# [2+2+2] cyclotrimerisation as a convenient route to 6N-doped nanographenes: a synthetic introduction to hexaazasuperbenzenes

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## Supporting information

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### S1. Materials and methods

**General Methods:** Unless otherwise stated, all reactions were carried out under nitrogen or argon with dry solvent, freshly distilled under anhydrous conditions. All chemicals were purchased from Sigma Aldrich unless otherwise stated.

NMR spectra were recorded in $CDCl_3$ with (i) Bruker Avance DPX-400 spectrometer (operating at 400.1 MHz for $^1H$, 100.6 MHz for $^{13}C$), (ii) Bruker AV-600 spectrometer (600.1 MHz for $^1H$, 150.6 MHz for $^{13}C$). $^1H$ and $^{13}C$ NMR spectra were referenced relative to TMS ($\delta = 0.00$ ppm) $^{13}C$ NMR spectra were proton-decoupled. Chemical shifts ($\delta$) are reported in ppm and coupling constants in Hz. IR spectra (reported in $cm^{-1}$) of neat samples were recorded with a Perkin–Elmer Spectrum-One FT-IR spectrometer equipped with a Universal-ATR sampling accessory. Electrospray mass spectra were recorded with a Micromass-LCT spectrometer, and accurate mass spectra were referenced against leucine enkephalin (555.6 g $mol^{-1}$) and reported to within 5 ppm. MALDI-TOF mass spectra were recorded with a Waters MALDI-QTOF Premier spectrometer by using an α-cyano-4-hydroxycinnamic acid matrix, and accurate mass spectra were referenced against [Glu1]-fibrinopeptide B (1570.6 g $mol^{-1}$) and reported to within 5 ppm. Elemental analyses were performed in the Microanalytical Laboratory, University College Dublin.

**Electrochemical Measurements:** Cyclic voltammetry was performed by using a CH instruments Electrochemical Analyser Model 600B. Cyclic voltammograms were measured on 1 mM solutions of ligands in $CH_2Cl_2$ by using tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) as supporting electrolyte. A standard three-electrode cell was employed with a glassy carbon working electrode, a Pt wire counter electrode, and an SCE as the reference electrode. Potentials are quoted vs. the ferrocene/ferrocenium couple (0.0 V), and all potentials were referenced to internal ferrocene added at the end of each experiment. Solutions were degassed for several minutes by nitrogen bubbling before the experiments were performed, and a flow of nitrogen over the solution was maintained for the duration of the experiment.

**Photophysical Measurements:** UV/Vis absorption spectra were recorded as optically dilute solutions ($10^{-5}$ to $10^{-6}$ M) in 1x1 $cm^2$ quartz cuvettes with a Shimadzu UV-2450 spectrophotometer. Corrected steady-state solution (ca. $10^{-6}$ M) spectra at 298K were recorded with a Horiba–Jobin–Yvon Fluorolog 3-22 spectrometer with double grating emission and excitation monochromators. Low temperature measurements were carried out within a thin tube in a quartz Dewar filled with liquid nitrogen. A Jobin–Yvon FluoroHub single-photon counting controller fitted with a 340 nm Jobin–Yvon NanoLED was used to measure lifetimes, which were determined from the observed decays by using DataStation v2.4. Emission quantum yields of **4** was measured by the Demas and Crosby[1] method relative to quinine sulfate in 0.5 M $H_2SO_4$ ($\Phi$em = 0.546) [2] as the reference. Corrections were made for the difference in refractive index of the sample and reference solutions.

### Crystal structure determination:

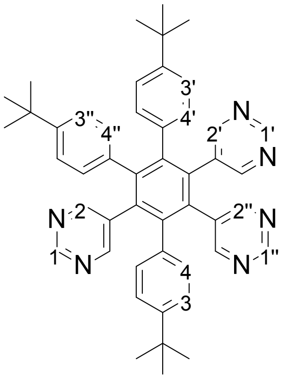
Single crystal analyses were carried out on a Bruker SMART APEX CCD diffractometer using graphite monochromised Mo-Kα (λ = 0.71073Å) radiation at the temperatures given following data. Data reduction was performed using SAINT. Intensities were corrected for Lorentz and polarization effects and for absorption by SADABS. The structures were solved by direct methods using SHELXS and refined on $F^2$ using all data by full-matrix least-squares procedures with SHELX-97. All non-hydrogen atoms were refined with anisotropic displacement parameters 1.3 times the isotropic equivalent of their carrier carbons.

## S2. Synthetic procedures

### Cyclotrimerisation of (4-*tert*-butylphenyl)(5-pyrimidyl)acetylene

(4-*Tert*-butylphenyl)(5-pyrimidyl)acetylene[3] (150 mg, 0.63 mmol) and dicobalt octacarbonyl (43.3 mg, 0.13 mmol) were heated at reflux temperature in dioxane (7 mL) for 24 h. The solvent was reduced in *vacuo*, dissolved in $CH_2Cl_2$ and filtered through celite to remove cobalt particles. The products were purified by column chromatography ($SiO_2$, $CH_2Cl_2$:$CH_3OH$, 25:1). Both asymmetric **1** ($R_f$ = 0.31) and symmetric **2** ($R_f$ = 0.57) products were isolated as white crystalline solids, with respective yields of: **1** (102 mg, 0.144 mol, 68%); **2** (40.5 mg, 0.057 mmol, 27%).

**3,5,6-Tri-(4-*tert*-butylphenyl)-1,2,4-tri-(5-pyrimidyl)benzene (1)**



**$^1$H-NMR** (400 MHz, $CDCl_3$, δ in ppm): 8.81 (s, 2H, $H^{1'}$ and $H^{1''}$), 8.74 (s, 1H, $H^1$), 8.27 (s, 2H, $H^{2'}$ or $H^{2''}$), 8.26 (s, 2H, $H^{2'}$ or $H^{2''}$), 8.24 (s, 2H, $H^2$), 7.04 (d, 2H, $^3J_{HH}$ = 8.0 Hz, $H^3$), 6.95 (d, 4H, $^3J_{HH}$ = 8.0 Hz, $H^{3'}$ and $H^{3''}$), 6.77 (d, 2H, $^3J_{HH}$ = 8.0 Hz, $H^4$), 6.70 (m, 4H, $H^{4'}$ and $H^{4''}$), 1.15 (s, 9H, $C(CH_3)_3$), 1.12 (s, 18H, $C(CH_3)_3$).

**$^{13}$C-NMR** (150 MHz, $CDCl_3$, δ in ppm ): 157.83 (2C, $C^{2'}$or $C^{2''}$), 157.81 (2C, $C^{2'}$or $C^{2''}$), 157.5 (2C, $C^2$), 156.2 (2C, $C^{1'}$and $C^{1''}$), 155.6 (1C, $C^1$), 150.3 ($C_{quat}$), 149.6 ($C_{quat}$), 149.5 ($C_{quat}$), 143.5 ($C_{quat}$), 142.6 ($C_{quat}$), 141.9 ($C_{quat}$), 135.2 ($C_{quat}$), 134.9 ($C_{quat}$), 134.8 ($C_{quat}$), 134.6 ($C_{quat}$), 134.2 ($C_{quat}$), 134.0 ($C_{quat}$), 133.7 ($C_{quat}$), 133.6 ($C_{quat}$), 133.4 ($C_{quat}$), 130.6 (2C, $C^3$), 130.5 (2C, $C^{3'}$or $C^{3''}$), 130.4 (2C, $C^{3'}$or $C^{3''}$), 125.1 (2C, $C^4$), 124.4 (2C, $C^{4'}$or $C^{4''}$), 124.3 (2C, $C^{4'}$or $C^{4''}$), 34.2 (3C,-$C(CH_3)_3$), 31.0 (9C, -$C(CH_3)_3$).

**HRMS** (ESI-MS, $CHCl_3$): calculated for $C_{48}H_{49}N_6$, $[M+H]^+$ *m/z,* 709.4019; found 709.3990.

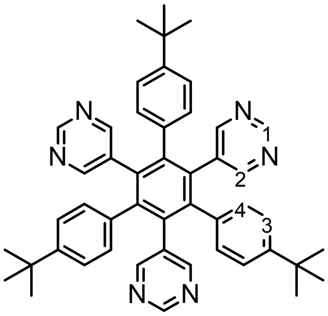
**M.p** > 360 ºC.

**IR** (neat) νbar in $cm^{-1}$: 3047 ($CH_{aromatic}$), 2868, 1578, 1548 (C=N), 1418 (C=C), 1388 ($CH_3$), 1269, 1174, 1019, 837, 786, 732.

**CHN**: Calculated (%) for $C_{48}H_{49}N_6$: C, 82.32; H, 6.82, N, 11.85. Found: C, 81.10; H, 6.68, N, 11.94. **UV-vis** ($CHCl_3$, nm): 270 ($\lambda_{max}^{abs}$).

**Fluorescence** ($CHCl_3$, nm, $\lambda_{exc}$ = 300 nm, RT): 357 ($\lambda_{max}^{em}$).

### 2,4,6-Tri-(4-*tert*-butylphenyl)-1,3,5-tri-(5-pyrimidyl)benzene (2)



**$^1$H-NMR** (400 MHz, $CDCl_3$, δ in ppm): 8.73 (s, 3H, $H^1$), 8.22 (s, 6H, $H^2$), 7.04 (d, 6H, $^3J_{HH}$ = 8.5 Hz, $H^3$), 6.77 (d, 6H, $^3J_{HH}$ = 8.5 Hz, $H^4$), 1.14 (s, 27H, $C(CH_3)_3$).

**$^{13}$C-NMR** (150 MHz, $CDCl_3$, δ in ppm): 157.5 (6C, $C^2$), 155.7 (3C, $C^1$), 150.3 ($C_{quat}$), 142.9 ($C_{quat}$), 134.4 ($C_{quat}$), 134.3 ($C_{quat}$), 133.8 ($C_{quat}$), 130.5 (6C, $C^4$), 125.1 (6C, $C^3$), 34.3 (3C, -$C(CH_3)_3$) and 31.0 (9C, -$C(CH_3)_3$).

**HRMS** (ESI-MS, $CHCl_3$): calculated for $C_{48}H_{49}N_6$, $[M+H]^+$ *m/z*, 709.4019; found 709.3983.

**M.p** > 360 ºC.

**IR** (neat) νbar in $cm^{-1}$: 3038 ($CH_{aromatic}$), 2904, 2868, 1576, 1548 (C=N), 1508, 1464, 1390 ($CH_3$), 1185, 833, 783.

**CHN**: Calculated (%) for $C_{48}H_{49}N_6$: C, 82.32; H, 6.82, N, 11.85. Found: C, 81.09; H, 6.88, N, 12.03.

**UV-vis** ($CHCl_3$, nm): 270 ($\lambda_{max}^{abs}$).

**Fluorescence** ($CHCl_3$, nm, $\lambda_{exc}$ = 300 nm, RT): 369 ($\lambda_{max}^{em}$).

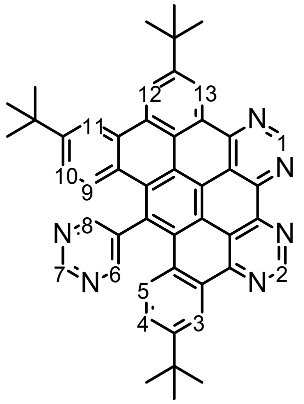
### Procedure for oxidative cyclodehydrogenation

Oxidative cyclodehydrogenation of **1** was carried out *via* three methods; **Method A** - $FeCl_3$ route and **Method B** – $AlCl_3/CuCl_2$ route and **Method C** – (i) $DDQ/CH_3SO_3H$ route and also by (ii) $DDQ/CF_3SO_3H$ route.[4]

**Method A**

A solution of iron(III) trichloride (602 mg, 3.70 mmol), in nitromethane (3 mL) was added dropwise to a stirred solution of **1** (100 mg, 0.14 mmol) in $CH_2Cl_2$ (40 mL). After stirring for 72 h under argon at room temperature, the reaction was quenched with $CH_3OH$ (20 mL) and was left stirring for another 30 min. The solvent was reduced *in vacuo*, and was redissolved in $CHCl_3$. The organic solution was washed with saturated $NaHCO_3$ (1 x 25 mL), water (2 x 25 mL) and finally dried over $MgSO_4$. Preparative thin layer chromatography ($SiO_2$, $C_7H_8$:$CH_3OH$, 25:1,) was used to isolate the products. Two main bands were observed: an orange band closer to the baseline and a yellow band above it. $^5/_6$-Asym-HASB (**4**) (five C-C bonds fused) was isolated as an orange solid in 20 % yield (20 mg, 0.03 mmol) and $^2/_3$-asym-HASB (**3**) (four C-C bonds fused) as a dark yellow solid in 10 % yield (10 mg, 0.014 mmol).

**⅔-Asym-HASB (3)**



**$^1$H-NMR** (600 MHz, 20 °C, $CDCl_3$, δ in ppm): 10.01 (s, 1H, $H^{13}$), 9.93 (s, 2H, $H^{12}$ and $H^1$), 9.81 (s, 1H, $H^7$), 9.70 (s, 1H, $H^8$), 9.56 (s, 1H, $H^6$), 9.53 (s, 1H, $H^3$), 9.49 (s, 1H, $H^2$), 9.31 (s, 1H, $H^{11}$), 8.58 (d, 1H, $^3J_{HH}$ = 8.1 Hz, $H^5$), 8.41 (d, 1H, $^3J_{HH}$ = 8.8 Hz, $H^9$), 7.71 (d, 1H, $^3J_{HH}$ = 7.4 Hz, $H^{10}$), 7.61 (d, 1H, $^3J_{HH}$ = 8.8 Hz, $H^4$), 1.78 (s, 9H, $C(CH_3)_3$), 1.62 (s, 9H, $C(CH_3)_3$), 1.60 (s, 9H, $C(CH_3)_3$).

**$^{13}$C-NMR** (150 MHz, 20 °C, $CDCl_3$, δ in ppm): 157.67 (1C, C), 156.88 (1C, C), 156.63 (1C, $C^1$), 156.22 (1C, $C^1$), 155.79 (1C, $C^1$), 154.03 ($C_{quat}$), 153.32 ($C_{quat}$), 152.22 ($C_{quat}$), 152.07 ($C_{quat}$), 151.98 ($C_{quat}$), 151.55 ($C_{quat}$),151.08 ($C_{quat}$), 134.30 ($C_{quat}$) , 131.77 ($C_{quat}$), 130.46 ($C_{quat}$), 130.43 ($C_{quat}$), 129.94 ($C_{quat}$), 129.83 ($C_{quat}$), 129.60 ($C_{quat}$), 129.19 ($C_{quat}$), 128.88 ($C_{quat}$), 128.85

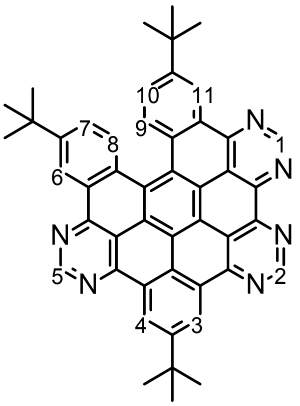
($C_{quat}$), 128.40 ($C_{quat}$), 128.07 ($C_{quat}$), 128.03, 127.46, 127.23, 127.18, 126.08 (1C, C), 125.46 (1C, C), 125.15 ($C_{quat}$), 124.29 ($C_{quat}$), 123.67 ($C_{quat}$), 122.97 ($C_{quat}$), 122.60 ($C_{quat}$), 121.62 ($C_{quat}$), 121.52 ($C_{quat}$), 121.39 (1C, C), 121.17 (1C, C), 120.17 ($C_{quat}$), 115.21 ($C_{quat}$), 35.89 (1C,-*C*($CH_3$)$_3$), 35.28 (1C,-*C*($CH_3$)$_3$), 35.24 (1C,-*C*($CH_3$)$_3$), 31.62 (3C, -C(*C*$H_3$)$_3$), 31.29 (3C, -C(*C*$H_3$)$_3$), 31.21(3C, -C(*C*$H_3$)$_3$).

**HRMS** (ESI-MS, $C_7H_8$) calculated for $C_{48}H_{41}N_6$, $[M+H]^+$ *m/z* 701.3393; found 701.3390.

**UV-vis** ($C_7H_8$, nm): 323 ($\lambda_{max}^{abs}$), 352, 385, 440, 468.

**Fluorescence** ($C_7H_8$, nm, $\lambda_{exc}$ = 360 nm, RT): 495 ($\lambda_{max}^{em}$).

**$^5/_6$-Asym-HASB (4)**



**$^1$H-NMR** (600 MHz, 20 °C, $CDCl_3$, δ in ppm): 10.20 (s, 1H, $H^1$), 10.09 (s, 1H, $H^2$), 10.05 (s, 1H, $H^5$), 10.03 (s, 1H, $H^3$), 9.98 (s, 1H, $H^4$), 9.56 (s, 1H, $H^{11}$), 9.54 (s, 1H, $H^8$), 8.72 (d, $^3J_{HH}$ = 8.6 Hz, 1H, $H^9$), 8.68 (d, $^3J_{HH}$ = 8.6 Hz, 1H, $H^8$), 7.72 (m, 2H, $H^7$ and $H^{10}$), 1.87 (s, 9H, -C(C*H*$_3$)$_3$) 1.67 (s, 9H, -C(C*H*$_3$)$_3$), 1.65 (s, 9H, -C(C*H*$_3$)$_3$).

**$^{13}$C NMR** (150 MHz, 20 °C, $CDCl_3$, δ in ppm): 157.09 (1C, $C^1$), 157.01 (1C, $C^2$), 156.04 (1C, $C^5$), 154.32 ($C_{quat}$), 154.14 ($C_{quat}$), 153.50 ($C_{quat}$), 153.38 ($C_{quat}$), 152.50 ($C_{quat}$), 152.37 ($C_{quat}$), 151.24 ($C_{quat}$), 151.03 ($C_{quat}$), 131.19 ($C_{quat}$), 130.83 (1C, $C^{10}$), 130.76 (1C, $C^7$), 129.54 ($C_{quat}$), 128.16 ($C_{quat}$), 127.31 (1C, $C^8$), 127.05 (1C, $C^9$), 126.90 (1C, $C^3$), 126.88 ($C_{quat}$), 126.71 ($C_{quat}$), 126.33 (1C, $C^4$) , 124.34 ($C_{quat}$), 121.96 (1C, $C^{11}$), 121.76 (1C, $C^6$), 121.35 ($C_{quat}$), 121.29 ($C_{quat}$), 119.66 ($C_{quat}$), 119.11($C_{quat}$), 118.14 ($C_{quat}$), 118.07 ($C_{quat}$), 117.16 ($C_{quat}$), 114.87 ($C_{quat}$), 36.11 (1C,-*C*($CH_3$)$_3$), 35.40 (1C,-*C*($CH_3$)$_3$), 35.35 (1C,-*C*($CH_3$)$_3$), 31.7 (3C, -C(*C*$H_3$)$_3$), 31.33 (3C, -C(*C*$H_3$)$_3$), 31.27 (3C, -C(*C*$H_3$)$_3$).

**HRMS** (ESI-MS, $C_7H_8$): calculated for $C_{48}H_{38}N_6$, $[M+Na]^+$ *m/z*, 721.3056; found 721.3060.

**M.p** > 360 ° C.

**IR** (neat) νbar in $cm^{-1}$: 2958 (C-H), 1603, 1560, 1528, 1465, 1395, 1367, 1296, 1252, 1121, 910, 887, 845, 792.

**UV-vis** ($C_7H_8$, nm): 323 ($\lambda_{max}^{abs}$), 352, 385, 440, 468.

**Fluorescence** ($C_7H_8$, nm, $\lambda_{exc}$ = 360 nm, RT): 495 ($\lambda_{max}^{em}$).

**Method B**

A solution mixture of **1** (50 mg, 0.07 mmol), $AlCl_3$ (140 mg, 1.05 mmol), and $CuCl_2$ (141 mg, 1.05 mmol) in $CS_2$ (15 mL) was stirred for 72 h at room temperature. The resulting black solid was allowed to settle and $CS_2$ was removed. The black solid was suspended in an aqueous 10 % ammonia solution (35 mL), extracted into chloroform and washed with water and the organic layer was dried over $MgSO_4$. The preliminary mass spectral results showed a mixture of products including ⅓rd fused (two C-C bonds), ½ fused (three C-C bonds), ⅔rd fused (four C-C bonds) and $^5/_6$th fused (five C-C bonds) products. Purification was carried out using preparative thin-layer chromatography ($SiO_2$, $C_7H_8$:$CH_3OH$, 25:1). The preparative plate showed a myriad of bands and only $^5/_6$-Asym-HASB (**4**) was successfully isolated as an orange solid in low yield (5 mg, 0.007 mmol, 5%).

The analyses of the products $^5/_6$-Asym-HASB (**4**), was consistent with the results obtained by **Method A**.

**Method C**

**(i) DDQ/$CH_3SO_3H$**

Compound **1** (50 mg, 0.071 mmol) was dissolved in $CH_2Cl_2$ (10 mL), and methanesulfonic acid (1.0 mL) was added. The reaction mixture rapidly changed colour to a yellow upon addition of acid and the mixture was cooled at 0 °C for 15 min. DDQ (6 eq.) was dissolved in $CH_2Cl_2$ (4 mL) and was added dropwise to the reaction mixture. The reaction mixture gradually changed to a dark green coloration (after 2 hrs), and was stirred at 0 °C for 5 h and left stirring at room temperature under argon for 48 h. After completion of the reaction, it was quenched with addition of saturated aqueous solution of $NaHCO_3$ (20 mL). The organic layer was separated and washed with brine solution and water, and dried over $Na_2SO_4$. The removal of solvent *in vacuo* afforded a yellow precipitate. Thin layer preparative plate ($SiO_2$, $C_7H_8$:$CH_3OH$, 20:1) separation, resulted in the isolation of the $^5/_6$th-Asym-HASB (**4**) as a yellow solid. In addition, the $^5/_6$*th* product was isolated by precipitating it from the mother liquor, giving an overall yield of 60 %, (30 mg, 0.042 mmol).

**(ii) DDQ/$CF_3SO_3H$**

Compound **1** (14 mg, 0.020 mmol) was dissolved in $CH_2Cl_2$ (10 mL) under an atmosphere of nitrogen, and DDQ (27 mg, 0.118 mmol) was added. Trifluoromethanesulfonic acid (0.01 mL, 0.118 mmol) was subsequently added, upon the addition of which a dark red colour was immediately observed. The reaction mixture slowly changed colour to a dark green over two hours. After completion of the reaction, it was quenched by the addition of a saturated aqueous solution of $K_2CO_3$. The organic layer was separated and washed with $H_2O$ (10 ml). The resulting solution was reduced *in vacuo* and upon addition of methanol, the product was precipitated as a yellow/orange solid, in a yield of 58% (8 mg, 0.012 mmol). NMR and HRMS confirmed the presence of a single species, the $^5/_6$th-Asym-HASB (**4**), consistent with the product yielded from (i).

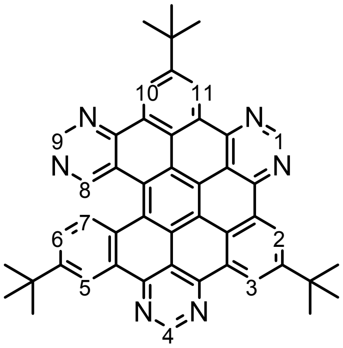
The analysis of the product obtained by **Method C** ((i) and (ii)), $^5/_6$-Asym-HASB (**4**), was consistent with the results obtained by **Method A**.

**Cyclodehydrogenation of 2**

Oxidative cyclodehydrogenation of **2** was carried out *via* three methods; **Method A** - $FeCl_3$ route and **Method B** - $AlCl_3$/$CuCl_2$ route and **Method C** - DDQ/$H^+$ route.

**Method A** discussed above for **1** was followed using a solution of iron(III) trichloride (602 mg, 3.70 mmol), in nitromethane (3 mL) which was added dropwise to a stirred solution of **2** (100 mg, 0.14 mmol) in $CH_2Cl_2$ (40 mL). A similar work up was followed and preparative thin layer chromatography ($SiO_2$, $C_7H_8$:$CH_3OH$, 10:0.4) resulted in successful isolation of $^5/_6$-Sym-HASB (**5**) as a yellow solid in 23 % yield. (23 mg, 0.03 mmol).

## $^5/_6$-Sym-HASB (5)



**$^1$H-NMR** (600 MHz, 20 °C, $CDCl_3$, δ in ppm): 10.37 (s, 2H, $H^1$ and $H^4$), 10.29 (s, 2H, $H^2$ and $H^3$), 10.18 (s, 1H, $H^9$), 9.76 (s, 1H, $H^5$), 9.66 (s, 1H , $H^{10}$ or $H^{11}$ ), 8.98 (d, J= 8.1Hz, 1H, $H^7$), 8.85 (s, 1H, $H^8$), 7.85 (m, 2H, $H^6$ and $H^{10}$ or $H^{11}$) 1.88 (s, 9H, $C(CH_3)_3$), 1.67 (s, 9H, $C(CH_3)_3$), 1.64 (s, 9H, $C(CH_3)_3$).

**HRMS** (ESI-MS, $C_7H_8$): calculated for $C_{48}H_{38}N_6$, $[M+H]^+$ *m/z*, 699.3236; found 699.3236.

**UV-vis** ($C_7H_8$, nm): 323 ($\lambda_{max}^{abs}$), 352, 385, 440, 468.

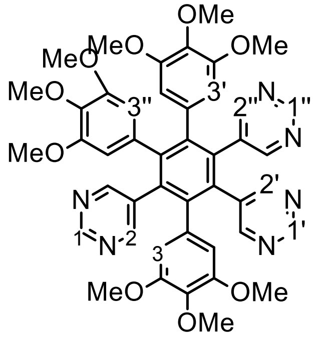
**Fluorescence** ($C_7H_8$, nm, $\lambda_{exc}$ = 360 nm, RT): 495 ($\lambda_{max}^{em}$).

**Method B** and **Method C** were also attempted for **2**, however these were unsuccessful.

### Cyclotrimerisation of (3,4,5-trimethoxyphenyl)(5-pyrimidyl)acetylene

(3,4,5-Trimethoxyphenyl)(5-pyrimidyl)acetylene[5] (150 mg, 0.55 mmol) and dicobalt octacarbonyl (43.3 mg, 0.13 mmol) were heated at reflux temperature in dioxane (7 mL) for 24 h. The solvent was reduced in *vacuo,* dissolved in $CH_2Cl_2$ and filtered through celite to remove cobalt particles. The products were purified by column chromatography ($SiO_2$, $CH_2Cl_2$:$CH_3OH$, 25:1). Both asymmetric **6** ($R_f$ = 0.24) and symmetric **7** ($R_f$ = 0.33) products were isolated as white crystalline solids with respective yields of: **6** (95 mg, 0.12 mmol, 63 %); **7** (25 mg, 0.03 mmol, 17 %).

### 3,5,6-Tri-(3,4,5-trimethoxyphenyl)-1,2,4-tri-(5-pyrimidyl)benzene (6)



$^1$**H-NMR** (600 MHz, 20 °C, $CDCl_3$, δ in ppm): 8.84 (s, 1H, H1’/H”), 8.82 (s, 1H, H1’/H”), 8.81 (s, 1H, H1), 8.28 (m, 6H, H2, H2’ and H2”), 3.66, 3.49, 3.48, 3.46, 3.43 (-OC$H_3$).

$^{13}$**C-NMR** (150 MHz, 20 °C, $CDCl_3$, δ in ppm): 157.36 (1C, $C^{2'}$or $C^{2''}$), 157.26 (1C, $C^{2'}$or $C^{2''}$), 156.75 (1C, $C^{2'}$or $C^{2''}$), 156.68 (1C, $C^{2'}$or $C^{2''}$), 156.47 (2C, $C^2$), 156.41 (1C, $C^1$), 156.06 (1C, $C^{1'}$or $C^{1''}$), 156.01 (1C, $C^{1'}$or $C^{1''}$), 152.83 ($C_{quat}$), 152.79 ($C_{quat}$), 152.58 ($C_{quat}$), 152.55 ($C_{quat}$), 142.72 ($C_{quat}$), 142.63 ($C_{quat}$), 141.83 ($C_{quat}$), 137.27 ($C_{quat}$) , 137.24 ($C_{quat}$), 137.05 ($C_{quat}$) , 135.01 ($C_{quat}$), 134.67 ($C_{quat}$), 134.01 ($C_{quat}$), 133.94 ($C_{quat}$), 133.79 ($C_{quat}$), 133.67 ($C_{quat}$), 133.23 ($C_{quat}$), 132.98 ($C_{quat}$), 132.94 ($C_{quat}$), 132.77 ($C_{quat}$), 132.09 ($C_{quat}$), 131.90 ($C_{quat}$), 108.72 (2C, $C^3$), 108.64 (2C, $C^3$), 108.61 (2C, $C^3$), 60.73 (3C, –O$CH_3$), 55.95 (6C, –O$CH_3$).

**HRMS** (MALDI-TOF, $CHCl_3$): calculated for $C_{45}H_{42}N_6O_9$, $[M+H]^+$ *m/z,* 810.3013; found 810.2988.

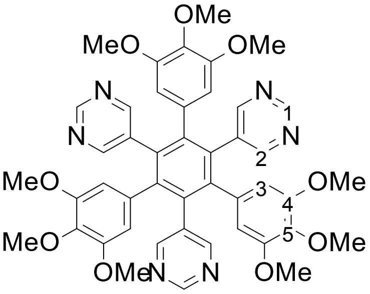
**M.p.** 243 - 245 ºC.

**IR** (neat) νbar in $cm^{-1}$: 2960 (C-H), 1580, 1452, 1411, 1294, 1321, 1238, 1118 (C-OR), 1000, 972, 830, 767.

**UV-vis** ($CHCl_3$, nm): 270 ($\lambda_{max}^{abs}$).

**Fluorescence** ($CHCl_3$, nm, $\lambda_{exc}$ = 300 nm, RT): 357 ($\lambda_{max}^{em}$).

**2,4,6-tri-(3,4,5-Trimethoxyphenyl)-1,3,5-tri-(5-pyrimidyl)benzene (7)**



$^1$**H-NMR** (600 MHz, 20 °C, $CDCl_3$, δ in ppm): 8.87 (s, 3H, $H^1$), 8.34 (s, 6H, $H^2$), 6.04 (s, 6H, $H^3$), 3.72 (s, 9H, -$C^5OCH_3$), 3.54 (s, 18H, -$C^4OCH_3$).

$^{13}$**C-NMR** (150 MHz, $CDCl_3$, δ in ppm): 156.74 (6C, $C^2$), 156.04 (3C, $C^1$), 152.86 ($C_{quat}$), 142.73 ($C_{quat}$), 137.34 ($C_{quat}$), 132.04 ($C_{quat}$), 108.69 (6C, $C^3$), 60.80 (6C–$C^5OCH_3$), 56.07 (3C, –$C^4OCH_3$).

**HRMS** (MALDI-TOF, $CHCl_3$): calculated for $C_{45}H_{42}N_6O_9$, $[M+H]^+$ *m/z,* 810.3013; found 810.2986.

**M.p** 240 - 242 ºC.

**IR** (neat) νbar in $cm^{-1}$: 2961 (C-H), 1579, 1452, 1411, 1294, 1321, 1238, 1118 (C-OR), 1000, 972, 830, 767.

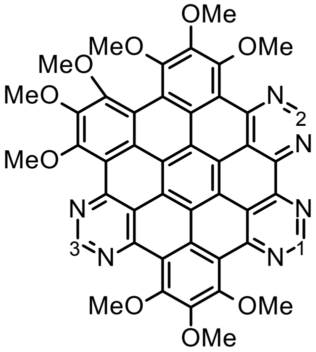
**UV-vis** ($CHCl_3$, nm): 270 ($\lambda_{max}^{abs}$).

**Fluorescence** ($CHCl_3$, nm, $\lambda_{exc}$ = 300 nm, RT): 357 ($\lambda_{max}^{em}$).

**Cyclodehydrogenation of 6**

**Method A,** discussed above for compound **1,** was followed using a solution of iron(III) trichloride (602 mg, 3.70 mmol), in nitromethane (3 mL), which was added dropwise to a stirred solution of **6** (100 mg, 0.12 mmol) in $CH_2Cl_2$ (40 mL). After 24 hrs the reaction was quenched with $CH_3OH$ and was stirred for 30 min. The solvent was removed *in vacuo*, and yielded a brownish red solid. Preliminary mass spectral analysis of the crude material indicated the presence of a mixture of products, showing mainly the presence of the fully-fused product (six C-C bonds closed) **8** as the predominant product, along with a $^5/_6$th-fused product (five C-C bonds closed). Thin layer preparative plate ($SiO_2$, $C_7H_8$:$CH_3OH$, 20:1) resulted in isolation of the fully fused **8** in 10 % yield. (10 mg, 0.012 mmol).

### 7, 8, 9, 10, 11, 12, 16, 17, 18-Non-(methoxy)-1, 3, 4, 6, 13, 15 –hexaazasuperbenzene (8)

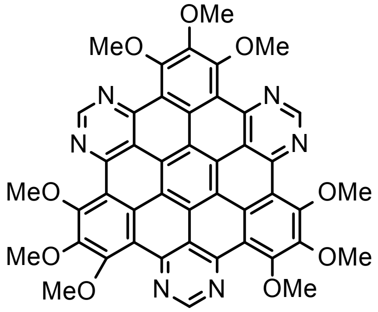


$^1$**H-NMR** (600 MHz, 20 °C, $CDCl_3$, δ in ppm): 10.49 (s, 1H , H1 or H2) , 10.46 (s, 1H , H1 or H2), 10.33 (s, 1H , H3), 4.56 - 4.20 (27 H, - OC*$H_3$*).
**HRMS** (ESI-MS, $CHCl_3$): calculated for $C_{45}H_{31}N_6O_9$, $[M+H]^+$ *m/z* 799.2147; found 799.2144.
**UV-vis** ($C_7H_8$, nm): 325, 365 ($\lambda_{max}^{abs}$), 386, 462, 492.
**Fluorescence** ($C_7H_8$, nm, $\lambda_{exc}$ = 360 nm, RT): 514 ($\lambda_{max}^{em}$).
(Due to low yield, it was not possible to obtain a $^{13}$C NMR of **8**.)

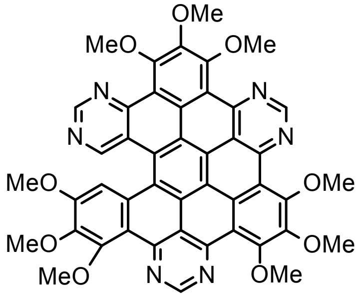
### Cyclodehydrogenation of 7

**Method A** discussed above for compound **1** was followed using a solution of iron(III) trichloride (602 mg, 3.70 mmol) in nitromethane (3 mL) which was added dropwise to a stirred solution of **7** (100 mg, 0.12 mmol) in $CH_2Cl_2$ (40 mL). A similar work-up was carried out as discussed in **Method A** for **1**. The preliminary mass spectral analysis of the crude product resulted in both the fully-fused **9** and $^5/_6{}^{th}$-fused **10**. However, despite several attempts using thin layer preparative plate in various solvent systems ($CH_2Cl_2$:$CH_3OH$, 10:0.1)/ $CH_2Cl_2$:$CH_3OH$, 10:0.2)/ ($C_7H_8$:$CH_3OH$, 20:1) the two products could not be separated.

### 4, 5, 6, 10, 11, 12, 16, 17, 18-Non-(methoxy)-1, 3, 7, 9, 13, 15 –hexaazasuperbenzene (9) and $^{5}/_{6}$-Sym-HASB (9)



**9**



**$^{5}/_{6}$-Sym-HASB (9)**

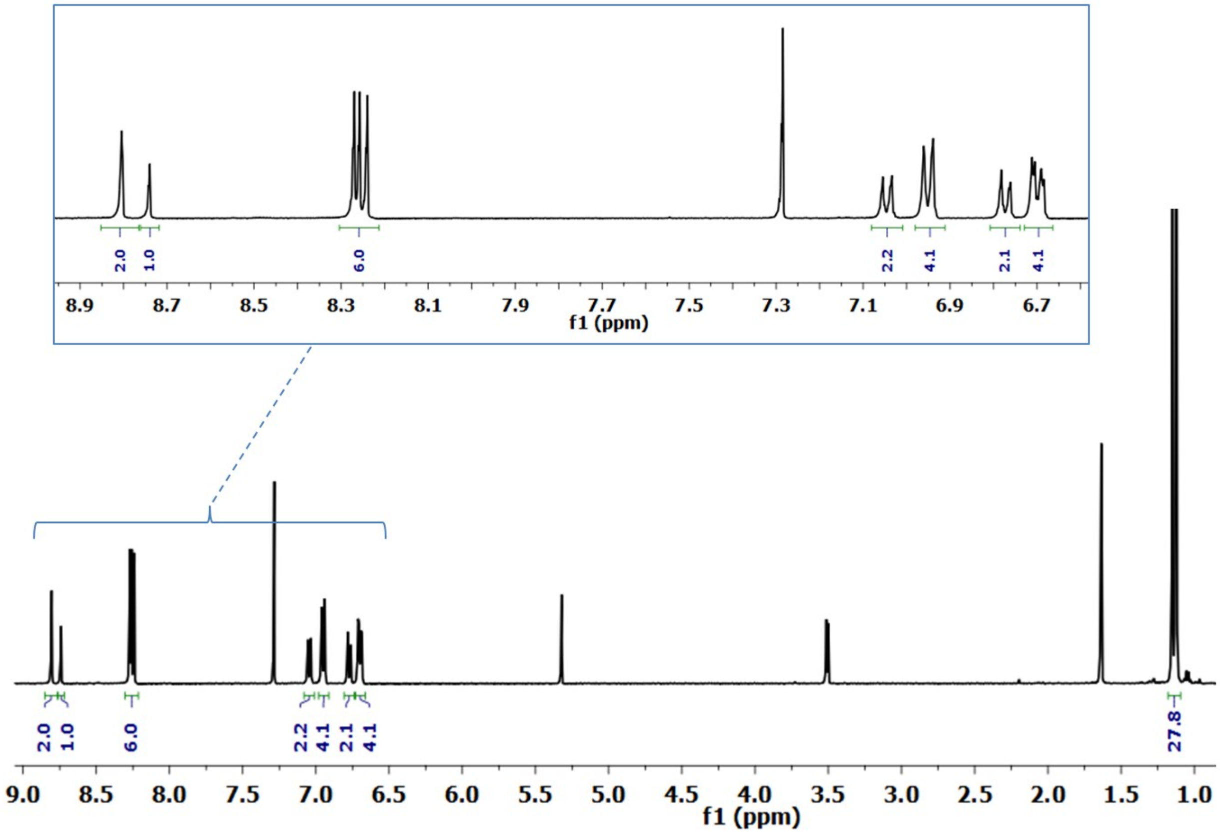
**HRMS** (ESI-MS, $CHCl_3$): calculated for $C_{45}H_{31}N_6O_9$, $[M+H]^+$ *m/z*, 799.2153; found 799.2134 (**9**).

**HRMS** (ESI-MS, $CHCl_3$): calculated for $C_{45}H_{33}N_6O_9$, $[M+H]^+$ *m/z,* 801.2309; found 801. 2332 **$^{5}/_{6}$-Sym-HASB (9).**

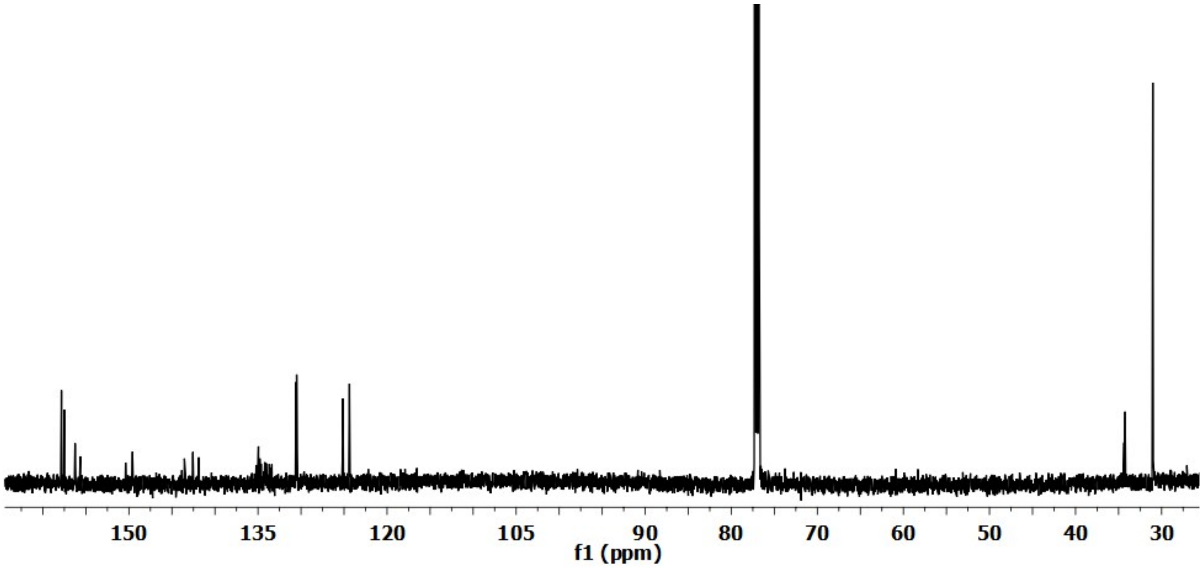
## S3. $^{1}$H and $^{13}$C NMR Spectra

**1** in $CDCl_3$

$^{1}$H –NMR

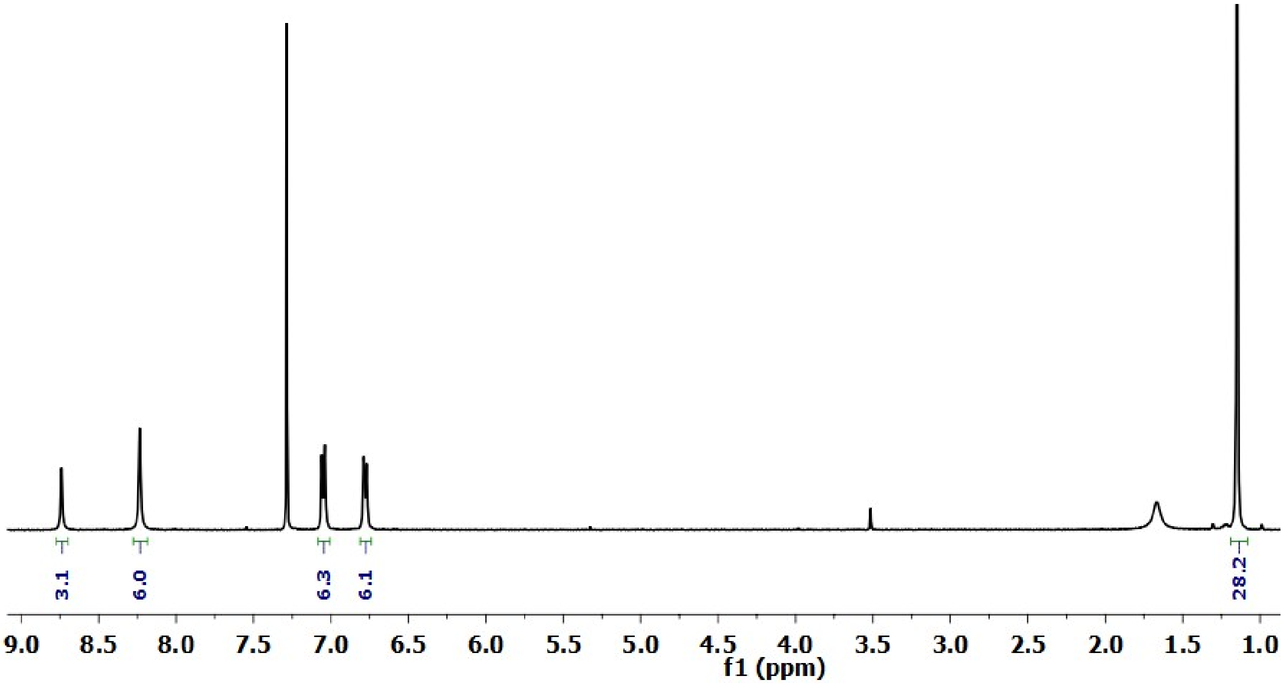


$^{13}$C-NMR

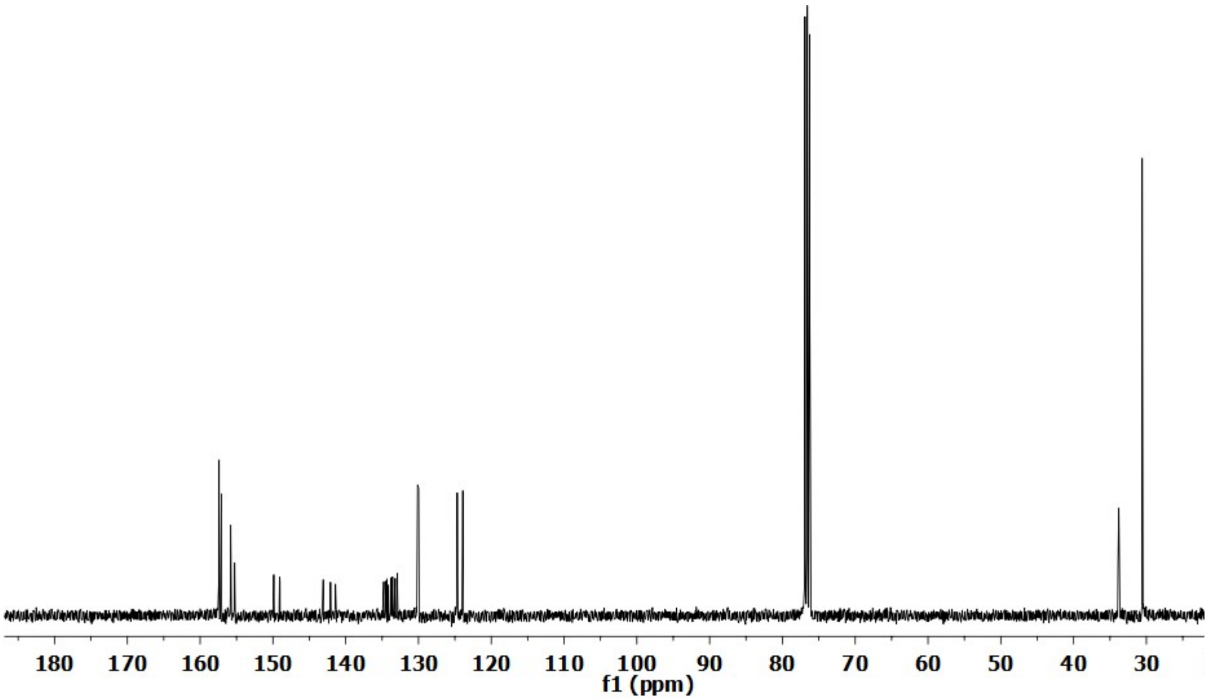


**2** in $CDCl_3$

$^1H$-NMR

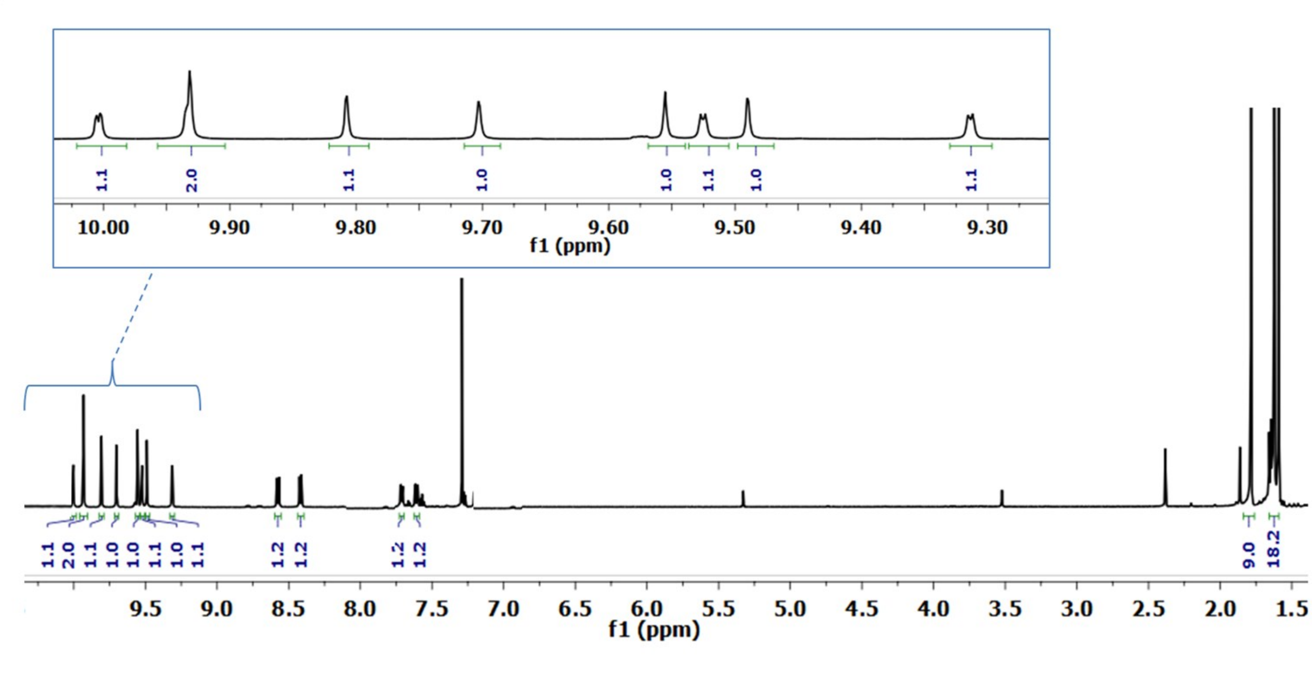


$^{13}C$-NMR

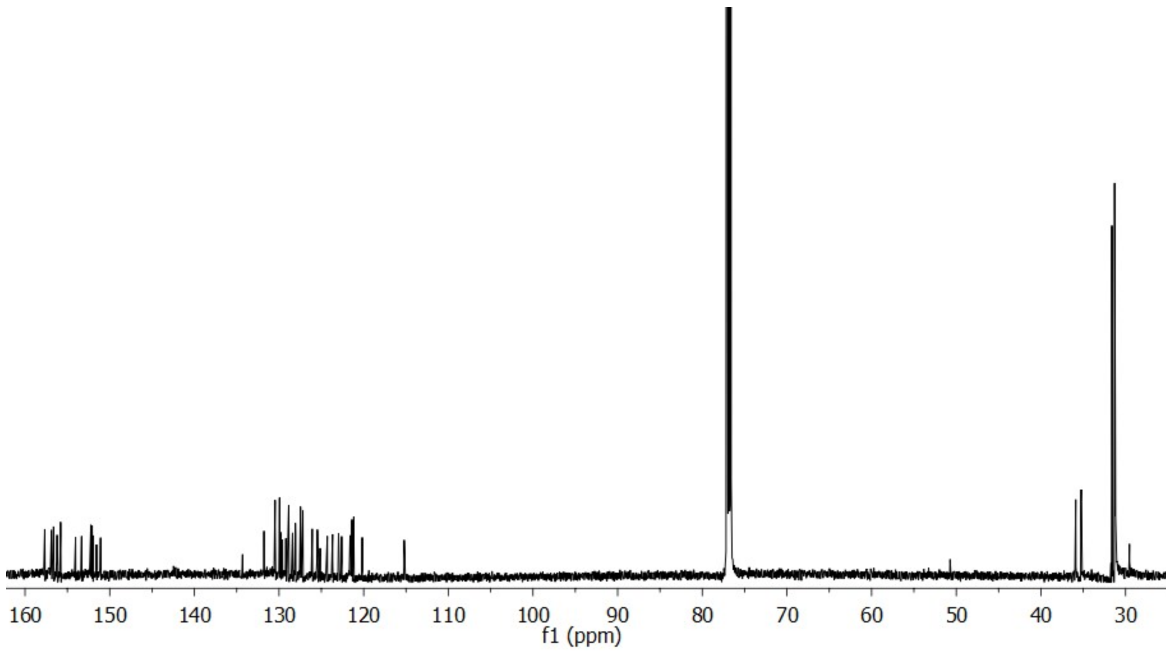


**3** in $CDCl_3$

$^1$H-NMR

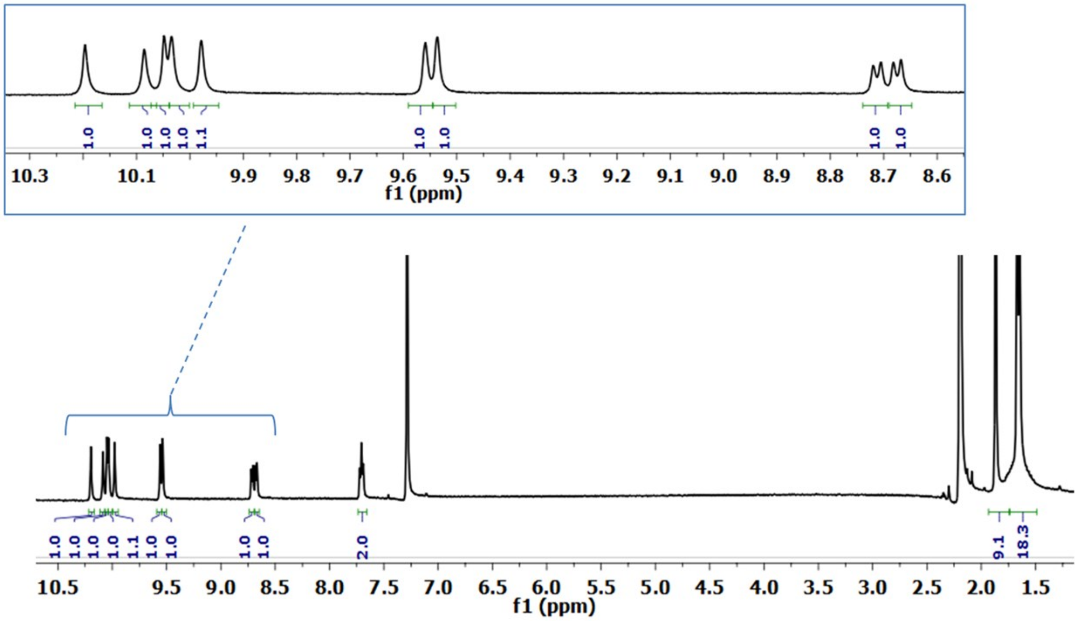


$^{13}$C-NMR

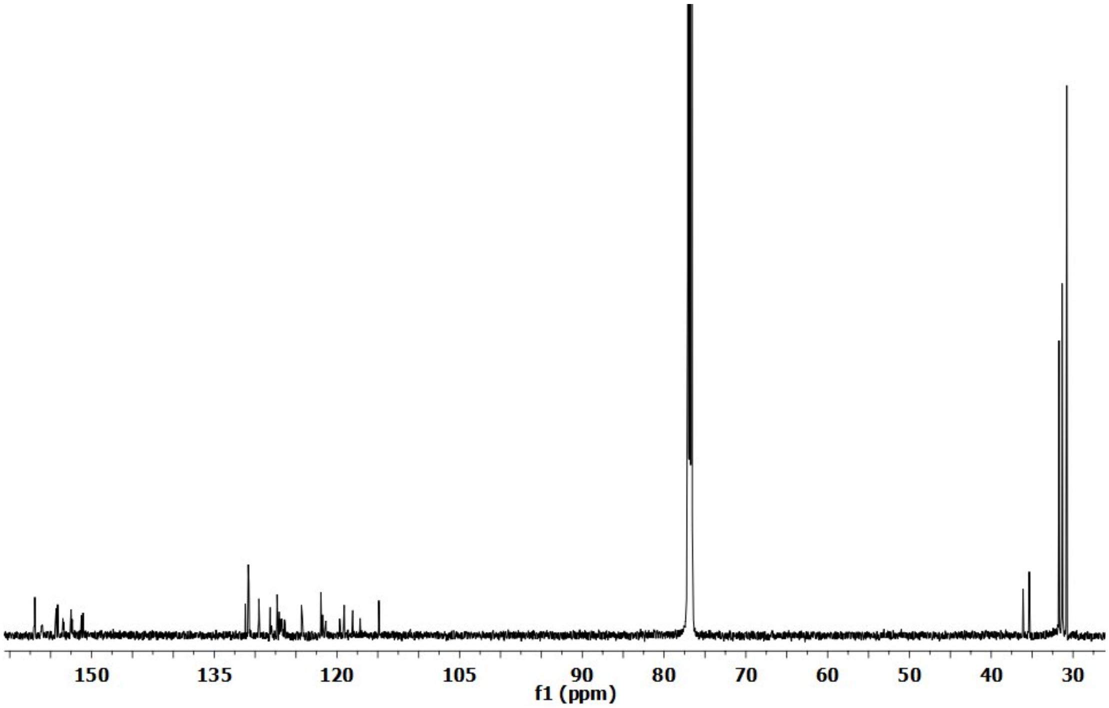


**4** in $CDCl_3$

$^1$H-NMR

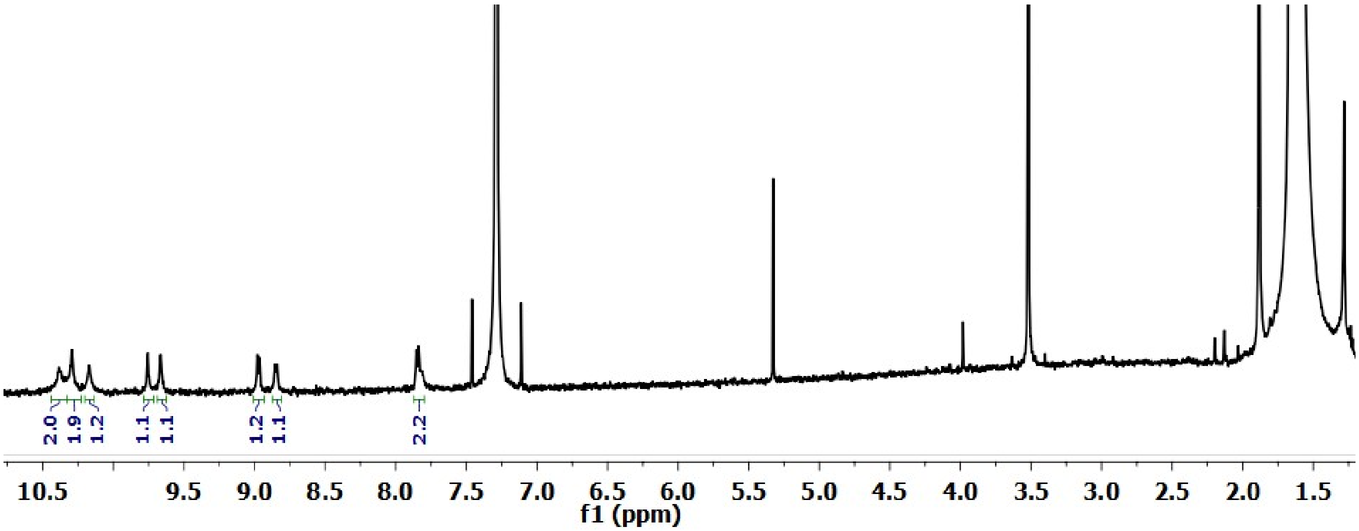


$^{13}$C-NMR



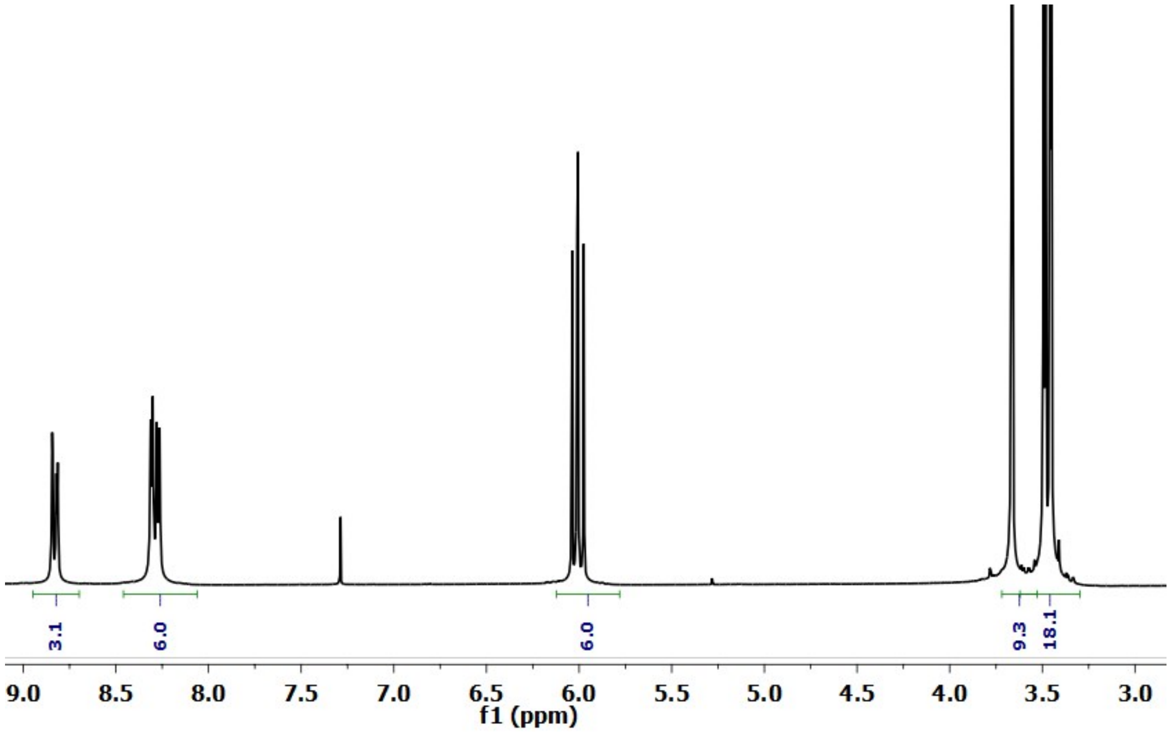
**5** in $CDCl_3$

$^1$H-NMR



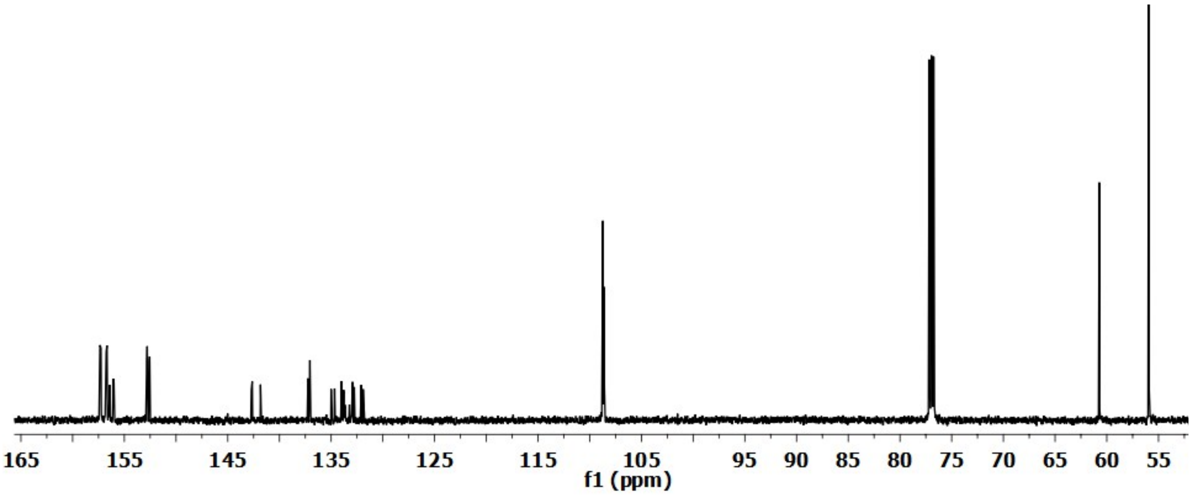
**6** in $CDCl_3$

$^1$H-NMR



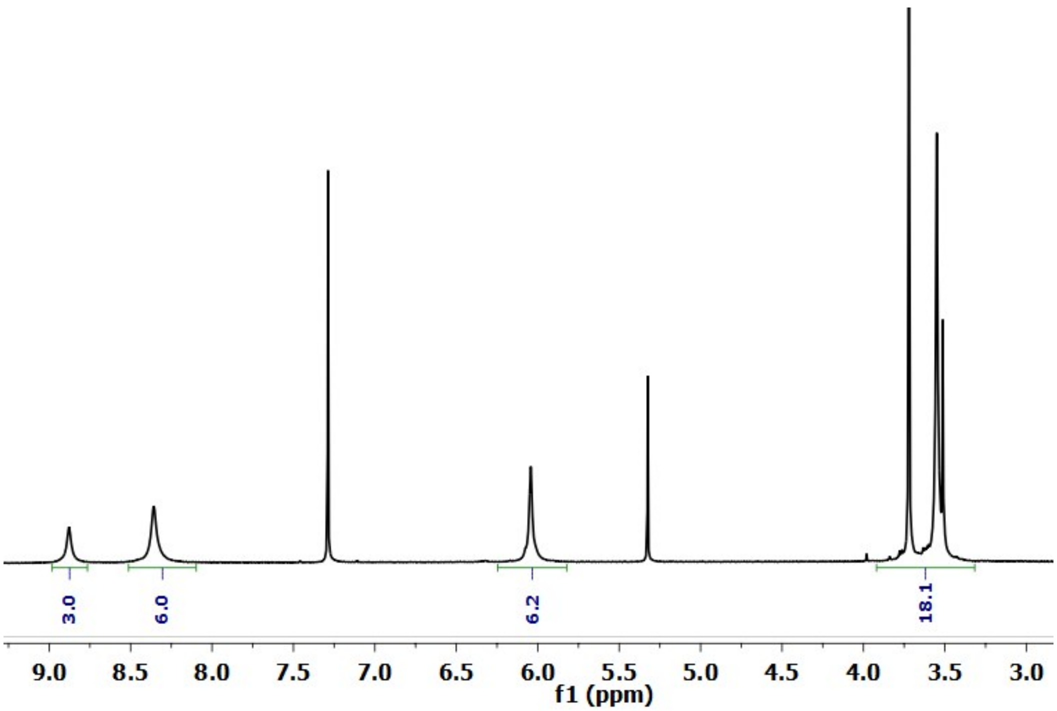
**6** in CDCl$_3$

$^{13}$C-NMR



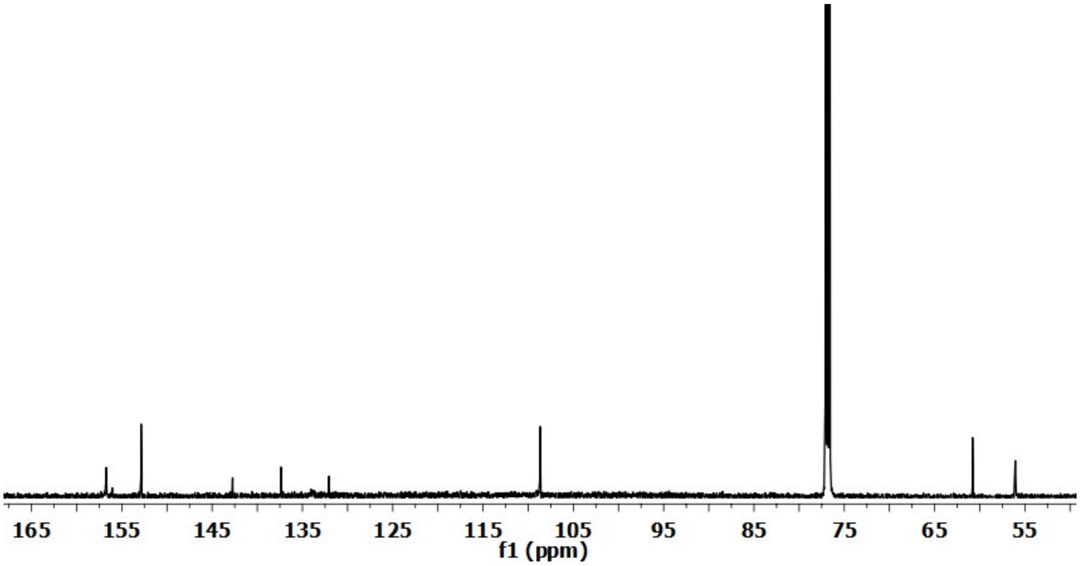
**7** in CDCl$_3$

$^{1}$H-NMR



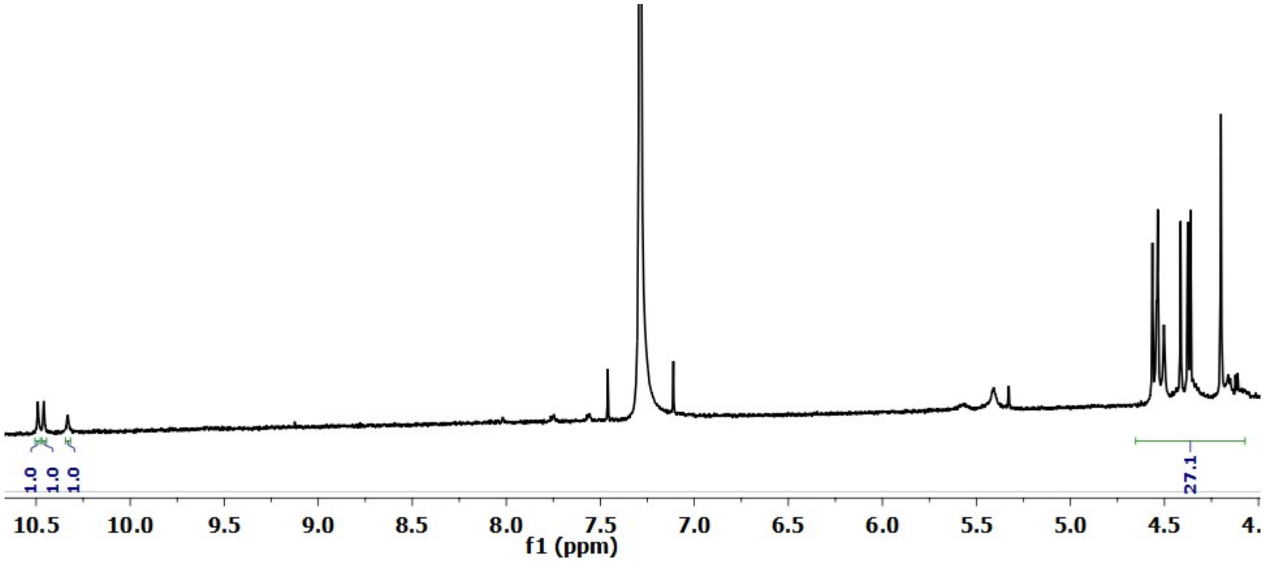
**7** in $CDCl_3$

$^{13}C$-NMR



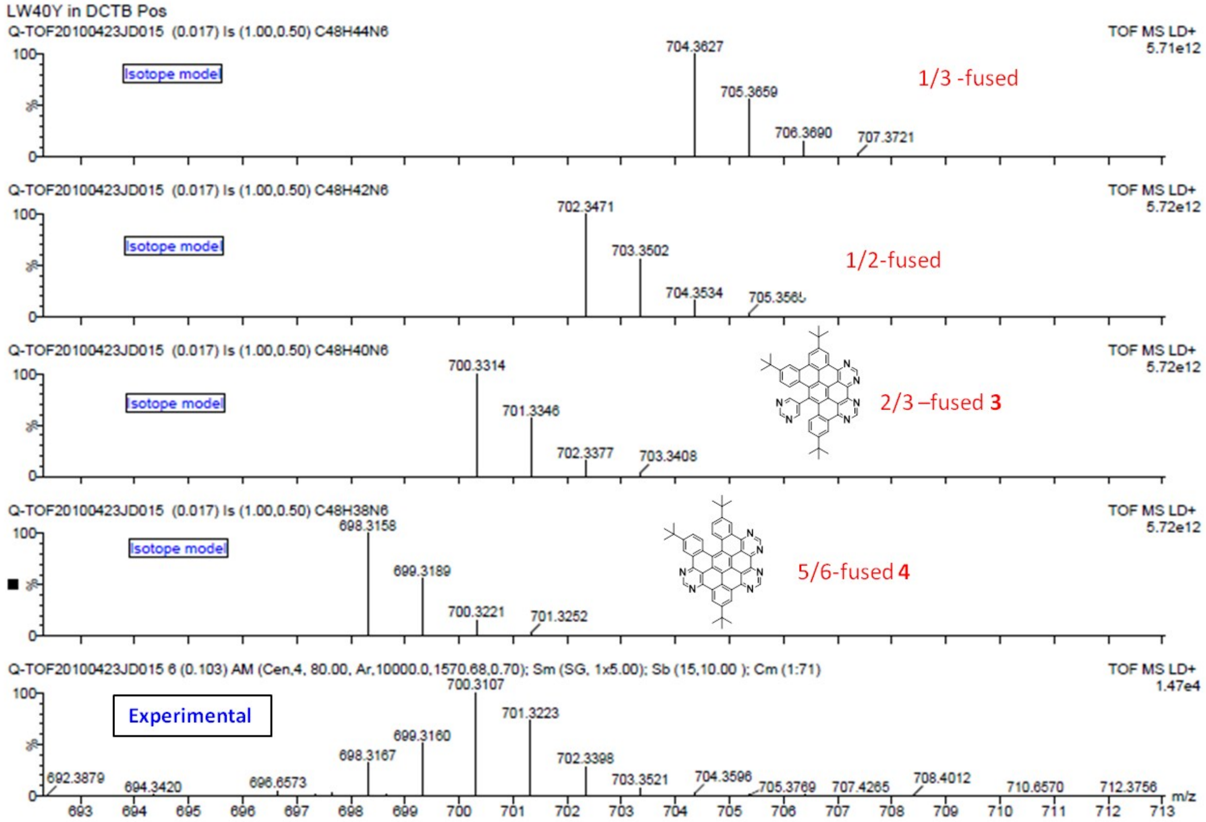
**8** in $CDCl_3$

<sup>1</sup>H-NMR

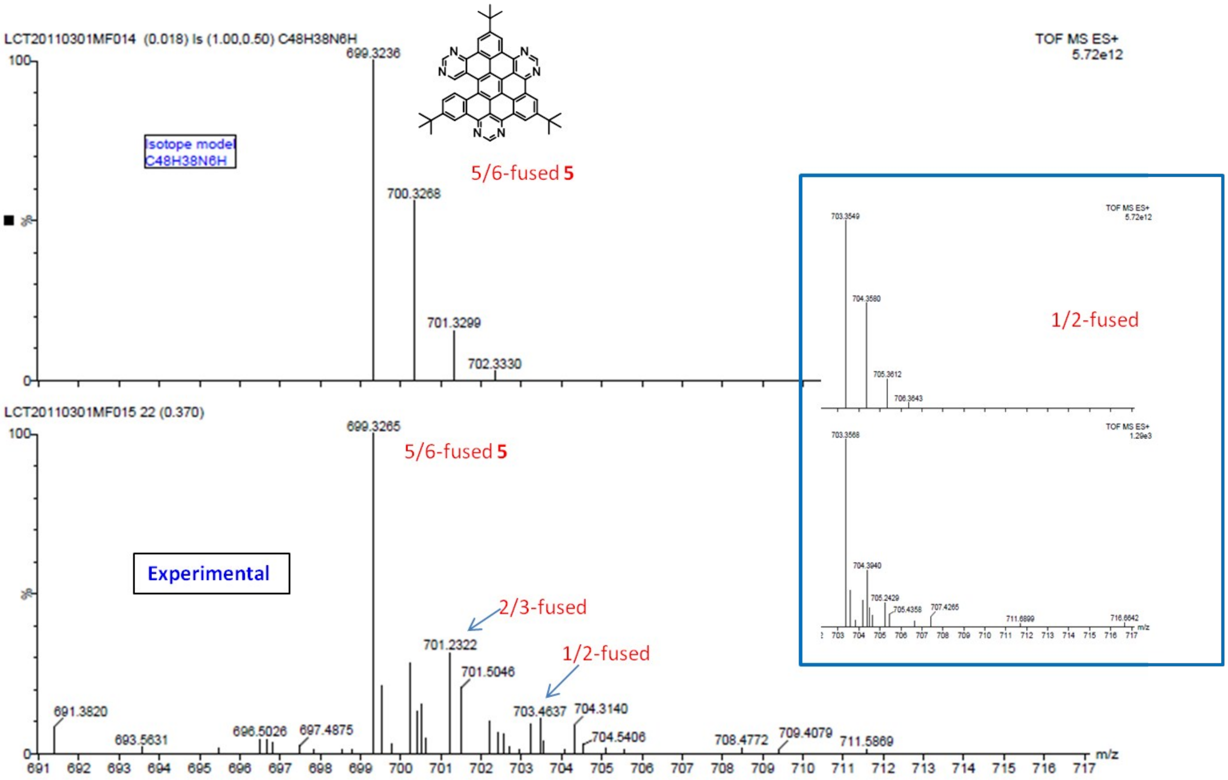


## S4. Mass spectra of reaction mixtures

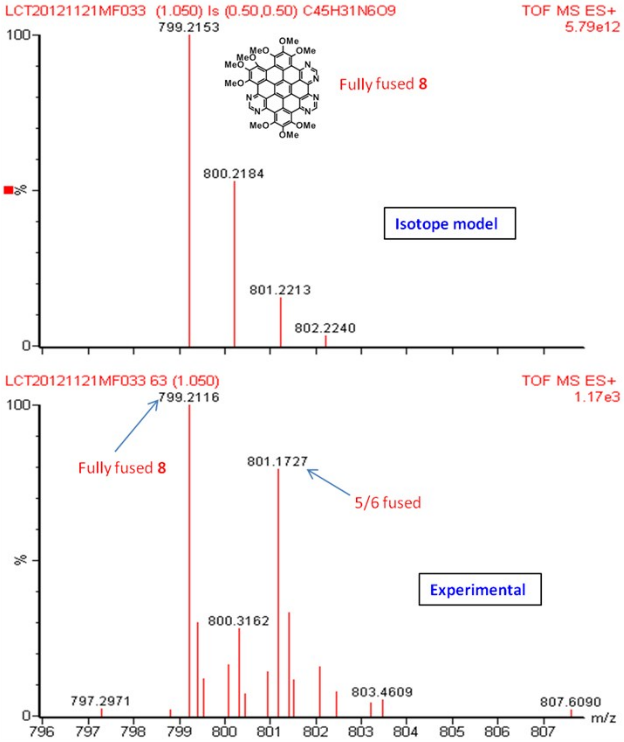
(a) Crude mass spectral analysis - cyclodehydrogenation of **1**



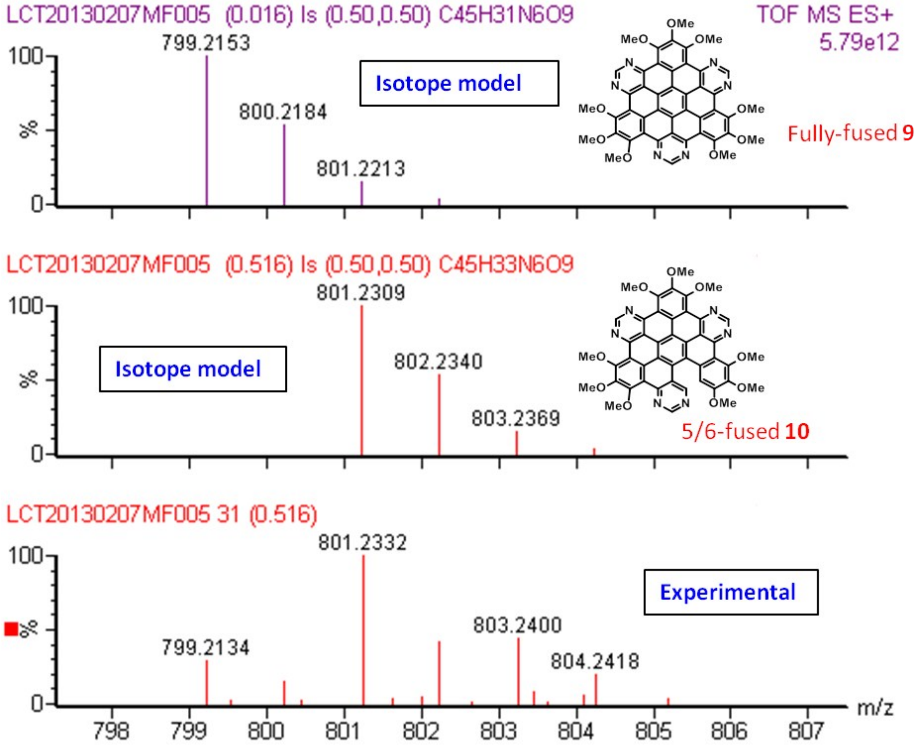
(b) Crude mass spectral analysis – cyclodehydrogenation of **2**



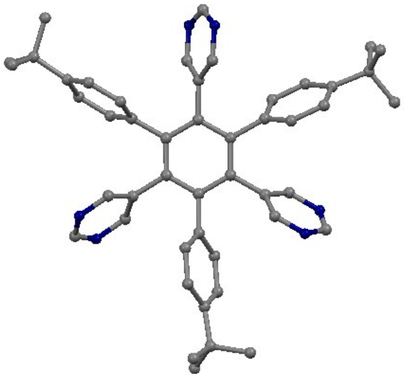
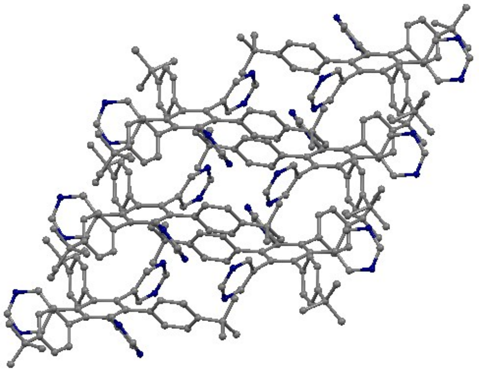
(c) Crude mass spectral analysis – cyclodehydrogenation of **6**



(d) Crude mass spectral analysis – cyclodehydrogenation of **7**



## S5. X-ray crystal structures of 2

| | |
|---|---|
|  Asymmetric unit |  Molecular packing arrangement along' b' axis |

| | |
|---|---|
| Identification code | **2** |
| Empirical formula | C48 H48 N6 |
| Formula weight | 708.92 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |

| | | |
|---|---|---|
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 6.1779(12) Å | α= 77.28(3)°. |
| | b = 18.260(4) Å | β= 84.37(3)°. |
| | c = 18.962(4) Å | γ = 81.29(3)°. |
| Volume | 2057.8(7) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.144 Mg/m$^3$ | |
| Absorption coefficient | 0.068 mm$^{-1}$ | |
| F(000) | 756 | |
| Crystal size | 0.60 x 0.20 x 0.08 mm$^3$ | |
| Theta range for data collection | 1.75 to 25.14°. | |
| Index ranges | -7<=h<=7, -21<=k<=21, -22<=l<=22 | |
| Reflections collected | 22203 | |
| Independent reflections | 7321 [R(int) = 0.0542] | |
| Completeness to theta = 25.14° | 99.3 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9946 and 0.9603 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 7321 / 0 / 487 | |
| Goodness-of-fit on F$^2$ | 1.005 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0504, wR2 = 0.1182 | |
| R indices (all data) | R1 = 0.0890, wR2 = 0.1346 | |
| Largest diff. peak and hole | 0.669 and -0.234 e.Å$^{-3}$ | |

## S6. UV-visible absorption and emission spectra

### S6a: Polyphenylenes

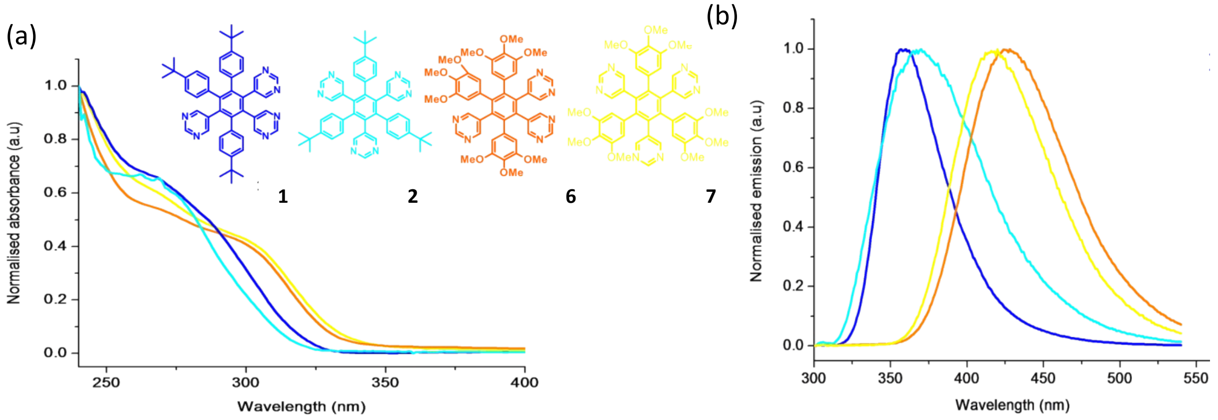
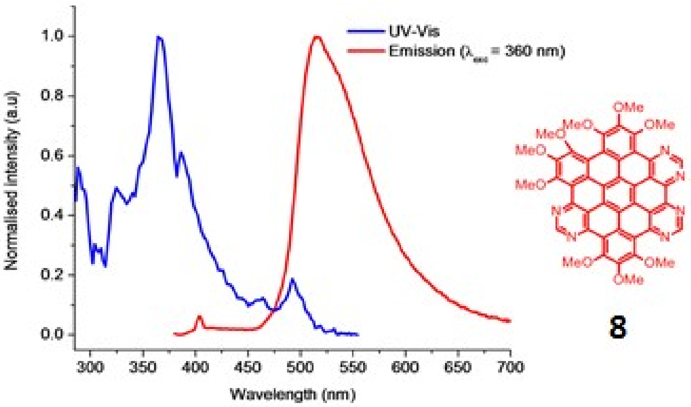


*Figure 1: The (a) absorption and (b) emission spectra of 6N polyphenylenes in chloroform (~$10^{-6}$ M) at RT*

*Table 1: The absorption and emission data observed for 6N polyphenylenes **1**, **2**, **6** and **7** in chloroform (~$10^{-5}$M).*

| Compound | $\lambda_{max}$ [nm] ($\varepsilon$ x $10^4$ [$M^{-1}$ $cm^{-1}$]) | $\lambda_{em}$ [nm] ($\lambda_{exc}$ [nm]) |
|---|---|---|
| **1** | 270 (2.6) | 357 (300) |
| **2** | 270 (2.4) | 369 (300) |
| **6** | 297 (3.3) | 415 (300) |
| **7** | 297 (3.4) | 426 (300) |

### S6b: Photophysical data for 6N fused systems



**8**

*Figure 2: The overlaid absorption and emission spectra of **8** in toluene with $\lambda_{exc}$ = 360 nm (~$10^{-6}$M).*

## S7: Electrochemical data for 6N fused systems

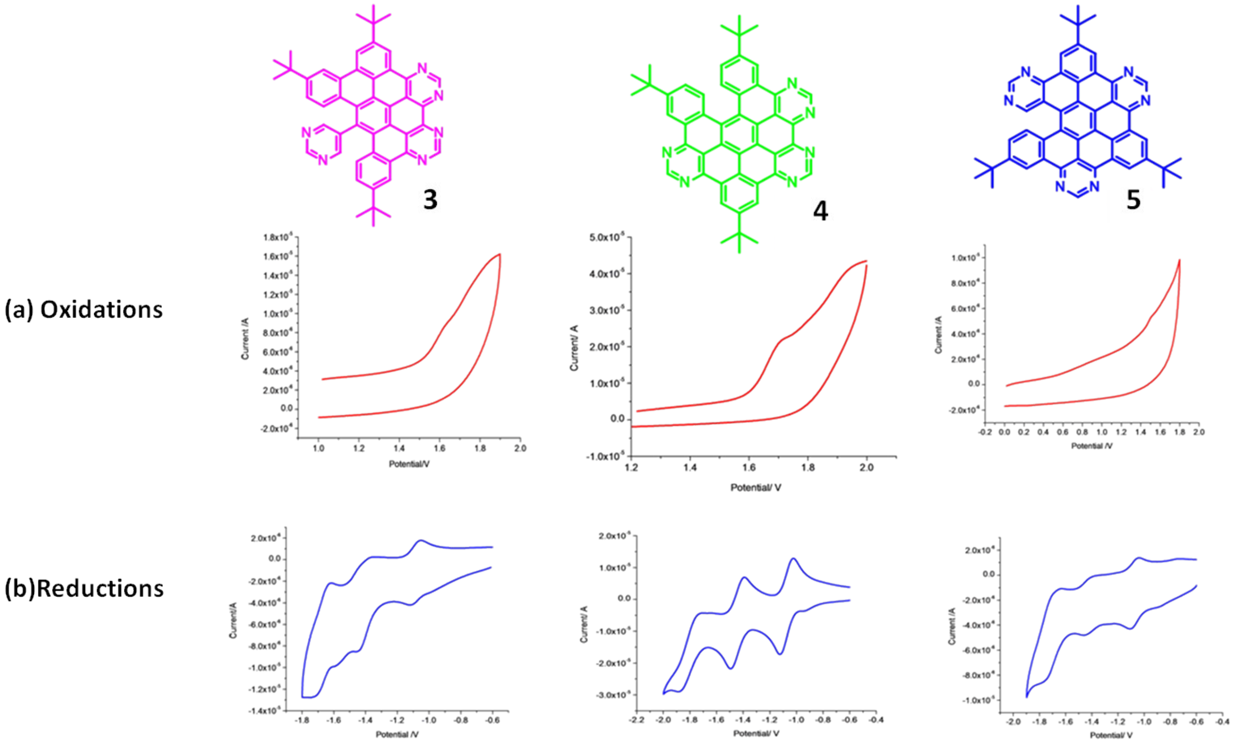


*Figure 3: Cyclic voltammograms of* ***3****,* ***4*** *and* ***5*** *showing (a) oxidation and (b) reduction in 1 mM solutions of $CH_2Cl_2$ (0.1 M $nBu_4NPF_6$) using Ag/AgCl electrode as the reference electrode, scan rate = 100 $mVs^{-1}$ at 298K.*

## References

1. G. A. Crosby and J. N. Demas, *The Journal of Physical Chemistry*, 1971, **75**, 991-1024.
2. D. F. Eaton, *Pure Appl. Chem.*, 1988, **60**, 1107-1114.
3. S. Nagarajan, C. Barthes and A. Gourdon, *Tetrahedron*, 2009, **65**, 3767-3772.
4. D. J. Jones, B. Purushothaman, S. Ji, A. B. Holmes and W. W. H. Wong, *Chemical Communications*, 2012, **48**, 8066-8068.
5. L. P. Wijesinghe, B. S. Lankage, G. M. O. Maille, S. D. Perera, D. Nolan, L. Wang and S. M. Draper, *Chemical Communications*, 2014, **50**, 10637-10640.