Electronic Supplementary Material (ESI) for ChemComm.

Supplementary information

Glucose selective bis-boronic acid *click-fluor*

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1. General information

Commercially available solvents and reagents were purchased and used without further purification. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker AVIII300 NMR spectrometer, ^{11}B NMR spectra at 128 MHz on a Bruker AVIII400 NMR spectrometer. ^{13}C NMR spectra at 101 MHz on a Bruker AVIII400 NMR spectrometer. Data was processed with Topspin 3.5pl6. Chemical shifts (δ) are reported in ppm relative to TMS (δ 0.00) for the ^{1}H NMR spectra, to chloroform (δ 77.0) for the ^{13}C NMR spectra and to $BF_3 \cdot Et_2O$ (δ 0.00) for the ^{11}B NMR spectra measurements, coupling constant *J* are expressed in Hertz, pendant technique was used for ^{13}C NMR assignment. Mass spectra were recorded with electrospray MS Waters LCT Time of Flight Mass Spectrometer and with EI (GC/MS) Waters GCT Premier Time of Flight Mass Spectrometer. Infrared Spectra were recorded on a PerkinElmer 100FT-IR spectrometer at room temperature.

2. Fluorescence study

Fluorescence spectra were recorded on both Shimadzu RF-5301PC and Gilden Photonic FluorSENS fluorimeters. All the measurements were carried out in pH 8.21 methanolic buffer. The buffer was prepared in a 1 L volumetric flask according to a literature procedure and consisted of: 52.1 *wt*% HPLC grade methanol, in deionised water with KCl (0.7456 g, 0.01000 mol/L), KH_2PO_4 (0.3745 g, 0.002752 mol/L) and Na_2HPO_4 (0.3914g, 0.002757 mol/L).[1]

Quartz cuvette with 10 mm path lengths, four faces polished was used for fluorescence test. All pH measurements taken during fluorescence experiments were on pH meter which was calibrated using standard buffer solutions (pH 4 and pH 7). All solvents used in fluorescence measurements were HPLC or fluorescent grade. All saccharides used in fluorescent measurements were certified as ≥99% pure.

A 0.15 M stock solution of fructose (and glucose) was prepared in deionised water and stored at room temperature overnight before use. A 2×10^{-4} M stock solution of the synthesised compound **14** was prepared in methanol and kept in dark place before fluorescence test. 20 μL stock solution of **14** was added in 3 mL of methanolic buffer to give a concentration of 1.67 μM. 20 μL saccharide stock solution was added to this solution and allowed to kept at room temperature for 30 minutes before the fluorescence spectrum was recorded.

3. Isothermal titration calorimetry (ITC) study

ITC experiment was carried out with a MicorCal VP-ITC instrument (MicroCal). All the experiments were conducted in pH 8.21 PBS buffer with 20% DMSO. To compensate, the same batch of buffer stock solution was used for preparing all boronic acids and D-fructose (or D-glucose) samples in all experiments. The concentrations of each boronic acid compound and fructose were optimised for each individual experiment. The ITC cell volume was 1.474 mL. Experiments were performed at a constant cell temperature of 25 °C. The reference power was set to 30 $\mu Cal \cdot s^{-1}$. Each titration comprised 49 separate injections of 5 μL of concentrated saccharide solution at time intervals of 180 s. In the case of compound **8b** and **8c** binding with D-glucose, the time interval was extended to allow the signal return to the baseline. Data was analysed using Origin 7E (OriginLab). The first injection point was routinely discarded. Data were fit using "One Sites" model.[2]

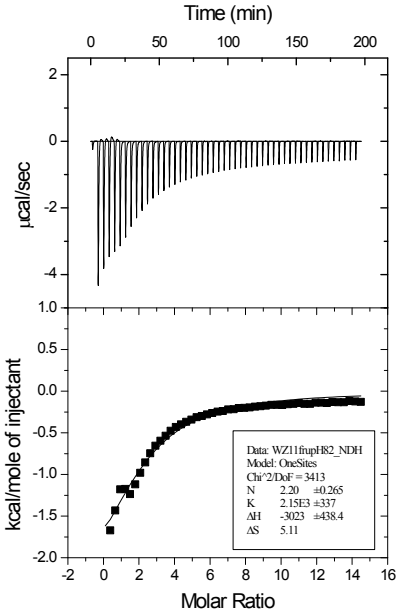


Figure S 1. ITC study of compound **8a** (2.5×10^{-5} M) titrating with D-fructose (0.02 M) in pH 8.21 PBS buffer with 20% DMSO.

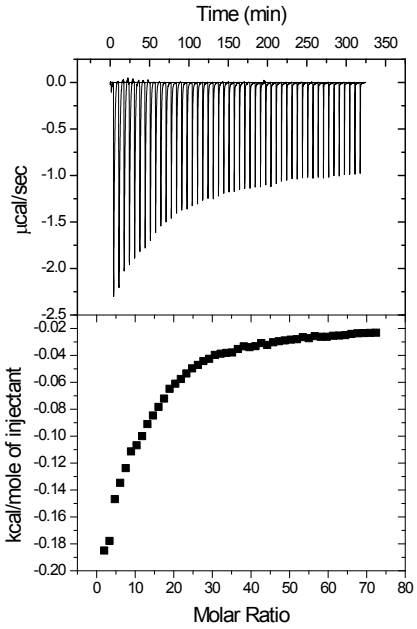


Figure S 2. ITC study of compound **8a** (5×10^{-4} M) titrating with D-glucose (0.2 M) in pH 8.21 PBS buffer with 20% DMSO.

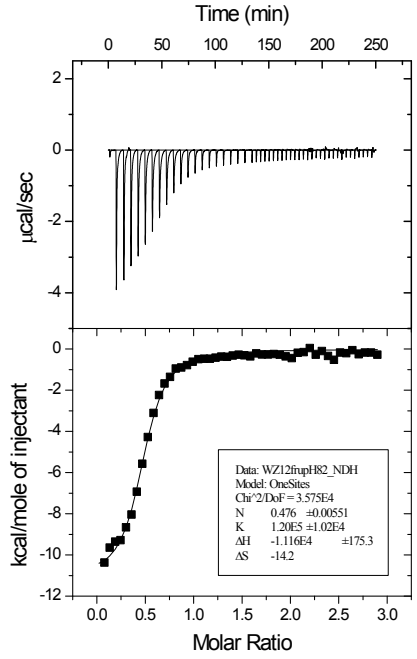


Figure S 3. ITC study of compound **8b** (2.5×10^{-5} M) titrating with D-fructose (0.02 M) in pH 8.21 PBS buffer with 20% DMSO.

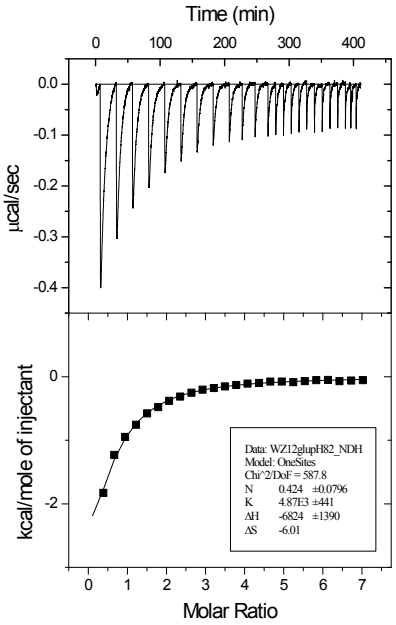


Figure S 4. ITC study of compound **8b** (2.5×10^{-5} M) titrating with D-glucose (0.02 M) in pH 8.21 PBS buffer with 20% DMSO.

4. Synthetic procedures and characterisation data

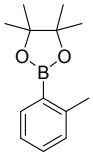
4.1 Synthesis of compound 5

o-Tolylboronic acid (1.36 g, 10.0 mmol) and pinacol (1.54 g, 12 mmol) were mixed in toluene (100 mL). The reaction mixture was heated under reflux for 2 h, water was removed using a Dean-Stark apparatus. The reaction solution was cooled to room temperature and toluene was removed by rotary evaporator. The crude product was dissolved in ethyl acetate (50 mL), and washed with deionised water (5 × 50 mL) and Brine (50 mL), dried over magnesium sulfate and filtered. The solvent was removed *in vacuo* to obtain *o*-tolylboronic acid pinacol ester as a colourless oil.

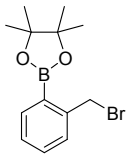
o-Tolylboronic acid pinacol ester (1.74 g, 8.0 mmol), *N*-bromosuccinimide (1.57 g, 8.8 mmol), and benzoyl peroxide (19 mg, 1 mol%) were added in 100 mL of acetonitrile and refluxed at 90 ^{0}C for 4 h. After the reaction was completed, the mixture was allowed to cool at room temperature and the solvent was removed by rotary evaporator. Hexane was added to dissolve the product and the remaining solid was removed after filtration. The filtrate was concentrated by rotary evaporator and dried *in vacuo* to obtain the bromination product as a light brown solid.[1]

Bromo-substituted starting material (1.00 g, 3.4 mmol) and sodium azide (might be explosive, deal with particular care!) (0.30 g, 5.1 mmol) were carefully charged into a round-bottom flask. 5 mL DMSO was added and the reaction mixture was stirred at room temperature overnight (16 h). After that, water was added and the reaction mixture was extracted with diethyl ether (3 × 50 mL). The product was concentrated *in vacuo* to obtain compound **5** as a colourless oil. Sample contained small amount of DMSO. Considering the potential risk of dealing with organic azide, no further purification was carried out (DMSO was used as the reaction solvent in the next step, so it should not cause any problem for the upcoming CuAAC reaction).

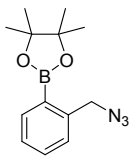
4,4,5,5-Tetramethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane $C_{13}H_{19}BO_2$ colourless oil (99% yield), R_f = 0.90 (PE/EtOAc, 6:1). δ_H (300 MHz, $CDCl_3$) 7.80 (dd, *J* = 7.5, 1.6 Hz, 1H) , 7.35 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.25 - 7.16 (m, 2H), 2.58 (s, 2H), 1.38 (s, 12H). δ_C (101 MHz, $CDCl_3$) 144.8, 135.9, 130.8, 129.8, 124.7, 83.4, 24.9, 22.3. M/z: (ES$^+$) 241.1 [M + Na]$^+$ *ν*/cm^{-1} 2963, 1601, 1477, 1435, 1379, 1343, 1302, 1276, 1217, 1144.



2-(2-(Bromomethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane $C_{13}H_{18}BBrO_2$ light brown solid (99% yield), R_f = 0.81 (PE/EtOAc, 6:1). mp 79 – 80 °C. δ_H (300 MHz, $CDCl_3$) 7.86 (d, *J* = 7.2 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.36 – 7.27 (m, 1H), 4.96 (s, 2H), 1.41 (s, 12H). δ_C (101 MHz, $CDCl_3$) 144.3, 136.4, 131.3, 130.1, 127.6, 83.9, 34.0, 24.9. M/z: (ES$^+$) 319.0 [M + Na]$^+$ *ν*/cm^{-1} 2979, 1598, 1443, 1387, 1333, 1270, 1143.



2-(2-(Azidomethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5) $C_{13}H_{18}BN_3O_2$ colourless oil (99% yield), R_f = 0.78 (PE/EtOAc, 6:1). δ_H (300 MHz, $CDCl_3$) 7.93 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.54 – 7.46 (m, 1H), 7.42 – 7.34 (m, 2H), 4.70 (s, 2H), 1.40 (s, 12H). δ_C (101 MHz, $CDCl_3$) 141.27, 136.19, 131.23, 129.06, 127.29, 83.71, 53.76, 24.64. M/z: (ES$^+$) 282.1 [M + Na]$^+$ *ν*/cm^{-1} 3597, 3039, 2979, 2092, 1601, 1345, 1210, 1143, 961, 848, 752, 656.

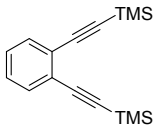


4.2 **Synthesis of compound 6c**

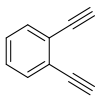
A three-neck round-bottom flask was dried in oven overnight. 1,2-diborombenzene (3.00 g, 12.7 mmol) was dissolved in 20 mL dry TEA, then added into the sealed flask *via* syringe. After bubbling with argon gas for 15 min, $Pd(PPh_3)_2Cl_2$ (421 mg, 0.6 mmol), and CuI (133 mg, 0.7 mmol) was charged into the flask. After bubbling with argon gas for another 15 min, trimethylsilylacetylene (5.4 mL, 38.1 mmol) was injected *via* syringe. The mixture was refluxed under argon protection for 20 h, diluted with DCM, filtered, and concentrated by rotary evaporator. The crude product was purified by chromatography on silica gel using hexane as eluent.[3]

In a round bottom flask, 1,2-bis((trimethylsilyl)ethynyl)benzene (1.35 g, 5 mmol) was dissolved in THF (20 mL). The flask was cooled to 0 °C and a 1 M solution of TBAF in THF (15.00 mL, 15 mmol) was slowly added *via* syringe. The reaction mixture was stirred for 2 h at room temperature, washed with water (3 × 50 mL) and brine (50 mL), dried over $MgSO_4$, filtered and concentrated by rotary evaporator. The crude product was purified by flash chromatography on silica gel ((hexane/EtOAc) 95:5, *v*/*v*).

1,2-Bis((trimethylsilyl)ethynyl)benzene $C_{16}H_{22}Si_2$ brown oil (95% yield), R_f = 0.90 (hexane). δ_H (300 MHz, $CDCl_3$) 7.49 (dd, *J* = 5.8, 3.4 Hz, 2H), 7.25 (dd, *J* = 5.8, 3.4 Hz, 2H), 0.32 (s, 18H). δ_C (101 MHz, $CDCl_3$) 132.3, 128.1, 125.8, 103.3, 98.4, 0.1. M/z: (ES^+) 293.1 $[M + Na]^+$. *v*/cm^{-1} 2960, 2900, 2160, 1474, 1441, 1248, 1228, 1201, 1099, 1038, 861, 835, 755, 698.



1,2-Diethynylbenzene (6c) $C_{10}H_6$ brown oil (90% yield), R_f = 0.82 (hexane). δ_H (300 MHz, $CDCl_3$) 7.55 (dd, *J* = 5.7, 3.4 Hz, 2H), 7.33 (dd, *J* = 5.8, 3.4 Hz, 2H), 3.38 (s, 2H). δ_C (101 MHz, $CDCl_3$) 132.6, 128.5, 125.0, 81.8, 81.2. M/z: (ES^+) 149.0 $[M + Na]^+$. *v*/cm^{-1} 2957, 2102, 1475, 1239, 1223, 1198, 1087, 1042, 867, 745, 702.

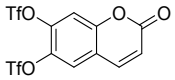


4.3 **Synthesis of compound 12**

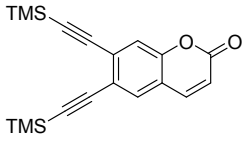
6,7-Dihydroxycoumarin (1.00 g, 5.6 mmol) was initially combined with anhydrous pyridine (20 mL). The reaction mixture was placed on ice and allowed to cool prior to the addition of trifluoromethanesulfonic anhydride (2.10 mL, 12.0 mmol). The mixture was stirred on ice bath for 4 h, after which diethyl ether (100 mL) was added. The first precipitate was separated by filtration and discarded. Following a second precipitation after the addition of aq HCl (1 M, 5 mL), the product was collected by filtration, and dried under vacuum to obtain compound **10**.[4]

For Sonogashira cross-coupling reaction and TMS deprotection, the same procedures were followed as previously described. The final product was purified using chromatography on silica gel ((hexane/EtOAc, 9:1, *v*/*v*).

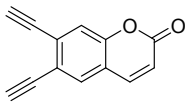
2-Oxo-2*H*-chromene-6,7-diyl bis(trifluoromethanesulfonate) (10) $C_{11}H_4F_6O_8S_2$ white solid (97% yield), R_f = 0.76 (PE/EtOAc, 9:1). mp 87 – 89 °C. δ_H (300 MHz, $CDCl_3$) 7.74 (d, *J* = 9.7 Hz, 1H), 7.65 (s, 1H), 7.49 (s, 1H), 6.62 (d, *J* = 9.7 Hz, 1H). δ_C (101 MHz, $CDCl_3$) 158.1, 153.0, 141.9, 141.0, 136.6, 122.2, 120.1, 119.4, 119.1, 116.9, 112.8. δ_F (282 MHz, $CDCl_3$) -72.76, -72.77, -72.81, -72.82. M/z: (ES^+) 442.9 $[M + H]^+$. High resolution MS calc. for formula $C_{11}H_5F_6O_8S_2^+$: 442.9325; found: 442.9326. *v*/cm^{-1} 3089, 3057, 1721, 1614, 1435, 1393, 1207, 1141, 975, 833, 697.



6,7-Bis((trimethylsilyl)ethynyl)-2*H*-chromen-2-one (11) $C_{19}H_{22}O_2Si_2$ light brown solid (75% yield), R_f = 0.85 (hexane/EtOAc, 6:1). mp 189 – 191 °C. δ_H (300 MHz, $CDCl_3$) 7.38 (d, *J* = 9.6 Hz, 1H), 7.35 (s, 1H), 7.13 (s, 1H), 6.17 (d, *J* = 9.6 Hz, 1H), 0.06 (s, 9H), 0.04 (s, 9H). δ_C (101 MHz, $CDCl_3$) 160.0, 153.1, 142.3, 131.7, 129.1, 122.4, 120.5, 118.8, 117.8, 102.9, 101.8, 101.6, 99.3, 0.1, 0.0. M/z: (EI^+) 338.1 $[M]^+$. High resolution MS calc. for formula $C_{19}H_{22}O_2Si_2^+$: 338.1153; found: 338.1164. *ν*/cm^{-1} 3102, 3097, 2955, 1733, 1713, 1612, 1346, 1266, 1154, 978, 863, 741.



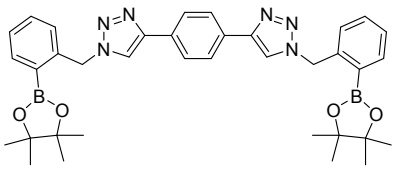
6,7-Diethynyl-2*H*-chromen-2-one (12) $C_{13}H_6O_2$ light brown solid (82% yield), R_f = 0.75 (PE/EtOAc, 8:1). mp 131 – 133 °C. δ_H (300 MHz, $CDCl_3$) 7.67 (d, *J* = 9.6 Hz, 1H), 7.66 (s, 1H), 7.47 (s, 1H), 6.49 (d, *J* = 9.6 Hz, 1H), 3.54 (s, 1H), 3.37 (s, 1H). δ_C (101 MHz, $CDCl_3$) 159.6, 153.2, 141.9, 131.9, 128.2, 121.4, 120.9, 119.1, 118.1, 84.4, 81.7, 80.5, 80.2. M/z: (EI^+) 194.0 $[M]^+$. High resolution MS calc. for formula $C_{13}H_6O_2^+$: 194.0362; found: 194.0364. *ν*/cm^{-1} 2970, 2105, 2093, 1694, 1562, 1368, 1245, 1082, 967, 855, 776.



4.4 CuAAC reaction

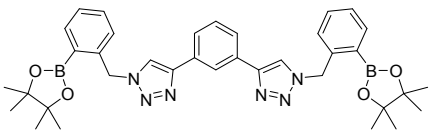
Azide substrate (**5**) (1.30 g, 5.0 mmol) and alkyne substrate (**6a-c**, **12**) (2.0 mmol) were dissolved in dimethyl sulfoxide (5 mL). Copper (I) iodide (38 mg, 0.2 mmol) and TBTA (159 mg, 0.3 mmol) were added. The reaction mixture was stirred at room temperature overnight (16 h). During work-up, deionised water (50 mL) was added into the reaction flask. Ethyl acetate was used to extract the crude product (3 × 50 mL). After washing with Brine and removing water using magnesium sulfate, the product was concentrated by rotary evaporator. Flash chromatography was employed to purify the crude product (hexane/EtOAc as the eluent). The appropriate fractions were combined together, and the solvents were removed under reduced pressure to give the corresponding triazole compounds.

1,4-Bis(1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1*H*-1,2,3-triazol-4-yl)benzene



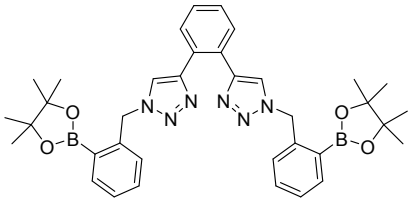
(7a) $C_{36}H_{42}B_2N_6O_4$ white solid (68% yield), R_f = 0.63 (hexane/EtOAc, 4:1). mp 156 – 159 °C. δ_H (300 MHz, $CDCl_3$) 7.94 (dd, *J* = 7.4, 1.4 Hz, 2H), 7.83 (s, 4H), 7.79 (s, 2H), 7.47 (td, *J* = 7.4, 1.4 Hz, 2H), 7.38 (td, *J* = 7.4, 1.4 Hz, 2H), 7.31 (m, 2H), 7.28 (s, 2H), 5.92 (s, 4H), 1.38 (s, 24H). δ_C (101 MHz, $CDCl_3$) 147.2, 140.8, 136.7, 131.9, 130.4, 129.3, 127.9, 125.9, 119.9, 84.2, 53.4, 24.9. δ_B (128 MHz, $CDCl_3$) 31.3. M/z: (ES^+) 645.4 $[M + H]^+$. High resolution MS calc. for formula $C_{36}H_{43}B_2N_6O_4^+$: 645.3536; found: 645.3538. *ν*/cm^{-1} 2923, 1592, 1541, 1483, 1452, 1398, 1272, 1265, 1139, 953, 871, 643.

1,3-Bis(1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1*H*-1,2,3-triazol-4-yl)benzene



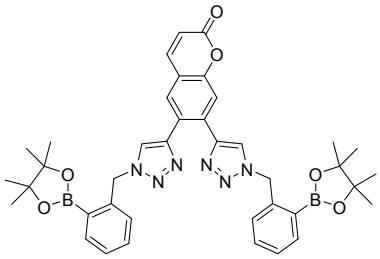
(7b) $C_{36}H_{42}B_2N_6O_4$ white solid (52% yield), R_f = 0.52 (hexane/EtOAc, 3:1). mp 170 – 171 °C. δ_H (300 MHz, $CDCl_3$) 8.08 (s, 1H), 7.85 (dd, *J* = 7.3, 1.3 Hz, 2H), 7.70 (s, 2H), 7.67 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.40 – 7.32 (m, 3H), 7.32 – 7.24 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 5.83 (s, 4H), 1.27 (s, 24H). δ_C (101 MHz, $CDCl_3$) 147.2, 140.8, 136.7, 131.9, 130.4, 129.3, 127.9, 125.9, 119.9, 84.2, 53.4, 24.9. δ_B (128 MHz, $CDCl_3$) 31.2. M/z: (ES^+) 645.4 $[M + H]^+$. High resolution MS calc. for formula $C_{36}H_{43}B_2N_6O_4^+$: 645.3536; found: 645.3540. *ν*/cm^{-1} 2956, 1602, 1543, 1377, 1321, 1284, 1145, 1062, 1033, 954, 802, 774, 652.

1,2-Bis(1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1*H*-1,2,3-triazol-4-yl)benzene



(7c) $C_{36}H_{42}B_2N_6O_4$ light brown solid (33% yield), R_f = 0.39 (hexane/EtOAc, 4:1). mp 183 – 185 °C. δ_H (300 MHz, $CDCl_3$) 7.90 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.73 – 7.70 (m, 2H), 7.46 – 7.38 (m, 4H), 7.34 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.32 (s, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 5.78 (s, 4H), 1.35 (s, 24H). δ_C (101 MHz, $CDCl_3$) 147.2, 140.8, 136.7, 131.9, 130.4, 129.3, 127.9, 125.9, 119.9, 84.2, 53.4, 24.9. δ_B (128 MHz, $CDCl_3$) 31.0. M/z: (ES^+) 645.4 $[M + H]^+$. High resolution MS calc. for formula $C_{36}H_{43}B_2N_6O_4^+$: 645.3536; found: 645.3538. *v*/cm^{-1} 2947, 1586, 1578, 1442, 1358, 1272, 1243, 1131, 977, 669.

6,7-Bis(1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1*H*-1,2,3-triazol-4-yl)-2*H*-chromen-2-one (13)

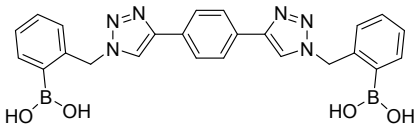


$C_{39}H_{42}B_2N_6O_6$ white solid (36% yield), R_f = 0.35 (PE/EtOAc, 3:1). mp 191 – 192 °C. δ_H (300 MHz, $CDCl_3$) 7.91 (d, *J* = 7.3 Hz, 2H), 7.85 (s, 1H), 7.72 (d, *J* = 9.6 Hz, 1H), 7.67 (s, 1H), 7.41 (td, *J* = 3.7, 1.8 Hz, 3H), 7.38 – 7.30 (m, 3H), 7.15 (dd, *J* = 7.3, 2.9 Hz, 2H), 6.44 (d, *J* = 9.6 Hz, 1H), 5.78 (s, 2H), 5.76 (s, 2H), 1.33 (s, 12H), 1.32 (s, 12H). δ_C (101 MHz, $CDCl_3$) 160.5, 153.5, 144.8, 142.9, 140.9, 140.6, 136.8, 136.8, 133.5, 131.8, 129.6, 129.0, 128.8, 127.9, 127.8, 126.4, 123.3, 123.1, 118.6, 117.9, 117.3, 84.2, 53.4, 53.3, 24.9. δ_B (128 MHz, $CDCl_3$) 31.2. M/z: (ES^+) 713.3 $[M + H]^+$. High resolution MS calc. for formula $C_{39}H_{43}B_2N_6O_6^+$: 713.3425; found: 713.3438. *v*/cm^{-1} 2947, 1743, 1712, 1553, 1467, 1262, 1198, 1124, 963, 769.

4.5 **Pinacol deprotection**

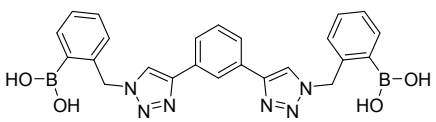
The synthesised triazole substrate (64.4 mg, 0.10 mmol) was dissolved in 10 mL 1,4-dioxane. *o*-Tolylboronic acid (163.0 mg, 1.20 mmol) and aq HCl (5 M, 2 mL) were added. The reaction mixture was heated at 100 °C for 24 h. After cooling to room temperature, the solvent was removed by rotatory evaporator. The crude product was washed with ethyl acetate, acetonitrile and diethyl ether for multiple times. The final purification was performed by flash chromatography (DCM/methanol as the eluent) to afford the free boronic acid products.

(((1,4-Phenylenebis(1*H*-1,2,3-triazole-4,1-diyl))bis(methylene))bis(2,1-phenylene))diboronic acid (8a)



$C_{24}H_{22}B_2N_6O_4$ white solid (81% yield), R_f = 0.60 (DCM/methanol, 95:5). mp 136 – 139 °C. δ_H (300 MHz, MeOD) 8.58 (s, 2H), 7.94 (s, 4H), 7.59 – 7.37 (m, 8H), 5.82 (s, 4H). δ_C (101 MHz, MeOD) 145.1, 137.3, 133.0, 129.5, 129.3, 127.9, 126.9, 126.5, 122.9, 55.1. δ_B (128 MHz, MeOD) 29.3. M/z: (ES^+) 481.2 $[M + H]^+$. High resolution MS calc. for formula $C_{24}H_{23}B_2N_6O_4^+$: 481.1961; found: 481.1968. *v*/cm^{-1} 3307, 3148, 3064, 2924, 1598, 1568, 1496, 1480, 1444, 1378, 1346, 1266, 1246, 1130.

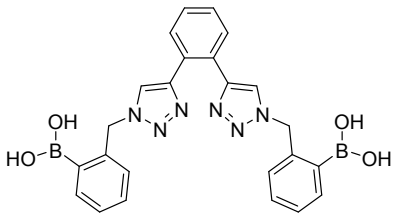
(((1,3-Phenylenebis(1*H*-1,2,3-triazole-4,1-diyl))bis(methylene))bis(2,1-phenylene))diboronic acid (8b)



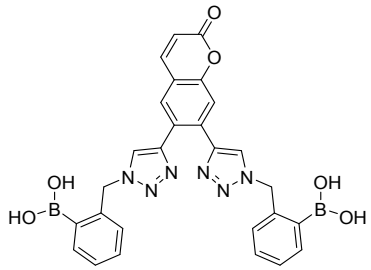
$C_{24}H_{22}B_2N_6O_4$ white solid (88% yield), R_f = 0.72 (DCM/methanol, 9:1). mp 149 – 151 °C. δ_H (300 MHz, MeOD)

8.19 (s, 2H), 8.11 (s, 1H), 7.69 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.41 – 7.24 (m, 9H), 5.60 (s, 4H). δ_C (101 MHz, MeOD) 148.2, 139.4, 133.7, 132.0, 130.9, 130.7, 130.3, 129.0, 126.7, 124.0, 122.9, 55.6. δ_B (128 MHz, MeOD) 29.3. M/z: (ES^+) 481.2 $[M + H]^+$. High resolution MS calc. for formula $C_{24}H_{23}B_2N_6O_4^+$: 481.1961; found: 481.1966. *v*/cm^{-1} 3318, 3137, 1599, 1571, 1446, 1376, 1325, 1277, 1250, 1132, 1079, 1049, 1028, 973, 793, 754, 690.

(((1,2-Phenylenebis(1*H*-1,2,3-triazole-4,1-diyl))bis(methylene))bis(2,1-phenylene))diboronic acid (8c) $C_{24}H_{22}B_2N_6O_4$ white solid (72% yield), R_f = 0.69 (DCM/methanol, 9:1). mp 164 – 165 °C. δ_H (300 MHz, DMSO-*d6*) 8.35 (s, 4H), 7.70 (s, 2H), 7.68 – 7.60 (m, 4H), 7.51 – 7.41 (m, 2H), 7.32 (pd, *J* = 7.4, 1.6 Hz, 4H), 6.91 (dd, *J* = 6.9, 1.8 Hz, 2H), 5.73 (s, 4H). δC (101 MHz, MeOD) 146.1, 138.1, 132.3, 129.7, 129.4, 128.5, 127.4, 123.2, 119.4, 115.0, 53.8. δ_B (128 MHz, MeOD) 29.2. M/z: (ES^+) 503.2 $[M + Na]^+$. High resolution MS calc. for formula $C_{24}H_{22}B_2N_6O_4Na^+$: 503.1781; found: 503.1785. *v*/cm^{-1} 3314, 3139, 2944, 1596, 1577, 1450, 1369, 1267, 1130, 974, 672.

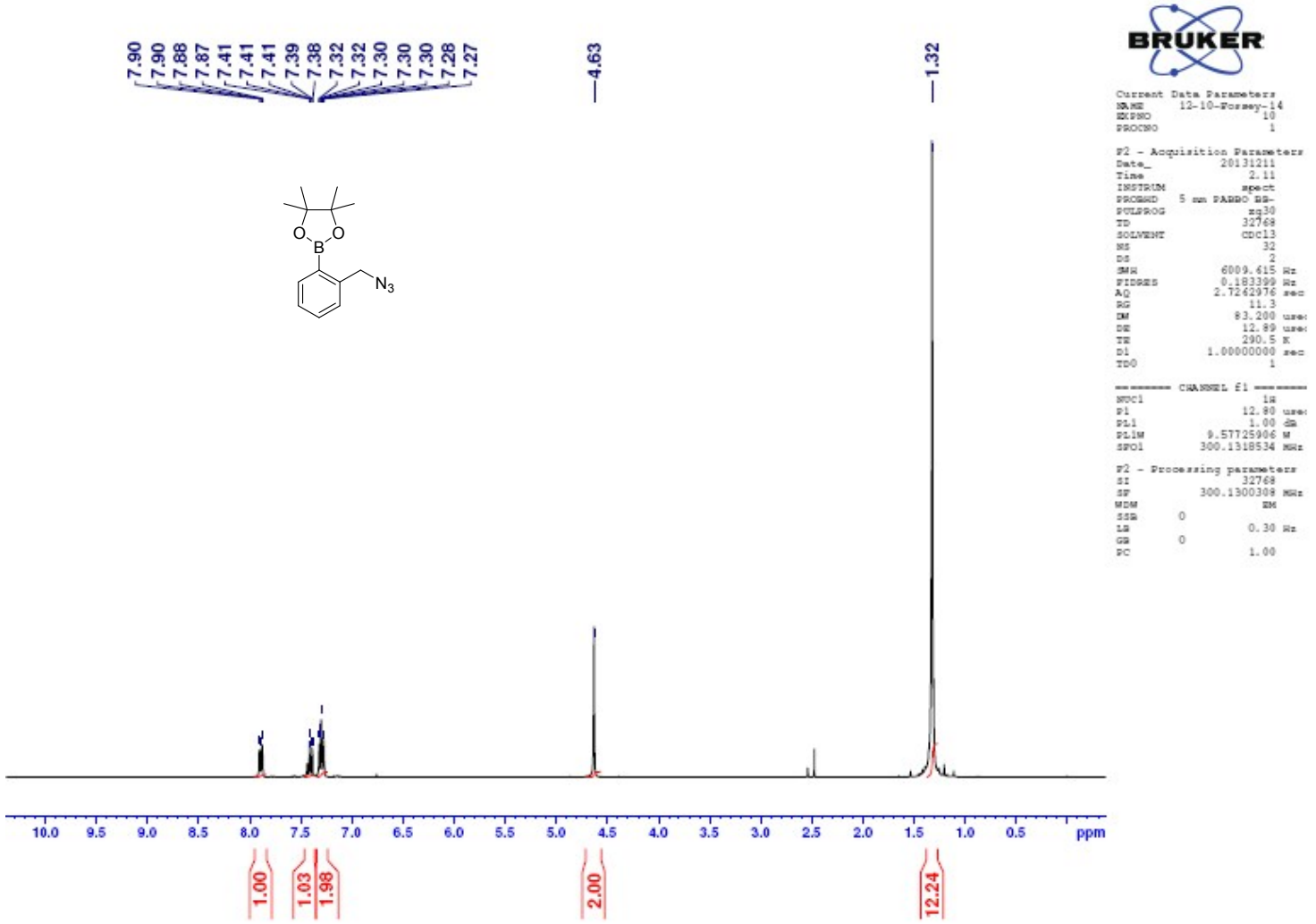


((((2-Oxo-2*H*-chromene-6,7-diyl)bis(1*H*-1,2,3-triazole-4,1-diyl))bis(methylene))bis(2,1-phenylene))diboronic acid (14) $C_{27}H_{22}B_2N_6O_6$ white solid (77% yield), R_f = 0.42 (DCM/methanol, 95:5). mp 172 – 173 °C. δ_H (300 MHz, DMSO-*d6*) 8.35 (s, 2H), 8.33 (s, 2H), 8.13 (d, *J* = 9.6 Hz, 1H), 7.98 (s, 1H), 7.86 (s, 1H), 7.73 (s, 1H), 7.71 (s, 1H), 7.64 (dd, *J* = 6.9, 1.8 Hz, 2H), 7.35 – 7.30 (m, 4H), 6.97 (dd, *J* = 6.9, 1.8 Hz, 2H), 6.57 (d, *J* = 9.6 Hz, 1H), 5.77 (s, 2H), 5.75 (s, 2H). δ_C (101 MHz, DMSO-*d6*) 160.3, 153.6, 144.1, 140.3, 140.0, 134.9, 133.6, 130.6, 130.2, 129.1, 128.2, 128.0, 127.6, 127.5, 124.8, 124.4, 119.0, 117.4, 116.9, 53.4. δ_B (128 MHz, DMSO-*d6*) 29.2. M/z: (ES^+) $[M + Na]^+$ 571.2. High resolution MS calc. for formula $C_{27}H_{22}B_2N_6O_6Na^+$: 571.1679; found: 571.1687. IR (cm^{-1}): 3308, 3148, 2924, 1714, 1624, 1441, 1335, 1055, 904, 831, 758, 714.

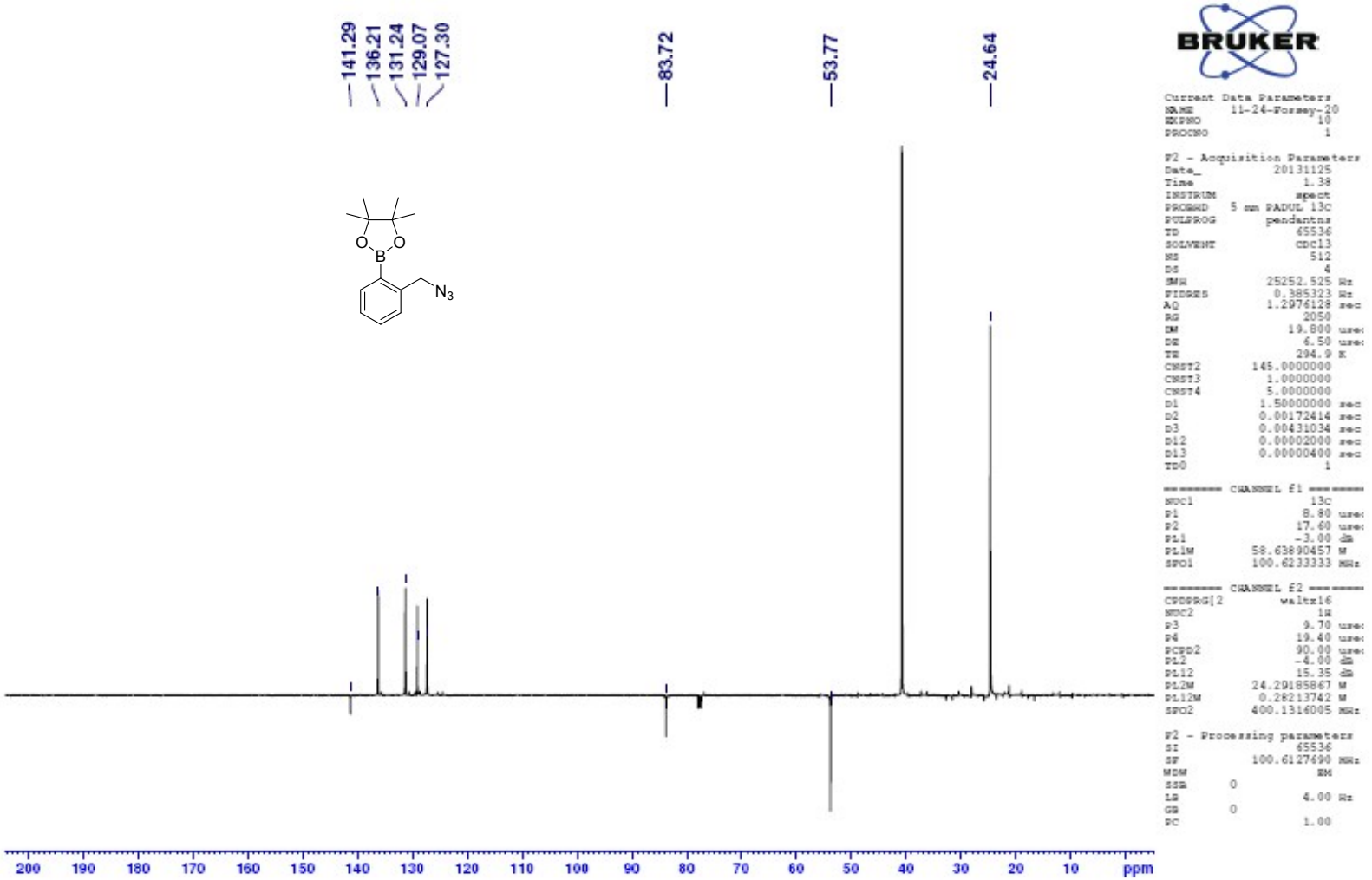


5. NMR spectra of the synthesised compounds

2-(2-(Azidomethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5) ^{1}H NMR spectrum



2-(2-(Azidomethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5) ^{13}C NMR spectrum



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PROCNO              1

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TD              65536
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976128 sec
RG                 2050
DW                19.800 usec
DE                 6.50 usec
TE                294.9 K
CNST2         145.0000000
CNST3           1.0000000
CNST4           5.0000000
D1              1.50000000 sec
D2              0.00172414 sec
D3              0.00431034 sec
D12             0.00002000 sec
D13             0.00000400 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.80 usec
P2                17.60 usec
PL1               -3.00 dB
PL1M          58.63890457 W
SFO1         100.6233333 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                1H
P3                 9.70 usec
P4                19.40 usec
PCPD2             90.00 usec
PL2               -4.00 dB
PL12              15.35 dB
PL2M          24.29185867 W
PL12M          0.28213742 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127690 MHz
WDW                   EM
SSB       0
LB                 4.00 Hz
GB        0
PC                 1.00
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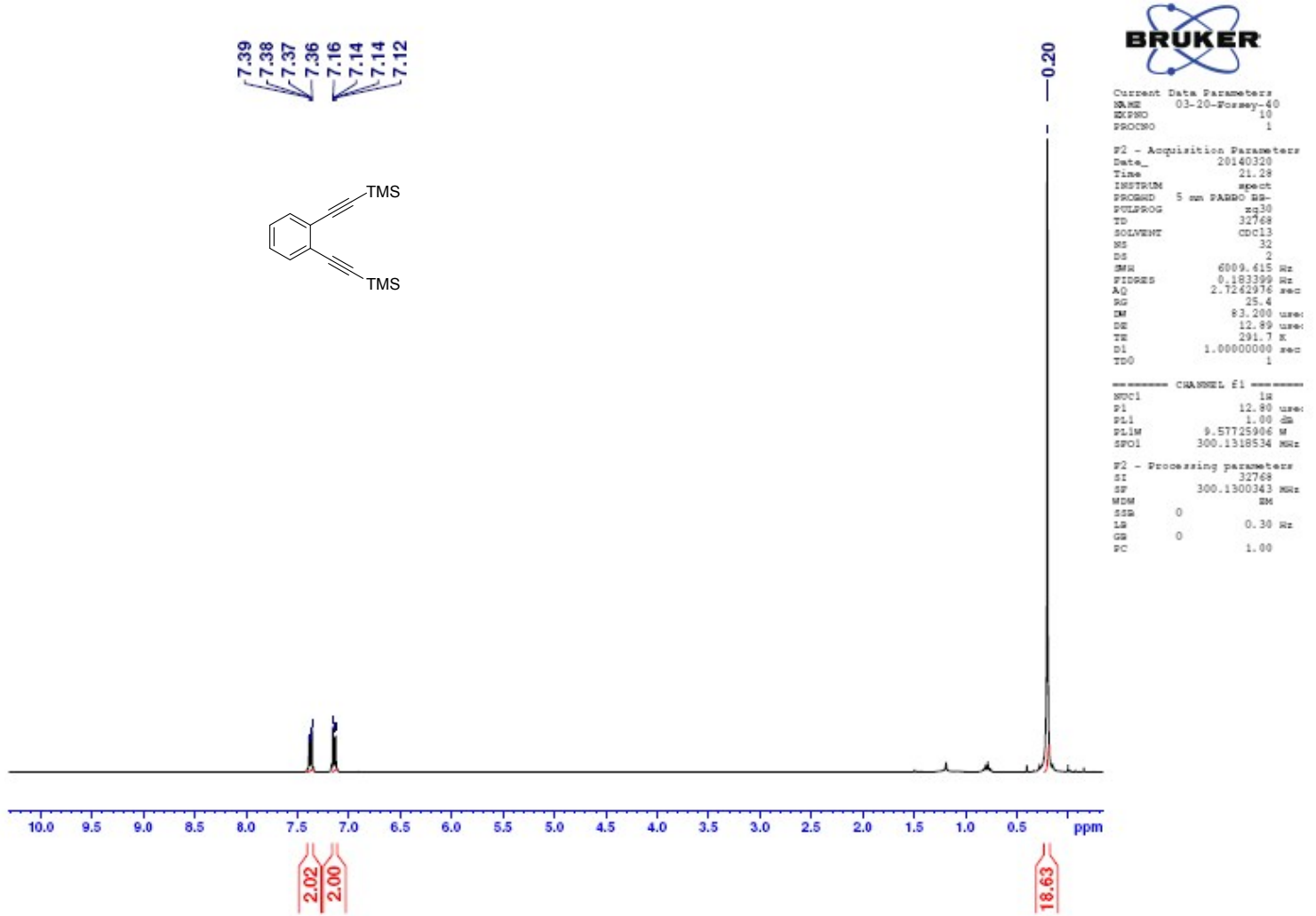
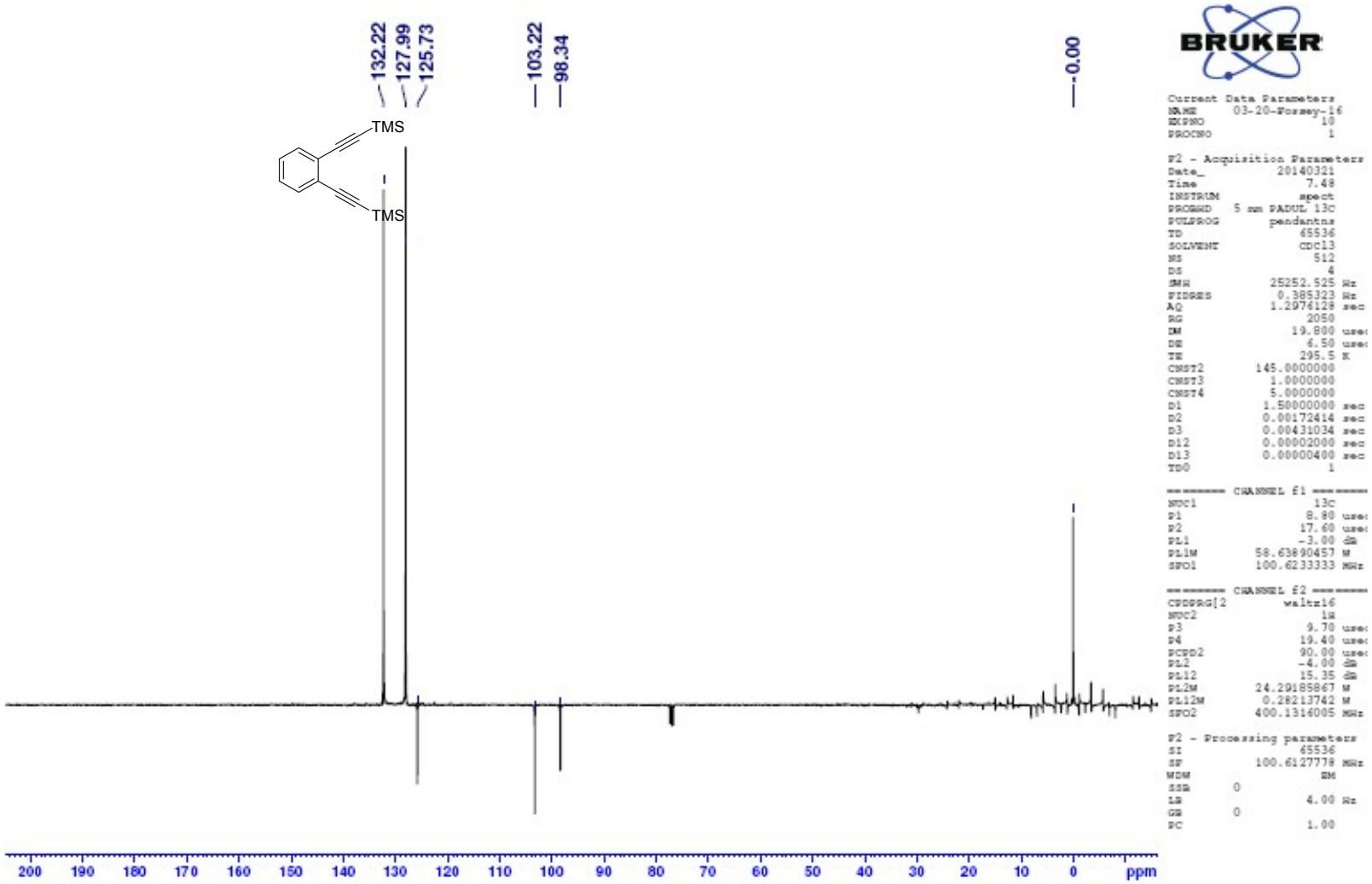
1,2-Bis((trimethylsilyl)ethynyl)benzene ^{1}H NMR spectrum



1,2-Bis((trimethylsilyl)ethynyl)benzene ^{13}C NMR spectrum

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PROCNO                 1

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PULPROG        pendantns
TD                 65536
SOLVENT             CDCl3
NS                    512
DS                      4
SWH           25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976128 sec
RG                   2050
DW                19.800 use
DE                 6.50 use
TE                295.5 K
CNST2        145.0000000
CNST3          1.0000000
CNST4          5.0000000
D1             1.50000000 sec
D2             0.00172414 sec
D3             0.00431034 sec
D12            0.00002000 sec
D13            0.00000400 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.80 use
P2                  17.60 use
PL1                 -3.00 dB
PL1M         58.63890457 W
SFO1         100.6233333 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
P3                   9.70 use
P4                  19.40 use
PCPD2               90.00 use
PL2                 -4.00 dB
PL12                15.35 dB
PL2M         24.29185867 W
PL12M         0.28213742 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127778 MHz
WDW                   EM
SSB      0
LB                 4.00 Hz
GB       0
PC                 1.00
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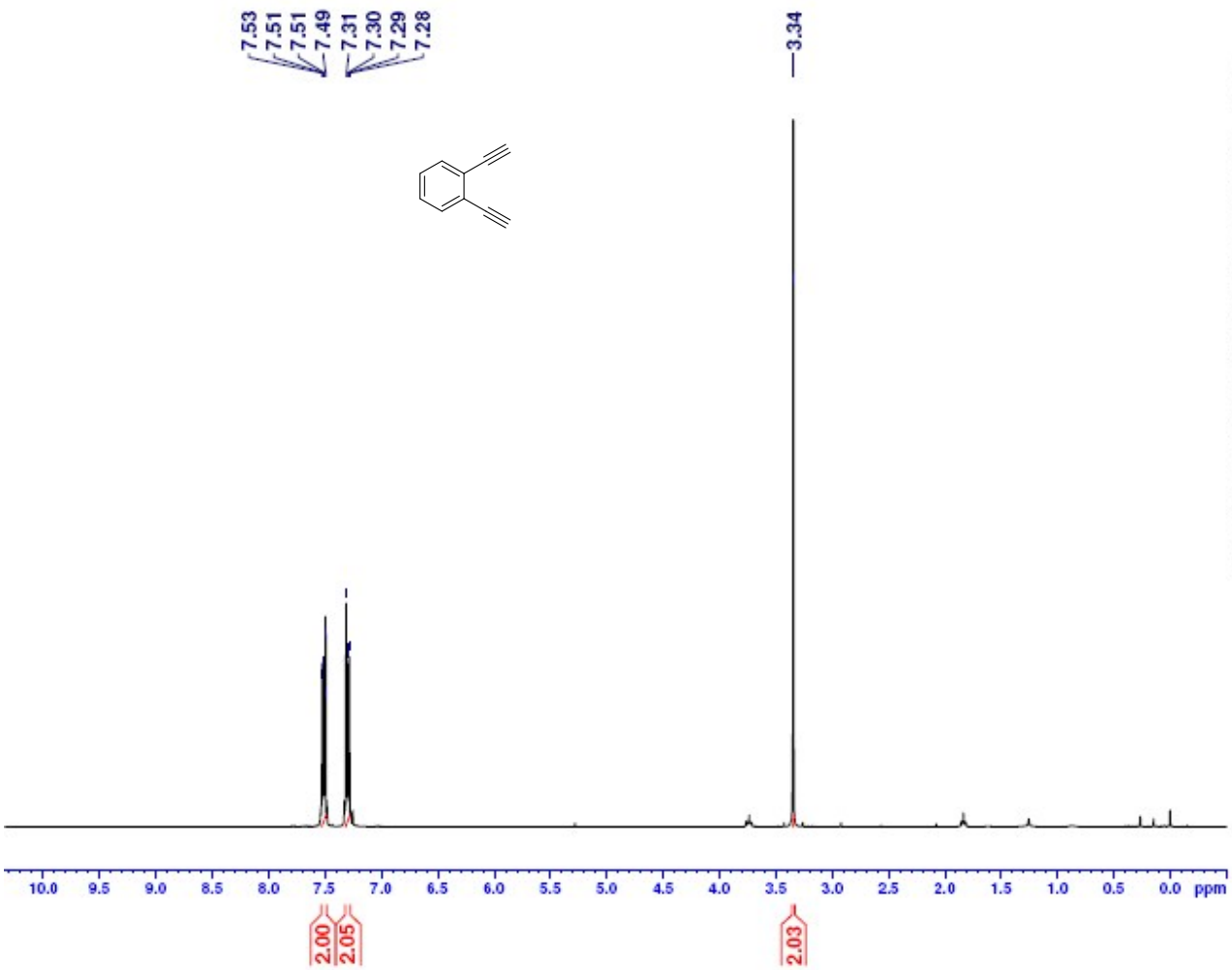
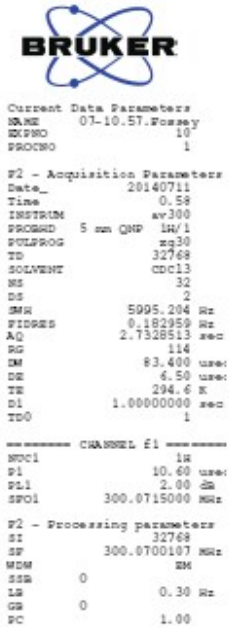
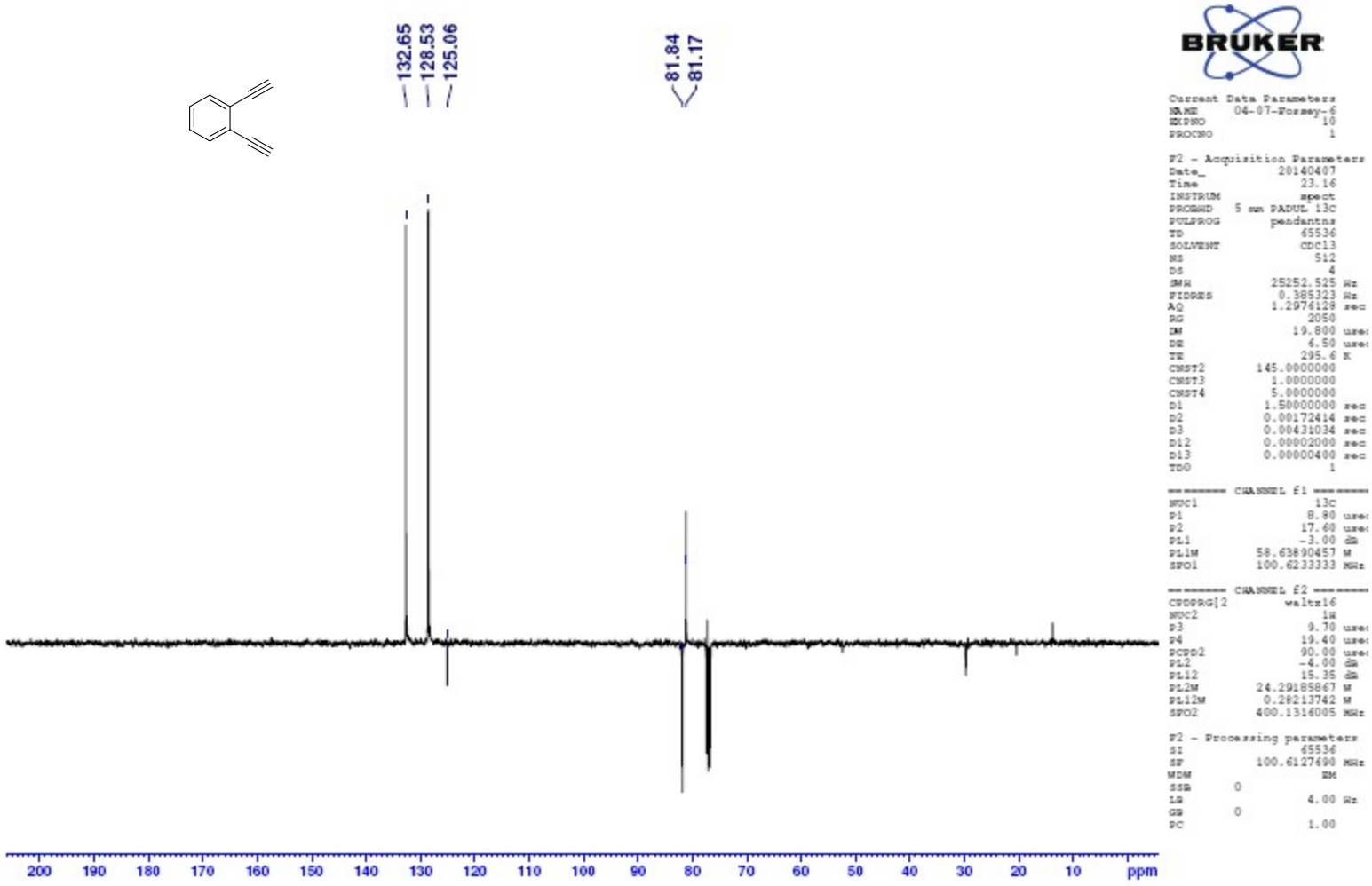
1,2-Diethynylbenzene (6c) ^{1}H NMR spectrum





1,2-Diethynylbenzene (6c) ^{13}C NMR spectrum

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PROCNO              1

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DS                  4
SWH           25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976128 sec
RG                2050
DW               19.800 usec
DE                6.50 usec
TE              295.6 K
CNST2         145.0000000
CNST3           1.0000000
CNST4           5.0000000
D1              1.50000000 sec
D2              0.00172414 sec
D3              0.00431034 sec
D12             0.00002000 sec
D13             0.00000400 sec
TD0                 1

======== CHANNEL f1 ========
NUC1              13C
P1                8.80 usec
P2               17.60 usec
PL1              -3.00 dB
PL1W       58.63890457 W
SFO1       100.6233333 MHz

======== CHANNEL f2 ========
CPDPRG[2       waltz16
NUC2              1H
P3                9.70 usec
P4               19.40 usec
PCPD2            90.00 usec
PL2              -4.00 dB
PL12             15.35 dB
PL2W       24.29185867 W
PL12W       0.28213742 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                65536
SF         100.6127690 MHz
WDW                EM
SSB       0
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GB        0
PC                1.00
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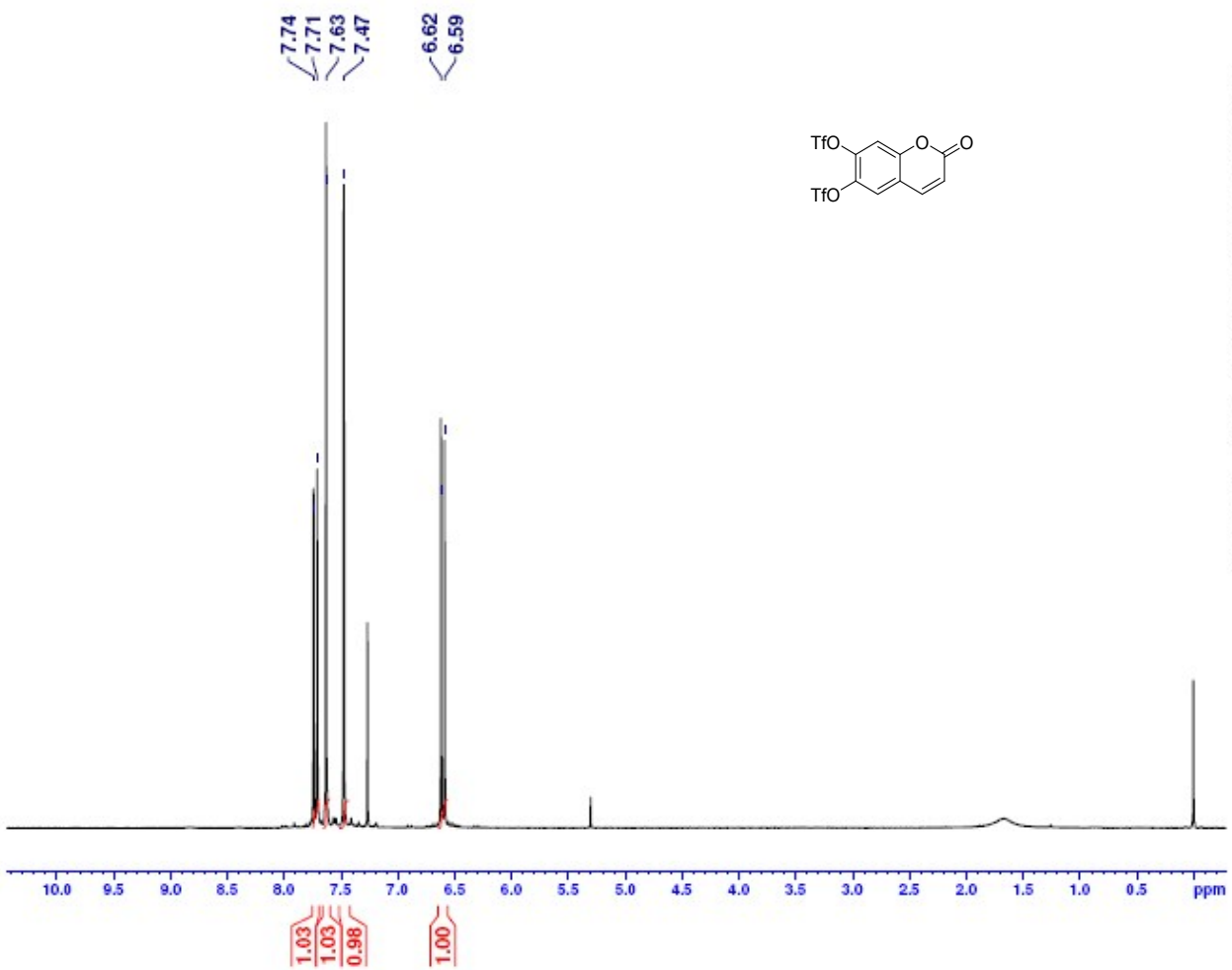
2-Oxo-2*H*-chromene-6,7-diyl bis(trifluoromethanesulfonate) (10) ^{1}H NMR spectrum

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EXPNO                 10
PROCNO                 1

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INSTRUM             spect
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PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ              2.7262976 sec
RG                   575
DW                83.200 usec
DE                12.89 usec
TE                294.2 K
D1              1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         300.1318534 MHz
NUC1                   1H
P1                 12.80 usec
PLW1          9.57730007 W

F2 - Processing parameters
SI                 32768
SF           300.1300055 MHz
WDW                   EM
SSB        0
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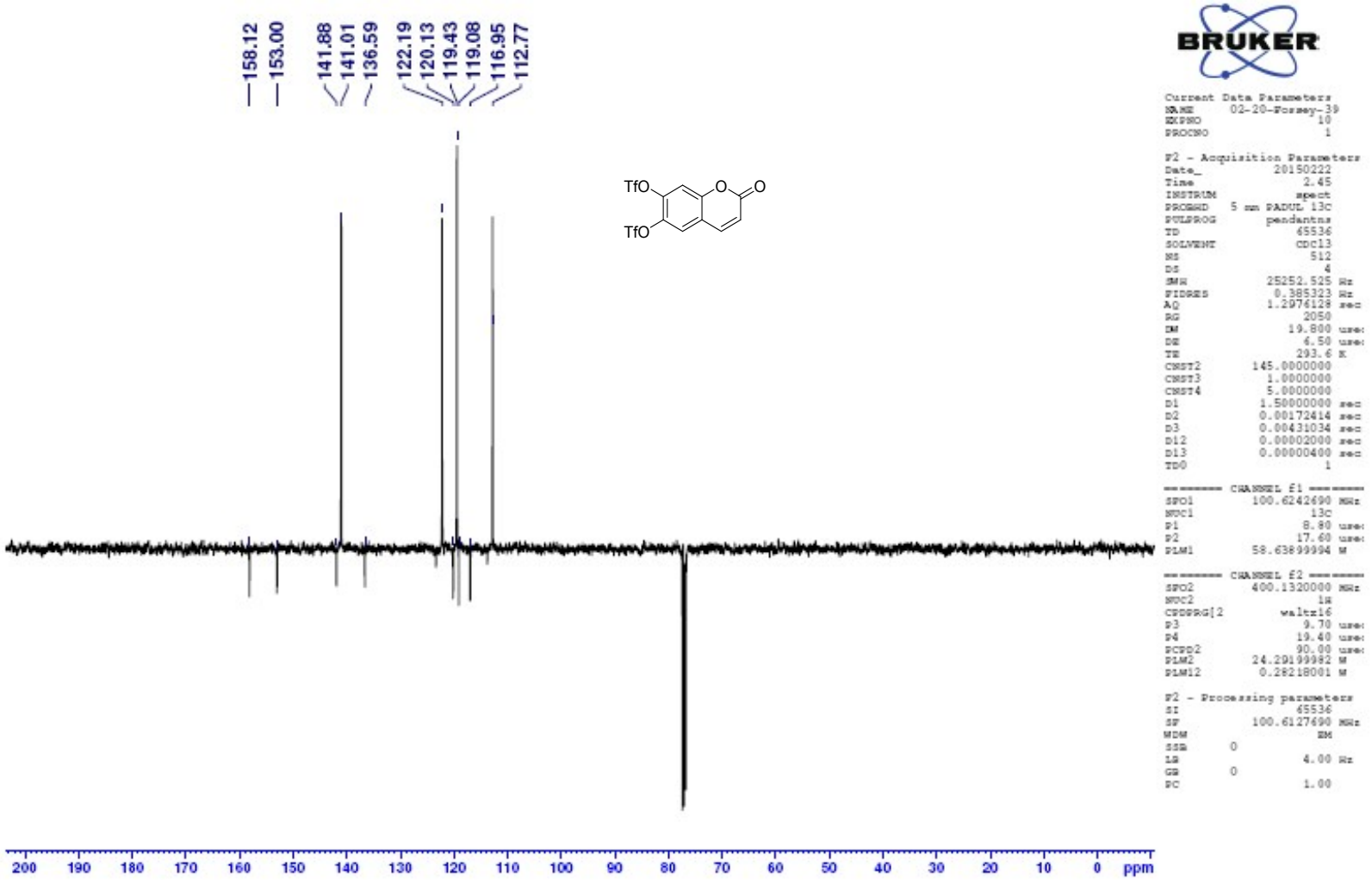
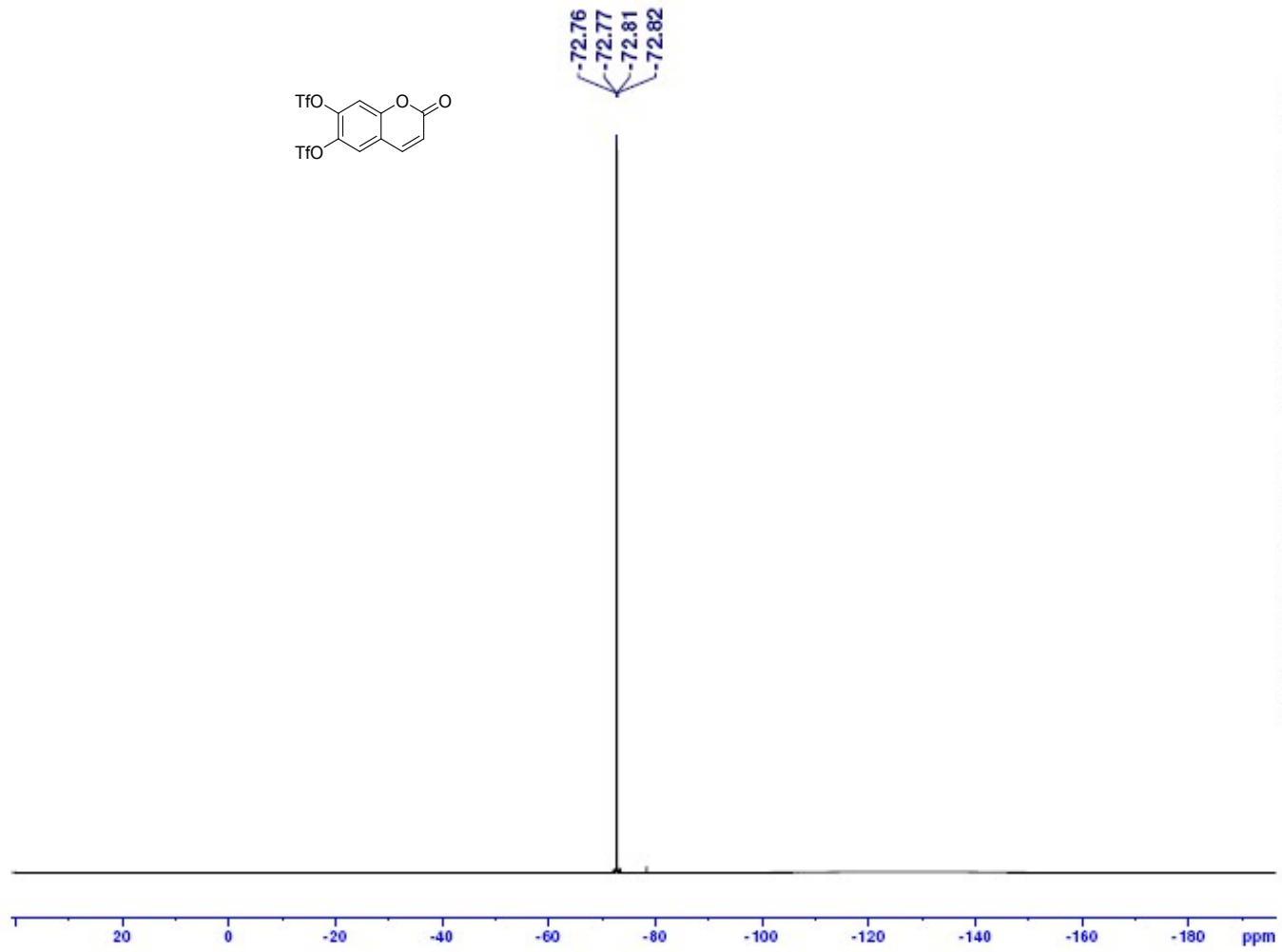
2-Oxo-2*H*-chromene-6,7-diyl bis(trifluoromethanesulfonate) (10) ^{13}C NMR spectrum



2-Oxo-2*H*-chromene-6,7-diyl bis(trifluoromethanesulfonate) (10) ^{19}F NMR spectrum



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Current Data Parameters
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EXPNO                        11
PROCNO                        1

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PULPROG                   zgig
TD                      131072
SOLVENT                   cdcl3
NS                           32
DS                            4
SWH                   66964.289 Hz
FIDRES                0.510897 Hz
AQ                    0.9784710 sec
RG                          406
DW                        7.467 use
DE                         7.27 use
TE                        295.0 K
D1                   3.00000000 sec
D11                  0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                282.3823550 MHz
NUC1                        19F
P1                         8.70 use
PLW1                30.58200073 W

======== CHANNEL f2 ========
SFO2                300.1312005 MHz
NUC2                        1H
CPDPRG[2                waltz16
PCPD2                     90.00 use
PLW2                 9.57730007 W
PLW12                0.19372000 W

F2 - Processing parameters
SI                          131072
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WDW                           EM
SSB         0
LB                         0.50 Hz
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PC                         1.00
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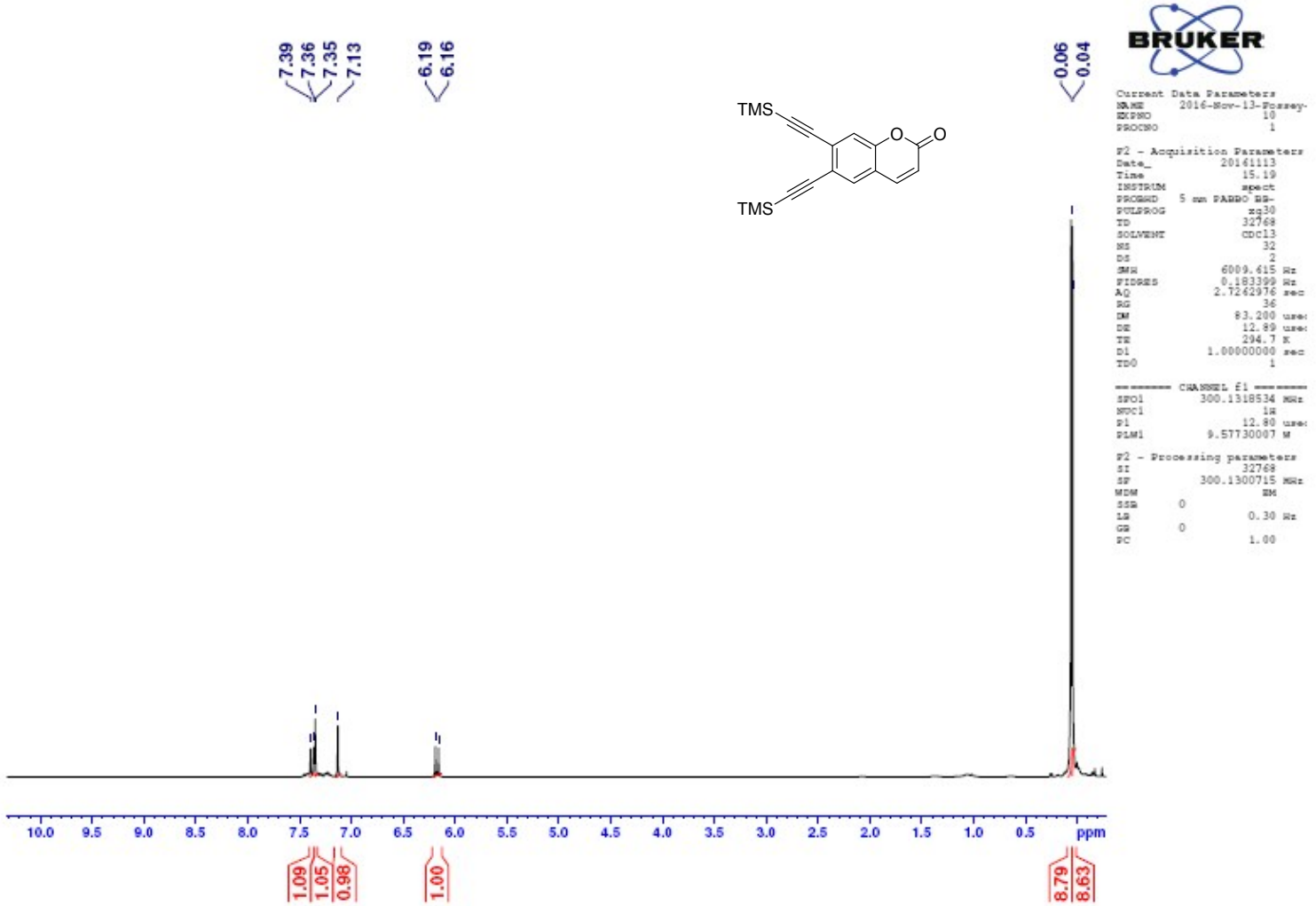
6,7-Bis((trimethylsilyl)ethynyl)-2*H*-chromen-2-one (11) ^{1}H NMR spect



BRUKER

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PROCNO 1

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FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 36
DW 83.200 use
DE 12.89 use
TE 294.7 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
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NUC1 1H
P1 12.80 use
PLW1 9.57730007 W

F2 - Processing parameters
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WDW EM
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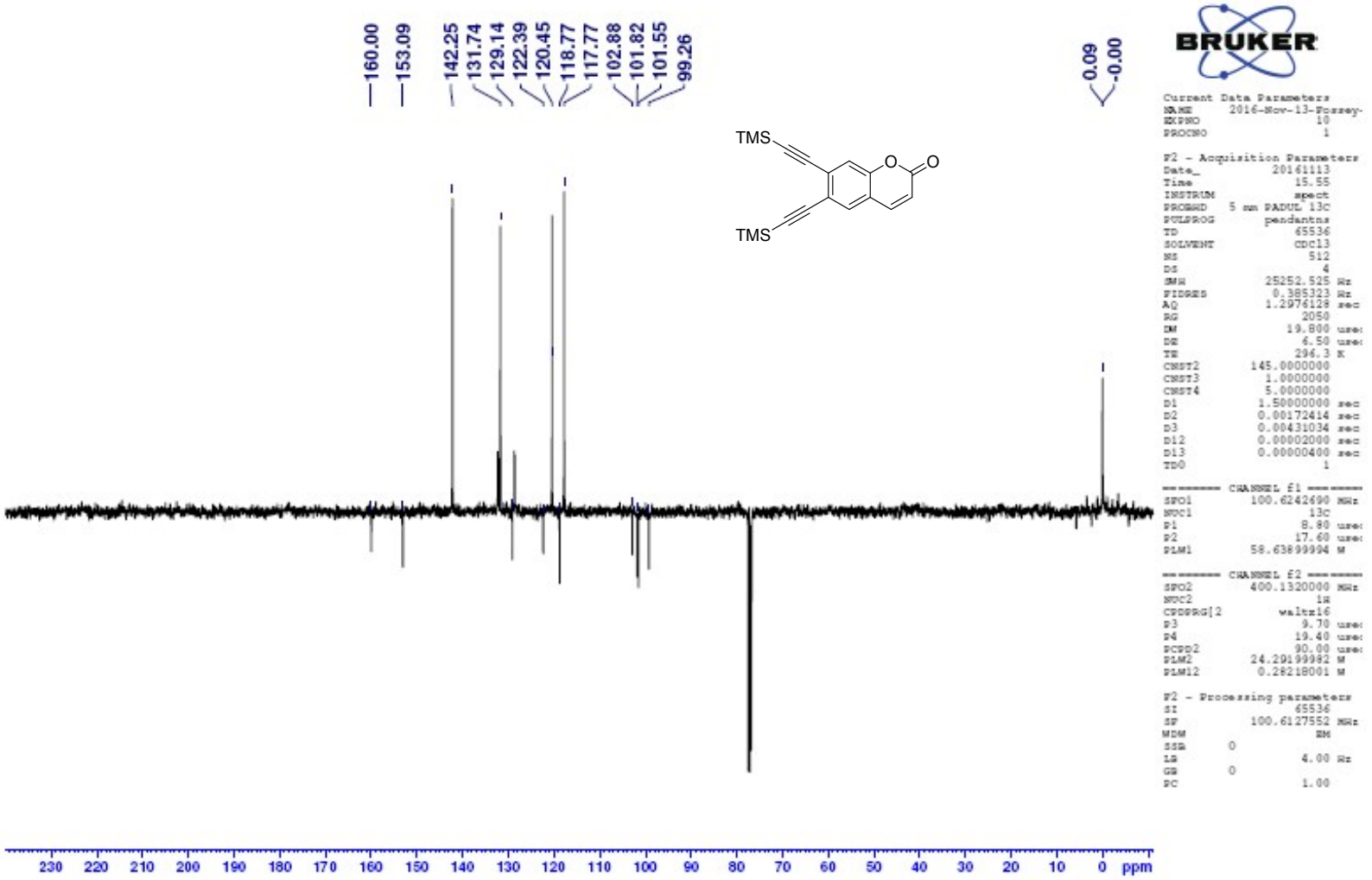
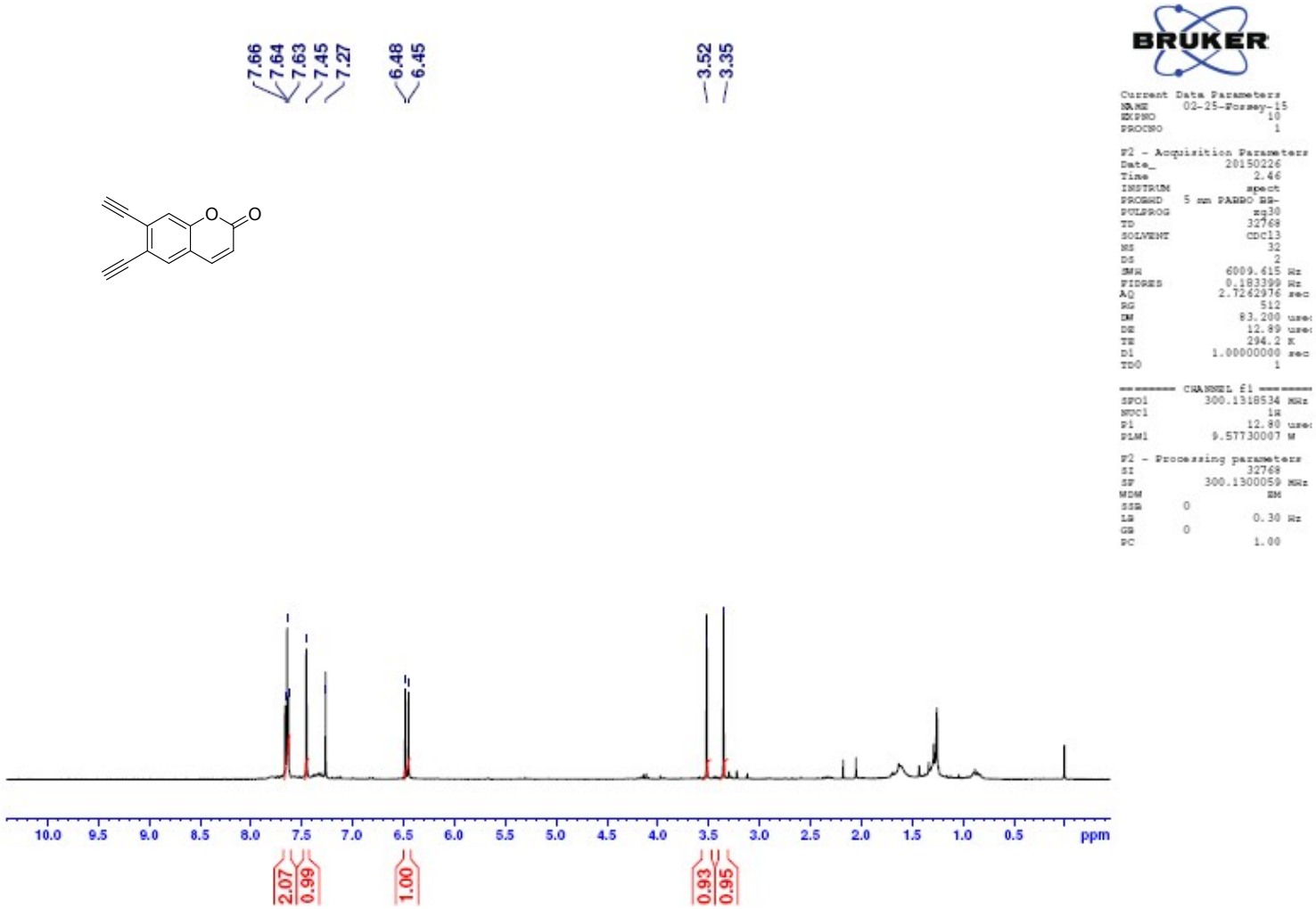
PC 1.00

6,7-Bis((trimethylsilyl)ethynyl)-2*H*-chromen-2-one (11) ^{13}C NMR spectrum



6,7-Diethynyl-2*H*-chromen-2-one (12) ^{1}H NMR spectrum

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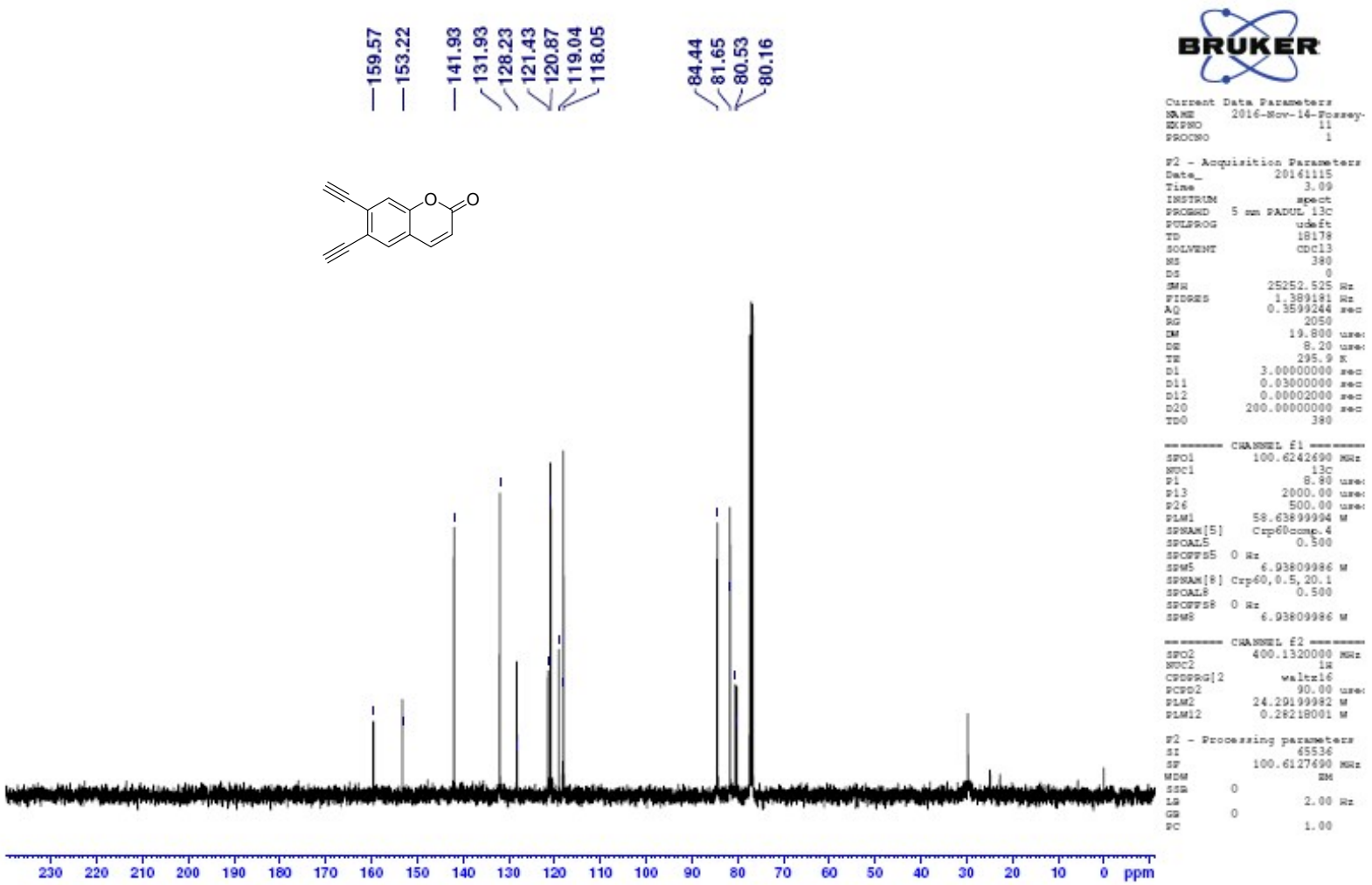
NAME      02-25-Forsey-15
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150226
Time               2.46
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    2
SWH            6009.615 Hz
FIDRES         0.183399 Hz
AQ             2.7262976 sec
RG                  512
DW                83.200 usec
DE                12.89 usec
TE                294.2 K
D1             1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         300.1318534 MHz
NUC1               1H
P1                12.80 usec
PLW1          9.57730007 W

F2 - Processing parameters
SI                32768
SF           300.1300059 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

6,7-Diethynyl-2*H*-chromen-2-one (12) ^{13}C NMR spectrum

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Current Data Parameters
NAME      2016-Nov-14-Fossey-
EXPNO                      11
PROCNO                      1

F2 - Acquisition Parameters
Date_                20161115
Time                     3.09
INSTRUM                  spect
PROBHD   5 mm PADUL 13C
PULPROG                  udeft
TD                       18178
SOLVENT                  CDCl3
NS                         380
DS                           0
SWH                  25252.525 Hz
FIDRES               1.389181 Hz
AQ                   0.3599244 sec
RG                        2050
DW                      19.800 use
DE                       8.20 use
TE                      295.9 K
D1                   3.00000000 sec
D11                  0.03000000 sec
D12                  0.00002000 sec
D20                200.00000000 sec
TD0                        380

======== CHANNEL f1 ========
SFO1               100.6242690 MHz
NUC1                       13C
P1                        8.80 use
P13                    2000.00 use
P26                     500.00 use
PLW1                58.63899994 W
SPNAM[5]            Crp60comp.4
SPOAL5                   0.500
SPOFFS5  0 Hz
SPW5                 6.93809986 W
SPNAM[8]  Crp60,0.5,20.1
SPOAL8                   0.500
SPOFFS8  0 Hz
SPW8                 6.93809986 W

======== CHANNEL f2 ========
SFO2               400.1320000 MHz
NUC2                       1H
CPDPRG[2                waltz16
PCPD2                     90.00 use
PLW2                24.29199982 W
PLW12                0.28218001 W

F2 - Processing parameters
SI                        65536
SF                 100.6127690 MHz
WDW                          EM
SSB          0
LB                        2.00 Hz
GB           0
PC                        1.00
```
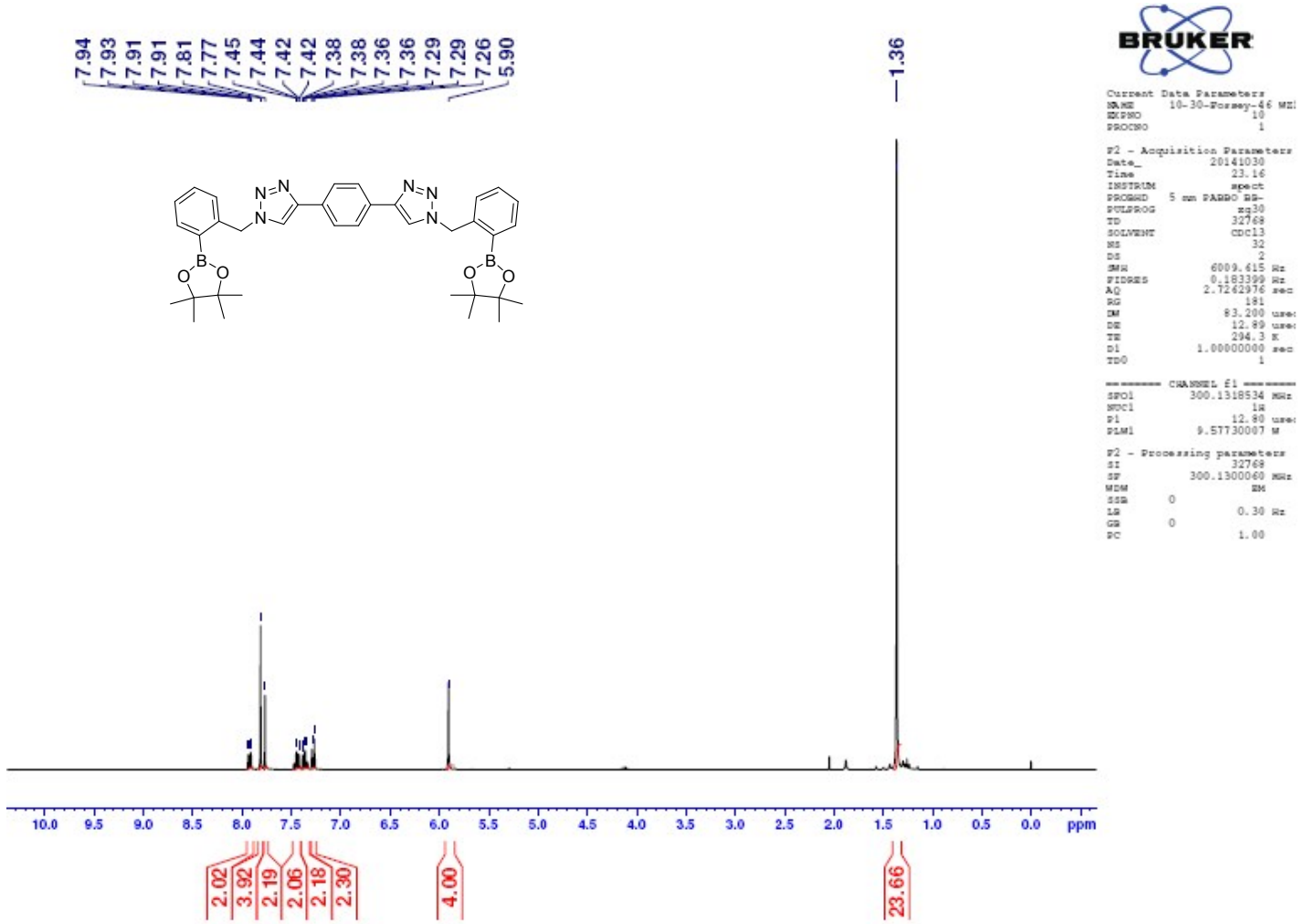
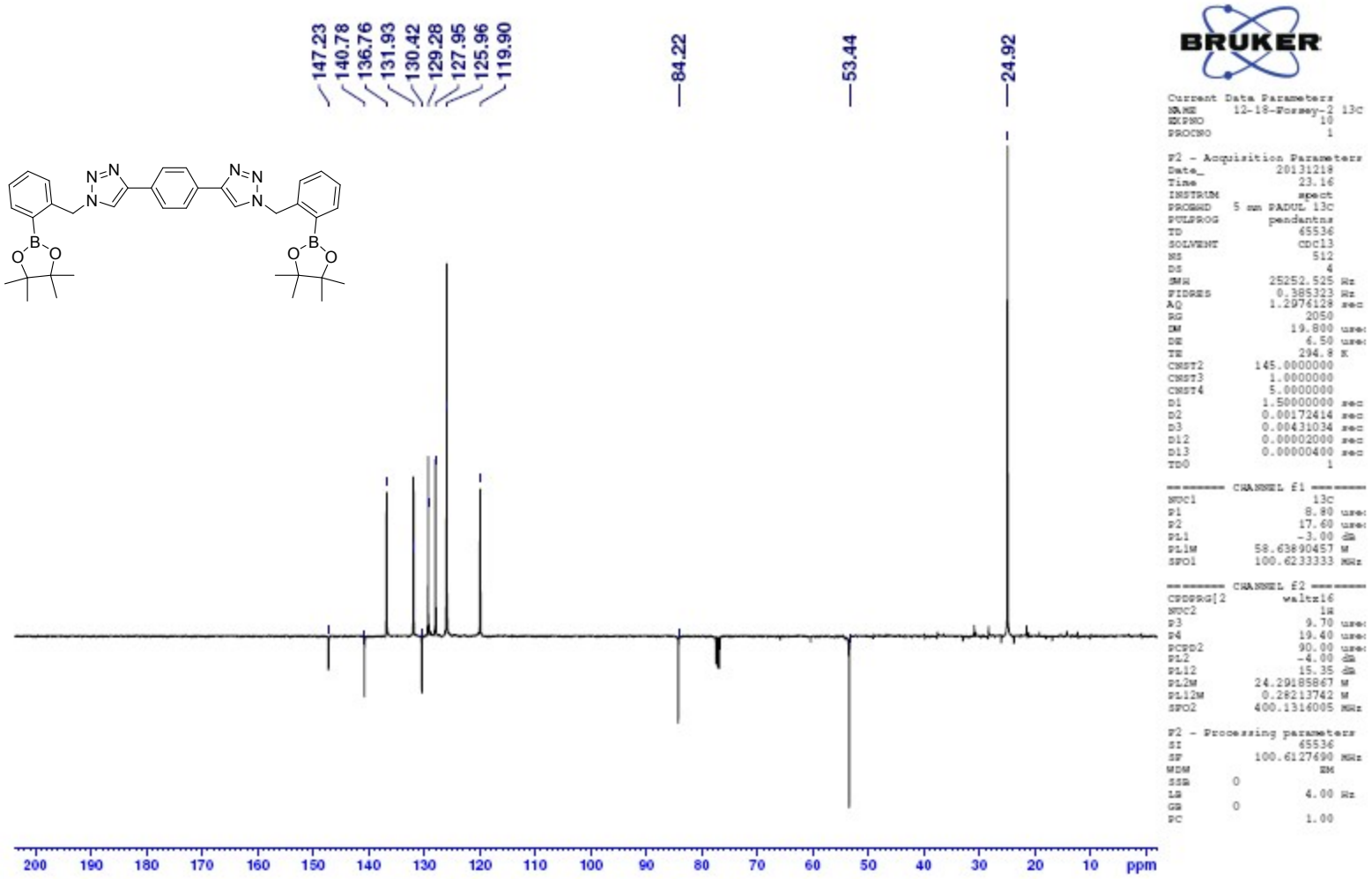
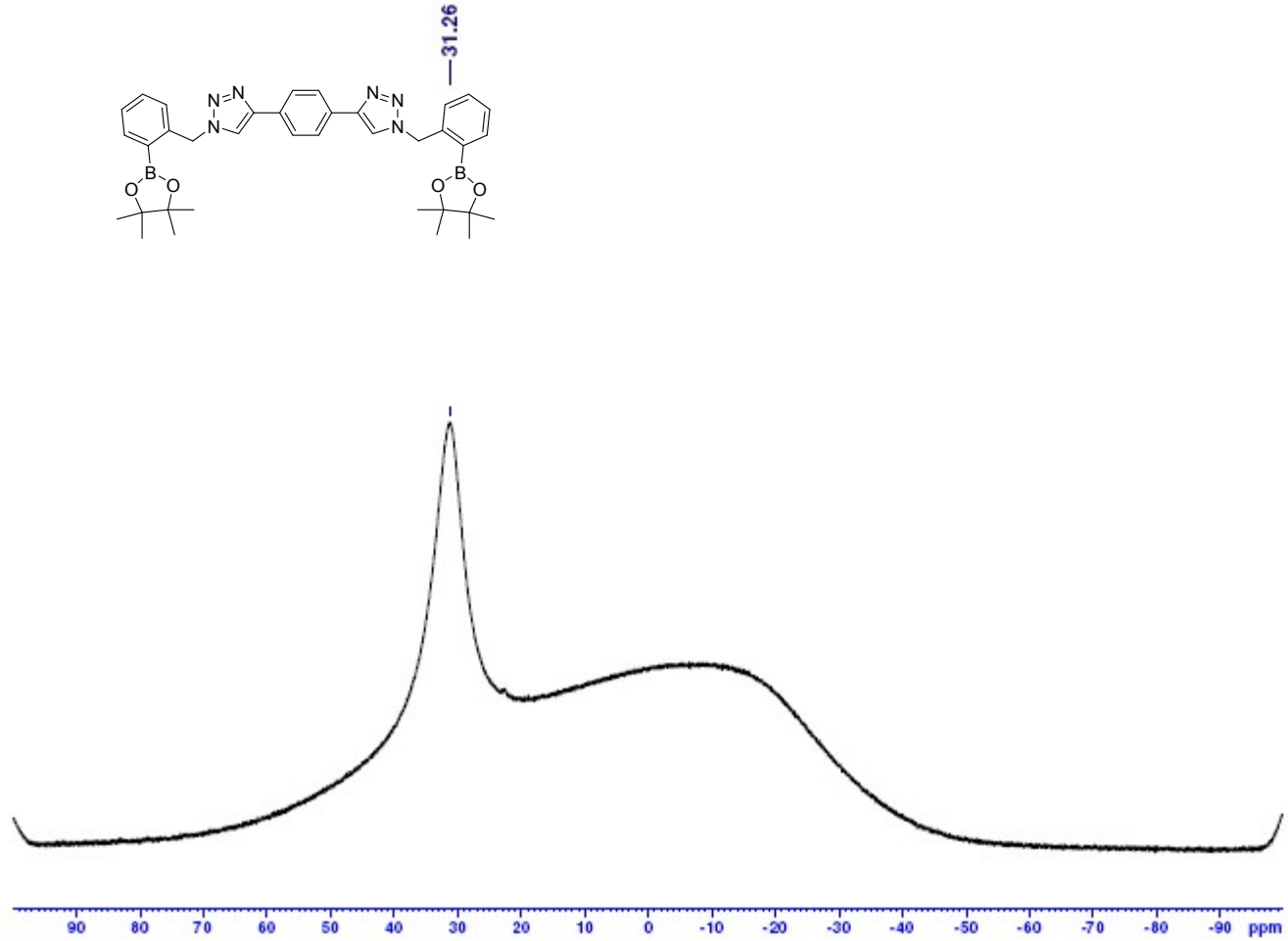

1,4-Bis(1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1*H*-1,2,3-triazol-4-yl)benzene (7a) ^{1}H NMR spectrum



1,4-Bis(1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1*H*-1,2,3-triazol-4-yl)benzene (7a) ^{13}C NMR spectrum

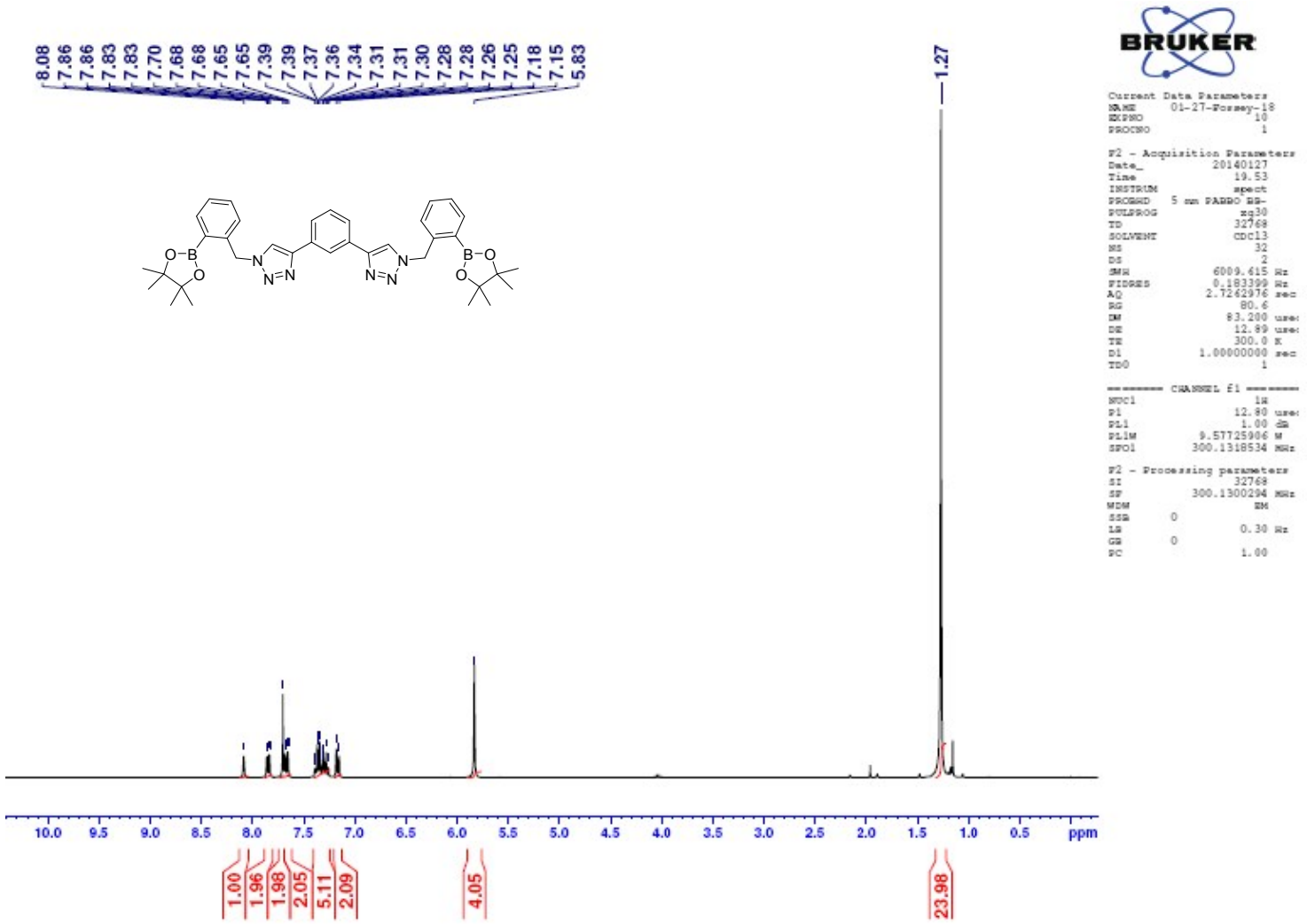


1,4-Bis(1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1*H*-1,2,3-triazol-4-yl)benzene (7a) ^{11}B NMR spectrum

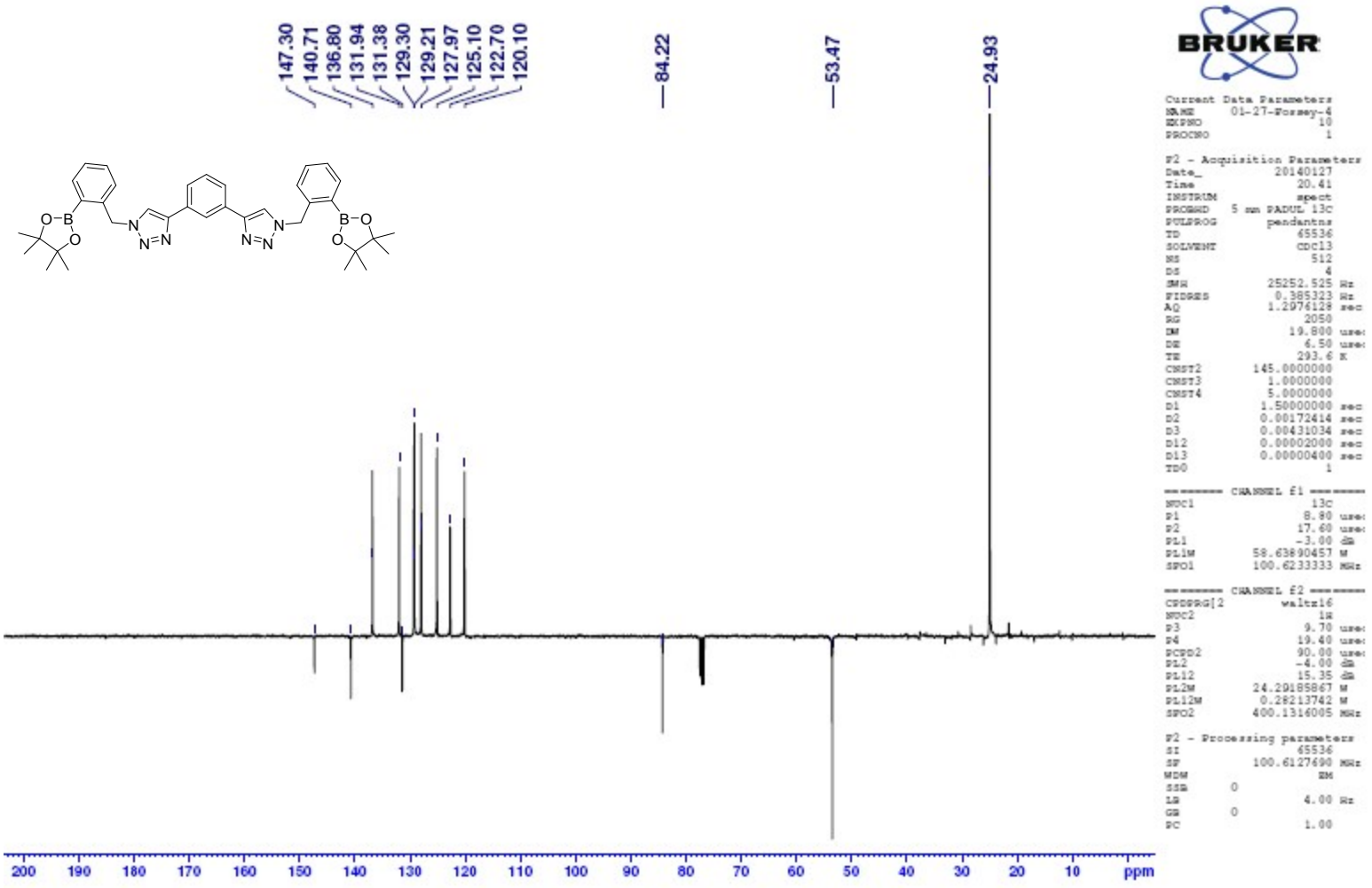



```
Current Data Parameters
NAME                  WE11-01
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20160323
Time                   22.26
INSTRUM                av400
PROBHD     5 mm BBO BB-1H
PULPROG                zgpg
TD                     32768
SOLVENT                CDCl3
NS                      1000
DS                         0
SWH                25641.025 Hz
FIDRES             0.782502 Hz
AQ                 0.6389760 sec
RG                       128
DW                    19.500 usec
DE                     6.50 usec
TE                    296.4 K
D1                 5.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     11B
P1                      7.37 usec
PL1                     8.00 dB
SFO1             128.3583550 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                     2.00 dB
PL12                   23.20 dB
PL13                   25.00 dB
SFO2             400.0720004 MHz

F2 - Processing parameters
SI                       32768
SF               128.3583540 MHz
WDW                         EM
SSB          0
LB                      2.00 Hz
GB           0
PC                      0.50
```

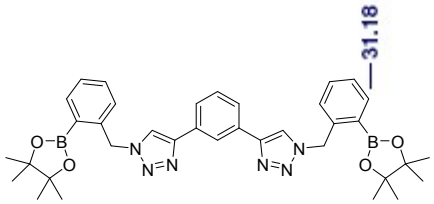
1,3-Bis(1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1*H*-1,2,3-triazol-4-yl)benzene (7b) ^{1}H NMR spectrum

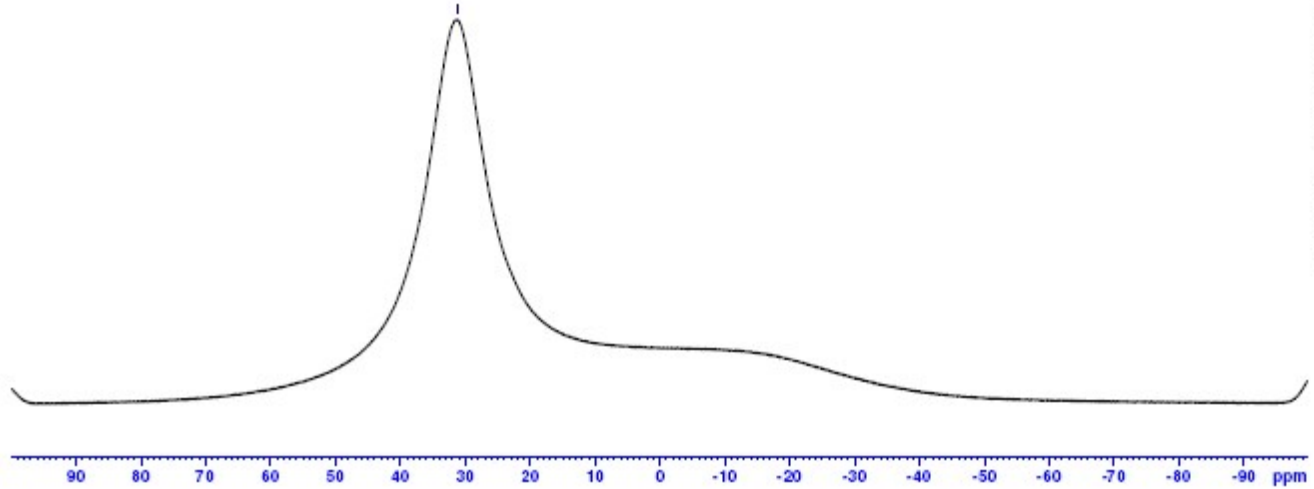


1,3-Bis(1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1*H*-1,2,3-triazol-4-yl)benzene (7b) ^{13}C NMR spectrum



1,3-Bis(1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1*H*-1,2,3-triazol-4-yl)benzene (7b) ^{11}B NMR spectrum





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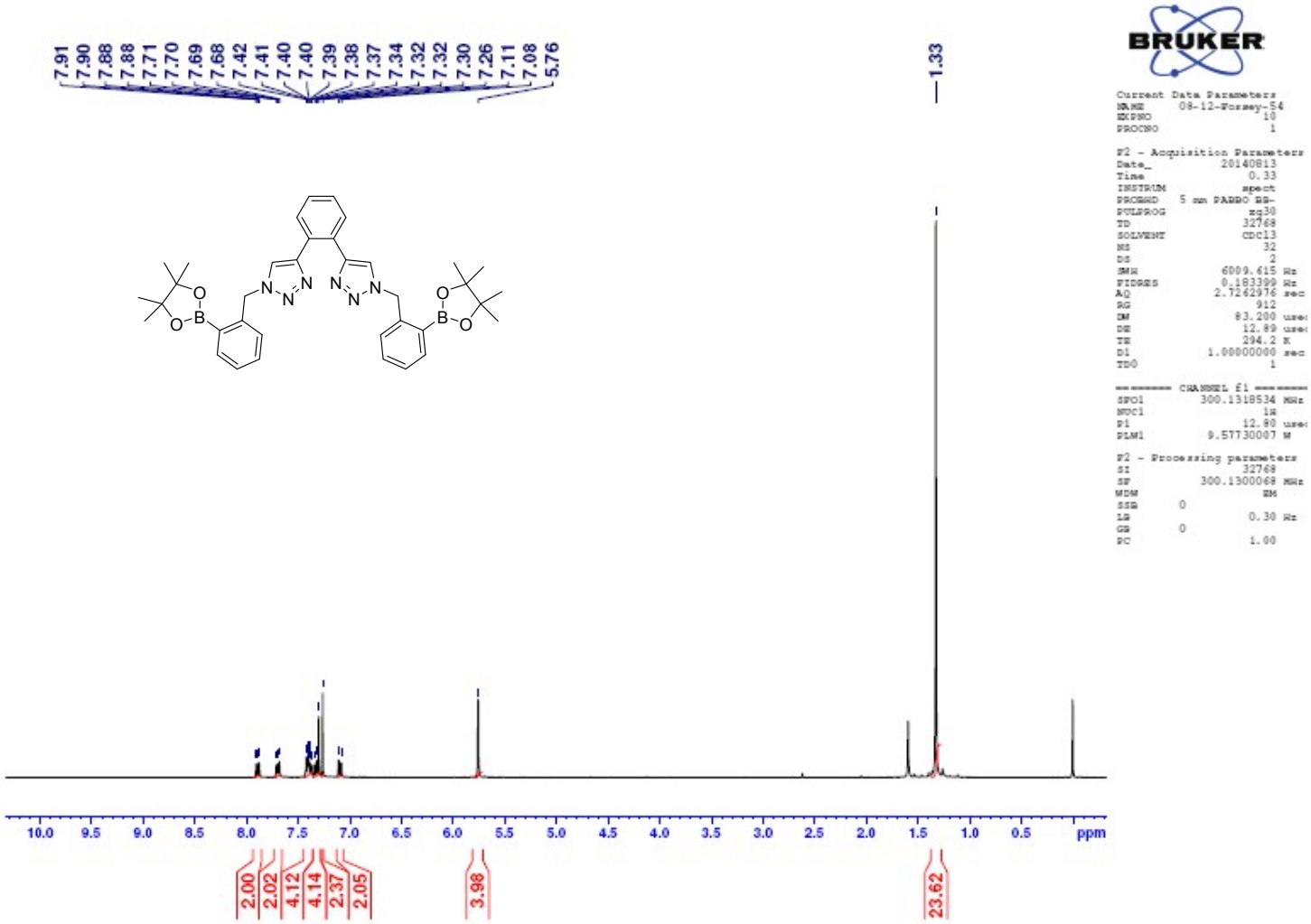
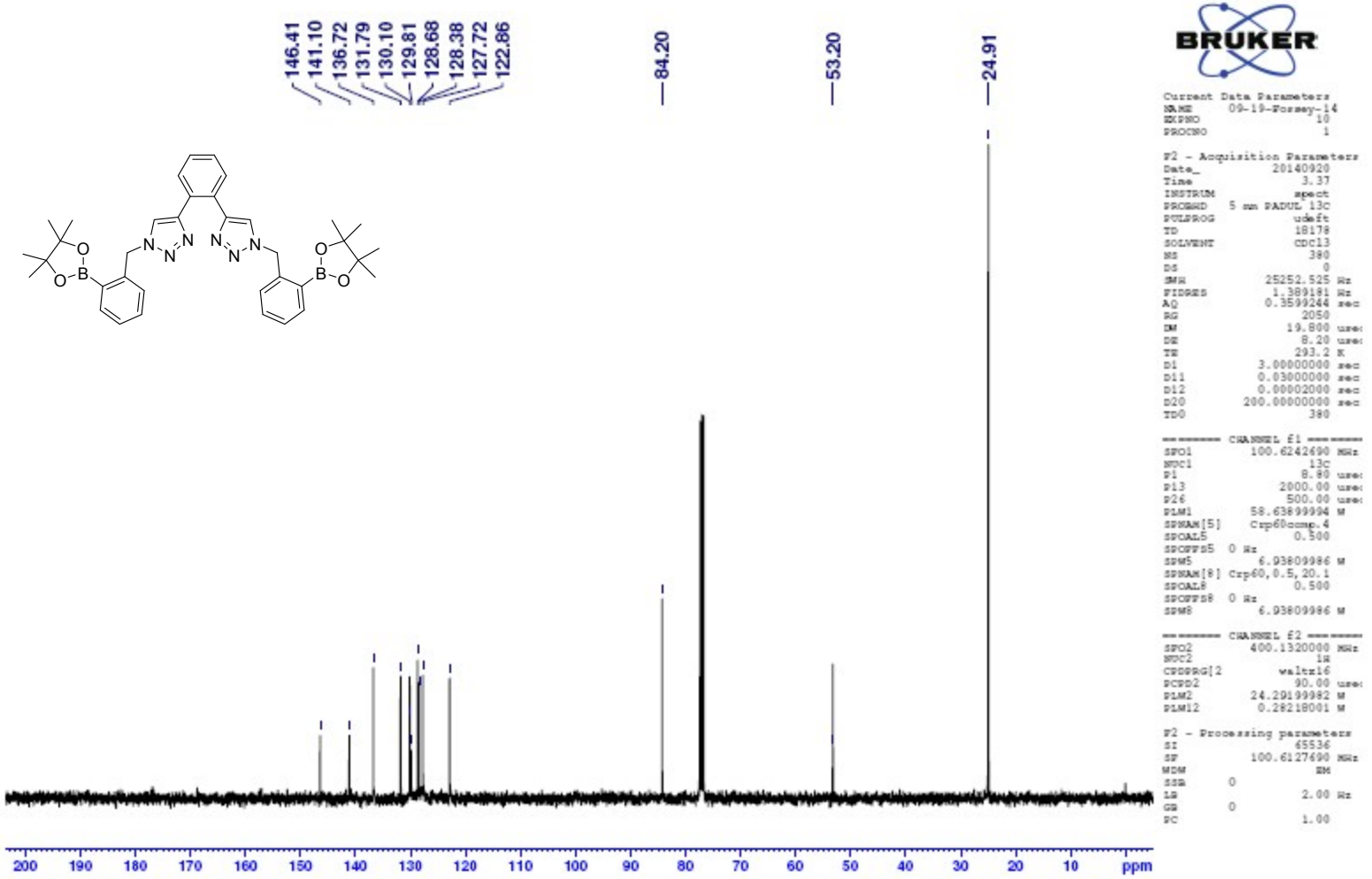
```
Current Data Parameters
NAME      MZ4-50(MZ12-01)
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160212
Time                1.54
INSTRUM           av400
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg
TD                32768
SOLVENT           CDCl3
NS                 1000
DS                    0
SWH           25641.025 Hz
FIDRES         0.782502 Hz
AQ            0.6389760 sec
RG                  128
DW                19.500 use
DE                 6.50 use
TE                296.6 K
D1            5.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                11B
P1                 7.37 use
PL1                8.00 dB
SFO1         128.3583550 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                1H
PCPD2            100.00 use
PL2                2.00 dB
PL12              23.20 dB
PL13              25.00 dB
SFO2         400.0T20004 MHz

F2 - Processing parameters
SI                 32768
SF           128.3583540 MHz
WDW                   EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 0.50
```

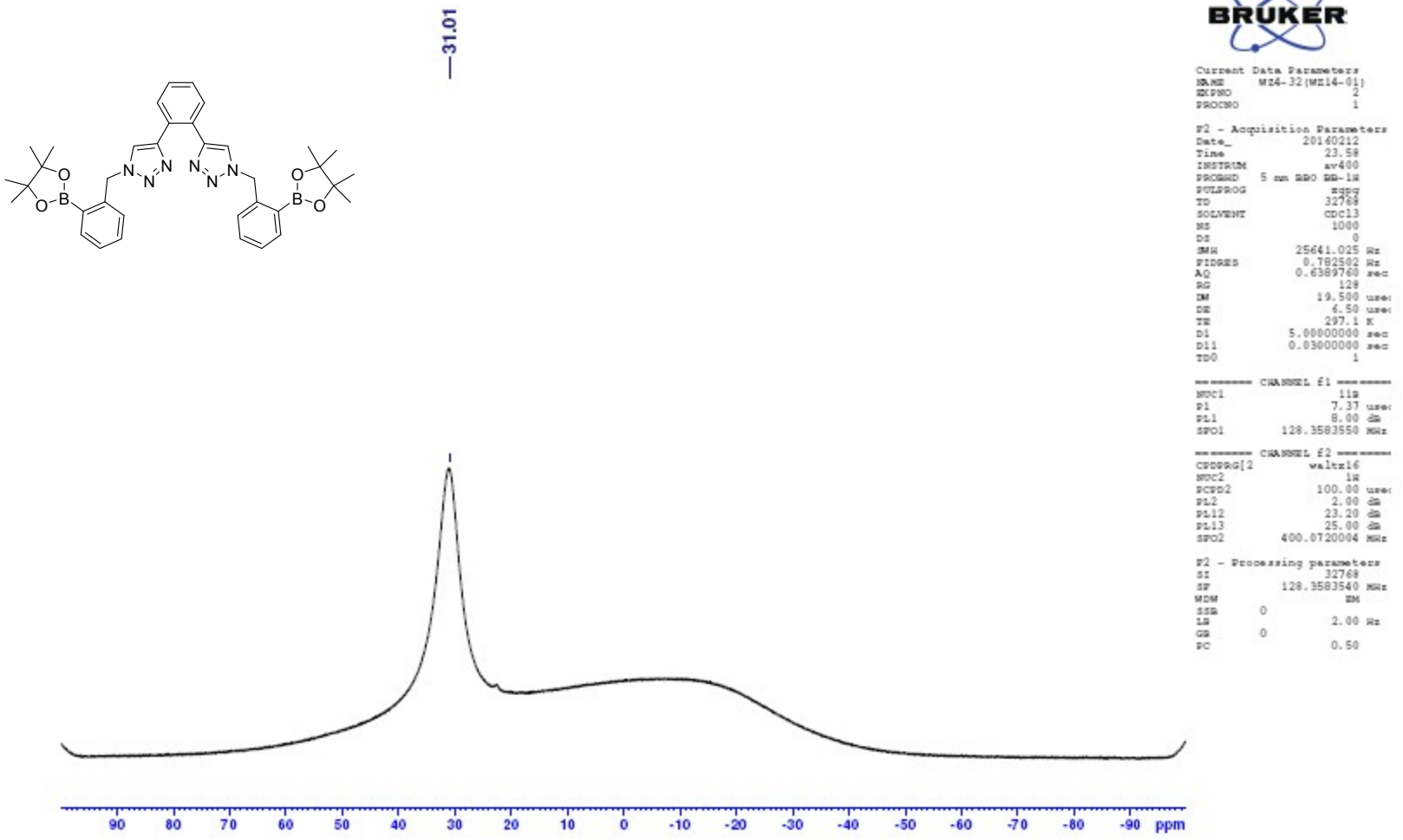
1,2-Bis(1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1*H*-1,2,3-triazol-4-yl)benzene (7c) ^{1}H NMR spectrum



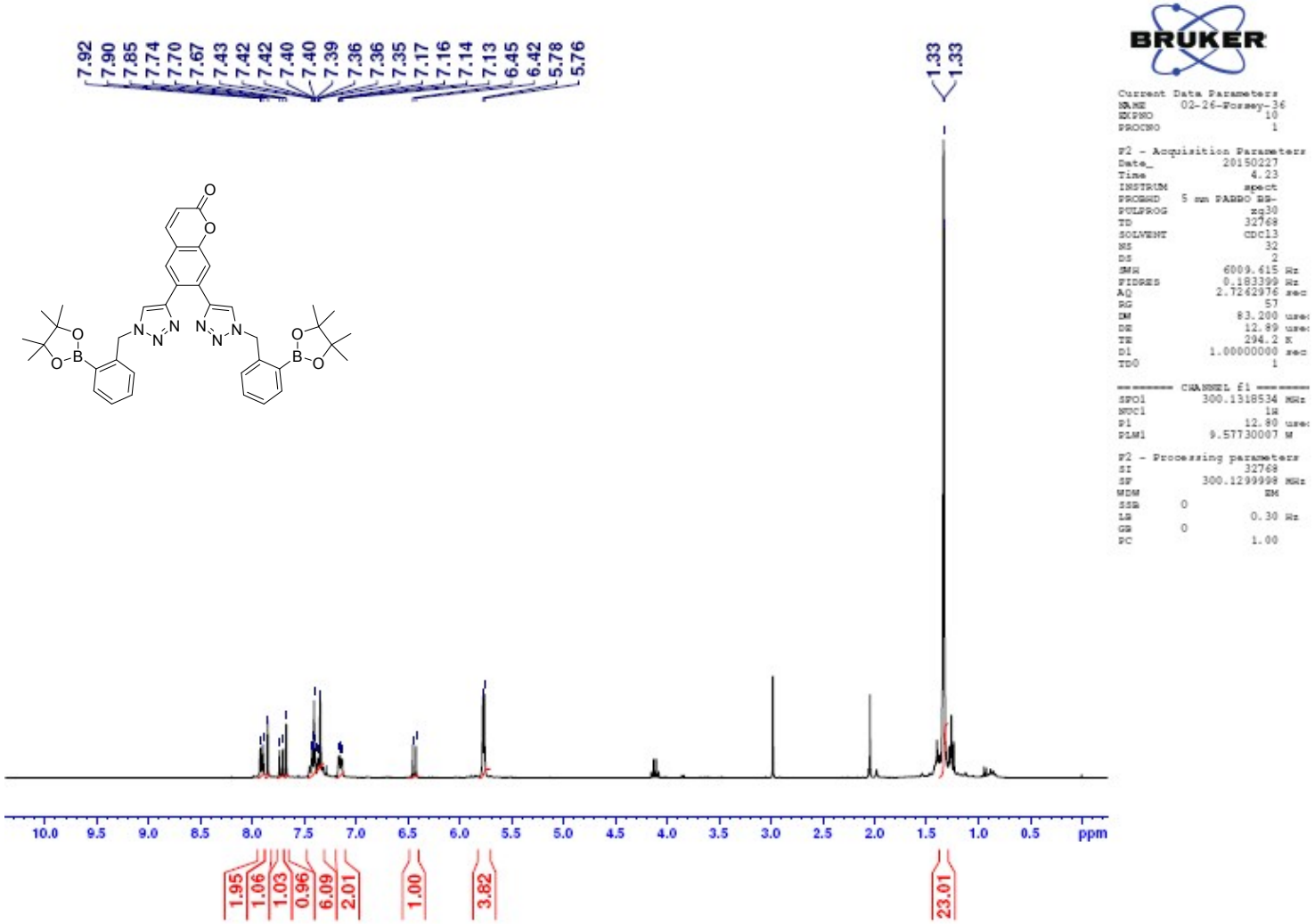
1,2-Bis(1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1*H*-1,2,3-triazol-4-yl)benzene (7c) ^{13}C NMR spectrum



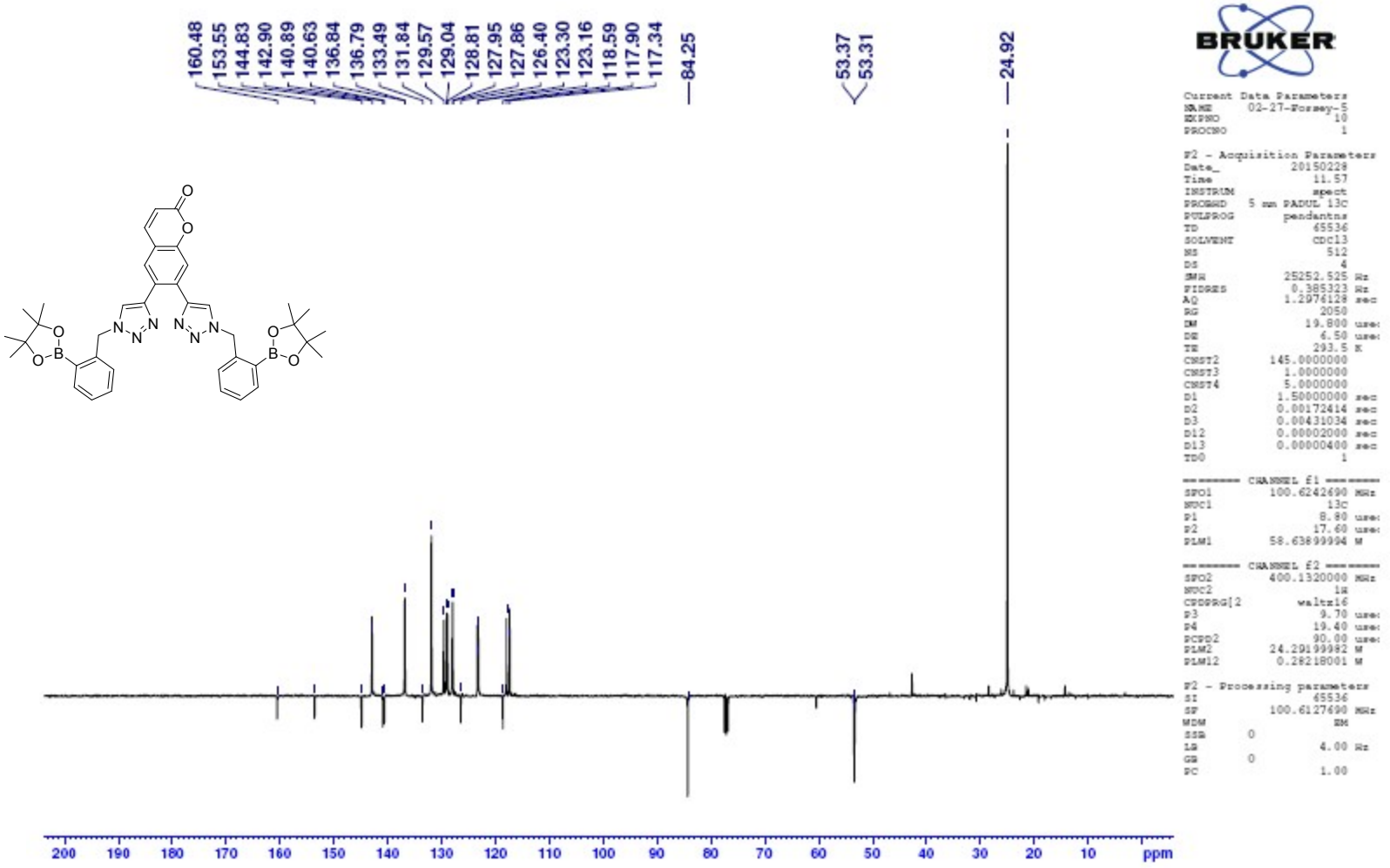
1,2-Bis(1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1*H*-1,2,3-triazol-4-yl)benzene (7c) ^{11}B NMR spectrum



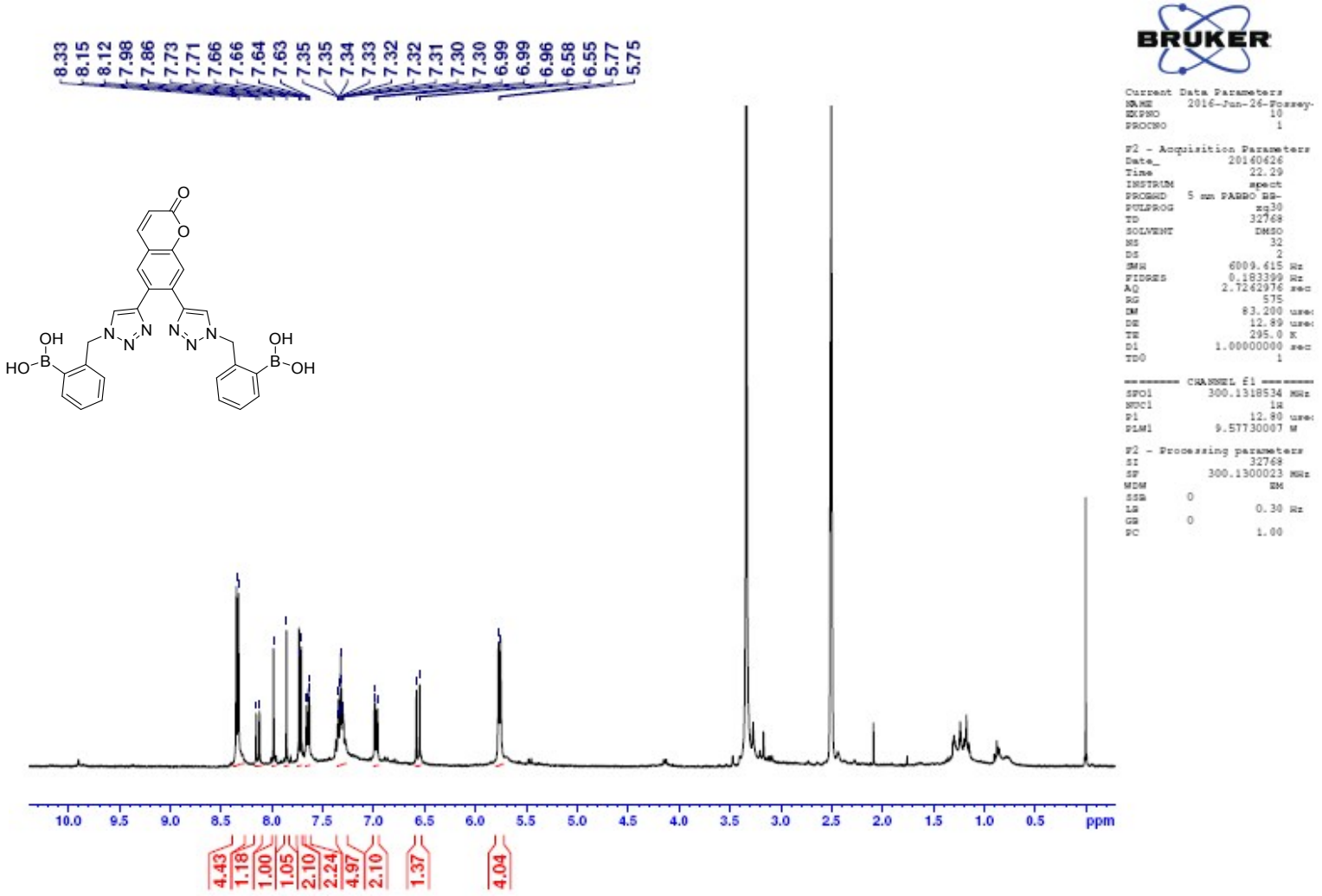
6,7-Bis(1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1*H*-1,2,3-triazol-4-yl)-2*H*-chromen-2-one (13) ^{1}H NMR spectrum



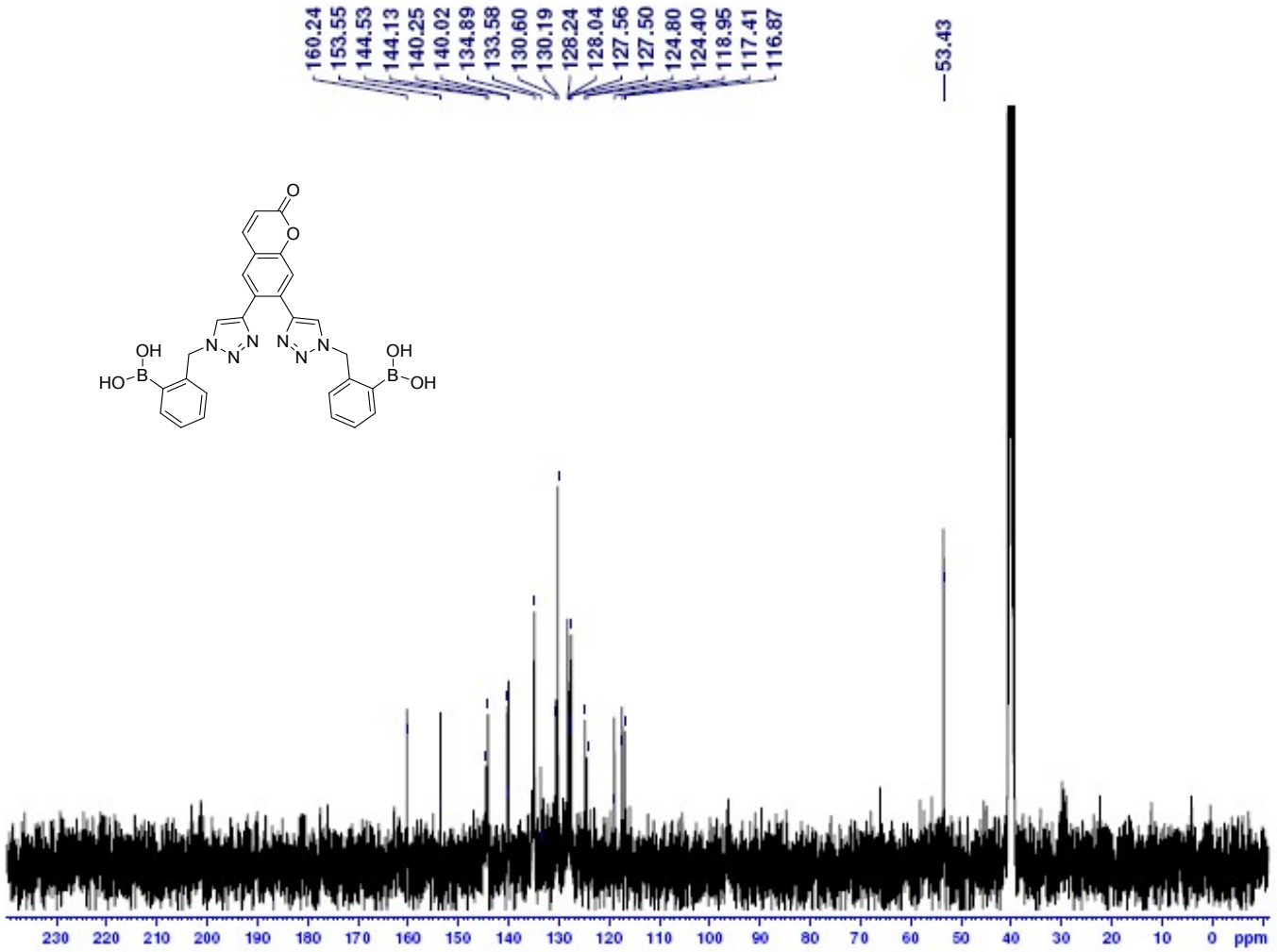
6,7-Bis(1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1*H*-1,2,3-triazol-4-yl)-2*H*-chromen-2-one (13) ^{13}C NMR spectrum



((((2-Oxo-2*H*-chromene-6,7-diyl)bis(1*H*-1,2,3-triazole-4,1-diyl))bis(methylene))bis(2,1-phenylene))diboronic acid (14) ^{1}H NMR spectrum



((((2-Oxo-2*H*-chromene-6,7-diyl)bis(1*H*-1,2,3-triazole-4,1-diyl))bis(methylene))bis(2,1-phenylene))diboronic acid (14) ^{13}C NMR spectrum



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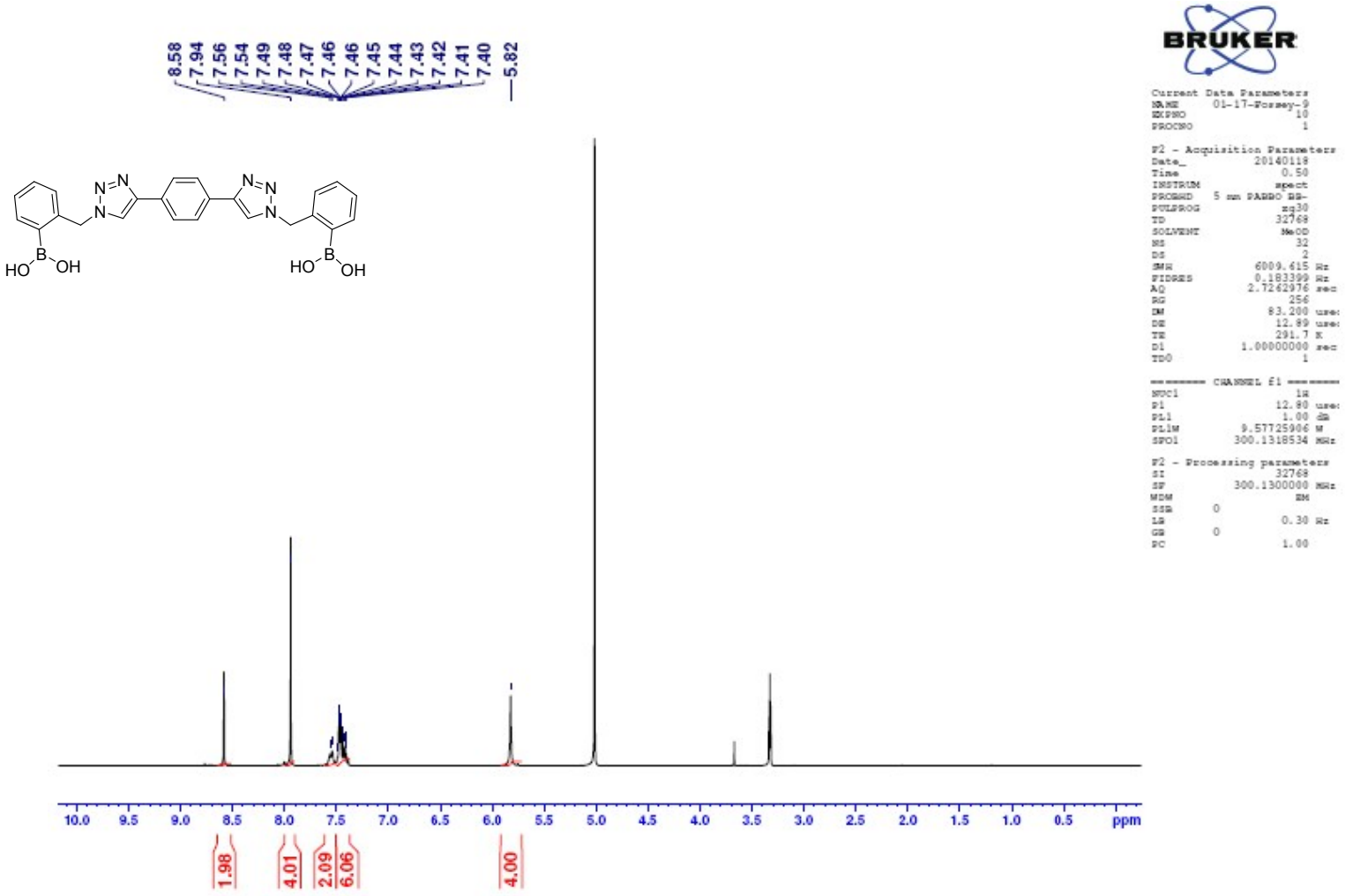
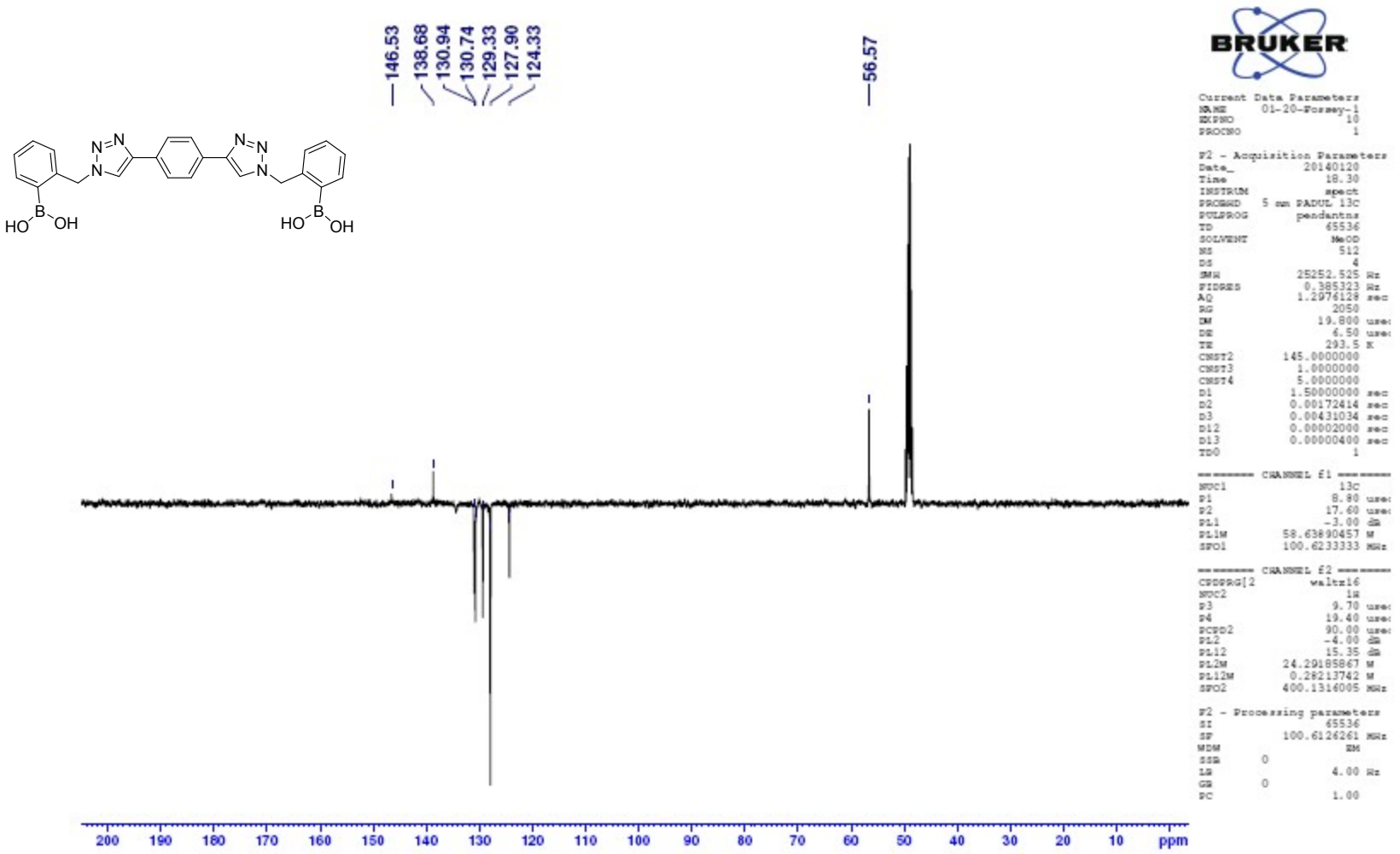
```
Current Data Parameters
NAME        2016-Nov-11-Fossey-
EXPNO                        10
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20161111
Time                      14.09
INSTRUM                    spect
PROBHD     5 mm PADUL 13C
PULPROG                   udeft
TD                        18178
SOLVENT                    DMSO
NS                          380
DS                            0
SWH                   25252.525 Hz
FIDRES                1.389181 Hz
AQ                    0.3599244 sec
RG                         2050
DW                       19.800 use
DE                        8.20 use
TE                       296.0 K
D1                  3.00000000 sec
D11                 0.03000000 sec
D12                 0.00002000 sec
D20                 200.00000000 sec
TD0                         380

======== CHANNEL f1 ========
SFO1               100.6242690 MHz
NUC1                       13C
P1                        8.80 use
P13                    2000.00 use
P26                     500.00 use
PLW1                58.63899994 W
SPNAM[5]            Crp60comp.4
SPOAL5                   0.500
SPOFFS5    0 Hz
SPW5                6.93809986 W
SPNAM[8]  Crp60,0.5,20.1
SPOAL8                   0.500
SPOFFS8    0 Hz
SPW8                6.93809986 W

======== CHANNEL f2 ========
SFO2               400.1320000 MHz
NUC2                        1H
CPDPRG[2                waltz16
PCPD2                     90.00 use
PLW2                24.29199982 W
PLW12                0.28218001 W

F2 - Processing parameters
SI                         65536
SF                 100.6127690 MHz
WDW                           EM
SSB         0
LB                        2.00 Hz
GB          0
PC                        1.00
```

(((1,4-Phenylenebis(1*H*-1,2,3-triazole-4,1-diyl))bis(methylene))bis(2,1-phenylene))diboronic acid (8a) ^{1}H NMR spectrum



(((1,4-Phenylenebis(1*H*-1,2,3-triazole-4,1-diyl))bis(methylene))bis(2,1-phenylene))diboronic acid (8a) ^{13}C NMR spectrum



BRUKER

Current Data Parameters
NAME 01-20-Forsey-1
EXPNO 10
PROCNO 1

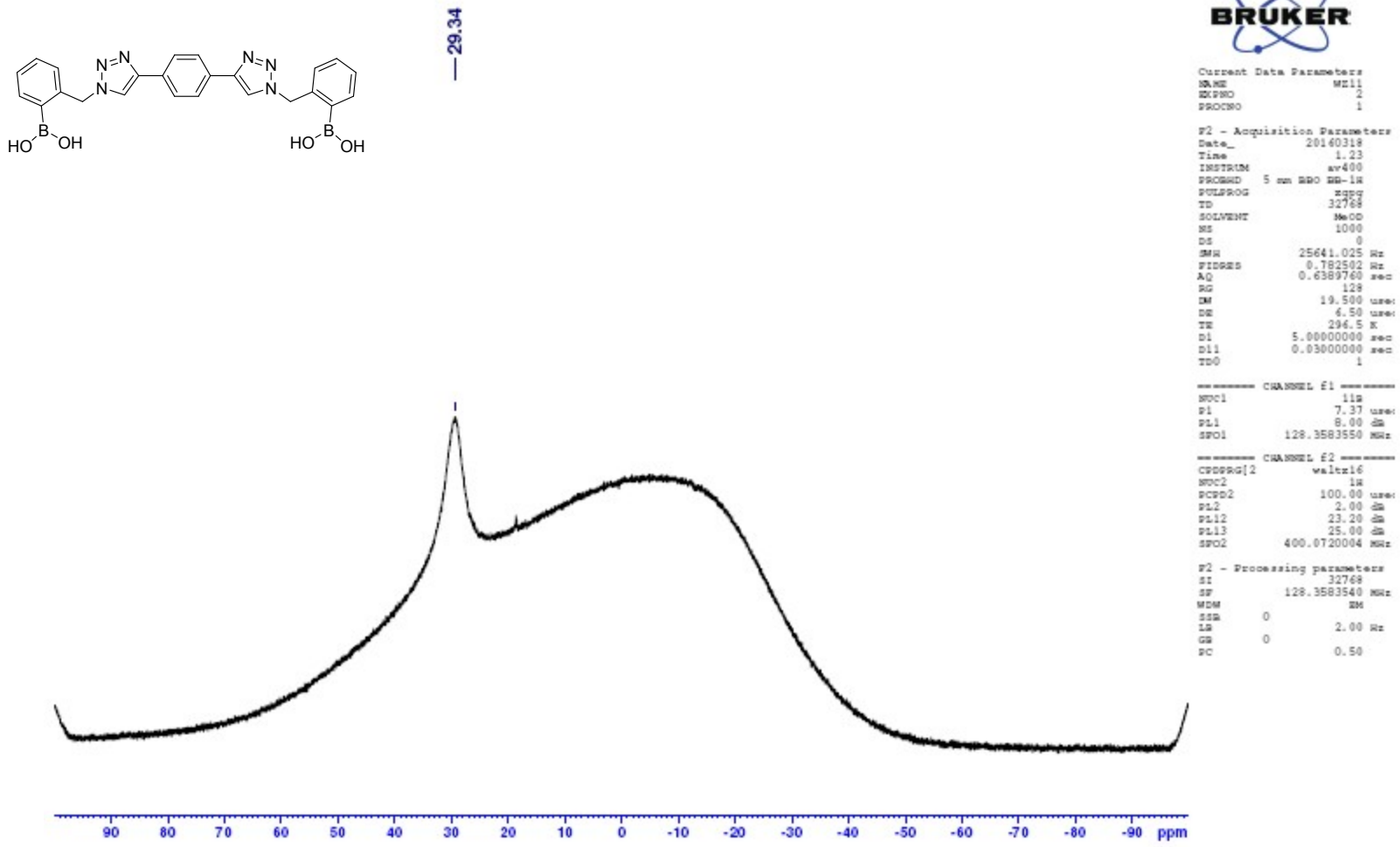
F2 - Acquisition Parameters
Date_ 20140120
Time 18.30
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG pendantns
TD 65536
SOLVENT MeOD
NS 512
DS 4
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 use
DE 6.50 use
TE 293.5 K
CNST2 145.0000000
CNST3 1.0000000
CNST4 5.0000000
D1 1.50000000 sec
D2 0.00172414 sec
D3 0.00431034 sec
D12 0.00002000 sec
D13 0.00000400 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.80 use
P2 17.60 use
PL1 -3.00 dB
PL1M 58.63890457 W
SFO1 100.6233333 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
P3 9.70 use
P4 19.40 use
PCPD2 90.00 use
PL2 -4.00 dB
PL12 15.35 dB
PL2M 24.29185867 W
PL12M 0.28213742 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 65536
SF 100.6126261 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

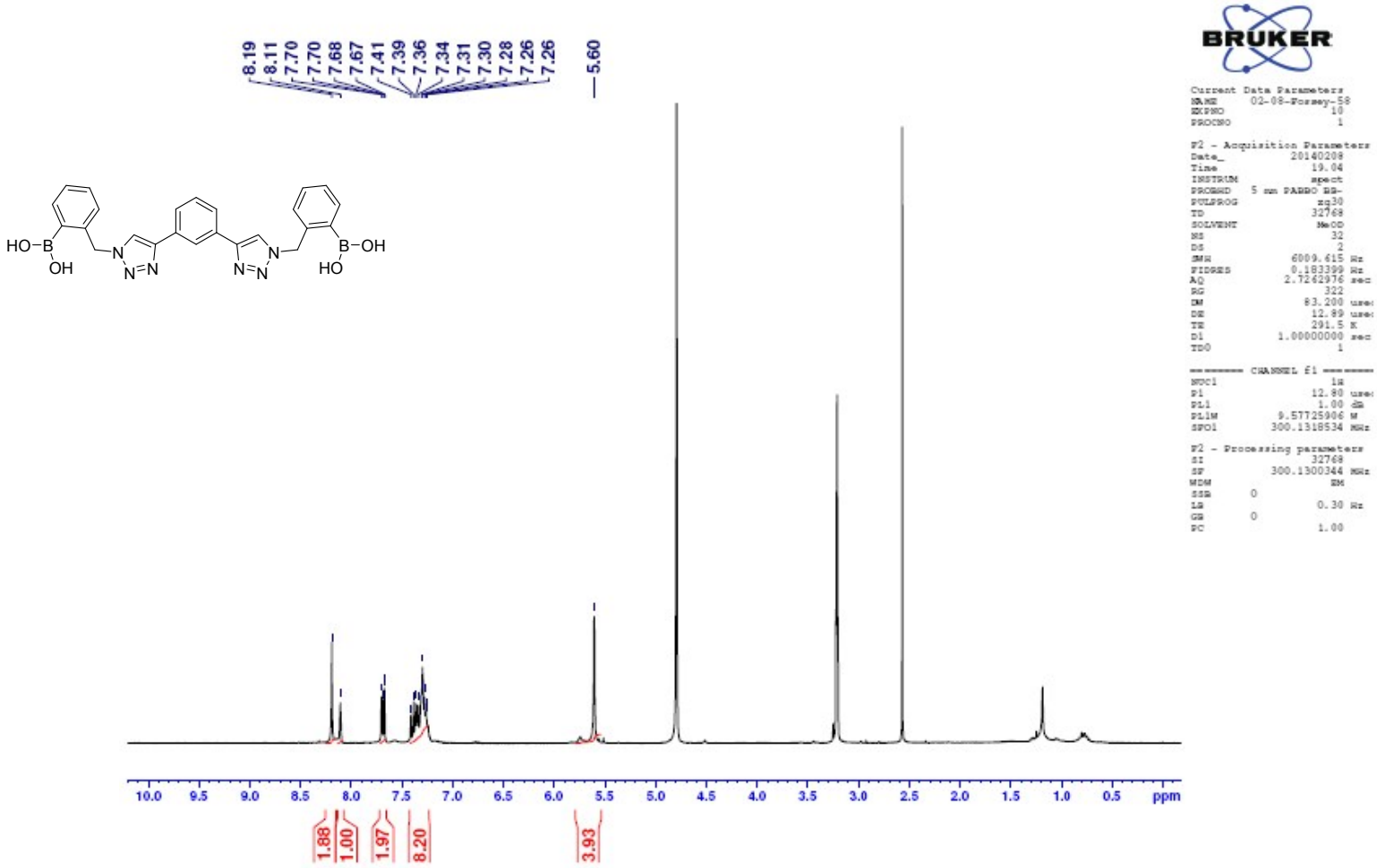
(((1,4-Phenylenebis(1*H*-1,2,3-triazole-4,1-diyl))bis(methylene))bis(2,1-phenylene))diboronic acid (8a) ^{11}B NMR spectrum



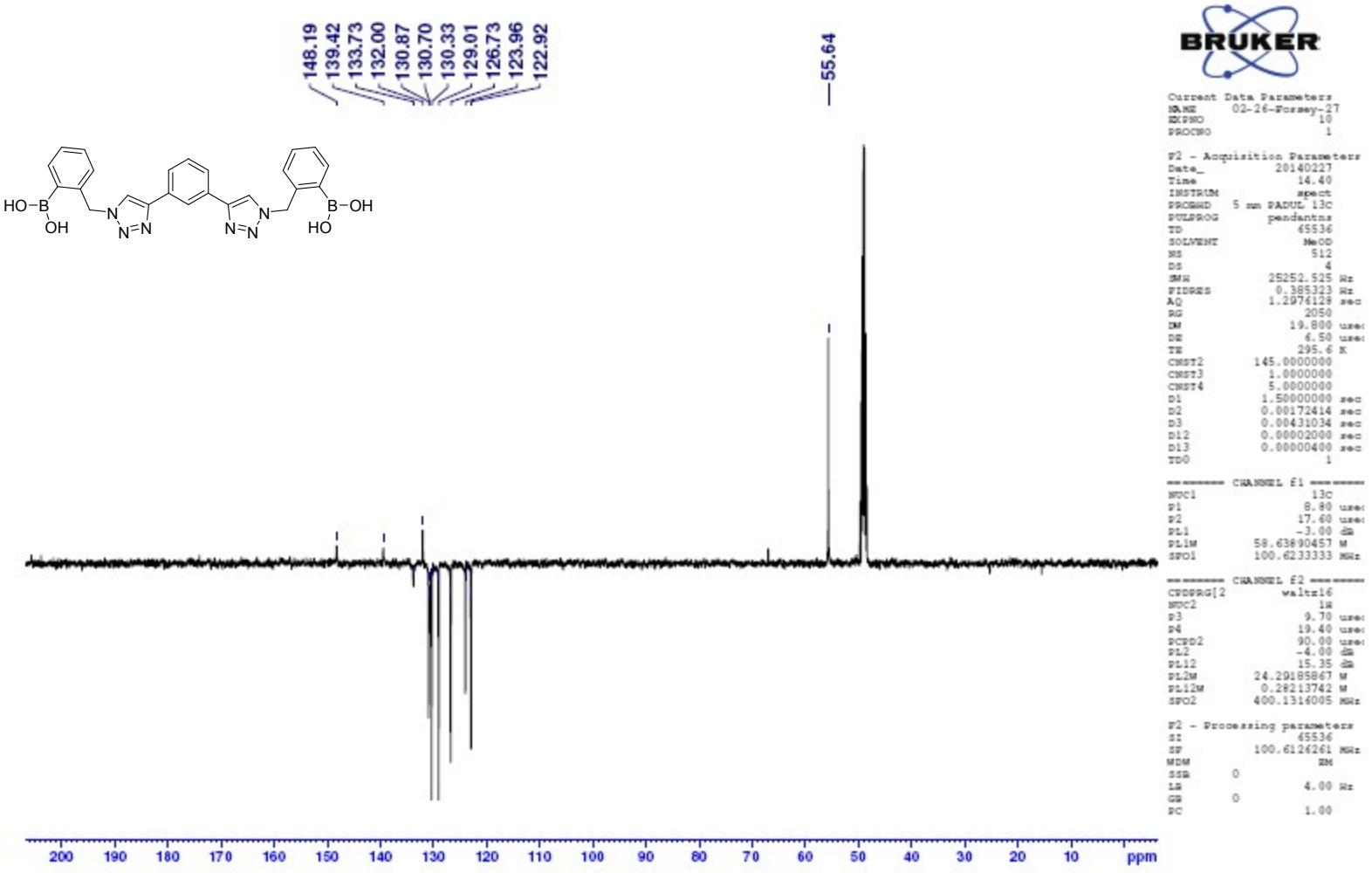
BRUKER

```
Current Data Parameters
NAME                  MZ11
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20140318
Time                   1.23
INSTRUM               av400
PROBHD   5 mm BBO BB-1H
PULPROG               zgpg
TD                   32768
SOLVENT               MeOD
NS                    1000
DS                       0
SWH               25641.025 Hz
FIDRES             0.782502 Hz
AQ                0.6389760 sec
RG                     128
DW                  19.500 use
DE                   6.50 use
TE                  296.5 K
D1                5.00000000 sec
D11               0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    11B
P1                    7.37 use
PL1                   8.00 dB
SFO1         128.3583550 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                    1H
PCPD2               100.00 use
PL2                   2.00 dB
PL12                 23.20 dB
PL13                 25.00 dB
SFO2         400.0720004 MHz

F2 - Processing parameters
SI                   32768
SF           128.3583540 MHz
WDW                     EM
SSB       0
LB                    2.00 Hz
GB        0
PC                    0.50
```

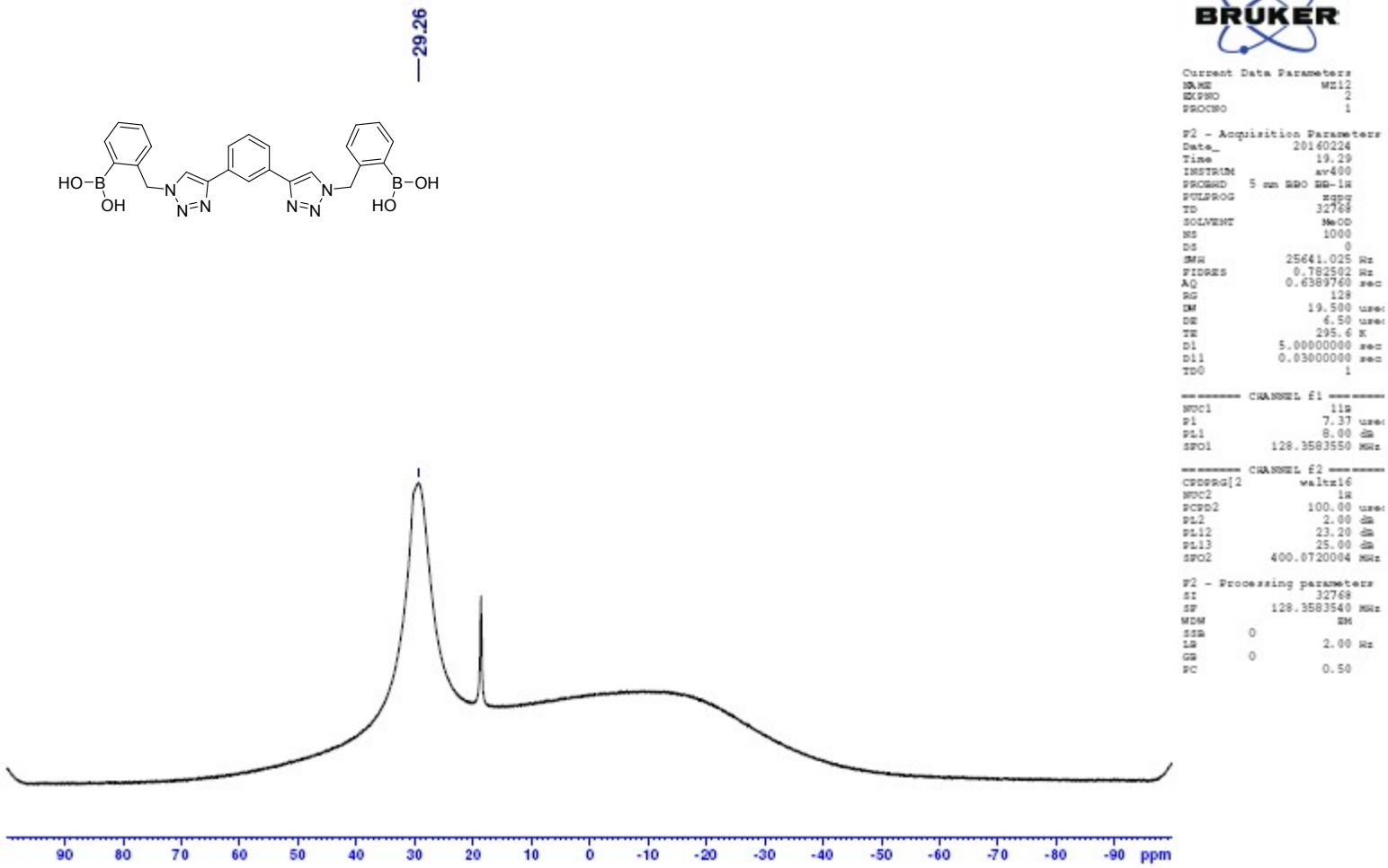
(((1,3-Phenylenebis(1*H*-1,2,3-triazole-4,1-diyl))bis(methylene))bis(2,1-phenylene))diboronic acid (8b) ^{1}H NMR spectrum



(((1,3-Phenylenebis(1*H*-1,2,3-triazole-4,1-diyl))bis(methylene))bis(2,1-phenylene))diboronic acid (8b) ^{13}C NMR spectrum



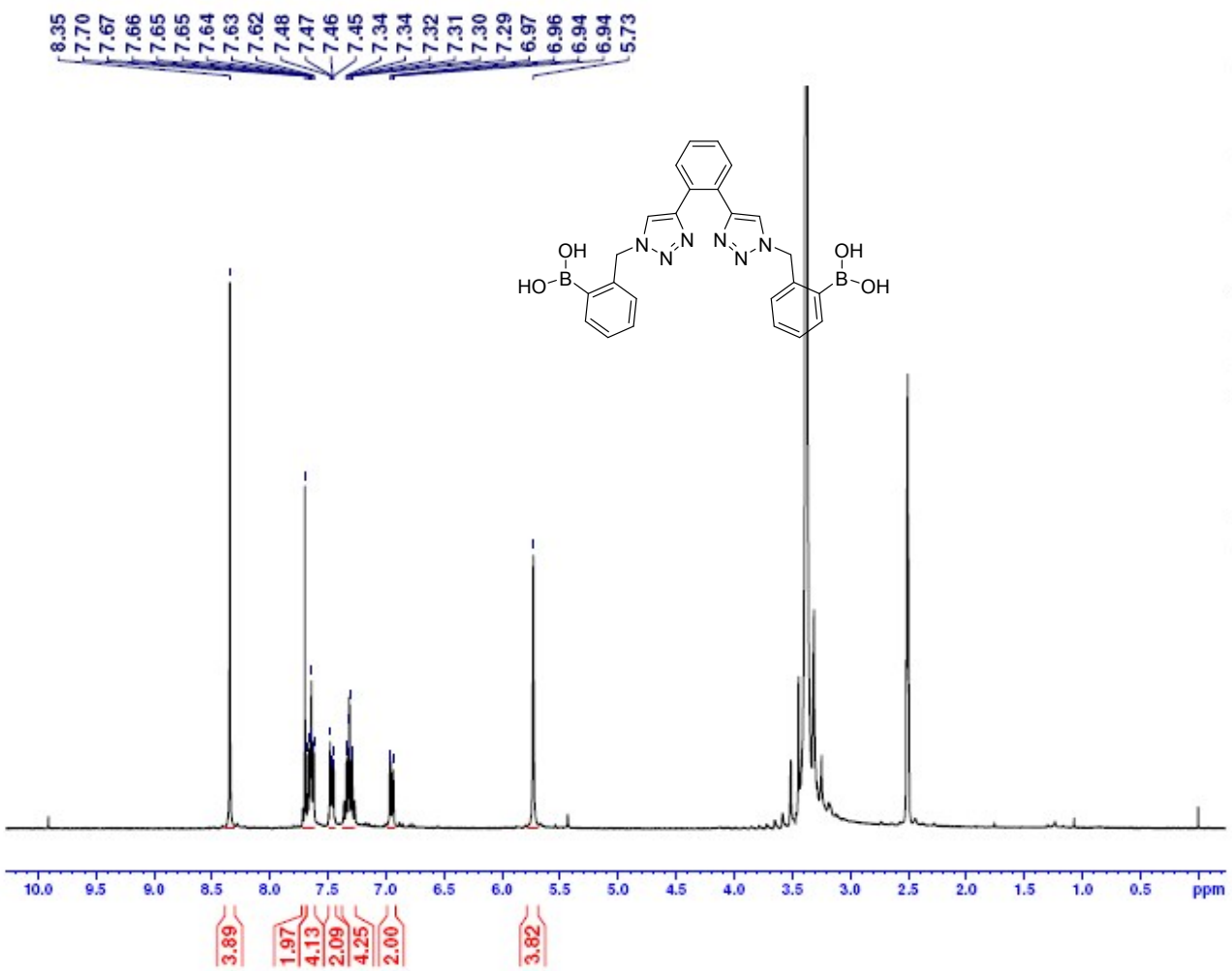
(((1,3-Phenylenebis(1*H*-1,2,3-triazole-4,1-diyl))bis(methylene))bis(2,1-phenylene))diboronic acid (8b) ^{11}B NMR spectrum

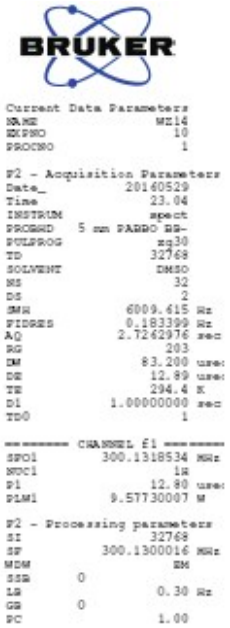


BRUKER

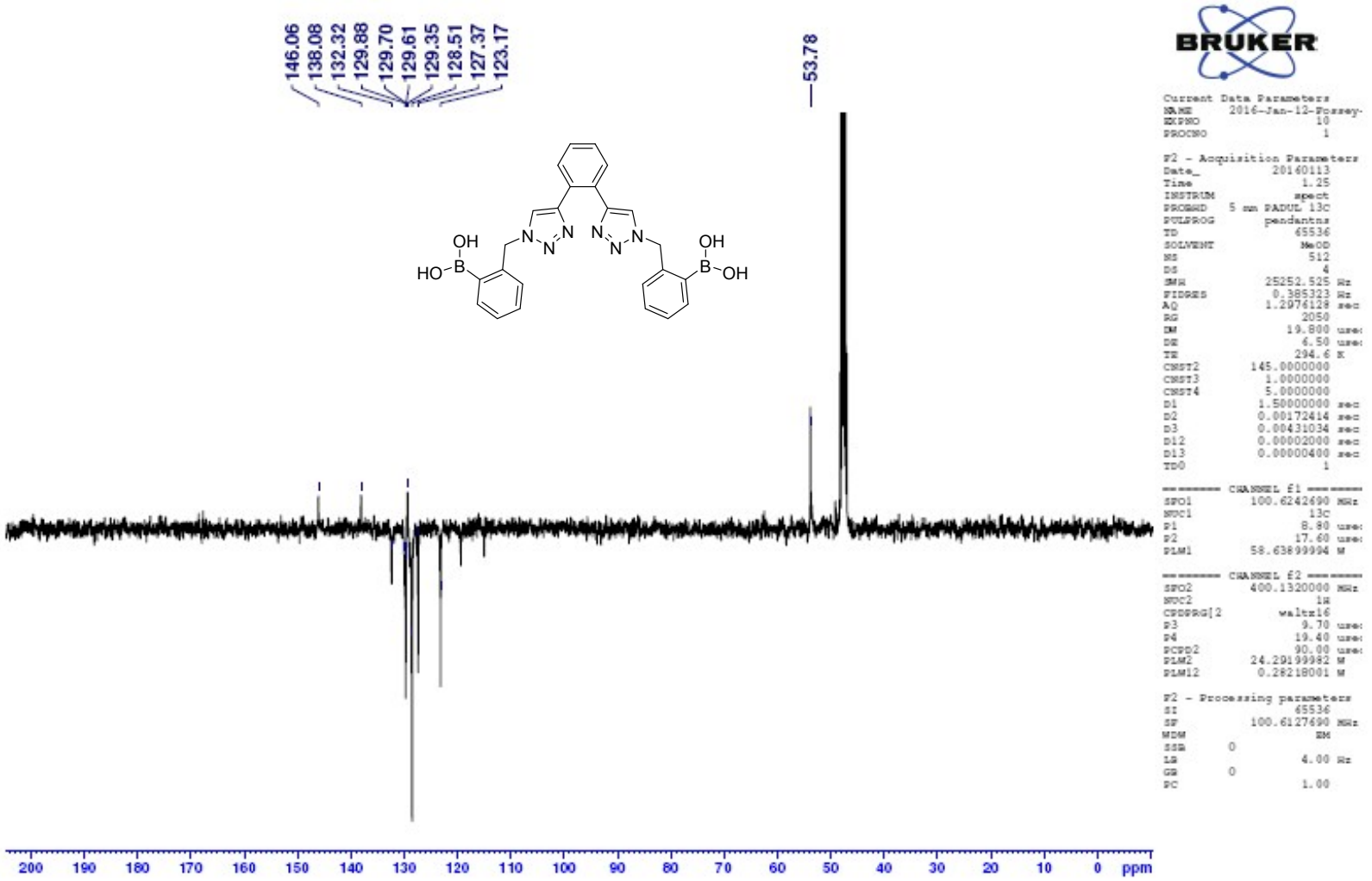
```
Current Data Parameters
NAME                  MZ12
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20140224
Time                 19.29
INSTRUM              av400
PROBHD    5 mm BBO BB-1H
PULPROG              zgpg
TD                  32768
SOLVENT              MeOD
NS                   1000
DS                      0
SWH              25641.025 Hz
FIDRES            0.782502 Hz
AQ                0.6389760 sec
RG                    128
DW                 19.500 use
DE                  6.50 use
TE                 295.6 K
D1              5.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   11B
P1                    7.37 use
PL1                   8.00 dB
SFO1          128.3583550 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                   1H
PCPD2                100.00 use
PL2                   2.00 dB
PL12                 23.20 dB
PL13                 25.00 dB
SFO2          400.0720004 MHz

F2 - Processing parameters
SI                    32768
SF            128.3583540 MHz
WDW                      EM
SSB       0
LB                    2.00 Hz
GB        0
PC                    0.50
```

(((1,2-Phenylenebis(1*H*-1,2,3-triazole-4,1-diyl))bis(methylene))bis(2,1-phenylene))diboronic acid (8c) ^{1}H NMR spectrum

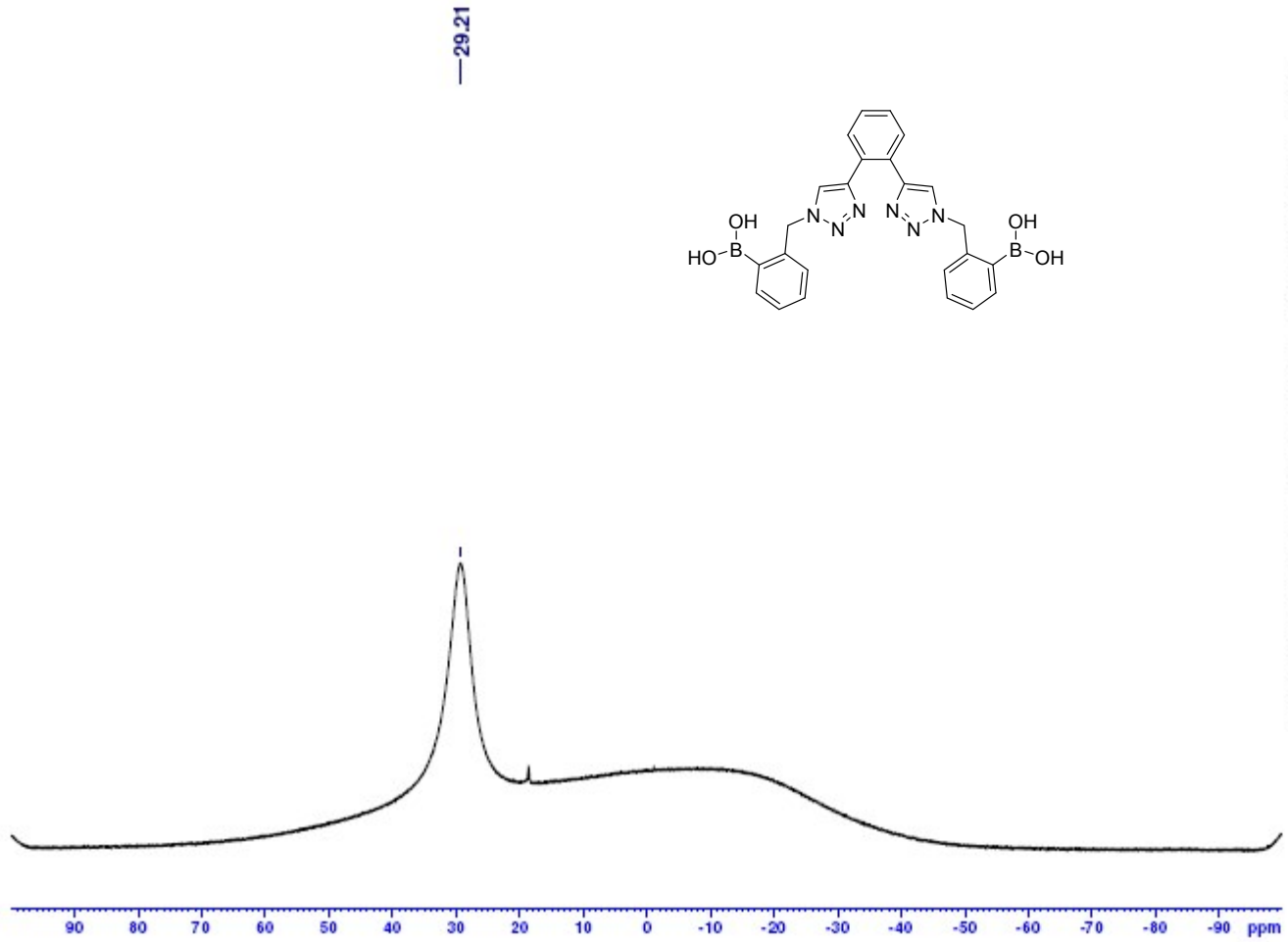




(((1,2-Phenylenebis(1*H*-1,2,3-triazole-4,1-diyl))bis(methylene))bis(2,1-phenylene))diboronic acid (8c) ^{13}C NMR spectrum



(((1,2-Phenylenebis(1*H*-1,2,3-triazole-4,1-diyl))bis(methylene))bis(2,1-phenylene))diboronic acid (8c) ^{11}B NMR spectrum

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PROCNO                 1

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DE                 6.50 use
TE                296.4 K
D1             5.00000000 sec
D11            0.03000000 sec
TD0                    1

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PL1                8.00 dB
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======== CHANNEL f2 ========
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PCPD2             100.00 use
PL2                2.00 dB
PL12              23.20 dB
PL13              25.00 dB
SFO2        400.0T20004 MHz

F2 - Processing parameters
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WDW                   EM
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PC                 0.50
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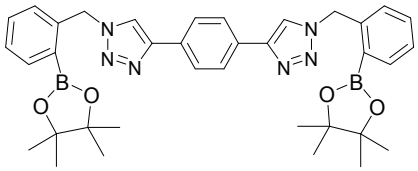
6. X-Ray crystallographic information

The datasets were measured on an Agilent SuperNova diffractometer using an Atlas detector. The data collections were driven and processed and numerical absorption corrections based on gaussian integration over multifaceted crystal models were applied using CrysAlisPro.[5] The structures were solved using ShelXS [6] and refined by a full-matrix least-squares procedure on F^2 in ShelXL.[6] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (U_{eq}) of the parent atom. In **7a** the molecule is located on an inversion centre such that only half is crystallographically-unique. In **7c** the molecule is located on a 2-fold rotation axis such that only half is crystallographically-unique. Also in **7c** part of the boronic ester group O(1), O(2), C(2), C(3), C(5), C(6)/O(1'), O(2'), C(2'), C(3'), C(5'), C(6') is disordered over two positions, with the refined occupancy ratio being 0.813 (5) : 0.187 (5). Figures were produced using OLEX2.[7] The CIFs for **7a**, **7b**, and **7c** have been deposited with the CCDC and have been given the deposition numbers 1510897-1510899 respectively.

6.1 Compound 7a



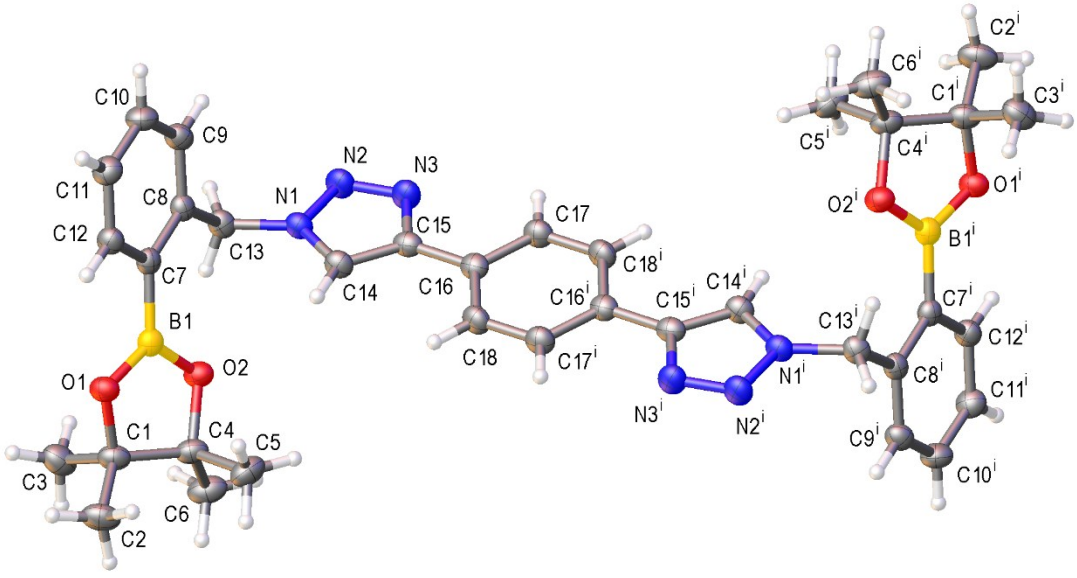
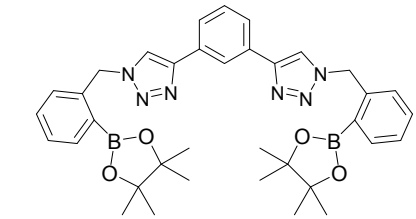


Figure S 5. Crystal structure of **7a** with ellipsoids drawn at the 50 % probability level. The molecule is located on an inversion centre such that only half is crystallographically-unique. Symmetry code used to generate equivalent atoms: (i): -x, 1-y, 2-z.

Crystal Data for **7a**, $C_{36}H_{42}B_2N_6O_4$ (M =644.37 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 6.27417(14) Å, b = 21.9593(5) Å, c = 12.6125(3) Å, β = 96.237(2)°, V = 1727.42(7) Å^3, Z = 2, T = 100.00(10) K, μ(CuKα) = 0.648 mm^{-1}, *Dcalc* = 1.239 g/cm^3, 11755 reflections measured (8.052° ⩽ 2Θ ⩽ 140.132°), 3280 unique (R_{int} = 0.0263, R_{sigma} = 0.0216) which were used in all calculations. The final R_1 was 0.0413 (I > 2σ(I)) and wR_2 was 0.1070 (all data).

6.2 **Compound 7b**



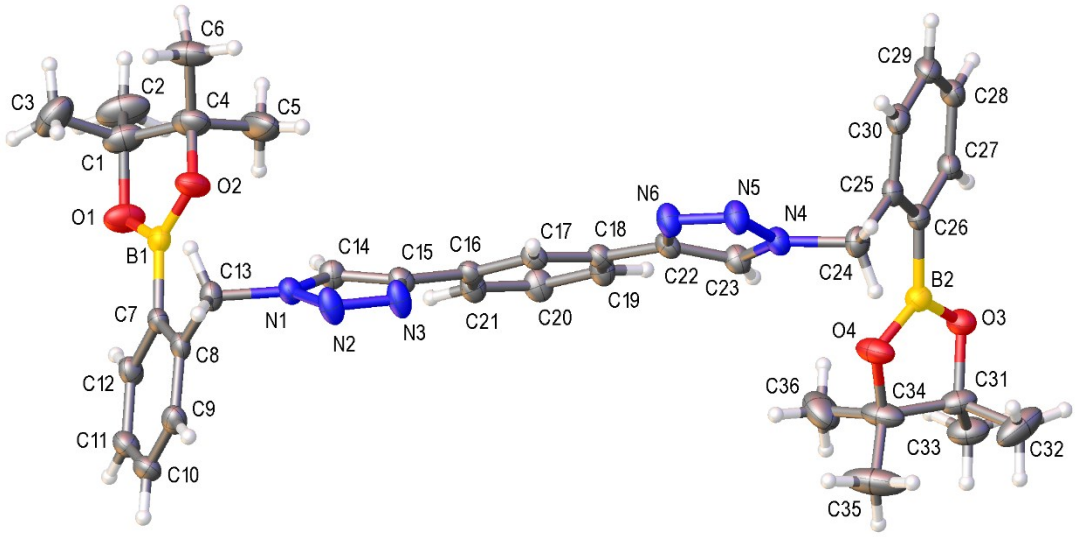
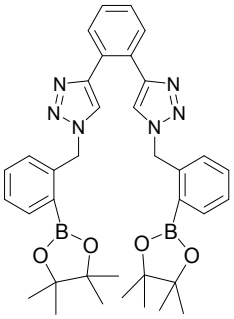


Figure S 6. Crystal structure of **7b** with ellipsoids drawn at the 50 % probability level.

Crystal Data for **7b**, $C_{36}H_{42}B_2N_6O_4$ (M =644.37 g/mol): orthorhombic, space group $Pna2_1$ (no. 33), a = 26.0090(3) Å, b = 6.56488(9) Å, c = 20.4434(3) Å, V = 3490.62(8) Å^3, Z = 4, T = 100.00(10) K, μ(CuKα) = 0.642 mm^{-1}, *Dcalc* = 1.226 g/cm^3, 13862 reflections measured (6.798° ⩽ 2Θ ⩽ 149.176°), 5551 unique (R_{int} = 0.0217, R_{sigma} = 0.0236) which were used in all calculations. The final R_1 was 0.0404 (I > 2σ(I)) and wR_2 was 0.1046 (all data).

6.3 Compound 7c



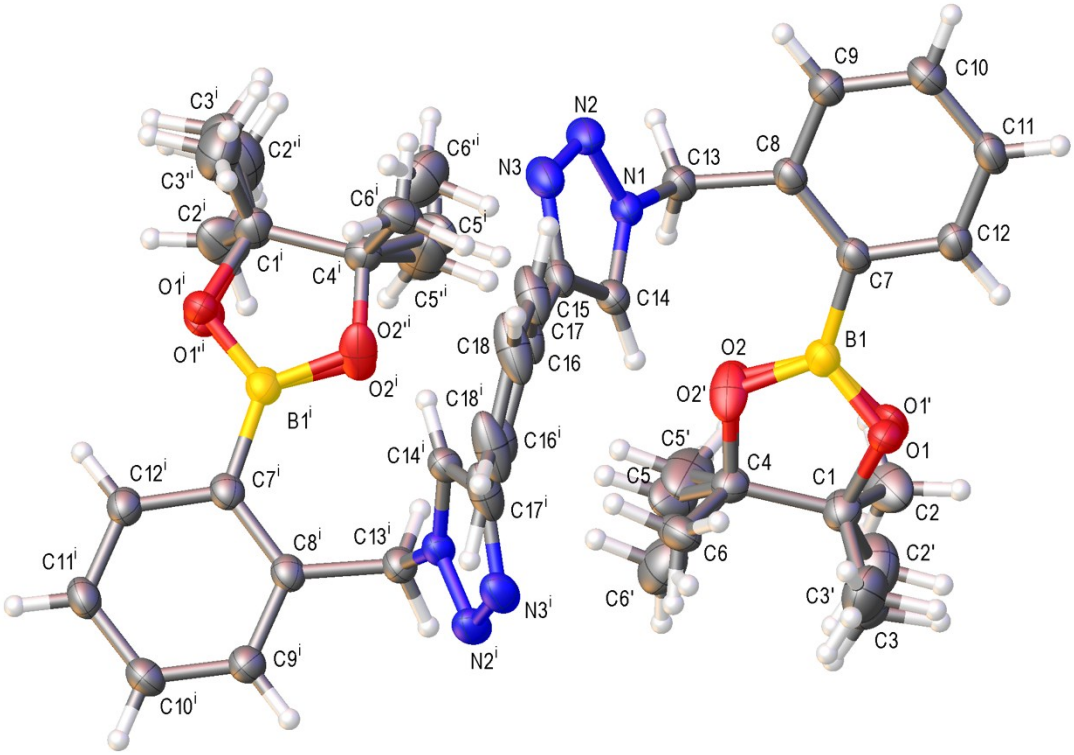


Figure S 7. Crystal structure of **7c** with ellipsoids drawn at the 50 % probability level. The molecule is located on a 2-fold rotation axis such that only half is crystallographically-unique. Part of the boronic ester group O(1), O(2), C(2), C(3), C(5), C(6)/O(1'), O(2'), C(2'), C(3'), C(5'), C(6') is disordered over two positions, with the refined occupancy ratio being 0.813 (5) : 0.187 (5). Symmetry code used to generate equivalent atoms: (i): -x, y, 0.5-z.

Crystal Data for **7c**, $C_{36}H_{42}B_2N_6O_4$ (M =644.37 g/mol): monoclinic, space group C2/c (no. 15), a = 16.3223(5) Å, b = 12.4005(4) Å, c = 17.5981(5) Å, β = 103.806(3)°, V = 3459.04(19) Å^3, Z = 4, T = 100.0(2) K, μ(CuKα) = 0.648 mm^{-1}, *Dcalc* = 1.237 g/cm^3, 6813 reflections measured (9.054° ⩽ 2Θ ⩽ 148.648°), 3428 unique (R_{int} = 0.0204, R_{sigma} = 0.0253) which were used in all calculations. The final R_1 was 0.0393 (I > 2σ(I)) and wR_2 was 0.1023 (all data).

7. References for ESI

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5. CrysAlisPro, Agilent Technologies, Version 1.171.36.28, 2013.
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