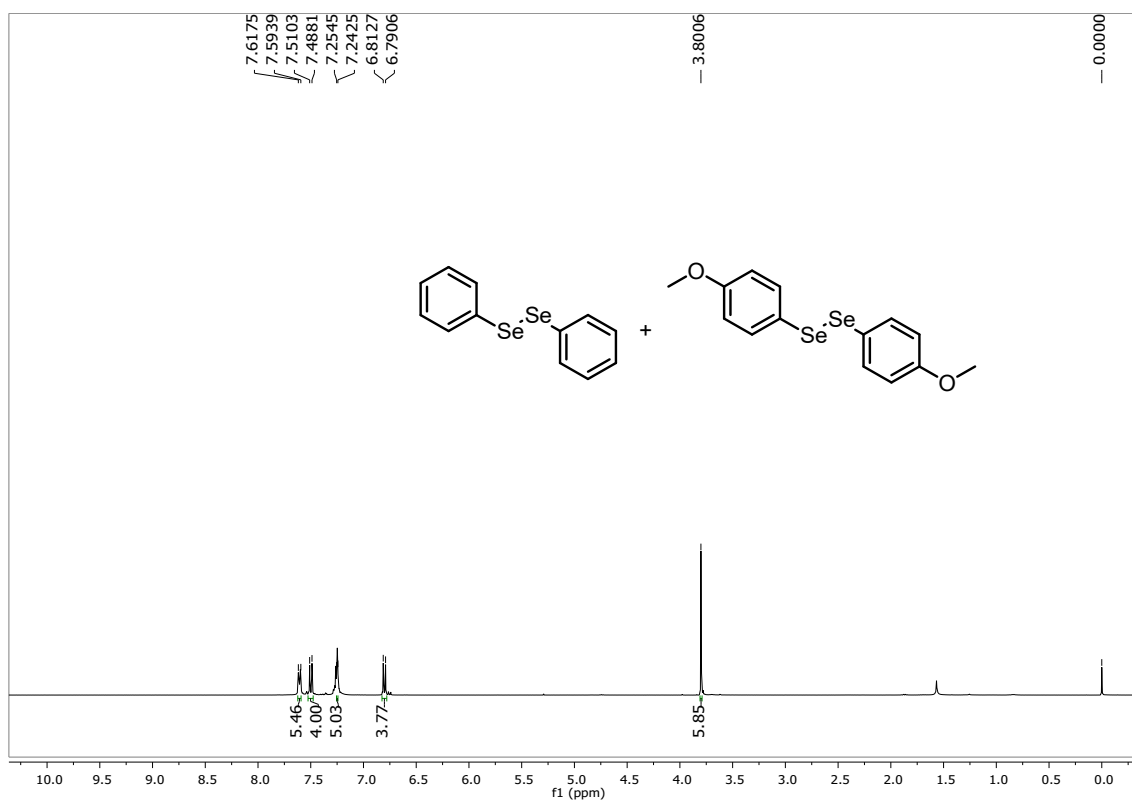
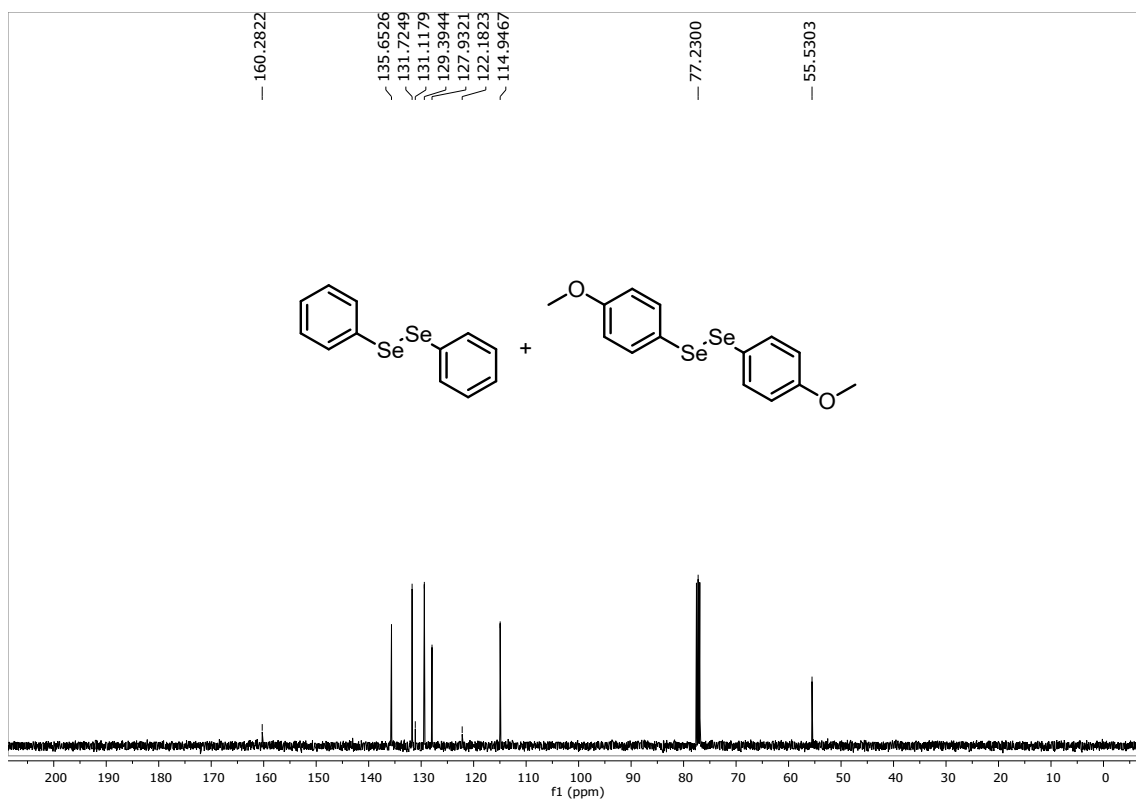


Figure S15: ¹H NMR (400 MHz, CDCl₃) spectrum of (*p*-CH₃OPhSe)₂ using a capillary of (PhSe)₂.



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e S16: ¹³C{¹H} NMR (100 MHz, CDCl₃) spectrum of (*p*-CH₃OPhSe)₂ using a capillary of (PhSe)₂.

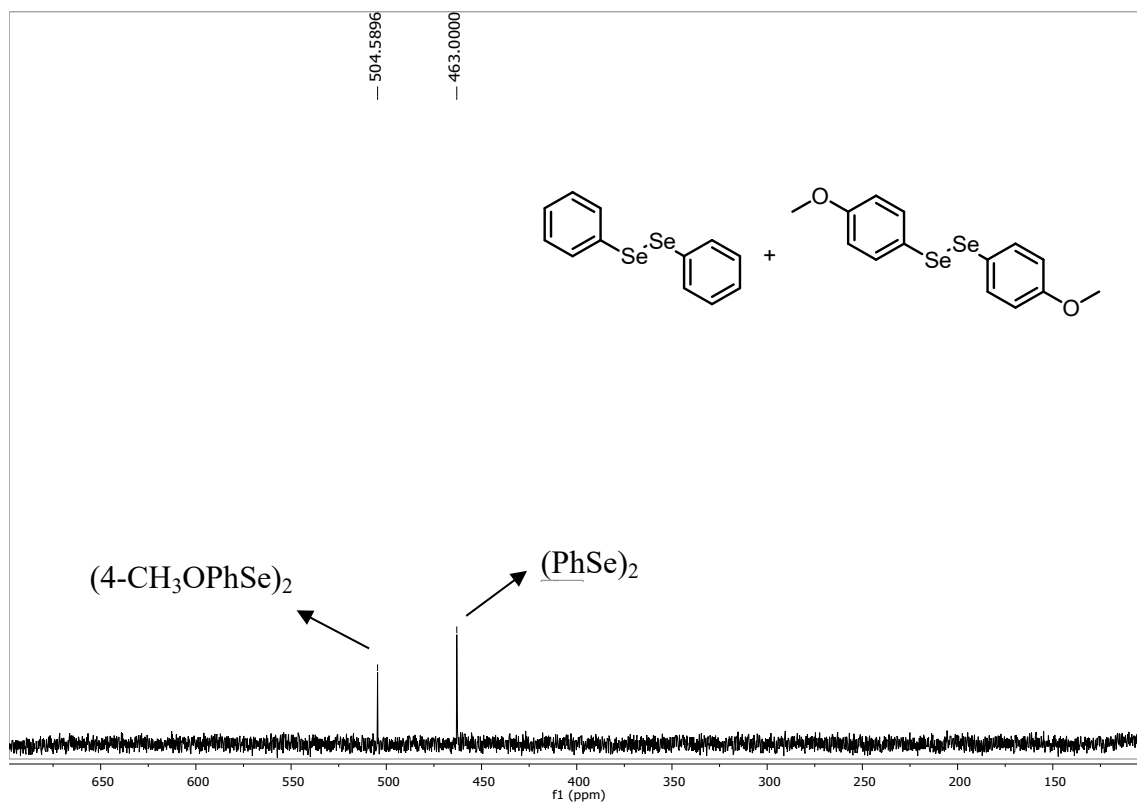


Figure S17: $^{77}\text{Se}\{^1\text{H}\}$ NMR (76 MHz, CDCl_3) spectrum of $(p\text{-CH}_3\text{OPhSe})_2$ using a capillary of $(\text{PhSe})_2$.

Cartesian Coordinates of gas phase optimized dimethylselenide and diphenyldiselenide

Me₂Se

Se	0.384500000	0.308000000	-0.140800000
C	-0.593700000	1.851600000	-0.790900000
H	-0.518300000	1.827100000	-1.881500000
H	-1.646400000	1.792300000	-0.502000000
H	-0.146000000	2.777600000	-0.420400000
C	0.093500000	0.590000000	1.755900000
H	-0.973300000	0.556200000	1.992900000
H	0.602300000	-0.229500000	2.270800000
H	0.527600000	1.540700000	2.076800000

Ph₂Se₂, open conformer

Se	3.943900000	3.878500000	13.278200000
Se	5.197400000	1.989400000	12.792600000
C	2.777400000	3.287900000	14.684900000
C	1.747100000	2.379600000	14.436100000
C	0.882600000	2.016700000	15.462200000
C	1.030100000	2.568100000	16.732900000
C	2.050600000	3.480600000	16.977700000
C	2.929700000	3.837300000	15.958700000
C	6.593700000	2.034400000	14.110600000
C	6.605600000	1.064900000	15.114400000
C	7.646800000	1.035800000	16.038200000
C	8.668200000	1.977300000	15.970300000
C	8.652900000	2.946800000	14.970200000
C	7.623800000	2.973600000	14.036200000
H	1.624000000	1.958400000	13.440900000
H	0.081700000	1.305700000	15.264900000
H	0.346900000	2.285900000	17.532100000
H	2.172400000	3.913300000	17.969500000
H	3.737500000	4.539800000	16.152500000
H	5.799300000	0.337000000	15.174000000
H	7.652700000	0.276600000	16.818800000
H	9.479100000	1.956000000	16.696300000
H	9.453500000	3.682600000	14.910300000
H	7.617900000	3.723300000	13.248200000

Ph₂Se₂, closed conformer

Se	3.146100000	1.707000000	13.463300000
Se	5.131700000	2.270300000	14.443000000
C	2.999400000	-0.201000000	13.668500000
C	1.963100000	-0.800400000	12.949200000
C	1.761900000	-2.173000000	13.044500000
C	2.590200000	-2.951900000	13.846800000
C	3.622000000	-2.346200000	14.556400000
C	3.829600000	-0.972900000	14.473600000
C	4.695400000	2.694700000	16.268700000
C	3.475700000	2.411400000	16.873200000
C	3.276800000	2.748000000	18.208500000

C	4.287400000	3.358200000	18.944500000
C	5.506200000	3.637000000	18.333600000
C	5.714200000	3.311500000	16.997900000
H	1.312600000	-0.204100000	12.310400000
H	0.952800000	-2.633900000	12.480000000
H	2.433000000	-4.026400000	13.916500000
H	4.277000000	-2.945700000	15.187000000
H	4.640100000	-0.505000000	15.027600000
H	2.680900000	1.937700000	16.301700000
H	2.318500000	2.525800000	18.675800000
H	4.125600000	3.617900000	19.988800000
H	6.304500000	4.119200000	18.895700000
H	6.669600000	3.545100000	16.529300000

Linear Correlation Between the Computed and Experimental Chemical Shift

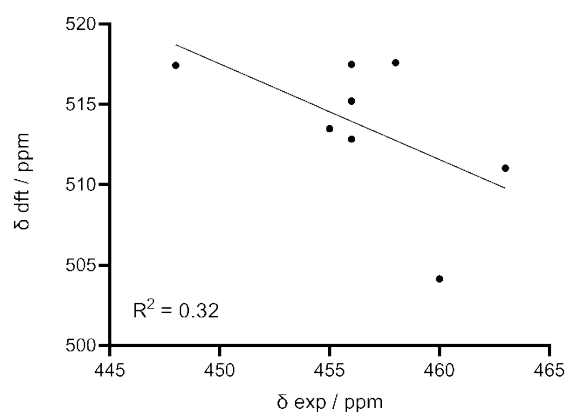


Figure S18: Linear correlation between the computed (COSMO-ZORA-OPBE/QZ4P-ae // ZORA-OPBE/TZ2P) and experimental chemical shift of diphenyl diselenide in solvents of different polarity. R^2 is reported on the plot.

Figure S19. Open (left) vs closed (right) conformation of diphenyl diselenide (level of theory: ZORA-OPBE/TZ2P).



Table S3. Shielding constants for both Se (Se1 and Se2) nuclei and both conformations (open and close) in different solvents. COSMO-ZORA-OPBE/QZ4P-ae // ZORA-OPBE/TZ2P

		Se1	Se2
benzene	open	1112.71	1112.25
	close	1312.63	1318.80
cdcl3	open	1116.96	1117.65
	close	1320.60	1314.59
cdco2d	open	1118.87	1118.16
	close	1314.90	1320.79
thf	open	1119.47	1118.70
	close	1315.34	1321.29
Py	open	1120.75	1119.92
	close	1315.87	1321.78
CD3OD	open	1122.45	1121.39
	close	1316.08	1321.95
cd3cn	open	1122.50	1121.40
	close	1316.24	1322.04
dmso	open	1122.36	1121.45
	close	1322.25	1316.41