New approach to stereochemical structure determination of bis-selenium-subsituted alkenes

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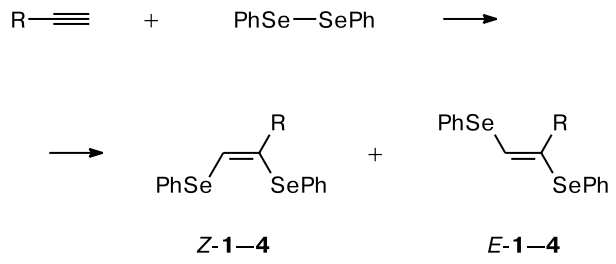
A new approach to determination of the stereochemical structure of bis-selenium-substituted alkenes using experimental ^{77}Se NMR studies and B3LYP/6-311G(d) quantum-chemical calculations is developed. Joint analysis of experimental and calculated data allows assignment of signals in the ^{77}Se NMR spectrum. The method was evaluated taking the model compounds (PhSe)HC=C(SePh)R (R = COOMe, CH_2NMe_2, CH_2OH, Ph) as examples.

Key words: stereochemistry, selenium compounds, ^{77}Se NMR spectroscopy, quantum-chemical calculations.

Element—element bond addition to acetylene hydrocarbons catalyzed by transition metal complexes is a promising method for stereoselective and regioselective synthesis of bis-element-substituted alkenes (Scheme 1).[1,2] In this case activation of the triple bond in alkyne molecules can proceed by two mechanisms, namely, insertion and nucleophilic attack.[1—4] The first type of reactions occurs as *syn*-addition and results in *Z*-products. External nucleophilic attack leads to the corresponding *E*-isomers. The *Z*-/*E*-isomer ratio can be strongly effected by the isomerization reactions and noncatalytic side processes. Therefore, determination of the stereochemical structure of reaction products is of great importance for investigations of the mechanisms of catalytic processes.

Scheme 1



Z-**1—4** *E*-**1—4**

R = COOMe (**1**), CH_2NMe_2 (**2**), CH_2OH (**3**), Ph (**4**)

Fast procedures for determining the substitution type of the double bond most often involve[5] the use of NMR spectroscopy. As a rule, the stereochemical structure of reaction products is analyzed using the results of experiments based on the measurements of the nuclear Overhauser effect (NOE).[6,7]

Since the intensity of the NOE is usually at most 5% of the total signal intensity, low sensitivity of the NOESY (Nuclear Overhauser Effect Spectroscopy) experiments sometimes strongly complicates analysis of the stereochemical structure.

Recently, considerable progress has been achieved of quantum-chemical computational methods for calculations of NMR parameters. In particular, the GIAO (Gauge-Independent Atomic Orbital) approximation[8,9] provides a good accuracy of DFT calculations with the B3LYP hybrid potential.[10] This aproach was evaluated[11—14] taking calculations of the chemical shifts of heteronuclei in complex molecules as an example.

In this work we propose a new method for determination of the stereochemical structure of bis-element-substituted alkenes based on joint NMR experiments and quantum-chemical calculations. Bis(phenylseleno)alkenes **1—4** (see Scheme 1) synthesized earlier[15,16] were chosen as model compounds.

Results and Discussion

Experimental determination of stereochemical structure of model compounds. *Determination of stereochemical structure of the Z-1 and E-1 isomers in the reaction mixture.* Unfortunately, the NOESY NMR spectra of these compounds recorded over a wide range of mixing times (0.2—2.0 s) exhibited no NOE between the vinyl and methyl protons. Attempts to detect the corresponding cross

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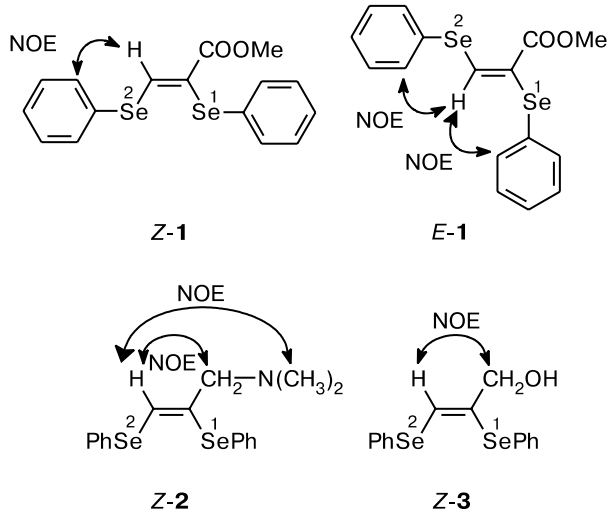
peak in the 2D ROESY (Rotating Frame Overhauser Effect Spectroscopy) NMR spectra also failed.

Determination of the stereochemical structure and assignment of signals can be made based on the analysis of the 2D NOESY NMR spectrum in the region of aromatic and vinyl proton signals (Scheme 2). The vinyl proton of the *Z*-isomer (δ 9.00) is characterized by one cross peak with *ortho*-protons of the Ph group (δ 7.26). The spectrum of the *E*-isomer esxhibits cross peaks of the vinyl proton (δ 7.96) with *ortho*-protons of both Ph groups (δ 7.38 and 7.24).

Scheme 2



The $^{1}H—^{77}Se$ spin—spin coupling constants (J) provide an alternative source of information on the molecular structure of the systems under study. For the vinyl system one can expect the following order of changes in the J values: $^{3}J_{trans} > {}^{3}J_{cis} > {}^{2}J_{gem}$. The largest splitting (J_{H-Se} = 9.7 Hz) is observed for the signal at δ 9.00 assigned to the vinyl proton of the *Z* isomer (Fig. 1, *a*). Most likely, this corresponds to the largest spin—spin coupling constant, $^{3}J_{trans}$, and confirms the stereochemical structure determined by analysing the NOESY spectrum.

Determination of the stereochemical structure of Z-2. Since the signal of the vinyl proton of the *Z*-**2** molecule (δ 7.28) appears in the region of aromatic protons, it was assigned using the 2D LR-COSY (Long Range Correlation Spectroscopy). Observing the NOE between the vinyl proton and the protons of methylene and methyl groups in the 2D NOESY spectrum indicates the *Z*-configuration of the isomer (see Scheme 2).

An independent confirmation of the structure of the *Z*-**2** isomer was obtained in the X-ray diffraction study of the crystalline salt $HC(SePh)=C(SePh)—CH_2N^+HMe_2 \cdot HOOC—COO^-$ (*Z*-**2** · HOOC—COOH).[15]

Determination of the stereochemical structure of Z-3. This compound is characterized by separate signals of the vinyl (δ 7.41) and methylene (δ 4.17) protons. The *Z*-geometry of the double bond was established based on the results of analysis of the NOESY spectrum (see Scheme 2).

Attempts to determine the stereochemical structure of the *Z*-**4** and *E*-**4** isomers of addition products of diphenyldiselenide to phenylacetylene failed because of strong overlap of the signals.

Alternative strategy of the stereochemical structure determination using the 2D HMQC NMR technique and quantum-chemical calculations. The classical method for solving the problem is to use NMR spectroscopy (see above). However, it is time-consuming and in some cases gives ambiguous results. A drawback of the classical procedure is a low sensitivity of the NOESY technique and severe difficulties in the interpretation of the NMR spectra in the case of strong overlap of signals.

An improved method for determination of the stereochemical structure proposed in this work is based on the inverse $^{1}H—^{77}Se$ HMQC (Heteronuclear Multiple Quantum Coherence) NMR technique. The use of pulsed field gradients for choosing the pathways of magnetization transfer provides rather high sensitivity. In particular, the 2D $^{1}H—^{77}Se$ HMQC NMR spectrum of a mixture of the *Z*-**1** and *E*-**1** isomers (total weight 10 mg) can be acquired during 3—5 min (see Fig. 1, *a*). Much stronger (compared to protons) dependence of the chemical shifts of heteronuclei on the molecular structure allows elimination of the signal overlap problem in the 2D spectrum. Even in the most difficult case (mixture of the *Z*-**4** and *E*-**4** isomers) the spectrum recorded exhibits no overlap of the signals due to a larger chemical shift difference for the heteronucleus (see Fig. 1, *b*).

Therefore, the use of the $^{1}H—^{77}Se$ HMQC NMR spectrum allows reliable determination of the presence of two isomers in the mixture and measurements of the chemical shifts. However, we still cannot determine the stereochemical structure and make unambiguous assignment of the spectral lines. Solving this problem requires quantum-chemical calculations.

The molecular geometry of the *Z*-**1** and *E*-**1** isomers was optimized by density functional calculations with the B3LYP hybrid potential and the Lanl2dz basis set. The ^{77}Se NMR chemical shifts were calculated using the GIAO approach at the B3LYP/6-311G(d) level.

Good correlation between the experimental and calculated ^{77}Se NMR chemical shifts and a nearly unity slope of the straight line obtained (Fig. 2) is achieved only in the case of correct determination of the stereochemical structure and assignment of signals in the ^{77}Se NMR spectrum. If the signal assignment for at least one isomer is incorrect, the correlation coefficient is at most 0.5. Comparison of the calculated chemical shifts with the values obtained in the $^{1}H—^{77}Se$ HMQC experiments (see

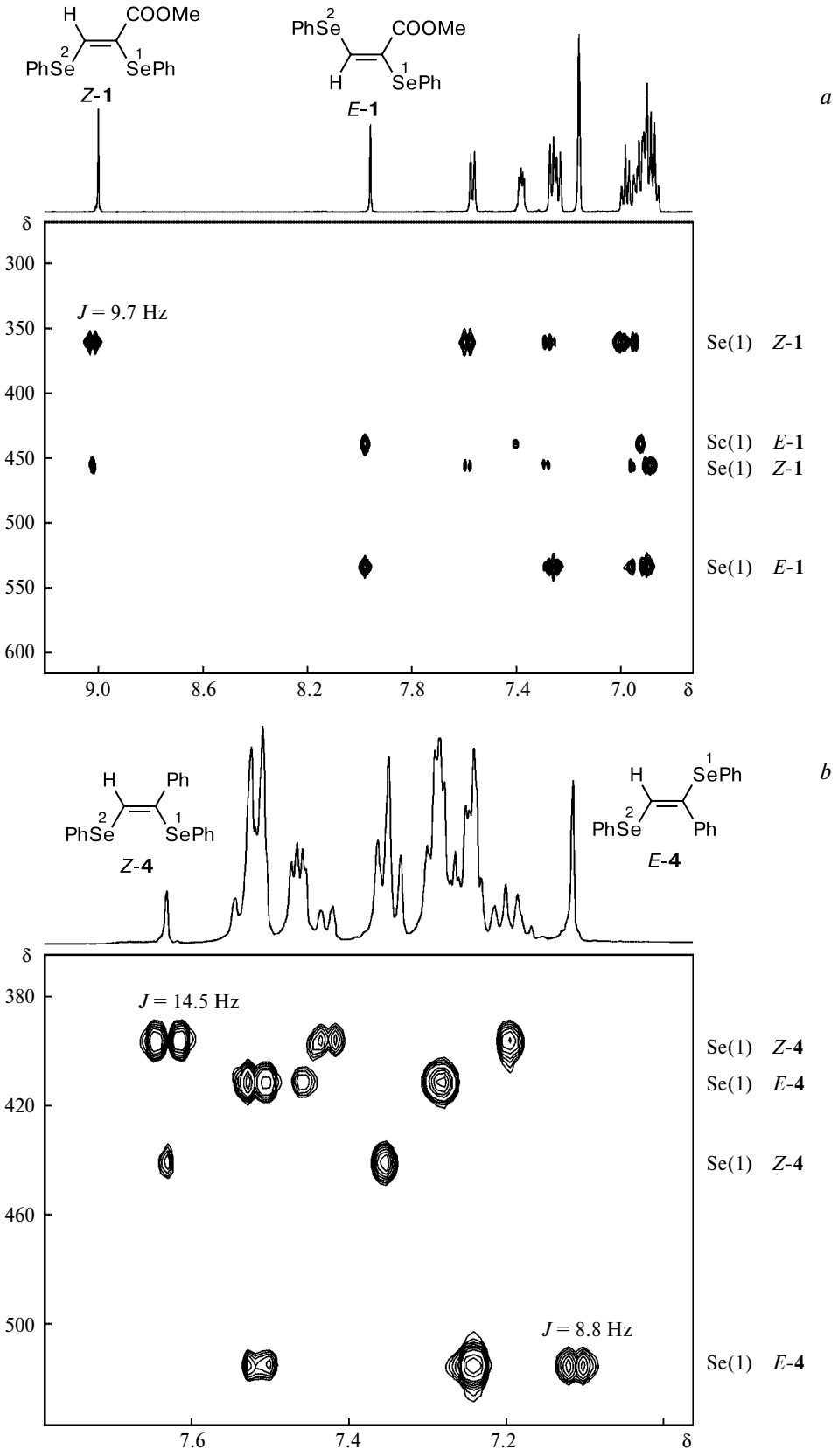


Fig. 1. Experimental $^{1}H—^{77}Se$ HMQC NMR spectra of a mixture of *Z*-**1**/*E*-**1** (*a*) and *Z*-**4**/*E*-**4** (*b*) isomers. Shown are the signals of vinyl protons of the corresponding isomers in the ^{1}H NMR spectra.

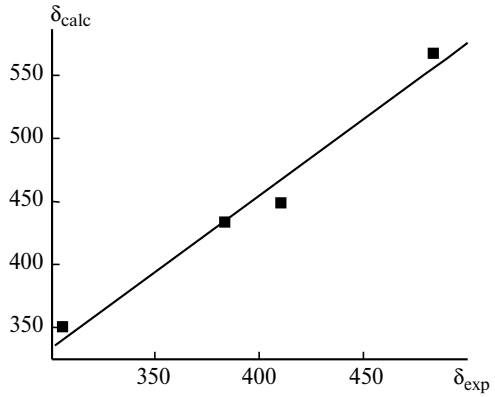


Fig. 2. Correlation between experimental and calculated (B3LYP/6-311G(d)) ^{77}Se NMR chemical shifts of the *Z*-**1** and *E*-**1** isomers. The parameters of linear regression $Y = A + BX$ are as follows: $A = -87\pm62$, $B = 1.2\pm0.1$; correlation coefficient, R, is 0.987 ($n = 4$).

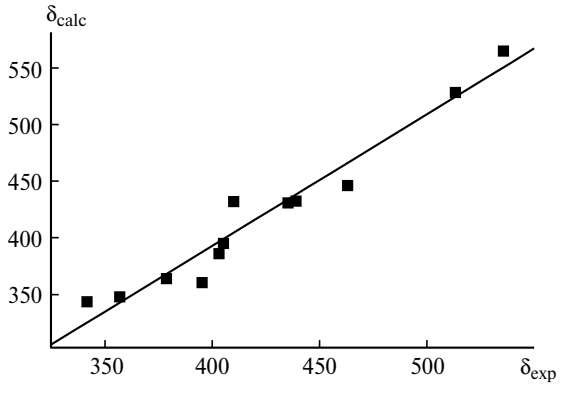


Fig. 3. Correlation between experimental and calculated ^{77}Se NMR chemical shifts of bis(phenylseleno)alkenes **1—4**. The parameters of linear regression $Y = A + BX$ are as follows: $A = -73\pm36$, $B = 1.2\pm0.1$, and $R = 0.975$ ($n = 12$).

Fig. 1, *a*) shows that the signal of the vinyl proton at δ 9.00 corresponds to the *Z*-**1** isomer while the signal at δ 7.96 corresponds to the *E*-**1** isomer. This is in excellent agreement with the above-mentioned independent assignment.

By analyzing a mixture of the *Z*-**4** and *E*-**4** isomers in a similar way we established that the signal of the vinyl proton at δ 7.63 corresponds to the *Z*-**4** isomer while the signal at δ 7.12 corresponds to the *E*-**4** isomer (see Fig. 1, *b*). The *Z*-**4** : *E*-**4** ratio is 1 : 4. It should be emphasized that determination of the stereochemical structure of addition products of aryl derivatives to phenylacetylene is a challenge to the classical experimental procedure. Joint analysis of the experimental and calculated data essentially simplifies the solution of this problem.

Thus, a comparison of the experimental and calculated ^{77}Se NMR chemical shifts permits not only unambiguous determination of the stereochemical structure but also assignment of lines in the ^{77}Se NMR spectrum. As should be expected, in the experimental ^{1}H—^{77}Se HMQC NMR spectra of the *Z*-**1**/*E*-**1** and *Z*-**4**/*E*-**4** mixtures the largest separation between the components of the cross peak of vinyl protons is observed for the *Z*-**1**—Se(1) and *Z*-**4**—Se(1) interactions, thus corresponding to the spin—spin coupling constants ^{1}H—^{77}Se $^{3}J_{trans} = 14.5$ Hz and $^{3}J_{cis} = 8.8$ Hz (see Fig. 1, *b*). This can serve as a independent confirmation of correct assignment of the lines in the ^{77}Se NMR spectrum.

Analysis of the parameters of the correlation between the experimental and calculated ^{77}Se NMR chemical shifts of compounds **1—4** (Fig. 3) suggests a universal character of the approach proposed.

Choice of optimum procedure for quantum-chemical calculations. The accuracy of prediction of the experimental NMR chemical shifts achieved in quantum-chemical calculations depends on the choice of reference compounds. The greater the structural similarity of the reference compound to the compound under study, the better accuracy can be expected due to the mutual cancellation of errors. The data listed in Table 1 show that the results obtained using Me_2Se as a reference compound are the least accurate (mean deviation is 29.7 ppm). Much better accuracy can be achieved by taking Ph_2Se and Ph—Se—CH=CH_2 as reference compounds (mean deviations from the experimental values are 13.1 and 14.7 ppm, respectively). The Ph—Se—CH=CH_2 compound is most structurally similar to the vinylselenides studied and provides a good accuracy when normalizing the ^{77}Se NMR chemical shifts at optimum computational cost.

Since the approach proposed involves determination of the stereochemical structure based on the results of correlation analysis (see Fig. 3), the efficiency of the method employed is independent of the choice of reference compounds. When varying the reference compound, the errors of the chemical shift calculations affect the *Y*-intercept value only. In particular, for all the reference compounds employed (see Table 1) we obtained the same signal assignment. It is possible to directly use the calculated chemical shifts without normalizing them to the standard NMR scale (see below). This is a considerable advantage of the approach proposed.

It is desired to perform geometry optiization using a basis set with a pseudopotential both to reduce the com-

Table 1. ^{77}Se NMR chemical shifts (δ_{calc}) calculated by the B3LYP/6-311G(d) method using different reference compounds

Compound	Atom	δ_{calc}			δ_{exp}
		Me_2Se	Ph_2Se	PhSeCH=CH_2	
Z-**1**	Se(1)	318.2	351.1	348.0	356.7
	Se(2)	416.6	449.4	446.4	462.9
E-**1**	Se(1)	401.3	434.2	431.1	435.1
	Se(2)	535.2	568.0	565.0	535.5

Table 2. Calculated (δ_{calc}) and experimental (δ_{exp}) ^{77}Se chemical shifts of compounds **2—4**

Compound	Atom	δ_{calc}*	δ_{exp}
Z-**2**	Se(1)	364.1	378.4
	Se(2)	386.2	403.0
E-**2**	Se(1)	469.8	—
	Se(2)	397.6	—
Z-**3**	Se(1)	395.2	405.1
	Se(2)	343.7	341.5
E-**3**	Se(1)	408.5	—
	Se(2)	454.7	—
Z-**4**	Se(1)	360.8	395.1
	Se(2)	432.5	438.8
E-**4**	Se(1)	528.7	513.1
	Se(2)	432.2	409.9

* Obtained from B3LYP/6-311G(d) calculations with $PhSeCH{=}CH_2$ as a reference.

putational cost and to improve the accuracy of determination of geometric parameters. However, such a basis set is unsuitable for the NMR chemical shift calculations. It is the core electrons that contribute mostly to the nucleear shielding, so description of the system using the core pseudopotential makes the obtaining of correct results impossible. When using the B3LYP/Lanl2dz calculations within the GIAO approximation, the differences in the ^{77}Se NMR chemical shifts of compounds **1—4** are at most 10 ppm (*cf.* the experimentally observed differences of the order of 200 ppm, see Tables 1 and 2). Single-point GIAO calculations using the extended full-electron basis sets significantly improve the accuracy of calculations. As can be seen in Table 3, the use of the 6-31G(d) basis set provides a rather low accuracy (mean deviation is 38.1 ppm). An acceptable solution is to perform B3LYP/6-311G(d) calculations, which allow one to achieve a mean deviation of 14.7 ppm between the calculated and experimental NMR chemical shifts (see Table 1). Further extension of the basis set does not essentially improve the accuracy of calculations while adding diffuse and polarization p-functions causes small changes in the chemical shifts (see Table 3).

Table 3. ^{77}Se NMR chemical shifts (δ_{calc}) obtained from B3LYP calculations with different basis sets (the results obtained by the B3LYP/6-311G(d) method are listed in Table 1)*

Compound	Atom	6-31G(d)	6-311+ G(d)	6-311+ G(dp)	6-311++ G(dp)
Z-**1**	Se(1)	302.7	346.6	343.8	342.6
	Se(2)	455.2	435.7	433.2	430.8
E-**1**	Se(1)	372.3	431.0	428.6	428.1
	Se(2)	563.3	560.1	557.3	556.3

* With $PhSeCH{=}CH_2$ as a reference.

The experimental and calculated NMR chemical shifts listed in Tables 1 and 2 are in good agreement (see Fig. 3); the error of calculations is at most 10%. Much better accuracy can be achieved in the calculations of the differences, $\Delta\delta = \delta_{Se(1)} - \delta_{Se(2)}$, which serves as the basis for good applicability of the method employed.

The approach proposed to determine the stereochemical structure and to assign the chemical shifts in the heteronuclear NMR spectra can be useful in studies of not only selenium derivatives but also a number of other bis-element-substituted alkenes. Detailed investigation of the scope of this technique is currently in progress.

Experimental

NMR experiments. The chemical shifts of the compounds under study (δ_{exp}) were calculated using the formula

$$\delta_{exp} = \delta_{comp} - \delta_{ref} + \delta^0_{ref}, \quad (1)$$

where δ_{comp} is the experimental chemical shift of the compound under study, δ_{ref} is the experimental chemical shift of the reference compound, and δ^0_{ref} is the chemical shift assigned to the reference compound.

NMR spectra were recorded on a Bruker DRX-500 spectrometer operating at 500.1 (^{1}H), 125.8 (^{13}C), and 95.4 (^{77}Se) MHz with $CDCl_3$ as solvent. All measurements were carried out at ~20 °C. Homonuclear NMR experiments were performed using the NOESY [17,18] and LR-COSY [19] techniques.

^{1}H—^{77}Se HMQC experiment.[20,21] The spectrum was recorded at the durations of the 90° pulses of 12.5 μs (^{1}H) and 16.0 μs (^{77}Se); the relaxation delay was 2 s; the evolution time, $\Delta = (2J_{H-Se})^{-1}$, was 100 ms (optimized for J_{H-Se} = 5 Hz). The acquisition time of the free induction decay signal was 0.35 s, the width of the spectral window was 3000 and 25000 Hz for ^{1}H(F2) and ^{77}Se(F1), respectively. Eight transients for each out of 256 t_1 increments were recorded. The pathway of magnetization transfer was chosen using pulsed field gradients in the 50.0 : 30.0 : 35.3 ratio (pulse duration was 1 ms and the recovery delay was 100 μs). The 2D matrix was filled with zeroes until a size of 2048×2048 and processed using the linear prediction algorithm before Fourier transformation.

Compounds **1—4** were synthesized by Pd complex-catalyzed addition of diphenyldiselenide to alkynes according to a known procedure.[15] Attempts to separate the ***Z/E*-α,β-bis(phenylseleno)styrene (*Z/E*-4)** by chromatography failed and ^{1}H—^{77}Se NMR HMQC experiment was carried out using the reaction mixture.

Methyl-(*Z*)-2,3-bis(phenylseleno) acrylate (*Z*-1). ^{1}H NMR, δ: 8.92 (s, 1 H, HC=); 7.62, 7.51 (both m, 2 H, Ph); 7.38, 7.29 (both m, 3 H, Ph); 3.71 (s, 3 H, OMe). ^{13}C{^{1}H} NMR, δ: 164.0, 158.7, 133.6, 131.5, 129.9, 129.8, 129.6, 129.2, 128.6, 127.2, 120.2, 52.7.

Methyl-(*E*)-2,3-bis(phenylseleno) acrylate (*E*-1). ^{1}H NMR, δ: 7.92 (s, 1 H, HC=); 7.49 (m, 4 H, Ph); 7.32 (m, 6 H, Ph); 3.83 (s, 3 H, OMe). ^{13}C{^{1}H} NMR (126 MHz), δ: 166.5, 151.8, 132.9, 132.8, 132.7, 130.2, 129.4, 129.3, 128.2, 127.7, 114.4, 52.8.

(*Z*)-*N*,*N*-Dimethyl-2,3-bis(phenylseleno)allylamine (*Z*-2). ^{1}H NMR, δ: 7.59 (m, 4 H, Ph); 7.31 (m, 6 H, Ph); 7.28 (s, 1 H,

HC=); 3.04 (s, 2 H, $-CH_2-$); 2.22 (s, 6 H, Me). $^{13}C\{^1H\}$ NMR, δ: 133.0, 132.9, 132.8, 131.2, 130.9, 129.4, 129.3, 129.1, 127.5, 127.2, 67.3, and 45.0.

(*Z*)-2,3-Bis(phenylseleno)allyl alcohol (*Z*-3). ^1H NMR, δ: 7.60, 7.56 (both m, 2 H, Ph); 7.41 (s, 1 H, HC=); 7.31 (m, 6 H, Ph); 4.17 (s, 2 H, $-CH_2-$). $^{13}C\{^1H\}$ NMR (δ): 133.5, 133.2, 132.4, 132.1, 130.3, 129.4, 129.3, 128.6, 127.8, 127.5, 67.5.

Procedure for qantum-chemical calculations. Geometry optimization and calculations of the NMR chemical shifts were carried out by the density functional method using the B3LYP hybrid potential.[22—24] The molecular geometry of the compounds under study was optimized by the B3LYP/Lanl2dz method. The stationary points located were checked for the absence of imaginary eigenvalues in the matrix of the second derivatives of energy. The NMR chemical shifts were calculated in the GIAO approximation[8] using the standard DZ and TZ basis sets.[25,26] All calculations were carried out using the GAUSSIAN-98 program.[27]

To determine the chemical shifts, quantum-chemical calculations of the reference compound and of the compound under study were performed using the same method. Stable compounds with known chemical shifts were chosen as reference compounds. These were Me_2Se (δ^0_{ref} = 0.0),[28] Ph_2Se (δ^0_{ref} = 416.5),[28] and $PhSeCH{=}CH_2$ (δ^0_{ref} = 395.5).[14] The calculated chemical shift of a compound (δ_{calc}) was determined by the formula

$$\delta_{calc} = \delta^*_{ref} - \delta^*_{comp} + \delta^0_{ref}, \qquad (2)$$

where δ^*_{ref} is the calculated chemical shift of the reference compound and δ^*_{comp} is the calculated chemical shift of the compound under study. The difference in signs in Eq. (2) compared to Eq. (1) accounts a convention about the low-field shift of NMR signals with an increase in the resonance frequency (for NMR chemical shift scales, see Ref. 29; for relative signs of the resonance frequencies, see Ref. 30).

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