Electronic Supplementary Material (ESI) for New Journal of Chemistry.

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1. General remarks

1.1. Instrumentation

Thin layer chromatography (TLC) was conducted on pre-coated aluminum sheets with 0.20 mm *Merk Millipore* Silica gel 60 with fluorescent indicator F254. *Column chromatography* was carried out using *Merck Gerduran* silica gel 60 (particle size 40-63 μm). ***Melting points*** (mp) were measured on a *Gallenkamp* apparatus in open capillary tubes and have not been corrected. ***Nuclear magnetic resonance:*** (NMR) spectra were recorded on a Bruker Fourier 300 MHz spectrometer equipped with a dual (^{13}C, ^{1}H) probe, a Bruker AVANCE III HD 400MHz NMR spectrometer equipped with a Broadband multinuclear (BBFO) SmartProbe™, a Bruker AVANCE III HD 500MHz Spectrometer equipped with Broadband multinuclear (BBO) Prodigy CryoProbe or a Bruker Avance III 600 MHz NMR spectrometer equipped with an inverse QCI Cryoprobe. ^{1}H spectra were obtained at 300, 400, 500 or 600 MHz, ^{13}C spectra were obtained at 75, 100 or 125 MHz. All spectra were obtained at room temperature. Chemical shifts were reported in ppm according to tetramethylsilane using the solvent residual signal as an internal reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.52 ppm). Coupling constants (*J*) were given in Hz. Resonance multiplicity was described as *s* (singlet), *d* (doublet), *t* (triplet), *dd* (doublet of doublets), *ddd* (doublet of doublets of doublets), *td* (triplet of doublets), *m* (multiplet) and *bs* (broad signal). Carbon spectra were acquired with a complete decoupling for the proton. ***Infrared spectra*** (IR) were recorded on a Shimadzu IR Affinity 1S FTIR spectrometer in ATR mode with a diamond mono-crystal. ***Mass spectrometry:*** (i) High-resolution mass spectra (HRMS) were performed on a Waters LCT HR TOF mass spectrometer in the positive ion mode. All analyses were carried out at Cardiff university. ***Photophysical analysis:*** Absorption spectra of compounds were recorded on air equilibrated solutions at room temperature with a Agilent Cary 5000 UV-Vis spectrophotometer, using quartz cells with path length of 1.0 cm. ***X-ray measurements:*** Single crystals of $\mathbf{9}_{\mathbf{C\text{-}Se}}$, $\mathbf{11}_{\mathbf{C\text{-}Te}}$ and $\mathbf{11}_{\mathbf{N\text{-}Te}}$ were grown by slow evaporation of $CHCl_3$, $\mathbf{9}_{\mathbf{N\text{-}Te}}$ from cooling down a hot solution of *p*-xylene. Crystallographic studies were undertaken on single crystal mounted in paratone and studied on an Agilent SuperNova Dual three-circle diffractometer using Cu-Kα (λ = 1.540598 Å) or Mo-Kα (λ = 0.7093187 Å) radiation and a CCD detector. Measurements were typically made at 150(2) K with temperatures maintained using an Oxford Cryostream unless otherwise stated. Data were collected, integrated and corrected for absorption using a numerical absorption correction based on gaussian integration over a multifaceted crystal model within CrysAlisPro.[1] The structures were solved by direct methods and refined against F^2 within SHELXL-2013.[2]

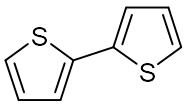
1.2. Materials and methods

Synthesis. Chemicals were purchased from *Sigma Aldrich*, *Acros Organics*, *TCI, Apollo Scientific, ABCR, Alfa Aesar, Carbosynth* and *Fluorochem* and were used as received. Solvents were purchased from

Fluorochem, Fisher Chemical and *Sigma Aldrich*, while deuterated solvents from *Eurisotop* and *Sigma Aldrich*. THF, Et_2O and CH_2Cl_2 were dried on a Braun MB SPS-800 solvent purification system. MeOH and acetone were purchased as reagent-grade and used without further purification. $CHCl_3$ was distilled from $CaCl_2$ and stored over $CaCl_2$. NEt_3 was distilled from CaH_2 and then stored over KOH. Anhydrous dioxane and pyridine were purchased from *Sigma Aldrich*. Sulfuric acid (H_2SO_4 > 95%) was purchased from *Fluorochem*. Solution of iso-propyl magnesium chloride in THF was freshly prepared according to a procedure of Lin et al.[3] and titrated with the Paquette method.[4] Low temperature baths were prepared using different solvent mixtures depending on the desired temperature: -78 °C with acetone/dry ice, and 0 °C with ice/H_2O. Anhydrous conditions were achieved by flaming two necked flasks with a heat gun under vacuum and purging with nitrogen. The inert atmosphere was maintained using nitrogen-filled balloons equipped with a syringe and needle that was used to penetrate the silicon stoppers closing the flask's necks. Additions of liquid reagents were performed using plastic syringes. All reactions were performed in dry conditions and under inert atmosphere unless otherwise stated.

2. Synthetic procedures

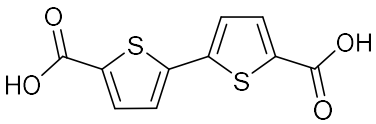
2.1. Synthesis of 2,2'-bithiophene 1



1

In a Schlenk flask magnesium turnings (940 mg, 39 mmol) was added, then the system was dried under vacuum at 100 °C for 20 minutes and refilled with N_2. The solid was covered with dry Et_2O (40 mL) and 2-bromothiophene (4.8 g, 2.9 mL, 30 mmol) was added dropwise at 0 °C. The mixture was heated to reflux and stirred for 1 hour, then added dropwise to a solution of 2-bromothiophene (4 g, 2.4 mL, 25 mmol) and Ni(dppp)Cl_2 (27 mg, 1.25 mmol) in dry Et_2O (30 mL). The reaction was heated to reflux and stirred overnight, then quenched by slow addition of water (30 mL). The aqueous phase was extracted with Et_2O (3 × 50 mL), then the combined organic extracts were washed with brine (30 mL), dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The crude was purified by silica gel chromatography (petr. ether) to give pure **1** as a white solid (2.9 g, 71% yield). m.p.: 30-31 °C (lit. 34-35 °C – from petr. ether); ^{1}H-NMR (300 MHz, DMSO-d_6) δ_H: 7.62 (d, J = 5.1 Hz, 2H, ArH), 7.48 (m, 2H, ArH), 7.34 (d, J = 3.9 Hz, 2H, ArH); ^{13}C-NMR (75 MHz, DMSO-d_6) δ_C: 143.0 × 2, 135.5 × 2, 132.6 × 2, 127.4 × 2; Spectral properties were in agreement with those reported in the literature.[5]

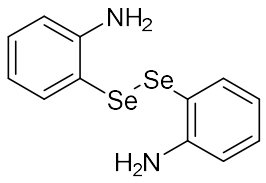
2.2. Synthesis of [2,2'-bithiophene]-5,5'-dicarboxylic acid 2



2

[2,2'-bithiophene]-5,5'-dicarboxylic acid **2** has been synthesized taking inspiration from the procedure of Yu et al.[6] To a solution of 2,2'-bithiophene **1** (1.66 g, 10 mmol) in dry Et_2O (85 mL) under N_2, a solution of *n*-butyllithium (2.5 M in hexanes, 8.8 mL, 22 mmol) in dry Et_2O (10 mL) was added dropwise at -78 °C. The mixture was stirred at 0 °C for 2 hours, then the system was cooled down to -78 °C and a stream of CO_2 passed through the flask (generated by slow addition of HCl to an aqueous solution of $NaHCO_3$, having the resulting gas dried passing through a 95% H_2SO_4 trap and a plug of $CaCl_2$). The reaction was stirred at -78 °C for 2 hours, then at room temperature overnight. The formed precipitate was recovered by filtration, washed several times with Et_2O, placed in suspension in a 3% HCl solution (30 mL), then stirred at room temperature for 30 minutes and filtrated. The obtained solid was suspended in MeOH (20 mL), stirred at room temperature for 2 hours and filtrated to give pure **2** as a brown powder (935 mg, 37% yield). m.p.: > 300 °C (lit. 371 °C – from MeOH); ^{1}H-NMR (300 MHz, DMSO-*d*$_6$) δ_H: 7.66 (d, *J* = 3.9 Hz, 2H, ArH), 7.34 (d, *J* = 3.9 Hz, 2H, ArH); ^{13}C-NMR (75 MHz, DMSO-*d*$_6$) δ_C: 162.8 × 2, 134.4 × 2, 128.8 × 2, 126.0 × 2, 124.7 × 2; Spectral properties were in agreement with those reported in the literature.[7]

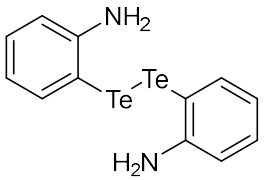
2.3. Synthesis of 2,2'-diselanediyldianiline 4_{Se}



4_{Se}

2,2'-diselanediyldianiline **4_{Se}** has been synthesized according to the procedure of Engman et al.[8] To a solution of 2-bromoaniline **3** (1.76 g, 10 mmol) in dry THF (50 mL) under N_2, *t*-butyllithium (1.7 M in hexanes, 17.6 mL, 30 mmol) was added dropwise at -78 °C. The reaction was stirred at -78 °C for 1 hour, then freshly grounded elemental selenium powder (780 mg, 10 mmol) was added in once while a brisk flux of nitrogen was passed through the flask. The reaction was stirred at room temperature for 1 hour, then poured into a solution of $[K_3Fe(CN)_6]$ (3.29 g, 10 mmol) in water (180 mL) and stirred for 10 minutes. The aqueous phase was extracted with Et_2O (6 × 50 mL), then the combined organic extracts were washed with water (2 × 30 mL) and brine (2 × 30 mL), dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The crude was purified by silica gel chromatography (cyclohexane/EtOAc 8:2) to give pure **6_{Se}** as a red powder (1.4 g, 83% yield). m.p.: 83 °C (lit. 80-83 °C – from EtOH); ^{1}H-NMR (300 MHz, DMSO-*d*$_6$) δ_H: 7.23 (d, *J* = 7.6 Hz, 2H, ArH), 7.06 (t, *J* = 7.6 Hz, 2H, ArH), 6.72 (d, *J* = 7.4 Hz, 2H, ArH), 6.41 (t, *J* = 7.4 Hz, 2H, ArH), 5.34 (bs, 4H, NH_2); ^{13}C-NMR (75 MHz, DMSO-*d*$_6$) δ_C: 149.9 × 2, 136.8 × 2, 130.9 × 2, 116.4 × 2, 114.4 × 2, 113.1 × 2. Spectral properties were in agreement with those reported in the literature.[9]

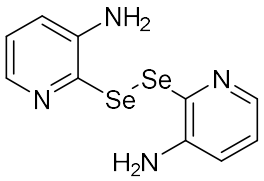
2.4. Synthesis of 2,2'-ditellanediyldianiline 4_{Te}



4_{Te}

2,2'-ditellanediyldianiline **4_{Te}** has been synthesized according to the procedure of Junk et al. with slight modifications.[10] A suspension of NaH (60% in oil, 1.44 g, 60 mmol) and freshly grounded elemental tellurium powder (2.55 g, 20 mmol) in dry and degassed NMP (20 mL) under N_2 was heated to 155 °C for 30 minutes. To the resulting deep purple solution, a solution of 2-bromoaniline **3** (3.44 g, 20 mmol) in dry and degassed NMP (6 mL) was added dropwise at 155 °C, then the reaction was stirred at 185 °C for 3.5 hours. The system was allowed to cool down to room temperature and poured into a solution of NH_4Cl (3.3 g) in water (120 mL) and air bubbled through for 2 hours. The aqueous phase was extracted with Et_2O (9 × 50 mL), then the combined organic extracts were washed with water (2 × 30 mL) and brine (2 × 30 mL), dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The crude was purified by recrystallization (hot toluene) to give pure **4_{Te}** as a deep red solid (2.08 g, 47% yield). m.p.: 101-102 °C (lit. 99-101 °C – from $CHCl_3$); ^{1}H-NMR (300 MHz, DMSO-d_6) δ_H: 7.58 (d, J = 8.0 Hz, 2H, ArH), 7.03 (t, J = 7.6 Hz, 2H, ArH), 6.70 (d, J = 8.0 Hz, 2H, ArH), 6.38 (t, J = 7.6 Hz, 2H, ArH), 5.17 (bs, 4H, NH_2); ^{13}C-NMR (75 MHz, DMSO-d_6) δ_C: 151.4 x 2, 141.6 x 2, 130.6 x 2, 117.5 x 2, 113.5 x 2, 93.8 x 2. Spectral properties were in agreement with those reported in the literature.[10]

2.5. Synthesis of 2,2'-diselanediylbis(pyridin-3-amine) 6_{Se}

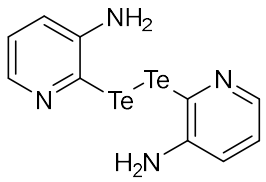


6_{Se}

2,2'-diselanediylbis(pyridin-3-amine) **6_{Se}** has been synthesized according to the procedure of Biot et al.[11] To a solution of 3-amino-2-bromopyridine **5** (3.46 g, 20 mmol) in dry THF (20 mL) under N_2, freshly prepared *i*-propyl magnesium chloride (2.14 M, 21 mL, 44 mmol) was added dropwise at 0 °C. The reaction was stirred at room temperature for 3 hours, then freshly grounded elemental selenium powder (1.58 g, 20 mmol) was added in once while a brisk flux of nitrogen was passed through the flask. The reaction was stirred at room temperature overnight, then poured into a solution of $[K_3Fe(CN)_6]$ (6.6 g, 20 mmol) in water (320 mL) and stirred for 10 minutes. The aqueous phase was extracted with Et_2O (6 × 50 mL), then the combined organic extracts were washed with water (2 × 30 mL) and brine (2 × 30 mL), dried over Na_2SO_4, filtered and the solvents removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH

2%) to give pure $\mathbf{6_{Se}}$ as a brown powder (180 mg, 5% yield). m.p.: 189-190 °C (lit. 187-188 °C – from $CHCl_3$); ^{1}H-NMR (300 MHz, DMSO-d_6) δ_H: 7.74 (dd, J = 4.4, 1.6 Hz, 2H, ArH), 7.08 (dd, J = 8.0, 4.4 Hz, 2H, ArH), 6.99 (dd, J = 8.0, 1.6 Hz, 2H, ArH), 5.85 (bs, 4H, NH_2); ^{13}C-NMR (75 MHz, DMSO-d_6) δ_C: 145.7 x 2, 137.4 x 2, 135.8 x 2, 124.5 x 2, 120.7 x 2. Spectral properties were in agreement with those reported in the literature.[11]

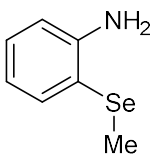
2.6. Synthesis of 2,2'-ditellanediylbis(pyridin-3-amine) $\mathbf{6_{Te}}$



$\mathbf{6_{Te}}$

2,2'-ditellanediylbis(pyridin-3-amine) $\mathbf{6_{Te}}$ has been synthesized according to the procedure of Biot et al.[11] To a solution of 3-amino-2-bromopyridine **5** (3.46 g, 20 mmol) in dry THF (20 mL) under N_2, freshly prepared *i*-propyl magnesium chloride (1.62 M, 27 mL, 44 mmol) was added dropwise at 0 °C. The reaction was stirred at room temperature for 3 hours, then freshly grounded elemental tellurium powder (2.54 g, 20 mmol) was added in once while a brisk flux of nitrogen was passed through the flask. The reaction was stirred at room temperature for 24 hours, poured into a solution of NH_4Cl (3.3 g) in water (200 mL) and air bubbled through for 2 hours. The aqueous phase was extracted with Et_2O (9 × 50 mL), then the combined organic extracts were washed with water (2 × 30 mL) and brine (2 × 30 mL), dried over Na_2SO_4, filtered and the solvents removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH 2%) to give pure $\mathbf{6_{Te}}$ as a dark red powder (554 mg, 12% yield). m.p.: 152-153 °C (lit. 153-154 °C – from $CHCl_3$); ^{1}H-NMR (300 MHz, DMSO-d_6) δ_H: 7.73 (dd, J = 4.3, 1.3 Hz, 2H, ArH), 7.01 (dd, J = 8.0, 4.3 Hz, 2H, ArH), 6.90 (dd, J = 8.0, 1.3 Hz, 2H, ArH), 5.71 (bs, 4H, NH_2); ^{13}C-NMR (75 MHz, DMSO-d_6) δ_C: 148.1 x 2, 138.6 x 2, 124.1 x 2, 120.0 x 2, 119.0 x 2. Spectral properties were in agreement with those reported in the literature.[11]

2.7. Synthesis of 2-(methylselanyl)aniline $\mathbf{7_{C\text{-}Se}}$

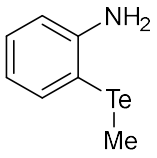


$\mathbf{7_{C\text{-}Se}}$

To a solution of 2,2'-diselanediyldianiline $\mathbf{4_{Se}}$ (1 g, 2.9 mmol) in dry and degassed THF (80 mL) under N_2, were added $NaBH_4$ (329 mg, 8.7 mmol) and MeOH (464 mg, 0.58 mL, 14.5 mmol). The mixture was stirred at room temperature for 75 minutes (the red colour turned orange), then MeI (904 mg, 0.4 mL, 6.4 mmol) was added. The reaction was stirred at room temperature for 1.5 hours under exclusion of light, then water (50 mL) was slowly added and the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic extracts

were washed with brine (20 mL), dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The crude was purified by silica gel chromatography (petr. ether/CH_2Cl_2 1:3) to give pure **$7_{C\text{-}Se}$** as a yellow oil (1.05 g, 97% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H: 7.50 (dd, *J* = 7.5, 1.5 Hz, 1H, ArH), 7.13 (ddd, *J* = 7.9, 7.5, 1.5 Hz, 1H, ArH), 6.80 (dd, *J* = 7.9, 1.2 Hz, 1H, ArH), 6.70 (td, *J* = 7.5, 1.2 Hz, 1H, ArH), 4.12 (bs, 2H, NH_2), 2.22 (s, 3H, Me); ^{13}C-NMR (75 MHz, $CDCl_3$) δ_C: 147.0, 136.3, 129.7, 119.6, 116.2, 115.3, 8.2. Spectral properties were in agreement with those reported in the literature.[12]

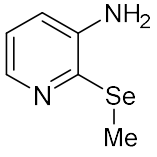
2.8. Synthesis of 2-(methyltellanyl)aniline $7_{C\text{-}Te}$



$7_{C\text{-}Te}$

To a solution of 2,2'-ditellanediyldianiline **4_{Te}** (1 g, 2.3 mmol) in dry and degassed THF (63 mL) under N_2, were added $NaBH_4$ (261 mg, 6.9 mmol) and MeOH (368 mg, 0.47 mL, 11.5 mmol). The mixture was stirred at room temperature for 75 minutes (the dark red colour turned light orange), then MeI (718 mg, 0.31 mL, 5.1 mmol) was added. The reaction was stirred at room temperature for 1.5 hours under exclusion of light, then water (50 mL) was slowly added and the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with brine (20 mL), dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The crude was purified by silica gel chromatography (petr. ether/CH_2Cl_2 1:3) to give pure **$7_{C\text{-}Te}$** as a red oil (791 mg, 73% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H: 7.72 (dd, *J* = 7.5, 1.5 Hz, 1H, ArH), 7.15 (td, *J* = 7.9, 1.5 Hz, 1H, ArH), 6.77 (dd, *J* = 7.9, 1.2 Hz, 1H, ArH), 6.58 (td, *J* = 7.5, 1.2 Hz, 1H, ArH), 4.28 (bs, 2H, NH_2), 2.05 (s, 3H, Me); ^{13}C-NMR (75 MHz, $CDCl_3$) δ_C: 149.1, 140.8, 129.8, 118.6, 112.9, 98.7, -16.4. Spectral properties were in agreement with those reported in the literature.[12]

2.9. Synthesis of 2-(methylselanyl)pyridin-3-amine $7_{N\text{-}Se}$

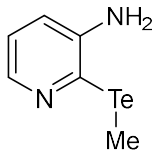


$7_{N\text{-}Se}$

To a solution of 2,2'-diselanediylbis(pyridin-3-amine) **6_{Se}** (300 mg, 0.87 mmol) in dry and degassed THF (20 mL) under N_2, were added $NaBH_4$ (100 mg, 2.62 mmol) and MeOH (140 mg, 0.18 mL, 4.35 mmol). The mixture was stirred at room temperature for 1.5 hours (the brown colour turned orange), then MeI (270 mg, 0.12 mL, 1.9 mmol) was added. The reaction was stirred at room temperature for 1.5 hours under exclusion of light, then water (20 mL) was slowly added and the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered and the solvents removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH 1%) to

give pure $\mathbf{7_{N\text{-}Se}}$ as an orange oil (160 mg, 50% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H: 7.99 (dd, J = 4.5, 1.6 Hz, 1H, ArH), 6.93 (dd, J = 7.9, 4.5 Hz, 1H, ArH), 6.87 (dd, J = 7.9, 1.6 Hz, 1H, ArH), 3.83 (bs, 2H, NH_2), 2.48 (s, 3H, Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: 142.4, 141.0, 140.5, 121.5, 120.4, 6.1. Spectral properties were in agreement with those reported in the literature.[11]

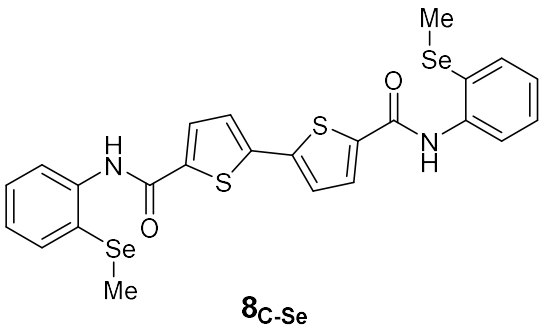
2.10. Synthesis of 2-(methyltellanyl)pyridin-3-amine $\mathbf{7_{N\text{-}Te}}$



$\mathbf{7_{N\text{-}Te}}$

To a solution of 2,2'-ditellanediylbis(pyridin-3-amine) $\mathbf{6_{Te}}$ (800 mg, 1.8 mmol) in dry and degassed THF (42 mL) under N_2, were added $NaBH_4$ (200 mg, 5.4 mmol) and MeOH (280 mg, 0.36 mL, 9 mmol). The mixture was stirred at room temperature for 1.5 hours (the dark red colour turned light red), then MeI (560 mg, 0.25 mL, 3.96 mmol) was added. The reaction was stirred at room temperature for 1.5 hours under exclusion of light, then water (30 mL) was slowly added and the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered and the solvents removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH 1%) to give pure $\mathbf{7_{N\text{-}Te}}$ as an orange oil (649 mg, 76% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H: 8.03 (dd, J = 4.5, 1.6 Hz, 1H, ArH), 6.94 (dd, J = 8.0, 4.5 Hz, 1H, ArH), 6.86 (dd, J = 8.0, 1.6 Hz, 1H, ArH), 3.85 (bs, 2H, NH_2), 2.29 (s, 3H, Me); ^{13}C-NMR (75 MHz, $CDCl_3$) δ_C: 145.7, 141.8, 128.6, 122.2, 119.6, -15.5. Spectral properties were in agreement with those reported in the literature.[11]

2.11. Synthesis of N^5,$N^{5'}$-bis(2-(methylselanyl)phenyl)-[2,2'-bithiophene]-5,5'-dicarboxamide $\mathbf{8_{C\text{-}Se}}$

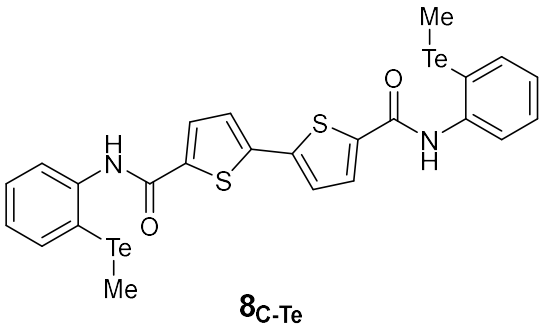


$\mathbf{8_{C\text{-}Se}}$

A two-necked flask was loaded with [2,2'-bithiophene]-5,5'-dicarboxylic acid **2** (102 mg, 0.4 mmol) under N_2. The solid was dissolved in $SOCl_2$ (2.4 mL), then the mixture was heated to reflux and stirred overnight. The system was allowed to cool down to room temperature and the solvent was removed under vacuum. To a solution of the resulting acyl chloride and DMAP (2 mg, 0.02 mmol) in dry $CHCl_3$ (1.1 mL), a solution of 2-(methylselanyl)aniline $\mathbf{7_{C\text{-}Se}}$ (310 mg, 0.88 mmol) and dry NEt_3 (130 mg, 0.18 mL, 1.28 mmol) in dry $CHCl_3$

(1 mL) was added dropwise at 0 °C. The reaction was heated to reflux and stirred for 24 hours, then water (20 mL) was added and extracted with $CHCl_3$ (3 × 30 mL). The combined organic extracts were washed with brine (20 mL), dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH 0.4%) to give the desired product and the monoamide in a mixture. The obtained solid was dissolved in $CHCl_3$ (20 mL) and washed with a saturated solution of $NaHCO_3$ (3 × 20 mL), then the organic phase was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure, to give pure **8**$_{C\text{-}Se}$ as a brown powder (68 mg, 28% yield). m.p.: 154 °C (from CH_2Cl_2); IR (ATR) ν_{max} (cm^{-1}): 3325 (w, NH), 2922 (w, Alk), 1640 (s, C=O), 1578 (m), 1516 (s), 1506 (s), 1425 (s), 1304 (s), 1234 (s), 1094 (m), 907 (w), 795 (m), 741 (s), 660 (w), 575 (w), 529 (w); ^{1}H-NMR (400 MHz, DMSO-*d*$_6$) δ_H: 10.17 (s, 2H, O=C-NH), 7.96 (d, *J* = 3.8 Hz, 2H, ArH), 7.55 (dd, *J* = 3.8, 0.9 Hz, 2H, ArH), 7.53 – 7.46 (m, 2H, AHr), 7.34 (m, 2H, ArH) 7.31 – 7.24 (m, 4H, ArH), 2.27 (s, 6H, Me); ^{13}C-NMR (100 MHz, DMSO-*d*$_6$) δ_C: 159.6 x 2, 140.4 x 2, 139.0 x 2, 136.2 x 2, 131.2 x 2, 130.2 x 2, 129.8 x 2, 127.4 x 2, 126.3 x 2, 126.1 x 2, 6.5 x 2 (one peak missing probably due to overlap); ESI-HRMS: $[M+H]^+$ calcd for $[C_{24}H_{21}N_2O_2S_2Se_2]^+$: 586.9443; found: 586.9420.

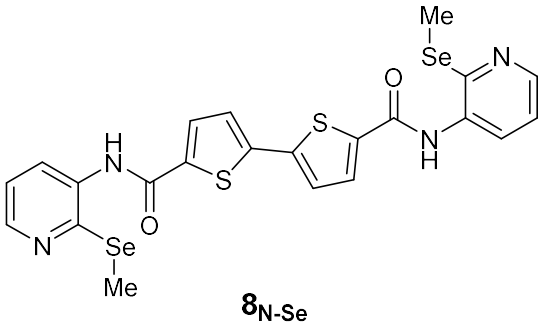
2.12. Synthesis of *N*^{5},*N*$^{5'}$-bis(2-(methyltellanyl)phenyl)-[2,2'-bithiophene]-5,5'-dicarboxamide 8$_{C\text{-}Te}$



8$_{C\text{-}Te}$

A two-necked flask was loaded with [2,2'-bithiophene]-5,5'-dicarboxylic acid **2** (102 mg, 0.4 mmol) under N_2. The solid was dissolved in $SOCl_2$ (2.4 mL), then the mixture was heated to reflux and stirred overnight. The system was allowed to cool down to room temperature and the solvent was removed under vacuum. To a solution of the resulting acyl chloride and DMAP (2 mg, 0.02 mmol) in dry $CHCl_3$ (1.1 mL), a solution of 2-(methyltellanyl)aniline **7**$_{C\text{-}Te}$ (207 mg, 0.88 mmol) and dry NEt_3 (130 mg, 0.18 mL, 1.28 mmol) in dry $CHCl_3$ (1 mL) was added dropwise at 0 °C. The reaction was heated to reflux and stirred for 24 hours, then water (20 mL) was added and extracted with $CHCl_3$ (3 × 30 mL). The combined organic extracts were washed with brine (20 mL), dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The crude material was used in the next step without further purification.

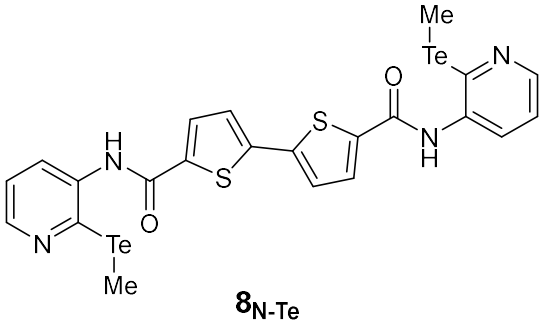
2.13. Synthesis of *N*^{5},*N*$^{5'}$-bis(2-(methylselanyl)pyridin-3-yl)-[2,2'-bithiophene]-5,5'-dicarboxamide 8$_{N\text{-}Se}$



$\mathbf{8_{N\text{-}Se}}$

A two-necked flask was loaded with [2,2'-bithiophene]-5,5'-dicarboxylic acid **2** (102 mg, 0.4 mmol) under N_2. The solid was dissolved in $SOCl_2$ (2.4 mL), then the mixture was heated to reflux and stirred overnight. The system was allowed to cool down to room temperature and the solvent was removed under vacuum. To a solution of the resulting acyl chloride and DMAP (2 mg, 0.02 mmol) in dry $CHCl_3$ (1.1 mL), a solution of 2-(methylselanyl)pyridin-3-amine $\mathbf{7_{N\text{-}Se}}$ (164 mg, 0.88 mmol) and dry NEt_3 (130 mg, 0.18 mL, 1.28 mmol) in dry $CHCl_3$ (1 mL) was added dropwise at 0 °C. The reaction was heated to reflux and stirred for 24 hours, then water (20 mL) was added and extracted with $CHCl_3$ (3 × 30 mL). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered and the solvents removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH 2%) to give pure $\mathbf{8_{N\text{-}Se}}$ as a golden powder (41 mg, 18% yield). m.p.: 262-263 °C (from CH_2Cl_2); IR (ATR) ν_{max} (cm^{-1}): 3252 (m, NH), 2928 (w, Alk), 2558 (w), 1921 (w), 1634 (2, C=O), 1560 (m), 1505 (s), 1449 (m), 1381 (s), 1263 (s), 1199 (m), 1101 (m), 1053 (m), 961 (w), 799 (s), 725 (s), 667 (m), 617 (m), 578 (m); ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H: 10.32 (s, 2H, O=C-NH), 8.45 (bs, 2H, ArH), 7.99 (bs, 2H, ArH), 7.65 (d, J = 7.2 Hz, 2H, ArH), 7.59 (bs, 2H, ArH), 7.26 (s, 2H, ArH), 2.36 (s, 6H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C: 159.9 x 2, 154.1 x 2, 148.0 x 2, 140.6 x 2, 138.6 x 2, 135.1 x 2, 133.0 x 2, 130.6 x 2, 126.3 x 2, 120.3 x 2, 5.1 x 2; ESI-HRMS: $[M+H]^+$ calcd for $[C_{22}H_{19}N_4O_2S_2{}^{76}Se^{77}Se]^+$: 587.9341; found: 587.9347.

2.14. Synthesis of N^5,$N^{5'}$-bis(2-(methyltellanyl)pyridin-3-yl)-[2,2'-bithiophene]-5,5'-dicarboxamide $\mathbf{8_{N\text{-}Te}}$

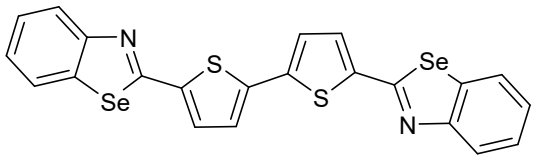


$\mathbf{8_{N\text{-}Te}}$

A two-necked flask was loaded with [2,2'-bithiophene]-5,5'-dicarboxylic acid **2** (102 mg, 0.4 mmol) under N_2. The solid was dissolved in $SOCl_2$ (2.4 mL), then the mixture was heated to reflux and stirred overnight. The system was allowed to cool down to room temperature and the solvent was removed under vacuum. To a solution of the resulting acyl chloride and DMAP (2 mg, 0.02 mmol) in dry $CHCl_3$ (1.1 mL), a solution of 2-

(methyltellanyl)pyridin-3-amine **7$_{N-Te}$** (207 mg, 0.88 mmol) and dry NEt_3 (130 mg, 0.18 mL, 1.28 mmol) in dry $CHCl_3$ (1 mL) was added dropwise at 0 °C. The reaction was heated to reflux and stirred for 24 hours, then the obtained solid was filtered off and washed with a saturated solution of Na_2CO_3 to give pure **8$_{N-Te}$** as a brown solid (43 mg, 16% yield). m.p.: > 300 °C (from $CHCl_3$); IR (ATR) ν_{max} (cm^{-1}): 3296 (m, NH), 2931 (w, Alk), 1638 (s, C=O), 1568 (m), 1514 (s), 1464 (s), 1427 (m), 1393 (m), 1300 (w), 1262 (m), 1063 (m), 949 (w), 885 (w), 813 (m), 785 (s), 725 (s), 657 (m); ^{1}H-NMR (500 MHz, DMSO-*d*$_6$) δ_H: 8.14 (bs, 2H. ArH), 7.86 (bs, 2H, ArH), 7.34 (bs, 2H, ArH), 7.16 (bs, 2H, ArH), 6.86 (bs, 2H, ArH), 1.80 (s, 6H, Me); ^{13}C-NMR could not be measured due to low solubility issues; ESI-HRMS: $[M+H]^+$ calcd for $[C_{22}H_{19}N_4O_2S_2{}^{124}Te_2]^+$: 682.9006; found: 682.9022.

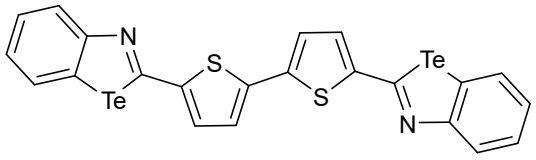
2.15. Synthesis of 5,5'-bis(benzo[d][1,3]selenazol-2-yl)-2,2'-bithiophene 9$_{C-Se}$



9$_{C-Se}$

To a suspension of *N*^{5},*N*$^{5'}$-bis(2-(methylselanyl)phenyl)-[2,2'-bithiophene]-5,5'-dicarboxamide **8$_{C-Se}$** (30 mg, 0.05 mmol) and NEt_3 (69 mg, 90 µL, 0.68 mmol) in dry 1,4-dioxane (3.8 mL) under N_2, a solution of $POCl_3$ (53 mg, 32 µL, 0.23 mmol) in dry 1,4-dioxane (0.23 mL) was added dropwise at room temperature. The reaction was heated to reflux and stirred overnight. The mixture was diluted with $CHCl_3$ (20 mL), washed with a saturated solution of $NaHCO_3$ (2 × 20 mL) and the aqueous phase extracted with $CHCl_3$ (3 × 30 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$) to give pure **9$_{C-Se}$** as a yellow solid (12 mg, 45% yield). m.p.: 240-243 °C (from $CHCl_3$): IR (ATR) ν_{max} (cm^{-1}): 2920 (w), 1820 (w), 1765 (w), 1587 (w), 1479 (m), 1439 (s), 1304 (s), 1229 (m), 1193 (m), 1112 (w), 1045 (m), 903 (m), 866 (m), 793 (s), 746 (s), 718 (s), 661 (m), 542 (m), 465 (m); ^{1}H-NMR (600 MHz, DMSO-*d*$_6$) δ_H: 8.18 (d, *J* = 7.7 Hz, 2H, ArH), 8.02 (d, *J* = 7.7 Hz, 2H, ArH), 7.94 (d, *J* = 4.0 Hz, 2H, ArH), 7.64 (d, *J* = 4.0 Hz, 2H, ArH), 7.52 (t, *J* = 7.7 Hz, 2H, ArH), 7.37 (t, *J* = 7.7 Hz, 2H, ArH); ^{13}C-NMR could not be measured due to low solubility issues; ESI-HRMS: $[M+H]^+$ calcd for $[C_{22}H_{13}N_2S_2{}^{77}Se_2]^+$: 522.8919; found: 522.8892. Crystal suitable for X-Ray diffraction was obtained by slow evaporation of solvent from a $CHCl_3$ solution.

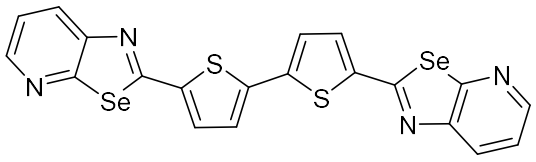
2.16. Synthesis of 5,5'-bis(benzo[d][1,3]tellurazol-2-yl)-2,2'-bithiophene 9$_{C-Te}$



9$_{C-Te}$

To a suspension of N^5,$N^{5'}$-bis(2-(methyltellanyl)phenyl)-[2,2'-bithiophene]-5,5'-dicarboxamide **8$_{C-Te}$** (73 mg, 0.11 mmol) and NEt_3 (134 mg, 0.17 mL, 1.32 mmol) in dry 1,4-dioxane (8 mL) under N_2, a solution of $POCl_3$ (101 mg, 60 µL, 0.44 mmol) in dry 1,4-dioxane (0.44 mL) was added dropwise at room temperature. The reaction was heated to reflux and stirred overnight. The mixture was diluted with $CHCl_3$ (20 mL), washed with a saturated solution of $NaHCO_3$ (3 × 20 mL) and the aqueous phase extracted with $CHCl_3$ (5 × 30 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$) to give pure **9$_{C-Te}$** as a red solid (18 mg, 7% yield over two steps). m.p.: 269-270 °C (from $CHCl_3$); IR (ATR) ν_{max} (cm^{-1}): 2920 (w), 2355 (w), 1690 (w), 1478 (m), 1427 (m), 1306 (w), 1290 (w), 1215 (m), 1065 (w), 990 (m), 897 (m), 864 (m), 791 (s), 783 (s), 745 (s), 604 (w), 579 (w), 449 (m); ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H: 8.12 (d, J = 7.8 Hz, 2H, ArH), 8.02 (d, J = 7.5 Hz, 2H, ArH), 7.93 (d, J = 4.0 Hz, 2H, ArH), 7.59 (d, J = 4.0 Hz, 2H, ArH), 7.48 – 7.44 (m, 2H, ArH), 7.19 (t, J = 7.5 Hz, 2H, ArH); ^{13}C-NMR could not be measured due to low solubility issues; ESI-HRMS: $[M+H]^+$ calcd for $[C_{22}H_{13}N_2S_2{}^{124}Te_2]^+$: 616.8577; found: 616.8479. Crystal suitable for X-Ray diffraction was obtained by slow cooling of a hot solution of *p*-xylene.

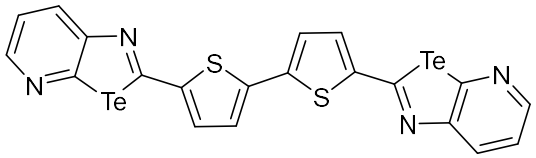
2.17. Synthesis of 5,5'-bis([1,3]selenazolo[5,4-β]pyridin-2-yl)-2,2'-bithiophene 9$_{N-Se}$



9$_{N-Se}$

To a suspension of N^5,$N^{5'}$-bis(2-(methylselanyl)pyridin-3-yl)-[2,2'-bithiophene]-5,5'-dicarboxamide **8$_{N-Se}$** (25 mg, 0.05 mmol) and NEt_3 (109 mg, 0.14 mL, 1.08 mmol) in dry 1,4-dioxane (3.2 mL) under N_2, a solution of $POCl_3$ (83 mg, 50 µL, 0.36 mmol) in dry 1,4-dioxane (0.36 mL) was added dropwise at room temperature. The reaction was heated to reflux and stirred overnight. The mixture was diluted with $CHCl_3$ (10 mL), washed with a saturated solution of $NaHCO_3$ (3 × 20 mL) and the aqueous phase extracted with $CHCl_3$ (8 × 30 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The crude was purified by preparative TLC ($CHCl_3$/MeOH 3%) to give pure **9$_{N-Se}$** as an orange solid (6 mg, 27% yield). m.p.: 230-232 °C (from $CHCl_3$); IR (ATR) ν_{max} (cm^{-1}): 2922 (w), 2849 (w), 2361 (w), 1651 (w), 1573 (m), 1470 (m), 1435 (m), 1373 (m), 1307 (s), 1270 (w), 1197 (w), 1065 (m), 907 (w), 812 (m), 798 (s), 785 (s), 727 (m), 662 (m), 600 (m), 556 (w), 434 (s); ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H: 8.54 – 8.51 (m, 4H, ArH), 7.82 (d, J = 4.0 Hz, 2H, ArH), 7.67 – 7.61 (m, 2H, ArH), 7.42 – 7.38 (m, 2H, ArH); ^{13}C-NMR could not be measured due to low solubility issues; EI-HRMS: $[M]^+$ calcd for $[C_{20}H_{10}N_4S_2{}^{80}Se_2]^+$: 529.8677; found: 529.8675.

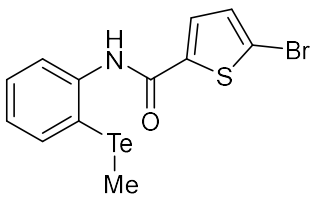
2.18. Synthesis of 5,5'-bis([1,3]tellurazolo[5,4-β]pyridin-2-yl)-2,2'-bithiophene 9$_{N-Te}$



$9_{N\text{-}Te}$

To a suspension of N^5,$N^{5'}$-bis(2-(methyltellanyl)pyridin-3-yl)-[2,2'-bithiophene]-5,5'-dicarboxamide **$8_{N\text{-}Te}$** (41 mg, 0.06 mmol) and NEt_3 (146 mg, 0.18 mL, 1.44 mmol) in dry 1,4-dioxane (4.7 mL) under N_2, a solution of $POCl_3$ (111 mg, 70 µL, 0.48 mmol) in dry 1,4-dioxane (0.48 mL) was added dropwise at room temperature. The reaction was heated to reflux and stirred overnight. The mixture was diluted with $CHCl_3$ (20 mL), washed with a saturated solution of $NaHCO_3$ (3 × 20 mL) and the aqueous phase extracted with $CHCl_3$ (10 × 30 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH 3% to 5%) to give pure **$9_{N\text{-}Te}$** as a red solid (20 mg, 53% yield). m.p.: 251-232 °C (from $CHCl_3$); IR (ATR) ν_{max} (cm^{-1}): 2922 (w), 2496 (w), 1684 (w), 1541 (w), 1460 (s), 1430 (m), 1397 (m), 1364 (s), 1260 (w), 1207 (m), 1173 (m), 1036 (s), 903 (w), 813 (w), 793 (s), 777 (s), 725 (m), 669 (w), 580 (w), 453 (m); ^{1}H-NMR (300 MHz, DMSO-d_6) δ_H: 8.51 – 8.50 (m, 2H, ArH), 8.34 – 8.32 (m, 2H, ArH), 8.08 – 8.06 (m, 2H, ArH), 7.68 – 7.66 (m, 2H, ArH), 7.58 – 7.54 (m, 2H, ArH); ^{13}C-NMR could not be measured due to low solubility issues; ESI-HRMS: $[M+H]^+$ calcd for $[C_{20}H_{11}N_4S_2{}^{124}Te_2]^+$: 618.8482; found: 618.8479.

2.19. Synthesis of 5-bromo-*N*-(2-(methyltellanyl)phenyl)thiophene-2-carboxamide $10_{C\text{-}Te}$

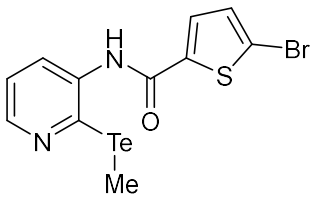


$10_{C\text{-}Te}$

A two-necked flask was loaded with 5-bromothiophene-2-carboxylic acid (720 mg, 3.5 mmol) under N_2. The solid was dissolved in $SOCl_2$ (5 mL), then the mixture was heated to reflux and stirred overnight. The system was allowed to cool down to room temperature and the solvent was removed under vacuum. To a solution of the resulting acyl chloride in dry CH_2Cl_2 (4 mL), a solution of 2-(methyltellanyl)aniline **$7_{C\text{-}Te}$** (820 mg, 3.5 mmol) and dry NEt_3 (390 mg, 0.54 mL, 3.85 mmol) in dry CH_2Cl_2 (6 mL) was added dropwise at 0 °C. The reaction stirred at 0°C for 5 minutes, then at room temperature for 3 hours. The system was diluted with EtOAc (30 mL), washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The crude was washed with Et_2O (2 × 20 mL) to give pure **$10_{C\text{-}Te}$** as a beige powder (670 mg, 45% yield). m.p: 126-127 °C (from $CHCl_3$); IR (ATR) ν_{max} (cm^{-1}): 3219 (m, NH), 2363 (w), 1624 (s, C=O), 1530 (s), 1460 (s), 1323 (m), 1292 (m), 1225 (w), 1119 (m), 1088 (w), 974 (m), 833 (m), 797 (m), 740 (s), 708 (m), 646 (m), 576 (m), 451 (m); ^{1}H-NMR (400 MHz, DMSO-d_6) δ_H: 10.33 (s, 1H, O=C-NH), 7.79 (bs, 1H, ArH), 7.64 (d, J = 7.5 Hz, 1H, ArH), 7.38 (d, J = 4.0 Hz, 1H, ArH), 7.29 – 7.25 (m, 2H, ArH),

7.18 – 7.15 (m, 1H, ArH), 2.02 (s, 3H, Me); ^{13}C-NMR (100 MHz, DMSO-d_6) δ_C: 159.1, 141.0, 139.4, 135.4, 131.8, 130.0, 127.4, 1273, 126.5, 117.7, 116.3, -15.8; API-HRMS: $[M+H]^+$ calcd for $[C_{12}H_{11}NOSBr^{122}Te]^+$: 417.8775; found: 417.8774.

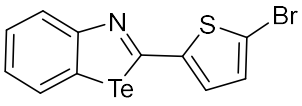
2.20. Synthesis of 5-bromo-*N*-(2-(methyltellanyl)pyridin-3-yl)thiophene-2-carboxamide $\mathbf{10_{N\text{-}Te}}$



$\mathbf{10_{N\text{-}Te}}$

A two-necked flask was loaded with 5-bromothiophene-2-carboxylic acid (390 mg, 1.88 mmol) under N_2. The solid was dissolved in $SOCl_2$ (3 mL), then the mixture was heated to reflux and stirred overnight. The system was allowed to cool down to room temperature and the solvent was removed under vacuum. To a solution of the resulting acyl chloride in dry CH_2Cl_2 (3 mL), a solution of 2-(methyltellanyl)pyridin-3-amine $\mathbf{7_{N\text{-}Te}}$ (370 mg, 1.57 mmol) and dry pyridine (137 mg, 0.14 mL, 1.73 mmol) in dry CH_2Cl_2 (4 mL) was added dropwise at 0 °C. The reaction was stirred at 0°C for 5 minutes, then at room temperature overnight. The system was diluted with EtOAc (30 mL), washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered and the solvents removed under reduced pressure. The crude was washed with Et_2O (2 × 20 mL) to give pure $\mathbf{10_{N\text{-}Te}}$ as a beige powder (290 mg, 36% yield). m.p.: 145 °C (from $CHCl_3$); IR (ATR) ν_{max} (cm^{-1}): 3215 (m, NH), 2980 (w, Alk), 2571 (w), 1628 (C=O), 1568 (m), 1526 (m), 1497 (s), 1410 (s), 1387 (s), 1323 (m), 1289 (m), 1063 (m), 978 (m), 812 (m), 785 (s), 725 (m), 653 (m), 586 (m); ^{1}H-NMR (400 MHz, DMSO-d_6) δ_H: 10.39 (s, 1H, O=C-NH), 8.45 (dd, J = 4.7, 1.6 Hz, 1H, ArH), 7.82 (d, J = 3.9 Hz, 1H, ArH), 7.54 (dd, J = 7.9, 1.6 Hz, 1H, ArH), 7.40 (d, J = 3.9 Hz, 1H, ArH), 7.23 (dd, J = 7.9, 4.7 Hz, 1H, ArH), 2.15 (s, 3H, Me); ^{13}C-NMR (100 MHz, DMSO-d_6) δ_C: 159.4, 148.8, 143.3, 140.5, 137.0, 133.9, 131.9, 130.4, 120.9, 118.2, -14.7; ESI-HRMS: $[M+H]^+$ calcd for $[C_{11}H_{10}N_2OS^{79}Br^{122}Te]^+$: 418.8728; found: 418.8733.

2.21. Synthesis of 2-(5-bromothiophen-2-yl)benzo[d][1,3]tellurazole $\mathbf{11_{C\text{-}Te}}$

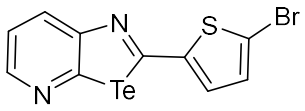


$\mathbf{11_{C\text{-}Te}}$

To a solution of 5-bromo-*N*-(2-(methyltellanyl)phenyl)thiophene-2-carboxamide $\mathbf{10_{C\text{-}Te}}$ (770 mg, 1.8 mmol) and NEt_3 (1.09 g, 1.4 mL, 10.8 mmol) in dry 1,4-dioxane (36 mL) under N_2, $POCl_3$ (830 mg, 0.52 mL, 3.6 mmol) was added dropwise at room temperature, the reaction was heated to reflux and stirred overnight. The mixture was diluted with $CHCl_3$ (20 mL), washed with a saturated solution of $NaHCO_3$ (3 × 30 mL) and the aqueous phase extracted with $CHCl_3$ (3 × 50 mL). The combined organic extracts were washed with water (20

mL) and brine (20 mL), dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH 1%) to give pure **$11_{C\text{-}Te}$** as a yellow solid (570 mg, 81% yield). m.p.: 137-138 °C (from $CHCl_3$); IR (ATR) ν_{max} (cm^{-1}): 3046 (w, Ar), 1740 (w), 1578 (w), 1479 (m), 1418 (s), 1292 (s), 1206 (s), 1111 (m), 970 (m), 874 (s), 799 (m), 785 (s), 756 (m), 708 (m), 606 (w), 573 (m); ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 8.10 (ddd, J = 8.0, 1.3, 0.4 Hz, 1H, ArH), 7.85 (ddd, J = 8.0, 1.3, 0.4 Hz, 1H, ArH), 7.46 – 7.43 (m, 1H, ArH), 7.18 (d, J = 4.0 Hz, 1H, ArH), 7.17 – 7.14 (m, 1H, ArH), 7.07 (d, J = 4.0 Hz, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: 161.3, 161.1, 147.3, 133.7, 131.6, 130.8, 130.5, 127.4, 126.4, 125.4, 118.0; EI-HRMS: $[M]^+$ calcd for $[C_{11}H_6NSBr^{130}Te]^+$: 392.8467; found: 392.8449. Crystal suitable for X-Ray diffraction was obtained by slow evaporation of solvent from a $CHCl_3$ solution.

2.22. Synthesis of 2-(5-bromothiophen-2-yl)-[1,3]tellurazolo[5,4-β]pyridine $11_{N\text{-}Te}$



$11_{N\text{-}Te}$

To a solution of 5-bromo-*N*-(2-(methyltellanyl)pyridin-3-yl)thiophene-2-carboxamide **$10_{N\text{-}Te}$** (325 mg, 0.77 mmol) and NEt_3 (940 mg, 1.2 mL, 9.24 mmol) in dry 1,4-dioxane (15 mL) under N_2, $POCl_3$ (710 mg, 0.44 mL, 3.08 mmol) was added dropwise at room temperature, the reaction was heated to reflux and stirred overnight. The mixture was diluted with $CHCl_3$ (20 mL), washed with a saturated solution of $NaHCO_3$ (3 x 30 mL) and the aqueous phase extracted with $CHCl_3$ (3 x 50 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH 1%) to give pure **$11_{N\text{-}Te}$** as a yellow solid (200 mg, 66% yield). m.p.: 206-207 °C (from $CHCl_3$); IR (ATR) ν_{max} (cm^{-1}): 3061 (w, Ar), 1917 (w), 1570 (w), 1468 (m), 1362 (s), 1271 (m), 1204 (m), 1105 (m), 1053 (w), 975 (m), 791 (s), 723 (s), 656 (m), 455 (m), 430 (w); ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 8.43 (dd, J = 4.6, 1.6 Hz, 1H, ArH), 8.21 (dd, J = 8.1, 1.6 Hz, 1H, ArH), 7.40 (dd, J = 8.1, 4.6 Hz, 1H, ArH), 7.25 (d, J = 4.0 Hz, 1H, ArH), 7.10 (d, J = 4.0 Hz, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: 165.6, 162.8, 157.1, 147.4, 146.4, 131.9, 131.2, 131.0, 122.1, 119.1; EI-HRMS: $[M]^+$ calcd for $[C_{10}H_5N_2SBr^{130}Te]^+$: 393.8419; found: 393.8405. Crystal suitable for X-Ray diffraction was obtained by slow evaporation of solvent from a $CHCl_3$ solution.

3. ^{1}H and ^{13}C spectra

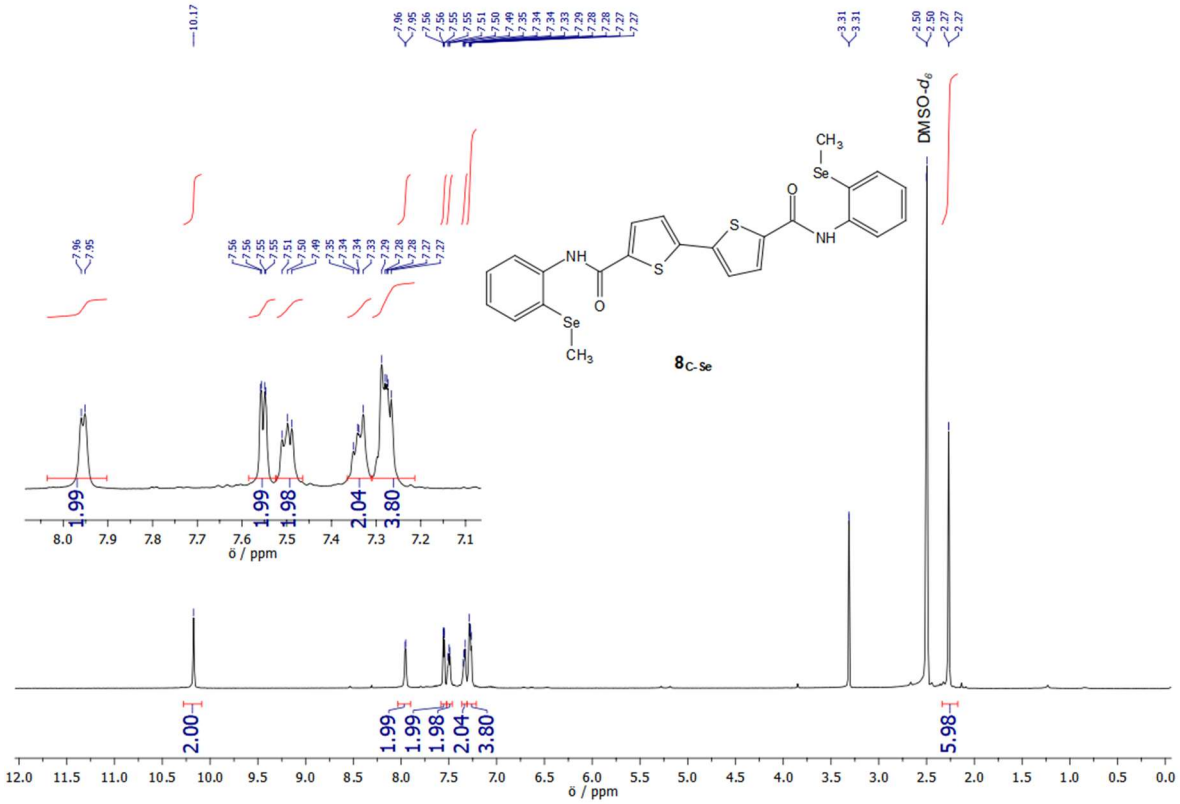


Figure 1S – 400 MHz ^{1}H-NMR in DMSO-d_6 of molecule $\mathbf{8}_{\mathbf{C\text{-}Se}}$.

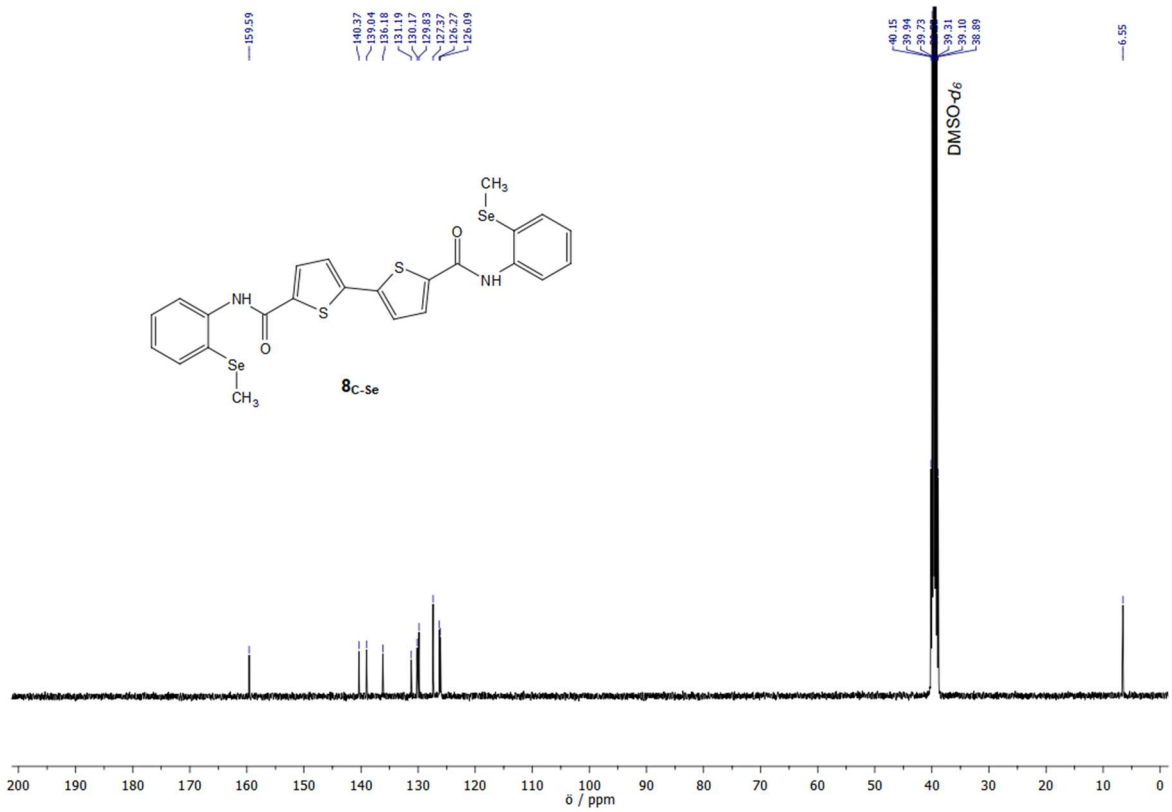


Figure 2S – 100 MHz ^{13}C-NMR in DMSO-*d*$_6$ of molecule **8**$_{C\text{-}Se}$.

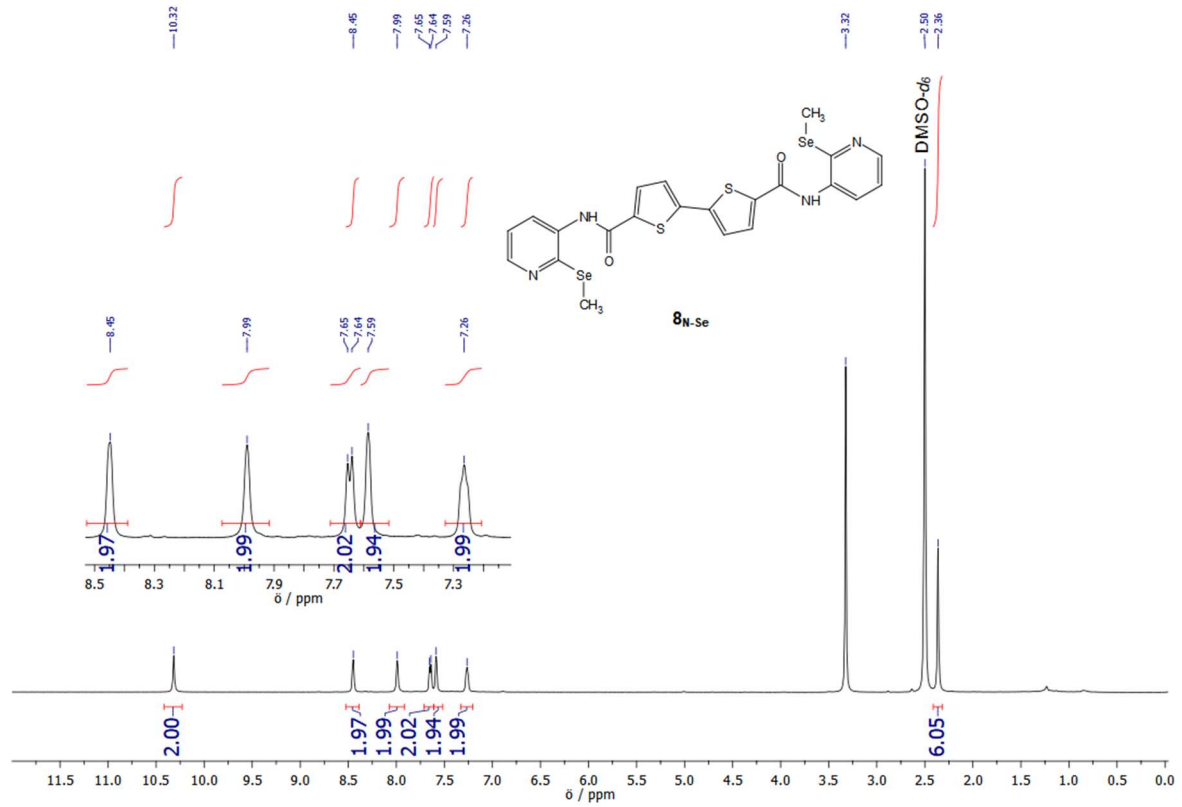


Figure 3S – 500 MHz ^{1}H-NMR in DMSO-*d*$_6$ of molecule **8**$_{N\text{-}Se}$.

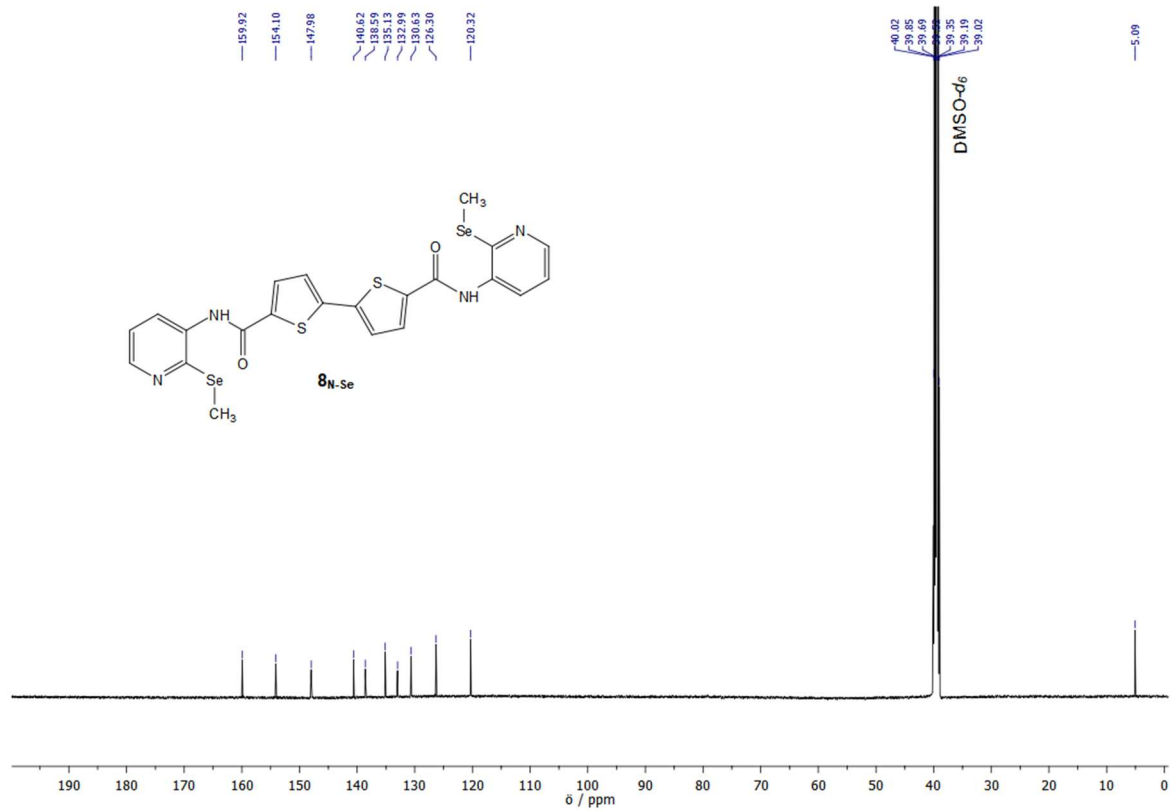


Figure 4S – 125 MHz ^{13}C-NMR in DMSO-*d*$_6$ of molecule **8**$_{N\text{-}Se}$.

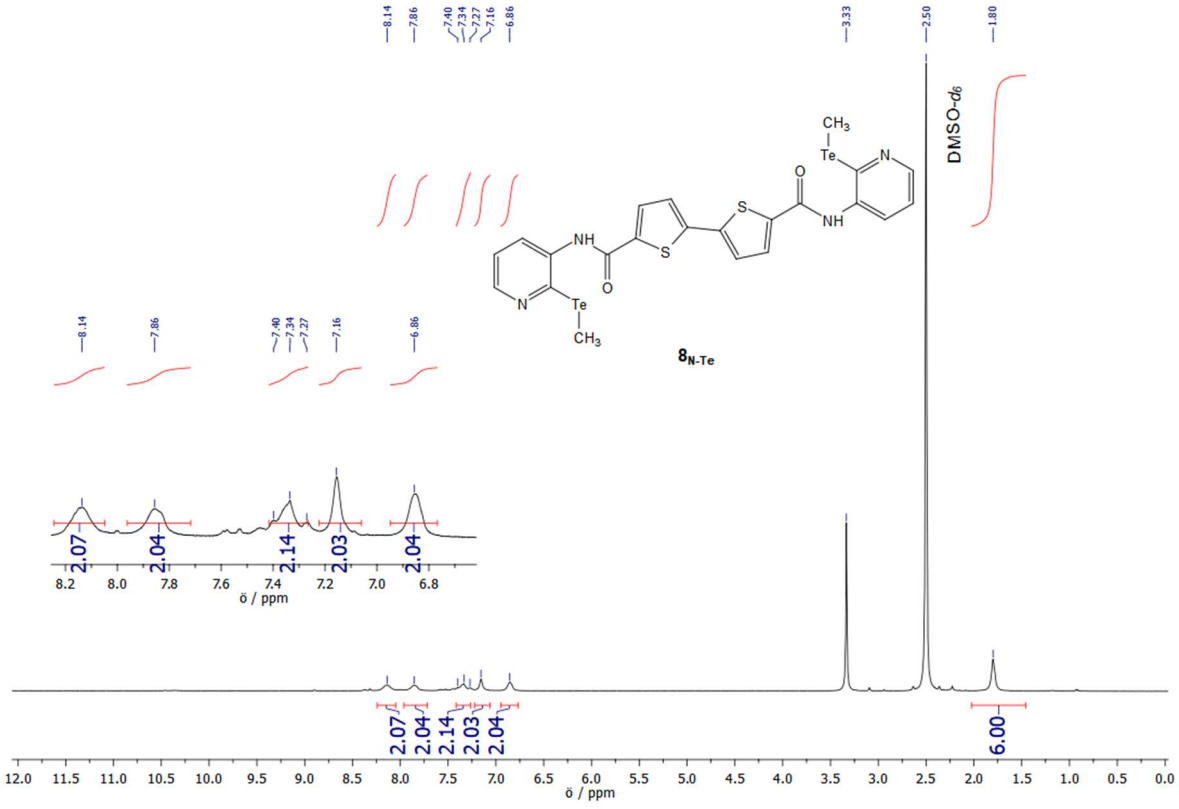


Figure 5S – 500 MHz ^{1}H-NMR in DMSO-*d*$_6$ of molecule **8**$_{N\text{-}Te}$.

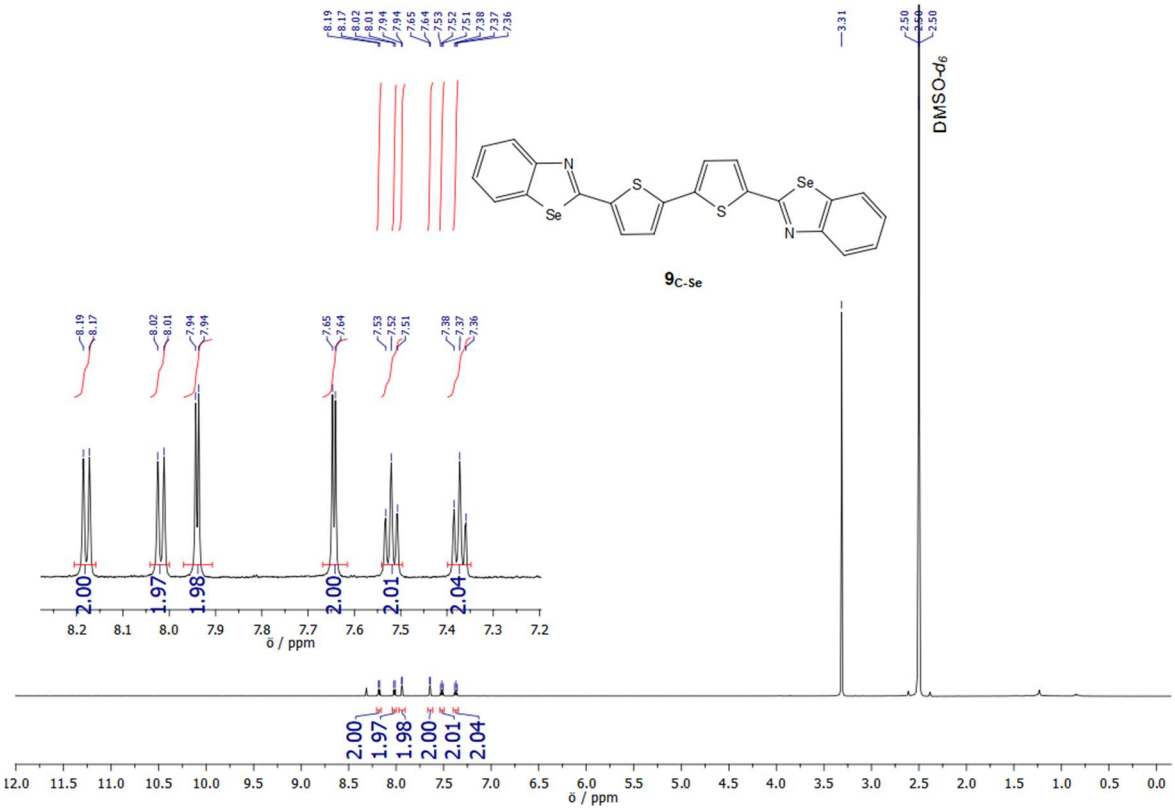


Figure 6S – 600 MHz ^{1}H-NMR in DMSO-d_6 of $\mathbf{9}_{\text{C-Se}}$.

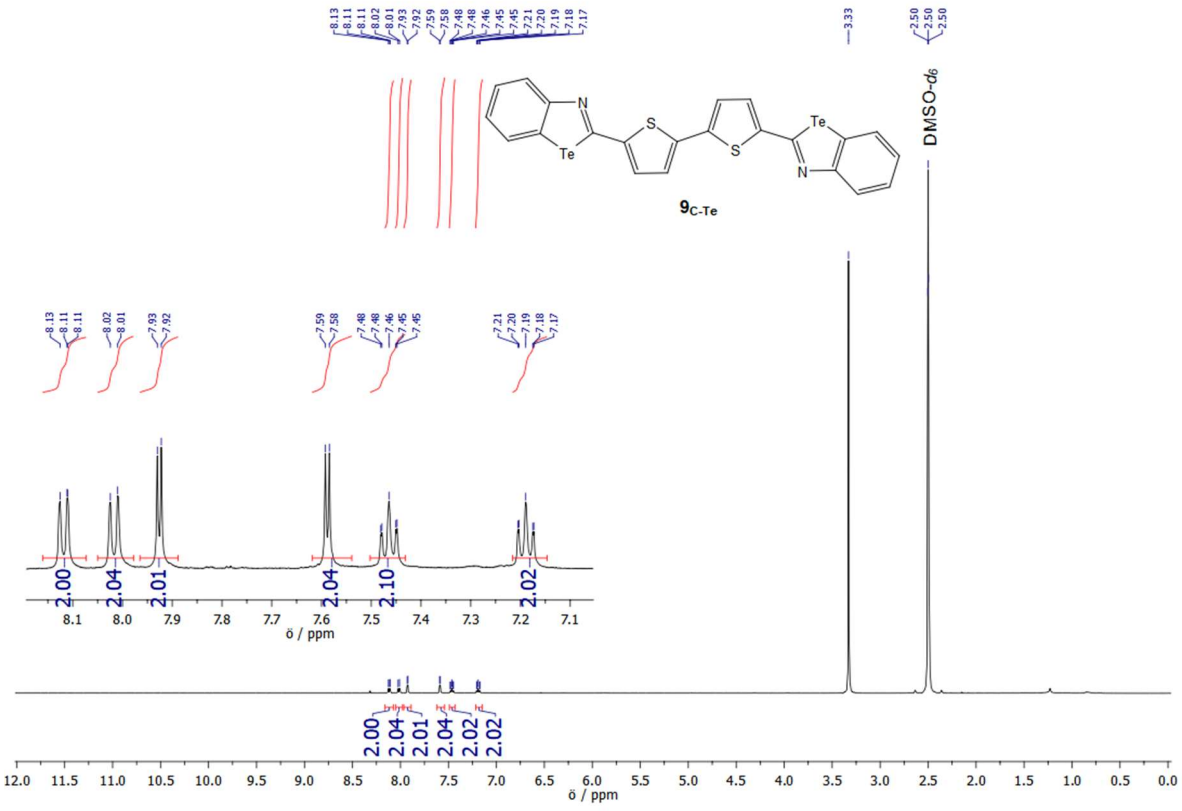


Figure 7S – 500 MHz ^{1}H-NMR in DMSO-d_6 of molecule $\mathbf{9}_{\text{C-Te}}$.

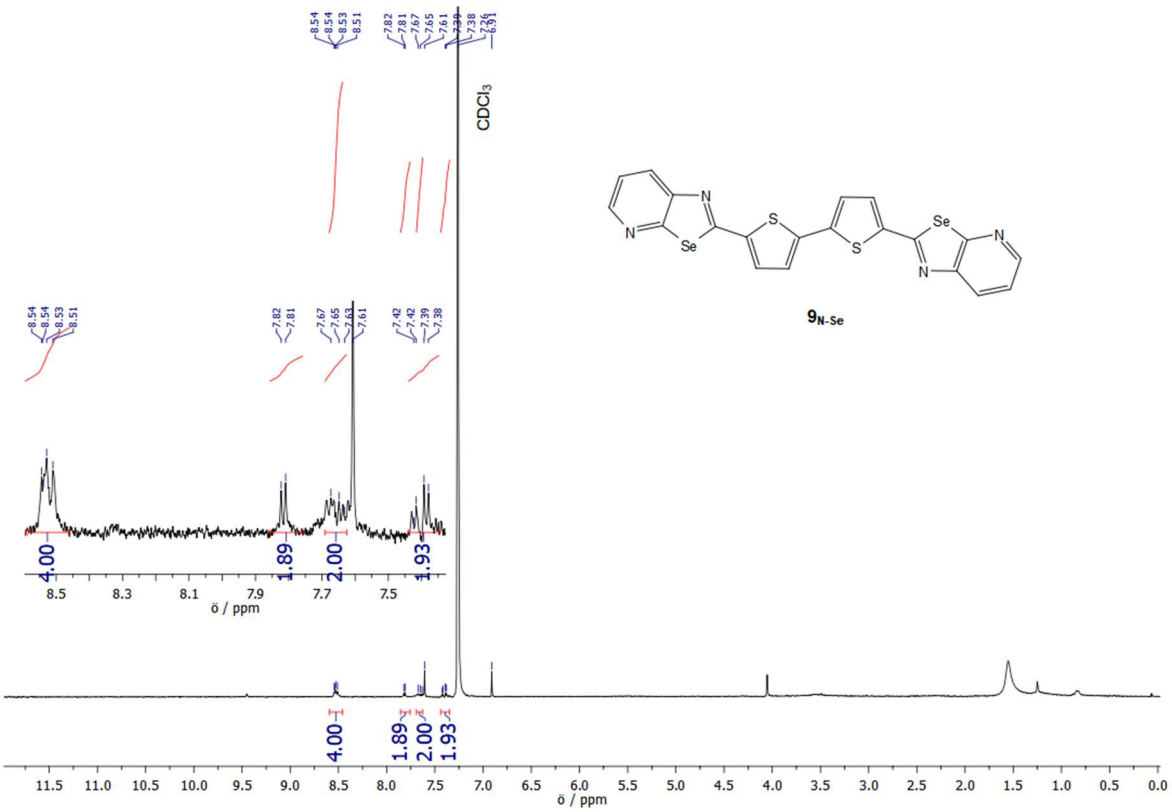


Figure 8S – 300 MHz ^{1}H-NMR in $CDCl_3$ of molecule $\mathbf{9_{N\text{-}Se}}$.

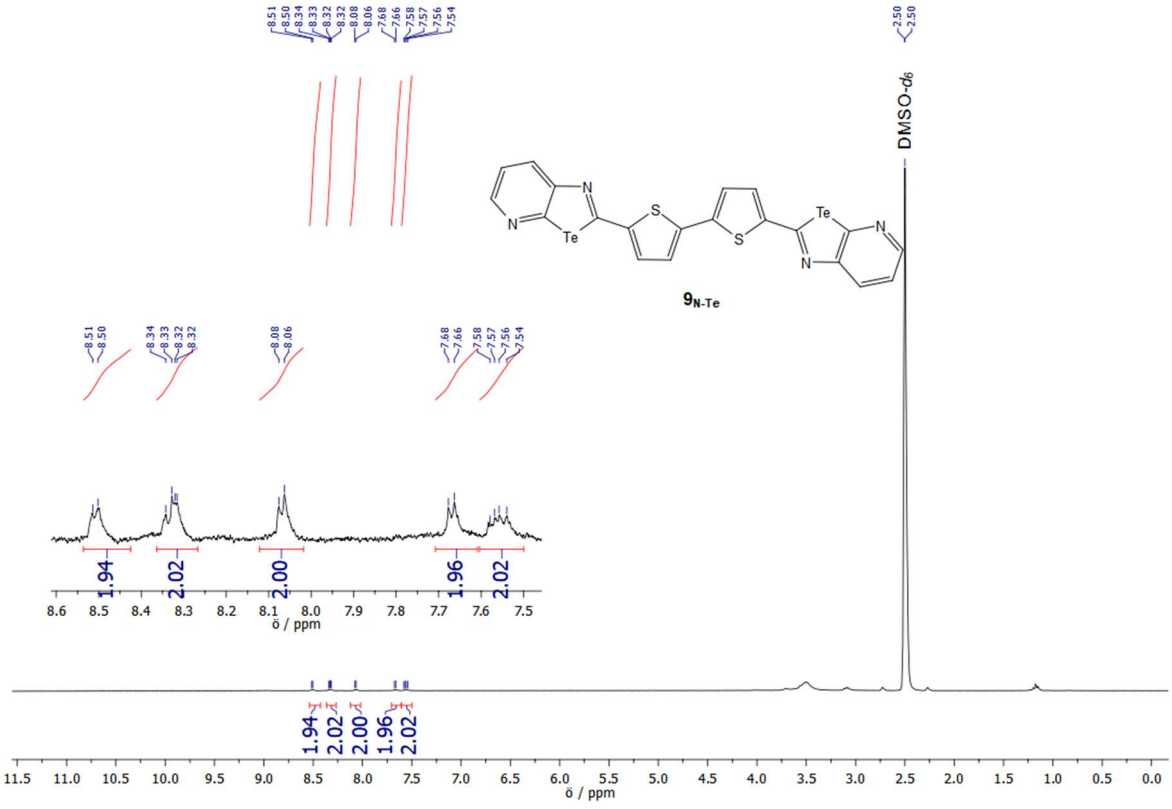


Figure 9S – 300 MHz ^{1}H-NMR in DMSO-d_6 of molecule $\mathbf{9_{N\text{-}Te}}$.

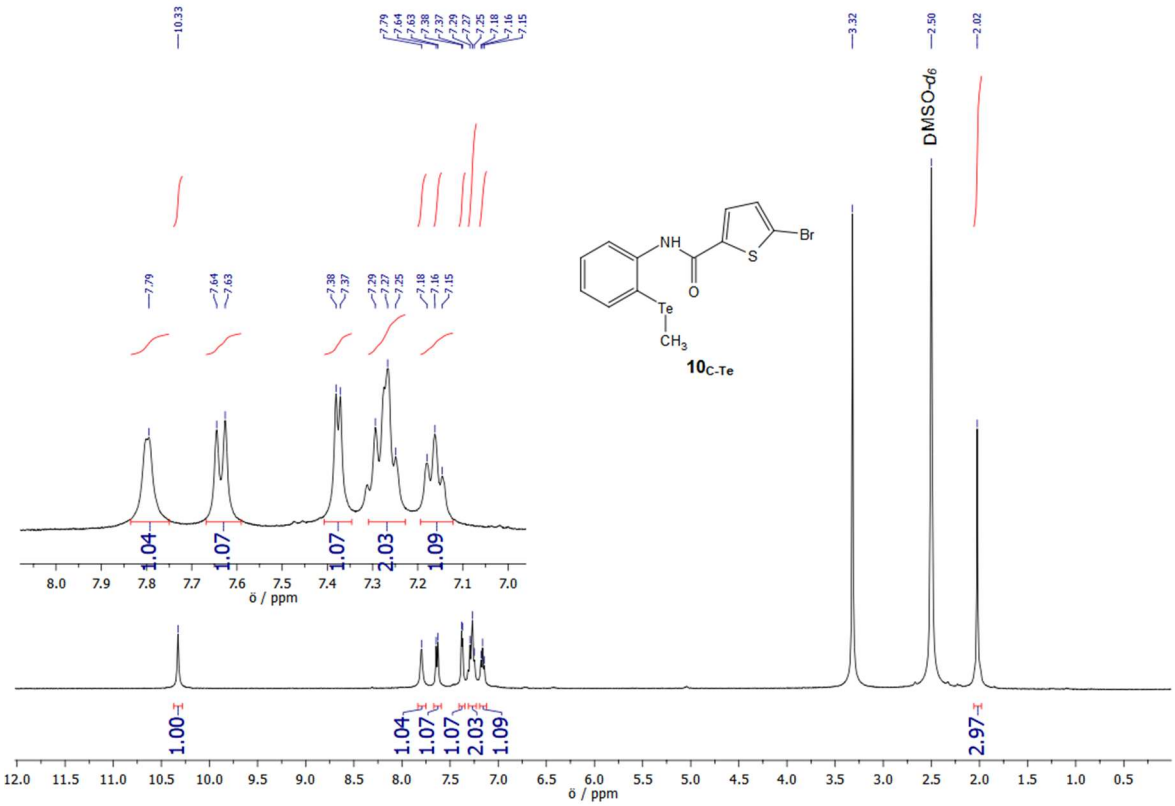


Figure 10S – 400 MHz ^{1}H-NMR in DMSO-*d*$_6$ of molecule **10**$_{\text{C-Te}}$.

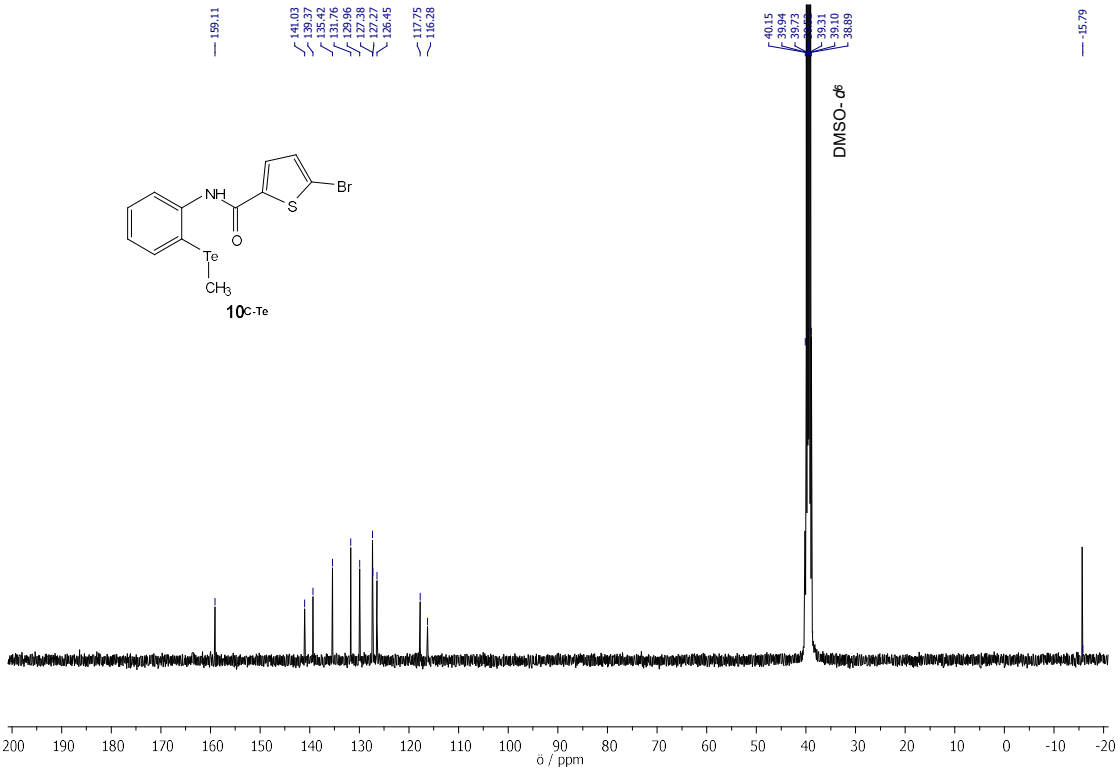


Figure 11S – 100 MHz ^{13}C-NMR in DMSO-*d*$_6$ of molecule **10**$_{\text{C-Te}}$.

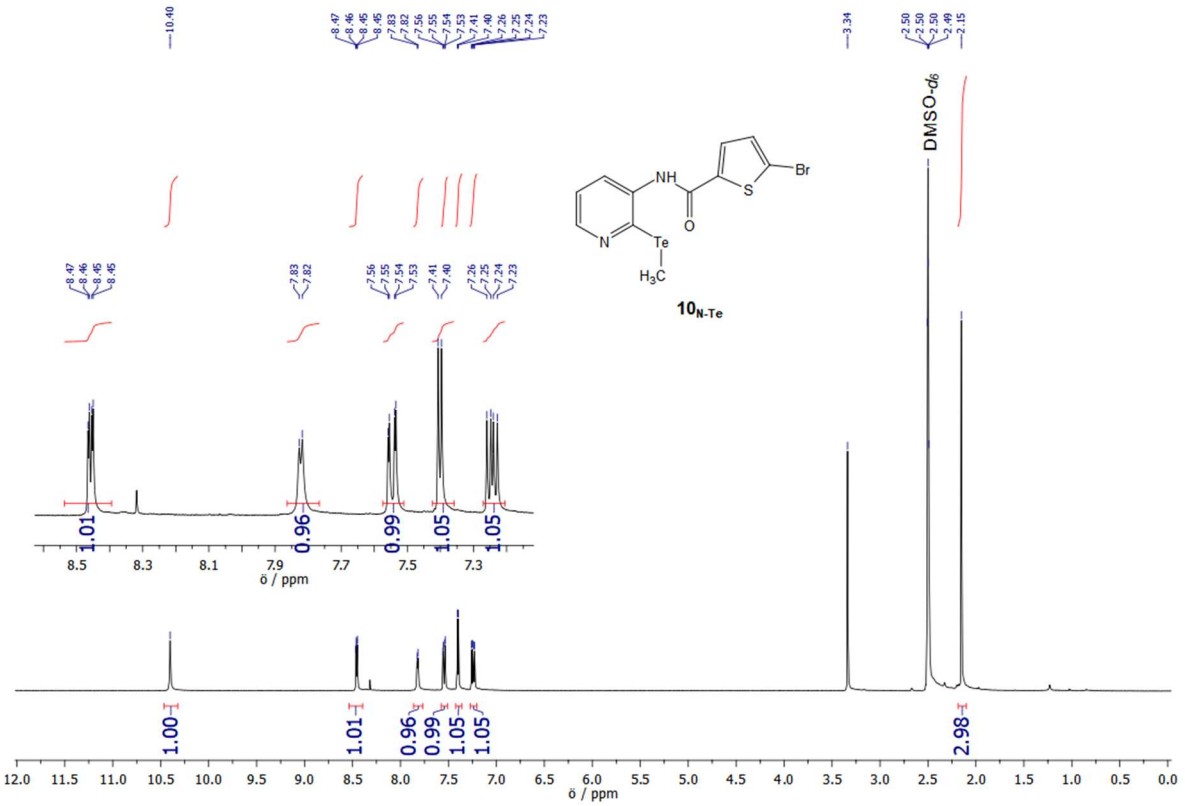


Figure 12S – 400 MHz ^{1}H-NMR in DMSO-*d*$_6$ of molecule **10$_{N\text{-}Te}$**.

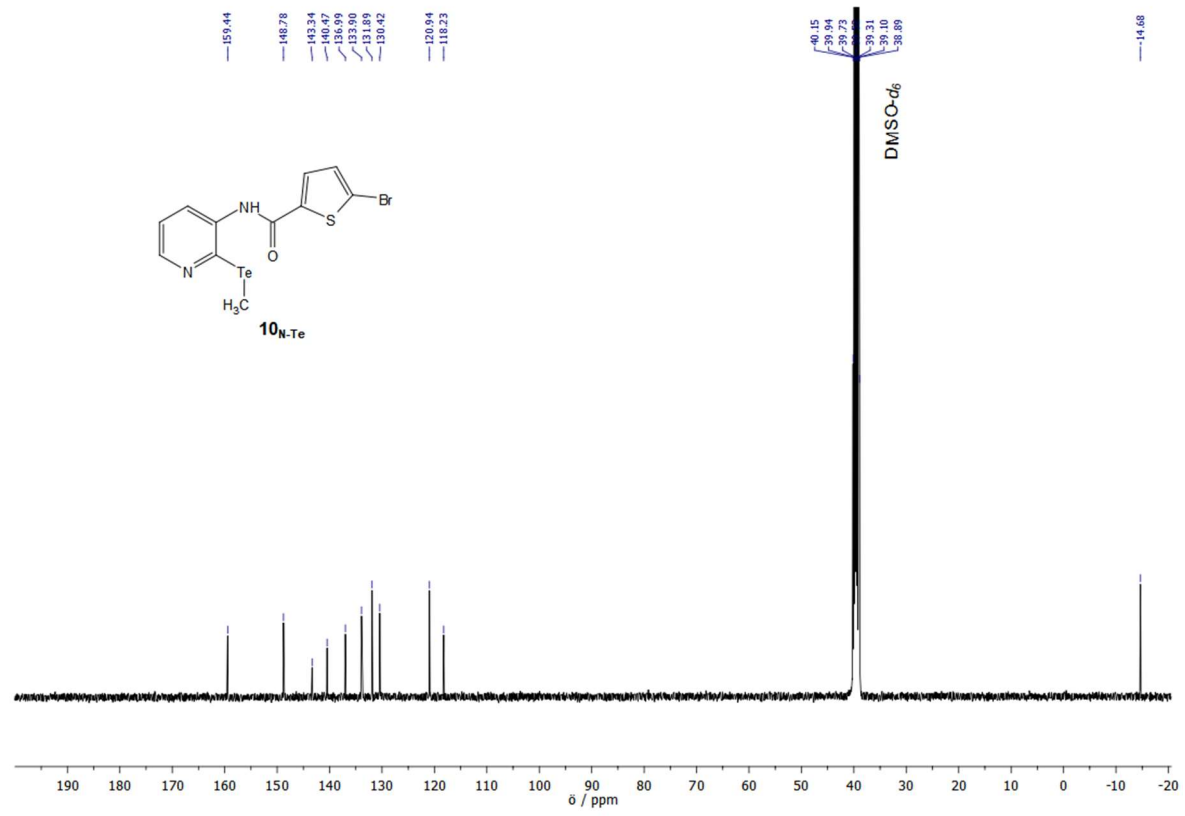


Figure 13S – 100 MHz ^{13}C-NMR in DMSO-*d*$_6$ of molecule **10$_{N\text{-}Te}$**.

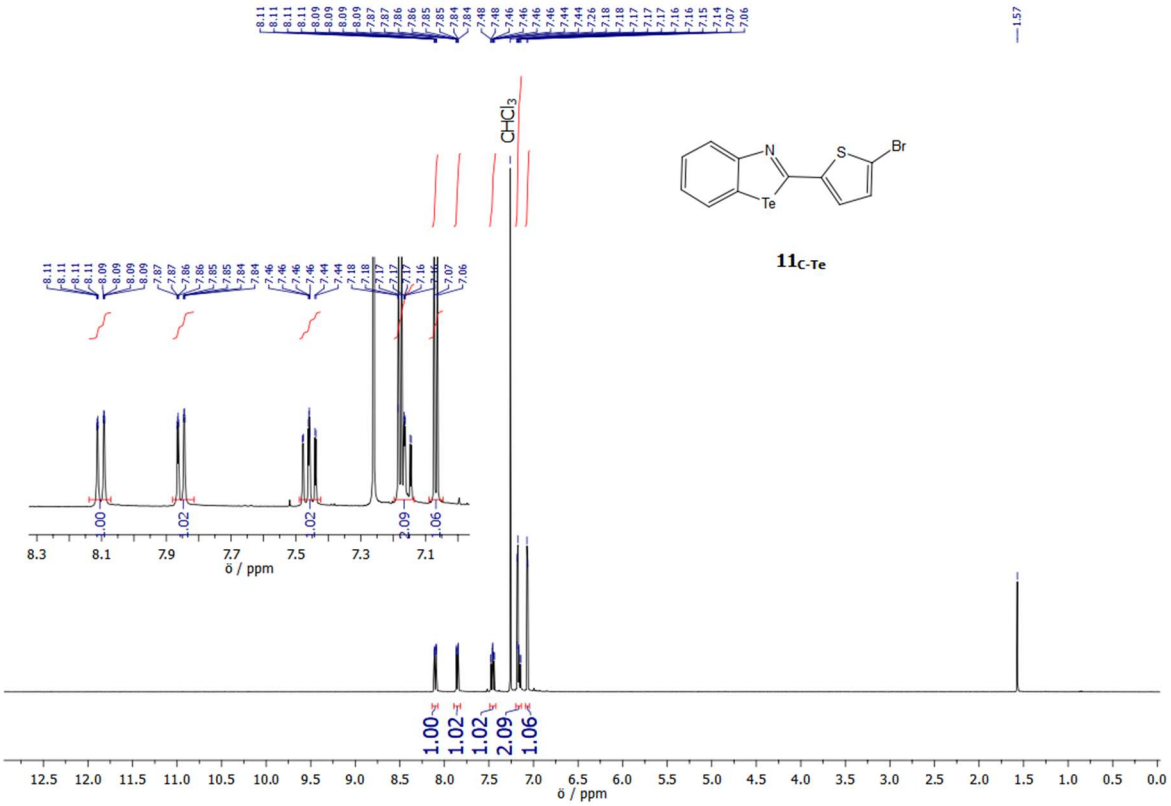


Figure 14S – 400 MHz ^{1}H-NMR in $CDCl_3$ of molecule **11$_{C\text{-}Te}$**.

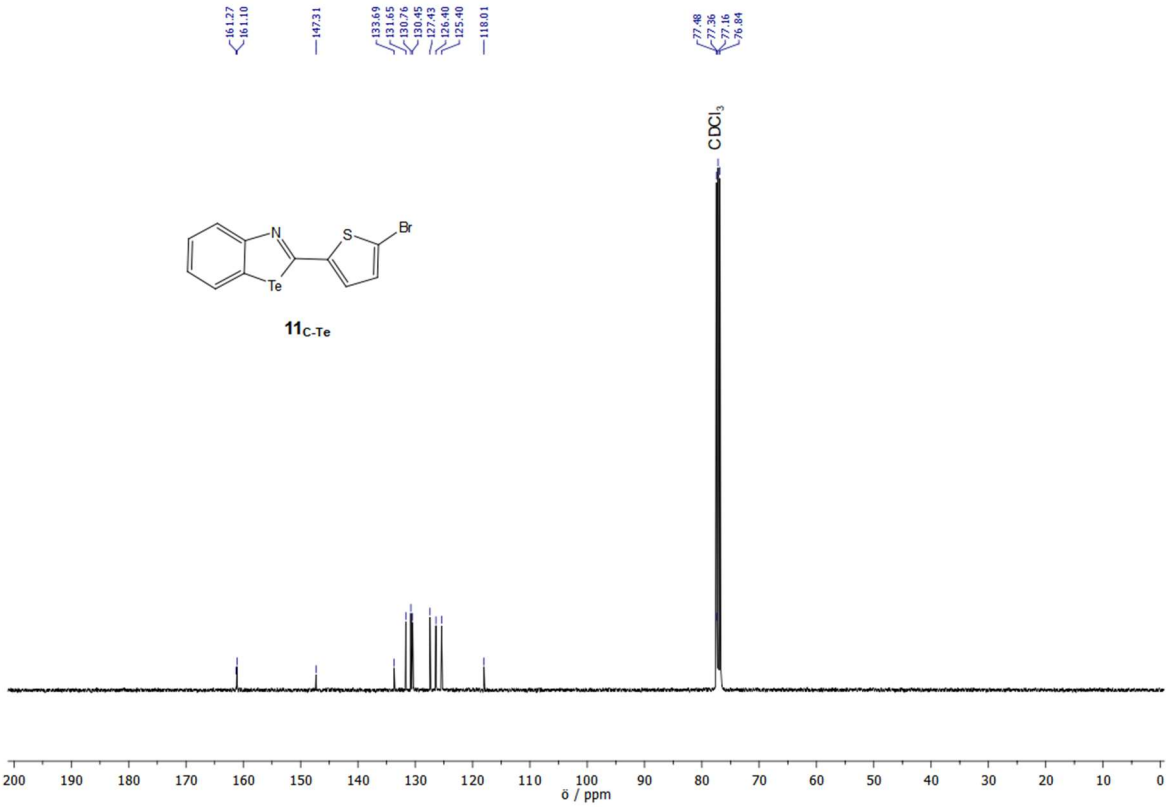


Figure 15S – 100 MHz ^{13}C-NMR in $CDCl_3$ of molecule **11$_{C\text{-}Te}$**.

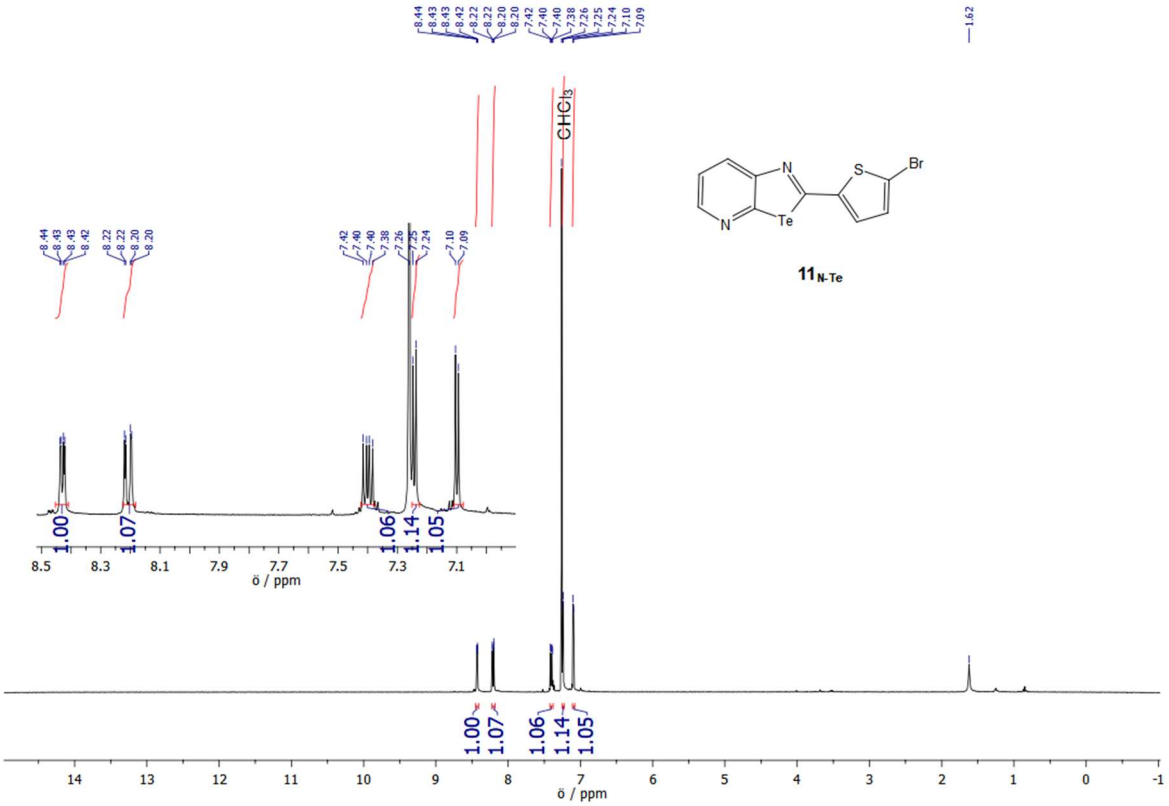


Figure 16S – 400 MHz ^{1}H-NMR in $CDCl_3$ of molecule $\mathbf{11_{N\text{-}Te}}$.

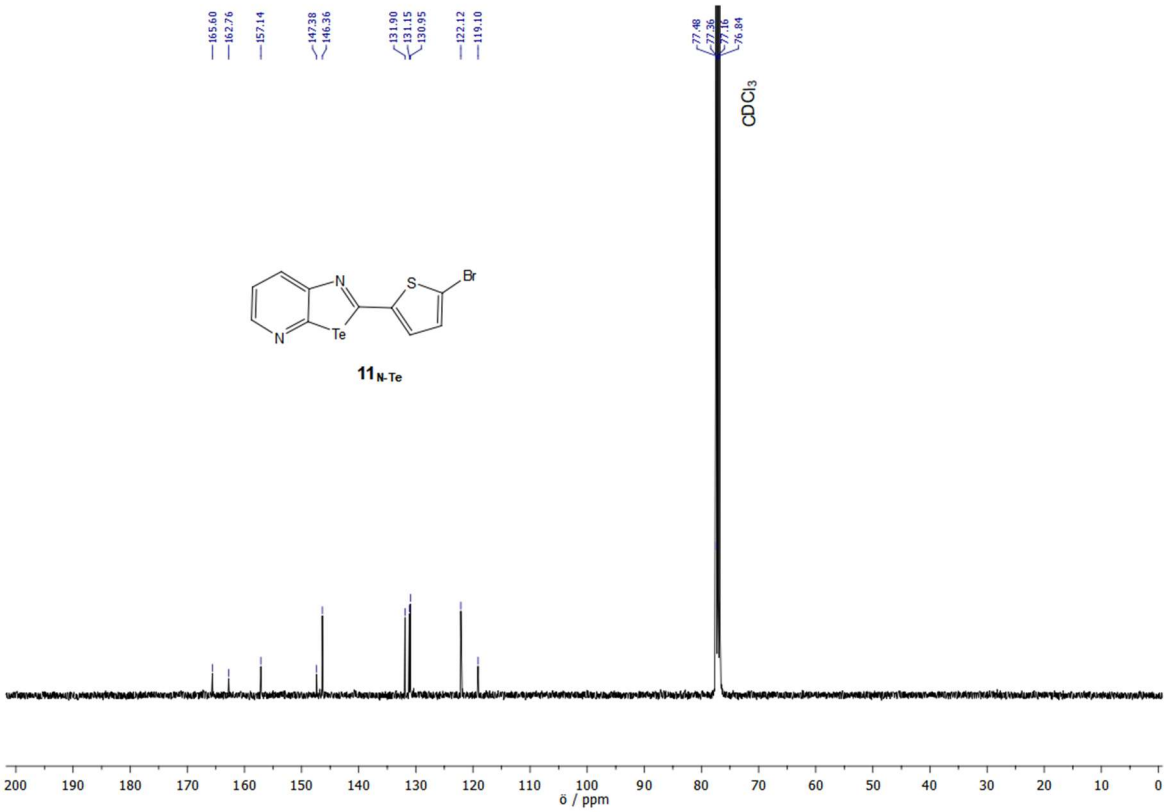
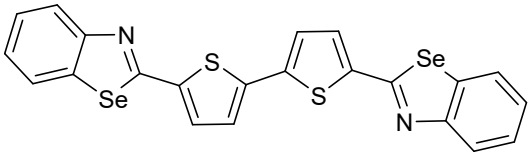


Figure 17S – 100 MHz ^{13}C-NMR in $CDCl_3$ of molecule $\mathbf{11_{N\text{-}Te}}$.

4. Crystal data and structure refinement

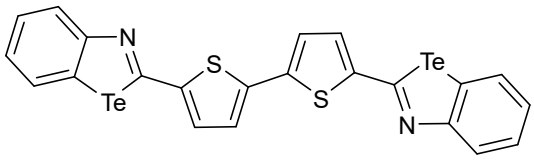
Table S1. Crystal data and structure refinement for **9**$_{C\text{-}Se}$ (1970771).



9$_{C\text{-}Se}$

Crystal data		
Empirical formula	C_{12} H_7 Cl_3 N S Se	
Formula weight	382.56	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.9982(6) Å	α = 71.952(8)°.
	b = 10.1384(8) Å	β = 82.221(8)°.
	c = 12.3690(12) Å	γ = 73.411(8)°.
Volume	684.50(12) Å^3	
Z	2	
Density (calculated)	1.856 Mg/m^3	
Absorption coefficient	3.459 mm^{-1}	
F(000)	374	
Crystal size	0.887 x 0.083 x 0.050 mm^3	
Data collection		
Temperature	150(2) K	
Wavelength	0.71073 Å	
Theta range for data collection	3.469 to 29.843°.	
Index ranges	-8<=h<=8, -13<=k<=13, -16<=l<=16	
Reflections collected	5201	
Independent reflections	3207 [R(int) = 0.0401]	
Completeness to theta = 25.242°	99.7 %	
Refinement		
Absorption correction	Gaussian	
Max. and min. transmission	0.994 and 0.952	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3207 / 0 / 163	
Goodness-of-fit on F^2	1.096	
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.0767	
R indices (all data)	R1 = 0.0671, wR2 = 0.0932	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.573 and -0.642 e.Å^{-3}	

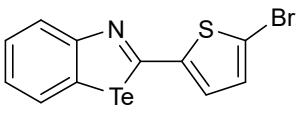
Table S2. Crystal data and structure refinement for **9**$_{C\text{-}Te}$ (1970772).



9$_{C\text{-}Te}$

Crystal data		
Empirical formula	$C_{22}H_{12}N_2S_2Te_2$	
Formula weight	623.66	
Crystal system	Monoclinic	
Space group	P $2_1/c$	
Unit cell dimensions	a = 20.6424(7) Å	α = 90°.
	b = 4.15880(10) Å	β = 91.535(3)°.
	c = 11.6051(4) Å	γ = 90°.
Volume	995.91(5) Å^3	
Z	2	
Density (calculated)	2.080 Mg/m^3	
Absorption coefficient	3.150 mm^{-1}	
F(000)	588	
Crystal size	0.167 x 0.118 x 0.018 mm^3	
Data collection		
Temperature	150(2) K	
Wavelength	0.71073 Å	
Theta range for data collection	3.512 to 29.713°.	
Index ranges	-28<=h<=27, -5<=k<=5, -15<=l<=15	
Reflections collected	15566	
Independent reflections	2596 [R(int) = 0.0282]	
Completeness to theta = 25.242°	99.8 %	
Refinement		
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.837	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2596 / 0 / 127	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0221, wR2 = 0.0450	
R indices (all data)	R1 = 0.0319, wR2 = 0.0491	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.358 and -0.386 e.Å^{-3}	

Table S3. Crystal data and structure refinement for **11**$_{C\text{-}Te}$ (1970774).



11$_{C\text{-}Te}$

Crystal data

Empirical formula	C_{11} H_6 Br N S Te	
Formula weight	391.74	
Crystal system	Orthorhombic	
Space group	P n a 2_1	
Unit cell dimensions	a = 11.2104(6) Å	a = 90°.
	b = 4.0802(2) Å	b = 90°.
	c = 48.882(3) Å	γ = 90.000(6)°.
Volume	2235.9(2) Å^3	
Z	8	
Density (calculated)	2.327 Mg/m^3	
Absorption coefficient	6.384 mm^{-1}	
F(000)	1456	
Crystal size	0.164 x 0.108 x 0.084 mm^3	

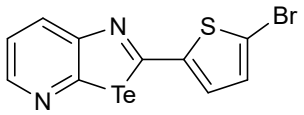
Data collection

Temperature	150(2) K
Wavelength	0.71073 Å
Theta range for data collection	3.334 to 29.798°.
Index ranges	-15<=h<=14, -5<=k<=4, -42<=l<=66
Reflections collected	7650
Independent reflections	3971 [R(int) = 0.0553]
Completeness to theta = 25.242°	99.9 %

Refinement

Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.935
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3971 / 7 / 271
Goodness-of-fit on F^2	1.056
Final R indices [I>2sigma(I)]	R1 = 0.0683, wR2 = 0.1513
R indices (all data)	R1 = 0.0918, wR2 = 0.1740
Extinction coefficient	n/a
Largest diff. peak and hole	4.231 and -2.153 e.Å^{-3}

Table S4. Crystal data and structure refinement for **11**$_{N\text{-}Te}$ (1970773).



11$_{N\text{-}Te}$

Crystal data

Empirical formula	C_{10} H_5 Br N_2 S Te	
Formula weight	392.73	
Crystal system	Orthorhombic	
Space group	P b c n	
Unit cell dimensions	a = 11.9421(6) Å	a= 90°.
	b = 7.2245(4) Å	b= 90°.
	c = 24.8025(11) Å	g = 90°.
Volume	2139.85(19) Å^3	
Z	8	
Density (calculated)	2.438 Mg/m^3	
Absorption coefficient	6.673 mm^{-1}	
F(000)	1456	
Crystal size	0.120 x 0.063 x 0.063 mm^3	

Data collection

Temperature	150(2) K
Wavelength	0.71073 Å
Theta range for data collection	3.285 to 29.800°.
Index ranges	-16<=h<=12, -9<=k<=9, -23<=l<=34
Reflections collected	7594
Independent reflections	2621 [R(int) = 0.0260]
Completeness to theta = 25.242°	99.9 %

Refinement

Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.728
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2621 / 0 / 136
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0253, wR2 = 0.0485
R indices (all data)	R1 = 0.0346, wR2 = 0.0516
Extinction coefficient	n/a
Largest diff. peak and hole	0.549 and -0.743 e.Å^{-3}

5. Reference

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