

SUPPORTING INFORMATION

Selective Base-Promoted Synthesis of Substituted Selenophenes by Carbocyclization of (Z)-Benzylselenoenynes

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Materials and Methods

Proton nuclear magnetic resonance spectra (¹H NMR) were obtained at 200 MHz or at 400 MHz NMR spectrometer. Spectra were recorded in CDCl₃ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl₃ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (*J*) in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (¹³C NMR) were obtained either at 50 MHz or at 100 MHz NMR spectrometer. Spectra were recorded in CDCl₃ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl₃. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sex (sextet), dd (double doublet), and m (multiplet). High resolution mass spectra (HRMS-ESI-TOF) was performed on an High-Speed Liquid Chromatograph Mass

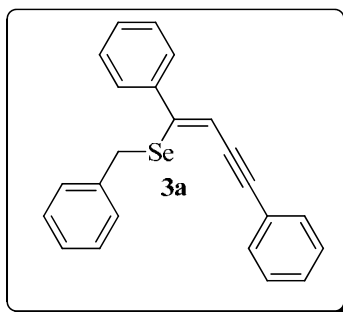
Spectrometer LC-MS-IT-TOF. Elemental analysis (CHN analysis) was recorded on a EA 1110 Elemental Analyzer. Column chromatography was performed using Merck Silica Gel (230-400 mesh) following the methods described by Still.¹ Thin layer chromatography (TLC) was performed using Merck Silica Gel GF₂₅₄, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. Most reactions were monitored by TLC for disappearance of starting material. The following solvents were dried and purified by distillation from the reagents indicated: tetrahydrofuran from sodium with a benzophenone ketyl indicator. All other solvents were ACS or HPLC grade unless otherwise noted. Air- and moisture-sensitive reactions were conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry nitrogen or argon. Reagents and solvents were handled using standard syringe techniques. Temperatures above room temperature were maintained by use of a mineral oil bath with an electrically heated coil connected to a Variac controller.

General Procedure for the Preparation of the (Z)-benzylselenoenynes 3a-q.²

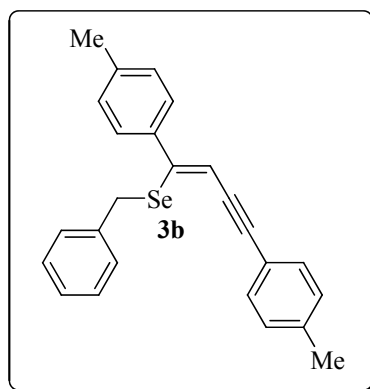
To a solution of the diyne (2.0 mmol) in THF (10 mL) and appropriate dibenzyl diselenide (1 mmol) in 95% ethanol (25 mL) under an argon atmosphere, NaBH₄ (0.12g; 3.2 mmol) was added at room temperature, under vigorous stirring. Gas evolution was observed during addition. The reaction mixture was stirred under reflux for 5 hours, allowed to reach room temperature, diluted with ethyl acetate (30 mL) and washed with brine (3 x 20 mL) and water (3 x 20 mL). After drying the organic phase over anhydrous MgSO₄, the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel using hexane as eluent.

⁽¹⁾ Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

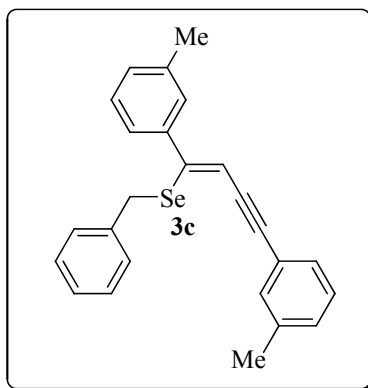
⁽²⁾ Dabdoub, M. J.; Baroni, A. C.; Lenardão, E. J.; Gianeti, T. R.; Hurtado, G. R. *Tetrahedron*, **2001**, *57*, 4271.



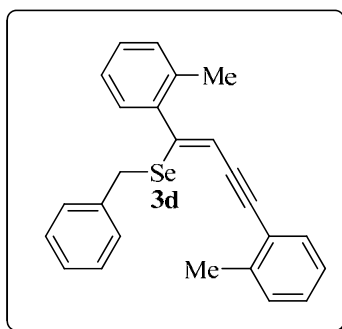
(Z)-benzyl(1,4-diphenylbut-1-en-3-ynyl)selane (3a). Yield: 0.524 g (70%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.60-7.28 (m, 9H), 7.23-7.04 (m, 6H), 6.23 (s, 1H), 3.87 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.6, 140.0, 138.3, 131.4, 128.9, 128.5, 128.4, 128.3, 128.2, 128.1, 126.7, 123.3, 111.6, 97.3, 88.3, 30.5. MS (relative intensity) m/z : 373 (28), 282 (13), 215 (16), 202 (50), 91 (100), 65 (13). Elem. Anal. (%) Calcd for $\text{C}_{23}\text{H}_{18}\text{Se}$: C 73.99, H 4.86. Found: C 74.26, H 4.92.



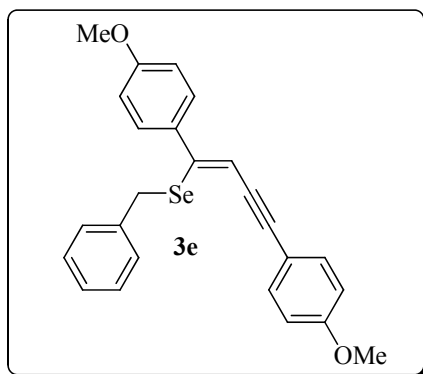
(Z)-benzyl(1,4-dip-tolylbut-1-en-3-ynyl)selane (3b). Yield: 0.680g (85%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.40-7.28 (m, 4H), 7.23-6.96 (m, 9H), 6.21 (s, 1H), 3.88 (s, 2H), 2.37(s, 3H), 2.35 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.1, 138.6, 138.5, 138.3, 137.4, 131.3, 129.2, 129.1, 128.9, 128.3, 128.2, 126.7, 120.4, 111.2, 97.3, 87.9, 30.6, 21.5, 21.2. MS (relative intensity) m/z : 402 (60), 311 (18), 296 (42), 230 (35), 215 (58), 115 (20), 91 (100). Elem. Anal. (%) Calcd for $\text{C}_{25}\text{H}_{22}\text{Se}$: C 74.80, H 5.52. Found: C 74.85, H 5.57.



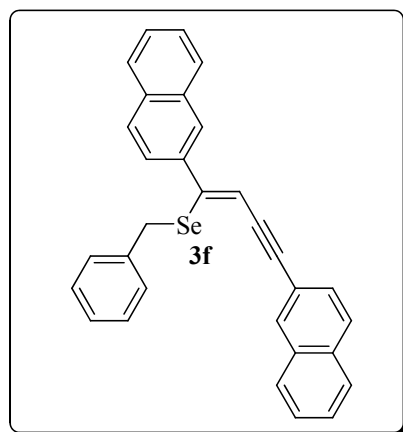
(Z)-benzyl(1,4-dim-tolylbut-1-en-3-ynyl)selane (3c). Yield: 0.584g (73%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.45-7.02 (m, 13H), 6.21 (s, 1H), 3.87 (s, 2H), 2.36 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.6, 140.0, 138.5, 138.1, 137.9, 131.9, 129.2, 129.1, 128.9, 128.5, 128.3, 128.2, 126.7, 125.4, 123.2, 111.4, 97.3, 87.9, 30.6, 21.3, 21.2. MS (relative intensity) m/z : 402 (49), 296 (24), 229 (27), 215 (45), 115 (15), 91 (100). HRMS calcd for $\text{C}_{25}\text{H}_{22}\text{Se}$: 420.0887. Found: 402.0890.



(Z)-benzyl(1,4-dio-tolylbut-1-en-3-ynyl)selane (3d). Yield: 0.408g (51%). ^1H NMR (CDCl_3 , 400 MHz): δ 7.47-7.45 (m, 1H), 7.28-7.10 (m, 11H), 7.01-6.99 (m, 2H), 5.98 (s, 1H), 3.52 (s, 2H), 2.50 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 148.3, 140.0, 138.9, 137.8, 136.0, 131.7, 130.2, 129.3, 129.2, 128.9, 128.3, 128.2, 128.1, 126.7, 125.6, 125.4, 123.0, 108.8, 96.4, 90.7, 26.6, 21.1, 19.6. MS (relative intensity) m/z : 401 (51), 310 (21), 230 (32), 215 (48), 115 (47), 91 (100). Elem. Anal. (%) Calcd for $\text{C}_{25}\text{H}_{22}\text{Se}$: C 74.80, H 5.52. Found: C 74.95, H 5.60.

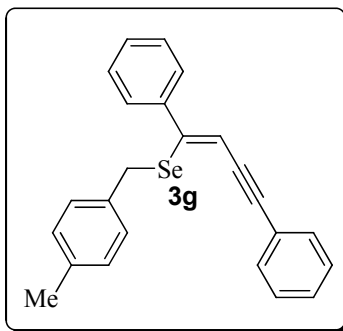


(Z)-benzyl(1,4-bis(4-methoxyphenyl)but-1-en-3-ynyl)selane (3e). Yield: 0.730g (84%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.48-7.34 (m, 4H), 7.25-7.07 (m, 5H), 6.91-6.83 (m, 4H), 6.18 (s, 1H), 3.89 (s, 2H), 3.83 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 159.8, 159.5, 145.9, 138.5, 133.9, 132.7, 129.4, 128.8, 128.2, 126.6, 115.5, 113.9, 113.7, 110.7, 96.8, 87.4, 55.2, 55.1, 30.5. MS (relative intensity) m/z : 433 (100), 341 (51), 326 (13), 247 (32), 91 (76). HRMS calcd for $\text{C}_{25}\text{H}_{22}\text{O}_2\text{Se}$: 434.0785. Found: 434.0806.

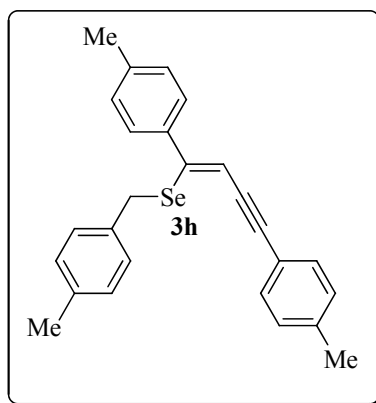


(Z)-benzyl(1,4-di(naphthalen-2-yl)but-1-en-3-ynyl)selane (3f). Yield: 0.488g (52%). ^1H NMR (CDCl_3 , 200 MHz): δ 8.03 (s, 1H), 7.93 (s, 1H), 7.90-7.77 (m, 7H), 7.64-7.46 (m, 7H), 7.16 (s, 3H), 6.42 (s, 1H), 3.93 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.6, 138.3, 137.5, 133.3, 133.2, 132.9, 132.8, 131.2, 128.9, 128.8, 128.5, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 126.8, 126.6, 126.5, 126.4, 125.9, 120.7, 112.3, 97.9, 88.9, 30.8. MS (relative intensity) m/z : 472 (25), 382

(20), 302 (100), 151 (21), 91 (77). Elem. Anal. (%) Calcd for C₃₁H₂₂Se: C 78.64, H 4.68. Found: C 78.90, H 4.72.

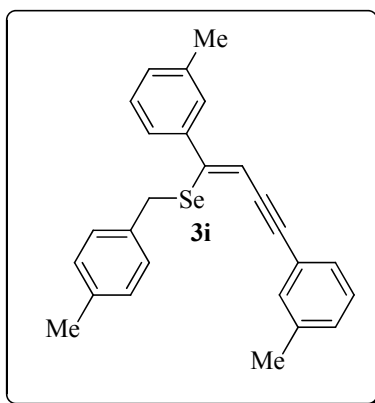


(Z)-(1,4-diphenylbut-1-en-3-ynyl)(4-methyl)selane (3g). Yield: 0.423g (55%). ¹H NMR (CDCl₃, 200 MHz): δ 7.52-7.45 (m, 4H), 7.38-7.30 (m, 6H), 7.25-7.23 (m, 1H), 7.02 (s, 3H), 6.22 (s, 1H), 3.84 (s, 2H), 2.28 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 147.9, 140.1, 136.4, 135.1, 131.4, 129.0, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 123.4, 111.4, 97.2, 88.3, 30.4, 21.0. MS (relative intensity) *m/z*: 388 (13), 202 (16), 105 (100), 77 (9). Elem. Anal. (%) Calcd for C₂₄H₂₀Se: C 74.41, H 5.20. Found: C 74.68, H 5.16.

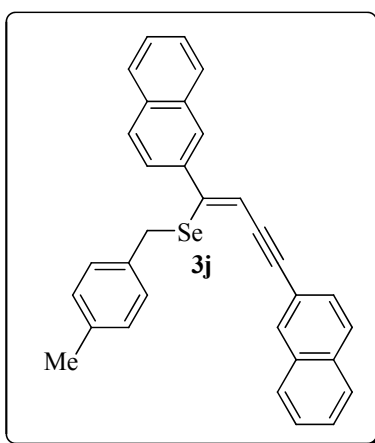


(Z)-(1,4-dip-tolylbut-1-en-3-ynyl)(4-methylbenzyl)selane (3h). Yield: 0.664g (80%). ¹H NMR (CDCl₃, 200 MHz): δ 7.40-7.35 (m, 4H), 7.22-6.98 (m, 8H), 6.21 (s, 1H), 3.85 (s, 2H), 2.38 (s, 3H), 2.35 (s, 3H), 2.28 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 147.4, 138.5, 138.3, 137.4, 136.4, 135.3, 131.2, 129.1, 129.0, 128.8, 128.2, 125.9, 120.4, 110.9, 97.2, 87.9, 30.4, 21.5, 21.2, 21.1. MS (relative

intensity) m/z : 416 (21), 230 (7), 215 (15), 105 (100), 79 (11). HRMS calcd for $C_{26}H_{24}Se$: 416.1043. Found: 416.1050.

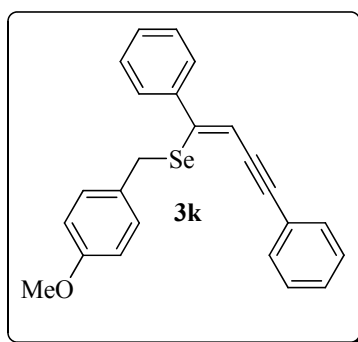


(Z)-(1,4-dim-tolylbut-1-en-3-ynyl)(4-methylbenzyl)selane (3i). Yield: 0.523g (63%). 1H NMR ($CDCl_3$, 200 MHz): δ 7.40-7.35 (m, 4H), 7.22-6.98 (m, 8H), 6.21 (s, 1H), 3.85 (s, 2H), 2.38 (s, 3H), 2.35 (s, 3H), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 147.8, 139.9, 138.0, 137.8, 136.2, 135.2, 131.8, 129.2, 129.0, 128.9, 128.8, 128.7, 128.4, 128.2, 128.1, 125.3, 123.1, 111.1, 97.2, 87.9, 30.3, 21.3, 21.1, 21.0. MS (relative intensity) m/z : 416 (15), 230 (5), 215 (11), 105 (100), 79 (9). Elem. Anal. (%) Calcd for $C_{26}H_{24}Se$: C 75.17, H 5.82. Found: C 75.29, H 5.85.

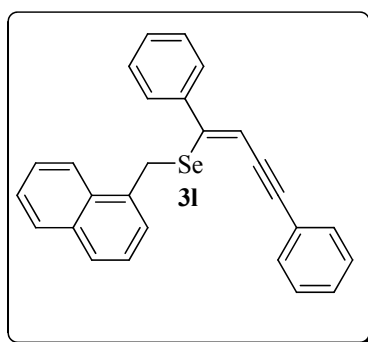


(Z)-(1,4-di(naphtalen-2-yl)but-1-en-3-ynyl)(4-methylbenzyl)selane (3j). Yield: 0.669g (69%). 1H NMR ($CDCl_3$, 200 MHz): δ 8.02 (s, 1H), 7.95 (s, 1H), 7.87-7.77 (m, 6H), 7.66-7.47 (m, 6H), 7.08-6.96 (m, 4H), 6.41 (s, 1H), 3.89 (s, 2H), 2.27 (s,

3H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 147.9, 137.5, 136.4, 135.1, 133.2, 133.2, 133.0, 132.8, 131.2, 129.1, 128.8, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 126.6, 126.5, 126.4, 126.0, 120.7, 112.1, 97.9, 97.5, 88.9, 30.6, 21.0. MS (relative intensity) m/z : 488 (20), 384 (14), 302 (28), 151 (10), 105 (100). Elem. Anal. (%) Calcd for $\text{C}_{32}\text{H}_{24}\text{Se}$: C 78.84, H 4.96. Found: C 78.79, H 4.92.

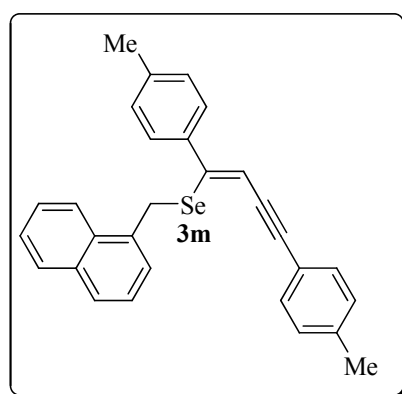


(Z)-(1,4-diphenylbut-1-en-3-ynyl)(4-methoxybenzyl)selane (3k). Yield: 0.558g (69%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.52-7.44 (m, 9H), 7.41-7.27 (m, 6H), 7.06 (d, J = 8.5 Hz, 2H), 6.74 (d, J = 8.4 Hz, 2H), 6.22 (s, 1H), 3.84 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 158.4, 147.8, 140.1, 131.3, 130.2, 130.1, 128.5, 128.4, 128.3, 128.2, 128.1, 123.4, 113.7, 111.4, 97.1, 88.3, 55.1, 30.1. **MS (relative intensity) m/z :** 403 (8), 202 (5), 121 (100), 91 (3), 77 (4). HRMS calcd for $\text{C}_{24}\text{H}_{20}\text{OSe}$: 404.0679. Found: 404.0692.

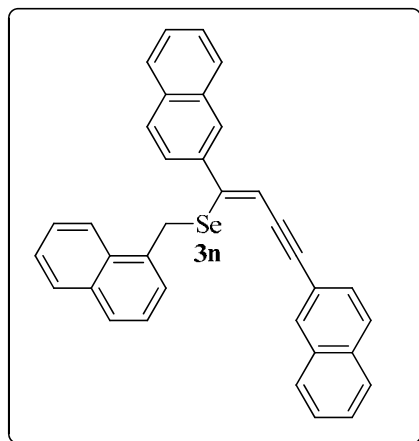


(Z)-(1,4-diphenylbut-1-en-3-ynyl)(naphthalen-1-ylmethyl)selane (3l). Yield: 0.622g (74%). ^1H NMR (CDCl_3 , 200 MHz): δ 8.12-8.08 (m, 1H), 7.85-7.69 (m, 2H), 7.57-7.35 (m, 9H), 7.30-7.27 (m, 4H), 7.19-7.16 (m, 1H), 6.30 (s, 1H), 4.34 (s, 2H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 147.8, 140.2, 134.0, 133.8, 131.4, 131.3, 128.7, 128.6, 128.5, 128.3, 128.2, 127.9, 127.2, 125.9, 125.7, 125.3, 124.0, 123.3, 111.9, 97.2, 88.4, 28.6. MS (relative intensity) m/z : 422 (100), 345 (33), 325 (18), 265 (40), 70 (43). Elem. Anal. (%) Calcd for $\text{C}_{27}\text{H}_{20}\text{Se}$: C 76.59, H 4.76. Found: C 76.72, H 4.80.

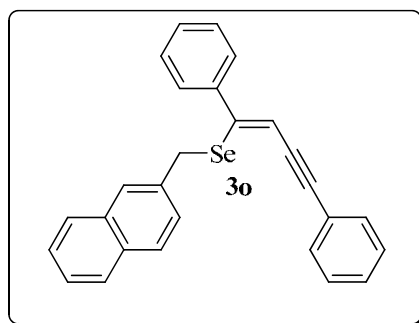


(Z)-(1,4-dip-tolylbut-1-en-3-ynyl)(naphthalen-1-ylmethyl)selane (3m). Yield: 0.675g (75%). ^1H NMR (CDCl_3 , 200 MHz): δ 8.13-8.08 (m, 1H), 7.85-7.80 (m, 1H), 7.72-7.68 (m, 1H), 7.56-7.41 (m, 4H), 7.33-7.17 (m, 6H), 7.10-7.06 (m, 2H), 6.28 (s, 1H), 4.35 (s, 2H), 2.38 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.4, 138.6, 138.3, 137.4, 134.2, 133.8, 131.3, 129.5, 129.2, 129.0, 128.6, 128.2, 127.8, 127.2, 125.9, 125.7, 125.3, 124.1, 120.3, 111.4, 97.3, 87.9, 28.6, 21.5, 21.2. MS (relative intensity) m/z : 450 (100), 357 (25), 337 (19), 266 (12), 170 (26). Elem. Anal. (%) Calcd for $\text{C}_{29}\text{H}_{24}\text{Se}$: C 77.15, H 5.36. Found: C 77.45, H 5.40.



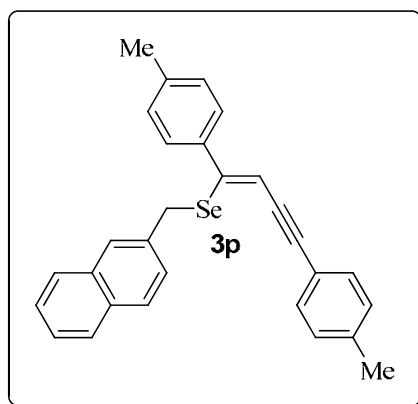
(Z)-(1,4-di(naphtalen-2-yl)but-1-en-3-ynyl)(naphtlalen-1-ylmethyl)selane (3n).

Yield: 0.239g (23%). ^1H NMR (CDCl_3 , 200 MHz): δ 8.19-8.13 (m, 1H), 8.02-7.64 (m, 12H), 7.55-7.46 (m, 7H), 7.23-7.17 (m, 1H), 6.49 (s, 1H), 4.40 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.7, 137.7, 134.1, 133.9, 133.4, 133.2, 133.0, 132.8, 131.5, 131.3, 128.7, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.3, 126.7, 126.6, 126.5, 126.4, 126.0, 125.9, 125.7, 125.3, 124.1, 120.7, 112.9, 97.9, 89.1, 28.8. MS (relative intensity) m/z : 522 (5), 382 (18), 302 (49), 151 (10), 141 (100). Elem. Anal. (%) Calcd for $\text{C}_{35}\text{H}_{24}\text{Se}$: C 80.30, H 4.62. Found: C 80.27, H 4.59.

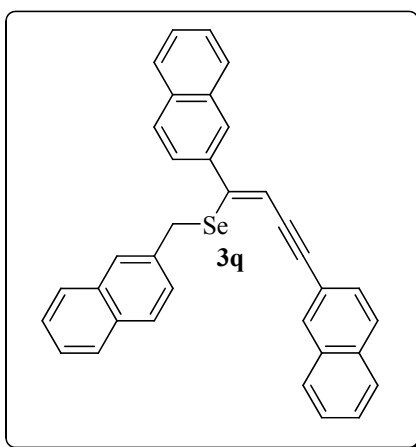


(Z)-(1,4-diphenylbut-1-en-3-ynyl)(naphtlalen-2-ylmethyl)selane (3o).

Yield: 0.551g (65%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.77-7.58 (m, 3H), 7.51-7.17 (m, 14H), 6.20 (s, 1H), 4.01 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.5, 139.9, 135.7, 133.1, 132.3, 131.4, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.6, 127.3, 127.2, 125.9, 125.6, 123.4, 111.7, 97.3, 88.3, 30.9. MS (relative intensity) m/z : 424 (84), 344 (31), 282 (11), 141 (100), 77 (15). Elem. Anal. (%) Calcd for $\text{C}_{27}\text{H}_{20}\text{Se}$: C 76.59, H 4.76. Found: C 76.72, H 4.80.



(Z)-(1,4-dip-tolylbut-1-en-3-ynyl)(naphthalen-2-ylmethyl)selane (3p). Yield: 0.540g (60%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.79-7.46 (m, 4H), 7.44-7.34 (m, 8H), 7.19-7.10 (m, 4H), 6.19 (s, 1H), 4.03 (s, 2H), 2.38 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.1, 138.5, 138.4, 137.3, 135.9, 133.2, 132.3, 131.3, 129.1, 129.0, 128.3, 128.1, 127.6, 127.4, 127.3, 125.9, 125.6, 120.4, 111.3, 97.3, 87.9, 30.9, 21.5, 21.2. MS (relative intensity) m/z : 452 (100), 356 (16), 296 (28), 141 (41), 115 (49). Elem. Anal. (%) Calcd for $\text{C}_{29}\text{H}_{24}\text{Se}$: C 77.15, H 5.36. Found: C 77.11, H 5.31.

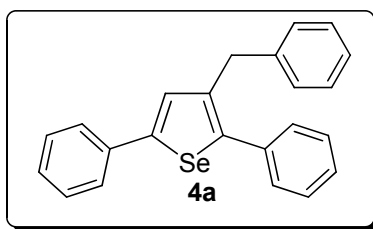


(Z)-(1,4-di(naphthalen-2-yl)-but-1-en-3-ynyl)(naphthalen-2-ylmethyl)selane (3q). Yield: 0.728g (70%). ^1H NMR (CDCl_3 , 200 MHz): δ 8.01 (s, 1H), 7.93 (s, 1H), 7.89-7.68 (m, 8H), 7.64-7.63 (m, 1H), 7.60-7.46 (m, 6H), 7.41-7.32 (m, 4H), 6.38 (s, 1H), 4.06 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.6, 137.6, 135.8, 133.3,

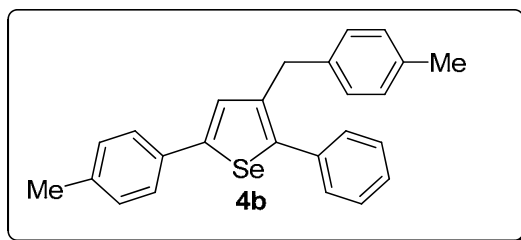
133.3, 133.2, 133.0, 132.9, 132.4, 131.1, 128.4, 128.3, 128.1, 127.9, 127.8, 127.76, 127.72, 127.6, 127.5, 127.4, 127.2, 126.65, 126.60, 126.52, 126.51, 126.0, 125.9, 125.6, 120.8, 112.5, 97.9, 88.9, 31.2. MS (relative intensity) m/z : 524 (12), 384 (7), 302 (15), 141 (100), 115 (13). Elem. Anal. (%) Calcd for $C_{35}H_{24}Se$: C 80.30, H 4.62. Found: C 80.27, H 4.59.

General Procedure for the Preparation of the 3-benzyl-2,5-diarylselenophenes 4a-q.

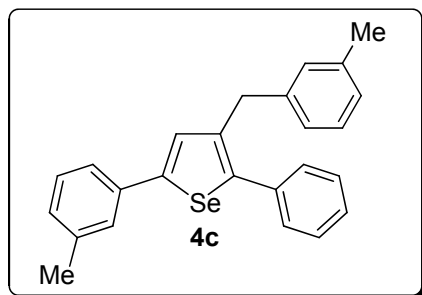
To a Schlenk tube, under argon, containing the appropriate (Z)-benzylselenoenyne **3** (0.4 mmol) in DMF (4 mL) was added the *t*-BuOk (0.4 mmol) and the resulting solution was stirred at 90°C for 2-6 h. After this the mixture was diluted with ethyl acetate (10 mL), and washed with brine (3x10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexane or ethyl acetate/hexane as the eluent.



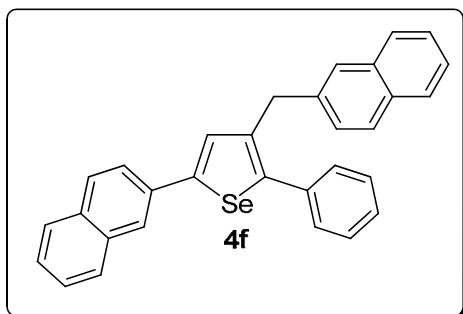
3-benzyl-2,5-diphenylselenophene (4a). Yield: 0.104g (70%). 1H NMR ($CDCl_3$, 200 MHz): δ 7.53-7.16 (m, 16H), 3.99 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.4, 144.1, 140.8, 138.6, 136.2, 136.1, 129.2, 128.9, 128.8, 128.6, 128.5, 128.4, 127.6, 127.5, 126.0, 125.9, 35.7. MS (relative intensity) m/z : 370 (100), 293 (19), 212 (43), 114 (11), 90 (14). Elem. Anal. (%) Calcd for $C_{23}H_{18}Se$: C 73.99, H 4.86. Found: C 74.03, H 4.90.



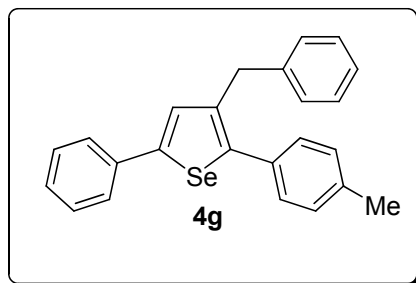
3-(4-methylbenzyl)-2-phenyl-5-p-tolylselenophene (4b). Yield: 0.088g (55%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.48-7.30 (m, 6H), 7.27-7.23 (m, 3H), 7.15-7.09 (m, 5H), 3.94 (s, 2H), 2.34 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 148.4, 143.3, 138.8, 137.8, 137.4, 136.2, 135.5, 133.5, 129.4, 129.2, 129.1, 128.5, 128.4, 128.3, 127.4, 125.9, 35.4, 21.2, 20.9. MS (relative intensity) m/z : 402 (100), 322 (19), 310 (14), 229 (26), 215 (23), 105 (18). Elem. Anal. (%) Calcd for $\text{C}_{25}\text{H}_{22}\text{Se}$: C 74.80 H 5.52. Found: C 74.83, H 5.53.



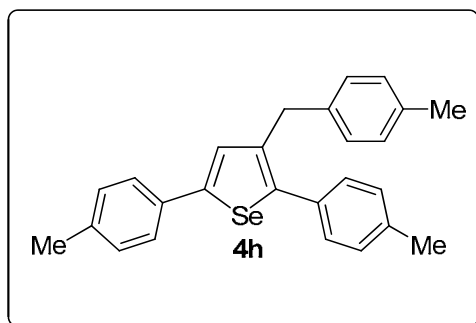
3-(3-methylbenzyl)-2-phenyl-5-m-tolylselenophene (4c). Yield: 0.090g (56%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.49-7.15 (m, 10H), 7.09-6.96 (m, 4H), 3.95 (s, 2H), 2.36 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 148.4, 143.8, 140.8, 138.6, 138.4, 138.0, 136.1, 136.0, 129.2, 128.9, 128.7, 128.5, 128.4, 128.3, 127.5, 126.8, 126.7, 125.5, 123.2, 35.7, 21.4, 21.3. MS (relative intensity) m/z : 401 (100), 322 (19), 310 (13), 229 (27), 215 (24), 105 (14). Elem. Anal. (%) Calcd for $\text{C}_{25}\text{H}_{22}\text{Se}$: C 74.80, H 5.52. Found: C 74.91, H 5.58.



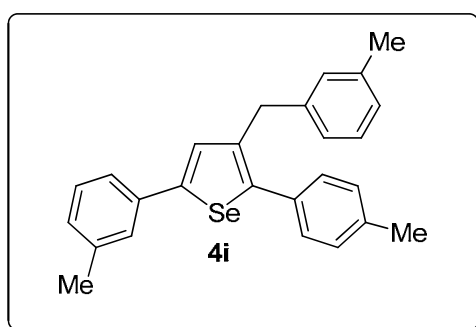
5-(naphthalen-2-yl)-3-(naphthalen-2-ylmethyl)-2-phenylselenophene (4f). Yield: 0.079g (40%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.94-7.89 (m, 1H), 7.83-7.70 (m, 5H), 7.63-7.58 (m, 2H), 7.54-7.21 (m, 12H), 4.16 (s, 2H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 148.4, 144.4, 138.6, 138.4, 136.0, 133.6, 133.5, 133.4, 132.7, 132.0, 129.3, 129.2, 128.6, 128.5, 128.4, 128.1, 127.9, 127.64, 127.62, 127.60, 127.2, 126.6, 126.5, 125.6, 125.9, 125.3, 124.4, 124.2, 36.0. MS (relative intensity) m/z : 473 (22), 281 (46), 207 (100), 191 (17), 147 (24). Elem. Anal. (%) Calcd for $\text{C}_{31}\text{H}_{22}\text{Se}$: C 78.64, H 4.68. Found: C 78.59, H 4.64.



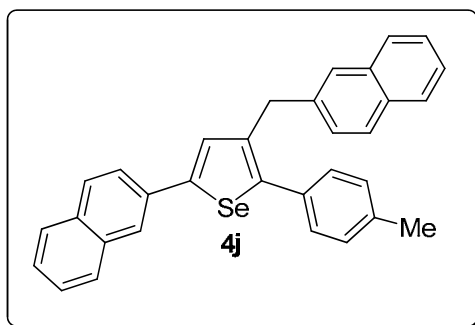
3-benzyl-5-phenyl-2-p-tolylselenophene (4g). Yield: 0.105g (70%). ^1H NMR (CDCl_3 , 400 MHz): δ 7.50-7.48 (m, 2H), 7.36-7.29 (m, 5H), 7.27-7.23 (m, 3H), 7.22-7.17 (m, 5H), 3.98 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.9, 144.3, 140.9, 138.4, 137.4, 136.3, 133.2, 129.3, 129.1, 128.9, 128.8, 128.5, 128.4, 127.4, 126.0, 125.9, 35.77, 21.2. MS (relative intensity) m/z : 388 (100), 311 (11), 215 (39), 115 (13), 91 (17). Elem. Anal. (%) Calcd for $\text{C}_{24}\text{H}_{20}\text{Se}$: C 74.41, H 5.20. Found: C 74.46, H 5.24.



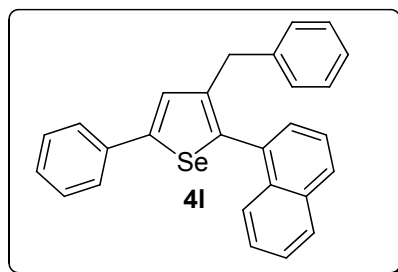
3-(4-methylbenzyl)-2,5-dip-tolylselenophene (4h). Yield: 0.102g (64%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.41-7.32 (m, 4H), 7.21-7.09 (m, 9H), 3.93 (s, 2H), 2.37 (s, 3H), 2.33 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 148.0, 143.5, 138.5, 137.9, 137.3, 136.2, 135.4, 133.5, 133.3, 129.4, 129.2, 129.1, 129.0, 128.4, 128.3, 125.8, 35.3, 21.2, 21.1, 20.9. MS (relative intensity) m/z : 416 (100), 325 (11), 243 (16), 229 (19), 105 (18). Elem. Anal. (%) Calcd for $\text{C}_{26}\text{H}_{24}\text{Se}$: C 75.17, H 5.82. Found: C 75.21, H 5.87.



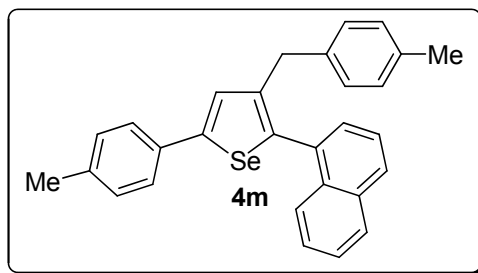
3-(3-methylbenzyl)-5-m-tolyl-2-p-tolylselenophene (4i). Yield: 0.040g (25%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.37-7.14 (m, 9H), 7.10-6.96 (m, 4H), 3.94 (s, 2H), 2.37 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 148.0, 143.9, 140.8, 138.4, 138.3, 138.0, 137.3, 136.1, 133.2, 129.2, 129.0, 128.8, 128.7, 128.3, 128.2, 126.8, 126.7, 125.5, 123.1, 35.7, 21.4, 21.3, 21.2. MS (relative intensity) m/z : 416 (100), 325 (12), 243 (15), 229 (16), 105 (13). Elem. Anal. (%) Calcd for $\text{C}_{26}\text{H}_{24}\text{Se}$: C 75.17, H 5.82. Found: C 75.01, H 5.79.



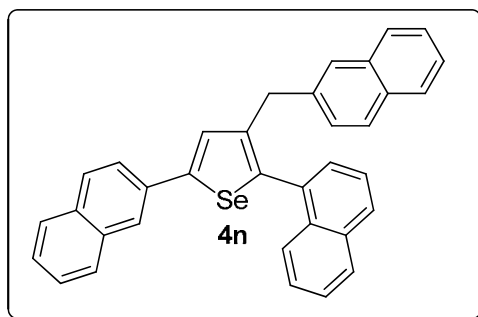
5-(naphthalen-2-yl)-3-(naphthalen-2-ylmethyl)-2-p-tolyl-selenophene (4j). Yield: 0.038g (20%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.92-7.75 (m, 5H), 7.65-7.31 (m, 6H), 7.26-7.07 (m, 8H), 3.68 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 148.1, 144.6, 138.5, 138.3, 137.5, 136.2, 136.1, 133.6, 133.2, 132.7, 132.1, 129.3, 129.2, 129.1, 128.9, 128.3, 128.1, 127.9, 127.7, 127.6, 127.3, 126.6, 126.5, 125.9, 125.8, 125.3, 124.4, 124.3, 36.1, 21.1. MS (relative intensity) m/z : 487 (100), 315 (26), 265 (30), 141 (23), 115 (24). Elem. Anal. (%) Calcd for $\text{C}_{32}\text{H}_{24}\text{Se}$: C 78.84, H 4.96. Found: C 78.92, H 5.01.



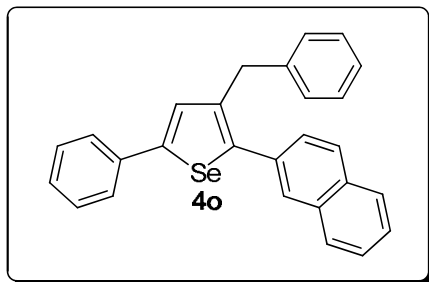
3-benzyl-2-(naphthalen-1-yl)-5-phenylselenophene (4l). Yield: 0.061g (36%). ^1H NMR (CDCl_3 , 400 MHz): δ 8.01-7.99 (m, 1H), 7.89-7.85 (m, 2H), 7.56-7.46 (m, 6H), 7.35-7.29 (m, 3H), 7.25-7.16 (m, 3H), 7.13-7.09 (m, 1H), 7.05-7.03 (m, 2H), 3.65 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 149.3, 141.6, 140.8, 140.6, 136.2, 133.6, 133.3, 132.7, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 127.6, 127.5, 126.3, 126.2, 126.1, 126.0, 125.9, 125.1, 36.28. MS (relative intensity) m/z : 423 (100), 343 (25), 265 (41), 252 (27), 91 (15). Elem. Anal. (%) Calcd for $\text{C}_{27}\text{H}_{20}\text{Se}$: C 76.59, H 4.76. Found: C 76.28, H 4.69.



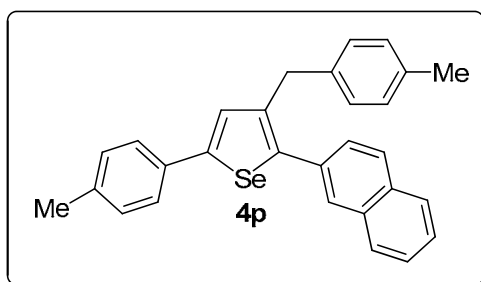
3-(4-methylbenzyl)-2-(naphthalen-1-yl)-5-p-tolylselenophene (4m). Yield: 0.104g (58%). ^1H NMR (CDCl_3 , 200 MHz): δ 8.04-7.99 (m, 1H), 7.92-7.86 (m, 2H), 7.59-7.46 (m, 4H), 7.41 (d, J = 8.0 Hz, 2H), 7.29 (s, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 3.60 (s, 2H), 2.34 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 149.4, 141.7, 139.9, 137.6, 137.4, 135.2, 133.6, 133.5, 133.4, 132.7, 129.5, 128.9, 128.8, 128.5, 128.4, 128.2, 127.0, 126.4, 126.3, 126.0, 125.9, 125.1, 35.8, 21.1, 20.9. MS (relative intensity) m/z : 451 (100), 359 (19), 279 (24), 265 (18), 105 (18). Elem. Anal. (%) Calcd for $\text{C}_{29}\text{H}_{24}\text{Se}$: C 77.15, H 5.36. Found: C 77.29, H 5.40.



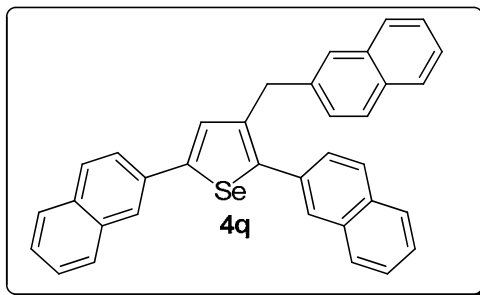
2-(naphthalen-1-yl)-5-(naphthalen-2-yl)-3-(naphthalen-2-ylmethyl)selenophene (4n). Yield: 0.080g (38%). ^1H NMR (CDCl_3 , 200 MHz): δ 8.10-8.02 (m, 1H), 7.94-7.88 (m, 3H), 7.85-7.70 (m, 8H), 7.57-7.36 (m, 9H), 7.24-7.17 (m, 1H), 3.85 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 149.5, 141.6, 141.2, 138.1, 133.7, 133.6, 133.5, 133.4, 133.3, 132.8, 132.7, 131.9, 128.8, 128.7, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 127.3, 126.8, 126.5, 126.4, 126.3, 126.1, 125.9, 125.8, 125.2, 125.1, 124.5, 124.4, 36.6. MS (relative intensity) m/z : 524 (100), 395 (18), 315 (46), 302 (23), 141 (24). HRMS calcd for $\text{C}_{26}\text{H}_{24}\text{Se}$: 524.1043. Found: 524.1038.



3-benzyl-2-(naphthalen-2-yl)-5-phenylselenophene (4o). Yield: 0.150g (88%). ^1H NMR (CDCl_3 , 400 MHz): δ 7.90 (s, 1H), 7.86-7.79 (m, 3H), 7.59-7.56 (m, 1H), 7.54-7.46 (m, 4H), 7.37-7.31 (m, 4H), 7.30-7.26 (m, 2H), 7.22-7.19 (m, 3H), 4.05 (s, 2H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 148.6, 144.0, 140.8, 138.9, 136.1, 133.4, 133.2, 132.4, 129.0, 128.8, 128.5, 128.4, 128.1, 128.0, 127.9, 127.6, 127.5, 127.4, 126.4, 126.1, 126.0, 125.9, 35.8. MS (relative intensity) m/z : 424 (100), 346 (15), 265 (45), 252 (20), 91 (14). Elem. Anal. (%) Calcd for $\text{C}_{27}\text{H}_{20}\text{Se}$: C 76.59, H 4.76. Found: C 76.29, H 4.71.



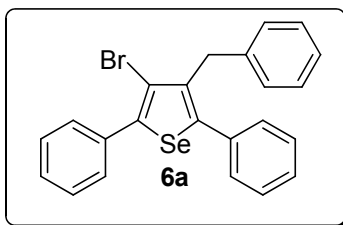
3-(4-methylbenzyl)-2-(naphthalen-2-yl)-5-p-tolylselenophene (4p). Yield: 0.137g (76%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.90-7.78 (m, 4H), 7.60-7.38 (m, 5H), 7.28 (s, 1H), 7.16-7.10 (m, 6H), 4.00 (s, 2H), 2.35 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 148.7, 143.2, 139.2, 137.8, 137.5, 135.5, 133.6, 133.4, 133.3, 132.5, 129.5, 129.2, 128.6, 128.4, 128.1, 128.0, 127.9, 127.6, 127.5, 126.4, 126.1, 125.9, 35.5, 21.2, 21.0. MS (relative intensity) m/z : 451 (100), 356 (15), 279 (25), 139 (16), 105 (17). Elem. Anal. (%) Calcd for $\text{C}_{29}\text{H}_{24}\text{Se}$: C 77.15, H 5.36. Found: C 77.37, H 5.41.



2,5-di(naphthalen-2-yl)-3-(naphthalen-2-ylmethyl)selenophene (4q). Yield: 0.080g (76%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.95 (s, 2H), 7.89-7.77 (m, 9H), 7.67-7.62 (m, 3H), 7.52-7.34 (m, 8H), 4.05 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 148.8, 144.5, 139.0, 138.4, 133.7, 133.6, 133.5, 133.3, 132.7, 132.6, 132.1, 129.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 126.7, 126.6, 126.5, 126.3, 126.0, 125.9, 125.4, 124.5, 124.3, 36.2. MS (relative intensity) m/z : 523 (100), 315 (59), 302 (16), 141 (19), 128 (28). Elem. Anal. (%) Calcd for $\text{C}_{35}\text{H}_{24}\text{Se}$: C 80.30, H 4.62. Found: C 80.52, H 4.70.

General Procedure for the Preparation of the 3-benzyl-4-bromo-2,5-diphenylselenophene (6a).³

A solution of bromine (2.0g, 12.5 mmol) in CHCl_3 (15 mL) was added dropwise to a solution of 3-benzyl-2,5-diphenylselenophene **4a** (1.870g, 5 mmol) in CHCl_3 (40 mL) at room temperature. After the addition was complete, the reaction was stirred at room temperature for 1 h. After this the mixture was diluted with CHCl_2 (30 mL), and washed with brine (3 x 20 mL). The organic phase was separated, dried over MgSO_4 , and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexane as the eluent.

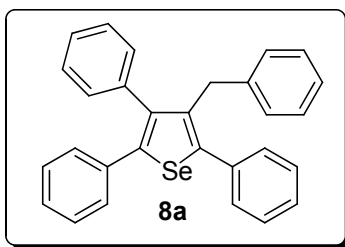


⁽³⁾ Chen, Z.; Mocharia, V. P.; Farmer, J. M.; Pettit, G. R.; Hamel, E.; Pinney, K. G. *J. Org. Chem.* **2000**, *65*, 8811.

3-benzyl-4-bromo-2,5-diphenylselenophene (6a). Yield: 2.079g (92%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.66-7.61 (m, 2H), 7.45-7.28 (m, 9H), 7.22-7.12 (m, 4H), 4.11 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 145.2, 142.2, 139.8, 136.8, 135.7, 135.2, 129.5, 128.9, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 125.9, 112.4, 36.2. MS (relative intensity) m/z : 452 (100), 373 (19), 293 (72), 215 (92), 138 (22), 91 (58). Elem. Anal. (%) Calcd for $\text{C}_{23}\text{H}_{17}\text{Se}$: C 61.08, H 3.79. Found: C 61.25, H 3.82.

General procedure for the palladium-catalyzed coupling reaction of 6a with arylboronic acids.⁴

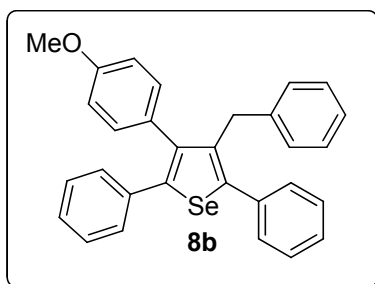
To a Schlenk tube, under argon, containing a solution of 3-benzyl-4-bromo-2,5-diphenylselenophene **5a** (0.180g, 0.40 mmol) in Toluene/Dioxane (1:1, 3.2 mL) was added to $\text{Pd}(\text{PPh}_3)_4$ (0.023g, 0.02 mmol). The resulting solution was stirred for 30 minutes at room temperature. After this time appropriate arylboronic acid (0.6 mmol) and a solution of K_3PO_4 (0.211g, 1 mmol) in H_2O (0.5 mL) were added. The mixture was stirred at 90 °C for 3 h. After this the mixture was diluted with ethyl acetate (20 mL), and washed with brine (3x20 mL). The organic phase was separated, dried over MgSO_4 , and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using ethyl acetate/hexane as the eluent.



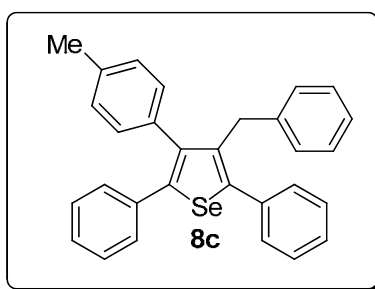
3-benzyl-2,4,5-triphenylselenophene (8a). Yield: 0.155g (86%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.52-7.47 (m, 2H), 7.41-7.28 (m, 4H), 7.18-7.03 (m, 10H), 6.96-6.92 (m, 2H), 6.78-6.73 (m, 2H), 3.84 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 145.1, 144.3, 142.3, 140.8, 138.5, 138.4, 136.6, 136.3, 130.5, 129.5, 129.2, 128.5, 128.2, 128.0, 127.9, 127.8, 127.5, 126.8, 126.7, 125.4, 35.0. MS (relative intensity) m/z :

⁽⁴⁾Dang, T. T.; Rasool, N.; Reinke T. T. D, H.; Langer, P. *Tetrahedron Lett.* **2007**, *48*, 845.

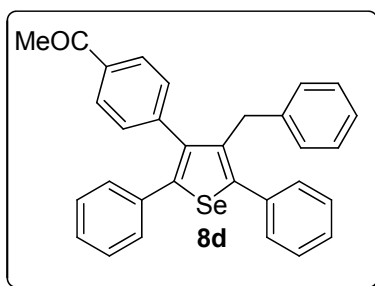
450 (100), 370 (14), 291 (39), 145 (29), 91 (19). Elem. Anal. (%) Calcd for $C_{29}H_{22}Se$: C 77.50, H 4.93. Found: C 77.69, H 4.99.



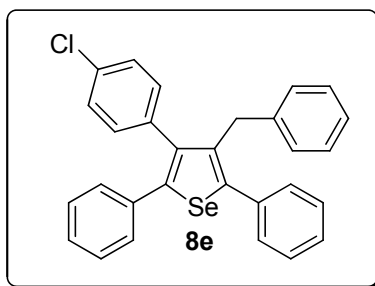
3-benzyl-4-(4-methoxyphenyl)-2,5-diphenylselenophene (8b). Yield: 0.177g (93%). 1H NMR ($CDCl_3$, 200 MHz): δ 7.51-7.43 (m, 3H), 7.39-7.28 (m, 3H), 7.17-7.05 (m, 7H), 6.98-6.72 (m, 4H), 6.69-6.62 (m, 2H), 3.83 (s, 2H), 3.74 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.6, 145.0, 144.1, 142.0, 141.0, 138.7, 136.7, 136.5, 131.5, 130.8, 129.4, 129.2, 128.5, 128.2, 128.1, 127.9, 127.7, 127.5, 125.4, 113.5, 55.1, 35.0. MS (relative intensity) m/z : 480 (100), 291 (12), 191 (14), 153 (14), 91 (15). Elem. Anal. (%) Calcd for $C_{30}H_{24}OSe$: C 75.15, H 5.05. Found: C 75.28, H 5.17.



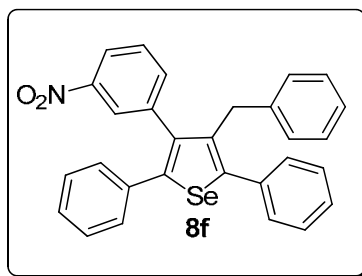
3-benzyl-2,5-diphenyl-4-p-tolylselenophene (8c). Yield: 0.160g (89%). 1H NMR ($CDCl_3$, 200 MHz): δ 7.50-7.45 (m, 2H), 7.37-7.22 (m, 3H), 7.19-7.01 (m, 8H), 6.94-6.72 (m, 6H), 3.83 (s, 2H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 144.8, 144.1, 142.2, 140.9, 138.4, 136.5, 136.3, 136.2, 135.1, 130.1, 129.3, 129.2, 128.6, 128.5, 128.1, 128.0, 127.8, 127.4, 126.7, 125.3, 34.8, 21.2. MS (relative intensity) m/z : 464 (100), 384 (12), 291 (21), 191 (15), 145 (29). Elem. Anal. (%) Calcd for $C_{30}H_{24}Se$: C 77.74, H 5.22. Found: C 77.85, H 5.29.



1-(4-(4-benzyl-2,5-diphenylselenophen-3-yl)-phenyl)ethanone (8d). Yield: 0.152g (80%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.70 (d, J = 8.5 Hz, 2H), 7.52-7.47 (m, 2H), 7.42-7.32 (m, 3H), 7.13 (s, 5H), 7.08-7.02 (m, 5H), 6.77-6.72 (m, 2H), 3.84 (s, 2H), 2.54 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.6, 145.7, 145.0, 143.6, 141.1, 140.4, 137.7, 136.2, 135.8, 135.5, 130.7, 129.4, 129.2, 128.5, 128.2, 128.1, 127.9, 127.8, 127.7, 127.1, 125.5, 34.9, 26.3. MS (relative intensity) m/z : 492 (100), 291 (39), 191 (22), 145 (27), 91 (41). Elem. Anal. (%) Calcd for $\text{C}_{31}\text{H}_{24}\text{OSe}$: C 75.76, H 4.92. Found: C 75.91, H 4.98.



3-benzyl-4-(4-chlorophenyl)-2,5-diphenylselenophene (8e). Yield: 0.180g (95%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.51-7.45 (m, 2H), 7.40-7.26 (m, 3H), 7.21-7.03 (m, 10H), 6.86-6.70 (m, 4H), 3.82 (s, 2H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 145.4, 144.5, 140.7, 140.5, 137.9, 136.7, 136.2, 135.8, 132.7, 131.7, 129.3, 129.2, 128.5, 128.2, 128.1, 128.0, 127.9, 127.6, 127.0, 125.5, 34.9. MS (relative intensity) m/z : 484 (100), 291 (36), 191 (20), 145 (72), 91 (27). Elem. Anal. (%) Calcd for $\text{C}_{29}\text{H}_{21}\text{Se}$: C 71.98, H 4.37. Found: C 72.21, H 4.43.



3-benzyl-4-(3-nitrophenyl)-2,5-diphenylselenophene (8f). Yield: 0.162g (90%).
 ^1H NMR (CDCl_3 , 200 MHz): δ 8.02-7.96 (m, 1H), 7.78-7.74 (m, 1H), 7.55-7.46 (m, 2H), 7.46-7.33 (m, 3H), 7.27-7.04 (m, 10H), 6.75-6.67 (m, 2H), 3.83 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.8, 146.5, 145.3, 140.2, 140.0, 139.5, 137.6, 136.6, 136.0, 135.4, 129.5, 129.3, 128.7, 128.6, 128.3, 128.1, 128.0, 127.9, 127.4, 125.8, 125.4, 121.7, 35.1. MS (relative intensity) m/z : 495 (100), 289 (35), 169 (21), 145 (37), 91 (33). HRMS calcd for $\text{C}_{29}\text{H}_{21}\text{NO}_2\text{Se}$: 495.0738. Found: 495.0742.

SELECTED SPECTRA

