

Electronic Supplementary Information

The [3+2] Cycloaddition Reaction of Thiazole Carbene-derived C-C-Se 1,3-Dipoles: a Concise and Highly Efficient Strategy for the Construction of Multifunctional Dihydroselenophenes and Selenopheno[2,3-b]pyrazines

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General procedure for the preparation of 2-arylselenocarbamoylthiazolium inner salts 4.

At $-20\text{ }^{\circ}\text{C}$ and under nitrogen atmosphere, the mixture of *N*-alkyl thiazolium bromide or thiazolium chloride **1** (1 mmol) with aryl isoselenocyanates **3** (1 mmol) in THF (50 mL) was stirred for 15-20 min. Then NaH (1.5 mmol, 50% in mineral oil) was added in portions and the mixture was stirred for 2.5-3.5 h at $-20\text{ }^{\circ}\text{C}$. After removal of the solvent under vacuum at room temperature, the residue was chromatographed on a neutral Al_2O_3 column eluting with a mixture of petroleum ether (30-60 $^{\circ}\text{C}$) and acetone (from 3:1 to 1:1). The eluent was evaporated under vacuum at room temperature to give 2-arylselenocarbamoylthiazolium inner salts **4** in 55-88% yields. The products were recrystallized with dichloromethane and petroleum ether.

3-Benzyl-4-methyl-2-phenylselenocarbamoylthiazolium inner salt 4a: 65%, red crystals, mp 180-181 $^{\circ}\text{C}$; $\nu_{\text{max}}/\text{cm}^{-1}$ 3041, 1659, 1514, 1495, 1479; δ_{H} (400 MHz, CDCl_3) 7.32-7.40 (m, 7H, Ph-H), 7.26-7.30 (m, 2H, Ph-H), 7.19 (d, $J = 0.8\text{ Hz}$, 1H, thiazolyl-H), 7.11 (tt, $J = 6.7, 1.8\text{ Hz}$, 1H, Ph-H), 6.22 (s, 2H, CH_2Ph), 2.38 (d, $J = 0.9\text{ Hz}$, 3H, thiazolyl- CH_3); δ_{C} (100 MHz, CDCl_3) 180.8, 163.4, 152.3, 145.5, 132.8, 129.3, 128.7, 128.6, 127.3, 124.3, 121.1, 118.7, 54.1, 15.0; MS (ESI): 373 (M+1). Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{SSe}$: C 58.22, H 4.34, N 7.54; Found: C 58.13, H 4.20, N 7.43.

3-Benzyl-4-methyl-2-(4-chlorophenyl)selenocarbamoylthiazolium inner salt 4b: 69%, dark crystals, mp 160-161 $^{\circ}\text{C}$; $\nu_{\text{max}}/\text{cm}^{-1}$ 1571, 1521, 1478; δ_{H} (400 MHz, CD_3COCD_3) 7.66 (d, $J = 0.9\text{ Hz}$, 1H, thiazolyl-H), 7.22-7.29 (m, 7H, Ar-H), 7.12 (d, $J = 8.8\text{ Hz}$, 2H, Ar-H), 6.20 (s, 2H, CH_2Ph), 2.32 (d, $J = 1.0\text{ Hz}$, 3H, thiazolyl- CH_3); δ_{C} (100 MHz, CDCl_3) 180.4, 164.1, 150.6,

145.7, 132.7, 129.3, 128.7, 128.6, 127.1, 122.7, 119.1, 54.2, 14.9; MS (ESI): 407 (M+1). Anal. Calcd for C₁₈H₁₅ClN₂SSe: C 53.28, H 3.73, N 6.90; Found: C 53.38, H 3.48, N 6.99.

3-Benzyl-4-methyl-2-(3,4-dichlorophenyl)selenocarbamoylthiazolium inner salt 4c: 73%, red crystals, mp 187-188 °C; $\nu_{\max}/\text{cm}^{-1}$ 3116, 1580, 1501, 1461, 1454; δ_{H} (400 MHz, CDCl₃) 7.37 (s, 1H, thiazolyl-H), 7.29-7.34 (m, 4H, Ar-H), 7.13-7.17 (m, 4H, Ar-H), 6.09 (s, 2H, CH₂Ph), 2.28 (s, 3H, thiazolyl-CH₃); δ_{C} (100 MHz, CDCl₃) 180.5, 165.9, 151.7, 145.7, 132.5, 132.1, 130.2, 129.3, 128.9, 127.1, 123.2, 121.0, 118.9, 54.2, 14.9; MS (ESI): 441 (M+1). Anal. Calcd for C₁₈H₁₄Cl₂N₂SSe: C 49.11, H 3.21, N 6.36; Found: C 49.15, H 3.03, N 6.32.

3-Benzyl-4-methyl-2-(4-trifluoromethylphenyl)selenocarbamoylthiazolium inner salt 4d: 76%, red crystals, mp 115-116 °C; $\nu_{\max}/\text{cm}^{-1}$ 3118, 1606, 1516, 1498; δ_{H} (400 MHz, CDCl₃) 7.58 (d, $J = 8.3$ Hz, 2H, Ar-H), 7.34-7.41 (m, 5H, Ar-H), 7.25-7.33 (m, 3H, Ar-H), 6.20 (s, 2H, CH₂Ph), 2.36 (d, $J = 0.84$ Hz, 3H, thiazolyl-CH₃); δ_{C} (100 MHz, CDCl₃) 180.2, 165.8, 155.6, 145.8, 132.5, 129.3, 128.8, 127.1, 126.0, 125.93, 125.90, 125.86, 125.7, 125.4, 123.2, 121.0, 119.1, 54.1, 15.0; MS (ESI): 441 (M+1). Anal. Calcd for C₁₉H₁₅F₃N₂SSe: C 51.94, H 3.44, N 6.38; Found: C 51.82, H 2.98, N 6.31.

4-Methyl-3-(4-methylbenzyl)-2-(4-chlorophenyl)selenocarbamoylthiazolium inner salt 4e: 61%, dark crystals, mp 169-170 °C; $\nu_{\max}/\text{cm}^{-1}$ 1566, 1525, 1479; δ_{H} (400 MHz, CDCl₃) 7.32 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.29 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.20 (s, 1H, thiazolyl-H), 7.18 (d, $J = 9.0$ Hz, 2H, Ar-H), 7.15 (d, $J = 8.9$ Hz, 2H, Ar-H), 6.13 (s, 2H, CH₂Ph), 2.34 (s, 6H, thiazolyl-CH₃+Ph-CH₃); δ_{C} (100 MHz, CDCl₃) 180.4, 164.3, 150.7, 145.6, 138.7, 129.9, 129.6, 129.2, 128.6, 127.2, 122.7, 118.7, 54.0, 21.1, 14.9; MS (ESI): 421 (M+1). Anal. Calcd for C₁₉H₁₇ClN₂SSe: C 54.36, H 4.08, N 6.67; Found: C 54.18, H 3.72, N 6.61.

4-Methyl-3-(4-methylbenzyl)-2-(4-trifluoromethylphenyl)selenocarbamoylthiazolium inner salt 4f: 70%, red crystals, mp 155-156 °C; $\nu_{\max}/\text{cm}^{-1}$ 3103, 1602, 1576, 1525, 1496; δ_{H} (400 MHz, CDCl₃) 7.58 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.34 (brs, 2H, Ar-H), 7.30 (s, 1H, thiazolyl-H), 7.18 (d, $J = 8.3$ Hz, 2H, Ar-H), 7.15 (d, $J = 8.4$ Hz, 2H, Ar-H), 6.13 (s, 2H, CH₂Ph), 2.37 (d, $J = 0.6$ Hz, 3H,

CH₃Ar), 2.35 (s, 3H, CH₃Ar); δ_{C} (100 MHz, CDCl₃) 180.0, 165.8, 155.6, 145.8, 138.8, 130.0, 129.5, 127.2, 126.0, 125.95, 125.9, 125.88, 125.7, 125.4, 123.2, 121.0, 119.0, 54.0, 21.1, 15.0; HRMS (TOF-ESI): 455.0303 (M+1). Anal. Calcd for C₂₀H₁₈F₃N₂SSe: 455.0308 (M+1).

3-(4-Methoxybenzyl)-4-methyl-2-phenylselenocarbamoylthiazolium inner salt 4g: 55%, dark crystals, mp 161-162 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 2988, 1567, 1538, 1511; δ_{H} (400 MHz, CDCl₃) 7.35-7.38 (m, 4H, Ar-H), 7.27 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.16 (s, 1H, thiazolyl-H), 7.10-7.14 (m, 1H, Ar-H), 6.89 (d, $J = 8.7$ Hz, 2H, Ar-H), 6.12 (s, 2H, CH₂Ph), 3.80 (s, 3H, OCH₃), 2.34 (d, $J = 0.9$ Hz, 3H, thiazolyl-CH₃); δ_{C} (100 MHz, CDCl₃) 180.3, 163.6, 159.8, 152.4, 145.4, 129.0, 128.6, 124.6, 124.3, 121.1, 118.6, 114.6, 55.4, 53.7, 15.0; MS (ESI): 403 (M+1). Anal. Calcd for C₁₉H₁₈N₂OSSe: C 56.85, H 4.52, N 6.98; Found: C 56.53, H 4.24, N 6.84.

3-(4-Methoxybenzyl)-4-methyl-2-(4-chlorophenyl)selenocarbamoylthiazolium inner salt 4h: 80%, red crystals, mp 175-176 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 3099, 1612, 1575, 1515, 1505, 1480; δ_{H} (400 MHz, CDCl₃) 7.35 (brs, 2H, Ar-H), 7.30 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.25 (s, 1H, thiazolyl-H), 7.24 (d, $J = 8.8$ Hz, 2H, Ar-H), 6.89 (d, $J = 8.7$ Hz, 2H, Ar-H), 6.07 (s, 2H, CH₂Ph), 3.80 (s, 3H, OCH₃), 2.37 (d, $J = 0.7$ Hz, 3H, thiazolyl-CH₃); δ_{C} (125 MHz, CDCl₃) 180.2, 164.3, 159.9, 150.6, 145.5, 129.3, 128.9, 128.7, 124.5, 122.8, 118.7, 114.6, 55.4, 53.8, 15.0; MS (ESI): 537 (M+1). Anal. Calcd for C₁₉H₁₇ClN₂OSSe: C 52.36, H 3.93, N 6.43; Found: C 52.53, H 3.54, N 6.38.

3-(4-Methoxybenzyl)-4-methyl-2-(4-trifluoromethylphenyl)selenocarbamoylthiazolium inner salt 4i: 88%, red crystals, mp 145-146 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 3110, 1608, 1530, 1514; δ_{H} (400 MHz, CDCl₃) 7.60 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.36 (br, 2H, Ar-H), 7.28 (s, 1H, thiazolyl-H), 7.24 (d, $J = 8.7$ Hz, 2H, Ar-H), 6.89 (d, $J = 8.7$ Hz, 2H, Ar-H), 6.08 (s, 2H, CH₂Ph), 3.80 (s, 3H, OCH₃), 2.38 (d, $J = 0.7$ Hz, 3H, thiazolyl-CH₃); δ_{C} (100 MHz, CDCl₃) 180.0, 165.9, 160.0, 155.6, 145.6, 128.9, 126.0, 125.95, 125.92, 125.88, 125.5, 124.4, 123.2, 121.0, 118.7, 114.7, 55.3, 53.7, 15.0; MS (ESI): 471 (M+1), 493 (M+Na⁺). Anal. Calcd for C₂₀H₁₇F₃N₂OSSe: C 51.18, H 3.65, N 5.97; Found: C 51.09, H 3.08, N 5.97.

3-(4-Chlorobenzyl)-4-methyl-2-phenylselenocarbamoylthiazolium inner salt 4j: 69%, red crystals, mp 107-108 °C; $\nu_{\max}/\text{cm}^{-1}$ 3036, 1589, 1570, 1517, 1491; δ_{H} (400 MHz, CDCl_3) 7.34-7.36 (m, 6H, Ar-H), 7.31 (s, 1H, thiazolyl-H), 7.24 (d, $J = 8.6$ Hz, 2H, Ar-H), 7.11-7.16 (m, 1H, Ar-H), 6.16 (s, 2H, CH_2Ph), 2.34 (s, 3H, thiazolyl- CH_3); δ_{C} (100 MHz, CDCl_3) 180.7, 163.2, 152.1, 145.4, 134.8, 131.3, 129.4, 128.7, 128.6, 124.5, 121.1, 119.2, 53.4, 15.0; MS (ESI): 407 (M+1). Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{ClN}_2\text{SSe}$: C 53.28, H 3.73, N 6.90; Found: C 53.15, H 3.35, N 6.86.

3-(4-Chlorobenzyl)-4-methyl-2-(4-chlorophenyl)selenocarbamoylthiazolium inner salt 4k: 55%, dark crystals, mp 165-166 °C; $\nu_{\max}/\text{cm}^{-1}$ 1565, 1522, 1492, 1478; δ_{H} (400 MHz, CD_3COCD_3) 7.81 (s, 1H, thiazolyl-H), 7.39-7.46 (m, 6H, Ar-H), 7.26 (d, $J = 8.7$ Hz, 2H, Ar-H), 6.32 (s, 2H, CH_2Ph), 2.47 (d, $J = 0.8$ Hz, 3H, thiazolyl- CH_3); δ_{C} (100 MHz, CDCl_3) 180.6, 164.0, 150.4, 145.5, 134.9, 131.2, 129.5, 128.7, 128.6, 122.8, 119.3, 53.5, 15.0; MS (ESI): 441 (M+1). Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{N}_2\text{SSe}$: C 49.11, H 3.21, N 6.36; Found: C 49.07, H 3.23, N 6.33.

3-(4-Chlorobenzyl)-4-methyl-2-(4-trifluoromethylphenyl)selenocarbamoylthiazolium inner salt 4l: 71%, red crystals, mp 142-143 °C; $\nu_{\max}/\text{cm}^{-1}$ 3114, 1607, 1518, 1496; δ_{H} (400 MHz, CDCl_3) δ (ppm) 7.51 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.29 (d, $J = 8.5$ Hz, 2H, Ar-H), 7.22-7.24 (br, 2H, Ar-H), 7.21 (s, 1H, thiazolyl-H), 7.15 (d, $J = 8.5$ Hz, 2H, Ar-H), 6.08 (s, 2H, CH_2Ph), 2.28 (s, 3H, thiazolyl- CH_3); δ_{C} (125 MHz, CDCl_3) 180.3, 165.7, 155.4, 145.6, 135.0, 131.0, 129.6, 128.6, 126.0, 125.97, 125.6, 125.4, 123.5, 121.0, 119.5, 53.5, 15.0; MS (ESI): 475 (M+1). Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{ClF}_3\text{N}_2\text{SSe}$: C 48.16, H 2.98, N 5.91; Found: C 48.27, H 2.70, N 5.91.

3-(4-Bromobenzyl)-4-methyl-2-phenylselenocarbamoylthiazolium inner salt 4m: 66%, red crystals, mp 178-179 °C; $\nu_{\max}/\text{cm}^{-1}$ 3035, 1589, 1570, 1517, 1489, 1480; δ_{H} (400 MHz, CDCl_3) 7.50 (d, $J = 8.1$ Hz, 2H, Ar-H), 7.30-7.37 (m, 5H, Ar-H), 7.17 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.13 (t, $J = 7.2$ Hz, 1H, Ar-H), 6.15 (s, 2H, CH_2Ph), 2.33 (s, 3H, thiazolyl- CH_3); δ_{C} (100 MHz, CDCl_3) 180.7, 163.2, 152.1, 145.4, 132.4, 131.8, 129.0, 128.6, 124.5, 122.9, 121.1, 119.2, 53.5, 14.9; MS (ESI): 451 (M+1). Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{BrN}_2\text{SSe}$: C 48.02, H 3.36, N 6.22; Found: C 47.96, H 3.30, N 6.11.

3-(4-Bromobenzyl)-4-methyl-2-(4-chlorophenyl)selenocarbamoylthiazolium inner salt 4n:

68%, dark crystals, mp 174-175 °C; $\nu_{\max}/\text{cm}^{-1}$ 1565, 1523, 1478; δ_{H} (400 MHz, CDCl_3) 7.51 (d, $J = 8.5$ Hz, 2H, Ar-H), 7.34 (s, 1H, thiazolyl-H), 7.35 (br, 2H, Ar-H), 7.30 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.16 (d, $J = 8.4$ Hz, 2H, Ar-H), 6.10 (s, 2H, CH_2Ph), 2.35 (d, $J = 0.7$ Hz, 3H, thiazolyl- CH_3); δ_{C} (100 MHz, CDCl_3) 180.5, 164.0, 150.3, 145.5, 132.4, 131.7, 129.5, 128.9, 128.7, 122.9, 122.8, 119.4, 53.6, 15.0; MS (ESI): 485 (M+1). Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{BrClN}_2\text{SSe}$: C 44.60, H 2.91, N 5.78; Found: C 44.68, H 2.81, N 5.78.

3-(4-Bromobenzyl)-4-methyl-2-(3,4-dichlorophenyl)selenocarbamoylthiazolium inner salt 4o:

61%, dark crystals, mp 164-165 °C; $\nu_{\max}/\text{cm}^{-1}$ 3096, 1577, 1501, 1487; δ_{H} (400 MHz, CDCl_3) 7.51 (d, $J = 8.4$ Hz, 3H, Ar-H), 7.38 (d, $J = 8.4$ Hz, 1H, Ar-H), 7.31 (s, 1H, $\text{HC}=\text{C}$), 7.25 (s, 1H, Ar-H), 7.13 (d, $J = 8.4$ Hz, 2H), 6.04 (s, 2H, CH_2Ph), 2.34 (s, 3H, thiazolyl- CH_3); δ_{C} (100 MHz, CDCl_3) 180.7, 163.2, 152.1, 145.4, 132.4, 131.8, 129.0, 128.6, 124.5, 122.9, 122.3, 121.1, 119.2, 53.5, 14.9; MS (ESI): 519 (M+1). Anal. Calcd for $\text{C}_{18}\text{H}_{13}\text{BrCl}_2\text{N}_2\text{SSe}$: C 41.64, H 2.52, N 5.40; Found: C 41.60, H 2.29, N 5.34.

3-Ethyl-4-methyl-2-(3,4-dichlorophenyl)selenocarbamoylthiazolium inner salt 4p:

81%, dark crystals, mp 121-122 °C; $\nu_{\max}/\text{cm}^{-1}$ 3071, 1573, 1522, 1479; δ_{H} (400 MHz, CDCl_3) 7.54 (s, 1H, $\text{HC}=\text{C}$), 7.43 (d, $J = 8.5$ Hz, 1H, Ar-H), 7.33 (dd, $J = 8.7, 1.8$ Hz, 1H, Ar-H), 7.27 (d, $J = 0.64$ Hz, 1H, Ar-H), 4.82 (q, $J = 7.2$ Hz, 2H, CH_2CH_3), 2.53 (d, $J = 0.8$ Hz, 3H, thiazolyl- CH_3), 1.57 (t, $J = 7.2$ Hz, 3H, CH_2CH_3); δ_{C} (100 MHz, CDCl_3) 179.6, 165.8, 152.1, 144.5, 132.1, 130.2, 126.9, 123.1, 119.1, 46.6, 14.7, 14.5; MS (ESI): 379 (M+1). Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{Cl}_2\text{N}_2\text{SSe}$: C 41.29, H 3.20, N 7.41; Found: C 41.53, H 2.84, N 7.31.