

Supporting Information

Linear and angular heteroacenes from double-electrophilic-cyclization (DEC) and DEC-reductive-elimination of diynes

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Experimental details:

All reactions were performed under an inert atmosphere of anhydrous N₂ (g), unless otherwise stated. Solvents used for various reactions were dried using a commercial solvent purification system. 1,2-Dichloroethane (DCE) was purchased in an anhydrous form and stored under nitrogen. Solvents used in reaction extractions and chromatography and all other reagents were used as supplied by commercial vendors without further purifications or drying. Petroleum spirits with a boiling point range of 40–60 °C was used in chromatography. Column (flash) chromatography was performed on either 40–60 or 20–40 micron silica gel. ¹H NMR spectra were recorded at 300 or 400 MHz, as indicated. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets, dt = doublet of triplets. ¹³C NMR spectra were recorded at 75 or 101 MHz, as indicated. ⁷⁷Se NMR and ¹²⁵Te NMR spectra were recorded at 76.3 and 126.30 MHz, respectively. All chemical shifts were calibrated using residual non-deuterated solvent as an internal reference and are reported in parts per million (δ) relative to trimethylsilane (δ = 0). Thin layer chromatography (TLC) was performed using 0.25 mm thick plates pre-coated with Merck Kieselgel 60 F₂₅₄ silica gel, and visualised using UV light (254 nm and 365 nm). Melting points were measured using a Gallenkamp MPD350 digital melting point apparatus and are uncorrected. For high-resolution mass spectra (HRMS), atmospheric-pressure chemical ionization (APCI) experiments were carried out on a Thermo Scientific Q-Exactive FTMS, ionizing by APCI from an atmospheric solids analysis probe (ASAP).

The following materials were prepared according to literature procedures: SCl₂,^{S1} SeCl₂,^{S2} methyl(2-(phenylethynyl)phenyl)sulfane (**6**),^{S3} (2-ethynylphenyl)(methyl)sulfane (**9**),^{S3} and (2-iodophenyl)(methyl)selane (**19**).^{S4}

Synthetic procedures:

Bis(2-phenylbenzo[*b*]thiophen-3-yl)sulfane (7a)

Methyl(2-(phenylethynyl)phenyl)sulfane (**6**) (150 mg, 0.67 mmol) was dissolved in anhydrous DCE (12.0 mL) and the resulting yellow solution was heated to 60 °C. Sulfur dichloride (SCl₂) (34 mg, 0.33 mmol) in DCE (5.0 mL) was added dropwise and the resulting red solution was stirred for 5 h. The reaction mixture was cooled to room temperature and was quenched with saturated Na₂S₂O₃ (20.0 mL). The organic layer was separated, washed with water followed by brine, dried over anhydrous MgSO₄, and recovered to get crude mass which was subjected to column chromatography on silica (5% diethyl ether in hexane) to afford title compound **7a** (170 mg, 56.3%) as a light yellow solid: m.p. = 120.5–121.7 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.68 (d, *J* = 8.2 Hz, 2H), 7.52–7.45 (m, 6H), 7.38–7.34 (m, 6H), 7.26–7.22 (m, 2H), 7.18–7.14 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 144.6, 140.7, 138.1, 133.6, 130.1, 128.6, 128.2, 124.7, 124.6, 123.4, 122.1, 120.3; HRMS (APCI): calculated for C₂₈H₁₈S₃ [M]⁺ (m/z) 450.0565; found = 450.0564

Bis(2-phenylbenzo[*b*]thiophen-3-yl)selane (7b)

This material was prepared using the procedure described above for **7a** using compound **6** (100 mg, 0.45 mmol) and selenium dichloride (SeCl₂) (0.23 mmol in tetrahydrofuran). The crude residue was purified by flash chromatography on silica (30% diethyl ether in hexanes) to get 140 mg (62.5%) of **7b** as a yellow solid: m.p. = 115.3–116.7 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.69–7.67 (m, 2H), 7.46–7.42 (m, 4H), 7.40–7.36 (m, 8H), 7.25–7.21 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 2H), 7.15–7.11 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 145.5, 141.7, 138.7, 134.3, 130.3, 128.6, 128.2, 124.6, 124.7, 124.6, 121.9, 116.8; HRMS (APCI): calculated for C₂₈H₁₈S₂[74]Se M⁺ (m/z) 492.0069; found = 492.0075

Bis(2-phenylbenzo[*b*]thiophen-3-yl)tellane (7d)

This material was prepared using the procedure described above for **7a** using compound **6** (80 mg, 0.35 mmol) and tellurium tetrachloride (TeCl₄) (47 mg, 0.18 mmol). The crude residue was purified by flash chromatography on silica (50% diethyl ether in hexanes) to get 131 mg (68.5%) of **7d** as a light yellow solid: m.p. = 229.5–230.4 °C; ¹²⁵Te NMR (126.30 MHz, CDCl₃) δ (ppm): 219.13; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.85–7.83 (d, *J* = 8.2 Hz, 2H), 7.71–7.68 (m, 4H), 7.63–7.59 (m, 6H), 7.35–7.33 (d, *J* = 8.2 Hz, 2H), 7.25–7.21 (m, 2H), 6.91–6.86 (ddd, *J* = 8.2, 7.2, 1.0 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 153.1, 139.8, 139.4, 134.0, 130.8, 129.8, 129.7, 126.3, 125.4, 124.7, 122.2, 119.8; HRMS (APCI): calculated for C₂₈H₁₈S₂Te M⁺ (m/z) 547.9907; found = 547.9897.

2,2'-Diphenyl-3,3'-bibenzo[*b*]thiophene (8)

This material was prepared using the procedure described above for **7a** using compound **6** (56 mg, 0.25 mmol) and gold (III) chloride (AuCl₃) (39 mg in 1:1 solvent mixture of DCE and tetrahydrofuran, 0.13 mmol). The crude residue was purified by column chromatography on silica (10% diethyl ether in hexanes) to get 64 mg (61.2%) of **8** as an off-white solid: m.p. = 148.5–151.4 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.91–7.89 (m, 2H), 7.38–7.34 (m, 4H), 7.27–7.23 (m, 2H), 7.12–7.02 (m, 10H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 142.5, 140.8, 138.9, 134.2, 128.5, 128.3, 127.8, 126.5, 124.7, 124.6, 123.8, 122.3; HRMS (APCI): calculated for C₂₈H₁₈S₂ M⁺ (m/z) 418.0844; found = 418.0845.

1,4-Bis(2-(methylthio)phenyl)buta-1,3-diyne (10)

Copper(II) acetate monohydrate [Cu(CH₃COO)₂·H₂O] (3.23 g, 16.22 mmol) was taken in 1:1 solvent mixture of pyridine and methanol (30 mL), and the resulting blue suspension was heated to 80 °C. To this suspension was added (2-ethynylphenyl)(methyl)sulfane **9** (1.20 g, 8.11 mmol), and the resulting green reaction mixture was heated to reflux for 4 h. The reaction solution was cooled down to 10 °C and was slowly diluted with 2N H₂SO₄ (30 mL) followed by the addition of diethyl ether (50 mL). The organic layer was separated, washed with water twice followed by brine, dried over anhydrous MgSO₄, and recovered to afford title compound **10** (1.47 g, 61.6%) as a light yellow solid: m.p. = 98.6–100.4 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.5 (d, *J* = 8.3 Hz, 2H), 7.40 (dd, *J* = 8.3, 7.6 Hz, 2H), 7.18 (dd, *J* = 8.3, 7.6 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 2.51 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 143.3, 133.7, 129.7, 124.6, 124.5, 120.2, 80.7, 80.0, 15.4; HRMS (APCI): calculated for C₁₈H₁₄S₂ M⁺ (m/z) 294.0531; found = 294.0534.

Bis((2-(methylthio)phenyl)ethynyl)selane (11)

n-Butyllithium (1.10 mL, 2.20 mmol (2.0 M solution in hexanes)) was added dropwise to a solution of (2-ethynylphenyl) (methyl)sulfane **9** (296 mg, 2 mmol) in anhydrous tetrahydrofuran (THF) (10.0 mL) at –78 °C (dry ice-acetone bath) and the resultant yellow suspension left to stir at this temperature for 0.5 h. The dry ice-acetone bath was replaced with ice-bath and the reaction mixture was allowed to warm to 0 °C and stirred for 1 h at this temperature. The reaction mixture was placed back in dry ice-acetone bath and SeCl₂ (1 mmol in THF) was added dropwise, and the resulting reddish reaction mixture was left to stir overnight. Saturated ammonium chloride (20 mL) and diethyl ether (50 mL) were added to the reaction mixture and the organic layer was separated. Organic layer was washed with water (2 × 30 mL) followed by brine (30 mL), dried over anhydrous MgSO₄, and concentrated to a red oil which was subjected to chromatography on silica eluting with 2% diethyl ether in petroleum spirits providing **11** as a dark yellow oil (386 mg, 51% yield). ⁷⁷Se NMR (76.3 MHz, CDCl₃) δ (ppm): 183.79; ¹H NMR (401 MHz, CDCl₃) δ (ppm): 7.44 (dd, *J* = 7.7, 1.1 Hz, 2H), 7.32–7.27 (m, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.09 (t, *J* = 7.7 Hz, 2H), 2.49 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 142.4, 133.0, 129.4, 124.7, 124.4, 121.1, 97.9, 71.5, 15.4; HRMS (APCI): calculated for C₁₈H₁₅S₂[⁷⁴Se] [M+H]⁺ (m/z) 368.9833; found = 368.9834

Bis(benzothieno)[3,2-*b*:2',3'-*d*]thiophene (14a)

Compound **10** (74 mg, 0.25 mmol) and SCl₂ (26 mg, 0.25 mmol) were separately dissolved in anhydrous DCE (each substrate in 2.0 mL DCE), and were simultaneously added to heated DCE (2.0 mL) at 60 °C over the period of 2 h. The reaction solution was stirred for additional 1 h, cooled to room temperature and was quenched with saturated Na₂S₂O₃ (5.0 mL). Dichloromethane (5.0 mL) was added to the reaction mixture and the organic layer was separated, washed with water followed by brine, dried over anhydrous MgSO₄, and recovered to give a crude red solid which was subjected to column chromatography on silica (20% diethyl ether in petroleum spirits) to afford title compound **14a** (48 mg, 65%) as a red solid: m.p. = 304–306 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.86–7.80 (m, 4H), 7.47 (ddd, *J* = 8.0, 7.2, 1.1 Hz, 2H), 7.42–7.38 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 138.6, 137.1, 134.1, 125.9, 125.5, 123.5, 122.9, 120.9; HRMS (APCI): calculated for C₁₆H₈S₃ M⁺ (m/z) 295.9788; found = 295.9783

Selenolo[3,2-*b*:4,5-*b'*]bis[1]benzothiophene (14b)

Compound **10** (74 mg, 0.25 mmol) and SeCl₂ (0.25 mmol) were taken in anhydrous DCE (2.0 mL) and anhydrous THF (2.0 mL), respectively, and were simultaneously added to heated DCE

(2.0 mL) at 70 °C over the period of 2 h. The reaction solution was stirred for additional 1 h, cooled to room temperature and was quenched with saturated Na₂S₂O₃ (5.0 mL). The work-up of this reaction was carried out using the procedure described above for **14a**. Titled compound **14b** was obtained as a brick-red solid (59 mg, 68%): m.p. = 182.6–183.1 °C; ⁷⁷Se NMR (76.3 MHz, CDCl₃) δ (ppm): 221.46; ¹H NMR (401 MHz, CDCl₃) δ (ppm): 7.83 (ddd, *J* = 8.6, 1.8, 0.8 Hz, 4H), 7.48 (ddd, *J* = 8.0, 7.2, 1.1 Hz, 2H), 7.40 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 138.9, 138.7, 135.8, 125.8, 125.5, 124.7, 122.7, 114.7; HRMS (APCI): calculated for C₁₆H₈S₂Se M⁺ (m/z) 343.9226; found = 343.9217.

Tellurolo[3,2-*b*:4,5-*b'*]bis[1]benzothiophene (14d)

This material was prepared using the procedure described above for **14b** using compound **10** (74 mg, 0.25 mmol) and tellurium tetrachloride (TeCl₄) (68 mg, 0.25 mmol). The crude reaction mass was subjected to flash chromatography to afford **14d** as a yellow solid (74 mg, 76%): m.p. = 286.2–287.9 °C; ¹²⁵Te NMR (126.30 MHz, CDCl₃) δ (ppm): 189.54; ¹H NMR (401 MHz, CDCl₃) δ (ppm): 7.93–7.90 (m, 2H), 7.74–7.71 (m, 2H), 7.46–7.37 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 140.7, 140.2, 135.8, 125.3, 125.1, 123.9, 123.8, 122.7; HRMS (APCI): calculated for C₁₆H₈S₂Te [M+H]⁺ (m/z) 394.9204; found = 394.9205

[1,4]Diselenino[2,3-*b*:6,5-*b'*]bibenzo[*b*]thiophene (15)

This material was prepared using the procedure described above for **14b** using compound **11** (100 mg, 0.26 mmol) and SeCl₂ (0.26 mmol). The crude reaction mass was subjected to column chromatography on silica (5% diethyl ether in petroleum spirits) to afford title compound **15** as a yellow solid (66 mg, 60%): m.p. = 166–168 °C; ⁷⁷Se NMR (76.3 MHz, CDCl₃) δ (ppm): 352.94, 295.92; ¹H NMR (401 MHz, CDCl₃) δ (ppm): 7.84–7.81 (ddd, *J* = 8.0, 1.2, 0.7 Hz, 2H), 7.79–7.76 (m, 2H), 7.44–7.40 (m, 2H), 7.37–7.32 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 143.1, 138.6, 127.1, 126.0, 125.1, 125.1, 122.4, 122.4; HRMS (APCI): calculated for C₁₆H₈S₂Se₂ M⁺ (m/z) 423.8392; found = 423.8394

Selenopheno[2,3-*b*:5,4-*b'*]bibenzo[*b*]thiophene (16)

This material was prepared using the procedure described above for **14b** using compound **11** (100 mg, 0.26 mmol) and gold (III) chloride (AuCl₃) (78 mg, 0.26 mmol). The crude reaction mass was subjected to column chromatography on silica (2% diethyl ether in petroleum spirits) to afford title compound **16** as an off white solid (46 mg, 51%): m.p. = 172.5–177.4 °C; ⁷⁷Se NMR (76.3 MHz, CDCl₃) δ (ppm): 507.01; ¹H NMR (401 MHz, CDCl₃) δ (ppm): 8.75–8.73 (d, *J* = 8.1 Hz, 2H), 7.93–7.91 (d, *J* = 8.1 Hz, 2H), 7.58–7.54 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 2H), 7.43–7.39 (ddd, *J* = 7.2, 5.2, 1.1 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 144.3, 139.4, 136.2, 133.9, 124.6, 123.7, 123.4, 123.4; HRMS (APCI): calculated for C₁₆H₉S₂[⁷⁴Se] [M+H]⁺ (m/z) 338.9365; found = 338.9365.

(2-(Buta-1,3-diyn-1-yl)phenyl)(methyl)sulfane (18)

(Iodoethynyl)trimethylsilane (464 mg, 2.07 mmol) was dissolved in triethylamine (15 mL) and the reaction solution was degassed. To this reaction mixture was added Pd(PPh₃)₄ (68 mg, 3 mol%) and CuI (23.5 mg, 6 mol%), and the resultant suspension was degassed and stirred for 15 min at room temperature. Then (2-ethynylphenyl)(methyl)sulfane (**9**) (337 mg, 2.27 mmol) in triethylamine was added dropwise over the period of 30 min and the resulting reaction mixture was left to stir overnight. The mixture was filtered and concentrated to a residue which was taken in diethyl ether and washed with water twice followed by brine. The organic layer was taken in a conical flask containing a mixture of anhydrous MgSO₄ and carbon, stirred well for 10 min, filtered through Celite, and concentrated to a brown liquid (535 mg), which was

immediately taken up in methanol (20 mL) and KF (255 mg, 4.40 mmol) was added to this solution at room temperature. The reaction mixture was stirred overnight and was diluted with water. Diethyl ether was added and the organic layer was separated, washed with water twice followed by brine, and was concentrated to afford a crude brown mass which was subjected to silica gel column chromatography (petroleum spirits: diethyl ether 9.9: 0.5) to afford title compound **18** as a tan oil (160 mg, 41%). ¹H NMR (401 MHz, CDCl₃) δ (ppm): 7.49 – 7.45 (m, 1H), 7.33 (ddd, *J* = 8.0, 7.5, 1.5 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.09 (td, *J* = 7.6, 1.1 Hz, 1H), 2.61 (s, 1H), 2.50 (s, 3H). The NMR data of **18** matched with the literature reported spectrum.^{S5}

Methyl(2-((2-(methylselanyl)phenyl)buta-1,3-diyn-1-yl)phenyl)sulfane (**20**)

(2-Iodophenyl)(methyl)selane (121 mg, 0.41 mmol) was dissolved in diisopropylamine (10 mL) and the reaction solution was degassed. To this reaction mixture was added Pd(PPh₃)₄ (14 mg, 3 mol%) and CuI (4.7 mg, 6 mol%), and the resultant suspension was degassed and stirred for 15 min at room temperature. Then compound **18** (70 mg, 0.41 mmol) in THF was added dropwise over the period of 30 min and the resulting reaction mixture was left to stir overnight. The mixture was filtered and concentrated to a residue which was taken in diethyl ether and washed with water twice followed by brine. The organic layer was taken in a conical flask containing a mixture of anhydrous MgSO₄ and carbon, stirred well for 10 min, filtered through Celite, and concentrated to a brown liquid which was subjected to column chromatography on silica gel (5% diethyl ether in petroleum spirits) to afford title compound **20** as a light brown oil (50 mg, 35%). ⁷⁷Se NMR (76.3 MHz, CDCl₃) δ (ppm): 212.78; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.52–7.48 (m, 2H), 7.35–7.27 (m, 3H), 7.19–7.08 (m, 3H), 2.52 (s, 3H), 2.38 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 143.4, 137.6, 133.8, 133.7, 129.7, 128.2, 125.5, 124.7, 124.5, 123.6, 122.8, 120.3, 81.6, 80.7, 79.9, 79.2, 15.4, 6.7; HRMS (APCI): calculated for C₁₈H₁₅S[⁷⁴Se] [M+H]⁺ (*m/z*) 337.0114; found = 337.0114

Benzo[*b*]selenopheno[2',3':4,5]telluropheno[3,2-*b*]benzo[*b*]thiophene (**21**)

This material was prepared using the procedure described above for **14d** using compound **20** (50 mg, 0.14 mmol) and tellurium tetrachloride (TeCl₄) (37 mg, 0.14 mmol). The crude reaction mass was subjected to flash chromatography on silica gel (5% diethyl ether in petroleum spirits) to afford **21** as a yellow solid (38 mg, 62%): m.p. = 254–256 °C; ⁷⁷Se NMR (76.3 MHz, CDCl₃) δ (ppm): 547.15; ¹²⁵Te NMR (126.3 MHz, CDCl₃) δ (ppm): 222.97; ¹H NMR (401 MHz, CDCl₃) δ (ppm): 7.96–7.94 (m, 1H), 7.92–7.89 (m, 1H), 7.73–7.70 (m, 2H), 7.45–7.39 (m, 3H), 7.34–7.30 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 142.3, 141.3, 140.9, 140.3, 139.1, 134.5, 133.4, 127.7, 126.8, 125.8, 125.4, 125.2, 125.0, 124.4, 123.8, 122.9; HRMS (APCI): calculated for C₁₆H₈SSeTe M⁺ (*m/z*) 439.8559; found = 439.8559

3,3'-Diiodo-2,2'-bibenzo[*b*]thiophene (**22**)

Compound **10** (300 mg, 1.02 mmol) was dissolved in anhydrous DCE (20.0 mL), and iodine (545 mg, 2.14 mmol) was added at room temperature. The reaction mixture was stirred at 50 °C for 5 h, cooled to room temperature and was quenched with saturated Na₂S₂O₃ (20.0 mL). The organic layer was separated, washed with brine, dried over anhydrous MgSO₄, and recovered to get **22** as a light brown solid (450 mg, 85% yield): m.p. = 216–218 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.87–7.83 (m, 4H), 7.54–7.45 (dtd, *J* = 14.9, 7.2, 1.3 Hz, 4H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 141.1, 140.3, 135.4, 126.6, 126.5, 125.8, 122.4, 86.7; HRMS (APCI): calculated for C₁₆H₈I₂S₂ M⁺ (*m/z*) 517.8151; found = 517.8153.

4-Benzylidene-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]bibenzo[*b*]thiophene (23)

Compound **22** (52 mg, 0.10 mmol) was dissolved in dimethylformamide (5.0 mL) at room temperature under N_2 (g) atmosphere. To this solution was added $Pd(OAc)_2$ (1.2 mg, 5 mol%), triphenylphosphine (37 mg, 0.14 mmol), potassium acetate (98 mg, 1.0 mmol), and styrene (31 mg, 0.30 mmol), and the resulting reaction mixture was stirred at 80 °C for 18 h. The reaction mixture was cooled to room temperature, diluted with water (15 mL), and extracted with ethyl acetate (2×15 mL). The organic layer was washed with water followed by brine, dried (anhydrous $MgSO_4$), and concentrated to get reddish-brown solid which was subjected to column chromatography on silica (10% diethyl ether in petroleum spirits) to get **23** (23 mg, 62%) as a dark red solid: m.p. = 139–142 °C; 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.10–8.07 (m, 2H), 7.86–7.84 (d, J = 8.0 Hz, 1H), 7.73–7.71 (m, 1H), 7.59–7.56 (m, 2H), 7.47–7.41 (m, 4H), 7.30–7.27 (m, 1H), 7.11–7.07 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H), 6.91–6.86 (ddd, J = 8.3, 7.1, 1.2 Hz, 1H), 6.26–6.23 (d, J = 8.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 143.9, 143.2, 142.5, 141.9, 141.5, 139.7, 138.5, 137.9, 137.2, 134.5, 134.1, 134.0, 131.7, 130.7, 129.0, 128.9, 125.7, 124.5, 124.4, 123.7, 123.6, 123.5, 123.1, 121.3; HRMS (APCI): calculated for $C_{24}H_{15}S_2$ $[M+H]^+$ (m/z) 367.0610; found = 367.0604.

2-(11*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*d*]pyrrol-11-yl)-*N,N*-dimethylethane-1-amine (24)

Compound **22** (52 mg, 0.10 mmol) was dissolved in dry toluene (7.0 mL). To this mixture was added Cs_2CO_3 (81 mg, 0.25 mmol) and CuI (48 mg, 0.25 mmol), and the resulting suspension was stirred for 15 min while N_2 (g) was bubbled through the mixture. Then *N,N*-dimethylethane-1,2-diamine (62 mg, 0.70 mmol) was added to the stirred solution and the resulting reaction mixture was stirred overnight at 100 °C. The reaction mixture was cooled to room temperature, diluted with ethyl acetate (20.0 mL), and washed with water (2×20.0 mL) followed by brine (20.0 mL). The organic layer was dried ($MgSO_4$) and concentrated to get crude brown mass which was subjected to column chromatography on silica (20% methanol/ethyl acetate) to afford title compound **24** (15 mg, 42%) as a light brown solid: m.p. = 152–154 °C; 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.90 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 4.82 (t, J = 7.0 Hz, 2H), 2.88 (J = 7.0 Hz, 2H), 2.43 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 141.9, 137.4, 127.4, 124.6, 124.5, 123.3, 118.7, 114.9, 59.3, 46.2, 46.0; HRMS (APCI): calculated for $C_{20}H_{19}N_2S_2$ $[M+H]^+$ (m/z) 351.0984; found = 351.0990.

11,11-Dimethyl-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*d*]germole (25)

n-Butyllithium (0.21 mL, 0.42 mmol (2.0 M solution in hexanes)) was added dropwise to a solution of compound **22** (104 mg, 0.2 mmol) in anhydrous tetrahydrofuran (THF) (10.0 mL) at –78 °C, and the resultant yellow suspension was left to stir at this temperature for 5 min. Dichlorodimethylgermane (38 mg, 0.22 mmol) was added at once and the resulting reaction mixture was left to stir overnight. Saturated ammonium chloride (20 mL) and diethyl ether (30 mL) were added to the reaction mixture and the organic layer was separated. Organic layer was washed with water (2×30 mL) followed by brine (30 mL), dried over anhydrous $MgSO_4$, and concentrated to a light yellow oil which was subjected to chromatography on silica eluting with 2% diethyl ether in petroleum spirits providing **25** as an off-white semi-solid (44 mg, 60% yield). 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.91–7.88 (dd, J = 8.0, 0.8 Hz, 2H), 7.75–7.72 (m, 2H), 7.40–7.36 (m, 2H), 7.32–7.28 (ddd, J = 8.2, 7.2, 1.2 Hz, 2H), 0.81 (s, 6H); ^{13}C NMR

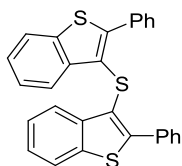
(101 MHz, CDCl₃) δ (ppm): 146.5, 143.5, 141.7, 140.6, 125.1, 123.9, 123.7, 123.4, 29.8;
HRMS (APCI): calculated for C₁₈H₁₄S₂[70]Ge M⁺ (m/z) 363.9774; found = 363.9775

References:

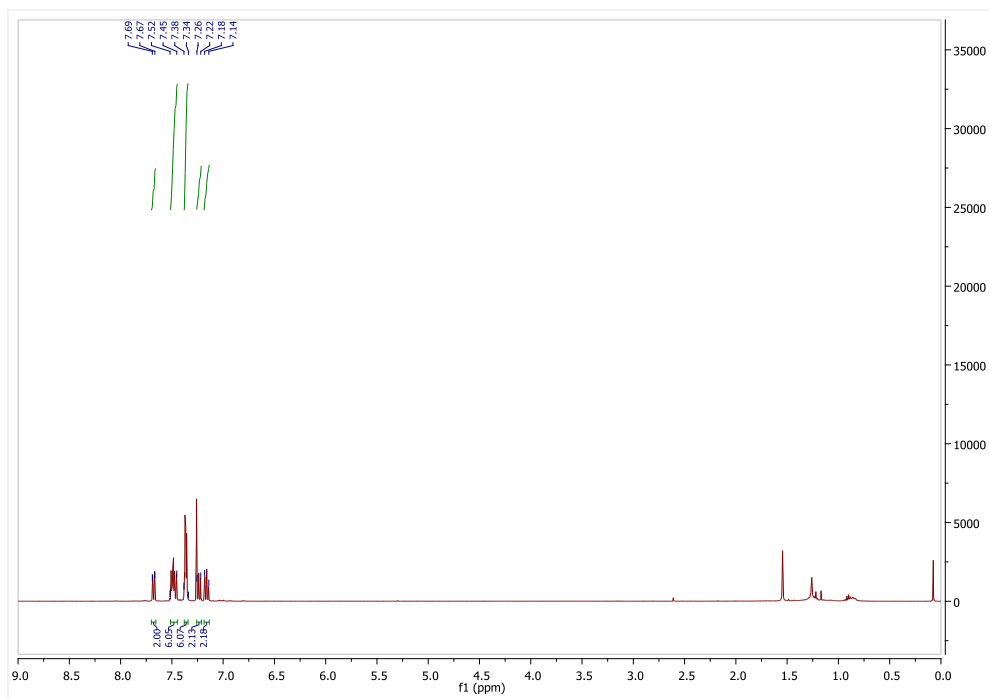
- S1. R. Bishop, *Org. Synth.*, 1992, **70**, 120–128
- S2. A. Maaninen, T. Chivers, M. Parvez, J. Pietikäinen and R. S. Laitinen, *Inorg. Chem.*, 1999, **38**, 4093–4097
- S3. A. Gupta and B. L. Flynn, *J. Org. Chem.* 2016, **81**, 4012–4019.
- S4. T. Kesharwani, S. A. Worlikar and R. C. Larock, *J. Org. Chem.* 2006, **71**, 2307–2312
- S5. R. A. Aitken and S. Seth, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2461–2466

NMR Spectra

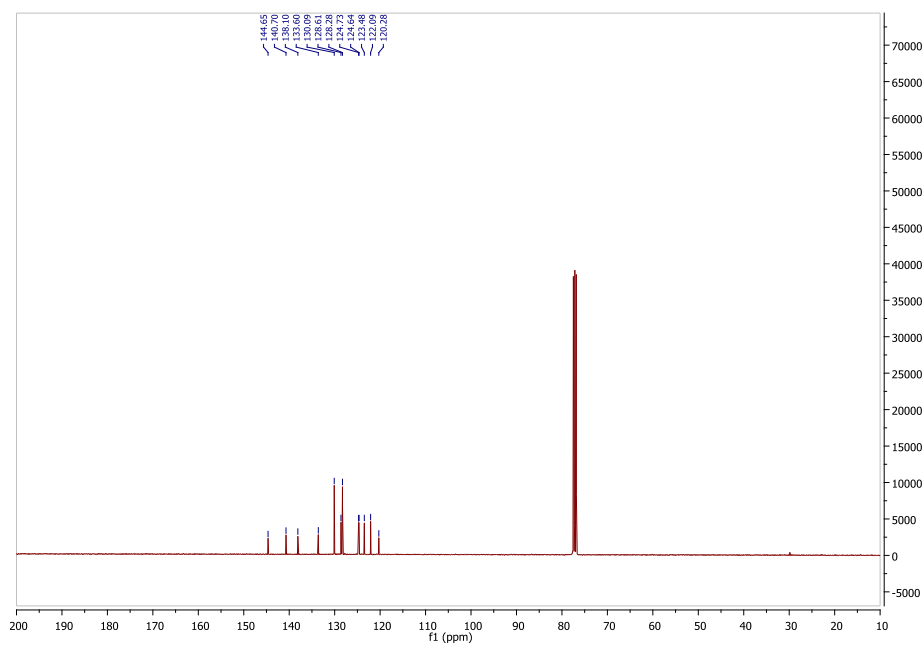
Bis(2-phenylbenzo[*b*]thiophen-3-yl)sulfane (7a)



¹H NMR:



¹³C NMR:

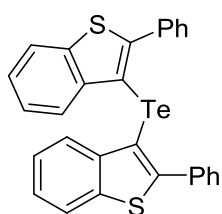


Chemical structure of compound 10b is shown in the top left corner. The structure is a substituted benzene ring with a carboxylic acid group (-COOH) and a side chain containing a double bond and a methyl group.

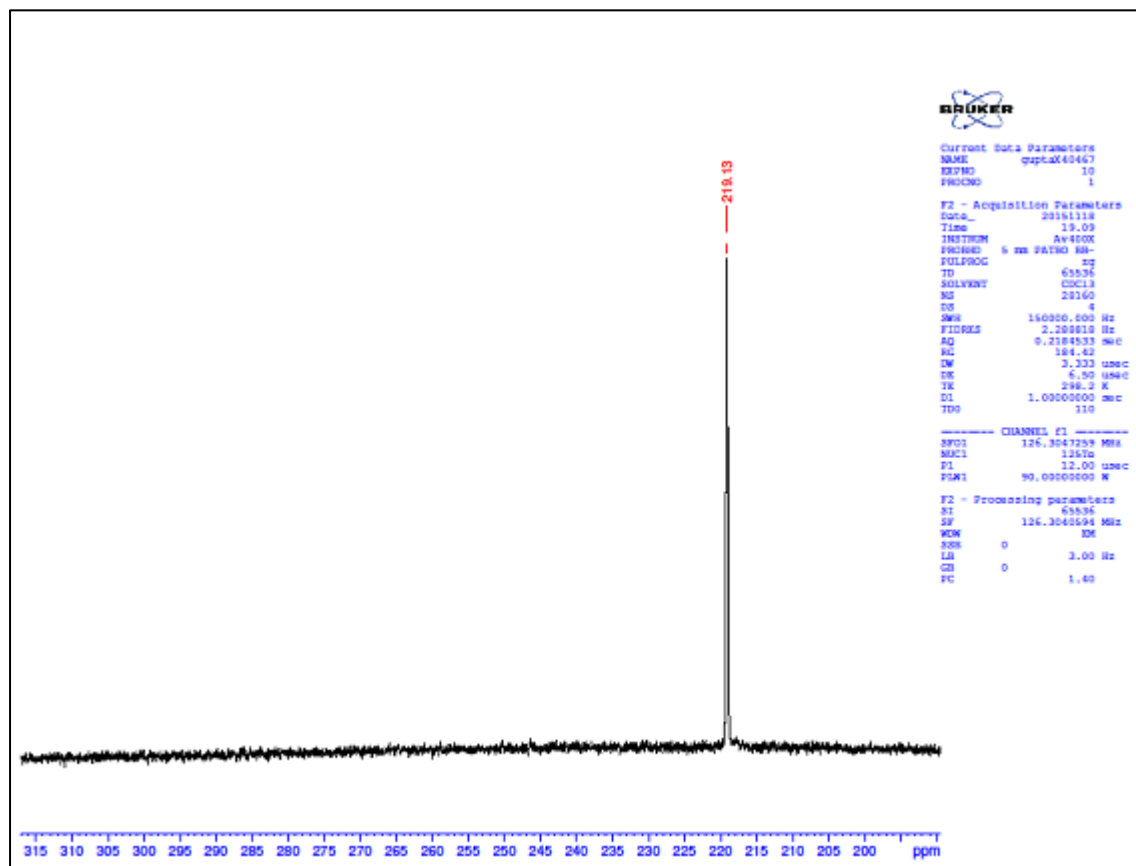
The ^1H NMR spectrum (CDCl₃) shows the following peaks and integrations:

- Peak at $\delta \approx 7.7$ ppm (integration 2.04)
- Peak at $\delta \approx 7.6$ ppm (integration 4.02)
- Peak at $\delta \approx 7.5$ ppm (integration 8.12)
- Peak at $\delta \approx 7.4$ ppm (integration 2.18)
- Peak at $\delta \approx 7.3$ ppm (integration 2.19)
- Peak at $\delta \approx 1.5$ ppm (integration 1.00)
- Peak at $\delta \approx 0.1$ ppm (integration 1.00)

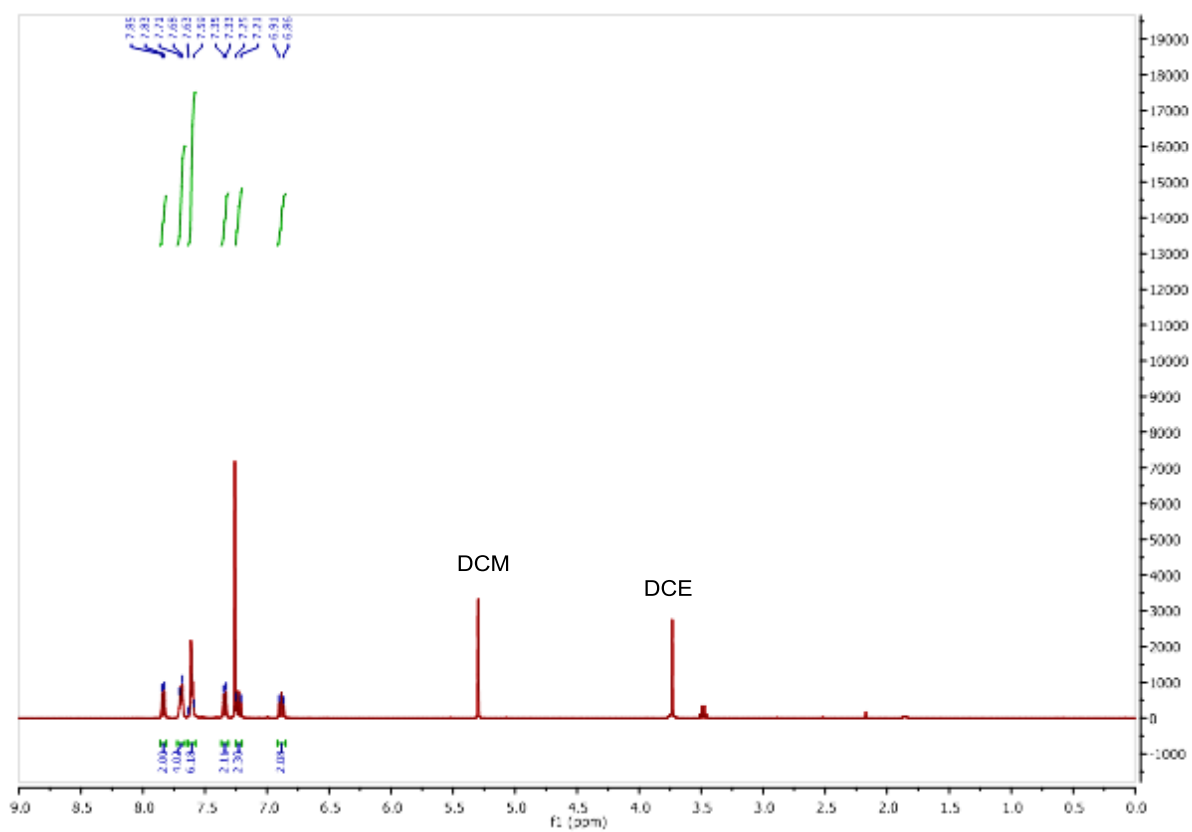
Bis(2-phenylbenzo[b]thiophen-3-yl)tellane (7d)



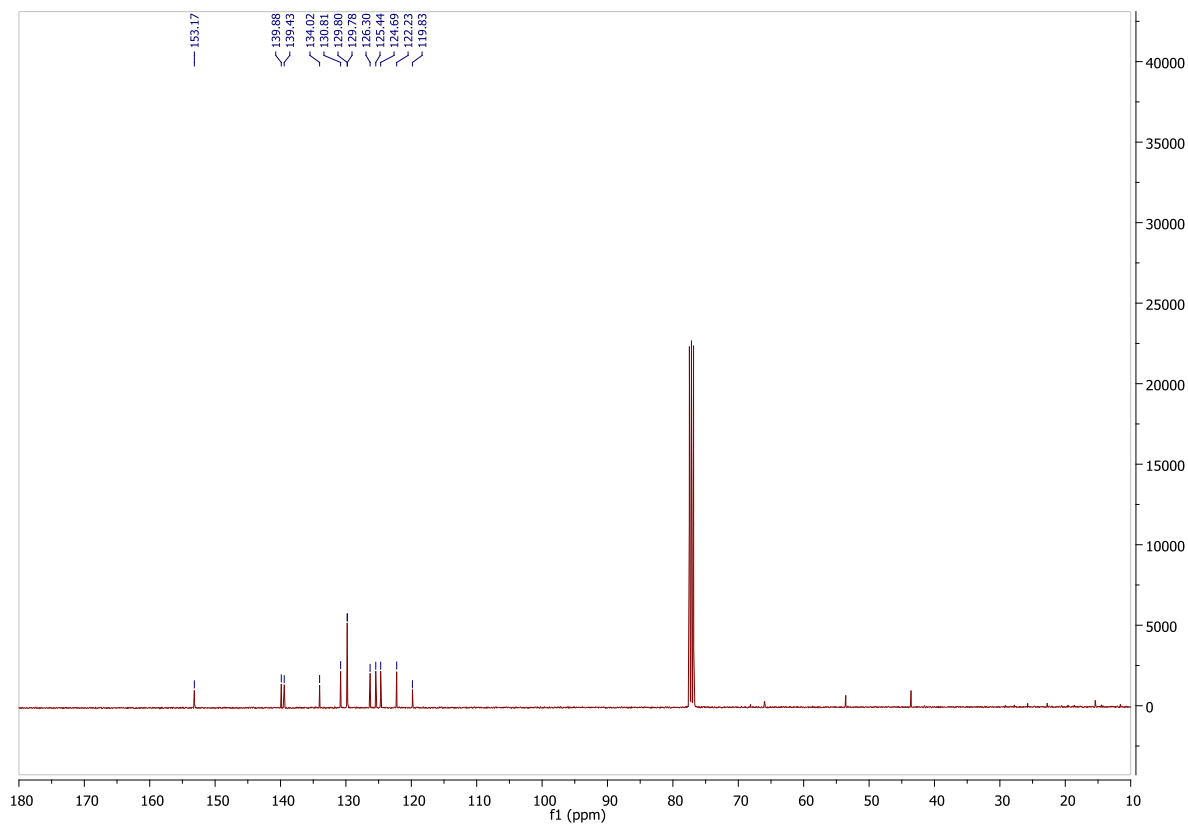
^{125}Te NMR:



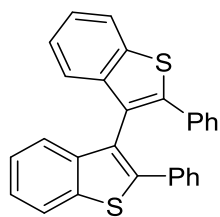
¹H NMR:



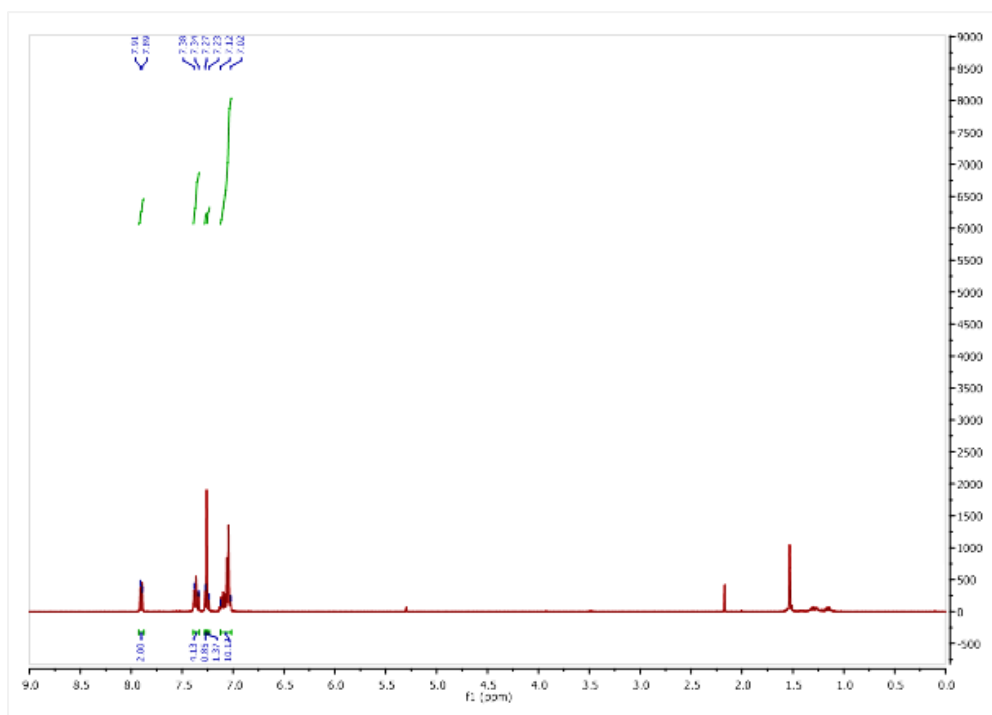
¹³C NMR:



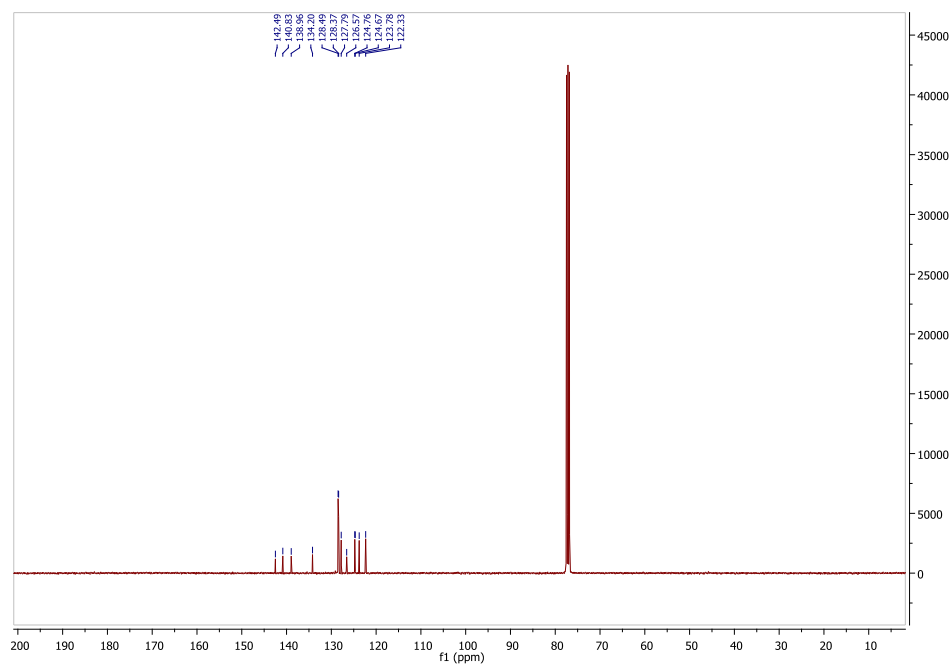
2,2'-Diphenyl-3,3'-bibenzo[b]thiophene (8)



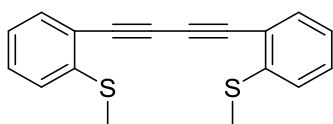
^1H NMR:



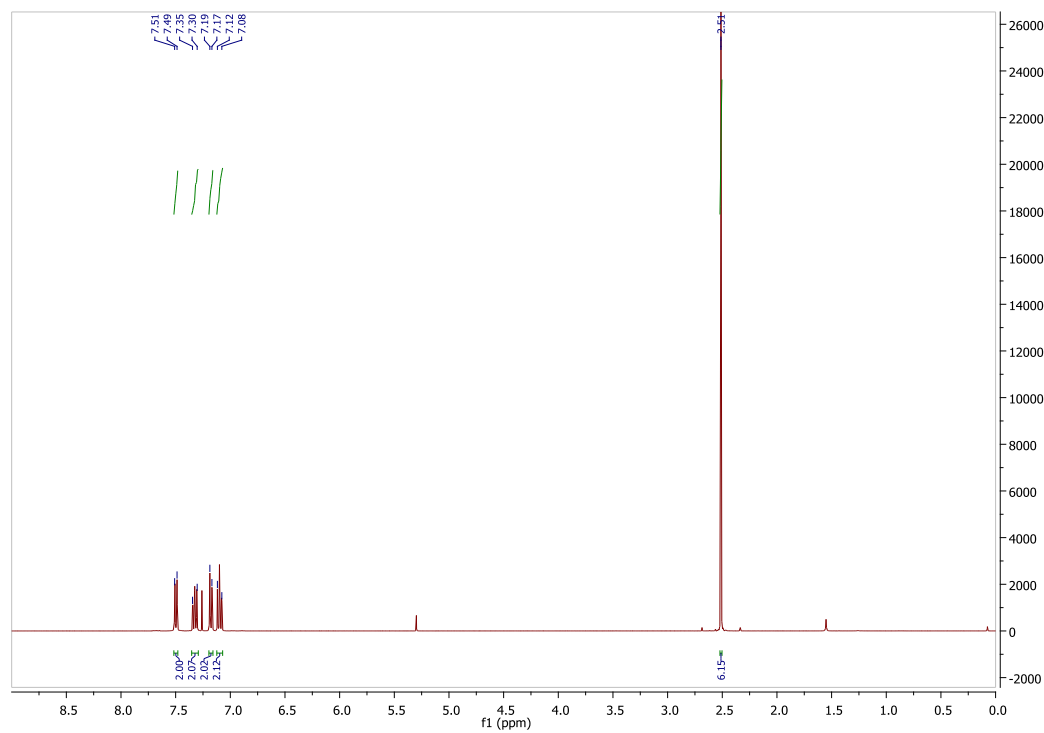
^{13}C NMR:



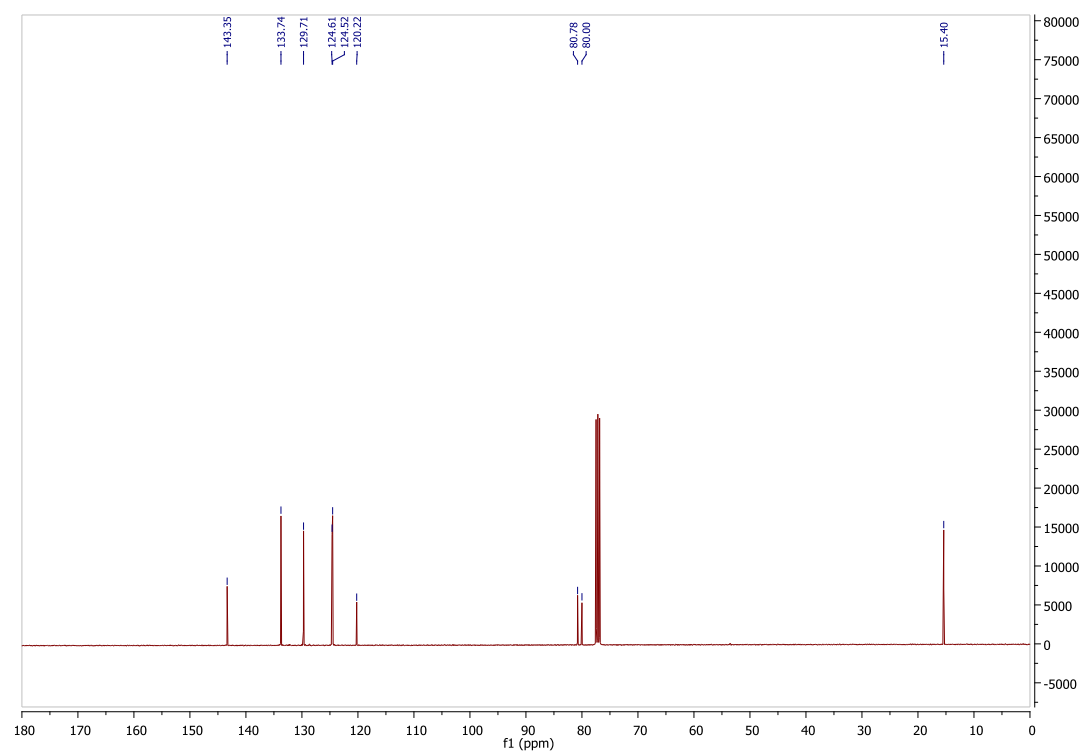
1,4-Bis(2-(methylthio)phenyl)buta-1,3-diyne (10)



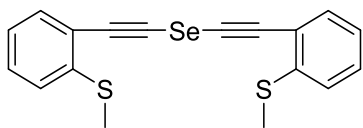
^1H NMR:



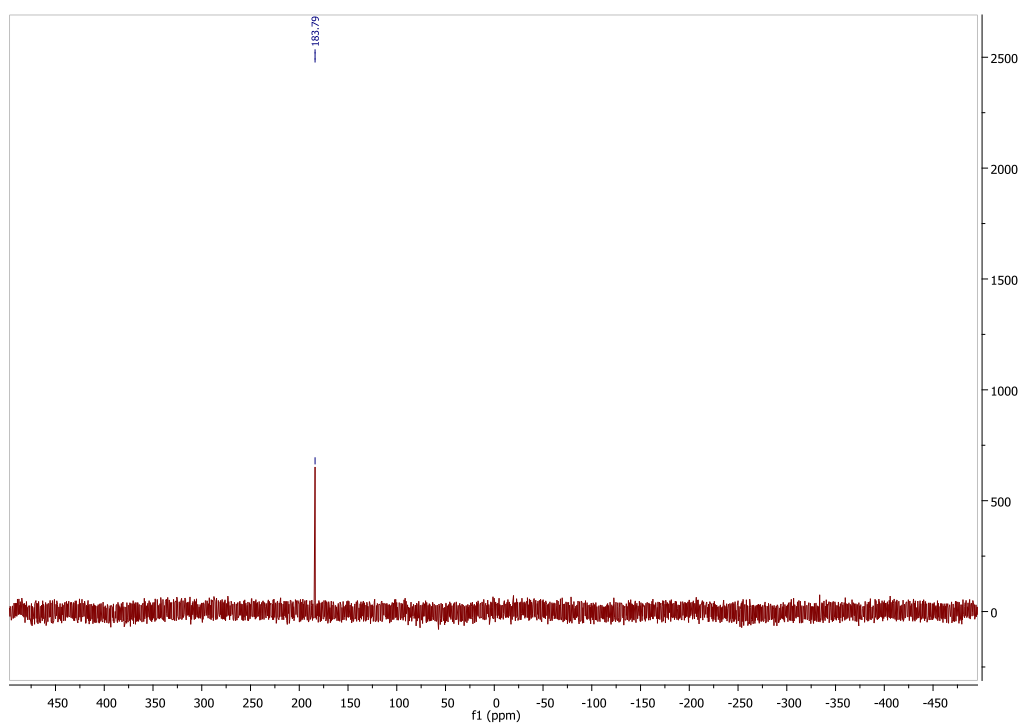
^{13}C NMR:



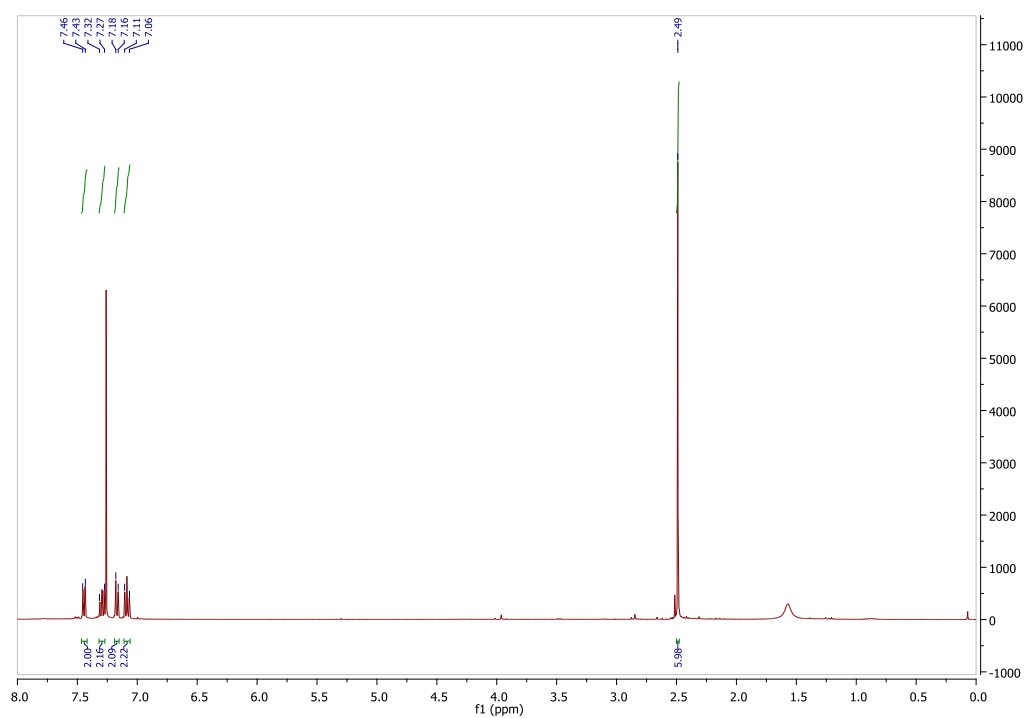
Bis((2-(methylthio)phenyl)ethynyl)selane (11)



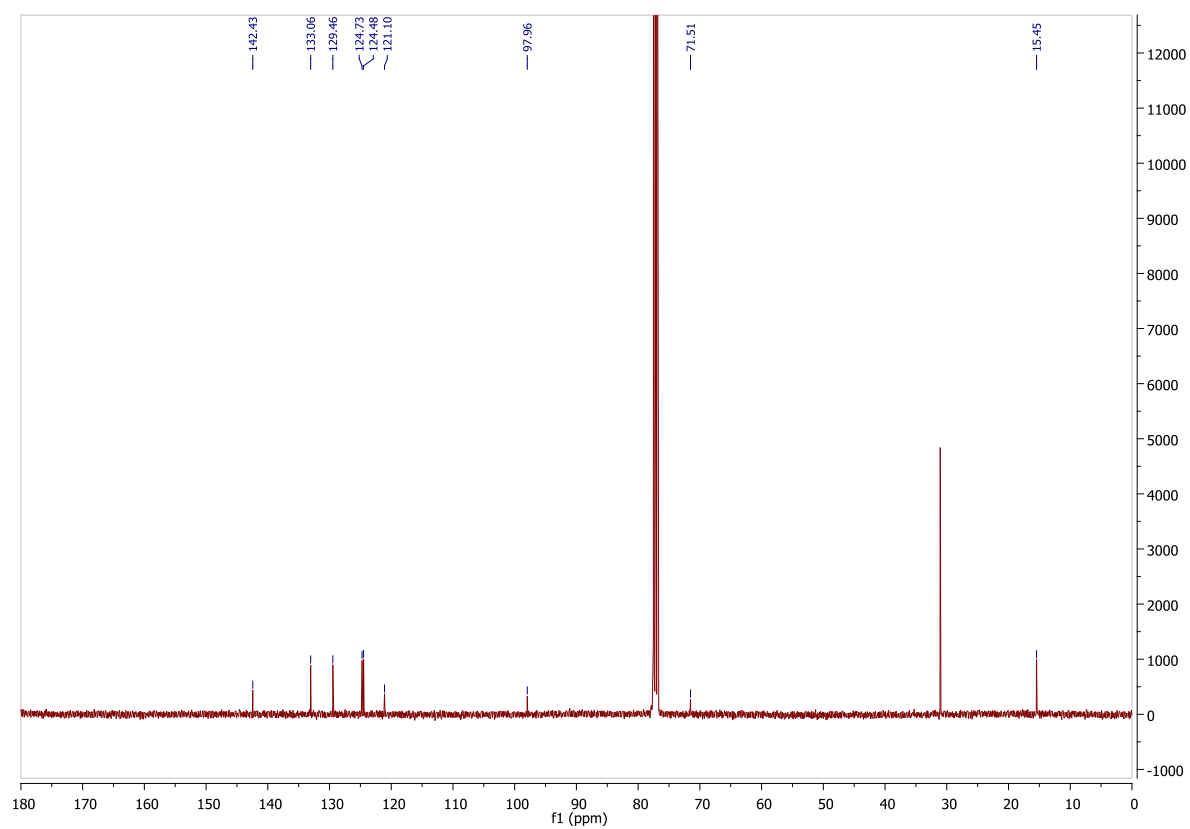
^{77}Se NMR:



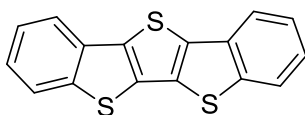
^1H NMR:



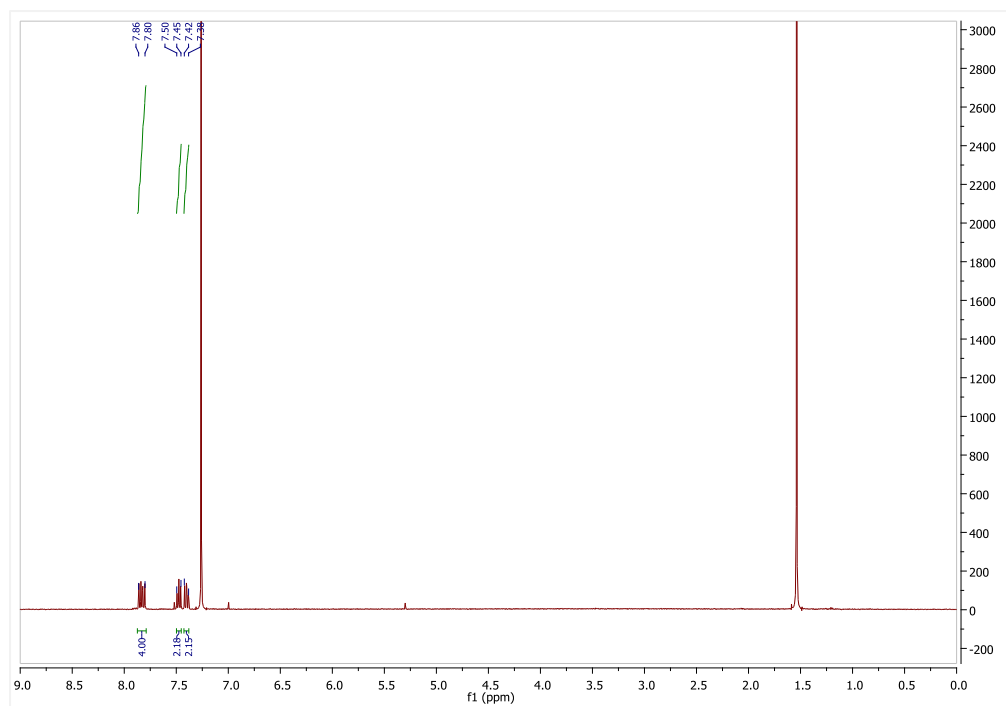
^{13}C NMR:



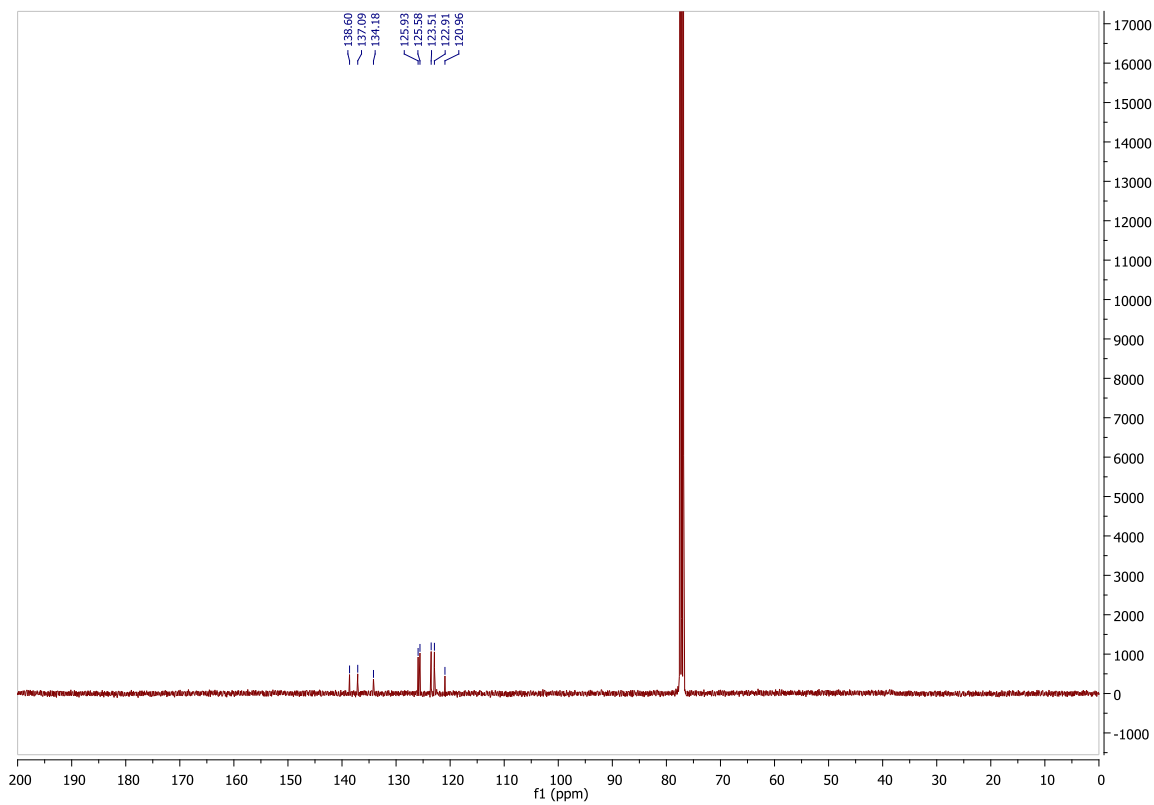
Bis(benzothieno)[3,2-*b*:2',3'-*d*]thiophene (14a)



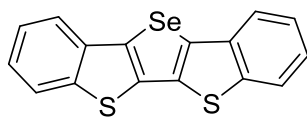
^1H NMR:



^{13}C NMR:



Selenolo[3,2-*b*:4,5-*b'*]bis[1]benzothiophene (14b)



⁷⁷Se NMR:

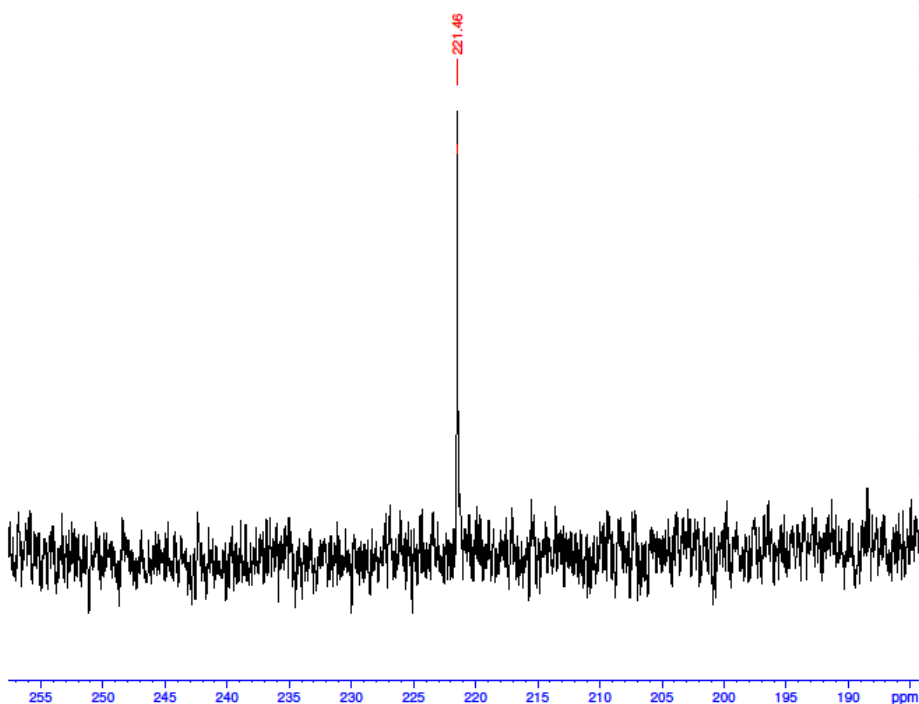
CSIRO Akhil Gupta
S-Se-S
Av400_77Se CDCl₃ C:\gup016 26



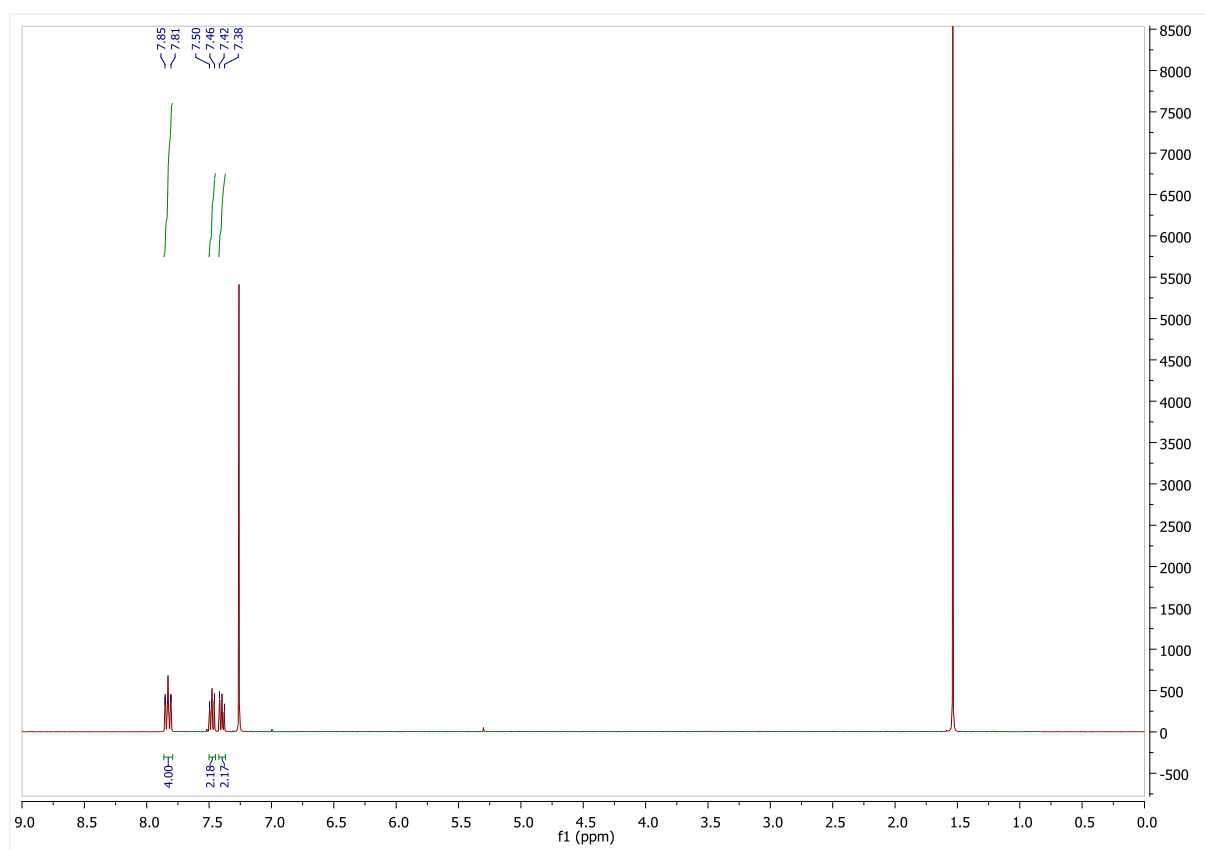
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PROCNO 1

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FIDRES 1.155969 Hz
AQ 0.8650752 sec
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RW 6.600 usec
RX 6.50 usec
TK 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
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NUC1 77Se
P1 11.00 usec
PLW1 90.00000000 W
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PLW2 20.00000000 W
PLW12 0.75616997 W

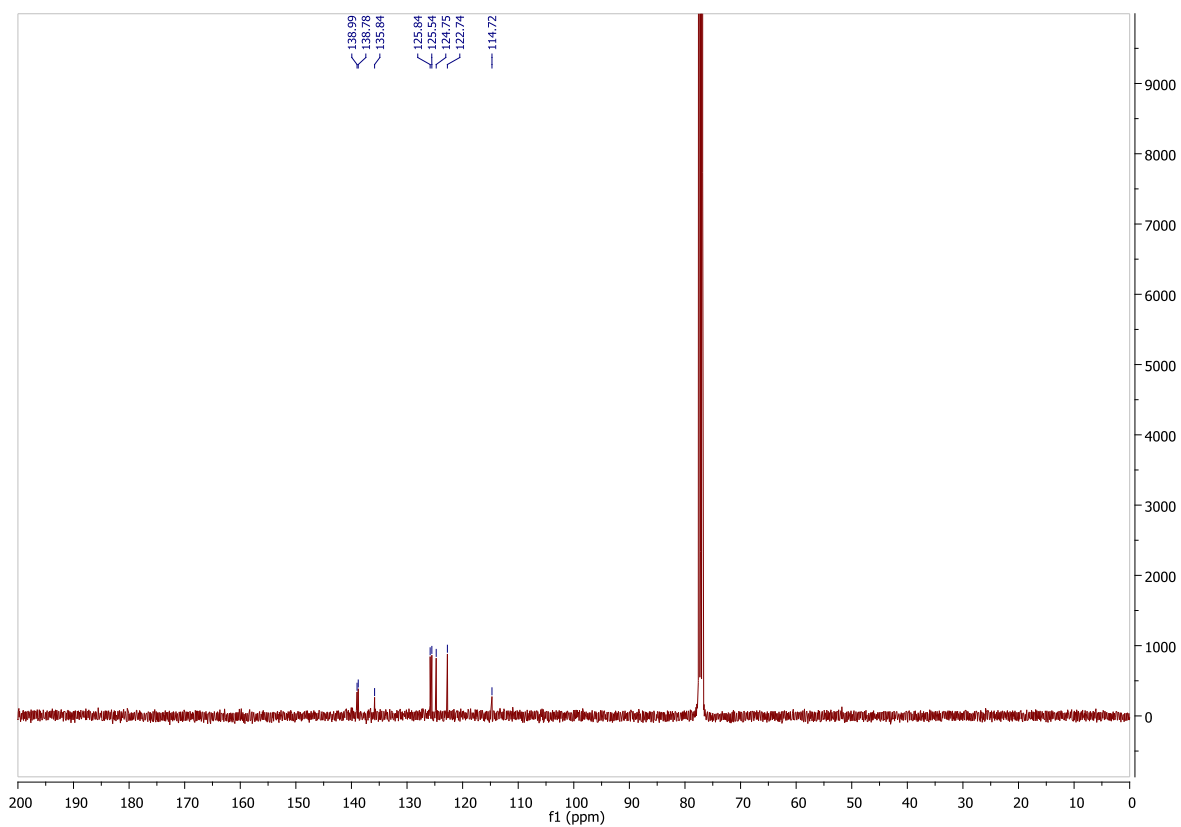
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CB 0
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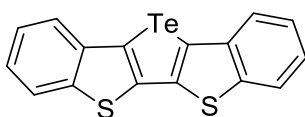
¹H NMR:



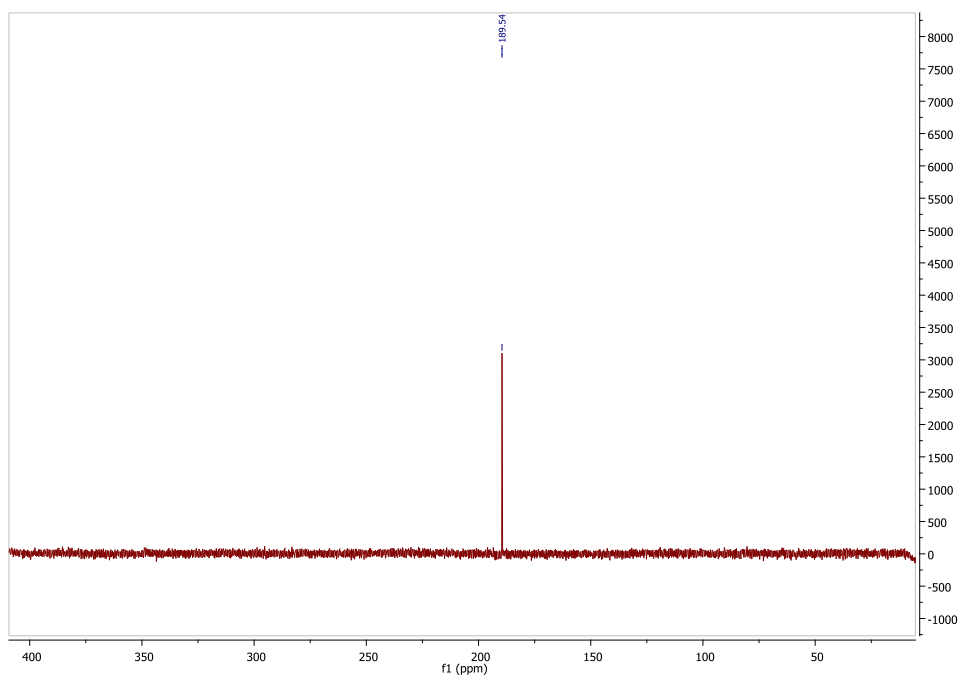
¹³C NMR:



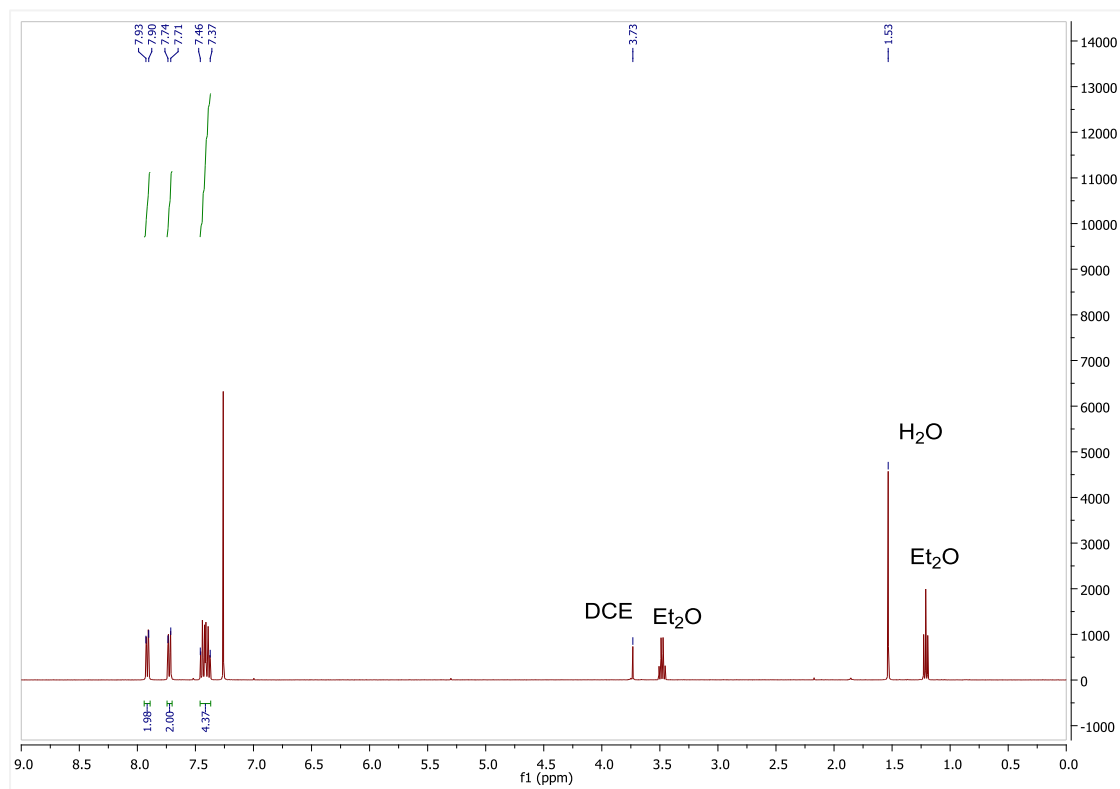
Tellurolo[3,2-*b*:4,5-*b'*]bis[1]benzothiophene (14d)



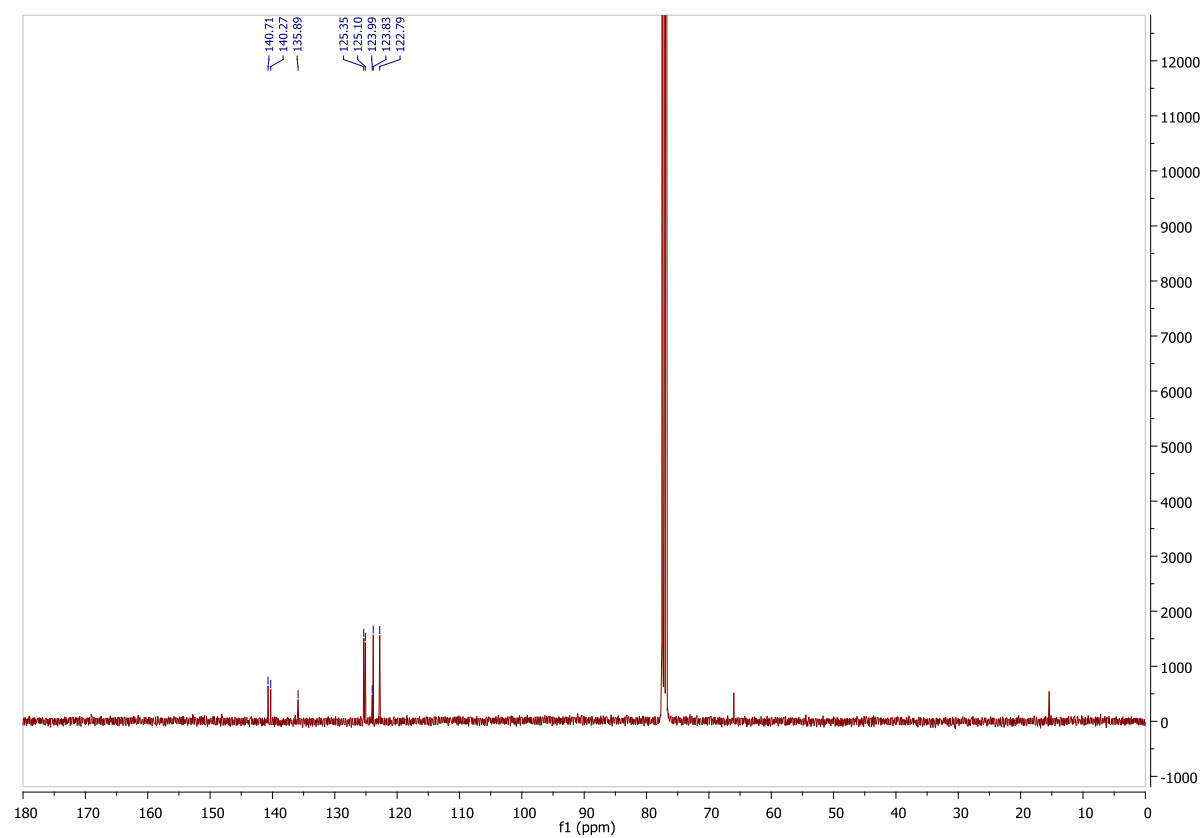
^{125}Te NMR:



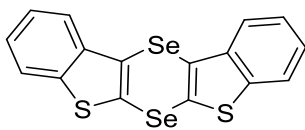
^1H NMR:



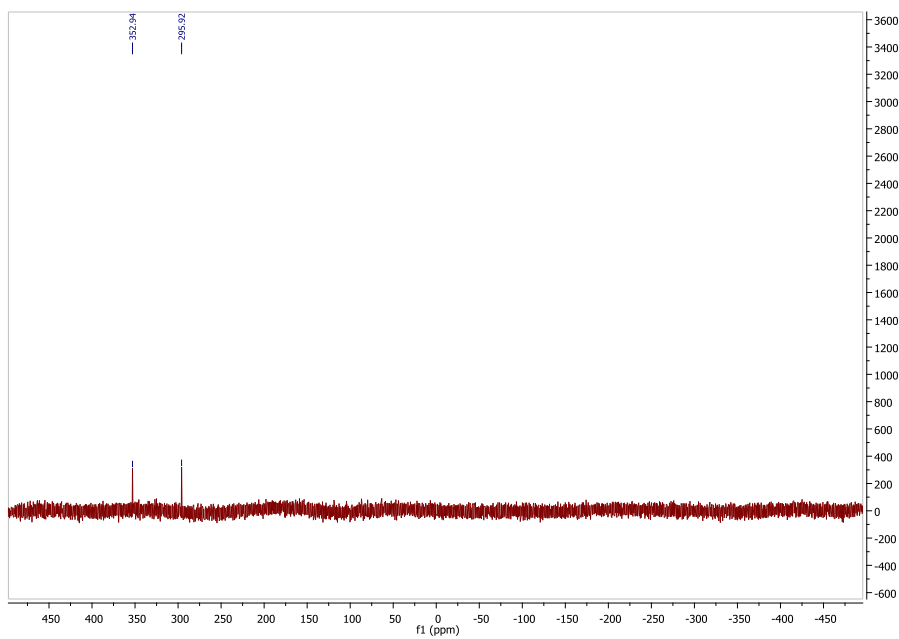
^{13}C NMR:



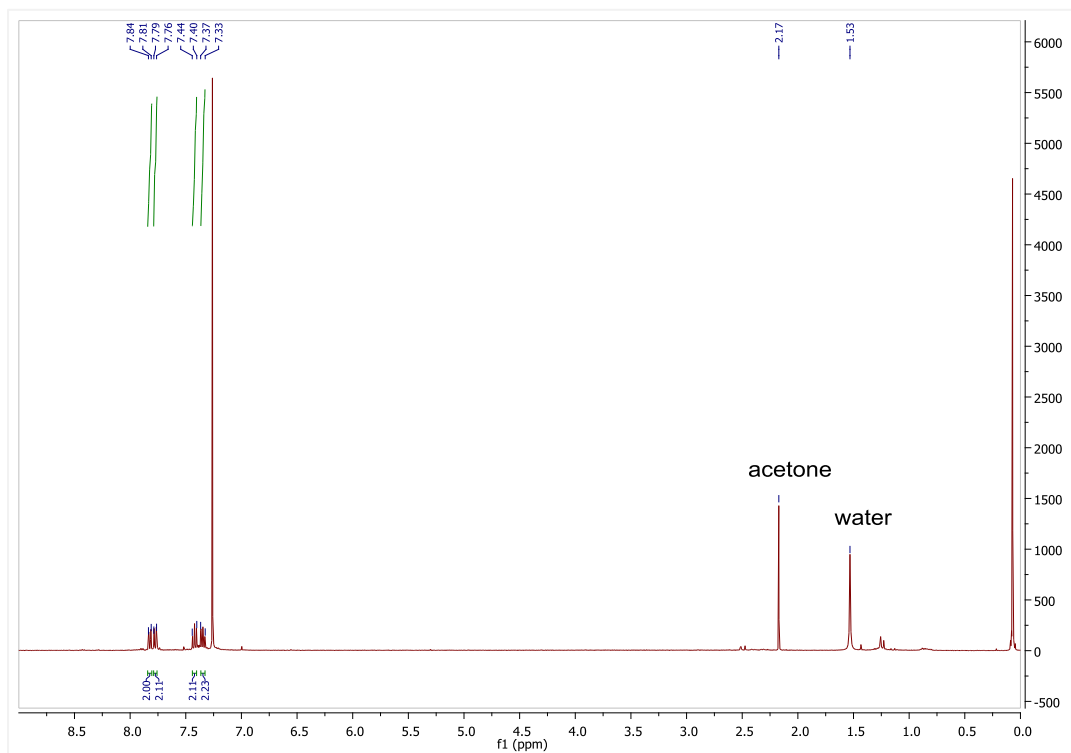
[1,4]diselenino[2,3-*b*:6,5-*b'*]bibenzo[*b*]thiophene (15)



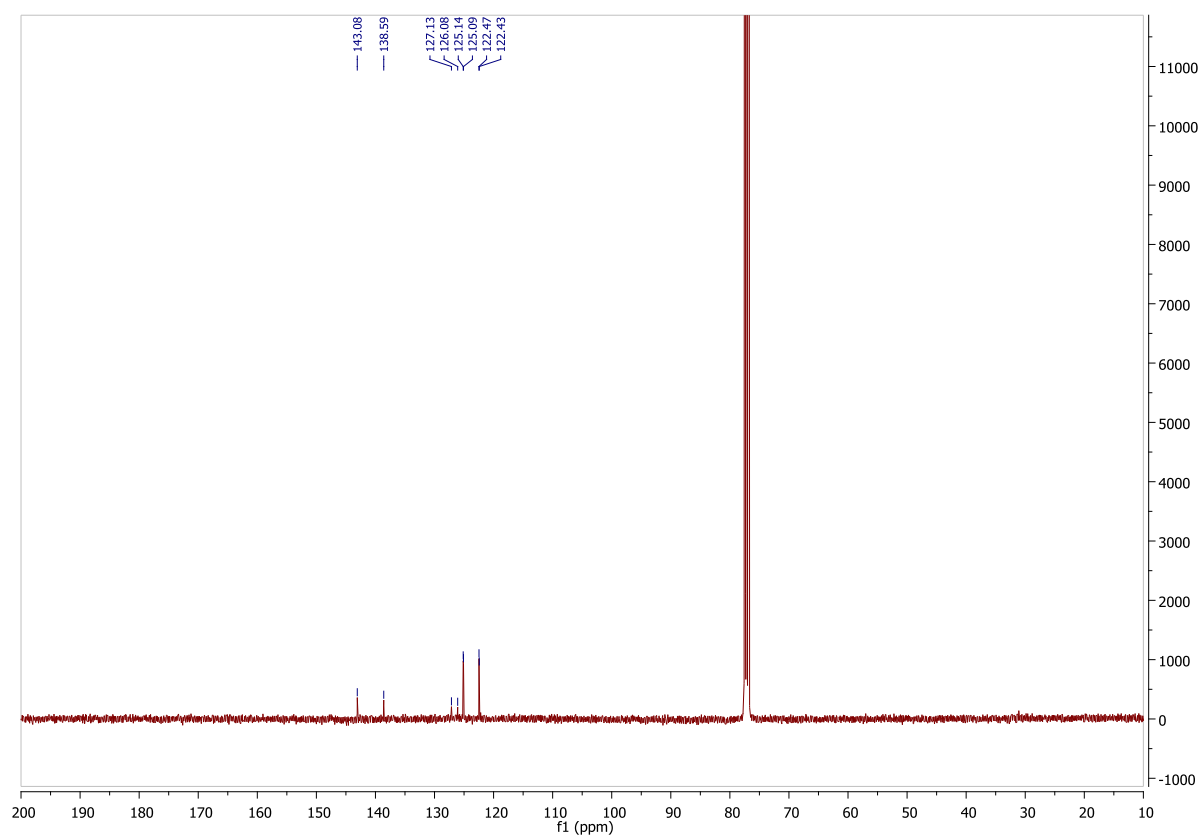
⁷⁷Se NMR:



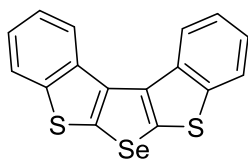
¹H NMR:



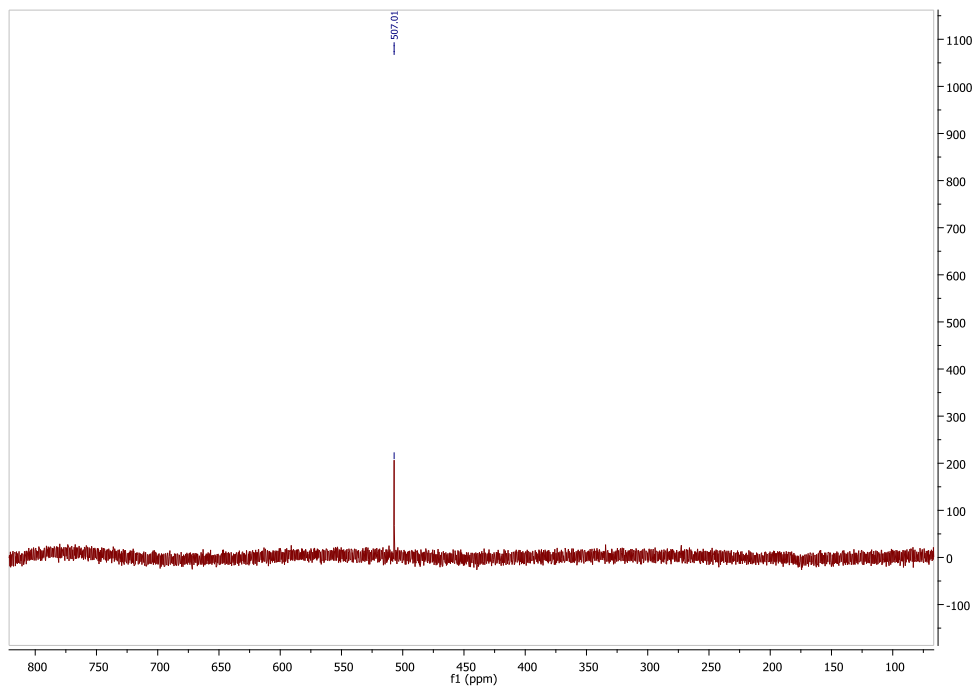
^{13}C NMR:



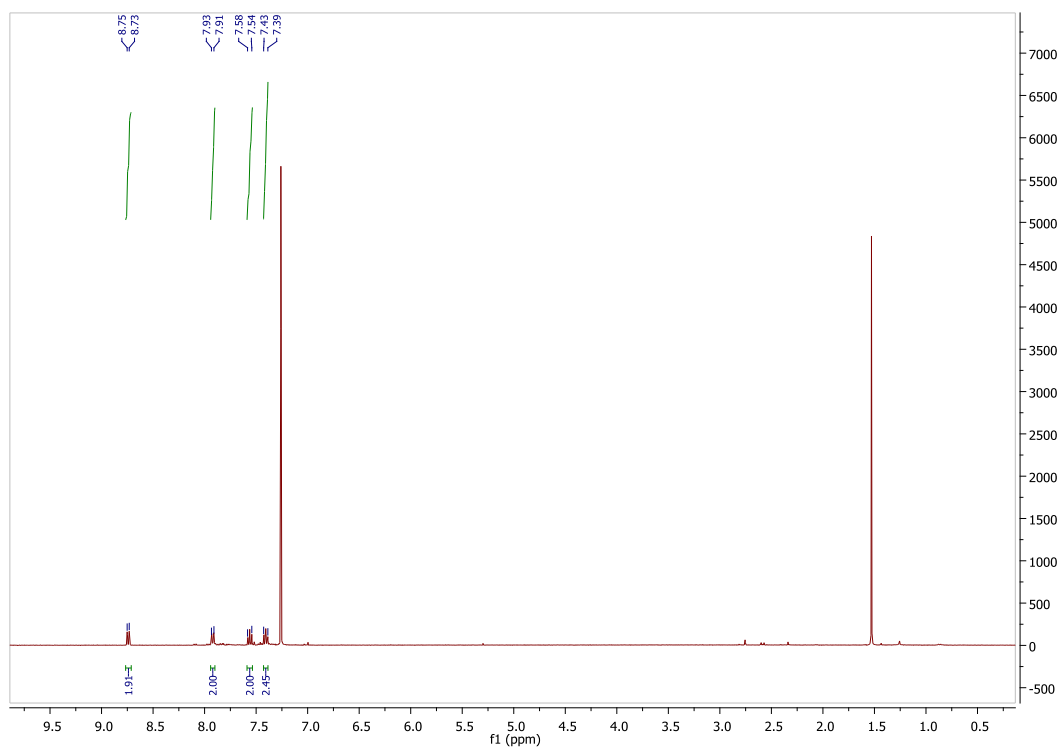
Selenopheno[2,3-*b*:5,4-*b'*]bibenzo[*b*]thiophene (16)



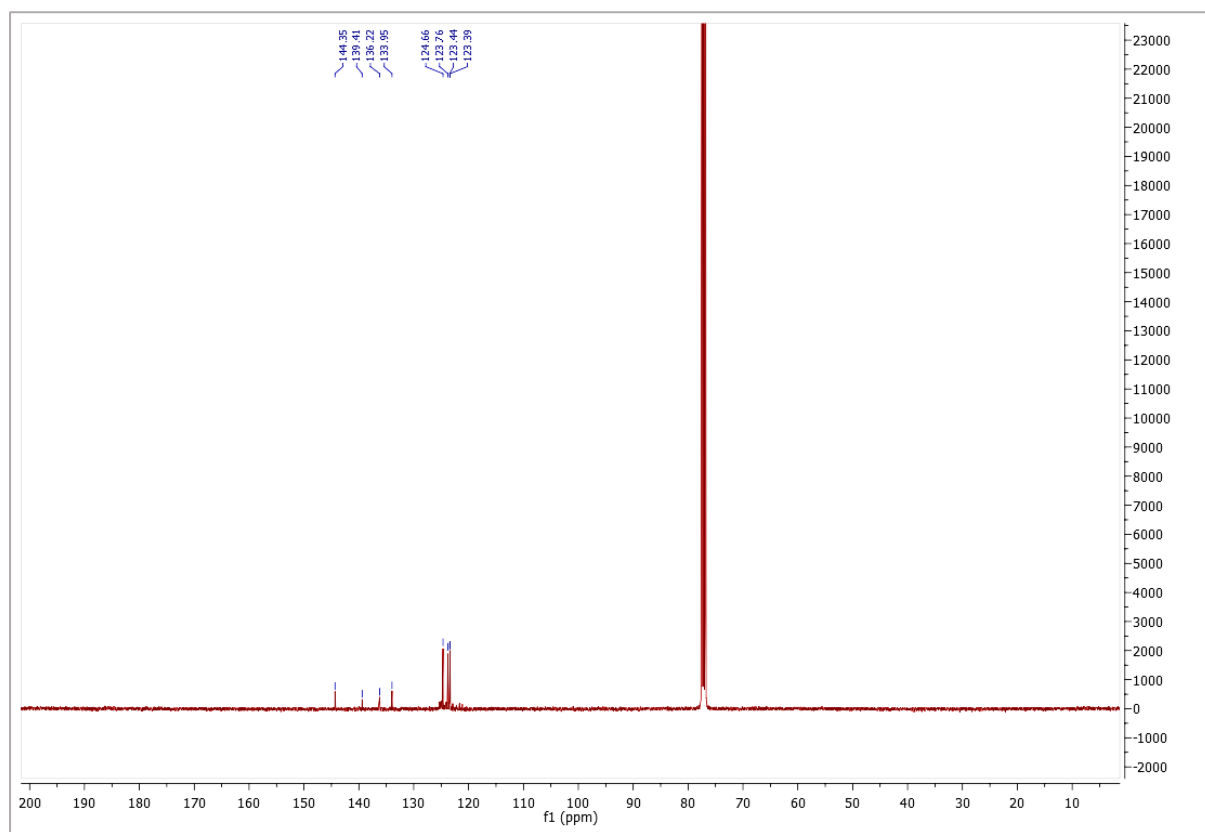
^{77}Se NMR:



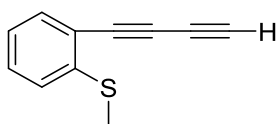
^1H NMR:



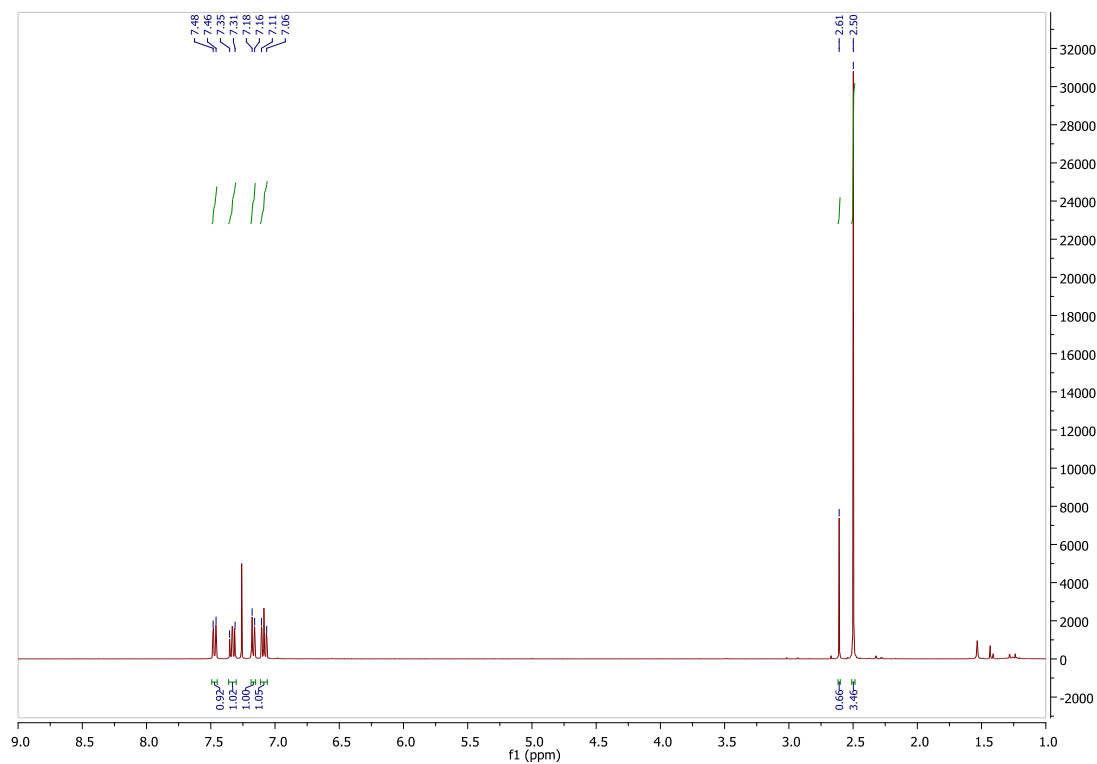
^{13}C NMR:



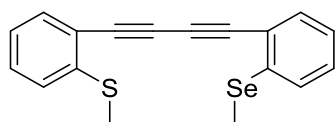
(2-(Buta-1,3-diyn-1-yl)phenyl)(methyl)sulfane (18)



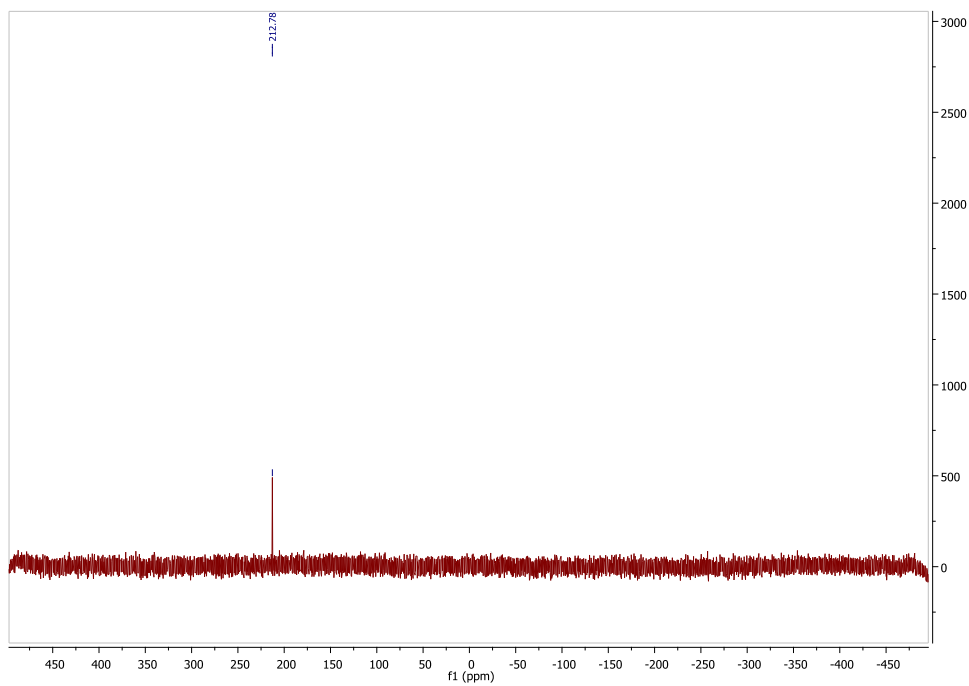
¹H NMR:



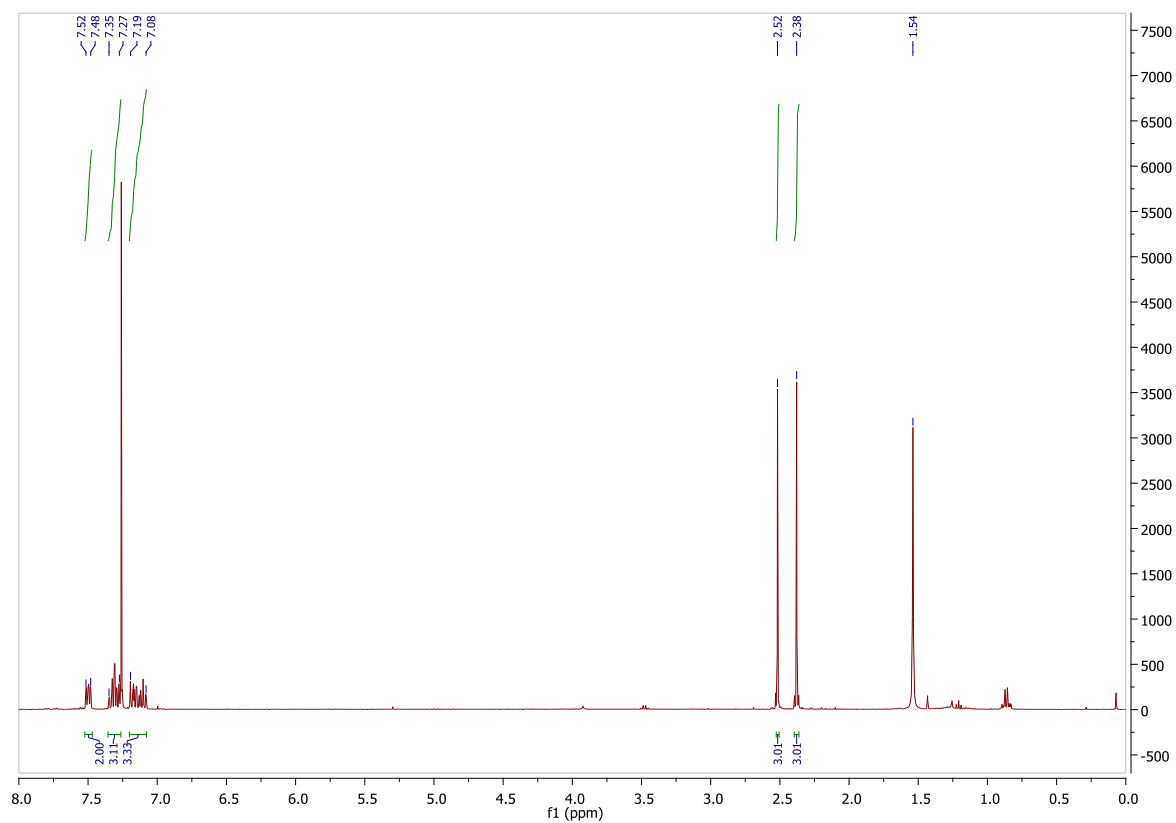
Methyl(2-((2-(methylselanyl)phenyl)buta-1,3-diy-1-yl)phenyl)sulfane (20)



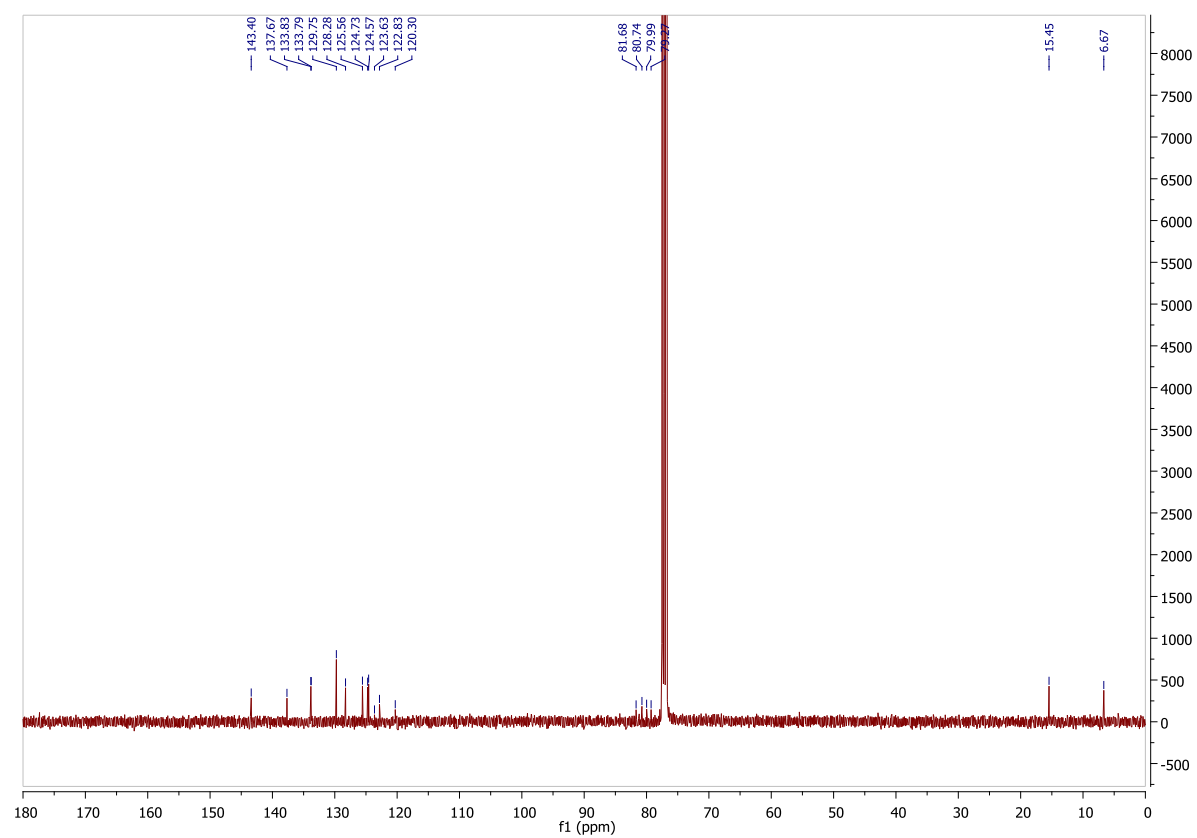
^{77}Se NMR:



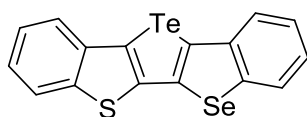
^1H NMR:



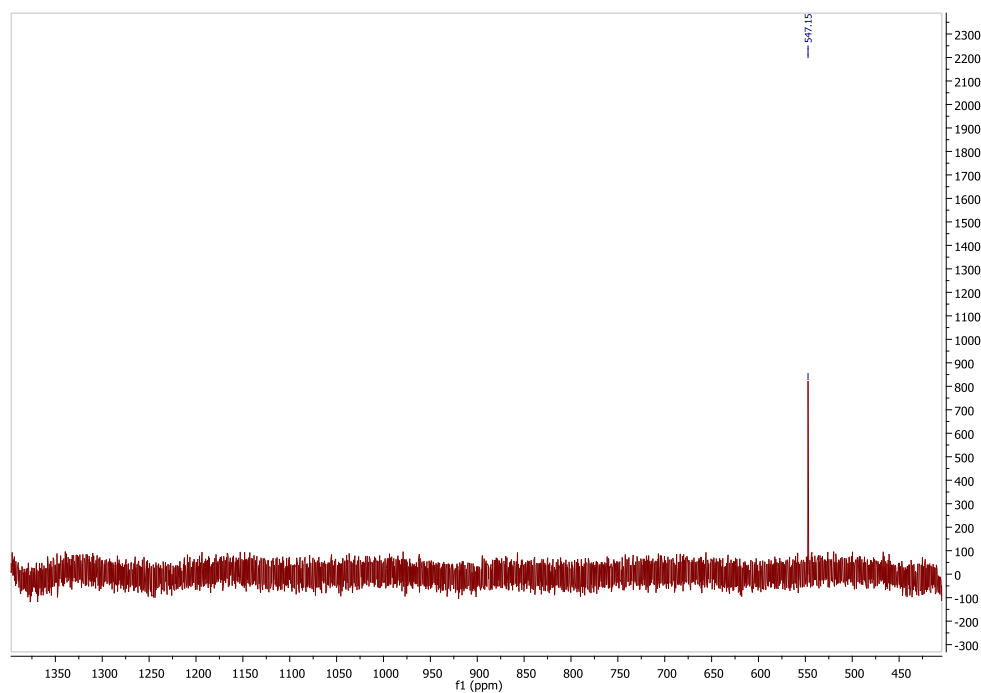
^{13}C NMR:



Benzo[*b*]selenopheno[2',3':4,5]telluropheno[3,2-*b*]benzo[*b*]thiophene (21)



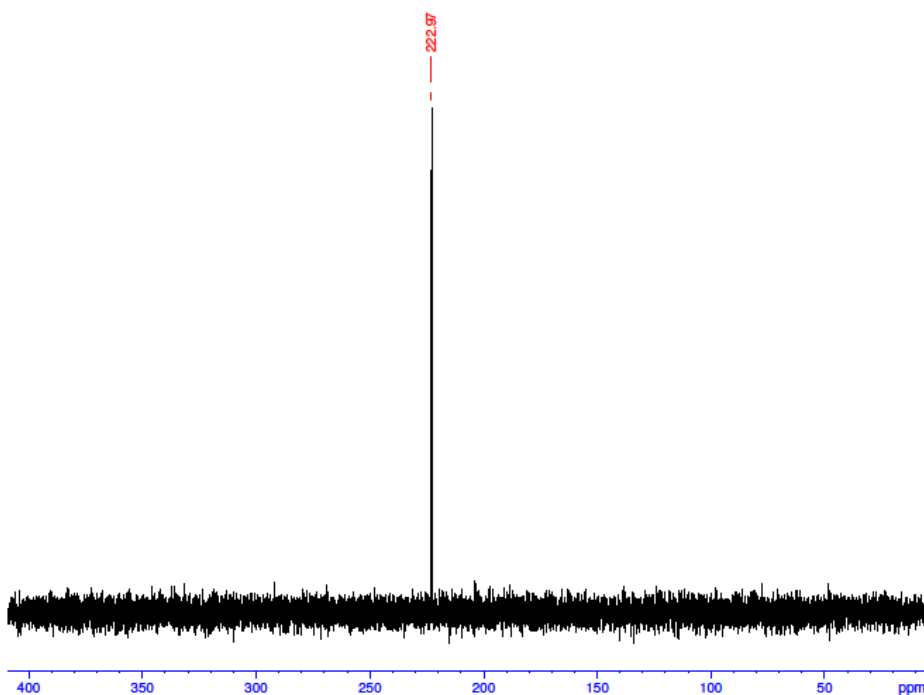
⁷⁷Se NMR:



¹²⁵Te NMR:



Akhil Gupta
Av400_125Te CDCl3 C:\1 gup016 26

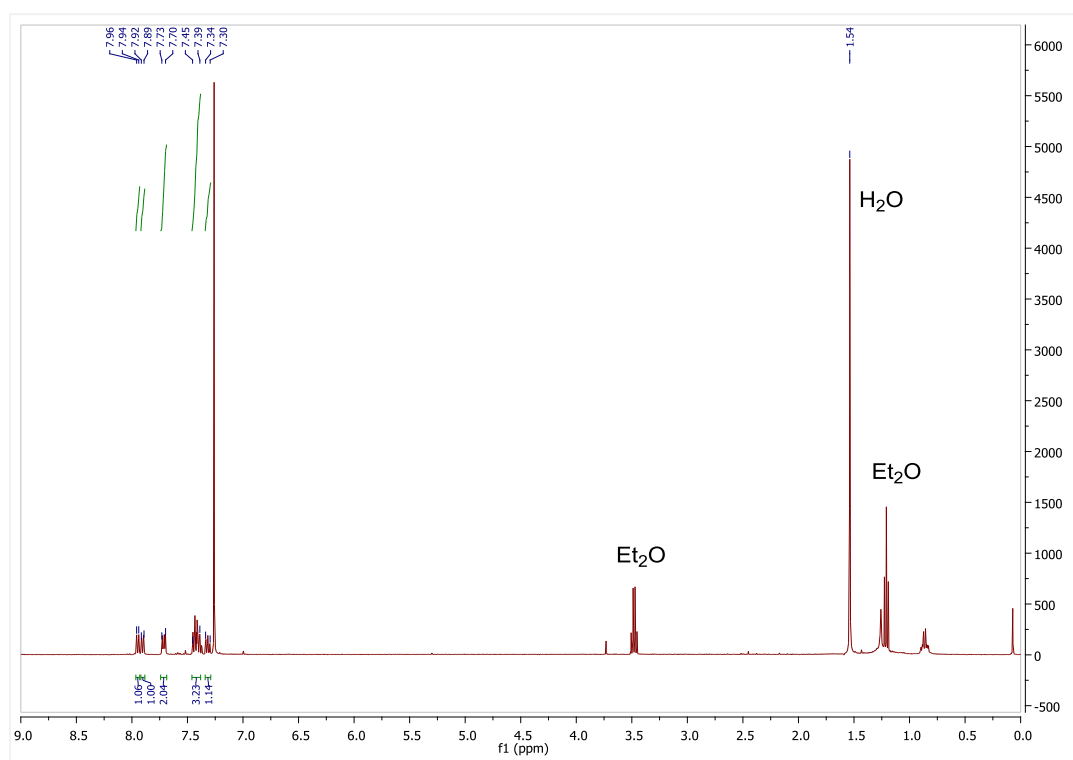


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PROCNO 1

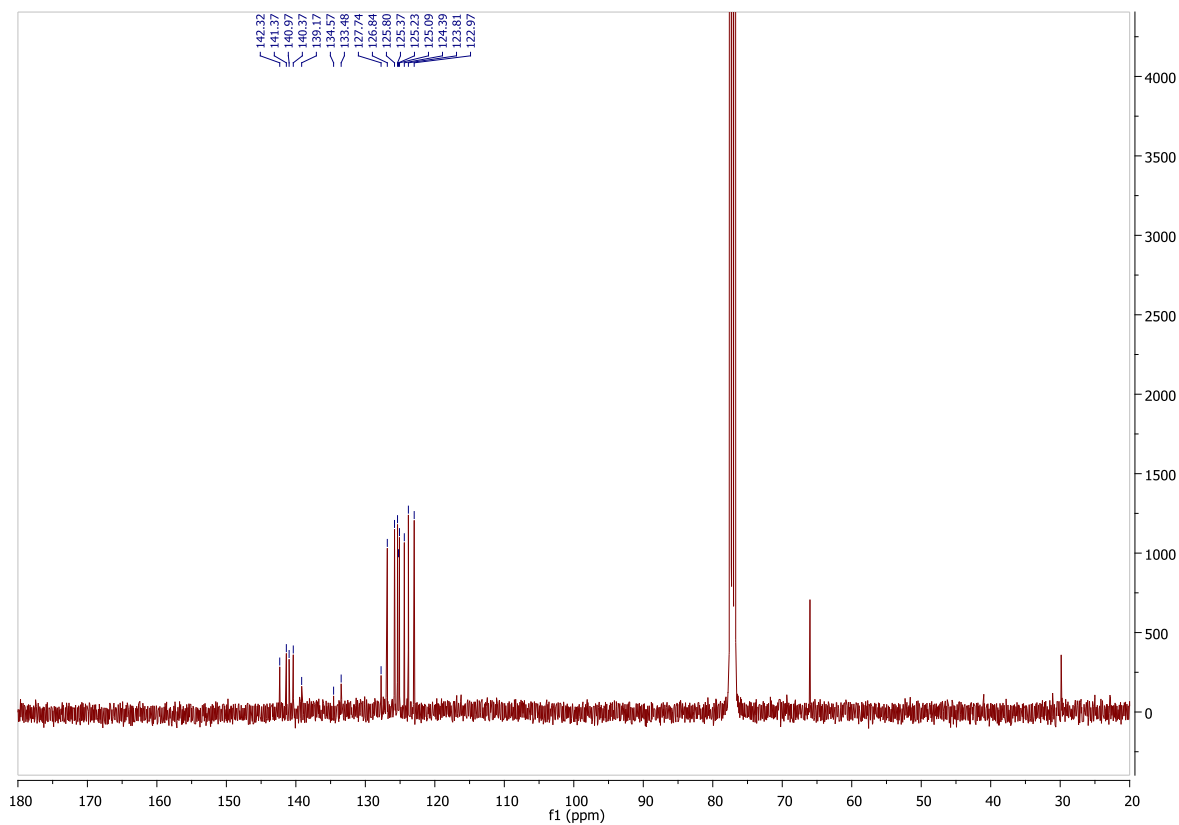
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DK 6.50 usec
TX 298.2 K
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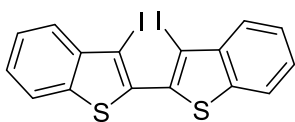
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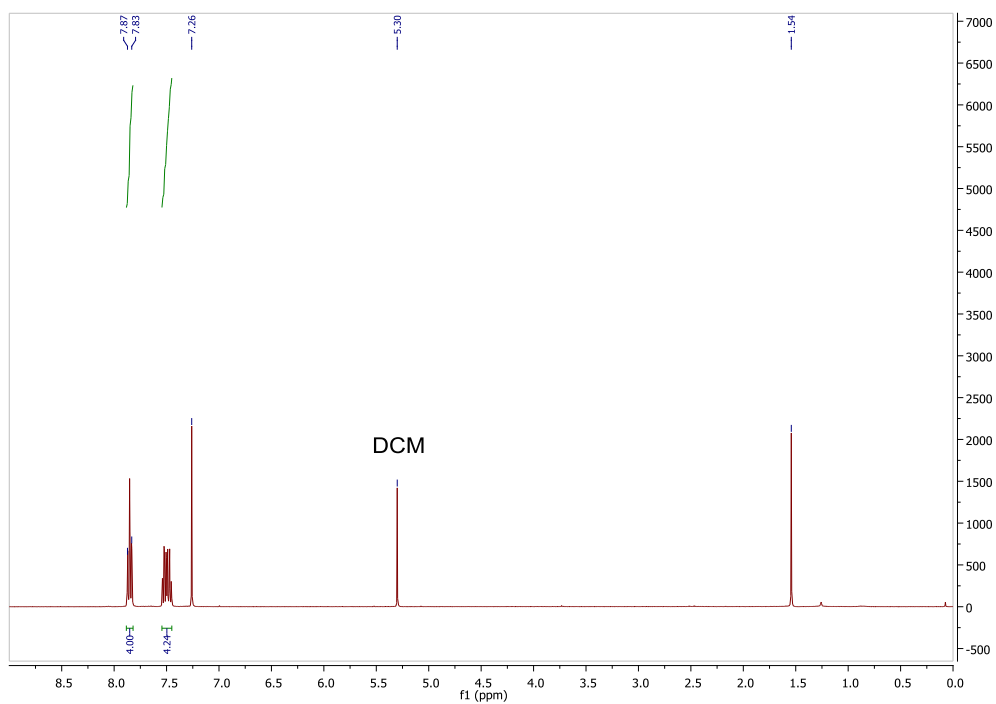
¹³C NMR:



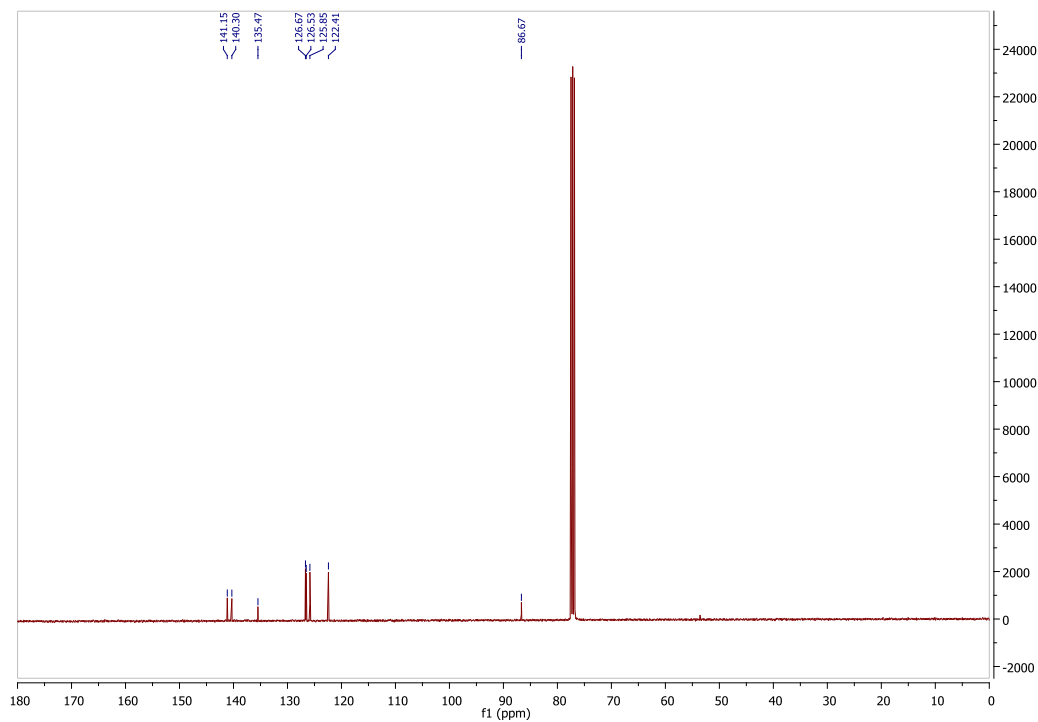
3,3'-Diiodo-2,2'-bibenzo[*b*]thiophene (22)



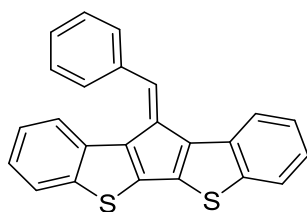
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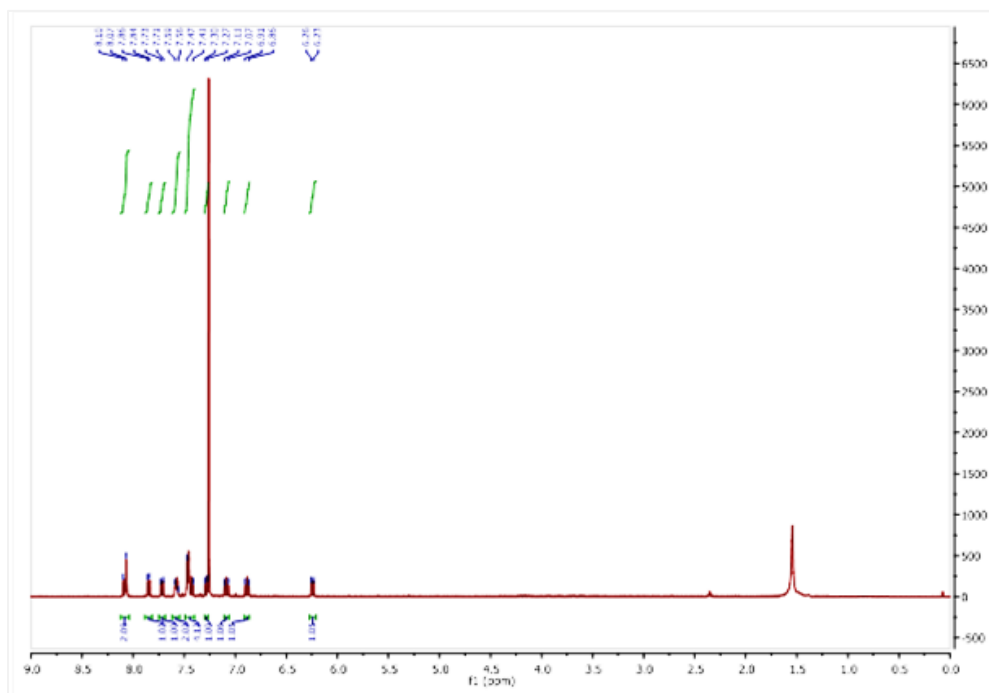
¹³C NMR:



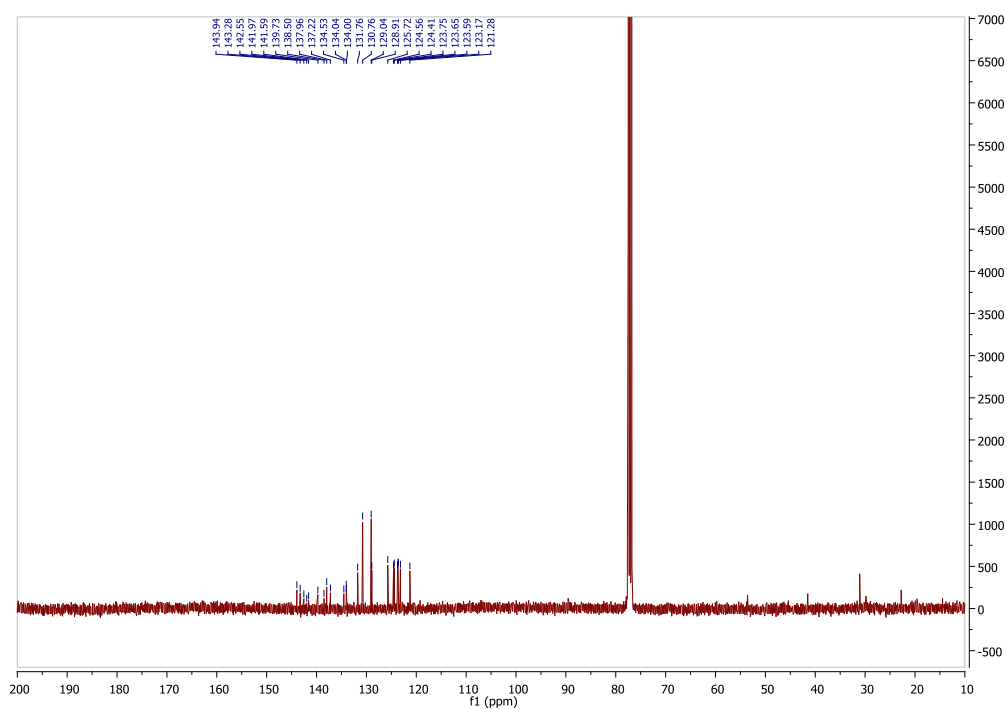
4-Benzylidene-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]bibenzo[*b*]thiophene (23)



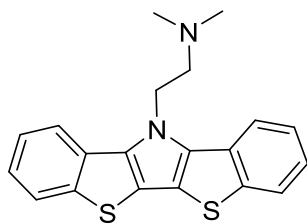
¹H NMR:



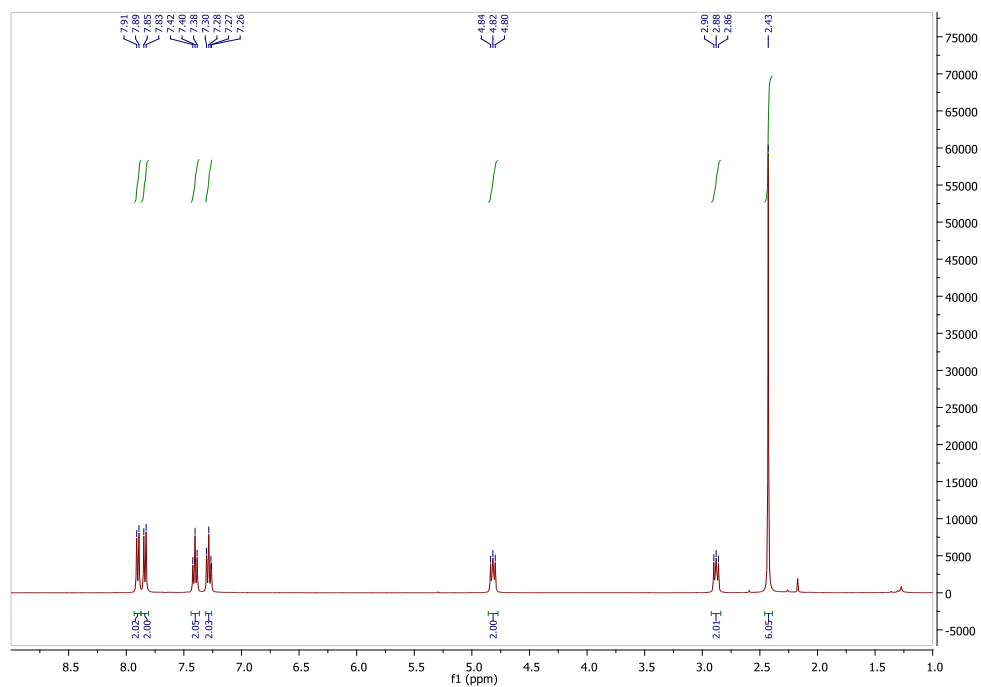
¹³C NMR:



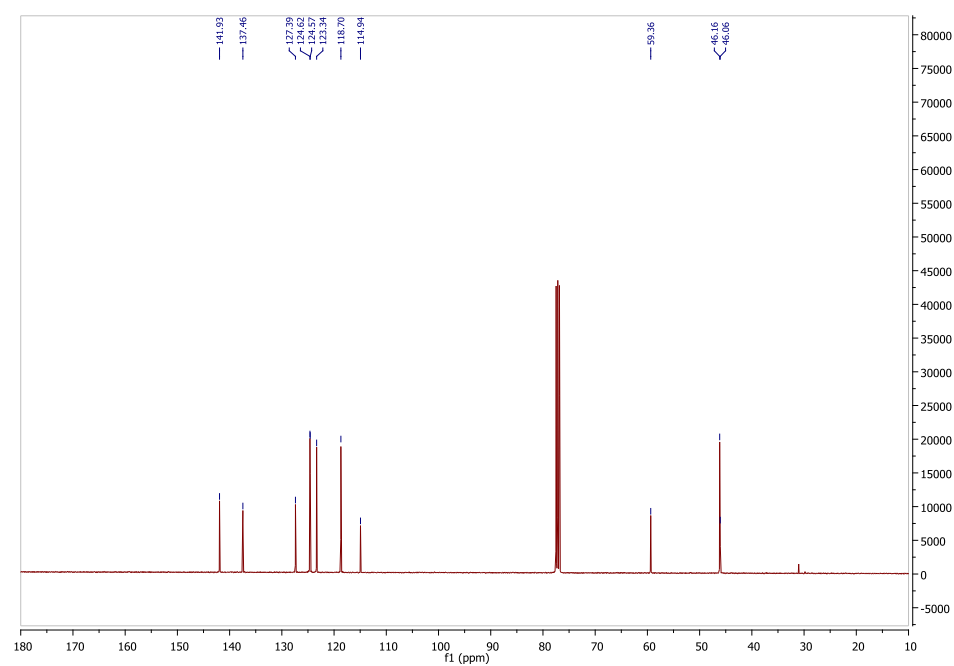
2-(11*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*d*]pyrrol-11-yl)-*N,N*-dimethylethan-1-amine (24)



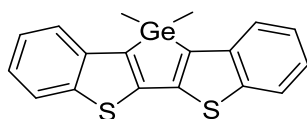
¹H NMR:



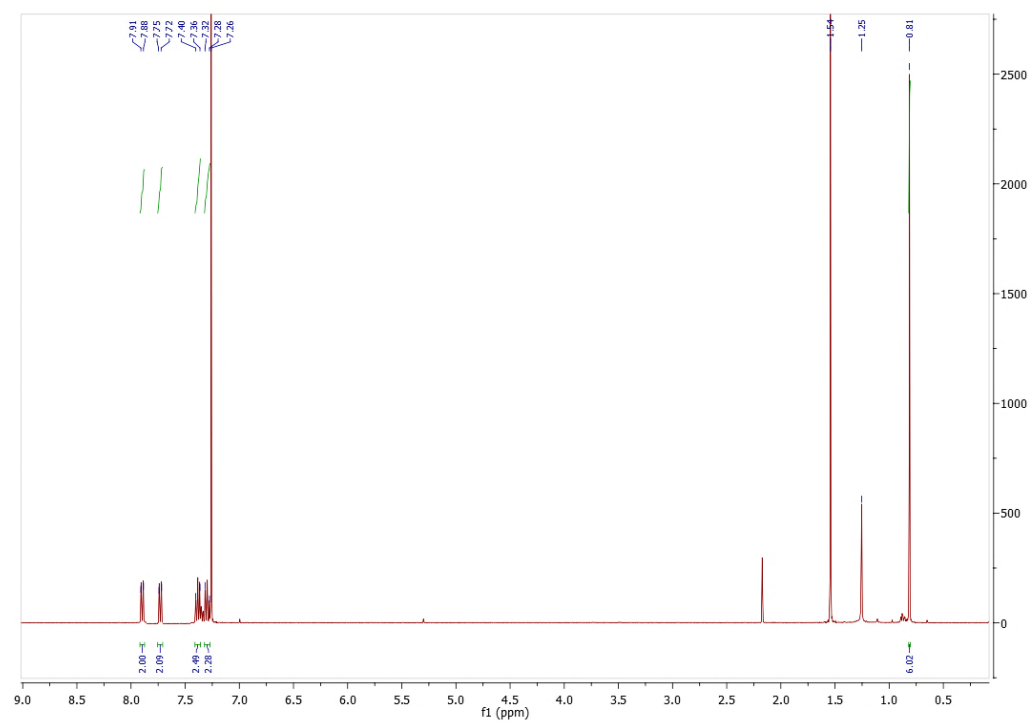
¹³C NMR:



11,11-Dimethyl-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*d*]germole (25)



¹H NMR:



¹³C NMR:

