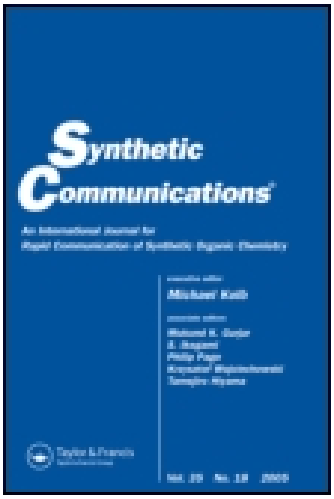

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Metal Triflate-Catalyzed Se-Se Bond Cleavage and the Selective Additions Under Mild Conditions

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METAL TRIFLATE–CATALYZED Se-Se BOND CLEAVAGE AND THE SELECTIVE ADDITIONS UNDER MILD CONDITIONS

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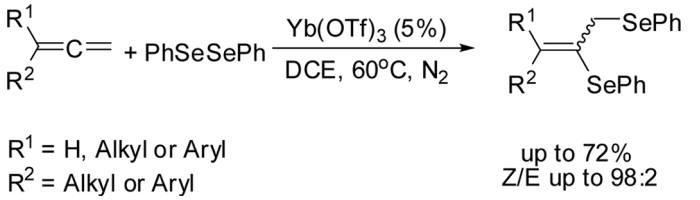
GRAPHICAL ABSTRACT



Abstract *Metal triflate–catalyzed Se-Se bond cleavage would generate selenyl cations, which could add to activated C=C double bond selectively. The reaction conditions were mild and could be easily handled. The cleavage of Se-Se bond in this novel way under mild conditions might expand the view of organic synthesis and facilitate new synthetic strategies.*

Keywords Allenes; electrophilic addition; regioselectivity; selenium; stereoselectivity

Selenium-containing organic compounds have attracted chemists' attention for a long period because of their wide applications in organic synthesis and their activity in bioorganic chemistry.[1] Ordinarily, the free radical additions or transition metal–catalyzed additions of diphenyldiselenide to unsaturated organic compounds are convenient methods of introducing selenium atoms.[2] Besides these methods, recently we have found that Lewis acids could also catalyze Se-Se bond cleavage. Because of the totally different mechanisms, the Lewis acid–catalyzed additions of diphenyldiselenide might bring quite different results. The Lewis acid–catalyzed addition of diphenyldiselenide to methylenecyclopropanes (MCPs) leads to cyclobutane-1,1-diylbis(phenylselane) derivatives,[3] which are different from the products of free radical addition (Scheme 1).[2h,2k] Encouraged by previous works, we are interested in investigating the Lewis acid–catalyzed additions of diphenyldiselenide to other activated olefins.

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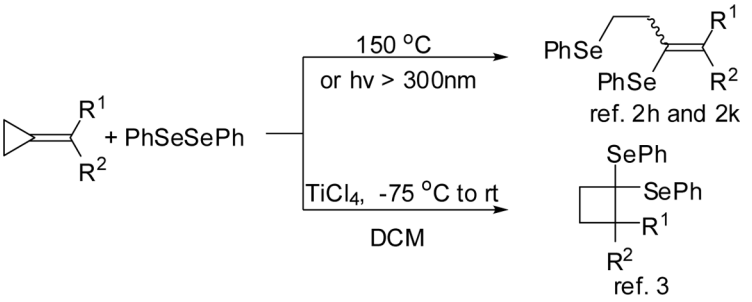
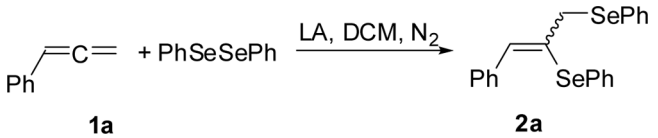


Scheme 1. Reaction of MCPs with PhSeSePh under different conditions.

Allenes are a kind of organic compounds that have attracted attentions from chemists for years.[4] Containing cumulated carbon–carbon double bonds, allenes are highly activated and could undergo a variety of reactions with high selectivity under mild conditions. These include electrophilic additions,[5] free radical additions,[6] transition metal–catalyzed reactions,[7] and so on. Herein, we report the Lewis acid–catalyzed addition of diphenyldiselenide to allenes.

We initially investigated the reaction of 1-phenylallene (**1a**) with diphenyldiselenide catalyzed by $TiCl_4$ at $-75\,^{\circ}C$ to rt. However, no desired adduct was observed (Table 1, entry 1). Metal triflates are a kind of Lewis acids that could catalyze a variety of reactions under mild conditions.[8] Therefore, we tried to employ $Cu(OTf)_2$ as Lewis acid catalyst. After stirring in dichloromethane (DCM) for 9 h, the regioselective 2,3-adduct **2a** could be separated in 21% yield with poor stereoselectivity

Table 1. Addition of PhSeSePh to 1-phenylallene (**1a**) catalyzed by different Lewis acids[a]



1a **2a**

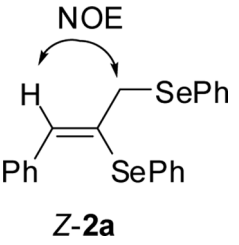
Entry	LA[b]	Temperature	Time (h)[c]	Yield of **2a** (Z/E)[d]
1	$TiCl_4$	$-75\,^{\circ}C$ to rt	Overnight	0
2	$Cu(OTf)_2$	rt	9	21 (63/37)
3	$Zn(OTf)_2$	rt	24	36 (82/18)
4	$Co(OTf)_2$	rt	24	37 (81/19)
5	$Be(OTf)_2$	rt	10	Trace
6	$Mg(OTf)_2$	rt	10	44 (74/26)
7	$Y(OTf)_3$	rt	24	56 (79/21)
8	$Yb(OTf)_3$	rt	30	58 (90/10)
9	$Sm(OTf)_3$	rt	20	58 (78/22)

[a]0.24 mmol of **1a** (20% excess), 0.2 mmol of PhSeSePh, and 1 mL of DCM were employed. The dosage of LA was 0.5 equiv in entry 1 and 0.2 equiv in entries 2 to 9.

[b]LA = Lewis acid.

[c]The reaction was monitored by TLC (eluent: petroleum ether).

[d]Isolated yields based on PhSeSePh. Z/E ratio was calculated from ^{1}H NMR spectrum.



Z-**2a**

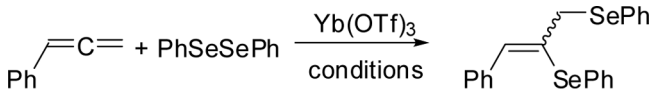
Scheme 2. Configuration of Z-**2a**.

($Z/E = 63/37$, Table 1, entry 2). The configuration of **2a** was established by the nuclear overhauser effect spectroscopy (NOESY) spectrum studies (Scheme 2). Further screening demonstrated that the stereoselectivity could be obviously enhanced when $Zn(OTf)_2$, $Co(OTf)_2$, or $Mg(OTf)_2$ was employed (Table 1, entries 3, 4, and 6). Catalyzed by rare-earth metal triflates, the reaction could be further optimized (Table 1, entries 7–9), especially when $Yb(OTf)_3$ was employed (Table 1, entry 8).

We then tried to examine the $Yb(OTf)_3$-catalyzed reactions under different conditions. The experimental results showed that dichloroethane (DCE) was a better solvent, and the reaction could be further optimized at a higher temperature (Table 2, entries 5–7). The dosage of $Yb(OTf)_3$ could be cut to 5% without the decrease of product yield (Table 2, entries 7–9). The Lewis acid catalyst was essential, and the reaction did not happen in the absence of $Yb(OTf)_3$ (Table 2, entry 10).

Allyl derivatives are important building blocks in organic synthesis.[9] Containing selenium element and an allyl structure unit, 2,3-diphenylselenyl-1-propene

Table 2. Optimization of the reactions catalyzed by $Yb(OTf)_3$[a]

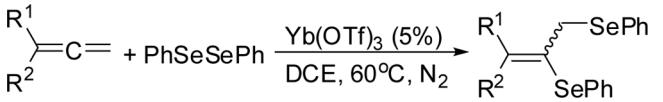


1a **2a**

Entry	Solvent	LA (%)	Temperature (°C)	Time (h)[b]	Yield of **2a** (Z/E)[c]
1	DCM	20	rt	30	58 (90/10)
2	THF	20	rt	24	0
3	Cyclohexane	20	rt	48	21 (80/20)
4	CCl_4	20	rt	50	30 (75/25)
5	DCE	20	rt	36	52 (86/14)
6	DCE	20	40	28	56 (85/15)
7	DCE	20	60	10	63 (80/20)
8	DCE	10	60	10	61 (80/20)
9	DCE	5	60	10	67 (83/17)
10	DCE	0	60	24	NR

[a]0.24 mmol of **1a** (20% excess), 0.2 mmol of PhSeSePh, and 1 mL of solvent were employed.
[b]The reaction was monitored by TLC (eluent: petroleum ether).
[c]Isolated yields based on PhSeSePh. Z/E ratio was calculated from ^{1}H NMR spectrum.

Table 3. Synthesis of 2,3-diphenylselenyl-1-propenes

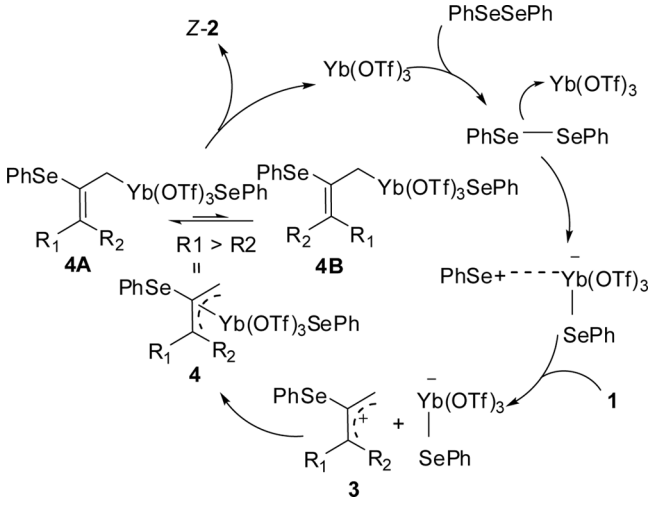


1 2

Entry	R^1, R^2	Yield of **2** (Z/E)[a]
1	H, C_6H_5 (**1a**)	67 (83/17) (**2a**)
2	H, 1-$C_{10}H_7$ (**1b**)	50 (70/30) (**2b**)
3	H, Bn (**1c**)	57 (81/19) (**2c**)
4	H, *c*-C_6H_{11} (**1d**)	55 (75/25) (**2d**)
5	H, *n*-C_5H_{11} (**1e**)	52 (74/26) (**2e**)
6	C_6H_5, C_6H_5 (**1f**)	72 (–) (**2f**)
7	C_2H_5, C_6H_5 (**1g**)	64 (87/13) (**2g**)
8	*c*-C_6H_{11}, C_6H_5 (**1h**)	70 (98/2) (**2h**)

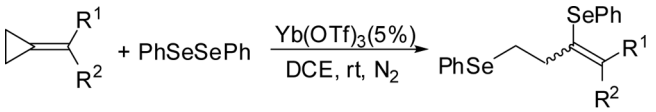
[a]Isolated yields. The configuration of **2** was established by the NOESY spectrum studies as well as Ref. 2i, and the Z/E ratio was calculated from the ^{1}H NMR spectrum.

might be of potential applicable value.[10] Therefore, we then tried to examine the application scope of this reaction. A series of allenes were employed to give the corresponding 2,3-diphenylselenyl-1-propenes, and the results are listed in Table 3. It is notable that the reaction had excellent regioselectivity and only 2,3-adducts were generated. Meanwhile, in most cases, the stereoselectivity of this reaction was high, especially when disubstituted allenes were employed (Table 3, entries 7 and 8). Disulfides have properties similar to diselenides. However, when diaryl disulfide was employed, no reaction was observed.



Scheme 3. Possible mechanism for the $Yb(OTf)_3$-catalyzed addition of PhSeSePh to allenes.

Table 4. Additions of PhSeSePh to MCPs catalyzed by $Yb(OTf)_3$



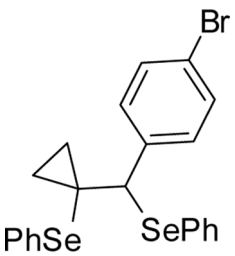
5 **6**

Entry	R^1, R^2	Yield of **6** (Z/E)[a]
1	H, C_7H_{15} (**5a**)	56 (36/64) (**6a**)
2	H, C_9H_{19} (**5b**)	81 (39/61) (**6b**)
3	-$(CH_2)_5$- (**5c**)	30 (–) (**6c**)
4	-$CH_2CH_2CH(Ph)CH_2CH_2$- (**5d**)	24 (–) (**6d**)
5	*p*-BrC_6H_5 (**5e**)	0[b]

[a]Isolated yields. The configuration of **6** was established by the NOESY spectrum studies as well as Ref. 2 h, and the Z/E ratio was calculated from the ^{1}H NMR spectrum.
[b]Compound **7** was obtained (Fig. 1).

On the basis of references as well as the experimental results mentioned previously, here we propose the possible mechanisms. $Yb(OTf)_3$-mediated reaction of diphenyldiselenide with allenes **1** gave the intermediate allylic carbon cation **3** and $Yb(OTf)_3SePh$ anion,[3,11] which could be transformed to the π-allylic metal complex **4**. When $R^1 > R^2$, the intermediate **4A** should be the more stable than **4B**. Further reductive elimination led to **2** with *Z*-configuration as the major product (Scheme 3).

$Yb(OTf)_3$ is an environmentally friendly Lewis acid catalyst that is tolerance to moisture. Compared with the traditional Lewis acid catalysts (e.g., $AlCl_3$, $TiCl_4$, $ZnCl_2$), the dosage of $Yb(OTf)_3$ could be lower. Therefore, we also tried to optimize the Lewis acid–catalyzed addition of diphenyldiselenide to MCPs, reported by us recently,[3] by employing $Yb(OTf)_3$ as catalyst. However, the products were quite different from that of the $TiCl_4$-catalyzed reaction. Instead of the ring-enlarged product cyclobutane-1,1-diylbis(phenylselane) derivatives, ring-opened product 2,4-diphenylselenyl-1-butene derivatives **6** were obtained when alkyl-substituted MCPs were employed (Table 4, entries 1–4). Compared with the reported free radical additions,[2h,2k] the stereoselectivity was slightly higher when unsymmetric MCPs



7, 20%

Figure 1. Structure of compound **7**.

were employed (Table 4, entries 1 and 2). When aryl-substituted MCP **5e** was employed, only cyclopropyl ring intact adduct **7** was obtained in 20% yield (entry 5, Table 4; Fig. 1).

In conclusion, we found that, when catalyzed by $Yb(OTf)_3$, diphenyldiselenide could add to allenes through electrophilic addition, providing a novel and efficient method for the synthesis of 2,3-diphenylselenyl-1-propene derivatives. The mild conditions, the high regio- and stereoselectivities, and the low dosage of the catalyst are the advantages. We also found that when $Yb(OTf)_3$ was employed as Lewis acid catalyst, the products were different from those of the $TiCl_4$-catalyzed addition of diphenyldiselenide to MCPs. The cleavage of Se-Se bond in this novel way under mild conditions will expand the view of organic synthesis and facilitate new synthetic strategies.

EXPERIMENTAL

^1H NMR spectra were recorded on a Bruker Avance (600-MHz) spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. ^{13}C NMR spectra were recorded on a Bruker Avance (150 MHz) spectrometer in $CDCl_3$. Infrared (IR) spectra were recorded on a Shimadzu IR-408 spectrometer. Electron impact mass spectrometry (EIMS) was run on an HP 5989B mass spectrometer.

General Procedure for the $Yb(OTf)_3$-Catalyzed Additions of Diphenyldiselenide to Allenes

In a Schlenk tube, 0.24 mmol of **1**, 0.2 mmol of diphenyldiselenide (62.4 mg), 0.01 mmol of $Yb(OTf)_3$ (5%, 6.2 mg), and 1 mL of 1,2-dichloroethane (DCE) were added. The mixture was stirred at 60 °C under a nitrogen atmosphere and was monitored by thin-layer chromatography (TLC; eluent: petroleum ether). When the reaction terminated, the solvent was evaporated under vacuum. The residue was isolated by preparative TLC (eluent: petroleum ether/EtOAC 20:1) to give the corresponding adduct **2**.

General Procedure for the $Yb(OTf)_3$-Catalyzed Additions of Diphenyldiselenide to MCPs

In a Schlenk tube, 0.24 mmol of **5**, 0.2 mmol of diphenyldiselenide (62.4 mg), 0.01 mmol of $Yb(OTf)_3$ (5%, 6.2 mg), and 1 mL of DCE were added. The mixture was stirred at room temperature under a nitrogen atmosphere and was monitored by TLC (eluent: petroleum ether). When the reaction terminated, the solvent was evaporated under vacuum. The residue was isolated by preparative TLC (eluent: petroleum ether/EtOAC 12:1) to give the corresponding adduct **6** (for substrate **5a**–**5d**) or **7** (for substrate **5e**).

Data

Compound 2a. Oil. IR (film): 3055, 1637, 1578, 1476, 1438, 1022, 913, 738, 691 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.22–7.55 (m, 15H), 6.68 (s, 1H), 3.73 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 38.3, 127.5, 127.6, 127.9, 128.0,

128.6, 128.9(d), 129.2, 129.9, 131.2, 133.5,134.6, 134.7, 137.0. MS (apci): m/z (%) 430 (8) [M^+], 390 (100), 273 (14) [M^+-PhSe].

Compound 2b. Oil. IR (film): 3055, 1657, 1578, 1507, 1475, 1437, 1388, 1067, 1021, 999, 800, 780, 737, 691 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, TMS): (*Z* isomer) δ 7.05–7.82 (m, 18H), 3.86 (s, 2H). (*E* isomer) δ7.05–7.82 (m, 18H), 3.94 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): (*Z* and *E* mixtures) δ 32.2, 36.9, 124.7(d), 125.1, 125.3, 125.8, 126.0, 126.2, 126.9, 127.3, 127.7, 127.9, 128.0, 128.1, 128.4, 128.9, 129.1, 129.5, 131.4, 133.2, 133.6, 134.2, 134.5, 134.7, 134.9. MS (EI, 70 eV): m/z (%) 480 (3) [M^+], 323 (25) [M^+-PhSe], 165 (100). Anal. calcd. for $C_{25}H_{20}Se_2$: C, 62.77; H, 4.21. Found: C, 62.50; H, 4.53.

Compound 2c. Oil. IR (film): 3058, 3026, 2976, 2925, 1476, 1437, 1180, 1121, 1069, 1022, 736, 692 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.00–7.48 (m, 15H), 5.92 (t, $J = 6.6$ Hz, 1H), 3.73 (s, 2H), 3.569 (d, $J = 6.6$ Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 37.8, 38.4, 126.1, 127.2, 127.4, 128.3, 128.4, 128.5(d), 128.9, 129.0, 129.2, 129.3, 132.8, 134.2, 136.3. MS (EI, 70 eV): m/z (%) 444 (3) [M^+], 286 (16) [M^+-PhSe-1], 129 (100).

Compound 2d. Oil. IR (film): 3057, 2976, 2924, 2860, 1578, 1475, 1440, 1411, 1120, 1069, 1022, 736, 690 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, TMS): δ7.24–7.45 (m, 10H), 5.54 (d, $J = 9.0$ Hz, 1H), 3.63 (s, 2H), 2.47–2.48 (m, 1H), 0.95–1.63 (m, 10H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 25.6, 25.9, 32.5, 37.9, 41.0, 126.5, 127.0, 127.4, 128.8, 129.0, 129.2, 132.3, 132.7, 134.6, 144.1. MS (EI, 70 eV): m/z (%) 436 (6) [M^+], 279 (18) [M^+-PhSe], 79 (100).

Compound 2e. Oil. IR (film): 3057, 2955, 2926, 2855, 1578, 1475, 1437, 1067, 1022, 999, 736, 690, 669 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.24–7.47 (m, 10H), 5.76 (t, $J = 6.0$ Hz, 1H), 3.69 (s, 2H), 0.85–2.19 (m, 11H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.0, 22.5, 28.7, 31.3, 32.0, 38.0, 126.9, 127.3, 128.8, 128.9, 129.1, 132.6, 132.7, 134.1, 134.6, 138.6. MS (apci): m/z (%) 425 (100) [$M^+ + 1$], 424 (50) [M^+]. Anal. calcd. for $C_{20}H_{24}Se_2$: C, 56.88; H, 5.73. Found: C, 57.13; H, 5.44.

Compound 2f. Oil. IR (film): 3055, 2978, 2867, 1578, 1476, 1440, 1383, 1123, 1073, 1022, 1000, 763, 737, 697 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 6.98–7.52 (m, 20H), 3.87 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 34.1, 127.1, 127.3, 127.4, 127.6, 127.8, 128.1, 128.8, 129.0, 129.2(d), 129.3, 129.7, 130.1, 131.0, 134.4, 141.1, 143.0, 146.6. MS (EI, 70 eV): m/z (%) 506 (1) [M^+], 349 (27) [M^+-PhSe], 192 (100). Anal. calcd. for $C_{27}H_{22}Se_2$: C, 64.29; H, 4.40. Found: C, 63.94; H, 4.57.

Compound 2g. Oil. IR (film): 3056, 2967, 2930, 2871, 1577, 1476, 1438, 1381, 1180, 1069, 1022, 765, 737, 695 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 6.96–7.52 (m, 15H), 3.66 (s, 2H), 2.71 (q, $J = 7.2$ Hz, 2H), 0.85 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 12.6, 32.8, 35.4, 126.4, 127.0(d), 127.1, 128.1, 128.2, 128.8, 129.2, 130.5, 130.7, 132.5, 134.0, 140.7, 150.9. MS (EI, 70 eV): m/z (%) 458 (3) [M^+], 301 (24) [M^+-PhSe], 143 (100). Anal. calcd. for $C_{23}H_{22}Se_2$: C, 60.54; H, 4.86. Found: C, 60.37; H, 4.60.

Compound 2h. Oil. IR (film): 3055, 2926, 2851, 2361, 2338, 1640, 1577, 1475, 1440, 1384, 1069, 1022, 976, 913, 774, 737, 691 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$,

TMS): δ6.76–7.54 (m, 15H), 3.48 (s, 2H), 3.16 (t, $J = 12$ Hz, 1H), 1.53–1.65 (m, 6H), 1.23–1.28 (m, 2H), 0.90–0.96 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 27.0, 27.5, 32.8, 36.6, 47.3, 128.0, 128.1, 128.3, 128.4, 129.0, 130.0(d), 130.4, 131.7, 132.1, 134.0, 135.5, 140.1, 155.0. MS (EI, 70 eV): m/z (%) 512 (4) [M^+], 355 (36) [M^+-PhSe], 115 (100). Anal. calcd. for $C_{27}H_{28}Se_2$: C, 63.53; H, 5.53. Found: C, 63.38; H, 5.27.

Compound 6a. Oil. IR (film): 2925, 2863, 1636, 1579, 1475, 1438, 1383, 1069, 1022, 735, 691 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): (*E* isomer) δ 7.19–7.42 (m, 10H), 6.07 (t, $J = 7.5$ Hz, 1H), 3.03 (t, $J = 8.4$ Hz, 2H), 2.58–2.63 (m, 2H), 2.02–2.04 (m, 2H), 0.86–1.38 (m, 13H); (*Z* isomer) δ 7.19–7.42 (m, 10H), 5.90 (t, $J = 6.9$ Hz, 1H), 3.04 (t, $J = 7.2$ Hz, 2H), 2.58–2.63 (m, 2H), 2.28–2.31 (m, 2H), 0.86–1.38 (m, 13H). ^{13}C NMR (150 MHz, $CDCl_3$): (*E* and *Z* mixture) δ 14.1, 18.2, 22.7, 26.3, 27.0, 28.5, 29.1, 29.2(d), 29.3, 29.4(d), 29.6, 31.8, 31.9, 33.5, 36.1, 39.9, 126.6, 126.7(d), 126.9, 128.8, 128.9, 129.0(d), 129.1, 130.0, 130.2, 130.6, 131.2, 132.2, 132.3(d), 133.8, 134.5, 137.9, 140.7. MS (EI, 70 eV): m/z (%) 466 (12) [M^+], 309 (45) [M^+-PhSe], 67 (100). Anal. calcd. for $C_{23}H_{30}Se_2$: C, 59.48; H, 6.51. Found: C, 59.17; H, 6.26.

Compound 6b. Oil. IR (film): 3070, 2924, 2853, 1579, 1475, 1437, 1144, 1070, 1022, 1000, 735, 691, 669 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): (*E* isomer) δ 7.19–7.41 (m, 10H), 6.06 (t, $J = 7.5$ Hz, 1H), 3.01–3.04 (m, 2H), 2.59–2.63 (m, 2H), 2.01–2.05 (m, 2H), 1.26–1.36 (m, 14H), 0.86–0.90 (m, 3H). (*Z* isomer) δ 7.19–7.41 (m, 10H), 5.89 (t, $J = 6.9$ Hz, 1H), 3.01–3.04 (m, 2H), 2.59–2.63 (m, 2H), 2.29–2.31 (m, 2H), 1.26–1.36 (m, 14H), 0.86–0.90 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): (*E* and *Z* mixture) δ 14.1, 18.2, 22.7, 26.3, 27.0, 28.4, 29.2, 29.3(d), 29.4, 29.5(d), 29.6(d), 31.9, 33.5, 36.1, 39.9, 126.5, 126.6, 126.7, 126.9, 128.8, 128.9(d), 129.0, 129.1, 130.0, 130.2, 130.5, 131.2, 132.2(d), 132.3, 133.8, 134.5, 137.9, 140.7. MS (EI, 70 eV): m/z (%) 494 (9) [M^+], 337 (45) [M^+-PhSe], 67 (100). Anal. calcd. for $C_{25}H_{34}Se_2$: C, 60.97; H, 6.96. Found: C, 60.79; H, 6.73.

Compound 6c. Oil. IR (film): 3069, 2926, 2851, 1578, 1476, 1438, 1384, 1022, 998, 734, 690, 669 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.20–7.42 (m, 10H), 3.03 (t, $J = 7.8$ Hz, 2H), 2.74 (t, $J = 7.8$ Hz, 2H), 2.56 (t, $J = 5.7$ Hz, 2H), 2.27 (t, $J = 5.7$ Hz, 2H), 1.56–1.57 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.6, 26.7, 28.3, 28.4, 31.3, 35.8, 36.2, 121.8, 126.2, 126.5, 129.0, 129.1, 130.5, 131.0, 132.0, 132.1, 148.9. MS (EI, 70 eV): m/z (%) 436 (11) [M^+], 279 (45) [M^+-PhSe], 79 (100).

Compound 6d. Oil. IR (film): 3058, 2924, 2853, 1631, 1579, 1476, 1437, 1384, 1119, 1068, 1022, 1000, 735, 693, 668 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ7.20–7.44 (m, 15H), 3.36–3.38 (m, 1H), 3.06 (t, $J = 7.2$ Hz, 2H), 2.72–2.82 (m, 4H), 1.99–2.12 (m, 4H), 1.51–1.55 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.8, 30.9, 35.3, 35.5, 35.8, 35.9, 44.4, 122.8, 126.2, 126.3, 126.6, 126.8, 128.4, 129.0, 129.1, 130.4, 131.3, 131.8, 132.2, 146.3, 147.2. MS (EI, 70 eV): m/z (%) 512 (7) [M^+], 355 (27) [M^+-PhSe], 91 (100).

Compound 7. Oil. IR (film): 1638, 1479, 1436, 1385, 1134, 1070, 1015, 913, 740, 691. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.15–7.34 (m, 14H), 4.55 (s, 1H), 1.13–1.39 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): (*E* and *Z* mixture) δ 14.5, 15.6, 27.1, 56.3, 121.0, 127.3, 127.4, 128.7, 128.9, 129.0, 130.1, 130.3, 131.3, 133.3,

133.5, 140.8. MS (EI, 70 eV): m/z (%) 522 (2) [M^+], 365 (29) [M^+-PhSe], 128 (100). HRMS (ESI): m/z calcd. for $C_{22}H_{19}BrNaSe_2$ $(M + Na)^+$ 544.8898, Found 544.8885.

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