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Supplementary Information

Versatile Telluracycle Synthesis via Sequential Electrophilic Telluration of $C(sp^2)$ -Zn and $C(sp^2)$ -H Bonds

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Material and Methods

General. All reactions dealing with air- or moisture-sensitive compound were performed by standard Schlenk techniques in oven-dried reaction vessels under nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Flash chromatography was performed using 40–63 μ m silica gel (Si 60, Merck). ¹H and ¹³C{¹H} nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV-400 (400 MHz) NMR spectrometers. ¹H and ¹³C{¹H} NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and CHCl₃ (77.0 ppm), respectively. Gas chromatographic (GC) analysis was performed on a Shimadzu GC-2010 system equipped with an FID detector and a capillary column, DB-5 (Agilent J&W, 0.25 mm i.d. x 30 m, 0.25 μ m film thickness). High-resolution mass spectra (HRMS) were obtained with a Q-Tof Premier LC HR mass spectrometer. Melting points were determined using a capillary melting point apparatus and are uncorrected. UV and fluorescence spectra were recorded on Shimadzu UV-1800 spectrophotometer and Shimadzu RF-5301PC spectrofluorophotometer, respectively.

Materials. Unless otherwise noted, commercial reagents were purchased from Aldrich, Alfa Aesar, and other commercial suppliers and were used as received. Anhydrous CoCl₂ (97%) and TeCl₄ (99%) were purchased from Alfa Aesar and were used as received. THF was distilled over Na/benzophenone. Grignard reagents (approx. 1 M) were prepared from the corresponding halides and magnesium turnings in anhydrous THF and titrated before use. 1-Butyl-4-(ptolylethynyl) benzene, ¹ 4-((4-butylphenyl)ethynyl)-1,1'-biphenyl, ² 1-methoxy-4-(oct-1-yn-1vl)benzene,³ 2-(but-1-vn-1-vl)-1,3-dimethylbenzene,⁴ 2-(hex-1-vn-1-vl)thiophene,⁵ 1-fluoro-4-6 1-chloro-4-(hex-1-vn-1-vl)benzene. 7 (hex-1-vn-1-vl)benzene. 1-(hex-1-vn-1-vl)-3-(trifluoromethyl)benzene, ⁸ 2-(hex-1-yn-1-yl)naphthalene, ⁹ 2-(2-iodophenyl)thiophene, ¹⁰ 2-(2iodophenyl)naphthalene, 10 2-(2-bromophenyl)-1-methyl-1*H*-indole, 11 1-(2-iodophenvl)-3methyl-1*H*-indole¹² were prepared according the literature procedures and their ¹H and ¹³C{¹H} NMR spectra showed good agreement with the literature data.

Synthesis of Benzotellurophene Derivatives

Procedures for the preparation of arylzinc reagents and their addition to alkynes

An arylzinc reagent was prepared either by transmetalation between ZnCl₂•TMEDA and the corresponding aryl Grignard reagent (type I and II reagents) or by Co–Xantphos-catalyzed insertion of Zn•LiCl into the corresponding aryl bromide (type III reagent).¹³ The resulting arylzinc reagent was subjected to the reaction with an alkyne under Co–Xantphos catalysis as described previously, thus furnishing an *ortho*-alkenylarylzinc reagent.⁴ Below are brief descriptions of three different procedures used in the present study.



Type I reagent: In a 10 mL Schlenk tube was placed ZnCl₂•TMEDA (139 mg, 0.55 mmol). The Schlenk tube was submerged in an ice bath for 15 min, followed by dropwise addition of a THF solution of an aryl Grignard reagent (0.55 mmol). The resulting mixture was stirred for 1 h at 0 °C and then allowed to warm to room temperature. To the arylzinc reagent was added Xantphos (14.5 mg, 0.025 mmol), CoCl₂ (3.2 mg, 0.025 mmol) followed by stirring for 5 min and addition of an alkyne (0.50 mmol). The resulting mixture was stirred at 60 °C, monitored by TLC until starting materials were consumed, and then allowed to cool to room temperature.

Type II reagent: In a 10 mL Schlenk tube was placed ZnCl₂•TMEDA (139 mg, 0.55 mmol). The Schlenk tube was submerged in an ice bath for 15 min, followed by dropwise addition of a THF solution of an aryl Grignard reagent (1.1 mmol). The resulting mixture was stirred for 1 h at 0 °C and then allowed to warm to room temperature. To the arylzinc reagent was added Xantphos (14.5 mg, 0.025 mmol), CoCl₂ (3.2 mg, 0.025 mmol) followed by stirring for 5 min and addition of an alkyne (0.50 mmol). The resulting mixture was stirred at 60 °C, monitored by TLC until starting materials were consumed, and then allowed to cool to room temperature.

Type III reagent: Anhydrous LiCl (42.4 mg, 1.0 mmol) was placed in a 10 mL Schlenk tube, dried under vacuum (1 mbar) at 150 °C for 20 min, and cooled down to room temperature under N₂. To the Schlenk tube was added zinc powder (98.1 mg, 1.5 mmol), and the heterogeneous mixture of Zn and LiCl was dried under vacuum (1 mbar) at 150 °C for 15 min. While cooling to room temperature, the reaction tube was evacuated and backfilled with N₂ for three times. The mixture was suspended with THF (1 mL), followed by the activation of Zn with BrCH₂CH₂Br (5 μ L, 0.05 mmol) and Me₃SiCl (1.5 μ L, 0.01 mmol) and stirring for 5 min. Then Xantphos (28.9 mg, 0.050 mmol) and CoCl₂ (6.5 mg, 0.050 mmol) were added sequentially. After stirring for additional 5 min, an aryl halide (1 mmol) was added in one portion. The reaction was stirred at room temperature. After complete conversion of the starting material, alkyne (0.50 mmol) was added to the arylzinc reagent. The resulting solution was stirred at 60 °C, monitored by TLC until starting materials were consumed, and then allowed to cool to room temperature.

General procedure for benzotellurophene synthesis

To a THF solution (0.2 M) of TeCl₄ (269 mg, 1.0 mmol for Type I reagent and 404 mg, 1.5 mmol for Type II and III reagent; weighed into a Schlenk tube inside a glove box) was added the solution of the *ortho*-alkenyl arylzinc reagent at room temperature. The resulting solution was stirred at 90 °C for 12 h, followed by the addition of a saturated aqueous solution of Na₂S (1 mL) at 0 °C. The mixture was stirred at room temperature for 3 h, diluted with ethyl acetate (5 mL), and filtered through a pad of silica gel with additional ethyl acetate (15 mL) as the eluent. The filtrate was washed with water (10 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.



2,3-Dibutyl-6-methoxybenzo[*b*]tellurophene (3aa): Type I arylzinc reagent was used; Yellow oil (58% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 7.49 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 2.4 Hz, 1H), 7.00 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.86 (s, 3H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.74 (t,

J = 7.6 Hz, 2H), 1.72 - 1.63 (m, 2H), 1.61 - 1.56 (m, 2H), 1.55 - 1.44 (m, 4H), 1.02 (t, J = 7.2 Hz, 3H), 1.01 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃): δ 156.5, 142.7, 140.9, 136.9, 131.7, 126.3, 115.9, 113.4, 55.5, 36.8, 33.5, 32.0, 29.6, 23.0, 22.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for C₁₇H₂₅OTe [M + H]⁺ 375.0968, found 375.0966.



2,3-dibutylbenzo[*b*]**tellurophene (3ba):** Type I arylzinc reagent was used; Yellow oil (62% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.89 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.61 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.16 – 7.12 (m, 1H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 1.71 – 1.67 (m, 2H), 1.61 – 1.56 (m, 2H), 1.54 – 1.45 (m, 4H), 1.01 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 148.8, 141.7, 140.6, 132.2, 130.8, 125.8, 125.0, 123.8, 36.9, 33.7, 31.9, 29.4, 23.0, 22.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for C₁₆H₂₃Te [M + H]⁺ 345.0862, found 345.0853.



2,3-Dibutyl-6-(trifluoromethyl)benzo[*b*]tellurophene (3ca): Type III arylzinc reagent was used; Yellow oil (53% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.11 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 1.69 – 1.63 (m, 2H), 1.55 – 1.41 (m, 6H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 151.5, 145.3, 141.3, 130.9, 129.0 (q, ³*J*_{C-F} = 4.0 Hz), 127.6, 127.2 (q, ¹*J*_{C-F} = 270.2 Hz), 125.7, 121.8 (q, ³*J*_{C-F} = 3.6 Hz), 36.8, 33.8, 31.8, 29.4, 22.9, 22.6, 14.0 (two signals overlapped); HRMS (ESI) Calcd for C₁₇H₂₂F₃Te [M + H]⁺ 413.0736, found 413.0742.



2,3-Dibutyl-6-fluorobenzo[*b*]**tellurophene (3da):** Type I arylzinc reagent was used; Yellow oil (48% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 7.55 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.12 – 7.07 (m, 1H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 1.69 – 1.61 (m, 2H), 1.57 – 1.53 (m, 2H), 1.51 – 1.42 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.6 (d, ¹*J*_{C-F} = 245.4 Hz), 145.2 (d, ⁴*J*_{C-F} = 2.1 Hz), 140.7, 139.6, 131.4 (d, ³*J*_{C-F} = 7.1 Hz), 126.5 (d, ³*J*_{C-F} = 8.0 Hz), 118.3 (d, ²*J*_{C-F} = 22.9 Hz), 113.2 (d, ²*J*_{C-F} = 22.8 Hz), 36.7, 33.6, 31.8, 29.7, 23.0, 22.6, 14.0 (two signals overlapped); HRMS (ESI) Calcd for C₁₆H₂₂TeF [M + H]⁺ 363.0768, found 363.0765.



Ethyl 2,3-dibutylbenzo[*b*]tellurophene-6-carboxylate (3ea): Type II arylzinc reagent was used; Yellow oil (47% yield, eluent = hexane/EtOAc (50:1)); ¹H NMR (400 MHz, CDCl₃): δ 8.54 (d, J = 1.6 Hz, 1H), 8.02 (dd, J = 8.4, 1.6 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 4.40 (q, J = 7.2 Hz, 2H), 2.92 (t, J = 7.6 Hz, 2H), 2.75 (t, J = 7.6 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.61 – 1.45 (m, 6H), 1.41 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H), 0.96 (t, J = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 166.7, 152.3, 146.1, 141.7, 133.7, 130.5, 129.5, 126.1, 125.3, 60.9, 36.8, 34.0, 31.8, 29.5, 22.9, 22.6, 14.4, 14.0 (two signals overlapped); HRMS (ESI) Calcd for C₁₉H₂₇O₂Te [M + H]⁺ 417.1073, found 417.1074.



1-(2,3-Dibutylbenzo[*b***]tellurophen-6-yl)ethanone (3fa):** Type **III** arylzinc reagent prepared from (*E*)-*N*-(1-(4-bromophenyl)ethylidene)-4-methoxyaniline was used. After the reaction was completed, aqueous HCl (1.5 mL, 1 M) was added, and the resulting mixture was stirred for 1 h. Silica gel chromatography of the crude product afforded the title compound as a brown oil (50% yield, eluent = hexane/EtOAc (50:1)); ¹H NMR (400 MHz, CDCl₃): δ 8.46 (d, *J* = 1.6 Hz, 1H), 7.94 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.61 (d, *J* = 8.4Hz, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.63 (s, 3H), 1.71 – 1.63 (m, 2H), 1.56 – 1.41 (m, 6H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 197.7, 152.5, 147.0, 141.7, 132.7, 132.2, 130.9, 125.5, 125.1, 36.8, 34.0, 31.8, 29.4, 26.7, 22.9, 22.6, 14.0 (two signals overlapped); HRMS (ESI) Calcd for C₁₈H₂₅OTe [M + H]⁺ 387.0968, found 387.0967.



2,3-Dibutyl-6-methylbenzo[*b*]**tellurophene (3ga):** Type I arylzinc reagent was used; Yellow oil (55% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 7.71 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.18 (dd, *J* = 8.4, 1.2 Hz, 1H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 1.71 – 1.63 (m, 2H), 1.60 – 1.56 (m, 2H), 1.54 – 1.43 (m, 4H), 1.00 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 146.5, 141.4, 138.9, 133.6, 132.4, 130.9, 126.4, 125.4, 41.0, 36.8, 33.6, 31.9, 29.4, 23.0, 22.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for C₁₇H₂₅Te [M + H]⁺ 359.1019, found 359.1014.



2,3-Dibutyl-6-phenylbenzo[*b*]**tellurophene (3ha):** Type I arylzinc reagent was used; Yellow oil (52% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.12 (d, *J* = 1.6 Hz, 1H), 7.69 – 7.61 (m, 4H), 7.49 – 7.45 (m, 2H), 7.39 – 7.35 (m, 1H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.64 – 1.57 (m, 2H), 1.55 – 1.47 (m, 4H), 1.02 (t, *J* = 7.2 Hz, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 148.0, 141.5, 141.1, 141.0, 136.8, 131.5, 130.6, 128.8, 127.2, 127.1, 125.9, 124.4, 36.9, 33.8, 31.9, 29.5, 23.0, 22.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for C₂₂H₂₇Te [M + H]⁺ 421.1175, found 421.1176.



(2,3-Dibutylbenzo[*b*]tellurophen-6-yl)trimethylsilane (3ia): Type III arylzinc reagent was used; Yellow oil (52% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.03 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.48 (dd, *J* = 7.6, 1.2 Hz, 1H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 1.67 – 1.61 (m, 2H), 1.57 – 1.53 (m, 2H), 1.51 – 1.41 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.30 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.2, 141.8, 141.4, 137.1, 135.6, 131.1, 129.6, 125.3, 36.8, 33.7, 31.8, 29.2, 23.0, 22.5, 14.0 (two signals overlapped), -1.0; HRMS (ESI) Calcd for C₁₉H₃₁TeSi [M + H]⁺ 417.1257, found 417.1257.



2,3-Dibutyl-N,N-dimethylbenzo[b]tellurophen-6-amine (3ja): Type I arylzinc reagent was

used; Brown oil (54% yield, eluent = hexane/EtOAc (50:1)); ¹H NMR (400 MHz, CDCl₃): δ 7.42 (d, *J* = 8.8 Hz, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.4 Hz, 1H), 2.98 (s, 6H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 1.68 – 1.60 (m, 2H), 1.58 – 1.53 (m, 2H), 1.49 – 1.40 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 147.8, 141.0, 139.5, 134.2, 132.0, 125.9, 115.4, 111.8, 41.0, 36.8, 33.4, 32.0, 29.4, 23.0, 22.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for C₁₈H₂₈NTe [M + H]⁺ 388.1284, found 388.1290.



tert-Butyl((2,3-dibutylbenzo[*b*]tellurophen-6-yl)oxy)dimethylsilane (3ka): Type I arylzinc reagent was used; Yellow oil (41% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 7.38 (d, *J* = 8.8 Hz, 1H), 7.32 (d, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.4 Hz, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.66 – 1.58 (m, 2H), 1.55 – 1.51 (m, 2H), 1.49 – 1.40 (m, 4H), 1.00 (s, 9H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.21 (s, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 152.3, 143.0, 140.9, 137.0, 131.1, 126.1, 123.0, 118.3, 36.7, 33.5, 31.8, 29.6, 25.7, 23.0, 22.6, 18.2, 14.0 (two signals overlapped), -4.4; HRMS (ESI) Calcd for C₂₂H₃₇OSiTe [M + H]⁺ 475.1676, found 475.1678.



2,3-Dibutylbenzo[*b*]**tellurophen-6-ol (3la):** Type **III** arylzinc reagent prepared from 4bromophenyl *tert*-butyl carbonate was used. The Boc group was removed during the reaction; Brown oil (58% yield, eluent = hexane/EtOAc (30:1)); ¹H NMR (400 MHz, CDCl₃): δ 7.40 (d, *J* = 8.8 Hz, 1H), 7.31 (d, *J* = 2.4 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.86 (s, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.68 – 1.58 (m, 2H), 1.55 – 1.51 (m, 2H), 1.49 – 1.40 (m,

4H), 0.96 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 152.2, 142.8, 140.8, 136.8, 131.6, 126.4, 118.1, 113.8, 36.7, 33.4, 31.9, 29.5, 23.0, 22.5, 14.0 (two signals overlapped); HRMS (ESI) Calcd for C₁₆H₂₃OTe [M + H]⁺ 361.0811, found 361.0812.



2,3-Dibutyl-5,7-dimethoxybenzo[*b*]tellurophene (3ma): Type I arylzinc reagent was used; Yellow oil (46% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 6.79 (d, *J* = 1.6 Hz, 1H), 6.33 (d, *J* = 2.0 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 1.68 – 1.59 (m, 2H), 1.55 – 1.51 (m, 2H), 1.50 – 1.38 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 160.5, 160.4, 149.9, 142.0, 141.4, 109.7, 102.5, 94.1, 55.8, 55.7, 36.8, 33.7, 31.8, 29.6, 22.9, 22.6, 14.0 (two signals overlapped); HRMS (ESI) Calcd for C₁₈H₂₇O₂Te [M + H]⁺ 405.1073, found 405.1079.



2,3-Dibutyl-5-methylbenzo[*b*]**tellurophene (3na):** Type I arylzinc reagent was used; Brown oil (51% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.43 (s, 1H), 7.00 (dd, *J* = 7.6, 1.2 Hz, 1H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.49 (s, 1H), 1.72 - 1.64 (m, 2H), 1.61 - 1.55 (m, 2H), 1.54 - 1.44 (m, 4H), 1.00 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.1, 141.5, 140.6, 134.6, 131.9, 126.7, 126.3, 125.4, 36.8, 33.7, 31.9, 29.4, 23.0, 22.6, 21.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for C₁₇H₂₅Te [M + H]⁺ 359.1019, found 359.1026.



6,7-Dibutyltelluropheno[**2'**,**3'**:**3**,**4**]**benzo**[**1**,**2**-*d*][**1**,**3**]**dioxole** (**3oa**): Type I arylzinc reagent was used; Yellow oil (66% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 7.10 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.02 (s, 2H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 1.67 – 1.59 (m, 2H), 1.55 – 1.50 (m, 2H), 1.48 – 1.40 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.5, 145.2, 142.3, 141.3, 137.0, 119.1, 107.1, 106.6, 100.9, 36.7, 33.5, 31.9, 29.8, 23.0, 22.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for C₁₇H₂₃O₂Te [M + H]⁺ 389.0760, found 389.0768.



2,3-Dibutyl-6,7-difluorobenzo[*b*]**tellurophene (3pa):** Type **III** arylzinc reagent was used; Orange oil (55% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 7.30 – 7.27 (m, 1H), 7.25 – 7.18 (m, 1H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 1.71 – 1.64 (m, 2H), 1.60 – 1.41 (m, 6H), 1.01 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 151.1 (dd, ¹*J*_{C-F} = 240.5 Hz, ²*J*_{C-F} = 13.7 Hz), 146.7 (dd, ³*J*_{C-F} = 5.5, 2.6 Hz), 146.0 (dd, ¹*J*_{C-F} = 246.6 Hz, ²*J*_{C-F} = 13.9 Hz), 141.0, 140.8 (d, ⁴*J*_{C-F} = 2.4 Hz), 121.3 (dd, ³*J*_{C-F} = 6.0 Hz, ⁴*J*_{C-F} F = 2.9 Hz), 117.9 (d, ²*J*_{C-F} = 25.7 Hz), 115.5 (d, ²*J*_{C-F} = 18.9 Hz), 36.7, 33.5, 31.9, 29.8, 22.9, 22.6, 14.0 (two signals overlapped); HRMS (ESI) Calcd for C₁₆H₂₁TeF₂ [M + H]⁺ 381.0674, found 381.0669.



2,3-DibutyInaphtho[**2,3-***b*]**tellurophene (3qa):** Type I arylzinc reagent was used; Orange oil (38% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.31 (s, 1H), 8.04 (s, 1H), 7.95 – 7.93 (m, 1H), 7.79 – 7.76 (m, 1H), 7.48 – 7.45 (m, 2H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.85 (t, *J* = 7.6 Hz, 2H), 1.71 – 1.61 (m, 4H), 1.56 – 1.46 (m, 4H), 1.01 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 147.8, 140.9, 139.3, 131.4, 131.2, 130.9, 128.4, 126.8, 126.4, 125.3, 125.2, 123.9, 36.4, 34.0, 31.8, 29.4, 23.0, 22.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for C₂₀H₂₅Te [M + H]⁺ 395.1019, found 395.1014.



2,3-Dibutyltelluropheno[**2,3-***b*]**quinoline (3ra):** Type **III** arylzinc reagent was used; Orange oil (46% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.06 – 8.04 (m, 2H), 7.87 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.52 – 7.48 (m, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 1.72 – 1.65 (m, 2H), 1.62 – 1.54 (m, 2H), 1.51 – 1.42 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 160.7, 146.3, 143.3, 142.0, 137.6, 129.8, 128.7, 128.4, 127.9, 126.1, 125.5, 36.3, 34.1, 31.8, 28.7, 22.9, 22.6, 14.1, 14.0; HRMS (ESI) Calcd for C₁₉H₂₄NTe [M + H]⁺ 396.0971, found 396.0973.



4,5-Dibutyltelluropheno[2,3-b]thiophene (3sa): Type III arylzinc reagent was used; Brown oil

(46% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 7.42 (d, *J* = 4.8 Hz, 1H), 7.19 (d, *J* = 4.8 Hz, 1H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.7 Hz, 2H), 1.66 – 1.53 (m, 4H), 1.51 – 1.37 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 156.4, 142.5, 137.9, 129.5, 123.9, 115.7, 37.0, 33.3, 32.2, 30.6, 22.8, 22.5, 14.0 (two signals overlapped); HRMS (ESI) Calcd for C₁₄H₂₁STe [M + H]⁺ 351.0426, found 351.0421.



6-Methyl-7-phenyltelluropheno[2',3':3,4]benzo[1,2-*d***][1,3]dioxole (3ob): Type II arylzinc reagent was used; Yellow solid (56% yield, eluent = hexane); m.p. = 104-105 °C; ¹H NMR (400 MHz, CDCl₃): \delta 7.44 – 7.38 (m, 4H), 7.34 – 7.30 (m, 1H), 7.23 (d,** *J* **= 8.4 Hz, 1H), 7.00 (d,** *J* **= 8.0 Hz, 1H), 6.07 (s, 2H), 2.31 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): \delta 149.3, 145.5, 143.2, 140.1, 137.5, 131.6, 129.7, 128.5, 127.2, 120.4, 108.0, 107.5, 101.1, 16.5; HRMS (ESI) Calcd for C₁₆H₁₃O₂Te [M + H]⁺ 366.9978, found 366.9973.**



6-Butyl-7-(*p***-tolyl)telluropheno[2',3':3,4]benzo[1,2-***d***][1,3]dioxole (3oc): Type III arylzinc reagent was used; Yellow gum (47% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): \delta 7.31 (d,** *J* **= 8.0 Hz, 2H), 7.23 (d,** *J* **= 8.4 Hz, 1H), 7.20 (d,** *J* **= 8.0 Hz, 2H), 6.98 (d,** *J* **= 8.4 Hz, 1H), 6.06 (s, 2H), 2.68 (t,** *J* **= 8.0 Hz, 2H), 2.38 (s, 3H), 1.63 – 1.55 (m, 2H), 1.37 – 1.26 (m, 2H), 0.87 (t,** *J* **= 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): \delta 149.3, 144.5, 142.8, 142.7, 137.3, 137.0, 132.1, 129.2, 129.1, 120.4, 108.7, 107.4, 101.0, 32.5, 29.9, 22.8, 21.2, 13.8; HRMS (ESI) Calcd for C₂₀H₂₁O₂Te [M + H]⁺ 423.0604, found 423.0601.**



7-([1,1'-Biphenyl]-4-yl)-6-butyltelluropheno[2',3':3,4]benzo[1,2-*d***][1,3]dioxole (3od): Type II** arylzinc reagent was used; Yellow solid (58% yield, eluent = hexane); m.p. = $133-134 \,^{\circ}$ C; ¹H NMR (400 MHz, CDCl₃): δ 7.68 – 7.64 (m, 4H), 7.52 – 7.47 (m, 4H), 7.41 – 7.37 (m, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.08 (s, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.42 – 1.33 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.3, 144.5, 143.1, 142.9, 140.6, 140.0, 139.3, 131.5, 129.8, 128.9, 127.5, 127.1, 127.0, 120.6, 108.9, 107.5, 101.1, 32.6, 30.0, 22.9, 13.9; HRMS (ESI) Calcd for C₂₅H₃O₂Te [M + H]⁺ 485.0760, found 485.0767. Recrystallization from EtOAc/hexane afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of the compound (Figure S1 and S2).¹⁴



Figure S1. ORTEP drawing of **3od** with thermal ellipsoids presented at 50% probability (grey = carbon, red = oxygen, orange = tellurium). Hydrogen atoms are omitted for clarity.



Figure S2. Packing diagram of 3od. The shortest Te-Te distance is 3.671 Å.



6-Butyl-7-(4-fluorophenyl)telluropheno[2',3':3,4]benzo[1,2-*d***][1,3]dioxole (3oe): Type III arylzinc reagent was used; Yellow solid (46% yield, eluent = hexane); m.p. = 101-102 °C; ¹H NMR (400 MHz, CDCl₃): \delta 7.39 – 7.36 (m, 2H), 7.23 (d,** *J* **= 8.4 Hz, 1H), 7.10 – 7.06 (m, 2H), 6.99 (d,** *J* **= 8.0 Hz, 1H), 6.06 (s, 2H), 2.64 (t,** *J* **= 8.0 Hz, 2H), 1.60 – 1.54 (m, 2H), 1.35 – 1.26 (m, 2H), 0.85 (t,** *J* **= 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): \delta 162.0 (d, ¹***J***_{C-F} = 245.5 Hz), 149.3, 144.1, 143.4, 143.0,136.2, 130.9 (d, ³***J***_{C-F} = 8.0 Hz), 130.3, 120.6, 115.3 (d, ²***J***_{C-F} = 21.4 Hz), 108.7, 107.5, 101.0, 32.4, 29.8, 22.8, 13.8; HRMS (ESI) Calcd for C₁₉H₁₈O₂TeF [M + H]⁺ 427.0353, found 427.0354.**



6-Butyl-7-(4-chlorophenyl)telluropheno[2',3':3,4]benzo[1,2-*d***][1,3]dioxole (3of): Type III arylzinc reagent was used; Yellow solid (58% yield, eluent = hexane); m.p. = 106-107 °C; ¹H NMR (400 MHz, CDCl₃): \delta 7.38 – 7.32 (m, 4H), 7.24 (d,** *J* **= 8.4 Hz, 1H), 7.00 (d,** *J* **= 8.4 Hz, 1H), 6.06 (s, 2H), 2.65 (t,** *J* **= 8.0 Hz, 2H), 1.61 – 1.53 (m, 2H), 1.36 – 1.27 (m, 2H), 0.86 (t,** *J* **= 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): \delta 149.3, 144.1, 143.5, 143.0, 138.8, 133.2, 130.6, 130.0, 128.6, 120.7, 108.8, 107.6, 101.1, 32.5, 29.9, 22.8, 13.8; HRMS (ESI) Calcd for C₁₉H₁₈O₂CITe [M + H]⁺ 443.0058, found 443.0053.**



6-Butyl-7-(3-(trifluoromethyl)phenyl)telluropheno[2',3':3,4]benzo[1,2-*d*][1,3]dioxole (3og): Type II arylzinc reagent was used; Yellow solid (52% yield, eluent = hexane); m.p. = 65-66 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.71 (s, 1H), 7.61 – 7.59 (m, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.08 (s, 2H), 2.66 (t, *J* = 8.0 Hz, 2H), 1.65 – 1.58 (m, 2H), 1.38 – 1.29 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.3, 144.2, 143.9, 143.2, 141.2, 132.8, 130.9 (q, ²*J*_{C-F} = 32.1 Hz), 129.2, 129.0, 125.9 (q, ³*J*_{C-F} = 3.7 Hz), 124.0 (q, ¹*J*_{C-F} = 271.0 Hz), 123.9 (q, ³*J*_{C-F} = 3.8 Hz), 120.9, 108.8, 107.6, 101.1, 32.5, 29.9, 22.8, 13.7; HRMS (ESI) Calcd for C₂₀H₁₈O₂TeF₃ [M + H]⁺ 477.0321, found 477.0321.



6-Hexyl-7-(4-methoxyphenyl)telluropheno[2',3':3,4]benzo[1,2-*d***][1,3]dioxole (3oh):** Type **II** arylzinc reagent was used; Brown solid (46% yield, eluent = hexane); m.p. = 75-76 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.34 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H),

6.92 (d, J = 8.8 Hz, 2H), 6.05 (s, 2H), 3.85 (s, 3H), 2.65 (t, J = 7.6 Hz, 2H), 1.63 – 1.56 (m, 2H), 1.33 – 1.20 (m, 6H), 0.86 (t, J = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 158.8, 149.3, 144.5, 142.8, 132.6, 131.8, 130.4, 129.9, 120.4, 113.8, 108.7, 107.4, 101.0, 55.4, 31.5, 30.3, 30.2, 29.5, 22.6, 14.1; HRMS (ESI) Calcd for C₂₂H₂₅O₃Te [M + H]⁺ 467.0866, found 467.0861.



6-Butyl-7-(naphthalen-2-yl)telluropheno[2',3':3,4]benzo[1,2-*d***][1,3]dioxole (3oi): Type II arylzinc reagent was used; Yellow solid (41% yield, eluent = hexane); m.p. = 87-88 °C; ¹H NMR (400 MHz, CDCl₃): \delta 7.86 – 7.82 (m, 4H), 7.53 – 7.48 (m, 3H), 7.24 (d,** *J* **= 2.4 Hz, 1H), 6.98 (d,** *J* **= 8.4 Hz, 1H), 6.05 (s, 2H), 2.71 (t,** *J* **= 8.0 Hz, 2H), 1.64 – 1.58 (m, 2H), 1.31 – 1.23 (m, 2H), 0.81 (t,** *J* **= 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): \delta 149.3, 144.4, 143.3, 142.9, 137.7, 133.3, 132.4, 131.8, 128.0 (2C), 127.9, 127.7, 127.6, 126.5, 126.1, 120.6, 109.0, 107.5, 101.0, 32.5, 30.0, 22.8, 13.8; HRMS (ESI) Calcd for C₂₃H₂₁O₂Te [M + H]⁺ 459.0604, found 459.0604.**



7-(2,6-Dimethylphenyl)-6-ethyltelluropheno[2',3':3,4]benzo[1,2-*d***][1,3]dioxole (3oj): Type II arylzinc reagent was used; Yellow gum (40% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): \delta 7.24 (d,** *J* **= 8.4 Hz, 1H), 7.17 – 7.21 (m, 1H), 7.12 (d,** *J* **= 7.6 Hz, 2H), 6.99 (d,** *J* **= 8.0 Hz, 1H), 6.07 (s, 2H), 2.41 (q,** *J* **= 7.6 Hz, 2H), 2.20 (s, 6H), 1.08 (t,** *J* **= 7.6 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): \delta 149.7, 143.8, 143.7, 142.9, 138.3, 136.7, 130.2, 127.7, 127.6, 120.1, 109.3, 107.1, 101.0, 23.7, 20.8, 13.6; HRMS (ESI) Calcd for C₁₉H₁₉O₂Te [M + H]⁺ 409.0447, found 409.0450.**



6-Butyl-7-(thiophen-2-yl)telluropheno[2',3':3,4]benzo[1,2-*d***][1,3]dioxole (3ok): Type II arylzinc reagent was used; Orange oil (38% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): \delta 7.34 (dd,** *J* **= 4.4, 2.0 Hz, 1H), 7.23 (d,** *J* **= 8.4 Hz, 1H), 7.06 – 7.05 (m, 2H), 6.98 (d,** *J* **= 8.4 Hz, 1H), 6.06 (s, 2H), 2.89 (t,** *J* **= 8.0 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.52 – 1.39 (m, 2H), 0.97 (t,** *J* **= 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): \delta 149.2, 144.6, 144.1, 143.3, 142.3, 127.5, 127.2, 125.9, 122.0, 120.7, 108.5, 107.6, 101.1, 32.3, 30.6, 23.0, 13.9; HRMS (ESI) Calcd for C₁₇H₁₇O₂STe [M + H]⁺ 415.0012, found 415.0005.**



6-Methoxy-3-methylbenzo[*b*]tellurophene (3al): Type I arylzinc reagent and 1-trimethylsilyl-1-propyne were used. The crude product was treated with KOH (3 equiv) in MeOH solution at 75 °C for 3 h to completely remove the silyl group; Light yellow solid (53% yield, eluent = hexane); m.p. = 57-58 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.99 (s, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.48 (s, 1H), 7.02 (d, *J* = 8.8 Hz, 1H), 3.87 (s, 3H), 2.37 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 157.1, 142.4, 141.3, 133.5, 126.7, 115.9, 113.6, 111.1, 55.6, 19.9; HRMS (ESI) Calcd for C₁₀H₁₁OTe [M + H]⁺ 276.9872, found 276.9870.



3-Methylbenzo[*b*]tellurophene (3bl): Type I arylzinc reagent and 1-trimethylsilyl-1-propyne were used. The crude product was treated with KOH (3 equiv) in MeOH solution at 75 °C for 3 h to completely remove the silyl group; Light yellow gum (52% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.23 (s, 1H), 7.97 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.39 (m, 1H), 7.26 – 7.12 (m, 1H), 2.41 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 147.3,

143.0, 132.5, 126.3, 125.0, 124.5, 114.7, 19.8 (one carbon missing due to overlap); HRMS (ESI) Calcd for $C_9H_9Te [M + H]^+ 246.9767$, found 246.9763.



3-Methyl-6-(trifluoromethyl)benzo[*b*]**tellurophene (3cl):** Type **II** arylzinc reagent and 1trimethylsilyl-1-propyne were used. The crude product was treated with KOH (3 equiv) in MeOH solution at 75 °C for 3 h to completely remove the silyl group; Orange oil (48% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.46 (s, 1H), 8.25 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 2.47 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.9, 142.5, 137.4, 132.7, 129.3 (q, ³*J*_{C-F} = 4.1 Hz), 126.3, 124.4 (q, ¹*J*_{C-F} = 270.6 Hz), 121.9 (d, ³*J*_{C-F} = 3.5 Hz), 119.1, 19.8; HRMS (ESI) Calcd for C₁₀H₈F₃Te [M + H]⁺ 314.9640, found 314.9639.

Benzotellurophene synthesis through Ni-catalyzed arylmagnesiation of alkyne

A 25 mL Schlenk tube equipped with a stirrer bar was charged with NiCl₂ (3.2 mg, 0.025 mmol) and diphenylacetylene (89 mg, 0.50 mmol). The Schlenk tube was evacuated and backfilled with N₂ for three times, followed by the addition of toluene (2 mL) and a THF solution of aryl Grignard reagent (0.6 mmol). The resulting mixture was stirred at 60 °C for 2 h and then allowed to cool to room temperature. ZnCl₂•TMEDA (151.6 mg, 0.6 mmol) was added, and the mixture was stirred at 80 °C for 1 h and then cooled to room temperature. To the Schlenk tube was added a THF solution (0.2 M) of TeCl₄ (269 mg, 1.0 mmol). The reaction mixture was stirred at 90 °C for 12 h, and then quenched by the addition of a saturated aqueous solution of Na₂S (1 mL) at 0 °C. The mixture was stirred at room temperature for 3 h, diluted with ethyl acetate (5 mL), and filtered through a pad of silica gel with additional ethyl acetate (15 mL) as the eluent. The filtrate was washed with water (10 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.



6-Methoxy-2,3-diphenylbenzo[*b*]**tellurophene (3am):** Light yellow solid (38% yield, eluent = hexane); m.p. = 150-151 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, *J* = 2.4 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.29 – 7.25 (m, 3H), 7.20 – 7.14 (m, 5H), 6.93 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.89 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 157.3, 143.7, 143.2, 139.8, 139.1, 134.7, 133.1, 130.8, 130.0, 129.4, 128.4, 128.1, 127.1, 126.7, 115.3, 113.9, 55.6; HRMS (ESI) Calcd for C₂₁H₁₇OTe [M + H]⁺ 415.0342, found 415.0345.



2,3-Diphenylbenzo[*b*]**tellurophene (3bm):** Yellow solid (56% yield, eluent = hexane); m.p. = 117-118 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.34 (m, 6H), 7.31 – 7.27 (m, 2H), 7.25 – 7.19 (m, 5H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.3, 144.4, 139.8, 138.9, 138.6, 132.2, 131.8, 130.9, 130.0, 128.9, 128.5, 128.2, 127.2, 127.0, 125.3, 124.9; HRMS (ESI) Calcd for C₂₀H₁₅Te [M + H]⁺ 385.0236, found 385.0242.



N,N-Dimethyl-2,3-diphenylbenzo[*b*]tellurophen-6-amine (3jm): Yellow solid (35% yield, eluent = hexane/EtOAc (30:1)); m.p. = 157-158 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.34 – 7.31 (m, 3H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.25 – 7.23 (m, 2H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.13 – 7.09 (m, 5H), 6.75 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.00 (s, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 148.5, 143.8, 104.2, 140.0, 139.4, 133.5, 131.5, 130.8, 130.0, 128.9, 128.3, 128.0, 126.9, 126.4, 114.3, 111.8, 40.7; HRMS (ESI) Calcd for C₂₂H₂₀NTe [M + H]⁺ 428.0658, found 428.0653.

Transformation of Benzotellurophenes 3al-3cl



2-(6-Methoxy-3-methylbenzo[b]tellurophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a): To a solution of 3al (54.8 mg, 0.20 mmol) in THF (1 mL) was added n-BuLi (1.6 M in hexane, 0.15 mL, 0.24 mmol) dropwise at 0 °C. The resulting mixture was stirred at 0 °C for 1 h, followed by the addition of trimethylborate (44.6 µL, 0.40 mmol). The reaction mixture was allowed to room temperature and stirred for 2 h. The reaction was quenched with 3M HCl solution, and then extracted with diethyl ether. The extracts were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. To the residue was added pinacol (47.2 mg, 0.40 mmol), molecular sieves 4Å (200 mg) and dry diethyl ether. The resulting mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with 5 mL of ethyl acetate and filtered through a pad of silica gel with additional ethyl acetate (15 mL) as the eluent. The filtrate was washed with water (10 mL), dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent = hexane) to afford the title compound as a yellow solid (37.7 mg, 47% yield); m.p. = 119-120 °C; ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3)$: $\delta 8.00 (d, J = 1.2 \text{ Hz}, 1\text{H}), 7.67 (d, J = 8.8 \text{ Hz}, 1\text{H}), 7.02 (d, J = 8.8 \text{ Hz}, 1\text{H}),$ 3.90 (s, 3H), 2.35 (s, 3H), 1.41 (s, 12H); ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃): δ 162.9, 143.1, 141.6, 141.3, 129.6, 115.0, 109.7, 84.3, 56.7, 25.1, 20.4 (The carbon bonded to the boron atom was not detected due to quadrupolar relaxation); HRMS (ESI) Calcd for $C_{16}H_{22}BO_{3}Te [M + H]^{+}$ 403.0724, found 403.0726.



4,4,5,5-Tetramethyl-2-(3-methylbenzo[*b*]**tellurophen-2-yl)-1,3,2-dioxaborolane (4b):** Yellow solid (50% yield, eluent = hexane); m.p. = 101-102 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 2.62 (s, 3H), 1.39 (s, 12H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 153.4, 150.2, 134.8, 132.4, 127.5, 125.4, 124.7, 84.0, 24.9, 19.2 (The carbon bonded to the boron atom was not detected due to

quadrupolar relaxation); HRMS (ESI) Calcd for $C_{15}H_{20}BO_2Te [M + H]^+$ 373.0619, found 373.0619.



4,4,5,5-Tetramethyl-2-(3-methyl-6-(trifluoromethyl)benzo[*b*]**tellurophen-2-yl)-1,3,2dioxaborolane (4c):** Yellow solid (41% yield, eluent = hexane); m.p. = 102-103 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.23 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 2.61 (s, 3H), 1.36 (s, 12H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 152.5, 152.4, 134.9, 129.2 (q, ³*J*_{C-F} = 4.1 Hz), 127.5, 126.8 (q, ²*J*_{C-F} = 31.9 Hz), 124.4 (d, ¹*J*_{C-F} = 268.7 Hz), 121.6 (d, ³*J*_{C-F} = 3.6 Hz), 84.3, 24.9, 19.2 (The carbon bonded to the boron atom was not detected due to quadrupolar relaxation); HRMS (ESI) Calcd for C₁₆H₁₉BO₂TeF₃ [M + H]⁺ 441.0492, found 441.0495.



1,1-Dibutyl-3-methyl-1H-benzo[b]stannole (5): To a solution of **3bl** (48.8 mg, 0.20 mmol) in hexane (1 mL) was added *n*-BuLi (1.6 M in hexane, 0.28 mL, 0.44 mmol) dropwise at room temperature. The resulting mixture was stirred for 3 h and then cooled to 0 °C. Dibutyltin dichloride (182 mg, 0.60 mmol) was added, and the reaction mixture was allowed to room temperature and stirred for 12 h. The reaction was quenched with saturated NH₄Cl solution, and then extracted with ethyl acetate. The extracts were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent = hexane) to afford the title compound as a yellow oil (35.1 mg, 60% yield); ¹H NMR (400 MHz, CDCl₃): δ 8.23 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.24 – 7.20 (m, 1H), 2.41 (s, 3H), 1.52 – 1.44 (m, 4H), 1.36 – 1.27 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 6H), 0.84 – 0.80 (m, 4H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 147.3, 143.0, 132.4, 128.8, 126.2, 124.9, 124.5, 114.6, 29.3, 27.4, 19.8, 13.7, 8.8; ¹¹⁹Sn{¹H} NMR (149 MHz, CDCl₃) δ -11.6; HRMS (ESI) Calcd for C₁₂H₂₇Sn [M + H]⁺ 291.1135, found 291.1143.





Figure S3. UV-vis spectrum of 4c in THF. $[4c] = 600 \mu M$.



Figure S4. Fluorescence (excited at 375 nm) spectrum of 4c in THF/water (10:90). $[4c] = 600 \mu$ M.

Measurement of photoluminescence lifetime of 4c

The time-resolved fluorescence lifetime of compound **4c** in THF/water (10/90) solution ($c = 600 \mu$ M) was measured using a time-correlated single photon counting (TCSPC) spectrofluorometer (FluoroCube, Horiba Jobin Yvon). The samples were excited at 375 nm using a pulsed diode laser (NanoLED-375L, Horiba Jobin Yvon) and the photons emitted at 525 (± 16) nm were collected to construct the fluorescence decay profile. The fluorescence decay profile was analyzed using the Horiba Jobin Yvon Datastation software and the goodness of fit was assessed by considering the reduced chi-square values and the randomness of the weighted residuals. The measurement was performed at ambient conditions. Three-exponential decay function was used to fit the lifetime decay curve and three components are 0.18 ns (39.96%), 0.88 ns (45.09%), and 3.68 ns (14.95%), respectively.



Figure S5. Time-resolved photoluminescence of 4c in THF/water (10:90). $[4c] = 600 \mu M$.

Synthesis of Tellurium-Bridged Heterobiaryls

Preparation of 2-iodoheterobiaryls



General procedure for the preparation of 2-aminoheterobiaryls: A 50 mL three-necked flask was charged with 2-bromoaniline (0.86 g, 5.0 mmol), heteroarylboronic acid (7.5 mmol), aqueous solution of K_2CO_3 (2 M, 5 mL), and DME (20 mL) under a gentle stream of nitrogen. The resulting mixture was stirred for 30 min at room temperature, followed by the addition of $PdCl_2(PPh_3)_2$ (109 mg, 0.25 mmol). The reaction mixture was stirred at 80 °C for 12 h, cooled to room temperature, and diluted with EtOAc. The organic layer was washed with water, dried over MgSO₄, and concentrated under reduced pressure. The residue was subjected to flash chromatography on silica gel to afford the desired 2-aminoheterobiaryl.

General procedure for the preparation of 2-iodoheterobiaryls: To a solution of *p*-TsOH (1.15 g, 6.0 mmol) in MeCN (15 mL) was added 2-aminoheterobiaryl (2.0 mmol). The resulting suspension was cooled to 10-15 °C, followed by the slow addition of a solution of NaNO₂ (272 mg, 4.0 mmol) and KI (830 mg, 5.0 mmol) in H₂O (5 mL). The mixture was stirred for 10 min, allowed to room temperature for 4 h. An aqueous solution of NaHCO₃ was added until the pH of the mixture reached 9, and then Na₂S₂O₃ was added until complete reduction of the residual iodine. The crude mixture was extracted with EtOAc, and the extracts were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired 2-iodoheterobiaryl.



2-([2,2'-Bithiophen]-5-yl)aniline: Yellow gum (54% yield, eluent = hexane/EtOAc (10:1)); ¹H NMR (400 MHz, CDCl₃): δ 7.30 (dd, J = 7.6, 1.2 Hz, 1H), 7.23 (dd, J = 5.2, 0.8 Hz, 1H), 7.20 – 7.17 (m, 2H), 7.15 (dd, J = 7.6, 1.2 Hz, 1H), 7.12 (d, J = 3.6 Hz, 1H), 7.03 (dd, J = 4.8, 3.6 Hz, 1H), 6.83 – 6.77 (m, 2H), 4.05 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.1, 140.1, 137.3,

137.1, 130.7, 129.2, 127.9, 126.5, 124.4, 124.1, 123.7, 119.7, 118.7, 116.0; HRMS (ESI) Calcd for $C_{14}H_{12}NS_2 [M + H]^+$ 258.0411, found 258.0417.



5-(2-IodophenyI)-2,2'-bithiophene: Colourless oil (63% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 7.98 (dd, J = 8.0, 1.2 Hz, 1H), 7.46 (dd, J = 8.0, 1.6 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.24 – 7.22 (m, 2H), 7.18 (d, J = 3.6 Hz, 1H), 7.12 (d, J = 3.6 Hz, 1H), 7.06 – 7.01 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.7, 140.3, 139.0, 138.1, 137.3, 131.3, 129.5, 128.6, 128.3, 128.0, 124.6, 123.9, 123.6, 99.2; HRMS (ESI) Calcd for C₁₄H₁₀S₂I [M + H]⁺ 368.9269, found 368.9266.



2-(4-Methylthiophen-3-yl)aniline: Yellow oil (69% yield, eluent = hexane/EtOAc (15:1)); ¹H NMR (400 MHz, CDCl₃): δ 7.28 – 7.23 (m, 2H), 7.15 – 7.13 (m, 2H), 6.90 – 6.81 (m, 1H), 6.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.63 (s, 2H), 2.22 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.7, 140.1, 137.6, 130.8, 128.8, 123.8, 122.6, 121.9, 118.1, 115.2, 14.8; HRMS (ESI) Calcd for C₁₁H₁₂NS [M + H]⁺ 190.0690, found 190.0693.



3-(2-Iodophenyl)-4-methylthiophene: Colourless oil (65% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 7.34 (d, *J* = 6.4 Hz, 1H), 6.91 – 6.88 (m, 1H), 6.81 – 6.78 (m, 1H), 6.68 – 6.61 (m, 3H), 2.64 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 145.5, 142.5, 139.0, 136.7, 130.5, 129.1, 128.0, 123.8, 121.2, 100.7, 15.1; HRMS (ESI) Calcd for C₁₁H₁₀SI [M + H]⁺ 300.9548, found 300.9548.



2-(Furan-3-yl)aniline: Light yellow oil (65% yield, eluent = hexane/EtOAc (15:1)); ¹H NMR (400 MHz, CDCl₃): δ 7.73 (s, 1H), 7.59 (t, *J* = 1.6 Hz, 1H), 7.28 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.22 – 7.18 (m, 1H), 6.90 – 6.86 (m, 1H), 6.81 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.71 – 6.70 (m, 1H), 3.90 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.1, 143.3, 139.8, 129.8, 128.4, 123.5, 118.8, 118.4, 115.8, 110.9; HRMS (ESI) Calcd for C₁₀H₁₀NO [M + H]⁺ 160.0762, found 160.0762.



3-(2-Iodophenyl)furan: Colorless oil (48% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, *J* = 7.6 Hz, 1H), 7.73 (s, 1H), 7.50 (t, *J* = 1.6 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.03 – 6.99 (m, 1H), 6.67 – 6.66 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 142.4, 140.5, 140.0, 137.9, 130.4, 128.8, 128.2, 128.1, 111.9, 98.5; HRMS (ESI) Calcd for C₁₀H₈OI [M + H]⁺ 270.9620, found 270.9625.



2-(Benzo[*b***]thiophen-2-yl)aniline:** Pale yellow solid (85% yield, eluent = hexane/EtOAc (10:1)); m.p. = 129-130 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.87 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.44 (s, 1H), 7.42 – 7.34 (m, 3H), 7.23 – 7.19 (m, 1H), 6.87 – 6.80 (m, 2H), 4.12 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.3, 141.6, 140.4, 139.8, 131.2, 129.6, 124.5, 124.3, 123.5, 122.5, 122.2, 119.8, 118.6, 116.1; HRMS (ESI) Calcd for C₁₄H₁₂NS [M + H]⁺ 226.0690, found 226.0689.



2-(2-Iodophenyl)benzo[*b***]thiophene:** Yellow solid (76% yield, eluent = hexane); m.p. = 43-44 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.03 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.54 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.46 – 7.39 (m, 4H), 7.12 – 7.08 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 145.2, 140.3, 140.1, 139.8, 139.5, 131.5, 129.9, 128.2, 124.6, 124.4, 124.0, 122.3, 99.2 (one carbon missing due to overlap); HRMS (ESI) Calcd for C₁₄H₁₀SI [M + H]⁺ 336.9548, found 336.9563.



2-(Benzo[*b***]thiophen-3-yl)aniline:** Orange gum (89% yield, eluent = hexane/EtOAc (10:1)); ¹H NMR (400 MHz, CDCl₃): δ 8.02 – 8.00 (m, 1H), 7.74 – 7.72 (m, 1H), 7.50 (s, 1H), 7.49 – 7.42 (m, 2H), 7.34 – 7.30 (m, 2H), 6.97 – 6.93 (m, 1H), 6.90 – 6.87 (m, 1H), 3.73 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.8, 140.4, 138.3, 135.0, 131.2, 129.2, 124.8, 124.7, 124.4, 123.5, 122.9, 121.0, 118.4, 115.6; HRMS (ESI) Calcd for C₁₄H₁₂NS [M + H]⁺ 226.0690, found 226.0690.



3-(2-Iodophenyl)benzo[*b*]**thiophene:** Pale yellow oil (73% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.15 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.15 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.62 (dd, *J* = 6.8, 2.0 Hz, 1H), 7.56 – 7.46 (m, 5H), 7.24 – 7.20 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 141.0, 139.9, 139.8, 139.7, 138.4, 131.3, 129.7, 128.3, 125.4, 124.7, 124.5, 123.5, 122.9, 100.4; HRMS (ESI) Calcd for C₁₄H₁₀SI [M + H]⁺ 336.9548, found 336.9543.



2-(Benzofuran-2-yl)aniline: Orange solid (64% yield, eluent = hexane/EtOAc (15:1)); m.p. =

67-68 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.68 (dd, J = 8.0, 1.2 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.25 – 7.21 (m, 1H), 6.98 (d, J = 0.8 Hz, 1H), 6.91 – 6.86 (m, 1H), 6.82 (d, J = 8.0 Hz, 1H), 4.52 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 155.7, 154.3, 144.2, 129.9, 128.9, 128.6, 124.0, 123.0, 120.7, 118.5, 116.9, 115.5, 111.0, 103.0; HRMS (ESI) Calcd for C₁₄H₁₂NO [M + H]⁺ 210.0919, found 201.0923.



2-(2-Iodophenyl)benzofuran: Orange oil (81% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.11 (dd, J = 8.0, 1.2 Hz, 1H), 7.89 (dd, J = 8.0, 1.6 Hz, 1H), 7.77 (dd, J = 7.6, 0.8 Hz, 1H), 7.68 (dd, J = 7.6, 0.8 Hz, 1H), 7.53 – 7.52 (m, 1H), 7.51 – 7.38 (m, 3H), 7.14 – 7.09 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 155.7, 154.7, 141.1, 135.2, 130.3, 130.0, 128.7, 128.3, 124.9, 123.2, 121.6, 111.4, 106.4, 95.5; HRMS (ESI) Calcd for C₁₄H₁₀OI [M + H]⁺ 320.9776, found 320.9783.



2-Iodobenzo[*b*]selenophene: A 50 mL three-necked flask equipped with a stirrer bar was charged with benzo[*b*]selenophen-2-yltrimethylsilane¹⁵ (1.27 g, 5.0 mmol) and purged with nitrogen. Dry CH₂Cl₂ (20 mL) was added, and the resulting suspension was cooled to -30 °C. To the suspension was added iodine monochloride in CH₂Cl₂ solution (1M, 5.0 mL) via syringe. The mixture was stirred at -30 °C for 1 h and then warmed up to room temperature for further 12 h. Saturated Na₂S₂O₃ solution was added until the color did not change. The mixture was extracted with CH₂Cl₂ and the organic phase was washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was subjected to flash chromatography on silica gel (eluent = hexane) to afford the title compound as a light yellow

solid (1.32 g, 86%). m.p. = 70-71 °C; ¹H NMR (400 MHz, acetone- d_6): δ 8.00 (dd, J = 8.0, 0.8 Hz, 1H), 7.96 (s, 1H), 7.82 (dd, J = 8.0, 0.8 Hz, 1H), 7.36 – 7.27 (m, 2H); ¹³C{¹H} NMR (100 MHz, acetone- d_6): δ 146.5, 143.5, 138.4, 125.0, 124.9, 124.8, 124.2, 77.3; HRMS (ESI) Calcd for C₈H₆ISe [M + H]⁺ 308.8679, found 308.8678.

2-(Benzo[b]selenophen-2-yl)aniline: A mixture of 2-iodobenzo[*b*]selenophene (0.92 g, 3.0 mmol), 2-aminophenylboronic acid pinacol ester (0.99 g, 4.5 mmol), (2-biphenyl)-dicyclohexylphosphine (CyJohnPhos, 210.3 mg, 0.60 mmol), Pd(OAc)₂ (67.4 mg, 0.30 mmol), K₂CO₃ (1.24 g, 9.0 mmol), MeCN (15 mL) and H₂O (10 mL) was heated at 80 °C for 12 h. The mixture was diluted with water, and the aqueous layer was separated and then extracted with EtOAc. The combined organic extracts were washed with brine, dried over MgSO₄, and evaporated under reduced pressure. The residue was subjected to flash chromatography on silica gel (eluent = hexane/EtOAc (15:1)) to afford the title compound as a yellow solid (0.42 g, 52%). m.p. = 124-125 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.57 (s, 1H), 7.41 – 7.33 (m, 2H), 7.30 – 7.28 (m, 1H), 7.21 – 7.17 (m, 1H), 6.85 – 6.78 (m, 2H), 4.11 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.7, 143.9, 142.8, 141.8, 131.2, 129.5, 126.3, 125.4, 125.3, 124.8, 124.4, 121.9, 118.6, 116.0; HRMS (ESI) Calcd for C₁₄H₁₂NSe [M + H]⁺ 274.0135, found 274.0131.

2-(2-Iodophenyl)benzo[*b*]**selenophene:** The title compound was obtained by using a similar procedure as described above. Colorless oil (73% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.00 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.43 – 7.38 (m, 2H), 7.33 – 7.29 (m, 1H), 7.09 – 7.04 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 148.7, 142.5, 142.1, 141.4, 140.0, 131.2, 129.7, 128.1, 128.0, 125.8, 125.4, 124.8, 124.7, 99.0; HRMS (ESI) Calcd for C₁₄H₁₀SeI [M + H]⁺ 384.8992, found 384.9000.



2-(8-Iodonaphthalen-1-yl)thiophene: To a 25 mL three-necked bottom flask, equipped with a magnetic stir bar, 1,8-diiodonaphthalene (417.9 mg, 1.1 mmol), thiophen-2-ylboronic acid (128 mg, 1 mmol), K_2CO_3 (828 mg, 6.0 mmol), and Pd(PPh_3)₄ (115.5 mg, 0.1 mmol) were dissolved in 8 mL of THF followed by the addition of 3 mL of H₂O and 3 mL of EtOH. The resulting

mixture was refluxed for 12 h. After cooling to room temperature, the biphasic solution was diluted with 10 mL of saturated aqueous NH₄Cl and 15 mL of EtOAc. The aqueous phase was extracted with EtOAc, and the combined organic layers were washed with water and brine. The organic phase was dried over MgSO₄ and filtered. The filtrate was concentrated in vacuo and purified by column chromatography (eluent = hexane) to afford the desired product as a yellow gum (100.1 mg, 30%). ¹H NMR (400 MHz, CDCl₃): δ 8.27 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.92 – 7.88 (m, 2H), 7.66 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.15 – 7.10 (m, 2H), 7.03 (dd, *J* = 3.6, 1.2 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 142.8, 141.4, 135.4, 133.3, 132.5, 132.2, 130.9, 130.3, 129.8, 127.0, 126.7, 126.3, 124.9, 91.6; HRMS (ESI) Calcd for C₁₄H₉IS [M + H]⁺ 336.9548, found 336.9536.



1-(8-Iodonaphthalen-1-yl)-3-methyl-1*H***-indole:** The reaction was performed according to the literature procedure.¹² A mixture of 3-methyl-1*H*-indole (288.4 mg, 2.2 mmol), 1,8-diiodonaphthalene (759.9 mg, 2.0 mmol), CuI (38.0 mg, 0.20 mmol), benzotriazole (47.6 mg, 0.40 mmol), K₃PO₄ (849.1 mg, 4.0 mmol) and DMSO (8 mL) was heated at 120 °C for 30 h. The reaction mixture was washed with ethyl acetate and water. The organic layer was then washed with brine and dried over MgSO₄ and evaporated under reduced pressure. The residue was subjected to flash chromatography on silica gel (eluent = hexane/EtOAc (20:1)) to afford the title compound as a yellow solid (306.4 mg, 40%). m.p. = 92-93 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.30 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.30 – 7.19 (m, 3H), 7.05 (s, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 2.58 (s, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 142.9, 140.6, 136.5, 136.0, 130.3, 130.2, 129.8, 129.4, 129.3, 128.8, 127.2, 125.9, 122.3, 119.5, 118.9, 112.9, 111.0, 87.2, 9.9; HRMS (ESI) Calcd for C₁₉H₁₅NI [M + H]⁺ 384.0249, found 384.0251.

General procedure for tellurative cyclization: An oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with 2-iodoheterobiaryl (0.3 mmol). *i*-PrMgBr or *i*-PrMgCl·LiCl in THF (0.36 mmol, 1.2 equiv) was slowly added at 0 °C, and the resulting mixture

was stirred at 0 °C for 2 h. ZnCl₂•TMEDA (91.0 mg, 0.36 mmol) was added, and the mixture was stirred further for 30 min. The resulting organozinc solution was added to a solution of TeCl₄ (161 mg, 0.60 mmol) in THF (4 mL) via syringe, and the reaction mixture was stirred at 90 °C for 12 h. The mixture was diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel with additional ethyl acetate (15 mL) as the eluent. The filtrate was washed with water (10 mL), dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.



Benzo[4,5]telluropheno[3,2-*b***]thiophene (6):** *i*-PrMgBr was used; Yellow solid (66% yield, eluent = hexane); m.p. = 70-71 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.86 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.34 – 7.32 (m, 1H), 7.18 – 7.14 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.7, 139.4, 133.1, 131.1, 128.3, 126.0, 125.8, 124.8, 124.4, 120.3; HRMS (ESI) Calcd for C₁₀H₇STe [M + H]⁺ 288.9331, found 288.9328.



2-(Thiophen-2-yl)benzo[4,5]telluropheno[3,2-*b***]thiophene (7):** *i***-PrMgBr was used; Yellow solid (47% yield, eluent = hexane); m.p. = 97-98 °C; ¹H NMR (400 MHz, CDCl₃): \delta 7.90 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.28 – 7.26 (m, 2H), 7.17 – 7.13 (m, 1H), 7.07 – 7.05 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): \delta 142.2, 139.4, 138.0, 137.1, 133.0, 131.1, 128.0, 126.1, 124.9, 124.8, 124.6, 124.2, 124.1, 121.2; HRMS (ESI) Calcd for C₁₄H₉S₂Te [M + H]⁺ 370.9208, found 370.9202.**



3-Methylbenzo[4,5]telluropheno[2,3-*b***]thiophene (8):** *i*-PrMgBr was used; Yellow solid (51% yield, eluent = hexane); m.p. = 72-73 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.16 (d, J = 8.0 Hz,

1H), 7.89 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.14 (s, 1H), 2.71 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 148.3, 140.9, 135.4, 133.2, 132.8, 127.6, 125.6, 124.9, 124.2, 117.8, 16.9; HRMS (ESI) Calcd for C₁₁H₉STe [M + H]⁺ 302.9487, found 302.9487.



Benzo[4,5]telluropheno[2,3-*b*]furan (9): *i*-PrMgCl·LiCl was used; Yellow oil (47% yield, eluent = hexane); ¹H NMR (400 MHz, CDCl₃): δ 7.83 – 7.77 (m, 2H), 7.77 (d, J = 2.0 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.12 – 7.08 (m, 1H), 6.96 (d, J = 2.0 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 150.2, 136.2, 135.6 (2C), 132.9, 131.6, 126.2, 124.4, 124.2, 107.5; HRMS (ESI) Calcd for C₁₀H₇OTe [M + H]⁺ 272.9559, found 272.9564.



Benzo[*b*]**benzo**[4,5]**telluropheno**[2,3-*d*]**thiophene (10):** *i*-PrMgCl·LiCl was used; Pale yellow solid (54% yield, eluent = hexane); m.p. = 158-159 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.94 – 7.89 (m, 2H), 7.69 – 7.67 (m, 1H), 7.48 – 7.38 (m, 3H), 7.23 – 7.19 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 141.9, 140.2, 139.9, 139.7, 133.1, 130.9, 130.8, 126.1, 125.3, 125.2, 125.0, 124.9, 123.5, 123.4; HRMS (ESI) Calcd for C₁₄H₉STe [M + H]⁺ 338.9487, found 338.9482. Recrystallization from EtOAc/hexane afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of the compound (Figure S6 and S7).¹⁴



Figure S6. ORTEP drawing of **10** with thermal ellipsoids presented at 50% probability (grey = carbon, yellow = sulfur, orange = tellurium). Hydrogen atoms are omitted for clarity.



Figure S7. Packing diagram of **10** illustrating a sandwiched herringbone structure. The shortest Te-Te distance is 6.796 Å.



Benzo[*b*]**benzo**[4,5]**telluropheno**[3,2-*d*]**thiophene (11):** *i*-PrMgCl·LiCl was used; Pale yellow solid (52% yield, eluent = hexane); m.p. = 171-172 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.54 (dd, J = 8.0, 0.8 Hz, 1H), 8.50 (d, J = 8.0 Hz, 1H), 7.95 – 7.92 (m, 2H), 7.55 – 7.48 (m, 2H), 7.39 –

7.35 (m, 1H), 7.25 – 7.21 (m, 1H); ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃): δ 146.3, 142.7, 140.9, 136.4, 133.5, 132.8, 126.0, 124.8, 124.4, 123.8, 123.4, 122.6, 120.9 (one carbon missing due to overlap); HRMS (ESI) Calcd for C₁₄H₉STe [M + H]⁺ 338.9487, found 338.9491. Recrystallization from EtOAc/hexane afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of the compound (Figure S8 and S9).¹⁴



Figure S8. ORTEP drawing of **11** with thermal ellipsoids presented at 50% probability (grey = carbon, yellow = sulfur, orange = tellurium). Hydrogen atoms are omitted for clarity.



Figure S9. Packing diagram of **11** illustrating a π -stacked herringbone structure. The shortest Te-Te distance is 3.709 Å.



Benzo[4,5]telluropheno[3,2-*b***]benzofuran (12):** *i*-PrMgCl·LiCl was used; Light yellow solid (53% yield, eluent = hexane); m.p. = 105-106 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.05 (dd, *J* =
8.0, 0.8 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.60 (dd, J = 8.0, 0.8 Hz, 1H), 7.50 - 7.46 (m, 1H), 7.40 - 7.32 (m, 2H), 7.24 - 7.20 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 158.8, 156.5, 133.1, 131.4, 130.1, 129.1, 126.1, 125.6, 124.9, 123.7, 123.3, 120.7, 112.1, 99.7; HRMS (ESI) Calcd for C₁₄H₉OTe [M + H]⁺ 322.9716, found 322.9712.



10-Methyl-10*H***-benzo[4,5]telluropheno[3,2-***b***]indole (13):** *i***-PrMgCl·LiCl was used; Brown solid (54% yield, eluent = hexane/EtOAc (20:1)); m.p. = 174-175 °C; ¹H NMR (400 MHz, CDCl₃): \delta 8.20 (dd, J = 8.0, 0.4 Hz, 1H), 7.99 (dd, J = 7.6, 0.4 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.38 – 7.33 (m, 1H), 7.22 – 7.14 (m, 2H), 4.26 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): \delta 144.0, 140.9, 134.7, 134.1, 130.7, 128.6, 125.6, 124.3, 123.8, 123.0, 120.6, 119.7, 109.6, 96.5, 32.2; HRMS (ESI) Calcd for C₁₅H₁₂NTe [M + H]⁺ 336.0032, found 336.0037.**



Benzo[*b*]**benzo**[4,5]**telluropheno**[2,3-*d*]**selenophene (14):** *i*-PrMgCl·LiCl was used; Yellow solid (50% yield, eluent = hexane); m.p. = 139-140 °C; ¹H NMR (400 MHz, THF-*d*₈): δ 8.07 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.28 (t, J = 7.2 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H); ¹³C{¹H} NMR (100 MHz, THF-*d*₈): δ 143.6, 141.4, 140.9, 133.8, 131.6, 127.1, 126.6, 126.3, 125.9, 125.8, 125.6, 125.5, 124.4 (one carbon missing due to overlap); HRMS (ESI) Calcd for C₁₄H₉SeTe [M + H]⁺ 386.8932, found 386.8931.



Benzo[*b*]**naphtho**[2,1-*d*]**tellurophene (15):** *i*-PrMgBr was used; Pale yellow solid (67% yield, eluent = hexane); m.p. = 194-195 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.18 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.94 – 7.89 (m, 2H), 7.63 – 7.61 (m, 1H), 7.56

-7.49 (m, 3H), 7.34 - 7.30 (m, 1H); ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃): δ 145.4, 142.0, 135.7, 132.6, 132.5, 132.2, 129.5, 129.1, 128.9, 127.0, 126.9, 126.6, 126.5, 125.8, 125.1, 122.6; HRMS (ESI) Calcd for C₁₆H₁₁Te [M + H]⁺ 332.9923, found 332.9929.



11-Methylbenzo[**4**,**5**][**1**,**3**]**tellurazolo**[**3**,**2**-*a*]**indole** (**16**): *i*-PrMgCl·LiCl was used; Yellow solid (55% yield, eluent = hexane/EtOAc (30:1)); m.p. = 80-81 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.09 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.66 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.55 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.30 – 7.22 (m, 2H), 7.11 – 7.06 (m, 1H), 2.40 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 142.0, 136.1, 133.6, 132.3, 127.7, 122.8, 120.8, 120.6, 117.3, 115.1, 114.2, 113.0, 111.3, 111.1, 11.8; HRMS (ESI) Calcd for C₁₅H₁₂NTe [M + H]⁺ 336.0032, found 336.0033.



Benzo[4,5]tellurochromeno[3,2-*b***]thiophene (17):** *i*-PrMgCl·LiCl was used; Pale yellow solid (62% yield, eluent = hexane); m.p. = 74-75 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.72 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.59 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.51 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.42 (d, *J* = 5.2 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.14 (dd, *J* = 8.0, 7.2 Hz, 1H), 6.96 (d, *J* = 5.2 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 136.1, 132.2, 131.3, 130.7, 129.3, 129.0, 127.8, 127.5, 126.5, 126.2, 126.1, 123.1, 110.6, 101.1; HRMS (ESI) Calcd for C₁₄H₉STe [M + H]⁺ 338.9487, found 338.9483.



8-Methylnaphtho[1',8':4,5,6][1,3]tellurazino[3,2-a]indole (18): i-PrMgCl·LiCl was used;

Yellow solid (58% yield, eluent = hexane/EtOAc (30:1)); m.p. = 175-176 °C; ¹H NMR (400 MHz, THF- d_8): δ 8.09 (dd, J = 8.0, 0.8 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.73 – 7.66 (m, 3H), 7.58 (t, J = 8.0 Hz, 1H), 7.47 (dd, J = 7.6, 0.8 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.13 – 7.03 (m, 2H), 2.29 (s, 3H); ¹³C{¹H} NMR (100 MHz, THF- d_8): δ 139.8, 137.6, 136.6, 132.5, 131.8, 129.0, 128.1, 127.1, 126.4, 126.2, 125.9, 121.8, 121.4, 119.2, 118.3, 118.0, 112.1, 104.9, 11.4; HRMS (ESI) Calcd for C₁₉H₁₄NTe [M + H]⁺ 386.0189, found 386.0195.



2-Bromobenzo[**4**,**5**]**telluropheno**[**3**,**2**-*b*]**thiophene (19):** A solution of bromine (0.17 mL, 3.3 mmol) in dichloromethane (5 mL) was added dropwise to a vigorously stirred solution of **6** (0.86 g, 3.0 mmol) in dichloromethane (20 mL) at 0 °C. The resulting mixture was stirred at room temperature for 12 h, followed by quenching of excess bromine with saturated aqueous solution of Na₂S₂O₃. The mixture was extracted with dichloromethane, and the combined organic extracts were washed with brine and dried over anhydrous MgSO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane as eluent to afford **19** as a white solid (0.79 g, 72%). m.p. = 126-127 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.87 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.73 (d, *J* = 8.0, 0.8 Hz, 1H), 7.38 (td, *J* = 8.0, 0.8 Hz, 1H), 7.25 (s, 1H), 7.15 (td, *J* = 8.0, 0.8 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.4, 139.7, 133.0, 130.9, 130.8, 126.2, 125.0, 124.3, 119.6, 111.6; HRMS (ESI) Calcd for C₁₀H₆BrSTe [M + H]⁺ 366.8416, found 366.8407.

2-(Benzo[4,5]telluropheno[3,2-b]thiophen-2-yl)aniline (20): A 50 mL three-necked flask was

charged with **19** (1.09 g, 3.0 mmol), 2-aminophenylboronic acid pinacol ester (0.99 g, 4.5 mmol), aqueous solution of K₂CO₃ (2 M, 3 mL), and DME (12 mL) under a gentle stream of nitrogen. The resulting mixture was stirred for 30 min at room temperature, followed by the addition of PdCl₂(PPh₃)₂ (65 mg, 0.15 mmol). The reaction mixture was stirred at 80 °C for 12 h, cooled to room temperature, and diluted with EtOAc. The organic layer was washed with water, dried over MgSO₄, and concentrated under reduced pressure. The residue was subjected to flash chromatography on silica gel (eluent = hexane/EtOAc (20:1)) to afford **20** as a yellow gum (0.66 g, 58%). ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.24 – 7.18 (m, 2H), 6.88 – 6.82 (m, 2H), 4.12 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.2, 143.3, 142.0, 139.6, 133.0, 130.9, 129.5, 126.9, 126.1, 124.8, 124.4, 121.0, 119.6, 118.7, 116.1, 115.1; HRMS (ESI) Calcd for C₁₆H₁₂NSTe [M + H]⁺ 379.9753, found 379.9750.

2-(2-Iodophenyl)benzo[4,5]telluropheno[3,2-*b***]thiophene (21): To a solution of** *p***-TsOH (1.15 g, 6.0 mmol) in MeCN (15 mL) was added 20** (0.75 g, 2.0 mmol). The resulting suspension was cooled to 10-15 °C, followed by the slow addition of a solution of NaNO₂ (272 mg, 4.0 mmol) and KI (830 mg, 5.0 mmol) in H₂O (5 mL). The mixture was stirred for 10 min, allowed to room temperature for 4 h. An aqueous solution of NaHCO₃ was added until the pH of the mixture reached 9, and then Na₂S₂O₃ was added until complete reduction of the residual iodine. The crude mixture was extracted with EtOAc, and the extracts were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent = hexane) to afford **21** as a yellow solid (0.51 g, 52%). m.p. = 102-103 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.00 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.92 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.86 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.51 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.43 – 7.38 (m, 3H), 7.19 – 7.15 (m, 1H), 7.09 – 7.05 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 145.3, 144.1, 140.2, 139.5, 139.0, 133.0, 131.4, 131.1, 129.7, 128.8, 128.2, 126.1, 124.9, 124.4, 120.2, 99.3; HRMS (ESI) Calcd for C₁₆H₁₀STeI [M + H]⁺ 490.8610, found 490.8605.

Benzo[4,5]telluropheno[3,2-*b*]benzo[4,5]telluropheno[2,3-*d*]thiophene (22): An oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with 21 (146 mg, 0.30 mmol). BuLi (0.23 mL, 0.36 mmol, 1.6 M in hexane) was slowly added at -78 °C, and the resulting mixture was stirred for 30 min. ZnCl₂•TMEDA (91.0 mg, 0.36 mmol) was added at 0 °C and the mixture was stirred further for 30 min. The organozinc solution was added to a solution of TeCl₄

(161 mg, 0.60 mmol) in THF (4 mL) via syringe. The reaction mixture was stirred at 90 °C for 12 h, and then diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel with additional ethyl acetate (15 mL) as the eluent. The filtrate was washed with water (10 mL), dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **22** as a yellow solid (46.8 mg, 32%). m.p. > 300 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H); ¹³C NMR could not be measured due to the poor solubility of the compound in any solvent; HRMS (ESI) Calcd for C₁₆H₉STe₂ [M + H]⁺ 492.8550, found 492.8539.

UV-vis Spectra of Compounds 10–15 and 17



Figure S10. UV-vis absorption spectrum of 10 in MeOH (1.0×10^{-5} M).



Figure S11. UV-vis absorption spectrum of 11 in MeOH (1.0×10^{-5} M).



Figure S12. UV-vis absorption spectrum of 12 in MeOH (1.0×10^{-5} M).



Figure S13. UV-vis absorption spectrum of 13 in MeOH (1.0×10^{-5} M).



Figure S14. UV-vis absorption spectrum of 14 in MeOH (1.0×10^{-5} M).



Figure S15. UV-vis absorption spectrum of 15 in MeOH (1.0×10^{-5} M).



Figure S16. UV-vis absorption spectrum of 17 in MeOH (1.0×10^{-5} M).

DFT Calculations

DFT calculations were performed using Gaussian 09 program suite.¹⁶ Geometry optimization was performed employing the B3LYP functional and using the SDD effective core potential basis set for Te and Se¹⁷ and the 6-311G* basis set for the remaining atoms.¹⁸ TD-DFT calculations were performed for the optimized structures at the same level.



Figure S17. Energy diagrams and contour plots of Kohn–Sham molecular orbitals for the optimized structures of the compounds **10** and **12–14**, which feature the same type of molecular framework.



Figure S18. Energy diagrams and contour plots of Kohn–Sham molecular orbitals for the optimized structures of the compounds **11**, **15**, and **17**.

cmpd	transition energy	wavelength	major contributions	oscillator
	(eV)	(nm)	(coefficient)	strength
10	3.6491	339.76	HOMO→LUMO (0.66837)	0.0922
			HOMO–1→LUMO (0.18697)	
11	4.0812	303.79	HOMO→LUMO+1 (0.63970)	0.1116
			HOMO−1→LUMO+1 (-0.20793)	
			HOMO–1→LUMO+4 (–0.13646)	
12	3.7948	326.72	HOMO→LUMO (0.65423)	0.1493
			HOMO–1→LUMO (0.22494)	
			HOMO–1→LUMO+2 (0.10037)	
13	3.5596	348.31	HOMO→LUMO (0.67751)	0.1011
			HOMO–1→LUMO (0.15039)	
14	3.5853	345.82	HOMO→LUMO (0.67137)	0.0902
			HOMO–1→LUMO (0.18031)	
15	3.5772	346.60	HOMO→LUMO (0.66900)	0.0575
			HOMO–1→LUMO (0.15175)	
17	2.9811	401.10	HOMO→LUMO (0.69050)	0.1492

Table S1. Lowest transition energies of the compounds 10–15 and 17 calculated at the B3LYP/6-311G* level.

XYZ coordinates of optimized structures

==	===10===				
С	0.016450	1.024637	-0.000002		
С	-0.580049	-0.209814	-0.000021		
С	-2.013241	-0.174857	-0.000036		
С	-2.486631	1.161790	0.000005		
S	-1.167576	2.331024	0.000017		
С	1.455938	1.135766	0.000004		
С	2.201713	2.326151	0.000014		
С	2.149957	-0.099101	-0.000001		
С	3.587796	2.283141	0.000019		
Н	1.688137	3.282757	0.000017		
С	3.541808	-0.137522	0.000004		
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NMR Spectra





















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