Supporting Information

Photo-Induced Copper-Catalyzed C–H Chalcogenation of Azoles at Room Temperature

Parthasarathy Gandeepan, Jiayu Mo, and Lutz Ackermann*

Institut für Organische und Biomolekulare Chemie, Georg-August-Universität
Tammannstraße 2, 37077 Göttingen, Germany

Fax: +49/ 551-39-6777

Lutz.Ackermann@chemie.uni-goettingen.de

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General Remarks

Photo-induced catalytic reactions were performed under an atmosphere of ambient air in pre-dried quartz tubes using a Luzchem Lzc-ICh2 photoreactor with 254 nm irradiation. The temperature was determined to be 25–27 °C in the reaction mixture. The following starting materials were synthesized according to previously described methods: Benzothiazoles (1b-1c, 1f),[1] 5-phenylthiazole (1e).[2] Other chemicals were obtained from commercial sources, and were used without further purification. Yields refer to isolated compounds, estimated to be > 95% pure as determined by 1H-NMR. TLC: Macherey-Nagel, TLC plates Alugram® Sil G/UV254. Detection under UV light at 254 nm. Chromatography: Separations were carried out on Merck Silica 60 (0.040– 0.063 mm, 70–230 mesh ASTM). Melting points (M. p.): Stuart melting point apparatus SMP3, Barloworld Scientific, the reported values are not corrected. NMR: Spectra were recorded on Varian VX 300, Varian VNMRS 300, Bruker Avance 300, Bruker Avance 400 and 500 or Varian Inova 500 and 600 spectrometers in the solvent indicated; chemical shifts (δ) are given in ppm and referenced to the residual solvent peak. All IR spectra were recorded on a Bruker ATR FT-IR Alpha device. MS: ESI-MS-spectra as well as high resolution mass spectrometry (HRMS) were recorded with a microTOF (ESI-TOF-MS), Bruker Daltonik; EI-spectra were recorded with a AccuTOF (EI-TOF) instrument from Jeol.
General Procedure for Photo-Induced Copper-Catalyzed C–H Thioarylation:

To a pre-dried 10 mL quartz tube were added heterocycle 1 (0.40 mmol), haloarene 2 or 5 (1.20 mmol), copper(I) thiophene-2-carboxylate (15.3 mg, 20 mol %), LiOrBu (96.0 mg, 1.20 mmol), sulfur powder (26.0 mg, 0.80 mmol), and DMF (2.0 mL) under an ambient air atmosphere. The tube was sealed tightly and stirred under 254 nm irradiation in a Luzchem LZC-ICH2 photoreactor for 16 h at ambient temperature. The temperature was determined to be 25–27 °C in the reaction mixture. Afterwards the reaction mixture was diluted with Et₂O (100 mL) and washed with water (4 × 50 mL). The combined organic extracts were dried over Na₂SO₄. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (n-hexane/EtOAc) to yield the desired product 3.

General Procedure for Photo-Induced Copper-Catalyzed C–H Selenoarylation:

To a pre-dried 10 mL quartz tube were added heterocycle 1 (0.40 mmol), haloarene 2 or 5 (1.20 mmol), copper(I) thiophene-2-carboxylate (15.3 mg, 20 mol %), LiOrBu (96.0 mg, 1.20 mmol), selenium powder (63.2 mg, 0.80 mmol), and DMF (2.0 mL) under an ambient air atmosphere. The tube was sealed tightly and stirred under 254 nm irradiation in a Luzchem LZC-ICH2 photoreactor for 16 h at ambient temperature. The temperature was determined to be 25–27 °C in the reaction mixture. Afterwards the reaction mixture was diluted with Et₂O (100 mL) and washed with water (4 × 50 mL). The combined organic extracts were dried over Na₂SO₄. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (n-hexane/EtOAc) to yield the desired product 4.
Characterization Data for the Products 3 and 4:

2-(m-Tolylthio)benzo[d]thiazole (3aa): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 1-iodo-3-methylbenzene (2a) (262 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 3aa (51 mg, 50%) as a pale yellow liquid.

**1H-NMR** (600 MHz, CDCl₃): δ 7.86 (dd, J = 8.2, 1.0 Hz, 1H), 7.63 (dd, J = 7.9, 1.1 Hz, 1H), 7.54 (s, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.2 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 7.7 Hz, 1H), 2.39 (s, 3H).

**13C-NMR** (101 MHz, CDCl₃): δ 170.0 (C₉), 153.9 (C₉), 139.9 (C₉), 135.8 (CH), 135.5 (C₉), 132.3 (CH), 131.2 (CH), 129.7 (CH), 129.6 (C₉), 126.1 (CH), 124.2 (CH), 121.9 (CH), 120.7 (CH), 21.2 (CH₃). **IR** (ATR): 1455, 1423, 1236, 1019, 1006, 983, 779, 753, 725, 665, 428 cm⁻¹.

**MS** (ESI) m/z (relative intensity): 258 [M+H]⁺ (100), 166 [M-C₇H₈]⁺ (5). **HR-MS** (ESI) m/z calcd for C₁₄H₁₂NS₂⁺ [M+H]⁺ 258.0406, found 258.0408. The analytical data are in accordance with those reported in the literature.[3]

2-(Phenylthio)benzo[d]thiazole (3ab): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and iodobenzene (2b) (245.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 3ab (56 mg, 58%) as a pale yellow liquid.

**1H-NMR** (400 MHz, CDCl₃): δ 7.87 (ddd, J = 8.2, 1.2, 0.7 Hz, 1H), 7.73 (dd, J = 8.0, 1.6 Hz, 2H), 7.63 (ddd, J = 7.9, 1.3, 0.6 Hz, 1H), 7.53–7.43 (m, 3H), 7.39 (ddd, J = 8.4, 7.3, 1.3 Hz, 1H), 7.25 (ddd, J = 8.0, 7.2, 1.2 Hz, 1H). **13C-NMR** (101 MHz, CDCl₃): δ 169.6 (C₉), 153.8 (C₉), 135.5 (C₉), 135.3 (CH), 130.4 (CH), 129.9 (C₉), 129.8 (CH), 126.1 (CH), 124.2 (CH), 121.9 (CH), 120.7 (CH). **IR** (ATR): 3057, 1456, 1424, 1006, 982, 752, 726, 703, 689, 496 cm⁻¹. **MS** (ESI) m/z (relative intensity): 266 [M+Na]⁺ (15), 244 [M+H]⁺ (100). **HR-MS** (ESI) m/z calcd for C₁₃H₁₀NS₂⁺ [M+H]⁺ 244.0249, found 244.0255. The analytical data are in accordance with those reported in the literature.[4]
2-{(3-Fluorophenyl)thio}benzo[d]thiazole (3ac): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (2c) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 3ac (69.0 mg, 66%) as a pale yellow liquid. 

$^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ 7.89 (dt, $J = 8.2, 0.9$ Hz, 1H), 7.68 (ddd, $J = 8.0, 1.3, 0.7$ Hz, 1H), 7.49 (ddd, $J = 7.7, 1.7, 1.0$ Hz, 1H), 7.46–7.39 (m, 3H), 7.29 (ddd, $J = 8.3, 7.2, 1.2$ Hz, 1H), 7.18 (tdd, $J = 8.4, 2.6, 1.0$ Hz, 1H). 

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 167.2 (C$_q$), 162.7 (d, $^1$J$_{C-F} = 250.3$ Hz, C$_q$), 153.6 (C$_q$), 135.6 (C$_q$), 132.0 (d, $^3$J$_{C-F} = 7.9$ Hz, C$_q$), 131.0 (d, $^3$J$_{C-F} = 8.3$ Hz, CH), 130.3 (d, $^1$J$_{C-F} = 3.3$ Hz, CH), 126.2 (CH), 124.6 (CH), 122.2 (CH), 121.5 (d, $^2$J$_{C-F} = 22.6$ Hz, CH), 120.8 (CH), 117.3 (d, $^2$J$_{C-F} = 20.9$ Hz, CH). 

$^{19}$F-NMR (282 MHz, CDCl$_3$): $\delta$ -110.3 (td, $J = 8.4, 5.6$ Hz). 

IR (ATR): 1579, 1472, 1457, 1424, 1218, 1007, 879, 783, 726 cm$^{-1}$. 

MS (ESI) m/z (relative intensity): 262 [M+H]$^+$ (100), 166 [M-C$_6$H$_5$F]$^+$ (5). 

HR-MS (ESI) m/z calcd for C$_{13}$H$_9$FNS$_2$ $^+$ [M+H]$^+$ 262.0155, found 262.0156.

The analytical data are in accordance with those reported in the literature.$^{[3]}$

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2-{(3-Chlorophenyl)thio}benzo[d]thiazole (3ad): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 1-chloro-3-iodobenzene (2d) (286.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 3ad (79.0 mg, 71%) as a pale yellow liquid. 

$^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ 7.89 (ddd, $J = 8.2, 1.2, 0.6$ Hz, 1H), 7.71 (t, $J = 1.9$ Hz, 1H), 7.67 (ddd, $J = 8.0, 1.3, 0.6$ Hz, 1H), 7.59 (ddd, $J = 7.7, 1.8, 1.1$ Hz, 1H), 7.45 (ddd, $J = 8.1, 2.0, 1.1$ Hz, 1H), 7.41 (ddd, $J = 8.3, 7.3, 1.2$ Hz, 1H), 7.38 (t, $J = 7.9$ Hz, 1H), 7.28 (ddd, $J = 8.3, 7.3, 1.2$ Hz, 1H). 

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 167.0 (C$_q$), 153.5 (C$_q$), 135.5 (C$_q$), 135.2 (C$_q$), 134.2 (CH), 132.6 (CH), 131.8 (C$_q$), 130.6 (CH), 130.2 (CH), 126.2 (CH), 124.5 (CH), 122.1 (CH), 120.7 (CH). 

IR (ATR): 1565, 1456, 1424, 1401, 1019, 1007, 984, 780, 755 cm$^{-1}$. 

MS (ESI) m/z (relative intensity): 278 [M+H]$^+$ (100), 166 [M-C$_6$H$_5$Cl]$^+$ (5). 

HR-MS (ESI) m/z calcd for C$_{13}$H$_9$ClNS$_2$ $^+$ [M+H]$^+$ 277.9859, found 277.9860. The analytical data are in accordance with those reported in the literature.$^{[3]}$
Ethyl 3-(benzo[d]thiazol-2-ylthio)benzoate (3ae): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and ethyl 3-iodobenzoate (2e) (331.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/2) yielded 3ae (66.0 mg, 52%) as a colorless liquid. $^1$H-NMR (500 MHz, CDCl₃): δ 8.39 (s, 1H), 8.16 (dt, $J = 7.9$, 1.4 Hz, 1H), 7.91–7.88 (m, 1H), 7.87 (d, $J = 8.4$ Hz, 1H), 7.65 (d, $J = 7.9$ Hz, 1H), 7.54 (t, $J = 7.8$ Hz, 1H), 7.40 (ddd, $J = 8.4$, 7.3, 1.3 Hz, 1H), 7.27 (ddd, $J = 8.3$, 7.3, 1.2 Hz, 1H), 4.38 (q, $J = 7.1$ Hz, 2H), 1.38 (t, $J = 7.1$ Hz, 3H).

$^{13}$C-NMR (126 MHz, CDCl₃): δ 168.0 (C₆), 165.3 (C₆), 153.7 (C₆), 139.2 (CH), 136.0 (CH), 135.5 (C₆), 132.2 (C₆), 131.3 (CH), 130.6 (C₆), 129.8 (CH), 126.2 (CH), 124.5 (CH), 122.0 (CH), 120.8 (CH), 61.4 (CH₂), 14.2 (CH₃).

IR (ATR): 1716, 1457, 1424, 1279, 1258, 1124, 1007, 751 cm⁻¹.

MS (EI) m/z (relative intensity): [M]+ 315 (100), [M-C₂H₅]+ 286 (100), [M-CO₂Et]+ 243 (50). HR-MS (ESI) m/z calcd for C₁₆H₁₄NO₂S₂ [M+H]+ 316.0460, found 316.0460.

3-(Benzonitrile benzothiazol-2-ylthio)benzonitrile (3af): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 3-iodobenzonitrile (2f) (275.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/2) yielded 3af (73.0 mg, 68%) as a colorless solid. M. p.: 77–78 °C. $^1$H-NMR (500 MHz, CDCl₃): δ 7.97 (s, 1H), 7.93–7.87 (m, 2H), 7.73–7.69 (m, 2H), 7.54 (t, $J = 7.9$ Hz, 1H), 7.43 (dd, $J = 8.3$, 7.2 Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 1H). $^{13}$C-NMR (126 MHz, CDCl₃): δ 164.9 (C₆), 153.4 (C₆), 138.2 (CH), 137.1 (CH), 135.7 (C₆), 133.1 (CH), 132.5 (C₆), 130.3 (CH), 126.4 (CH), 125.0 (CH), 122.3 (CH), 120.9 (CH), 117.5 (C₆), 114.0 (C₆). IR (ATR): 2230, 1456, 1424, 1407, 1007, 986, 765, 757, 726 cm⁻¹. MS (ESI) m/z (relative intensity): 291 [M+Na]+ (5), 269 [M+H]+ (100). HR-MS (ESI) m/z calcd for C₁₆H₁₄N₂S₂ [M+H]+ 269.0202, found 269.0203.
2-{[3-(Trifluoromethyl)phenyl]thio}benzo[d]thiazole (3ag): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 1-iodo-3-(trifluoromethyl)benzene (2g) (326.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 3af (90.0 mg, 72%) as a colorless solid. M. p.: 57–59 °C. \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.98 (d, \(J = 0.9\) Hz, 1H), 7.91–7.87 (m, 2H), 7.72 (dd, \(J = 7.9, 0.9\) Hz, 1H), 7.68 (dd, \(J = 8.0, 0.9\) Hz, 1H), 7.60–7.55 (m, 1H), 7.41 (ddt, \(J = 8.3, 7.2, 1\) Hz, 1H), 7.29 (ddd, \(J = 8.3, 7.2, 1.1\) Hz, 1H). \(^13\)C-NMR (126 MHz, CDCl\(_3\)): \(\delta\) 166.4 (C\(_s\)), 153.6 (C\(_q\)), 137.8 (CH), 135.6 (C\(_q\)), 132.2 (q, \(^3J_{C-F} = 3.2\) Hz, C\(_q\)), 131.6 (C\(_q\)), 131.2 (q, \(^1J_{C-F} = 3.7\) Hz, CH), 130.2 (CH), 126.7 (q, \(^1J_{C-F} = 3.7\) Hz, CH), 126.3 (CH), 125.5 (d, \(^1J_{C-F} = 273.1\) Hz, C\(_q\)), 124.8 (CH), 122.2 (CH), 120.9 (CH). \(^19\)F-NMR (282 MHz, CDCl\(_3\)): \(\delta\) -62.8 (s). IR (ATR): 1458, 1420, 1319, 1273, 1167, 1122, 1067, 1007, 983 cm\(^{-1}\). MS (ESI) m/z (relative intensity): 312 [M+H]\(^+\) (100). HR-MS (ESI) m/z calcd for C\(_{14}\)H\(_9\)F\(_3\)NS\(_2\): [M+H]\(^+\) 312.0123, found 312.0126. The analytical data are in accordance with those reported in the literature.[3]

2-{[4-(Fluorophenyl)thio]benzo[d]thiazole (3ah): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 1-fluoro-4-iodobenzene (2h) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 3ah (59.0 mg, 56%) as a pale yellow liquid. \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.86 (dt, \(J = 8.2, 0.9\) Hz, 1H), 7.72 (dd, \(J = 8.8, 5.2\) Hz, 2H), 7.65 (ddd, \(J = 8.0, 1.3, 0.7\) Hz, 1H), 7.39 (ddd, \(J = 8.3, 7.3, 1.3\) Hz, 1H), 7.26 (ddd, \(J = 8.2, 7.2, 1.2\) Hz, 1H), 7.19–7.14 (m, 2H). \(^13\)C-NMR (101 MHz, CDCl\(_3\)): \(\delta\) 169.4 (C\(_q\)), 164.1 (d, \(^1J_{C-F} = 252.1\) Hz, C\(_q\)), 153.9 (C\(_q\)), 137.7 (d, \(^3J_{C-F} = 8.8\) Hz, CH), 135.4 (C\(_q\)), 126.2 (CH), 125.1 (d, \(^4J_{C-F} = 3.5\) Hz, C\(_q\)), 124.3 (CH), 121.9 (CH), 120.7 (CH), 117.2 (d, \(^2J_{C-F} = 22.2\) Hz, CH). \(^19\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -108.94 (tt, \(J = 8.4, 5.2\) Hz). IR (ATR): 2924, 1588, 1489, 1458, 1425, 1322, 1156, 1020, 1006, 983, 755 cm\(^{-1}\). MS (ESI) m/z (relative intensity): 262 [M+H]\(^+\) (100), 166 [M-C\(_4\)H\(_3\)F]\(^+\) (5). HR-MS (ESI) m/z calcd for C\(_{13}\)H\(_6\)FNS\(_2\):
[M+H]$^+$ 262.0155, found 262.0154. The analytical data are in accordance with those reported in the literature.\[^3\]

2-{(4-Chlorophenyl)thio}benzo[d]thiazole (3ai): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 1-chloro-4-iodobenzene (2i) (286.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 3ai (66.0 mg, 59\%) as a pale yellow liquid. $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.87 (dt, $J = 8.2$, 0.9 Hz, 1H), 7.69–7.61 (m, 3H), 7.45–7.42 (m, 2H), 7.40 (ddd, $J = 8.4$, 7.3, 1.3 Hz, 1H), 7.27 (ddd, $J = 8.2$, 7.3, 1.2 Hz, 1H). $^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta$ 168.3 (C$_q$), 153.7 (C$_q$), 136.9 (C$_q$), 136.3 (CH), 135.4 (C$_q$), 130.1 (CH), 128.3 (C$_q$), 126.2 (CH), 124.5 (CH), 122.0 (CH), 120.8 (CH). IR (ATR): 1571, 1474, 1456, 1425, 1092, 1004, 986, 820, 755, 725, 501 cm$^{-1}$. MS (ESI) m/z (relative intensity): 262 [M+H]$^+$ (100), 244 [M-Cl]$^+$ (10), 166 [M-C$_6$H$_5$Cl]$^+$ (10). HR-MS (ESI) m/z calcd for C$_{13}$H$_9$ClNS$_2^+$ [M+H]$^+$ 277.9859, found 277.9861. The analytical data are in accordance with those reported in the literature.\[^4\]

4-(Benzo[d]thiazol-2-ylthio)benzonitrile (3aj): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 4-iodobenzonitrile (2j) (275.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/2) yielded 3aj (65.0 mg, 61\%) as a colorless solid. M. p.: 110–113 °C. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 7.93 (ddd, $J = 8.2$, 1.2, 0.7 Hz, 1H), 7.76 (ddd, $J = 8.3$, 7.2, 1.3 Hz, 1H), 7.72 (d, $J = 8.8$ Hz, 2H), 7.69 (d, $J = 8.8$ Hz, 2H), 7.45 (ddd, $J = 8.2$, 7.3, 1.3 Hz, 1H), 7.35 (ddd, $J = 8.0$, 7.3, 1.3 Hz, 1H). $^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta$ 163.3 (C$_q$), 153.2 (C$_q$), 137.4 (C$_q$), 135.9 (C$_q$), 132.9 (CH), 132.8 (CH), 126.4 (CH), 125.2 (CH), 122.5 (CH), 120.9 (CH), 117.8 (C$_q$), 112.7 (C$_q$).
IR (ATR): 2229, 1591, 1455, 1423, 1398, 1273, 1079, 1007, 987, 883, 755, 723, 553 cm$^{-1}$. MS (ESI) m/z (relative intensity): 269 [M+H]$^+$ (100), 291 [M+Na]$^+$ (7). HR-MS (ESI) m/z calcd for C$_{14}$H$_{9}$N$_2$S$_2^+$ [M+H]$^+$ 269.0202, found 269.0202.

2-{(2,5-Difluorophenyl)thio}benzo[d]thiazole (3ak): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 1,4-difluoro-2-iodobenzene (2k) (289.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/2) yielded 3ak (57.0 mg, 51%) as a pale yellow solid. M. p.: 86–87 °C. $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.86 (dt, $J$ = 8.2, 0.8 Hz, 1H), 7.76–7.69 (m, 1H), 7.66 (dt, $J$ = 8.1, 0.9 Hz, 1H), 7.40 (ddd, $J$ = 8.3, 7.2, 1.2 Hz, 1H), 7.27 (ddd, $J$ = 8.2, 7.3, 1.2 Hz, 1H), 7.04–6.97 (m, 2H). $^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta$ 167.0 (C$_q$), 165.1 (dd, $J_{C-F}$ = 214.0, 11.4 Hz, C$_q$), 163.1 (dd, $J_{C-F}$ = 225.5, 12.7, C$_q$), 153.7 (C$_q$), 138.7 (d, $J_{C-F}$ = 10.7 Hz, CH), 135.5 (C$_q$), 126.2 (CH), 124.5 (CH), 122.0 (CH), 120.8 (CH), 112.9 (dd, $J_{C-F}$ = 21.8, 3.9 Hz, CH), 112.6 (dd, $J_{C-F}$ = 18.7, 4.1 Hz, C$_q$), 105.5 (t, $J_{C-F}$ = 26.1 Hz, CH). $^{19}$F NMR (471 MHz, CDCl$_3$): $\delta$ -99.4–-99.5 (m), -103.5 (dt, $J$ = 18.7, 7.7 Hz). IR (ATR): 1594, 1484, 1460, 1423, 1266, 1143, 1006, 755, 726 cm$^{-1}$. MS (EI) m/z (relative intensity): 279 [M]$^+$ (60), 260 [M-F]$^+$ (100). HR-MS (ESI) m/z calcd for C$_{13}$H$_8$F$_2$NS$_2^+$ [M+H]$^+$ 280.0061, found 280.0060.

2-(Naphthalen-1-ylthio)benzo[d]thiazole (3al): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 1-iodonaphthalene (2l) (305.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 3al (59.0 mg, 50%) as a pale yellow solid. M. p.: 98–99 °C. $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 8.48 (dd, $J$ = 6.3, 3.5 Hz, 1H), 8.06-8.04 (m 2H), 7.93 (dd, $J$ = 6.1, 3.4 Hz, 1H), 7.87 (d, $J$ = 8.5 Hz, 1H), 7.57–7.54 (m, 3H), 7.50 (dt, $J$ = 7.9, 0.9 Hz, 1H), 7.37 (ddd, $J$ = 8.4, 7.2, 1.2 Hz, 1H), 7.19 (ddd, $J$ = 8.2, 7.2, 1.2 Hz, 1H). $^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta$ 170.0 (C$_q$), 153.8
(C₆H₅), 136.3 (CH), 135.5 (C₆), 134.4 (C₆), 134.2 (C₆), 132.1 (CH), 128.7 (CH), 127.8 (CH), 126.9 (CH), 126.7 (C₆), 126.0 (CH), 125.8 (CH), 125.4 (CH), 124.1 (CH), 121.7 (CH), 120.6 (CH). IR (ATR): 3054, 1502, 1456, 1424, 1006, 786, 770, 755, 726, 664 cm⁻¹. MS (ESI) m/z (relative intensity): 294 [M+H]^+ (100), 166 [M-C₁₆H₅S₃] (5). HR-MS (ESI) m/z calcd for C₁₁H₁₂NS₂⁺ [M+H]^+ 294.0406, found 294.0405. The analytical data are in accordance with those reported in the literature.³

2-{(3-Fluorophenyl)thio}-6-methylbenzo[d]thiazole (3bc): The representative procedure was followed using 6-methylbenzo[d]thiazole (1b) (60.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (2c) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 3bc (65.0 mg, 58%) as a yellow liquid.¹H-NMR (400 MHz, CDCl₃): δ 7.77 (d, J = 8.3 Hz, 1H), 7.48–7.44 (m, 2H), 7.43–7.36 (m, 2H), 7.22 (ddd, J = 8.3, 1.7, 0.6 Hz, 1H), 7.15 (tdd, J = 8.3, 2.6, 1.1 Hz, 1H), 2.42 (s, 3H).¹H-NMR (101 MHz, CDCl₃): δ 165.4 (C₆H₅), 162.8 (d, ¹JC₆F = 250.5 Hz, C₆), 151.8 (C₆), 135.9 (C₆), 134.9 (C₆), 132.4 (d, ³JC₆F = 8.2 Hz, C₆), 130.9 (d, ³JC₆F = 8.3 Hz, CH), 129.9 (d, 4JC₆F = 3.2 Hz, CH), 127.8 (CH), 121.8 (CH), 121.2 (d, ²JC₆F = 22.6 Hz, CH), 120.7 (CH), 117.1 (d, ²JC₆F = 21.1 Hz, CH), 21.4 (CH₃).¹F-NMR (376 MHz, CDCl₃): δ -110.4 (dd, J = 8.5, 5.8 Hz). IR (ATR): 1595, 1579, 1471, 1440, 1263, 1218, 1012, 990, 879 cm⁻¹. MS (ESI) m/z (relative intensity): 298 [M+Na]^+ (15), 276 [M+H]^+ (100). HR-MS (ESI) m/z calcd for C₁₄H₁₁FNS₂⁺ [M+H]^+ 276.0311, found 276.0312.

6-Fluoro-2-{(3-fluorophenyl)thio}benzo[d]thiazole (3cc): The representative procedure was followed using 6-fluorobenzo[d]thiazole (1c) (60.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (2c) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 3cc (60.0 mg, 54%) as a yellow liquid.¹H-NMR (400 MHz, CDCl₃): δ 7.82 (ddd, J = 9.0, 4.8, 0.5 Hz, 1H), 7.50–7.39 (m, 3H), 7.36 (ddd, J = 8.0, 2.6, 0.4 Hz, 1H), 7.21–7.10 (m, 2H).¹C-NMR (101 MHz, CDCl₃): δ 166.7 (C₆H₅), 162.8 (d, ²JC₆F = 251.0 Hz, C₆H₅), 160.1 (d, ³JC₆F = 245.9 Hz, C₆H₅), 150.3 (C₆H₅), 136.6 (d, ²JC₆F = 11.1 Hz, C₆H₅), 131.7
(d, $J_{CF} = 7.9$ Hz, C$_q$), 131.2 (d, $J_{CF} = 8.3$ Hz, CH), 130.3 (d, $J_{CF} = 3.3$ Hz, CH), 123.1 (d, $J_{CF} = 9.3$ Hz, CH), 121.5 (d, $J_{CF} = 22.6$ Hz, CH), 117.5 (d, $J_{CF} = 21.0$ Hz, CH), 114.8 (d, $J_{CF} = 24.6$ Hz, CH), 107.3 (d, $J_{CF} = 26.9$ Hz, CH). $^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$ -110.1 (td, $J = 8.4, 5.6$ Hz), -116.2 (td, $J = 8.4, 4.7$ Hz). IR (ATR): 1595, 1579, 1567, 1443, 1420, 1250, 1217, 1192 cm$^{-1}$. MS (EI) m/z (relative intensity): 278 [M]$^+$ (100), 260 [M-F]$^+$ (5). HR-MS (EI) m/z calcd for C$_{13}$H$_7$F$_2$NS$_2$ [M]$^+$ 278.9988, found 278.9985.

![Image of 2-{(3-Fluorophenyl)thio}-6-methoxybenzo[d]thiazole](image)

2-{(3-Fluorophenyl)thio}-6-methoxybenzo[d]thiazole (3dc): The representative procedure was followed using 6-methoxybenzo[d]thiazole (1d) (66.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (2c) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/2) yielded 3dc (86.0 mg, 74%) as a yellow liquid. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.78 (dd, $J = 8.9, 0.4$ Hz, 1H), 7.44–7.34 (m, 3H), 7.14 (d, $J = 2.4$ Hz, 1H), 7.14–7.09 (m, 1H), 7.01 (dd, $J = 9.0, 2.4$ Hz, 1H), 3.80 (s, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ 162.8 (C$_q$), 162.7 (d, $J_{CF} = 251.3$ Hz, C$_q$), 157.4 (C$_q$), 148.1 (C$_q$), 137.3 (C$_q$), 132.8 (d, $J_{CF} = 7.9$ Hz, C$_q$), 130.9 (d, $J_{CF} = 8.3$ Hz, CH), 129.4 (d, $J_{CF} = 3.2$ Hz, CH), 122.8 (CH), 120.7 (d, $J_{CF} = 22.7$ Hz, CH), 116.7 (d, $J_{CF} = 21.0$ Hz, CH), 115.3 (CH), 103.8 (CH), 55.7 (CH). $^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$ -110.46 (td, $J = 8.5, 5.7$ Hz). IR (ATR): 1597, 1473, 1452, 1432, 1260, 1221, 1027, 1011, 878, 782, 520 cm$^{-1}$. MS (ESI) m/z (relative intensity): 314 [M+Na]$^+$ (5), 292 [M+H]$^+$ (100). HR-MS (ESI) m/z calcd for C$_{14}$H$_{11}$FNO$_3$S$_2$ [M+H]$^+$ 292.0261, found 292.0261.

![Image of 5-Phenyl-2-(phenylthio)thiazole](image)

5-Phenyl-2-(phenylthio)thiazole (3eb): The representative procedure was followed using 5-phenylthiazole (1e) (64.0 mg, 0.40 mmol) and iodobenzene (2b) (245.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 3eb (60.0 mg, 56%) as a yellow liquid. $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.83 (s, 1H), 7.65–7.63 (m, 2H), 7.43–7.41 (m, 5H), 7.35–7.31 (m, 2H), 7.29–7.25 (m, 1H). $^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta$ 164.8 (C$_q$), 140.7 (C$_q$), 138.6 (CH), 133.7 (CH), 131.8 (C$_q$), 130.9 (C$_q$), 129.7 (CH), 129.5 (CH), 129.0 (CH), 128.2 (CH), 126.4 (CH). IR (ATR): 1475, 1444, 1389, 1041, 1016, 754,
2-(Quinolin-3-ylthio)benzo[d]thiazole (3am): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 3-bromoquinoline (5m) (250.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/3) yielded 3am (71.0 mg, 60%) as a colorless solid. M. p.: 138–139 °C.

1H-NMR (400 MHz, CDCl3): δ 9.08 (d, J = 2.2 Hz, 1H), 8.53 (dd, J = 2.3, 0.8 Hz, 1H), 8.15 (dd, J = 8.5, 1.0 Hz, 1H), 7.89–7.76 (m, 3H), 7.67–7.55 (m, 2H), 7.39 (ddd, J = 8.3, 7.3, 1.3 Hz, 1H), 7.25 (ddd, J = 8.1, 7.2, 1.2 Hz, 1H). 13C-NMR (101 MHz, CDCl3): δ 167.0 (C_q), 154.0 (CH), 153.6 (C_q), 147.9 (C_q), 142.6 (CH), 135.5 (C_q), 131.1 (CH), 129.5 (CH), 128.0 (C_q), 127.9 (CH), 127.6 (CH), 126.3 (CH), 124.6 (CH), 123.8 (C_q), 122.1 (CH), 120.8 (CH). IR (ATR): 3060, 1561, 1488, 1455, 1423, 1354, 1310, 1019, 1005, 977, 776, 751 cm⁻¹. MS (ESI) m/z (relative intensity): 295 [M+H]+ (100), 317 [M+Na]+ (10). HR-MS (ESI) m/z calcd for C_{16}H_{11}NS_{2}+ [M+H]+ 295.0358, found 295.0364.

2-(Isoquinolin-4-ylthio)benzo[d]thiazole (3an): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 4-bromoisoquinoline (5n) (250.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/3) yielded 3an (61.0 mg, 52%) as a pale yellow solid. M. p.: 136–138 °C. 1H-NMR (400 MHz, CDCl3): δ 9.39 (s, 1H), 8.97 (s, 1H), 8.35 (dd, J = 8.4, 1.0 Hz, 1H), 8.06 (ddd, J = 8.1, 1.4, 0.8 Hz, 1H), 7.85 (ddd, J = 8.2, 1.2, 0.6 Hz, 1H), 7.76 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.68 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.53 (ddd, J = 8.0, 1.3, 0.6 Hz, 1H), 7.37 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.21 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H). 13C-NMR (101 MHz, CDCl3): δ 167.9 (C_q), 155.7 (CH), 153.7 (C_q), 150.7 (CH), 136.9 (C_q), 135.5 (C_q), 132.2 (CH), 129.3 (C_q), 128.4 (2 CH), 126.2 (CH), 124.5 (CH), 124.4 (CH), 122.4 (C_q), 122.0 (CH), 120.8 (CH). IR (ATR): 1616, 1564, 1455, 1423, 1376, 1321, 1018, 1005, 977, 776, 751 cm⁻¹. MS (ESI) m/z (relative intensity): 295 [M+H]+ (100), 130 [M-C_{7}H_{4}NS_{2}]^{+} (10). HR-MS (ESI) m/z calcd for C_{16}H_{11}NS_{2}+ [M+H]+ 295.0358, found 295.0361.
2-(Phenylselanyl)benzo[d]thiazole (4ab): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and iodobenzene (2b) (245.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/2) yielded 4ab (63.0 mg, 54%) as a pale yellow liquid. $^1$H-NMR (301 MHz, CDCl$_3$): $\delta$ 7.91 (ddd, $J$ = 8.2, 1.2, 0.6 Hz, 1H), 7.84–7.80 (m, 2H), 7.67 (ddd, $J$ = 8.0, 1.3, 0.6 Hz, 1H), 7.53–7.35 (m, 4H), 7.29–7.22 (m, 1H). $^{13}$C-NMR (76 MHz, CDCl$_3$): $\delta$ 162.7 (C$_q$), 154.6 (C$_q$), 136.6 (CH), 132.4 (C$_q$), 130.1 (CH), 129.9 (CH), 126.6 (C$_q$), 126.0 (CH), 124.3 (CH), 121.9 (CH), 120.8 (CH). IR (ATR): 3055, 1454, 1437, 1421, 1232, 972, 755, 740, 726, 689 cm$^{-1}$. MS (ESI) m/z (relative intensity): 292 [M+H]$^+$ (100), 214 [M-Ph]$^+$ (5). HR-MS (ESI) m/z calcd for C$_{13}$H$_{10}$NSSe$^+$ [M+H]$^+$ 291.9694, found 291.9694. The analytical data are in accordance with those reported in the literature.$^{[4]}$

2-{(3-Fluorophenyl)selanyl}benzo[d]thiazole (4ac): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (2c) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 4ac (73.0 mg, 59%) as a yellow liquid. $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.93 (ddd, $J$ = 8.2, 1.2, 0.7 Hz, 1H), 7.70 (ddd, $J$ = 8.0, 1.3, 0.7 Hz, 1H), 7.57 (ddd, $J$ = 7.7, 1.6, 0.9 Hz, 1H), 7.53 (ddd, $J$ = 8.2, 2.6, 1.5 Hz, 1H), 7.43–7.35 (m, 2H), 7.29 (ddd, $J$ = 8.0, 7.2, 1.2 Hz, 1H), 7.16 (dd, $J$ = 8.5, 2.6, 1.0 Hz, 1H). $^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta$ 162.6 (d, $^1$J$_{C,F}$ = 251.5 Hz, C$_q$), 160.6 (C$_q$), 154.3 (C$_q$), 136.7 (C$_q$), 131.7 (d, $^4$J$_{C,F}$ = 3.3 Hz, CH), 131.1 (d, $^3$J$_{C,F}$ = 8.0 Hz, CH), 127.9 (d, $^1$J$_{C,F}$ = 7.1 Hz, C$_q$), 126.1 (CH), 124.7 (CH), 122.9 (d, $^2$J$_{C,F}$ = 22.2 Hz, CH), 122.2 (CH), 120.8 (CH), 117.0 (d, $^2$J$_{C,F}$ = 21.0 Hz, CH). $^{19}$F-NMR (471 MHz, CDCl$_3$): $\delta$ -110.2 (td, $J$ = 8.3, 5.8 Hz). IR (ATR): 3060, 1586, 1470, 1455, 1422, 1212, 973, 858, 781, 756, 726, 679 cm$^{-1}$. MS (ESI) m/z (relative intensity): 310 [M+H]$^+$ (100), 213 [M-PhF]$^+$ (5). HR-MS (ESI) m/z calcd for C$_{13}$H$_9$FNSSe$^+$ [M+H]$^+$ 309.9599, found 309.9602.
3-(Benzo[d]thiazol-2-ylselanyl)benzonitrile (4af): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 3-iodobenzonitrile (2f) (275.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 4af (71.0 mg, 56%) as a colorless liquid. ¹H-NMR (300 MHz, CDCl₃): δ 8.08 (dt, J = 1.7, 0.8 Hz, 1H), 8.01 (ddd, J = 7.9, 1.7, 1.2 Hz, 1H), 7.96 (ddd, J = 8.2, 1.3, 0.6 Hz, 1H), 7.77–7.71 (m, 2H), 7.51 (td, J = 7.8, 0.6 Hz, 1H), 7.45 (ddd, J = 8.2, 7.3, 1.3 Hz, 1H), 7.34 (ddd, J = 7.9, 7.3, 1.2 Hz, 1H). ¹³C-NMR (126 MHz, CDCl₃): δ 158.4 (Cₗ), 154.2 (Cₗ), 139.7 (CH), 138.6 (CH), 136.7 (Cₗ), 133.0 (CH), 130.4 (CH), 128.5 (Cₗ), 126.4 (CH), 125.1 (CH), 122.4 (CH), 120.9 (CH), 117.6 (Cₗ), 114.0 (Cₗ). IR (ATR): 3057, 2229, 1454, 1421, 1404, 973, 793, 757, 727, 681 cm⁻¹. MS (ESI) m/z (relative intensity): 317 [M+H]⁺ (100), 339 [M+Na]⁺ (5). HR-MS (ESI) m/z calcd for C₁₄H₉N₂SSe⁺ [M+H]⁺ 316.9646, found 316.9641.

2-[[3-(Trifluoromethyl)phenyl]selanyl]benzo[d]thiazole (4ag): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 1-iodo-3-(trifluoromethyl)benzene (2g) (326.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 4ag (86.0 mg, 60%) as a pale yellow solid. M. p.: 64–66 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.08 (dq, J = 1.7, 0.9 Hz, 1H), 7.99 (ddt, J = 7.8, 1.7, 1.2, 0.6 Hz, 1H), 7.94 (ddd, J = 8.2, 1.2, 0.6 Hz, 1H), 7.74–7.69 (m, 2H), 7.54 (ddt, J = 8.5, 7.8, 0.7 Hz, 1H), 7.42 (ddd, J = 8.3, 7.3, 1.3 Hz, 1H), 7.31 (ddd, J = 8.0, 7.2, 1.2 Hz, 1H). ¹³C-NMR (101 MHz, CDCl₃): δ 159.9 (Cₗ), 154.3 (Cₗ), 139.3 (CH), 136.7 (Cₗ), 132.7 (q, ³J_C-F = 3.8 Hz, CH), 132.2 (d, ²J_C-F = 32.9 Hz, Cₗ), 130.2 (CH), 127.7 (Cₗ), 126.6 (q, ³J_C-F = 3.7 Hz, CH), 126.3 (CH), 124.8 (CH), 122.3 (CH), 123.4 (d, ¹J_C-F = 274.0 Hz, Cₗ), 120.9 (CH). ¹⁹F-NMR (376 MHz, CDCl₃): δ -62.75 (s). IR (ATR): 1455, 1421, 1320, 1272, 1167, 1128, 1080, 1066, 973 cm⁻¹. MS (ESI) m/z (relative intensity): 360 [M+H]⁺ (100), 381 [M+Na]⁺ (5). HR-MS (ESI) m/z calcd for C₁₄H₉F₃NSSe⁺ [M+H]⁺ 359.9568, found 359.9565. The analytical data are in accordance with those reported in the literature.[⁴]
2-{(4-Fluorophenyl)selenyl}benzo[d]thiazole (4ah): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 1-fluoro-4-iodobenzene (2h) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 4ah (70.0 mg, 57%) as a pale yellow liquid. \( ^1H\)-NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.90 (ddd, \( J = 8.2, 1.2, 0.6 \) Hz, 1H), 7.82--7.78 (m, 2H), 7.68 (ddd, \( J = 8.0, 7.3, 1.3 \) Hz, 1H), 7.26 (ddd, \( J = 8.0, 7.2, 1.2 \) Hz, 1H), 7.16--7.07 (m, 2H). \( ^13C\)-NMR (101 MHz, CDCl\(_3\)): \( \delta \) 164.0 (d, \( ^1J_{C-F} = 251.4 \) Hz, C\(_q\)), 162.5 (C\(_q\)), 154.5 (C\(_q\)), 138.9 (d, \( ^1J_{C-F} = 8.5 \) Hz, CH), 136.5 (C\(_q\)), 126.1 (CH), 124.4 (CH), 121.9 (CH), 121.2 (d, \( ^4J_{C-F} = 3.5 \) Hz, C\(_q\)), 120.8 (CH), 117.3 (d, \( ^2J_{C-F} = 21.9 \) Hz, CH). \( ^19F\)-NMR (376 MHz, CDCl\(_3\)): \( \delta \) -109.66 (tt, \( J = 8.5, 5.2 \) Hz). IR (ATR): 1582, 1485, 1454, 1422, 1396, 1228, 1156, 971, 827, 811 cm\(^{-1}\). MS (ESI) m/z (relative intensity): 310 [M+H]\(^+\) (100), 292 [M-C\(_6\)H\(_4\)F]\(^+\) (13), 213 [M-C\(_6\)H\(_4\)Cl]\(^+\) (10). HR-MS (ESI) m/z calcd for C\(_{13}\)H\(_9\)FNSSe\(^+\) [M+H]\(^+\) \( 309.9608 \), found 309.9599. The analytical data are in accordance with those reported in the literature.\[^{[4]}\]

2-{(4-Chlorophenyl)selenyl}benzo[d]thiazole (4ai): The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 1-chloro-4-iodobenzene (2i) (286.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 4ai (70.0 mg, 54%) as a pale yellow solid. M. p.: 55--56 °C. \( ^1H\)-NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.91 (ddd, \( J = 8.2, 1.2, 0.7 \) Hz, 1H), 7.76--7.72 (m, 2H), 7.69 (ddd, \( J = 8.0, 1.3, 0.6 \) Hz, 1H), 7.43--7.36 (m, 3H), 7.28 (ddd, \( J = 8.1, 7.3, 1.2 \) Hz, 1H). \( ^13C\)-NMR (101 MHz, CDCl\(_3\)): \( \delta \) 161.5 (C\(_q\)), 154.5 (C\(_q\)), 137.7 (CH), 136.6 (C\(_q\)), 136.5 (C\(_q\)), 130.2 (CH), 126.1 (CH), 124.7 (C\(_q\)), 124.6 (CH), 122.1 (CH), 120.8 (CH). IR (ATR): 1586, 1470, 1454, 1440, 1422, 1212, 1193, 1088, 1011, 857 cm\(^{-1}\). MS (ESI) m/z (relative intensity): 325 [M+H]\(^+\) (100), 292 [M-Cl]\(^+\) (13), 213 [M-C\(_6\)H\(_4\)Cl]\(^+\) (10). HR-MS (ESI) m/z calcd for C\(_{13}\)H\(_9\)ClNSSe\(^+\) [M+H]\(^+\) \( 325.9304 \), found 325.9302. The analytical data are in accordance with those reported in the literature.\[^{[4]}\]
6-Fluoro-2-\{(3-fluorophenyl)selanyl\}benzo[d]thiazole (4cc): The representative procedure was followed using 6-fluorobenzo[d]thiazole (1c) (61.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (2c) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/2) yielded 4cc (80.0 mg, 61%) as a yellow oil. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.86 (dd, $J$ = 8.9, 4.8 Hz, 1H), 7.56 (ddd, $J$ = 7.7, 1.6, 1.0 Hz, 1H), 7.52 (ddd, $J$ = 8.2, 2.6, 1.6 Hz, 1H), 7.41–7.35 (m, 2H), 7.19–7.10 (m, 2H). $^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ 162.7 (d, $J_{CF}$ = 251.7 Hz, C$_q$), 160.1 (d, $J_{CF}$ = 246.1 Hz, C$_q$), 159.8 (d, $J_{CF}$ = 2.9 Hz, C$_q$), 151.0 (d, $J_{CF}$ = 1.7 Hz, C$_q$), 137.6 (d, $J_{CF}$ = 11.0 Hz, C$_q$), 131.7 (d, $J_{CF}$ = 3.3 Hz, CH), 131.2 (d, $J_{CF}$ = 8.0 Hz, CH), 127.7 (d, $J_{CF}$ = 7.1 Hz, C$_q$), 123.1 (d, $J_{CF}$ = 4.7 Hz, CH), 122.9 (d, $J_{CF}$ = 17.5 Hz, CH), 117.2 (d, $J_{CF}$ = 20.9 Hz, CH), 114.7 (d, $J_{CF}$ = 24.7 Hz, CH), 107.2 (d, $J_{CF}$ = 26.9 Hz, CH). $^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$ -110.05 (td, $J$ = 8.3, 5.8 Hz), -116.22 (td, $J$ = 8.5, 4.8 Hz). IR (ATR): 1586, 1564, 1468, 1440, 1407, 1247, 1212, 1193, 898, 856, 813, 781, 679 cm$^{-1}$. MS (ESI) m/z (relative intensity): 327 [M+H]$^+$ (100), 177 [M-C$_3$H$_2$FNS]$^+$ (10). HR-MS (ESI) m/z calcd for C$_{13}$H$_8$F$_2$NSSe$^+$ [M+H]$^+$ 327.9505, found 327.9511.

2-\{(3-fluorophenyl)selanyl\}-6-methoxybenzo[d]thiazole (4dc): The representative procedure was followed using 6-methoxybenzo[d]thiazole (1d) (66.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (2c) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/2) yielded 4dc (92.0 mg, 68%) as a pale yellow liquid. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (dd, $J$ = 8.9, 0.4 Hz, 1H), 7.52 (ddd, $J$ = 7.7, 1.6, 0.9 Hz, 1H), 7.48 (ddd, $J$ = 8.3, 2.5, 1.5 Hz, 1H), 7.37–7.31 (m, 1H), 7.17 (dd, $J$ = 2.5, 0.4 Hz, 1H), 7.11 (tdd, $J$ = 8.4, 2.6, 1.0 Hz, 1H), 7.01 (dd, $J$ = 9.0, 2.6 Hz, 1H), 3.81 (s, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ 162.6 (d, $^1J_{CF}$ = 251.3 Hz, C$_q$), 157.4 (C$_q$), 155.8 (C$_q$), 148.9 (C$_q$), 138.3 (C$_q$), 131.0 (d, $^4J_{CF}$ = 2.1 Hz, CH), 130.9 (d, $^3J_{CF}$ = 6.9 Hz, CH), 128.6 (d, $^3J_{CF}$ = 7.1 Hz, C$_q$), 122.8 (CH), 122.3 (d, $^2J_{CF}$ = 22.3 Hz, CH), 116.6 (d, $^2J_{CF}$ = 21.0 Hz, CH), 115.3 (CH), 103.6 (CH), 55.7 (CH$_3$). $^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$ -110.42 (td, $J$ = 8.3, 5.8 Hz). IR (ATR): 1587, 1470, 1449, 1429, 1408, 1256, 1219, 1060, 1025, 974.
cm\(^{-1}\). **MS** (ESI) m/z (relative intensity): 340 [M+H]\(^{+}\) (100), 362 [M+Na]\(^{+}\) (15). **HR-MS** (ESI) m/z calcd for \(\text{C}_{14}\text{H}_{11}\text{FNOSSe}\)^{+} [M+H]\(^{+}\) 339.9705, found 339.9703.

![Image of a molecule](image)

**2-((3-Fluorophenyl)selanyl)-5-phenylthiazole (4ec):** The representative procedure was followed using 5-phenylthiazole (1e) (65.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (2c) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/2) yielded 4ec (82.0 mg, 61%) as a pale yellow liquid. **\(^{1}\)H-NMR** (400 MHz, CDCl\(_3\)): \(\delta\) 7.90 (s, 1H), 7.49–7.40 (m, 4H), 7.38–7.26 (m, 4H), 7.07 (tdd, \(J = 8.4, 2.5, 1.0\) Hz, 1H). **\(^{13}\)C-NMR** (101 MHz, CDCl\(_3\)): \(\delta\) 162.7 (d, \(\text{J}_{\text{C-F}} = 251.0\) Hz, C\(_q\)), 154.05 (C\(_q\)), 143.2 (C\(_q\)), 139.6 (CH), 130.9 (d, \(\text{J}_{\text{C-F}} = 8.0\) Hz, CH), 130.7 (C\(_q\)), 130.0 (d, \(\text{J}_{\text{C-F}} = 7.1\) Hz, C\(_q\)), 129.8 (d, \(\text{J}_{\text{C-F}} = 3.2\) Hz, CH), 129.1 (CH), 128.5 (CH), 126.7 (CH), 121.2 (d, \(\text{J}_{\text{C-F}} = 22.4\) Hz, CH), 116.1 (d, \(\text{J}_{\text{C-F}} = 21.1\) Hz, CH). **\(^{19}\)F-NMR** (376 MHz, CDCl\(_3\)): \(\delta\) -110.56 (td, \(\text{J}_{\text{F-F}} = 8.3, 5.8\) Hz).

**IR** (ATR): 3059, 1586, 1470, 1445, 1424, 1384, 1262, 1211, 988, 856, 780, 757, 689, 678 cm\(^{-1}\). **MS** (ESI) m/z (relative intensity): 336 [M+H]\(^{+}\) (100), 358 [M+Na]\(^{+}\) (60). **HR-MS** (ESI) m/z calcd for \(\text{C}_{15}\text{H}_{11}\text{FNOSSe}\)^{+} [M+H]\(^{+}\) 335.9756, found 335.9765.

![Image of a molecule](image)

**6-Chloro-2-((3-fluorophenyl)selanyl)benzo[d]thiazole (4fc):** The representative procedure was followed using 6-chlorobenzo[d]thiazole (1f) (66.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (2c) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/2) yielded 4fc (70.0 mg, 51%) as a pale yellow liquid. **\(^{1}\)H-NMR** (400 MHz, CDCl\(_3\)): \(\delta\) 7.81 (dd, \(J = 8.7, 0.5\) Hz, 1H), 7.67 (dd, \(J = 2.1, 0.5\) Hz, 1H), 7.57 (ddd, \(J = 7.7, 1.6, 1.0\) Hz, 1H), 7.53 (ddd, \(J = 8.2, 2.6, 1.5\) Hz, 1H), 7.43–7.39 (m, 1H), 7.36 (dd, \(J = 8.7, 2.1\) Hz, 1H), 7.18 (ddd, \(J = 8.4, 2.6, 1.0\) Hz, 1H). **\(^{13}\)C-NMR** (101 MHz, CDCl\(_3\)): \(\delta\) 162.6 (d, \(\text{J}_{\text{C-F}} = 251.9\) Hz, C\(_q\)), 161.6 (C\(_q\)), 152.9 (C\(_q\)), 137.7 (C\(_q\)), 131.8 (d, \(\text{J}_{\text{C-F}} = 3.3\) Hz, CH), 131.2 (d, \(\text{J}_{\text{C-F}} = 8.0\) Hz, CH), 130.7 (C\(_q\)), 127.4 (d, \(\text{J}_{\text{C-F}} = 7.1\) Hz, C\(_q\)), 126.9 (CH), 123.2 (d, \(\text{J}_{\text{C-F}} = 22.2\) Hz, CH), 122.8 (CH), 120.5 (CH), 117.3 (d, \(\text{J}_{\text{C-F}} = 21.0\) Hz, CH). **\(^{19}\)F-NMR** (376 MHz, CDCl\(_3\)) \(\delta\) -109.97 (td, \(J = 8.3, 5.8\) Hz).
The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol) and 4-bromoisoquinoline (5n) (250.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/3) yielded 4an (72.0 mg, 53%) as a pale yellow solid. M. p.: 84–86 °C. 1H-NMR (300 MHz, Chloroform-d): δ 9.39 (s, 1H), 9.08 (s, 1H), 8.36 (dd, J = 8.4, 1.2 Hz, 1H), 8.04 (ddd, J = 8.0, 1.4, 0.8 Hz, 1H), 7.90 (ddd, J = 8.2, 1.2, 0.7 Hz, 1H), 7.77 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.69 (ddd, J = 8.1, 6.9, 1.3 Hz, 1H), 7.56 (ddd, J = 8.0, 1.3, 0.7 Hz, 1H), 7.38 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.22 (ddd, J = 7.9, 7.2, 1.2 Hz, 1H). 13C-NMR (101 MHz, CDCl3): δ 160.9 (Cq), 155.5 (CH), 154.3 (Cq), 151.5 (CH), 137.3 (Cq), 136.5 (Cq), 132.1 (CH), 129.5 (Cq), 128.3 (CH), 128.3 (CH), 126.8 (CH), 126.0 (CH), 124.4 (CH), 121.9 (CH), 121.2 (Cq), 120.7 (CH). IR (ATR): 1615, 1561, 1487, 1454, 1422, 1375, 1309, 752 cm⁻¹. MS (EI) m/z (relative intensity): 341 [M]+ (100), 262 (95), 235 (20), 181 (25). HR-MS (ESI) m/z calcd for C13H11N2SSe+[M+H]+ 343.9210, found 343.9192.

2-(m-Tolylselanyl)benzo[d]thiazole (4aa): Yellow liquid. 1H-NMR (400 MHz, CDCl3): δ 7.91 (ddd, J = 8.2, 1.2, 0.7 Hz, 1H), 7.69–7.60 (m, 3H), 7.39 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.34–7.22 (m, 3H), 2.38 (s, 3H). 13C-NMR (101 MHz, CDCl3): δ 163.0 (Cq), 154.6 (Cq), 139.9 (Cq), 137.1 (CH), 136.6 (Cq), 133.5 (CH), 130.8 (CH), 129.6 (CH), 126.2 (Cq), 125.9 (CH), 124.2 (CH), 121.9 (CH), 120.7 (CH), 21.2 (CH3). IR (ATR): 3054, 1454, 1421, 1232, 972, 775, 755, 726, 687, 428 cm⁻¹. MS (ESI) m/z (relative intensity): 306 [M+H]+ (100), 214 [M-C3H3]+ (5). HR-MS (ESI) m/z calcd for C14H12NSSe+[M+H]+ 305.9850, found 305.9859. The analytical data are in accordance with those reported in the literature.6}
Phenyl disulfide (7a): Colorless solid. M. p.: 59–60 °C. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.49 (dd, \(J = 7.0, 1.3\) Hz, 4H), 7.29 (td, \(J = 8.0, 2.4\) Hz, 4H), 7.21 (ddd, \(J = 7.6, 2.5, 1.3\) Hz, 2H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)): \(\delta\) 137.0 (C\(_q\)), 129.0 (CH), 127.5 (CH), 127.1 (CH). IR (ATR): 3056, 1575, 1473, 1436, 1020, 735, 685, 464 cm\(^{-1}\). MS (EI) m/z (relative intensity): 218 [M]+ (100), 185 (30), 154 (35), 109 (90). HR-MS (EI) m/z calcd for C\(_{12}\)H\(_{10}\)S\(_2\) [M]+ 218.0224, found 218.0232.\(^7\)

\[\begin{array}{c}
\text{Ph-S-S-Ph} \\
\text{(Phenyl disulfide)}
\end{array}\]

Diphenyl sulfide (8a): Colorless liquid. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.36 (dd, \(J = 7.0, 1.7\) Hz, 4H), 7.31 (dt, \(J = 7.0, 1.4\) Hz, 4H), 7.28–7.23 (m, 2H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)): \(\delta\) 135.7 (C\(_q\)), 130.9 (CH), 129.1 (CH), 126.9 (CH). IR (ATR): 3057, 1578, 1474, 1438, 1023, 736, 688, 516, 463 cm\(^{-1}\). MS (EI) m/z (relative intensity): 186 [M]+ (100), 152 (15), 109 (10). HR-MS (EI) m/z calcd for C\(_{12}\)H\(_{10}\)S [M]+ 186.0503, found 186.0498.\(^8\)

\[\begin{array}{c}
\text{Ph-S-Ph} \\
\text{(Diphenyl sulfide)}
\end{array}\]
Competition Experiment:

The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol), 1-iodo-3-methylbenzene (2a) (131.0 mg, 0.6 mmol) and 1-fluoro-3-iodobenzene (2c) (133.0 mg, 0.6 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 3aa (13.0 mg, 13%) and 3ac (50.0 mg, 48%).

The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol), 1-iodo-3-methylbenzene (2a) (131.0 mg, 0.6 mmol) and 1-fluoro-3-iodobenzene (2c) (133.0 mg, 0.6 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 4aa (18.0 mg, 15%) and 4ac (47.0 mg, 38%).
Probing SET-Type Mechanism:

\[
\begin{align*}
1a & \quad + \quad 2c & \quad \overset{\text{cat. CuTc}}{\text{LiOEtBu, DMF}} & \quad \text{hv, 25 °C, 16 h} & \quad \text{air} \quad \rightarrow \\
& & & & \text{3ac} \\
& & & & \text{standard conditions: 66%} \\
& & & & \text{galvinoxyl (1.0 equiv): 36%} \\
& & & & \text{galvinoxyl (3.0 equiv): 0%}
\end{align*}
\]

The representative procedure was followed using benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol), 1-fluoro-3-iodobenzene (2c) (266.0 mg, 1.2 mmol) and galvinoxyl (169 mg, 100 mol %; or 506 mg, 300 mol %, respectively). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (n-hexane/EtOAc: 10/1) yielded 3ac (38.0 mg, 36% or 0 mg, 0%, respectively).

Probing a Reaction Intermediate:

\[
\begin{align*}
1a & \quad + \quad 6a & \quad \overset{\text{cat. CuTc}}{\text{LiOEtBu, DMF}} & \quad \text{hv, 25 °C, 16 h} & \quad \text{air} \quad \rightarrow \\
& & & & \text{3ab}
\end{align*}
\]

To a pre-dried 10 mL quartz tube were added benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol), thiophenol (6a) (88.0 mg, 0.8 mmol), copper(I) thiophene-2-carboxylate (15.3 mg, 20 mol %), LiOEtBu (96.0 mg, 1.20 mmol), and DMF (2.0 mL) under an air atmosphere. The tube was sealed tightly and stirred under 254 nm irradiation in a Luzchem LZC-ICH2 photoreactor for 16 h at ambient temperature. The temperature was determined to be 25–27 °C in the reaction mixture. Afterwards the reaction mixture was diluted with Et2O (100 mL) and washed with water (4 × 50 mL). The combined organic extracts were dried over Na2SO4 and concentrated under reduced pressure. The NMR and GC analysis of the crude mixture showed only a trace amount of the desired product 3ab.
To a pre-dried 10 mL quartz tube were added benzo[d]thiazole (1a) (54.0 mg, 0.40 mmol), diphenyl disulfide 7a (87.0 mg, 0.40 mmol), copper(I) thiophene-2-carboxylate (15.3 mg, 20 mol%), LiOrBu (96.0 mg, 1.20 mmol), and DMF (2.0 mL) under an air atmosphere. The tube was sealed tightly and stirred under 254 nm irradiation in a Luzchem LZC-ICH2 photoreactor for 16 h at ambient temperature. The temperature was determined to be 25–27 °C in the reaction mixture. Afterwards the reaction mixture was diluted with Et₂O (100 mL) and washed with water (4 × 50 mL). The combined organic extracts were dried over Na₂SO₄. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (n-hexane/EtOAc) to yield the product 3ab (76.0 mg, 78%).

To a pre-dried 10 mL quartz tube were added sulfur powder (15.0 mg, 0.46 mmol), iodobenzene (2b) (282.0 mg, 1.38 mmol), copper(I) thiophene-2-carboxylate (18.0 mg, 20 mol%), LiOrBu (110.0 mg, 1.38 mmol), and DMF (2.0 mL) under an air atmosphere. The tube was sealed tightly and stirred under 254 nm irradiation in a Luzchem LZC-ICH2 photoreactor for 16 h at ambient temperature. The temperature was determined to be 25–27 °C in the reaction mixture. Afterwards the reaction mixture was diluted with Et₂O (100 mL) and washed four times with water. The combined organic extracts were dried over Na₂SO₄. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (n-hexane/EtOAc) to yield the product 7a (29.0 mg, 29%) and 8a (15.0 mg, 17%).
References:


$^1$H-, $^{13}$C-, and $^{19}$F-NMR Spectra

3aa

(CDCl$_3$, 600 MHz)

3aa

(CDCl$_3$, 101 MHz)
3ac
(CDCl$_3$, 600 MHz)

3ac
(CDCl$_3$, 126 MHz)
3ac
(282 MHz, CDCl$_3$)

3ad
(CDCl$_3$, 600 MHz)
3ad
(CDCl₃, 126 MHz)

3ae
(CDCl₃, 500 MHz)
3ae  
(CDCl$_3$, 126 MHz)

3af  
(CDCl$_3$, 500 MHz)
3af
(CDCl₃, 126 MHz)

3ag
(CDCl₃, 600 MHz)
3ag
(CDCl₃, 126 MHz)

3ag
(282 MHz, CDCl₃)
3ah
(CDCl₃, 600 MHz)

3ah
(CDCl₃, 101 MHz)
3ai
(126 MHz, CDCl₃)

3aj
(300 MHz, CDCl₃)
3aj
(126 MHz, CDCl₃)

3ak
(500 MHz, CDCl₃)
3ak
(126 MHz, CDCl₃)

3ak
(471 MHz, CDCl₃)
3bc
(400 MHz, CDCl₃)

3bc
(101 MHz, CDCl₃)
3cc
(101 MHz, CDCl₃)

3cc
(376 MHz, CDCl₃)
3dc
(376 MHz, CDCl₃)

3eb
(500 MHz, CDCl₃)
3eb
(126 MHz, CDCl₃)

3am
(400 MHz, CDCl₃)
$3\text{am}$

$(101 \text{ MHz, CDCl}_3)$

$\begin{align*}
\text{N} & \text{S} \\
\text{S} & \text{N} \\
\end{align*}$

$3\text{an}$

$(400 \text{ MHz, CDCl}_3)$

$\begin{align*}
\text{N} & \text{S} \\
\text{S} & \text{N} \\
\end{align*}$
4aa
(101 MHz, CDCl₃)

4ab
(301 MHz, CDCl₃)
4af
(300 MHz, CDCl₃)

4af
(126 MHz, CDCl₃)
4ag

(376 MHz, CDCl₃)

4ah

(400 MHz, CDCl₃)
4cc
(400 MHz, CDCl₃)

4cc
(101 MHz, CDCl₃)
**4cc**  
(376 MHz, CDCl₃)

**4dc**  
(400 MHz, CDCl₃)
4dc
(101 MHz, CDCl₃)

4dc
(376 MHz, CDCl₃)
$^\text{4fc}$

(101 MHz, CDCl$_3$)

$^\text{4fc}$

(376 MHz, CDCl$_3$)
7a

(400 MHz, CDCl₃)

7a

(101 MHz, CDCl₃)
The UV-visible absorption spectra of reaction components and combination were measured in DMF (1×10⁻⁵ M). The results showed that the reagents, catalyst and the reaction mixture are absorbing light under UV region which facilitate the Cu-catalyzed C–H chalcogenation process.

**Benzothiazole (1a):**

![UV-visible absorption spectra for Benzothiazole (1a)](image)

**3-Iodotoluene (2a):**

![UV-visible absorption spectra for 3-Iodotoluene (2a)](image)
Copper(I)-thiophene-2-carboxylate (CuTc):

Product 3aa:
Mixture of 1a and CuTc:

- Absorption peak at 270 nm

Mixture of 1a and LiO\textsubscript{t}Bu:

- Absorption peak at 275 nm

Mixture of 1a, LiO\textsubscript{t}Bu and CuTc:

- Absorption peak at 265 nm
Mixture of 2a and CuTc:

Mixture of 3aa and CuTc:

Diphenyl disulfide (7a):
Reaction mixture for the synthesis of 3aa—Before light irradiation:

![Graph](image1)

Reaction mixture for the synthesis of 3aa—after 1 h light irradiation:

![Graph](image2)

Reaction mixture for the synthesis of 3aa—after 3 h light irradiation:

![Graph](image3)
Reaction mixture for the synthesis of 3aa—after 16 h light irradiation: