

Supporting Information

Influence of bromine substitution pattern on the singlet oxygen generation efficiency of two-photon absorbing chromophores

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General procedures: All reactions were routinely performed under argon. THF was dried and degassed on a solvent station by passage through an activated alumina column followed by argon flush. Other solvents were used without further purification. All reagents were purchased from Sigma Aldrich®, Acros® or Alfa Aesar® with the best available quality grade. NMR spectra (¹H, ¹³C) were recorded at 298K on a BRUKER® AC 200 operating at 200.13 and 50.32 MHz for ¹H and ¹³C respectively and on a BRUKER® 500 Ultra Shield operating at 500.1 and 126.3 MHz for ¹H and ¹³C respectively. Data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (¹H, ¹³C), residual solvent peaks being used as internal standard (CHCl₃ ¹H: 7.26 ppm, ¹³C: 77.36 ppm). Analytical HPLC experiments were performed on a Varian ProStar unit composed of a Varian ProStar210 pump, Varian ProStar UV-vis 320 detector, and Varian Chrompack 250X4.6 mm column filled with Inertsil 5SI. Eluant was Heptane (HPLC grade), and flow rate was of 1 ml/min for all experiments. Laure Guy is acknowledged for her kind assistance on HPLC measurements. UV-visible spectra were recorded on a JascoV-670® spectrophotometer in diluted chloroform solution. Luminescence spectra were measured using a Horiba-Jobin-Yvon Fluorolog-3® spectrofluorimeter, equipped with a three-slit double-grating excitation and emission monochromator with dispersions of 2.1 nm.mm⁻¹ (1200 grooves.mm⁻¹). In the visible range [400-845 nm] the R928 detector was used. Spectra were reference corrected for both the excitation source light intensity variation (lamp and grating) and the emission spectral response (detector and grating). Fluorescence quantum yields *Q* were measured in diluted chloroform solutions with an optical density lower than 0.1 using the relative method (comparison with a reference compound), according the following equation:

$$Q_x/Q_r = [A_r(\lambda)/A_x(\lambda)][n_x^2/n_r^2][D_x/D_r]$$

Where *A* is the absorbance at the excitation wavelength (λ), *n* the refractive index and *D* the integrated luminescence intensity. "r" and "x" stand for reference and sample. Here, reference is coumarine 153 in MeOH (*Q_r* = 0.45). Time-gated (0.65 μ s) phosphorescence measurements were performed at 77K in a glassy solution of methanol : ethanol / 1 : 4. Singlet-oxygen phosphorescence were recorded using a liquid nitrogen cooled, solid Indium/Gallium/Arsenic detector (850-1600 nm), and singlet oxygen generation quantum yield were deduced from the same relative method as depicted for fluorescence QY (see above) using phenalenone as a reference (ϕ_{Δ} = 0.98 in CHCl₃). Excitation of reference and sample in diluted chloroform solutions compounds was performed at the same wavelength. Fluorescence lifetime measurements were performed in chloroform at 290K on a Horiba-Jobin-Yvon Fluorolog-3® spectrofluorimeter, equipped with a NanoLED 440L source operating at 440 nm with 250ps pulses, a iHR320 emission monochromator with 1200 grooves.mm⁻¹ gratings and a R928 detector. The TPA cross-section spectra were obtained by two-photon excited fluorescence measurement of diluted dichloromethane solutions of the compound using a Ti:sapphire femtosecond laser in the range 700-900 nm. The excitation beam (5 mm diameter) was focalized with a lens (focal length 10 cm) at the middle of the fluorescence cell (10 mm). The fluorescence, collected at 90° to the excitation beam, was focused into an optical fiber (diameter 600 μ m) connected to an Ocean Optics S2000 spectrometer. The incident beam intensity was adjusted to 50 mW in order to ensure an intensity-squared dependence of the fluorescence over the whole

spectral range. The detector integration time was fixed to 1 s. Calibration of the spectra was performed by comparison with the published 700-900 nm Coumarin-307 and fluorescein two photon absorption spectra.^{[1][1]} The measurements were done at room temperature in dichloromethane and at concentrations *ca* 10⁻⁴ to 10⁻⁵ M. HRMS measurements were performed by ESI-TOF or by MALDI TOF. In the case of ESI-TOF a Bruker Daltonics® Micro TOF-Q II was used with a resolution of 8000, in positive mode with a capillary tension of 4500V, a source temperature of 180°C, and a cone tension of 60V. The internal reference used for calibration was sodium formate. In the case of MALDI-TOF a Bruker Daltonics® Ultraflex III was used with a solid YAG Laser, in positive reflectron mode. Dithranol was used as a matrix for all MALDI samples. Elemental analyses were performed on a Flash EA1112 CHNS/O Thermo Electron micro-analyzer.

Figure S1 Target molecules

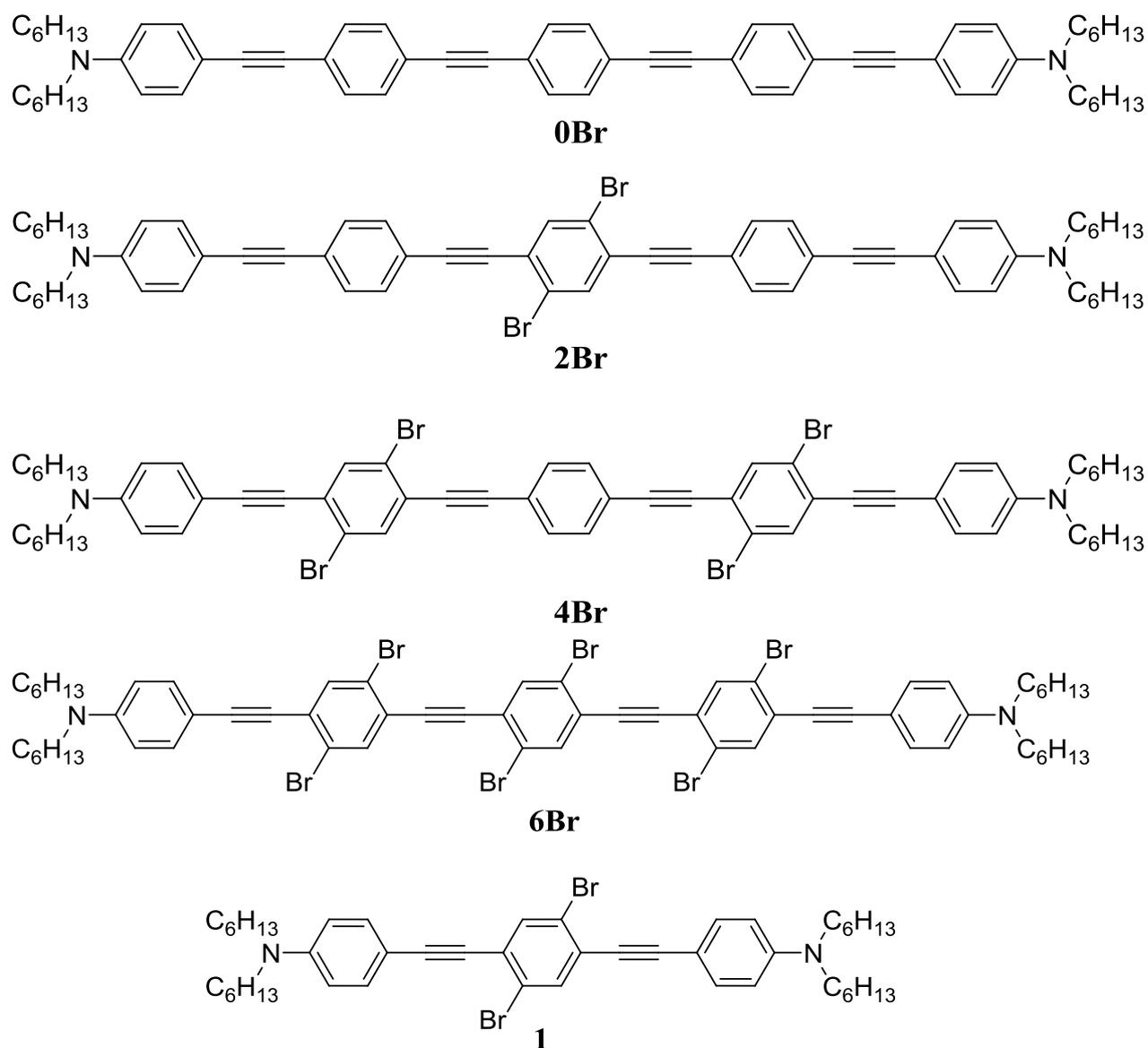
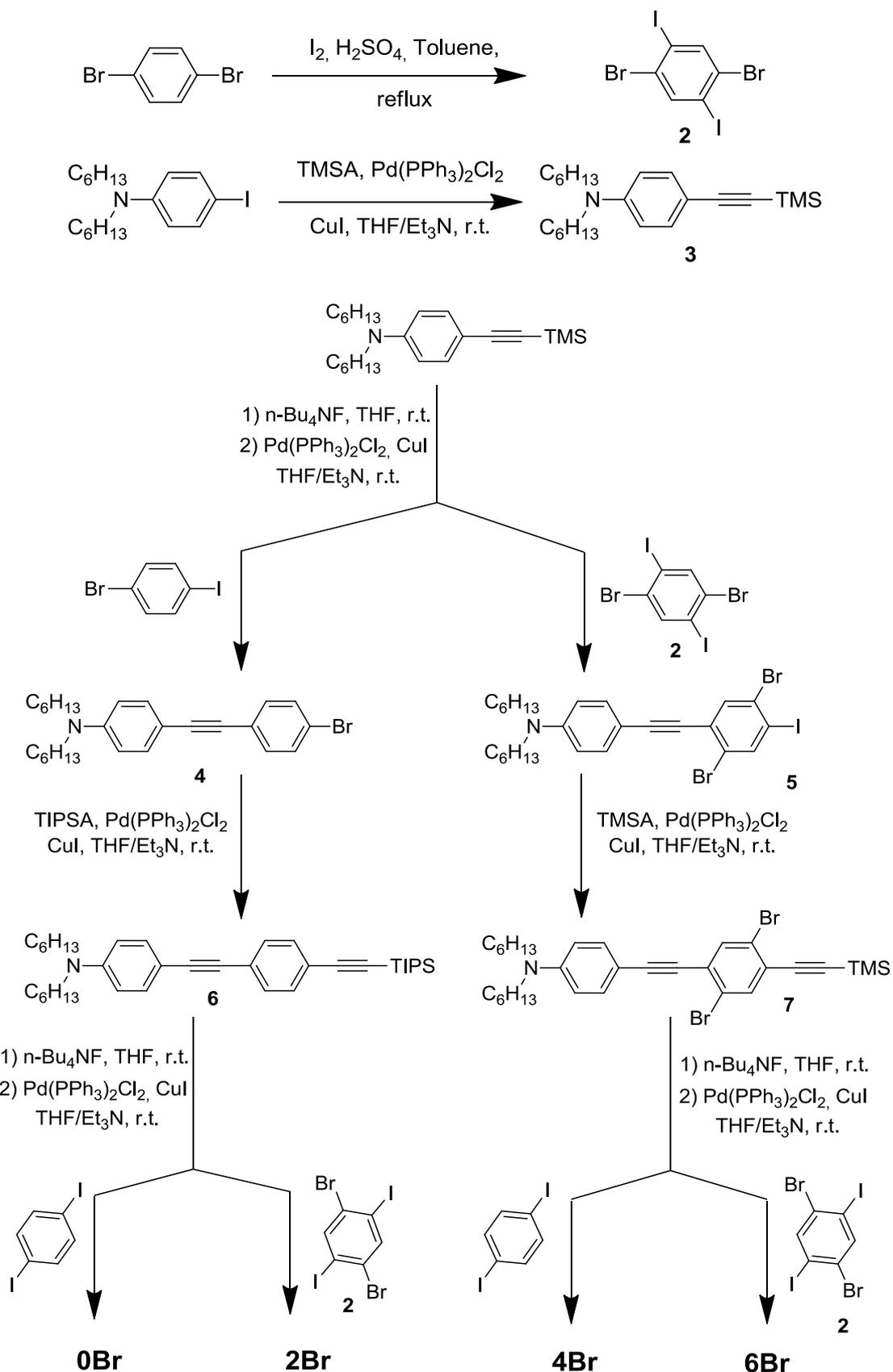


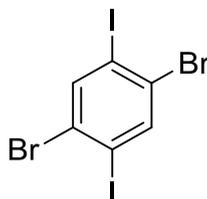
Figure S2 Synthesis scheme:



Experimental procedures

Synthesis of N,N-dihexyl-4-iodoaniline² and of **1**³ have been described previously in literature.

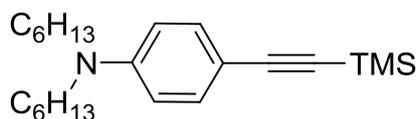
1,4-diiodo-2,5-dibromobenzene (**2**)



From a modified literature protocol⁴: To a solution of dibromobenzene (10,8 g, 47 mmol) in concentrated sulfuric acid (250 mL) in a 500 mL flask fitted with a reflux condenser, iodine (40 g, 150 mmol) was added, the mixture was heated at 135°C for 48h. p-dibromobenzene and iodine that sublimed on the reflux condenser were regularly scratched off into the solution during the reaction. The mixture was poured into an ice bath and quenched with a solution of NaHCO₃. The solution's pH was controlled with pH paper. After neutralization (pH= 7-8) sodium thiosulfate (50 g) was added. The product was extracted three times from the aqueous layer using ether, the organic layer were gathered and dried with Na₂SO₄, filtered and solvent was evaporated under reduced pressure. The crude product was recrystallized in hot CH₂Cl₂/MeOH to provide, upon cooling, a white solid that was collected by filtration (9,6 g, 45%).

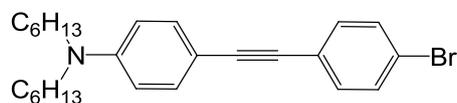
¹H NMR (200 MHz CDCl₃) δ ppm : 8.02 (s, 2H); ¹³C NMR (50 MHz, CDCl₃) δ ppm 142.5, 129.4, 101.5. IR(ATR) : ν= 3057, 1736, 1430, 1407, 1279, 1104 , 1000, 875, 486 , 423 cm⁻¹; mp: 159°C (litt. 160-162°C in ref 4)

N,N-dihexyl-4-((trimethylsilyl)ethynyl)-aniline (**3**)



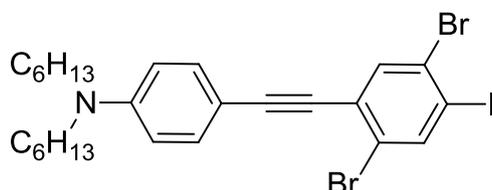
From modified literature protocol⁵: N,N-dihexyl-4-iodo-aniline (400 mg, 1.03 mmol) was dissolved in a mixture of THF/Et₃N (10 mL, v/v, 1/1); the solution was degassed by argon bubbling (20 min). Pd(PPh₃)₂Cl₂ (35 mg, 5 · 10⁻² mmol) and CuI (10 mg, 5 · 10⁻² mmol) were added to the solution following TMSA (165 μL, 1.14 mmol). The mixture was stirred overnight at room temperature. Et₂O was added and the mixture was filtered through a celite pad, eluted with Et₂O. Solvents were removed under vacuum. A column chromatography (SiO₂, petroleum ether / dichloromethane, 9 /1, v/v) afforded the desired compound as a colorless oil (310 mg, 84%). ¹H NMR (200 MHz CDCl₃) δ ppm 7.27 (d, J = 9.2 Hz, 2H), 6.48 (d, J =9.2 Hz, 2H), 3.25 (t, J = 7.7 Hz, 4 H), 1.52 (m, 4H), 1.30 (m, 12H), 0.87 (t, 3J=6.62 Hz, 6 H), 0.21 (s, 9H); ¹³C NMR (50 MHz, CDCl₃) δ ppm 148.08, 133.26, 111.00, 108.55, 106.85, 90.77, 50.92, 31.71, 27.16, 26.80, 22.67, 14.04, 0.27. HRMS calcd. for [C₂₃H₃₉NSi+H⁺] 358.2925, found 358.2910

4-(4-Bromo-1-(ethynyl)phenyl)-N,N-dihexylaniline (**4**)



A solution of tetrabutylammonium fluoride (2.8 mL of 1 M solution in THF), was added to a solution of *N,N*-dihexyl-4-(trimethylsilyl)ethynyl-aniline **3** (1 g, 2.8 mmol) in 30 mL of THF. After full conversion of the reactant was achieved (TLC), Et₂O was added and the mixture was filtered through a celite pad. Solvents were removed under reduced pressure. The crude material was dissolved in a mixture of THF/Et₃N (25 mL/mmol, v/v, 1/1) and 1-Bromo-4-iodobenzene (1.584 mg, 5.6 mmol) was added. The solution was degassed by bubbling argon, then Pd(PPh₃)₂Cl₂ (98 mg, 0.14 mmol) and CuI (27 mg, 0.14 mmol) were added. The solution was stirred overnight (16H) at room temperature. Et₂O was added and the mixture was filtered through celite, eluted with Et₂O. Solvents were removed under vacuum. The crude material was purified by column chromatography on SiO₂ (petroleum ether/CH₂Cl₂, from 10/0 to 8/2) to give a yellowish oil (712 mg, 58%). ¹H NMR (200 MHz, CDCl₃): 7.44 (2H, d, *J* = 8.8 Hz), 7.35 (4H, m), 6.57 (2H, d, *J* = 8.8 Hz), 3.27 (4H, dd, *J*₁ = *J*₂ = 7.6 Hz), 1.58 (16H, m), 0.88 (6H, m). ¹³C NMR (50 MHz, CDCl₃-*d*) δ ppm 148.13, 132.92, 132.67, 131.46, 123.43, 121.31, 111.24, 108.27, 92.24, 86.15, 51.00, 31.75, 27.23, 26.85, 22.73, 14.11. HRMS calcd. for [C₂₆H₃₄BrN+H⁺] 440.1947, found 440.1937.

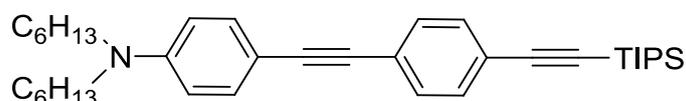
4-(3,5-dibromo-4-iodo-1-(ethynyl)phenyl)-*N,N*-dihexylaniline (**5**)



A solution of tetrabutylammonium fluoride (630 μL of 1 M solution in THF) was added to a solution of the *N,N*-dihexyl-4-(trimethylsilyl)ethynyl-aniline **3** (150 mg, 0.42 mmol) in 8 mL of THF. After full conversion of the reactant was achieved (TLC), Et₂O was added and the mixture was filtered through a celite pad. Solvents were removed under reduced pressure. The crude material was dissolved in a mixture of THF/Et₃N (3.6 mL/mmol, v/v, 1/1) and 1,4-dibromo-2,6-diiodobenzene **2** (225mg, 0.46 mmol, 1 eq.) was added. The solution was degassed by bubbling argon (20 min), and Pd(PPh₃)₂Cl₂ (15 mg, 0.02 mmol) and CuI (2 mg, 0.02 mmol) were added. The mixture was stirred at room temperature until full conversion of the reactants was achieved (TLC). Et₂O was added and the mixture was filtered through celite, eluted with Et₂O. Solvents were removed under vacuum. The crude material was purified by column chromatography (petroleum ether/CH₂Cl₂, from 10/0 to 7/3) to give a yellowish oil (139 mg, 51%).

¹H NMR (200 MHz, CDCl₃) δ ppm 8.04 (1 H, s), 7.72 (1 H, s), 7.38 (2 H, d, *J* = 8.8 Hz), 6.55 (2 H, d, *J* = 8.8 Hz), 3.28 (2 H, t, *J* = 7.6 Hz), 1.57 (4 H, m), 1.32 (16 H, s), 0.89 (6 H, m). ¹³C NMR (126 MHz, CDCl₃) δ ppm 148.70, 142.50, 135.17, 133.35, 128.21, 128.15, 123.90, 111.28, 107.47, 99.43, 98.86, 84.84, 51.11, 31.84, 27.31, 26.91, 22.83, 14.20. HRMS (ESI) calcd. for [C₂₆H₃₂Br₂I₂N+H⁺] 645.9946, found 645.9982.

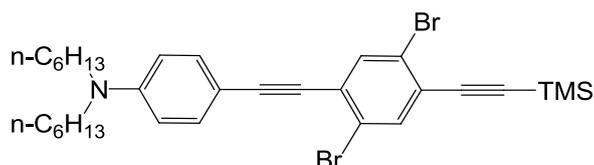
4-(4-(trisopropylsilyl)ethynyl-1-(ethynyl)phenyl)-*N,N*-dihexylaniline (**6**)



4-(4-Bromo-1-(ethynyl)phenyl)-*N,N*-dihexylaniline **4** (105 mg, 0.24 mmol) was dissolved in a mixture of toluene/Et₃N (10 mL, v/v, 1/1); the solution was degassed by argon bubbling (20 min). Pd(PPh₃)₂Cl₂

(6 mg, 9×10^{-3} mmol) and CuI (2 mg, 9×10^{-3} mmol) were added to the solution following TIPSA (60 μ L, 0.26 mmol). The mixture was stirred at 90°C overnight. Et₂O was added and the mixture was filtered through a short celite pad, eluted with Et₂O. Solvents were removed under vacuum. A column chromatography (SiO₂, petroleum ether/CH₂Cl₂, from 10/0 to 8/2) afforded the desired compound as yellowish oil (109 mg, 84%). ¹H NMR (200 MHz CDCl₃) δ ppm 7.38 (6H, m), 6.57 (2H, d, $J = 8.8$ Hz), 3.27 (4H, m), 1.32 (4H, dd, $J_1 = J_2 = 6.4$ Hz), 1.32 (b, 15H), 1.13 (15H, s), 0.88 (6 H, m) ¹³C NMR (50 MHz, CDCl₃) δ ppm 148.34, 133.2, 133.15, 132.89, 132.13, 131.70, 131.16, 111.42, 94.43, 93.24, 92.28, 51.22, 31.97, 27.45, 27.07, 22.95, 18.96, 14.31, 11.15. HRMS calcd. for [C₃₇H₅₅NSi+H⁺] 541.4104, found 542.4169 [M+H]⁺.

4-((2,5-dibromo-4-((trimethylsilyl)ethynyl)phenyl)ethynyl)-N,N-dihexylaniline (7)



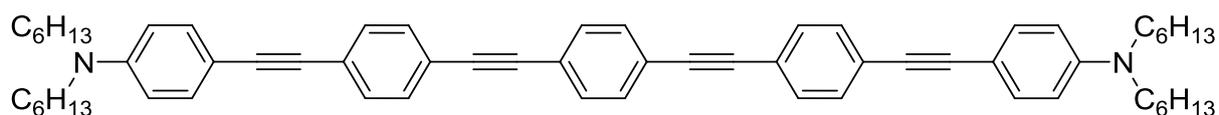
4-(3,5-dibromo-4-iodo-1-(ethynyl)phenyl)-N,N-dihexylaniline **5** (300 mg, 0.46 mmol) was dissolved in a mixture of THF/Et₃N (6 mL, v/v, 1/1); the solution was degassed by argon bubbling (20 min). Pd(PPh₃)₂Cl₂ (16 mg, 2.3×10^{-2} mmol) and CuI (4 mg, 2.3×10^{-2} mmol) were added to the solution following TMSA (65 μ L, 0.46 mmol). The mixture was stirred overnight at room temperature. Et₂O was added and the mixture was filtered through a short celite pad, eluted with Et₂O. Solvents were removed under vacuum. A column chromatography (SiO₂, petroleum ether/CH₂Cl₂, from 10/0 to 7/3) afforded the desired compound as a yellowish oil (120 mg, 44%). ¹H NMR (200 MHz, CDCl₃) δ ppm 7.69 (2 H, s), 7.40 (2 H, d, $J=8.8$ Hz), 6.58 (2 H, d, $J=8.8$ Hz), 3.29 (4 H, t, $J=7.5$ Hz), 1.59 (4 H, m), 1.33 (12 H, m), 0.92 (6 H, m), 0.28 (9 H, m). ¹³C NMR (50 MHz, CDCl₃) δ ppm 149.39, 137.09, 136.06, 134.11, 125.61, 124.51, 123.76, 111.92, 108.18, 100.12, 93.00, 92.42, 86.05, 51.73, 32.45, 27.92, 23.43, 14.78, 0.27. HRMS (MALDI) m/z , calcd for [M]⁺ 613.1375, found 613.1370

General procedure for the alkyne deprotection following by the Sonogashira-Higihara cross coupling reactions between arylhalide and silyl-protected phenylethynyl :

In a typical procedure, solution of TBAF (1 eq.) was added to a *ca* 55 mM solution of the silyl protected alkyne in THF. After full conversion of the reactant (TLC), Et₂O was added and the mixture was filtered through a celite pad. Solvents were removed under reduced pressure. The crude material was dissolved in a mixture of THF/Et₃N (3.6 mL/mmol, v/v, 1/1) and the suitable aryl iodide ($\frac{1}{2}$ eq) was added. The solution was degassed by bubbling argon (20 min), and Pd(PPh₃)₂Cl₂ (5%) and CuI (5%) were added. The mixture was stirred at room temperature until full conversion of the reactants (TLC). Et₂O was added and the mixture was filtered through celite, eluted with Et₂O. Solvents were removed under vacuum. The crude material was purified by column chromatography (SiO₂).

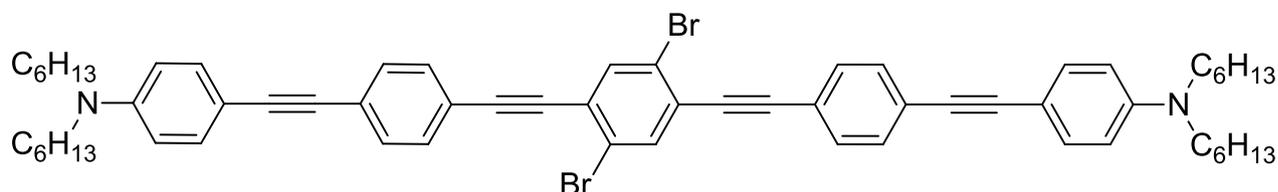
Further details about the quantities of reactant/reagent/catalyst/solvent involved in each reaction, purification conditions, yields of isolated products and analytical data are given below for each product (see below):

0Br



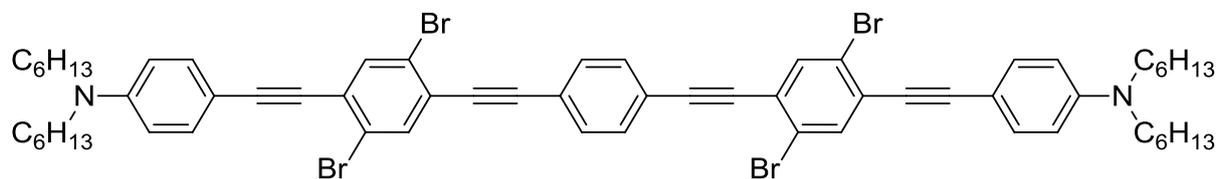
TBAF (730 μL of 1 M solution in THF), 4-(4-(triisopropylsilyl)ethynyl-1-(ethynyl)phenyl)-N,N-dihexylaniline **6** (395 mg, 0.73 mmol). 1,4-diiodobenzene (63 mg, 0.19 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (14 mg, 2.10^{-2} mmol) and CuI (4 mg, $0.2 \cdot 10^{-2}$ mmol). Column chromatography on SiO_2 (petroleum ether/ CH_2Cl_2 , from 10/0 to 7/3) gives a yellow oil (19 mg, 12 %). ^1H NMR (500 MHz, CDCl_3) δ ppm 7.53 (4H, s), 7.49 (8H, b), 7.39 (4H, d, $J = 10$ Hz), 6.60 (4H, d, $J = 10$ Hz), 3.30 (8H, dd, $J_1 = 5$ Hz, $J_2 = 5$ Hz), 1.61 (8H, m), 1.35 (24 H, m), 0.93 (12 H, dd, $J_3 = 6$ Hz, $J_4 = 7$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ ppm 148.12, 132.98, 131.54, 131.48, 124.59, 123.15, 121.71, 111.24, 108.33, 93.31, 91.41, 90.55, 87.04, 50.99, 31.73, 27.20, 26.82, 22.71, 14.06. Elemental analysis calcd for $\text{C}_{62}\text{H}_{72}\text{N}_2$, $\text{C}_6\text{H}_{14} + \frac{1}{2} \text{H}_2\text{O}^6$: C, 86.85; H, 9.32; N, 2.98. Found: C, 87.17; H, 8.99; N, 3.29. HRMS (MALDI) m/z , calcd for $[\text{M}]^+$ 844.5696, found 844.5690

2Br



TBAF (350 μL of 1 M solution in THF), 4-(4-(triisopropylsilyl)ethynyl-1-(ethynyl)phenyl)-N,N-dihexylaniline **6** (128 mg, 0.24 mmol). 1,4-diBromo-2,5-diiodobenzene **2** (57 mg, 0.12 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (7 mg, 1.10^{-2} mmol) and CuI (2 mg, 0.110^{-2} mmol). Column chromatography on SiO_2 (petroleum ether/ CH_2Cl_2 , from 10/0 to 7/3) gives a yellow oil (8mg, 3 %). ^1H NMR (500 MHz, CDCl_3) δ ppm 7.53 (4H, s), 7.49 (6H, s), 7.39 (4H, d, $J = 8.2$ Hz), 6.57 (4H, d, $J = 8.2$ Hz), 3.27 (8H, dd, $J_1 = J_2 = 7.8$ Hz), 1.58 (8H, m), 1.32 (24H, m), 0.90 (12H, m). ^{13}C NMR (126 MHz, CDCl_3) δ ppm 148.26, 133.12, 131.68, 131.62, 131.27, 130.86, 124.69, 123.23, 121.79, 111.33, 108.44, 91.55, 90.66, 89.24, 87.17, 51.12, 31.86, 27.34, 26.96, 22.83, 14.20. HRMS (MALDI) m/z , calcd for $[\text{M}]^+$ 1000.3906, found 1000.3900

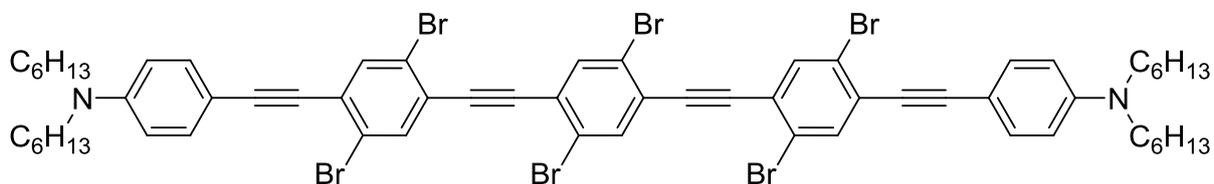
4Br



TBAF (220 μL of 1 M solution in THF), 4-(4-(trimethyl)ethynyl-(2,5-dibromo-1-ethynyl)-phenyl)-N,N-dihexylaniline **7** (132 mg, 0.22 mmol). 1,4-diiodobenzene (36 mg, 0.11 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (5 mg, 6.10^{-3} mmol) and CuI (1 mg, 6.10^{-3} mmol). Column chromatography on SiO_2 (petroleum ether/ CH_2Cl_2 , from 10/0 to 7/3) gives a yellow oil (36 mg, 40 %). ^1H NMR (500 MHz, CDCl_3) δ ppm 7.75 (2H, s), 7.72 (2H, s), 7.55 (4H, s), 7.40 (4H, d, $J = 8.5$ Hz), 6.58 (4H, d, $J = 8.5$ Hz), 3.29 (8H, dd, $J_1 = 5$ Hz, $J_2 = 5$ Hz), 1.57 (8H, br), 1.32 (24H, s), 0.91 (12H, m). ^{13}C NMR (126 MHz, CDCl_3) δ ppm 148.75, 136.11, 135.49, 133.45, 131.88, 128.06, 124.81, 123.82, 123.34, 123.15, 120.76, 117.66, 111.32, 107.57, 99.76, 95.68,

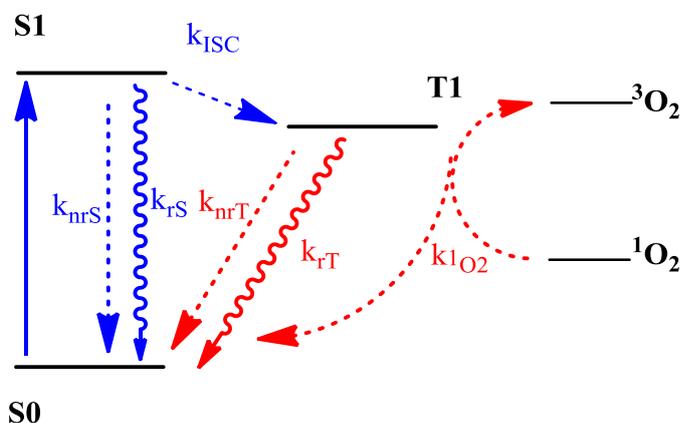
89.42, 85.58, 51.14, 31.85, 27.32, 26.94, 22.83, 14.20. Elemental analysis calcd for $C_{62}H_{68}N_2Br_4 + 2/3 C_6H_{14}$: C, 65.07; H, 6.40; N, 2.32. Found: C, 65.13; H, 6.22; N, 2.45. HRMS (MALDI) m/z , calcd for $[M]^+$ 1156.2116, found 1156.2111

6Br



TBAF (100 μ L of 1 M solution in THF), 4-((2,5-dibromo-4-((trimethylsilyl)ethynyl)phenyl)ethynyl)-N,N-dihexylaniline **7** (62 mg, 0.10 mmol), 1,4-dibromo-2,5-diiodobenzene **2** (25 mg, 0.05 mmol), $Pd(PPh_3)_2Cl_2$ (21 mg, 3.10^{-2} mmol) and CuI (6 mg, 3.10^{-2} mmol). Column chromatography on SiO_2 (petroleum ether/ CH_2Cl_2 , from 10/0 to 7/3) gives a yellow oil (15 mg, 30%). 1H NMR (500 MHz, $CDCl_3$) δ ppm 7.80 (2H, s), 7.77 (2H, s), 7.72 (2H, s), 7.39 (4H, d, $J = 9$ Hz), 6.57 (4H, d, $J = 9$ Hz), 3.29 (8H, dd, $J_1 = 7.5$ Hz, $J_2 = 8$ Hz), 1.58 (8H, br), 1.29 (24H, m), 0.90 (12H, m). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 148.81, 136.64, 136.51, 135.55, 133.51, 128.76, 126.48, 124.05, 123.85, 123.813, 123.31, 121.20, 120.40, 111.31, 107.47, 100.36, 94.49, 92.90, 85.69, 51.14, 31.95, 29.86, 27.32, 26.94, 22.83, 14.20. Elemental analysis calcd for $C_{62}H_{66}N_2Br_6$, C_6H_{14} , H_2O : C, 57.40; H, 5.81; N, 1.97. Found: C, 57.10; H, 6.24; N, 1.76. HRMS (MALDI) m/z , calcd for $[M]^+$ 1312.0326, found 1312.0321

Discussion on the evolution of photophysical kinetic parameters among the series



Considering Perrin-Jablonski diagram shown above, fluorescence quantum yields, lifetime and ISC quantum yields can be expressed as a function of a set of kinetic constants, as shown in the equations (1), (2) and (3) below

$$(1) \quad \phi_{in} = k_{rs(n)} / (k_{rs(n)} + k_{nrs(n)} + k_{ISC(n)})$$

$$(2) \quad \tau_f = 1 / (k_{rs(n)} + k_{nrs(n)} + k_{ISC(n)})$$

$$(3) \quad \phi_{ISC} = k_{ISC(n)} / (k_{rS(n)} + k_{nrS(n)} + k_{ISC(n)})$$

With $n = 0, 2, 4, 6$ for **0Br**, **2Br**, **4Br**, **6Br** respectively.

Our strategy is based on the assumption that the structural similarity between the four structures reported in this study allow us to consider that the differences in the kinetics of the excited state will be related to the extent of spin orbit coupling only, which will vary with the position of the ISC promoters (2,5-dibromophenyl moieties). This leads us to consider k_r and k_{nr} as being independent of substitution pattern. This assumptions allows us to introduce constant terms a and b in equation (1), (2) and (3), which then transform into

$$(1) \quad \phi_{f(n)} = a / (b + k_{ISC(n)})$$

$$(2) \quad \tau_{f(n)} = 1 / (b + k_{ISC(n)})$$

$$(3) \quad \phi_{ISC(n)} = k_{ISC(n)} / (b + k_{ISC(n)})$$

With $a = k_{rS}$, $b = (k_{rS} + k_{nrS})$.

Within this hypothesis, it is easy to deduce that, for all values of n and n' we should have

$$\phi_{f(n)} / \phi_{f(n')} = \tau_{f(n)} / \tau_{f(n')}$$

By testing the validity of this equation, we find, for the different combinations of n and n' ,

$n ; n'$	0 ; 2	0 ; 4	0 ; 6	2 ; 4	2 ; 6	4 ; 6
$\phi_{f(n)} / \phi_{f(n')}$	1.14	2.65	1.50	2.33	1.32	0.56
$\tau_{f(n)} / \tau_{f(n')}$	1.08	1.96	1.44	1.80	1.32	0.70

In spite of some discrepancies, which are unavoidable considering the various experimental uncertainties associated with measurements of the different parameters involved in this equation, the observed general evolution roughly confirms our initial hypothesis.

Then, if one consider the sum of $\phi_{f(n)}$ and $\phi_{ISC(n)}$, it can be noticed that

$$(4) \quad \phi_{f(n)} + \phi_{ISC(n)} = (a + k_{ISC(n)}) / (b + k_{ISC(n)})$$

-A second order development into a power series of $k_{ISC(n)}$ leads to rewrite equation (4) as :

$$(4) \quad \phi_{f(n)} + \phi_{ISC(n)} = (a + k_{ISC(n)}) / (b + k_{ISC(n)}) = a/b + k_{ISC(n)} [(b-a)/b^2] - k_{ISC(n)}^2 [(b-a)/b^3]$$

-Moreover, from eq. (1) we know that $\phi_{f(0)} = a/b = 0.8$ or $a = 0.8b$, which leads to

$$(4) \quad \phi_{f(n)} + \phi_{ISC(n)} = (a + k_{ISC(n)}) / (b + k_{ISC(n)}) = a/b + k_{ISC(n)} [(0.2)/b] - k_{ISC(n)}^2 [(0.2)/b^2]$$

-It can be demonstrated that the value $k_{ISC(n)} [(0.2)/b] - k_{ISC(n)}^2 [(0.2)/b^2]$ remains small compared to a/b for $k_{ISC(n)} \leq b (= k_{rS} + k_{nrS})$. From eq (4), it comes that, in our series, $\phi_{f(n)} + \phi_{ISC(n)} \approx a/b = 0.8$

-Now, if we consider the sum of $\phi_{f(n)}$ and $\phi_{^1O_2(n)}$ it can be noticed that

$\phi_{f(n)}$ and $\phi_{^1O_2(n)}$

n	0	2	4	6
$\phi_{f(n)} + \phi_{^1O_2(n)}$	0.8	0.8	0.8	0.88

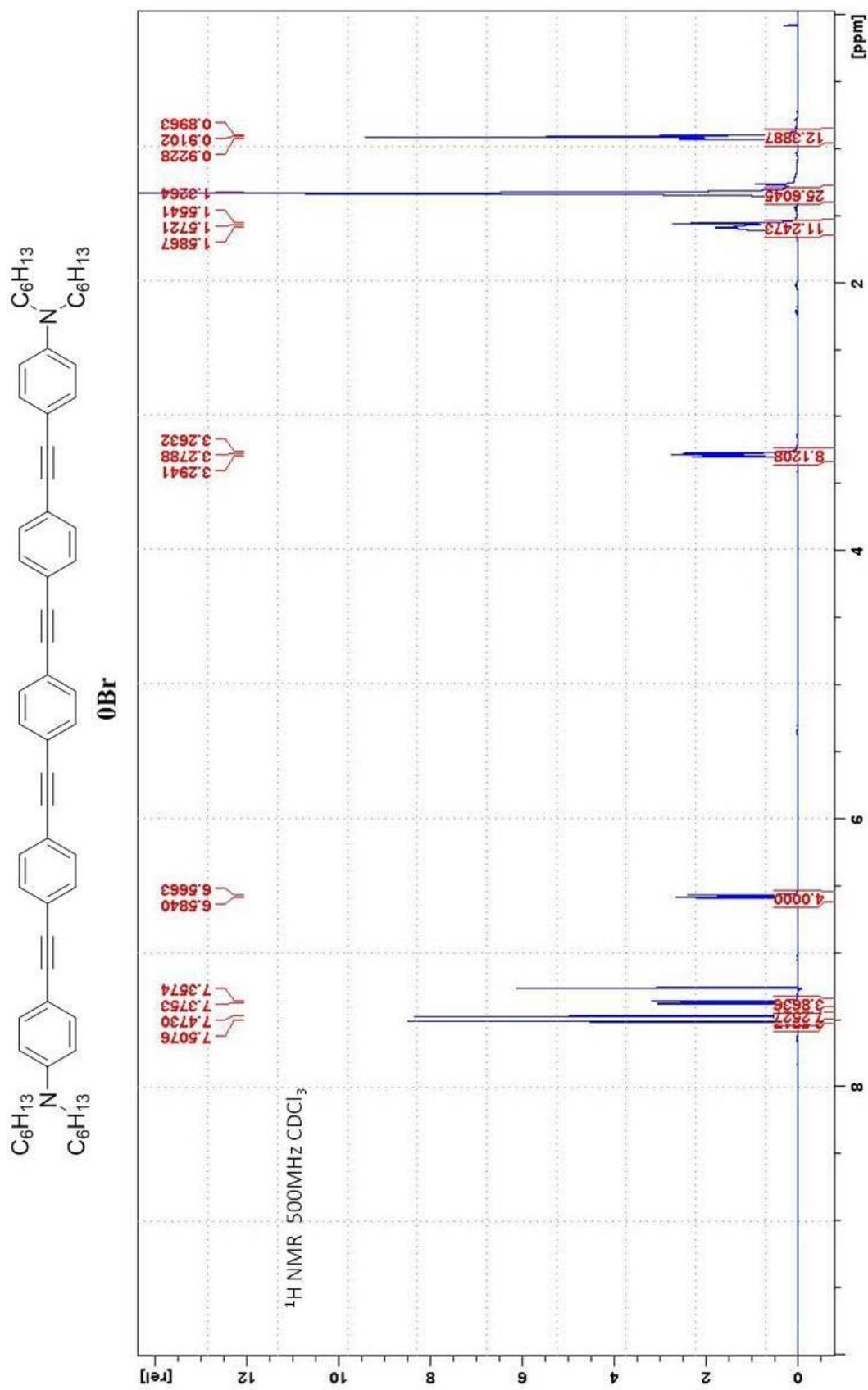
Again, within experimental uncertainties, it can be noticed that the value of $\phi_{f(n)} + \phi_{^1O_2(n)}$ is close to 0.8. From equation (4), it then appears that :

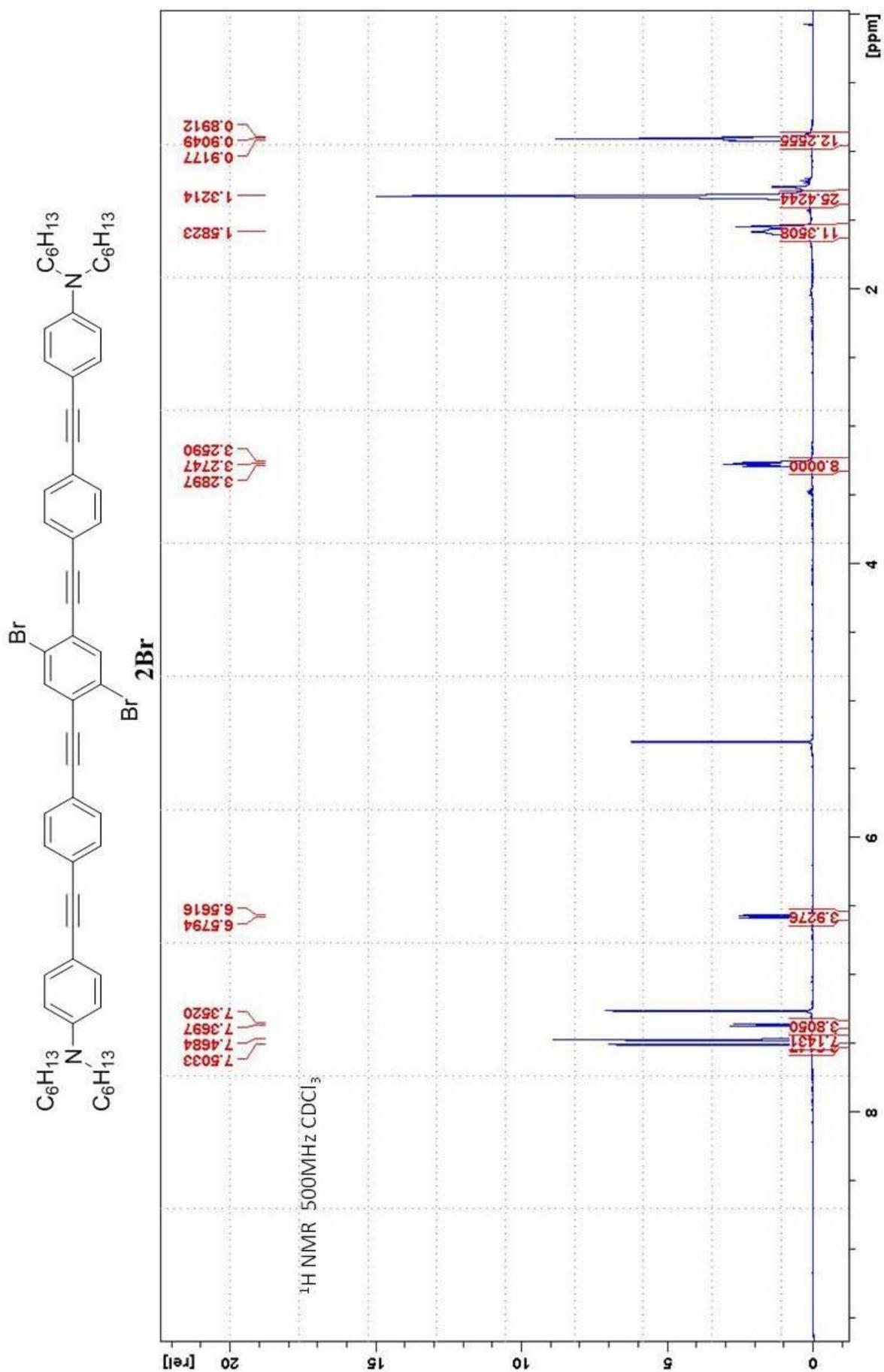
$$(5) \quad \phi_{ISC(n)} \approx \phi_{^1O_2(n)}$$

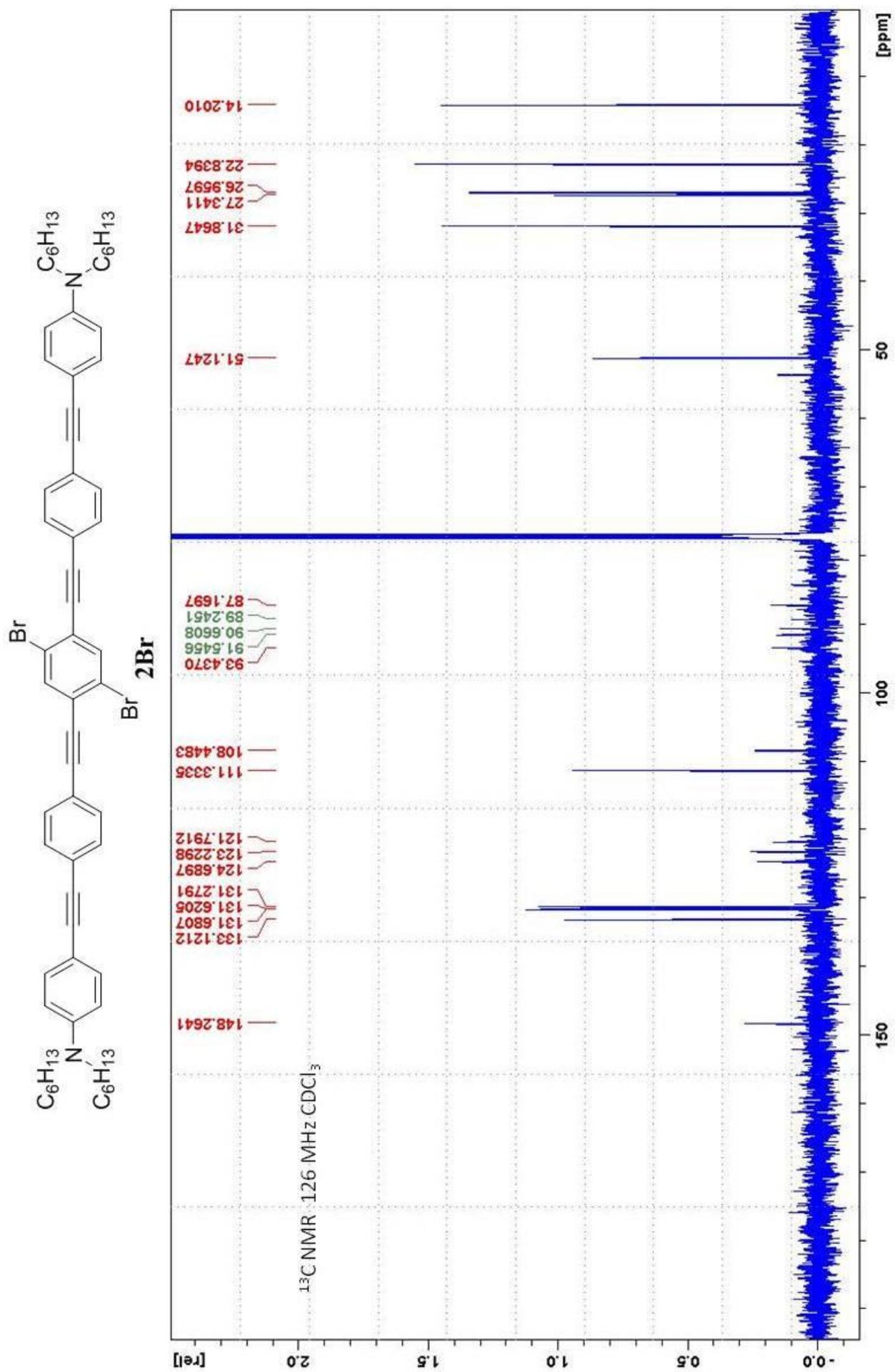
Which leads us to conclude that the singlet oxygen generation efficiency from the triplet state of each molecule of the series has a value that is close to unity, and that all radiative and non-radiative events other than singlet oxygen sensitization can be neglected, or, in other words kinetic constants of radiative (k_{rT}) and non-radiative (k_{nrT}) deactivation of the triplet state are negligible to the kinetic constant associated to singlet oxygen sensitization. Thus, we can state that the measured value for singlet oxygen generation quantum efficiency corresponds to a good approximation of the ISC quantum efficiency within our series of molecules.

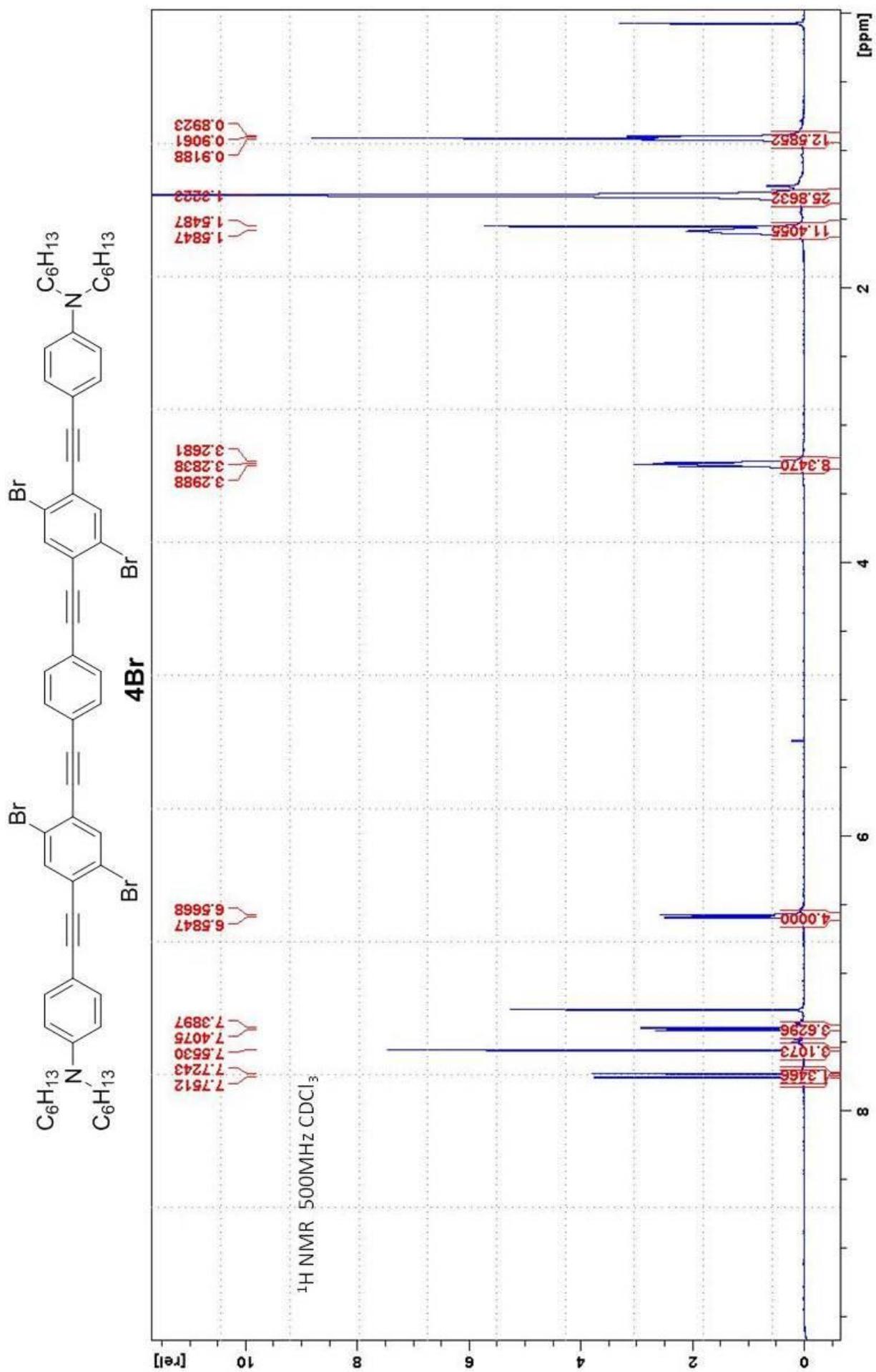
The fact that the sum of those two parameters remain constant results in the fact that a quasi mirror evolution is observed for those parameters, with $\phi_{^1O_2(n)} = 0.8 - \phi_{f(n)}$, whatever the value of n is. Similarly, $\phi_{f(n)}$ and $\tau_{f(n)}$ are connected via a proportionality relationships (the term k_{rS} , which remain constant according to our demonstration, being the proportionality factor), which explains their quasi parallel evolution, hence the remark "The fact that fluorescence quantum yields and lifetimes evolve opposite to (and almost mirror) the 1O_2 generation quantum yield is thus in excellent agreement with the fact that, as a result of the structural similarity of all chromophores within the series, 1O_2 quantum efficiency can be directly connected to ISC efficiency".

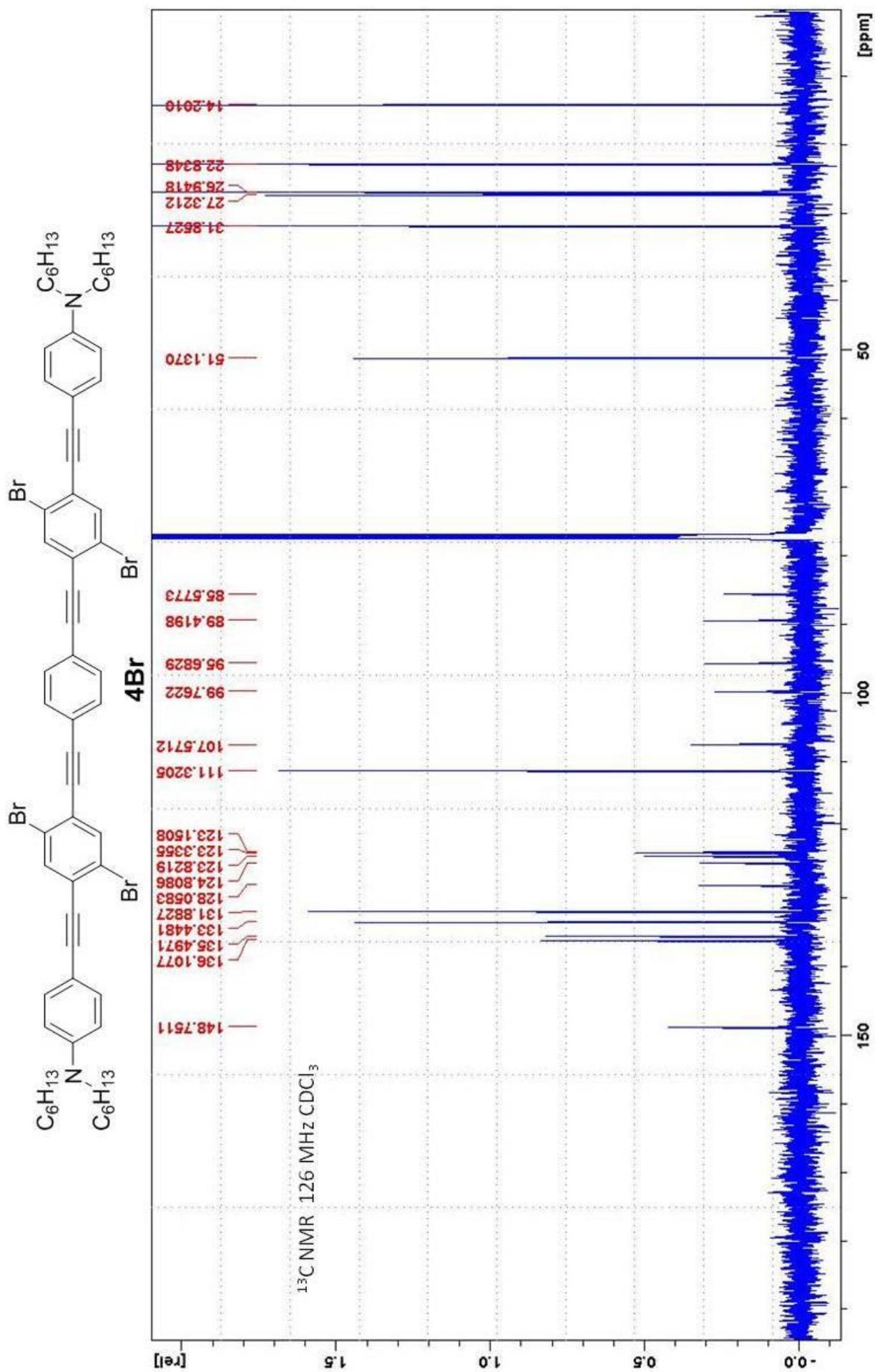
^1H and ^{13}C NMR spectra of 0Br, 2Br, 4Br and 6Br

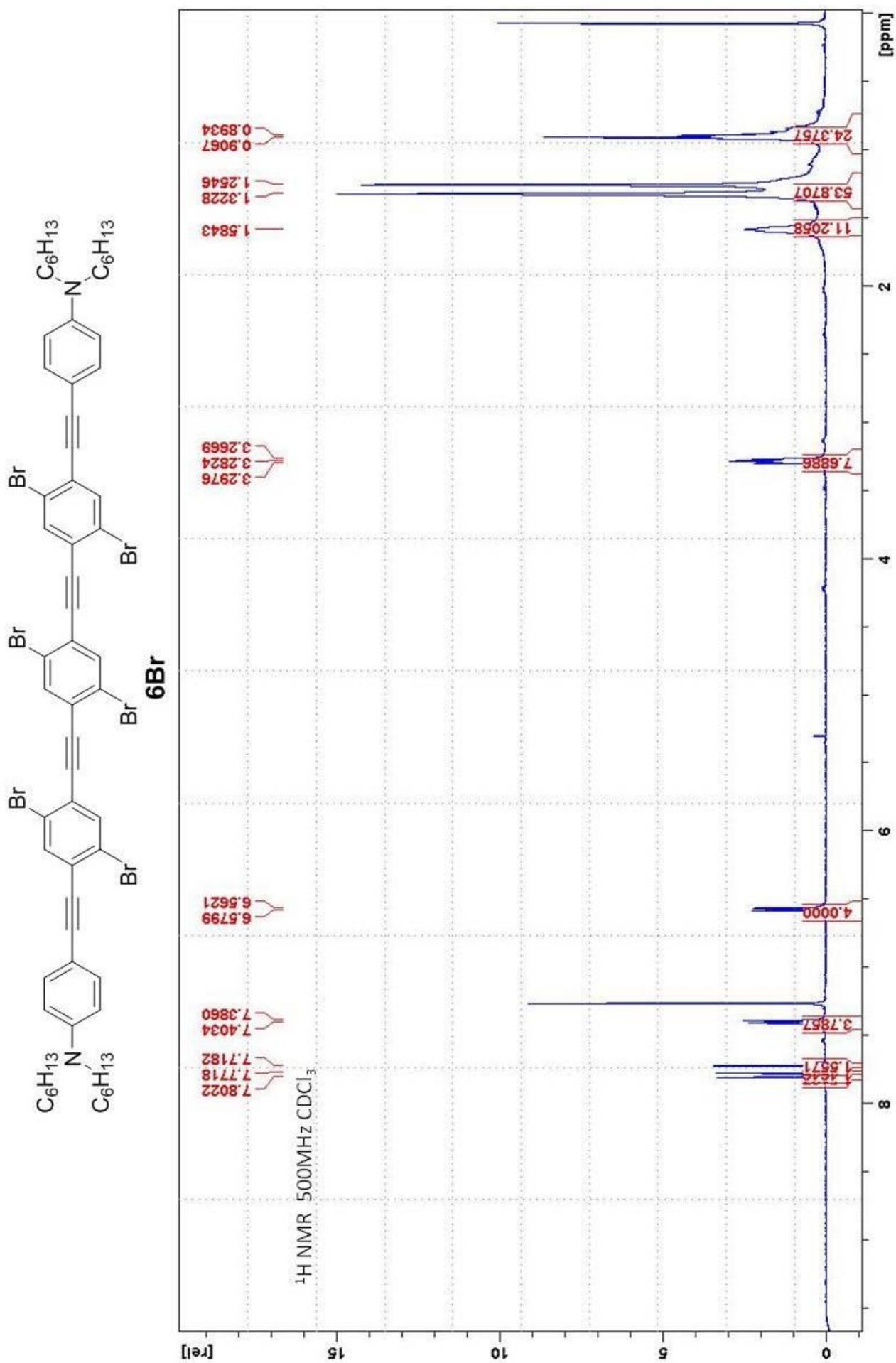


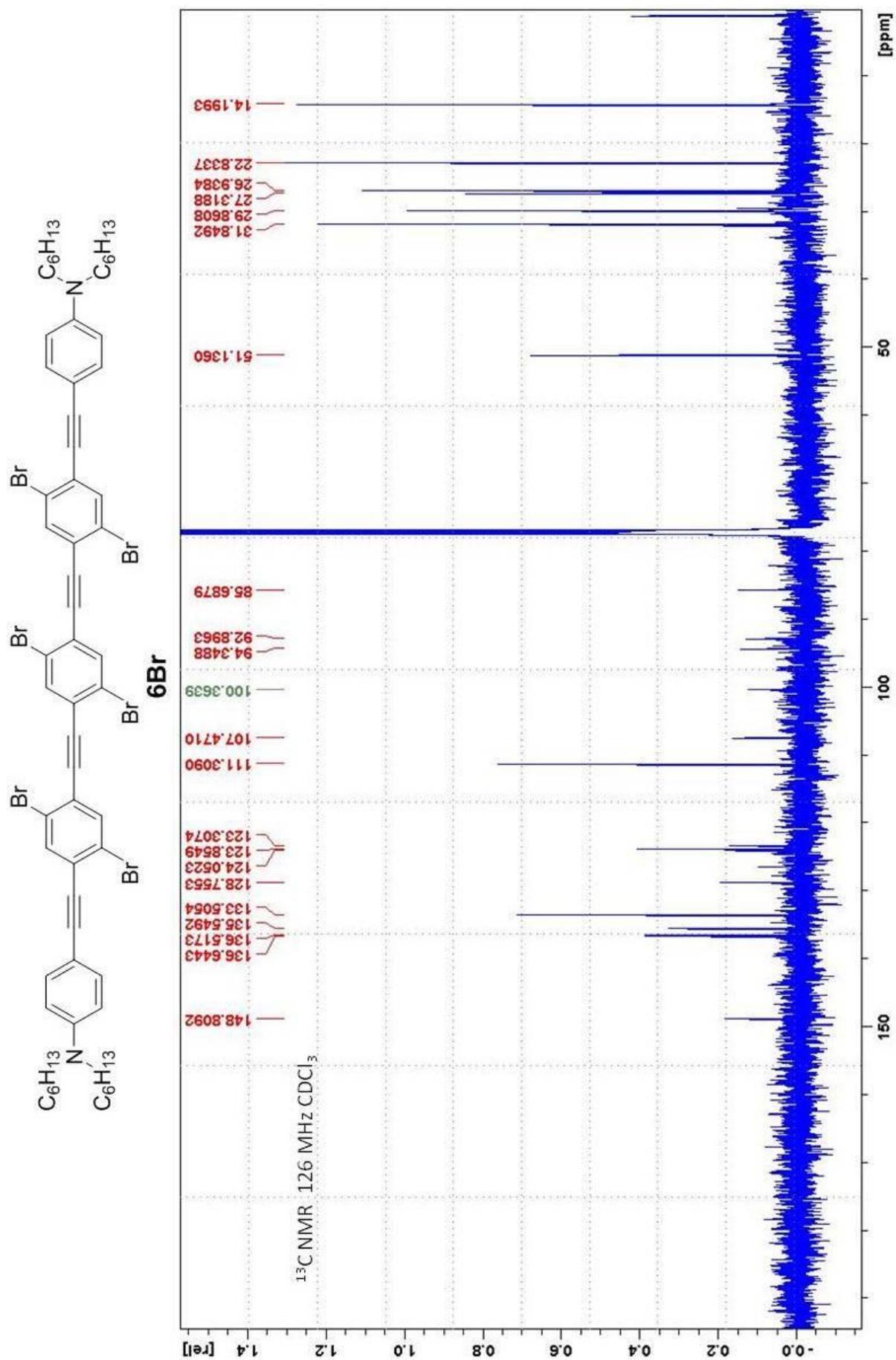












FigureS3 HPLC traces of all compounds with their retention time

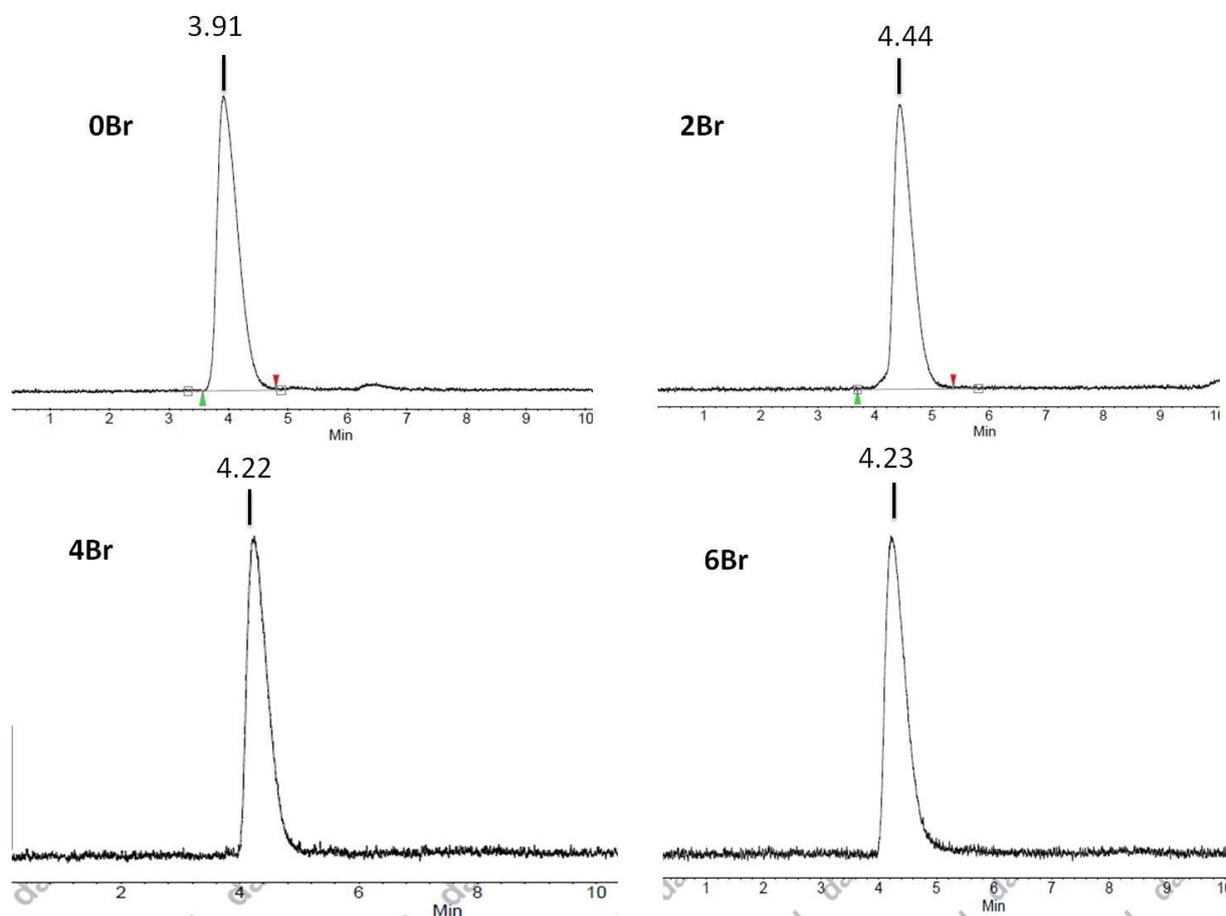
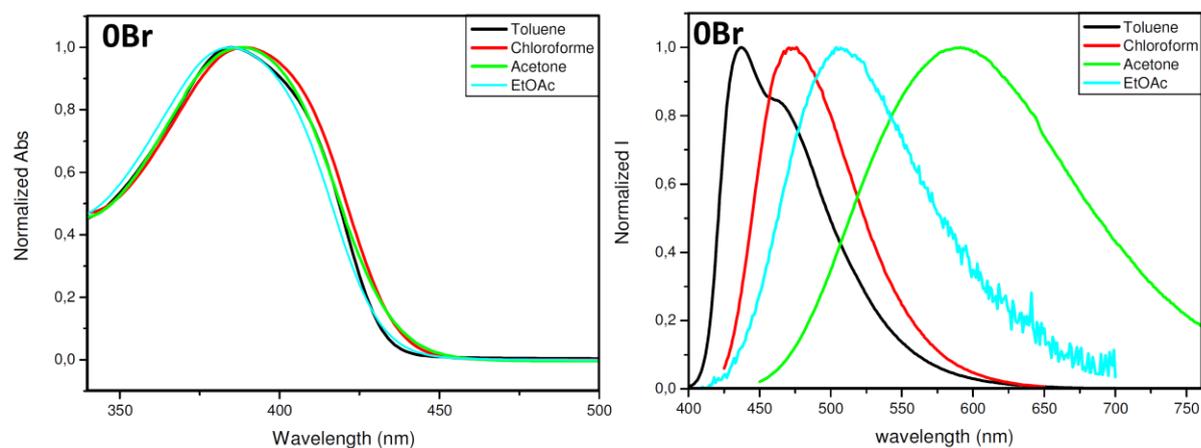


Figure S4 Solvatochromism Study at room temperature (left absorption, right emission), λ_{exc} used for each compounds was the maximum of the CT band.



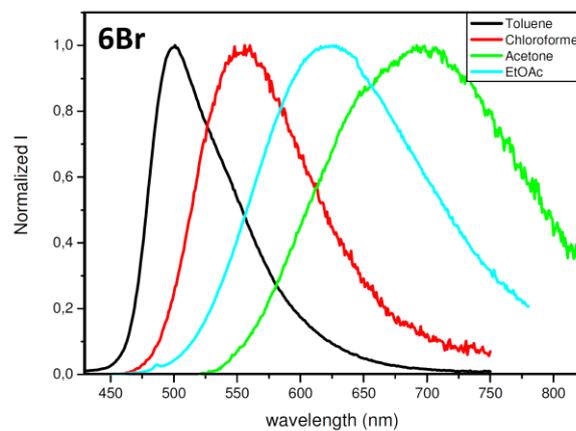
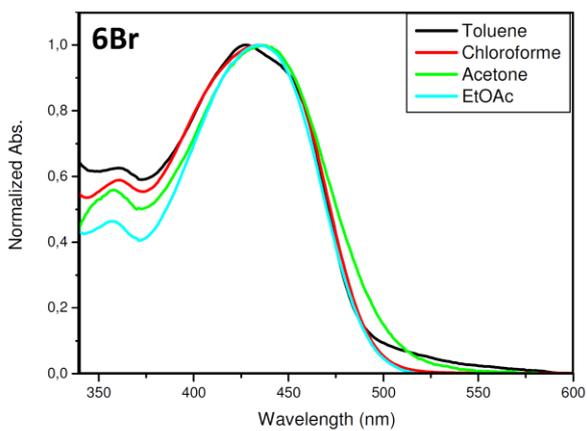
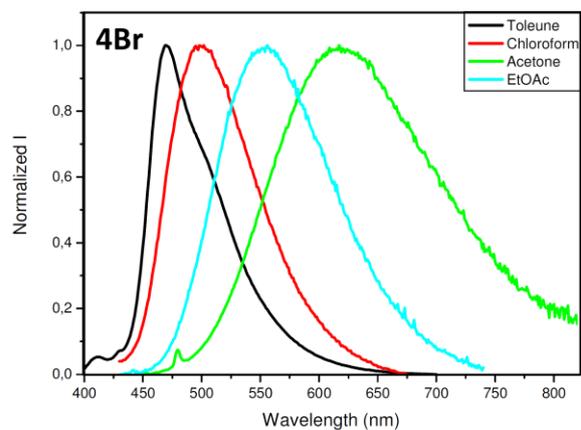
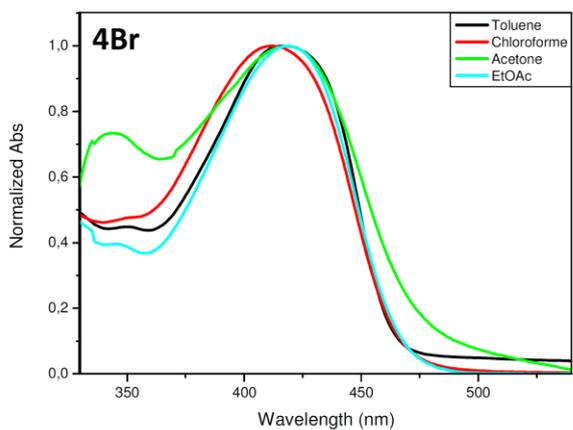
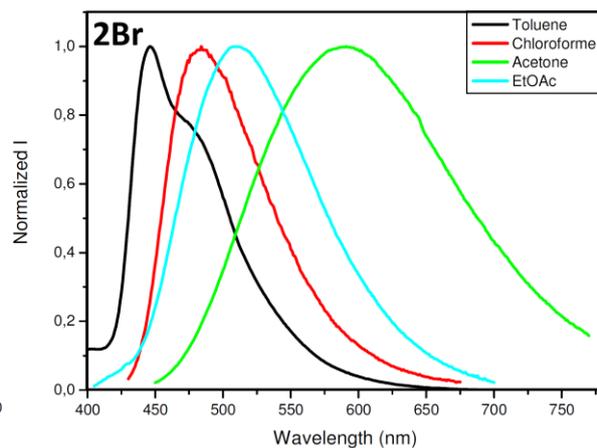
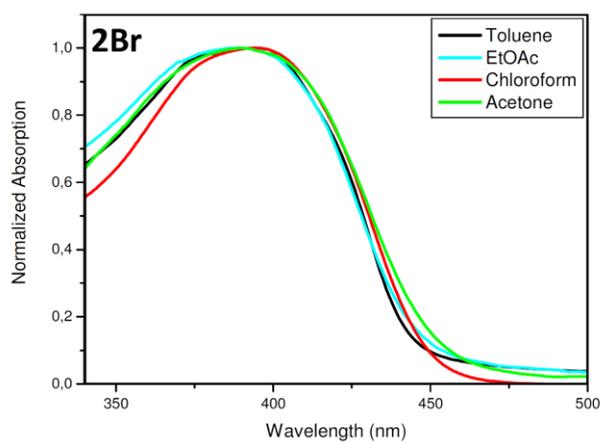
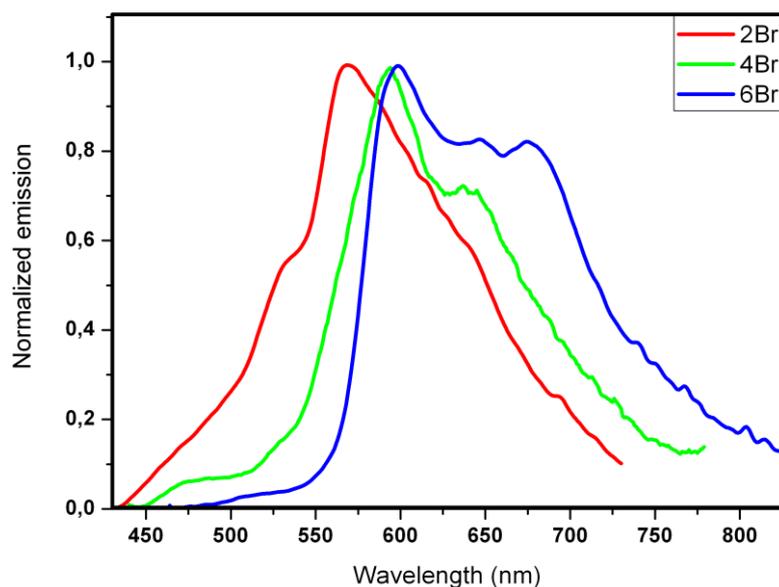
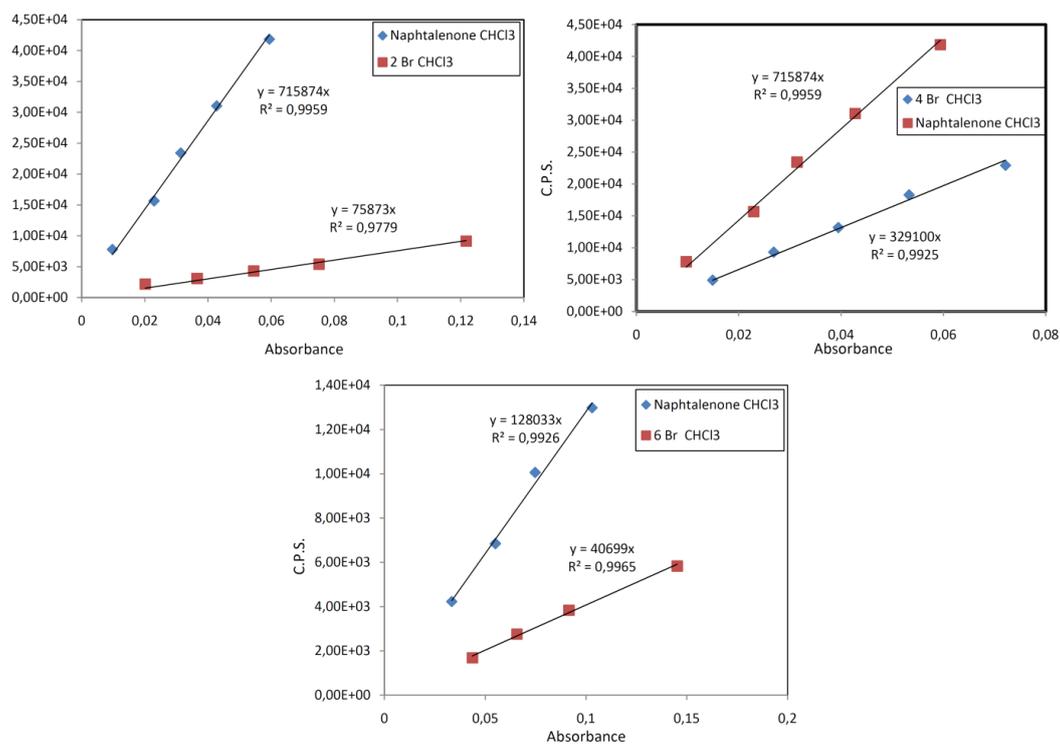


Figure S5 Phosphorescence spectra of molecules 2Br, 4Br, 6Br



time gated 77K phosphorescence (0.65 μ s delay) in a methanol : ethanol / 1 : 4 glassy solution

Figure S6 Singlet oxygen generation quantum yields measurements : plots of the 1270 nm $^1\text{O}_2$ phosphorescence signal against reference and product OD @ 410 nm



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- (5) Traber, B.; Wolff, J. J.; Rominger, F.; Oeser, T.; Gleiter, R.; Goebel, M.; Wortmann, R. *Chem. Eur. J.* **2004**, *10*, 1227-1238.
- (6) Residual presence of water in most samples has been attested, and is due to the fact that a non-dessicated argon flow has been used to pre-dry most of the samples