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Article

Addition of Thiols to Phenylselenoalkynes using KF/Alumina under Solvent-Free Conditions

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Um método simples e eficiente foi desenvolvido para a hidrotiolação de fenilselenoalquinos utilizando KF/Al_2O_3 em meio livre de solvente. O método é geral e permite a preparação seletiva de (*Z*)-1-fenilseleno-2-organotio-1-alquenos a partir de tióis aromáticos e alifáticos em rendimentos de razoáveis a bons. A presença do grupamento organosselênio direcionou a regioquímica da adição do tiol. O sistema catalítico pode ser reutilizado mais quatro vezes sem tratamento prévio.

We present herein the results of a simple and efficient protocol for the hydrothiolation of phenylselenoalkynes promoted by KF/Al_2O_3 using solvent-free conditions. This improved method furnishes selectively the corresponding (*Z*)-1-phenylseleno-2-organylthio-1-alkenes in reasonable to good yields starting from selenoalkynes and aliphatic or aromatic thiols. The presence of the phenylselenium group in the alkyne directed the regiochemistry of the thiol addition. The catalytic system can be reused up to 4 times without previous treatment.

Keywords: selenium, green chemistry, solvent-free reaction, hydrothiolation, vinyl selenides

Introduction

The development of new preparative methods for vinyl chalcogenides is still being of interest in organic synthesis and in materials science.[1] Among the vinyl chalcogenides the densely functionalized 1,2-bis-chalcogenide alkenes are of special interest, because they can be used as a versatile precursor to enediynes and other functionalized olefins.[2] The methods for preparation of vicinal bis-chalcogenide alkenes involve the addition of two identical organochalcogenium groups in alkynes. This reaction can be catalyzed by transition metal complexes $[Pd(PPh_3)_4]$ and $[Pt(PR_3)_4]$,[3] gallium trichloride,[4] or under photochemical,[5] thermal[6] or basic conditions.[7] Because the difference in reactivity of the organoselenium and organosulfur groups attached at the double bond, the preparation of mixed (S, Se) bis-chalcogenide alkenes was also developed.[3,5]

Recently, the *in situ* addition of chalcogenides to propargylic alcohols (alkynyl-lithium species) to afford bis-chalcogenide alkenes (S and Se) in very good yields was described.[8] The authors observed that the presence of the acidic hydrogen from hydroxyl group is essential for the selectivity control of the addition. An alternative method to obtain mixed vinyl bis-chalcogenides is the hydrochalcogenation of chalcogenoalkynes.[9,10] In this way, sodium phenylseleno-(triethoxy)borate, generated *in situ* in the presence of refluxing ethanol, was used for the hydroselenation of phenylthioalkynes to prepare (*Z*)-1-phenylseleno-2-phenylthio-1-organylethenes.[9] The authors observed that the phenylthio group acts as a directing and activating group for the nucleophilic addition of the selenolate species. Recently, the solvent-free hydrothiolation of thioacetylenes catalyzed by PhSeBr was used for the selective formation of (*Z*)-1,2-bis-organylthio alkenes in good yields.[10] The authors studied also the hydrothiolation of methylselenoalkyne (only one example) and they observed the exclusive formation of the respective (*Z*)-1-phenylthio-2-methylseleno-1-organylalkene.[10]

On other hand, the use of potassium fluoride supported on alumina (KF/Al_2O_3) as a green catalytic system for a number of transformations has been increased.[11] By using KF/Al_2O_3, the products can be easily isolated by filtration and the generation of large amounts of salts at the end of the synthesis, as well as the use of stoichiometric strong bases, can be avoided.

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Our major research goal has been the development of new and cleaner protocols for the preparation and synthetic applications of organochalcogenium compounds.[12] More recently, we have described several efficient approaches using KF/Al_2O_3.[13] As a continuation of our studies, we report herein the results of the hydrothiolation of phenylselenoalkynes **1** using KF/Al_2O_3 for the selective synthesis of (*Z*)-1-organylthio-2-phenylseleno-1-organylalkenes **3** (Scheme 1).

Results and Discussion

Initially, we chose 1-phenylseleno-2-phenylethyne **1a** and benzenethiol **2a** as standard starting materials to establish the best reaction conditions (Table 1). We examined the temperature, amount of KF/Al_2O_3 (50%)[14] and the use of N_2 atmosphere. It was found that stirring a mixture of **1a** (1 mmol) and **2a** (1 mmol) in presence of 0.08 g of KF/Al_2O_3 (50%) at room temperature, the products of hydrothiolation **3a** were obtained in a overall yield of 30% after 3.5 h, together with great amount of diphenyl disulfide (Table 1, entry 1). When the same protocol was performed at gently heating (60 ºC) and under N_2 atmosphere, the yield increased to 58% yield (Table 1, entry 3). On the other hand, using 1.2, 1.5 and 2 equiv. of **2a**, the yield increased to 68, 78 and 90%, respectively (Table 1, entries 5, 6 and 7). When an excess of phenylselenoalkyne **1a** was used, unsatisfactory yields were obtained (Table 1, entries 2 and 4), while using 0.10 g of the catalyst (entry 8) or prolonged reaction time (entry 9) also did not increase significantly the vinyl sulfides yields. It was also observed that the catalytic system can be re-used for several cycles, just by washing it with ethyl acetate and drying under vacuum. The product **3a** was obtained in 90, 87, 78, 67 and 60% yields after successive cycles.

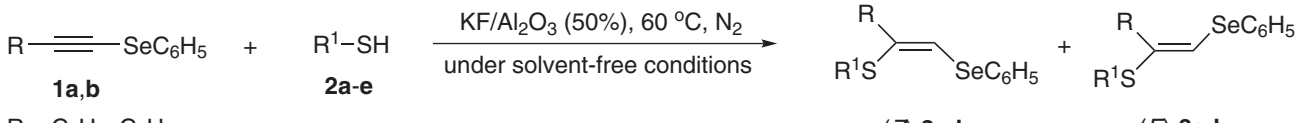
Using the optimized conditions, the protocol was extended to other thiols (Table 2, entries 2-4) and 1-phenylseleno heptyne **1b** (Table 2, entries 5-8).[15] Starting from disubstituted selenoalkynes **1a** and **1b**, the hydrothiolation reaction afforded trisubstituted olefins, which can be present as four different isomers. However, we observed here that, except for the reaction between **1b** and **2a**, which formed also the *gem*-1,2-bis-chalcogenide (trace amount detected by GC), for all the studied examples, it was obtained exclusively the 1-phenylseleno-2-phenylthio-1-organylethenes **3** (Table 2). This observation showed that the phenylselenium moiety acts as a directing and activating group for the nucleophilic addition of the thiolate anion. This influence in the regiochemistry of the reaction is similar to that observed for the hydrochalcogenation of thioacetylenes.[9] Regarding the stereochemistry of product **3**, the (*Z*)-isomer was obtained preferentially, with a *Z*:*E* ratio around of 70:30 in all the studied examples. The best yields were obtained using the benzenethiol **2a**. Thus, for example, from the reaction of phenylselenoalkyne derived from phenylacetylene, **1a** or 1-heptyne, **1b** with benzenethiol **2a**, the respective products **3a** and **3e** were obtained in 90% yield (Table 2, entries 1 and 5). When benzylic (**2c** and **2e**) and aliphatic thiols (**2d**) were used, the product **3** were obtained in 49-60% yields (Table 2, entries 3-4 and 7-8).

The low yield observed for the aliphatic thiols **2c-e** compared with benzenethiol **2a** can be attributed to a competition between the hydrothiolation reaction and the thiol oxidation to afford the respective disulfides. For all the studied examples, a variable amount of disulfide was isolated. This is in agreement with a recently report of our group describing the clean oxidation of thiols to disulfide in the presence of KF/Al_2O_3.[13] Thus, the unreacted excess of thiol employed was easily recovered at the end of the reaction as the corresponding disulfide. A plausible mechanism for the formation of **3a**-**h** is outlined in

Table 1. Optimization of the synthesis of **3a**

entry	**1a** (equiv.)	**2a** (equiv.)	Temp.	time (h)	Yield (%)[a]
1	1	1	r.t.	3.5	30
2[b]	2	1	r.t.	3.5	38
3[b]	1	1	60 °C	3.5	58
4[b]	2	1	60 °C	3.0	65
5[b]	1	1.2	60 °C	3.0	68
6[b]	1	1.5	60 °C	3.0	78
7[b]	1	2	60 °C	3.0	90
8[c]	1	2	60 °C	3.0	91
9[b]	1	2	60 °C	24.0	90

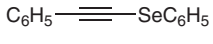
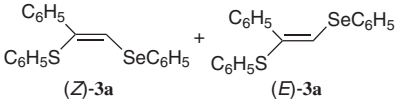
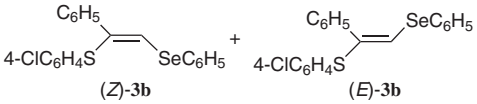
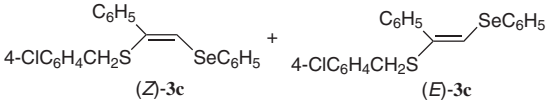
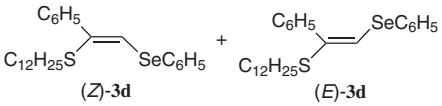
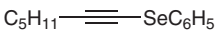
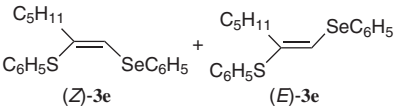
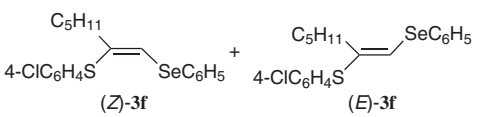
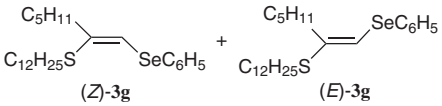
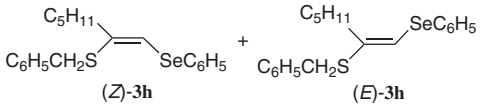
[a]Obtained as a mixture of (*Z*)-**3a** and (*E*)-**3a** (ratio = 70:30). [b]Reactions accomplished under of N_2 atmosphere. [c]Reaction using 0.10 g of KF/Al_2O_3.



R = C_6H_5, C_5H_{11}
R^1 = C_6H_5, 4-ClC_6H_4, 4-$ClC_6H_4CH_2$, $C_6H_5CH_2$, $C_{12}H_{25}$

Scheme 1.

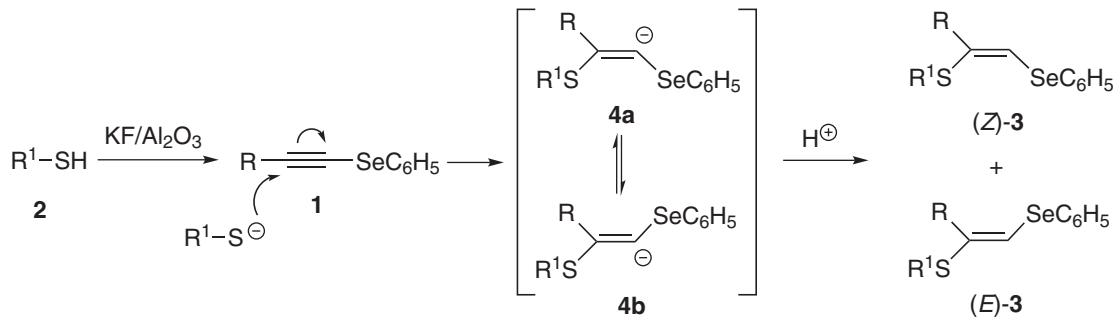
Table 2. Hydrothiolation of phenylselenoalkynes using KF/Al_2O_3 under solvent-free condition

entry	Alkyne **1**	Thiol **2**	Product **3**	time (h)	Ratio[a] (*Z*):(*E*)	Yield[b] %
1	 **1a**	C_6H_5SH **2a**	 (*Z*)-**3a** (*E*)-**3a**	3	70 : 30	90
2	**1a**	4-ClC_6H_4SH **2b**	 (*Z*)-**3b** (*E*)-**3b**	2.5	72 : 28	68
3	**1a**	4-$ClC_6H_4CH_2SH$ **2c**	 (*Z*)-**3c** (*E*)-**3c**	2.5	75 : 25	55
4	**1a**	$CH_3(CH_2)_{11}SH$ **2d**	 (*Z*)-**3d** (*E*)-**3d**	3	62 : 38	58
5	 **1b**	**2a**	 (*Z*)-**3e** (*E*)-**3e**	3	72 : 28	90
6	**1b**	**2b**	 (*Z*)-**3f** (*E*)-**3f**	2.5	69 : 31	75
7	**1b**	**2d**	 (*Z*)-**3g** (*E*)-**3g**	3	74 : 26	49
8	**1b**	$C_6H_5CH_2SH$ **2e**	 (*Z*)-**3h** (*E*)-**3h**	3	67 : 33	60

[a]Determined by ^1H NMR of the crude reaction mixture and confirmed after isolation of pure products. [b]Yields of pure products isolated by column chromatography (hexanes/AcOEt).

Scheme 2. The reaction was initiated by addition of the thiolate anion to give the intermediate **4a** and **4b** which by abstraction of proton to give the desired products **3**.

In conclusion, several (*Z*)-1-organylthio-2-phenylseleno-1-organylalkenes could be selectively prepared starting from thiol and selenoalkynes under solvent-free conditions using KF/Al_2O_3. This regio- and stereocontrolled method is general and can be used for aromatic and aliphatic thiols with reasonable to good yields. This green protocol consists in low consumption of solvent in the overall process, short



Scheme 2.

reaction time, mild reaction conditions and simplicity, with non-aqueous work-up. The catalytic system was re-used up to 4 times with a slight declining in yields.

Acknowledgments

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14. *Preparation of alumina supported potassium fluoride*:[16] To a 100 mL beaker was added alumina (4.0 g of Al_2O_3 90, 0.063-0.200 mm, Merck), KF·$2H_2O$ (6.0 g) and water (10 mL). The suspension was stirred for 1 h at 65 °C, dried at 80 °C for 1 h and for an additional 4 h at 300 °C in an oven and then cooled in a desiccator. The content of KF is about 50% (m/m).
15. *General procedure for the synthesis of 1,2-bis-chalcogeno-alkenes **3***: To a mixture of phenylselenoalkyne **1** (1 mmol) and the appropriate thiol **2** (2 mmol) under N_2 atmosphere, KF/Al_2O_3[14] (0.08 g) was added at room temperature. Then, the temperature was slowly raised to 60 °C. The reaction progress was followed by TLC. After consumption the starting materials (see Table 2), the crude product was filtered off the solid supported catalyst by washing with ethyl acetate (10 mL). The solvent was evaporated under reduced pressure and the residue was purified by column chromatography over silica gel eluting with hexane/ethyl acetate (98:2). (*Z*)- and (*E*)-**3a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ *Z* isomer: 7.13-764 (m, 15H), 7.60 (s, 1H); *E* isomer: 7.08-764 (m, 15H), 7.07 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ *E* + *Z* isomers: 140.5, 138.6, 137.2, 136.1, 135.6, 134.3, 133.6, 133.2, 133.1, 131.0, 130.9, 130.8, 130.4, 129.4, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 126.7, 126.6, 125.9, 125.8; MS *m/z* (rel. int., %) *Z* isomer: 368 (M^+, 36.4), 259 (11.2), 209 (10.8), 178 (100.0); *E* isomer: 368 (M^+, 29.5), 259 (8.3), 209 (13.5), 178 (100.0); HRMS (ESI):

m/z calcd for $C_{20}H_{16}SSe$ $[M + H]^+$: 369.0216; found: 369.0222. (*Z*)- and (*E*)-**3b**: ^1H NMR (300 MHz, $CDCl_3$) δ *Z* isomer: 7.11-758 (m, 14H), 7.51 (s, 1H); *E* isomer: 7.10-7.64 (m, 14H), 7.14 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ *E* + *Z* isomers: 126.6, 126.7, 127.1, 127.5, 128.0, 128.1, 128.3, 128.5, 128.5, 128.6, 128.8, 128.8, 128.9, 129.0, 129.3, 129.4, 129.4, 129.5, 129.6; MS *m/z* (rel. int., %) *Z* isomer: 402 (M^+, 17.4), 259 (31.4), 179 (100.0), 157 (30.0), 77 (54.5); *E* isomer: 402 (M^+, 20.8), 210 (100.0), 77 (32.3); HRMS (ESI): *m/z* calcd for $C_{20}H_{15}ClSSe$ $[M + K - Cl]^+$: 405.9697; found: 405.2175. (*Z*)- and (*E*)-**3c**: ^1H NMR (300 MHz, $CDCl_3$) δ *Z* isomer: 7.12-7.63 (m, 14H), 7.60 (s, 1H); 3.55 (s, 2H); *E* isomer: 7.00-7.63 (m, 14H), 7.03 (s, 1H); 3.92 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ *Z* + *E* isomers: 42.4, 126.6, 127.2, 127.4, 127.8, 128.2, 128.6, 129.1, 129.3, 130.6, 130.8, 133.1, 133.3, 135.7, 136.1. MS *m/z* (rel. int., %) *Z* isomer: 416 (M^+, 15.2), 259 (39.2), 178 (100.0), 157 (42.9); *E* isomer: 416 (M^+, 17.4), 259 (35.2), 178 (100.0), 157 (32.1); HRMS (ESI): *m/z* calcd for $C_{21}H_{17}ClSSe$ $[M + Na - Cl]^+$: 405.0147; found: 405.2218. (*Z*)- and (*E*)-**3d**: ^1H NMR (300 MHz, $CDCl_3$) δ *Z* isomer: 7.14-7.65 (m, 10H); 7.60 (s, 1H); 1.53-1.55 (m, 2H); 1.25-1.31 (m, 20H); 0.88 (t, *J* 7.0, 3H); *E* isomer: 7.11-7.65 (m, 10H); 7.06 (s, 1H); 1.53-1.55 (m, 2H); 1.25-1.31 (m, 20H); 0.88 (t, *J* 7.0, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ *E* + *Z* isomers: 28.1, 29.08, 29.1, 29.12, 29.16, 29.26, 29.31, 29.33, 29.38, 29.55, 29.58, 29.61, 29.65, 126.6, 127.2, 127.5, 127.6, 127.7, 127.8, 128.0, 128.1, 128.2, 128.7, 128.8, 129.1, 129.2, 129.4, 130.8, 133.2, 133.6, 134.3, 136.0, 138.6, 140.5. MS *m/z* (rel. int., %) *Z* isomer: 304 (M^+ - C_6H_5Se, 32.5), 136 (100.0), 91 (29.7); HRMS (ESI): *m/z* calcd for $C_{26}H_{36}SSe$ $[M + H - S]^+$: 429.2060; found: 429.3037. (*Z*)- and (*E*)-**3e**: ^1H NMR (300 MHz, $CDCl_3$) δ *Z* isomer: 7.54-7.58 (m, 3H); 7.21-7.43 (m, 7H); 6.82 (s, 1H); 2.22 (t, *J* 7.5, 2H); 1.45-1.54 (m, 2H); 1.11-1.25 (m, 4H); 0.84 (t, *J* 7.0, 3H); *E* isomer: 7.54-7.58 (m, 3H); 7.21-7.43 (m, 7H); 6.56 (s, 1H); 2.25 (t, *J* 7.5, 2H); 1.45-1.54 (m, 2H); 1.11-1.25 (m, 4H); 0.84 (t, *J* 7.0, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ *Z* isomer: 14.0, 22.4, 28.1, 31.0, 37.7, 126.7, 128.5, 129.0, 129.1, 129.2, 130.2, 131.0, 132.8, 133.8, 135.9; *E* isomer: 14.0, 22.4, 28.2, 30.9, 37.1, 126.4, 128.8, 129.1, 129.2, 129.7, 130.5, 131.2, 132.9, 134.3, 136.4. MS *m/z* (rel. int., %) *Z* isomer: 362 (M^+, 46.3), 252 (19.0), 77 (76.0), 43 (100.0); *E* isomer: 362 (M^+, 7.55), 205 (7.73), 147 (100.0), 135 (57.5); HRMS (ESI): *m/z* calcd. for $C_{19}H_{22}SSe$ $[M + H]^+$: 363.0686; found: 363.0672. (*Z*)- and (*E*)-**3f**: ^1H NMR (300 MHz, $CDCl_3$) δ *Z* isomer: 7.21-7.62 (m, 9H), 6.85 (t, *J* 1.0, 1H), 2.21 (dt, *J* 1.0 and 7.5, 2H), 1.49 (qui, *J* 7.5, 2H), 1.17-1.32 (m, 4H), 0.84 (t, *J* 7.5, 3H); *E* isomer: 7.21-7.62 (m, 9H), 6.50 (t, *J* 1.0, 1H), 2.22 (dt, *J* 1.0 and 7.5, 2H), 1.60 (qui, *J* 7.5, 2H), 1.17-1.32 (m, 4H), 0.85 (t, *J* 7.5, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ *Z*+*E* isomers: 13.9, 22.3, 22.4, 28.0, 28.1, 30.9, 31.0, 37.0, 37.7, 127.5, 128.5, 129.0, 129.1, 129.2, 129.7, 130.9, 131.2, 131.6, 132.7, 132.8, 135.0, 135.1; MS *m/z* (rel. int., %) *Z* isomer: 396 (M^+, 34.8), 253 (10.5), 77 (51.7), 43 (100.0); *E* isomer: 396 (M^+, 27.8), 209 (15.0), 147 (44.3), 77 (53.6), 43 (100); HRMS (ESI): *m/z* calcd. for $C_{19}H_{21}ClSSe$ $[M + H - Cl]^+$: 360.0615; found: 360.2335. (*Z*)- and (*E*)-**3g**: ^1H NMR (300 MHz, $CDCl_3$) δ *Z* isomer: 7.50-7.57 (m, 2H); 7.25-7.32 (m, 3H); 6.93 (t, *J* 1.0, 1H); 2.28 (td, *J* 7.5 and 1.0, 2H); 1.43-1.55 (m, 4H); 1.17-1.26 (m, 24H); 0.83 (t, *J* 7.0, 6H); *E* isomer: 7.49-7.58 (m, 2H); 7.23-7.34 (m, 3H); 6.04 (s, 1H); 2.68 and 2.72 (2t, *J* 7.5, 2H); 1.43-1.68 (m, 4H); 1.17-1.26 (m, 24H); 0.88 (t, *J* 7.0, 3H); 0.83 (t, *J* 7.0, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ *Z* + *E* isomer: 14.0, 14.1, 22.3, 22.7, 28.6, 29.2, 29.3, 29.4, 29.5, 29.6, 29.61, 29.62, 29.64, 29.68, 29.7, 30.9, 31.2, 31.9, 39.9, 127.2, 127.3, 127.8, 129.1, 129.2, 129.5, 131.2, 132.6, 132.9, 136.4; MS *m/z* (rel. int., %) *Z* isomer: 454 (M^+, 21.5), 252 (13.6), 91 (91.4), 55 (100.0); *E* isomer: 454 (M^+, 22.5), 252 (15.0), 91 (50.7), 55 (100.0); HRMS (ESI): *m/z* calcd. for $C_{25}H_{42}SSe$ $[M + Na - S]^+$: 443.2357; found: 443.3385. (*Z*)- and (*E*)-**3h**: ^1H NMR (300 MHz, $CDCl_3$) δ *Z* isomer: 7.19-7.50 (m, 10H); 6.56 (s, 1H); 3.58 (s, 2H); 2.22 (t, *J* 7.5, 2H); 1.45-1.58 (m, 2H); 1.17-1.32 (m, 4H); 0.87 (t, *J* 7.0, 3H); *E* isomer: 7.19-7.50 (m, 10H); 6.14 (s, 1H); 4.0 (s, 2H); 2.42 (t, *J* 7.5, 2H); 1.45-1.58 (m, 2H); 1.17-1.32 (m, 4H); 0.89 (t, *J* 7.0, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ *Z*+*E* isomers: 14.0, 22.4, 28.0, 28.4, 31.1, 31.2, 35.4, 36.5, 37.9, 43.2, 125.7, 126.4, 127.0, 127.2, 127.3, 128.3, 128.4, 128.5, 128.7, 128.8, 129.1, 129.3, 130.6, 131.3, 132.5, 132.8, 136.7, 137.3, 137.7; MS *m/z* (rel. int., %) *Z* isomer: 376 (M^+, 9.6), 205 (8.0), 147 (18.6), 91 (100.0); *E* isomer: 376 (M^+, 7.6), 204 (6.8), 147 (16.7), 91 (100); HRMS (ESI): *m/z* calcd. for $C_{20}H_{24}SSe$ $[M + K]^+$: 413.0409; found: 413.2725.

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