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Twisted Pyrene-fused Azaacenes

Sandeep More,[a,b,c] Sunil Choudhary,[b,c] Alexander Higelin,[d] Ingo Krossing,[b,d] Manuel Melle-Franco[e] and Aurelio Mateo-Alonso[a,f]*

[a] POLYMAT, University of the Basque Country UPV/EHU, Avenida de Tolosa 72, E-20018 Donostia-San Sebastian, Spain. E-mail: amateo@polymat.eu
[b] School of Soft Matter Research, Freiburg Institute for Advanced Studies (FRIAS), Albert-Ludwigs-Universität Freiburg, Albertstraße 19, 79104 Freiburg, Germany
[c] Institut für Organische Chemie und Biochemie, Albert-Ludwigs-Universität Freiburg, Albertstraße 21, 79104 Freiburg, Germany
[d] Institut für Anorganische und Analytische Chemie, Albert-Ludwigs-Universität Freiburg, Albertstraße 21, 79104 Freiburg, Germany
[e] Centro de Ciências e Tecnologias de Computação, CCTC Universidade do Minho, 4710-057 Braga, Portugal
[f] Ikerbasque, Basque Foundation for Science, Bilbao, Spain

Supporting Information

Reagents, Solvents and Equipment

Reagents for synthesis were, if not otherwise specified, purchased from Aldrich, Fluka or Acros. All reactions were carried out under argon, with magnetic stirring. Commercial chemicals and solvents were used as received. Petrol ether refers to the fraction that distills between 40-60 °C. Anhydrous solvents were dried using a *MB SPS* Solvent Purification System. In the case of dry THF the first and second column is charged with molecular sieves (2Å) type II. Compounds **4**, **1a**, **6a**, **6b**, **3a** and **3b** were prepared according previously reported procedures.[1]

Chromatographic Methods

Column chromatography was carried out using silica gel 60 (40-63 μm) from Fluka. Analytical thin layer chromatography (TLC) was done using aluminum sheets (20x20 cm) pre-coated with silica gel RP-18W 60 F254 from Merck, aluminum foils (20x20 cm) covered with nano-silica gel from Fluka. Column chromatography was carried out by using Merck silica gel with particle size 40-63 μm. UV-active compounds were detected with a UV-lamp from CAMAG at wavelength λ = 254 or 366 nm.

UV-Vis-NIR and Emission

Spectra were recorded on a Perkin-Elmer *Lambda 950* spectrometer, and a *LS55* Perkin-Elmer Fluorescence spectrometer, respectively.

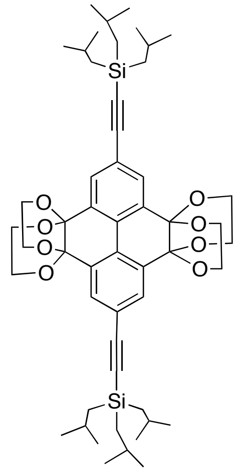
Cyclic Voltammetry.

Electrochemical measurements were carried out on a Princeton Applied Research Parstat 2273 in a 3-electrode single compartment cell with Pt disc working electrode (Ø = 0.5 mm), a platinum wire counter electrode (Ø = 0.5 mm) and a silver wire pseudoreference electrode. The cell and the electrodes were custom made. The reduction potentials were referred to SCE using ferrocene (Fc) as internal reference ($E_{1/2\ Fc}^{SCE}$ = +0.48 V) after the measurements. Anhydrous THF were dried using a *MB SPS* Solvent Purification System.

X-Ray Diffraction.

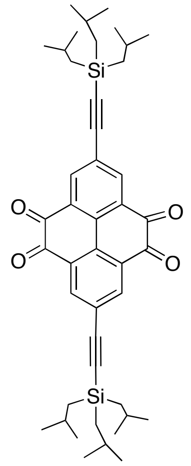
Data for the crystal structures were collected on a Bruker SMART APEX2 CCD area detector diffractometer with Mo-Kα radiation. The single crystals were coated at room temperature with perfluoroether oil and mounted on 0.1 mm micromounts. The structures were solved by direct or dual space methods in SHELX[4] and OLEX2[5] and refined by least squares on weighted F^2 values for all reflections. All hydrogen atoms were included in the refinement in calculated positions by a riding model. The graphical representations were prepared with mercury.

Compound 5b



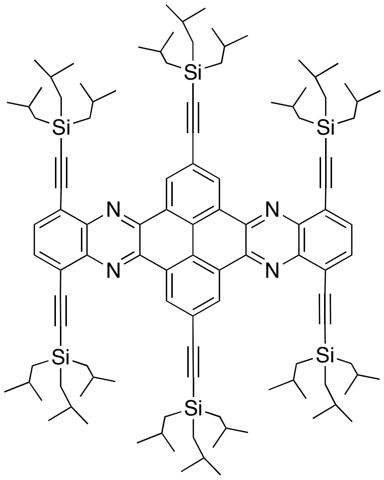
Compound **4** (100 mg, 0.14 mmol) was added to a degassed solution of *i*-Pr_2NH (10 mL) and dry THF (10 mL) and the solution was degassed. Subsequently CuI (2.061 mg, 0.0108 mmol) and $[Pd(PPh_3)_2Cl_2]$ (7.70 mg, 0.0108 mmol) were added and degassed. Then triisobutylsilyl acetylene (0.129 mL, 0.57 mmol) was added, the solution was once again degassed and heated at 80 °C under Argon overnight. The resulting mixture was filtered over celite and washed with 200 mL of CH_2Cl_2. Removal of the solvent under vacuum and purification of the crude product by column chromatography (petrol ether : ethyl acetate = 20 : 1) yielded **5b** as white solid (80 mg, 62 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm = 7.78 (s, 4H); 4.18 (br s, 8H); 3.65 (br s, 8H); 1.90 (m, 6H); 1.01 (d, 36H, *J*=10Hz); 0.68 (d, 12H, *J*=10Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 133.33, 130.40, 128.56, 125.27, 106.27, 96.09, 92.30, 61.51, 29.82, 26.45, 25.21. MS: Found 883.3 $[M]^+$ Calculated Mass: 883.31

Compound 2b



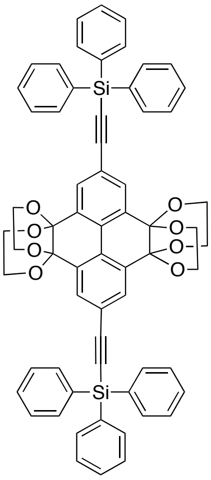
A solution of **5b** (100 mg, 0.125 mmol) in a mixture of TFA-H_2O (9:1, 10 ml) was stirred at room temperature for 8 hrs and reaction was monitored by TLC. After completion, the reaction mixture was poured in ice cold water and the precipitate was filtered then the solid was washed with water, which after drying purified by column chromatography (petrol ether : CH_2Cl_2; 7 : 3) offered **2b** as dark orange solid (64 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm = 8.37 (s, 4H); 1.85 (m, 6H); 0.95 (d, 36H, *J*=15Hz); 0.70 (d, 12H, *J*=15Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 177.07, 139.20, 132.76, 130.73, 127.32, 102.52, 102.05, 26.27, 25.07, 24.70. MS: Found 707.6 $[M]^+$ Calculated Mass: 707.10

Compound 1b



In a dry argon flushed Schlenk flask the compound **2b** (50 mg, 0.07 mmol) and amine **3b** (156.43 mg, 0.28 mmol) were suspended in the mixture of acetic acid (3 ml) and ethanol (10 ml). The reaction mixture was heated at 80°C overnight. After completion the reaction, mixture was allowed to cool down to room temperature. Then filtered and the solid was washed with ethanol, which after drying purified by column chromatography (petrol ether : CH_2Cl_2; 7 : 3) under vacuum yielded compound **1b** (56 mg, 78%) as yellow solid. ^{1}H NMR: (300 MHz, $CDCl_3$) δ ppm = 9.72 (s, 4H); 7.97 (s, 4H); 2.08 (m, 18H); 1.14(d, 108H); 0.90 (d, 36H). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 142.60, 141.97, 134.01, 131.64, 130.08, 124.28, 103.87, 103.30, 26.44, 25.27, 25.13. MS: Found 1740.9 $[M]^+$ Calculated Mass: 1741.08. UV-Vis (THF, nm): 269, 320, 335, 408, 432

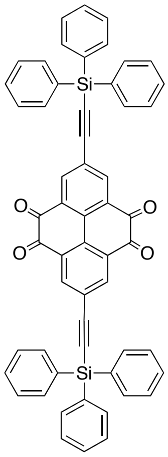
Compound 5c



Compound **4** (100 mg, 0.144 mmol) was added to a degassed solution of *i*-Pr_2NH (10 mL) and dry THF (10 mL) and the solution was degassed. Subsequently CuI (1.37 mg, 0.007 mmol) and $[Pd(PPh_3)_2Cl_2]$ (5.14 mg, 0.007 mmol) were added and degassed. Triphenylsily acetylene (164 mg, 0.57 mmol) was added, the solution was once again degassed and heated at 80 °C under Argon overnight. The resulting mixture was filtered over celite and washed with 200 mL of CH_2Cl_2. Removal of the solvent under vacuum and purification of the crude product by column chromatography ($CHCl_3$: MeOH = 20 : 1) yielded **5c** as white solid (30 mg, 20 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 7.96

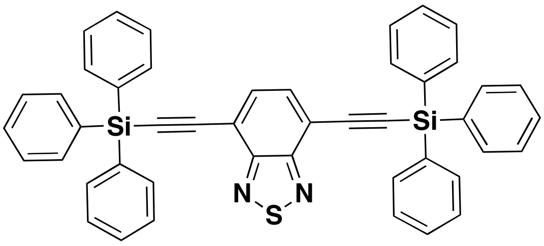
(s, 4H); 7.7 (m, 6H); 7.43 (m, 24H); 4.22 (br s, 8H); 3.68 (br s, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 135.76, 133.75, 133.42, 130.95, 130.14, 128.21, 128.16, 124.50, 101.36, 92.23. MS: Found 1002.9 $[M-1]^+$ Calculated Mass: 1003.24

Compound 2c



A solution of **5c** (20 mg, 0.009 mmol) in a mixture of TFA-H_2O- CH_2Cl_2 (5:1:4, 10 ml) was stirred at 40^{o}C for 24 hrs and reaction was monitored on TLC. After completion, the reaction mixture was poured in ice cold water and extracted with CH_2Cl_2 (10 ml) 2-3 times the organic layer was dried over Na_2SO_4. After removal of solvent under reduced pressure yielded **2c** as orange solid (12 mg, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm = 8.61 (s, 4H); 7.69 (m, 6H); 7.46 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 176.94, 139.77, 135.72, 132.39, 131.00, 130.5, 128.35, 128.28, 126.84, 104.79, 97.28. MS: Found 897.1 $[M + 2NH_4OH]^+$ Calculated Mass: 827.03

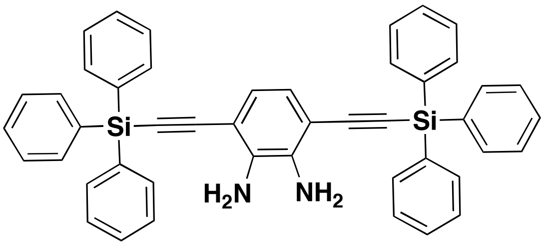
Compound 6c



To an oven-dried Schlenk flask was added dry THF (20 mL) and triethylamine (20 mL), which was then vacuum degassed three times. 4,7-dibromobenzo[c][1,2,5] thiadiazole (0.5 gm, 1.70 mmol), triphenylsilylacetylene (1.065 gm, 3.74 mmol), copper (I) iodide (9.26 mg, 0.05 mmol), and bis(triphenylphosphine)palladium(II) chloride (35.10 mg, 0.05 mmol) were all added at room temperature. The Schlenk flask was sealed and heated to 80^{0}C, whereupon the solution was stirred for 12 h. After the reaction was cooled to room temperature, water (200 mL) was added to the mixture and the aqueous solution was extracted with dichloromethane (2 x 100mL). The combined organic layers were washed with water (3 x 200mL), dried with sodium sulfate, filtered, and dried in vacuo. The residue was purified by column chromatography on silica gel using pure hexane. Compound **6c** (0.900 g, 75% yield) was isolated as yellow crystals. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.805 (s, 2H); 7.792-7.769 (m, 6H), 7.477-7.362 (m, 24H). ^{13}C

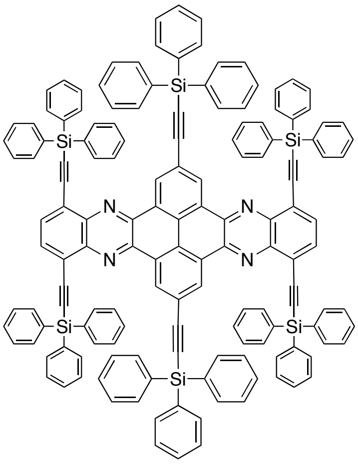
NMR (100 MHz, $CDCl_3$): δ 155.201, 136.409, 133.847, 133.683, 130.804, 128.780, 118.145, 104.959 and 99.477. ESI-MS calcd. For $C_{46}H_{32}N_2SSi_2$ (M^+) 701.2, found 700.2

Compound 3c



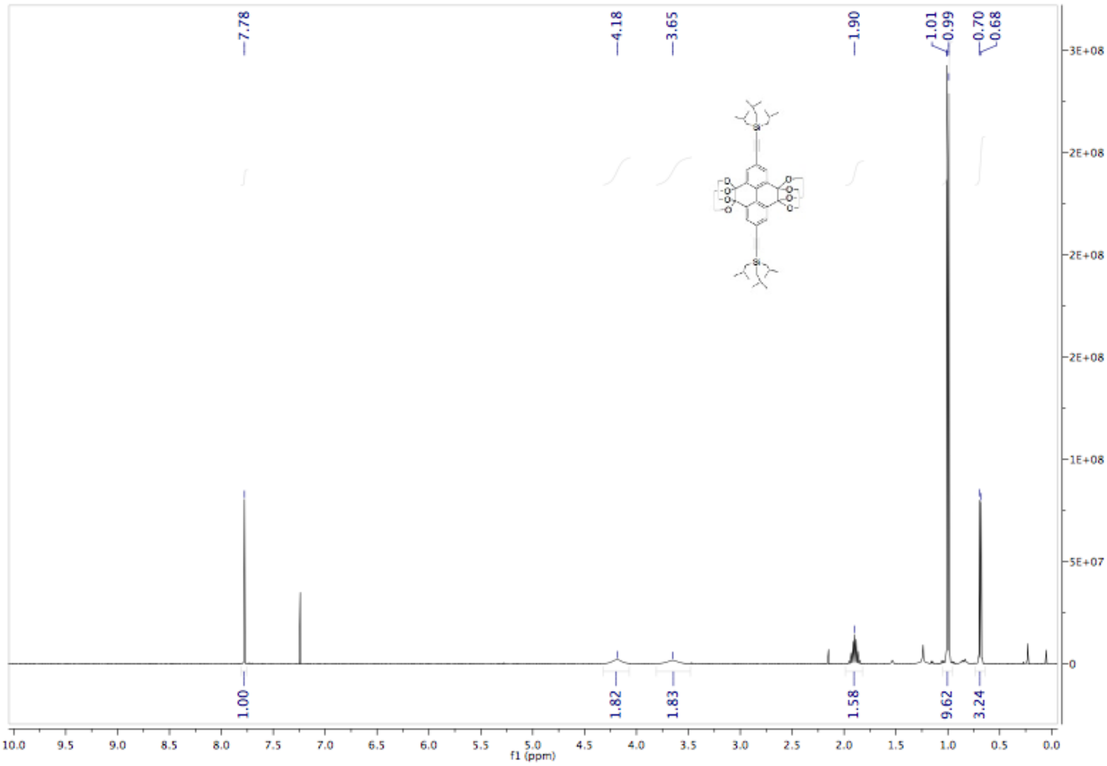
To a solution of **6c** (0.5 g, 0.714 mmol) in THF (20 mL) was added $LiAlH_4$ (108.38 mg, 2.856 mmol) at 0 °C and the mixture was stirred at room temperature for 12 h. The mixture was quenched with saturated NH_4Cl solution and extracted with diethyl ether (3 x 200 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo* to give a light yellow solid (0.920 g, 96%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.708-7.688 (m, 6H), 7.465-7.368 (m, 24H), 6.925 (s, 2H), 3.639 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.867, 135.272, 133.640, 130.426, 130.340, 128.506, 128.371, 128.345 and 128.227. ESI-MS calcd. For $C_{46}H_{36}N_2Si_2$ (M^+) 672.6, found 672.2

Compound 1c



In a dry argon-flushed Schlenk flask, compound **2c** (40 mg, 0.04 mmol) and amine **3c** (92.4 mg, 0.13 mmol) were dissolved in the mixture of acetic acid (3 ml) and ethanol (10 ml). The reaction mixture was heated at 80°C for overnight. After completion the reaction, mixture was allowed to cool down to room temperature. Then filtered and the solid was washed with ethanol. The obtained product was purified by column chromatogryphy (CH_2Cl_2 : petrol ether = 4 : 1) which gave compound **5c** (52 mg, 51%) as yellow solid.

^1H NMR: (500 MHz, $CDCl_3$) δ ppm = 10.06 (s, 4H); 8.19 (s, 4H); 7.91 (m, 24H); 7.26 (m, 48H); 7.14 (m, 6H); 6.98 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 142.54, 135.89, 135.78, 135.65, 135.34, 133.37, 133.04, 132.42, 130.34, 130.19, 129.74, 128.35, 128.32, 128.00, 124.19, 108.24, 106.30, 99.68, 93.45. MS: Found: 2101.654 [M + 3] Calculated Mass: 2098.64. UV-Vis (THF, nm): 280, 334, 348, 411, 436.



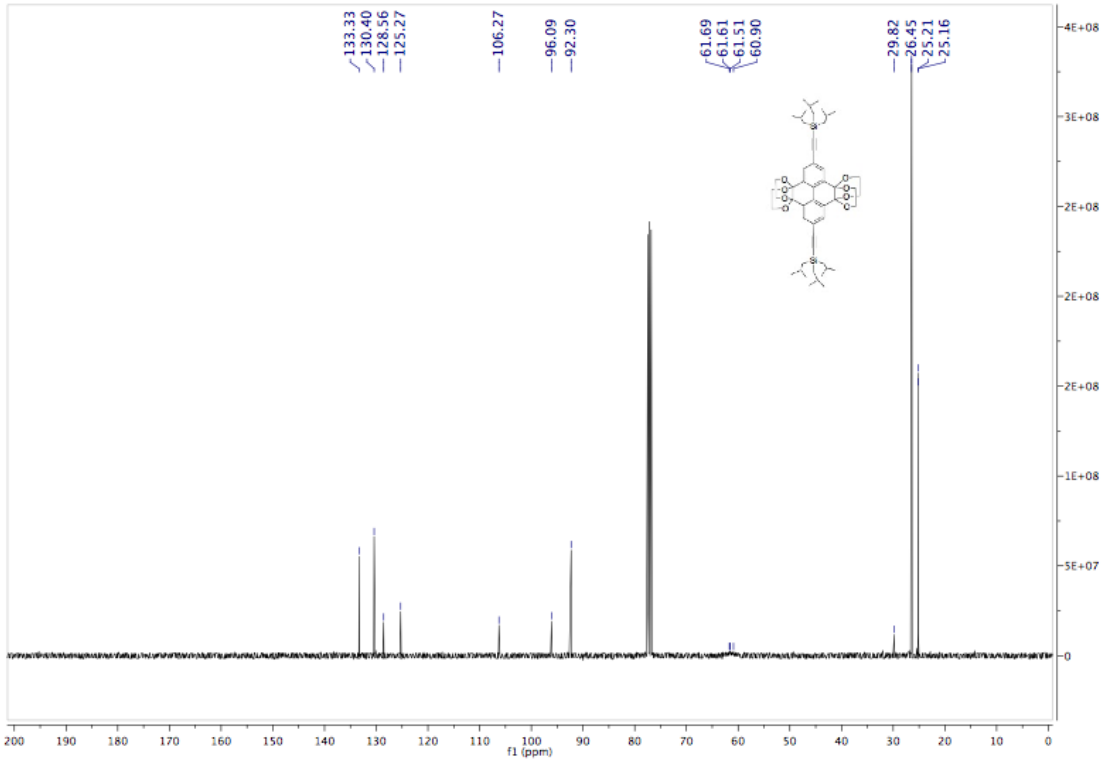


Fig. S1: ^{1}H NMR and ^{13}C NMR of compound **5b** in $CDCl_3$.

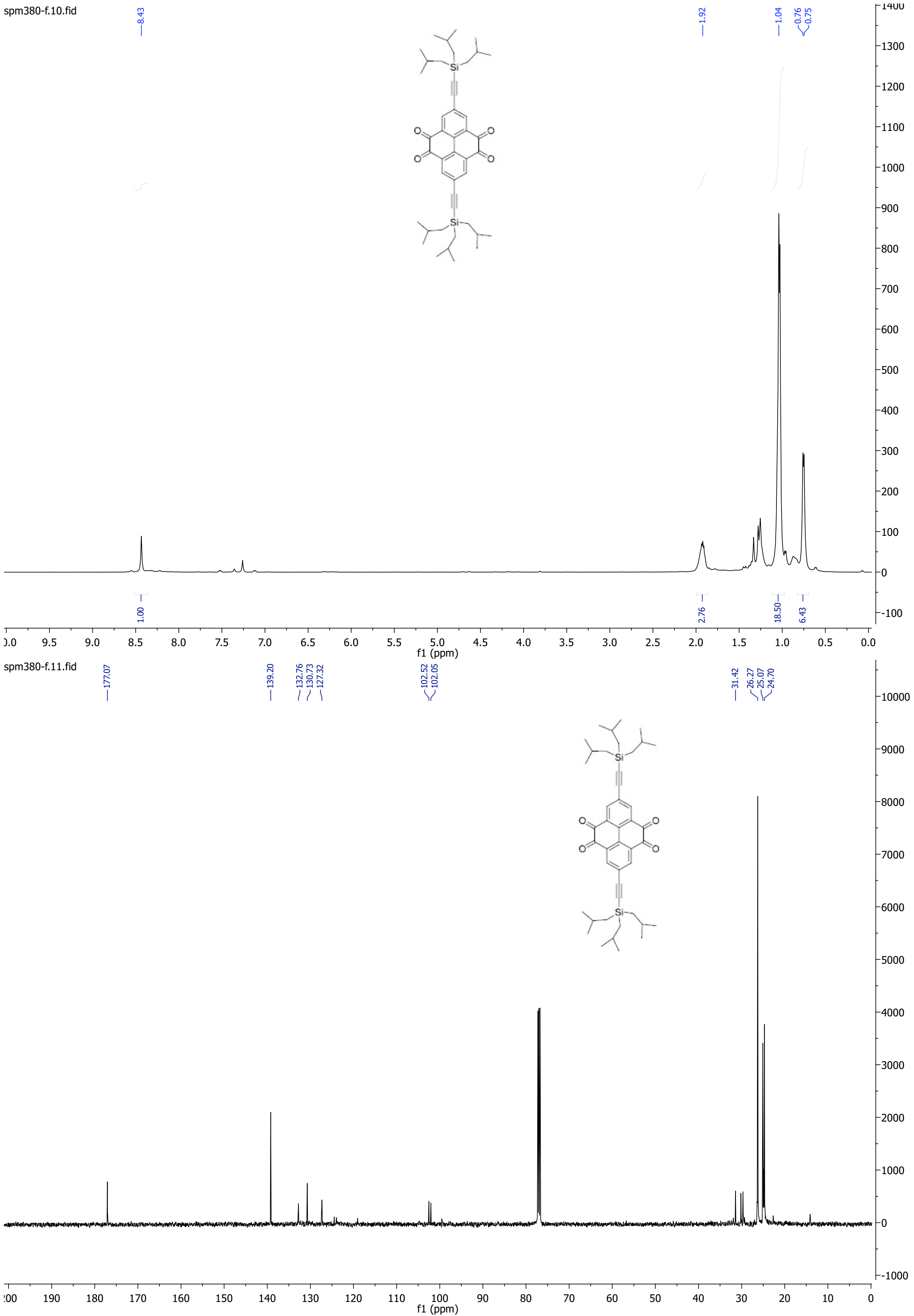


Fig. S2: ^{1}H NMR and ^{13}C NMR of compound **2c** in $CDCl_3$.

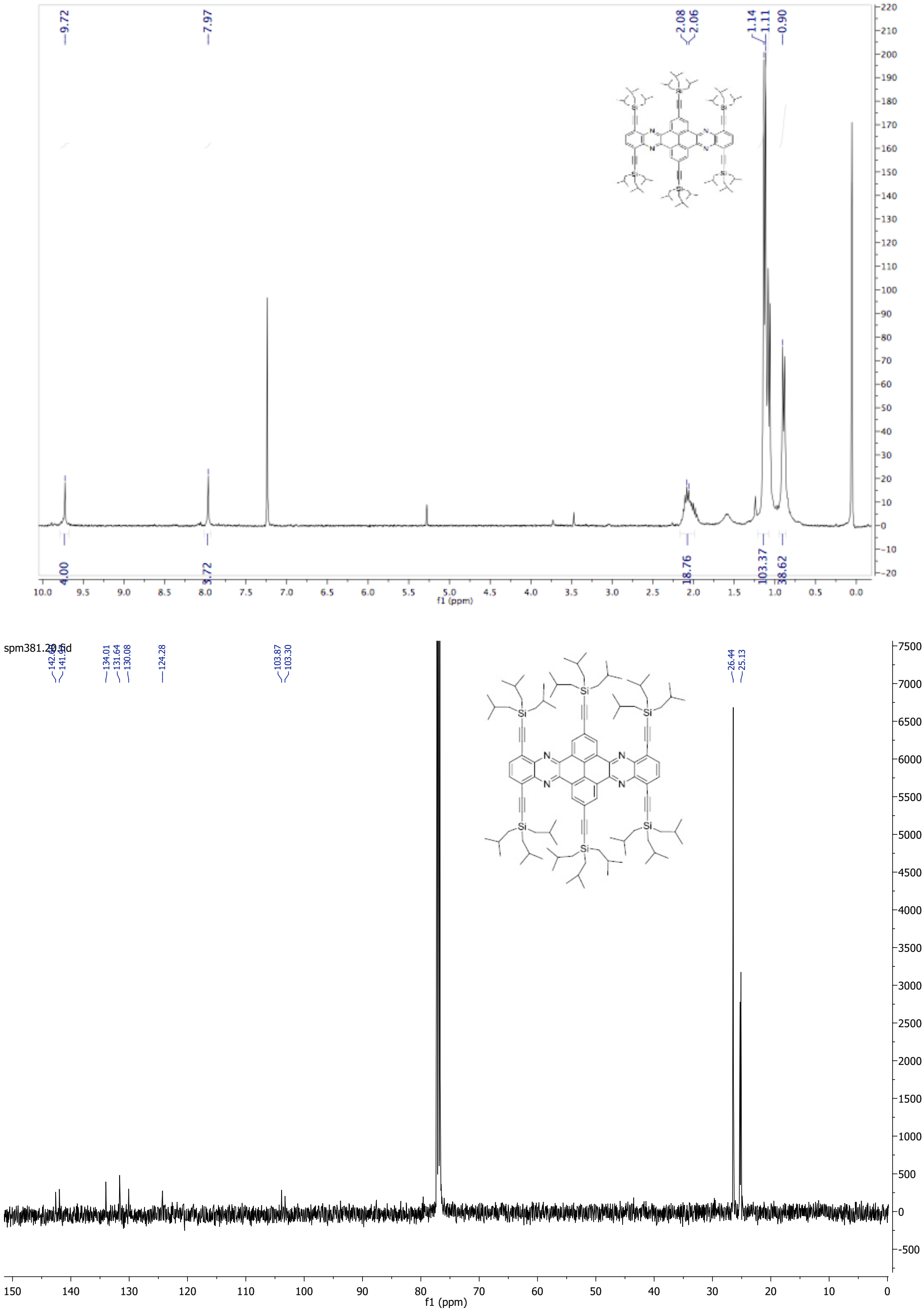


Fig. S3: ^{1}H NMR and ^{13}C NMR of compound **1b** in $CDCl_3$.

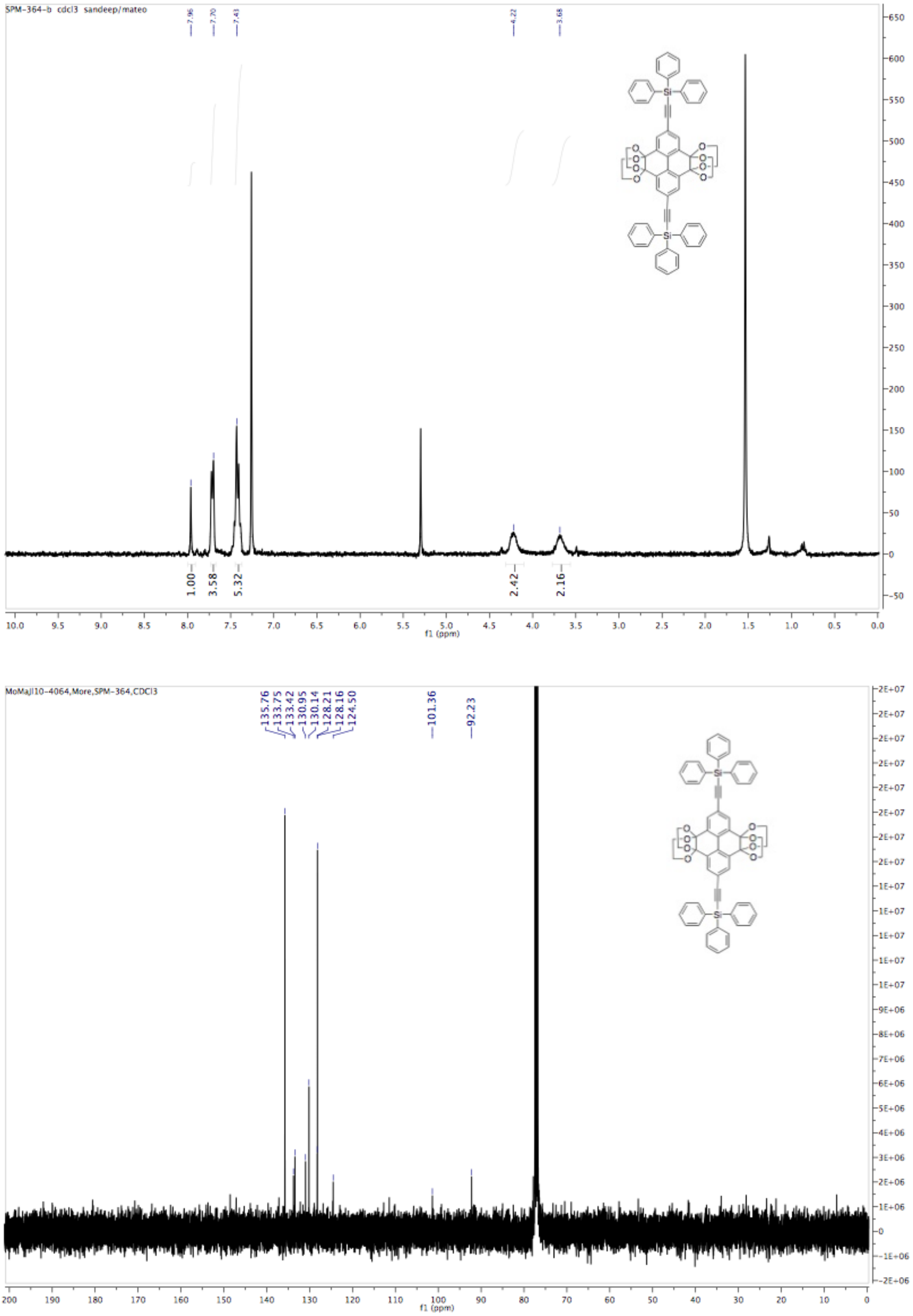


Fig. S4: ^{1}H NMR and ^{13}C NMR of compound **5c** in CDCl$_3$.

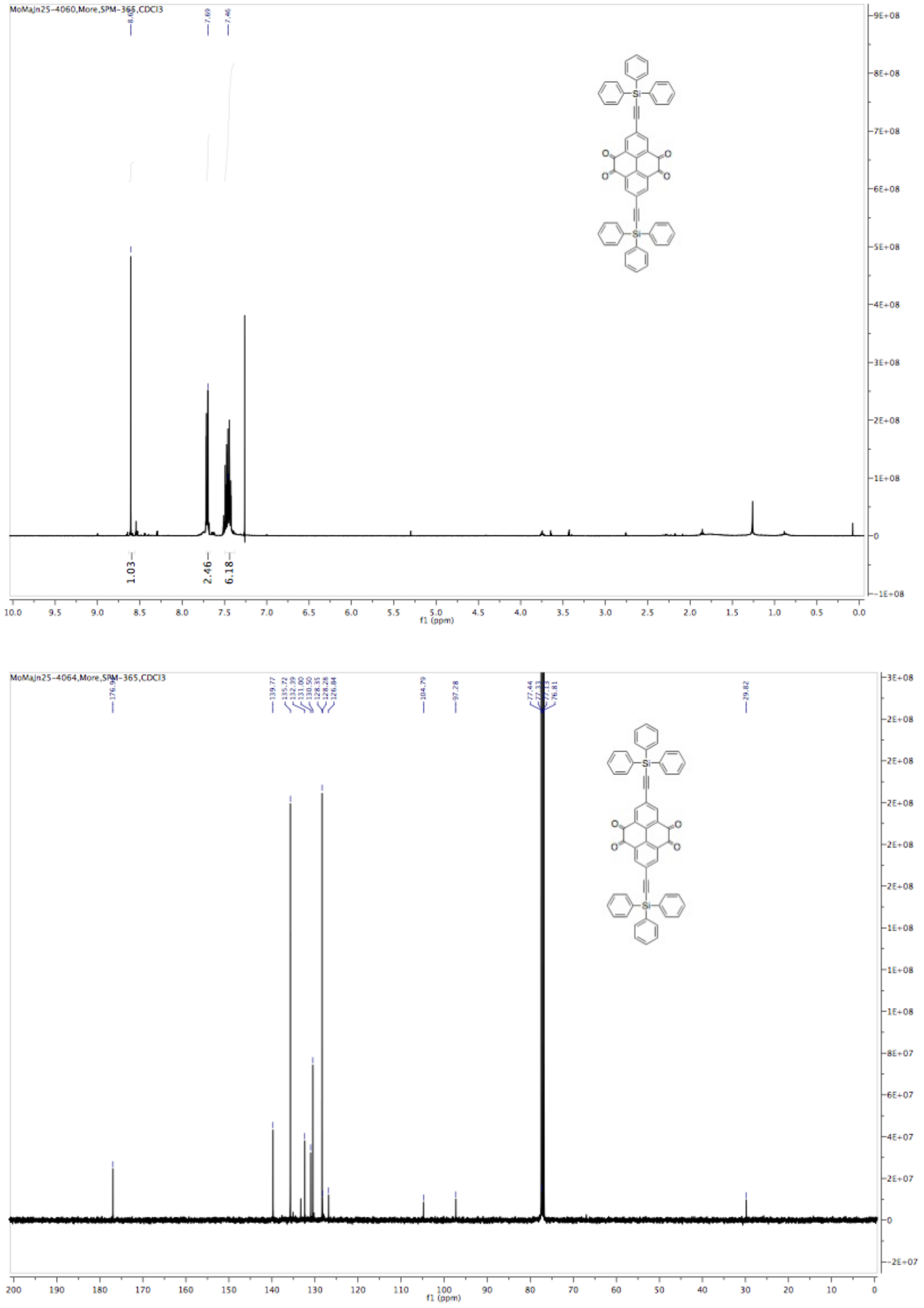
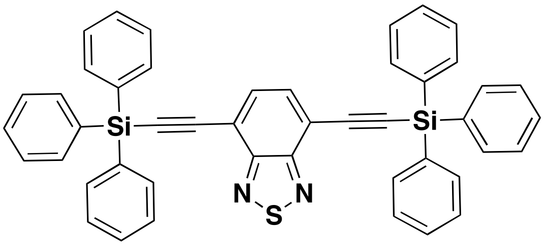


Fig. S5: ^{1}H NMR and ^{13}C NMR of compound **5c** in $CDCl_3$.



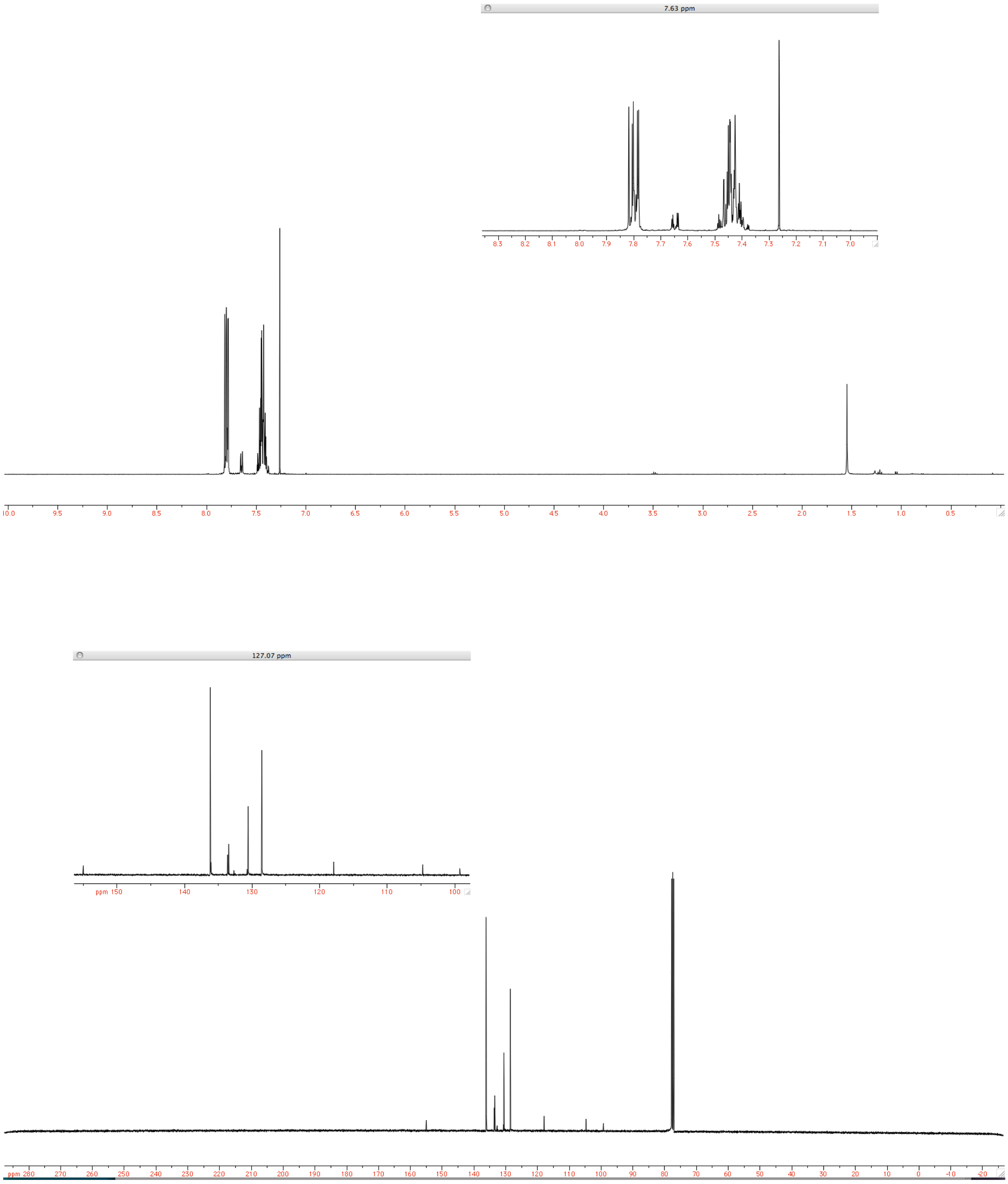
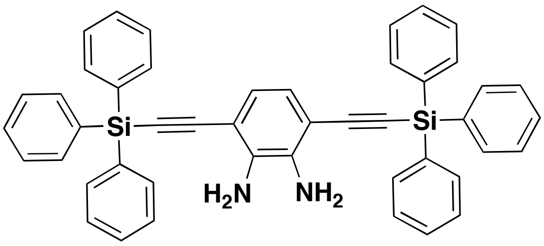


Fig. S6: ^{1}H NMR and ^{13}C NMR of compound **6c** in $CDCl_3$.



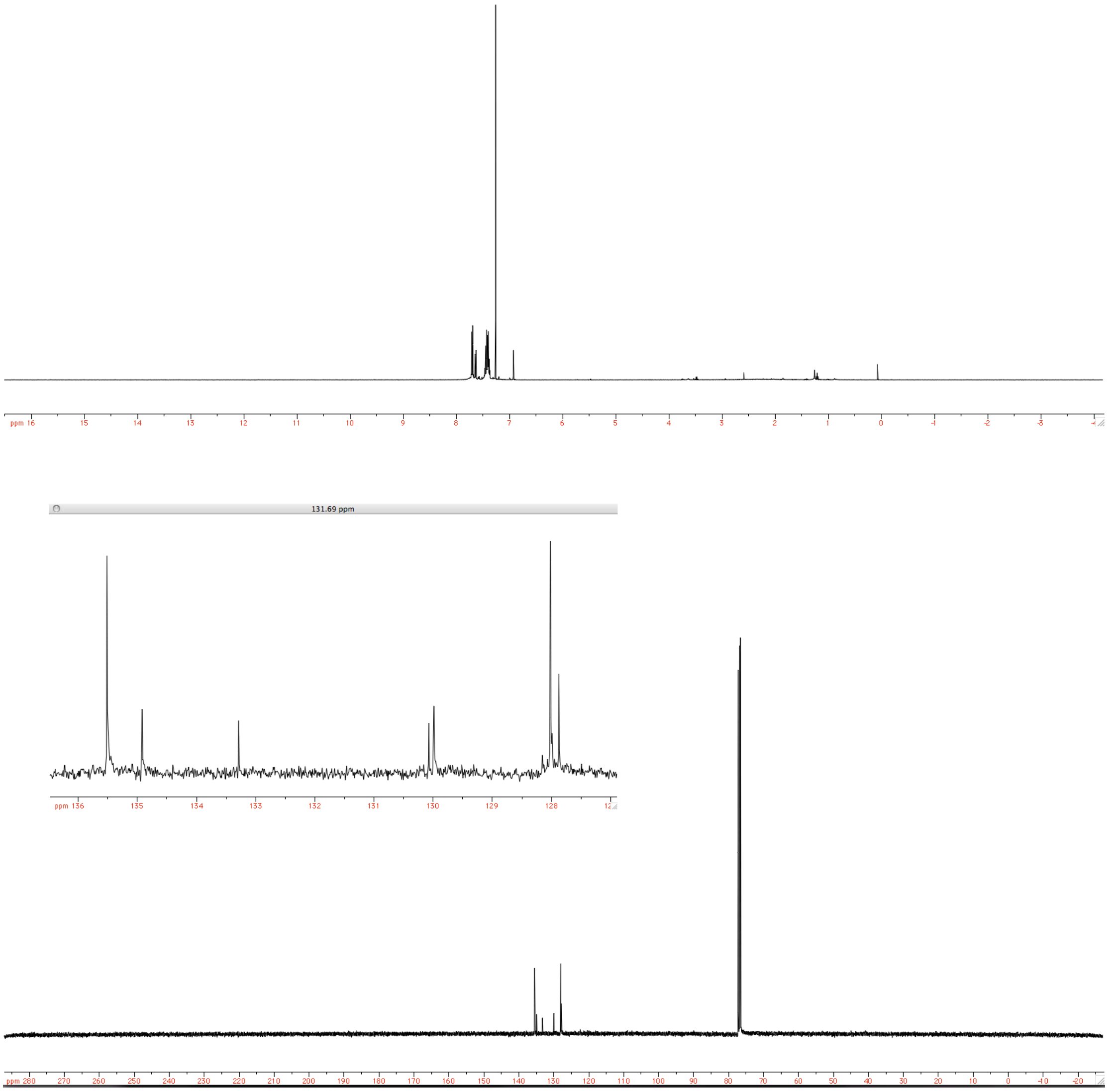


Fig. S7: ^{1}H NMR and ^{13}C NMR of compound **3c** in $CDCl_3$.

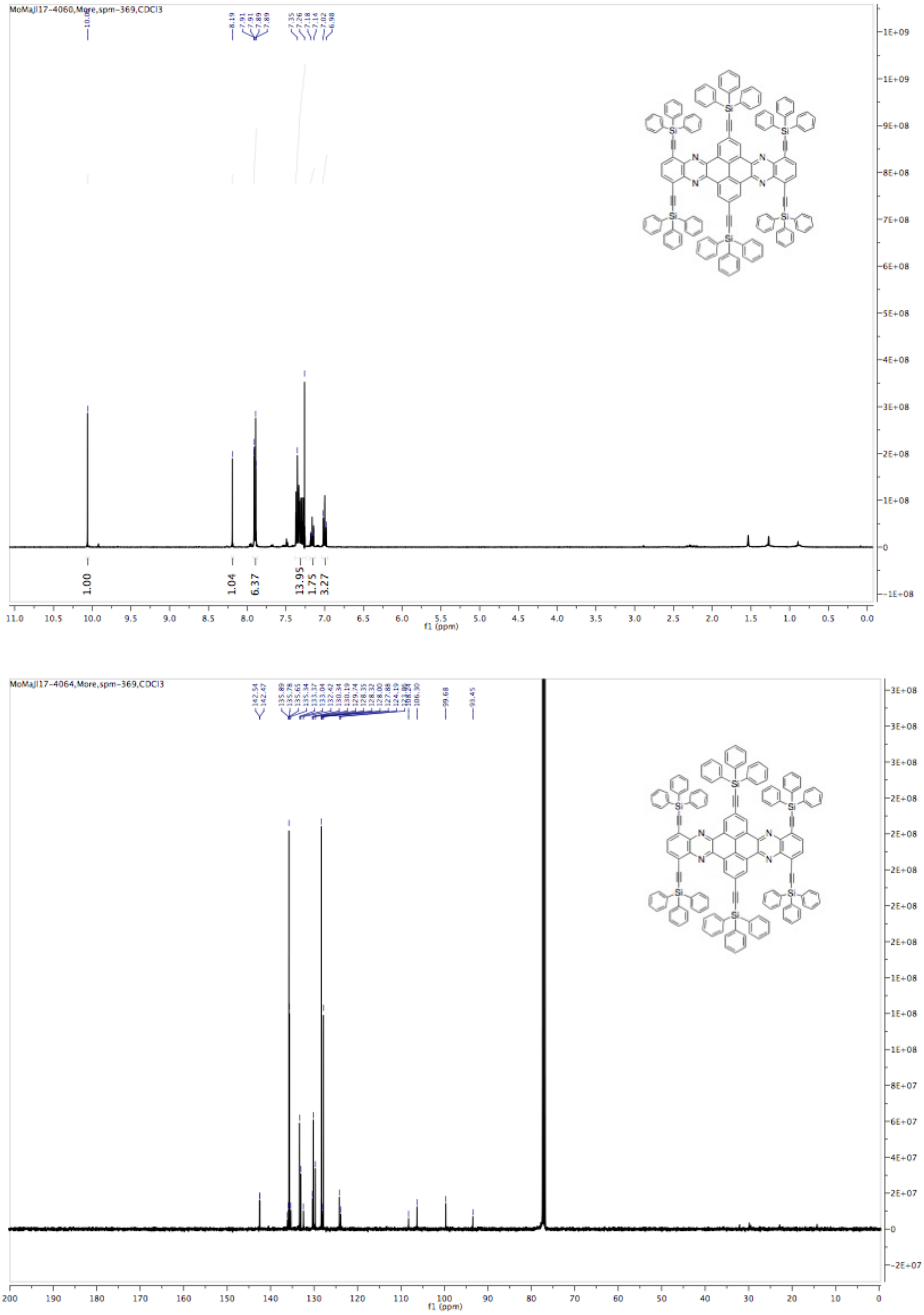


Fig. S8: ^{1}H NMR and ^{13}C NMR of compound **1c** in $CDCl_3$.

Computer modelling

The geometry of compounds **1a-c** was optimized with Spartan10 and Gaussian09 with a B3LYP 6-31g* basis set yielding similar results.

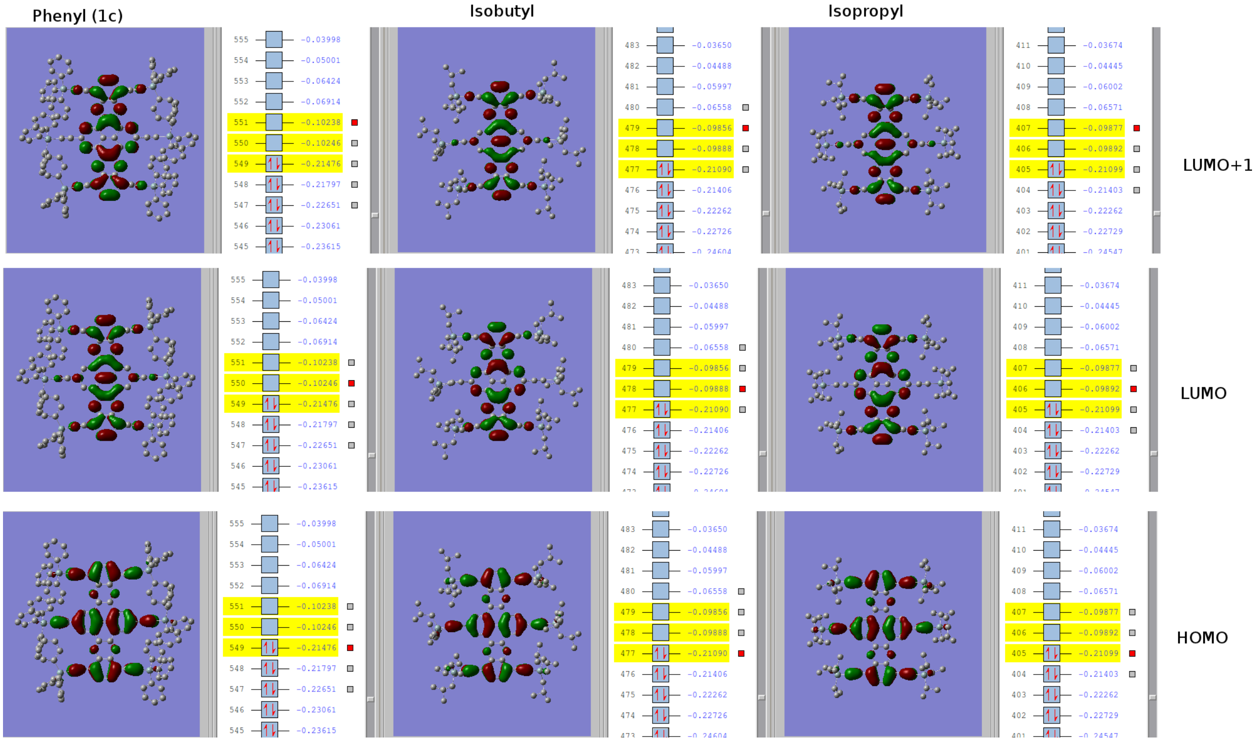
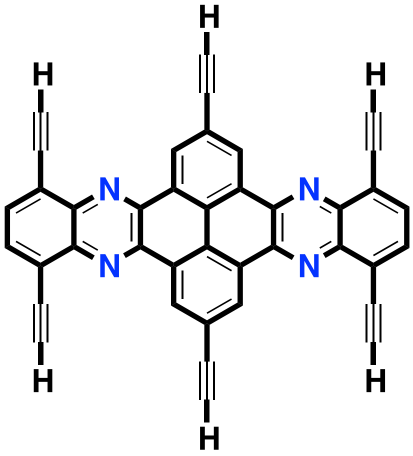


Fig. S9. HOMO, LUMO y LUMO+1 orbitals for **1a-c**.

	1a	**1b**	**1c**	**Units**
LUMO+1	-2.7	-2.7	-2.8	eV
LUMO	-2.7	-2.7	-2.8	eV
HOMO	-5.8	-5.8	-5.9	eV
HOMO-1	-5.7	-5.7	-5.8	eV
HOMO/LUMO gap	3.1	3.1	3.1	eV
LUMO(B_{1g})/LUMO(B_{3u}) ΔE	**4**	**9**	**–2**	**meV**

Table S1. B3LYP energy levels for **1a-c**.

Twist effects



Compound S1

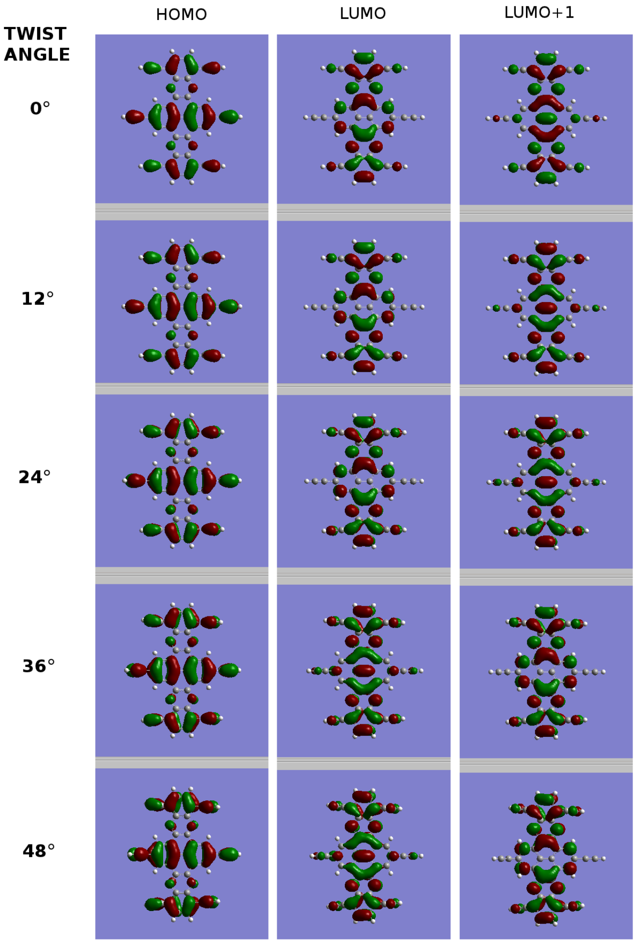


Fig. S10. HOMO, LUMO y LUMO+1 orbitals for **S1** with varying twist angles.

Twist angle	**0º**	**12º**	**24º**	**36º**	**48º**	**Units**
LUMO+1	-2.696	-2.699	-2.705	-2.701	-2.695	eV
LUMO	-2.711	-2.711	-2.707	-2.717	-2.736	eV
HOMO	-5.919	-5.917	-5.914	-5.907	-5.896	eV
HOMO-1	-6.046	-6.045	-6.040	-6.033	-6.022	eV
HOMO/LUMO gap	3.2	3.2	3.2	3.2	3.2	eV
LUMO(B_{1g})/LUMO(B_{3u}) ΔE	**15**	**12**	**2**	**–16**	**–41**	**meV**

Table S2. B3LYP energy levels for **S1** with different twist angles.

References

1. a) S. More, R. Bhosale, S. Choudhary and A. Mateo-Alonso, *Org. Lett.*, 2012, **14**, 4170-4173; b) A. L. Appleton, S. Miao, S. M. Brombosz, N. J. Berger, S. Barlow, S. R. Marder, B. M. Lawrence, K. I. Hardcastle and U. H. F. Bunz, *Org. Lett.*, 2009, **11**, 5222-5225; c) B. D. Lindner, J. U. Engelhart, M. Maerken, O. Tverskoy, A. L. Appleton, F. Rominger, K. I. Hardcastle, M. Enders and U. H. F. Bunz, *Chem. Eur.J.*, 2012, **18**, 4627-4633.