Therapeutic targeting of SETD2-deficient cancer cells with the small-molecule compound RITA

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Supplementary information

Synthesis of Compounds -General Experimental information:

Unless otherwise noted, all solvents and reagents were commercially available and used without further purification. Where specified, solvents were degassed by passing a stream of nitrogen or argon through the solvent while subjecting it to sonication for a minimum of 15 minutes. Compounds should be stored at −20 °C at a minimum due to their instability and should not be stored for long periods. When removing solvent via rotary evaporation it is recommended to keep the temperature of the water bath <40 °C if possible.

NMR spectra were recorded on a Bruker AVIIIHD 400 Nanobay (400 MHz) NMR spectrometer, equipped with a 5 mm z-gradient multinuclear BBFO probe using the software TopSpin (version 3, Bruker BioSpin); a Bruker Avance NEO Nanobay 400 MHz NMR spectrometer, equipped with a 5 mm z-gradient broadband multinuclear SMART probe using the software TopSpin (version 4, Bruker BioSpin); a Bruker AVIII HD 500 MHz NMR spectrometer, equipped with a 5 mm z-gradient broadband X–^{19}F/^{1}H BBFO SMART probe using the software TopSpin (version 3, Bruker BioSpin) or a Bruker Avance NEO (600 MHz) NMR spectrometer, equipped with a 5 mm BB-F/^{1}H helium-cooled cryoprobe using the software TopSpin (version 4, Bruker BioSpin). Chemical shifts (in parts per million (ppm)) were determined relative to an internal deuterium lock NMR solvent as specified using the solvent peak provided by Fulmer *et al.*[16] The multiplicity of each signal is indicated by: s (singlet); br s (broad singlet); d (doublet); t (triplet); q (quartet); qn (quintet), dd (doublet of doublets); or m (multiplet). Coupling constants (*J*) are quoted in Hz and are recorded to the nearest 0.1 Hz. Identical proton coupling constants (*J*) are averaged in each spectrum and reported to the nearest 0.1 Hz and were determined by analysis using Bruker TopSpin v4.5.0 software and/or MestReNova v14.1.0 software.

High-resolution mass spectra were acquired on a Bruker MicroTOF spectrometer from solutions of methanol, water or acetonitrile (ESI) filtered through a 0.2 μM, 13 mm nylon syringe filter. For compounds that did not ionise well, flow injection analysis was performed on

an ACQUITY UPLC System (Waters, Milford, MA, USA) coupled to an Exactive Orbitrap mass spectrometer (Thermo Scientific, San Jose, CA, USA) equipped with an APCI probe in positive ion mode. The flow rate was set to 0.200 mL/min using a 90% methanol$_{(aq)}$ + 0.1% formic acid eluent. ESI Source parameters: sheath gas flow rate, 20; aux gas flow rate, 0; sweep gas flow rate, 0; discharge current, 5.00 mA; capillary temperature, 250 °C; capillary voltage, 30.00 V; tube lens voltage, 110.00 V; skimmer voltage, 20.00 V; and vaporizer temperature, 250 °C. MS scan parameters: microscans, 1; resolution, high; AGC target, ultimate mass accuracy; maximum IT, 50 ms; and scan range, 80-1600 *m/z*. Low-resolution mass spectra were recorded on a Waters LCT Premier spectrometer or Agilent 6120 Quadrupole LC/MS spectrometer (ESI). *m/z* values are reported in Daltons and followed by their percentage abundance in parentheses. Where low resolution mass spectrometry is not reported, the corresponding $[M+H]^+$ peak or equivalent adduct could not be found by ESI+ and was taken directly to HRMS.

IR spectra were obtained from a solid or thin film from $CHCl_3$ using a diamond ATR module as indicated. The spectra were recorded on either a Bruker Tensor 27 spectrometer or a Perkin Elmer Two FTIR spectrometer. Absorption maxima are reported in wavenumbers (cm^{-1}) for major peaks only.

Melting points were determined using either a Gallenkamp melting point apparatus or an Electrothermal IA9100X1 and are uncorrected.

Normal phase silica gel flash column chromatography was performed manually using Geduran Silica gel 60 (40-63 μm) under a positive pressure of compressed nitrogen. Analytical thin layer chromatography (TLC) was carried out on Merck silica gel 60 F^{254} aluminium-supported thin layer chromatography sheets. Visualisation was by absorption of UV light at 254 nm or 365 nm, or thermal development after dipping in an aqueous solution of potassium permanganate, potassium carbonate and sodium hydroxide.

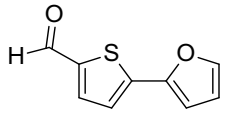
Analytical HPLC was carried out on a PerkinElmer Flexar system with a Binary LC Pump and UV/VIS LC Detector. For determination of compound purity, a Dionex Acclaim® 120 column (C18, 5 μm, 120 Å, 4.6 × 150 mm) was employed, with a 10 minute gradient of 95% H_2O +0.1% TFA (Solvent A) to 95% MeCN +0.1% TFA (Solvent B), flow rate 1.5 mL/min and detection at 254 nm (unless stated otherwise). Samples were injected (10 μL or as indicated) in acetonitrile, isopropanol or methanol or as DMSO solutions in these solvents. The gradient used is as described below and has a 5 minute hold at 95% solvent A after the run to return to equilibrium conditions:

Elapsed time (min)	% Solvent A	% Solvent B
1	95	5
11	5	95
14	5	95
15	95	5

The following abbreviations are used: brine (refers to a saturated aqueous solution of sodium chloride); eq. (equivalents); MeCN (acetonitrile); PE (Petroleum ether boiling fraction between 40-60 °C); TFA (trifluoroacetic acid); DMF (dimethylformamide); XPhos (2-dicyclohexylphosphino-2′,4′,6′- triisopropylbiphenyl) and NBS (*N*-bromosuccinimide).

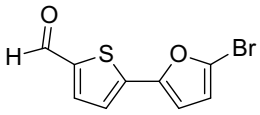
Synthesis of compounds:

5-(Furan-2-yl)thiophene-2-carbaldehyde (RV-1)



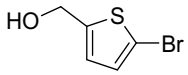
5-(Furan-2-yl)thiophene-2-carbaldehyde was prepared as per Lin *et al.*[2] 5-Bromo-2-thiophenecarboxaldehyde (1.0 g, 5.2 mmol, 1.0 eq.) was combined with XPhos (50 mg, 0.10 mmol, 0.02 eq.), $Pd(OAc)_2$ (12 mg, 0.05 mmol, 0.01 eq.) and K_2CO_3 (2.2 g, 15.7 mmol, 3 eq.) in degassed MeCN/H_2O (1.5:1, 25 mL) under an argon environment. After 5 mins, 2-furanylboronic acid (0.88 g, 7.85 mmol, 1.5 eq.) was added and the reaction was left to stir under argon for 28 h at rt. Once complete, the solvent was reduced *in vacuo* and the residue extracted in CH_2Cl_2 (3×30 mL). The organic layers were collected, washed with brine (100 mL), dried (Na_2SO_4) and the solvent removed *in vacuo*. The residue was purified using silica gel flash column chromatography (1:1 to 3:2, CH_2Cl_2:hexane) to give the title compound as a golden/dark brown oil that solidified on standing (0.57 g, 61%). mp 39-40 °C (from hexane) [38 °C,[18] 39-40 °C[19]]. R_f = 0.19 (CH_2Cl_2:hexane, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.88 (s, 1H), 7.69 (d, *J* = 4.0 Hz, 1H), 7.51-7.48 (m, 1H,), 7.32 (d, *J* = 4.0 Hz, 1H), 6.76-6.73 (m, 1H), 6.51 (dd, *J* = 3.4, 1.8 Hz, 1H). LRMS (ESI+) *m/z* 179.0 $[M + H]^+$ (100%). HPLC retention time (no TFA) (9.16 mins, purity >99%). ^{1}H NMR data are in agreement with reported literature.[2]

5-(5-Bromofuran-2-yl)thiophene-2-carbaldehyde (**RV-2**)



5-(5-Bromofuran-2-yl)thiophene-2-carbaldehyde (RV-2) was prepared as per Lin *et al.* with minor modifications.[2] 5-(Furan-2-yl)thiophene-2-carbaldehyde (RV-1, 0.50 g, 2.81 mmol, 1 eq.) was combined with dibenzoyl peroxide (10 mg, 0.042 mmol, 0.015 eq.) in toluene (10 mL) and cooled to −15 °C before NBS (0.5 g, 2.81 mmol, 1 eq.) was added portion wise over 30 mins in the dark. After 3.5 h, the solvent was removed *in vacuo* and the residue purified using silica gel flash column chromatography (1:1 hexane:CH_2Cl_2 to 100% CH_2Cl_2) to give the title compound as a dark yellow/brown powder (0.438 g, 61%). mp 124-126 °C (CH_2Cl_2) [literature 137-139 °C][2]. R_f = 0.26 (Hexane:CH_2Cl_2, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.88 (s, 1H), 7.68 (d, *J* = 4.0 Hz, 1H), 7.31 (d, *J* = 4.0 Hz, 1H), 6.68 (d, *J* = 3.5 Hz, 1H), 6.43 (d, *J* = 3.5 Hz, 1H). LRMS (ESI+) *m/z* 259 [M+H, ^{81}Br]$^+$ (100%), 257 [M + H, ^{79}Br]$^+$ (95%). HPLC retention time (10.31 mins, purity >97%). ^{1}H NMR data is in agreement with reported literature values.[2]

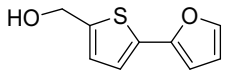
(5-Bromothien-2-yl)methanol (RV-3)



(5-Bromothien-2-yl)methanol (**RV-3**) was prepared using a modified literature procedure for related substrates.[2] 5-Bromothiophene-2-carbaldehyde (0.124 mL, 0.2 g, 1.05 mmol, 1 eq.) was dissolved in MeOH:CH_2Cl_2 (1:1, 6 mL) and the reaction cooled to 0 °C before $NaBH_4$ (19 mg, 0.5 mmol, 0.5 eq.) was added portion wise. The reaction mixture was allowed to stir at 0 °C for 30 mins. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed with H_2O (20 mL), which was added slowly. The layers were separated and the CH_2Cl_2 layer washed with HCl (aq. 1 M, 2×20 mL). The organic layer was separated and the solvent was removed *in vacuo* when it was determined that the reaction had not gone to completion. The residue was diluted in MeOH:CH_2Cl_2 (1:1, 6 mL) and the reaction cooled to 0 °C before a second portion of $NaBH_4$ (19 mg, 0.5 mmol, 0.5 eq.) was added portion wise. The reaction mixture was allowed to warm to room temperature and then to stir for 4 h. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed with HCl (aq. 1 M, 20 mL) which was added slowly. The layers were separated and the CH_2Cl_2 layer washed a further 1× with HCl (aq. 1 M, 20 mL). The CH_2Cl_2 layer was separated, dried (Mg_2SO_4), filtered, and the solvent removed *in vacuo*. The residue was purified using silica gel flash column chromatography (100% PE to 60:40 PE:EtOAc) to give the title compound as an oil (14%, 27 mg). R_f 0.35 (60:40 PE/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.92 (d, *J* = 3.7 Hz, 2H), 6.76 (dt, *J* = 3.7, 0.9 Hz, 2H), 4.75 (apparent d, *J* = 5.9 Hz, 2H), 1.80 (t, *J* = 5.9 Hz, 1H). ^{13}C NMR (101 MHz,

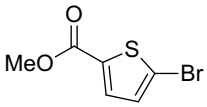
$CDCl_3$) δ_C 145.8, 129.7, 125.8, 112.4, 60.3. HPLC retention time (5.50 mins, purity >98%). NMR data are in agreement with reported literature values.[20,21]

5-(Furan-2-yl)thiophene-2-methanol (RV-27)



5-(Furan-2-yl)thiophene-2-carbaldehyde (**RV-1**, 500 mg, 2.81 mmol, 1 eq.) was dissolved in CH_2Cl_2 (3 mL) before MeOH (3 mL) was added and the mixture cooled to 0 °C. $NaBH_4$ (53 mg, 1.40 mmol, 0.5 eq.) was added portion wise and the reaction mixture stirred for a further 30 mins. The reaction was quenched by the addition of HCl (1 M, 20 mL) and CH_2Cl_2 (20 mL). The organic layer was separated and the aqueous layer washed with further CH_2Cl_2 (3×30 mL). The organic layers were combined, dried (Na_2SO_4), filtered, and the solvent was removed *in vacuo* to give a beige solid (0.455 g, 90%). mp undetermined, compound decomposed before melting as evidence by change in colour to black. R_f = 0.4 (EtOAc/Hexane 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.40 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.10 (d, *J* = 3.6 Hz, 1H), 6.92 (dt, *J* = 3.6, 0.8 Hz, 1H), 6.48 (dd, *J* = 3.4, 0.7 Hz, 1H), 6.43 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.87 – 4.72 (m, 2H), 2.05 (br t, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 149.4, 142.9, 141.9, 134.1, 126.2, 122.4, 111.8, 105.3, 60.2. HRMS (ESI+) *m/z* calculated for $C_9H_8O_2Na^{32}S$: 203.0143, found: 203.0144 $[M + Na]^+$, $|\Delta\ m/z|$ = 0.5 ppm. A significant peak was observed corresponding to $[M\text{-}H_2O+H]^+$: HRMS (ESI+) *m/z* calculated for $C_9H_7O^{32}S$: 163.0218, found: 163.0213 $[M\text{-}H_2O+H]^+$, $|\Delta\ m/z|$ = –3.1 ppm. ν_{max} (solid)/cm^{-1} 3233, 2928, 2869, 1504, 1362, 1213, 1148, 1013, 799, 728. HPLC retention time (8.17 mins, purity >99%).

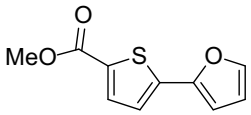
5-Bromo-2-thiophenecarboxylic acid methyl ester (RV-7)



5-Bromo-2-thiophenecarboxylic acid methyl ester was prepared as previously described by Kranich *et al*.[15] 5-Bromo-2-thiophenecarboxylic acid (1.5 g, 7.24 mmol, 1 eq.) was combined with H_2SO_4 (390 µL, 7.24 mmol, 1 eq.) in MeOH (11 mL) and the reaction mixture was stirred under reflux (85 °C) for 24 h, followed by 3 h at 90 °C. The solvent was removed *in vacuo* and EtOAc (50 mL) and saturated aqueous $NaHCO_3$ (50 mL) was added. The organic layer was separated and washed a further twice with saturated aqueous $NaHCO_3$ (2×50 mL). The combined saturated $NaHCO_3$ layers were washed with EtOAc (100 mL). The combined organic layers were washed with water (100 mL) followed by brine (100 mL), dried ($MgSO_4$),

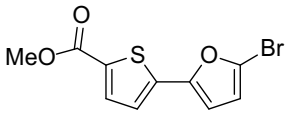
filtered, and the solvent removed *in vacuo* to give the title compound as a yellow oil that crystallised upon standing (1.34 g, 84%). mp. 61-62 °C from ethyl acetate [59-60 °C from hexane,[22] 56-57 °C,[23] 61-62 °C,[24]]. R_f = 0.73 (PE:EtOAc:acetic acid, 75:20:5). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.54 (d, J = 4.0 Hz, 1H), 7.06 (d, J = 4.0 Hz, 1H), 3.87 (s, 3H). ^{13}C (101 MHz, $CDCl_3$) δ_C 161.7, 134.8, 133.8, 131.0, 120.4, 52.5. HRMS (ESI+) *m/z* calculated for $C_6H_6O_2{}^{81}Br^{32}S$: 222.92459 (^{81}Br), found: 222.92458 [M + H, ^{81}Br]$^+$. Calculated for $C_6H_6O_2{}^{79}Br^{32}S$: 220.92664 (^{79}Br), found: 220.92661 [M + H, ^{79}Br]$^+$, |Δ *m/z*| = −0.15 ppm for ^{79}Br. HPLC retention time (9.72 mins, purity 100%). The ^{1}H NMR spectrum is in agreement with reported literature.[15,22,23]

5-Furan-2-yl-thiophene-2-carboxylic acid methyl ester (RV-8)



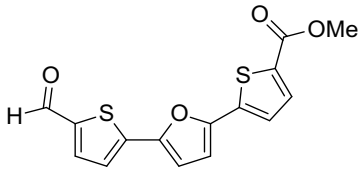
5-Furan-2-yl-thiophene-2-carboxylic acid methyl ester was prepared using a related literature procedure.[2] Methyl-5-bromothiophene-2-carboxylate (**RV-7**, 1 g, 4.5 mmol, 1 eq.) was combined with XPhos (91 mg, 0.19 mmol, 0.04 eq.), $Pd(OAc)_2$ (22 mg, 0.098 mmol, 0.02 eq.) and K_2CO_3 (2.0 g, 14.4 mmol, 3.2 eq.) in degassed MeCN:H_2O (1.5:1, 12.5 mL). After 5 mins, 2-furanylboronic acid (0.65 g, 5.8 mmol, 1.3 eq.) was added and the reaction mixture was left to stir for 26 h at room temperature. Once complete, the reaction mixture was filtered through Celite and washed with CH_2Cl_2 (30 mL) before H_2O (30 mL) was added. The aqueous layer was washed with CH_2Cl_2 (2×30 mL) and the organic layers were combined, dried ($MgSO_4$), filtered, and the solvent removed *in vacuo*. The residue was purified using silica gel flash column chromatography (95:5 PE:Et_2O). A second silica gel flash column was undertaken on the product using the same solvent system and relevant fractions combined to give 5-furan-2-yl-thiophene-2-carboxylic acid methyl ester as a dark orange/brown solid (0.35 g, 35%). mp 63-65 °C from PE:diethyl ether. R_f = 0.27 (95:5 PE:Et_2O).^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.71 (d, J = 4.0 Hz, 1H), 7.45 (dd, J = 1.8, 0.6 Hz, 1H), 7.21 (d, J = 4.0 Hz, 1H), 6.65 (dd, J = 3.4, 0.6 Hz, 1H), 6.48 (dd, J = 3.4, 1.8 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 162.8, 148.7, 143.0, 140.3, 134.3, 131.3, 122.7, 112.2, 107.5, 52.3. HRMS (ESI+) *m/z* calculated for $C_{10}H_9O_3{}^{32}S$: 209.02669, found: 209.02684, |Δ *m/z*| = 0.71 ppm. ν_{max} (solid)/cm^{-1} 2981, 2360, 2341, 1714, 1443, 1270. HPLC retention time (9.89 mins, purity 100%). Exceptions to the reported NMR data are found (^{1}H NMR shift and ^{13}C NMR data) but presence of carbonyl ^{13}C shift at 162.8 and 2D NMR data (not shown) supports the synthesis of compound **RV-8**.[25]

Methyl 5-(5-bromofuran-2-yl)thiophene-2-carboxylate (RV-9)



Methyl 5-(5-bromofuran-2-yl)thiophene-2-carboxylate was prepared using a related literature procedure.[2] 5-Furan-2-yl-thiophene-2-carboxylic acid methyl ester (**RV-8**) (0.32 g, 1.50 mmol, 1 eq.) was combined with dibenzoyl peroxide (5.5 mg, 0.02 mmol, 0.015 eq.) in toluene (10 mL) and cooled to −20 °C before NBS (0.27 g, 1.5 mmol, 1 eq.) was added portion wise over 30 mins in the dark. After allowing the reaction to stir at room temperature overnight, the solvent was removed under a stream of N_2 gas, and the residue purified using silica gel column chromatography (95:5 toluene:CH_2Cl_2) to give the title compound as yellow powder that decomposes over time (0.363 g, 84 %). mp 73-76 °C from toluene:CH_2Cl_2. R_f = 0.42 (97:3 toluene:CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.70 (d, *J* = 4.0 Hz, 1H), 7.19 (d, *J* = 4.0 Hz, 1H), 6.59 (d, *J* = 3.5 Hz, 1H), 6.40 (d, *J* = 3.5 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 162.7, 150.5, 138.9, 134.2, 131.7, 123.0, 122.9, 113.9, 109.7, 52.4. HRMS (APCI+) *m/z* calculated for $C_{10}H_8{}^{81}BrO_3{}^{32}S$: 288.93516 (^{81}Br), found 288.93489 [M+H$^+$, ^{81}Br]. *m/z* calculated for $C_{10}H_8{}^{79}BrO_3{}^{32}S$: 286.93720 (^{79}Br), found 286.93710 [M+H$^+$, ^{79}Br], |Δ *m/z*| = −0.35 ppm for ^{79}Br. ν_{max} (solid)/cm^{-1} 2981, 2360, 1722, 1251. HPLC retention time (11.49 mins, purity >95%).

Methyl 5-[5-(5-formylthiophen-2-yl)furan-2-yl]thiophene-2-carboxylate (RV-11)

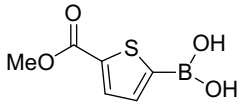


Methyl 5-[5-(5-formylthiophen-2-yl)furan-2-yl]thiophene-2-carboxylate was prepared using a related literature procedure.[2] Methyl 5-(5-bromofuran-2-yl)thiophene-2-carboxylate (**RV-9**, 100 mg, 0.35 mmol, 1 eq.) was combined with XPhos (6.7 mg, 0.014 mmol, 0.04 eq.), $Pd(OAc)_2$ (1.57 mg, 0.007 mmol, 0.02 eq.) and K_2CO_3 (145 mg, 1.05 mmol, 3 eq.) in degassed MeCN:H_2O (1.5:1, 5 mL). After 5 mins, 5-formylthiophene-2-boronic acid (81 mg, 0.52 mmol, 1.5 eq.) was added and the reaction mixture was left to stir for 18.5 h at room temperature. The reaction mixture was filtered through Celite and washed with CH_2Cl_2 (30 mL) before H_2O (30 mL) was added. The layers were separated and the aqueous layer was washed with further CH_2Cl_2 (2×30 mL). The organic layers were combined, washed with H_2O (100 mL), then brine (100 mL) before they were dried ($MgSO_4$), filtered, and the solvent removed *in vacuo*. The residue was purified using silica gel flash column chromatography (100% PE to

4:1 PE:Et_2O) to give a bright yellow solid. Due to the presence of ^{1}H/silicon grease (Fulmer *et al.*),[16] the product was dissolved in CH_2Cl_2 (20 mL) and washed several times with hexane and the product reisolated as a yellow powder (0.025 g, 22%) with minor ^{1}H/silicon grease impurities in the aliphatic region. mp. 118-120 °C from CH_2Cl_2. R_f = 0.58 (2:3 EtOAc:PE), 0.09 (4:1 PE:Et_2O). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.90 (s, 1H), 7.74 (d, *J* = 4.0 Hz, 2H), 7.71 (d, *J* = 4.0 Hz, 1H) 7.40 (d, *J* = 4.0 Hz, 1H), 7.31 (d, *J* = 4.0 Hz, 1H), 6.82 (d, *J* = 3.6 Hz, 2H), 6.74 (d, *J* = 3.6 Hz), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 182.7, 162.6, 149.5, 148.5, 142.2, 141.8, 138.9, 137.2, 134.3, 123.8, 123.7, 111.2, 110.0, 52.5. HRMS (APCI+) *m/z* calculated for $C_{15}H_{11}O_4{}^{32}S_2$: 319.00933, found 319.00890 $[M+H]^+$, $|\Delta\ m/z|$ = −1.3 ppm. ν_{max} (thin film)/cm^{-1} 2361, 2341, 1733, 1654, 1443. HPLC retention time (11.21 mins, purity >95%).

COSY, HSQC and HMBC correlations allowed full characterisation of thiophene, ester, and aldehyde protons and their corresponding ^{13}C chemical shifts. Due to strong ^2J and ^3J couplings (HMBC) that were close in ppm shift, full characterisation for the central furan ring and quaternary carbons was not obtained due to relatively high symmetry of the central molecule.

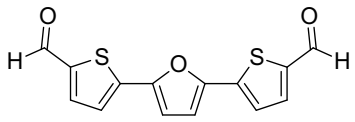
5-(Methoxycarbonyl)thiophen-2-ylboronic acid (RV-10)



5-(Methoxycarbonyl)thiophen-2-ylboronic acid was prepared using a related literature procedure for 5-bromo-2-thiophenecarboxylic acid methyl ester **(RV-7)**.[15] 5-Di(hydroxybenzyl)-2-thiophenecarboxylic acid (1 g, 5.8 mmol, 1 eq.) was combined with H_2SO_4 (312 µL, 5.8 mmol, 1 eq.) in MeOH (9 mL) and the reaction mixture was stirred at 70 °C overnight. The solvent was removed *in vacuo* and the residue dissolved in EtOAc (30 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (3×30 mL). The organic layer was then washed with water (100 mL), then brine (100 mL). The organic layer was dried ($MgSO_4$), filtered, and the solvent removed *in vacuo* to give the title compound as a pale orange solid (0.20 g, 19%). mp 196-200°C from ethyl acetate. R_f = 0.59 (EtOAc+0.1% acetic acid). ^{1}H NMR (400 MHz, D_6-DMSO) δ_H 8.54 (s, 2H), 7.80 (d, *J* = 3.7 Hz, 1H), 7.67 (d, *J* = 3.7 Hz, 1H), 3.82 (s, 3H). ^{11}B NMR{1H} (128.4 MHz, D_6-DMSO) δ_B 25.82. ^{13}C NMR (101 MHz, D_6-DMSO) δ_C 162.0, 143.9, 137.3, 136.3, 134.2, 52.2. HRMS (ESI−) *m/z* calculated for $C_6H_6{}^{10}BO_4{}^{32}S$: 184.01216, found: 184.01157, $|\Delta\ m/z|$ = −3.25 ppm. ν_{max} (thin film)/cm^{-1} 3339, 2360, 1685, 1300. HPLC retention time (6.41 mins, purity >98%). Spectroscopic data (^{1}H, ^{13}C) has been provided by Witschel *et al.* in D_6-DMSO prepared by an analogous method, however,

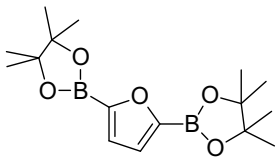
we observe $B(OH)_2$ at 8.54 ppm by ^1H NMR and C5 at 143.9 ppm by ^{13}C NMR.[26] Wang *et al.* report spectroscopic data (^1H, ^{13}C) in $CDCl_3$.[27]

2,5-Bis(5-formylthiophen-2-yl)furan (RV-6)



5-(5-Bromofuran-2-yl)thiophene-2-carbaldehyde (**RV-2**) (150 mg, 0.58 mmol, 1 eq.) was combined with XPhos (11 mg, 0.024 mmol, 0.04 eq.), $Pd(OAc)_2$ (2.6 mg, 0.012 mmol, 0.02 eq.), and K_2CO_3 (242 mg, 1.75 mmol, 3 eq.) in degassed DMF (5 mL). To this, 5-formylthiophene-2-boronic acid (109 mg, 0.70 mmol, 1.2 eq.) in degassed DMF (2 mL) was added slowly dropwise over 15 mins and the reaction mixture allowed to stir at room temperature for 18 h. The reaction mixture was filtered through Celite and washed with an excess of CH_2Cl_2 and the solvent removed *in vacuo*. The residue was purified using silica gel column chromatography (EtOAc:PE, 2:3 to 100:0) to give the title compound as a yellow solid (21.2 mg, 13%). mp.: >250 °C [literature: 186-187 °C].[2] R_f = 0.14 (80:20 PE:EtOAc). ^1H NMR (400 MHz, D_6-DMSO) δ_H 9.93 (s, 2H), 8.06 (d, J = 4.0 Hz, 2H), 7.71 (d, J = 4.0 Hz, 2H), 7.34 (s, 2H). ^{13}C NMR (101 MHz, D_6-DMSO) δ_C 184.1, 148.4, 141.9, 139.8, 139.0, 125.2, 112.5. HRMS (ESI+) *m/z* calculated for $C_{14}H_9O_3{}^{32}S_2$: 288.99876, found: 288.99881 $[M+H]^+$, $|\Delta\ m/z|$ = 0.17 ppm. ν_{max} (thin film)/cm^{-1} 1674, 1999, 765. HPLC retention time (8.37 mins, purity >99%). ^1H NMR and ^{13}C NMR data matches reported literature when prepared by an analogous Suzuki coupling method[2] and alternative method.[1]

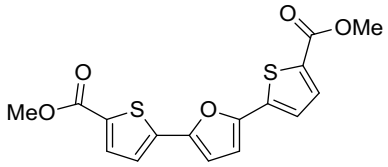
2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan (RV-15)



2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan was prepared as per Ishiyama *et al.* with a modification to the work up procedure.[17] Furan (0.213 mL, 2.93 mmol, 1 eq.) was combined with $[Ir(OMe)COD]_2$ (29 mg, 0.044 mmol, 0.015 eq.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (24 mg, 0.088 mmol, 0.03 eq.) in hexane (5.1 mL) in flame dried glassware. To this, bis(pinacolato)diboron (818 mg, 3.22 mmol, 1.1 eq.) was added and the reaction mixture stirred for 1.5 h at room temperature. The resultant red solution was filtered through Celite and

washed with hexane (200 mL). The hexane was disposed and the Celite pad washed with CH_2Cl_2 (200 mL). The CH_2Cl_2 was removed *in vacuo* to give a brown solid (0.9116 g, 97%) that was used without further purification. R_f 0.26 (50:50 PE:EtOAc) mp 129-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.05 (s, 2H), 1.32 (s, 24H). ^{11}B NMR {^{1}H} (128 MHz, $CDCl_3$) δ_B 26.98. ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 123.3, 84.3, 24.8. LRMS (ESI+) *m/z* 662 $[2M]^+$ (100%), 581 (95%), 343 $[M+Na]^+$ (92%). ν_{max} (thin film)/cm^{-1} 1569, 1338, 1139, 1010, 854. ^{1}H NMR data matches reported literature where 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan was prepared in an independent manner.[28]

Dimethyl 5,5'-(furan-2,5-diyl)bis(thiophene-2-carboxylate) RV-12



Dimethyl 5,5'-(furan-2,5-diyl)bis(thiophene-2-carboxylate) was prepared in two different ways.

Route A (RV-12A)

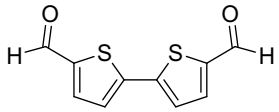
Methyl 5-(5-bromofuran-2-yl)thiophene-2-carboxylate (**RV-9**, 200 mg, 0.7 mmol, 1 eq.) was combined with XPhos (13.3 mg, 0.028 mmol, 0.04 eq.), $Pd(OAc)_2$ (3 mg, 0.014 mmol, 0.02 eq.), and K_2CO_3 (290 mg, 2.1 mmol, 3 eq.) in degassed DMF (5-10 mL). After 5 mins, [5-(methyoxycarbonyl)thiophen-2-yl)boronic acid (**RV-10**) (0.194 mg, 1.04 mmol, 1.5 eq.) was added and the reaction mixture was left to stir for 25 h at room temperature. The reaction mixture was filtered through Celite and the DMF removed under a stream of N_2 overnight. The residue was dissolved in CH_2Cl_2 (100 mL) before H_2O (100 mL) was added. The layers were separated and the aqueous layer was washed with further CH_2Cl_2 (2×100 mL). The organic layers were combined and the solvent removed *in vacuo*. The residue was purified using silica gel flash column chromatography (4:1 PE:Et_2O to 3:2 PE:Et_2O). After this first column (0.045, 18%), the product was purified a second time using silica gel flash column chromatography (100% PE to 60:40 PE:EtOAc) and the product isolated as a bright yellow solid (0.018 g, 7%). R_f 0.38 (80:20 PE:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.73 (d, J = 4.0 Hz, 2H), 7.27 (d, J = 4.0 Hz, 2H), 6.71 (s, 2H), 3.90 (s, 6H). ^{13}C NMR (152 MHz, $CDCl_3$) δ_C 162.6, 148.8, 139.1, 134.3, 131.9, 123.5, 109.8, 52.4.

Route B (RV-12B)

Methyl-5-bromothiophene-2-carboxylate (**RV-7**, 160 mg, 0.7 mmol, 2.2 eq.) was combined with XPhos (35 mg, 0.074 mmol, 0.08 eq.), $Pd(OAc)_2$ (9 mg, 0.037 mmol, 0.04 eq.) and K_2CO_3

(77 mg, 5.6 mmol, 6 eq.) in degassed DMF (20 mL). After stirring at room temperature for 5 mins, 5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan (**RV-15**, 105 mg, 0.33 mmol, 1 eq.) was added and the reaction solution allowed to stir at room temperature for 5 h. The solution was allowed to stand for 16 h at room temperature before stirring started again for 2 h. The solution was filtered through Celite and washed with CH_2Cl_2. The solvent was removed under a stream of nitrogen and the residue reconstituted in EtOAc. The solution was purified using silica gel column chromatography (9:1 toluene:acetone). After this first column, the product (0.084 g, 73%) was purified a second time by flash column chromatography (100% PE to 60:40 PE:EtOAc) and the product isolated as a bright yellow solid (0.057 g, 50%). ^{1}H and ^{13}C NMR matches the characterisation above with minor impurities in the aliphatic and aromatic region. HRMS (APCI+) *m/z* calculated for $C_{16}H_{13}O_5{}^{32}S_2$: 349.01989, found: 349.01933 $[M+H]^+$, $|\Delta\ m/z| = -1.64$ ppm. ν_{max} (thin film)/cm^{-1} 2360, 1701, 1442, 1250. Purity was determined by ^{1}H NMR, as it appeared that peak doubling and product degradation on the HPLC column occurred.

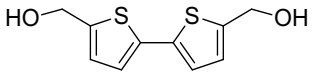
[2,2']Bithiophenyl-5,5'-dicarbaldehyde (RV-13)



5-Bromo-thiophene-2-carbaldehyde (200 mg, 1.05 mmol, 1 eq.) was combined with XPhos (20 mg, 0.042 mmol, 0.04 eq.), $Pd(OAc)_2$ (5 mg, 0.02 mmol, 0.02 eq.) and K_2CO_3 (435 mg, 3.15 mmol, 3 eq.) in degassed DMF (5 mL) before 5-formylthiophene-2-boronic acid (245 mg, 1.57 mmol, 1.5 eq.) was added. The reaction mixture was allowed to stir at room temperature for 35 mins before further DMF (2 mL) was added and the reaction allowed to stir overnight for 12 h at room temperature. The reaction mixture was filtered through Celite and washed with CH_2Cl_2. Upon standing, a strong yellow solid precipitated. The crystals were isolated by filtration and were used without further purification (66.2 mg, 28%). R_f 0.18 (80:20 PE:EtOAc). mp 195-198 °C from CH_2Cl_2:DMF [Literature 190-192 °C[29]; 212.5-214 °C[30]]. ^{1}H NMR (400 MHz, D_6-DMSO) δ_H 9.94 (s, 2H), 8.06 (d, J = 4.0 Hz, 2H), 7.78 (d, J = 4.0 Hz, 2H). ^{13}C NMR (101 MHz, D_6-DMSO) δ_C 184.8, 144.0, 143.9, 139.4, 128.4. HRMS (APCI+) *m/z* calculated for $C_{10}H_6O_2{}^{32}S_2$: 221.9804, found: 221.9802 $[M]^+$, $|\Delta\ m/z| = -0.77$ ppm. ν_{max} (solid)/cm^{-1} 1653, 1436, 1224. HPLC retention time (6.45 mins, purity 100%). ^{1}H NMR data matches reported literature where [2,2']bithiophenyl-5,5'-dicarbaldehyde was prepared in an independent manner.[30] ^{1}H and ^{13}C NMRs were also run in $CDCl_3$ (data not shown) and

correspond to reported literature where [2,2']bithiophenyl-5,5'-dicarbaldehyde was prepared in an independent manner.[29]

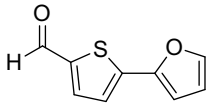
2,2'-Bithiophene-5,5'-diyldimethanol (RV-14)

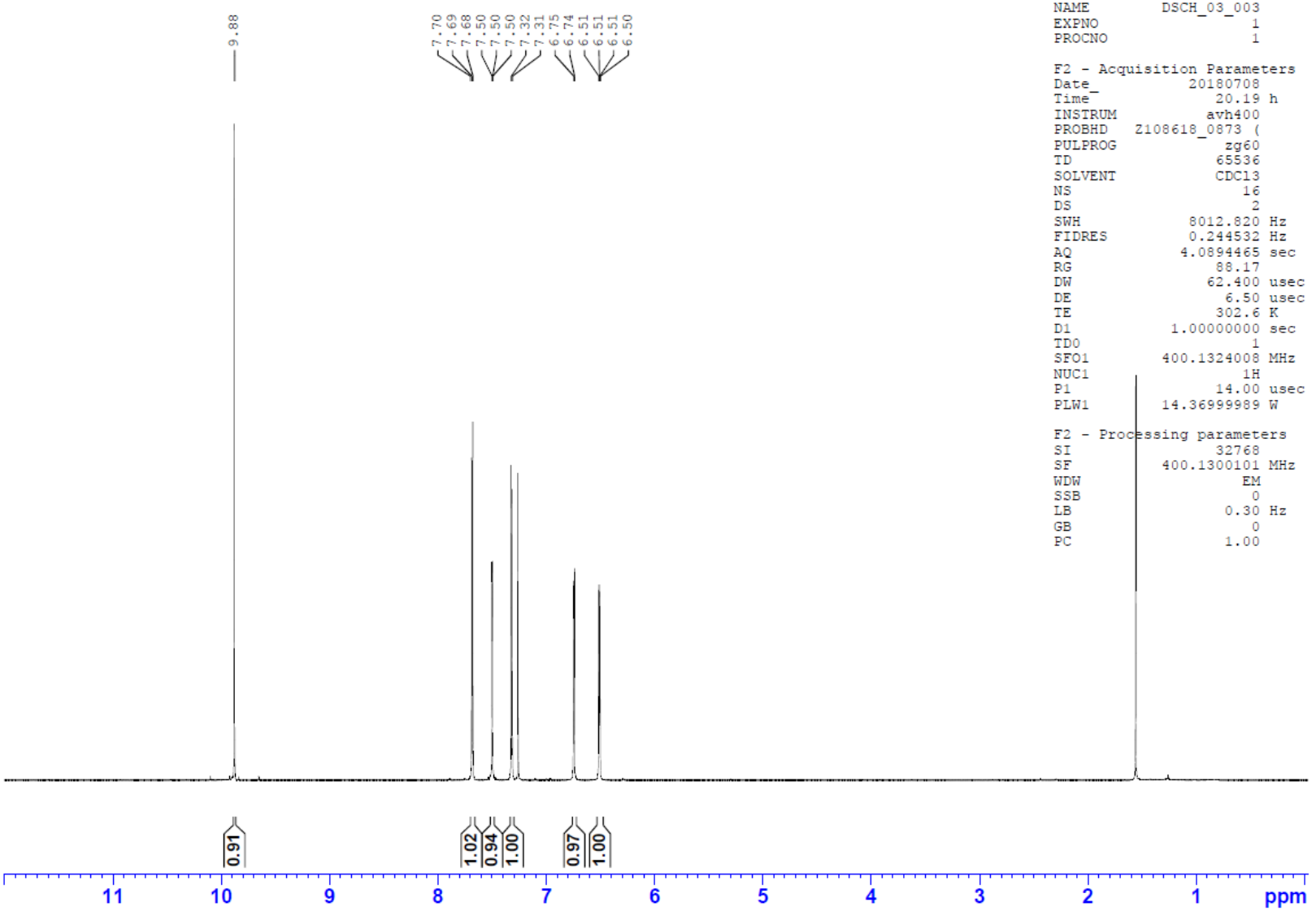


[2,2']Bithiophenyl-5,5'-dicarbaldehyde (**RV-13** 50 mg, 0.22 mmol, 1 eq.) was combined in 1:1 tetrahydrofuran:methanol (6 mL) and cooled to 0 °C before $NaBH_4$ (13 mg, 0.22 mmol, 1 eq.) was added portion wise over 30 mins. The reaction mixture was allowed to stir at 0 °C for 50 mins and was determined complete by TLC analysis. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and extracted with HCl (aq. 1 M, 50 mL) which was added slowly. The layers were separated and the CH_2Cl_2 layer washed with further 2 HCl (aq. 1 M, 2×50 mL). During the extraction a yellow solid precipitated that was isolated separately (5.9 mg, 12%). R_f 0.33 (50:50 PE:EtOAc). mp 141-144 °C from CH_2Cl_2 [literature 158-160 °C, solvent not specified[31]]. ^{1}H NMR (400 MHz, D_6-DMSO) δ_H 7.08 (d, J = 3.6 Hz, 2H), 6.91-6.87 (m, 2H), 5.50 (t, J = 5.8 Hz, 2H), 4.62-4.58 (m, 4H). ^{13}C NMR (101 MHz, D_6-DMSO) δ_C 146.0, 136.1, 125.4, 123.4, 58.8. ν_{max} (solid)/cm^{-1} 3338, 3254, 1004, 794. HPLC retention time (5.34 mins, purity 100%). The product mass could not be determined by APCI or ESI in positive mode. Further product (crude yield, 12 mg) was found in the filtrate but this portion was not carried forward. ^{1}H NMR data corresponds to reported literature values.[32]

^{1}H and ^{13}C NMR spectra

^{1}H NMR, $CDCl_3$, 400 MHz: 5-(furan-2-yl)thiophene-2-carbaldehyde (RV-1)



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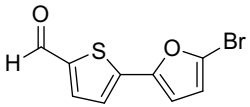
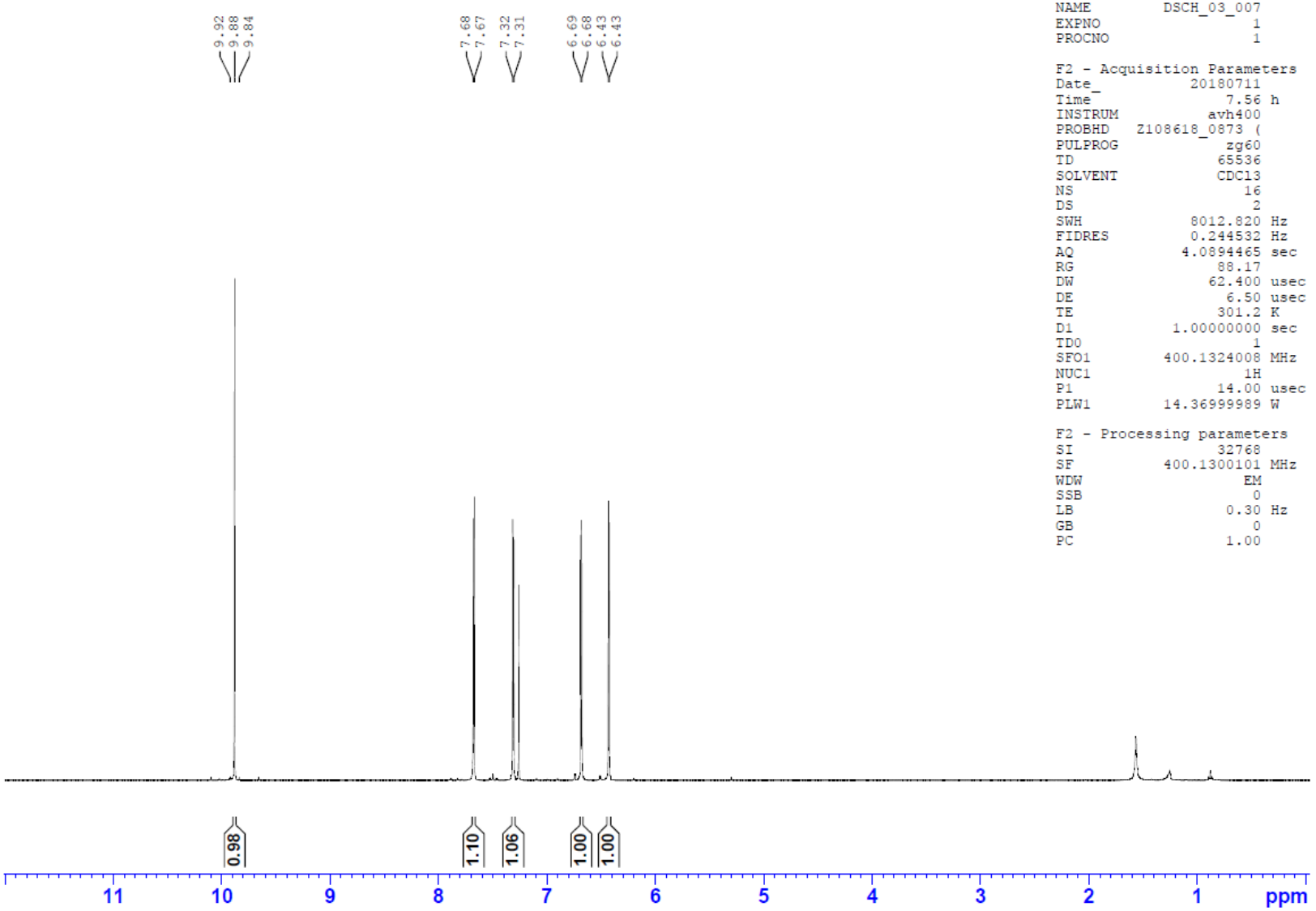
^{1}H NMR, $CDCl_3$, 400 MHz: 5-(5-bromofuran-2-yl)thiophene-2-carbaldehyde (RV-2)



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F2 - Processing parameters
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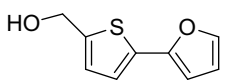
^{1}H NMR, $CDCl_3$, 400 MHz: 5-(Furan-2-yl)thiophene-2-methanol (RV-27)

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FIDRES                  0.244532 H
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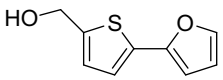
^{13}C NMR, $CDCl_3$, 101 MHz: 5-(Furan-2-yl)thiophene-2-methanol (RV-27)

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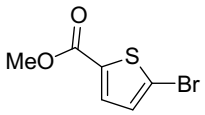
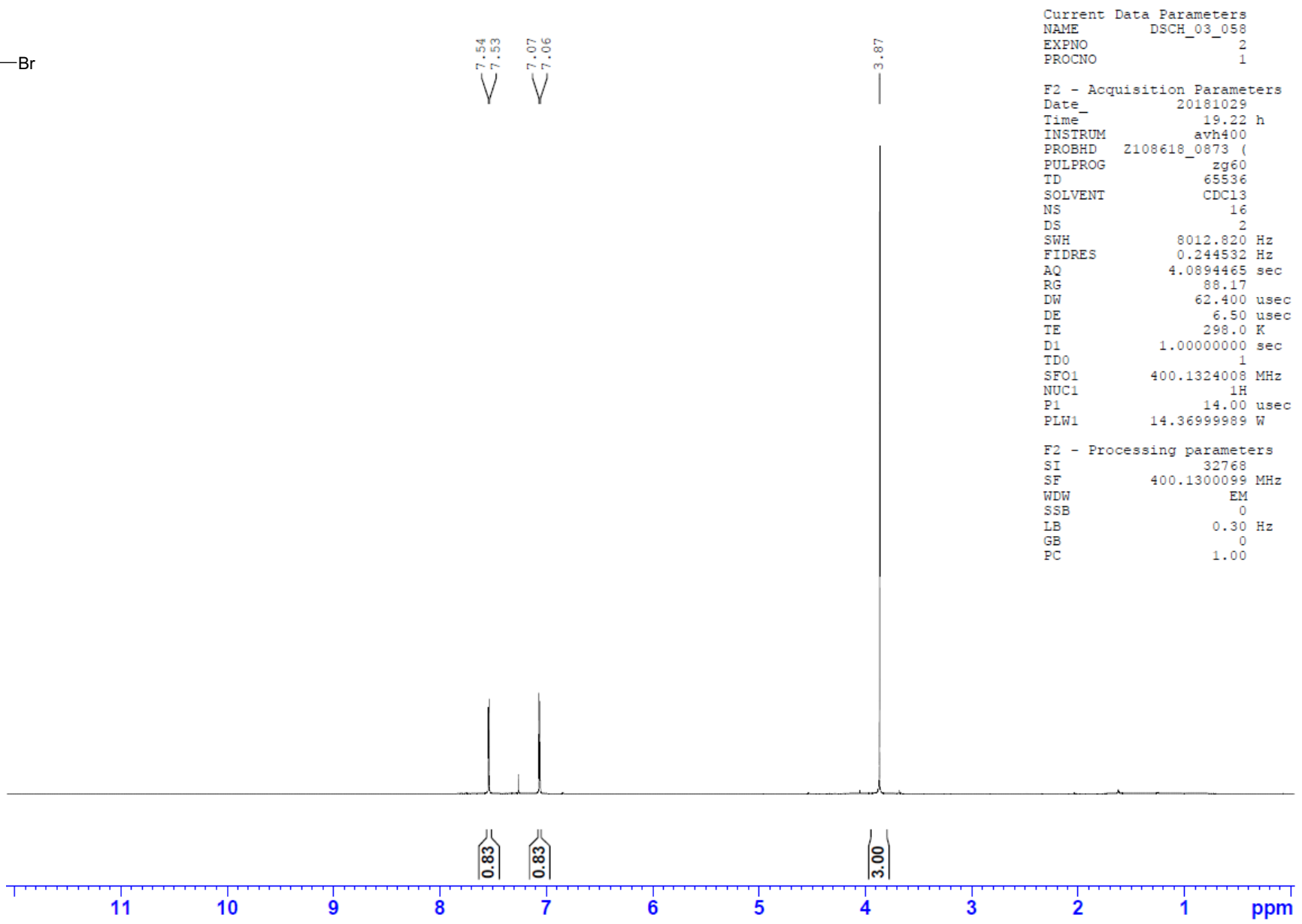
^{1}H NMR, $CDCl_3$, 400 MHz: Methyl-5-bromothiophene-2-carboxylate (RV-7)



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F2 - Processing parameters
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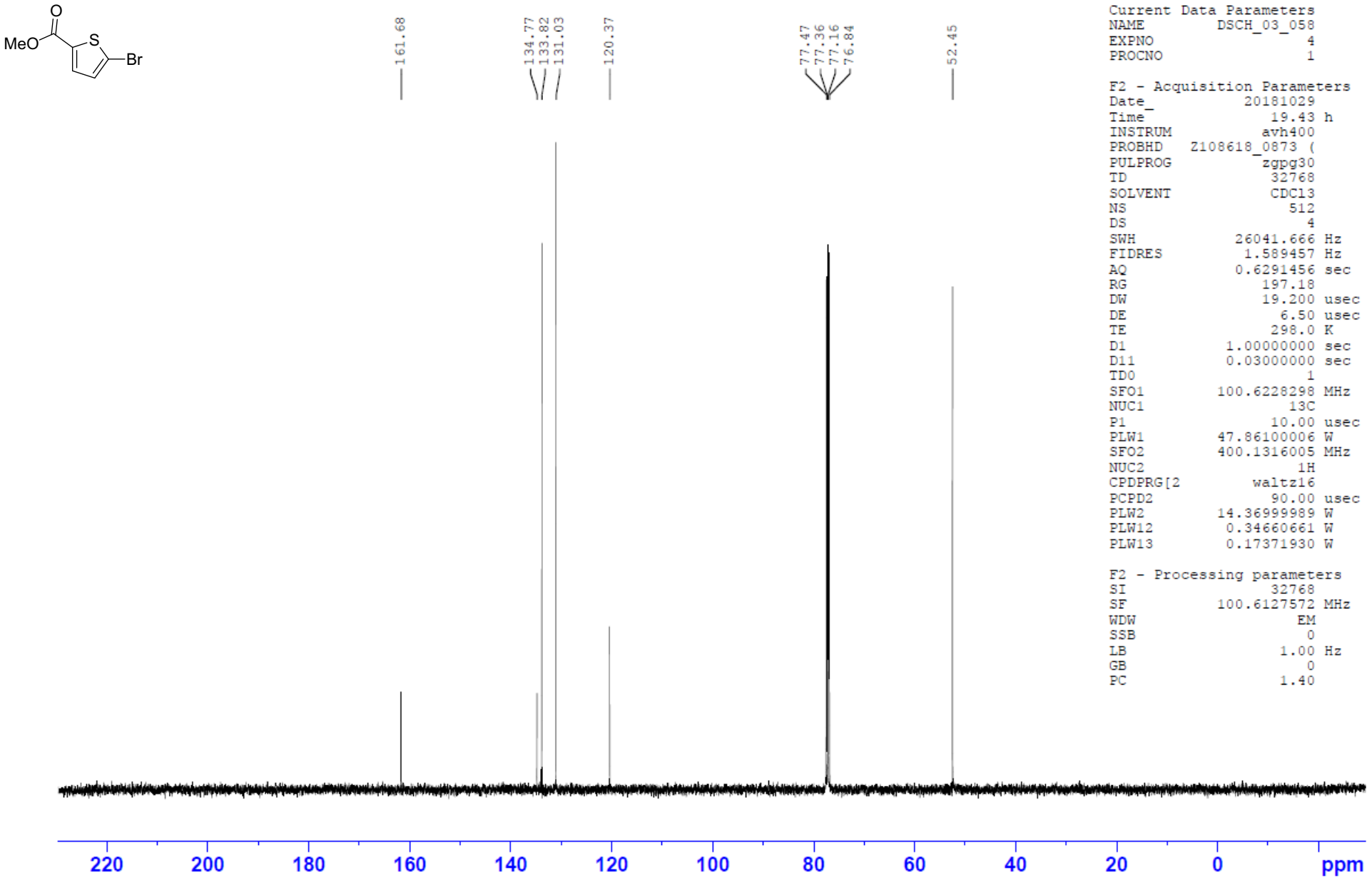
^{13}C NMR, $CDCl_3$, 101 MHz: Methyl-5-bromothiophene-2-carboxylate (RV-7)

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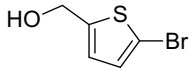
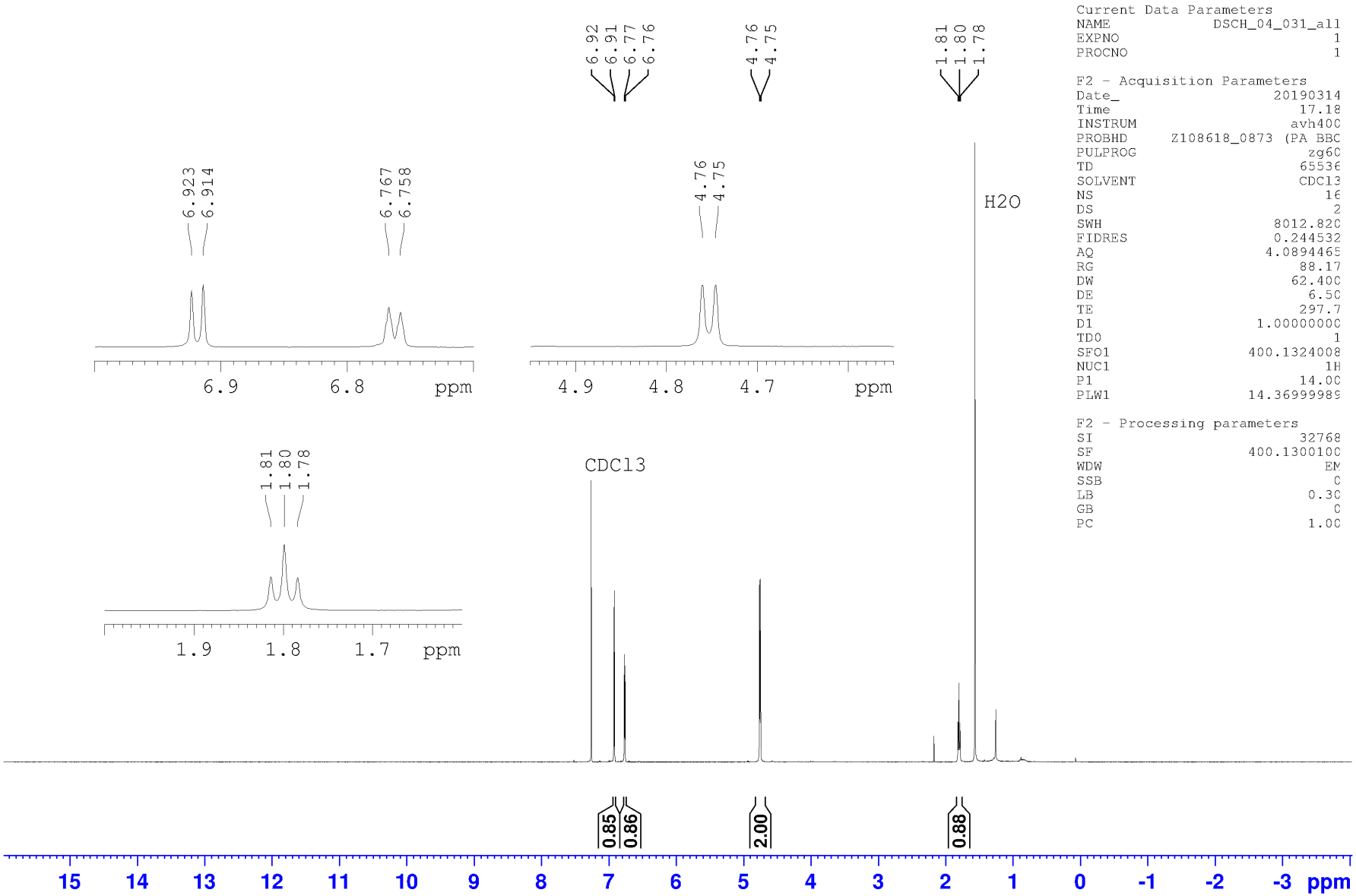
^{1}H NMR, $CDCl_3$, 400 MHz: (5-bromothien-2-yl)methanol (RV-3)



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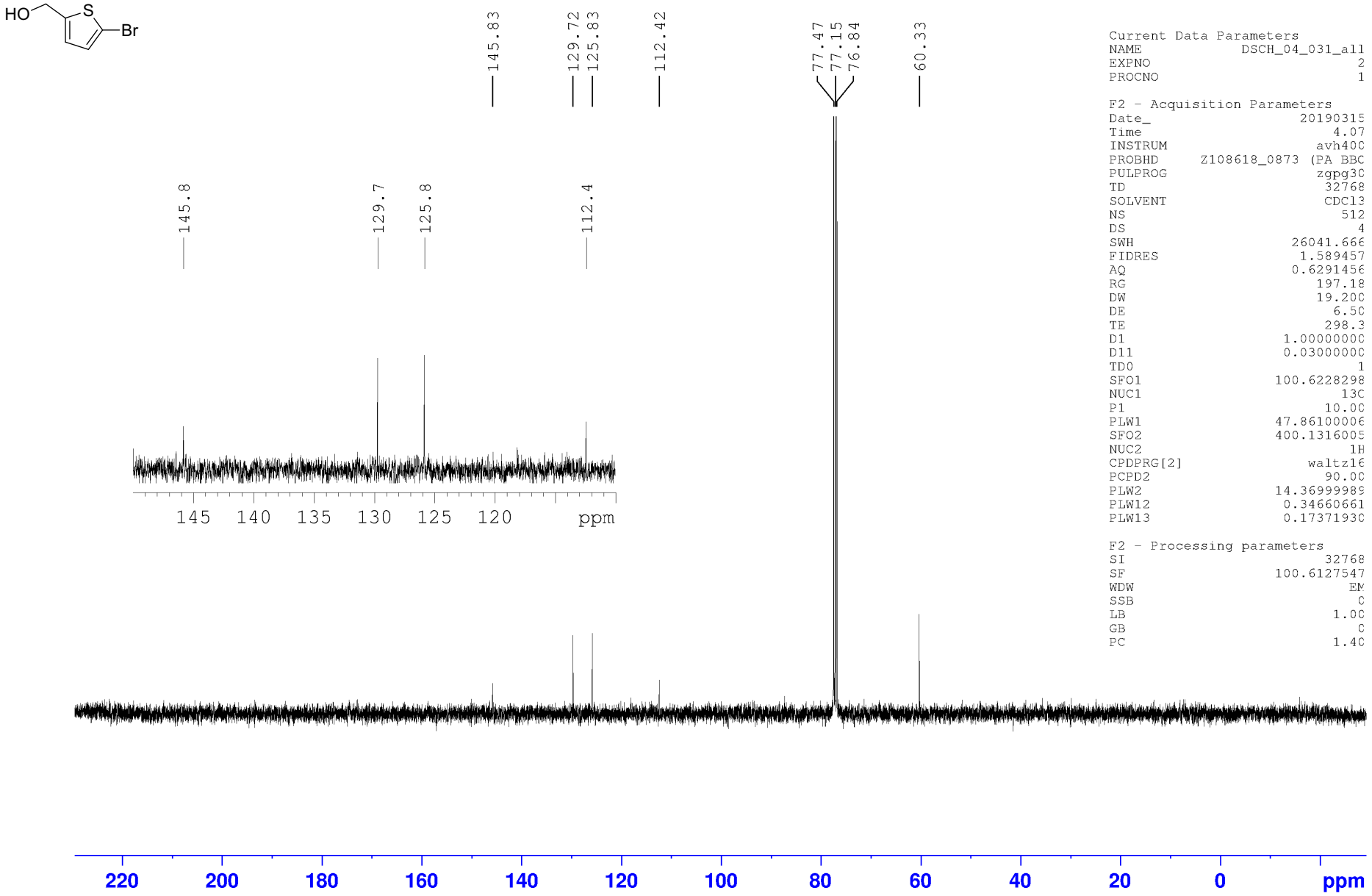
Current Data Parameters
NAME                  DSCH_04_031_all
EXPNO                               1
PROCNO                              1

F2 - Acquisition Parameters
Date_                        20190314
Time                            17.18
INSTRUM                       avh400
PROBHD       Z108618_0873 (PA BBC
PULPROG                         zg60
TD                             65536
SOLVENT                        CDCl3
NS                                16
DS                                 2
SWH                         8012.820
FIDRES                      0.244532
AQ                          4.0894465
RG                              88.17
DW                              62.400
DE                               6.50
TE                              297.7
D1                          1.00000000
TD0                                1
SFO1                      400.1324008
NUC1                             1H
P1                              14.00
PLW1                      14.36999989

F2 - Processing parameters
SI                                32768
SF                          400.1300100
WDW                                EM
SSB                                 0
LB                               0.30
GB                                  0
PC                               1.00
```

^{13}C NMR, $CDCl_3$, 101 MHz: (5-bromothien-2-yl)methanol (RV-3)

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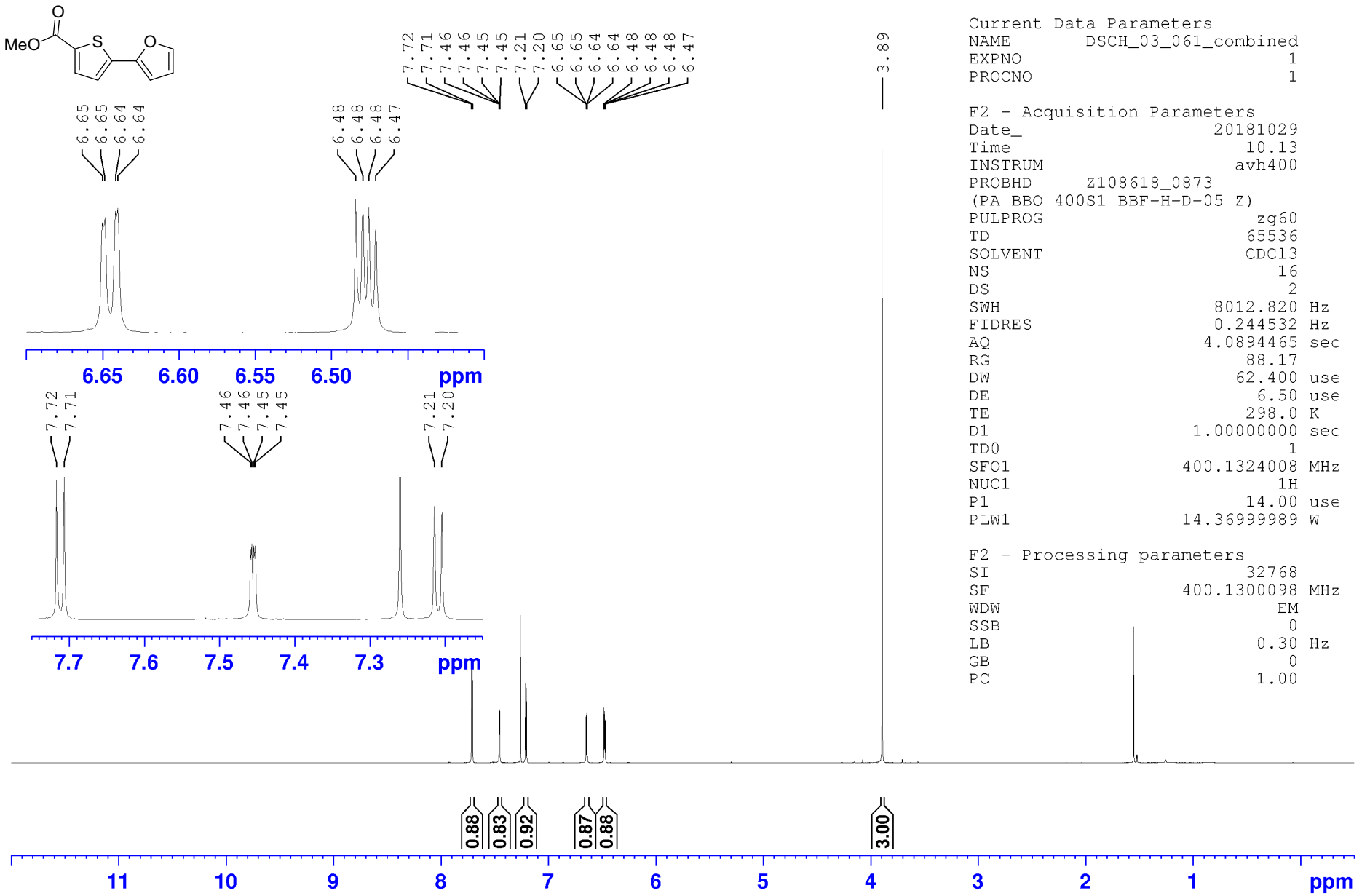
Current Data Parameters
NAME                  DSCH_04_031_all
EXPNO                               2
PROCNO                              1

F2 - Acquisition Parameters
Date_                        20190315
Time                             4.07
INSTRUM                       avh400
PROBHD      Z108618_0873 (PA BBC
PULPROG                       zgpg30
TD                            32768
SOLVENT                       CDCl3
NS                              512
DS                                4
SWH                       26041.666
FIDRES                    1.589457
AQ                        0.6291456
RG                            197.18
DW                            19.200
DE                              6.50
TE                             298.3
D1                        1.00000000
D11                       0.03000000
TD0                               1
SFO1                    100.6228298
NUC1                            13C
P1                             10.00
PLW1                    47.86100006
SFO2                    400.1316005
NUC2                            1H
CPDPRG[2]                  waltz16
PCPD2                          90.00
PLW2                    14.36999989
PLW12                   0.34660661
PLW13                   0.17371930

F2 - Processing parameters
SI                            32768
SF                      100.6127547
WDW                            EM
SSB                             0
LB                             1.00
GB                              0
PC                             1.40
```

^{1}H NMR, $CDCl_3$, 400 MHz: Methyl 5-(furan-2-yl)thiophene-2-carboxylate (RV-8)

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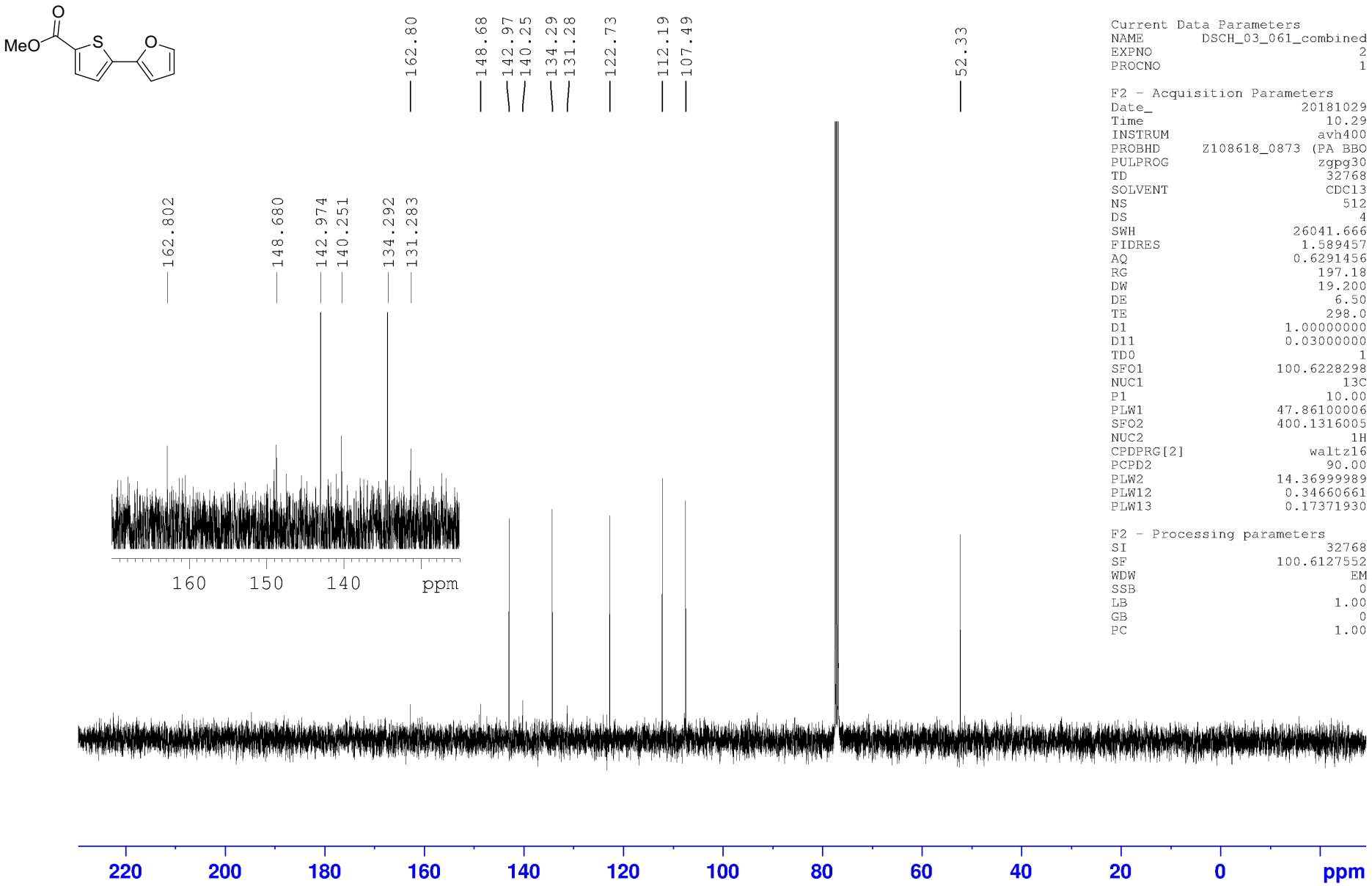
Current Data Parameters
NAME        DSCH_03_061_combined
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20181029
Time                       10.13
INSTRUM                  avh400
PROBHD      Z108618_0873
(PA BBO 400S1 BBF-H-D-05 Z)
PULPROG                    zg60
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8012.820 Hz
FIDRES                 0.244532 Hz
AQ                     4.0894465 sec
RG                         88.17
DW                        62.400 use
DE                         6.50 use
TE                        298.0 K
D1                     1.00000000 sec
TD0                           1
SFO1                 400.1324008 MHz
NUC1                         1H
P1                        14.00 use
PLW1                 14.36999989 W

F2 - Processing parameters
SI                        32768
SF                   400.1300098 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```

^{13}C NMR, $CDCl_3$, 101 MHz: Methyl 5-(furan-2-yl)thiophene-2-carboxylate (RV-8)

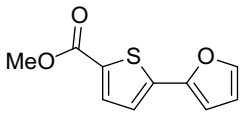



```
Current Data Parameters
NAME        DSCH_03_061_combined
EXPNO                          2
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20181029
Time                       10.29
INSTRUM                 avh400
PROBHD      Z108618_0873 (PA BBO
PULPROG                 zgpg30
TD                      32768
SOLVENT                 CDCl3
NS                      512
DS                      4
SWH                     26041.666
FIDRES                  1.589457
AQ                      0.6291456
RG                      197.18
DW                      19.200
DE                      6.50
TE                      298.0
D1                      1.00000000
D11                     0.03000000
TD0                     1
SFO1                    100.6228298
NUC1                    13C
P1                      10.00
PLW1                    47.86100006
SFO2                    400.1316005
NUC2                    1H
CPDPRG[2]               waltz16
PCPD2                   90.00
PLW2                    14.36999989
PLW12                   0.34660661
PLW13                   0.17371930

F2 - Processing parameters
SI                      32768
SF                      100.6127552
WDW                     EM
SSB                     0
LB                      1.00
GB                      0
PC                      1.00
```

^{13}C NMR, $CDCl_3$, 101 MHz: Methyl 5-(furan-2-yl)thiophene-2-carboxylate (RV-8)

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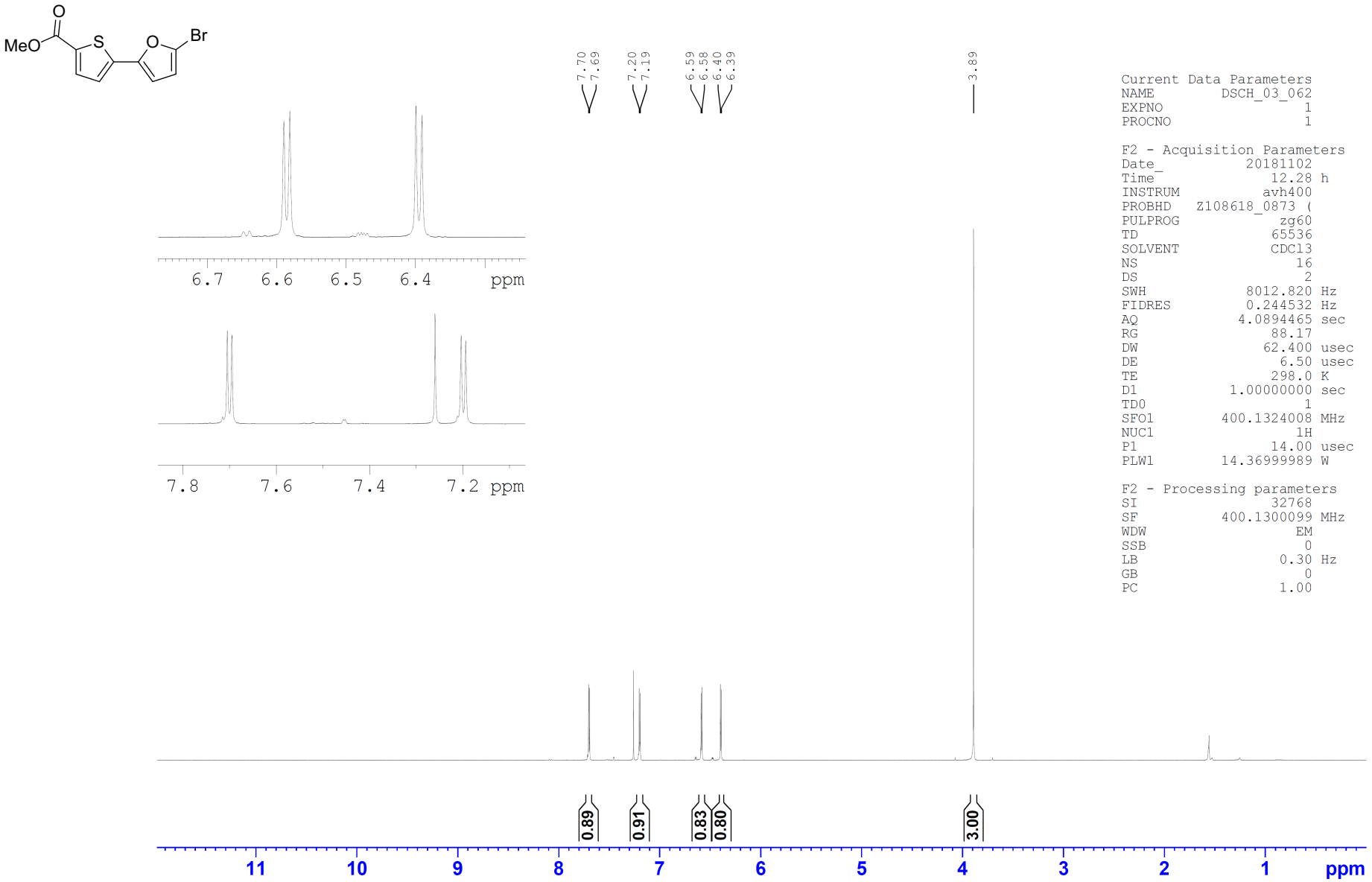
Current Data Parameters
NAME       DSCH_01_041_c1_f30-39
EXPNO                          9
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20250715
Time                      20.06 h
INSTRUM                  Avance
PROBHD             Z163739_1071
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                  23809.524 Hz
FIDRES                0.726609 Hz
AQ                    1.3762560 sec
RG                          101
DW                     21.000 usec
DE                      6.50 usec
TE                      298.7 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1
SFO1                100.4485574 MHz
NUC1                       13C
P0                     2.67 usec
P1                     8.00 usec
PLW1                100.51000000 W
SFO2                399.4385977 MHz
NUC2                       1H
CPDPRG2                waltz65
PCPD2                  90.00 usec
PLW2                24.01400000 W
PLW12                0.18974000 W
PLW13                0.09543800 W

F2 - Processing parameters
SI                         32768
SF                  100.4385025 MHz
WDW                           EM
SSB                            0
LB                      1.00 Hz
GB                             0
PC                          1.40
```

^{1}H NMR, $CDCl_3$, 400 MHz: Methyl 5-(5-bromofuran-2-yl)thiophene-2-carboxylate (RV-9)

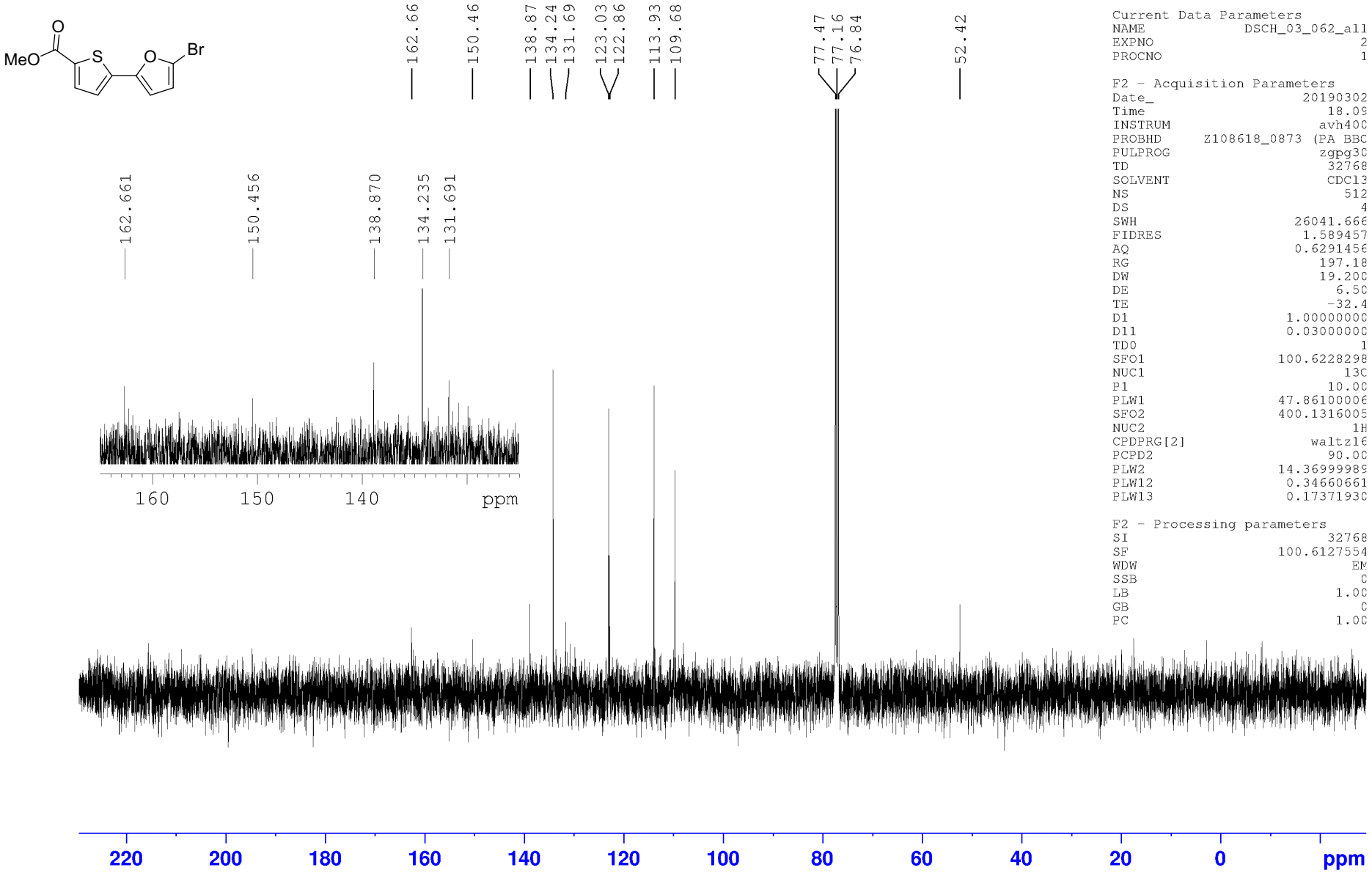



```
Current Data Parameters
NAME         DSCH_03_062
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20181102
Time               12.28 h
INSTRUM          avh400
PROBHD   Z108618_0873 (
PULPROG             zg60
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ              4.0894465 sec
RG                 88.17
DW                 62.400 usec
DE                  6.50 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1
SFO1         400.1324008 MHz
NUC1                  1H
P1                 14.00 usec
PLW1         14.36999989 W

F2 - Processing parameters
SI                 32768
SF           400.1300099 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{13}C NMR, $CDCl_3$, 101 MHz: Methyl 5-(5-bromofuran-2-yl)thiophene-2-carboxylate (RV-9)

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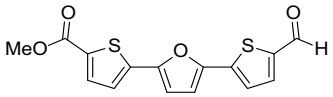
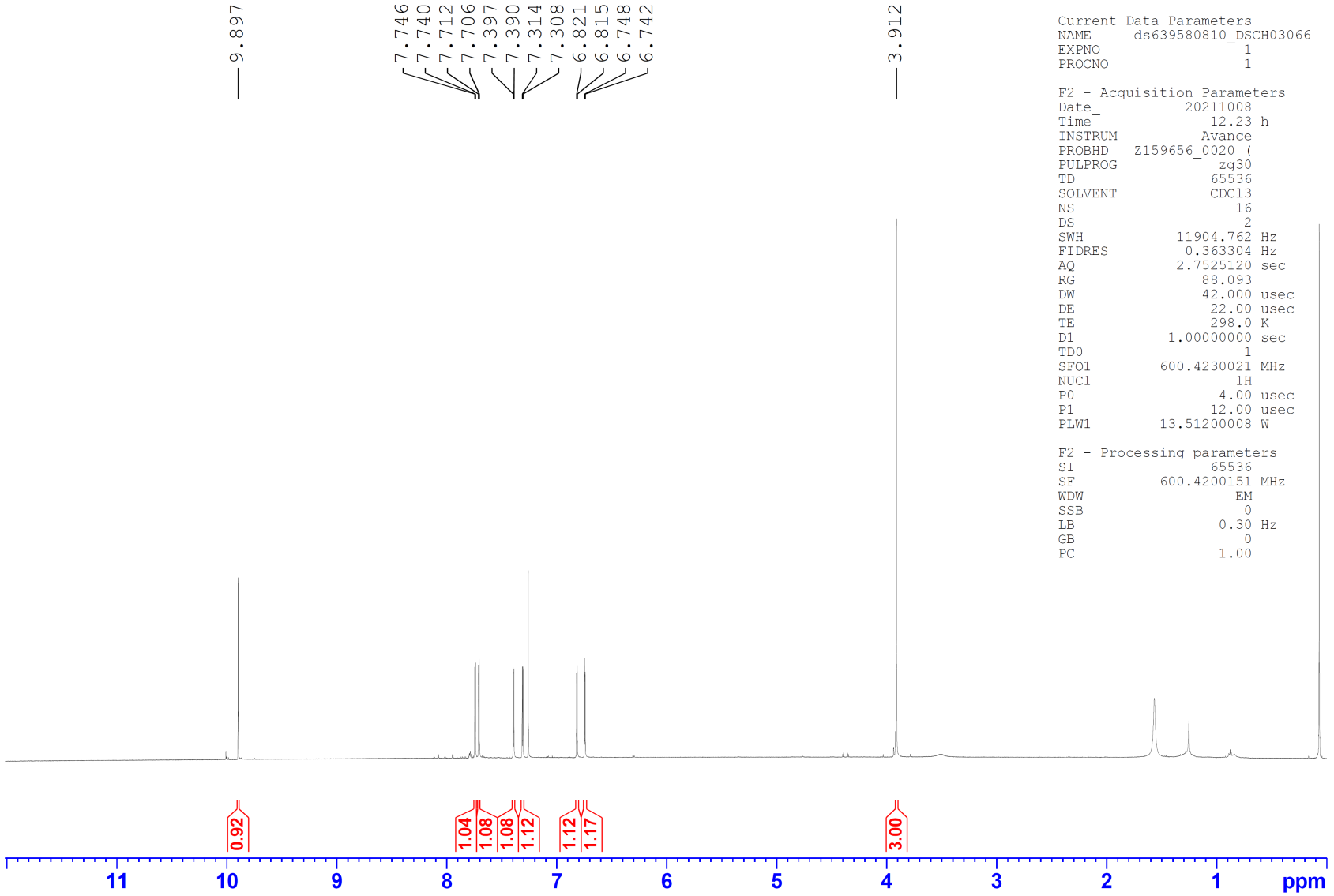
Current Data Parameters
NAME                  DSCH_03_062_all
EXPNO                               2
PROCNO                              1

F2 - Acquisition Parameters
Date_                        20190302
Time                            18.09
INSTRUM                       avh400
PROBHD       Z108618_0873 (PA BBC
PULPROG                       zgpg30
TD                               32768
SOLVENT                         CDCl3
NS                                512
DS                                  4
SWH                         26041.666
FIDRES                       1.589457
AQ                          0.6291456
RG                              197.18
DW                              19.200
DE                                6.50
TE                               -32.4
D1                          1.00000000
D11                         0.03000000
TD0                                 1
SFO1                      100.6228298
NUC1                              13C
P1                              10.00
PLW1                      47.86100006
SFO2                      400.1316005
NUC2                              1H
CPDPRG[2]                    waltz16
PCPD2                           90.00
PLW2                      14.36999989
PLW12                      0.34660661
PLW13                      0.17371930

F2 - Processing parameters
SI                               32768
SF                        100.6127554
WDW                               EM
SSB                                0
LB                              1.00
GB                                 0
PC                              1.00
```

^{1}H NMR, $CDCl_3$, 600 MHz: Methyl 5-[5-(5-formylthiophen-2-yl)furan-2-yl]thiophene-2-carboxylate (RV-11)



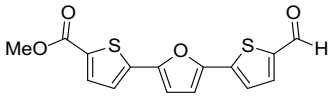


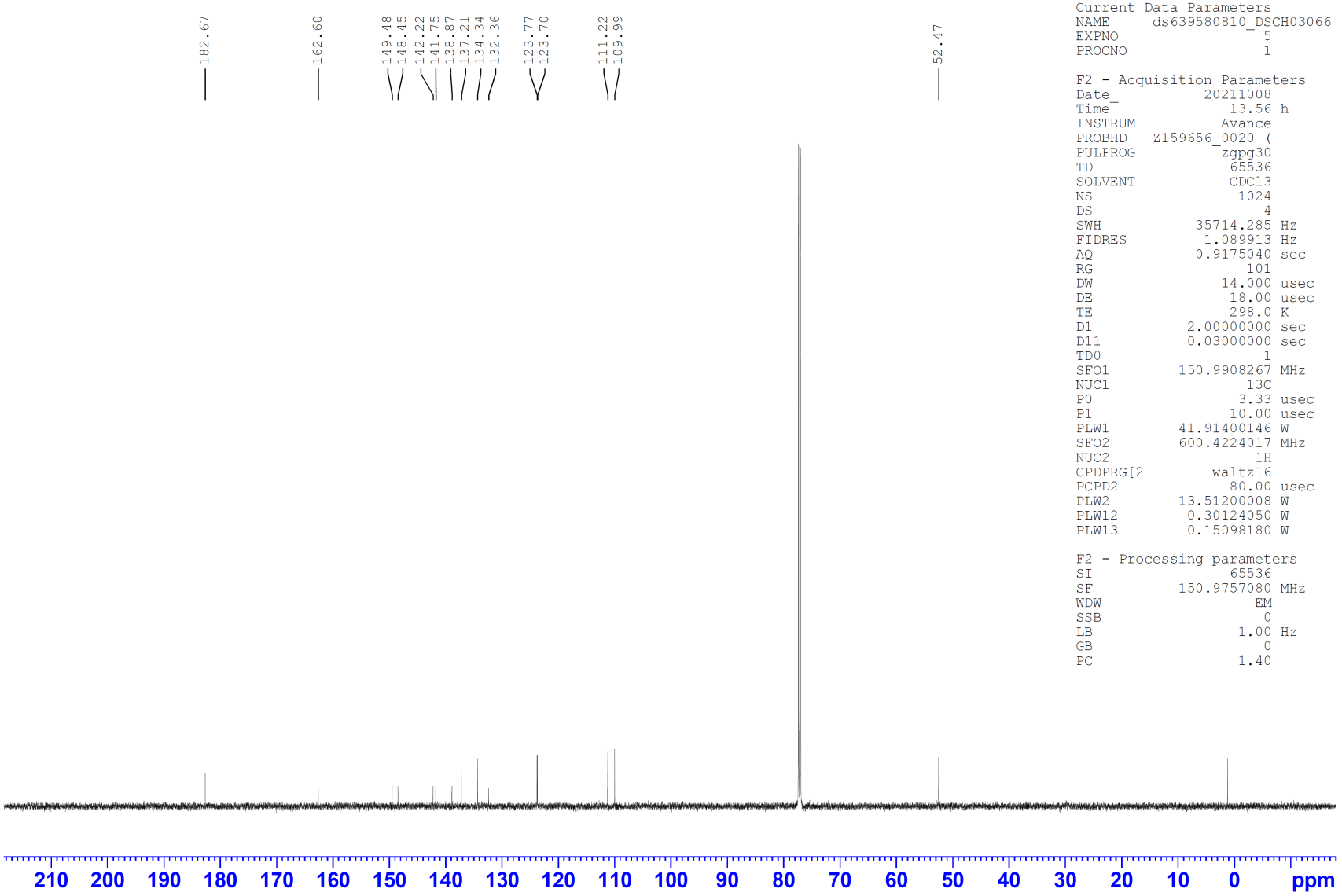

```
Current Data Parameters
NAME      ds639580810_DSCH03066
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20211008
Time                 12.23 h
INSTRUM              Avance
PROBHD    Z159656_0020 (
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              11904.762 Hz
FIDRES            0.363304 Hz
AQ               2.7525120 sec
RG                  88.093
DW                  42.000 usec
DE                  22.00 usec
TE                  298.0 K
D1               1.00000000 sec
TD0                      1
SFO1           600.4230021 MHz
NUC1                    1H
P0                   4.00 usec
P1                  12.00 usec
PLW1           13.51200008 W

F2 - Processing parameters
SI                   65536
SF             600.4200151 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

^{13}C NMR, $CDCl_3$, 151 MHz: Methyl 5-[5-(5-formylthiophen-2-yl)furan-2-yl]thiophene-2-carboxylate (RV-11)



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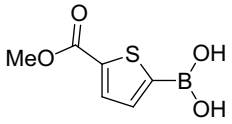
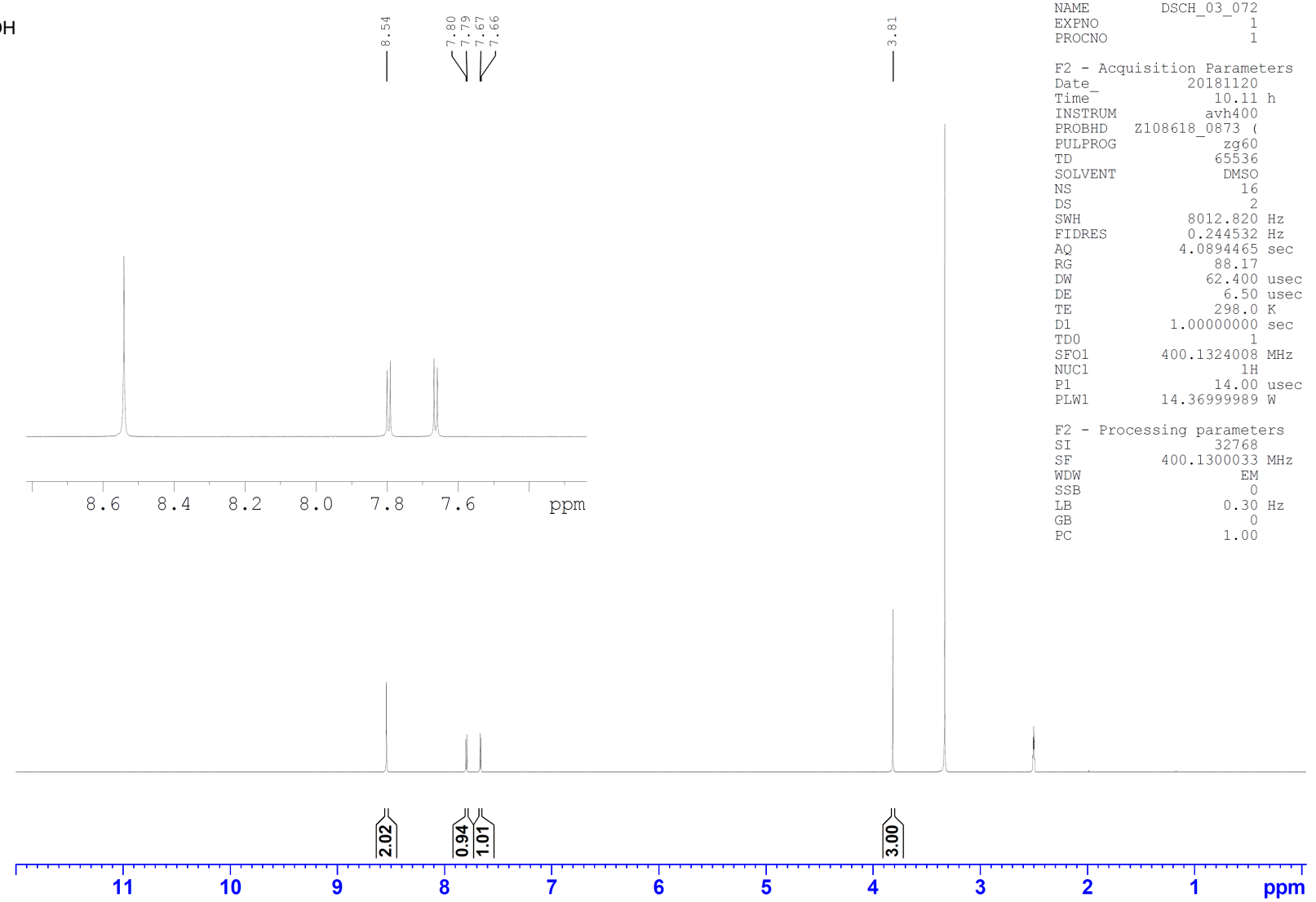
Current Data Parameters
NAME      ds639580810_DSCH03066
EXPNO                         5
PROCNO                        1

F2 - Acquisition Parameters
Date_               20211008
Time                  13.56 h
INSTRUM               Avance
PROBHD    Z159656_0020 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              35714.285 Hz
FIDRES            1.089913 Hz
AQ               0.9175040 sec
RG                     101
DW                  14.000 usec
DE                  18.00 usec
TE                  298.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1
SFO1           150.9908267 MHz
NUC1                   13C
P0                   3.33 usec
P1                  10.00 usec
PLW1           41.91400146 W
SFO2           600.4224017 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2           13.51200008 W
PLW12           0.30124050 W
PLW13           0.15098180 W

F2 - Processing parameters
SI                   65536
SF             150.9757080 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^{1}H NMR, D_6-DMSO, 400 MHz: [5-(methyoxycarbonyl)thiophen-2-yl)boronic acid (RV-10)



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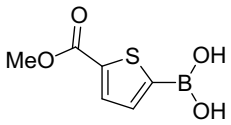
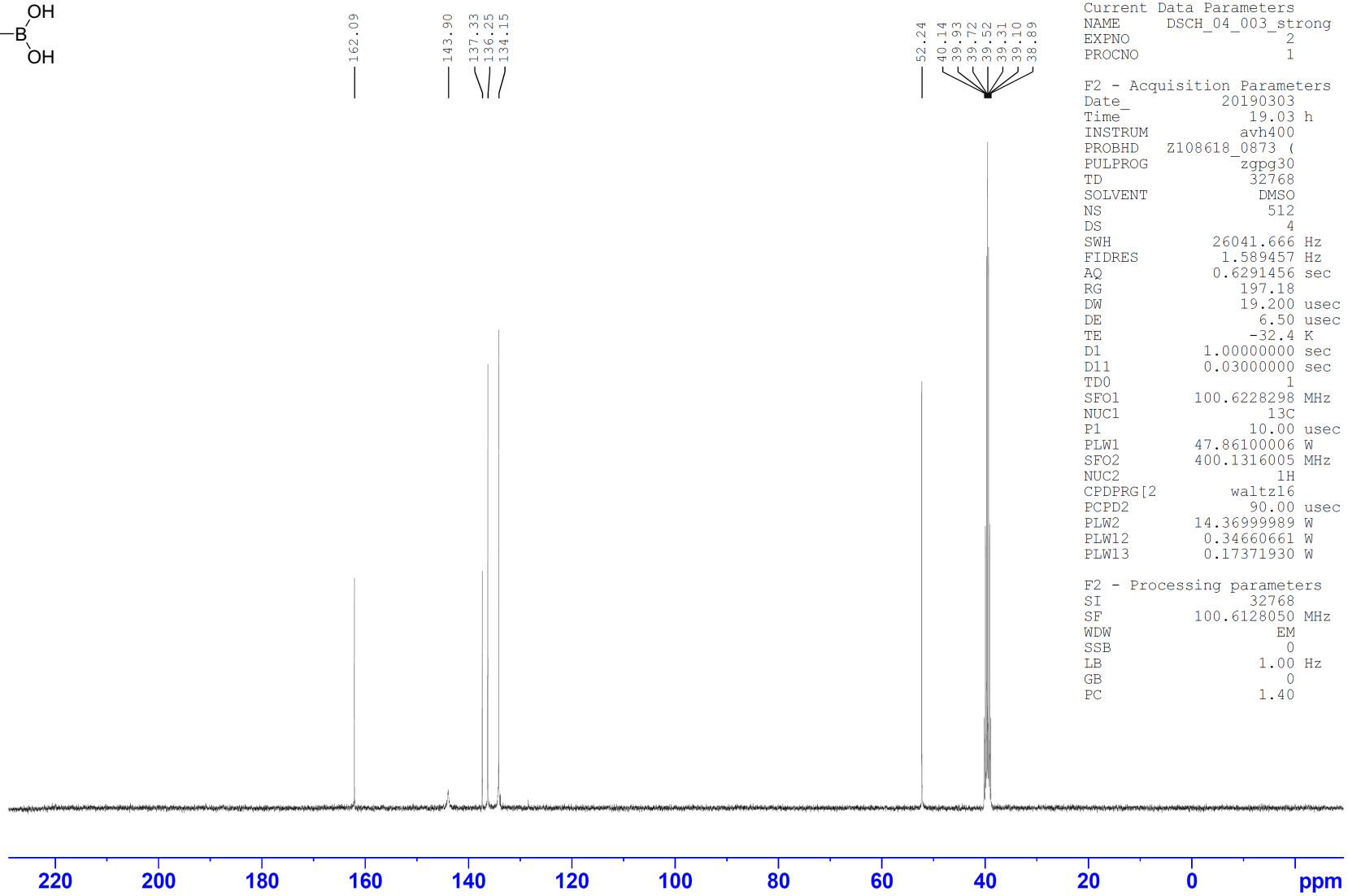
Current Data Parameters
NAME         DSCH_03_072
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20181120
Time              10.11 h
INSTRUM           avh400
PROBHD   Z108618_0873 (
PULPROG             zg60
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ             4.0894465 sec
RG                 88.17
DW                62.400 usec
DE                 6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1
SFO1         400.1324008 MHz
NUC1                  1H
P1                14.00 usec
PLW1         14.36999989 W

F2 - Processing parameters
SI                 32768
SF          400.1300033 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.00
```

^{13}C NMR, D_6-DMSO, 101 MHz: [5-(methyoxycarbonyl)thiophen-2-yl)boronic acid (RV-10)



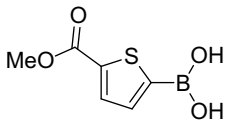



```
Current Data Parameters
NAME      DSCH_04_003_strong
EXPNO                      2
PROCNO                     1

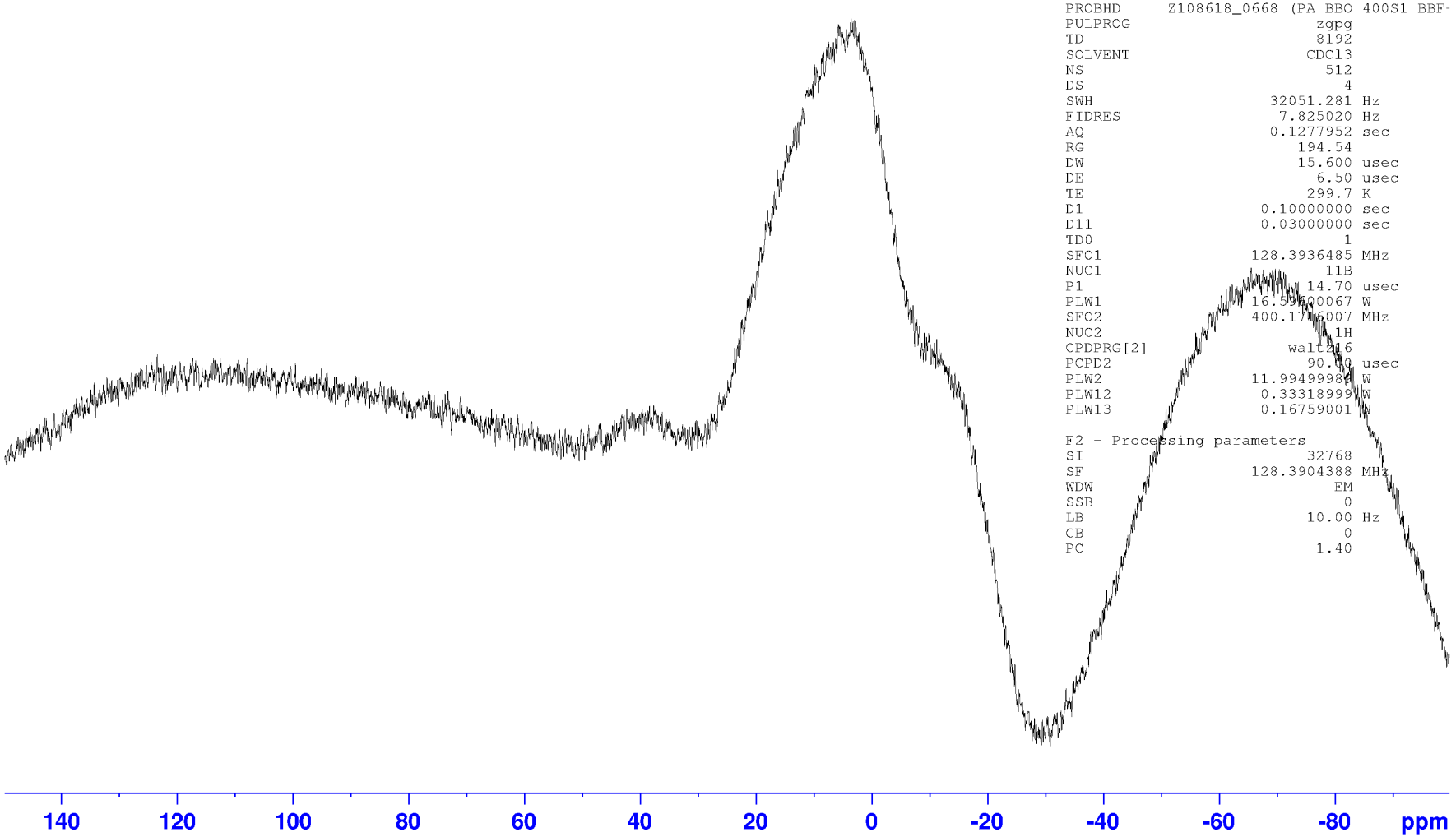
F2 - Acquisition Parameters
Date_           20190303
Time              19.03 h
INSTRUM           avh400
PROBHD   Z108618_0873 (
PULPROG          zgpg30
TD                32768
SOLVENT             DMSO
NS                    512
DS                      4
SWH           26041.666 Hz
FIDRES         1.589457 Hz
AQ            0.6291456 sec
RG               197.18
DW               19.200 usec
DE                 6.50 usec
TE                -32.4 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1        100.6228298 MHz
NUC1                13C
P1                10.00 usec
PLW1        47.86100006 W
SFO2        400.1316005 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        14.36999989 W
PLW12        0.34660661 W
PLW13        0.17371930 W

F2 - Processing parameters
SI                32768
SF          100.6128050 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

^{11}B NMR{^{1}H}, $CDCl_3$, 128 MHz: [5-(methyoxycarbonyl)thiophen-2-yl)boronic acid (RV-10)



^{11}B NMR {^{1}H}, $CDCl_3$, 128 MHz with decoupling blank

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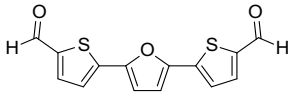
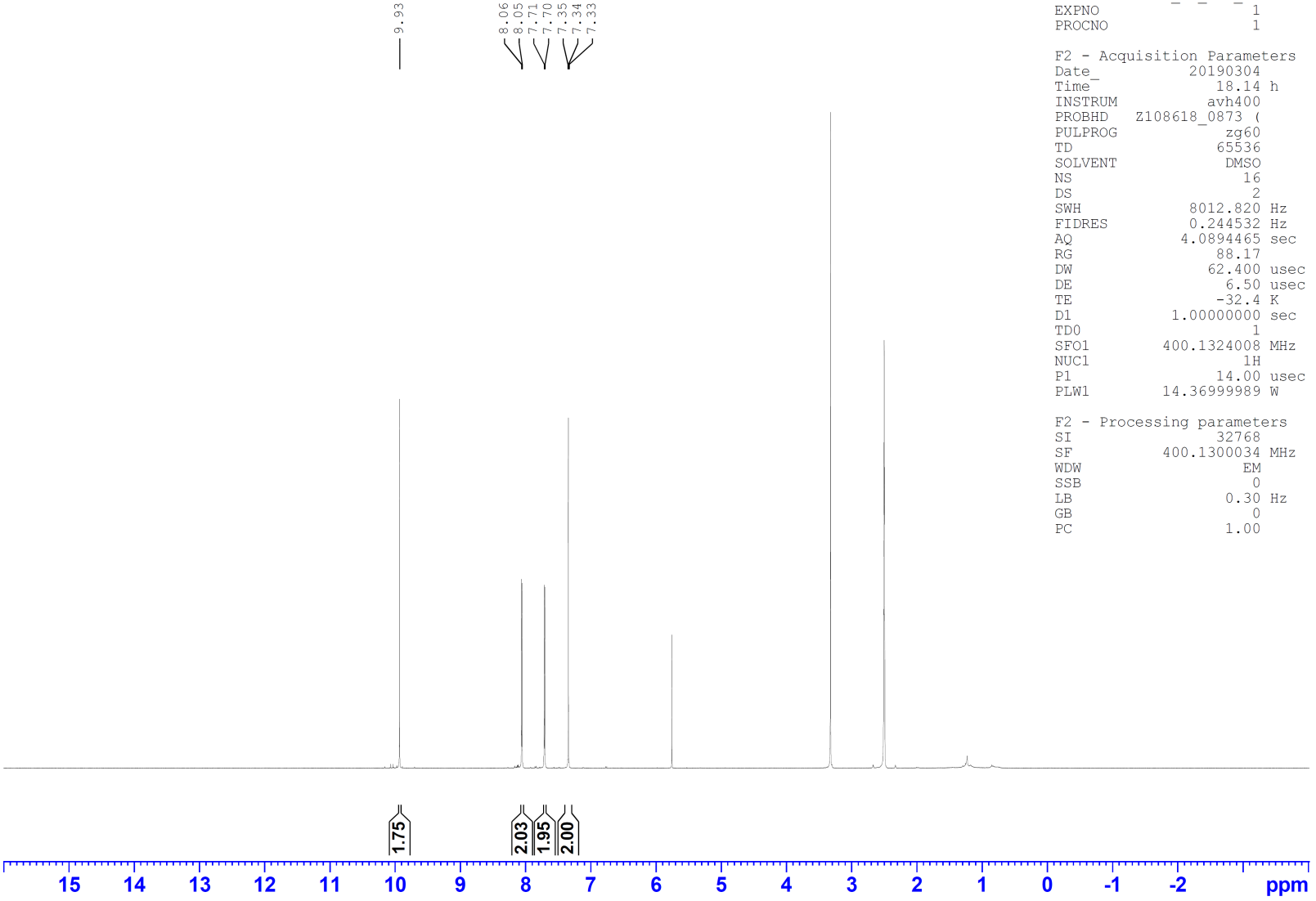
Current Data Parameters
NAME                  DSCH_boron_CDCl3
EXPNO                                2
PROCNO                               1

F2 - Acquisition Parameters
Date_                         20210731
Time                             19.21
INSTRUM                          Hg400
PROBHD       Z108618_0668 (PA BBO 400S1 BBF-
PULPROG                          zgpg
TD                               8192
SOLVENT                          CDCl3
NS                                512
DS                                  4
SWH                         32051.281 Hz
FIDRES                       7.825020 Hz
AQ                           0.1277952 sec
RG                              194.54
DW                              15.600 usec
DE                               6.50 usec
TE                              299.7 K
D1                          0.10000000 sec
D11                         0.03000000 sec
TD0                                 1
SFO1                      128.3936485 MHz
NUC1                              11B
P1                              14.70 usec
PLW1                      16.59900067 W
SFO2                      400.1716007 MHz
NUC2                              1H
CPDPRG[2]                      waltz16
PCPD2                           90.00 usec
PLW2                      11.99499989 W
PLW12                      0.33318999 W
PLW13                      0.16759001 W

F2 - Processing parameters
SI                              32768
SF                        128.3904388 MHz
WDW                                EM
SSB                                 0
LB                              10.00 Hz
GB                                  0
PC                               1.40
```

^{1}H NMR, D_6-DMSO, 400 MHz: 2,5-bis(5-formylthiophen-2-yl)furan (RV-6)



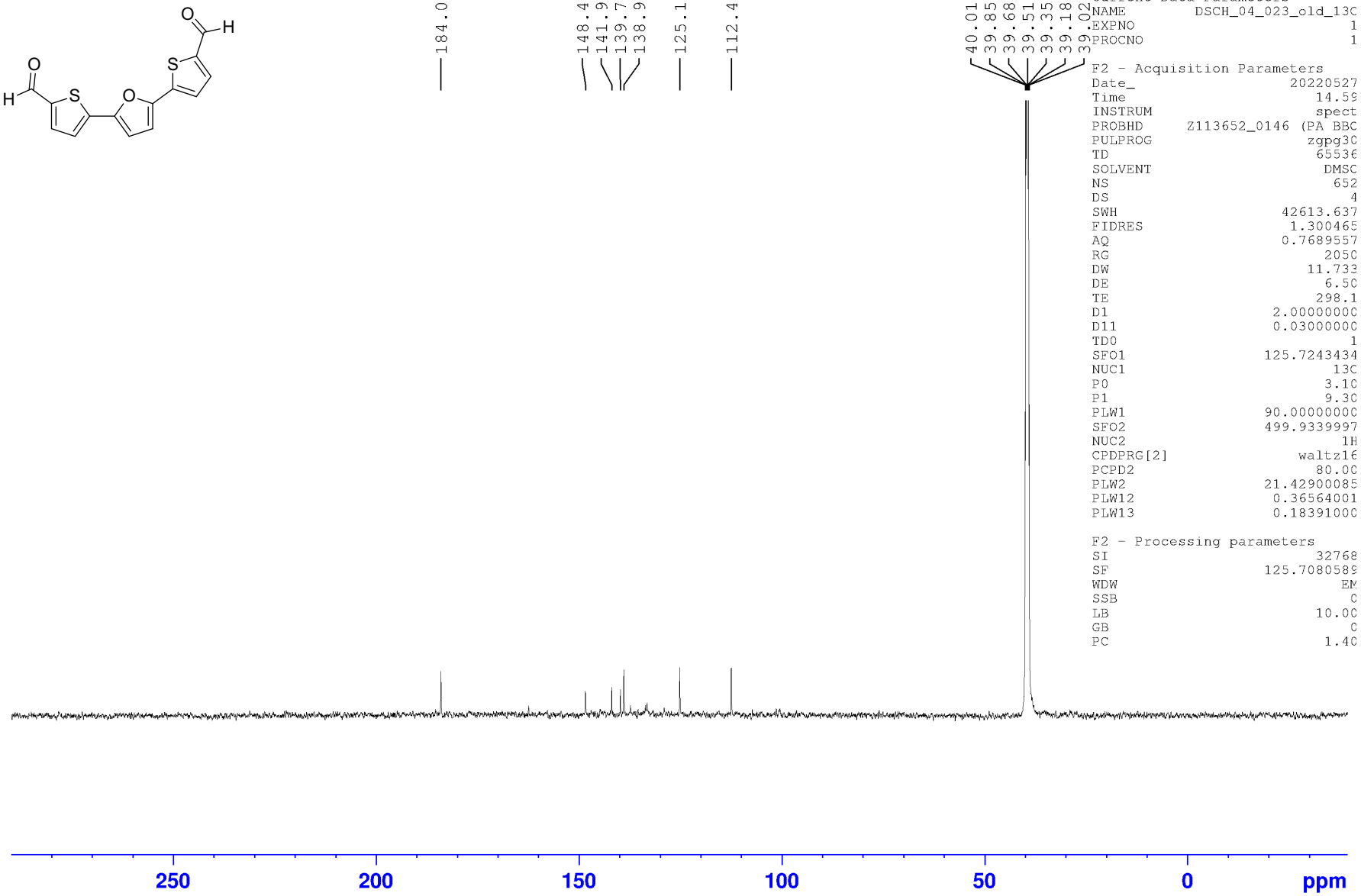



```
Current Data Parameters
NAME      DSCH_04_023_colend
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190304
Time                 18.14 h
INSTRUM            avh400
PROBHD   Z108618_0873 (
PULPROG              zg60
TD                  65536
SOLVENT               DMSO
NS                      16
DS                       2
SWH               8012.820 Hz
FIDRES           0.244532 Hz
AQ               4.0894465 sec
RG                   88.17
DW                 62.400 usec
DE                  6.50 usec
TE                 -32.4 K
D1            1.00000000 sec
TD0                      1
SFO1          400.1324008 MHz
NUC1                    1H
P1                 14.00 usec
PLW1          14.36999989 W

F2 - Processing parameters
SI                   32768
SF            400.1300034 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                  1.00
```

^{13}C NMR, D_6-DMSO, 126 MHz: 2,5-bis(5-formylthiophen-2-yl)furan (RV-6)

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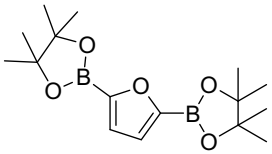
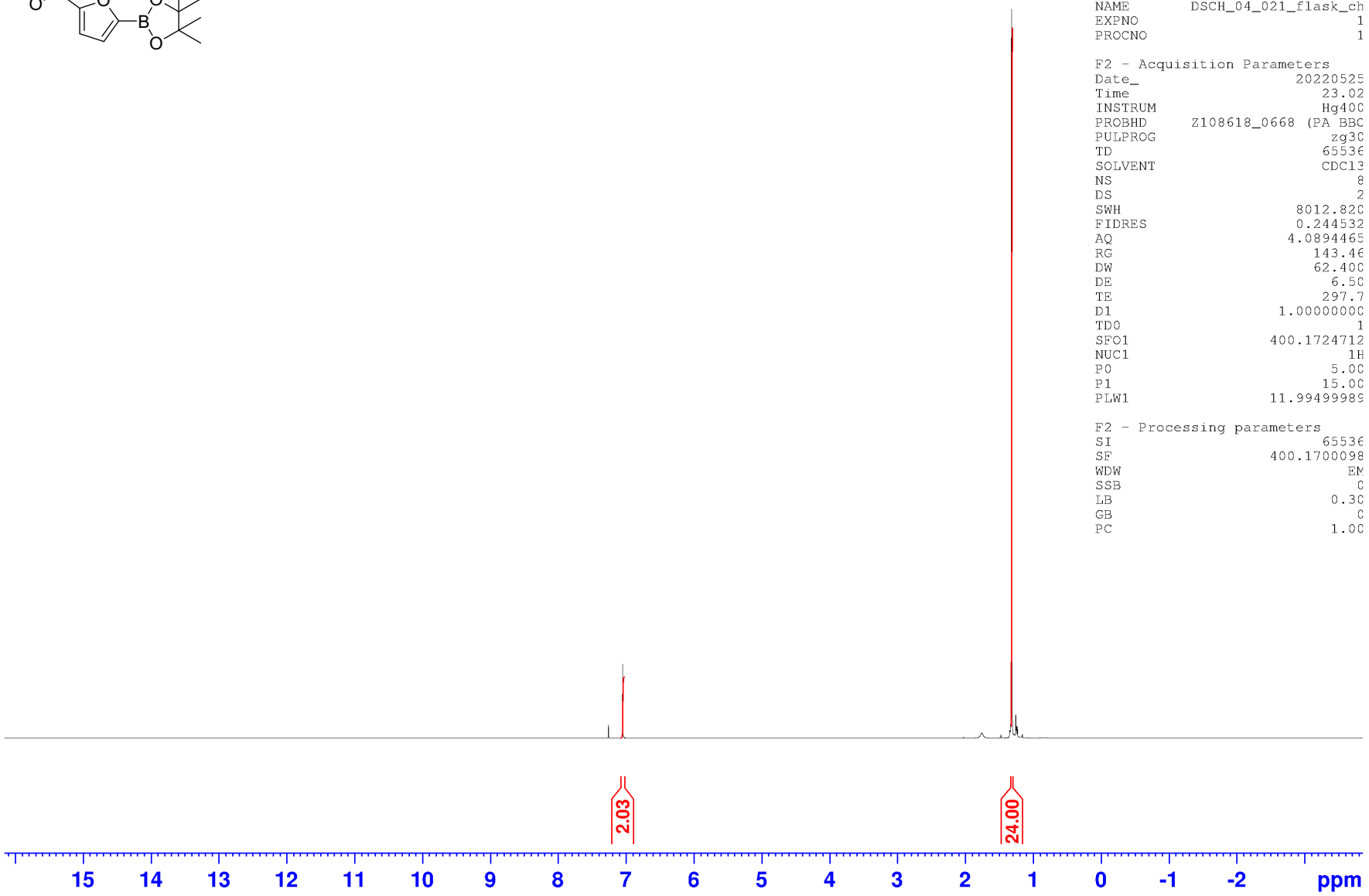
Current Data Parameters
NAME          DSCH_04_023_old_13C
EXPNO                           1
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20220527
Time                        14.59
INSTRUM                     spect
PROBHD      Z113652_0146 (PA BBC
PULPROG                  zgpg30
TD                        65536
SOLVENT                    DMSO
NS                          652
DS                            4
SWH                     42613.637
FIDRES                  1.300465
AQ                      0.7689557
RG                         2050
DW                         11.733
DE                          6.50
TE                         298.1
D1                     2.00000000
D11                    0.03000000
TD0                           1
SFO1                125.7243434
NUC1                        13C
P0                          3.10
P1                          9.30
PLW1                90.00000000
SFO2                499.9339997
NUC2                        1H
CPDPRG[2]               waltz16
PCPD2                      80.00
PLW2                21.42900085
PLW12                0.36564001
PLW13                0.18391000

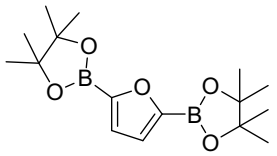
F2 - Processing parameters
SI                          32768
SF                  125.7080589
WDW                            EM
SSB                             0
LB                          10.00
GB                              0
PC                           1.40
```

^{1}H NMR, $CDCl_3$, 400 MHz: 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan (RV-15)





^{13}C NMR, $CDCl_3$, 101 MHz: 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan (RV-15)

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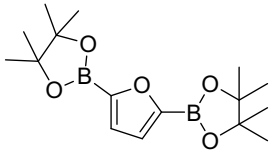
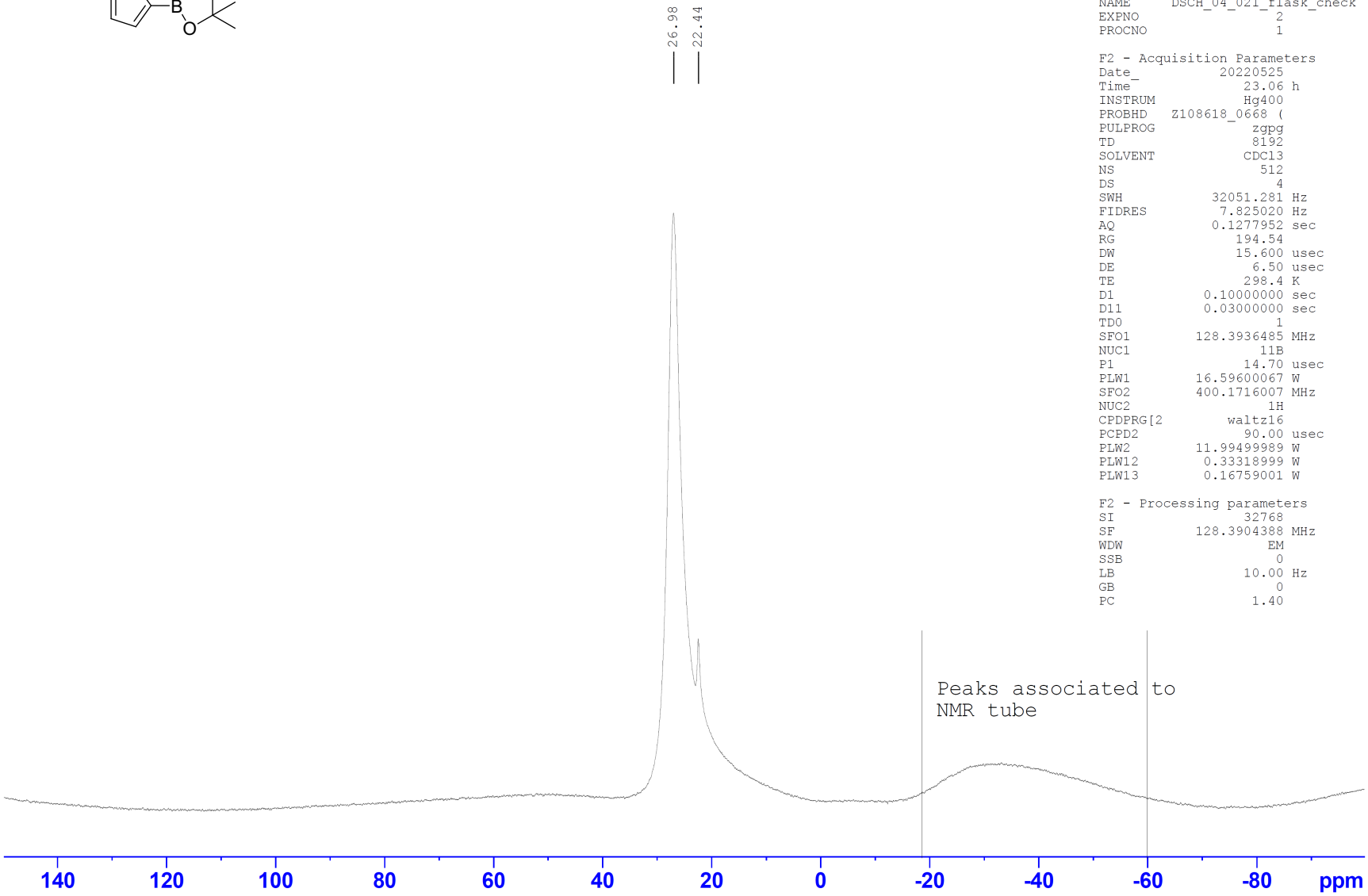
Current Data Parameters
NAME        DSCH_04_021_flask_ch
EXPNO                          2
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20220526
Time                       22.53
INSTRUM                  avh400
PROBHD      Z108618_0873 (PA BBO
PULPROG                  zgpg30
TD                        32768
SOLVENT                   CDCl3
NS                          512
DS                            4
SWH                   26041.666
FIDRES                 1.589457
AQ                    0.6291456
RG                        197.1
DW                        19.200
DE                          6.50
TE                         -32.4
D1                   1.00000000
D11                  0.03000000
TD0                           1
SFO1                100.6228298
NUC1                        13C
P0                         3.33
P1                        10.00
PLW1                47.86100006
SFO2                400.1316005
NUC2                        1H
CPDPRG[2]               waltz16
PCPD2                     90.00
PLW2                14.36999989
PLW12                0.34772000
PLW13                0.17490000

F2 - Processing parameters
SI                        32768
SF                  100.6127551
WDW                         EM
SSB                          0
LB                        1.00
GB                           0
PC                        1.40
```

^{11}B NMR {1H}, $CDCl_3$, 128 MHz: 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan (RV-15)



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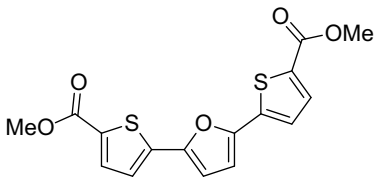
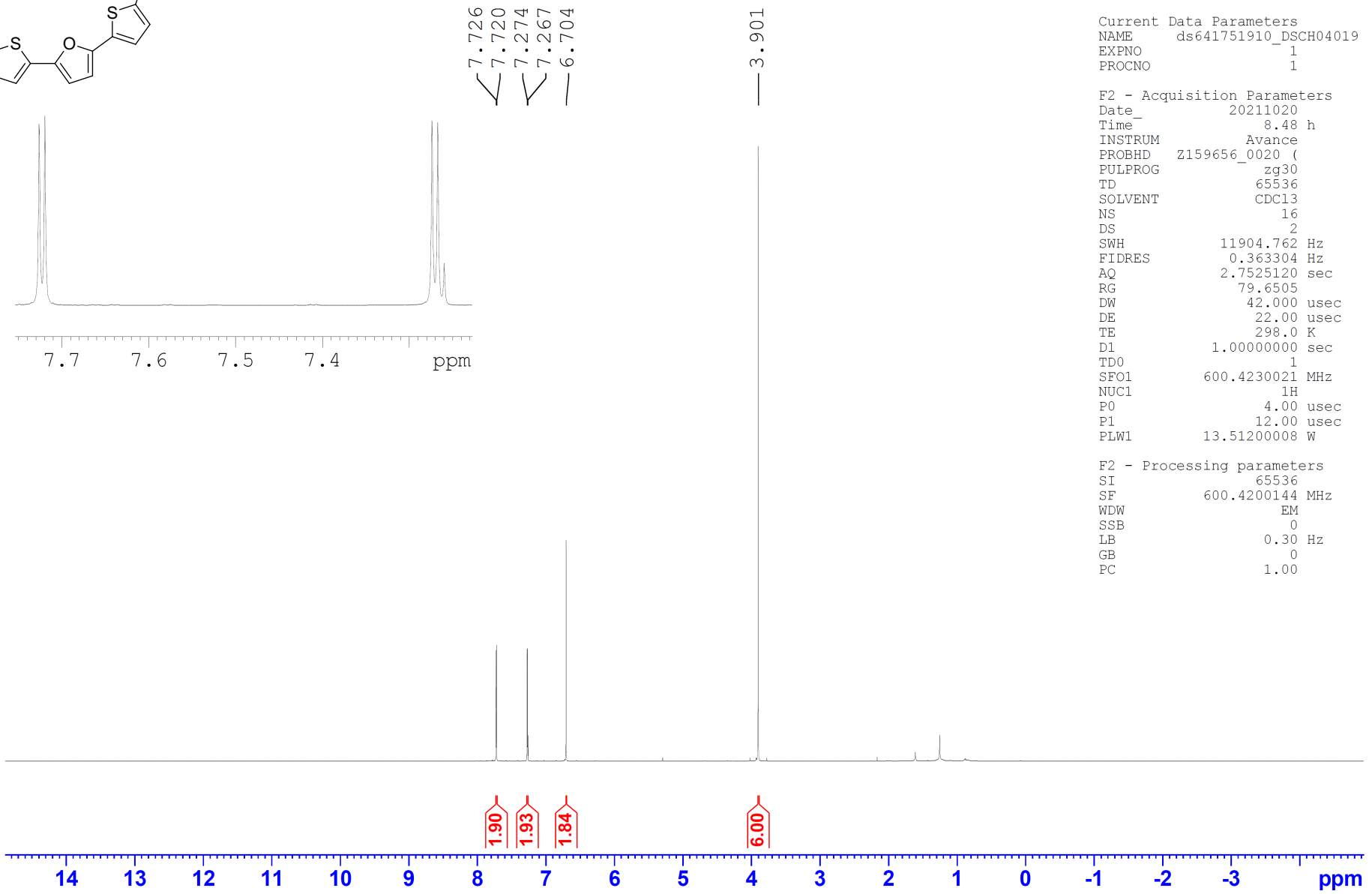
Current Data Parameters
NAME      DSCH_04_021_flask_check
EXPNO                           2
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20220525
Time                       23.06 h
INSTRUM                    Hg400
PROBHD   Z108618_0668 (
PULPROG                     zgpg
TD                          8192
SOLVENT                    CDCl3
NS                           512
DS                             4
SWH                    32051.281 Hz
FIDRES                  7.825020 Hz
AQ                     0.1277952 sec
RG                        194.54
DW                        15.600 usec
DE                         6.50 usec
TE                        298.4 K
D1                   0.10000000 sec
D11                  0.03000000 sec
TD0                            1
SFO1                128.3936485 MHz
NUC1                        11B
P1                        14.70 usec
PLW1                16.59600067 W
SFO2                400.1716007 MHz
NUC2                        1H
CPDPRG[2                waltz16
PCPD2                     90.00 usec
PLW2                11.99499989 W
PLW12                0.33318999 W
PLW13                0.16759001 W

F2 - Processing parameters
SI                         32768
SF                  128.3904388 MHz
WDW                           EM
SSB                            0
LB                        10.00 Hz
GB                             0
PC                         1.40
```

^{1}H NMR, $CDCl_3$, 600 MHz: Dimethyl 5,5'-(furan-2,5-diyl)bis(thiophene-2-carboxylate) (RV-12A)



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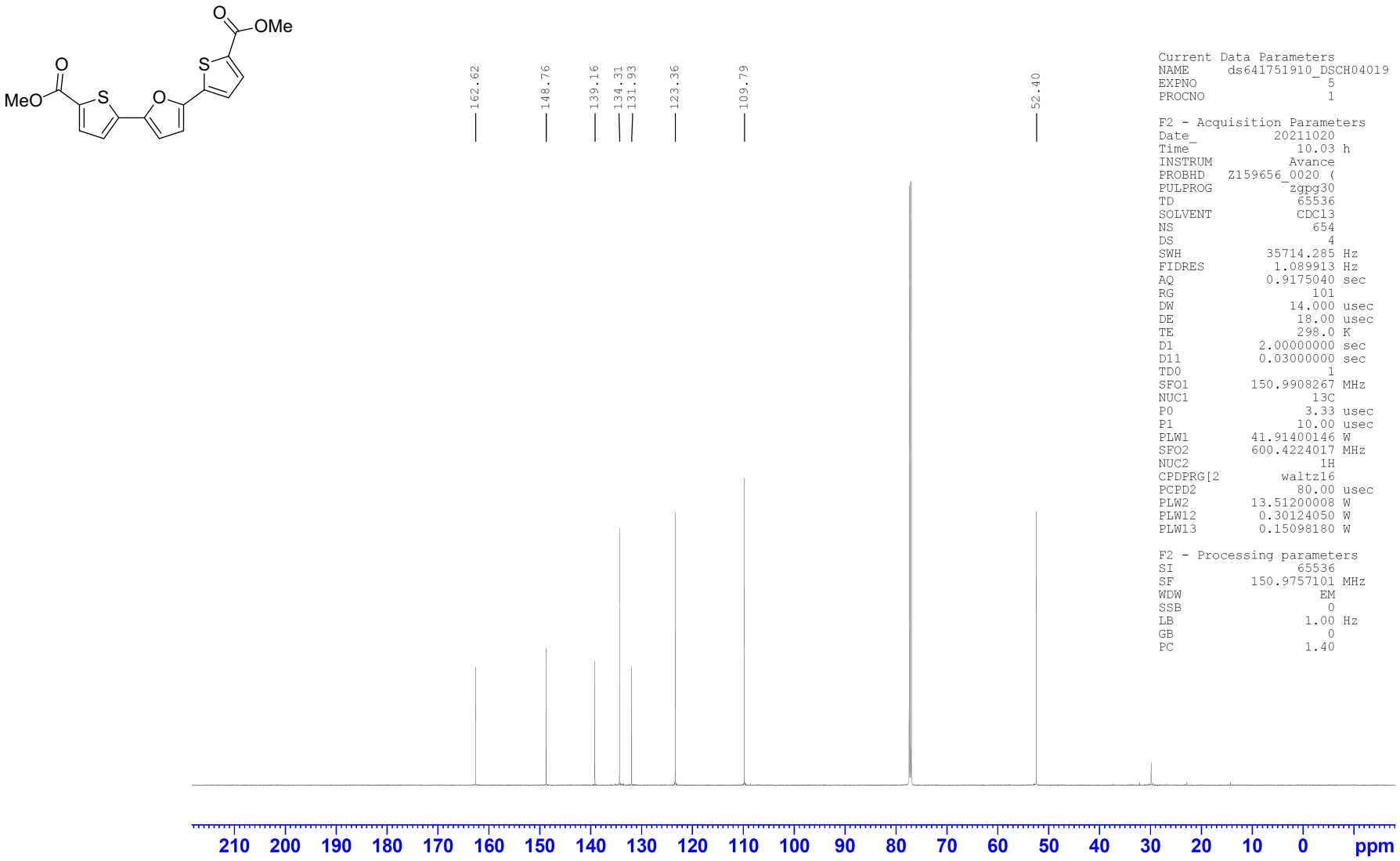
Current Data Parameters
NAME      ds641751910_DSCH04019
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_               20211020
Time                    8.48 h
INSTRUM                Avance
PROBHD    Z159656_0020 (
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                11904.762 Hz
FIDRES              0.363304 Hz
AQ                  2.7525120 sec
RG                    79.6505
DW                    42.000 usec
DE                    22.00 usec
TE                    298.0 K
D1                 1.00000000 sec
TD0                         1
SFO1              600.4230021 MHz
NUC1                       1H
P0                    4.00 usec
P1                   12.00 usec
PLW1              13.51200008 W

F2 - Processing parameters
SI                      65536
SF                600.4200144 MHz
WDW                        EM
SSB                         0
LB                   0.30 Hz
GB                          0
PC                       1.00
```

^{13}C NMR, $CDCl_3$, 151 MHz Dimethyl 5,5'-(furan-2,5-diyl)bis(thiophene-2-carboxylate) (RV-12A)

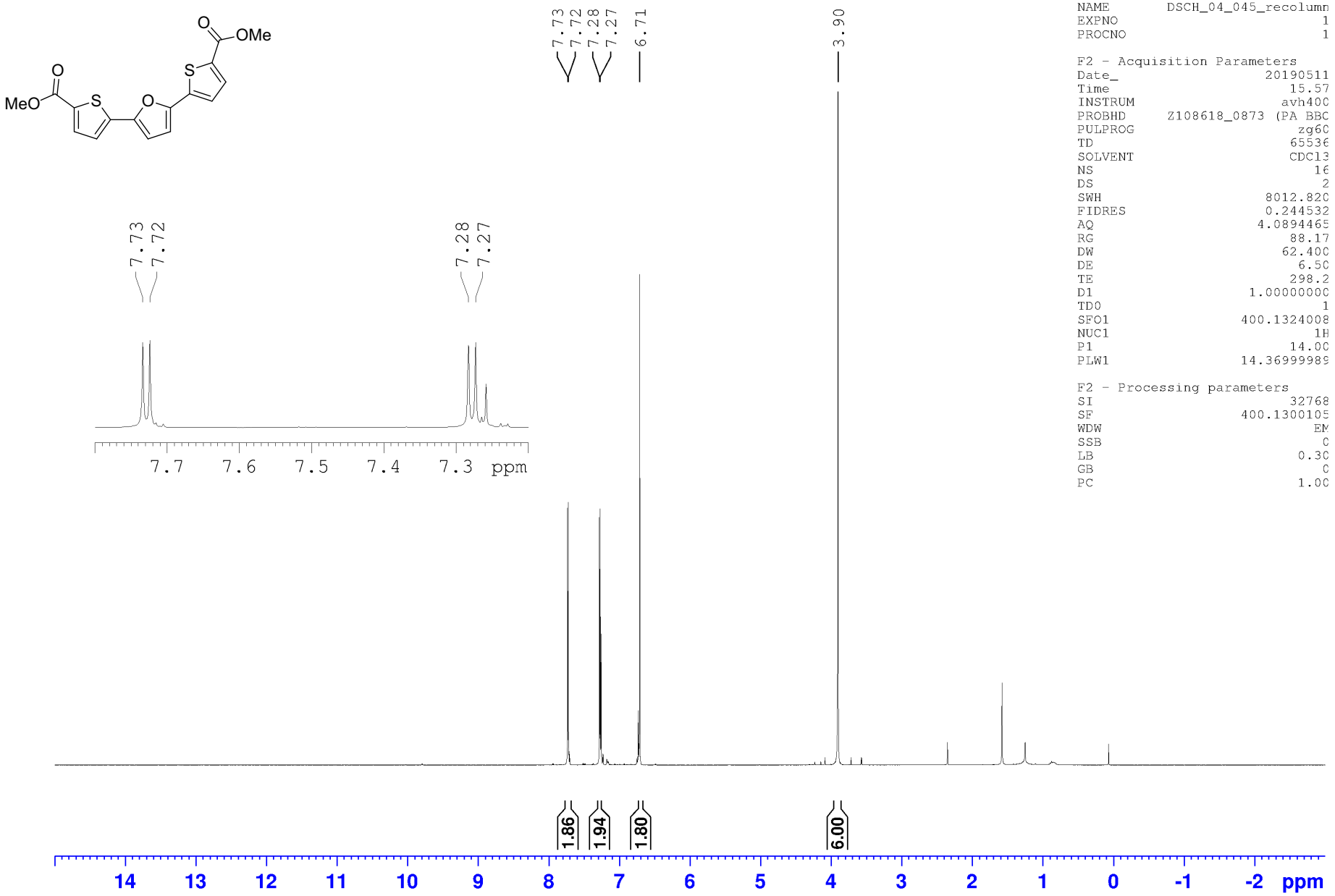



```
Current Data Parameters
NAME      ds641751910_DSCH04019
EXPNO                         5
PROCNO                        1

F2 - Acquisition Parameters
Date_              20211020
Time                 10.03 h
INSTRUM              Avance
PROBHD   Z159656_0020 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      654
DS                        4
SWH              35714.285 Hz
FIDRES            1.089913 Hz
AQ               0.9175040 sec
RG                      101
DW                 14.000 usec
DE                 18.00 usec
TE                 298.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1
SFO1           150.9908267 MHz
NUC1                    13C
P0                  3.33 usec
P1                 10.00 usec
PLW1           41.91400146 W
SFO2           600.4224017 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2              80.00 usec
PLW2           13.51200008 W
PLW12           0.30124050 W
PLW13           0.15098180 W

F2 - Processing parameters
SI                    65536
SF             150.9757101 MHz
WDW                      EM
SSB                       0
LB                 1.00 Hz
GB                        0
PC                     1.40
```

^{1}H NMR, $CDCl_3$, 600 MHz: Dimethyl 5,5'-(furan-2,5-diyl)bis(thiophene-2-carboxylate) (RV-12B)

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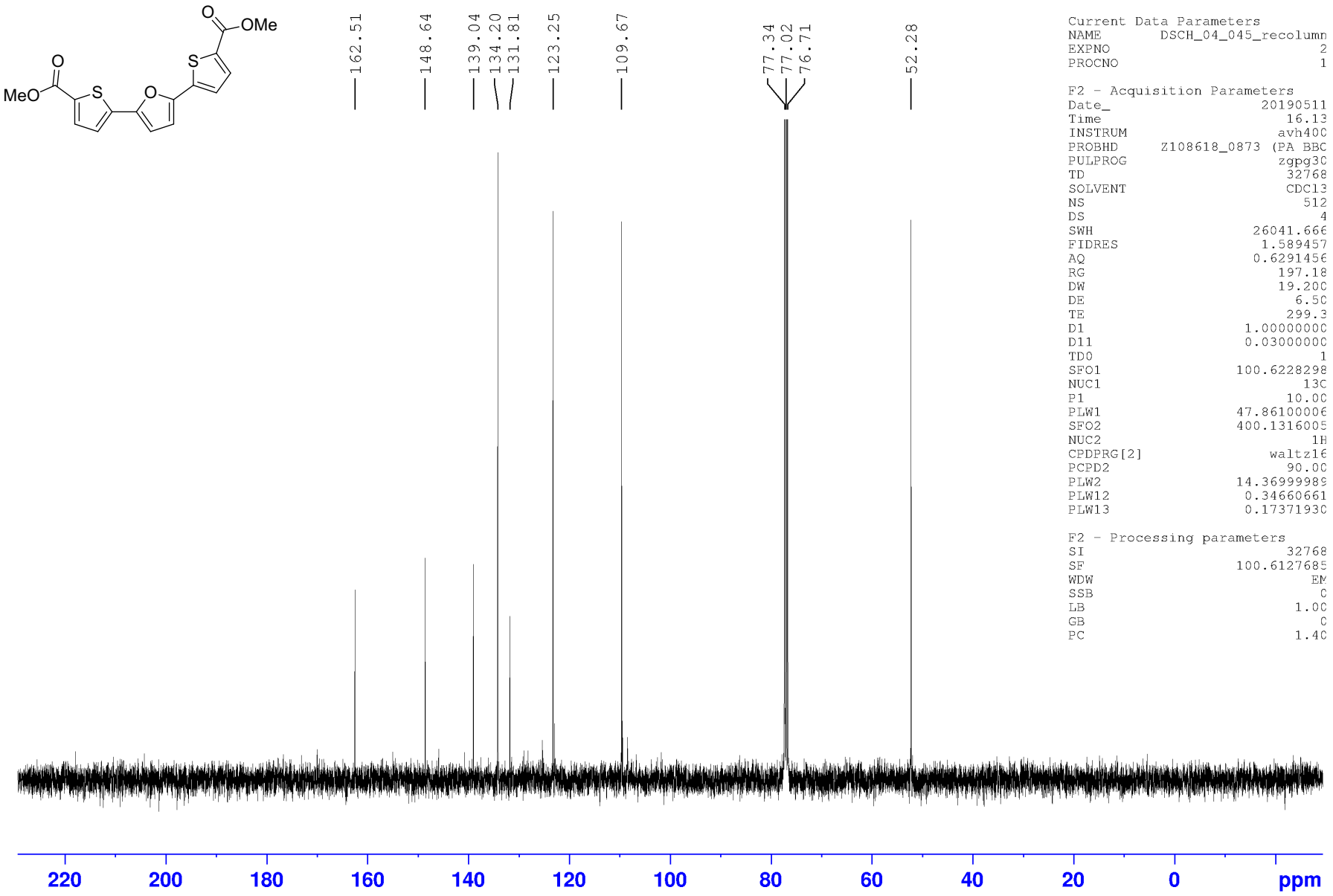
Current Data Parameters
NAME        DSCH_04_045_recolumn
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20190511
Time                       15.57
INSTRUM                  avh400
PROBHD      Z108618_0873 (PA BBC
PULPROG                    zg60
TD                        65536
SOLVENT                    CDCl3
NS                            16
DS                             2
SWH                     8012.820
FIDRES                  0.244532
AQ                     4.0894465
RG                         88.17
DW                         62.400
DE                          6.50
TE                         298.2
D1                    1.00000000
TD0                            1
SFO1                400.1324008
NUC1                        1H
P1                         14.00
PLW1                14.36999989

F2 - Processing parameters
SI                         32768
SF                  400.1300105
WDW                        EM
SSB                            0
LB                          0.30
GB                             0
PC                          1.00
```

^{13}C NMR, $CDCl_3$, 101 MHz Dimethyl 5,5'-(furan-2,5-diyl)bis(thiophene-2-carboxylate) (RV-12B)

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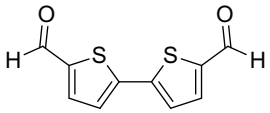
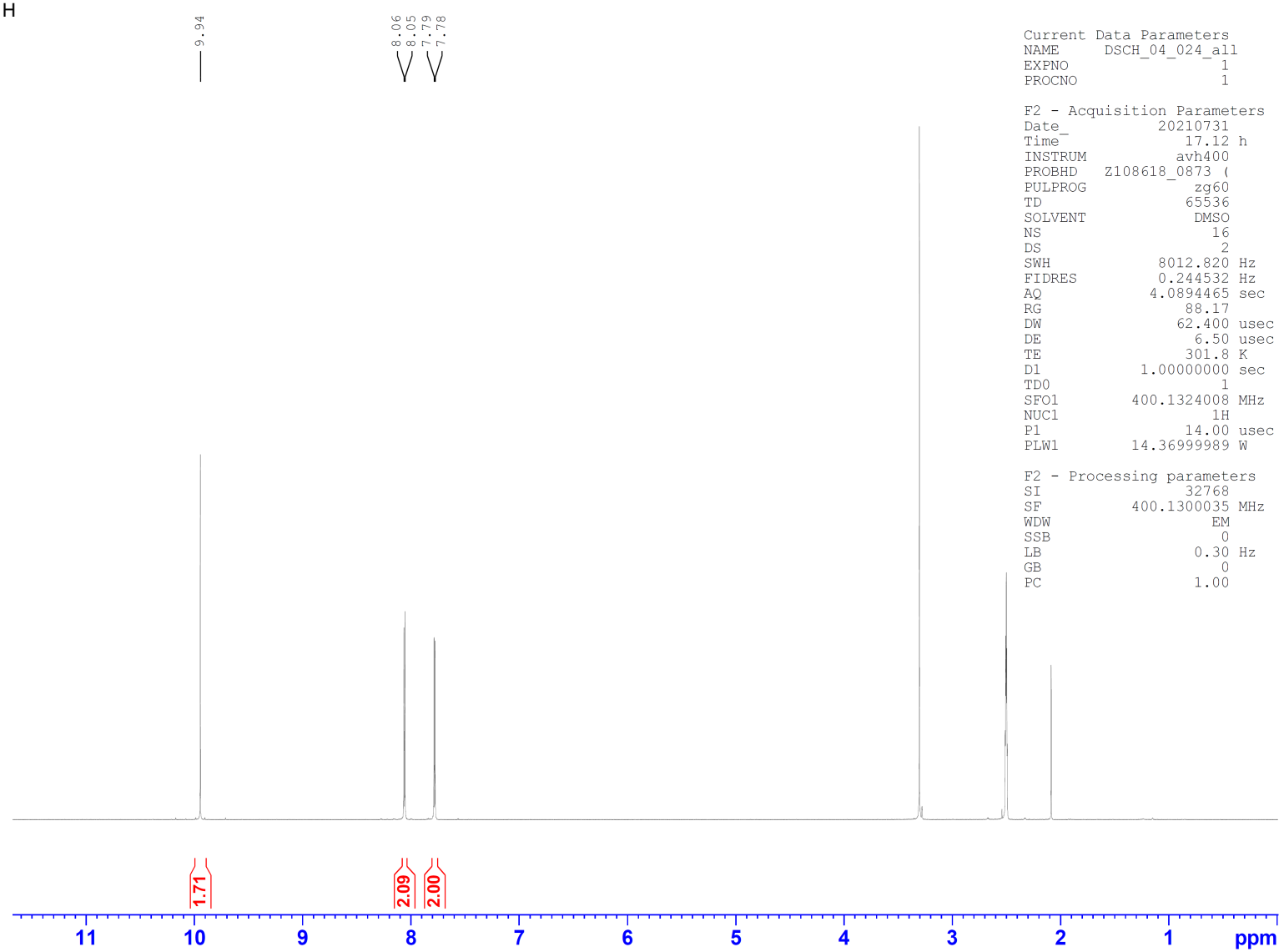
Current Data Parameters
NAME        DSCH_04_045_recolumn
EXPNO                          2
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20190511
Time                       16.13
INSTRUM                  avh400
PROBHD      Z108618_0873 (PA BBC
PULPROG                 zgpg30
TD                         32768
SOLVENT                  CDCl3
NS                           512
DS                             4
SWH                    26041.666
FIDRES                 1.589457
AQ                     0.6291456
RG                        197.18
DW                        19.200
DE                          6.50
TE                         299.3
D1                    1.00000000
D11                   0.03000000
TD0                            1
SFO1                 100.6228298
NUC1                         13C
P1                         10.00
PLW1                 47.86100006
SFO2                 400.1316005
NUC2                         1H
CPDPRG[2]                waltz16
PCPD2                      90.00
PLW2                 14.36999989
PLW12                 0.34660661
PLW13                 0.17371930

F2 - Processing parameters
SI                         32768
SF                   100.6127685
WDW                           EM
SSB                            0
LB                          1.00
GB                             0
PC                          1.40
```

^{1}H NMR, D_6-DMSO, 400 MHz: [2,2']bithiophenyl-5,5'-dicarbaldehyde (RV-13)



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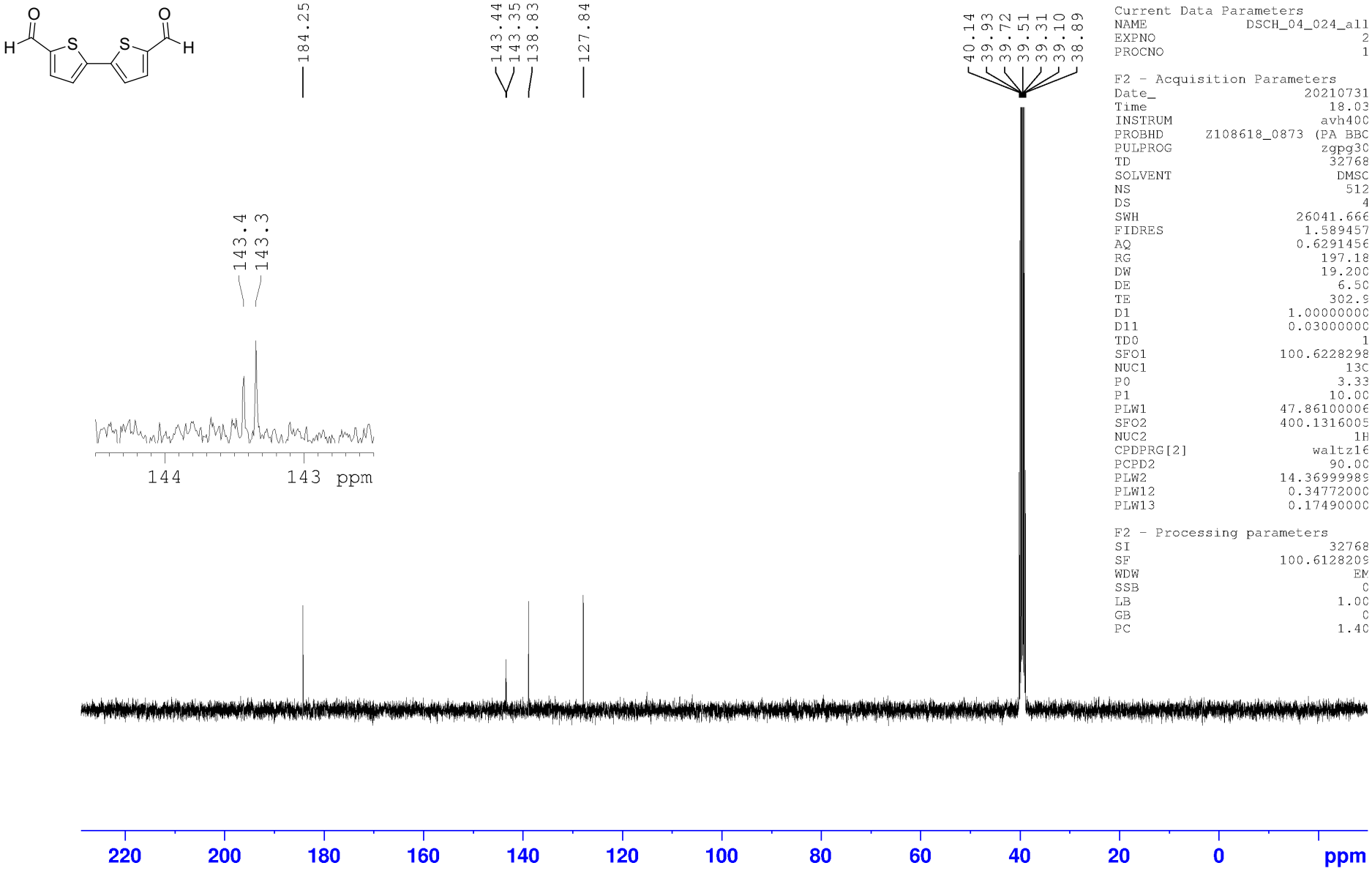
Current Data Parameters
NAME      DSCH_04_024_all
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20210731
Time              17.12 h
INSTRUM           avh400
PROBHD   Z108618_0873 (
PULPROG            zg60
TD                65536
SOLVENT            DMSO
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.244532 Hz
AQ             4.0894465 sec
RG                88.17
DW               62.400 usec
DE                6.50 usec
TE               301.8 K
D1            1.00000000 sec
TD0                   1
SFO1         400.1324008 MHz
NUC1                 1H
P1                14.00 usec
PLW1         14.36999989 W

F2 - Processing parameters
SI                32768
SF           400.1300035 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

^{1}H NMR, D_6-DMSO, 101 MHz: [2,2']bithiophenyl-5,5'-dicarbaldehyde (RV-13)

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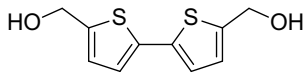
Current Data Parameters
NAME                  DSCH_04_024_a11
EXPNO                               2
PROCNO                              1

F2 - Acquisition Parameters
Date_                        20210731
Time                            18.03
INSTRUM                       avh400
PROBHD       Z108618_0873 (PA BBC
PULPROG                       zgpg30
TD                               32768
SOLVENT                         DMSO
NS                                512
DS                                  4
SWH                         26041.666
FIDRES                       1.589457
AQ                          0.6291456
RG                             197.18
DW                             19.200
DE                               6.50
TE                              302.9
D1                         1.00000000
D11                        0.03000000
TD0                                 1
SFO1                     100.6228298
NUC1                             13C
P0                              3.33
P1                             10.00
PLW1                     47.86100006
SFO2                     400.1316005
NUC2                             1H
CPDPRG[2]                    waltz16
PCPD2                          90.00
PLW2                     14.36999989
PLW12                     0.34772000
PLW13                     0.17490000

F2 - Processing parameters
SI                               32768
SF                       100.6128209
WDW                               EM
SSB                                0
LB                              1.00
GB                                 0
PC                              1.40
```

^{1}H NMR, D_6-DMSO, 400 MHz: 2,2'-bithiophene-5,5'-diyldimethanol (RV-14)

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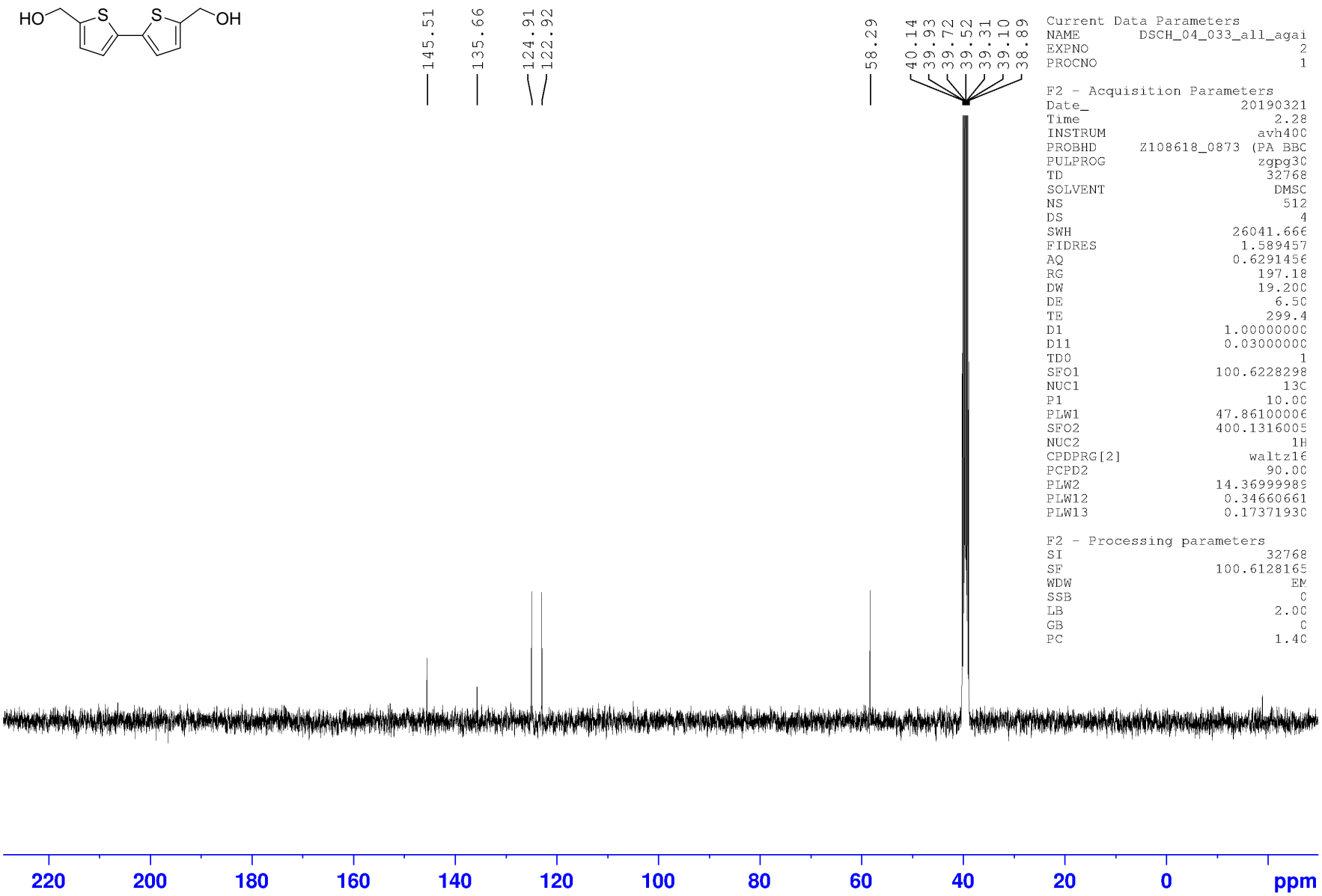
Current Data Parameters
NAME        DSCH_04_033_precip_check
EXPNO                              1
PROCNO                             1

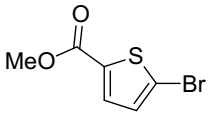
F2 - Acquisition Parameters
Date_                       20210922
Time                           20.39
INSTRUM                        Hg400
PROBHD      Z108618_0668 (PA BBO 400
PULPROG                        zg30
TD                            65536
SOLVENT                        DMSO
NS                                8
DS                                2
SWH                        8012.820 Hz
FIDRES                     0.244532 Hz
AQ                         4.0894465 sec
RG                            194.54
DW                            62.400 use
DE                             6.50 use
TE                            298.2 K
D1                         1.00000000 sec
TD0                               1
SFO1                   400.1724712 MHz
NUC1                             1H
P0                             5.00 use
P1                            15.00 use
PLW1                  11.99499989 W

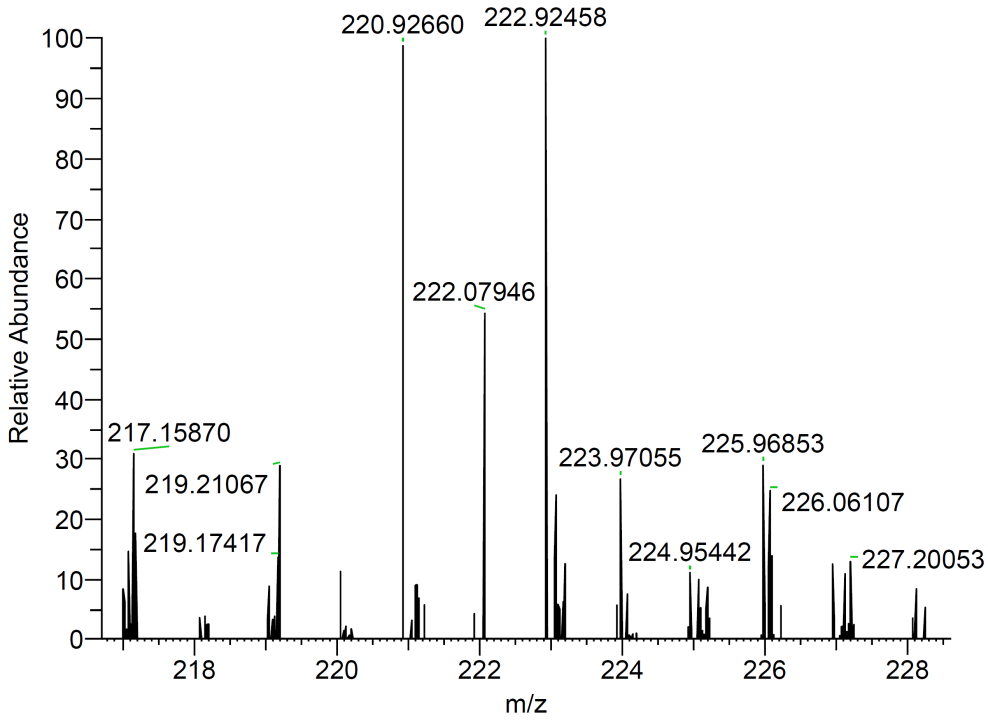
F2 - Processing parameters
SI                            65536
SF                     400.1700032 MHz
WDW                              EM
SSB                               0
LB                             0.30 Hz
GB                                0
PC                             1.00
```

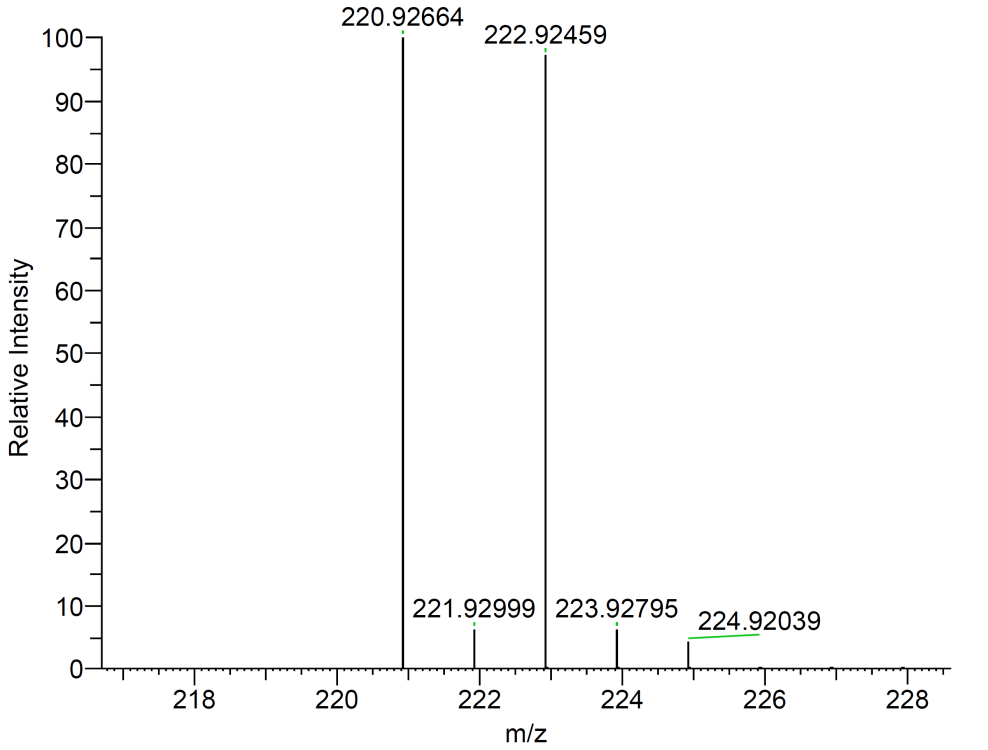
^{13}C NMR, D_6-DMSO, 400 MHz 2,2'-bithiophene-5,5'-diyldimethanol (RV-14)



High resolution mass spectraMethyl-5-bromothiophene-2-carboxylate (RV-7)

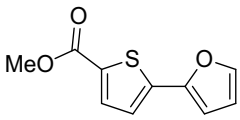


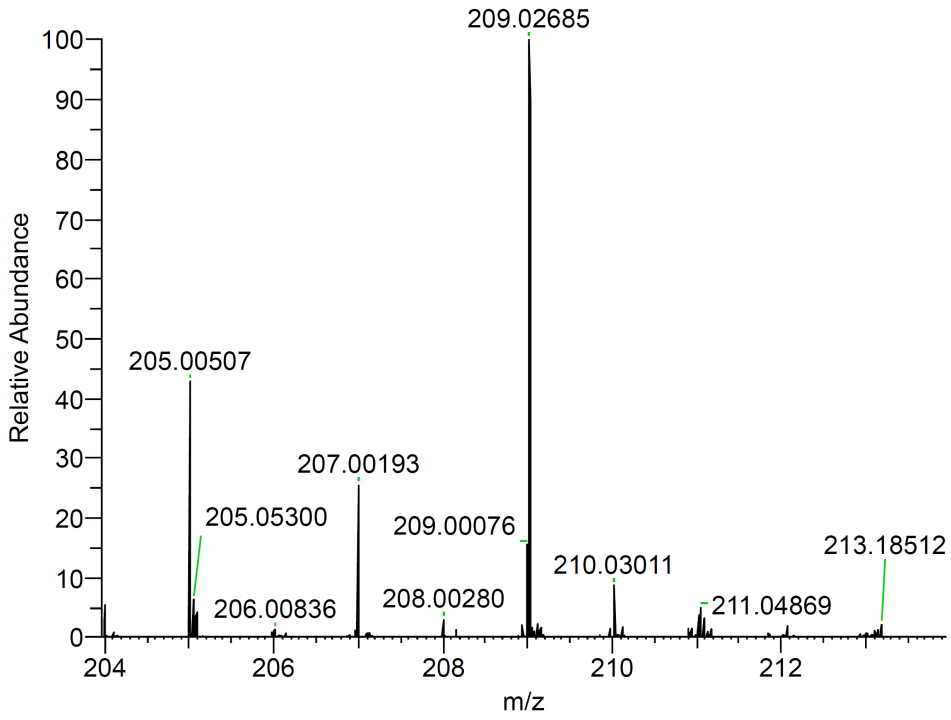




m/z	Formula	RDB	Delta ppm	Theo. Mass
220.92661	$C_6H_6O_2{}^{79}Br^{32}S$	3.5	-0.15	220.92664

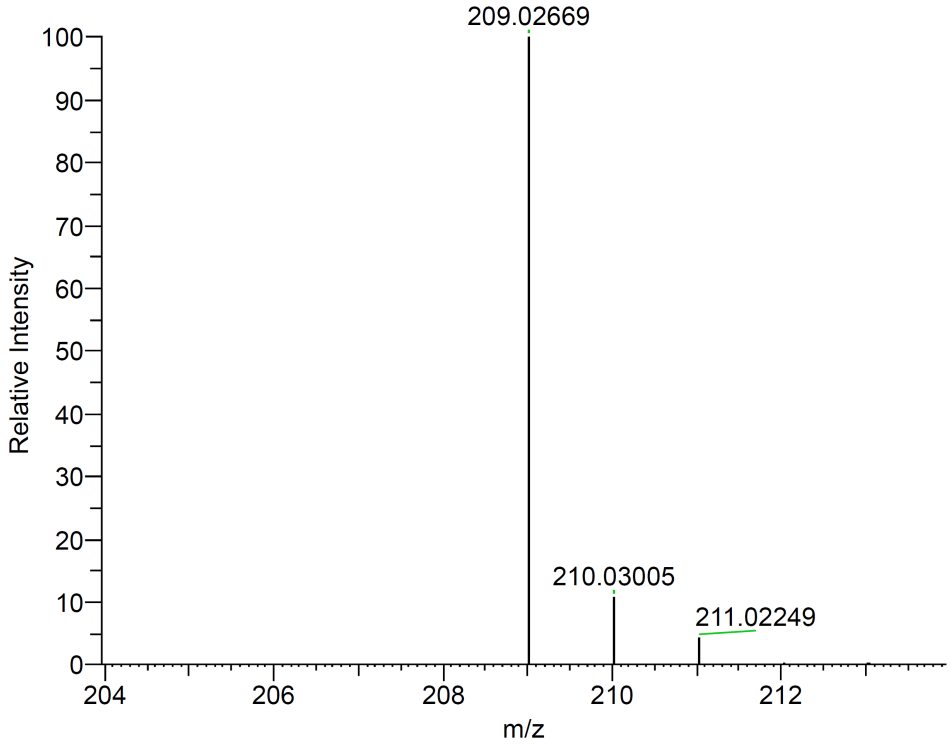
Methyl 5-(furan-2-yl)thiophene-2-carboxylate (RV-8)





NL: 1.73E5
MSSesi21804 #13-26 RT: 0.15-0.29 AV: 7
NL: 1.36E+006
T: FTMS {1,1} + p ESI Full lock ms
[80.00-1600.00]

Measured Spectrum

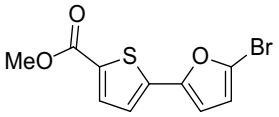


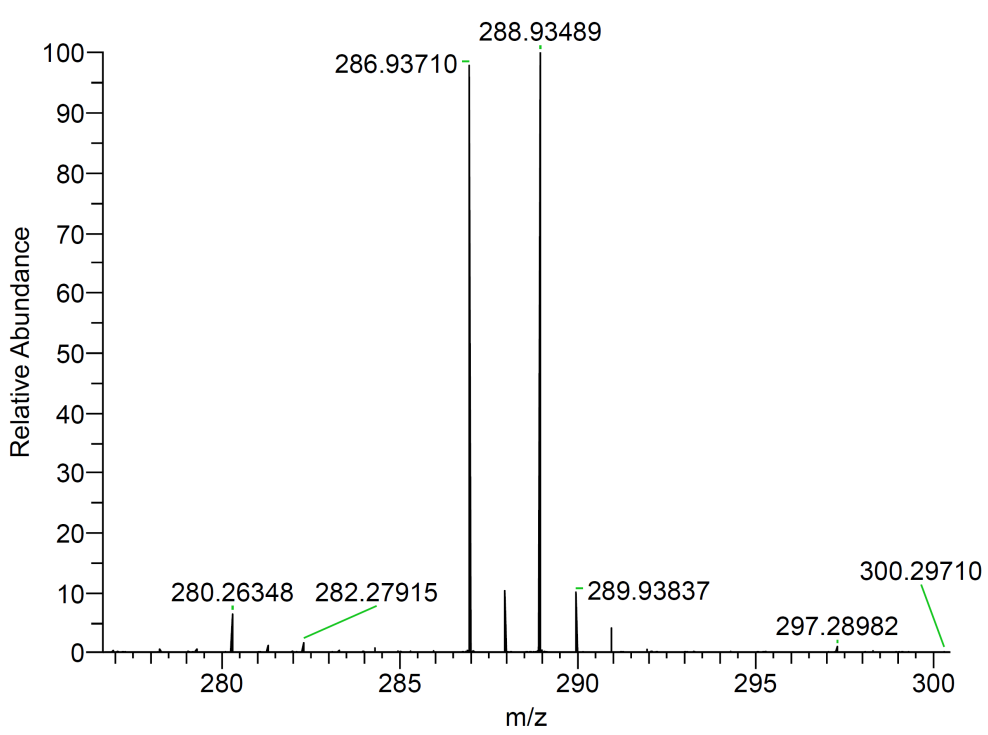
NL: 8.45E5
C10H9O3S1: C_{10} H_9 O_3 S Chrg 1 R:
1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
209.02684	$C_{10}H_9O_3{}^{32}S$	6.5	0.71	209.02669

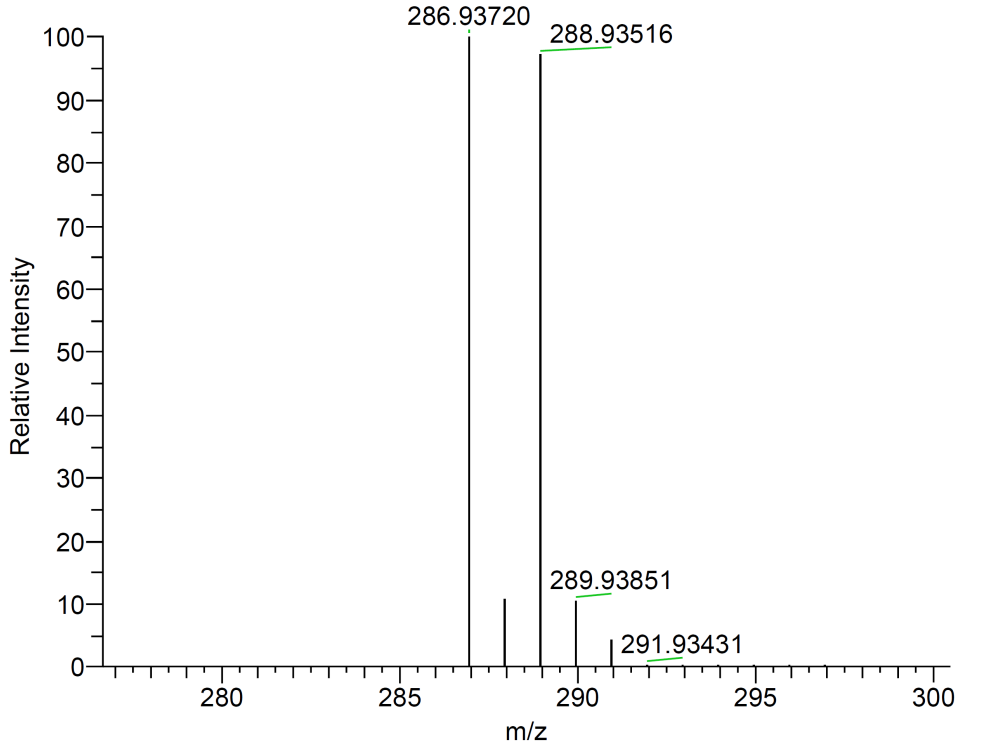
Methyl 5-(5-bromofuran-2-yl)thiophene-2-carboxylate (RV-9)





NL: 1.55E7
MSSapci21984 #11-27 RT: 0.12-0.31 AV: 9
NL: 1.55E+007
T: FTMS {1,1} + p APCI corona Full ms
[80.00-1600.00]

Measured Spectrum

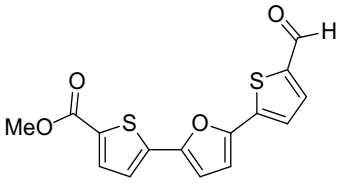


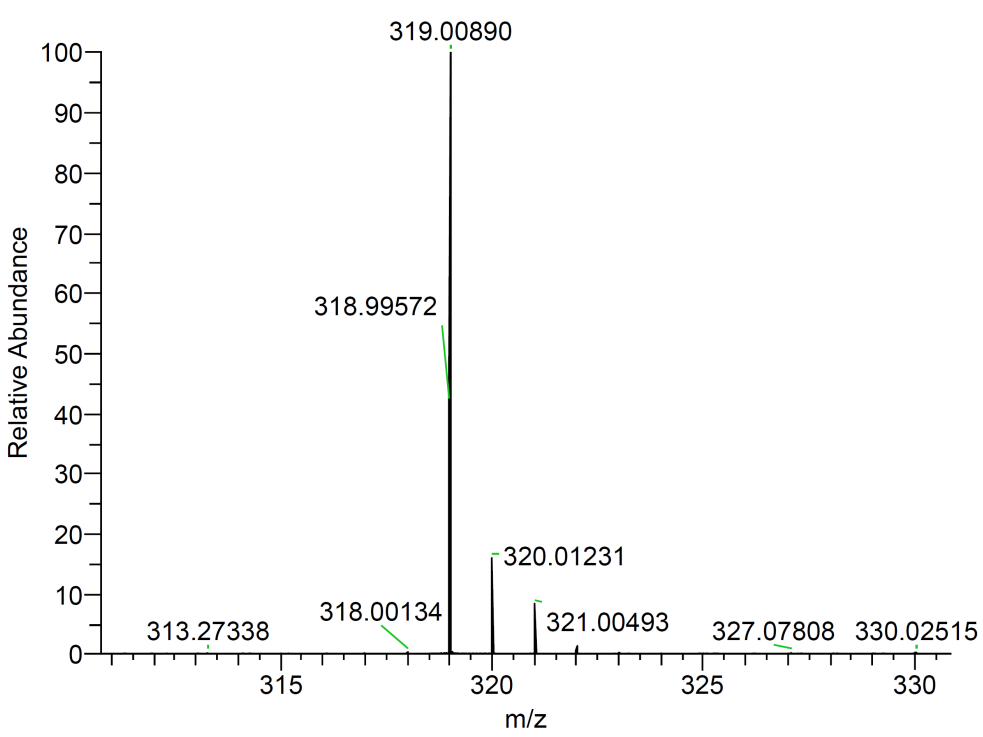
NL: 4.29E5
C10H8O3Br1S1: C_{10} H_8 O_3 Br S Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
286.93710	$C_{10}H_8O_3{}^{79}Br^{32}S$	6.5	-0.35	286.93720

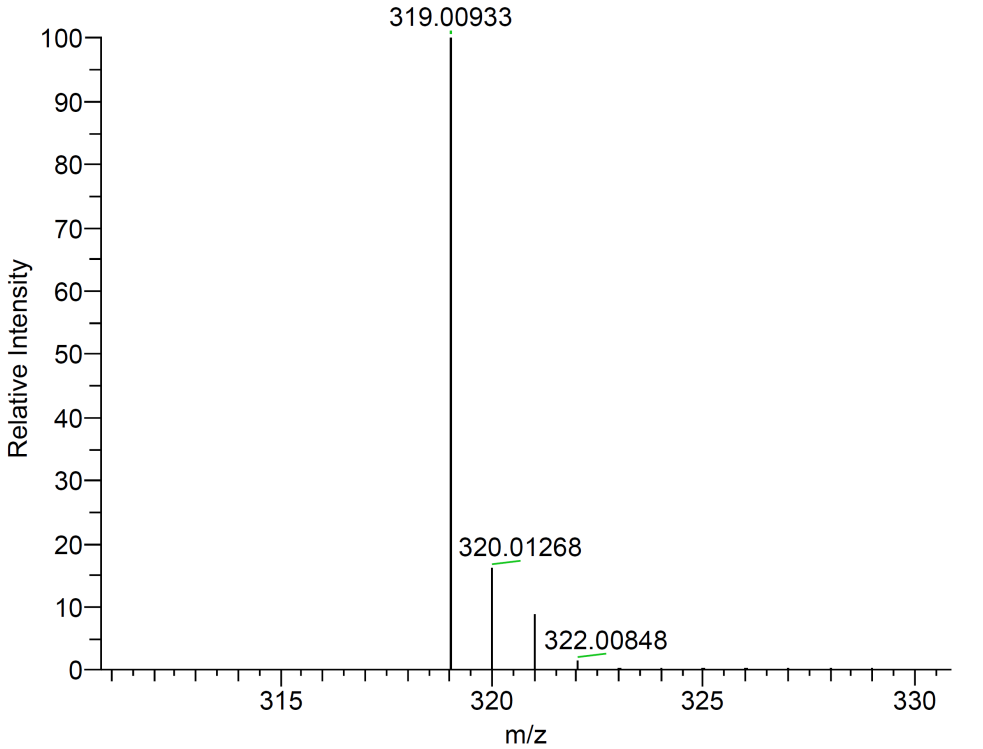
Methyl 5-[5-(5-formylthiophen-2-yl)furan-2-yl]thiophene-2-carboxylate (RV-11)





NL: 4.24E7
MSSapci21985 #11-27 RT: 0.13-0.31 AV: 9
NL: 4.24E+007
T: FTMS {1,1} + p APCI corona Full ms
[80.00-1600.00]

Measured Spectrum

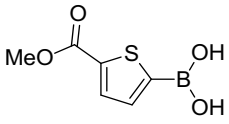


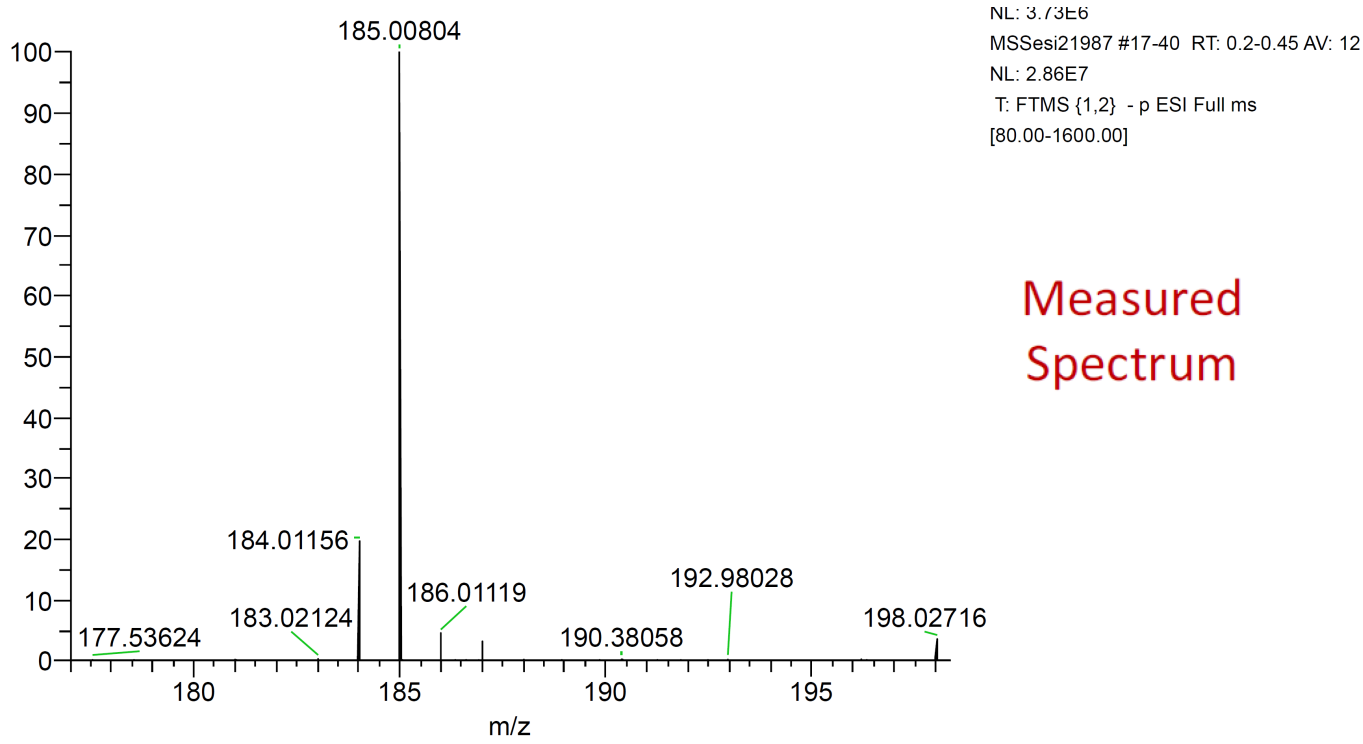
NL: 7.58E5
C15H11O4S2: $C_{15}H_{11}O_4S_2$ Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
319.00891	$C_{15}H_{11}O_4{}^{32}S_2$	10.5	-1.3	319.00933

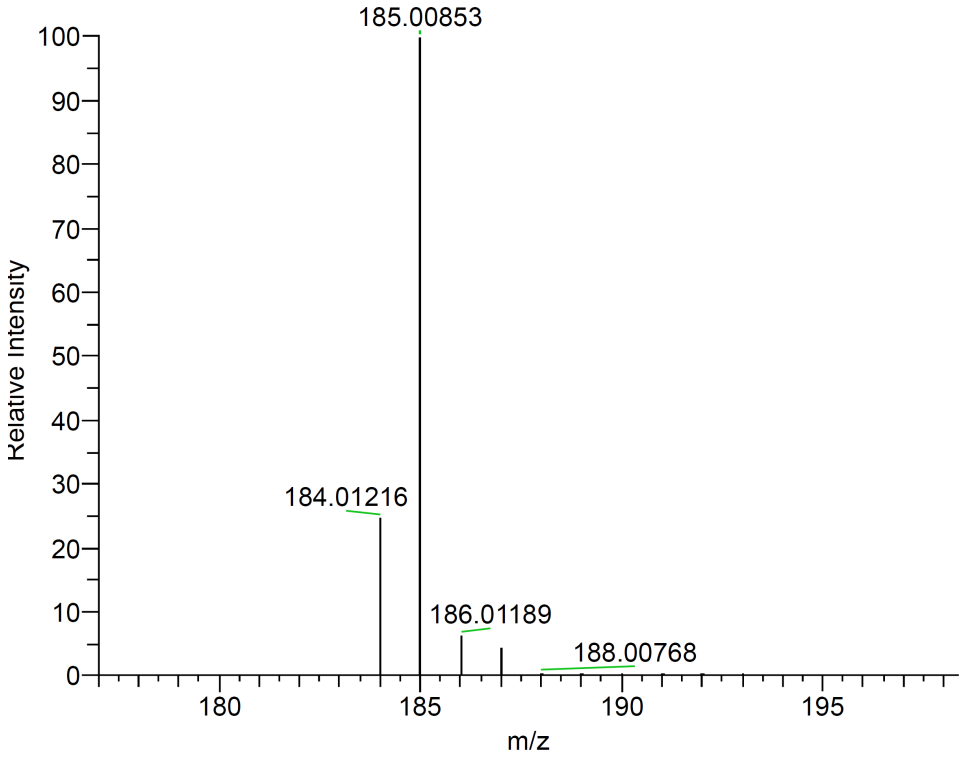
[5-(methyoxycarbonyl)thiophen-2-yl)boronic acid (RV-10)





NL: 3.73E6
MSSesi21987 #17-40 RT: 0.2-0.45 AV: 12
NL: 2.86E7
T: FTMS {1,2} - p ESI Full ms
[80.00-1600.00]

Measured Spectrum

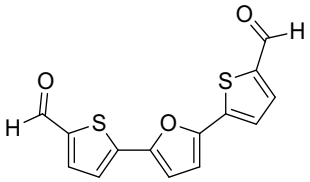


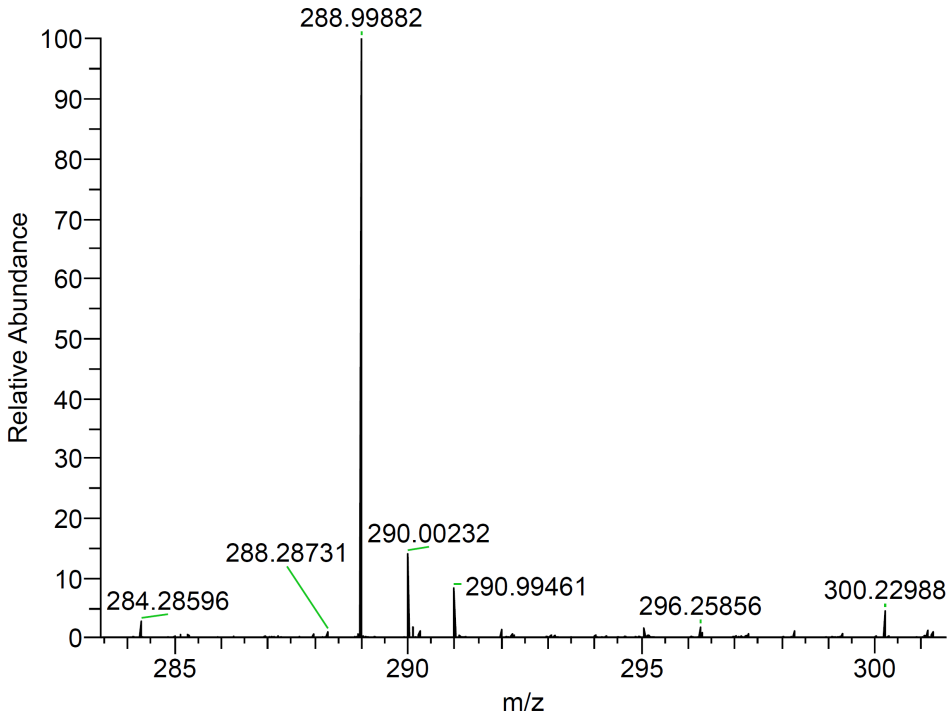
NL: 7.05E5
C6H6O4B1S1: C_6 H_6 O_4 B S Chrg -1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

n/z	Formula	RDB	Delta ppm	Theo. Mass
184.01157	$C_6H_6O_4{}^{10}B^{32}S$	4	-3.25	184.01216

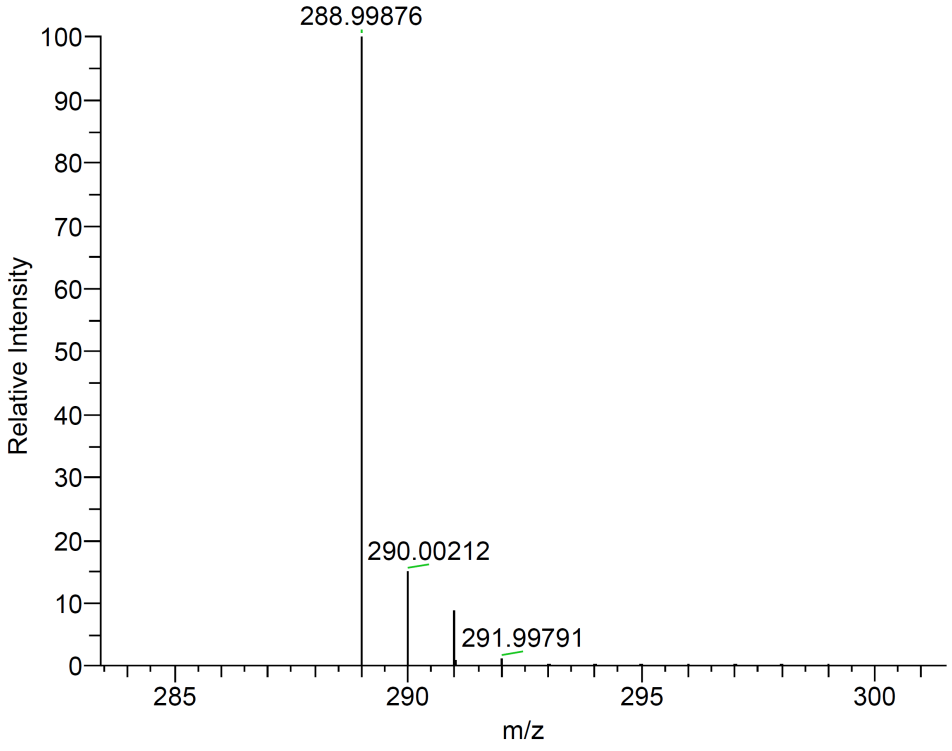
2,5-bis(5-formylthiophen-2-yl)furan (RV-6)





NL: 1.55E6
MSSesi21988 #13-27 RT: 0.15-0.31 AV: 8
NL: 2.96E+006
T: FTMS {1,1} + p ESI Full lock ms
[80.00-1600.00]

Measured Spectrum

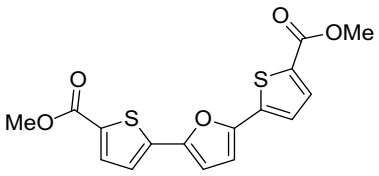


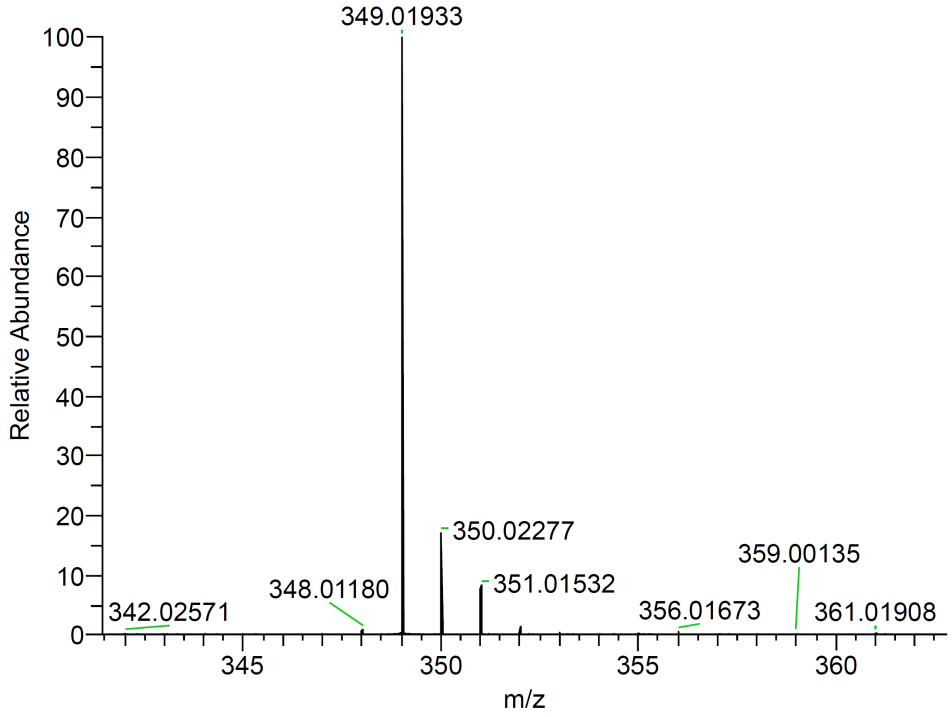
NL: 7.69E5
C14H9O3S2: $C_{14}H_9O_3S_2$ Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
288.99881	$C_{14}H_9O_3{}^{32}S_2$	10.5	0.17	288.99876

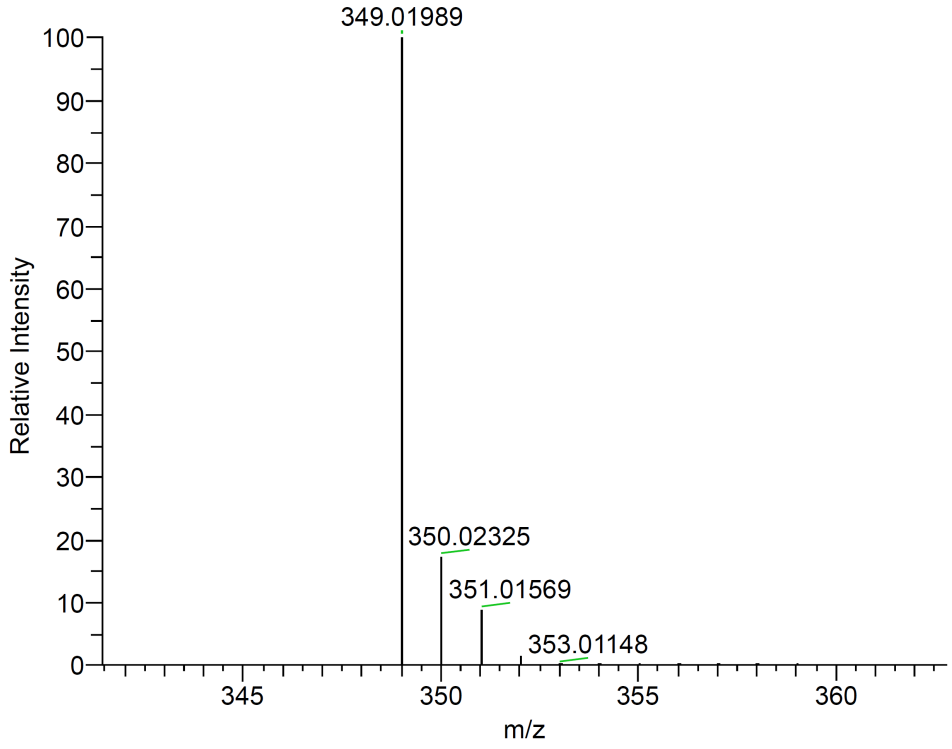
Dimethyl 5,5'-(furan-2,5-diyl)bis(thiophene-2-carboxylate) (RV-12)





NL: 5.17E7
MSSapci21986 #11-27 RT: 0.13-0.31 AV: 9
NL: 5.17E+007
T: FTMS {1,1} + p APCI corona Full ms
[80.00-1600.00]

Measured Spectrum

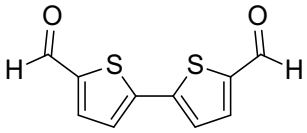


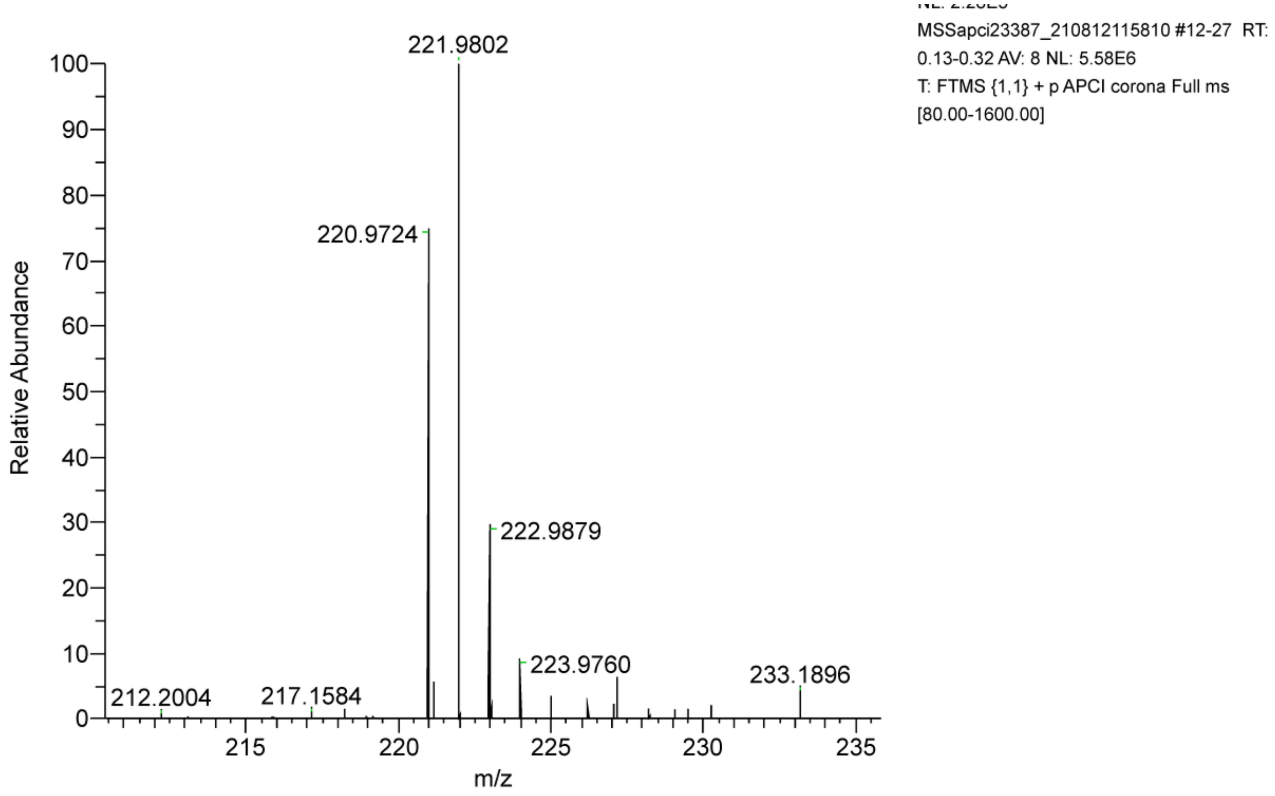
NL: 7.48E5
C16H13O5S2: $C_{16}H_{13}O_5S_2$ Chrg 1 R: 1000000 Res. Pwr. @FWHM

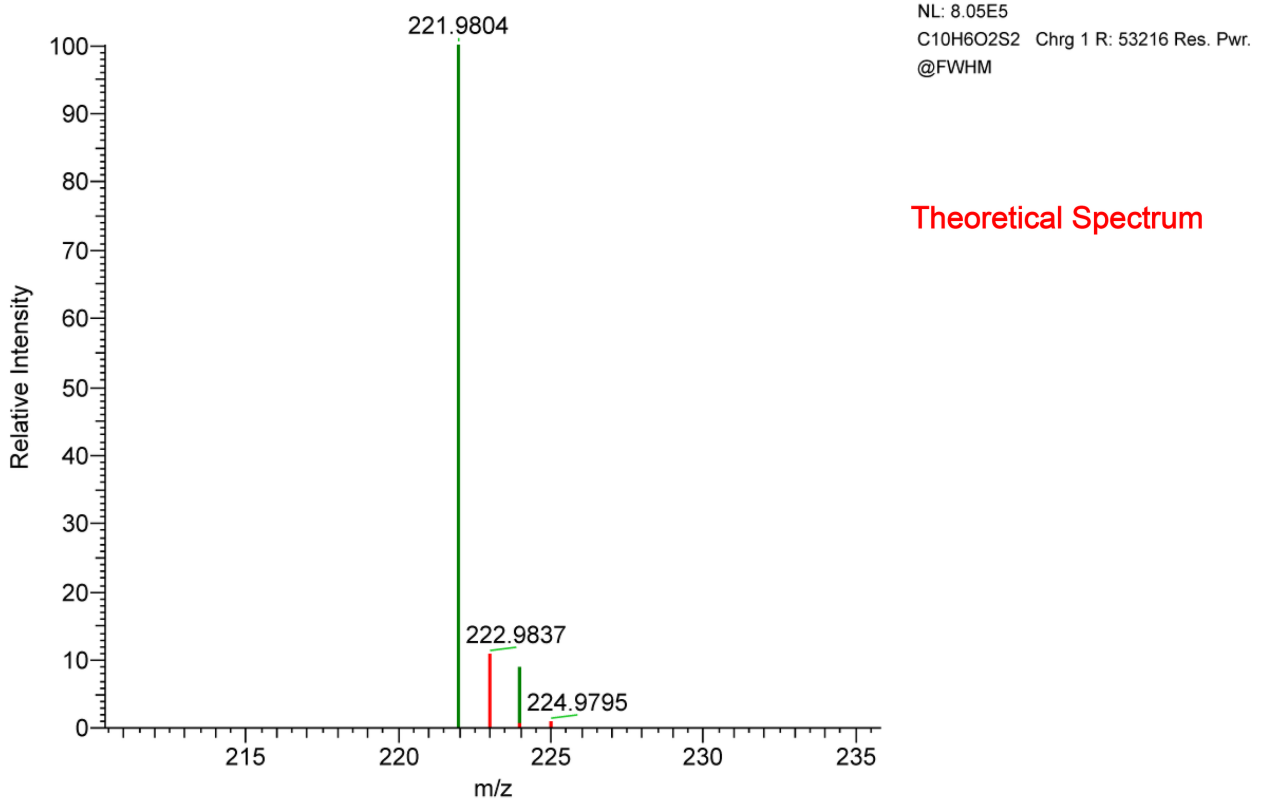
Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
349.01932	$C_{16}H_{13}O_5{}^{32}S_2$	10.5	-1.64	349.01989

[2,2']bithiophenyl-5,5'-dicarbaldehyde (RV-13)



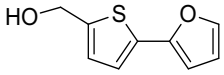




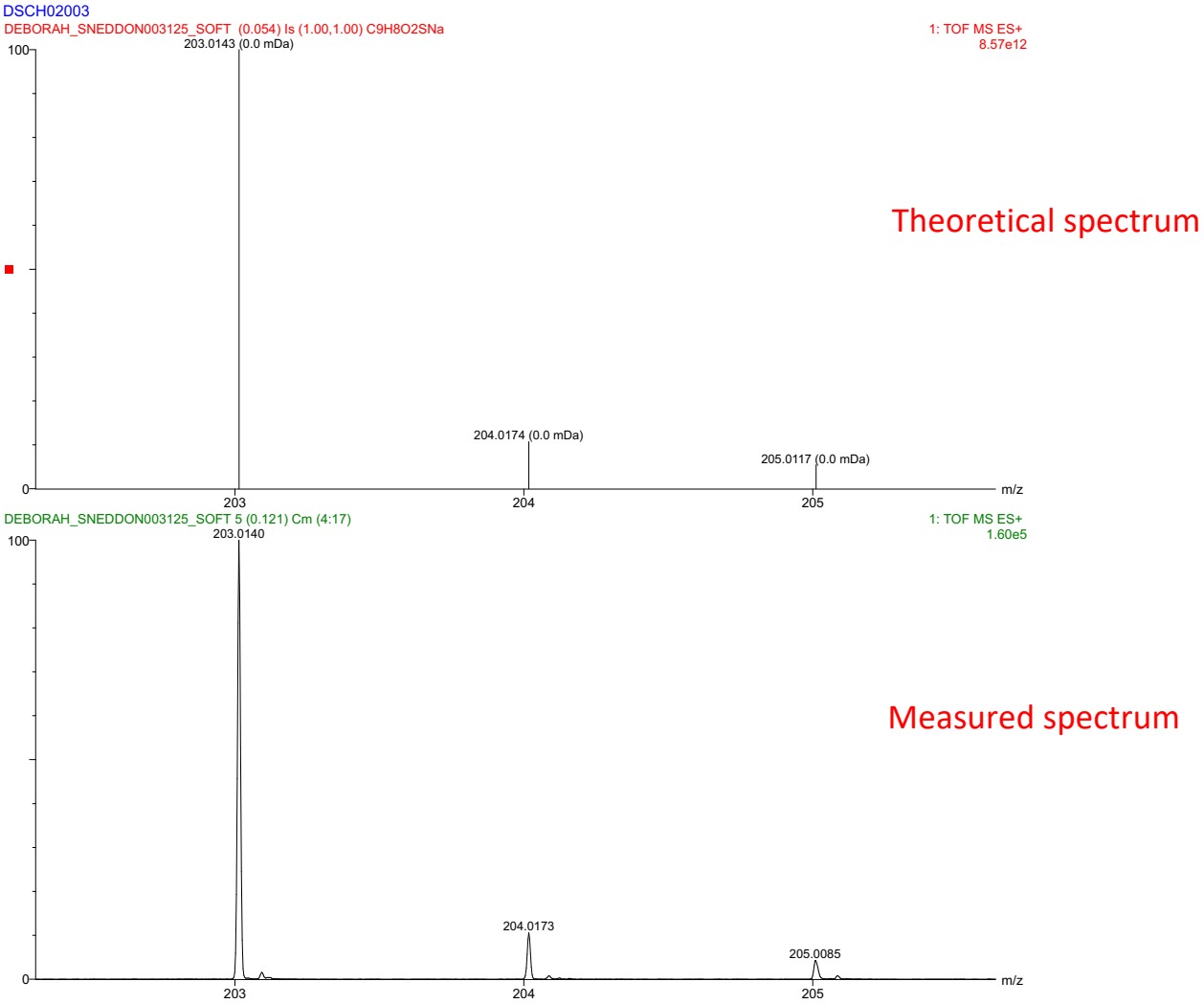
Theoretical Spectrum

Peak Mass	Display...	Combin...	RDB	Delta [p...	Theo. m...	Rank	Combin...	# Match...	# Misse...	MS Cov....	Pattern...	MSMS...
221.9802	$C_{10}H_6O...$	21.531...	8.00	-0.77	221.98...	1	67.833...	2	3	70.406...	89.482...	(Collec...

5-(Furan-2-yl)thiophene-2-methanol (RV-27)



For this sample ESI mass spectra were obtained using a Waters Xevo G2 Q-ToF HRMS (Wilmslow, UK) equipped with analytical flow ESI source. ESI experimental parameters were: capillary voltage 0.85 kV, sampling cone 5 au, extraction cone 2.5 au, source temperature 100 °C and desolvation gas 200 °C with a desolvation gas flow of 600 L h-1 and no cone gas. MS conditions were MS1 in resolution mode between 100-750 Da. Accurate mass data were obtained using MassLynx software.



Elemental Composition Report

Single Mass Analysis

Tolerance = 10000.0 PPM / DBE: min = -80.0, max = 250.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

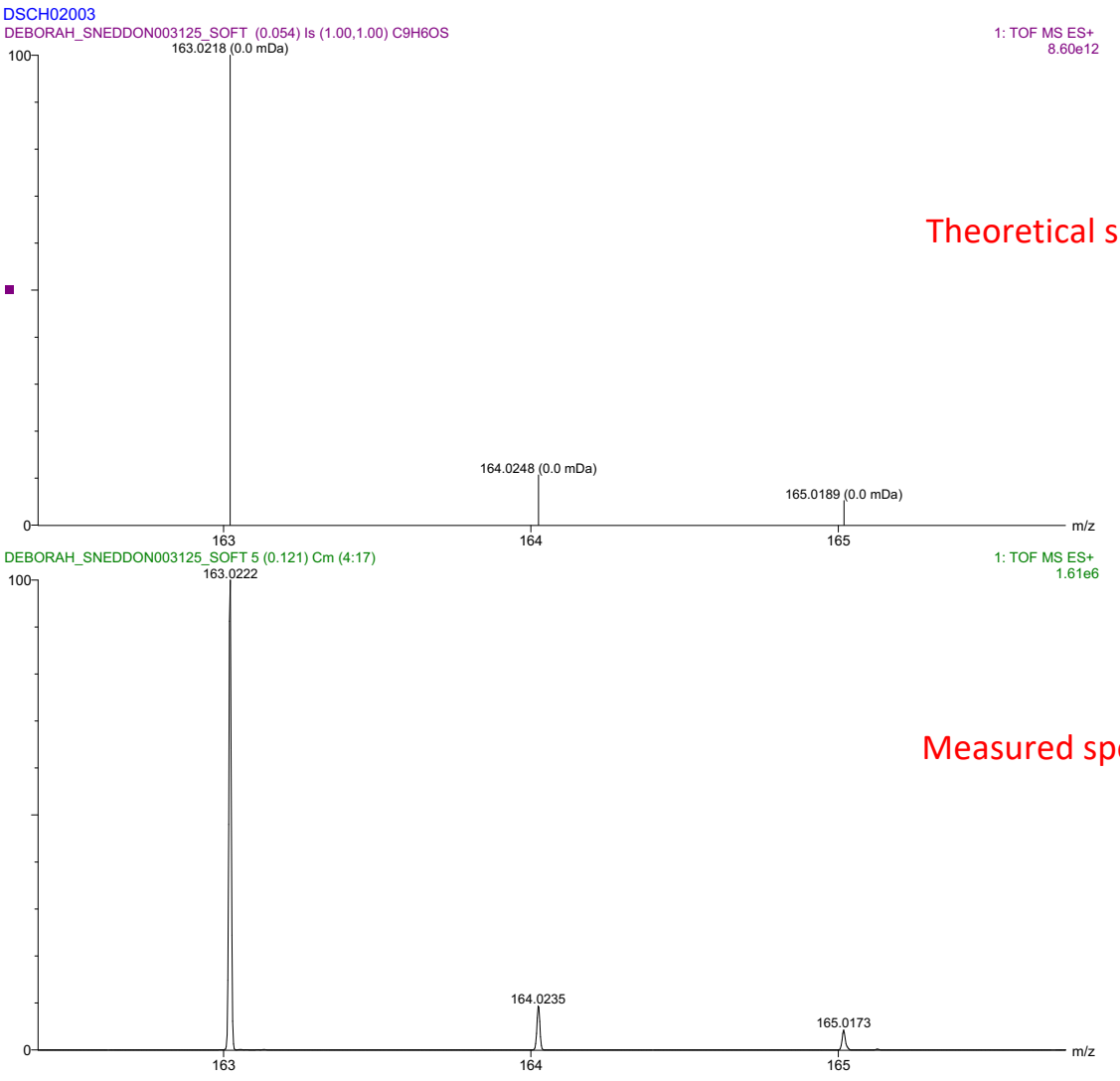
1 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 9-9 H: 0-150 O: 2-2 Na: 1-1 S: 1-1

Minimum:				-80.0					
Maximum:		5.0	10000.0		250.0				
Mass	Calc. Mass	mDa	PPM		DBE	i-FIT	Norm		Conf(%) Formula
203.0144	203.0143	0.1	0.5	5.5	698.7		n/a	n/a	C9 H8 O2 Na S

Please note that in this sample, a significant peak was observed corresponding to $[M\text{-}H_2O+H]^+$ in ESI positive. Spectrum shown below.



Elemental Composition Report

Single Mass Analysis

Tolerance = 10000.0 PPM / DBE: min = -80.0, max = 250.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

1 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

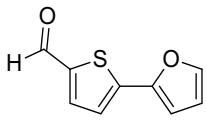
Elements Used:

C: 9-9 H: 0-150 O: 1-1 S: 1-1

Minimum:				-80.0						
Maximum:		5.0	10000.0		250.0					
Mass	Calc. Mass	mDa	PPM		DBE	i-FIT	Norm		Conf(%)	Formula
163.0213	163.0218	-0.5	-3.1	6.5	916.5		n/a	n/a	C9 H7 O S	

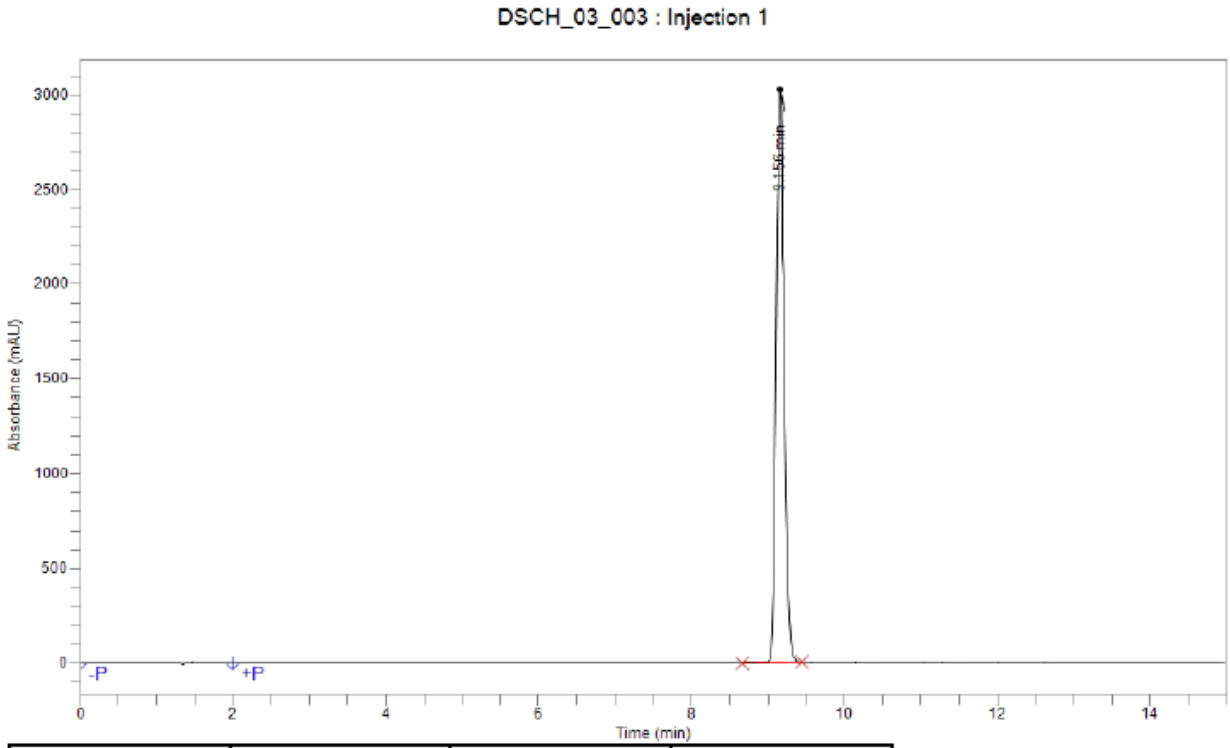
HPLC traces

5-(furan-2-yl)thiophene-2-carbaldehyde (RV-1)



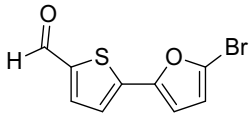
Method and gradient as described in General Experimental *without* TFA (0.1%) (254 nm).

Acquisition Method	Purity short run @254 nm
Acquisition Date/Time	7/18/2018 3:00 pm
Injection Volume	10
Sample Name	DSCH_03_003
Sample Description	
Batch Description	



Time	Height	Area	Area %
8.763	3,762.6	25,572.9	0.12
9.156	3,060,092.6	21,751,553.4	99.88
Total		21,777,126.3	100.00

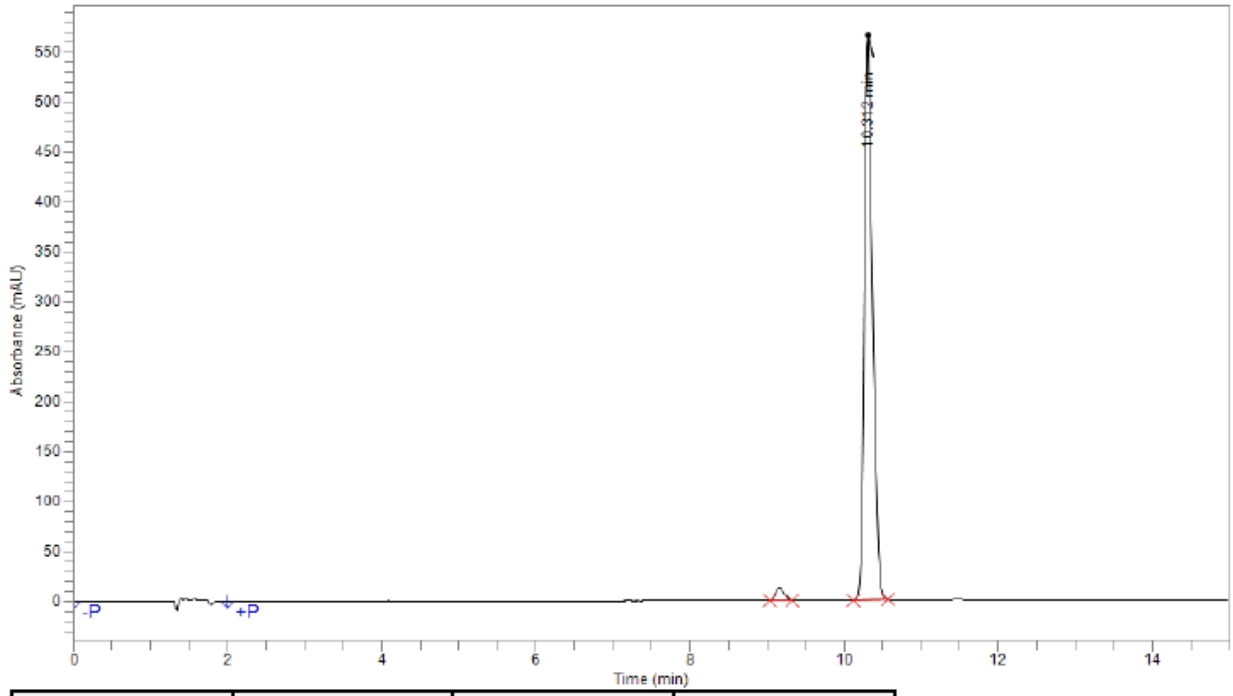
5-(5-bromofuran-2-yl)thiophene-2-carbaldehyde (RV-2)



Method and gradient as described in General Experimental *with* TFA (0.1%) (254 nm).

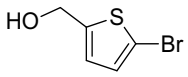
Acquisition Method	Purity short run @254 nm	
Acquisition Date/Time	7/18/2018 3:36 pm	
Injection Volume	10	
Sample Name	DSCH_03_006	(named in error, sample is DSCH_03_007)
Sample Description		
Batch Description		

DSCH_03_006 : Injection 1



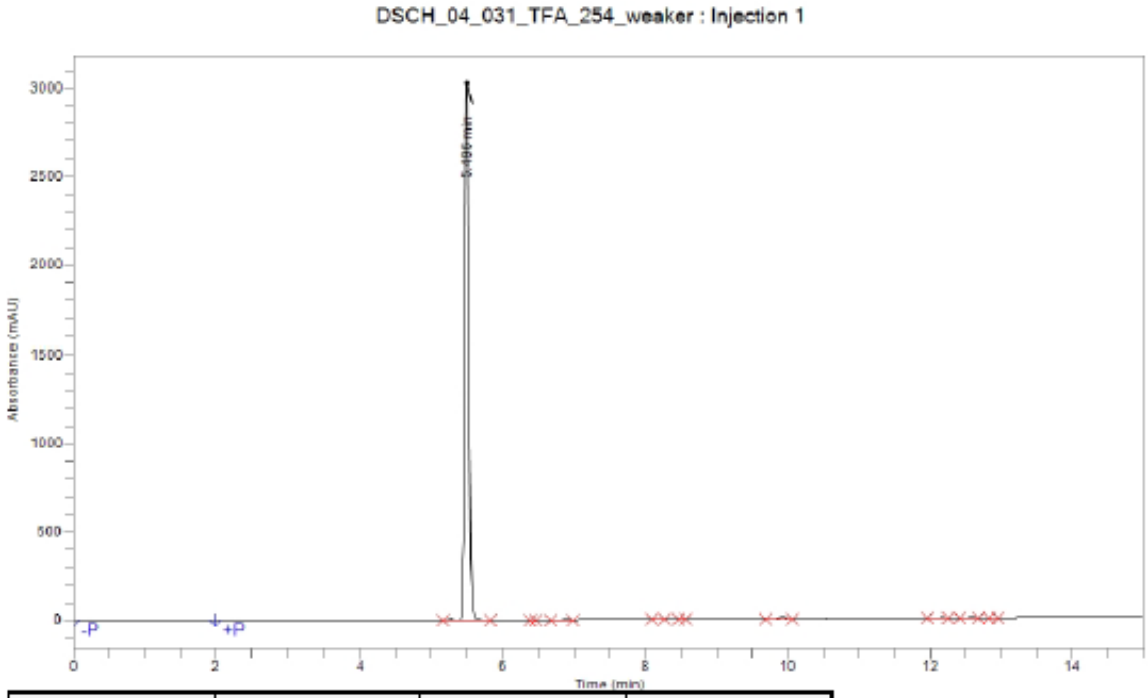
Time	Height	Area	Area %
9.164	12,758.3	88,245.7	2.01
10.312	566,848.0	4,292,181.0	97.99
Total		4,380,426.8	100.00

(5-bromothien-2-yl)methanol (RV-3)



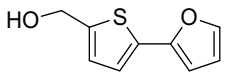
Method and gradient as described in General Experimental *with* TFA (0.1%) (254 nm).

Acquisition Method	Purity short run @254 nm
Acquisition Date/Time	3/14/2019 3:54 pm
Injection Volume	5
Sample Name	DSCH_04_031_TFA_254_weaker
Sample Description	
Batch Description	



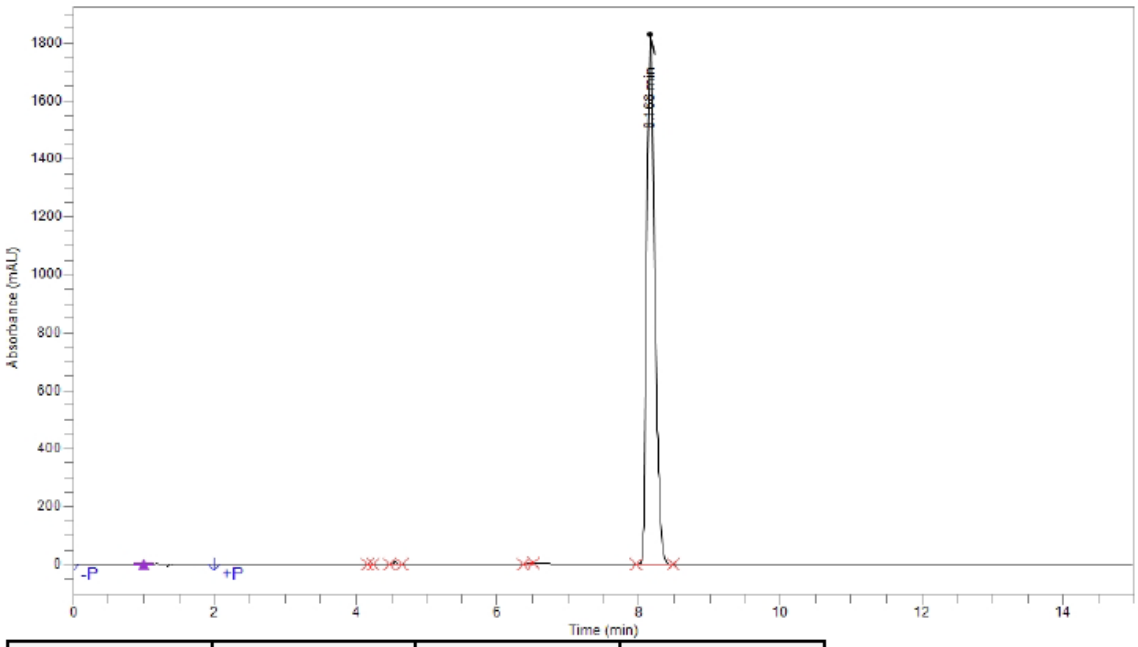
Time	Height	Area	Area %
5.269	12,373.4	49,559.2	0.39
5.496	3,070,862.9	12,381,030.7	98.36
6.435	104.6	327.7	0.00
6.738	250.4	926.5	0.01
6.892	3,694.0	14,526.3	0.12
8.194	967.2	4,473.0	0.04
8.533	133.7	500.2	0.00
9.925	17,663.4	98,345.1	0.78
12.163	2,506.7	11,003.1	0.09
12.581	5,782.5	25,496.9	0.20
12.898	275.3	1,107.8	0.01
Total		12,587,296.5	100.00

5-(Furan-2-yl)thiophene-2-methanol (RV-27)



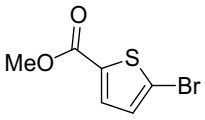
Acquisition Method	Purity short run @254 nm
Acquisition Date/Time	7/18/2018 7:45 pm
Injection Volume	10
Sample Name	DSCH_03_010
Sample Description	
Batch Description	

DSCH_03_010 : Injection 1



Time	Height	Area	Area %
4.230	205.5	995.0	0.01
4.564	8,776.8	36,724.1	0.27
6.495	290.3	3,553.8	0.03
8.168	1,832,303.8	13,740,063.8	99.70
Total		13,781,336.8	100.00

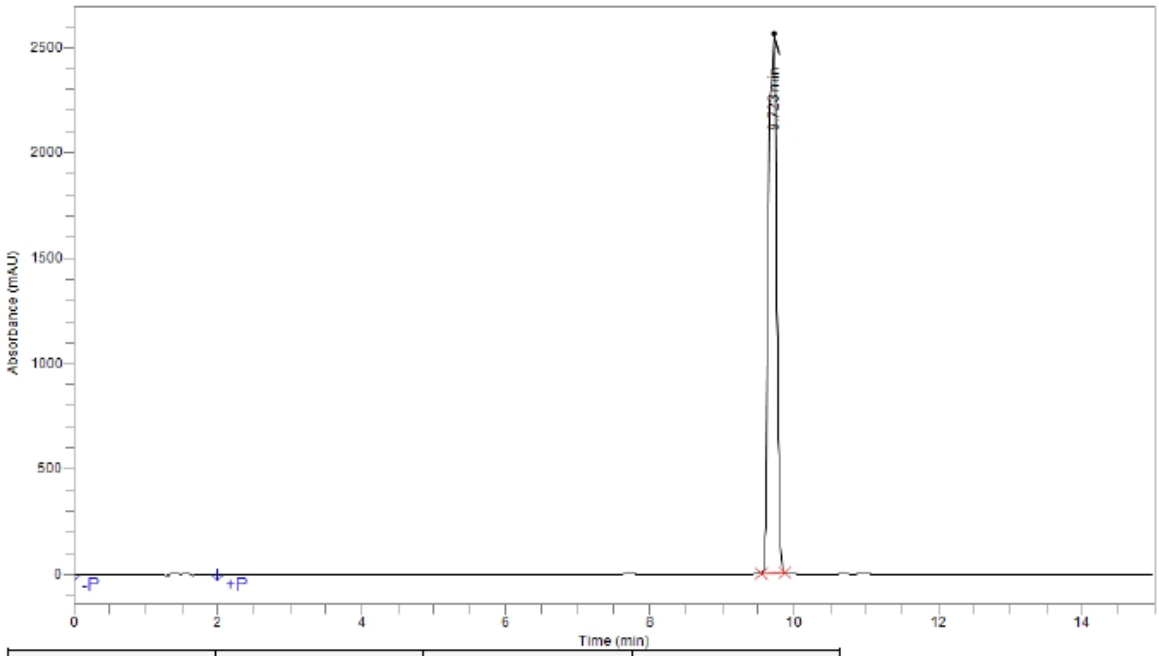
Methyl-5-bromothiophene-2-carboxylate (RV-7)



Method and gradient as described in General Experimental *with* TFA (0.1%) (254 nm).

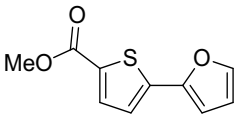
Acquisition Method	Purity short run @254 nm
Acquisition Date/Time	10/31/2018 2:14 pm
Injection Volume	10
Sample Name	DSCH_03_058
Sample Description	
Batch Description	For start up

DSCH_03_058 : Injection 1



Time	Height	Area	Area %
9.723	2,558,975.4	19,705,779.8	100.00
Total		19,705,779.8	100.00

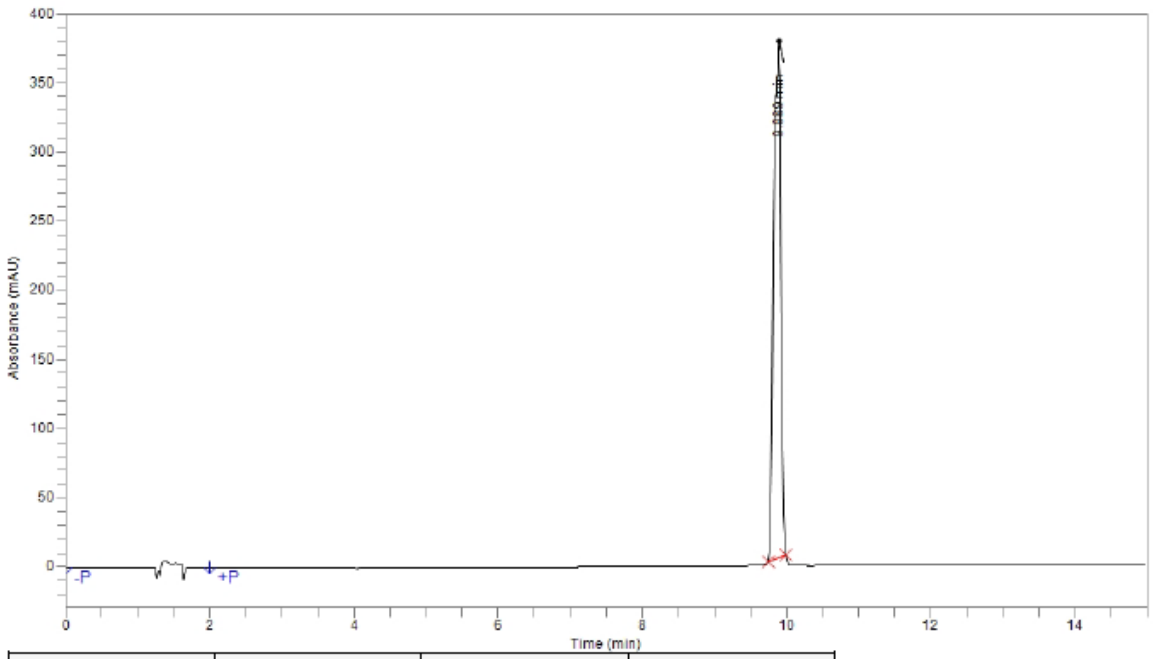
Methyl 5-(furan-2-yl)thiophene-2-carboxylate (RV-8)



Method and gradient as described in General Experimental *with* TFA (0.1%) (254 nm).

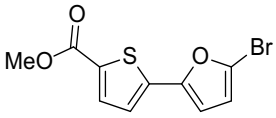
Acquisition Method	Purity short run @254 nm
Acquisition Date/Time	10/31/2018 2:49 pm
Injection Volume	10
Sample Name	DSCH_03_061
Sample Description	
Batch Description	For start up

DSCH_03_061 : Injection 1



Time	Height	Area	Area %
9.889	373,651.5	2,668,545.5	100.00
Total		2,668,545.5	100.00

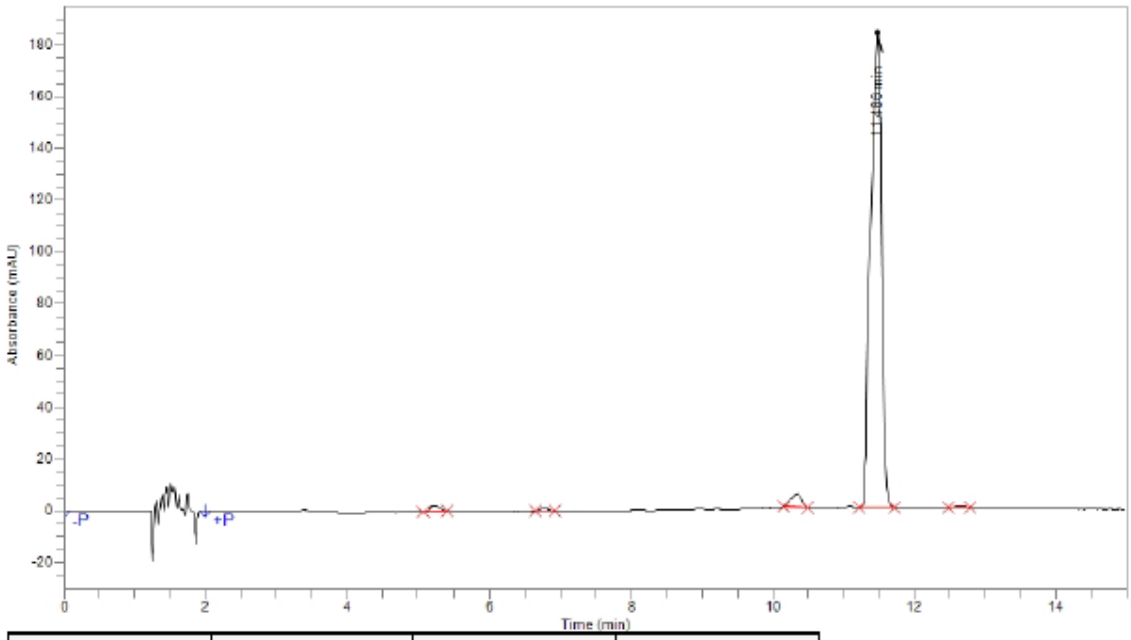
Methyl 5-(5-bromofuran-2-yl)thiophene-2-carboxylate (RV-9)



Method and gradient as described in General Experimental *without* TFA (0.1%) (254 nm) with injection volume increased to 50 µL.

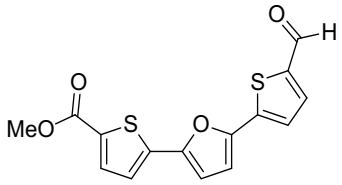
Acquisition Method	Purity short run @254 nm
Acquisition Date/Time	11/26/2018 5:42 pm
Injection Volume	50
Sample Name	DSCH_03_062_noTFA_50uL
Sample Description	
Batch Description	

DSCH_03_062_noTFA_50uL : Injection 1



Time	Height	Area	Area %
5.199	2,366.5	23,750.9	1.16
6.775	936.2	8,468.0	0.41
10.348	5,094.5	51,776.8	2.53
11.486	183,859.9	1,955,078.7	95.52
12.674	767.0	7,790.3	0.38
Total		2,046,864.7	100.00

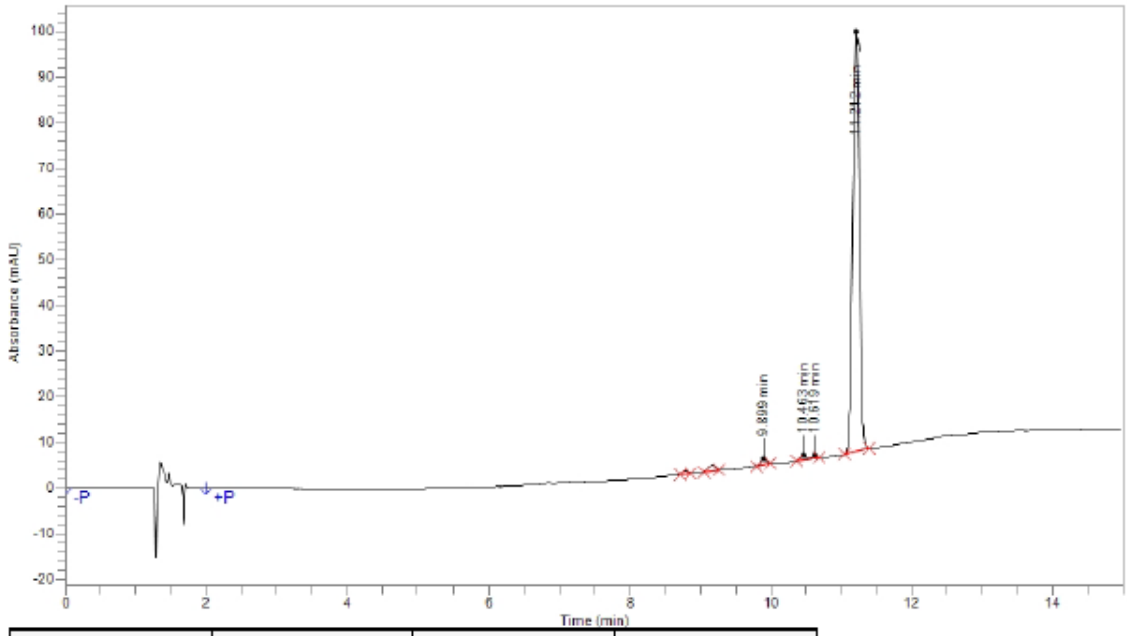
Methyl 5-[5-(5-formylthiophen-2-yl)furan-2-yl]thiophene-2-carboxylate (RV-11)



Method and gradient as described in General Experimental *with* TFA (0.1%) (254 nm).

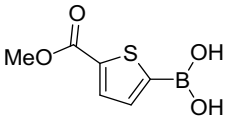
Acquisition Method	Purity short run @254 nm
Acquisition Date/Time	11/15/2018 10:05 am
Injection Volume	10
Sample Name	DSCH_03_066_f107-122_TFA_254
Sample Description	
Batch Description	

DSCH_03_066_f107-122_TFA_254 : Injection 1



Time	Height	Area	Area %
8.787	637.7	3,158.2	0.51
9.162	1,234.7	7,645.9	1.24
9.899	1,426.5	7,050.1	1.15
10.463	1,211.4	6,272.7	1.02
10.619	820.7	4,263.6	0.69
11.212	92,057.4	586,269.8	95.38
Total		614,660.3	100.00

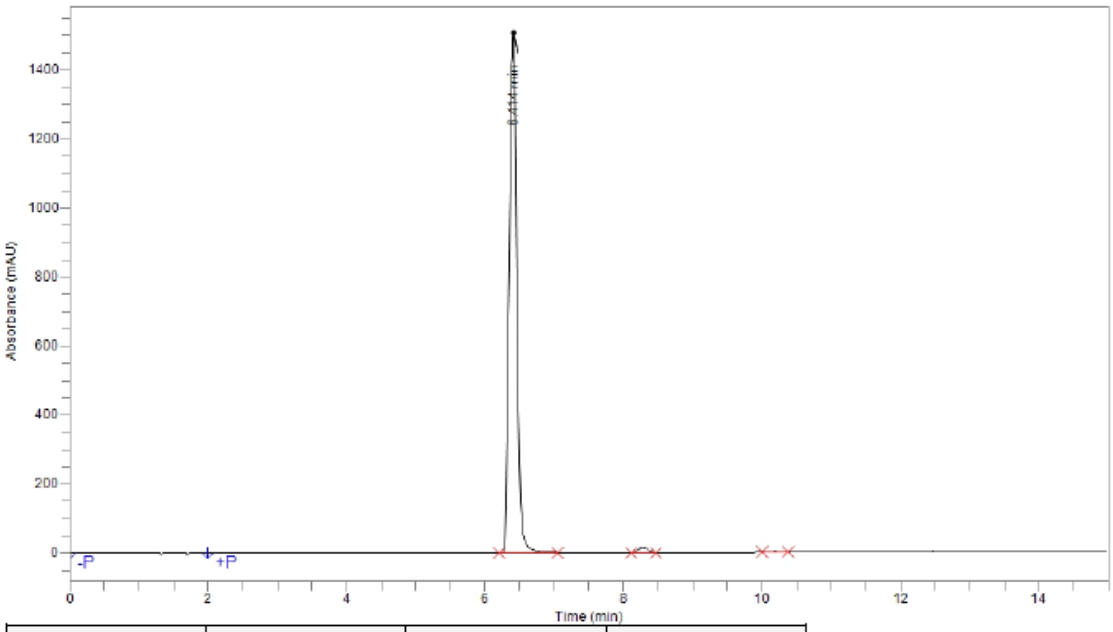
[5-(methyoxycarbonyl)thiophen-2-yl)boronic acid (RV-10)



Method and gradient as described in General Experimental *with* TFA (0.1%) (254 nm) and injection volume reduced to 2.5 µL.

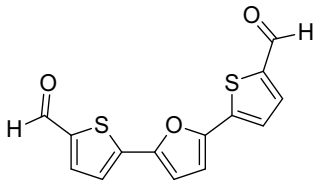
Acquisition Method	Purity short run @254 nm
Acquisition Date/Time	11/23/2018 3:38 pm
Injection Volume	2.5
Sample Name	DSCH_03_072_TFA_2pt5uL_REAL
Sample Description	
Batch Description	

DSCH_03_072_TFA_2pt5uL_REAL : Injection 1



Time	Height	Area	Area %
6.414	1,508,320.4	12,064,617.3	98.50
8.281	14,967.6	153,729.4	1.26
10.192	2,696.2	29,828.4	0.24
Total		12,248,175.1	100.00

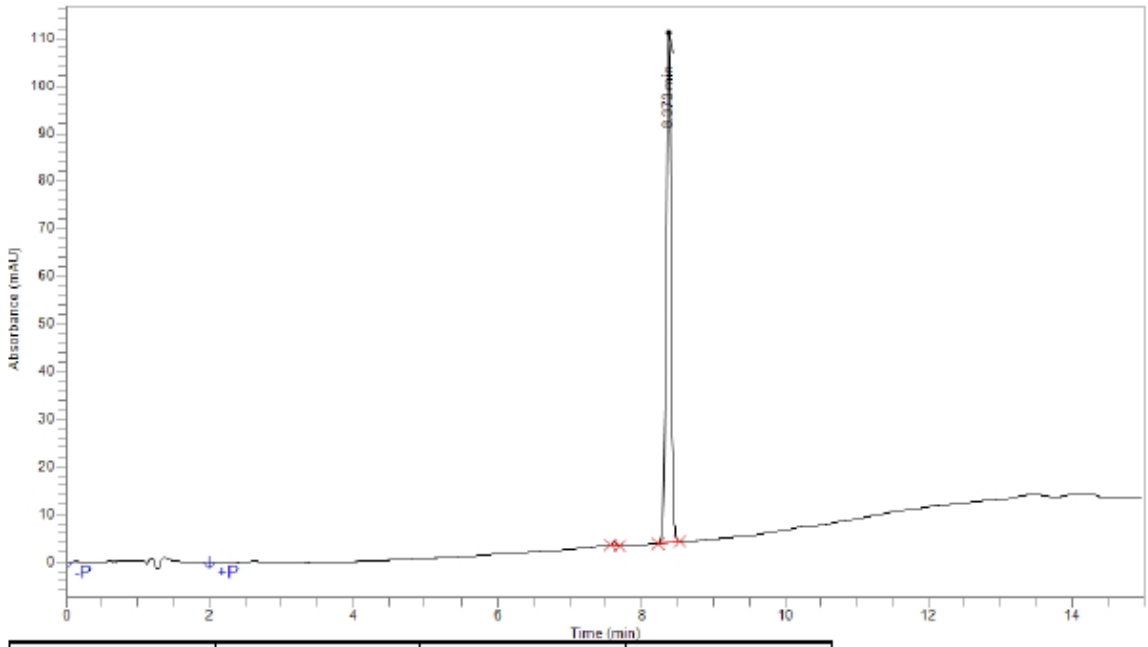
2,5-bis(5-formylthiophen-2-yl)furan (RV-6)



Method and gradient as described in General Experimental *with* TFA (0.1%) (254 nm).

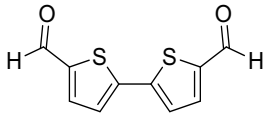
Acquisition Method	Purity short run @254 nm
Acquisition Date/Time	3/13/2019 5:45 pm
Injection Volume	10
Sample Name	DSCH_04_023_colend1_TFA_254_check
Sample Description	
Batch Description	

DSCH_04_023_colend1_TFA_254_check : Injection 1



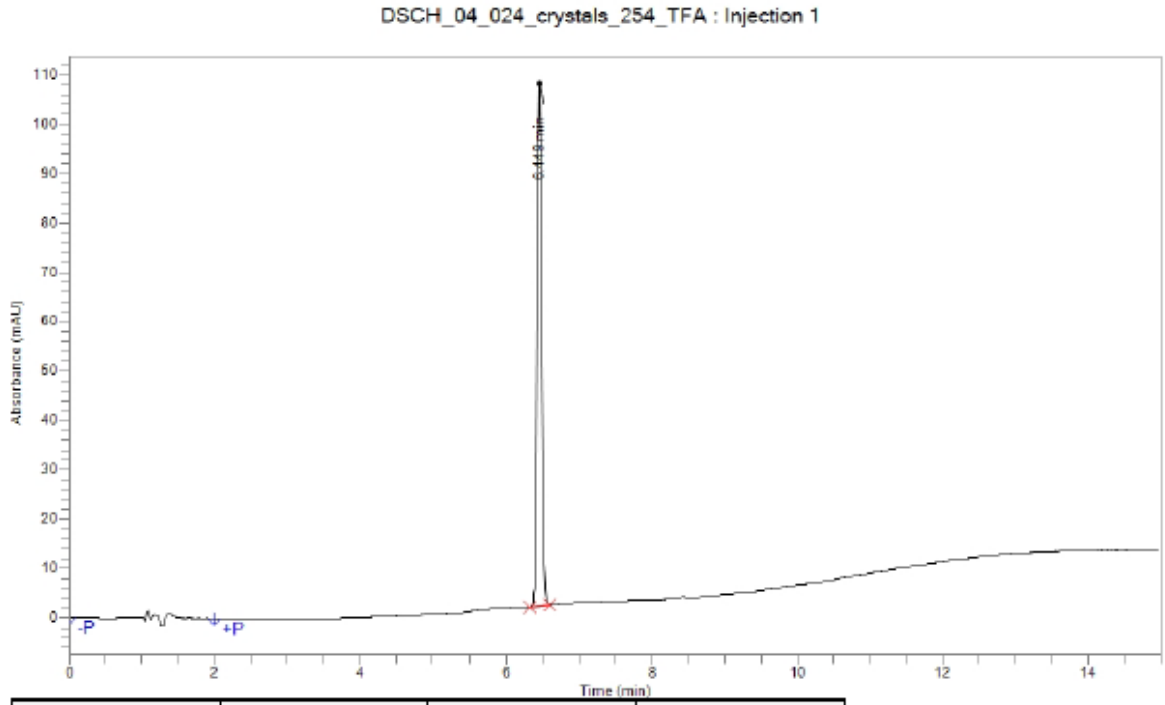
Time	Height	Area	Area %
7.623	678.7	2,644.1	0.52
8.373	107,180.3	509,259.9	99.48
Total		511,904.0	100.00

[2,2']bithiophenyl-5,5'-dicarbaldehyde (RV-13)



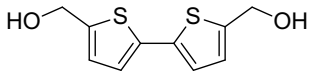
Method and gradient as described in General Experimental *with* TFA (0.1%) (254 nm).

Acquisition Method	Purity short run @254 nm
Acquisition Date/Time	3/13/2019 7:22 pm
Injection Volume	10
Sample Name	DSCH_04_024_crystals_254_TFA
Sample Description	
Batch Description	



Time	Height	Area	Area %
6.449	105,933.1	438,946.0	100.00
Total		438,946.0	100.00

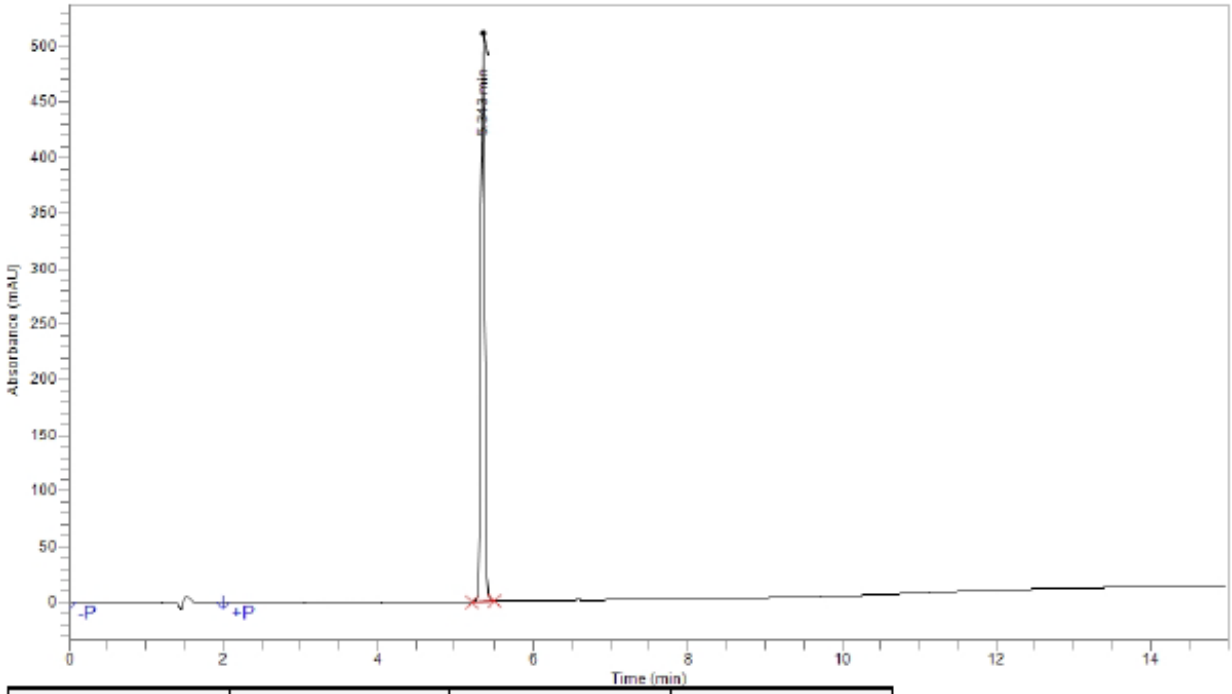
2,2'-bithiophene-5,5'-diyldimethanol (RV-14)



Method and gradient as described in General Experimental *with* TFA (0.1%) (254 nm).

Acquisition Method	Purity short run @254 nm
Acquisition Date/Time	3/14/2019 12:35 pm
Injection Volume	10
Sample Name	DSCH_04_033_TFA_precipitate
Sample Description	
Batch Description	

DSCH_04_033_TFA_precipitate : Injection 1



Time	Height	Area	Area %
5.343	511,809.4	1,809,730.8	100.00
Total		1,809,730.8	100.00

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