Supporting Information for

Inhibition of Stannane-Mediated Radical Rearrangements by a Recoverable, Minimally Fluorous Selenol

by

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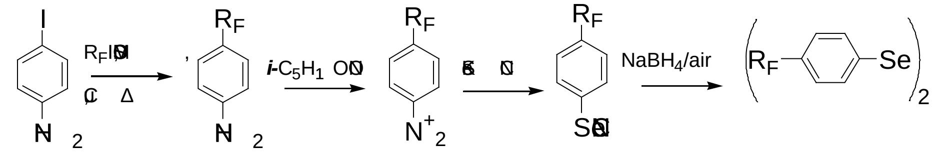


1: $R_F = C_6F_{13}$
2: $R_F = C_8F_{17}$
3: $R_F = C_{10}F_{21}$

4: $R_F = C_6F_{13}$
5: $R_F = C_8F_{17}$
6: $R_F = C_{10}F_{21}$

7: $R_F = C_6F_{13}$
8: $R_F = C_8F_{17}$
9: $R_F = C_{10}F_{21}$

10: $R_F = C_6F_{13}$
11: $R_F = C_8F_{17}$
12: $R_F = C_{10}F_{21}$

4-Perfluorodecylaniline (3). A mixture of 4-iodoaniline (1.53 g, 7 mmol), perfluorodecyl iodide (5 g, 7.7 mmol) and copper (1.48 g, 23.3 mmol) in DMSO (8 mL) was heated to 140 °C under Ar for 6h. After filtration, the filtrate was diluted with ether (100 mL), washed with water and brine and dried over sodium sulfate. Removal of the solvent followed by column chromatography (Hexane/EtOAc, 5/1) gave **3** as a white solid (3.0 g, 71%). M.p. 78-79 °C; ^{1}H-NMR δ: 3.96 (br s, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H); ^{13}C-NMR δ: 106.5-109.0 (m), 110.0-112.0(m), 114.3, 118.3 (m), 128.4, 149.7; ^{19}F-NMR δ: -53.7, -50.3, -49.5, -49.3, -48.9, -37.1 (m), -8.3 (m); Anal. Calcd. for $C_{16}H_6F_{21}N$: C, 31.44, H, 0.99; Found: C, 31.32, H, 0.90.

4-Perfluorohexylbenzenediazonium Tetrafluoroborate (4). A solution of 4-perfluorohexylaniline[1] (1.5 g, 3.6 mmol) and 48% HBF_4 (1.4 mL, 10.8 mmol) in EtOH

(30 mL) at 0 °C was treated with isoamyl nitrite (0.96 g, 8.2 mmol). After 30 min, a white crystalline solid was obtained by filtration and washed with water and ether several times (1.77 g, 95%). M.p. 165 ° C (decomp.); ^{1}H-NMR (d_6 acetone) δ: 8.44 (d, J = 8.9 Hz, 2H), 8.95 (d, J = 8.8 Hz, 2H); ^{19}F-NMR δ: -71.0 (m), -48.5, -45.3, -44.0 (m), -33.8 (m), -3.0 (m).

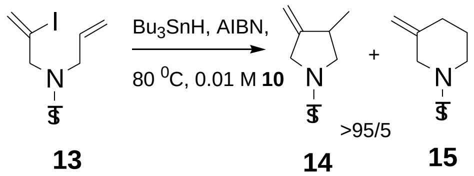
4-Perfluorohexylphenylselenocyanate (7). To a solution of **4** (2.5 g, 4.9 mmol) in DMF (7 mL) at 0 °C was added KSeCN (0.7 g, 6.1 mmol) in DMF (7 mL) dropwise, followed by stirring at room temperature overnight. The reaction mixture was then diluted with EtOAc (100 mL) and washed with water, brine and dried. Removal of solvent followed by column chromatography gave **7** as a yellow solid (0.93 g, 37%). M.p. 55-57 °C; ^{1}H-NMR δ: 7.63 (d, J =8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H); ^{13}C-NMR δ: 100.2, 105.0-120.0, 127.6, 128.9, 130.4 (t), 131.8; ^{19}F-NMR δ: -53.5 (m), -50.3, -49.3, -48.9, -38.6 (m), -8.3 (m); ^{77}Se-NMR δ: 330.4; Anal. Calcd. for $C_{13}H_4F_{13}NSe$: C, 31.22, H, 0.81; Found: C, 31.36, H, 0.88.

Bis-(4-perfluorohexylphenyl) Diselenide (10). A solution of **7** (500 mg, 1.0 mmol) in a mixture of ether (6 mL), THF (1 mL) and EtOH (3 mL) at 0 °C was treated with $NaBH_4$ (64 mg, 1.2 mmol) followed by stirring at room temperature for 1h. Quenching with 3N HCl at 0 °C followed by ether extraction gave a clear yellow solution. Air was bubbled through this solution. After removing the solvent, **10** was obtained as a yellow solid (440 mg, 92%). M.p. 95-97 °C; ^{1}H-NMR δ: 7.49 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H); ^{13}C-NMR δ: 105.0-120.0 (m), 127.8, 128.0 (t), 130.7, 135.5; ^{19}F-NMR δ: -53.8 (m), -

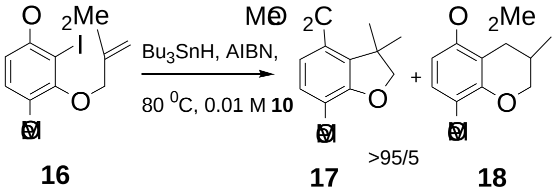
50.4, -49.5, -49.1, -38.4 (m), -8.4 (m); ^{77}Se-NMR δ: 450.8; Anal. Calcd. for $C_{24}H_8F_{26}Se_2$: C, 30.40, H, 0.85; Found: C, 30.74, H, 0.87.

Bis-(4-perfluorooctylphenyl) Diselenide (11). 11 was prepared analogously to **10**, via **2**,[1] **5** and **8**. M.p. 122-124 °C; ^{1}H-NMR δ: 7.49 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H); ^{13}C-NMR δ: 100-120 (m), 127.8, 130.6; ^{19}F-NMR δ: -53.7, -50.3, -49.4, -48.8, -38.3 (m), -8.3 (m); Anal. Calcd. for $C_{28}H_8F_{34}Se_2$: C, 29.29, H, 0.70; Found: C, 29.78, H, 0.69.

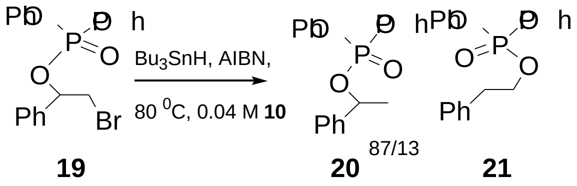
Bis-(4-perfluorodecylphenyl) Diselenide (12). 12 was prepared analogously to **10,** via **3**, **6** and **9**. M.p. 142-144 °C; **8** is insoluble in all solvents for NMR. Anal. Calcd. for $C_{32}H_8F_{42}Se_2$: C, 28.51, H, 0.60; Found: C, 28.80, H, 0.68.



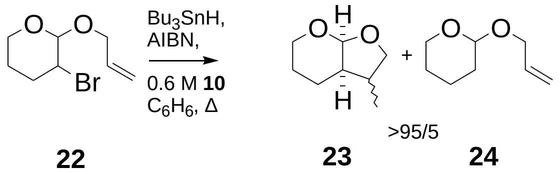
Reaction of *N*-(2-Iodo-2-propenyl)-*N*-(2-propenyl)benzenesulfonamide (13) with Bu_3SnH and 10. A solution of **13**[2] (18.1 mg, 0.05 mmol), Bu_3SnH (29 μL, 0.11 mmol), **10** (47 mg, 0.05 mmol) and AIBN (1.5 mg, 0.006 mmol) in benzene (5 mL) was irradiated with a 250 W sunlamp for 3h in such a way that the heat generated by the lamp maintained the solution at reflux. After removal of the solvent under reduced pressure the crude reaction mixture was analyzed by ^{1}H-NMR spectroscopy which indicated the exclusive formation of **14**.[2] Diselenide **10** was recovered by fluorous extraction in the jacketed continuous extractor (45 mg, 96%).



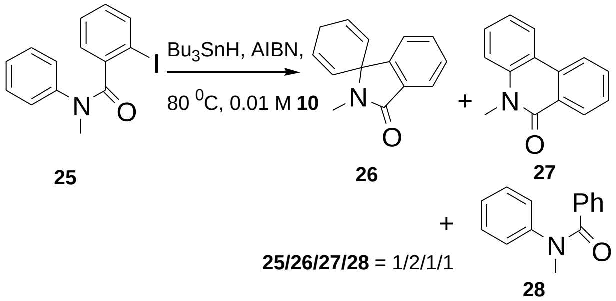
Reaction of Methyl-2-Iodo-3-Methallyloxy-4-Methoxybenzoate (16) with Bu$_3$SnH and 10. A solution of **16**[3] (22 mg, 0.06 mmol), Bu$_3$SnH (40 μL, 0.15 mmol), **10** (57 mg, 0.06 mmol) and AIBN (1 mg, 0.004 mmol) in benzene (6 mL) was irradiated as described for **13**. After removal of the solvent, ^{1}H-NMR spectroscopy indicated that only the exo-product **17**[3] was obtained. **10** was recovered by fluorous extraction in the jacketed continuous extractor (55 mg, 96%).



Reaction of 2-Bromo-1-Phenylethyl-Diphenylphosphate (19) with Bu$_3$SnH and 10. A solution of Bu$_3$SnH (120 μL, 0.45 mmol) and AIBN (1.5 mg, 0.013 mmol) in benzene (4 mL) was added over 4h with the syringe pump to a solution of **19**[4] (81 mg, 0.19 mmol) and **10** (178 mg, 0.19 mmol) at reflux under Ar in benzene (5 mL). After a further 1h at reflux the reaction mixture was cooled to room temperature and the solvent was removed in vacuum. Examination of the crude reaction mixture by ^{1}H-NMR revealed the formation of products **20**[4] and **21**[4] in the ratio of 87:13. **10** was recovered by fluorous extraction in the jacketed continuous extractor (160 mg, 90%).

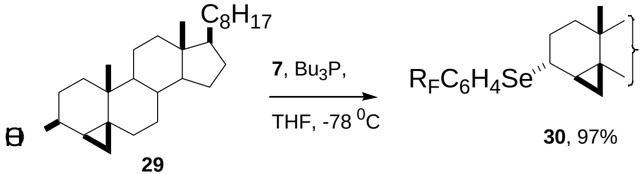


Reaction of 3-Bromo-2-Allyloxytetrahydropyran (16) with Bu$_3$SnH and 6. To a solution of **16**[3] (50 mg, 0.23 mmol) and **6** (1.89 g, 2 mmol) in benzene (3.5 mL) at reflux under Ar was added a solution of Bu$_3$SnH (661 μL, 2.54 mmol) and AIBN (10 mg, 0.05 mmol) in benzene (1.5 mL) over 6 min followed by heating to reflux for 30 min leading to the exclusive formation of the reduction product **17**.[3] **6** was recovered by fluorous extraction in the jacketed continuous extractor (1.63 g, 86%).



Reaction of *o*-Iodo-*N*-Methylbenzanilide (25) with Bu$_3$SnH and 10. To a 0.01M solution of **25**[5] (50 mg, 0.15 mmol) and **10** (140 mg, 0.15 mmol) in benzene (15 mL) at reflux under Ar was added a solution of Bu_3SnH (88 μL, 0.33 mmol) and AIBN (3.2 mg, 0.022 mmol) in benzene (6 mL) by means of a syringe pump over for 48h. After a further 1h at reflux, the reaction mixture was cooled and the solvent was removed under reduced pressure. ^{1}H-NMR spectroscopy indicated that a mixture of **25**,[5] **27**,[5] **28**[5] and **26**[5] was formed in the ratio of **1:1:1:2**. **10** was recovered by fluorous extraction in the jacketed continuous extractor (135 mg, 95%).

Standard Method for Recovery of the Fluorous Diselenide 10 from Stannane-Mediated Reactions. Benzoyl peroxide (0.5-1.0 equiv. of **10**) was added to the crude reaction mixture followed by heating to reflux for 6h. The solvent was then removed under reduced pressure and the residue was dissolved in 5 mL DCM or toluene. Continuous extraction in the jacketed extractor with perfluoromethylcyclohexane gave **10** as a yellow solid in 86% to 97% yield.

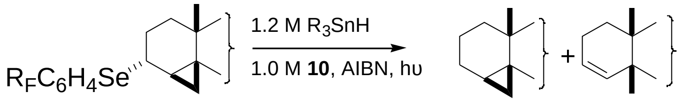


29

30, 97%

7 = 4-$R_FC_6H_4SeCN$; R_F = C_6F_{13}

4β,5β-Methano-3α-(4-perfluorohexylphenylseleno)-5α-Cholestane (30). A solution of **7** (300 mg, 0.6 mmol) in dry THF (1.6 mL) was added over 1h to 4β,5β-methano-5α-cholestan-3β-ol (**29**)[6] (120 mg, 0.3 mmol) and Bu_3P (0.15 mL, 0.6 mmol) in dry THF (1 mL) at –78 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 4h. Removal of the solvent followed by column chromatography on silica gel (eluent: pentane) gave a mixture of the product **30** and **10** (350 mg) as a yellow solid. This solid was dissolved in toluene (3 mL) and the solution extracted continuously with perfluoromethylcyclohexane until the upper layer was colorless. Concentration of the toluene layer then gave pure **10** as a white solid. M.p. 77-79 ^{0}C; (250 mg, 97%). ^{1}H-NMR δ: 0.29 (dd, *J* = 9.2, 4.8 Hz, 1H), 0.40 (t, *J* = 4.8 Hz, 1H), 0.49 (d, *J* = 13.6 Hz, 1H), 0.66 (s, 3H), 0.85-1.99 (m, 40H), 3.61 (dd, *J* = 10.6, 8.1 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H); ^{13}C-NMR δ: 12.0, 18.3, 18.8, 21.4, 21.6, 22.7, 22.9, 23.9, 24.4, 24.5, 27.2, 28.2, 28.4, 30.4, 30.6, 30.8, 33.2, 34.9, 35.86, 35.91, 36.3, 38.7, 39.7, 40.2, 42.5, 46.2, 56.3, 56.6, 105-120 (m), 127.0, 127.3, 132.6, 137.2; ^{19}F-NMR δ: -53.7 (m), -50.4, -49.4 (m), -49.0, -38.2 (m), -8.37 (m); ^{77}Se-NMR δ: 452.5; Anal. Calcd. for $C_{40}H_{51}F_{13}Se$: C, 56.01, H, 5.99; Found: C, 56.01, H, 5.90.



30 **31** **32**

$R_F = C_6F_{13}$ R = $MeOCH_2CH_2O(CH_2)_3$ **31/32** = 58/42

Reaction of 25 with Tris[3-(2-methoxyethoxy)propyl]stannane and 10. A mixture of **10** (190 mg, 0.21mmol), **30** (17.2 mg, 0.02 mmol), tris[3-(2-methoxyethoxy)propyl]-stannane[7,8] (100 μL, 0.25 mmol) and AIBN (1 mg, 0.004 mmol) in benzene (0.2 mL) was stirred at room temperature for 30 min under Ar. The resulting clear solution was irradiated analogously to **13**. **10** was recovered by fluorous extraction in the jacketed continuous extractor (185 mg, 97%) Column chromatography of the non-fluorous layer on silica gel (eluent: pentane) gave a mixture of reduction product **31**[9] and rearrangement product **32**[10] as in the ratio of 58: 42 (5mg, 65%).

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