

Supporting Information

Synthesis of Alkynyl and Vinyl Selenides via Selenodecarboxylation of Arylpropionic and Cinnamic Acids

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1. General methods:

^1H and ^{13}C (200 MHz) NMR spectra were recorded on a BRUKER-AC 200 MHz and ^1H (400 MHz) NMR spectra (for compounds **1b** & **2b**) were recorded on a VARIAN VXR 400 spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuteriochloroform: δ 7.27 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constant (Hz). ESI-MS spectra were taken using Waters LCT mass spectrometer. Elemental analyses were carried out using a CHNS/O Analyzer Perkin Elmer 2400 Series II instrument. Melting points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected. UV-vis measurement was carried out using Jasco V530 spectrophotometer.

All the reactions were performed under an inert atmosphere of argon. All the starting materials were >98% pure vide NMR. Pre-coated silica gel 60F₂₅₄ (Merck) was used for thin layer chromatography and silica gel 100-200 mesh (SRL) was used for column chromatography. Attempted photochemical reactions were done in a quartz photoreactor employing medium pressure 100W UV lamp. Dichloromethane and acetonitrile were refluxed over phosphorous pentoxide and distilled. Diphenyl diselenide and bis-4-tolyl diselenide were prepared by standard Grignard route and recrystallized to obtain analytical grade purity. Iodosobenzene diacetate (IBDA) was prepared by literature procedure (Kazmierczak, P.; Skulski, L. *Synthesis*, **1998**, 1721) and recrystallized from AcOH/Ac₂O/EtOAc. Iodosylbenzene (IB) was prepared by literature procedure (*Vogel's Textbook of Practical Organic Chemistry*; ELBS-Addison Wesley Longman Ltd.: England, 1997; pp. 869). Substituted α,β -unsaturated carboxylic acids were prepared from the corresponding aldehydes by malonic acid condensation reaction using standard protocol. Substituted aromatic propiolic acids were synthesized from the corresponding aldehydes via Corey's method (Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 36, 3769) and is described below. The purity of the acids was >98% (based on NMR).

2. General procedure for the preparation of arylpropiolic acids:

Triphenylphosphine (20 mmol) was added to a well-stirred solution of carbon tetrabromide (10 mmol) in dry dichloromethane (50 mL). Upon addition of aldehyde (5 mmol), the orange colored solution slowly faded away. The reaction mixture was stirred at ambient temperature for 4-6 hours till completion (TLC monitoring). After removal of solvent, the residue was repeatedly triturated with hexane (10 x 25 mL) and hexane solution was concentrated. This cycle was continued three times. Finally the mixture was subjected to column chromatography (silica gel 60-120 mesh, eluent hexane) to afford the 1,1-dibromoolefin.

A solution of 1,1-dibromoolefin (6 mmol) in 10 mL of dry THF at $-78\text{ }^\circ\text{C}$ was treated with a solution of n-BuLi in hexane (1.6 M, 7.5 mL, 12 mmol) under argon atmosphere. After stirring for 1h

at -78°C , the reaction mixture was warmed to 25°C during 1 h, and again cooled to -60°C . Solid carbon dioxide (5 g) was added to the above solution at -60°C and the mixture was allowed to warm gradually to room temperature. The mixture was poured into water, and ethyl acetate was added. The aqueous layer was separated and washed further with ethyl acetate. The aqueous part was acidified with 6(N) HCl and extracted with ethyl acetate (3 x 50 mL). The organic layer was washed with brine and dried over anhydrous magnesium sulfate. Evaporation of solvent afforded pure arylpropionic acid in 70-75% yield.

3. General procedure for the synthesis of alkynyl selenides using IBDA/ArSeSeAr:

To a solution of arylpropionic acid (1 mmol) in acetonitrile (3 mL), IBDA (161 mg, 0.5 mmol) and diaryl diselenide (0.3 mmol) was added. The reaction mixture was stirred at room temperature till completion (TLC monitoring for ArSeSeAr, precoated silica gel 60 F₂₅₄ TLC sheets, eluent: n-hexane-EtOAc 9:1). After completion of the reaction solvent was removed under reduced pressure, and the mixture was subjected to column chromatography over silica gel (100-200 mesh, eluent hexane) to afford the corresponding acetylenic selenides. The isolated yields are reported with respect to diaryl diselenide. The products showed satisfactory spectral and analytical data and were compared to authentic samples wherever possible.

4. General procedure for the synthesis of vinyl selenides using IBDA/ArSeSeAr:

To a solution of α,β -unsaturated aromatic carboxylic acid (1 mmol) in acetonitrile (3 mL), IBDA (161 mg, 0.5 mmol) was added and the solution was stirred for 10 min at 60°C temperature. Following the addition of diaryl diselenide (0.4 mmol) the reaction mixture was stirred at 60°C till completion (TLC monitoring for ArSeSeAr, precoated silica gel 60 F₂₅₄ TLC sheets, eluent: n-hexane-EtOAc 9:1). After removing solvent under reduced pressure the mixture was subjected to column chromatography over silica gel (100-200 mesh, eluent 1% ethyl acetate in hexane) to afford the corresponding vinyl selenides. The isolated yields are reported with respect to diaryl diselenide. The products showed satisfactory spectral and analytical data and were compared to authentic samples wherever possible.

5. Iodosylbenzene (IB) promoted selenodecarboxylation of phenylpropionic acid 1:

To a solution of phenylpropionic acid **1** (1 mmol, 146 mg) in acetonitrile (3 mL), IB (0.5 mmol, 110 mg) and diphenyl diselenide (0.3 mmol, 94 mg) was added. The reaction mixture was stirred at room temperature till completion (TLC monitoring for ArSeSeAr, precoated silica gel 60 F₂₅₄ TLC sheets, eluent: n-hexane-EtOAc 9:1). After completion of the reaction solvent was removed under reduced pressure, and the mixture was subjected to column chromatography over silica gel (100-200 mesh, eluent hexane) to afford **1a** (88% w.r.t. diphenyl diselenide).

6. Iodosylbenzene (IB) promoted selenodecarboxylation of 4-methoxycinnamic acid **6**:

To a solution of 4-methoxycinnamic acid **6** (1 mmol, 178 mg) in acetonitrile (3 mL), IB (0.5 mmol 110 mg) was added and the solution was stirred for 10 min at 60 °C temperature. Following the addition of dipheyl diselenide (0.4 mmol, 125 mg) the reaction mixture was stirred at 60 °C for 8 hours. Then the solvent was evaporated under reduced pressure and the mixture was subjected to column chromatography over silica gel (100-200 mesh, eluent 1% ethylacetate in hexane) to afford **6a** (65% w.r.t. Diphenyl diselenide).

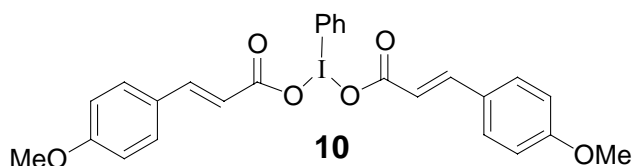
7. General procedure for solid-state selenodecarboxylation of arylpropionic acids using IBDA:

A mixture of the acid (1 mmol), IBDA (0.5 mmol, 161 mg) and diphenyl diselenide (0.3 mmol, 94 mg) was ground in a mortar for 10 min. The formation of acetic acid and wetting of the reaction mixture was observed. Extraction of the product into dichloromethane followed by chromatography (silica gel: 100-200 mesh, eluent: hexane) led to the pure alkynyl selenides.

8. General procedure for solid-state selenodecarboxylation of cinnamic acids using IBDA:

A mixture of the acid (1 mmol), IBDA (0.5 mmol, 161 mg) and diphenyl diselenide (0.4 mmol, 125 mg) was ground in a mortar for 15 min. The formation of acetic acid and wetting of the reaction mixture was observed. Extraction of the product into dichloromethane followed by chromatography (silica gel: 100-200 mesh, eluent: 1% ethyl acetate in hexane) led to the pure vinyl selenides.

9. Isolation and characterization of hypervalent iodonium intermediate (**10**):



To a solution of 4-methoxycinnamic acid (89 mg, 0.5 mmol) in acetonitrile (3 mL), IBDA (89 mg, 0.275 mmol) was added and the solution was stirred at 60 °C temperature. After 10 minutes a white solid precipitated. The stirring was continued for another 1 hour. The precipitate was collected by filtration, and washed repeatedly with acetonitrile to remove unreacted starting materials and acetic acid. After drying in vacuum, 122 mg (80 % w.r.t. Acid) of phenyliodosobenzene dicinnamate salt **10** was isolated. White solid, mp 165 °C.

¹H NMR (CDCl₃) δ: 3.81 (s, 6H, -OCH₃), 6.26 (d, 2H, J = 16Hz), 6.86 (d, 4H, J = 8Hz), 7.41 (d, 4H, J = 8 Hz, H_b), 7.49 (d, J = 16Hz, 2H), 7.53-7.58 (m, 3H-Ph), 8.19 (d, J = 7Hz, 2H, Ph)

¹³C NMR (CDCl₃) δ: 55.32, 94.26, 114.27, 116.1, 127.19, 127.44, 129.64, 130.22, 137.37, 144.47, 161.24, 169.3.

ESI-MS: for C₂₆H₂₃IO₆[M], [M]⁺ = 559.15

Anal. Calcd. for C₂₆H₂₃IO₆: C, 55.87; H, 4.12; Found: C, 55.32; H, 3.92.

10. In-situ generation of benzeneselenenyl sulfate:

Tiecco, M.; Testaferri, L.; Tingoli, M.; Bartoli, D.; Balducci, R. *J. Org. Chem.* **1990**, 55, 429.

Diphenyl diselenide (156 mg, 0.5 mmol) and ammoniumperoxy disulfate (137 mg, 0.6 mmol) in MeOH or in MeCN were stirred at reflux for 2h. After cooling to room temperature, the mixture was used in further reaction. $(\text{Et}_4\text{N})_2\text{S}_2\text{O}_8$ and $[\{\text{CH}_3(\text{CH}_2)_5\}\text{Et}_3\text{N}]_2\text{S}_2\text{O}_8$ were also used in place of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to generate benzeneselenenyl sulfate.

11. Attempted reaction of 4-methoxycinnamic acid with 4-tolyl diselenide under photolytic condition:

4-tolyl diselenide (85 mg, 0.25 mmol), 4-methoxycinnamic acid (89 mg, 0.5 mmol) and AIBN (8 mg, 0.05 mmol in 2-potions) were dissolved in 5 mL of chloroform in a quartz photoreactor attached to a condenser and argon line. The solution was degassed for 10 minutes with a stream of argon and a positive pressure of argon was maintained through out the course of the experiment. The solution was irradiated for 20 hours using medium pressure UV lamp, while maintaining the internal temperature of the solution at 35 °C. ^1H NMR of the mixture, after solvent removal, showed only the starting material peaks. Further work up by chromatography led to recovery of the starting material in quantitative yield.

12. Attempted reaction of phenylpropionic acid with 4-tolyl diselenide under photolytic condition:

Using identical procedure as above, but using 4-tolyl diselenide (82 mg, 0.24 mmol), phenylpropionic acid (73 mg, 0.5 mmol) and AIBN (8 mg, 0.05 mmol in 2-potions) in 5 mL of chloroform failed to show selenodecarboxylation. ^1H NMR of the mixture, after solvent removal, showed only the starting material peaks. Further work up by chromatography led to recovery of the starting material in quantitative yield.

13. Salient observations on attempted selenodecarboxylation under other conditions:

(i) Reactions with electrophilic organoselenium reagents (ArSe^+):

Electrophilic selenenylating agents are well known in literature. Most important among them are organoselenenyl halides, acetates, triflates, sulfates. We therefore attempted a number of experiments utilizing these selenenylating reagents. For all the experiments 4-methoxycinnamic acid **6** was chosen as the model substrate. Major observations are summarized in Table-S1. Reaction of **6** with PhSeCl (1 equiv.) and Et_3N (1 equiv.) in MeCN as solvent afforded the selenodecarboxylated product (*E*)-(2-(4-methoxyphenyl)-vinylseleno)benzene **6a** in 21% isolated yield (entry a). In presence of other additives such as Bu_3N or LiOAc , negligible yield of **6a** was observed (entries b, c). Decarboxylative chlorination and formation of diphenyl diselenide are major side reactions in these cases, as evident by the isolation of 4-methoxy- β -chlorostyrene and diphenyl diselenide during work up. We associate the above difficulties to the nucleophilic chloride counterion of PhSeCl . Henceforth we explored

selenenylating agents that do not contain nucleophilic counterions such as PhSeOTf, (PhSe)₂SO₄, and *N*-phenylseleno phthalimide (PthNSePh). However, in all cases the desired vinyl selenide **6a** was obtained in poor yields (entries d-k).

Table S1. Attempted Selenodecarboxylation of 4-methoxycinnamic acid **6** with various selenenylating reagents.^a

Entry	Reagents ^b	Additive (equiv) ^c	Solvent	Time (h)	Yield (%)
a	PhSeCl	Et ₃ N (1)	MeCN	4	21
b	PhSeCl	Bu ₃ N (1)	MeCN	4	20
c	PhSeCl	LiOAc (1)	MeCN	4	5
d	PhSeOTf	-	DCM	24	20
e	(PhSe) ₂ SO ₄	-	MeCN	24	5
f	(PhSe) ₂ SO ₄	Et ₃ N (1)	MeCN	24	10
g	(PhSe) ₂ SO ₄	Et ₂ NH (1)	MeCN	24	17
h ^d	(PhSe) ₂ SO ₄	Et ₂ NH (1)	MeCN	24	25
i	(PhSe) ₂ SO ₄	Et ₂ NH (0.1)	MeCN	24	10
j ^d	(PhSe) ₂ SO ₄	Et ₂ NH (0.1)	MeOH	24	15
k	PthNSePh	Et ₂ NH (1)	DCM	24	10

^a Unless otherwise stated, reactions were carried out at 40 °C, ^c With respect to **6**, ^d Under reflux.

(ii) Reactions under free radical (ArSe[•]) condition:

The selenodecarboxylation was also attempted under radical condition. An easy entry into ArSe radical is by the photolysis or thermolysis of ArSeSeAr, often in the presence of AIBN. Thus, a solution of 4-methoxycinnamic acid (0.5 mmol) **6**, diphenyl diselenide (0.25 mmol) and AIBN (0.05 mmol in two portions) in chloroform (5 mL) and under argon was irradiated in a photochemical reactor with medium pressure UV-lamp. After 20 h, the starting materials were recovered back nearly quantitatively. As shown in Table S2, various attempts to modify the reaction condition by changing additive, temperature, and dilution did not afford the desired selenodecarboxylated product.

Table S2. Attempted Selenodecarboxylation of 4-methoxycinnamic acid **6** under free radical condition in chloroform.^a

Entry	Reagents	Additive	Condition	Observation
a	PhSeSePh	AIBN	<i>hν</i>	No reaction. Starting materials recovered in all the cases after 20h.
b	PhSeSePh	AIBN	Reflux	
c	TolSeSeTol	AIBN	<i>hν</i>	
d	PhSeSePh	Bz ₂ O ₂	Reflux	
e	PhSeSePh	Bz ₂ O ₂	<i>hν</i>	
f ^b	PhSeSePh	AIBN	<i>hν</i>	

^a Condition: Acid **6** (0.5 mmol)/ArSeSeAr (0.25mmol)/additive (0.05 mmol in two portions) in chloroform (5 mL). ^b In 10 mL chloroform.

The results from the above are summarized below.

1. None of the reactions with electrophilic selenenylating reagents is preparatively useful.
2. Use of additives could not improve the yields.
3. Reactions under free radical condition failed with the recovery of the starting materials.

14. General kinetics procedure for selenodecarboxylation of arylpropionic acids

The UV-vis spectra of unsymmetrical alkynyl selenides **1a**, **2a**, and **3a** in chloroform show a weak but distinct peak at 313-315 nm (ϵ 3760-5290 $\text{litmol}^{-1}\text{cm}^{-1}$, Table S3), at which IBDA and PhSeSePh are nearly transparent ($\epsilon < 50 \text{ litmol}^{-1}\text{cm}^{-1}$). In each case linear Beer plot of absorbance versus concentration afforded the corresponding molar extinction constant ϵ -values, which were utilized to evaluate concentration of product in reaction mixture.

A 10 mL flask equipped with a magnetic bar was charged with diphenyl diselenide, iodosobenzene diacetate and arylpropionic acid in 1:5:10 molar ratio in chloroform (4 mL). The flask was degassed with argon and placed into a constant temperature bath at 25 °C and vigorously stirred. Known volume of aliquots were withdrawn periodically, diluted to 10 mL in a volumetric flask and washed with saturated sodium bicarbonate solution in order to make the solution free from excess arylpropionic acids. UV-vis monitoring of solutions were carried out at 315 nm for alkynyl selenide **1a** and at 313 nm for **2a** and **3a** respectively to determine product concentration (P_t). As shown in Figure S1, linear plot of $\ln[a_0/(a_0-x)]$ vs. time (t) indicated pseudo first order kinetics with respect to diselenide in accordance with the following equation.

$$k_R t = \ln[a_0/(a_0-x)]$$

a_0 = initial concentration of PhSeSePh

(a_0-x) = concentration of PhSeSePh at time t

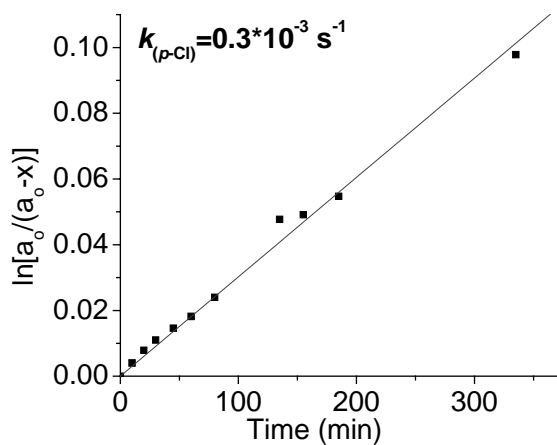
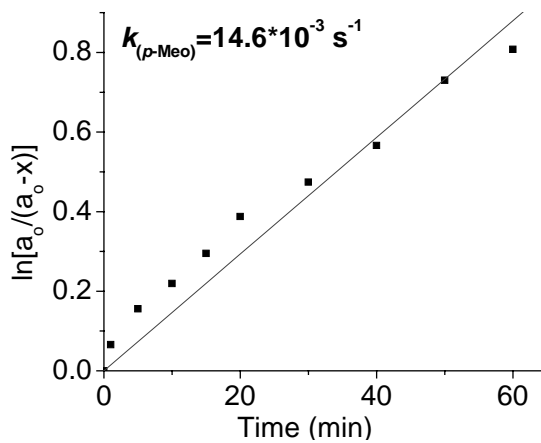
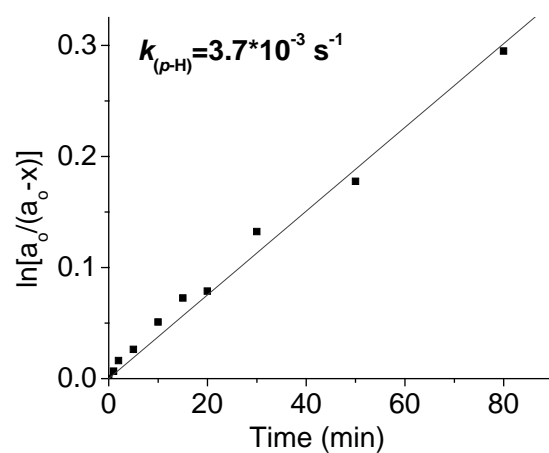
$$x = 0.5P_t$$

The rate constants k_R were determined for the first 20% conversion of the reaction.

Table S3. Kinetic data for the selenodecarboxylation of arylpropionic acids with PhSeSePh/IBDA

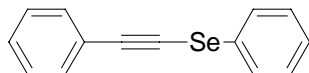
entry	a_0	Product			R	$k_R \times 10^3 \text{ (s}^{-1}\text{)}$
		No.	λ (nm)	ϵ		
1	0.04 M	1a	315	5290	H	3.7
2	0.04 M	2a	313	3760	OMe	14.6
3	0.02 M	3a	313	4590	Cl	0.3

Figure S1: Pseudo-first order rate plots for the selenodecarboxylation of 1, 2 and 3



15. REFERENCES, SPECTROSCOPIC AND ANALYTICAL DATA OF PRODUCTS

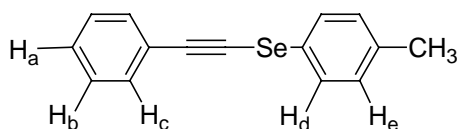
1-phenylseleno-2-phenylacetylene (1a):



Braga, A. L.; Comasseto, J. V.; Petragnani, N. *Synthesis* **1984**, 240.

¹H NMR (CDCl₃) δ : 7.05-7.65 (m, 10H); **ESI-MS**: for C₁₄H₁₀Se [M], [M+H]⁺ = 259.00, [M+MeCN+H]⁺ = 300.03; **Anal.** Calcd. for C₁₄H₁₀Se: C, 65.37; H, 3.89; Found: C, 65.77; H, 3.76.

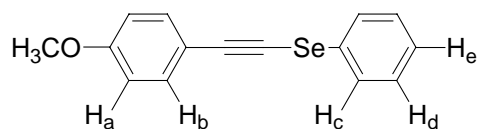
1-(*p*-Tolylseleno)-2-phenylacetylene (1b):



Zhang, J. L.; Chen, Z. C. *Synth. Commun.* **1997**, 27, 3757

¹H NMR (CDCl₃) δ : 2.34 (s, 3H, -CH₃), 7.15 (d, 2H, J = 8 Hz, H_e), 7.30-7.34 (m, 3H, H_a, H_b), 7.46-7.53 (m, 4H, H_c, H_d); **ESI-MS**: for C₁₅H₁₂Se [M], [M+H]⁺ = 273.00, [M+MeCN+H]⁺ = 314.03; **Anal.** Calcd. for C₁₅H₁₂Se: C, 66.42; H, 4.43; Found: C, 66.73; H, 4.22.

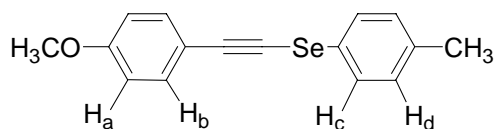
1-(phenylseleno)-2-(*p*-meo-phenyl)acetylene (2a):



Braga, A. L.; Comasseto, J. V.; Petragnani, N. *Synthesis* **1984**, 240.

¹H NMR (CDCl₃) δ : 3.82 (s, 3H, -OCH₃), 6.86 (d, 2H, J = 9 Hz, H_a), 7.22-7.38 (m, 3H, H_d, H_e), 7.46 (d, 2H, J = 9 Hz, H_b), 7.52-7.63 (m, 2H, H_c); **ESI-MS**: for C₁₅H₁₂OSe: [M], [M+H]⁺ = 289.02; **Anal.** Calcd. for C₁₅H₁₂OSe: C, 62.72; H, 4.18; Found: C, 63.05; H, 4.08.

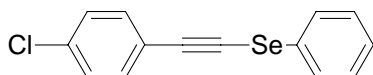
1-(*p*-tolylseleno)-2-(*p*-methoxyphenyl)acetylene (2b):



Latypova, V. Z.; Yakovleva, O. G.; Rydvanskii, Y. V.; Kataeva, L. M.; Kargin, Y. M. *Zhurnal Obshchei Khimi* **1984**, *54*, 848

¹H NMR (CDCl₃) δ: 2.33 (s, 3H, -CH₃), 3.81 (s, 3H, -OCH₃), 6.85 (d, 2H, J= 9 Hz, H_a), 7.13 (d, 2H, J= 8 Hz, H_d), 7.43 (d, 2H, J= 9 Hz, H_b), 7.47 (d, 2H, J= 8 Hz, H_c); **ESI-MS:** for C₁₆H₁₄OSe: [M], [M+H]⁺ = 303.01; **Anal.** Calcd. for C₁₆H₁₄OSe: C, 63.79; H, 4.65; Found: C, 63.83; H, 4.67.

1-(phenylseleno)-2-(*p*-chlorophenyl)acetylene (3a):

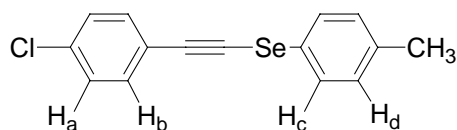


Braga, A. L.; Comasseto, J. V.; Petragnani, N. *Synthesis* **1984**, 240.

Husebye, S.; Meyers, E. A.; Zingaro, R. A.; Braga, A. L.; Comasseto, J. V.; Petragnani, N. *Acta Cryst.* **1986**, *C42*, 1789-1792

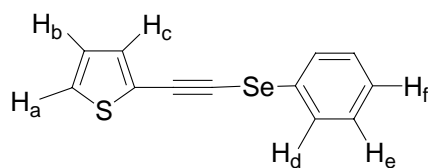
¹H NMR (CDCl₃) δ: 7.18-7.67(m, 9H); **ESI-MS:** for C₁₄H₉ClSe [M], [M+H]⁺ = 292.96 (³⁵Cl) & 294.95 (³⁷Cl), [M+H-Cl]⁺ = 257.99(³⁵Cl) & 255.99(³⁷Cl); **Anal.** Calcd. for C₁₄H₉ClSe: C, 57.63; H, 3.09; Found: C, 58.01; H, 2.83.

1-(*p*-tolylseleno)-2-(*p*-chlorophenyl)acetylene (3b):



¹H NMR (CDCl₃) δ: 2.34 (s, 3H, -CH₃), 7.15 (d, 2H, J= 8Hz, H_d), 7.28 (d, 2H, J= 9Hz, H_b), 7.39 (d, 2H, J= 9Hz, H_a), 7.47 (d, 2H, J= 8Hz, H_c); **¹³C NMR (CDCl₃) δ:** 21.01, 71.25, 100.97, 121.75, 124.59, 128.62, 129.68, 130.38, 132.82, 134.42, 137.42; **ESI-MS:** for C₁₅H₁₁ClSe [M], [M+H]⁺ = 306.98 (³⁵Cl) & 308.98 (³⁷Cl), [M+H-Cl]⁺ = 272.01(³⁵Cl) & 270.01(³⁷Cl), [M+MeCN+H]⁺ = 348.01(³⁵Cl) & 350.01(³⁷Cl); **Anal.** Calcd. for C₁₅H₁₁ClSe: C, 58.92; H, 3.60; Found: C, 58.87; H, 3.42.

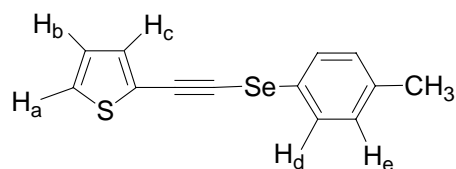
1-(Phenylseleno)-2-(2'-thienyl)acetylene (4a):



Braga, A. L.; Comasseto, J. V.; Petragnani, N. *Synthesis* **1984**, 240.

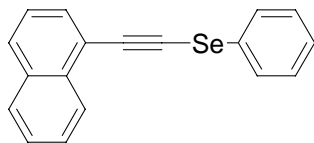
¹H NMR (CDCl₃) δ: 7.00 (dd, 1H, J = 5, 5.1 Hz, H_b), 7.14-7.42 (m, 4H, H_a, H_c, H_e, H_f), 7.45-7.62 (m, 2H, H_d); **ESI-MS:** for C₁₂H₈SSe [M], [M+H]⁺ = 264.96; **Anal.** Calcd. for C₁₂H₈SSe: C, 54.75; H, 3.04; Found: C, 54.88; H, 2.97.

1-(*p*-Tolylseleno)-2-(2'-thienyl)acetylene (4b):



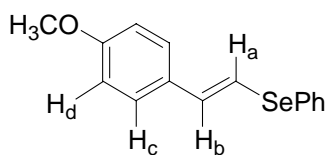
¹H NMR (CDCl₃) δ: 2.33 (s, 3H, -CH₃), 6.98 (dd, 1H, J = 4, 5 Hz, H_b), 7.14 (d, 2H, J = 8Hz, H_e), 7.21-7.30 (m, 2H, H_a & H_c), 7.45 (d, 2H, J = 8Hz, H_d); **¹³C NMR (CDCl₃) δ:** 21.00, 74.48, 94.93, 123.35, 124.83, 126.89, 127.96, 129.59, 130.35, 133.12, 137.36; **ESI-MS:** for C₁₃H₁₀SSe [M], [M+H]⁺ = 278.97; **Anal.** Calcd. for C₁₃H₁₀SSe: C, 56.32; H, 3.61; Found: C, 56.65; H, 3.53.

1-Phenylselanylethynyl-naphthalene (5a):



¹H NMR (CDCl₃) δ: 7.20-8.00 (m, 11H), 8.30-8.45 (m, 1H); **¹³C NMR (CDCl₃) δ:** 73.97, 101.13, 120.79, 125.20, 126.17, 126.47, 126.94, 127.16, 128.30, 129.09, 129.62, 130.81, 133.16, 133.44; **ESI-MS:** for C₁₈H₁₂Se [M], [M+H]⁺ = 309.02; **Anal.** Calcd. for C₁₈H₁₂Se: C, 70.36; H, 3.91; Found: C, 70.53; H, 3.96.

(E)-(2-(p-Methoxyphenyl)vinylseleno)benzene (6a):

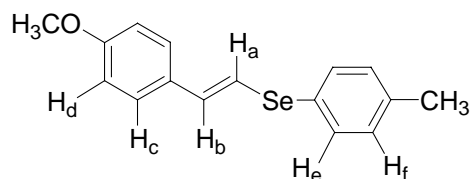


Yu, Y.; Xian, H. *Synth. Commun.* **1997**, 27, 345

Shin, W. S.; Lee, K.; Oh, D. Y. *Bull. Of the Korean chem. Soc.* **1996**, 17, 981

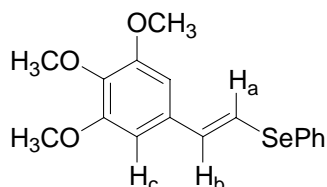
¹H NMR (CDCl₃) δ: 3.81 (s, 3H, -OCH₃), 6.86 (d, 2H, J = 9 Hz, H_d), 6.88 (d, 1H, J = 16 Hz, H_a), 7.03 (d, 1H, J = 16 Hz, H_b), 7.25-7.34 (m, 3H-Ph + 2H-H_c), 7.49-7.56 (m, 2H, Ph); **¹³C NMR (CDCl₃) δ:** 55.28, 114.06, 115.90, 127.10, 127.37, 129.24, 129.87, 130.73, 131.99, 135.87, 159.35; **ESI-MS:** for C₁₅H₁₄OSe [M], [M]⁺ = 290.04; **Anal.** Calcd. for C₁₅H₁₄OSe: C, 62.28; H, 4.84; Found: C, 62.40; H, 4.73; Light yellow solid, mp 50-51 °C.

(E)-(2-(p-Methoxyphenyl)vinylseleno)toluene (6b):



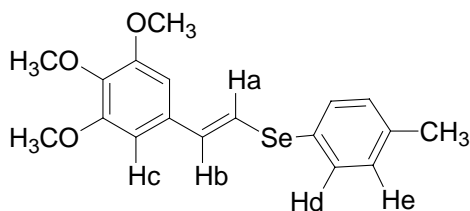
¹H NMR (CDCl₃) δ: 2.34 (s, 3H, -CH₃), 3.80 (s, 3H, -OCH₃), 6.79 (d, 1H, J = 18 Hz, H_a), 6.84 (d, 2H, J = 9 Hz, H_d), 7.00 (d, 1H, J = 18 Hz, H_b), 7.12 (d, 2H, J = 8 Hz, H_f), 7.26 (d, 2H, J = 9 Hz, H_c), 7.43 (d, 2H, J = 8 Hz, H_e); **ESI-MS:** for C₁₆H₁₆OSe [M], [M]⁺ = 304.02; **Anal.** Calcd. for C₁₆H₁₆OSe : C, 63.37; H, 5.28; Found : C, 63.58; H, 5.11; Light yellow solid, mp 69.5-70.5 °C.

(E)-(2-(3,4,5-Trimethoxyphenyl)vinylseleno)benzene (7a):



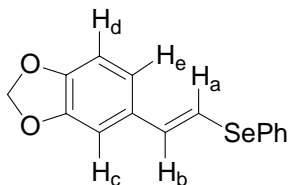
¹H NMR (CDCl₃) δ: 3.85 (s, 3H, -OCH₃), 3.87 (s, 6H, -OCH₃), 6.55 (s, 2H, H_c), 6.8 (d, 1H, J = 16 Hz, H_a), 7.09 (d, 1H, J = 16 Hz, H_b), 7.28-7.37 (m, 3H, Ph), 7.52-7.60 (m, 2H, Ph); **ESI-MS:** for C₁₇H₁₈O₃Se [M], [M+H]⁺ = 351.03, [M+MeCN+H]⁺ = 392.05, [M+MeCN+Na]⁺ = 414.03; **Anal.** Calcd. for C₁₇H₁₈O₃Se: C, 58.45; H, 5.16; Found: C, 58.78; H, 5.44; Light yellow solid, mp 50.6-51.5 °C.

(E)-(2-(3,4,5-Trimethoxyphenyl)vinylseleno)toluene (7b):



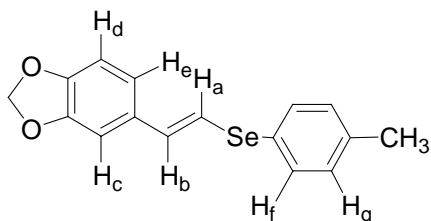
¹H NMR (CDCl₃) δ: 2.35 (s, 3H, -CH₃), 3.84 (s, 3H, -OCH₃), 3.85 (s, 6H, -OCH₃), 6.52 (s, 2H, H_c), 6.74 (d, 1H, J = 18 Hz, H_a), 7.07 (d, 1H, J = 18 Hz, H_b), 7.14 (d, 2H, J = 8 Hz, H_e), 7.45 (d, 2H, J = 8 Hz, H_d); **¹³C NMR (CDCl₃) δ:** 21.10, 56.07, 60.87, 103.15, 119.48, 125.93, 130.16, 132.86, 133.18, 134.12, 137.67, 137.88, 153.34; **ESI-MS:** for C₁₈H₂₀O₃Se [M], [M+H]⁺ = 365.05, [M+MeCN+H]⁺ = 406.08; **Anal.** Calcd. for C₁₈H₂₀O₃Se: C, 59.50; H, 5.51; Found: C, 59.73; H, 5.26; oil.

(E)-5-(2-Phenylselanyl-vinyl)-benzo[1,3]dioxole (8a):



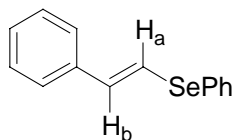
¹H NMR (CDCl₃) δ: 5.95 (s, 2H, -O-CH₂-O-), 6.76-6.88 (m, 4H, H_a, H_c, H_d, H_e), 6.99 (d, 1H, J = 16 Hz, H_b), 7.25-7.35 (m, 3H, Ph), 7.50-7.54 (m, 2H, Ph); **¹³C NMR (CDCl₃) δ:** 101.10, 105.40, 108.31, 116.76, 120.86, 127.21, 129.26, 130.45, 131.51, 132.16, 135.46, 147.32, 148.05; **ESI-MS:** for C₁₅H₁₂O₂Se [M], [M]⁺ = 304.00; **Anal.** Calcd. for C₁₅H₁₂O₂Se: C, 59.41; H, 3.96; Found: C, 59.23; H, 4.05; oil.

(E)-5-(2-*p*-tolylselanyl-vinyl)-benzo[1,3]dioxole (8b):



¹H NMR (CDCl₃) δ: 2.35 (s, 3H, -CH₃), 5.94 (s, 2H, -O-CH₂-O-), 6.73 (d, 1H, J = 16 Hz, H_a), 6.74 (m, 2H, H_d, H_e), 6.86 (s, 1H, H_c), 6.96 (d, 1H, J = 16 Hz, H_b), 7.12 (d, 2H, J = 8 Hz, H_g), 7.43 (d, 2H, J = 8 Hz, H_f); **ESI-MS:** for C₁₆H₁₄O₂Se [M], [M]⁺ = 318.00; **Anal.** Calcd. for C₁₆H₁₄O₂Se: C, 60.57; H, 4.42; Found: C, 60.38; H, 4.26; White solid, mp 50-50.6 °C.

(*E*)-(2-(phenyl)vinylseleno)benzene (9a):

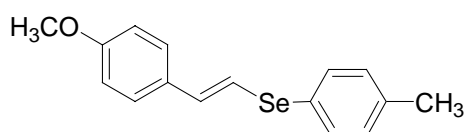


Comasseto, J. V.; Ferreira, J. T. B. *J. Organomet. Chem.* **1984**, 240.

¹H NMR (CDCl₃) δ: 6.73 (d, 1H, J = 16 Hz, H_a), 6.90 (d, 1H, J = 16 Hz, H_b), 7.1-7.6 (m, 10H, Ph);

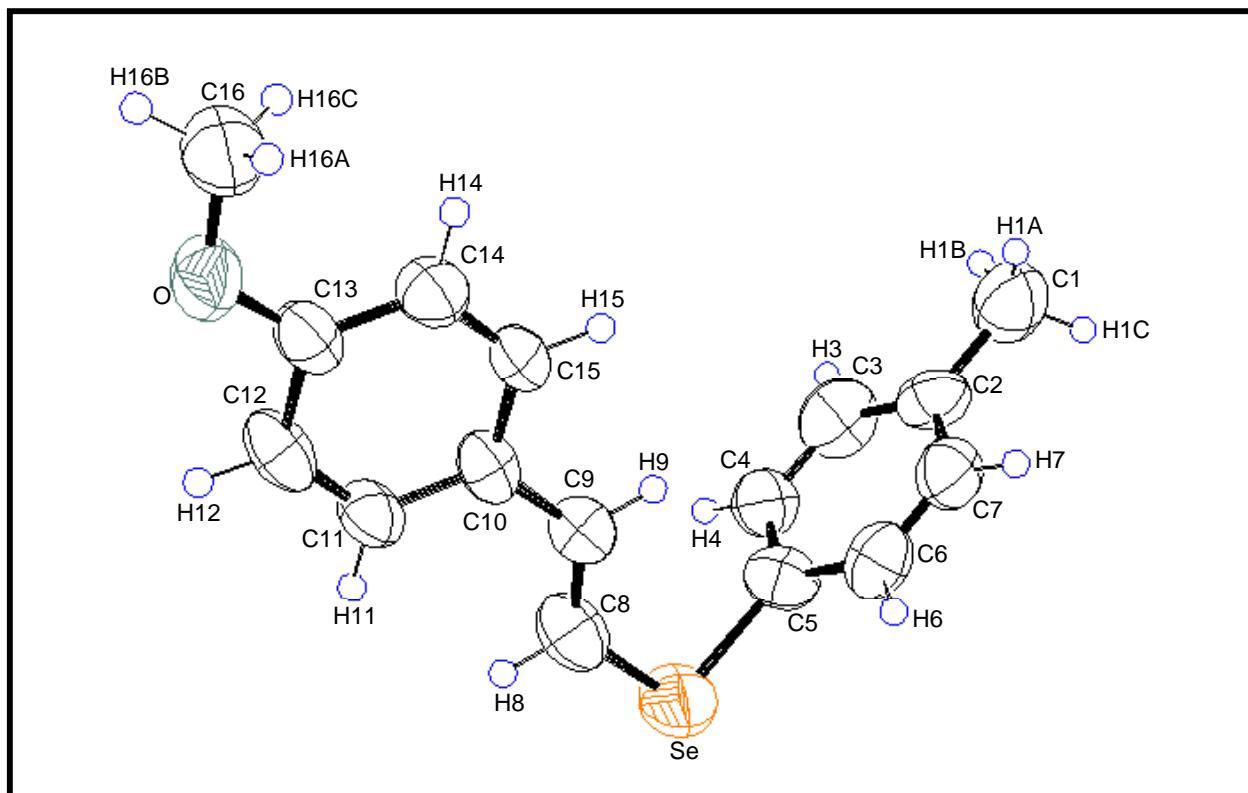
Anal. Calcd. for C₁₄H₁₂Se: C, 64.87; H, 4.67; Found: C, 65.12; H, 4.39; Oil.

16. X-ray Crystallographic Structure of (*E*)-(2-(p-Methoxyphenyl)vinylseleno)toluene (6b):



Crystals of **6b** suitable for structure determination was grown from hexane at 4 °C.

ORTEP diagram of **6b**.



Crystal data and structure refinement for 6b.

Identification code	6b	
Empirical formula	C ₁₆ H ₁₆ O Se	
Formula weight	303.25	
Temperature	293(2) K	
Wavelength	0.71073 Å (Mo K α)	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 5.960(18) Å	alpha = 90deg
	b = 7.710(10) Å	beta = 90deg
	c = 31.23(3) Å	gamma = 90deg
Volume	1435(5) Å ³	
Z	4	
Density (calculated)	1.404 Mg/m ³	
Absorption coefficient	2.603 mm ⁻¹	
F (000)	616	
Crystal size	0.16 x 0.14 x 0.03 mm	
Theta range for data collection	2.72 to 24.96 deg.	
Index ranges	0 ≤ h ≤ 7; 0 ≤ k ≤ 9; 0 ≤ l ≤ 37	
Reflections collected	1402	
Independent reflections	1402 [R(int) = 0.0000]	
Reflections observed (>2sigma)	849	
Data Completeness	0.933	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1402 / 0 / 165	
Goodness-of-fit on F ²	1.016	
Final R indices [I>2sigma(I)]	R = 0.0812	wR = 0.1816
R indices (all data)	R = 0.1438	wR = 0.2146
Absolute structure parameter	-0.07(6)	
Largest diff. Peak and hole	0.824 and -0.490 e.Å ⁻³	

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U (eq)
Se(1)	2500(2)	5135(2)	8978(1)	88(1)
O(1)	9481(13)	4441(12)	6654(2)	75(2)
C(13)	8660(20)	4353(14)	7059(4)	61(3)
C(9)	5606(18)	330(14)	8305(3)	59(3)
C(12)	6653(18)	5233(15)	7129(4)	65(3)
C(2)	6520(20)	434(13)	9561(4)	68(3)
C(10)	6649(18)	4358(13)	7864(3)	53(3)
C(14)	9618(19)	3480(15)	7401(3)	61(3)
C(7)	7290(20)	2090(17)	9584(4)	70(3)
C(8)	3862(19)	5208(18)	8438(4)	78(4)
C(11)	5697(16)	5264(15)	7527(3)	58(3)
C(5)	4150(20)	3243(15)	9211(4)	67(3)
C(15)	8662(19)	3505(16)	7796(3)	64(3)
C(4)	3330(20)	1597(17)	9170(4)	70(3)
C(16)	11450(20)	3540(20)	6546(4)	87(4)
C(3)	4440(20)	199(19)	9347(4)	86(4)
C(1)	7820(30)	-1102(18)	9729(4)	96(5)
C(6)	6220(20)	3444(18)	9423(4)	70(3)

Table S4. Bond length [Å] for **6b**.

Se(1)-C(8)	1.870(12)	Se(1)-C(5)	1.903(12)
O(1)-C(13)	1.359(13)	O(1)-C(16)	1.408(14)
C(13)-C(14)	1.387(14)	C(13)-C(12)	1.390(18)
C(9)-C(8)	1.308(16)	C(9)-C(10)	1.512(15)
C(9)-H(9)	0.9300	C(12)-C(11)	1.368(15)
C(12)-H(12)	0.9300	C(2)-C(7)	1.357(17)
C(2)-C(3)	1.42(2)	C(2)-C(1)	1.51(2)
C(10)-C(15)	1.385(15)	C(10)-C(11)	1.385(13)
C(14)-C(15)	1.359(14)	C(14)-H(14)	0.9300
C(7)-C(6)	1.321(18)	C(7)-H(7)	0.9300
C(8)-H(8)	0.9300	C(11)-H(11)	0.9300
C(5)-C(4)	1.366(17)	C(5)-C(6)	1.412(18)
C(15)-H(15)	0.9300	C(4)-C(3)	1.381(18)
C(4)-H(4)	0.9300	C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600	C(16)-H(16C)	0.9600
C(3)-H(3)	0.9300	C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600	C(1)-H(1C)	0.9600
C(6)-H(6)	0.9300		

Table S5. Bond angles [°] for **6b**.

C(8)-C(9)-C(10)	127.4(11)	C(8)-C(9)-H(9)	116.3
C(10)-C(9)-H(9)	116.3	C(11)-C(12)-C(13)	120.6(10)
C(11)-C(12)-H(12)	119.7	C(13)-C(12)-H(12)	119.7
C(7)-C(2)-C(3)	116.0(12)	C(7)-C(2)-C(1)	123.1(13)
C(3)-C(2)-C(1)	120.8(12)	C(15)-C(10)-C(11)	118.6(10)
C(15)-C(10)-C(9)	119.3(9)	C(11)-C(10)-C(9)	122.1(10)
C(15)-C(14)-C(13)	121.3(10)	C(15)-C(14)-H(14)	119.4
C(13)-C(14)-H(14)	119.4	C(6)-C(7)-C(2)	124.2(13)
C(6)-C(7)-H(7)	117.9	C(2)-C(7)-H(7)	117.9
C(9)-C(8)-Se(1)	127.9(10)	C(9)-C(8)-H(8)	116.0
Se(1)-C(8)-H(8)	116.0	C(12)-C(11)-C(10)	120.8(10)
C(12)-C(11)-H(11)	119.6	C(10)-C(11)-H(11)	119.6
C(4)-C(5)-C(6)	117.3(11)	C(4)-C(5)-Se(1)	119.5(10)
C(6)-C(5)-Se(1)	123.2(10)	C(14)-C(15)-C(10)	120.6(10)
C(14)-C(15)-H(15)	119.7	C(10)-C(15)-H(15)	119.7
C(5)-C(4)-C(3)	121.0(11)	C(5)-C(4)-H(4)	119.5
C(3)-C(4)-H(4)	119.5	O(1)-C(16)-H(16A)	109.5
O(1)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
O(1)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5	C(4)-C(3)-C(2)	120.6(12)
C(4)-C(3)-H(3)	119.7	C(2)-C(3)-H(3)	119.7
C(2)-C(1)-H(1A)	109.5	C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5	C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5	H(1B)-C(1)-H(1C)	109.5
C(7)-C(6)-C(5)	120.8(12)	C(7)-C(6)-H(6)	119.6
C(5)-C(6)-H(6)	119.6		

Symmetry transformations used to generate equivalent atoms

Table S6. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6b**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U_{11} + \dots + 2 hka^*b^*U_{12}]$

Atom	U11	U22	U33	U23	U13	U12
Se(1)	76(1)	104(1)	84(1)	-1(1)	12(1)	25(1)
O(1)	72(5)	99(6)	54(4)	14(4)	8(4)	14(5)
C(13)	66(7)	49(6)	69(7)	9(5)	-12(6)	3(6)
C(9)	55(6)	58(6)	64(6)	6(6)	0(6)	2(6)
C(12)	36(4)	72(7)	85(8)	18(7)	-19(5)	0(6)
C(2)	90(8)	41(7)	72(7)	-4(5)	10(7)	-6(6)
C(10)	44(5)	51(5)	63(6)	10(5)	-12(5)	-10(5)
C(14)	54(7)	70(7)	60(6)	8(6)	11(6)	9(6)
C(7)	57(7)	84(8)	69(7)	-8(6)	-4(8)	1(8)
C(8)	48(7)	93(9)	92(8)	7(8)	-14(6)	12(7)
C(11)	43(5)	67(7)	63(6)	7(6)	-1(5)	12(6)
C(5)	57(7)	63(7)	80(8)	5(7)	12(6)	2(6)
C(15)	61(7)	75(7)	56(6)	2(6)	-11(6)	25(7)
C(4)	47(6)	78(8)	85(8)	-12(7)	-13(6)	-2(6)
C(16)	65(7)	119(11)	76(8)	16(8)	12(7)	20(9)
C(3)	82(9)	75(9)	101(9)	-10(8)	-2(8)	-30(9)
C(1)	124(14)	80(9)	85(8)	-3(7)	-11(10)	-5(10)
C(6)	72(8)	76(8)	61(7)	-4(7)	1(6)	-16(7)

Table S7. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6b**.

Atom	x	y	z	U (eq)
H(9)	6283	3605	8505	71
H(12)	5958	5807	6903	78
H(14)	10943	2865	7359	74
H(7)	8644	2283	9723	84
H(8)	3221	5961	8240	93
H(11)	4393	5901	7572	69
H(15)	9367	2945	8023	77
H(4)	1998	1414	9020	84
H(16A)	12735	4166	6650	130
H(16B)	11552	3422	6241	130
H(16C)	11423	2407	6675	130
H(3)	3821	-905	9326	103
H(1A)	9277	-1134	9597	145
H(1B)	7028	-2152	9664	145
H(1C)	7994	-997	10034	145
H(6)	6848	4543	9449	84

17. ^1H , ^{13}C NMR and ESI-MS Spectra of Acetylenic and Vinyl Selenides^a

