Supporting information

Typical experimental procedure

General. All ^{1}H NMR spectra were measured in $CDCl_3$ and recorded on Brucker Avance – 400 (400MHz) spectrometer and all ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on Brucker Avance – 400 (100MHz for ^{13}C) spectrometer or on Brucker Avance – 500 spectrometer (125MHz for ^{13}C) with TMS as the internal standard. Chemical shifts are expressed in ppm and J values are given in Hz. IR spectra were run on a Bruck vector 22 spectrometer. EIMS were determined with a HP5989B mass spectrometer. Melting points are uncorrected. All the reactions in this paper were performed under nitrogen atmosphere. Solvents used in the reaction described here were dried over appropriate drying agents (Na for THF, toluene, CaH_2 for CH_2Cl_2 and P_2O_5 for CH_3CN) and distilled immediately before use. Acetylenic sulfones were prepared by literature method. Aldehydes in liquid state were purified by distillation before use. Aldehydes in solid state were used without further purification.

The tandem reaction of phenylselenomagnesium bromide with acetylenic sulfones and aldehydes. Preparation of 4. General procedure. To a colorless solution of phenylselenomagnesium bromide (0.6mmol) in THF/CH_2Cl_2 (v/v=1:4, 5ml), prepared in situ from phenylmagnesium bromide and powder selenium, was added acetylenic sulfone (0.5mmol) and aldehyde (0.5 mmol) at –20°C with stirring. The reaction mixture turned to a pale yellow solution, which was maintained stirring at -20°C for 50-90min. After the reaction was complete (monitored by TLC), the reaction was quenched with saturated NH_4Cl and

extracted with CH_2Cl_2 (3 × 10ml). The organic phase was washed with saturated brine and dried over $MgSO_4$. After filtration and removal of the solvent in vacuo, crude product was purified with flash chromatography (silica/hexanes - ethyl acetate 8:1 v/v) and the desired tandem adduct **4** was obtained.

(*Z*)–3–phenyl–3–phenylseleno–2–(*p*–tolylsulfonyl)–1–(*p*–chlorophenyl)–2–propenyl alcohol (*Z*-4a): mp 153°C; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.74 (d, 2H, J = 8.3Hz), 7.21 (d, 2H, J = 8.0Hz), 7.10- 6.74 (m, 13H), 6.74 (s, 1H), 5.45 (d, 1H, J = 11.1Hz), 4.32 (d, 1H, 11.4Hz), 2.44 (s, 3H); ^{13}C NMR (125MHz, $CDCl_3$) δ 157.9, 144.6, 139.5, 138.3, 137.5, 137.3, 136.6, 133.1, 129.3, 128.9, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 127.2, 73.3, 21.8; IR (KBr) 3489, 1296, 1136cm^{-1}; mass spectrum, m/e (relative intensity, %) 399 (7.43, M^+ – PhSe, ^{37}Cl), 397 (18.36, M^+ – PhSe, ^{35}Cl), 244 (5.83, M^+ – PhSe – SO_2Tol, ^{37}Cl), 243 (34.18, M^+ – PhSeH – SO_2Tol, ^{37}Cl), 242 (17.97, M^+ – PhSe– SO_2Tol, ^{35}Cl), 241 (100, M^+ – PhSeH– SO_2Tol, ^{35}Cl); Anal. Calcd. For $C_{28}H_{23}ClO_3SSe$: C, 60.71; H, 4.18. Found: C, 60.48; H, 4.30.

(E)–3–phenyl–3–phenylseleno–2–(*p*–tolylsulfonyl)–1–(*p*–chlorophenyl)–2–propenyl alcohol (*E*-4a): mp 173°C; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.61 (d, 2H, J = 7.8Hz), 7.44 (d, 2H, J = 8.5Hz), 7.12 – 7.06 (m, 3H), 6.98 – 6.88 (m, 8H), 6.74 (m, 2H), 6.44 (m, 2H), 4.70 (d, 1H, 10.8Hz), 2.31 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 156.4, 143.6, 140.1, 139.6, 138.4, 137.0, 134.7, 133.5, 129.6, 129.4, 129.0, 128.9, 128.7, 128.6, 127.8, 127.5, 127.3, 126.9, 126.7, 126.6, 74.9, 21.5; IR (KBr) 3487, 1295, 1133cm^{-1}; mass spectrum, m/e (relative intensity, %) 539 (3.67, M^+ – OH, ^{37}Cl), 537 (7.56, M^+ – OH, ^{35}Cl), 399 (6.90, M^+ – PhSe, ^{37}Cl), 397 (16.93, M^+ – PhSe, ^{35}Cl), 243 (33.87, M^+ – PhSe – SO_2Tol, ^{37}Cl), 242 (19.45, M^+ – PhSe– SO_2Tol, ^{35}Cl), 241 (100, M^+ – PhSeH– SO_2Tol, ^{35}Cl); Anal. Calcd. For $C_{28}H_{23}ClO_3SSe$: C, 60.71; H, 4.18. Found: C, 60.97; H, 4.43.

(*Z*)–1,3–diphenyl–3–phenylseleno–2–(*p*–tolylsulfonyl)–2–propenyl alcohol (*Z*–4b): mp 130°C; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.70 (d, 2H, J = 8.2Hz), 7.25–7.18 (m, 7H,), 7.10–6.91 (m, 9H), 6.76 (s, 1H), 5.51 (d, 1H, J = 10.9Hz), 4.35 (d, 1H, J = 11.5Hz), 2.43 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 156.9, 144.2, 140.8, 138.2, 138.1, 137.1, 136.7, 129.1, 128.7, 128.5, 128.2, 128.1, 127.9, 127.1, 125.7, 73.8, 21.7; IR (KBr) 3510, 1299, 1136cm^{-1}; mass spectrum, m/e (relative intensity, %) 503 (10.6, M^+ – OH), 363(21.5, M^+ – PhSe,), 208 (18.38, M^+ – PhSe – SO_2Tol), 207 (100, M^+ – PhSeH – SO_2Tol); Anal. Calcd. For $C_{28}H_{24}O_3SSe$: C, 64.73; H, 4.66. Found: C, 64.89;H, 4.78.

(*Z*)–3–phenyl–3–phenylseleno–2–(*p*–tolylsulfonyl)–1–(*p*–methoxyphenyl)–2–propenyl alcohol (*Z*-4c): mp 144°C; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.77 (d, 2H, J = 8.3Hz), 7.22 (d, 2H, J = 8.1Hz), 7.15- 6.91(m, 11H), 6.72 (d, 3H, J = 8.7Hz), 5.45 (d, 1H, J = 11.4Hz), 4.28 (d, 1H, J = 11.8Hz), 3.77 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125MHz, $CDCl_3$) δ 158.9, 156.6, 144.3, 138.5, 138.4, 137.3, 136.8, 133.1, 129.2, 129.0, 128.8, 128.6, 128.2, 128.1, 127.8, 127.0, 113.7, 73.7, 55.5, 21.9; IR (KBr) 3498, 1287, 1136cm^{-1}; mass spectrum, m/e (relative intensity, %) 533 (0.16, M^+ – OH), 393(8.66, M^+ – PhSe,), 238 (18.66, M^+ – PhSe – SO_2Tol), 237 (100, M^+ – PhSeH – SO_2Tol); Anal. Calcd. For $C_{29}H_{26}O_4SSe$: C, 63.38; H, 4.77. Found: C, 63.54; H, 4.60.

(*Z*)–3–phenyl–3–phenylseleno–2–(*p*–tolylsulfonyl)–1–furyl–2–propenyl alcohol (*Z*-4d): mp 135°C; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.73 (d, 2H, J = 8.3Hz), 7.26 (d, 2H, J = 8.1Hz), 7.12 (d, 1H, J = 0.8Hz), 7.06- 6.90 (m, 10H), 6.42 (d, 1H, J = 1.2Hz), 6.33 (dd, 1H, J = 3.1 Hz, 1.7Hz)**,** 5.39 (d, 1H, J = 11.7Hz), 4.61(d, 1H, J = 11.7Hz), 2.44 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 158.4, 153.8, 144.4, 141.9, 137.7, 137.0, 136.4, 135.9, 129.3, 128.7, 128.6, 128.5, 128.4, 128.2, 128.0, 127.6, 110.8, 107.5, 69.8, 21.8; IR (film) 3490, 1304, 1139cm^{-1}; mass

spectrum, m/e (relative intensity, %) 493 (2.5, M^+ – OH), 353 (11.1, M^+ – PhSe,), 198 (15.4, M^+ – PhSe – SO_2Tol), 197 (100, M^+ – PhSeH – SO_2Tol); Anal. Calcd. For $C_{26}H_{22}O_4SSe$: C, 61.29; H, 4.35. Found: C, 61.48; H, 4.38.

(*Z*)–3–phenyl–3–phenylseleno–2–(*p*–tolylsulfonyl)–1–(*n*–butyl)–2–propenyl alcohol (*Z*-4e): mp 71°C; ^{1}H NMR (400MHz, $CDCl_3$) δ 8.20 (d, 2H, J = 8.3Hz), 7.40 (d, 2H, J = 8.1Hz), 7.05- 6.98 (m, 4H), 6.89 – 6.85 (m, 3H), 6.78 (d, 2H, J = 7.7Hz), 6.72 (s, 1H,), 4.28(m, 1H), 3.50 (d, 1H, J = 11.5Hz), 2.49 (s, 3H), 1.95 (m, 1H), 1.80 (m, 1H), 1.17 – 0.95(m, 4H), 0.75 (t, 3H, J = 6.8Hz); ^{13}C NMR(100MHz, $CDCl_3$) δ 153.9, 144.2, 140.1, 138.4, 136.8, 136.7, 129.1, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 73.6, 37.1, 28.1, 22.0, 21.7, 13.8; IR (film) 3529, 1285, 1135cm^{-1}; mass spectrum, m/e (relative intensity, %) 500 (4.0, M^+), 483 (6.78, M^+ – OH), 343 (12.55, M^+ – PhSe,), 257 (49.12, M^+ – PhSe – C_4H_9CHO), 188 (3.54, M^+ – PhSe – SO_2Tol), 187 (22.09, M^+ – PhSeH – SO_2Tol), 91 (100, $PhCH_2^+$); Anal. Calcd. For $C_{26}H_{28}O_3SSe$: C, 62.52; H, 5.65. Found: C, 62.88; H, 5.58.

(*Z*)–3–phenylseleno–2–(*p*–tolylsulfonyl)–1–(*p*–chlorophenyl)–2–heptenyl alcohol (*Z*-4f): mp 122°C; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.71 (d, 2H, J = 8.3Hz), 7.44 (d, 2H, J = 7.0Hz), 7.39 (d, 1H, J = 7.3Hz), 7.33 – 7.20 (m, 8H), 5.93 (d, 1H, J = 10.5Hz), 4.20(d, 1H, J = 10.5Hz), 2.43(s, 3H), 2.37 – 2.25 (m, 2H), 1.32 – 1.28 (m, 2H), 0.92 – 0.89 (m, 2H), 0.58 (t, 3H, J = 7.3Hz); ^{13}C NMR(100MHz, $CDCl_3$) δ 158.8, 144.2, 139.8, 138.3, 137.1, 136.8, 133.2, 129.6, 129.4, 129.1, 128.3, 127.9, 127.8, 127.2, 71.6, 34.8, 31.8, 22.2, 21.6, 13.3; IR (KBr) 3498, 1274, 1145cm^{-1}; mass spectrum, m/e (relative intensity, %) 379 (4.43, M^+ – PhSe, ^{37}Cl), 377 (10.95, M^+ – PhSe, ^{35}Cl), 223 (31.55, M^+ – PhSeH – SO_2Tol, ^{37}Cl), 222 (14.98, M^+ – PhSe– SO_2Tol, ^{35}Cl), 221 (100, M^+ – PhSeH– SO_2Tol, ^{35}Cl); Anal. Calcd. For $C_{26}H_{27}ClO_3SSe$: C, 58.48; H, 5.10. Found: C, 58.23; H, 5.06.

(*Z*)–3–phenylseleno–2–(*p*–tolylsulfonyl)–1–phenyl–2–heptenyl alcohol (*Z*-4g): mp 121°C; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.69 (d, 2H, J = 8.3Hz), 7.46 – 7.22 (m, 10H), 7.17 (d, 2H, J = 12.0Hz), 6.0 (s, 1H), 4.25 (br, 1H), 2.44 (s, 3H), 2.40 – 2.24 (m, 2H), 1.33 –1.25 (m, 2H), 0.93 – 0.85 (m, 2H), 0.57 (t, 3H, J = 7.3Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ 158.2, 144.1, 141.3, 138.3, 137.7, 137.0, 129.5, 129.4, 129.1, 128.3, 128.2, 128.1, 127.3, 125.8, 72.2, 34.8, 31.7, 22.2, 21.6, 13.4;IR (KBr) 3491, 1282, 1131cm^{-1}; mass spectrum, m/e (relative intensity, %) 483 (0.54, M^+ – OH), 343 (15.1, M^+ – PhSe), 188 (15.14, M^+ – PhSe – SO_2Tol), 187 (100, M^+ – PhSeH– SO_2Tol, ^{35}Cl); Anal. Calcd. For $C_{26}H_{28}O_3SSe$: C, 62.52; H, 5.65. Found: C, 62.68; H, 5.42.

(*Z*)–3–phenylseleno–2–(*p*–tolylsulfonyl)–1–(*p*–dimethylaminephenyl–2–heptenyl lcohol (*Z*-4h): mp 56°C; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.75 (d, 2H, J = 8.2Hz), 7.40 – 7.35 (m, 3H), 7.30 – 7.25 (m, 2H), 7.20 – 7.17 (m, 4H), 6.64 (d, 2H, J = 8.7Hz), 5.92 (d, 1H, J = 10.7Hz), 4.20 (d, 1H, J = 10.7Hz), 2.93 (s, 6H), 2.40 (s, 3H), 2.32 – 2.27 (m, 2H), 1.44 – 1.22 (m**,** 2H), 0.93 – 0.90 (m, 2H), 0.58 (t, 3H, J = 7.3Hz); ^{13}C NMR(100MHz, $CDCl_3$) δ 156.6, 150.0, 143.6, 138.7, 138.2, 136.9, 129.4, 129.3, 129.0, 128.9, 128.4, 128.1, 126.7, 112.5, 72.2, 40.7, 34.7, 31.8, 22.2, 21.6, 13.4; IR (KBr) 3504, 1287, 1130cm^{-1}; mass spectrum, m/e (relative intensity, %) 543 (0.74, M^+), 526 (0.28, M^+ – OH), 368 (15.1, M^+ – PhSe – H_2O), 231 (17.78, M^+ – PhSe – SO_2Tol), 230(100, M^+ – PhSeH– SO_2Tol); Anal. Calcd. For $C_{28}H_{33}NO_3SSe$: C, 61.98; H, 6.13; N, 2.58. Found: C, 62.28; H, 6.19; N, 2.82.

(*Z*)–3–phenylseleno–2–(*p*–tolylsulfonyl)–1–furyl–2–heptenyl alcohol (*Z*-4i): mp 111°C; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.65 (d, 2H, J = 8.2Hz), 7.30 – 7.26 (m, 3H), 7.20 – 7.13 (m, 5H), 6.39 (d, 1H, J = 3.2Hz), 6.28 (dd, 1H, J = 3.1Hz, 1.9Hz), 5.80 (s, 1H), 4.52 (br, 1H), 2.32 (s, 3H), 2.25 – 2.21 (m, 2H), 1.29 – 1.21 (m, 2H), 0.92 – 0.85 (m, 2H), 0.52 (t, 3H, J = 7.3Hz);

^{13}C NMR (100MHz, $CDCl_3$) δ 158.9, 153.9, 143.9, 141.9, 137.9, 136.9, 135.4, 129.5, 129.4, 129.0, 128.1, 128.0, 110.8, 107.7, 67.9, 34.6, 31.8, 22.2, 21.6, 13.4; IR (KBr) 3440, 1288, 1135cm^{-1}; mass spectrum, m/e (relative intensity, %) 473 (3.05, M^+ – OH), 333 (7.87, M^+ – PhSe,), 178 (13.5, M^+ – PhSe – SO_2Tol), 177 (100, M^+ – PhSeH – SO_2Tol); Anal. Calcd. For $C_{24}H_{26}O_4SSe$: C, 58.89; H, 5.35. Found: C, 58.68; H, 5.40.

(*Z*)–3–phenylseleno–2–(*p*–tolylsulfonyl)–1–styryl–2–heptenyl alcohol (*Z*-4j): mp 102°C; ^{1}H NMR (400MHz, $CDCl_3$) δ 8.03 (d, 2H, J = 8.2Hz), 7.39 – 7.25 (m, 12H), 6.64 (d, 1H, J = 15.8Hz), 6.35 (dd, 1H, J = 15.9Hz, 5.3Hz), 5.47 (dd, 1H, J = 9.3Hz, 5.3Hz), 4.02 (d, 1H, J = 10.1Hz), 2.41 – 2.29 (m, 5H), 1.42 – 1.34 (m, 2H), 1.01 – 0.96 (m, 2H), 0.62 (t, 3H, J = 7.3Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ 157.5, 144.2, 138.6, 137.0, 136.8, 136.3, 131.2, 129.7, 129.5, 129.4, 129.3, 128.6, 128.2, 128.0, 127.9, 126.7, 71.9, 34.6, 31.9, 22.3, 21.7, 13.4; IR (film) 3440, 1302, 1143cm^{-1}; mass spectrum, m/e (relative intensity, %) 509 (10.83, M^+ – OH), 369(10.03, M^+ – PhSe,), 214 (16.22, M^+ – PhSe – SO_2Tol), 213 (100, M^+ – PhSeH – SO_2Tol); Anal. Calcd. For $C_{28}H_{30}O_3SSe$: C, 63.99; H, 5.75. Found: C, 64.16, H, 5.90.

(*Z*)–3–phenylseleno–2–(*p*–tolylsulfonyl)–1–(*p*–chlorophenyl)–2–octylenyl alcohol (*Z*-4k): mp 133°C; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.72 (d, 2H, J = 8.3Hz), 7.44 – 7.38 (m, 3H), 7.32 – 7.20 (m, 8H), 5.94 (s, 1H), 3.78 (br, 1H), 2.42 (s, 3H), 2.34 – 2.25 (m, 2H), 1.31 – 1.27 (m, 2H), 1.01 - 0.95(m, 2H), 0.84 – 0.79 (m, 2H), 0.69 (t, 3H, J = 7.2Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ 159.05, 144.4, 139.9, 138.3, 137.1, 136.9, 133.2, 129.7, 129.5, 129.2, 128.4, 128.0, 127.9, 127.3, 71.7, 35.1, 31.3, 29.6, 22.0, 21.7, 13.9; IR (KBr) 3498, 1276, 1143cm^{-1}; mass spectrum, m/e (relative intensity, %) 533 (1.72, M^+ – OH, ^{37}Cl), 531 (3.35, M^+ – OH, ^{35}Cl), 393 (6.33, M^+ – PhSe, ^{37}Cl), 391 (16.27, M^+ – PhSe, ^{35}Cl), 238 (5.64, M^+ – PhSe – SO_2Tol, ^{37}Cl), 237 (32.99, M^+ – PhSeH– SO_2Tol, ^{35}Cl), 236 (17.63, M^+ – PhSe – SO_2Tol, ^{37}Cl), 235

(100, M^+ – PhSeH– SO_2Tol, ^{35}Cl); Anal. Calcd. For $C_{27}H_{29}ClO_3SSe$: C, 59.18; H, 5.33. Found: C, 59.02; H, 5.37.

(*Z*)–3–phenylseleno–2–(*p*–tolylsulfonyl)–1–phenyl–2–octylenyl alcohol (*Z*-4l): mp 113°C; ^1H NMR (400MHz, $CDCl_3$) δ 7.69 (d, 2H, J = 8.3Hz), 7.42 – 7.21 (m, 10H), 7.17 (d, 2H, J = 8.1Hz), 6.0 (s, 1H), 4.24 (s, 1H), 2.40 (s, 3H), 2.38 – 2.24 (m, 2H), 1.32 –1.28 (m, 2H), 1.00 – 0.94 (m, 2H), 0.85 – 0.78 (m, 2H), 0.68 (t, 3H, J = 7.20Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ 158.2, 144.0, 141.3, 138.3, 137.7, 137.0, 129.4, 129.3, 129.1, 128.3, 128.2, 128.1, 127.3, 125.8, 72.1, 35.1, 31.2, 29.4, 22.0, 21.6, 13.8;;IR (KBr) 3489, 1278, 1134cm^{-1}; mass spectrum, m/e (relative intensity, %) 497 (0.39, M^+ – OH), 357 (15.01, M^+ – PhSe), 202 (16.83, M^+ – PhSe – SO_2Tol), 201 (100, M^+ – PhSeH– SO_2Tol); Anal. Calcd. For $C_{27}H_{30}O_3SSe$: C, 63.15; H, 5.89. Found: C, 63.38; H, 5.68.

(*Z*)–3–phenylseleno–2–(*p*–tolylsulfonyl)–1–(*p*–methoxyphenyl)–2–octylenyl alcohol (*Z*-4 m): colorless oil; ^1H NMR (400MHz, $CDCl_3$) δ 7.74 (d, 2H, J = 8.1Hz), 7.41 – 7.37 (m, 3H), 7.31 – 7.25 (m, 4H), 7.20 (d, 2H, J = 8.3Hz), 6.81 (d, 2H, J = 8.7Hz), 5.95 (d, 1H, J = 10.5Hz), 4.24 (d, 1H, J = 10.5Hz), 3.80 (s, 3H), 2.41 (s, 3H), 2.32 – 2.25 (m, 2H), 1.32 – 1.28 (m, 2H), 1.00 – 0.95 (m, 2H), 0.85 – 0.80 (m, 2H), 0.68 (t, 3H, J = 7.2Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ 157.9, 156.6, 142.9, 137.4, 136.7, 135.9, 132.4, 128.4, 128.3, 128.0, 127.1, 127.0, 126.0, 112.7, 70.9, 54.3, 34.0, 30.2, 28.4, 20.9, 20.6, 12.8; IR (film) 3500, 1294, 1131cm^{-1}; mass spectrum, m/e (relative intensity, %) 527 (9.73, M^+ – OH), 387 (5.27, M^+ – PhSe), 369 (57.79, M^+ – PhSe – H_2O), 232 (13.83, M^+ – PhSe – SO_2Tol), 231 (80.25, M^+ – PhSeH– SO_2Tol,), 213 (100, M^+ – PhSe – SO_2Tol – H_2O); Anal. Calcd. For $C_{28}H_{32}O_4SSe$: C, 61.87; H, 5.93. Found: C, 61.75; H, 5.97.

(*Z*)–3–phenylseleno–2–(*p*–tolylsulfonyl)–1–furyl–2–octylenyl alcohol (*Z*-4n): mp 100°C;

^{1}H NMR (400MHz, $CDCl_3$) δ 7.74 (d, 2H, J = 8.3Hz), 7.43-7.33 (m, 3H), 7.29-7.23 (m, 5H), 6.49 (d, 1H, J = 2.2Hz), 6.37 (dd, 1H, J = 2.8Hz, 1.6Hz), 5.88 (d, 1H, J=10.1Hz), 4.64 - 4.0 (m, 1H), 2.42 (s, 3H), 2.32 –2.28 (m, 2H), 1.37 – 1.33 (m, 2H), 1.03 – 0.99 (m, 2H), 0.91 –0.88 (m, 2H), 0.71 (t, 3H, J = 7.2Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ 159.0, 153.9, 144.0, 141.9, 137.9, 136.9, 135.4, 129.5, 129.4, 129.0, 128.1, 128.0, 110.8, 107.7, 67.6, 34.9, 31.2, 29.5, 22.0, 21.7, 13.8; IR (KBr) 3442, 1286, 1139cm^{-1}; mass spectrum, m/e (relative intensity, %) 487 (0.87, M^+ – OH), 347 (8.0, M^+ – PhSe,), 192 (14.43, M^+ – PhSe – SO_2Tol), 191 (100, M^+ – PhSeH – SO_2Tol); Anal. Calcd. For $C_{25}H_{28}O_4SSe$: C, 59.63; H, 5.61. Found: C, 59.46; H, 5.57.

(*Z*)–3–phenylseleno–2–(*p*–tolylsulfonyl)–1–styryl–2–octylenyl alcohol (*Z*-4o): mp 89°C; ^{1}H NMR (400MHz, $CDCl_3$) δ 8.03 (d, 2H, J = 8.2Hz), 7.38 – 7.21 (m, 12H), 6.63 (d, 1H, J = 15.9Hz), 6.35 (dd, 1H, J = 15.9Hz, 5.2Hz), 5.51 – 5.50 (m, 1H), 4.11 (d, 1H, J = 9.6Hz), 2.37 – 2.32 (m, 5H), 1.41 – 1.36 (m, 2H), 1.02 – 0.87 (m, 4H), 0.69 (t, 3H, J = 7.2Hz); ^{13}C NMR(100MHz, $CDCl_3$) δ 157.9, 144.2, 138.6, 137.0, 136.8, 136.4, 131.0, 129.8, 129.5, 129.4, 129.3, 128.6, 128.1, , 127.9, 126.7, 71.8, 34.8, 31.3, 29.7, 22.1, 21.7, 13.9; IR (film) 3443, 1300, 1145cm^{-1}; mass spectrum, m/e (relative intensity, %) 523 (12.87, M^+ – OH), 383 (3.81, M^+ – PhSe,), 365 (15.53, M^+ – PhSe – H_2O), 227 (17.73, M^+ – PhSeH – SO_2Tol), 209 (100, M^+ – PhSeH – SO_2Tol – H_2O); Anal. Calcd. For $C_{29}H_{32}O_3SSe$: C, 64.55; H, 5.98. Found: C, 64.36; H, 5.85.

(*Z*)–3–phenylseleno–2–(*p*–tolylsulfonyl)–1– (*n*–butyl)–2–octylenyl alcohol (*Z*-4p): colorless oil; ^{1}H NMR (400MHz, $CDCl_3$) δ 8.06 (d, 2H, J = 8.3Hz), 7.35 – 7.31(m, 3H), 7.27 – 7.20 (m, 4H), 4.71 – 4.66 (m, 1H), 3.62 (d, 1H, J = 11.1Hz), 2.45 (s, 3H), 2.29 – 2.13 (m, 3H), 1.85 – 1.74 (m, 1H), 1.42 – 1.31 (m, 6H), 1.15 – 1.04 (m, 2H), 1.08 – 0.88 (m, 5H), 0.75

(t, 3H, J = 7.6Hz);^{13}C NMR(100MHz, $CDCl_3$) δ 154.6, 143.9, 139.8, 138.8, 136.6, 129.2, 129.0, 128.1, 72.3, 37.6, 34.6, 31.3, 29.5, 28.7, 22.4, 22.0, 21.6, 14.0, 13.8; IR (film) 3519, 1285, 1132cm^{-1}; mass spectrum 477(20.99, M^+ – OH), 337 (7.66, M^+ – PhSe), 182 (6.75, M^+ – PhSe – SO_2Tol), 181 (42.19, M^+ – PhSeH – SO_2Tol), 91 (100, $PhCH_2^+$); Anal. Calcd. For $C_{25}H_{34}O_3SSe$: C, 60.84; H, 6.94. Found: C, 60.58; H, 7.08.

General procedure for the synthesis of (1*E*, 3*E*)–2–(*p*–tolylsulfonyl)–3–phenylselenoocta –1, 3–dienes 5 from 4k. $BF_3{\cdot}Et_2O$ (0.5mmol) was added to Ac_2O (1ml) solution of **4k** (0.26g, 0.5mmol) at 0°C. The mixture was stirred for 20min and poured into $CHCl_3$ (15ml). The organic layer was washed with a saturated $NaHCO_3$ and dried over $MgSO_4$. The solvent was removed in vacuo. The residue was purified by preparative TLC on silica gel (hexanes/ethyl acetate = 10:1) to afford **5** as colorless crystal (254mg, 96%). mp 89°C. ^{1}H NMR (400MHz, $CDCl_3$) δ 7.83 (d, 2H, J = 8.2Hz), 7.68 (s, 1H), 7.49–7.45 (m, 4H), 7.32–7.19 (m, 7H), 5.79 (t, 1H, J = 7.3Hz), 2.43 (s, 3H), 1.64–1.42 (m, 2H), 0.96–0.87 (m, 4H), 0.65 (t, 3H, J = 7.0Hz); IR (KBr) 1280, 1149cm^{-1}; mass spectrum, m/e (relative intensity, %) 530 (2.86, M^+, ^{35}Cl), 373 (10.29, M^+ – PhSe, ^{35}Cl), 219 (34.36, M^+ – PhSeH – SO_2Tol, ^{37}Cl), 217 (100, M^+ – PhSeH – SO_2Tol, ^{35}Cl); Anal. Calcd. For $C_{27}H_{27}ClO_2SSe$: C, 61.19; H, 5.13. Found: C, 61.35; H, 5.38.