Supporting Information

Substituent-controlled tailoring of chalcogen-bonded supramolecular nanoribbons in the solid state.

Nicolas Biot[†], Deborah Romito[‡] and Davide Bonifazi[‡]*

[†]School of Chemistry; Cardiff University, Park Place, CF10 3AT, Cardiff, United Kingdom; [‡]Institute of Organic Chemistry, University of Vienna, 1090 Vienna, Austria. E-mail: davide.bonifazi@univie.ac.at

1. General remarks

1.1. Instrumentation

Thin layer chromatography (TLC) was conducted on pre-coated aluminum sheets with 0.20 mm *Merck Millipore* Silica gel 60 with fluorescent indicator F254. *Column chromatography* was carried out using *Merck Gerduran* silica gel 60 (particle size 40-63 μm). ***Microwave reactions*** were performed on a *Biotage AB Initiator microwave instrument* producing controlled irradiation at 2.450 GHz. ***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™ or a Bruker AVANCE III HD 500MHz Spectrometer equipped with Broadband multinuclear (BBO) Prodigy CryoProbe. ^{1}H spectra were obtained at 300, 400 or 500 MHz, ^{13}C spectra were obtained at 75, 100 or 125 MHz NMR and ^{19}F spectra were obtained at 376 or 470 MHz. All spectra were obtained at r.t. otherwise stated. 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; C_6D_6: δ_H = 7.16 ppm, δ_C = 128.06 ppm). Coupling constants (*J*) were given in Hz. Resonance multiplicity was described as *s* (singlet), *d* (doublet), *t* (triplet), *dd* (doublet of doublets), *q* (quartet), *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 ESI mass spectra (HRMS) were performed on a Waters LCT HR TOF mass spectrometer in the positive or negative ion mode. All analyses were carried out at Cardiff university. ***X-ray measurements:*** 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] A summary of crystallographic data are available as ESI and the structures deposited with the Cambridge Structural Database (CCDC) deposition

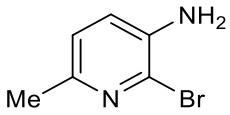
numbers: **Me-Te-CF$_3$** (1954271), **Cl-Se-CF$_3$** (2015557), **Cl-Te-CF$_3$** (1954275), **Cl-Te-Ph** (1954273), **Cl-Te-Th** (1954278), **I-Se-CF$_3$** (2015556), **I-Te-CF$_3$** (1954276), **I-Te-Ph** (1954274), **Ox-Se-CF$_3$** (2015558), and **Ox-Te-CF$_3$** (1954277). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1.2. Materials and methods

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, $CHCl_3$ and acetone were purchased as reagent-grade and used without further purification. Et_3N was distilled from CaH_2 and then stored over KOH. Anhydrous dioxane and pyridine were purchased from *Sigma Aldrich*. Solution of iso-propyl magnesium chloride in THF were freshly prepared according to a procedure of Lin et al.[3] and titrated with the Paquette method,[4] or directly purchased from *Sigma Aldrich*. Low temperature baths were prepared using different solvent mixtures depending on the desired temperature: 0 °C with ice/H_2O. Anhydrous conditions were achieved by flaming two necked flasks with a heat gun under vacuum and purging with N_2. 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 dried plastic or glass syringes. All reactions were performed in dry conditions and under inert atmosphere unless otherwise stated.

2. Synthetic procedure and spectral data

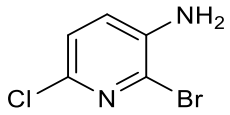
2.1. 2-bromo-6-methylpyridin-3-amine 2_{Me}



2_{Me}

2-bromo-6-methylpyridin-3-amine **2_{Me}** was synthesised following a procedure developed by Dunn et al.[5] To a solution of 6-methylpyridin-3-amine **1_{Me}** (5.41 g, 50 mmol) in MeCN (250 mL) was added portion wise NBS (8.89 g, 50 mmol). The reaction was stirred at room temperature for 5 minutes (orange colour turned dark red). The solvent was evaporated under reduced pressure and the crude material mixture was purified by silica gel chromatography ($CHCl_3$/MeOH 1%) to afford the desired product **2_{Me}** as a beige solid (6.95 g, 37 mmol, 74%). mp = 80-82 °C. IR: υ (cm^{-1}): 3443, 3294, 3175, 1616, 1553, 1472, 1377, 1310, 1260, 1142, 1109, 1053, 988, 867, 822, 671; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 6.90 (d, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 3.98 (s, NH_2, 2H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 148.2, 138.8, 128.5, 123.2, 123.1, 22.9; ESI-HRMS: $[M + H]^+$ cacld for $[C_6H_8N_2Br]^+$: 186.9871; found: 186.9863.

2.2. 2-bromo-6-chloropyridin-3-amine 2_{Cl}

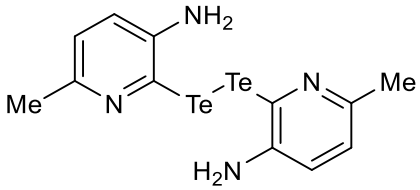


2_{Cl}

2-bromo-6-chloropyridin-3-amine **2_{Cl}** was synthesised following a procedure developed by Dunn et al.[5] To a solution of 6-chloropyridin-3-amine **1_{Cl}** (3.21 g, 25 mmol) in MeCN (125 mL) was added portion wise NBS (4.45 g, 25 mmol). The reaction was stirred at room temperature for 5

minutes. The solvent was evaporated under reduced pressure and the crude material mixture was purified by silica gel chromatography ($CHCl_3$) to afford the desired product **2$_{Cl}$** as a white solid (5.02 g, 24.2 mmol, 97%). mp = 140-142 °C. IR: υ (cm^{-1}): 3441, 3325, 1609, 1543, 1441, 1373, 1304, 1267, 1142, 1105, 1047, 851, 827, 696, 644; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.07 (d, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 4.17 (s, NH_2, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 140.7, 137.8, 126.9, 124.6, 124.0; ESI-HRMS: $[M + H]^+$ cacld for $[C_5H_5N_2ClBr]^+$: 206.9325; found: 206.9328.

2.3. 2,2'-ditellanediylbis(6-methylpyridin-3-amine) 3$_{Me-Te}$

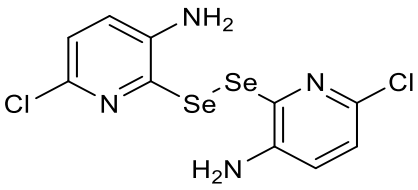


3$_{Me-Te}$

To a diluted solution of *i*-PrMgCl (2 M, 3.0 mL, 6 mmol) in dry THF (13.2 mL) under anhydrous condition, *n*-BuLi (1.6 M, 7.5 mL, 12 mmol) was added dropwise at 0 °C. The resulting mixture was stirred at the same temperature for 10 minutes. In parallel, to a solution of 2-bromo-6-methylpyridin-3-amine **2$_{Me}$** (1.13 g, 6 mmol) in dry THF (47 mL) under anhydrous condition, *n*-BuLi (1.6 M, 3.8 mL, 6 mmol) was added dropwise at 0 °C. The reaction was stirred 10 minutes at the same temperature then the tri-alkyl magnesate solution freshly prepared was added dropwise. The reaction was stirred for 1 h at 0 °C, freshly grounded elemental tellurium powder (2.29 g, 18 mmol) was added in once while a brisk flux of nitrogen was passed through the flask. The resulting mixture was stirred overnight, poured in a solution of NH_4Cl (1.00 g) in water (70 mL) and air bubbled through for 2 h. The aqueous phase was extracted with Et_2O (6 × 30 mL). The combined organic extracts were washed with water (25 mL), brine (25 mL), and dried over Na_2SO_4. The solvents were removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH 2%) to give pure **3$_{Me-Te}$** as a dark red solid (667 mg, 47%); mp = 132-136 °C. IR: υ (cm^{-1}): 3400, 3362, 3312, 3169, 2916, 1624, 1591, 1574, 1541, 1447, 1285, 1250, 1132, 1036, 984, 822; ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: 6.88 (d, *J* = 8.2 Hz, 2H), 6.84 (d,

J = 8.2 Hz, 2H), 5.55 (s, NH_2, 4H); 2.29 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 146.4 (two peaks overlap, 2C), 145.8 (two peaks overlap, 2C), 123.5 (two peaks overlap, 2C), 120.0 (two peaks overlap, 2C), 119.3 (two peaks overlap, 2C), 22.3 (two peaks overlap, 2C); ESI-HRMS: $[M + H]^+$ cacld for $[C_{12}H_{15}N_4{}^{128}Te_2]^+$: 470.9386; found: 470.9398.

2.4. 2,2'-diselanediylbis(6-chloropyridin-3-amine) $\mathbf{3_{Cl\text{-}Se}}$

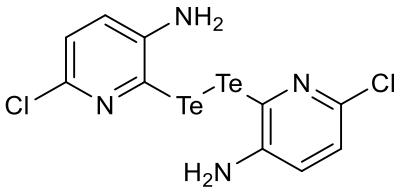


$\mathbf{3_{Cl\text{-}Se}}$

To a solution of *i*-PrMgCl (2 M, 1.9 mL, 3.81 mmol) in dry THF (7.6 mL) under anhydrous condition, *n*-BuLi (2.5 M, 3.0 mL, 7.62 mmol) was added dropwise at 0 °C. The resulting mixture was stirred at the same temperature for 10 minutes. In parallel, to a solution of 2-bromo-6-chloropyridin-3-amine **$\mathbf{2_{Cl}}$** (790 mg, 3.81 mmol) in dry THF (30 mL) under anhydrous condition, *n*-BuLi (2.5 M, 1.5 mL, 3.81 mmol) was added dropwise at 0 °C. The reaction was stirred 10 minutes at the same temperature then the tri-alkyl magnesate solution freshly prepared was added dropwise. The mixture was stirred for 30 minutes at 0 °C, freshly grounded elemental selenium powder (903 mg, 11.4 mmol) was added in once while a brisk flux of nitrogen was passed through the flask. The resulting mixture was stirred overnight, then poured in a solution of K_3FeCN_6 (1.25 g, 3.81 mmol) in water (60 mL) for 10 minutes. The aqueous phase was extracted with Et_2O (6 × 30 mL). The combined organic extracts were washed with water (25 mL), brine (25 mL), and dried over Na_2SO_4. The solvents were removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH 1%) to give pure **$\mathbf{3_{Cl\text{-}Se}}$** as a red solid (440 mg, 28% yield). mp = 198-200 °C. IR: ν (cm^{-1}): 3453, 3306, 3202, 3171, 2363, 1773, 1611, 1560, 1437, 1306, 1261, 1144, 1113, 851, 822, 691, 635, 570, 478; ^1H NMR (300 MHz, DMSO-d_6) δ_H: 7.18 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.01 (s, 4H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 145.9 (two peaks overlap, 2C), 135.7 (two peaks overlap, 2C), 134.5 (two peaks overlap, 2C), 125.2 (two peaks

overlap, 2C), 124.9 (two peaks overlap, 2C); ESI-HRMS: $[M+H]^+$ calcd for $[C_{10}H_9N_4Cl_2{}^{76}Se^{78}Se]^+$: 408.8569: found: 408.8577.

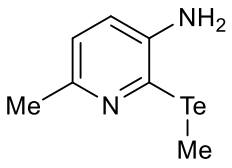
2.5. 2,2'-ditellanediylbis(6-chloropyridin-3-amine) $\mathbf{3_{Cl\text{-}Te}}$



$\mathbf{3_{Cl\text{-}Te}}$

To a diluted solution of *i*-PrMgCl (2 M, 0.5 mL, 1 mmol) in dry THF (2 mL) under anhydrous condition, *n*-BuLi (2.5 M, 0.8 mL, 2 mmol) was added dropwise at 0 °C. The resulting mixture was stirred at the same temperature for 10 minutes. In parallel, to a solution of 2-bromo-6-chloropyridin-3-amine $\mathbf{2_{Cl}}$ (207 mg, 1 mmol) in dry THF (8 mL) under anhydrous condition, *n*-BuLi (2.5 M, 0.4 mL, 1 mmol) was added dropwise at 0°C. The reaction was stirred 10 minutes at the same temperature then the tri-alkyl magnesate solution freshly prepared was added dropwise. The reaction was stirred for 1 h at 0 °C, freshly grounded elemental tellurium powder (381 mg, 3 mmol) was added in once while a brisk flux of nitrogen was passed through the flask. The resulting mixture was stirred overnight, poured in a solution of NH_4Cl (495 mg) in water (40 mL) and air bubbled through for 2 h. The aqueous phase was extracted with Et_2O (5 × 20 mL). The combined organic extracts were washed with water (15 mL), brine (15 mL), and dried over Na_2SO_4. The solvents were removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH 2%) to give pure $\mathbf{3_{Cl\text{-}Te}}$ as a dark red solid (141 mg, 55%); mp = 162-164 °C. IR: υ (cm^{-1}): 3460, 3362, 1599, 1558, 1539, 1296, 1244, 1142, 1117, 1030, 841, 824, 673, 635; ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: 7.10 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 5.83 (s, NH_2, 4H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 147.8 (two peaks overlap, 2C), 135.8 (two peaks overlap, 2C), 124.1 (two peaks overlap, 2C), 122.2 (two peaks overlap, 2C), 117.8 (two peaks overlap, 2C); ESI-HRMS: $[M + H]^+$ cacld for $[C_{10}H_9N_4{}^{128}Te^{130}Te]^+$: 512.8311; found: 512.8297.

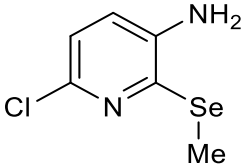
2.6. 6-methyl-2-(methyltellanyl)pyridin-3-amine $4_{Me\text{-}Te}$



$4_{Me\text{-}Te}$

To a solution of 2,2'-ditellanediylbis(6-methylpyridin-3-amine) **$3_{Me\text{-}Te}$** (469 mg, 1 mmol) in dry and degassed THF (25 mL) under anhydrous condition, were added $NaBH_4$ (114 mg, 3 mmol) and MeOH (0.20 mL, 160 mg, 5 mmol) and the reaction was stirred at room temperature for 1 h (the dark orange colour turned lighter). MeI (0.14 mL, 312 mg, 2.2 mmol) was added ant the mixture was stirred at room temperature for 1.5 h more, under exclusion of light. Water (10 mL) was slowly added to the solution and extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with water (15 mL), brine (15 mL) and dried over Na_2SO_4. The solvents were removed under reduce pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH 1%) to give pure amine **$4_{Me\text{-}Te}$** as yellow oil (450 mg, 90%). IR: υ (cm^{-1}): 3318, 3204, 2920, 2363, 2313, 1609, 1558, 1508, 1445, 1373, 1281, 1213, 1138, 1099, 1049, 820, 662; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 6.79 (s, 2H), 3.72 (s, NH_2, 2H), 2.43 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 150.3, 143.2, 127.6, 121.7, 120.7, 23.50, -15.37; API-HRMS: $[M + H]^+$ cacld for $[C_7H_{11}N_2{}^{122}Te]^+$: 244.9953; found: 244.9954.

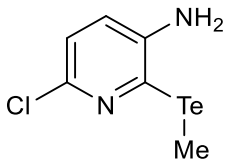
2.7. 6-chloro-2-(methylselanyl)pyridin-3-amine $4_{Cl\text{-}Se}$



$4_{Cl\text{-}Se}$

To a solution of 2,2'-diselanediylbis(6-chloropyridin-3-amine) **3**$_{\mathbf{Cl\text{-}Se}}$ (185 mg, 0.45 mmol) in dry and degassed THF (12 mL) under anhydrous conditions, were added $NaBH_4$ (51 mg, 1.34 mmol) and MeOH (0.09 mL, 72 mg, 2.25 mmol) and the reaction was stirred at room temperature for 1 h (the dark red colour turned dark orange). MeI (0.06 mL, 140 mg, 0.99 mmol) was added and the mixture was stirred at room temperature for 1.5 h more, under exclusion of light. Water (15 mL) was slowly added to the solution and extracted with Et_2O (3 × 50 mL). The combined organic extracts were washed with water (20 mL), brine (20 mL) and dried over Na_2SO_4. The solvents were removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH 0.5%) to give pure amine **4**$_{\mathbf{Cl\text{-}Se}}$ as orange oil (145 mg, 72%). IR: ν (cm^{-1}): 3395, 3319, 3221, 2930, 1867, 1620, 1568, 1418, 1377, 1290, 1256, 1128, 1105, 910, 847, 810, 694, 633, 571, 478, 430; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 6.92 (d, *J* = 8.2 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 3.80 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 141.1, 140.8, 140.1, 123.0, 121.0, 6.5; ESI-HRMS: $[M+H]^+$ cacld for $[C_6H_8N_2Cl^{76}Se]^+$: 218.9568; found: 218.9559.

2.8. 6-chloro-2-(methyltellanyl)pyridin-3-amine 4$_{\mathbf{Cl\text{-}Te}}$

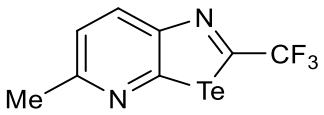


4$_{\mathbf{Cl\text{-}Te}}$

To a solution of 2,2'-ditellanediylbis(6-chloropyridin-3-amine) **3**$_{\mathbf{Cl\text{-}Te}}$ (714 mg, 1.4 mmol) in dry and degassed THF (35 mL) under N_2, were added $NaBH_4$ (159 mg, 4.2 mmol) and MeOH (0.28 mL, 224 mg, 5 mmol) and the reaction was stirred at room temperature for 1 h (the dark orange colour turned lighter). MeI (0.19 mL, 437 mg, 3.1 mmol) was added ant the mixture was stirred at room temperature for 1.5 h more, under exclusion of light. Water (15 mL) was slowly added to the solution and extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with water (15 mL), brine (15 mL) and dried over Na_2SO_4. The solvents were removed under reduce pressure. The crude was purified by silica gel chromatography ($CHCl_3$) to give pure amine **4**$_{\mathbf{Cl\text{-}Te}}$ as yellow oil (745 mg, 98%). IR: υ (cm^{-1}): 3422, 3316, 6026, 2926, 1607,1557, 1418, 1366, 1281,

1250, 1215, 1121, 1090, 1042, 843, 816, 679, 637; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 6.92 (d, J = 8.3 Hz, 1H), 6.81 (d, J = 8.3 Hz, 1H), 3.80 (s, NH_2, 2H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 144.8, 141.1, 127.7, 122.4, 122.0, -14.37; ESI-HRMS: $[M + H]^+$ cacld for $[C_6H_8N_2Cl^{122}Te]^+$: 264.9407; found: 264.9418.

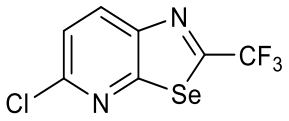
2.9. 5-methyl-2-(trifluoromethyl)-[1,3]tellurazolo[5,4-β]pyridine Me-Te-CF_3



Me-Te-CF_3

To a solution of 6-methyl-2-(methyltellanyl)pyridin-3-amine **4$_{Me-Te}$** (333 mg, 1.3 mmol) in dry pyridine (4 mL) and dry CH_2Cl_2 (4 mL) under anhydrous condition at 0 °C, trifluoroacetic anhydride (0.22 mL, 335 mg, 1.6 mmol) was added dropwise. The reaction was stirred 5 minutes at the same temperature then at room temperature overnight. Liquids were removed under reduced pressure, the yellow solid residue was dissolved in dry 1,4-dioxane (10 mL) and dry DIPEA (10 mL), then $POCl_3$ (0.48 mL, 799 mg, 5.3 mmol) was added dropwise. The reaction was heated to reflux and stirred overnight. The resulting mixture was allowed to cool down to room temperature, diluted with $CHCl_3$ (70 mL), washed with a saturated solution of $NaHCO_3$ (25 mL), water (20 mL), brine (20 mL) and dried over Na_2SO_4. The solvents were removed under reduced pressure. The crude was purified twice by silica gel chromatography ($CHCl_3$/MeOH 0 to 1%) to give pure **Me-Te-CF_3** as an off-white solid (189 mg, 45%); mp = 110-112 °C. IR: υ (cm^{-1}): 3017, 2970, 1738, 1549, 1495, 1300, 1157, 1126, 1065, 968, 833, 716, 640; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.36 (d, J = 8.3 Hz, 1H), 7.37 (d, J = 8.3 Hz, 1H), 2.67 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3$) δ_F: -62.5 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C: 164.4, 162.6 (q, J_{CF} = 41 Hz, 1C), 158.2, 153.3, 134.9, 123.6 (q, J_{CF} = 274 Hz, 1C), 122.5, 24.66; ESI-HRMS: $[M + H]^+$ cacld for $[C_8H_6N_2F_3{}^{130}Te]^+$: 316.9545; found: 316.9547. Single crystals suitable for X-ray diffraction analysis were grown from slow evaporation of $CHCl_3$ solution.

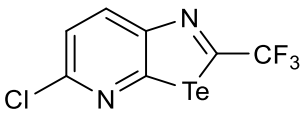
2.10. 5-chloro-2-(trifluoromethyl)-[1,3]selenazolo[5,4-β]pyridine Cl-Se-CF_3



Cl-Se-CF_3

To a mixture of 6-chloro-2-(methylselanyl)pyridin-3-amine **$4_{Cl\text{-}Se}$** (140 mg, 0.63 mmol) in dry pyridine (2.6 mL) and dry CH_2Cl_2 (2.6 mL) under anhydrous condition at 0 °C, trifluoroacetic acid anhydride (0.1 mL, 146 mg, 0.69 mmol) was added dropwise. The reaction was stirred 5 minutes at the same temperature, then at room temperature overnight. Liquids were removed under reduced pressure, the yellow solid residue was dissolved in dry 1,4-dioxane (2.3 mL) and dry DIPEA (2.3 mL), then $POCl_3$ (0.23 mL, 386 mg, 2.52 mmol) was added dropwise. The reaction was heated to reflux and stirred overnight. The resulting mixture was allowed to cool down to room temperature, diluted with $CHCl_3$ (50 mL), washed with a saturated solution of $NaHCO_3$ (20 mL), water (20 mL), brine (20 mL) and dried over Na_2SO_4. The solvents were removed under reduced pressure. The crude was purified by Silica Gel Chromatography ($CHCl_3$) to give pure **Cl-Se-CF_3** as a yellow solid (38 mg, 38%). mp: 118-120 °C. IR: ν (cm^{-1}): 2976, 2936, 2363, 2158, 1703, 1574, 1503, 1408, 1348, 1314, 1261, 1123, 1076, 991, 837, 746, 719, 662, 534, 436; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 8.40 (d, J = 8.6 Hz, 1H), 7.57 (d, J = 8.6 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -62.3 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 162.5 (q, J_{CF} = 42 Hz, 1C), 161.7, 150.3, 146.7, 135.7, 123.5, 122.3 (q, J_{CF} = 274 Hz, 1C); ASAP-HRMS: $[M+H]^+$ cacld for $[C_7H_3N_2F_3Cl^{76}Se]^+$: 282.9129; found: 282.9135. Single crystals suitable for X-ray diffraction analysis were grown from slow evaporation of $CHCl_3$ solution.

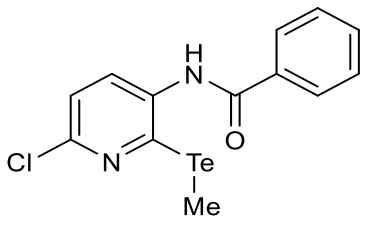
2.11. 5-chloro-2-(trifluoromethyl)-[1,3]tellurazolo[5,4-β]pyridine Cl-Te-CF_3



Cl-Te-CF_3

To a solution of 6-chloro-2-(methyltellanyl)pyridin-3-amine **4$_{Cl\text{-}Te}$** (736 mg, 2.7 mmol) in dry pyridine (6 mL) and dry CH_2Cl_2 (6 mL) under anhydrous condition at 0 °C, trifluoroacetic acid anhydride (0.46 mL, 693 mg, 3.3 mmol) was added dropwise. The reaction was stirred 5 minutes at the same temperature, then overnight at room temperature. Liquids were removed under reduced pressure, the yellow solid residue was dissolved in dry 1,4-dioxane (25 mL) and dry DIPEA (25 mL), then $POCl_3$ (0.98 mL, 1.62 g, 10.8 mmol) was added dropwise. The reaction was heated to reflux and stirred overnight. The resulting mixture was allowed to cool down to room temperature, diluted with $CHCl_3$ (150 mL), washed with a saturated solution of $NaHCO_3$ (35 mL), water (25 mL), brine (25 mL), and dried over Na_2SO_4. The solvents were removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$) to give pure **Cl-Te-CF$_3$** as a white solid (746 mg, 83%); mp = 140-142°C. IR: υ (cm^{-1}): 3021, 1562, 1524, 1485, 1396, 1354, 1296, 1250, 1233, 1128, 1119, 1061, 968, 854, 835, 737, 704, 640; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.42 (d, J = 8.5 Hz, 1H), 7.54 (d, J = 8.5 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -62.6 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 164.8 (q, J_{CF} = 42 Hz, 1C), 164.0, 154.5, 149.1, 136.7, 123.4, 123.2 (q, J_{CF} = 275 Hz, 1C); EI-HRMS: $[M]^+$ cacld for $[C_7H_2N_2ClF_3{}^{130}Te]^+$: 335.8921; found: 335.8916. Single crystals suitable for X-ray diffraction analysis were grown from slow evaporation of $CHCl_3$ solution.

2.12. *N*-(6-chloro-2-(methyltellanyl)pyridin-3-yl)benzamide 5$_{Cl\text{-}Ph}$

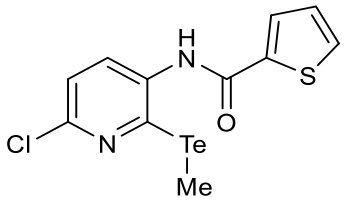


5$_{Cl\text{-}Ph}$

To a solution of 6-chloro-2-(methyltellanyl)pyridin-3-amine **4$_{Cl\text{-}Te}$** (95 mg, 0.35 mmol) in dry pyridine (1 mL) and dry CH_2Cl_2 (1 mL) under anhydrous condition at 0 °C, benzoyl chloride (0.05 mL, 59 mg, 0.42 mmol) was added dropwise. The reaction was stirred 5 minutes at the same

temperature, then at room temperature overnight. The resulting mixture was diluted with EtOAc (30 mL) and washed with water (10 mL), extracted with EtOAc (2 x 10 mL), organic phases were combined and washed with brine (10 mL) and dried over Na_2SO_4. The solvents were removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH 1%) to give pure amide **5$_{Cl\text{-}Ph}$** as a white solid (120 mg, 92%); mp = 138-140 °C. IR: υ (cm^{-1}): 3229, 1647, 1558, 1501, 1485, 1339, 1215, 1126, 1107, 1051, 907, 827, 710; ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: 10.38 (s, 1H), 8.00-7.96 (m, 2H), 7.65-7.53 (m, 4H), 7.35 (d, J = 8.2 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 165.9, 147.8, 144.4, 137.6, 136.4, 133.4, 132.2, 128.6 (two peaks overlap, 2C), 127.8 (two peaks overlap, 2C), 120.9, -13.57; ESI-HRMS: $[M + H]^+$ cacld for $[C_{13}H_{12}N_2OCl^{130}Te]^+$: 376.9700; found: 376.9708.

2.13. *N*-(6-chloro-2-(methyltellanyl)pyridin-3-yl)thiophene-2-carboxamide 5$_{Cl\text{-}Th}$

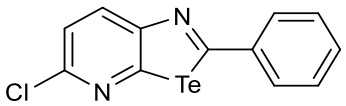


5$_{Cl\text{-}Th}$

To a solution of 6-chloro-2-(methyltellanyl)pyridin-3-amine **4$_{Cl\text{-}Te}$** (656 mg, 2.43 mmol) in dry pyridine (6 mL) and dry CH_2Cl_2 (6 mL) under anhydrous condition at 0 °C, thiophene-2-carbonyl chloride (0.31 mL, 427 mg, 2.91 mmol) was added dropwise. The reaction was stirred 5 minutes at the same temperature, then at room temperature overnight. The resulting mixture was diluted with EtOAc (75 mL) and washed with water (25 mL), extracted with EtOAc (2 x 15 mL), organic phases were combined and washed with brine (25 mL) and dried over Na_2SO_4. The solvents were removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$/MeOH 1%) to give pure amide **5$_{Cl\text{-}Th}$** as a bright yellow solid (794 mg, 86%); mp = 154-156 °C. IR: υ (cm^{-1}): 3237, 2970, 1739, 1632, 1557, 1520, 1489, 1404, 1352, 1331, 1287, 1217, 1125, 1094, 1057, 901, 808, 738, 714; ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: 10.39 (s, 1H), 7.99 (dd, J = 3.8, 1.0 Hz, 1H), 7.91 (dd, J = 5.0, 1.0 Hz, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.34 (d, J = 8.2 Hz,

1H), 7.25 (dd, J = 5.0, 3.8 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 160.5, 148.0, 144.5, 138.4, 137.1, 136.6, 132.5, 129.9, 128.3, 120.9, -13.53; ESI-HRMS: $[M + H]^+$ cacld for $[C_{11}H_{10}N_2OSCl^{130}Te]^+$: 382.9265; found: 382.9254.

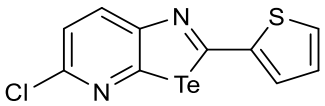
2.14. 5-chloro-2-phenyl-[1,3]tellurazolo[5,4-β]pyridine Cl-Te-Ph



Cl-Te-Ph

To a solution of *N*-(6-chloro-2-(methyltellanyl)pyridin-3-yl)benzamide **5$_{Cl-Ph}$** (105 mg, 0.28 mmol) in dry DIPEA (3 mL) in dry 1,4-dioxane (3 mL) under anhydrous condition, $POCl_3$ (0.1 mL, 172 mg, 1.12 mmol) was added dropwise. The reaction was heated to reflux and stirred overnight. The resulting mixture was allowed to cool down to room temperature, diluted with $CHCl_3$ (30 mL), washed with a saturated solution of $NaHCO_3$ (10 mL), water (10 mL), brine (10 mL) and dried over Na_2SO_4. The solvents were removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$) to give pure 5-chloro-2-phenyl-[1,3]tellurazolo[5,4-β]pyridine **Cl-Te-Ph** as a yellowish solid (87 mg, 91%); mp = 166-168 °C. IR: υ (cm^{-1}): 1557, 1476, 1385, 1329, 1115, 1084, 1057, 916, 829, 758, 729, 685, 559; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 8.20 (d, J = 8.5 Hz, 1H), 7.87-7.82 (m, 2H), 7.55-7.42 (m, 3H), 7.40 (d, J = 8.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 178.2, 162.3, 157.3, 146.7, 140.8, 134.0, 131.8, 129.4, 128.7, 122.4; ESI-HRMS: $[M]^+$ cacld for $[C_{12}H_8N_2Cl^{130}Te]^+$: 344.9438; found: 344.9436. Single crystals suitable for X-ray diffraction analysis were grown from slow evaporation of $CHCl_3$ solution.

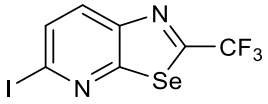
2.15. 5-chloro-2-(thiophen-2-yl)-[1,3]tellurazolo[5,4-β]pyridine Cl-Te-Th



Cl-Te-Th

To a solution of *N*-(6-chloro-2-(methyltellanyl)pyridin-3-yl)thiophene-2-carboxamide **5$_{Cl\text{-}Th}$** (761 mg, 2 mmol) in dry DIPEA (20 mL) in dry dioxane (20 mL) under anhydrous condition, $POCl_3$ (0.73 mL, 1.20 g, 8 mmol) was added dropwise. The reaction was heated to reflux and stirred overnight. The resulting mixture was allowed to cool down to room temperature, diluted with $CHCl_3$ (100 mL), washed with a saturated solution of $NaHCO_3$ (40 mL), water (40 mL), brine (40 mL), and dried over Na_2SO_4. The solvents were removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$) to give pure 5-chloro-2-(thiophen-2-yl)-[1,3]tellurazolo[5,4-β]pyridine **Cl-Te-Th** as a yellow solid (598 mg, 86%); mp = 168-170 °C. IR: υ (cm^{-1}): 1740, 1566, 1526, 1466, 1416, 1385, 1337, 1274, 1059, 1047, 887, 856, 839, 827, 716, 696; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 8.12 (d, *J* = 8.5 Hz, 1H), 7.54 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.49 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.11 (dd, *J* = 5.1, 3.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 167.5, 161.8, 156.5, 146.6, 145.8, 133.4, 131.5, 130.7, 128.1, 122.5; ESI-HRMS: $[M + H]^+$ cacld for $[C_{10}H_6N_2SCl^{130}Te]^+$: 350.9003; found: 350.8991. Single crystals suitable for X-ray diffraction analysis were grown from slow evaporation of $CHCl_3$ solution.

2.16. 5-iodo-2-(trifluoromethyl)-[1,3]selenazolo[5,4-β]pyridine I-Se-CF$_3$

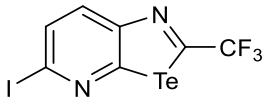


I-Se-CF$_3$

5-iodo-2-(trifluoromethyl)-[1,3]selenazolo[5,4-β]pyridine **I-Se-CF$_3$** was synthesised following a procedure inspired by the work of *Bissember* and *Banwell*.[6] A microwave was loaded with, in that order, NaI (195 mg, 1.3 mmol), 5-chloro-2-(trifluoromethyl)-[1,3]selenazolo[5,4-β]pyridine **Cl-Se-CF$_3$** (38 mg, 0.13 mmol), dry MeCN (0.65 mL) and acetyl chloride (0.01 mL, 16 mg, 0.2 mmol) under nitrogen atmosphere. The reaction was stirred under microwave irradiation at 80 °C for 9 hours. The resulting mixture was diluted with MeCN (10 mL), washed with a saturated solution of K_2CO_3 (15 mL) brine (15 mL), and dried over Na_2SO_4. The solvents were removed under reduced pressure. The crude was purified by silica gel chromatography ($CHCl_3$) to give pure

I-Se-CF$_3$ as a yellow solid (27 mg, 55% yield); mp = 128-130 °C. IR: υ (cm^{-1}): 3005, 2978, 2832, 1750, 1612, 1580, 1489, 1313, 1250, 1189, 1132, 1082, 1059, 958, 850, 812, 750; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 8.08 (d, J = 8.7 Hz, 1H), 7.94 (d, J = 8.7 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -62.3 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 162.6, 162.5 (q, J_{CF} = 42 Hz, 1C), 150.3, 146.7, 135.7, 123.5, 120.5 (q, J_{CF} = 275 Hz, 1C); ASAP-HRMS: $[M+H]^+$ cacld for $[C_7H_3N_2F_3{}^{76}SeI]^+$: 374.8484; found: 374.8485. Single crystals suitable for X-ray diffraction analysis were grown from slow evaporation of $CHCl_3$ solution.

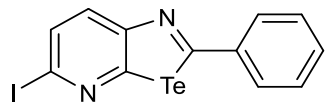
2.17. 5-iodo-2-(trifluoromethyl)-[1,3]tellurazolo[5,4-β]pyridine I-Te-CF$_3$



I-Te-CF$_3$

5-iodo-2-(trifluoromethyl)-[1,3]tellurazolo[5,4-β]pyridine **I-Te-CF$_3$** was synthesised following a procedure inspired by the work of *Bissember* and *Banwell*.[6] A microwave vial was loaded with, in that order, NaI (750 mg, 5 mmol), 5-chloro-2-(trifluromethyl)-[1,3]tellurazolo[5,4-β]pyridine **Cl-Te-CF$_3$** (167 mg, 0.5 mmol), dry MeCN (2.5 mL) and acetyl chloride (0.05 mL, 59 mg, 0.75 mmol) under nitrogen atmosphere. The reaction was stirred under micro-wave irradiation at 80 °C for 12 h. The resulting mixture was diluted with MeCN (5 mL), washed with a saturated solution of K_2CO_3 (5 mL), brine (5 mL), and dried over Na_2SO_4. The solvents were removed under reduced pressure. The crude material was purified by silica gel chromatography ($CHCl_3$) to give pure **I-Te-CF$_3$** as a white solid (109 mg, 51 %); mp = 170-172 °C. IR: υ (cm^{-1}): 3032, 2970, 1738, 1557, 1489, 1383, 1292, 1237, 1182, 1132, 1088, 1059, 964, 849, 829, 725; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 8.12 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -62.6 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 165.3, 165.1 (q, J_{CF} = 42 Hz, 1C), 154.9, 135.9, 133.6, 123.4 (q, J_{CF} = 276 Hz, 1C), 115.5; ESI-HRMS: $[M + H]^+$ cacld for $[C_7H_3N_2F_3{}^{130}Te^{127}I]^+$: 428.8355; found: 428.8355. Single crystals suitable for X-ray diffraction analysis were grown from slow evaporation of $CHCl_3$ solution.

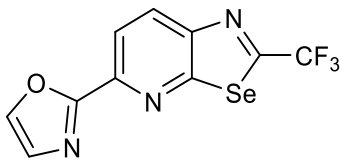
2.18. 5-iodo-2-phenyl-[1,3]tellurazolo[5,4-β]pyridine I-Te-Ph



I-Te-Ph

5-iodo-2-phenyl-[1,3]tellurazolo[5,4-β]pyridine **I-Te-Ph** was synthesised following a procedure inspired by the work of *Bissember* and *Banwell*.[6] A microwave vial was loaded with, in that order, NaI (360 mg, 2.4 mmol), 5-chloro-2-phenyl-[1,3]tellurazolo[5,4-β]pyridine **Cl-Te-Ph** (84 mg, 0.24 mmol), dry MeCN (1.2 mL) and acetyl chloride (0.03 mL, 28 mg, 0.36 mmol) under nitrogen atmosphere. The reaction was stirred under micro-wave irradiation at 80 °C for 12 h. The resulting mixture was diluted with MeCN (10 mL), washed with a saturated solution of K_2CO_3 (10 mL), a saturated solution of $Na_2S_2O_6$ (10 mL), brine (10 mL), and dried over Na_2SO_4. The solvents were removed under reduced pressure. The crude material was purified by silica gel chromatography ($CHCl_3$) to give pure **I-Te-Ph** as a yellowish solid (87 mg, 84 %); mp = 164-168 °C. IR: υ (cm^{-1}): 2922, 1557, 1495, 1474, 1443, 1329, 1211, 1082, 1055, 829, 758, 727, 685, 559; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.92 (d, *J* = 8.4 Hz, 1H), 7.88-7.84 (m, 2H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.56-7.43 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 178.5, 164.0, 157.8, 140.9, 133.4, 132.8, 131.9, 129.4 (two peaks overlap, 2C), 128.8 (two peaks overlap, 2C), 112.5; ESI-HRMS: $[M + H]^+$ cacld for $[C_{12}H_8N_2{}^{130}Te^{127}I]^+$: 436.8795; found: 436.8802. Single crystals suitable for X-ray diffraction analysis were grown from slow evaporation of $CHCl_3$ solution.

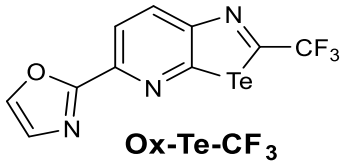
2.19. 2-(2-(trifluoromethyl)-[1,3]selenazolo[5,4-β]pyridin-5-yl)oxazole Ox-Se-CF_3



Ox-Se-CF_3

2-(2-(trifluoromethyl)-[1,3]selenazolo[5,4-β]pyridin-5-yl)oxazole **Ox-Se-CF$_3$** was synthesised following a procedure inspired by the work of Piersanti *et al.*[7] To a solution of oxazole (0.03 mL, 35 mg, 0.5 mmol) in dry and degassed THF (0.5 mL) under anhydrous condition was added *n*-BuLi (2.5 M, 0.2 mL, 0.5 mmol) dropwise at -84 °C. The reaction was stirred at the same temperature for 30 minutes and a solution of $ZnCl_2$ in Et_2O (1 M, 1.5 mL, 1.5 mmol) added dropwise. The mixture was stirred further at 0 °C for 1 h (white suspension). A separated flask was loaded with 5-iodo-2-(trifluoromethyl)-[1,3]selenazolo[5,4-β]pyridine **I-Se-CF$_3$** (85 mg, 0.20 mmol) and [$Pd(PPh_3)_4$] (23 mg, 0.02 mmol) in dry and degassed THF under anhydrous condition and oxazolylzinc chloride suspension (1.2 mL) was added. The reaction was stirred at reflux for 2 h. The resulting mixture was diluted with EtOAc (20 mL), washed with water (10 mL), brine (10 mL) and dried over Na_2SO_4. The solvents were evaporated under reduced pressure. The crude was purified by silica gel chromatography (petr. ether/EtOAc 6:4) to give pure **Ox-Se-CF$_3$** as a yellow solid (13 mg, 59% yield); mp = 180-184 °C. IR: ν (cm^{-1}): 3136, 3038, 2918, 2849, 1726, 1686, 1581, 1560, 1506, 1466, 1414, 1313, 1283, 1180, 1138, 1090, 989, 914, 862, 841, 785, 741, 719, 696, 660, 538; ^{1}H NMR (300 MHz, C_6D_6) δ_H: 8.06 (d, J = 8.6 Hz, 1H), 7.70 (d, J = 8.6 Hz, 1H), 7.02 (d, J = 0.7 Hz, 1H), 6.91 (d, J = 0.7 Hz, 1H); ^{19}F NMR (376 MHz, C_6D_6) δ_F: -62.3 (s, 3F); ^{13}C NMR (100 MHz, C_6D_6) δ_C: 163.8, 162.8 (q, J_{CF} = 42 Hz), 160.4, 147.9, 145.2, 140.6, 134.0, 129.5, 121.3 (q, J_{CF} = 274 Hz), 121.1; ESI-HRMS: $[M+H]^+$ calcd for $[C_{10}H_5N_3OF_3{}^{76}Se]^+$: 315.9577; found: 315.9576. Single crystals suitable for X-ray diffraction analysis were grown from slow evaporation of C_6H_6 solution.

2.20. 2-(2-(trifluoromethyl)-[1,3]tellurazolo[5,4-β]pyridin-5-yl)oxazole Ox-Te-CF$_3$

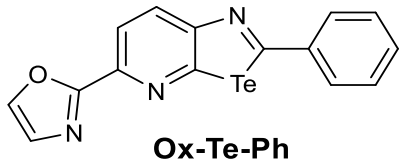


Ox-Te-CF$_3$

2-(2-(trifluoromethyl)-[1,3]tellurazolo[5,4-β]pyridin-5-yl)oxazole **Ox-Te-CF$_3$** was synthesised following a procedure inspired by the work of Piersanti *et al.*[7] To a solution of oxazole (0.03 mL,

35 mg, 0.5 mmol) in dry and degassed THF (0.5 mL) under anhydrous condition was added *n*-BuLi (2.5 M, 0.2 mL, 0.5 mmol) dropwise at -84 °C. The reaction was stirred at the same temperature for 30 minutes and a solution of $ZnCl_2$ in Et_2O (1M, 1.5 mL, 1.5 mmol) added dropwise. The mixture was stirred further at 0 °C for 1 h (white suspension). A separated flask was loaded with 5-iodo-2-(trifluoromethyl)-[1,3]tellurazolo[5,4-β]pyridine **I-Te-CF$_3$** (85 mg, 0.20 mmol) and $[Pd(PPh_3)_4]$ (23 mg, 0.02 mmol) in dry and degassed THF under anhydrous condition and oxazolylzinc chloride suspension (1.2 mL) was added. The reaction was stirred at reflux for 2 h. The resulting mixture was diluted with EtOAc (20 mL), washed with water (10 mL), brine (10 mL) and dried over Na_2SO_4. The solvents were evaporated under reduced pressure. The crude material was purified by silica gel chromatography (petroleum ether/EtOAc 6:4) to give pure **Ox-Te-CF$_3$** as a yellow solid (51 mg, 70%); mp = 200-204°C. IR: υ (cm^{-1}): 3022, 1574, 1553, 1543, 1487, 1398, 1346, 1302, 1252, 1163, 1126, 1114, 1053, 970, 910, 849, 762, 735; ^{1}H NMR (300 MHz, C_6D_6) δ_H: 8.06 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.03 (d, J = 0.8 Hz, 1H) , 6.92 (d, J = 0.8 Hz, 1H); ^{19}F NMR (470 MHz, $CDCl_3$) δ_F: -62.7 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C: 166.3 (q, J_{CF} = 40 Hz, 1C), 165.1, 160.0, 155.7, 143.9, 140.6, 135.6, 129.7, 123.5 (q, J_{CF} = 274 Hz, 1C), 121.0; ESI-HRMS: $[M + H]^+$ cacld for $[C_{10}H_5N_3OF_3{}^{130}Te]^+$: 369.9447; found: 369.9442. Single crystals suitable for X-ray diffraction analysis were grown from slow evaporation of EtOH solution.

2.21. 2-(2-(phenyl)-[1,3]tellurazolo[5,4-β]pyridin-5-yl)oxazole Ox-Te-Ph



Ox-Te-Ph

2-(2-(phenyl)-[1,3]tellurazolo[5,4-β]pyridin-5-yl)oxazole **Ox-Te-Ph** was synthesised following a procedure inspired by the work of Piersanti *et al*.[7] To a solution of oxazole (35 mg, 0.03 mL, 0.5 mmol) in dry and degassed THF (0.5 mL) under anhydrous condition was added *n*-BuLi (2.5 M, 0.2 mL, 0.5 mmol) dropwise at -84°C. The reaction was stirred at the same temperature for 30 minutes and a solution of $ZnCl_2$ in Et_2O (1M, 1.5 mL, 1.5 mmol) added dropwise. The mixture

was stirred further at 0 °C for 1 h (white suspension). A separated flask was loaded with 5-iodo-2-(trifluoromethyl)-[1,3]tellurazolo[5,4-β]pyridine **I-Te-Ph** (85 mg, 0.20 mmol) and [$Pd(PPh_3)_4$] (23 mg, 0.02 mmol) in dry and degassed THF under anhydrous condition and oxazolylzinc chloride suspension (1.2 mL) was added. The reaction was stirred at reflux for 2 h. The resulting mixture was diluted with EtOAc (20 mL), washed with water (10 mL), brine (10 mL), and dried over Na_2SO_4.The solvents were evaporated under reduced pressure. The crude material was purified by silica gel chromatography (petroleum ether/EtOAc 6:4) to afford 2-(2-(phenyl)-[1,3]tellurazolo[5,4-β]pyridin-5-yl)oxazole **Ox-Te-Ph** as a yellow solid (54 mg, 72%); mp = 180-182°C. IR: υ (cm^{-1}): 1555, 1470, 1396, 1340, 1271, 1252, 1211, 1111, 1082, 1055, 912, 847, 752, 719, 683, 663, 596; ^{1}H NMR (300 MHz, C_6D_6) δ_H: 8.18 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.74-7.70 (m, 2H), 7.10-6.95 (m, 5H); ^{13}C NMR (75 MHz, C_6D_6) δ_C: 178.7, 163.2, 160.9, 158.6, 142.4, 141.3, 139.6, 132.1, 131.2, 129.0, 128.9 (two peaks overlap, 2C), 128.7 (two peaks overlap, 2C), 120.6; ESI-HRMS: $[M]^+$ cacld for $[C_{15}H_{10}N_3O^{130}Te]^+$: 377.9886; found: 377.9882.

3. ^{1}H, ^{13}C and ^{19}F spectra

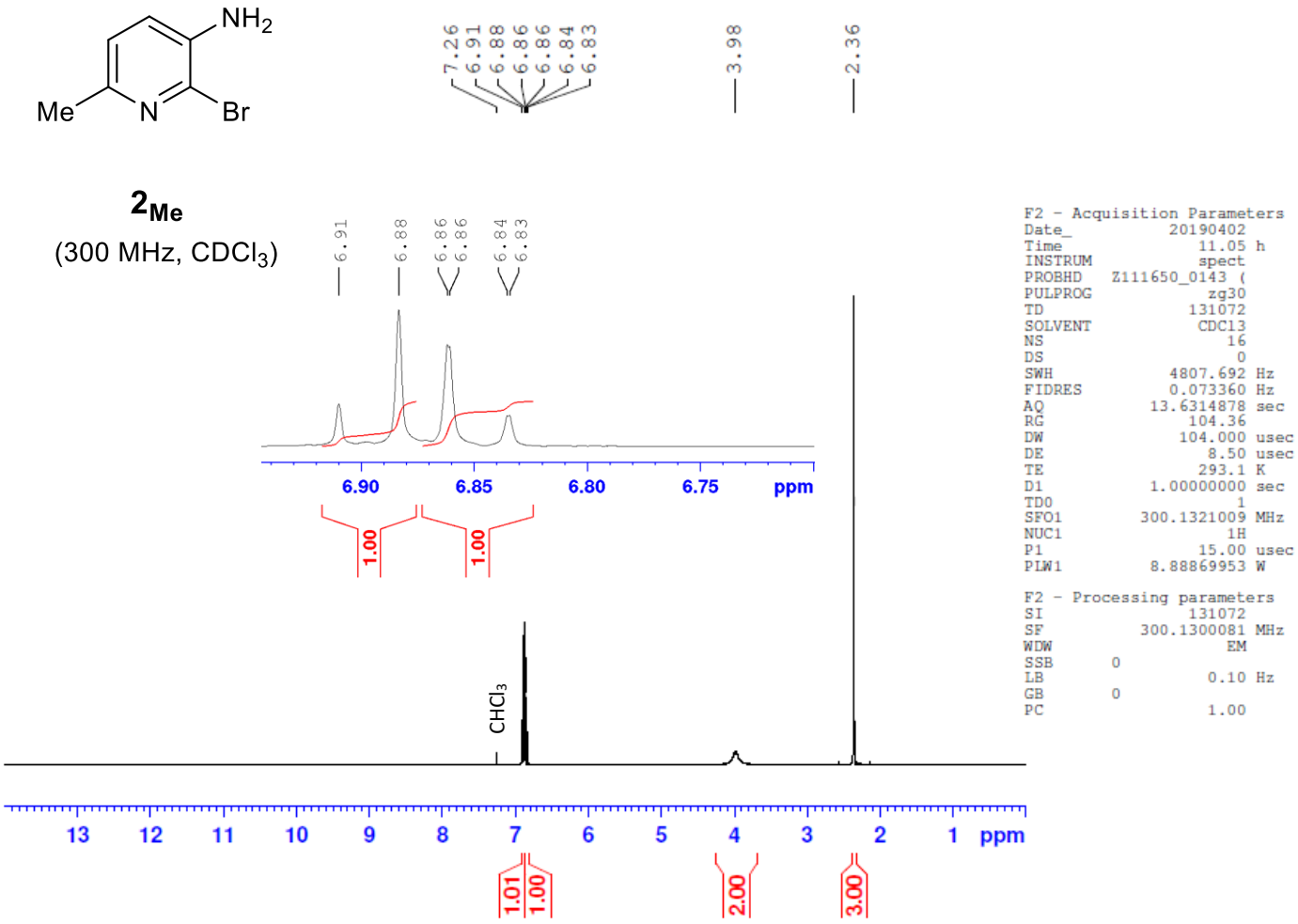


Figure S1: 300 MHz ^{1}H NMR in $CDCl_3$ of molecule ***2$_{Me}$.***

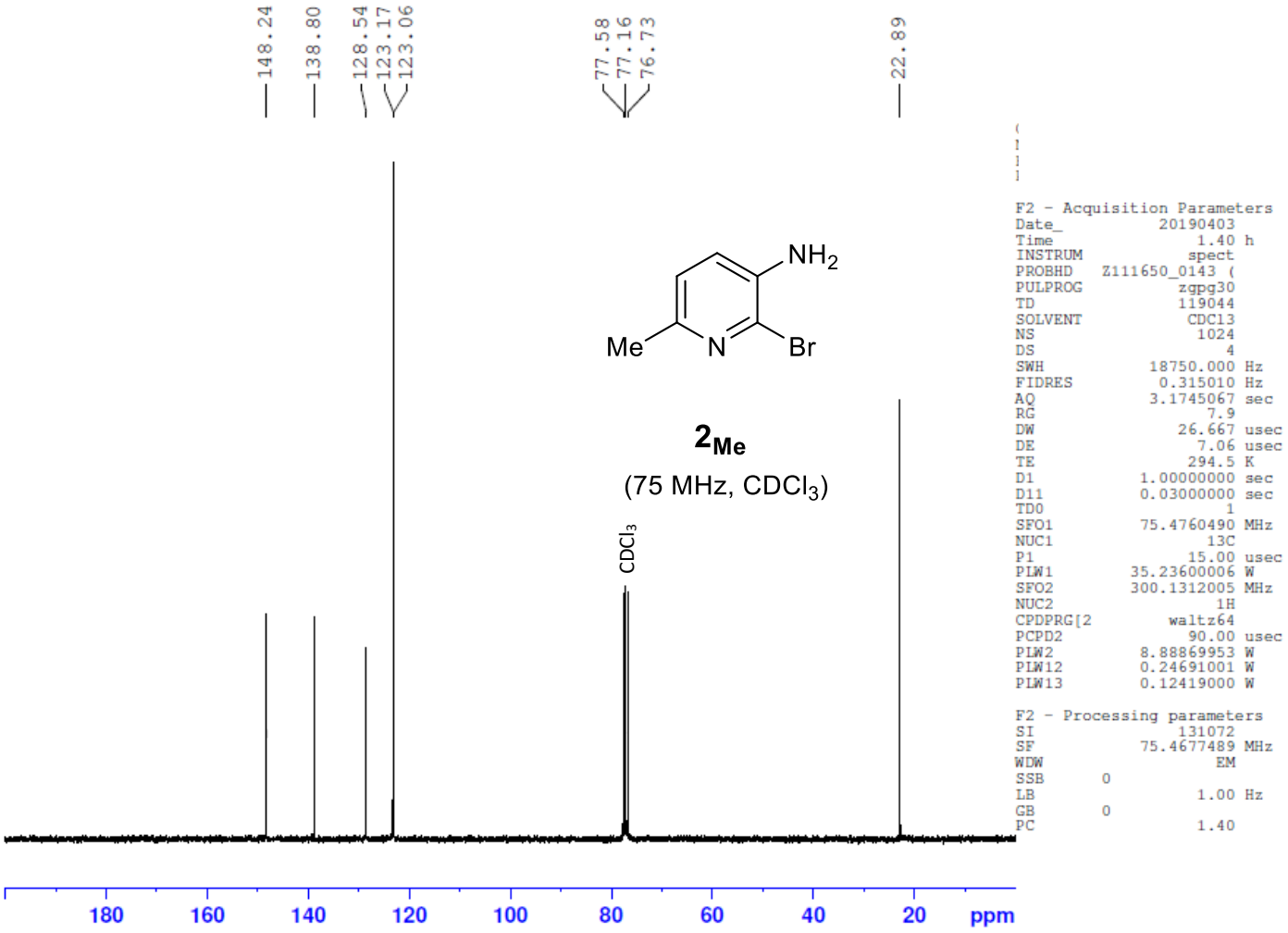


Figure S2: 75 MHz ^{13}C NMR in $CDCl_3$ of molecule ***2Me*****.**

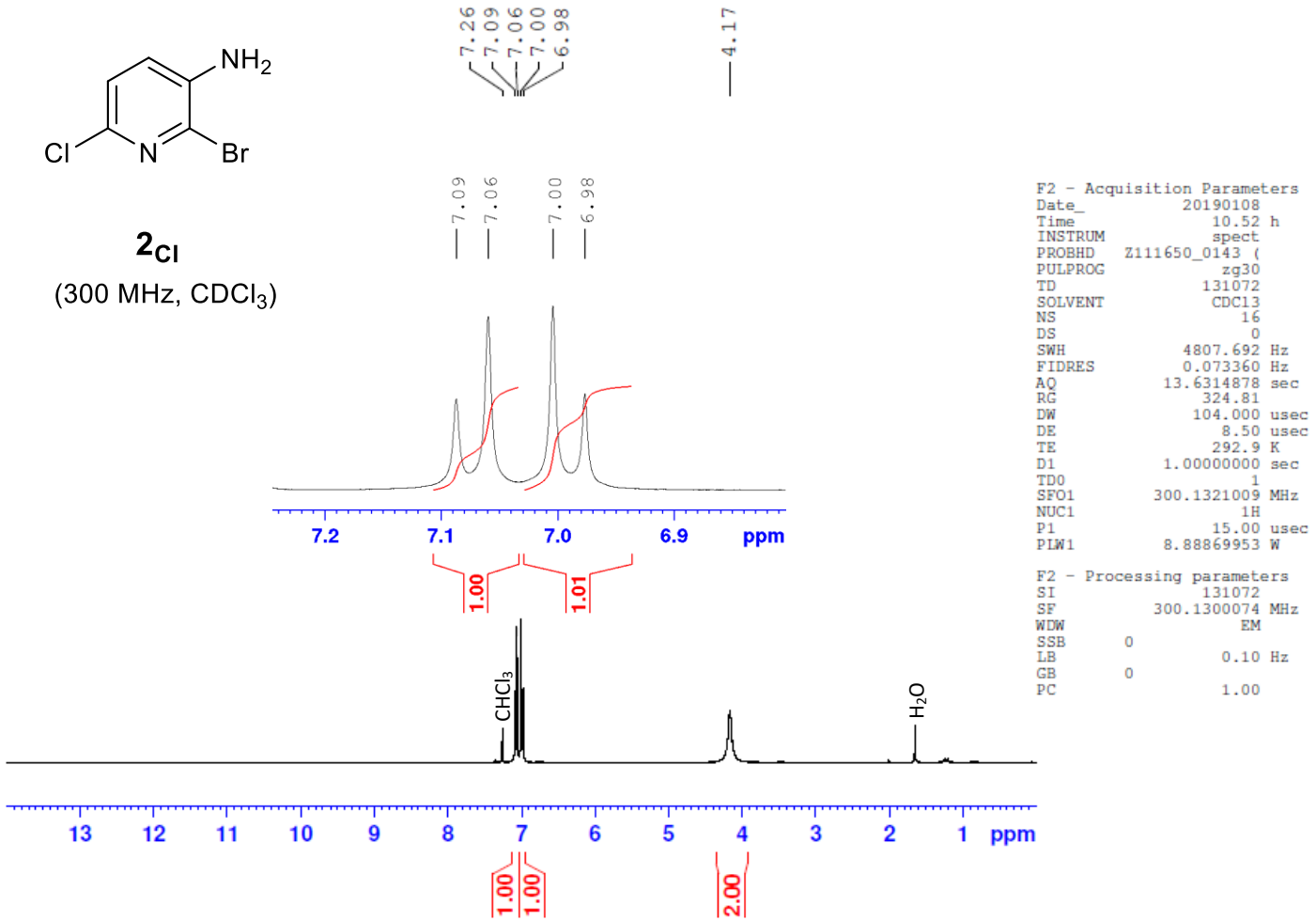
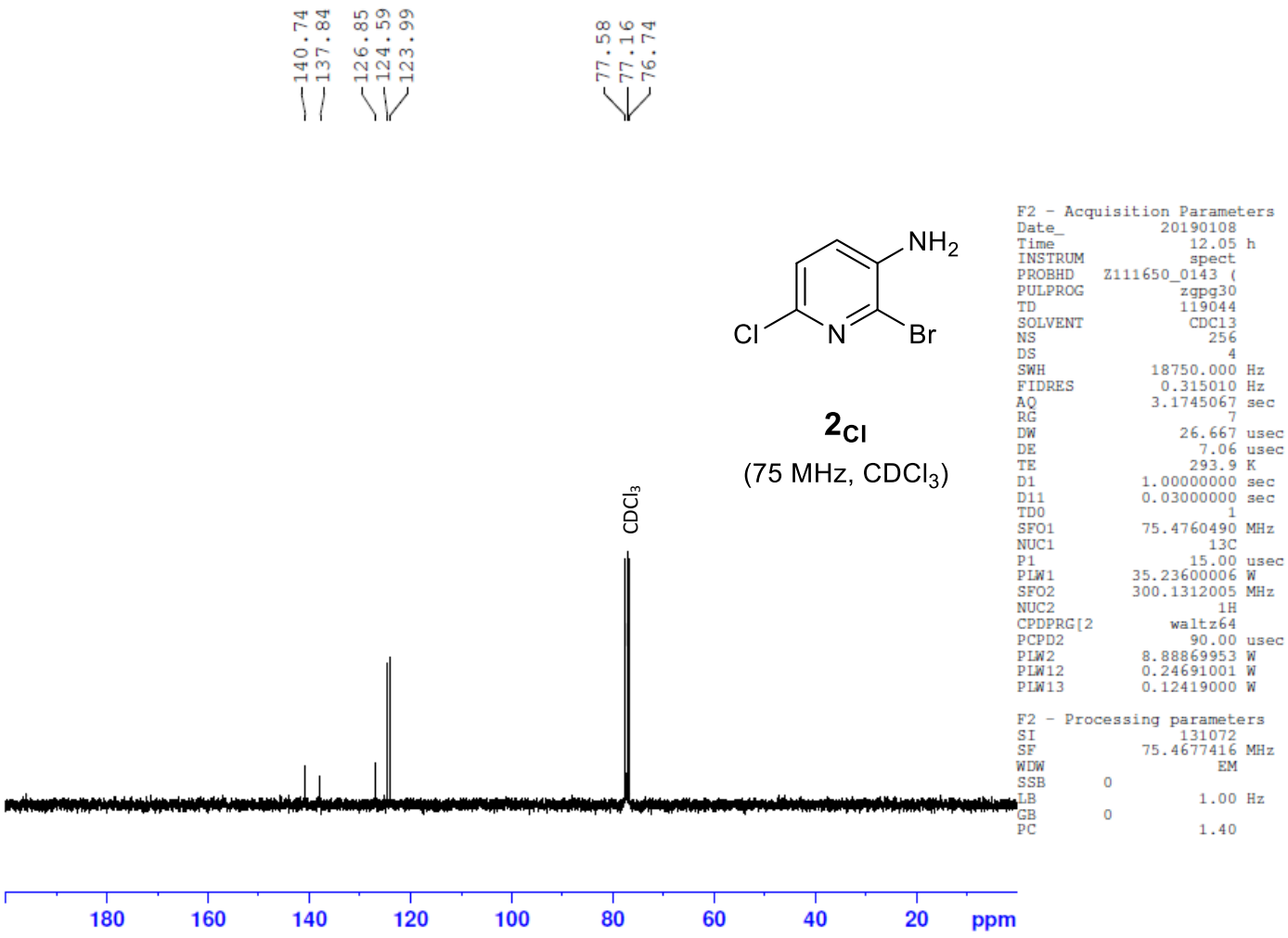


Figure S3: 300 MHz ^1H NMR in $CDCl_3$ of molecule ***2*****$_{CI}$**.



F2 - Acquisition Parameters

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PULPROG	zgpg30
TD	119044
SOLVENT	CDCl3
NS	256
DS	4
SWH	18750.000 Hz
FIDRES	0.315010 Hz
AQ	3.1745067 sec
RG	7
DW	26.667 usec
DE	7.06 usec
TE	293.9 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	75.4760490 MHz
NUC1	13C
P1	15.00 usec
PLW1	35.23600006 W
SFO2	300.1312005 MHz
NUC2	1H
CPDPRG[2	waltz64
PCPD2	90.00 usec
PLW2	8.88869953 W
PLW12	0.24691001 W
PLW13	0.12419000 W

F2 - Processing parameters

SI	131072
SF	75.4677416 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Figure S4: 75 MHz ^{13}C NMR in $CDCl_3$ of molecule $\mathbf{2_{CI}}$.

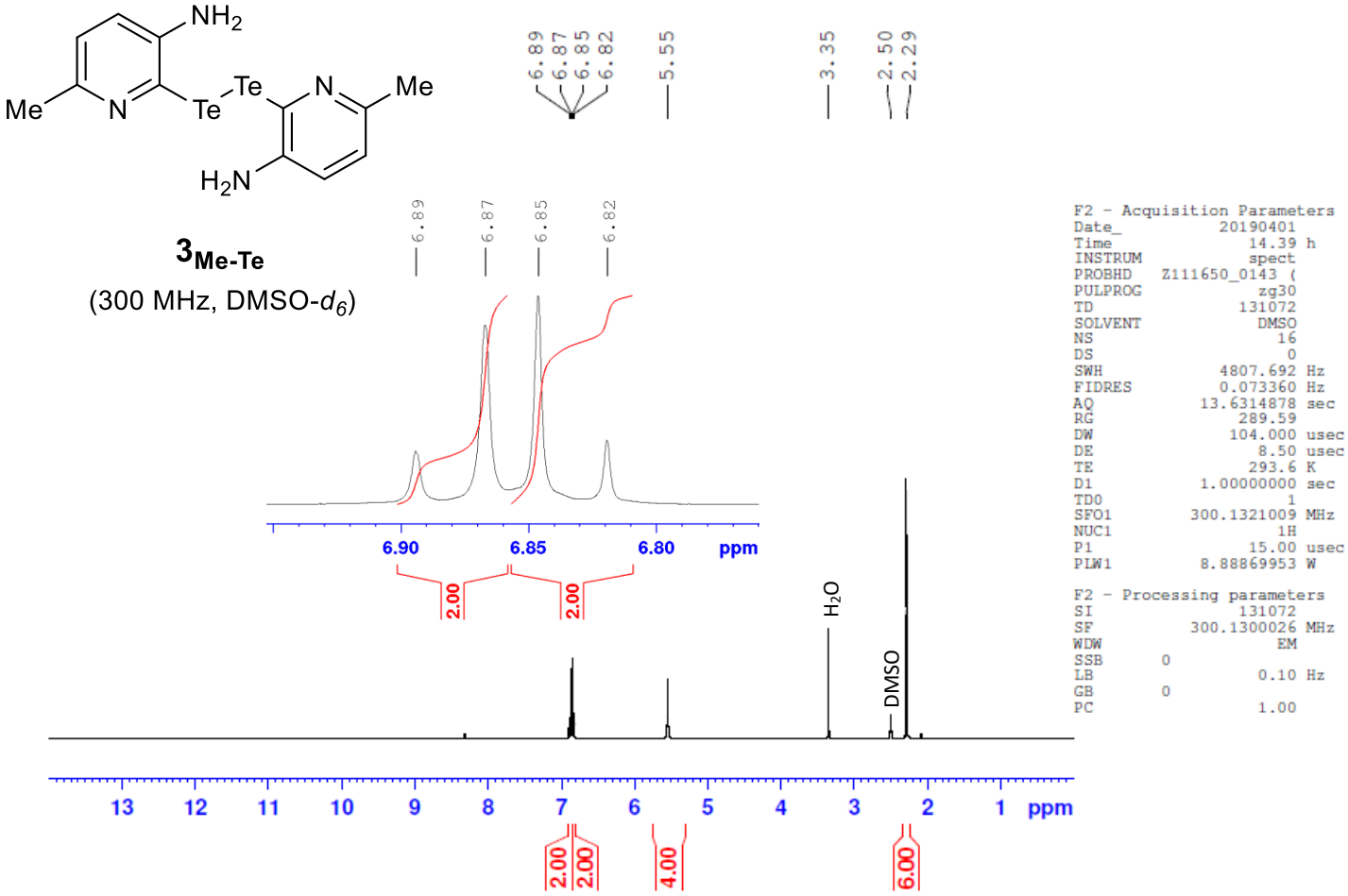


Figure S5: 300 MHz ^{1}H NMR in DMSO-d_6 of molecule $\mathbf{3_{Me\text{-}Te}}$.

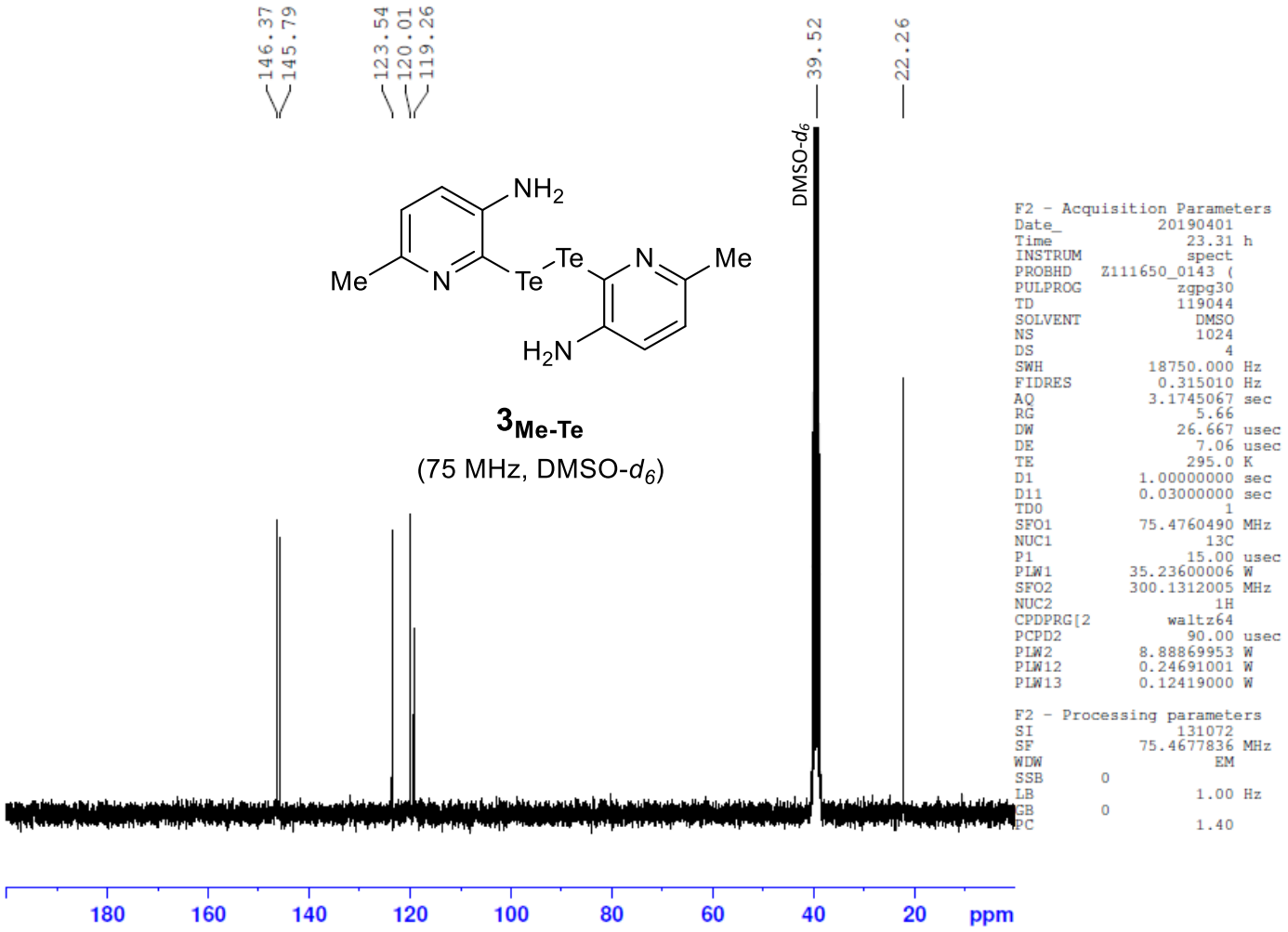
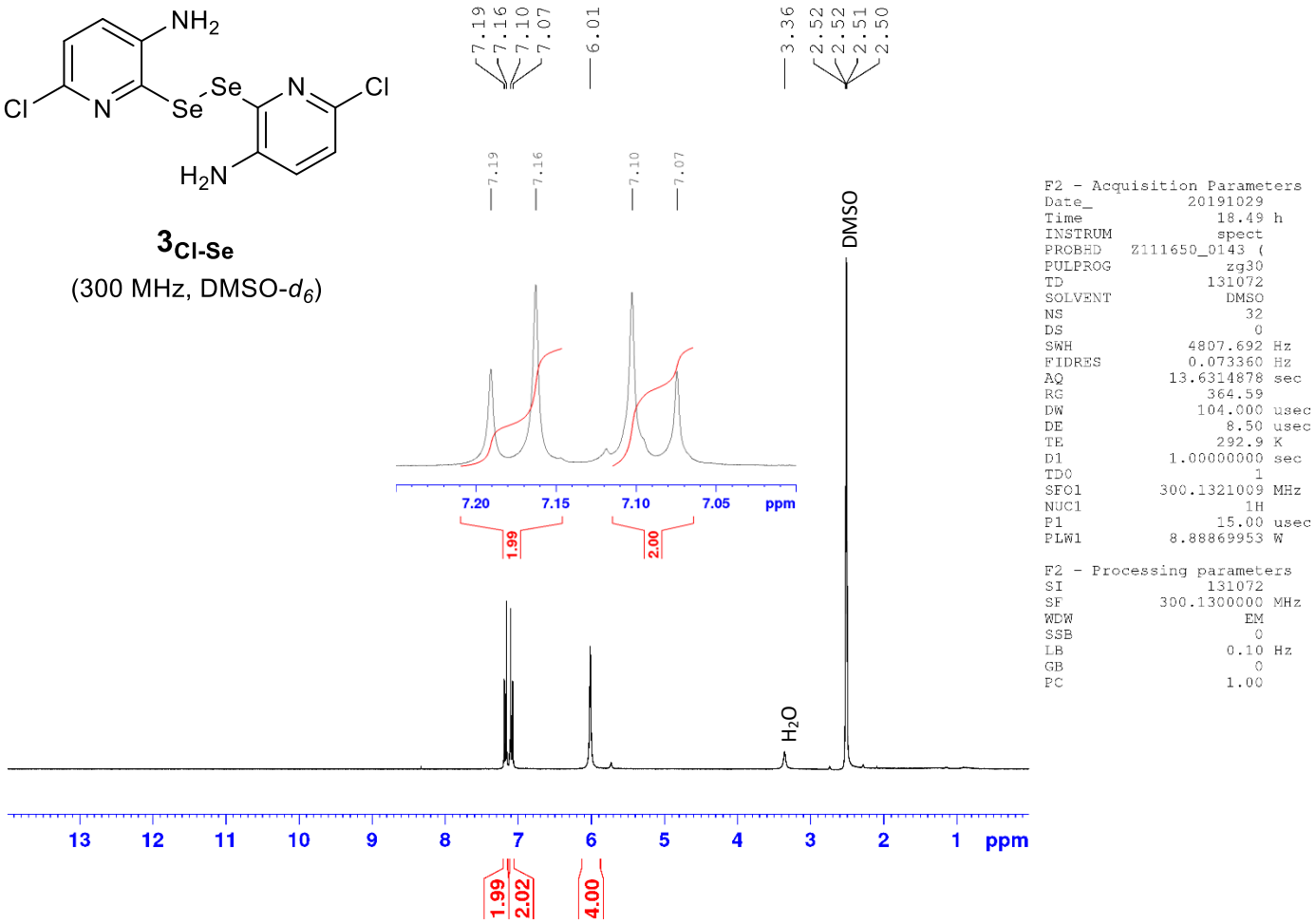


Figure S6: 75 MHz ^{13}C NMR in DMSO-d_6 of molecule $\mathbf{3}_{\mathbf{Me\text{-}Te}}$.




```
F2 - Acquisition Parameters
Date_              20191029
Time                 18.49 h
INSTRUM                spect
PROBHD    Z111650_0143 (
PULPROG                zg30
TD                   131072
SOLVENT                DMSO
NS                       32
DS                        0
SWH                4807.692 Hz
FIDRES             0.073360 Hz
AQ                13.6314878 sec
RG                   364.59
DW                  104.000 usec
DE                    8.50 usec
TE                   292.9 K
D1                1.00000000 sec
TD0                       1
SFO1           300.1321009 MHz
NUC1                     1H
P1                    15.00 usec
PLW1           8.88869953 W

F2 - Processing parameters
SI                   131072
SF              300.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.10 Hz
GB                        0
PC                     1.00
```

Figure S7: 300 MHz ^{1}H NMR in DMSO-d$_6$ of molecule ***3*** $_{\textbf{Cl-Se}}$.

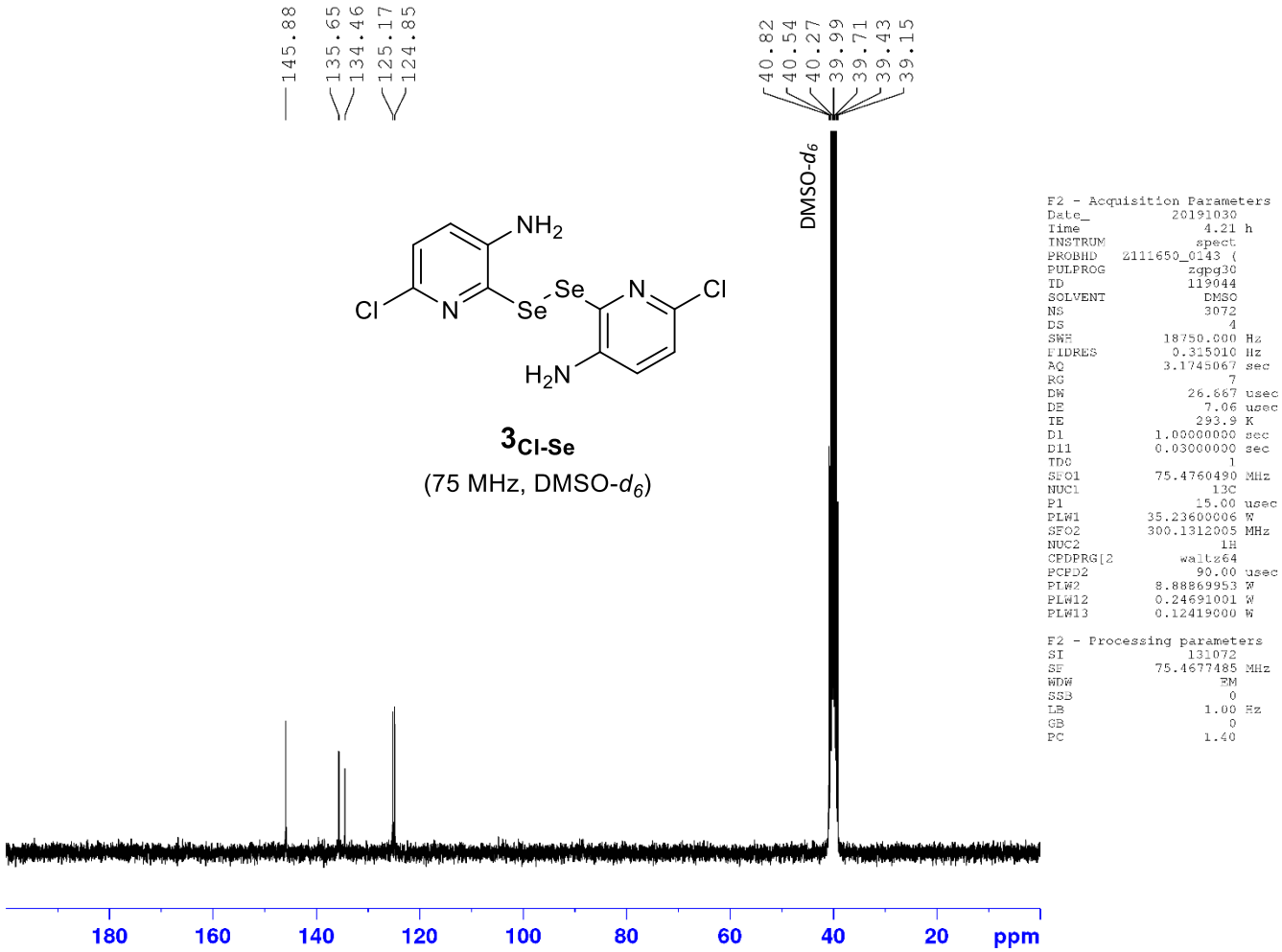


Figure S8: 75 MHz ^{13}C NMR in DMSO-d_6 of molecule $\mathbf{3_{Cl\text{-}Se}}$.

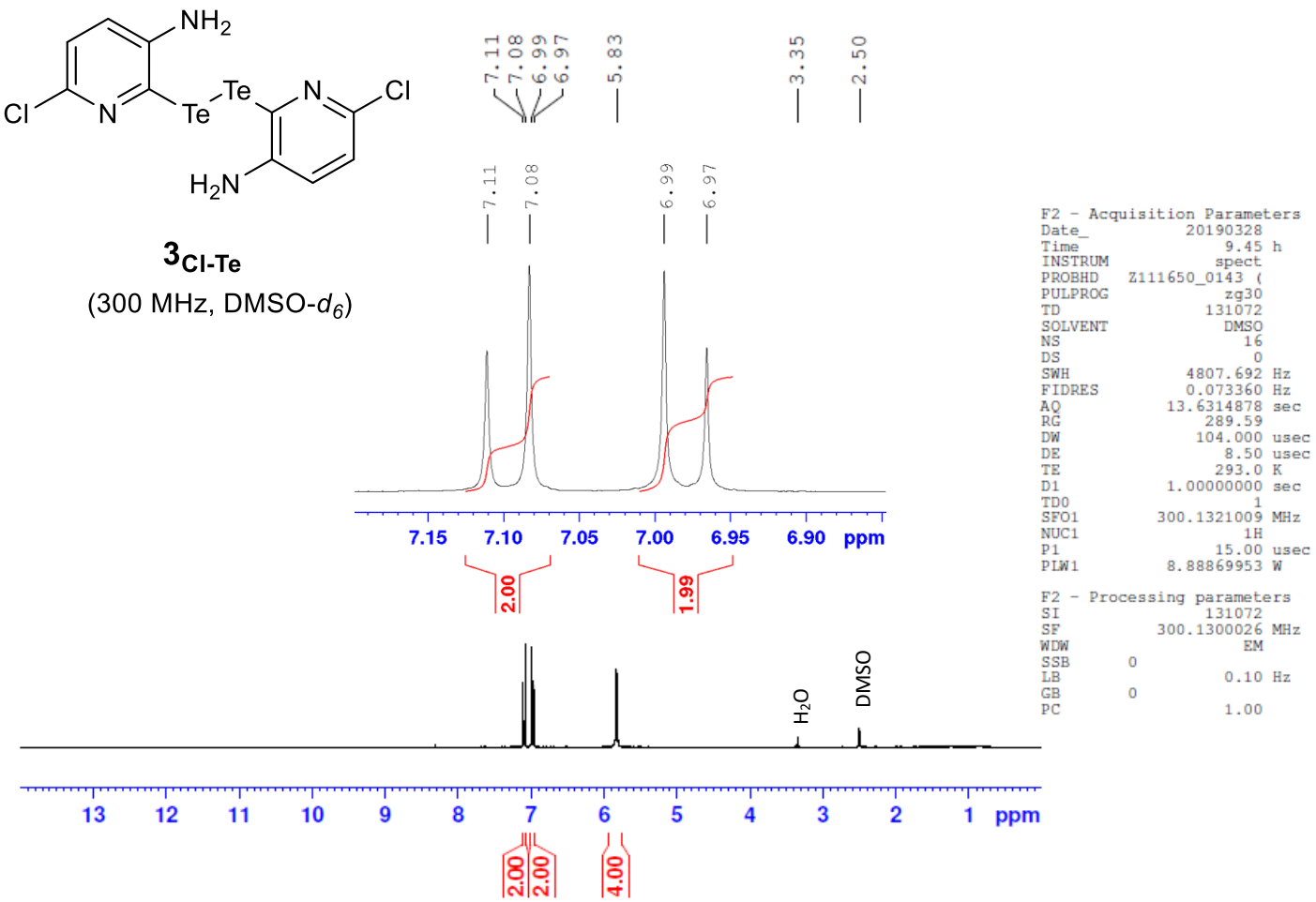


Figure S9: 300 MHz ^{1}H NMR in DMSO-d_6 of molecule $\mathbf{3_{Cl\text{-}Te}}$.

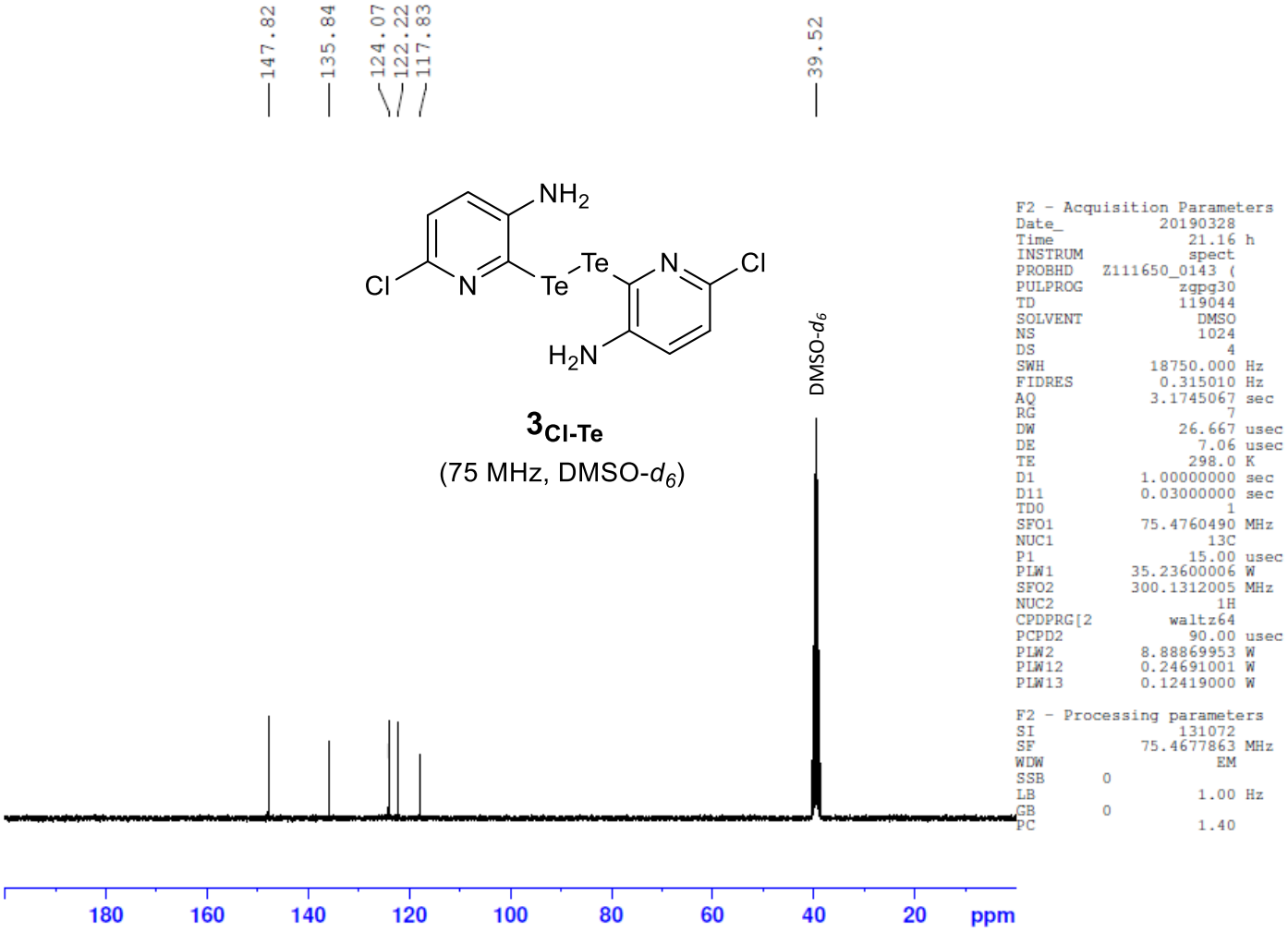


Figure S10: 75 MHz ^{13}C NMR in DMSO-d_6 of molecule ***3*** $_{\textbf{CI-Te}}$.

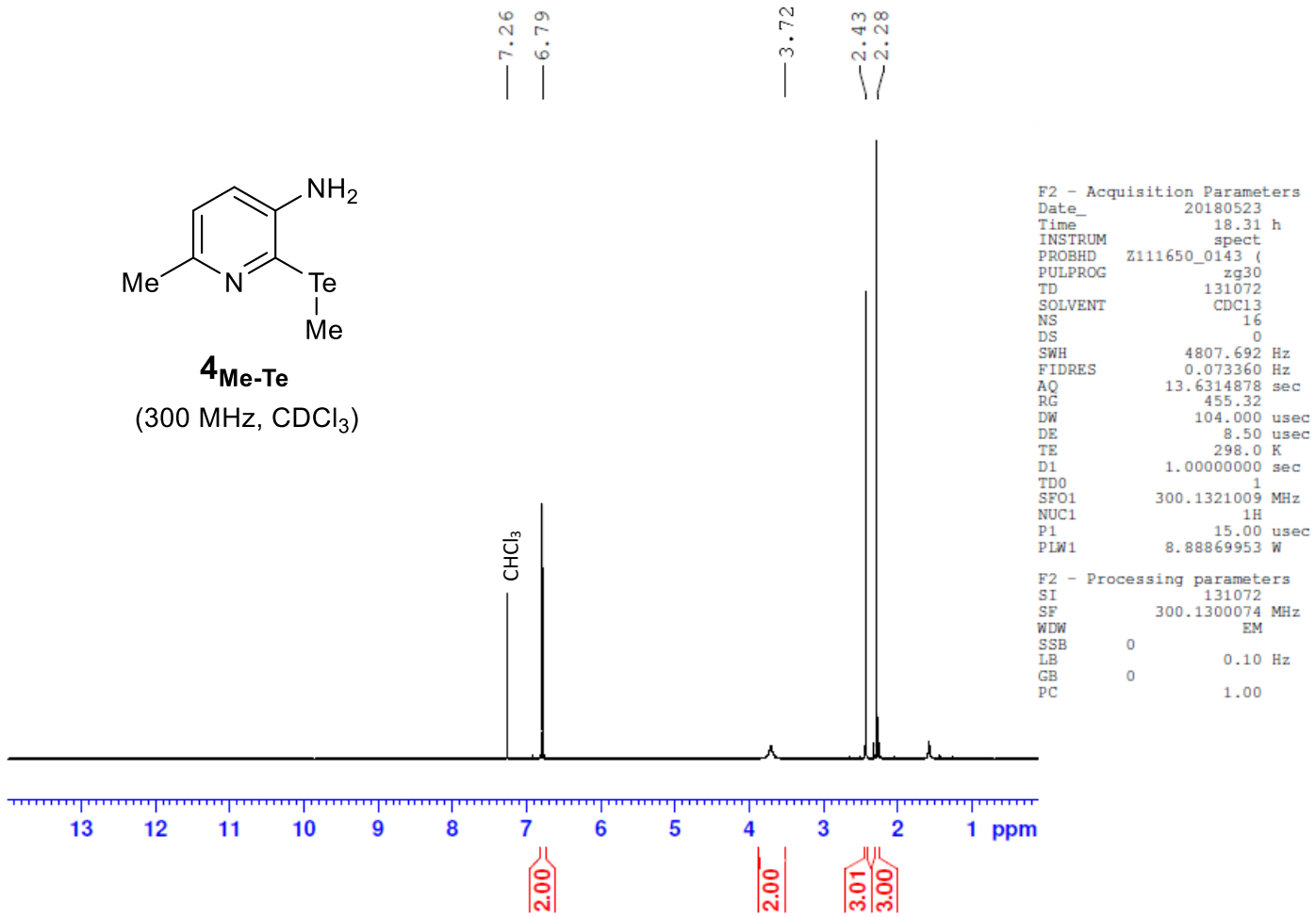
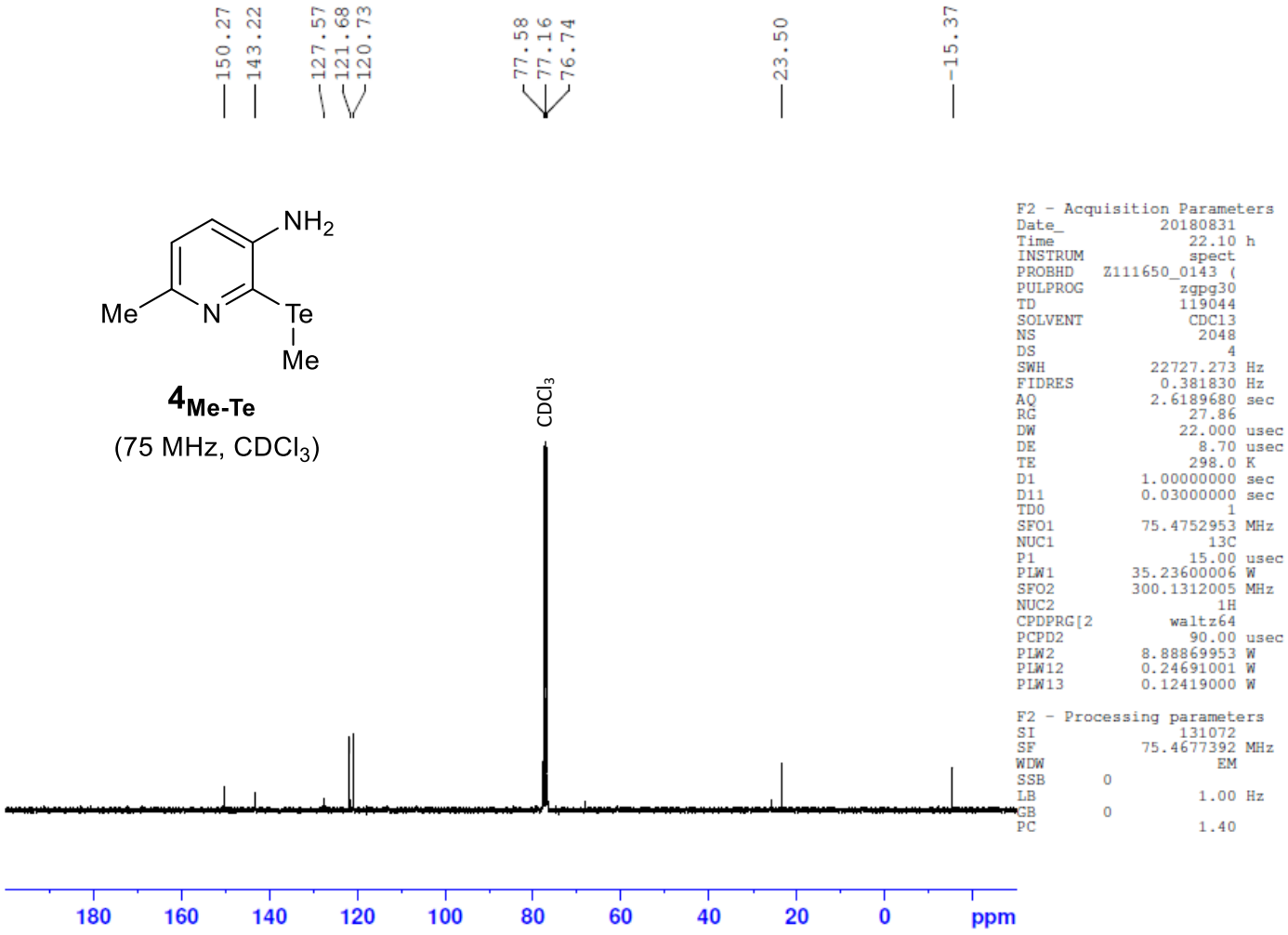


Figure S11: 300 MHz ^{1}H NMR in $CDCl_3$ of molecule ***4*** *Me-Te.*

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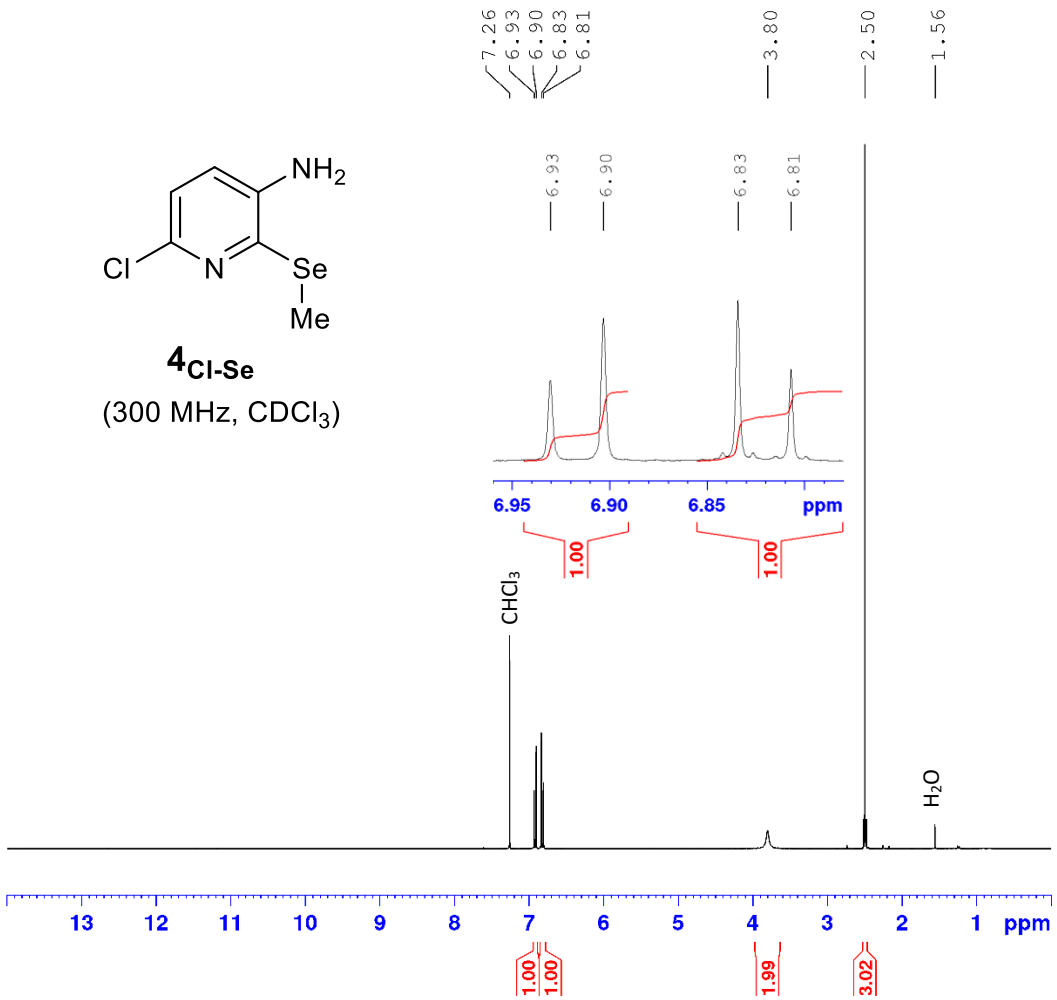
F2 - Acquisition Parameters
Date_           20180831
Time              22.10 h
INSTRUM             spect
PROBHD    Z111650_0143 (
PULPROG           zgpg30
TD                119044
SOLVENT             CDCl3
NS                   2048
DS                      4
SWH             22727.273 Hz
FIDRES          0.381830 Hz
AQ              2.6189680 sec
RG                  27.86
DW                22.000 usec
DE                 8.70 usec
TE                298.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1
SFO1           75.4752953 MHz
NUC1                  13C
P1                 15.00 usec
PLW1          35.23600006 W
SFO2          300.1312005 MHz
NUC2                  1H
CPDPRG[2          waltz64
PCPD2              90.00 usec
PLW2           8.88869953 W
PLW12          0.24691001 W
PLW13          0.12419000 W

F2 - Processing parameters
SI                  131072
SF            75.4677392 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure S12: 75 MHz ^{13}C NMR in $CDCl_3$ of molecule ***4*** *Me-Te.*




```
F2 - Acquisition Parameters
Date_            20190322
Time               17.28 h
INSTRUM             spect
PROBHD   %111650_0143 (
PULPROG             zg30
TD                131072
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              4807.692 Hz
FIDRES           0.073360 Hz
AQ              13.6314878 sec
RG                 455.32
DW                104.000 usec
DE                  8.50 usec
TE                 294.3 K
D1              1.00000000 sec
TD0                     1
SFO1          300.1321009 MHz
NUC1                   1H
P1                  15.00 usec
PLW1           8.88869953 W

F2 - Processing parameters
SI                 131072
SF            300.1300082 MHz
WDW                    EM
SSB                     0
LB                   0.10 Hz
GB                      0
PC                   1.00
```

Figure S13: 300 MHz ^{1}H NMR in $CDCl_3$ of molecule ***4CI-Se*****.**

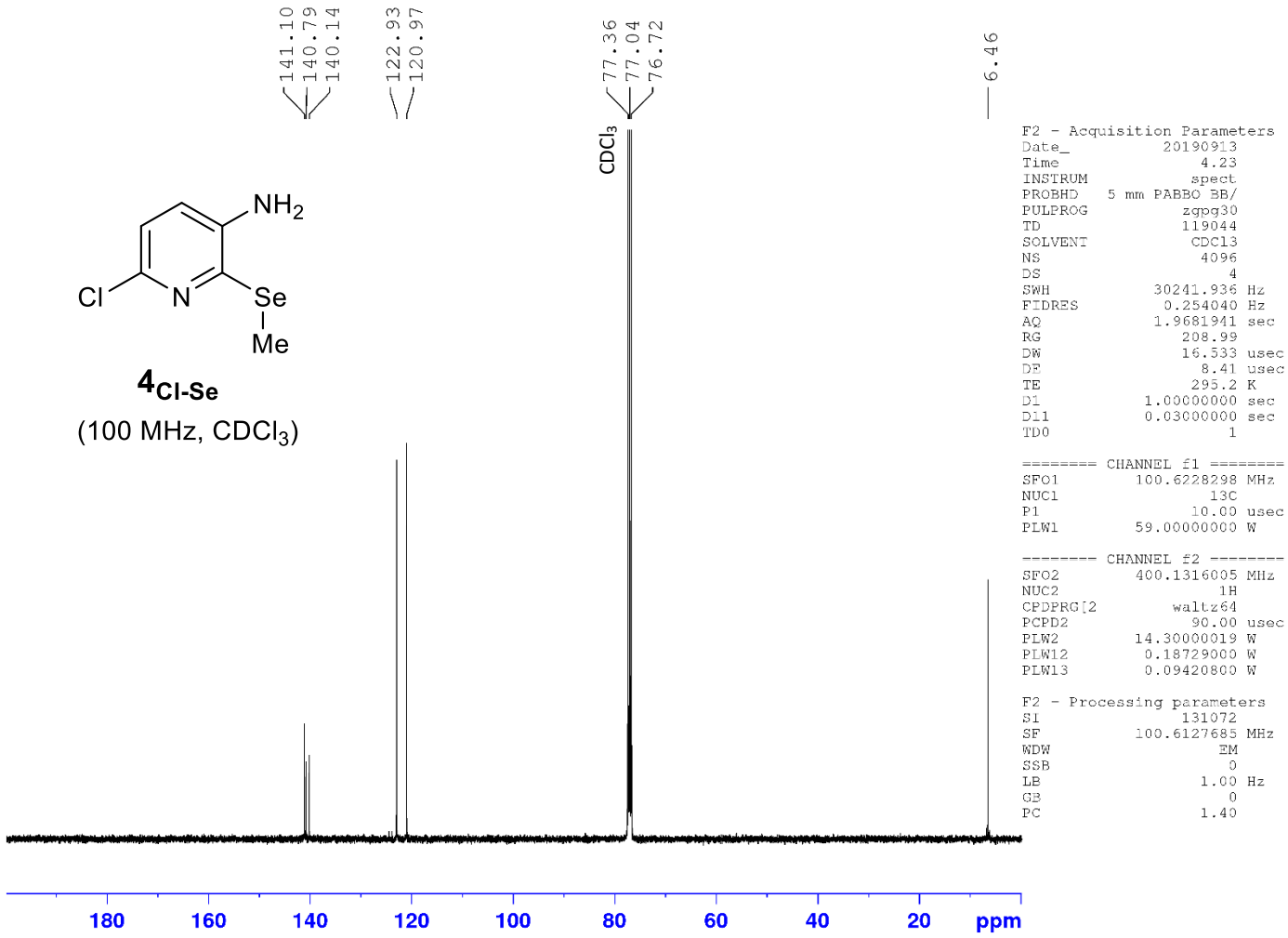


Figure S14: 100 MHz ^{13}C NMR in $CDCl_3$ of molecule ***4CI-Se*.**

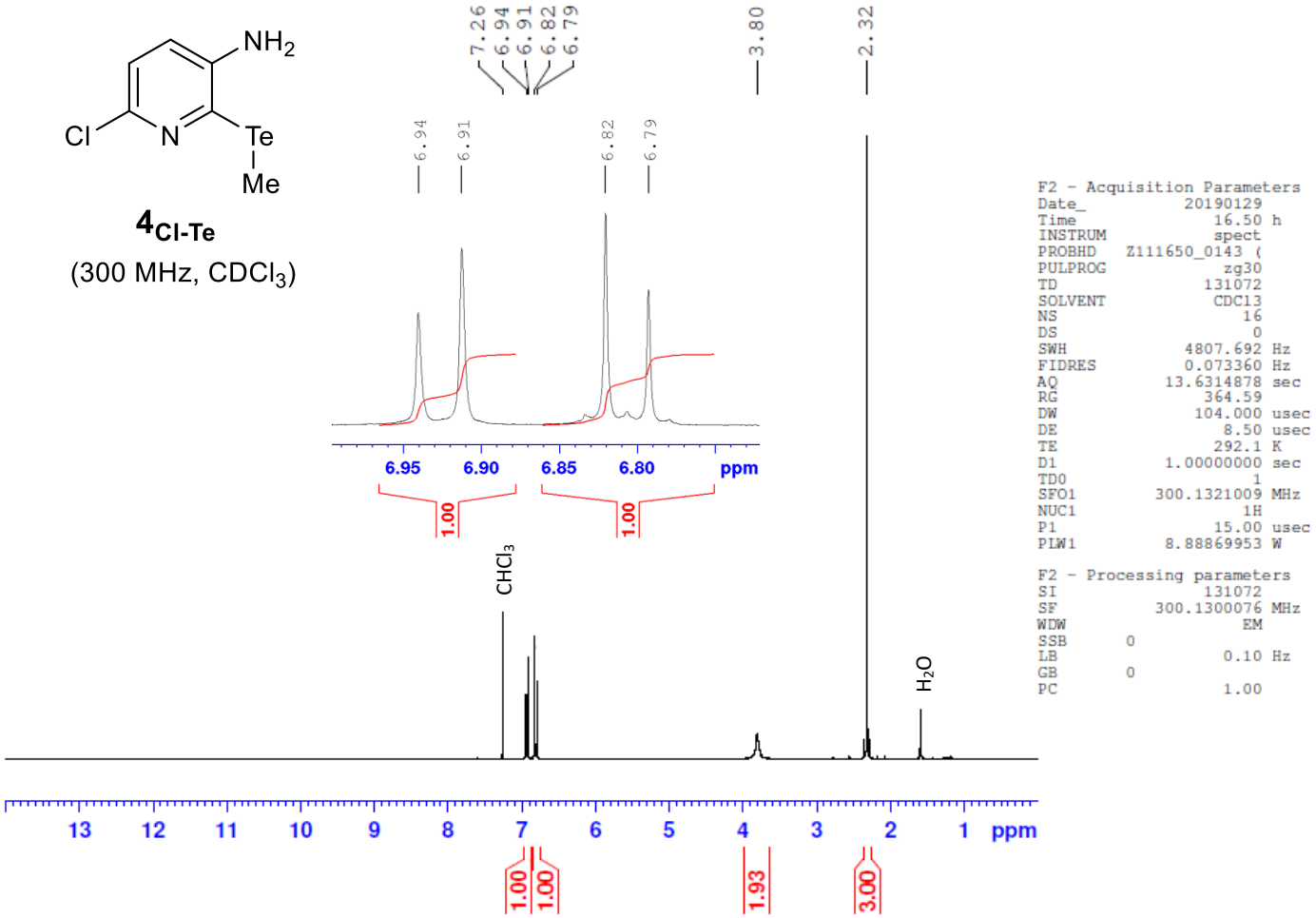


Figure S15: 300 MHz ^1H NMR in $CDCl_3$ of molecule ***4*** $_{CI\text{-}Te}$.

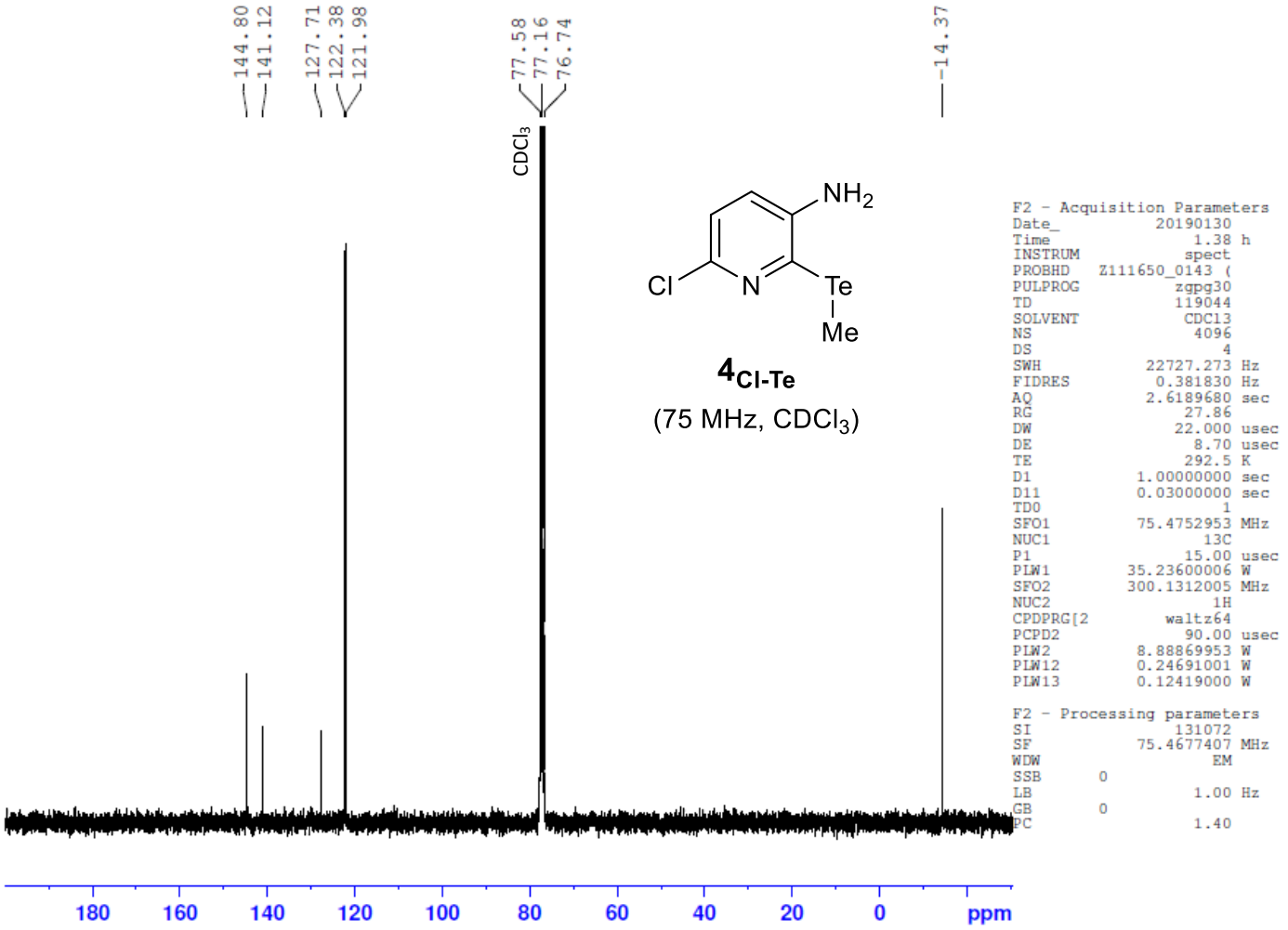


Figure S16: 75 MHz ^{13}C NMR in $CDCl_3$ of molecule $\mathbf{4_{Cl\text{-}Te}}$.

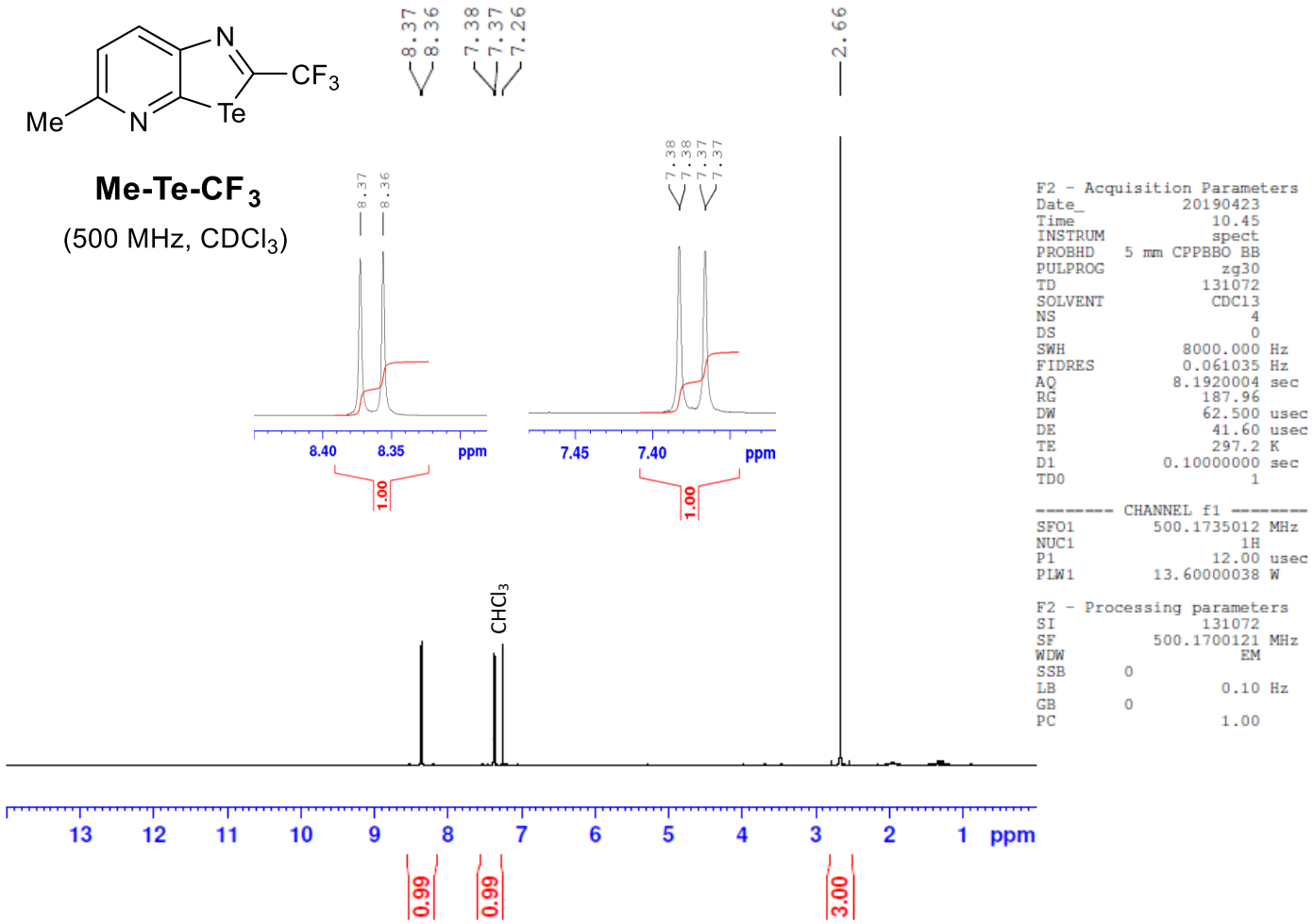


Figure S17: 500 MHz ^{1}H NMR in $CDCl_3$ of molecule ***Me-Te-CF$_3$.***

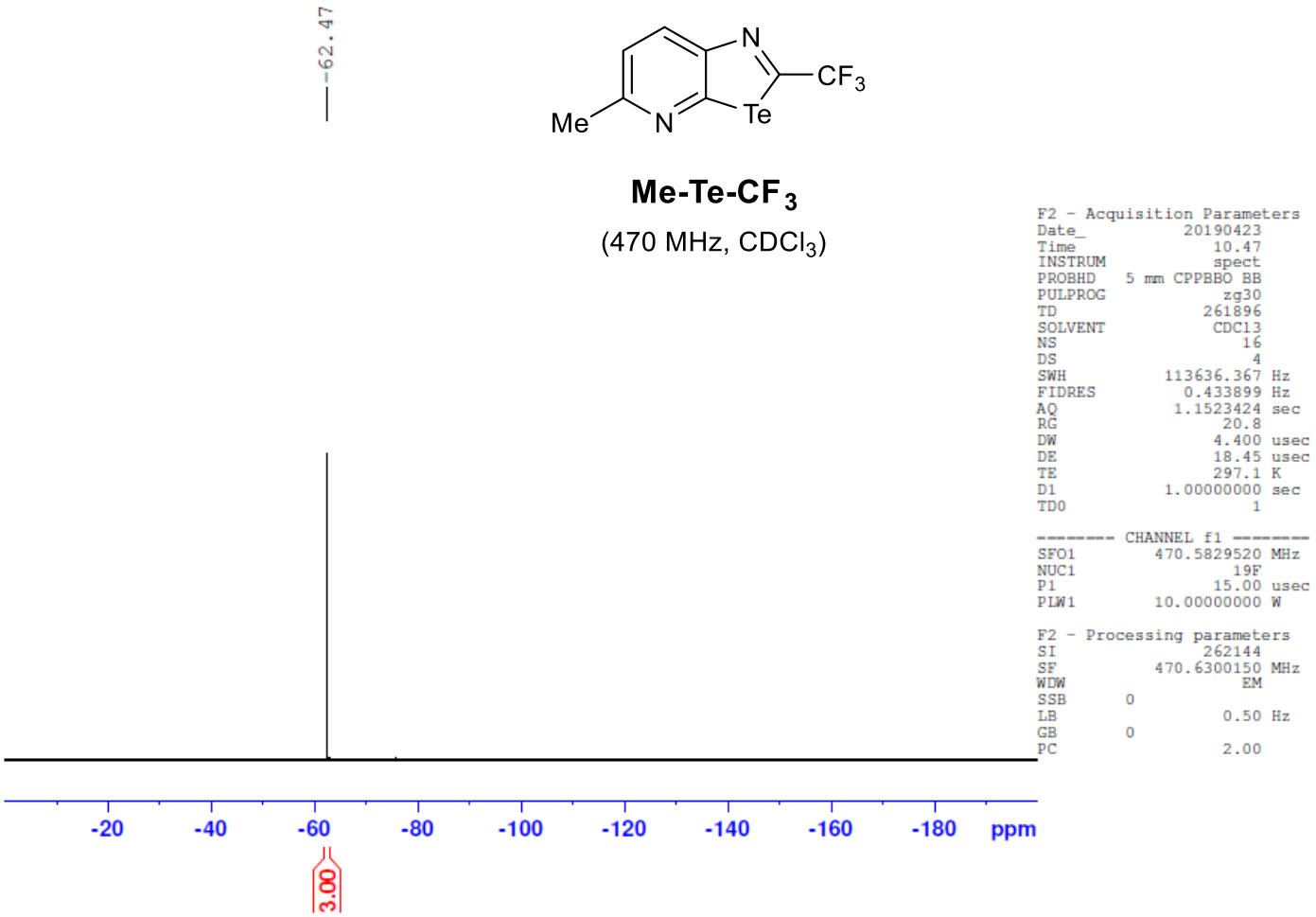


Figure S18: 470 MHz ^{19}F NMR in $CDCl_3$ of molecule ***Me-Te-CF3.***

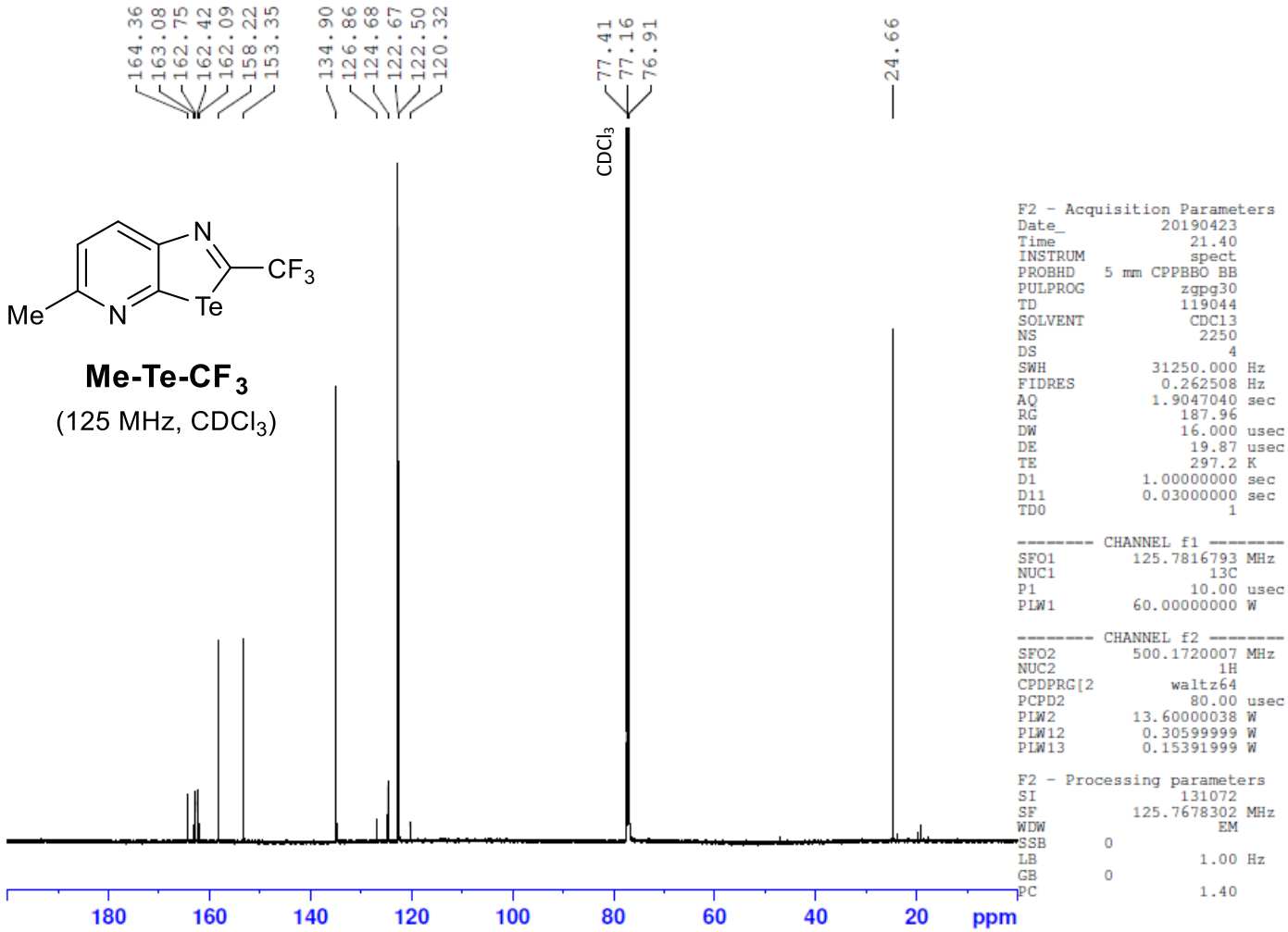
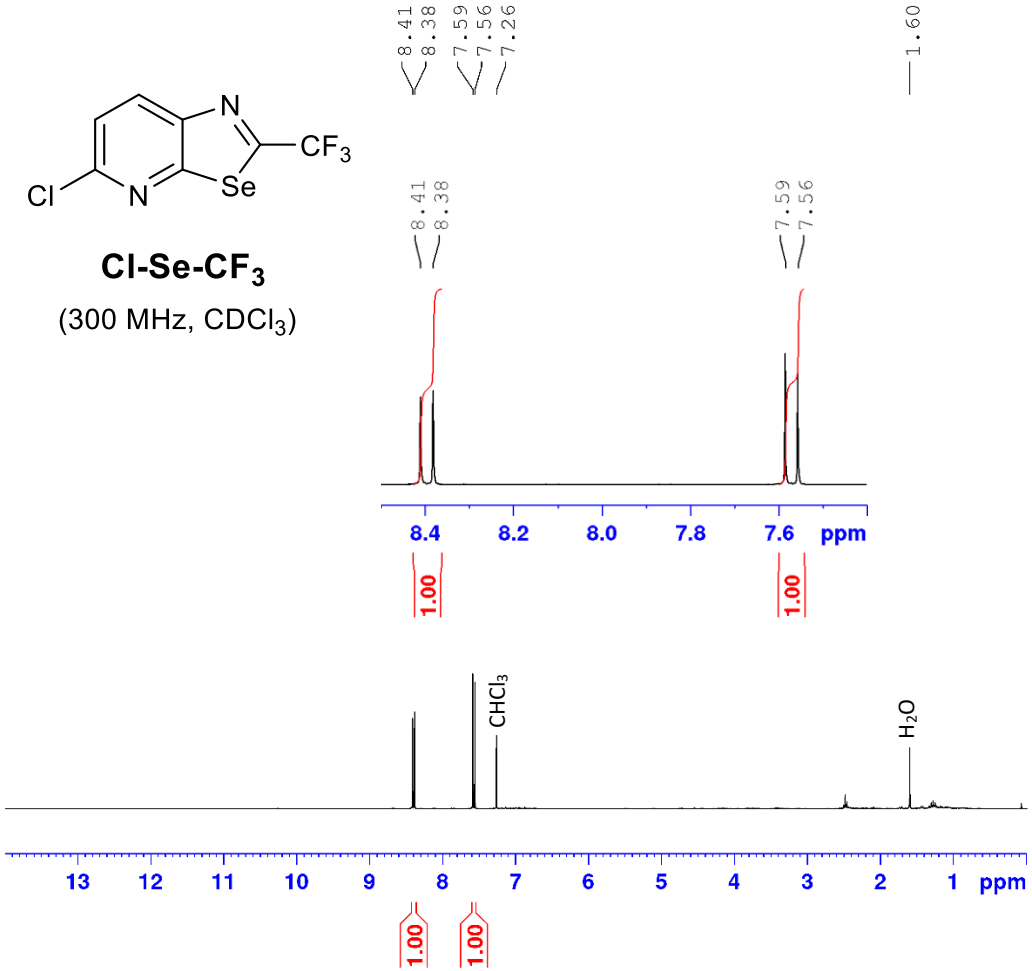


*Figure S19: 125 MHz ^{13}C NMR in $CDCl_3$ of molecule **Me-Te-CF$_3$**. Due to ^{13}C-^{19}F coupling: Peak 162.6 splits into 163.08, 163.45, 162.75 and 162.42; Peak 123.6 splits into 126.86, 124.68, 122.50 and 120.32.*

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TD                131072
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             4807.692 Hz
FIDRES          0.073360 Hz
AQ             13.6314878 sec
RG                396.43
DW                104.000 usec
DE                  8.50 usec
TE                292.4 K
D1             1.00000000 sec
TD0                    1
SFO1          300.1321009 MHz
NUC1                  1H
P1                15.00 usec
PLW1           8.88869953 W

F2 - Processing parameters
SI                131072
SF            300.1300083 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```
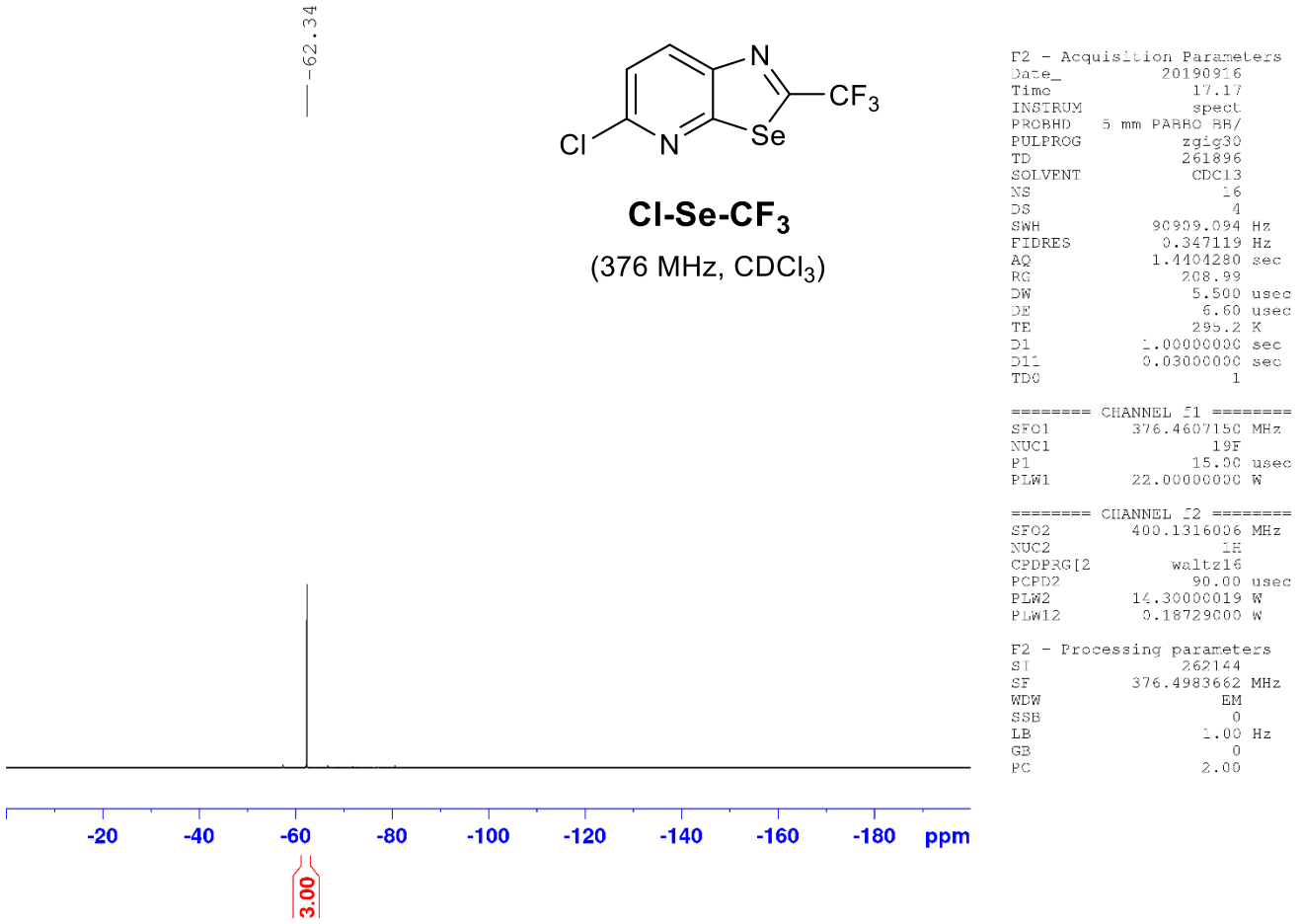

Figure S20: 300 MHz ^{1}H NMR in $CDCl_3$ of molecule ***Cl-Se-CF$_3$.***




```
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PULPROG          zgig30
TD               261896
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NS                    16
DS                     4
SWH            90909.094 Hz
FIDRES         0.347119 Hz
AQ             1.4404280 sec
RG                208.99
DW                 5.500 usec
DE                 6.60 usec
TE                295.2 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         376.4607150 MHz
NUC1               19F
P1                15.00 usec
PLW1         22.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316006 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         14.30000019 W
PLW12         0.18729000 W

F2 - Processing parameters
SI                262144
SF           376.4983662 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                2.00
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Figure S21: 376 MHz ^{19}F NMR in $CDCl_3$ of molecule ***Cl-Se-CF3.***

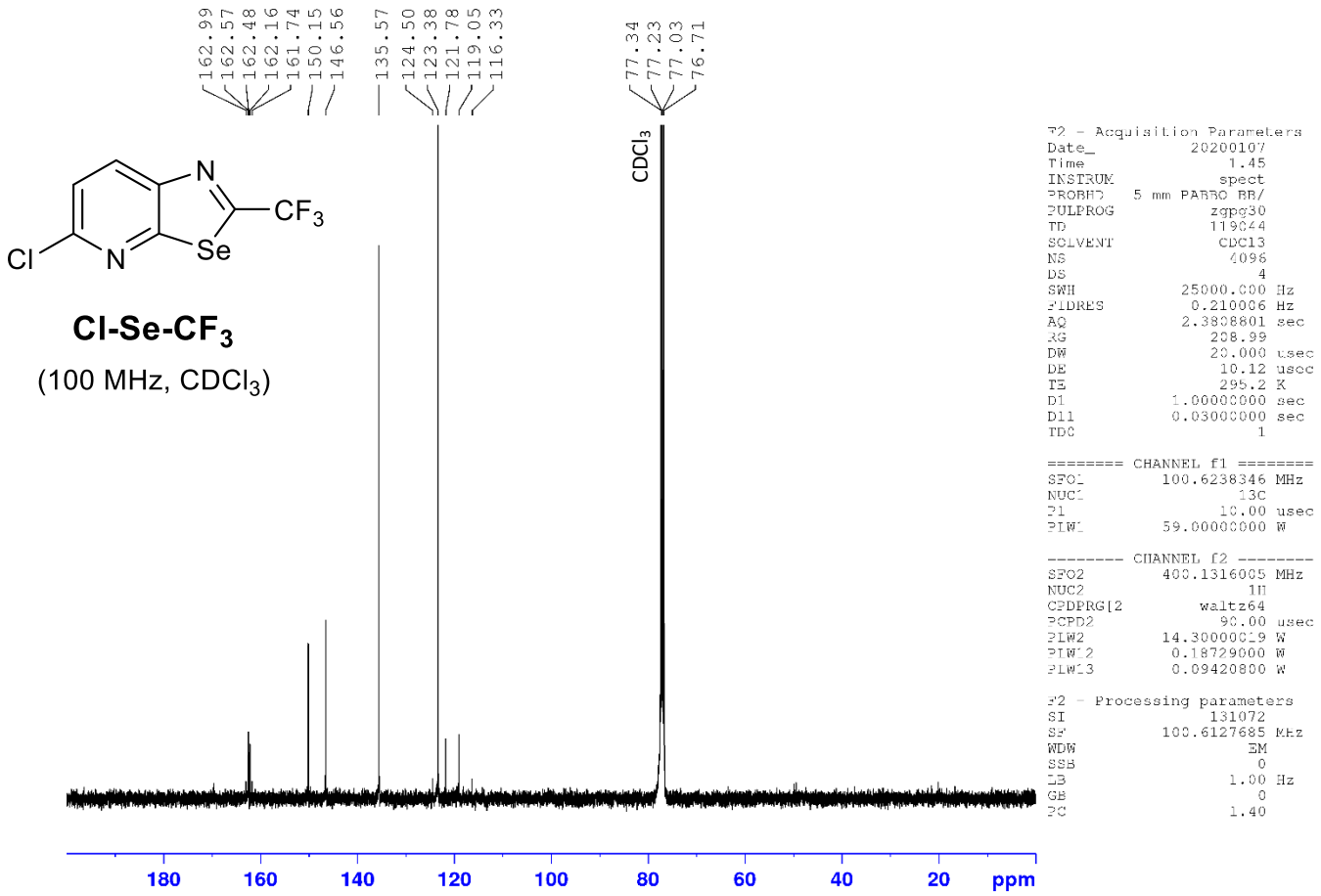


*Figure S22: 100 MHz ^{13}C NMR in $CDCl_3$ of molecule **Cl-Se-CF3**. Due to ^{13}C-^{19}F coupling: Peak 162.5 splits into 162.99, 162.57, 162.48 and 162.16; Peak 122.6 splits into 123.38, 121.78, 119.05 and 116.33.*

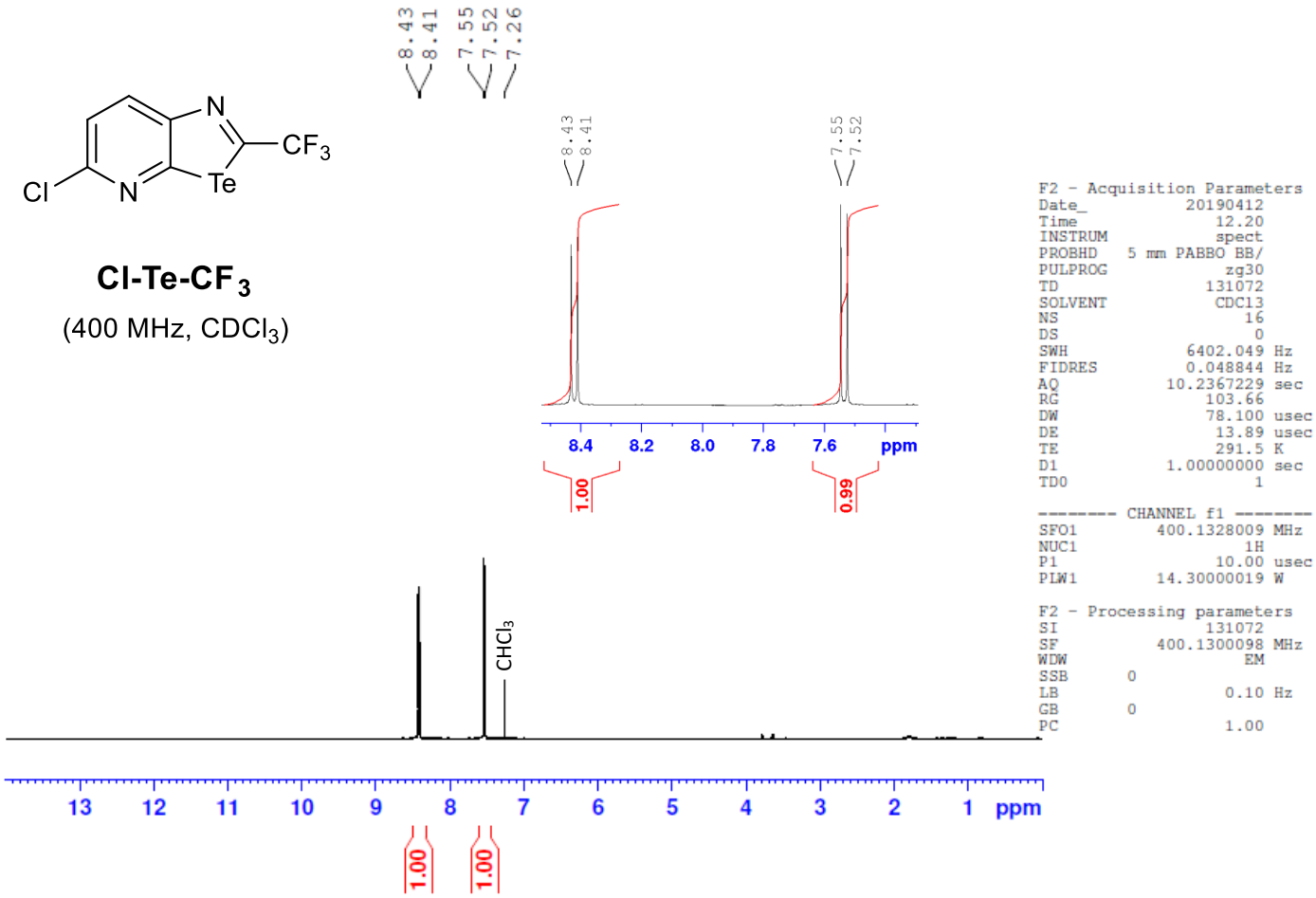


Figure S23: 400 MHz ^{1}H NMR in $CDCl_3$ of molecule ***Cl-Te-CF$_3$.***

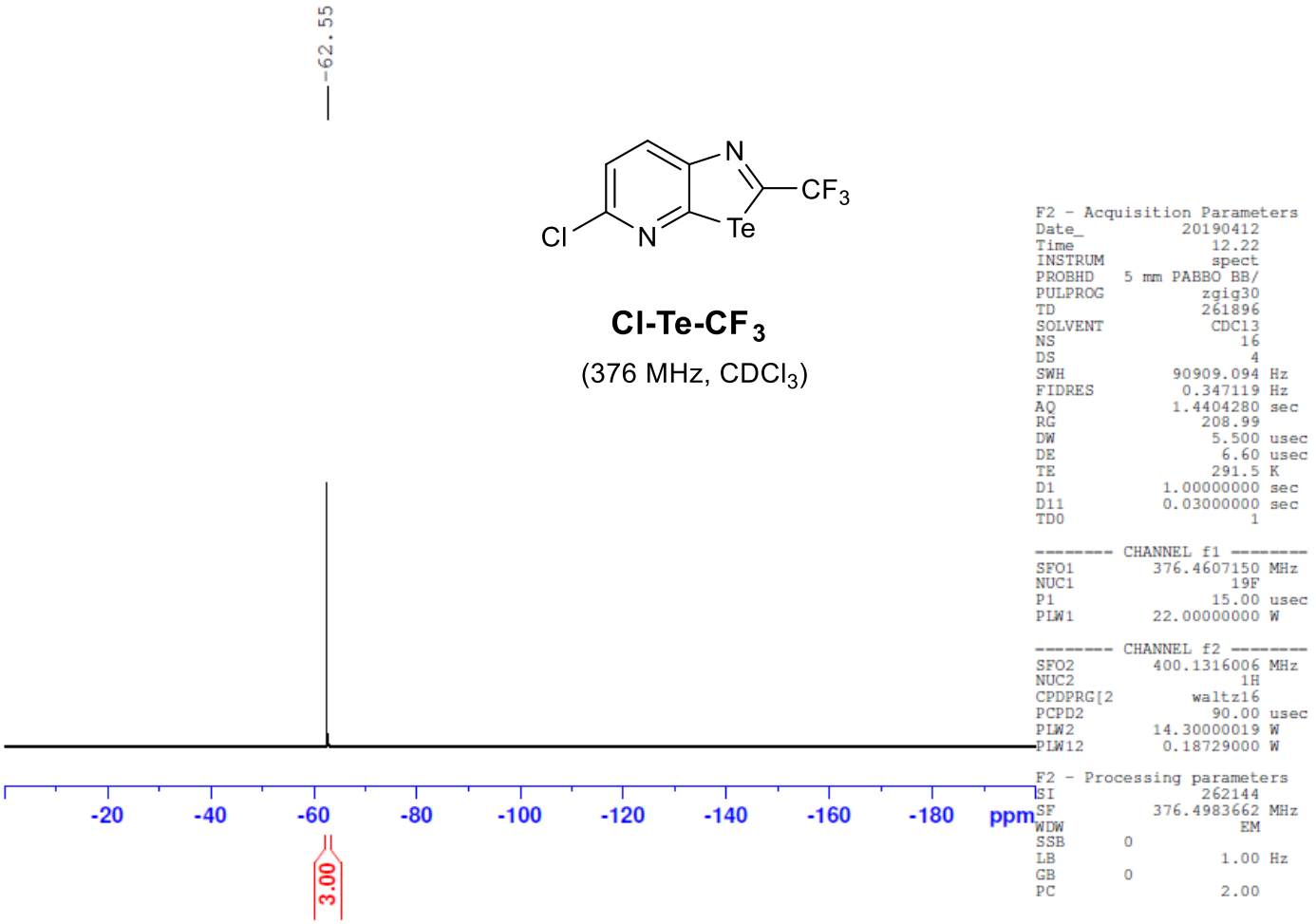


Figure S24: 376 MHz ^{19}F NMR in $CDCl_3$ of molecule ***Cl-Te-CF3.***

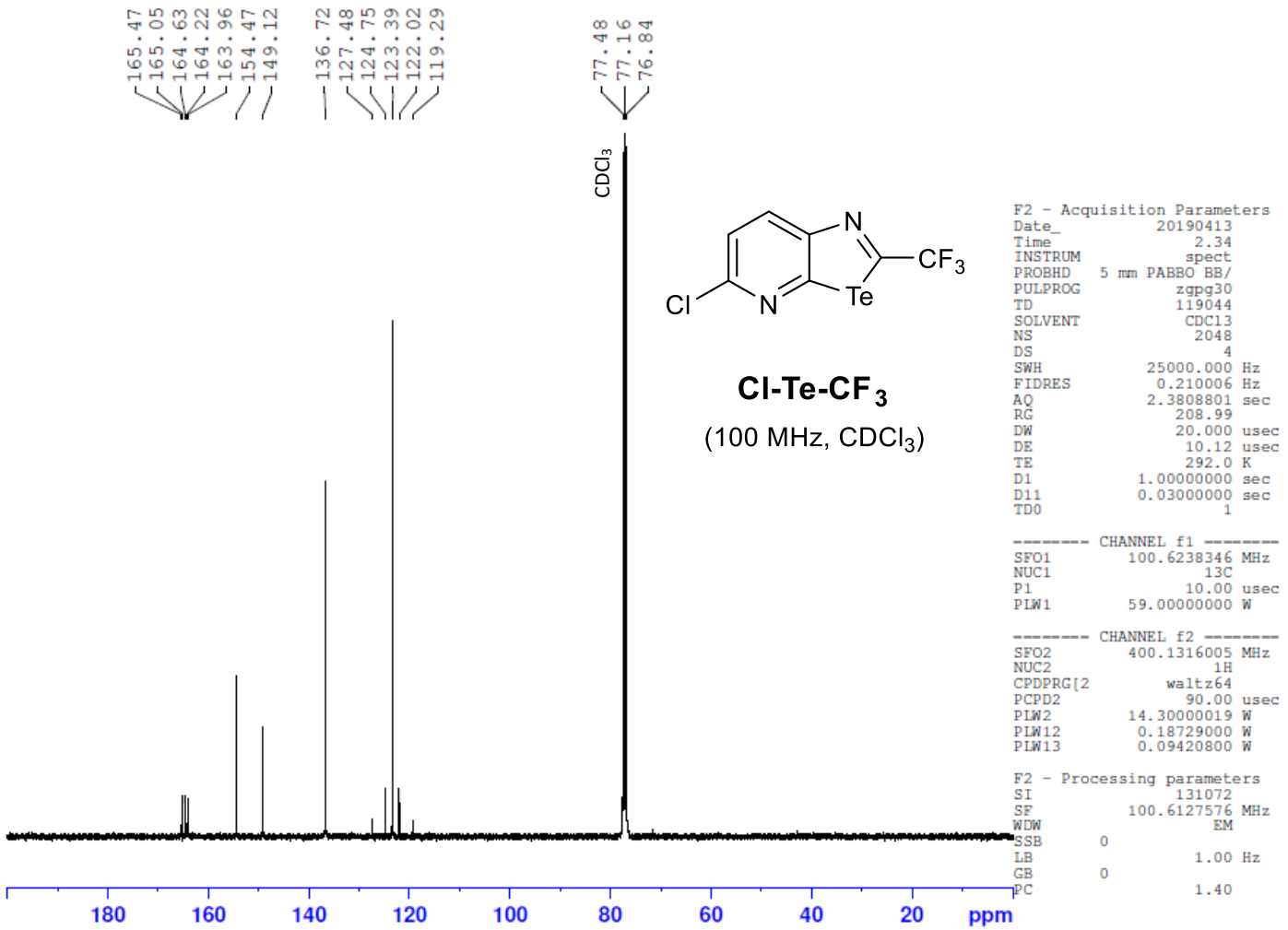


*Figure S25: 100 MHz ^{13}C NMR in $CDCl_3$ of molecule **Cl-Te-CF$_3$**. Due to ^{13}C-^{19}F coupling: Peak 164.8 splits into 165.47, 165.05, 164.63 and 164.22; Peak 123.2 splits into 127.48, 124.75, 122.02 and 119.29.*

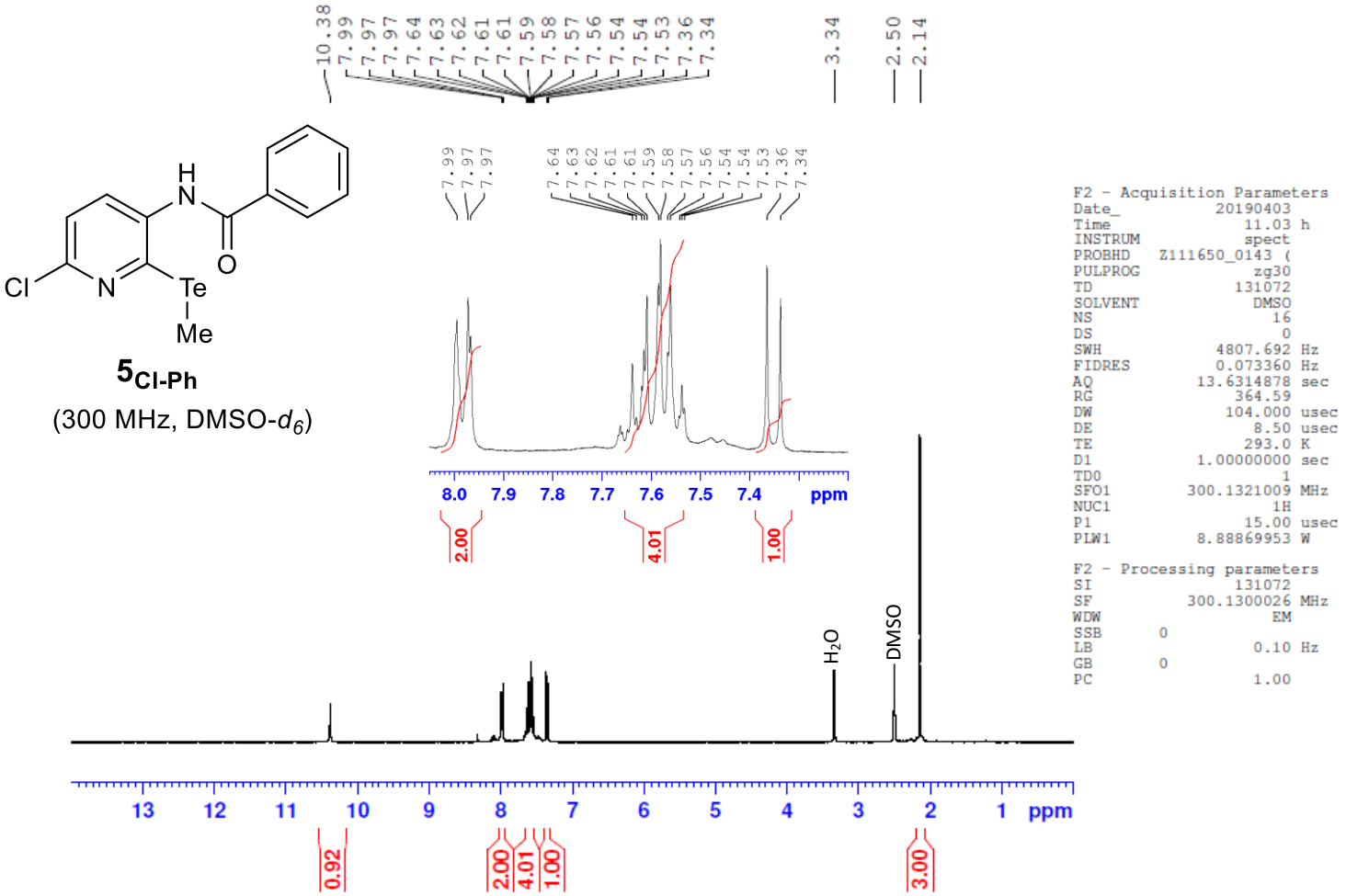


Figure S26: 300 MHz ^{1}H NMR in DMSO-d_6 of molecule $\mathbf{5_{CI\text{-}Ph}}$.

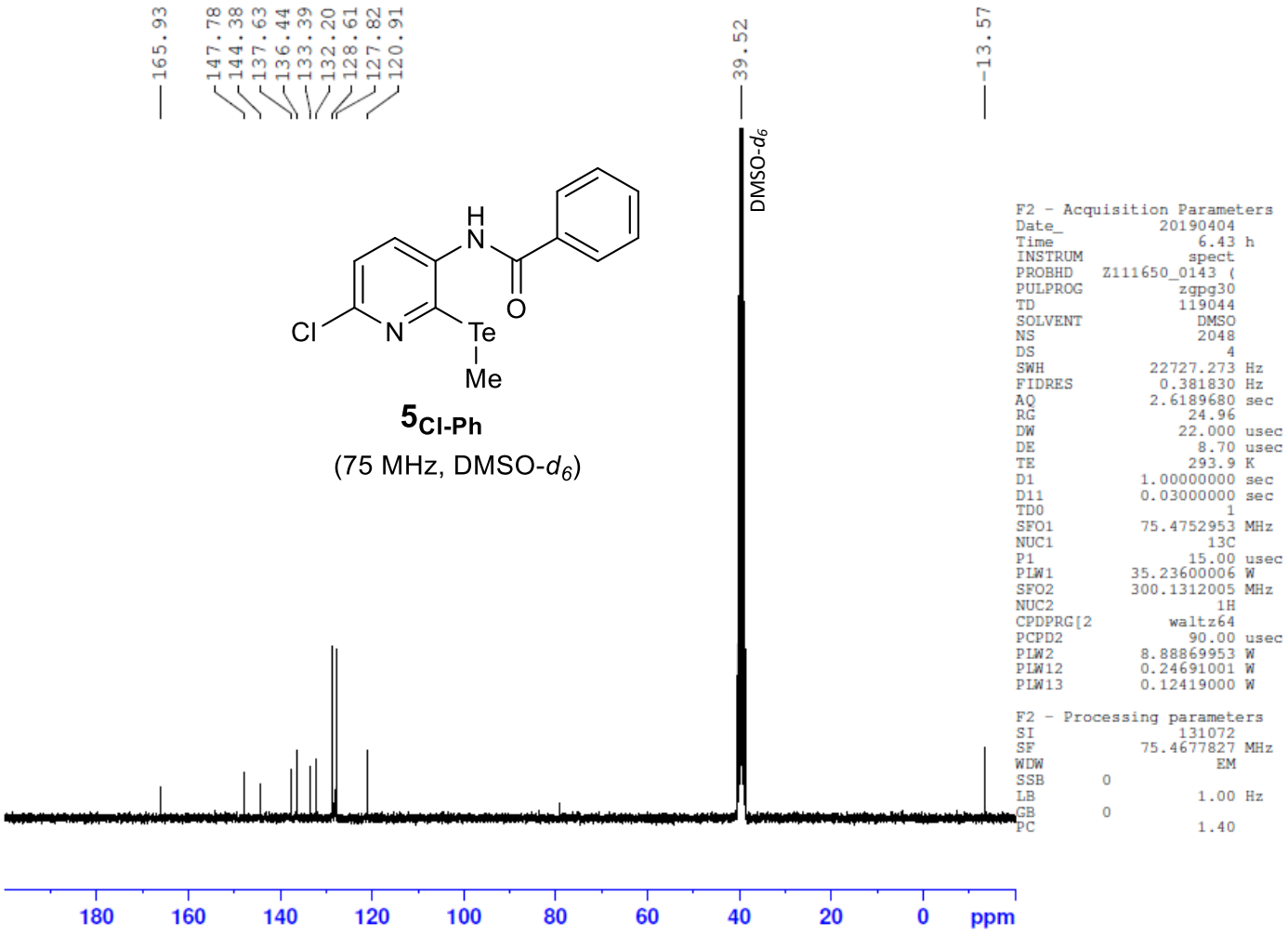


Figure S27: 75 MHz ^{13}C NMR in DMSO-d_6 of molecule $\mathbf{5_{Cl\text{-}Ph}}$.

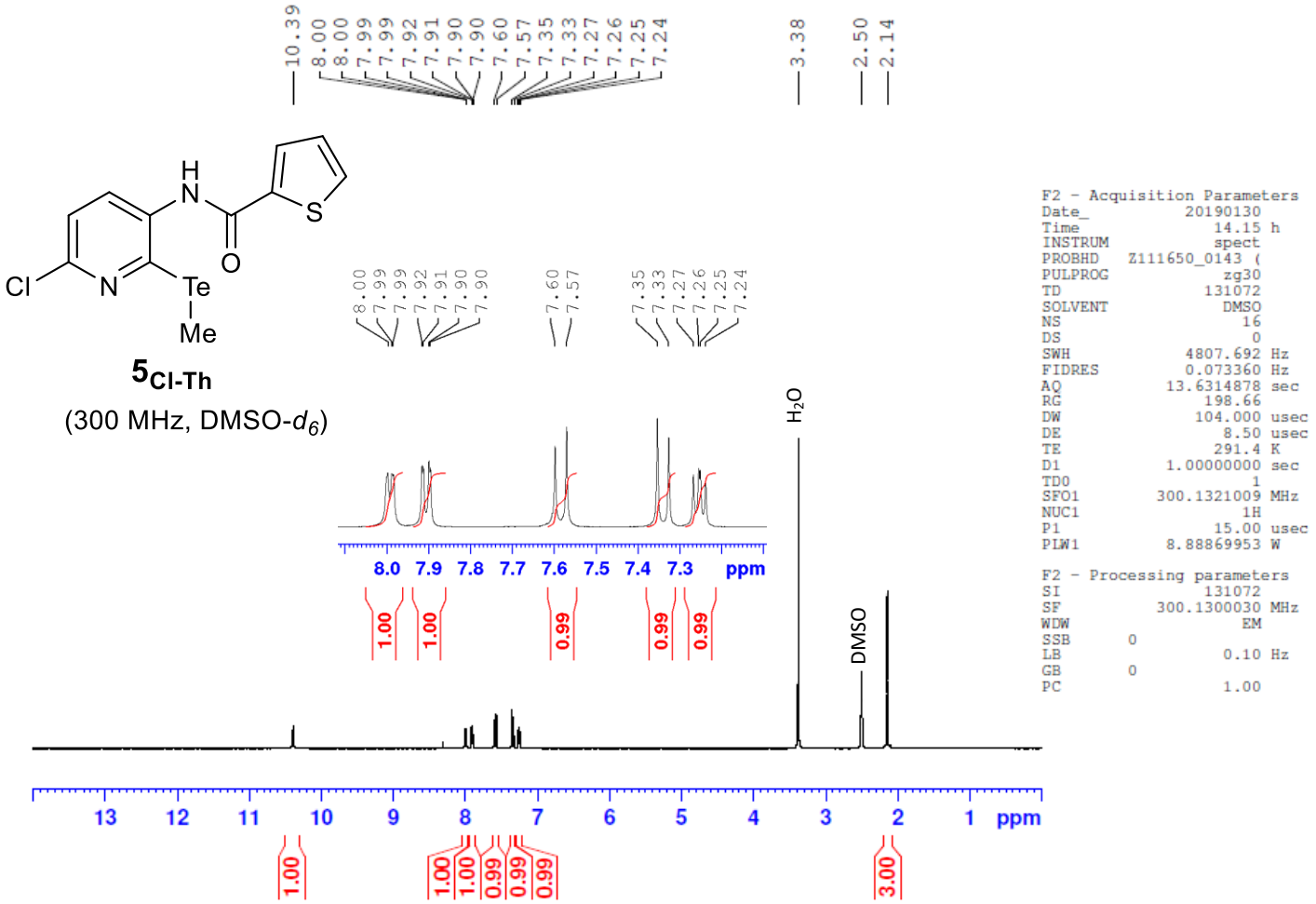


Figure S28: 300 MHz ^{1}H NMR in DMSO-d_6 of molecule **5**$_{CI\text{-}Th}$.

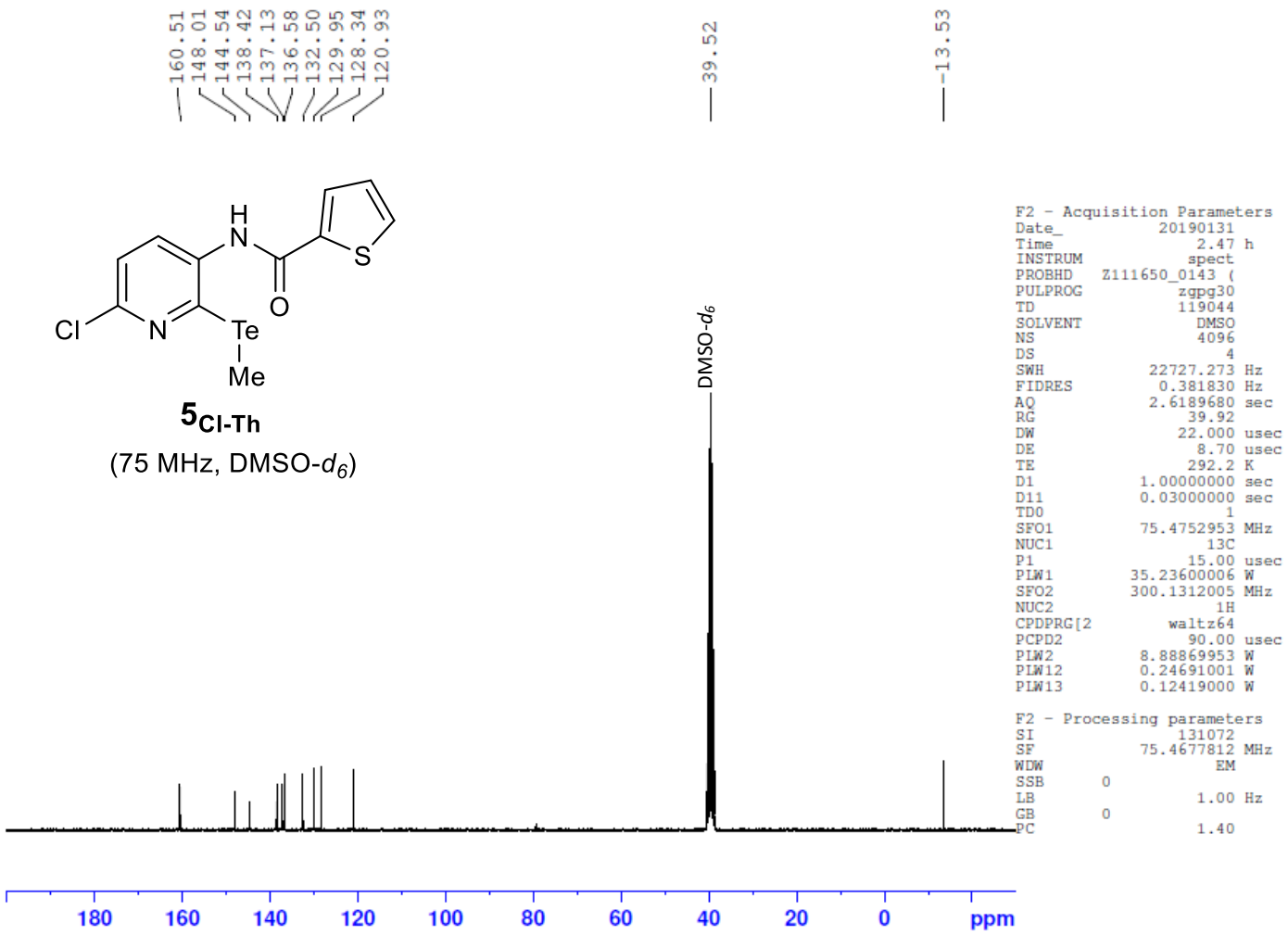


Figure S29: 75 MHz ^{13}C NMR in DMSO-d_6 of molecule $\mathbf{5_{Cl\text{-}Th}}$.

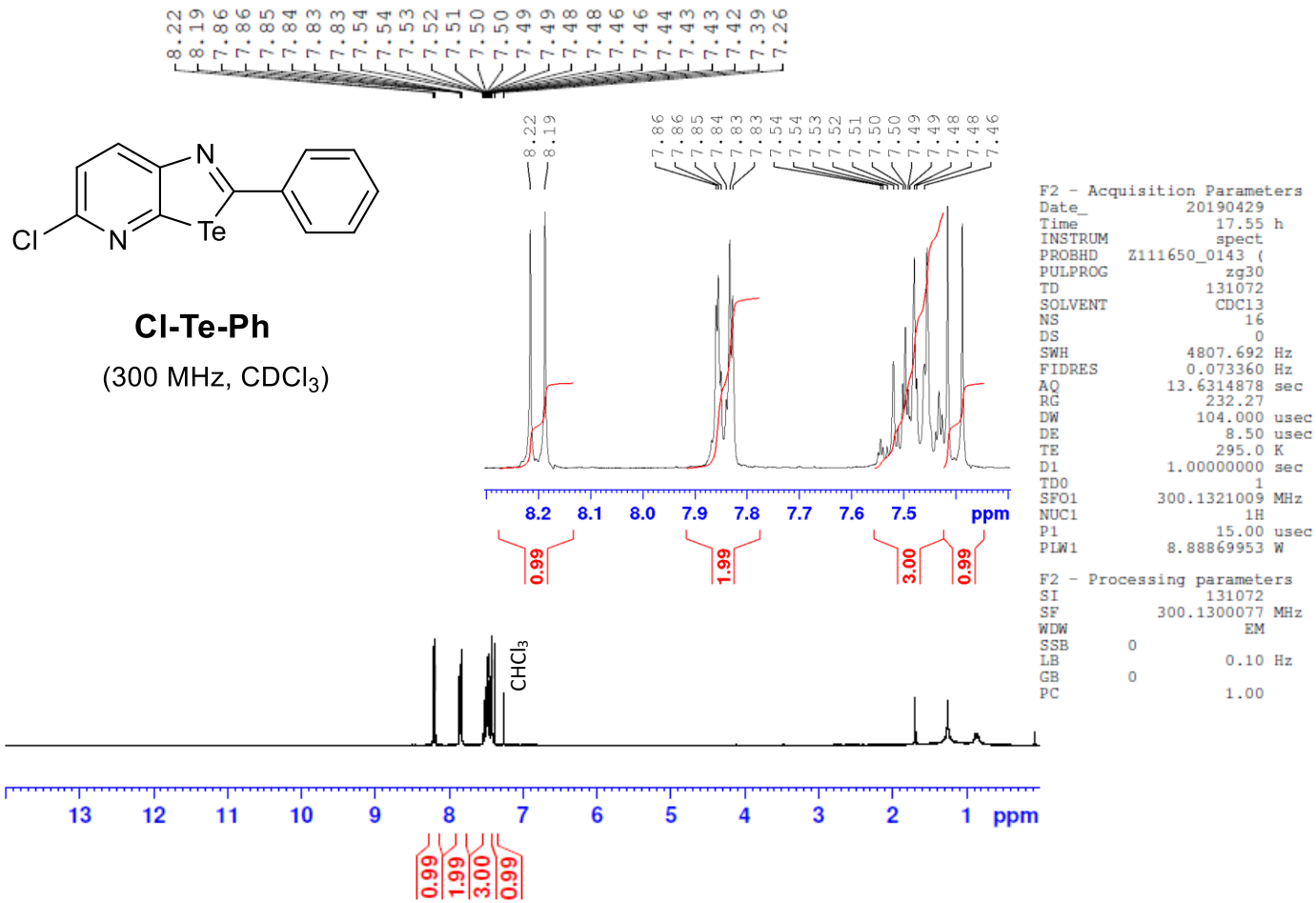


Figure S30: 300 MHz ^{1}H NMR in $CDCl_3$ of molecule ***Cl-Te-Ph****.*

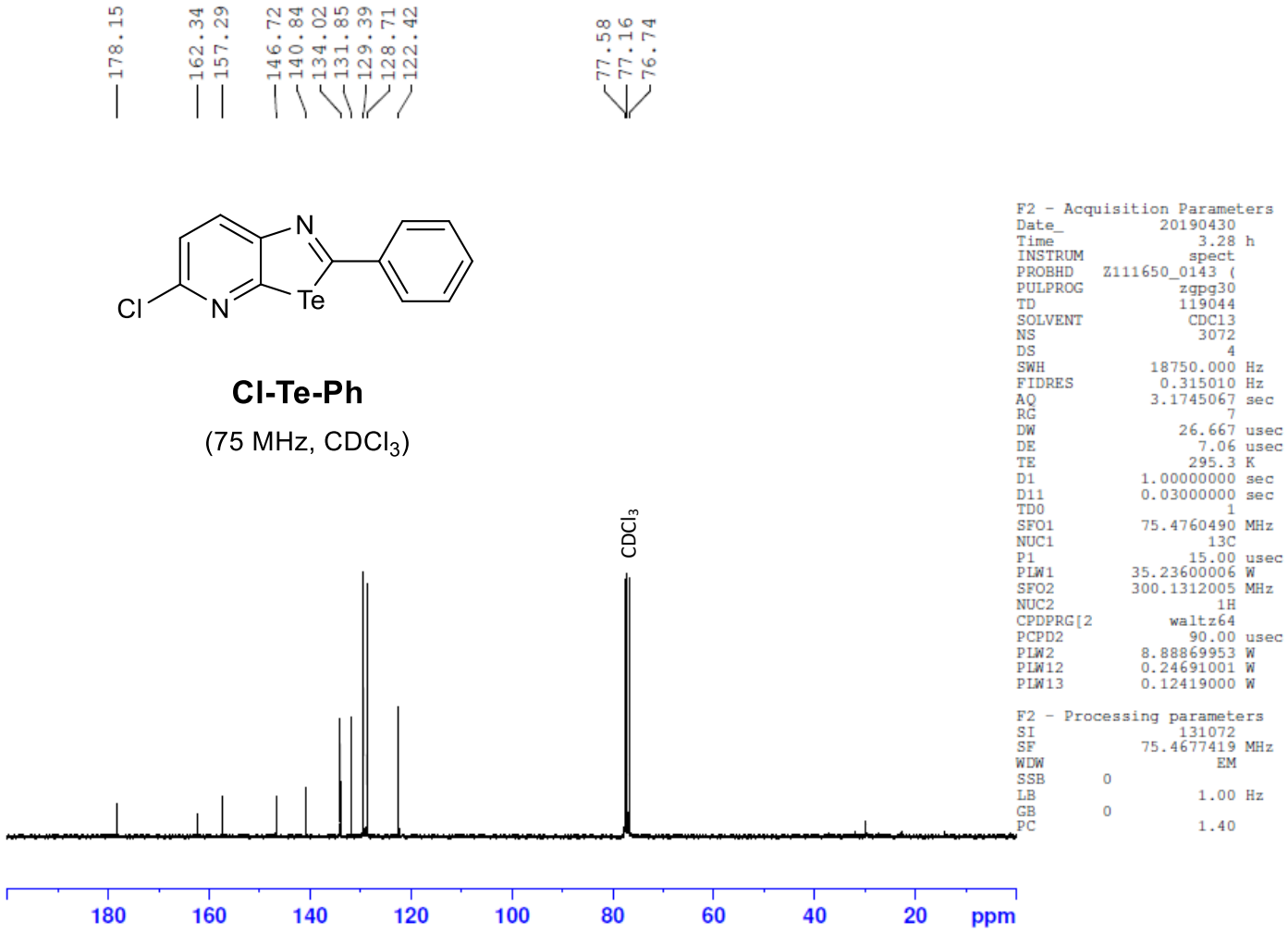


Figure S31: 75 MHz ^{13}C NMR in $CDCl_3$ of molecule ***Cl-Te-Ph****.*

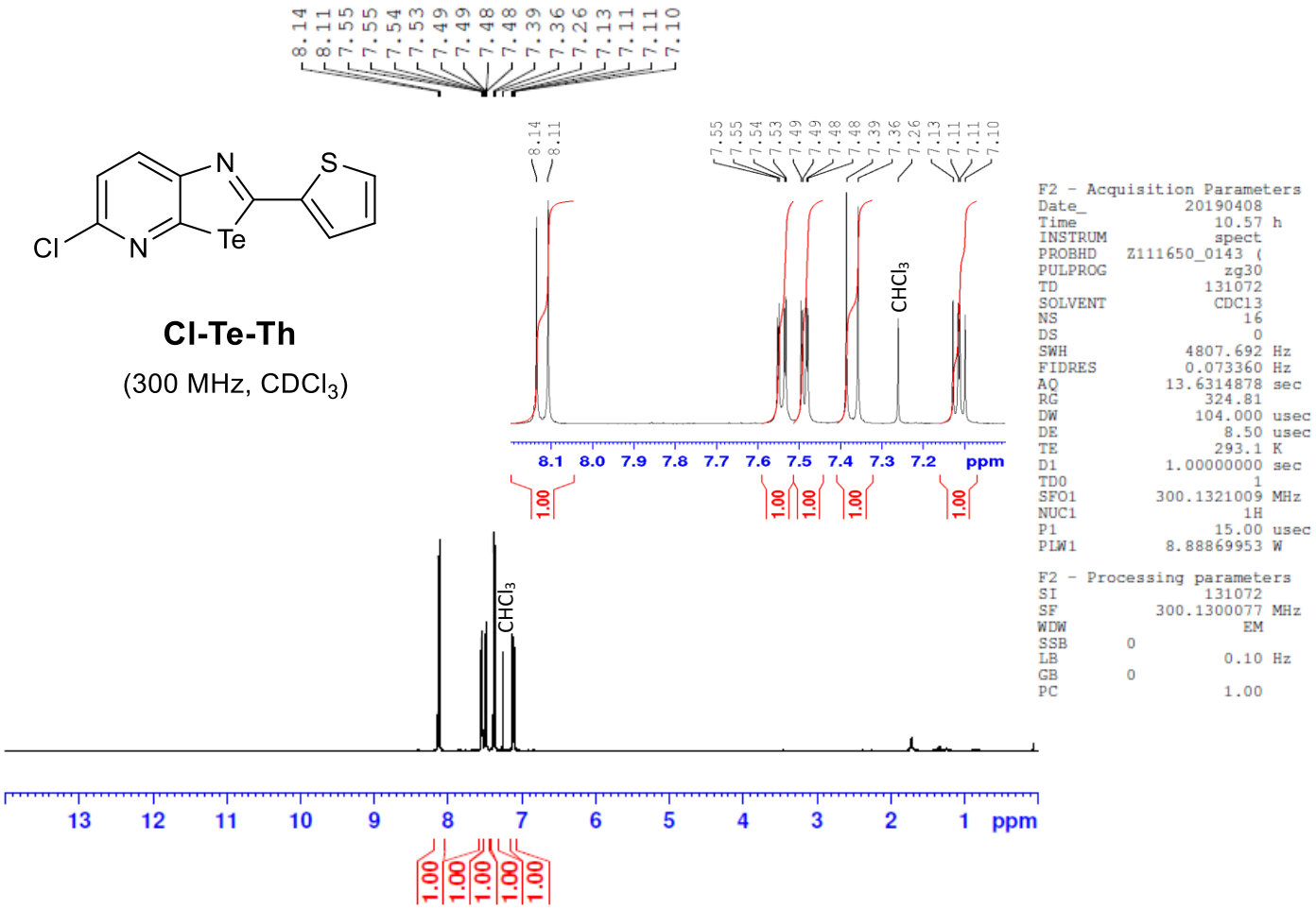


Figure S32: 300 MHz ^{1}H NMR in $CDCl_3$ of molecule ***Cl-Te-Th***.

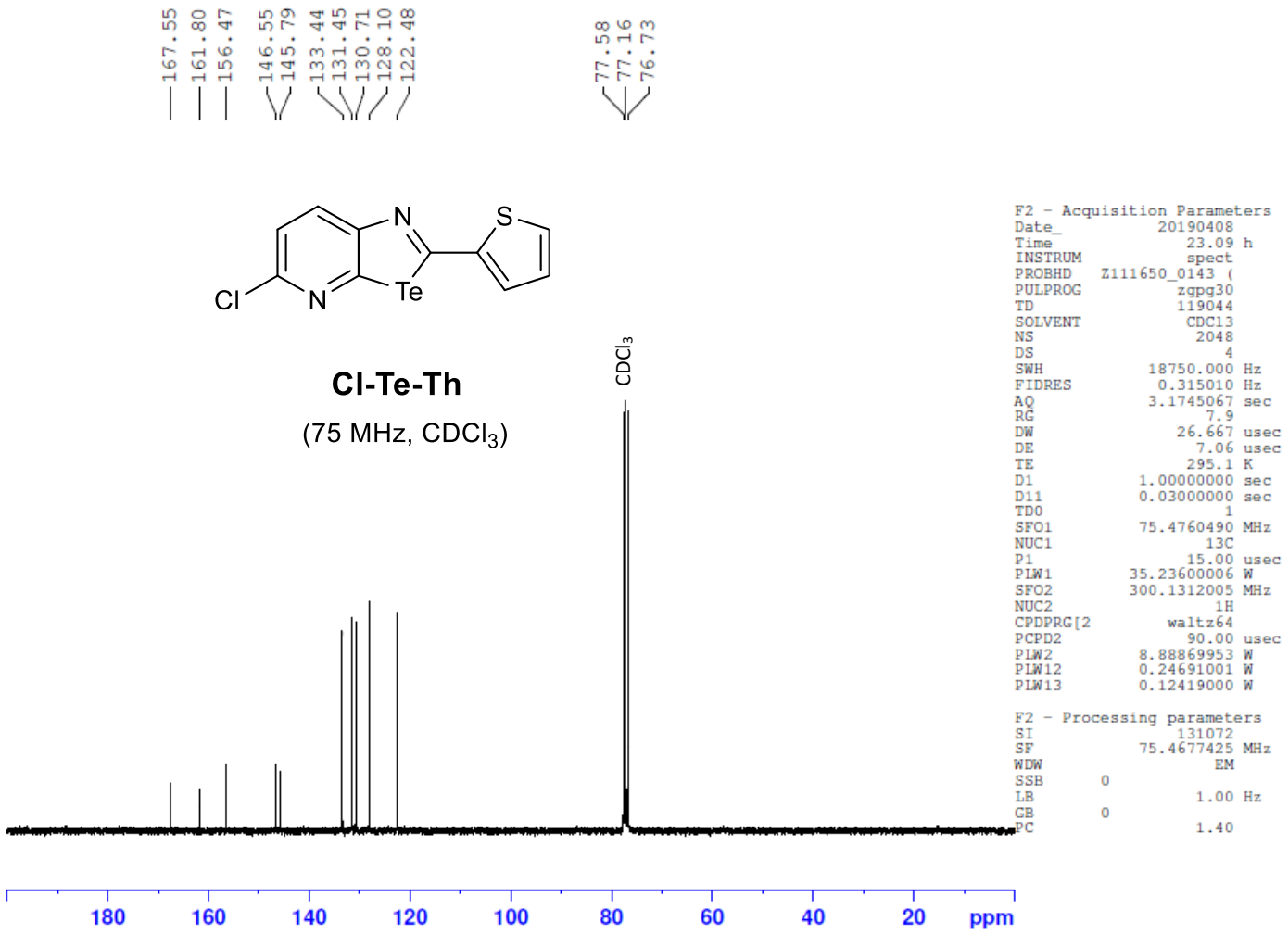
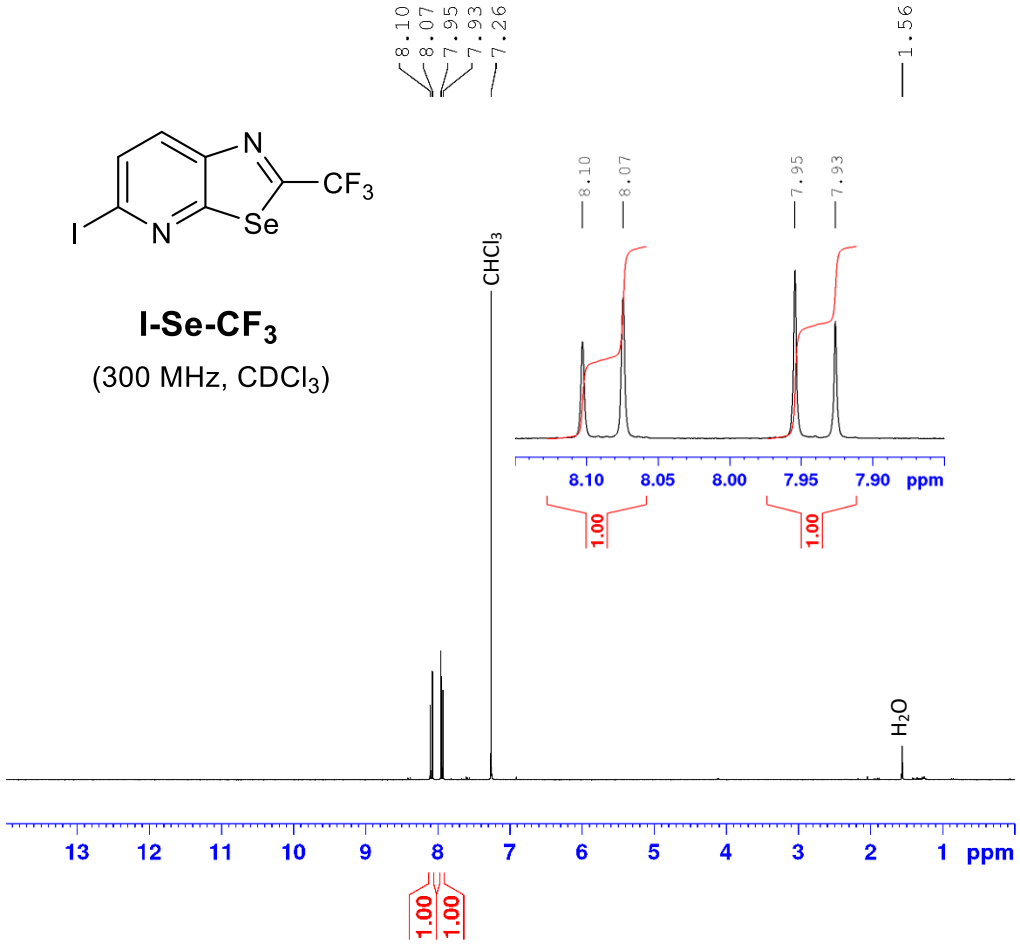


Figure S33: 75 MHz ^{13}C NMR in $CDCl_3$ of molecule ***Cl-Te-Th****.*

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INSTRUM             spect
PROBHD    Z111650_0143 (
PULPROG             zg30
TD                131072
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              4807.692 Hz
FIDRES           0.073360 Hz
AQ              13.6314878 sec
RG                 455.32
DW                104.000 usec
DE                  8.50 usec
TE                 294.4 K
D1              1.00000000 sec
TD0                     1
SFO1          300.1321009 MHz
NUC1                   1H
P1                  15.00 usec
PLW1           8.88869953 W

F2 - Processing parameters
SI                 131072
SF            300.1300079 MHz
WDW                    EM
SSB                     0
LB                   0.10 Hz
GB                      0
PC                   1.00
```
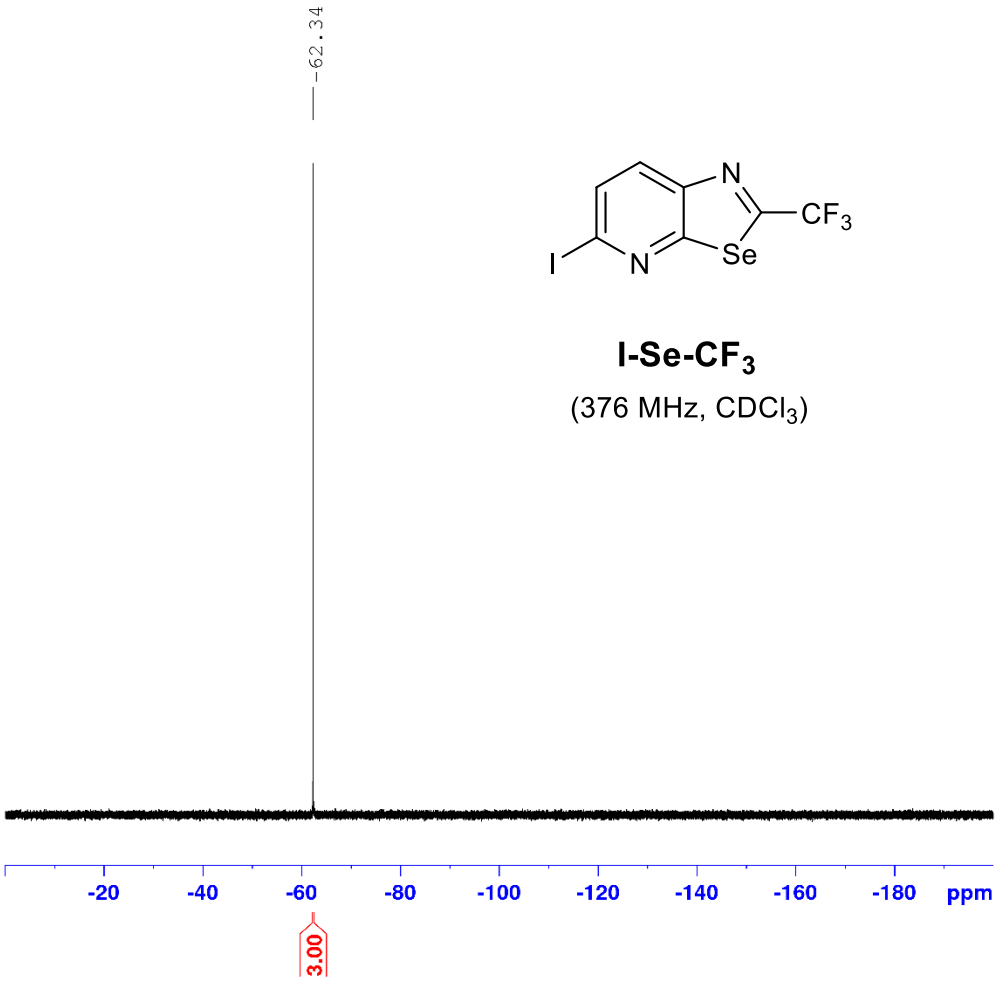

Figure S34: 300 MHz ^{1}H NMR in $CDCl_3$ of molecule ***I-Se-CF₃.***

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PULPROG            zqig30
TD                 261896
SOLVENT              CDCl3
NS                      16
DS                       4
SWH              90909.094 Hz
FIDRES           0.347119 Hz
AQ               1.4404280 sec
RG                  208.99
DW                   5.500 usec
DE                   6.60 usec
TE                   291.6 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          376.4607150 MHz
NUC1                   19F
P1                   15.00 usec
PLW1          22.00000000 W

======== CHANNEL f2 ========
SFO2          400.1316006 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2                90.00 usec
PLW2          14.30000019 W
PLW12          0.18729000 W

F2 - Processing parameters
SI                  262144
SF            376.4983662 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    2.00
```

*Figure S35: 376 MHz ^{19}F NMR in $CDCl_3$ of molecule **I-Se-CF$_3$**.*

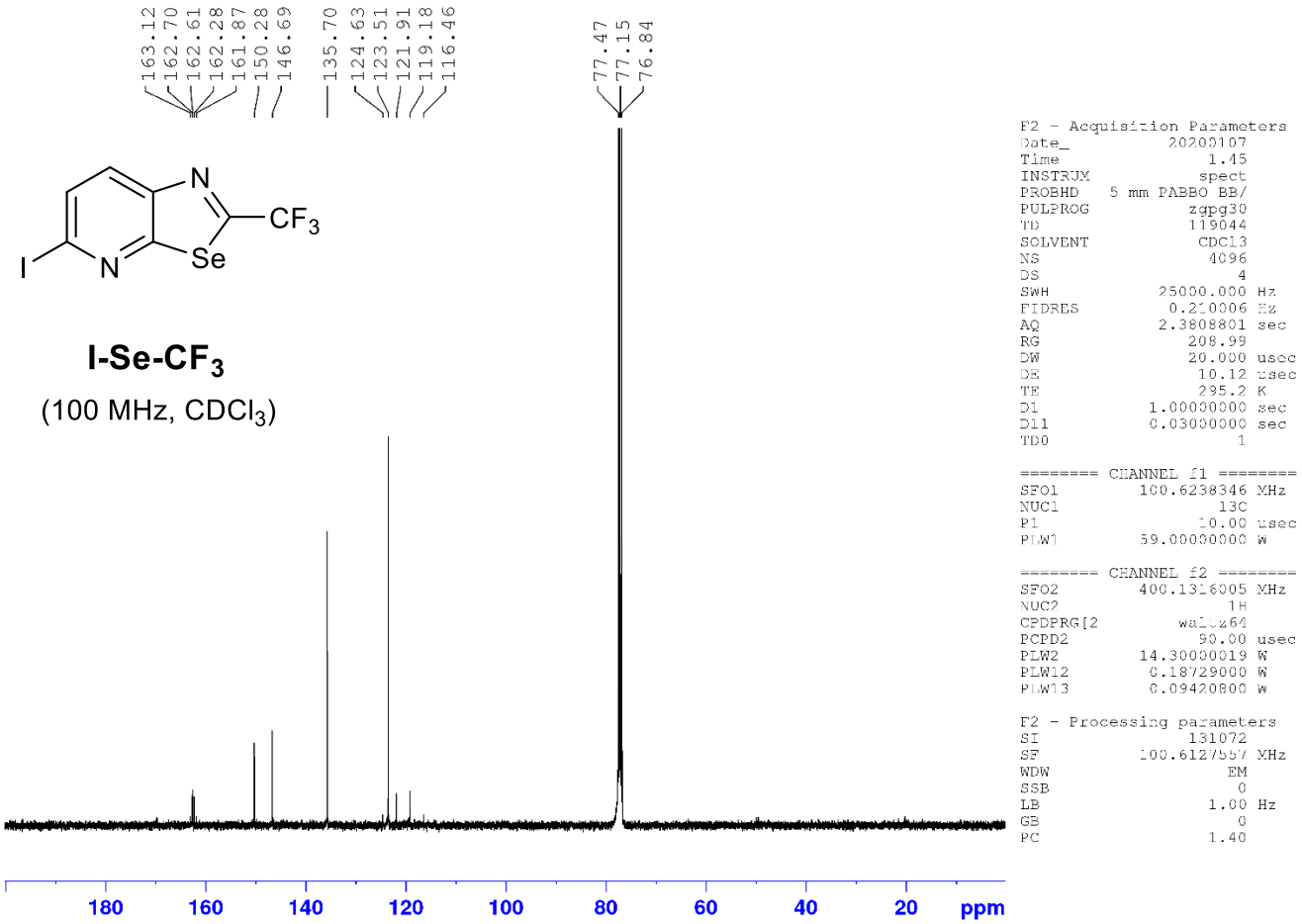


*Figure S36: 100 MHz ^{13}C NMR in $CDCl_3$ of molecule **I-Se-CF$_3$**. Due to ^{13}C-^{19}F coupling: Peak 162.5 splits into 163.12, 162.70, 162.28 and 161.87; Peak 122.5 splits into 124.63, 121.91, 119.81 and 116.46.*

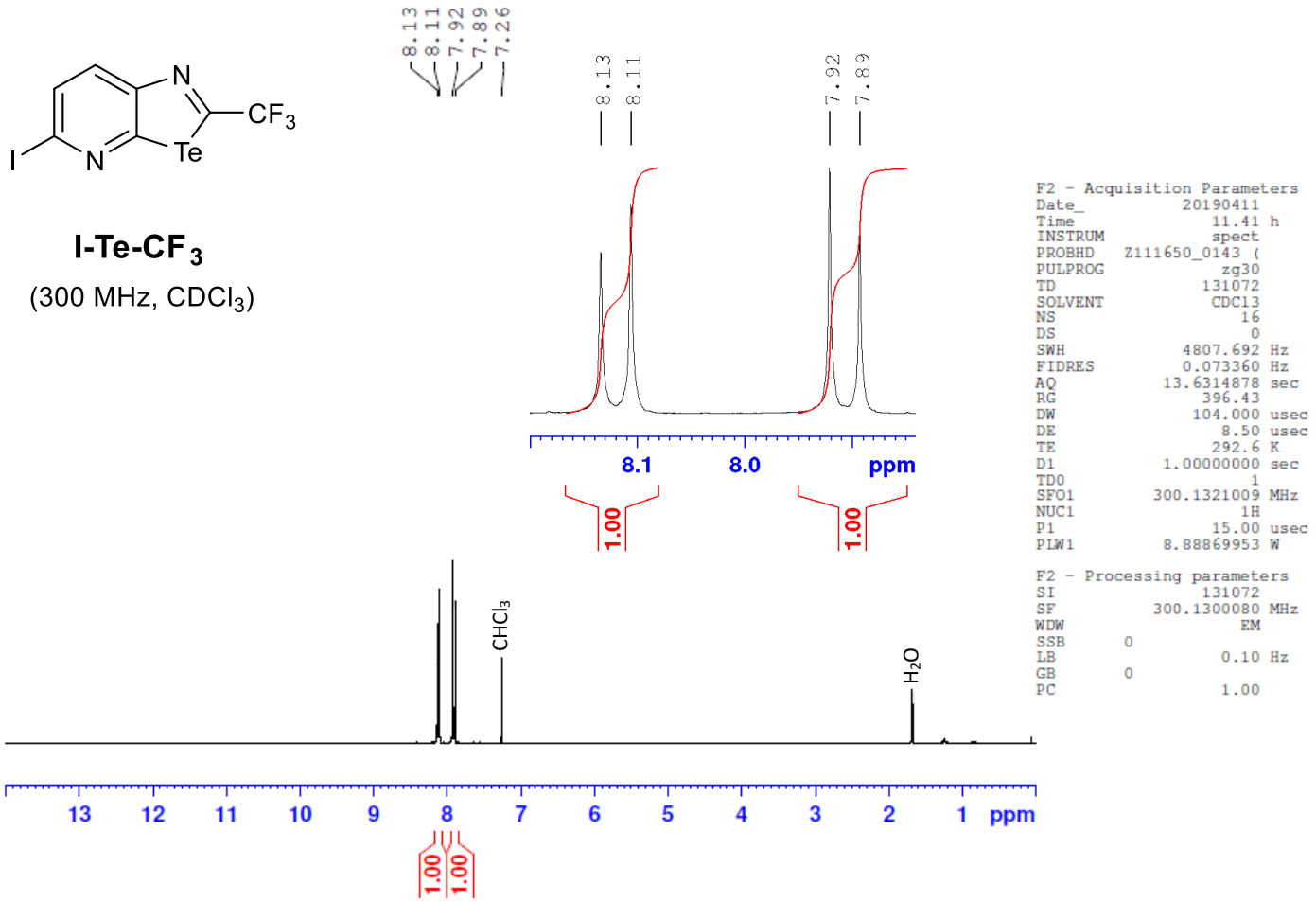


Figure S37: 300 MHz ^{1}H NMR in $CDCl_3$ of molecule ***I-Te-CF₃.***

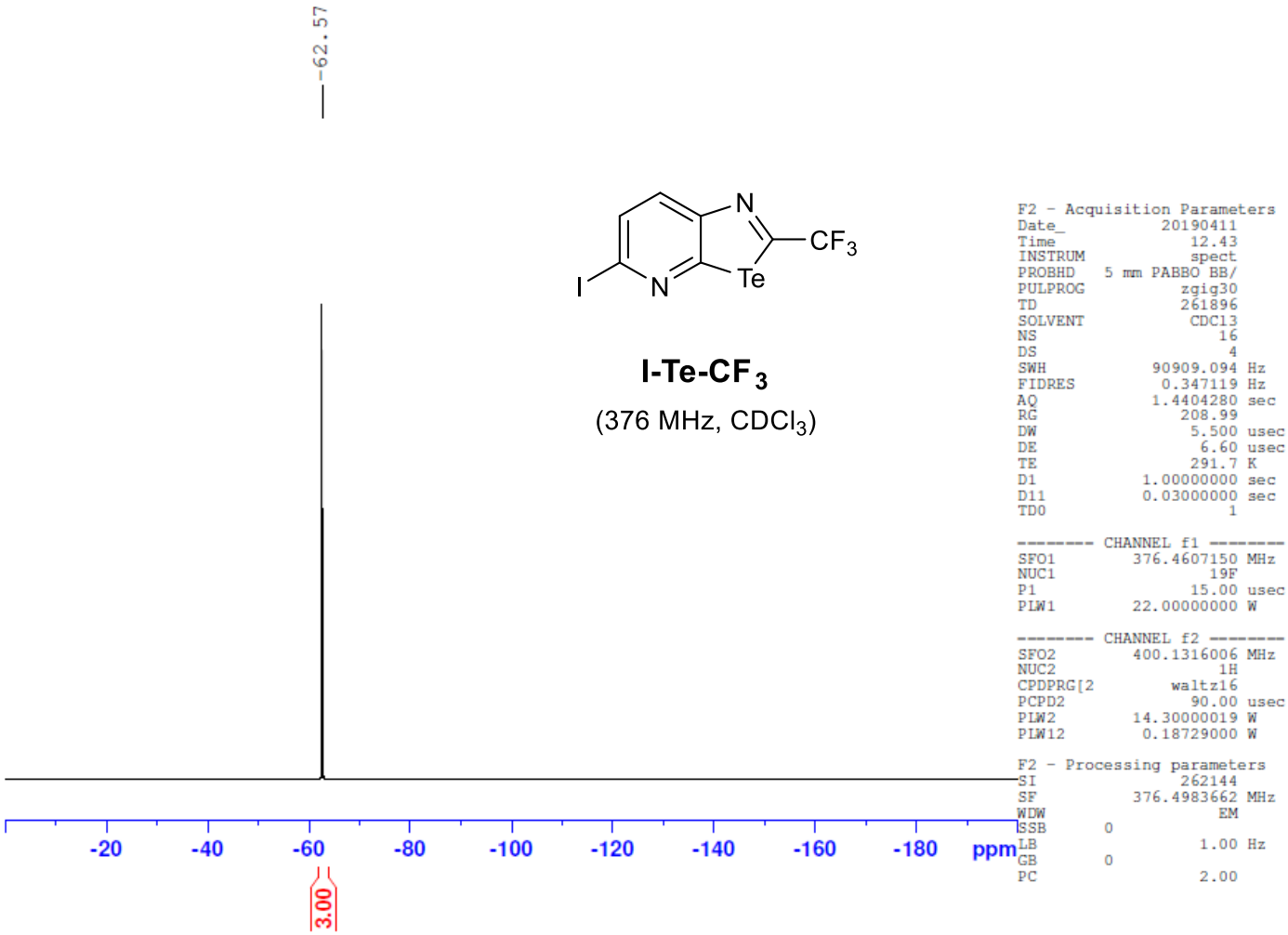


Figure S38: 376 MHz ^{19}F NMR in $CDCl_3$ of molecule ***I-Te-CF$_3$.***

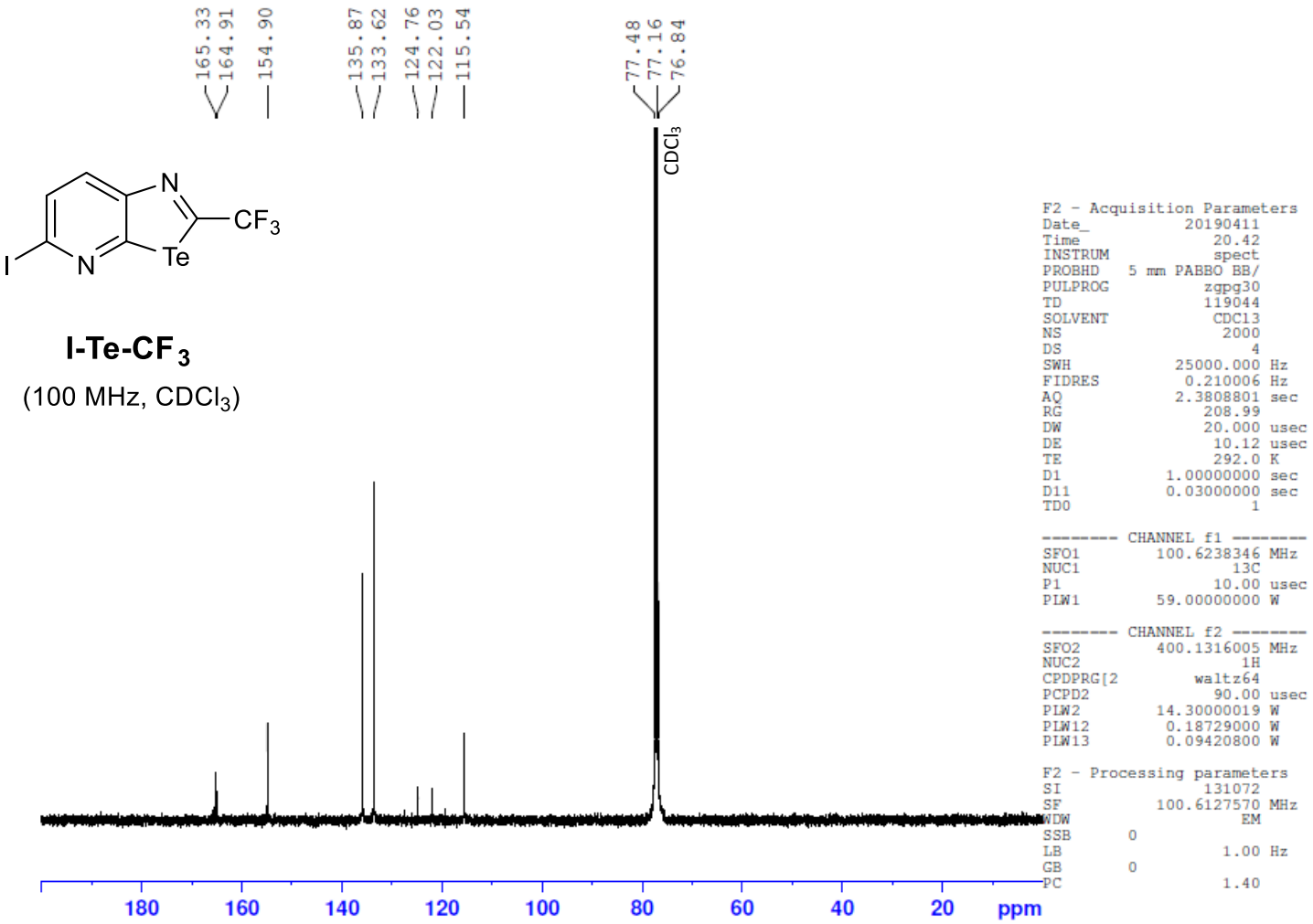


*Figure S39: 100 MHz ^{13}C NMR in $CDCl_3$ of molecule **I-Te-CF$_3$**. Due to ^{13}C-^{19}F coupling: Peak 165.1 splits into 165.33 and 164.91; Peak 123.4 splits into 124.76 and 122.03.*

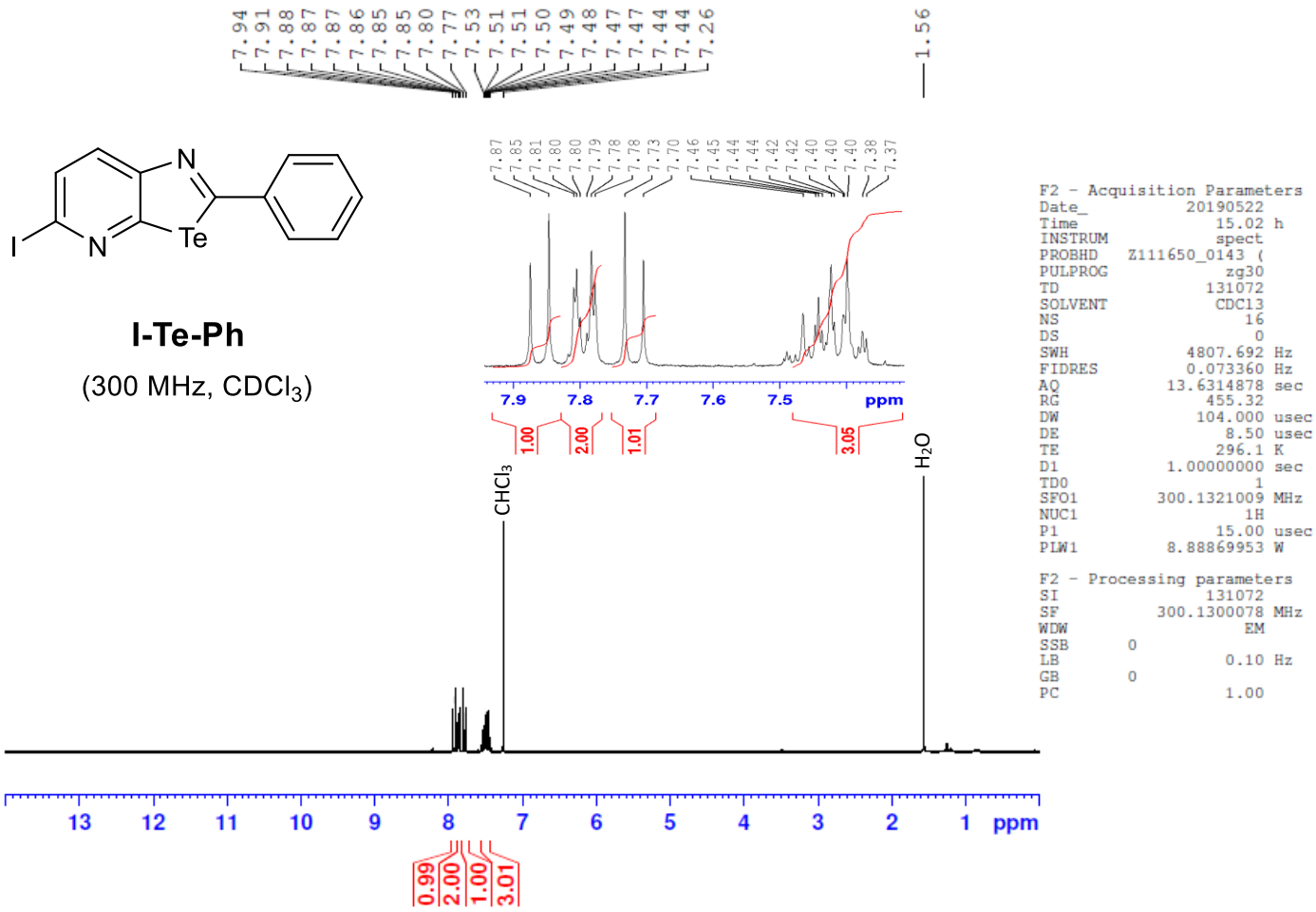


Figure S40: 300 MHz ^{1}H NMR in $CDCl_3$ of molecule ***I-Te-Ph*****.**

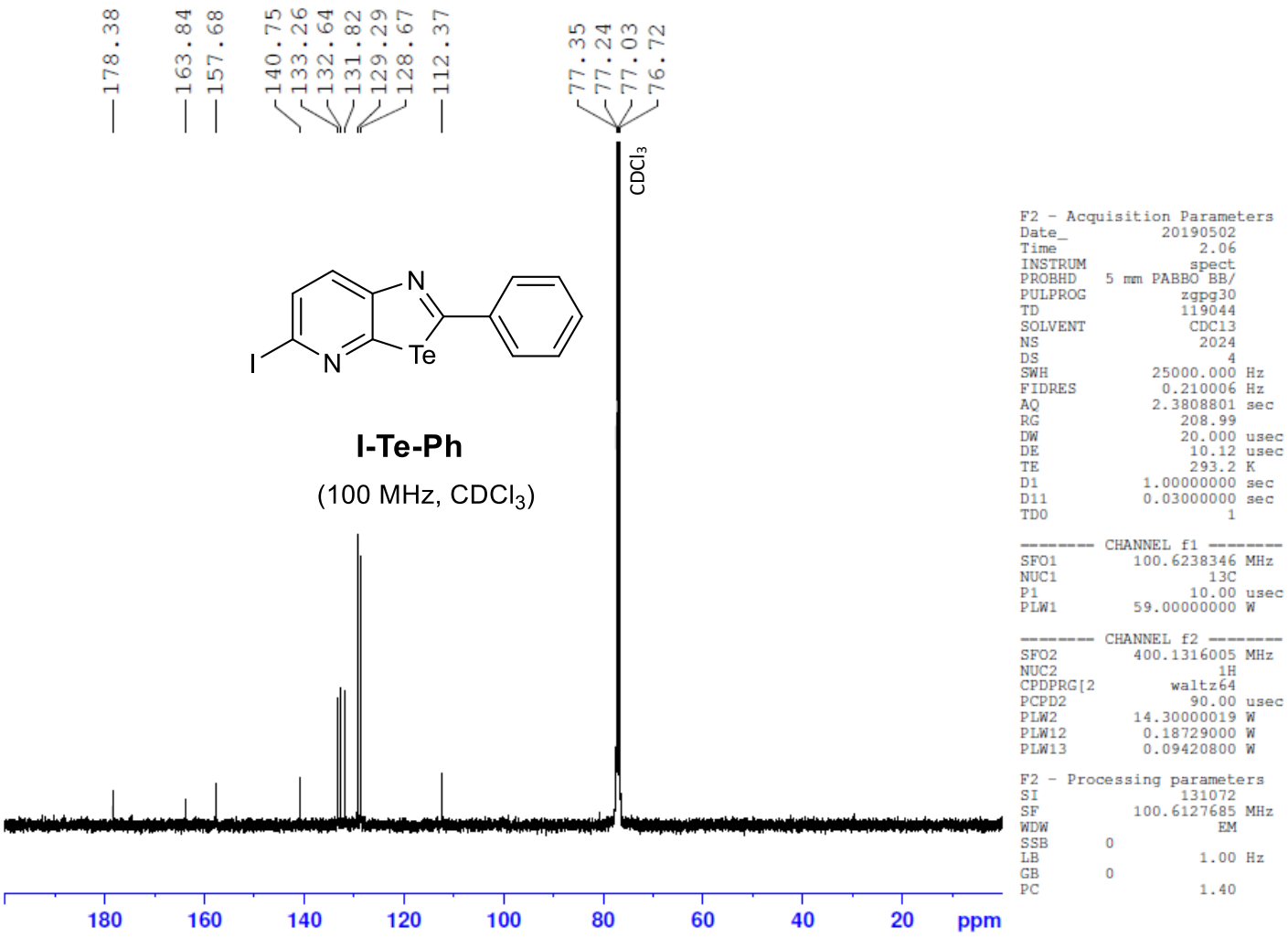


*Figure S41: 100 MHz ^{13}C NMR in $CDCl_3$ of molecule **I-Te-Ph**.*

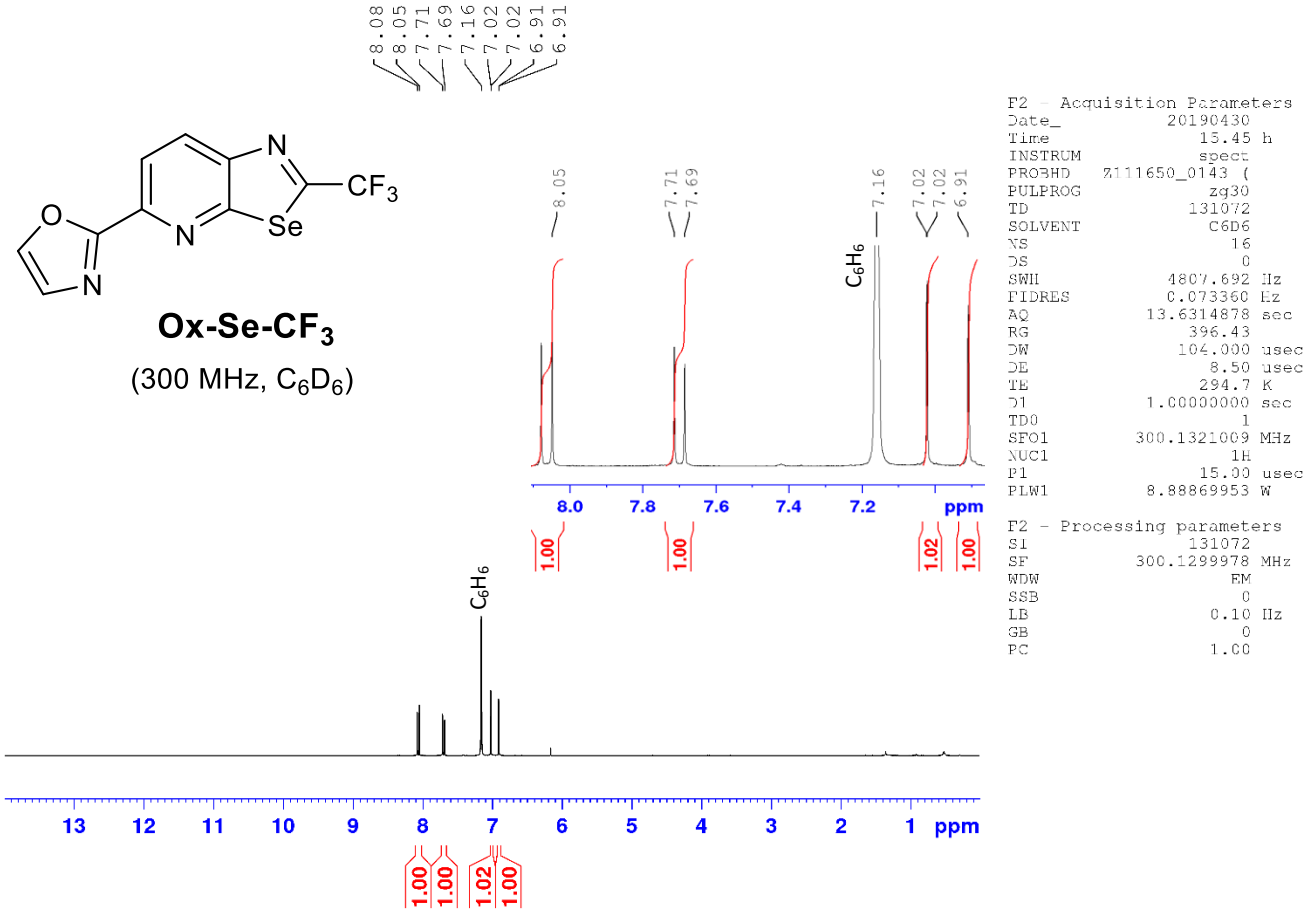
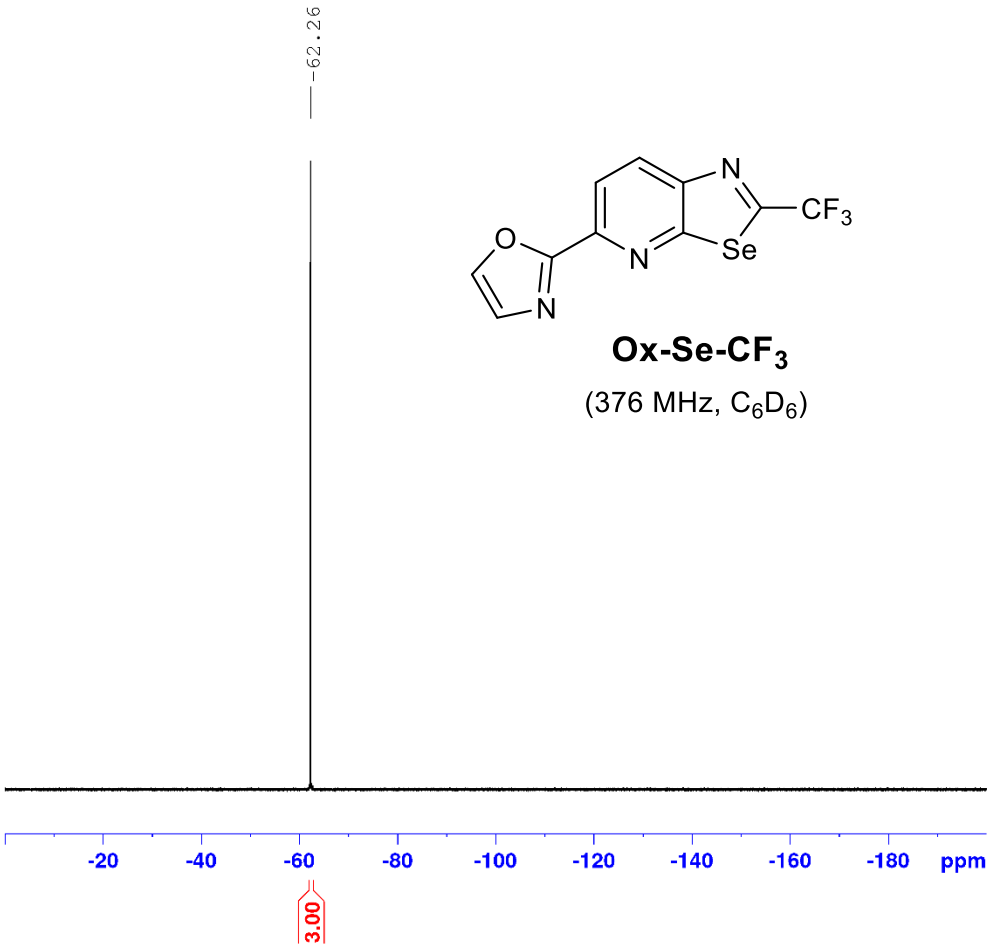


Figure S42: 300 MHz ^1H NMR in C_6D_6 of molecule ***Ox-Se-CF₃.***

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PULPROG          zgig30
TD               261896
SOLVENT            C6D6
NS                   32
DS                    4
SWH           90909.094 Hz
FIDRES        0.347119 Hz
AQ            1.4404280 sec
RG               208.99
DW                5.500 usec
DE                6.60 usec
TE               291.3 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         376.4607150 MHz
NUC1                19F
P1                15.00 usec
PLW1         22.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316006 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         14.30000019 W
PLW12         0.18729000 W

F2 - Processing parameters
SI                262144
SF           376.4983662 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                2.00
```
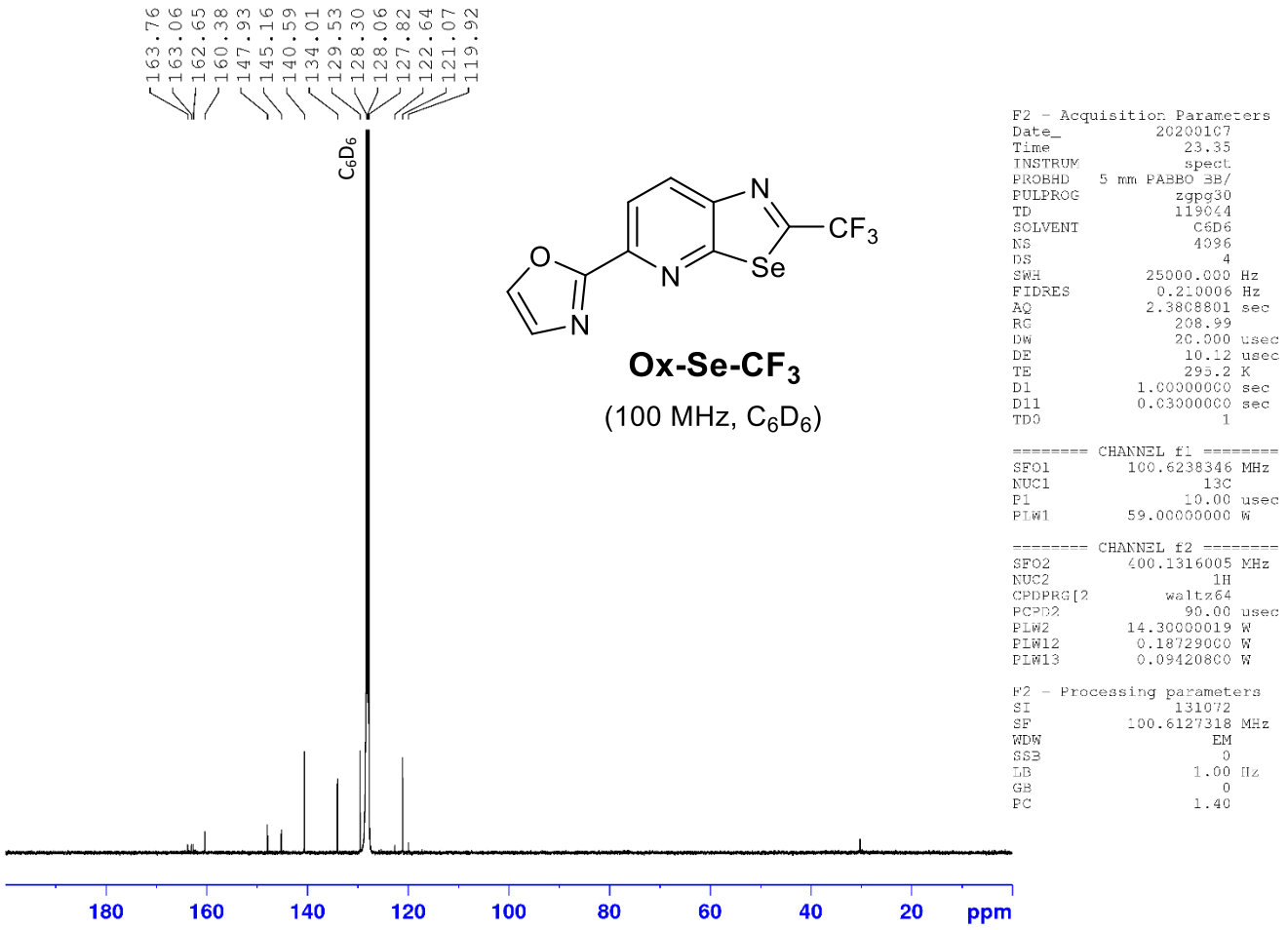

*Figure S43: 376 MHz ^{19}F NMR in C_6D_6 of molecule **Ox-Se-CF$_3$**.*

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F2 - Acquisition Parameters
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PULPROG           zgpg30
TD                119044
SOLVENT             C6D6
NS                  4096
DS                     4
SWH           25000.000 Hz
FIDRES         0.210006 Hz
AQ            2.3808801 sec
RG               208.99
DW               20.000 usec
DE                10.12 usec
TE                295.2 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6238346 MHz
NUC1                13C
P1                10.00 usec
PLW1        59.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz64
PCPD2             90.00 usec
PLW2        14.30000019 W
PLW12        0.18729000 W
PLW13        0.09420800 W

F2 - Processing parameters
SI                131072
SF           100.6127318 MHz
WDW                 EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```

*Figure S44: 100 MHz ^{13}C NMR in C_6D_6 of molecule **Ox-Se-CF$_3$**. Due to ^{13}C-^{19}F coupling: Peak 162.8 splits into 163.06 and 162.65; Peak 121.3 splits into 122.64 and 119.92.*

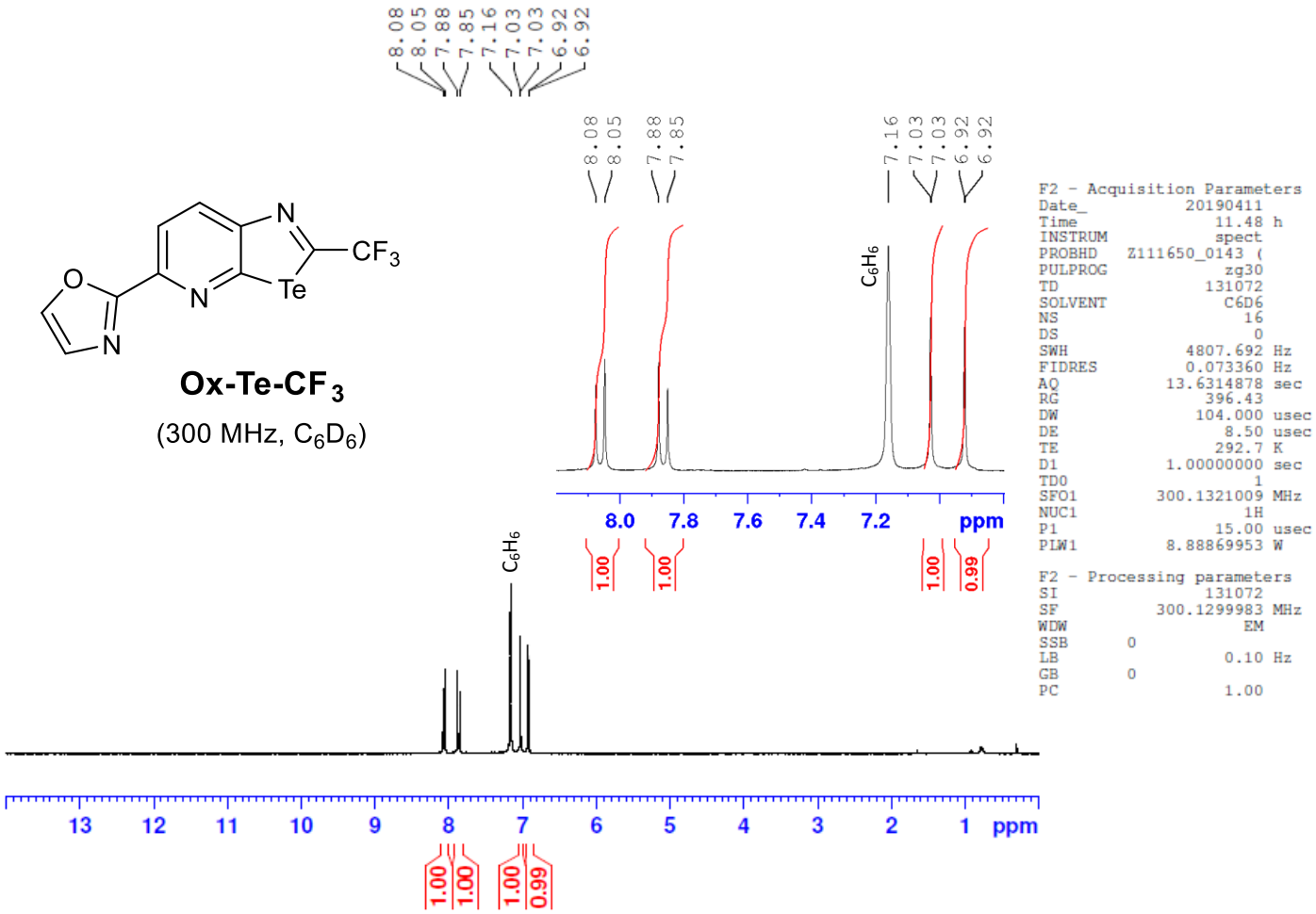
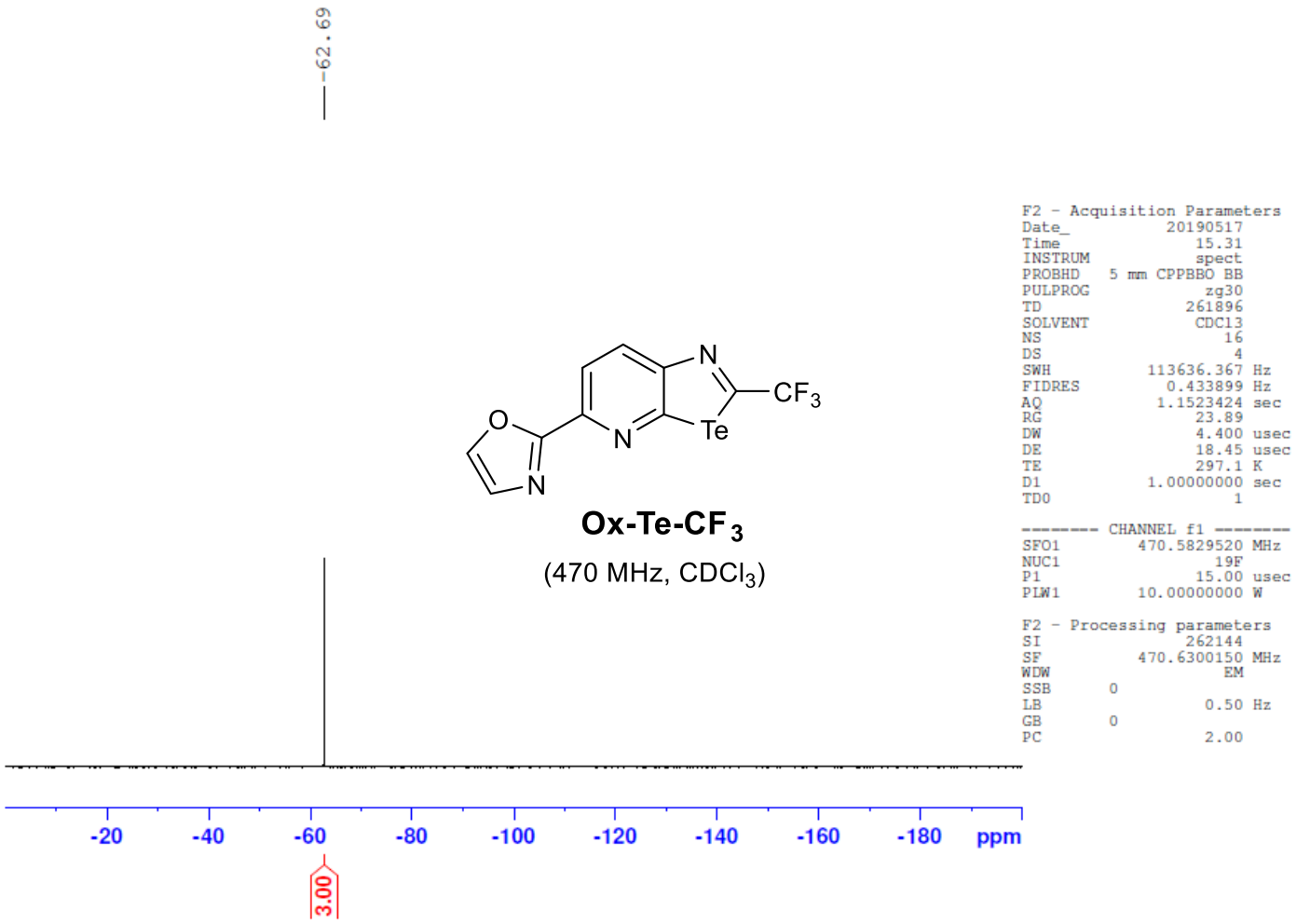


Figure S45: 300 MHz ^{1}H-NMR in C_6D_6 of molecule ***Ox-Te-CF$_3$.***

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F2 - Acquisition Parameters
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PULPROG           zg30
TD              261896
SOLVENT           CDCl3
NS                  16
DS                   4
SWH          113636.367 Hz
FIDRES         0.433899 Hz
AQ           1.1523424 sec
RG                23.89
DW                4.400 usec
DE                18.45 usec
TE                297.1 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        470.5829520 MHz
NUC1              19F
P1               15.00 usec
PLW1        10.00000000 W

F2 - Processing parameters
SI              262144
SF          470.6300150 MHz
WDW               EM
SSB      0
LB              0.50 Hz
GB       0
PC              2.00
```

Figure S46: 470 MHz ^{19}F NMR in $CDCl_3$ of molecule ***Ox-Te-CF$_3$.***

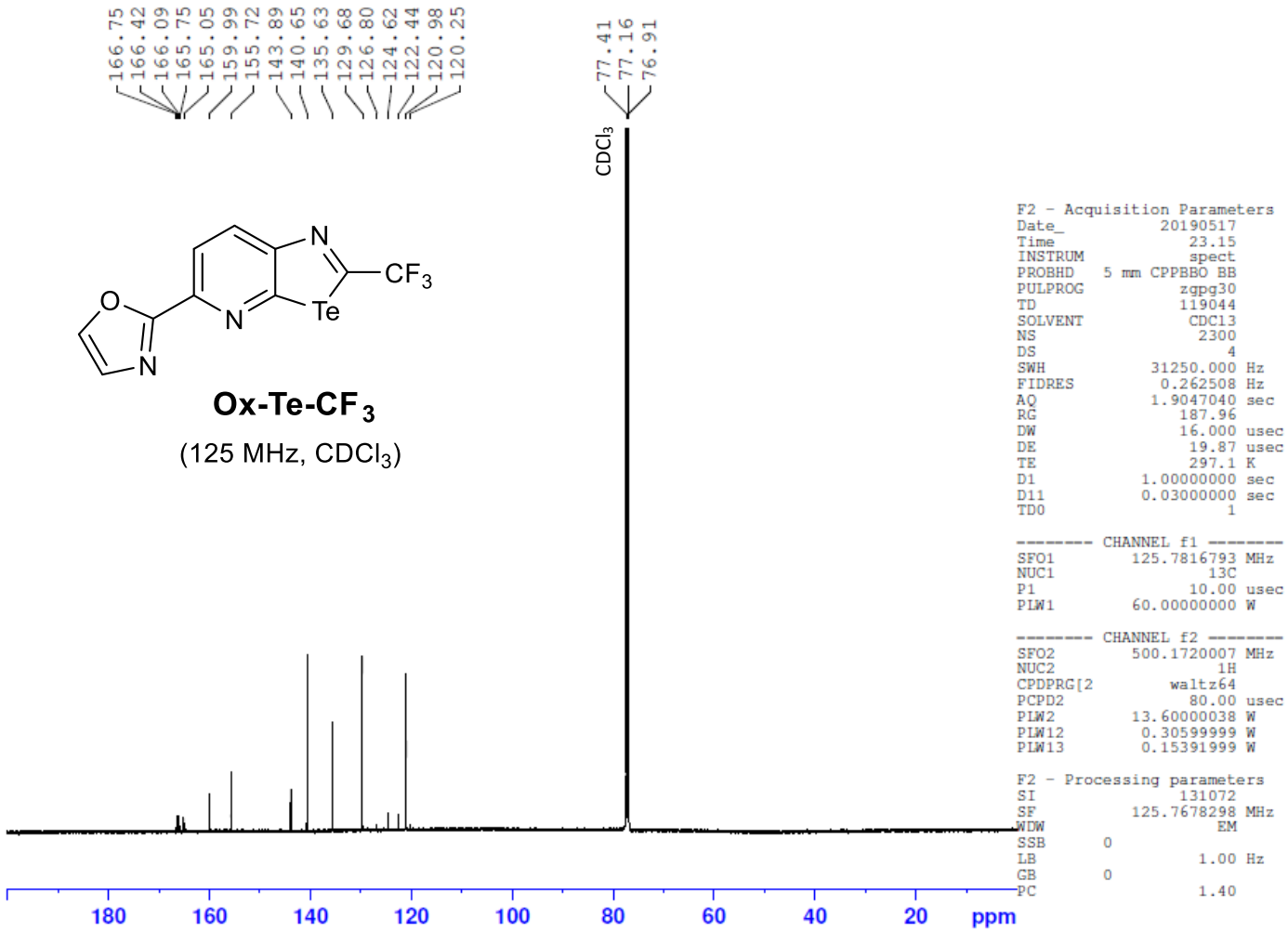


*Figure S47: 125 MHz ^{13}C NMR in $CDCl_3$ of molecule **Ox-Te-CF$_3$**. Due to ^{13}C-^{19}F coupling: Peak 166.3 splits into 166.75, 166.42, 166.09 and 165.75; Peak 123.5 splits into 126.80, 124.62, 122.44 and 120.25.*

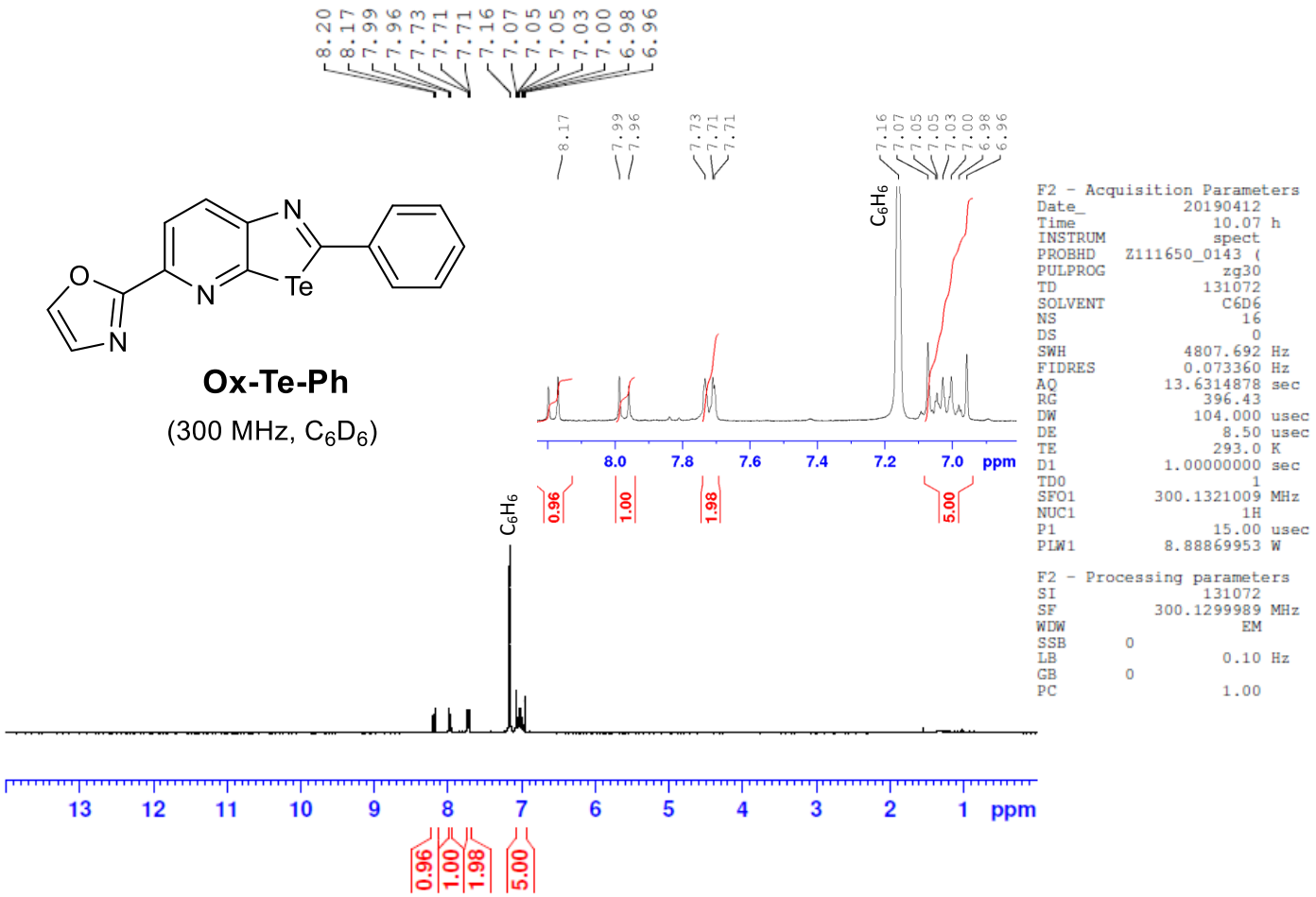


Figure S48: 300 MHz ^{1}H NMR in C_6D_6 of molecule ***Ox-Te-Ph***.

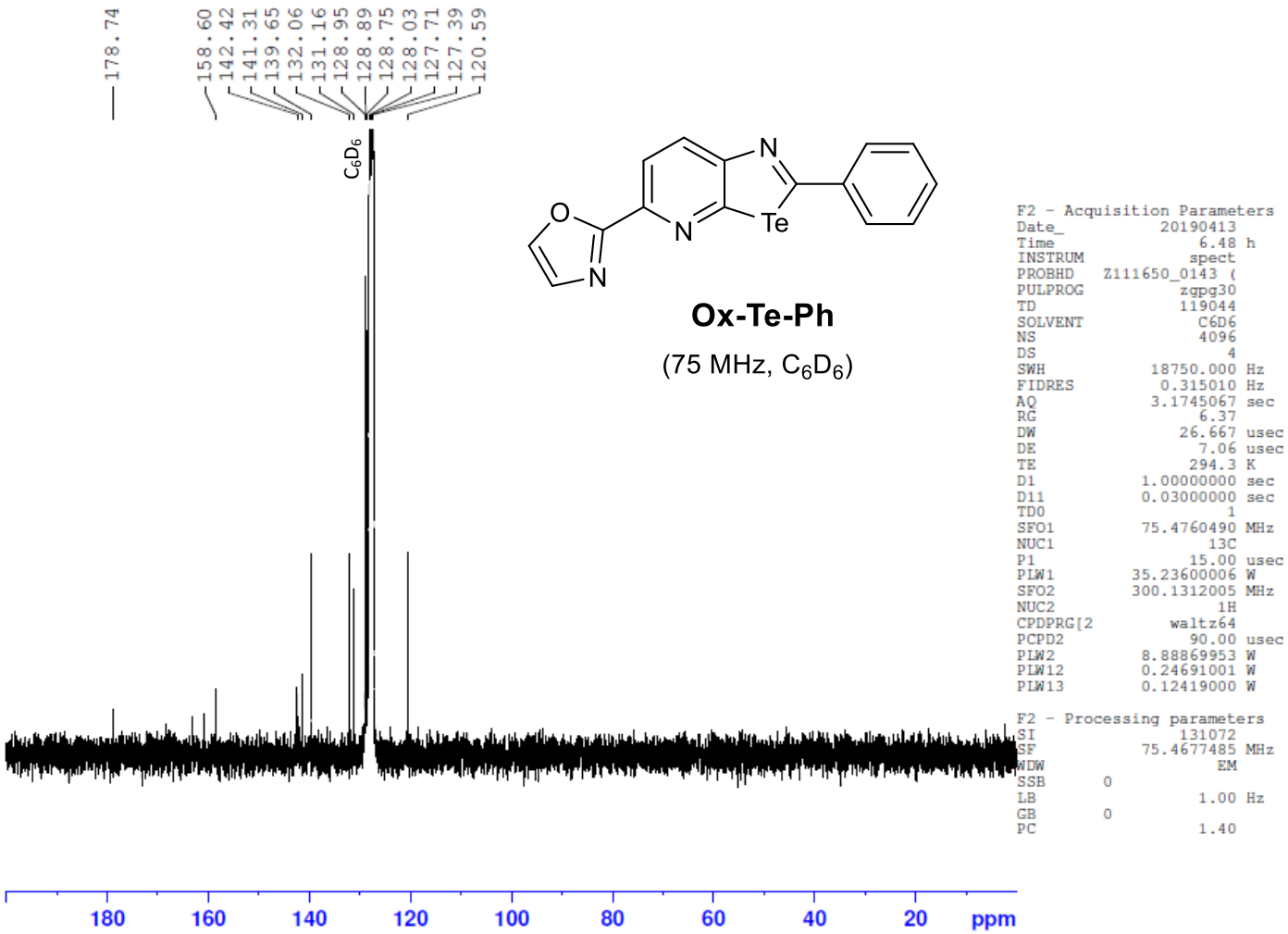
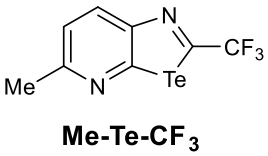
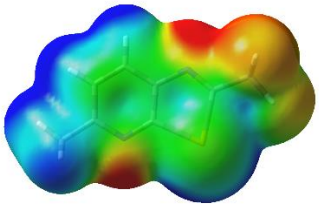
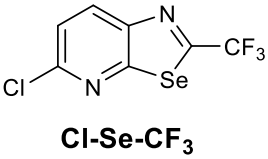
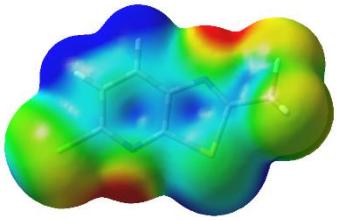


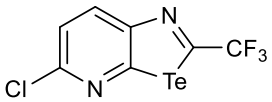
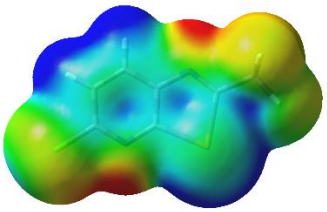
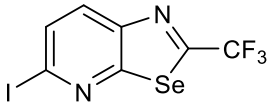
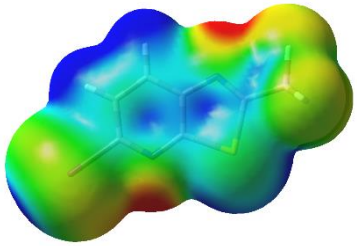
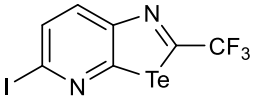
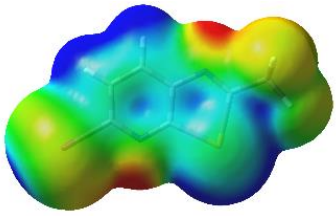
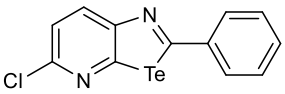
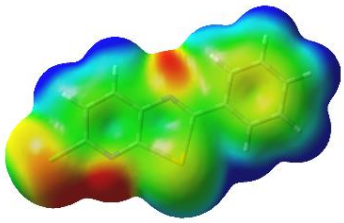
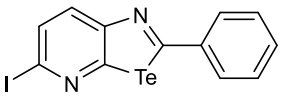
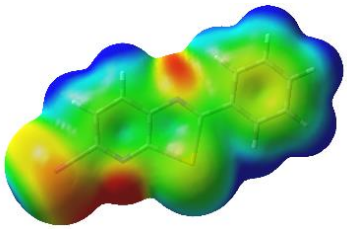
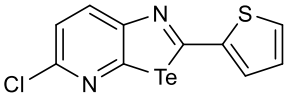
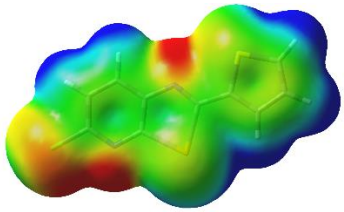
Figure S49: 75 MHz ^{13}C NMR in C_6D_6 of molecule ***Ox-Te-Ph***.

4. Calculations

Calculations were carried out using Gaussian 09 including the D01 revision.[8] Geometries optimizations were firstly carried out at B97-D3/LanL2DZ level of theory and frontier orbitals were obtained at the same level.[9] Then structures were optimized again at B97-D3/Def2-TZVP level of theory and electrostatic surface potential were created at the same level.[10] ESP surfaces were mapped on the van der Waals surface of molecules up to an electron density of 0.001 electron.bohr^{-3}. $V_{s,max}$ were determined with a classical method.[11] Frontier orbitals images were obtained using the Avogadro software and ESP figures with Gaussview4.

*Table S1: Representation of selected molecules **Me-Te-CF$_3$**, **X-E-CF$_3$** and **X-Te-R** and their respective ESP map with their associated $V_{s,max}$ values (expressed in kcal mol^{-1}) for N_p, N_c, σ hole [α] of the Te atom and σ hole of the halogen if applicable.*

Compound	ESP map	$V_{s,max}$ N_p	$V_{s,max}$ N_c	σ hole (α)	σ hole halogen
 **Me-Te-CF$_3$**		-21.6	-23.2	+17.6	-
 **Cl-Se-CF$_3$**		-21.9	-20.8	+15.0	+10.1

 **Cl-Te-CF$_3$**		-21.9	-19.6	+21.9	+9.5
 **I-Se-CF$_3$**		-20.1	-19.6	+14.6	+20.5
 **I-Te-CF$_3$**		-20.1	-19.4	+22.3	+19.1
 **Cl-Te-Ph**		-28.8	-14.1	+10.5	+13.8
 **I-Te-Ph**		-26.3	-13.8	+11.0	+13.9
 **Cl-Te-Th**		-28.5	-18.8	+12.5	+3.8

5. Crystal data and structure refinement

*Table S2: Crystal data and structure refinement for **Me-Te-CF$_3$** (1954271).*

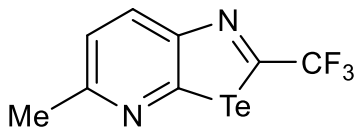
	Crystal data	 **Me-Te-CF$_3$**
Empirical formula	$C_8 H_5 F_3 N_2 Te$	
Formula weight	313.74	
Crystal system	Monoclinic	
Space group	P 2_1/m	
Unit cell dimensions	a = 6.2430(5) Å	α = 90°.
	b = 7.0585(7) Å	β = 97.461(7)°.
	c = 10.5317(8) Å	γ = 90°.
Volume	460.16(7) Å^3	
Z	2	
Density (calculated)	2.264 Mg/m^3	
Absorption coefficient	3.237 mm^{-1}	
F(000)	292	
Crystal size	0.241 x 0.118 x 0.033 mm^3	
	Data collection	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Theta range for data collection	3.484 to 29.493°.	
Index ranges	-8<=h<=5, -9<=k<=8, -14<=l<=12	
Reflections collected	2129	
Independent reflections	1163 [R(int) = 0.0242]	
Completeness to theta = 25.242°	99.8 %	
	Refinement	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.825	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1163 / 0 / 82	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0294, wR2 = 0.0599	
R indices (all data)	R1 = 0.0328, wR2 = 0.0635	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.666 and -0.981 e.Å^{-3}	

*Table S3: Crystal data and structure refinement for **Cl-Se-CF$_3$** (2015557).*

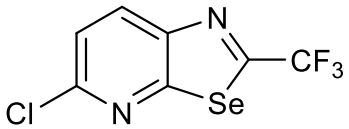
	Crystal data	
Empirical formula	$C_7 H_2 Cl F_3 N_2 Se$	
Formula weight	285.52	
Crystal system	Monoclinic	
Space group	P 2_1/m	**Cl-Se-CF$_3$**
Unit cell dimensions	a = 6.1459(5) Å	a = 90°.
	b = 6.8360(8) Å	b = 95.864(7)°.
	c = 10.3772(8) Å	γ = 90°.
Volume	433.70(7) Å^3	
Z	2	
Density (calculated)	2.186 Mg/m^3	
Absorption coefficient	4.641 mm^{-1}	
F(000)	272	
Crystal size	0.270 x 0.107 x 0.063 mm^3	
	Data collection	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Theta range for data collection	3.575 to 29.703°.	
Index ranges	-8<=h<=6, -9<=k<=8, -7<=l<=13	
Reflections collected	2140	
Independent reflections	1123 [R(int) = 0.0272]	
Completeness to theta = 25.242°	99.8 %	
	Refinement	
Absorption correction	Gaussian	
Max. and min. transmission	0.889 and 0.428	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1123 / 0 / 82	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	R1 = 0.0395, wR2 = 0.1002	
R indices (all data)	R1 = 0.0513, wR2 = 0.1063	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.912 and -0.547 e.Å^{-3}	

*Table S4: Crystal data and structure refinement for **Cl-Te-CF$_3$** (1954275).*

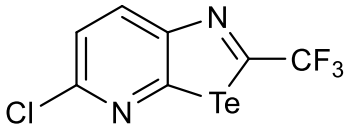
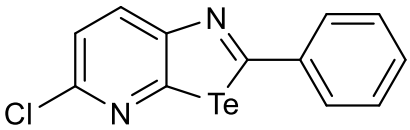
	Crystal data	
Empirical formula	$C_7 H_2 Cl F_3 N_2 Te$	
Formula weight	334.16	
Crystal system	Monoclinic	
Space group	P 2_1/m	**Cl-Te-CF$_3$**
Unit cell dimensions	a = 6.1992(4) Å	α = 90°.
	b = 6.9684(6) Å	β = 95.722(7)°.
	c = 10.4885(9) Å	γ = 90°.
Volume	450.83(6) Å^3	
Z	2	
Density (calculated)	2.462 Mg/m^3	
Absorption coefficient	3.599 mm^{-1}	
F(000)	308	
Crystal size	0.124 x 0.092 x 0.050 mm^3	
	Data collection	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Theta range for data collection	3.303 to 29.580°.	
Index ranges	-8<=h<=8, -9<=k<=9, -13<=l<=13	
Reflections collected	4037	
Independent reflections	1229 [R(int) = 0.0371]	
Completeness to theta = 25.242°	99.9 %	
	Refinement	
Absorption correction	Gaussian	
Max. and min. transmission	0.840 and 0.595	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1229 / 430 / 150	
Goodness-of-fit on F^2	1.113	
Final R indices [I>2sigma(I)]	R1 = 0.0309, wR2 = 0.0483	
R indices (all data)	R1 = 0.0427, wR2 = 0.0532	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.728 and -0.806 e.Å^{-3}	

*Table S5: Crystal data and structure refinement for **Cl-Te-Ph** (1954273).*



Cl-Te-Ph

	Crystal data	
Empirical formula	C_{12} H_7 Cl N_2 Te	
Formula weight	342.25	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 12.4328(6) Å	α = 90°.
	b = 8.4466(5) Å	β = 90°.
	c = 21.1948(16) Å	γ = 90°.
Volume	2225.8(2) $Å^3$	
Z	8	
Density (calculated)	2.043 Mg/m^3	
Absorption coefficient	2.882 mm^{-1}	
F(000)	1296	
Crystal size	0.439 x 0.049 x 0.044 mm^3	
	Data collection	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Theta range for data collection	3.493 to 29.648°.	
Index ranges	-17<=h<=11, -11<=k<=9, -28<=l<=19	
Reflections collected	7941	
Independent reflections	2620 [R(int) = 0.0312]	
Completeness to theta = 25.242°	97.2 %	
	Refinement	
Absorption correction	multi-scan	
Max. and min. transmission	1.00000 and 0.66818	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2620 / 0 / 145	
Goodness-of-fit on F^2	1.091	
Final R indices [I>2sigma(I)]	R1 = 0.0290, wR2 = 0.0558	
R indices (all data)	R1 = 0.0459, wR2 = 0.0664	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.067 and -0.953 e.$Å^{-3}$	

*Table S6: Crystal data and structure refinement for **Cl-Te-Th** (1954278).*

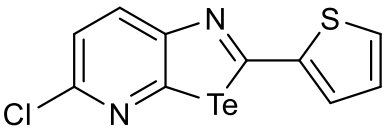
	Crystal data	
Empirical formula	C_{10} H_5 Cl N_2 S Te	
Formula weight	348.27	
Crystal system	Monoclinic	**Cl-Te-Th**
Space group	P $2_1/c$	
Unit cell dimensions	a = 11.0278(5) Å	α = 90°.
	b = 18.0069(8) Å	β = 104.168(5)°.
	c = 11.1423(5) Å	γ = 90°.
Volume	2145.30(17) $Å^3$	
Z	8	
Density (calculated)	2.157 Mg/m^3	
Absorption coefficient	3.180 mm^{-1}	
F(000)	1312	
Crystal size	0.333 x 0.255 x 0.178 mm^3	
	Data collection	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Theta range for data collection	3.751 to 29.792°.	
Index ranges	-13<=h<=15, -18<=k<=24, -15<=l<=10	
Reflections collected	10688	
Independent reflections	5177 [R(int) = 0.0278]	
Completeness to theta = 25.242°	99.8 %	
	Refinement	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.758	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5177 / 0 / 271	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0319, wR2 = 0.0554	
R indices (all data)	R1 = 0.0475, wR2 = 0.0646	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.701 and -0.710 $e.Å^{-3}$	

*Table S7: Crystal data and structure refinement for **I-Se-CF$_3$** (2015556).*

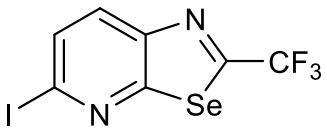
	Crystal data	
Empirical formula	$C_7 H_2 F_3 I N_2 Se$	
Formula weight	376.97	
Crystal system	Orthorhombic	
Space group	C m c a	**I-Se-CF$_3$**
Unit cell dimensions	a = 7.2272(6) Å	a = 90°.
	b = 6.2016(5) Å	b = 90°.
	c = 43.222(2) Å	γ = 90°.
Volume	1937.2(2) Å^3	
Z	8	
Density (calculated)	2.585 Mg/m^3	
Absorption coefficient	30.424 mm^{-1}	
F(000)	1376	
Crystal size	0.184 x 0.090 x 0.040 mm^3	
	Data collection	
Temperature	298(2) K	
Wavelength	1.54184 Å	
Theta range for data collection	4.091 to 72.689°.	
Index ranges	-4<=h<=8, -7<=k<=7, -52<=l<=53	
Reflections collected	5798	
Independent reflections	1032 [R(int) = 0.0396]	
Completeness to theta = 67.684°	99.9 %	
	Refinement	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.591	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1032 / 0 / 83	
Goodness-of-fit on F^2	1.213	
Final R indices [I>2sigma(I)]	R1 = 0.0680, wR2 = 0.1970	
R indices (all data)	R1 = 0.0728, wR2 = 0.2033	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.572 and -1.156 e.Å^{-3}	

*Table S8: Crystal data and structure refinement for **I-Te-CF$_3$** (1954276).*

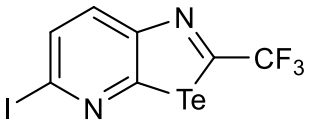
	Crystal data	
Empirical formula	$C_7 H_2 F_3 I N_2 Te$	
Formula weight	425.61	
Crystal system	Monoclinic	
Space group	C 2/c	**I-Te-CF$_3$**
Unit cell dimensions	a = 19.4935(10) Å	α = 90°.
	b = 4.5147(4) Å	β = 98.020(6)°.
	c = 22.524(2) Å	γ = 90°.
Volume	1962.9(3) Å^3	
Z	8	
Density (calculated)	2.880 Mg/m^3	
Absorption coefficient	6.181 mm^{-1}	
F(000)	1520	
Crystal size	0.192 x 0.091 x 0.066 mm^3	
	Data collection	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Theta range for data collection	3.654 to 29.465°.	
Index ranges	-26<=h<=16, -6<=k<=4, -31<=l<=29	
Reflections collected	4346	
Independent reflections	2313 [R(int) = 0.0220]	
Completeness to theta = 25.242°	99.8 %	
	Refinement	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.938	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2313 / 0 / 127	
Goodness-of-fit on F2	1.148	
Final R indices [I>2sigma(I)]	R1 = 0.0421, wR2 = 0.0930	
R indices (all data)	R1 = 0.0539, wR2 = 0.1020	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.188 and -1.443 e.Å^{-3}	

*Table S9: Crystal data and structure refinement for **I-Te-Ph** (1954274).*

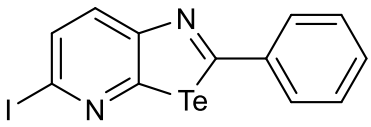
	Crystal data	
Empirical formula	C_{12} H_7 I N_2 Te	
Formula weight	433.70	
Crystal system	Monoclinic	**I-Te-Ph**
Space group	P $2_1/c$	
Unit cell dimensions	a = 12.5510(6) Å	α = 90°.
	b = 8.2204(5) Å	β = 104.881(6)°.
	c = 23.8900(14) Å	γ = 90°.
Volume	2382.2(2) $Å^3$	
Z	8	
Density (calculated)	2.419 Mg/m^3	
Absorption coefficient	5.061 mm^{-1}	
F(000)	1584	
Crystal size	0.599 x 0.060 x 0.036 mm^3	
	Data collection	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Theta range for data collection	3.359 to 29.660°.	
Index ranges	-17<=h<=17, -10<=k<=10, -32<=l<=33	
Reflections collected	13008	
Independent reflections	5678 [R(int) = 0.0380]	
Completeness to theta = 25.242°	99.7 %	
	Refinement	
Absorption correction	Gaussian	
Max. and min. transmission	0.840 and 0.595	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5678 / 0 / 289	
Goodness-of-fit on F2	1.072	
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.0794	
R indices (all data)	R1 = 0.0604, wR2 = 0.0940	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.083 and -1.355 e.$Å^{-3}$	

*Table S10: Crystal data and structure refinement for **Ox-Se-CF$_3$** (2015558).*

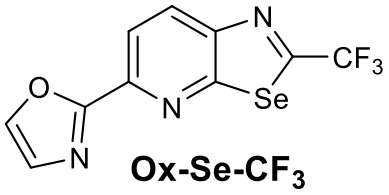
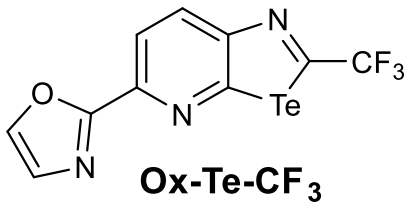
	Crystal data	 **Ox-Se-CF$_3$**
Empirical formula	C_{10} H_4 F_3 N_3 O Se	
Formula weight	318.12	
Crystal system	Monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 6.2405(3) Å	a = 90°.
	b = 25.298(3) Å	b = 91.703(5)°.
	c = 6.7009(7) Å	γ = 90°.
Volume	1057.42(16) Å^3	
Z	4	
Density (calculated)	1.998 Mg/m^3	
Absorption coefficient	3.584 mm^{-1}	
F(000)	616	
Crystal size	0.314 x 0.191 x 0.072 mm^3	
	Data collection	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Theta range for data collection	3.364 to 29.721°.	
Index ranges	-8<=h<=8, -34<=k<=34, -6<=l<=8	
Reflections collected	7842	
Independent reflections	7842 [R(int) = ?]	
Completeness to theta = 25.242°	99.8 %	
	Refinement	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.371	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7842 / 0 / 163	
Goodness-of-fit on F^2	0.869	
Final R indices [I>2sigma(I)]	R1 = 0.0385, wR2 = 0.0823	
R indices (all data)	R1 = 0.0726, wR2 = 0.0874	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.886 and -0.501 e.Å^{-3}	

*Table S11: Crystal data and structure refinement for **Ox-Te-CF$_3$** (1954277).*

	Crystal data
Empirical formula	C_{10} H_4 F_3 N_3 O Te
Formula weight	366.76
Crystal system	Orthorhombic
Space group	P n m a
Unit cell dimensions	a = 26.0295(14) Å α = 90°.
	b = 6.6541(5) Å β = 90°.
	c = 6.2290(3) Å γ = 90°.
Volume	1078.88(11) Å^3
Z	4
Density (calculated)	2.258 Mg/m^3
Absorption coefficient	2.789 mm^{-1}
F(000)	688
Crystal size	0.233 x 0.046 x 0.039 mm^3
	Data collection
Temperature	150(2) K
Wavelength	0.71073 Å
Theta range for data collection	3.363 to 29.727°.
Index ranges	-34<=h<=35, -6<=k<=8, -6<=l<=8
Reflections collected	4463
Independent reflections	1452 [R(int) = 0.0408]
Completeness to theta = 25.242°	99.8 %
	Refinement
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.47820
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1452 / 0 / 106
Goodness-of-fit on F^2	1.106
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.0755
R indices (all data)	R1 = 0.0521, wR2 = 0.0856
Extinction coefficient	n/a
Largest diff. peak and hole	0.894 and -0.878 e.Å^{-3}



Ox-Te-CF$_3$

6. References

[1] A. T. CrysAlisPro, Version 1.171.37.33 (release 27-03-2014 CrysAlis171 .NET).

[2] G. M. Sheldrick, *SHELX-2013: Program for the Solution of Crystal Structures, University of Göttingen* **2013**.

[3] W. Lin, L. Chen, P. Knochel, *Tetrahedron* **2007**, *63*, 2787-2797.

[4] H.-S. Lin, L. A. Paquette, *Synth. Commun.* **1994**, *24*, 2503-2506.

[5] A. D. Dunn, A. Currie, L. E. Hayes, *J. Prakt. Chem.* **1989**, *331*, 369-374.

[6] A. C. Bissember, M. G. Banwell, *J. Org. Chem.* **2009**, *74*, 4893-4895.

[7] G. Piersanti, L. Giorgi, F. Bartoccini, G. Tarzia, P. Minetti, G. Gallo, F. Giorgi, M. Castorina, O. Ghirardi, P. Carminati, *Org. Biomol. Chem.* **2007**, *5*, 2567-2571.

[8] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian, Inc., Wallingford, CT*.

[9] a) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465; b) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270-283; c) A. F. Cozzolino, I. Vargas-Baca, S. Mansour, A. H. Mahmoudkhani, *J. Am. Chem. Soc.* **2005**, *127*, 3184-3190.

[10] a) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305; b) G. E. Garrett, G. L. Gibson, R. N. Straus, D. S. Seferos, M. S. Taylor, *J. Am. Chem. Soc.* **2015**, *137*, 4126-4133.

[11] P. Politzer, J. S. Murray, T. Clark, *Phys. Chem. Chem. Phys.* **2013**, *15*, 11178-11189.