Supplementary Material

Radical-Mediated 5-*exo*-Trig Cyclizations of 3-Silylhepta-1,6-dienes

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General Methods.

^1H NMR and ^{13}C NMR were recorded at 250 and 62.9 MHz respectively or at 300 and 75.5 MHz respectively; other ^1H NMR spectrums were also recorded at 400 MHz. CDCl_3 was used as internal reference unless otherwise indicated. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz respectively. Infrared (IR) spectra were obtained using a FTIR spectrophotometer. Data are presented as frequency of absorption (cm^{-1}). Melting points were not corrected. Flash chromatography was performed employing 230-400 mesh silica gel.

CH_2Cl_2 , Et_3N , $(i\text{-Pr})_2\text{NH}$ were distilled from CaH_2 . Benzene was distilled from sodium and THF, hexane and Et_2O were distilled from sodium and benzophenone. Chlorosilanes were distilled from magnesium. Photochemical reactions used a 300 W sunlamp or a middle pressure mercury lamp.

Dimethylphenyl-(1-vinylpent-4-enyl)-silane 3a. To a suspension of $\text{CH}_3\text{PPh}_3\text{Br}$ (2.690 g, 7.53 mmol) in THF (53 mL) under nitrogen atmosphere was added LiHMDS (preparation: A 2.5 M solution of $n\text{-BuLi}$ in hexane (2.7 mL, 6.72 mmol) was added dropwise at $-78\text{ }^\circ\text{C}$ to hexamethyldisilazane (1.5 mL, 7.06 mmol) in THF (7 mL). After the addition, the temperature was allowed to warm to $0\text{ }^\circ\text{C}$ and was stirred for 15 min at this temperature before use). The resulting yellow mixture was stirred at room temperature for 15 min before being cooled to $0\text{ }^\circ\text{C}$, and to which was added a solution of 4-(dimethylphenylsilyl)-hex-5-enal¹ (781 mg, 3.36 mmol) in THF (8 mL). The reaction mixture was kept at $0\text{ }^\circ\text{C}$ for 15 min and was then quenched with saturated aqueous NH_4Cl . The mixture was extracted with pentane and the organic layers were combined and washed

¹ James, P.; Felpin, F.-X.; Landais, Y.; Schenk, K. *J. Org. Chem.* **2005**, *70*, 7985-7995.

with brine, dried with MgSO_4 . Removal of solvent under reduced pressure followed by flash chromatography (Petroleum ether) afforded **3a** as a colorless oil (93 %, 717 mg). IR (neat) $\nu = 3070$, 2958, 2925, 2849, 1639, 1624, 1427, 1248, 1114, 997, 896, 833, 812, 774, 730, 699, 654 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) $\delta = 7.50$ (m, 2 H), 7.35 (m, 3 H), 5.73 (ddd, $J = 10.1, 7.0, 6.3$, 1 H), 5.58 (ddd, $J = 17.1, 10.4, 9.5$, 1 H), 4.99-4.87 (m, 2 H), 4.83 (ddd, $J = 17.1, 2.1, 0.9$, 2 H), 2.11 (m, 2 H), 1.85 (m, 1 H), 1.45 (m, 2 H), 0.28 (s, 3 H), 0.27 (s, 3 H). ^{13}C NMR (CDCl_3 , 75.5 MHz) $\delta = 139.4$, 138.8, 137.7, 134.1, 128.9, 127.6, 114.5, 112.9, 33.8, 33.2, 27.8, -4.5, -5.3. Anal. calcd. for $\text{C}_{15}\text{H}_{22}\text{Si}$ C, 78.19; H, 9.62. Found C, 77.79; H, 9.72.

2-Allyl-3-(dimethyl-phenyl-silyl)-pent-4-enoic acid methyl ester 3b. A solution of DIPA (729 μL , 5.2 mmol) in freshly distilled THF (5.7 mL) at -78°C was treated with a 2.5 M solution of *n*-BuLi in hexanes (2.1 mL, 5.2 mmol) under nitrogen atmosphere. The solution was brought to 0°C for 10 min and then recooled to -78°C . A solution of 3-(dimethyl-phenyl-silyl)-pent-4-enoic acid methyl ester¹ (1 g, 4.0 mmol) in THF (1.5 mL) was added via syringe to the cooled solution (-78°C) of LDA. The light yellow solution was stirred for 30 min and allylbromide (692 μL , 8.0 mmol) in THF (1 mL) was added. The reaction mixture was allowed to warm slowly to room temperature and stirred for 10 h before being diluted with saturated NH_4Cl . The mixture was extracted with EtOAc. The combined organic layers were washed with saturated brine and dried over MgSO_4 , filtered and the solvent was removed under vacuum to afford crude product, which was then purified by flash chromatography (Petroleum ether/EtOAc 95/5) to give **3b** as a colorless oil (1.007 g, 88 %). IR (neat) $\nu = 3071$, 2950, 1735, 1640, 1625, 1428, 1358, 1249, 1193, 1171, 1148, 1113, 997, 911, 835,

814, 775, 735, 701, 656 cm^{-1} . ^1H NMR (250 MHz, CDCl_3) δ = 7.53 (m, 2 H), 7.37 (m, 3 H), 5.75-5.45 (m, 2 H), 5.05-4.85 (m, 4 H), 3.40 (s, 3 H), 2.59 (ddd, J = 10.1, 9.5, 4.0, 1 H), 2.40-2.15 (m, 3 H), 0.36 (s, 3 H), 0.31 (s, 3 H). ^{13}C NMR (62.9 MHz, CDCl_3) δ = 174.8, 136.9, 136.2, 135.4, 134.2, 130.0, 127.5, 116.4, 115.1, 50.8, 45.5, 37.1, 36.1, -3.6, -4.6. MS (FAB+): m/z (%) = 311 ($\text{M}+\text{Na}^+$, 23), 288 (M^+ , 50), 247 (100), 211 (98). HRMS (FAB+): calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_2\text{Si} + \text{Na}^+$ 288.1545. Found 288.1541.

5-(dimethylphenylsilyl)-hepta-1,6-dien-3-ol 3c. To a solution of $(\text{COCl})_2$ (5.4 mL, 60.5 mmol) in CH_2Cl_2 (400 mL) at -78°C was added DMSO (7.6 mL, 144 mmol). The resulting mixture was stirred at -78°C for 30 min before a solution of 3-(dimethyl(phenyl)silyl)pent-4-en-1-ol² (10.43 g, 47.3 mmol) in CH_2Cl_2 (80 mL) was added. The reaction mixture was kept at -78°C for another 30 min and Et_3N (33 mL, 237 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for 1 h before being quenched with H_2O . The aqueous layer was extracted with CH_2Cl_2 . The organic layers were combined and washed with brine, dried over MgSO_4 . Removal of the solvent under reduced pressure and purification by chromatography (Petroleum ether/EtOAc 96/4) afforded 3-(dimethyl(phenyl)silyl)pent-4-enal as a colorless oil (90 %, 9.3 g). IR (neat) ν = 3070, 2957, 2899, 2812, 2715, 1723, 1626, 1427, 1409, 1250, 1114, 1020, 998, 900, 835, 814, 778, 735, 700, 654 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ = 9.61 (dd, J = 2.6, 1.5, 1 H), 7.53 (m, 2 H), 7.39 (m, 3 H), 5.80 (ddd, J = 17.7, 10.2, 7.5, 1 H), 5.01 (d, J = 10.2, 1 H), 4.85 (d, J = 17.0, 1 H), 2.55-2.35 (m, 3 H), 0.36 (s, 3 H), 0.34 (s, 3 H). ^{13}C NMR (CDCl_3 , 62.9 MHz) δ = 202.6, 137.3, 136.1, 133.8, 129.3, 127.7, 113.9, 41.8, 27.7, -4.9, -5.7. To a stirred solution of 3-

² Akiyama, T.; Ishida, Y. *Synlett* **1998**, 10, 1150.

(dimethyl(phenyl)silyl)pent-4-enal (1.22 g, 5.59 mmol) in dry THF (50 mL) under a nitrogen atmosphere was added a 1.0 M solution of vinylmagnesium bromide in THF (5.59 mL, 5.6 mmol) at 0 °C. After 2 h stirring, an aqueous solution of NH₄Cl was added. The organic layer was then extracted with ether, washed with brine, dried over MgSO₄, filtered and the solvent was removed under reduced pressure. The reaction mixture contained a 64:36 mixture of the two diastereoisomers **3c/3d**. Separation by flash chromatography (Petroleum ether/EtOAc 9/1) gave both diastereoisomers as colorless oils (670 mg, 49 % global yield **3c** + **3d**). **3c**. IR (neat) ν = 3343, 3070, 2957, 2924, 1624, 1427, 1248, 1114, 994, 896, 839, 814, 783, 731, 699, 654 cm⁻¹. ¹H NMR (CDCl₃, 250 MHz) δ = 7.52 (m, 2 H), 7.39 (m, 3 H), 5.78-5.58 (m, 2 H), 5.17 (m, 1 H), 5.10 (m, 1 H), 4.93 (dd, J = 10.4, 1.8, 1 H), 4.87 (ddd, J = 17.1, 1.8, 0.9, 1 H), 4.11 (br q, 1 H), 1.87 (br s, 1 H), 1.85-1.65 (m, 2 H), 1.55 (br ddd, 1 H), 0.31 (s, 3 H), 0.30 (s, 3 H). ¹³C NMR (CDCl₃, 62.9 MHz) δ = 140.1, 139.3, 137.0, 134.0, 129.1, 127.6, 115.7, 113.1, 73.5, 35.5, 31.4, -4.7, -5.5. MS (CI⁺): m/z (%) = 264 (MH⁺+NH₃, 4), 247 (M+H⁺, 6), 233 (5), 219 (21), 169 (6), 152 (100), 135 (18), 128 (3), 109 (5), 95 (19), 84 (8), 78 (17), 58 (16).

5-(dimethylphenylsilyl)-hepta-1,6-dien-3-ol 3d. IR (neat) ν = 3394, 3070, 2958, 2924, 1624, 1487, 1427, 1411, 1248, 1113, 997, 919, 895, 843, 813, 776, 731, 700, 655 cm⁻¹. ¹H NMR (CDCl₃, 250 MHz) δ = 7.52 (m, 2 H), 7.39 (m, 3 H), 5.85 (ddd, J = 17.4, 10.7, 5.5, 1 H), 5.65 (dt, J = 17.1, 10.1, 1 H), 5.19 (dt, J = 17.4, 1.5, 1 H), 5.07 (dt, J = 10.7, 1.5, 1 H), 4.99 (dd, J = 10.7, 1.8, 1 H), 4.93 (dd, J = 17.1, 0.9, 1 H), 4.15 (m, 1 H), 2.17 (dt, J = 10.0, 4.9, 1 H), 1.68 (br s, 1 H), 1.57 (m, 2 H), 0.31 (s, 3 H), 0.30 (s, 3 H). ¹³C NMR (CDCl₃, 62.9 MHz) δ = 141.4, 139.0, 137.1, 134.01, 133.95, 129.0, 127.6, 113.8, 113.5, 70.9, 35.7, 30.0, -4.7, -5.3. MS (CI⁺) m/z (%) = 264 (MH⁺+NH₃, 6), 247

(M+H⁺, 9), 229 (6) 186 (3), 169 (14), 152 (100), 135 (34), 123 (3), 112 (6), 95 (61), 78 (16), 58 (5).

Anal. calcd. for C₁₅H₂₂OSi C, 73.11; H, 9.00. Found C, 72.86; H, 8.97.

Dimethylphenyl-[3-phenylselenenylmethyl-2-(toluene-4-sulfonylmethyl)-cyclopentyl]-silane 4a.

Following the general procedure, diene **3a** (52.7 mg, 0.23 mmol), *p*-TolSO₂SePh (78 mg, 0.25 mmol) in degassed CH₂Cl₂ (18 mL) were irradiated for 5 h at - 70 °C. After usual treatment, the residue contained a 90:10 mixture of the two regioisomers **4a/5a**. Chromatography (Petroleum ether) afforded **4a** as a pale yellow oil [(**4a+5a**: 72 mg, 58 % overall yield); pure **4a** (65 mg, 52 %)]. IR (neat) ν = 3067, 2925, 2868, 1597, 1578, 1477, 1437, 1428, 1404, 1312, 1301, 1250, 1148, 1114, 1087, 1021, 998, 939, 813, 772, 735, 701, 692, 662, 632 cm⁻¹. ¹H NMR (400 MHz) δ = 7.63 (d, *J* = 8.2 Hz, 2 H), 7.54 (m, 2 H), 7.48-7.20 (m, 10 H), 3.09 (dd, ABX, *J*_{AB} = 11.2, *J*_{BX} = 4.6, $\Delta\nu/J$ = 17, 1 H), 3.07 (dd, ABX, *J*_{AB} = 14.4, *J*_{AX} = 9.2, $\Delta\nu/J$ = 8, 1 H), 2.87 (dd, ABX, *J*_{AB} = 14.4, *J*_{BX} = 4.1, $\Delta\nu/J$ = 8, 1 H), 2.75 (dd, ABX, *J*_{AB} = 11.2, *J*_{AX} = 10.5, $\Delta\nu/J$ = 17, 1 H), 2.55-2.40 (m, 5 H), 1.95-1.84 (m, 1 H), 1.83-1.72 (m, 1 H), 1.67-1.52 (m, 2 H), 1.38-1.29 (m, 1 H), 0.27 (s, 6 H). ¹³C NMR (CDCl₃, 75.5 MHz) δ = 144.4, 137.7, 136.7, 133.9, 132.3, 130.3, 129.7, 129.1, 126.6, 56.3, 41.7, 39.2, 31.5, 28.0, 28.0, 24.5, 21.6, -3.9, -5.4. RMN ⁷⁷Se (CDCl₃, 76.3 MHz) δ = 269.1. MS (FAB⁺): *m/z* (%) = 565 (M+Na⁺, 77), 564 (17), 542 (M⁺, 49), 541 (15), 465 (78), 421 (59), 385 (30), 321 (95), 307 (32), 288 (21), 273 (17), 251 (20), 227 (22), 213 (88), 211 (100). HRMS (FAB⁺): calcd. for C₂₈H₃₄O₂SSeSi 542.1214. Found 542.1203.

Methyl 2-(dimethyl(phenyl)silyl)-4-((phenylselenanyl)methyl)-3-(tosylmethyl)cyclopentane-carboxylate 4b. Following the general procedure, **3b** (300 mg, 1.04 mmol), *p*-TolSO₂-SePh (356 mg, 1.14 mmol) in degassed CH₂Cl₂ (82 mL) were irradiated for 1.3 h. After usual treatment, the crude mixture contained a 77:23 mixture of the two regioisomers **4b/5b**. Chromatography (Petroleum ether/EtOAc 8/2) yielded pure **4b** as a colorless oil (378 mg, 61 %) and pure **5b** as a colorless oil (119 mg, 19 %). IR (neat) ν = 3049, 2950, 2925, 1728, 1596, 1578, 1478, 1436, 1312, 1302, 1257, 1207, 1148, 1113, 1087, 1021, 949, 818, 737, 702, 692, 667 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ = 7.63 (d, *J* = 8.3 Hz, 2 H), 7.48-7.21 (m, 12 H), 3.58 (s, 3 H), 3.11 (dd, *J* = 14.3, 6.8, 1 H), 3.02 (dd, *J* = 14.3, 7.2, 1 H), 2.96 (dd, *J* = 12.0, 6.2, 1 H), 2.75 (m, 1 H), 2.71 (dd, *J* = 9.2, 2.1, 1 H), 2.59 (quint, *J* = 6.4, 1 H), 2.45 (s, 3 H), 2.24 (m, 1 H), 2.01 (t, *J* = 6.8, 1 H), 1.92 (m, 2 H), 0.29 (s, 3 H), 0.28 (s, 3 H). ¹³C NMR (CDCl₃, 75.5 MHz) δ = 177.0, 144.3, 137.0, 136.6, 133.9, 132.4, 129.7, 129.2, 128.9, 127.8, 127.7, 126.7, 55.9, 51.8, 45.5, 42.6, 38.9, 35.6, 33.0, 27.5, 21.5, -4.2, -5.0. MS (FAB⁺): *m/z* (%) = 623 (M+Na⁺, 100), 600 (M⁺, 12), 569 (3), 523 (61), 443 (21), 365 (7), 329 (3), 311 (7), 289 (4), 251 (32). HRMS (ES⁺): calcd. for C₃₀H₃₆O₄SSeSi + Na⁺ 623.1152 . Found 623.1167. Mp (CH₂Cl₂): + 116.8 °C.

4-(Dimethyl-phenyl-silyl)-2-phenylselenenylmethyl-3-(toluene-4-sulfonylmethyl)-cyclopentanol

4c. Following the general procedure, diene **3c** (117 mg, 0.47 mmol), *p*-TolSO₂-SePh (163 mg, 0.52 mmol) in degassed CH₂Cl₂ (37 mL) were irradiated for 5 h. After usual treatment, the crude reaction mixture contained a 85:15 mixture of the two regioisomers **4c/5c**, which were inseparable by chromatography (Petroleum ether/EtOAc 8/2) (228 mg, 87 %). IR (neat) ν = 3516, 3067, 2951, 2923, 1596, 1578, 1477, 1437, 1426, 1403, 1311, 1300, 1250, 1145, 1111, 1086, 1041, 1021, 871,

813, 771, 736, 701, 660 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ = 7.65 (d, J = 8.3, 2 H), 7.43 (m, 4 H), 7.35-7.20 (m, 8 H), 4.06 (m, 1 H), 3.27 (dd, J = 13.9, 4.9, 1 H), 3.19 (dd, J = 13.9, 7.5, 1 H), 2.96 (m, 2 H), 2.67 (m, 1 H), 2.41 (s, 3 H), 2.01 (br s, 1 H), 1.90 (m, 2 H), 1.83 (m, 1 H), 1.71 (m, 1 H), 0.28 (s, 3 H), 0.24 (s, 3 H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 144.3, 137.6, 137.5, 134.0, 132.6, 129.8, 129.8, 129.1, 129.1, 127.8, 127.0, 74.2, 58.9, 48.1, 36.6, 36.0, 28.4, 23.9, 21.6, -4.2, -4.6. ^{77}Se NMR (CDCl_3 , 76.3 MHz) δ = 281.4. MS (FAB+): m/z (%) = 581 ($\text{M}+\text{Na}^+$, 14), 558 (M^+ , 11), 481 (16), 423 (3), 401 (7), 323 (3), 267 (3), 251 (12), 211 (17), 171(9), 149 (51), 135 (100). HRMS (ES+): calcd. for $\text{C}_{28}\text{H}_{34}\text{O}_3\text{SSeSi} + \text{Na}^+$ 581.1058. Found 581.1061.

4-(Dimethyl-phenyl-silyl)-2-phenylselenenylmethyl-3-(toluene-4-sulfonylmethyl)-cyclopentanol

4d. Following the general procedure, diene **3d** (190 mg, 0.77 mmol), *p*-TolSO₂-SePh (264 mg, 0.85 mmol) in degassed CH_2Cl_2 (61 mL) were irradiated for 5 h. After usual treatment, the crude reaction mixture contained a 90:10 mixture of the two regioisomers **4d/5d**. Chromatography (Petroleum ether/EtOAc 9/1 then 8/2) yielded pure **4d** as a pale yellow oil (204 mg, 61 %). IR (neat) ν = 3519, 3067, 2951, 2927, 1596, 1578, 1478, 1427, 1312, 1301, 1250, 1145, 1112, 1085, 1021, 814, 773, 736, 702, 692, 668 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ = 7.58 (d, J = 8.2 Hz, 2 H), 7.52 (m, 2 H), 7.40-7.23 (m, 10 H), 4.25 (m, 1 H), 3.13 (dd, ABX, J_{AB} = 11.6, J_{BX} = 4.9, $\Delta\nu/J$ = 25, 1 H), 2.99 (dd, ABX, J_{AB} = 14.4, J_{AX} = 10.4, $\Delta\nu/J$ = 8, 1 H), 2.79 (dd, ABX, J_{AB} = 14.4, J_{BX} = 3.4 Hz, $\Delta\nu/J$ = 8, 1 H), 2.63 (t, ABX, J_{AB} = 11.4, J_{AX} = 11.4, $\Delta\nu/J$ = 25, 1 H), 2.44 (s, 3 H), 2.35 (m, 1 H), 2.14 (m, 1 H), 1.50 (br s, 1 H), 1.45 (m, 1 H), 1.22 (m, 1 H), 0.21 (s, 6 H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 144.5, 137.5, 136.4, 133.8, 132.4, 129.8, 129.3, 129.2, 128.0, 126.9, 77.8, 55.9, 49.7, 37.2, 34.4, 27.1, 26.4,

21.6, -3.7, -5.7. ^{77}Se NMR (CDCl_3 , 76.3 MHz) δ = 261.3. MS (FAB+): m/z (%) = 581 ($\text{M}+\text{Na}^+$, 33), 558 (M^+ , 30), 481 (25), 323 (22), 281 (23), 251 (100). HRMS (FAB+): calcd. for $\text{C}_{28}\text{H}_{34}\text{O}_3\text{SSeSi}$ 558.1163. Found 558.1152.

Dimethyl-phenyl-[2-phenylselenenylmethyl-3-(toluene-4-sulfonylmethyl)-cyclopentyl]-silane 5a.

Following the general procedure, diene **3a** (110 mg, 0.48 mmol), *p*-TolSO₂SePh (150 mg, 0.48 mmol) and AIBN (8 mg, 0.05 mmol) in degassed benzene (38 mL) were refluxed for 6 h. After usual treatment, the crude reaction mixture contained a 38:62 mixture of the two regioisomers **4a/5a**. Chromatography (Petroleum ether) afforded **5a** a pale yellow oil [**4a+5a** (139 mg, 53 % overall yield), pure **5a** (112 mg, 43 %)]. IR (neat) ν = 2923, 2853, 1597, 1460, 1376, 1314, 1301, 1248, 1144, 1113, 1087, 1021, 815, 770, 735, 700, 665 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ = 7.80 (m, 2 H), 7.47 (m, 2 H), 7.43-7.24 (m, 10 H), 3.30 (dd, ABX, J_{AB} = 14.0, J_{BX} = 4.2, $\Delta\nu/J$ = 9, 1 H), 3.10 (dd, ABX, J_{AB} = 13.9, J_{AX} = 9.5, $\Delta\nu/J$ = 9, 1 H), 2.76 (dd, ABX, J_{AB} = 11.7, J_{BX} = 6.3, $\Delta\nu/J$ = 5, 1 H), 2.64 (dd, ABX, J_{AB} = 11.7, J_{AX} = 8.0, $\Delta\nu/J$ = 5, 1 H), 2.48 (s, 3 H), 2.32 (m, 1 H), 2.25 (m, 1 H), 1.93 (m, 1 H), 1.79 (m, 1 H), 1.68 (m, 1 H), 1.55 (m, 1 H), 1.27 (m, 1 H), 0.27 (s, 6 H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 144.4, 137.8, 136.6, 133.7, 132.4, 129.8, 130.0, 128.9, 128.0, 127.7, 126.8, 55.9, 43.7, 38.0, 30.7, 30.5, 29.5, 25.9, 21.6, -4.2, -4.9. ^{77}Se NMR (CDCl_3 , 76.3 MHz) δ = 268.1. MS (FAB+): m/z (%) = 565 ($\text{M}+\text{Na}^+$, 81), 564 (17), 542 (M^+ , 34), 541 (11), 465 (50), 385 (100), 307 (13), 275 (7), 251 (12), 227 (7), 213 (92), 211 (31). HRMS (FAB+): calcd. for $\text{C}_{28}\text{H}_{34}\text{O}_2\text{SSeSi}$ 542.1214. Found 542.1223.

Methyl 2-(dimethyl(phenyl)silyl)-3-((phenylselenanyl)methyl)-4-(tosylmethyl)cyclopentane-carboxylate 5b. Following the general procedure, diene **3b** (109 mg, 0.38 mmol), *p*-TolSO₂-SePh (129 mg, 0.42 mmol) and AIBN (6 mg, 0.04 mmol) in degassed benzene (30 mL) were refluxed for 1 h. After usual treatment, the crude reaction mixture contained a 38:62 mixture of the two regioisomers **4b/5b**. Chromatography (Petroleum ether/EtOAc 8/2) yielded pure **4b** (82 mg, 36 %) and pure **5b** (128 mg, 56 %). IR (neat) ν = 3050, 2951, 2923, 2853, 1728, 1596, 1578, 1477, 1436, 1312, 1301, 1251, 1207, 1168, 1147, 1113, 1087, 1021, 815, 773, 736, 702, 668 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ = 7.74 (d, *J* = 8.3 Hz, 2 H), 7.48-7.22 (m, 12 H), 3.57 (s, 3 H), 3.28 (dd, *J* = 13.9, 4.5, 1 H), 3.15 (dd, *J* = 13.9, 8.7, 1 H), 2.78 (m, 2 H), 2.72 (m, 1 H), 2.47 (s, 3 H), 2.30 (m, 2 H), 2.00 (m, 2 H), 1.79 (dd, *J* = 7.9, 6.0, 1 H), 0.27 (s, 3 H), 0.26 (s, 3 H). ¹³C NMR (CDCl₃, 75.5 MHz) δ = 176.6, 144.5, 136.6, 136.6, 133.8, 132.4, 129.7, 129.2, 129.0, 127.8, 127.8, 126.8, 56.0, 51.8, 44.4, 44.1, 38.0, 34.9, 34.0, 30.2, 21.5, -4.4, -4.7. MS (FAB⁺): *m/z* (%) = 623 (M+Na⁺, 26), 600 (M⁺, 29), 523 (32), 443 (77), 365 (14), 289 (18), 251 (100), 226 (25). HRMS (ES⁺): calcd. for C₃₀H₃₆O₄SSeSi + Na⁺ 623.1178. Found 623.1167.

4-(Dimethyl-phenyl-silyl)-3-phenylselenylmethyl-2-(toluene-4-sulfonylmethyl)-cyclopentanol

5c. Following the general procedure, diene **3c** (102 mg, 0.41 mmol), *p*-TolSO₂-SePh (128 mg, 0.41 mmol) and AIBN (6.6 mg, 0.04 mmol) in degassed benzene (33 mL) were refluxed for 6 h. After usual treatment, the crude reaction mixture contained a 25:75 mixture of the two regioisomers **4c/5c**, which were inseparable by chromatography (Petroleum ether/EtOAc 8/2) (110 mg, 49 %). IR (neat) ν = 3517, 3050, 2950, 1596, 1576, 1477, 1437, 1426, 1404, 1300, 1249, 1144, 1112, 1086, 1046, 1021, 919, 813, 770, 735, 701, 660 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ = 7.76 (d, *J* = 8.3, 2 H),

7.45-7.18 (m, 12 H), 4.41 (m, 1 H), 3.47 (dd, $J = 13.8, 10.0$, 1 H), 3.37 (dd, $J = 13.8, 3.5$, 1 H), 2.93 (dd, $J = 12.2, 6.0$, 1 H), 2.81 (dd, $J = 12.2, 6.7$, 1 H), 2.65 (d, $J = 4.5$, 1 H), 2.47 (s, 3 H), 2.32 (m, 2 H), 1.92 (ddd, $J = 13.8, 8.7, 1.7$, 1 H), 1.70 (ddd, $J = 13.9, 10.4, 5.2$, 1 H), 1.55 (m, 1 H), 0.21 (s, 6 H). ^{13}C NMR (CDCl_3 , 75.5 MHz) $\delta = 144.7, 137.4, 136.5, 134.0, 133.8, 132.8, 132.6, 129.9, 129.7, 129.1, 129.0, 127.8, 126.9, 73.8, 53.4, 42.9, 42.4, 35.9, 32.2, 29.1, 21.6, -4.3, -4.6$. ^{77}Se NMR (CDCl_3 , 76.3 MHz) $\delta = 278.4$. MS (FAB+): m/z (%) = 581 ($\text{M}+\text{Na}^+$, 95), 558 (M^+ , 75), 481 (83), 403 (74), 323 (24), 251 (77), 213 (100). HRMS (FAB+): calcd. for $\text{C}_{28}\text{H}_{34}\text{O}_3\text{SSeSi}$ 558.1163. Found 558.1166.

4-(Dimethyl-phenyl-silyl)-3-phenylselenylmethyl-2-(toluene-4-sulfonylmethyl)-cyclopentanol

5d. Following the general procedure, diene **3d** (134 mg, 0.54 mmol), *p*-TolSO₂-SePh (168 mg, 0.54 mmol) and AIBN (8 mg, 0.05 mmol) in degassed benzene (43 mL) were refluxed for 3.5 h. After usual treatment, the crude reaction mixture contained a 11:89 mixture of the two regioisomers **4d/5d**. Chromatography (Petroleum ether/EtOAc 9/1 then 8/2) yielded **5d** as a pale yellow oil [pure **5d** (120 mg, 41 %), 50 % overall yield]. IR (neat) $\nu = 3506, 3066, 2952, 2919, 1596, 1578, 1477, 1437, 1426, 1404, 1312, 1301, 1250, 1143, 1111, 1086, 1021, 938, 814, 771, 735, 701, 666\text{ cm}^{-1}$. ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.76$ (d, $J = 8.3$, 2 H), 7.42 (m, 2 H), 7.33 (m, 5 H), 7.23 (m, 5 H), 4.24 (m, 1 H), 3.36 (dd, ABX, $J_{\text{AB}} = 14.2, J_{\text{BX}} = 5.0, \Delta\nu/J = 8$, 1 H), 3.18 (dd, ABX, $J_{\text{AB}} = 14.2, J_{\text{AX}} = 8.9, \Delta\nu/J = 8$, 1 H), 2.77 (dd, ABX, $J_{\text{AB}} = 11.8, J_{\text{BX}} = 5.6, \Delta\nu/J = 8$, 1 H), 2.66 (d, $J = 3.8$, 1 H), 2.59 (dd, ABX, $J_{\text{AB}} = 11.8, J_{\text{AX}} = 7.8, \Delta\nu/J = 8$, 1 H), 2.46 (s, 3 H), 2.44 (m, 1 H), 2.19 (m, 2 H), 1.45 (ddd, $J = 13.1, 10.6, 7.4$, 1 H), 1.24 (m, 1 H), 0.25 (s, 3 H), 0.24 (s, 3 H). ^{13}C NMR (CDCl_3 , 75.5 MHz) $\delta =$

144.8, 137.5, 136.1, 133.8, 132.7, 129.9, 129.9, 129.1, 128.1, 127.9, 127.0, 76.7, 55.8, 45.4, 41.2, 35.6, 31.0, 27.8, 21.6, -4.2, -5.0. ^{77}Se NMR (CDCl_3 , 76.3 MHz) δ = 264.9. MS (FAB+): m/z (%) = 581 ($\text{M}+\text{Na}^+$, 70), 558 (M^+ , 56), 541 (100), 403 (37), 323 (27), 251 (97). HRMS (FAB+): calcd. for $\text{C}_{28}\text{H}_{34}\text{O}_3\text{SSeSi}$ 558.1163. Found 558.1139.

5-(dimethyl(phenyl)silyl)-6-(phenylselanyl)-7-tosylhept-1-en-3-ol 6d. Following the general procedure, diene **3d** (58.2 mg, 0.24 mmol), *p*-TolSO₂-SePh (81 mg, 0.26 mmol) in degassed CH_2Cl_2 (19 mL) were irradiated for 5 h. After usual treatment, the crude reaction mixture contained a 68:10:22 mixture of **4d/5d/6d**. **6d** was isolated by chromatography (Petroleum ether/EtOAc 9/1 then 8/2) as a pale yellow oil (10 mg, 7 %); **4d** (55 mg 41 % yield). **6d**: ^1H NMR (CDCl_3 , 300 MHz) δ = 7.62 (m, 2 H), 7.52 (d, J = 8.3, 2 H), 7.38 (m, 3 H), 7.33-7.12 (m, 7 H), 5.83 (ddd, J = 12.1, 10.6, 5.3, 1 H), 5.20 (d, J = 17.0, 1 H), 5.08 (br d, J = 10.2, 1 H), 4.28 (m, 1 H), 3.89 (ddd, J = 10.2, 3.8, 1.9, 1 H), 3.30 (dd, J = 14.5, 10.3, 1 H), 3.18 (dd, J = 14.5, 3.6, 1 H), 2.46 (br s, 1 H), 2.44 (s, 3 H), 2.26 (dt, J = 11.3, 2.3, 1 H), 1.90 (ddd, J = 14.7, 11.7, 3.0, 1 H), 1.61 (ddd, J = 14.3, 9.8, 2.6, 1 H), 0.47 (s, 3 H), 0.41 (s, 3 H). ^{13}C NMR (CDCl_3 , 62.9 MHz) δ = 144.6, 140.6, 137.5, 136.2, 134.6, 134.2, 129.8, 129.5, 129.4, 129.3, 128.0, 127.9, 127.7, 114.3, 69.2, 61.0, 40.7, 36.4, 26.6, 21.6, -1.9, -2.5. MS (FAB+): m/z (%) = 581 ($\text{M}+\text{Na}^+$, 34), 541 (5), 425 (27), 401 (37), 349 (6), 291 (3), 251 (24), 213 (100). HRMS (FAB+): calcd. for $\text{C}_{28}\text{H}_{34}\text{O}_3\text{SSeSi} + \text{Na}^+$ 581.1060. Found 581.1063.

Dimethyl(phenyl)((E)-8-phenyl-2-(phenylselanyl)-1-tosyloct-6-en-3-yl)silane 8a and 1-(8-phenylocta-2,6-dienylsulfonyl)-4-methylbenzene 8b. Following the general procedure, diene **7** (203 mg, 0.63 mmol), *p*-TolSO₂-SePh (394 mg, 1.27 mmol) in CH_2Cl_2 (12.6 mL), were irradiated

for 2 h at -70 °C. Evaporation of the solvent gave a mixture of **8a** and **8b**. Chromatography (Petroleum ether/EtOAc 9/1 then 8/2) gave **8b** as a colorless oil (76 mg, 35 %). IR (neat) ν = 3026, 2922, 2851, 1597, 1493, 1452, 1316, 1302, 1148, 1136, 1087, 969, 815, 744, 714, 628 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ = 7.76 (d, J = 7.9, 2 H), 7.35-7.32 (m, 7 H), 5.73 (m, 1 H), 5.58-5.25 (m, 3 H), 3.82 (d, J = 7.6, 2 H), 3.19 (d, J = 6.4, 2 H), 2.41 (s, 3 H), 1.84 (m, 4 H). ^{13}C NMR (CDCl_3 , 62.9 MHz) δ = 144.5, 140.6, 138.5, 130.2, 129.8, 129.6, 128.4, 128.34, 128.28, 125.9, 115.6, 55.2, 38.8, 31.5, 27.0, 21.5. MS (FAB+): m/z (%) = 363 ($\text{M}+\text{Na}^+$, 100). HRMS (FAB+): calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_2\text{S} + \text{Na}^+$ 363.1394. Found 363.1392. **8a (major stereoisomer)**. ^1H NMR (CDCl_3 , 300 MHz) δ = 7.48-6.86 (m, 19 H), 5.38-5.20 (m, 2 H), 3.72-3.60 (m, 1 H), 3.12-3.09 (m, 2 H), 2.97-2.91 (m, 2H), 2.20 (s, 3H), 2.0-1.28 (m, 4H), 1.15-1.10 (m, 1H), 0.25 (s, 3H), 0.21 (s, 3H). ^{13}C NMR (CDCl_3 , 62.9 MHz) δ = 146.1, 142.6, 139.7, 136.1, 135.9, 132.7, 131.4, 131.3, 131.0, 130.9, 130.8, 130.2, 130.1, 130.0, 129.6, 129.5, 129.4, 127.6, 62.2, 43.2, 40.7, 33.5, 32.1, 30.8, 23.3, 0.0, -0.8. MS (FAB+): m/z (%) = 655 ($\text{M}+\text{Na}^+$, 100).

(Tetrahydro-2-methyl-5-vinylfuran-3-yl)dimethyl(phenyl)silane 9. $\text{Mn}_2(\text{CO})_{10}$ (18 mg, 0.046 mmol) was added to a stirred solution of BrCCl_3 (137 μL , 1.39 mmol) and diene **3c** (114 mg, 0.46 mmol) in degassed CH_2Cl_2 (10.7 mL) under a nitrogen atmosphere. After photolysis (sunlamp) for 2 h at 10 °C, DBU (90 μL , 0.60 mmol) was added dropwise and the solution stirred a further 1 h. The crude reaction mixture was then purified by column chromatography to afford **9** as a colorless oil (49 mg, 43 %). IR (neat) ν = 3069, 2955, 2924, 2854, 1456, 1427, 1250, 1114, 986, 918, 828, 732, 699 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ = 7.51 (m, 2 H), 7.48 (m, 3 H), 5.77 (ddd, J = 6.8, 10.2, 17.0, 1

H), 5.20 (br d, $J = 17.3$, 1 H), 5.07 (br d, $J = 10.6$, 1 H), 4.31 (m, 1 H), 4.02 (m, 1 H), 2.15 (m, 1 H), 1.56 (dt, $J = 9.4$, 12.8, 1 H), 1.31 (ddd, $J = 6.8$, 10.2, 12.8, 1 H), 1.16 (d, $J = 6.0$, 3 H), 0.35 (s, 3 H), 0.34 (s, 3 H). ^{13}C NMR (CDCl_3 , 75.5 MHz) $\delta = 139.3$, 137.4, 133.7, 129.2, 127.8, 115.2, 79.7, 77.7, 37.4, 35.6, 22.1, -4.3, -4.4.

(Hexahydro-1H-cyclopenta[c]thiophen-6-yl)dimethyl(phenyl)silane 10a. Following the general procedure, diene **3a** (36 mg, 0.16 mmol) and di-*tert*-butyldisulfide (150 μL , 0.78 mmol) in degassed hexane (3 mL) were irradiated for 3 h at +10 °C, using a middle pressure mercury lamp. After usual treatment, chromatography of the crude reaction mixture (Petroleum ether) gave **10a** as a yellow oil (22 mg, 54 %). ^1H NMR (CDCl_3 , 300 MHz) $\delta = 7.52$ (m, 2 H), 7.36 (m, 3 H), 2.83 (dd, $J = 11.3$, 6.8, 1 H), 2.76 (dd, $J = 11.7$, 6.8, 1 H), 2.65 (m, 2 H), 2.54 (dd, $J = 11.3$, 2.3, 1 H), 2.29 (d, $J = 11.7$, 1 H), 1.87 (m, 2 H), 1.32 (m, 2 H), 1.06 (m, 1 H), 0.3 (s, 6 H). ^{13}C NMR (CDCl_3 , 75.5 MHz) $\delta = 138.4$, 133.8, 128.9, 127.7, 50.1, 49.6, 39.5, 38.7, 34.2, 32.9, 29.8, -4.3, -4.5. MS (FAB+): m/z (%) = 263 ($\text{M}+\text{H}^+$, 84), 261 (100), 243 (36). HRMS (FAB+): calcd. for $\text{C}_{15}\text{H}_{22}\text{SSi} + \text{H}^+$ 263.1289. Found 263.1289.

Hexahydro-6-(dimethyl(phenyl)silyl)-1H-cyclopenta[c]thiophen-4-ol 10b. Following the general procedure, diene **3b** (639 mg, 2.59 mmol) and di-*tert*-butyldisulfide (2.7 mL, 13 mmol) in degassed hexane (50 mL) were irradiated for 3 h at +10 °C, using a middle pressure mercury lamp. After usual treatment, chromatography of the crude reaction mixture (Petroleum ether/EtOAc 9/1) gave **10b** as a yellow oil (484 mg, 67 %). IR (neat) $\nu = 3429$, 3067, 2952, 2923, 1426, 1248, 1112, 1011, 849, 829, 767, 732, 700, 650 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.51$ (m, 2 H), 7.36 (m, 3 H), 4.16 (m, 1

H), 3.01 (d, $J = 10.9$, 1 H), 2.78-2.60 (m, 4 H), 2.27 (d, $J = 10.9$, 1 H), 1.88 (dd, $J = 13.2$, 6.0, 1 H), 1.63 (br s, 1 H), 1.45 (dt, $J = 13.9$, 4.1, 1 H), 1.16 (m, 1 H), 0.33 (s, 6 H). ^{13}C NMR (CDCl_3 , 62.9 MHz) $\delta = 137.7$, 133.9, 133.8, 129.1, 127.8, 127.7, 75.8, 52.7, 49.6, 39.4, 39.0, 33.3, 29.7, -4.3, -4.6. MS (FAB+): m/z (%) = 279 ($\text{M}+\text{H}^+$, 100), 261 (51). HRMS (FAB+): calcd. for $\text{C}_{15}\text{H}_{22}\text{OSSi} + \text{H}^+$ 279.1238. Found 279.1236.

Hexahydro-6-(dimethyl(phenyl)silyl)-1H-cyclopenta[c]thiophen-4-ol 10c. Following the general procedure, diene **3d** (236 mg, 0.96 mmol) and di-*tert*-butyldisulfide (990 μL , 4.8 mmol) in degassed hexane (18 mL) were irradiated for 3 h at +10 $^\circ\text{C}$, using a middle pressure mercury lamp. After usual treatment, chromatography of the crude reaction mixture (Petroleum ether/EtOAc 9/1) gave **10c** as a yellow oil (152 mg, 57 %). IR (neat) $\nu = 3352$, 3067, 2951, 2918, 2853, 1426, 1249, 1112, 1077, 1040, 848, 824, 763, 735, 700, 640 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.51$ (m, 2 H), 7.36 (m, 3 H), 3.89 (br q, 1 H), 2.75 (m, 4 H), 2.44 (m, 1 H), 2.18 (d, $J = 11.0$, 1 H), 2.03 (dt, $J = 13.6$, 6.0, 1 H), 1.72 (m, 1 H), 1.36 (dt, $J = 9.5$, 13.6, 1 H), 1.05 (ddd, $J = 13.5$, 9.3, 6.4, 1 H), 0.32 (s, 6 H). ^{13}C NMR (CDCl_3 , 62.9 MHz) $\delta = 137.7$, 133.8, 129.1, 127.8, 79.2, 56.8, 47.5, 39.6, 37.7, 37.0, 29.2, -4.5, -4.7. MS (FAB+): m/z (%) = 279 ($\text{M}+\text{H}^+$), 201 (33), 176 (29). HRMS (FAB+): calcd. for $\text{C}_{15}\text{H}_{22}\text{OSSi} + \text{H}^+$ 279.1238. Found 279.1235.

(1-benzyl-hexahydro-1H-cyclopenta[c]thiophen-4-yl)dimethyl(phenyl)silane 10d. Following the general procedure, diene **7** (499 mg, 1.56 mmol) and di-*tert*-butyldisulfide (1.5 mL, 7.78 mmol) in degassed hexane (31 mL) were irradiated for 8 h at +10 $^\circ\text{C}$, using a middle pressure mercury lamp. After usual treatment, chromatography of the crude reaction mixture (Petroleum ether) gave **10d** as a

yellow oil (316 mg, 58 %, 2:1 mixture of diastereoisomers). IR (neat) ν = 3066, 2924, 2856, 1453, 1248, 1112, 828, 812, 734 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ = 7.53 (m, 2 H), 7.42-7.17 (m, 8 H, aromatic H), 2.95 (dd, J = 11.8, 7.4, 1 H), 2.87 (m, 2 H), 2.74 (m, 1 H), 2.45 (m, 1 H), 2.37 (dd, J = 11.8, 4.8, 1 H), 1.90 (m, 1 H), 1.75 (m, 1 H), 1.40-1.10 (m, 3 H), 0.31 (s, 6 H). ^{13}C NMR (CDCl_3 , 62.9 MHz) δ = 140.3, 138.3, 133.9, 129.0, 128.96, 128.3, 127.8, 126.3, 56.5, 56.0, 50.7, 42.4, 38.0, 33.6, 32.7, 29.8, -4.3, -4.5. MS (FAB+) : m/z (%) = 353 ($\text{M}+\text{H}^+$, 63), 351 (100), 333 (18), 307 (22), 261 (38), 241 (11), 225 (17), 217 (21). HRMS (FAB+): calcd. for $\text{C}_{22}\text{H}_{28}\text{SSi} + \text{H}^+$ 353.1759. Found 353.1767.

Selenosulfonylation of Diene 7 by irradiation. A mixture containing diene 7 (150 mg, 0.47 mmol) and *p*-TolSO₂SePh (160 mg, 0.51 mmol) under a nitrogen atmosphere in degassed CH_2Cl_2 (37 mL) was irradiated for 2 h at -70 °C. The solvent was then evaporated and the residue purified by chromatography (Petroleum ether/EtOAc 9/1) to afford a colorless oil, which contained the desired product along with non identified products (188 mg).

Dimethyl(3-phenethyl-2- (tosylmethyl)cyclopentyl)(phenyl) silane. The preceding mixture (122 mg, 0.19 mmol) was diluted in benzene (5.8 mL) under a nitrogen atmosphere and *n*-Bu₃SnH (156 μL , 0.58 mmol) was

added. The solution was degassed, AIBN (3 mg by portions, 0.02 mmol) was added and the mixture refluxed for 4 h then concentrated under vacuum. Purification by chromatography (Petroleum ether/EtOAc 9/1) gave the above cyclopentane as a colorless oil (23 mg, 25 %). IR (neat) ν = 3065, 3024, 2925, 2864, 1598, 1495, 1453, 1426, 1404, 1313, 1301, 1289, 1249, 1149, 1113, 1087, 814,

771, 736, 700, 660, 633 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ = 7.56 (d, J = 8.3, 2 H), 7.40-7.05 (m, 12 H), 2.97 (dd, J = 14.3, 8.3, 1 H), 2.72 (dd, J = 14.3, 4.9, 1 H), 2.47 (m, 2 H), 2.40 (s, 3 H), 2.33 (m, 1 H), 2.00 (m, 1 H), 1.80 (m, 1 H), 1.62 (m, 1 H), 1.51 (m, 1 H), 1.50-1.42 (m, 2 H), 1.35-1.15 (m, 2 H). ^{13}C NMR (CDCl_3 , 62.9 MHz) δ = 144.3, 142.4, 138.0, 137.1, 133.9, 129.7, 129.0, 128.3, 127.9, 127.8, 125.7, 56.5, 41.8, 38.9, 34.1, 30.4, 30.3, 28.1, 24.4, 21.6, -3.8, -4.9. MS (FAB+): m/z (%) = 499 ($\text{M}+\text{Na}^+$, 15), 461 (10), 425 (4), 399 (100), 291 (9). HRMS (FAB+): calcd. for $\text{C}_{29}\text{H}_{36}\text{O}_2\text{SSi} + \text{Na}^+$ 499.2103. Found 499.2093.

Dimethyl(phenyl)(3-styryl-2-(tosylmethyl)cyclopentyl)silane.

The

mixture resulting from selenosulfonylation of **7** (83 mg, 0.13 mmol) was diluted in THF (1 mL) and treated with 30 % H_2O_2 (74 μL , 0.73 mmol) at

0 °C. The mixture was stirred for 4 h at room temperature and a 3 % solution of Na_2SO_3 was added.

The organic layer was extracted with EtOAc, washed with brine, dried over MgSO_4 , filtered and concentrated under vacuum. Purification by chromatography (Petroleum ether/EtOAc 8/2) gave the above cyclopentane as a colorless oil (16 mg, 26 %). IR (neat) ν = 3026, 2923, 2853, 1597, 1452,

1313, 1301, 1250, 1146, 1115, 1087, 968, 813, 735, 700, 674, 621 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz)

δ = 7.61 (d, J = 8.3, 2 H), 7.49 (m, 2 H), 7.40-7.28 (m, 10 H), 6.34 (d, J = 16.2, 1 H), 6.00 (dd, J = 15.8, 9.0, 1 H), 3.08 (dd, J = 14.3, 9.8, 1 H), 3.01 (m, 1 H), 2.77 (dd, J = 14.3, 2.3, 1 H), 2.51 (m, 1

H), 2.45 (s, 3 H), 2.00 (m, 1 H), 1.75-1.55 (m, 3 H), 1.23 (m, 1 H), 0.32 (s, 3 H), 0.31 (s, 3 H). ^{13}C

NMR (CDCl_3 , 62.9 MHz) δ = 144.2, 137.8, 137.5, 137.3, 134.0, 132.3, 129.7, 129.2, 128.5, 128.0,

127.9, 127.1, 126.1, 57.2, 46.4, 40.1, 32.0, 28.1, 25.0, 21.6, -3.8, -5.4. MS (FAB+): m/z (%) = 497

(M+Na⁺, 62), 455 (25), 397 (43), 265 (45), 211 (100). HRMS (FAB⁺): calcd. for C₂₉H₃₄O₂SSi + Na⁺ 497.1927. Found 497.1946.

Dimethylphenyl-(1-vinylpent-4-enyl)-silane 3a

Dimethylphenyl-(1-vinylpent-4-enyl)-silane 3a

2-Allyl-3-(dimethyl-phenyl-silyl)-pent-4-enoic acid methyl ester 3b

2-Allyl-3-(dimethyl-phenyl-silyl)-pent-4-enoic acid methyl ester 3b

3-dimethyl(phenyl)silyl)pent-4-enal

3-dimethyl(phenyl)silyl)pent-4-enal

5-(dimethylphenylsilyl)-hepta-1,6-dien-3-ol 3c

5-(dimethylphenylsilyl)-hepta-1,6-dien-3-ol 3c

5-(dimethylphenylsilyl)-hepta-1,6-dien-3-ol 3d

5-(dimethylphenylsilyl)-hepta-1,6-dien-3-ol 3d

Dimethylphenyl-[3-phenylselenenylmethyl-2-(toluene-4-sulfonylmethyl)-cyclopentyl]-silane 4a

Dimethylphenyl-[3-phenylselenenylmethyl-2-(toluene-4-sulfonylmethyl)-cyclopentyl]-silane 4a

Methyl 2-(dimethyl(phenyl)silyl)-4-((phenylselanyl)methyl)-3-(tosylmethyl)cyclopentane carboxylate 4b

Methyl 2-(dimethyl(phenyl)silyl)-4-((phenylselanyl)methyl)-3-(tosylmethyl)cyclopentane-carboxylate 4b

4-(Dimethyl-phenyl-silyl)-2-phenylselenenylmethyl-3-(toluene-4-sulfonylmethyl)-cyclopentanol 4c

4-(Dimethyl-phenyl-silyl)-2-phenylselenenylmethyl-3-(toluene-4-sulfonylmethyl)-cyclopentanol 4c

4-(Dimethyl-phenyl-silyl)-2-phenylselenenylmethyl-3-(toluene-4-sulfonylmethyl)-cyclopentanol 4d

4-(Dimethyl-phenyl-silyl)-2-phenylselenenylmethyl-3-(toluene-4-sulfonylmethyl)-cyclopentanol 4d

Dimethyl-phenyl-[2-phenylselenenylmethyl-3-(toluene-4-sulfonylmethyl)-cyclo-pentyl]-silane 5a

Dimethyl-phenyl-[2-phenylselenenylmethyl-3-(toluene-4-sulfonylmethyl)-cyclo-pentyl]-silane 5a

Methyl 2-(dimethyl(phenyl)silyl)-3-((phenylselanyl)methyl)-4-(tosylmethyl)cyclo-pentane-carboxylate 5b

Methyl 2-(dimethyl(phenyl)silyl)-3-((phenylselanyl)methyl)-4-(tosylmethyl)cyclopentane-carboxylate 5b

4-(Dimethyl-phenyl-silyl)-3-phenylselenenylmethyl-2-(toluene-4-sulfonylmethyl)-cyclopentanol 5c

4-(Dimethyl-phenyl-silyl)-3-phenylselenenylmethyl-2-(toluene-4-sulfonylmethyl)-cyclopentanol 5c

4-(Dimethyl-phenyl-silyl)-3-phenylselenenylmethyl-2-(toluene-4-sulfonylmethyl)-cyclopentanol 5d

4-(Dimethyl-phenyl-silyl)-3-phenylselenenylmethyl-2-(toluene-4-sulfonylmethyl)-cyclopentanol 5d

5-(dimethyl(phenyl)silyl)-6-(phenylselanyl)-7-tosylhept-1-en-3-ol 6d

5-(dimethyl(phenyl)silyl)-6-(phenylselanyl)-7-tosylhept-1-en-3-ol 6d

1-(8-phenylocta-2,6-dienylsulfonyl)-4-methylbenzene 8b

1-(8-phenylocta-2,6-dienylsulfonyl)-4-methylbenzene 8b

(Tetrahydro-2-methyl-5-vinylfuran-3-yl)dimethyl(phenyl)silane 9

(Tetrahydro-2-methyl-5-vinylfuran-3-yl)dimethyl(phenyl)silane 9

(Hexahydro-1H-cyclopenta[c]thiophen-6-yl)dimethyl(phenyl)silane 10a

(Hexahydro-1H-cyclopenta[c]thiophen-6-yl)dimethyl(phenyl)silane 10a

Hexahydro-6-(dimethyl(phenyl)silyl)-1H-cyclopenta[c]thiophen-4-ol 10b

Hexahydro-6-(dimethyl(phenyl)silyl)-1H-cyclopenta[c]thiophen-4-ol 10b

Hexahydro-6-(dimethyl(phenyl)silyl)-1H-cyclopenta[c]thiophen-4-ol 10c

Hexahydro-6-(dimethyl(phenyl)silyl)-1H-cyclopenta[c]thiophen-4-ol 10c

(1-benzyl-hexahydro-1H-cyclopenta[c]thiophen-4-yl)dimethyl(phenyl)silane 10d

(1-benzyl-hexahydro-1H-cyclopenta[c]thiophen-4-yl)dimethyl(phenyl)silane 10d

Dimethyl(3-phenethyl-2-(tosylmethyl)cyclopentyl)(phenyl)silane

Dimethyl(3-phenethyl-2-(tosylmethyl)cyclopentyl)(phenyl)silane

Dimethyl(phenyl)(3-styryl-2-(tosylmethyl)cyclopentyl)silane

Dimethyl(phenyl)(3-styryl-2-(tosylmethyl)cyclopentyl)silane

Dimethyl(phenyl)((E)-8-phenyl-2-(phenylselanyl)-1-tosyloct-6-en-3-yl)silane 8a

Dimethyl(phenyl)((E)-8-phenyl-2-(phenylselanyl)-1-tosyloct-6-en-3-yl)silane 8a

^1H - ^{13}C Correlations **4a**

^1H - ^{13}C Correlations **4a** (Enlargment)

^1H - ^{13}C Correlations **5a**

^1H - ^{13}C Correlations **5a** (Enlargement)

77SE/PJ349F4

 ^{77}Se NMR **5a**

HMGC 1H-77Se/ PJ349F4 /CDC13 mix=100ms

¹H-⁷⁷Se Correlations **5a**