Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Direct formation of 4,5-disubstituted carbazoles via regioselective dilithiation

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General experimental

All reagents were bought commercially from either Sigma-Aldrich (Merck), Alfa Aesar, Acros Organics, Fisher Scientific, VWR, or Fluorochem, and were used as sold unless stated. *n*BuLi was bought as a 2.5 M solution in hexanes and titrated with menthol and 'blue'.[1] All reactions were performed under an atmosphere of argon in oven or flame dried flasks. All solvents were bought from one of the above suppliers, and used without further drying or purification unless stated. Any solvents that were dried were stored under argon. MeOH, Toluene, THF, CH_2Cl_2 and MeCN were dried over 3Å molecular sieves for at least 24 h before use. *N*,*N*,*N*',*N*'-Tetramethylethylenediamine (TMEDA) was distilled from CaH_2 and stored over KOH. Iodomethane, dichlorodimethylsilane and dimethylgermanium dichloride were distilled prior to use. Sulfur was recrystallized from hot toluene prior to use. Silica gel on aluminium-backed TLC plates were used for reaction monitoring, supplied from Merck. The plates were visualised in UV (254 nm) and standard laboratory visualizing agents: $KMnO_4$, anisaldehyde, vanillin, curcumin, iodine powder. Purification by flash column chromatography was performed on Sigma-Aldrich or Fluorochem silica gel, pore size 60 Å, 230–400 mesh particle size, 40–63 µm particle size. Automated flash column chromatography was performed using a Teledyne ISCO Combi*Flash*® NextGen 300+ utilising Interchim PuriFlash® dryload columns filled with Sigma-Aldrich or Fluorochem silica gel, pore size 60 Å, 230–400 mesh particle size, 40–63 µm particle size. Infra-red spectra were recorded neat (oil) or with the aid of an ATR-attachment (solid) on a Perkin Elmer Spectrum 100 FT-IR spectrometer, only selected absorbances (νmax, cm^{-1}) are reported. The following abbreviations are used when describing the data: w (weak), m (medium), s (strong), br (broad). Melting points were recorded using open glass capillaries on a Gallenkamp melting point apparatus and are uncorrected. MS data are reported as m/z (%) (relative intensity except in cases where only the parent ion is observed). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVIII300, Bruker AVIII400, Bruker NEO400 and Bruker AV4-500 in the solvents indicated. The solvent signals were used as references: ^{1}H NMR: residual $CHCl_3$ (7.26 ppm), CH_2Cl_2 (5.32 ppm) and C_6H_6 (7.16 ppm); ^{13}C NMR; $CDCl_3$ (77.16 ppm), CD_2Cl_2 (53.84 ppm) and C_6D_6 (128.06 ppm). ^{11}B MNR was referenced at 0 ppm using a solution of 15% $BF_3{\cdot}OEt_2$ (0.00 ppm) in $CDCl_3$ in a sealed capillary. ^{19}F NMR was indirectly referenced to 0 ppm (chemical shift of CCl_3F) using 0.05% trifluorotoluene in $CDCl_3$ at –64.72 ppm. Coupling constants (J) are reported in Hz, and are reported as observed, not averaged between the two environments that share them. The following abbreviations are used to describe multiplicity in 1H-NMR: m (multiplet), s (singlet), d (doublet), t (triplet), hept (heptet), ap. (apparent). The distinction between multiplet and stack is as follows: a multiplet is a single environment that is too convoluted to establish its multiplicity correctly, a stack is where multiple environments overlap and their fidelity is lost.

Experimental procedures and analytical data

General Procedure 1 – *N*-silylation of carbazoles

Lithium hexamethyldisilazide (1 M in THF, 1.1 eq.) was added to a solution of functionalized carbazole in THF (0.1 M), and allowed to stir at room temperature for 15 min. Chloro(trialkyl)silane (1.2 eq.) was added and the mixture allowed to stir for 16 h. Water was added and the mixture extracted with EtOAc (× 3) and the combined organic extracts washed with brine. The organic layer was dried over sodium sulfate, filtered and concentrated under reduced pressure to give the crude product. The crude product was purified by flash column chromatography or recrystallization.

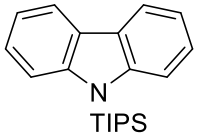
General Procedure 2 – 4,5-difunctionalisation of *N*-silylated carbazoles

A solution of *n*-butyllithium in hexane (4 eq.) was added to a solution of *N*-silylated carbazole derivative in TMEDA (4 eq.) and the mixture heated to 60 °C for 6 h. The reaction mixture was cooled to –78 °C, diluted with THF (0.22 M wrt. *N*-silylated carbazole derivative), and treated with the electrophile. After 10 min the cooling bath was removed and the resulting mixture allowed to stir for 17 h. The mixture was subjected to, electrophile-dependent, work-up and purification.

Deuteration study (Table 1, Entry 2)

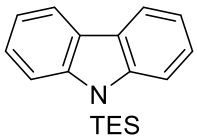
n-Butyllithium solution in hexane (1.24 mmol) was added to a solution of **1a** (0.31 mmol) in TMEDA (1.24 mmol) and the mixture heated at 60 °C for 6 h. The reaction mixture was cooled to –78 °C, diluted with THF (1.34 mL), and treated with deuterium oxide (0.75 mL, 41.6 mmol). After 10 min the cooling bath was removed and the resulting mixture allowed to stir for 17 h. The reaction mixture was poured into $HCl_{(aq)}$ (1 M, 5 ml) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed sequentially with H_2O (10 mL) and brine (10 mL), dried over sodium sulfate, filtered and concentrated under reduced pressure. The extent of deuteration of **1a** was determined by relative integration of aromatic hydrogen signals in the ^1H NMR.

9-(Triisopropylsilyl)-9H-carbazole [1a][2]



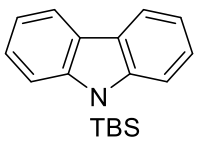
Following General Procedure 1: [From 11.93 mmol carbazole with chlorotriisopropylsilane.] Purified by recrystallization (EtOH), **1a** (3.20 g, 83%) was obtained as a colourless solid. R_f = 0.27 (hexane); mp 88 – 90 °C (EtOH); ν_{max} (solid, cm^{-1}) 2945 br, 2866 br, 1592 w, 1465 m, 1442 s, 1255 m, 1195 m, 954 s, 881 m, 750 s, 720 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.07 (dd, *J* 7.8 Hz, 0.8 Hz, 2 H), 7.69 (d, *J* 8.5 Hz, 2 H), 7.36 (ddd, *J* 8.5 Hz, 7.1 Hz, 1.4 Hz, 2 H), 7.23 (ddd, *J* 7.7 Hz, 7.1 Hz, 0.8 Hz, 2 H), 2.00 (hept, *J* 7.5 Hz, 3 H), 1.20 (d, *J* 7.5 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 145.2, 126.6, 125.4, 119.8, 119.6, 114.2, 18.7, 14.0; m/z (TOF ASAP$^+$) calculated for $C_{121}H_{30}NSi$ $[M+H]^+$; 324.2148, found 324.2142 (PPM error –1.9).

9-(Triethylsilyl)-9H-carbazole [1c][3]



Following General Procedure 1: [From 6.04 mmol carbazole with chlorotriethylsilane.] Purified by flash column chromatography (hexane), **1c** (1.36 g, 80%) was obtained as a colourless oil that solidified on standing. R_f = 0.30 (hexane); mp 37 – 39 °C (hexane); ν_{max} (solid, cm^{-1}) 2954 br, 2874 br, 1592 w, 1471 m, 1444 s, 1263 s, 1210 s, 961 s, 752 s, 722 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.07 (d, *J* 7.7 Hz, 2 H), 7.50 (d, *J* 8.3 Hz, 2 H), 7.37 (ddd, *J* 8.4 Hz, 7.2 Hz, 1.4 Hz, 2 H), 7.23 (ddd, *J* 7.9 Hz, 7.1 Hz, 0.8 Hz, 2 H), 1.25 (dd, *J* 15.7 Hz, 7.8 Hz, 6 H), 1.00 (t, *J* 7.8 Hz, 9 H); ^{13}C NMR (101 MHz) δ_C 144.8, 126.3, 125.5, 120.1, 119.6, 113.2, 7.1, 5.4; m/z (TOF EI+) calculated for $C_{18}H_{23}NSi$ $[M]^+$; 281.1600, found 281.1602 (PPM error 0.7).

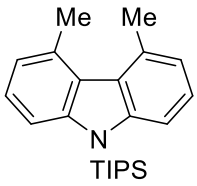
9-(*tert*-Butyldimethylsilyl)-9H-carbazole [1d][4]



Following General Procedure 1: [From 6.01 mmol carbazole with *tert*-butyldimethylchlorosilane.] Purified by flash column chromatography (hexane), **1d** (1.64 g,

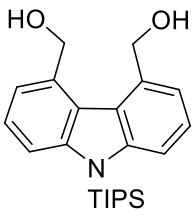
97%) was obtained as a colourless solid. R_f = 0.31 (hexane); mp 116 – 118 °C (EtOH); ν_{max} (solid, cm^{-1}) 2928 br, 2856 br, 1594 w, 1471 m, 1443 s, 1256 s, 1208 s, 965 s, 806 s, 751 s, 722 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.07 (d, *J* 7.8 Hz, 2 H), 7.60 (d, *J* 8.4 Hz, 2 H), 7.36 (ddd, *J* 8.4 Hz, 7.2 Hz, 1.3 Hz, 2 H), 7.23 (ddd, *J* 7.8 Hz, 6.9 Hz, 0.8 Hz, 2 H), 1.05 (s, 9 H), 0.75 (s, 6 H); ^{13}C NMR (101 MHz) δ_C 145.2, 126.4, 125.3, 119.9, 119.6, 114.2, 26.7, 20.7, –1.1; m/z (TOF EI+) calculated for $C_{18}H_{23}NSi$ $[M]^+$; 281.1600, found 281.1606 (PPM error 2.1).

4,5-Dimethyl-9-(triisopropylsilyl)-9H-carbazole [2a]

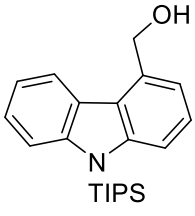


Following General Procedure 2: [From 0.78 mmol **1a**, using iodomethane as the electrophile (8 eq.).] The reaction mixture was poured into sat. $NH_4Cl_{(aq)}$ (15 mL) and extracted with CH_2Cl_2 (2 × 15 mL). The combined organic extracts were washed sequentially with H_2O (15 mL) and brine (15 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure to give an orange oil. The orange oil was purified by flash column chromatography (hexane) to give **2a** (103.8 mg, 38%) as a colourless solid. R_f = 0.19 (hexane); mp 58 – 60 °C (hexane); ν_{max} (solid, cm^{-1}) 2946 br, 2866 br, 1576 w, 1446 m, 1412 s, 1278 s, 1058 m, 983 m, 884 s, 771 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.58 (d, *J* 8.4 Hz, 2 H), 7.24 (dd, *J* 8.4 Hz, 7.3 Hz, 2 H), 7.02 (d, *J* 7.2 Hz, 2 H), 2.98 (s, 6 H), 2.00 (hept, *J* 7.5 Hz, 3 H), 1.17 (d, *J* 7.5 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 146.3, 131.7, 126.0, 124.6, 123.2, 111.8, 26.6, 18.8, 14.0; m/z (TOF ASAP+) calculated for $C_{23}H_{34}NSi$ $[M+H]^+$; 352.2461, found 352.2465 (PPM error 1.2).

(9-(Triisopropylsilyl)-9H-carbazole-4,5-diyl)dimethanol [3a] and (9-(Triisopropylsilyl)-9H-carbazol-4-yl)methanol [22a]



3a



22a

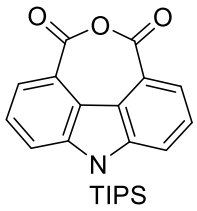
Following General Procedure 2: [From 6.46 mmol **1a**, using paraformaldehyde as the electrophile (10 eq.).] The reaction mixture was poured into sat. $NH_4Cl_{(aq)}$ (100 mL) and

extracted with EtOAc (3 × 80 mL). The combined organic extracts were washed with brine (3 × 80 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give an orange oil. The orange oil was purified by flash column chromatography (hexane/EtOAc; 3:1 to 1:1) to give **22a** (524 mg, 23%) as a yellow oil followed by **3a** (1.05 g, 43%) as an off-white crystalline solid.

Analytical data for [3a] R_f = 0.30 (hexane:EtOAc, 1:1); mp 95 – 96 °C (hexane); ν_{max} (solid, cm^{-1}) 3304 br, 2948 m, 2869 m, 1604 w, 1585 m, 1464 m, 1420 s, 1272 s 1236 m, 1037 w, 1010 s, 982 m, 883 m, 846 m, 778 s, 728 s, 719 s, 682 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.74 (dd, *J* 8.4 Hz, 0.9 Hz, 2 H), 7.34 (dd, *J* 8.4 Hz, 7.3 Hz, 2 H), 7.24 (dd, *J* 7.2 Hz, 0.8 Hz, 2 H), 5.22 (s, 4 H), 3.47 (br s, 2 H) 1.99 (hept, *J* 7.5 Hz, 3 H), 1.17 (d, *J* 7.5 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 146.7, 134.7, 124.8, 123.8, 122.9, 114.1, 67.0, 18.6, 13.9; m/z (TOF ES+) calculated for $C_{23}H_{33}NO_2SiNa$ $[M+Na]^+$; 406.2178, found 406.2190 (PPM error −3.0).

Analytical data for [22a] R_f = 0.31 (hexane:EtOAc, 3:1); ν_{max} (oil, cm^{-1}) 3357 br, 2949 m, 2868 m, 1725 w, 1588 w, 1450 s, 1427 s, 1265 s, 1209 s, 1002 s, 881 s, 726 s, 682 m; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.24 (dd, *J* 7.9 Hz, 0.7 Hz, 1 H), 7.76 (d, *J* 8.5 Hz, 1 H), 7.71 (d, *J* 8.3 Hz, 1 H), 7.42 – 7.34 (stack, 2 H), 7.30–7.25 (stack, 2 H), 5.29 (s, 2 H), 2.02 (hept, *J* 7.5 Hz, 3 H), 1.21 (d, *J* 7.6 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 145.7, 145.4, 134.9, 125.8, 125.2, 125.0, 124.0, 123.0, 120.0, 119.3, 114.1, 114.0, 64.7, 18.8, 14.0; m/z (TOF MS Cl+) calculated for $C_{22}H_{35}N_2OSi$ $[M+NH_4]^+$; 371.2519, found 371.2533 (PPM error 3.8)

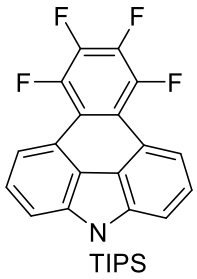
4-(Triisopropylsilyl)-4H-oxepino[3,4,5,6-def]carbazole-8,10-dione [4a]



Following General Procedure 2: [From, 4.75 mmol **1a**, using carbon dioxide (dry ice) as the electrophile (>100 eq.).] The reaction mixture was poured into concentrated HCl (37 w/w%, 8 mL) at 0 °C and allowed to stir at this temperature for 1 h prior to diluting with H_2O (80 mL) and extracting with CH_2Cl_2 (3 × 80 mL). The combined organic extracts were washed with brine (3 × 80 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure to give a brown solid. The brown solid was purified by trituration with hexane, to give **4a** (1.17 g, 63%) as a beige solid. R_f = 0.29 (CH_2Cl_2:MeOH, 9:1); mp 207 – 209 °C

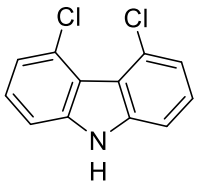
(hexane); ν_{max} (solid, cm^{-1}) 2951 br, 2869 br, 1692 s, 1421 m,1302 s, 1263 s, 1028 w, 880 w, 754 w, 735 w; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.96 (d, *J* 8.5 Hz, 2H), 7.77 (d, *J* 7.3 Hz, 2 H), 7.45 (dd, J 8.4 Hz, 7.6 Hz, 2 H), 2.02 (hept, J 7.5 Hz, 3 H), 1.22 (d, *J* 7.5 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 176.6, 146.5, 127.5, 125.2, 122.2, 122.0, 118.4, 18.7, 14.1; m/z (TOF ES+) calculated for $C_{23}H_{28}NO_3Si$ $[M+H]^+$; 394.1838, found 394.1839 (PPM error 0.3).

8,9,10,11-Tetrafluoro-4-(triisopropylsilyl)-4H-naphtho[1,2,3,4-def]carbazole [5a]



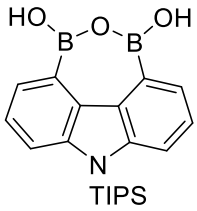
Following General Procedure 2: [From, 0.65 mmol **1a**, using hexafluorobenzene as the electrophile (8 eq).] The mixture was poured into ice/water (8 mL) and extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with brine (20 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure to give an orange solid. The crude material was purified by automated flash column chromatography (hexane) to give **5a** (103.6 mg, 34%) as a white solid. R_f = 0.31 (hexane); mp 207 − 208 °C (hexane); ν_{max} (solid, cm^{-1}) 2950 m, 2870 m, 1570 m, 1489 s, 1451 s, 1369 m, 1256 m, 1112 m, 952 s, 864 s, 778 s, 767 s, 718 s; ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 8.45 (d, *J* 7.7 Hz, 2 H), 7.88 (d, *J* 8.0 Hz*,* 2 H), 7.81 (t, *J* 7.9 Hz, 2 H), 2.12 (hept, *J* 7.5 Hz, 3 H), 1.27 (d, *J* 7.5 Hz, 18 H). ^{13}C NMR ($CDCl_3$,126 MHz) δc 147.4 (dm, *J* 250.5 Hz), 144.0, 139.2 (dm, *J* 253.1 Hz), 127.5, 124.0, 122.2, 117.9 (m) 117.5 (m), 112.6, 18.6, 13.8; ^{19}F NMR ($CDCl_3$, 471 MHz) δ -139.3 (d, *J* 16.5 Hz), -158.1 (d, *J* 16.4 Hz); m/z (TOF ASAP+) calculated for $C_{27}H_{28}NSiF_4$ $[M+H]^+$;470.1927, found 470.1937 (PPM error 2.1).

4,5-Dichloro-9H-carbazole [6b]



Following General Procedure 2: [From 0.64 mmol **1a**, using hexachloroethane as the electrophile (10 eq.).] The reaction mixture was poured into H_2O (20 mL) and extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with 10 w/w% $NaHCO_{3(aq)}$ (40 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give a brown oil. The brown oil was dissolved in THF (6.4 mL), treated with tetrabutylammonium fluoride solution (1.0 M in THF, 0.96 mL, 0.96 mmol), and allowed to stir for 15 min at rt. The solvent was removed under reduced pressure and the residue dissolved in EtOAc (10 mL). The mixture was sequentially washed with H_2O (2 × 10 mL) and brine (2 × 10 mL), and the organic extracts dried over sodium sulfate, filtered, and concentrated under reduced pressure to give a brown oil. The brown oil was purified by automated flash column chromatography (hexane/EtOAc 95:5) to give 4-chloro-9H-carbazole[5] (16.4 mg, 13%) as yellow solid followed by **6b** (52.6 mg, 35%) as a beige crystalline solid. R_f = 0.30 (hexane:EtOAc, 85:15); mp 173 – 175 °C (hexane); ν_{max} (solid, cm^{-1}) 3417 s, 2957 w, 2925 w, 2855 m, 1603 m, 1561 m, 1493 w, 1476 m, 1427 s, 1380 w, 1305 s, 1148 m, 1133 m,934 m, 845 w, 765 s, 712 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.33 (br s, 1 H), 7.35 – 7.33 (m, 4 H), 7.33 – 7.29 (m, 2 H); ^{13}C NMR (101 MHz) δ_C 141.3, 128.1, 127.0, 123.0, 119.9, 109.2; m/z (TOF ES+) calculated for $C_{12}H_7{}^{35}Cl_2N$ $[M+]^+$; 234.9956, found 234.9955 (PPM error −0.4).

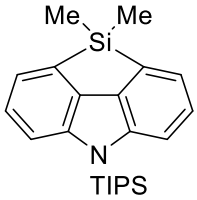
4-(Triisopropylsilyl)-4H-[1,2,7]oxadiborepino[3,4,5,6-def]carbazole-8,10-diol [7a]



Following General Procedure 2: [From 4.67 mmol **1a**, using trimethyl borate as the electrophile (10 eq.).] The reaction mixture was poured into $HCl_{(aq)}$ (3 M, 80 mL) and allowed to stir for 3 h at rt. The mixture was diluted with H_2O (100 mL) and extracted with EtOAc (3 × 100 mL). The combined organic extracts were washed with brine (100 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude material was purified by trituration using hexane to give **7a** (1.21 g, 66%) as a beige solid. R_f = 0.30 (hexane:EtOAc, 7:3; visualized using curcumin dip,[6] appears as orange spot with heating); mp 175 – 177 °C (hexane); ν_{max} (solid, cm^{-1}) 2947 br, 2867 br, 1595 w, 1294 w, 1331 w, 1258 s, 1016 w, 957 w, 919 w, 879 s, 732 s, 638 m; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.93 (app d, *J* 7.8 Hz, 4 H), 7.49 (app t, *J* 7.8 Hz, 2 H), 4.74 (s, 2 H), 2.03 (hept, *J* 7.5. Hz, 3 H), 1.20 (d, *J* 7.5 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 145.0, 132.2, 127.8, 125.2, 117.4, 18.7, 14.0, missing one quaternary

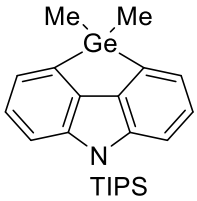
carbon signal; ^{11}B NMR (128.37 MHz) δ_B 28.5; m/z (TOF ES+) calculated for $C_{21}H_{30}{}^{10}B^{11}BNO_3Si$ $[M+H]^+$; 393.2217, found 393.2228 (PPM error 2.8).

8,8-Dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [8a]



Following General Procedure 2: [From 0.31 mmol **1a**, using dichlorodimethylsilane as the electrophile (4 eq.).] The reaction mixture was poured into sat. $NaHCO_{3(aq)}$ (20 mL) and extracted with CH_2Cl_2 (2 × 10 mL). The combined organic extracts were washed with brine (20 mL), dried over sodium sulfate, filtered and concentrated under reduced pressure to give an orange oil. The orange oil was purified by flash column chromatography (hexane) to give **8a** (86.8 mg, 74%) as a colourless solid. R_f = 0.29 (hexane); mp 115 – 117 °C (EtOH); ν_{max} (solid, cm^{-1}) 2948 br, 2867 br, 1603 w, 1499 w, 1439 w, 1388 w, 1204 m, 1145 m, 1014 w, 870 m, 840 s, 759 s, 645 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.46 (dd, *J* 7.6 Hz, 0.6 Hz, 2 H), 7.36–7.30 (stack, 4 H), 1.94 (hept, *J* 7.6 Hz, 3 H), 1.20 (d, *J* 7.6 Hz, 18 H), 0.63 (s, 6 H); ^{13}C NMR (101 MHz) δ_C 141.6, 140.5, 132.9, 127.2, 123.5, 115.5, 18.5, 13.5, –1.5; m/z (TOF ASAP+) calculated for $C_{23}H_{33}NSiNa$ $[M]^+$; 402.2044, found 402.2037 (PPM error 1.8).

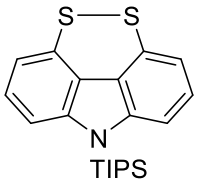
8,8-Dimethyl-4-(triisopropylsilyl)-4,8-dihydrogermolo[2,3,4,5-def]carbazole [9a]



Following General Procedure 2: [From 0.77 mmol **1a**, using dimethylgermanium dichloride as the electrophile (4 eq.).] The reaction mixture was poured into sat. $NaHCO_{3(aq)}$ (30 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with brine (30 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure to give a red oil. The red oil was purified by flash column chromatography (hexane) to give **9a** (125.8 mg, 39%) as a colourless solid. R_f = 0.22 (hexane); mp 114 – 116 °C (hexane); ν_{max} (solid, cm^{-1}) 2941 br, 2865 br, 1393 w, 1220 w, 990 w, 867 w, 721 m, 648 m; ^{1}H NMR ($CDCl_3$, 400

MHz) δ_H 7.45 (dd, *J* 7.3 Hz, 1.2 Hz, 2 H), 7.36–7.30 (stack, 4 H), 1.94 (hept, *J* 7.6 Hz, 3 H), 1.20 (d, *J* 7.6 Hz, 18 H), 0.80 (s, 6 H); ^{13}C NMR (101 MHz) δ_C 140.8, 140.7, 135.3, 127.1, 123.5, 114.7, 18.6, 13.5, –0.4; m/z (TOF ASAP$^+$) calculated for $C_{23}H_{32}NSi^{72}Ge$ $[M]^+$; 422.1703, found 422.1713 (PPM error 2.4).

9-(Triisopropylsilyl)-9H-[1,2]dithiino[3,4,5,6-def]carbazole [10a]



Following General Procedure 2: [From 3.1 mmol **1a**, using sulfur as the electrophile (8 eq).] The reaction mixture was poured into $NaOH_{(aq)}$ (2 M, 100 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed sequentially with H_2O (50 mL) and brine (50 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure to give an orange oil. The orange oil was purified by flash column chromatography (hexane) to give **10a** (638.1 mg, 54%) as a yellow solid.

Following General Procedure 2 followed by sodium borohydride reduction of di:trisulfide mixture: [From 6.2 mmol **1a**, using sulfur as the electrophile (8 eq).] The reaction mixture was poured into $HCl_{(aq)}$ (1 M, 50 mL) and stirred rapidly, open to the air, for 20 min. The mixture was partitioned and the aqueous layer extracted with CH_2Cl_2 (4 × 50 mL). The combined organic extracts were washed with brine (50 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure to give an orange oil. The orange oil was partially purified by flash column chromatography (hexane) to give a mixture of **10a**:**11a** (1.42 g, 1:~2.2 ratio by integration of ^{1}H NMR*) as a yellow oil that solidified on standing. The yellow solid was dissolved in THF:EtOH (1:1, 0.1 M, 35 mL), treated with sodium borohydride (661.1 mg, 17.5 mmol) and the resulting mixture heated at 50 °C for 3.5 h. The mixture was cooled to rt and treated with $NaOH_{(aq)}$ (1 M, 50 mL). The mixture was partitioned and the aqueous layer extracted with CH_2Cl_2 (3 × 75 mL). The combined organic extracts were concentrated under reduced pressure and the residue dissolved in CH_2Cl_2 (100 mL). The solution was washed sequentially with H_2O (100 mL) and brine (100 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure to give **10a** (1.05 g, 44% over 2 steps) as a yellow solid.

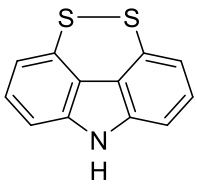
*Trisulfide **11a** additionally identified by low resolution mass spectroscopy.

Analytical data for [10a] R_f = 0.25 (hexane); mp 141 – 143 °C (hexane); ν_{max} (solid, cm^{-1}) 2946 br, 2866 br, 1610 w, 1556 w, 1464 m, 1425 s, 1253 s, 1183 m, 1151 m, 997 s, 880 s, 764 s, 719 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.47 (d, *J* 8.5 Hz, 2 H), 7.28 (dd, *J* 8.5 Hz, 7.5 Hz, 2 H), 7.00 (d, *J* 7.4 Hz, 2 H), 1.94 (hept, *J* 7.5 Hz, 3 H), 1.19 (d, *J* 7.5 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 144.2, 127.5, 124.2, 123.5, 116.9, 113.8, 18.6, 13.8; m/z (TOF ASAP+) calculated for $C_{21}H_{28}NSiS_2$ $[M+H]^+$; 386.1432, found 386.1436 (PPM error 1.0).

Peaks assignable to trisulfide [11a] in ^{1}H NMR prior to sodium borohydride reduction

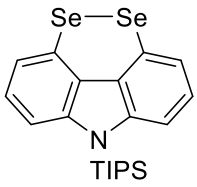
^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.77 (dd, *J* 8.2 Hz, 1.3 Hz, 2 H), 7.35 (dd, *J* 7.5 Hz, 1.2 Hz, 2 H), 7.30 (dd, *J* 8.2 Hz, 7.5 Hz, 2 H), 1.99 (hept, J 7.4 Hz, 3 H), 2.01 (d, J 7.4 Hz, 18 H).

9-(Triisopropylsilyl)-9H-[1,2]dithiino[3,4,5,6-def]carbazole [10b]



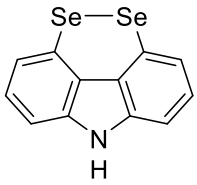
Tetrabutylammonium fluoride solution (1 M in THF, 6.48 mL, 6.48 mmol) was added to a solution of **10a** (1.00 g, 2.59 mmol) in THF (26 mL). The mixture was allowed to stir for 15 min prior to concentrating under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 mL) and washed sequentially with water (2 × 10 mL) and brine (20 mL). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give a red solid. The red solid was purified by flash column chromatography (hexane:EtOAc, 9:1) to give **10b** (389 mg, 66%) as a yellow solid; R_f = 0.08 (hexane:EtOAc, 9:1); mp 98 – 100 °C (EtOH); ν_{max} (solid, cm^{-1}) 3388 br, 1709 m, 1594 m, 1420 m, 1317 m, 1152 m, 761 s, 709 s; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 8.01 (br s, 1 H), 7.33 (dd, *J* 8.1 Hz, 7.5 Hz, 2 H), 7.22 (d, *J* 7.8 Hz, 2 H), 6.99 (dd, *J* 7.4 Hz, 0.4 Hz, 2 H); ^{13}C NMR (101 MHz) δ_C 138.0, 128.1, 124.4, 120.9, 116.5, 110.2; m/z (TOF AP+) calculated for $C_{12}H_8NS_2$ $[M]^+$; 230.0098, found 230.0097 (PPM error –0.4).

9-(Triisopropylsilyl)-9H-[1,2]diselenino[3,4,5,6-def]carbazole [12a]



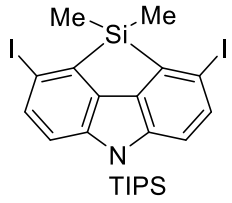
Following General Procedure 2: [From 2.5 mmol **1a**, using selenium as the electrophile (8 eq.).] The reaction mixture was poured into H_2O (50 mL) and extracted with Et_2O (3 × 40 mL). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude material was purified by flash column chromatography (hexane) to give **12a** (512 mg, 43%) as a dark burgundy crystalline solid. R_f = 0.43 (hexane); mp 140 – 141 °C (hexane); ν_{max} (solid, cm^{-1}) 2946 br , 2864 br, 1578 w, 1460 m, 1420 s, 1256 s, 1185 m, 989 s, 881 m, 765 s, 713 s, 648 s, 586s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.53 (dd, *J* 8.5 Hz, 0.5 Hz, 2 H), 7.29 (dd, *J* 8.5 Hz, 7.4 Hz, 2 H), 7.16 (dd, *J* 7.4 Hz, 0.6 Hz, 2 H), 1.99 (hept, *J* 7.6 Hz, 3 H), 1.22 (d, *J* 7.5 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 144.8, 127.2, 125.5, 119.4, 116.6, 113.9, 18.7, 13.9; ^{77}Se NMR (76 MHz, $CDCl_3$) 244.6; m/z (TOF ASAP+) calculated for $C_{21}H_{28}NSi^{80}Se_2$ $[M+H]^+$; 482.0321, found 482.0328 (PPM error 1.5).

9H-[1,2]diselenino[3,4,5,6-def]carbazole [12b]



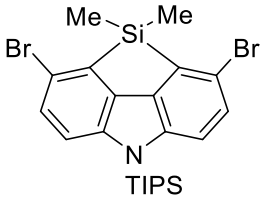
Tetrabutylammonium fluoride solution (1 M in THF, 7.51 mL, 7.51 mmol) was added to a solution of **12a** (361.0 mg, 7.50 mmol) in THF (15 mL). The mixture was allowed to stir for 2.5 h then treated with H_2O (10 mL) and extracted with Et_2O (2 × 20 mL). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give **12b** (210 mg, 86%) as a red crystalline solid. R_f = 0.43 (hexane:Et_2O, 4:1); mp 143 – 144 °C (hexane); ν_{max} (solid, cm^{-1}) 3392 br s, 1586 s, 1427 s, 1421 s, 1378 w, 1306 s, 1275 m, 1189 w, 1169 s, 1134 w, 888 m, 865 m, 757 s, 710 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.04 (br s, 1 H), 7.32 (dd, *J* 8.1 Hz, 7.4 Hz, 2 H), 7.23 (dd, *J* 8.1 Hz, 0.7 Hz, 2 H), 7.13 (dd, *J* 7.4 Hz, 0.7 Hz, 2 H); ^{13}C NMR (101 MHz) δ_C 138.6, 128.0, 122.9, 118.7, 116.8, 110.3; ^{77}Se NMR (76 MHz, $CDCl_3$) 265.6; m/z (TOF EI$^+$) calculated for $C_{12}H_8N^{76}Se^{78}Se$ $[M+H]^+$; 319.9022, found 319.9031 (PPM error 2.8).

1,7-Diiodo-8,8-dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [13a]



N-Iodosuccinimide (130.1 mg, 0.58 mmol) was added to a solution of **8a** (100.4 mg, 0.26 mmol) in acetic acid (2.6 mL) and the resultant mixture allowed to stir for 22 h. Water (10 mL) was added to the mixture and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with brine (10 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure to give a beige solid. The beige solid was purified by automated flash column chromatography (hexane) to give **13a** (117.7 mg, 70%) as a colourless solid. R_f = 0.61 (hexane); mp 162 – 164 °C (hexane); ν_{max} (solid, cm^{-1}) 2946 br, 2865 br, 1597 w, 1482 w, 1459 w, 1436 m, 1421 m, 1391 m, 1286 w, 1241 m, 1214 m, 1189 s, 1151 m, 1070 w, 1013 s, 991 m, 882 m, 841 s, 800 s, 841 s, 783 s, 748 s, 701 s, 674 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.53 (d, *J* 8.3 Hz, 2 H), 7.19 (d, *J* 8.3 Hz, 2 H), 1.85 (hept, *J* 7.5 Hz, 3 H), 1.17 (d, *J* 7.5 Hz, 18 H), 0.68 (s, 6H); ^{13}C NMR (101 MHz) δ_C 142.7, 141.4, 140.1, 135.7, 118.1, 87.5, 18.4, 13.3, –4.3; m/z (TOF ASAP+) calculated for $C_{23}H_{32}NSi_2I_2$ $[M+H]^+$; 632.0163, found 632.0168 (PPM error 0.8).

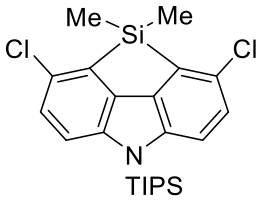
1,7-Dibromo-8,8-dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [14a]



N-Bromosuccinimide (104.7 mg, 0.59 mmol) was added to a solution of **8a** (100.8 mg, 0.27 mmol) in acetic acid (2.7 mL) and the resultant mixture allowed to stir for 22 h. Water (15 mL) was added to the mixture and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with brine (20 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure to give a colourless solid. The solid was purified by automated flash column chromatography (hexane) to give **14a** (129.9 mg, 91%) as a colourless solid. R_f = 0.57 (hexane); mp 174 – 176 °C (hexane); ν_{max} (solid, cm^{-1}) 2948 br, 2866 br, 1600 w, 1488 w,

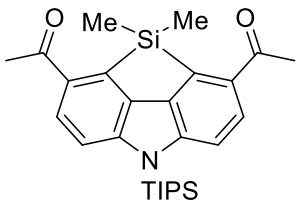
1459 w, 1440 m, 1425 m, 1391 m, 1366 w, 1288 w, 1247 m, 1214 m, 1190 s, 1152 m, 1071 w, 1032 m, 1014 m, 992 m, 924 w, 881 s, 842 s, 801 m, 784 s, 752 s, 704 m, 677 m, 654 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.34 (d, *J* 8.5 Hz, 2 H), 7.29 (d, *J* 8.4 Hz, 2 H), 1.86 (hept, *J* 7.5 Hz, 3 H), 1.17 (d, *J* 7.5 Hz, 18 H), 0.72 (s, 6H); ^{13}C NMR (101 MHz) δ_C 142.2, 139.8, 134.6, 130.3, 118.0, 117.3, 18.4, 13.3, –4.3; m/z (TOF ASAP+) calculated for $C_{23}H_{32}NSi_2Br_2$ $[M+H]^+$; 536.0440, found 536.0446 (PPM error 1.1).

1,7-Dichloro-8,8-dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [15a]



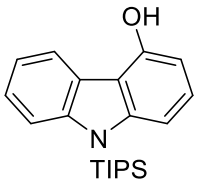
N-Chlorosuccinimide (82.0 mg, 0.61 mmol) was added to a solution of **8a** (99.4 mg, 0.26 mmol) in acetic acid (2.6 mL) and the resultant mixture heated at 50 °C for 24 h. Water (15 mL) was added to the mixture and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with brine (10 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude material was purified by automated flash column chromatography (hexane) to give **15a** (103.5 mg, 88%) as a colourless solid. R_f = 0.45 (hexane); mp 149 – 151 °C (hexane); ν_{max} (solid, cm^{-1}) 2951 br, 2868 br, 1605 w, 1494 w, 1391 m, 1447 m, 1430 m, 1391 w, 1369 w, 1244 m, 1214 m, 1191 s, 1151 w, 1071 w, 1050 s, 1012 m, 878 s, 837 s, 787 s, 758 s, 708 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.43 (d, *J* 8.4 Hz, 2 H), 7.20 (d, *J* 8.4 Hz, 2 H), 1.86 (hept, *J* 7.5 Hz, 3 H), 1.17 (d, *J* 7.5 Hz, 18 H), 0.74 (s, 6 H); ^{13}C NMR (101 MHz) δ_C 141.9, 139.6, 131.0, 129.7, 127.7, 117.6, 18.4, 13.4, –2.9; m/z (TOF ASAP+) calculated for $C_{23}H_{32}NSi_2Cl_2$ $[M+H]^+$; 448.1457, found 448.1450 (PPM error 1.6).

1,1'-(8,8-Dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole-1,7-diyl)bis(ethan-1-one) [16a]



8,8-Dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole **8a** (101.0 mg, 0.27 mmol) was added to a suspension of aluminium chloride (108.8 mg, 0.82 mmol) in acetyl chloride (0.04 mL, 0.56 mmol) and CH_2Cl_2 (1.3 mL), and the resultant mixture allowed to stir for 30 min. The reaction mixture was treated with $HCl_{(aq)}$ (1 M, 10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with brine (10 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure to give a beige solid. The beige solid was purified by automated flash column chromatography (hexane:EtOAc, 9:1) to give **16a** (61.2 mg, 50%) as a colourless solid. R_f = 0.26 (hexane:EtOAc, 9:1); mp 205 – 207 °C (hexane); ν_{max} (solid, cm^{-1}) 2948 br, 2867 br, 1665 m, 1603 m, 1530 w, 1489 m, 1461 m, 1423 m, 1384 m, 1353 m, 1253 m, 1199 s, 1152 m, 1071 w, 1015 m, 961 w, 880 s, 842 s, 802 s, 787 s, 748 s, 704 s, 674 s, 652 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.98 (d, *J* 8.4 Hz, 2 H), 7.50 (d, *J* 8.4 Hz, 2 H), 2.69 (s, 6 H), 1.95 (hept, *J* 7.6 Hz, 3 H), 1.22 (d, *J* 7.5 Hz, 18 H), 0.77 (s, 6 H); ^{13}C NMR (101 MHz) δ_C 198.0, 144.0, 142.0, 136.1, 135.2, 129.6, 115.0, 27.0, 18.4, 13.4, –4.2; m/z (TOF ASAP+) calculated for $C_{27}H_{38}NO_2Si_2$ $[M+H]^+$; 464.2441, found 464.2450 (PPM error 1.9).

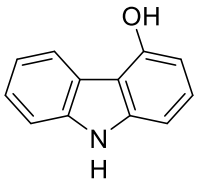
9-(Triisopropylsilyl)-9H-carbazol-4-ol [17a]



Potassium fluoride dihydrate (173.6 mg, 1.84 mmol) and potassium hydrogen carbonate (183.3 mg, 1.83 mmol) were added to a solution of **8a** (169.4 mg, 0.45 mmol) in THF:MeOH (1:1, 2 mL) at 0 °C. To this mixture was added hydrogen peroxide solution (30%, 1.37 mL, 13.4 mmol), after 10 min the cooling bath was removed, and the mixture allowed to stir for 21 h. Sat. $Na_2S_2O_{3(aq)}$ (25 mL) was added dropwise and the resultant mixture extracted with EtOAc (3 × 25 mL). The combined organic extracts were washed sequentially with H_2O (25 mL) and brine (25 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure to give an orange oil. The orange oil was purified by automated flash column chromatography (hexane to hexane:EtOAc, 9:1) to give**17a** (87.6 mg, 58%) as a colourless oil. R_f = 0.29 (hexane:EtOAc, 9:1); ν_{max} (oil, cm^{-1}) 3516 br, 2948 br, 2867 br, 1630 w, 1580 w, 1437 s, 1242 m, 1047 s, 880 m, 785 m, 754 s, 717 s, 645 m; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.36 (ddd, *J* 7.7 Hz, 1.5 Hz, 0.9 Hz, 1 H), 7.68 (d, *J* 8.4 Hz, 1 H), 7.34 (ddd, *J* 8.4 Hz, 7.2 Hz, 1.5 Hz, 1 H), 7.29 (d, *J* 8.4 Hz, 1 H), 7.24 (ddd, *J* 7.9 Hz, 7.0 Hz, 0.9 Hz, 1 H), 7.18 (dd, *J* 8.4 Hz, 7.8 Hz, 1 H), 6.58 (d, *J* 7.5 Hz, 1 H), 5.24 (s, 1 H), 1.99 (hept, *J* 7.6 Hz, 3 H), 1.20 (d, *J*

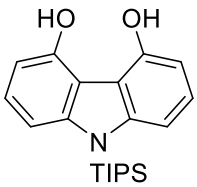
7.6 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 151.8, 147.2, 144.6, 133.7, 125.7, 124.6, 122.8, 119.8, 114.9, 113.6, 107.2, 105.4, 18.7, 14.0; m/z (TOF ASAP+) calculated for $C_{21}H_{30}NOSi$ $[M+H]^+$; 340.2097, found 340.2101 (PPM error 1.2).

9H-Carbazol-4-ol [17b][7]



Tetrabutylammonium fluoride solution (1 M in THF, 0.27 mL, 0.27 mmol) was added to a solution of **17a** (61.4 mg, 0.18 mmol) in THF (0.9 mL). The mixture was allowed to stir for 2.5 h then treated with saturated $NH_4Cl_{(aq)}$ (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed sequentially with H_2O (10 mL) and brine (10 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure to give a yellow oil. The yellow oil was purified by automated flash column chromatography (CH_2Cl_2 to CH_2Cl_2:MeOH, 9:1) to give **17b** (30.4 mg, 92%) as a colourless solid. R_f = 0.52 (CH_2Cl_2); mp 171 – 172 °C (CH_2Cl_2); ν_{max} (solid, cm^{-1}) 3395 br, 3211 br, 1637 w, 1608 m, 1586 m, 1505 m, 1446 s, 1330 m, 1306 m, 1268 m, 1205 m, 1043 s, 999 m, 930 m, 783 m, 751 s, 718 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.28 (dd, *J* 7.8 Hz, 0.7 Hz, 1 H), 8.06 (br s, 1 H), 7.42 – 7.40 (stack, 2 H), 7.28 – 7.22 (stack, 2 H), 7.02 (dd, *J* 8.1 Hz, 0.6 Hz, 1 H), 6.59 (dd, *J* 7.8 Hz, 0.5 Hz, 1 H), 5.39 (s, 1 H); ^{13}C NMR (101 MHz) δ_C 152.0, 141.5, 139.0, 126.7, 125.3, 122.9, 122.5, 119.9, 111.9, 110.2, 106.3, 103.5; m/z (TOF ASAP$^+$) calculated for $C_{12}H_{10}NO$ $[M+H]^+$; 184.0762, found 184.0757 (PPM error –2.7).

9-(triisopropylsilyl)-9H-carbazole-4,5-diol [18a]

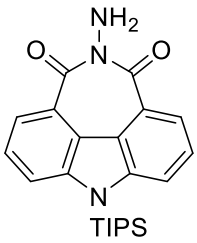


N-Methylmorpholine *N*-oxide (207 mg, 1.768 mmol) was added to a suspension of **7a** (139.1 mg, 0.353 mmol) in anhydrous acetonitrile (2.7 mL) and the mixture heated to reflux for 3 h. The reaction was monitored by TLC, using curcumin dip[6] with heating to visualize disappearance of the boronic anhydride **7a**. The mixture was then concentrated under reduced

pressure and the resulting residue purified by automated flash column chromatography (hexane to hexane:EtOAc, 9:1) to give **18a** (15.8 mg, 13%) as a colourless oil followed by **17a** 39.1 mg (31%) as a beige solid.

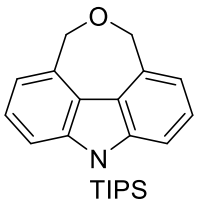
Analytical data for [18a] R_f = 0.30 (hexane:EtOAc, 85:15); mp 156 – 158 °C (hexane); ν_{max} (solid, cm^{-1}) 3212 br, 2950 m, 2869 m, 1610 m, 1585 m, 1446 s, 1393 w, 1271 w, 1237 m, 1092 m, 1062 m, 1036 w, 900 w, 770 m, 718 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.26 (s, 2 H), 7.28 (dd, *J* 8.4 Hz, 0.5 Hz, 2 H), 7.21 (dd, *J* 8.4 Hz, 7.7 Hz, 2 H), 6.70 (dd, *J* 7.6 Hz, 0.5 Hz, 2 H), 1.98 (hept, *J* 7.5 Hz, 3 H), 1.19 (d, *J* 7.5 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 149.2, 146.8, 126.1, 113.5, 107.0, 105.9, 18.8, 14.0; m/z (TOF ES−) calculated for $C_{21}H_{28}NO_2Si$ $[M-H]^-$; 354.1889, found 354.1891 (PPM error 0.6).

9-Amino-4-(triisopropylsilyl)azepino[3,4,5,6-def]carbazole-8,10(4H,9H)-dione [19a]



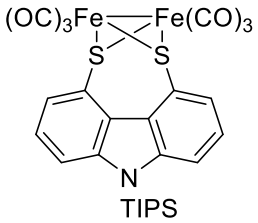
Hydrazine monohydrate (0.02 mL, 0.411 mmol) was added to a solution of **4a** (115.2 mg, 0.292 mmol) in methanol (9 mL) and the mixture heated at reflux for 24 h. The mixture was allowed to cool and the resulting precipitate was filtered, washed with methanol and dried under reduced pressure to give **19a** (35.7 mg, 30%) as a white powder which required no further purification. R_f = 0.31 (CH_2Cl_2/EtOAc, 2:8); mp 169 − 170 °C (MeOH); ν_{max} (solid, cm^{-1}) 3624 w br, 3356 w, 3269 w, 2949 m, 2866 m, 1695 m, 1574 m, 1464 w, 1421 w, 1381 w, 1263 s, 1031 s, 990 m, 878 m, 842 m, 807 s, 756 s; ^{1}H NMR (DMSO-d_6, 500 MHz) δ_H 7.80 (d, *J* 8.0 Hz, 2 H), 7.48 (d, *J* 6.8 Hz, 2 H), 7.37 (app t, *J* 7.3 Hz, 2 H), 9 − 6.5 (br, 2 H), 2.05 (hept, *J* 6.9 Hz, 3 H), 1.16 (d, *J* 6.7 Hz, 18 H); ^{13}C NMR (126 MHz) δ_C 172.4, 145.4, 134.13, 124.4, 122.7, 120.1, 115.0, 18.4, 13.2; m/z (TOF ASAP+) calculated for $C_{23}H_{30}N_3O_2Si$ $[M+H]^+$;408.2107, found 408.2097 (PPM error –2.4).

4-(Triisopropylsilyl)-8,10-dihydro-4H-oxepino[3,4,5,6-def]carbazole [20a]



Diol **3a** (131.0 g, 0.34 mol) was suspended in 50% $H_3PO_{4(aq)}$ (2 mL) and heated at 90 °C for 11 h. The mixture was cooled to rt, diluted with H_2O (20 mL) and extracted by EtOAc (3 × 20 ml). The combined organic extracts were washed with sat. $NaHCO_{3(aq)}$ (20 mL), and dried over sodium sulfate, filtered and the solvent removed under reduced pressure to afford an off-white solid, which was purified by automated flash column chromatography (hexane:EtOAc, 95:5) to give **20a** (69.2 mg, 56%) as an off-white crystalline solid. R_f = 0.31 (hexane:EtOAc, 95:5); mp 133 − 134 °C (hexane), ν_{max} (solid, cm^{-1}) 2946 m, 2866 m, 1610 w, 1583 w, 1464 m, 1433 s, 1375 m, 1308 m, 1287 m, 1262 s, 1244 s, 1112 m, 1069 m, 1016 m, 879 s, 768 s, 729 s, 676 s, 668 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.59 (dd, *J* 8.5 Hz, 2 H), 7.27 (dd, *J* 8.4 Hz, 7.3 Hz, 2H), 6.94 (dd, *J* 7.2 Hz, 0.5 Hz, 2 H), 5.31 (s, 4H), 2.01 (hept, *J* 7.5 Hz, 3 H), 1.20 (d, *J* 7.5 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 145.2, 136.2, 125.1, 124.2, 116.1, 112.9, 77.6, 18.7, 14.0; m/z (TOF MS) calculated for $C_{23}H_{32}NOSi$ $[M+H]^+$; 366.2253, found 366.2264 (PPM error 3.0).

Iron hexacarbonyl complex [21a]



Triiron dodecacarbonyl (132.0 mg, 0.26 mmol) was added to a solution of **10a** (100.0 mg, 0.26 mmol) in toluene (10 mL), and the mixture heated to reflux for 1 h. The reaction mixture was then concentrated under reduced pressure to give a red solid. The red solid was purified by flash column chromatography (hexane) to give **21a** (113 mg, 66%) as a red solid. R_f = 0.25 (hexane); mp 164 °C dec. (hexane); ν_{max} (solid, cm^{-1}) 2952 w, 2871 w, 2071 s, 2028 s, 2008 s, 1978 s, 1972 s, 1597 m, 1571 m, 1461 m, 1412 m, 1348 m, 1270 m, 1246 m, 994 m, 880 m, 773 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.03 (d, *J* 7.6 Hz, 2 H), 7.85 (d, *J* 8.2 Hz, 2 H), 7.31 (dd, *J* 8.2 Hz, 7.8 Hz, 2 H), 2.00 (hept, *J* 7.5 Hz, 3 H), 1.14 (d, *J* 7.5 Hz, 18 H); ^{13}C NMR (101

MHz) δ_C 207.5, 146.9, 136.4, 130.3, 124.4, 123.4, 115.1, 18.6, 14.1; m/z (TOF ASAP+) calculated for $C_{27}H_{28}NO_6SiS_2{}^{54}Fe^{56}Fe$ $[M+H]^+$; 663.9873, found 663.9868 (PPM error –0.8).

Electrophile and substrate screen

Electrophile screen

In an initial screen, the following electrophiles reacted poorly (<10% 4,5-disubstitution):

DMF;[8] 9% lactone (from trapping and concomitant Cannizzaro reaction[9]), 22% mono aldehyde

$Cl(CO)CO_2Et$;[10] 4% diketone

$Br_2CHCHBr_2$;[11] 2% dibromide with concomitant desilylation

I_2;[12] 2% diiodide with concomitant desilylation

Tellurium;[13] provides trace ditelluride.

Carbon disulfide;[14] provides <5% mixture of **10a**:**11a**.

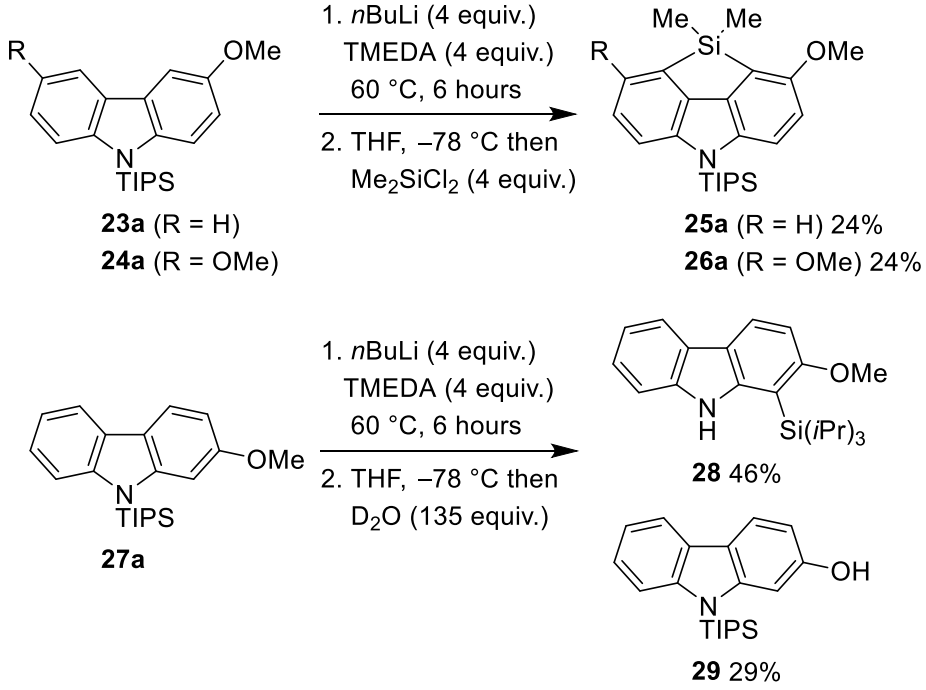
Formaldehyde (0.5 M) in THF;[15] 5% **3a**, 10% **29a** and 29% **1a**.

In an initial screen, the following electrophiles underwent no appreciable reaction and starting material was evident in the ^{1}H NMR of the crude reaction mixture:

$SiCl_4$,[16] $MeSiHCl_2$,[17] $(C_3H_6)SiCl_2$,[18] $PhPCl_2$,[19] $MgCl_2$•LiCl with $PhP(O)Cl_2$,[20] Me_2SnCl_2,[21] *N*-fluorobenzenesulfonimide (NSFI),[22-23] allyl bromide, $ZnCl_2$ and Br_2,[23] $ZnCl_2$ and CuCN•2LiCl with allyl bromide,[23] CuCN•2LiCl with allyl bromide, *p*-toluenesulfonyl azide,[24] benzyl bromide, $PhS(O)_2SPh$,[25] benzophenone,[26] oxalyl chloride,[10] diethyl oxalate,[10] *N*,*N*-dimethylcarbamyl chloride.[27]

Substrate screen

The *n*BuLi-TMEDA-directed metalation conditions were also investigated on methoxy-substituted *N*-TIPS carbazoles (Scheme S1). 3-Methoxycarbazole **23a** and 3,6-dimethoxycarbazole **24a** were converted into the corresponding silafluorenes **25a** and **26a** respectively, albeit in lower yield than for unsubstituted silafluorene **8a**. The 2-methoxycarbazole **27a** did not give any silafluorene. Subsequent investigation into the feasibility of the 4,5-dilithiation of **27a** using D_2O as a trap gave two compounds, with no evidence of deuterium incorporation. The aromatic silane **28** presumably arises from a retro [1,3]-aza-Brook rearrangement of a 1-lithiocarbazole, where the inherent preference of carbazoles for C1-lithiation coupled with the directing effect of the 2-OMe group is presumably sufficient to overcome the bulk of the TIPS group.[28] Demethylation of **27a** to phenol **29** was also a significant pathway.



23a (R = H)
24a (R = OMe)

25a (R = H) 24%
26a (R = OMe) 24%

27a

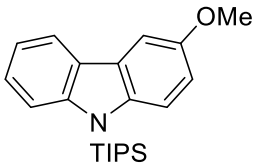
28 46%

29 29%

Scheme S1 Reactions of methoxy-substituted *N*-TIPS carbazoles.

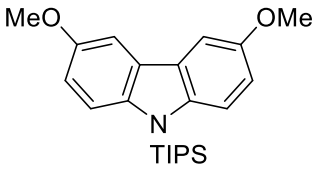
Experimental procedures and analytical data for **23-29** are reported below.

3-Methoxy-9-(triisopropylsilyl)-9H-carbazole [23a]



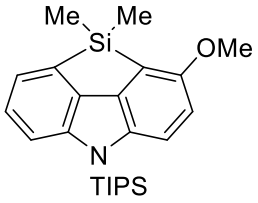
Following General Procedure 1: [From 17.3 mmol 3-methoxycarbazole with chlorotriisopropylsilane.] Purified by automated flash column chromatography (hexane:CH_2Cl_2, 9:1), **23a** (4.03 g, 66%) was obtained as a colourless oil that solidified on standing. R_f = 0.09 (hexane:CH_2Cl_2, 9:1); mp 73 – 75 °C (hex); ν_{max} (solid, cm^{-1}) 2947 br, 2866 br, 1627 w, 1595 w, 1481 s, 1449 s, 1439 s, 1391 w, 1301 w, 1263 m, 1239 s, 1198 s, 1176 s, 1119 w, 1070 w, 1039 s, 957 s, 921 w, 880 s, 851 s, 800 s, 747 s, 724 m, 686 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.02 (dd, *J* 7.8 Hz, 0.9 Hz, 1 H), 7.67 (d, *J* 8.5 Hz, 1 H), 7.59 (d, *J* 9.0 Hz, 1 H), 7.53 (d, *J* 2.7 Hz, 1 H), 7.34 (ddd, *J* 8.5 Hz, 7.1 Hz, 1.4 Hz, 1 H), 7.20 (ddd, *J* 7.8 Hz, 6.9 Hz, 0.7 Hz, 1 H), 6.99 (dd, *J* 9.1 Hz, 2.7 Hz, 1 H), 3.93 (s, 3 H), 1.97 (hept, J 7.5 Hz, 3 H), 1.19 (d, J 7.5 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 153.8, 145.9, 139.8, 127.2, 126.6, 125.4, 119.8, 119.2, 114.9, 114.3, 114.2, 102.4, 56.0, 18.7, 14.0; m/z (TOF ASAP+) calculated for $C_{22}H_{32}NOSi$ $[M+H]^+$; 354.2253, found 354.2260 (PPM error 2.0).

3,6-Dimethoxy-9-(triisopropylsilyl)-9H-carbazole [24a]



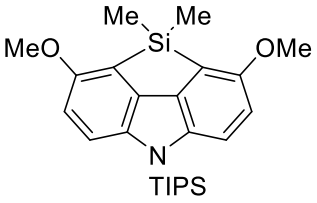
Following General Procedure 1: [From 9.01 mmol 3,6-dimethoxycarbazole with chlorotriisopropylsilane.] Purified by automated flash column chromatography (hexane:CH_2Cl_2, 9:1), **24a** (3.03 g, 88%) was obtained as a colourless solid. R_f = 0.44 (Hex:EtOAc, 9:1); mp 97 – 99 °C (hex); ν_{max} (solid, cm^{-1}) 2947 br, 2867 br, 1607 w, 1576 w, 1485 s, 1458 s, 1431 s, 1392 w, 1341 w, 1296 m, 1254 m, 1228 s, 1194 s, 1162 s, 1034 s, 1019 s, 960 s, 908 s, 885 s, 842 s, 800 s, 785 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.56 (d, *J* 9.1 Hz, 2 H), 7.47 (d, *J* 2.7 Hz, 2 H), 6.96 (dd, *J* 9.1Hz, 2.7 Hz, 2 H), 3.93 (s, 6 H), 1.94 (hept, *J* 7.5 Hz, 3 H), 1.18 (d, *J* 7.6 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 153.6, 140.6, 127.1, 115.1, 114.5, 102.2, 56.0, 18.7, 14.0; m/z (TOF ASAP+) calculated for $C_{23}H_{34}NO_2Si$ $[M+H]^+$; 384.2359, found 384.2362 (PPM error 0.8).

1-Methoxy-8,8-dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [25a]



Following General Procedure 2: [From 0.70 mmol **23a**, using dichlorodimethylsilane as the electrophile (4 eq.).] The reaction mixture was poured into sat. $NaHCO_{3(aq)}$ (15 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with brine (15 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude material was purified by automated flash column chromatography (hexane:CH_2Cl_2, 9:1) to give **25a** 68.2 mg (24%) as a yellow oil. R_f = 0.08 (hexane:CH_2Cl_2, 9:1); ν_{max} (oil, cm^{-1}) 2947 br, 2867 br, 1606 w, 1502 w, 1470 s, 1447 s, 1423 m, 1382 m, 1331 w, 1230 s, 1171 m, 1072 m, 1042 m, 1014 m, 957 w, 881 m, 861 m, 838 s, 799 s, 756 s, 685 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.45 – 7.41 (m, 1 H), 7.38 (d, *J* 8.5 Hz, 1 H), 7.31 (brs, 1 H), 7.30 (d, *J* 1.6 Hz, 1 H), 6.85 (d, *J* 8.6 Hz, 1 H), 3.93 (s, 6 H), 1.90 (hept, *J* 7.6 Hz, 3 H), 1.18 (d, *J* 7.6 Hz, 18 H), 0.69 (S, 6 H); ^{13}C NMR (101 MHz) δ_C 158.2, 141.9, 141.3, 141.0, 135.3, 132.1, 127.2, 122.8, 117.7, 116.1, 115.5, 112.5, 56.5, 18.5, 13.5, 0.2; m/z (TOF ASAP+) calculated for $C_{24}H_{36}NOSi_2$ $[M+H]^+$; 410.2335, found 410.2343 (PPM error 2.0).

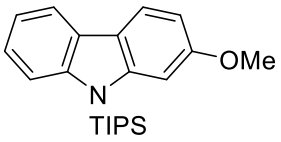
1,7-Dimethoxy-8,8-dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [26a]



Following General Procedure 2: [From 0.31 mmol **24a** with 1.87 mmol TMEDA, using dichlorodimethylsilane as the electrophile (4 eq.).] The reaction mixture was poured into sat. $NaHCO_{3(aq)}$ (15 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with brine (15 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude material was purified by automated flash column chromatography (hexane:CH_2Cl_2, 1:1) to give **26a** 32.1 mg (24%) as a colourless solid. R_f = 0.43 (hexane:CH_2Cl_2, 1:1); mp 103 – 105 °C (hexane); ν_{max} (solid, cm^{-1}) 2948 br, 2865 br,

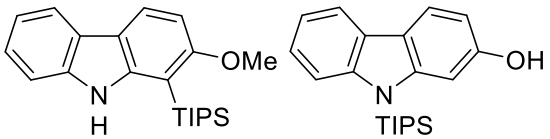
1592 w, 1542 w, 1474 m, 1451 s, 1426 m, 1371 w, 1331 w, 1300 w, 1224 s, 1207 s, 1178 m, 1140 w, 1059 m, 1013 m, 990 w, 948 w, 883 m, 836 m, 769 s, 705 m; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.36 (d, *J* 8.6 Hz, 2 H), 6.85 (d, *J* 8.6 Hz, 2 H), 3.93 (s, 6 H), 1.87 (hept, *J* 7.5 Hz, 3 H), 1.18 (d, *J* 7.5 Hz, 18 H), 0.77 (s, 6 H); ^{13}C NMR (101 MHz) δ_C 157.6, 141.6, 136.0, 117.5, 115.5, 112.7, 56.7, 18.5, 13.5, 1.5; m/z (TOF ASAP+) calculated for $C_{25}H_{38}NO_2Si_2$ $[M+H]^+$; 440.2441, found 440.2448 (PPM error 1.6).

2-Methoxy-9-(triisopropylsilyl)-9H-carbazole [27a]



Following General Procedure 1: [From 2.53 mmol 2-methoxycarbazole with chlorotriisopropylsilane.] Purified by automated flash column chromatography (hexane:CH_2Cl_2, 9:1), **27a** (843.5 mg, 94%) was obtained as a colourless oil that solidified on standing. R_f = 0.65 (hexane:EtOAc, 9:1); mp 75 – 77 °C (hex); ν_{max} (solid, cm^{-1}) 2951 br, 2865 br, 1627 w, 1597 w, 1573 w, 1494 w, 1457 s, 1422 w, 1350 w, 1329 w, 1268 m, 1187 s, 1150 s, 1128 s, 1044 m, 1011 m, 963 s, 914 m, 882 s, 839 m, 795 m, 759 s, 732 m, 648 s, 680 s; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.96 (dd, *J* 7.6 Hz, 0.9 Hz, 1 H), 7.93 (d, *J* 8.5 Hz, 1 H), 7.64 (d, *J* 8.4 Hz, 1 H), 7.28 (ddd, *J* 8.5 Hz, 7.1 Hz, 1.4 Hz, 1 H), 7.22 (d, *J* 2.3 Hz, 1 H), 7.20 (ddd, *J* 8.5 Hz, 7.1 Hz, 0.7 Hz, 1 H), 6.87 (dd, *J* 8.5 Hz, 2.1 Hz, 1 H), 3.90 (s, 3 H), 1.99 (hept, J 7.5 Hz, 3 H), 1.21 (d, J 7.5 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 158.5, 146.5, 145.2, 126.7, 124.2, 120.7, 120.1, 119.7, 119.0, 114.0, 107.4, 99.5, 55.8, 18.8, 13.9; m/z (TOF ES+) calculated for $C_{22}H_3NOSi$ $[M+H]^+$; 354.253, found 354.2263 (PPM error 2.8).

2-Methoxy-1-(triisopropylsilyl)-9H-carbazole [28] and 9-(Triisopropylsilyl)-9H-carbazol-2-ol [29]



[28] **[29]**

Following General Procedure 2: [From 0.42 mmol **27a** with 2.26 mmol TMEDA, using D_2O as the electrophile (89 eq.).] The reaction mixture was poured into sat. $NH_4Cl_{(aq)}$ (20 mL) and extracted with CH_2Cl_2 (4 × 15 mL). The combined organic extracts were washed with brine

(20 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude material was purified by automated flash column chromatography (hexane:CH_2Cl_2, 1:0 to 1:1) to give **28** (67.9 mg, 46%) as a colourless solid followed by **29** (41.3 mg, 29%) as a tan solid.

Analytical data for [28] R_f = 0.71 (hexane:CH_2Cl_2, 1:1); mp 87 – 89 °C (hexane); ν_{max} (solid, cm^{-1}) 3488 m, 2945 br, 2867 br, 1601 m, 1563 m, 1459 m, 1395 s, 1313 m, 1267 m, 1214 s, 1171 s, 1143 m, 1070 m, 1014 m, 883 s, 802 m, 780 m, 771 m, 745 s, 733 s, 685 m; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.25 (br s, 1 H), 8.05 (d, *J* 8.6 Hz, 1 H), 7.98 (d, *J* 7.7 Hz, 1 H), 7.35 − 7.40 (m, 1 H), 7.32 − 7.36 (m, 1 H), 7.20 (ddd, *J* 8.6 Hz, 7.7 Hz, 0.9 Hz, 1 H), 6.85 (d, *J* 8.6 Hz, 1 H), 3.87 (s, 3 H), 1.60 (hept, *J* 7.4 Hz, 3 H), 1.16 (d, *J* 7.4 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 164.4, 146.4, 139.5, 124.6, 123.2, 122.3, 119.4, 119.3, 117.7, 110.2, 103.2, 103.1, 55.2, 19.3, 13.5; m/z (TOF ASAP+) calculated for $C_{22}H_{32}NOSi$ $[M+H]^+$; 354.2253, found 354.2259 (PPM error 1.7).

Analytical data for [29] R_f = 0.11 (hexane:CH_2Cl_2, 1:1); mp 148 – 150 °C (hexane); ν_{max} (solid, cm^{-1}) 3273 br, 2949 br, 2867 m, 1631 m, 1599 m, 1579 m, 1470 m, 1456 s, 1435 s, 1365 m, 1274 s, 1145 s, 1125 s, 1071 m, 1017 m, 927 s, 882 s, 834 s, 803 m, 762 m, 747 s, 726 s, 680; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.94 (dd, *J* 1.0 Hz, 7.6 Hz, 1 H), 7.88 (d, *J* 8.4 Hz, 1 H), 7.63 (d, *J* 8.5 Hz, 1 H), 7.28 (ddd, *J* 8.4 Hz, 7.2 Hz, 1.4 Hz, 1 H), 7.19 (dd, *J* 7.6 Hz, 7.4 Hz, 1 H), 7.16 (d, *J* 1.7 Hz, 1 H), 6.74 (dd, *J* 8.3 Hz, 2.1 Hz, 1 H), 4.75 (s, 1 H), 1.98 (hept, *J* 7.5 Hz, 3 H), 1.20 (d, *J* 7.5 Hz, 18 H); ^{13}C NMR (101 MHz) δ_C 154.6, 147.0, 145.7, 127.1, 124.7, 121.3, 120.7, 120.2, 119.4, 114.5, 109.0, 101.2, 19.2, 14.4; m/z (TOF ASAP+) calculated for $C_{21}H_{29}NOSi$ $[M]^+$; 339.2018, found 339.2027 (PPM error 2.7).

X-ray crystallography

CCDC 2079909 – CCDC 2079912 (**1a**, **8a**, **10b** and **12b** respectively) and CCDC 2080733-2080736 (**3a**, **5a**, **6b** and **20a** respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The datasets for **1a**, **3a**, **5a**, **6b**, **8a**, **10b**, **12b** and **20a** were measured on an Agilent SuperNova diffractometer using an Atlas detector. The data collections were driven and processed and absorption corrections were applied using CrysAlisPro.[29] The structures were solved using ShelXT.[30] All structures were refined by a full-matrix least-squares procedure on F^2 in ShelXL.[31] Figures and reports were produced using OLEX2.[32] All non-hydrogen atoms were refined with anisotropic displacement parameters. In **10b** the hydrogen atoms bonded to N(1) and N(101), and in **6b** and **12b** the hydrogen atom bonded to N(1), were located in the electron density and freely refined. All remaining hydrogen atoms in all structures were fixed as riding models and the isotropic thermal parameters (U_{iso}) were based on the U_{eq} of the parent atoms.

Crystal data for **1a**: $C_{21}H_{29}NSi$ (M =323.54 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 9.3498(4) Å, b = 7.3678(3) Å, c = 27.1186(10) Å, β = 98.469(4)°, V = 1847.76(12) Å^3, Z = 4, T = 100.01(10) K, μ(CuKα) = 1.093 mm^{-1}, *Dcalc* = 1.163 g/cm^3, 6721 reflections measured (9.564° ≤ 2Θ ≤ 140.102°), 3490 unique (R_{int} = 0.0354, R_{sigma} = 0.0476) which were used in all calculations. The final R_1 was 0.0581 (I > 2σ(I)) and wR_2 was 0.1522 (all data).

Crystals were obtained by slow evaporation from Et_2O.

The methyl group C(22) / C(22') is disordered over two positions at a refined percentage occupancy ratio of 84 (2) : 16 (2).

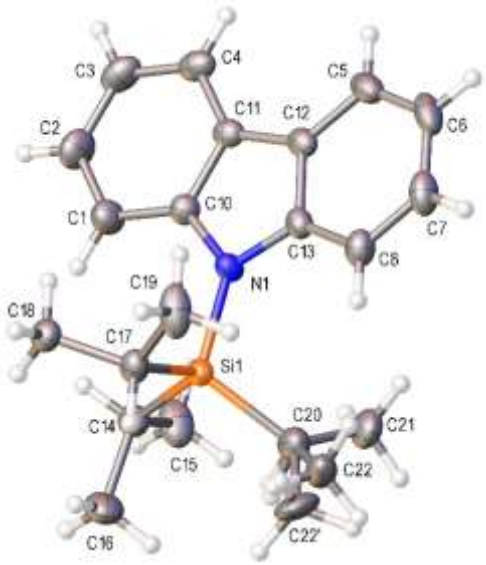


Figure S1 *Crystal structure of* ***1a*** *with ellipsoids drawn at the 50 % probability level. The methyl group C(22) / C(22') is disordered over two positions at a refined percentage occupancy ratio of 84 (2) : 16 (2).*

Crystal data for **3a**: $C_{23}H_{33}NO_2Si$ (*M* =383.59 g/mol): hexagonal, space group $P6_1$ (no. 169), *a* = 19.2612(6) Å, *c* = 9.9892(5) Å, *V* = 3209.4(3) Å^3, *Z* = 6, *T* = 100.00(10) K, μ(Cu Kα) = 1.092 mm^{-1}, *Dcalc* = 1.191 g/cm^3, 18641 reflections measured (9.182° ≤ 2Θ ≤ 140.086°), 3827 unique (R_{int} = 0.0319, R_{sigma} = 0.0270) which were used in all calculations. The final R_1 was 0.0611 (I > 2σ(I)) and wR_2 was 0.1764 (all data).

Crystals were obtained by slow evaporation from ethanol

The CH_2-OH group C(13)-O(1) / C(13A)-O(1A) is disordered over two positions, at a refined percentage occupancy ratio of 59 (2) : 49 (2).

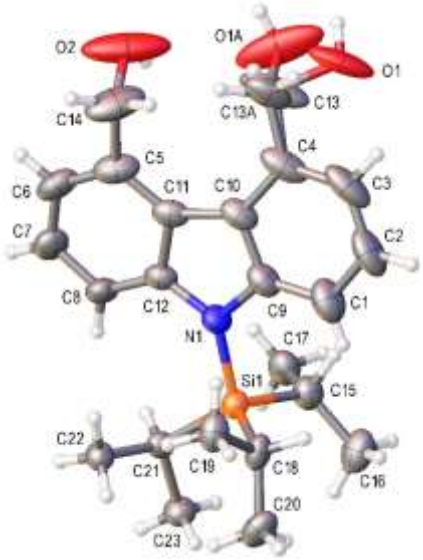


Figure S2 *Crystal structure of* ***3a*** *with ellipsoids drawn at the 50 % probability level. The CH_2-OH group C(13)-O(1) / C(13A)-O(1A) is disordered over two positions, at a refined percentage occupancy ratio of 59 (2) : 49 (2).*

Crystal data for **5a**: $C_{27}H_{27}F_4NSi$ (*M* =469.58 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 8.2725(4) Å, *b* = 19.9141(9) Å, *c* = 13.8083(7) Å, *β* = 101.265(5)°, *V* = 2230.95(19) $Å^3$, *Z* = 4, *T* = 100.01(10) K, μ(Cu Kα) = 1.359 mm^{-1}, *Dcalc* = 1.398 g/cm^3, 8851 reflections measured (7.896° ≤ 2Θ ≤ 146.254°), 4330 unique (R_{int} = 0.0280, R_{sigma} = 0.0344) which were used in all calculations. The final R_1 was 0.0377 (I > 2σ(I)) and wR_2 was 0.1036 (all data).

Crystals were obtained by slow evaporation from chloroform.

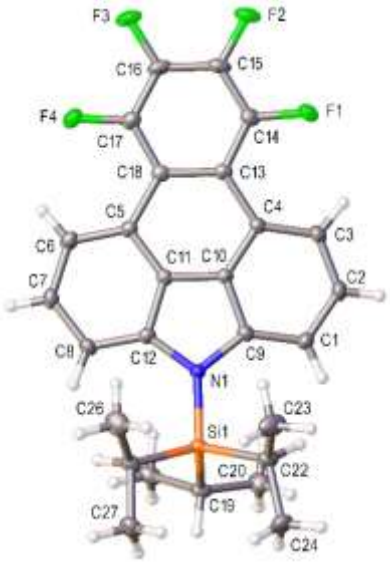


Figure S3 *Crystal structure of* ***5a*** *with ellipsoids drawn at the 50 % probability level.*

Crystal data for **6b**: $C_{12}H_7Cl_2N$ (*M* =236.09 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 3.8267(2) Å, *b* = 14.2898(6) Å, *c* = 17.5522(7) Å, *V* = 959.80(7) Å^3, *Z* = 4, *T* = 100.00(10) K, μ(Cu Kα) = 5.725 mm^{-1}, *Dcalc* = 1.634 g/cm^3, 9168 reflections measured (7.978° ≤ 2Θ ≤ 145.682°), 1895 unique (R_{int} = 0.0352, R_{sigma} = 0.0257) which were used in all calculations. The final R_1 was 0.0270 (I > 2σ(I)) and wR_2 was 0.0683 (all data).

Crystals were obtained by slow evaporation from CH_2Cl_2

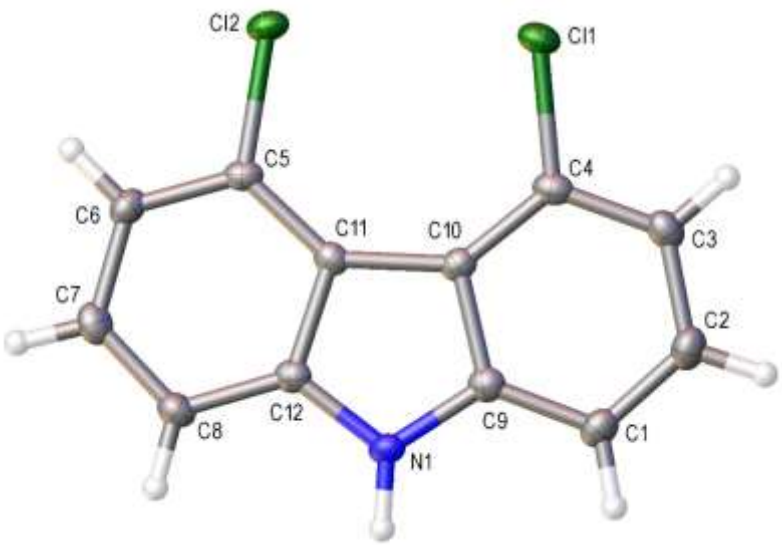


Figure S4 *Crystal structure of* ***6b*** *with ellipsoids drawn at the 50 % probability level.*

Crystal data for **8a**: $C_{23}H_{33}NSi_2$ (M =379.68 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 13.1260(5) Å, b = 15.4832(4) Å, c = 12.3174(5) Å, β = 117.891(5)°, V = 2212.51(16) Å^3, Z = 4, T = 100.01(10) K, μ(CuKα) = 1.483 mm^{-1}, $Dcalc$ = 1.140 g/cm^3, 8569 reflections measured (9.526° ≤ 2Θ ≤ 138.262°), 4107 unique (R_{int} = 0.0250, R_{sigma} = 0.0323) which were used in all calculations. The final R_1 was 0.0361 (I > 2σ(I)) and wR_2 was 0.1018 (all data).

Crystals obtained by recrystallisation of pure material from hot ethanol.

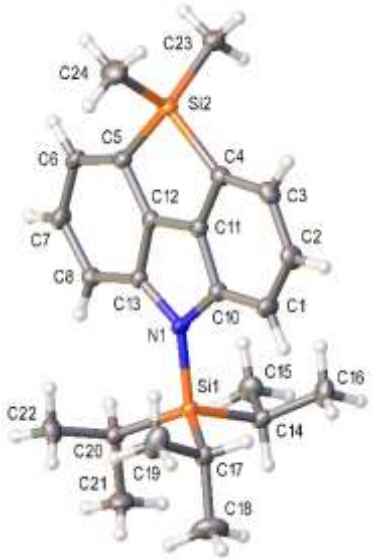


Figure S5 *Crystal structure of* ***8a*** *with ellipsoids drawn at the 50 % probability level.*

Crystal data for **10b**: $C_{12}H_7NS_2$ (M =229.31 g/mol): triclinic, space group P-1 (no. 2), a = 9.3372(6) Å, b = 10.5025(6) Å, c = 10.6156(6) Å, α = 92.683(4)°, β = 108.926(5)°, γ = 91.966(5)°, V = 982.30(10) Å^3, Z = 4, T = 100.00(10) K, μ(CuKα) = 4.559 mm^{-1}, *Dcalc* = 1.551 g/cm^3, 6804 reflections measured (8.44° ≤ 2Θ ≤ 149.248°), 3862 unique (R_{int} = 0.0234, R_{sigma} = 0.0301) which were used in all calculations. The final R_1 was 0.0292 (I > 2σ(I)) and wR_2 was 0.0776 (all data).

Crystals were obtained by slow evaporation from Et_2O.

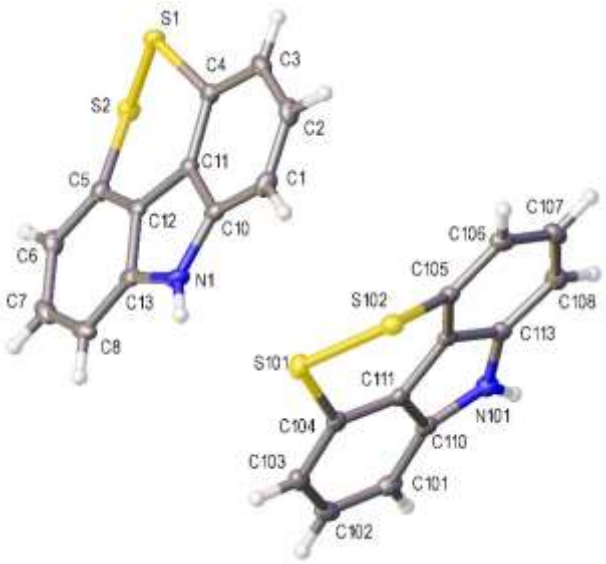


Figure S6 *Crystal structure of* ***10b*** *with ellipsoids drawn at the 50 % probability level. The structure contains two crystallographically-independent molecules.*

Crystal data for **12b**: $C_{12}H_7NSe_2$ (*M* =323.11 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 9.9907(4) Å, *b* = 6.7480(3) Å, *c* = 14.9843(6) Å, *β* = 95.086(4)°, *V* = 1006.22(7) Å^3, *Z* = 4, *T* = 100.00(10) K, μ(CuKα) = 8.847 mm^{-1}, *Dcalc* = 2.133 g/cm^3, 3677 reflections measured (10.238° ≤ 2Θ ≤ 148.818°), 1999 unique (R_{int} = 0.0172, R_{sigma} = 0.0207) which were used in all calculations. The final R_1 was 0.0215 (I > 2σ(I)) and wR_2 was 0.0561 (all data).

Crystals were obtained by slow evaporation for CH_2Cl_2

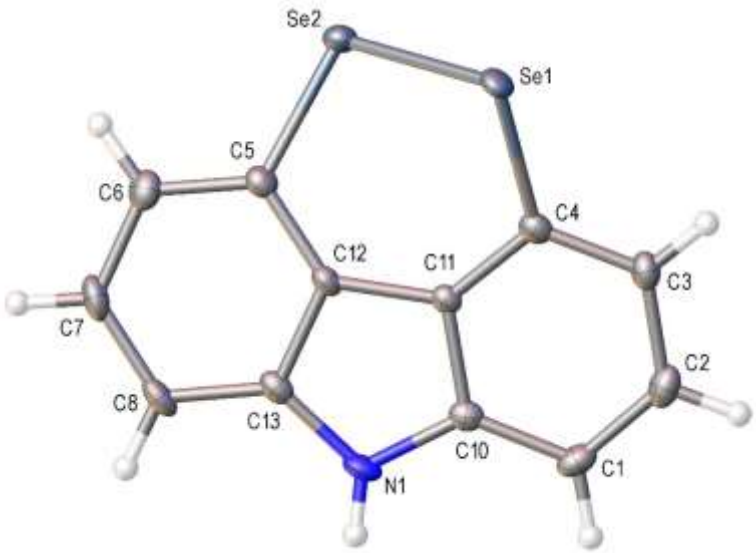


Figure S7 *Crystal structure of* ***12b*** *with ellipsoids drawn at the 50 % probability level.*

Crystal data for **20a**: $C_{23}H_{31}NOSi$ (*M* =365.58 g/mol): orthorhombic, space group Pbca (no. 61), *a* = 9.0996(3) Å, *b* = 14.8381(5) Å, *c* = 29.5722(8) Å, *V* = 3992.9(2) Å^3, *Z* = 8, *T* = 100.01(10) K, μ(Cu Kα) = 1.109 mm^{-1}, *Dcalc* = 1.216 g/cm^3, 9832 reflections measured (11.418° ≤ 2Θ ≤ 146.074°), 3879 unique (R_{int} = 0.0278, R_{sigma} = 0.0285) which were used in all calculations. The final R_1 was 0.0409 (I > 2σ(I)) and wR_2 was 0.1159 (all data).

Crystals were obtained by slow evaporation from EtOAc.

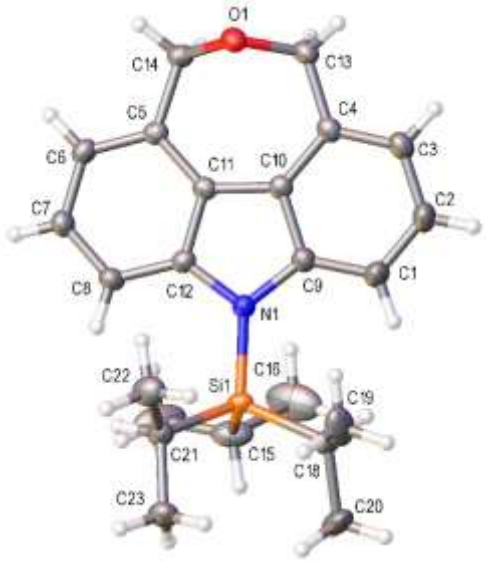
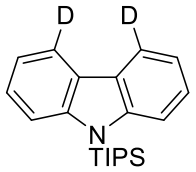


Figure S8 *Crystal structure of* ***20a*** *with ellipsoids drawn at the 50 % probability level.*

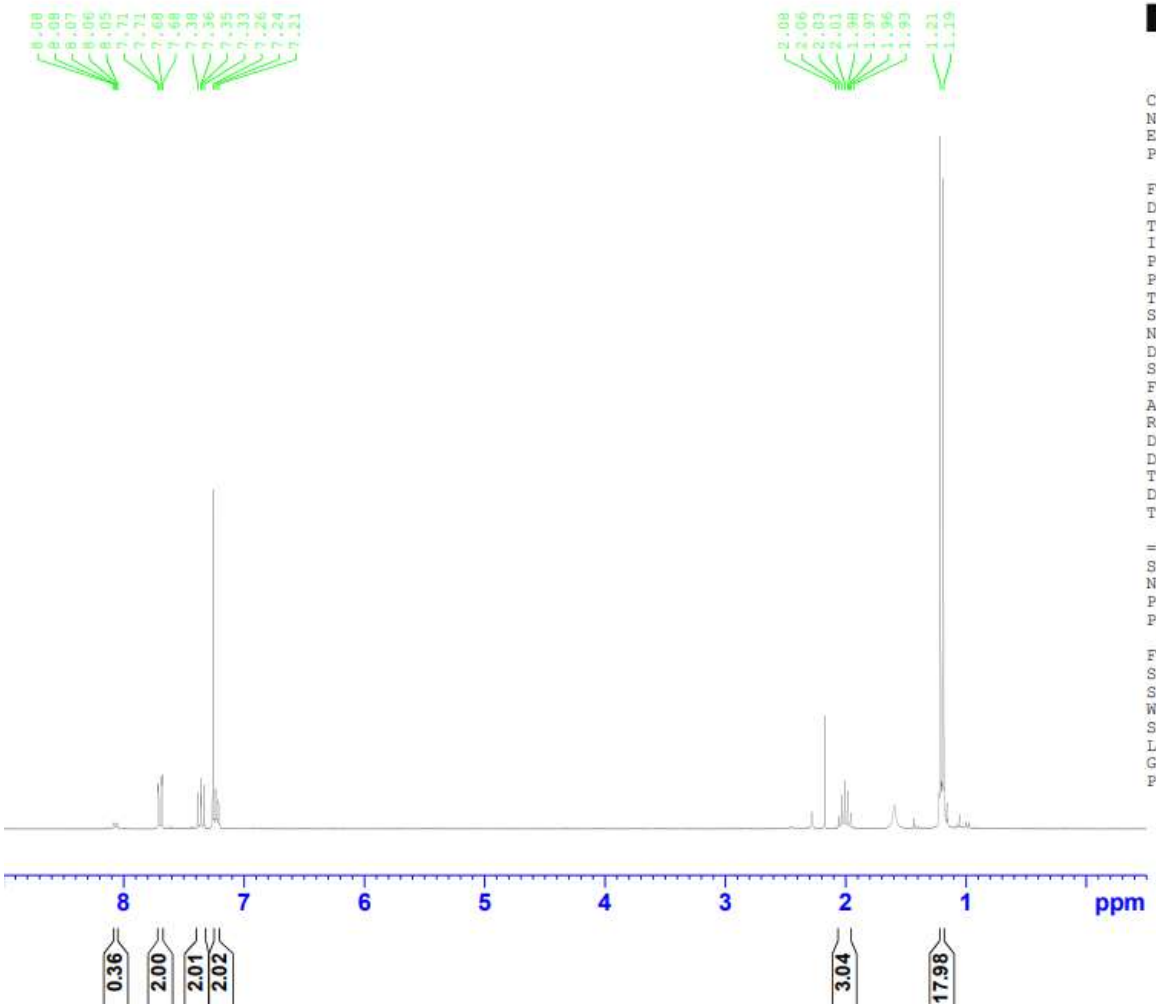
Copies of NMR spectra

Deuteration study (Table 1, Entry 2)



1a-D

(83% deuteration)

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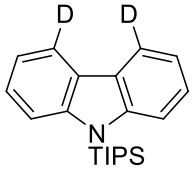

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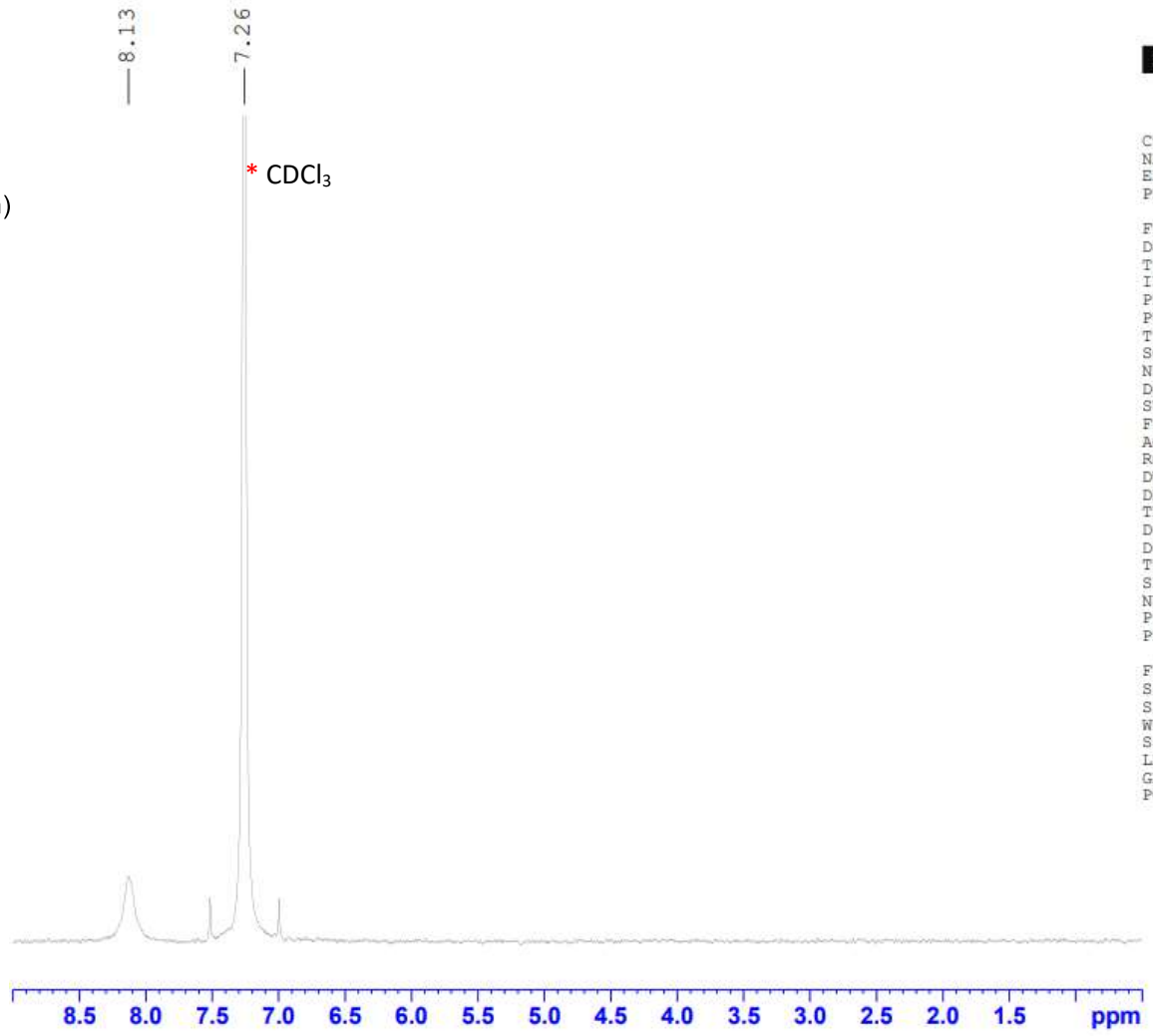

BRUKER

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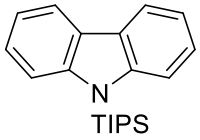
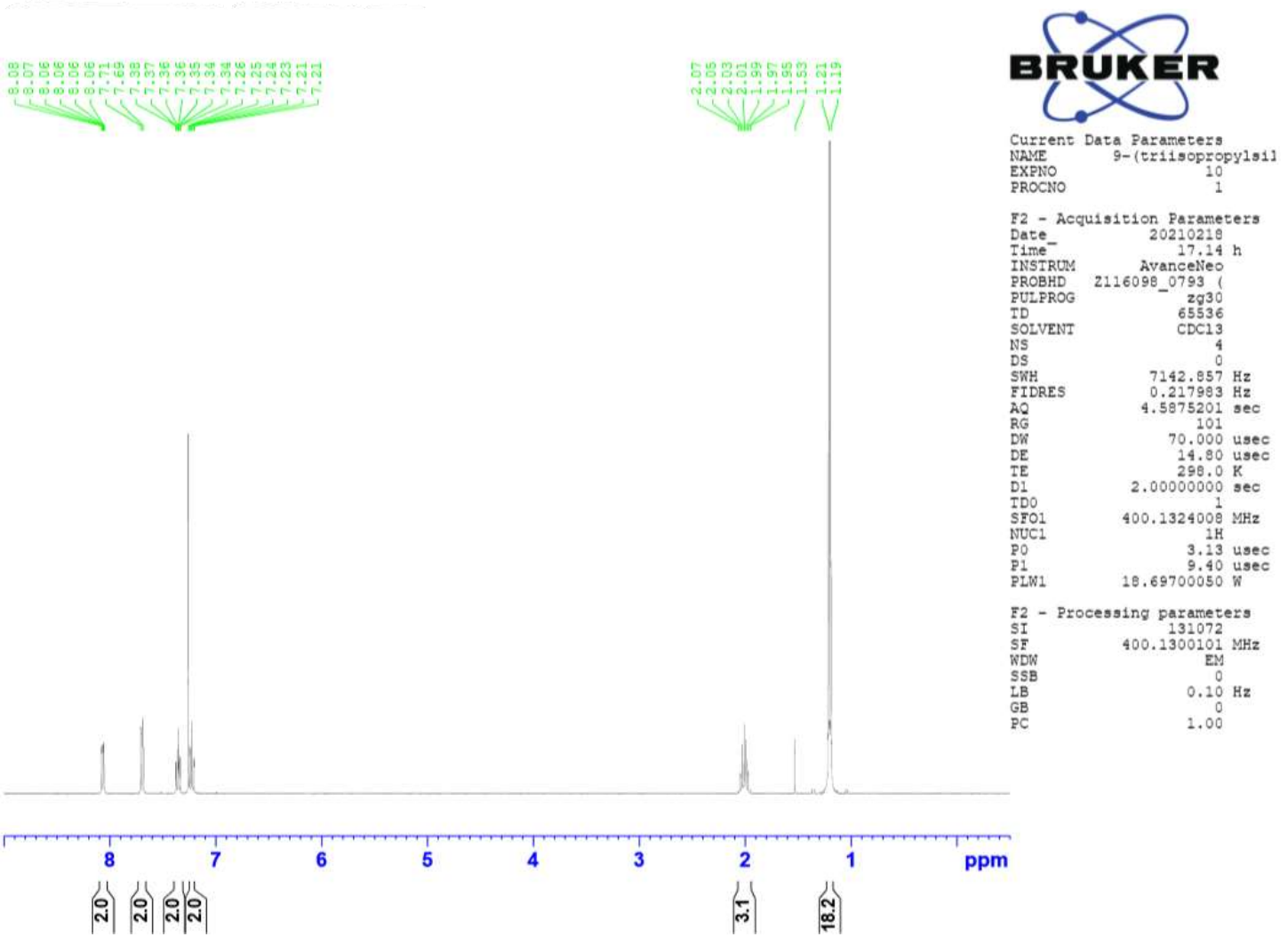
9-(Triisopropylsilyl)-9H-carbazole [1a]



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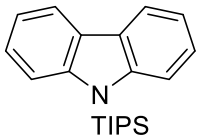
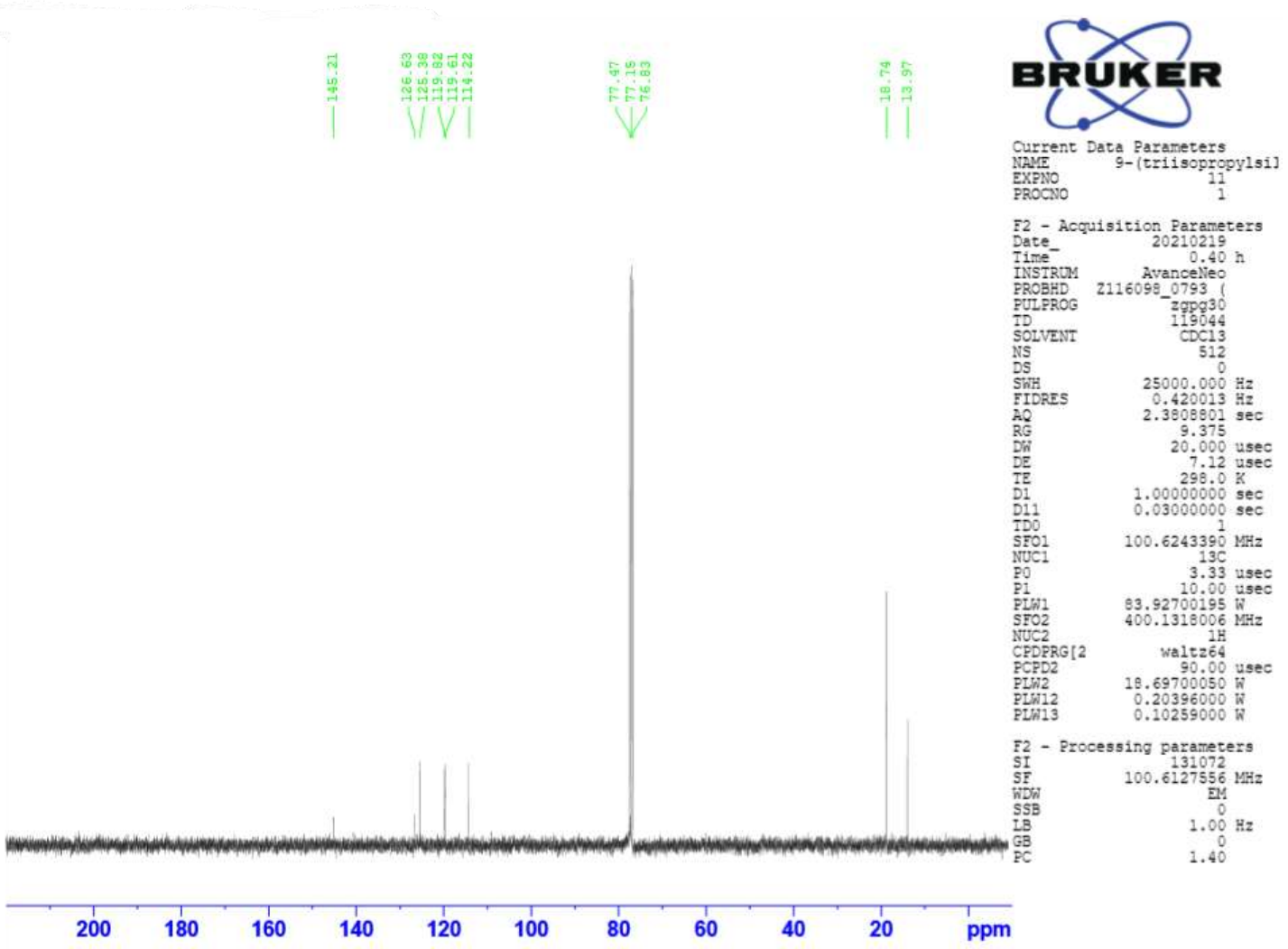
9-(Triisopropylsilyl)-9H-carbazole [1a]



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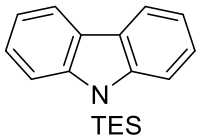
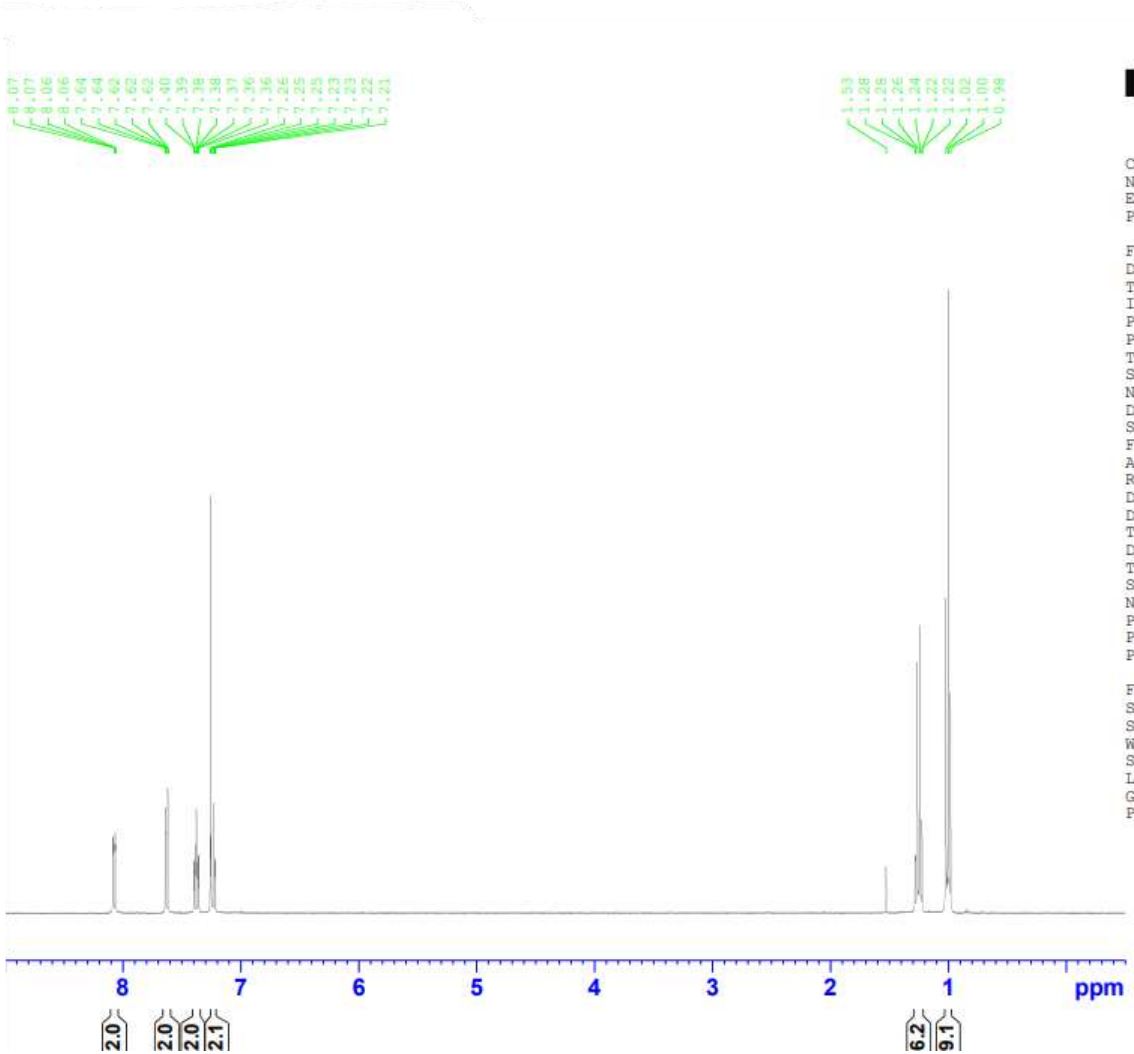
9-(Triethylsilyl)-9H-carbazole [1c]



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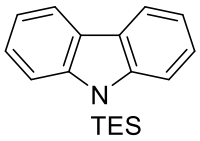
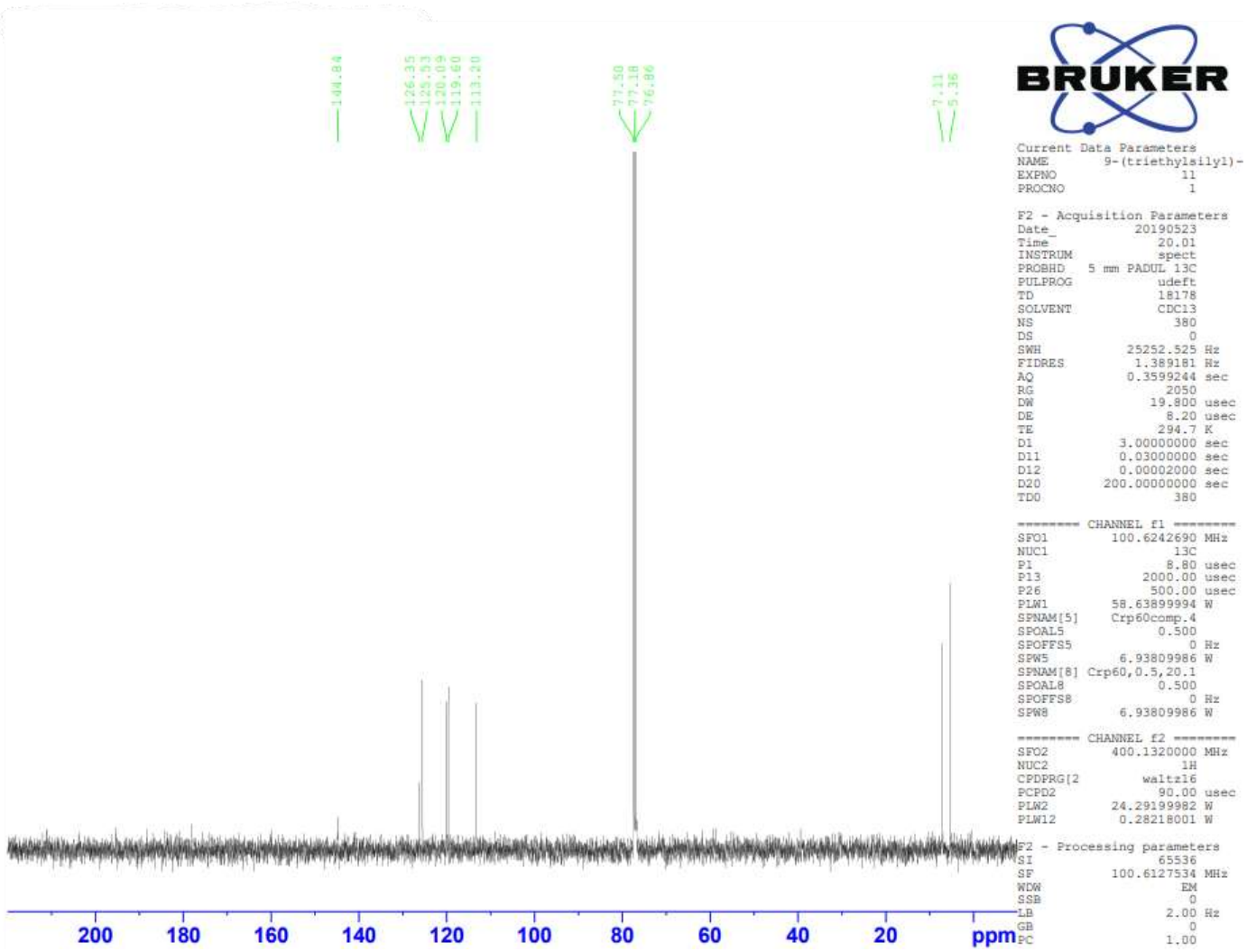
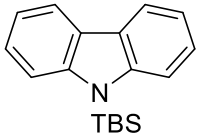
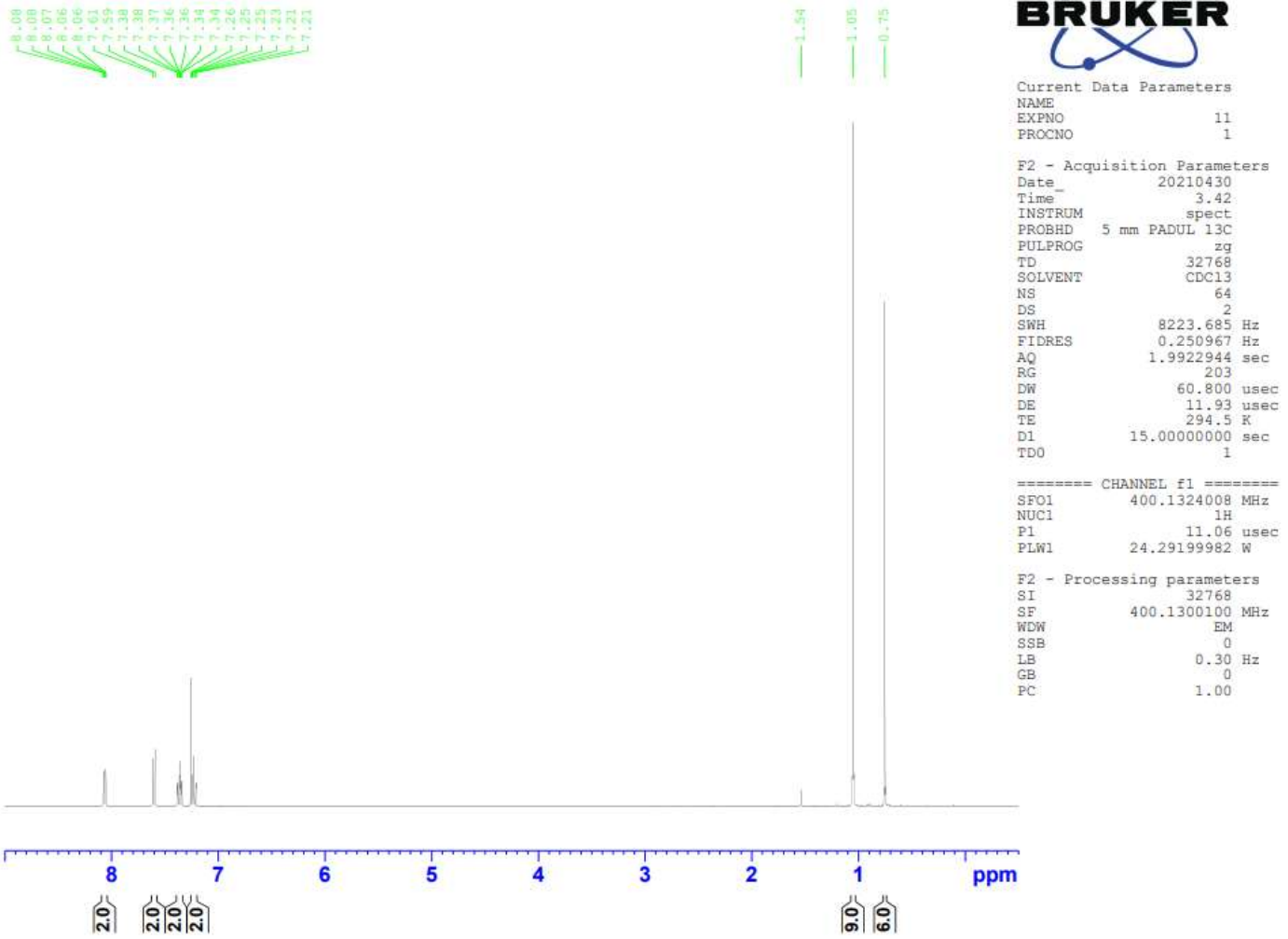
9-(Triethylsilyl)-9H-carbazole [1c]





9-(*tert*-Butyldimethylsilyl)-9H-carbazole [1d]





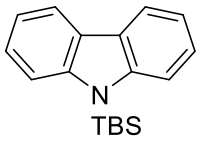

```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

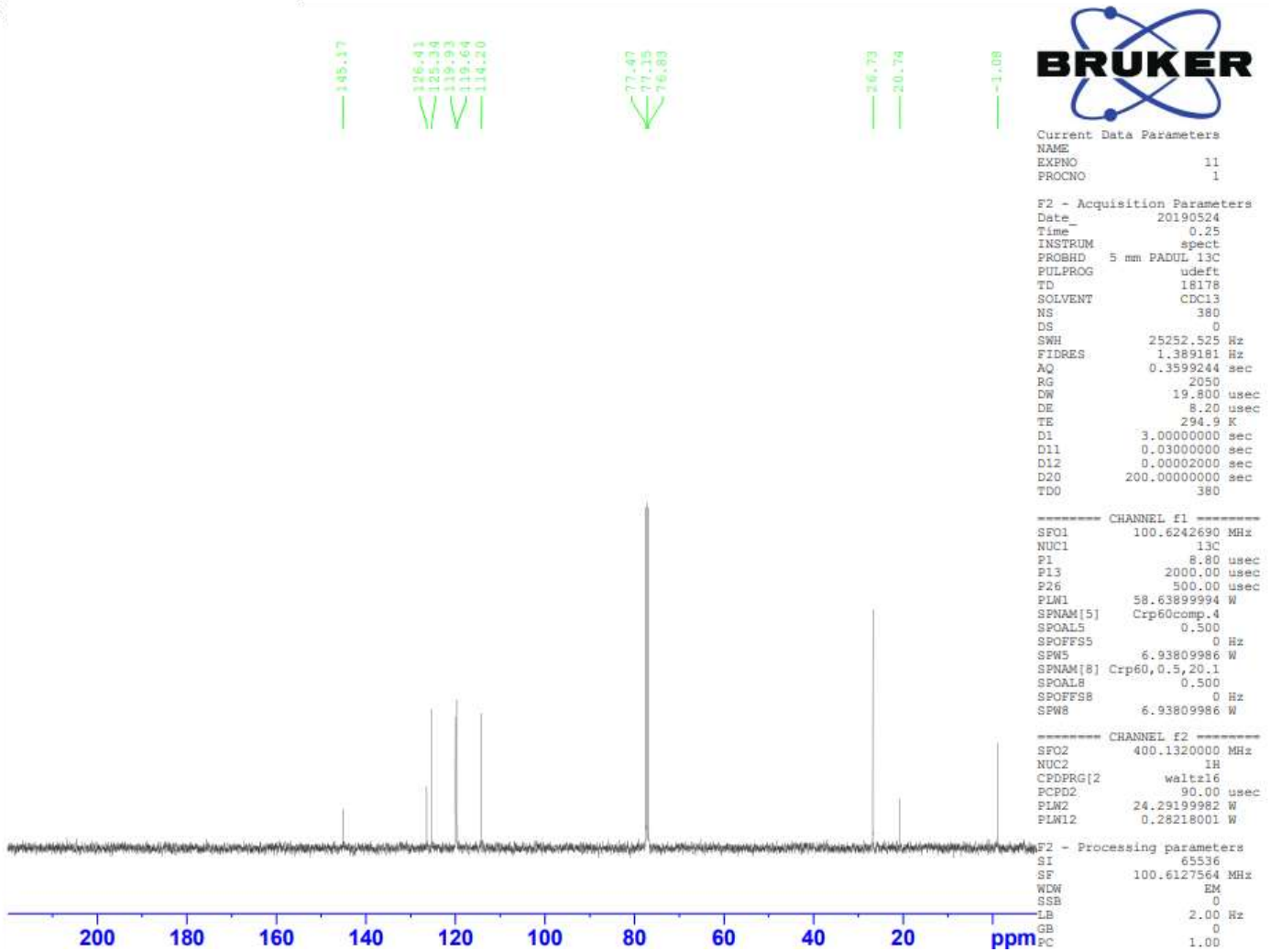
F2 - Acquisition Parameters
Date_            20210430
Time                3.42
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG                zg
TD                  32768
SOLVENT             CDCl3
NS                     64
DS                      2
SWH              8223.685 Hz
FIDRES           0.250967 Hz
AQ               1.9922944 sec
RG                    203
DW                 60.800 usec
DE                 11.93 usec
TE                 294.5 K
D1              15.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324008 MHz
NUC1                   1H
P1                  11.06 usec
PLW1          24.29199982 W

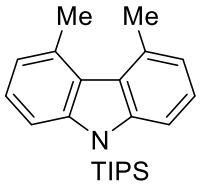
F2 - Processing parameters
SI                  32768
SF            400.1300100 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

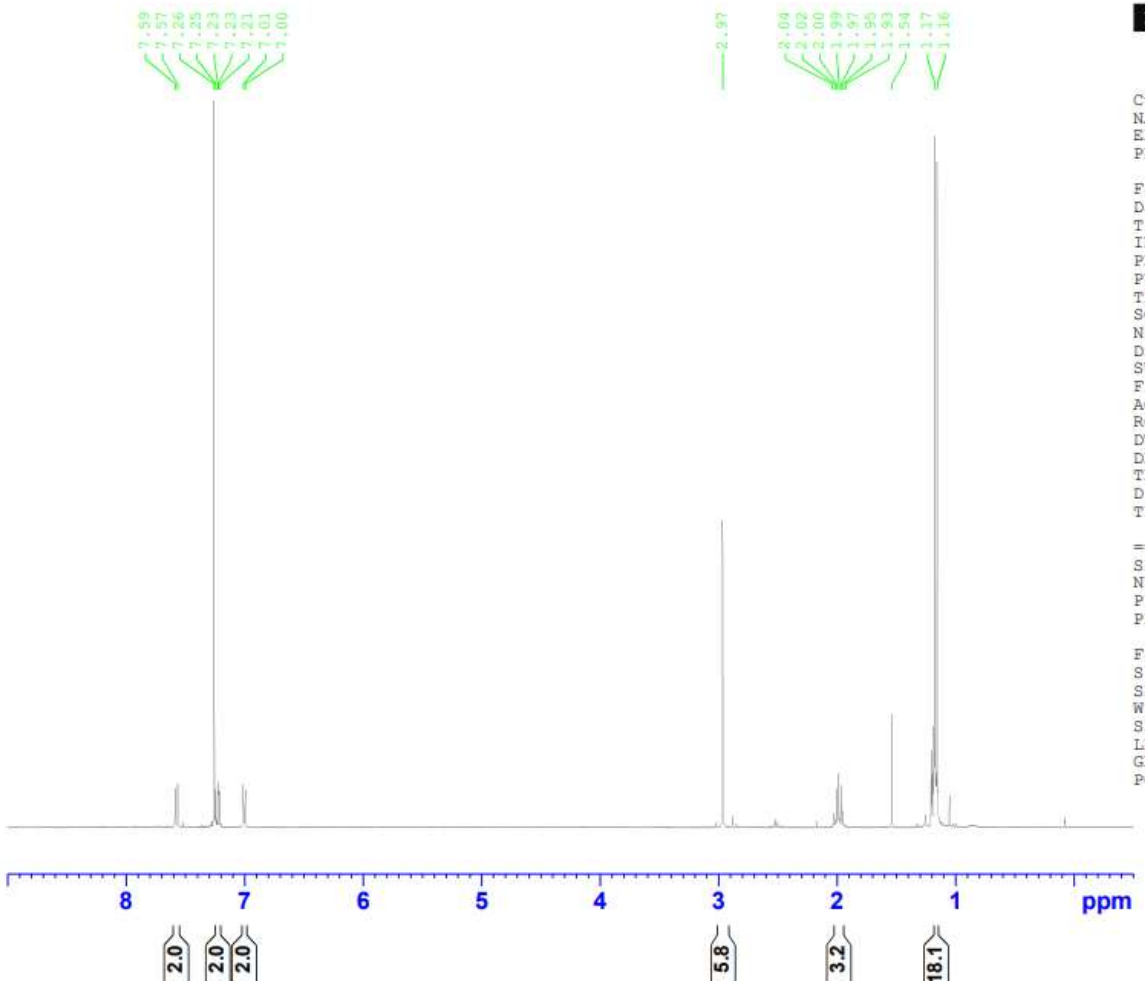
9-(*tert*-Butyldimethylsilyl)-9H-carbazole [1d]





4,5-Dimethyl-9-(triisopropylsilyl)-9H-carbazole [2a]





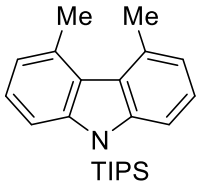

```
Current Data Parameters
NAME
EXPNO                 101
PROCNO                  1

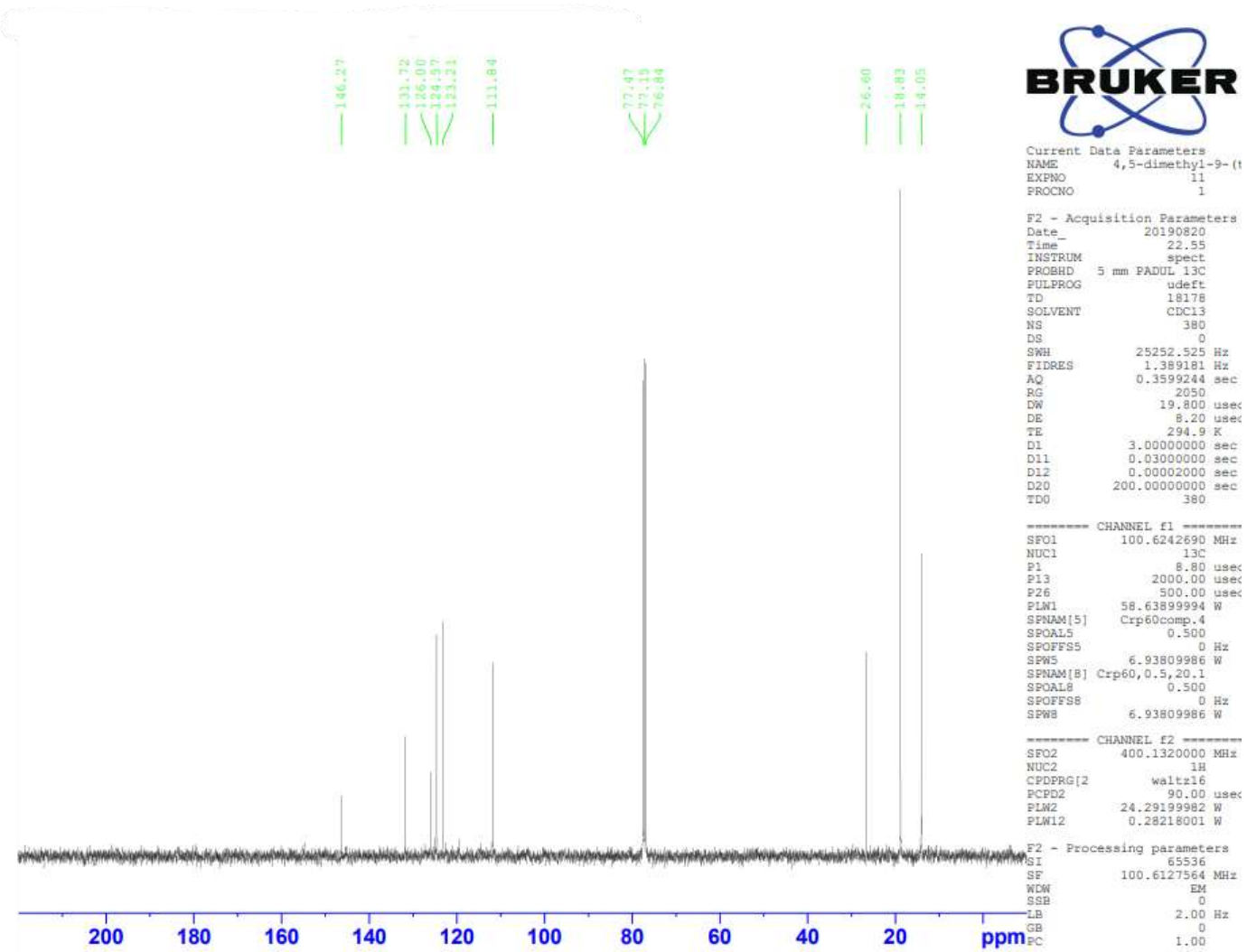
F2 - Acquisition Parameters
Date_            20210326
Time                18.23
INSTRUM             spect
PROBHD   5 mm PADUL 13C
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     32
DS                      2
SWH              8223.685 Hz
FIDRES           0.250967 Hz
AQ               1.9922944 sec
RG                    912
DW                 60.800 usec
DE                 16.65 usec
TE                 294.7 K
D1              1.50000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324008 MHz
NUC1                  1H
P1                 11.06 usec
PLW1          24.29199982 W

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

4,5-Dimethyl-9-(triisopropylsilyl)-9H-carbazole [2a]






```
Current Data Parameters
NAME        4,5-dimethyl-9-(t
EXPNO                 11
PROCNO                 1

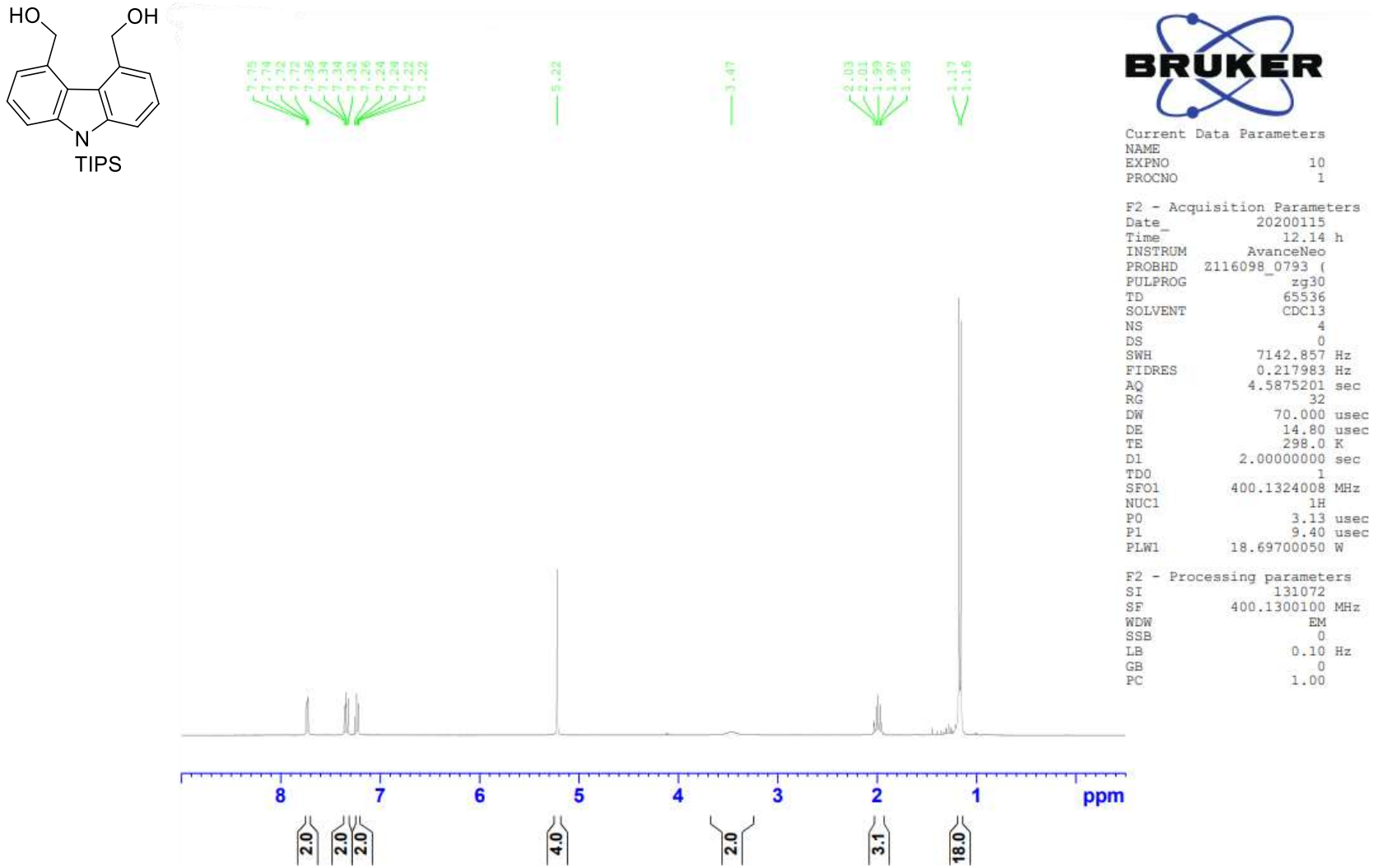
F2 - Acquisition Parameters
Date_           20190820
Time              22.55
INSTRUM           spect
PROBHD   5 mm PADUL 13C
PULPROG           udeft
TD                18178
SOLVENT           CDCl3
NS                  380
DS                    0
SWH           25252.525 Hz
FIDRES         1.389181 Hz
AQ            0.3599244 sec
RG                 2050
DW               19.800 usec
DE                8.20 usec
TE               294.9 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 usec
P13            2000.00 usec
P26             500.00 usec
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

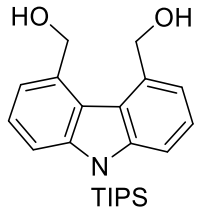
======== CHANNEL f2 ========
SFO2        400.1320000 MHz
NUC2              1H
CPDPRG[2         waltz16
PCPD2            90.00 usec
PLW2         24.29199982 W
PLW12         0.28218001 W

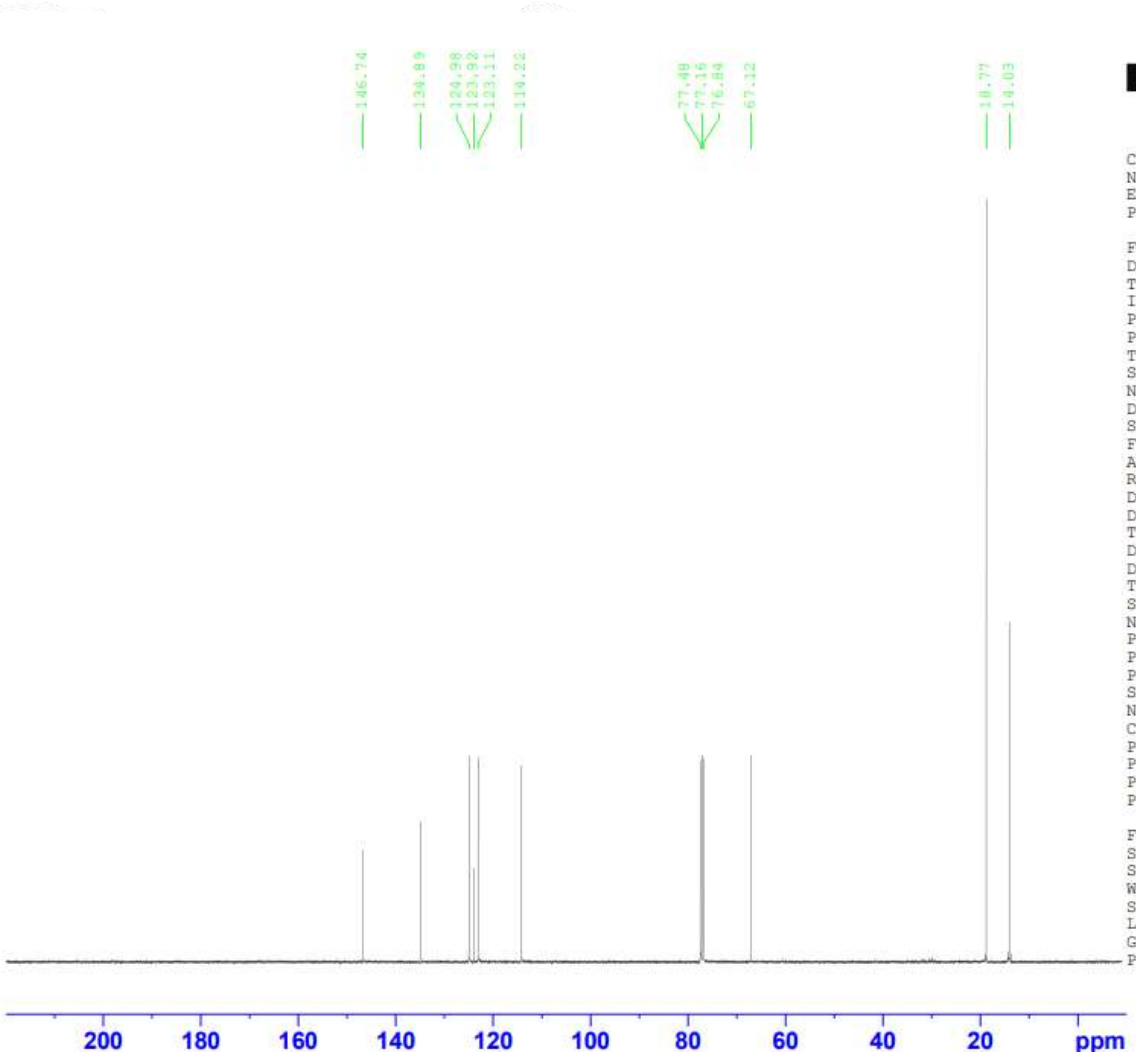
F2 - Processing parameters
SI                65536
SF          100.6127564 MHz
WDW                EM
SSB                0
LB                2.00 Hz
GB                 0
PC                1.00
```

(9-(Triisopropylsilyl)-9H-carbazole-4,5-diyl)dimethanol [3a]



(9-(Triisopropylsilyl)-9H-carbazole-4,5-diyl)dimethanol [3a]



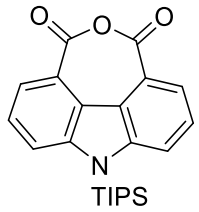


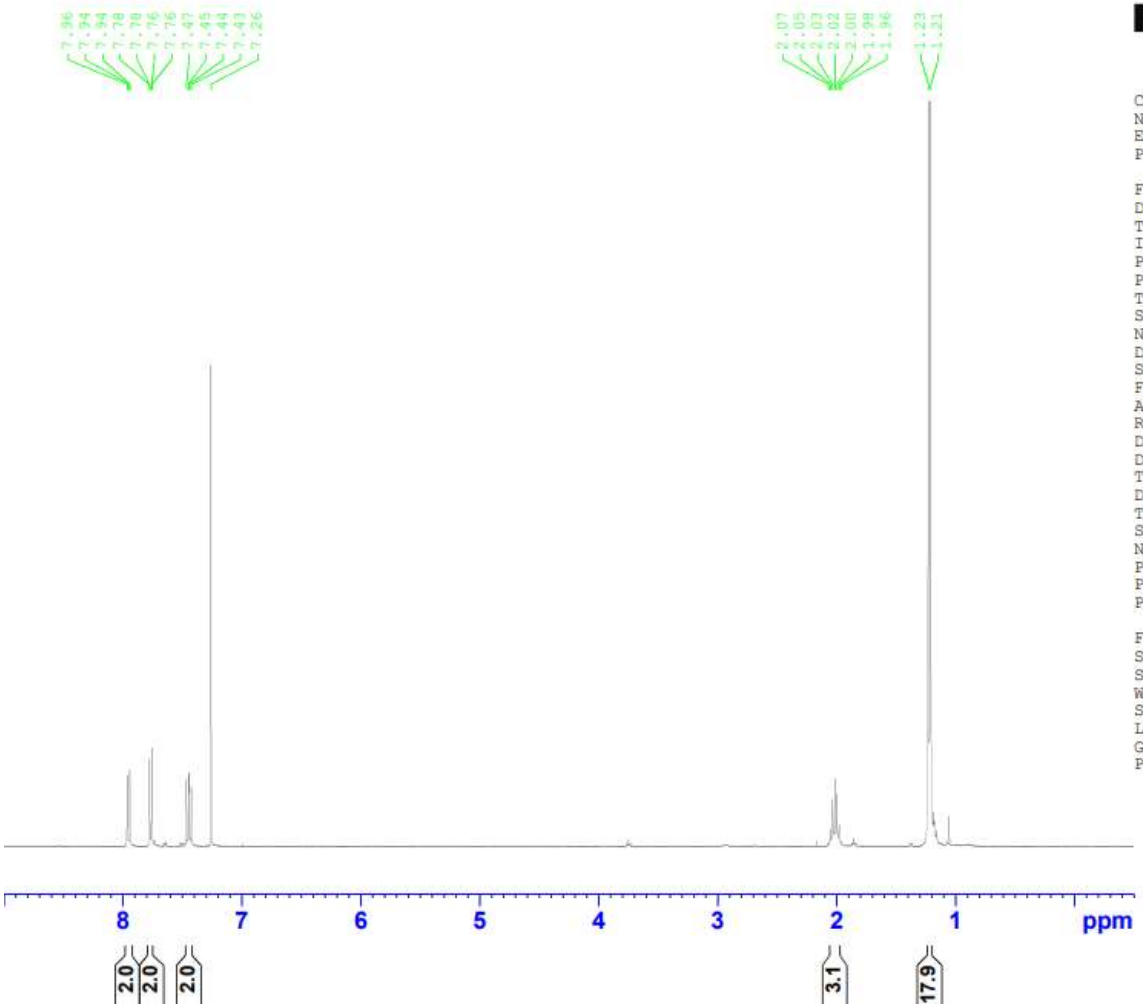

```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_            20200115
Time                18.10 h
INSTRUM         AvanceNeo
PROBHD    Z116098_0793 (
PULPROG            zgpg30
TD                 119044
SOLVENT             CDCl3
NS                    512
DS                      0
SWH             25000.000 Hz
FIDRES          0.420013 Hz
AQ              2.3808801 sec
RG                31.9602
DW                20.000 usec
DE                 7.12 usec
TE                298.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1
SFO1          100.6243390 MHz
NUC1                  13C
P0                 3.33 usec
P1                10.00 usec
PLW1          83.92700195 W
SFO2          400.1318006 MHz
NUC2                  1H
CPDPRG[2          waltz64
PCPD2             90.00 usec
PLW2          18.69700050 W
PLW12          0.20396000 W
PLW13          0.10259000 W

F2 - Processing parameters
SI                  131072
SF            100.6127598 MHz
WDW                   EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```

4-(Triisopropylsilyl)-4H-oxepino[3,4,5,6-def]carbazole-8,10-dione [4a]



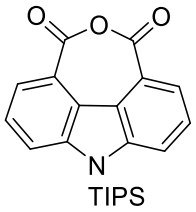


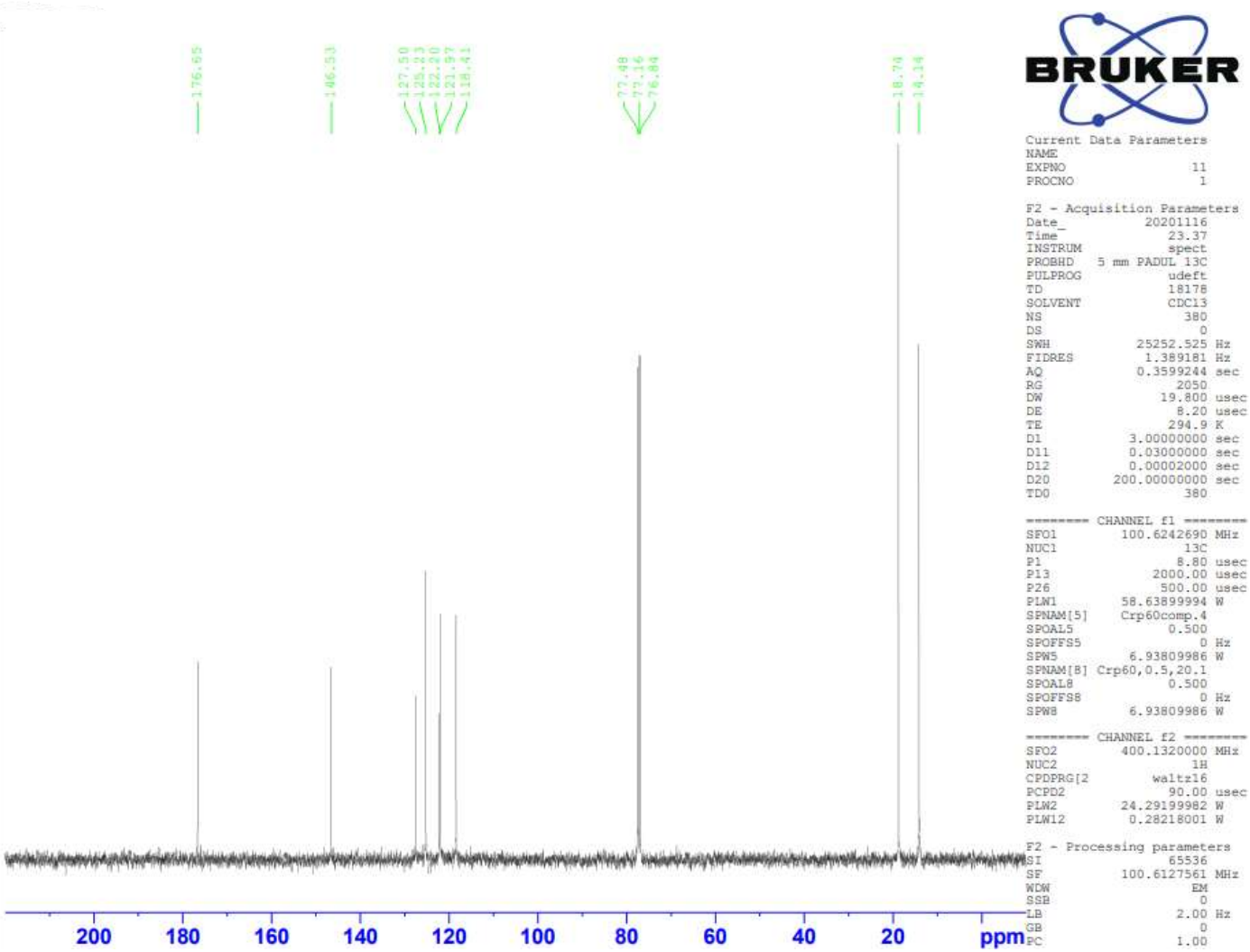

```
Current Data Parameters
NAME
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20000114
Time                21.24 h
INSTRUM         AvanceNeo
PROBHD    Z116098_0793 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      4
DS                      0
SWH              7142.857 Hz
FIDRES           0.217983 Hz
AQ               4.5875201 sec
RG                    101
DW                 70.000 usec
DE                 14.80 usec
TE                 298.0 K
D1              2.00000000 sec
TD0                     1
SFO1          400.1324008 MHz
NUC1                   1H
P0                 3.13 usec
P1                 9.40 usec
PLW1          18.69700050 W

F2 - Processing parameters
SI                 131072
SF            400.1300096 MHz
WDW                    EM
SSB                     0
LB                 0.10 Hz
GB                      0
PC                   1.00
```

4-(Triisopropylsilyl)-4H-oxepino[3,4,5,6-def]carbazole-8,10-dione [4a]






```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

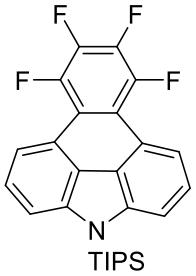
F2 - Acquisition Parameters
Date_            20201116
Time                23.37
INSTRUM             spect
PROBHD   5 mm PADUL 13C
PULPROG             udeft
TD                  18178
SOLVENT             CDCl3
NS                    380
DS                      0
SWH             25252.525 Hz
FIDRES          1.389181 Hz
AQ              0.3599244 sec
RG                   2050
DW                19.800 usec
DE                 8.20 usec
TE                294.9 K
D1             3.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec
D20          200.00000000 sec
TD0                   380

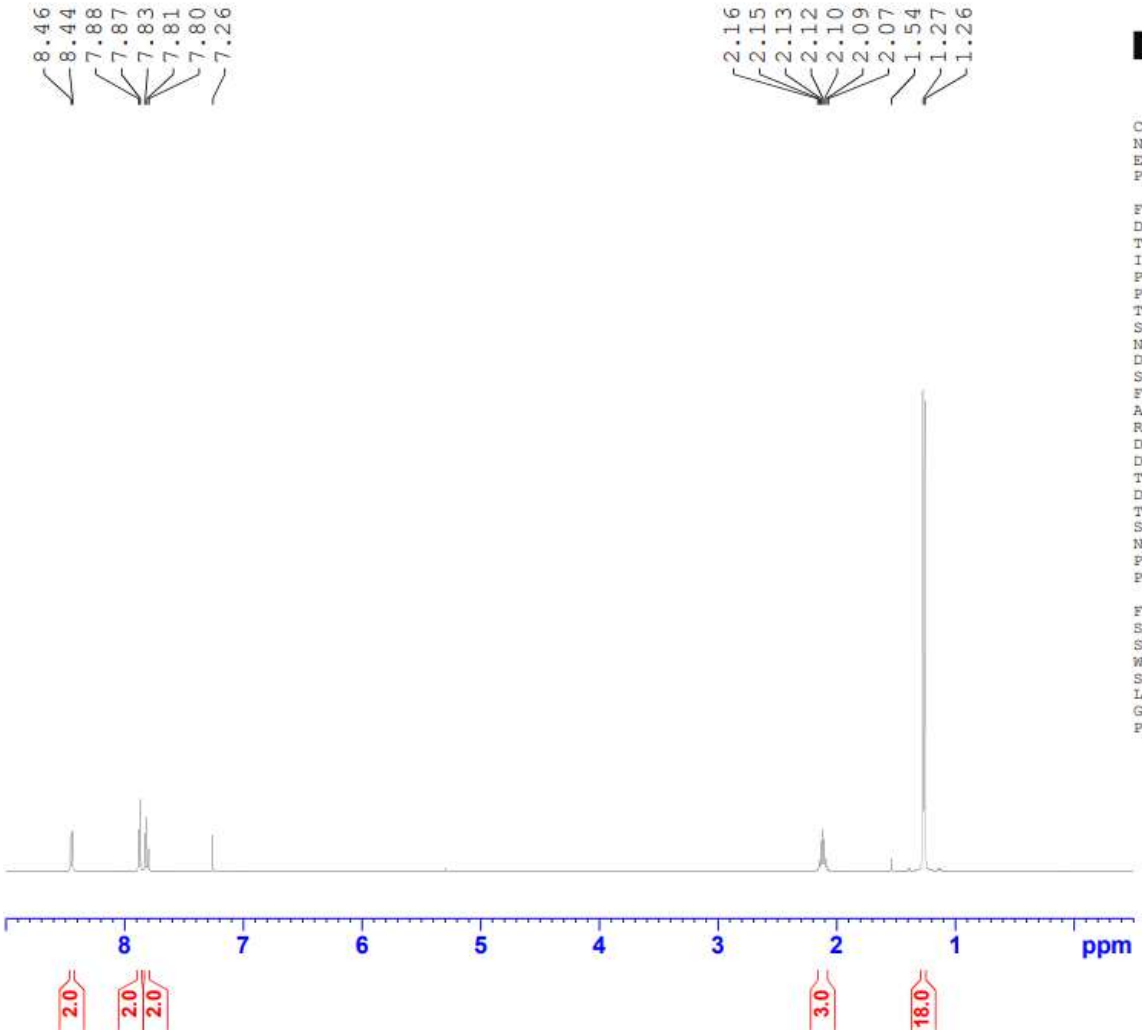
======== CHANNEL f1 ========
SFO1         100.6242690 MHz
NUC1                 13C
P1                  8.80 usec
P13              2000.00 usec
P26               500.00 usec
PLW1         58.63899994 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5                0 Hz
SPW5          6.93809986 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 usec
PLW2         24.29199982 W
PLW12         0.28218001 W

F2 - Processing parameters
SI                  65536
SF           100.6127561 MHz
WDW                    EM
SSB                     0
LB                   2.00 Hz
GB                      0
PC                   1.00
```

8,9,10,11-Tetrafluoro-4-(triisopropylsilyl)-4H-naphtho[1,2,3,4-def]carbazole [5a]



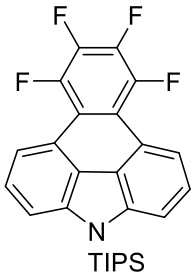


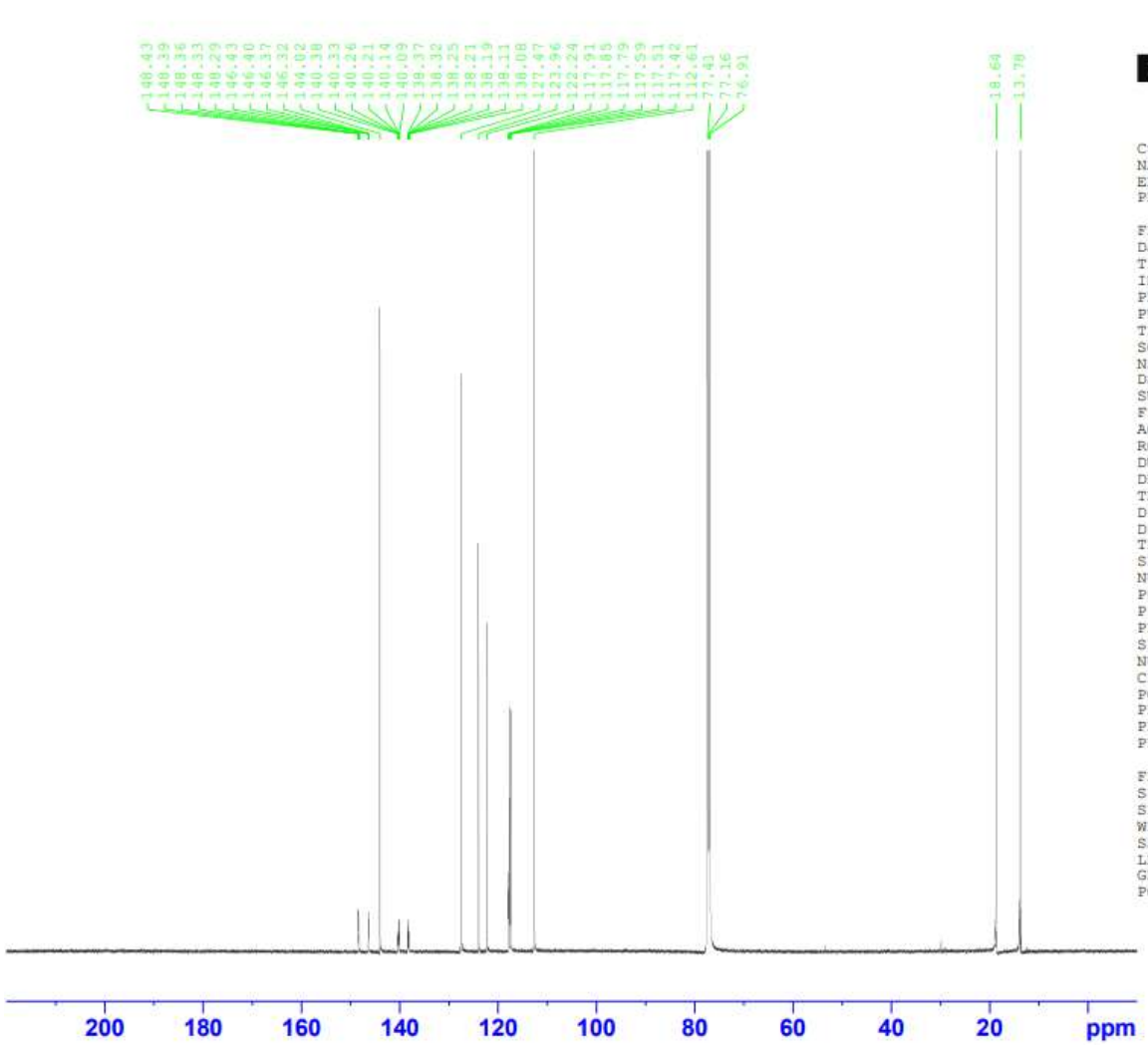

```
Current Data Parameters
NAME
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210315
Time                17.38 h
INSTRUM  CAB AV4 500 MHZ BASIC
PROBHD   Z150364_0007 (
PULPROG                 zg
TD                   66560
SOLVENT              CDCl3
NS                      16
DS                       0
SWH             10416.667 Hz
FIDRES          0.313001 Hz
AQ              3.1948800 sec
RG                 76.9231
DW                 48.000 usec
DE                 34.36 usec
TE                 298.0 K
D1             10.00000000 sec
TD0                      1
SFO1           500.0760004 MHz
NUC1                    1H
P1                 12.00 usec
PLW1           14.55099964 W

F2 - Processing parameters
SI                  131072
SF             500.0730123 MHz
WDW                     EM
SSB                      0
LB                  0.10 Hz
GB                       0
PC                  1.00
```

8,9,10,11-Tetrafluoro-4-(triisopropylsilyl)-4H-naphtho[1,2,3,4-def]carbazole [5a]



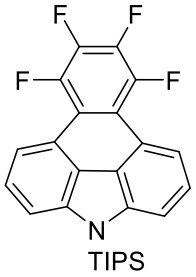


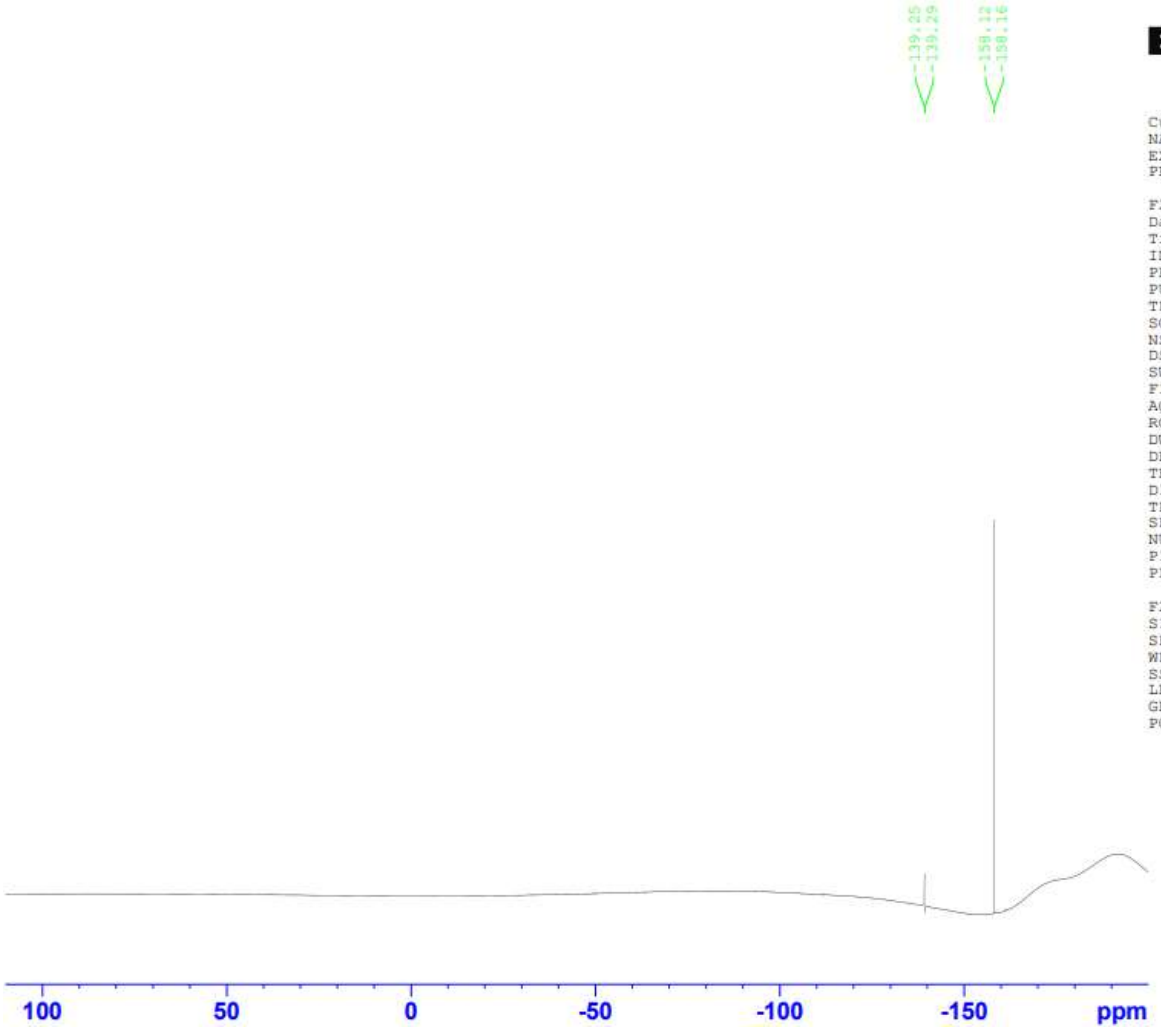

```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210317
Time                7.24 h
INSTRUM  CAB AV4 500 MHZ BASIC
PROBHD   Z150364_0007 (
PULPROG             zgpg30
TD                  119044
SOLVENT              CDCl3
NS                    4000
DS                       0
SWH              31250.000 Hz
FIDRES            0.525016 Hz
AQ               1.9047040 sec
RG                     101
DW                16.000 usec
DE                 18.29 usec
TE                 298.0 K
D1            32.00000000 sec
D11            0.03000000 sec
TD0                      1
SFO1          125.7572860 MHz
NUC1                  13C
P0                  3.33 usec
P1                 10.00 usec
PLW1          61.18099976 W
SFO2          500.0750003 MHz
NUC2                  1H
CPDPRG[2          waltz64
PCPD2              80.00 usec
PLW2          14.55099964 W
PLW12          0.32740000 W
PLW13          0.16468000 W

F2 - Processing parameters
SI                  131072
SF            125.7434386 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

8,9,10,11-Tetrafluoro-4-(triisopropylsilyl)-4H-naphtho[1,2,3,4-def]carbazole [5a]



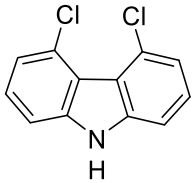


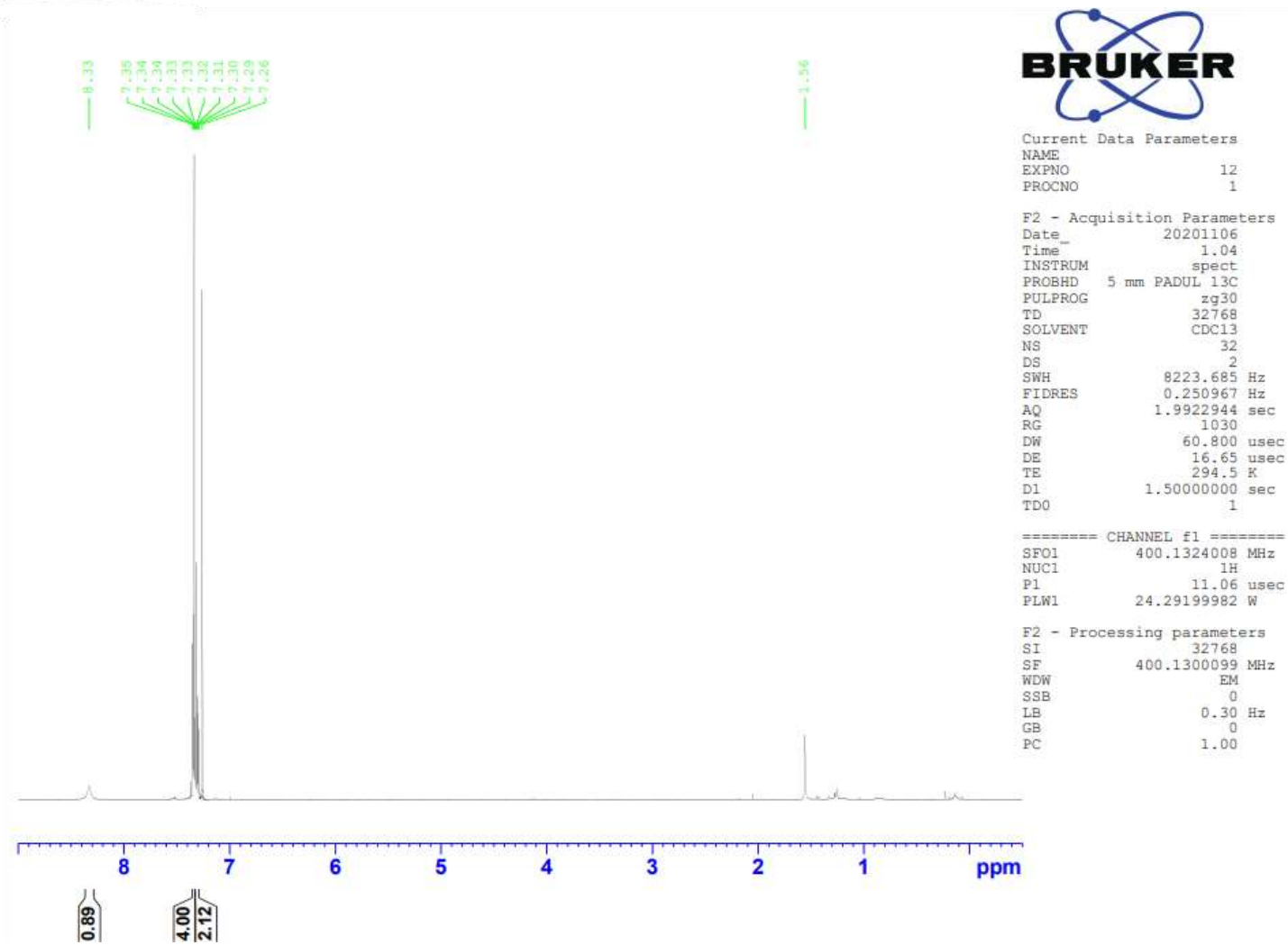

```
Current Data Parameters
NAME
EXPNO                  13
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210317
Time                8.47 h
INSTRUM  CAB AV4 500 MHZ BASIC
PROBHD   Z150364_0007 (
PULPROG                zg
TD                 134144
SOLVENT              CDCl3
NS                      32
DS                       0
SWH           200000.000 Hz
FIDRES          2.981870 Hz
AQ              0.3353600 sec
RG                40.6901
DW                 2.500 usec
DE                18.00 usec
TE                298.0 K
D1             3.00000000 sec
TD0                     1
SFO1          470.5387436 MHz
NUC1                  19F
P1                 15.00 usec
PLW1           9.63220024 W

F2 - Processing parameters
SI                 131072
SF            470.5387436 MHz
WDW                    EM
SSB                     0
LB                 2.00 Hz
GB                      0
PC                 1.00
```

4,5-Dichloro-9H-carbazole [6b]





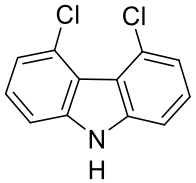

```
Current Data Parameters
NAME
EXPNO                  12
PROCNO                  1

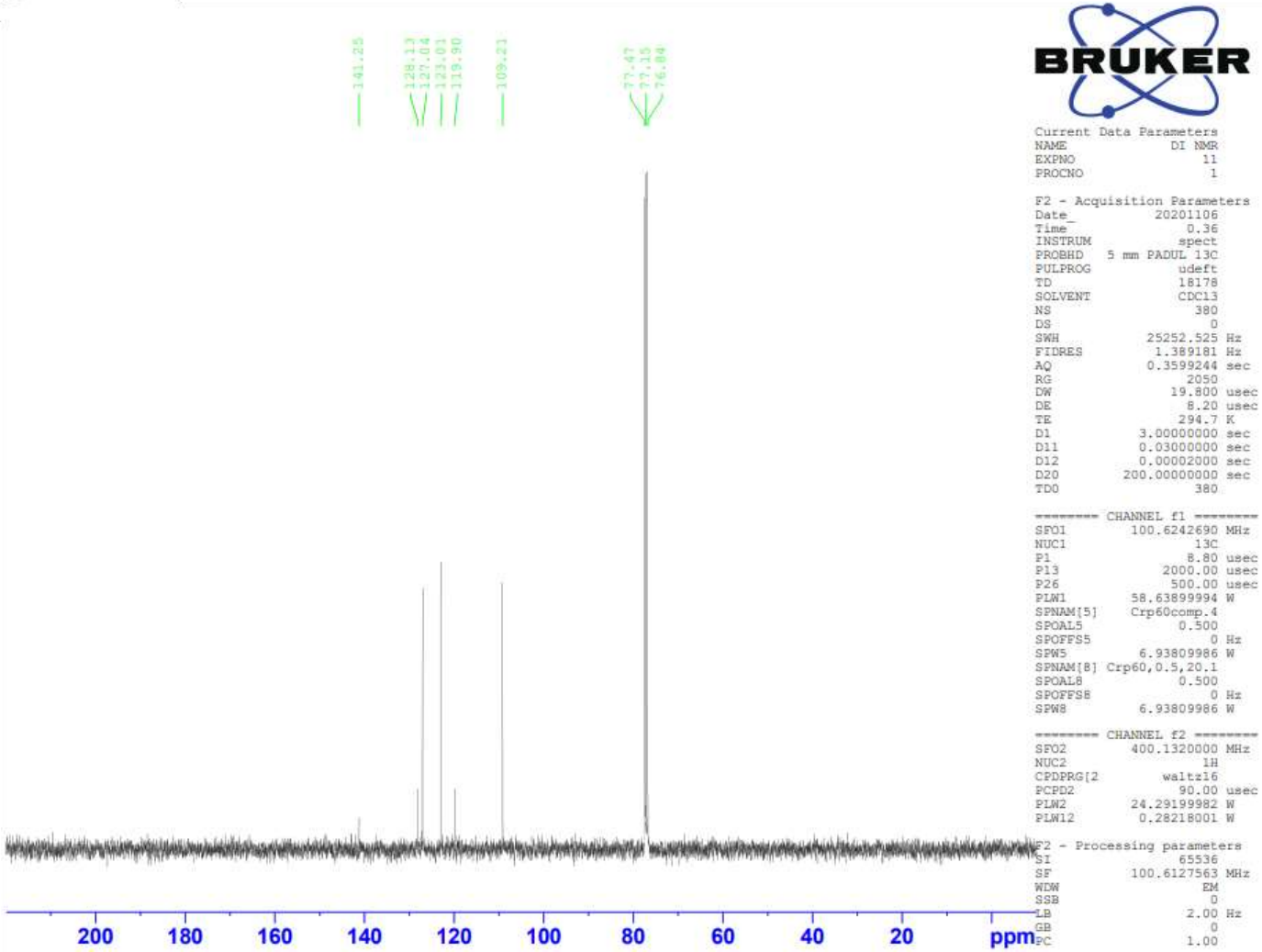
F2 - Acquisition Parameters
Date_            20201106
Time                1.04
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG              zg30
TD                  32768
SOLVENT             CDC13
NS                     32
DS                      2
SWH              8223.685 Hz
FIDRES           0.250967 Hz
AQ               1.9922944 sec
RG                   1030
DW                 60.800 usec
DE                 16.65 usec
TE                 294.5 K
D1              1.50000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324008 MHz
NUC1                   1H
P1                  11.06 usec
PLW1          24.29199982 W

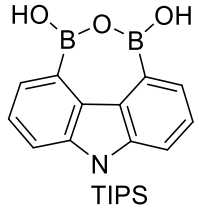
F2 - Processing parameters
SI                  32768
SF            400.1300099 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

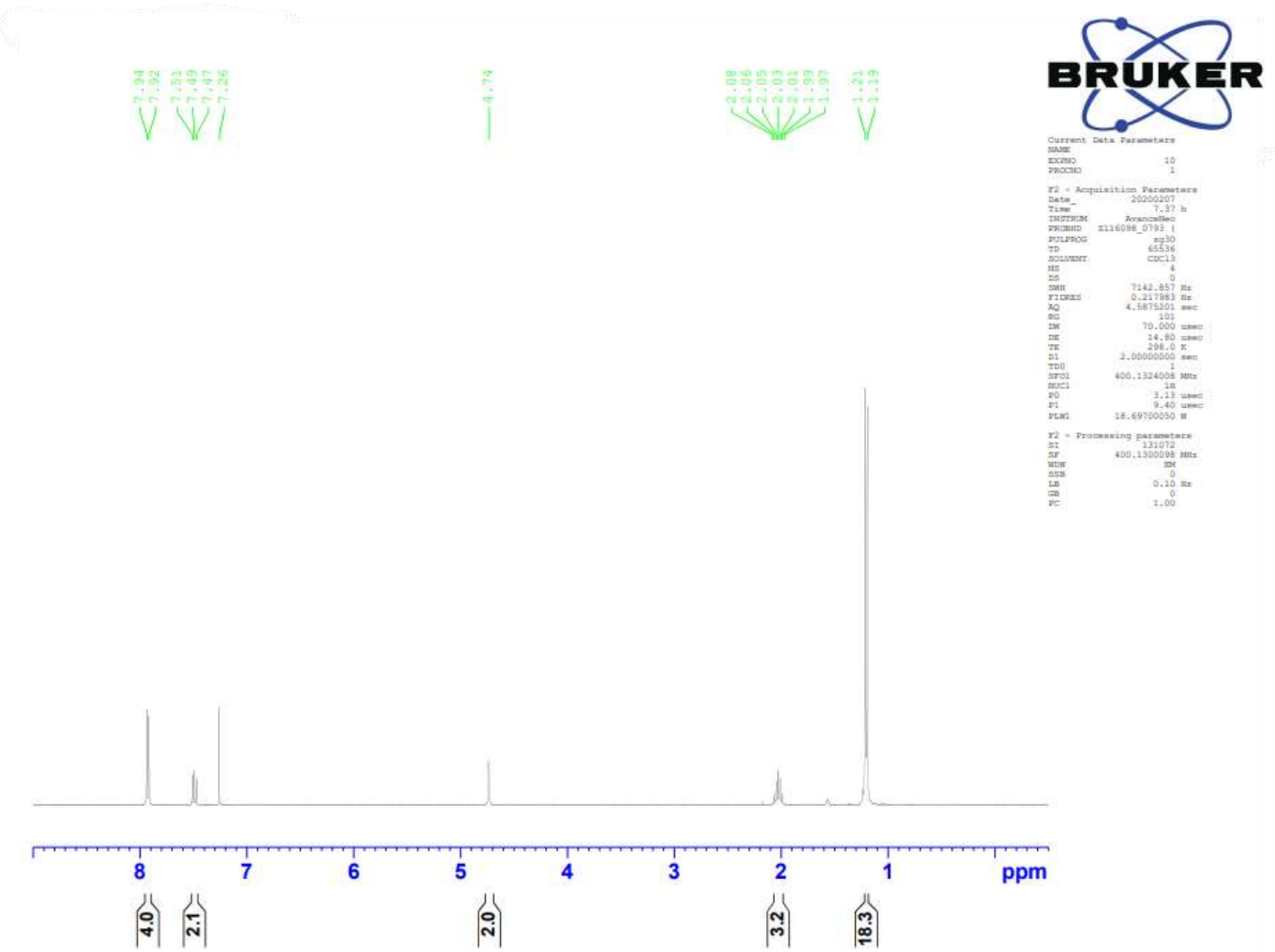
4,5-Dichloro-9H-carbazole [6b]



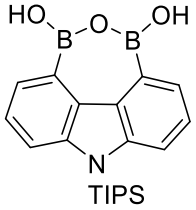


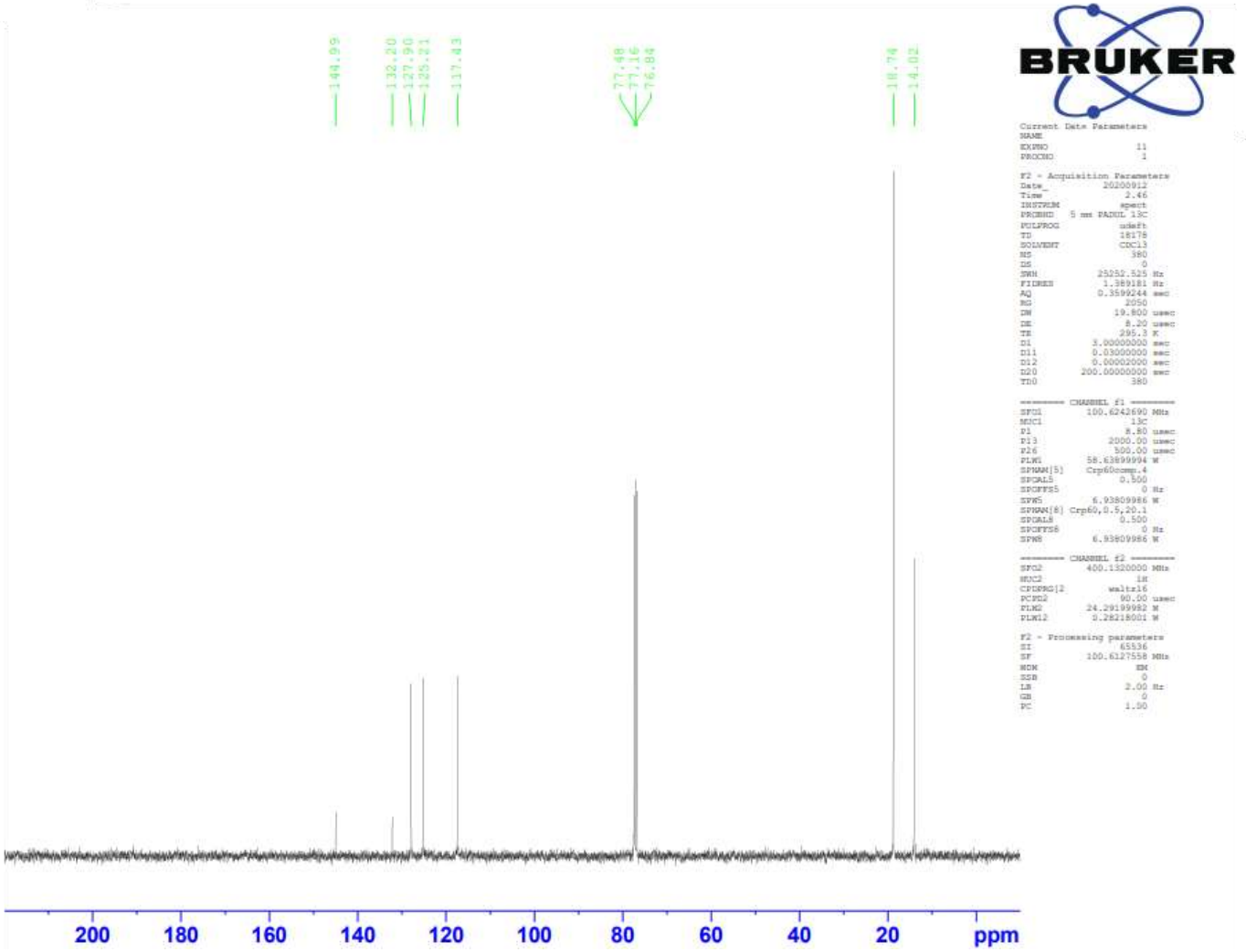
4-(Triisopropylsilyl)-4H-[1,2,7]oxadiborepino[3,4,5,6-def]carbazole-8,10-diol [7a]



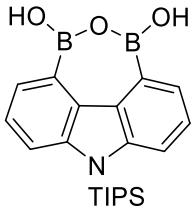


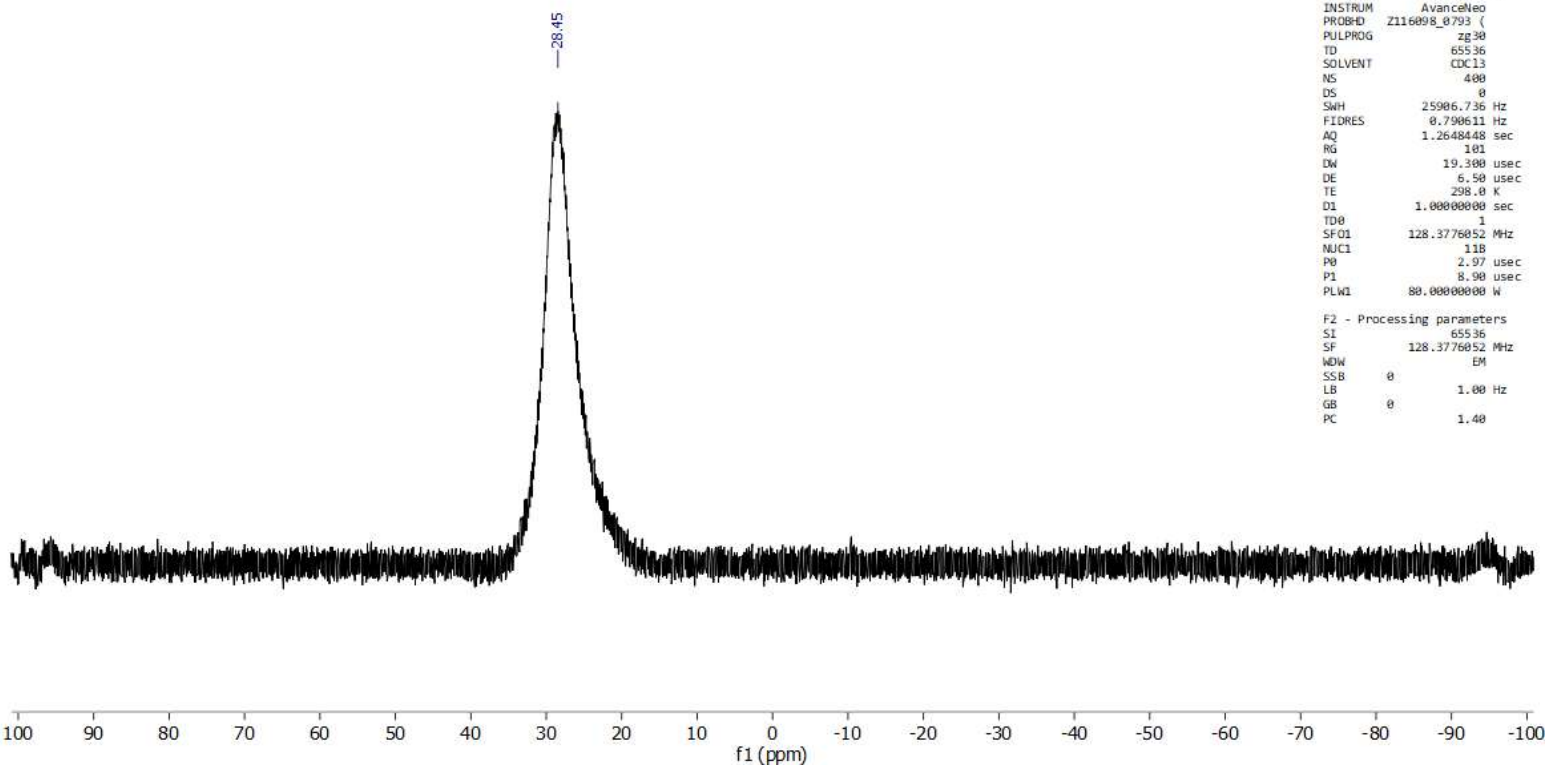
4-(Triisopropylsilyl)-4H-[1,2,7]oxadiborepino[3,4,5,6-def]carbazole-8,10-diol [7a]





4-(Triisopropylsilyl)-4H-[1,2,7]oxadiborepino[3,4,5,6-def]carbazole-8,10-diol [7a]



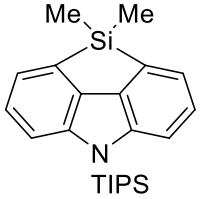


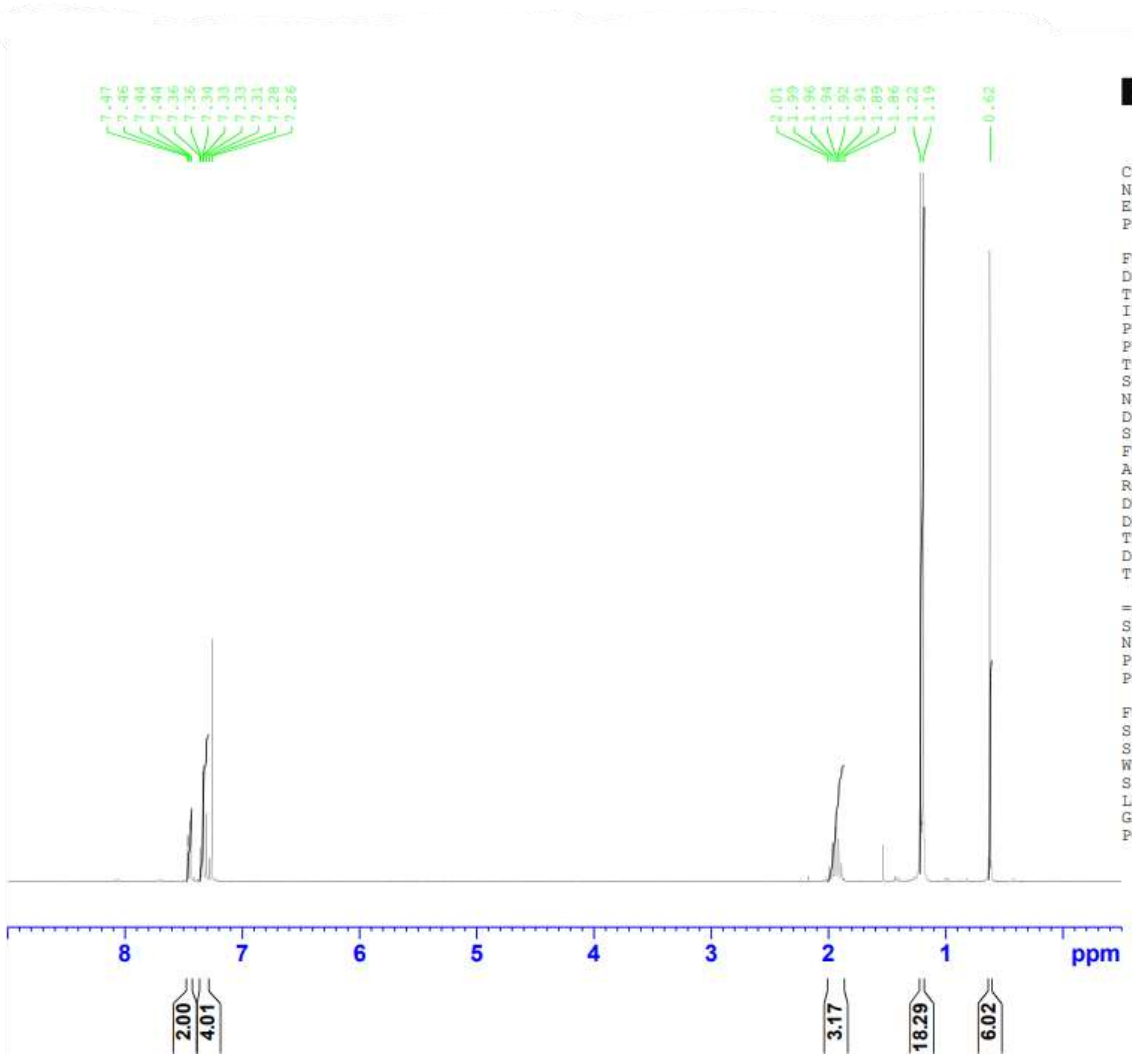

```
Current Data Parameters
NAME                AM70048-3
EXPNO                      13
PROCNO                      1

F2 - Acquisition Parameters
Date_                20191026
Time                     3.27 h
INSTRUM              AvanceNeo
PROBHD     Z116098_0793 (
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                        400
DS                          0
SWH                 25906.736 Hz
FIDRES               0.790611 Hz
AQ                   1.2648448 sec
RG                        101
DW                     19.300 usec
DE                      6.50 usec
TE                     298.0 K
D1                1.00000000 sec
TD0                         1
SFO1              128.3776052 MHz
NUC1                      11B
P0                      2.97 usec
P1                      8.90 usec
PLW1             80.00000000 W

F2 - Processing parameters
SI                      65536
SF                128.3776052 MHz
WDW                        EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```

8,8-Dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [8a]





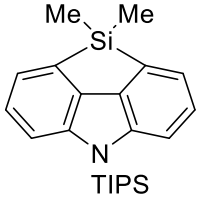

```
Current Data Parameters
NAME                 8,8-dimethy
EXPNO                       20
PROCNO                       1

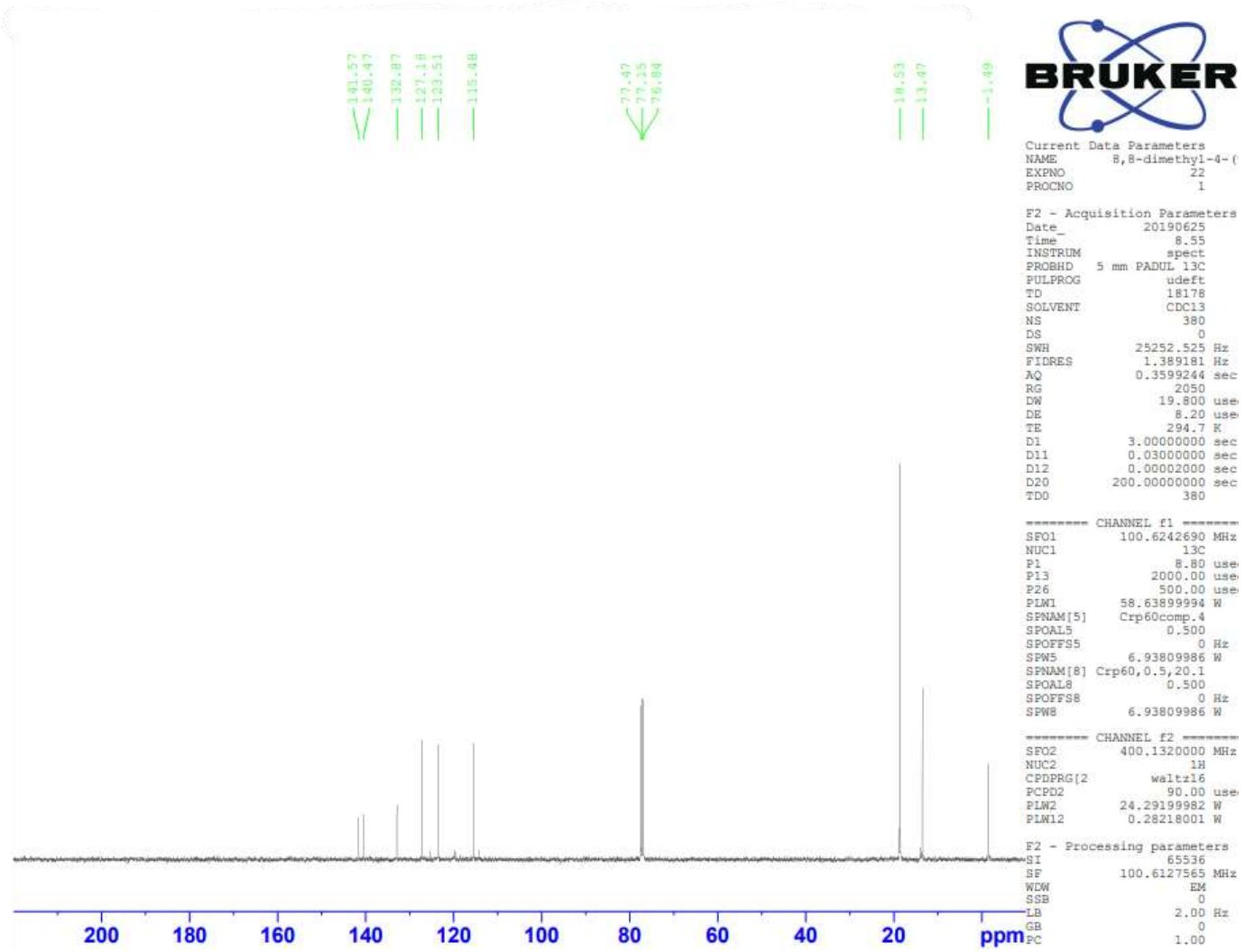
F2 - Acquisition Parameters
Date_               20200210
Time                   17.02
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     32768
SOLVENT                CDC13
NS                        32
DS                         2
SWH                 6009.615 Hz
FIDRES              0.183399 Hz
AQ                  2.7262976 sec
RG                       575
DW                    83.200 usec
DE                    13.27 usec
TE                    296.6 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1             300.0718531 MHz
NUC1                       1H
P1                      10.95 usec
PLW1            15.00000000 W

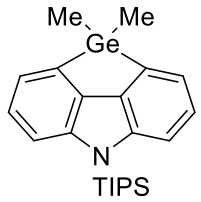
F2 - Processing parameters
SI                         32768
SF               300.0700073 MHz
WDW                          EM
SSB                           0
LB                       0.30 Hz
GB                            0
PC                         1.00
```

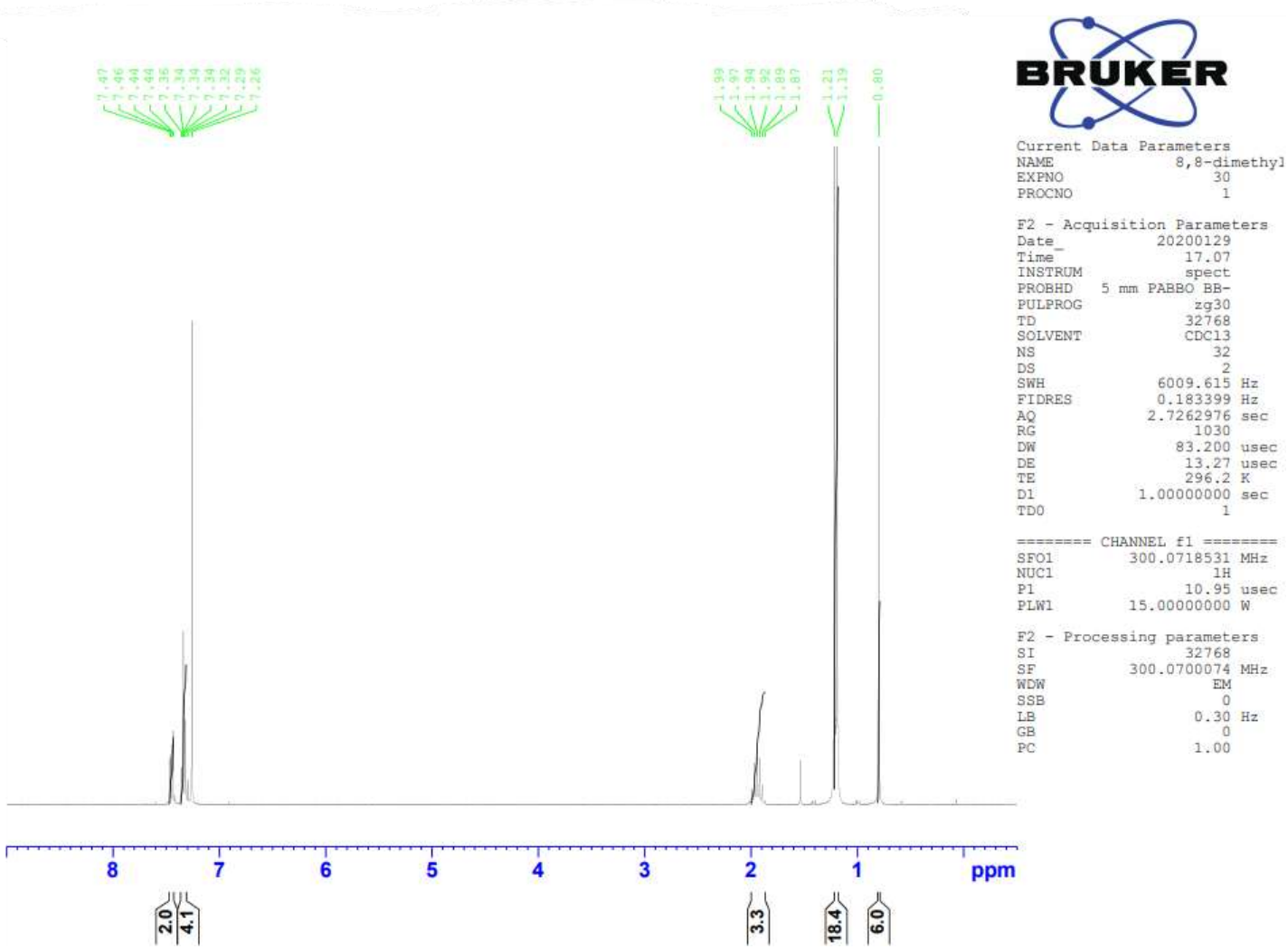
8,8-Dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [8a]





8,8-Dimethyl-4-(triisopropylsilyl)-4,8-dihydrogermolo[2,3,4,5-def]carbazole [9a]





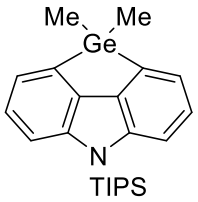

```
Current Data Parameters
NAME                  8,8-dimethyl
EXPNO                           30
PROCNO                           1

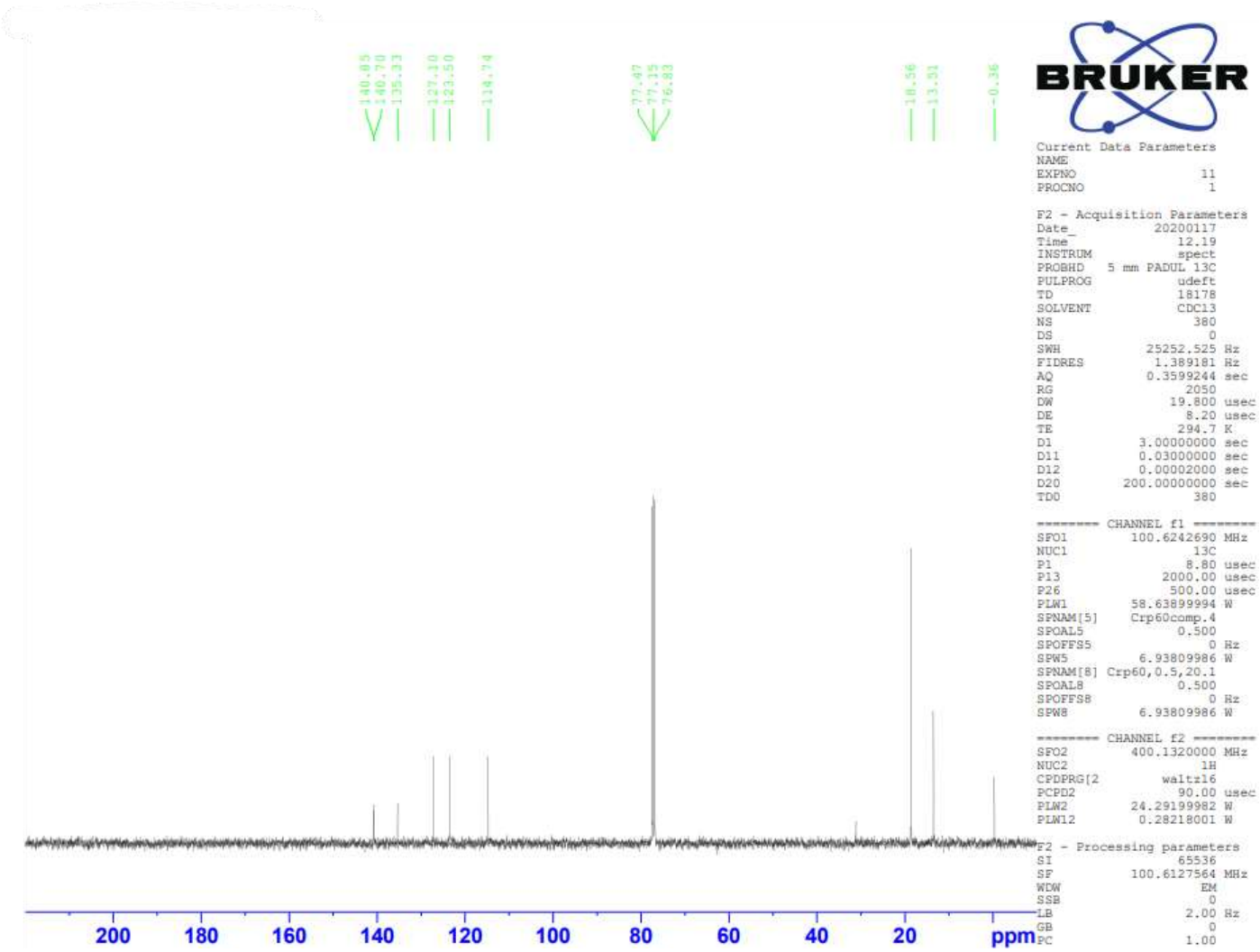
F2 - Acquisition Parameters
Date_                     20200129
Time                         17.07
INSTRUM                      spect
PROBHD    5 mm PABBO BB-
PULPROG                      zg30
TD                          32768
SOLVENT                     CDCl3
NS                             32
DS                              2
SWH                      6009.615 Hz
FIDRES                   0.183399 Hz
AQ                       2.7262976 sec
RG                           1030
DW                         83.200 usec
DE                          13.27 usec
TE                          296.2 K
D1                    1.00000000 sec
TD0                             1

======== CHANNEL f1 ========
SFO1                300.0718531 MHz
NUC1                        1H
P1                         10.95 usec
PLW1                15.00000000 W

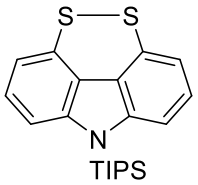
F2 - Processing parameters
SI                          32768
SF                  300.0700074 MHz
WDW                            EM
SSB                             0
LB                           0.30 Hz
GB                              0
PC                           1.00
```

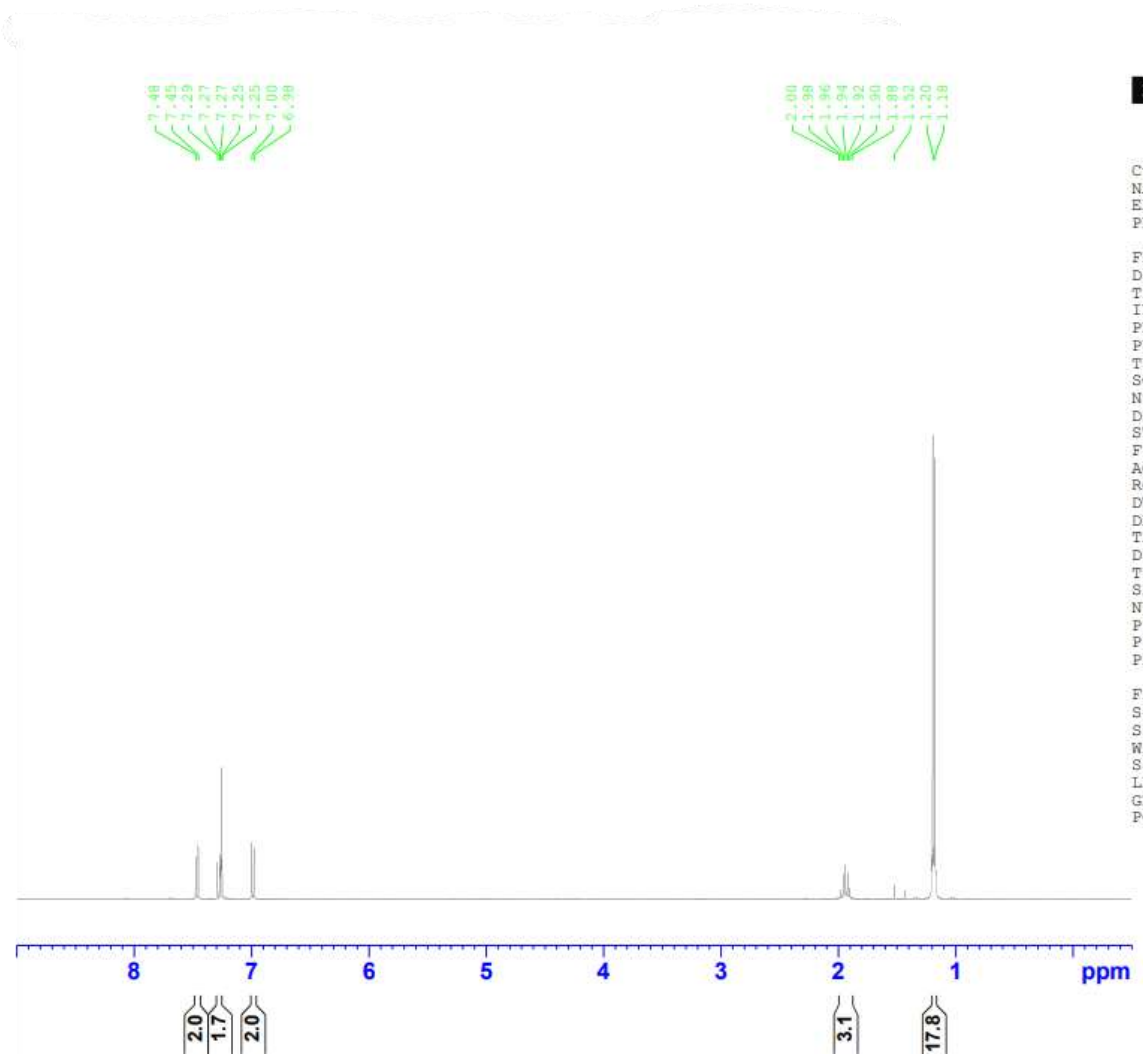
8,8-Dimethyl-4-(triisopropylsilyl)-4,8-dihydrogermolo[2,3,4,5-def]carbazole [9a]





9-(Triisopropylsilyl)-9H-[1,2]dithiino[3,4,5,6-def]carbazole [10a]



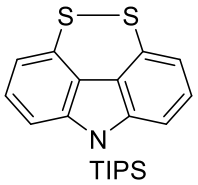


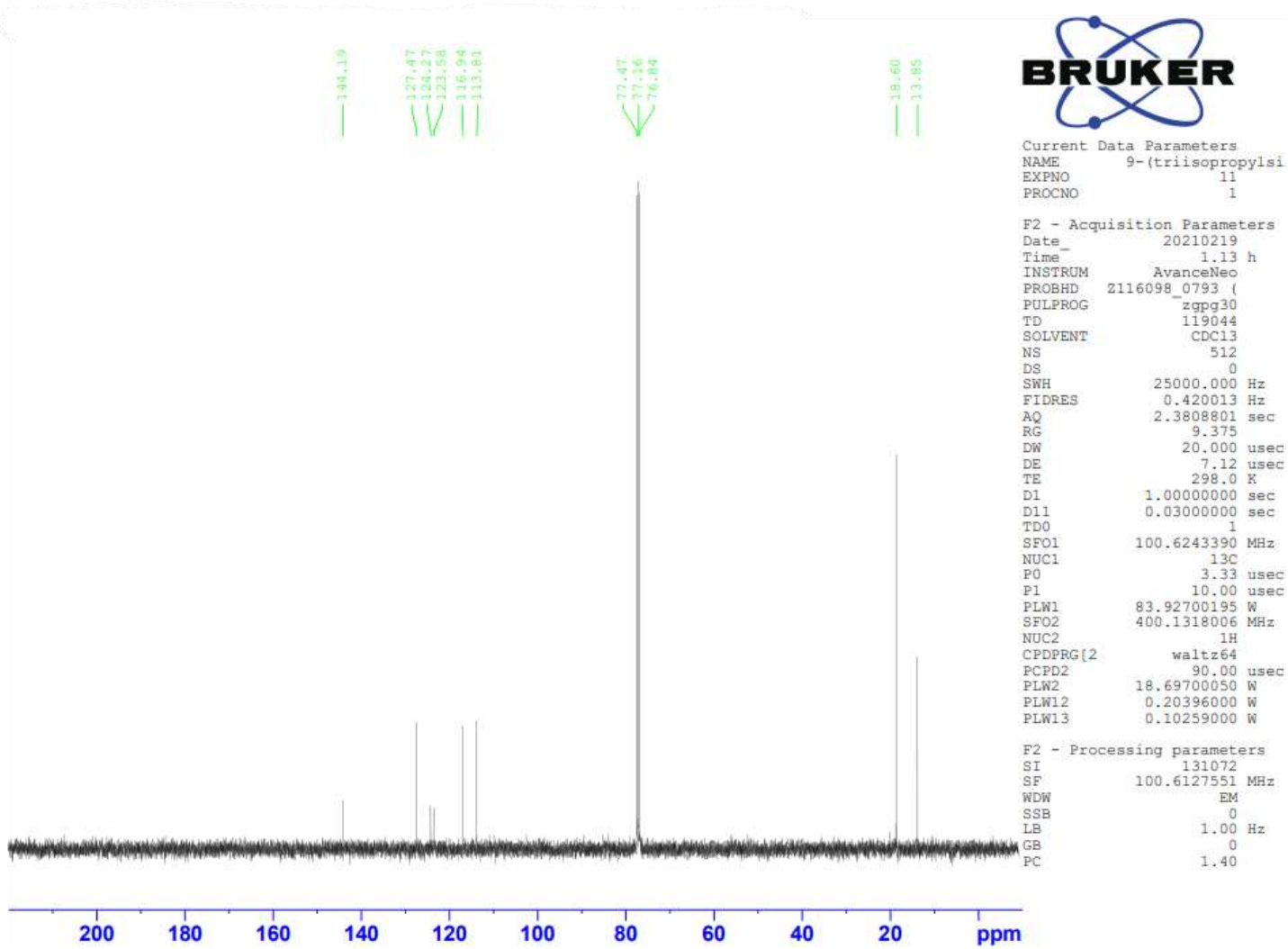

```
Current Data Parameters
NAME        9-(triisopropylsi
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20210218
Time                 17.19 h
INSTRUM          AvanceNeo
PROBHD    Z116098_0793 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        4
DS                        0
SWH                7142.857 Hz
FIDRES            0.217983 Hz
AQ                4.5875201 sec
RG                      101
DW                   70.000 usec
DE                   14.80 usec
TE                   298.0 K
D1              2.00000000 sec
TD0                       1
SFO1           400.1324008 MHz
NUC1                     1H
P0                   3.13 usec
P1                   9.40 usec
PLW1           18.69700050 W

F2 - Processing parameters
SI                   131072
SF             400.1300123 MHz
WDW                      EM
SSB                       0
LB                    0.10 Hz
GB                        0
PC                    1.00
```

9-(Triisopropylsilyl)-9H-[1,2]dithiino[3,4,5,6-def]carbazole [10a]



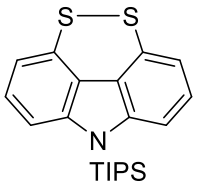



```
Current Data Parameters
NAME        9-(triisopropylsi
EXPNO                      11
PROCNO                      1

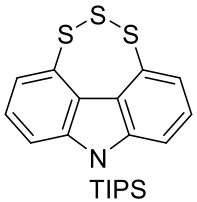
F2 - Acquisition Parameters
Date_                20210219
Time                     1.13 h
INSTRUM             AvanceNeo
PROBHD    Z116098_0793 (
PULPROG                zgpg30
TD                     119044
SOLVENT                 CDCl3
NS                        512
DS                          0
SWH                 25000.000 Hz
FIDRES                0.420013 Hz
AQ                    2.3808801 sec
RG                        9.375
DW                       20.000 usec
DE                        7.12 usec
TE                       298.0 K
D1                  1.00000000 sec
D11                 0.03000000 sec
TD0                         1
SFO1               100.6243390 MHz
NUC1                       13C
P0                        3.33 usec
P1                       10.00 usec
PLW1               83.92700195 W
SFO2               400.1318006 MHz
NUC2                       1H
CPDPRG[2               waltz64
PCPD2                    90.00 usec
PLW2               18.69700050 W
PLW12               0.20396000 W
PLW13               0.10259000 W

F2 - Processing parameters
SI                        131072
SF                 100.6127551 MHz
WDW                         EM
SSB                         0
LB                        1.00 Hz
GB                          0
PC                        1.40
```

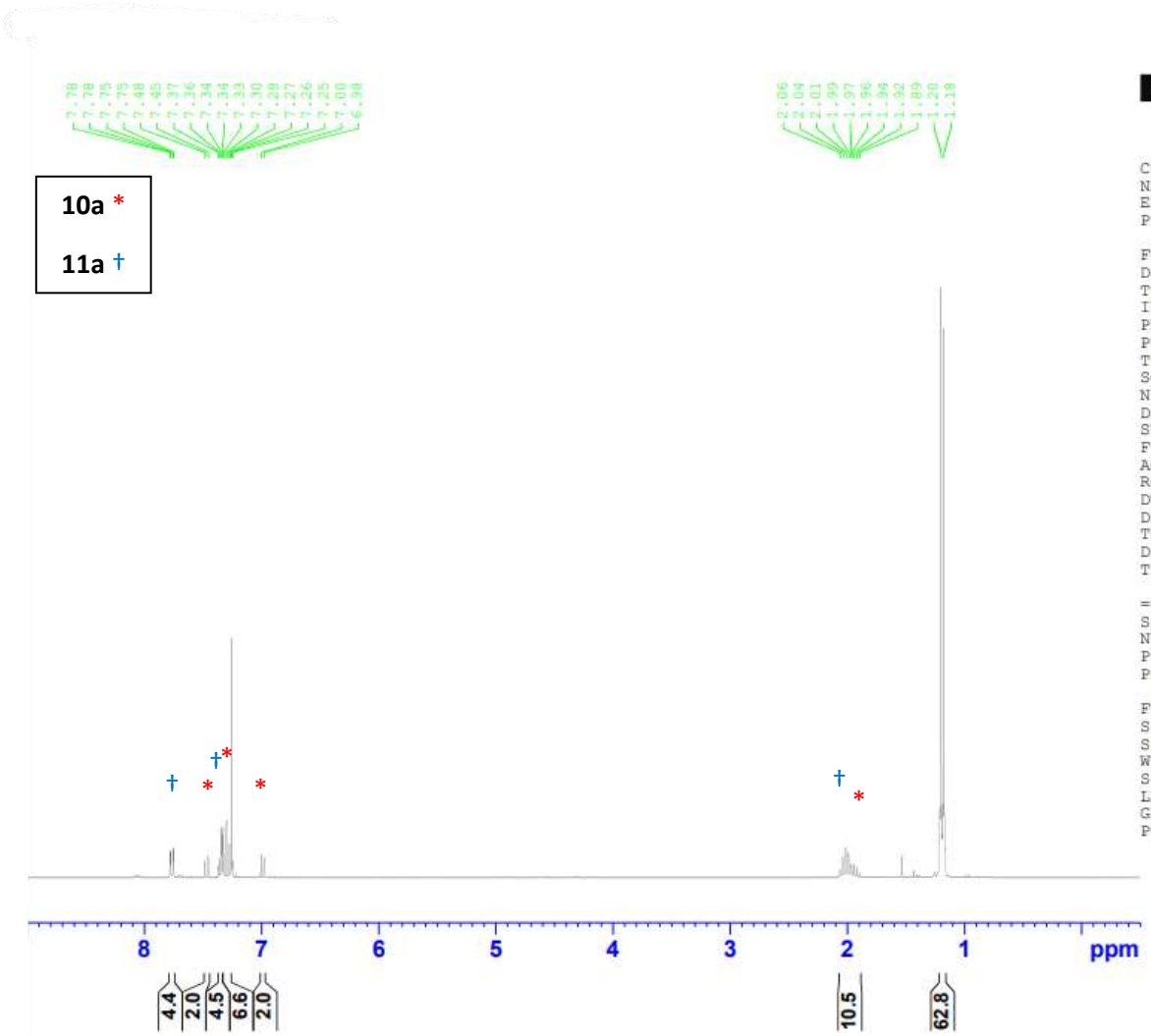
Mixture of 10a and 11a (1:~2.2 by integration of ^{1}H NMR)



10a



11a



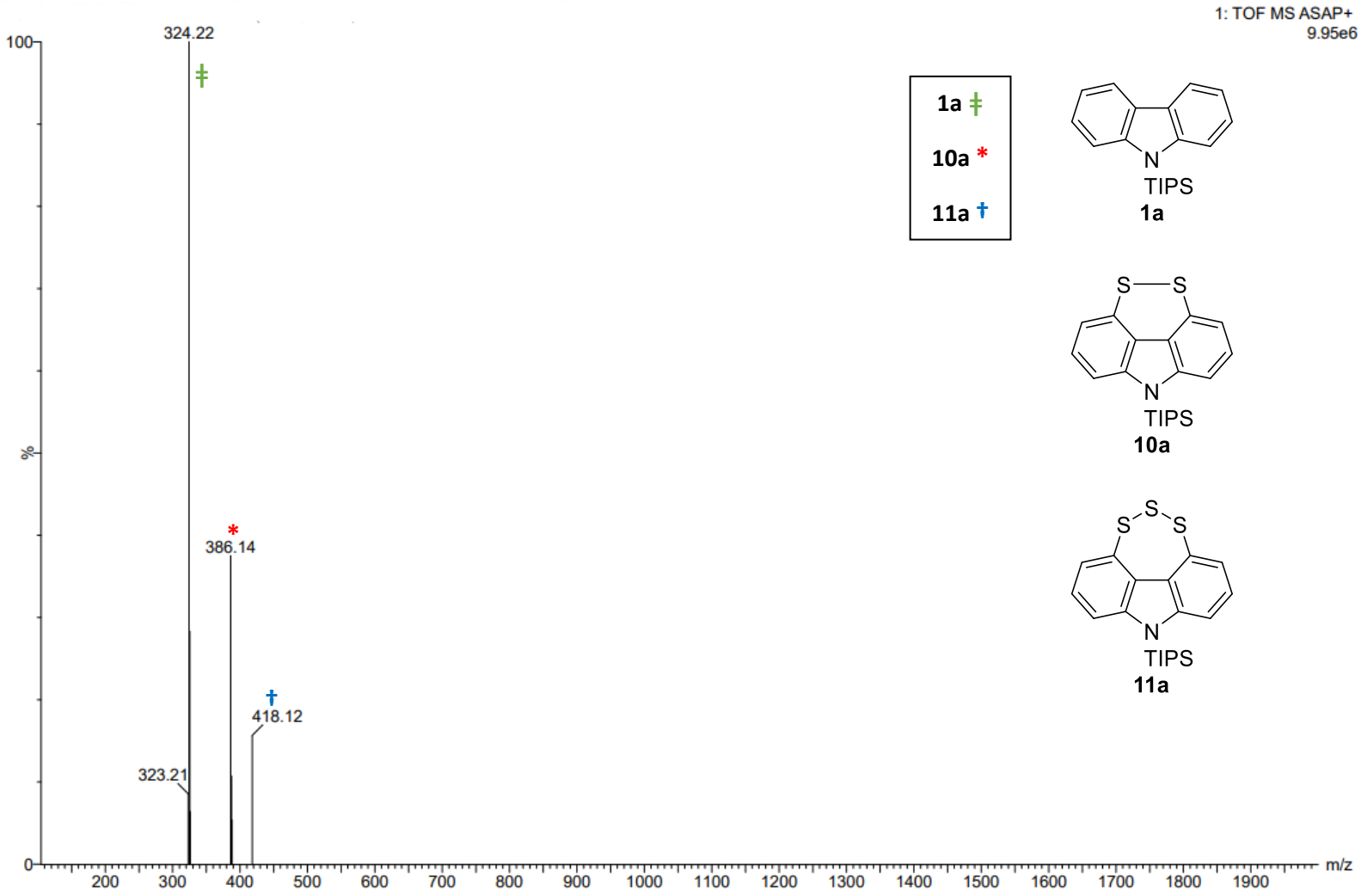

```
Current Data Parameters
NAME
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20201217
Time                10.02
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     32
DS                      2
SWH              6009.615 Hz
FIDRES           0.183399 Hz
AQ               2.7262976 sec
RG                    645
DW                 83.200 usec
DE                 13.05 usec
TE                 295.6 K
D1              1.00000000 sec
TD0                     1

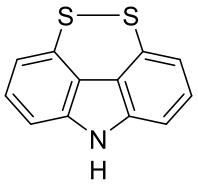
======== CHANNEL f1 ========
SFO1          300.0718531 MHz
NUC1                   1H
P1                  12.00 usec
PLW1          9.50000000 W

F2 - Processing parameters
SI                  32768
SF            300.0700083 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

Low resolution mass spectrum of mixture of 10a and 11a



9-(Triisopropylsilyl)-9H-[1,2]dithiino[3,4,5,6-def]carbazole [10b]

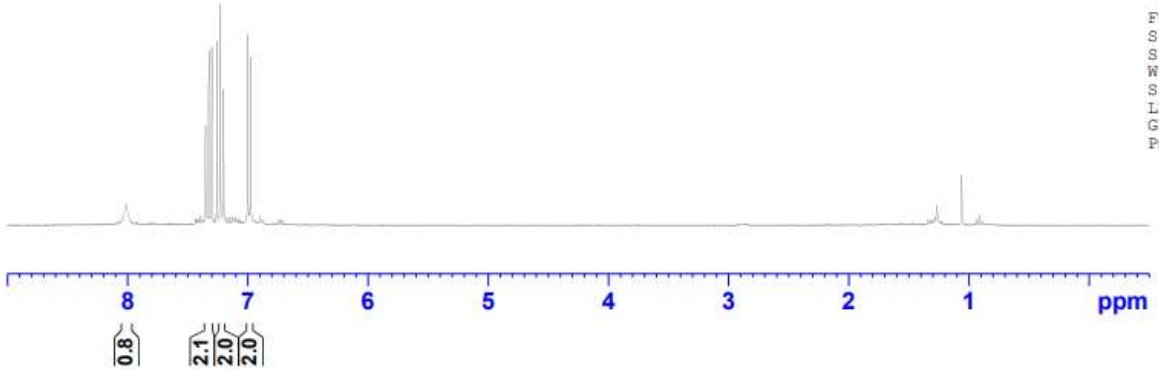



```
Current Data Parameters
NAME
EXPNO                  20
PROCNO                  1

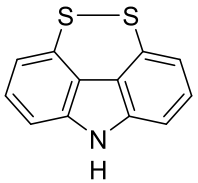
F2 - Acquisition Parameters
Date_           20210429
Time               16.26
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ              2.7262976 sec
RG                   645
DW                83.200 usec
DE                13.05 usec
TE                295.1 K
D1             1.00000000 sec
TD0                    1

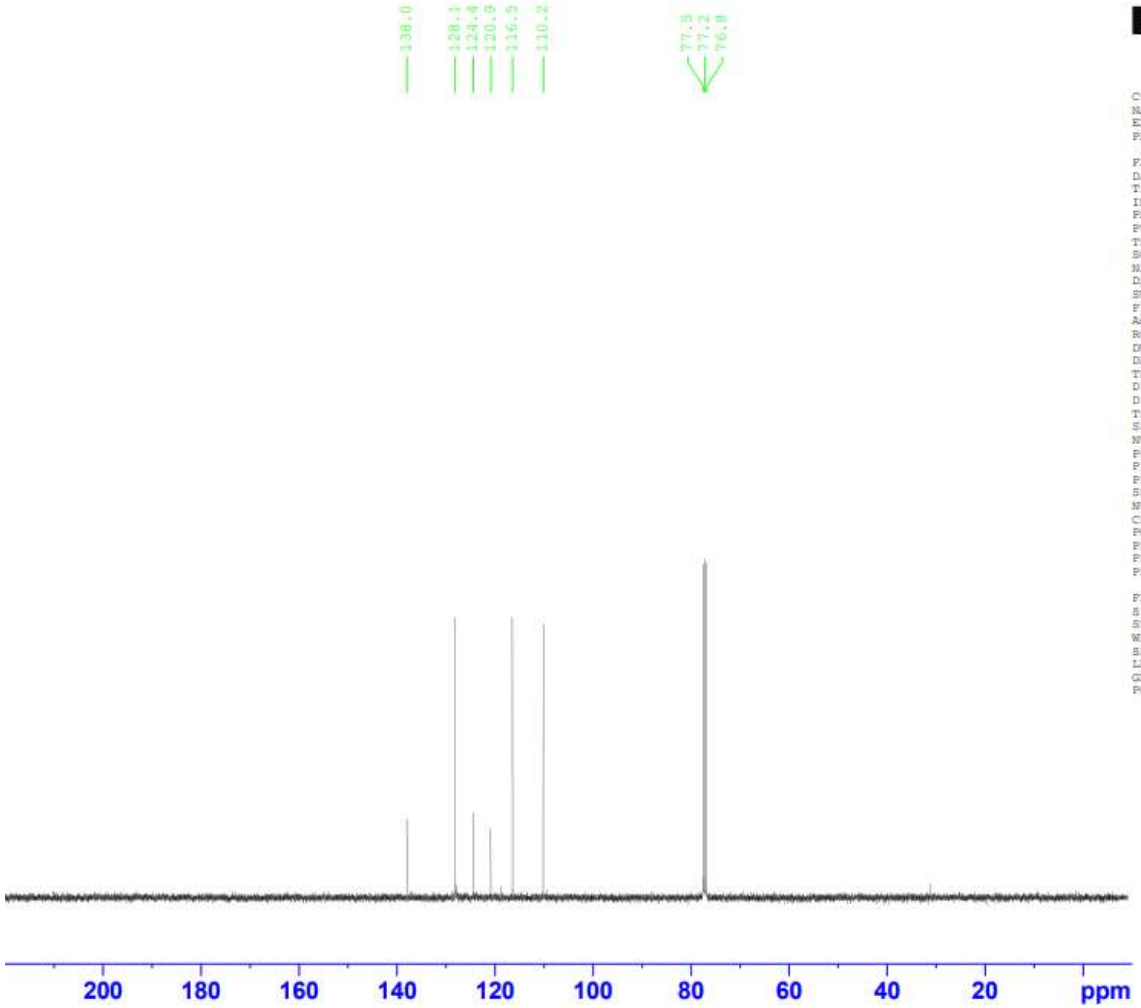
======== CHANNEL f1 ========
SFO1         300.0718531 MHz
NUC1                1H
P1                 12.00 usec
PLW1          9.50000000 W

F2 - Processing parameters
SI                 32768
SF           300.0700073 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



9-(Triisopropylsilyl)-9H-[1,2]dithiino[3,4,5,6-def]carbazole [10b]





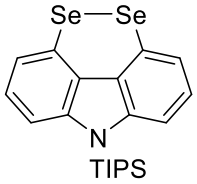
BRUKER

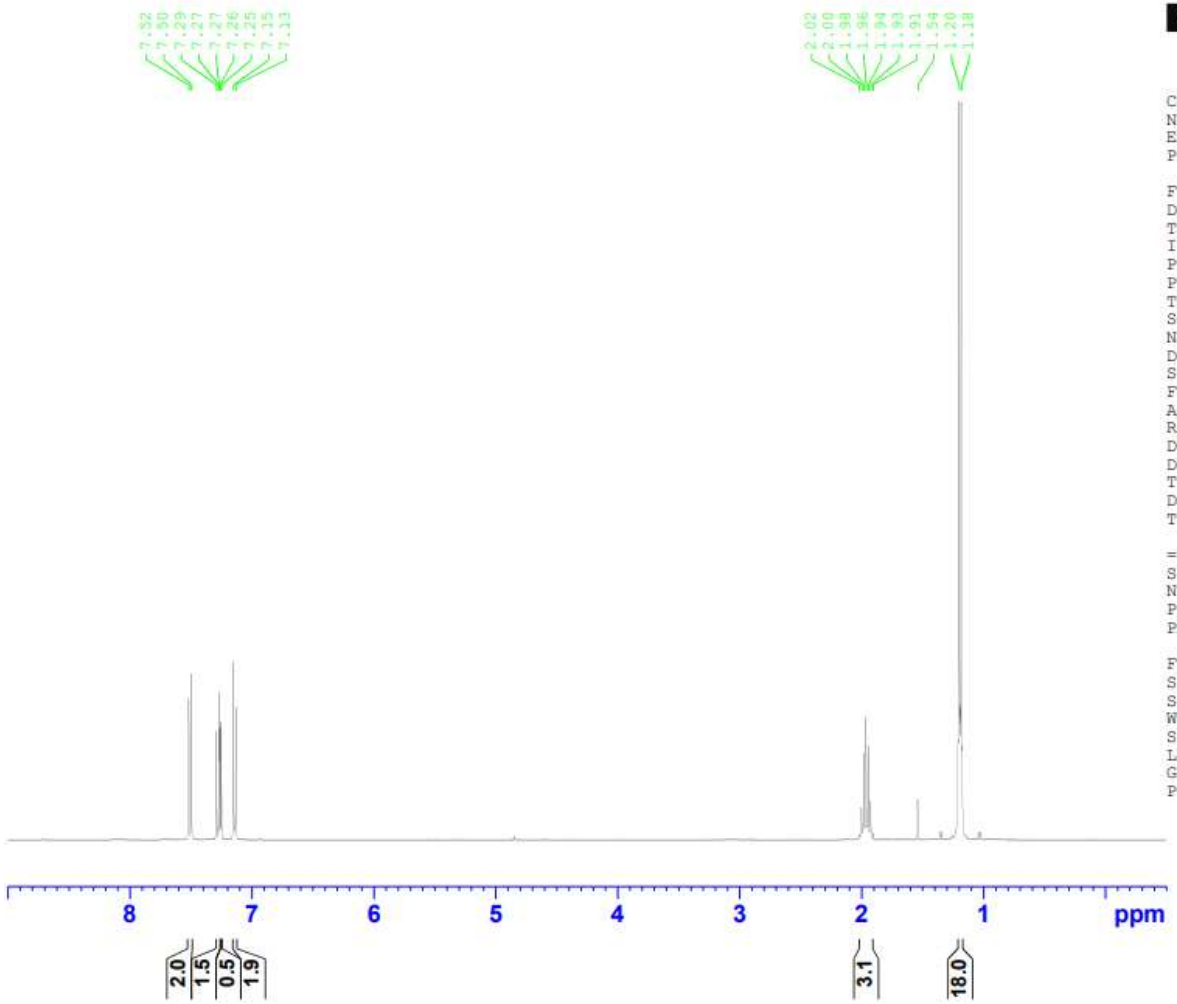
```
Current Data Parameters
NAME
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210501
Time                2.52 h
INSTRUM        AvanceNeo
PROBHD   Z116098_0793 (
PULPROG            zgpg30
TD                 119044
SOLVENT             CDCl3
NS                    512
DS                      0
SWH             25000.000 Hz
FIDRES              0.420013 Hz
AQ                2.3808801 sec
RG                    9.375
DW                   20.000 usec
DE                    7.12 usec
TE                  298.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1
SFO1          100.6243390 MHz
NUC1                  13C
P0                    3.33 usec
P1                   10.00 usec
PLW1          83.92700195 W
SFO2          400.1318006 MHz
NUC2                  1H
CPDPRG[2          waltz64
PCPD2                90.00 usec
PLW2          18.69700050 W
PLW12          0.20396000 W
PLW13          0.10259000 W

F2 - Processing parameters
SI                  131072
SF            100.6127583 MHz
WDW                   EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

9-(Triisopropylsilyl)-9H-[1,2]diselenino[3,4,5,6-def]carbazole [12a]





BRUKER

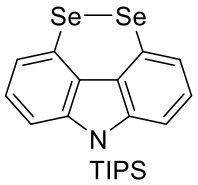
```
Current Data Parameters
NAME
EXPNO                  10
PROCNO                  1

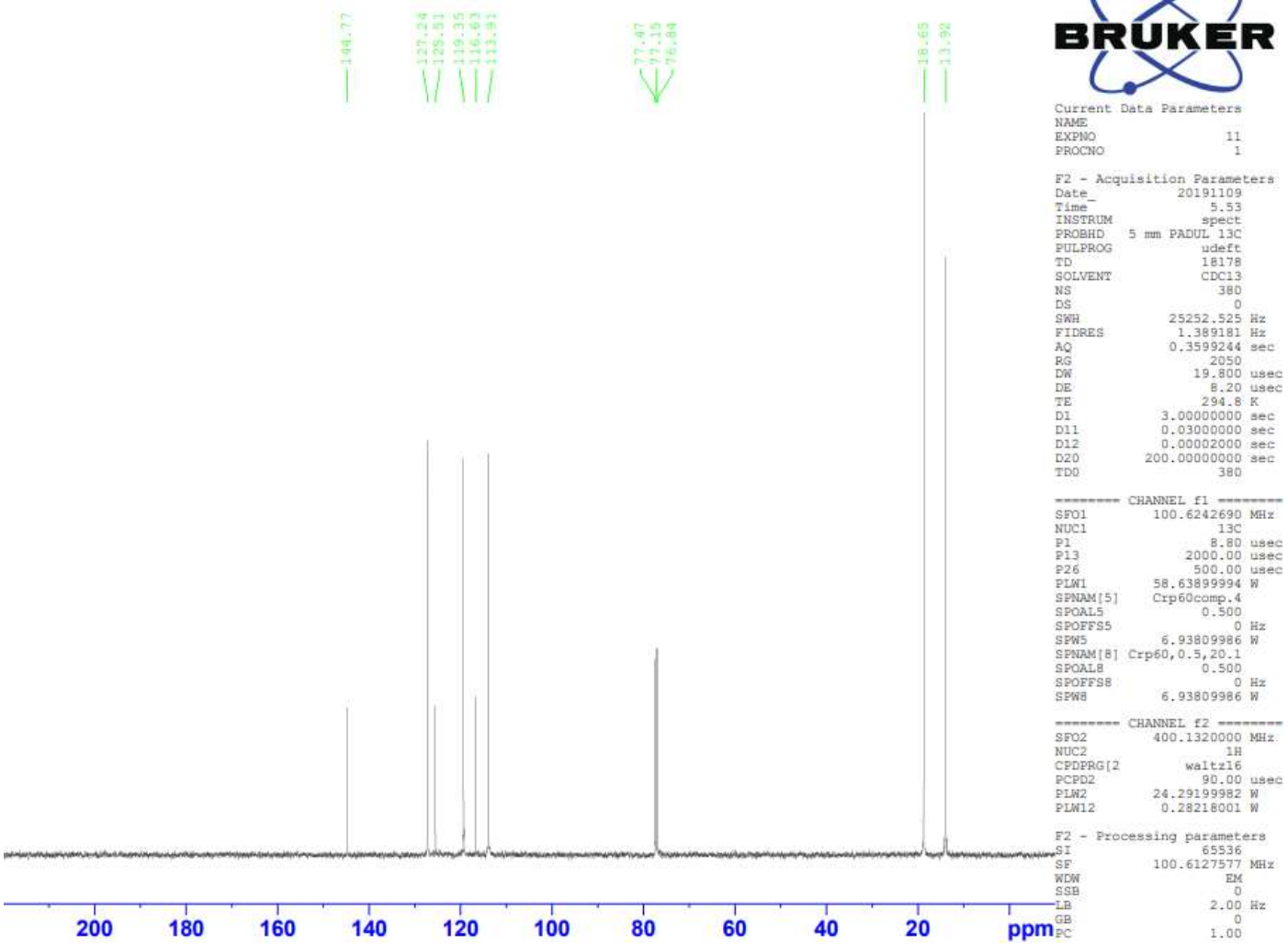
F2 - Acquisition Parameters
Date_            20191109
Time                5.43
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             8223.685 Hz
FIDRES          0.250967 Hz
AQ              1.9922944 sec
RG                   203
DW                60.800 usec
DE                16.65 usec
TE                294.8 K
D1             1.50000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          400.1324008 MHz
NUC1                  1H
P1                 11.06 usec
PLW1          24.29199982 W

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

9-(Triisopropylsilyl)-9H-[1,2]diselenino[3,4,5,6-def]carbazole [12a]





BRUKER

```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

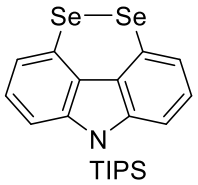
F2 - Acquisition Parameters
Date_            20191109
Time                5.53
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG            udeft
TD                 18178
SOLVENT            CDCl3
NS                   380
DS                     0
SWH            25252.525 Hz
FIDRES          1.389181 Hz
AQ              0.3599244 sec
RG                  2050
DW                19.800 usec
DE                 8.20 usec
TE                294.8 K
D1             3.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec
D20          200.00000000 sec
TD0                  380

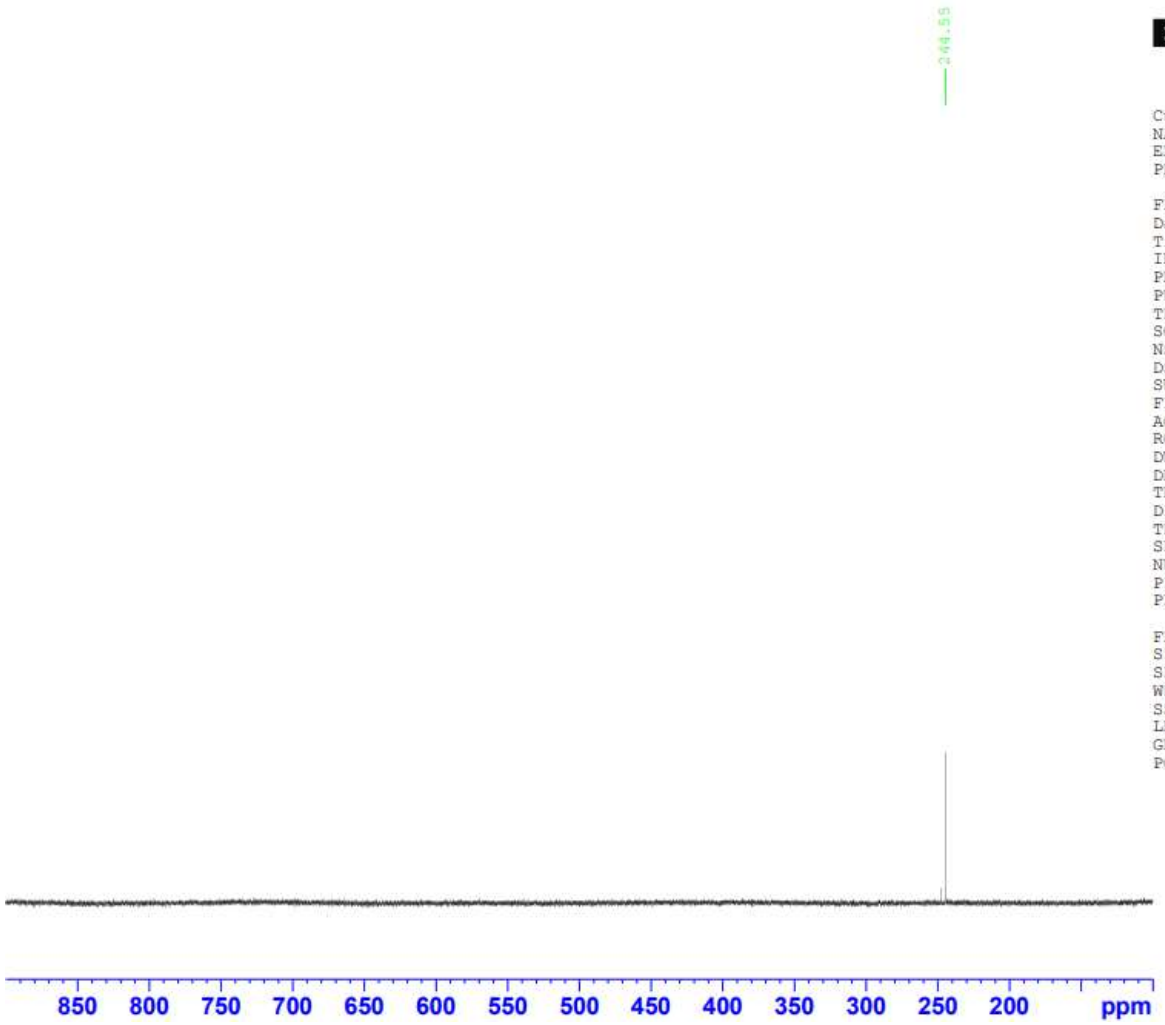
======== CHANNEL f1 ========
SFO1         100.6242690 MHz
NUC1                13C
P1                 8.80 usec
P13             2000.00 usec
P26              500.00 usec
PLW1          58.63899994 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5                0 Hz
SPW5           6.93809986 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 usec
PLW2         24.29199982 W
PLW12         0.28218001 W

F2 - Processing parameters
SI                 65536
SF           100.6127577 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.00
```

9-(Triisopropylsilyl)-9H-[1,2]diselenino[3,4,5,6-def]carbazole [12a]



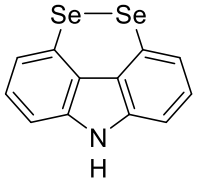


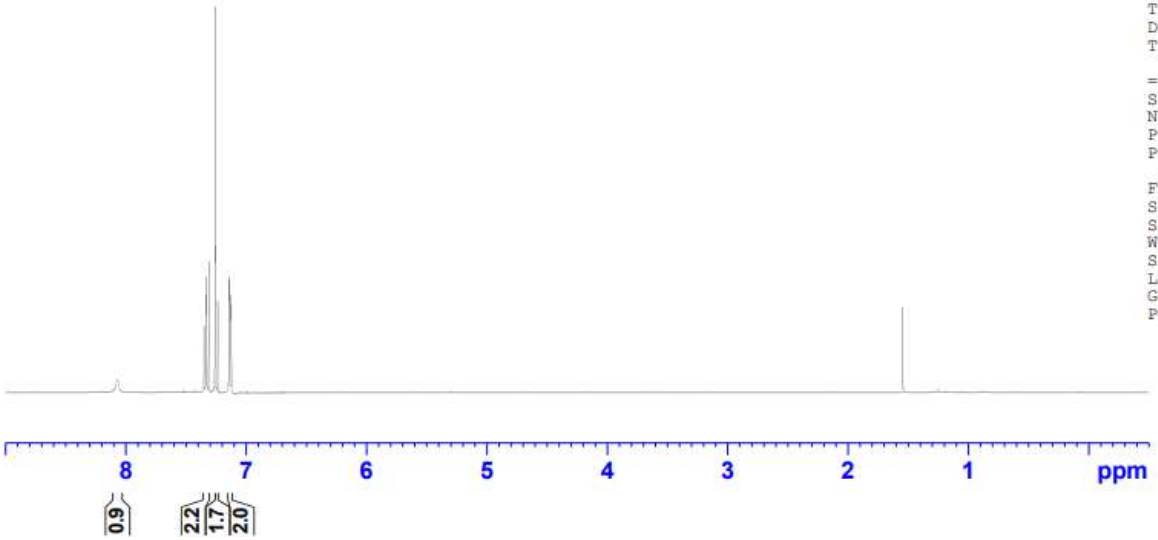

```
Current Data Parameters
NAME
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190317
Time                7.53 h
INSTRUM  AvanceNeo, Otter
PROBHD   Z116098_0793 (
PULPROG                zg
TD                  32768
SOLVENT             CDCl3
NS                   1500
DS                      0
SWH             62500.000 Hz
FIDRES          3.814697 Hz
AQ              0.2621440 sec
RG                5.20833
DW                  8.000 usec
DE                  6.50 usec
TE                 298.0 K
D1             0.50000000 sec
TD0                     1
SFO1           76.3490004 MHz
NUC1                 77Se
P1                 11.00 usec
PLW1          90.00000000 W

F2 - Processing parameters
SI                  65536
SF             76.3108450 MHz
WDW                    EM
SSB                     0
LB                  2.00 Hz
GB                      0
PC                  1.40
```

9H-[1,2]diselenino[3,4,5,6-def]carbazole [12b]





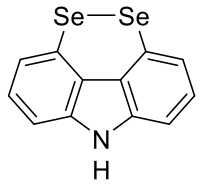

```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

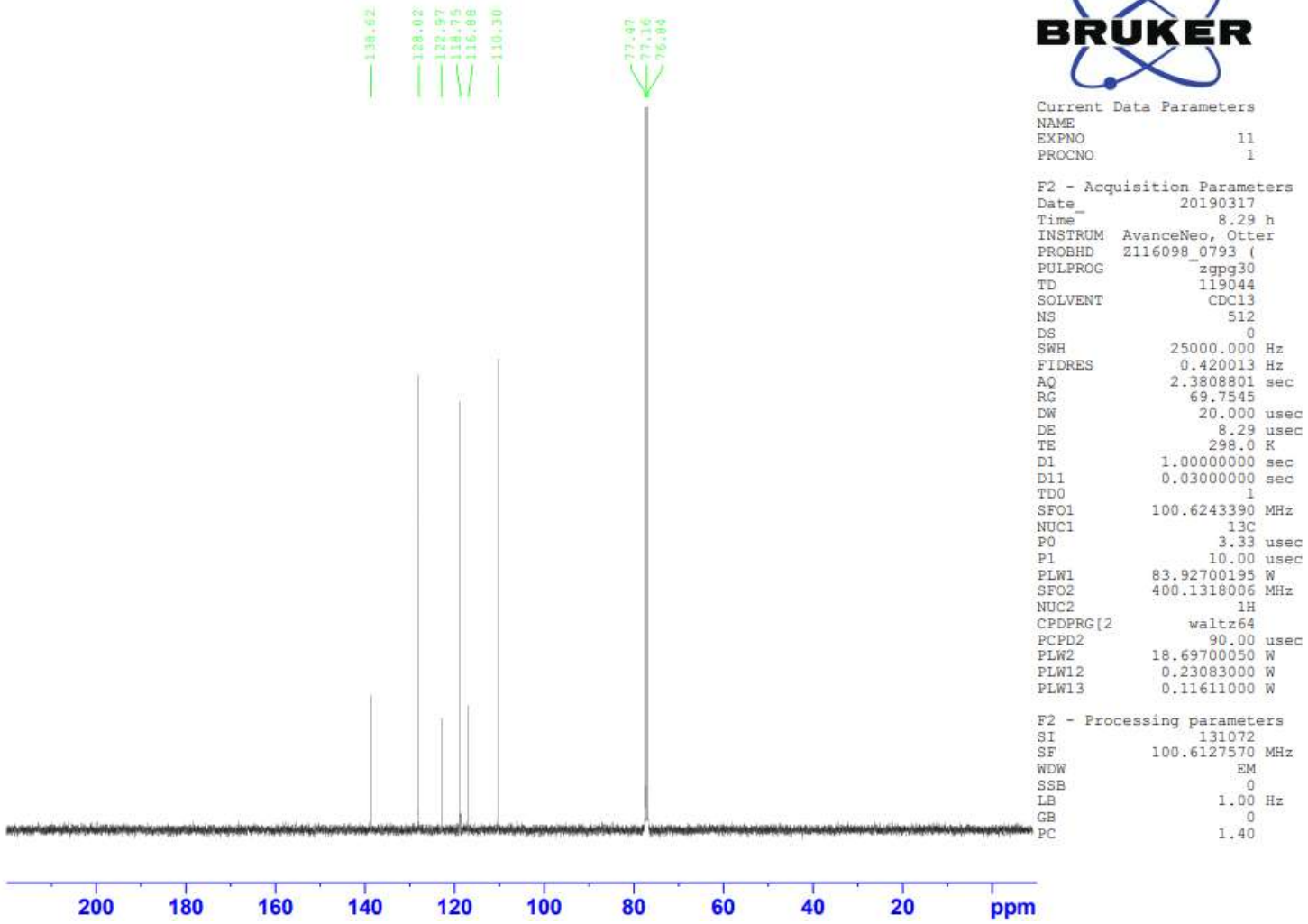
F2 - Acquisition Parameters
Date_           20210430
Time                4.53
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG                zg
TD                  32768
SOLVENT             CDCl3
NS                     64
DS                      2
SWH              8223.685 Hz
FIDRES           0.250967 Hz
AQ               1.9922944 sec
RG                    406
DW                 60.800 usec
DE                 11.93 usec
TE                 294.4 K
D1           15.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                   1H
P1                 11.06 usec
PLW1         24.29199982 W

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

9H-[1,2]diselenino[3,4,5,6-def]carbazole [12b]





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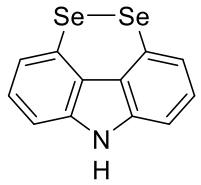
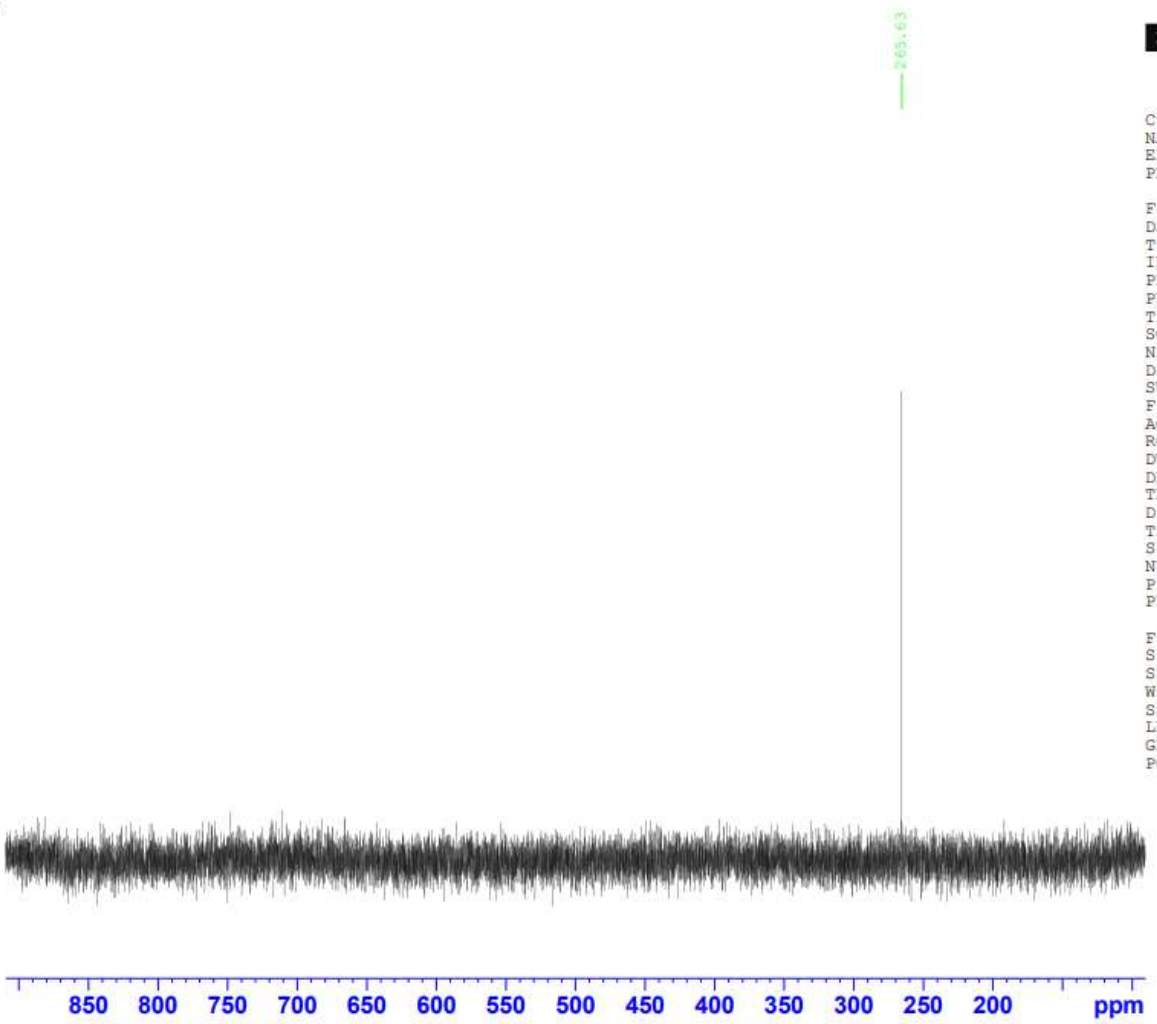
```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190317
Time                8.29 h
INSTRUM  AvanceNeo, Otter
PROBHD   Z116098_0793 (
PULPROG           zgpg30
TD                119044
SOLVENT             CDC13
NS                    512
DS                      0
SWH           25000.000 Hz
FIDRES         0.420013 Hz
AQ             2.3808801 sec
RG               69.7545
DW                20.000 usec
DE                 8.29 usec
TE                298.0 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                     1
SFO1        100.6243390 MHz
NUC1                  13C
P0                   3.33 usec
P1                  10.00 usec
PLW1         83.92700195 W
SFO2        400.1318006 MHz
NUC2                  1H
CPDPRG[2          waltz64
PCPD2               90.00 usec
PLW2         18.69700050 W
PLW12         0.23083000 W
PLW13         0.11611000 W

F2 - Processing parameters
SI                  131072
SF          100.6127570 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

9H-[1,2]diselenino[3,4,5,6-def]carbazole [12b]



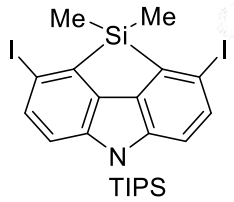


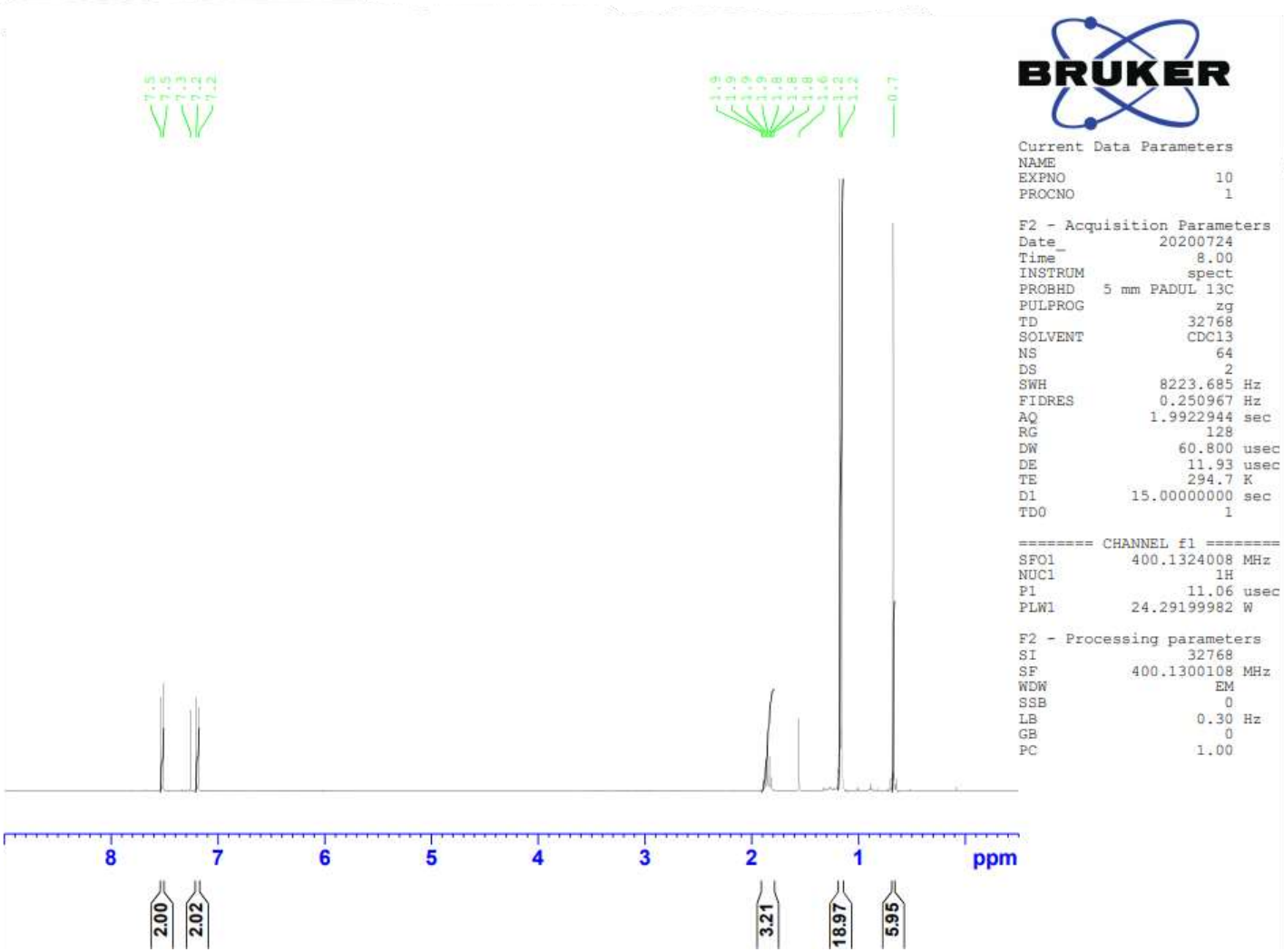

```
Current Data Parameters
NAME
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190317
Time                8.50 h
INSTRUM  AvanceNeo, Otter
PROBHD   Z116098_0793 (
PULPROG                zg
TD                  32768
SOLVENT             CDCl3
NS                   1500
DS                      0
SWH             62500.000 Hz
FIDRES          3.814697 Hz
AQ              0.2621440 sec
RG                 7.8125
DW                 8.000 usec
DE                 6.50 usec
TE                 298.0 K
D1              0.50000000 sec
TD0                     1
SFO1           76.3490004 MHz
NUC1                  77Se
P1                 11.00 usec
PLW1          90.00000000 W

F2 - Processing parameters
SI                  65536
SF             76.3108450 MHz
WDW                    EM
SSB                     0
LB                 2.00 Hz
GB                      0
PC                 1.40
```

1,7-Diiodo-8,8-dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [13a]





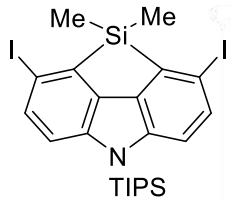

```
Current Data Parameters
NAME
EXPNO                  10
PROCNO                  1

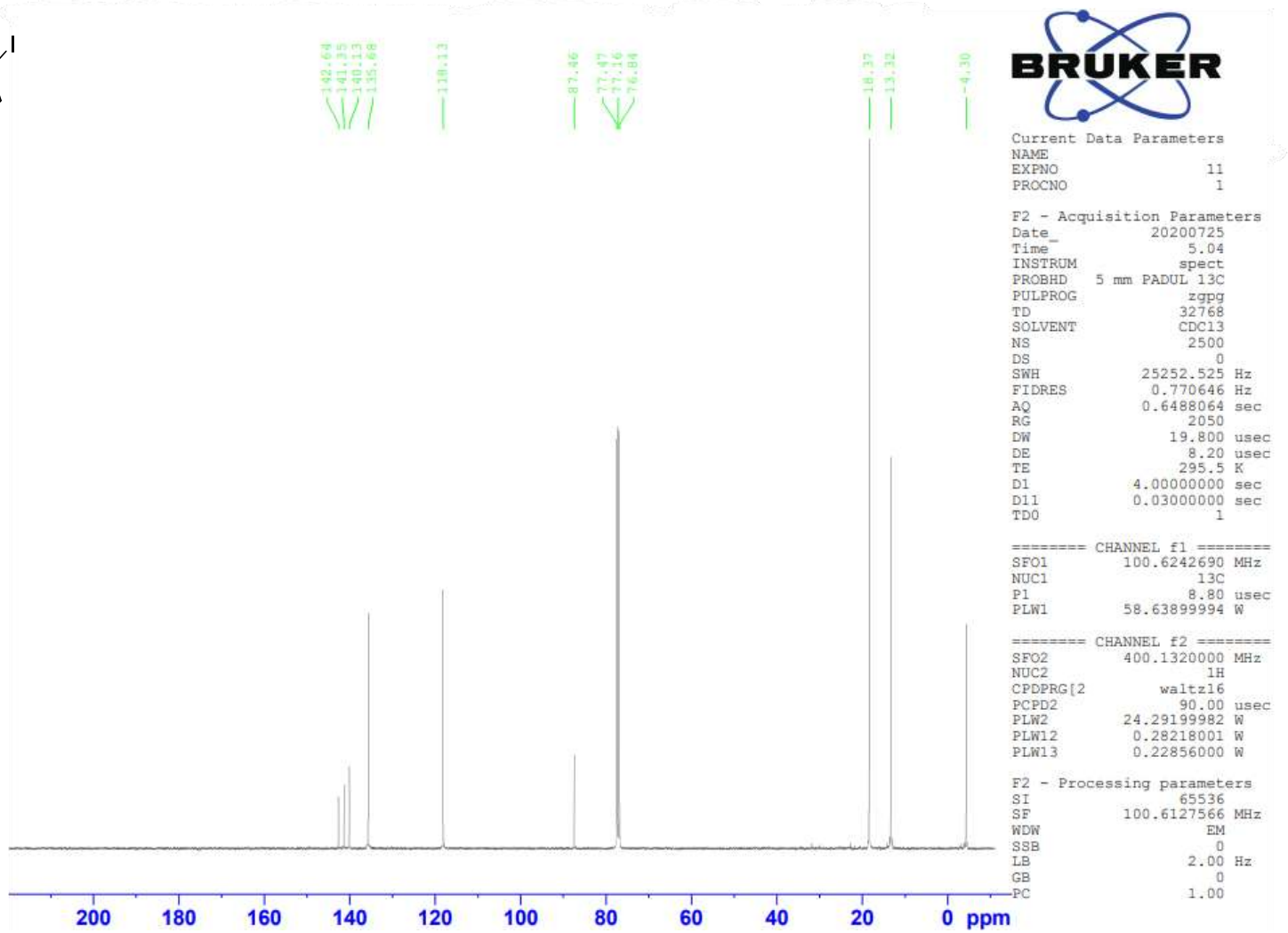
F2 - Acquisition Parameters
Date_            20200724
Time                8.00
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG                zg
TD                  32768
SOLVENT             CDC13
NS                     64
DS                      2
SWH              8223.685 Hz
FIDRES           0.250967 Hz
AQ               1.9922944 sec
RG                    128
DW                 60.800 usec
DE                 11.93 usec
TE                 294.7 K
D1           15.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                   1H
P1                 11.06 usec
PLW1         24.29199982 W

F2 - Processing parameters
SI                  32768
SF           400.1300108 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

1,7-Diiodo-8,8-dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [13a]





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```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

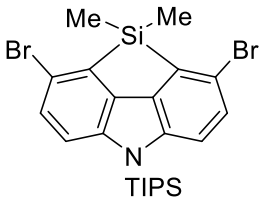
F2 - Acquisition Parameters
Date_           20200725
Time                5.04
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG             zgpg
TD                 32768
SOLVENT            CDCl3
NS                  2500
DS                     0
SWH            25252.525 Hz
FIDRES          0.770646 Hz
AQ              0.6488064 sec
RG                  2050
DW                19.800 usec
DE                 8.20 usec
TE                295.5 K
D1           4.00000000 sec
D11          0.03000000 sec
TD0                    1

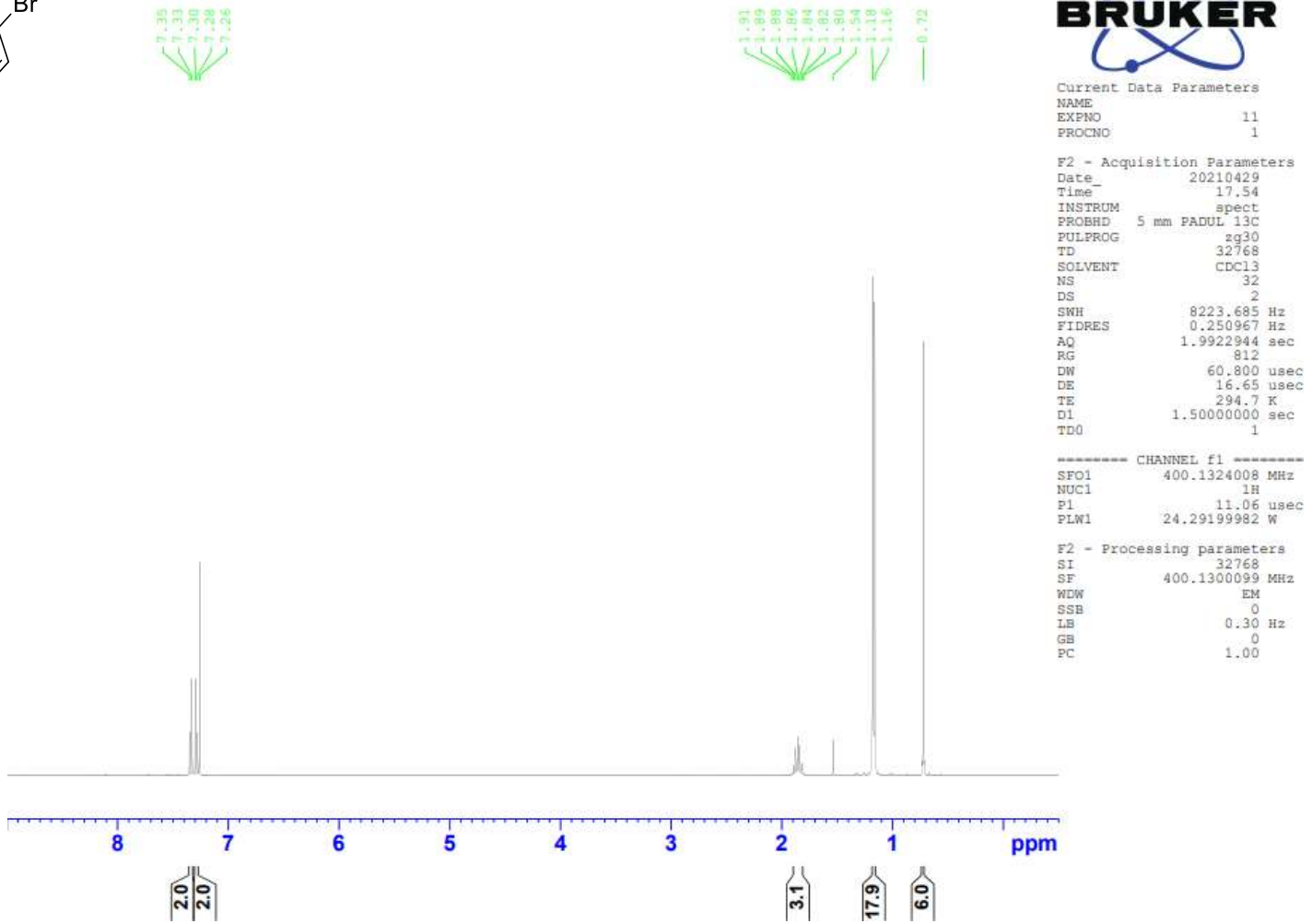
======== CHANNEL f1 ========
SFO1         100.6242690 MHz
NUC1                13C
P1                 8.80 usec
PLW1         58.63899994 W

======== CHANNEL f2 ========
SFO2         400.1320000 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         24.29199982 W
PLW12         0.28218001 W
PLW13         0.22856000 W

F2 - Processing parameters
SI                 65536
SF           100.6127566 MHz
WDW                  EM
SSB                   0
LB                 2.00 Hz
GB                    0
PC                 1.00
```

1,7-Dibromo-8,8-dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [14a]





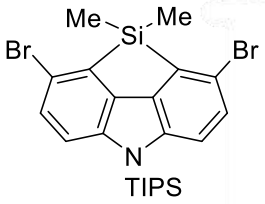

```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

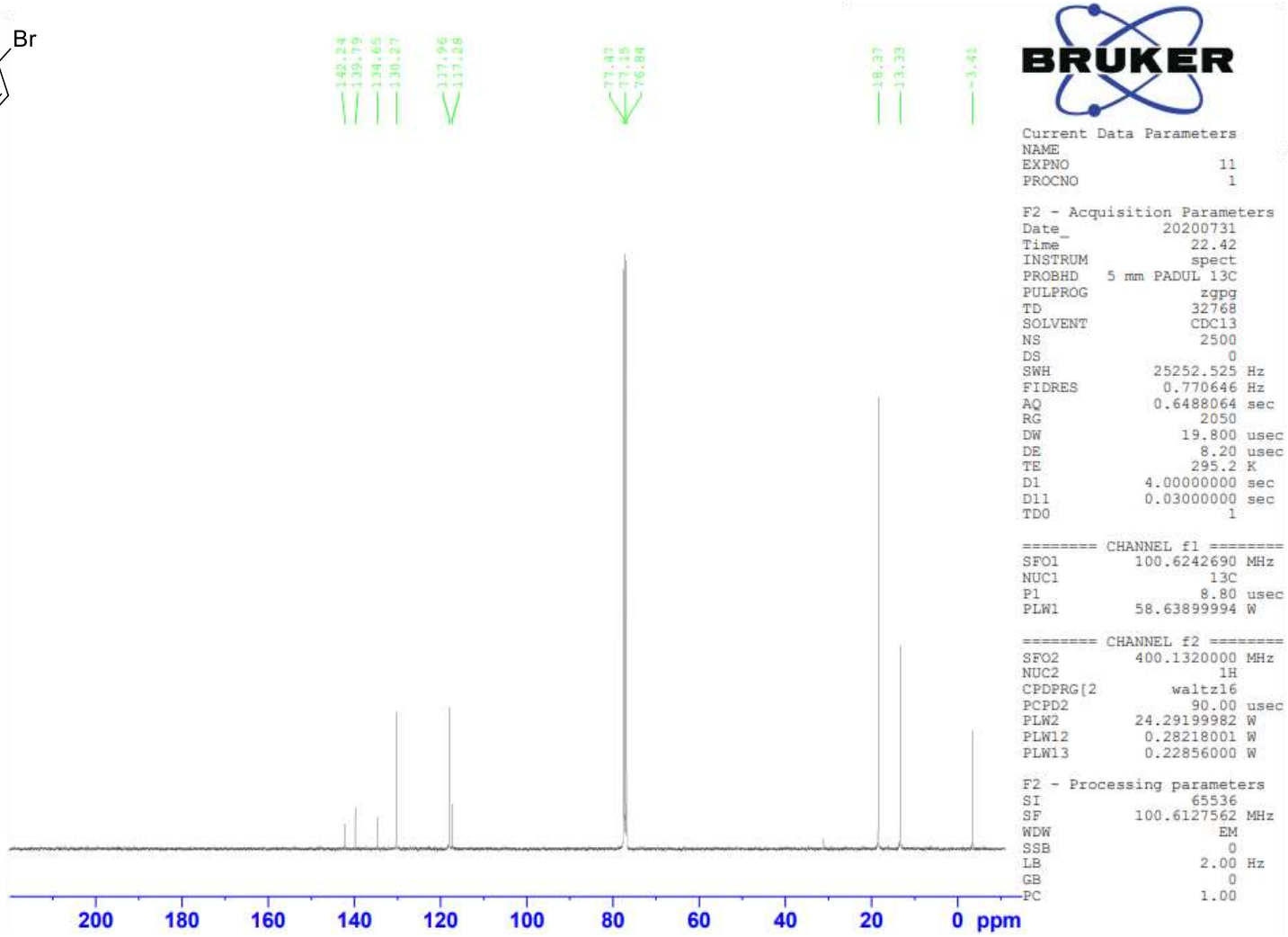
F2 - Acquisition Parameters
Date_            20210429
Time                17.54
INSTRUM             spect
PROBHD   5 mm PADUL 13C
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     32
DS                      2
SWH              8223.685 Hz
FIDRES           0.250967 Hz
AQ               1.9922944 sec
RG                    812
DW                 60.800 usec
DE                 16.65 usec
TE                 294.7 K
D1              1.50000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324008 MHz
NUC1                   1H
P1                  11.06 usec
PLW1         24.29199982 W

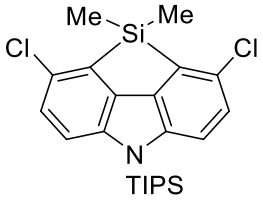
F2 - Processing parameters
SI                  32768
SF            400.1300099 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

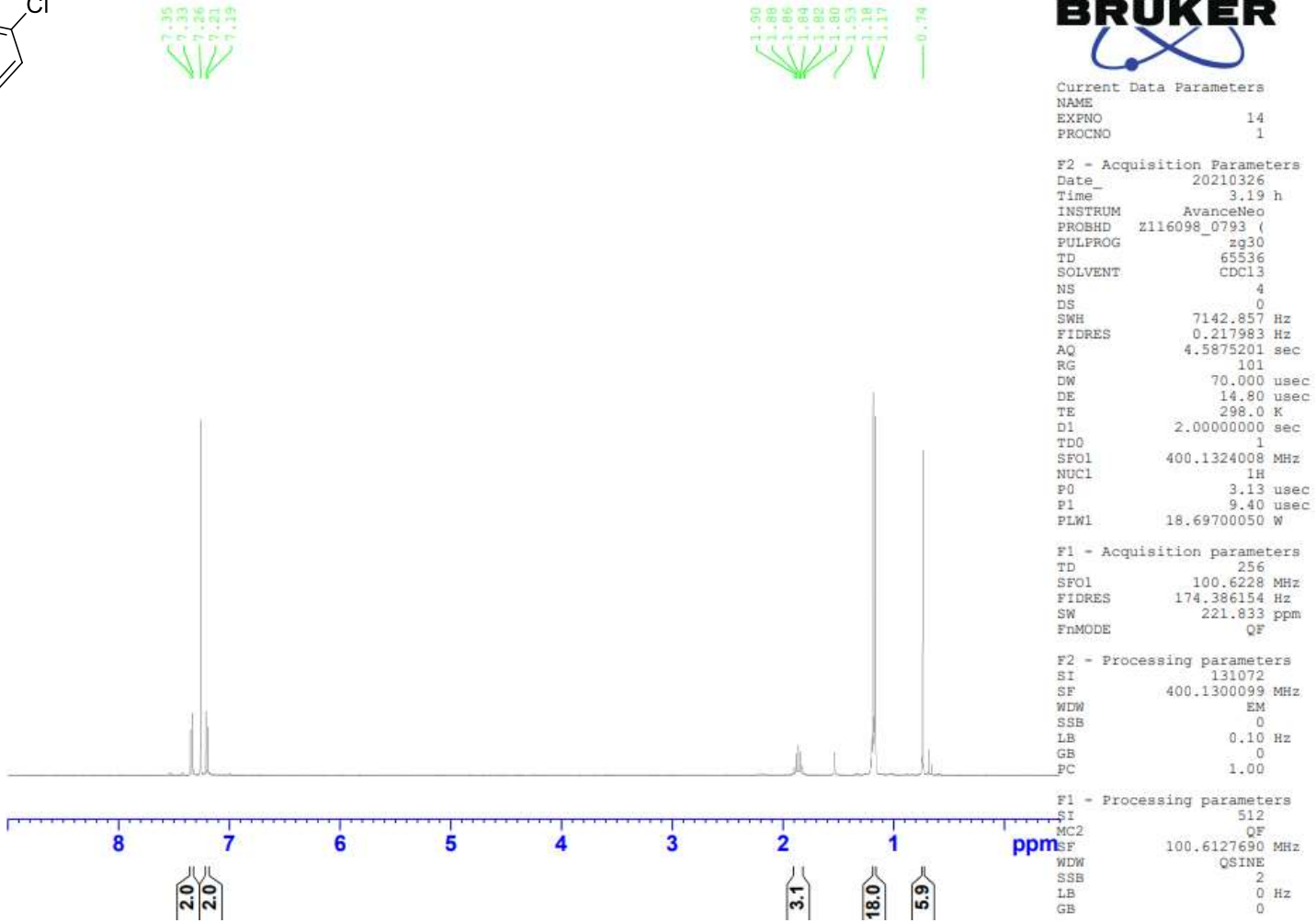
1,7-Dibromo-8,8-dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [14a]





1,7-Dichloro-8,8-dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [15a]






```
Current Data Parameters
NAME
EXPNO                  14
PROCNO                  1

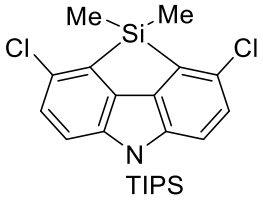
F2 - Acquisition Parameters
Date_            20210326
Time                3.19 h
INSTRUM         AvanceNeo
PROBHD    Z116098_0793 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     4
DS                     0
SWH             7142.857 Hz
FIDRES          0.217983 Hz
AQ              4.5875201 sec
RG                   101
DW                70.000 usec
DE                14.80 usec
TE                298.0 K
D1             2.00000000 sec
TD0                    1
SFO1          400.1324008 MHz
NUC1                  1H
P0                 3.13 usec
P1                 9.40 usec
PLW1          18.69700050 W

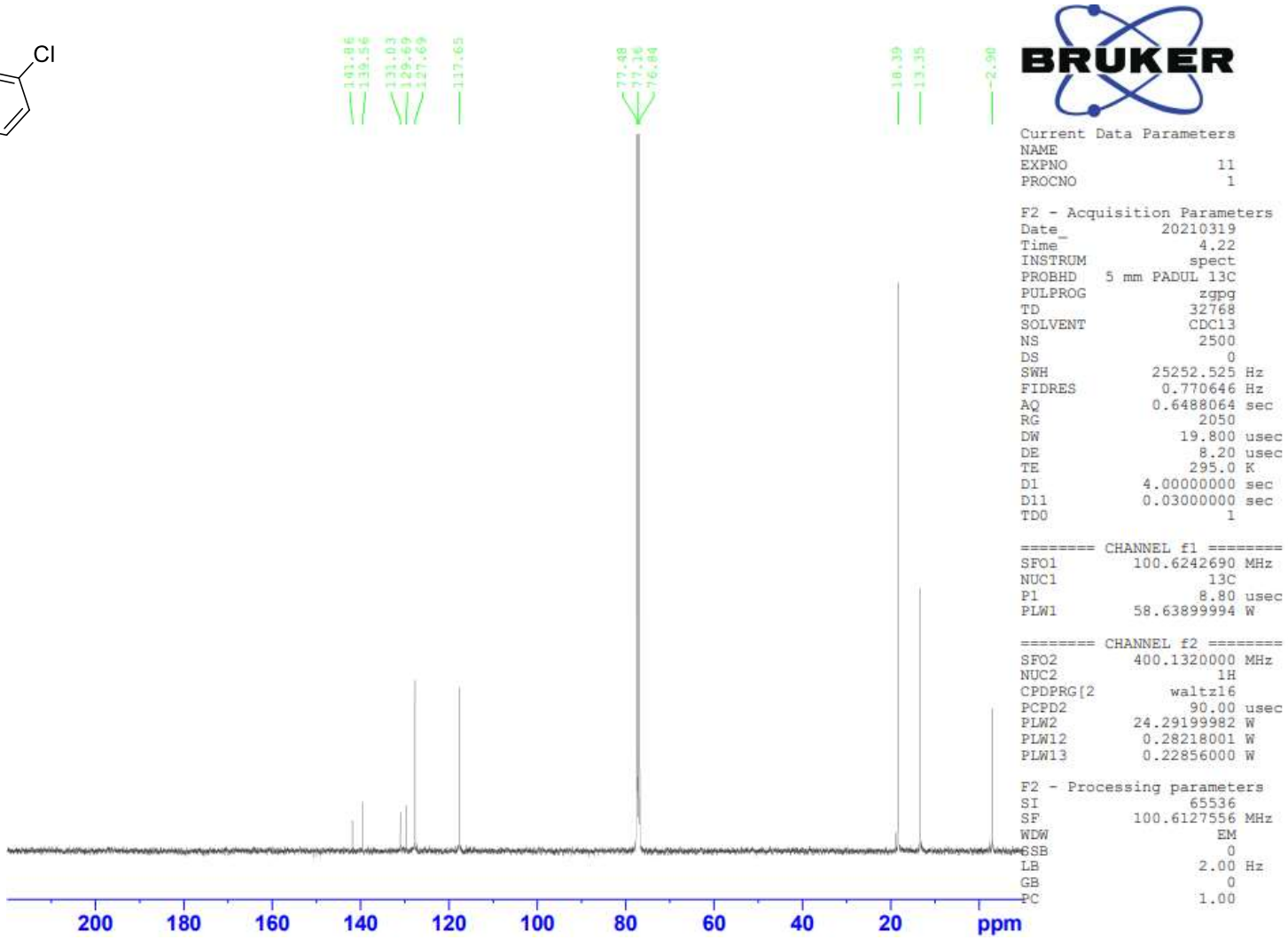
F1 - Acquisition parameters
TD                   256
SFO1           100.6228 MHz
FIDRES        174.386154 Hz
SW             221.833 ppm
FnMODE                QF

F2 - Processing parameters
SI                131072
SF          400.1300099 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00

F1 - Processing parameters
SI                   512
MC2                   QF
SF          100.6127690 MHz
WDW                QSINE
SSB                    2
LB                     0 Hz
GB                     0
```

1,7-Dichloro-8,8-dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [15a]






```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

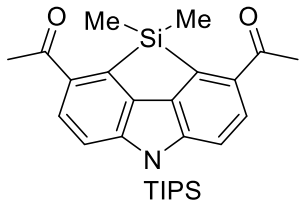
F2 - Acquisition Parameters
Date_            20210319
Time                4.22
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG             zgpg
TD                 32768
SOLVENT            CDCl3
NS                  2500
DS                     0
SWH           25252.525 Hz
FIDRES         0.770646 Hz
AQ             0.6488064 sec
RG                  2050
DW                19.800 usec
DE                 8.20 usec
TE                295.0 K
D1             4.00000000 sec
D11            0.03000000 sec
TD0                    1

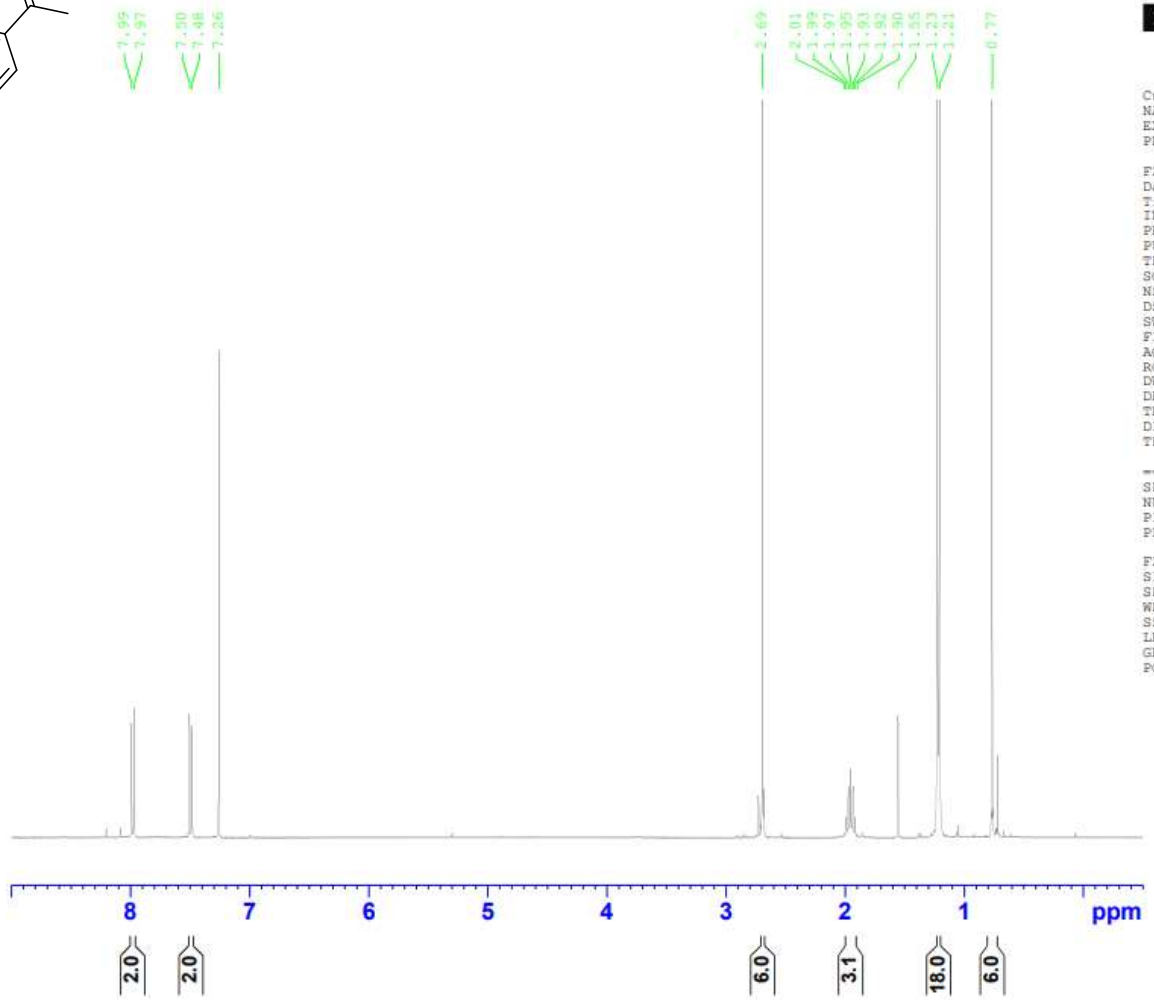
======== CHANNEL f1 ========
SFO1          100.6242690 MHz
NUC1                  13C
P1                   8.80 usec
PLW1          58.63899994 W

======== CHANNEL f2 ========
SFO2          400.1320000 MHz
NUC2                  1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2          24.29199982 W
PLW12          0.28218001 W
PLW13          0.22856000 W

F2 - Processing parameters
SI                  65536
SF            100.6127556 MHz
WDW                    EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.00
```

1,1'-(8,8-Dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole-1,7-diyl)bis(ethan-1-one) [16a]





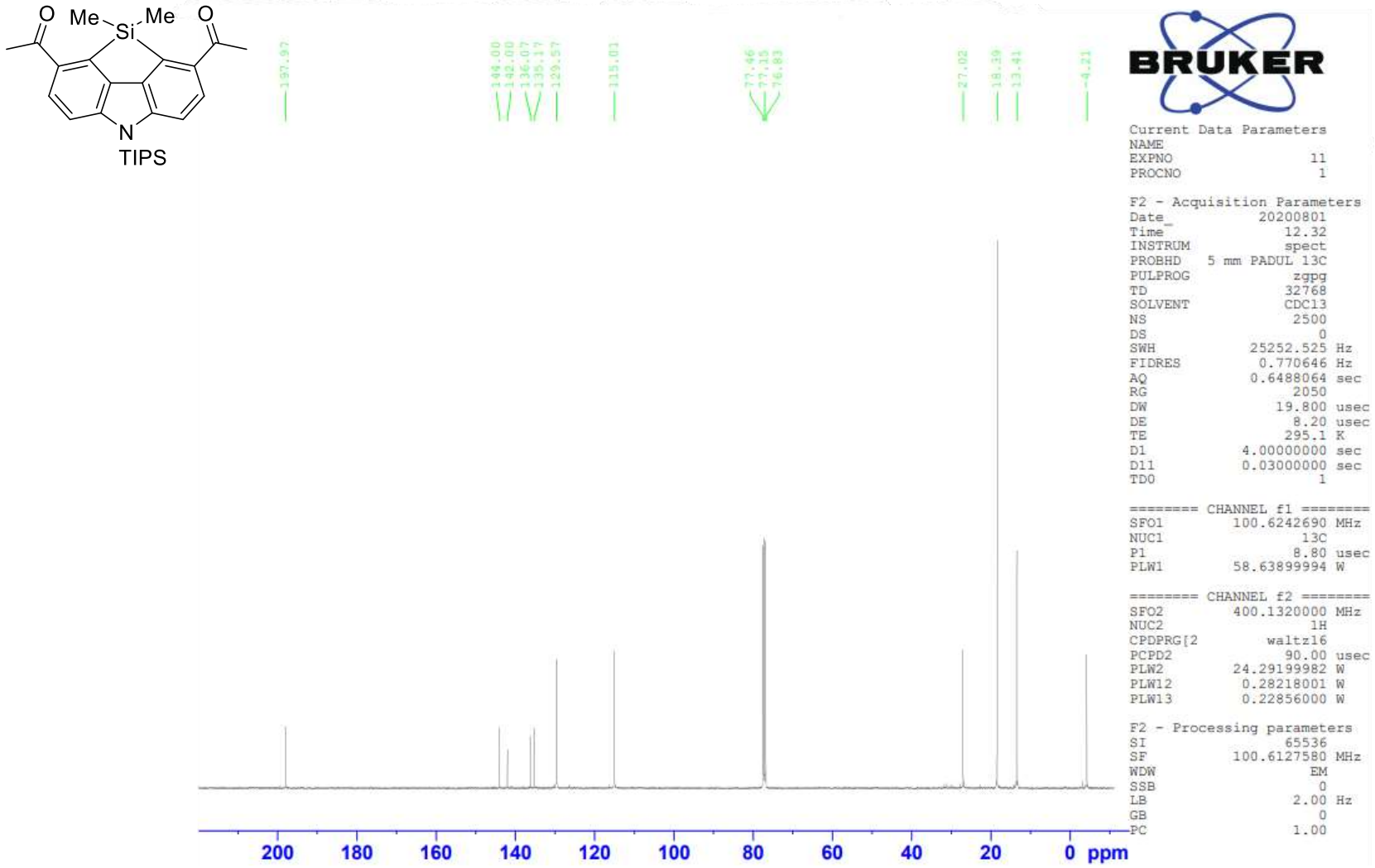

```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210430
Time                4.29
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG                zg
TD                  32768
SOLVENT             CDCl3
NS                     64
DS                      2
SWH              8223.685 Hz
FIDRES           0.250967 Hz
AQ               1.9922944 sec
RG                    322
DW                60.800 usec
DE                11.93 usec
TE                294.6 K
D1           15.00000000 sec
TD0                     1

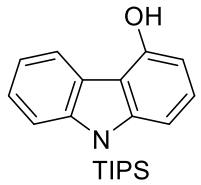
======== CHANNEL f1 ========
SFO1          400.1324008 MHz
NUC1                    1H
P1                  11.06 usec
PLW1         24.29199982 W

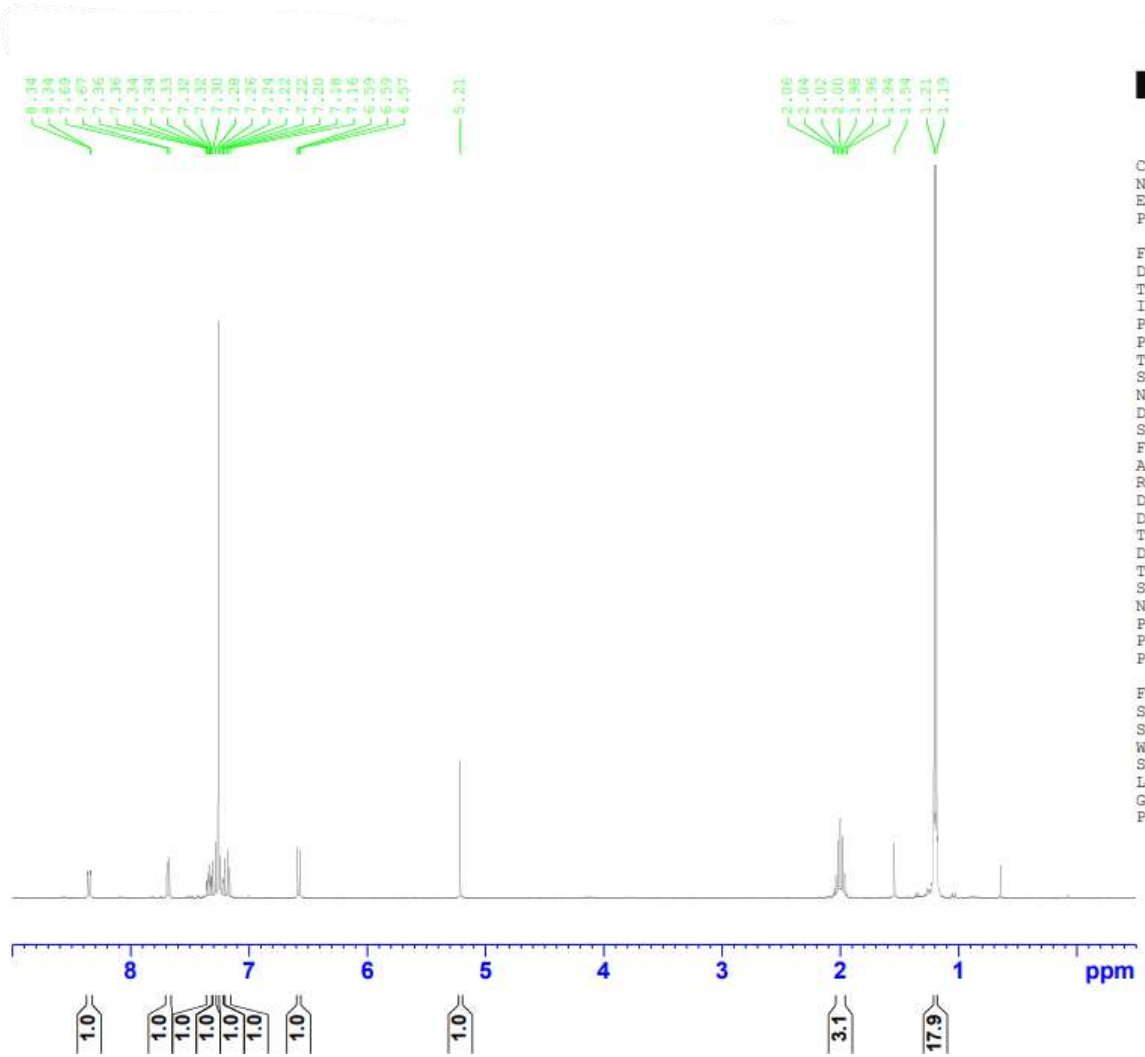
F2 - Processing parameters
SI                  32768
SF            400.1300101 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```

1,1'-(8,8-Dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole-1,7-diyl)bis(ethan-1-one) [16a]



9-(Triisopropylsilyl)-9H-carbazol-4-ol [17a]



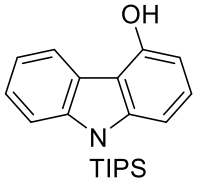


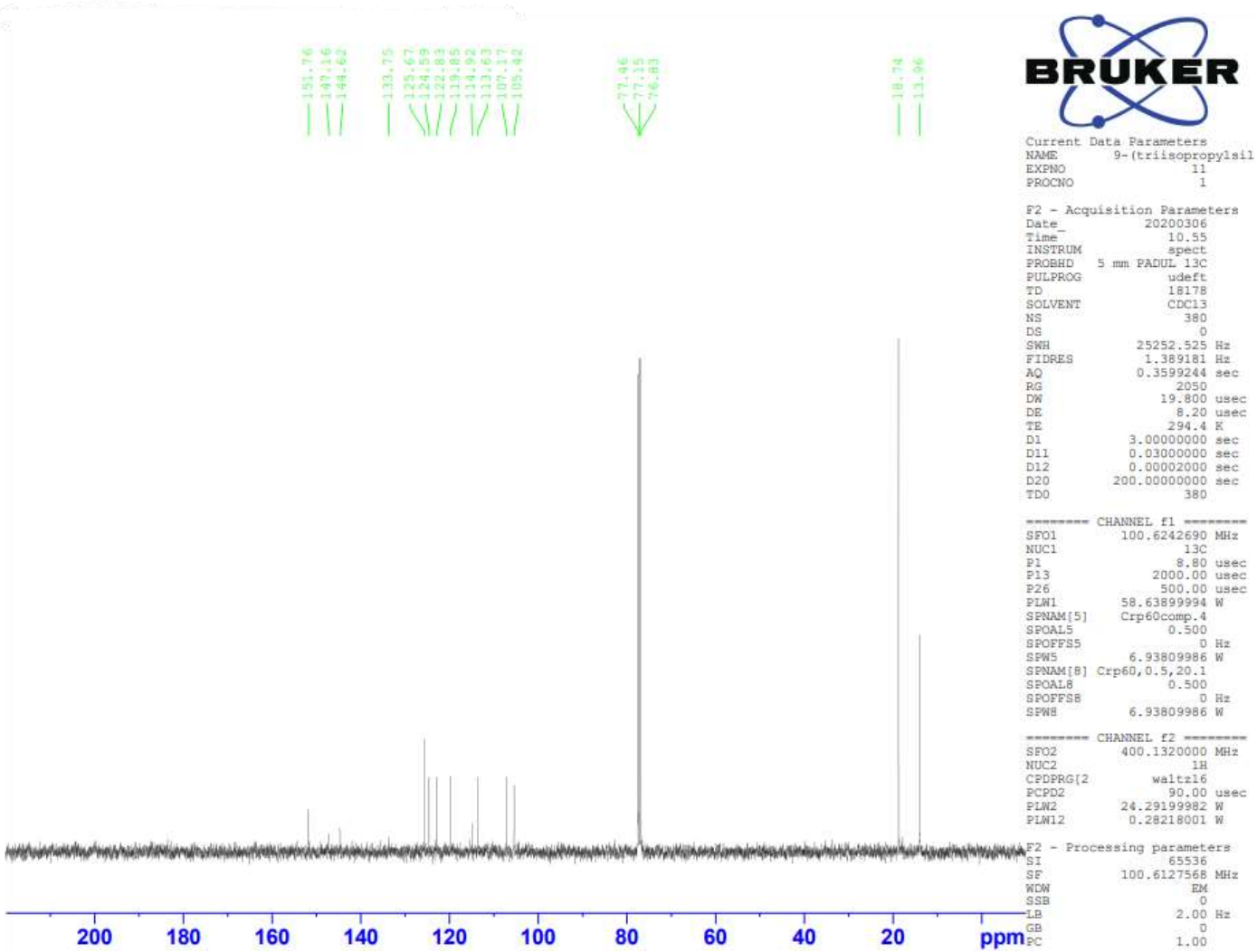

```
Current Data Parameters
NAME
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210224
Time                17.29 h
INSTRUM         AvanceNeo
PROBHD    Z116098_0793 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      4
DS                      0
SWH              7142.857 Hz
FIDRES           0.217983 Hz
AQ               4.5875201 sec
RG                    101
DW                 70.000 usec
DE                 14.80 usec
TE                 298.0 K
D1              2.00000000 sec
TD0                     1
SFO1          400.1324008 MHz
NUC1                   1H
P0                  3.13 usec
P1                  9.40 usec
PLW1          18.69700050 W

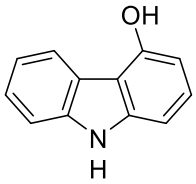
F2 - Processing parameters
SI                 131072
SF            400.1300099 MHz
WDW                    EM
SSB                     0
LB                 0.10 Hz
GB                      0
PC                   1.00
```

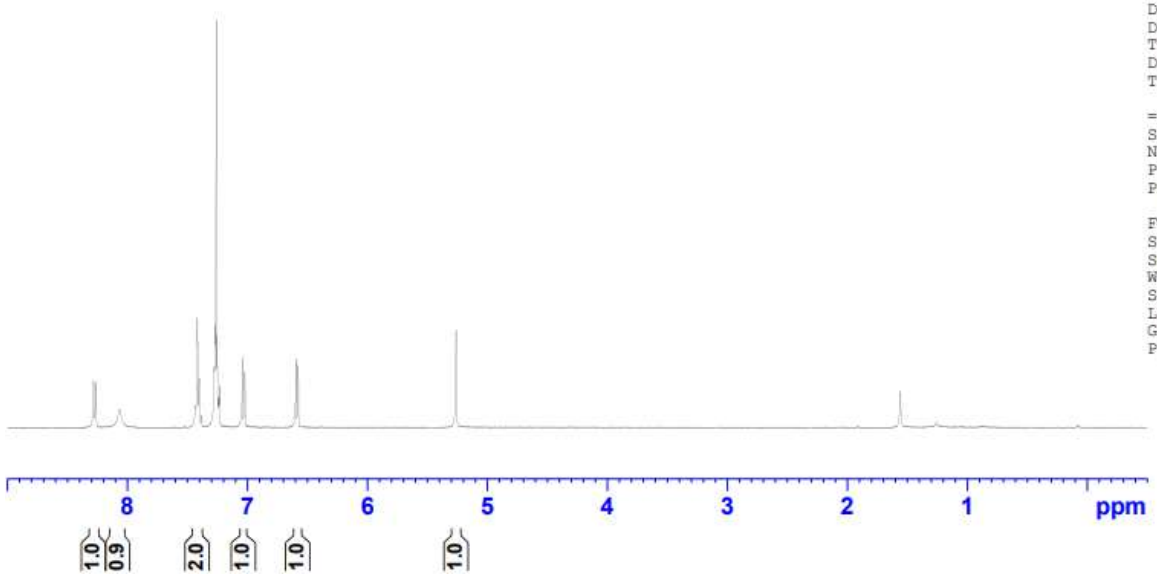
9-(Triisopropylsilyl)-9H-carbazol-4-ol [17a]





9H-Carbazol-4-ol [17b]





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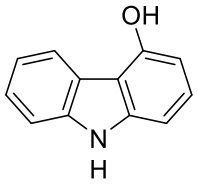
```
Current Data Parameters
NAME
EXPNO                 101
PROCNO                  1

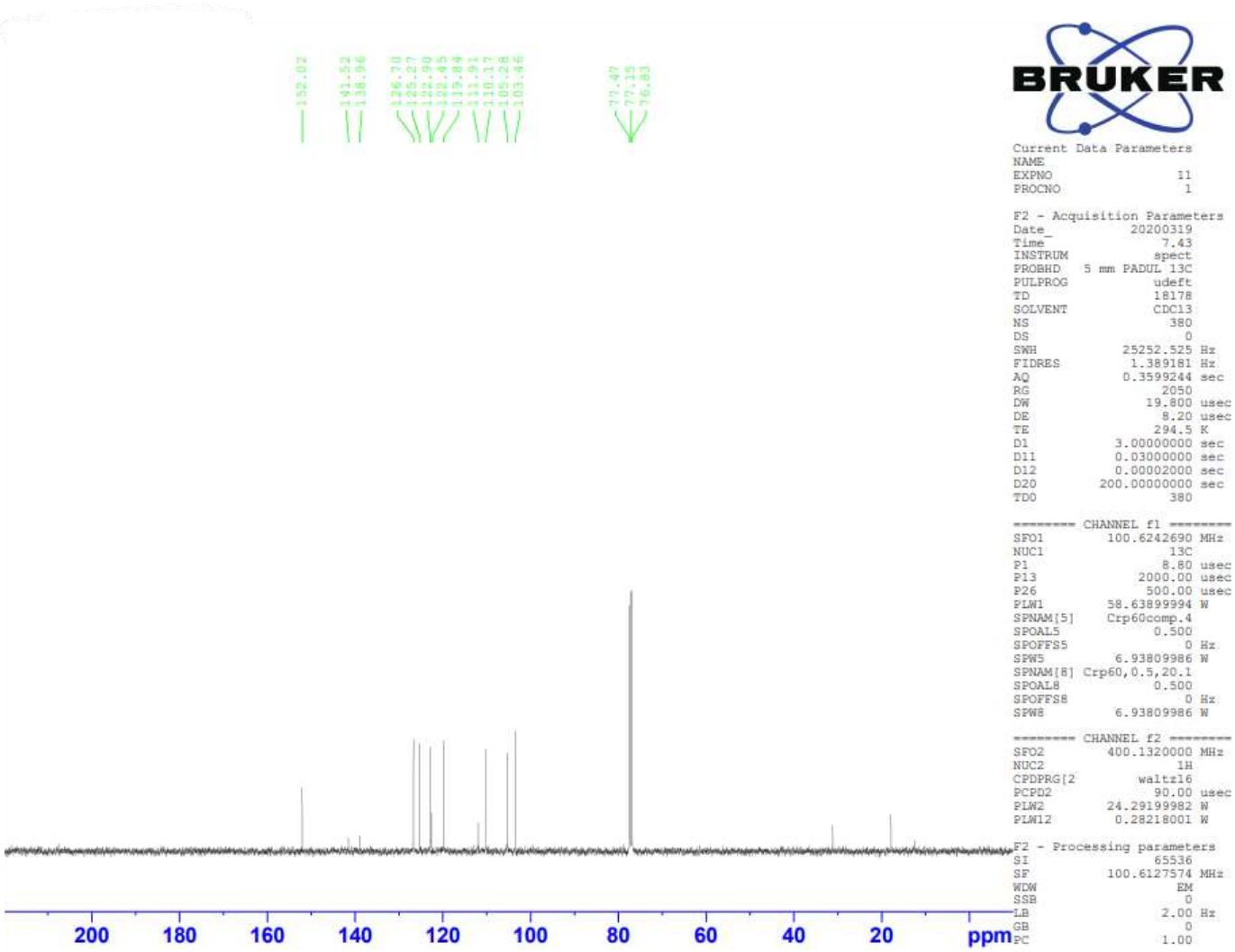
F2 - Acquisition Parameters
Date_           20210326
Time              18.17
INSTRUM           spect
PROBHD   5 mm PADUL 13C
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            8223.685 Hz
FIDRES         0.250967 Hz
AQ             1.9922944 sec
RG                  1030
DW                60.800 usec
DE                16.65 usec
TE                294.6 K
D1             1.50000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                   1H
P1                  11.06 usec
PLW1         24.29199982 W

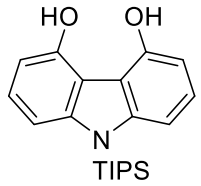
F2 - Processing parameters
SI                 32768
SF           400.1300094 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

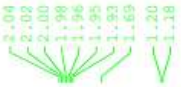
9H-Carbazol-4-ol [17b]





9-(Triisopropylsilyl)-9H-carbazole-4,5-diol [18a]



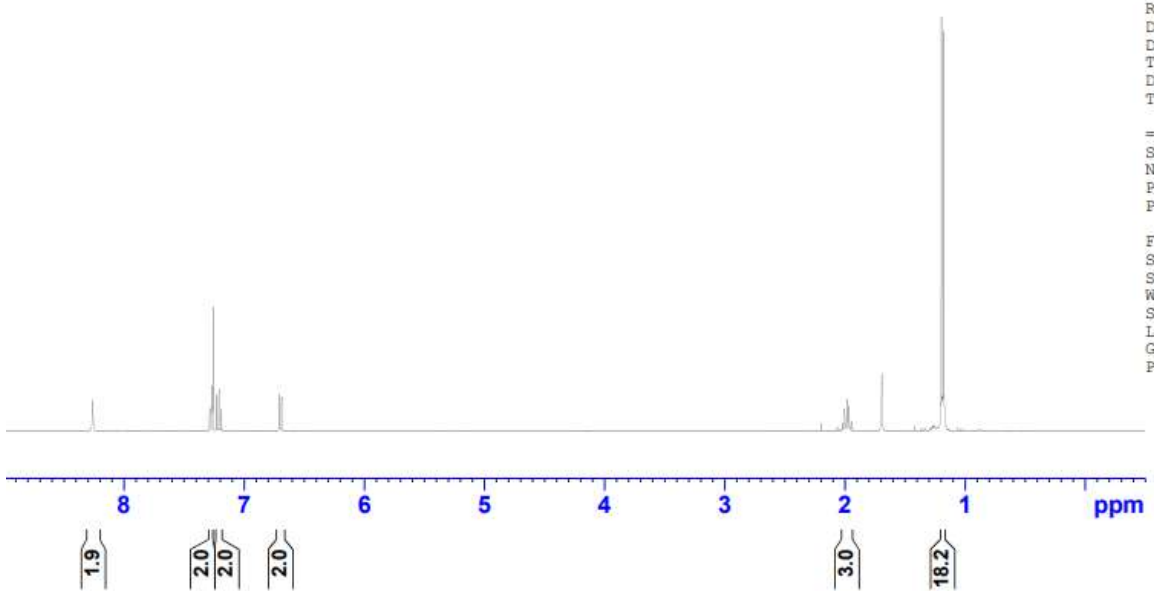



```
Current Data Parameters
NAME
EXPNO                  1
PROCNO                 1

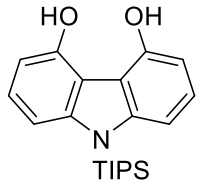
F2 - Acquisition Parameters
Date_           20201021
Time              12.32
INSTRUM           spect
PROBHD   5 mm PADUL 13C
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             8223.685 Hz
FIDRES          0.250967 Hz
AQ              1.9922944 sec
RG                   575
DW                60.800 usec
DE                16.65 usec
TE                294.3 K
D1             1.50000000 sec
TD0                    1

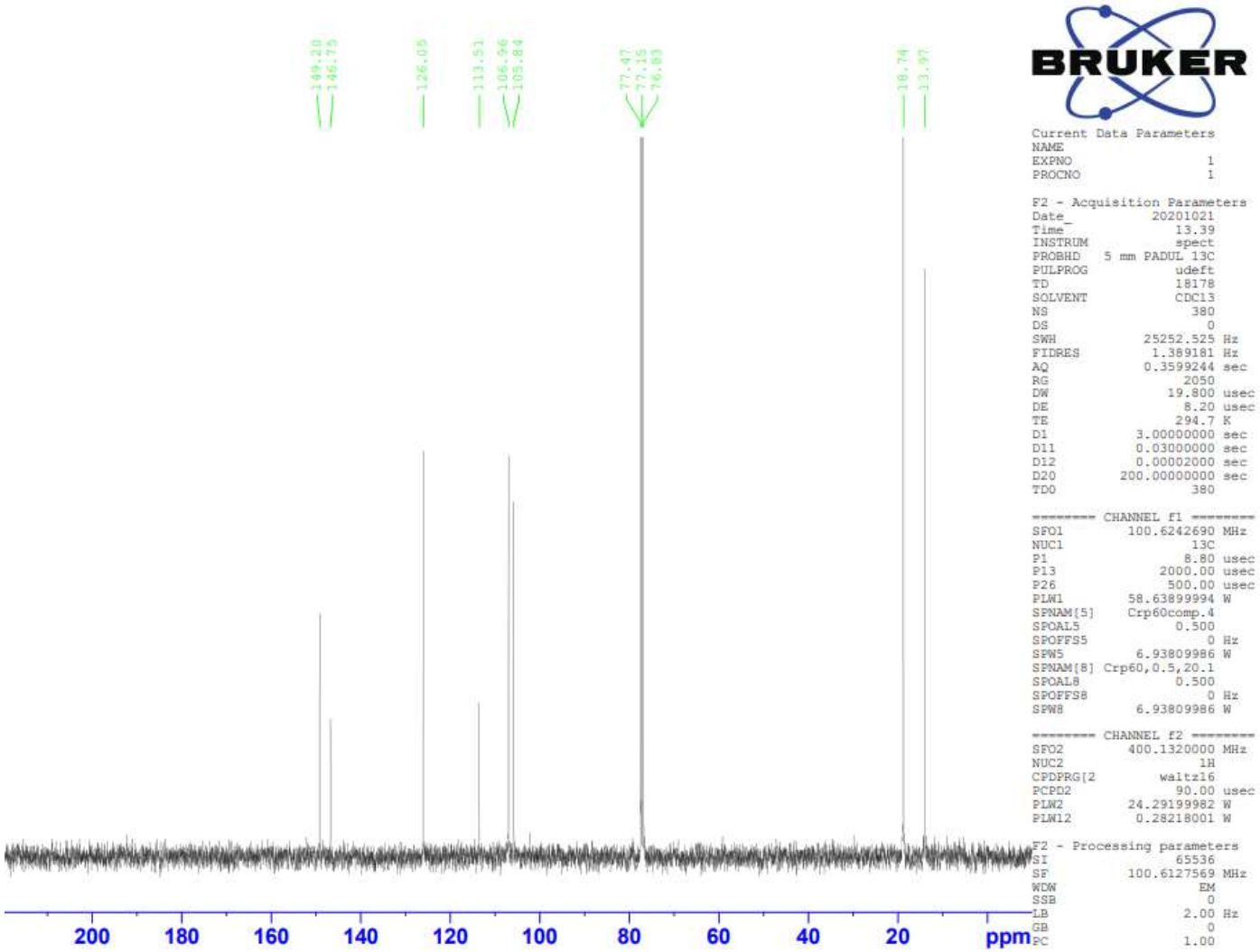
======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                   1H
P1                  11.06 usec
PLW1         24.29199982 W

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



9-(Triisopropylsilyl)-9H-carbazole-4,5-diol [18a]





BRUKER

```
Current Data Parameters
NAME
EXPNO                  1
PROCNO                 1

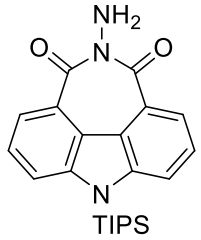
F2 - Acquisition Parameters
Date_           20201021
Time_              13.39
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG            udeft
TD                 18178
SOLVENT            CDCl3
NS                   380
DS                     0
SWH            25252.525 Hz
FIDRES         1.389181 Hz
AQ             0.3599244 sec
RG                  2050
DW                19.800 usec
DE                 8.20 usec
TE                294.7 K
D1             3.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec
D20          200.00000000 sec
TD0                  380

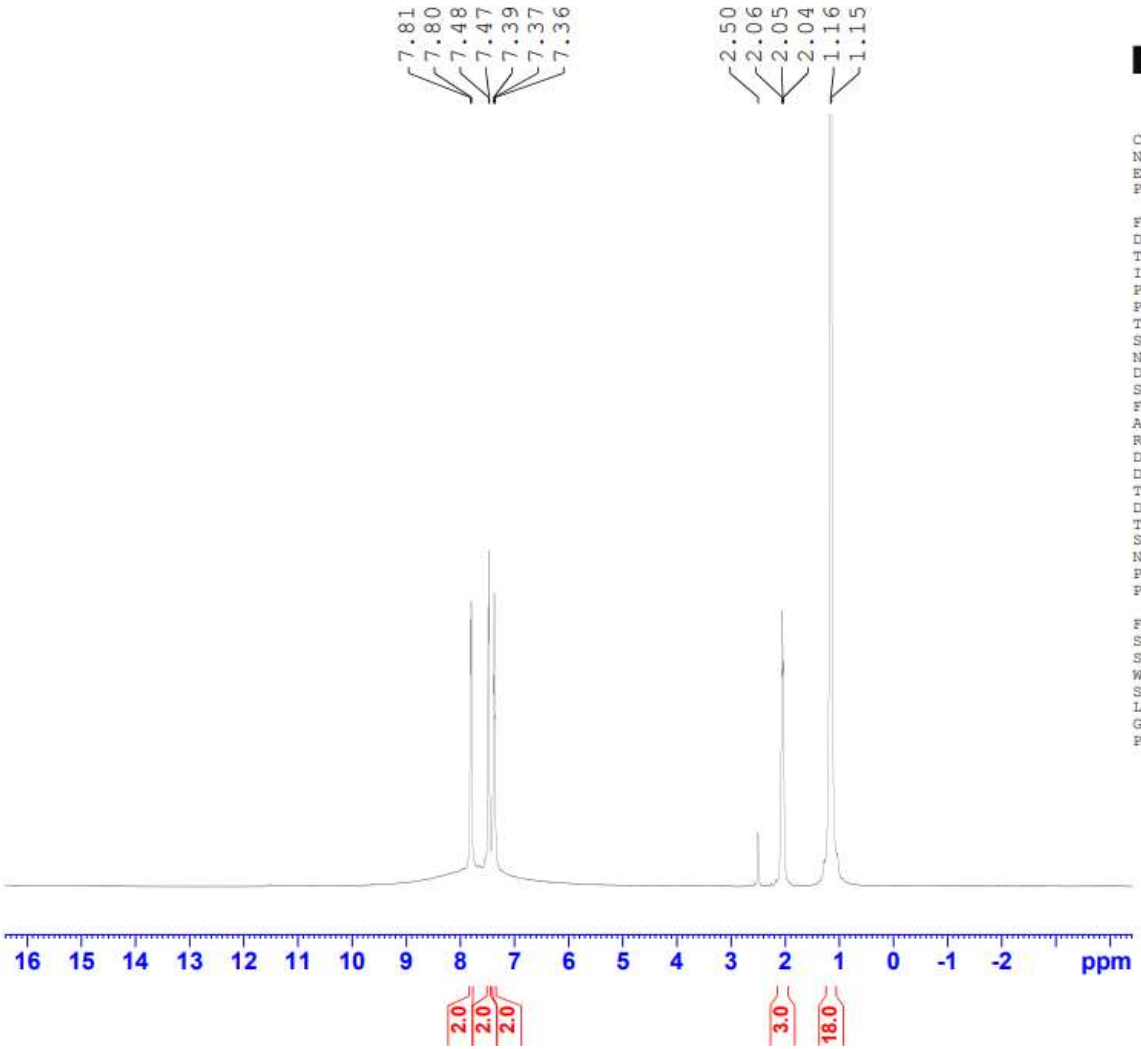
======== CHANNEL f1 ========
SFO1          100.6242690 MHz
NUC1                 13C
P1                  8.80 usec
P13              2000.00 usec
P26               500.00 usec
PLW1           58.63899994 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5                0 Hz
SPW5           6.93809986 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 usec
PLW2          24.29199982 W
PLW12          0.28218001 W

F2 - Processing parameters
SI                 65536
SF            100.6127569 MHz
WDW                  EM
SSB                   0
LB                 2.00 Hz
GB                    0
PC                 1.00
```

9-Amino-4-(triisopropylsilyl)azepino[3,4,5,6-def]carbazole-8,10(4H,9H)-dione [19a]





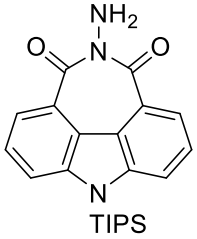
BRUKER

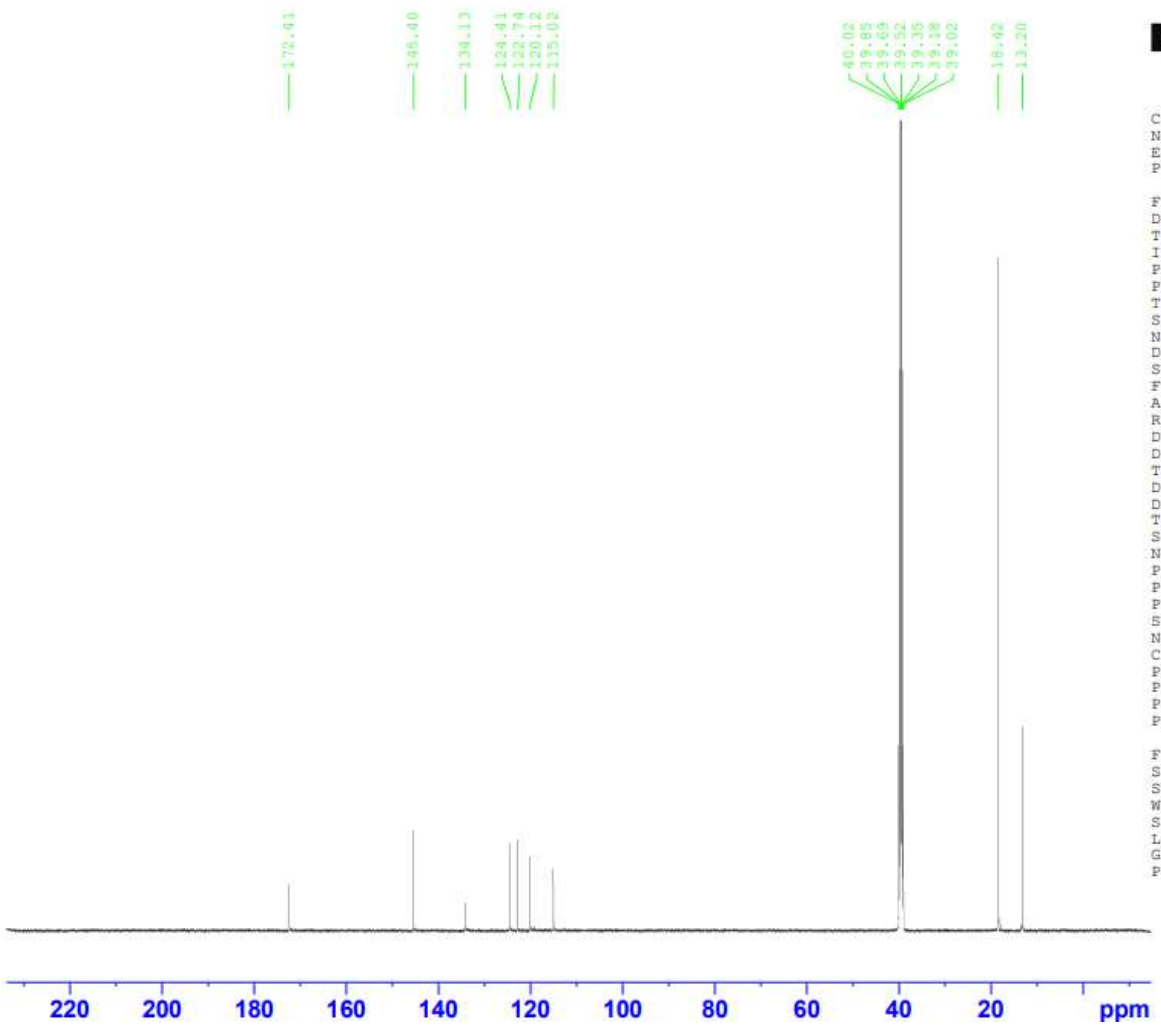
```
Current Data Parameters
NAME
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210427
Time                13.13 h
INSTRUM  CAB AV4 500 MHZ BASIC
PROBHD   Z150364_0007 (
PULPROG                zg
TD                  66560
SOLVENT              DMSO
NS                     16
DS                      0
SWH            10416.667 Hz
FIDRES          0.313001 Hz
AQ              3.1948800 sec
RG                   62.5
DW                 48.000 usec
DE                 34.36 usec
TE                 298.0 K
D1            10.00000000 sec
TD0                     1
SFO1          500.0760004 MHz
NUC1                   1H
P1                 12.00 usec
PLW1          14.55099964 W

F2 - Processing parameters
SI                 131072
SF            500.0730027 MHz
WDW                    EM
SSB                     0
LB                 0.10 Hz
GB                      0
PC                 1.00
```

9-Amino-4-(triisopropylsilyl)azepino[3,4,5,6-def]carbazole-8,10(4H,9H)-dione [19a]





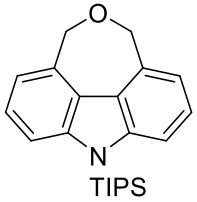
BRUKER

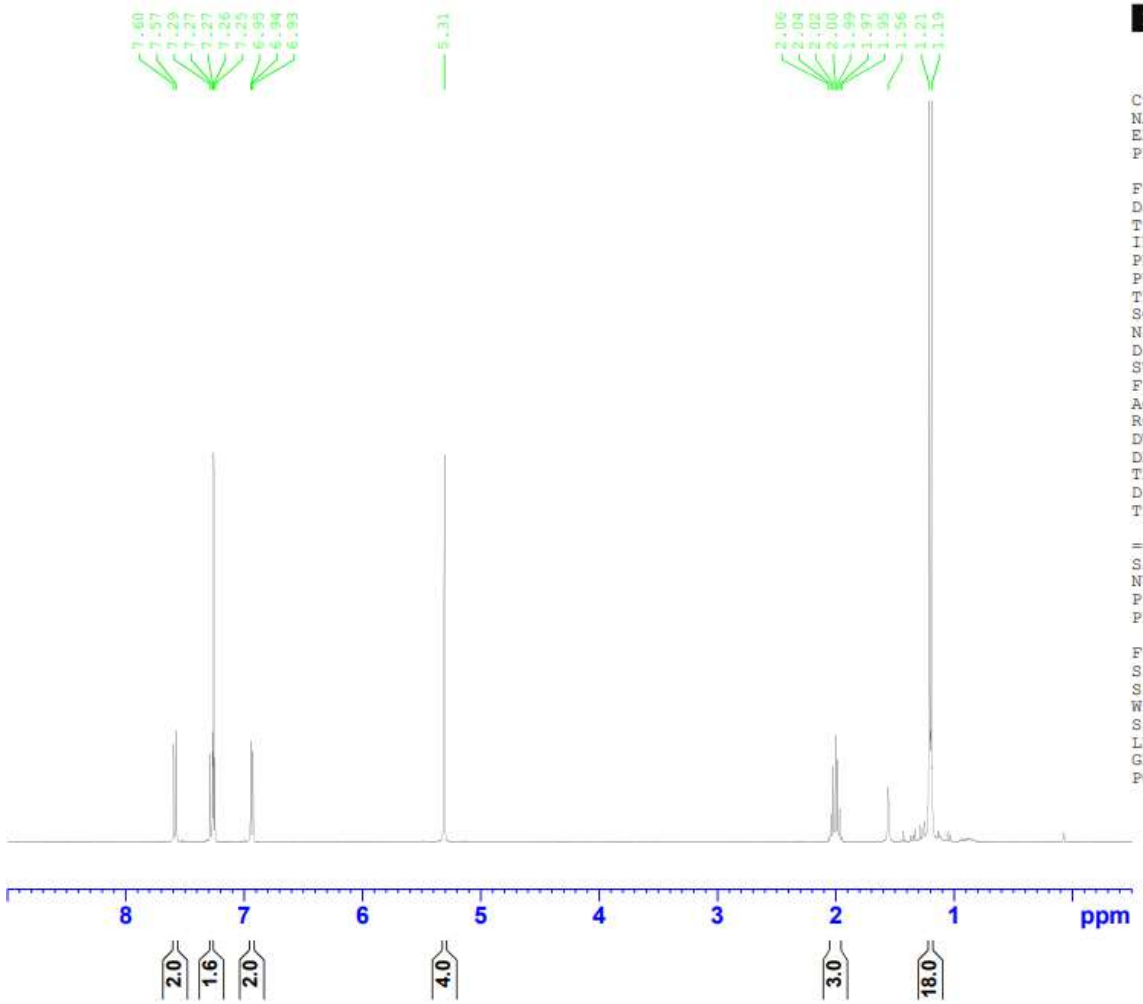
```
Current Data Parameters
NAME
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210427
Time                13.51 h
INSTRUM  CAB AV4 500 MHZ BASIC
PROBHD   Z150364_0007 (
PULPROG             zgpg30
TD                  119044
SOLVENT               DMSO
NS                      600
DS                        0
SWH               31250.000 Hz
FIDRES             0.525016 Hz
AQ                1.9047040 sec
RG                      101
DW                   16.000 usec
DE                   18.29 usec
TE                   298.0 K
D1                1.00000000 sec
D11               0.03000000 sec
TD0                       1
SFO1            125.7572860 MHz
NUC1                    13C
P0                    3.33 usec
P1                   10.00 usec
PLW1             61.18099976 W
SFO2            500.0750003 MHz
NUC2                    1H
CPDPRG[2             waltz64
PCPD2                80.00 usec
PLW2             14.55099964 W
PLW12             0.32740000 W
PLW13             0.16468000 W

F2 - Processing parameters
SI                    131072
SF              125.7435153 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

4-(Triisopropylsilyl)-8,10-dihydro-4H-oxepino[3,4,5,6-def]carbazole [20a]





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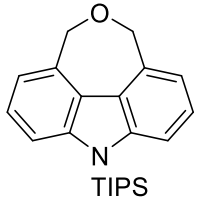
```
Current Data Parameters
NAME
EXPNO                  16
PROCNO                  1

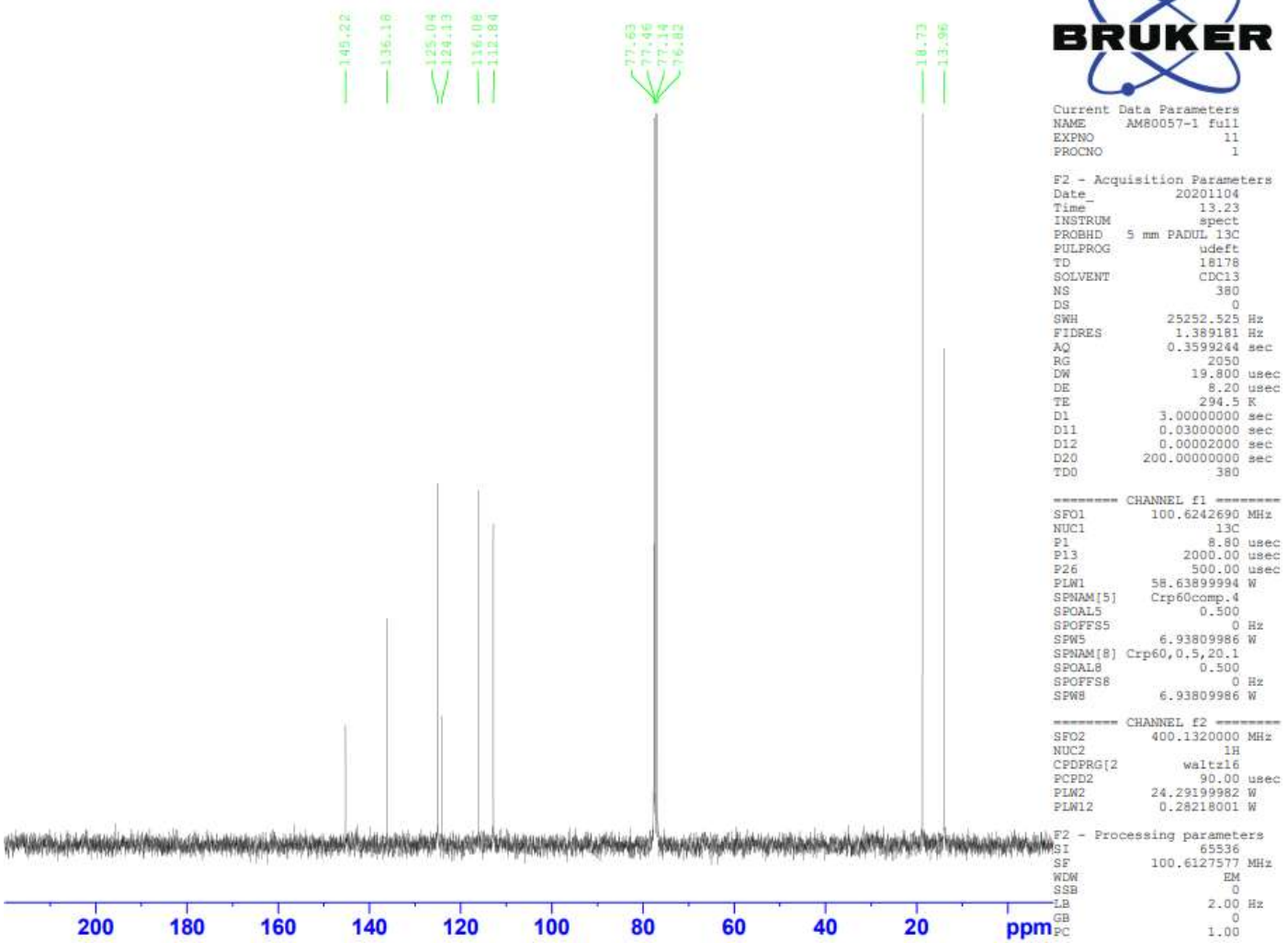
F2 - Acquisition Parameters
Date_           20201105
Time               19.35
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG                zg
TD                  32768
SOLVENT             CDC13
NS                     64
DS                      2
SWH              8223.685 Hz
FIDRES           0.250967 Hz
AQ               1.9922944 sec
RG                    203
DW                 60.800 usec
DE                 11.93 usec
TE                 294.8 K
D1              15.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                   1H
P1                  11.06 usec
PLW1         24.29199982 W

F2 - Processing parameters
SI                  32768
SF           400.1300104 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

4-(Triisopropylsilyl)-8,10-dihydro-4H-oxepino[3,4,5,6-def]carbazole [20a]






```
Current Data Parameters
NAME      AM80057-1 full
EXPNO                11
PROCNO                1

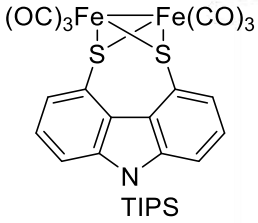
F2 - Acquisition Parameters
Date_          20201104
Time              13.23
INSTRUM           spect
PROBHD   5 mm PADUL 13C
PULPROG           udeft
TD                18178
SOLVENT           CDCl3
NS                  380
DS                    0
SWH           25252.525 Hz
FIDRES         1.389181 Hz
AQ            0.3599244 sec
RG                 2050
DW               19.800 usec
DE                8.20 usec
TE                294.5 K
D1           3.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
D20        200.00000000 sec
TD0                 380

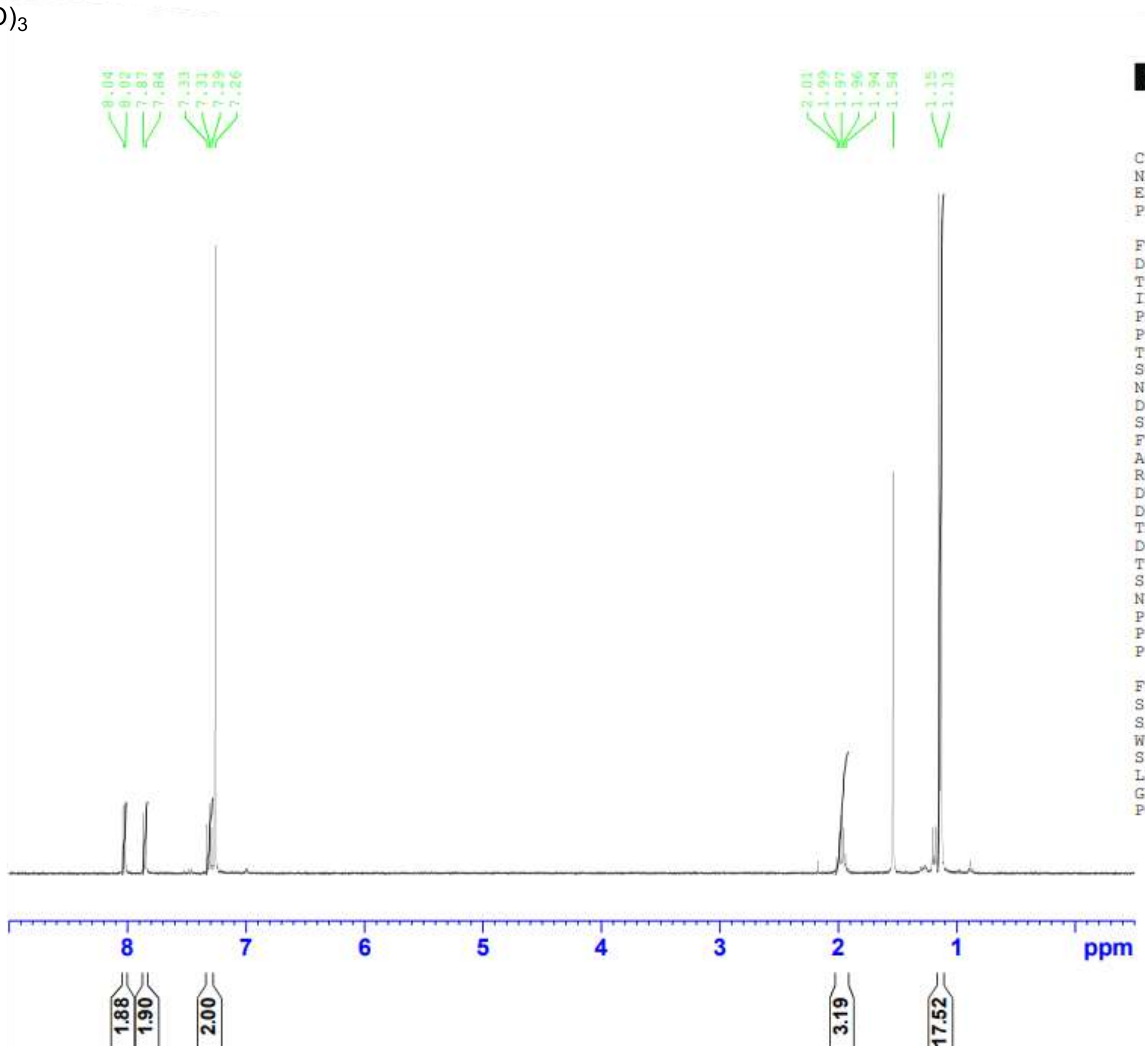
======== CHANNEL f1 ========
SFO1        100.6242690 MHz
NUC1                13C
P1                 8.80 usec
P13             2000.00 usec
P26              500.00 usec
PLW1         58.63899994 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5                0 Hz
SPW5          6.93809986 W
SPNAM[8] 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 usec
PLW2         24.29199982 W
PLW12         0.28218001 W

F2 - Processing parameters
SI                 65536
SF          100.6127577 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.00
```

Iron hexacarbonyl complex [21a]



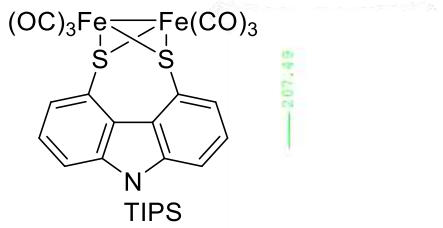



```
Current Data Parameters
NAME
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20190731
Time                11.36 h
INSTRUM         AvanceNeo
PROBHD    Z116098_0793 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      2
DS                      0
SWH              7142.857 Hz
FIDRES           0.217983 Hz
AQ               4.5875201 sec
RG                    101
DW                 70.000 usec
DE                 14.62 usec
TE                 298.0 K
D1              2.00000000 sec
TD0                     1
SFO1          400.1324008 MHz
NUC1                   1H
P0                  3.33 usec
P1                 10.00 usec
PLW1          18.69700050 W

F2 - Processing parameters
SI                 131072
SF            400.1300100 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```

Iron hexacarbonyl complex [21a]

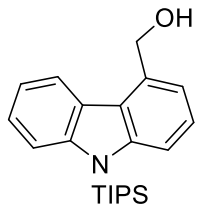


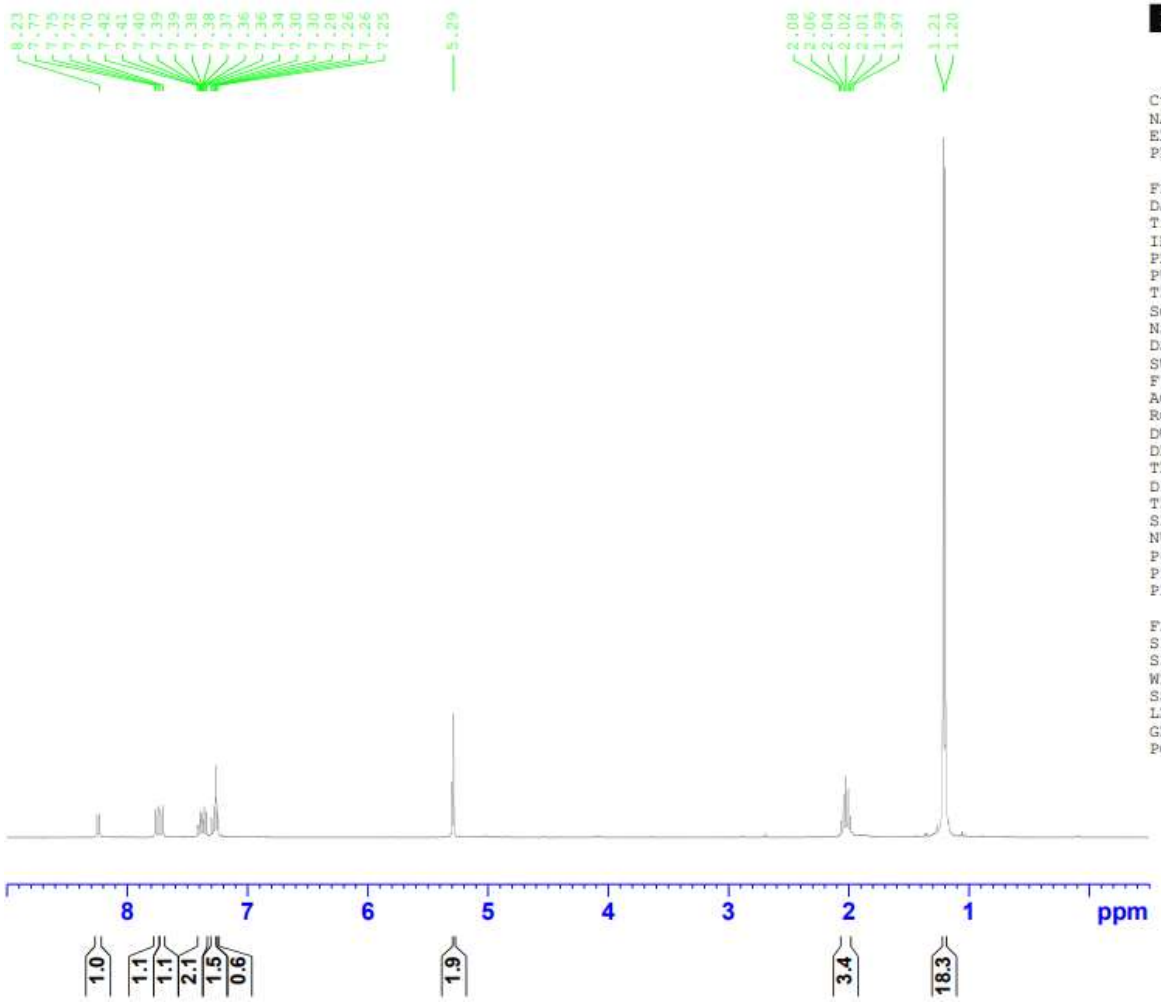

```
Current Data Parameters
NAME
EXPNO                  23
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190805
Time                20.15 h
INSTRUM          AvanceNeo
PROBHD    Z116098_0793 (
PULPROG            zgpg30
TD                 119044
SOLVENT             CDCl3
NS                    512
DS                      0
SWH             25000.000 Hz
FIDRES          0.420013 Hz
AQ              2.3808801 sec
RG                31.9602
DW                20.000 usec
DE                 7.12 usec
TE                298.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1
SFO1          100.6243390 MHz
NUC1                  13C
P0                 3.33 usec
P1                10.00 usec
PLW1          83.92700195 W
SFO2          400.1318006 MHz
NUC2                  1H
CPDPRG[2          waltz64
PCPD2              90.00 usec
PLW2          18.69700050 W
PLW12          0.23083000 W
PLW13          0.11611000 W

F2 - Processing parameters
SI                  131072
SF            100.6127572 MHz
WDW                   EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```

(9-(Triisopropylsilyl)-9H-carbazol-4-yl)methanol [22a]



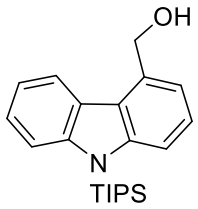


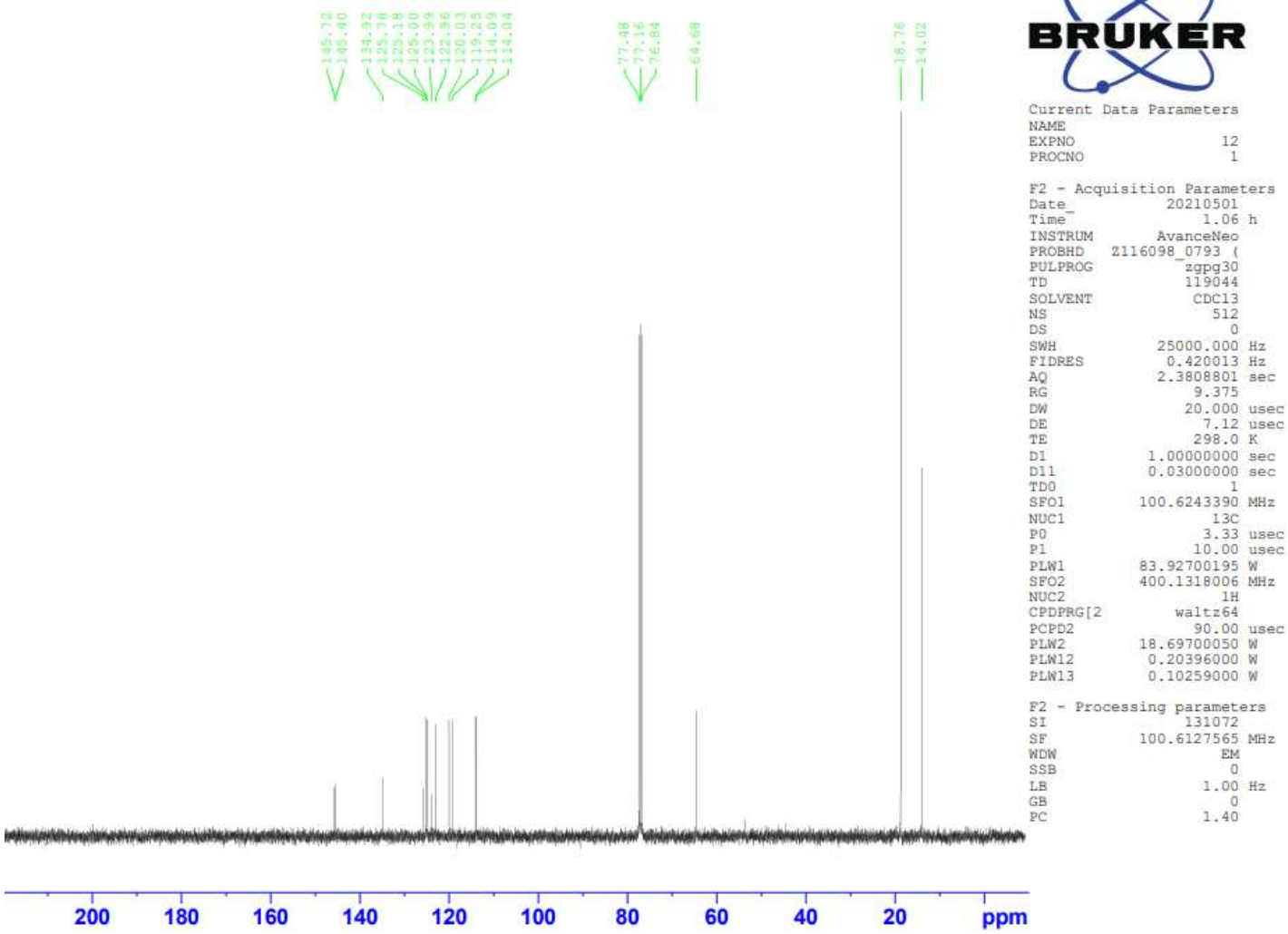

```
Current Data Parameters
NAME
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210430
Time                12.34 h
INSTRUM        AvanceNeo
PROBHD    Z116098_0793 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     4
DS                     0
SWH              7142.857 Hz
FIDRES           0.217983 Hz
AQ               4.5875201 sec
RG                92.3077
DW                  70.000 usec
DE                  14.80 usec
TE                  298.0 K
D1             2.00000000 sec
TD0                    1
SFO1          400.1324008 MHz
NUC1                   1H
P0                  3.13 usec
P1                  9.40 usec
PLW1          18.69700050 W

F2 - Processing parameters
SI                 131072
SF            400.1300098 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```

(9-(Triisopropylsilyl)-9H-carbazol-4-yl)methanol [22a]





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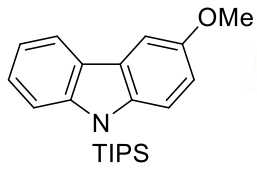
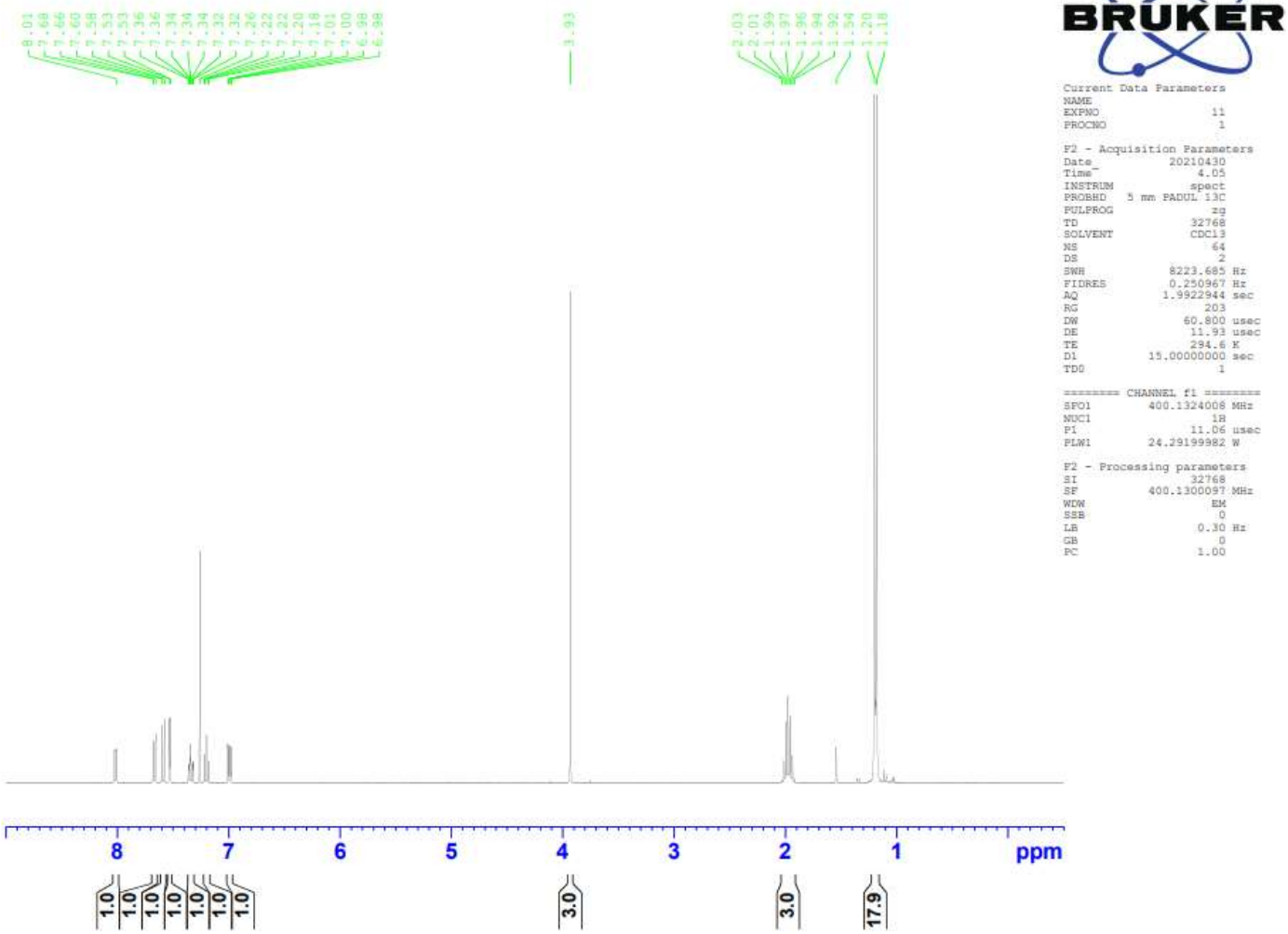
```
Current Data Parameters
NAME
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210501
Time                1.06 h
INSTRUM          AvanceNeo
PROBHD   Z116098_0793 (
PULPROG             zgpg30
TD                  119044
SOLVENT               CDC13
NS                      512
DS                        0
SWH               25000.000 Hz
FIDRES                0.420013 Hz
AQ                    2.3808801 sec
RG                        9.375
DW                       20.000 usec
DE                        7.12 usec
TE                       298.0 K
D1                1.00000000 sec
D11               0.03000000 sec
TD0                       1
SFO1             100.6243390 MHz
NUC1                     13C
P0                        3.33 usec
P1                       10.00 usec
PLW1             83.92700195 W
SFO2             400.1318006 MHz
NUC2                      1H
CPDPRG[2              waltz64
PCPD2                    90.00 usec
PLW2             18.69700050 W
PLW12             0.20396000 W
PLW13             0.10259000 W

F2 - Processing parameters
SI                      131072
SF               100.6127565 MHz
WDW                       EM
SSB                       0
LB                        1.00 Hz
GB                        0
PC                        1.40
```

3-Methoxy-9-(Triisopropylsilyl)-9H-carbazole [23a]





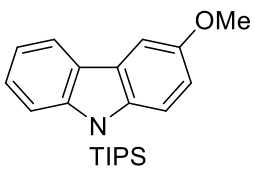

```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

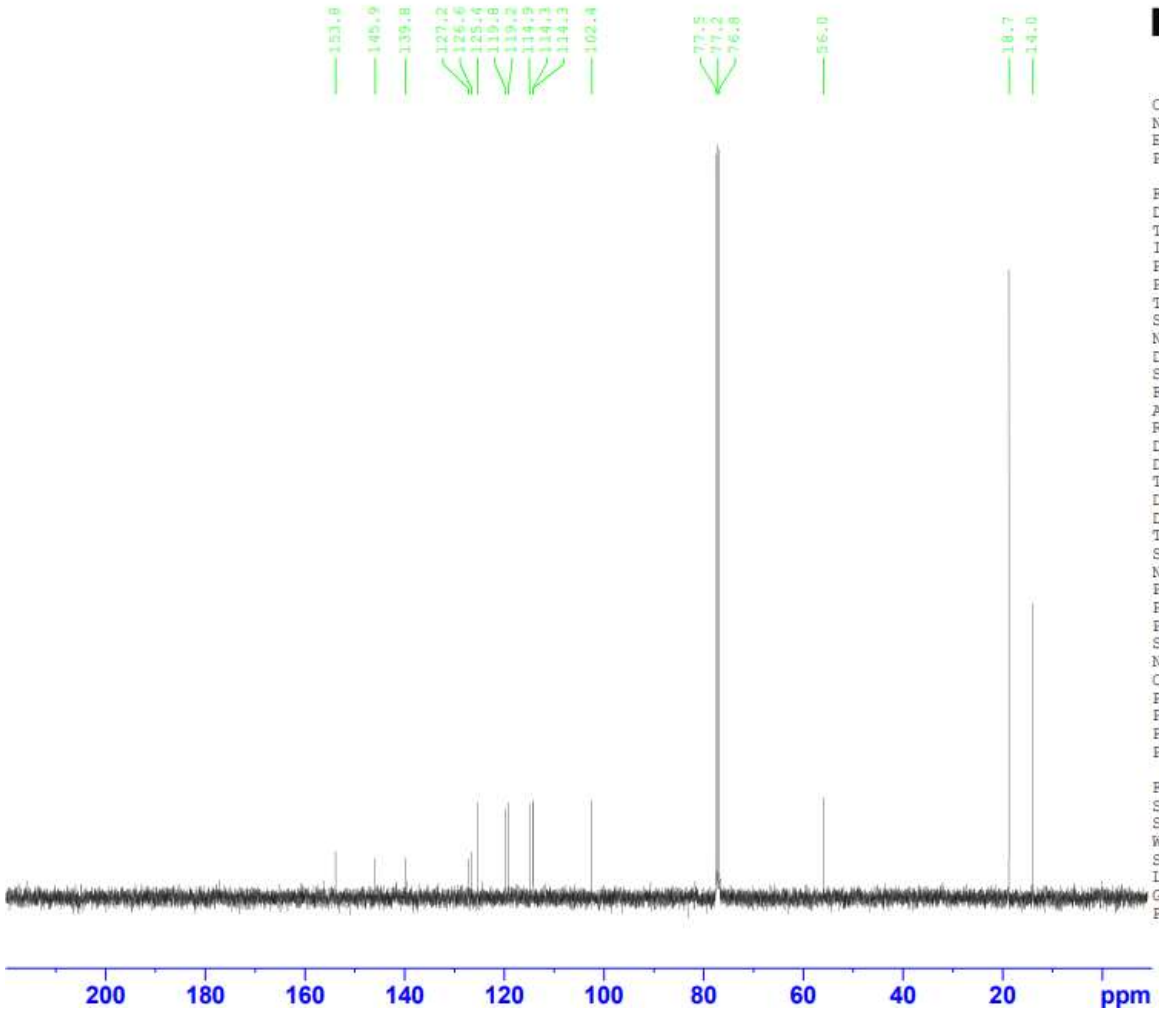
F2 - Acquisition Parameters
Date_            20210430
Time                 4.05
INSTRUM             spect
PROBHD   5 mm PADUL 13C
PULPROG                zg
TD                  32768
SOLVENT             CDCl3
NS                     64
DS                      2
SWH              8223.685 Hz
FIDRES           0.250967 Hz
AQ               1.9922944 sec
RG                    203
DW                 60.800 usec
DE                 11.93 usec
TE                 294.6 K
D1              15.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324008 MHz
NUC1                  1H
P1                 11.06 usec
PLW1          24.29199982 W

F2 - Processing parameters
SI                  32768
SF            400.1300097 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

3-Methoxy-9-(triisopropylsilyl)-9H-carbazole [23a]





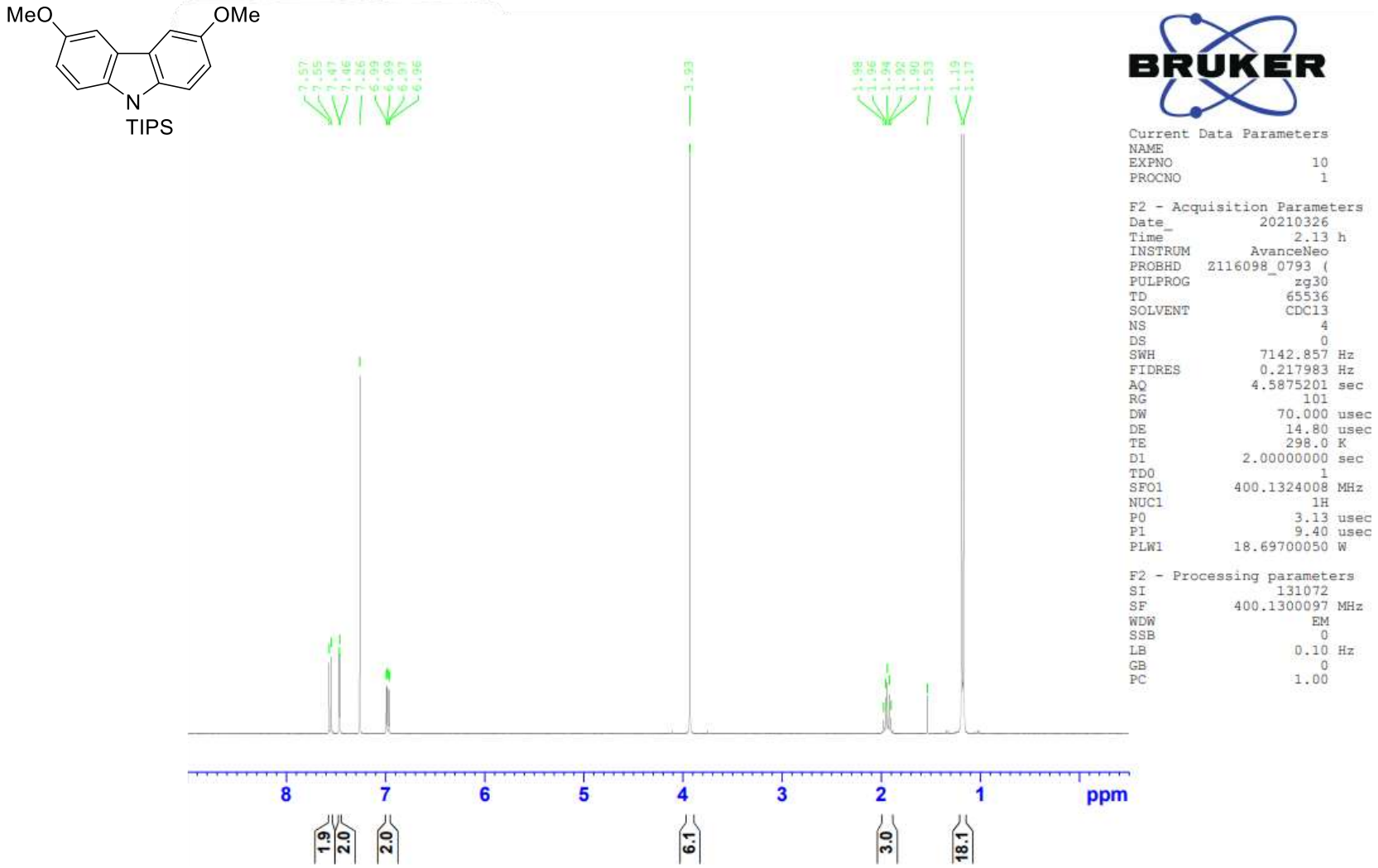
BRUKER

```
Current Data Parameters
NAME
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210501
Time                1.58 h
INSTRUM         AvanceNeo
PROBHD    Z116098_0793 (
PULPROG            zgpg30
TD                 119044
SOLVENT             CDCl3
NS                    512
DS                      0
SWH             25000.000 Hz
FIDRES              0.420013 Hz
AQ                2.3808801 sec
RG                    9.375
DW                   20.000 usec
DE                    7.12 usec
TE                   298.0 K
D1                1.00000000 sec
D11               0.03000000 sec
TD0                     1
SFO1            100.6243390 MHz
NUC1                   13C
P0                    3.33 usec
P1                   10.00 usec
PLW1            83.92700195 W
SFO2            400.1318006 MHz
NUC2                   1H
CPDPRG[2           waltz64
PCPD2                90.00 usec
PLW2            18.69700050 W
PLW12            0.20396000 W
PLW13            0.10259000 W

F2 - Processing parameters
SI                  131072
SF              100.6127555 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

3,6-Dimethoxy-9-(triisopropylsilyl)-9H-carbazole [24a]



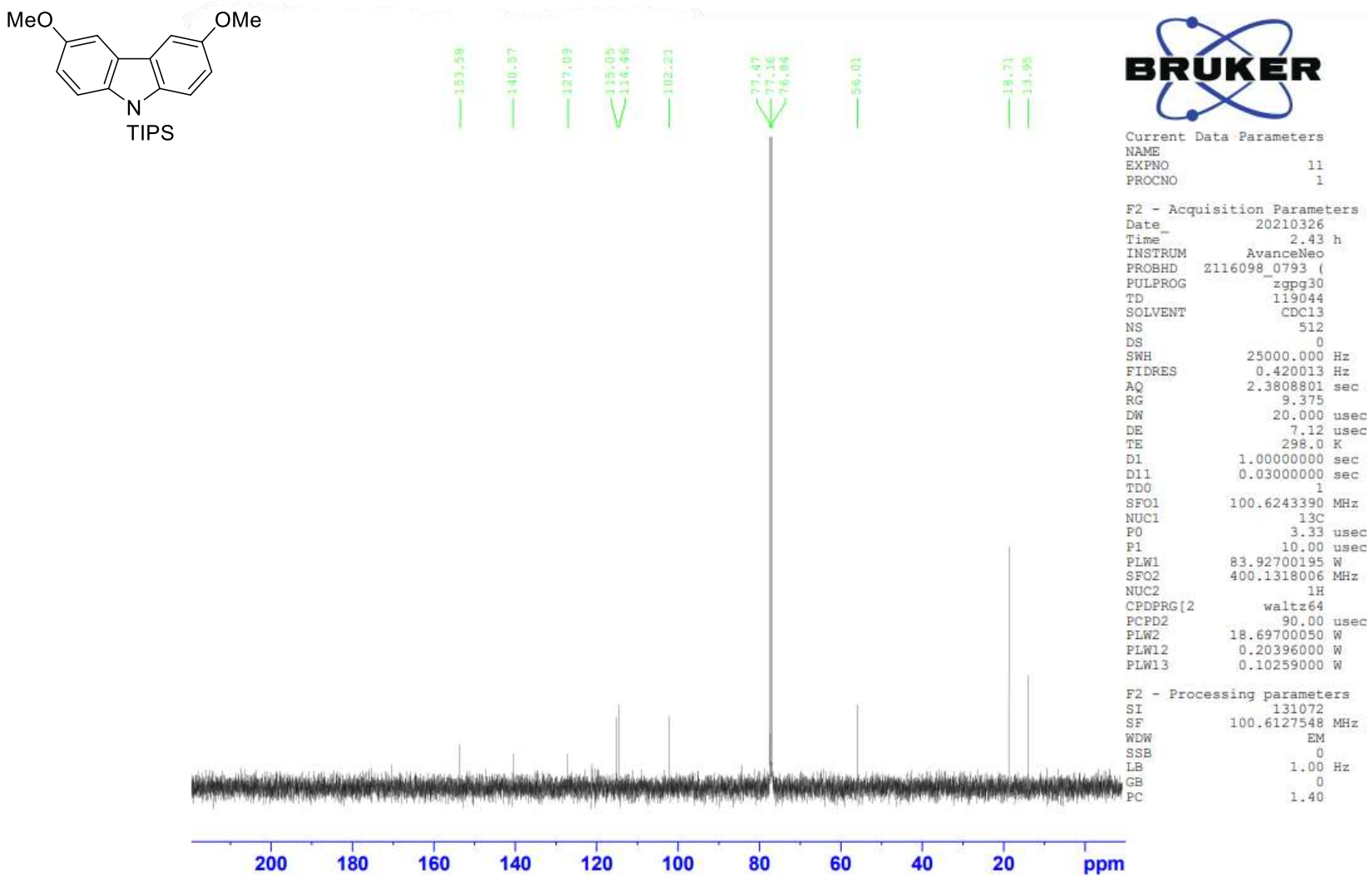
BRUKER

Current Data Parameters
NAME
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210326
Time 2.13 h
INSTRUM AvanceNeo
PROBHD Z116098_0793 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 0
SWH 7142.857 Hz
FIDRES 0.217983 Hz
AQ 4.5875201 sec
RG 101
DW 70.000 usec
DE 14.80 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 400.1324008 MHz
NUC1 1H
P0 3.13 usec
P1 9.40 usec
PLW1 18.69700050 W

F2 - Processing parameters
SI 131072
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

3,6-Dimethoxy-9-(triisopropylsilyl)-9H-carbazole [24a]

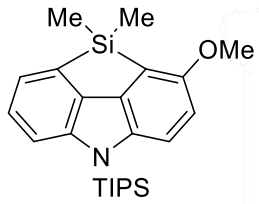


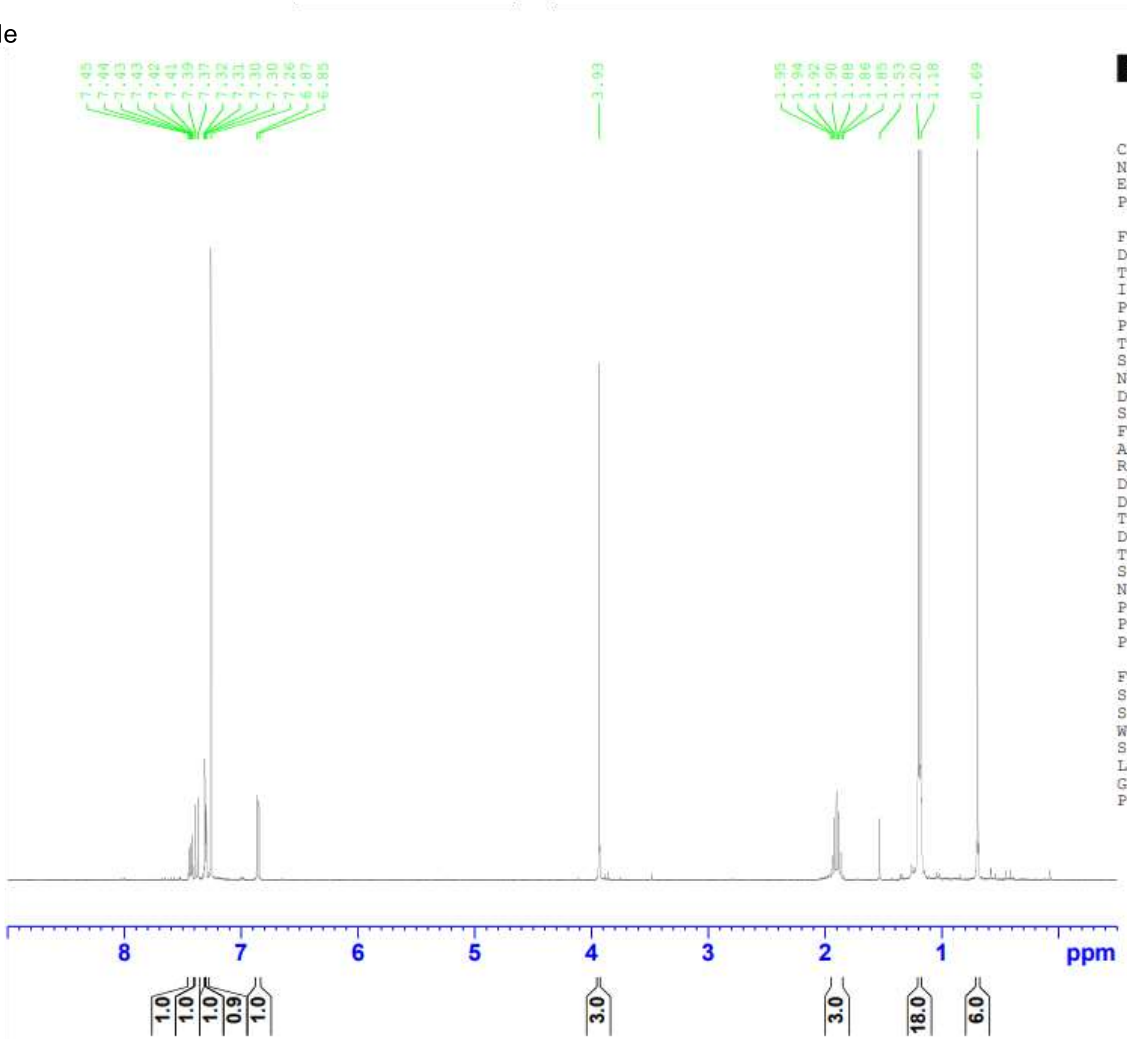

```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_           20210326
Time                2.43 h
INSTRUM         AvanceNeo
PROBHD    Z116098_0793 (
PULPROG            zgpg30
TD                 119044
SOLVENT             CDC13
NS                    512
DS                      0
SWH             25000.000 Hz
FIDRES          0.420013 Hz
AQ              2.3808801 sec
RG                  9.375
DW                 20.000 usec
DE                  7.12 usec
TE                 298.0 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                     1
SFO1          100.6243390 MHz
NUC1                  13C
P0                   3.33 usec
P1                  10.00 usec
PLW1          83.92700195 W
SFO2          400.1318006 MHz
NUC2                  1H
CPDPRG[2          waltz64
PCPD2               90.00 usec
PLW2          18.69700050 W
PLW12          0.20396000 W
PLW13          0.10259000 W

F2 - Processing parameters
SI                  131072
SF            100.6127548 MHz
WDW                   EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

1-Methoxy-8,8-dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [25a]





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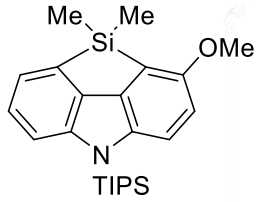
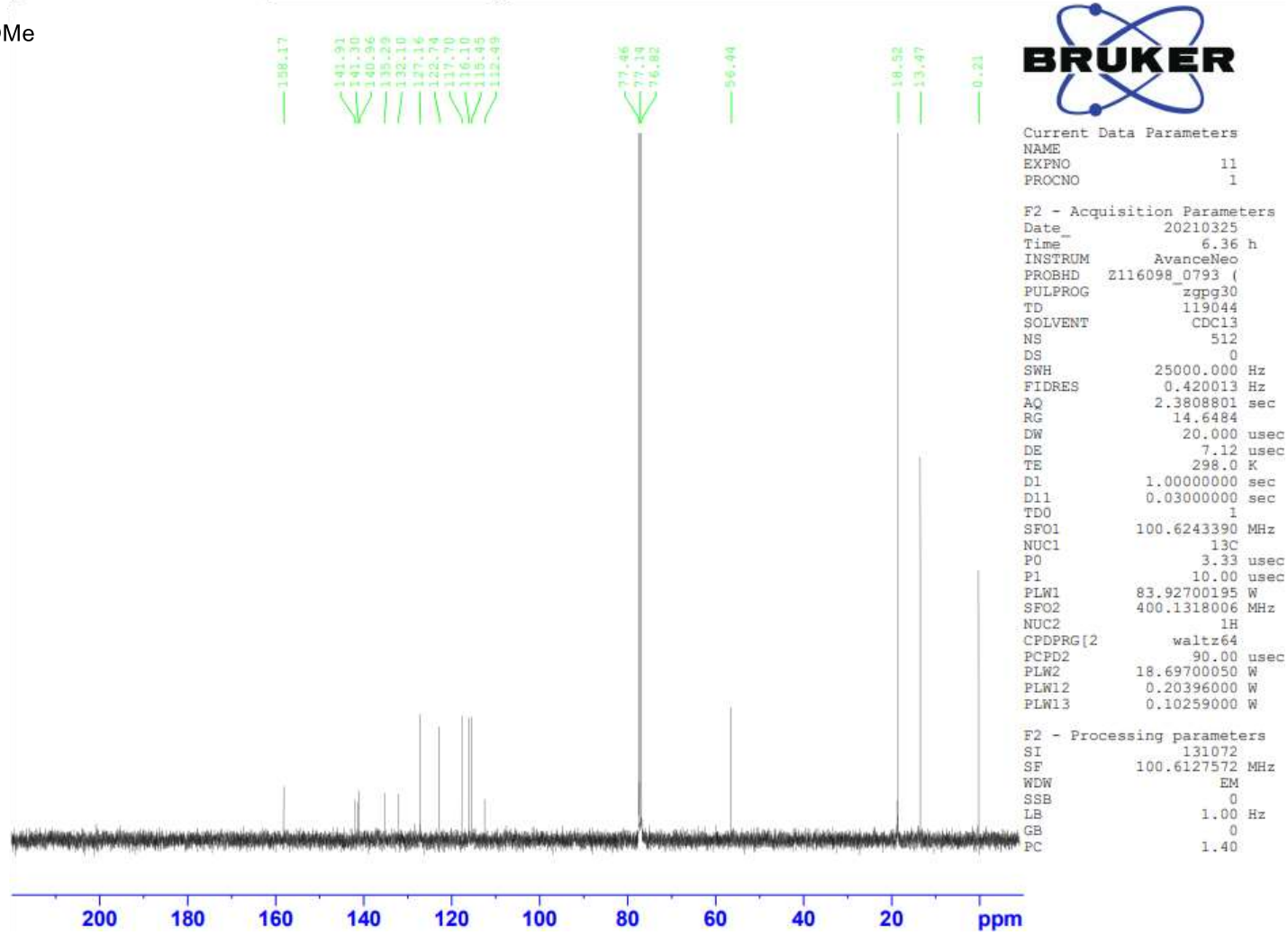
```
Current Data Parameters
NAME
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_           20210326
Time                3.53 h
INSTRUM       AvanceNeo
PROBHD   Z116098_0793 (
PULPROG             zg30
TD                 65536
SOLVENT            CDC13
NS                     4
DS                     0
SWH             7142.857 Hz
FIDRES          0.217983 Hz
AQ              4.5875201 sec
RG                   101
DW                70.000 usec
DE                14.80 usec
TE                298.0 K
D1             2.00000000 sec
TD0                    1
SFO1         400.1324008 MHz
NUC1                  1H
P0                 3.13 usec
P1                 9.40 usec
PLW1         18.69700050 W

F2 - Processing parameters
SI                131072
SF           400.1300102 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```

1-Methoxy-8,8-dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [25a]



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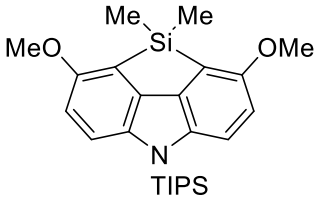
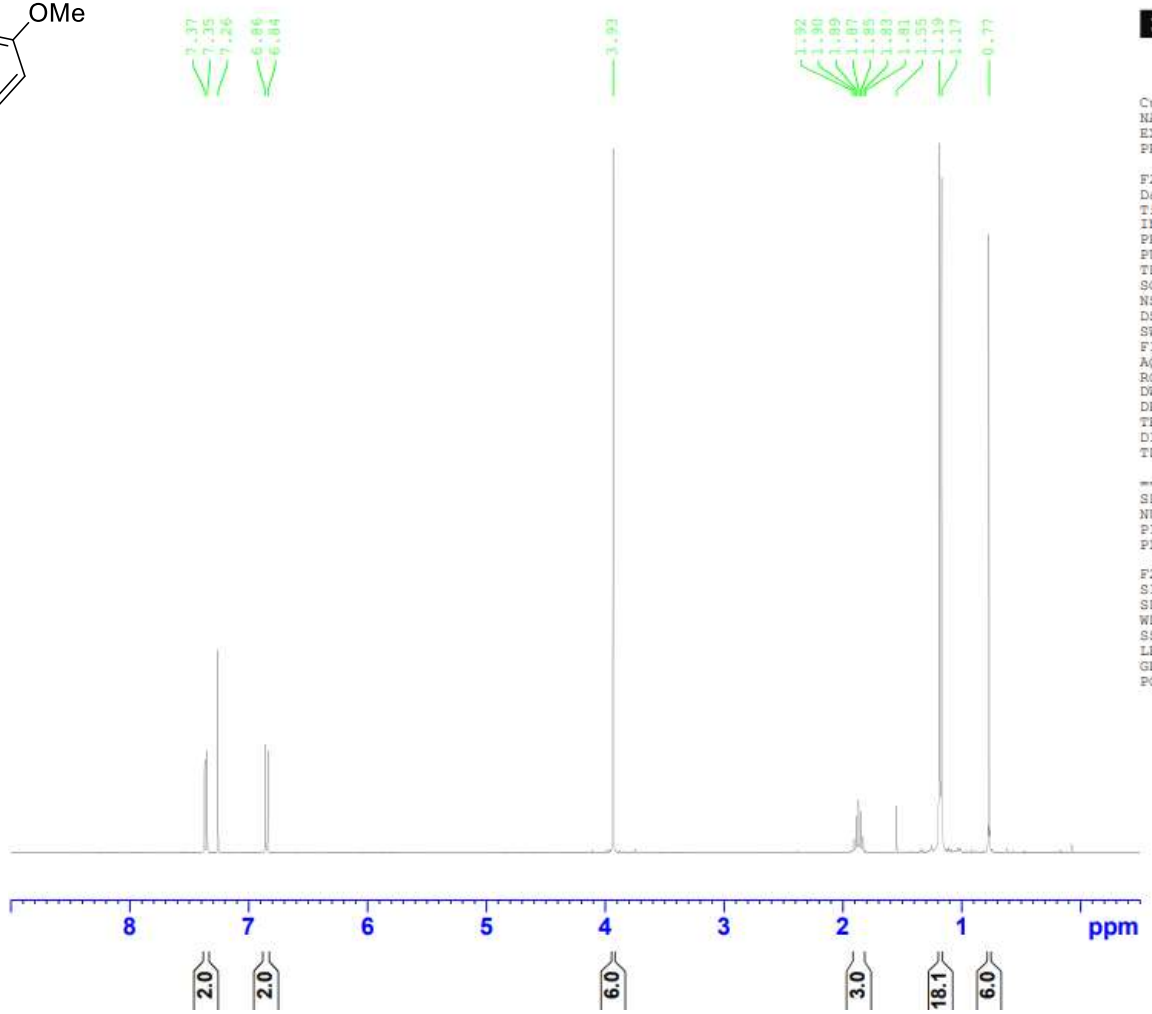
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210325
Time                6.36 h
INSTRUM         AvanceNeo
PROBHD    Z116098_0793 (
PULPROG            zgpg30
TD                 119044
SOLVENT             CDC13
NS                    512
DS                      0
SWH             25000.000 Hz
FIDRES          0.420013 Hz
AQ              2.3808801 sec
RG                14.6484
DW                20.000 usec
DE                 7.12 usec
TE                298.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1
SFO1          100.6243390 MHz
NUC1                  13C
P0                 3.33 usec
P1                10.00 usec
PLW1          83.92700195 W
SFO2          400.1318006 MHz
NUC2                  1H
CPDPRG[2         waltz64
PCPD2             90.00 usec
PLW2          18.69700050 W
PLW12          0.20396000 W
PLW13          0.10259000 W

F2 - Processing parameters
SI                  131072
SF            100.6127572 MHz
WDW                   EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```

1,7-Dimethoxy-8,8-dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [26a]





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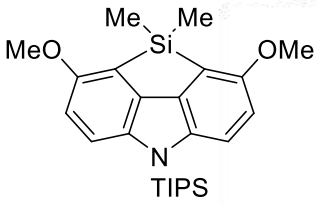
```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

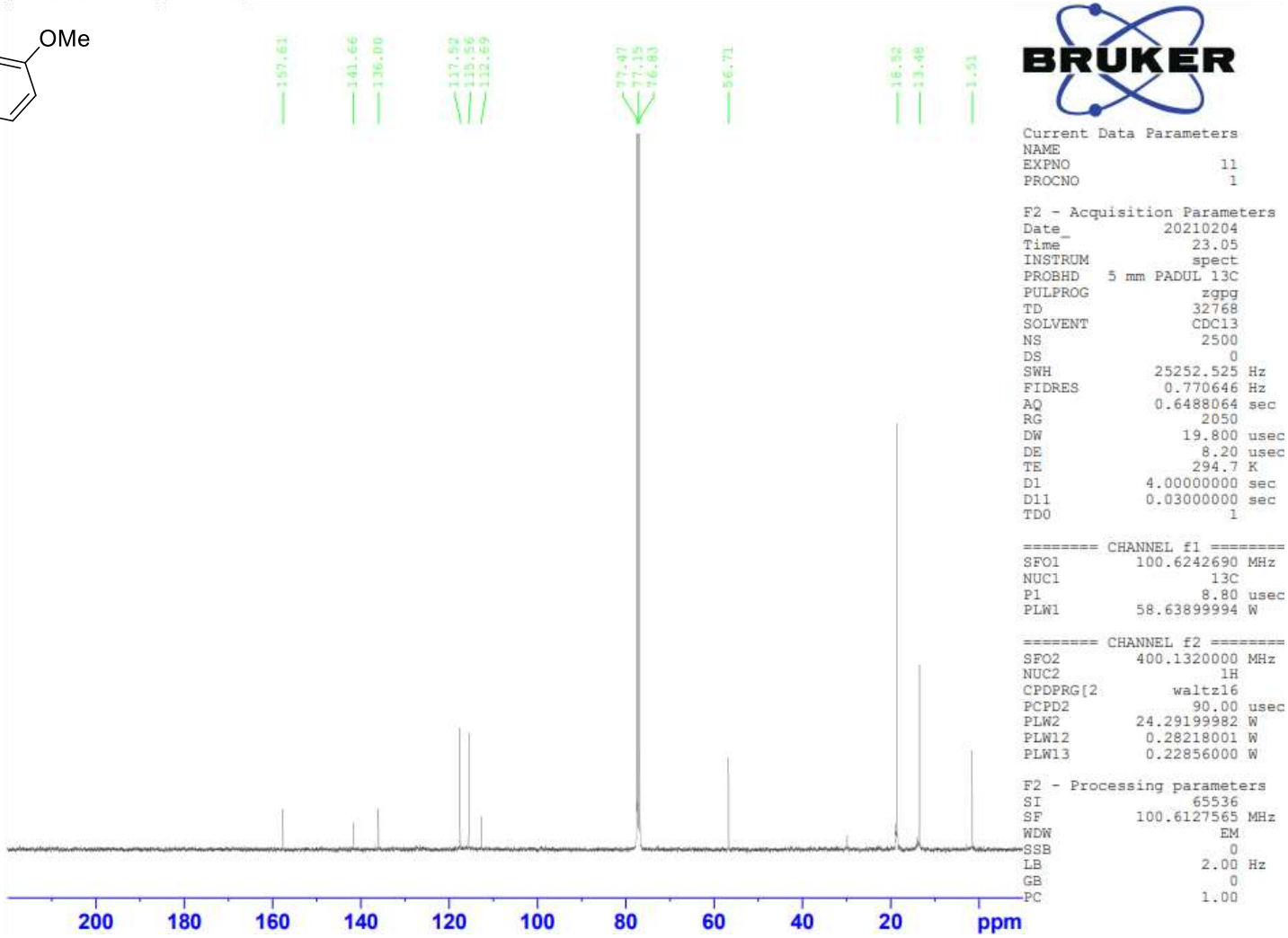
F2 - Acquisition Parameters
Date_            20210430
Time                5.16
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG                zg
TD                  32768
SOLVENT             CDCl3
NS                     64
DS                      2
SWH              8223.685 Hz
FIDRES           0.250967 Hz
AQ               1.9922944 sec
RG                    203
DW                60.800 usec
DE                11.93 usec
TE                294.3 K
D1           15.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                   1H
P1                  11.06 usec
PLW1         24.29199982 W

F2 - Processing parameters
SI                  32768
SF           400.1300103 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

1,7-Dimethoxy-8,8-dimethyl-4-(triisopropylsilyl)-4,8-dihydrosilolo[2,3,4,5-def]carbazole [26a]






```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

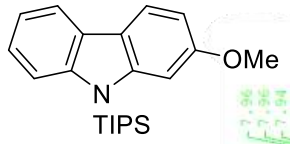
F2 - Acquisition Parameters
Date_            20210204
Time                23.05
INSTRUM             spect
PROBHD   5 mm PADUL 13C
PULPROG              zgpg
TD                  32768
SOLVENT             CDCl3
NS                   2500
DS                      0
SWH             25252.525 Hz
FIDRES          0.770646 Hz
AQ              0.6488064 sec
RG                   2050
DW                19.800 usec
DE                 8.20 usec
TE                294.7 K
D1             4.00000000 sec
D11            0.03000000 sec
TD0                     1

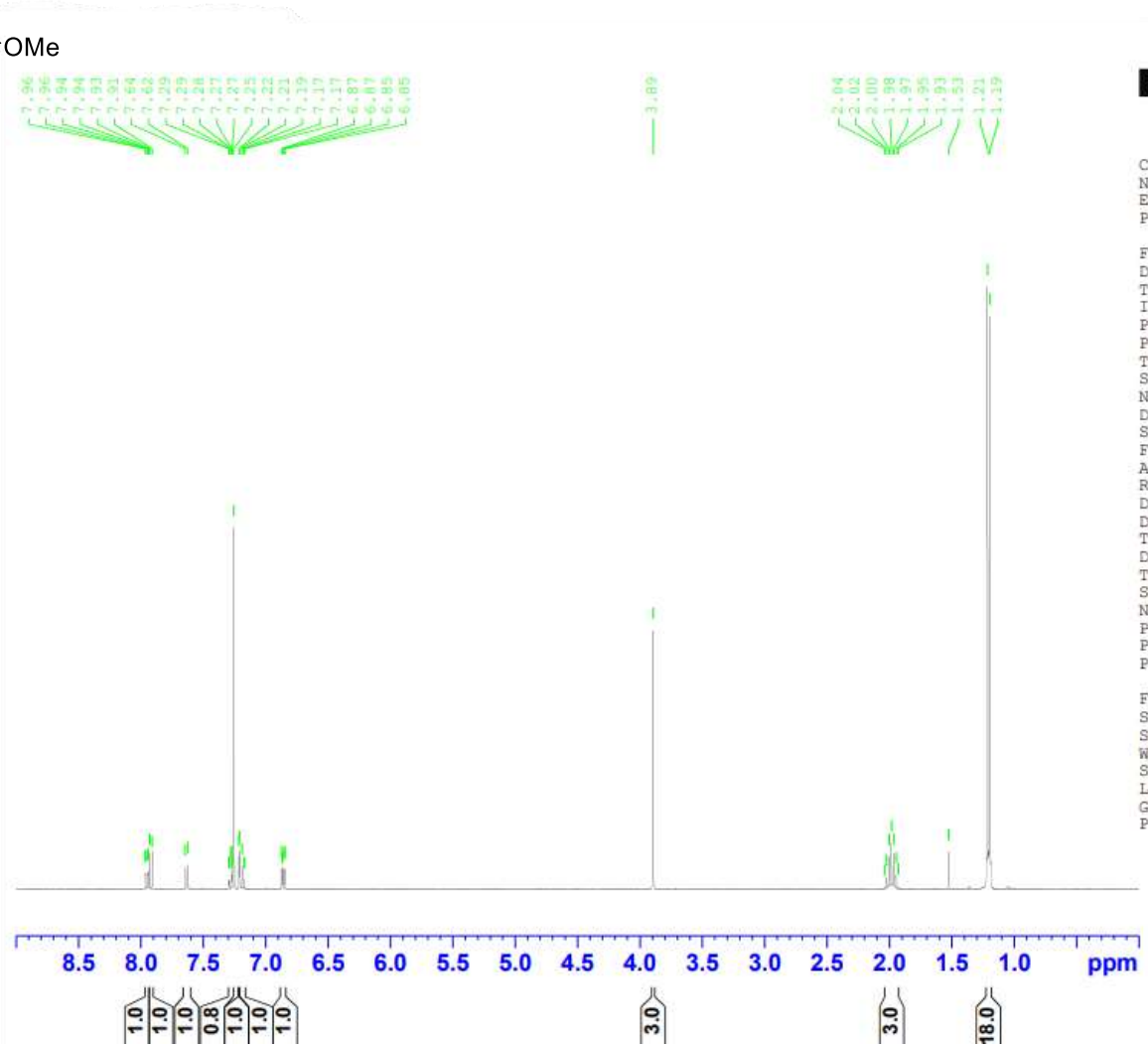
======== CHANNEL f1 ========
SFO1         100.6242690 MHz
NUC1                13C
P1                 8.80 usec
PLW1         58.63899994 W

======== CHANNEL f2 ========
SFO2         400.1320000 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         24.29199982 W
PLW12         0.28218001 W
PLW13         0.22856000 W

F2 - Processing parameters
SI                  65536
SF           100.6127565 MHz
WDW                    EM
SSB                     0
LB                 2.00 Hz
GB                      0
PC                   1.00
```

2-Methoxy-9-(triisopropylsilyl)-9H-carbazole [27a]



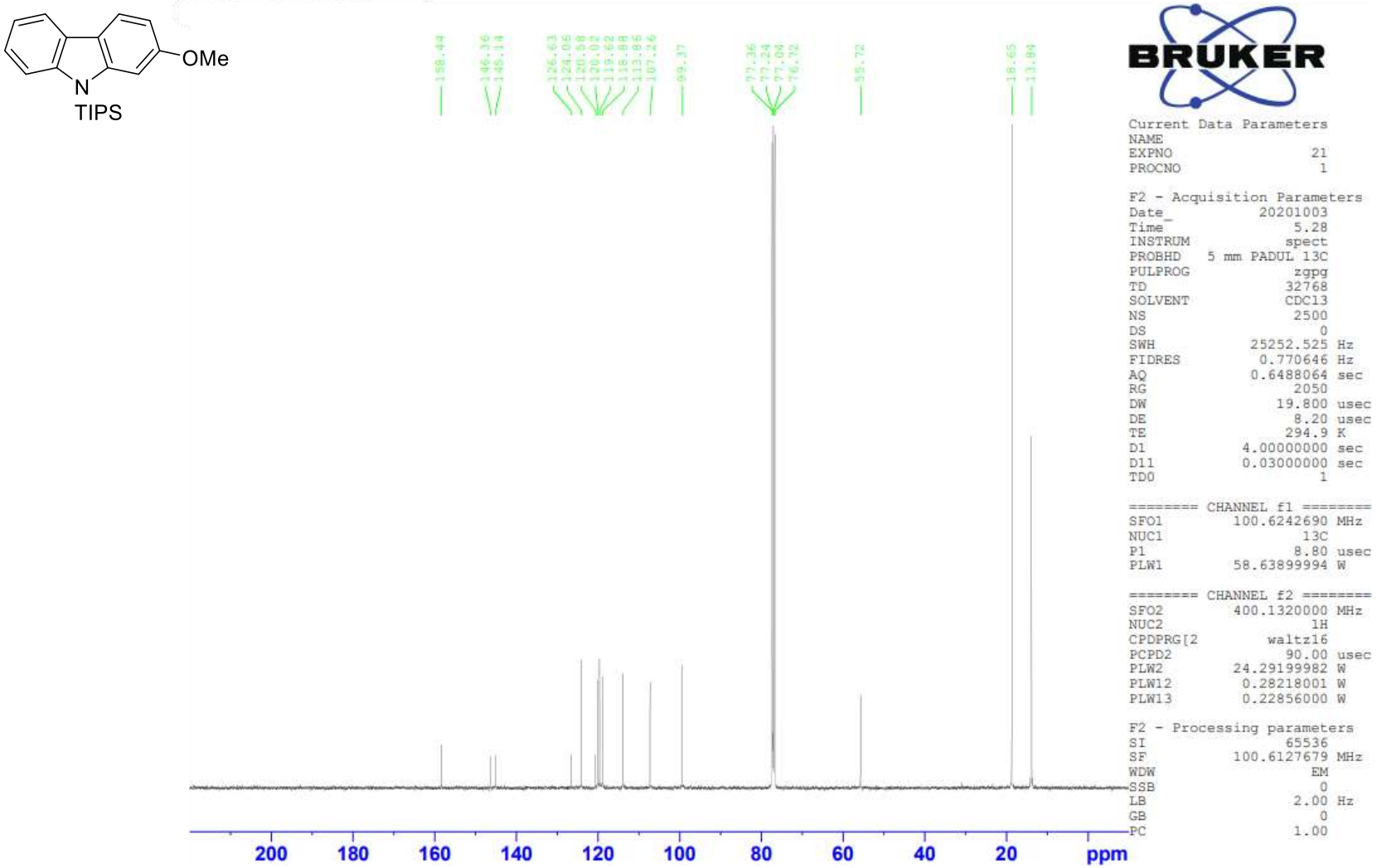



```
Current Data Parameters
NAME
EXPNO                  11
PROCNO                  1

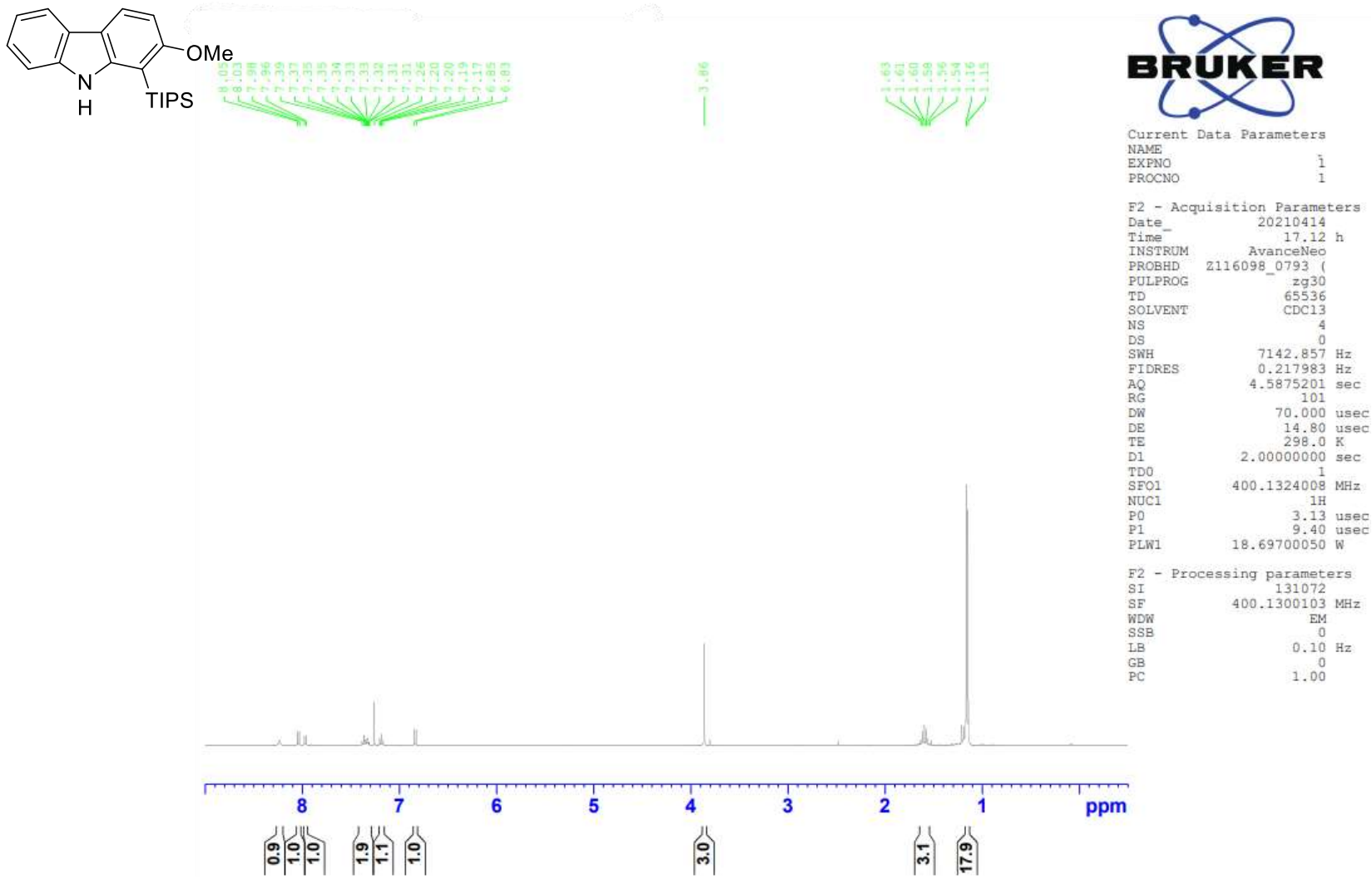
F2 - Acquisition Parameters
Date_            20210326
Time                2.09 h
INSTRUM         AvanceNeo
PROBHD    Z116098_0793 (
PULPROG             zg30
TD                 65536
SOLVENT            CDC13
NS                     4
DS                     0
SWH             7142.857 Hz
FIDRES          0.217983 Hz
AQ              4.5875201 sec
RG                   101
DW                70.000 usec
DE                14.80 usec
TE                298.0 K
D1             2.00000000 sec
TD0                    1
SFO1          400.1324008 MHz
NUC1                  1H
P0                 3.13 usec
P1                 9.40 usec
PLW1          18.69700050 W

F2 - Processing parameters
SI                131072
SF            400.1300116 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```

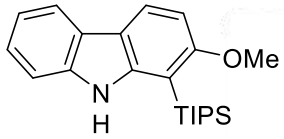
2-Methoxy-9-(triisopropylsilyl)-9H-carbazole [27a]

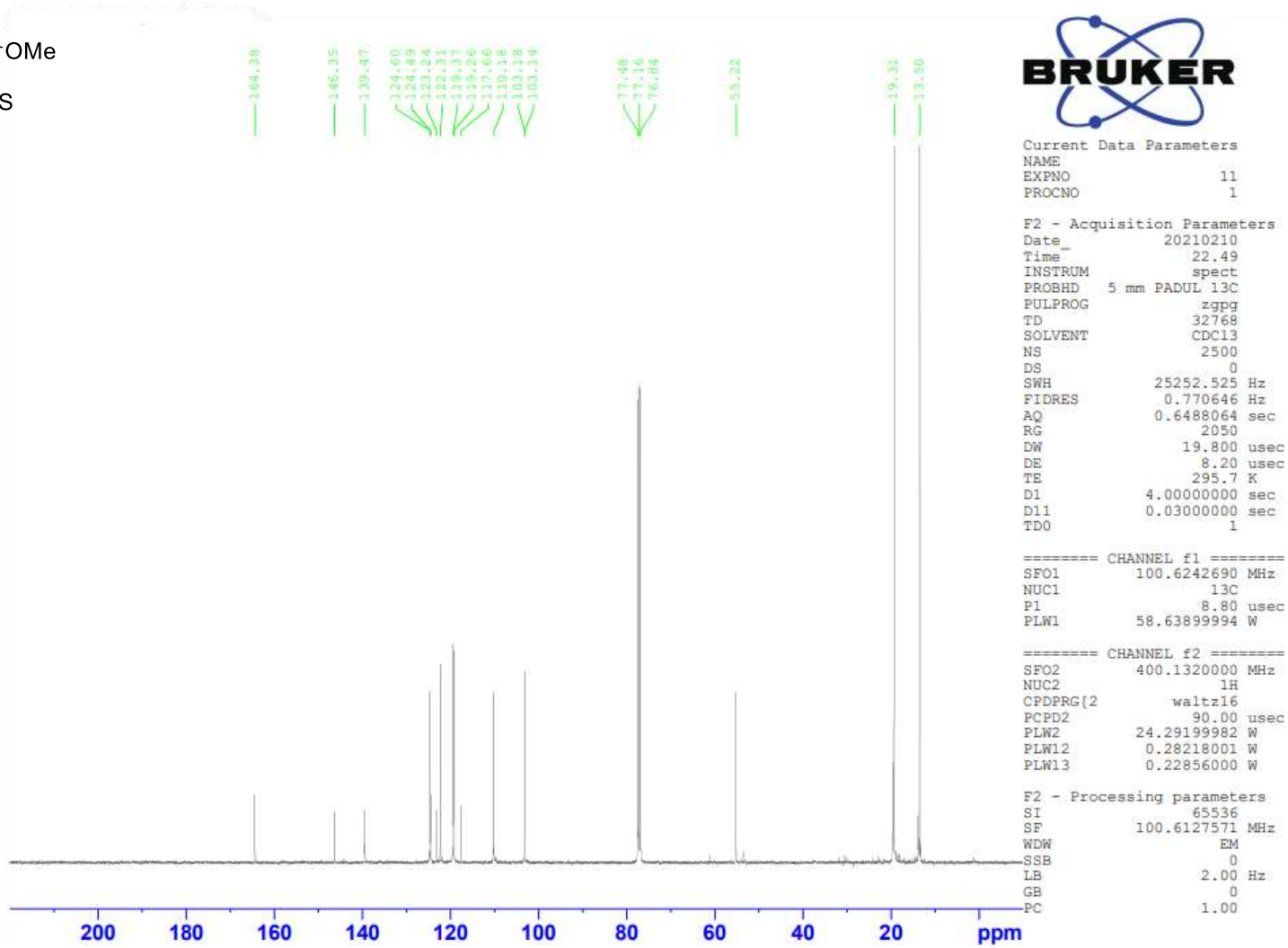


2-Methoxy-1-(triisopropylsilyl)-9H-carbazole [28]

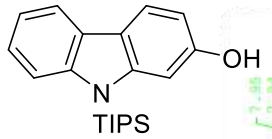


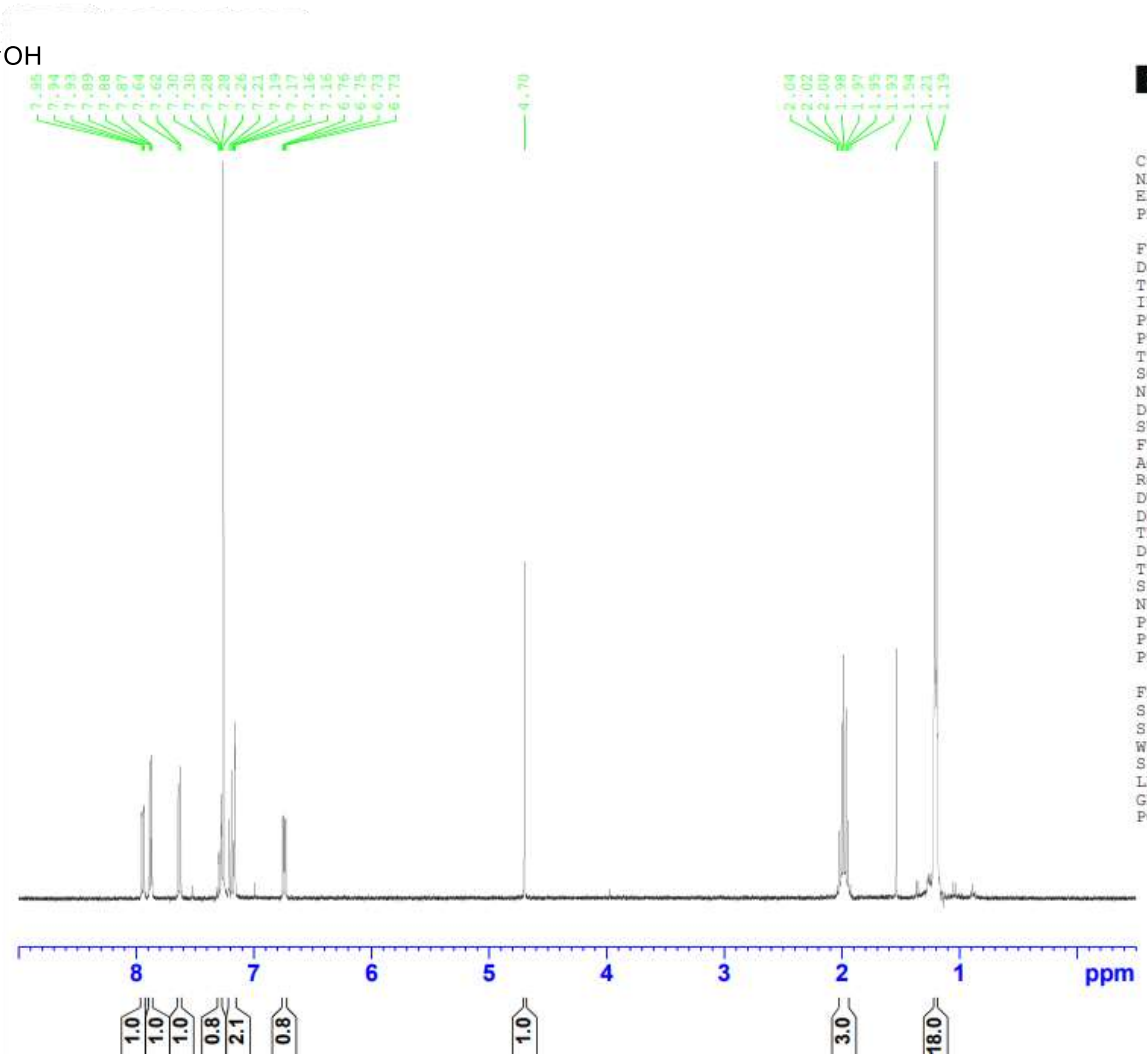
2-Methoxy-1-(triisopropylsilyl)-9H-carbazole [28]





9-(Triisopropylsilyl)-9H-carbazol-2-ol [29]



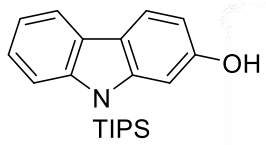


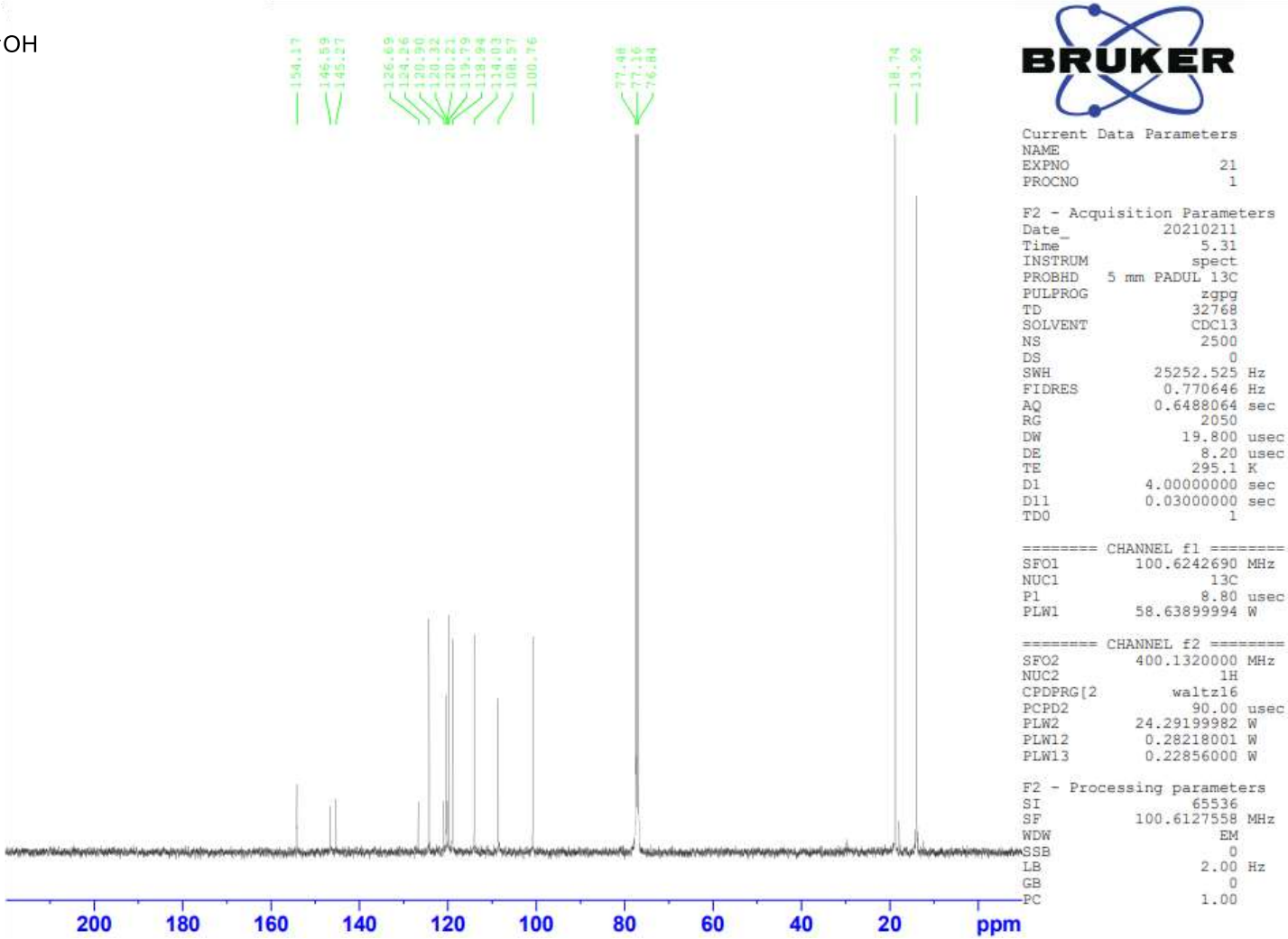

```
Current Data Parameters
NAME
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210414
Time              17.16 h
INSTRUM       AvanceNeo
PROBHD   Z116098_0793 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     4
DS                     0
SWH             7142.857 Hz
FIDRES          0.217983 Hz
AQ              4.5875201 sec
RG                   101
DW                70.000 usec
DE                14.80 usec
TE                298.0 K
D1             2.00000000 sec
TD0                    1
SFO1         400.1324008 MHz
NUC1                  1H
P0                 3.13 usec
P1                 9.40 usec
PLW1         18.69700050 W

F2 - Processing parameters
SI                131072
SF           400.1300096 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```

9-(Triisopropylsilyl)-9H-carbazol-2-ol [29]





BRUKER

```
Current Data Parameters
NAME
EXPNO                  21
PROCNO                  1

F2 - Acquisition Parameters
Date_           20210211
Time                5.31
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG             zgpg
TD                 32768
SOLVENT            CDC13
NS                  2500
DS                     0
SWH            25252.525 Hz
FIDRES          0.770646 Hz
AQ              0.6488064 sec
RG                  2050
DW                19.800 usec
DE                 8.20 usec
TE                295.1 K
D1             4.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6242690 MHz
NUC1                13C
P1                 8.80 usec
PLW1         58.63899994 W

======== CHANNEL f2 ========
SFO2         400.1320000 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         24.29199982 W
PLW12         0.28218001 W
PLW13         0.22856000 W

F2 - Processing parameters
SI                 65536
SF           100.6127558 MHz
WDW                   EM
SSB                    0
LB                 2.00 Hz
GB                     0
PC                  1.00
```

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