Quasi-planarDiazadithio and Diazadiseleno[8]circulenes: Synthesis, Structures and Properties

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Supporting Information

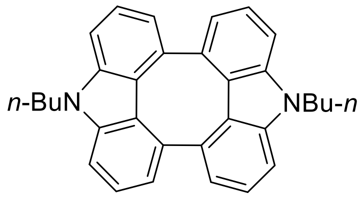
Contents

General Information:

All reagents and solvents were reagent grade. Further purification and drying by standard methods were employed when necessary. The plates used for thin-layer chromatography (TLC) were E. Merck silica gel 60 F_{254} (0.24 nm thickness) precoated on aluminum plates, and then visualized under UV light (365 nm and 254 nm) or through staining with acidic ceric ammonium molybdate and subsequent heating. Column chromatography was performed using E. Merck silica gel (230-400 mesh). NMR spectra were recorded on a Bruker Advance III 400 spectrometer (400.19 MHz for ^{1}H and 100.62 MHz for ^{13}C) and a Bruker 400 MHz NMR AV400Q (400.19 MHz for ^{1}H and 100.62 MHz for ^{13}C) at room temperature. Mass spectra (ESI, EI and FAB) were obtained with a ThermoFinnigan MAT 95 XL spectrometer and determined at an ionized voltage of 70 eV unless otherwise stated.Melting points were measured on a digital melting point apparatus and were uncorrected. UV/vis absorption spectrum was recorded on a UV-Vis-NIR spectrophotometer. Fluorescence spectrum was obtained on a fluorescence spectrophotometer at 22 °C.

1. Experimental Section

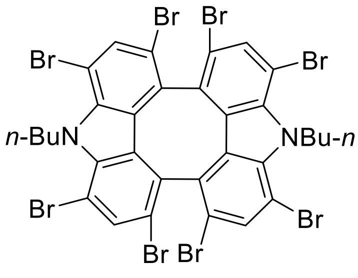
Synthesis of*N*,*N’*-Di-*n*-butyl-tetraphenyleno[*1,16-bcd:8,9-b'c'd'*]dipyrrole (6).



6

NaH (41.8 mg, 1.05 mmol of 60% dispersion in mineral oil) was added to a solution of **5** (313.5 mg, 0.95 mmol) in THF/DMF (1:1, 10 mL) at 0 °C. After stirring the mixture for 5 min, *n*-butyl bromide (135.6 mg, 0.99 mmol) was added, and the suspension was stirred for an additional 3 h. The reaction was diluted with dichloromethane (45 mL) and quenched with water (10 mL). The organic phase was washed with aqueous saturated NH_4Cl (20 mL), dried over Na_2SO_4 and concentrated under vacuum. Purification by column chromatography (eluting with hexane/ethyl acetate 30:1) afforded **6** (230.9 mg, 55%) as a yellow solid.M.p.: 258.8-260.2 °C; IR (KBr): 2942, 2851, 1570, 1447, 1319, 1151, 1036 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.48 (t, J = 8.0 Hz, 4H), 7.33 (d, J = 8.0 Hz, 4H), 7.11 (d, J = 7.6 Hz, 4H), 4.32 (t, J = 7.4 Hz, 4H), 1.88-1.92 (m, 4H), 1.46-1.55 (m, 4H), 1.01 ppm (t, J = 7.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 137.5, 126.2, 124.3, 120.8, 107.4, 42.9, 30.9, 20.6, 13.9 ppm.HRMS (ESI) *m/z* calcd. for $C_{32}H_{30}N_2Na$ $[M+Na]^+$ 465.2301, found 465.2308.

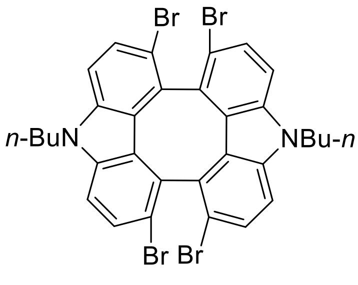
Synthesis of2,4,5,7,9,11,12,14-Octabromo-*N*,*N'*-di-*n*-butyl-tetraphenyleno-[*1,16-bcd:8,9-b'c'd'*]dipyrrole (7).



7

To a 250 mL round-bottomed flask was placed $CHCl_3$ (100 mL), tetraphenylene**6**(663.4 mg, 1.5 mmol) and trifluoroacetic acid (0.5 mL). The mixture was stirred vigorously at 0 °C, and NBS (2.3 g, 12.6 mmol) was added in portions over 30 minutes. Then the reaction mixture was stirred at room temperature for 10 h, and poured into ice water (50 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (30 mL × 3). The combined organic phase was washed with sat. $NaHCO_3$ and brine, and was dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluting with hexane) to give **7** (1.3 g, 82%) as a yellow solid. M.p> 300 °C; IR (KBr): 2934, 2864, 1536, 1452, 1364, 1253, 1049 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 4H), 5.18 (t, J = 7.8 Hz, 4H), 1.82-1.89 (m, 4H), 1.28-1.34 (m, 4H), 0.94 ppm (t, J = 7.4 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ138.5, 137.4, 132.3, 126.6, 118.6, 103.7, 44.8, 33.8, 19.7, 14.0 ppm. HRMS (ESI) *m/z* calcd. for $C_{32}H_{22}Br_8N_2Na$ $[M+Na]^+$ 1088.5142, found 1088.5147.

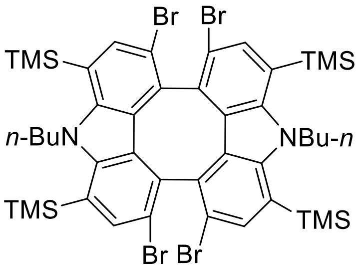
Synthesis of 4,5,11,12-tetrabromo-*N*,*N'*-Di-*n*-butyl-tetraphenyleno[*1,16-bcd:8,9-b'c'd'*]dipyrrole (8).



8

To a solution of 2,4,5,7,9,11,12,14-octabromotetraphenylene **7** (536.5 mg, 0.5 mmol) in dry THF (150 mL) was added dropwise *n*-BuLi (1.31 mL, 2.1 mmol, 4.2 eq, 1.6 M in hexane) at –78 °C under N_2 and stirred for 2 h at the same temperature. Then H_2O (0.18 mL, 10.0 mmol, 20.0 eq) was added at –78 °C and stirred for 1 h at this same temperature. The resulting mixture was then allowed to warm to room temperature and stirred for another 2 h. The reaction was quenched by addition of aqueous ammonium chloride solution (30 mL), the aqueous solution was extracted with dichloromethane (25 mL × 3). The combined organic phases was washed with water(20 mL) and brine (20 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate 30:1) to give the desired product **8**(169.7 mg, 45%) as a yellow solid. M.p>300 °C; IR (KBr): 2948, 2855, 1639, 1545, 1375, 1103 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.4 Hz, 4H), 7.20 (d, J = 8.4 Hz, 4H), 4.28-4.32 (m, 4H), 1.86-1.93 (m, 4H), 1.39-1.46 (m, 4H), 0.98 ppm (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 134.0, 132.2, 123.6, 117.6, 109.2, 43.6, 31.2, 29.8, 20.7, 14.0 ppm. HRMS (ESI) *m/z* calcd. for $C_{32}H_{26}N_2Br_4Na[M+Na]^+$ 776.8722, found 776.8725.

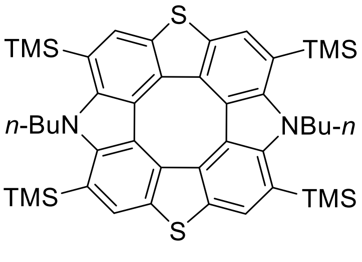
Synthesis of 4,5,11,12-tetrabromo-*N*,*N'*-di-*n*-butyl-2,7,9,14-tetrakis(trimethylsilyl)tetraphenyleno[*1,16-bcd:8,9-b'c'd'*]dipyrrole (9).



9

To a solution of 2,4,5,7,9,11,12,14-octabromotetraphenylene **7** (858.5 mg, 0.8 mmol) in dry THF (300 mL) was added dropwise *n*-BuLi (2.1 mL, 3.36 mmol, 4.2 eq, 1.6 M in hexane) at –78 °C and stirred for 2 h at the same temperature. Then Me_3SiCl (0.65 mL, 4.8 mmol, 6.0 eq) was added at –78 °C and stirred for 1 h at the same temperature. The resulting mixture was allowed to warm to room temperature and stirred for another 2 h. The reaction was quenched by addition of aqueous ammonium chloride solution (30 mL). The aqueous solution was extracted with dichloromethane (25 mL × 3). The combined organic phases was washed with water(20 mL) and brine (20 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate 60:1) to give the desired product **9**(541.8 mg, 65%) as a yellow solid. M.p> 300 °C; IR (KBr): 2947, 2856, 1639, 1385, 1285 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 4H), 4.38 (t, J = 6.4 Hz, 4H), 1.13-1.22 (m, 4H), 0.73-0.77 (m, 4H), 0.60 (t, J = 6.8 Hz, 6H), 0.51 ppm (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 139.1, 134.8, 127.3, 124.9, 119.0, 51.2, 30.3, 20.3, 14.2, 0.6 ppm. HRMS (ESI) *m/z* calcd. for $C_{44}H_{58}N_2Si_4Br_4$ Na[M+ Na]$^+$ 1065.0303, found 1065.0307.

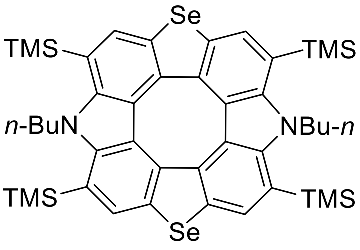
Synthesis of dithiophene[*2',3',4',5':4,5;2'',3'',4'',5'':12,13*]tetraphenyleno[*1,16-bcd:8,9-b'c'd'*]dipyrrole, 3,4,8,18-tetra(trimethylsilyl)-4,10-dihydro-4,10-dibutyl (10).



10

To a solution of tetraphenylene**9** (208.4 mg, 0.2 mmol) in dry THF (60 mL) was added dropwise *n*-BuLi (0.6 mL, 0.96 mmol, 4.8 eq, 1.6 M in hexane) at –78 °C under N_2, and the mixture was stirred for 3 h at the same temperature. Then S powder (96.0 mg, 3.0 mmol, 15.0 eq) was added in one portion at – 78°C and stirred for 2 h at the same temperature. The resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by addition of aqueous ammonium chloride solution (20 mL), and the aqueous solution was extracted with dichloromethane (15 mL × 3). The combined organic phases were dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate 20:1) to give **10**(118.5 mg, 75%) as a yellow solid. M.p>300 °C; IR (KBr): 2947, 2876, 1634, 1450, 1351, 1254, 1171 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 4H), 4.74 (t, *J* = 7.2 Hz, 4H), 0.88-0.99 (m, 4H), 0.81-0.89 (m, 4H), 0.65 (s, 36H), 0.41-0.49 ppm (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 133.9, 129.7, 129.4, 123.1, 120.6, 53.6, 29.9, 20.1, 14.1, 1.3 ppm. HRMS (ESI) *m/z* calcd. for $C_{44}H_{58}S_2N_2Si_4Na$ $[M+ Na]^+$813.3011, found 813.3015.

Synthesis of diselenine[*2',3',4',5':4,5;2'',3'',4'',5'':12,13*]tetraphenyleno[*1,16-bcd:8,9-b'c'd'*]dipyrrole, 3,4,8,18-tetra(trimethylsilyl)-4,10-dihydro-4,10-dibutyl (11).



11

To a solution of tetraphenylene**9** (312.6 mg, 0.3 mmol) in dry THF (100 mL) was added dropwise *n*-BuLi (0.9 mL, 1.44 mmol, 4.8 eq, 1.6 M in hexane) at –78 °C under N_2, and the mixture was stirred for 3 h at the same temperature. Then Se powder (355.3 mg, 4.5 mmol, 15.0 eq) was added at –78 °C and stirred for 2 h at the same temperature. The resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by addition of aqueous ammonium chloride solution (30 mL), the aqueous solution was extracted with dichloromethane (20 mL × 3). The combined organic phases was washed with water(20 mL) and brine (20 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate 20:1) to give the desired product **11**(207.3 mg, 78%) as an orange solid. M.p>300 °C; IR (KBr): 2945, 2858, 1351, 1261, 1167 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 4H), 4.71 (t, *J* = 7.2 Hz, 4H), 0.92-0.99 (m, 4H), 0.84-0.91 (m, 4H), 0.65 (s, 36H), 0.49-0.61 ppm (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 134.4, 133.0, 132.9, 122.8, 122.7, 52.78, 29.8, 20.1, 14.1, 1.4ppm.HRMS (ESI) *m/z* calcd. for $C_{44}H_{58}Se_2N_2Si_4Na$ $[M + Na]^+$909.1899, found 909.1905.

2. X-Ray Crystal Structure Analyses

Single crystals of **7**(clear yellow),**10** (clear yellow) and**11**(clear orange)were obtained by slow evaporation of their CH_2Cl_2 solution at room temperature. The single crystal X-ray diffraction was conducted on Agilent SuperNova diffractometer. The crystal structure was solved by direct methods *SIR2004* and refined by fullmatrixleast-squares on *F*2 by means of *SHELXL97*. The calculated positions of thehydrogen atoms were included in the final refinement.

Crystallographic data for **7**: $C_{32}H_{22}Br_8N_2$ (1065.53), Triclinic, P-1, 0.40 × 0.30 × 0.20 mm^3, a = 10.8503(5), b = 12.4427(5), c = 12.9897(5) Å, a = 100.3(2), β = 91.3(2), γ = 108.6(2)°, T= 296 K, V = 1628.82(12) $Å^3$, Z = 2,35914 reflections collected.The final R_1= 0.0405 (I >2σ(I)), andthe final R_1= 0.0558 (for all data). The goodness of fit on F^2 was 1.028

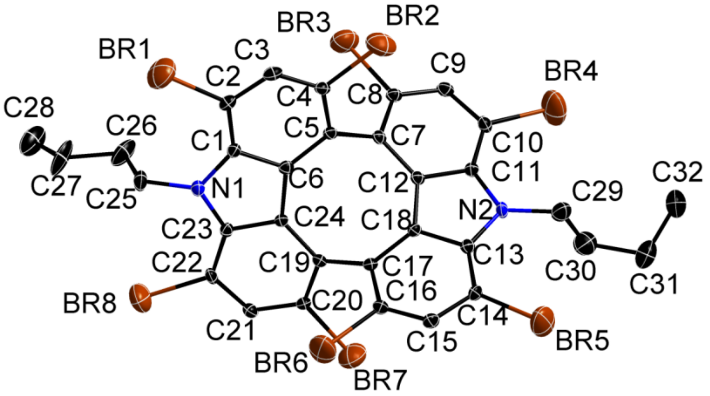


Figure S1. Crystal structure of **7**.

Crystallographic data for **10**: $C_{44}H_{58}N_2S_2Si_4$ (791.40), Monoclinic, P2(1)/n, 0.40 × 0.30 × 0.20 mm^3, a = 14.2494(6), b = 14.1245(6), c = 22.4876(9) Å, a = 90.0, β = 98.800(2), γ = 90.0°, T = 296 K, V = 4472.7(3) $Å^3$, Z = 4,53972 reflections collected. The final R_1= 0.0569 (I >2σ(I)), andthe final R_1= 0.0919 (for all data). The goodness of fit on F^2 was 1.023.

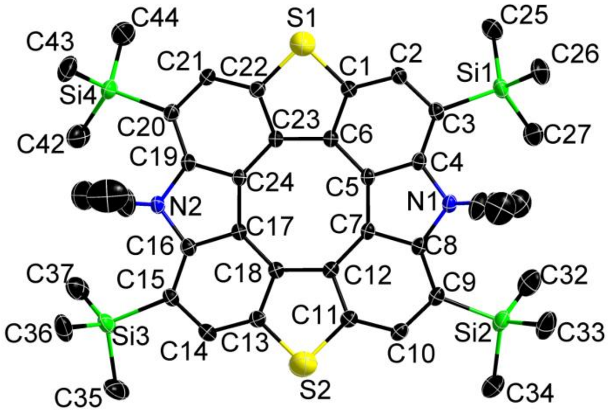


Figure S2. Crystal structure of **10**.

Crystallographic data for **11**: $C_{44}H_{58}N_2Se_2Si_4$(885.20), Monoclinic, P2(1)/n, 0.40 × 0.30 × 0.20 mm^3, a = 14.2771(2), b = 14.2280(2), c = 22.6224(4) Å, a = 90.0, β = 99.4270(10), γ = 90.0°, T = 296(2) K, V = 4533.33(12) Å^3, Z = 4,57800reflections collected. The final R_1= 0.0471 (I >2σ(I)), andthe final R_1= 0.1114 (for all data). The goodness of fit on F^2 was 1.010.

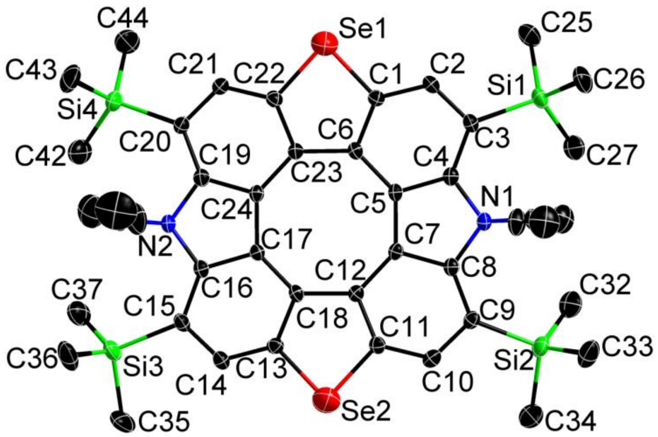


Figure S3. Crystal structure of **11**.

3. Photophysical Study

UV-vis absorption spectra were recorded on a Varian CARY 1E UV-vis spectrophotometer.

Fluorescence spectra were taken on a Hitachi F-4500 spectrofluorometer.

The fluorescence quantum yields (Φ) of **10** and **11** were determined by comparing the photoluminescence integrated intensities (area) and absorbance intensities with anthracene, a reference compound with Φ = 0.28.[1] The quantum yield was calculated by using the following equation:[2]

$$\Phi(\mathrm{sample}) = \left(\frac{F\mathrm{sample}}{F\mathrm{ref}}\right)\left(\frac{A\mathrm{ref}}{A\mathrm{sample}}\right)\left(\frac{\eta\mathrm{sample}}{\eta\mathrm{ref}}\right)^2\Phi_{(\mathrm{ref})}$$

Where *F* is the integrated intensities (area under emission peak), *A* is the absorbance, η is the refractive index and Φ is the quantum yield, the subscript ref refers to reference.

Anthracene was dissolved in EtOH (η = 1.36) and heterocycle [8]circulene **10**, **11** were dissolved in CH_2Cl_2 (η = 1.42). All samples were measured by using UV-Vis spectrometer to obtain the absorbance, and the absorbance values were kept below 0.05 at the excitation wavelength in order to minimize re-absorption effects. The samples were then measured by photoluminescence spectrometer in order to get the photoluminescence emission intensity at the excitation wavelength (356 nm).

Table S1 Quantum yields of **10** and **11**.

Sample	Integrated intensities (F)	Absorbance intensity at 356 nm (A)	Refractive index (η)	Quantum yield (Φ)
Anthracene	6214.14	0.038	1.36	0.28
10	553.63	0.018	1.42	0.057
11	183.29	0.017	1.42	0.019

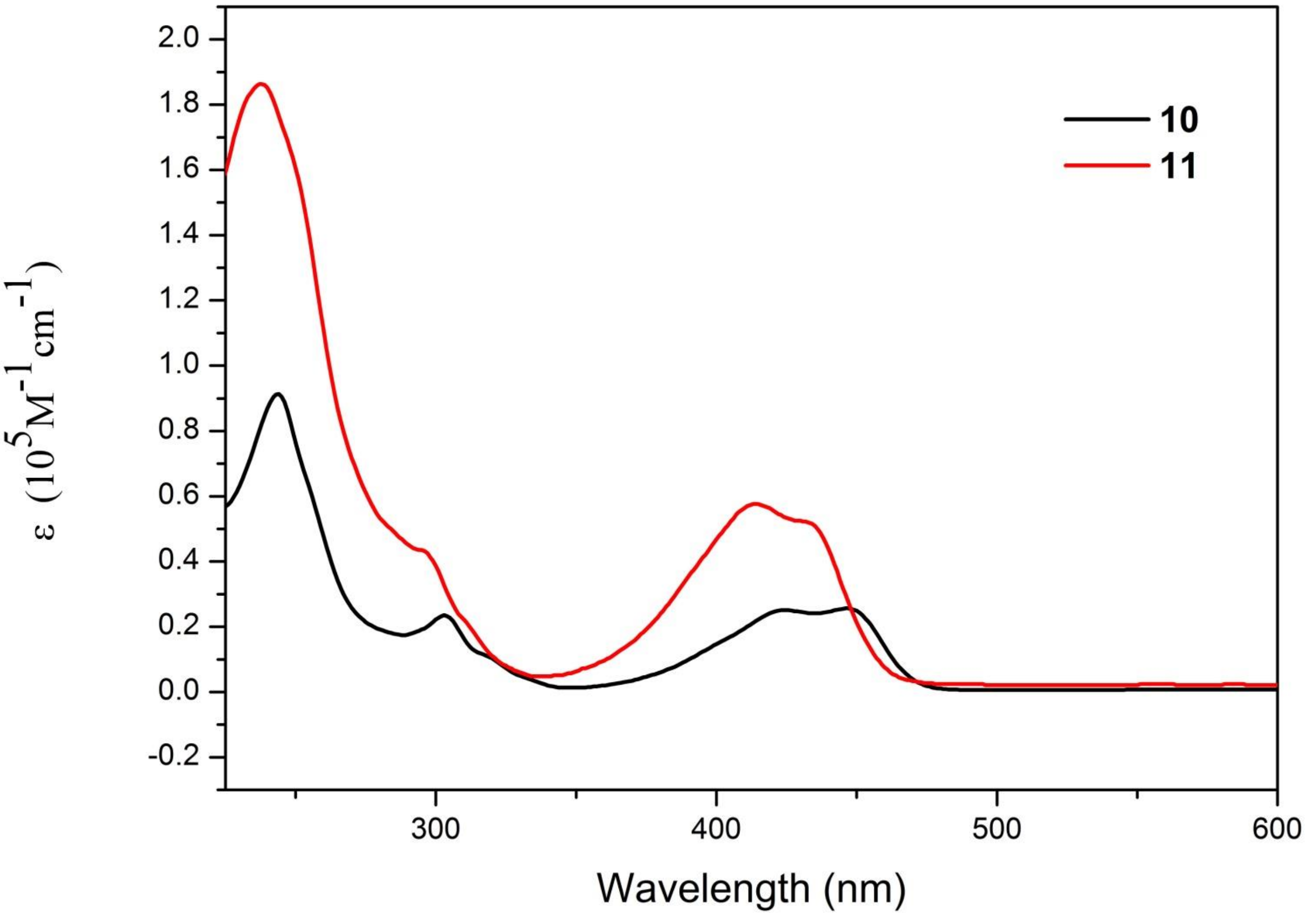


Figure S4. The absorption spectra of **10** and **11** recorded in CH_2Cl_2 at 20 ^oC.

4. Electrochemical Study

The cyclic voltammetry was performed in a solution of anhydrous CH_3CN with 0.1 M tetrabutylammoniumhexafluorophosphate (Bu_4NBF_4) as supporting electrolyte, at a scan rate of 50mV/s. A platinum bead was used as a working electrode, a platinum wire was used as an auxiliary electrode, and a silver wire was used as a psedo-reference. Ferrocene/ferrocenium($FeCp_2^+/FeCp_2^0$) was used as an internal standard, and potentials were recorded versus $FeCp_2^+/FeCp_2°$, temperature, 20 °C.

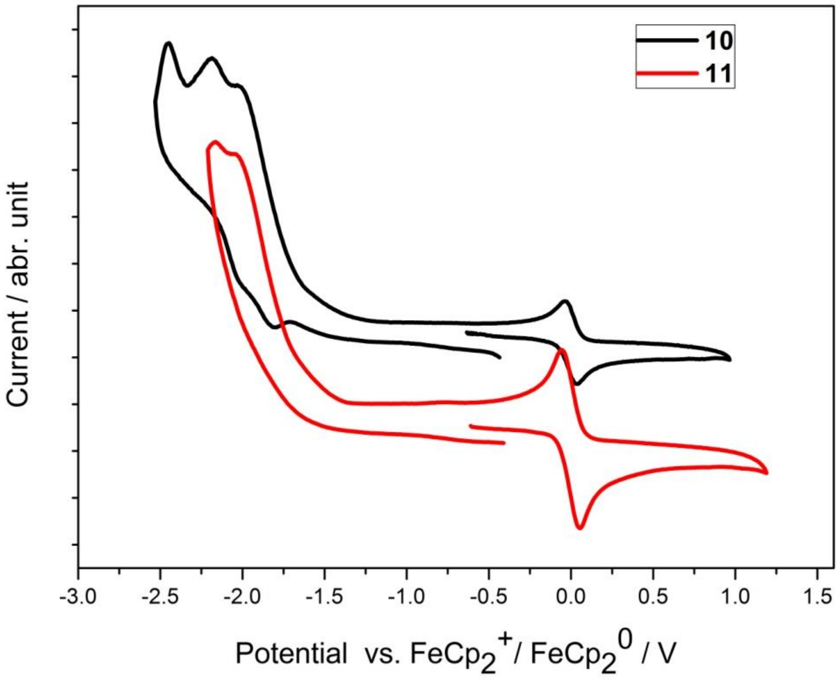


Figure S5. Cyclic voltammogram of **10** and **11** recorded from a solution in CH_3CN

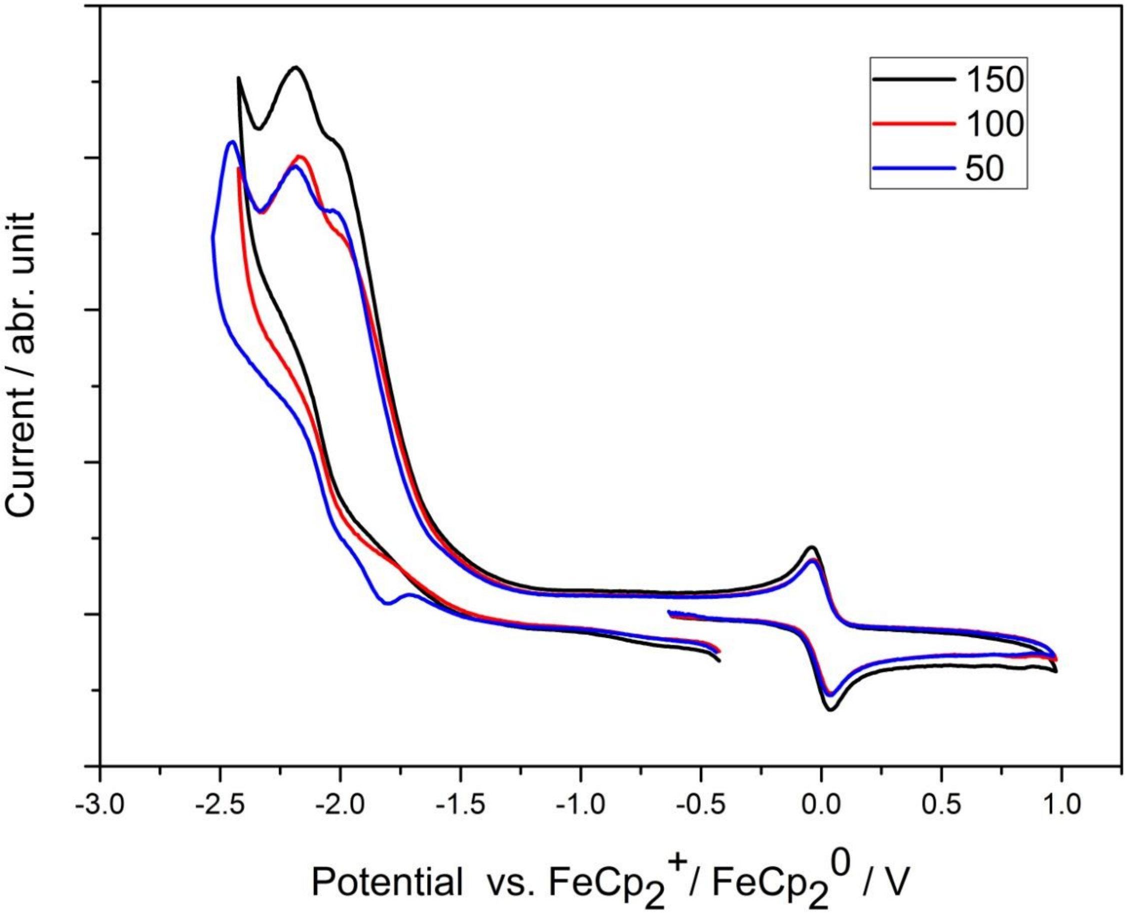


Figure S6. Cyclic voltammogram of **10** recorded from a solution in CH_3CN with varying scan rate (mV/s).

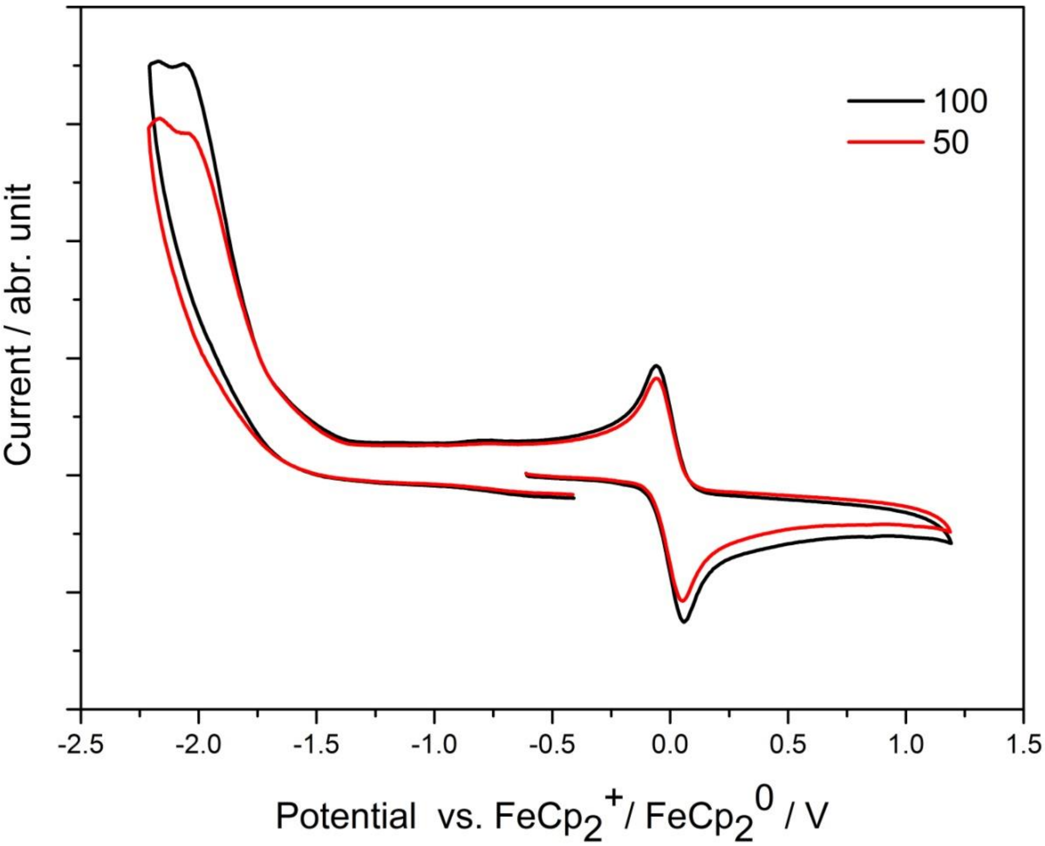
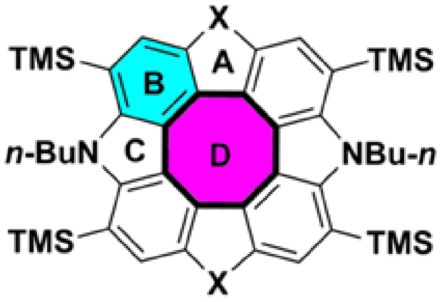


Figure S7. Cyclic voltammogram of **11** recorded from a solution in CH_3CN with varying scan rate (mV/s).

5. Theoretical calculation

All calculations were carried out using the Gaussian 09 software package at the density functional theory (DFT) level with the Becke’s three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) employing the 6-311++G(d,p) basis set for all atoms, and the results correlated well with the crystal bond lengths and bond angles. The shape and energy of the frontier molecular orbitals of **7**, **8** and **9** were calculated using the same method tacking into account the CH_2Cl_2 solvent effect using the polarized continuum model (PCM).



10 X= S, 11 X= Se

Figure S8.NICS values calculated for **10**and **11**.

Table S2. NICS values calculated for **10** and **11**.

	Compound **10**			Compound **11**		
species	–2	0	+2	–2	0	+2
A	–1.1	–8.6	25.7	0.4	–7.6	31.9
B	–7.5	–7.6	49.1	–7.7	–7.2	44.6
C	–4.7	–8.7	54.5	–5.5	–8.1	51.0
D	–13.1	7.7	32.5	–13.1	7.5	29.8

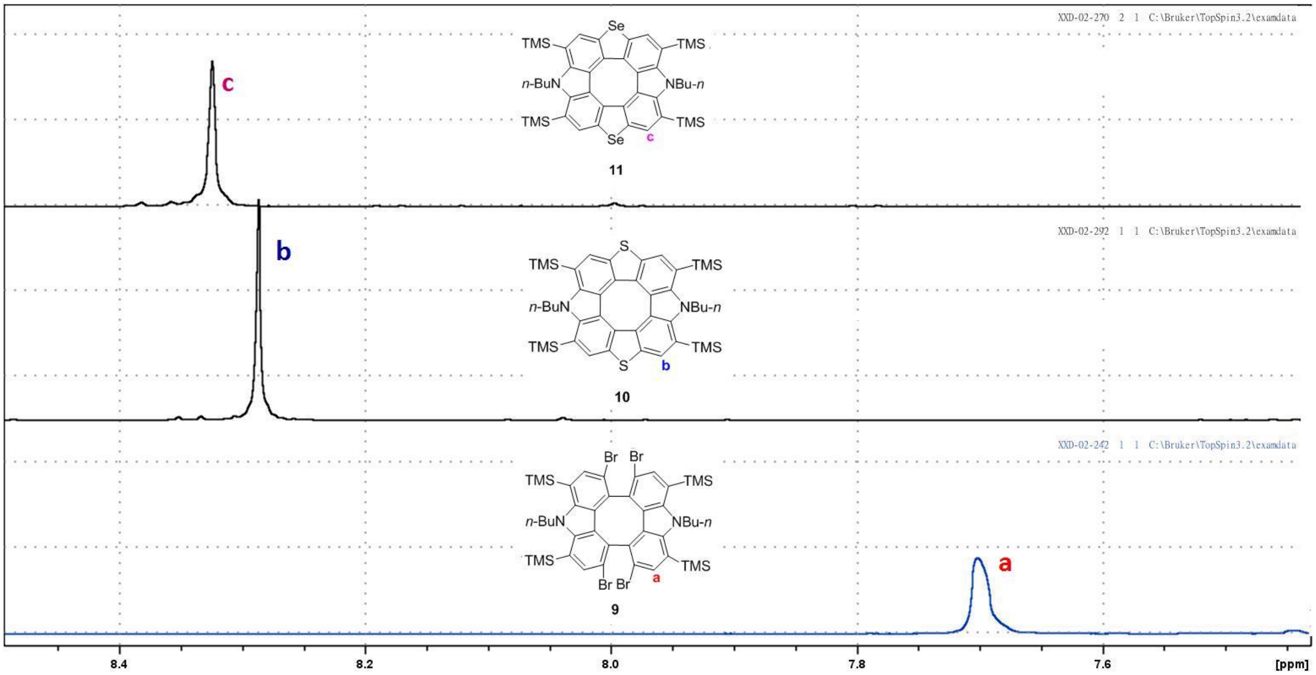
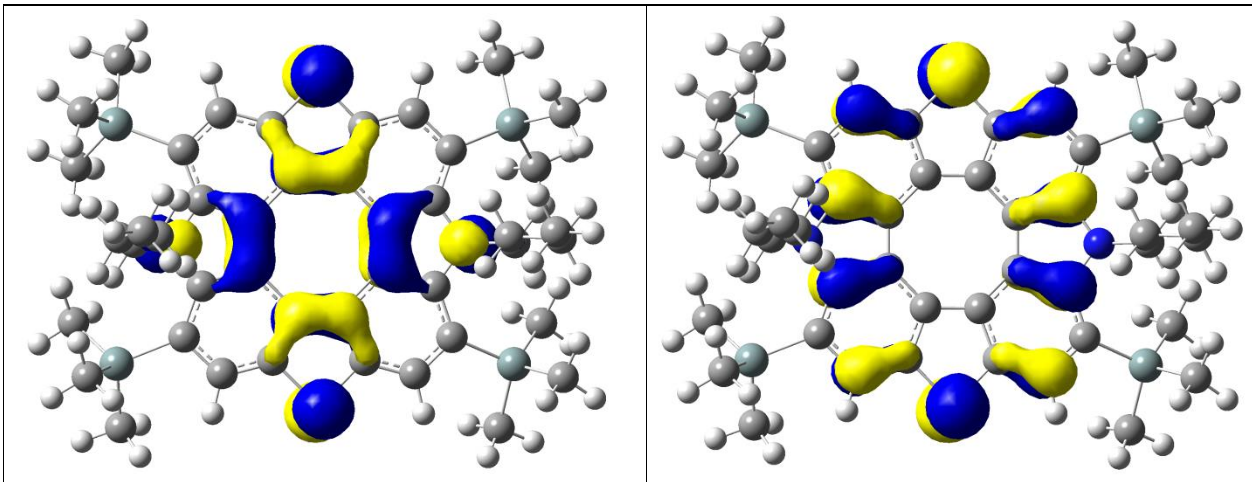
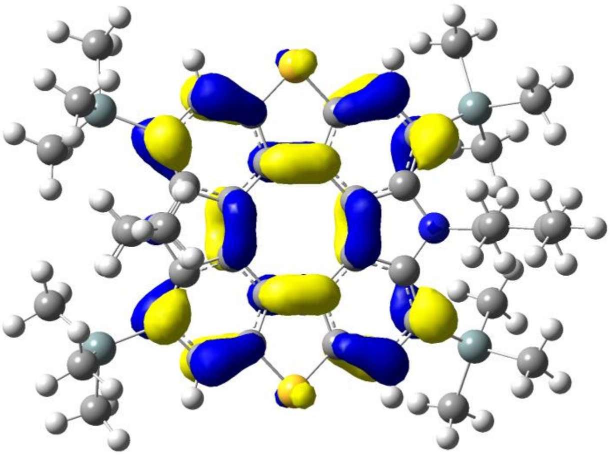


Figure S9. Aromatic regions of the ^{1}H NMR spectra of **9**, **10** and **11** in $CDCl_3$ at room temperature.



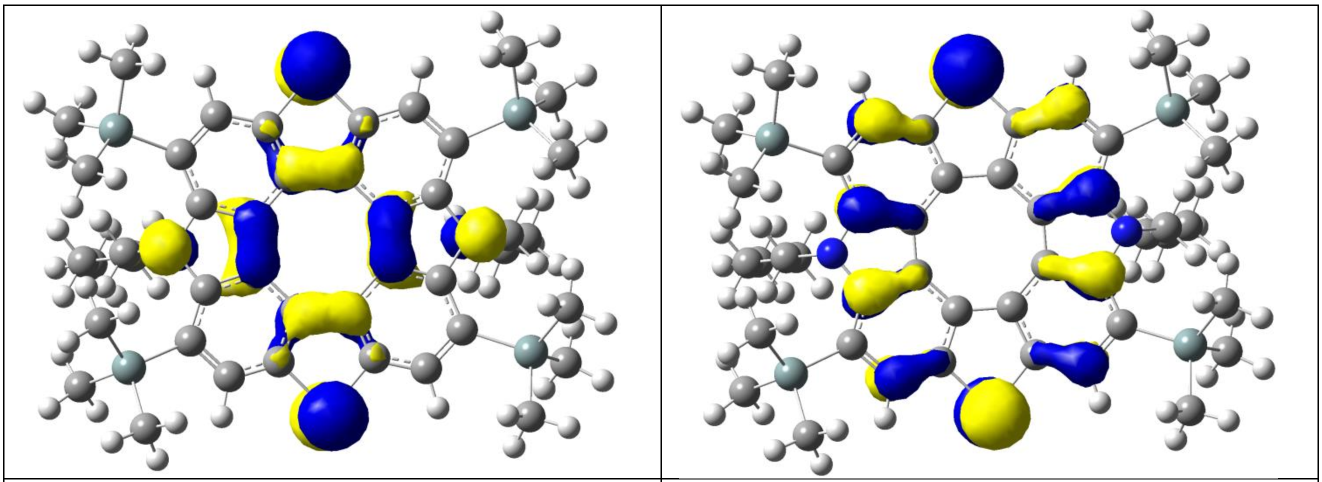
HOMO-1 (-5.61 eV)

HOMO (-5.53 eV)



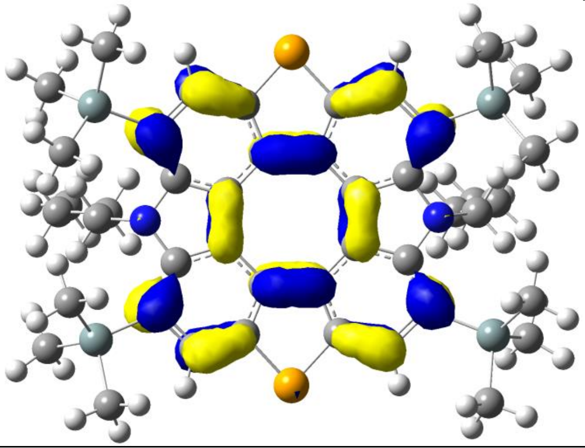
LUMO (-2.18 eV)

Figure S10. Calculated frontier molecular orbitals of **10**.



HOMO-1 (-5.55 eV)

HOMO (-5.45 eV)



LUMO (-2.20 eV)

Figure S11. Calculated frontier molecular orbitals of **11**.

Table S2 Coordinate data sets and absolute energies for DFT optimized complexes at B3LYP/6-311++G(d,p).

10-3776.3183166 a.u.

S	-0.00000500	-4.30771700	-0.08539200
S	0.00003700	4.29984600	-0.24094100
Si	-5.30838700	-3.17027500	-0.67184800
Si	-5.30758100	3.13131000	-0.80266900
Si	5.30761900	3.13125700	-0.80290100
Si	5.30835700	-3.17033200	-0.67211400
N	-3.92859600	-0.00347700	-0.14830900
N	3.92862900	-0.00351900	-0.14849300
C	-1.23121000	-3.07501800	-0.13394000
C	-2.57729600	-3.42876400	-0.19343700
C	-3.57857700	-2.46986700	-0.24938600
C	-3.10881600	-1.13373600	-0.18232400
C	-1.73731200	-0.73373600	-0.19488400
C	-0.73385200	-1.74975400	-0.17515000
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C	-6.25461300	-2.07321200	-1.88493200
C	-5.08715200	0.01056000	0.76244500
C	-4.69908700	0.14687900	2.24209900
C	-5.91035200	0.09664200	3.18093100
C	-5.52313800	0.24275400	4.65573400
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C	-6.44071800	3.42837200	0.68882300
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C	5.91055600	0.09657300	3.18064500
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C	6.25452300	-2.07328400	-1.88526000
C	6.35833300	-3.53281600	0.86370900
C	5.05578100	-4.83410400	-1.54080200
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H	2.81959500	-4.48317500	-0.24327900
H	-6.02556400	-5.19590000	-1.89804600
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H	-6.68646500	-2.64184500	1.40355100
H	-5.80127900	-4.15863300	1.56783500
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H	-6.81112700	2.52173200	1.17037600
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H	-4.72698500	5.59283900	-0.90289500
H	-6.04355200	5.16949900	-1.99057600
H	6.04356100	5.16942800	-1.99085900
H	4.72703200	5.59278900	-0.90313800
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H	6.81121000	2.52169500	1.17011400
H	5.92076000	4.01817600	1.44957300
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H	7.11071500	2.46132400	-2.37408100
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H	7.10552100	-2.63446000	-2.28515300
H	6.68657400	-2.64191100	1.40319600
H	7.25622600	-4.08640400	0.56901000
H	5.80137100	-4.15868200	1.56754500

H	4.64988200	-5.60558100	-0.88093300
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Si	-4.10452800	4.83129300	-1.69897900
Si	-1.76381400	5.15641200	4.08725300
Si	5.05987300	-2.73312600	1.82523700
Si	2.94442200	-2.83926100	-4.05135600
N	-2.41328300	3.56579700	1.06815000
N	2.68763200	-2.16448100	-0.64847400
C	-1.78105600	1.51320500	-2.39179000
C	-2.73905000	2.52024400	-2.42850900
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C	-2.25645500	2.95654200	-0.17506700
C	-1.21943700	1.96906600	-0.11045000
C	-0.94724700	1.19828300	-1.28923000
C	-0.69072000	2.02897900	1.25665000
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C	-1.21374000	3.53563800	3.23388300
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C	1.55062900	-0.51008100	0.50626800
C	1.25745400	0.23958100	1.69386000
C	1.80714900	-1.55686800	-1.54108500
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C	1.04284100	-0.54840600	-0.86946100
C	-3.96373100	5.19829500	-3.55201100
C	-5.94105800	4.50362400	-1.36612400
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C	-3.77532700	3.76966700	1.59646900
C	-4.50119400	2.45951600	1.93416300
C	-5.90510900	2.68700000	2.50737500
C	-6.63391200	1.37760600	2.82450300
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C	-3.36159800	4.97644300	5.09273600
C	-0.42158300	5.63168700	5.33575100
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H	-2.44661100	6.52827000	-0.91360000
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H	-5.83690200	3.29278900	3.41864700
H	-7.63109300	1.56557900	3.23166300
H	-6.07962400	0.78576600	3.55923600
H	-6.75032700	0.76396800	1.92602300
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H	-2.68845100	6.46785100	2.13015300
H	-3.50441200	5.87185800	5.70707300
H	-3.29119000	4.12058800	5.77101700
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H	-0.36283600	4.94401200	6.18394500
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H	5.57970000	-2.20937900	4.24735700
H	6.16635200	-0.92289700	3.18251700
H	4.37178000	-5.16180700	1.44480900
H	4.22507800	-4.68487900	3.13587200
H	5.81515500	-5.01588400	2.44525700
H	5.69995000	-2.88926500	-0.62450500
H	7.10391900	-2.97627000	0.44282200
H	6.31890300	-1.42477700	0.12857400
H	3.71732900	-3.92587800	-0.15423400
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H	1.51229800	-4.06861400	1.01572900
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H	1.71959300	-6.14999900	-1.22691300
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H	-0.46743700	-6.26367900	0.02853800
H	0.41931000	-6.35762500	1.55256500
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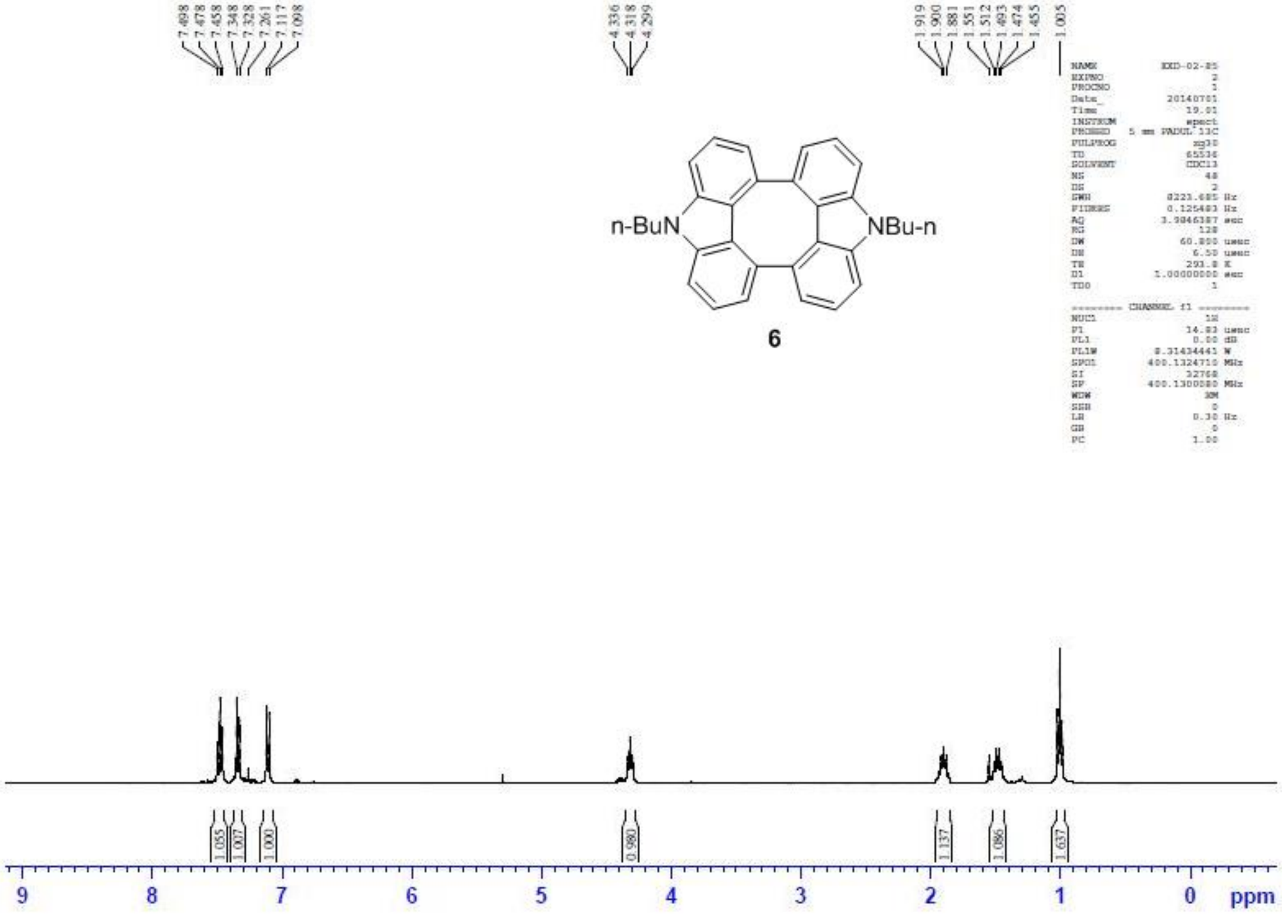
H	3.05992800	-5.10205900	-5.07616800	H	3.07156800	-0.95241200	-5.71007700
H	1.39531100	-4.70905800	-4.63625800				

References

1. A. M. Brouwer, *Pure Appl. Chem.* 2011, **83**, 2213.
2. D. F. Eaton, *Pure Appl. Chem.* 1988, **60**, 1107.

6. NMR spectra



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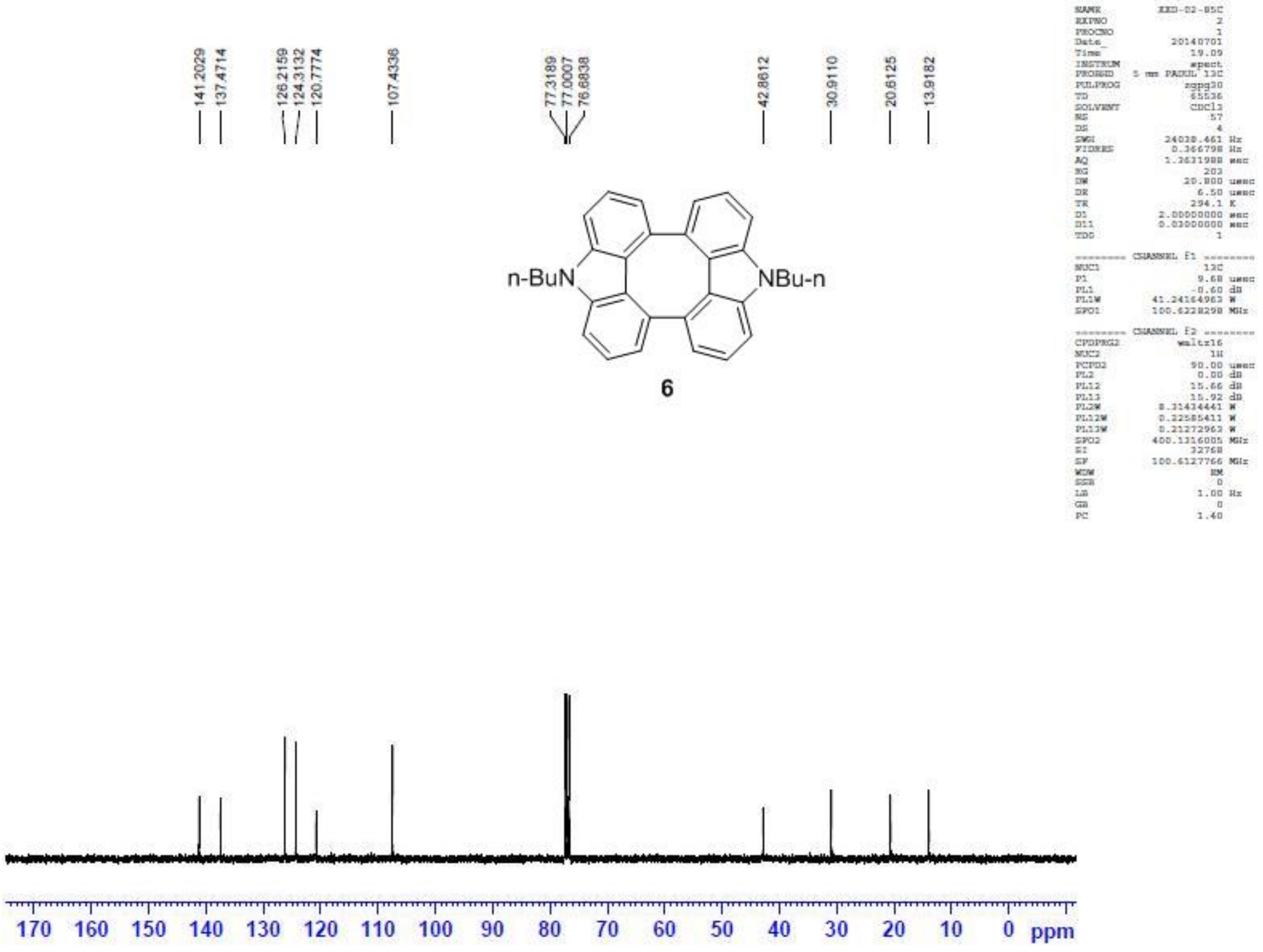

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PROCNO                 1
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PULPROG          zgpg30
TD                65536
SOLVENT            CDCl3
NS                    57
DS                     4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                   203
DW               20.800 usec
DE                 6.50 usec
TE                294.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.68 usec
PL1                -0.60 dB
PL1W         41.24164963 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                 0.00 dB
PL12               15.66 dB
PL13               15.92 dB
PL2W          8.31434441 W
PL12W         0.22585411 W
PL13W         0.21272963 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127766 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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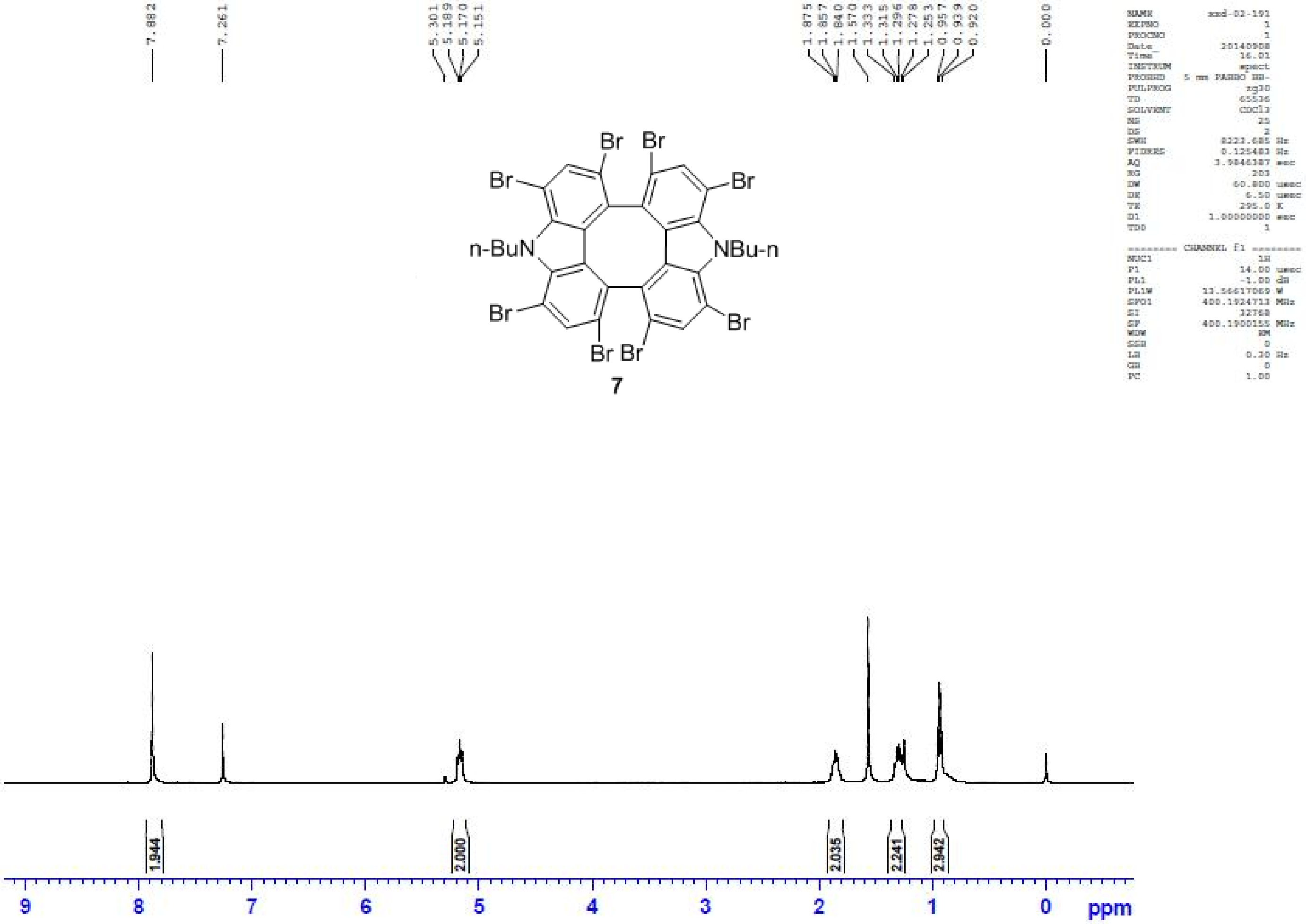

7

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PROCNO                 1
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INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    25
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                   203
DW                60.800 usec
DE                  6.50 usec
TE                 295.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.00 usec
PL1                -1.00 dB
PL1W         13.56617069 W
SFO1         400.1924713 MHz
SI                 32768
SF           400.1900155 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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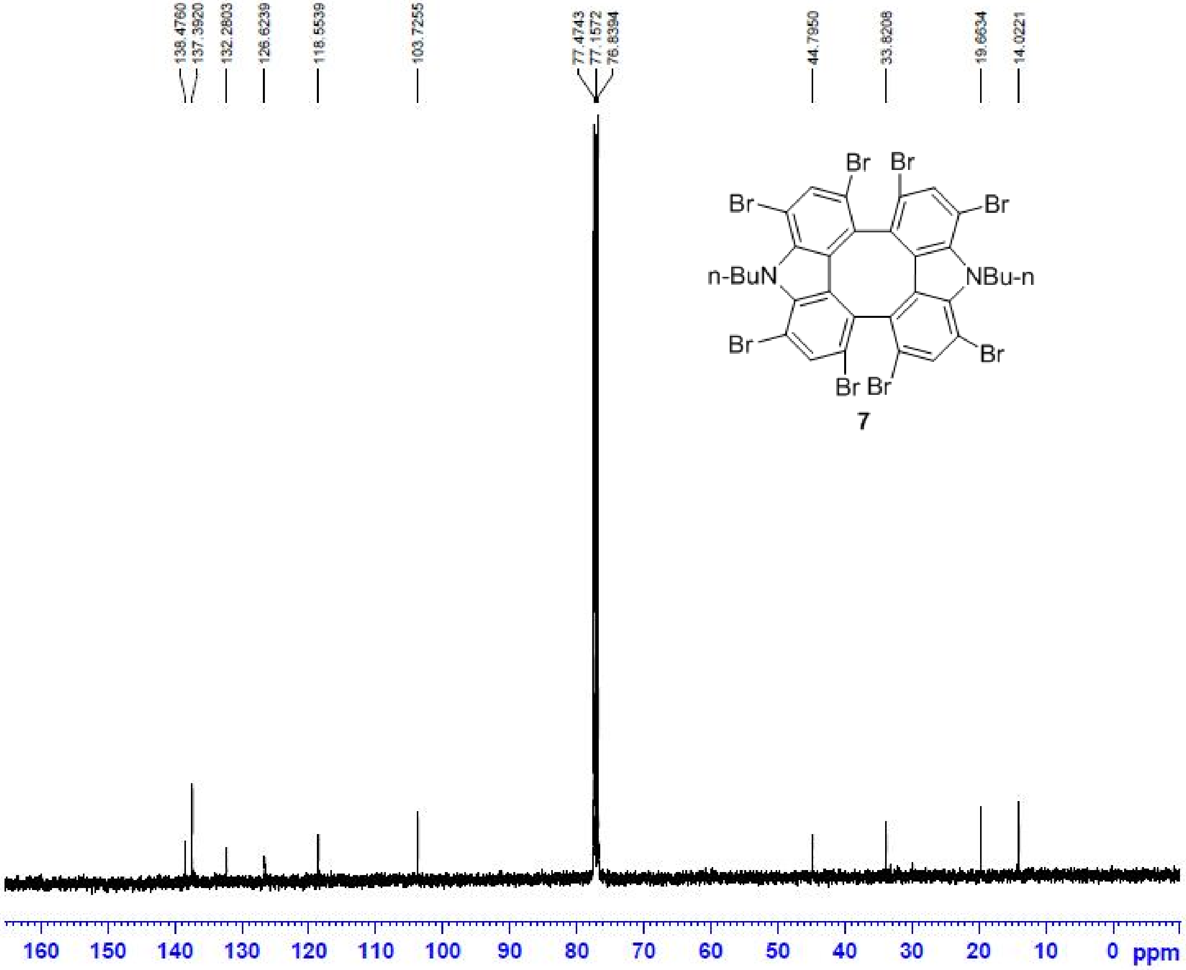

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Bruker AdvanceIII 400

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PROCNO                  1
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Time                16.05
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    476
DS                      4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                    161
DW                 20.800 usec
DE                   6.50 usec
TE                  295.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.90 usec
PL1                 -2.00 dB
PL1W         55.33689499 W
SFO1         100.6379183 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -1.00 dB
PL12                15.16 dB
PL13                18.62 dB
PL2W         13.56617069 W
PL12W         0.32844096 W
PL13W         0.14806664 W
SFO2         400.1916008 MHz
SI                  32768
SF           100.6278441 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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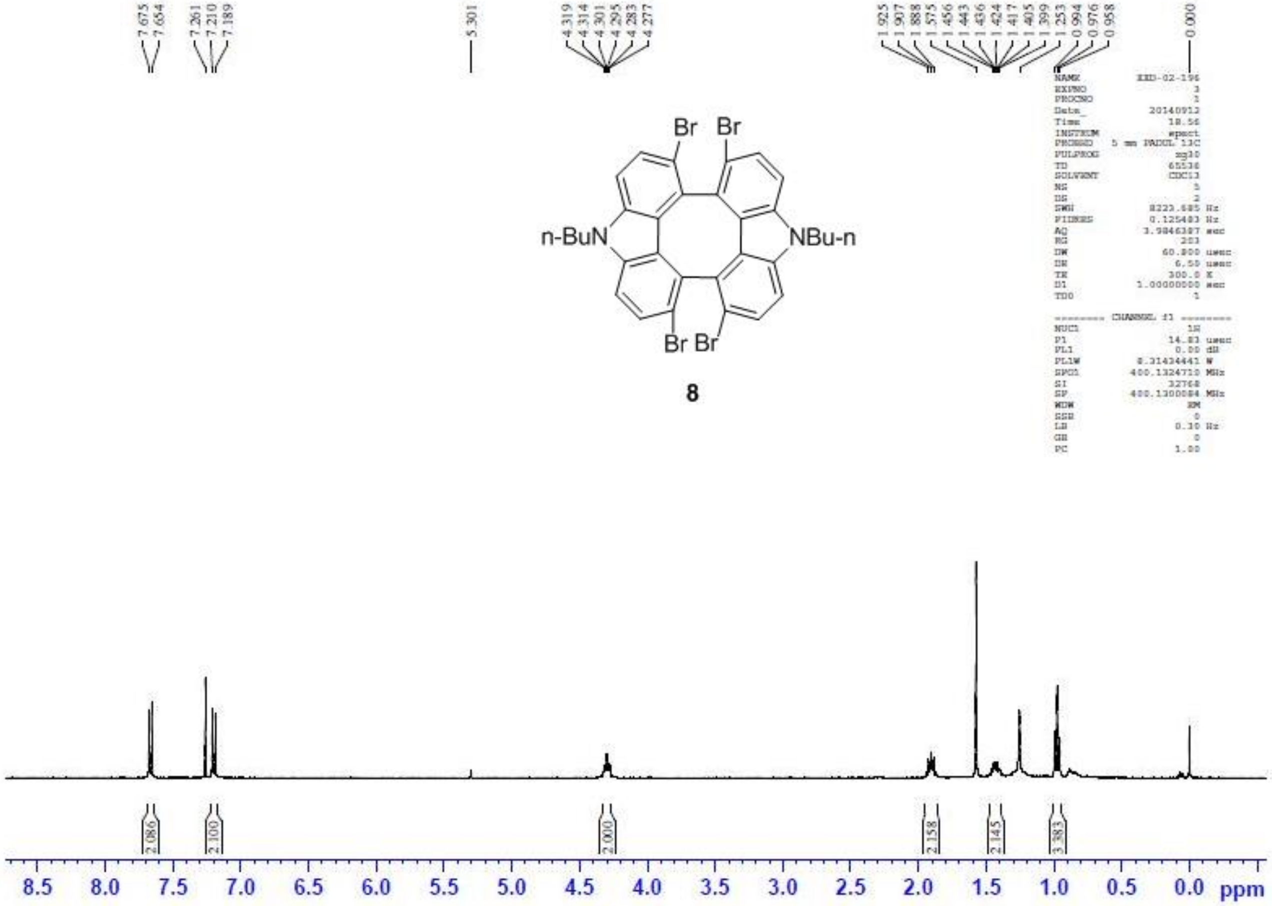
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1.925
1.907
1.888
1.575
1.456
1.443
1.436
1.424
1.417
1.405
1.399
1.253
0.994
0.976
0.958
0.000
Br
Br
n-BuN
NBu-n
Br
Br
8
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EXPNO 3
PROCNO 1
Date_ 20140912
Time 18.56
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.83 usec
PL1 0.00 dB
PL1W 8.31434441 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300084 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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2.100
2.000
2.158
2.145
3.383
8.5
8.0
7.5
7.0
6.5
6.0
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1.5
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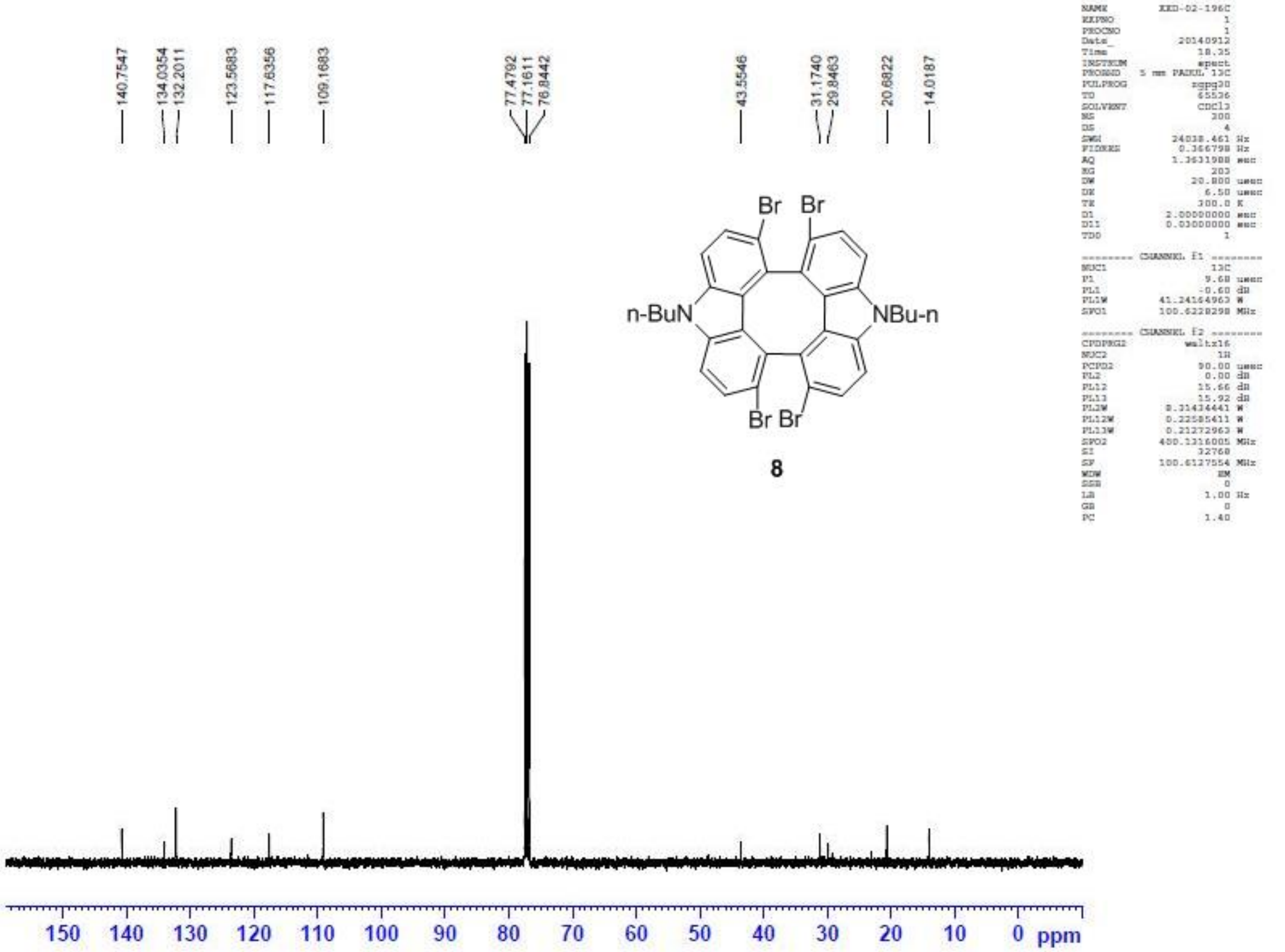

8

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PROCNO                  1
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Time                18.35
INSTRUM             spect
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PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    300
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.68 usec
PL1                 -0.60 dB
PL1W          41.24164963 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                  0.00 dB
PL12                15.66 dB
PL13                15.92 dB
PL2W           8.31434441 W
PL12W          0.22585411 W
PL13W          0.21272963 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127554 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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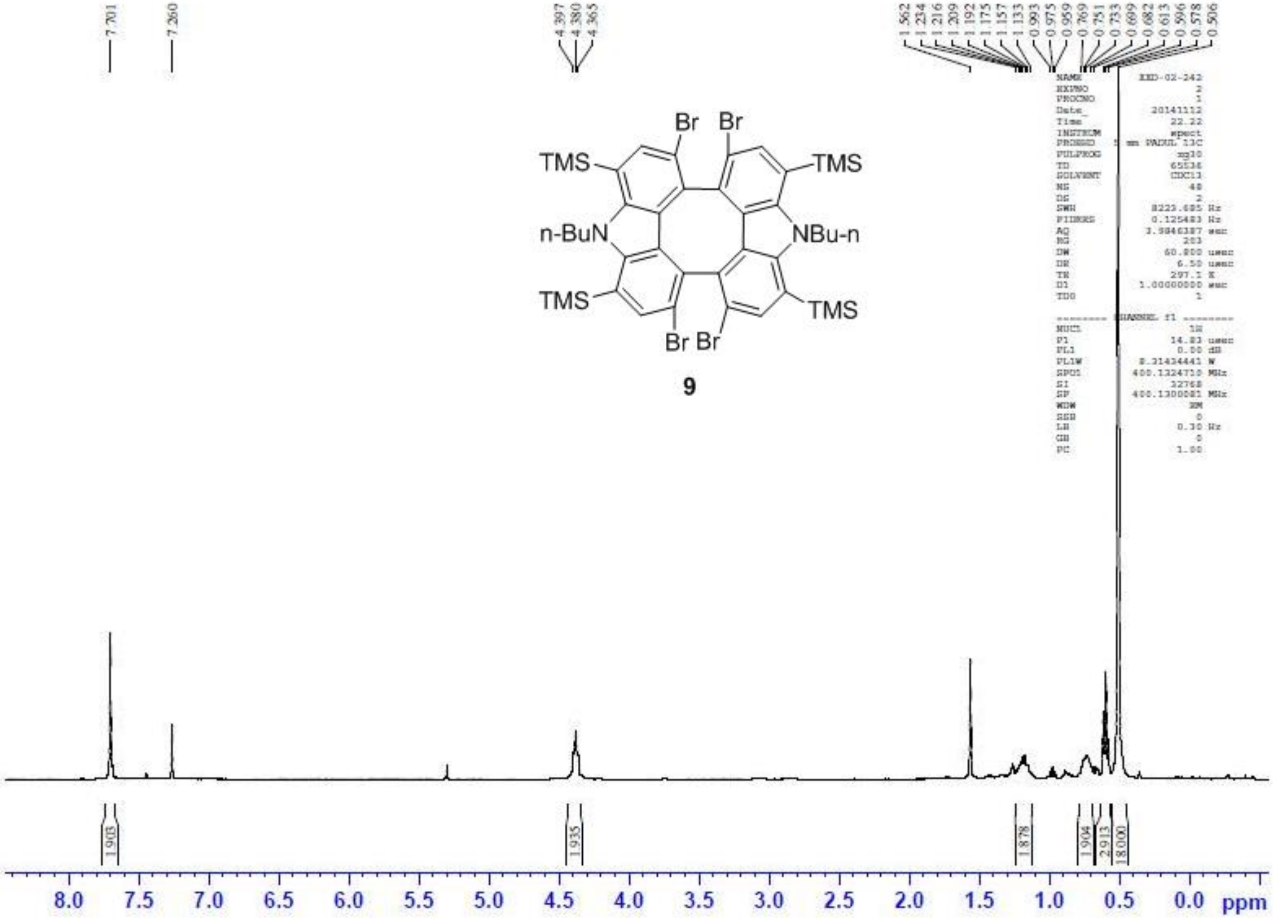
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1.157
1.133
0.993
0.975
0.959
0.769
0.751
0.733
0.699
0.682
0.613
0.596
0.578
0.506
Br
Br
TMS
TMS
n-BuN
NBu-n
TMS
TMS
Br
Br
NAME XXD-02-242
EXPNO 2
PROCNO 1
Date_ 20141112
Time 22.22
INSTRUM spect
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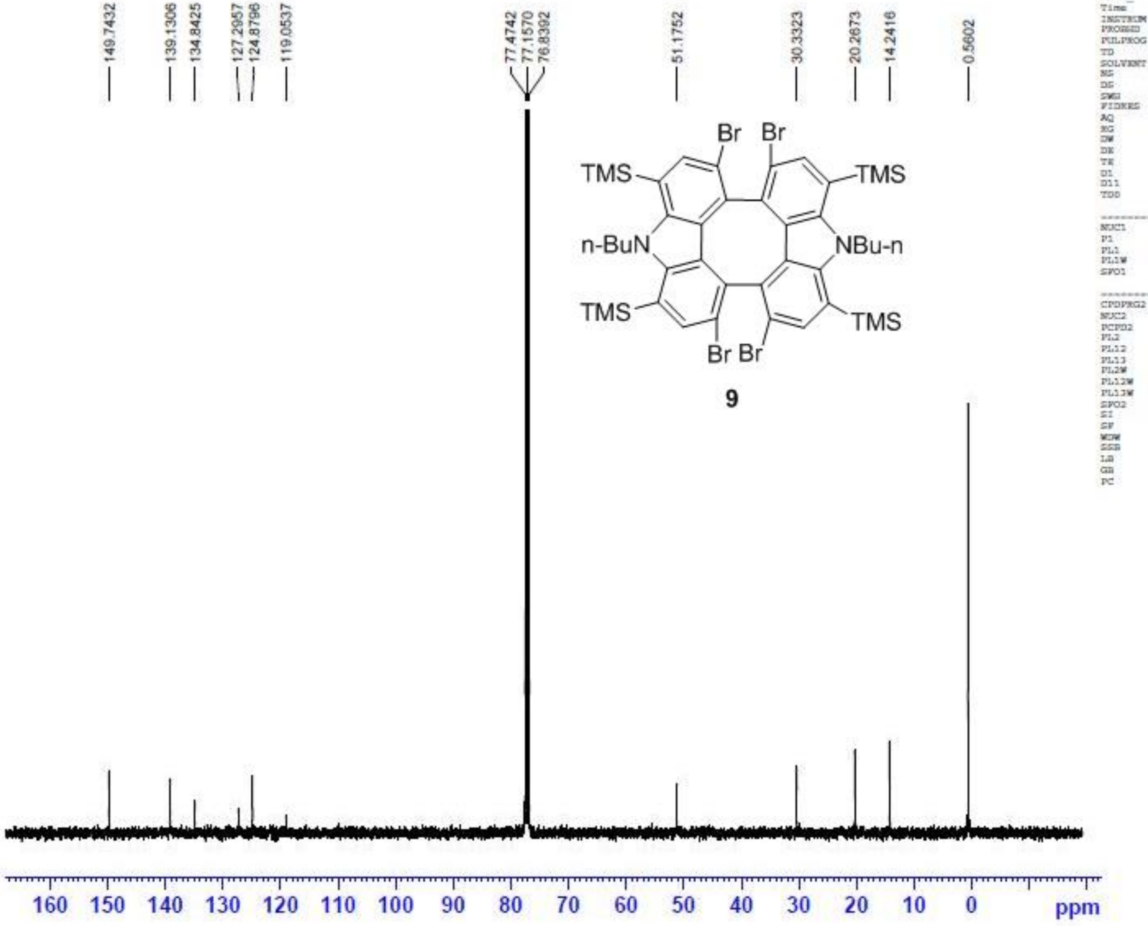
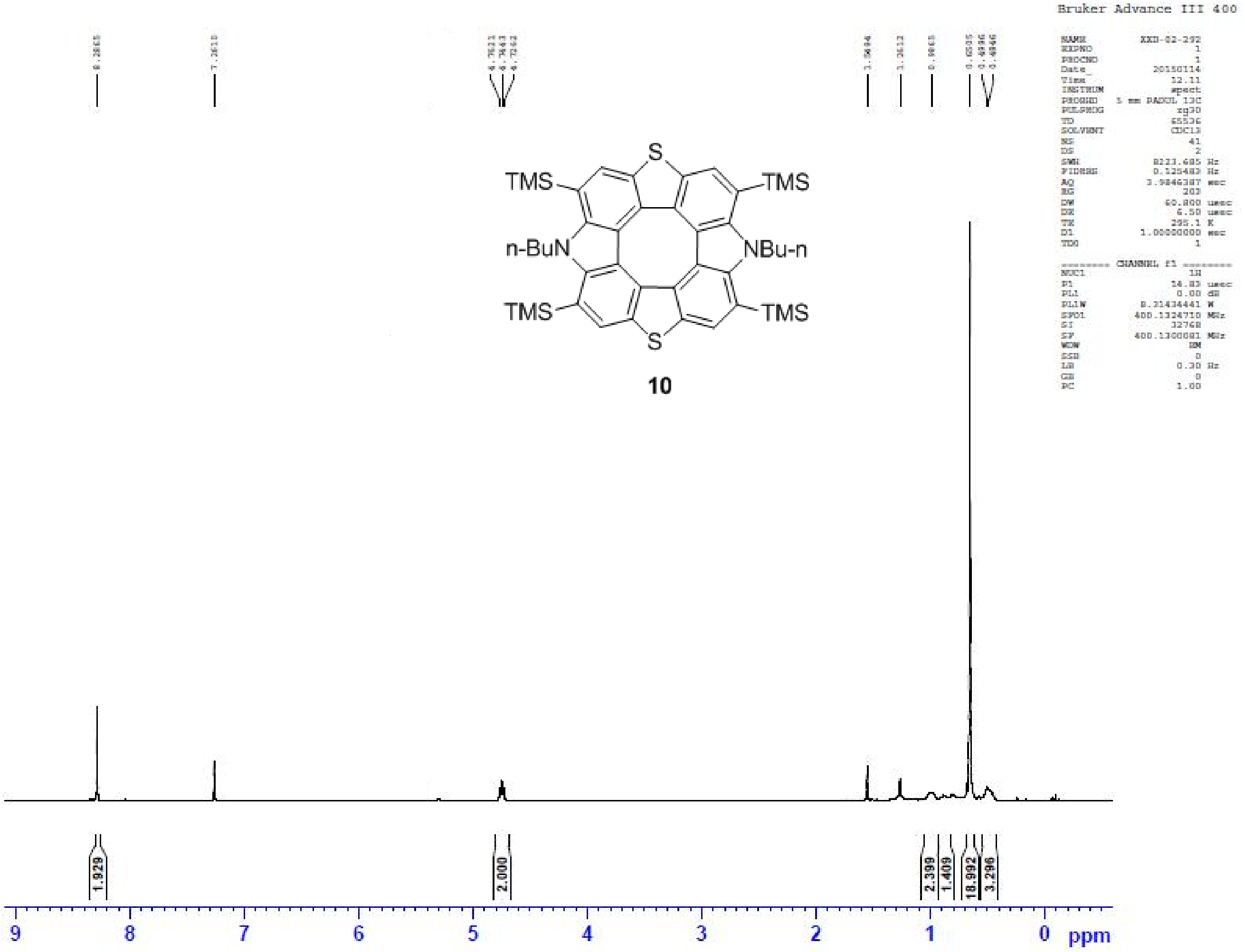
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 48
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 297.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.83 usec
PL1 0.00 dB
PL1W 8.31434441 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300081 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.903
1.935
1.878
1.904
2.913
18.000
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

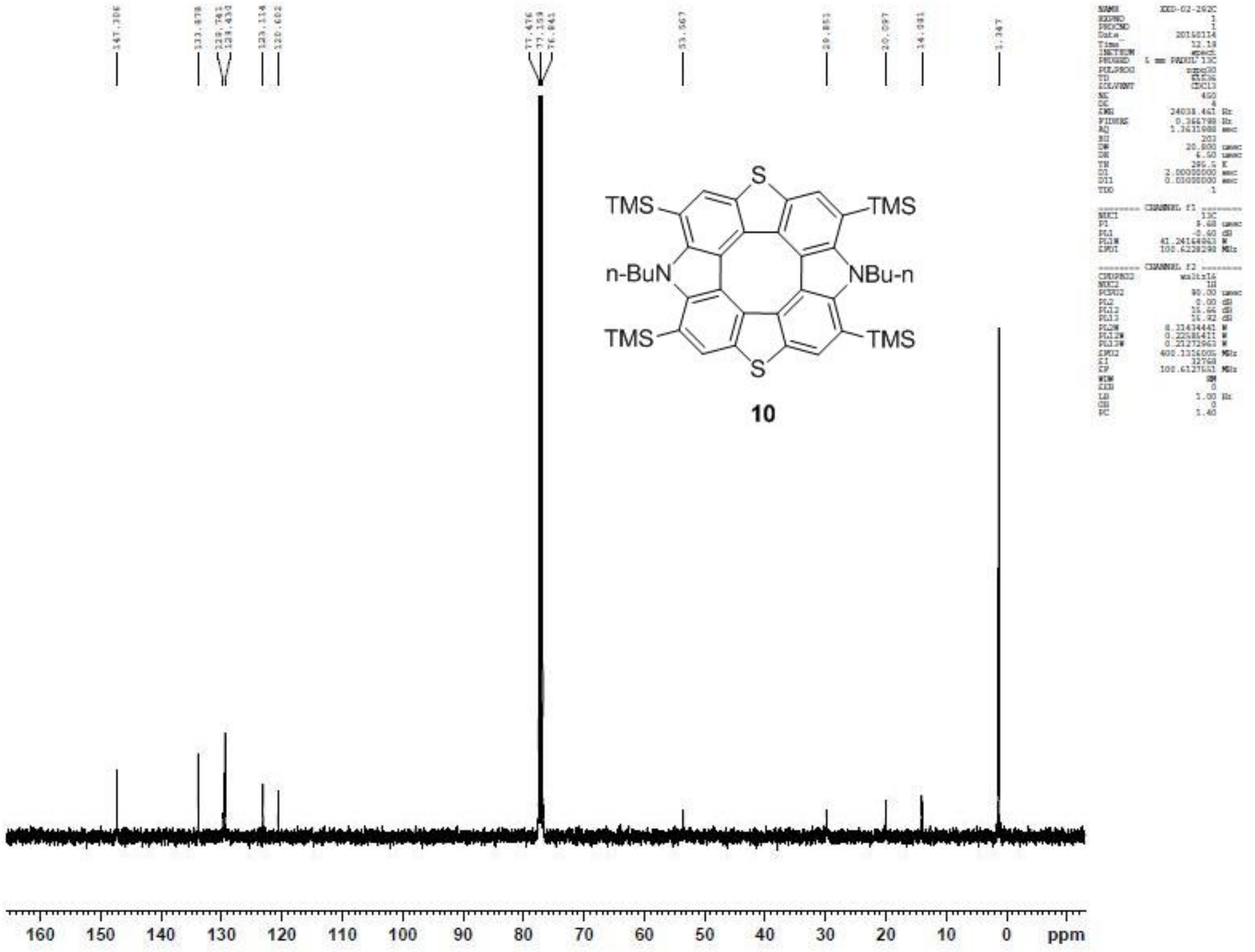
9



9

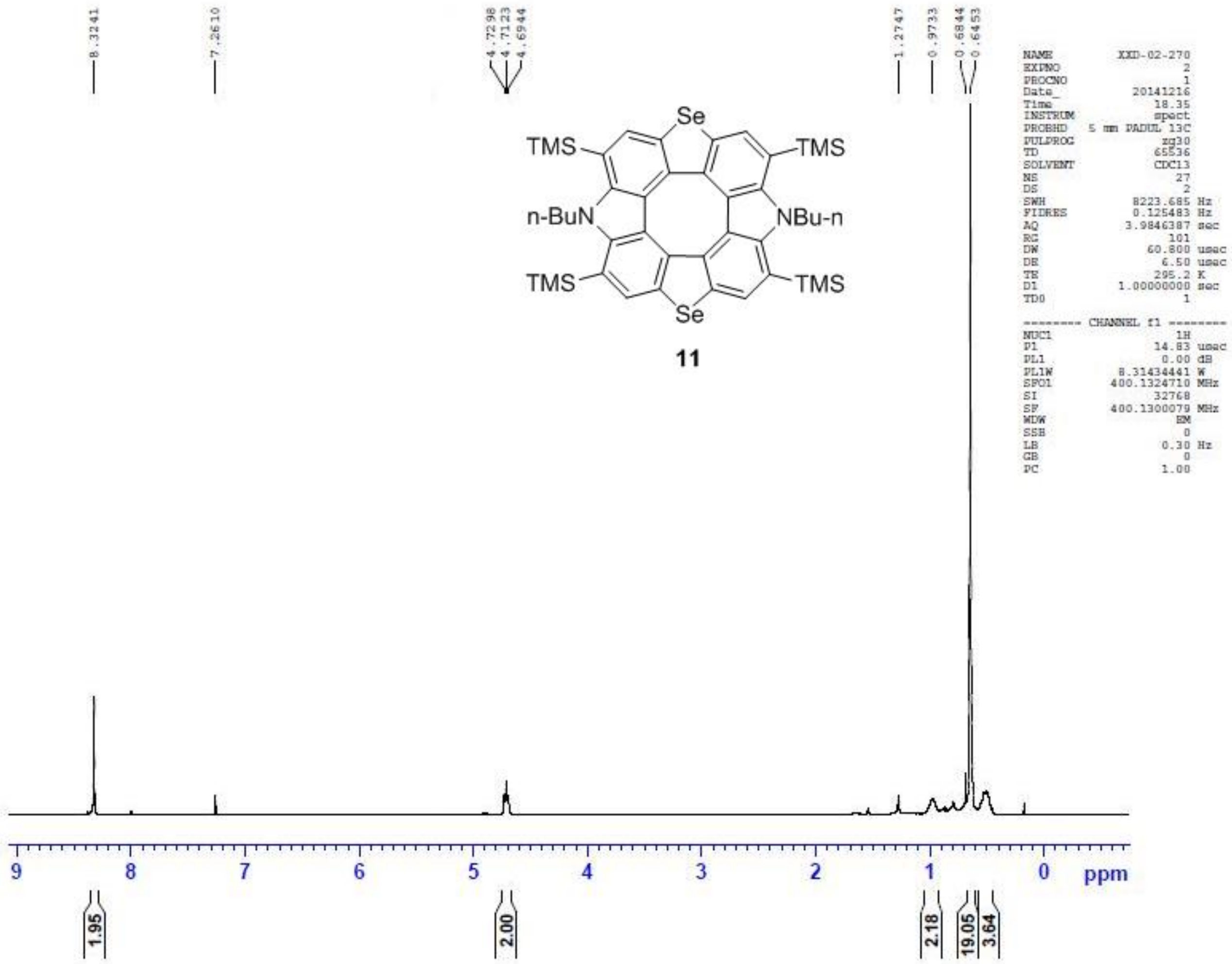
```
NAME           XXD-02-242C
EXPNO                    1
PROCNO                   1
Date_             20141112
Time                 21.40
INSTRUM              spect
PROBHD   5 mm PADUL 13C
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    623
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  296.7 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.68 usec
PL1                 -0.60 dB
PL1W          41.24164963 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                  0.00 dB
PL12                15.66 dB
PL13                15.92 dB
PL2W           8.31434441 W
PL12W          0.22585411 W
PL13W          0.21272963 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127546 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```


8.2865
7.2610
4.7621
4.7443
4.7262
1.5694
1.2613
0.9865
0.6535
0.4996
0.4846
TMS
TMS
TMS
TMS
S
S
n-BuN
NBu-n
10
1.929
2.000
2.399
1.409
18.992
3.296
9
8
7
6
5
4
3
2
1
0
ppm
Bruker Advance III 400
NAME XXD-02-292
EXPNO 1
PROCNO 1
Date_ 20150114
Time 12.11
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 41
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 295.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.83 usec
PL1 0.00 dB
PL1W 8.31434441 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300081 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

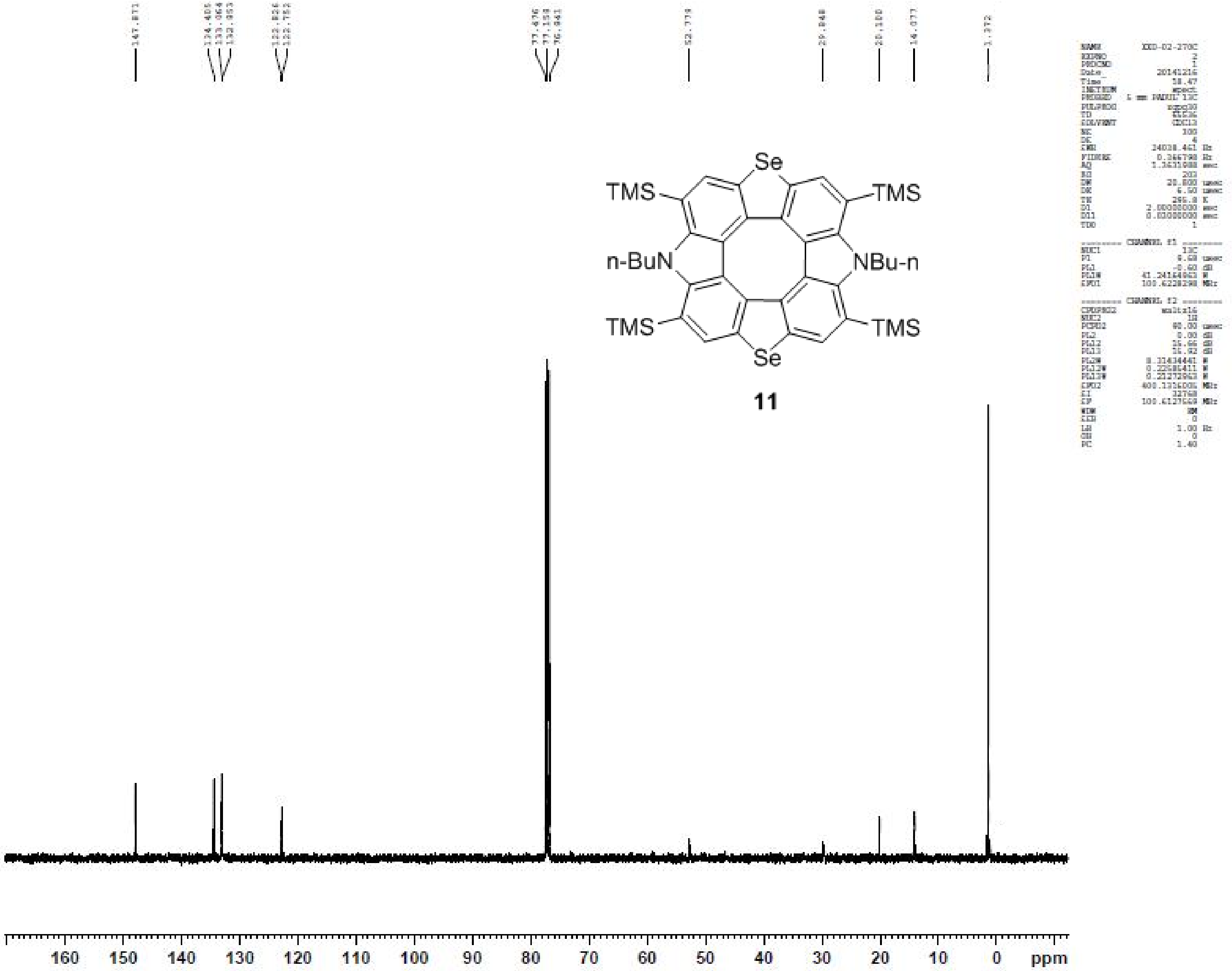


10

```
NAME          XXD-02-292C
EXPNO                   1
PROCNO                  1
Date_            20160114
Time                12.18
INSTRUM             spect
PROBHD   5 mm PABBO 13C
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    450
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  295.5 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.60 usec
PL1                 -0.60 dB
PL1W          41.24164963 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                  0.00 dB
PL12                15.66 dB
PL13                15.92 dB
PL2W           8.31434441 W
PL12W          0.22685411 W
PL13W          0.21272963 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127661 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



```
NAME          XXD-02-270
EXPNO                  2
PROCNO                 1
Date_           20141216
Time               18.35
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    27
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                   101
DW                60.800 usec
DE                  6.50 usec
TE                 295.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.83 usec
PL1                 0.00 dB
PL1W          8.31434441 W
SFO1         400.1324710 MHz
SI                 32768
SF           400.1300079 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```


11

147.873
134.405
133.064
132.853
122.826
122.752
77.476
77.158
76.841
52.779
29.848
20.100
14.077
1.372
Se
TMS
TMS
n-BuN
NBu-n
TMS
TMS
Se
NAME XXD-02-270C
EXPNO 2
PROCNO 1
Date_ 20141216
Time 18.47
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 300
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 295.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.68 usec
PL1 -0.60 dB
PL1W 41.24164963 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 16.66 dB
PL13 16.92 dB
PL2W 8.31434441 W
PL12W 0.22586411 W
PL13W 0.21272963 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127569 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm