Electronic Supplementary Information

A bisalkynylated 3,6-diiminocyclohexa-1,4-diene-1,4-diamine

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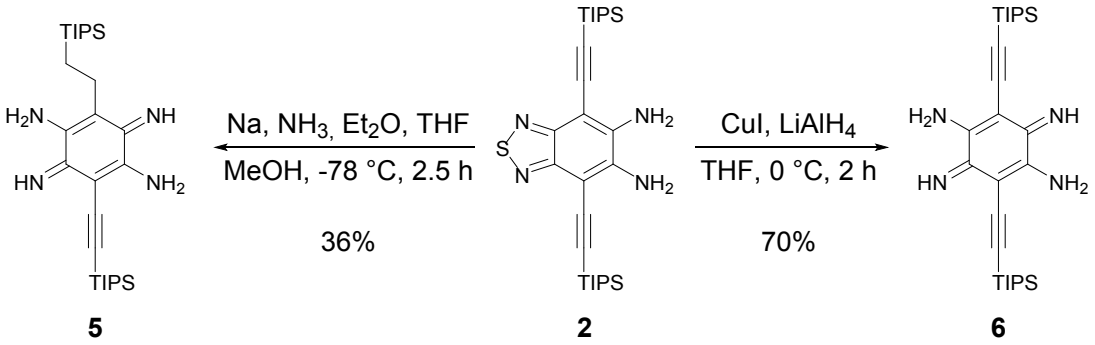
S1. General methods

All reagents and solvents were obtained from Fisher Scientific, ABCR, Sigma-Aldrich or Merck and were used as purchased. Absolute solvents were dried by a MB SPS-800 solvent purification system using drying columns. Thin layer chromatography (TLC) was carried out on Polygram® SIL G/UV_{254} plates from Macherey, Nagel & Co. KG, Düren (Germany) and examined under ultraviolet light irradiation (254 nm and 365 nm). Column chromatography was performed using silica gel from Macherey, Nagel & Co. KG, Düren (Germany) (particle size: 0.032-0.062 mm). Melting points were determined in glass capillaries with a Melting Point Apparatus MEL-TEMP (Electrothermal, Rochford, UK) and were kept uncorrected. Deuterated solvents were purchased from Deutero GmbH, Kastellaun. NMR spectra (^{1}H, ^{13}C) were recorded at room temperature on a Bruker Avance III 400 (400 MHz) at the NMR Spectroscopy Facility of the University of Heidelberg. The spectra were integrated and processed using TopSpin 3.2 (Bruker). Chemical shifts (δ) are given in parts per million (ppm) relative to solvent signals.[1] The following abbreviations describe the signal multiplicity: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet. The ^{13}C-NMR signal structure was analyzed by DEPT and is described as follows: + = primary or tertiary C-atom (positive signal), – = secondary C-atom (negative signal), and C_{quart} = quaternary C-atom (no signal). Obvious peak assignments are made by comparison to known substances.[2] IR spectra were recorded as a solid on a Jasco FT/IR-4100 spectrometer. The intensities are characterized as follows: vs = very strong 0–10% transmission (T), s = strong 10–40% T, m = middle 40–70% T, w = weak 70–90% T, vw = very weak 90–100% T. High resolution mass spectra (HRMS) were obtained by positive matrix-assisted laser desorption/ionization (MALDI), electrospray ionization (ESI) or direct analysis in real time (DART) experiments on a Bruker ApexQe hybrid 9.4 T FT-ICR at the Mass Spectrometry Facility of the University of Heidelberg. Elemental Analysis was accomplished on an Elementar vario MIKRO cube machine by the Microanalytical Laboratory of the University of Heidelberg. Crystal structure analysis was performed on a Bruker Smart CCD or a Bruker APEX-II Quazar diffractometer. Absorption spectra were recorded on a Jasco UV/VIS V-670 spectrophotometer. Emission spectra were recorded on a Jasco FP-6500 spectrofluorometer in solution. Cyclic voltammetry was performed on a VersaSTAT3-200 potentiostat (Princeton Applied Research). Computational studies were carried out using DFT calculations on Gaussian09.[3] Geometry optimization was found by B3LYP functional and 6-311+G* basis set and checked for imaginary frequencies. Using this geometry the absolute energy and FMO energies were assigned on single point approach by employing B3LYP/6-311++G**.

S2. Synthetic procedures and analytical data

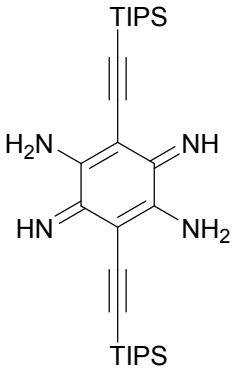
4,7-bis((triisopropylsilyl)ethynyl)benzo[c][1,2,5]thiadiazole-5,6-diamine **2**[4] and triptycene-2,3-dione **16**[5] were synthesized according to literature procedures.

Reduction of 4,7-bis((triisopropylsilyl)ethynyl)benzo[c][1,2,5]thiadiazole-5,6-diamine:



Scheme 1 Reduction of benzothiadiazole-diamine **2** leads to different products.

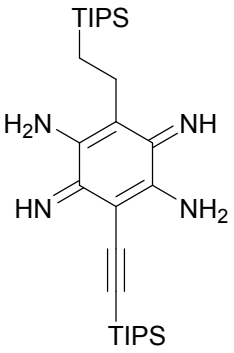
3,6-diimino-2,5-bis((triisopropylsilyl)ethynyl)cyclohexa-1,4-diene-1,4-diamine (6)



Under an atmosphere of argon, **2** (114 mg, 216 µmol) was dissolved in dry THF (12 mL). After addition of CuI (103 mg, 541 µmol, 2.5 eq), the mixture was cooled to 0 °C. $LiAlH_4$ (82.1 mg, 2.16 mmol, 10 eq) was added in small portions over 10 min. The mixture was stirred for additional 1.5 h at 0 °C. Complete conversion was detected by UPLC/MS analysis. At 0 °C, a saturated solution of sodium potassium tartrate in H_2O (20 mL) was added dropwise, and the mixture was extracted with diethyl ether (3x30 mL). The organic phase was stirred for 15 min over MnO_2 (tip of a spatula). After filtration over Celite, the filtrate was concentrates under reduced pressure. The crude product was purified by column chromatography (SiO_2, petrol ether/ dichloromethane 2:1 → 1:1 + 1 % trimethylamine) to yield **6** as a red solid (74.4 mg, 70 %).

R_f-value = 0.30 (dichloromethane) – mp > 238 °C decomp. – ν_{max}/cm^{-1} = 3437 (w), 3247 (w), 3061 (w, br), 2940 (m), 2862 (m), 2134 (m), 1627 (m), 1541 (s), 1459 (w), 1358 (s), 1224 (s), 1065 (w), 994 (w), 961 (w), 876 (s), 707 (m), 674 (m), 587 (w), 473 (w), 449 (w) – ^{1}H-NMR (THF-d8, 500 MHz, 298 K): δ [ppm] = 1.14–1.20 (m; 42H), 5.47 (s; br; 2H), 6.75 (s; br; 2H), 9.59 (s; br; 2H) – ^{13}C-NMR (250 MHz, THF-d8, 298 K): δ [ppm] = 12.0, 18.9, 91.6, 100.5, 103.3, 150.2, 159.7 – HRMS (DART (+) FT-ICR) *m/z*: $[M+H]^+$ Calc. for $C_{28}H_{49}N_4Si_2$: 497.3490; Found 497.3488 correct isotope distribution.

3,6-diimino-2-{2-[tri(propan-2-yl)silyl]ethyl}-5-{[tri(propan-2-yl)silyl]ethynyl}cyclohexa-1,4-diene-1,4-diamine (5)

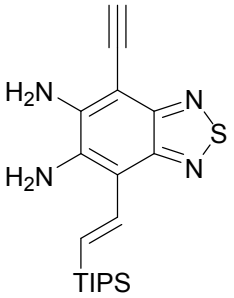


Under an atmosphere of argon, ammonia gas was condensed into a Schlenk tube at -78 °C to give 5 mL of liquid ammonia. Sodium (40 mg, 1.74 mmol, 7.5 eq) was added and stirred for 10 min until everything was dissolved. A solution of **2** (122 mg, 232 µmol) in a mixture of dry diethyl ether (1.5 mL), dry THF (1.0 mL), and dry MeOH (50.0 µL) was added dropwise. After stirring for 2 h at -78 °C, NH_4Cl (2.00 g) was added in portions and ammonia was allowed to volatilize under warming to r.t. H_2O was added and the mixture was extracted with dichloromethane (2x). After drying over Na_2SO_4, filtration and concentration, the crude product was purified by column chromatography (SiO_2, petrol ether/ethyl acetate 100:1 → 4:1). The resulting product was recrystallized from a mixture of diethyl ether and petrol ether to yield **5** as red needles (42 mg, 36 %).

R_f-value = 0.10 (dichloromethane) – mp > 128 °C decomp. – ν_{max}/cm^{-1} = 3491 (w), 3464 (w), 3281 (m, br), 3244 (w), 2940 (S), 2888 (m), 2863 (s), 2125 (m), 1618 (m), 1530 (s), 1460 (m), 1347 (s), 1216 (m), 997 (m), 876 (s), 838 (w), 740 (w), 699 (s), 671 (s), 657 (s), 590 (w), 574 (w), 442 (w), 427 (s), 417 (w) – ^{1}H-NMR ($CDCl_3$, 500 MHz, 298 K): δ [ppm] = 0.68–0.76 (m; 2H), 1.04–1.20 (m; 42H), 2.27–2.35 (m; 2H), 4.88 (s; br; 2H), 5.58 (s; br; 2H), 9.13 (s; br; 1H), 9.47 (s; br; 1H) – ^{13}C-NMR (125 MHz, $CDCl_3$, 298 K): δ [ppm] = 7.7, 11.0, 11.4, 18.9, 19.1, 19.5, 91.8, 99.2, 103.5, 110.7, 140.7, 149.3, 160.7, 160.9 – HRMS (ESI (+) FT-ICR) *m/z*: $[M+H]^+$ Calc. for $C_{28}H_{53}N_4Si_2$: 501.3803; Found 501.3812 correct isotope distribution.

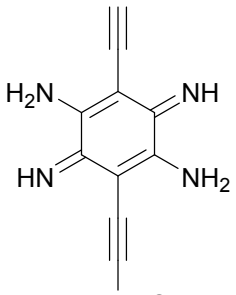
Analytical data of isolated byproducts

4-ethynyl-7-{(E)-2-[tri(propan-2-yl)silyl]ethenyl}-2,1,3-benzothiadiazole-5,6-diamine (7)



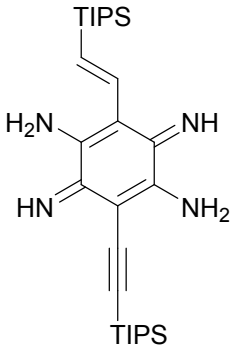
R_f-value = 0.72 (dichloromethane) – mp > 82 °C decomp. – ν_{max}/cm^{-1} = 3362 (w), 3303 (m), 3235 (w), 2940 (s), 2888 (w), 2862 (s), 2126 (w), 2094 (w), 1615 (m), 1535 (m), 1448 (s), 1364 (m9, 1312 (m), 1230 (w), 1007 (w), 995 (w), 881 (m), 819 (w), 790 (w), 707 (w), 654 (m), 561 (w), 514 (w) – ^{1}H-NMR (THF-d8, 500 MHz, 298 K): δ [ppm] = 1.14–1.21 (m; 21H), 4.14 (s; 1H), 5.19 (s; 2H), 5.63 (s; 2H), 7.12 (d; *J* = 19.7 Hz; 2H), 7.34 (d; *J* = 19.7 Hz; 2H) – ^{13}C-NMR (125 MHz, THF-d8, 298 K): δ [ppm] = 11.7, 19.0, 78.6, 88.1, 92.2, 110.7, 129.8, 138.7, 138.8, 146.7, 150.7, 152.1 – HRMS (DART (+) FT-ICR) *m/z*: $[M+H]^+$ Calc. for $C_{19}H_{29}N_4SSi$: 373.1877; Found 373.1874 correct isotope distribution.

2-ethynyl-3,6-diimino-5-{[tri(propan-2-yl)silyl]ethynyl}cyclohexa-1,4-diene-1,4-diamine (8)



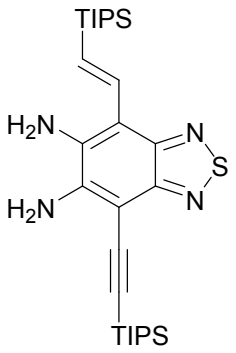
R_f-value = 0.13 (dichloromethane/methanol 95:5, v/v) – mp > 129 °C decomp. – ν_{max}/cm^{-1} = 3453 (w), 3275 (m), 3243 (m), 2940 (m), 2862 (m), 2115 (w), 1625 (m), 1535 (s), 1457 (w), 1538 (w), 1357 (s), 1213 (m), 989 (w), 878 (w), 865 (s), 695 (w), 660 (s), 590 (w), 55 (w), 431 (w), 450 (m), 413 (w), 404 (w) – ^{1}H-NMR (THF-d8, 400 MHz, 298 K): δ [ppm] = 1.14–1.20 (m; 21H), 4.18 (s; 1H), 6.39 (s; br; 4H), 9.56 (s; br; 2H) – ^{13}C-NMR (100 MHz, THF-d8, 298 K): δ [ppm] = 12.0, 19.0, 77.0, 90.1, 90.4, 91.6, 100.6, 103.2, 150.3, 150.4, 159.7, 159.8 – HRMS (ESI (+) FT-ICR) *m/z*: $[M+H]^+$ Calc. for $C_{19}H_{29}N_4Si$: 341.2156; Found 341.2158 correct isotope distribution.

3,6-diimino-2-{(E)-2-[tri(propan-2-yl)silyl]ethenyl}-5-{[tri(propan-2-yl)silyl]ethynyl}cyclohexa-1,4-diene-1,4-diamine (9)



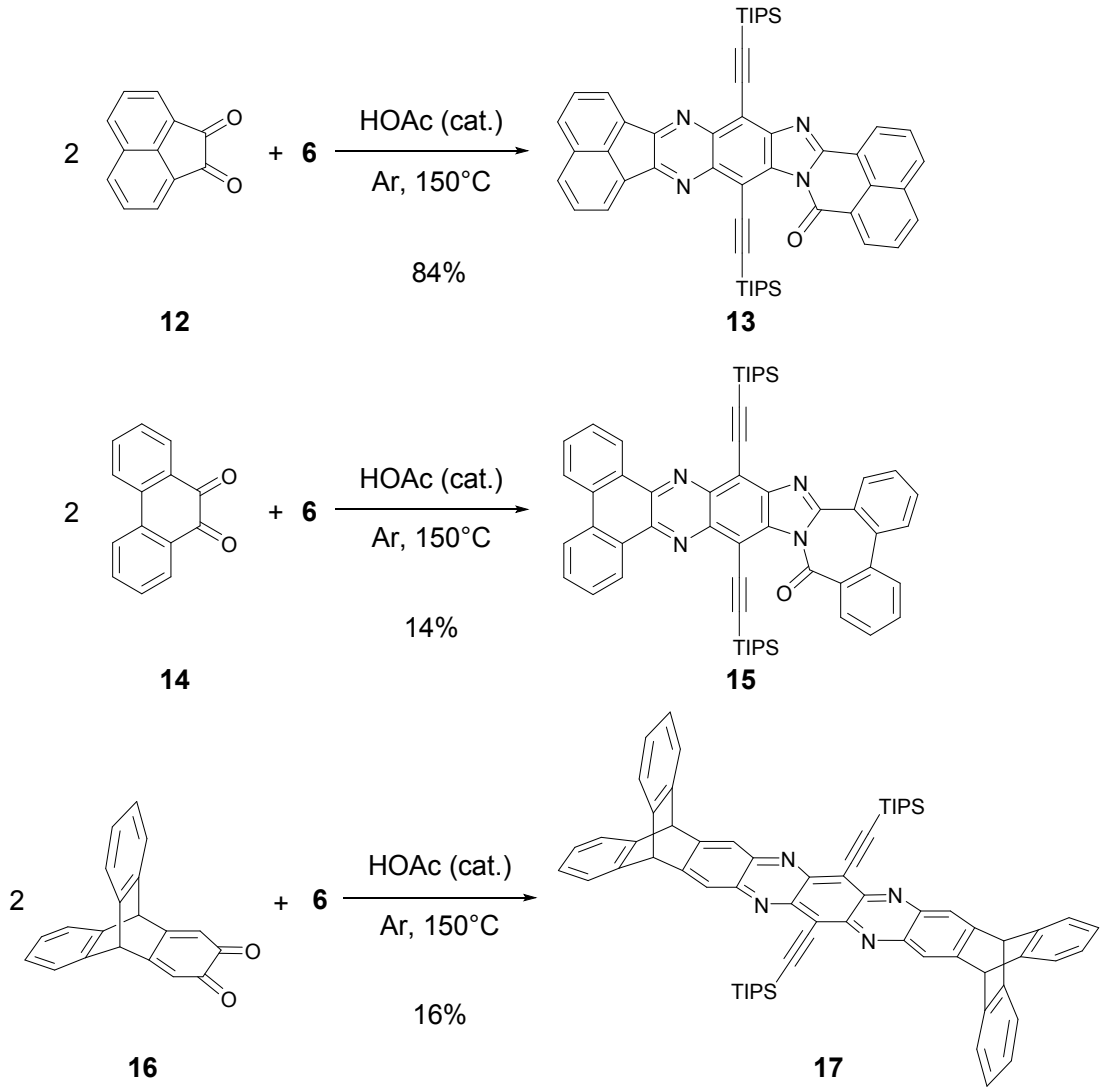
R_f-value = 0.21 (petroleum ether/diethyl ether 4:1, v/v) – mp > 170 °C decomp. – ν_{max}/cm^{-1} = 3443 (w), 34247 (w), 3095 (w, br), 2940 (m), 2863 (m), 2133 (w), 1732 (w), 1625 (m), 1529 (s), 1461 (m), 1355 (s), 1222 (w), 1069 (w), 1039 (w), 1011 (w), 994 (w), 878 (s), 706 (w), 668 (w), 492 (w), 469 (w), 448 (w), 435 (w), 410 (w) – ^{1}H-NMR (THF-d8, 500 MHz, 295 K): δ [ppm] = 1.13–1.16 (m; 21H), 1.16–1.19 (m; 21H), 5.68 (s; br; 4H), 6.00 (d; *J* = 19.9 Hz; 1H), 6.69 (d; *J* = 19.9 Hz; 1H), 9.46 (s; br; 1H), 9.56 (s; br; 1H) – ^{13}C-NMR (125 MHz, THF-d8, 295 K): δ [ppm] = 11.5, 12.0, 19.0, 91.1, 101.0, 102.4, 107.4, 131.1, 139.5, 142.7, 150.7, 160.3, 160.7 – HRMS (DART (+) FT-ICR) *m/z*: $[M+H]^+$ Calc. for $C_{28}H_{51}N_4Si_2$: 499.3647; Found 499.3641 correct isotope distribution.

4-{(E)-2-[tri(propan-2-yl)silyl]ethenyl}-7-{[tri(propan-2-yl)silyl]ethynyl}-2,1,3-benzothiadiazole-5,6-diamine (10)



R_f-value = 0.08 (dichloromethane) – mp > 150 °C decomp. – ν_{max}/cm^{-1} = 3459 (w), 3370 (w), 2940 (s), 2887 (w), 2863 (s), 2137 (w), 1648 (w), 1621 (w), 1586 (w), 1451 (s), 1366 (m), 1314 (w), 1072 (w), 1012 (w), 994 (m), 882 (s), 734 (m), 674 (m), 508 (w), 501 (w), 494 (w), 463 (w), 435 (w), 420 (m), 413 (w) – ^{1}H-NMR (THF-d8, 500 MHz, 295 K): δ [ppm] = 1.14–1.19 (m; 21H), 1.20–1.22 (m; 21H), 5.16 (s; 2H), 5.48 (s; 2H), 7.12 (d; *J* = 19.5 Hz; 2H), 7.35 (d; *J* = 19.5 Hz; 2H) – ^{13}C-NMR (125 MHz, THF-d8, 295 K): δ [ppm] = 11.7, 12.1, 19.0, 19.1, 93.8, 100.7, 102.3, 110.9, 130.0, 138.6, 138.8, 146.3, 150.7, 151.9 – HRMS (DART (+) FT-ICR) *m/z*: $[M+H]^+$ Calc. for $C_{28}H_{49}N_4SSi_2$: 529.3211; Found 529.3211 correct isotope distribution.

Condensation reactions of diaminoquinoneimine 6:

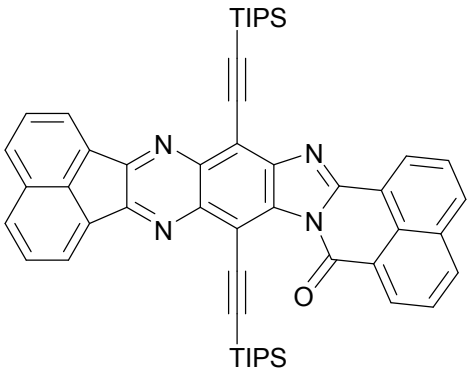


Scheme 2 Condensation reactions of diaminoquinoneimine **6** with commercially available *ortho*-quinones **13** and **15** and triptycene-2,3-dione **17**.

General Procedure (GP):

In a heat-gun dried thin schlenk tube *ortho*-quinone and diaminoquinoneimine were mixed and rinsed down with three drops of acetic acid under an argon atmosphere. The tube was closed with a glass stopper and tightened with a screw clamp and the reaction was heated for 16 h at 150 °C under stirring. The mixture was cooled to room temperature and directly subjected to column chromatography.

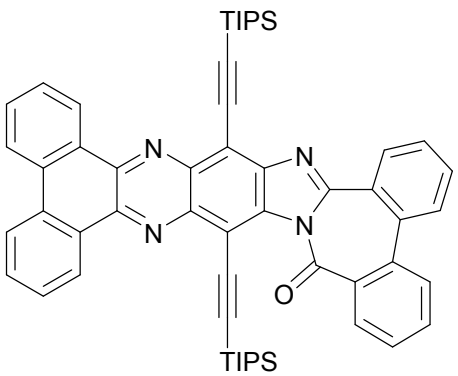
8,18-bis((triisopropylsilyl)ethynyl)-16H-acenaphtho[1,2-b]benzo[4',5']isoquinolino[2',1':1,2] imidazo[4,5-g]quinoxalin-16-one (13)



GP was carried out with 26.0 mg (143 µmol, 2.00 eq.) 1,2-acenaphthylenedione and 35.5 mg (71.4 µmol, 1.00 eq.) diaminoquinoneimine **6**. Column chromatography (silica gel; 25 × 3; petroleum ether/ethyl acetate gradient from 1:0 to 2:1, v/v) to yield an orange fluorescent solid. Yield: 39.4 mg (48.8 µmol, 84%).

R_f-value = 0.28 (petroleum ether/ethyl acetate 9:1, v/v) – mp > 335 °C decomp. – ν_{max}/cm^{-1} = 3060 (vw), 2924 (w), 2862 (w), 2162 (vw), 1722 (w), 1615 (vw), 1596 (w), 1543 (vw), 1506 (vw), 1462 (w), 1437 (w), 1422 (vw), 1396 (vw), 1363 (vw), 1339 (w), 1328 (w), 1299 (vw), 1265 (vw), 1206 (vw), 1177 (vw), 1167 (vw), 1129 (w), 1111 (w), 1072 (w), 1032 (w), 1016 (w), 999 (w), 908 (w), 882 (w), 835 (vw), 823 (w), 800 (w), 768 (m), 759 (m), 732 (vw), 716 (vw), 698 (vw), 673 (w), 659 (w), 611 (vw), 596 (w), 579 (w), 557 (w), 531 (vw), 518 (vw), 505 (vw), 488 (vw), 466 (w), 454 (w), 420 (vw), 402 (vw) – ^{1}H-NMR ($CDCl_3$, 500.13 MHz, 295.0 K): δ [ppm] = 1.38–1.40 (m, 21 H, ^{i}Pr-*H*), 1.40–1.42 (m, 21 H, ^{i}Pr-*H*), 7.84–7.87 (m, 4 H), 8.11 (dd, 2 H, *J* = 2.7, 8.0 Hz), 8.19 (d, 1 H, *J* = 8.0 Hz), 8.27 (d, 1 H, *J* = 8.0 Hz), 8.42 (t, 2 H, *J* = 6.6 Hz), 8.72 (d, 1 H, *J* = 6.6 Hz), 8.96 (d, 1 H, *J* = 6.6 Hz) – ^{13}C-NMR (150.95 MHz, $CDCl_3$, 295.0 K): δ [ppm] = 11.88 (+, *C*HCH$_3$), 11.93 (+, *C*HCH$_3$), 19.12 (+, CH*C*H$_3$), 19.16 (+, CH*C*H$_3$), 100.90 (C_{quart}, C*C*Si), 101.08 (C_{quart}, C*C*Si), 105.59 (C_{quart}, *C*CSi), 109.57 (C_{quart}, *C*CSi), 111.12 (C_{quart}), 114.35 (C_{quart}), 120.84 (C_{quart}), 122.25 (+), 122.27 (+), 124.30 (C_{quart}), 127.31 (+), 127.59 (+), 127.85 (C_{quart}), 128.53 (+), 128.83 (+), 128.88 (+), 129.46 (+), 129.59 (+), 130.16 (C_{quart}), 131.62 (+), 132.25 (C_{quart}), 132.34 (C_{quart}), 132.63 (+), 133.96 (C_{quart}), 134.72 (+), 137.27 (C_{quart}), 132.63 (C_{quart}), 140.99 (C_{quart}), 142.16 (C_{quart}), 148.10 (C_{quart}), 153.81 (C_{quart}), 154.03 (C_{quart}), 154.08 (C_{quart}), 158.73 (C_{quart}) – HRMS (MALDI FT-ICR) *m/z*: $[M+H]^+$ Calc. for $C_{52}H_{55}N_4OSi_2$: 807.3908; Found 807.3903 correct isotope distribution.

10,22-bis((triisopropylsilyl)ethynyl)-20H-dibenzo[a,c]dibenzo[3',4':5',6']azepino[1',2':1,2]imidazo [4,5-i]phenazin-20-one (15)

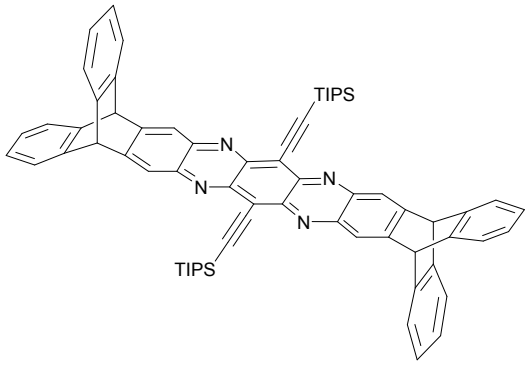


GP was carried out with 25.2 mg (121 µmol, 2.05 eq.) 9,10-phenanthrenequinone and 29.3 mg (59.0 µmol, 1.00 eq.) diaminoquinoneimine **6**. Column chromatography (silica gel; 20 × 2; petroleum ether/dichloromethane gradient from 1:0 to 2:1, v/v)

to yield an orange fluorescent solid. Yield: 7 mg (8.30 µmol, 14%).

R_f-value = 0.21 (petroleum ether/dichloromethane 2:1, v/v) – m.p. 243 °C – ν_{max}/cm^{-1} = 3070 (vw), 2939 (w), 2925 (w), 2862 (w), 2360 (w), 2342 (w), 2162 (vw), 2141 (vw), 1731 (w), 1597 (vw), 1516 (vw), 1493 (vw), 1459 (w), 1449 (w), 1382 (vw), 1356 (w), 1333 (w), 1284 (w), 1265 (w), 1248 (w), 1200 (vw), 1187 (vw), 1162 (vw), 1144 (vw), 1118 (w), 1092 (w), 1073 (w), 1042 (vw), 1017 (w), 995 (w), 960 (w), 914 (w), 881 (w), 818 (vw), 797 (vw), 781 (w), 760 (m), 733 (m), 725 (m), 706 (w), 674 (w), 658 (w), 628 (w), 582 (w), 551 (w), 529 (vw), 500 (w), 482 (vw), 471 (vw), 458 (vw), 432 (vw), 418 (vw), 403 (vw) – ^{1}H-NMR ($CDCl_3$, 600.25 MHz, 295.0 K): δ [ppm] = 1.36–1.39 (m, 21 H, ^{i}Pr-*H*), 1.40–1.43 (m, 21 H, ^{i}Pr-*H*), 7.59 (t, *J* = 7.8 Hz, 1 H), 7.67–7.82 (m, 8 H), 7.86 (d, 1 H, *J* = 7.8 Hz), 8.19 (d, 1 H, *J* = 6.8 Hz), 8.57 (dd, 2 H, *J* = 3.3, 7.8 Hz), 8.88 (d, 1 H, *J* = 7.8 Hz), 9.61–9.65 (m, 2 H) – ^{13}C-NMR (150.95 MHz, $CDCl_3$, 295.0 K): δ [ppm] = 11.83 (+, *C*HCH$_3$), 12.27 (+, *C*HCH$_3$), 19.09 (+, CH*C*H$_3$), 19.17 (+, CH*C*H$_3$), 99.68 (C_{quart}, C*C*Si), 101.07 (C_{quart}, C*C*Si), 105.91 (C_{quart}, *C*CSi), 106.86 (C_{quart}, *C*CSi), 110.57 (C_{quart}), 113.46 (C_{quart}), 122.98 (+), 123.02 (+), 126.12 (C_{quart}), 127.07 (+), 127.40 (+), 127.60 (+), 127.92(+), 128.69 (+), 129.27 (+), 129.70 (+), 129.82 (+), 130.53 (+), 130.55 (+), 130.59 (C_{quart}), 130.66 (C_{quart}), 130.99 (+), 132.34 (C_{quart}), 132.44 (C_{quart}), 132.53 (+), 132.62 (+), 133.30 (+), 135.14 (C_{quart}), 135.68 (C_{quart}), 135.97 (C_{quart}), 137.20 (C_{quart}), 140.39 (C_{quart}), 141.87 (C_{quart}), 141.93 (C_{quart}), 141.98 (C_{quart}), 148.14 (C_{quart}), 154.98 (C_{quart}), 166.01 (C_{quart}) – HRMS (DART FT-ICR) *m/z*: $[M+H]^+$ Calc. for $C_{56}H_{59}N_4OSi_2$ 859.4222; Found 859.4255 correct isotope distribution.

8,19-Bis(triisopropylsilylethynyl)-9,14-dihydro-5,22[1´,2´],11,16[1´,2´]-dibenzeno-7,9,18,20-tetraazanonacene (17)



GP was carried out with 26.4 mg (92.7 µmol, 4.85 eq.) 9,10-phenanthrenequinone and 9.5 mg (19.1 µmol, 1.00 eq.) diaminoquinoneimine **6**. Column chromatography (silica gel; 30 × 3; petroleum ether/ethyl acetate gradient from 1:0 to 2:1, v/v) to yield a darkish green solid, which could only be characterized by single crystal X-ray structure and mass spectrometry due to the small isolated amount. Yield: 2 mg (not NMR pure).

HRMS (MALDI FT-ICR) *m/z*: $[M+H_2]^+$ Calc. for $C_{68}H_{68}N_4Si_2$: 996.4977; Found 996.4955 correct isotope distribution.

S3. Full scaled absorption and emission spectra

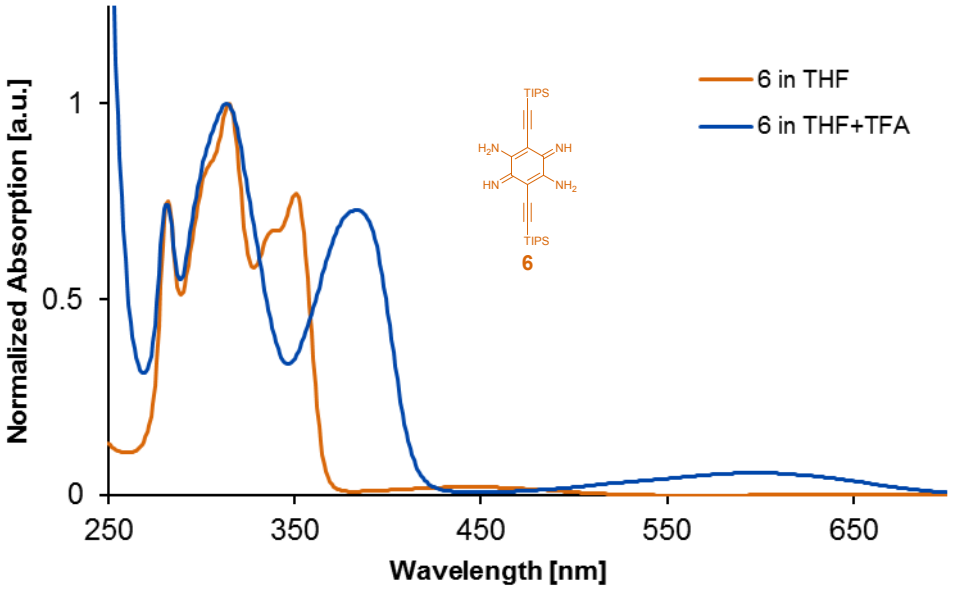


Figure 1 UV/Vis-absorption spectrum of **6** in tetrahydrofuran (orange) and with trifluoracetic acid (blue).

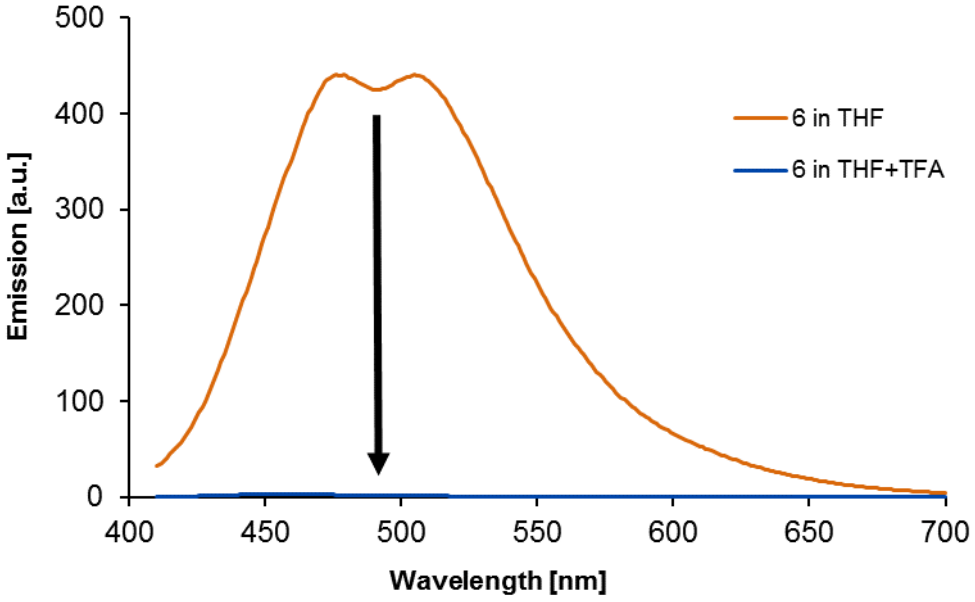


Figure 2 UV/Vis-absorption spectrum of **6** in tetrahydrofuran (orange) and with trifluoracetic acid (blue).

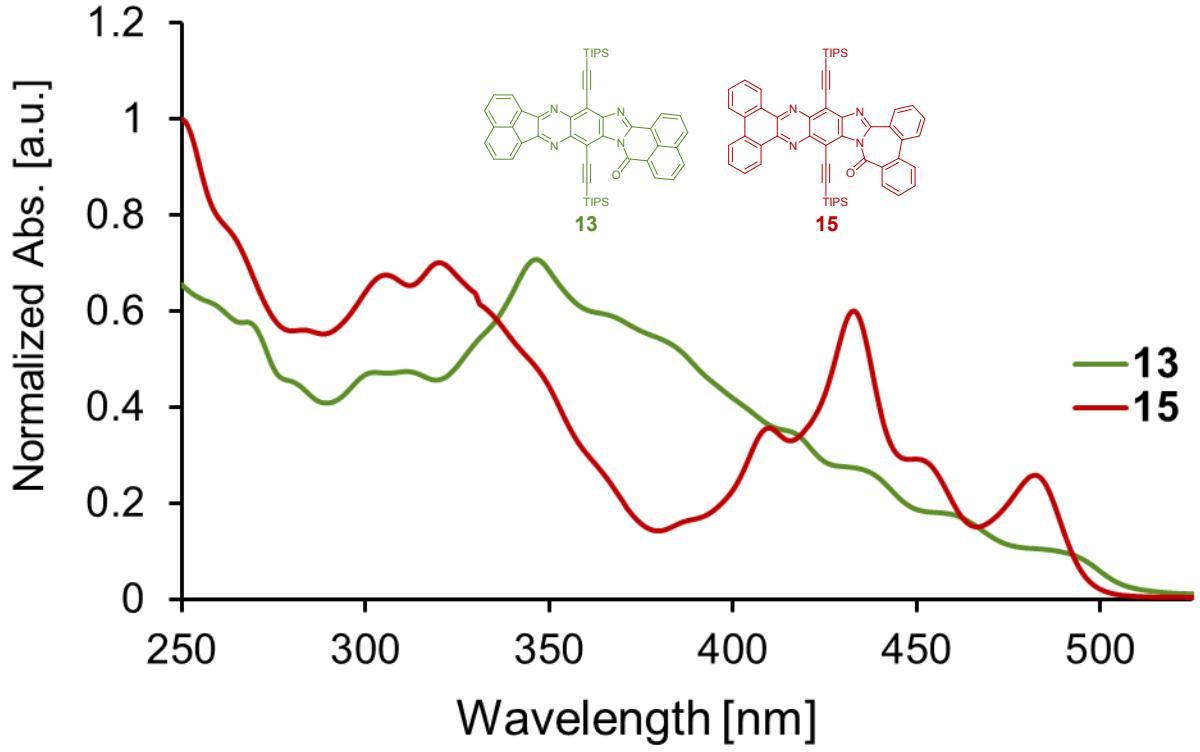


Figure 3 UV/Vis-absorption spectra of **13** and **15** in hexane.

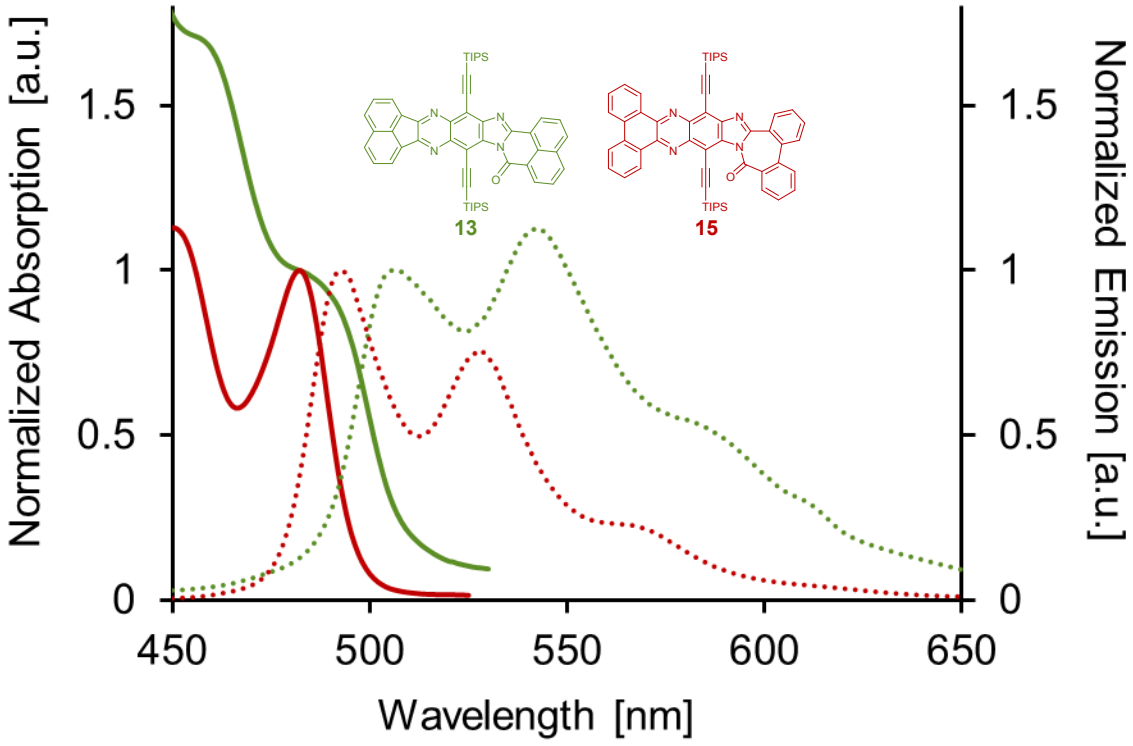


Figure 4 Long-wavelength absorption and emission spectra of **13** and **15** in hexane.

S4. Cyclic voltammograms

The cyclic voltammetry experiments were carried out using a platinum working electrode, a platinum/titanium wire auxiliary electrode, a silver wire pseudo-reference electrode, a 0.1 M NBu_4PF_6 solution in degassed dry tetrahydrofuran and ferrocene/ferrocenium as reference redox system and internal standard (–5.1 eV[6]). For determining the first and second reduction potential $E^{(0/-)}$ of **13** and **15** and the first oxidation potential of ferrocene the half-wave potentials were used.

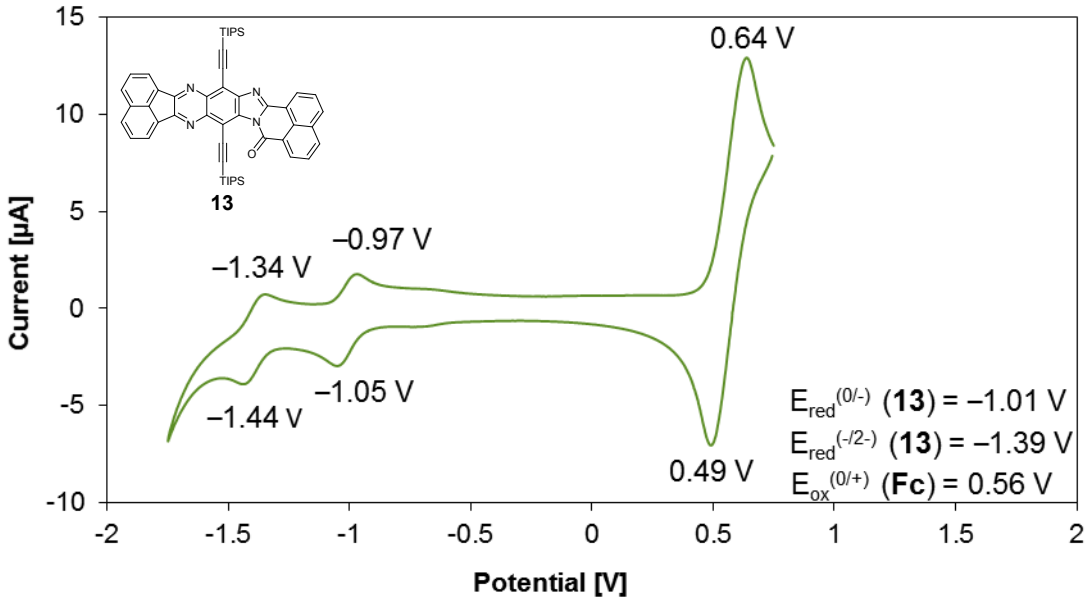
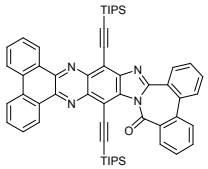


Figure 5 Cyclic voltammogram of **13**.



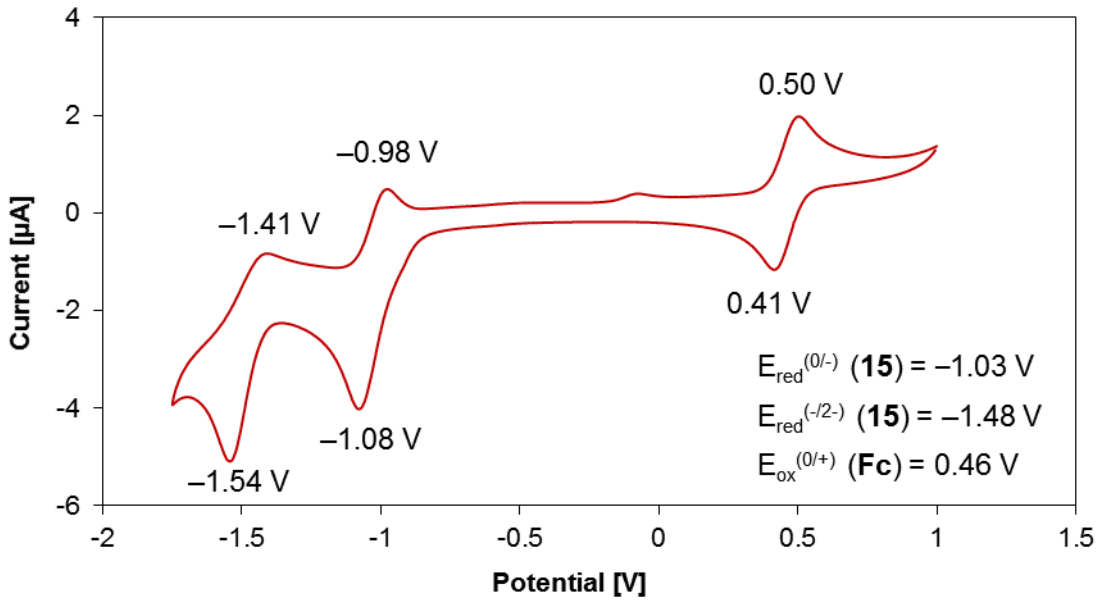
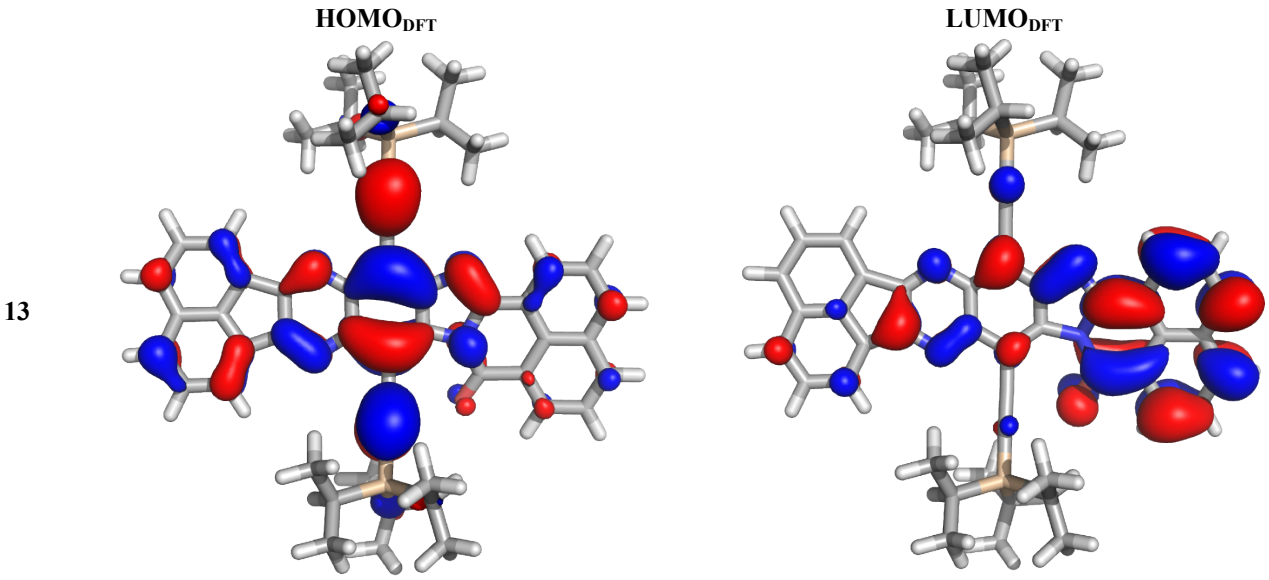
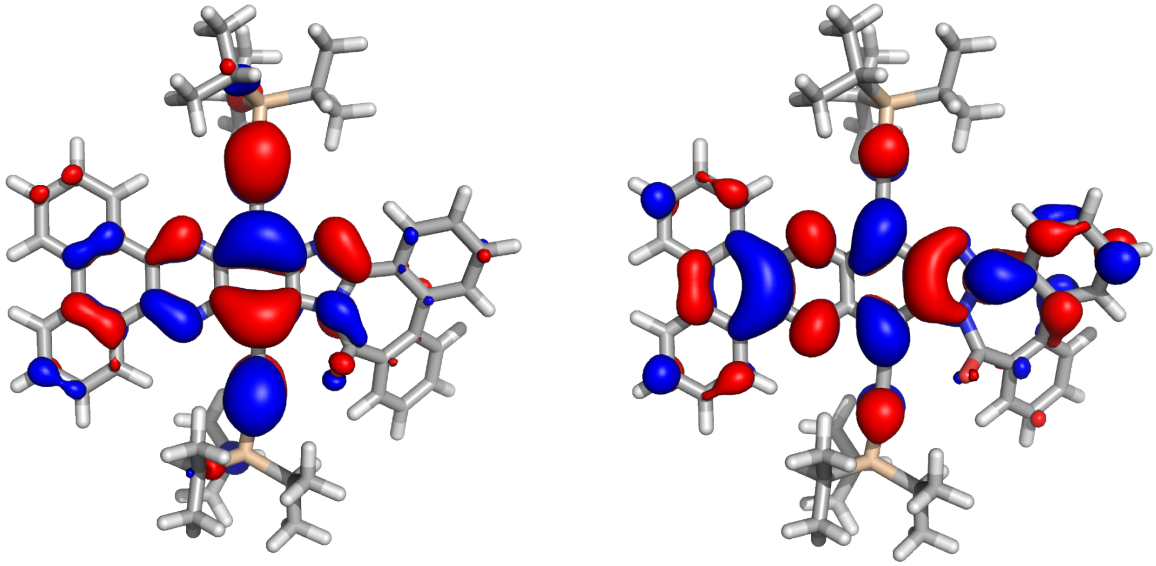


Figure 6 Cyclic voltammogram of **15**.

S5. Calculated frontier molecular orbitals (FMOs)



15



The geometry optimization was performed by Gaussian09 employing B3LYP 6-311+G*, and a single-point energy calculation (Gaussian09, B3LYP 6-311++G**) followed.[2]

Figure 7 Quantum-chemical calculations (B3LYP 6-311+G*//B3LYP 6-311++G**) of the FMOs for compounds **13** and **15**.[2]

S6. Crystallographic experiments

Crystal data for **1**: $C_{28}H_{42}N_4S_2Si_2$, M = 554.95, purple crystal (plate) obtained by slow evaporation of deuterated chloroform, dimensions 0.130 x 0.070 x 0.060 mm^3, monoclinic, a = 8.5203(3) Å, b = 15.4125(6) Å, c = 11.7589(5) Å, α = 90 °, β = 99.3033(9) °, γ = 90 °, V = 1523.86(10) Å^3, ρ = 1.209 g/cm^3, T = 200(2) K, space group $P2_1/n$, Z = 2, θ_{max} = 26.449 °, radiation Mo K_α, λ = 0.71073 Å, 0.5 ° omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 4.48 and a completeness of 98.3% to a resolution of 0.80 Å, 14317 reflections measured, 3094 unique (R_{int} = 0.0302), 2623 observed (I > 2σ(I)), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS (2012/1)[7] based on the Laue symmetry of the reciprocal space, μ = 0.28mm^{-1}, T_{min} = 0.87, T_{max} = 0.96, structure refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2014/7 (Sheldrick, 2014) software[8], 163 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.07 for observed reflections, final residual values $R_1(F)$ = 0.037, $wR(F^2)$ = 0.092 for observed reflections, residual electron density -0.21 to 0.36 eÅ^{-3}. CCDC 1408361 contains 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.

Crystal data for **5**: $C_{28}H_{52}N_4Si_2$, M = 500.91, orange crystal (needle) obtained by slow evaporation of a 1:1 mixture of diethyl ether/petroleum ether, dimensions 0.150 x 0.080 x 0.070 mm^3, triclinic, a = 7.8130(18) Å, b = 12.886(3) Å, c = 15.976(4) Å, α = 102.557(5) °, β = 96.908(6) °, γ = 93.896(6) °, V = 1551.2(6) Å^3, ρ = 1.072 g/cm^3, T = 200(2) K, space group $P\bar{1}$, Z = 2, θ_{max} = 21.942 °, radiation Mo K_α, λ = 0.71073 Å, 0.5 ° omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 2.86 and a completeness of 99.9% to a resolution of 0.95 Å, 10797 reflections measured, 3777 unique (R_{int} = 0.0627), 2334 observed (I > 2σ(I)), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS (2012/1)[7] based on the Laue symmetry of the reciprocal space, μ = 0.14mm^{-1}, T_{min} = 0.84, T_{max} = 0.96, structure refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2014/7 (Sheldrick, 2014) software[8], 359 parameters refined, hydrogen atoms were treated using appropriate riding models, except those at the nitrogen atoms, which were refined restrained, goodness of fit 1.04 for observed reflections, final residual values $R_1(F)$ = 0.059, $wR(F^2)$ = 0.122 for observed reflections, residual electron density -0.20 to 0.22 eÅ^{-3}. CCDC 1408362 contains 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.

Crystal data for **6**: $C_{28}H_{48}N_4Si_2$, M = 496.88, orange crystal (block) obtained by slow evaporation of a 1:1 mixture of diethyl ether/petroleum ether, dimensions 0.180 x 0.130 x 0.110 mm^3, monoclinic, a = 19.958(2) Å, b = 14.9301(16) Å, c = 14.7268(16) Å, α = 90 °, β = 132.098(2) °, γ = 90 °, V = 3256.1(6) Å^3, ρ = 1.014 g/cm^3, T = 200(2) K, space group C2/c, Z = 4, θ_{max} = 25.037 °, radiation Mo K_α, λ = 0.71073 Å, 0.5 ° omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 3.51 and a completeness of 99.7% to a resolution of 0.84 Å, 10051 reflections measured, 2866 unique (R_{int} = 0.0500), 1938 observed (I > 2σ(I)), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS (2012/1)[7] based on the Laue symmetry of the reciprocal space, μ = 0.13 mm^{-1}, T_{min} = 0.67, T_{max} = 0.96, structure refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2014/7 (Sheldrick, 2014) software[8], 248 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.21 for observed reflections, final residual values $R_1(F)$ = 0.086, $wR(F^2)$ = 0.239 for observed reflections, residual electron density -0.19 to 0.28 eÅ^{-3}. CCDC 1408363 contains 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.

Crystal data for **8**: $C_{19}H_{28}N_4Si$, M = 340.54, yellow crystal (needle) obtained by slow evaporation of a 1:1 mixture of diethyl ether/petroleum ether, dimensions 0.080 x 0.050 x 0.030 mm^3, monoclinic, a = 37.446(8) Å, b = 7.8246(18) Å, c = 30.575(7) Å, α = 90 °, β = 116.744(5) °, γ = 90 °, V = 8000(3) Å^3, ρ = 1.131 g/cm^3, T = 200(2) K, space group C2/c, Z = 16, θ_{max} = 17.222 °, radiation Mo K_α, λ = 0.71073 Å, 0.5 ° omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 6.24 and a completeness of 100.0% to a resolution of 1.20 Å, 15868 reflections measured, 2428 unique (R_{int} = 0.1858), 1347 observed (I > 2σ(I)), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS (2012/1)[7] based on the Laue symmetry of the reciprocal space, μ = 0.12mm^{-1}, T_{min} = 0.82, T_{max} = 0.96, structure refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2014/7 (Sheldrick, 2014) software[8], 474 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.02 for observed reflections, final residual values $R_1(F)$ = 0.066, $wR(F^2)$ = 0.134 for observed reflections, residual electron density -0.28 to 0.22 eÅ^{-3}. CCDC 1408364 contains 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.

Crystal data for **10**: $C_{28}H_{48}N_4SSi_2$, M = 528.94, yellow crystal (plate) obtained by slow evaporation of deuterated chloroform, dimensions 0.210 x 0.170 x 0.040 mm^3, monoclinic, a = 15.4408(14) Å, b =

13.9268(12) Å, c = 14.8221(13) Å, α = 90 °, β = 103.112(3) °, γ = 90 °, V = 3104.3(5) Å^3, ρ = 1.132 g/cm^3, T = 200(2) K, space group P2$_1$/c, Z = 4, θ_{max} = 20.816 °, radiation Mo K_α, λ = 0.71073 Å, 0.5 ° omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 7.29 and a completeness of 100.0% to a resolution of 1.00 Å, 24289 reflections measured, 3257 unique (R_{int} = 0.0758), 2347 observed (I > 2σ(I)), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS (2012/1)[7] based on the Laue symmetry of the reciprocal space, μ = 0.20mm^{-1}, T_{min} = 0.81, T_{max} = 0.86, structure refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2014/7 (Sheldrick, 2014) software[8], 345 parameters refined, hydrogen atoms were treated using appropriate riding models, except those at the NH2-groups, which were refined isotropically, goodness of fit 1.04 for observed reflections, final residual values $R_1(F)$ = 0.054, $wR(F^2)$ = 0.107 for observed reflections, residual electron density -0.31 to 0.24 eÅ^{-3}. CCDC 1408365 contains 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.

Crystal data for **15**: $C_{56}H_{58}N_4OSi_2$, M = 859.24, orange crystal (needle) obtained by slow evaporation of a 1:1 mixture of dichloromethane/petroleum ether, dimensions 0.170 x 0.030 x 0.030 mm^3, monoclinic, a = 37.073(4) Å, b = 11.0554(13) Å, c = 26.576(3) Å, α = 90°, β = 118.358(3)°, γ = 90°, V = 9585.2(19) Å^3, ρ = 1.191 g/cm^3, T = 200(2) K, space group C2/c, Z = 8, θ_{max} = 19.588°, radiation Mo K_α, λ = 0.71073 Å, 0.5° omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 5.98 and a completeness of 100.0% to a resolution of 1.06 Å, 26024 reflections measured, 4224 unique (R_{int} = 0.1494), 2239 observed (I > 2σ(I)), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS1 (2012/1)[7] based on the Laue symmetry of the reciprocal space, μ = 0.12 mm^{-1}, T_{min} = 0.82, T_{max} = 0.96, structure refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2014/7 (Sheldrick, 2014) software[8], 650 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.02 for observed reflections, final residual values $R_1(F)$ = 0.075, $wR(F^2)$ = 0.152 for observed reflections, residual electron density -0.32 to 0.43 eÅ^{-3}. CCDC 1408366 contains 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.

Crystal data for **17**: $C_{68}H_{66}N_4Si_2$, M = 995.47, green crystal (plate) obtained by slow evaporation of a 1:1 mixture of dichloromethane/petroleum ether, dimensions 0.140 x 0.100 x 0.030 mm^3, monoclinic, a = 18.0690(12) Å, b = 24.9858(17) Å, c = 29.3954(19) Å, α = 90°, β = 101.4712(17)°, γ = 90°, V =

13006.0(15) Å^3, ρ = 1.017 g/cm^3, T = 200(2) K, space group P2$_1$/n, Z = 8, θ_{max} = 20.816°, radiation Mo K_α, λ = 0.71073 Å, 0.5° omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 5.66 and a completeness of 100.0% to a resolution of 1.00 Å, 78017 reflections measured, 13606 unique (R_{int} = 0.1000), 8280 observed (I > 2σ(I)), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS (2012/1)[7] based on the Laue symmetry of the reciprocal space, μ = 0.09mm^{-1}, T_{min} = 0.81, T_{max} = 0.96, structure refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2014/7 (Sheldrick, 2014) software[8], 1443 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.03 for observed reflections, final residual values $R_1(F)$ = 0.086, $wR(F^2)$ = 0.197 for observed reflections, residual electron density -0.25 to 0.48 eÅ^{-3}. CCDC 1408367 contains 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.

S7. Full scaled crystal structures and packing motifs

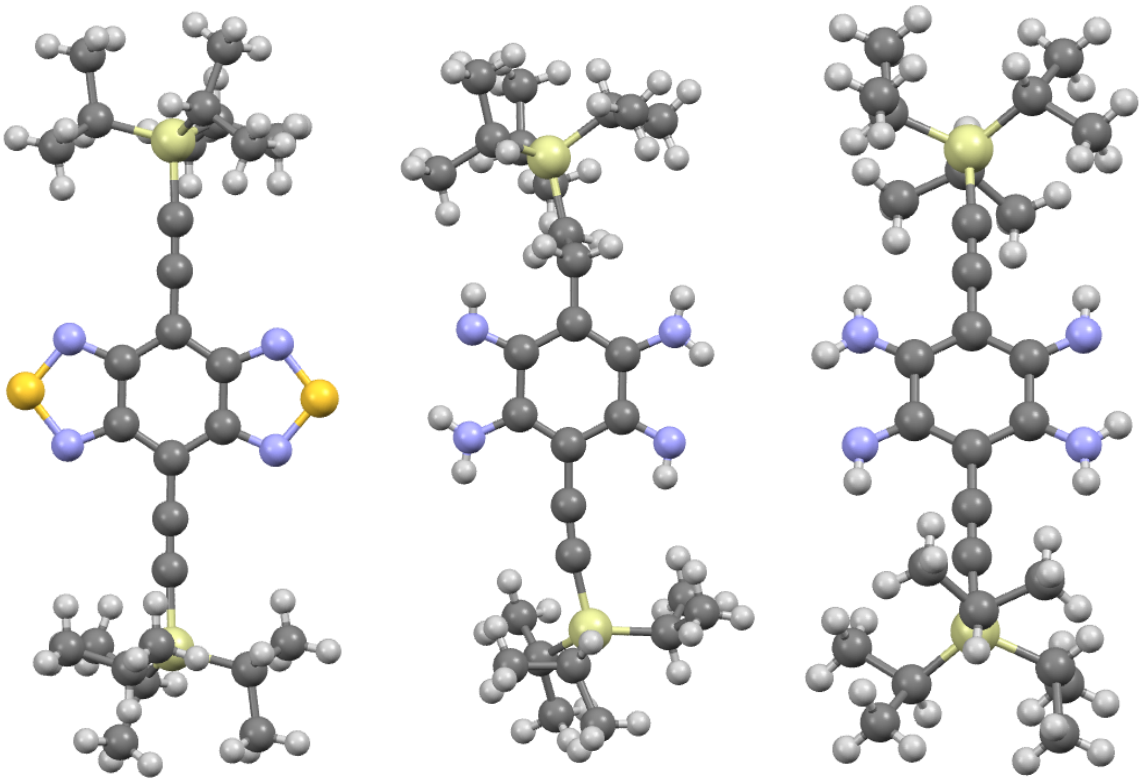


Figure 8 X-Ray crystal structures of **1**, **5** and **6.**

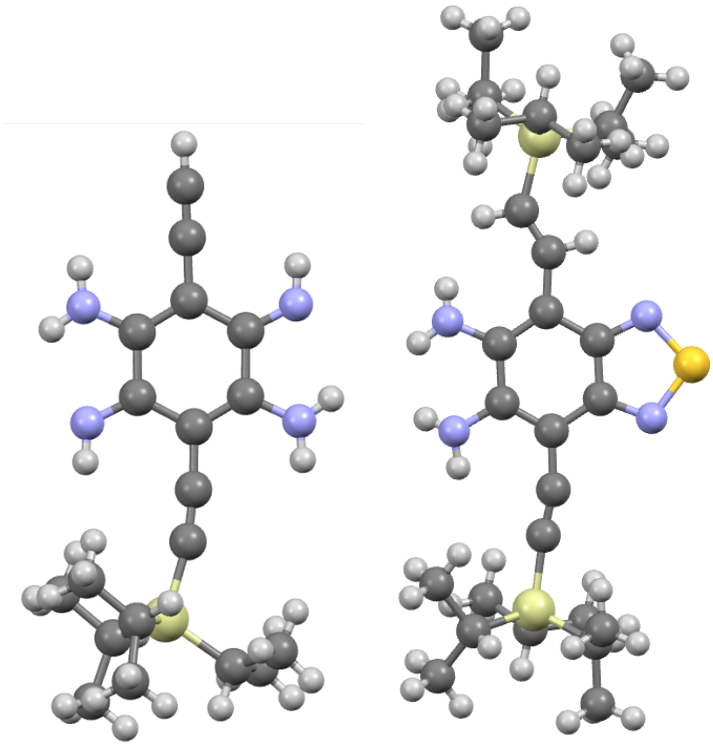


Figure 9 X-Ray crystal structure of **8** and **10**.

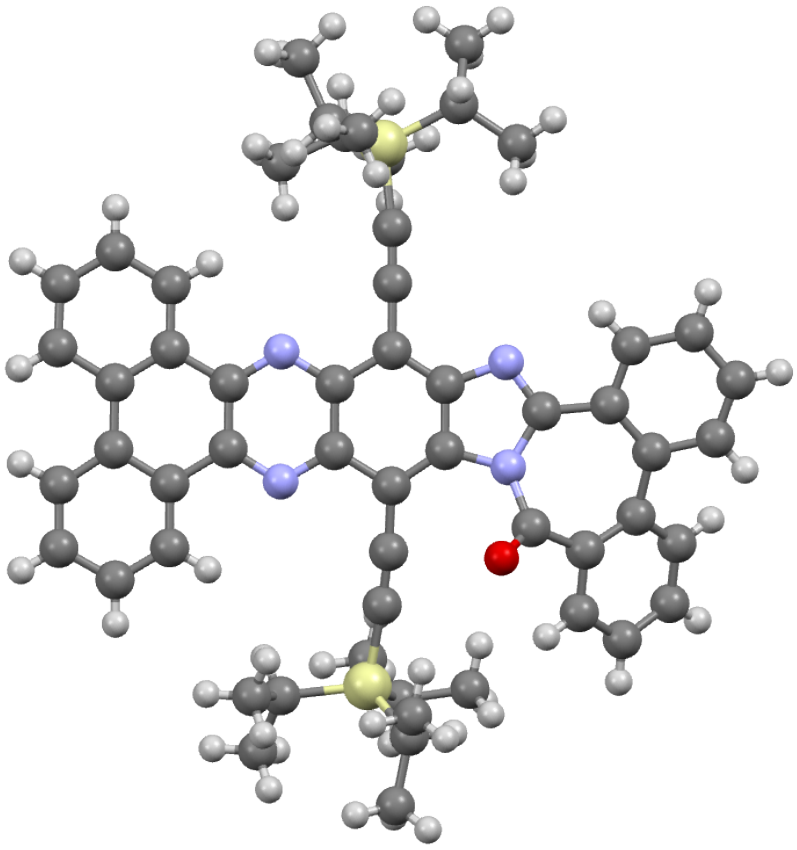


Figure 10 X-Ray crystal structure of **15**.

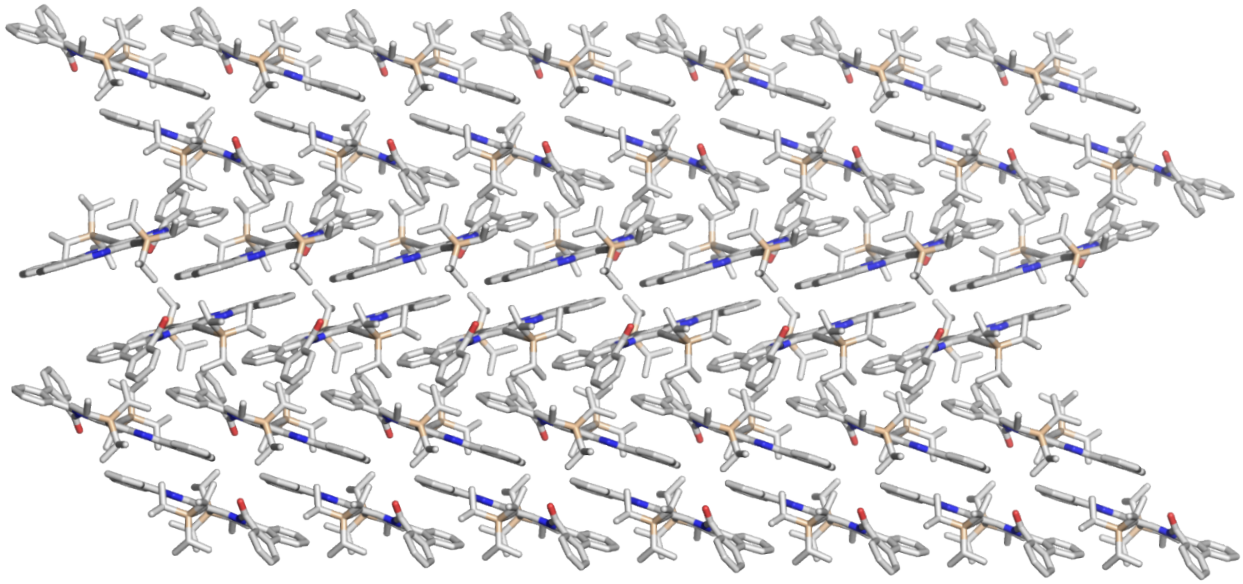


Figure 11 Herringbone arrangement of **15** from side-view (hydrogen atoms have been omitted for clarity).

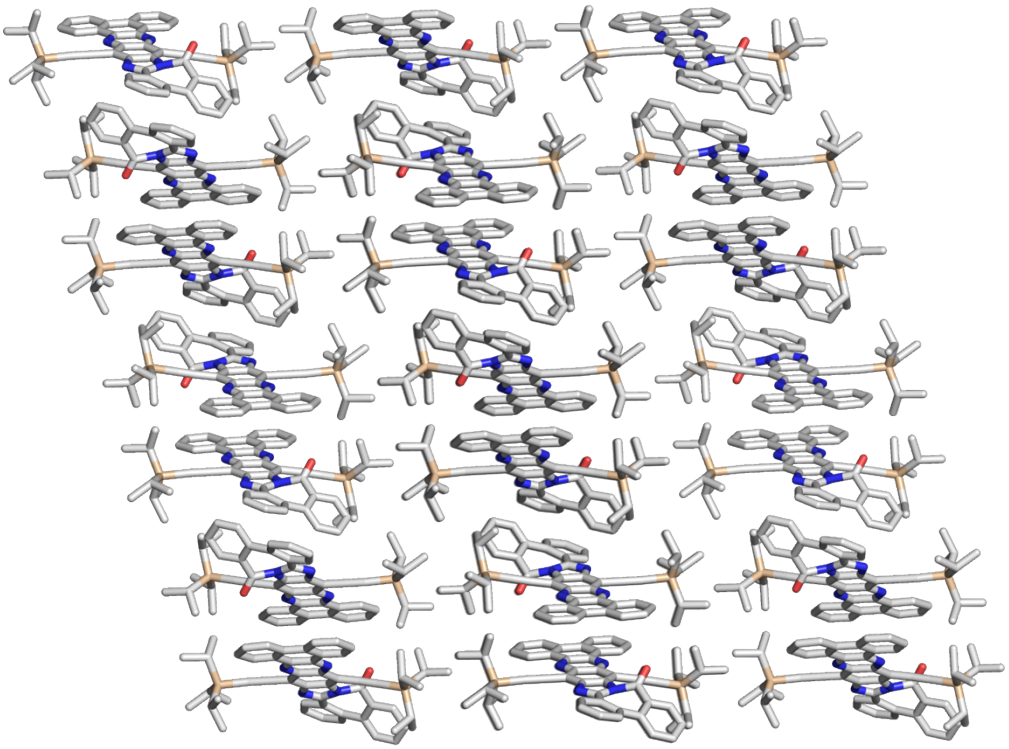


Figure 12 Arrangement of **15** from front-view (hydrogen atoms have been omitted for clarity).

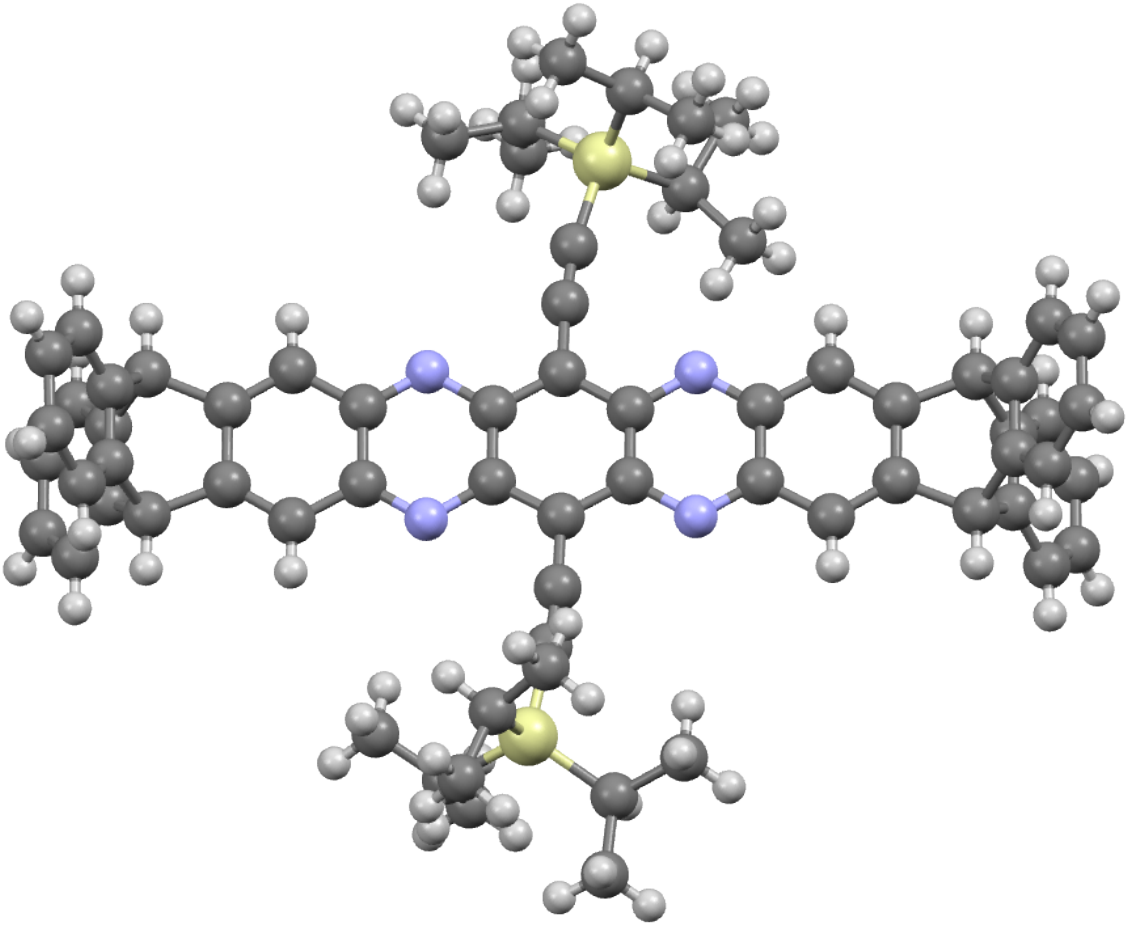


Figure 13 X-Ray crystal structure of **17**.

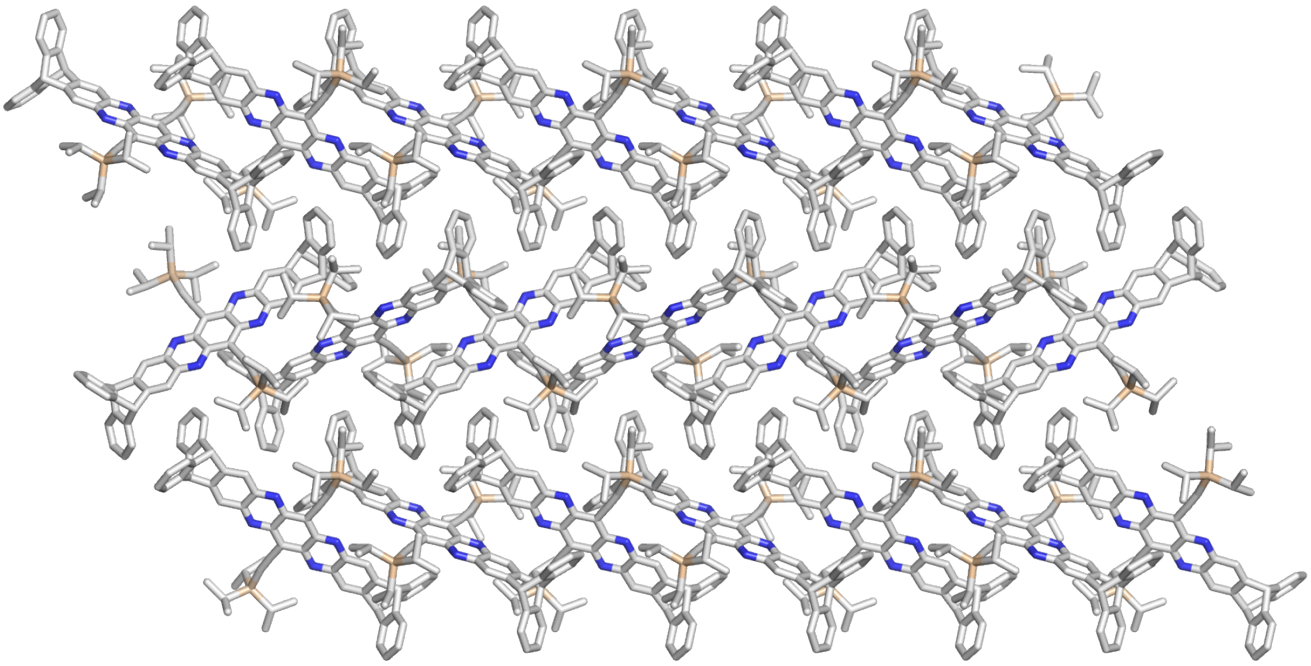


Figure 14 Arrangement of **17** from side-view (hydrogen atoms have been omitted for clarity).

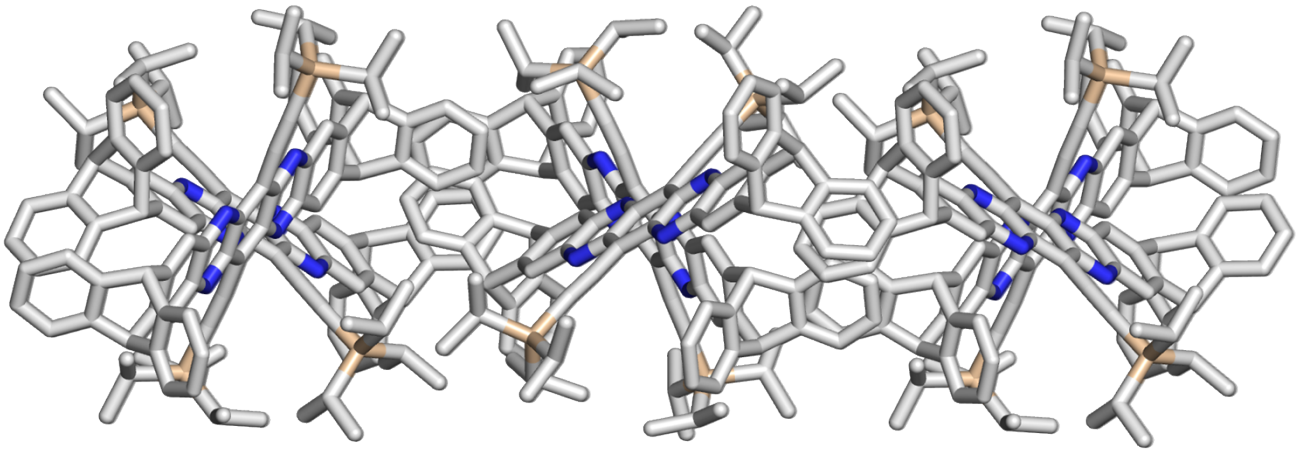


Figure 15 Twisted arrangement of **17** from front-view (hydrogen atoms have been omitted for clarity).

S8. ^{1}H- and ^{13}C-NMR spectra

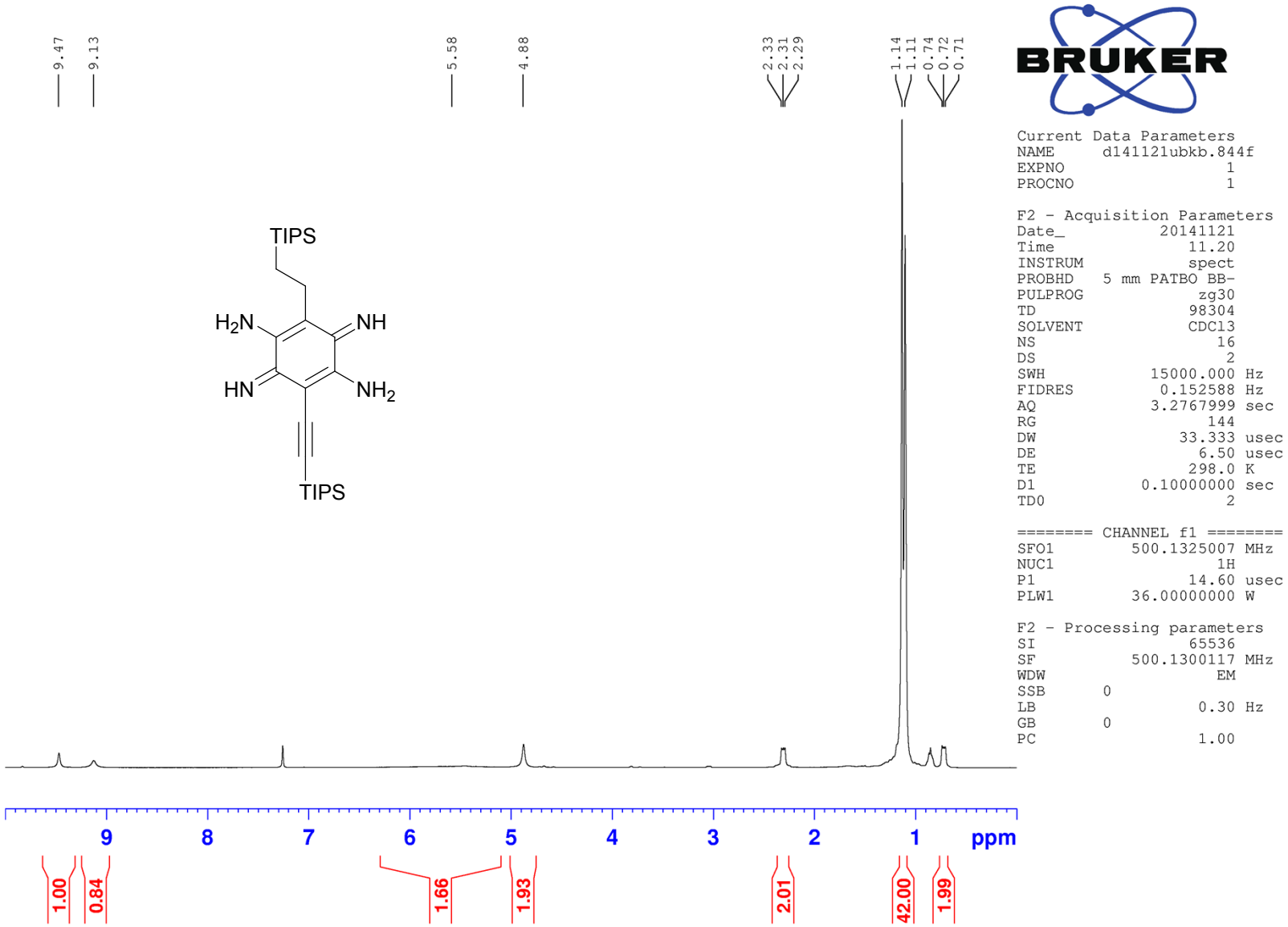


Figure 16 ^{1}H-NMR spectrum of **5** in $CDCl_3$.

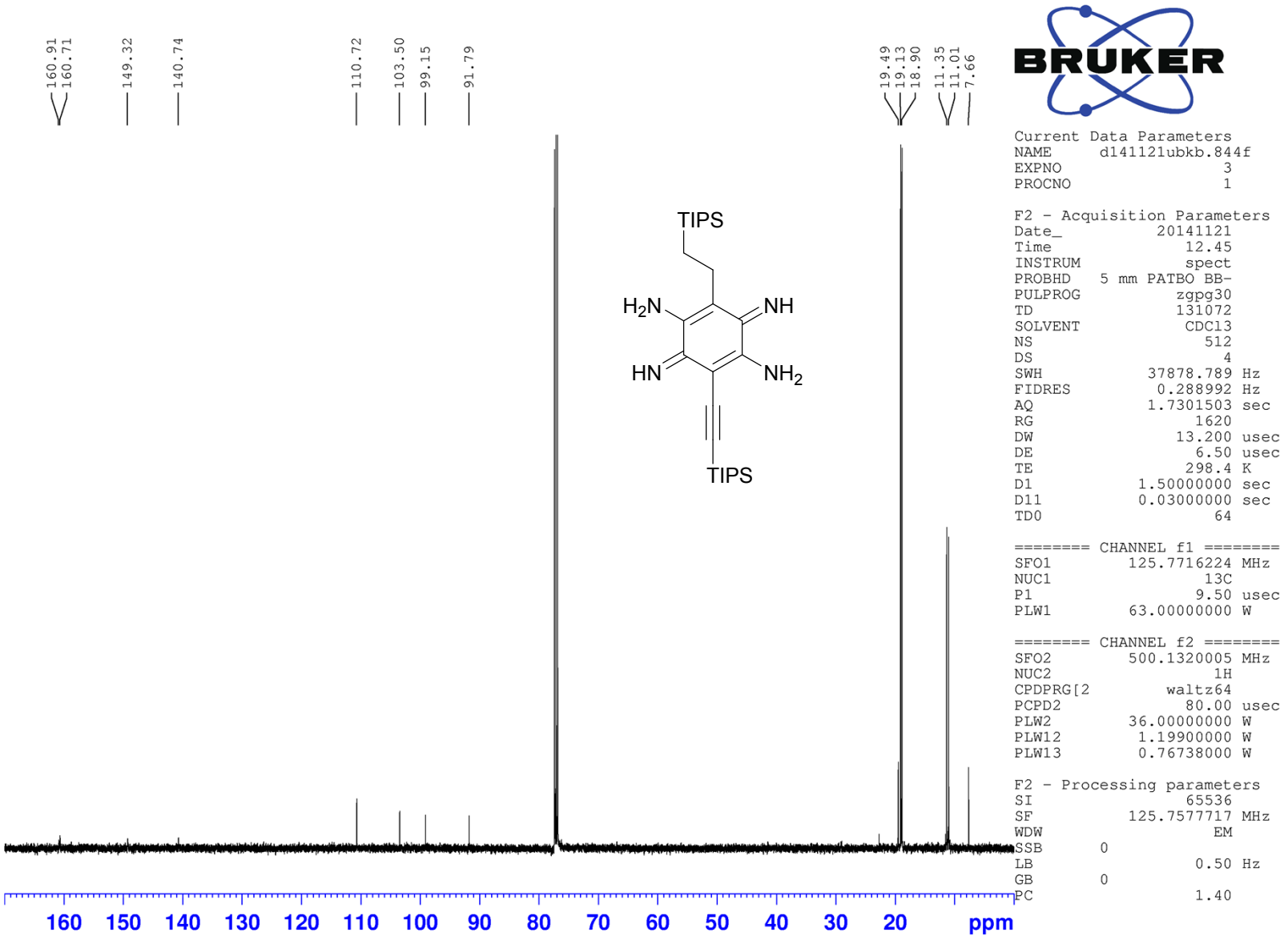


Figure 17 $^{13}C\{^{1}H\}$-NMR spectrum of **5** in $CDCl_3$.

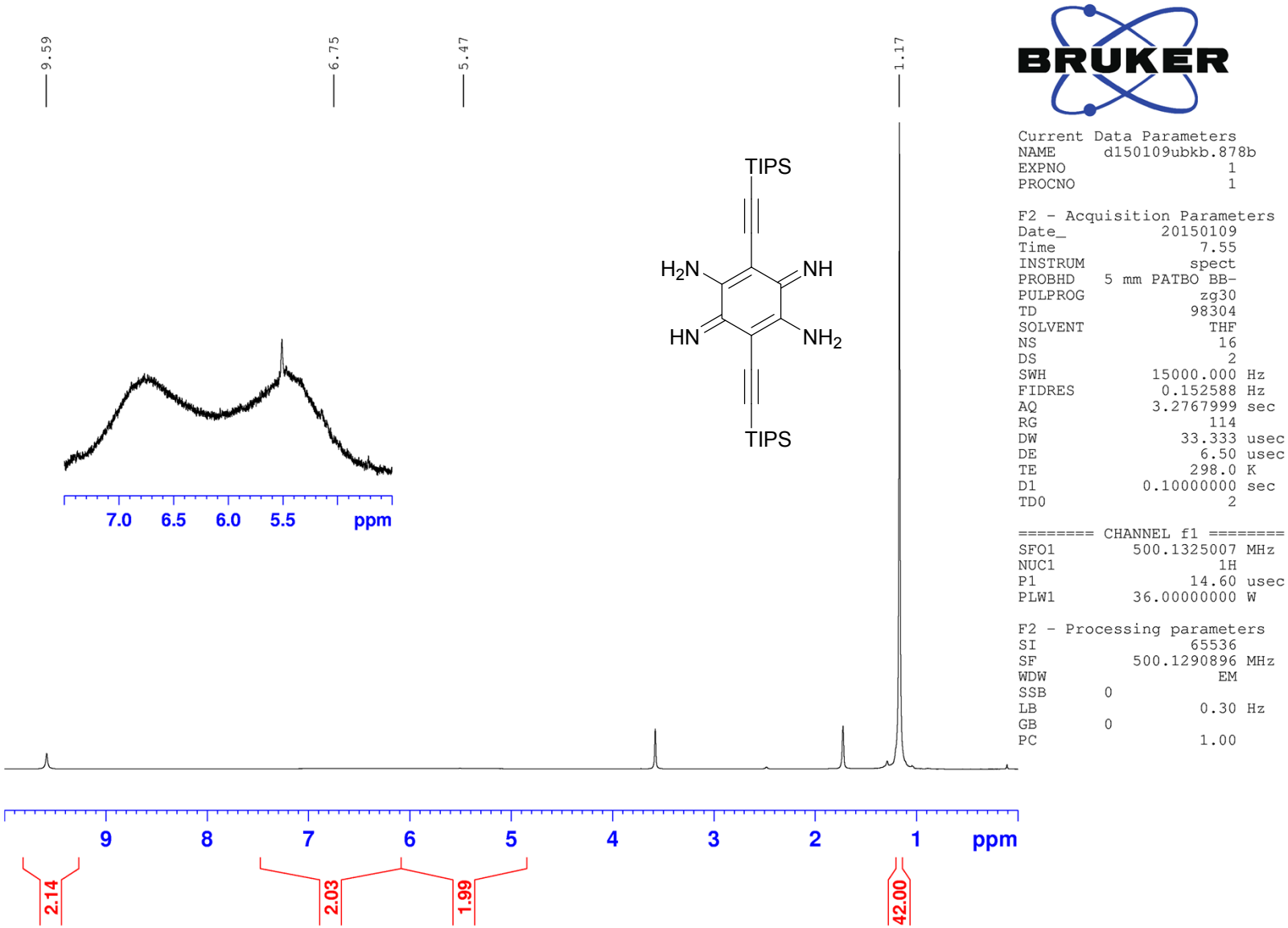



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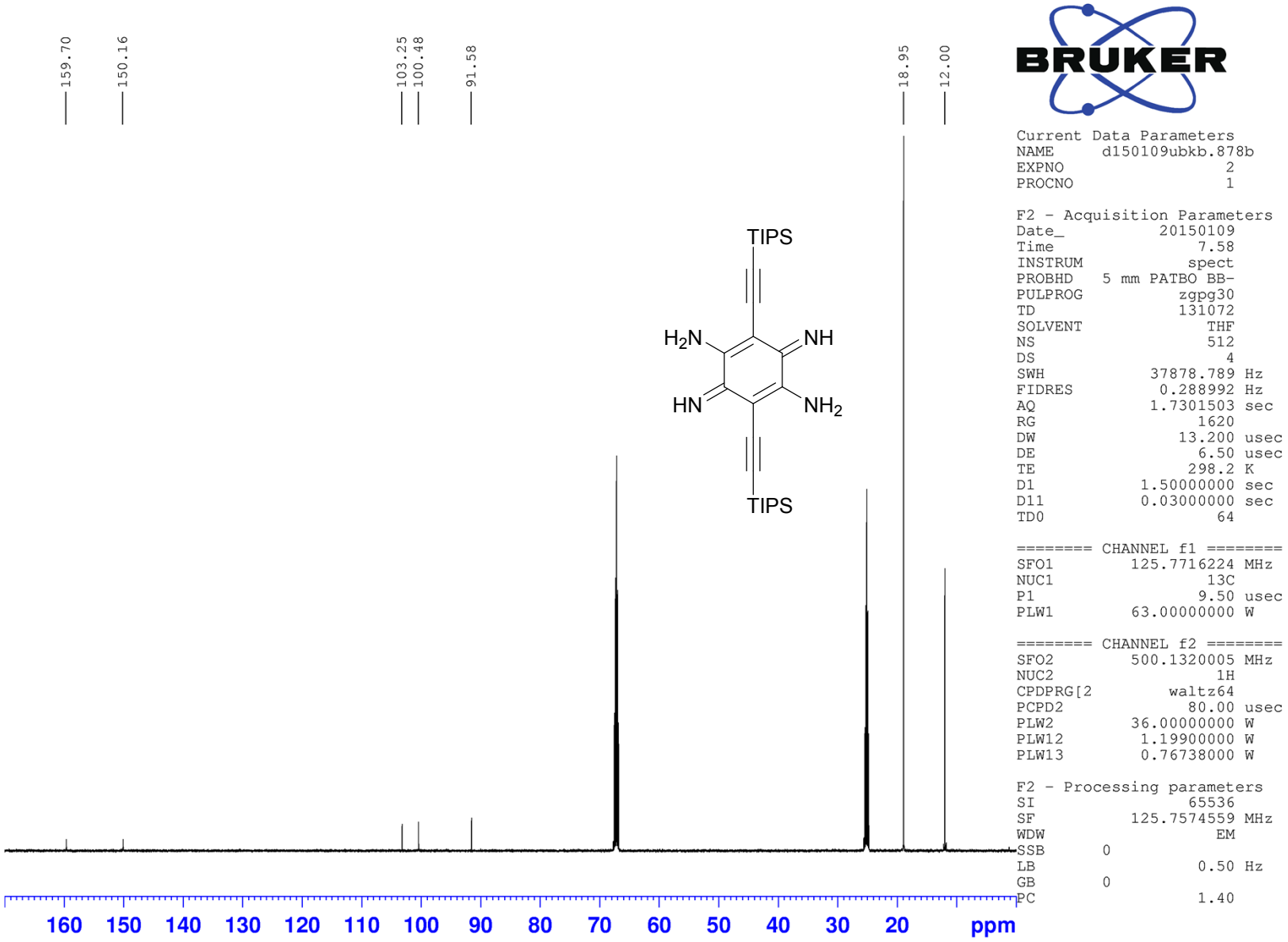
Figure 18 ^{1}H-NMR spectrum of **6** in THF-d8.

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PC                1.40
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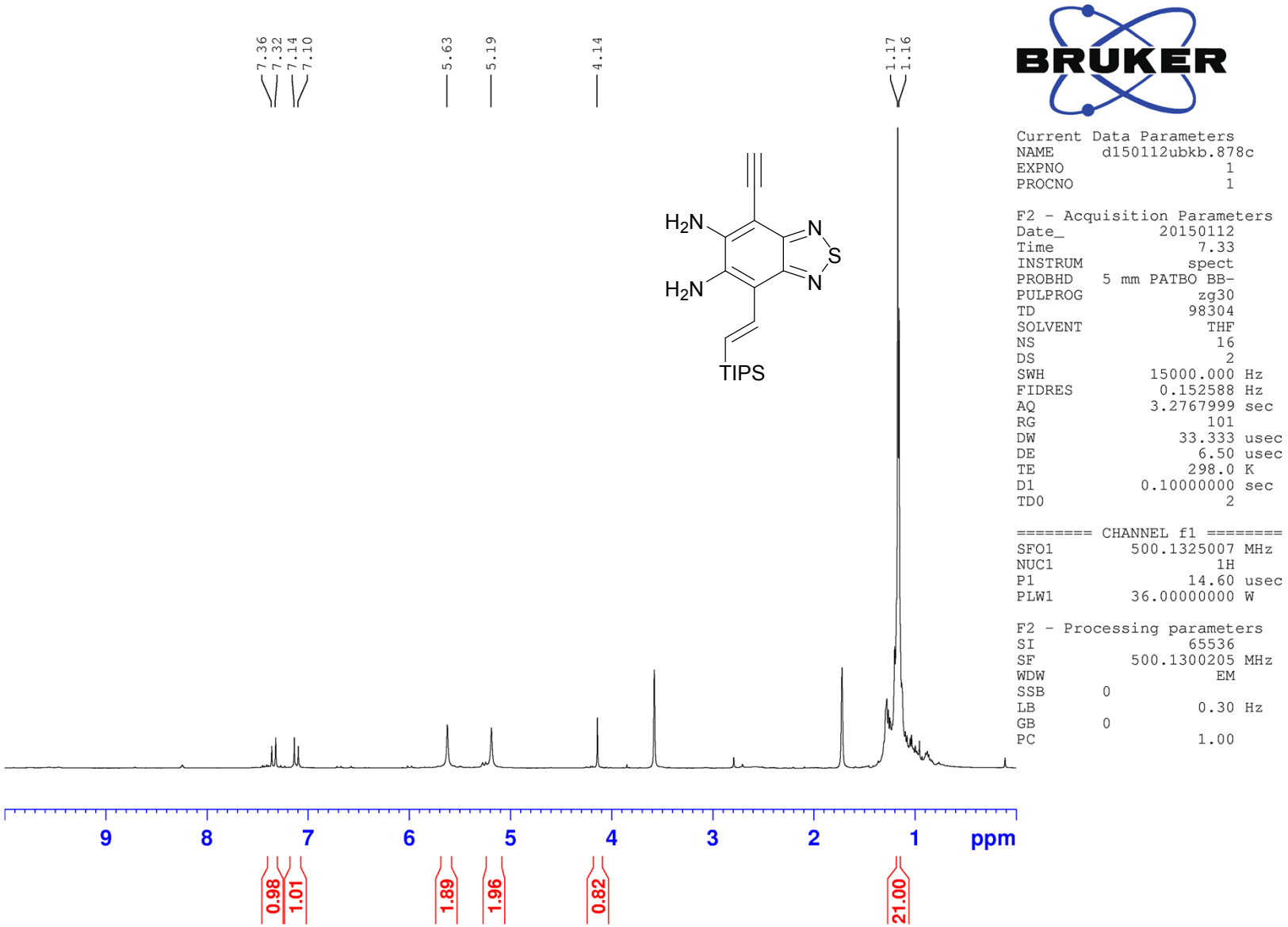
Figure 19 $^{13}C\{^{1}H\}$-NMR spectrum of **6** in THF-d8.



BRUKER

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F2 - Acquisition Parameters
Date_           20150112
Time                7.33
INSTRUM            spect
PROBHD   5 mm PATBO BB-
PULPROG             zg30
TD                 98304
SOLVENT              THF
NS                    16
DS                     2
SWH            15000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2767999 sec
RG                   101
DW                33.333 usec
DE                 6.50 usec
TE                298.0 K
D1           0.10000000 sec
TD0                    2

======== CHANNEL f1 ========
SFO1         500.1325007 MHz
NUC1                   1H
P1                 14.60 usec
PLW1         36.00000000 W

F2 - Processing parameters
SI                 65536
SF           500.1300205 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

Figure 20 ^{1}H-NMR spectrum of **7** in THF-d8.

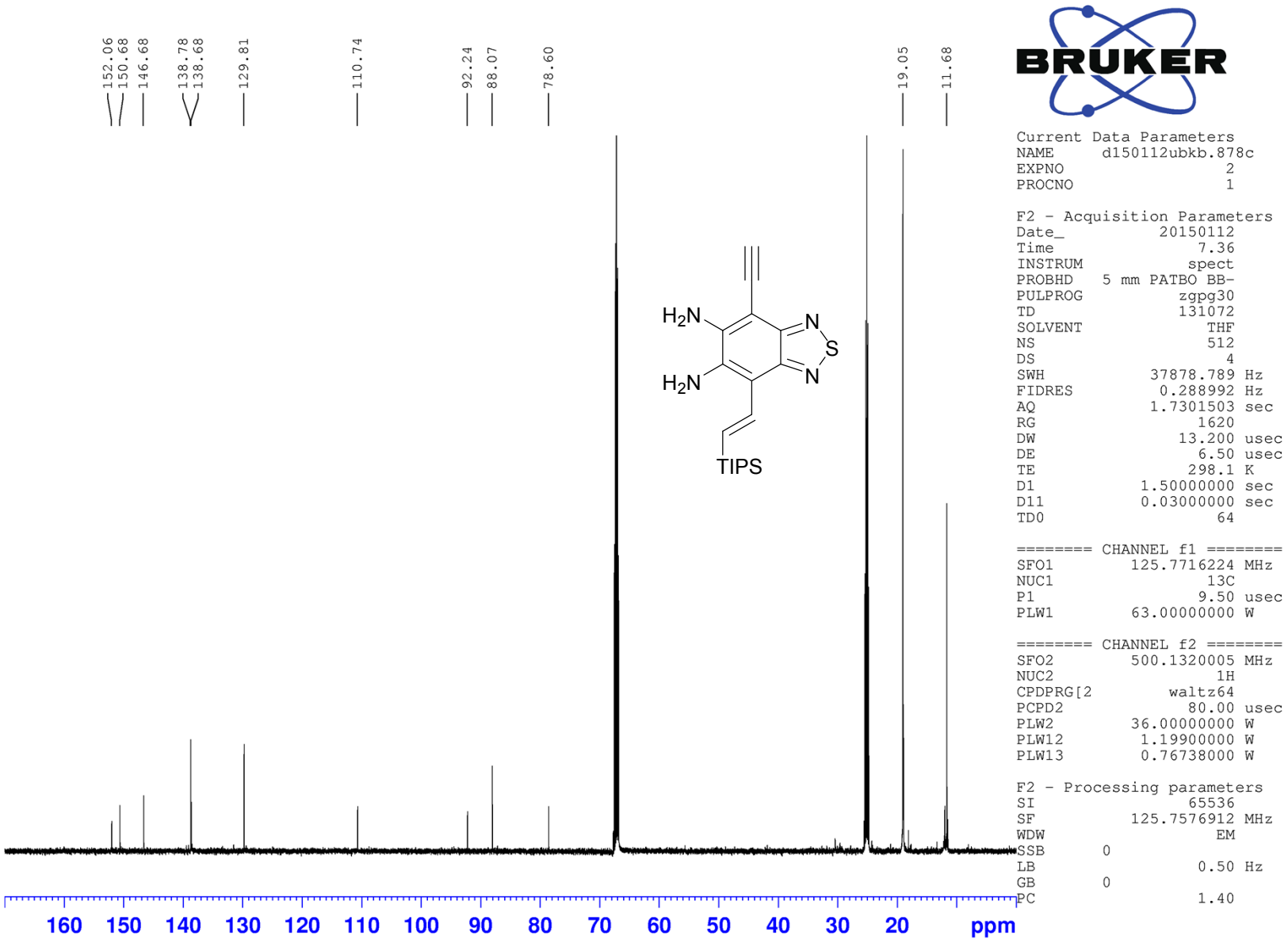
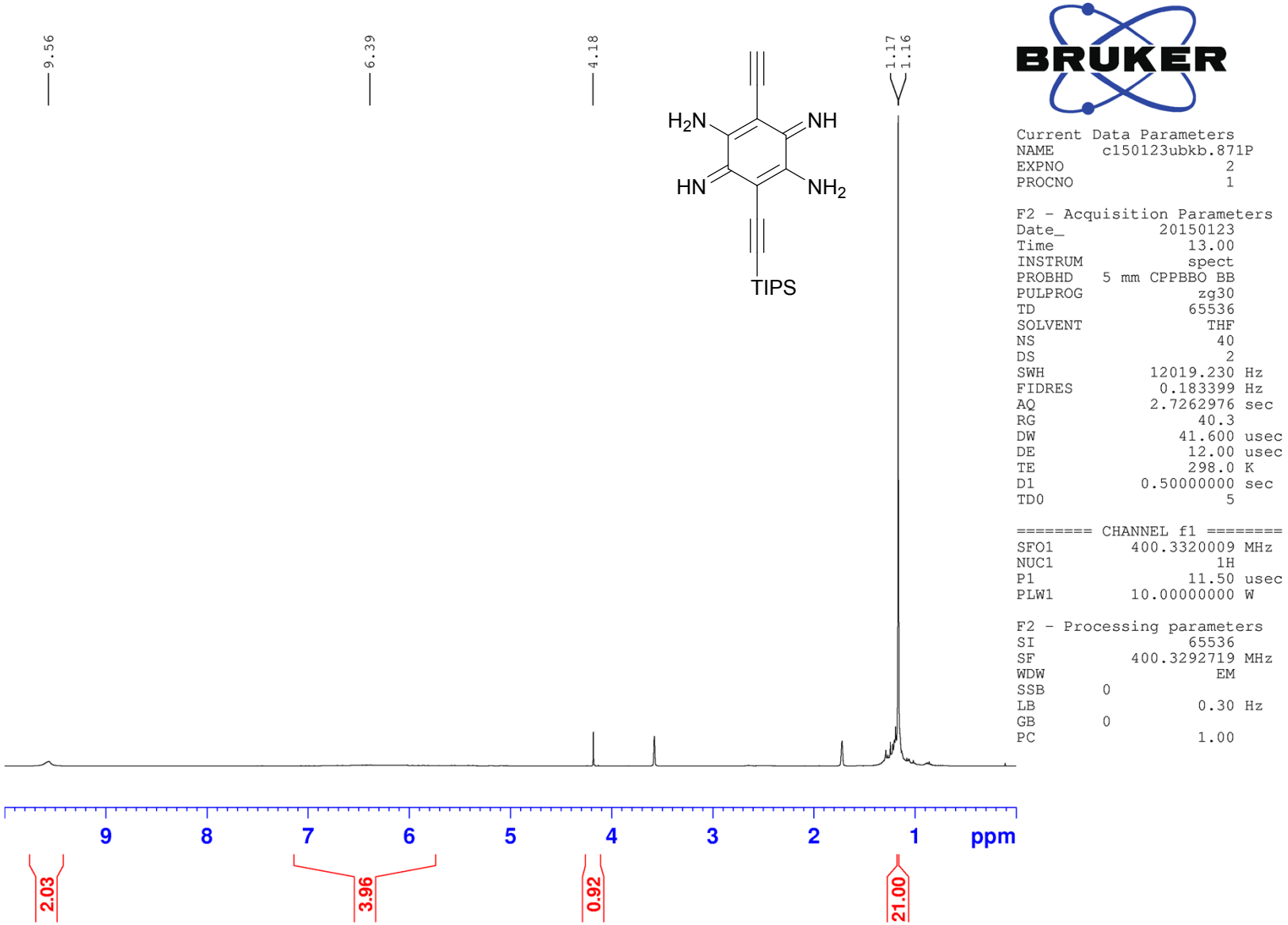


Figure 21 $^{13}C\{^{1}H\}$-NMR spectrum of **7** in THF-d8.



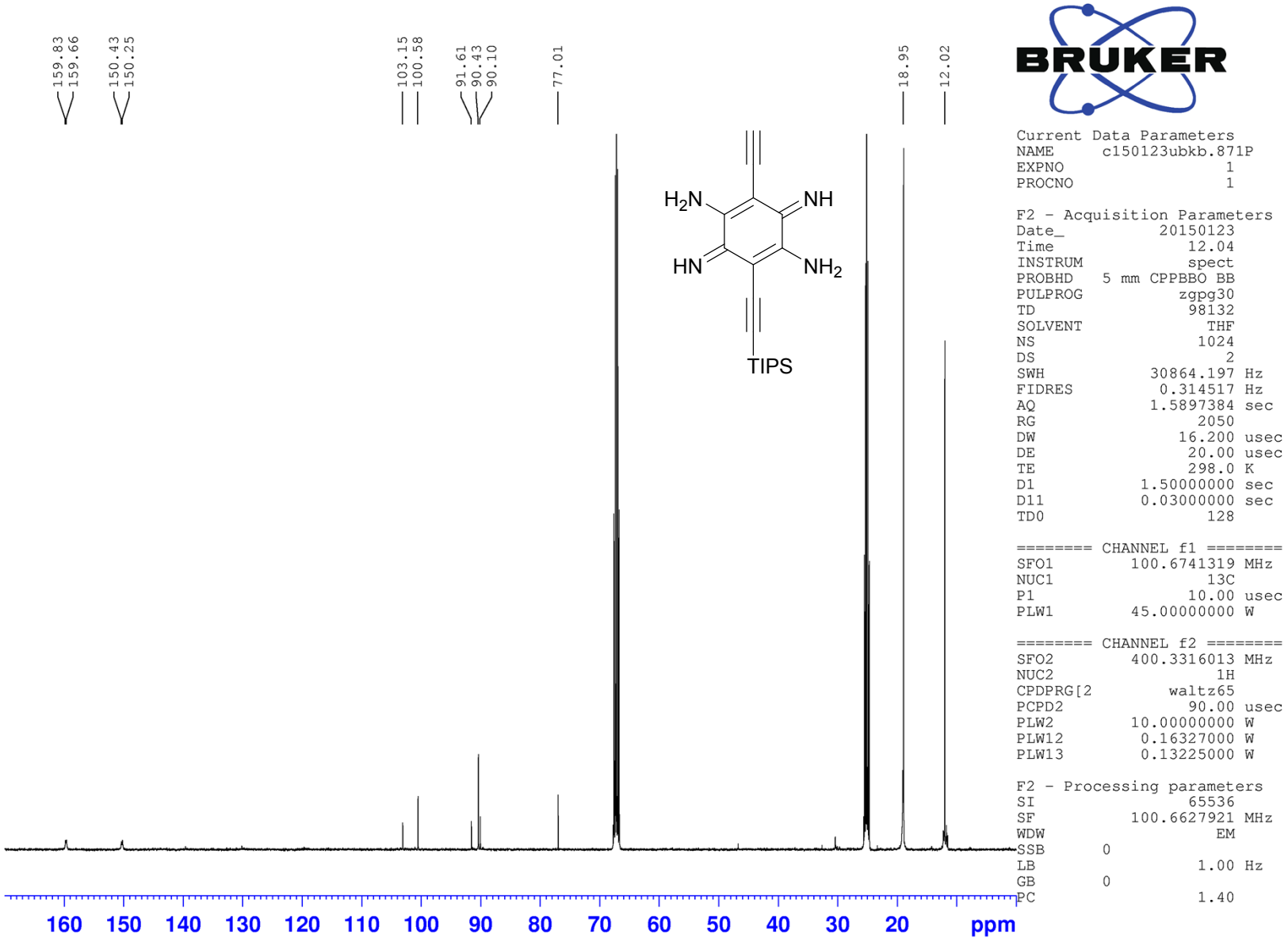

```
Current Data Parameters
NAME      c150123ubkb.871P
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_           20150123
Time               13.00
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG             zg30
TD                 65536
SOLVENT              THF
NS                    40
DS                     2
SWH            12019.230 Hz
FIDRES          0.183399 Hz
AQ             2.7262976 sec
RG                  40.3
DW                41.600 usec
DE                12.00 usec
TE                298.0 K
D1            0.50000000 sec
TD0                    5

======== CHANNEL f1 ========
SFO1         400.3320009 MHz
NUC1                   1H
P1                 11.50 usec
PLW1         10.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.3292719 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

Figure 22 ^{1}H-NMR spectrum of **8** in THF-d8.




```
Current Data Parameters
NAME      c150123ubkb.871P
EXPNO                    1
PROCNO                   1

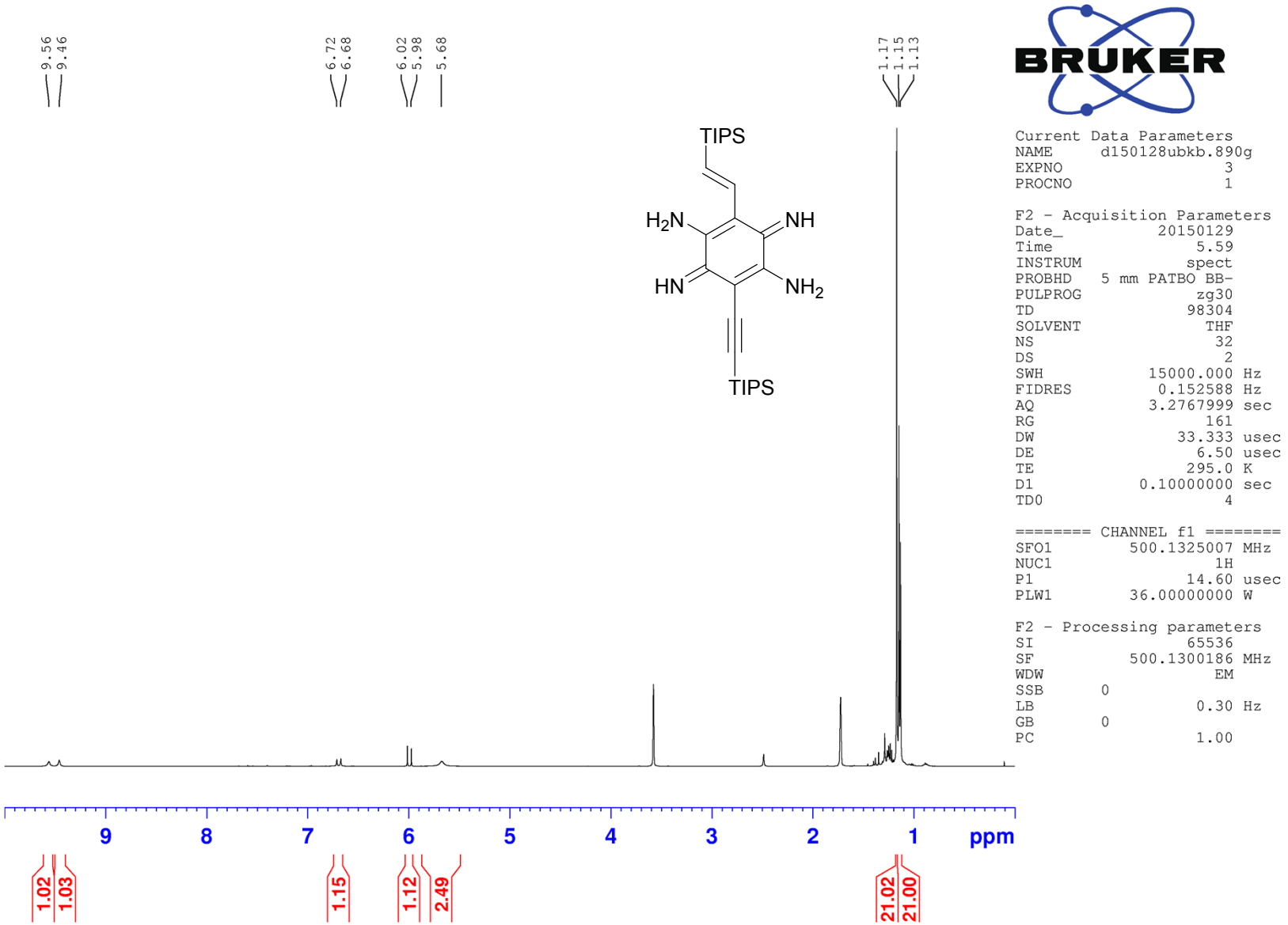
F2 - Acquisition Parameters
Date_           20150123
Time               12.04
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG          zgpg30
TD                98132
SOLVENT             THF
NS                 1024
DS                    2
SWH           30864.197 Hz
FIDRES         0.314517 Hz
AQ            1.5897384 sec
RG                 2050
DW               16.200 usec
DE               20.00 usec
TE               298.0 K
D1           1.50000000 sec
D11          0.03000000 sec
TD0                 128

======== CHANNEL f1 ========
SFO1        100.6741319 MHz
NUC1                13C
P1                10.00 usec
PLW1        45.00000000 W

======== CHANNEL f2 ========
SFO2        400.3316013 MHz
NUC2                1H
CPDPRG[2         waltz65
PCPD2             90.00 usec
PLW2        10.00000000 W
PLW12        0.16327000 W
PLW13        0.13225000 W

F2 - Processing parameters
SI                 65536
SF          100.6627921 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure 23 $^{13}C\{^{1}H\}$-NMR spectrum of **8** in THF-d8.




```
Current Data Parameters
NAME      d150128ubkb.890g
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_           20150129
Time                5.59
INSTRUM            spect
PROBHD   5 mm PATBO BB-
PULPROG             zg30
TD                 98304
SOLVENT              THF
NS                    32
DS                     2
SWH           15000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                   161
DW               33.333 usec
DE                6.50 usec
TE                295.0 K
D1           0.10000000 sec
TD0                    4

======== CHANNEL f1 ========
SFO1         500.1325007 MHz
NUC1                   1H
P1                 14.60 usec
PLW1         36.00000000 W

F2 - Processing parameters
SI                 65536
SF           500.1300186 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

Figure 24 ^{1}H-NMR spectrum of **9** in THF-d8.

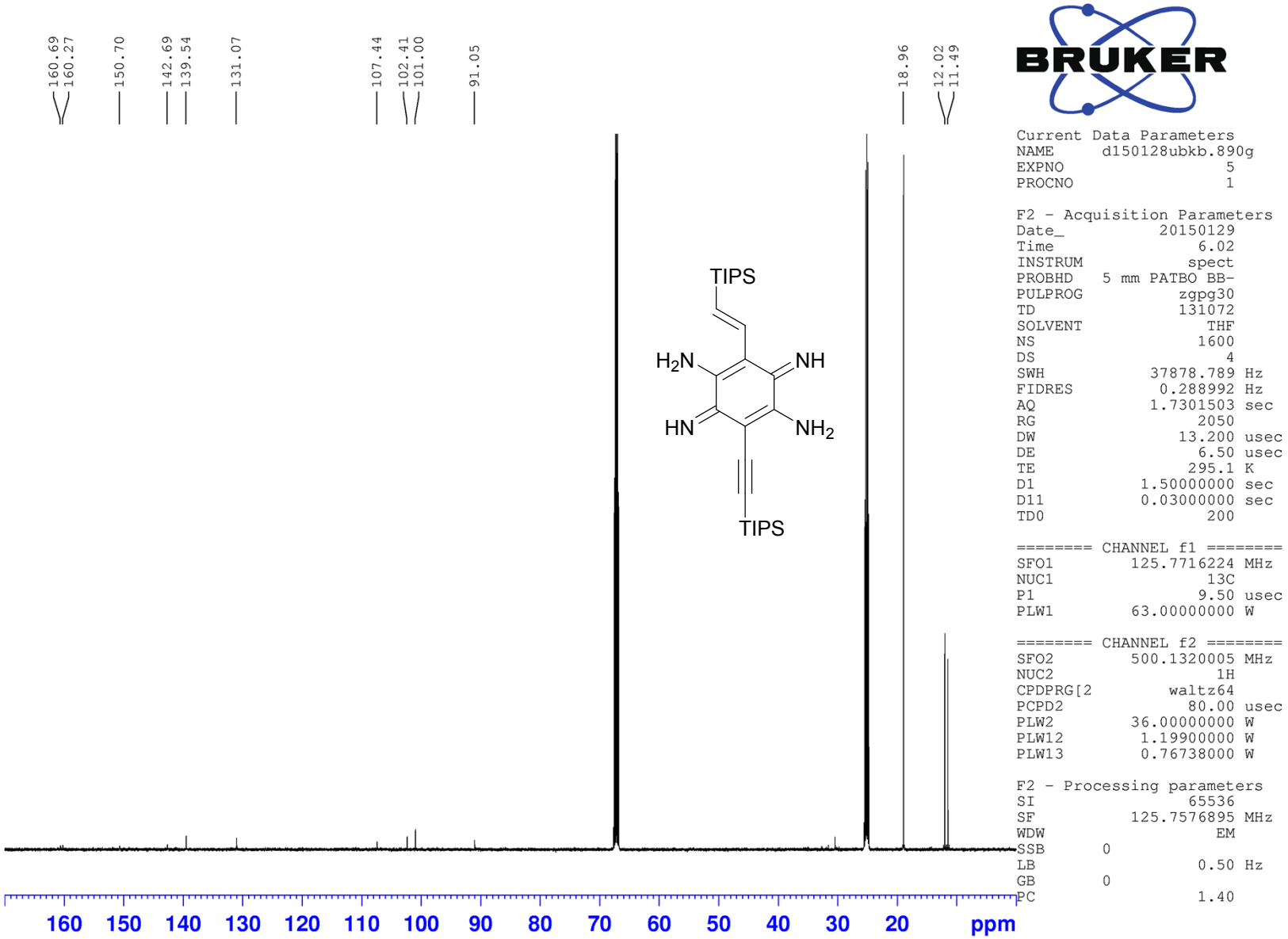
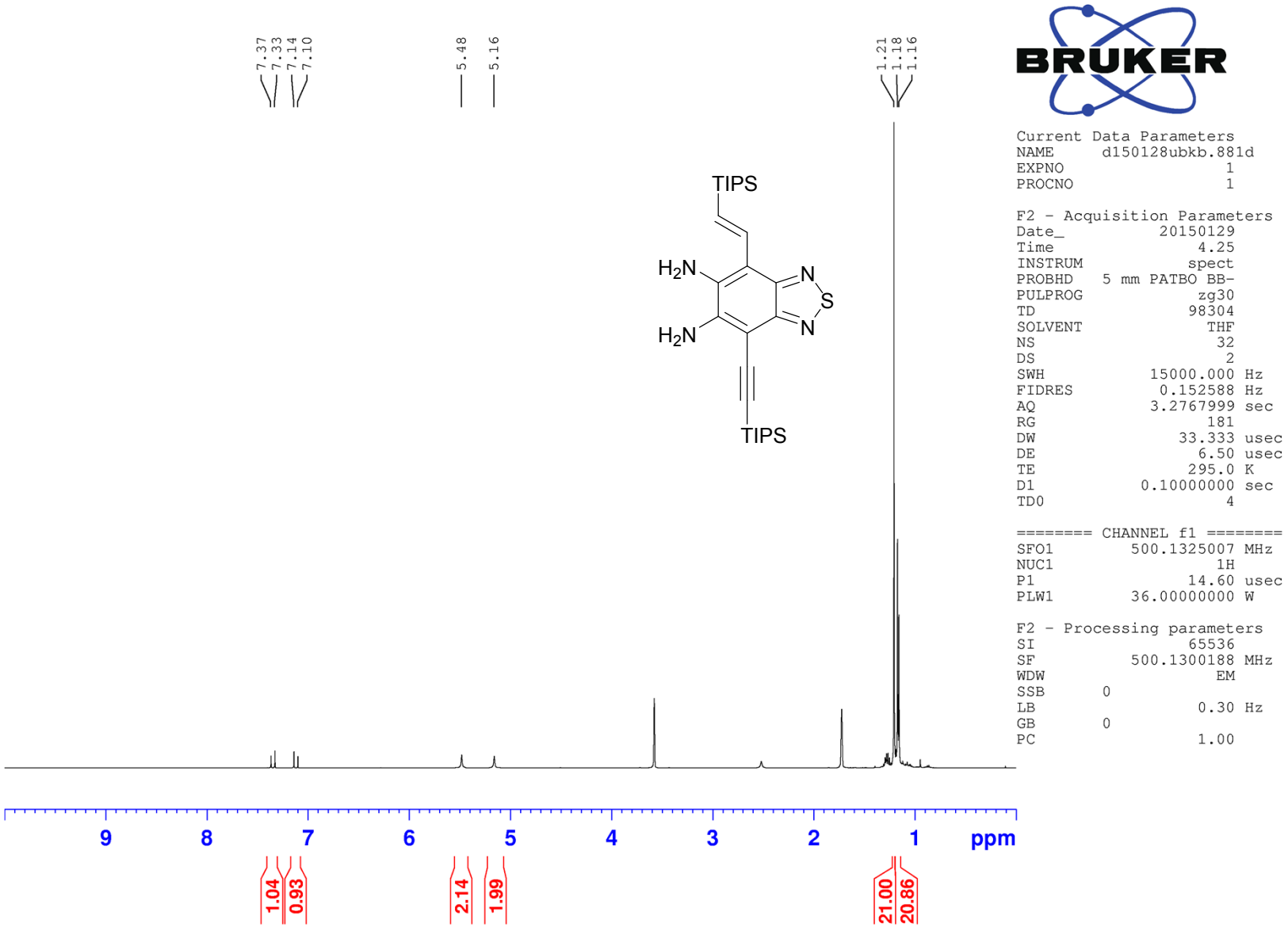


Figure 25 $^{13}C\{^{1}H\}$-NMR spectrum of **9** in THF-d8.



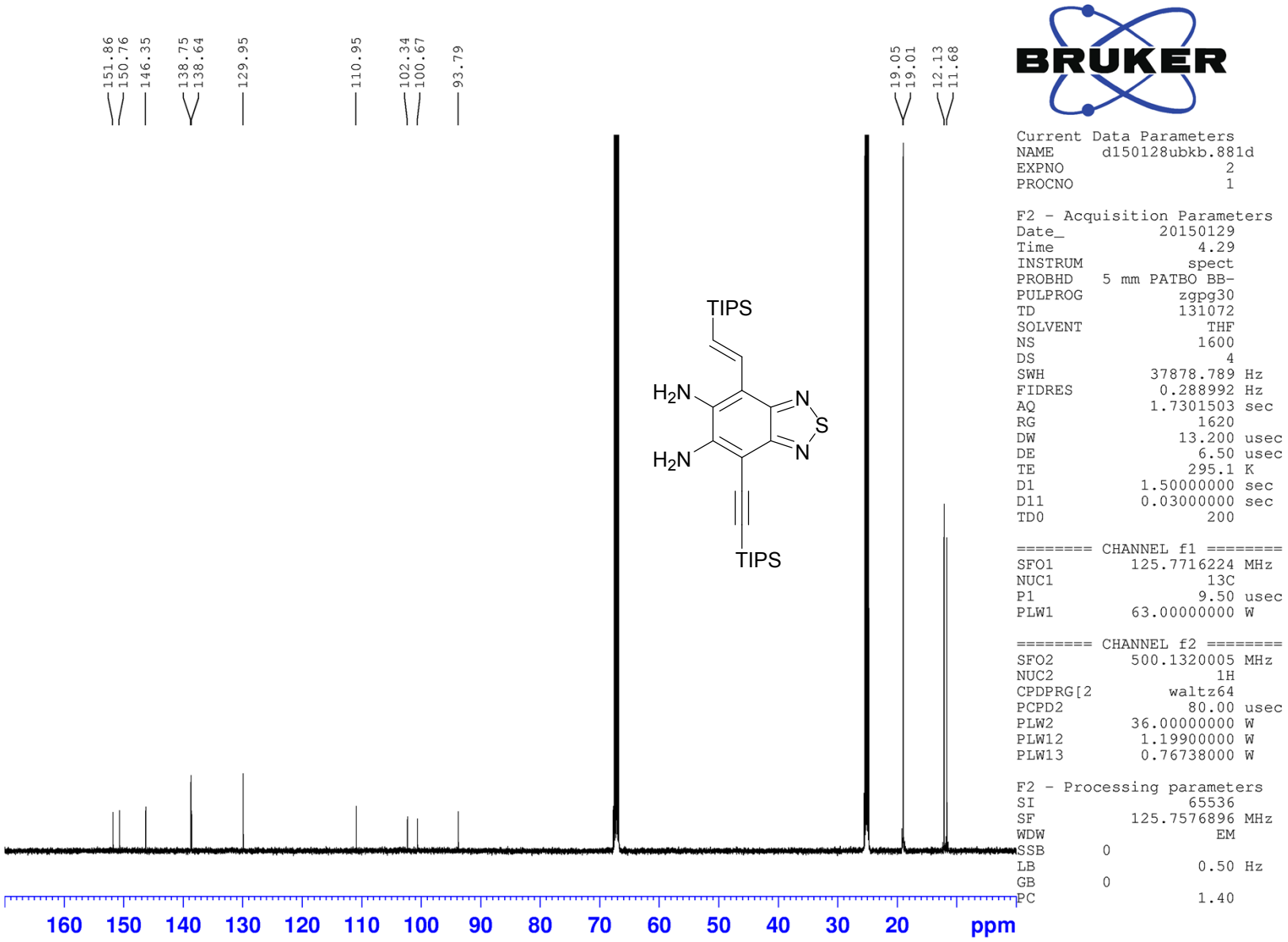

```
Current Data Parameters
NAME      d150128ubkb.881d
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20150129
Time                4.25
INSTRUM            spect
PROBHD   5 mm PATBO BB-
PULPROG             zg30
TD                 98304
SOLVENT              THF
NS                    32
DS                     2
SWH            15000.000 Hz
FIDRES          0.152588 Hz
AQ              3.2767999 sec
RG                   181
DW                33.333 usec
DE                 6.50 usec
TE                295.0 K
D1           0.10000000 sec
TD0                    4

======== CHANNEL f1 ========
SFO1         500.1325007 MHz
NUC1                   1H
P1                 14.60 usec
PLW1         36.00000000 W

F2 - Processing parameters
SI                 65536
SF           500.1300188 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

Figure 26 ^{1}H-NMR spectrum of **10** in THF-d8.




```
Current Data Parameters
NAME      d150128ubkb.881d
EXPNO                    2
PROCNO                   1

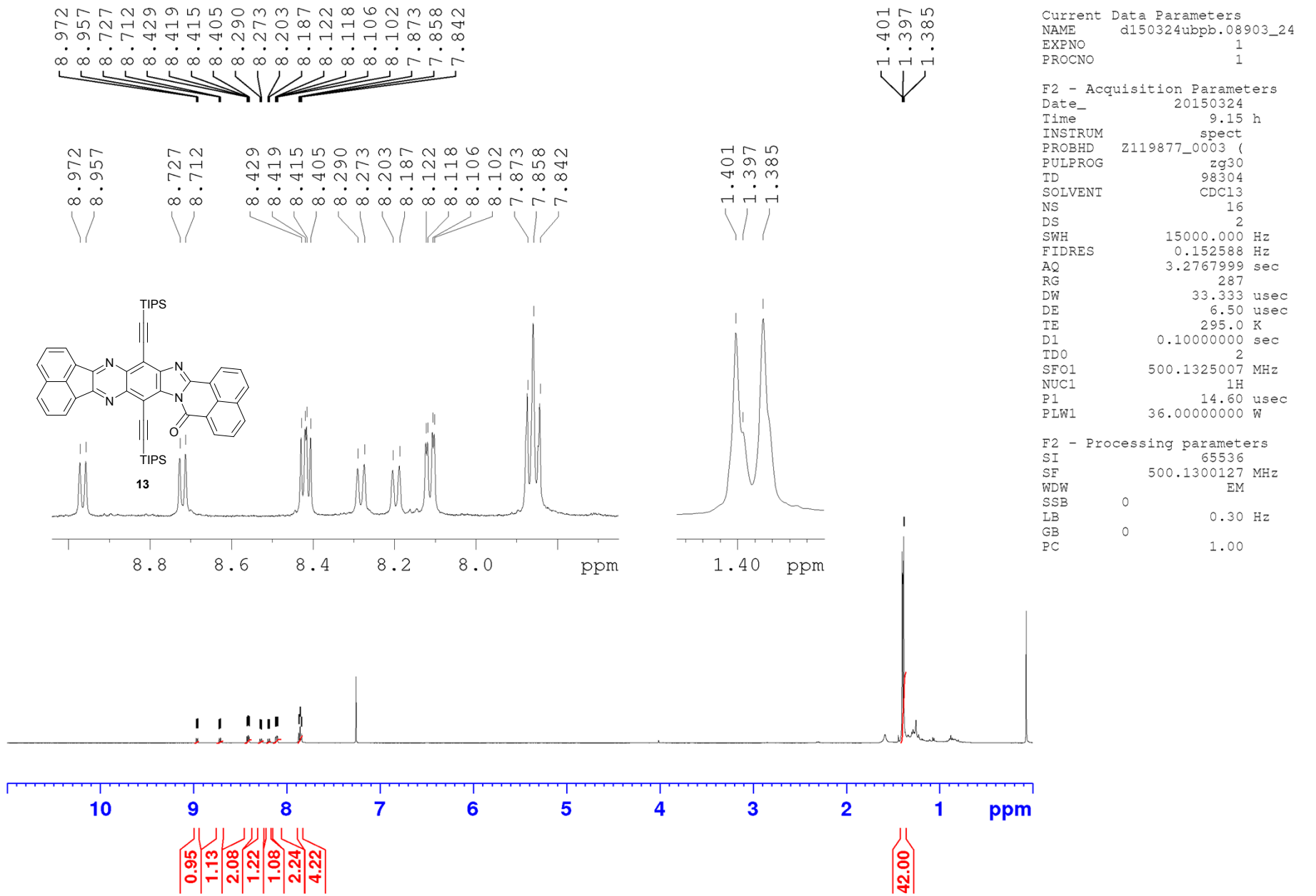
F2 - Acquisition Parameters
Date_           20150129
Time                4.29
INSTRUM            spect
PROBHD   5 mm PATBO BB-
PULPROG           zgpg30
TD                131072
SOLVENT              THF
NS                  1600
DS                     4
SWH            37878.789 Hz
FIDRES          0.288992 Hz
AQ            1.7301503 sec
RG                  1620
DW                13.200 usec
DE                 6.50 usec
TE                295.1 K
D1           1.50000000 sec
D11          0.03000000 sec
TD0                  200

======== CHANNEL f1 ========
SFO1         125.7716224 MHz
NUC1                 13C
P1                  9.50 usec
PLW1         63.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                 1H
CPDPRG[2         waltz64
PCPD2              80.00 usec
PLW2         36.00000000 W
PLW12         1.19900000 W
PLW13         0.76738000 W

F2 - Processing parameters
SI                  65536
SF           125.7576896 MHz
WDW                    EM
SSB       0
LB                  0.50 Hz
GB        0
PC                  1.40
```

Figure 27 $^{13}C\{^{1}H\}$-NMR spectrum of **10** in THF-d8.

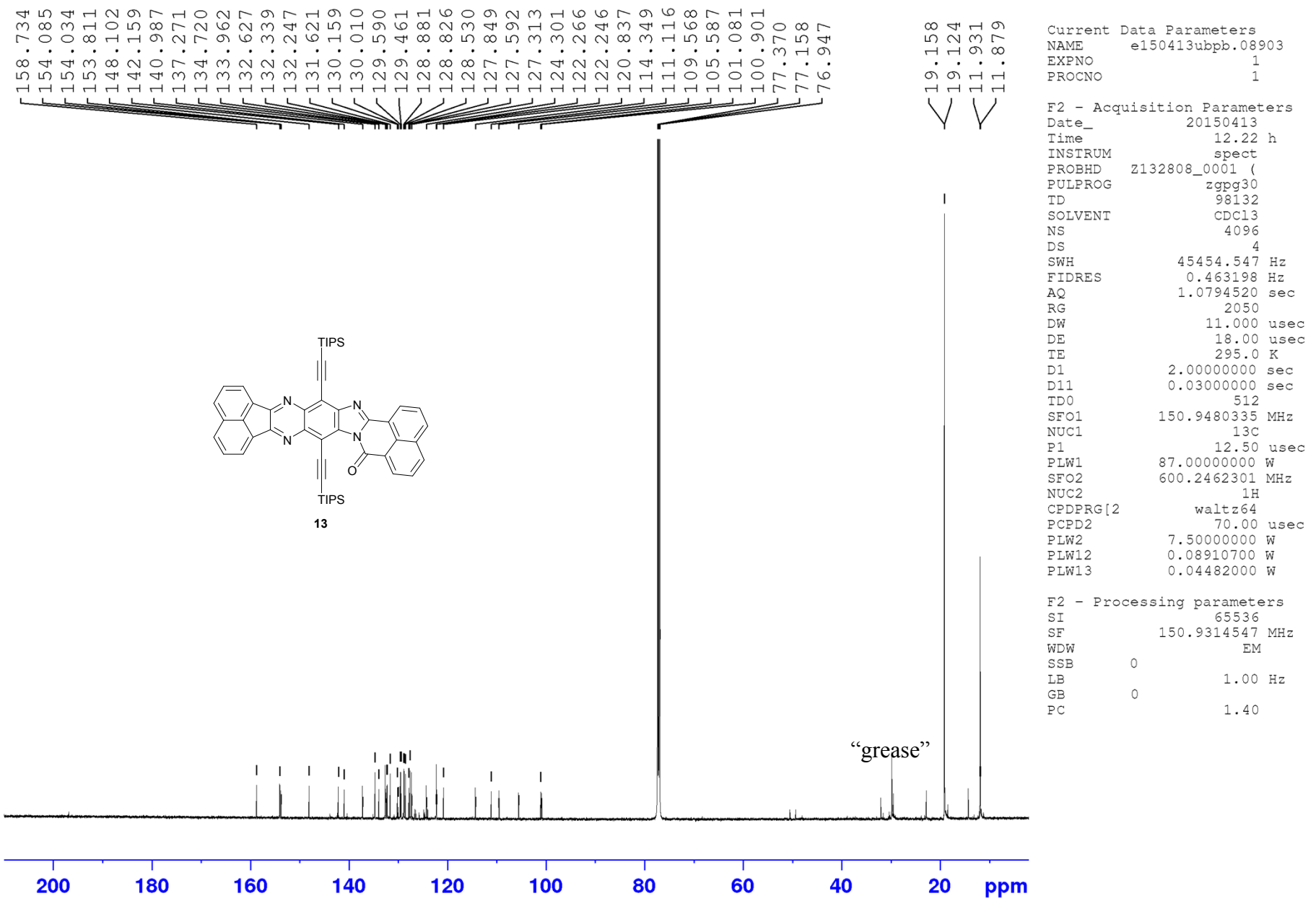



```
Current Data Parameters
NAME      d150324ubpb.08903_24
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20150324
Time                   9.15 h
INSTRUM               spect
PROBHD    Z119877_0003 (
PULPROG                zg30
TD                    98304
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               15000.000 Hz
FIDRES             0.152588 Hz
AQ                3.2767999 sec
RG                      287
DW                   33.333 usec
DE                    6.50 usec
TE                   295.0 K
D1              0.10000000 sec
TD0                       2
SFO1           500.1325007 MHz
NUC1                     1H
P1                    14.60 usec
PLW1           36.00000000 W

F2 - Processing parameters
SI                    65536
SF             500.1300127 MHz
WDW                      EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```

Figure 28 ^{1}H-NMR spectrum of **13** in $CDCl_3$.

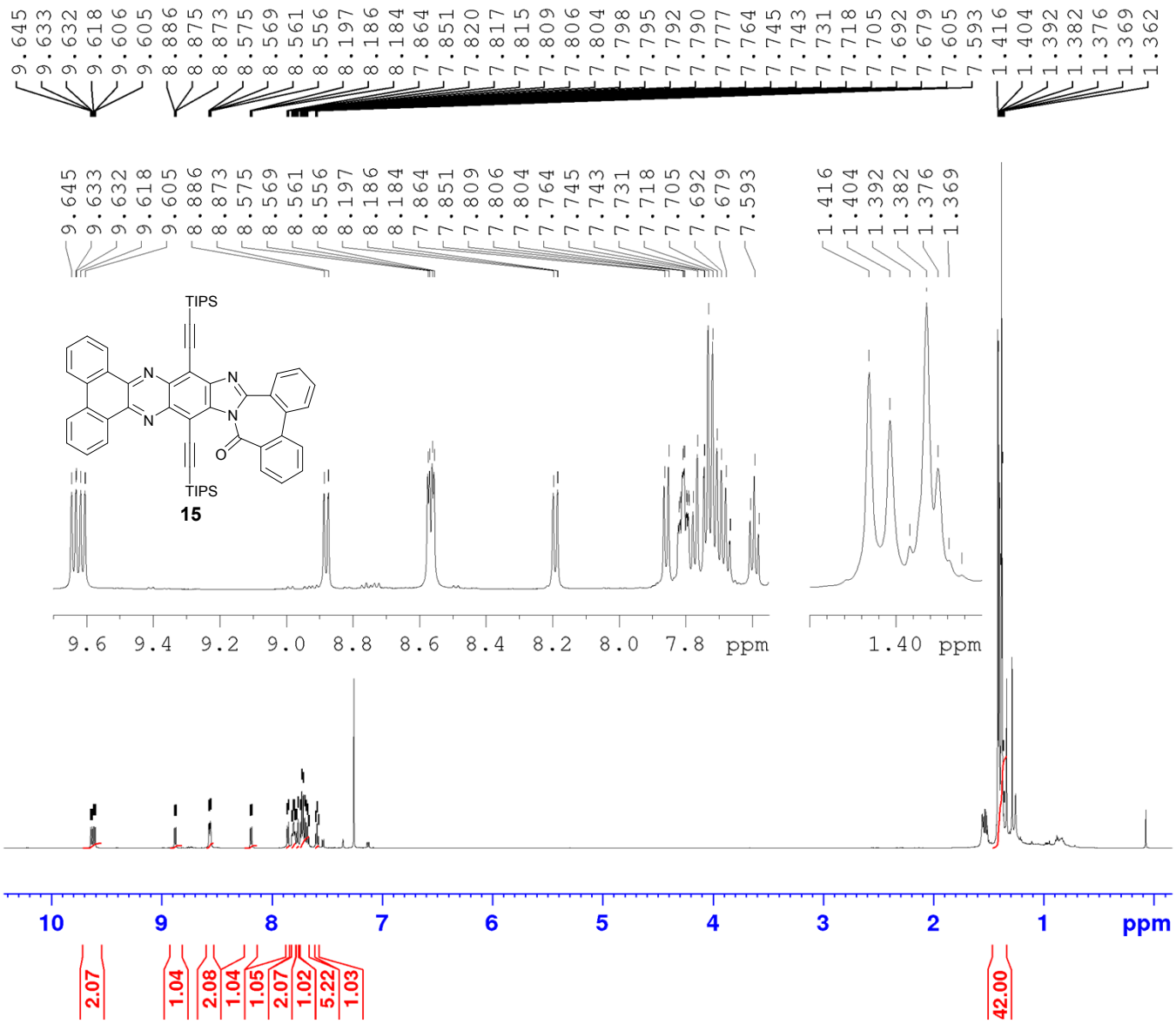



```
Current Data Parameters
NAME      e150413ubpb.08903
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150413
Time                12.22 h
INSTRUM              spect
PROBHD    Z132808_0001 (
PULPROG            zgpg30
TD                  98132
SOLVENT             CDCl3
NS                   4096
DS                      4
SWH            45454.547 Hz
FIDRES          0.463198 Hz
AQ             1.0794520 sec
RG                   2050
DW                 11.000 usec
DE                 18.00 usec
TE                 295.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   512
SFO1          150.9480335 MHz
NUC1                 13C
P1                 12.50 usec
PLW1          87.00000000 W
SFO2          600.2462301 MHz
NUC2                 1H
CPDPRG[2          waltz64
PCPD2              70.00 usec
PLW2           7.50000000 W
PLW12          0.08910700 W
PLW13          0.04482000 W

F2 - Processing parameters
SI                   65536
SF            150.9314547 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

Figure 29 $^{13}C\{^{1}H\}$-NMR spectrum of **13** in $CDCl_3$.

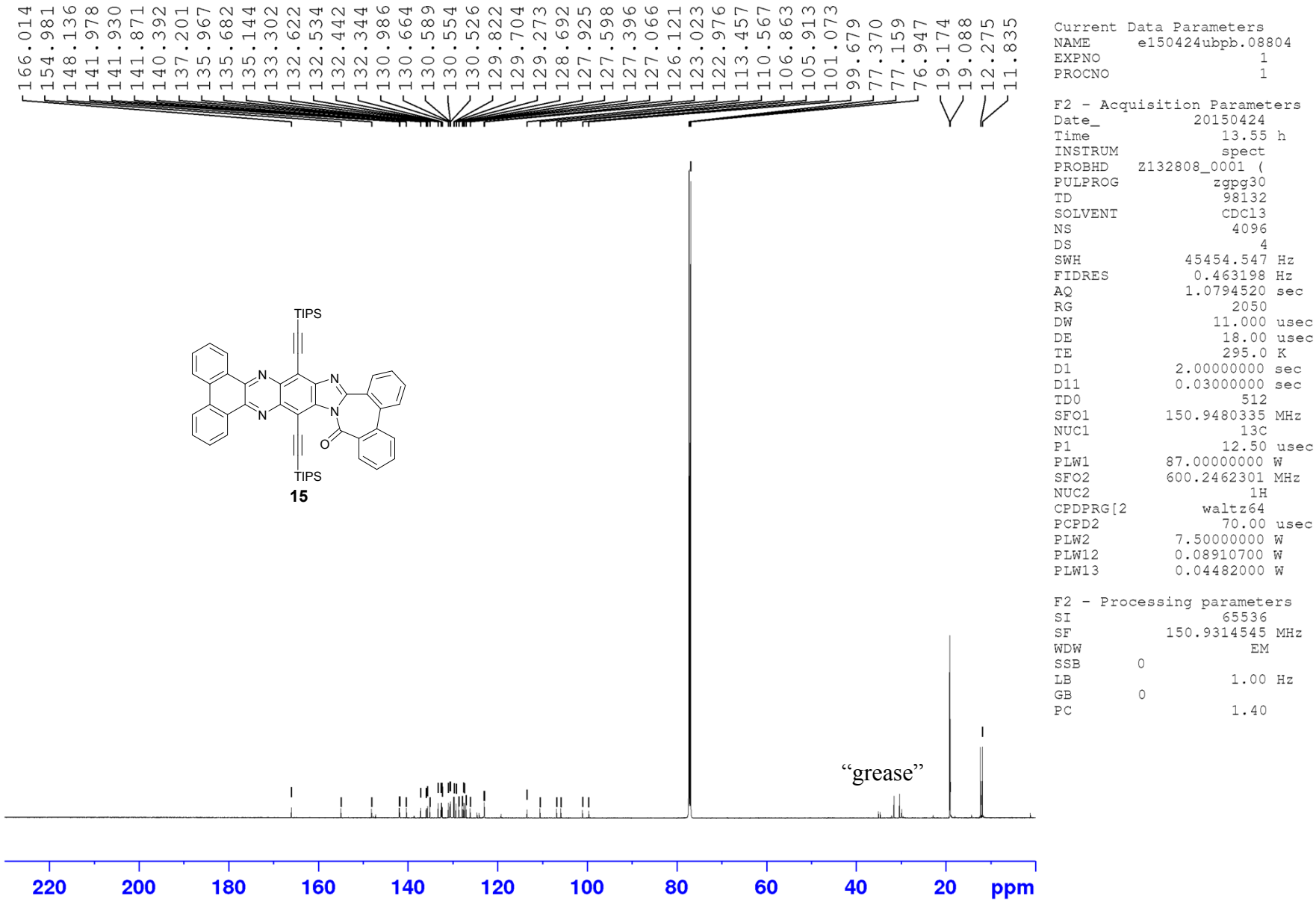



```
Current Data Parameters
NAME      e150424ubpb.08804
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20150424
Time                 17.31 h
INSTRUM              spect
PROBHD    Z132808_0001 (
PULPROG               zg30
TD                  131072
SOLVENT              CDCl3
NS                     128
DS                       2
SWH             18028.846 Hz
FIDRES           0.137549 Hz
AQ               3.6350634 sec
RG                   13.85
DW                 27.733 usec
DE                 12.00 usec
TE                 295.0 K
D1              0.10000000 sec
TD0                     16
SFO1          600.2468302 MHz
NUC1                   1H
P1                   7.63 usec
PLW1           7.50000000 W

F2 - Processing parameters
SI                   65536
SF            600.2440159 MHz
WDW                    EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.00
```

Figure 30 ^{1}H-NMR spectrum of **15** in $CDCl_3$.




```
Current Data Parameters
NAME      e150424ubpb.08804
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150424
Time                13.55 h
INSTRUM             spect
PROBHD    Z132808_0001 (
PULPROG           zgpg30
TD                 98132
SOLVENT            CDCl3
NS                  4096
DS                     4
SWH           45454.547 Hz
FIDRES         0.463198 Hz
AQ            1.0794520 sec
RG                  2050
DW                11.000 usec
DE                18.00 usec
TE                295.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  512
SFO1        150.9480335 MHz
NUC1                13C
P1                12.50 usec
PLW1        87.00000000 W
SFO2        600.2462301 MHz
NUC2                1H
CPDPRG[2         waltz64
PCPD2             70.00 usec
PLW2         7.50000000 W
PLW12        0.08910700 W
PLW13        0.04482000 W

F2 - Processing parameters
SI                 65536
SF          150.9314545 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure 31 $^{13}C\{^{1}H\}$-NMR spectrum of **15** in $CDCl_3$.

S9. Cartesian coordinates of computational studied molecules

Cartesian coordinates of compound **13**

C	-1.10697	0.92078	-0.31171
C	-1.10925	-0.51746	-0.38062
C	0.11424	-1.27375	-0.43969
C	1.28615	-0.52103	-0.51183
C	1.29564	0.89563	-0.36050
C	0.12130	1.64367	-0.26349
C	0.15779	3.05114	-0.12167
C	0.05494	-2.68264	-0.31432
C	-0.03976	-3.87977	-0.12871
C	0.22144	4.25934	-0.00086
N	-2.27380	1.63381	-0.26089
C	-3.37378	0.93523	-0.27684
C	-3.37712	-0.51615	-0.32989
N	-2.28043	-1.22046	-0.37405
N	2.64889	-0.86953	-0.59000
C	3.36240	0.33693	-0.43153
N	2.58935	1.37614	-0.30389
C	3.24519	-2.05036	-1.10297
C	4.72907	-2.07696	-1.00802
C	5.46858	-0.90865	-0.68120
C	4.81154	0.32285	-0.41453
C	6.89366	-0.96354	-0.64931
C	7.61489	0.22100	-0.35212
C	6.95445	1.40507	-0.10498
C	5.54878	1.46165	-0.13631
C	5.39040	-3.25821	-1.28986
C	6.79607	-3.32048	-1.23949
C	7.53206	-2.19849	-0.92876
O	2.58575	-2.93807	-1.59041
C	-5.56072	0.21349	-0.27310
C	-4.77120	1.39055	-0.24174
C	-5.39940	2.61514	-0.19096
C	-6.81900	2.64540	-0.17152
C	-7.58643	1.49401	-0.20228
C	-6.96444	0.21598	-0.25536
C	-7.59207	-1.05985	-0.29342
C	-6.82961	-2.21382	-0.34543
C	-5.40999	-2.18868	-0.36303
C	-4.77597	-0.96641	-0.32578
Si	0.29972	6.10138	0.11580
C	-0.01870	6.58810	1.94720
C	-1.00745	6.70448	-1.15361
C	2.07155	6.60407	-0.42915
C	-0.42795	8.06081	2.14317
C	-1.00747	5.66040	2.67732
C	-2.43869	6.27744	-0.77878
C	-0.95717	8.19818	-1.51939
C	2.45618	8.05856	-0.09726
C	3.14615	5.64502	0.11753
Si	-0.12886	-5.70847	0.10923
C	0.08276	-6.51277	-1.62359
C	1.37152	-6.12393	1.23190
C	-1.85944	-6.10570	0.84214
C	-0.60788	-5.70221	-2.73602
C	-0.36305	-7.98558	-1.69433
C	1.75922	-7.61144	1.30521
C	1.25798	-5.51670	2.64186
C	-2.40694	-5.00634	1.77194
C	-1.95233	-7.48113	1.53120
H	8.69962	0.18317	-0.32615
H	7.51771	2.30473	0.11818
H	5.02781	2.39075	0.06273

H	4.80716	-4.13317	-1.55192
H	7.29717	-4.25824	-1.45357
H	8.61649	-2.24646	-0.90051
H	-4.83281	3.53963	-0.16668
H	-7.31696	3.60884	-0.13147
H	-8.66984	1.56687	-0.18604
H	-8.67577	-1.12917	-0.28191
H	-7.33212	-3.17533	-0.37425
H	-4.84718	-3.11477	-0.40467
H	0.96164	6.45372	2.42857
H	-0.73378	6.14234	-2.05872
H	2.06620	6.50158	-1.52428
H	0.26570	8.76434	1.67646
H	-0.47128	8.30845	3.21031
H	-1.42230	8.25796	1.73183
H	-0.70958	4.61196	2.61619
H	-1.07392	5.92950	3.73831
H	-2.01702	5.73574	2.26230
H	-2.50152	5.20814	-0.56017
H	-3.13226	6.48843	-1.60159
H	-2.80770	6.82184	0.09643
H	0.02132	8.49803	-1.90263
H	-1.69118	8.42517	-2.30172
H	-1.19092	8.84283	-0.66710
H	1.74743	8.79258	-0.48796
H	3.43840	8.30178	-0.51933
H	2.53016	8.21578	0.98341
H	2.95586	4.60680	-0.16065
H	4.13686	5.92346	-0.26254
H	3.20200	5.68665	1.21127
H	1.16422	-6.47926	-1.81936
H	2.19402	-5.60129	0.72161
H	-2.51729	-6.13677	-0.03957
H	-0.24393	-4.67449	-2.77863
H	-0.43162	-6.16338	-3.71517
H	-1.69349	-5.66120	-2.59280
H	0.12651	-8.62159	-0.95249
H	-0.13662	-8.40714	-2.68073
H	-1.44353	-8.08395	-1.55011
H	1.95368	-8.03748	0.31773
H	2.67273	-7.74129	1.89782
H	0.98349	-8.21927	1.77997
H	1.02777	-4.44847	2.61226
H	2.19854	-5.63509	3.19315
H	0.47883	-6.00694	3.23381
H	-2.41173	-4.02598	1.29137
H	-3.43450	-5.23903	2.07752
H	-1.81472	-4.91819	2.68804
H	-1.61972	-8.30338	0.89311
H	-2.98703	-7.69593	1.82339
H	-1.35284	-7.51149	2.44564

Cartesian coordinates of compound **15**

C	-0.98963	0.93500	0.53420
C	-0.90928	-0.50217	0.52305
C	0.33284	-1.19289	0.26434
C	1.44453	-0.37274	0.09272
C	1.36129	1.05284	0.06539
C	0.16681	1.73732	0.27639
C	0.10390	3.14927	0.22120
C	0.31731	-2.60448	0.15053
C	0.21661	-3.81114	0.02913
C	0.07729	4.36363	0.15763
N	-2.16510	1.54785	0.77111
C	-3.23993	0.81103	0.99285
C	-3.16325	-0.62096	0.97627
N	-2.01489	-1.23646	0.74307

C	-4.51840	1.47237	1.25458	C	-0.91466	8.40260	1.63762
C	-5.67987	0.69773	1.48937	C	2.33257	8.11177	-0.09636
C	-5.60268	-0.77251	1.46952	C	2.49267	6.08022	-1.60558
C	-4.36668	-1.41669	1.21830	C	-1.13989	5.63969	-2.56609
C	-4.58928	2.87659	1.27350	C	-0.88590	8.08631	-1.99315
C	-5.78711	3.52182	1.52003	Si	-0.10445	-5.63201	-0.07425
C	-6.94239	2.76640	1.75292	C	-0.92506	-5.94575	-1.78512
C	-6.88587	1.38284	1.73730	C	1.61171	-6.48305	0.00960
C	-6.73145	-1.58498	1.69533	C	-1.30669	-6.05967	1.36201
C	-6.64552	-2.96689	1.67554	C	-1.87667	-4.81170	-2.20983
C	-5.41833	-3.59275	1.42726	C	-1.65152	-7.29966	-1.90177
C	-4.29391	-2.82074	1.20122	C	1.63929	-7.97115	-0.38506
N	2.78963	-0.64440	-0.20165	C	2.33225	-6.25619	1.35141
C	3.42057	0.60183	-0.36380	C	-1.07640	-5.23372	2.64188
N	2.59310	1.60006	-0.20953	C	-1.36356	-7.56106	1.70775
C	3.44885	-1.90995	-0.05284	H	-3.68037	3.43635	1.09179
C	4.37357	-2.27399	-1.16409	H	-5.83009	4.60596	1.53357
C	5.35437	-1.42375	-1.71065	H	-7.88815	3.26211	1.94750
C	5.75871	-0.13389	-1.09750	H	-7.79830	0.83032	1.92217
C	4.86702	0.79438	-0.51416	H	-7.69603	-1.13411	1.89030
C	7.12700	0.19423	-1.11515	H	-7.53536	-3.56222	1.85387
C	7.60340	1.39863	-0.61867	H	-5.34950	-4.67560	1.41308
C	6.71081	2.32789	-0.08556	H	-3.33216	-3.27815	1.00776
C	5.36155	2.02115	-0.03240	H	7.83315	-0.52788	-1.50706
C	4.17145	-3.55536	-1.69279	H	8.66810	1.60668	-0.64044
C	4.88016	-3.98885	-2.80453	H	7.06647	3.27620	0.30266
C	5.81005	-3.13499	-3.39408	H	4.65259	2.72224	0.38836
C	6.04772	-1.88132	-2.84485	H	3.43265	-4.19432	-1.22544
O	3.13942	-2.65454	0.84007	H	4.69909	-4.97690	-3.21371
Si	0.09864	6.20615	0.00475	H	6.35430	-3.44461	-4.28023
C	-0.51887	6.91406	1.68044	H	6.77649	-1.23111	-3.31414
C	1.94780	6.63270	-0.27606	H	0.34086	6.81692	2.35970
C	-1.10089	6.67056	-1.42260	H	2.44345	6.07135	0.52990
C	-1.67228	6.08865	2.28056	H	-2.09301	6.65798	-0.94675

H	-1.40876	5.03671	2.40425	H	-2.29634	-5.77909	0.97069
H	-1.95803	6.48167	3.26342	H	-1.37959	-3.84052	-2.23332
H	-2.56702	6.13070	1.64913	H	-2.28447	-5.00593	-3.20884
H	-0.12316	9.04932	1.25125	H	-2.72989	-4.72242	-1.52888
H	-1.16439	8.76178	2.64275	H	-1.01868	-8.15338	-1.64880
H	-1.80155	8.56151	1.01618	H	-2.00960	-7.45450	-2.92619
H	2.06004	8.49464	0.89037	H	-2.53073	-7.33785	-1.25125
H	3.41643	8.24010	-0.20207	H	1.24340	-8.14340	-1.38916
H	1.86249	8.75766	-0.84363	H	2.66868	-8.34848	-0.37554
H	2.28900	5.01282	-1.72094	H	1.06717	-8.59479	0.30750
H	3.57943	6.21468	-1.66379	H	2.38757	-5.19849	1.61729
H	2.06171	6.59952	-2.46717	H	3.35983	-6.63633	1.30696
H	-1.36561	4.63440	-2.20569	H	1.83419	-6.78473	2.17011
H	-1.90646	5.91238	-3.30125	H	-1.10127	-4.15947	2.45151
H	-0.18617	5.58915	-3.09991	H	-1.84875	-5.46008	3.38646
H	-0.88844	8.86291	-1.22481	H	-0.11028	-5.46116	3.10178
H	-1.67894	8.33539	-2.70792	H	-1.56495	-8.19526	0.84144
H	0.06200	8.16214	-2.53441	H	-2.15472	-7.75358	2.44181
H	-0.08833	-5.95576	-2.49970	H	-0.42708	-7.90434	2.15693
H	2.18462	-5.94431	-0.76013				

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