Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information for Synthesis and properties of spiro-type heterasumanenes containing group 14 elements as bridging atoms

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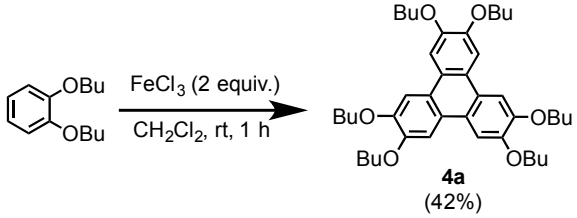
1. General consideration for synthesis and characterization

NMR spectra were recorded on Bruker AVANCE500 spectrometer (^{1}H NMR, 500 MHz; ^{13}C NMR, 125 MHz), Bruker AVANCE400 spectrometer (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) and Bruker AVANCE500T spectrometer (^{29}Si NMR, 99 MHz; ^{119}Sn NMR, 186 Hz). Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane, and referenced internally to the residual proton in the solvent ($CDCl_3$: δ 7.26). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane, and are referenced to the ^{13}C resonance of the NMR solvent ($CDCl_3$: δ 77.16). Chemical shifts for ^{29}Si NMR spectra are reported in parts per million (ppm, δ scale) downfield and are referenced to an external tetramethylsilane as the standard. Chemical shifts for ^{119}Sn NMR spectra are reported in parts per million (ppm, δ scale) downfield and are referenced to an external tetramethylstannane as the standard. The data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), coupling constant in hertz (Hz), and integration. Mass spectra were obtained with Bruker AutoflexIII (MALDI-TOF) mass spectrometer. Cyclic voltammetry measurements were performed with Gamry Interface 1000 using a glassy carbon working electrode, a Pt counter electrode and an $Ag/AgNO_3$ reference electrode at room temperature in CH_2Cl_2 containing 0.1 M *n*-Bu_4NClO_4 as the supporting electrolyte. Melting points were measured by Yanaco MP-S3 instrument. The intensity data for X-ray crystallographic analyses were collected at –173 °C on Bruker SMART APEX II equipped with a CCD area detector with graphite-monochromated MoKα radiation (λ = 0.71073 Å). Column chromatography was performed using Kanto silica gel 60N. Thin layer chromatography was performed using Merck Silica Gel 60 F254, TLC Plates. Medium pressure liquid chromatography was performed with Yamazen Corporation EPCLC AI-580 instrument using Universal columns premium. UV-vis absorption spectra were obtained with JASCO V-770 spectrometer. Electron spin resonance (ESR) spectra were recorded on Bruker EMX6/1 spectrometer.

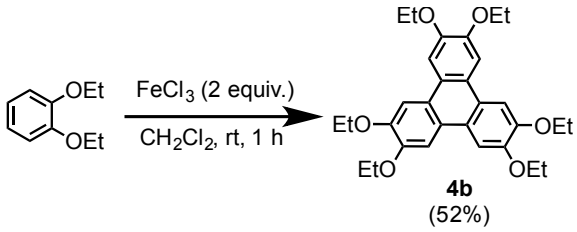
2. Synthetic procedures for all compounds

Synthesis of 2,3,6,7,10,11-hexabutoxytriphenylene (4a)[1]



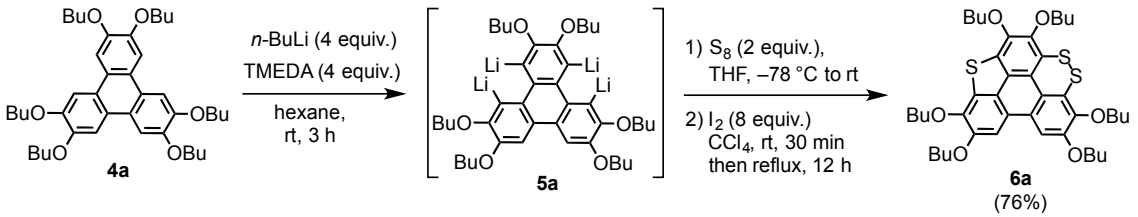
Anhydrous iron(III) chloride (39.1 g, 241 mmol) was added to a dichloromethane (400 mL) solution of 1,2-dibutoxybenzene (26.7 g, 120 mmol) for 40 min at room temperature. After stirring for 20 min at the same temperature, ethanol (320 mL) was added to the reaction mixture. The mixture was cooled in an ice-bath and then the resulting solid was corrected by suction filtration. The products were purified by silica gel column chromatography (eluents: hexane : $CHCl_3$ = 2 : 3, *v*/*v*) to give **4a** (11.2 g, 16.9 mmol, 42%) as a colorless solid.

Synthesis of 2,3,6,7,10,11-hexaethoxytriphenylene (4b)[1]



A dichloromethane (140 mL) solution of 1,2-diethoxybenzene (36.5 g, 220 mmol) was added to a suspension of anhydrous iron(III) chloride (71.5 g, 441 mmol) in dichloromethane (360 mL) dropwise for 40 min at room temperature. After stirring for 45 min at the same temperature, ethanol (350 mL) was added to the reaction mixture. The mixture was cooled in an ice-bath and then the resulting solid was corrected by suction filtration. The products were purified by silica gel column chromatography ($CHCl_3$) to give **4b** (19.0 g, 38.6 mmol, 52%) as a colorless solid.

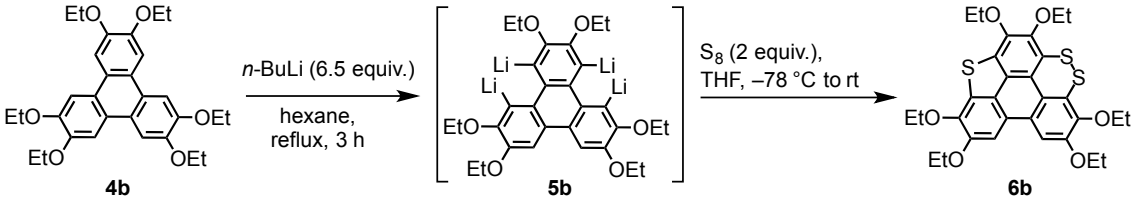
Synthesis of 2,3,6,7,10,11-hexabutoxy[4,5-*b,c,d*]thienotriphenyleno[8,9-*c′,d′,e′*]1′,2′-dithiine (6a)



Anhydrous hexane (28 mL) and TMEDA (6.4 mL, 43.0 mmol) were added to **4a** (7.06 g, 10.7

mmol) in a dried three-necked-flask under argon atmosphere. *n*-BuLi in hexane (2.66 M, 16.1 mL, 42.8 mmol) was added dropwise to the suspension for 20 min. The suspension was stirred at room temperature for 3 hours. Volatiles were removed under reduced pressure. THF (210 mL) was added to the resulting solid and then cooled to under −70 °C. Sulfur powder (5.50 g, 21.4 mmol) was added to the suspension. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for 12 hours. After stirring, aqueous NH_4Cl was added to the mixture, and insoluble materials were removed by suction filtration. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown viscous solid (9.54 g). Carbon tetrachloride (180 mL) and iodine (19.0 g, 75.0 mmol) were added to the viscous solid under argon atmosphere, and the mixture was stirred at room temperature for 50 min. After heating under reflux conditions for 14 hours, the mixture was cooled to room temperature, then aqueous sodium sulfite was added. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a dark yellow solid. The products were purified by silica gel column chromatography (eluent, hexane: $CHCl_3$, 2:3, *v/v*) to give **6a** (6.16 g, 8.18 mmol, 76%) as a yellow solid. mp. 105-107 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01-1.08 (m, 18H), 1.58-1.67 (m, 12H), 1.83-1.90 (m, 8H), 1.91–1.97 (m, 4H), 4.20–4.28 (m, 8H), 4.34-4.39 (m, 4H), 7.74 (s, 1H), 7.76 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.07-14.14 (m, CH_3), 19.42 (CH_2), 19.46 (CH_2), 19.51 (CH_2), 19.59 (CH_2), 31.57 (CH_2), 31.85 (CH_2), 32.57, 32.59 (CH_2), 32.60 (CH_2), 32.62 (CH_2), 68.84 (CH_2), 70.32 (CH_2), 73.22 (CH_2), 73.29 (CH_2), 73.86 (CH_2), 74.74 (CH_2), 105.08 (CH), 105.83 (CH), 120.53 (C), 121.30 (C), 122.56 (C), 123.43 (C), 123.91 (C), 126.49 (C), 127.11 (C), 128.30 (C), 128.34 (C), 130.71 (C), 143.29 (C), 145.01 (C), 146.28 (C), 146.47 (C), 152.36 (C), 152.82 (C); MS (MALDI) *m*/*z* calcd for $C_{42}H_{56}O_6S_3$ ([M]$^+$) 752.3, found: 752.2; elemental analysis calcd for $C_{42}H_{56}O_6S_3$: C, 66.98; H, 7.50, found: C, 66.99; H, 7.55.

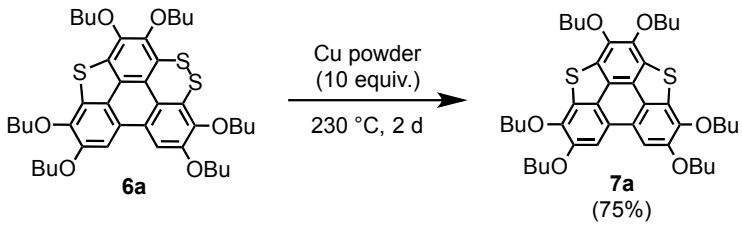
Synthesis of 2,3,6,7,10,11-hexaethoxy[4,5-*b*,*c*,*d*]thienotriphenyleno[8,9-*c*′,*d*′,*e*′]1′,2′-dithiine (6b)



Anhydrous hexane (250 mL) was added to **4b** (5.01 g, 10.2 mmol) in a dried three-necked-flask under argon atmosphere. *n*-BuLi in hexane (2.66 M, 24.0 mL, 63.8 mmol) was added dropwise to the suspension. The suspension was refluxed for 3 hours. Volatiles were removed under reduced pressure. THF (200 mL) was added to the resulting solid and then the mixture was cooled to under

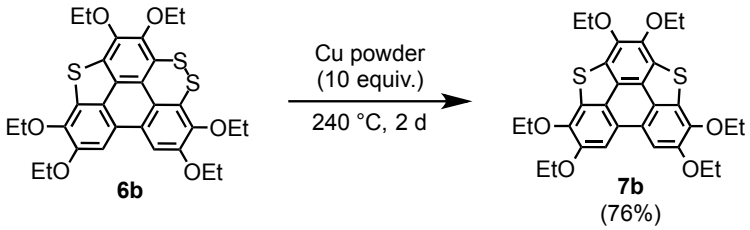
−70 °C. Sulfur powder (5.32 g, 20.7 mmol) was added to the suspension, and stirred for 30 min at −70 °C. The mixture was allowed to warm to room temperature and stirred for 12 hours. After stirring, aqueous NH_4Cl was added to the mixture, and insoluble materials were removed by suction filtration. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown solid. The products were purified by silica gel column chromatography (eluent, hexane: CH_2Cl_2 = 2 : 3, *v/v*) to give **6b** (3.04 g, 5.20 mmol, 51%) as a yellow solid. mp. 169-170 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48-1.53 (m, 12H), 1.57 (t, *J* = 7.0 Hz, 6H), 4.27–4.34 (m, 8H), 4.43 (q, *J* = 7.0 Hz, 4H), 4.47 (q, *J* = 7.0 Hz, 4H), 7.71 (s, 1H), 7.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.02 (CH_3), 15.27 (CH_3), 15.92 (CH_3), 15.96 (CH_3), 16.12 (CH_3), 64.72 (CH_2), 66.07 (CH_2), 68.94 (CH_2), 68.98 (CH_2), 69.76 (CH_2), 70.49 (CH_2), 105.03 (CH), 105.83 (CH), 120.43 (C), 121.18 (C), 122.39 (C), 123.31 (C), 123.77 (C), 126.30 (C), 127.01 (C), 128.24 (C), 128.26 (C), 130.65 (C), 142.87 (C), 144.75 (C), 145.98 (C), 146.13 (C), 152.01 (C), 152.53 (C); MS (MALDI) *m/z* calcd for $C_{30}H_{32}O_6S_3$ ($[M]^+$) 584.1, found: 584.4; elemental analysis calcd for $C_{30}H_{32}O_6S_3$: C, 61.62; H, 5.52, found: C, 61.29; H, 5.44.

Synthesis of 2,3,6,7,10,11-hexabutoxy[4,5-*b*,*c*,*d*:8,9-*b′*,*c′*,*d′*]dithiophene (7a)



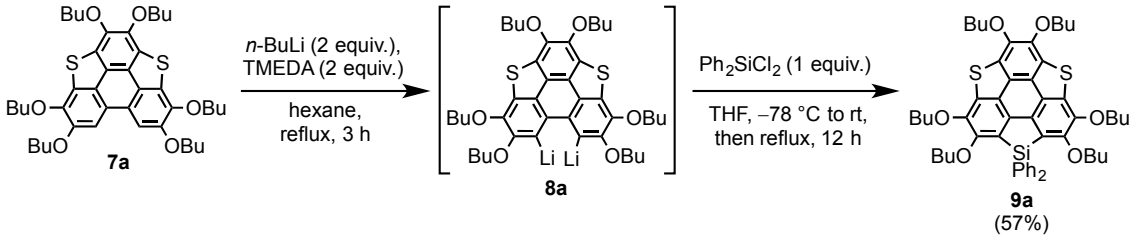
Compound **6a** (4.18 g, 5.55 mmol) and copper powder (3.70 g, 58.3 mmol) were mixed in a flask, and the mixture was heated at 230 °C for 2 days under argon atmosphere. After cooled to room temperature, dichloromethane was added to the reaction mixture, and the resulting insoluble solid was removed by suction filtration. The filtrate was concentrated and further purified by column chromatography on silica (eluent, hexane : CH_2Cl_2 = 3 : 2, *v/v*) to give **7a** as a yellow solid (3.00 g, 4.16 mmol, 75%). mp. 111-112 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02-1.08 (m, 18H), 1.61-1.69 (m, 12H), 1.85-1.98 (m, 12H), 4.28 (t, *J* = 6.5 Hz, 4H), 4.41 (t, *J* = 6.5 Hz, 4H), 4.45 (t, *J* = 6.5 Hz, 4H), 7.84 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.09 (CH_3), 14.11 (CH_3), 19.43 (CH_2), 19.46 (CH_2), 19.60 (CH_2), 31.93 (CH_2), 32.50 (CH_2), 32.59 (CH_2), 70.58 (CH_2), 72.89 (CH_2), 73.08 (CH_2), 106.68 (CH), 123.11 (C), 123.56 (C), 125.09 (C), 127.52 (C), 132.49 (C), 143.70 (C), 145.99 (C), 152.24 (C); MS (MALDI) *m/z* calcd for $C_{42}H_{56}O_6S_2$ ($[M]^+$) 720.4, found: 720.2; elemental analysis calcd for $C_{42}H_{56}O_6S_2$: C, 69.96; H, 7.83, found: C, 69.82; H, 7.88.

Synthesis of 2,3,6,7,10,11-hexaethoxy[4,5-*b*,*c*,*d*:8,9-*b*′,*c*′,*d*′]dithiophene (7b)



Compound **6b** (2.30 g, 3.94 mmol) and copper powder (2.49 g, 3.92 mmol) were mixed in a flask, and the mixture was heated at 240 °C for 2 days under argon atmosphere. After cooled to room temperature, dichloromethane was added to the reaction mixture, and the resulting insoluble solid was removed by suction filtration. The filtrate was concentrated and further purified by column chromatography on silica (eluent, hexane : CH_2Cl_2 = 2 : 5, *v*/*v*) to give **7b** as a pale yellow solid (1.676 g, 3.03 mmol, 75%). mp. 174 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52 (t, *J* = 8.5 Hz, 6H), 1.54 (t, *J* = 8.5 Hz, 6H), 1.58 (t, *J* = 8.5 Hz, 6H), 4.35 (q, *J* = 8.5 Hz, 4H), 4.49 (q, *J* = 8.5 Hz, 4H), 4.52 (q, *J* = 8.5 Hz, 4H), 7.85 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.36 (CH_3), 16.02 (CH_3), 16.08 (CH_3), 66.47 (CH_2), 68.68 (CH_2), 68.85 (CH_2), 106.92 (CH), 123.19 (C), 123.58 (C), 125.11 (C), 127.57 (C), 132.52 (C), 143.48 (C), 145.70 (C), 151.97 (C); MS (MALDI) *m*/*z* calcd for $C_{30}H_{32}O_6S_2$ ($[M]^+$) 552.2, found: 552.2; elemental analysis calcd for $C_{30}H_{32}O_6S_2$: C, 65.19; H, 5.84, found: C, 64.97; H, 5.75.

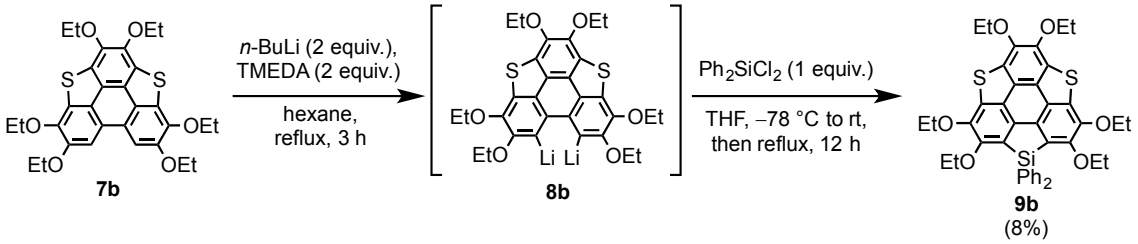
Synthesis of 2,3,6,7,10,11-hexabutoxytriphenyleno[4,5-2′,3′,4′,5′]1′,1′-diphenyl-1*H*-silolo[8,9-*b*,*c*,*d*:12,1-*b*′,*c*′,*d*′]dithiophene (9a)



Anhydrous hexane (4.4 mL) and TMEDA (0.40 mL, 2.68 mmol) were added to **7a** (948 mg, 1.32 mmol) in a dried three-necked-flask under argon atmosphere. *n*-BuLi in hexane (2.66 M, 1.00 mL, 2.66 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (26 mL) was added to the resulting solid and then the mixture was cooled to under −70 °C. Dichlorodiphenylsilane (0.28 mL, 1.33 mmol) was added slowly to the solution and stirred for 30 min at −70 °C. The mixture was allowed to warm to room temperature and stirred for an hour then was refluxed for 12 hours. After cooling to room temperature, aqueous NH_4Cl was added to the mixture. The reaction mixture was extracted with

chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give an orange solid. The products were purified by silica gel column chromatography (eluent, hexane : CH_2Cl_2 = 1:1, *v/v*) to give **9a** (681 mg, 0.755 mmol, 57%) as a yellow solid. mp. 128-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (t, *J* = 9.0 Hz, 6 H), 1.02 (t, *J* = 9.5 Hz, 6H), 1.04 (t, *J* = 9.0 Hz, 6H), 1.19 (sext, *J* = 9.5 Hz, 4H), 1.51-1.68 (m, 12H), 1.85-1.93 (m, 8H), 3.92 (t, *J* = 9.0 Hz, 4H), 4.40 (t, *J* = 8.0 Hz, 4H), 4.43 (t, *J* = 8.0 Hz, 4H), 7.32-7.43 (m, 6H), 7.81-7.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.84 (CH_3), 14.02 (CH_3), 19.03 (CH_2), 19.41 (CH_2), 32.03 (CH_2), 32.39 (CH_2), 32.43 (CH_2), 72.43 (CH_2), 72.93 (CH_2), 73.53 (CH_2), 120.07 (C), 125.78 (C), 126.05 (C), 126.97 (C), 128.28 (CH), 130.42 (CH), 133.09 (C), 133.36 (C), 135.05 (C) 135.82 (CH), 146.40 (C), 146.49 (C), 156.25 (C); ^{29}Si NMR (99 MHz, $CDCl_3$) δ –0.04; MS (MALDI) *m/z* calcd for $C_{54}H_{64}O_6S_2Si$ ([M]$^+$) 900.4, found: 900.5; elemental analysis calcd for $C_{54}H_{64}O_6S_2Si$: C, 71.97; H, 7.16, found: C, 71.88; H, 7.21.

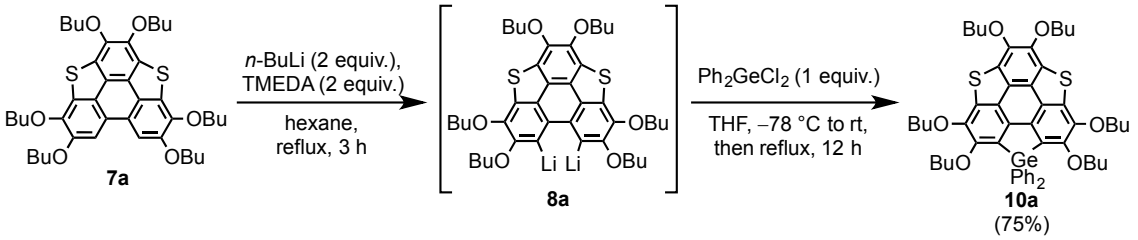
Synthesis of 2,3,6,7,10,11-hexaethoxytriphenyleno[4,5-2′,3′,4′,5′]1′,1′-diphenyl-1*H*-silolo[8,9-*b*,*c*,*d*:12,1-*b*′,*c*′,*d*′]dithiophene (9b)



Anhydrous hexane (15 mL) and TMEDA (0.30 mL, 2.01 mmol) were added to **7b** (510 mg, 0.92 mmol) in dried a three-necked-flask under argon atmosphere. *n*-BuLi in hexane (2.66 M, 0.72 mL, 1.91 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (15 mL) was added to the resulting solid and then cooled to under −70 °C. A THF (5 mL) solution of dichlorodiphenylsilane (0.20 mL, 0.96 mmol) was transferred to the reaction mixture via a PTFE tube over 10 min. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour then was refluxed for 12 hours. After cooling to room temperature, aqueous NH_4Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown solid. The products were purified by silica gel column chromatography (eluent, hexane : CH_2Cl_2 = 2 : 3, *v/v*) to give **9b** (53 mg, 0.073 mmol, 8%) as a yellow solid. mp. 216-217 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16 (t, *J* = 7.0 Hz, 6 H), 1.52 (t, *J* = 7.0 Hz, 6H), 1.54 (t, *J* = 7.0 Hz, 6H), 4.02 (q, *J* = 7.0 Hz, 4H), 4.48 (q, *J* = 7.0 Hz, 4H), 4.51 (q, *J* = 7.0 Hz, 4H), 7.34-7.37 (m, 4H), 7.40-7.44 (m, 2H), 7.82-7.84

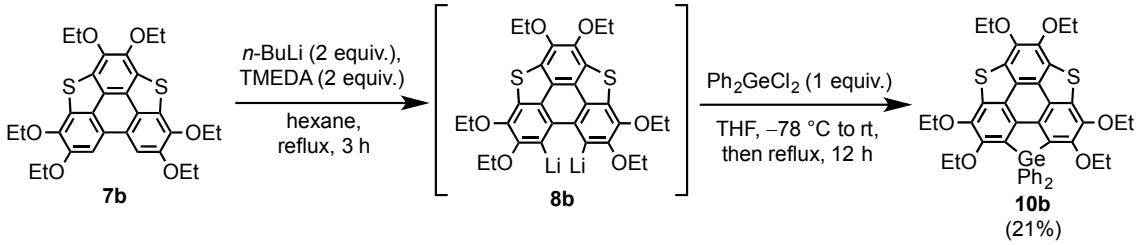
(m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.38 (CH_3), 15.95 (CH_3), 15.97 (CH_3), 68.33 (CH_2), 68.85 (CH_2), 69.38 (CH_2), 120.78 (C), 126.01 (C), 126.19 (C), 127.19 (C), 128.33 (CH), 130.50 (CH), 133.11 (C), 133.14 (C), 135.14 (C) 135.78 (CH), 146.30 (C), 146.44 (C), 155.93 (C); ^{29}Si NMR (99 MHz, $CDCl_3$) δ 0.037; MS (MALDI) *m*/*z* calcd for $C_{42}H_{40}O_6S_2Si$ ([M]$^+$) 732.2, found: 732.2; elemental analysis calcd for $C_{42}H_{40}O_6S_2Si$: C, 68.82; H, 5.50, found: C, 68.68; H, 5.46.

Synthesis of 2,3,6,7,10,11-hexabutoxytriphenyleno[4,5-2′,3′,4′,5′]1′,1′-diphenyl-1*H*-germolo[8,9-*b*,*c*,*d*:12,1-*b*′,*c*′,*d*′]dithiophene (10a)



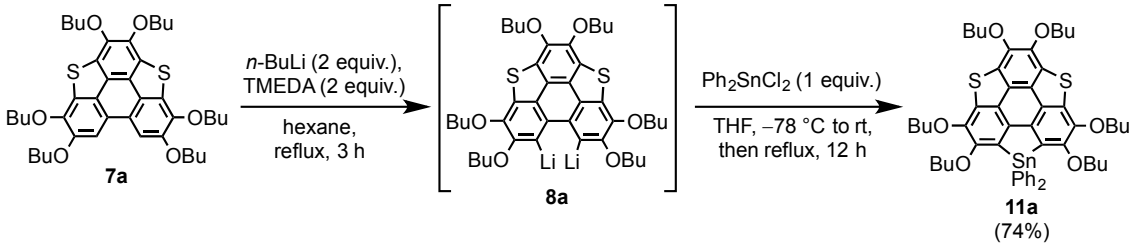
Anhydrous hexane (4.5 mL) and TMEDA (0.35 mL, 2.35 mmol) were added to **7a** (827 mg, 1.15 mmol) in dried a three-necked-flask under argon atmosphere. *n*-BuLi in hexane (2.66 M, 0.87 mL, 2.31 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (22 mL) was added to the resulting solid and then cooled to under −70 °C. Dichlorodiphenylgermane (0.25 mL, 1.20 mmol) was added slowly to the solution. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour. Then the mixture was refluxed for 12 hours. After cooling to room temperature, aqueous NH_4Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give an orange solid. The products were purified by silica gel column chromatography (eluent, hexane : CH_2Cl_2 = 2 : 3, *v*/*v*) to give **10a** (813 mg, 0.859 mmol, 75%) as a pale yellow solid. mp. 126 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.74 (t, *J* = 7.5 Hz, 6 H), 1.02 (t, *J* = 7.5 Hz, 6H), 1.04 (t, *J* = 7.5 Hz, 6H), 1.21 (sext, *J* = 7.5 Hz, 4H), 1.56-1.68 (m, 12H), 1.85-1.93 (m, 8H), 3.97 (t, *J* = 7.5 Hz, 4H), 4.40 (t, *J* = 7.5 Hz, 4H), 4.44 (t, *J* = 7.5 Hz, 4H), 7.35-7.42 (m, 6H), 7.72-7.73 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.84 (CH_3), 14.08 (CH_3), 19.07 (CH_2), 19.44 (CH_2), 32.04 (CH_2), 32.43 (CH_2), 32.48 (CH_2), 72.54 (CH_2), 73.00 (CH_2), 73.07 (CH_2), 121.13 (C), 125.40 (C), 125.81 (C), 126.92 (C), 128.78 (CH), 129.97 (CH), 132.44 (C), 134.10 (C), 134.95 (CH), 136.16 (C), 146.05 (C), 146.48 (C), 155.95 (C); MS (MALDI) *m*/*z* calcd for $C_{54}H_{65}O_6S_2Ge$ ([M]$^+$) 946.3, found: 992.3; elemental analysis calcd for $C_{54}H_{64}O_6S_2Ge$: C, 68.57; H, 6.82, found: C, 68.47; H, 6.82.

Synthesis of 2,3,6,7,10,11-hexaethoxytriphenyleno[4,5-2′,3′,4′,5′]1′,1′-diphenyl-1*H*-germolo[8,9-*b*,*c*,*d*:12,1-*b*′,*c*′,*d*′]dithiophene (10b)



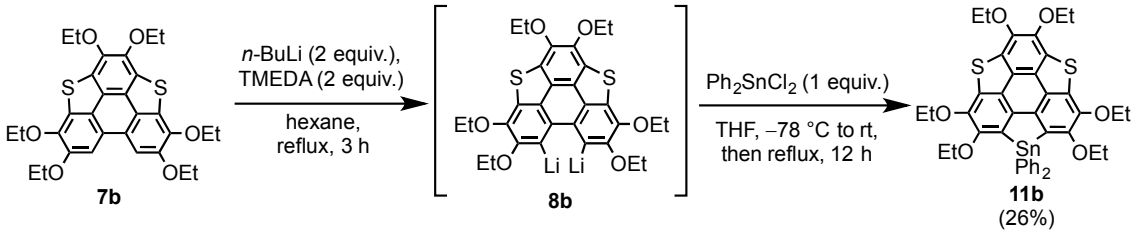
Anhydrous hexane (15 mL) and TMEDA (0.40 mL, 2.60 mmol) were added to **7b** (678 mg, 1.23 mmol) in dried a three-necked-flask under argon atmosphere. *n*-BuLi in hexane (2.65 M, 0.87 mL, 2.31 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (15 mL) was added to the resulting solid and the mixture was cooled to under −78 °C. Dichlorodiphenylgermane (0.26 mL, 1.25 mmol) was added slowly to the solution at −78 °C and stirred for 30 min at the same temperature. The mixture was allowed to warm to room temperature and stirred for an hour then was refluxed for 12 hours. After cooling to room temperature, aqueous NH_4Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown solid. The products were purified by silica gel column chromatography (eluent, hexane : CH_2Cl_2 = 1 : 1, *v/v*) to give **10b** (198 mg, 0.255 mmol, 21%) as a pale yellow solid. mp. 224-225 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (t, *J* = 7.0 Hz, 6 H), 1.53 (t, *J* = 7.0 Hz, 6H), 1.55 (t, *J* = 7.0 Hz, 6H), 4.07 (q, *J* = 7.0 Hz, 4H), 4.49 (q, *J* = 7.0 Hz, 4H), 4.53 (q, *J* = 7.0 Hz, 4H), 7.35-7.42 (m, 6H), 7.73-7.75 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.41 (CH_3), 15.96 (CH_3), 16.00 (CH_3), 68.38 (CH_2), 68.82 (CH_2), 69.02 (CH_2), 122.04 (C), 125.61 (C), 125.94 (C), 127.18 (C), 128.78 (CH), 130.00 (CH), 132.48 (C), 134.17 (C), 134.90 (CH) 135.95 (C), 146.25 (C), 146.27 (C), 155.62 (C); MS (MALDI) *m/z* calcd for $C_{42}H_{40}O_6S_2Ge$ ($[M]^+$) 778.1, found: 778.2; elemental analysis calcd for $C_{42}H_{40}O_6S_2Ge$: C, 64.88; H, 5.19, found: C, 65.04; H, 5.12.

Synthesis of 2,3,6,7,10,11-hexabutoxytriphenyleno[4,5-2′,3′,4′,5′]1′,1′-diphenyl-1*H*-stannolo[8,9-*b*,*c*,*d*:12,1-*b*′,*c*′,*d*′]dithiophene (11a)



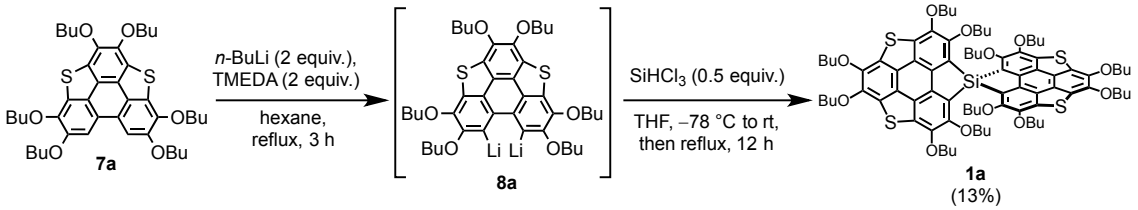
Anhydrous hexane (4.0 mL) and TMEDA (0.32 mL, 2.15 mmol) were added to **7a** (764 mg, 1.32 mmol) in dried a three-necked-flask under argon atmosphere. *n*-BuLi in hexane (2.66 M, 0.80 mL, 2.13 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (16 mL) was added to the resulting solid and the mixture was cooled to under −70 °C. A THF (7 mL) solution of dichlorodiphenylstannane (384 mg, 1.12 mmol) was transferred to the reaction mixture via a PTFE tube over 10 min. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour. The solution was refluxed for 12 hours. After cooling to room temperature, aqueous NH_4Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give an orange solid. The products were purified by silica gel column chromatography (eluent, hexane : CH_2Cl_2 = 2 : 3, *v/v*) to give **11a** (782 mg, 0.788 mmol, 74%) as a pale yellow solid. mp. 125-126 °C (dec.); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.75 (t, *J* = 7.5 Hz, 6 H), 1.02 (t, *J* = 7.5 Hz, 6H), 1.04 (t, *J* = 7.0 Hz, 6H), 1.27 (sext, *J* = 7.5 Hz, 4H), 1.58-1.70 (m, 12H), 1.85-1.93 (m, 8H), 4.08 (t, *J* = 7.0 Hz, 4H), 4.40 (t, *J* = 6.5 Hz, 4H), 4.46 (t, *J* = 6.5 Hz, 4H), 7.37-7.42 (m, 6H), 7.67-7.69 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.78 (CH_3), 14.09 (CH_3), 19.19 (CH_2), 19.45 (CH_2), 30.06 (CH_2), 32.03 (CH_2), 32.45 (CH_2), 32.56 (CH_2), 71.56 (CH_2), 72.65 (CH_2), 72.97 (CH_2), 118.71 (C), 124.22 (C), 125.23 (C), 127.05 (C), 129.25 (CH), 129.98 (CH), 133.07 (C), 134.94 (C), 137.05 (CH), 138.87 (C), 145.37 (C), 146.35 (C), 157.46 (C); ^{119}Sn NMR (186 MHz, $CDCl_3$) δ −62.96; MS (MALDI) *m*/*z* calcd for $C_{54}H_{64}O_6S_2Sn$ ($[M]^+$) 992.3, found: 992.3; elemental analysis calcd for $C_{54}H_{64}O_6S_2Sn$: C, 65.39; H, 6.50, found: C, 65.25; H, 6.53.

Synthesis of 2,3,6,7,10,11-hexaethoxytriphenyleno[4,5-2′,3′,4′,5′]1′,1′-diphenyl-1*H*-stannolo[8,9-*b*,*c*,*d*:12,1-*b*′,*c*′,*d*′]dithiophene (11b)



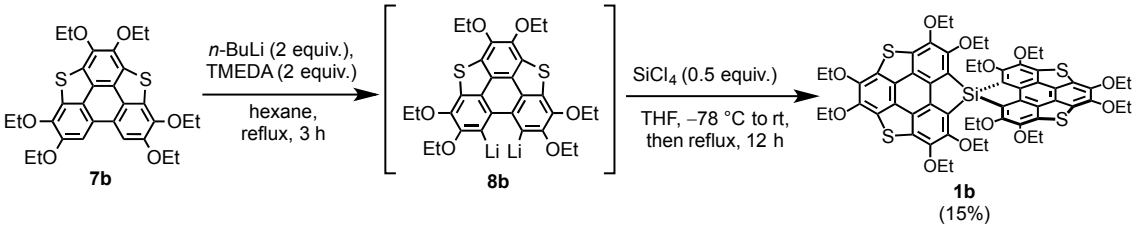
Anhydrous hexane (50 mL) and TMEDA (0.60 mL, 4.03 mmol) were added to **7b** (1.00 g, 1.82 mmol) in dried a three-necked-flask under argon atmosphere. *n*-BuLi in hexane (2.66 M, 1.40 mL, 3.72 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (50 mL) was added to the resulting solid and the mixture was cooled to under −70 °C. A THF (10 mL) solution of dichlorodiphenylstannane (635 mg, 1.85 mmol) was transferred to the reaction mixture via a PTFE tube over 5 min. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour then was refluxed for 12 hours. After cooling to room temperature, aqueous NH_4Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown solid. The products were purified by silica gel column chromatography (eluent, hexane : CH_2Cl_2 = 1 : 1, *v/v*) to give **11b** (386 mg, 0.47 mmol, 26%) as a pale yellow solid. mp. 237-238 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16 (t, *J* = 7.0 Hz, 6 H), 1.52 (t, *J* = 7.0 Hz, 6H), 1.54 (t, *J* = 7.0 Hz, 6H), 4.02 (q, *J* = 7.0 Hz, 4H), 4.48 (q, *J* = 7.0 Hz, 4H), 4.51 (q, *J* = 7.0 Hz, 4H), 7.34-7.37 (m, 4H), 7.40-7.43 (m, 2H) , 7.82-7.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.52 (CH_3), 15.98 (CH_3), 16.07 (CH_3), 67.64 (CH_2), 68.48 (CH_2), 68.77 (CH_2), 119.70 (C), 124.38 (C), 125.31 (C), 127.26 (C), 129.28 (CH), 130.02 (CH), 133.07 (C), 134.99 (C), 137.02 (CH) 138.67 (C), 145.38 (C), 146.09 (C), 157.17 (C); ^{119}Sn NMR (186 MHz, $CDCl_3$) δ −62.13; MS (MALDI) *m*/*z* calcd for $C_{42}H_{40}O_6S_2Sn$ ($[M]^+$) 824.1, found: 824.1; elemental analysis calcd for $C_{42}H_{40}O_6S_2Sn$: C, 61.25; H, 4.90, found: C, 61.25; H, 4.73.

Synthesis of spirobi{2,3,6,7,10,11-hexabutoxytriphenyleno[4,5-2′,3′,4′,5′]1′,1′-diphenyl -1*H*-silolo[8,9-*b*,*c*,*d*:12,1-*b*′,*c*′,*d*′]dithiophene} (1a)



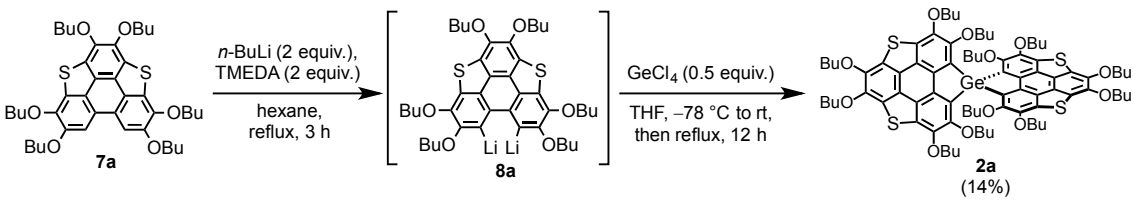
Anhydrous hexane (4.0 mL) and TMEDA (0.32 mL, 2.15 mmol) were added to **7a** (764 mg, 1.32 mmol) in dried a three-necked-flask under argon atmosphere. *n*-BuLi in hexane (2.66 M, 0.80 mL, 2.13 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (16 mL) was added to the resulting solid and the mixture was cooled to under −70 °C. A THF (7 mL) solution of dichlorodiphenylstannane (384 mg, 1.12 mmol) was transferred to the reaction mixture via a PTFE tube over 10 min. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour then was refluxed for 12 hours. After cooling to room temperature, aqueous NH_4Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give an orange solid. The products were purified by silica gel column chromatography (eluent, hexane : CH_2Cl_2 = 2 : 3, *v/v*) to give **1a** (782 mg, 0.788 mmol, 74%) as a pale yellow solid. mp. 84-85 °C (dec.); ^{1}H NMR (500 MHz, $CDCl_3$) δ –0.06 (t, *J* = 7.5 Hz, 12 H), –0.01-0.05 (m, 8H), 0.97 (t, *J* = 7.5 Hz, 12H), 1.03-1.11 (m, 8H), 1.06 (t, *J* = 7.5 Hz, 12H), 1.51-1.59 (m, 8H), 1.66 (sext, *J* = 7.5 Hz, 8H), 1.79 (quin, *J* = 7.5 Hz, 8H), 1.92 (quint, *J* = 7.5 Hz, 8H), 3.60 (t, *J* = 7.0 Hz, 12H), 4.29 (t, *J* = 6.5 Hz, 12H), 4.47 (t, *J* = 6.5 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.88 (CH_3), 14.02 (CH_3), 14.07 (CH_3), 17.71 (CH_2), 19.35 (CH_2), 19.45 (CH_2), 30.96 (CH_2), 32.38 (CH_2), 32.40 (CH_2), 70.21 (CH_2), 72.76 (CH_2), 73.09 (CH_2), 114.81 (C), 125.31 (C), 125.68 (C), 126.27 (C), 134.57 (C), 134.95 (C), 144.68 (C), 146.69 (C), 156.94 (C); ^{29}Si NMR (99 MHz, $CDCl_3$) δ 3.39; MS (MALDI) *m*/*z* calcd for $C_{84}H_{109}O_{12}S_4Si$ ($[M+H]^+$) 1465.6, found: 1465.3; elemental analysis calcd for $C_{84}H_{108}O_{12}S_4Si$: C,68.82; H, 7.42, found: C,68.79; H, 7.46.

Synthesis of spirobi{2,3,6,7,10,11-hexaethoxytriphenyleno[4,5-2′,3′,4′,5′]1′,1′-diphenyl-1*H*-silolo[8,9-*b*,*c*,*d*:12,1-*b*′,*c*′,*d*′]dithiophene} (1b)



Anhydrous hexane (34 mL) and TMEDA (0.58 mL, 3.89 mmol) were added to **7b** (1.03 g, 1.87 mmol) in dried a three-necked-flask under argon atmosphere. *n*-BuLi in hexane (2.66 M, 1.40 mL, 3.72 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (34 mL) was added to the resulting solid and the mixture was cooled to under −70 °C. A toluene (21 mL) solution of tetrachlorosilane (0.12 mL, 1.05 mmol) was transferred to the reaction mixture via a PTFE tube over 15 min. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour then was refluxed for 12 hours. After cooling to room temperature, aqueous NH_4Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown solid. The products were purified by silica gel column chromatography (eluent, hexane : CH_2Cl_2 = 1 : 4, *v/v*) to give **1b** (158 mg, 0.140 mmol, 15%) as a yellow solid. mp. 226 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.61 (t, *J* = 7.0 Hz, 12 H), 1.44 (t, *J* = 7.0 Hz, 12H), 1.59 (t, *J* = 7.0 Hz, 12H), 3.71 (q, *J* = 7.0 Hz, 8H), 4.40 (q, *J* = 7.0 Hz, 8H), 4.57 (q, *J* = 7.0 Hz, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.92 (CH_3), 15.89 (CH_3), 15.99 (CH_3), 66.41 (CH_2), 68.48 (CH_2), 68.89 (CH_2), 114.64 (C), 125.05 (C), 125.14 (C), 125.78 (C), 134.00 (C), 134.47 (C), 144.91 (C), 146.54 (C), 156.72 (C); ^{29}Si NMR (99 MHz, $CDCl_3$) δ 2.72; MS (MALDI) *m*/*z* calcd for $C_{60}H_{61}O_{12}S_4Si$ ([M+H]$^+$) 1129.3, found: 1129.1; elemental analysis calcd for $C_{60}H_{60}O_{12}S_4Si$: C,63.80; H, 5.35, found: C,63.44; H, 5.29.

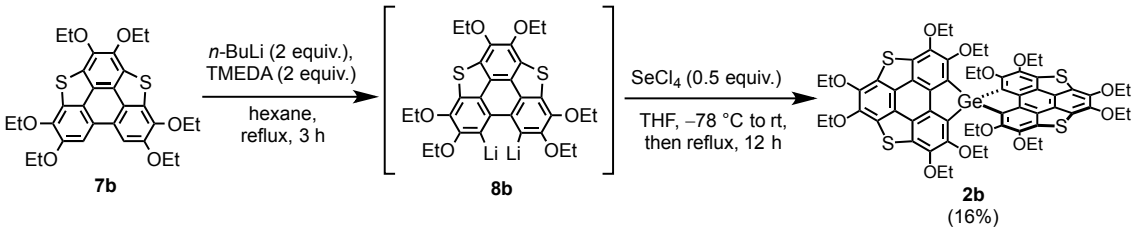
Synthesis of spirobi{2,3,6,7,10,11-hexabutoxytriphenyleno[4,5-2′,3′,4′,5′]1′,1′-diphenyl-1*H*-germolo[8,9-*b*,*c*,*d*:12,1-*b*′,*c*′,*d*′]dithiophene} (2a)



Anhydrous hexane (7.0 mL) and TMEDA (0.57 mL, 3.83 mmol) were added to **7a** (1.37 g, 1.90 mmol) in dried a three-necked-flask under argon atmosphere. *n*-BuLi in hexane (2.66 M, 1.45 mL,

3.86 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (25 mL) was added to the resulting solid and the mixture was cooled to under −70 °C. A THF (10 mL) solution of tetrachlorogermane (0.11 mL, 0.964 mmol) was transferred to the reaction mixture via a PTFE tube over 15 min. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour then was refluxed for 12 hours. After cooling to room temperature, aqueous NH_4Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give an orange solid. The products were purified by silica gel column chromatography (eluent, hexane : CH_2Cl_2 = 2 : 3, *v/v*) to give **2a** (209 mg, 0.138 mmol, 14%) as a yellow solid. mp. 113-115 °C (dec.) °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ –0.07 (t, *J* = 7.5 Hz, 12H), 0.09 (sext, *J* = 7.5 Hz, 8H), 0.97 (t, *J* = 7.5 Hz, 12H), 1.06 (t, *J* = 7.5 Hz, 12H), 1.13 (quint, *J* = 7.5 Hz, 8H), 1.55-1.60 (m, 8H), 1.66 (sext, *J* = 7.5 Hz, 12H), 1.80 (quint, *J* = 8.0 Hz, 8H), 1.93 (quint, *J* = 7.0 Hz, 8H), 3.67 (t, *J* = 7.5 Hz, 12H), 4.31 (t, *J* = 6.5 Hz, 12H), 4.48 (t, *J* = 6.5 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.82 (CH_3), 14.03 (CH_3), 14.09 (CH_3), 17.79 (CH_2), 19.37 (CH_2), 19.46 (CH_2), 30.97 (CH_2), 32.41 (CH_2), 70.15 (CH_2), 72.81 (CH_2), 73.06 (CH_2), 117.06 (C), 124.95 (C), 125.36 (C), 126.22 (C), 132.75 (C), 134.23 (C), 144.85 (C), 146.68 (C), 156.14 (C); MS (MALDI) *m/z* calcd for $C_{84}H_{109}O_{12}S_4Ge$ ($[M+H]^+$) 1511.6, found: 1511.7; elemental analysis calcd for $C_{84}H_{108}O_{12}S_4Ge$: C,66.79; H, 7.21, found: C,66.60; H, 7.26.

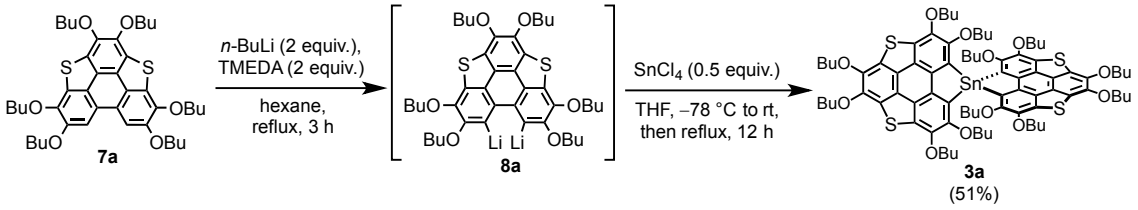
Synthesis of spirobi{2,3,6,7,10,11-hexaethoxytriphenyleno[4,5-2′,3′,4′,5′]1′,1′-diphenyl-1*H*-germolo[8,9-*b*,*c*,*d*:12,1-*b*′,*c*′,*d*′]dithiophene } (2b)



Anhydrous hexane (14 mL) and TMEDA (0.27 mL, 1.81 mmol) were added to **7b** (482 mg, 0.872 mmol) in dried a three-necked-flask under argon atmosphere. *n*-BuLi in hexane (2.66 M, 0.66 mL, 1.76 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (14 mL) was added to the resulting solid and the mixture was cooled to under −70 °C. A toluene (10 mL) solution of tetrachlorogermane (60 μL, 0.52 mmol) was transferred to the reaction mixture via a PTFE tube over 10 min. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour

then was refluxed for 12 hours. After cooling to room temperature, aqueous NH_4Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown solid. The products were purified by silica gel column chromatography (eluent, hexane : CH_2Cl_2 = 1 : 3, *v/v*) to give **2b** (80 mg, 69.8 μmol, 16%) as a pale yellow solid. mp. 236 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.68 (t, *J* = 7.0 Hz, 12H), 1.45 (t, *J* = 7.0 Hz, 12H), 1.59 (t, *J* = 7.0 Hz, 12H), 3.78 (q, *J* = 7.0 Hz, 8H), 4.42 (q, *J* = 7.0 Hz, 8H), 4.58 (q, *J* = 7.0 Hz, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.01 (CH_3), 15.91 (CH_3), 16.01 (CH_3), 66.29 (CH_2), 68.53 (CH_2), 68.87 (CH_2), 116.99 (C), 124.77 (C), 124.96 (C), 125.78 (C), 132.21 (C), 133.79 (C), 145.02 (C), 146.55 (C), 155.92 (C); MS (MALDI) *m/z* calcd for $C_{60}H_{60}O_{12}S_4Ge$ ($[M]^+$) 1174.2, found: 1174.6; elemental analysis calcd for $C_{60}H_{60}O_{12}S_4Ge$: C,61.38; H, 5.15, found: C,61.40; H, 5.00.

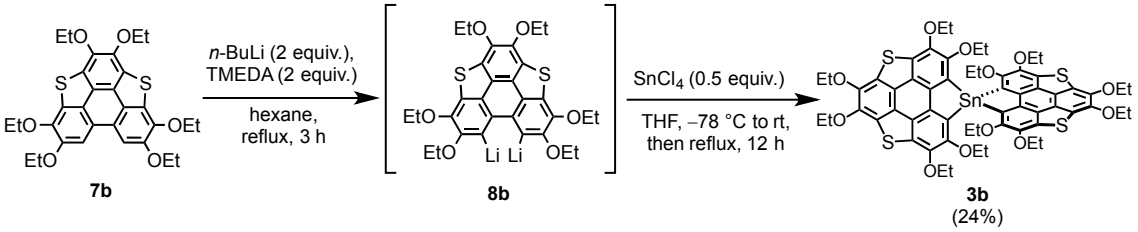
Synthesis of spirobi{2,3,6,7,10,11-hexabutoxytriphenyleno[4,5-2′,3′,4′,5′]1′,1′-diphenyl-1*H*-stannolo[8,9-*b*,*c*,*d*:12,1-*b*′,*c*′,*d*′]dithiophene } (3a)



Anhydrous hexane (4.0 mL) and TMEDA (0.37 mL, 2.48 mmol) were added to **7a** (873 mg, 1.21 mmol) in dried a three-necked-flask under argon atmosphere. *n*-BuLi in hexane (2.66 M, 0.92 mL, 2.45 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (18 mL) was added to the resulting solid and the mixture was cooled to under −70 °C. A toluene (8 mL) solution of tetrachlorostannane (76 μL, 0.650 mmol) was transferred to the reaction mixture via a PTFE tube over 15 min. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour. The solution was refluxed for 12 hours. After cooling to room temperature, aqueous NH_4Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give an orange solid. The products were purified by silica gel column chromatography (eluent, hexane : CH_2Cl_2 = 1:1, *v/v*) to give **3a** (480 mg, 0.308 mmol, 51%) as a yellow solid. mp. 126 °C (dec.); ^{1}H NMR (500 MHz, $CDCl_3$) δ0.04 (t, *J* = 7.5 Hz, 12H), 0.38 (sext, *J* = 7.5 Hz, 8H), 0.98 (t, *J* = 7.5 Hz, 12H), 1.06 (t, *J* = 7.5 Hz, 12H), 1.28 (quint, *J* = 7.5 Hz, 8H), 1.58 (sext, *J* = 7.5 Hz, 8H), 1.67 (sext, *J* = 7.5 Hz, 8H), 1.82 (quint, *J* = 7.5 Hz, 8H), 1.93 (quint, *J* = 7.5 Hz, 8H), 3.84 (t, *J* = 7.5 Hz, 12H), 4.34 (t, *J* = 6.5 Hz, 12H), 4.50 (t, *J* = 6.5 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.88 (CH_3),

14.03 (CH_3), 14.09 (CH_3), 18.19 (CH_2), 19.38 (CH_2), 19.47 (CH_2), 30.08 (CH_2), 32.45 (CH_2), 32.47 (CH_2), 70.13 (CH_2), 72.81 (CH_2), 73.01 (CH_2), 116.65 (C), 124.05 (C), 124.86 (C), 126.71 (C), 133.05 (C), 134.30 (C), 145.04 (C), 146.57 (C), 157.12 (C); ^{119}Sn NMR (186 MHz, $CDCl_3$) δ –25.86; MS (MALDI) *m*/*z* calcd for $C_{84}H_{109}O_{12}S_4Sn$ ($[M+H]^+$) 1557.6, found: 1557.4; elemental analysis calcd for $C_{84}H_{108}O_{12}S_4Sn$: C,64.81; H, 6.99, found: C,64.82; H, 6.99.

Synthesis of spirobi{2,3,6,7,10,11-hexaethoxytriphenyleno[4,5-2′,3′,4′,5′]1′,1′-diphenyl-1*H*-stannolo[8,9-*b*,*c*,*d*:12,1-*b*′,*c*′,*d*′]dithiophene } (3b)



Anhydrous hexane (44 mL) and TMEDA (0.76 mL, 5.10 mmol) were added to **7b** (1.36 g, 2.49 mmol) in dried a three-necked-flask under argon atmosphere. *n*-BuLi in hexane (2.66 M, 1.87 mL, 4.97 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (44 mL) was added to the resulting solid and the mixture was cooled to under –70 °C. A toluene (15 mL) solution of tetrachlorostannane (0.15 mL, 1.28 mmol) was transferred to the reaction mixture via a PTFE tube over 10 min. After stirring for 30 min at –70 °C, the mixture was allowed to warm to room temperature and stirred for an hour. The solution was refluxed for 12 hours. After cooling to room temperature, aqueous NH_4Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown solid. The products were purified by silica gel column chromatography (eluent, hexane : CH_2Cl_2 = 1 : 3, *v*/*v*) to give **3b** (364 mg, 0.299 mmol, 24%) as a pale yellow solid. mp. 236 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 12H), 1.48 (t, *J* = 7.0 Hz, 12H), 1.59 (t, *J* = 7.0 Hz, 12H), 3.94 (q, *J* = 7.0 Hz, 8H), 4.46 (q, *J* = 7.0 Hz, 8H), 4.58 (q, *J* = 7.0 Hz, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.21 (CH_3), 15.98 (CH_3), 16.02 (CH_3), 66.14 (CH_2), 68.59 (CH_2), 68.89 (CH_2), 117.04 (C), 124.19 (C), 124.88 (C), 126.60 (C), 132.92 (C), 134.12 (C), 145.11 (C), 146.41 (C), 156.86 (C); ^{119}Sn NMR (186 MHz, $CDCl_3$) δ –28.72; MS (MALDI) *m*/*z* calcd for $C_{60}H_{60}O_{12}S_4Sn$ ($[M]^+$) 1174.2, found: 1174.6; elemental analysis calcd for $C_{60}H_{60}O_{12}S_4Sn$: C,61.38; H, 5.15, found: C,61.40; H, 5.00.

3. X-ray crystallographic analysis

Table S1. Crystal data for **1b, 2b** and **3b.**

	1b	**2b**	**3c**
crystal system	triclinic	triclinic	monoclinic
space group	*P*-1	*P*-1	$P2_1/n$
a/Å	9.7198(13)	9.7680(7)	9.2728(7)
b/Å	13.5510(18)	11.2196(8)	21.8232(16)
c/Å	21.616(3)	25.3543(18)	27.505(2)
α/deg	104.724(2)	88.261(1)	–
β/deg	100.877(1)	82.947(1)	88.261(1)
γ/deg	95.266(2)	86.248(1)	–
V/Å^3	2674.7(6)	2751.0(3)	5523.1(7)
Z	2	2	4
D_{calc}/g cm^{-3}	1.402	1.502	1.569
R_1 ($I>2\sigma(I)$)	0.0395	0.0352	0.0295
R_2 (all data)	0.1104	0.0888	0.0723
goodness of fit	1.023	1.032	1.016
T/K	100	100	100

4. Electrochemical study

Table S2. Electrochemical properties of **9b**–**11b** and **1b**–**3b.**

	E^1_{pa} [V]	E^1_{pc} [V]	$E^1_{1/2}$ [V]	E^2_{pa} [V]	E^2_{pc} [V]	$E^2_{1/2}$ [V]
9b	0.45	0.36	0.40	NA	NA	NA
10b	0.44	0.35	0.40	0.74	—	—
11b	0.47	0.34	0.41	0.72	—	—
1b	0.44	0.37	0.40	0.57	0.50	0.54
2b	0.45	0.38	0.41	0.59	0.51	0.55
3b	0.44	0.38	0.41	0.58	0.50	0.54

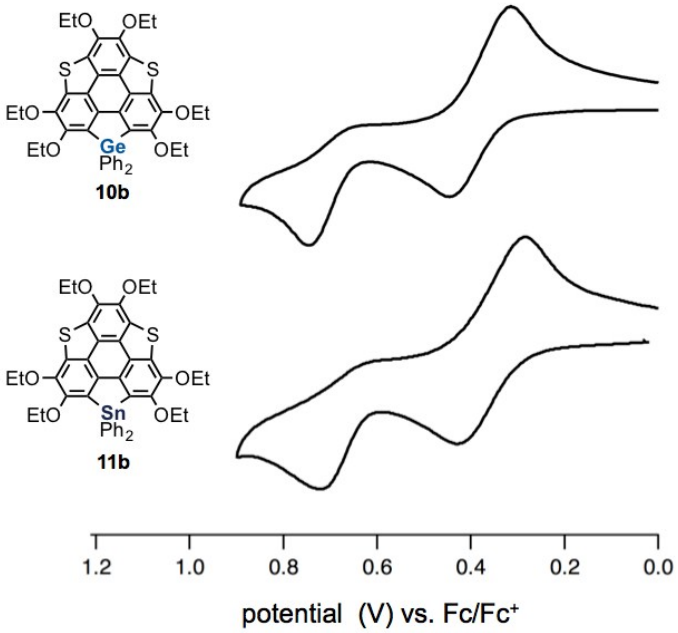
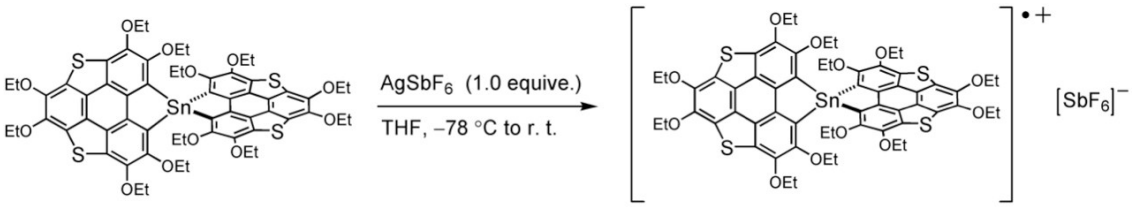


Fig. S1 Cyclic voltammograms of **10b** (0.62 mM) and **11b** (0.67 mM) in CH_2Cl_2 containing 0.1 M *n*-Bu_4NClO_4 at scan rate of 100 mV s^{-1}.

5. Chemical oxidation of spirobistannasumanene 3b

Scheme S1 Chemical oxidation of **3b** using $AgSbF_6$ as an oxidant.



3b **3b**$^{\bullet+}$

An anhydrous THF (1 mL) solution of silver hexafluoroantimonate(V) (8.1 mg, 23.6 μmol) was added dropwise to a THF (3 mL) solution of **9b** (26 mg, 21.3 μmol) at −78 °C. After stirring for 30 min at the same temperature, the mixture was allowed to warm to room temperature and stirred for an hour. The reaction mixture was concentrated under reduced pressure to give a blue solid. The solid was extracted with dichloromethane and the extract was concentrated under reduced pressure to give a green solid (30.9 mg). An ESR spectrum of the product in CH_2Cl_2 showed a signal at *g* value of 2.0061 (Fig. S2).

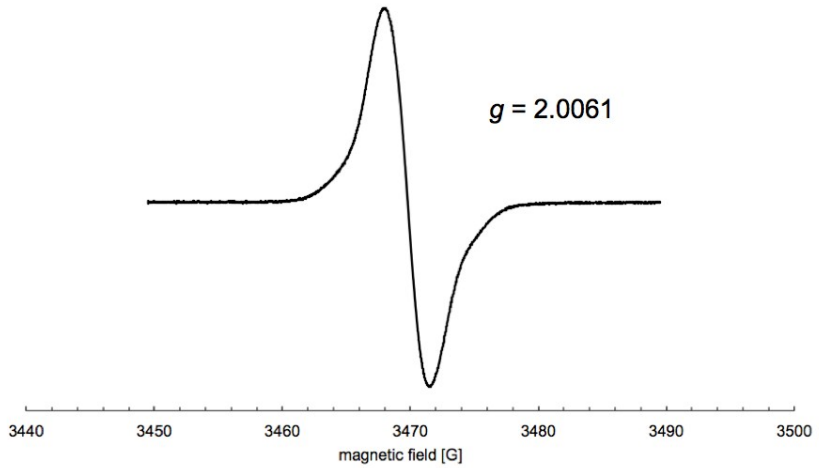


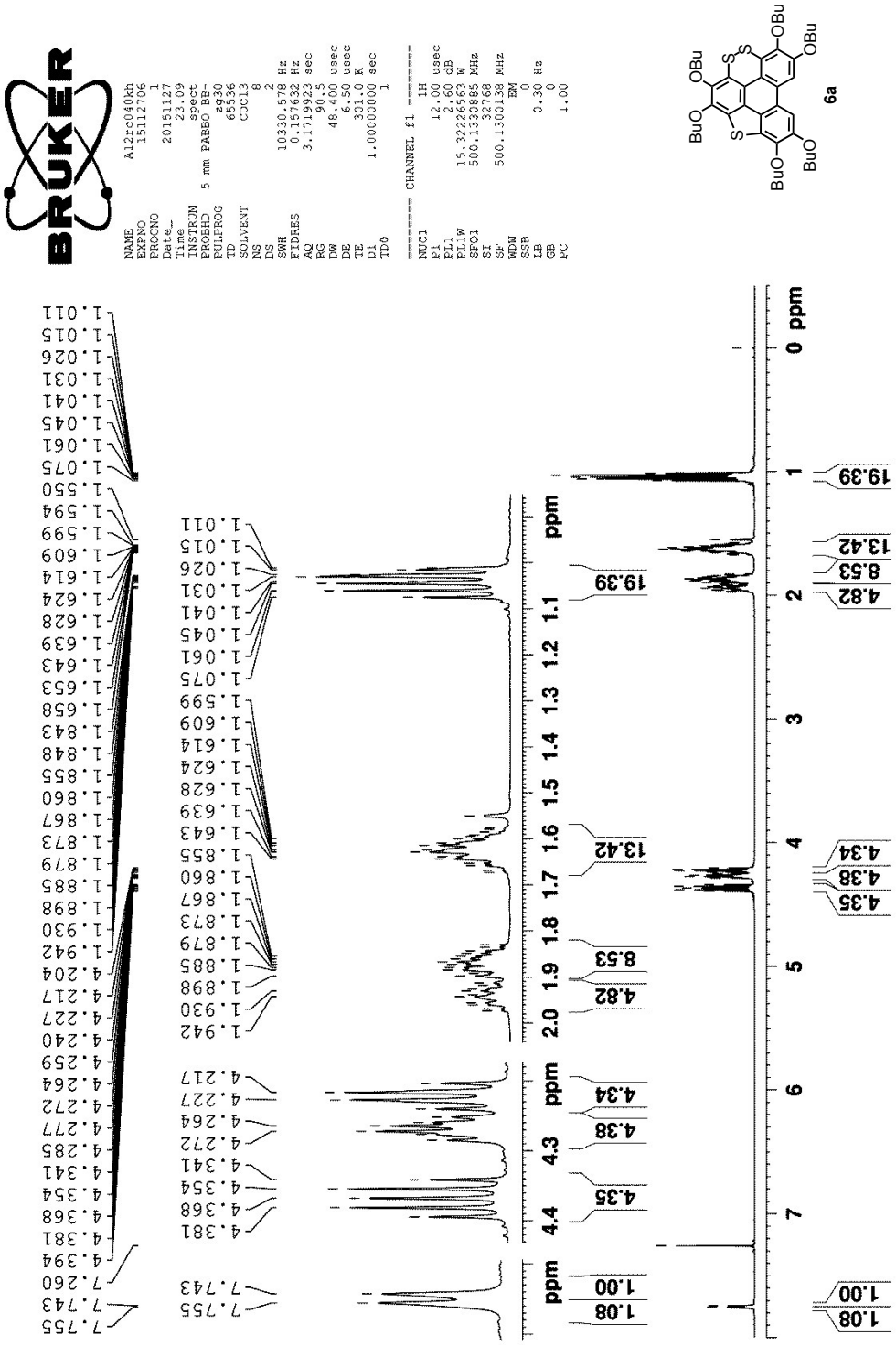
Fig. S2 ESR spectrum of the product of the oxidation reaction of **3b** using 1 equiv. of $AgSbF_6$, measured in CH_2Cl_2 at room temperature.

6. Reference

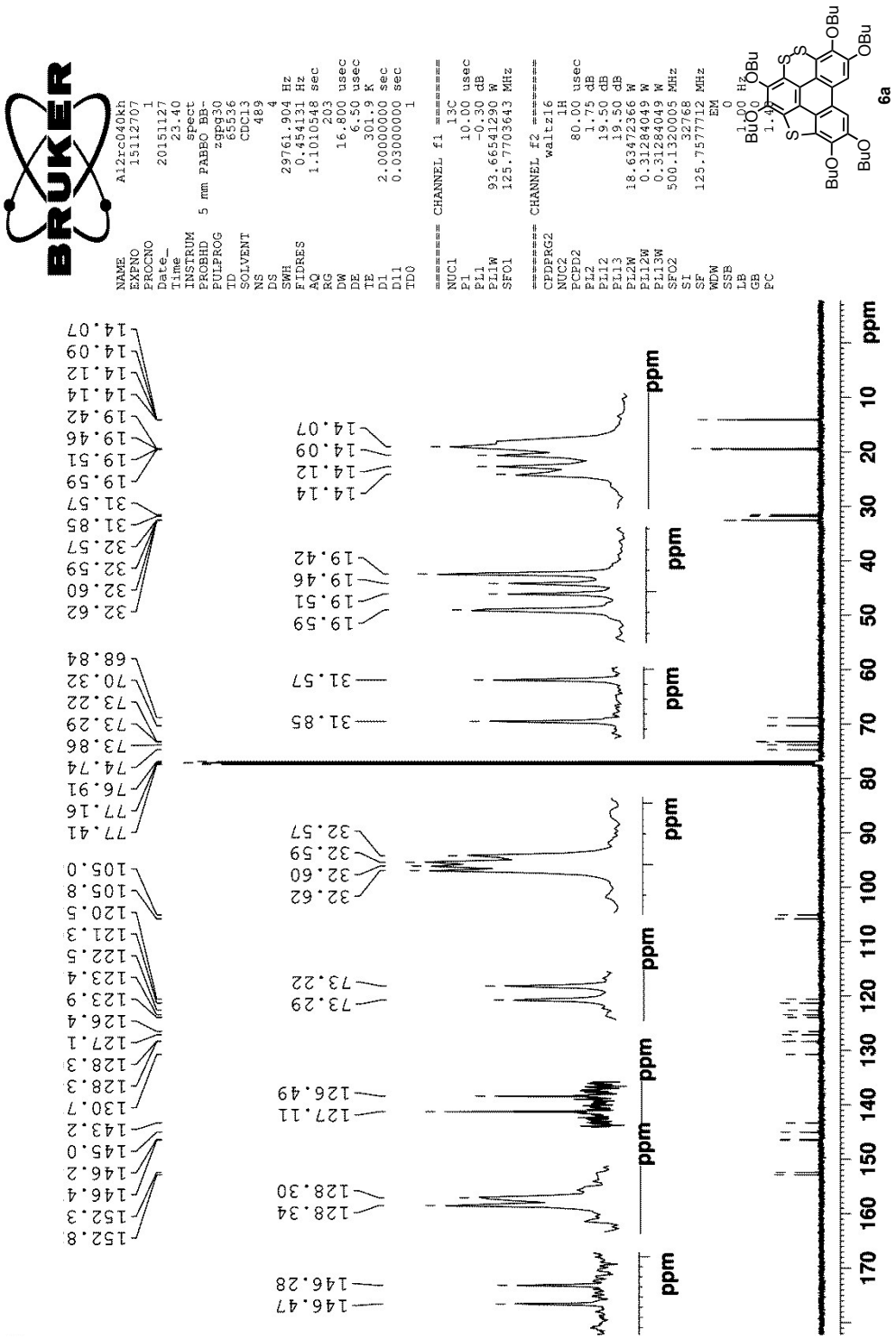
1) Wang, Y.; Zhang, C.; Wu, H.; Pu, J. *J. Mater. Chem. C.*, **2014**, *2*, 1667.

7. NMR charts

^{1}H NMR spectrum of 6a in $CDCl_3$



^{13}C NMR spectrum of 6a in $CDCl_3$



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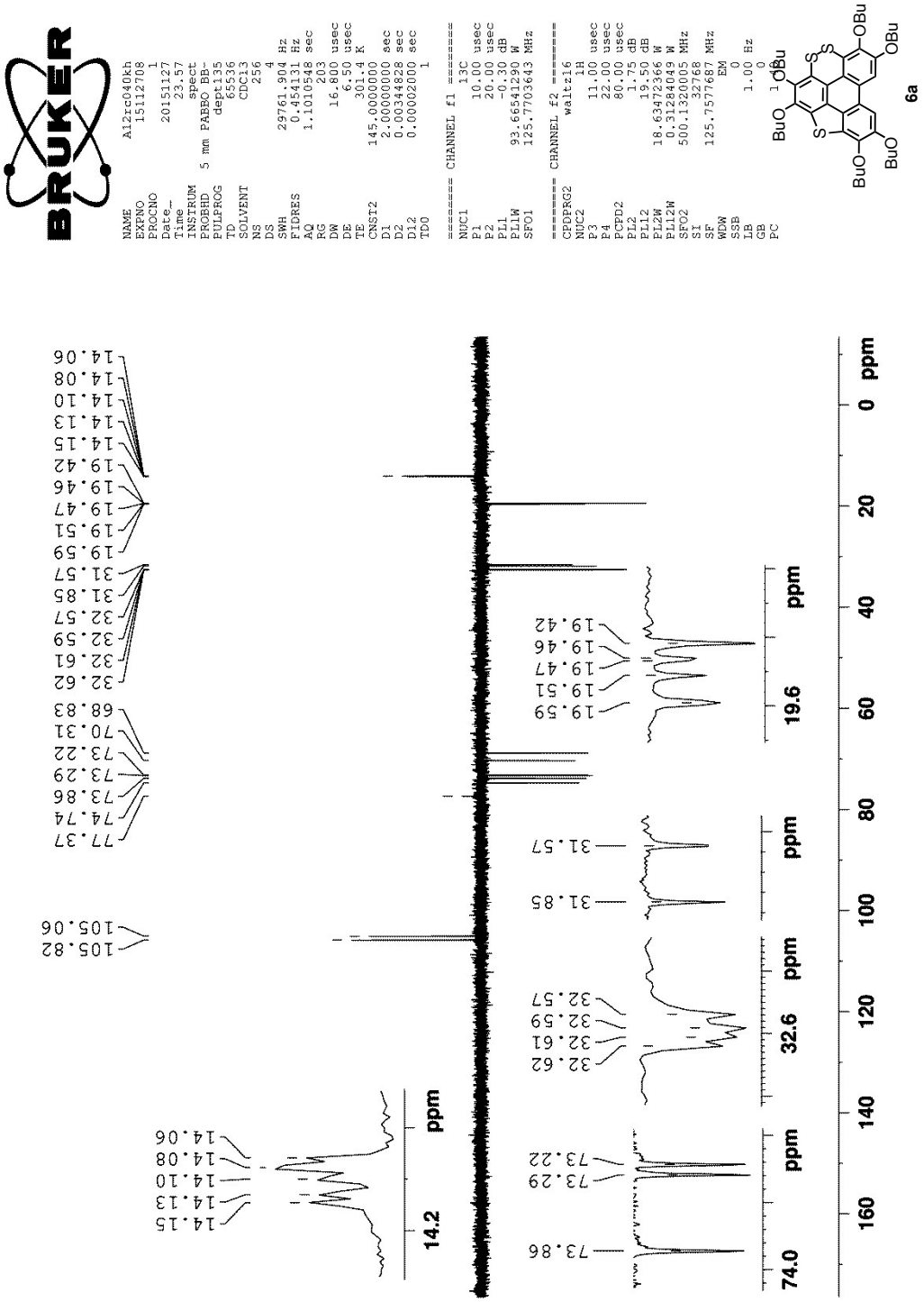

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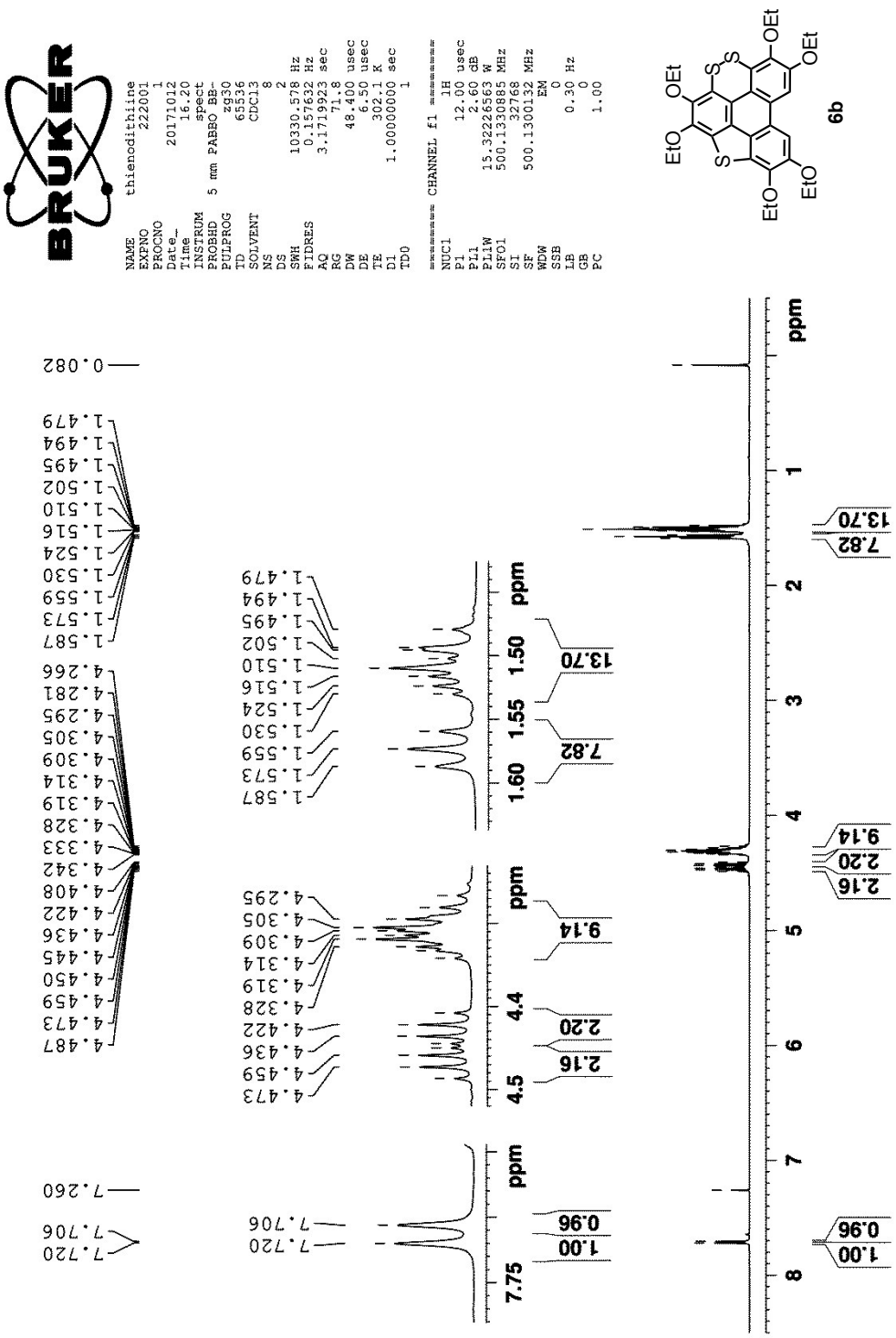
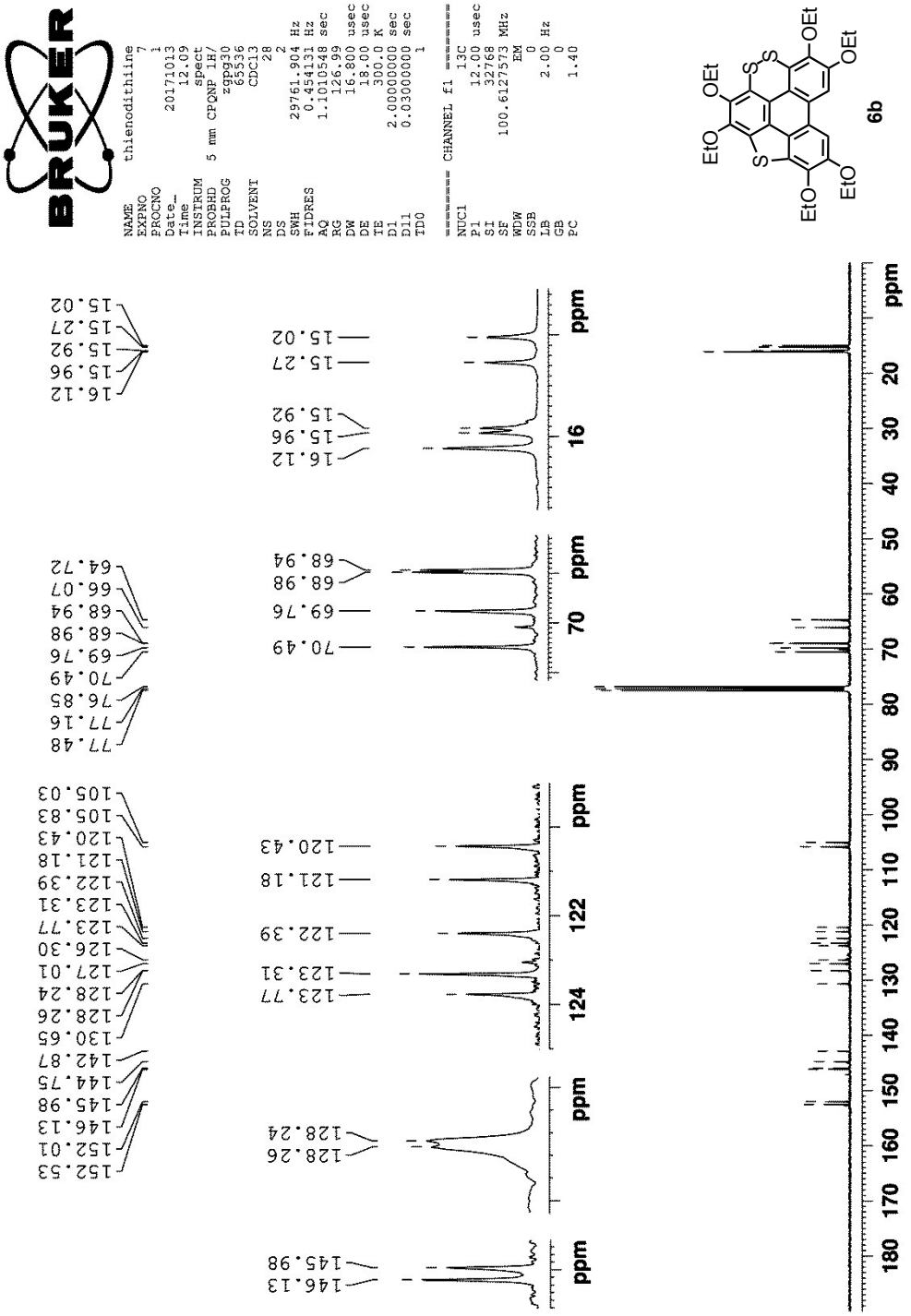


^{13}C NMR spectrum of 6b in $CDCl_3$



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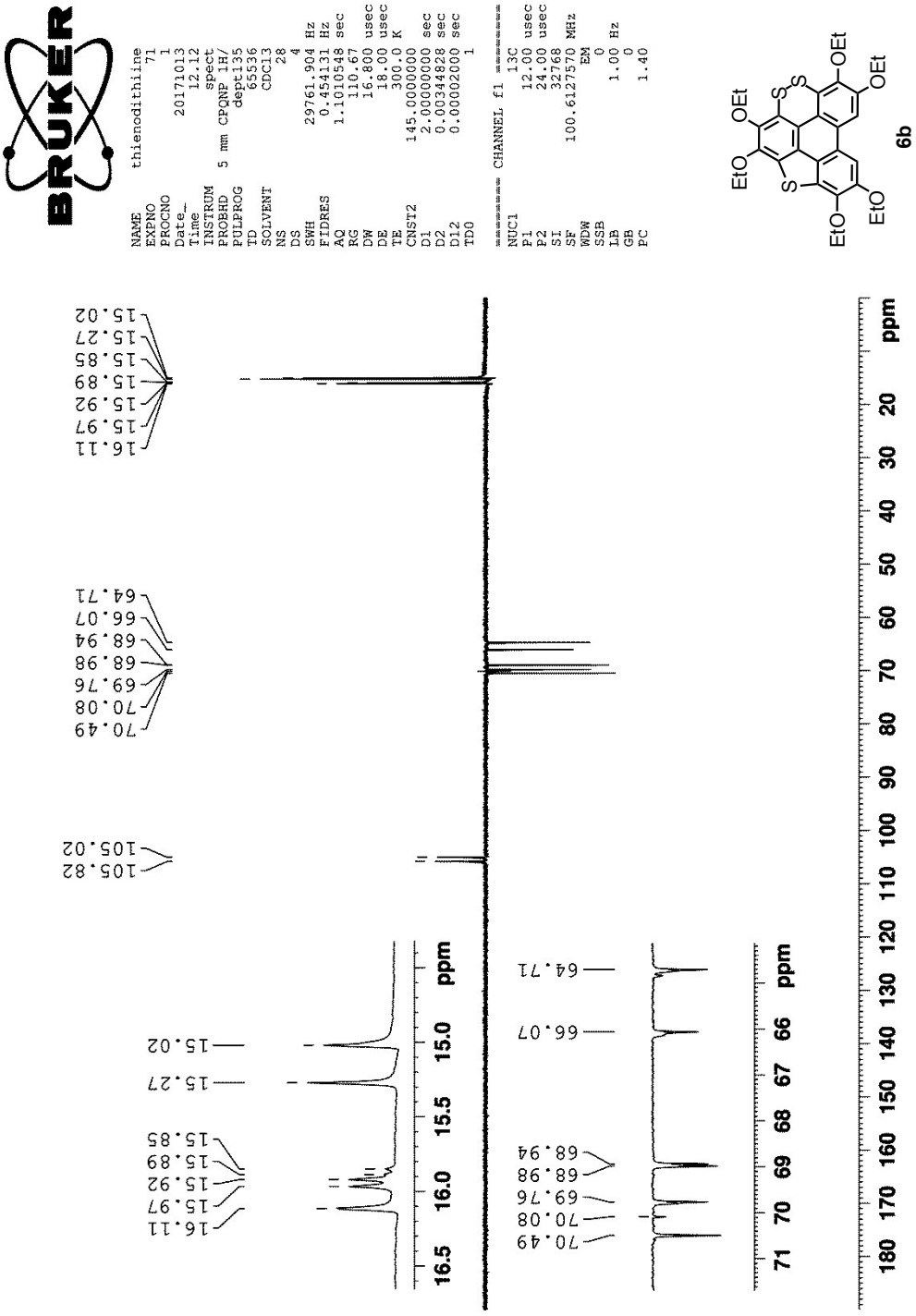
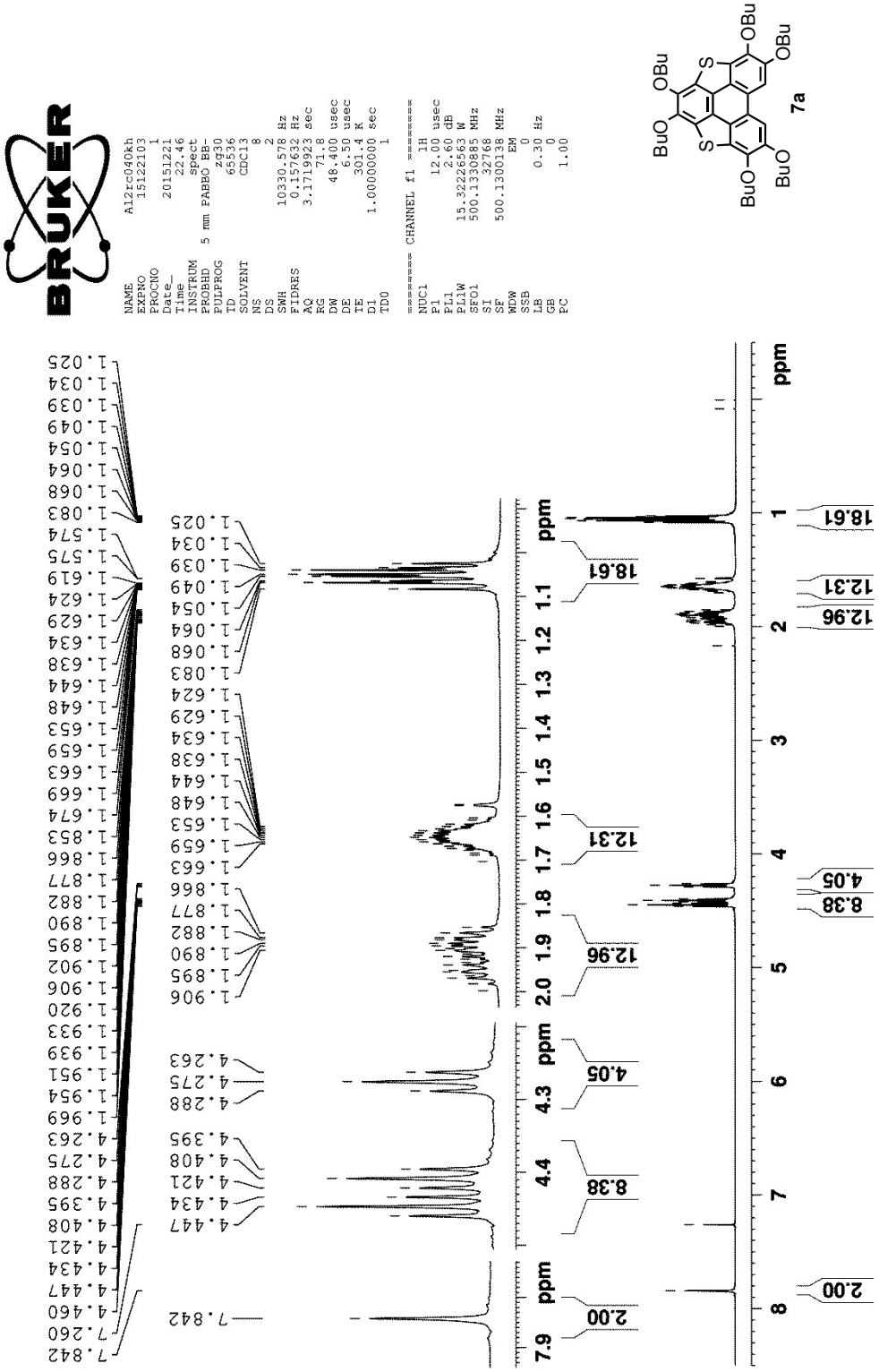


^{1}H NMR spectrum of 7a in $CDCl_3$



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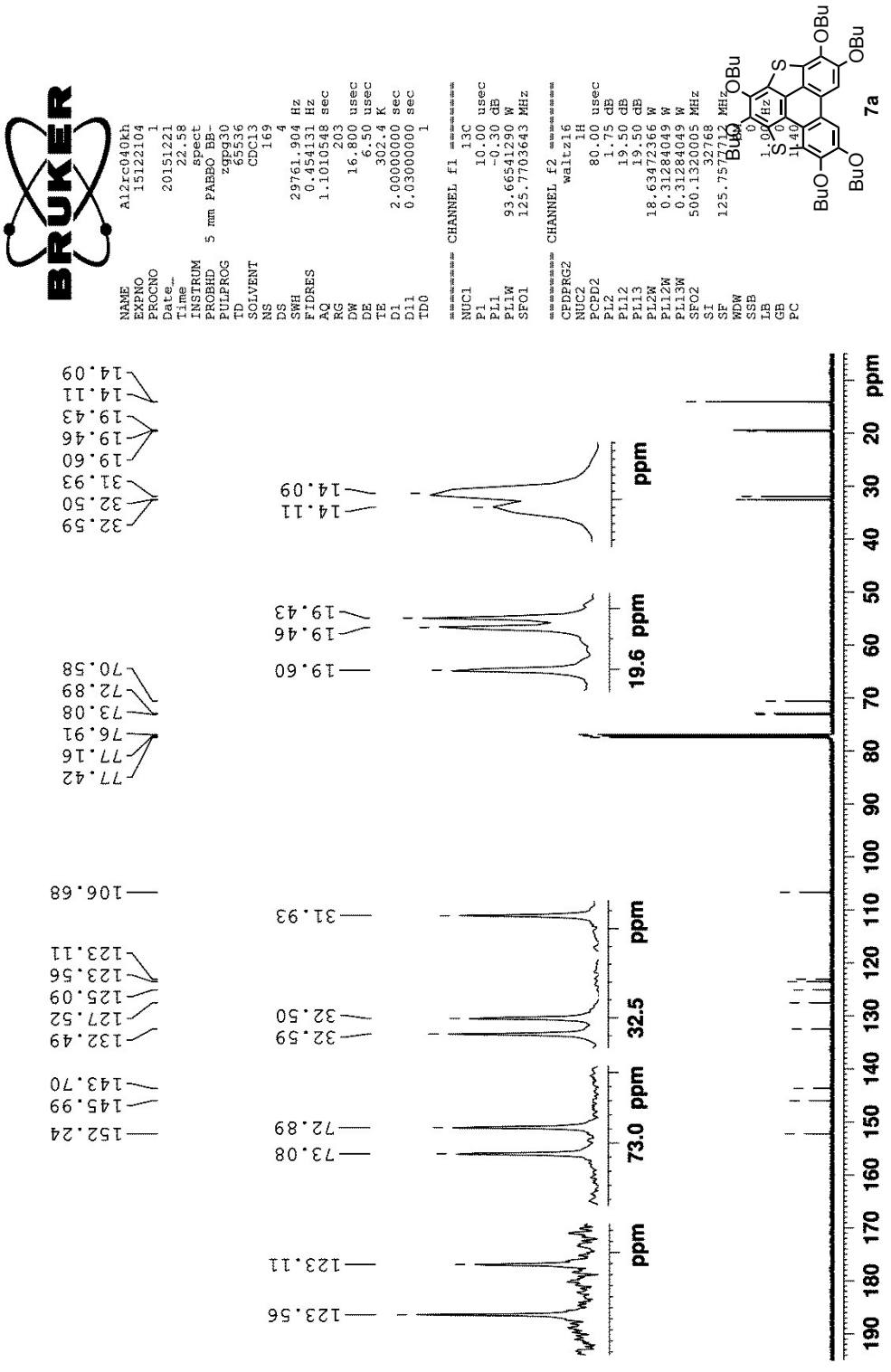

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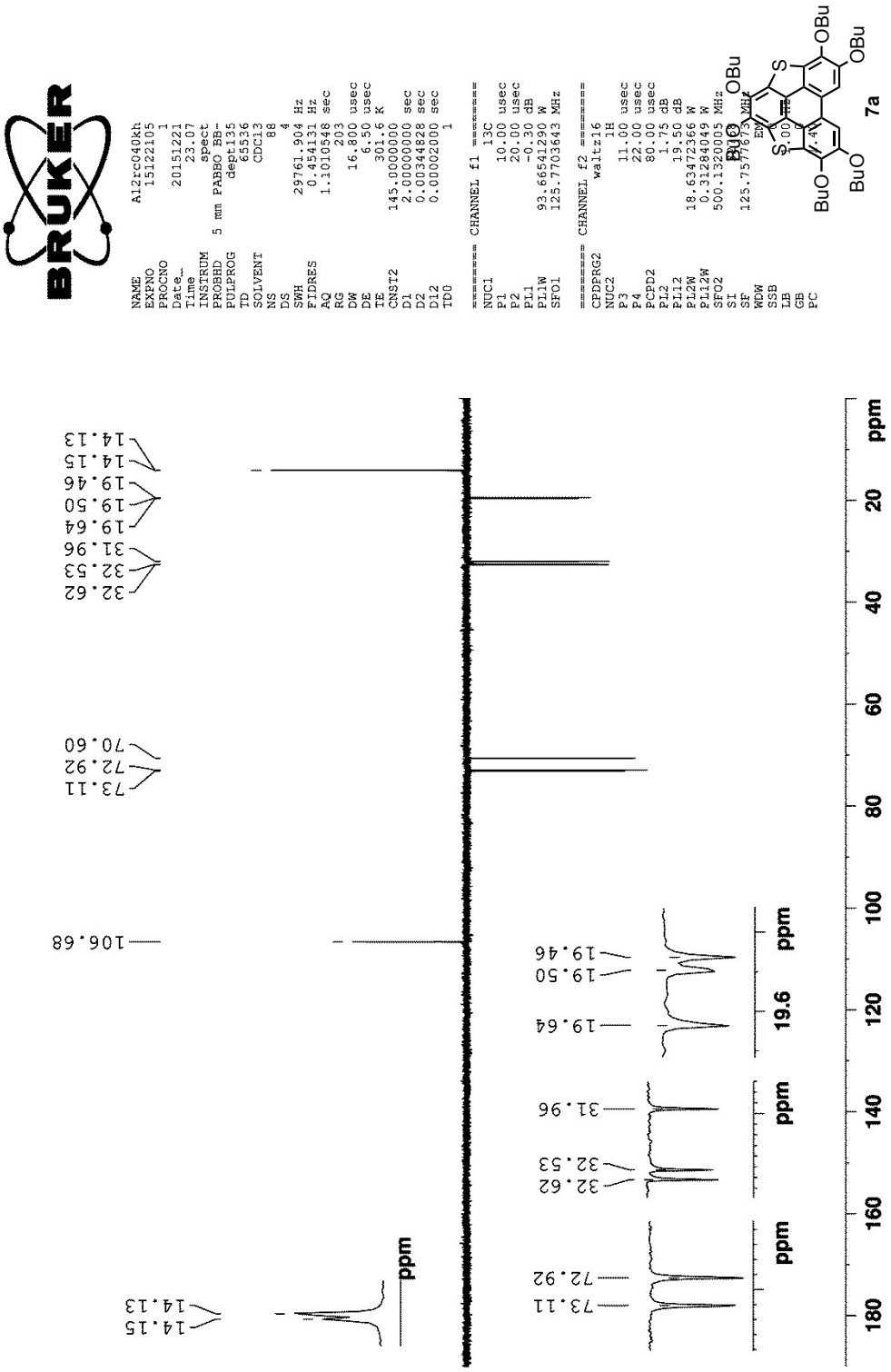

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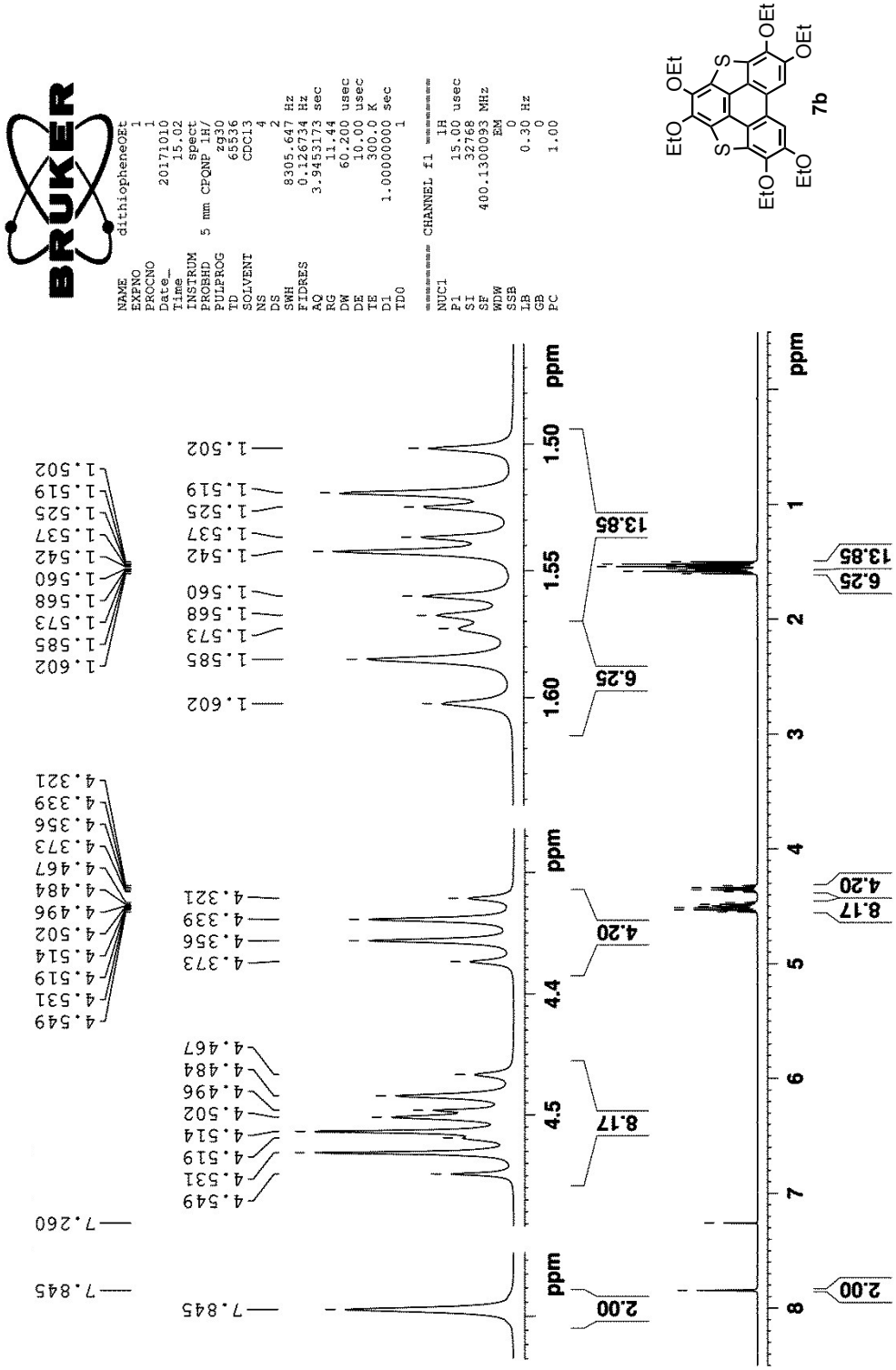

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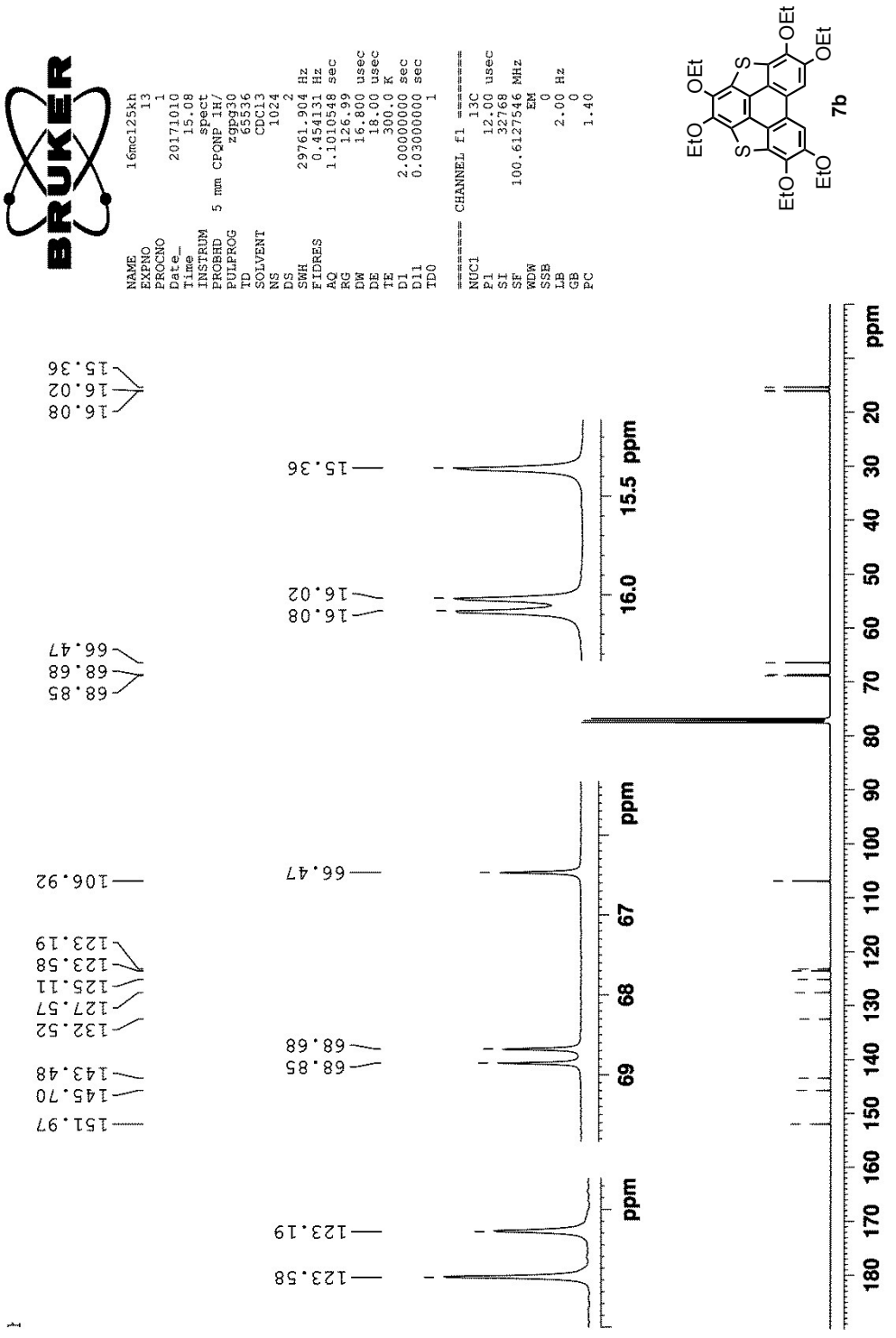

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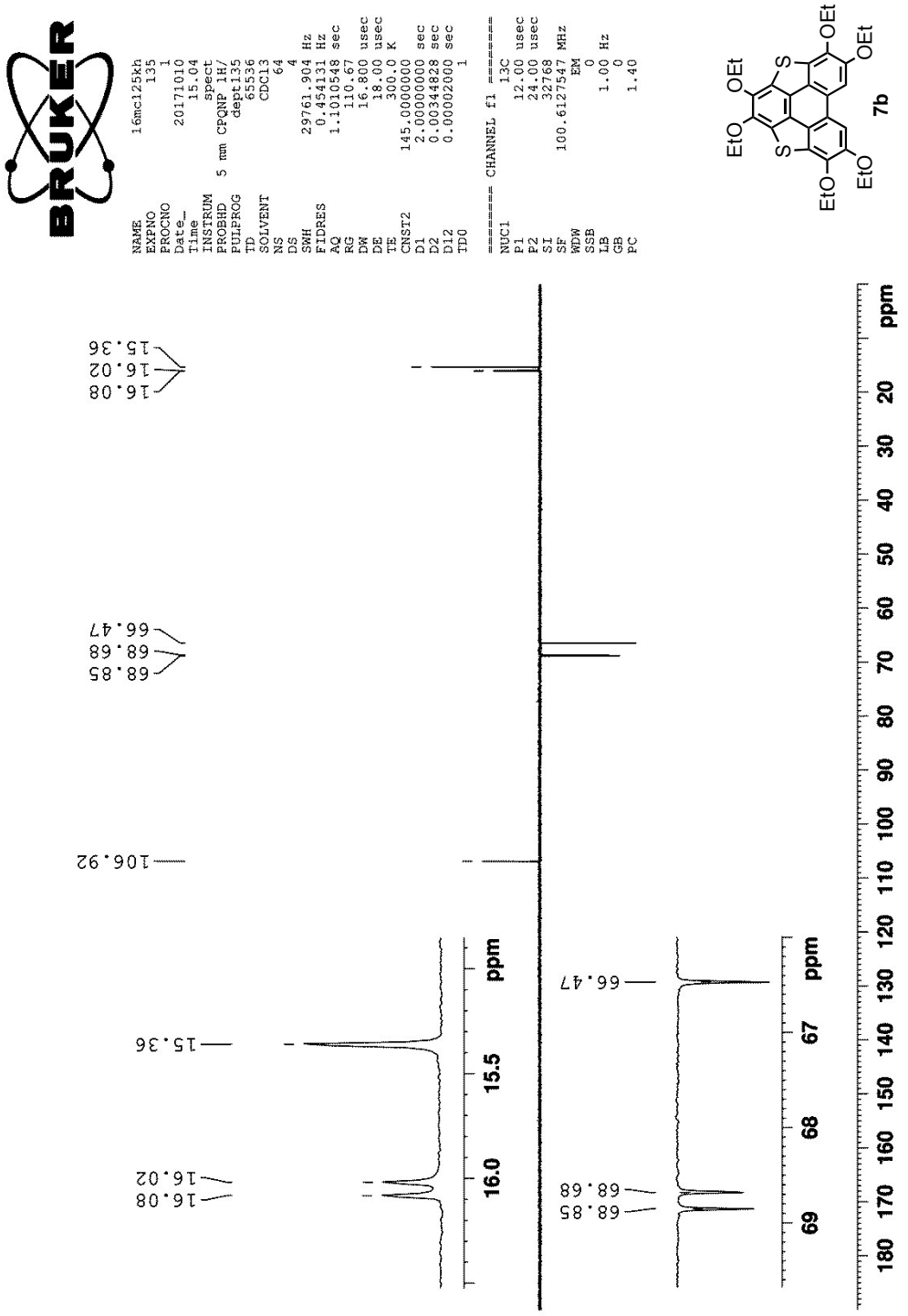

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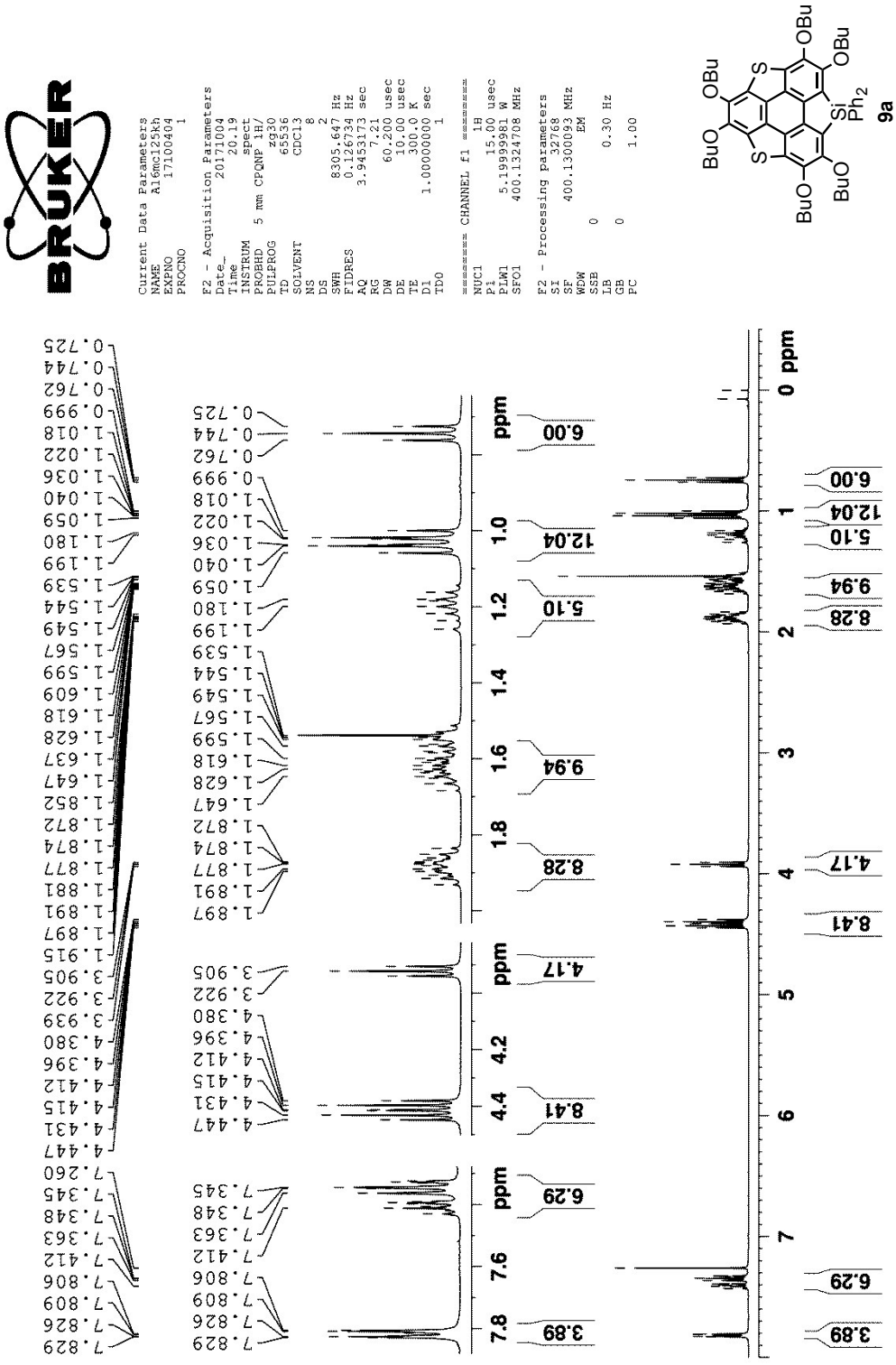

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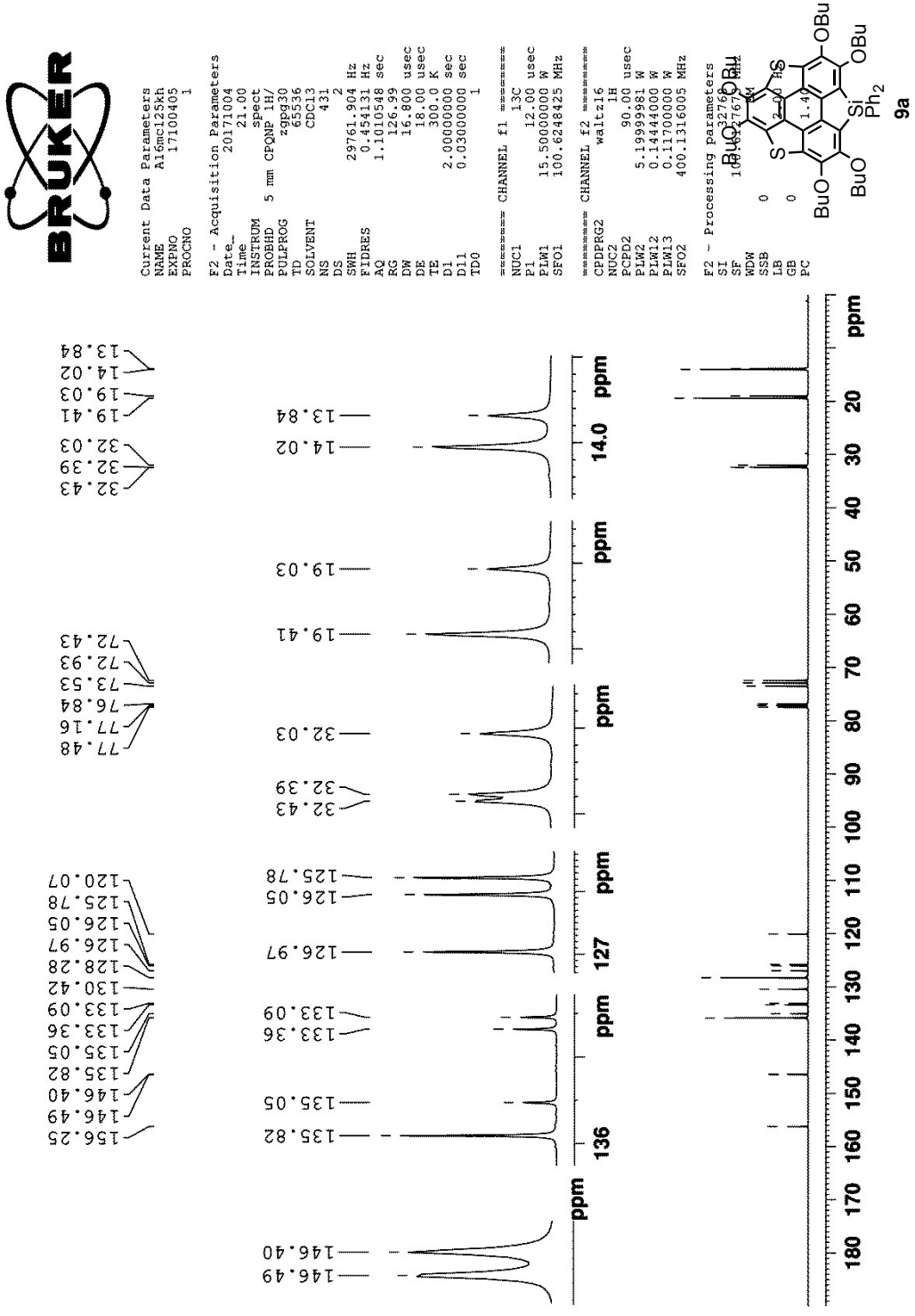

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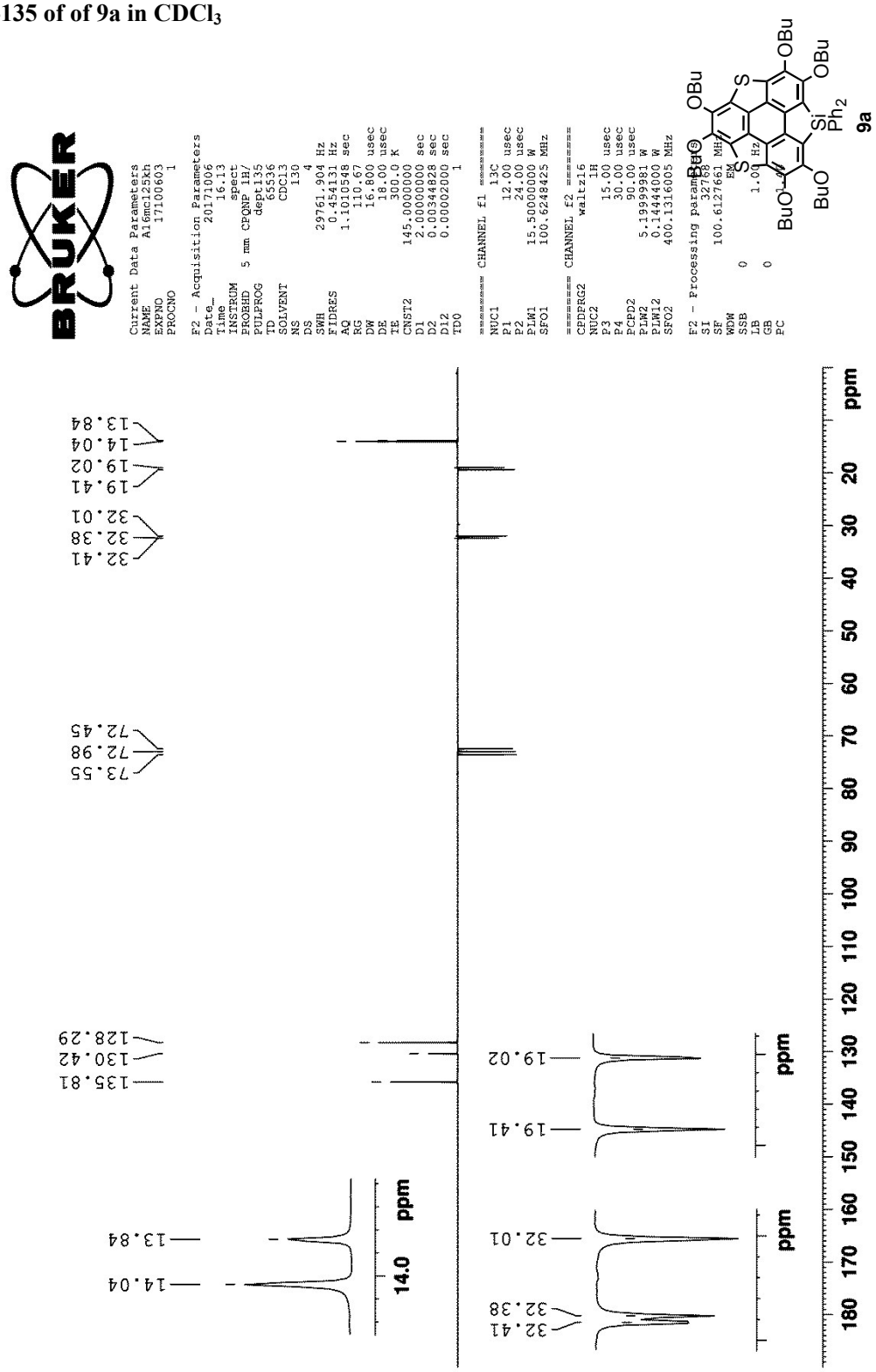
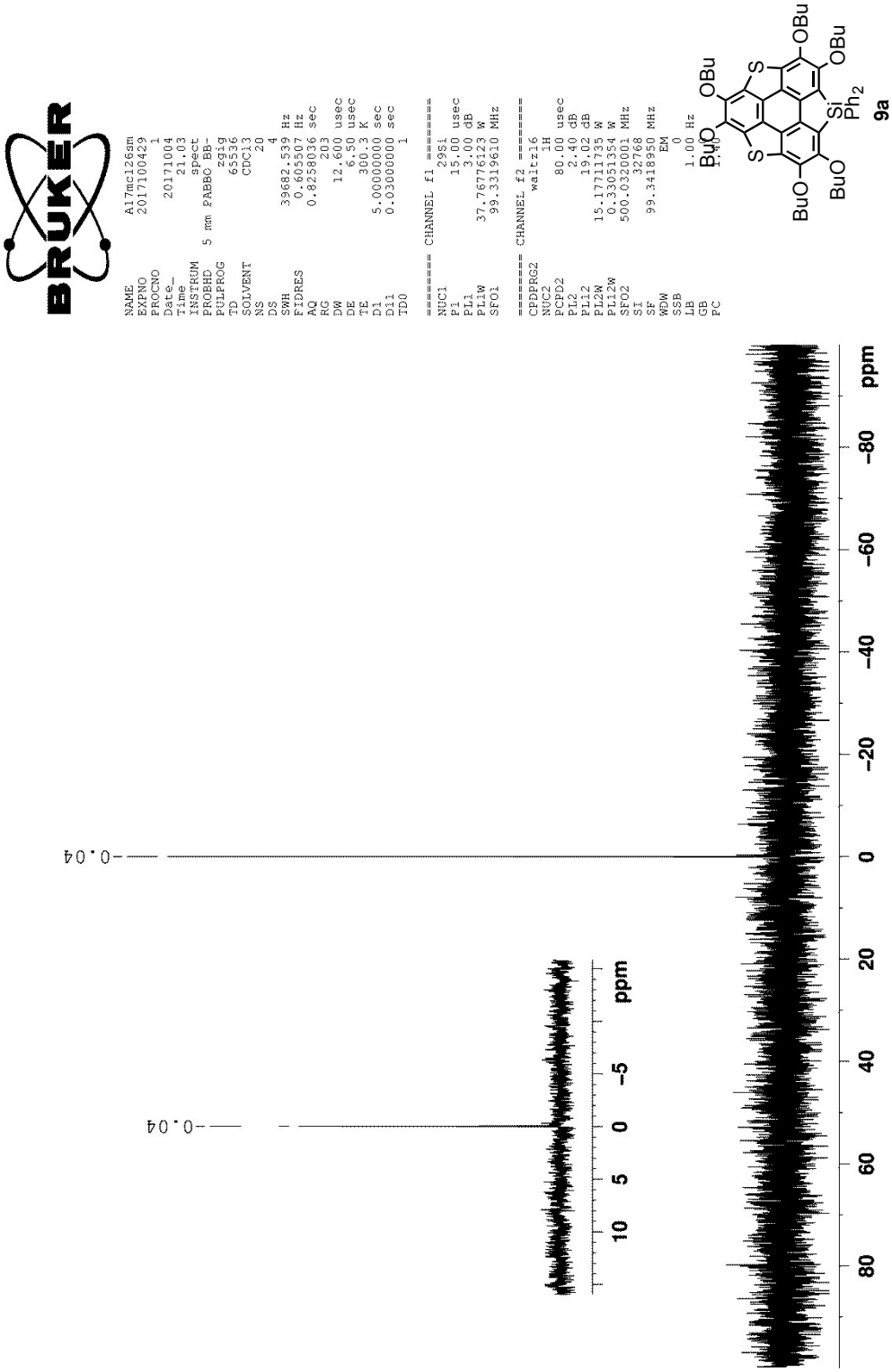


^{29}Si NMR spectrum of 9a in $CDCl_3$



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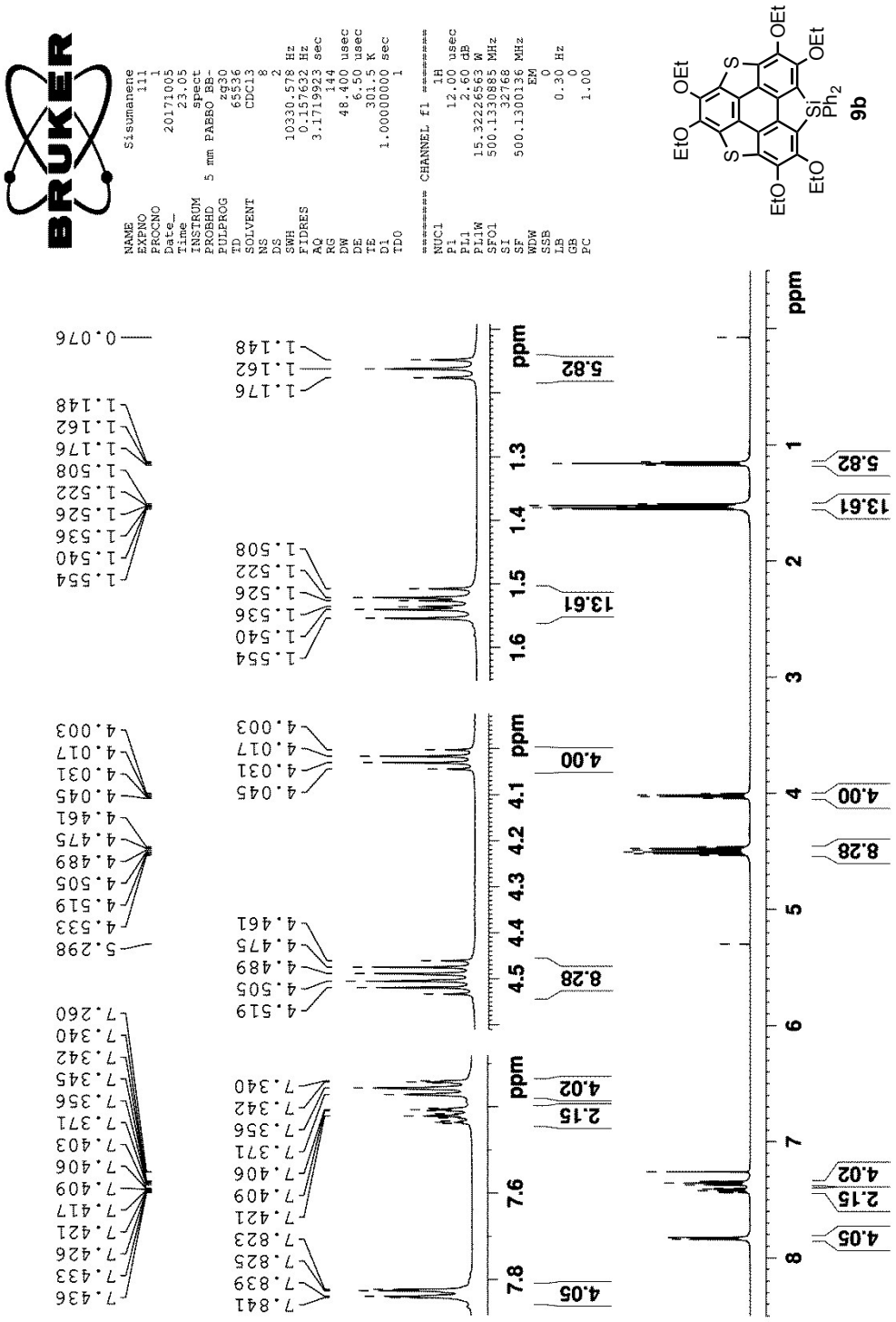

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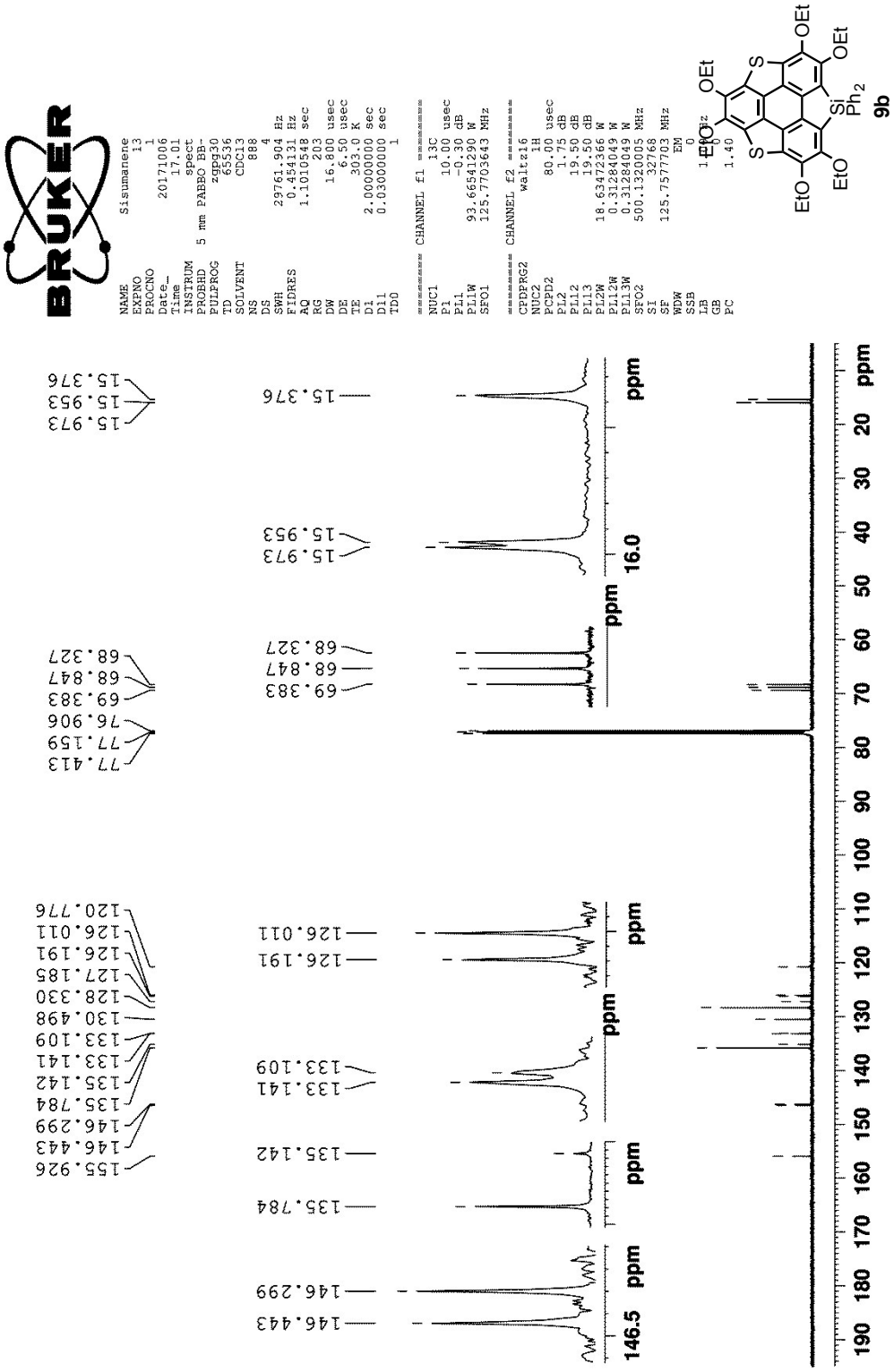

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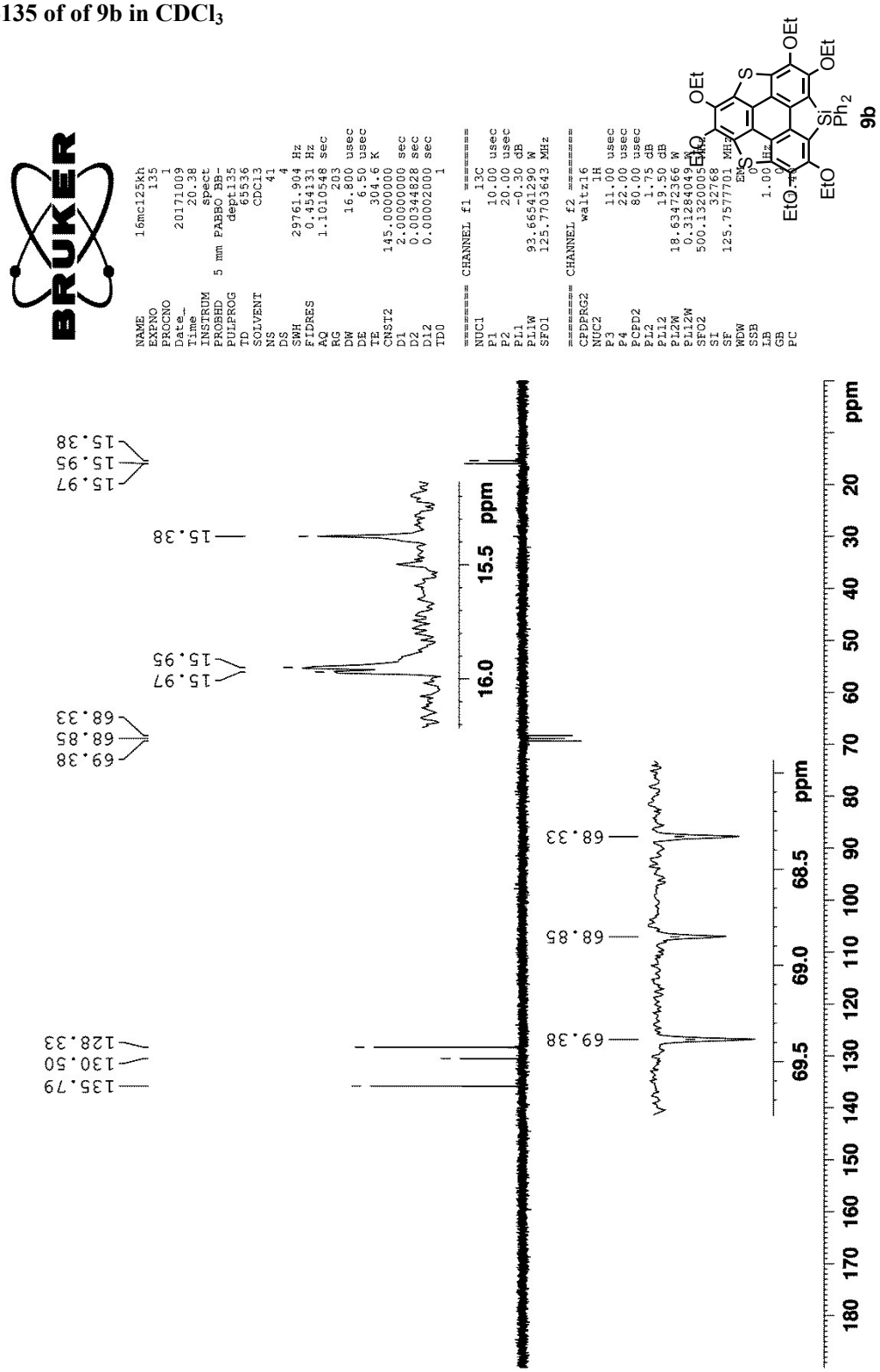

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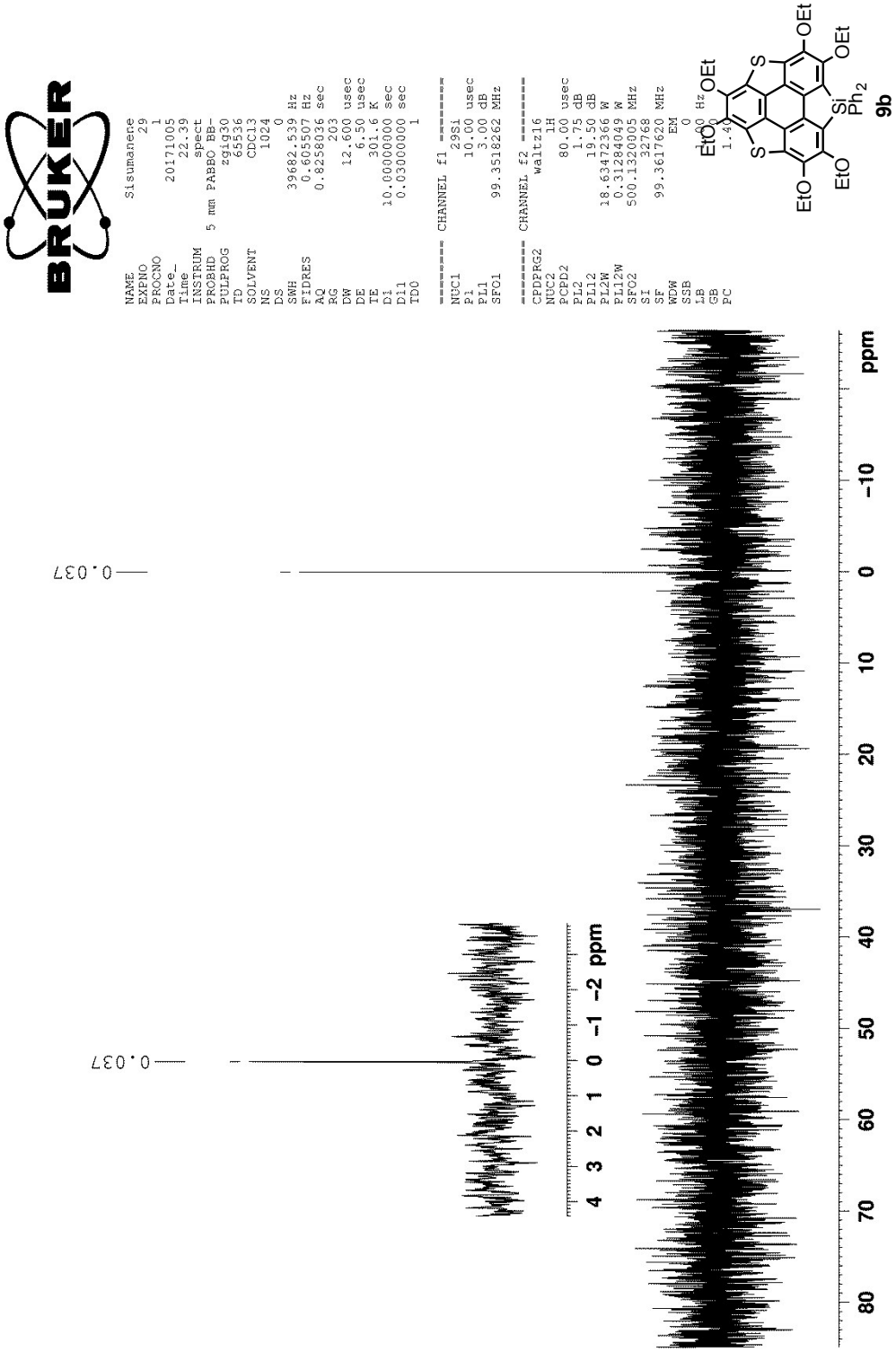

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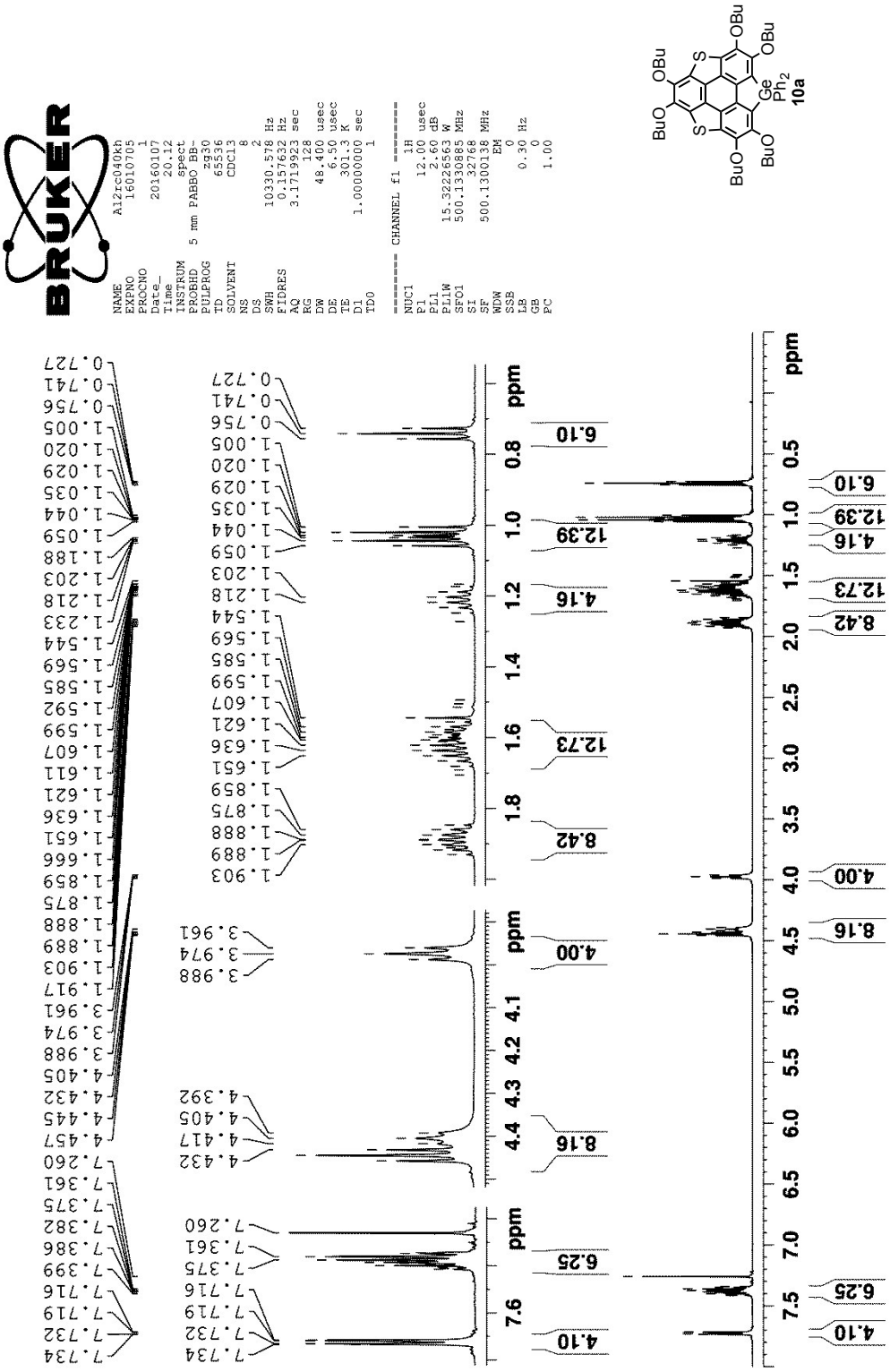

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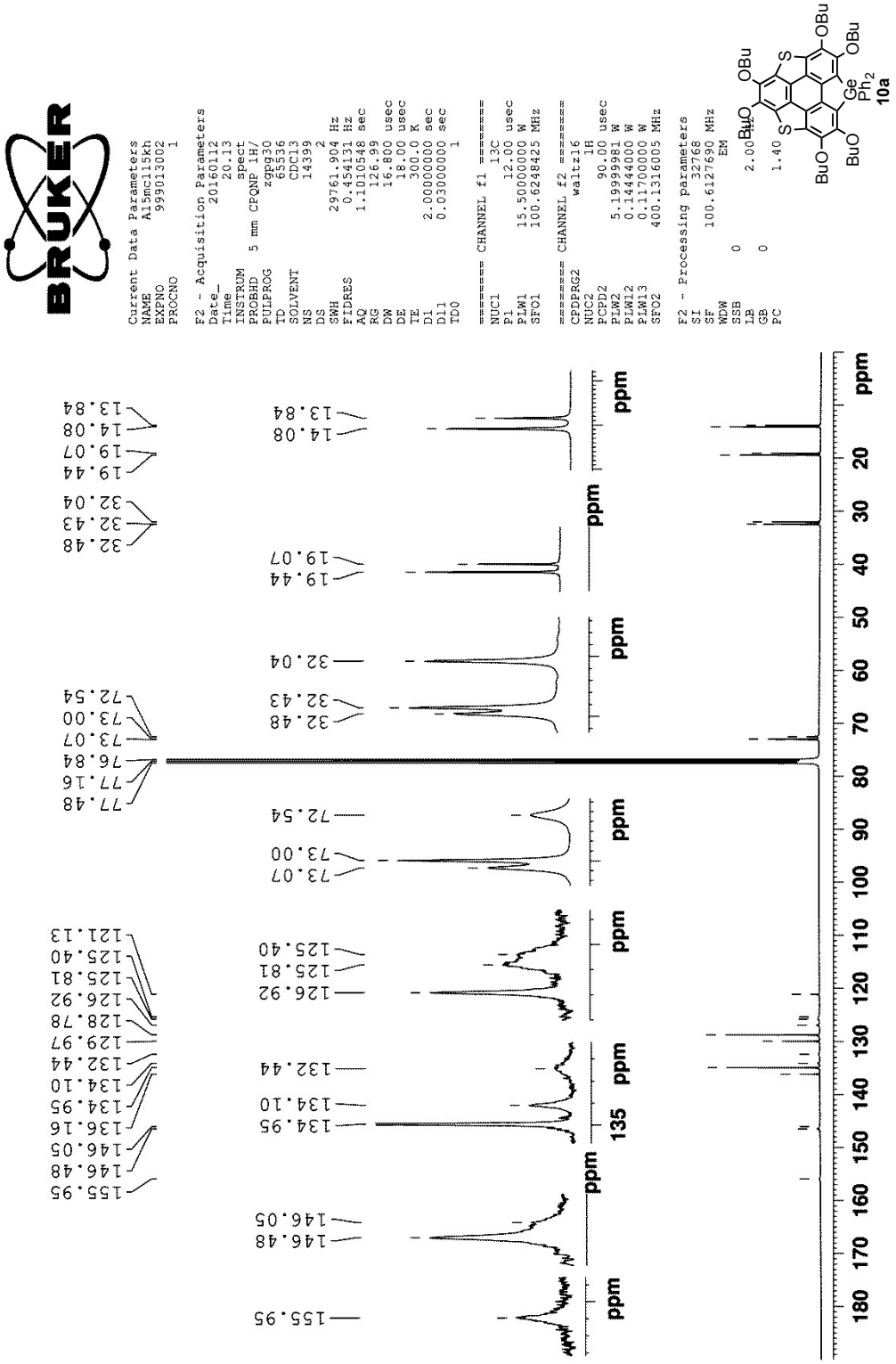

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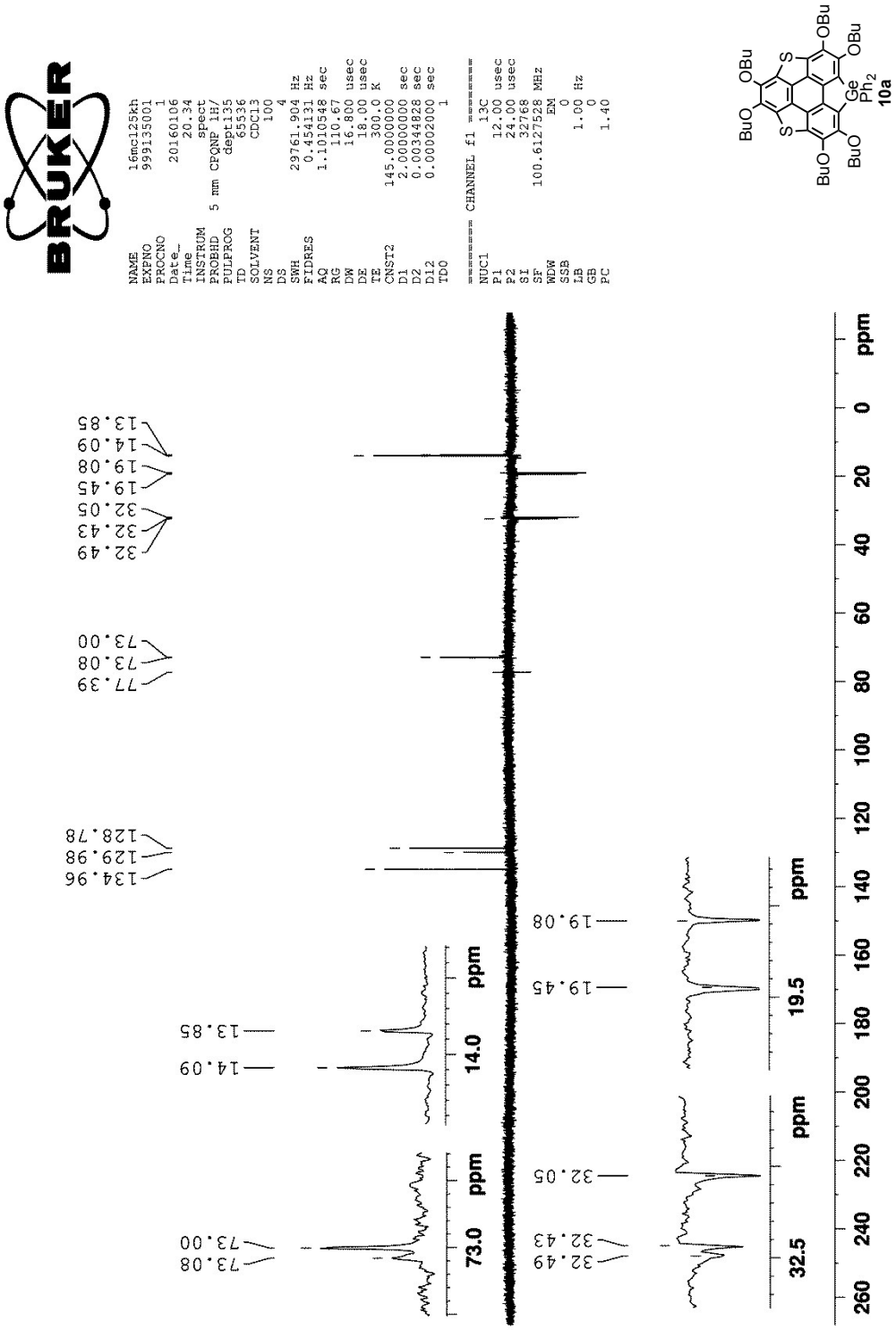

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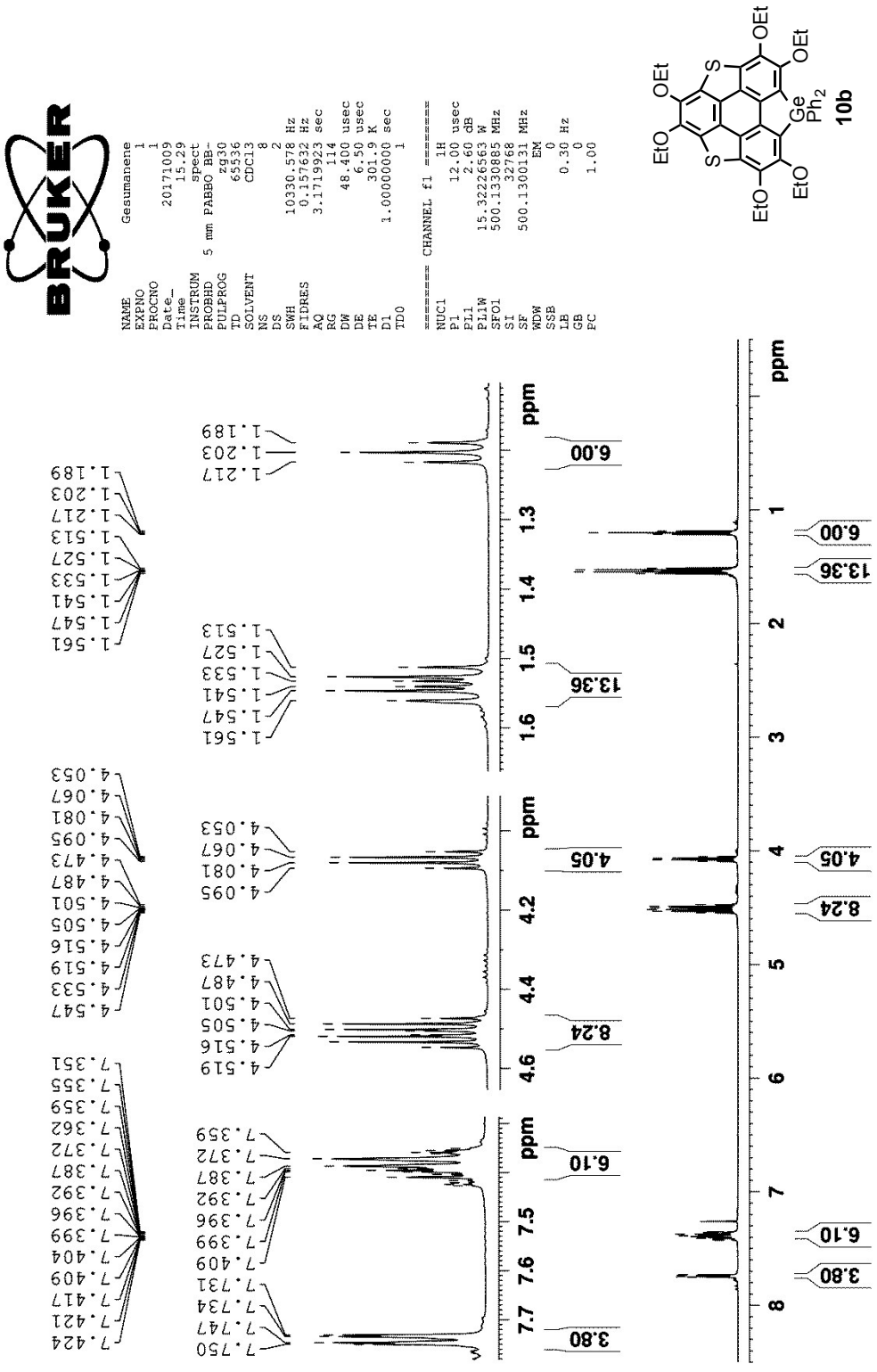

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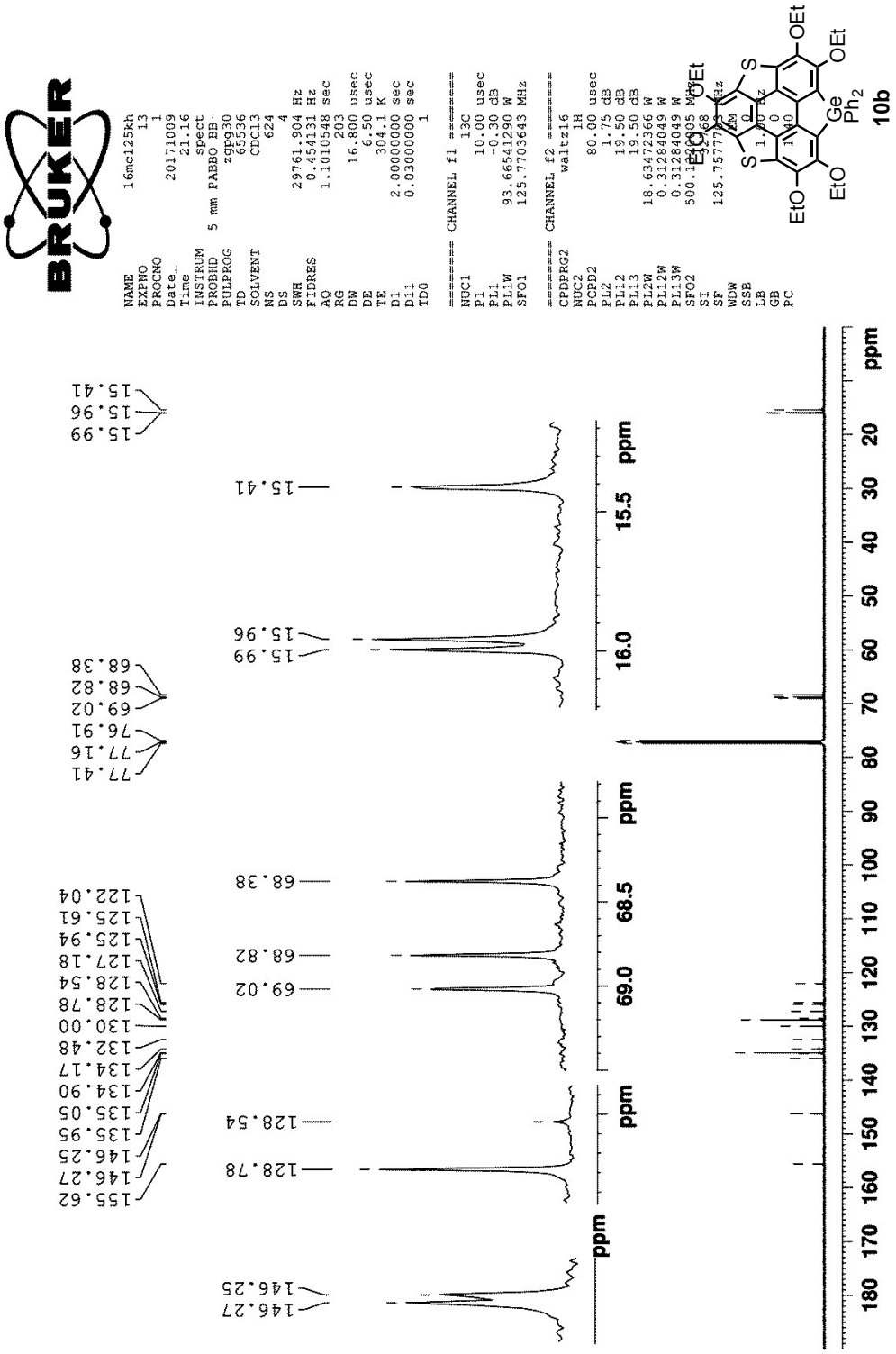

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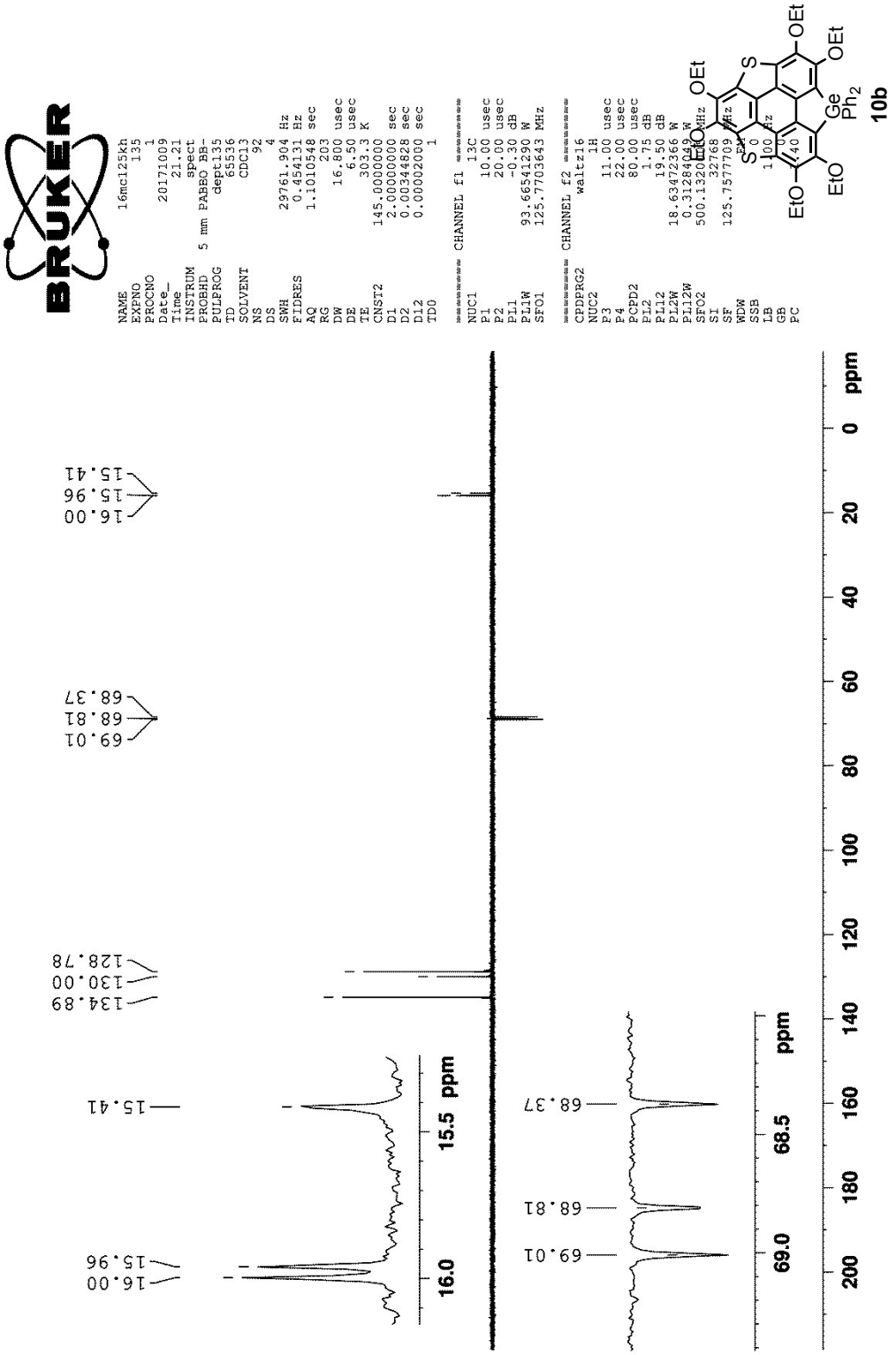

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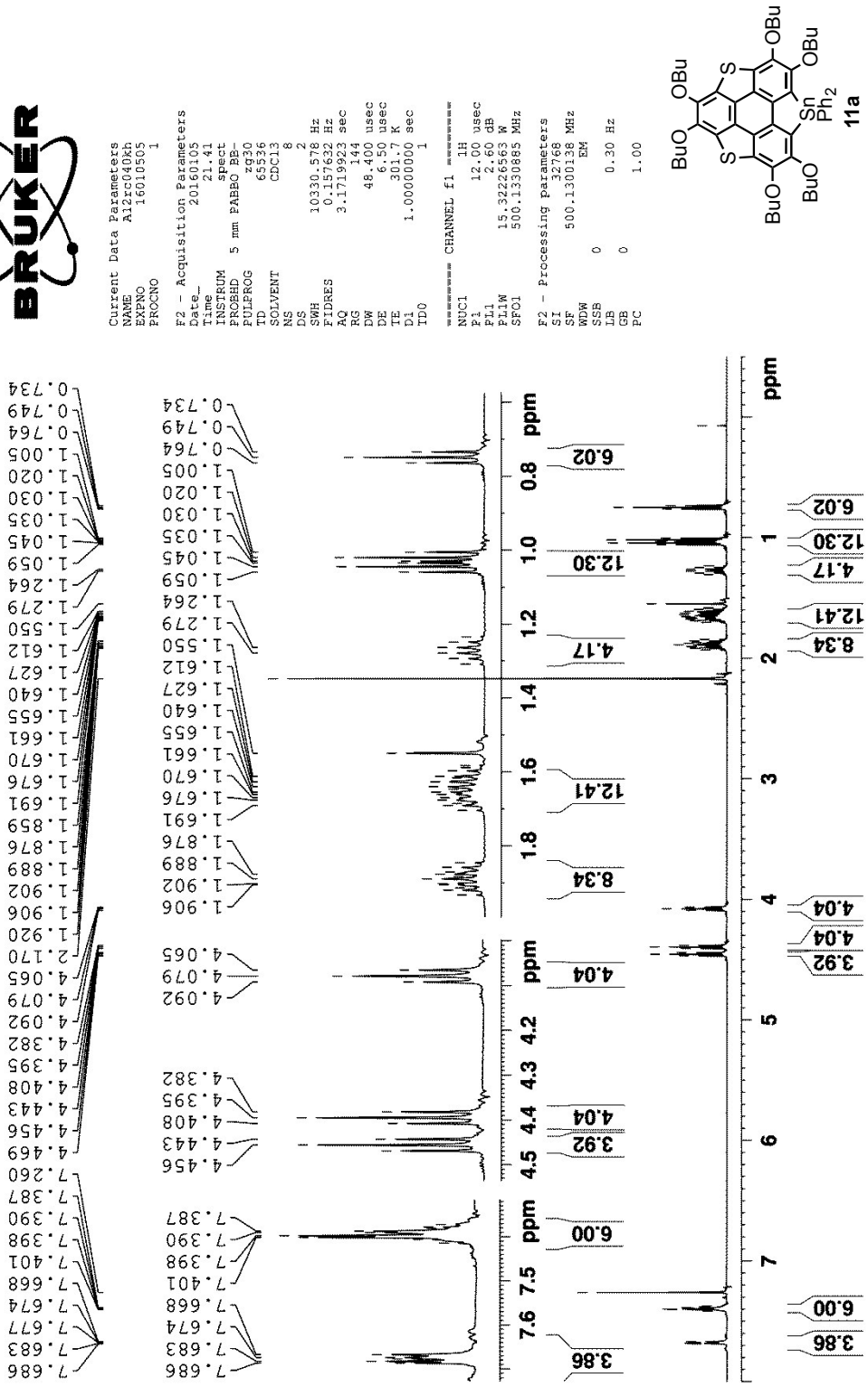

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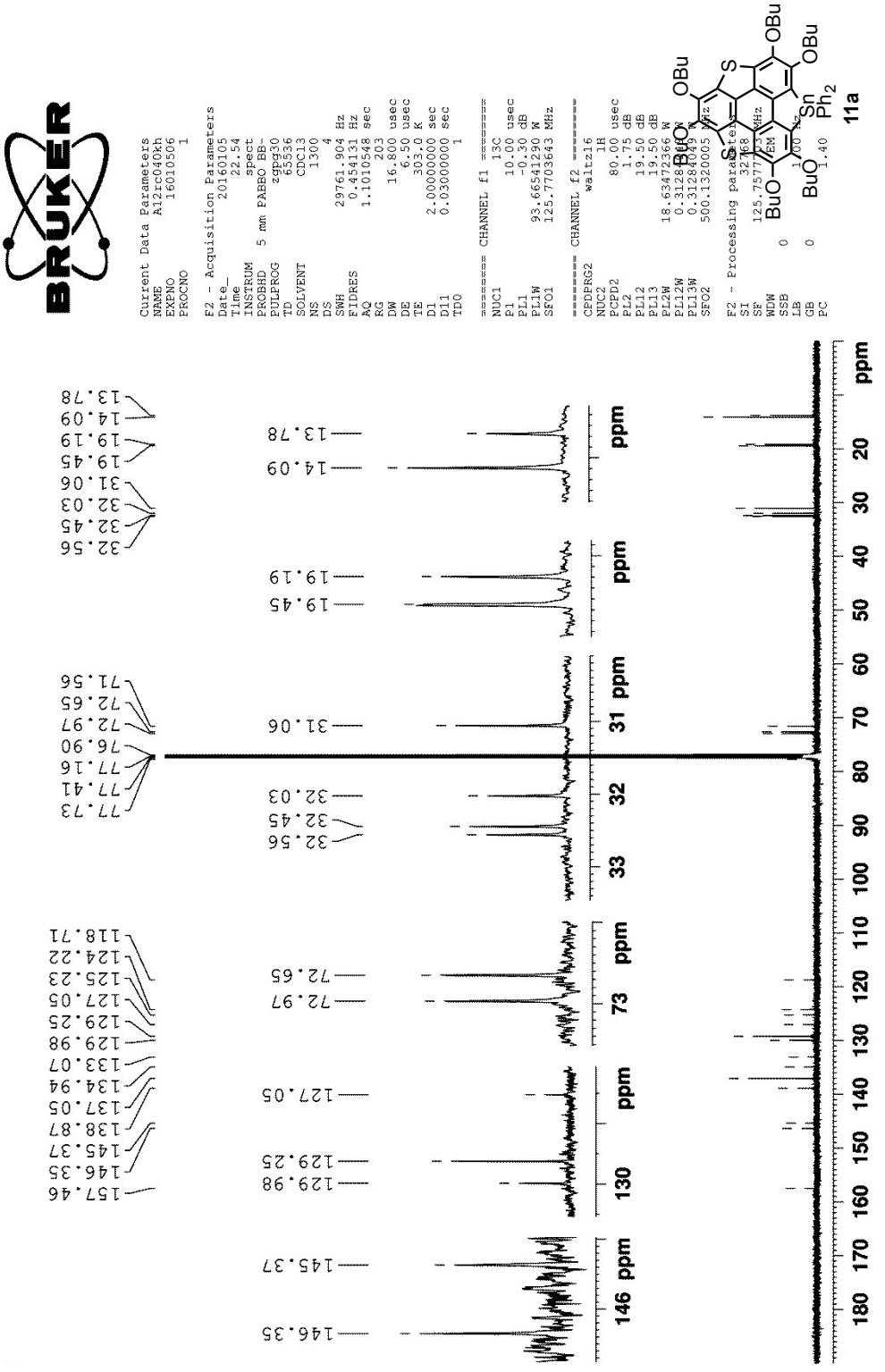

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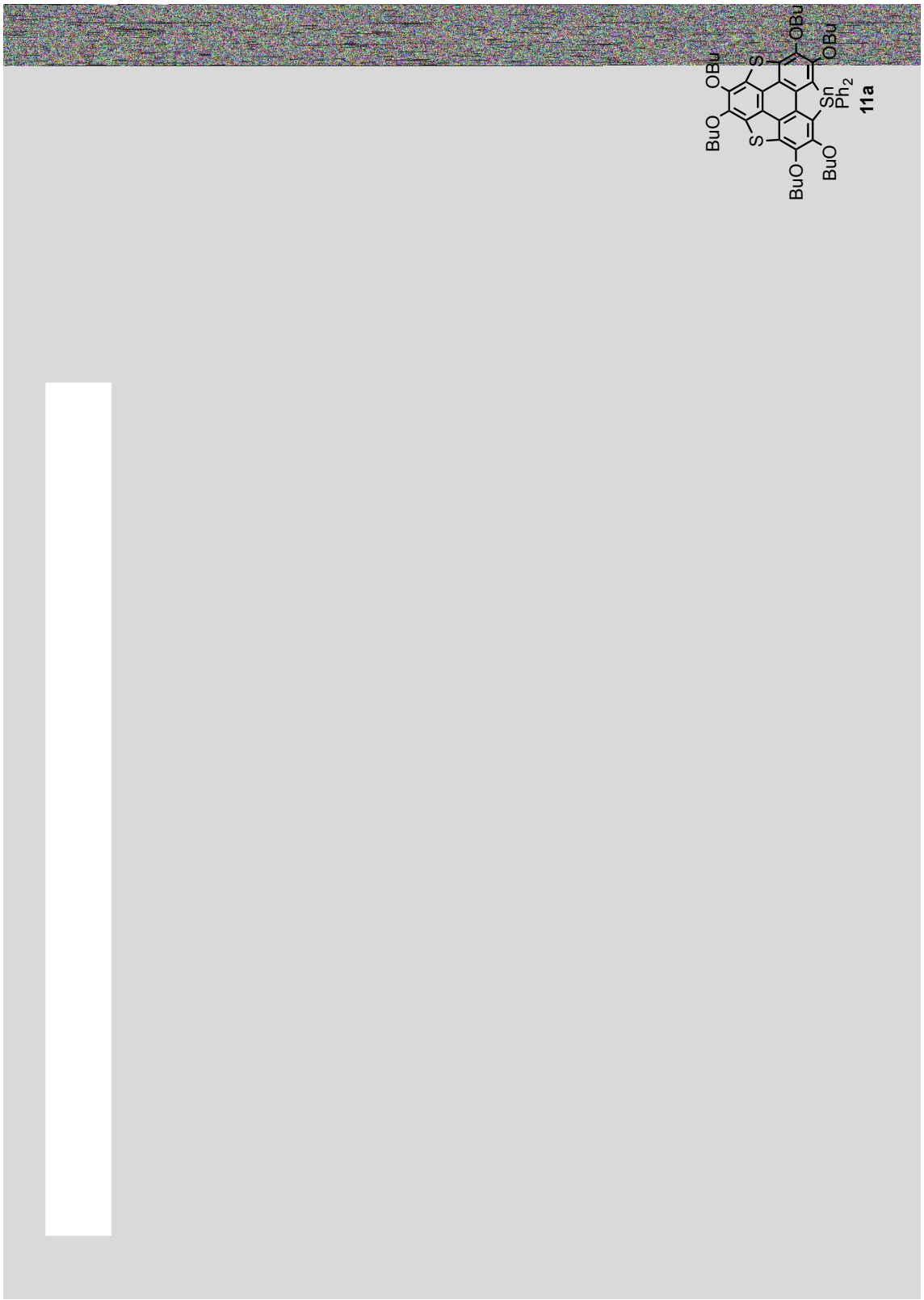

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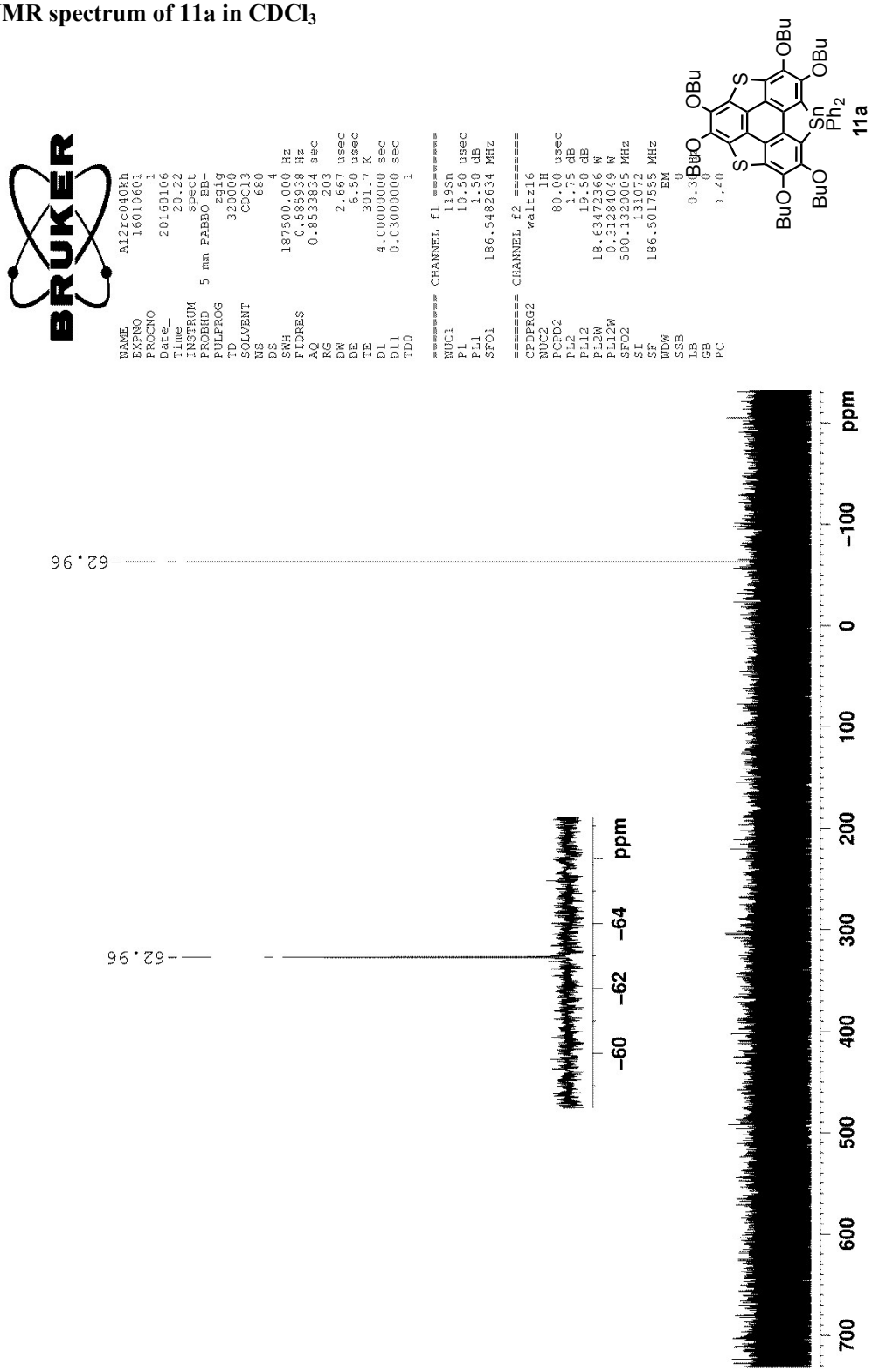

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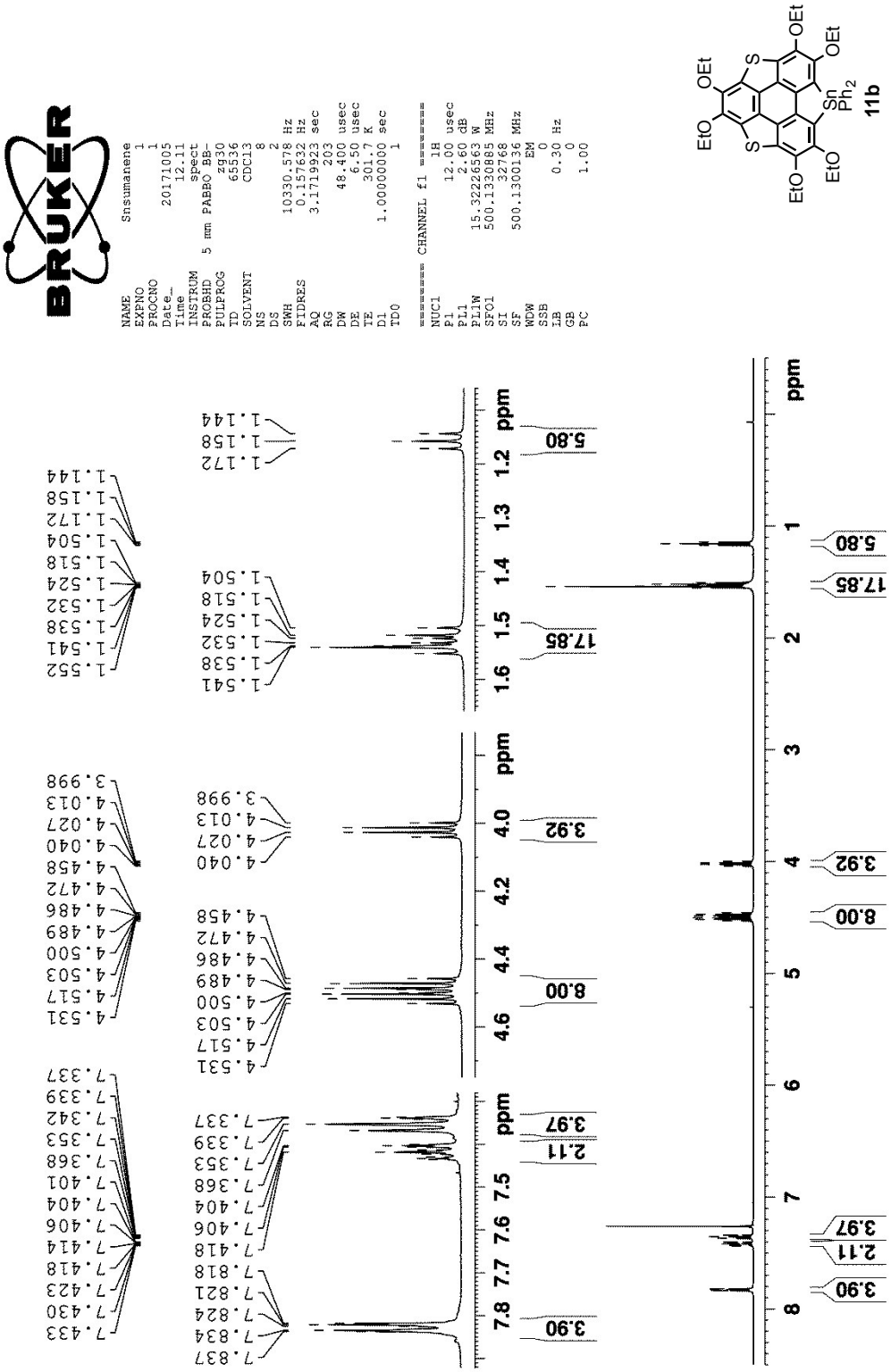

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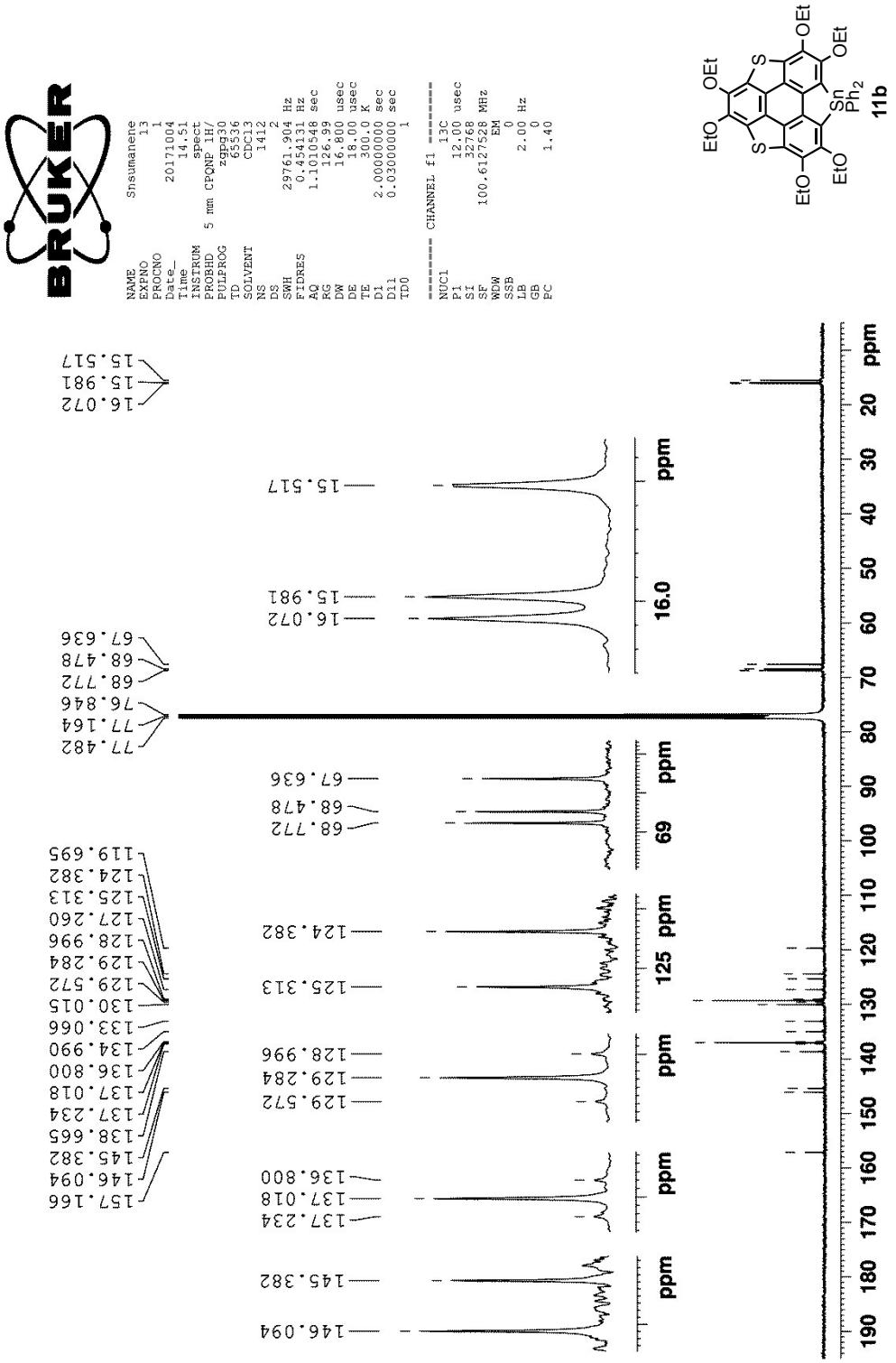

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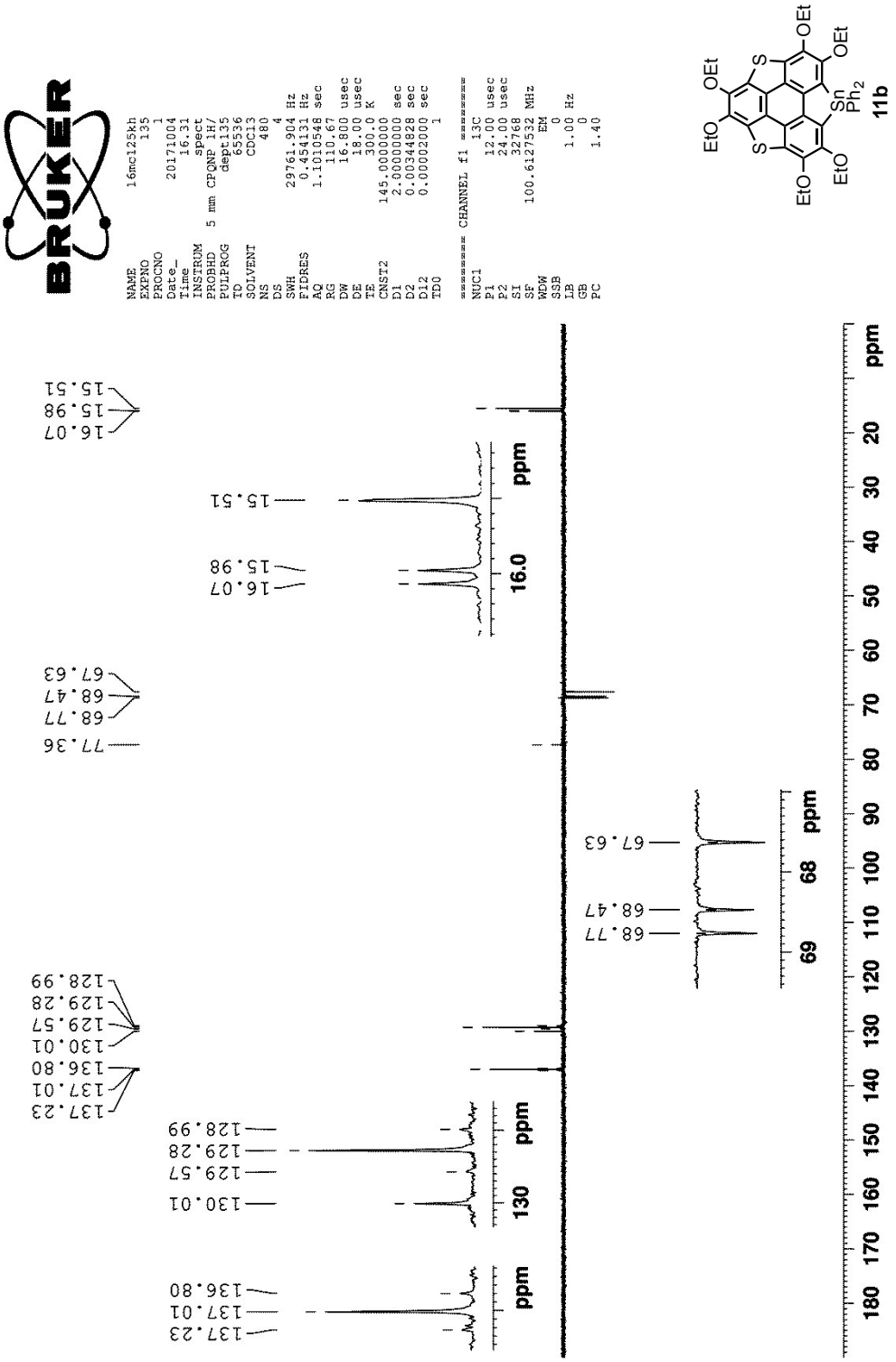

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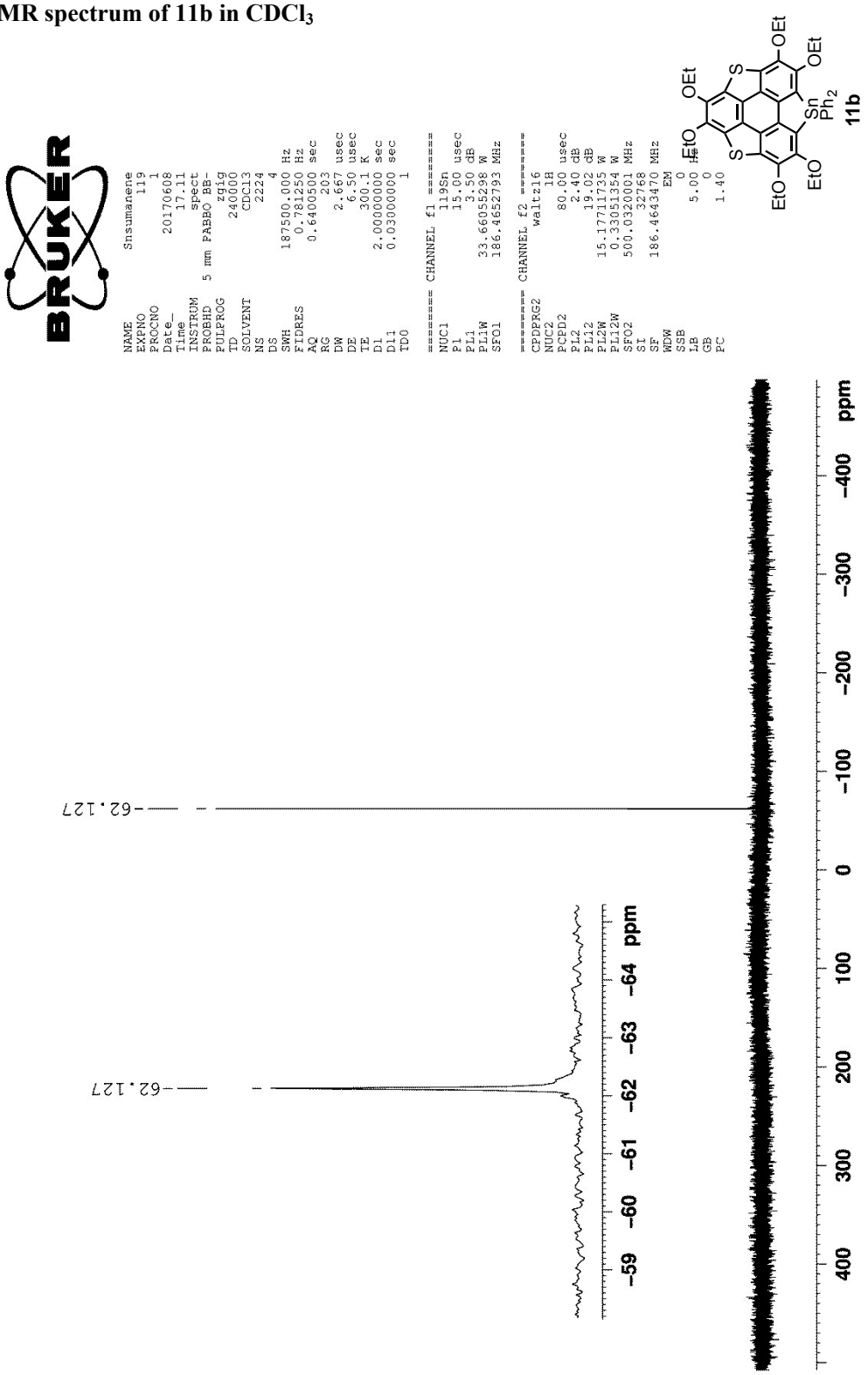

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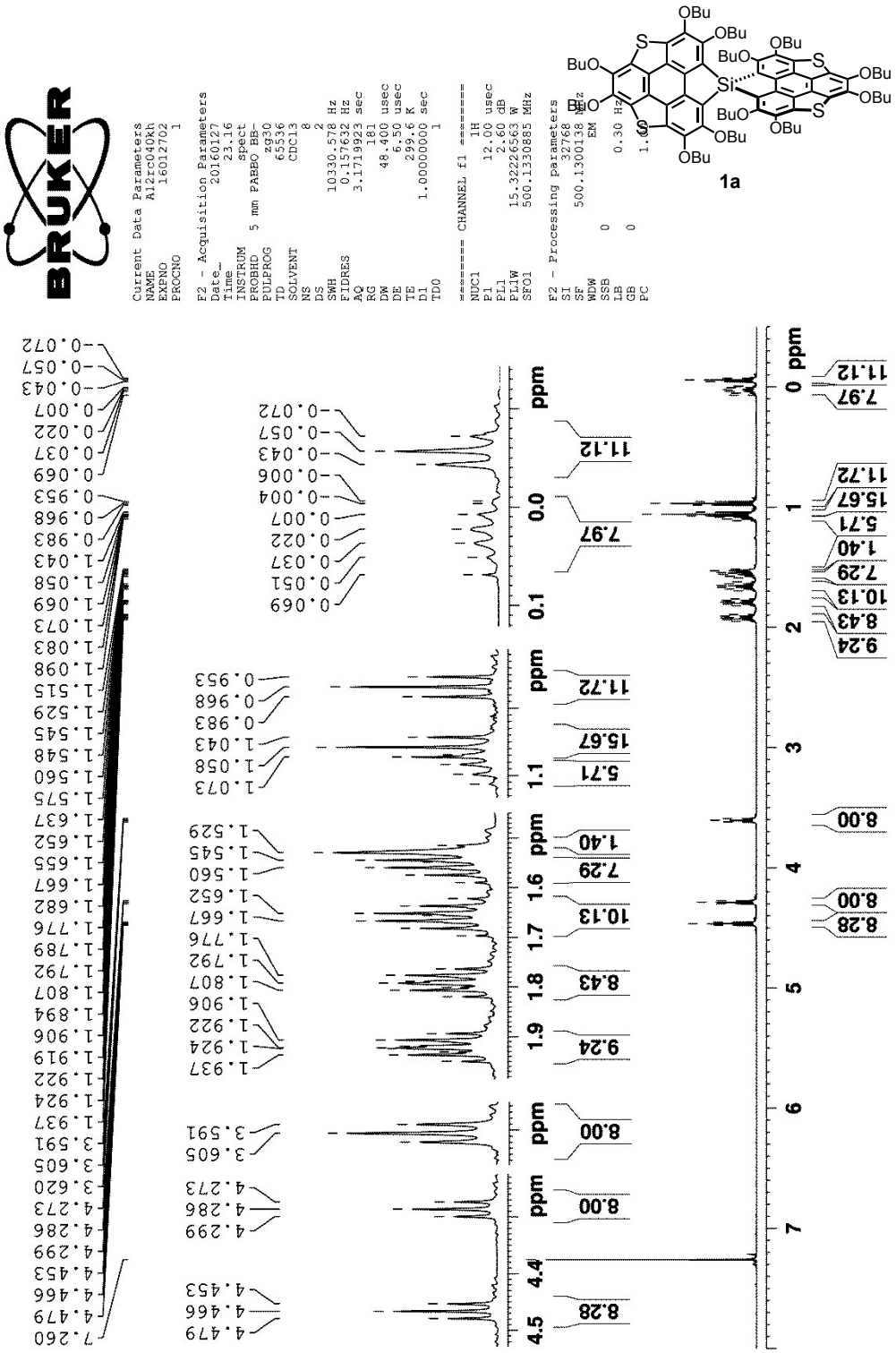

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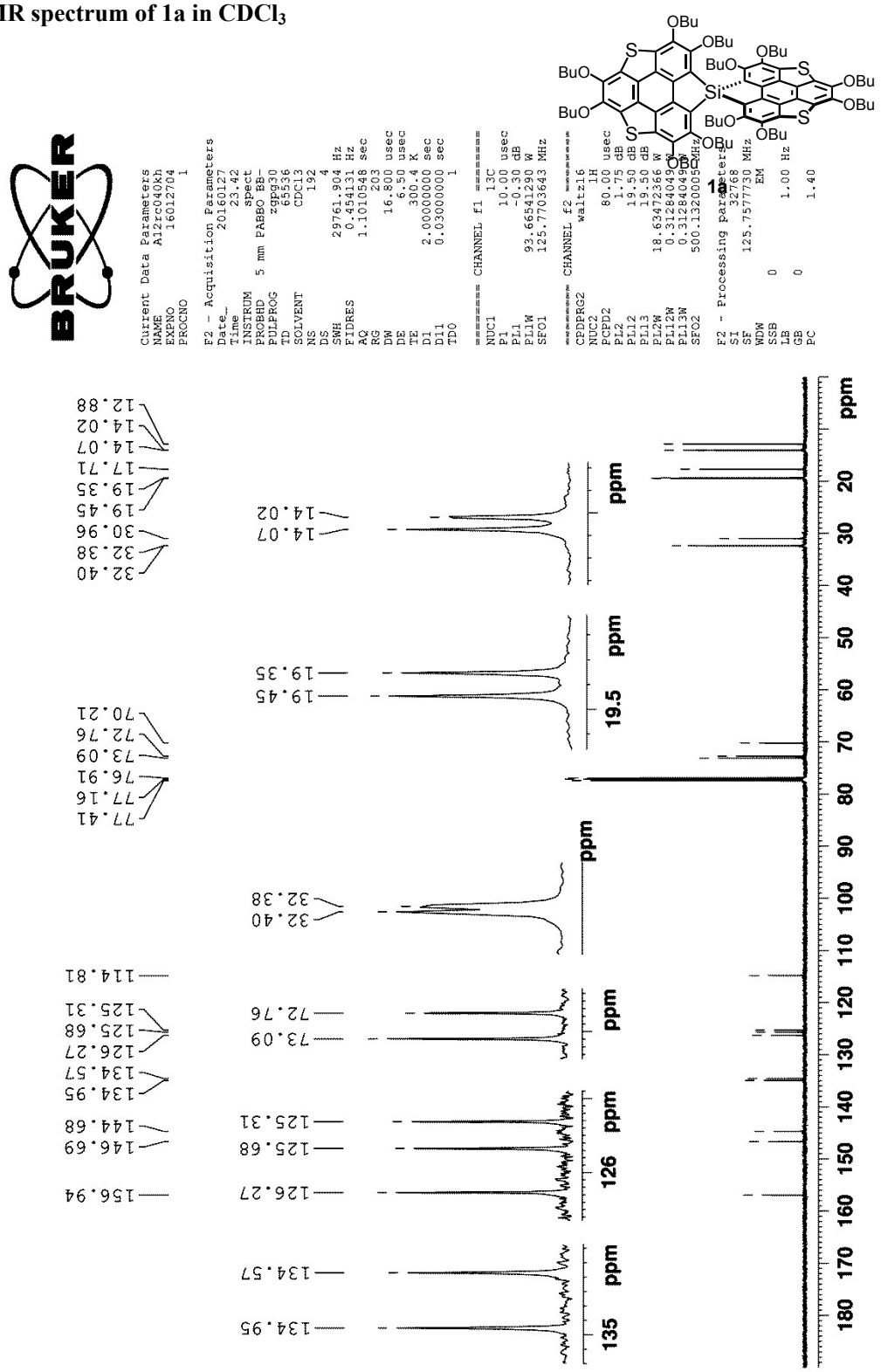

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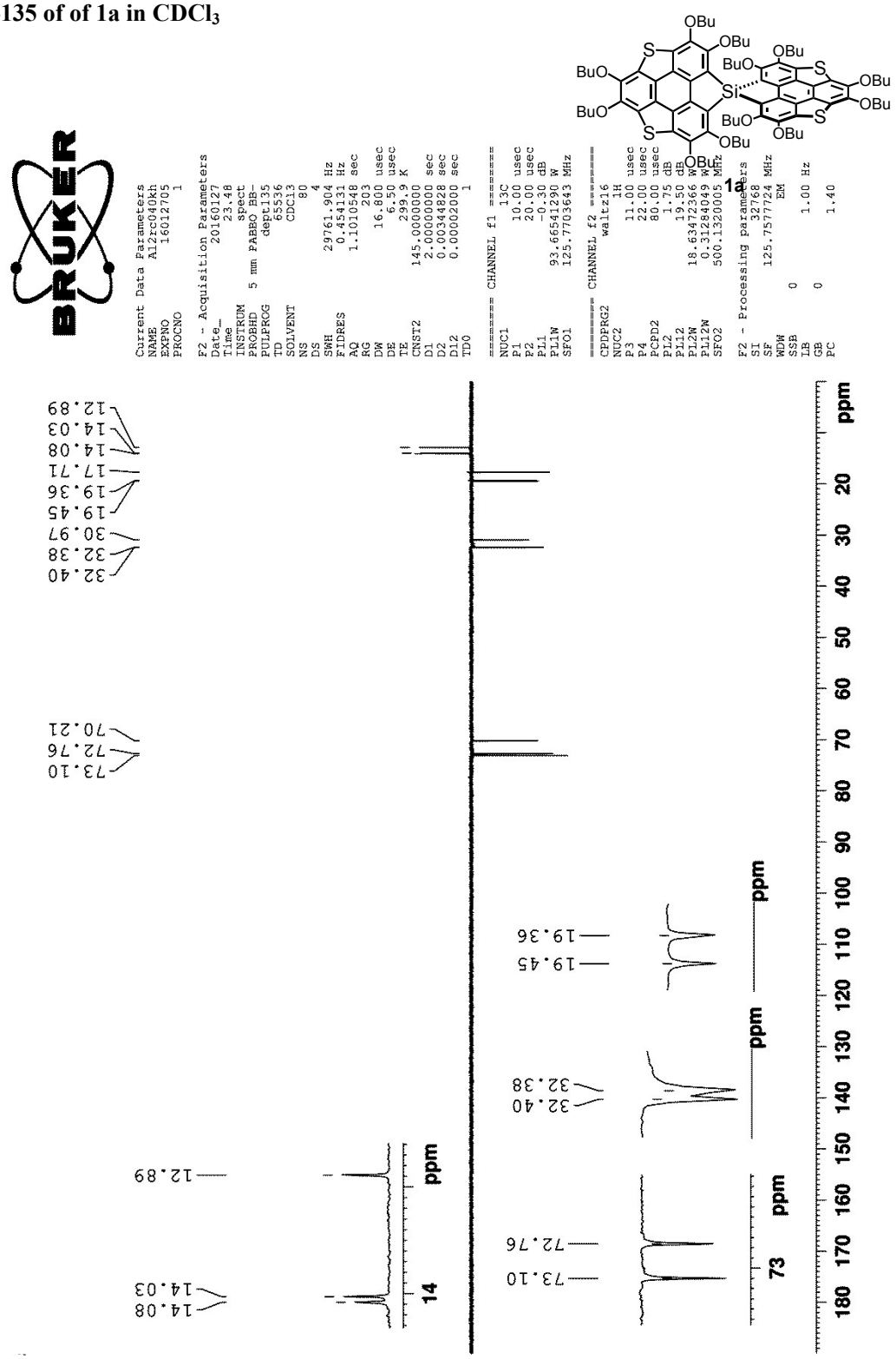
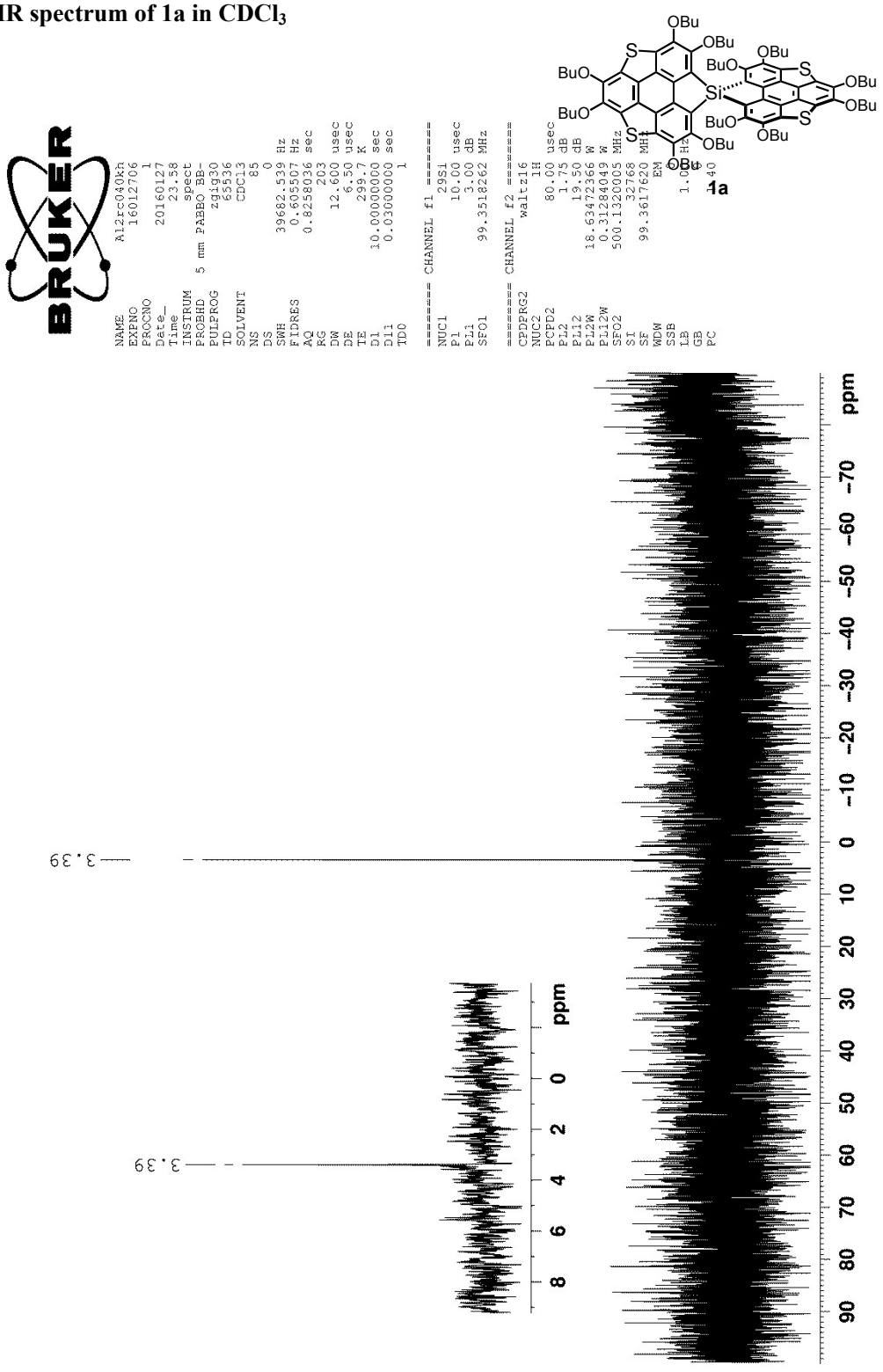


^{29}Si NMR spectrum of 1a in $CDCl_3$



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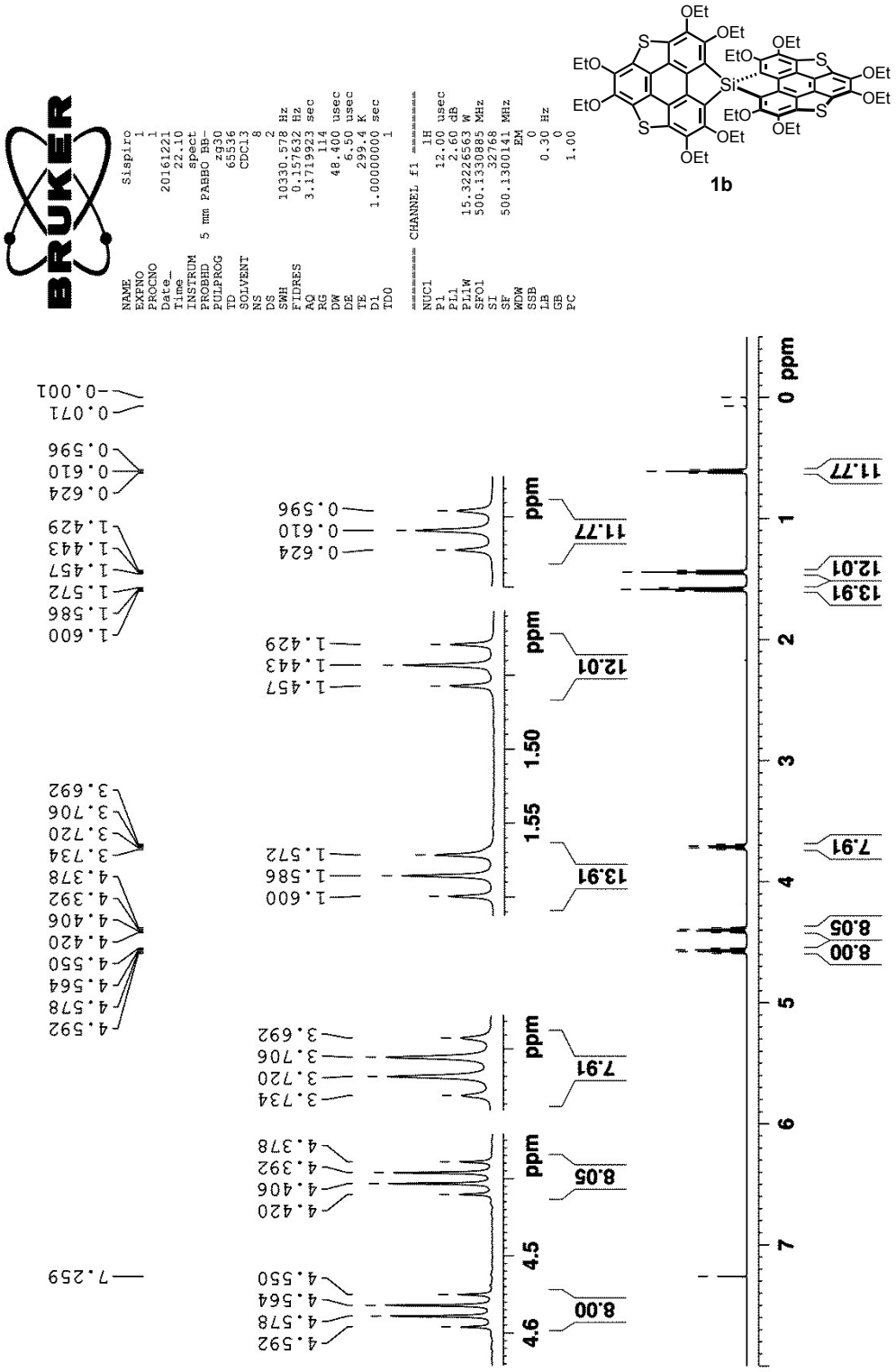
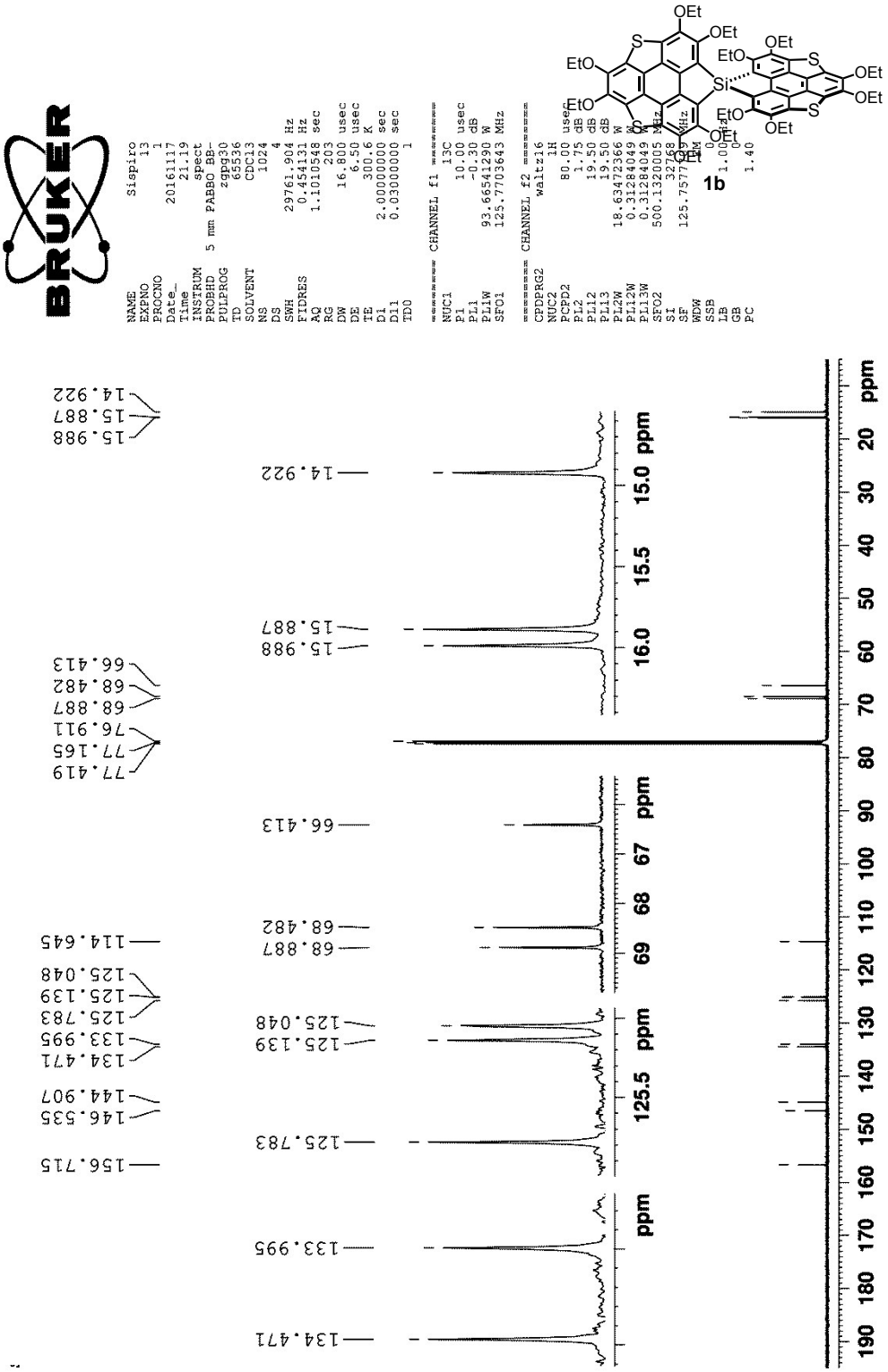
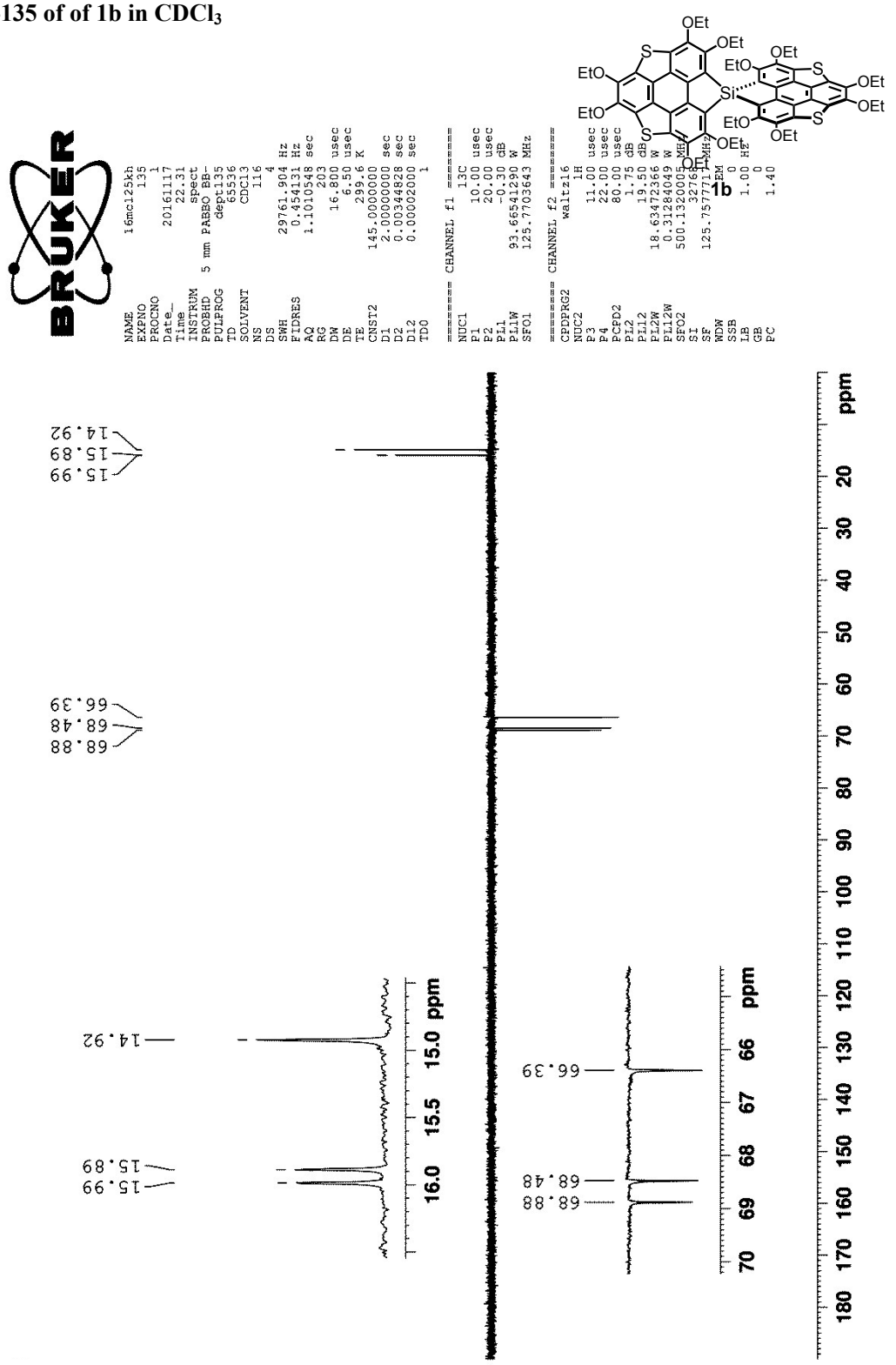


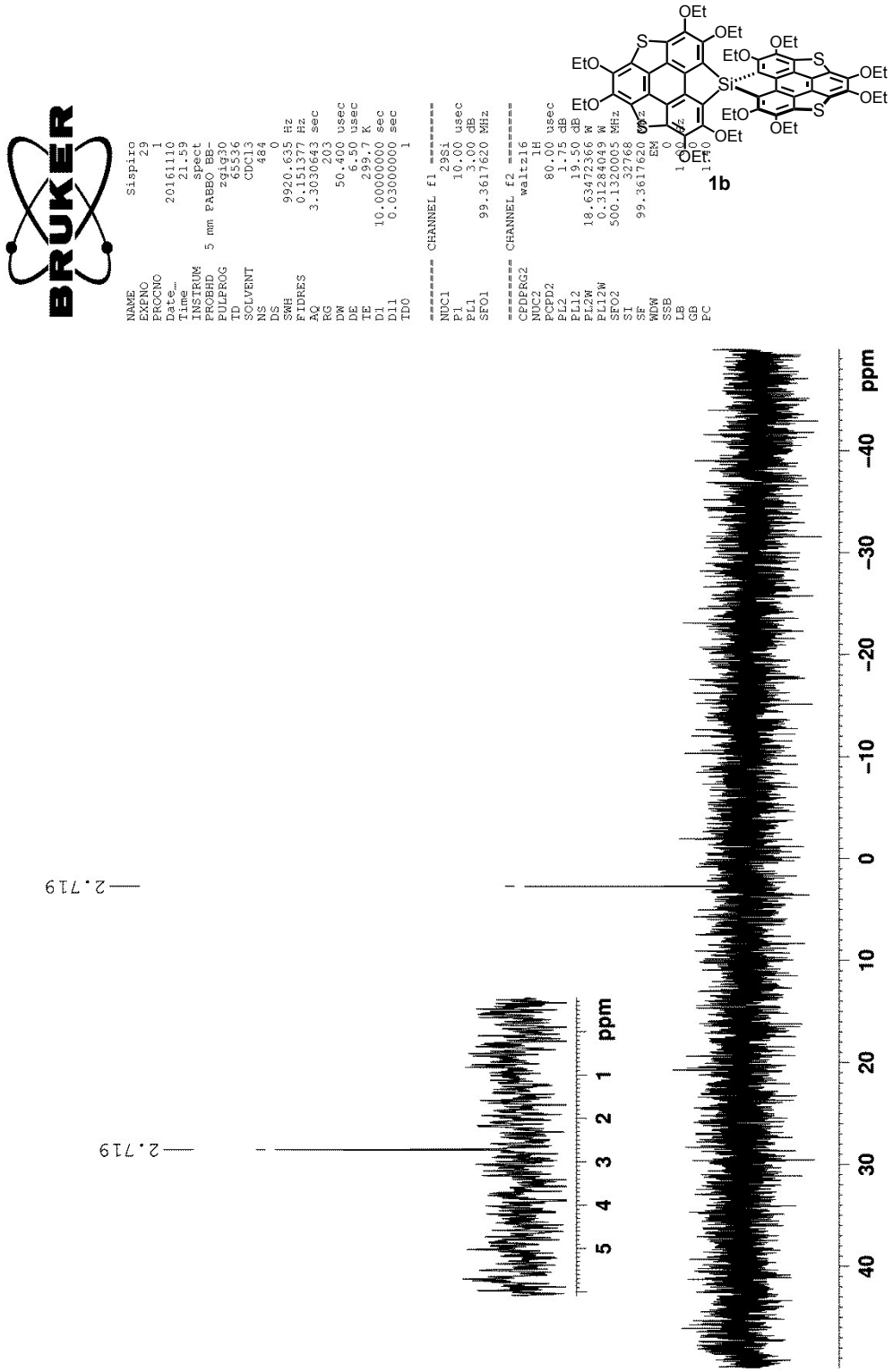
^{13}C NMR spectrum of 1b in $CDCl_3$



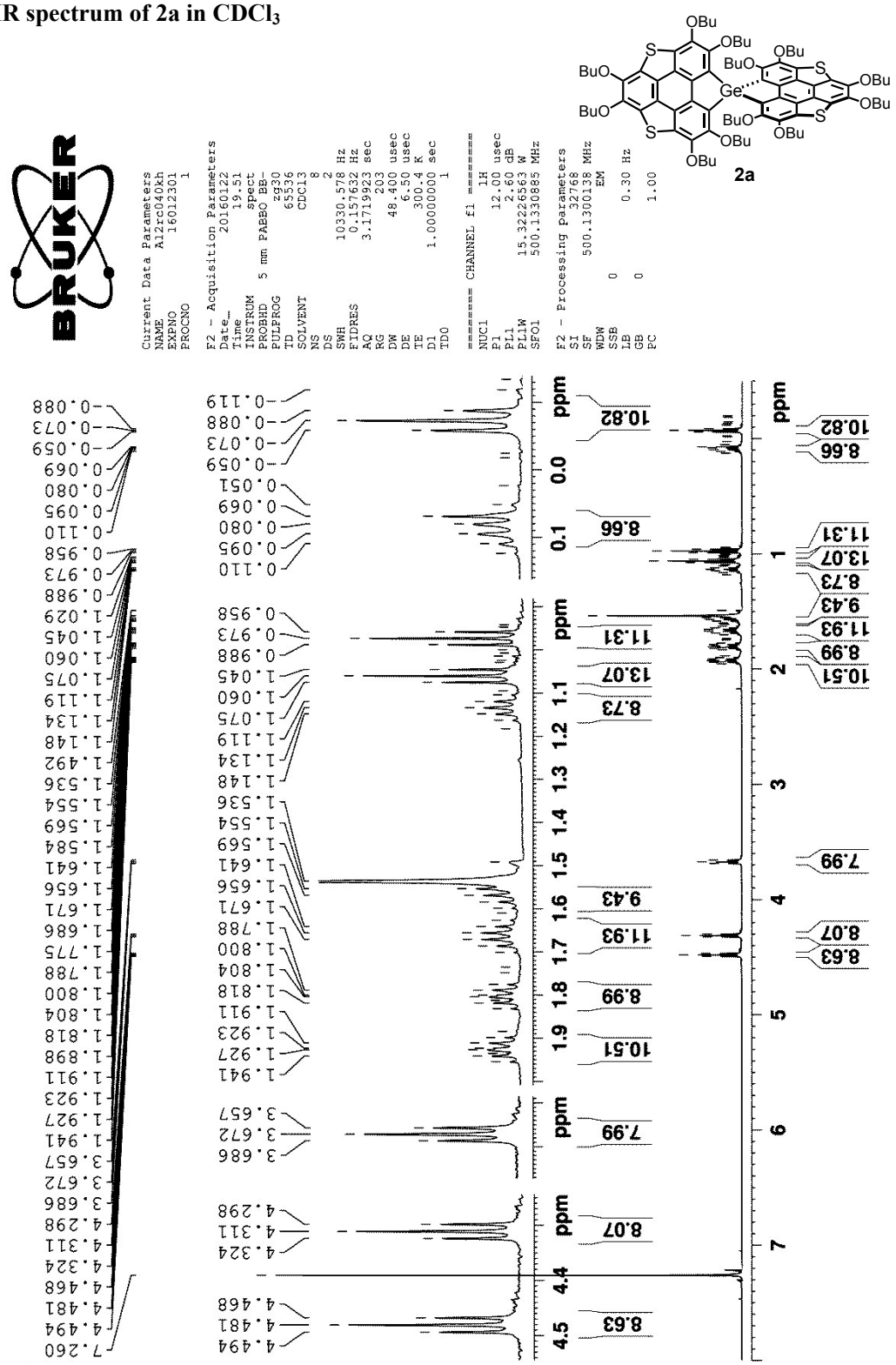
DEPT-135 of of 1b in $CDCl_3$



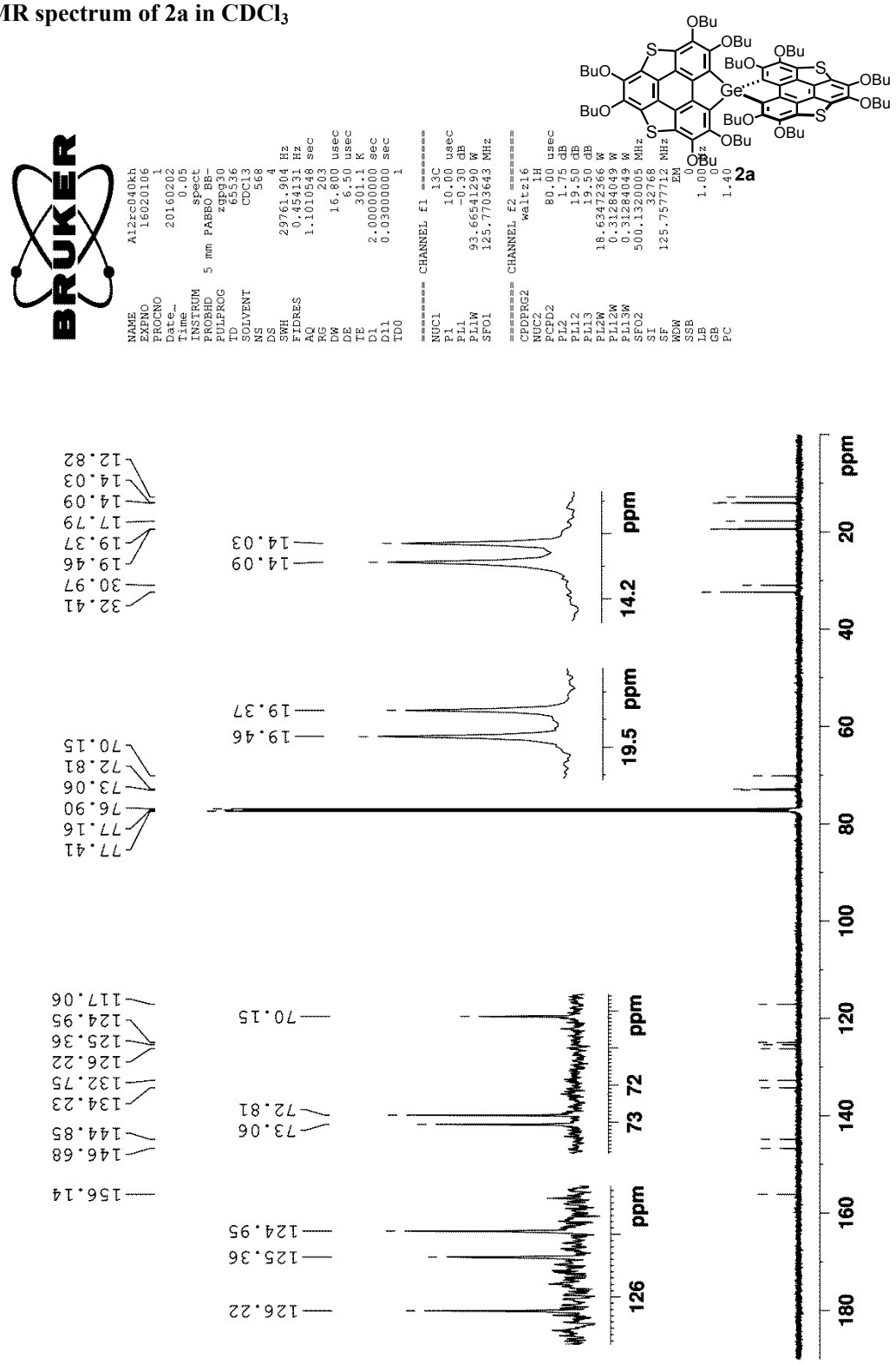
^{29}Si NMR spectrum of 1b in $CDCl_3$



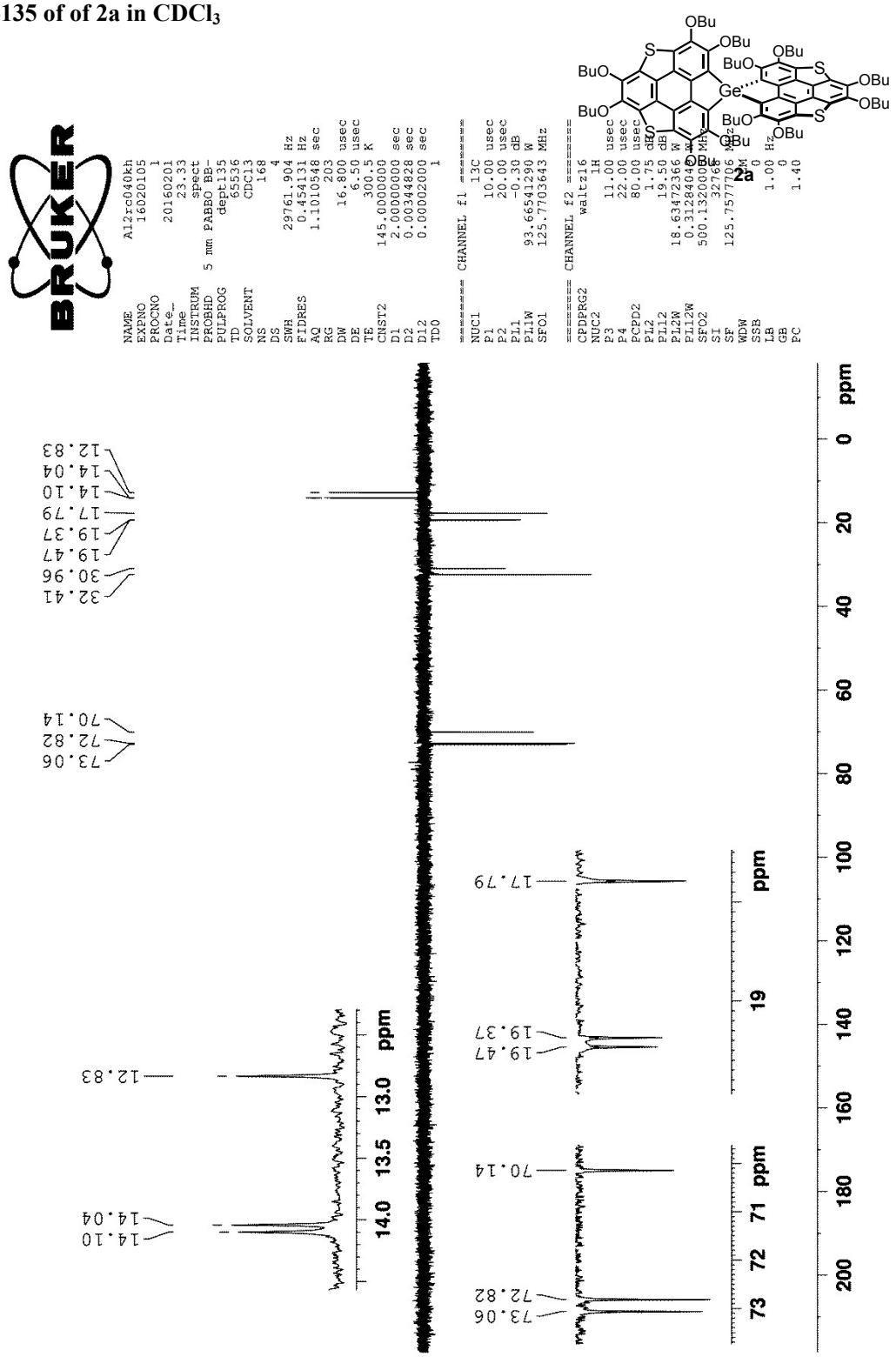
^{1}H NMR spectrum of 2a in $CDCl_3$



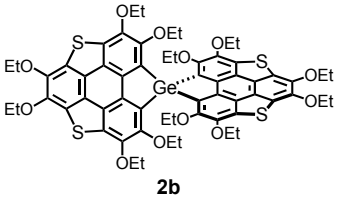
^{13}C NMR spectrum of 2a in $CDCl_3$

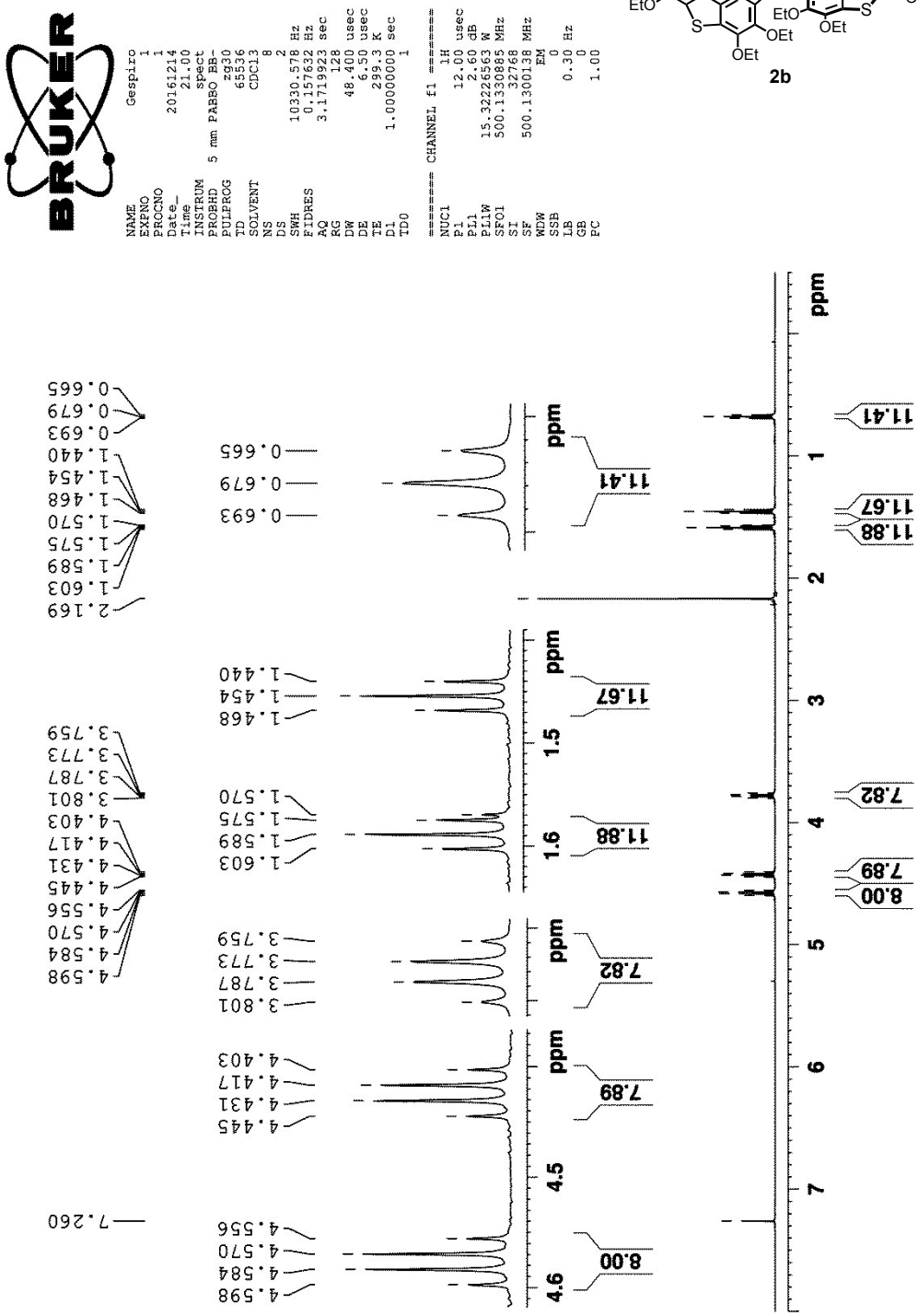


DEPT-135 of of 2a in $CDCl_3$

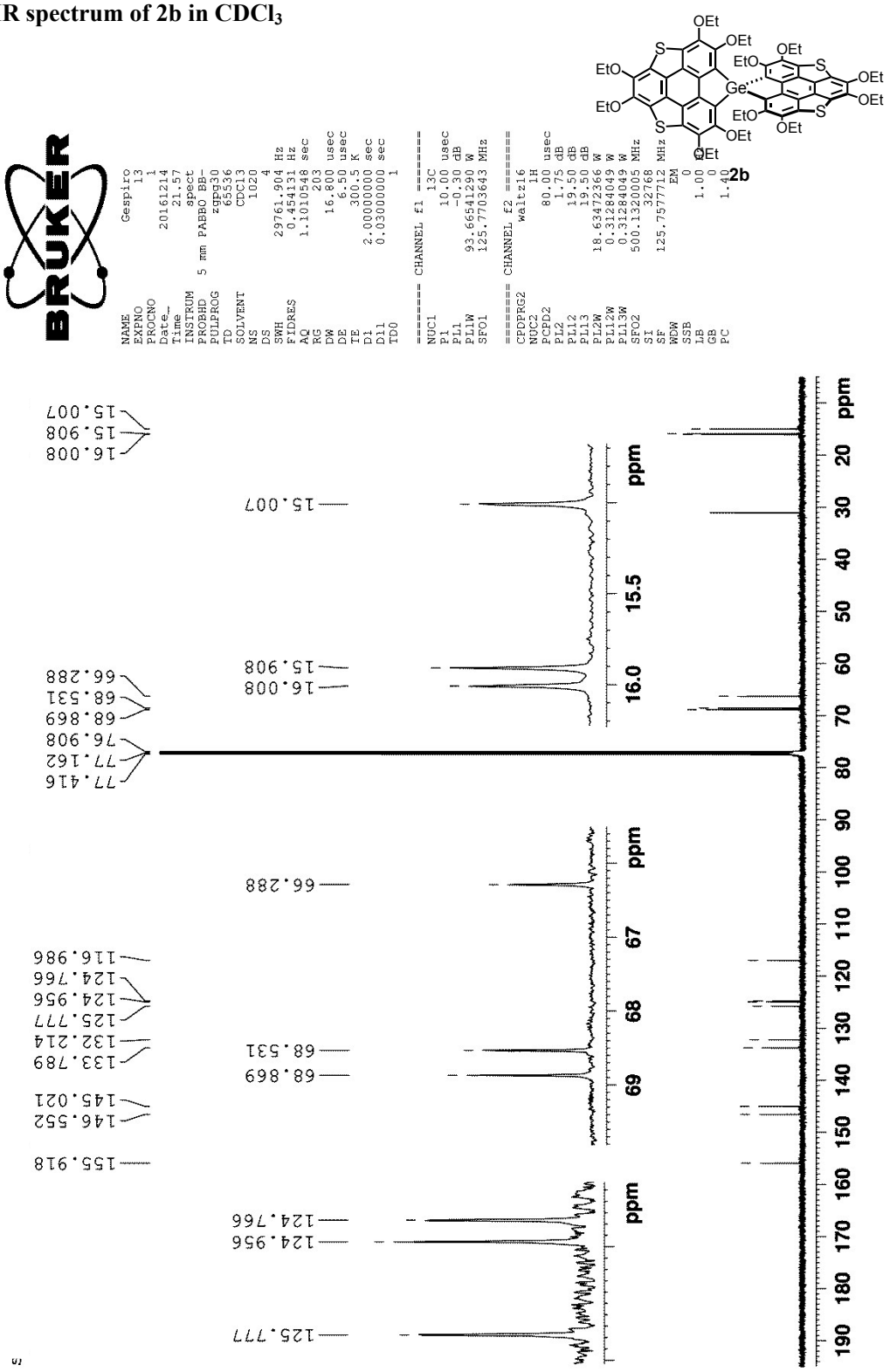


^{1}H NMR spectrum of 2b in $CDCl_3$

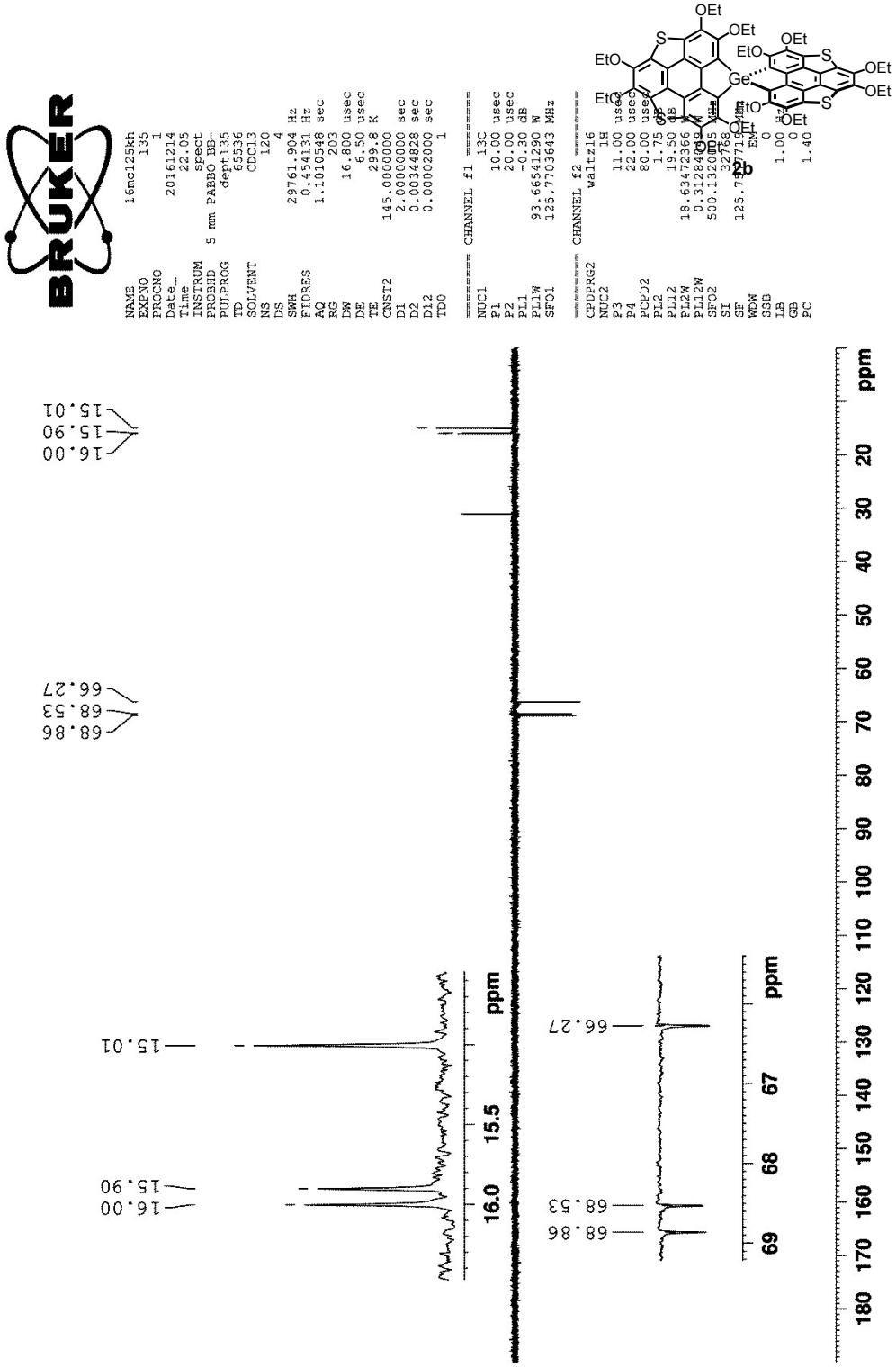




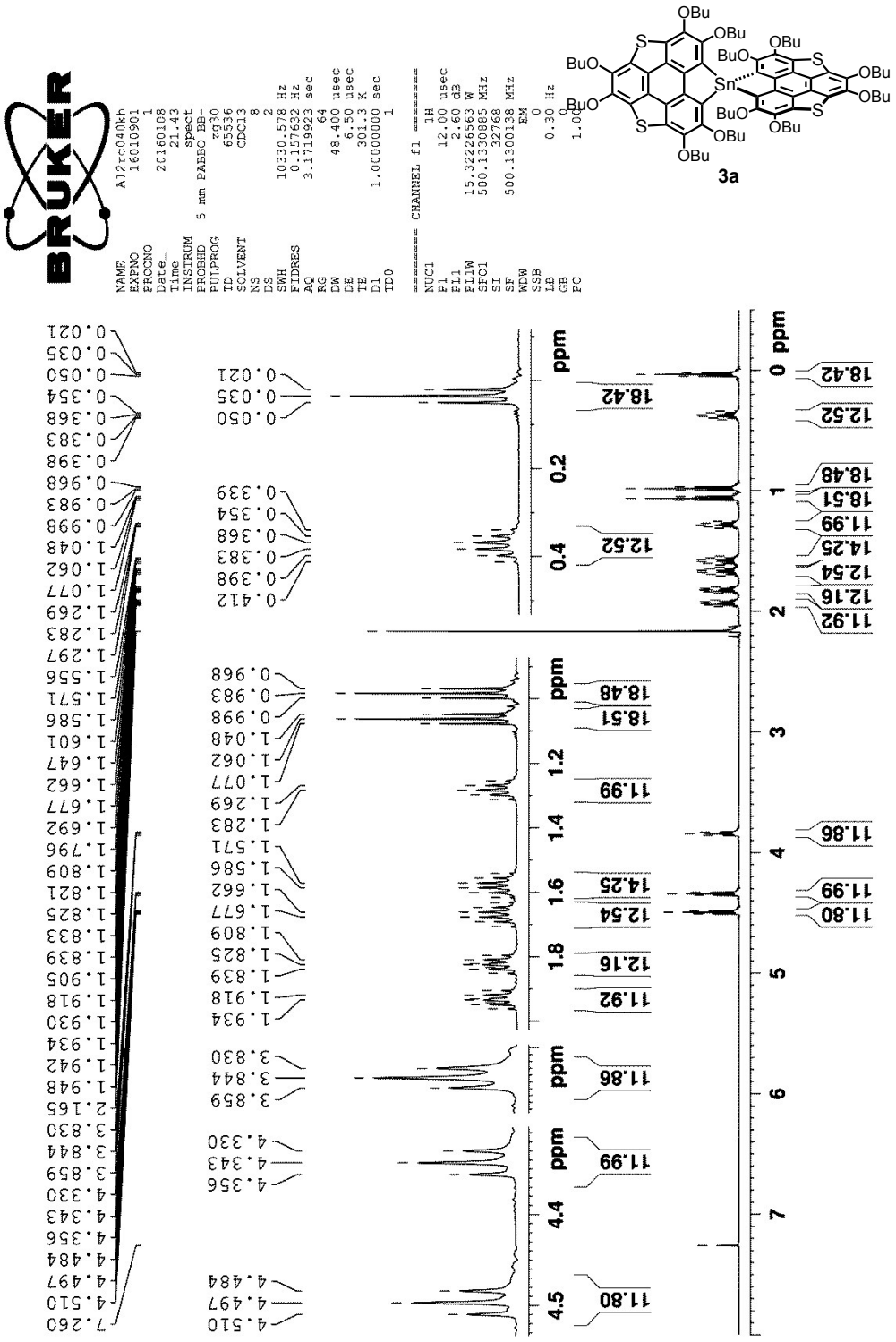
^{13}C NMR spectrum of 2b in $CDCl_3$



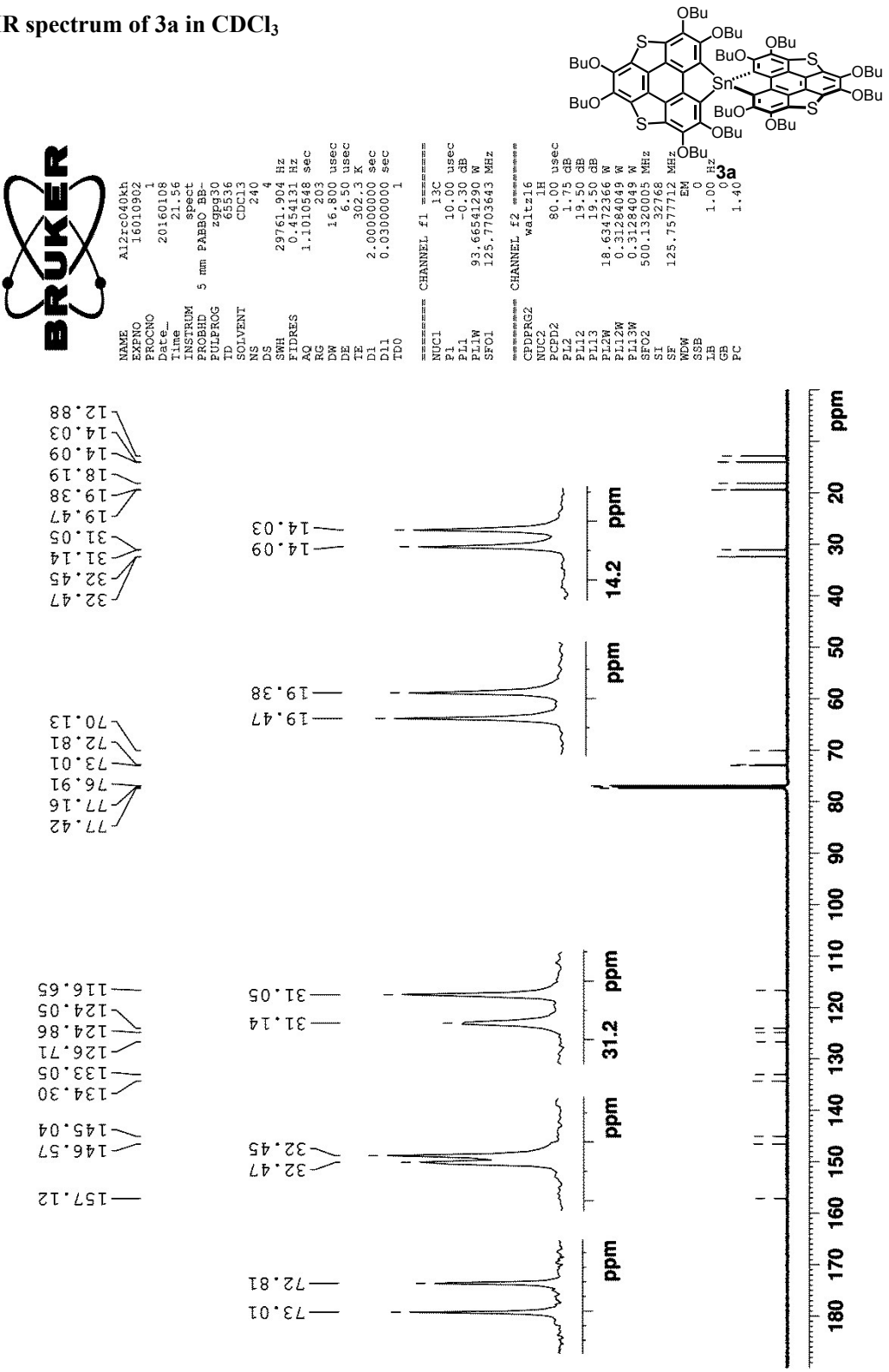
DEPT-135 of of 2b in $CDCl_3$



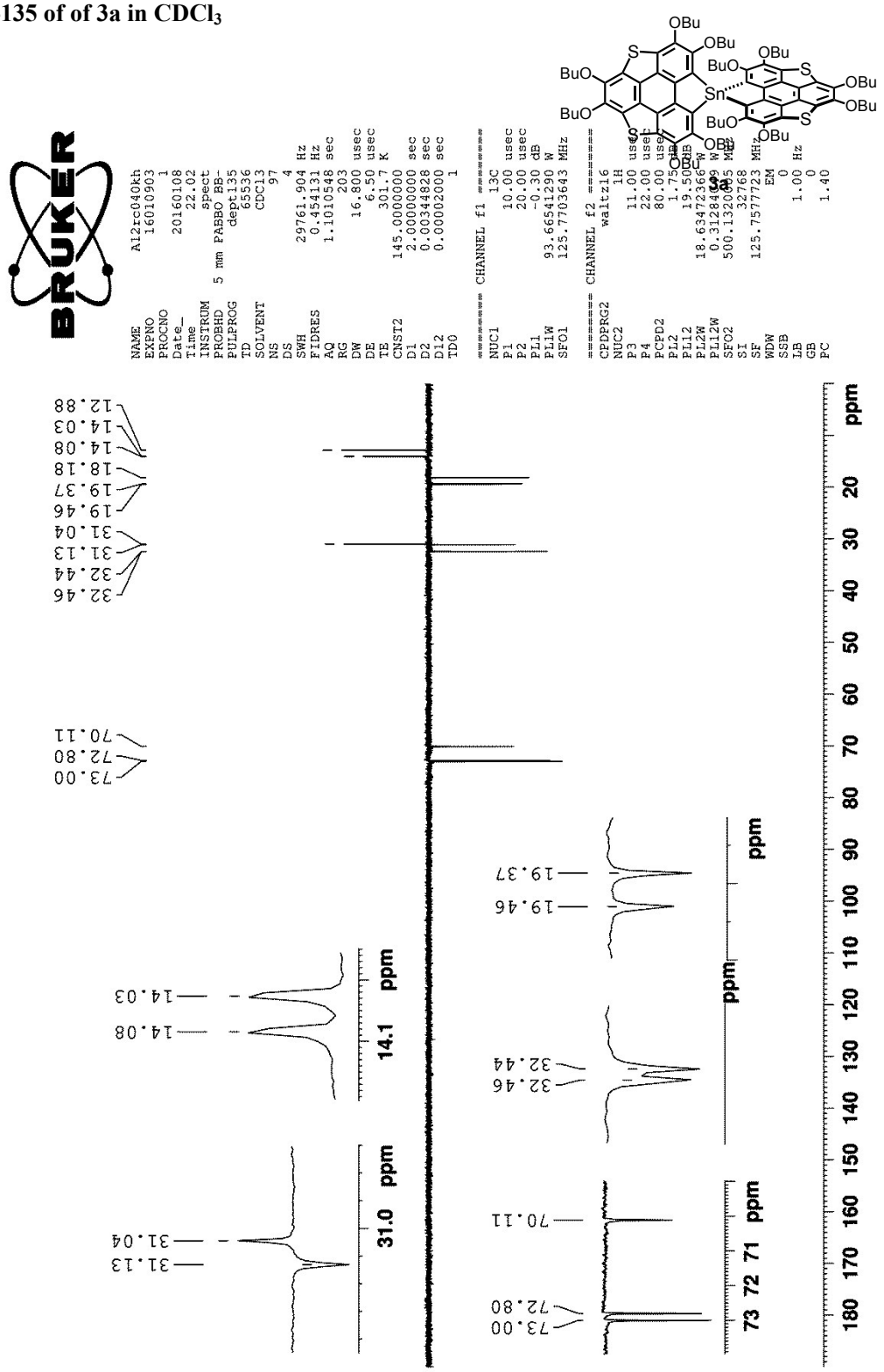
^{1}H NMR spectrum of 3a in $CDCl_3$



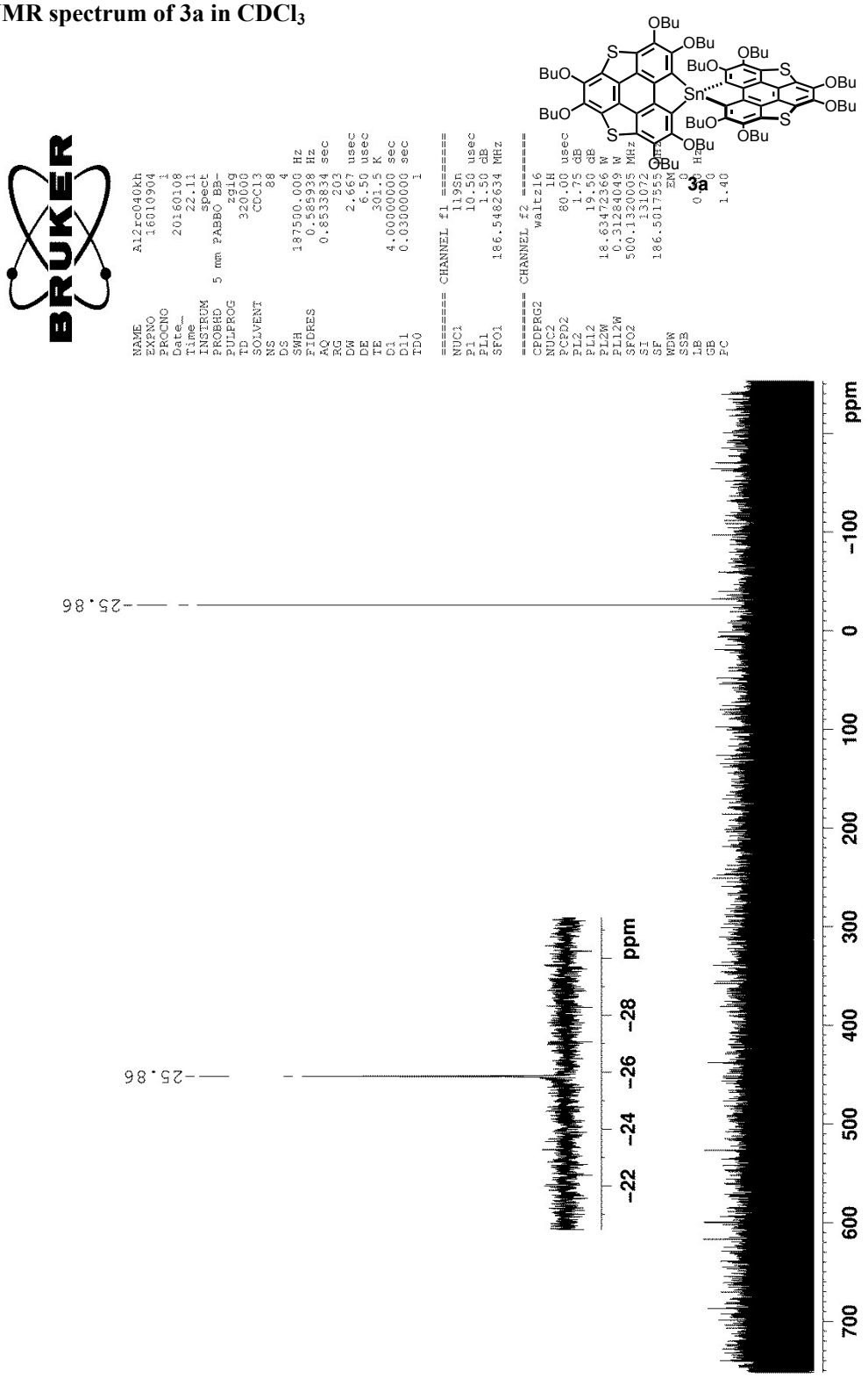
^{13}C NMR spectrum of 3a in $CDCl_3$



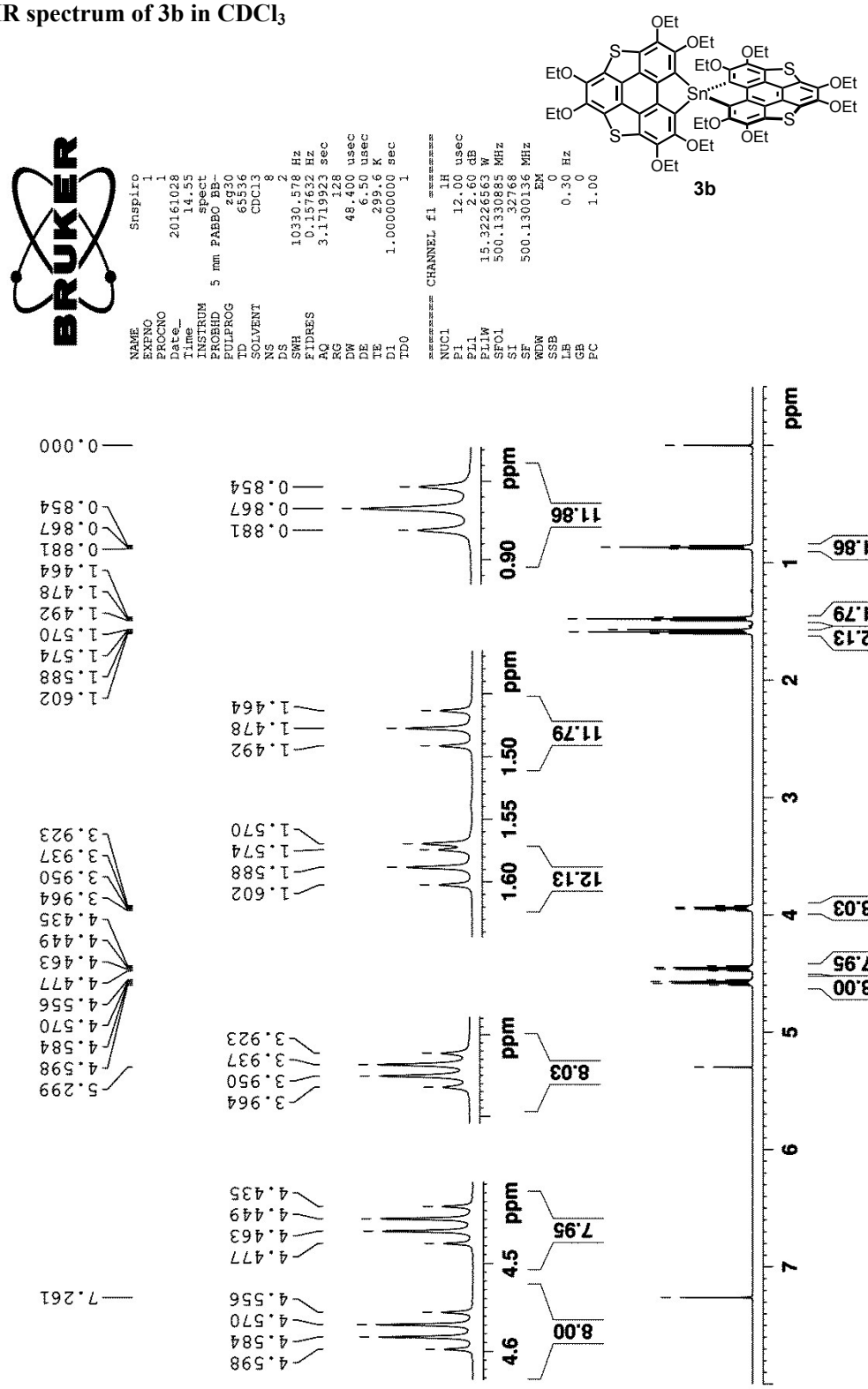
DEPT-135 of of 3a in $CDCl_3$



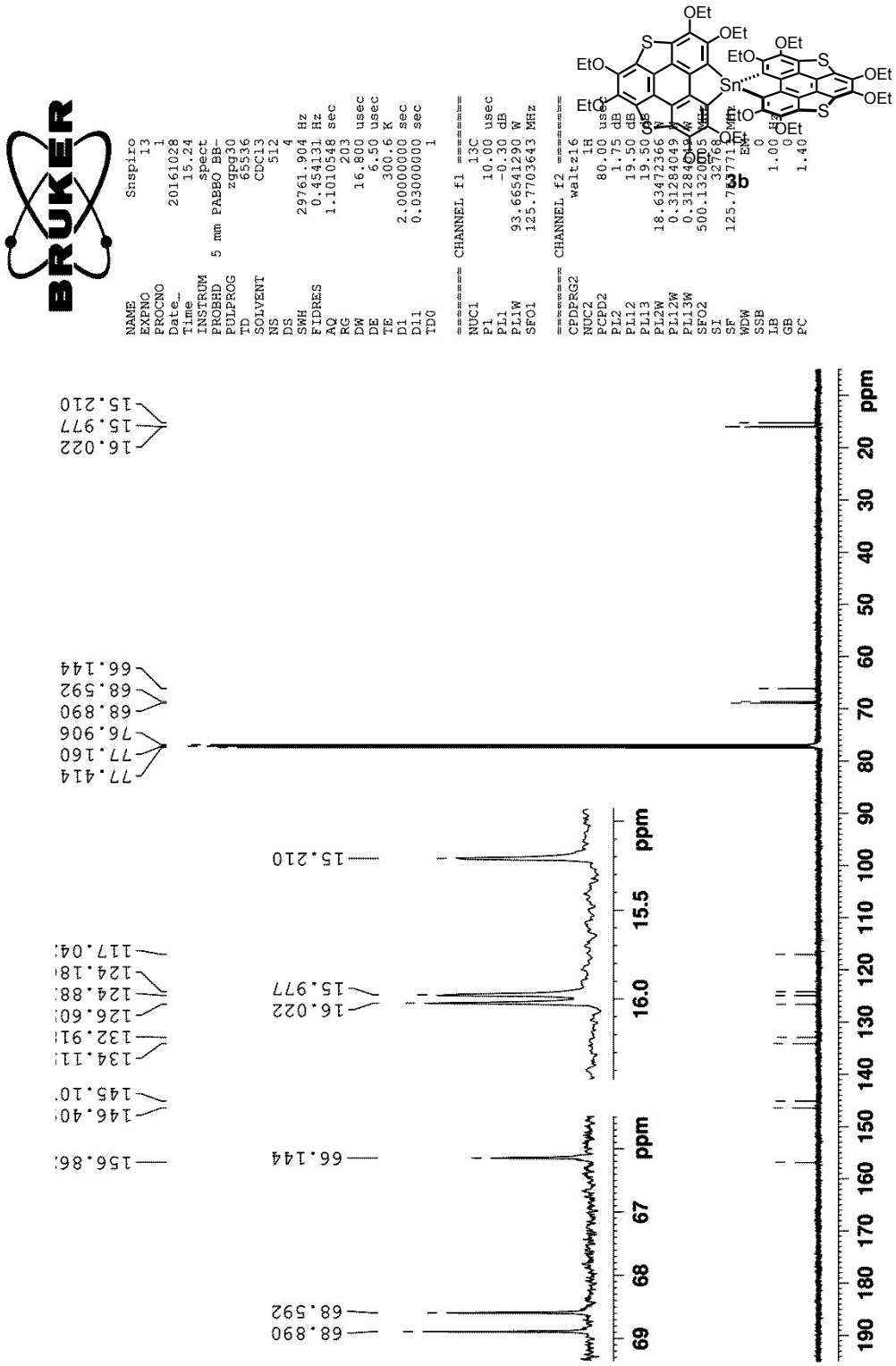
^{119}Sn NMR spectrum of 3a in $CDCl_3$



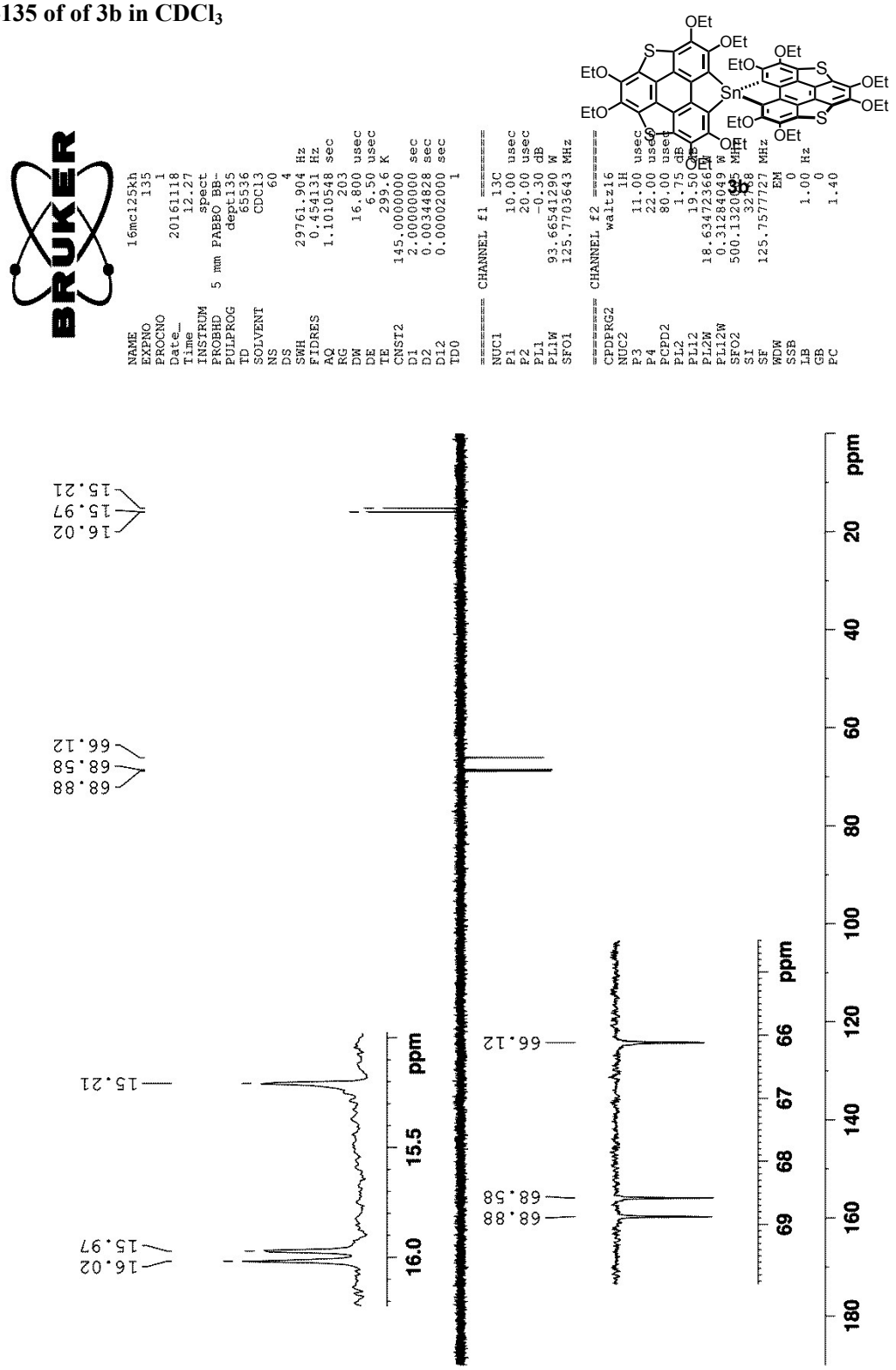
^{1}H NMR spectrum of 3b in $CDCl_3$



^{13}C NMR spectrum of 3b in $CDCl_3$



DEPT-135 of of 3b in $CDCl_3$



^{119}Sn NMR spectrum of 3b in $CDCl_3$