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Selenostannylation of Arynes Produced by Silylaryl Triflates under Mild Reaction Conditions

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General methods

^{1}H and ^{13}C NMR spectra were obtained on a Varian INOVA 300 spectrometer (^{1}H at 300 MHz and ^{13}C at 75 MHz) and on a Bruker DRX-500 spectrometer (^{1}H at 500 MHz and ^{13}C at 125 MHz). The spectra were taken in deuterated solvents and the chemical shifts were given in ppm using residual undeuterated solvents or tetramethylsilane (TMS) as internal standard. ^{77}Se NMR spectra were taken on a Bruker DRX-500 spectrometer at 95 MHz using $CDCl_3$ as solvent. The chemical shifts were given in ppm using diphenyl diselenide (PhSeSePh) diluted in $CDCl_3$ (1 mol L^{-1}) as an external standard (δ 463 ppm at 25ºC). Low-resolution mass spectra were obtained on a Shimadzu CG-17A/CGMS-QP5050A instrument. Elemental analyses were obtained on a Perkin-Elmer CHN 2400 equipment. Near-IR spectra were obtained on a Bomem MB-100 spectrometer. The melting point value obtained is uncorrected. Reagents and solvents were used as obtained commercially or when necessary were purified and/or dried using procedures described in the literature.[1] THF was distilled under nitrogen from sodium/benzophenone and CH_3CN was distilled from calcium hydride. Both solvents were distilled prior to use. Oxygen and moisture sensitive materials were manipulated under a nitrogen atmosphere. Column chromatography and preparative thin layer chromatography separations were carried out using silica gel 60. Tributyl(phenylselanyl) stannane (**1**),[2] 2-(trimethylsilyl)phenyl triflate (**2a**),[3] 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate (**2b**),[4] 4-fluoro-2-(trimethylsilyl)phenyl triflate (**2c**),[5] 1-(trimethylsilyl)-2-naphtyl triflate (**2d**),[6] and 2-(trimethylsilyl)-1-naphtyl triflate (**2e**)[7] were prepared according to literature procedures.

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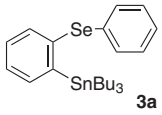
General procedure for selenostannylation of arynes

To a vial (10 mL) were added the tributyl(phenylselanyl) stannne **1** (0.3 mmol), the appropriate aryne precursor **2a-e** (0.6 mmol), 18-crown-6 ether (158 mg, 0.6 mmol), and THF (3 mL). The mixture was cooled to 0 ºC and potassium fluoride (34.8 mg, 0.6 mmol) was added. The vial was sealed using a cap, and the reaction mixture was stirred for 24 h at 0 ºC. Afterwards, the reaction was added to a saturated solution of ammonium chloride (30 mL), which was extracted with ethyl acetate (3 × 30 mL). The organic phase was dried over $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure. The residue was purified by preparative TLC using silica gel as stationary phase and hexane as eluent unless otherwise indicated, affording the desired products **3a-d**.

Iododestannylation of aromatic selenostannane

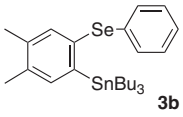
To a vial (10 mL) were added the tributyl[2-(phenylselanyl)phenyl]stannane **3a** (47.5 mg, 0.09 mmol), dichloromethane (1 mL), and iodine (23 mg, 0.09 mmol). The vial was sealed using a cap, and the mixture was stirred for 4 h at room temperature. Afterwards, the reaction was diluted with ethyl acetate (10 mL) and washed with a saturated solution of sodium thiosulfate (10 mL). The organic phase was stirred with an 1 mol.L^{-1} aqueous solution of potassium fluoride (10 mL) for 30 min at room temperature. The insoluble materials were filtered off through a celite pad. The organic phase was dried over $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure. The residue was purified by preparative TLC using silica gel as stationary phase and hexane as eluent, affording the desired product **4**.

Characterization data



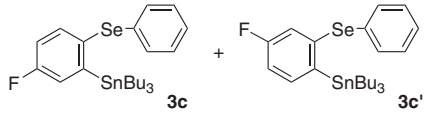
3a

*Tributyl[2-(phenylselanyl)phenyl]stannane (**3a**):* Yield 97.1 mg (62%); light yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.52 (dd, *J* 7.5 Hz, *J* 1.3 Hz, 1H), 7,45 (dd, *J* 7.5 Hz, *J* 1.6 Hz, 1H), 7.30-7.13 (m, 7H), 1.55-1.44 (m, 6H), 1.27 (sext, *J* 7.3 Hz, 6H), 1.08-1.03 (m, 6H), 0.84 (t, *J* 7.3 Hz, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 151.4, 139.2, 137.5, 135.8, 134.0, 130.5, 129.3, 129.1, 127.3, 126.3, 29.1, 27.4, 13.7, 11.2; IR (film) ν_{max}/cm^{-1}: 2956, 2923, 1926, 1849, 1793, 1732, 1578, 1470, 1441, 1070, 736, 689; Elemental Analysis: calc. for $C_{24}H_{36}SeSn$: C 55.20; H 6.95%; found: C 55.20; H, 6.85%.



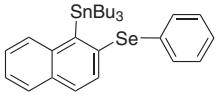
3b

*Tributyl[4,5-dimethyl-2-(phenylselanyl)phenyl] stannane (**3b**):* Yield 99.0 mg (60%); light yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.25-7.13 (m,7H), 2.26 (s, 3H), 2.23 (s, 3H), 1.52-1.42 (m, 6H), 1.25 (sext, *J* 3 Hz, 6H), 1.04-0.98 (m, 6H), 0.84 (t, *J* 3 Hz, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 148.7, 140.3, 138.9, 138.1, 137.7, 137.0, 136.0, 129.6, 129.0, 125.8, 29.1, 27.4, 19.9, 19.2, 13.6, 11.1; IR (film) ν_{max}/cm^{-1}: 2956, 2924, 1605, 1579, 1420, 1212, 843, 733, 689; Elemental Analysis: calc. for $C_{26}H_{40}SeSn$: C 56.75; H, 7.33%; found: C 56.60; H, 7.16%.



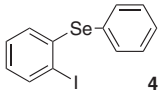
3c **3c'**

*Mixture of tributyl[5-fluoro-2-(phenylselanyl)phenyl] stannane (**3c**) and tributyl[4-fluoro-2-(phenylselanyl) phenyl]stannane (**3c'**):* yield 55.1 mg (34%); light yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.54 (dd, *J* 8.5 Hz, *J* 5.5 Hz, 1H), 7.43-7.37 (m, 0.5H), 7.36-7.32 (m, 1H), 7.28-7.22 (m, 1.5 H), 7.21-7.13 (m, 6.5H), 6.97-6.95 (m, 0.5H), 6.94-6.90 (m, 1H), 1.54-1.44 (m, 9H), 1.27 (sext, *J* 7.5 Hz, 6H), 1.26 (sext, *J* 7.5 Hz, 3H), 1.12-1.03 (m, 9H), 0.86 (t, *J* 7.5 Hz, 9H), 0.84 (t, *J* 7.5 Hz, 4.5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 163.4 (d, *J* 248 Hz), 162.5 (d, *J* 250 Hz), 155.6 (d, *J* 2 Hz), 141.3 (d, *J* 6Hz), 138.4 (d, *J* 7Hz), 138.2 (d, *J* 7 Hz), 136.0, 134.3, 133.0 (d, *J* 3 Hz), 131.8, 129.7, 194.4 129.2, 127.6, 127.1, 125.2, 123.9 (d, *J* 18 Hz), 121.3 (d, *J* 20 Hz), 116.6 (d, *J* 22 Hz), 114.4 (d, *J* 19 Hz), 29.1, 29.0, 27.3, 13.6, 11.3, 11.2; ^{77}Se RMN ($CDCl_3$, 95 MHz) δ: 437.2, 437.1; IR (film) ν_{max}/cm^{-1}: 2956, 2926, 1942, 1882, 1735, 1568, 1455, 1091, 845, 733, 689; Elemental Analysis: calc. for $C_{24}H_{35}FSeSn$: C 53.36; H, 6.53%; found: C 53.06; H, 6.31%.



3d

*Tributyl[2-(phenylselanyl)naphthalen-1-yl]stannane (**3d**):* yield 94.4 mg (55%); light yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.27 (d, *J* 8.0 Hz, 1H), 7.83 (d, *J* 8.0 Hz, 1H), 7.77 (d, *J* 8.0 Hz, 1H), 7.54 (d, *J* 8.0 Hz, 1H), 7.43-7.36 (m, 2H), 7.05-6.98 (m, 3H), 6.99-6.93 (m, 2H), 1.47-1.40 (m, 6H), 1.19 (sext, *J* 7.5 Hz, 6H), 1.08-0.97 (m, 6H), 0.77 (t, *J* 7.5 Hz, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 155.7, 136.8, 135.5, 134.6, 134.3, 133.5, 129.2, 129.0, 128.9, 128.5, 127.9, 127.1, 126.3, 125.3, 29.1, 27.4, 13.6, 11.7; ^{77}Se RMN ($CDCl_3$, 95 MHz) δ: 383.3; IR (film) ν_{max}/cm^{-1}: 2955, 2923, 1933, 1851, 1794, 1733, 1578, 1476, 1069, 1019, 702, 689; Elemental Analysis: calc. for $C_{28}H_{38}SeSn$: C 58.77; H 6.69%; found: C 58.43; H, 7.02%.



4

*(2-Iodophenyl)(phenyl)selenide (**4**) (CAS Number 363617-27-0):* yield 21.6 mg (67%); white solid; mp 76-78 °C (Lit.[8] mp 73-74 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.76 (dd, *J* 7.5 Hz, *J* 1.2 Hz,1H), 7.66-7.61 (m, 2H), 7.45-7.35 (m, 3H), 7.12 (dd. *J* 7.5 Hz, *J* 1.5 Hz, 1H), 6.90-6.83 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 140.6; 139.4, 135.8, 130.2, 129.8, 128.8, 128.7, 127.4, 99.4; IR (KBr) ν_{max}/cm^{-1}: 1949, 1877, 1436, 999, 741, 687; LRMS (*m/z*, %): $[M+1]^+$ 360 (11), 232 (28), 152 (100), 116 (70), 77 (54), 51 (93), 50 (87).

Copies of [1]H and [13]C NMR spectra

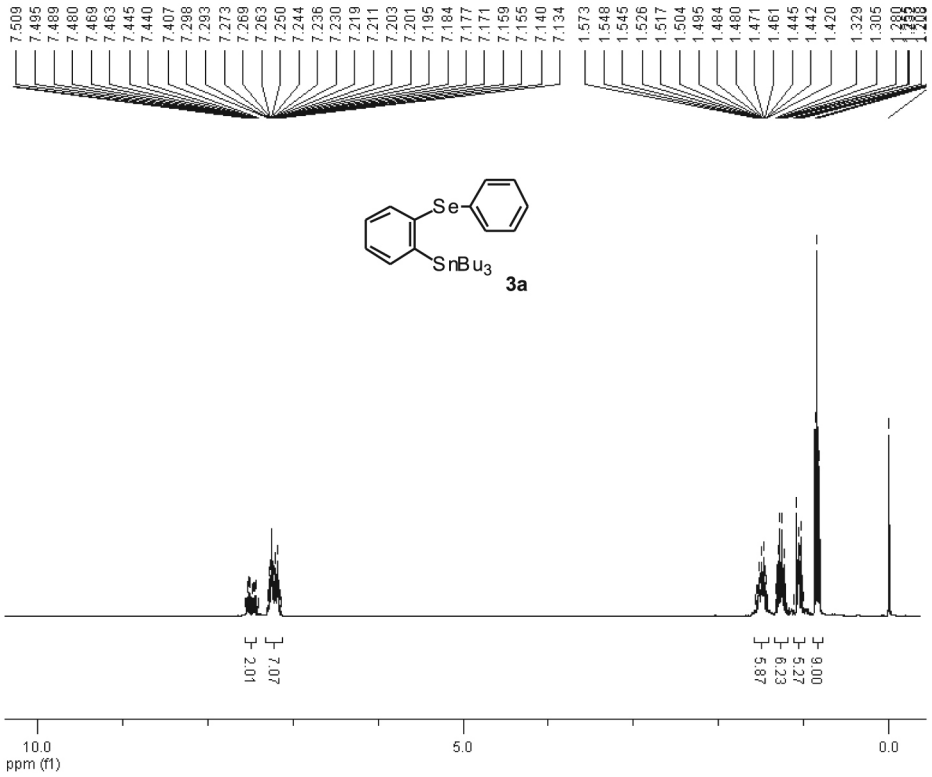


Figure S1. [1]H NMR for compound **3a**.

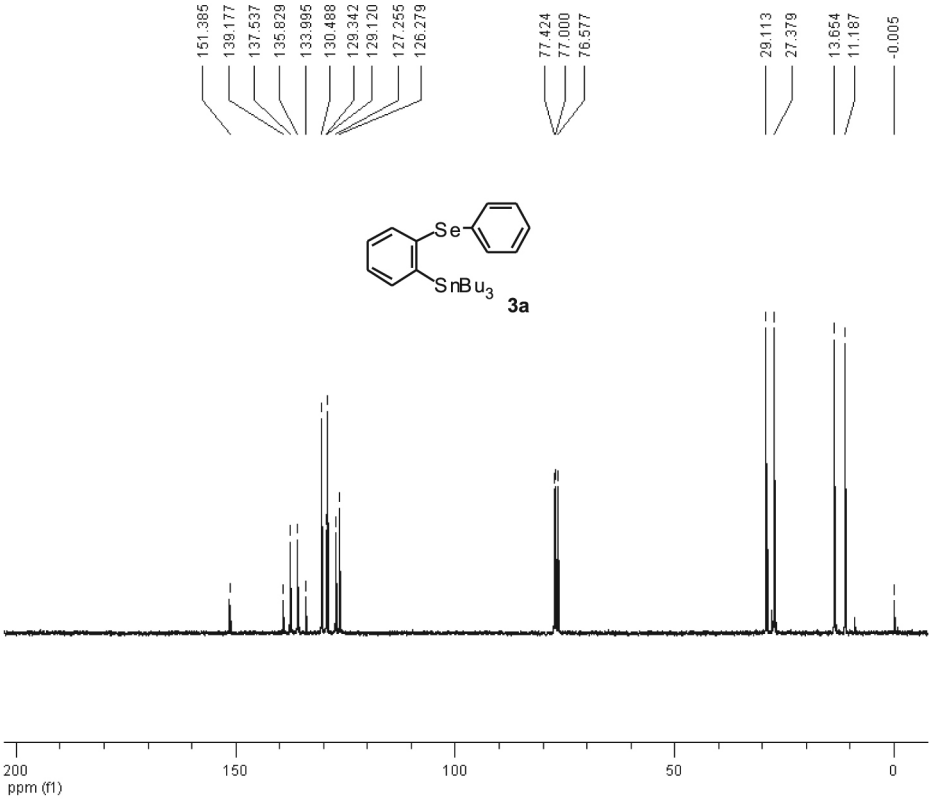


Figure S2. [13]C NMR for compound **3a**.

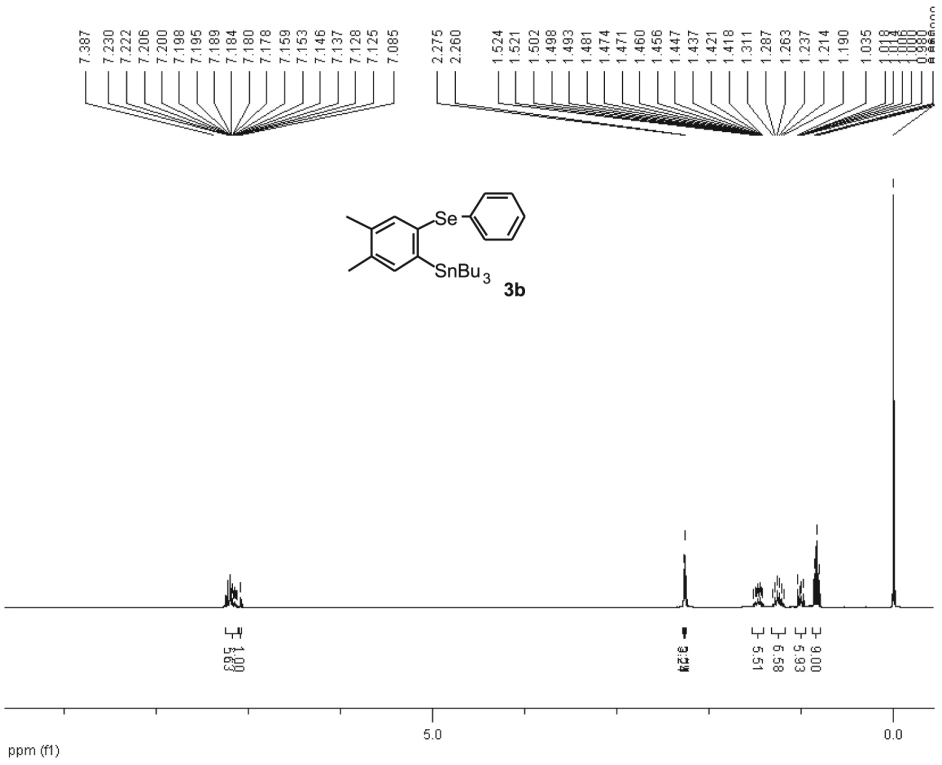


Figure S3. [1]H NMR for compound **3b**.

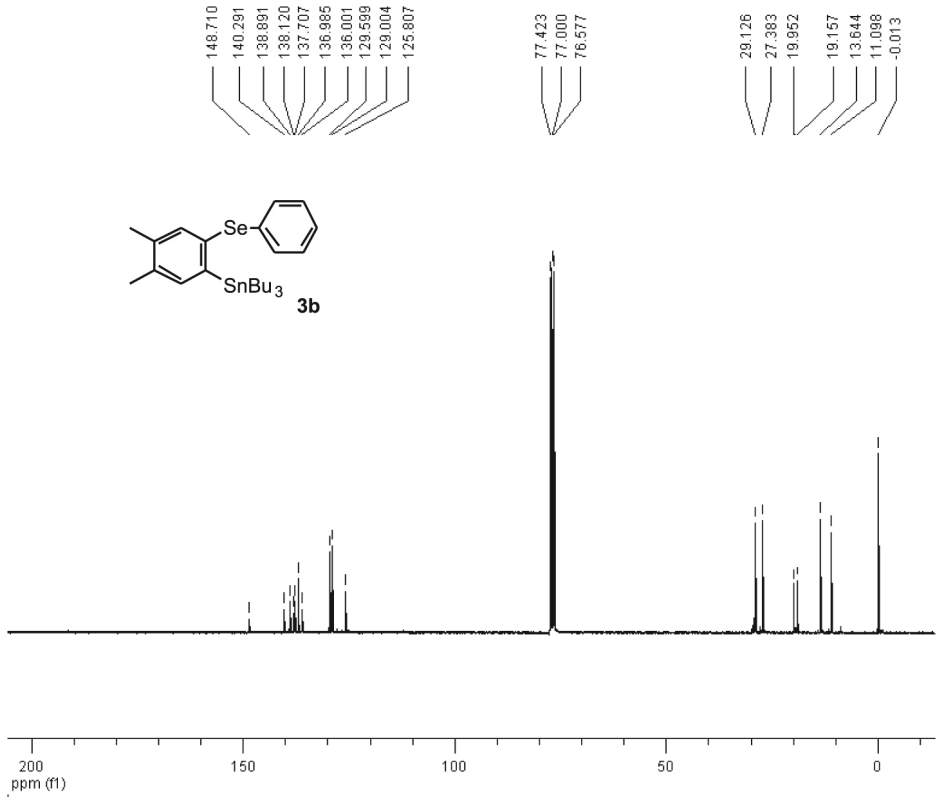


Figure S4. [13]C NMR for compound **3b**.

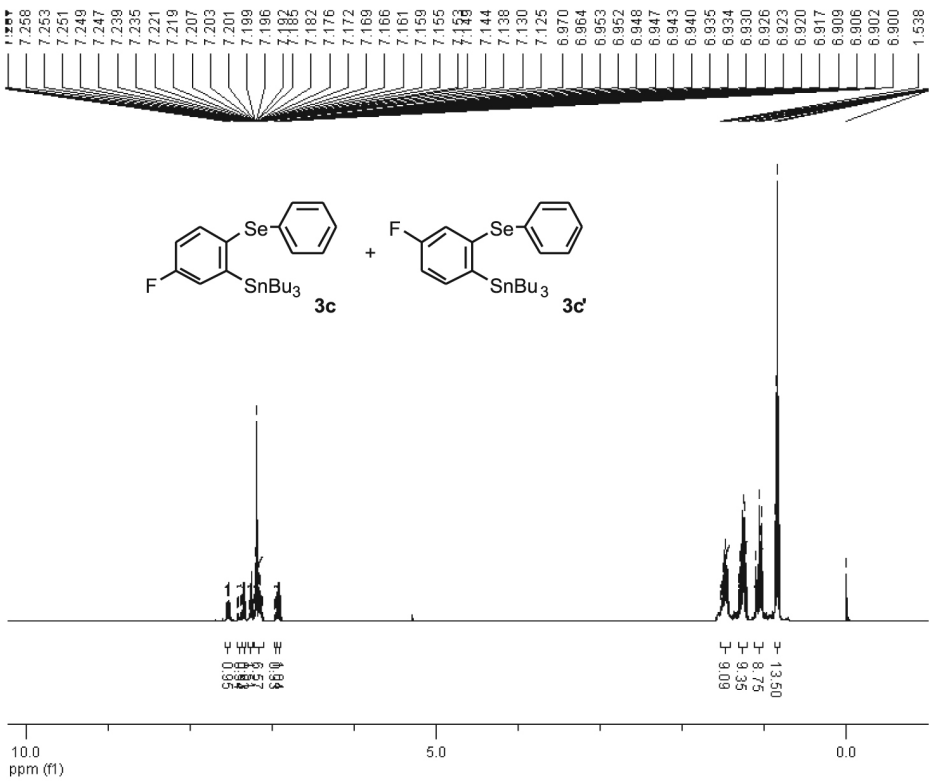


Figure S5. [1]H NMR for mixture of compounds **3c** and **3c'**.

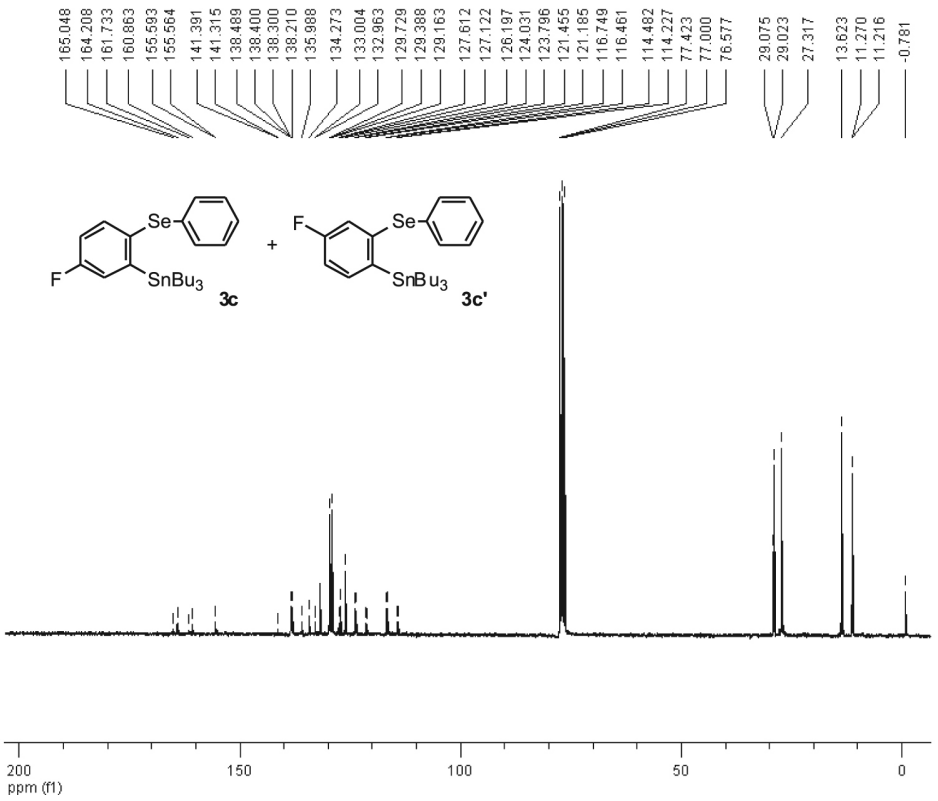


Figure S6. [13]C NMR for mixture of compounds **3c** and **3c'**.

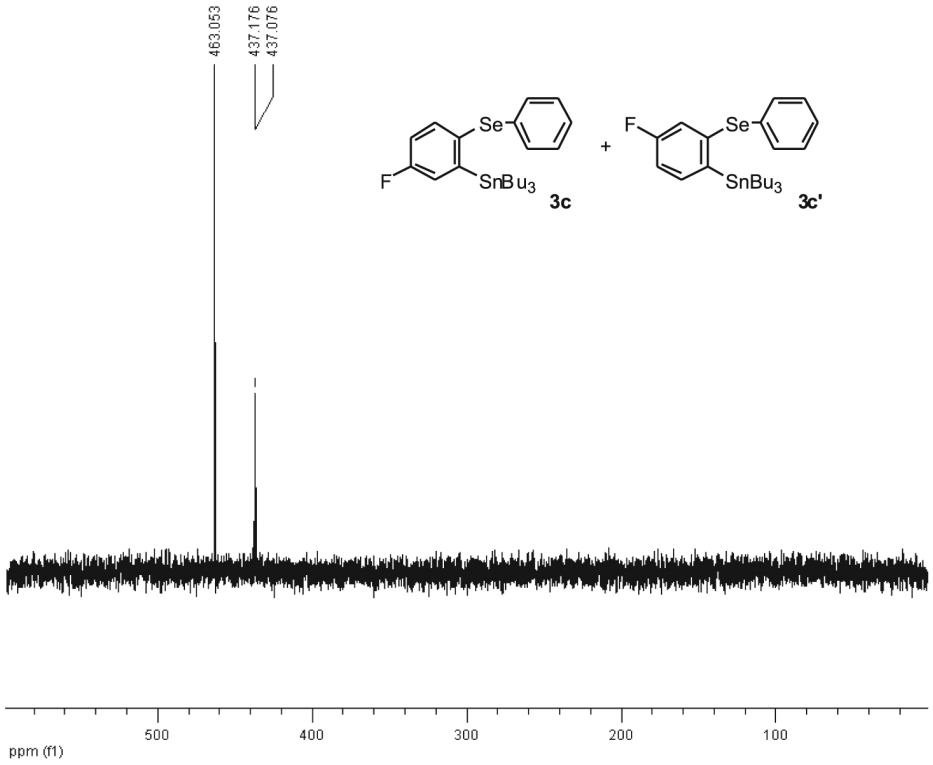


Figure S7. ^{77}Se NMR for mixture of compounds **3c** and **3c'**.

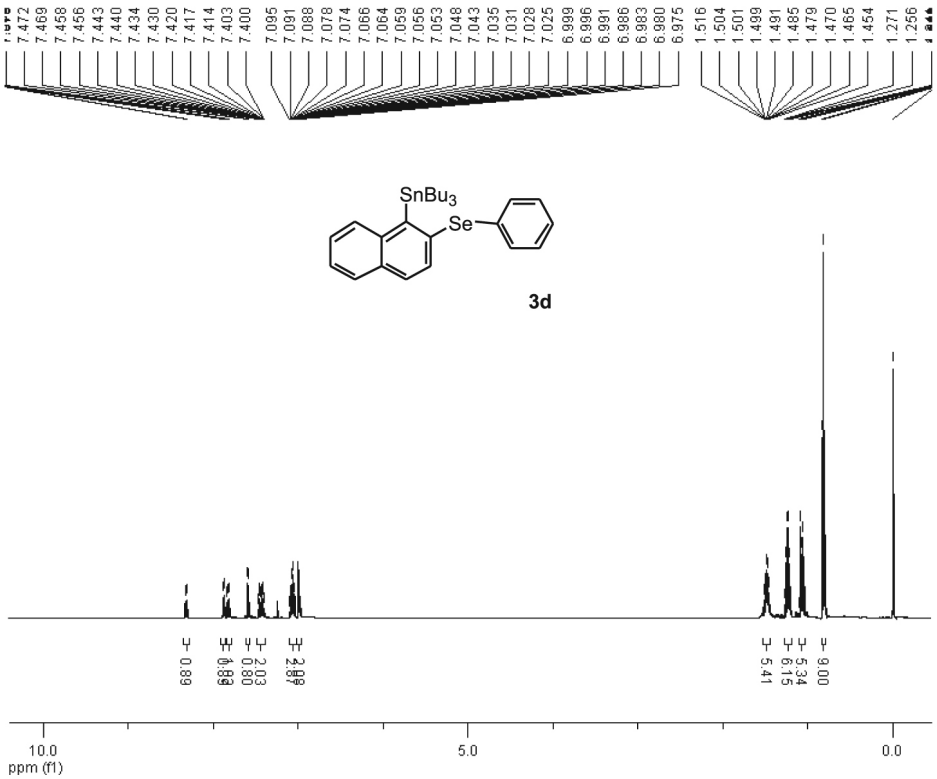


Figure S8. ^{1}H NMR for compound **3d**.

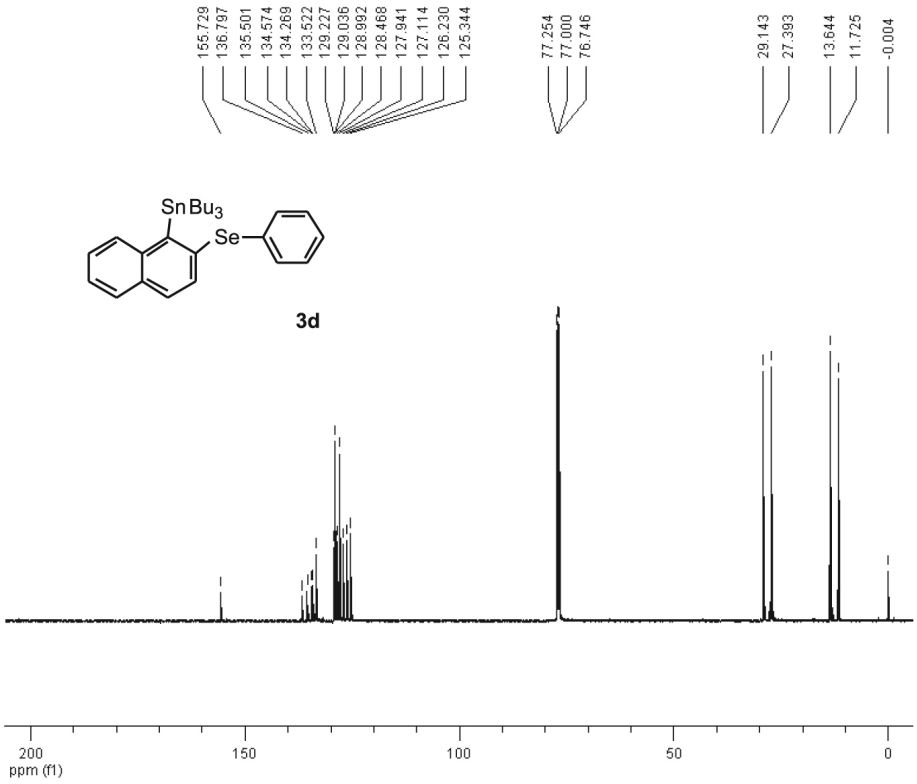


Figure S9. ^{13}C NMR for compound **3d**.

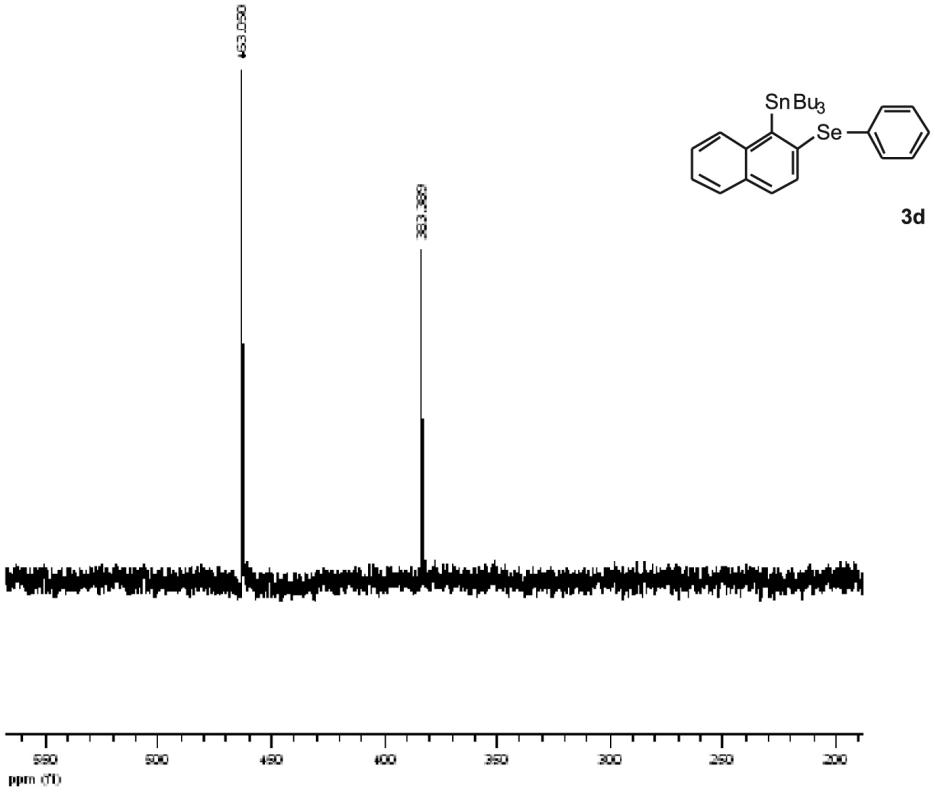


Figure S10. ^{77}Se NMR for compound **3d**.

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