Chemical Science

Electronic Supplementary Information

Donor-substituted Octacyano[4]dendralenes: a New Class of Cyano-rich Nonplanar Organic Acceptors

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Table of Contents **Page**

Experimental Section:

Materials and general methods:

Reagents and solvents were purchased at reagent grade from GFS Chemicals, Acros, ABCR, Aldrich, and Fluka and used as received. THF was freshly distilled from Na/benzophenone under N_2 atmosphere. For all aqueous solutions, deionised water was used. Hay catalyst refers to a freshly prepared solution of CuCl (400 mg, 4.0 mmol) and TMEDA (*N,N,N′,N′*-tetramethylethylenediamine, 464 mg, 4.0 mmol) in acetone (100 cm^3). All reactions, except Hay couplings, were performed under an inert atmosphere by applying a positive pressure of argon. Drying was performed *in vacuo* at 10^{-2} Torr. Compounds **10**,[1] **14**,[2] as well as 4-iodo-*N*-isopropylaniline[3] for the synthesis of **15**, *N*-butyl-4-ethynylaniline[4] for the synthesis of **9**, 4-ethynyl-*N*,*N*-diisopropylaniline[5] for the synthesis of **11** and 9-iodo-1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinoline[6] for the synthesis of **16** were prepared according to literature procedures. Solvents for column chromatography (CC), plug filtrations

and extractions were of technical quality. The chromatographic separations were carried out on SiO_2 60 (particle size 0.040–0.063 mm, 230–400 mesh; Silicycle). CC was carried out at an overpressure of 0.1–0.6 bar. MPLC (medium-pressure LC) was performed with a Büchi Sepacore system consisting of a Büchi Pump manager C-615, a Büchi Pump Module C-601 and a Büchi Fraction collector C-660. Thin-layer chromatography (TLC) was conducted on SiO_2-layered glass plates (60 F_{254}, Merck); visualisation with UV light (254 or 366 nm). Compounds were prepared according to literature procedures. Melting points (mp.) were measured on a Büchi B-540 melting-point apparatus in open capillaries and are uncorrected; "decomp." refers to decomposition. ^{1}H NMR and ^{13}C NMR spectra were measured on Varian Mercury 300, Bruker ARX 300, Bruker DRX400, Bruker AV400 or Bruker DRX 500 instruments at 298 K, unless otherwise stated. Chemical shifts are reported in ppm relative to the signal of tetramethylsilane. Residual solvent signals in the ^{1}H and ^{13}C NMR spectra were used as an internal reference. Coupling constants (*J*) are given in Hz. The apparent resonance multiplicity is described as s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplets), t (triplet), q (quartet), sep (septet) and m (multiplet). Infrared spectra (IR) were recorded neat on a Varian 800 FT-IR instrument. Absorption bands are reported in cm^{-1}. UV/Vis spectra were recorded on a Varian Cary-5 spectrophotometer. The spectra were measured in CH_2Cl_2 in a quartz cuvette (1 cm) at 298 K. The absorption wavelengths are reported in nm with the molar extinction coefficient ε ($dm^3\ mol^{-1}\ cm^{-1}$) in parenthesis; shoulders are indicated as sh. High-resolution- (HR) EI-MS spectra were measured on a Waters Micromass AutoSpec-Ultima spectrometer, HR-ESI-TOF-MS spectra on a Bruker maXis ESI-Q-TOF spectrometer and HR-FT-ICR-MALDI-MS and ESI-MS spectra on a Varian IonSpec Fourier Transform (FT) ICR instrument with (3-

hydroxypyridine-2-carboxylic acid) (3-HPA) as matrix. The most important signals are reported in *m*/*z* units with M^+ or M^- as the molecular ion. The nomenclature was generated with ACD Name 9 by Advanced Chemistry Development Inc.

Electrochemistry:

Electrochemical measurements were carried out at 20 °C in CH_2Cl_2 containing 0.1 M $^nBu_4NPF_6$ in a classical three-electrode cell. CH_2Cl_2 was purchased in spectroscopic grade from Merck, dried over molecular sieves (4 Å) and stored under Ar prior to use. $^nBu_4NPF_6$ was purchased in electrochemical grade from Fluka and used as received. The working electrode was a glassy carbon disk electrode (3 mm in diameter) used either motionless for cyclic voltammetry (CV; 0.1 to 10 V s^{-1}) or as rotating-disk electrode for rotating disk voltammetry (RDV). The auxiliary electrode was a Pt wire, and the reference electrode was either an aqueous Ag/AgCl electrode or a platinum wire used as a pseudo-reference electrode. All potentials are referenced to the ferricinium/ferrocene (Fc^+/Fc) couple, used as an internal standard, and are uncorrected from ohmic drop. The cell was connected to an Autolab PGSTAT 30 potentiostat (Eco Chemie BV, Utrecht, The Netherlands) driven by a GPSE software running on a personal computer.

Variable-temperature NMR and EPR spectroscopies and magnetic susceptibility:

CD_3CN was obtained from Sigma-Aldrich and used as supplied. ^1H NMR experiments were performed on a Bruker AVANCE 200 MHz DPX NMR spectrometer equipped with a 5 mm BBO (BB-1H) probehead and a temperature controller (BVT 3200). EPR spectra were taken on a Bruker EMX spectrometer (variable temperature unit), and the magnetic susceptibility was determined with a SUS-10 (Anton Paar KG, Austria).

X-ray data analysis:

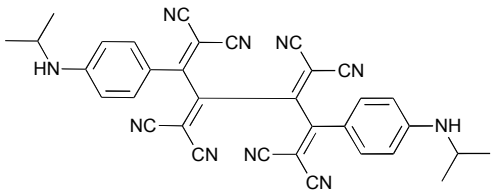
Suitable crystals were measured on a Bruker-Nonius Kappa-CCD diffractometer, MoKa radiation, l = 0.71073 Å, with a graphite monochromator. All diagrams and calculations were performed using maXus (Bruker Nonius, Delft & MacScience, Japan). Structures were solved by direct methods (SIR97)[7] and refined by full-matrix least-squares analysis (SHELXL-97).[8] All heavy atoms were refined anisotropically; H-positions are based on stereochemical considerations and were included in the structure factor calculation with constrained isotropic thermal parameters. CCDC-775678 (**5**) and CCDC-775679 (**7**) 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.

Synthetic Protocols:

General Procedure for double [2+2] cycloaddition of TCNE to dianilino-end-capped buta-1,3-diynes

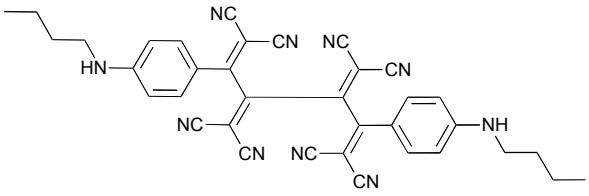
TCNE was added to a solution of the appropiate dianilinobutadiyne in $C_2H_2Cl_4$, and the mixture was stirred under Ar. The solvent was evaporated *in vacuo*, and the residue was purified according to the experimental details below.

3,4-Bis(dicyanomethylidene)-2,5-bis{4-[(1-methylethyl)amino]phenyl}hexa-1,5-diene-1,1,6,6-tetracarbonitrile (1)



General Procedure, starting from **8** (170 mg, 0.49 mmol) and TCNE (516 mg, 4.0 mmol) in $C_2H_2Cl_4$ (25 cm^3), stirring for 48 h at 80 °C and purification by column chromatography (CC) (SiO_2, CH_2Cl_2/CH_3CN 20:1) to give **1** (243 mg, 82%) as a brown solid. Mp. > 400 ºC; $\lambda_{max}(CH_2Cl_2)$/nm 475 (ε / dm^3 mol^{-1} cm^{-1} 69000); ν_{max}(neat)/cm^{-1} 3339, 2971, 2214, 1605, 1436, 1168, 833; δ_H (500 MHz, $C_2D_2Cl_4$, 80 °C): 1.35 (12 H, br s), 3.86 (2 H, br s), 4.91 (2 H, br s), 6.69 (4H, d, *J* 8.0 Hz), 7.47 (4H, d, *J* 7.8 Hz); δ_C (100 MHz, $C_2D_2Cl_4$, 80 °C): 22.4, 44.8, 98.7, 109.3, 109.7, 112.7, 113.8, 120.2, 132.0, 154.0, 156.4; HR-MALDI-MS m/z (%): calcd for $C_{34}H_{24}N_{10}^-$ (M^-): 572.2191; found: 572.2192 (100); elemental analysis calcd for $C_{34}H_{24}N_{10}$ + 0.25 CH_2Cl_2 + 0.25 pentane: C 69.68, H 4.53, N 22.89; found: C 69.63, H 4.56, N 22.78.

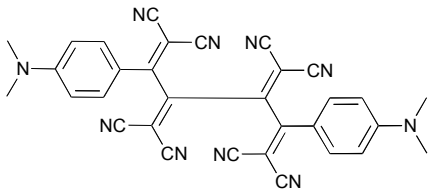
2,5-Bis[4-(butylamino)phenyl]-3,4-bis(dicyanomethylidene)hexa-1,5-diene-1,1,6,6-tetracarbonitrile (2)



General Procedure, starting from **9** (150 mg, 0.49 mmol) and TCNE (496 mg, 3.9 mmol) in $C_2H_2Cl_4$ (20 cm^3), stirring for 48 h at 80 °C and purification by CC (SiO_2, CH_2Cl_2 → CH_2Cl_2/EtOAc 20:1) to give **2** (243 mg, 82%) as a brown solid. Mp. >

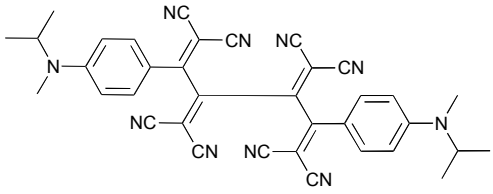
400 ºC; $\lambda_{max}(CH_2Cl_2)$/nm 474 (ε / dm^3 mol^{-1} cm^{-1} 60 100); ν_{max}(neat)/cm^{-1} 3379, 3334, 2959, 2932, 2865, 2207, 1605, 1434, 1337, 1178, 831; δ_H(500 MHz; $C_2D_2Cl_4$, 80 °C): 1.04 (6 H, t, *J* 7.1), 1.36 (4 H, br m), 1.59 (4 H, br m), 3.34 (4 H, br s), 5.05 (2 H, br s), 6.70 (4 H, d, *J* 6.6), 7.47 (4 H, d, *J* 6.3); δ_C(100 MHz; $C_2D_2Cl_4$, 80 °C): 13.4, 19.9, 31.0, 43.1, 98.7, 109.3, 109.7, 113.5, 116.3, 131.9, 154.9, 156.5; HR-MALDI-MS *m/z* (%): calcd for $C_{36}H_{28}N_{10}^-$ (M^-): 600.2504; found: 600.2504 (100).

3,4-Bis(dicyanomethylidene)-2,5-bis[4-(dimethylamino)phenyl]hexa-1,5-diene-1,1,6,6-tetracarbonitrile (3)



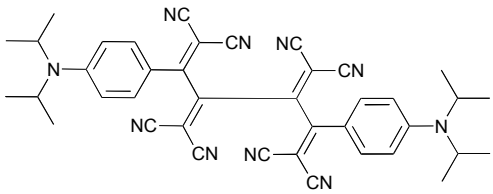
General Procedure, starting from **10**[1] (50 mg, 0.173 mmol) and TCNE (111 mg, 0.87 mmol) in $C_2H_2Cl_4$ (40 cm^3); stirring for 100 h at 95 °C. During the time of the reaction, dark insoluble precipitates were formed. The solvent was removed under vacuum, and the residue was triturated with Et_2O (8 cm^3, 3 x) and subsequently acetone (8 cm^3, 4 x) in a centrifuge tube to afford **3** as a black solid (152 mg, 80%). Mp. > 400 ºC; $\lambda_{max}(CH_2Cl_2)$/nm 494 (ε / dm^3 mol^{-1} cm^{-1} 36700, the number is approximate, due to the very poor solubility); ν_{max}(neat)/cm^{-1} 2923, 2212, 1603, 1453, 1383, 1337, 1220, 1170, 830; δ_H (500 MHz, $C_2D_2Cl_4$, 80 °C): = 3.23 (12 H, br s), 6.80 (4 H, d, *J* 9.2), 7.54 (4 H, d, *J* 9.5); δ_C(100 MHz; $C_2D_2Cl_4$, 80 °C): not available due to low solubility; HR-MALDI-MS *m/z* (%): calcd for $C_{32}H_{20}N_{10}^-$ (M^-): 544.1878; found: 544.1878 (100).

3,4-Bis(dicyanomethylidene)-2,5-bis{4-[methyl(1-methylethyl)amino]phenyl}hexa-1,5-diene-1,1,6,6-tetracarbonitrile (4)



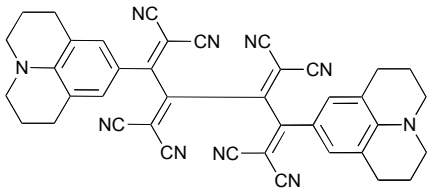
General Procedure, starting from **11** (50 mg, 0.15 mmol) and TCNE (154 mg, 1.2 mmol) in $C_2H_2Cl_4$ (25 cm^3), stirring for 24 h at 80 °C and purification by CC (SiO_2, CH_2Cl_2/CH_3CN 20:1) to give **4** (71.5 mg, 82%). Mp. > 400 ºC; $\lambda_{max}(CH_2Cl_2)$/nm 501 (ε / dm^3 mol^{-1} cm^{-1} 65 800); ν_{max}(neat)/cm^{-1} 2978, 2933, 2208, 1600, 1444, 1395, 1126, 827; δ_H(500 MHz; $C_2D_2Cl_4$, 80 °C)): δ = 1.34 (12 H, d, *J* 6.0 Hz); 3.01 (6 H, s), 4.3 (2 H, s), 6.85 (4 H, d, *J* 7.1 Hz), 7.53 (4 H, d, *J* 7.3 Hz); δ_C (100 MHz, $C_2D_2Cl_4$, 80 °C): δ = 20.7, 49.0, 98.5, 109.7, 109.9, 113.5, 115.3, 131.4, 154.2, 155.6; δ_C(100 MHz; $C_2D_2Cl_4$): δ = 19.5, 30.4, 49.6, 98.5, 109.5, 109.7, 113.0, 113.2, 115.5, 131.2, 155.0, 155.7; HR-MALDI-MS *m/z* (%): calcd for $C_{36}H_{28}N_{10}^-$ (M^-) : 600.2504; found: 600.2515 (100).

3,4-Bis(dicyanomethylene)-2,5-bis[4-(diisopropylamino)phenyl]hexa-1,5-diene-1,1,6,6-tetracarbonitrile (5):



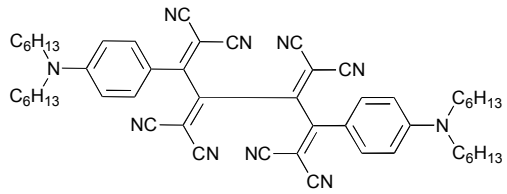
General Procedure, starting from **12** (200 mg, 0.49 mmol) and TCNE (522 mg, 4.0 mmol) in $C_2H_2Cl_4$ (25 cm^3), stirring for 24 h at 80 °C and purification by CC (SiO_2, CH_2Cl_2) to give **5** (266 mg, 81%) as a green solid. Mp. > 350 °C (decomp.); $\lambda_{max}(CH_2Cl_2)$/nm 281 (ε / dm^3 mol^{-1} cm^{-1} 29 600) 506 (50 700); ν(neat)/cm^{-1} 2972, 2930, 2360, 2342, 2215, 2125,1597, 1521, 1482, 1448, 1381, 1334, 1312, 1222, 1211, 1190, 1166, 1118, 1088, 1014 937, 903, 864, 822, 790, 729, 694, 653, 631; δ_H (500 MHz, $C_2D_2Cl_4$ 80 °C): 1.38 (24 H, d, *J* 6.9 Hz); 4.1-4.0 (4 H, m), 6.85 (4 H, d, *J* 8.8 Hz), 7.42 (4 H, d, *J* 8.1 Hz); δ_C (100 MHz, $C_2D_2Cl_4$, 80 °C): 20.7, 49.0, 98.5, 109.7, 109.9, 113.5, 115.3, 131.4, 154.2, 155.6; HR-MALDI-TOF (DCTB) *m/z* (%): calcd for $C_{36}H_{28}N_{10}^-$ (M^-) : 656.3119; found: 656.3095 (100).

3,4-Bis(dicyanomethylene)-2,5-bis(-(1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinolin-9-yl))hexa-1,5-diene-1,1,6,6-tetracarbonitrile (6):



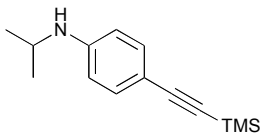
General Procedure, starting from **13** (200 mg, 0.5 mmol) and TCNE (523 mg, 4.1 mmol) in $C_2H_2Cl_4$ (25 cm^3), stirring for 24 h at 80 °C and purification by CC (SiO_2, CH_2Cl_2) to give **6** (283 mg, 87%) as a black greenish solid. Mp. dec > 350 °C; $\lambda_{max}(CH_2Cl_2)$/nm 297 (ε / dm^3 mol^{-1} cm^{-11} 26 400) 524 (45 200); ν_{max}(neat)/cm^{-1} 2923, 2851, 2360, 2339, 2206, 1605, 1543, 1484, 1434, 1417, 1364, 1301, 1259, 1209, 1171, 1096, 1021, 896, 859, 850;): δ_H (500 MHz, $C_2D_2Cl_4$, 80 °C): 2.04 (8 H, br s); 2.78 (8 H, br s), 3.46 (8 H, *J* 5.4), 7.15 (4H, s); δ_C (100 MHz, $C_2D_2Cl_4$, 80 °C): not available due to low solubility; HR-FT-ICR-MALDI-MS (DCTB) *m/z* (%): calcd for $C_{40}H_{28}N_{10}^-$ (M^-) 648.2504; found 648.2508 (100).

3,4-Bis(dicyanomethylene)-2,5-bis(4-(dihexylamino)phenyl)hexa-1,5-diene-1,1,6,6-tetracarbonitrile (7)



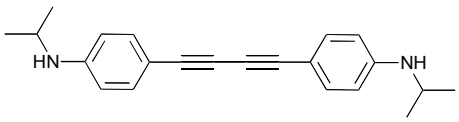
General Procedure, starting from **14**[2] (200 mg, 0.49 mmol) and TCNE (368 mg, 2.9 mmol) in $C_2H_2Cl_4$ (15 cm^3), stirring for 24 h at 80 °C and purification by CC (SiO_2, CH_2Cl_2 → CH_2Cl_2/EtOAc 20:1) to give **7** (257 mg, 82%) as green solid. Mp. dec > 350 °C; $\lambda_{max}(CH_2Cl_2)$/nm 296 (ε / dm^3 mol^{-1} cm^{-1} 22 900) 507 (65400); ν_{max}(neat)/cm^{-1} 2972, 2930, 2360, 2342, 2215, 2125,1597, 1521, 1482, 1448, 1381, 1334, 1312, 1222, 1211, 1190, 1166, 1118, 1088, 1014 937, 903, 864, 822, 790, 729, 694, 653, 631; δ_H (500 MHz, $C_2D_2Cl_4$, 80 °C): 0.91 (12 H, br s) 1.33 (24 H, br s), 1.63 (8 H, br s), 6.67 (4 H, d, *J* 8.0Hz), 7.44 (4 H, br s); δ_C (100 MHz, $C_2D_2Cl_4$, 80 °C): 13.8, 22.5, 26.6, 27.4, 31.4, 51.6, 98.5, 109.6, 109.8, 111.9, 113.5, 132.0, 154.1, 155.6; HR-MALDI-TOF (DCTB) *m/z* (%): calcd for $C_{52}H_{60}N_{10}^+$ (M^+) 825.0998; found 825.1024 (100).

***N*-(1-Methylethyl)-4-[(trimethylsilyl)ethynyl]aniline (15)**



Ethynyltrimethylsilane (3.8 cm^3, 27 mmol) was added to the deoxygenated solution of 4-iodo-*N*-isopropylaniline[3] (3.52 g, 13.5 mmol), $[Pd(PPh_3)_2Cl_2]$ (280 mg, 0.40 mmol) and CuI (150 mg, 0.79 mmol) in Et_3N (100 cm^3) under Ar atmosphere. The mixture was stirred at 25 °C overnight. The precipitate were removed by filtration, and the filtrate was concentrated and purified by CC (SiO_2; hexane/CH_2Cl_2 4:1) to give **15** as a brown solid (2.98 g, 96%). Mp. 37–38 ºC; ν_{max}(neat)/cm^{-1} 3417, 2961, 2144, 1608, 1513, 1245, 1176, 835, 822; δ_H(400 MHz; $CDCl_3$) 0.22 (9 H, s), 1.20 (6 H, d, *J* 6.3), 3.63 (1 H, septet, *J* 6.3), 3.70 (1 H, br), 6.47 (2 H, d, *J* 8.4), 7.27 (2 H, d, *J* 8.4); δ_C(100 MHz; $CDCl_3$) 0.19, 22.83, 44.08, 90.94, 106.47, 110.69, 112.59, 133.39, 147.52; HR-EI-MS *m/z* (%): calcd for $C_{14}H_{21}NSi^+$ (M^+): 231.1438; found: 231.1440 (100).

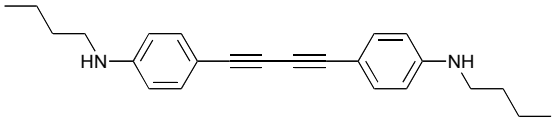
4,4'-Buta-1,3-diyne-1,4-diylbis[*N*-(1-methylethyl)aniline] (8)



K_2CO_3 (10 g, 72.6 mmol) was added to the solution of **15** (2.8 g, 12.1 mmol) in THF/MeOH (1:1, 200 cm^3). After stirring for 2 h at 25 °C, the silyl group of **15** was fully cleaved as confirmed by TLC. The solution was extracted with H_2O and CH_2Cl_2. The organic phase was collected, dried over Na_2SO_4 and concentrated by rotary evaporatoration. Without further purification, the residue was added to the freshly prepared Hay solution (CuCl 1.5 g, TMEDA 2.25 cm^3, acetone 375 cm^3). The mixture was stirred under air at 25 °C overnight. The green solution was first filtered through a SiO_2 plug to remove copper salts. After removal of solvents, the residue was recrystalised with hot ethyl acetate to give most of the product **8**, and the mother

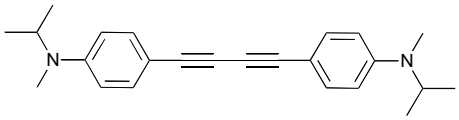
liquor was further purified by CC (SiO_2; hexane/CH_2Cl_2 2:1) to give another part of product as a yellow solid (totally 2.3 g, 82%). Mp. 193–194 ºC; ν_{max}(neat)/cm^{-1} 3413, 2964, 2137, 1605, 1512, 1326, 1172, 822; δ_H (400 MHz; $CDCl_3$) 1.21 (12 H, d, *J* 6.3), 3.64 (2 H, m), 3.72 (2 H, d, *J* 7.5), 6.47 (4 H, d, *J* 8.8), 7.31 (4 H, d, *J* 8.8); δ_C (100 MHz; $CDCl_3$) 22.86, 43.99, 72.35, 82.21, 109.35, 112.57, 133.91, 147.87; HR-EI-MS *m/z*: calcd for $C_{22}H_{24}N_2^+$ (M^+): 316.1934; found: 316.1937 (100).

4,4'-Buta-1,3-diyne-1,4-diylbis(*N*-butylaniline) (9)



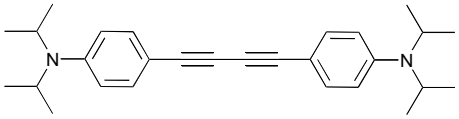
N-butyl-4-ethynylaniline[4] (1.1 g, 6.40 mmol) was dissolved in the freshly prepared Hay solution (CuCl 0.79 g, TMEDA 1.19 cm^3, acetone 200 cm^3). The mixture was stirred under air at 25 °C overnight. The purification was done in the same way as for **8** to afford **9** as a yellow solid (1.0 g, 92%). Mp. 123–124 ºC; ν_{max}(neat)/cm^{-1} 3397, 3384, 2996, 2866, 2138, 1602, 1512, 1320, 1172, 823; δ_H (300 MHz; $CDCl_3$) 0.96 (6 H, t, *J* 6.3), 1.42 (4 H, sextet), 1.60 (4 H, quintet), 3.12 (4 H, t, *J* 6.6), 3.86 (2 H, br, 6.49 (2 H, d, *J* 8.8), 7.32 (2 H, d, *J* 8.8); δ_C (75 MHz; $CDCl_3$) 13.84, 20.21, 31.44, 43.18, 72.36, 82.23, 109.39, 112.11, 133.83, 148.83; HR-MALDI-MS *m/z* (%): calcd for $C_{24}H_{28}N_2^+$ (M^+): 344.2247; found: 344.2251 (100).

4,4'-Buta-1,3-diyne-1,4-diylbis[*N*-methyl-*N*-(1-methylethyl)aniline] (10)



A mixture of **8** (180 mg, 0.57 mmol), formaldehyde (37% aqueous solution, 30 cm^3) and formic acid (36 cm^3) was heated to 120 ºC for 2 h. The solution was basified to pH ~ 12 with aqueous NaOH solution, and extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4 and concentrated to ca. 10 cm^3. The residue was passed through a SiO_2 plug to remove polymeric impurities, and the filtrate was concentrated and subjected to CC (SiO_2; hexane/CH_2Cl_2 2:1) to afford **10** as an off-white solid (22 mg, 22%). Mp. 200–202 ºC; ν_{max}(neat)/cm^{-1} 2978, 2924, 2138, 2117, 1598, 1510, 1121, 813; δ_H (300 MHz; $CDCl_3$) 1.19 (12 H, d, *J* 6.6), 2.77 (6 H, s), 4.13 (2 H, septet, *J* 6.6), 6.67 (4 H, d, *J* 8.8), 7.37 (4 H, d, *J* 8.8); δ_C (100 MHz; $CDCl_3$) 19.70, 29.83, 48.42, 82.36, 108.19, 111.92, 133.46, 149.67; HR-MALDI-MS *m/z* (%): calcd for $C_{24}H_{28}N_2^+$ (M^+):344.2247; found: 344.2243 (100).

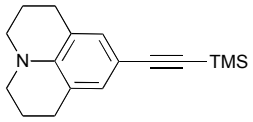
4,4'-(Buta-1,3-diyne-1,4-diyl)bis(*N*,*N*-diisopropylaniline) (11):



A solution of *Hay* catalyst in acetone (100 cm^3) was added to a solution of 4-ethynyl-*N*,*N*-diisopropylaniline[5] (470 mg, 2.34 mmol) in acetone (10 cm^3). The resulting mixture was stirred exposed to air for 18 h at 25 °C, filtered through a plug (SiO_2; acetone) and the solvent evaporated. The residue was purified by CC (hexane/CH_2Cl_2 2:1) to afford **11** (383 mg, 82%) as a yellow solid. Mp. 198–199 °C; ν_{max}(neat)/cm^{-1} 2970, 2931, 2133, 1597, 1538, 1507, 1469, 1416, 1370, 1325, 1291, 1250, 1179, 1152, 1115, 1017, 936 906, 855, 822, 775, 733, 646; δ_H (300 MHz, $CDCl_3$): δ = 1.28 (24 H, d, *J* 6.8 Hz) , 3.94-3.81 (4 H, m,), 6.74 (4 H, d, *J* 9.1 Hz), 7.33 (4 H, d, *J* 9.1

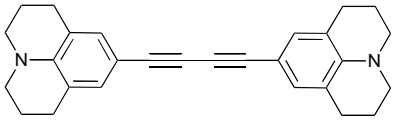
Hz); δ_C (100 MHz, $CDCl_3$): 21.3, 47.5, 72.6, 82.4, 108.4, 115.3, 132.9, 148.2 ppm; HR-EI-MS *m/z* (%): calcd for $C_{28}H_{36}N_2^+$ (M^+): 400.2878; found: 400.2874 (100).

9-((Trimethylsilyl)ethynyl)-1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinoline (16):



A solution of 9-iodo-1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinoline[6] (2.5 g, 8.36 mmol) in $HN(^iPr)_2$ (50 cm^3) was degassed with Ar for 30 min at 20 °C. $[Pd(PPh_3)_2Cl_2]$ (117 mg, 0.17 mmol) and CuI (47.7, 0.25 mmol) were added. Finally trimethylsilyacetylene (1.23 g, 12.54 mmol) was added, causing the solution to flocculate and slowly turn black. The resulting mixture was stirred for 14 h at 25 °C, hexane was added and the solution was filtered through a plug (SiO_2; CH_2Cl_2). The solvent was evaporated, and the residue was purified by CC (hexane/CH_2Cl_2 1:1) to afford **16** (2.16 g, 95%) as a colorless oil. ν_{max}(neat)/cm^{-1} 2947, 2842, 2131, 1747, 1676, 1602, 1494, 1455, 1446, 1313, 1247, 1206, 1183, 1078, 1031, 1016, 982, 912, 891, 837, 755, 735, 696, 648; δ_H (300 MHz, $CDCl_3$): 0.20 (9 H, s), 2.67 (4 H, t, *J* 6.4 Hz), 3.16 (4 H, t, *J* 5.7 Hz), 6.90 (2 H, s); δ_C (75 MHz, $CDCl_3$): 0.4, 21.9, 27.6, 50.0, 90.5, 107.4, 108.7, 120.9, 130.8, 143.2 ppm**;** HR-EI-MS *m/z* (%): calcd for $C_{17}H_{23}NSi^+$ (M^+): 269.1600; found: 269.1594 (100).

1,4-bis(1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinolin-9-yl)buta-1,3-diyne (13):



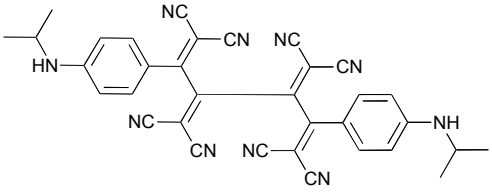
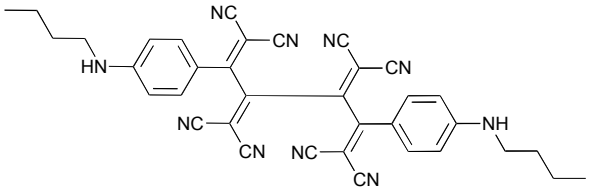
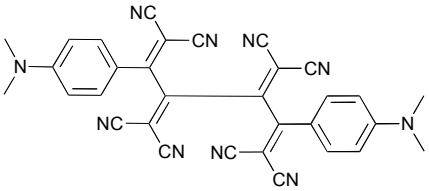
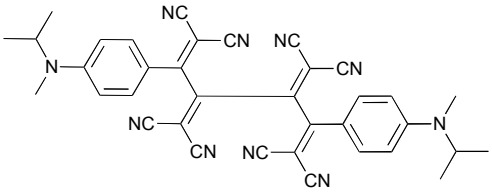
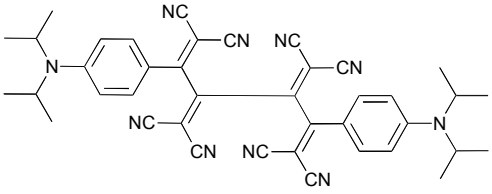
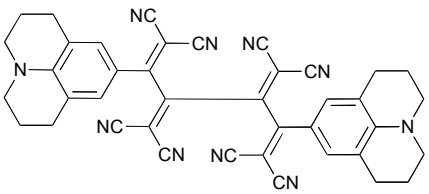
K_2CO_3 (4.62 g, 33.4 mmol) was added to the solution of **16** (2.0 g, 6.7 mmol) in THF/MeOH (1:1, 60 cm^3). After stirring for 2 h at 25 °C, the silyl group of **16** was fully cleaved as confirmed by TLC. The solution was extracted with H_2O and CH_2Cl_2. The organic phase was collected, dried over Na_2SO_4 and concentrated *in vacuo*. Without further purification, the residue was added to the freshly prepared of *Hay* catalyst in acetone (250 cm^3). The resulting mixture was stirred exposed to air for 14 h at 25 °C, filtered through a plug (SiO_2; acetone), and the solvent was evaporated. The residue was purified by CC (hexane/CH_2Cl_2 2:1) to afford **13** (478 mg, 78%) as a yellow solid. Mp. 207–209 °C; ν_{max}(neat)/cm^{-1} 2929, 2850, 2127, 1597, 1521, 1463, 1427, 1410, 1360, 1314, 1277, 1208, 1148, 1074, 1049, 1027, 887, 876, 864; δ_H (300 MHz, $CDCl_3$): 1.89-1.83 (8 H, m), 2.68 (8 H, t, *J* 6.4 Hz), 3.18 (8 H, t, *J* 5.7 Hz), 6.93 (4 H, s); δ_C (100 MHz, $CDCl_3$): 21.8, 27.7, 50.0, 72.4, 82.8, 107.7, 121.1, 131.2, 143.4 ppm; HR-EI-MS *m/z* (%): calcd for $C_{28}H_{28}N_2^+$ (M^+): 392.2252; found: 392.2244 (100).

Table 1 (ESI): Optical and electrochemical gaps of **1**–**7** determined from UV/Vis spectroscopy and CV in CH_2Cl_2.

	λ_{max} [nm (eV)]	λ_{end} [nm (eV)]	$\Delta(E_{ox,1}–E_{red,1})$ [V]
1	475 (2.61)	940 (1.33)	1.14
2	474 (2.62)	940 (1.33)	1.19
3	494 (2.51)	950 (1.31)	1.08
4	501 (2.47)	950 (1.31)	1.11

5	506 (2.45)	950 (1.31)	1.07
6	524 (2.37)	950 (1.31)	0.94
7	507 (2.45)	950 (1.31)	1.11

Table 2 (ESI): UV/Vis data for chromophores **1**–**7** in CH_2Cl_2 at 298 K.

Compound	λ_{max} [nm (eV)]	ε_{max} [dm^{-3} mol^{-1} cm^{-1}]
 **1**	280 (4.43) 475 (2.61)	15700 69000
 **2**	288 (4.31) 474 (2.62)	27600 60100
 **3**	291 (4.26) 494 (2.51)	14700 36700
 **4**	291 (4.26) 501 (2.47)	24500 65800
 **5**	281 (4.41) 506 (2.45)	29600 50740
	297 (4.17) 524 (2.37)	26400 45200

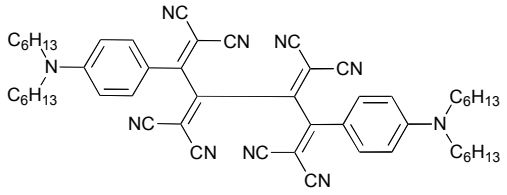
6  **7**	296 (4.19) 507 (2.45)	22900 65400

Table 3 (ESI): Cyclic voltammetry (CV; scan rate v = 0.1 V s^{-1}) and rotating disk voltammetry (RDV) data of **8**–**14** in CH_2Cl_2 (*vs*. Fc^+/Fc, + 0.1 M $^nBu_4NPF_6$).

	CV			RDV	
	$E°$ (V)[a]	ΔE_p (mV)[b]	E_{pc} (V)[c]	$E_{1/2}$ (V)[d]	Slope (mV)[e]
8			+0.37	+0.35 ($2e^-$)	70
9			+0.39	electrode inhibition	
10	+0.32 **Strong** electrode **inhibition** during the **second oxidation** step.	60		+0.33 ($1e^-$) Electrode inhibition during the second oxidation	60
11					
	+0.45	60		+0.45 ($1e^-$)	60
	+0.29	60		+0.30 ($1e^-$)	60
12					
	+0.44	60		+0.47 ($1e^-$)	60
	+0.29	60		+0.30 ($1e^-$)	60
13					
	+0.23	60		+0.24 ($1e^-$)	60
	+0.08	60		+0.09 ($1e^-$)	60
14					
	+0.45	90		+0.47 ($1e^-$)	70
	+0.26	100		+0.27 ($1e^-$)	65

[a] $E^o = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [b] $\Delta E_p = E_{pa} - E_{pc}$. [c] E_p = irreversible peak potential. [d] Logarithmic analysis of the wave obtained by plotting E versus $\log[I/(I_{lim} - I)]$. [e] Slope = Slope of the linearised plot of E *versus* $\log[I/(I_{lim} - I)]$, where I_{lim} is the limiting current and I the current.

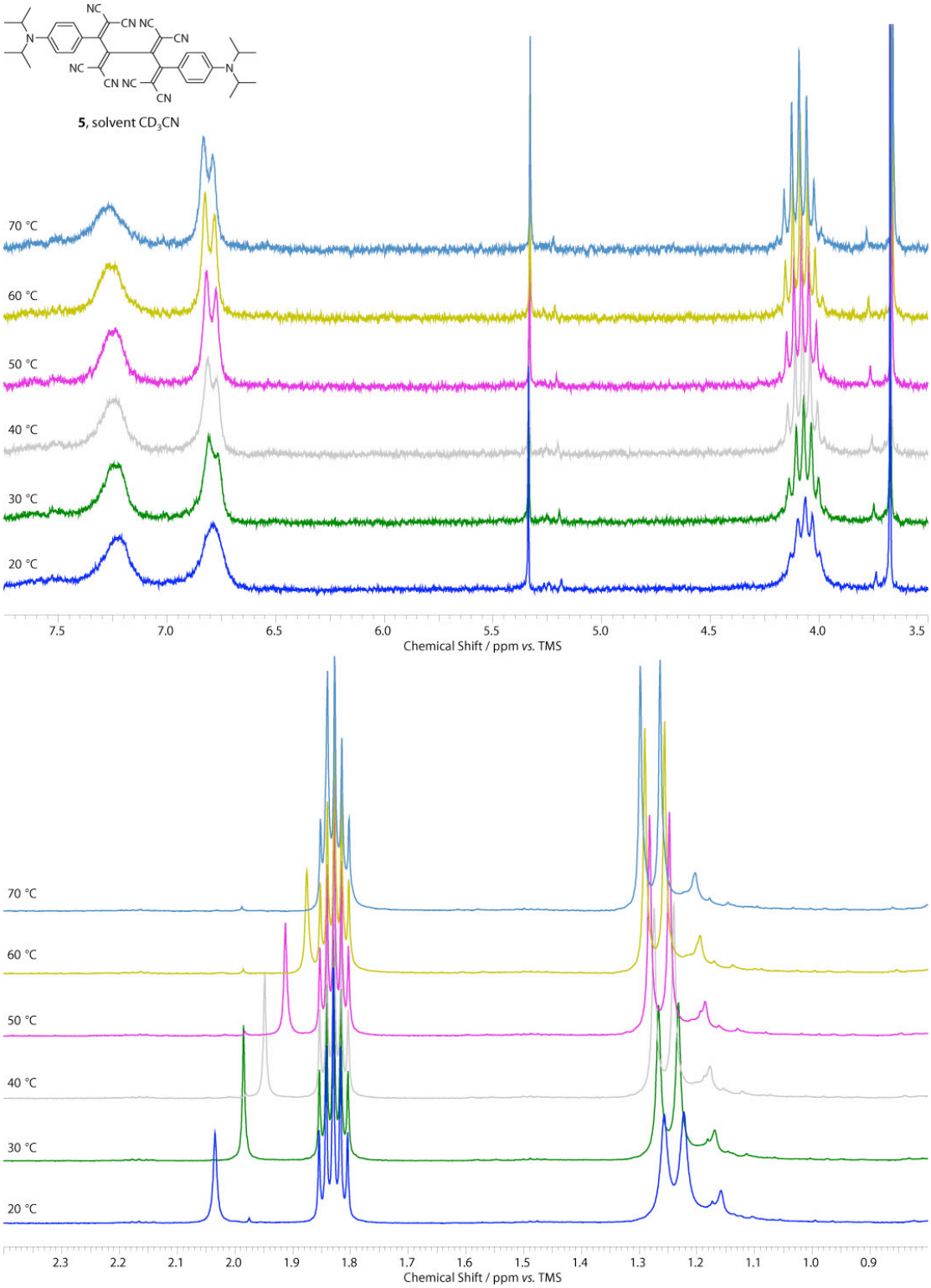


Figure 1 (ESI): Variable temperature ^{1}H NMR spectra of **5** in CD_3CN (200 MHz).

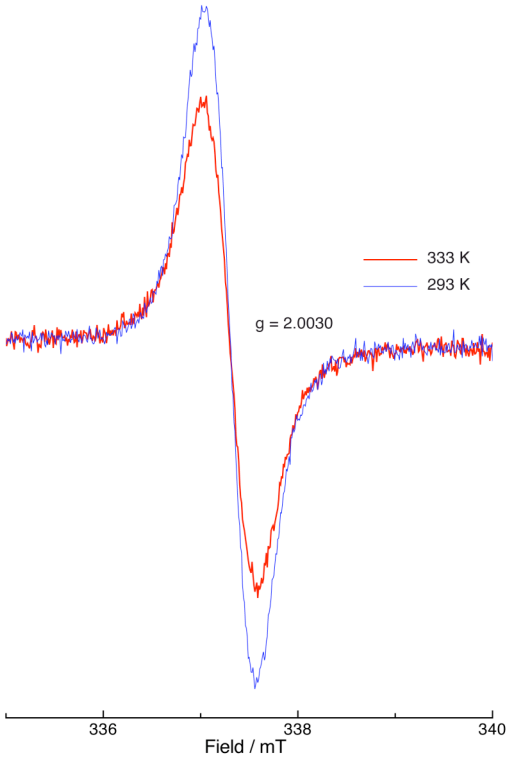


Figure 2 (ESI): EPR spectra of $\mathbf{5}^{\bullet-}$ in CD_3CN at 293 and 333 K.

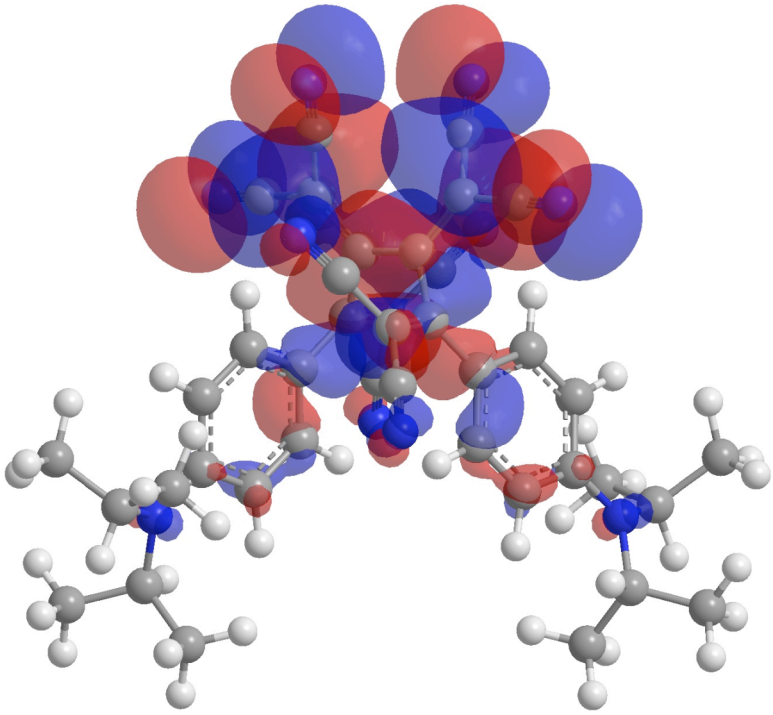


Figure 3 (ESI): LUMO of **5** (B3LYP/6-31G(d)).

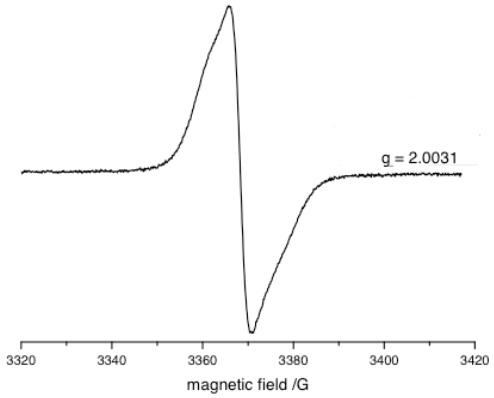


Figure 4 (ESI): EPR spectra of $\mathbf{5}^{\bullet-}$ in the solid state at 293.

Table 4 (ESI): Calculated geometries (Å) (B3LYP/6-31G(d)) for **3** and **5** in the compact and extended conformations, SCF energy and zero-point (ZPE, 0 K), enthalpy (*H*, 298 K) and free-energy-corrections (*G*, 298 K) (Hartrees). Geometries were optimised using Gaussian 09[9] and the resultant stationary states analysed with analytical harmonic frequencies to establish that they are minima.

Compound 5 (compact)
SCF = -2093.217772
ZPE = 0.678139
H = 0.730785
G = 0.588735

N 2.527685	2.937194	-2.507756
N 0.939734	-0.751882	-4.079862
N -4.531843	-2.463755	-0.264890
N -1.685669	5.779299	0.272271
N -2.400349	3.540171	-3.336581
N 1.685269	5.779527	-0.273230
N 2.400244	3.541433	3.336169
N 4.531558	-2.463971	0.265039
N -0.938199	-0.751399	4.080329
N -2.527416	2.937456	2.507705
C 0.626267	1.175270	-2.373240
C -0.391939	1.291459	-1.443158
C -0.385404	2.566057	-0.628099
C 0.385538	2.566270	0.627855
C 0.392232	1.291874	1.443204
C -0.625786	1.175735	2.373481
C 1.659798	2.161482	-2.454660
C 0.771029	0.101745	-3.305519
C -1.433664	0.325311	-1.155672
C -1.320442	-1.050769	-1.478625
C -2.316710	-1.956811	-1.183966
C -3.528956	-1.567495	-0.539923
C -3.628124	-0.190983	-0.195205
C -2.624392	0.706543	-0.485843
C -4.538104	-3.796108	-0.918536
C -5.533884	-2.257034	0.818067
C -1.143340	3.622277	-1.063032
C -1.410677	4.810011	-0.308426
C -1.829151	3.559946	-2.323826
C 1.143296	3.622718	1.062557
C 1.410447	4.810311	0.307666
C 1.829068	3.560833	2.323394
C 1.433874	0.325617	1.155719
C 2.624898	0.706797	0.486404
C 3.628506	-0.190891	0.195828
C 3.528833	-1.567500	0.540024
C 2.316268	-1.956740	1.183494

C 1.320155	-1.050532	1.478161
C 5.533843	-2.257469	-0.817741
C 4.537232	-3.796419	0.918484
C -0.770149	0.102330	3.305960
C -1.659488	2.161777	2.454816
H -0.412717	-1.431256	-1.928186
H -2.127032	-2.997696	-1.412546
H -4.519824	0.188415	0.280092
H -2.785243	1.738160	-0.198395
H 2.786066	1.738470	0.199335
H 4.520480	0.188410	-0.279027
H 2.126256	-2.997678	1.411568
H 0.412102	-1.430897	1.927177
H 5.959238	-3.252716	-0.968397
H 3.895323	-3.702005	1.795659
H -3.896459	-3.701774	-1.795896
H -5.959618	-3.252138	0.968692
C 6.714931	-1.351169	-0.422379
H 7.500132	-1.432482	-1.182518
H 6.442639	-0.295130	-0.348523
H 7.138988	-1.656365	0.538384
C 4.905862	-1.874216	-2.168497
H 4.109063	-2.573758	-2.440408
H 4.486613	-0.865816	-2.183692
H 5.677454	-1.920529	-2.944649
C 3.959667	-4.892972	0.009188
H 4.579659	-5.043468	-0.881910
H 3.915134	-5.847392	0.545687
H 2.947989	-4.638457	-0.323664
C 5.923476	-4.172666	1.466810
H 5.834217	-5.093671	2.052988
H 6.659759	-4.360888	0.678764
H 6.310314	-3.388855	2.125116
C -4.905510	-1.874167	2.168756
H -4.108939	-2.574061	2.440436
H -4.485865	-0.865931	2.183960
H -5.676967	-1.920245	2.945059
C -6.714650	-1.350207	0.423013
H -7.499665	-1.431107	1.183391
H -6.441863	-0.294299	0.349054
H -7.139124	-1.655247	-0.537611
C -5.924600	-4.171939	-1.466526
H -5.835657	-5.092830	-2.052929
H -6.660709	-4.360215	-0.678330
H -6.311477	-3.387921	-2.124566
C -3.960561	-4.892913	-0.009538
H -4.580328	-5.043270	0.881742
H -3.916456	-5.847324	-0.546100
H -2.948716	-4.638712	0.323045

Compound 5 (extended)
SCF = -2093.221927
ZPE = 0.677919
H = 0.730517
G = 0.589189

N -2.715169	-0.031893	2.595666
N 0.593087	-2.473679	3.773995
N 6.147003	-0.807980	0.319172
N -1.708456	4.406099	0.205648
N -0.089193	2.815562	3.887032
N 1.843422	4.255670	-0.877219
N 0.162119	2.123517	-4.242047
N -6.131946	-0.693420	-0.000247
N -0.662581	-3.037648	-3.270780
N 2.709556	-0.542015	-2.487469
C -0.188647	-0.519953	2.256040
C 0.640380	0.198460	1.410208
C 0.052000	1.360872	0.663871
C -0.015175	1.234716	-0.820185
C -0.637661	-0.019639	-1.362857
C 0.169890	-0.887358	-2.081186
C -1.582097	-0.233698	2.417694
C 0.270365	-1.595782	3.080317
C 2.037378	-0.088845	1.145487
C 2.588021	-1.391469	1.192934
C 3.917127	-1.628639	0.915883
C 4.820135	-0.575237	0.586612
C 4.263248	0.734167	0.556350
C 2.928622	0.960075	0.810207
C 6.750719	-2.119978	0.659656
C 6.975765	0.097703	-0.525150
C -0.397007	2.467350	1.331524
C -1.102096	3.542481	0.694513
C -0.228418	2.627425	2.748198
C 0.467298	2.197950	-1.663642
C 1.208427	3.341807	-1.215018
C 0.299441	2.123695	-3.087543
C -2.038576	-0.224774	-1.050524
C -2.895534	0.887060	-0.862915
C -4.230324	0.740758	-0.555133
C -4.819059	-0.543727	-0.372220
C -3.958427	-1.658907	-0.584674
C -2.629062	-1.504330	-0.910155
C -6.874385	0.457713	0.573190
C -6.925235	-1.920313	-0.277781
C -0.317469	-2.068862	-2.724373
C 1.570730	-0.672124	-2.281789
H 1.949881	-2.244461	1.390073
H 4.245678	-2.659261	0.896091
H 4.893854	1.587306	0.356395
H 2.577796	1.987359	0.799115
H -2.518995	1.893799	-1.014866
H -4.831886	1.637431	-0.486223
H -4.326031	-2.662359	-0.431332
H -2.022135	-2.396727	-1.001028
H -6.114054	1.167491	0.901310
H -7.959823	-1.597412	-0.136733
H 6.107356	-2.554516	1.426555
H 7.825946	-0.525225	-0.814251
C -6.836630	-2.379086	-1.742785
H -5.848610	-2.755658	-2.017369
H -7.558207	-3.186123	-1.910605
H -7.083207	-1.554832	-2.419709
C -6.702052	-3.066103	0.727918
H -5.741559	-3.571807	0.599108
H -6.751495	-2.699908	1.756897
H -7.487169	-3.819544	0.595493
C -7.771146	1.146911	-0.467100

H -8.246507	2.032593	-0.030908
H -7.193295	1.464726	-1.341313
H -8.570322	0.481381	-0.814284
C -7.649407	0.079283	1.845514
H -8.486355	-0.599945	1.652775
H -6.985930	-0.380659	2.583811
H -8.067117	0.990220	2.287708
C 8.130471	-1.974761	1.322110
H 8.081944	-1.306285	2.187204
H 8.460340	-2.958948	1.672082
H 8.897734	-1.601860	0.635874
C 6.787651	-3.074755	-0.544643
H 7.162895	-4.058025	-0.239305
H 5.790769	-3.205724	-0.977601
H 7.449617	-2.698609	-1.333020
C 6.297769	0.500697	-1.845246
H 5.906978	-0.376797	-2.368182
H 5.467360	1.197031	-1.713580
H 7.039958	0.985711	-2.489115
C 7.571492	1.296034	0.237362
H 6.824903	2.049974	0.501209
H 8.061691	0.971882	1.159928
H 8.321955	1.787373	-0.392491

Compound 3 (compact)
SCF = -1778.715523
ZPE = 0.450218
H = 0.492619
G = 0.37161

N -2.259726	2.236341	2.738810
N -0.480740	-1.417979	4.201518
N 4.518690	-3.183661	-0.122015
N 1.647662	5.061937	-0.458610
N 2.744384	2.830456	3.058642
N -1.646423	5.062412	0.457456
N -2.743541	2.830157	-3.059208
N -4.520149	-3.182090	0.122061
N 0.481602	-1.419205	-4.200655
N 2.260580	2.235306	-2.738526
C -0.375598	0.476804	2.433974
C 0.537338	0.581924	1.400392
C 0.449686	1.852421	0.583766
C -0.449118	1.852343	-0.584012
C -0.537013	0.581655	-1.400335
C 0.376160	0.476083	-2.433676
C -1.399169	1.461734	2.609136
C -0.410041	-0.579802	3.396123
C 1.543833	-0.391776	1.016678
C 1.449769	-1.765117	1.359709
C 2.412749	-2.678465	0.987283
C 3.556757	-2.284877	0.238675
C 3.645154	-0.915564	-0.128895
C 2.670528	-0.013814	0.242150
C 4.404718	-4.583631	0.270009
C 5.656993	-2.757199	-0.929765
C 1.252405	2.907660	0.931682
C 1.437694	4.093396	0.149770
C 2.068404	2.848420	2.112598
C -1.251628	2.907650	-0.932213
C -1.436653	4.093651	-0.150641
C -2.067616	2.848267	-2.113128
C -1.543916	-0.391606	-1.016596
C -2.670264	-0.013194	-0.241769
C -3.645314	-0.914475	0.129304
C -3.557769	-2.283761	-0.238562
C -2.414112	-2.677826	-0.987457
C -1.450697	-1.764947	-1.359898
C -5.658447	-2.755066	0.929519
C -4.406322	-4.582284	-0.269212
C 0.410741	-0.580771	-3.395540
C 1.399948	1.460784	-2.608847
H 0.590915	-2.131986	1.906031
H 2.274681	-3.714875	1.269042
H 4.483565	-0.555622	-0.711322
H 2.797859	1.013927	-0.074849
H -2.796970	1.014536	0.075509
H -4.483330	-0.554192	0.712096
H -2.276732	-3.714235	-1.269560
H -0.592219	-2.132215	-1.906530
H -6.305683	-3.612413	1.114882
H -4.347480	-4.689064	-1.359321
H -5.336264	-2.354042	1.898724
H -6.248799	-1.986869	0.414698
H -5.288886	-5.121345	0.075570
H -3.521330	-5.057267	0.174551
H 4.345230	-4.689732	1.360139
H 5.287552	-5.122826	-0.073874
H 3.520040	-5.058994	-0.174000
H 5.334594	-2.354948	-1.898372
H 6.303092	-3.615130	-1.116387
H 6.248598	-1.990125	-0.414672

Compound 3 (extended)
SCF = -1778.719823
ZPE = 0.450416
H = 0.492536
G = 0.373398

N 2.666177	-0.497090	-2.599878
N -0.686036	-2.995032	-3.504508
N -6.120148	-0.981370	-0.058297
N 1.765242	4.130973	-0.598188
N 0.043311	2.247707	-4.090788
N -1.764534	4.137216	0.557623
N -0.043193	2.288705	4.069052
N 6.119404	-0.981150	0.066053
N 0.687486	-2.959507	3.535303
N -2.665772	-0.471688	2.606280
C 0.141404	-0.925549	-2.175886
C -0.663140	-0.130882	-1.377103
C -0.048027	1.086490	-0.748729
C 0.048028	1.093984	0.738811
C 0.663225	-0.116954	1.379334
C -0.140951	-0.903716	2.186207
C 1.534369	-0.669197	-2.386868
C -0.342157	-2.063727	-2.896038
C -2.057418	-0.382289	-1.056703

C -2.617455	-1.680894	-0.984116	C -1.533952	-0.645611	2.394823
C -3.941121	-1.880447	-0.655720	H -1.994565	-2.552248	-1.145214
C -4.809991	-0.786397	-0.389058	H -4.304599	-2.897236	-0.578599
C -4.255463	0.519006	-0.476948	H -4.869711	1.390712	-0.291818
C -2.925785	0.704062	-0.787453	H -2.557495	1.722755	-0.856585
C -6.654753	-2.332461	0.066715	H 2.558288	1.731448	0.842787
C -6.955859	0.152143	0.322809	H 4.870333	1.393535	0.280458
C 0.402540	2.121802	-1.521418	H 4.303333	-2.891556	0.604033
C 1.136458	3.237465	-0.996606	H 1.993614	-2.540641	1.168543
C 0.205465	2.158725	-2.942973	H 7.954696	-0.214590	-0.566421
C -0.402305	2.137127	1.501050	H 6.534917	-2.886468	0.890026
C -1.135944	3.247641	0.965051	H 6.552768	0.661949	-1.207734
C -0.205279	2.188308	2.922169	H 7.048403	0.876753	0.489982
C 2.057460	-0.371588	1.061069	H 7.717879	-2.277938	-0.274963
C 2.926184	0.712051	0.782339	H 6.159978	-2.899858	-0.851342
C 4.255711	0.523722	0.473096	H -6.535761	-2.892620	-0.868211
C 4.809540	-0.782659	0.395955	H -7.720397	-2.274069	0.289793
C 3.940317	-1.873979	0.672420	H -6.164180	-2.892921	0.873923
C 2.616872	-1.671011	0.999637	H -6.553318	0.672589	1.201303
C 6.955494	0.148635	-0.325123	H -7.955410	-0.208481	0.566560
C 6.652614	-2.333641	-0.049431	H -7.047810	0.873436	-0.498452
C 0.343168	-2.034478	2.917583			

Table 5 (ESI): Calculated geometries (Å) (B3LYP/TZVP//BP86/SV(P)) for **5** in the compact and extended conformations. For the conformer energetics, single point calculations at the optimised geometries using the B3LYP-functional[10] in combination with a valence triple zeta basis set (TZVP)[11] were conducted. Additionally to account for dielectric solid state effects, a UPS/IEPS-calibrated version of the conductor like screening model (COSMO)[12] was used in conjunction with the single point calculations. Zero point energy corrections were taken from the BP86/SV(P) frequency calculations. Single point calculations to determine the ionisation potentials as well as the electron affinities at the optimised geometries of the charged and neutral species were performed on the BP86/TZVP level of theory including the same solid state correction as described above. The turbomole program package[13] was used throughout.

Compound 5 (compact)

N 1.75725226395151	0.15205027624153	-13.59124352375467
C 0.93926846390286	0.39815302535545	-11.12239298683728
C -1.65171417683156	0.02619971387816	-10.43179700646516
C -2.47956721170301	0.29313892661806	-7.95472275609216
C -0.77679827669809	0.86558034876303	-5.96197098569511
C 1.79872607802021	1.23992430829421	-6.61842926932158
C 2.62747248129375	1.04451216027566	-9.10365656458434
H -3.05876273786126	-0.44136856749915	-11.87752085401023

H -4.48871214328946	-0.03969395947033	-7.52706401936331
C -1.65325185081435	1.07935351625415	-3.33909342619452
H 3.17617885270149	1.74684091561351	-5.14184118831496
H 4.65103712082544	1.33469188050947	-9.46244739681963
C 4.28282671238548	1.11419046931013	-14.34332501632620
C 0.40901010590764	-1.41430281052207	-15.50289174984394
C -1.86349892002003	-0.08867377005302	-16.76330586155701
C -0.19298209287032	-4.10542149279494	-14.56644534623181
C 4.20275214132840	2.62945867966804	-16.82853468158620
C 6.29865694026891	-0.98591159543820	-14.39544341754054
C -0.30718979368924	-0.32390206158662	-1.35229701125074
C -3.77765971292209	2.58743196470033	-2.78072247644625
C -5.06565731531492	2.63638146389263	-0.40388199771277
C -4.85248776703059	4.24648471561188	-4.63227905644988
C 1.12426332422055	-2.48045523293511	-1.87631075316968
C 2.71845561014712	-3.56157513796694	0.03605523004481
C 1.15930638971992	-3.83834176951333	-4.22452617832510
N -5.78532328667373	5.67606289146905	-6.05617275857810
N -6.18384198452763	2.74993580098765	1.51546289491762
N 1.29737056900084	-5.18255849044560	-5.98875871377099
N 4.10817297781334	-4.42061549209957	1.54151158999739
H 4.82233326402362	2.49917713874046	-12.87010042736214
H 1.82848561005400	-1.66200011890879	-17.02605280607072
H -1.34615108375886	1.83632728668681	-17.41984342486903
H -2.47874451907335	-1.20074217640515	-18.43800220473107
H -3.52373429661665	0.09495606359154	-15.49366096020134
H -0.89130511595843	-5.25957360685689	-16.17810695578585
H 1.52924363134595	-5.02866863035236	-13.79894860940563
H -1.65573613301969	-4.15894882464167	-13.06571849870470
H 2.77202116810818	4.16335874627285	-16.73400113613370
H 6.07963677246240	3.51797070099448	-17.15017732147232
H 3.79086590884381	1.43542049279438	-18.50800313266706
H 8.19394152848320	-0.17208548543846	-14.80153191400707
H 6.39849334816177	-1.99065611405677	-12.55334507785657
H 5.89331129534751	-2.41180555779835	-15.88765601732506
N 1.53403445898836	0.34656145090159	13.63063777324457
C 0.80949705544197	-0.04791208528803	11.15219672373402
C -1.79623004500690	-0.19981551043164	10.42454185675696
C -2.51780267114251	-0.57915297947727	7.92738438218876
C -0.70891856477128	-0.76228451123001	5.95591129178784
C 1.88078396516469	-0.61829551327223	6.65189016653154
C 2.61699383845449	-0.30762727608033	9.15291179194043
H -3.30460994068939	-0.06707775184792	11.84413117726755
H -4.54685161590685	-0.65433229628175	7.47165495105623
C -1.48822763136200	-1.12871663228675	3.31961711858311
H 3.35341510119379	-0.81526568545884	5.19366348294664
H 4.64479078962325	-0.19971907318634	9.55817620482260
C 4.06006829585245	-0.38525234309955	14.62902098800294
C -0.34111752390544	1.21451370211341	15.53001115870063
C 0.65544738577477	3.41086357877067	17.16109626969267
C -1.37615901887398	-0.97791897680385	17.14157527543587
C 6.19027626626906	1.52096319370325	14.04514659472957
C 4.78014976399485	-3.14314151783218	14.02965622718098
C -0.41571320999628	0.51901208989442	1.35374432010780
C -3.25980719454449	-3.02847688484449	2.72450307584550
C -4.47512127279573	-3.32152739225856	0.32710619382954
C -4.00715900674065	-4.88215030686189	4.55251668565817
C 0.54897993042423	2.91602198874762	1.89790536602892
C 1.93162788319179	4.29319785470778	0.01126056556907
C 0.26925381306057	4.25090792899837	4.24253502907574

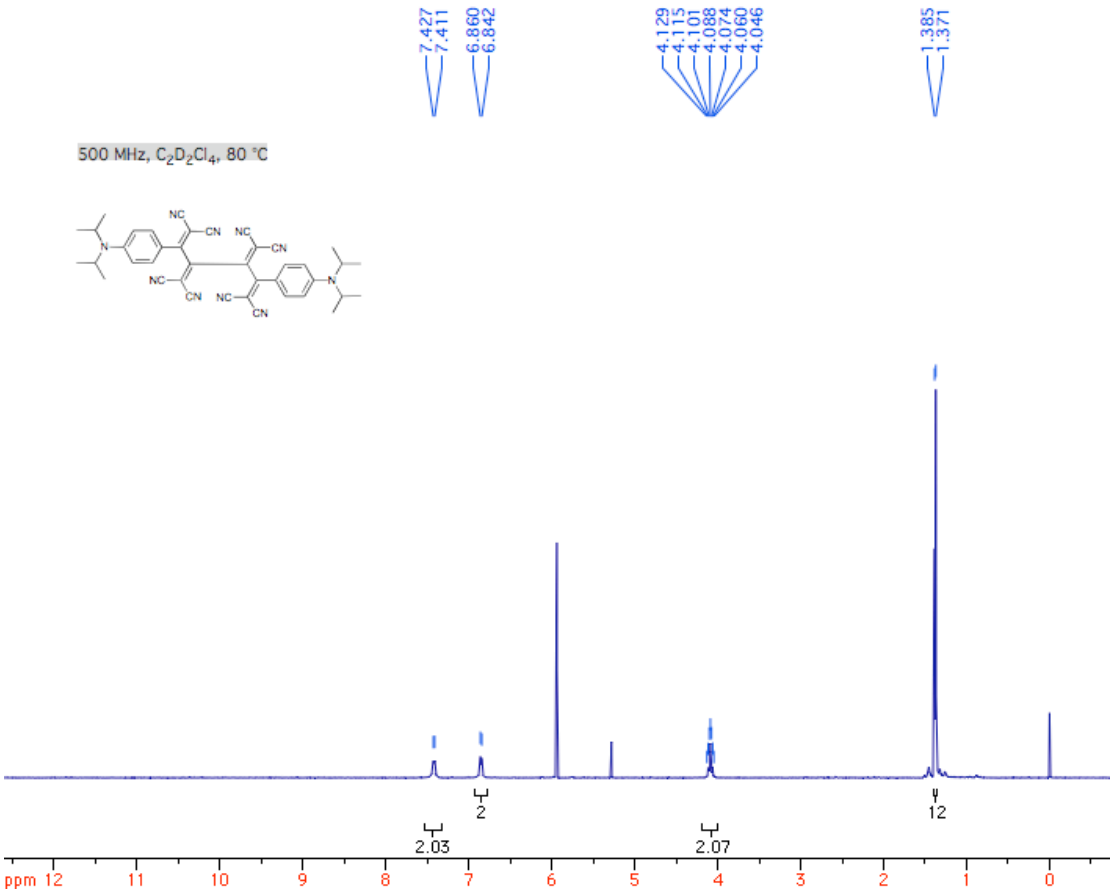
N	-4.65463234885745	-6.48073604612442	5.95497400678187
N	-5.51732229811473	-3.64718157824050	-1.61066574915410
N	0.10065943946294	5.59262711013394	6.00582862188566
N	3.15129843635086	5.40940901963415	-1.47268355735612
H	3.80539469822614	-0.32149584195802	16.70911067683059
H	-1.92766664768802	2.02144037989010	14.43033833150561
H	1.34066162663270	4.99268660439576	15.96245075988076
H	-0.91193088848202	4.14141364556585	18.35480220859818
H	2.20324936085893	2.83672517930883	18.46159437059974
H	-2.88797633931688	-0.28987605202067	18.42995699348220
H	-2.18797608624028	-2.49291541177580	15.93363954918450
H	0.12607839970132	-1.83762414483410	18.33721854705357
H	5.59867859821100	3.47885887108340	14.51375400242466
H	7.87936457423776	1.05794845696800	15.20813149387874
H	6.79188961770150	1.50101503698737	12.03538700248188
H	6.51921696774217	-3.65318448473365	15.09398100361347
H	3.24942299009189	-4.45422575775360	14.61915605459023
H	5.16133953227708	-3.48136170055966	11.99570225784711

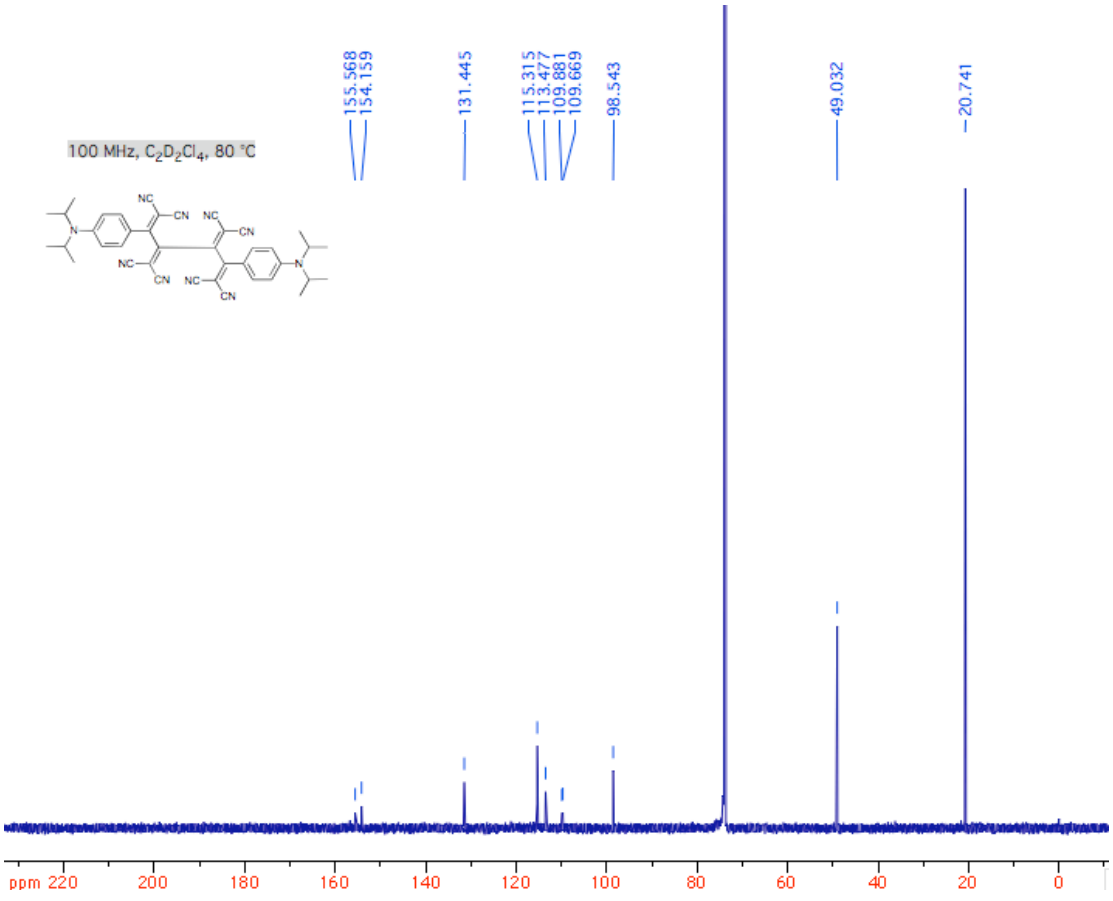
Compound 5 (extended)

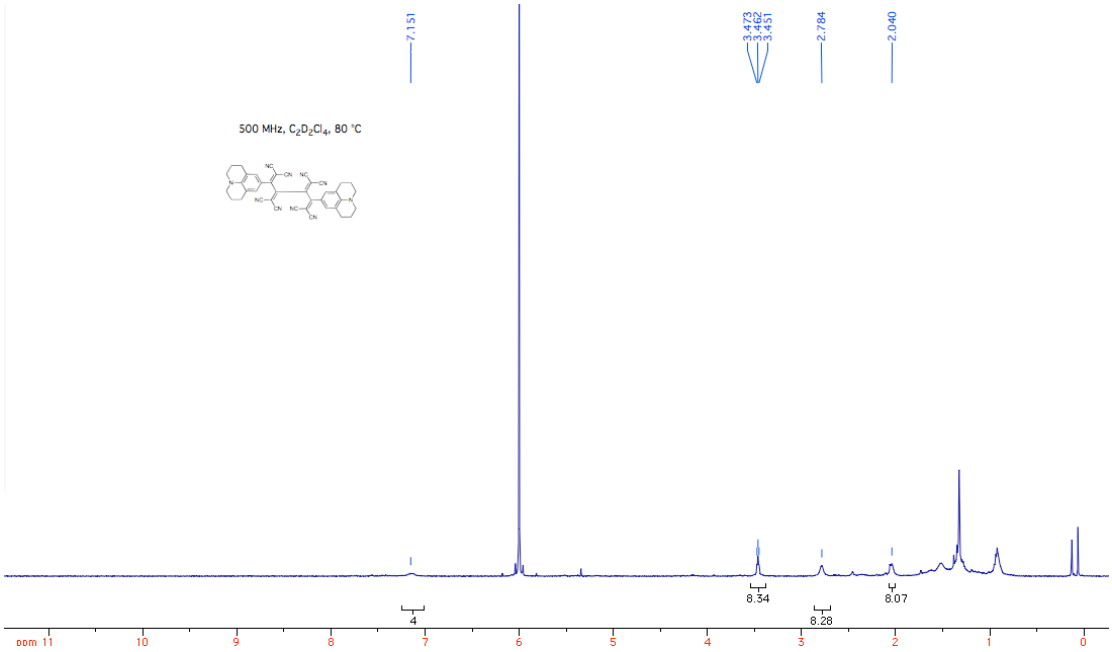
N	-5.37663739582548	-0.36484367280176	4.75097496717442
N	0.67007799725567	-5.43461023589887	6.53570354611448
N	11.50396121024796	-1.92020836261990	0.56567142470323
N	-3.25954964067769	8.37946506292918	1.26656854466433
N	-0.23842062457758	4.52162365512453	7.85927384780272
N	3.44858585127842	8.36022864557525	-0.71781064043377
N	0.31324225564411	5.15367794980529	-7.60063480859837
N	-11.42834427034220	-1.63517717234879	-0.12881508938809
N	-0.89854078996763	-4.85705520746353	-7.08751209394287
N	5.29584808513621	-0.09558638850399	-4.89917179899435
C	-0.60196610511953	-1.37515234856461	4.04550800139428
C	1.05364308869558	0.10549200265162	2.59330118957646
C	0.04046210718031	2.48724931503479	1.43719310041244
C	-0.02602705525037	2.60354593996341	-1.36841806519467
C	-1.11053406726036	0.35542578301666	-2.71159369896466
C	0.49712778679318	-1.04669560358092	-4.28984759789540
C	-3.22270542255200	-0.76830188896672	4.37822111741955
C	0.15972661026163	-3.60344230753130	5.38355637446386
C	3.68249841609747	-0.48087234300928	2.05909215029772
C	4.68037381873428	-2.98214831227828	2.00601130143169
C	7.20958696374808	-3.45308833922363	1.49895972905009
C	8.98708651861123	-1.45357593470992	1.03695632535609
C	7.97172794042394	1.05578518894507	1.09097498177029
C	5.43419182194711	1.50830942831155	1.56098220512757
C	12.59447237619352	-4.45624509478617	1.07753353776391
C	13.17679018648713	-0.10388577690788	-0.79350154034471
C	-0.79846803927098	4.45282435082915	2.95788675700260
C	-2.10753874133851	6.62663367695698	1.99256869408141
C	-0.49281153723203	4.42058810766879	5.65714301579582
C	0.87250215336220	4.66192704861226	-2.72343061667332
C	2.24532521207520	6.70851342957155	-1.58423976781358
C	0.56592558035549	4.86285514171854	-5.41525929524759
C	-3.74335376423487	-0.20849956068788	-2.17846553207015
C	-5.42563016829225	1.77654907428262	-1.47100359618414
C	-7.93900454108513	1.33529876451342	-0.87939573283474
C	-8.98319350068612	-1.16552364123470	-0.88138002536735
C	-7.30856553132969	-3.14393139631015	-1.67523440537082
C	-4.80376229595821	-2.68300806860016	-2.29545765058233
C	-12.83962647132222	0.29078932642701	1.35292085017648

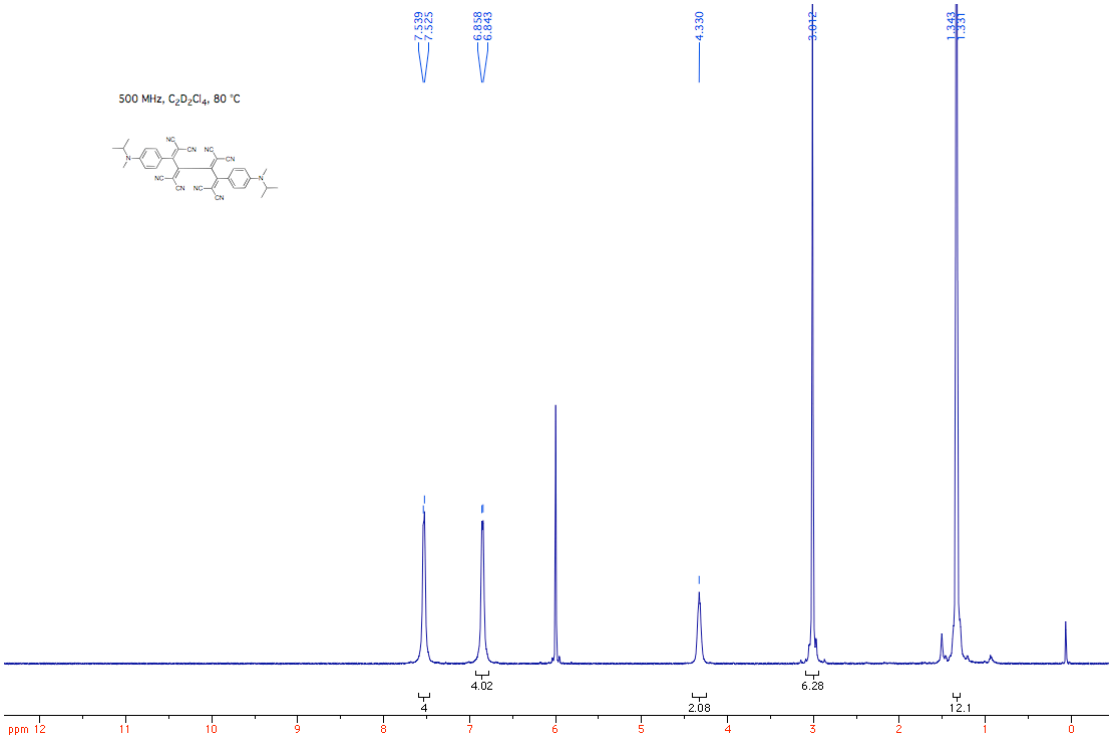
C	-12.87899352221658	-3.91413976911111	-0.91337905036700
C	-0.32896305424842	-3.13864808485108	-5.79762261556478
C	3.13191485647207	-0.48263068690811	-4.57364195082658
C	3.41989071732659	-4.61446937544806	2.25805396687771
H	7.79526787254621	-5.43921003148815	1.35415922963706
H	9.21101511864996	2.69051255850485	0.81430003827021
H	4.80362591056378	3.49169185443164	1.64787887006682
H	-4.75989187527825	3.75043118553290	-1.47718305636327
H	-9.12854836826735	2.97974633036206	-0.44677670195722
H	-7.95504167882316	-5.11149781329473	-1.67805317634350
H	-3.60570785117827	-4.31228968627938	-2.77122956181726
H	-11.39188995926581	1.62039947455909	2.06735513498774
H	-14.85943688501914	-3.42700577173122	-0.42600108171217
H	11.25356407495151	-5.39887761174849	2.37808634577726
H	14.85460978910895	-1.25923474933583	-1.28812441916926
H	-12.86923364860464	-4.33087923564605	-3.79483179556416
C	-10.98911020465911	-4.87936130538730	-4.54568953495955
H	-14.21817420846617	-5.86725958840097	-4.28110884759890
H	-13.47775771198556	-2.58967117456643	-4.79894125984732
H	-12.26989059078417	-6.33046707574104	0.60482085918062
C	-10.41857876995508	-7.18097510619530	0.10374324841963
H	-12.25849532261437	-5.94549434861095	2.66686759666350
H	-13.74367182297480	-7.78014702346268	0.22314467915236
H	-14.72550447137785	1.77918647046022	-0.28877877780642
C	-15.62852625432267	3.30475258803429	0.84027168442230
H	-13.76917537127382	2.66737475983416	-1.93531466975339
H	-16.26430409654788	0.54609260429363	-1.02193976172362
H	-14.08006646485246	-0.83444891767427	3.73357689919835
C	-15.64512974105998	-2.16780856840259	3.29780521971114
H	-12.65831842970878	-1.82128821287775	4.92136388631601
H	-14.89818251546267	0.72654133695130	4.87763803040577
H	15.10792604395188	-4.31195213402827	2.54050373493121
C	14.89884168121913	-3.17993464465086	4.29666087170023
H	15.69084816913169	-6.25392415078777	3.09194653724298
H	16.67615834615505	-3.49676375724856	1.40424122671121
H	12.80819264440442	-6.07142751649433	-1.33415576425448
C	13.47314291048172	-8.00830958286488	-0.85972167718468
H	10.95403187986550	-6.23519066719137	-2.30760256007454
H	14.18228291169164	-5.25016136331411	-2.69818011775469
H	12.07110712196689	0.78710292440413	-3.33388689590018
C	11.55239418394333	-0.85266988420111	-4.53607185076184
H	10.34732872494772	1.96188965973869	-3.13793604833809
H	13.51512469610219	1.92189346711516	-4.35607262470873
H	14.19451685616589	2.06724716730398	0.86822674313625
C	12.74796765011985	3.51636238668110	1.32522958690095
H	14.96532394046027	1.33696039987555	2.67877789590125
H	15.75151071705599	3.04658168643514	-0.14921777126142

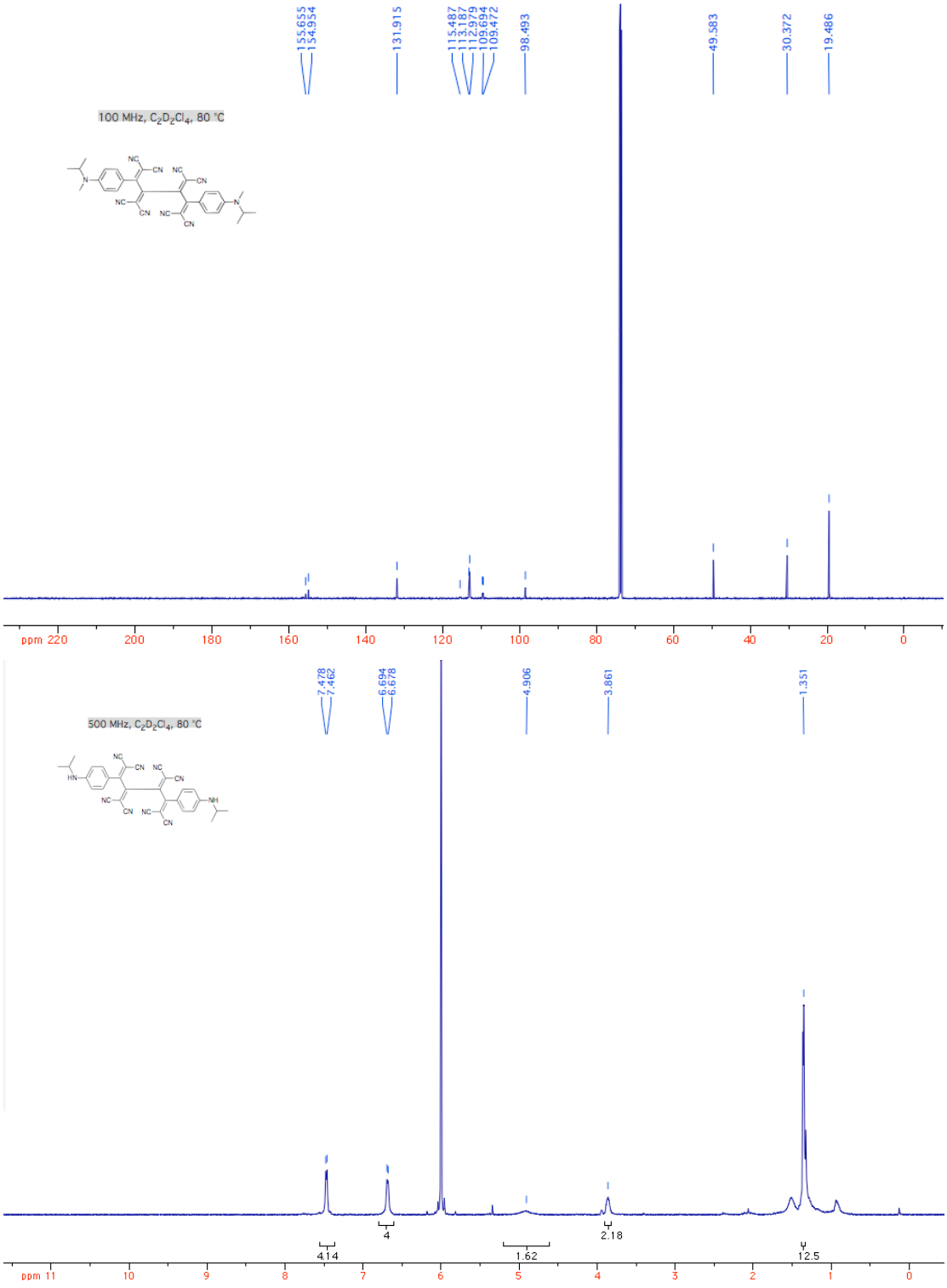
NMR Spectra:

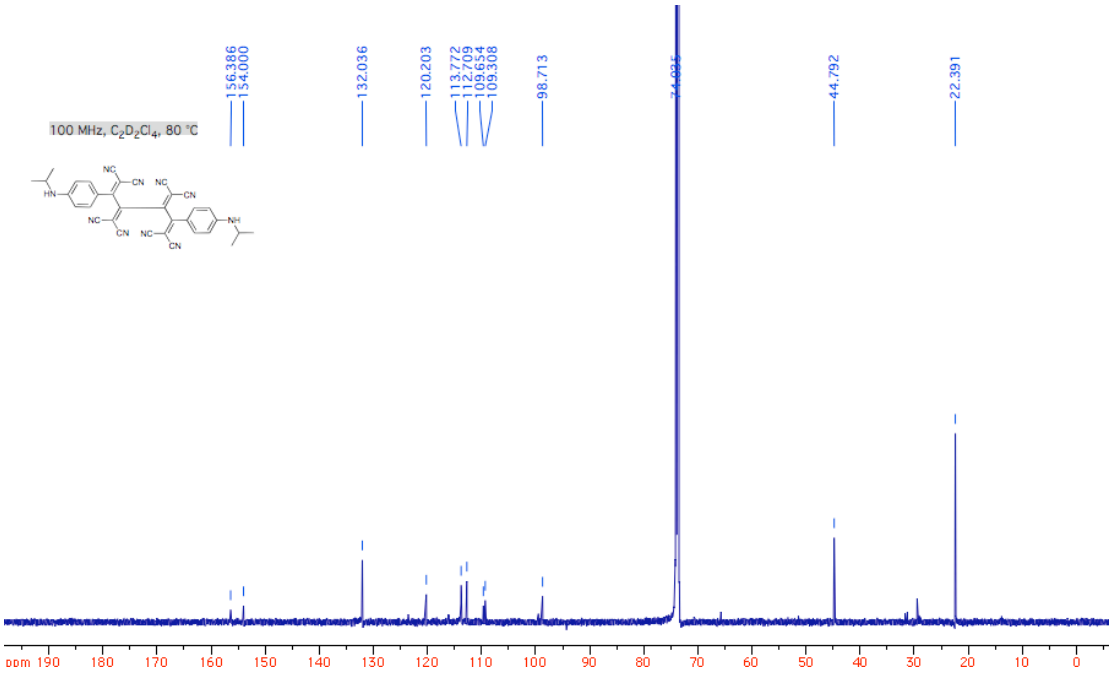

7.427
7.411
6.860
6.842
4.129
4.115
4.101
4.088
4.074
4.060
4.046
1.385
1.371
500 MHz, C2D2Cl4, 80 °C
2.03
2
2.07
12
ppm 12
11
10
9
8
7
6
5
4
3
2
1
0

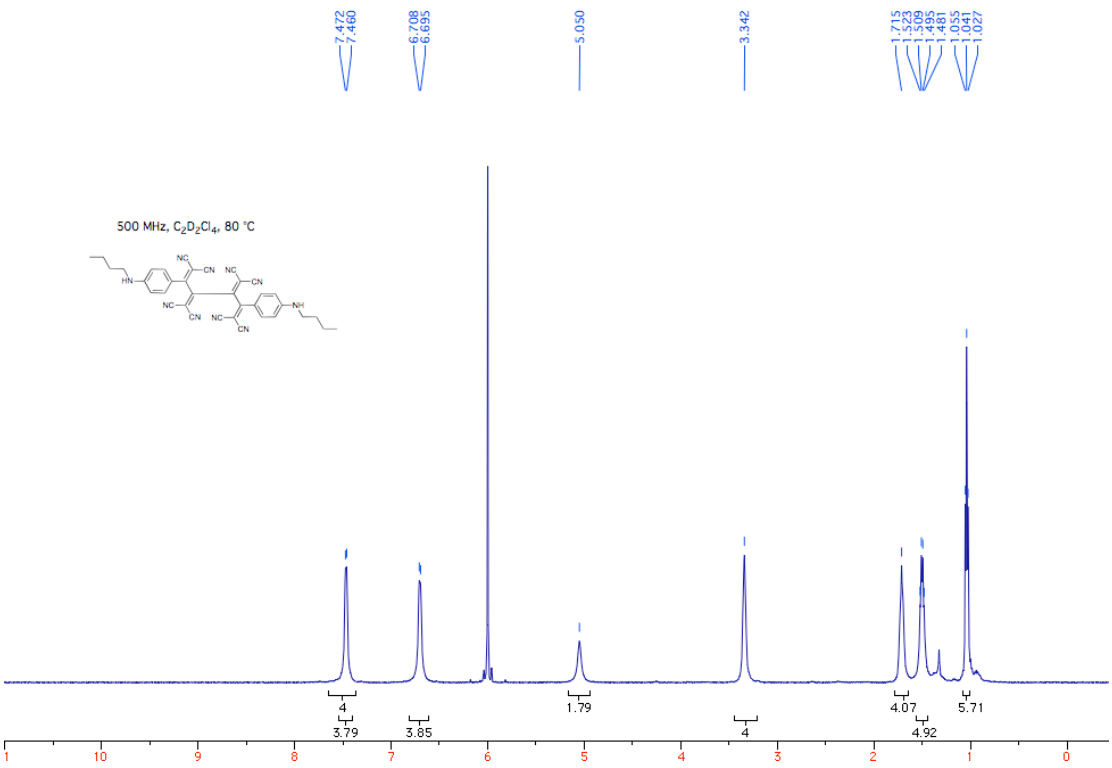

155.568
134.159
131.445
115.315
113.477
109.881
109.669
98.543
49.032
20.741
100 MHz, C2D2Cl4, 80 °C
ppm 220
200
180
160
140
120
100
80
60
40
20
0

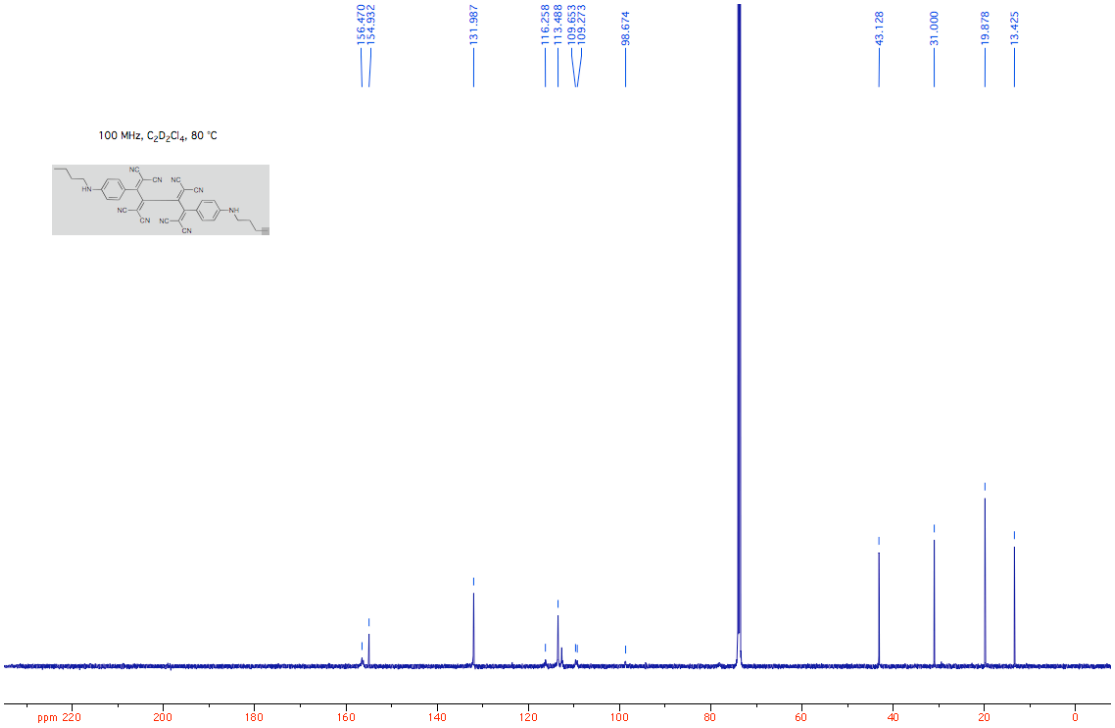

7.151
3.473
3.462
3.451
2.784
2.040
500 MHz, $C_2D_2Cl_4$, 80 °C
4
8.34
8.28
8.07
ppm 11 10 9 8 7 6 5 4 3 2 1 0

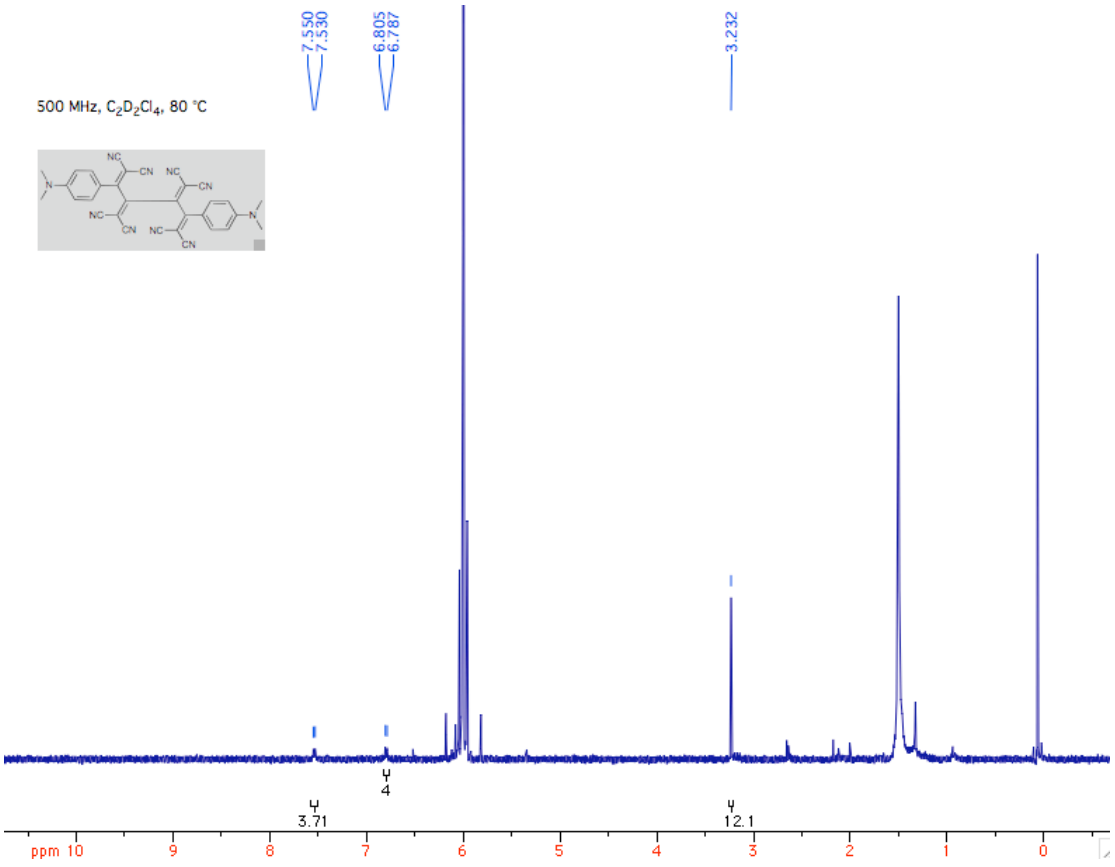

7.539
7.525
6.858
6.843
4.330
3.012
1.343
1.331
500 MHz, $C_2D_2Cl_4$, 80 °C
4
4.02
2.08
6.28
12.1
ppm 12 11 10 9 8 7 6 5 4 3 2 1 0

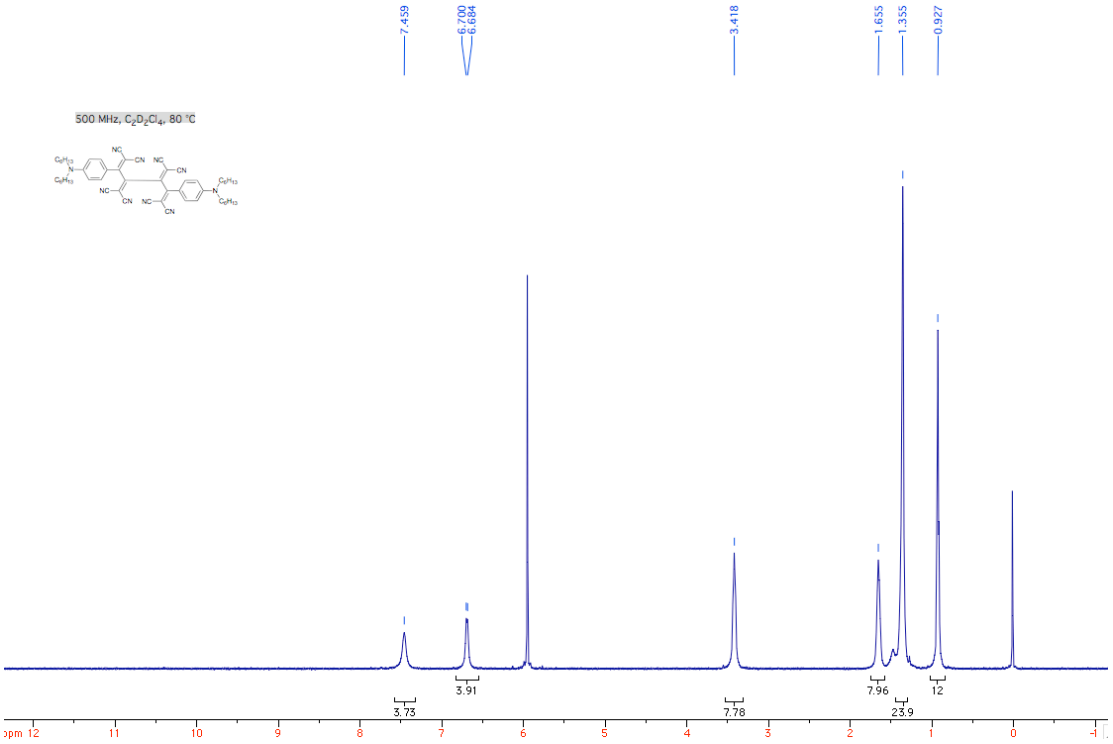

155.655
154.954
131.915
115.487
113.187
112.979
109.694
109.472
98.493
49.583
30.372
19.486
100 MHz, C2D2Cl4, 80 °C
ppm 220
200
180
160
140
120
100
80
60
40
20
0
7.478
7.462
6.694
6.678
4.906
3.861
1.351
500 MHz, C2D2Cl4, 80 °C
4.14
4
1.62
2.18
12.5
ppm 11
10
9
8
7
6
5
4
3
2
1
0

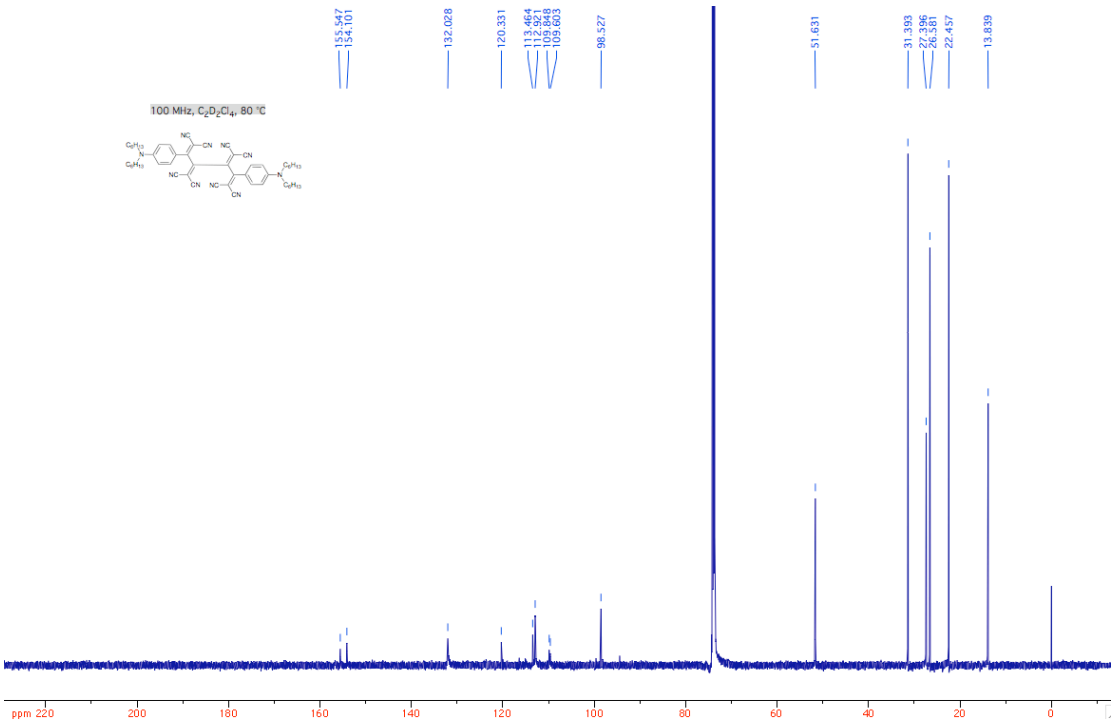

156.386
154.000
132.036
120.203
113.772
112.709
109.654
109.308
98.713
74.935
44.792
22.391
100 MHz, $C_2D_2Cl_4$, 80 °C
ppm 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

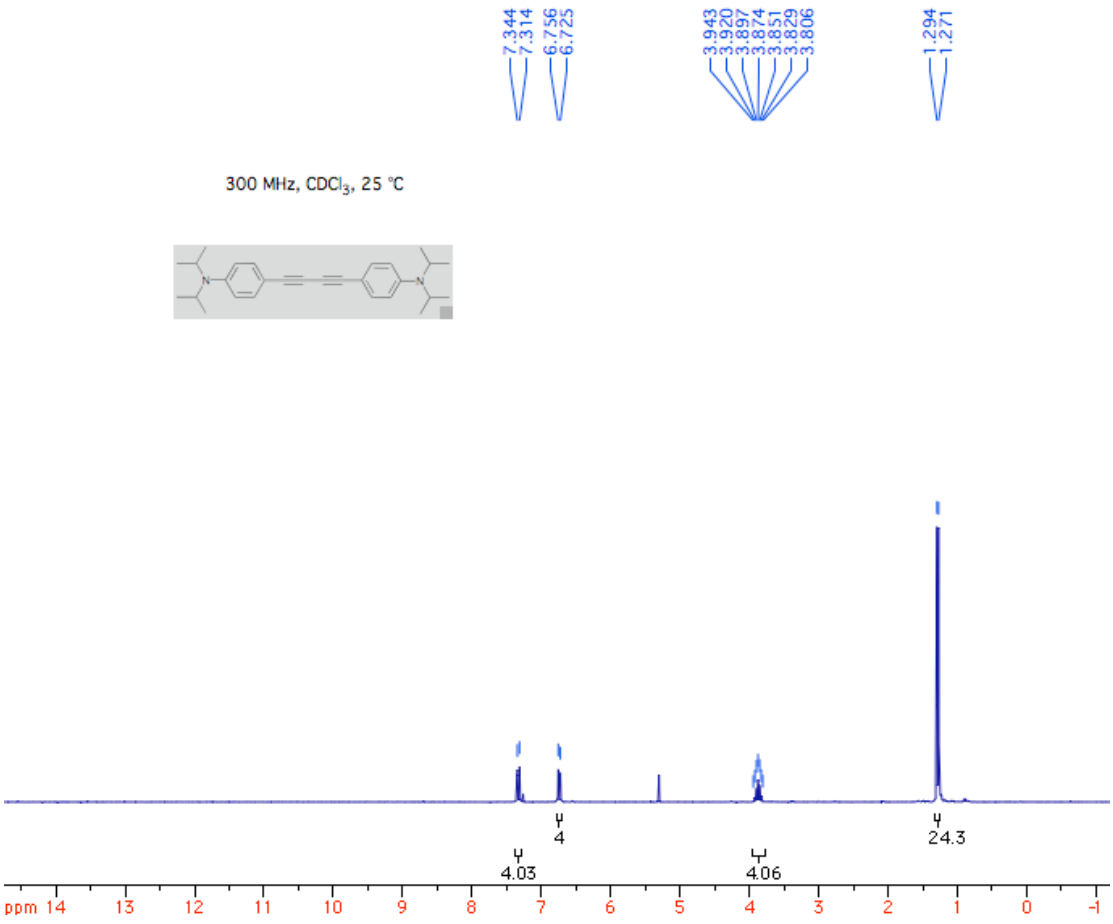

7.472
7.460
6.708
6.695
5.050
3.342
1.715
1.523
1.509
1.495
1.481
1.055
1.041
1.027
500 MHz, $C_2D_2Cl_4$, 80 °C
4
3.79
3.85
1.79
4
4.07
4.92
5.71
1 10 9 8 7 6 5 4 3 2 1 0

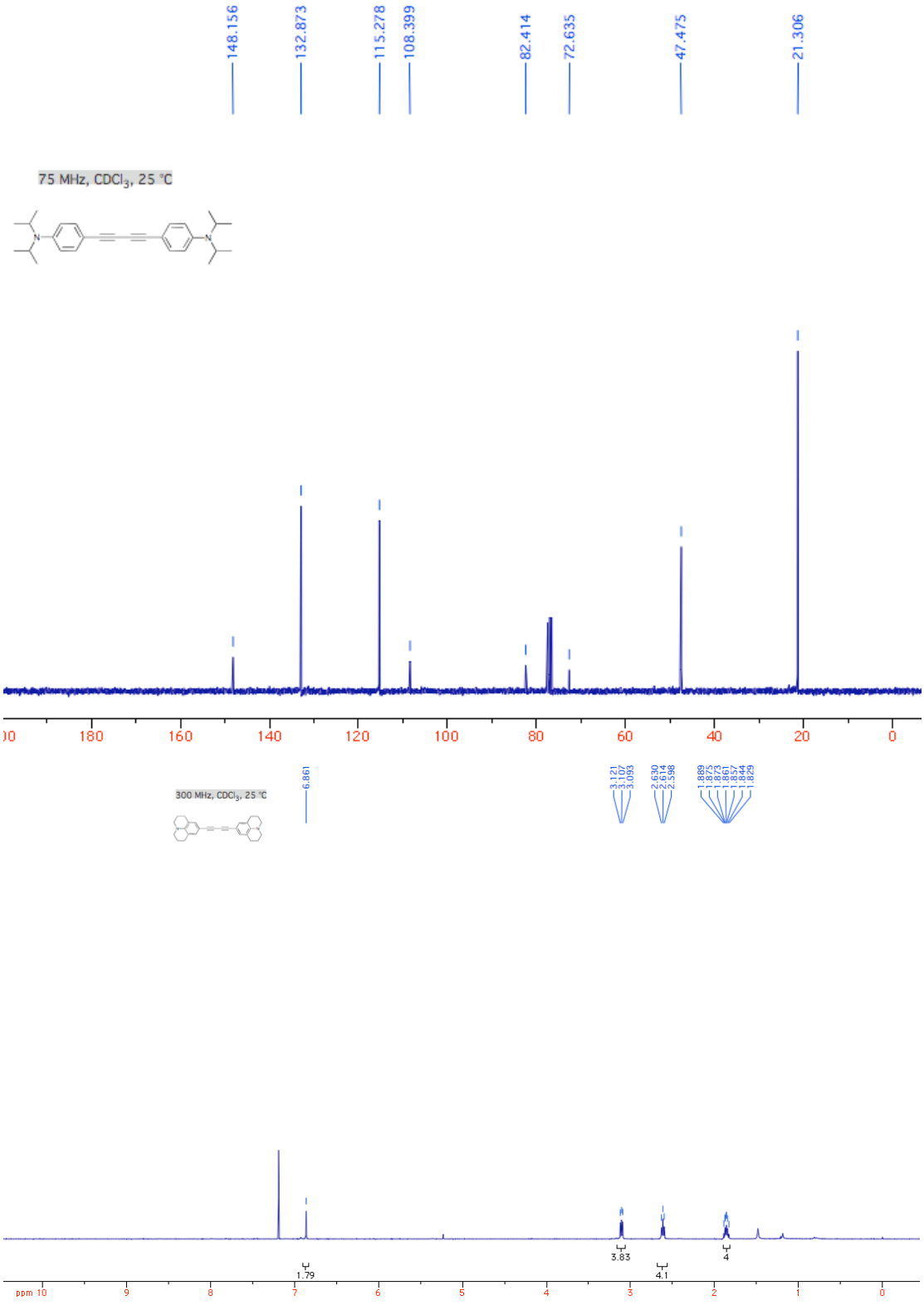

156.470
154.932
131.987
116.258
113.488
109.653
109.273
98.674
43.128
31.000
19.878
13.425
100 MHz, C2D2Cl4, 80 °C
ppm 220
200
180
160
140
120
100
80
60
40
20
0

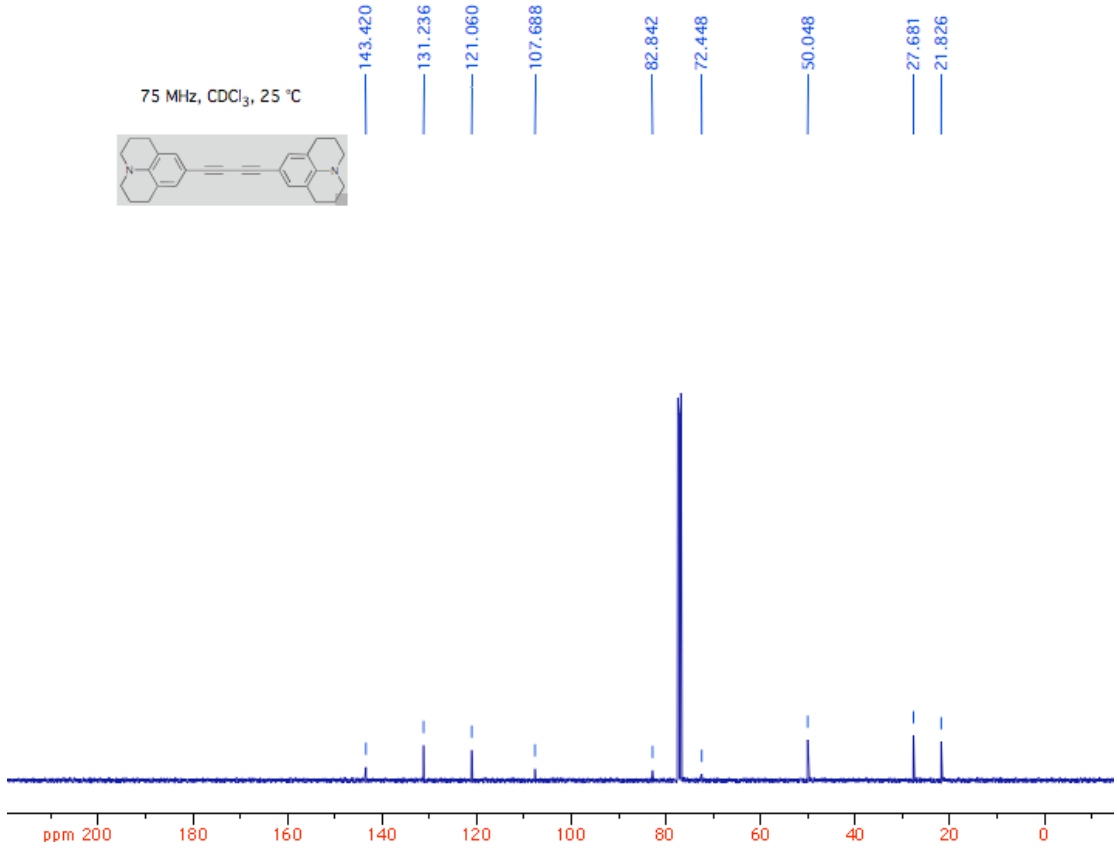

7.550
7.530
6.805
6.787
3.232
500 MHz, C2D2Cl4, 80 °C
4
3.71
12.1
ppm 10
9
8
7
6
5
4
3
2
1
0

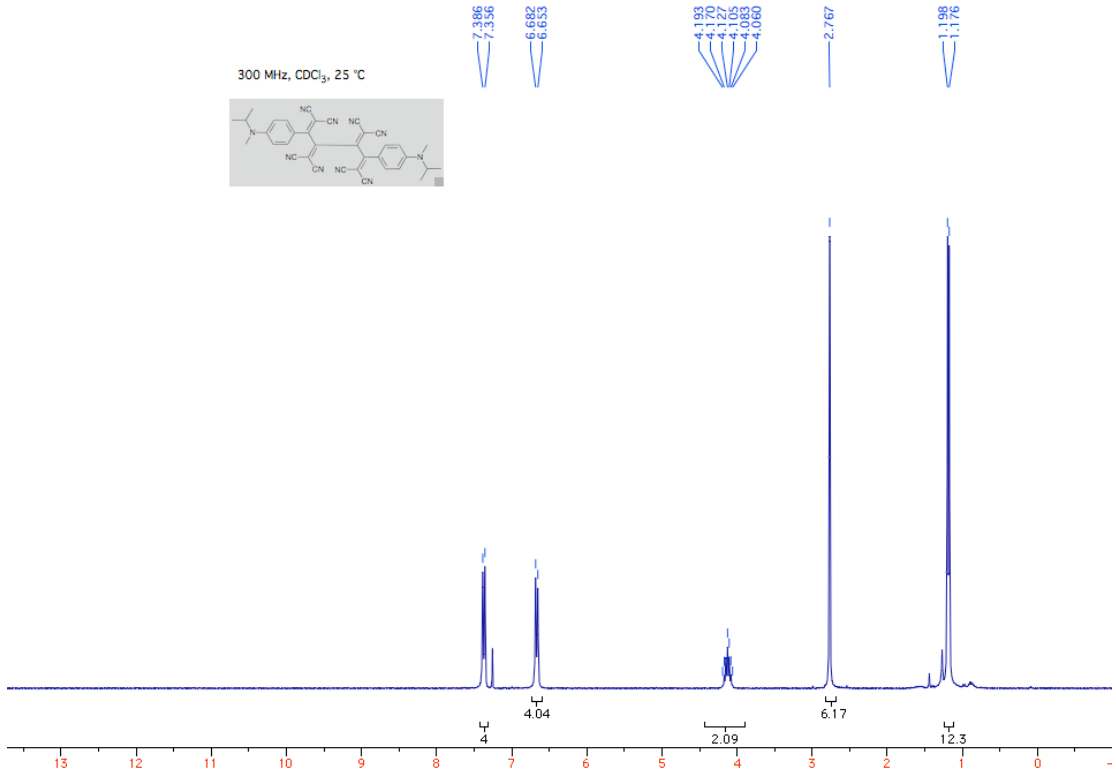

7.459
6.700
6.684
3.418
1.655
1.355
0.927
500 MHz, C2D2Cl4, 80 °C
3.73
3.91
7.78
7.96
23.9
12
ppm 12
11
10
9
8
7
6
5
4
3
2
1
0

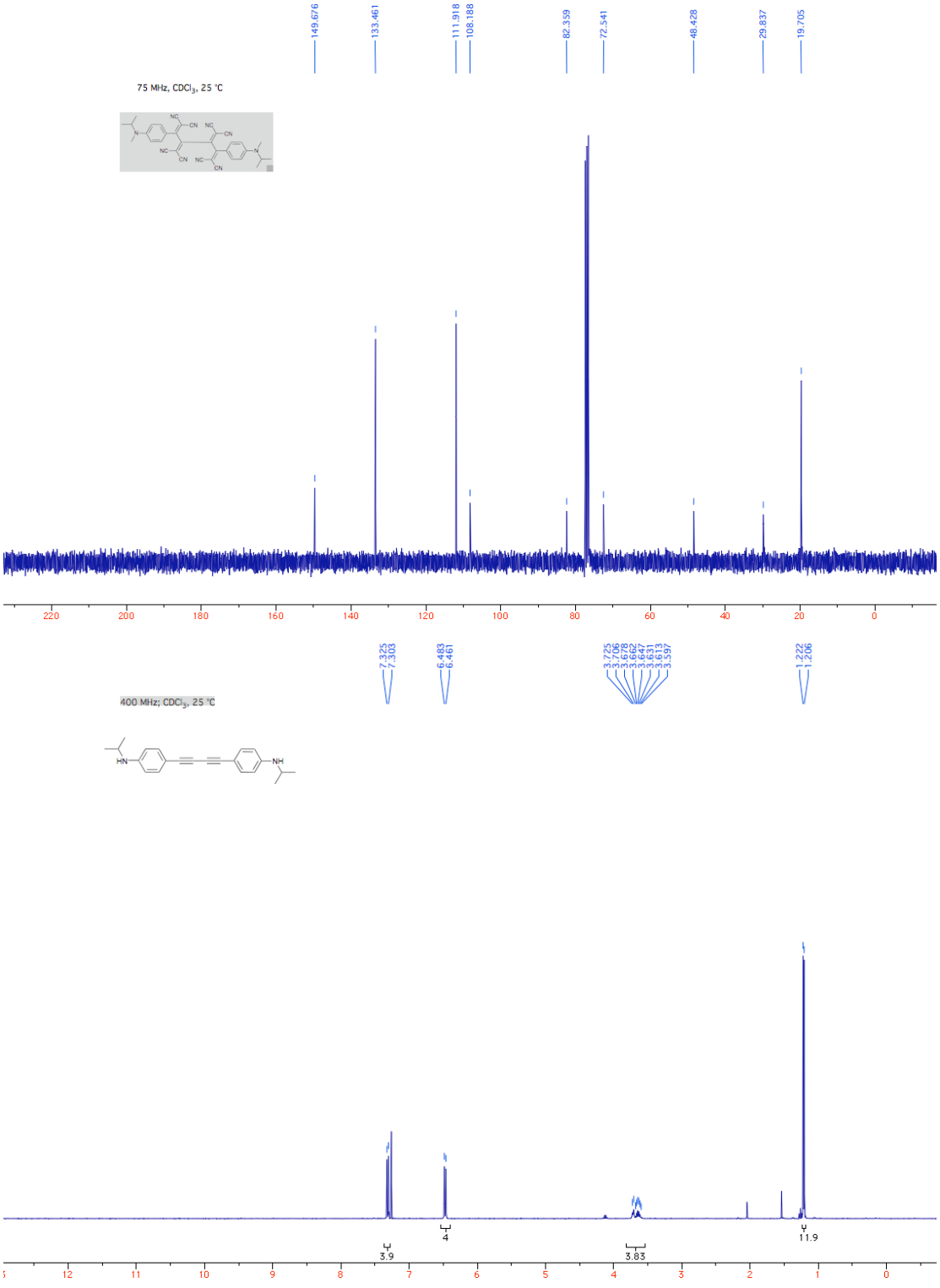

155.547
154.101
132.028
120.331
113.464
112.921
109.868
109.603
98.527
51.631
31.393
27.396
26.581
22.457
13.839
100 MHz, C2D2Cl4, 80 °C
ppm 220
200
180
160
140
120
100
80
60
40
20
0

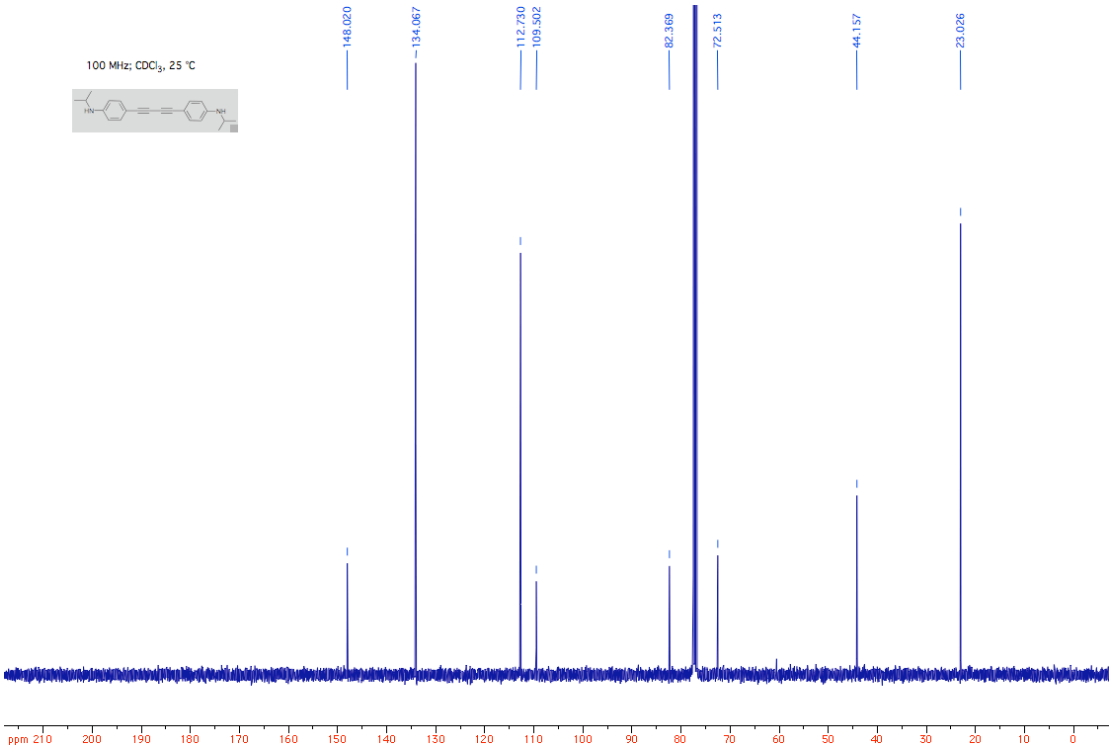

7.344
7.314
6.756
6.725
3.943
3.920
3.897
3.874
3.851
3.829
3.806
1.294
1.271
300 MHz, CDCl3, 25 °C
4
24.3
4.03
4.06
ppm 14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1

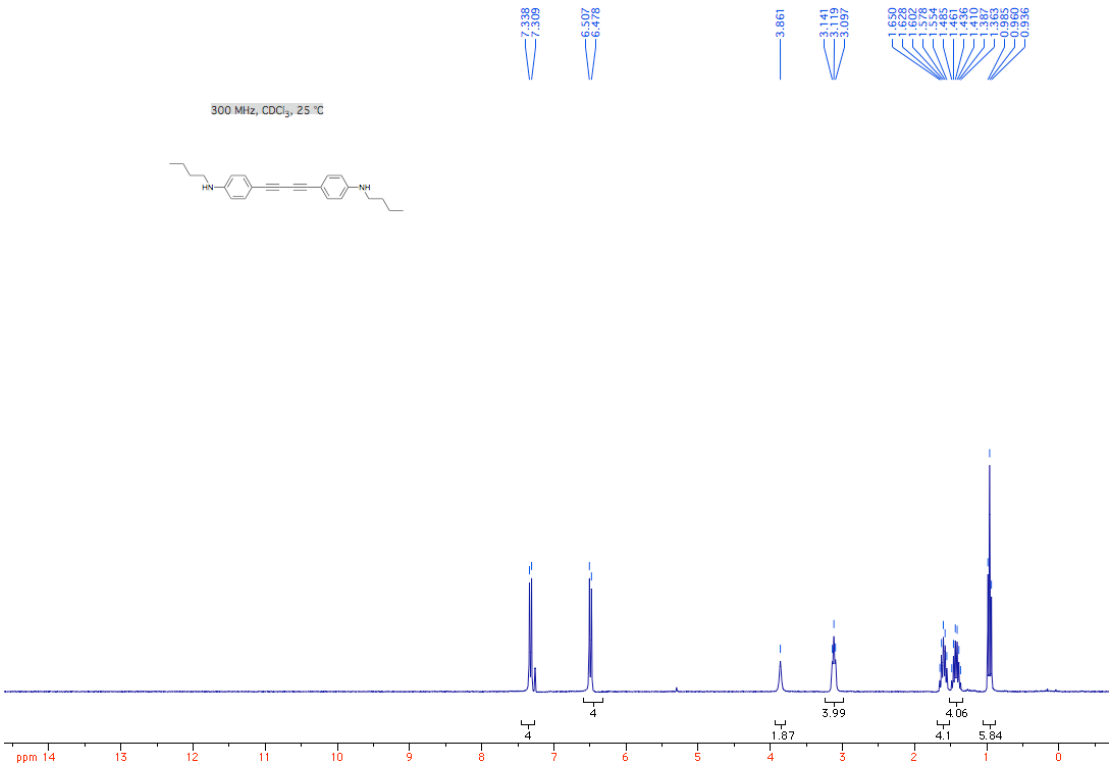

148.156
132.873
115.278
108.399
82.414
72.635
47.475
21.306
75 MHz, CDCl3, 25 °C
300 MHz, CDCl3, 25 °C
6.861
3.121
3.107
3.093
2.630
2.614
2.598
1.889
1.882
1.873
1.861
1.847
1.844
1.829
1.79
3.83
4.1
4
ppm

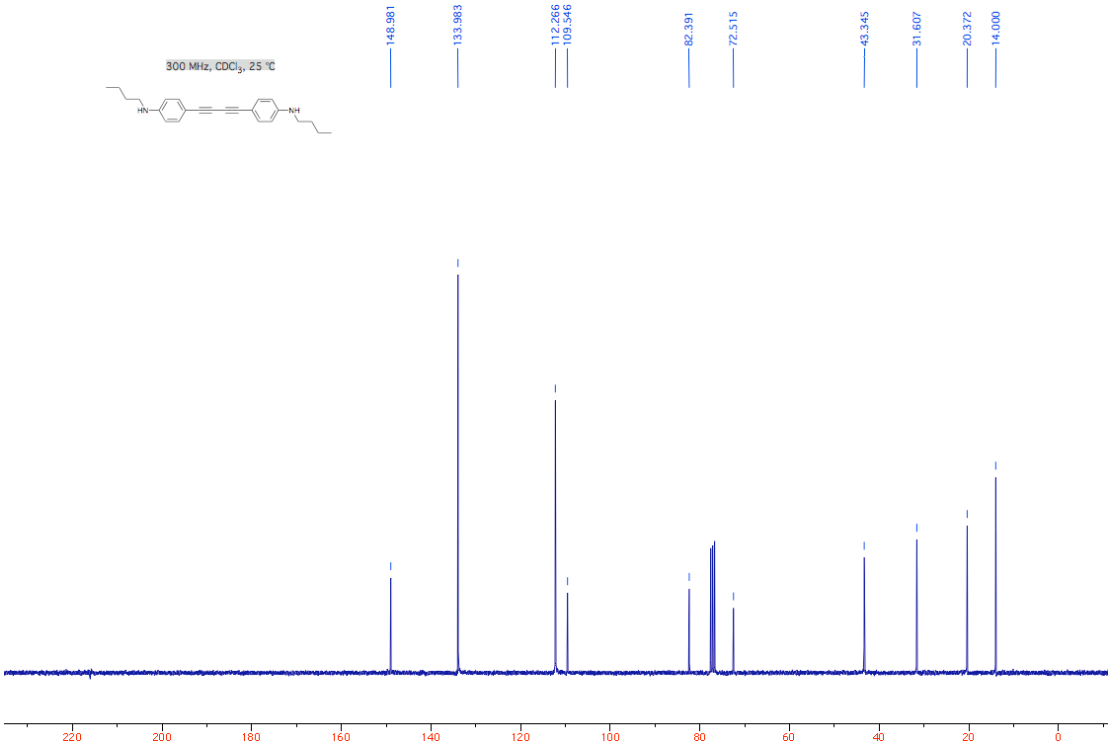

143.420
131.236
121.060
107.688
82.842
72.448
50.048
27.681
21.826
75 MHz, CDCl3, 25 °C
ppm 200
180
160
140
120
100
80
60
40
20
0

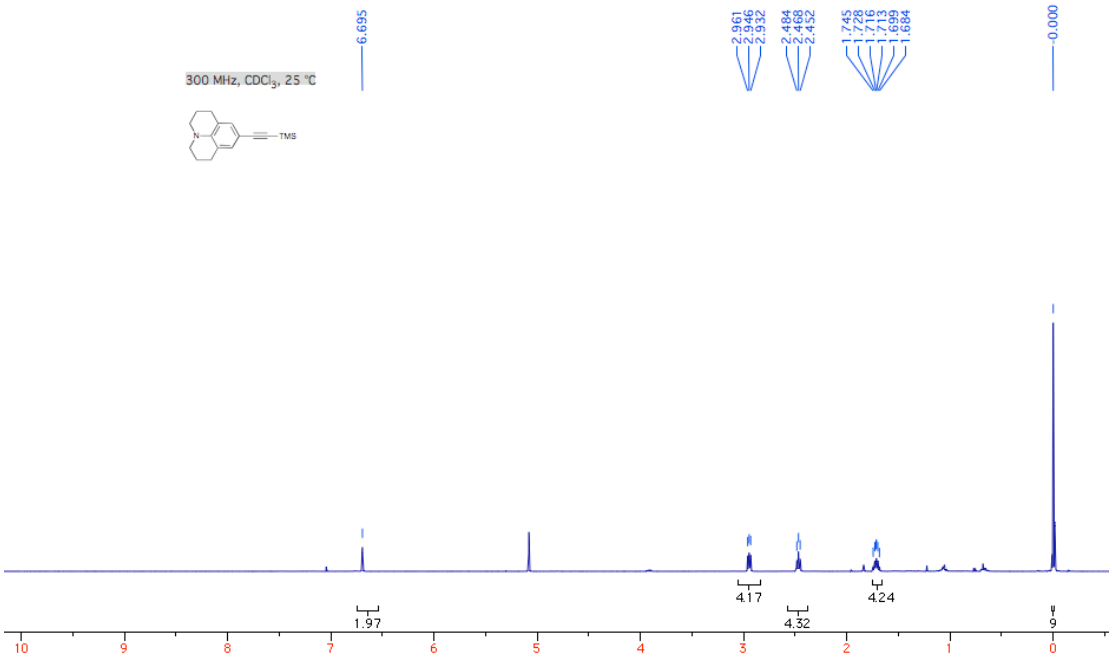

7.386
7.356
6.682
6.653
4.193
4.170
4.127
4.105
4.083
4.060
2.767
1.198
1.176
300 MHz, CDCl3, 25 °C
4
4.04
2.09
6.17
12.3
13
12
11
10
9
8
7
6
5
4
3
2
1
0

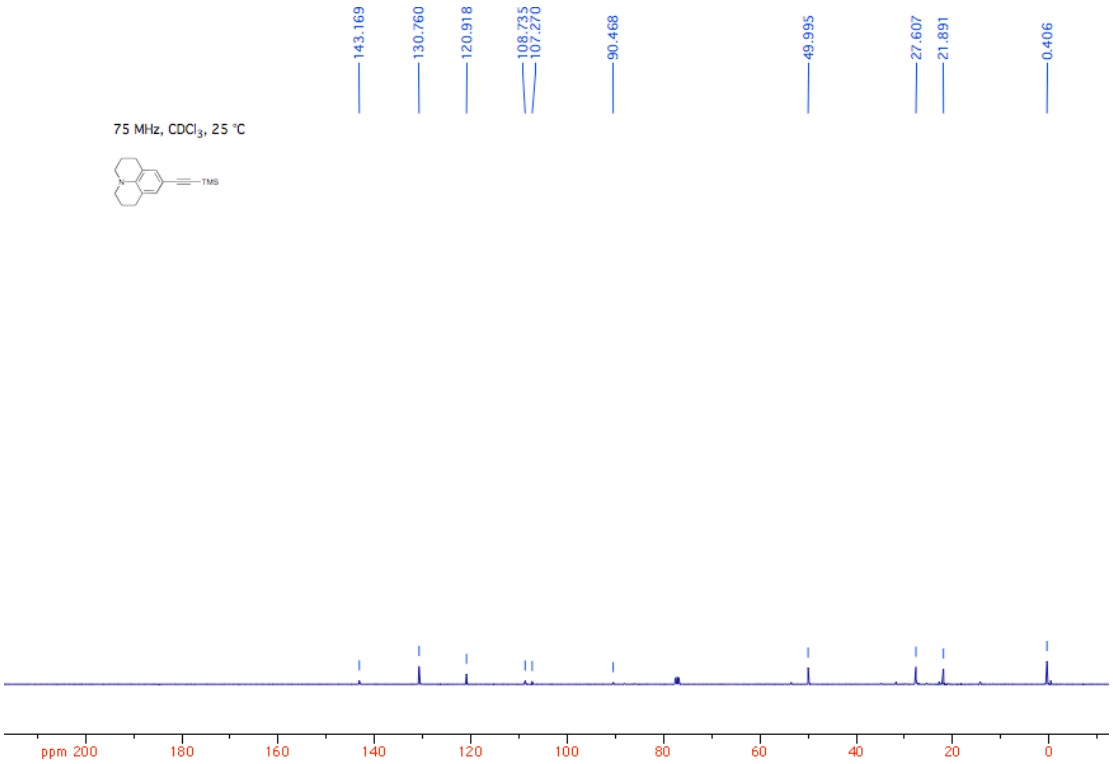

149.676
133.461
111.918
108.188
82.359
72.541
48.428
29.837
19.705
75 MHz, CDCl3, 25 °C
7.325
7.303
6.483
6.461
3.725
3.706
3.678
3.662
3.647
3.631
3.613
3.597
1.222
1.206
400 MHz; CDCl3, 25 °C
HN
NH
3.9
4
3.83
11.9

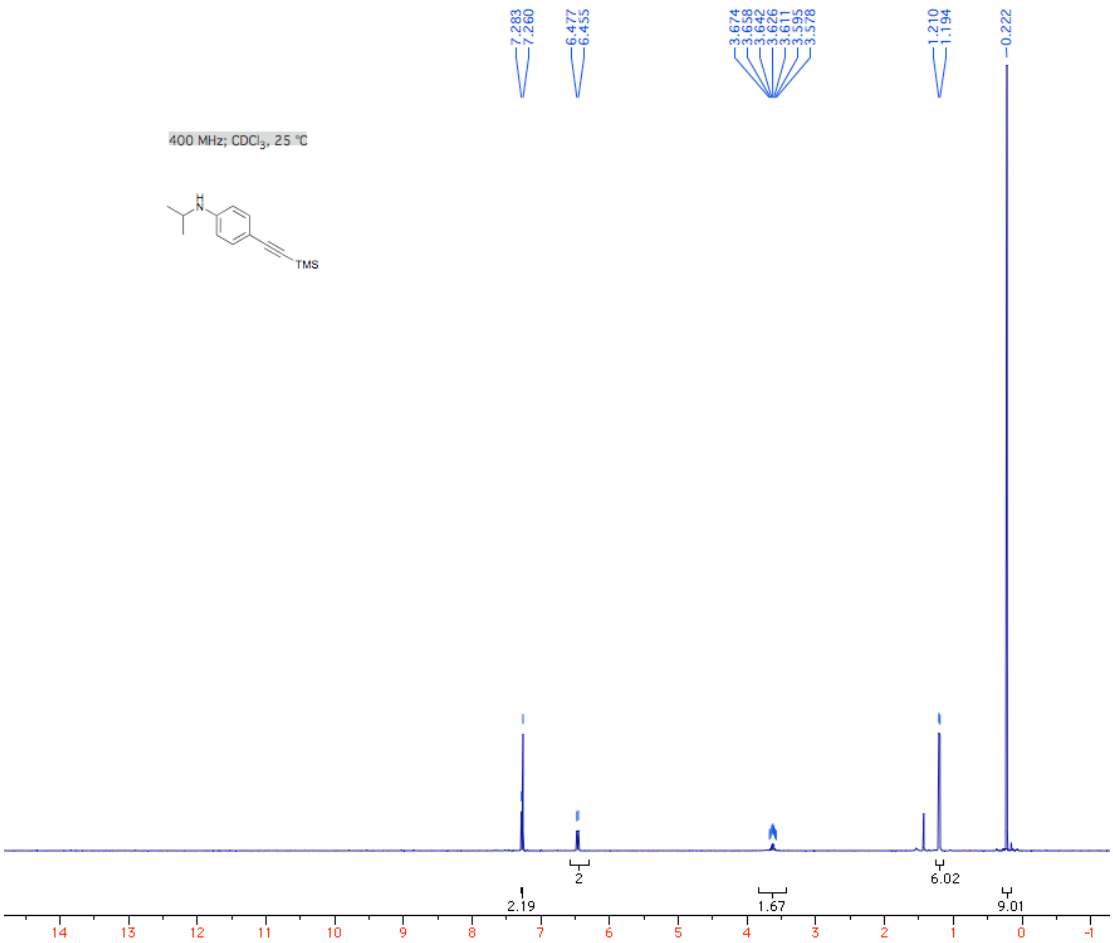

148.020
134.067
112.730
109.502
82.369
72.513
44.157
23.026
100 MHz; CDCl3, 25 °C
ppm 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

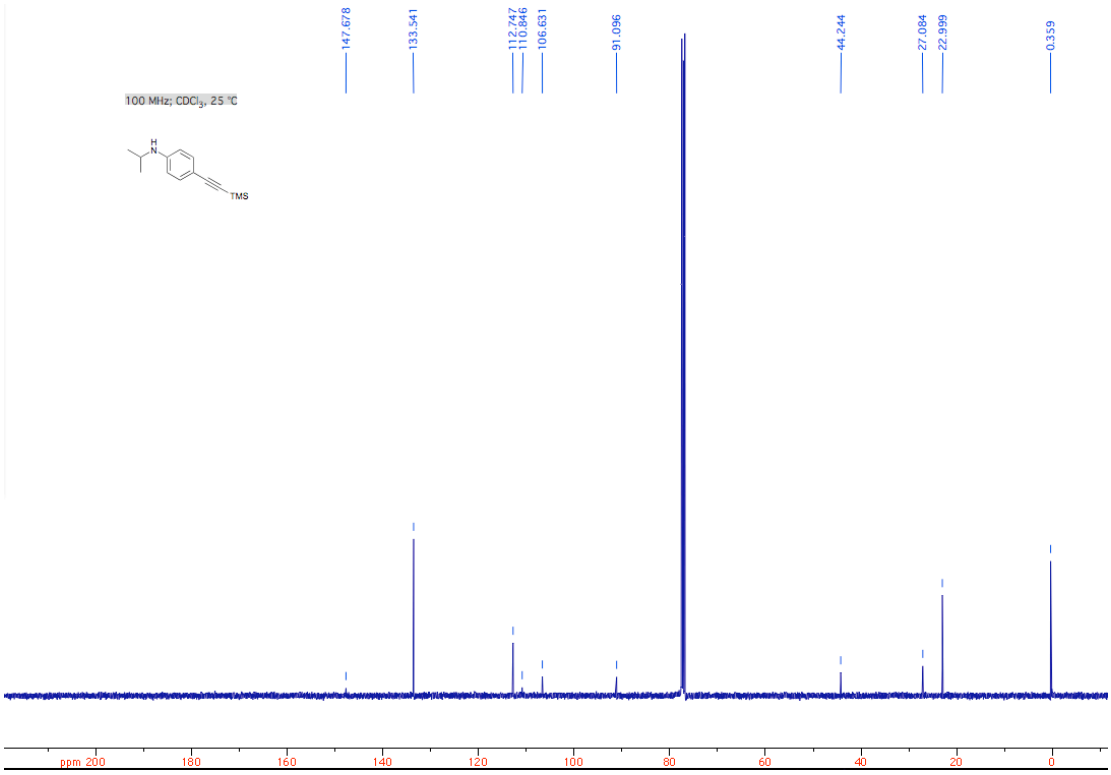

7.338
7.309
6.507
6.478
3.861
3.141
3.119
3.097
1.650
1.628
1.622
1.607
1.579
1.554
1.485
1.461
1.436
1.410
1.387
1.365
0.985
0.960
0.936
300 MHz, CDCl3, 25 °C
4
4
3.99
1.87
4.06
4.1
5.84
ppm 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0


300 MHz, CDCl3, 25 °C
148.981
133.983
112.266
109.546
82.391
72.515
43.345
31.607
20.372
14.000


300 MHz, CDCl3, 25 °C
6.695
2.961
2.946
2.932
2.484
2.468
2.452
1.745
1.728
1.716
1.711
1.699
1.684
0.000
1.97
4.17
4.32
4.24
9


143.169
130.760
120.918
108.735
107.270
90.468
49.995
27.607
21.891
0.406
75 MHz, CDCl3, 25 °C
TMS
ppm 200
180
160
140
120
100
80
60
40
20
0


7.283
7.260
6.477
6.455
3.674
3.658
3.642
3.626
3.611
3.595
3.578
1.210
1.194
0.222
400 MHz; CDCl3, 25 °C
H
N
TMS
2
6.02
2.19
1.67
9.01
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1



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