Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Comparative studies on the electronic properties of the representative benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole, [1,2,5]-thiadiazolo[3,4-g]quinoxaline and pyrazino[2,3-g]quinoxaline derivatives

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Experimental Details

Materials and Equipments. All reagents were purchased from Sigma-Aldrich and used without further purification, unless otherwise stated. Column chromatography was carried out with Merck silica (230 – 400 mesh) while thin layer chromatography (TLC) were performed on Merck silica 60 Al-backed plates (20 cm × 20 cm). ^{1}H and ^{13}C NMR data were obtained on a Bruker DPX 400 MHz spectrometer with chemical shifts referenced to $CDCl_3$. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Shimadzu Biotech AXIMA-TOF^2. Elemental analysis was obtained via a Thermo Scientific Flash 2000 Series CHNS/O Analyzer. UV-Vis absorption spectra were recorded on a Lambda 900 Spectrometer from Perkin Elmer. Emission spectra were recorded on a RF-5301Spectrofluorophotometer. Cyclic voltammetry experiments were

performed using a Multichannel Potentiostat (Model 1470E) from Solartron Analytical. All CV measurements were recorded in dichloromethane (DCM) with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte (scan rate of 100 $mV \cdot s^{-1}$). The experiments were performed at room temperature with a conventional three electrodes configuration consisting of a platinum wire working electrode, a gold counter electrode, and an Ag/AgCl in 3 M KCl reference electrode. The measured potentials were converted to orbital energies by using value of SCE (saturated calomel electrode) having potential of -4.4 eV relative to vacuum.

Calculation Method. Atomistic simulation, using density function theory (DFT) at B3LYP [1,2] and TD-B3LYP (which includes the gradient corrected exchange and correlation functionals along with the exact exchange) method with double-ζ quality basis functions 6-31G* (augmented with polarized function for all non-hydrogen atoms), was used to optimize the geometry of all the molecules. Geometry was fully relaxed and no symmetry constraints were imposed during optimization using Gaussian 09 code [3] with a convergence criterion of 10^{-3} a.u. on the gradient and displacement and 10^{-6} a.u on energy and electron density. Harmonic vibrational analyses showed no imaginary frequency, indicating these structures are a local minimum.

4,7-Dihexylbenzo[c][1,2,5]thiadiazole-5,6-diamine (2). Compound **1** (0.5 g, 1.54 mmol), n-hexylboronic acid (0.6 g, 4.62 mmol), $Pd(dppf)Cl_2$ (0.1g, 0.12 mmol), dioxane (30 ml) and $CsCO_3$ (2M aq, 20 ml) were added to a one neck round bottom flask purged with N_2 gas, the mixture were stirred at 60 °C for 1 d, cooled down and poured into water, then extracted with dichloromethane (DCM). The organic layer was collected, dried over anhydrous $MgSO_4$, and concentrated. The residue was recrystalized from methanol and used immediately without further purification due to its gradual decomposition in air.

4,7-Dihexylbenzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole (BBT-X1). N-thionylaniline (0.33 g, 2.39 mmol) was added dropwise to a solution of compound **2** (0.2 g, 0.60 mmol) in chloroform (15 ml) in a flask purged with N_2, followed by slow addition of TMSCl (0.26 g, 2.39 mmol) and pyridine (0.19 g, 2.39 mmol) at room temperature. The mixture was heated to reflux for 1 d, cooled down and poured into water, then extracted with DCM. The organic layer was collected, dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by chromatography**,** eluting with hexane/DCM (1/1) to yield 90 mg of a dark red solid (33% yield calculated from compound **1**). ^{1}H NMR ($CDCl_3$, δ ppm): 2.96 (t, 4 H, J = 7.6, PhC**H$_2$**), 1.65 (quintet, 4 H, J = 7.6 Hz, $PhCH_2C$**H$_2$**), 1.25-1.36 (m, 12 H, C**H$_2$**), 0.87 (t, 6 H, J = 6.8 Hz, C**H$_3$**). ^{13}C NMR ($CDCl_3$, δ ppm): 156.1, 134.7, 31.52, 29.51, 28.79, 28.60, 22.56, 14.07. MALDI-TOF-MS m/z: 362.1578 (M^+); calcd for $C_{18}H_{26}N_4S_2$: 362.1599. Anal calcd for $C_{18}H_{26}N_4S_2$: C, 59.63; H, 7.23; N, 15.45; S, 17.69; found: 59.46; H, 7.27; N, 15.86; S, 17.44.

4,7-Dihexyl-[1,2,5]selenadiazolo[3,4-f]-2,1,3-benzothiadiazole (SBT-X1). A mixture of compound **2** (0.2 g, 0.60 mmol) and SeO_2 (66 mg, 0.60 mmol) in EtOH (20 ml) was refluxed for 2 d. The cooled mixture was filtered, and the crude solid was eluted through silica with DCM to afford a dark purple solid (145 mg, 46 % calculated from compound **1**). ^{1}H NMR ($CDCl_3$, δ ppm): 3.08 (t, 4H, J = 8 Hz, PhC**H$_2$**), 1.79 (quintet, 4 H, J = 7.6 Hz, PhCH$_2$C**H$_2$**), 1.31-1.33 (m, 12H, C**H$_2$**), 0.89 (t, 6H, J = 7.6 Hz, C**H$_3$**). ^{13}C NMR ($CDCl_3$, δ ppm): 158.5, 155.8, 134.1, 32.8, 32.3, 30.3, 29.9, 23.3, 14.7. MALDI-TOF-MS m/z: 410.0904 (M^+); calcd for $C_{18}H_{26}N_4SSe$: 410.1043. Anal calcd for $C_{18}H_{26}N_4SSe$: C, 52.80; H, 6.40; N, 13.68; S, 7.83; found: C, 52.66; H, 6.49; N, 13.93, S, 7.96.

5,6-Dinitrobenzo[c][1,2,5]thiadiazole (4). N-thionylaniline (5.57 g, 40.0 mmol) was added dropwise into the suspension of compound **3** (2 g, 10.0 mmol) in chloroform(50 ml) in a flask purged with N_2, followed by slow addition of TMSCl (4.34 g, 40.0 mmol) and pyridine (3.16 g, 40.0 mmol) at room temperature. The whole solution was then heated to reflux for 1 d, cooled, poured into water, and then extracted with DCM. The organic layer was collected, dried over anhydrous $MgSO_4$ and concentrated. The crude product was recrystalized from a mixture of hexane with 10% of ethyl acetate to afford pale yellow crystals (1.47 g, 65 %). ^{1}H NMR ($CDCl_3$, δ ppm): 9.22 (s, 2H). ^{13}C NMR ($CDCl_3$, δ ppm): 171.7, 152.0, 110.9. Anal calcd for $C_6H_2N_4O_4S$: C, 31.86; H, 0.89; N, 24.77; S, 14.18; found: C, 31.65; H, 0.92; N, 25.01, S, 14.36.

3,6-Bis(3,5-di-tert-butylphenyl)phenanthrene-9,10-dione (6). Compound **5** (2 g, 5.46 mmol) and 3,5-di-tert-butylphenylboronic acid (2.81 g, 12.0 mmol), $Pd(PPh_3)_4$ (0.38 g, 0.33 mmol), toluene (40 ml) and K_2CO_3 (2M aq, 30 ml) were added to a one neck round bottom flask purged with N_2, the mixture was stirred at 85 °C for 1 d, cooled, poured into water, and then extracted with DCM. The organic layer was collected, dried over anhydrous $MgSO_4$ and concentrated. The crude was purified by chromatography**,** eluted with hexane/DCM (2/3) to afford yellow fluffy crystals (2.80 g, 88 %). ^{1}H NMR ($CDCl_3$, δ ppm): 8.30 (d, 2H, J = 7.6 Hz, Phenan-**H**), 8.29 (d, 2H, J = 7.6 Hz, Phenan-**H**), 7.72 (dd, 2H, J = 8 Hz, Phenan-**H**), 7.56 (s, 2H, Ph**H**), 7.54 (s, 4H, Ph**H**), 1.41 (s, 36H, C**H**$_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 180.9, 152.5, 150.5, 139.6, 136.8, 131.8, 130.4, 129.1, 123.9, 123.5, 122.3, 35.7, 32.1. MALDI-TOF-MS m/z: 584.70 (M^+); calcd for $C_{42}H_{48}O_2$: 584.37. Anal calcd for $C_{42}H_{48}O_2$: C, 86.26; H, 8.27; found: C, 86.02; H, 8.29.

4,7-Bis(thien-2'-yl)-[1,2,5]selenadiazolo[3,4-f]-2,1,3-benzothiadiazole (SBT-X2). A mixture of compound **8** (0.2 g, 0.61 mmol) and SeO_2 (67 mg, 0.61 mmol) in EtOH (20 ml) was refluxed for 1 d. The cooled mixture was filtered, and the crude solid was quickly filtered through silica with DCM to afford a dark purple solid with 53 % yield (130 mg). ^{1}H NMR ($CDCl_3$, δ ppm): 9.01 (dd, 2H, J = 4.8 Hz, Th**H**), 7.71 (d, 2H, J = 4.8 Hz, Th**H**), 7.33 (quartet, 2H, J = 4.8 Hz, Th**H**). MALDI-TOF-MS m/z: 405.9018 (M^+); calcd. for $C_{14}H_6N_4S_3Se$: 405.8920. Anal calcd for $C_{14}H_6N_4S_3Se$: C, 41.48; H, 1.49; N, 13.82; S, 23.73; found: C, 41.27; H, 1.45; N, 14.10; S, 23.51.

6,7-Bis(4'-butoxy-1',4-biphen-1-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (TQ-X0). Compound **4** (0.3 g, 1.33 mmol) and iron powder (1.48 g, 26.5 mmol) were suspended in acetic acid (30 ml) and the mixture was stirred at 60 °C for 6 hr under N_2 to form intermediate **7**. The excess iron powder was removed using magnetic bar, followed by addition of 1,2-bis(4'-butoxy-1',4-biphen-1-yl)-ethanedione (**9**) (0.67 g, 1.33 mmol) in one portion. The reaction was stirred at 80 °C for 2 d, then poured into water and extracted with DCM. The organic layer was collected, dried over anhydrous $MgSO_4$ and concentrated. The crude was purified by chromatography**,** eluted with hexane/DCM (1/2) to obtain red brown solid (0.60 g, 72 %). ^{1}H NMR ($CDCl_3$, δ ppm): 9.02 (s, 2H, Ph**H**), 7.74 (d, 4H, J = 8.4 Hz, BiPh**H**), 7.61 (d, 4H, J = 8.4 Hz, BiPh**H**), 7.58 (d, 4H, J = 8.4 Hz, BiPh**H**), 6.98 (d, 4H, J = 8.4 Hz, BiPh**H**), 4.02 (t, 4H, J = 6.4 Hz, OC**H$_2$**), 1.80 (quintet, 4H, J = 6.8 Hz, OCH_2C**H$_2$**), 1.51 (m, 4H, C**H$_2$**CH_3), 0.99 (t, 6H, J = 7.2 Hz, C**H$_3$**). ^{13}C NMR ($CDCl_3$, δ ppm): 160.0, 156.3, 153.0, 143.5, 138.8, 136.4, 132.8, 131.5, 128.8, 127.2, 115.6, 114.6, 68.5, 32.0, 19.9, 14.5. MALDI-TOF-MS m/z: 636.2851 (M^+); calcd for $C_{40}H_{36}N_4O_2S_2$: 636.2559. Anal calcd for $C_{40}H_{36}N_4O_2S_2$: C, 75.44; H, 5.70; N, 8.80; S, 5.04; found: 75.36; H, 5.72; N, 8.96; S, 5.14.

3,6-Bis(3,5-di-tert-butylphenyl)phenanthrene)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (TQ-Y0). **TQ-Y0** was prepared as **TQ-X0** above, substituting compound **6** for compound **9** to give an orange solid with yield of 75 %. ^{1}H NMR ($CDCl_3$, δ ppm): 9.28 (d, 2H, J = 8.4 Hz, Phenan-**H**), 8.81 (s, 2H, core-Ph**H**), 8.47 (s, 2H, Phenan-**H**), 8.00 (dd, 2H, J = 8.0 Hz, Phenan-**H**), 7.71 (s, 4H, Ph**H**), 7.57 (s,

2H, Ph**H**), 1.47 (s, 36H, C**H**$_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 152.6, 152.4, 146.8, 146.6, 140.3, 139.4, 134.1, 129.2, 128.8, 123.3, 122.6, 122.5, 114.4, 35.8, 32.2. MALDI-TOF-MS m/z: 714.3809 (M^+); calcd for $C_{48}H_{50}N_4S$: 714.3756. Anal calcd for $C_{48}H_{50}N_4S$: C, 80.63; H, 7.05; N, 7.84; S, 4.48; found: 80.51; H, 7.09; N, 7.98; S, 4.36.

Bis[(3,6-bis(3,5-di-tert-butylphenyl)phenanthrene)]-pyrazino[2,3-g]quinoxaline (PQ-Y0). A mixture of compound **10** (120 mg, 0.42 mmol) and compound **6** (494 mg, 0.84 mmol) was added to a round bottom flask containing glacial acetic acid (25 ml). The reaction was stirred at 130 °C for 2 d. The reaction mixture was cooled down and poured into water, filtered and the solids were washed with water and ethanol. Column chromatography was carried out using hexane/DCM (1/1) to obtain a red solid (340 mg, 65 % yield). ^{1}H NMR ($CDCl_3$, δ ppm): 9.66 (d, 4H, J = 8.4 Hz, Phenan-**H**), 9.62 (s, 2H, core-Ph**H**), 8.82 (s, 4H, Phenan-**H**), 8.15 (d, 4H, J = 8.4 Hz, Phenan-**H**), 7.88 (s, 8H, Ph**H**), 7.66 (s, 4H, Ph**H**), 1.48 (s, 72H, C**H**$_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 156.6, 152.3, 146.5, 145.4, 142.2, 140.6, 134.0, 129.2, 128.6, 128.5, 122.7, 122.6, 121.9, 35.8, 32.2. MALDI-TOF-MS m/z: 1237.8221 (M^+); calcd for $C_{90}H_{100}N_4$: 1237.7982. Anal calcd for $C_{90}H_{100}N_4$: C, 87.33; H, 8.14; N, 4.53; found: 87.08; H, 8.19; N, 4.65.

4,7-Bis(5'-hexylthien-2'-yl)-benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole (13). Compound **11** (0.4 g, 1.14 mmol), compound **12** (1.30 g, 2.84 mmol) and $Pd[PPh_3]_2Cl_2$ (48 mg, 0.068 mmol) were added to

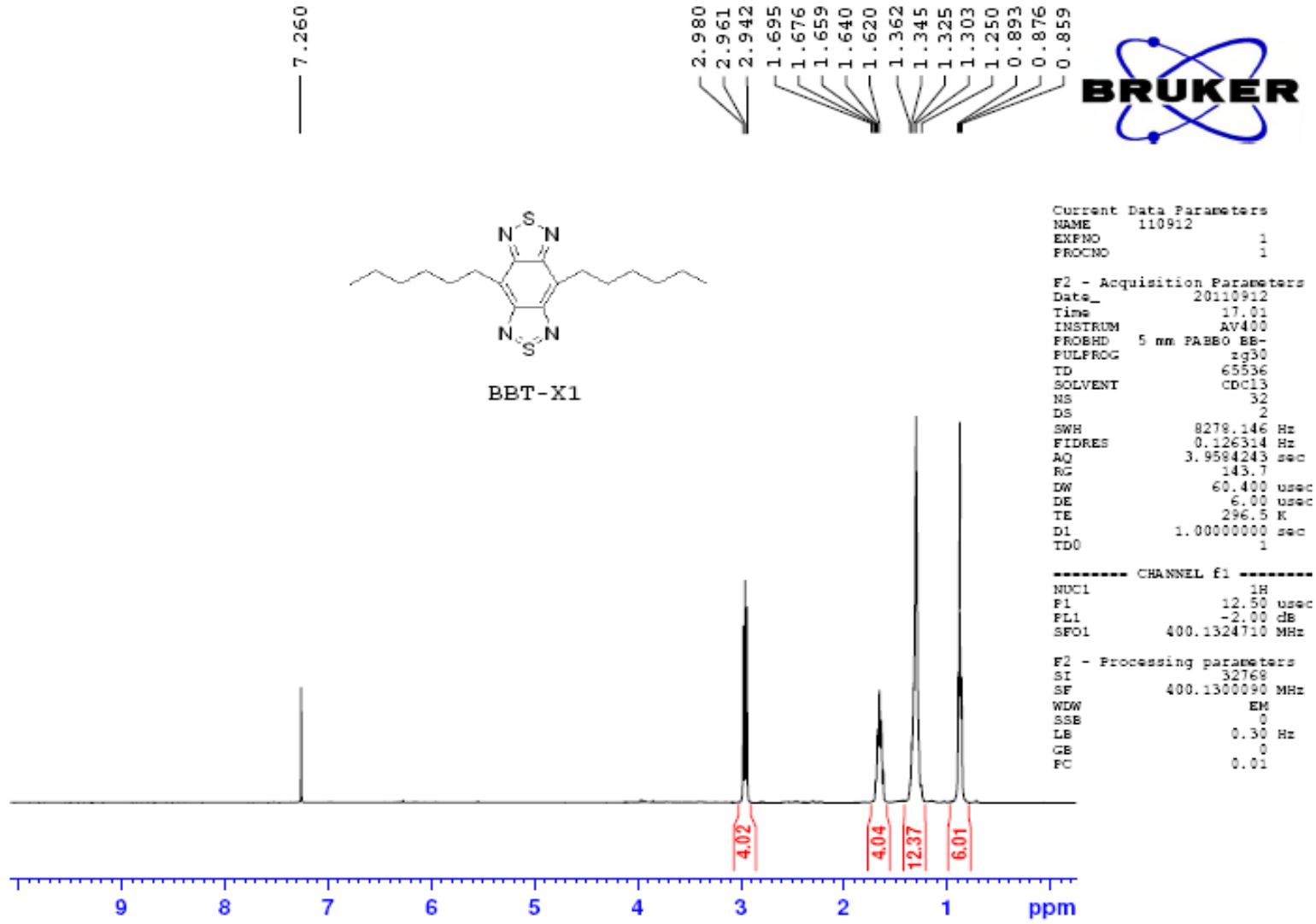
a round bottom flask purged with N_2, followed by injection of anhydrous THF (40 ml). The reaction was stirred under reflux for 2 d. The cooled mixture was poured into water, and extracted with DCM. The organic layer was collected, dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by chromatography, eluting with hexane/DCM (1/1) to obtain a dark blue solid (0.5 g, 84 %). ^{1}H NMR ($CDCl_3$, δ ppm): 8.70 (d, 2H, J = 4 Hz, Th**H**), 6.95 (d, 2H, J = 4 Hz, Th**H**), 2.94 (t, 4H, J = 7.6 Hz, ThC**H$_2$**), 1.81 (quintet, 4H, ThCH$_2$C**H$_2$**), 1.34-1.49 (m, 12H, C**H$_2$**), 0.92 (t, 6H, J = 7.2 Hz, C**H$_3$**). ^{13}C NMR ($CDCl_3$, δ ppm): 152.6, 151.5, 136.0, 133.4, 126.1, 113.8, 32.3, 32.2, 31.1, 29.6, 23.3, 14.8. MALDI-TOF-MS m/z: 526.1285 (M^+); calcd for $C_{26}H_{30}N_4S_4$: 526.1353. Anal calcd for $C_{26}H_{30}N_4S_4$: C, 59.28; H, 5.74; N, 10.64; S, 24.35; found: 59.10; H, 5.85; N, 10.89; S, 24.12.

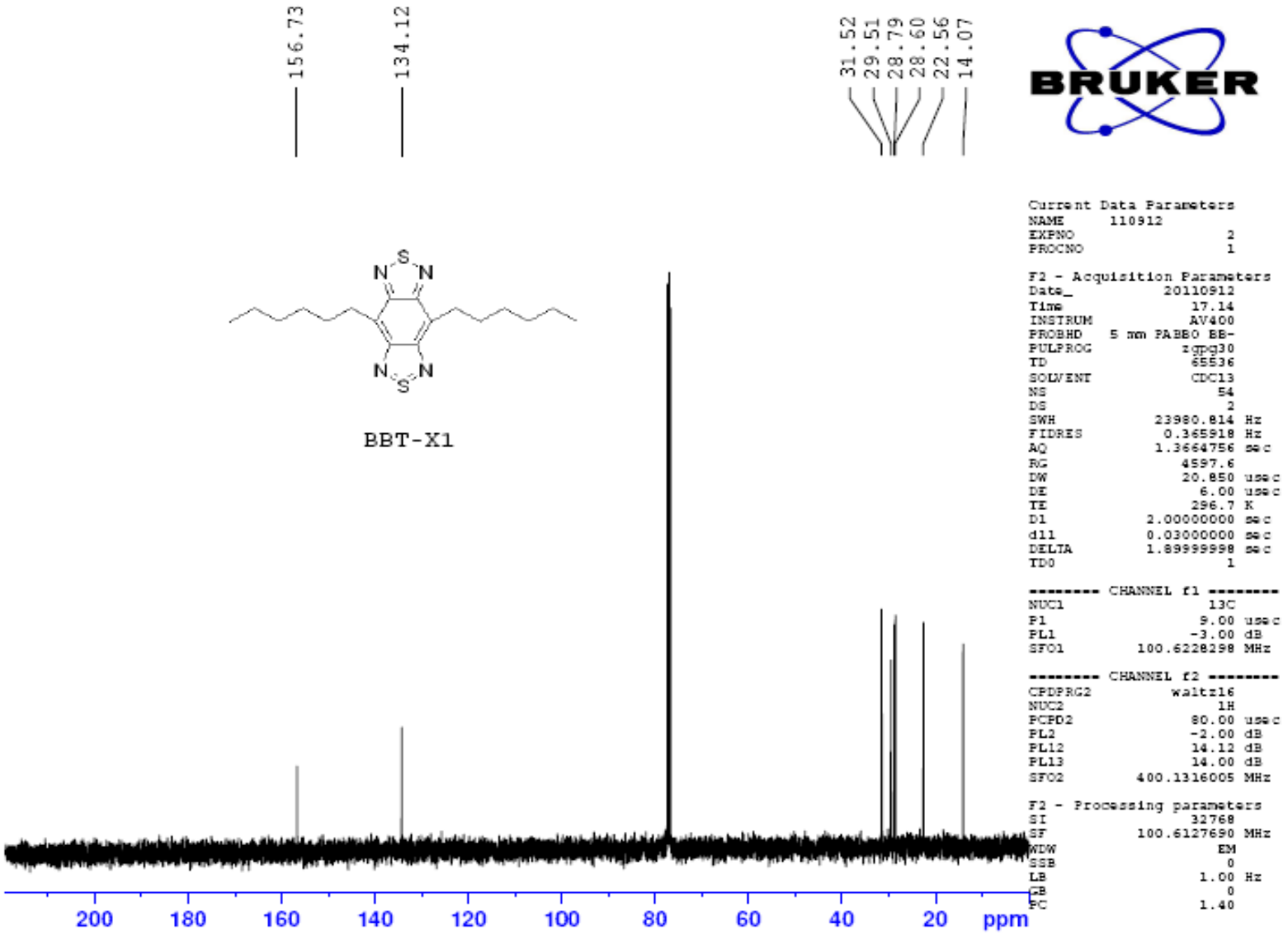
3,6-Bis(3,5-di-tert-butylphenyl)phenanthrene)-4,7-bis(5'-hexylthien-2'-yl)-[1,2,5]thiadiazolo [3,4-g]quinoxaline (TQ-Y2). Compound **13** (0.2 g, 0.38 mmol) and iron powder (0.42 g, 7.60 mmol) were suspended in glacial acetic acid (20 ml) and the mixture was stirred at 60 °C for 6 hr to form intermediate **14**, excess iron was removed using a magnetic bar, followed by addition of compound **6** (0.22 g, 0.38 mmol) in one portion. The reaction was stirred at 80 °C for 2 d, poured into water, and extracted with DCM. The organic layer was collected, dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by chromatography, eluting with hexane/DCM (3/1) to obtain a greenish or dark brown (colour depended on the molecular packing during drying) solid (0.26 g, 65 %). ^{1}H NMR ($CDCl_3$, δ ppm): 9.43 (d, 2H, J = 8 Hz, Phenan-**H**), 8.73 (d, 2H, J = 4 Hz, Th**H**), 8.69 (s, 2H, Phenan-

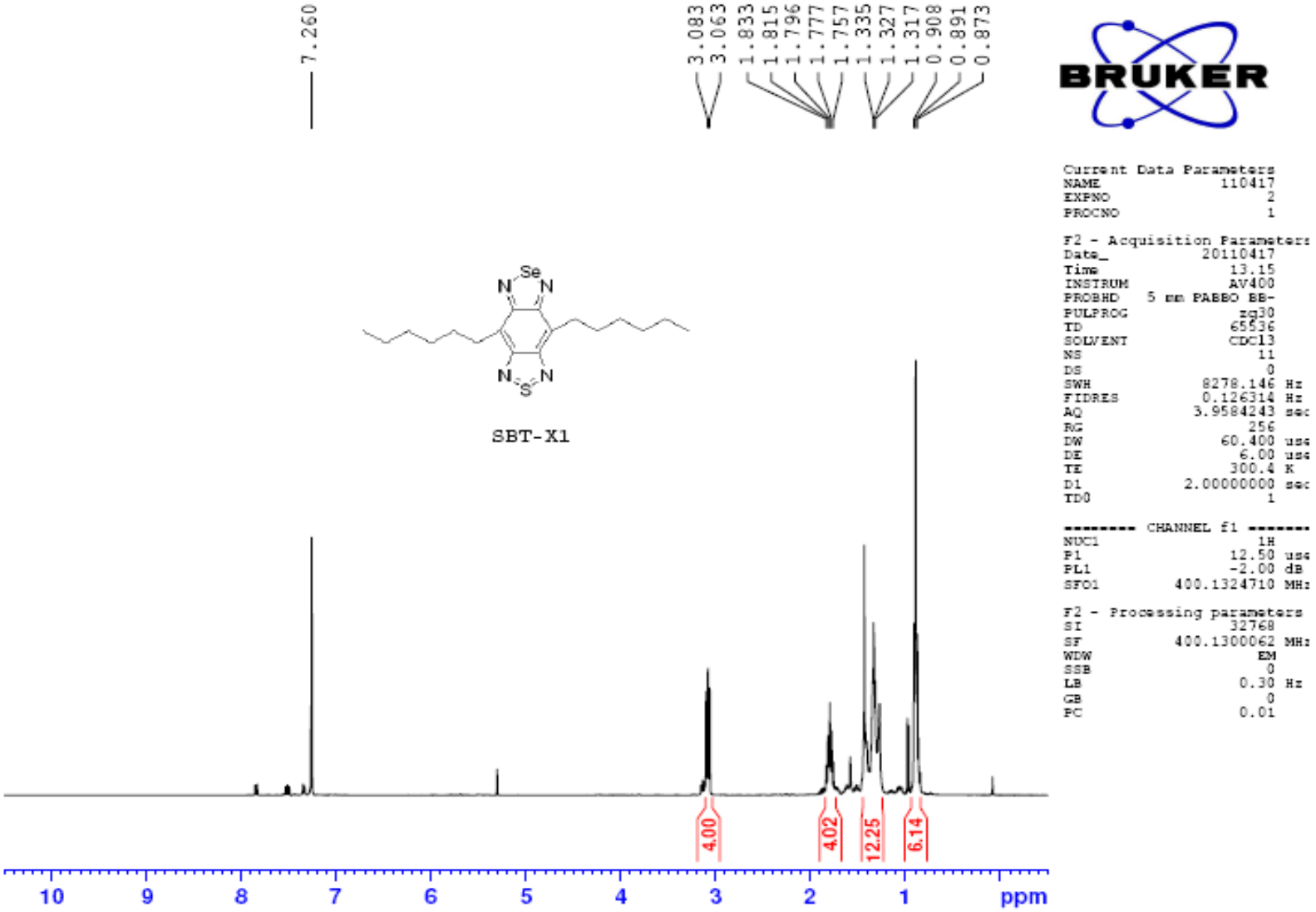
H), 7.91 (dd, 2H, J = 8 Hz, Phenan-**H**), 7.71 (s, 4H, Ph**H**), 7.58 (s, 2H, Ph**H**), 6.95 (d, 2H, J = 4 Hz, Th**H**), 3.00 (t, 4H, J = 7.6 Hz, ThC**H**$_2$), 1.88 (quintet, 4H, ThCH$_2$C**H**$_2$), 1.40-1.49 (m, 48H, C**H**$_2$ and t-Bu-C**H**$_3$), 0.92 (t, 6H, J = 7.2 Hz, C**H**$_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 152.5, 152.2, 151.9, 145.4, 144.1, 140.7, 136.4, 134.5, 134.1, 133.9, 130.1, 128.0, 125.0, 123., 122.6, 122.3, 121.3, 35.8, 32.4, 32.3, 31.0, 29.7, 23.3, 14.8. MALDI-TOF-MS m/z: 1046.5865 (M^+); calcd for $C_{68}H_{78}N_4S_3$: 1046.5389. Anal calcd for $C_{68}H_{78}N_4S_3$: C, 77.96; H, 7.50; N, 5.35; S, 9.18; found: 77.75; H, 7.57; N, 5.52; S, 9.09.

Bis[(3,6-bis(3,5-di-tert-butylphenyl)phenanthrene)]-4,7-bis(5'-hexylthien-2'-yl)-pyrazino[2,3-g]quinoxaline (PQ-Y2). Compound **13** (0.2 g, 0.38 mmol) and zinc powder (0.74 g, 11.4 mmol) were suspended in glacial acetic acid (20 ml) and the mixture was stirred at 90 °C for 12 hr to form intermediate **15** (whereas iron can be retrieved by a magnetic bar, the reaction for 12 hr to consume all excess zinc in the acid was required because could zinc can further reduce the later formed **PQ-Y2**), followed by addition of compound **6** (0.44 g, 0.76 mmol) in one portion. The reaction was stirred at 50 °C for 4 d, poured into water, and extracted with DCM. The organic layer was collected, dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by chromatography, eluting with hexane/DCM (3/1) to obtain a purple red solid (0.22 g, 37 %). 9.54 (d, 4H, J = 8 Hz, Phenan-**H**), 8.85 (s, 4H, J = 4 Hz, 2H, Phenan-**H**), 8.50 (d, 2H, J = 4 Hz, Th**H**), 8.07 (d, 4H, J = 8.4 Hz, Phenan-**H**), 7.72 (s, 8H, Ph**H**), 7.71 (dd, 2H, J = 4H, Th**H**), 7.57 (s, 4H, Ph**H**), 3.20 (t, 4H, J = 7.6 Hz, ThC**H**$_2$), 2.05 (quintet, 4H, ThCH$_2$C**H**$_2$), 1.67 (quintet, 4H, C**H**$_2$), 1.47 (s, 72H, t-Bu-C**H**$_3$), 1.25-1.42 (m, 8H,

C**H**$_2$), 0.96 (t, 6H, J = 7.2 Hz, C**H**$_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 163.8, 152.3, 145.4, 143.7, 140.8, 138.4, 135.4, 133.9, 133.8, 131.5, 130.7, 130.4, 129.4, 129.3, 128.3, 124.7, 122.9, 122.6, 35.8, 32.7, 32.5, 32.2, 29.7, 23.3, 14.8. MALDI-TOF-MS m/z: 1569.8923 (M^+); calcd for $C_{110}H_{128}N_4S_2$: 1569.9614. Anal calcd for $C_{110}H_{128}N_4S_2$: C, 84.13; H, 8.22; N, 3.57; S, 4.08; found: 83.89; H, 8.31; N, 3.72; S, 3.90.







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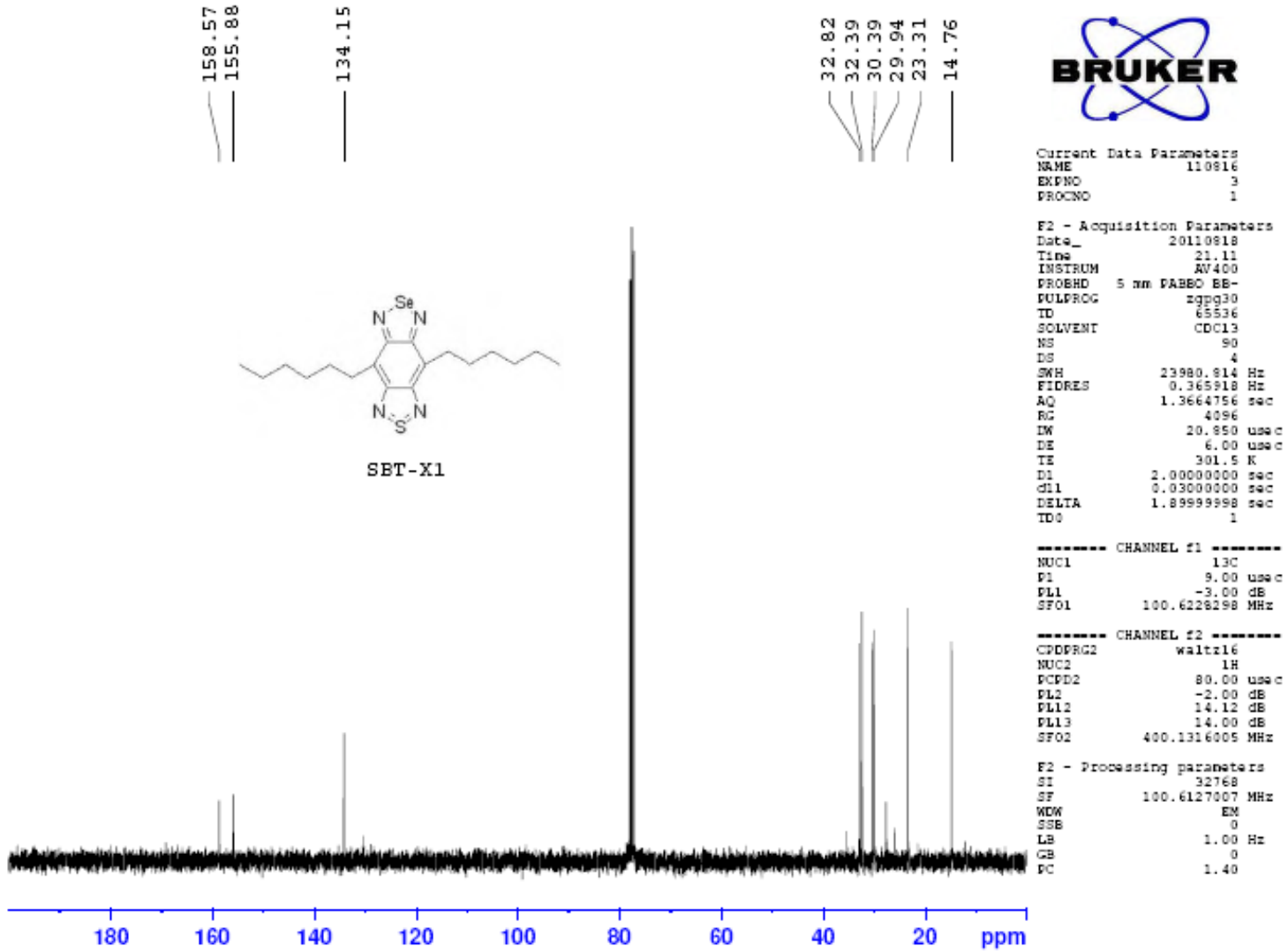

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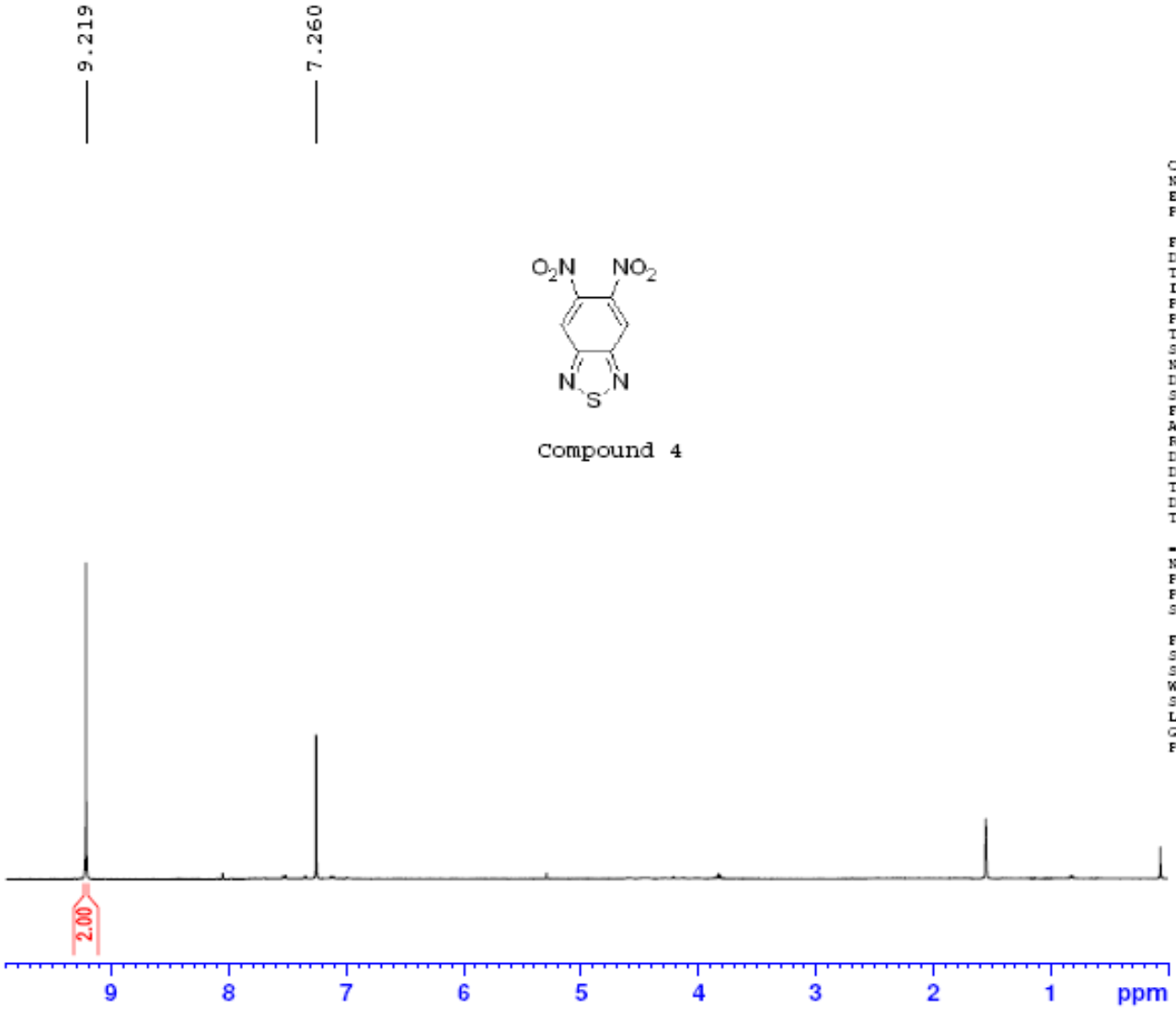


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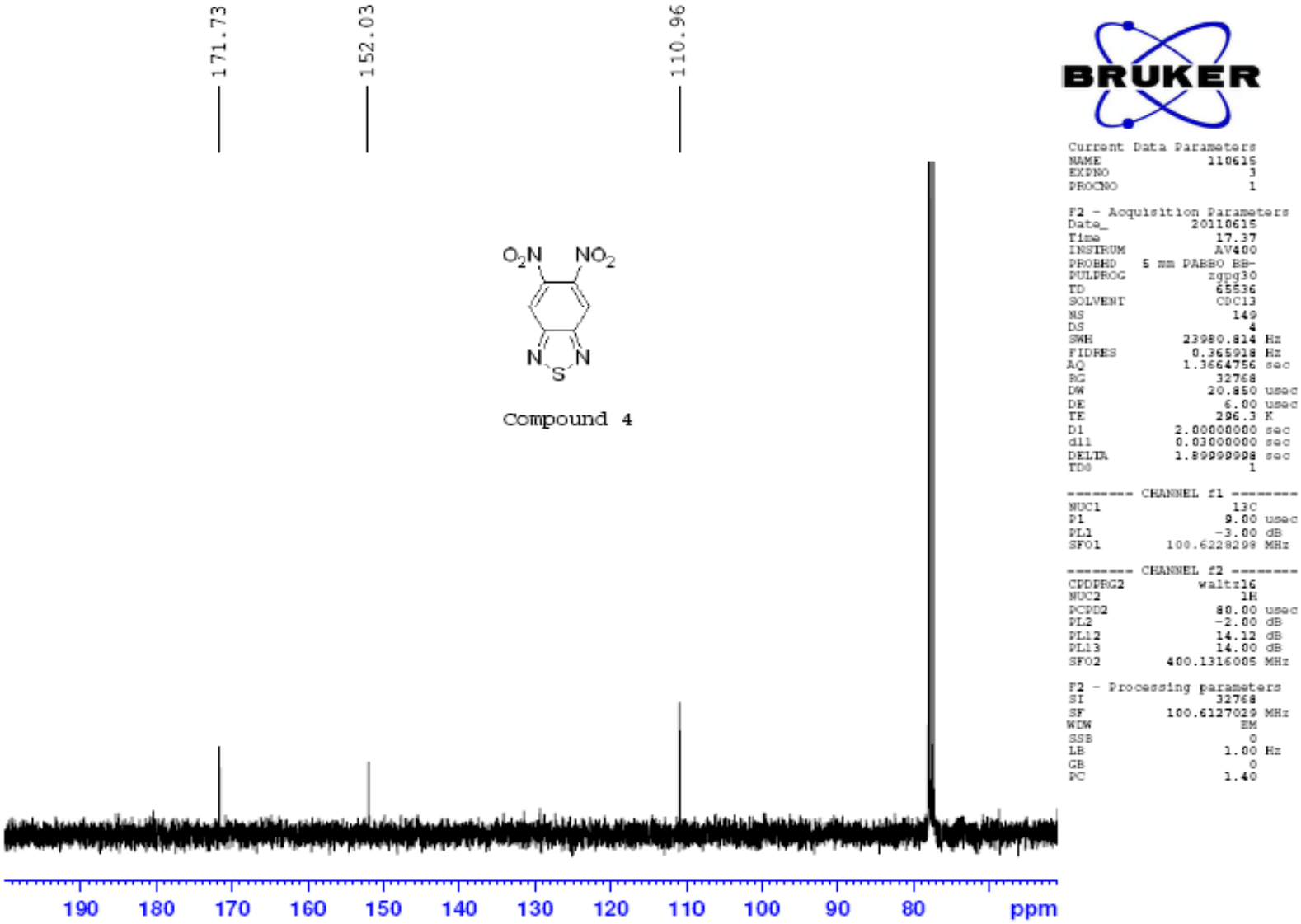

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NAME                 110615
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_             20110615
Time                 17.37
INSTRUM              AV400
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      149
DS                        4
SWH              23980.814 Hz
FIDRES               0.365918 Hz
AQ                1.3664756 sec
RG                    32768
DW                   20.850 usec
DE                    6.00 usec
TE                   296.3 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    9.00 usec
PL1                  -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -2.00 dB
PL12                 14.12 dB
PL13                 14.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                    32768
SF            100.6127029 MHz
WDW                      EM
SSB                       0
LB                    1.00 Hz
GB                        0
PC                    1.40
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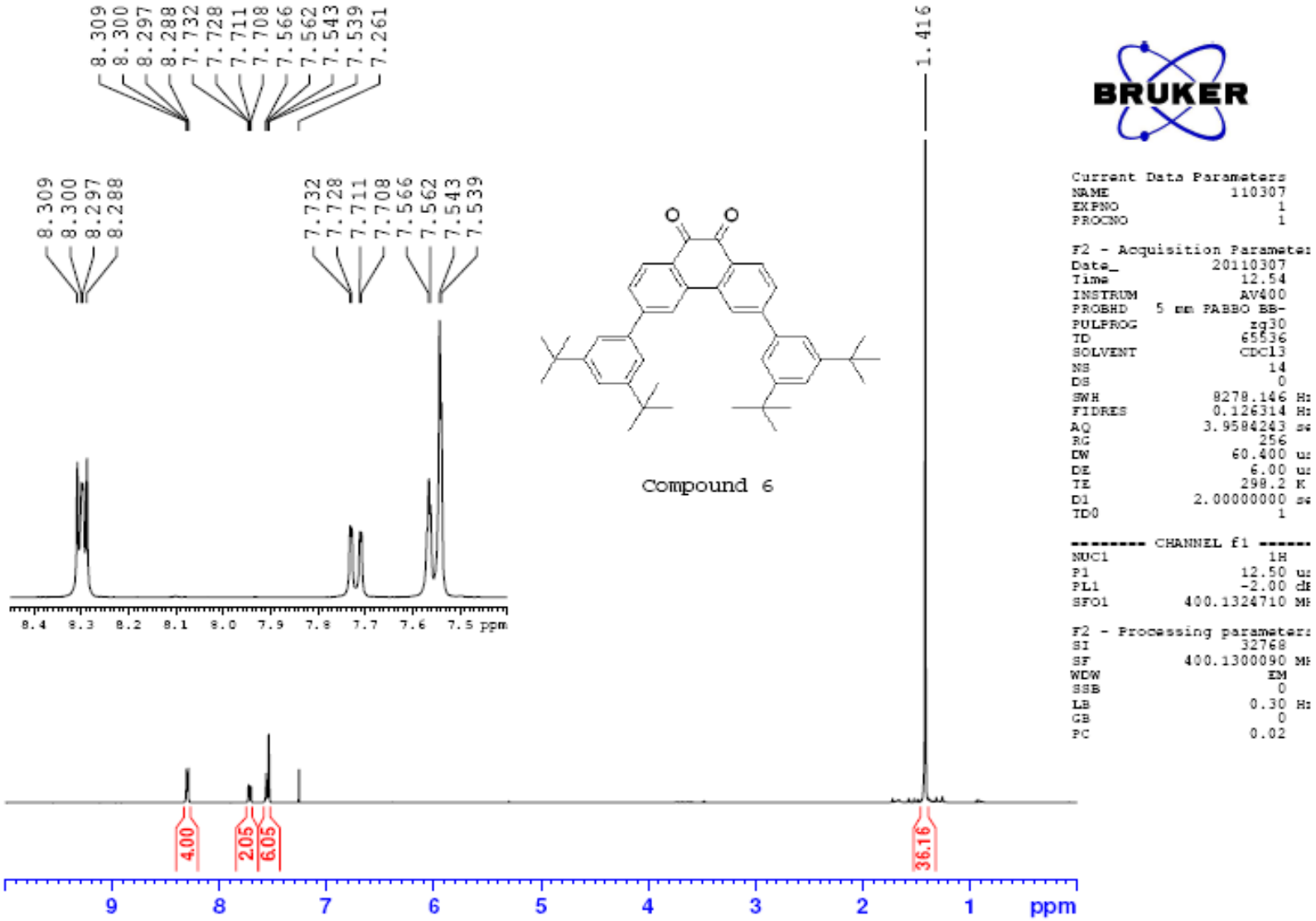

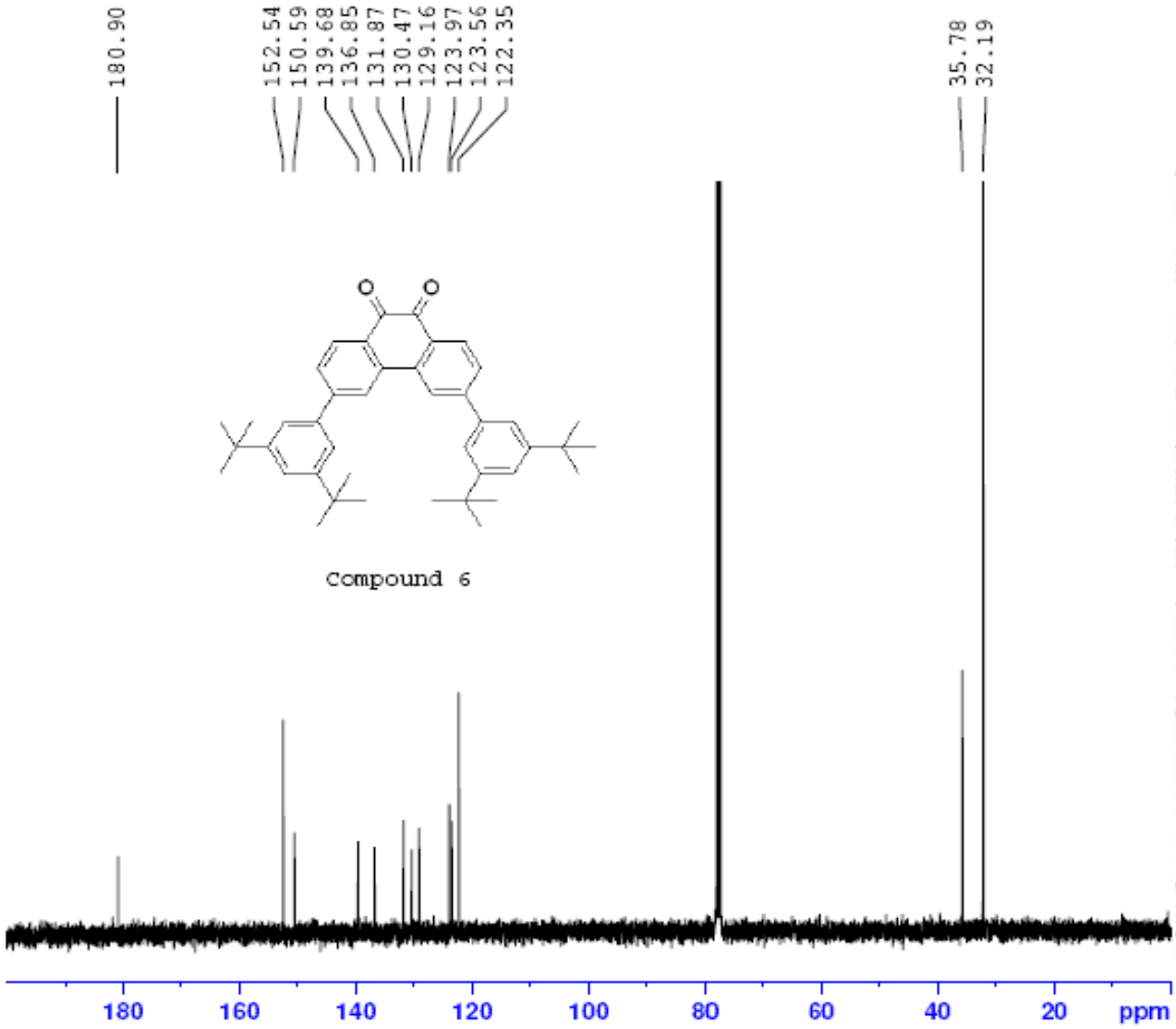

BRUKER

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Current Data Parameters
NAME                  110307
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20110307
Time                 13.05
INSTRUM              AV400
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      346
DS                        4
SWH               23980.814 Hz
FIDRES            0.365918 Hz
AQ                1.3664756 sec
RG                   3649.1
DW                   20.850 usec
DE                    6.00 usec
TE                   299.1 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    9.00 usec
PL1                  -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -2.00 dB
PL12                 14.12 dB
PL13                 14.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                    32768
SF            100.6127006 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    0.50
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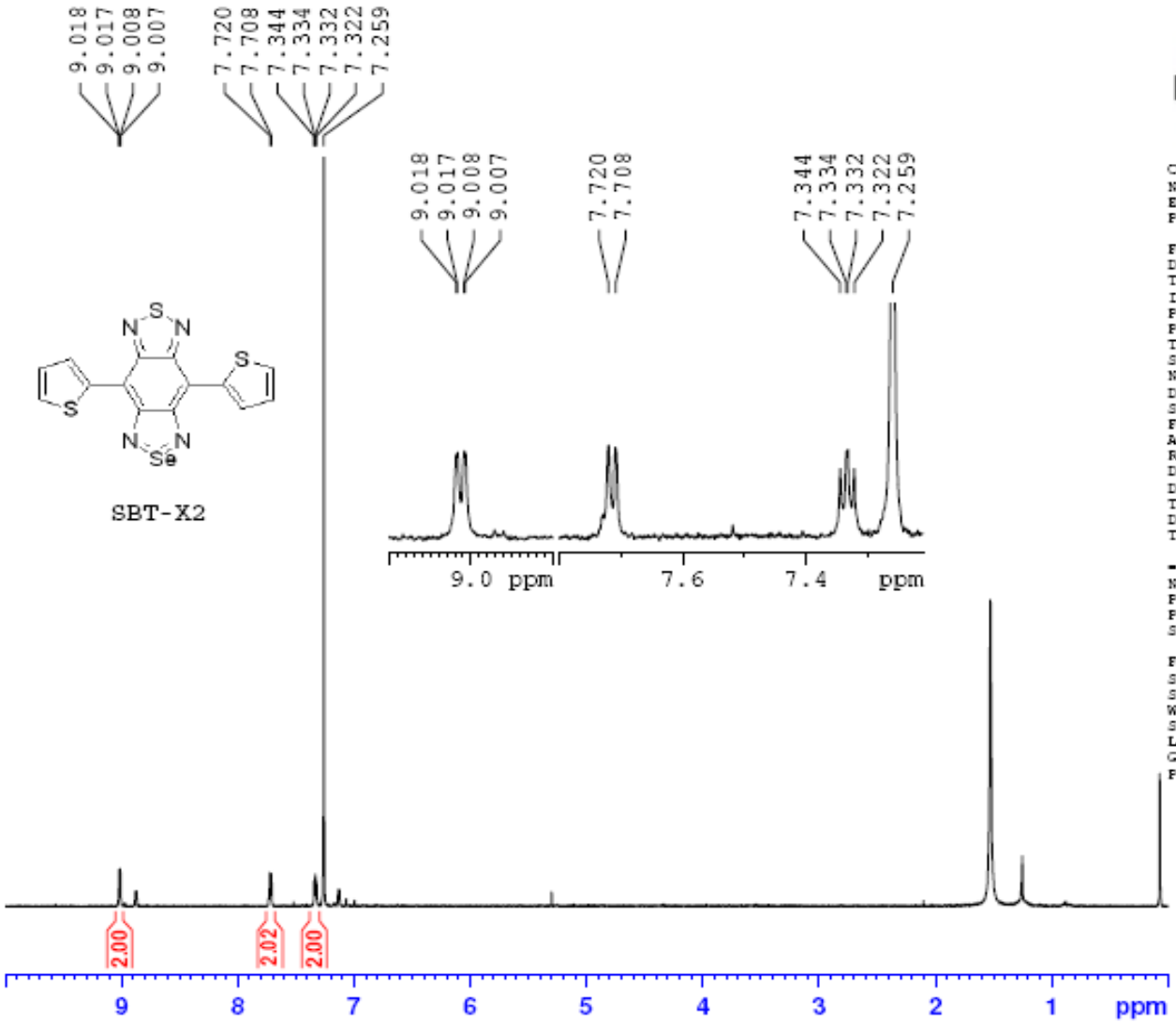


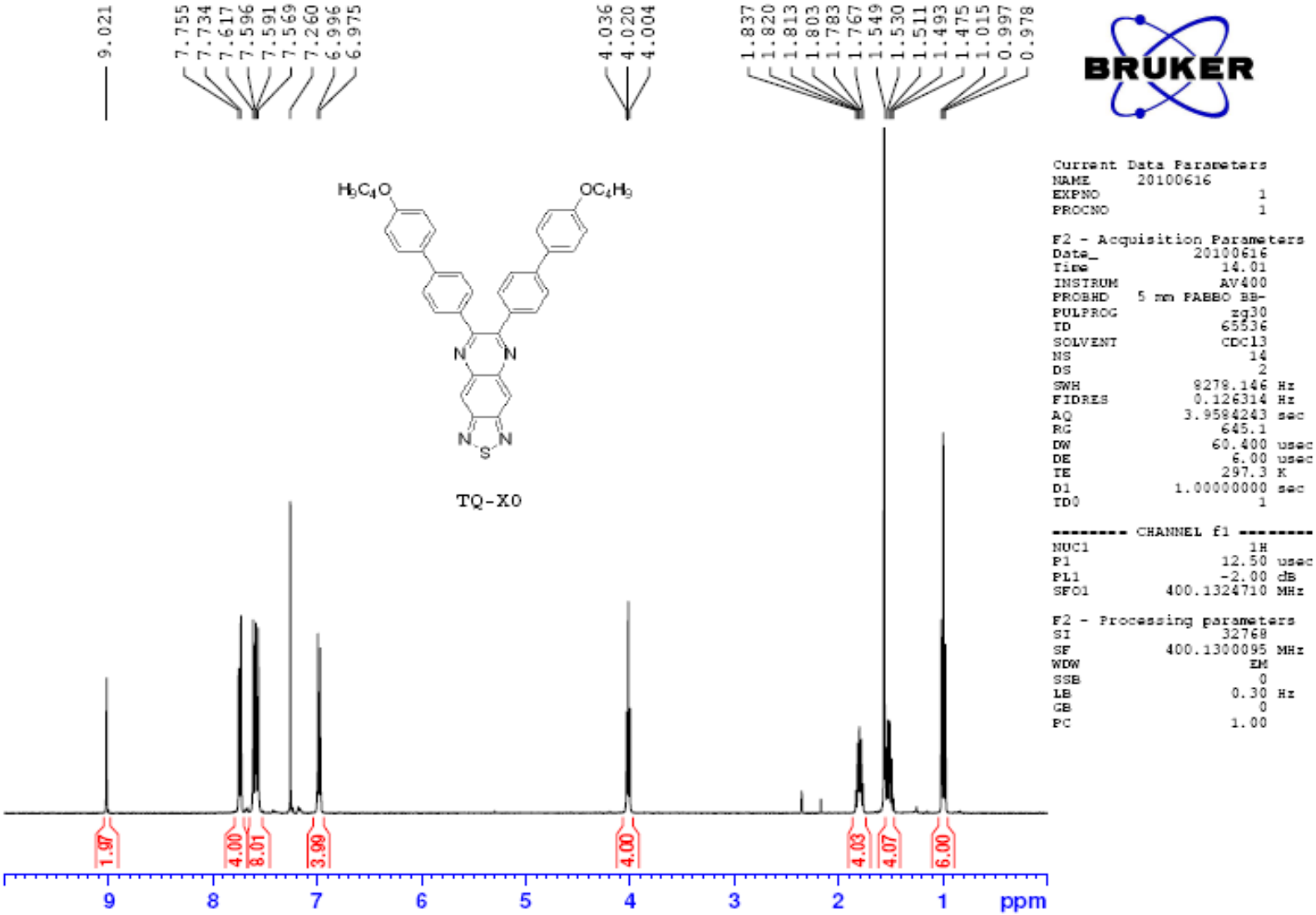
BRUKER

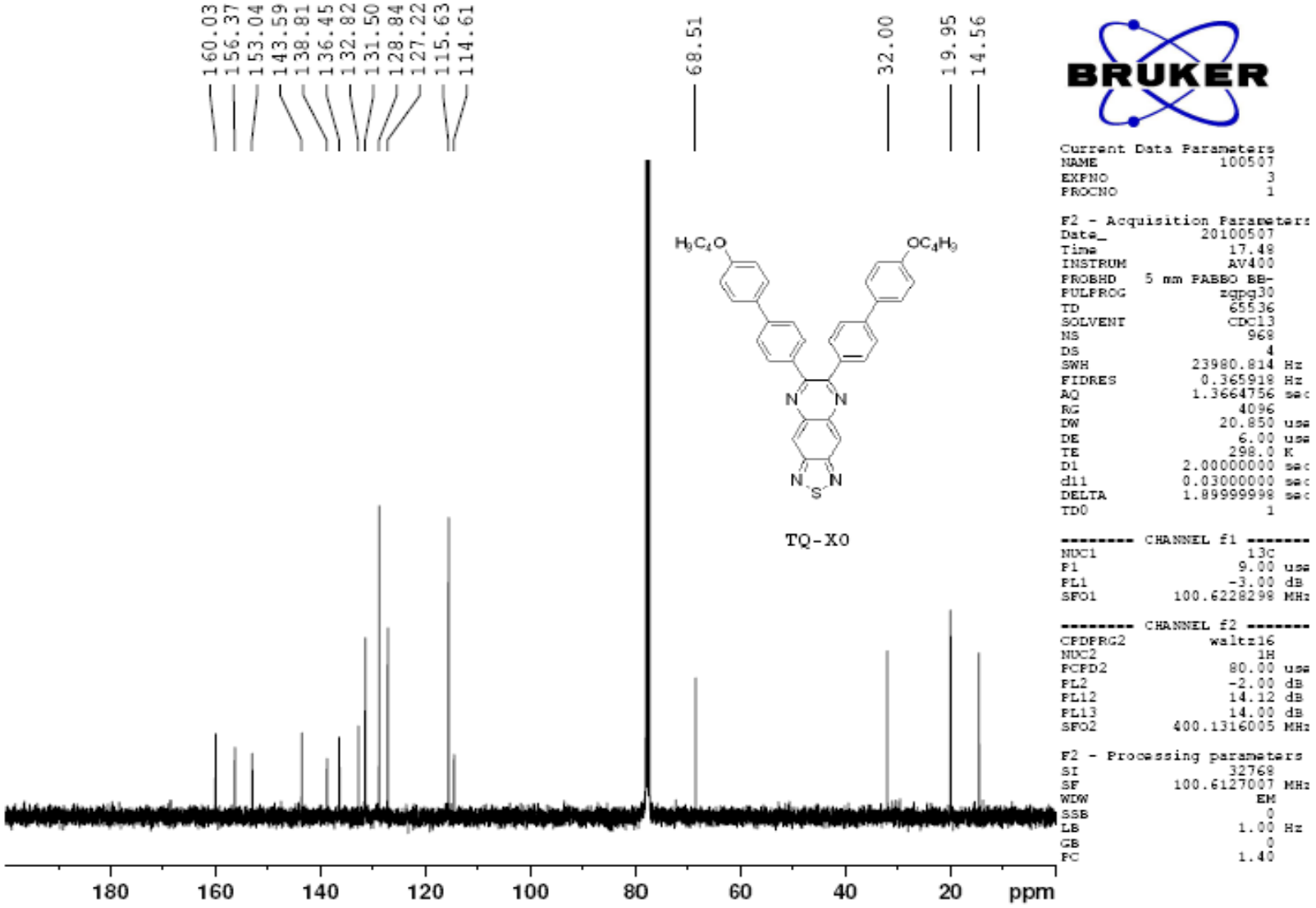
```
Current Data Parameters
NAME                 110406
EXPNO                     1
PROCNO                    1

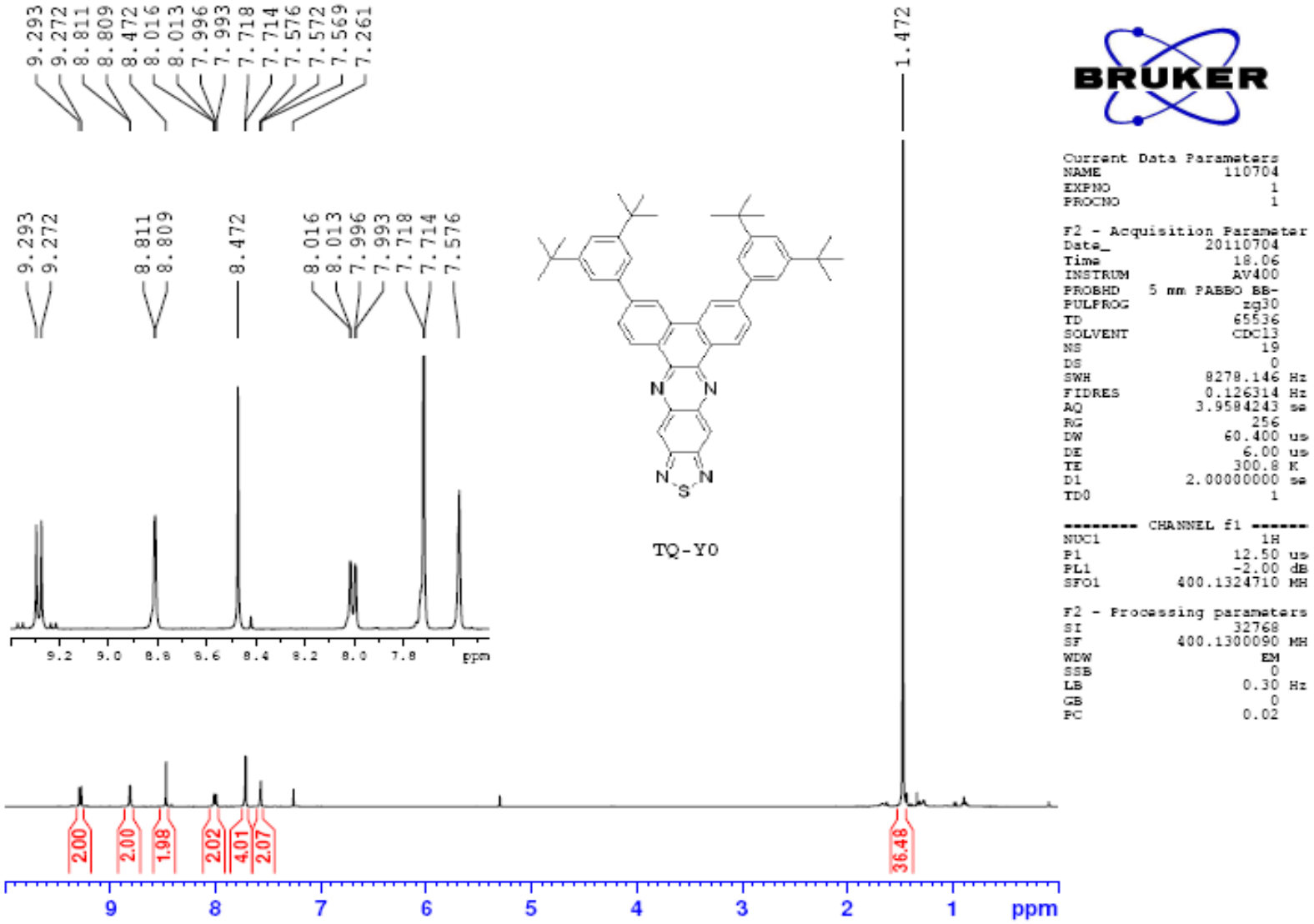
F2 - Acquisition Parameters
Date_             20110406
Time                 17.45
INSTRUM              AV400
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      14
DS                       0
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                     256
DW                  60.400 usec
DE                   6.00 usec
TE                  296.7 K
D1              2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.50 usec
PL1                 -2.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF            400.1300093 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   0.02
```







BRUKER

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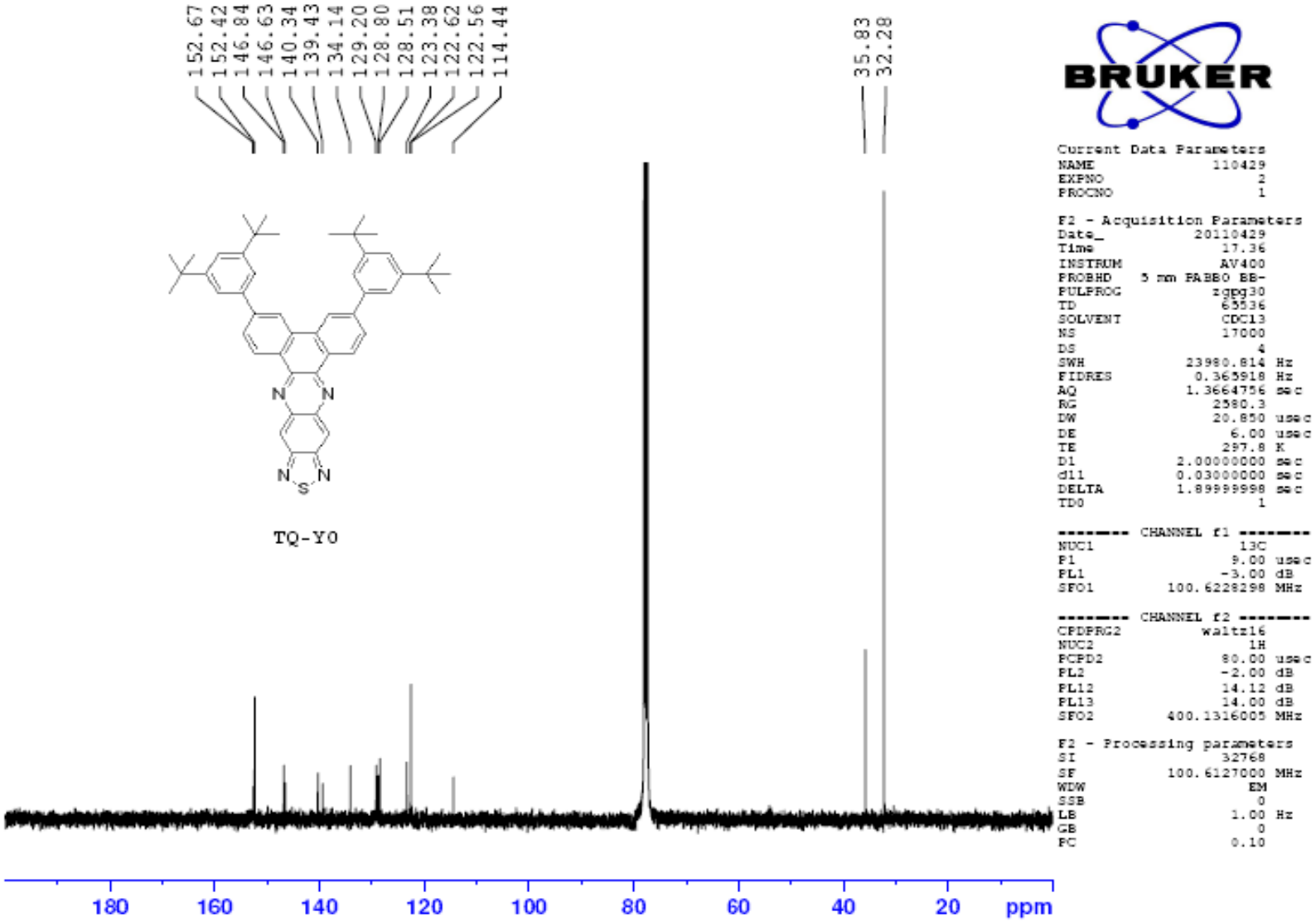
Current Data Parameters
NAME                  110704
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameter
Date_              20110704
Time                  18.06
INSTRUM               AV400
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       19
DS                        0
SWH                8278.146 Hz
FIDRES                0.126314 Hz
AQ                 3.9584243 sec
RG                      256
DW                   60.400 usec
DE                    6.00 usec
TE                   300.8 K
D1                 2.00000000 sec
TD0                       1

======== CHANNEL f1 ======
NUC1                      1H
P1                   12.50 usec
PL1                  -2.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF            400.1300090 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    0.02
```



BRUKER

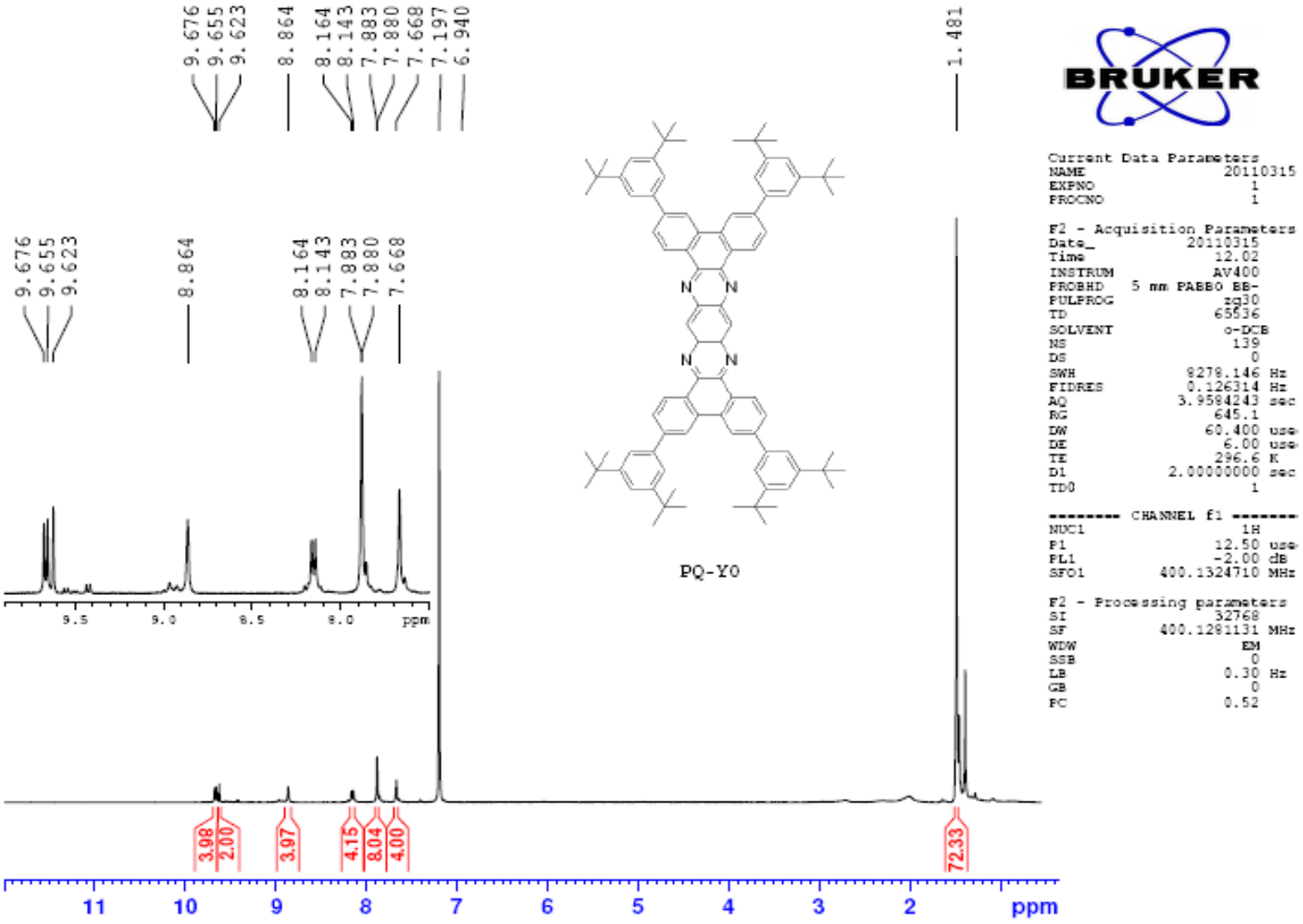
```
Current Data Parameters
NAME                  110429
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20110429
Time                  17.36
INSTRUM                 AV400
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                      17000
DS                          4
SWH                23980.814 Hz
FIDRES             0.365918 Hz
AQ                 1.3664756 sec
RG                     2580.3
DW                    20.850 usec
DE                     6.00 usec
TE                     297.8 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.00 usec
PL1                     -3.00 dB
SFO1             100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                     -2.00 dB
PL12                    14.12 dB
PL13                    14.00 dB
SFO2             400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF               100.6127000 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         0.10
```



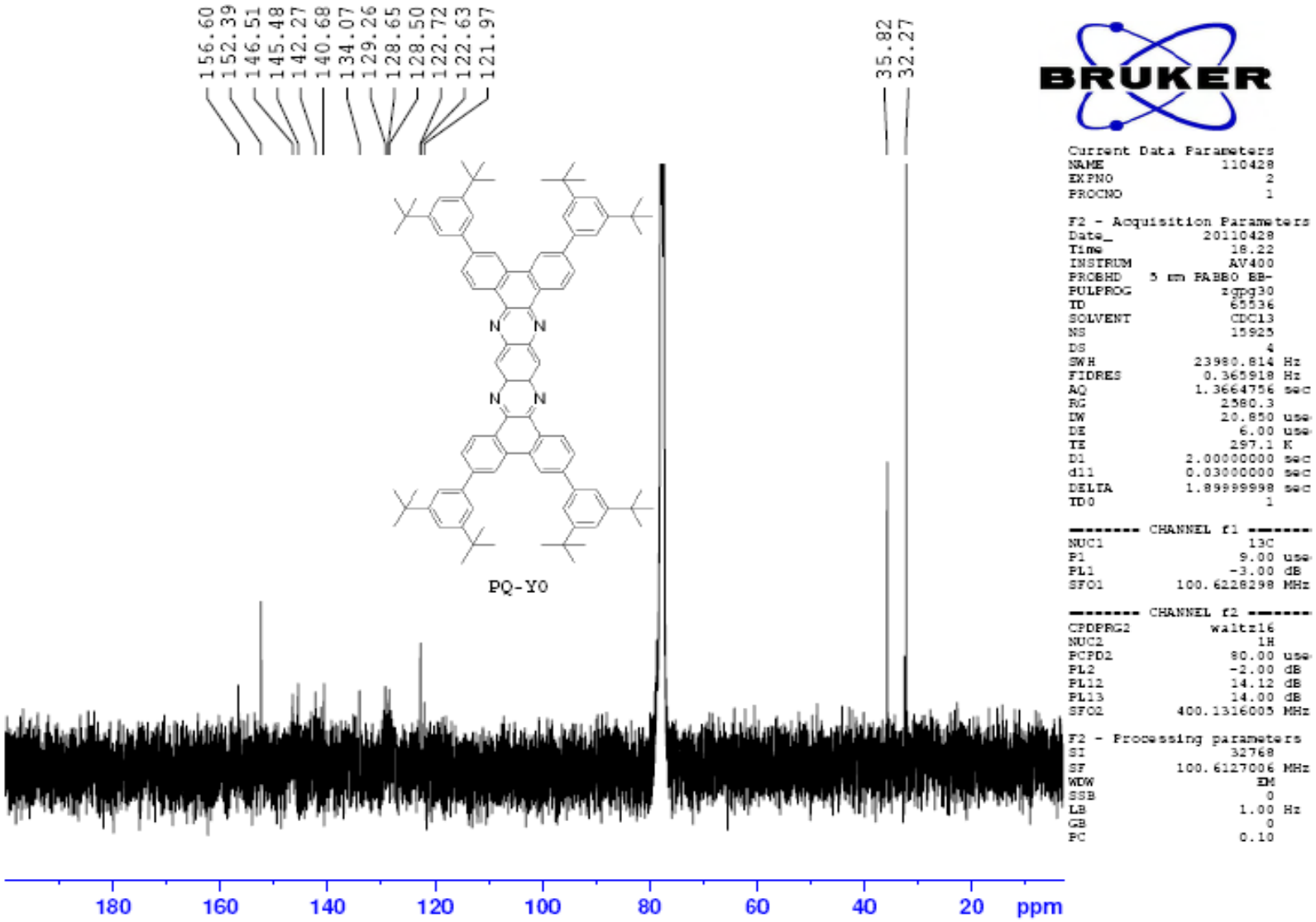
BRUKER

```
Current Data Parameters
NAME                  20110315
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20110315
Time                   12.02
INSTRUM                AV400
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT             o-DCB
NS                       139
DS                         0
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                 3.9584243 sec
RG                     645.1
DW                    60.400 use
DE                     6.00 use
TE                    296.6 K
D1                 2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     12.50 use
PL1                    -2.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF            400.1281131 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      0.52
```

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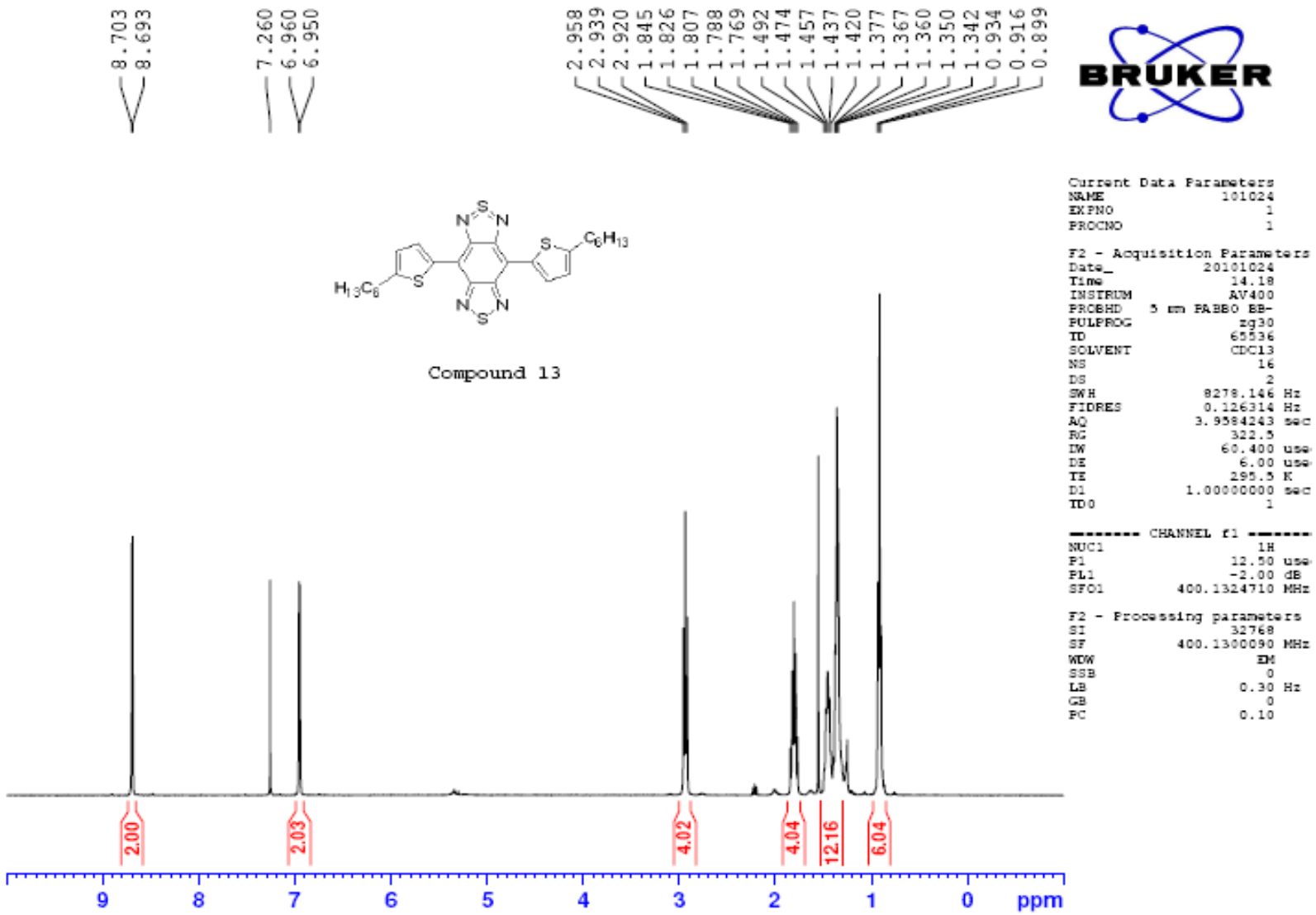
Current Data Parameters
NAME                  110428
EXPNO                      2
PROCNO                     1

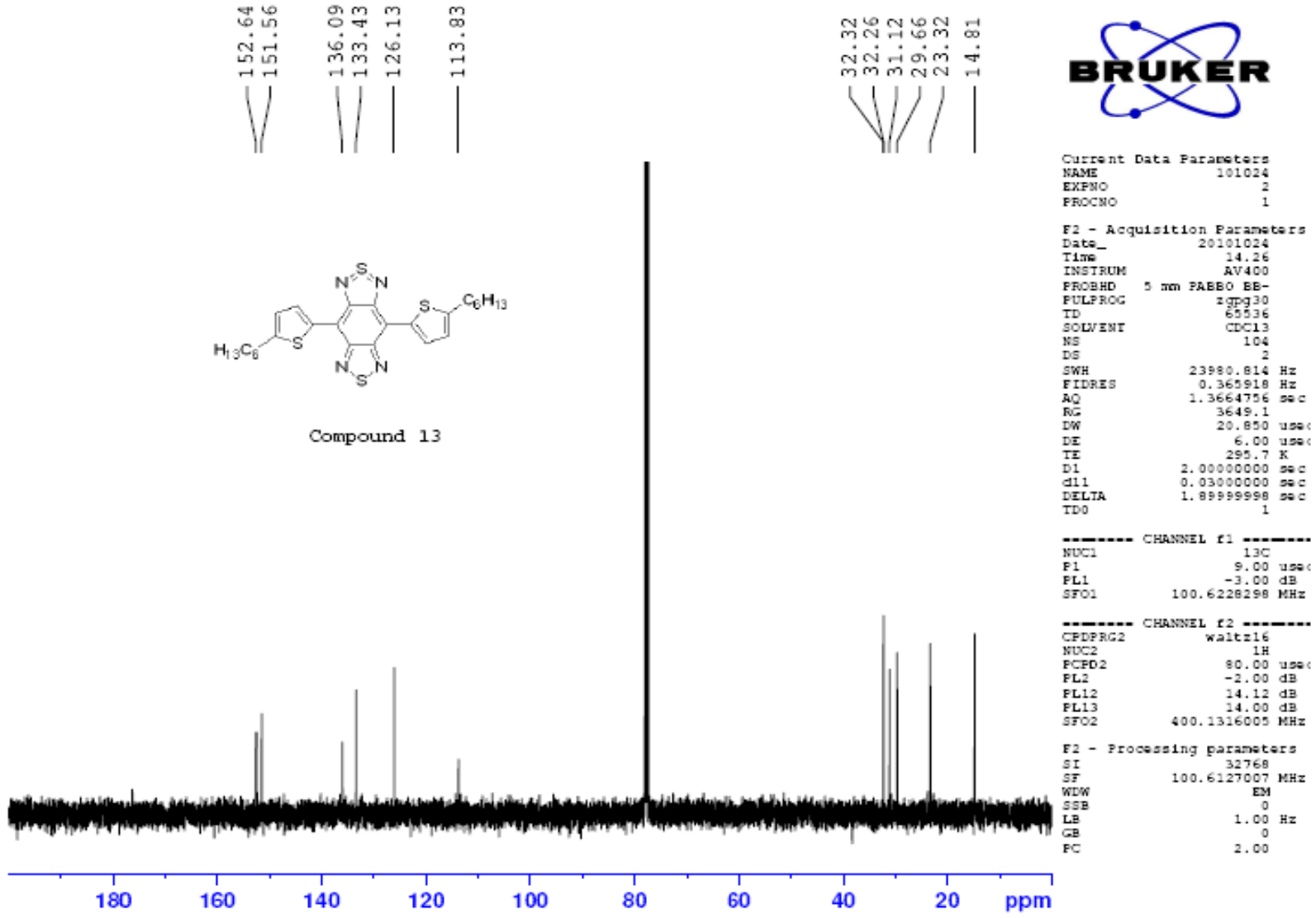
F2 - Acquisition Parameters
Date_              20110428
Time                   18.22
INSTRUM                AV400
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT                CDCl3
NS                     15925
DS                         4
SWH               23980.814 Hz
FIDRES            0.365918 Hz
AQ                1.3664756 sec
RG                    2580.3
DW                   20.850 use
DE                    6.00 use
TE                   297.1 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                      9.00 use
PL1                    -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                 80.00 use
PL2                   -2.00 dB
PL12                  14.12 dB
PL13                  14.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF            100.6127006 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       0.10
```





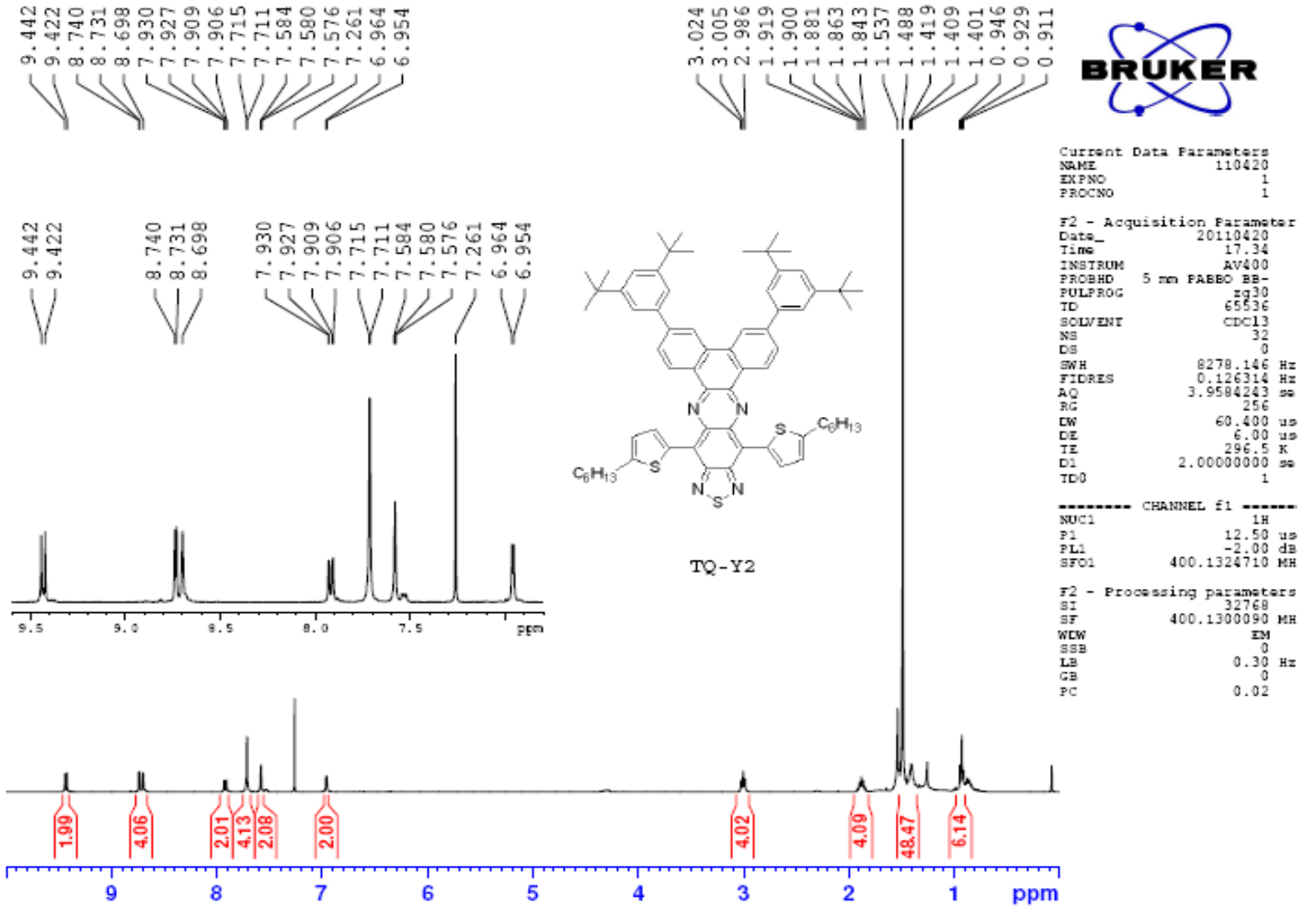

```
Current Data Parameters
NAME                  101024
EXPNO                      2
PROCNO                     1

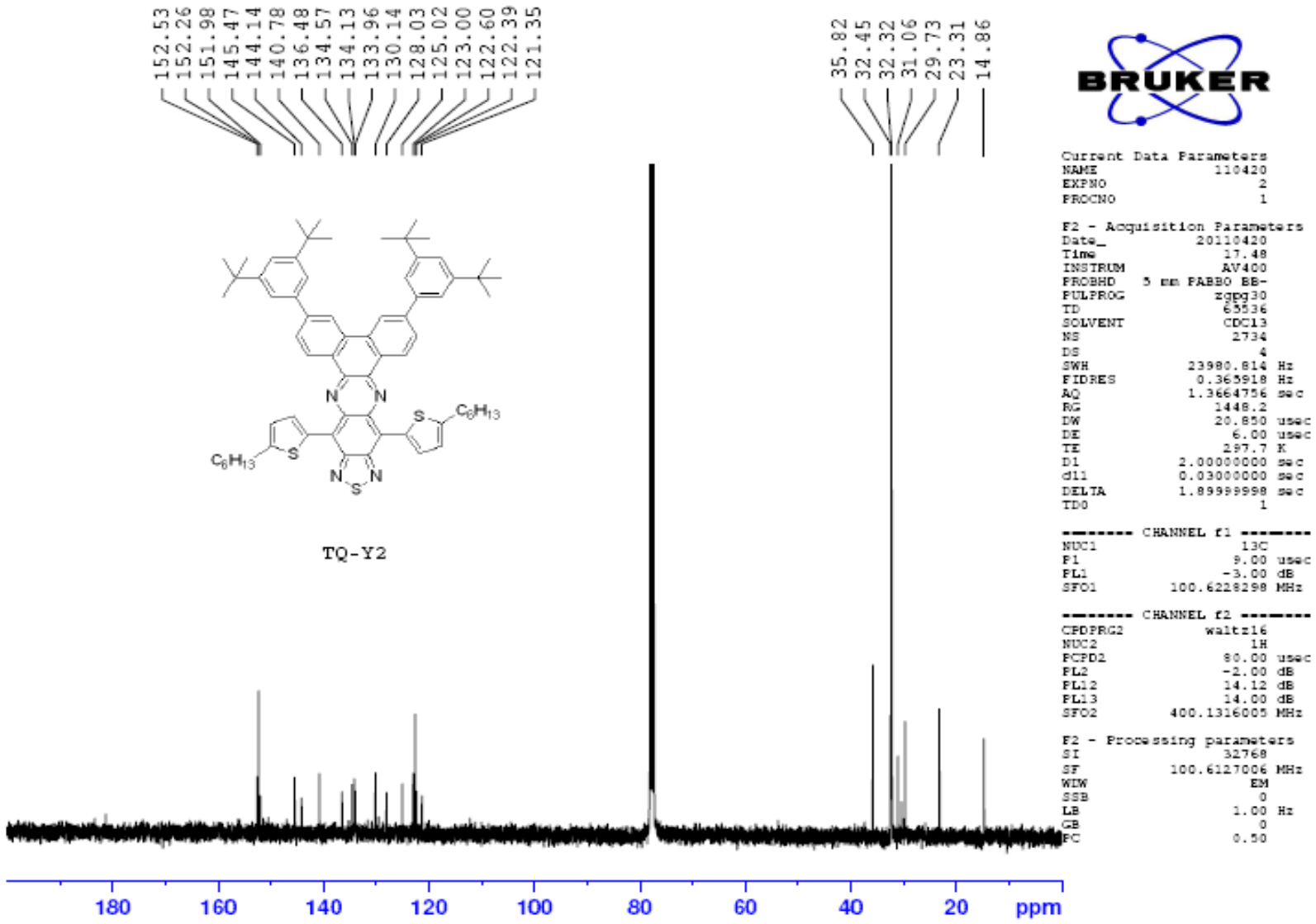
F2 - Acquisition Parameters
Date_              20101024
Time                  14.26
INSTRUM               AV400
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     104
DS                       2
SWH             23980.814 Hz
FIDRES              0.365918 Hz
AQ                1.3664756 sec
RG                   3649.1
DW                   20.850 usec
DE                    6.00 usec
TE                   295.7 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                    13C
P1                     9.00 usec
PL1                   -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                 80.00 usec
PL2                   -2.00 dB
PL12                  14.12 dB
PL13                  14.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                     32768
SF            100.6127007 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      2.00
```





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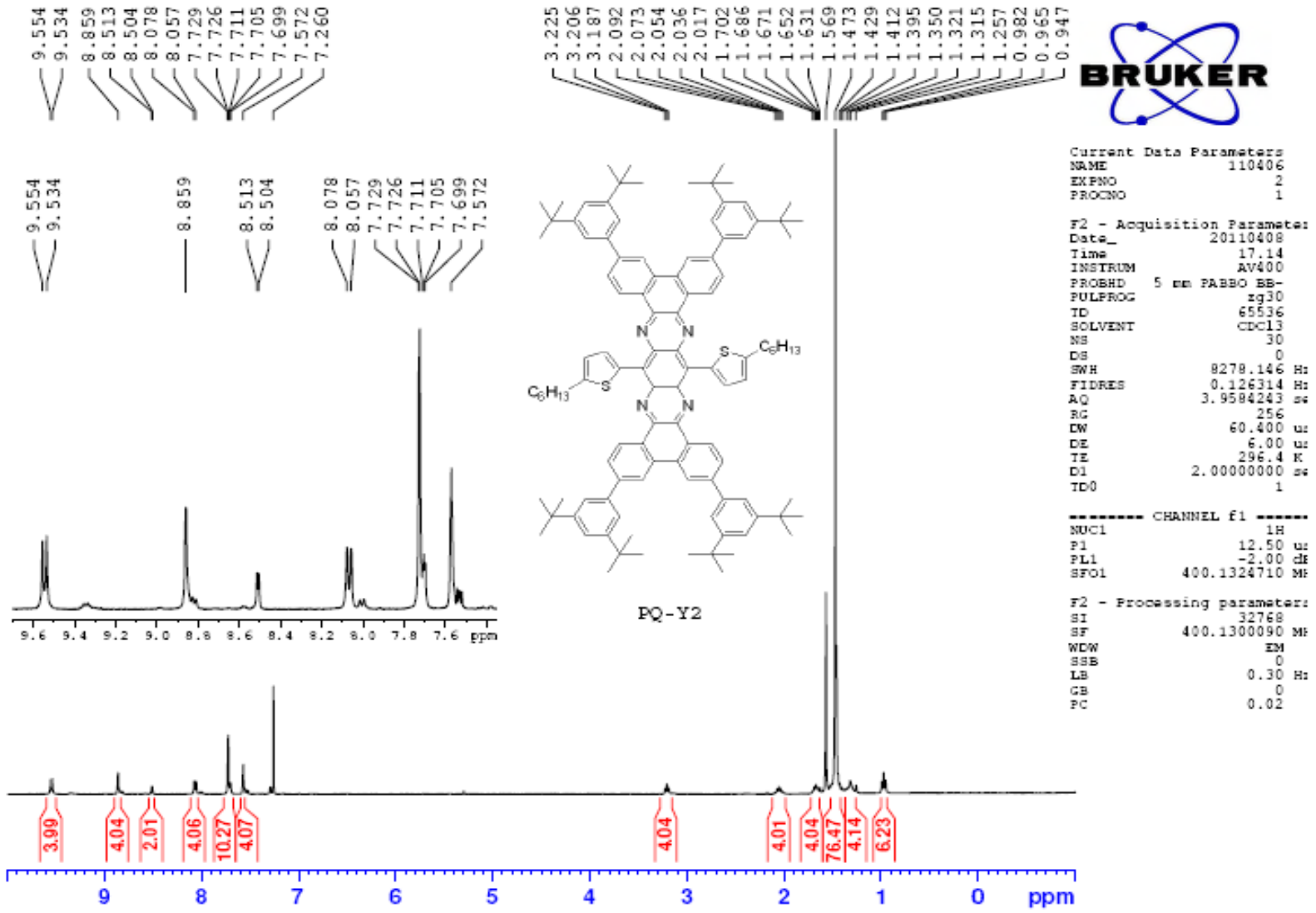
```
Current Data Parameters
NAME                 110420
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20110420
Time                 17.48
INSTRUM              AV400
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2734
DS                        4
SWH              23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                   1448.2
DW                  20.850 usec
DE                   6.00 usec
TE                  297.7 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                   9.00 usec
PL1                 -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2               80.00 usec
PL2                 -2.00 dB
PL12                14.12 dB
PL13                14.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                     32768
SF            100.6127006 MHz
WDW                       EM
SSB                       0
LB                   1.00 Hz
GB                        0
PC                    0.50
```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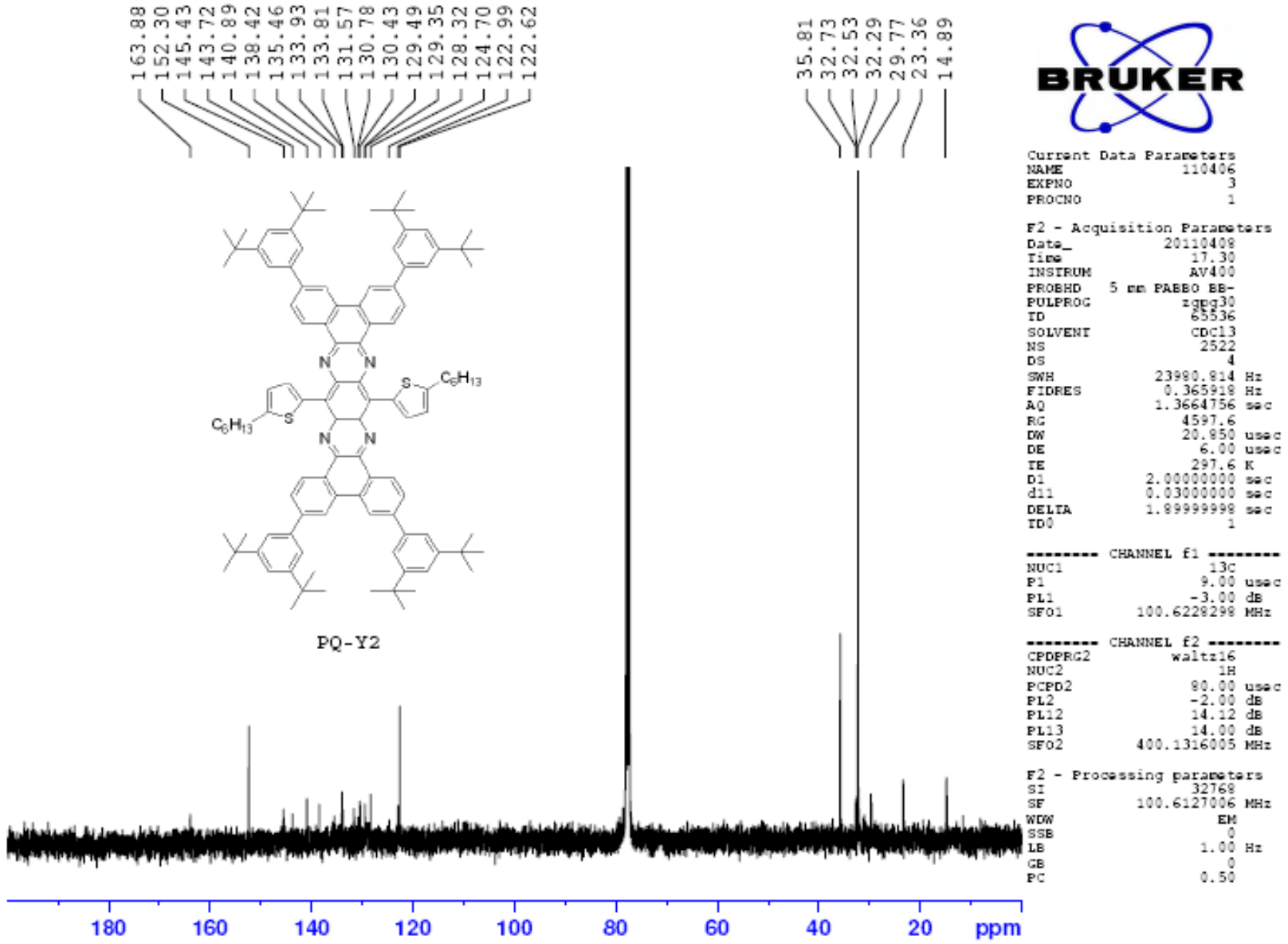
8.513
8.504
8.078
8.057
7.729
7.726
7.711
7.705
7.699
7.572
7.260
3.225
3.206
3.187
2.092
2.073
2.054
2.036
2.017
1.702
1.686
1.671
1.652
1.631
1.569
1.473
1.429
1.412
1.395
1.350
1.321
1.315
1.257
0.982
0.965
0.947
BRUKER
PQ-Y2
Current Data Parameters
NAME 110406
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110408
Time 17.14
INSTRUM AV400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 30
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 256
DW 60.400 usec
DE 6.00 usec
TE 296.4 K
D1 2.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 12.50 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300090 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.02
3.99
4.04
2.01
4.06
10.27
4.07
4.04
4.01
4.04
76.47
4.14
6.23
ppm



BRUKER

```
Current Data Parameters
NAME                  110406
EXPNO                      3
PROCNO                     1

F2 - Acquisition Parameters
Date_              20110408
Time                  17.30
INSTRUM                AV400
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    2522
DS                       4
SWH              23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                  4597.6
DW                  20.850 usec
DE                   6.00 usec
TE                  297.6 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                    13C
P1                    9.00 usec
PL1                  -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -2.00 dB
PL12                 14.12 dB
PL13                 14.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                     32768
SF            100.6127006 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                    0.50
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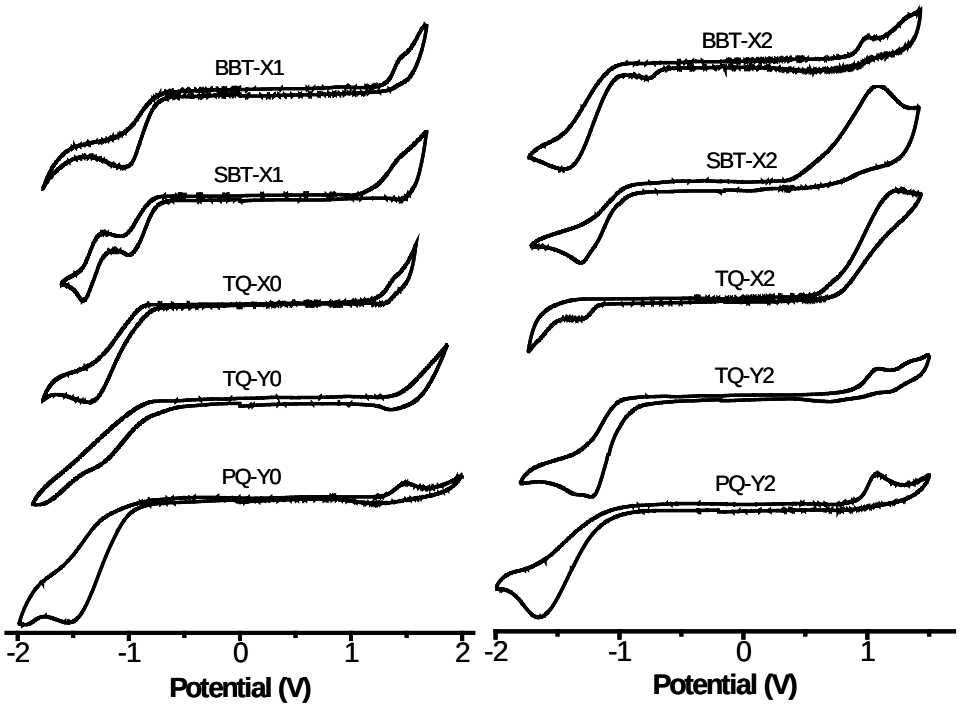

Figure S1. Cyclic voltammetry spectra for all newly synthesized BBT, TQ and PQ molecules (**PQ-X0** and **PQ-X2** can be found in our previous report [4]).

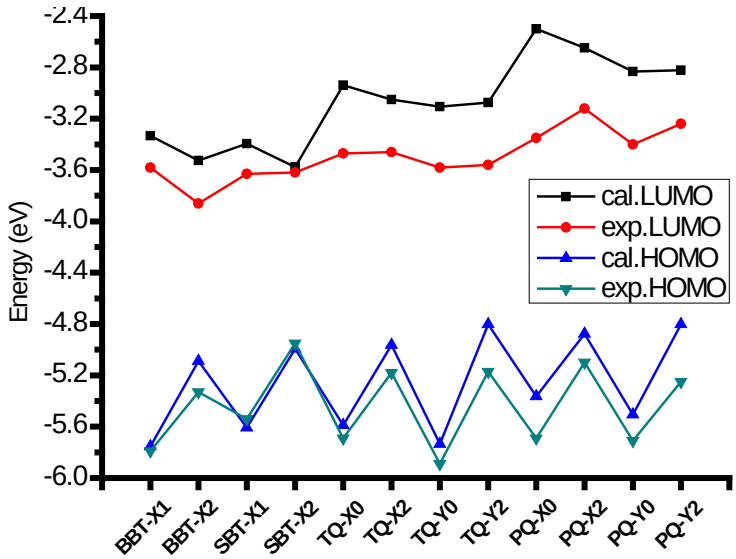

Figure S2. The plot of the calculated HOMO and LUMO energy together with the experimental data.

References

[1] Becke, A. D., *J. Chem. Phys.* **1993**, *98*, 5648.

[2] Lee, C.; W. Yang, W.; Parr, R. G., *Phys. Rev. B* **1988**, *37*, 785.

[3] Refer to the website http://www.gaussian.com/g_tech/g_ur/m_citation.html

[4] Tam, T. L.; Zhou, F.; Li, H.; Yu Pang, J. C.; Lam, Y. M.; Mhaisalkar, S. G.; Su, H.; Grimsdale, A. C., *J. Mater. Chem.* **2011,** *21*, 17798.