Supplementary Information (SI) for ChemComm.

Small cavitand macrocycles from direct C–C coupling of *s*-aryltetrazine units

Clève D. Mboyi, Henri Sabbadin, Marie-José Penouilh, Quentin Bonnin, Régine Amardeil, Hélène Cattey, Sophie Fournier, Charles H. Devillers, Julien Roger and Jean-Cyrille Hierso*

Table of contents

General conditions

All reagents were purchased from commercial suppliers and used without purifications. All the reagent and materials were mainly purchased from Sigma-Aldrich, Thermo Fisher Scientific, Acros and VWR chemicals. The solvents were obtained from a solvent purification system (PureSolv PS-MD-5) of Innovative Technology. The other solvents were obtained directly from the manufacturer or distilled from technical grade. Reactions were performed in Schlenk tubes or in a microwave reaction vessel. Microwave heating was carried out using a CEM Discover microwave reactor. The microwave reactions were run in closed reaction vessels with magnetic stirring and with the temperature controlled via IR detection. NMR spectra were recorded on Bruker spectrometers: Avance Neo 400 MHz equipped with a 5 mm TBO probe, Avance Neo 500 MHz equipped with a 5 mm BBOF iProbe and Avance III HD 600 MHz equipped with a 5 mm BBOF N_2 cryoprobe. NMR spectroscopy chemical shifts are quoted in parts per million (δ) relative to TMS (for ^{1}H, ^{13}C), $CFCl_3$ (for ^{19}F). For ^{1}H and ^{13}C spectra, calibration was made by using residual signals of the partially deuterated solvent summarized in 2010 by Fulmer *et al*. For all other nuclei, SR value obtained after zero-calibration of the corresponding reference was applied. Coupling constants *J* are given in Hz. High-resolution mass spectrometry analyses were recorded on a Orbitrap Exploris 240 mass spectrometer (Thermo Scientific) equipped with an electrospray ionization source (HESI). By default, the samples are injected via the HPLC Vanquish system composed of a binary pump, an autosampler (25 °C), and a column compartment (25 °C). The following MS source parameters were used in HPLC mode if no further specification is mentioned: Ion transfert tube Temperature: 320 °C; Gas Flow: Sheath 40 / Aux 5 / Sweep 0; Spray Voltage: 3.5 kV; Spray Current: 0.75 mA; Capillary Temperature: 275 °C; Resolution (m/z = 200): 240 000; Mass calibration in the 100-2000 Da mass range was operated using the commercially available Pierce Flexmix Calibration solution (Thermofisher Scientific ref 15988796), every month. Flash chromatography was performed on silica gel (230-400 mesh).

Synthesis and characterization

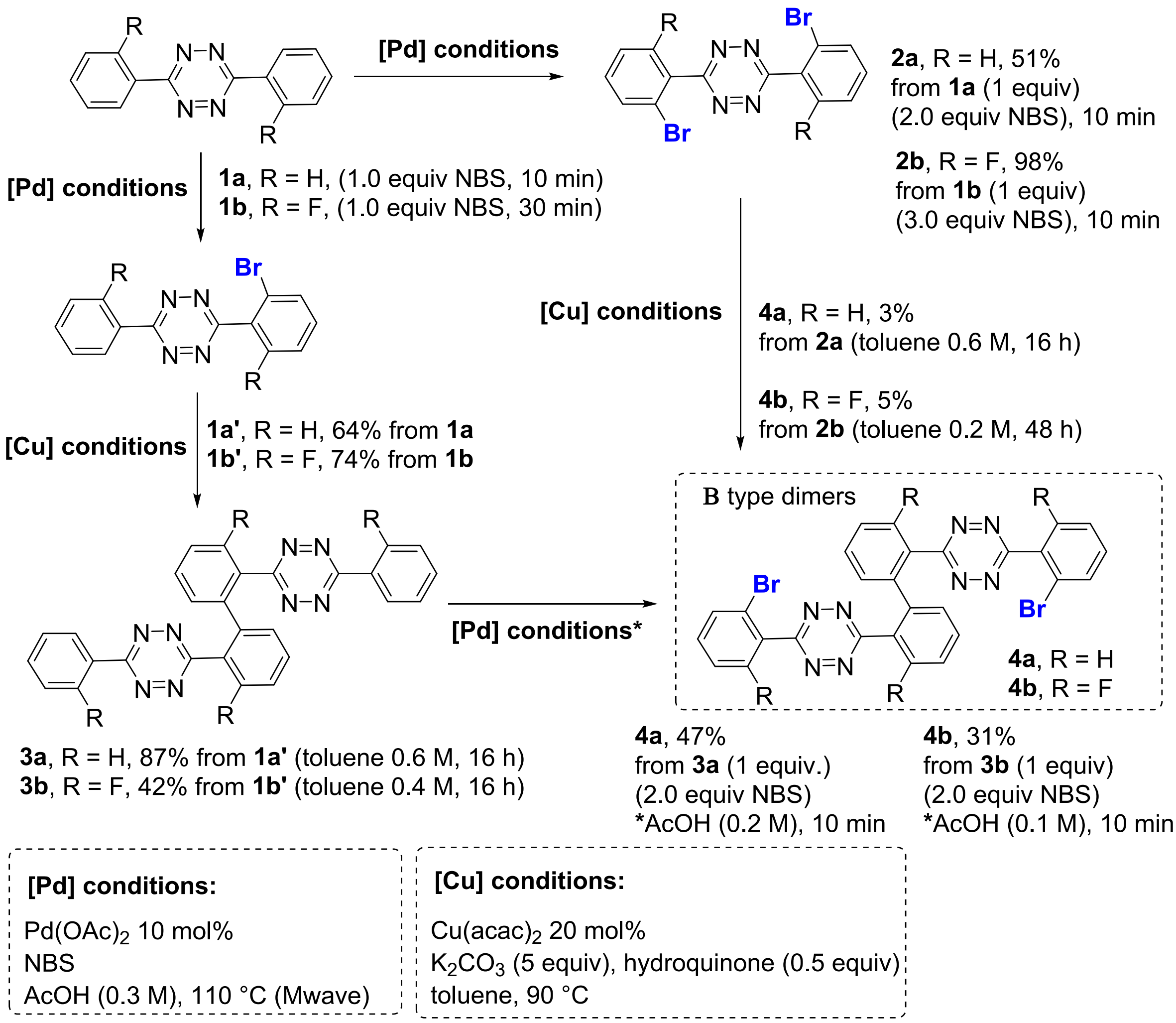


Figure S1. Detailed synthetic pathways to dibrominated **B**-type dimers.

The isolated yield of **2a** (51%, Fig. S1 right) is limited by the co-formation of either monobrominated (**1a'** and **1b'**) or tribrominated side-products (not described herein). Conversely, the compound **2b** is obtained quantitatively (98%). In our first approach, the homocoupling of **2a** and **2b** to **4a** and **4b**, respectively, was found unproductive, and the expected brominated **B**-type dimers **4a** (3%) and **4b** (5%) were obtained in low yields. We observed the concomitant formation of several compounds including various debromination products. We considered an alternative stepwise pathway to **B**-type dimers (Fig. S1, left) from monobrominated **1a'** and **1b'** (obtained in 64% and 74% yield, respectively, from **1a** and **1b**). The monobrominated **1a'** and **1b'** then achieve Cu-catalysed homocoupling to **3a** (87%) and **3b** (42%), respectively. These latter are subsequently dibrominated by Pd-catalysed C–H *ortho*-functionalization, in the presence of 2 equiv. NBS, to give **4a** (47%) and **4b** (31%), respectively.

Following this road, by tuning the amount of NBS to one equiv. and starting from **3a** the *o*-monobrominated analogue of **4a**, compound **4a'** was isolated (38%, Fig. S2). When a four equiv. excess of NBS was added to **3b**, the highly halogenated product **4c** (tetrabrominated, 61%) and **4a'** (tetrafluorinated, 61%) was obtained (Fig. S2).

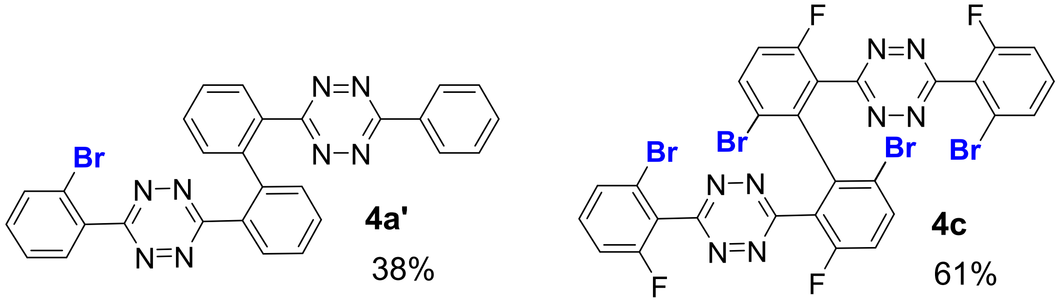


Figure S2. Mono- and tetrabrominated bis(tetrazine) **4a'** and **4c** (XRD in the following).

General procedure for palladium-catalyzed di-bromination of 1a and 1b

As a typical experiment, the tetrazine **1a** or **1b**, halogenated source (1-4 equiv), and $Pd(OAc)_2$ (10 mol%) were introduced in a 10 mL microwave reaction vessel, equipped with a magnetic stirring bar. The solvent (0.3 M) was added, and the reaction mixture was heated in the microwave at 110 °C for 10-30 min (200 W, 2 min ramp). After cooling down to room temperature, the reaction mixture was diluted with water, extracted three times with dichloromethane. The combined organic layer was washed with water and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography using an appropriate ratio of the eluent.

3-(2-bromophenyl)-6-phenyl-1,2,4,5-tetrazine (1a')

1a' was obtained according to the general procedure described above. For the reaction, 3,6-diaryl-1,2,4,5-tetrazine **1a** (1.31 g, 4.69 mmol, 1 equiv.) and NBS (0.799 g, 4.69 mmol, 1 equiv.) for10 min, was used, giving **1a'** as red solid (3.0 mmol, 64%), after purification by silica gel column chromatography using dichloromethane-heptane 7:3 ratio. For characteristic details of compounds **2a**, see described protocols in *ACS Catal.* **2017**, *7*, 8493.

3-(2-bromo-6-fluorophenyl)-6-(2-fluorophenyl)-1,2,4,5-tetrazine (1b')

1b' was obtained according to the general procedure described above. For the reaction, 3,6-bis(2-fluorophenyl)-1,2,4,5-tetrazine **1b** (0.821 g, 3.04 mmol, 1 equiv.) and NBS (0.845 g, 3.04 mmol, 1 equiv.) for10 min, was used, giving **1b'** as red solid (2.27 mmol, 74%), after purification by silica gel column chromatography using dichloromethane-heptane 7:3 ratio. For characteristic details of compounds **1b'**, see described protocols in *ACS Catal.* **2017**, *7*, 8493.

3,6-bis(2-bromophenyl)-1,2,4,5-tetrazine (2a)

2a was obtained according to the general procedure described above. For the reaction, 3,6-diaryl-1,2,4,5-tetrazine **1a** (0.8 g, 3.42 mmol, 1 equiv.) and NBS (1.22 g, 6.84 mmol, 2 equiv.) for10 min, was used, giving **2a** as red solid (1.74 mmol, 51%), after purification by silica gel column chromatography using dichloromethane-heptane 7:3 ratio. For characteristic details of compounds **2a**, see described protocols in *ACS Catal.* **2017**, *7*, 8493.

3,6-bis(2-bromo-6-fluorophenyl)-1,2,4,5-tetrazine (2b)

2b was obtained according to the general procedure described above. For the reaction, 3,6-bis(2-fluorophenyl)-1,2,4,5-tetrazine **1b** (1.0 g, 3.07 mmol, 1 equiv.) and NBS (2.56 g, 9.21 mmol, 3 equiv.) for10 min, was used, giving **2b** as red solid (3.04 mmol, 98%), after purification by silica gel column chromatography using dichloromethane-heptane 7:3 ratio. For characteristic details of compounds **2b**, see described protocols in *ACS Catal.* **2017**, *7*, 8493.

General procedure for palladium-catalyzed bromination of poly(aryl)-bis(tetrazines)

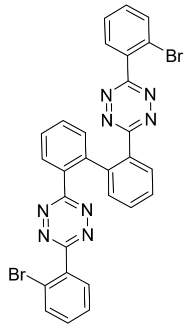
The synthetic procedure of **3a** and **3b** follows described protocols reported in *Angew. Chem. Int. Ed.*, **2020**, *59*, 1149.

In a microwave reaction vessel equipped with a magnetic stirring bar, symmetrical bridge-clamp bis(tetrazine) **3a** or **3b** (1 equiv.), $Pd(OAc)_2$ (10 mol%), NBS (1–4 equiv.) and acetic acid (0.12 M) were introduced, the vessel was placed in a microwave reactor (110 °C, 200 W, 10 min). After cooling down to room temperature, distilled water was added (10 mL) and the reaction mixture was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtrated and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to afford brominated bridge-clamp bis(tetrazine) **B**-type as red solids.

3,3'-bis[2,2'-bromophenyl]-6,6'-[1,1'-biphenyl-2,2'-diyl]-1,2,4,5-tetrazine (4a)

4a was obtained with 0.101 mmol, in 47% yield using 0.214 mmol of **3a** and 2 equivalents of NBS.

4a was obtained according to the general procedure described above. For the reaction, 3,3'-[(1,1'-biphenyl)-2,2'-diyl]-6,6'-bis[phenyl]-1,2,4,5-tetrazine **3a** (100 mg, 0.214 mmol, 1 equiv.) and NBS (76.17 mg, 0.428 mmol, 2 equiv.) for10 min, was used, giving **4a** as red solid (0.101 mmol, 47%), after purification by silica gel column chromatography using dichloromethane-heptane by gradient 7:3 to 3:7 ratio.



Rf = 0.45 (n-heptane/ethyl acetate = 7/3 (v/v)).

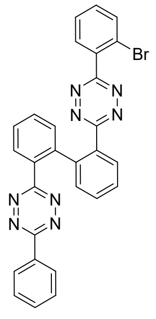
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.13 (dd, J = 7.8, 1.4 Hz, 2H), 7.91 (dd, J = 7.7, 1.7 Hz, 2H), 7.74 (dd, J = 8.0, 1.1 Hz, 2H), 7.67 (td, J = 7.6, 1.4 Hz, 2H), 7.62-7.54 (m, 4H), 7.50 (td, J = 7.6, 1.2 Hz, 2H), 7.41 (td, J = 7.8, 1.7 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 165.4, 165.1, 141.3, 134.2, 133.8, 132.4, 131.9, 131.8, 131.7, 130.8, 128.6, 127.9, 122.5.

HRMS + p ESI (m/z) [M+H$^+$] Calcd for $C_{28}H_{17}Br_2N_8$: 622.99374. Found: m/z = 622.99337.

3-[2-bromophenyl)-3'-phenyl]-6,6'-[(1,1'-biphenyl)-2,2'-diyl]-1,2,4,5-tetrazine (4a')

4a' was obtained according to the general procedure described above. For the reaction, 3,3'-[(1,1'-biphenyl)-2,2'-diyl]-6,6'-bis[phenyl]-1,2,4,5-tetrazine **3a** (49 mg, 0.107 mmol, 1 equiv.) and NBS (19.04 mg, 0.107 mmol, 1 equiv.) for10 min, was used, giving **4a'** as red solid (0.041 mmol, 38%), after purification by silica gel column chromatography using dichloromethane-heptane by gradient 7:3 to 3:7 ratio.



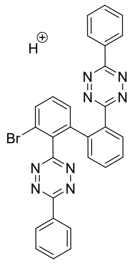
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.45-8.40 (m, 2H), 8.08 (dd, J = 7.8, 1.4 Hz, 1H), 7.98 (dd, J = 7.7, 1.4 Hz, 1H), 7.85 (dd, J = 7.7, 1.7 Hz, 1H), 7.67 (dd, J = 8.1, 1.1 Hz, 1H), 7.61-7.39 (m, 10H), 7.34 (td, J = 7.7, 1.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 166.31, 165.48, 165.01, 162.62, 141.54, 141.08, 134.26, 133.83, 132.79, 132.43, 132.32, 131.94, 131.91, 131.85, 131.76, 131.66, 130.73, 129.31, 128.52, 128.50, 128.36, 127.91, 122.57.

HRMS + p ESI (m/z) [M+H+] Calcd for $C_{28}H_{18}BrN_8$: 545.0823. Found: m/z = 545.08295.

3,3'-bis[phenyl]-6,6'-[bis(2-bromophenyl)-(1,1'-biphenyl)-2,2'-diyl]-1,2,4,5-tetrazine (4a")

4a" was obtained according to the general procedure described above. For the reaction, 3,3'-[(1,1'-biphenyl) -2,2'-diyl]-6,6'-bis[phenyl]-1,2,4,5-tetrazine **3a** (49 mg, 0.107 mmol, 1 equiv.) and NBS (19.04 mg, 0.107 mmol, 1 equiv.) for10 min, was used, giving **4a"** as red solid (0.044 mmol, 41%), after purification by silica gel column chromatography using dichloromethane-heptane by gradient 7:3 to 3:7 ratio.



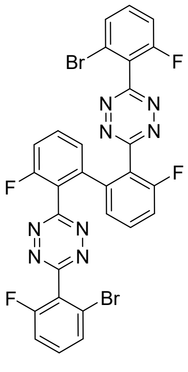
^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 8.61 (dd, J = 7.9, 1.7 Hz, 2H), 8.51 (dd, J = 7.7, 1.7 Hz, 2H), 8.06 (dd, J = 7.6, 1.4 Hz, 1H), 7.81 (dd, J = 7.5, 1.7 Hz, 1H), 7.69 – 7.54 (m, 9H), 7.52 – 7.44 (m, 2H).

^{13}C NMR (101MHz, CD_2Cl_2): δ (ppm) = 167.66, 166.10, 163.06, 143.79, 139.58, 133.81, 133.45, 133.15, 132.82, 132.67, 132.34, 132.20, 132.11, 131.92, 131.76, 130.93, 130.75, 129.72, 129.30, 128.69, 128.62, 123.50.

HRMS + p ESI (m/z) [M+H+] Calcd for $C_{28}H_{18}BrN_8$: 545.08323. Found: m/z = 545.08293.

3,3'-bis[(2,2'-fluoro-6,6'-bromophenyl)-(1,1'-biphenyl)-2,2'-diyl]-6,6'-bis[2,2'-fluorophenyl]-1,2,4,5-tetrazine (4b)

4b was obtained according to the general procedure described above. For the reaction, 3,3'-[(1,1'-biphenyl)-2,2'-diyl]-6,6'-bis[2,2'-fluorophenyl]-1,2,4,5-tetrazine **3b** (21.48 mg, 0.0427 mmol, 1 equiv.) and NBS (15.20 mg, 0.085 mmol, 2 equiv.) for10 min, was used, giving **4b** as red solid (0.0243 mmol, 57%), after purification by silica gel column chromatography using dichloromethane-heptane by gradient 7:3 to 3:7 ratio.



Rf = 0.32 (n-heptane/ethyl acetate = 7/3 (v/v)).

^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) = 7.65 – 7.54 (m, 4H), 7.49 (tt, J = 8.5, 5.5 Hz, 2H), 7.41 – 7.22 (m, 6H).

^{19}F NMR (470 MHz, CD_2Cl_2): δ (ppm) = -110.8 (bs, 2F), -114.5 (bs, 2F).

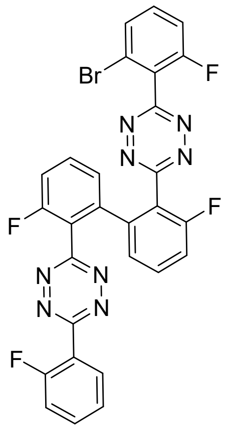
^{13}C NMR (126 MHz, CD_2Cl_2): δ (ppm) = 164.2 (d, J = 2.3 Hz), 163.5, 161.4 (d, J = 255.8 Hz), 161.1 (d, J = 255.8 Hz), 141.3, 133.8 (d, J = 9.2 Hz), 133.1 (d, J = 9.2 Hz), 129.5 (d, J = 3.7 Hz), 127.9 (d, J = 3.6 Hz), 123.8, 123.8 (d, J = 2.7 Hz), 123.7, 121.6 (d, J = 14.1 Hz), 116.6 (d, J = 21.3 Hz), 115.9 (d, J = 21.2 Hz).

HRMS + p ESI (m/z) [M+H$^+$] Calcd for $C_{28}H_{13}Br_2F_4N_8$: 695.95606. Found: m/z = 694.95712.

3-[(2-bromo-6-fluorophenyl)-3'-(2-fluorophenyl)]-6,6'-[bis(2,2'-fluorophenyl)-(1,1'-biphenyl)-2,2'-diyl]-1,2,4,5-tetrazine (4b')

4b' was obtained according to the general procedure described above. For the reaction, 3,3'-[(1,1'-biphenyl) -2,2'-diyl]-6,6'-bis[2,2'-fluorophenyl]-1,2,4,5-tetrazine **3b** (22 mg, 0.044 mmol, 1 equiv.) and NBS (15.56 mg, 0.088 mmol, 2 equiv.) for10 min, was used, giving **4b'** as red solid (0.0427 mmol, 31%), after purification by silica gel column chromatography using dichloromethane-heptane by gradient 7:3 to 3:7 ratio.

Rf = 0.34 (n-heptane/ethyl acetate = 7/3 (v/v)).



^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) = 8.27 (td, J = 7.6, 1.8 Hz, 1H), 7.68 – 7.54 (m, 4H), 7.50 (td, J = 8.4, 5.8 Hz, 1H), 7.40 (td, J = 7.6, 1.1 Hz, 1H), 7.36 – 7.28 (m, 5H), 7.28 – 7.23 (m, 1H).

^{19}F NMR (470 MHz, CD_2Cl_2): δ (ppm) = -110.8 (bs, 1F), -112.5 (bs, 1F), -114.6 (bs, 1F), -114.7 (bs, 1F).

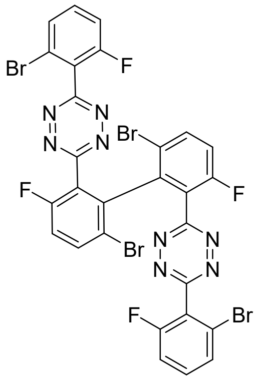
^{13}C NMR (126 MHz, CD_2Cl_2): δ (ppm) = 164.2 (d, J = 2.1 Hz), 163.5 (d, J = 5.4 Hz), 163.2 (d, J = 6.0 Hz), 161.9 (d, J = 259.6 Hz), 161.4 (d, J = 257.0 Hz), 161.2 (d, J = 254.0 Hz), 161.1 (d, J = 254.5 Hz), 141.6, 141.2, 134.8 (d, J = 8.8 Hz), 133.9 (d, J = 9.3 Hz), 133.2 (d, J = 9.3 Hz), 132.9 (d, J = 9.4 Hz), 132.1, 129.6 (d, J = 3.6 Hz), 128.0 (d, J = 3.5 Hz), 127.9 (d, J = 3.4 Hz), 125.3 (d, J = 3.9 Hz), 123.8 (d, J = 2.3 Hz), 123.7, 121.7 (d, J = 21.4 Hz), 121.5 (d, J = 21.4 Hz), 120.8 (d, J = 9.8 Hz).

HRMS + p ESI (m/z) [M+H$^+$] Calcd for $C_{28}H_{14}BrF_4N_8$: 617.04554. Found: m/z = 617.04633.

3,3'-bis[(2,2'-fluoro-6,6'-bromophenyl)-(1,1'-biphenyl)-2,2'-diyl]-6,6'-bis[2,2'-fluoro-5,5'-bromophenyl]-1,2,4,5-tetrazine (4c)

4c was obtained according to the general procedure described above. For the reaction, 3,3'-[(1,1'-biphenyl)-2,2'-diyl]-6,6'-bis[2,2'-fluorophenyl]-1,2,4,5-tetrazine **3b** (21.48 mg, 0.0427 mmol, 1 equiv.) and NBS (30.40 mg, 0.171 mmol, 4 equiv.) for10 min, was used, giving **4c** as red solid (0.026 mmol, 61%), after purification by silica gel column chromatography using dichloromethane-heptane by gradient 7:3 to 3:7

ratio.



Rf = 0.51 (n-heptane/ethyl acetate = 5/5 (v/v)).

^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) = 7.86 (dd, *J* = 9.0, 4.9 Hz, 2H), 7.70 – 7.55 (m, 2H), 7.49 (td, *J* = 8.3, 5.8 Hz, 2H), 7.41 – 7.20 (m, 4H).

^{19}F NMR (470 MHz, CD_2Cl_2): δ (ppm) = -110.8 (bs, 2F), -114.5 (bs, 2F).

^{13}C NMR (126 MHz, CD_2Cl_2): 163.5, 163.3 (d, *J* = 3.1 Hz), 161.3 (d, *J* = 255.8 Hz), 160.3 (d, *J* = 257.0 Hz), 140.2, 137.3 (d, *J* = 9.0 Hz), 133.9 (d, *J* = 9.2 Hz), 129.5 (d, *J* = 3.6 Hz), 123.8 (d, *J* = 2.6 Hz), 123.7, 123.5 (d, *J* = 5.5 Hz), 123.4, 121.3 (d, *J* = 3.7 Hz), 119.2 (d, *J* = 22.8 Hz), 115.9 (d, *J* = 21.2 Hz).

HRMS + p ESI (m/z) $[M+H]^+$ Calcd for $C_{28}H_{11}Br_4F_4N_8$: 852.77504. Found: m/z = 850.77594.

Copper-catalyzed homocoupling reaction for accessing macrocyclic and linear Tz oligomers

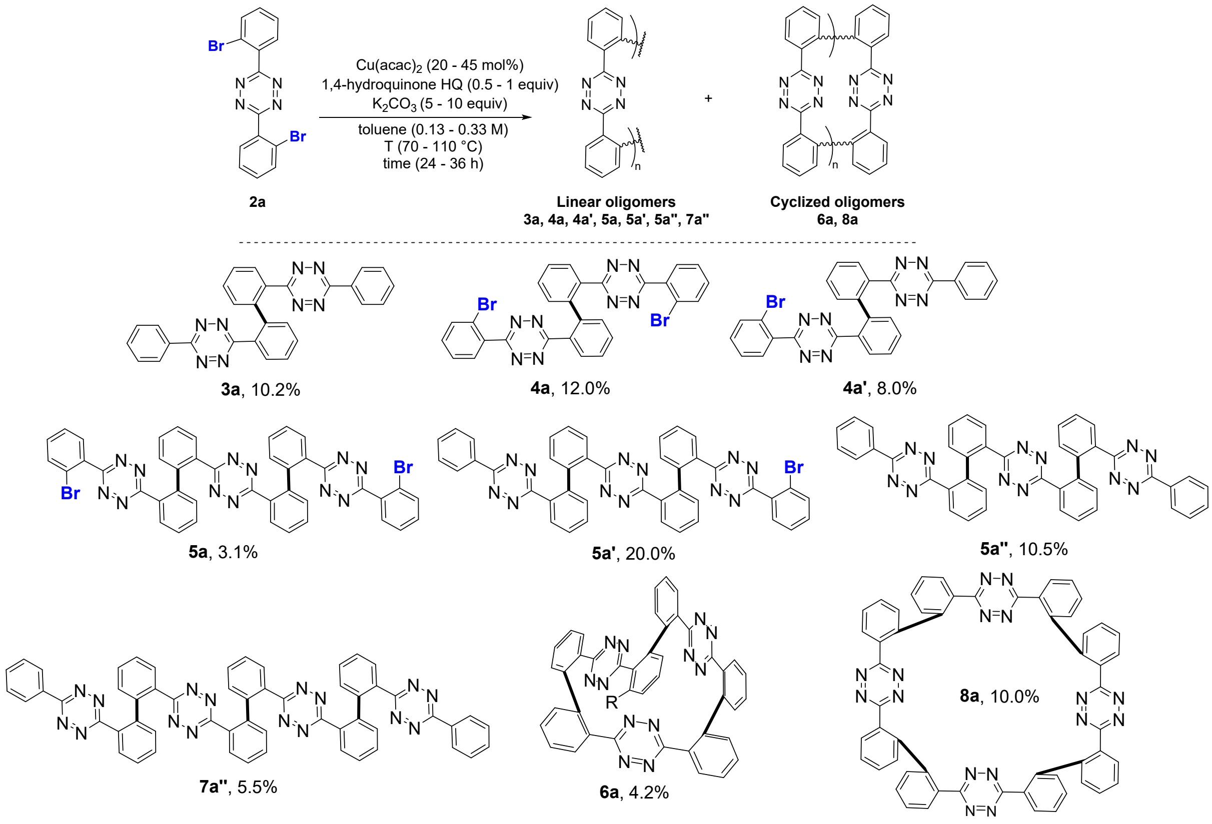


Figure S3. Linear and cyclized oligomers of poly(aryl-tetrazines) formed in non-fluorinated version.

Table S1. Screening of copper-catalyzed homocoupling reaction with 3,6-bis(2-bromophenyl)-1,2,4,5-tetrazine (**2a**).[a]

Entry	[Cu] %	K_2CO_3 (equiv.)	HQ (equiv)	Tol. (M)	T (°C)	Time (h)	**3a** (%)	**4a** (%)	**4a'** (%)	**5a** (%)	**5a'** (%)	**5a''** (%)	**6a** (%)	**7a''** (%)	**8a** (%)
1	20	5.0	0.5	0.15	90	24	-	9.5	-	-	19.7	-	-	-	8.6
2	20	5.0	0.5	0.33	90	24	1.4	3.2	4.1	1.5	2.1	1.4	-	-	1.5
3	45	5.5	0.55	0.15	90	24	4.9	12.0	3.3	-	-	1.6	-	-	9.7
4	40	9.5	1.0	0.15	110	36	10.2	4.1	8.0	-	-	10.5	-	5.5	1.0
5	20	5	0.5	0.7	90	16	nd	nd	nd	3.1	4.5	3.1	4.2	1.5	3.0

[a] Conditions: 3,6-bis(2-bromophenyl)-1,2,4,5-tetrazine **2a** (1 equiv).

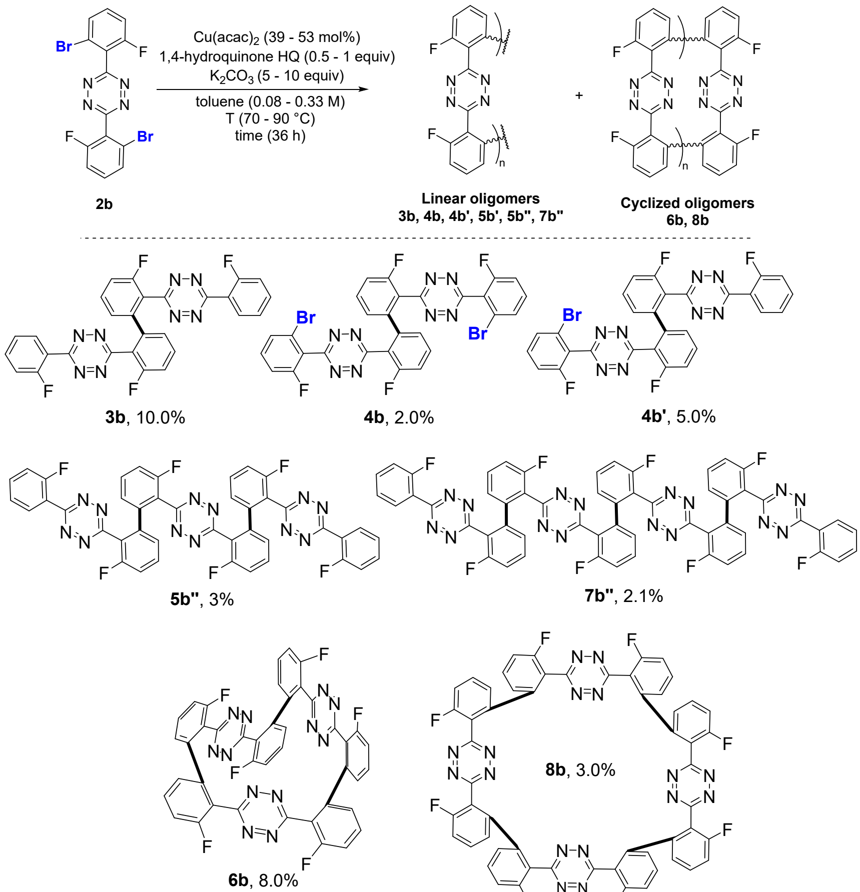


Figure S4. Linear and cyclized oligomers of poly(aryl-tetrazines) formed in fluorinated version.

Table S2. Screening of copper-catalyzed homocoupling reaction with 3,6-bis(2-bromo-6-fluorophenyl)-1,2,4,5-tetrazine (**2b**).[a]

Entry	[Cu] %	K_2CO_3 (equiv.)	HQ (equiv)	Tol. (M)	T (°C)	Time (h)	**3b** (%)	**4b** (%)	**4b'** (%)	**5b** (%)	**5b''** (%)	**6b** (%)	**7b''** (%)	**8b** (%)
1	40	10.0	1.0	0.08	70	36	-	-	-	-	-	-	-	-
2	39	10.0	1.0	0.08	90	36	2.8	-	-	-	-	11.9	-	-

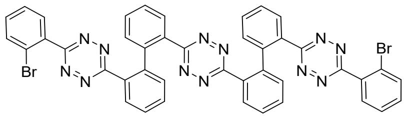
3	40	5	0.5	0.08	90	36	9.7	-	4.9		-	8.0	-	-
4	53	9.0	0.9	0.08	90	36	6.1	1.5	1.7	-	-	1.3	-	-
5	42	10.0	1.0	0.33	90	36	9.7	-	-	-	-	2.9	-	-
6	20	5	0.5	0.2	90	16	nd	nd	nd	-	3	4	2.1	2.5

[a] Conditions: 3,6-bis(2-bromophenyl)-1,2,4,5-tetrazine **2b** (1 equiv).

General procedure for copper-catalyzed homocoupling reaction with 2a

To a dried Schlenk tube were added 3,6-bis(2-bromophenyl)-1,2,4,5-tetrazine **2a** (2.653 g, 6.804 mmol, 1.0 equiv.), $Cu(acac)_2$ (0.356 g, 1.36 mmol, 20 mol%), 1.4-hydroquinone (0.375 g, 3.402 mmol, 0.5 equiv.) and K_2CO_3 (4.702 g, 34.02 mmol, 5 equiv.). After 3 standard cycles of evacuating and back-filling with argon, toluene (10 mL, 0.7 M) was added. The reaction mixture was stirred and heated at 90 °C for 16 hours. After allowing the reaction to cool to room temperature, the resulting mixture was diluted water and extracted with dichloromethane. The combined organic layer was dried over anhydrous $MgSO_4$, filtrated and the solvent was evaporated under reduced pressure. The Linear and cyclized oligomers were purified by silica gel column chromatography (eluent: heptane/dichloromethane and heptane/ethyl acetate by gradient). Note that, the bis(tetrazine) intermediates type **3a**, **3b**, **4a**, **4b**, **4a'** and **4b'** described in the previous section will not be described in this section. Only compounds **5a**, **5a'**, **5a''**, **6a**, **7a''** and **8a**, having a minimum of three *s*-tetrazines units are described in this part.

3,6''-bis[2,2'-bromophenyl]-3',6,3''6'-[(1,1',1'',1'''-biphenyl)-2,2',2'',2'''-diyl]-1,2,4,5-tetrazine 5a, was isolated as a red solid (0.211 mmol, 3.1%)



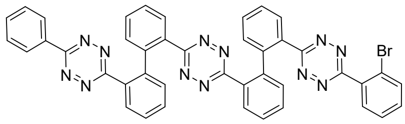
Rf = 0.41 (n-heptane/ethyl acetate = 7/3 (v/v)).

^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = ^1H NMR (500 MHz, $CDCl_3$) δ 8.59 – 8.46 (m, 2H), 8.16 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.06 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.93 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.75 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.70 – 7.49 (m, 10H), 7.42 (td, *J* = 7.7, 1.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 169.9, 165.8, 164.6, 156.5, 155.0, 146.7, 134.6, 134.0, 133.9, 132.8, 132.6, 132.5, 128.2, 124.9, 124.6, 123.1, 122.8, 120.8, 119.9.

HRMS + p ESI (m/z) [$M+H^+$] Calcd for $C_{42}H_{24}Br_2N_{12}$: 855.06864. Found: m/z = 855.06805.

3-[(2-bromophenyl)-6"-phenyl)]-3',6,3",6'-[(1,1',1",1"'-biphenyl)-2,2',2",2"'-diyl]-1,2,4,5-tetrazine 5a', isolated as red solid (0.306 mmol, 4.5%)



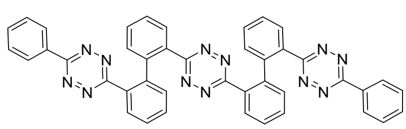
Rf = 0.40 (n-heptane/ethyl acetate = 7/3 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.13-8.08 (m, 1H), 8.00-7.80 (m, 3H), 7.85-7.80 (m, 1H), 7.77-7.67 (m, 3H), 7.63-7.53 (m, 5H), 7.52-7.33 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 165.2, 165.0, 164.8, 164.7, 164.6, 141.4, 141.1, 141.0, 140.8, 134.0, 133.95, 133.8, 133.7, 132.3, 132.2, 132.15, 132.1, 131.9, 131.7, 131.67, 131.53, 131.5, 131.4, 1313, 131.2, 130.74, 130.7, 130.6, 130.5,128.3, 128.2, 128.1, 127.7, 127.6, 122.4.

HRMS + p ESI (m/z) [M+H$^+$] Calcd for $C_{42}H_{26}BrN_{12}$: 777.15813. Found: m/z = 777.15767.

3,6"-[bis(phenyl]-3'6,3"6'-[(1,1',1",1"'-biphenyl)-2,2',2",2"'-diyl]-1,2,4,5-tetrazine 5a" was isolated as a red solid (0.211 mmol, 3.1%)

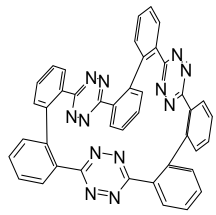


Rf = 0.38 (n-heptane/ethyl acetate = 7/3 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.16 – 8.07 (m, 1H), 7.97 (ddd, J = 9.9, 7.9, 1.4 Hz, 2H), 7.92 (dd, J = 7.8, 1.4 Hz, 1H), 7.83 (dd, J = 7.5, 1.9 Hz, 1H), 7.80 – 7.67 (m, 3H), 7.64 – 7.54 (m, 4H), 7.54 – 7.33 (m, 14H).

HRMS + p ESI (m/z) [M+H$^+$] Calcd for $C_{42}H_{27}N_{12}$: 699.24762. Found: m/z = 699.24719.

3',6,3",6',3,6"-[(1,1',1",1"',1"",1""'-biphenyl)-2,2',2",2"',2"",2""'-diyl]-1,2,4,5-tetrazine 6a, was isolated as a red solid (0.286 mmol, 4.2%)



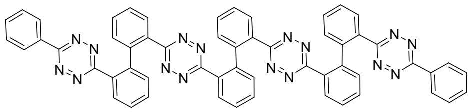
Rf = 0.39 (n-heptane/ethyl acetate = 7/3 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.46 (d, J = 7.4 Hz, 2H), 8.41 (d, J = 7.4 Hz, 2H), 8.08 (dd, J = 7.6, 1.5 Hz, 1H), 8.04 – 7.95 (m, 3H), 7.65 – 7.45 (m, 12H), 7.45 – 7.35 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 166.1, 166.0, 165.2, 164.9, 162.5, 162.4, 141.4, 141.3, 141.2, 141.1, 132.6, 132.5, 132.2, 132.0, 131.9, 131.8, 131.8, 131.6, 131.5, 131.5, 131.4, 131.3, 131.3, 130.8, 130.7, 130.7, 130.5, 129.2, 129.1, 128.4, 128.3, 128.2, 128.1.

HRMS + p ESI (m/z) [M+H$^+$] Calcd for $C_{42}H_{25}N_{12}$: 697.23197. Found: m/z = 697.23157.

3,6''''-[bis(phenyl]-3',6,3'',6',3''',6''-[(1,1',1'',1''',1'''',1'''''-biphenyl)-2,2',2'',2''',2'''',2'''''-diyl]-1,2,4,5-tetrazine 7a'' was isolated as a red solid (0.102 mmol, 1.5%)

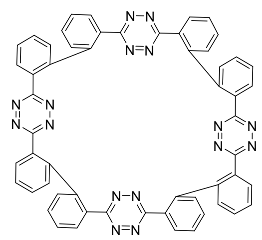


Rf = 0.24 (n-heptane/ethyl acetate = 7/3 (v/v)).

[1]H NMR (500 MHz, CD_2Cl_2): δ (ppm) = 8.59 – 8.36 (m, 2H), 7.99 (dd, J = 7.7, 1.4 Hz, 2H), 7.75 (dd, J = 7.8, 1.5 Hz, 2H), 7.69 – 7.22 (m, 28H).

HRMS + p ESI (m/z) [M+H$^+$] Calcd for $C_{56}H_{35}N_{16}$: 931.3251. Found: m/z = 931.31750.

3',6,3'',6',3''',6'',3,6''''-[(1,1',1'',1'''',1''''',1'''''',1'''''''-biphenyl)-2,2',2'',2''',2'''',2''''',2'''''',2'''''''-diyl]-1,2,4,5-tetrazine 8a, was isolated as a red solid (0.204 mmol, 3%)



Rf = 0.35 (n-heptane/ethyl acetate = 3/7 (v/v)).

[1]H NMR (500 MHz, CD_2Cl_2): δ (ppm) = 8.17 (dd, J = 7.9, 1.4 Hz, 6H), 7.54 (td, J = 7.7, 1.4 Hz, 10H), 7.46 (td, J = 7.5, 1.5 Hz, 10H), 7.25 (dd, J = 7.6, 1.3 Hz, 6H).

[13]C NMR (126 MHz, CD_2Cl_2): δ (ppm) = 163.7, 141.4, 132.1, 131.8, 130.9, 130.1, 128.3.

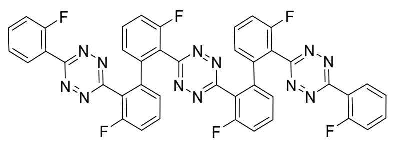
HRMS + p ESI (m/z) [M+H$^+$] Calcd for $C_{56}H_{33}N_{16}$: 929.30686. Found: m/z = 929.30177.

General procedure for copper-catalyzed homocoupling reaction with 2b

To a dried Schlenk tube were added 3,6-bis(2-bromo-6-fluorophenyl)-1,2,4,5-tetrazine **2b** (0.434 g, 1.02 mmol, 1.0 equiv), $Cu(acac)_2$ (0.053 g, 0.204 mmol, 20 mol%), 1.4-hydroquinone (0.056 g, 0.51 mmol, 0.5 equiv.) and K_2CO_3 (0.704 g, 5.09 mmol, 5 equiv.). After 3 standard cycles of evacuating and back-filling with argon, toluene (5 mL, 0.2 M) was added. The reaction mixture was stirred and heated at 90 °C for 16 hours. After allowing the reaction to cool to room temperature, the resulting mixture was diluted water and extracted with dichloromethane. The combined organic layer was dried over anhydrous $MgSO_4$, filtrated and the solvent was evaporated under reduced pressure. The Linear and cyclized oligomers were purified by silica gel column chromatography (eluent: heptane/ dichloromethane and heptane/ Ethyl acetate by gradient). Note that, the bis(tetrazine) intermediates type **3b**, **4b** and **4b'** described in the previous section will not be described in this section. Only compounds **5b''**, **6b**, **7b''** and **8b**, having a minimum of three *s*-

tetrazines units are described in this part.

3,6"bis[2,2'-fluorophenyl]-3'6,3"6'-[bis(2,2'-fluorophenyl)-(1,1',1",1"'-biphenyl)-2,2',2",2"'-diyl]-1,2,4,5-tetrazine 5b", was isolated as a orange-red solid (0.122 mmol, 3%)



Rf = 0.06 (n-heptane/ethyl acetate = 7/3 (v/v)).

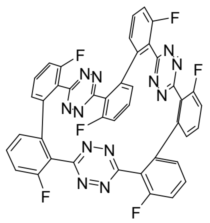
^{1}H NMR (500 MHz, CD_2Cl_2): 7.59 (td, J = 8.1, 5.5 Hz, 2H), 7.49 (m, 4H), 7.33 (ddd, J = 9.8, 8.4, 1.1 Hz, 2H), 7.27 (td, J = 7.2, 4.7 Hz, 6H), 7.18 (ddd, J = 9.8, 8.5, 1.3 Hz, 4H).

^{19}F NMR (470 MHz, CD_2Cl_2): δ (ppm) = -113.49 (bs, 2F), -114.7 (bs, 2F), -116.24 (2t, 6.0, 2F).

^{13}C NMR (126 MHz, CD_2Cl_2): δ (ppm) = 161.8 (d, J = 4.6 Hz), 161.7, 161.3 (d, J = 255.8 Hz), 160.5 (d, J = 257.0 Hz), 159.8, 159.6 (d, J = 4.5 Hz), 141.5 (d, J = 2.5 Hz), 141.37, 141.2 (d, J = 2.5 Hz), 132.7, 132.6 (d, J = 2.2 Hz), 132.5, 132.2 (d, J = 10.0 Hz), 129.3 (d, J = 3.3 Hz), 128.7 (d, J = 3.2 Hz), 128.4 (d, J = 3.4 Hz), 120.9 (d, J = 12.9 Hz), 119.8 (d, J = 11.6 Hz), 119.6 (d, J = 12.0 Hz), 117.2 (d, J = 22.6 Hz), 116.5, 116.3, 116.2.

HRMS + p ESI (m/z) [M+H$^+$] Calcd for $C_{42}H_{21}F_6N_{12}$: 807.19108. Found: m/z = 807.19036.

3',6,3",6',3,6"-[bis(2,2'-fluorophenyl)-(1,1',1",1"',1"",1""'-biphenyl)-2,2',2",2"',2"",2""'-diyl]-1,2,4,5-tetrazine 6b, isolated as red solid (0.041 mmol, 4%)



Rf = 0.07 (n-heptane/ethyl acetate = 7/3 (v/v)).

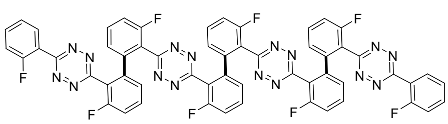
^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) = 7.99 – 7.51 (m, 6H), 7.52 – 7.04 (m, 12H).

^{19}F NMR (470 MHz, CD_2Cl_2): δ (ppm) = -114.15 (dd, J = 10.2, 5.4 Hz, 6F).

^{13}C NMR (126 MHz, CD_2Cl_2): δ (ppm) = 161.6 (d, J = 3.8 Hz), 161.3 (d, J = 257.1 Hz), 142.3, 132.9 (d, J = 9.6 Hz), 128.3 (d, J = 3.2 Hz), 120.1 (d, J = 12.0 Hz), 116.8 (d, J = 22.1 Hz).

HRMS + p ESI (m/z) [M+H$^+$] Calcd for $C_{42}H_{19}F_6N_{12}$: 805.17543. Found: m/z = 805.17682.

3,6"bis[2,2'-fluorophenyl]-3',6,3",6',3"',6"-[bis(2,2'-fluorophenyl)-(1,1',1",1"',1"",1""'-biphenyl)-2,2',2",2"',2"",2""'-diyl]-1,2,4,5-tetrazine 7b", isolated as pale red solid (0.021 mmol, 2.1%)



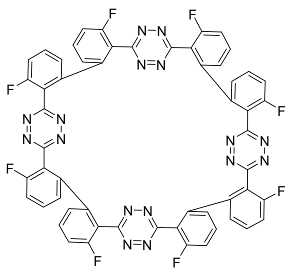
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.54 (td, J = 8.1, 5.4 Hz, 3H), 7.43 (m, 5H), 7.34 – 7.18 (m, 13H), 7.16 – 7.11 (m, 5H).

^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = -109.46 – -112.14 (m), -113.14, -114.22 – -115.05 (m).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 162.9 (d, J = 5.1 Hz), 162.8, 161.9 (d, J = 284.8 Hz), 160.8 (d, J = 255.0 Hz), 141.1, 134.4 (d, J = 8.7 Hz), 132.8 (d, J = 9.3 Hz), 132.0, 127.7 (d, J = 3.4 Hz), 124.9 (d, J = 3.9 Hz), 121.2 (d, J = 13.9 Hz), 120.6 (d, J = 9.9 Hz), 117.5 (d, J = 21.3 Hz), 116.4 (d, J = 21.7 Hz).

HRMS + p ESI (m/z) [M+Na$^+$] Calcd for $C_{56}H_{24}F_8N_{16}Na$: 1097.22963. Found: m/z = 1099.24493.

3',6,3'',6',3''',6'',3,6'''-[bis(2,2'-fluorophenyl)-(1,1',1'',1'',1'''',1''''',1'''''',1'''''''-biphenyl)-2,2',2'',2''',2'''',2''''',2'''''',2'''''''-diyl]-1,2,4,5-tetrazine 8b, was isolated as a red-orange solid (0.026 mmol, 2.5%)



Rf = 0.74 (n-heptane/ethyl acetate = 3/7 (v/v)).

^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) = 8.27 (m, 2H), 7.80 – 7.56 (m, 5H), 7.55 – 7.46 (m, 4H), 7.40 – 7.15 (m, 13H).

^{19}F NMR (470 MHz, CD_2Cl_2): δ (ppm) = -110.79, -112.55, -113.77 – -115.30 (m).

HRMS + p ESI (m/z) [M+Na$^+$] Calcd for $C_{56}H_{24}F_8N_{16}Na$: 1095.21343. Found: m/z = 1095.21343.

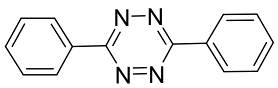
Oligomer monitoring by molecular weight using ECC-DOSY NMR

Each NMR tube contained about 10.0 mg of tetrazine and 0.6 ml of CD_2Cl_2. ^{1}H DOSY experiments were performed on a Bruker Avance III HD 600 spectrometer equipped with an ATMA 5 mm BBOF N_2 cryoprobe with a z-axis gradient coil operating at 600.13 MHz (^{1}H). The maximum gradient strength was 65.8 G/cm. Spectra were acquired in 5 mm NMR tubes and all experiments were recorded without spinning to avoid convection.

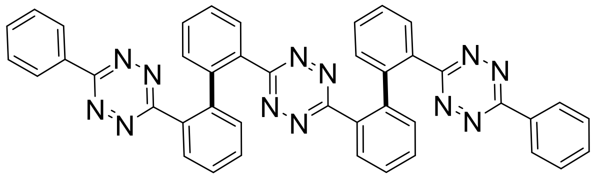
All DOSY experiments were performed using a double stimulated echo sequence with bipolar gradient pulses and three spoil gradients with convection compensation (dstebpgp3s). The diffusion time was 0.1 s (Δ). The duration of the magnetic field pulse gradients was adjusted for each tetrazine in a range of 500-1000 μs (δ/2). The delay for gradient recovery was 0.2 ms and the eddy current delay 5 ms. For each DOSY-NMR experiment, a series of 16 spectra with 16 scans on 32 K data points were collected. The pulse gradients were incremented from 2 to 98% of the maximum gradient strength in a linear ramp with a total experiment time of 23 min. The temperature was set and controlled at 298 K with an air flow of 400 l/h in order to avoid any temperature fluctuations due to sample heating during the magnetic field pulse gradients. After Fourier transformation and baseline correction, the diffusion dimension was processed with the Topspin 3.6.1 software and Dynamic Center 2.4.4.

Non-fluorinated compounds: 1a, 3a, 5a'' and 7a''

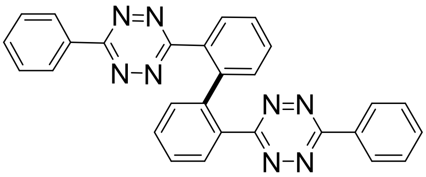
1a



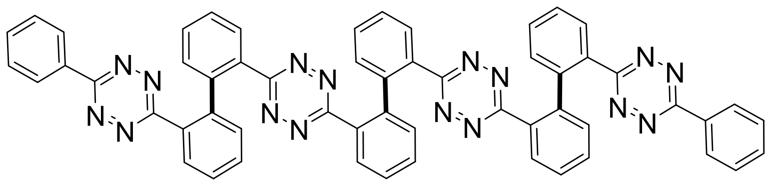
5a''



3a



7a''



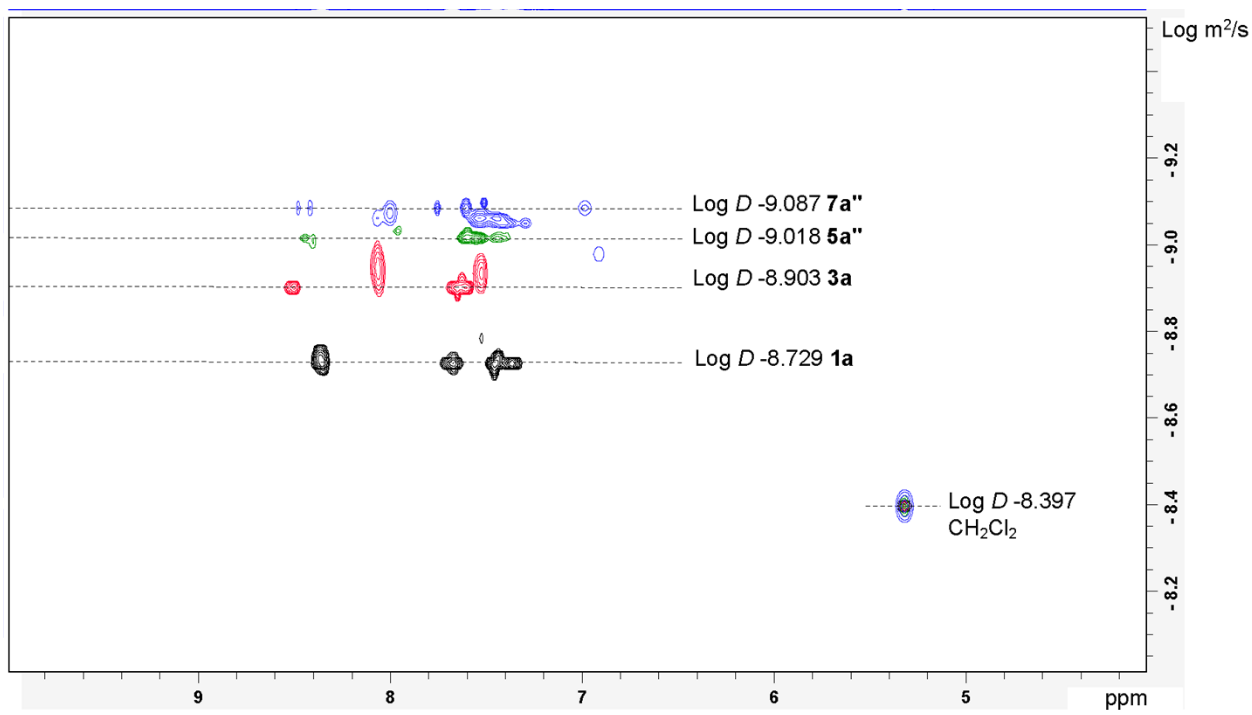


Figure S5. ^{1}H DOSY NMR spectrum of **1a**, **3a**, **5a''** and **7a''** and CH_2Cl_2. The spots represent resonance frequencies of each compound in the mixture; the associated values represent the log of the diffusion coefficient D of the compounds.

Table S3. Parameters of non-fluorinated compounds: diffusion coefficients and molecular weights (MW).

	$MW/g.mol^{-1}$	$log(M/g.mol^{-1})$	$log(D/\ m^2.s^{-1})$	$D/m^2.s^{-1}$
CH_2Cl_2	84.9	1.92890769	-8.397	$4.00867E^{-09}$
$C_{14}H_{10}N_{4,}$ **1a**	234	2.369215857	-8.729	$1.86638E^{-09}$
$C_{28}H_{18}N_8$, **3a**	466	2.668385917	-8.903	$1.25026E^{-09}$
$C_{42}H_{26}N_{12,}$ linear **5a''**	698	2.843855423	-9.018	$9.59401E^{-10}$
$C_{56}H_{34}N_{16}$ linear **7a''**	930	2.968482949	-9.087	$8.18465E^{-10}$

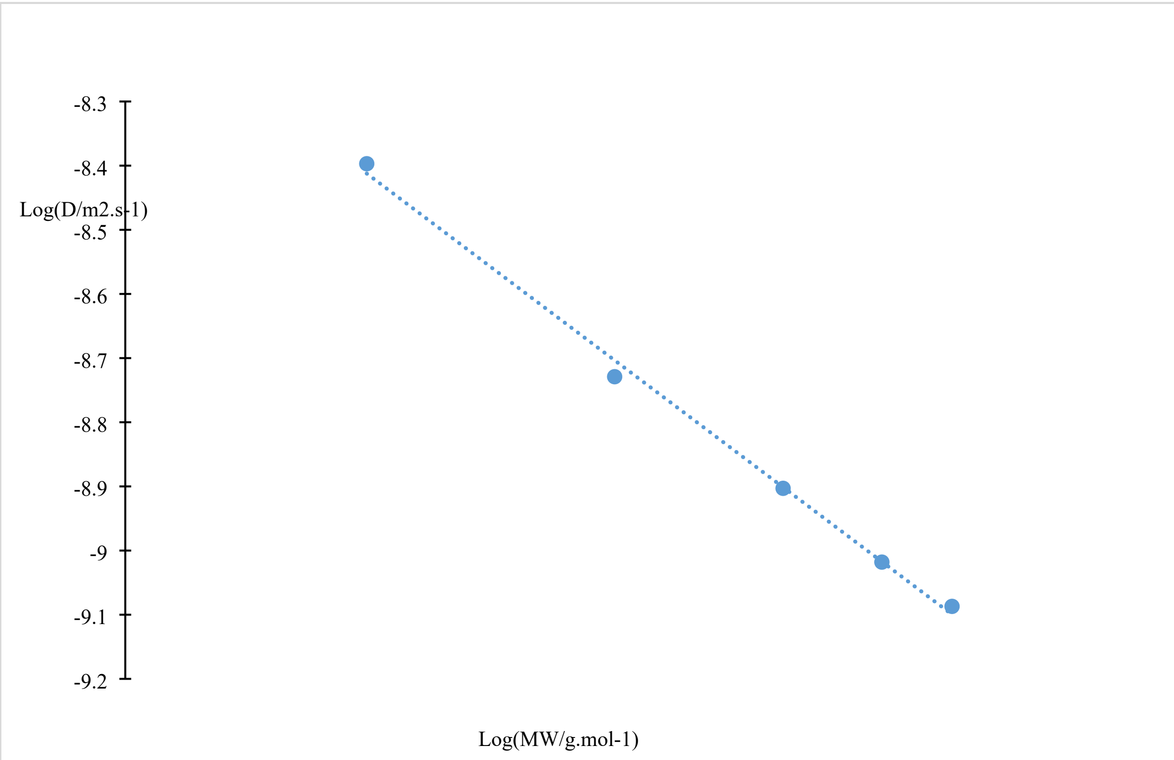
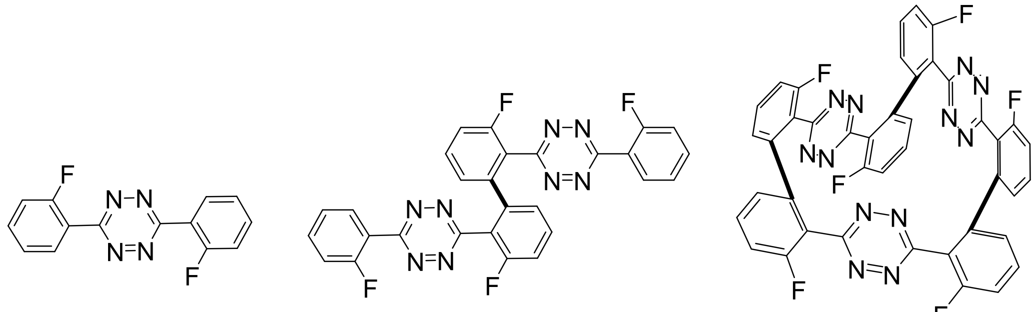


Figure S6. Plot of log(D) *vs.* log(MW) of **1a**, **3a**, **5a''** and **7a''** non-fluorinated poly(aryl)-tetrazines compounds in CH_2Cl_2.

Fluorinated compounds: 1b, 3b and 6b



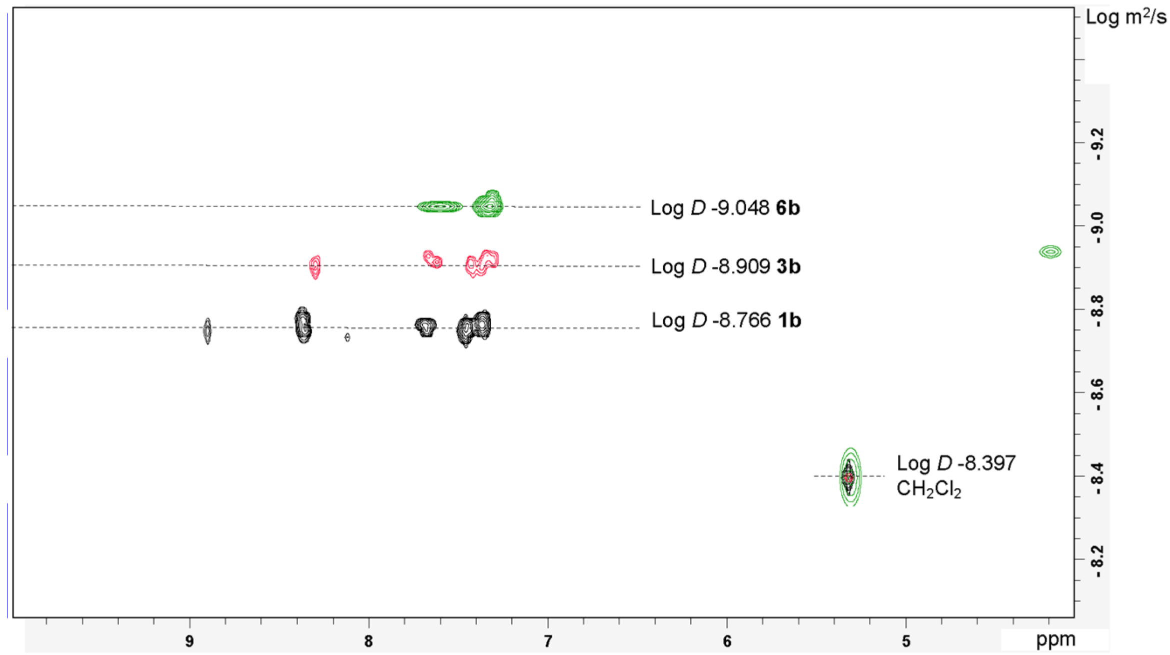


Figure S7. [1]H DOSY NMR spectrum of fluorinated **1b, 3b and 6b** and CH_2Cl_2. The spots represent resonance frequencies of each compound in the mixture; the associated values represent the log of the diffusion coefficient D of the compounds.

Table S4. Overview of the parameters of compounds in non-fluorinated version: diffusion coefficients and molecular weights (MW).

	MW/g.mol^{-1}	log(M/g.mol^{-1})	log(D/ m^2.s^{-1})	D/m^2.s^{-1}
CH_2Cl_2	84.9	1.92890769	-8.397	4.0087E^{-09}
$C_{14}H_8F_2N_4$, **1b**	270	2.43136376	-8.766	1.714E^{-09}
$C_{28}H_{14}F_4N_8$, **3b**	538	2.73078228	-8.909	1.2331E^{-09}
$C_{42}H_{18}F_6N_{12}$, cyclized **6b**	804	2.90525605	-9.048	8.9536E^{-10}

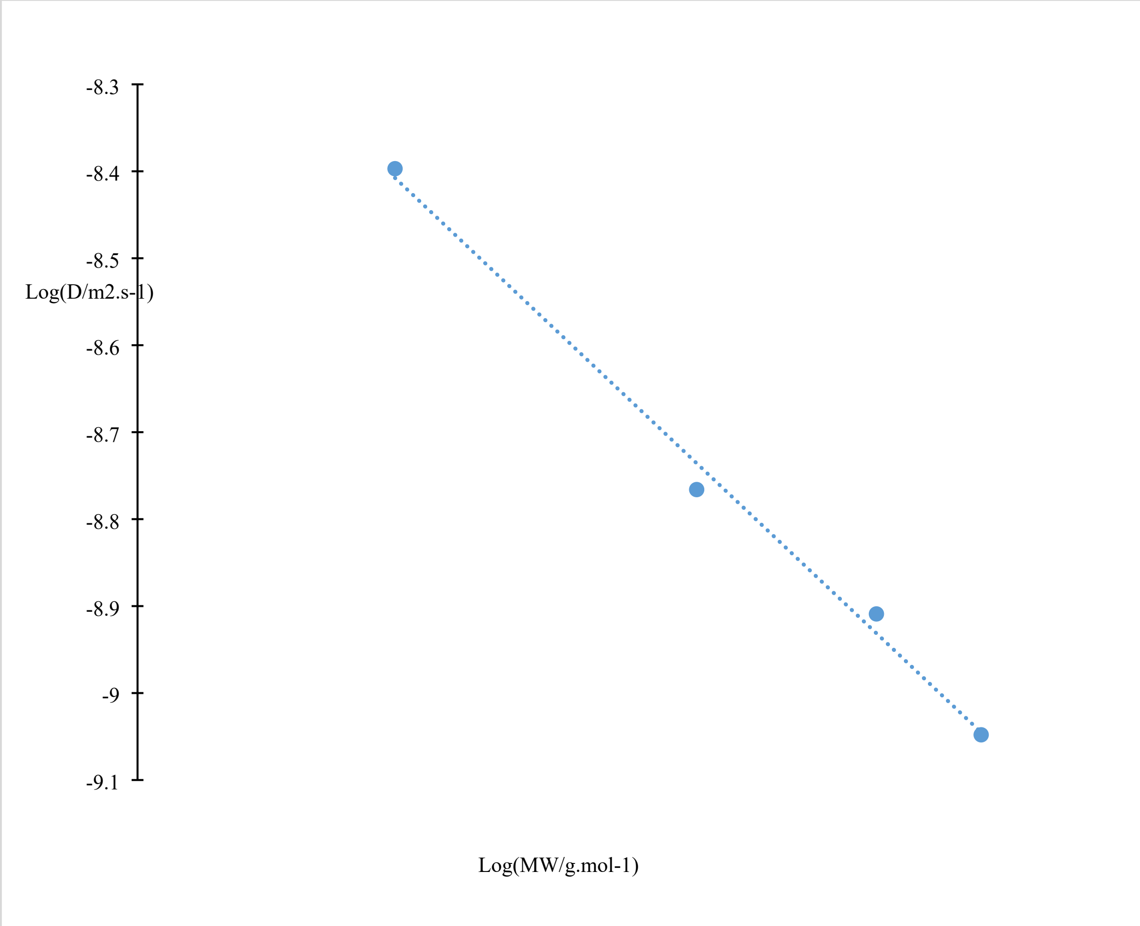


Figure S8. Plot of log(D) versus log(MW) of fluorinated **1b, 3b and 6b** compounds and CH_2Cl_2.

Compilated data

Table S5. Compiled correlated DOSY parameters diffusion coefficients (D) and molecular weights (MW).

Compound	MW/g.mol^{-1}	log(M/g.mol^{-1})	Log(D/ m^2.s^{-1})	D/m^2.s^{-1}
CH_2Cl_2	84.9	1.92890769	-8.397	4.00867E^{-09}
$C_{14}H_{10}N_4$ (**1a**)	234	2.369215857	-8.729	1.86638E^{-09}
$C_{14}H_8F_2N_4$ (**1b**)	270	2.431363764	-8.766	1.71396E^{-09}
$C_{28}H_{18}N_8$ **(3a)**	466	2.668385917	-8.903	1.25026E^{-09}
$C_{28}H_{14}F_4N_8$ **(3b)**	538	2.730782276	-8.909	1.2331E^{-09}
$C_{42}H_{26}N_{12}$ linear **(5a'')**	698	2.843855423	-9.018	9.59401E^{-10}
$C_{42}H_{18}F_6N_{12}$ cyclized (**6b**)	804	2.905256049	-9.048	8.95365E^{-10}
$C_{56}H_{34}N_{16}$ linear (**7a''**)	930	2.968482949	-9.087	8.18465E^{-10}

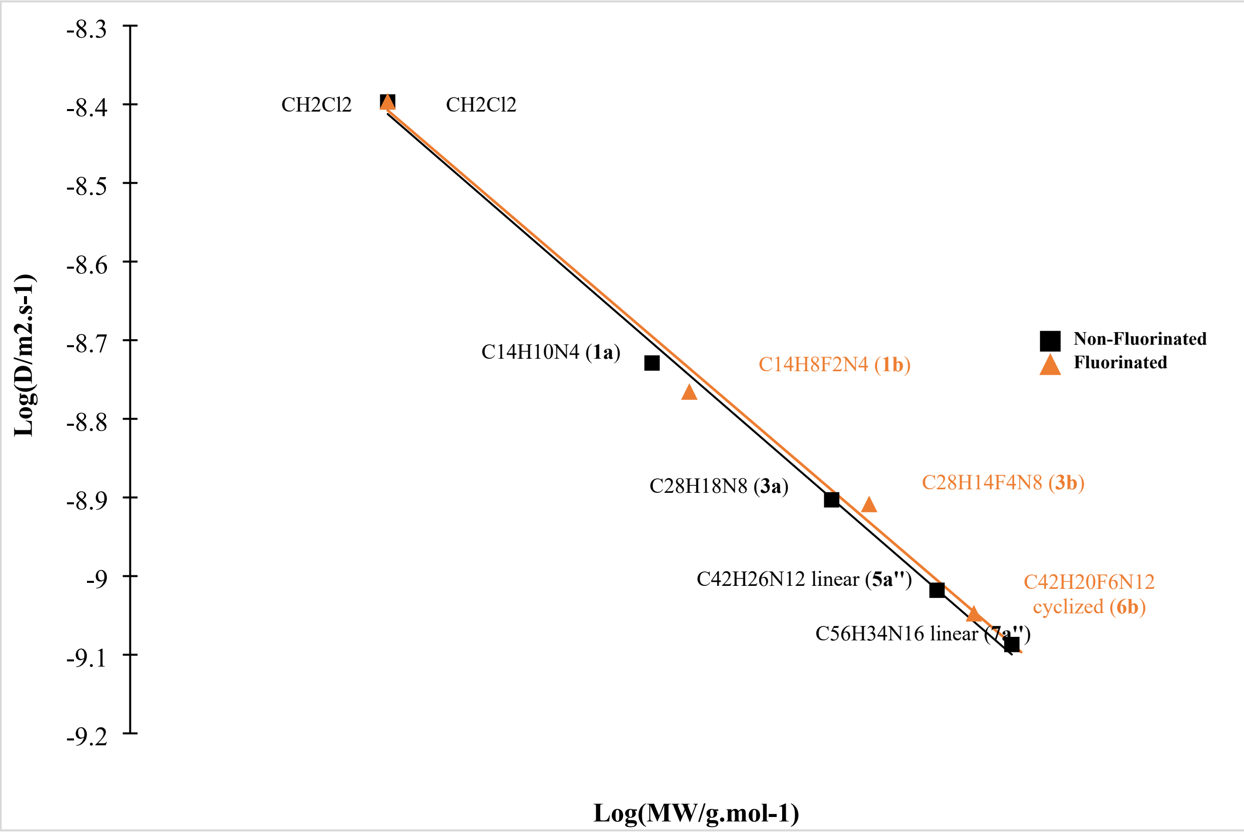


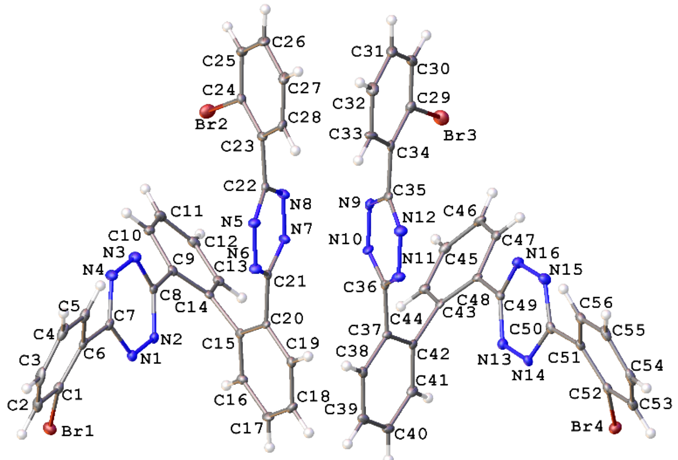
Figure S9. Compiled plot of log(D) versus log(MW) DOSY data.

Crystal data and structures analysis

Compound 4a

Report created with ReportPlus

R_1=2.94%



Experimental. Single clear light pink prism-shaped crystals of **4a** crystallized from a mixture of DCM and heptane by slow evaporation. A suitable crystal with dimensions 0.30 × 0.20 × 0.15 mm^3 was selected and mounted on a mylar loop with oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 115 K during data collection. The structure was solved with the **ShelXT** 2018/2 (Sheldrick, 2018) solution program using dual methods and by using **Olex2** 1.3 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on $\boldsymbol{F^2}$.

Crystal Data. $C_{28}H_{16}Br_2N_8$, M_r = 624.31, orthorhombic, $Pna2_1$ (No. 33), a = 14.2290(4) Å, b = 12.9685(4) Å, c = 26.3149(7) Å, $\alpha = \beta = \gamma$ = 90°, V = 4855.9(2) Å^3, T = 115 K, Z = 8, Z' = 2, μ(Mo K$_\alpha$) = 3.376, 120960 reflections measured, 11131 unique (R_{int} = 0.0539) which were used in all calculations. The final wR_2 was 0.0596 (all data) and R_1 was 0.0294 (I≥2 σ(I)).

Compound	**4a**
CCDC	
Formula	$C_{28}H_{16}Br_2N_8$
$D_{calc.}$/ g cm^{-3}	1.708
μ/mm^{-1}	3.376
Formula Weight	624.31
Colour	clear light pink
Shape	prism-shaped
Size/mm^3	0.30×0.20×0.15
T/K	115
Crystal System	orthorhombic
Flack Parameter	0.268(7)
Hooft Parameter	0.275(2)
Space Group	$Pna2_1$
a/Å	14.2290(4)
b/Å	12.9685(4)
c/Å	26.3149(7)
α/°	90
β/°	90
γ/°	90
V/Å^3	4855.9(2)
Z	8
Z'	2
Wavelength/Å	0.71073
Radiation type	Mo K$_\alpha$
Θ_{min}/°	2.629
Θ_{max}/°	27.505
Measured Refl's.	120960
Indep't Refl's	11131
Refl's I≥2 σ(I)	9206
R_{int}	0.0539
Parameters	686
Restraints	1
Largest Peak	0.716
Deepest Hole	-0.504
GooF	1.018
wR_2 (all data)	0.0596
wR_2	0.0548
R_1 (all data)	0.0467
R_1	0.0294

A clear light pink prism-shaped-shaped crystal with dimensions 0.30 × 0.20 × 0.15 mm^3 was mounted on a mylar loop with oil. Data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 115 K. Data were measured using ϕ and ω scans using Mo K_α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program APEX3 (Bruker, 2020). The maximum resolution that was achieved was Θ = 27.505° (0.77 Å).

The unit cell was refined using SAINT V8.40B (Bruker, 2016) on 9997 reflections, 8% of the observed reflections. Data reduction, scaling and absorption corrections were performed using SAINT V8.40B (Bruker, 2016). The final completeness is 99.90 % out to 27.505° in Θ. SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. wR_2(int) was 0.0892 before and 0.0495 after correction. The Ratio of minimum to maximum transmission is 0.7206. The $\lambda/2$ correction factor is Not present. The absorption coefficient μ of this material is 3.376 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.537 and 0.746.

The structure was solved and the space group $Pna2_1$ (# 33) determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using using dual methods and refined by full matrix least squares minimisation on $\boldsymbol{F^2}$ using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. It was refined as a 2-component inversion twin. The value of Z' is 2: this means that there are two independent molecules in the asymmetric unit. TWIN/BASF refinement type was used to determine absolute configuration from anomalous scattering using the Flack method. (Flack, 1983). The structure display a merohedral twinning and the twin law was found by using TwinRotMat implemented in Platon (Spek, 2009). The use of twin law (-1 0 0 0 -1 0 0 0 -1) with a population of 0.732(7)/0.268(7) reduced the R1 (for I > 2sigma(I)) from 3.25% to 2.94%. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

Table CD1: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Br1	5332.7(3)	9540.4(4)	7942.9(2)	24.27(11)
Br2	7112.0(3)	2945.7(4)	6217.9(2)	28.34(12)
C1	4288(3)	8645(3)	7861.0(16)	18.5(10)
C2	3458(3)	8953(4)	8094.4(17)	25.7(11)
C3	2675(3)	8339(5)	8074.7(18)	29.1(13)
C4	2708(4)	7399(4)	7830(2)	27.5(14)
C5	3527(3)	7088(4)	7587.6(18)	21.8(10)
C6	4334(3)	7715(4)	7595.0(18)	17.7(10)
C7	5156(4)	7348(4)	7305(2)	17.6(11)
C8	6615(3)	6677(3)	6815.1(16)	14.5(9)
C9	7515(3)	6324(3)	6598.2(16)	15.4(9)
C10	7958(3)	5480(3)	6829.6(17)	20.2(10)
C11	8871(3)	5220(4)	6698.2(18)	21.7(10)
C12	9353(3)	5807(3)	6344.5(17)	20.8(10)
C13	8907(3)	6614(3)	6098.9(17)	17.0(10)
C14	7977(3)	6866(3)	6212.0(16)	15.0(9)
C15	7502(3)	7680(3)	5907.0(17)	13.5(9)
C16	7870(3)	8670(3)	5884.1(16)	16.7(9)
C17	7392(4)	9447(4)	5625.7(18)	20.5(10)
C18	6550(3)	9232(4)	5388.2(18)	19.5(10)
C19	6187(3)	8251(3)	5393.6(17)	15.7(10)
C20	6660(3)	7465(3)	5645(2)	12.6(11)
C21	6295(3)	6393(3)	5624.5(16)	13.0(9)
C22	5724(3)	4518(3)	5646.1(16)	14.2(9)

Atom	x	y	z	U_{eq}
C23	5416(3)	3429(3)	5674.6(18)	15.5(10)
C24	5967(3)	2644(4)	5877.3(19)	17.3(11)
C25	5665(4)	1634(4)	5870.2(18)	21.8(11)
C26	4803(4)	1387(4)	5651.7(18)	25.9(12)
C27	4234(4)	2156(4)	5457.9(18)	23.3(11)
C28	4543(3)	3170(4)	5475.2(17)	19.2(10)
N1	5702(2)	8041(3)	7064.3(14)	16.8(8)
N2	6453(3)	7700(3)	6819.4(15)	15.7(8)
N3	6022(2)	5966(3)	7012.8(15)	20.0(8)
N4	5284(3)	6314(3)	7271.3(15)	21.3(9)
N5	5106(3)	5248(3)	5776.5(15)	18.4(8)
N6	5403(2)	6231(3)	5765.8(15)	17.8(9)
N7	6877(3)	5668(3)	5435.8(15)	17.8(9)
N8	6578(3)	4702(3)	5445.4(15)	20.0(9)
Br3	4683.7(3)	3061.0(4)	3814.0(2)	30.31(13)
Br4	2875.3(3)	9621.1(4)	2070.8(2)	23.18(11)
C29	3532(3)	2781(4)	4148.5(19)	20.0(11)
C30	3196(4)	1781(4)	4134.1(19)	25.6(11)
C31	2344(4)	1550(4)	4354.2(19)	26.8(12)
C32	1803(4)	2318(4)	4573(2)	26.5(12)
C33	2106(4)	3313(4)	4585.5(19)	23.9(11)
C34	3006(3)	3571(4)	4370.2(17)	16.8(10)
C35	3318(3)	4657(3)	4399.6(16)	16.1(9)
C36	3843(3)	6550(3)	4441.1(17)	14.3(9)
C37	4174(3)	7629(3)	4420(2)	13.4(10)
C38	3695(3)	8391(3)	4686.8(17)	17.3(10)
C39	4026(3)	9396(4)	4683.0(19)	21.1(11)
C40	4840(4)	9637(4)	4414.6(19)	23.0(11)
C41	5319(3)	8876(3)	4149.1(16)	18.5(9)
C42	4990(3)	7868(3)	4137.5(16)	15.3(9)
C43	5476(3)	7039(3)	3845.5(17)	14.8(9)
C44	6383(3)	6755(3)	3986.0(17)	17.7(10)
C45	6820(3)	5918(3)	3758.8(17)	20.1(10)
C46	6354(3)	5332(4)	3399.5(18)	22.0(10)
C47	5455(3)	5612(3)	3245.5(17)	17.9(9)
C48	5017(3)	6474(3)	3456.3(16)	13.8(9)
C49	4116(3)	6825(3)	3235.3(17)	14.8(10)
C50	2676(4)	7468(3)	2735(2)	15.9(11)
C51	1850(3)	7817(4)	2438.2(17)	16.4(10)
C52	1818(3)	8749(3)	2160.7(16)	18.3(10)
C53	1000(3)	9057(4)	1914.9(17)	23.5(11)
C54	203(3)	8444(4)	1943.6(17)	26.3(12)
C55	227(4)	7516(4)	2196(2)	23.4(13)
C56	1039(3)	7209(4)	2445.4(17)	19.1(10)
N9	4189(3)	4852(3)	4581.5(13)	18.0(8)
N10	4462(3)	5825(3)	4601.9(14)	18.2(9)
N11	2954(3)	6354(3)	4309.2(15)	19.7(9)
N12	2684(3)	5370(3)	4286.4(15)	20.7(9)
N13	3956(3)	7850(3)	3218.6(15)	17.2(9)
N14	3209(2)	8182(3)	2967.1(14)	15.1(8)
N15	2792(3)	6444(3)	2786.4(15)	20.5(9)
N16	3523(3)	6115(3)	3050.6(14)	19.3(8)

Table CD2: Anisotropic Displacement Parameters (×10^4) for **4a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	24.6(3)	22.9(3)	25.4(3)	-4.3(2)	3.1(2)	-2.6(2)
Br2	19.3(2)	28.6(3)	37.1(3)	3.8(2)	-7.1(2)	2.3(2)
C1	17(2)	22(2)	17(2)	4.8(19)	-2.0(18)	-0.9(18)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C2	25(3)	36(3)	16(2)	3(2)	3(2)	7(2)
C3	16(2)	55(4)	16(2)	11(2)	7.1(19)	6(2)
C4	16(3)	45(3)	21(4)	16(2)	-2(3)	-4(2)
C5	19(2)	29(3)	17(2)	7(2)	-2.4(19)	-1(2)
C6	18(3)	22(2)	13(2)	7(2)	-2.3(19)	-1(2)
C7	18(3)	22(3)	13(3)	5.6(19)	-4(2)	-4(2)
C8	18(2)	16(2)	10(2)	0.2(18)	-3.7(17)	1.5(18)
C9	15(2)	17(2)	14(2)	-3.3(18)	-3.3(17)	-1.9(18)
C10	28(3)	15(2)	18(2)	-0.6(18)	-3(2)	-1(2)
C11	26(2)	19(2)	21(2)	-3.1(19)	-8(2)	6.7(19)
C12	17(2)	21(2)	24(2)	-8(2)	-5.0(19)	3.5(19)
C13	17(2)	16(2)	19(2)	-2.8(17)	-0.7(18)	-3.6(19)
C14	19(2)	12(2)	14(2)	-3.4(18)	-2.8(19)	-2.9(17)
C15	14(2)	15(2)	12(2)	0.4(18)	5.5(18)	-0.5(18)
C16	17(2)	15(2)	18(2)	-1.4(18)	2.4(18)	-1.1(18)
C17	27(3)	13(2)	22(2)	1.2(19)	5(2)	-7.3(19)
C18	24(3)	16(2)	18(2)	6.0(19)	1(2)	3(2)
C19	17(2)	17(2)	13(2)	-0.9(18)	1.2(18)	-0.5(19)
C20	17(3)	11(2)	11(3)	1.2(16)	2(2)	-1.1(17)
C21	15(2)	14(2)	10(2)	-0.5(17)	-3.3(17)	-1.1(17)
C22	17(2)	16(2)	10(2)	-0.2(17)	-1.9(17)	-0.8(18)
C23	19(2)	12(2)	15(2)	-0.7(18)	5.0(19)	-0.9(18)
C24	19(3)	19(3)	13(3)	-2.0(19)	-3(2)	-2(2)
C25	33(3)	14(2)	18(3)	0.1(19)	0(2)	4(2)
C26	42(3)	14(2)	22(3)	2(2)	0(2)	-7(2)
C27	31(3)	21(3)	18(3)	2(2)	-2(2)	-9(2)
C28	23(3)	21(3)	13(2)	3.9(19)	-5.3(19)	-1(2)
N1	16.8(19)	18(2)	14.9(18)	-0.1(17)	-0.6(16)	-0.6(15)
N2	17(2)	18(2)	12(2)	1.2(16)	0.3(16)	1.6(17)
N3	21(2)	16(2)	23(2)	0.2(17)	3.0(18)	-3.8(16)
N4	24(2)	17(2)	23(2)	-0.1(17)	5.2(17)	-3.6(17)
N5	18.9(19)	14(2)	23(2)	0.6(16)	0.3(17)	-2.1(16)
N6	13.7(19)	15(2)	24(2)	0.1(16)	-0.1(16)	-3.8(15)
N7	22(2)	13(2)	19(2)	-2.3(16)	5.8(17)	-1.8(17)
N8	22(2)	15(2)	23(2)	-3.7(16)	5.7(17)	-2.8(16)
Br3	22.7(3)	33.0(3)	35.2(3)	-4.1(3)	6.4(2)	4.8(2)
Br4	24.7(2)	21.4(2)	23.4(2)	3.1(2)	-2.4(2)	-2.58(19)
C29	21(3)	22(3)	17(3)	4(2)	-2(2)	2(2)
C30	40(3)	18(3)	19(3)	-4(2)	-6(2)	5(2)
C31	43(3)	19(3)	19(3)	1(2)	-4(2)	-8(2)
C32	29(3)	26(3)	25(3)	0(2)	3(2)	-10(2)
C33	35(3)	11(2)	26(3)	-2(2)	-13(2)	1(2)
C34	23(2)	18(2)	10(2)	0.4(18)	-2.1(19)	-0.6(19)
C35	23(2)	14(2)	12(2)	1.3(18)	3.4(18)	-2.5(19)
C36	18(2)	15(2)	10(2)	-0.4(18)	2.0(18)	1.1(18)
C37	14(2)	12(2)	14(3)	1.8(17)	-4(2)	-0.4(17)
C38	20(2)	18(2)	14(2)	-1.0(18)	-3.2(19)	2.6(19)
C39	25(3)	17(2)	21(2)	-2.5(19)	-8(2)	5(2)
C40	32(3)	13(2)	24(3)	0(2)	-12(2)	-3(2)
C41	18(2)	19(2)	18(2)	3.3(18)	-6(2)	-5.8(19)
C42	20(2)	14(2)	11(2)	2.6(19)	-5.8(18)	-1(2)
C43	16(2)	15(2)	13(2)	5.3(18)	2.2(19)	-4.0(17)
C44	19(2)	14(2)	19(2)	2.6(18)	-0.8(18)	-1.4(18)
C45	15(2)	22(2)	23(2)	8(2)	-0.6(19)	-1.4(18)
C46	26(3)	17(2)	24(2)	7(2)	5(2)	6(2)
C47	22(2)	17(2)	15(2)	2.9(18)	1.4(19)	-1.3(19)
C48	16(2)	10(2)	15(2)	3.5(17)	1.6(17)	-2.3(17)
C49	17(2)	14(2)	13(2)	-1.6(18)	1.2(18)	-1.9(18)
C50	13(2)	21(3)	13(3)	-3.2(18)	2(2)	-1.0(18)
C51	17(2)	18(2)	14(2)	-4(2)	-2.3(19)	3(2)
C52	20(2)	22(2)	14(2)	-4.9(18)	-0.8(18)	1.2(19)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C53	29(3)	25(3)	16(2)	-4.7(19)	-4(2)	8(2)
C54	20(3)	41(3)	18(2)	-13(2)	-4.3(19)	7(2)
C55	19(3)	33(3)	18(3)	-10(2)	0(2)	-4(2)
C56	20(3)	21(3)	16(2)	-4.7(19)	3.3(19)	-5(2)
N9	22(2)	19(2)	13.7(19)	3.0(15)	-1.6(16)	-0.5(16)
N10	24(2)	13.1(19)	17(2)	4.5(16)	0.2(17)	-5.6(17)
N11	18(2)	14(2)	26(2)	1.8(16)	3.4(16)	-0.8(16)
N12	18.3(19)	17(2)	26(2)	1.1(17)	1.4(17)	-2.8(17)
N13	17(2)	19(2)	16(2)	0.5(18)	-1.6(16)	-1.0(18)
N14	15.0(18)	17.2(19)	13.3(18)	-3.0(16)	-1.6(16)	0.7(15)
N15	18(2)	20(2)	23(2)	-3.2(17)	-3.8(16)	0.8(17)
N16	19.6(19)	18(2)	20(2)	0.4(16)	-3.0(16)	0.3(16)

Table CD3: Bond Lengths in Å for **4a**.

Atom	Atom	Length/Å
Br1	C1	1.899(4)
Br2	C24	1.901(5)
C1	C2	1.389(6)
C1	C6	1.396(7)
C2	C3	1.370(7)
C3	C4	1.379(8)
C4	C5	1.388(7)
C5	C6	1.408(7)
C6	C7	1.476(7)
C7	N1	1.346(6)
C7	N4	1.355(6)
C8	C9	1.474(6)
C8	N2	1.346(6)
C8	N3	1.354(6)
C9	C10	1.402(6)
C9	C14	1.400(6)
C10	C11	1.386(6)
C11	C12	1.383(7)
C12	C13	1.384(6)
C13	C14	1.395(6)
C14	C15	1.489(6)
C15	C16	1.388(6)
C15	C20	1.409(7)
C16	C17	1.393(6)
C17	C18	1.380(7)
C18	C19	1.374(6)
C19	C20	1.390(6)
C20	C21	1.486(6)
C21	N6	1.339(5)
C21	N7	1.347(6)
C22	C23	1.481(6)
C22	N5	1.337(6)
C22	N8	1.346(6)
C23	C24	1.391(7)
C23	C28	1.390(6)
C24	C25	1.379(6)
C25	C26	1.391(7)
C26	C27	1.383(7)
C27	C28	1.386(7)
N1	N2	1.324(5)
N3	N4	1.331(5)
N5	N6	1.343(5)
N7	N8	1.324(5)

Atom	Atom	Length/Å
Br3	C29	1.895(5)
Br4	C52	1.897(5)
C29	C30	1.383(7)
C29	C34	1.397(7)
C30	C31	1.377(7)
C31	C32	1.384(7)
C32	C33	1.360(7)
C33	C34	1.439(7)
C34	C35	1.479(6)
C35	N9	1.352(6)
C35	N12	1.326(6)
C36	C37	1.477(6)
C36	N10	1.356(6)
C36	N11	1.337(6)
C37	C38	1.391(6)
C37	C42	1.414(7)
C38	C39	1.385(6)
C39	C40	1.393(7)
C40	C41	1.387(7)
C41	C42	1.388(6)
C42	C43	1.491(6)
C43	C44	1.393(6)
C43	C48	1.419(6)
C44	C45	1.387(6)
C45	C46	1.383(7)
C46	C47	1.390(7)
C47	C48	1.395(6)
C48	C49	1.480(6)
C49	N13	1.349(6)
C49	N16	1.341(5)
C50	C51	1.482(7)
C50	N14	1.343(6)
C50	N15	1.345(6)
C51	C52	1.412(6)
C51	C56	1.397(6)
C52	C53	1.390(6)
C53	C54	1.387(7)
C54	C55	1.376(8)
C55	C56	1.388(7)
N9	N10	1.321(5)
N11	N12	1.333(5)
N13	N14	1.324(5)
N15	N16	1.321(5)

Table CD4: Bond Angles in ° for **4a**.

Atom	Atom	Atom	Angle/°
C2	C1	Br1	116.1(4)
C2	C1	C6	120.7(4)
C6	C1	Br1	123.2(3)
C3	C2	C1	120.5(5)
C2	C3	C4	120.3(5)
C3	C4	C5	120.0(5)
C4	C5	C6	120.7(5)
C1	C6	C5	117.9(4)
C1	C6	C7	125.1(4)
C5	C6	C7	117.0(4)
N1	C7	C6	119.0(4)
N1	C7	N4	123.5(5)
N4	C7	C6	117.4(4)
N2	C8	C9	117.3(4)
N2	C8	N3	124.2(4)
N3	C8	C9	118.5(4)
C10	C9	C8	117.7(4)
C14	C9	C8	122.2(4)
C14	C9	C10	119.7(4)
C11	C10	C9	120.2(4)
C12	C11	C10	119.9(4)
C11	C12	C13	120.2(4)
C12	C13	C14	120.8(4)
C9	C14	C15	122.3(4)
C13	C14	C9	118.9(4)
C13	C14	C15	118.8(4)
C16	C15	C14	120.5(4)
C16	C15	C20	118.8(4)
C20	C15	C14	120.6(4)
C15	C16	C17	120.4(4)
C18	C17	C16	119.9(4)
C19	C18	C17	120.6(4)
C18	C19	C20	120.1(4)
C15	C20	C21	120.0(4)
C19	C20	C15	120.0(4)
C19	C20	C21	119.9(4)
N6	C21	C20	117.9(4)
N6	C21	N7	125.2(4)
N7	C21	C20	116.8(4)
N5	C22	C23	117.9(4)
N5	C22	N8	124.7(4)
N8	C22	C23	117.1(4)
C24	C23	C22	123.4(4)
C28	C23	C22	118.4(4)
C28	C23	C24	118.1(4)
C23	C24	Br2	120.9(3)
C25	C24	Br2	118.0(4)
C25	C24	C23	120.9(4)
C24	C25	C26	119.9(5)
C27	C26	C25	120.2(4)
C26	C27	C28	119.1(4)
C27	C28	C23	121.7(4)
N2	N1	C7	118.1(4)
N1	N2	C8	118.1(4)
N4	N3	C8	117.2(4)
N3	N4	C7	118.4(4)
C22	N5	N6	117.4(4)
C21	N6	N5	116.9(4)
N8	N7	C21	117.1(4)
N7	N8	C22	117.7(4)
C30	C29	Br3	117.8(4)
C30	C29	C34	120.9(5)
C34	C29	Br3	121.1(4)
C31	C30	C29	119.8(5)
C30	C31	C32	120.5(5)
C33	C32	C31	121.1(5)
C32	C33	C34	119.5(5)
C29	C34	C33	118.1(4)
C29	C34	C35	124.0(4)
C33	C34	C35	117.9(4)
N9	C35	C34	118.1(4)
N12	C35	C34	116.6(4)
N12	C35	N9	124.9(4)
N10	C36	C37	117.5(4)
N11	C36	C37	118.2(4)
N11	C36	N10	124.3(4)
C38	C37	C36	119.9(4)
C38	C37	C42	120.8(4)
C42	C37	C36	119.3(4)
C39	C38	C37	119.9(4)
C38	C39	C40	119.8(5)
C41	C40	C39	120.3(4)
C40	C41	C42	121.0(4)
C37	C42	C43	119.6(4)
C41	C42	C37	118.1(4)
C41	C42	C43	122.3(4)
C44	C43	C42	118.9(4)
C44	C43	C48	118.8(4)
C48	C43	C42	122.1(4)
C45	C44	C43	120.6(4)
C46	C45	C44	120.6(4)
C45	C46	C47	119.9(4)
C46	C47	C48	120.3(4)
C43	C48	C49	121.5(4)
C47	C48	C43	119.7(4)
C47	C48	C49	118.5(4)
N13	C49	C48	117.5(4)
N16	C49	C48	118.4(4)
N16	C49	N13	124.0(4)
N14	C50	C51	118.4(4)
N14	C50	N15	124.4(5)
N15	C50	C51	116.9(4)
C52	C51	C50	124.1(4)
C56	C51	C50	118.3(4)
C56	C51	C52	117.6(4)
C51	C52	Br4	123.3(3)
C53	C52	Br4	115.7(3)
C53	C52	C51	120.9(4)
C54	C53	C52	119.6(5)
C55	C54	C53	120.5(5)
C54	C55	C56	120.0(5)
C55	C56	C51	121.3(5)
N10	N9	C35	117.5(4)
N9	N10	C36	117.3(4)
N12	N11	C36	117.8(4)
C35	N12	N11	117.5(4)
N14	N13	C49	118.1(4)
N13	N14	C50	117.2(4)

Atom	Atom	Atom	Angle/˚
N16	N15	C50	117.9(4)

Atom	Atom	Atom	Angle/˚
N15	N16	C49	117.6(4)

Table CD5: Torsion Angles in ˚ for **4a**.

Atom	Atom	Atom	Atom	Angle/˚
Br1	C1	C2	C3	-177.3(4)
Br1	C1	C6	C5	176.1(3)
Br1	C1	C6	C7	-5.9(7)
Br2	C24	C25	C26	176.2(4)
C1	C2	C3	C4	1.2(7)
C1	C6	C7	N1	-34.1(7)
C1	C6	C7	N4	150.0(5)
C2	C1	C6	C5	-2.2(7)
C2	C1	C6	C7	175.7(4)
C2	C3	C4	C5	-2.3(8)
C3	C4	C5	C6	1.1(8)
C4	C5	C6	C1	1.1(7)
C4	C5	C6	C7	-177.0(5)
C5	C6	C7	N1	143.9(5)
C5	C6	C7	N4	-32.0(6)
C6	C1	C2	C3	1.1(7)
C6	C7	N1	N2	177.9(4)
C6	C7	N4	N3	-179.8(4)
C7	N1	N2	C8	1.6(6)
C8	C9	C10	C11	-169.3(4)
C8	C9	C14	C13	166.8(4)
C8	C9	C14	C15	-15.1(6)
C8	N3	N4	C7	2.1(6)
C9	C8	N2	N1	-172.4(4)
C9	C8	N3	N4	170.4(4)
C9	C10	C11	C12	1.2(7)
C9	C14	C15	C16	123.5(5)
C9	C14	C15	C20	-55.2(6)
C10	C9	C14	C13	-6.0(6)
C10	C9	C14	C15	172.1(4)
C10	C11	C12	C13	-3.9(7)
C11	C12	C13	C14	1.6(7)
C12	C13	C14	C9	3.4(6)
C12	C13	C14	C15	-174.8(4)
C13	C14	C15	C16	-58.4(6)
C13	C14	C15	C20	123.0(5)
C14	C9	C10	C11	3.8(6)
C14	C15	C16	C17	-175.8(4)
C14	C15	C20	C19	175.2(4)
C14	C15	C20	C21	-6.8(7)
C15	C16	C17	C18	-0.4(7)
C15	C20	C21	N6	127.6(5)
C15	C20	C21	N7	-56.2(6)
C16	C15	C20	C19	-3.5(7)
C16	C15	C20	C21	174.5(4)
C16	C17	C18	C19	-1.5(7)
C17	C18	C19	C20	0.9(7)
C18	C19	C20	C15	1.7(7)
C18	C19	C20	C21	-176.4(4)
C19	C20	C21	N6	-54.4(6)
C19	C20	C21	N7	121.9(5)
C20	C15	C16	C17	2.9(7)
C20	C21	N6	N5	-175.7(4)
C20	C21	N7	N8	175.9(4)

Atom	Atom	Atom	Atom	Angle/°
C21	N7	N8	C22	-0.6(6)
C22	C23	C24	Br2	8.3(7)
C22	C23	C24	C25	-176.6(4)
C22	C23	C28	C27	175.7(4)
C22	N5	N6	C21	0.0(6)
C23	C22	N5	N6	177.8(4)
C23	C22	N8	N7	-177.4(4)
C23	C24	C25	C26	0.9(7)
C24	C23	C28	C27	-2.5(7)
C24	C25	C26	C27	-2.3(7)
C25	C26	C27	C28	1.4(7)
C26	C27	C28	C23	1.1(7)
C28	C23	C24	Br2	-173.7(4)
C28	C23	C24	C25	1.5(7)
N1	C7	N4	N3	4.5(7)
N2	C8	C9	C10	143.1(4)
N2	C8	C9	C14	-29.9(6)
N2	C8	N3	N4	-7.1(6)
N3	C8	C9	C10	-34.6(6)
N3	C8	C9	C14	152.5(4)
N3	C8	N2	N1	5.2(6)
N4	C7	N1	N2	-6.4(7)
N5	C22	C23	C24	-136.2(5)
N5	C22	C23	C28	45.7(6)
N5	C22	N8	N7	9.0(7)
N6	C21	N7	N8	-8.1(7)
N7	C21	N6	N5	8.4(6)
N8	C22	C23	C24	49.8(6)
N8	C22	C23	C28	-128.2(5)
N8	C22	N5	N6	-8.7(7)
Br3	C29	C30	C31	-177.4(4)
Br3	C29	C34	C33	175.6(3)
Br3	C29	C34	C35	-4.7(6)
Br4	C52	C53	C54	177.5(3)
C29	C30	C31	C32	2.5(8)
C29	C34	C35	N9	-49.9(6)
C29	C34	C35	N12	135.9(5)
C30	C29	C34	C33	0.3(7)
C30	C29	C34	C35	-180.0(4)
C30	C31	C32	C33	-1.4(8)
C31	C32	C33	C34	-0.2(8)
C32	C33	C34	C29	0.7(7)
C32	C33	C34	C35	-179.0(4)
C33	C34	C35	N9	129.8(4)
C33	C34	C35	N12	-44.4(6)
C34	C29	C30	C31	-2.0(7)
C34	C35	N9	N10	179.5(4)
C34	C35	N12	N11	-179.8(4)
C35	N9	N10	C36	0.3(6)
C36	C37	C38	C39	177.5(4)
C36	C37	C42	C41	-176.2(4)
C36	C37	C42	C43	2.9(7)
C36	N11	N12	C35	0.4(6)
C37	C36	N10	N9	-174.7(4)
C37	C36	N11	N12	174.3(4)
C37	C38	C39	C40	-0.4(7)
C37	C42	C43	C44	-115.3(5)
C37	C42	C43	C48	59.5(6)
C38	C37	C42	C41	2.4(7)
C38	C37	C42	C43	-178.5(4)
C38	C39	C40	C41	0.3(7)

Atom	Atom	Atom	Atom	Angle/°
C39	C40	C41	C42	1.1(7)
C40	C41	C42	C37	-2.4(6)
C40	C41	C42	C43	178.5(4)
C41	C42	C43	C44	63.8(6)
C41	C42	C43	C48	-121.4(5)
C42	C37	C38	C39	-1.0(7)
C42	C43	C44	C45	173.3(4)
C42	C43	C48	C47	-170.8(4)
C42	C43	C48	C49	14.5(6)
C43	C44	C45	C46	-1.9(7)
C43	C48	C49	N13	30.7(6)
C43	C48	C49	N16	-151.3(4)
C44	C43	C48	C47	4.0(6)
C44	C43	C48	C49	-170.7(4)
C44	C45	C46	C47	3.1(7)
C45	C46	C47	C48	-0.7(7)
C46	C47	C48	C43	-2.8(6)
C46	C47	C48	C49	172.1(4)
C47	C48	C49	N13	-144.1(4)
C47	C48	C49	N16	33.9(6)
C48	C43	C44	C45	-1.7(6)
C48	C49	N13	N14	171.9(4)
C48	C49	N16	N15	-169.9(4)
C49	N13	N14	C50	-1.7(6)
C50	C51	C52	Br4	6.8(6)
C50	C51	C52	C53	-176.2(4)
C50	C51	C56	C55	176.9(5)
C50	N15	N16	C49	-2.2(6)
C51	C50	N14	N13	-178.2(4)
C51	C50	N15	N16	-179.9(4)
C51	C52	C53	C54	0.2(6)
C52	C51	C56	C55	-1.0(7)
C52	C53	C54	C55	-2.6(7)
C53	C54	C55	C56	3.1(8)
C54	C55	C56	C51	-1.3(8)
C56	C51	C52	Br4	-175.5(3)
C56	C51	C52	C53	1.5(6)
N9	C35	N12	N11	6.5(7)
N10	C36	C37	C38	-123.5(5)
N10	C36	C37	C42	55.1(6)
N10	C36	N11	N12	-6.9(7)
N11	C36	C37	C38	55.5(6)
N11	C36	C37	C42	-126.0(5)
N11	C36	N10	N9	6.4(6)
N12	C35	N9	N10	-6.9(6)
N13	C49	N16	N15	7.9(6)
N14	C50	C51	C52	34.1(7)
N14	C50	C51	C56	-143.6(5)
N14	C50	N15	N16	-5.4(7)
N15	C50	C51	C52	-151.1(4)
N15	C50	C51	C56	31.2(6)
N15	C50	N14	N13	7.4(7)
N16	C49	N13	N14	-6.0(6)

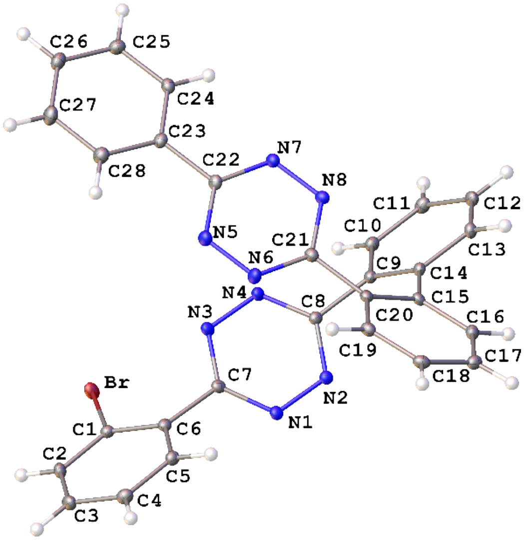
Table CD6: Hydrogen Fractional Atomic Coordinates (×10[4]) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H2	3433.48	9593.17	8269.01	31
H3	2107.91	8561.67	8230.11	35

Atom	x	y	z	U_{eq}
H4	2170.36	6964.74	7828	33
H5	3542	6445.72	7414.6	26
H10	7632.09	5085.59	7077.28	24
H11	9165.92	4640.58	6850.71	26
H12	9991.11	5654.99	6269.95	25
H13	9238.53	7001.55	5850.4	20
H16	8452.01	8817.91	6045.57	20
H17	7646.04	10124.38	5613.03	25
H18	6218.56	9768.19	5219.47	23
H19	5610.54	8109.06	5225.04	19
H25	6044.2	1107.03	6014.42	26
H26	4605.97	687.83	5635.57	31
H27	3638.85	1992.98	5314.92	28
H28	4147.48	3700.29	5347.61	23
H30	3551.97	1254.49	3972.83	31
H31	2124.97	857.73	4356.11	32
H32	1210.14	2148.49	4715.77	32
H33	1727.05	3833.19	4735.63	29
H38	3141.29	8223.23	4871.09	21
H39	3697.89	9918.8	4863.09	25
H40	5069.35	10324.76	4413.38	28
H41	5879.67	9047.74	3972.5	22
H44	6705.74	7137.74	4239.62	21
H45	7446.31	5744.76	3850.96	24
H46	6646.89	4739.91	3258.05	26
H47	5136.9	5214.23	2995.71	21
H53	987.29	9684.46	1728.37	28
H54	-363.8	8667.12	1787.76	32
H55	-312.68	7084.13	2199.5	28
H56	1044.82	6573.46	2624.66	23

Compound 4a'

R_1=4.65%



Compound	**4a'**
CCDC	
Formula	$C_{28}H_{17}BrN_8$
$D_{calc.}$/ g cm^{-3}	1.498
μ/mm^{-1}	1.735
Formula Weight	545.40
Colour	clear light red
Shape	prism-shaped
Size/mm^3	0.30×0.25×0.20
T/K	115
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	12.6054(7)
b/Å	13.4378(7)
c/Å	15.1105(8)
α/°	90
β/°	109.0940(10)
γ/°	90
V/Å^3	2418.7(2)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K_α
Θ_{min}/°	2.806
Θ_{max}/°	27.492
Measured Refl's.	51513
Indep't Refl's	5543
Refl's I≥2 σ(I)	4260
R_{int}	0.0495
Parameters	334
Restraints	0
Largest Peak	1.642
Deepest Hole	-0.455
GooF	1.136
wR_2 (all data)	0.1222
wR_2	0.1128
R_1 (all data)	0.0696
R_1	0.0465

Experimental. Single clear light red prism-shaped crystals of **4a'** recrystallised from a mixture of trichloromethane and heptane by slow evaporation. A suitable crystal with dimensions 0.30 × 0.25 × 0.20 mm^3 was selected and mounted on a mylar loop with oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 115 K during data collection. The structure was solved with the **ShelXT** 2018/2 (Sheldrick, 2018) solution program using dual methods and by using **Olex2** 1.3 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2.

Crystal Data. $C_{28}H_{17}BrN_8$, M_r = 545.40, monoclinic, $P2_1/c$ (No. 14), a = 12.6054(7) Å, b = 13.4378(7) Å, c = 15.1105(8) Å, β = 109.0940(10)°, α = γ = 90°, V = 2418.7(2) Å^3, T = 115 K, Z = 4, Z' = 1, μ(Mo K_α) = 1.735, 51513 reflections measured, 5543 unique (R_{int} = 0.0495) which were used in all calculations. The final wR_2 was 0.1222 (all data) and R_1 was 0.0465 (I≥2 σ(I)).

A clear light red prism-shaped-shaped crystal with dimensions 0.30 × 0.25 × 0.20 mm^3 was mounted on a mylar loop with oil. Data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 115 K.

Data were measured using ϕ and ω scans using Mo K$_\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program APEX3 (Bruker, 2020). The maximum resolution that was achieved was Θ = 27.492° (0.77 Å).

The unit cell was refined using SAINT V8.40B (Bruker, 2016) on 9972 reflections, 19% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using SAINT V8.40B (Bruker, 2016). The final completeness is 99.90 % out to 27.492° in Θ. SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. wR_2(int) was 0.0510 before and 0.0445 after correction. The Ratio of minimum to maximum transmission is 0.7028. The absorption coefficient μ of this material is 1.735 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.067 and 0.095.

The structure was solved and the space group $P2_1/c$ (# 14) determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using using dual methods and refined by full matrix least squares minimisation on $\boldsymbol{F}^2$ using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

Table CD7: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4a'**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Br	8631.3(3)	4669.8(3)	1545.3(3)	29.69(12)
C1	8362(3)	6051(3)	1652(2)	21.6(7)
C2	9268(3)	6683(3)	1788(2)	25.4(7)
C3	9116(3)	7703(3)	1847(3)	28.9(8)
C4	8075(3)	8087(3)	1769(3)	28.5(8)
C5	7172(3)	7449(3)	1621(2)	24.7(7)
C6	7293(3)	6418(3)	1556(2)	22.0(7)
C7	6272(3)	5800(2)	1376(2)	22.1(7)
C8	4422(3)	4851(2)	1135(2)	21.0(7)
C9	3366(3)	4326(2)	1049(2)	20.9(7)
C10	3326(3)	3297(3)	909(2)	25.3(7)
C11	2354(3)	2768(3)	813(2)	28.3(8)
C12	1412(3)	3263(3)	862(2)	27.2(8)
C13	1440(3)	4285(3)	1010(2)	24.9(7)
C14	2423(3)	4833(2)	1122(2)	21.2(7)
C15	2423(3)	5915(2)	1335(2)	20.1(7)
C16	1556(3)	6511(3)	772(2)	24.3(7)
C17	1520(3)	7525(3)	918(3)	26.4(7)
C18	2382(3)	7986(3)	1619(2)	27.0(8)
C19	3246(3)	7413(3)	2189(2)	24.7(7)
C20	3265(3)	6381(2)	2078(2)	20.8(7)
C21	4126(3)	5810(3)	2800(2)	22.6(7)
C22	5622(3)	4832(2)	4088(2)	23.0(7)
C23	6474(3)	4256(3)	4813(2)	23.4(7)
C24	6238(3)	3288(3)	5020(2)	25.1(7)
C25	7033(3)	2742(3)	5689(3)	29.1(8)
C26	8064(3)	3162(3)	6176(3)	32.1(8)
C27	8305(3)	4128(3)	5977(3)	35.1(9)
C28	7520(3)	4679(3)	5294(3)	30.9(8)
N1	5330(2)	6167(2)	739(2)	23.4(6)

Atom	x	y	z	U_{eq}
N2	4378(2)	5677(2)	618(2)	22.6(6)
N3	6334(2)	4940(2)	1838(2)	27.3(7)
N4	5375(2)	4447(2)	1707(2)	26.5(6)
N5	5920(2)	5710(2)	3816(2)	29.4(7)
N6	5151(2)	6211(2)	3150(2)	29.5(7)
N7	4579(2)	4445(2)	3753(2)	24.5(6)
N8	3808(2)	4947(2)	3098(2)	24.0(6)

Table CD8: Anisotropic Displacement Parameters (×10^4) for **4a'**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br	24.02(17)	24.00(18)	44.5(2)	-0.38(17)	15.92(15)	3.62(15)
C1	22.6(16)	21.9(16)	20.2(17)	0.8(13)	7.2(13)	0.1(13)
C2	17.7(16)	29.5(19)	28.6(18)	-0.5(15)	7.1(14)	-0.3(14)
C3	25.5(18)	28.9(19)	29.6(19)	0.1(15)	5.3(15)	-7.7(15)
C4	34.0(19)	22.4(17)	28.1(19)	-0.9(15)	8.7(15)	0.0(15)
C5	23.8(17)	25.2(18)	25.8(18)	0.8(14)	9.0(14)	3.8(14)
C6	21.8(16)	25.1(17)	20.7(17)	2.1(14)	9.0(13)	1.9(13)
C7	23.0(16)	22.3(17)	25.0(17)	0.6(14)	13.4(14)	2.9(13)
C8	21.1(16)	21.6(17)	21.4(16)	-0.4(13)	8.4(13)	2.0(13)
C9	19.4(15)	22.6(16)	20.0(16)	0.8(13)	5.5(13)	0.1(13)
C10	24.7(17)	24.7(18)	26.1(18)	1.3(14)	7.7(14)	4.1(14)
C11	30.8(19)	21.8(17)	27.6(19)	-2.6(15)	3.1(15)	-0.9(14)
C12	23.5(17)	26.2(18)	27.7(19)	-0.7(15)	2.7(14)	-6.6(14)
C13	19.0(16)	26.3(17)	28.0(18)	-1.9(15)	5.8(14)	0.5(14)
C14	18.4(15)	23.4(18)	19.8(16)	-0.3(13)	3.6(13)	-0.7(13)
C15	18.3(15)	20.1(16)	24.5(17)	-1.6(13)	10.6(13)	-2.2(12)
C16	19.9(16)	27.4(18)	25.4(18)	-0.8(14)	7.3(14)	0.7(14)
C17	27.1(18)	25.9(18)	27.8(18)	3.0(15)	11.3(15)	5.0(15)
C18	34.3(19)	21.1(17)	30.0(19)	0.1(15)	16.4(16)	-1.1(14)
C19	26.9(17)	24.2(17)	24.2(18)	-3.2(14)	10.1(14)	-5.2(14)
C20	20.1(15)	23.6(17)	20.6(16)	0.6(13)	9.1(13)	-1.5(13)
C21	24.0(17)	22.7(17)	21.7(17)	-3.1(14)	8.1(14)	-3.5(13)
C22	22.9(16)	23.3(18)	20.9(17)	-6.3(13)	4.4(13)	-2.1(13)
C23	24.0(17)	25.6(17)	19.4(16)	-3.6(14)	5.5(13)	1.6(14)
C24	22.1(16)	29.1(19)	24.6(18)	-4.0(14)	8.3(14)	-1.3(14)
C25	33.9(19)	26.3(18)	27.8(19)	1.8(15)	11.0(16)	2.2(15)
C26	29.2(19)	36(2)	28(2)	0.9(16)	5.0(16)	7.0(16)
C27	29.5(19)	35(2)	33(2)	-4.7(17)	0.1(16)	-0.5(17)
C28	32.0(19)	28.6(18)	29.2(19)	-2.4(16)	6.0(15)	-1.5(16)
N1	20.0(14)	26.7(15)	25.4(15)	1.7(12)	10.1(12)	2.4(11)
N2	20.7(14)	22.6(14)	25.6(15)	1.6(12)	9.2(12)	2.2(11)
N3	19.8(14)	29.3(15)	34.7(17)	8.2(13)	11.6(13)	3.0(12)
N4	18.9(14)	28.9(16)	32.1(16)	7.4(13)	8.7(12)	1.3(12)
N5	24.2(15)	28.6(16)	31.2(17)	2.7(13)	3.0(13)	-5.7(12)
N6	24.9(15)	28.1(16)	29.4(17)	2.6(13)	0.9(13)	-4.8(13)
N7	23.1(14)	25.9(16)	23.0(15)	0.2(12)	5.4(12)	-3.8(11)
N8	25.2(15)	23.3(14)	23.0(15)	0.0(12)	7.4(12)	-4.4(11)

Table CD9: Bond Lengths in Å for **4a'**.

Atom	Atom	Length/Å
Br	C1	1.903(3)
C1	C2	1.384(5)
C1	C6	1.397(4)
C2	C3	1.390(5)
C3	C4	1.379(5)
C4	C5	1.384(5)

Atom	Atom	Length/Å
C5	C6	1.402(5)
C6	C7	1.479(5)
C7	N1	1.354(4)
C7	N3	1.340(4)
C8	C9	1.475(4)
C8	N2	1.348(4)

Atom	Atom	Length/Å
C8	N4	1.344(4)
C9	C10	1.397(5)
C9	C14	1.405(4)
C10	C11	1.382(5)
C11	C12	1.383(5)
C12	C13	1.391(5)
C13	C14	1.403(5)
C14	C15	1.490(4)
C15	C16	1.397(5)
C15	C20	1.413(5)
C16	C17	1.383(5)
C17	C18	1.391(5)
C18	C19	1.381(5)
C19	C20	1.399(5)
C20	C21	1.478(5)

Atom	Atom	Length/Å
C21	N6	1.339(4)
C21	N8	1.351(4)
C22	C23	1.478(5)
C22	N5	1.342(4)
C22	N7	1.349(4)
C23	C24	1.391(5)
C23	C28	1.401(5)
C24	C25	1.380(5)
C25	C26	1.387(5)
C26	C27	1.388(6)
C27	C28	1.387(5)
N1	N2	1.329(4)
N3	N4	1.335(4)
N5	N6	1.329(4)
N7	N8	1.323(4)

Table CD10: Bond Angles in ° for **4a'**.

Atom	Atom	Atom	Angle/°
C2	C1	Br	116.7(2)
C2	C1	C6	121.3(3)
C6	C1	Br	121.9(3)
C1	C2	C3	119.4(3)
C4	C3	C2	120.7(3)
C3	C4	C5	119.4(3)
C4	C5	C6	121.4(3)
C1	C6	C5	117.7(3)
C1	C6	C7	124.9(3)
C5	C6	C7	117.3(3)
N1	C7	C6	115.8(3)
N3	C7	C6	119.3(3)
N3	C7	N1	124.9(3)
N2	C8	C9	118.5(3)
N4	C8	C9	117.1(3)
N4	C8	N2	124.4(3)
C10	C9	C8	118.2(3)
C10	C9	C14	120.1(3)
C14	C9	C8	121.6(3)
C11	C10	C9	120.7(3)
C10	C11	C12	119.6(3)
C11	C12	C13	120.4(3)
C12	C13	C14	120.8(3)
C9	C14	C15	123.4(3)
C13	C14	C9	118.2(3)
C13	C14	C15	118.4(3)
C16	C15	C14	118.9(3)
C16	C15	C20	117.7(3)
C20	C15	C14	123.4(3)

Atom	Atom	Atom	Angle/°
C17	C16	C15	121.9(3)
C16	C17	C18	120.1(3)
C19	C18	C17	119.1(3)
C18	C19	C20	121.3(3)
C15	C20	C21	122.4(3)
C19	C20	C15	119.8(3)
C19	C20	C21	117.6(3)
N6	C21	C20	117.6(3)
N6	C21	N8	124.6(3)
N8	C21	C20	117.7(3)
N5	C22	C23	118.7(3)
N5	C22	N7	124.0(3)
N7	C22	C23	117.3(3)
C24	C23	C22	120.0(3)
C24	C23	C28	119.8(3)
C28	C23	C22	120.3(3)
C25	C24	C23	120.3(3)
C24	C25	C26	120.1(3)
C25	C26	C27	120.0(4)
C28	C27	C26	120.5(4)
C27	C28	C23	119.4(4)
N2	N1	C7	117.4(3)
N1	N2	C8	117.7(3)
N4	N3	C7	117.1(3)
N3	N4	C8	118.1(3)
N6	N5	C22	118.0(3)
N5	N6	C21	117.7(3)
N8	N7	C22	118.2(3)
N7	N8	C21	117.4(3)

Table CD11: Torsion Angles in ° for **4a'**.

Atom	Atom	Atom	Atom	Angle/°
Br	C1	C2	C3	178.4(3)
Br	C1	C6	C5	-178.3(2)
Br	C1	C6	C7	0.7(5)
C1	C2	C3	C4	-0.2(6)
C1	C6	C7	N1	-137.6(3)
C1	C6	C7	N3	42.4(5)
C2	C1	C6	C5	-1.3(5)

Atom	Atom	Atom	Atom	Angle/°
C2	C1	C6	C7	177.7(3)
C2	C3	C4	C5	-0.7(5)
C3	C4	C5	C6	0.6(5)
C4	C5	C6	C1	0.4(5)
C4	C5	C6	C7	-178.7(3)
C5	C6	C7	N1	41.3(4)
C5	C6	C7	N3	-138.7(3)
C6	C1	C2	C3	1.2(5)
C6	C7	N1	N2	-174.4(3)
C6	C7	N3	N4	174.9(3)
C7	N1	N2	C8	-0.2(4)
C7	N3	N4	C8	-0.8(5)
C8	C9	C10	C11	-179.2(3)
C8	C9	C14	C13	178.4(3)
C8	C9	C14	C15	-3.1(5)
C9	C8	N2	N1	176.7(3)
C9	C8	N4	N3	-176.1(3)
C9	C10	C11	C12	-0.4(5)
C9	C14	C15	C16	130.8(3)
C9	C14	C15	C20	-48.6(5)
C10	C9	C14	C13	-2.7(5)
C10	C9	C14	C15	175.8(3)
C10	C11	C12	C13	-0.2(5)
C11	C12	C13	C14	-0.7(5)
C12	C13	C14	C9	2.1(5)
C12	C13	C14	C15	-176.4(3)
C13	C14	C15	C16	-50.7(4)
C13	C14	C15	C20	129.9(3)
C14	C9	C10	C11	1.9(5)
C14	C15	C16	C17	-178.4(3)
C14	C15	C20	C19	175.4(3)
C14	C15	C20	C21	-9.8(5)
C15	C16	C17	C18	2.2(5)
C15	C20	C21	N6	146.0(3)
C15	C20	C21	N8	-37.6(4)
C16	C15	C20	C19	-4.0(5)
C16	C15	C20	C21	170.8(3)
C16	C17	C18	C19	-2.5(5)
C17	C18	C19	C20	-0.5(5)
C18	C19	C20	C15	3.8(5)
C18	C19	C20	C21	-171.2(3)
C19	C20	C21	N6	-39.1(4)
C19	C20	C21	N8	137.3(3)
C20	C15	C16	C17	1.1(5)
C20	C21	N6	N5	178.4(3)
C20	C21	N8	N7	-179.2(3)
C22	C23	C24	C25	179.3(3)
C22	C23	C28	C27	179.6(3)
C22	N5	N6	C21	0.6(5)
C22	N7	N8	C21	0.9(4)
C23	C22	N5	N6	178.7(3)
C23	C22	N7	N8	-179.5(3)
C23	C24	C25	C26	1.5(5)
C24	C23	C28	C27	-0.5(5)
C24	C25	C26	C27	-1.2(6)
C25	C26	C27	C28	0.1(6)
C26	C27	C28	C23	0.8(6)
C28	C23	C24	C25	-0.7(5)
N1	C7	N3	N4	-5.0(5)
N2	C8	C9	C10	131.1(3)
N2	C8	C9	C14	-50.1(5)

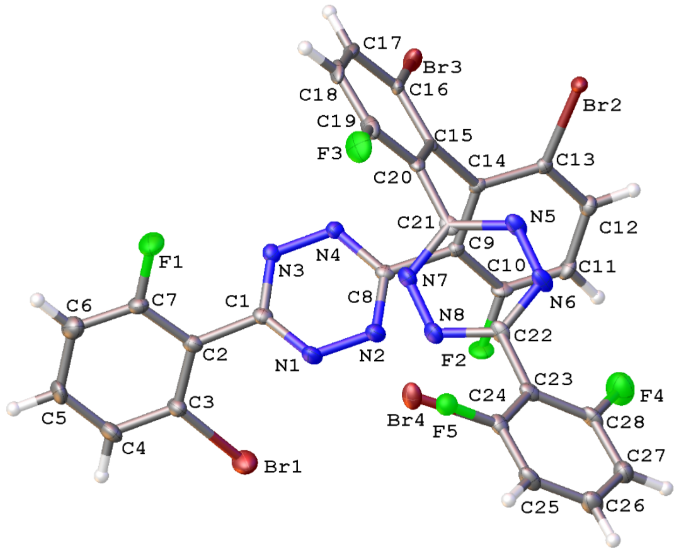
Atom	Atom	Atom	Atom	Angle/°
N2	C8	N4	N3	6.2(5)
N3	C7	N1	N2	5.6(5)
N4	C8	C9	C10	-46.8(4)
N4	C8	C9	C14	132.0(3)
N4	C8	N2	N1	-5.6(5)
N5	C22	C23	C24	-171.4(3)
N5	C22	C23	C28	8.6(5)
N5	C22	N7	N8	1.8(5)
N6	C21	N8	N7	-3.0(5)
N7	C22	C23	C24	9.9(5)
N7	C22	C23	C28	-170.2(3)
N7	C22	N5	N6	-2.6(5)
N8	C21	N6	N5	2.2(5)

Table CD12: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4a'**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H2	9986.48	6423.52	1839.48	30
H3	9735.95	8139.53	1942.17	35
H4	7978.91	8784.12	1817.13	34
H5	6453.71	7716.13	1561.47	30
H10	3973.93	2956.94	878.48	30
H11	2332.72	2069.27	713.53	34
H12	742.37	2901.32	793.65	33
H13	784.87	4616.9	1034.9	30
H16	974.01	6211.81	276.02	29
H17	906.15	7907.83	537.24	32
H18	2376.35	8686.33	1705.85	32
H19	3838.98	7726.17	2665.88	30
H24	5525.99	3003.31	4699.43	30
H25	6874.2	2076.14	5816.63	35
H26	8605.51	2789.03	6644.56	39
H27	9012.26	4413.27	6310.53	42
H28	7690.36	5336.52	5153.87	37

Compound 4c

R_1=4.41%



Compound	**4c**
CCDC	
Formula	$C_{28}H_{10}Br_{3.79}F_{4.21}N_8$
$D_{calc.}$/ g cm^{-3}	2.026
μ/mm^{-1}	5.598
Formula Weight	841.29
Colour	clear light red
Shape	prism
Size/mm^3	0.35×0.25×0.10
T/K	115
Crystal System	monoclinic
Space Group	$C2/c$
a/Å	27.3462(7)
b/Å	7.8804(2)
c/Å	25.6877(6)
α/°	90
β/°	94.7210(10)
γ/°	90
V/Å^3	5516.9(2)
Z	8
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K_α
Θ_{min}/°	2.691
Θ_{max}/°	27.491
Measured Refl's.	40594
Indep't Refl's	6318
Refl's I≥2 σ(I)	5525
R_{int}	0.0412
Parameters	402
Restraints	6
Largest Peak	0.769
Deepest Hole	-1.221
GooF	1.126
wR_2 (all data)	0.0979
wR_2	0.0945
R_1 (all data)	0.0545
R_1	0.0441

Experimental. Single clear light red prism crystals of **4c** recrystallised from DCM by slow evaporation. A suitable crystal with dimensions 0.35 × 0.25 × 0.10 mm^3 was selected and mounted on a mylar loop oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 115 K during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using the Instrinsic Phasing solution method and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on $\boldsymbol{F^2}$.

Crystal Data. $C_{28}H_{10}Br_{3.79}F_{4.21}N_8$, M_r = 841.29, monoclinic, $C2/c$ (No. 15), a = 27.3462(7) Å, b = 7.8804(2) Å, c = 25.6877(6) Å, β = 94.7210(10)°, α = γ = 90°, V = 5516.9(2) Å^3, T = 115 K, Z = 8, Z' = 1, μ(Mo K_α) = 5.598, 40594 reflections measured, 6318 unique (R_{int} = 0.0412) which were used in all calculations. The final wR_2 was 0.0979 (all data) and R_1 was 0.0441 (I≥2 σ(I)).

A clear light red prism-shaped crystal with dimensions 0.35 × 0.25 × 0.10 mm^3 was mounted on a mylar loop oil. Data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 115 K. Data were measured using ϕ and ω scans using Mo K_α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program APEX3 (Bruker, 2020). The maximum resolution that was achieved was Θ = 27.491° (0.77 Å).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program APEX3 (Bruker, 2020). The unit cell was refined using SAINT (Bruker, V8.40B, after 2013) on 9985 reflections, 25% of the observed reflections. Data reduction, scaling and absorption corrections were performed using SAINT (Bruker, V8.40B, after 2013). The final completeness is 99.90 % out to 27.491° in Θ. A multi-scan absorption correction was performed using SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. wR_2(int) was 0.1271 before and 0.0468 after correction. The Ratio of minimum to maximum transmission is 0.5491. The absorption coefficient μ of this material is 5.598 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.409 and 0.746.

The structure was solved and the space group $C2/c$ (# 15) determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using using the Instrinsic Phasing solution method and refined by full matrix least squares minimisation on $\boldsymbol{F}^2$ using version 2018/3 of ShelXL (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. A bromide and fluorine atom share the same position with occupancy factors converged around 0.79:0.21, with an isotropical refinement for the fluorine.

Table CD13: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4c**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	**x**	**y**	**z**	$\boldsymbol{U_{eq}}$
Br(1)	1771.3(2)	9148.9(6)	6695.4(2)	32.35(13)
Br(2)	4438.3(2)	5325.3(5)	4440.7(2)	16.96(10)
Br(3)	3697.8(2)	9445.2(5)	4209.0(2)	24.81(12)
F(1)	3187.8(10)	13421(3)	6412.7(11)	28.2(6)
F(2)	2576.6(9)	4912(3)	5493.1(10)	22.6(5)
F(3)	4885.4(10)	9579(3)	6270.5(10)	30.2(6)
F(4)	3961.4(12)	1190(4)	6544.9(11)	41.0(7)
N(1)	2853.4(14)	8644(4)	6461.6(13)	20.9(8)
N(2)	3020.1(13)	7429(4)	6164.1(14)	20.3(7)
N(3)	2918.6(12)	10638(4)	5775.1(13)	15.9(7)
N(4)	3102.3(12)	9439(4)	5485.2(13)	16.0(7)
N(5)	4473.1(13)	5236(5)	5969.0(13)	20.5(7)
N(6)	4452.1(14)	4052(5)	6335.1(13)	21.3(8)
N(7)	4074.8(14)	7174(4)	6503.0(13)	20.6(7)
N(8)	4043.0(14)	5987(4)	6863.1(13)	20.0(7)
C(1)	2785.0(14)	10186(5)	6245.0(15)	14.9(8)
C(2)	2550.5(15)	11497(5)	6556.0(15)	16.2(8)
C(3)	2113.8(15)	11225(5)	6787.9(16)	18.5(8)
C(4)	1901.4(17)	12480(6)	7073.6(17)	25.5(10)
C(5)	2121.2(19)	14047(6)	7127.0(17)	27.2(10)
C(6)	2558.7(18)	14377(6)	6896.1(18)	26.7(10)
C(7)	2757.2(15)	13114(5)	6619.6(16)	18.2(8)
C(8)	3119.7(14)	7854(5)	5680.5(14)	13.0(7)
C(9)	3279.1(14)	6486(5)	5334.8(14)	11.8(7)
C(10)	2990.8(14)	5040(5)	5247.7(16)	15.6(8)
C(11)	3102.3(15)	3778(5)	4908.9(16)	17.5(8)
C(12)	3525.9(15)	3926(5)	4651.1(15)	15.6(8)
C(13)	3831.3(14)	5319(5)	4747.3(14)	12.1(7)
C(14)	3714.7(14)	6616(4)	5080.5(14)	10.6(7)
C(15)	4050.0(13)	8086(5)	5200.4(15)	11.7(7)
C(16)	4082.6(15)	9449(5)	4856.6(15)	15.1(8)
C(17)	4376.8(15)	10843(5)	4987.5(18)	20.6(9)
C(18)	4642.9(16)	10904(5)	5469.1(18)	22.8(9)
C(19)	4613.4(15)	9558(5)	5803.9(17)	21.2(9)
C(20)	4325.6(14)	8148(5)	5684.7(15)	14.2(8)
C(21)	4295.5(14)	6768(5)	6074.0(14)	13.3(7)

Atom	x	y	z	U_{eq}
C(22)	4244.7(15)	4474(5)	6773.3(14)	15.6(8)
C(23)	4238.3(14)	3160(5)	7182.7(15)	15.9(8)
C(24)	4367.3(14)	3480(5)	7711.1(15)	16.6(8)
C(25)	4376.3(16)	2209(6)	8079.9(16)	21.2(9)
C(26)	4244.7(17)	569(6)	7924.9(17)	23.5(9)
C(27)	4108.9(16)	202(6)	7406.1(16)	22.1(9)
C(28)	4109.5(15)	1497(5)	7047.5(15)	18.7(8)
Br(4)	4539.0(2)	5740.6(9)	7957.6(2)	22.3(2)
F(5)	4518(4)	4870(20)	7877(5)	21(3)

Table CD14: Anisotropic Displacement Parameters (×10[4]) for **4c.** The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11}+ \ldots +2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	27.6(3)	29.4(2)	41.8(3)	-7.6(2)	13.1(2)	-9.52(19)
Br(2)	19.8(2)	12.24(17)	20.0(2)	-1.59(14)	9.12(15)	-2.73(15)
Br(3)	44.5(3)	14.07(19)	16.3(2)	0.75(15)	5.18(18)	0.59(18)
F(1)	21.6(14)	24.6(13)	38.8(15)	-1.8(11)	5.8(11)	-7.8(11)
F(2)	12.5(12)	26.5(13)	29.9(14)	-1.8(10)	7.4(10)	-8.4(10)
F(3)	24.2(14)	32.9(15)	31.7(15)	-13.8(12)	-8.2(11)	-7.6(11)
F(4)	54(2)	39.3(17)	29.3(15)	-5.2(13)	0.1(14)	3.0(15)
N(1)	28(2)	20.4(17)	15.7(17)	1.5(13)	9.7(15)	2.8(15)
N(2)	24(2)	19.0(17)	19.3(18)	2.0(14)	8.8(14)	2.8(15)
N(3)	14.1(17)	15.8(16)	17.9(17)	-0.3(13)	2.3(13)	1.8(13)
N(4)	16.0(17)	15.2(16)	17.2(17)	0.8(13)	4.9(13)	1.6(13)
N(5)	23.7(19)	25.5(18)	12.3(16)	1.0(14)	1.8(14)	8.6(15)
N(6)	26(2)	24.8(18)	13.4(16)	2.5(14)	2.7(14)	12.5(15)
N(7)	26(2)	19.4(17)	17.6(17)	-4.7(14)	7.4(14)	0.4(15)
N(8)	26(2)	20.0(17)	14.4(17)	-4.0(13)	5.0(14)	1.2(15)
C(1)	10.6(19)	18.7(19)	15.6(19)	0.0(15)	1.6(14)	-1.4(15)
C(2)	16(2)	18.7(19)	14.3(19)	-0.2(15)	3.1(15)	-1.0(16)
C(3)	19(2)	18.7(19)	19(2)	-3.8(15)	5.8(16)	-3.2(16)
C(4)	28(3)	29(2)	21(2)	-5.3(18)	12.5(18)	0.0(19)
C(5)	40(3)	19(2)	24(2)	-8.1(17)	14(2)	2.7(19)
C(6)	34(3)	23(2)	24(2)	-3.6(18)	6.7(19)	-4.8(19)
C(7)	18(2)	18.1(19)	19(2)	0.9(15)	5.0(16)	-3.5(16)
C(8)	8.1(18)	17.5(18)	13.3(18)	0.3(14)	0.7(14)	-1.1(14)
C(9)	11.5(19)	12.4(17)	11.3(17)	0.8(13)	0.3(14)	-0.6(14)
C(10)	7.5(18)	20.2(19)	19(2)	2.0(15)	1.6(14)	-3.3(15)
C(11)	16(2)	11.8(17)	24(2)	-1.0(15)	-1.8(16)	-3.8(15)
C(12)	16(2)	13.8(18)	16.3(19)	-2.6(14)	-1.5(15)	-1.3(15)
C(13)	12.1(18)	12.3(17)	11.5(17)	1.7(13)	-0.4(14)	0.4(14)
C(14)	9.5(18)	11.1(16)	10.9(17)	2.4(13)	-1.7(13)	-1.9(14)
C(15)	8.7(18)	10.7(16)	16.9(19)	-4.1(14)	7.6(14)	-1.7(13)
C(16)	19(2)	9.9(17)	17.1(19)	-2.7(14)	7.4(15)	0.6(15)
C(17)	20(2)	10.1(17)	34(2)	-0.6(16)	15.6(18)	-2.9(15)
C(18)	16(2)	12.7(18)	41(3)	-13.0(17)	9.4(18)	-5.6(16)
C(19)	15(2)	22(2)	27(2)	-11.6(17)	2.8(16)	-3.7(17)
C(20)	10.0(19)	14.0(17)	19.1(19)	-3.7(14)	5.6(15)	-2.6(14)
C(21)	7.0(17)	20.0(18)	12.1(17)	-4.6(14)	-4.2(13)	-2.1(14)
C(22)	14.5(19)	22(2)	9.1(17)	-4.0(15)	-4.2(14)	2.6(16)
C(23)	11.6(19)	22(2)	14.1(19)	0.7(15)	2.5(14)	4.4(15)
C(24)	11(2)	21(2)	17(2)	-4.6(15)	0.6(15)	3.4(15)
C(25)	24(2)	28(2)	11.3(19)	-1.3(16)	1.3(16)	8.2(18)
C(26)	29(2)	24(2)	17(2)	1.8(17)	3.4(17)	6.0(18)
C(27)	26(2)	20(2)	20(2)	-2.7(16)	5.2(17)	2.0(17)
C(28)	18(2)	28(2)	9.6(18)	-4.3(15)	0.6(15)	3.4(17)
Br(4)	29.9(4)	20.9(4)	15.2(3)	-4.0(2)	-3.4(2)	4.9(2)

Table CD15: Bond Lengths in Å for **4c**.

Atom	Atom	Length/Å
Br(1)	C(3)	1.890(4)
Br(2)	C(13)	1.895(4)
Br(3)	C(16)	1.894(4)
F(1)	C(7)	1.353(5)
F(2)	C(10)	1.345(4)
F(3)	C(19)	1.358(5)
F(4)	C(28)	1.343(5)
N(1)	N(2)	1.329(5)
N(1)	C(1)	1.344(5)
N(2)	C(8)	1.336(5)
N(3)	N(4)	1.327(4)
N(3)	C(1)	1.338(5)
N(4)	C(8)	1.345(5)
N(5)	N(6)	1.329(5)
N(5)	C(21)	1.337(5)
N(6)	C(22)	1.343(5)
N(7)	N(8)	1.323(5)
N(7)	C(21)	1.338(5)
N(8)	C(22)	1.342(5)
C(1)	C(2)	1.484(5)
C(2)	C(3)	1.394(5)
C(2)	C(7)	1.398(6)
C(3)	C(4)	1.387(6)
C(4)	C(5)	1.376(6)
C(5)	C(6)	1.403(6)
C(6)	C(7)	1.361(6)
C(8)	C(9)	1.485(5)
C(9)	C(10)	1.393(5)
C(9)	C(14)	1.409(5)
C(10)	C(11)	1.372(6)
C(11)	C(12)	1.386(6)
C(12)	C(13)	1.389(5)
C(13)	C(14)	1.387(5)
C(14)	C(15)	1.494(5)
C(15)	C(16)	1.398(5)
C(15)	C(20)	1.401(6)
C(16)	C(17)	1.386(5)
C(17)	C(18)	1.384(7)
C(18)	C(19)	1.372(6)
C(19)	C(20)	1.381(5)
C(20)	C(21)	1.484(5)
C(22)	C(23)	1.477(5)
C(23)	C(24)	1.397(6)
C(23)	C(28)	1.394(6)
C(24)	C(25)	1.378(6)
C(24)	Br(4)	1.935(4)
C(24)	F(5)	1.236(19)
C(25)	C(26)	1.391(6)
C(26)	C(27)	1.384(6)
C(27)	C(28)	1.375(6)

Table CD16: Bond Angles in ° for **4c**.

Atom	Atom	Atom	Angle/°
N(2)	N(1)	C(1)	117.2(3)
N(1)	N(2)	C(8)	117.4(3)
N(4)	N(3)	C(1)	117.5(3)
N(3)	N(4)	C(8)	117.1(3)
N(6)	N(5)	C(21)	117.0(3)
N(5)	N(6)	C(22)	117.7(3)
N(8)	N(7)	C(21)	117.9(3)
N(7)	N(8)	C(22)	117.1(3)
N(1)	C(1)	C(2)	117.3(3)
N(3)	C(1)	N(1)	125.1(4)
N(3)	C(1)	C(2)	117.6(3)
C(3)	C(2)	C(1)	123.1(4)
C(3)	C(2)	C(7)	116.3(4)
C(7)	C(2)	C(1)	120.6(4)
C(2)	C(3)	Br(1)	120.8(3)
C(4)	C(3)	Br(1)	117.3(3)
C(4)	C(3)	C(2)	121.8(4)
C(5)	C(4)	C(3)	119.6(4)
C(4)	C(5)	C(6)	120.3(4)
C(7)	C(6)	C(5)	118.4(4)
F(1)	C(7)	C(2)	118.3(4)
F(1)	C(7)	C(6)	118.1(4)
C(6)	C(7)	C(2)	123.5(4)
N(2)	C(8)	N(4)	125.2(4)
N(2)	C(8)	C(9)	117.8(3)
N(4)	C(8)	C(9)	117.0(3)
C(10)	C(9)	C(8)	120.0(3)
C(10)	C(9)	C(14)	118.3(3)
C(14)	C(9)	C(8)	121.7(3)
F(2)	C(10)	C(9)	118.3(3)
F(2)	C(10)	C(11)	118.9(3)
C(11)	C(10)	C(9)	122.8(4)
C(10)	C(11)	C(12)	118.7(4)
C(11)	C(12)	C(13)	119.7(4)
C(12)	C(13)	Br(2)	117.5(3)
C(14)	C(13)	Br(2)	120.5(3)
C(14)	C(13)	C(12)	121.8(3)
C(9)	C(14)	C(15)	119.3(3)
C(13)	C(14)	C(9)	118.6(3)
C(13)	C(14)	C(15)	122.0(3)
C(16)	C(15)	C(14)	122.4(3)
C(16)	C(15)	C(20)	118.5(3)
C(20)	C(15)	C(14)	119.1(3)
C(15)	C(16)	Br(3)	119.6(3)
C(17)	C(16)	Br(3)	118.9(3)
C(17)	C(16)	C(15)	121.4(4)
C(18)	C(17)	C(16)	119.8(4)
C(19)	C(18)	C(17)	118.7(4)
F(3)	C(19)	C(18)	119.2(4)
F(3)	C(19)	C(20)	117.8(4)
C(18)	C(19)	C(20)	123.0(4)
C(15)	C(20)	C(21)	121.1(3)

Atom	Atom	Atom	Angle/°
C(19)	C(20)	C(15)	118.7(4)
C(19)	C(20)	C(21)	120.1(4)
N(5)	C(21)	N(7)	125.3(4)
N(5)	C(21)	C(20)	119.0(3)
N(7)	C(21)	C(20)	115.7(3)
N(6)	C(22)	C(23)	117.0(3)
N(8)	C(22)	N(6)	124.9(4)
N(8)	C(22)	C(23)	118.1(3)
C(24)	C(23)	C(22)	123.3(4)
C(28)	C(23)	C(22)	120.0(4)
C(28)	C(23)	C(24)	116.8(4)

Atom	Atom	Atom	Angle/°
C(23)	C(24)	Br(4)	121.3(3)
C(25)	C(24)	C(23)	121.7(4)
C(25)	C(24)	Br(4)	117.0(3)
F(5)	C(24)	C(23)	123.0(7)
F(5)	C(24)	C(25)	115.0(7)
C(24)	C(25)	C(26)	119.3(4)
C(27)	C(26)	C(25)	120.8(4)
C(28)	C(27)	C(26)	118.4(4)
F(4)	C(28)	C(23)	117.3(4)
F(4)	C(28)	C(27)	119.6(4)
C(27)	C(28)	C(23)	123.1(4)

Table CD17: Torsion Angles in ° for **4c**.

Atom	Atom	Atom	Atom	Angle/°
Br(1)	C(3)	C(4)	C(5)	-176.3(4)
Br(2)	C(13)	C(14)	C(9)	-174.6(3)
Br(2)	C(13)	C(14)	C(15)	1.8(5)
Br(3)	C(16)	C(17)	C(18)	177.0(3)
F(2)	C(10)	C(11)	C(12)	179.1(4)
F(3)	C(19)	C(20)	C(15)	-178.7(3)
F(3)	C(19)	C(20)	C(21)	3.9(6)
N(1)	N(2)	C(8)	N(4)	5.6(6)
N(1)	N(2)	C(8)	C(9)	-176.6(3)
N(1)	C(1)	C(2)	C(3)	-50.7(6)
N(1)	C(1)	C(2)	C(7)	131.0(4)
N(2)	N(1)	C(1)	N(3)	-7.3(6)
N(2)	N(1)	C(1)	C(2)	173.8(4)
N(2)	C(8)	C(9)	C(10)	54.5(5)
N(2)	C(8)	C(9)	C(14)	-126.7(4)
N(3)	N(4)	C(8)	N(2)	-8.1(6)
N(3)	N(4)	C(8)	C(9)	174.1(3)
N(3)	C(1)	C(2)	C(3)	130.4(4)
N(3)	C(1)	C(2)	C(7)	-48.0(5)
N(4)	N(3)	C(1)	N(1)	4.9(6)
N(4)	N(3)	C(1)	C(2)	-176.2(3)
N(4)	C(8)	C(9)	C(10)	-127.5(4)
N(4)	C(8)	C(9)	C(14)	51.3(5)
N(5)	N(6)	C(22)	N(8)	2.2(6)
N(5)	N(6)	C(22)	C(23)	-178.1(4)
N(6)	N(5)	C(21)	N(7)	-4.0(6)
N(6)	N(5)	C(21)	C(20)	178.0(4)
N(6)	C(22)	C(23)	C(24)	134.2(4)
N(6)	C(22)	C(23)	C(28)	-44.3(5)
N(7)	N(8)	C(22)	N(6)	-3.7(6)
N(7)	N(8)	C(22)	C(23)	176.6(4)
N(8)	N(7)	C(21)	N(5)	2.5(6)
N(8)	N(7)	C(21)	C(20)	-179.5(3)
N(8)	C(22)	C(23)	C(24)	-46.1(6)
N(8)	C(22)	C(23)	C(28)	135.4(4)
C(1)	N(1)	N(2)	C(8)	2.0(6)
C(1)	N(3)	N(4)	C(8)	2.7(5)
C(1)	C(2)	C(3)	Br(1)	-2.6(6)
C(1)	C(2)	C(3)	C(4)	-179.5(4)
C(1)	C(2)	C(7)	F(1)	-3.2(6)
C(1)	C(2)	C(7)	C(6)	179.5(4)
C(2)	C(3)	C(4)	C(5)	0.8(7)
C(3)	C(2)	C(7)	F(1)	178.3(4)
C(3)	C(2)	C(7)	C(6)	1.0(6)
C(3)	C(4)	C(5)	C(6)	-0.3(7)

Atom	Atom	Atom	Atom	Angle/°
C(4)	C(5)	C(6)	C(7)	0.1(7)
C(5)	C(6)	C(7)	F(1)	-177.8(4)
C(5)	C(6)	C(7)	C(2)	-0.5(7)
C(7)	C(2)	C(3)	Br(1)	175.8(3)
C(7)	C(2)	C(3)	C(4)	-1.1(6)
C(8)	C(9)	C(10)	F(2)	-1.5(5)
C(8)	C(9)	C(10)	C(11)	176.0(4)
C(8)	C(9)	C(14)	C(13)	-177.5(3)
C(8)	C(9)	C(14)	C(15)	6.0(5)
C(9)	C(10)	C(11)	C(12)	1.6(6)
C(9)	C(14)	C(15)	C(16)	-104.7(4)
C(9)	C(14)	C(15)	C(20)	72.1(5)
C(10)	C(9)	C(14)	C(13)	1.3(5)
C(10)	C(9)	C(14)	C(15)	-175.1(3)
C(10)	C(11)	C(12)	C(13)	1.2(6)
C(11)	C(12)	C(13)	Br(2)	173.4(3)
C(11)	C(12)	C(13)	C(14)	-2.7(6)
C(12)	C(13)	C(14)	C(9)	1.4(5)
C(12)	C(13)	C(14)	C(15)	177.7(3)
C(13)	C(14)	C(15)	C(16)	79.0(5)
C(13)	C(14)	C(15)	C(20)	-104.2(4)
C(14)	C(9)	C(10)	F(2)	179.6(3)
C(14)	C(9)	C(10)	C(11)	-2.8(6)
C(14)	C(15)	C(16)	Br(3)	-0.9(5)
C(14)	C(15)	C(16)	C(17)	176.5(4)
C(14)	C(15)	C(20)	C(19)	-176.3(3)
C(14)	C(15)	C(20)	C(21)	1.1(5)
C(15)	C(16)	C(17)	C(18)	-0.5(6)
C(15)	C(20)	C(21)	N(5)	67.8(5)
C(15)	C(20)	C(21)	N(7)	-110.4(4)
C(16)	C(15)	C(20)	C(19)	0.6(5)
C(16)	C(15)	C(20)	C(21)	178.0(3)
C(16)	C(17)	C(18)	C(19)	1.0(6)
C(17)	C(18)	C(19)	F(3)	177.8(4)
C(17)	C(18)	C(19)	C(20)	-0.7(6)
C(18)	C(19)	C(20)	C(15)	-0.1(6)
C(18)	C(19)	C(20)	C(21)	-177.5(4)
C(19)	C(20)	C(21)	N(5)	-114.9(4)
C(19)	C(20)	C(21)	N(7)	67.0(5)
C(20)	C(15)	C(16)	Br(3)	-177.8(3)
C(20)	C(15)	C(16)	C(17)	-0.4(6)
C(21)	N(5)	N(6)	C(22)	1.6(6)
C(21)	N(7)	N(8)	C(22)	1.3(6)
C(22)	C(23)	C(24)	C(25)	-177.3(4)
C(22)	C(23)	C(24)	Br(4)	3.0(5)
C(22)	C(23)	C(24)	F(5)	-3.3(9)
C(22)	C(23)	C(28)	F(4)	-4.6(6)
C(22)	C(23)	C(28)	C(27)	178.2(4)
C(23)	C(24)	C(25)	C(26)	-1.2(6)
C(24)	C(23)	C(28)	F(4)	176.8(4)
C(24)	C(23)	C(28)	C(27)	-0.4(6)
C(24)	C(25)	C(26)	C(27)	0.4(7)
C(25)	C(26)	C(27)	C(28)	0.3(7)
C(26)	C(27)	C(28)	F(4)	-177.5(4)
C(26)	C(27)	C(28)	C(23)	-0.3(7)
C(28)	C(23)	C(24)	C(25)	1.2(6)
C(28)	C(23)	C(24)	Br(4)	-178.5(3)
C(28)	C(23)	C(24)	F(5)	175.3(8)
Br(4)	C(24)	C(25)	C(26)	178.5(3)
F(5)	C(24)	C(25)	C(26)	-175.7(8)

Table CD18: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4c.** U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

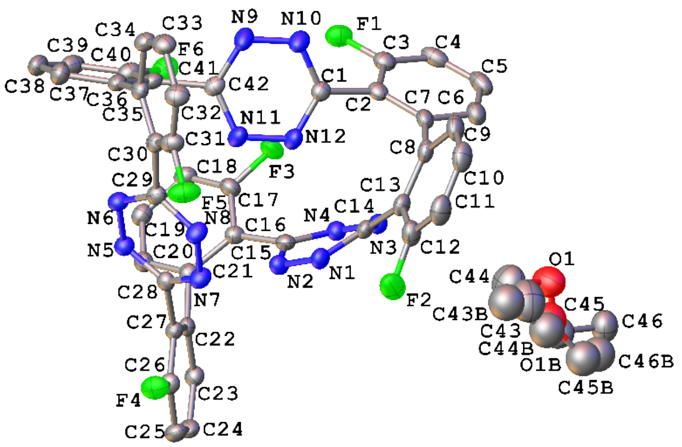
Atom	x	y	z	U_{eq}
H(4)	1605.77	12257.65	7231.49	31
H(5)	1975.87	14910.56	7321.22	33
H(6)	2712.77	15455.83	6931.9	32
H(11)	2893.27	2821.51	4852.29	21
H(12)	3607.13	3078.93	4409.64	19
H(17)	4395.71	11752.24	4747.24	25
H(18)	4842.04	11859.02	5566.08	27
H(25)	4471.32	2449.58	8436.26	25
H(26)	4248.04	-310.64	8178.22	28
H(27)	4017.47	-917.01	7300.47	27

Table CD19: Atomic Occupancies for all atoms that are not fully occupied in **4c.**

Atom	Occupancy	Atom	Occupancy
Br(4)	0.790(3)	F(5)	0.210(3)

Compound 6b

R_1=5.38%



Experimental. Single clear light red prism-shaped crystals of **6b** crystallised from a mixture of diethyl ether and DCM by slow evaporation. A suitable crystal with dimensions 0.30 × 0.25 × 0.20 mm^3 was selected and mounted on a mylar loop with oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 110 K during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using iterative methods and by using Olex2 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2019/3 (Sheldrick, 2015) using full matrix least squares minimisation on $\boldsymbol{F}^2$.

Crystal Data. $C_{46}H_{26}F_6N_{12}O$, M_r = 876.79, monoclinic, $P2_1/c$ (No. 14), a = 14.5165(8) Å, b = 12.9555(7) Å, c = 21.3838(11) Å, β = 101.2020(10)°, $\alpha = \gamma$ = 90°, V = 3945.0(4) Å^3, T = 110 K, Z = 4, Z' = 1, μ(Mo K$_\alpha$) = 0.114, 74654 reflections measured, 8675 unique (R_{int} = 0.0643) which were used in all calculations. The final wR_2 was 0.1596 (all data) and R_1 was 0.0538 (I≥2 σ(I)).

Compound	**6b**
CCDC	
Formula	$C_{46}H_{26}F_6N_{12}O$
$D_{calc.}$/ g cm^{-3}	1.476
μ/mm^{-1}	0.114
Formula Weight	876.79
Colour	clear light red
Shape	prism-shaped
Size/mm^3	0.30×0.25×0.20
T/K	110
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	14.5165(8)
b/Å	12.9555(7)
c/Å	21.3838(11)
α/°	90
β/°	101.2020(10)
γ/°	90
V/Å^3	3945.0(4)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K$_\alpha$
Θ_{min}/°	2.218
Θ_{max}/°	27.092
Measured Refl's.	74654
Indep't Refl's	8675
Refl's I≥2 σ(I)	5333
R_{int}	0.0643
Parameters	610
Restraints	95
Largest Peak	0.890
Deepest Hole	-0.586
GooF	1.021
wR_2 (all data)	0.1596
wR_2	0.1294
R_1 (all data)	0.1075
R_1	0.0538

A clear light red prism-shaped-shaped crystal with dimensions 0.30 × 0.25 × 0.20 mm^3 was mounted on a mylar loop with oil. Data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 110 K. Data were measured using ϕ and ω scans with Mo K_α radiation. . The maximum resolution that was achieved was Θ = 27.092° (0.78 Å). The unit cell was refined using SAINT V8.40B (Bruker, 2016) on 9968 reflections, 13% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using SAINT V8.40B (Bruker, 2016). The final completeness is 99.90 % out to 27.092° in Θ. SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. wR_2(int) was 0.0582 before and 0.0510 after correction. The Ratio of minimum to maximum transmission is 0.9333. The absorption coefficient μ of this material is 0.114 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.696 and 0.746.

The structure was solved and the space group $P2_1/c$ (# 14) determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using using iterative methods and refined by full matrix least squares minimisation on $\boldsymbol{F^2}$ using version 2019/3 of ShelXL (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. One diethylether was found disordered in several positions. Two main positions were defined with occupation factors converged to 0.75:0.25. The diethylether minor part atoms were isotropically refined and geometric. Constraints (SADI, SIMU) have been applied.

Table CD20: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **6b.** U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
F4	8775.8(11)	-714.5(13)	3225.9(7)	37.2(4)
F1	5372.8(11)	5922.0(13)	4185.8(7)	36.6(4)
F3	5221.3(11)	3898.1(12)	3318.6(8)	36.6(4)
F6	4623.6(11)	2866.7(14)	4580.6(7)	40.1(4)
F5	9869.2(11)	1174.4(14)	5687.3(7)	40.9(4)
F2	10163.1(12)	3837.1(14)	3458.9(9)	47.8(5)
N5	7042.6(15)	271.8(17)	4115.8(9)	26.3(5)
N7	8496.8(15)	1004.1(18)	3984.6(9)	28.8(5)
N4	6726.5(16)	4011.2(17)	2747.8(10)	27.3(5)
N6	7254.3(15)	493.2(17)	4739.3(9)	27.3(5)
N8	8677.9(15)	1280.0(18)	4587.8(9)	28.9(5)
N2	7633.7(15)	2593.8(17)	3193.1(10)	27.3(5)
N3	7471.3(16)	4623.3(17)	2916.8(10)	27.9(5)
N1	8376.0(16)	3197.3(17)	3359.3(10)	28.9(5)
N12	7138.2(17)	3965.5(18)	4224.8(10)	32.2(5)
N11	6904.5(17)	3098.4(18)	4495.5(11)	32.6(5)
N9	6542.9(18)	4079.1(19)	5339.8(10)	35.8(6)
N10	6796.1(18)	4935.5(19)	5076.1(10)	35.3(6)
C27	7433.1(18)	333.8(19)	3064.2(11)	22.8(5)
C22	6650.7(18)	732.0(19)	2640.5(11)	22.7(5)
C28	7654.4(18)	559.4(19)	3760.9(11)	22.8(5)
C2	6962.4(19)	5818(2)	4106.7(11)	25.7(6)
C41	6025.4(18)	2307(2)	5222.5(11)	24.2(6)
C42	6500.1(17)	3208(2)	5000.0(11)	24.1(6)
C7	7717.6(19)	6232(2)	3870.9(12)	27.2(6)
C23	6529.0(19)	470(2)	1996.3(11)	26.2(6)
C30	8236.3(18)	1414(2)	5617.5(11)	25.0(6)
C21	5888.2(17)	1351(2)	2846.2(11)	22.7(5)
C29	8037.2(18)	1038(2)	4946.5(11)	24.2(6)
C36	6497.8(19)	1603(2)	5665.4(11)	26.0(6)
C20	5040.9(18)	846(2)	2840.6(11)	26.6(6)
C1	6972.1(18)	4859(2)	4482.5(11)	24.0(6)

Atom	x	y	z	U_{eq}
C16	5947.8(18)	2420(2)	2983.0(11)	24.2(6)
C26	8039.2(18)	-300(2)	2814.0(12)	26.6(6)
C8	8690.3(19)	5789(2)	3991.4(12)	29.1(6)
C24	7155(2)	-173(2)	1768.8(12)	29.8(6)
C19	4269.8(19)	1355(2)	2984.0(12)	28.8(6)
C35	7519.5(18)	1725(2)	5937.8(11)	24.9(6)
C15	6799.3(18)	3047(2)	2989.6(11)	24.4(6)
C17	5159.4(19)	2888(2)	3141.1(12)	27.7(6)
C40	5070.6(19)	2166(2)	5003.2(12)	29.7(6)
C25	7917(2)	-577(2)	2183.6(12)	30.3(6)
C3	6108.9(19)	6338(2)	3971.3(12)	29.1(6)
C14	8222.4(19)	4219(2)	3309.7(12)	26.4(6)
C18	4331.0(19)	2386(2)	3147.0(12)	29.8(6)
C13	8937.3(19)	4899(2)	3684.2(12)	28.8(6)
C31	9156.0(19)	1520(2)	5953.0(12)	30.0(6)
C34	7753(2)	2162(2)	6543.3(12)	29.9(6)
C37	5995(2)	808(2)	5885.6(13)	32.9(6)
C33	8675(2)	2285(2)	6842.8(12)	33.6(7)
C32	9389(2)	1947(2)	6551.6(12)	33.3(6)
C6	7589(2)	7160(2)	3534.3(13)	34.7(7)
C39	4573(2)	1366(2)	5209.4(13)	34.5(7)
C12	9889(2)	4643(2)	3779.8(14)	35.4(7)
C4	5969(2)	7239(2)	3623.2(13)	36.6(7)
C9	9392(2)	6346(2)	4391.8(13)	36.8(7)
C38	5046(2)	695(2)	5659.5(13)	35.6(7)
C5	6729(2)	7654(2)	3412.0(13)	39.1(7)
C11	10580(2)	5193(3)	4174.3(15)	42.5(8)
C10	10327(2)	6043(3)	4491.0(15)	42.3(8)
O1	8132(3)	6886(3)	1502.0(16)	66.9(9)
C46	7788(4)	7519(4)	491(3)	58.6(13)
C45	8076(4)	6616(5)	882(3)	72.3(12)
C43	9501(6)	6098(6)	2107(4)	91.5(19)
C44	8542(4)	6122(5)	1946(3)	77.9(12)
C43B	9582(19)	5730(20)	2261(9)	83(3)
C44B	9547(12)	6184(15)	1683(8)	78(2)
O1B	8682(9)	6470(10)	1356(5)	75.5(13)
C45B	8771(13)	6706(14)	759(7)	76(2)
C46B	8032(14)	7126(16)	351(9)	76(3)

Table CD21: Anisotropic Displacement Parameters (×10[4]) for **6b.** The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F4	34.7(9)	42.8(10)	32.7(8)	3.7(7)	3.0(7)	15.1(8)
F1	30.0(9)	43.6(10)	36.0(8)	-5.5(7)	6.0(7)	4.0(7)
F3	38.9(10)	25.5(9)	48.5(9)	-6.3(7)	16.1(8)	3.7(7)
F6	31.6(9)	53.4(11)	33.3(8)	4.4(8)	1.1(7)	-0.7(8)
F5	31.3(9)	61.4(12)	28.4(8)	-7.7(8)	2.1(7)	13.8(8)
F2	34.9(10)	40.3(11)	73.3(12)	-4.6(9)	22.9(9)	-0.7(8)
N5	29.7(12)	26.5(12)	23.3(10)	0.5(9)	6.1(9)	0.0(10)
N7	30.3(13)	34.9(13)	20.9(10)	2.0(9)	4.4(9)	-1.3(10)
N4	32.4(13)	24.9(12)	25.8(11)	-0.2(9)	8.8(9)	-1.2(10)
N6	32.1(13)	28.6(13)	22.1(10)	-0.6(9)	7.3(9)	0.0(10)
N8	30.8(13)	35.7(14)	19.9(10)	2.9(9)	4.0(9)	-2.0(10)
N2	27.9(12)	24.4(12)	30.8(11)	-2.3(9)	9.2(9)	-2.0(10)
N3	33.1(13)	24.9(12)	27.6(11)	0.8(9)	10.6(10)	-1.7(10)
N1	30.3(13)	26.9(13)	31.8(12)	0.5(10)	11.5(10)	-4.2(10)
N12	42.7(14)	25.2(13)	33.2(12)	7.4(10)	18.4(10)	4.4(11)
N11	41.8(14)	26.9(13)	34.0(12)	7.8(10)	19.2(11)	6.3(11)
N9	50.5(16)	34.8(14)	23.8(11)	-1.8(10)	11.6(10)	-14.8(12)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N10	47.7(15)	36.3(14)	23.8(11)	-3.9(10)	11.0(10)	-12.5(12)
C27	27.4(14)	20.7(13)	21.4(11)	1.9(10)	7.8(10)	0.4(11)
C22	26.3(14)	19.1(13)	23.8(12)	1.5(10)	7.4(10)	-2.5(11)
C28	25.6(14)	20.2(13)	22.6(12)	2.9(10)	4.6(10)	2.6(11)
C2	34.3(15)	21.9(14)	19.6(11)	-3.2(10)	2.4(10)	-0.4(11)
C41	27.0(14)	27.1(14)	20.9(12)	-3.5(10)	10.0(10)	-1.3(11)
C42	22.8(13)	30.6(15)	17.9(11)	3.4(10)	1.6(10)	3.1(11)
C7	38.1(16)	19.7(14)	24.7(12)	-2.9(10)	8.0(11)	-6.1(12)
C23	29.5(14)	26.0(14)	22.9(12)	2.7(10)	4.5(10)	0.0(12)
C30	30.9(15)	23.6(14)	20.6(12)	4.0(10)	5.5(10)	2.5(11)
C21	25.3(14)	23.4(14)	18.8(11)	0.5(10)	3.0(10)	0.0(11)
C29	26.4(14)	23.9(14)	22.3(12)	3.1(10)	4.8(10)	4.3(11)
C36	33.4(15)	25.0(14)	22.4(12)	-2.3(10)	12.1(11)	-2.6(12)
C20	31.0(15)	23.8(14)	24.4(12)	1.1(10)	4.4(11)	-0.6(11)
C1	23.4(14)	26.3(14)	21.6(12)	-0.5(10)	2.6(10)	-2.1(11)
C16	25.1(14)	24.9(14)	22.7(12)	-1.5(10)	4.9(10)	0.8(11)
C26	26.4(14)	26.8(15)	26.2(12)	4.8(11)	3.9(11)	5.6(11)
C8	32.9(15)	25.6(15)	29.8(13)	6.1(11)	9.0(11)	-7.1(12)
C24	41.9(17)	28.1(15)	20.9(12)	-0.5(11)	9.9(11)	-0.1(13)
C19	27.6(15)	33.1(16)	26.0(13)	2.2(11)	5.7(11)	-3.0(12)
C35	31.9(15)	21.8(14)	22.2(12)	3.7(10)	8.0(10)	0.4(11)
C15	31.0(15)	22.8(14)	21.2(12)	-1.9(10)	9.2(10)	2.8(11)
C17	32.9(15)	21.3(14)	29.1(13)	-2.3(11)	6.9(11)	3.1(12)
C40	29.2(15)	37.3(16)	22.9(12)	-2.7(11)	5.6(11)	-0.6(13)
C25	35.7(16)	30.3(15)	27.9(13)	0.9(11)	13.6(12)	5.2(13)
C3	34.3(16)	27.3(15)	25.1(12)	-5.4(11)	4.1(11)	0.0(12)
C14	31.7(15)	24.2(14)	26.9(13)	2.1(11)	14.5(11)	-2.8(12)
C18	29.1(15)	33.2(16)	28.4(13)	0.8(12)	8.5(11)	6.0(12)
C13	28.5(15)	28.1(15)	32.0(13)	3.8(11)	11.4(11)	-6.3(12)
C31	31.8(15)	32.0(15)	26.4(13)	0.7(11)	6.0(11)	8.4(12)
C34	36.9(16)	30.2(15)	24.9(13)	0.4(11)	11.9(11)	1.0(13)
C37	39.1(17)	28.4(15)	34.3(14)	3.0(12)	15.2(13)	-0.6(13)
C33	43.6(18)	34.6(16)	22.4(13)	-1.7(11)	6.0(12)	1.9(14)
C32	34.9(16)	38.7(17)	24.3(13)	-1.2(12)	1.0(11)	3.4(13)
C6	47.5(18)	24.4(15)	32.4(14)	-1.2(12)	8.0(13)	-6.1(13)
C39	30.6(15)	41.5(18)	33.8(14)	-12.7(13)	12.3(12)	-10.7(13)
C12	33.3(16)	29.6(16)	45.0(16)	5.6(13)	11.6(13)	-4.0(13)
C4	47.7(18)	28.5(16)	29.7(14)	-7.8(12)	-2.3(13)	12.1(14)
C9	44.1(18)	28.6(16)	37.9(15)	1.5(12)	8.7(13)	-13.4(14)
C38	41.8(18)	32.6(16)	37.4(15)	-4.4(13)	20.6(13)	-9.6(14)
C5	61(2)	21.7(15)	31.9(15)	-1.6(12)	1.7(14)	3.2(14)
C11	30.9(17)	42.7(19)	53.8(19)	10.1(15)	8.1(14)	-8.6(14)
C10	39.1(18)	41.4(19)	44.3(17)	7.0(15)	3.1(14)	-16.1(15)
O1	83.4(19)	62.2(17)	54.5(16)	2.3(14)	12.1(15)	9.2(16)
C46	60(3)	52(3)	65(3)	6(2)	14(2)	-5(2)
C45	84(2)	69(2)	60.5(19)	-0.1(18)	6.6(18)	6.1(19)
C43	94(3)	88(4)	83(3)	3(3)	-4(3)	-15(3)
C44	83(2)	77(2)	71(2)	15.6(18)	11.4(18)	4.4(19)

Table CD22: Bond Lengths in Å for **6b.**

Atom	Atom	Length/Å
F4	C26	1.357(3)
F1	C3	1.354(3)
F3	C17	1.361(3)
F6	C40	1.355(3)
F5	C31	1.350(3)
F2	C12	1.351(3)
N5	N6	1.340(3)
N5	C28	1.329(3)

Atom	Atom	Length/Å
N7	N8	1.315(3)
N7	C28	1.352(3)
N4	N3	1.333(3)
N4	C15	1.348(3)
N6	C29	1.339(3)
N8	C29	1.352(3)
N2	N1	1.323(3)
N2	C15	1.341(3)

Atom	Atom	Length/Å
N3	C14	1.347(3)
N1	C14	1.343(3)
N12	N11	1.337(3)
N12	C1	1.324(3)
N11	C42	1.332(3)
N9	N10	1.328(3)
N9	C42	1.338(3)
N10	C1	1.346(3)
C27	C22	1.406(3)
C27	C28	1.491(3)
C27	C26	1.384(4)
C22	C23	1.396(3)
C22	C21	1.500(3)
C2	C7	1.399(4)
C2	C1	1.479(4)
C2	C3	1.390(4)
C41	C42	1.480(4)
C41	C36	1.395(4)
C41	C40	1.386(4)
C7	C8	1.499(4)
C7	C6	1.395(4)
C23	C24	1.389(4)
C30	C29	1.489(3)
C30	C35	1.411(4)
C30	C31	1.394(4)
C21	C20	1.391(4)
C21	C16	1.415(4)
C36	C35	1.493(4)
C36	C37	1.396(4)
C20	C19	1.384(4)
C16	C15	1.477(4)
C16	C17	1.393(4)
C26	C25	1.373(3)
C8	C13	1.408(4)
C8	C9	1.397(4)
C24	C25	1.379(4)
C19	C18	1.379(4)
C35	C34	1.393(3)
C17	C18	1.369(4)
C40	C39	1.383(4)
C3	C4	1.379(4)
C14	C13	1.474(4)
C13	C12	1.396(4)
C31	C32	1.375(4)
C34	C33	1.376(4)
C37	C38	1.377(4)
C33	C32	1.379(4)
C6	C5	1.382(4)
C39	C38	1.377(4)
C12	C11	1.378(4)
C4	C5	1.379(4)
C9	C10	1.389(4)
C11	C10	1.379(5)
O1	C45	1.358(6)
O1	C44	1.419(6)
C46	C45	1.452(7)
C43	C44	1.369(10)
C43B	C44B	1.359(18)
C44B	O1B	1.365(15)
O1B	C45B	1.342(15)
C45B	C46B	1.359(16)

Table CD23: Bond Angles in ° for **6b**.

Atom	Atom	Atom	Angle/°
C28	N5	N6	117.3(2)
N8	N7	C28	117.2(2)
N3	N4	C15	116.6(2)
C29	N6	N5	117.3(2)
N7	N8	C29	117.7(2)
N1	N2	C15	117.8(2)
N4	N3	C14	117.0(2)
N2	N1	C14	116.6(2)
C1	N12	N11	118.2(2)
C42	N11	N12	116.7(2)
N10	N9	C42	117.5(2)
N9	N10	C1	117.2(2)
C22	C27	C28	124.2(2)
C26	C27	C22	117.6(2)
C26	C27	C28	118.2(2)
C27	C22	C21	123.8(2)
C23	C22	C27	118.5(2)
C23	C22	C21	117.4(2)
N5	C28	N7	125.2(2)
N5	C28	C27	118.5(2)
N7	C28	C27	116.2(2)
C7	C2	C1	126.3(2)
C3	C2	C7	117.9(2)
C3	C2	C1	115.7(2)
C36	C41	C42	122.4(2)
C40	C41	C42	119.5(2)
C40	C41	C36	118.1(2)
N11	C42	N9	123.2(2)
N11	C42	C41	118.8(2)
N9	C42	C41	117.8(2)
C2	C7	C8	124.7(2)
C6	C7	C2	118.7(3)
C6	C7	C8	116.5(2)
C24	C23	C22	121.7(2)
C35	C30	C29	122.5(2)
C31	C30	C29	121.0(2)
C31	C30	C35	116.4(2)
C20	C21	C22	116.6(2)
C20	C21	C16	118.7(2)
C16	C21	C22	124.4(2)
N6	C29	N8	124.6(2)
N6	C29	C30	119.0(2)
N8	C29	C30	116.4(2)
C41	C36	C35	121.1(2)
C41	C36	C37	119.4(3)
C37	C36	C35	119.4(2)
C19	C20	C21	121.7(2)
N12	C1	N10	122.7(2)

Atom	Atom	Atom	Angle/°
N12	C1	C2	119.5(2)
N10	C1	C2	117.8(2)
C21	C16	C15	123.9(2)
C17	C16	C21	117.1(2)
C17	C16	C15	118.9(2)
F4	C26	C27	117.6(2)
F4	C26	C25	117.9(2)
C25	C26	C27	124.3(2)
C13	C8	C7	123.4(2)
C9	C8	C7	117.2(3)
C9	C8	C13	119.2(3)
C25	C24	C23	120.0(2)
C18	C19	C20	120.2(3)
C30	C35	C36	123.4(2)
C34	C35	C30	119.9(2)
C34	C35	C36	116.7(2)
N4	C15	C16	120.2(2)
N2	C15	N4	122.0(2)
N2	C15	C16	117.6(2)
F3	C17	C16	118.2(2)
F3	C17	C18	117.7(2)
C18	C17	C16	124.1(2)
F6	C40	C41	117.1(2)
F6	C40	C39	120.2(2)
C39	C40	C41	122.7(3)
C26	C25	C24	117.8(2)
F1	C3	C2	117.8(2)
F1	C3	C4	118.5(3)
C4	C3	C2	123.7(3)
N3	C14	C13	120.4(2)
N1	C14	N3	122.3(2)
N1	C14	C13	117.2(2)
C17	C18	C19	118.1(3)
C8	C13	C14	121.8(2)
C12	C13	C8	117.4(3)
C12	C13	C14	120.6(3)
F5	C31	C30	119.1(2)
F5	C31	C32	117.1(2)
C32	C31	C30	123.8(2)
C33	C34	C35	121.3(2)
C38	C37	C36	120.9(3)
C34	C33	C32	120.0(2)
C31	C32	C33	118.5(3)
C5	C6	C7	121.5(3)
C38	C39	C40	118.4(3)
F2	C12	C13	119.3(3)
F2	C12	C11	117.3(3)
C11	C12	C13	123.3(3)
C3	C4	C5	117.6(3)
C10	C9	C8	121.4(3)
C37	C38	C39	120.5(3)
C4	C5	C6	120.5(3)
C12	C11	C10	118.8(3)
C11	C10	C9	119.8(3)
C45	O1	C44	114.3(4)
O1	C45	C46	108.1(5)
C43	C44	O1	117.2(6)
C43B	C44B	O1B	116.9(18)
C45B	O1B	C44B	107.5(13)
O1B	C45B	C46B	119.5(17)

Table CD24: Torsion Angles in ° for **6b**.

Atom	Atom	Atom	Atom	Angle/°
F4	C26	C25	C24	178.5(2)
F1	C3	C4	C5	179.6(2)
F3	C17	C18	C19	-178.3(2)
F6	C40	C39	C38	-177.3(2)
F5	C31	C32	C33	-178.5(2)
F2	C12	C11	C10	177.7(3)
N5	N6	C29	N8	-7.7(4)
N5	N6	C29	C30	172.4(2)
N7	N8	C29	N6	3.5(4)
N7	N8	C29	C30	-176.6(2)
N4	N3	C14	N1	22.9(3)
N4	N3	C14	C13	-159.9(2)
N6	N5	C28	N7	4.0(4)
N6	N5	C28	C27	-179.4(2)
N8	N7	C28	N5	-8.2(4)
N8	N7	C28	C27	175.1(2)
N2	N1	C14	N3	-23.1(3)
N2	N1	C14	C13	159.6(2)
N3	N4	C15	N2	-22.9(3)
N3	N4	C15	C16	162.7(2)
N3	C14	C13	C8	42.2(4)
N3	C14	C13	C12	-141.9(3)
N1	N2	C15	N4	22.8(3)
N1	N2	C15	C16	-162.6(2)
N1	C14	C13	C8	-140.5(3)
N1	C14	C13	C12	35.4(3)

Atom	Atom	Atom	Atom	Angle/°
N12	N11	C42	N9	-18.1(4)
N12	N11	C42	C41	165.6(2)
N11	N12	C1	N10	16.4(4)
N11	N12	C1	C2	-162.7(2)
N9	N10	C1	N12	-17.7(4)
N9	N10	C1	C2	161.3(2)
N10	N9	C42	N11	16.8(4)
N10	N9	C42	C41	-166.9(2)
C27	C22	C23	C24	0.3(4)
C27	C22	C21	C20	-104.5(3)
C27	C22	C21	C16	81.8(3)
C27	C26	C25	C24	2.0(4)
C22	C27	C28	N5	61.8(3)
C22	C27	C28	N7	-121.3(3)
C22	C27	C26	F4	-177.7(2)
C22	C27	C26	C25	-1.2(4)
C22	C23	C24	C25	0.5(4)
C22	C21	C20	C19	-176.1(2)
C22	C21	C16	C15	-5.0(4)
C22	C21	C16	C17	177.2(2)
C28	N5	N6	C29	3.8(3)
C28	N7	N8	C29	4.2(3)
C28	C27	C22	C23	179.3(2)
C28	C27	C22	C21	-6.3(4)
C28	C27	C26	F4	3.0(4)
C28	C27	C26	C25	179.5(3)
C2	C7	C8	C13	75.7(3)
C2	C7	C8	C9	-109.6(3)
C2	C7	C6	C5	-2.3(4)
C2	C3	C4	C5	-1.5(4)
C41	C36	C35	C30	-80.7(3)
C41	C36	C35	C34	100.0(3)
C41	C36	C37	C38	1.7(4)
C41	C40	C39	C38	1.2(4)
C42	N9	N10	C1	1.2(4)
C42	C41	C36	C35	-0.2(4)
C42	C41	C36	C37	175.9(2)
C42	C41	C40	F6	1.1(3)
C42	C41	C40	C39	-177.4(2)
C7	C2	C1	N12	-62.3(4)
C7	C2	C1	N10	118.6(3)
C7	C2	C3	F1	178.3(2)
C7	C2	C3	C4	-0.6(4)
C7	C8	C13	C14	-11.8(4)
C7	C8	C13	C12	172.2(2)
C7	C8	C9	C10	-174.7(2)
C7	C6	C5	C4	0.2(4)
C23	C22	C21	C20	70.0(3)
C23	C22	C21	C16	-103.7(3)
C23	C24	C25	C26	-1.6(4)
C30	C35	C34	C33	-0.9(4)
C30	C31	C32	C33	0.5(4)
C21	C22	C23	C24	-174.5(2)
C21	C20	C19	C18	-1.0(4)
C21	C16	C15	N4	140.1(2)
C21	C16	C15	N2	-34.6(3)
C21	C16	C17	F3	175.4(2)
C21	C16	C17	C18	-2.6(4)
C29	C30	C35	C36	6.9(4)
C29	C30	C35	C34	-173.9(2)
C29	C30	C31	F5	-7.0(4)

Atom	Atom	Atom	Atom	Angle/˚
C29	C30	C31	C32	174.0(3)
C36	C41	C42	N11	88.9(3)
C36	C41	C42	N9	-87.6(3)
C36	C41	C40	F6	179.0(2)
C36	C41	C40	C39	0.5(4)
C36	C35	C34	C33	178.5(3)
C36	C37	C38	C39	0.1(4)
C20	C21	C16	C15	-178.6(2)
C20	C21	C16	C17	3.7(3)
C20	C19	C18	C17	2.1(4)
C1	N12	N11	C42	1.4(4)
C1	C2	C7	C8	-3.3(4)
C1	C2	C7	C6	-178.8(2)
C1	C2	C3	F1	-0.6(3)
C1	C2	C3	C4	-179.5(2)
C16	C21	C20	C19	-2.0(4)
C16	C17	C18	C19	-0.3(4)
C26	C27	C22	C23	0.0(4)
C26	C27	C22	C21	174.4(2)
C26	C27	C28	N5	-118.9(3)
C26	C27	C28	N7	58.0(3)
C8	C7	C6	C5	-178.1(2)
C8	C13	C12	F2	-175.4(2)
C8	C13	C12	C11	2.5(4)
C8	C9	C10	C11	2.1(4)
C35	C30	C29	N6	-34.5(4)
C35	C30	C29	N8	145.6(2)
C35	C30	C31	F5	175.9(2)
C35	C30	C31	C32	-3.1(4)
C35	C36	C37	C38	177.9(2)
C35	C34	C33	C32	-1.9(4)
C15	N4	N3	C14	0.2(3)
C15	N2	N1	C14	0.2(3)
C15	C16	C17	F3	-2.4(3)
C15	C16	C17	C18	179.5(2)
C17	C16	C15	N4	-42.2(3)
C17	C16	C15	N2	143.1(2)
C40	C41	C42	N11	-93.3(3)
C40	C41	C42	N9	90.2(3)
C40	C41	C36	C35	-178.1(2)
C40	C41	C36	C37	-1.9(4)
C40	C39	C38	C37	-1.5(4)
C3	C2	C7	C8	177.9(2)
C3	C2	C7	C6	2.4(4)
C3	C2	C1	N12	116.5(3)
C3	C2	C1	N10	-62.6(3)
C3	C4	C5	C6	1.6(4)
C14	C13	C12	F2	8.5(4)
C14	C13	C12	C11	-173.6(3)
C13	C8	C9	C10	0.2(4)
C13	C12	C11	C10	-0.2(4)
C31	C30	C29	N6	148.5(3)
C31	C30	C29	N8	-31.3(4)
C31	C30	C35	C36	-176.0(2)
C31	C30	C35	C34	3.2(4)
C34	C33	C32	C31	2.1(4)
C37	C36	C35	C30	103.1(3)
C37	C36	C35	C34	-76.2(3)
C6	C7	C8	C13	-108.8(3)
C6	C7	C8	C9	65.9(3)
C12	C11	C10	C9	-2.1(4)

Atom	Atom	Atom	Atom	Angle/°
C9	C8	C13	C14	173.6(2)
C9	C8	C13	C12	-2.4(4)
C45	O1	C44	C43	84.1(7)
C44	O1	C45	C46	-171.0(5)
C43B	C44B	O1B	C45B	-168.0(19)
C44B	O1B	C45B	C46B	-172.8(18)

Table CD25: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **6b.** U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

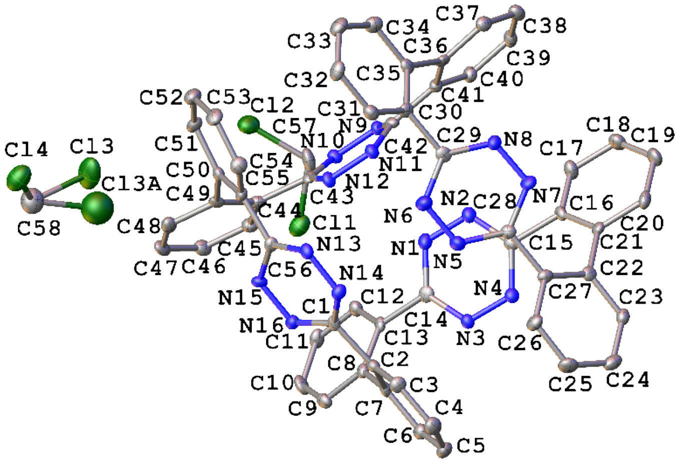
Atom	x	y	z	U_{eq}
H23	6004.27	738.14	1706.15	31
H20	4990.19	133.01	2735.6	32
H24	7058.98	-334.69	1327.57	36
H19	3696.89	993.21	2970.04	35
H25	8343.81	-1031.35	2037.83	36
H18	3813.13	2738.2	3260.24	36
H34	7267	2378.36	6753.53	36
H37	6312.61	339.47	6195.76	39
H33	8820.47	2603.25	7250.35	40
H32	10026.85	2008.01	6760	40
H6	8103.84	7459.55	3385.87	42
H39	3921.21	1281.43	5044.55	41
H4	5371.15	7563.15	3532.1	44
H9	9226.25	6945.81	4600.69	44
H38	4715.03	149.88	5815.13	43
H5	6659.92	8284.03	3180.46	47
H11	11220.01	4991.4	4227.07	51
H10	10789.82	6418.73	4776.24	51
H46A	7705.77	7331.47	39.54	88
H46B	8270.66	8055.5	589.59	88
H46C	7193.06	7780.98	579.66	88
H45	8203.28	5951.8	730.55	87
H43A	9755.38	5779.77	1760.51	137
H43B	9692.98	5692.52	2497.64	137
H43C	9742.64	6802.95	2178.04	137
H44	8165.48	5646.79	2123.73	93
H43D	9268.55	5058.07	2202.08	124
H43E	9264.05	6171.98	2524.94	124
H43F	10238.9	5635.89	2471.41	124
H44B	10098.51	6295.47	1515.49	94
H45B	9346.57	6579.97	623.77	91
H46D	7938.22	6757.54	-57.06	114
H46E	8160.17	7855.24	281.96	114
H46F	7464.5	7066.84	532.73	114

Table CD26: Atomic Occupancies for all atoms that are not fully occupied in **6b**.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
O1	0.75	H43B	0.75	H44B	0.25
C46	0.75	H43C	0.75	O1B	0.25
H46A	0.75	C44	0.75	C45B	0.25
H46B	0.75	H44	0.75	H45B	0.25
H46C	0.75	C43B	0.25	C46B	0.25
C45	0.75	H43D	0.25	H46D	0.25
H45	0.75	H43E	0.25	H46E	0.25
C43	0.75	H43F	0.25	H46F	0.25
H43A	0.75	C44B	0.25		

Compound 8a

R_1=7.49%



Experimental. Single clear light red prism-shaped crystals of **8a** crystallized from a mixture of dichloromethane and pentane by slow evaporation. A suitable crystal with dimensions 0.20 × 0.15 × 0.10 mm^3 was selected and mounted on a mylar loop with oil on a Bruker Kappa Apex II diffractometer. The crystal was kept at a steady T = 115 K during data collection. The structure was solved with the ShelXT (Sheldrick, 2015) solution program using dual methods and by using Olex2 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2019/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2.

Crystal Data. $C_{58}H_{36}Cl_4N_{16}$, M_r = 1098.83, monoclinic, $P2_1/c$ (No. 14), a = 12.5323(12) Å, b = 26.102(3) Å, c = 15.6284(15) Å, β = 101.219(3)°, α = γ = 90°, V = 5014.6(8) Å^3, T = 115 K, Z = 4, Z' = 1, μ(Mo K_α) = 0.296, 74552 reflections measured, 8869 unique (R_{int} = 0.0936) which were used in all calculations. The final wR_2 was 0.1460 (all data) and R_1 was 0.0749 (I≥2 σ(I)).

Compound	**8a**
Formula	$C_{58}H_{36}Cl_4N_{16}$
$D_{calc.}$/ g cm^{-3}	1.455
μ/mm^{-1}	0.296
Formula Weight	1098.83
Colour	clear light red
Shape	prism-shaped
Size/mm^3	0.20×0.15×0.10
T/K	115
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	12.5323(12)
b/Å	26.102(3)
c/Å	15.6284(15)
α/°	90
β/°	101.219(3)
γ/°	90
V/Å^3	5014.6(8)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K_α
Θ_{min}/°	2.445
Θ_{max}/°	25.077
Measured Refl's.	74552
Indep't Refl's	8869
Refl's I≥2 σ(I)	6248
R_{int}	0.0936
Parameters	708
Restraints	1
Largest Peak	0.427
Deepest Hole	-0.483
GooF	1.171
wR_2 (all data)	0.1460
wR_2	0.1225
R_1 (all data)	0.1226
R_1	0.0749

A clear light red prism-shaped-shaped crystal with dimensions 0.20 × 0.15 × 0.10 mm^3 was mounted on a mylar loop with oil. Data were collected using a Bruker Kappa Apex II diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 115 K.

Data were measured using ϕ and ω scans with Mo K_α radiation. . The maximum resolution that was achieved was Θ = 25.077° (0.84 Å). The unit cell was refined using SAINT V8.40B (Bruker, 2016) on 5142 reflections, 7% of the observed reflections. Data reduction, scaling and absorption corrections were performed using SAINT V8.40B (Bruker, 2016). The final completeness is 99.70 % out to 25.077° in Θ. SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. wR_2(int) was 0.0627 before and 0.0581 after correction. The Ratio of minimum to maximum transmission is 0.9534. The absorption coefficient μ of this material is 0.296 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.711 and 0.745.

The structure was solved and the space group $P2_1/c$ (# 14) determined by the ShelXT (Sheldrick, 2015) structure solution program using using dual methods and refined by full matrix least squares minimisation on $\boldsymbol{F^2}$ using version 2019/3 of ShelXL 2019/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. One chloride atom was found disordered over two positions with occupations factors converged to 0.88 :0.12.

Table CD27: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **8a.** U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
C1	5037(3)	7732.3(16)	5388(3)	12.9(9)
N1	3863(3)	7243.2(14)	2722(2)	18.2(8)
C2	4815(3)	8258.0(16)	5041(3)	14.6(9)
N2	2805(3)	7201.8(14)	2369(2)	17.9(8)
C3	4169(3)	8576.0(16)	5459(3)	16.8(10)
N3	3655(3)	8144.5(13)	2838(2)	14.2(8)
C4	3974(4)	9081.1(18)	5202(3)	21.7(10)
N4	2617(3)	8107.4(13)	2458(2)	15.5(8)
C5	4424(4)	9279.9(18)	4525(3)	22.9(11)
N5	1966(3)	7575.8(14)	4461(2)	20.8(9)
C6	5059(4)	8966.3(17)	4107(3)	18.3(10)
N6	2116(3)	7096.6(14)	4751(2)	22.4(9)
C7	5252(3)	8453.3(16)	4349(3)	14.2(9)
N7	343(3)	7323.2(14)	3485(2)	17.7(8)
C8	5922(3)	8137.8(16)	3841(3)	13.9(9)
N8	527(3)	6836.5(13)	3747(2)	15.9(8)
C9	7032(4)	8214.9(17)	3984(3)	18.1(10)
N9	3900(3)	6021.8(13)	2504(2)	14.6(8)
C10	7683(4)	7928.3(18)	3538(3)	22.1(11)
N10	4942(3)	6083.8(13)	2862(2)	14.5(8)
C11	7235(4)	7556.3(17)	2952(3)	19.6(10)
N11	3400(3)	6311.0(13)	3806(2)	15.3(8)
C12	6117(3)	7478.5(17)	2801(3)	16.8(10)
N12	4447(3)	6370.7(14)	4170(2)	15.5(8)
C13	5445(3)	7772.4(16)	3223(3)	13.3(9)
N13	4442(3)	7043.8(14)	6066(2)	14.7(8)
C14	4253(4)	7715.9(17)	2934(3)	15.1(9)
N14	4303(3)	7528.7(13)	5815(2)	15.5(8)
C15	2227(3)	7636.2(16)	2224(3)	15.3(9)
N15	6147(3)	7030.9(13)	5634(2)	14.8(8)
C16	1076(3)	7589.0(16)	1774(3)	14.0(9)
N16	6000(3)	7514.7(14)	5363(2)	15.7(8)
C17	799(4)	7210.3(18)	1141(3)	20.6(10)

Atom	x	y	z	U_{eq}
C18	-254(4)	7160.0(18)	685(3)	22.8(11)
C19	-1060(4)	7488.3(18)	851(3)	21.9(10)
C20	-806(4)	7862.7(17)	1485(3)	18.6(10)
C21	254(3)	7919.9(16)	1959(3)	14.5(9)
C22	485(3)	8321.7(16)	2642(3)	15.1(9)
C23	322(3)	8834.0(17)	2404(3)	17.8(10)
C24	653(4)	9225.8(18)	2995(3)	22.3(11)
C25	1131(4)	9109.5(17)	3844(3)	22.8(11)
C26	1266(4)	8603.8(16)	4109(3)	18.4(10)
C27	928(3)	8207.6(16)	3525(3)	14.4(9)
C28	1092(3)	7671.5(16)	3834(3)	14.1(9)
C29	1413(3)	6740.9(16)	4359(3)	14.7(9)
C30	1577(3)	6210.5(16)	4686(3)	14.6(9)
C31	1813(3)	6135.8(17)	5577(3)	18.0(10)
C32	1907(4)	5645.7(17)	5931(3)	20.3(10)
C33	1771(4)	5228.3(18)	5382(3)	23.8(11)
C34	1556(4)	5299.2(18)	4481(3)	20.9(10)
C35	1471(3)	5787.6(16)	4120(3)	14.0(9)
C36	1247(3)	5825.9(15)	3142(3)	14.2(9)
C37	211(4)	5675.6(16)	2702(3)	17.8(10)
C38	-63(4)	5663.8(17)	1804(3)	20.1(10)
C39	696(4)	5805.9(17)	1308(3)	19.3(10)
C40	1722(4)	5949.7(17)	1729(3)	18.1(10)
C41	2014(3)	5960.4(16)	2637(3)	13.8(9)
C42	3155(3)	6093.5(15)	3018(3)	13.2(9)
C43	5186(3)	6212.1(15)	3705(3)	12.8(9)
C44	6346(4)	6203.1(16)	4135(3)	15.9(9)
C45	7122(4)	6317.8(16)	3621(3)	18.0(10)
C46	8219(4)	6308.6(17)	3968(3)	20.0(10)
C47	8566(4)	6190.4(17)	4839(3)	21.4(10)
C48	7815(4)	6072.3(17)	5361(3)	20.0(10)
C49	6699(3)	6082.0(16)	5019(3)	14.2(9)
C50	5961(3)	5907.5(16)	5605(3)	14.1(9)
C51	5901(4)	5379.2(16)	5737(3)	19.0(10)
C52	5273(4)	5181.8(18)	6288(3)	24.0(11)
C53	4691(4)	5502.5(17)	6733(3)	21.4(10)
C54	4730(4)	6025.0(17)	6608(3)	18.6(10)
C55	5355(3)	6234.8(16)	6044(3)	14.8(9)
C56	5310(3)	6793.0(16)	5888(3)	13.4(9)
Cl4	7855.3(13)	5324.8(6)	9686.1(9)	42.9(4)
C58	8400(5)	5504(2)	8779(4)	41.1(14)
Cl1	7480.7(11)	6365.1(5)	1401.9(8)	29.9(3)
Cl2	7210.4(10)	5301.4(5)	1941.3(9)	32.3(3)
C57	6567(4)	5850.8(19)	1404(3)	26.9(12)
Cl3A	7602(16)	5805(8)	7857(11)	77(6)
Cl3	7438.1(17)	5463.9(8)	7816.4(11)	55.5(5)

Table CD28: Anisotropic Displacement Parameters (×10[4]) for **8a.** The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	13(2)	18(2)	7(2)	-2.4(17)	1.5(17)	2.1(18)
N1	15(2)	20(2)	19(2)	4.5(16)	2.4(16)	0.7(16)
C2	14(2)	16(2)	14(2)	0.5(18)	0.3(18)	-3.4(18)
N2	15(2)	20(2)	19(2)	2.1(16)	2.6(16)	-0.6(16)
C3	18(2)	18(2)	16(2)	-2.2(19)	7.5(19)	1.9(19)
N3	14(2)	17(2)	12.5(18)	-0.3(15)	2.3(15)	-0.2(15)
C4	18(3)	22(3)	26(3)	-4(2)	6(2)	4(2)
N4	14(2)	17(2)	16.0(19)	1.4(15)	4.3(15)	-0.7(16)
C5	25(3)	15(2)	27(3)	2(2)	0(2)	3(2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N5	21(2)	19(2)	20(2)	-0.6(16)	-1.6(17)	-2.8(17)
C6	20(2)	19(2)	15(2)	1.3(19)	0.1(19)	0.0(19)
N6	26(2)	16(2)	23(2)	1.0(17)	0.0(17)	-1.8(17)
C7	10(2)	19(2)	13(2)	-1.9(18)	0.1(17)	1.9(18)
N7	20(2)	15(2)	18(2)	4.7(16)	4.8(16)	-1.5(16)
C8	13(2)	16(2)	13(2)	5.4(18)	2.1(17)	0.7(18)
N8	14(2)	16(2)	17.8(19)	2.5(16)	3.5(15)	0.7(15)
C9	19(2)	21(2)	12(2)	1.2(19)	-0.7(18)	-5(2)
N9	12.3(19)	16.5(19)	14.9(19)	0.8(15)	2.6(15)	-0.8(15)
C10	10(2)	34(3)	22(2)	2(2)	1.9(19)	-2(2)
N10	13.8(19)	16.9(19)	13.4(19)	-0.8(15)	4.0(15)	-2.5(15)
C11	21(3)	23(3)	15(2)	-1.1(19)	4.5(19)	8(2)
N11	12.2(19)	18(2)	15.0(19)	0.3(15)	1.7(15)	-1.3(15)
C12	16(2)	20(2)	14(2)	-0.9(19)	0.8(18)	0.2(19)
N12	11.0(19)	20(2)	15.9(19)	1.0(16)	3.6(15)	-0.4(15)
C13	12(2)	18(2)	10(2)	4.9(18)	1.2(17)	2.0(18)
N13	14(2)	19(2)	10.4(18)	2.4(15)	1.9(15)	-0.7(16)
C14	20(2)	20(2)	6(2)	0.1(18)	5.2(18)	0.8(19)
N14	18(2)	15.4(19)	13.9(19)	1.1(15)	5.7(15)	2.7(16)
C15	17(2)	19(2)	11(2)	-0.3(18)	5.3(18)	-1.9(19)
N15	16(2)	12.3(19)	16.3(19)	-2.7(15)	4.5(15)	-3.9(15)
C16	13(2)	19(2)	9(2)	3.4(18)	-0.6(17)	-2.5(18)
N16	17(2)	14.7(19)	14.4(19)	0.2(15)	1.1(15)	0.4(16)
C17	16(2)	28(3)	17(2)	-1(2)	0.1(19)	2(2)
C18	23(3)	23(3)	21(2)	-5(2)	0(2)	-3(2)
C19	20(3)	27(3)	16(2)	-1(2)	-3.4(19)	-2(2)
C20	15(2)	22(2)	20(2)	7.4(19)	3.4(19)	5.1(19)
C21	17(2)	12(2)	14(2)	4.2(18)	1.3(18)	0.9(18)
C22	11(2)	18(2)	18(2)	0.0(19)	6.9(18)	0.2(18)
C23	15(2)	20(2)	19(2)	4.7(19)	2.9(19)	1.9(19)
C24	24(3)	15(2)	30(3)	3(2)	11(2)	1(2)
C25	28(3)	16(2)	25(3)	-7(2)	7(2)	-1(2)
C26	26(3)	15(2)	14(2)	3.4(19)	4.8(19)	2(2)
C27	16(2)	13(2)	16(2)	-1.7(18)	6.9(18)	0.4(18)
C28	17(2)	16(2)	11(2)	-0.3(18)	5.8(18)	-1.2(18)
C29	15(2)	19(2)	12(2)	-4.5(18)	7.8(18)	1.8(19)
C30	12(2)	14(2)	19(2)	-2.5(18)	6.3(18)	2.9(18)
C31	16(2)	21(2)	17(2)	-2.8(19)	2.2(18)	-1.3(19)
C32	25(3)	24(3)	13(2)	4(2)	4.9(19)	7(2)
C33	27(3)	20(3)	26(3)	8(2)	9(2)	3(2)
C34	22(3)	19(2)	23(3)	-2(2)	8(2)	1(2)
C35	9(2)	18(2)	15(2)	-3.6(18)	3.5(17)	1.7(18)
C36	18(2)	7(2)	18(2)	-1.1(17)	5.7(18)	2.2(17)
C37	15(2)	17(2)	22(2)	-0.5(19)	6.0(19)	0.3(19)
C38	18(2)	20(2)	22(3)	-6(2)	2(2)	0(2)
C39	20(3)	20(2)	16(2)	-1.2(19)	-1.7(19)	4(2)
C40	17(2)	19(2)	17(2)	2.9(19)	1.5(19)	1.0(19)
C41	13(2)	14(2)	15(2)	0.6(18)	2.7(18)	0.7(18)
C42	16(2)	11(2)	13(2)	1.0(17)	2.8(18)	-2.9(18)
C43	12(2)	12(2)	15(2)	5.6(17)	4.3(18)	-1.9(17)
C44	18(2)	13(2)	18(2)	-2.3(18)	6.1(19)	-3.5(18)
C45	19(2)	17(2)	18(2)	0.0(19)	5.2(19)	-2.8(19)
C46	16(2)	21(2)	25(3)	-3(2)	8(2)	-1.3(19)
C47	10(2)	21(3)	32(3)	-5(2)	3(2)	-0.8(19)
C48	20(3)	17(2)	22(3)	-4.5(19)	1(2)	3.3(19)
C49	17(2)	11(2)	15(2)	-5.5(17)	3.0(18)	-1.9(18)
C50	13(2)	16(2)	13(2)	0.4(18)	-0.6(17)	0.5(18)
C51	25(3)	13(2)	18(2)	-0.1(19)	1.8(19)	3.2(19)
C52	24(3)	18(2)	30(3)	5(2)	4(2)	0(2)
C53	22(3)	22(3)	21(2)	10(2)	5(2)	-2(2)
C54	21(3)	21(2)	16(2)	-0.4(19)	7.8(19)	1(2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C55	15(2)	13(2)	15(2)	2.1(18)	0.0(18)	1.3(18)
C56	15(2)	15(2)	10(2)	-2.2(17)	4.1(17)	2.6(18)
Cl4	57.1(10)	37.7(8)	35.8(8)	4.4(6)	13.9(7)	9.7(7)
C58	37(3)	48(4)	40(3)	2(3)	11(3)	4(3)
Cl1	38.9(7)	27.9(7)	24.8(6)	4.6(5)	10.9(5)	5.4(6)
Cl2	27.4(7)	28.2(7)	42.5(8)	2.1(6)	9.8(6)	-5.4(6)
C57	16(3)	43(3)	19(3)	-2(2)	-3(2)	6(2)
Cl3	71.9(13)	60.1(13)	26.5(9)	-7.2(8)	-10.2(8)	18.7(10)

Table CD29: Bond Lengths in Å for **8a**.

Atom	Atom	Length/Å
C1	C2	1.482(6)
C1	N14	1.346(5)
C1	N16	1.341(5)
N1	N2	1.338(5)
N1	C14	1.345(6)
C2	C3	1.405(6)
C2	C7	1.400(6)
N2	C15	1.340(5)
C3	C4	1.386(6)
N3	N4	1.324(5)
N3	C14	1.339(5)
C4	C5	1.392(6)
N4	C15	1.347(5)
C5	C6	1.390(6)
N5	N6	1.331(5)
N5	C28	1.344(5)
C6	C7	1.399(6)
N6	C29	1.343(6)
C7	C8	1.507(6)
N7	N8	1.341(5)
N7	C28	1.344(5)
C8	C9	1.380(6)
C8	C13	1.406(6)
N8	C29	1.340(5)
C9	C10	1.390(6)
N9	N10	1.327(5)
N9	C42	1.357(5)
C10	C11	1.377(6)
N10	C43	1.337(5)
C11	C12	1.390(6)
N11	N12	1.334(5)
N11	C42	1.336(5)
C12	C13	1.396(6)
N12	C43	1.348(5)
C13	C14	1.481(6)
N13	N14	1.326(5)
N13	C56	1.344(5)
C15	C16	1.483(6)
N15	N16	1.333(5)
N15	C56	1.344(5)
C16	C17	1.393(6)
C16	C21	1.416(6)
C17	C18	1.379(6)
C18	C19	1.387(6)
C19	C20	1.384(6)
C20	C21	1.397(6)
C21	C22	1.484(6)
C22	C23	1.392(6)
C22	C27	1.415(6)
C23	C24	1.386(6)
C24	C25	1.380(7)
C25	C26	1.384(6)
C26	C27	1.390(6)
C27	C28	1.482(6)
C29	C30	1.476(6)
C30	C31	1.380(6)
C30	C35	1.405(6)
C31	C32	1.389(6)
C32	C33	1.377(6)
C33	C34	1.392(6)
C34	C35	1.390(6)
C35	C36	1.502(6)
C36	C37	1.401(6)
C36	C41	1.401(6)
C37	C38	1.378(6)
C38	C39	1.390(6)
C39	C40	1.378(6)
C40	C41	1.396(6)
C41	C42	1.480(6)
C43	C44	1.478(6)
C44	C45	1.409(6)
C44	C49	1.402(6)
C45	C46	1.377(6)
C46	C47	1.381(6)
C47	C48	1.396(6)
C48	C49	1.396(6)
C49	C50	1.494(6)
C50	C51	1.398(6)
C50	C55	1.407(6)
C51	C52	1.375(6)
C52	C53	1.384(7)
C53	C54	1.380(6)
C54	C55	1.399(6)
C55	C56	1.476(6)
Cl4	C58	1.752(6)
C58	Cl3A	1.770(15)
C58	Cl3	1.739(6)
Cl1	C57	1.765(5)
Cl2	C57	1.775(5)

Table CD30: Bond Angles in ° for **8a**.

Atom	Atom	Atom	Angle/°
N14	C1	C2	116.7(4)
N16	C1	C2	119.2(4)
N16	C1	N14	123.6(4)
N2	N1	C14	117.4(4)
C3	C2	C1	117.4(4)
C7	C2	C1	123.1(4)
C7	C2	C3	119.4(4)
N1	N2	C15	117.4(4)
C4	C3	C2	120.8(4)
N4	N3	C14	118.0(4)
C3	C4	C5	120.0(4)
N3	N4	C15	117.4(4)
C6	C5	C4	119.4(4)
N6	N5	C28	117.6(4)
C5	C6	C7	121.4(4)
N5	N6	C29	117.3(4)
C2	C7	C8	123.3(4)
C6	C7	C2	118.9(4)
C6	C7	C8	117.8(4)
N8	N7	C28	116.9(4)
C9	C8	C7	118.8(4)
C9	C8	C13	119.4(4)
C13	C8	C7	121.8(4)
C29	N8	N7	117.6(4)
C8	C9	C10	120.8(4)
N10	N9	C42	117.9(3)
C11	C10	C9	120.7(4)
N9	N10	C43	117.5(3)
C10	C11	C12	118.8(4)
N12	N11	C42	118.2(4)
C11	C12	C13	121.4(4)
N11	N12	C43	117.1(4)
C8	C13	C14	123.1(4)
C12	C13	C8	118.8(4)
C12	C13	C14	117.8(4)
N14	N13	C56	118.0(3)
N1	C14	C13	117.6(4)
N3	C14	N1	124.8(4)
N3	C14	C13	117.4(4)
N13	N14	C1	117.4(3)
N2	C15	N4	124.8(4)
N2	C15	C16	117.0(4)
N4	C15	C16	118.2(4)
N16	N15	C56	117.6(4)
C17	C16	C15	118.7(4)
C17	C16	C21	119.2(4)
C21	C16	C15	122.1(4)
N15	N16	C1	117.5(4)
C18	C17	C16	121.0(4)
C17	C18	C19	120.2(4)
C20	C19	C18	119.7(4)
C19	C20	C21	121.1(4)
C16	C21	C22	122.0(4)
C20	C21	C16	118.7(4)
C20	C21	C22	119.3(4)
C23	C22	C21	119.3(4)
C23	C22	C27	118.1(4)
C27	C22	C21	122.5(4)
C24	C23	C22	121.5(4)
C25	C24	C23	119.7(4)
C24	C25	C26	120.2(4)
C25	C26	C27	120.6(4)
C22	C27	C28	121.3(4)
C26	C27	C22	119.7(4)
C26	C27	C28	118.9(4)
N5	C28	C27	117.1(4)
N7	C28	N5	125.2(4)
N7	C28	C27	117.7(4)
N6	C29	C30	117.1(4)
N8	C29	N6	125.1(4)
N8	C29	C30	117.5(4)
C31	C30	C29	118.0(4)
C31	C30	C35	120.0(4)
C35	C30	C29	121.9(4)
C30	C31	C32	121.1(4)
C33	C32	C31	119.3(4)
C32	C33	C34	120.1(4)
C35	C34	C33	121.2(4)
C30	C35	C36	124.4(4)
C34	C35	C30	118.3(4)
C34	C35	C36	117.3(4)
C37	C36	C35	116.9(4)
C37	C36	C41	117.7(4)
C41	C36	C35	125.2(4)
C38	C37	C36	122.0(4)
C37	C38	C39	120.0(4)
C40	C39	C38	118.9(4)
C39	C40	C41	121.7(4)
C36	C41	C42	123.2(4)
C40	C41	C36	119.7(4)
C40	C41	C42	117.0(4)
N9	C42	C41	116.9(4)
N11	C42	N9	122.8(4)
N11	C42	C41	120.1(4)
N10	C43	N12	124.0(4)
N10	C43	C44	117.4(4)
N12	C43	C44	118.6(4)
C45	C44	C43	117.7(4)
C49	C44	C43	123.1(4)
C49	C44	C45	119.3(4)
C46	C45	C44	121.3(4)
C45	C46	C47	119.4(4)
C46	C47	C48	120.5(4)
C47	C48	C49	120.7(4)
C44	C49	C50	123.9(4)
C48	C49	C44	118.9(4)
C48	C49	C50	116.9(4)
C51	C50	C49	116.6(4)
C51	C50	C55	118.5(4)
C55	C50	C49	124.8(4)
C52	C51	C50	121.0(4)
C51	C52	C53	120.7(4)
C54	C53	C52	119.3(4)
C53	C54	C55	121.1(4)
C50	C55	C56	121.7(4)
C54	C55	C50	119.4(4)
C54	C55	C56	118.8(4)
N13	C56	N15	123.1(4)

Atom	Atom	Atom	Angle/˚
N13	C56	C55	117.0(4)
N15	C56	C55	119.8(4)
Cl4	C58	Cl3A	122.0(8)
Cl3	C58	Cl4	111.7(3)
Cl1	C57	Cl2	112.3(2)

Table CD31: Torsion Angles in ˚ for **8a.**

Atom	Atom	Atom	Atom	Angle/˚
C1	C2	C3	C4	176.5(4)
C1	C2	C7	C6	-175.5(4)
C1	C2	C7	C8	4.8(6)
N1	N2	C15	N4	-4.4(6)
N1	N2	C15	C16	175.7(3)
C2	C1	N14	N13	174.5(3)
C2	C1	N16	N15	-176.2(3)
C2	C3	C4	C5	-0.4(7)
C2	C7	C8	C9	-105.6(5)
C2	C7	C8	C13	75.1(5)
N2	N1	C14	N3	1.9(6)
N2	N1	C14	C13	-172.6(3)
N2	C15	C16	C17	-34.2(6)
N2	C15	C16	C21	146.6(4)
C3	C2	C7	C6	1.8(6)
C3	C2	C7	C8	-177.9(4)
C3	C4	C5	C6	0.7(7)
N3	N4	C15	N2	1.9(6)
N3	N4	C15	C16	-178.2(3)
C4	C5	C6	C7	0.3(7)
N4	N3	C14	N1	-4.4(6)
N4	N3	C14	C13	170.0(3)
N4	C15	C16	C17	145.9(4)
N4	C15	C16	C21	-33.3(6)
C5	C6	C7	C2	-1.5(6)
C5	C6	C7	C8	178.2(4)
N5	N6	C29	N8	-5.5(6)
N5	N6	C29	C30	-179.6(4)
C6	C7	C8	C9	74.7(5)
C6	C7	C8	C13	-104.7(5)
N6	N5	C28	N7	1.2(6)
N6	N5	C28	C27	179.4(4)
N6	C29	C30	C31	43.5(6)
N6	C29	C30	C35	-138.2(4)
C7	C2	C3	C4	-0.9(6)
C7	C8	C9	C10	179.2(4)
C7	C8	C13	C12	-177.4(4)
C7	C8	C13	C14	8.4(6)
N7	N8	C29	N6	2.1(6)
N7	N8	C29	C30	176.2(4)
C8	C9	C10	C11	-0.9(7)
C8	C13	C14	N1	-147.3(4)
C8	C13	C14	N3	37.9(6)
N8	N7	C28	N5	-4.5(6)
N8	N7	C28	C27	177.4(4)
N8	C29	C30	C31	-131.0(4)
N8	C29	C30	C35	47.3(6)
C9	C8	C13	C12	3.2(6)
C9	C8	C13	C14	-170.9(4)
C9	C10	C11	C12	1.2(7)
N9	N10	C43	N12	-12.4(6)
N9	N10	C43	C44	170.8(4)

Atom	Atom	Atom	Atom	Angle/˚
C10	C11	C12	C13	0.8(7)
N10	N9	C42	N11	12.6(6)
N10	N9	C42	C41	-172.7(4)
N10	C43	C44	C45	31.3(6)
N10	C43	C44	C49	-148.1(4)
C11	C12	C13	C8	-2.9(6)
C11	C12	C13	C14	171.5(4)
N11	N12	C43	N10	11.9(6)
N11	N12	C43	C44	-171.3(4)
C12	C13	C14	N1	38.5(6)
C12	C13	C14	N3	-136.3(4)
N12	N11	C42	N9	-13.1(6)
N12	N11	C42	C41	172.3(4)
N12	C43	C44	C45	-145.7(4)
N12	C43	C44	C49	34.9(6)
C13	C8	C9	C10	-1.4(6)
C14	N1	N2	C15	2.4(6)
C14	N3	N4	C15	2.5(5)
N14	C1	C2	C3	25.7(6)
N14	C1	C2	C7	-157.0(4)
N14	C1	N16	N15	12.9(6)
N14	N13	C56	N15	13.8(6)
N14	N13	C56	C55	-170.4(4)
C15	C16	C17	C18	-178.1(4)
C15	C16	C21	C20	177.8(4)
C15	C16	C21	C22	-2.6(6)
C16	C17	C18	C19	0.0(7)
C16	C21	C22	C23	118.0(5)
C16	C21	C22	C27	-58.2(6)
N16	C1	C2	C3	-145.9(4)
N16	C1	C2	C7	31.4(6)
N16	C1	N14	N13	-14.3(6)
N16	N15	C56	N13	-15.2(6)
N16	N15	C56	C55	169.1(4)
C17	C16	C21	C20	-1.4(6)
C17	C16	C21	C22	178.2(4)
C17	C18	C19	C20	-0.9(7)
C18	C19	C20	C21	0.6(7)
C19	C20	C21	C16	0.5(6)
C19	C20	C21	C22	-179.1(4)
C20	C21	C22	C23	-62.4(6)
C20	C21	C22	C27	121.4(5)
C21	C16	C17	C18	1.2(7)
C21	C22	C23	C24	-171.8(4)
C21	C22	C27	C26	171.2(4)
C21	C22	C27	C28	-5.8(6)
C22	C23	C24	C25	-1.6(7)
C22	C27	C28	N5	145.0(4)
C22	C27	C28	N7	-36.7(6)
C23	C22	C27	C26	-5.1(6)
C23	C22	C27	C28	177.9(4)
C23	C24	C25	C26	-0.9(7)
C24	C25	C26	C27	0.4(7)
C25	C26	C27	C22	2.7(7)
C25	C26	C27	C28	179.8(4)
C26	C27	C28	N5	-32.0(6)
C26	C27	C28	N7	146.3(4)
C27	C22	C23	C24	4.6(6)
C28	N5	N6	C29	3.6(6)
C28	N7	N8	C29	2.7(5)
C29	C30	C31	C32	175.8(4)

Atom	Atom	Atom	Atom	Angle/°
C29	C30	C35	C34	-175.1(4)
C29	C30	C35	C36	3.4(6)
C30	C31	C32	C33	0.5(7)
C30	C35	C36	C37	-108.9(5)
C30	C35	C36	C41	76.5(6)
C31	C30	C35	C34	3.2(6)
C31	C30	C35	C36	-178.3(4)
C31	C32	C33	C34	0.9(7)
C32	C33	C34	C35	-0.2(7)
C33	C34	C35	C30	-1.8(7)
C33	C34	C35	C36	179.5(4)
C34	C35	C36	C37	69.7(5)
C34	C35	C36	C41	-105.0(5)
C35	C30	C31	C32	-2.6(7)
C35	C36	C37	C38	-175.8(4)
C35	C36	C41	C40	175.8(4)
C35	C36	C41	C42	-1.3(7)
C36	C37	C38	C39	-0.3(7)
C36	C41	C42	N9	155.0(4)
C36	C41	C42	N11	-30.0(6)
C37	C36	C41	C40	1.1(6)
C37	C36	C41	C42	-175.9(4)
C37	C38	C39	C40	1.0(7)
C38	C39	C40	C41	-0.6(7)
C39	C40	C41	C36	-0.5(7)
C39	C40	C41	C42	176.7(4)
C40	C41	C42	N9	-22.1(6)
C40	C41	C42	N11	152.8(4)
C41	C36	C37	C38	-0.7(6)
C42	N9	N10	C43	0.1(5)
C42	N11	N12	C43	0.9(5)
C43	C44	C45	C46	-178.8(4)
C43	C44	C49	C48	178.6(4)
C43	C44	C49	C50	5.3(7)
C44	C45	C46	C47	-0.7(7)
C44	C49	C50	C51	97.9(5)
C44	C49	C50	C55	-83.9(6)
C45	C44	C49	C48	-0.8(6)
C45	C44	C49	C50	-174.1(4)
C45	C46	C47	C48	1.1(7)
C46	C47	C48	C49	-1.4(7)
C47	C48	C49	C44	1.2(6)
C47	C48	C49	C50	175.0(4)
C48	C49	C50	C51	-75.5(5)
C48	C49	C50	C55	102.7(5)
C49	C44	C45	C46	0.6(7)
C49	C50	C51	C52	177.9(4)
C49	C50	C55	C54	-177.1(4)
C49	C50	C55	C56	6.4(6)
C50	C51	C52	C53	-0.7(7)
C50	C55	C56	N13	156.2(4)
C50	C55	C56	N15	-27.9(6)
C51	C50	C55	C54	1.2(6)
C51	C50	C55	C56	-175.3(4)
C51	C52	C53	C54	1.2(7)
C52	C53	C54	C55	-0.5(7)
C53	C54	C55	C50	-0.6(7)
C53	C54	C55	C56	176.0(4)
C54	C55	C56	N13	-20.4(6)
C54	C55	C56	N15	155.6(4)
C55	C50	C51	C52	-0.5(6)

Atom	Atom	Atom	Atom	Angle/°
C56	N13	N14	C1	0.9(5)
C56	N15	N16	C1	1.8(5)

Table CD32: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **8a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H3	3863.54	8443.11	5923.45	20
H4	3532.79	9291.6	5487.2	26
H5	4298.46	9626.83	4350.8	27
H6	5368.22	9103.14	3647.5	22
H9	7354.85	8466.83	4392.39	22
H10	8444.37	7989.6	3639.07	26
H11	7682.97	7356.37	2655.69	24
H12	5803.85	7219.84	2403.07	20
H17	1344.75	6983.28	1022.25	25
H18	-428.14	6899.68	255.54	27
H19	-1783.02	7456.34	530.4	26
H20	-1362	8084.58	1600.45	22
H23	-23.45	8916.84	1824.26	21
H24	550.4	9573.04	2815.24	27
H25	1368.43	9377.34	4248.28	27
H26	1591.91	8526.61	4696.03	22
H31	1911.76	6424.29	5955.1	22
H32	2063.17	5599.06	6545.4	24
H33	1824.32	4891.61	5617.17	29
H34	1466.11	5008.72	4107.99	25
H37	-317.62	5579.02	3032.19	21
H38	-770.96	5558.43	1524.95	24
H39	509.94	5804.03	688.66	23
H40	2245.66	6044.03	1391.38	22
H45	6883.03	6403.08	3023.28	22
H46	8732.41	6382.91	3611.16	24
H47	9321.7	6189.55	5084.07	26
H48	8064.77	5984.21	5956.34	24
H51	6301.48	5153.17	5441.93	23
H52	5237.77	4821.48	6363.43	29
H53	4268.7	5364.53	7121.59	26
H54	4326.22	6245.86	6908.68	22
H58A	8673.69	5860.28	8858.55	49
H58B	9022.8	5278.62	8738.07	49
H58C	8708.67	5190.65	8566.97	49
H58D	9019.88	5735.41	8996.22	49
H57A	6239.18	5760.2	794.02	32
H57B	5972.47	5960.45	1697.31	32

Table CD33: Atomic Occupancies for all atoms that are not fully occupied in **8a.**

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
H58A	0.90(9)	H58C	0.10(9)	Cl3A	0.11
H58B	0.90(9)	H58D	0.10(9)	Cl3	0.89

Electrochemical analysis

General procedure for electrochemistry analysis

All manipulations were performed using Schlenk techniques in an atmosphere of dry oxygen-free argon at room temperature (T = 20°C ± 3°C). The supporting electrolyte (tetraethylammonium tetrafluoroborate, $TEABF_4$) was degassed under vacuum before use and then dissolved in DMF (unless otherwise noted) to a concentration of 0.1 mol L^{-1}. The following electrolyte volumes (unless otherwise noted) were used for voltammetric analyses: anodic compartment: V = 5 mL; cathodic compartment: V = 5 mL; reference electrode compartment: V = 5 mL.

Voltammetric analyses were carried out in a standard three-electrode cell, with Autolab PGSTAT302N potentiostat and Nova 1.11 Software. The reference electrode was a KCl saturated calomel electrode (SCE) separated from the analyzed solution by a sintered glass disk filled with the background solution. The auxiliary electrode was a platinum foil separated from the analyzed solution by a sintered glass disk filled with the background solution. For all voltammetric measurements, the working electrode was a platinum electrode ($Ø$ = 2 mm, from ALS). Before each voltammetric analysis, the Pt electrode was polished with a diamond suspension (1 µm, diamond suspension Mono, alcohol based, from ATM Qness GmbH). In these conditions, when operating in DMF (0.1 M $TEABF_4$), the formal potential for the ferrocene (+/0) couple was 0.44 V *vs.* SCE.

For cyclic voltammetry measurements, a scan rate of 100 mV/s was used.

For differential pulse voltammetry, the following parameters were used:

-step potential: 0.010 V

-modulation amplitude: 0.025 V

-modulation time: 0.04 s

-interval time: 1 s

-scan rate: 10 mV/s

For rotating disk electrode voltammetry analysis, the following parameters were used:

-scan rate: 10 mV/s

-rotation speed: 1000 rpm

Cyclic Voltammetry Data

Products	E_{pc}(R1)	E_{pa}(R1)	$E_{1/2}$(R1)	E_{pc}(R2)	E_{pa}(R2)	$E_{1/2}$(R2)	E_{pc}(R3)	E_{pa}(R3)	$E_{1/2}$(R3)
1a	-0.866	-0.777	-0.82						
3a	-0.827	-0.783	-0.81	-0.994	-0.941	-0.97			
5a''	-0.826	-0.728	-0.78						
7a''	-0.819	-0.734	-0.78						
6a	-0.909	-0.793	-0.85						
8a	-0.787	-0.692	-0.74	-0.909	-0.801	-0.86	-1.197	-1.091	-1.14
1b	-0.621	-0.566	-0.59						
3b	-0.713	-0.652	-0.68	-0.848	-0.781	-0.81			
5b''	-0.731	-0.659	-0.70	-1.310	-1.191	-1.25			

6b	-0.731	-0.668	-0.70	-1.187	-1.103	-1.15			
4b	-0.663	-0.609	-0.64	-0.809	-0.745	0.78			
5a'	-0.821	-0.760	-0.79						

Differential Pulse Voltammetry Data

Products	E_{pc}(R1)	E_{pc}(R2)	E_{pc}(R3)
1a	-0.82		
3a	-0.80	-0.96	
5a''	-0.77		
7a''	-0.76	*ca.* -0.87	
6a	-0.86	-1.47	
8a	-0.70	-0.91	-1.14
1b	-0.58		
3b	-0.67	-0.81	
5b''	-0.68	-1.24	
6b	-0.69	-1.14	
4b	-0.62	-0.78	
5a'	-0.78		

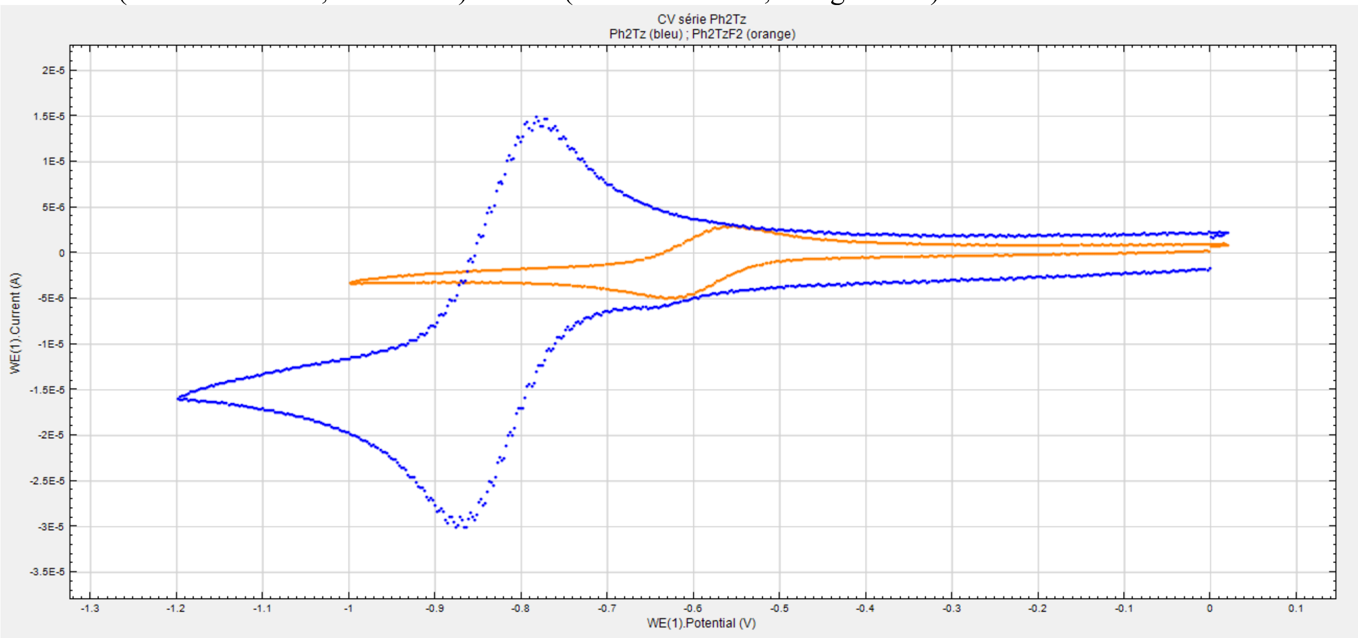
Rotating Disk Electrode Voltammetry Data

Products	$E_{1/2}$(R1)	$E_{1/2}$(R2)	$E_{1/2}$(R3)
1a	-0.82		
3a	-0.79	-1.04	
5a''	-0.77		
7a''	-0.79		
6a	-0.89	-1.51	
8a	-0.72	-0.92	-1.21
1b	-0.60		
3b	-0.68	-0.84	
5b''	-0.70	-1.26	
6b	-0.70	-1.20	
4b	-0.63	-0.80	
5a'	-0.78		

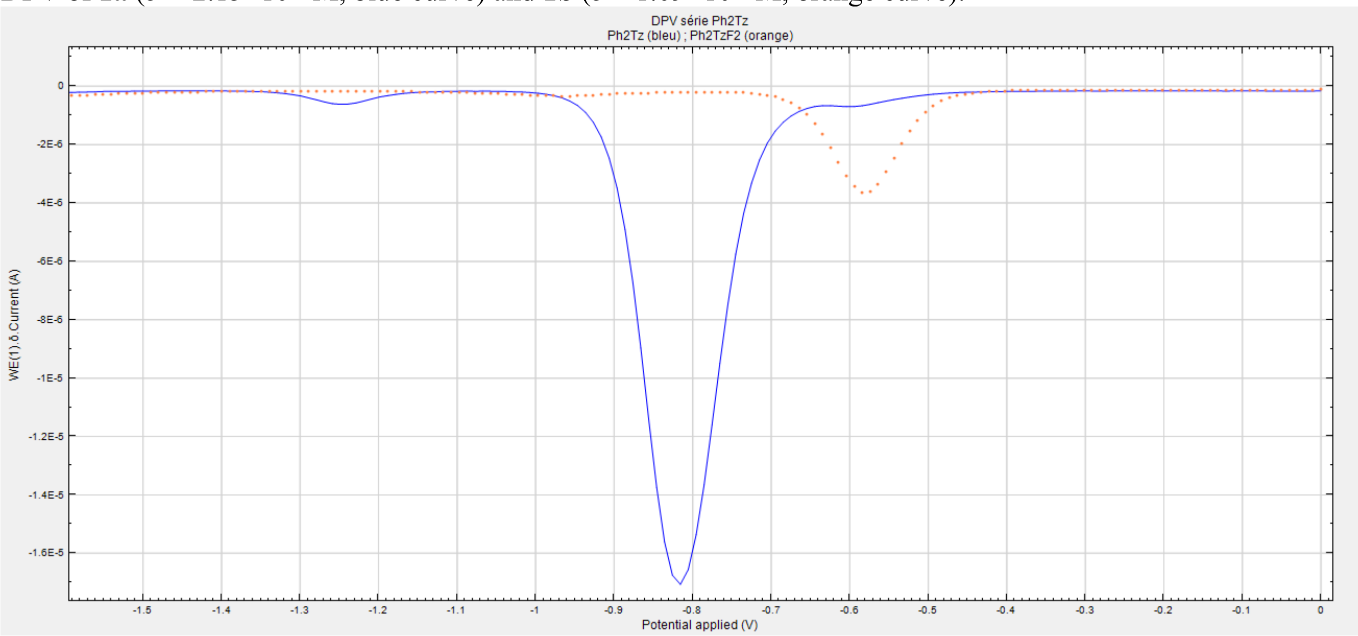
CV, DPV and RDE curves

Electrochemical Analyses of 1a and 1b

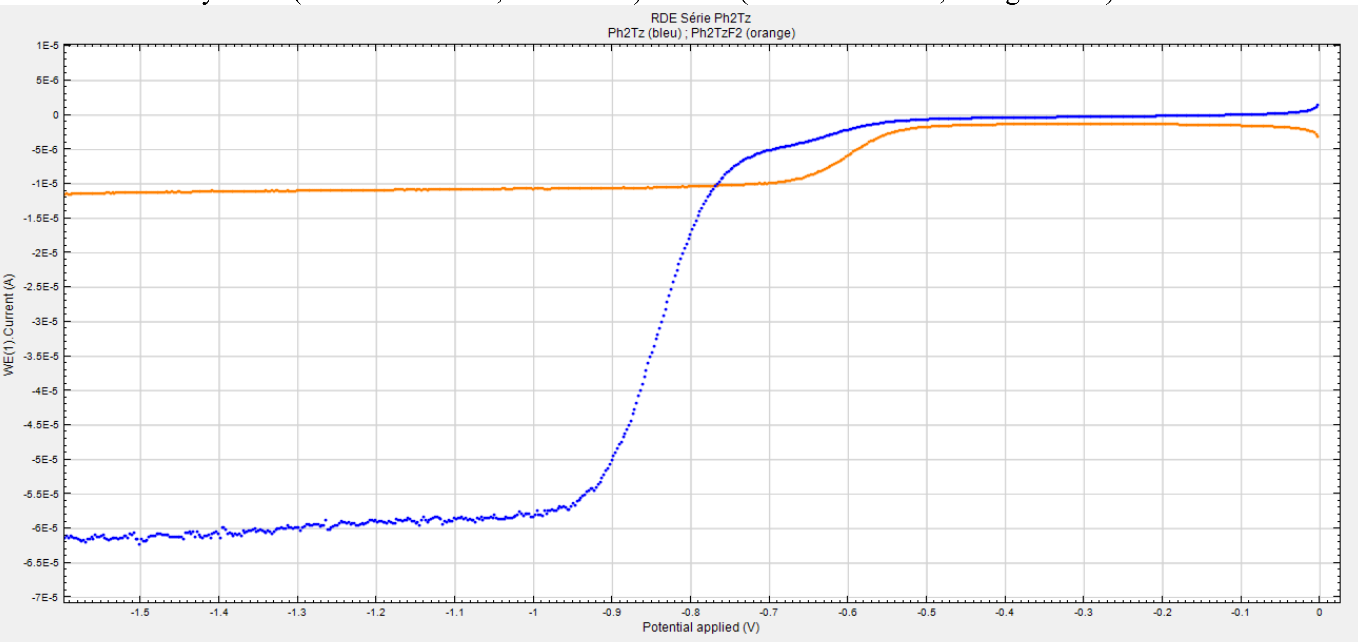
CV of **1a** (c = 2.15×10^{-3} M, blue curve) and **1b** (c = 1.09×10^{-3} M, orange curve).



DPV of **1a** (c = 2.15×10^{-3} M, blue curve) and **1b** (c = 1.09×10^{-3} M, orange curve).

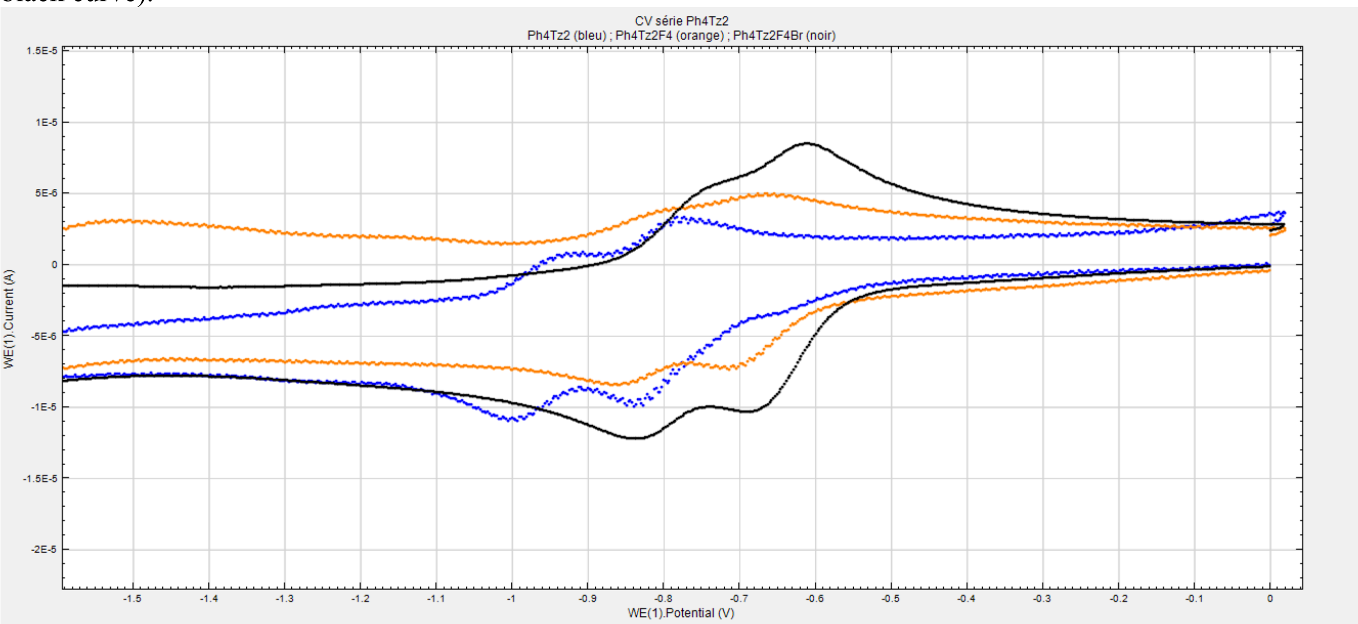


RDE voltammetry of **1a** (c = 2.15×10^{-3} M, blue curve) and **1b** (c = 1.09×10^{-3} M, orange curve).

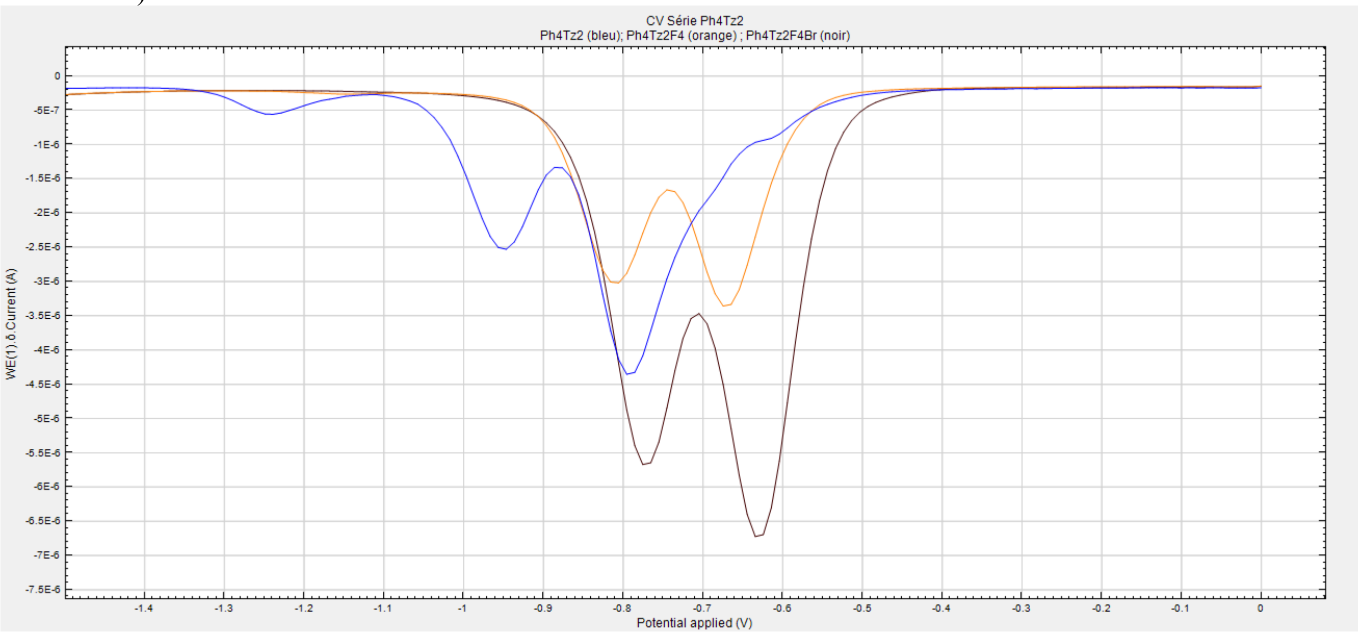


Electrochemical Analyses of 3a, 3b and 4b

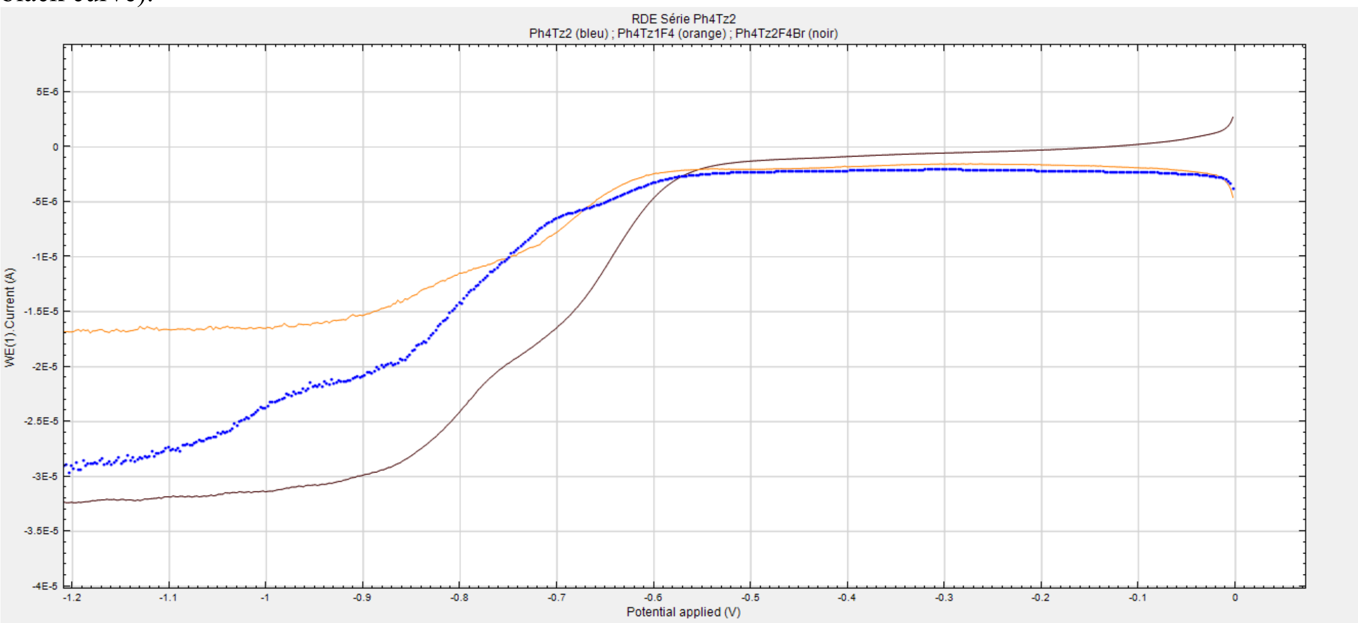
CV of **3a** (c = 2.22×10^{-3} M, blue curve), **3b** (c = 1.10×10^{-3} M, orange curve) and **4b** (c = 0.93×10^{-3} M, black curve).



DPV of **3a** (c = 2.22×10^{-3} M, blue curve), **3b** (c = 1.10×10^{-3} M, orange curve) and **4b** (c = 0.93×10^{-3} M, black curve).

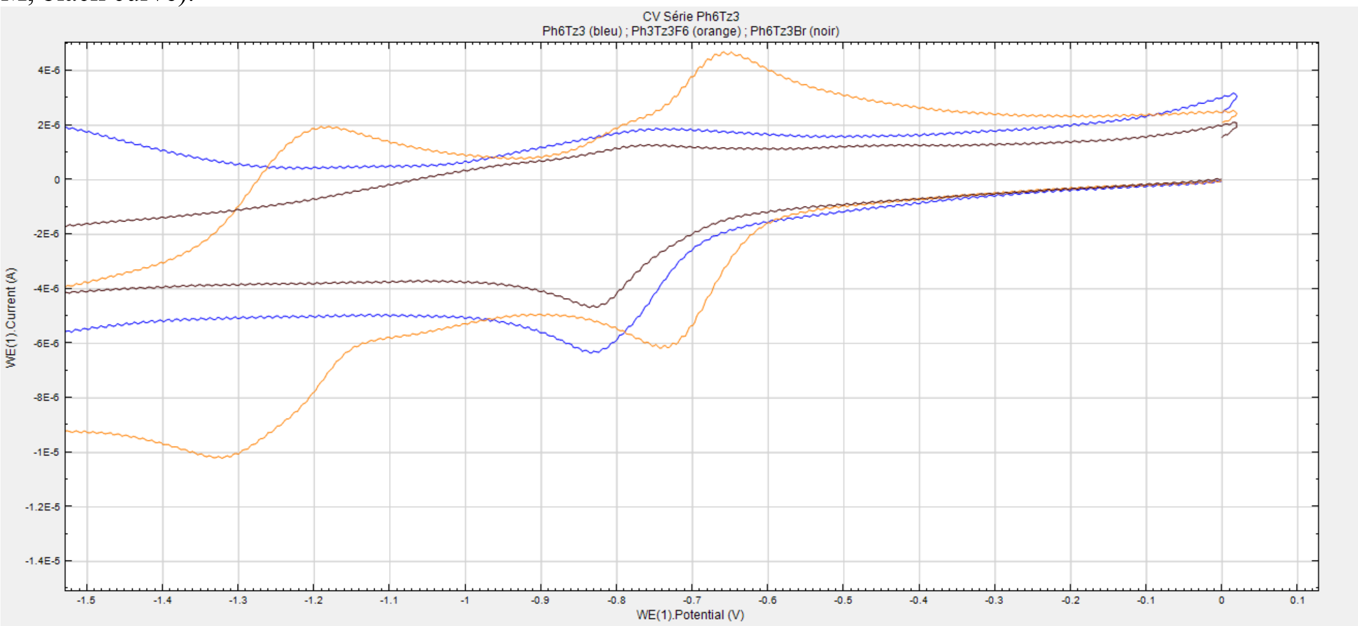


RDE of **3a** (c = 2.22×10^{-3} M, blue curve), **3b** (c = 1.10×10^{-3} M, orange curve) and **4b** (c = 0.93×10^{-3} M, black curve).

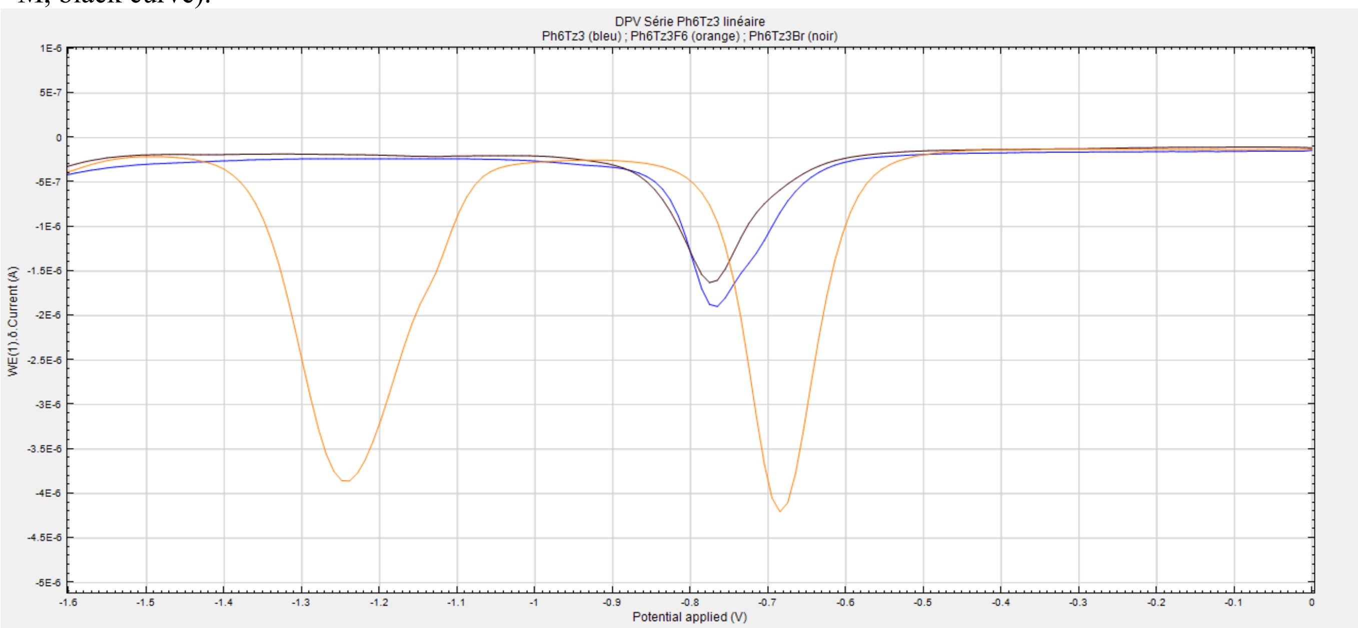


Electrochemical Analyses of 5a'', 5b'' and 5a'

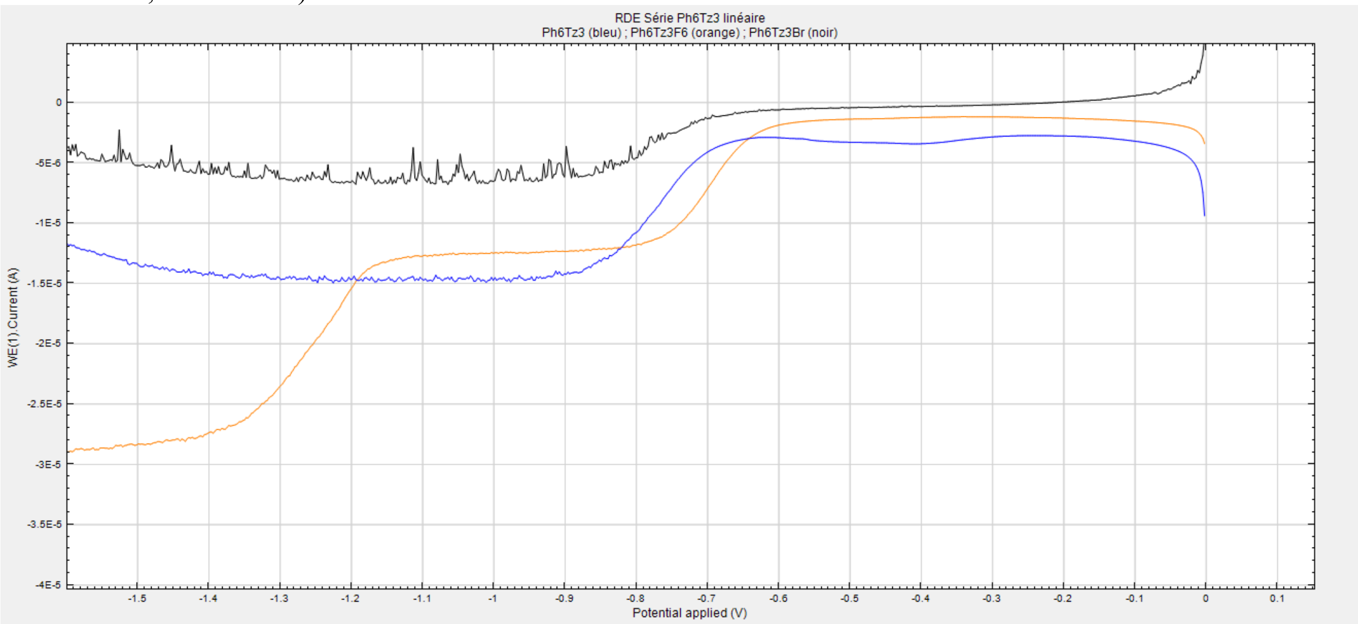
CV of **5a''** (c = 2.20×10^{-3} M, blue curve), **5b''.** (c = 1.12×10^{-3} M, orange curve) and **5a'** (c = 0.92×10^{-3} M, black curve).



DPV of **5a''** (c = 2.20×10^{-3} M, blue curve), **5b''** (c = 1.12×10^{-3} M, orange curve) and **5a'** (c = 0.92×10^{-3} M, black curve).

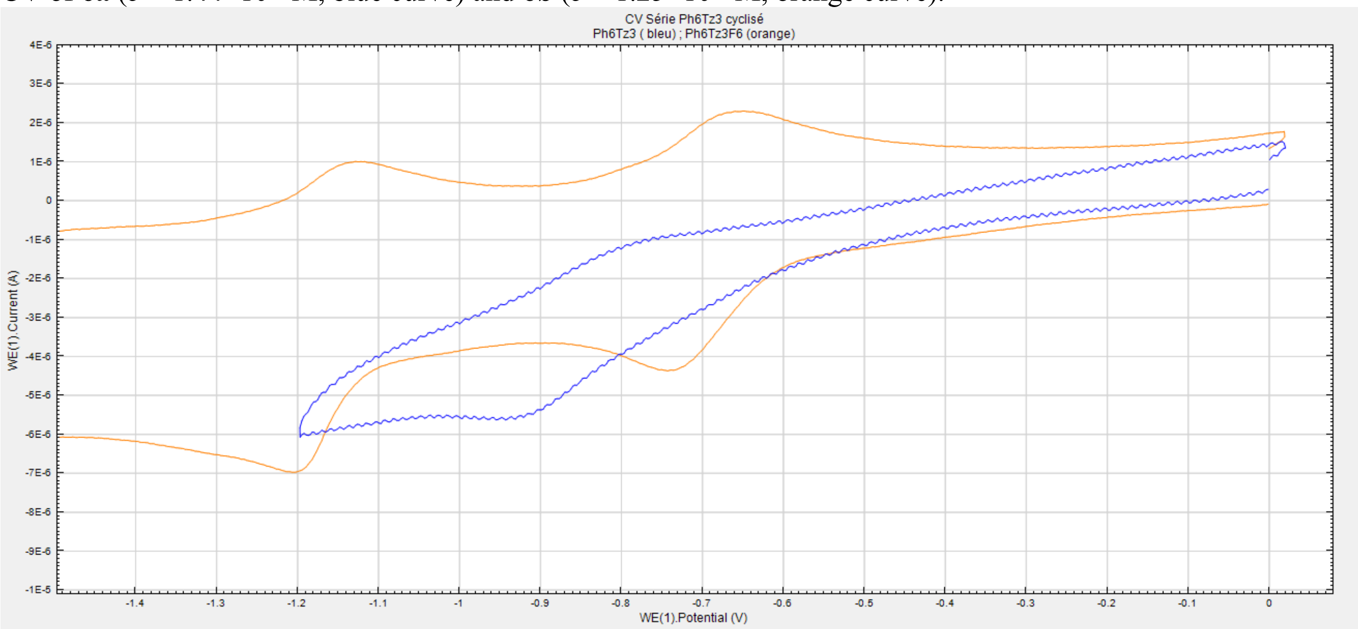


RDE of **5a''** (c = 2.20×10^{-3} M, blue curve), **5b''** (c = 1.12×10^{-3} M, orange curve) and **5a'** (c = 0.92×10^{-3} M, black curve). **3a** (c = 2.22×10^{-3} M, blue curve), **3b** (c = 1.10×10^{-3} M, orange curve) and **4b** (c = 0.93×10^{-3} M, black curve).

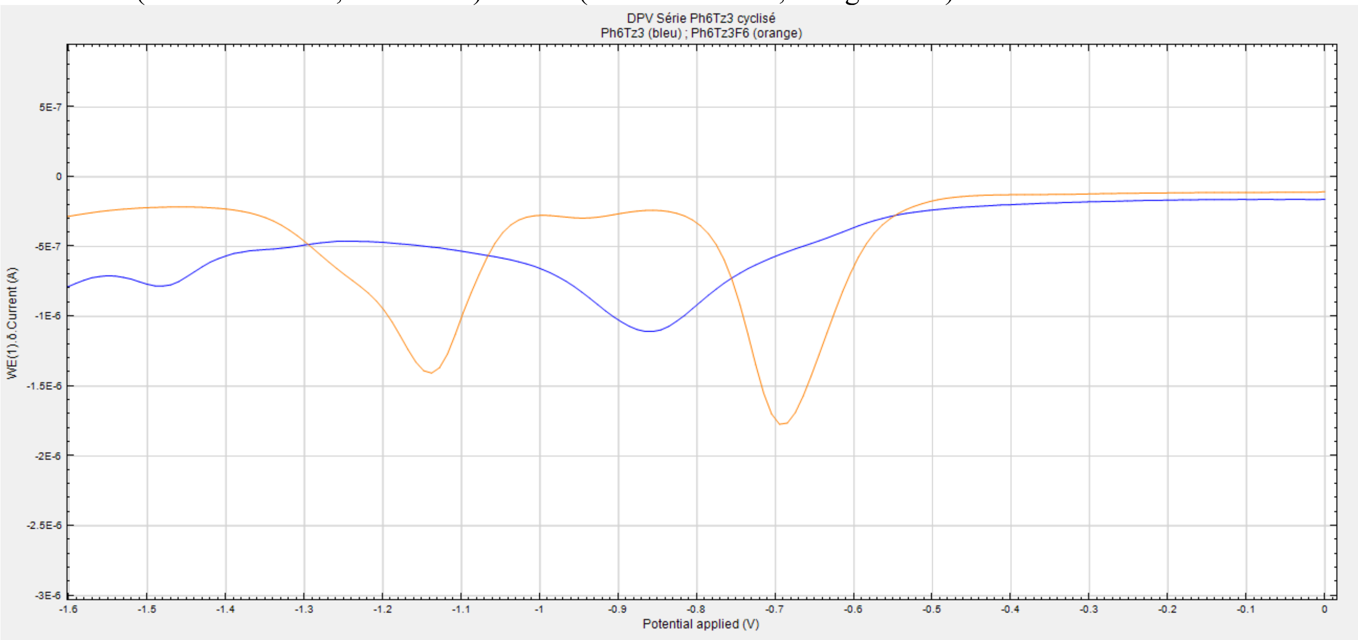


Electrochemical Analyses of 6a and 6b

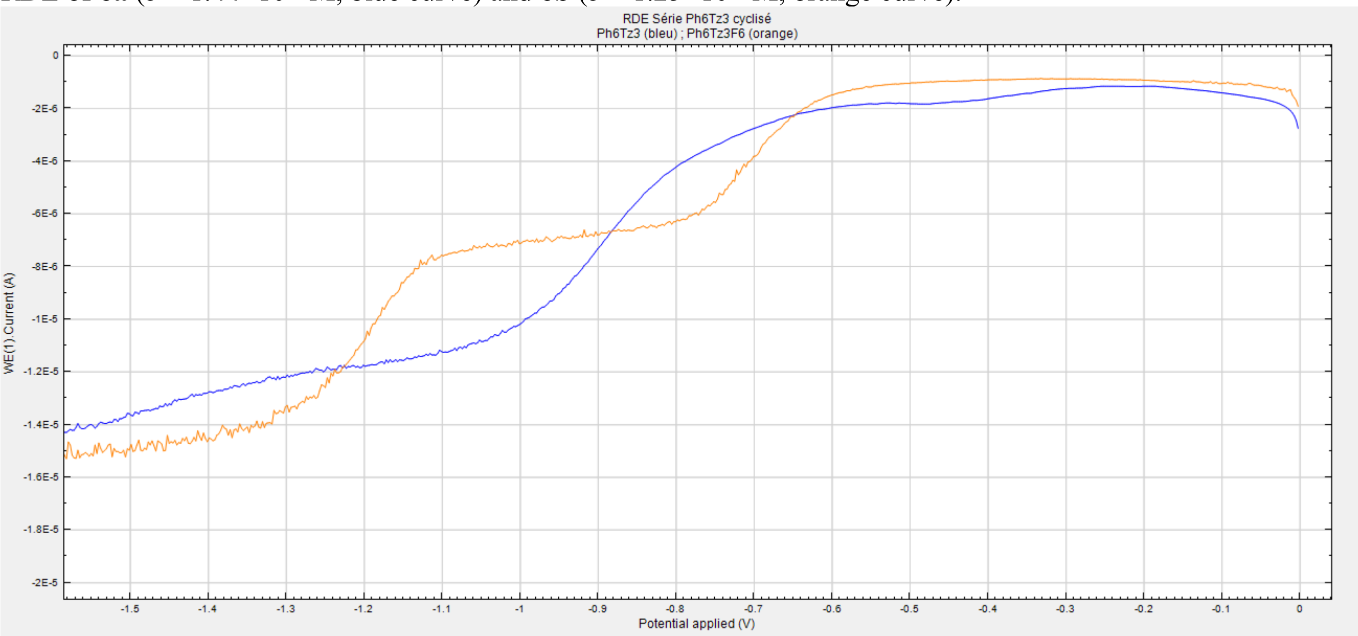
CV of **6a** (c = 1.44×10^{-3} M, blue curve) and **6b** (c = 1.25×10^{-3} M, orange curve).



DPV of **6a** (c = 1.44×10^{-3} M, blue curve) and **6b** (c = 1.25×10^{-3} M, orange curve).

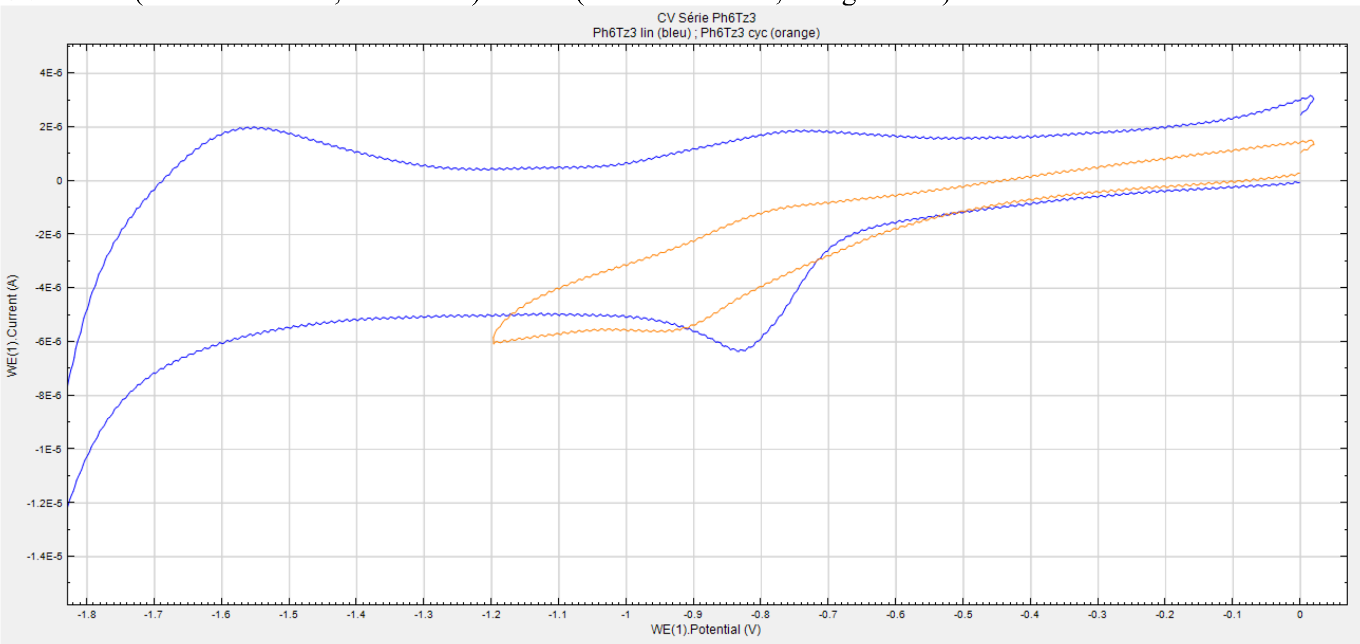


RDE of **6a** (c = 1.44×10^{-3} M, blue curve) and **6b** (c = 1.25×10^{-3} M, orange curve).

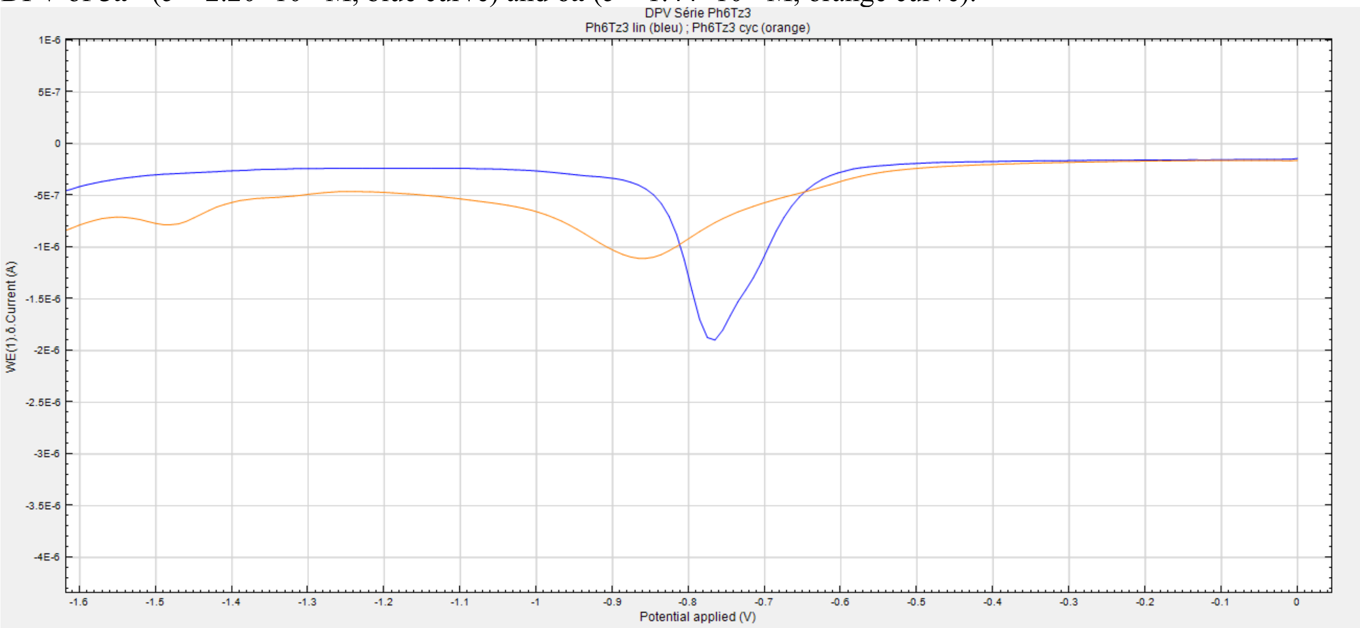


Comparison linear *vs.* cyclic tetrazine derivatives: 5a'' *vs.* 6a

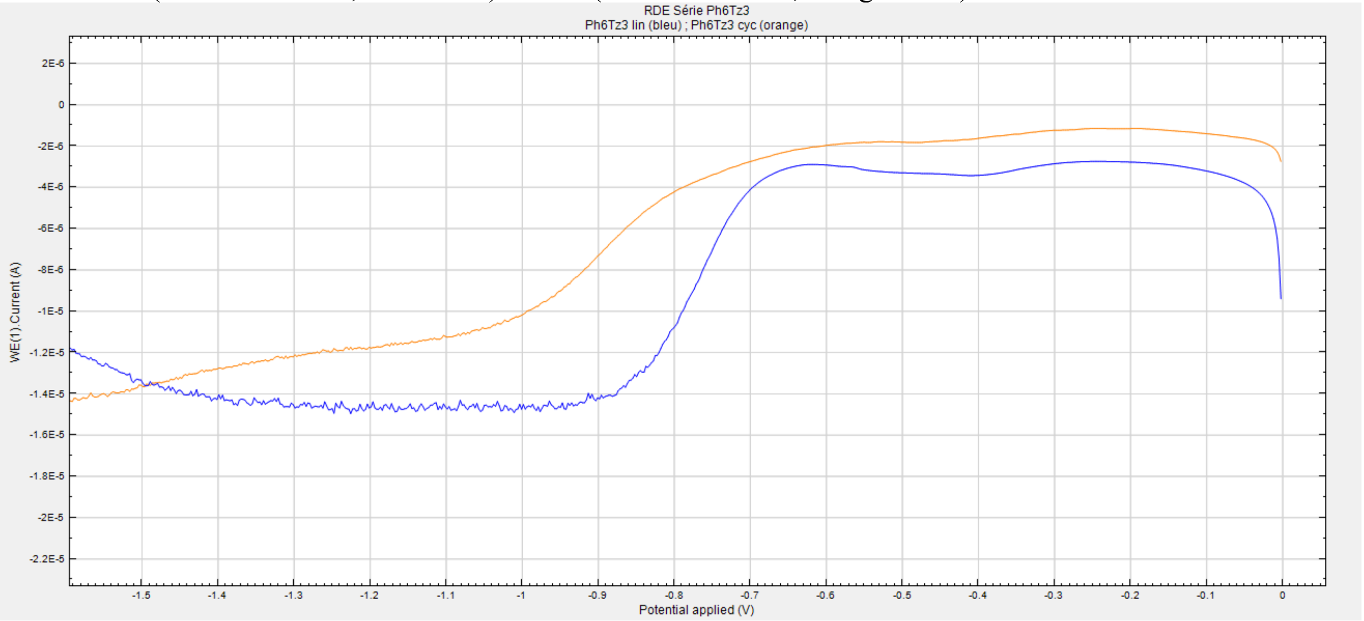
CV of **5a''** ($c = 2.20 \times 10^{-3}$ M, blue curve) and **6a** ($c = 1.44 \times 10^{-3}$ M, orange curve).



DPV of **5a''** ($c = 2.20 \times 10^{-3}$ M, blue curve) and **6a** ($c = 1.44 \times 10^{-3}$ M, orange curve).

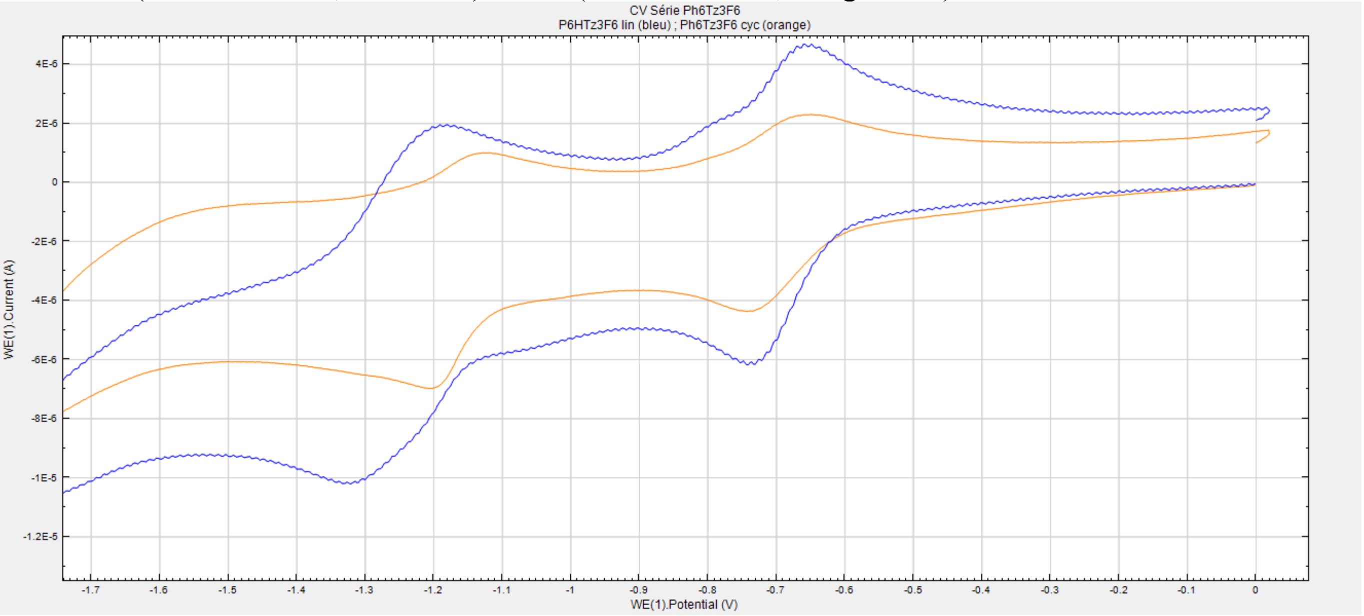


RDE of **5a''** (c = 2.20×10^{-3} M, blue curve) and **6a** (c = 1.44×10^{-3} M, orange curve).

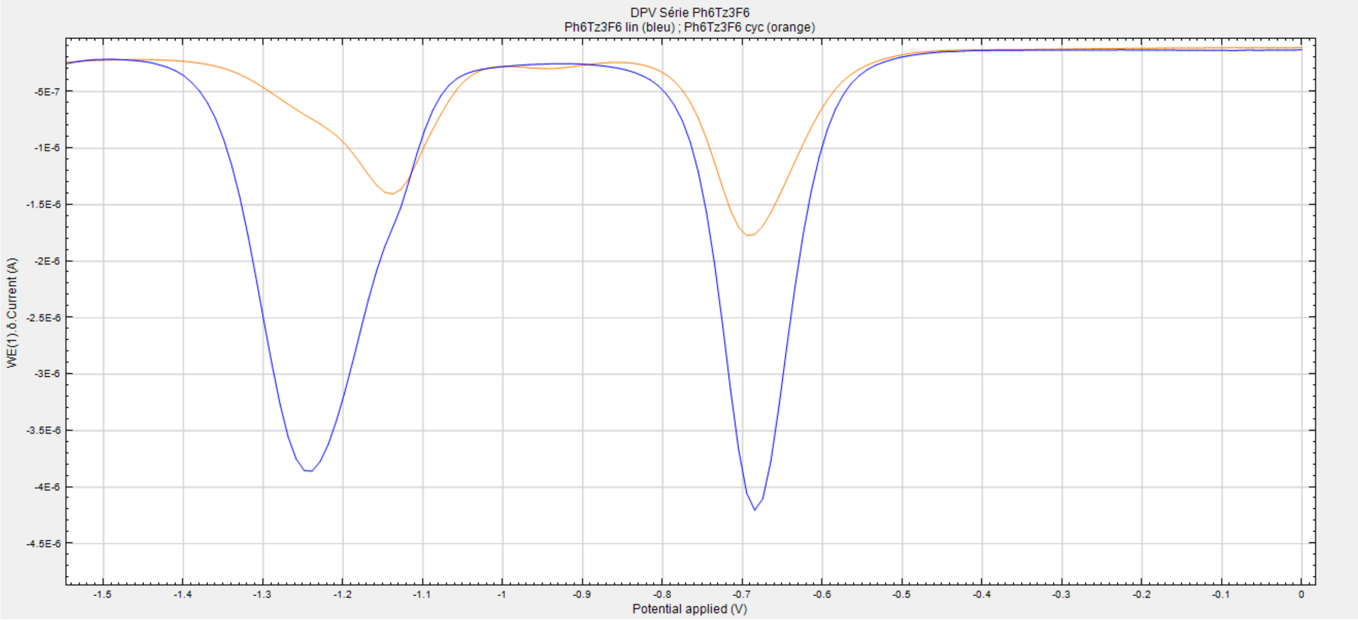


Comparison linear *vs.* cyclic tetrazine derivatives: 5b'' *vs.* 6b

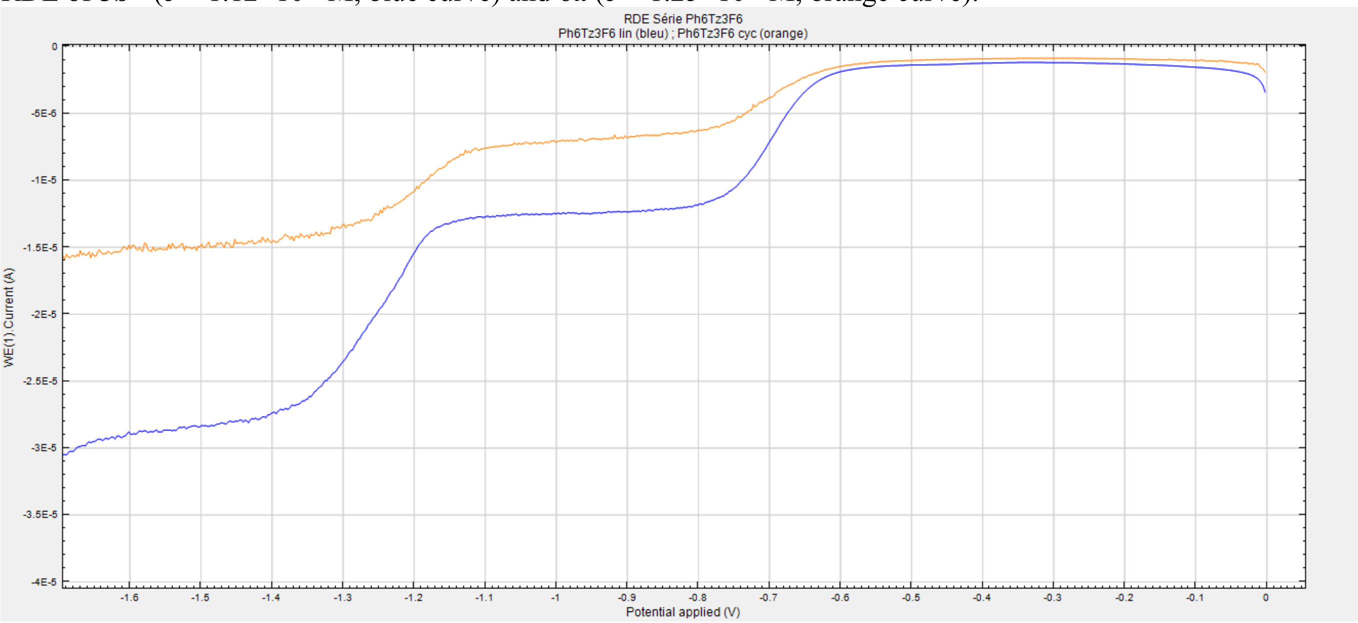
CV of **5b''** (c = 1.12×10^{-3} M, blue curve) and **6a** (c = 1.25×10^{-3} M, orange curve).



DPV of **5b''** (c = 1.12×10^{-3} M, blue curve) and **6a** (c = 1.25×10^{-3} M, orange curve).

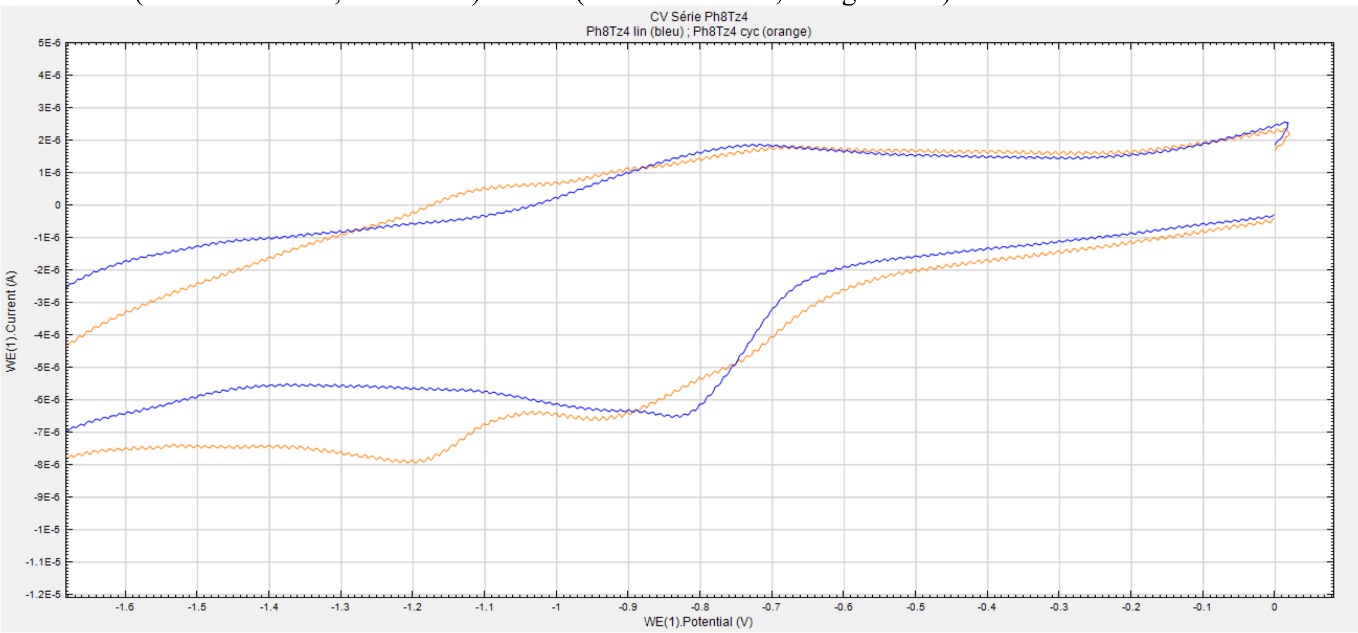


RDE of **5b''** (c = 1.12×10^{-3} M, blue curve) and **6a** (c = 1.25×10^{-3} M, orange curve).

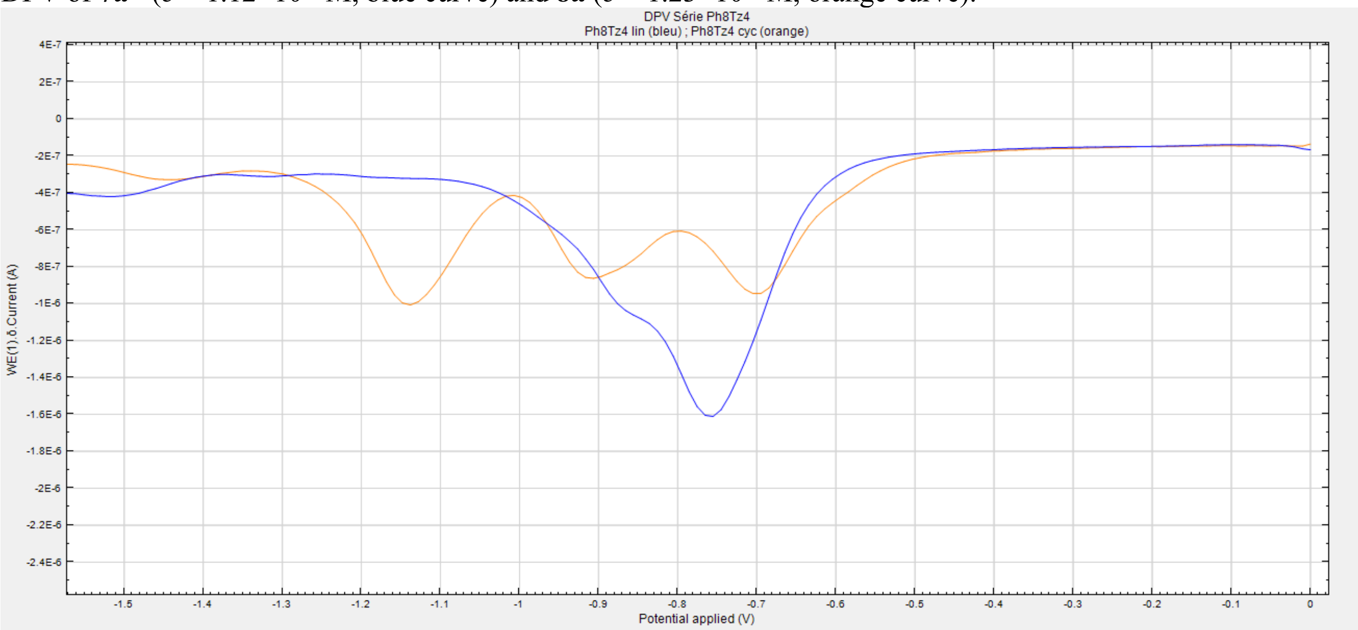


Comparison linear *vs.* cyclic tetrazine derivatives: 7a" *vs.* 8a

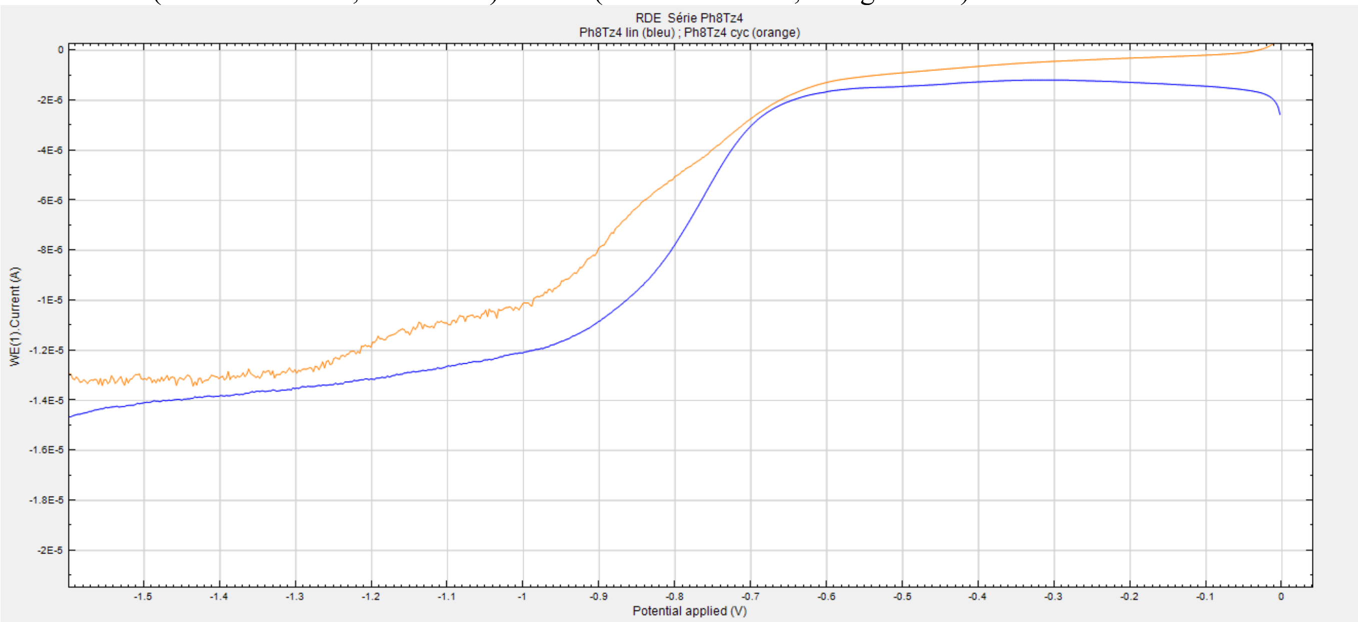
CV of **7a"** ($c = 1.12\times10^{-3}$ M, blue curve) and **8a** ($c = 1.23\times10^{-3}$ M, orange curve).



DPV of **7a"** ($c = 1.12\times10^{-3}$ M, blue curve) and **8a** ($c = 1.23\times10^{-3}$ M, orange curve).

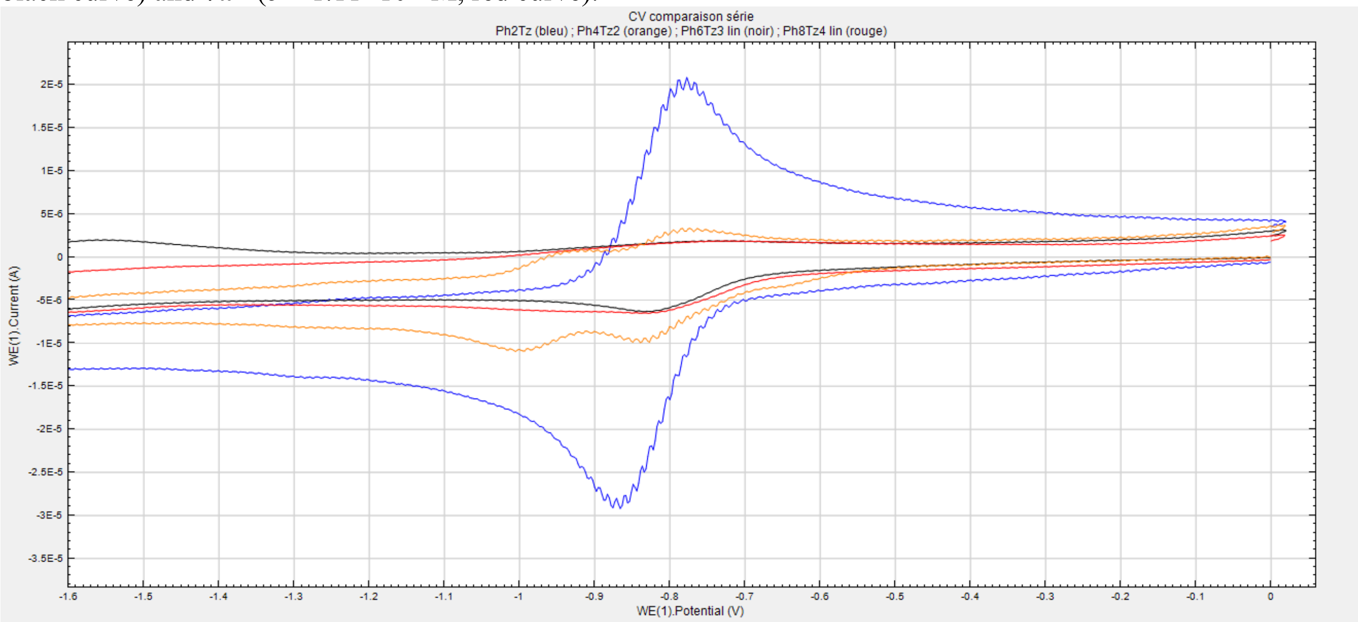


RDE of **7a''** (c = 1.12×10^{-3} M, blue curve) and **8a** (c = 1.23×10^{-3} M, orange curve).

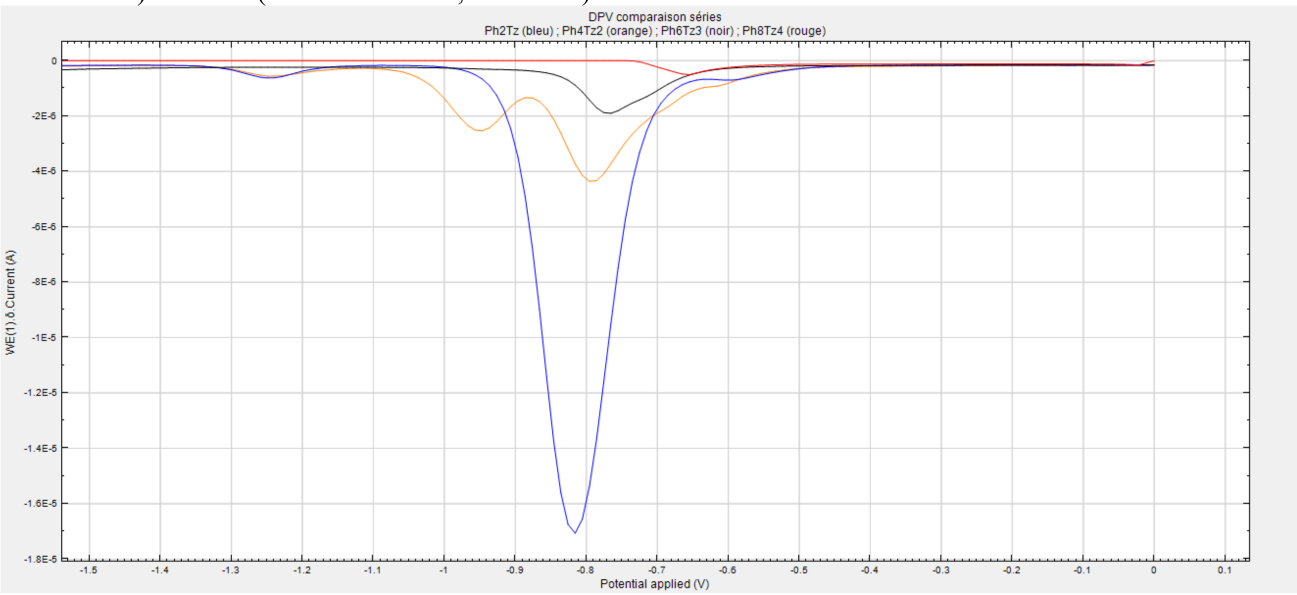


Comparison of the effect of increasing the number of tetrazine units in the non-fluorinated linear series: 1a, 3a, 5a'', 7a''

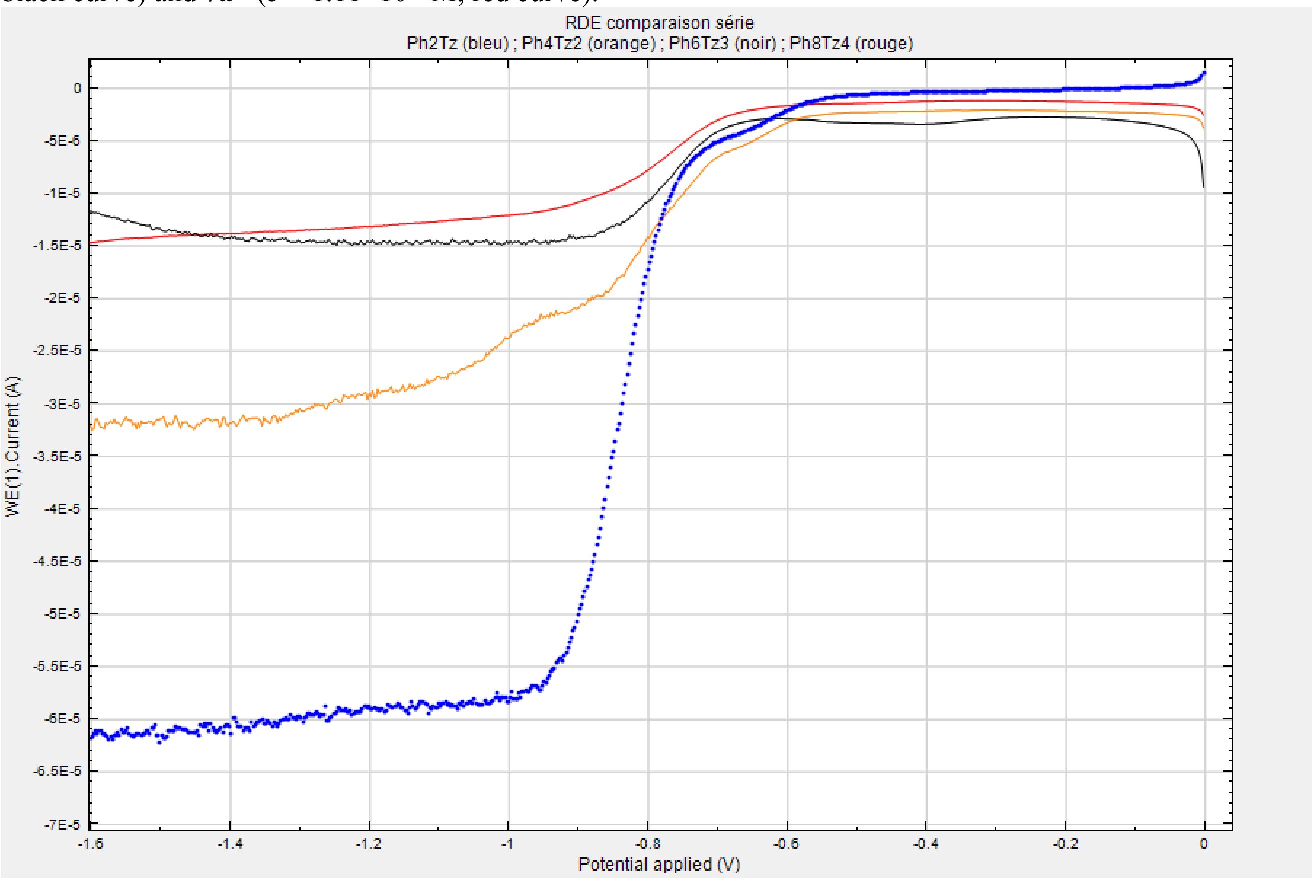
CV of **1a** (c = 2.15×10^{-3} M, blue curve), **3a** (c = 2.22×10^{-3} M, orange curve), **5a''** (c = 2.20×10^{-3} M, black curve) and **7a''** (c = 1.11×10^{-3} M, red curve).



DPV of **1a** (c = 2.15×10^{-3} M, blue curve), **3a** (c = 2.22×10^{-3} M, orange curve), **5a''** (c = 2.20×10^{-3} M, black curve) and **7a''** (c = 1.11×10^{-3} M, red curve).

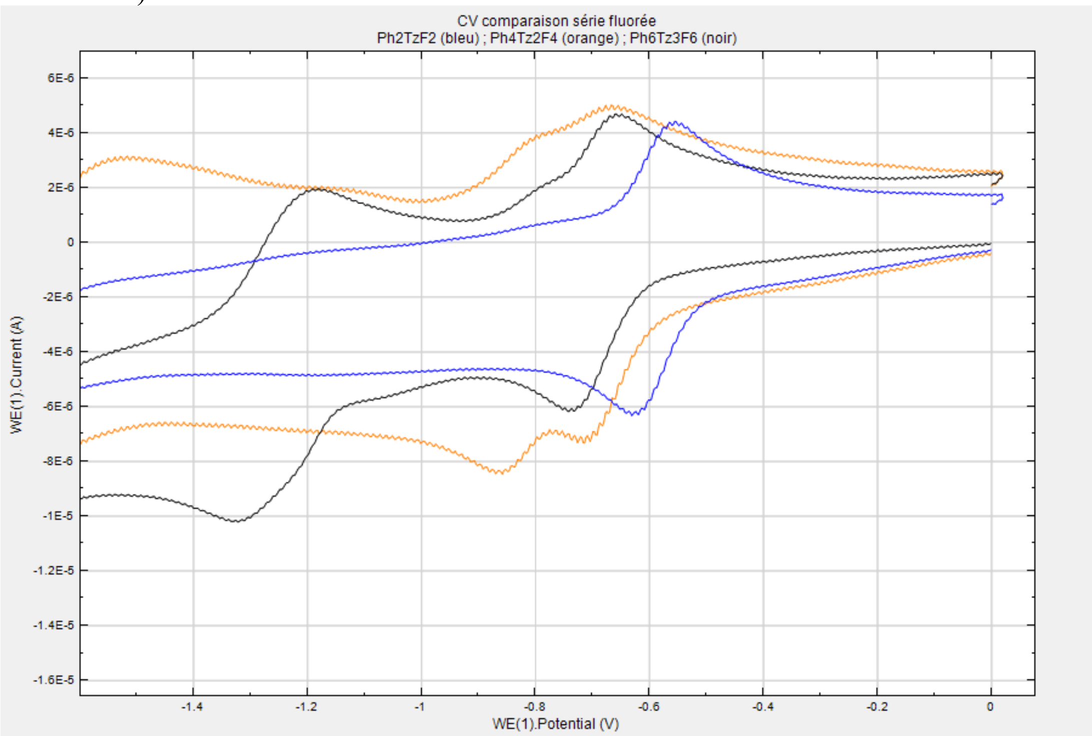


RDE of **1a** (c = 2.15×10^{-3} M, blue curve), **3a** (c = 2.22×10^{-3} M, orange curve), **5a''** (c = 2.20×10^{-3} M, black curve) and **7a''** (c = 1.11×10^{-3} M, red curve).

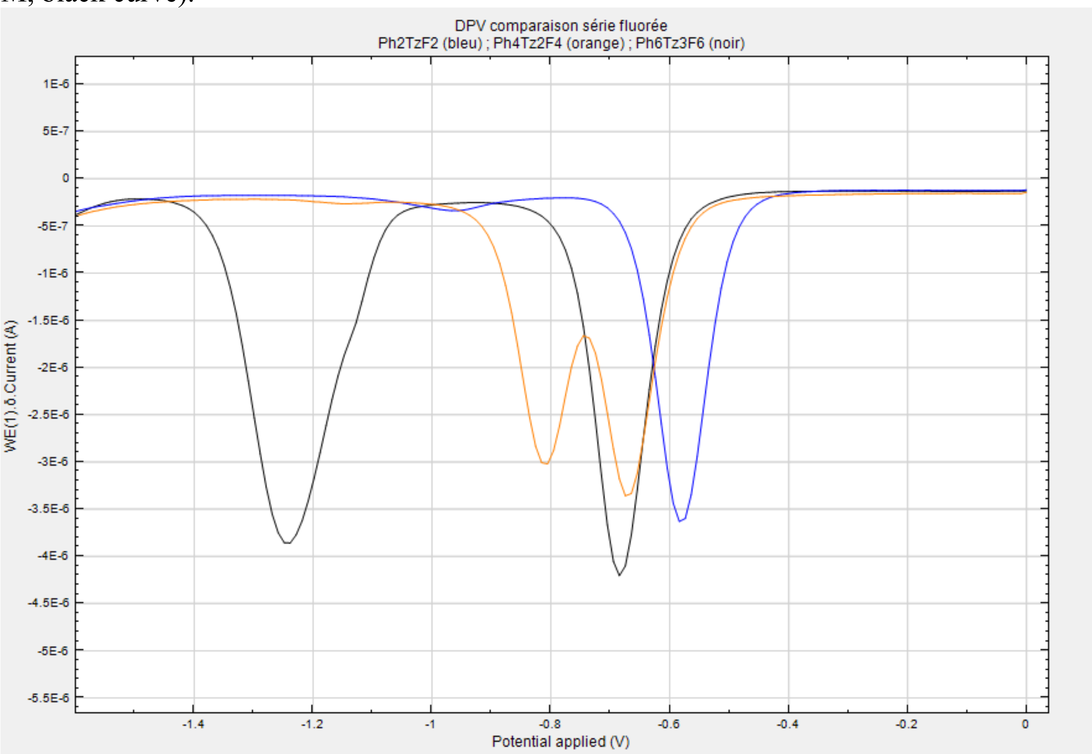


Comparison of the effect of increasing the number of tetrazine units in the fluorinated linear series: 1b, 3b, 5b".

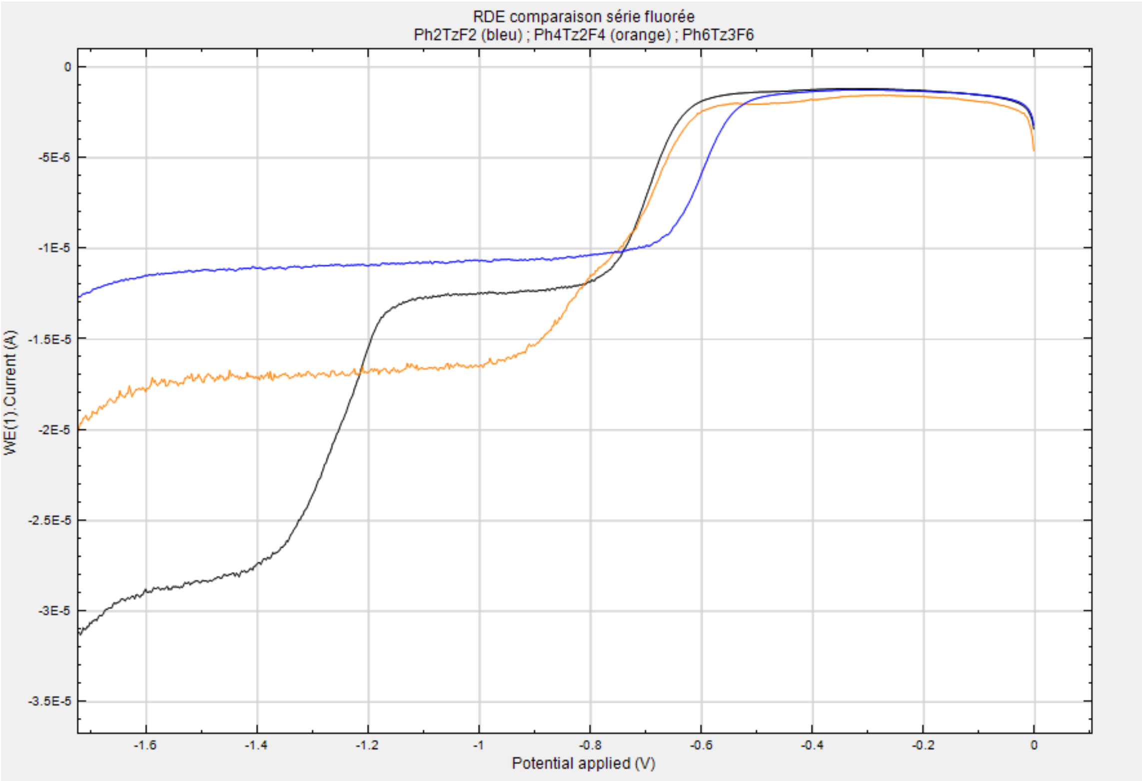
CV of **1b** (c = 1.09×10^{-3} M, blue curve), **3b** (c = 1.10×10^{-3} M, orange curve) and **5b"** (c = 1.12×10^{-3} M, black curve).



DPV of **1b** (c = 1.09×10^{-3} M, blue curve), **3b** (c = 1.10×10^{-3} M, orange curve) and **5b"** (c = 1.12×10^{-3} M, black curve).

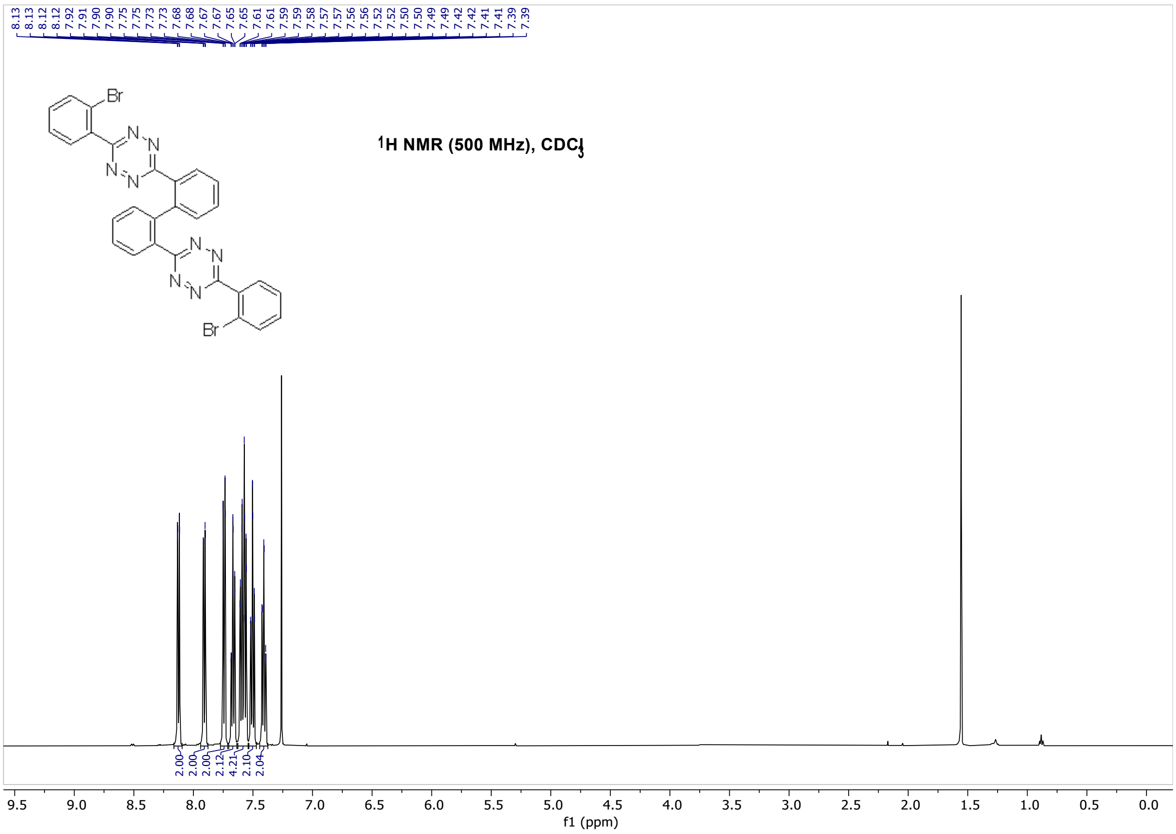


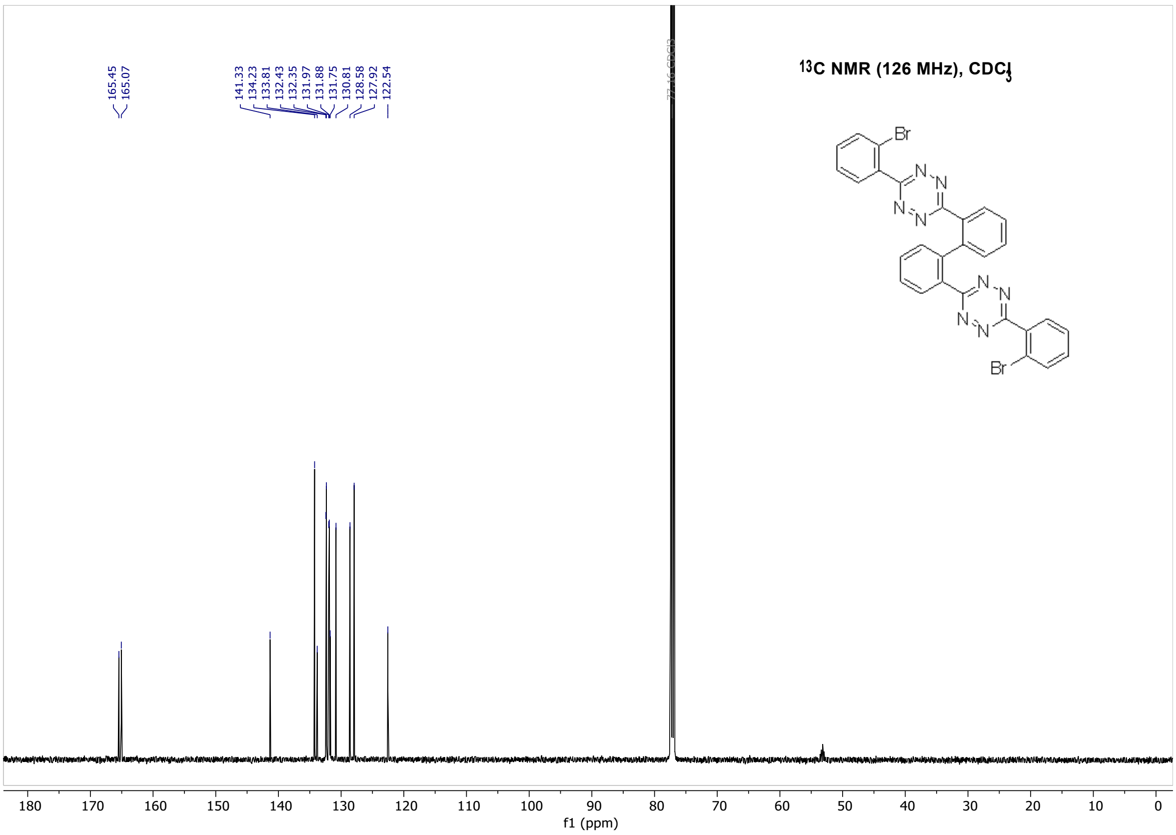
RDE of **1b** (c = 1.09×10^{-3} M, blue curve), **3b** (c = 1.10×10^{-3} M, orange curve) and **5b"** (c = 1.12×10^{-3} M, black curve).


RDE comparaison série fluorée
Ph2TzF2 (bleu) ; Ph4Tz2F4 (orange) ; Ph6Tz3F6
0
-5E-6
-1E-5
-1.5E-5
-2E-5
-2.5E-5
-3E-5
-3.5E-5
WE(1).Current (A)
-1.6
-1.4
-1.2
-1
-0.8
-0.6
-0.4
-0.2
0
Potential applied (V)

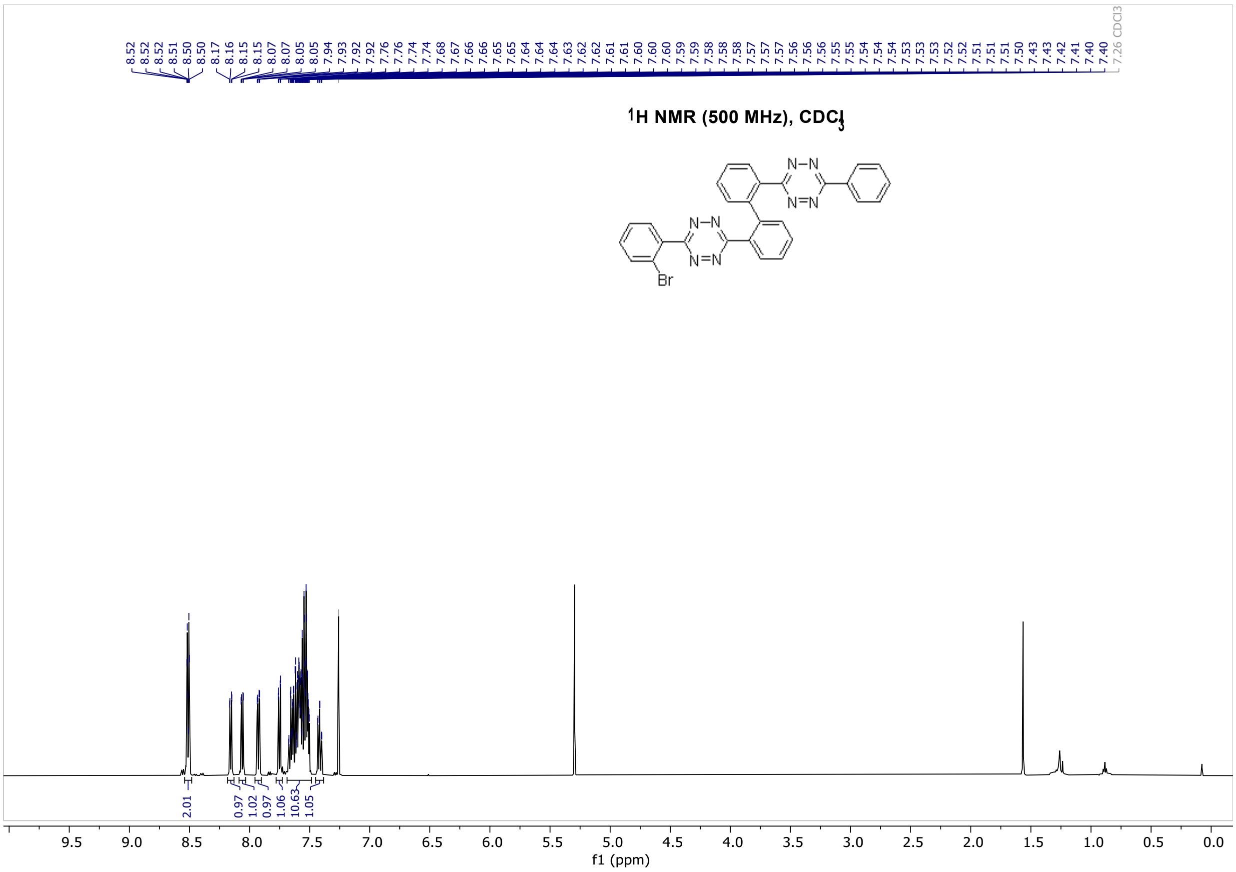
Copy of NMR and HRMS spectra

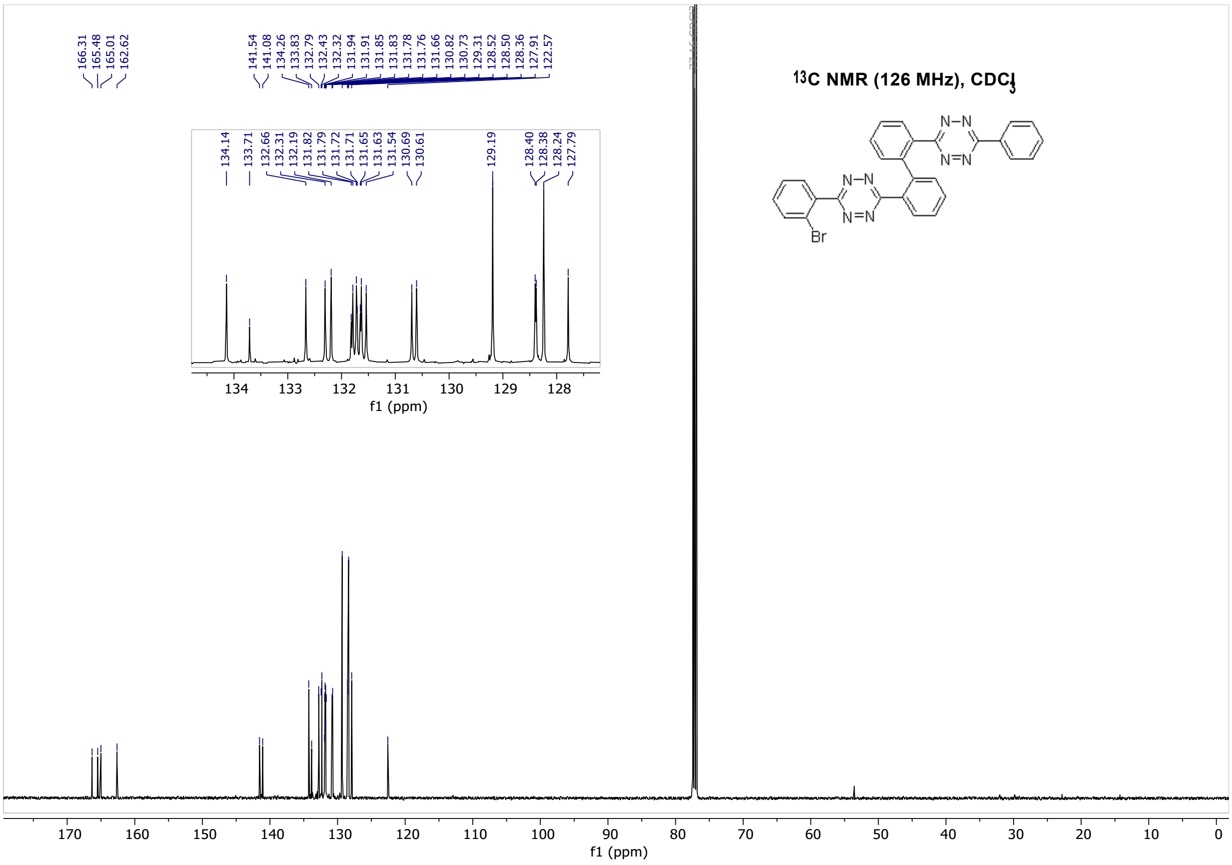
3,3'-bis[2,2'-bromophenyl]-6,6’-[1,1'-biphenyl-2,2'-diyl]-1,2,4,5-tetrazine (4a)

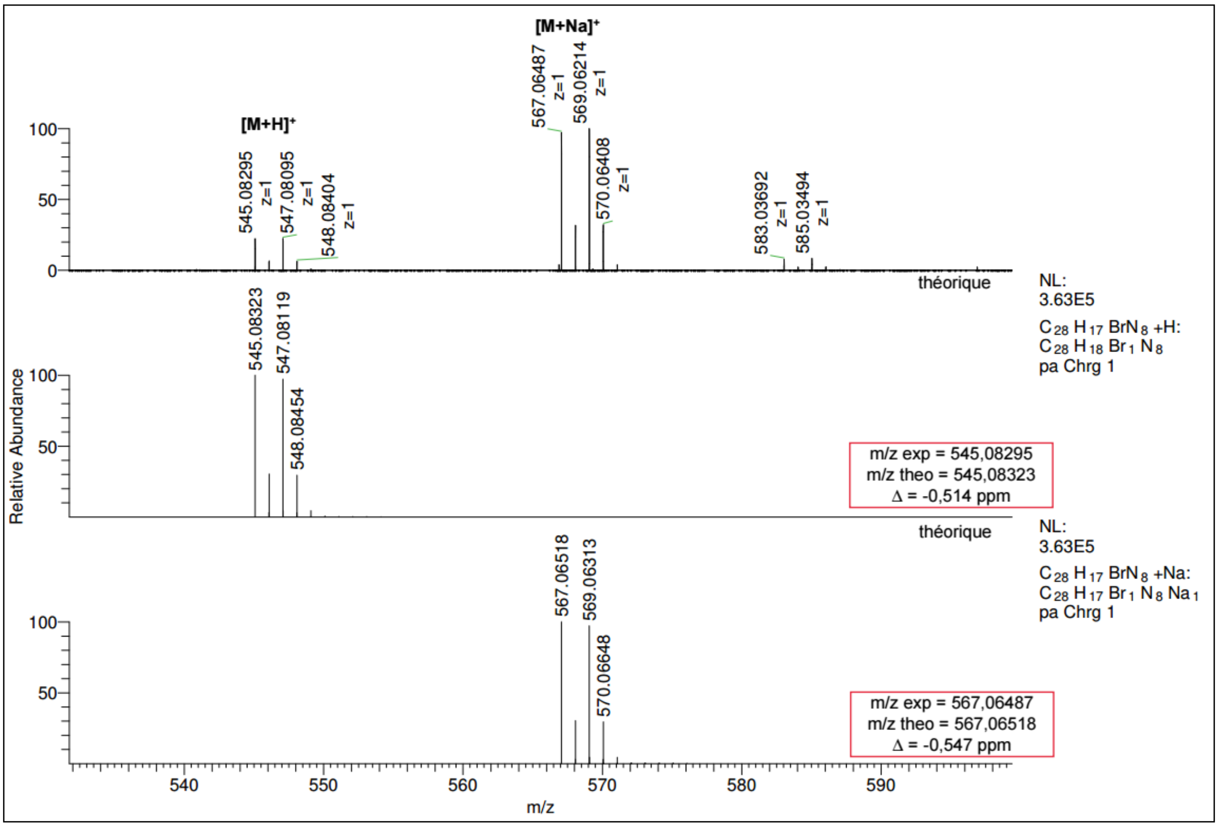




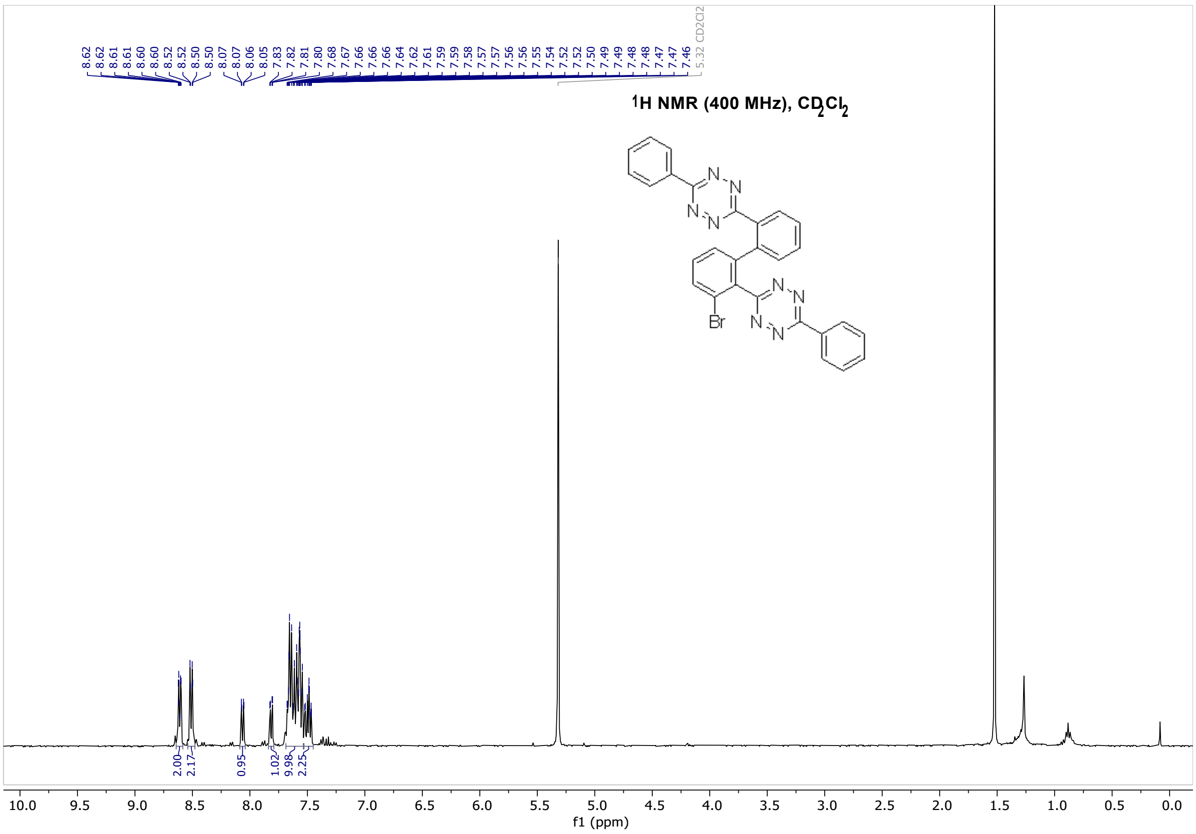
3,3’-bis[phenyl]-6,6’-[bis(2-bromophenyl)-(1,1'-biphenyl)-2,2'-diyl]-1,2,4,5-tetrazine (4a')

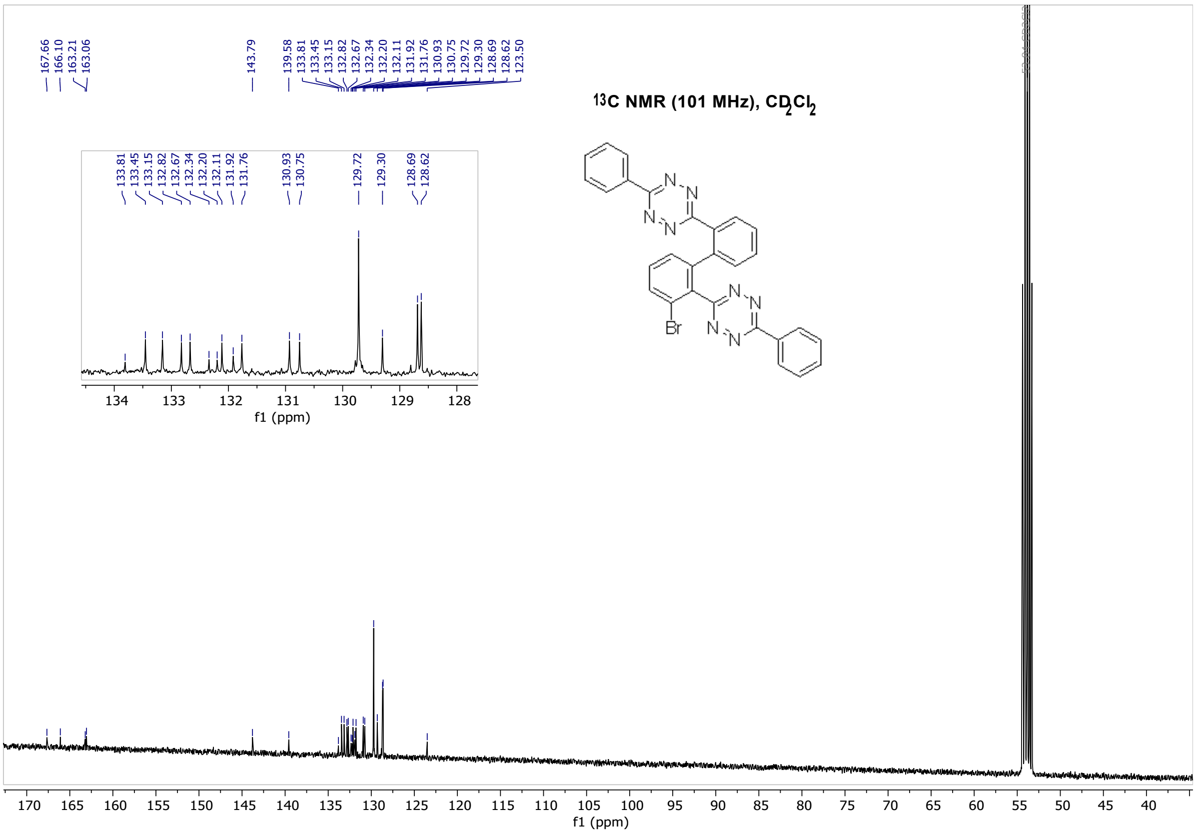


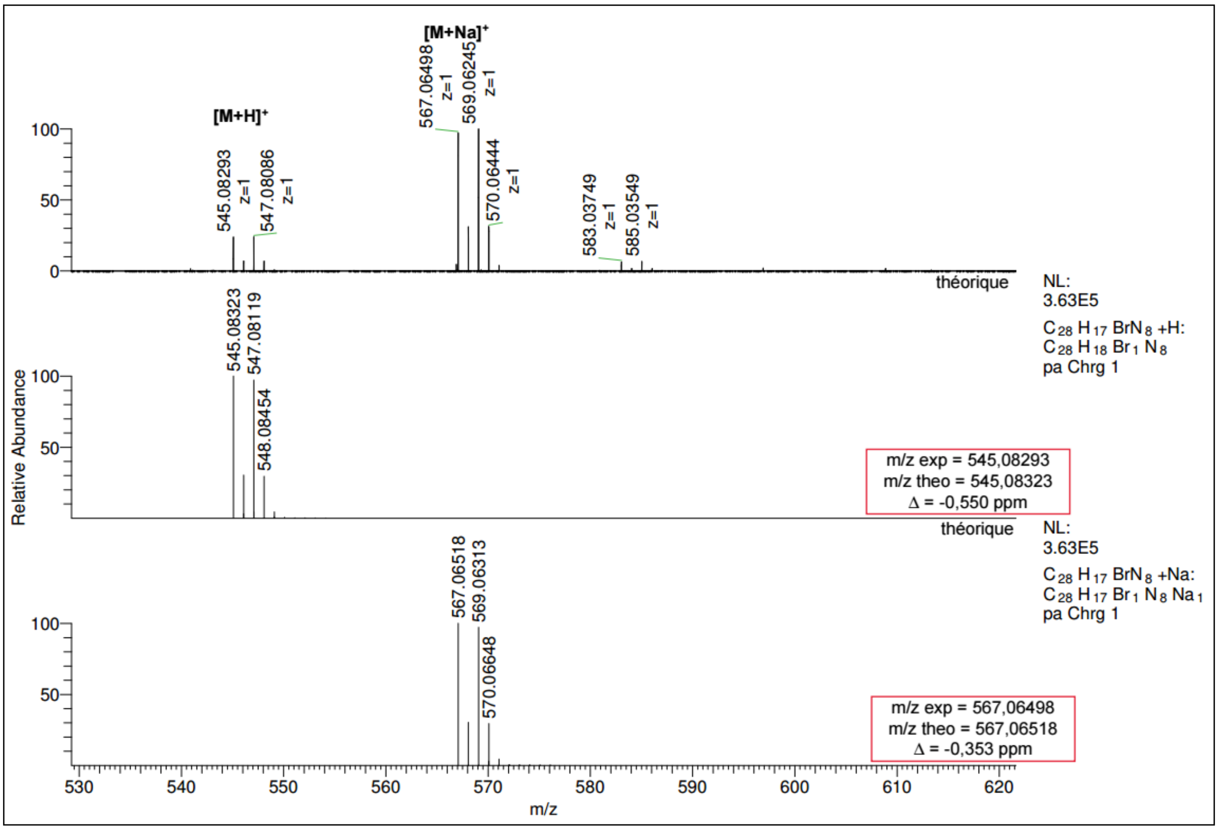




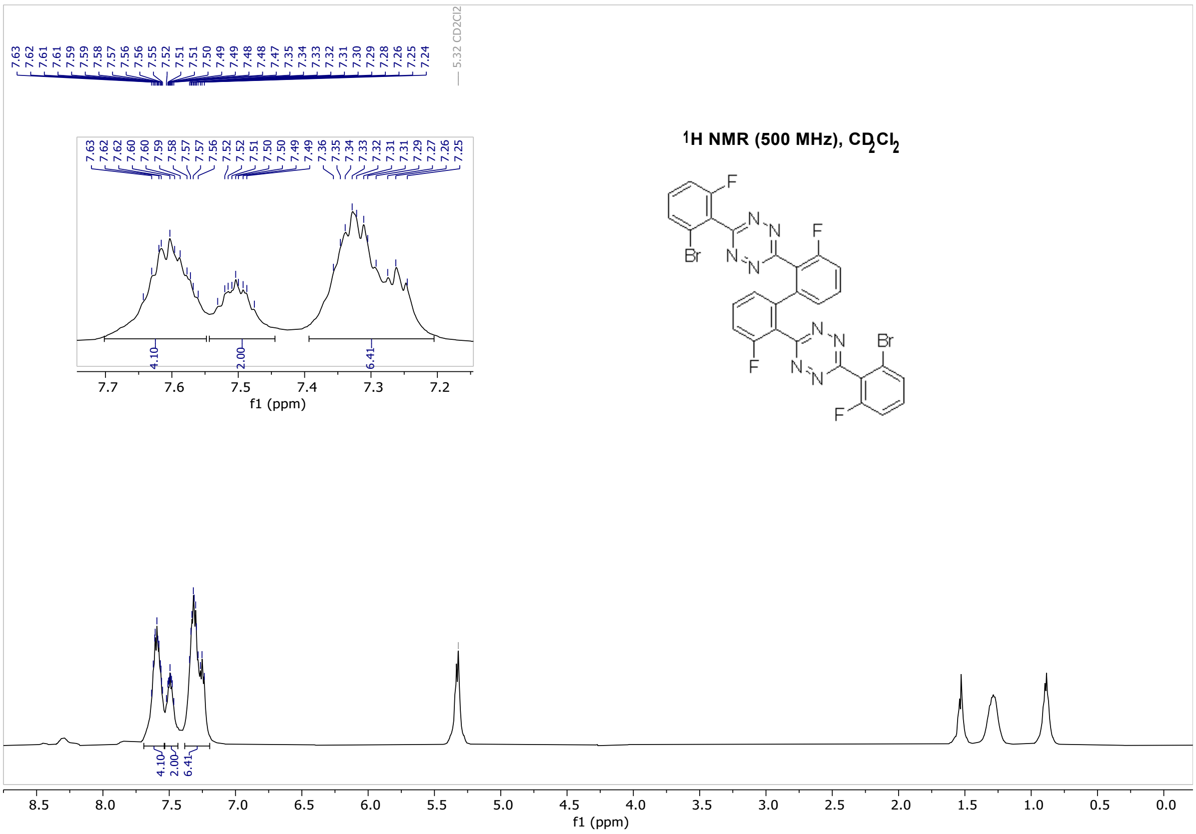
3,3'-bis[phenyl]-6,6'-[bis(2-bromophenyl)-(1,1'-biphenyl)-2,2'-diyl]-1,2,4,5-tetrazine (4a")

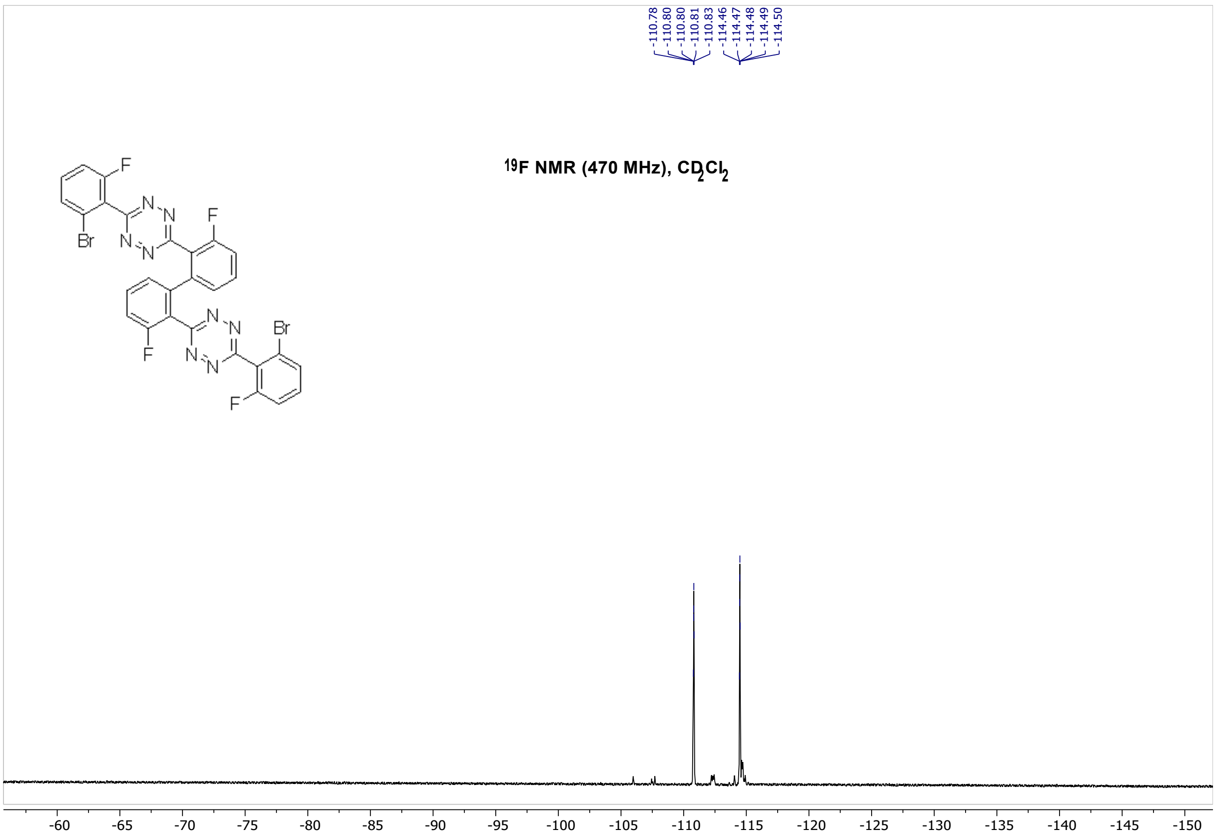


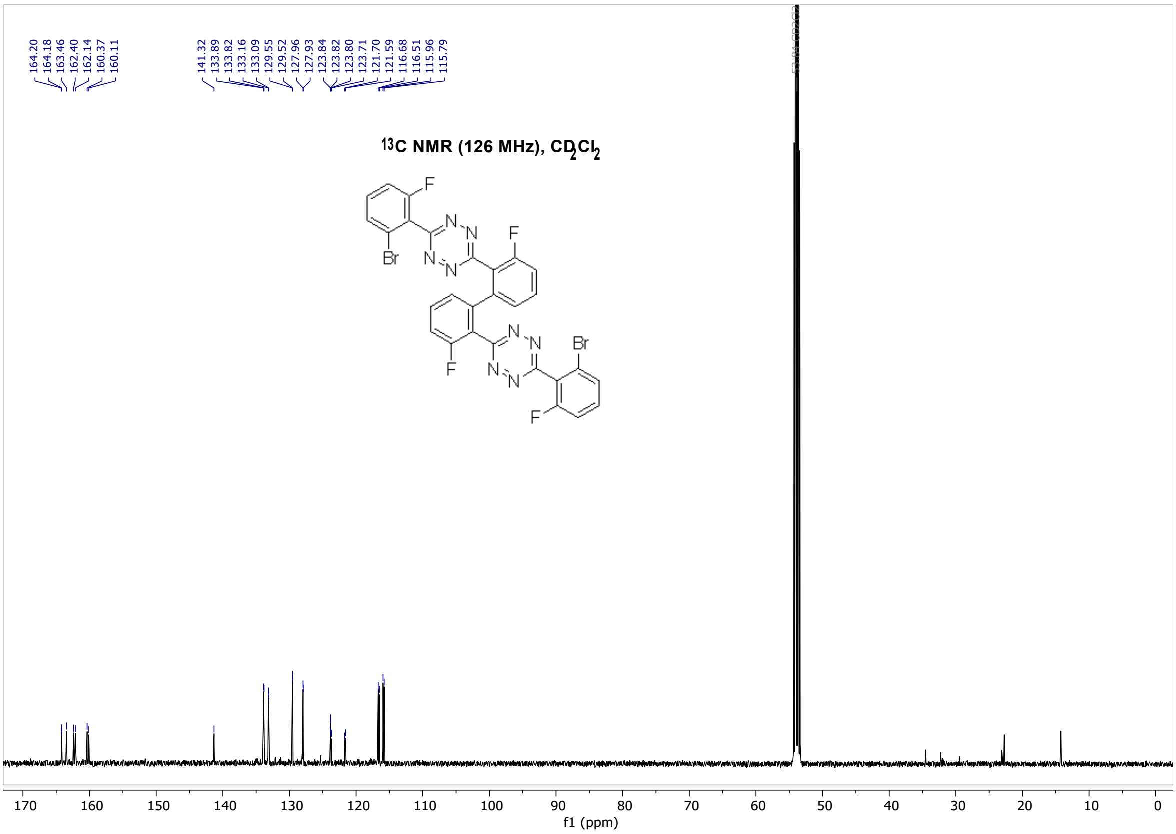

13C NMR (101 MHz), CD2Cl2
f1 (ppm)


[M+H]+
[M+Na]+
Relative Abundance
m/z
théorique
NL:
3.63E5
C28 H17 BrN8 +H:
C28 H18 Br1 N8
pa Chrg 1
m/z exp = 545,08293
m/z theo = 545,08323
Δ = -0,550 ppm
C28 H17 BrN8 +Na:
C28 H17 Br1 N8 Na1
m/z exp = 567,06498
m/z theo = 567,06518
Δ = -0,353 ppm

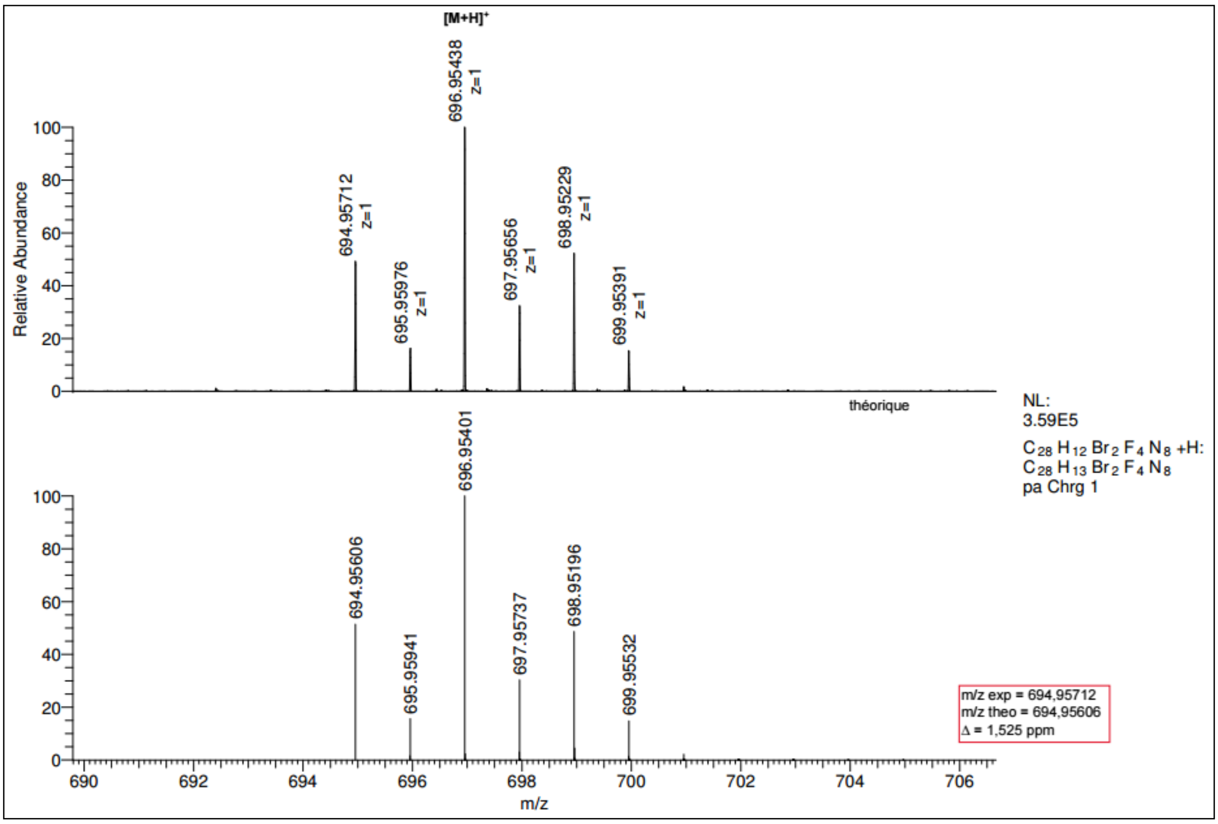
3,3’-bis[(2,2'fluoro-6,6'-bromophenyl)-(1,1'-biphenyl)-2,2'-diyl]-6,6'-bis[2,2'-fluorophenyl]-1,2,4,5-tetrazine (4b)





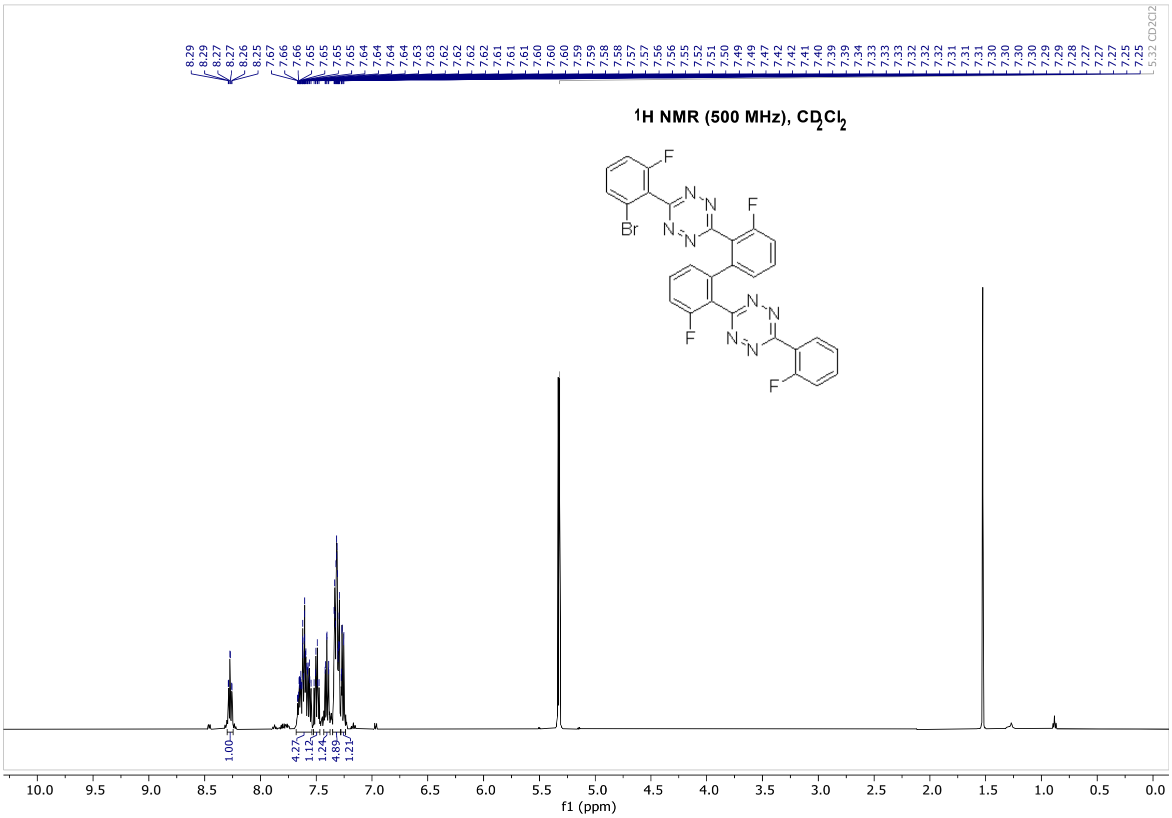


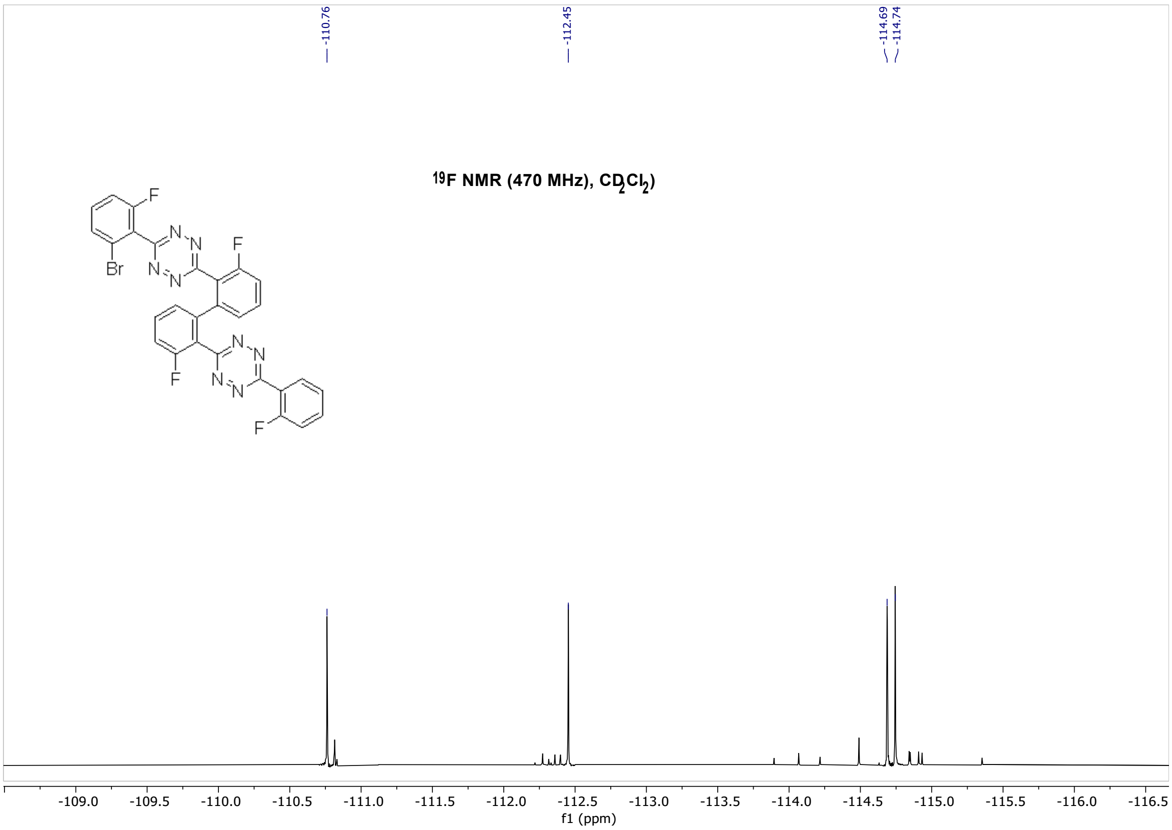
164.20
164.18
163.46
162.40
162.14
160.37
160.11
141.32
133.89
133.82
133.16
133.09
129.55
129.52
127.96
127.93
123.84
123.82
123.80
123.71
121.70
121.59
116.68
116.51
115.96
115.79
13C NMR (126 MHz), CD2Cl2
F
N
N
N
N
Br
F
F
N
N
N
N
Br
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

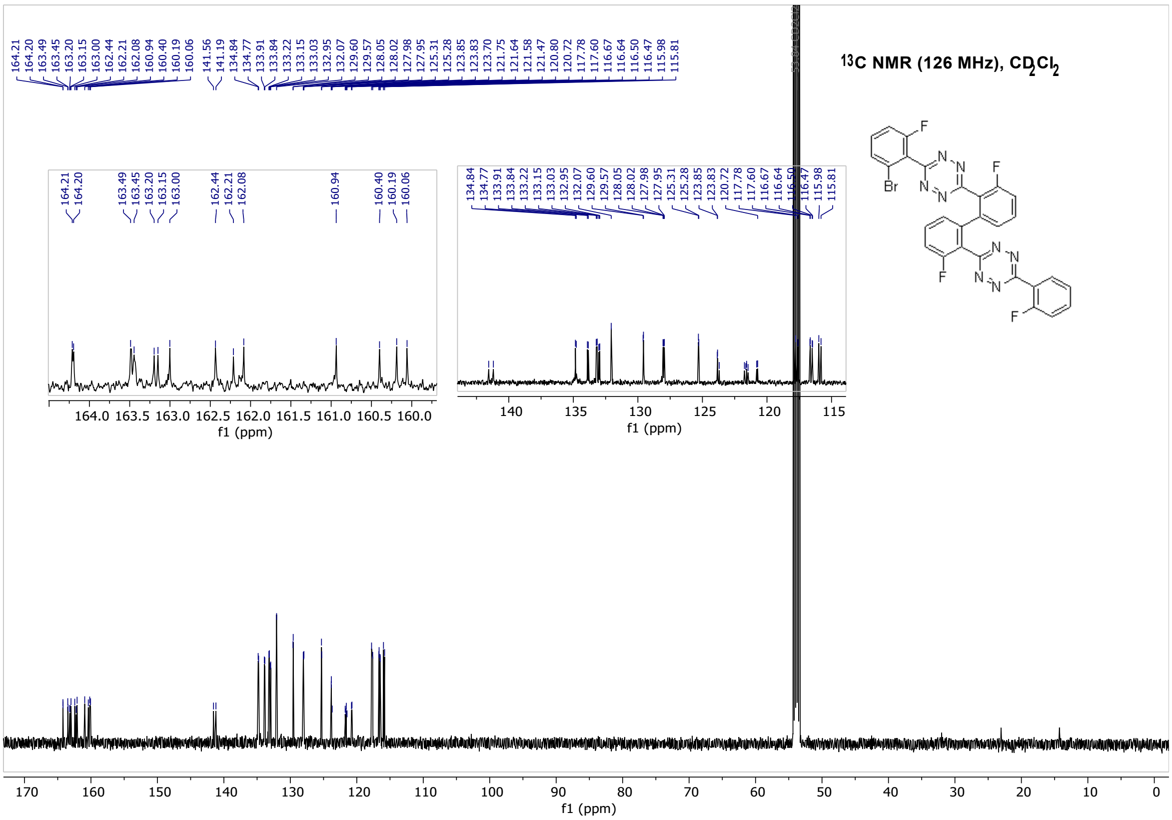


[M+H]+
696.95438
z=1
694.95712
z=1
695.95976
z=1
697.95656
z=1
698.95229
z=1
699.95391
z=1
Relative Abundance
théorique
NL:
3.59E5
C28 H12 Br2 F4 N8 +H:
C28 H13 Br2 F4 N8
pa Chrg 1
696.95401
694.95606
695.95941
697.95737
698.95196
699.95532
m/z exp = 694,95712
m/z theo = 694,95606
Δ = 1,525 ppm
690
692
694
696
698
700
702
704
706
m/z

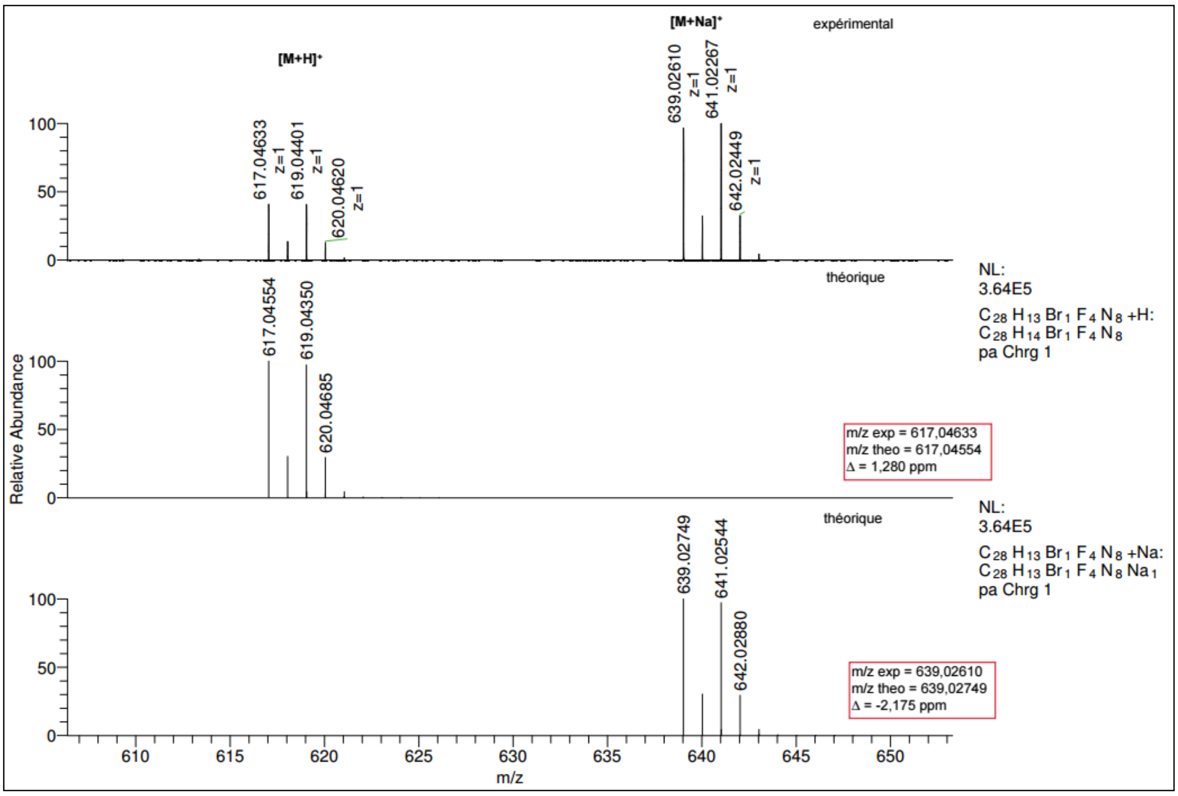
3-[(2-bromo-6-fluorophenyl)-3'-(2-fluorophenyl)]-6,6'-[bis(2,2'-fluorophenyl)-(1,1'-biphenyl) 2,2'-diyl]-1,2,4,5-tetrazine (4b')





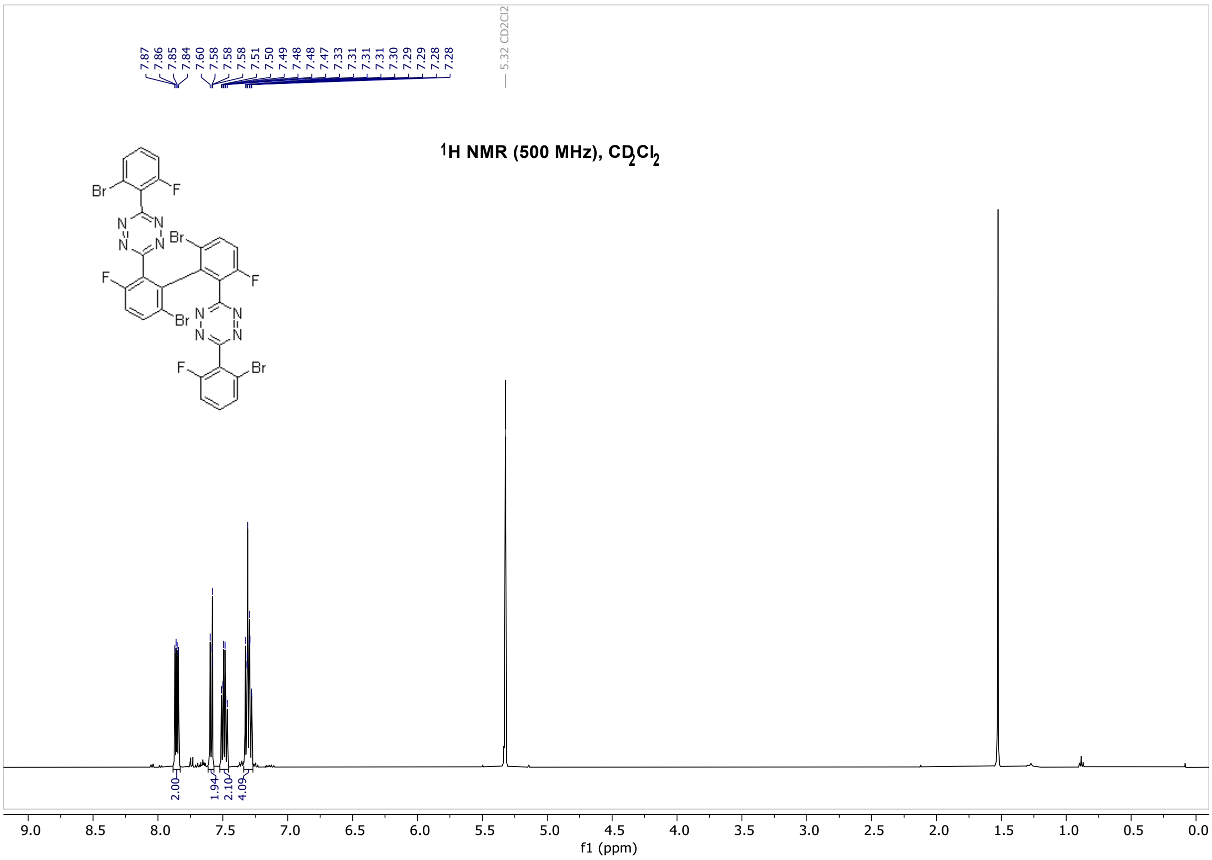


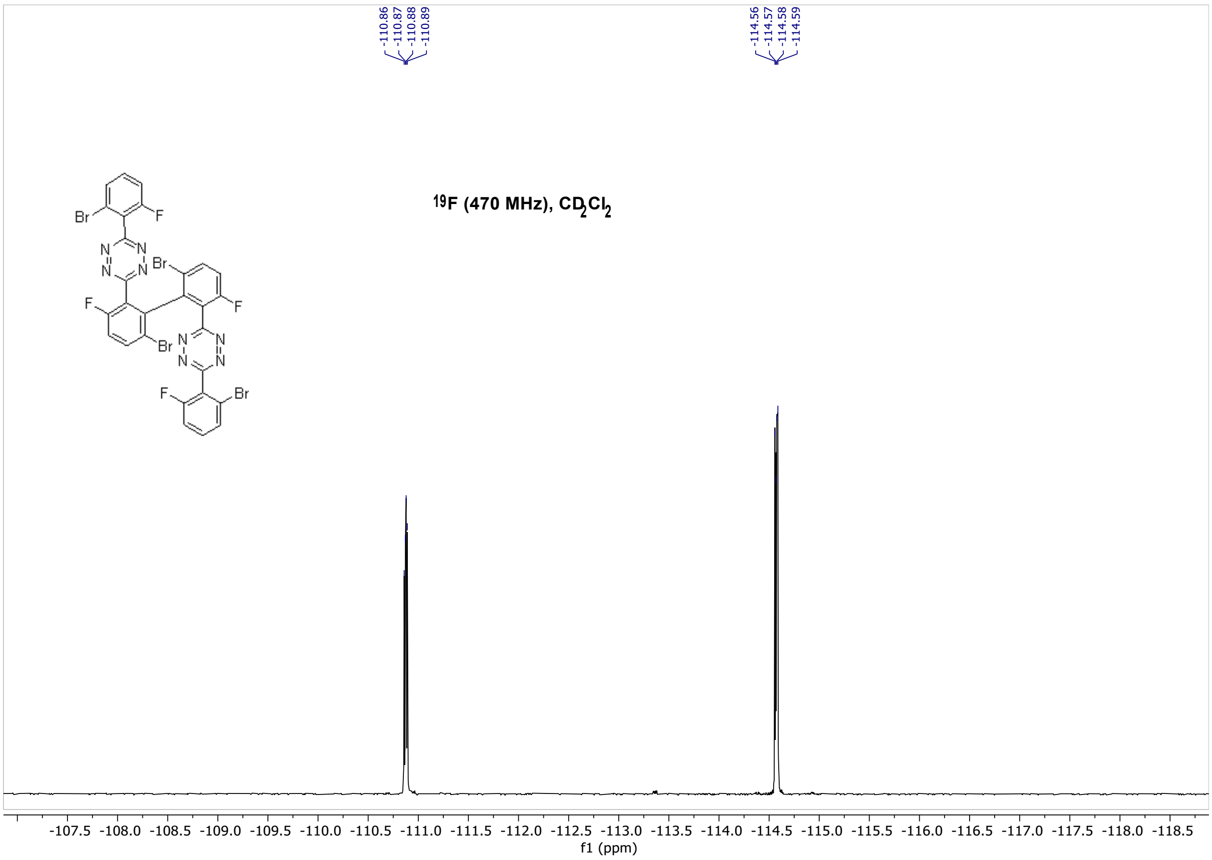
13C NMR (126 MHz), CD2Cl2
f1 (ppm)

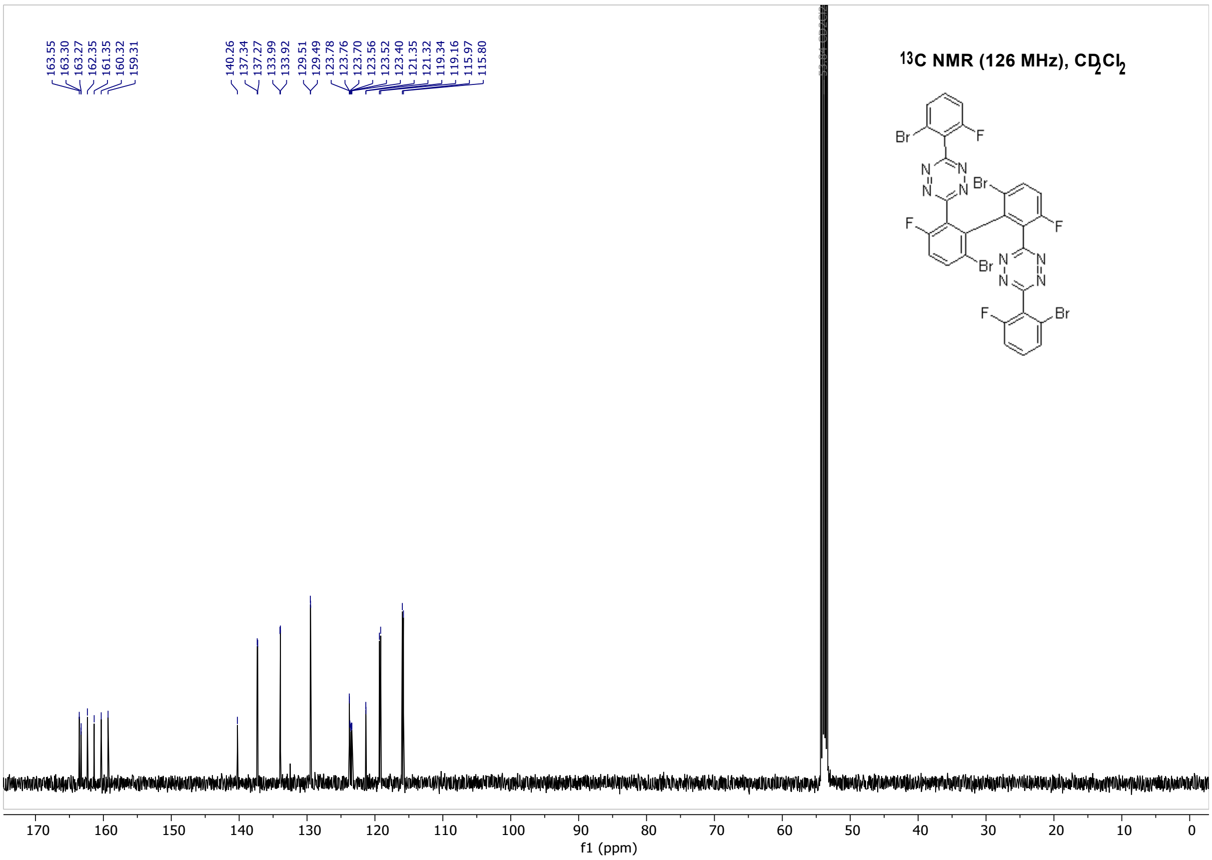


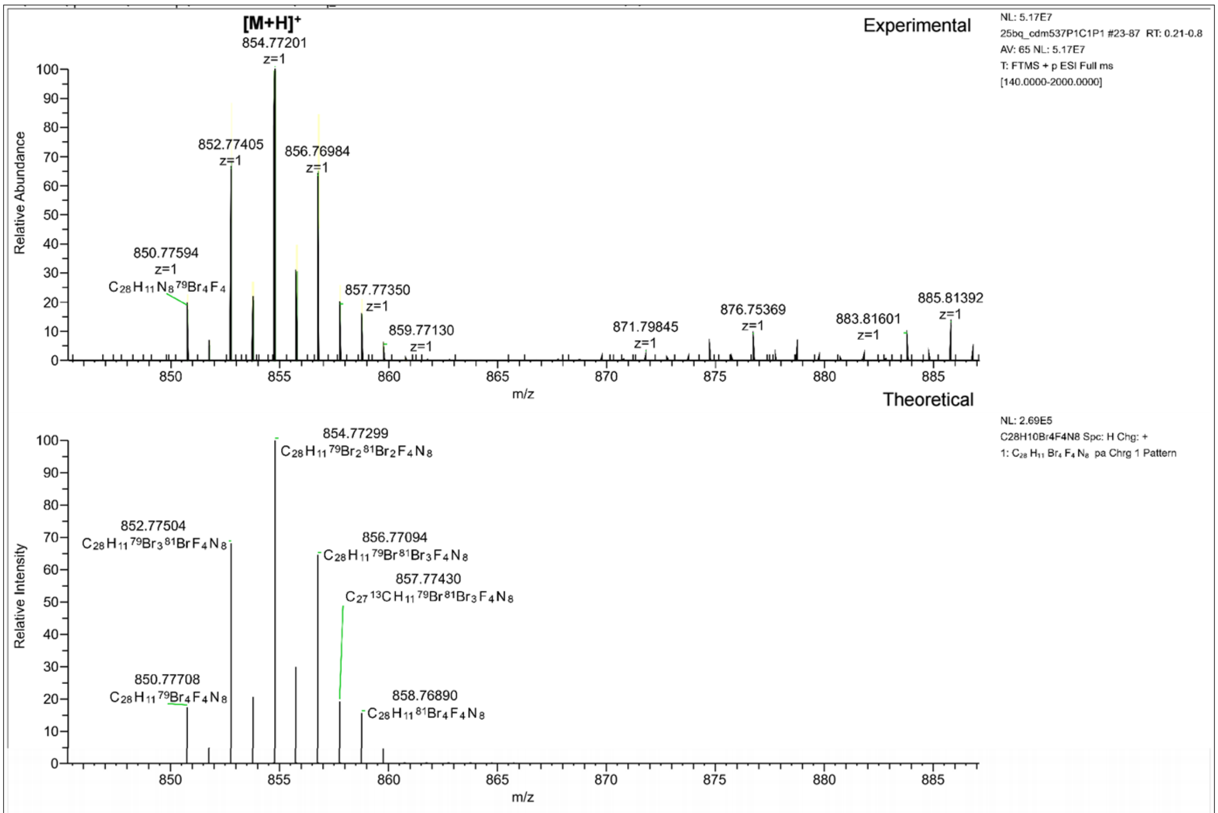
[M+Na]+
expérimental
[M+H]+
théorique
Relative Abundance
m/z
NL: 3.64E5
C28 H13 Br1 F4 N8 +H: C28 H14 Br1 F4 N8 pa Chrg 1
m/z exp = 617,04633
m/z theo = 617,04554
Δ = 1,280 ppm
C28 H13 Br1 F4 N8 +Na: C28 H13 Br1 F4 N8 Na1 pa Chrg 1
m/z exp = 639,02610
m/z theo = 639,02749
Δ = -2,175 ppm

3,3’-bis[(2,2’-fluoro-6,6’-bromophenyl)-(1,1'-biphenyl)-2,2'-diyl]-6,6'-bis[2,2'-fluoro-5,5’-bromophenyl]-1,2,4,5-tetrazine (4c)



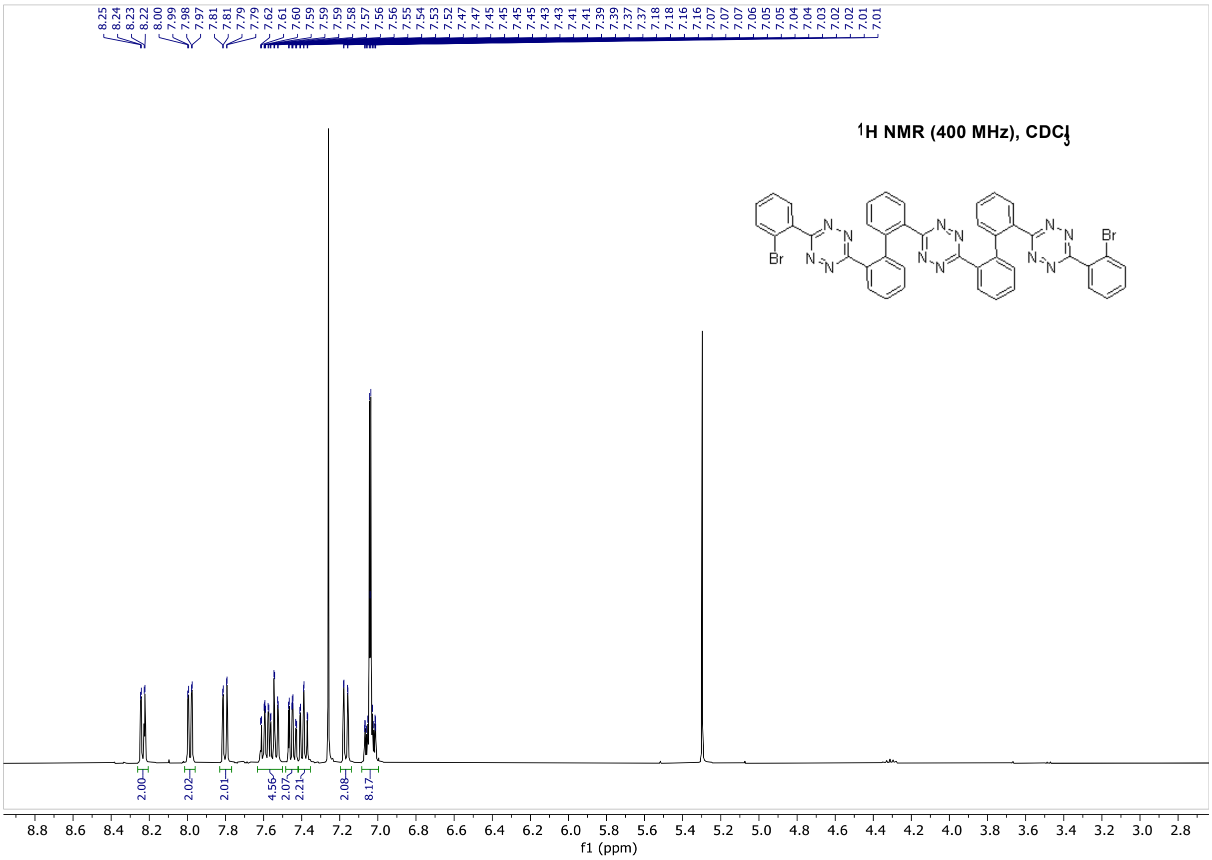


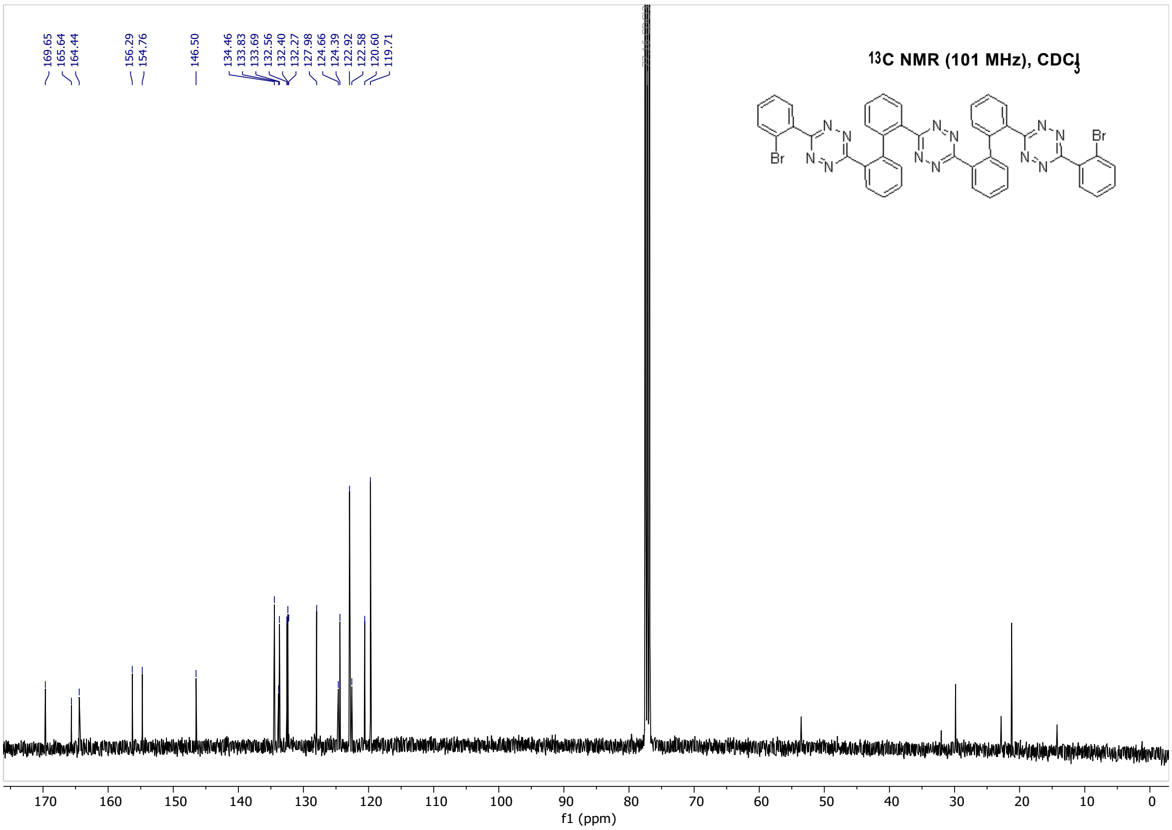


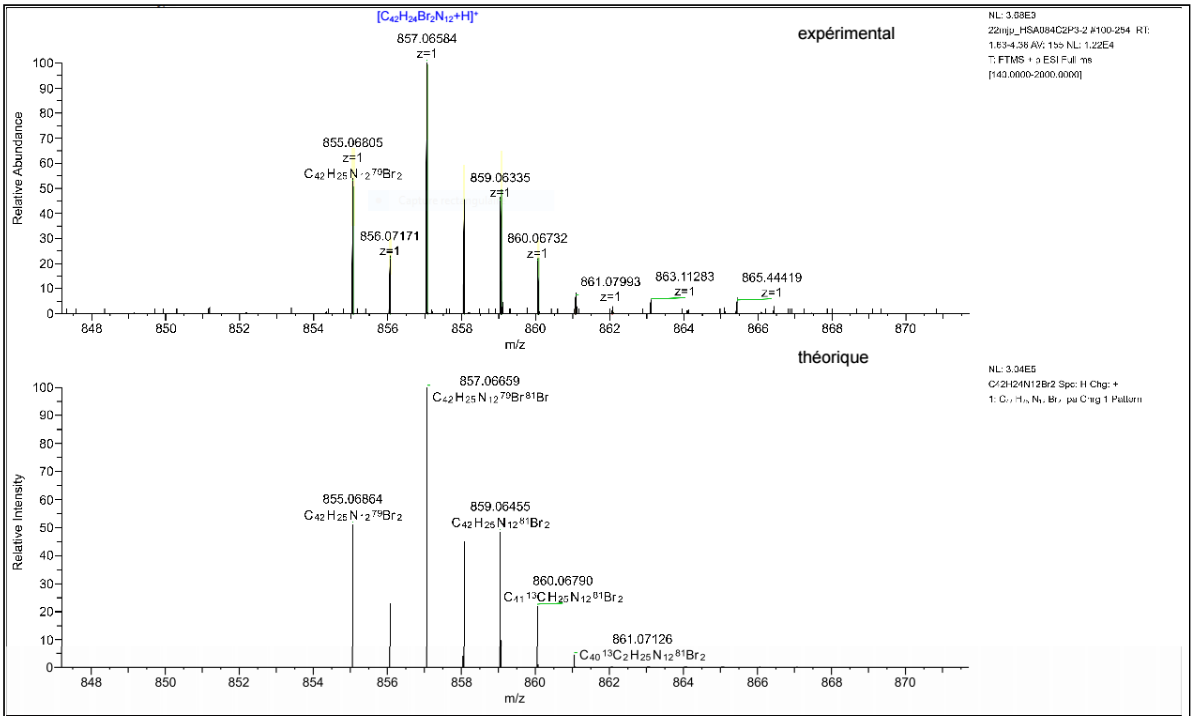


Display Formula	Peak Mass	Theo. mass	Delta [ppm]	RDB	MSMS Matched Fragments
$C_{28}H_{11}N_8{}^{79}Br_4F_4$	850.77594	850.77708	-1.34	23.50	(Collection)

3,6''-bis[2,2'-bromophenyl]-3',6,3''6'-[(1,1',1'',1'''-biphenyl)-2,2',2'',2'''-diyl]-1,2,4,5-tetrazine (5a)

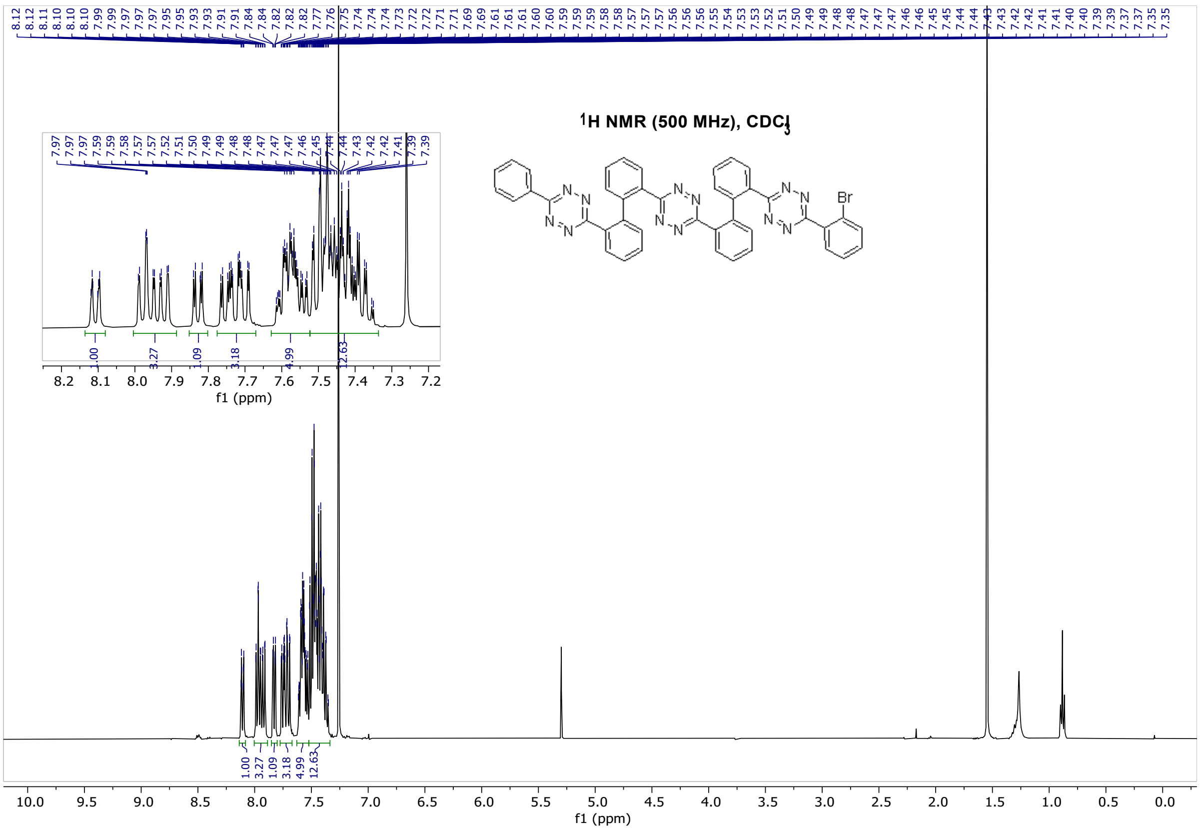


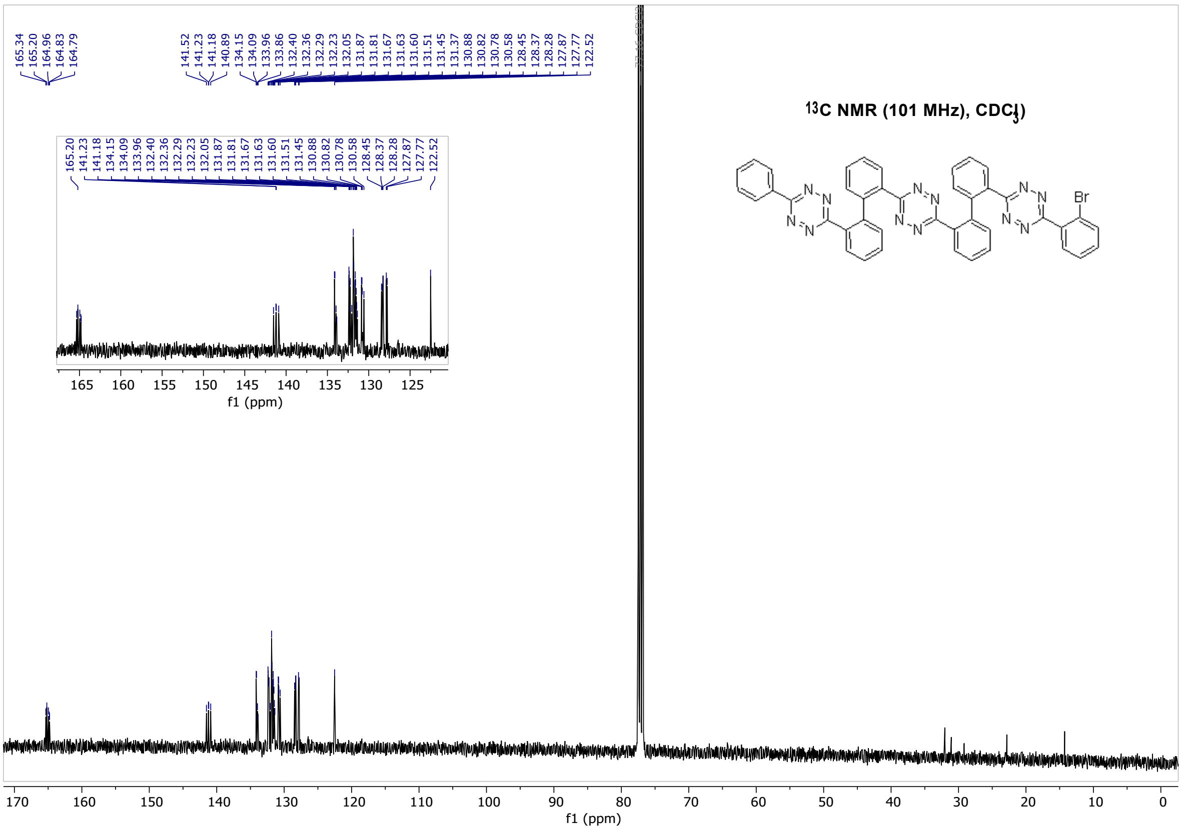




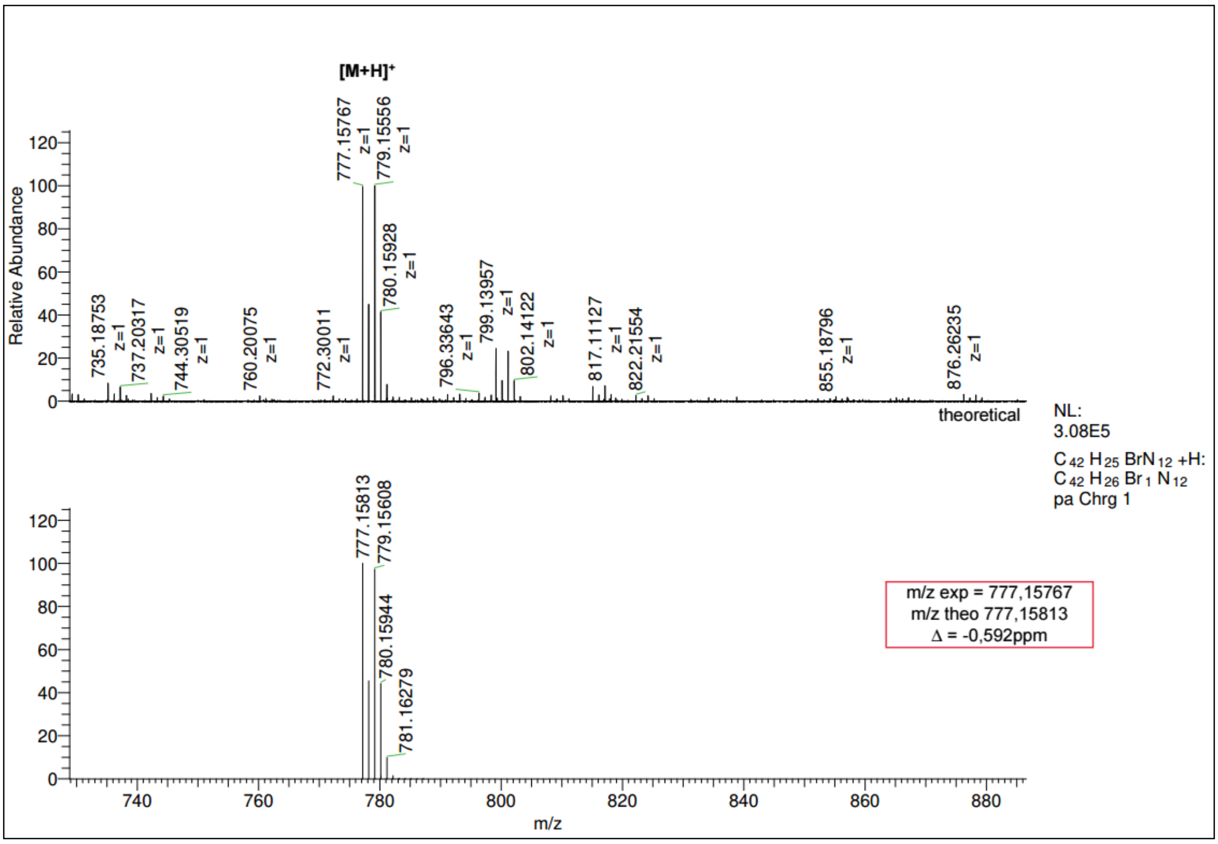
Peak Mass	Display Formula	RDB	Delta [ppm]	Theo. mass	Rank	Pattern Cov. [%]	MSMS Matched Fragm...
855.06805	$C_{42}H_{25}N_{12}{}^{79}Br_2$	35.50	-0.69	855.06864	1	98.06	(Collection)

3-[(2-bromophenyl)-6''-phenyl)]-3',6,3'',6'-[(1,1',1'',1'''-biphenyl)-2,2',2'',2'''-diyl]-1,2,4,5-tetrazine (5a')



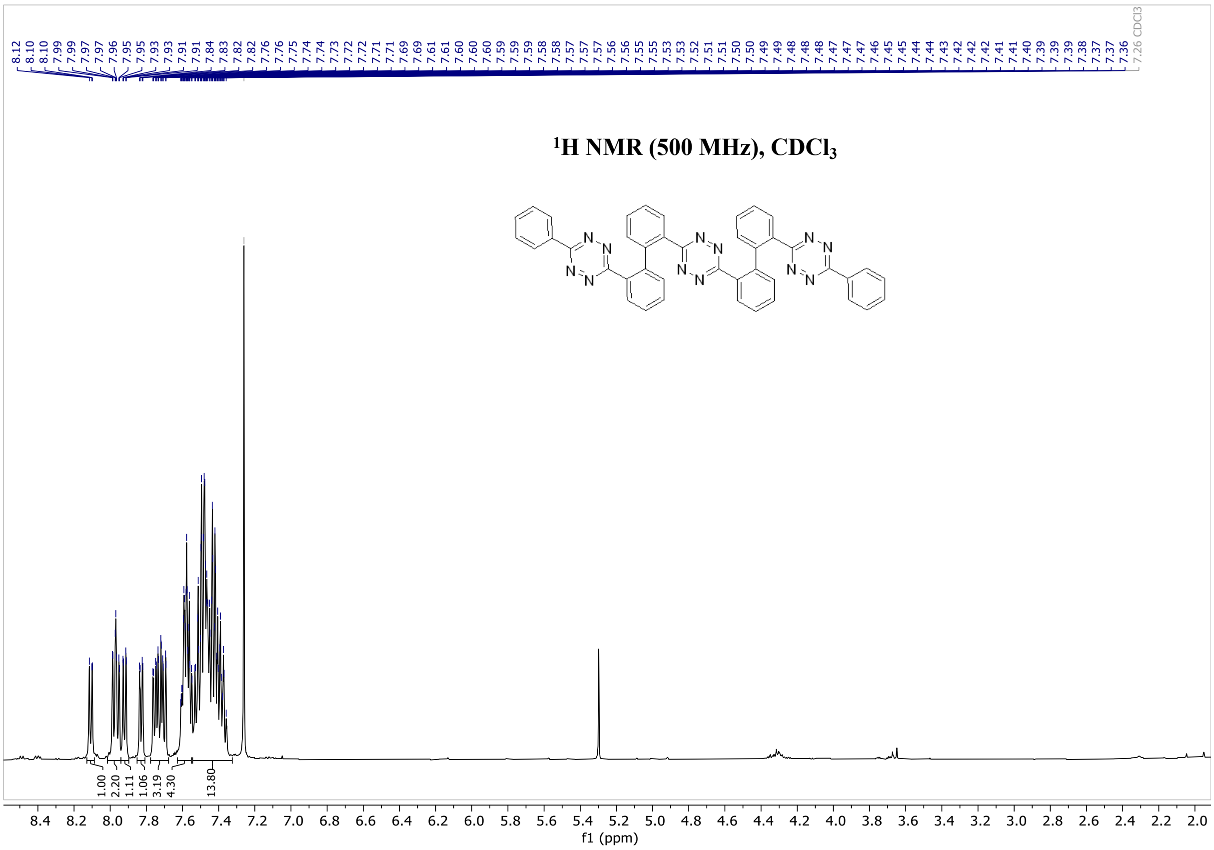


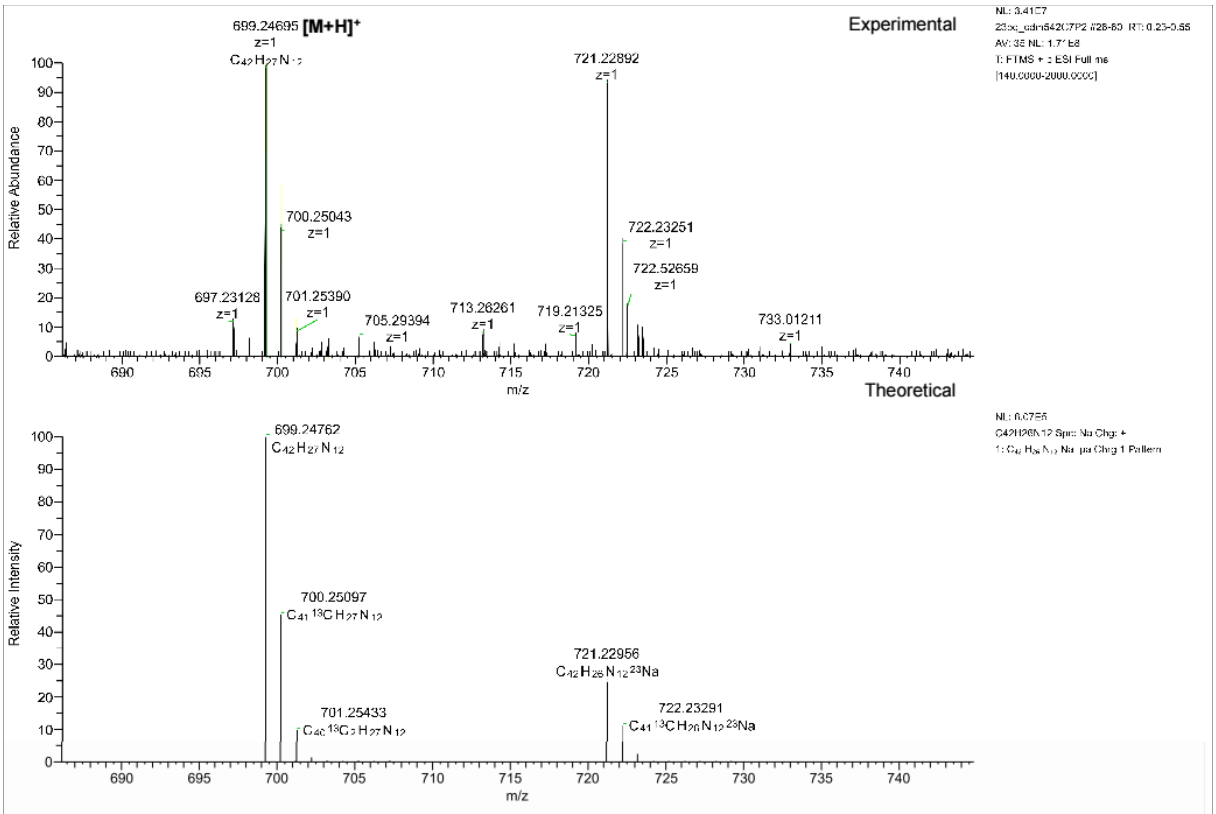
13C NMR (101 MHz), CDCl3
Br
N
f1 (ppm)



[M+H]+
Relative Abundance
theoretical
NL:
3.08E5
C 42 H 25 BrN 12 +H:
C 42 H 26 Br 1 N 12
pa Chrg 1
m/z exp = 777,15767
m/z theo 777,15813
Δ = -0,592ppm
m/z

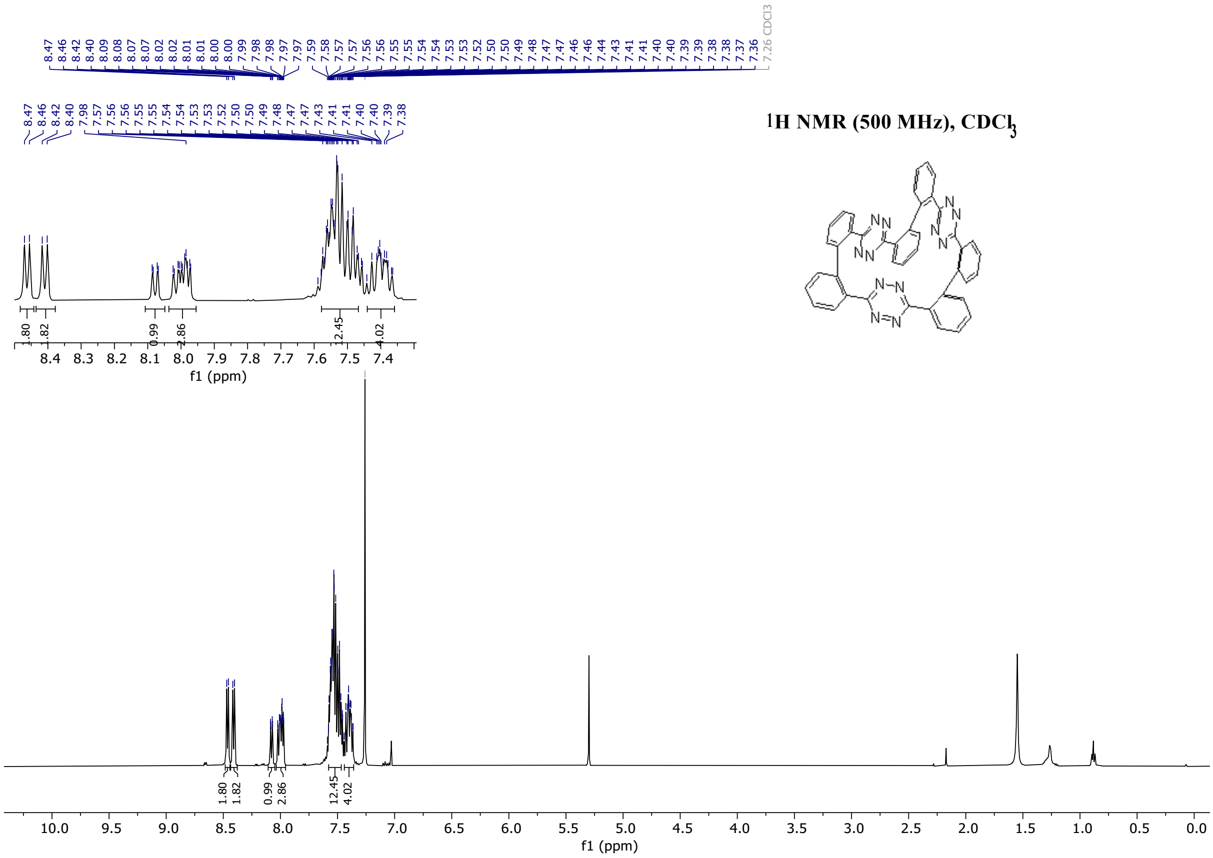
3,6''-[bis(phenyl]-3'6,3''6'-[(1,1',1'',1'''-biphenyl)-2,2',2'',2'''-diyl]-1,2,4,5-tetrazine (5a'')

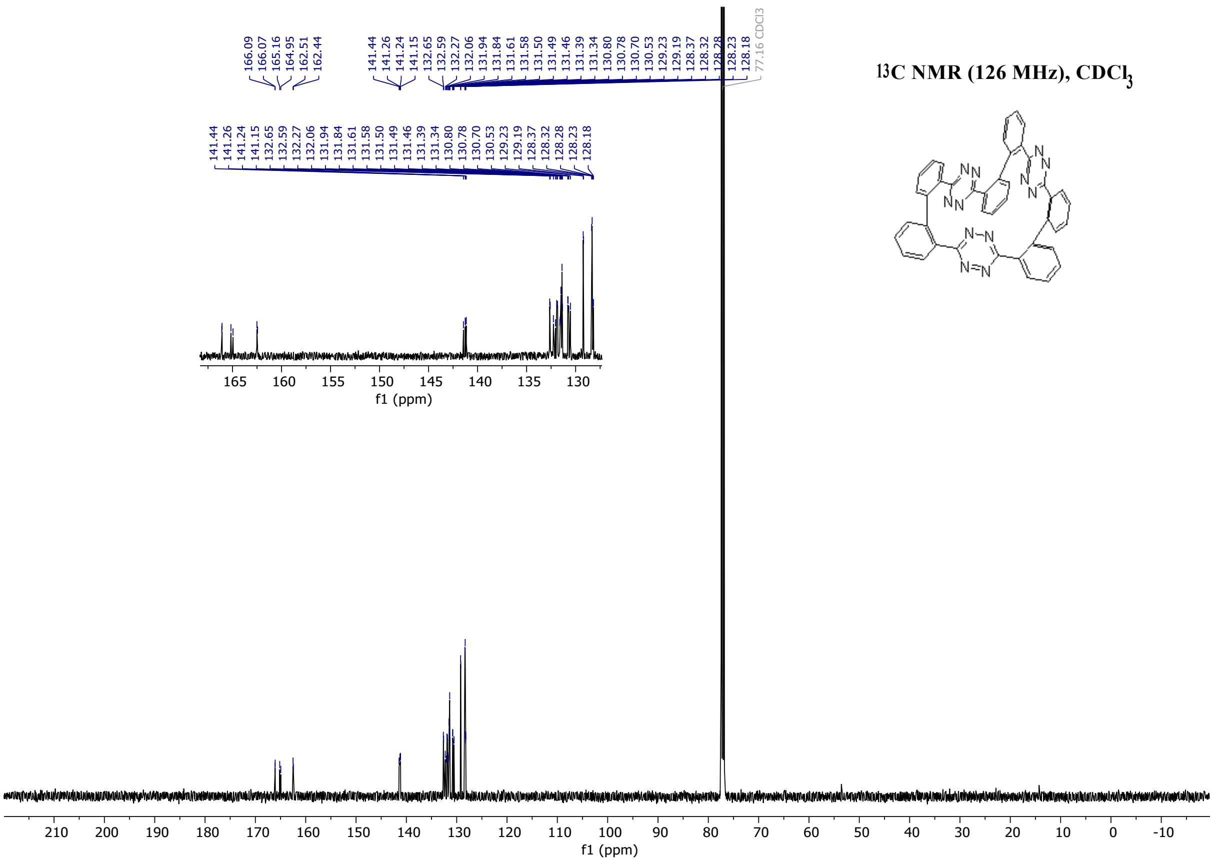


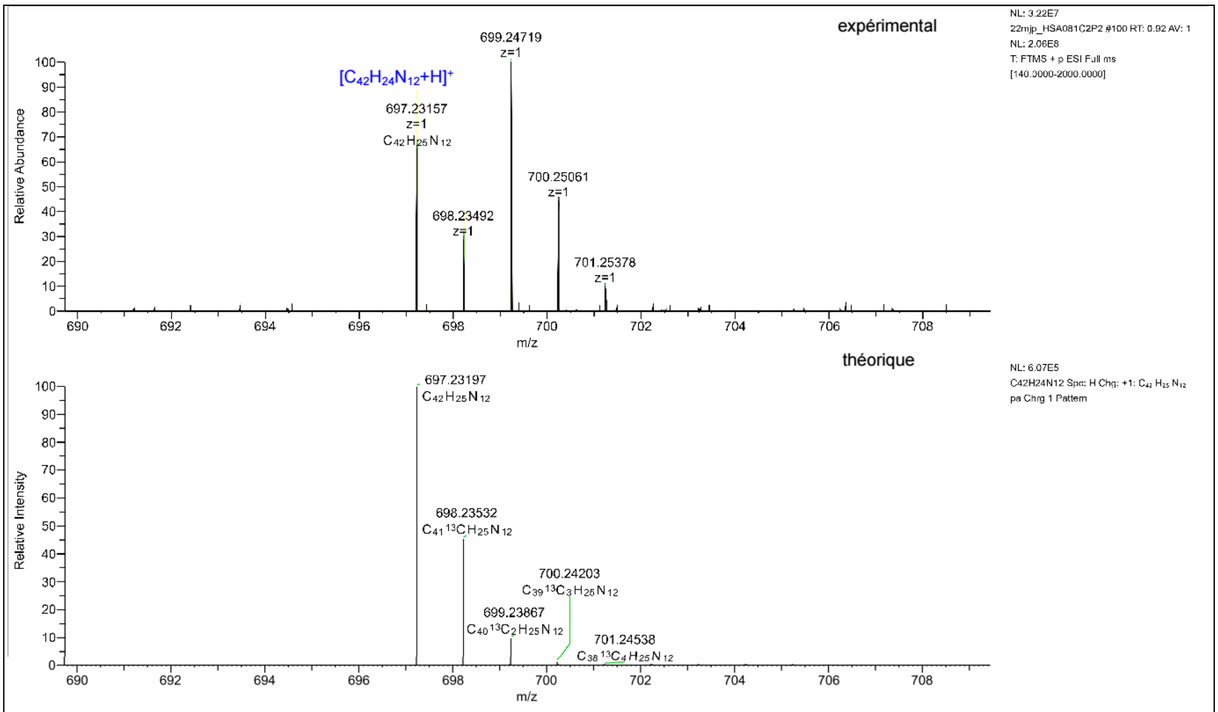


Display Formula	Peak Mass	Theo. mass	Delta [ppm]	RDB	MSMS Matched Fragments
$C_{42}H_{27}N_{12}$	699.24695	699.24762	-0.96	35.50	(Collection)

3',6,3",6',3,6"-[(1,1',1",1"',1"",1""'-biphenyl)-2,2',2",2"',2"",2""'-diyl]-1,2,4,5-tetrazine (6a)

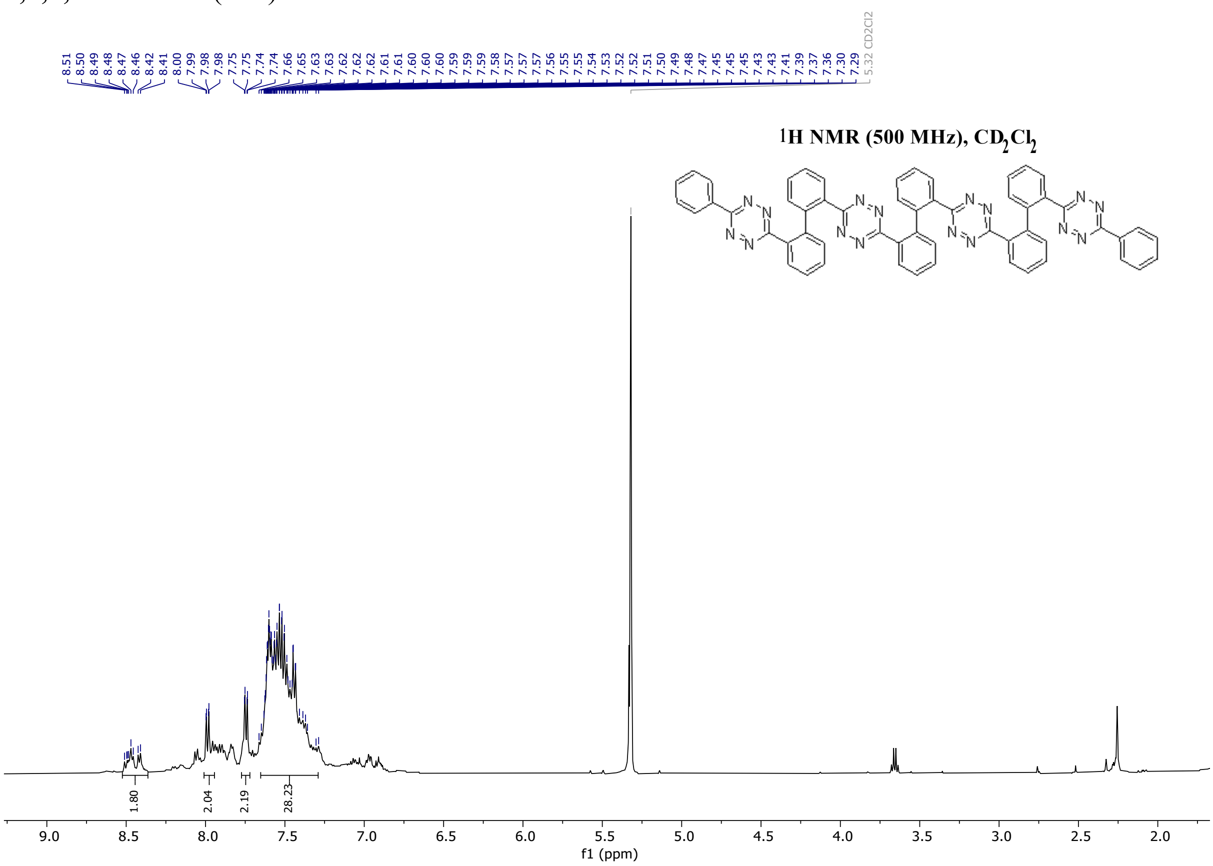


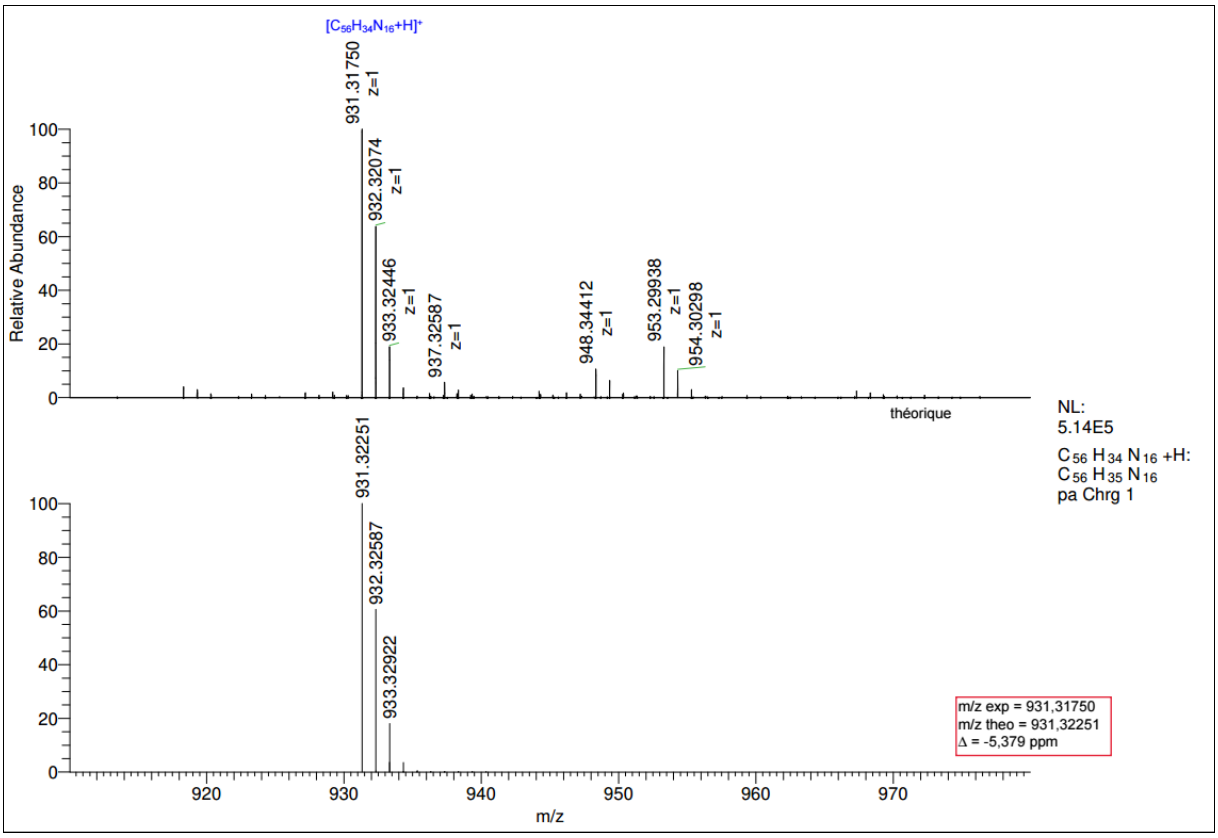




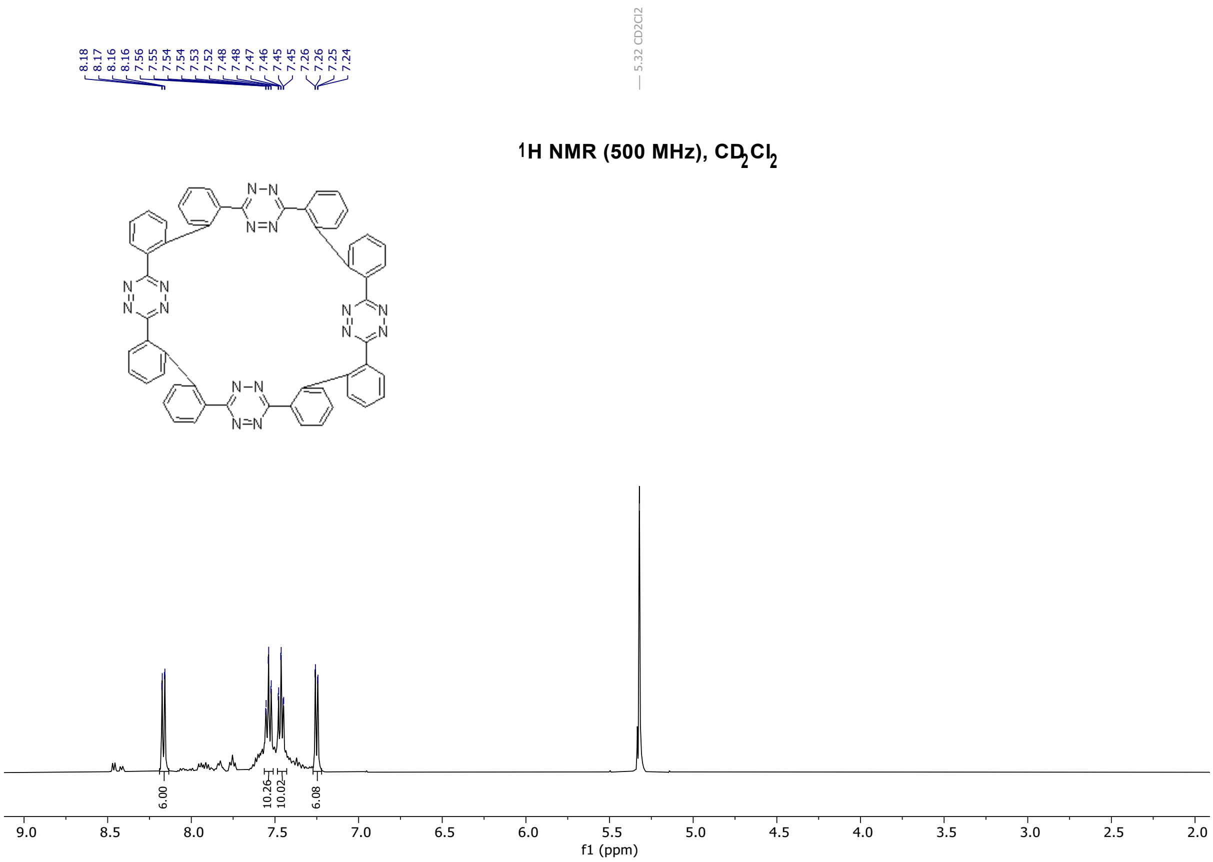
Peak Mass	Display Formula	RDB	Delta [ppm]	Theo. mass	Rank	Pattern Cov. [%]	MSMS Matched Fragm...
697.23157	$C_{42}H_{25}N_{12}$	36.50	-0.57	697.23197	1	99.06	(Collection)

3,6'''-[bis(phenyl]-3',6,3'',6',3''',6''-[(1,1',1'',1''',1'''',1'''''-biphenyl)-2,2',2'',2''',2'''',2'''''-diyl]-1,2,4,5-tetrazine (7a'')

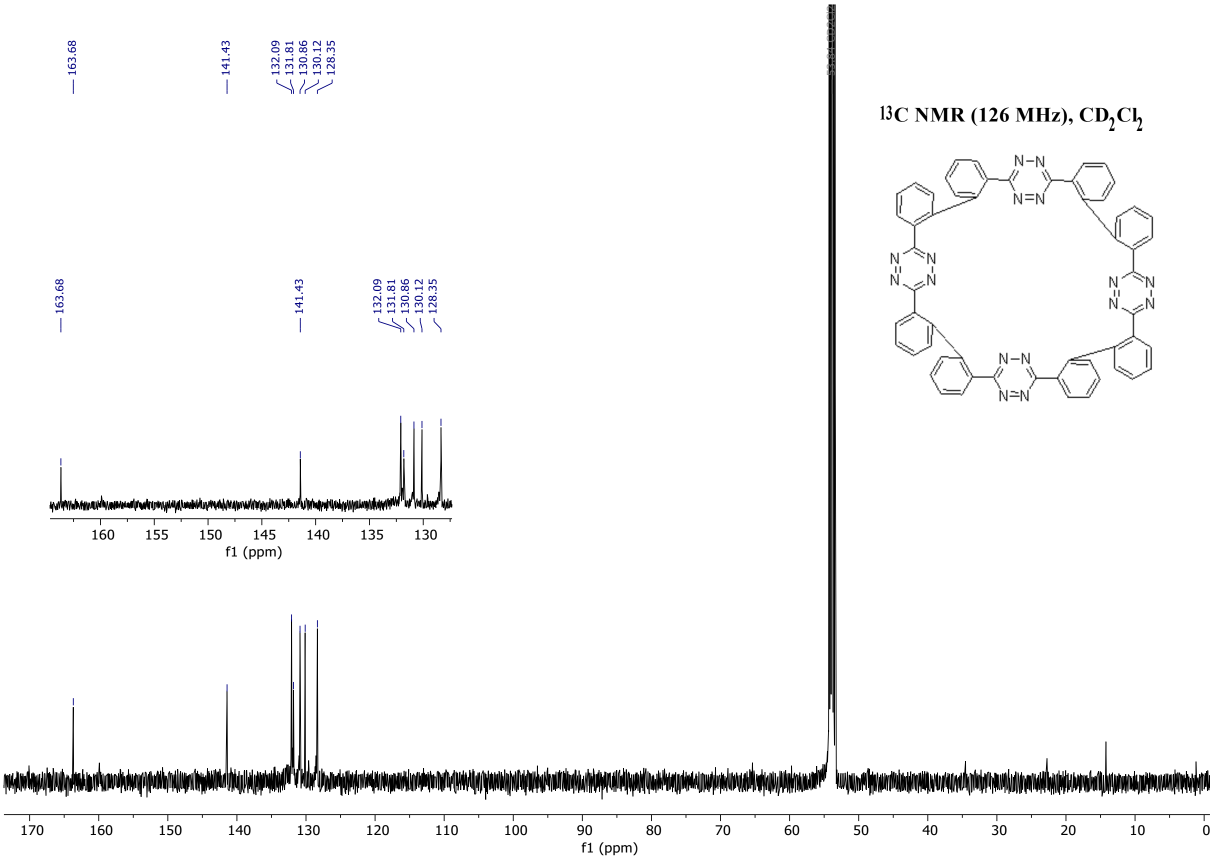


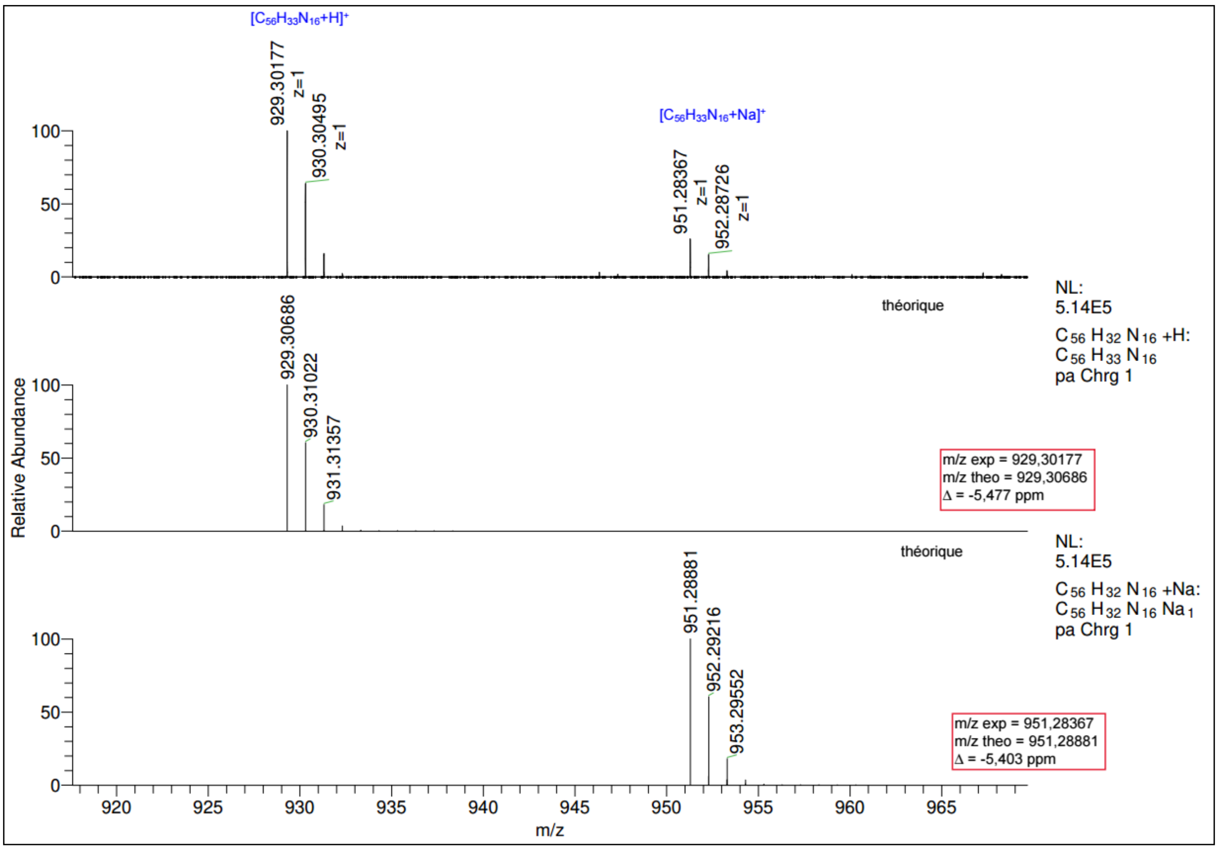


3',6,3'',6',3''',6'',3,6'''-[(1,1',1'',1'',1'''',1''''',1'''''',1''''''-biphenyl)-2,2',2'',2''',2'''',2''''',2'''''',-2''''''-diyl]-1,2,4,5-tetrazine (8a)

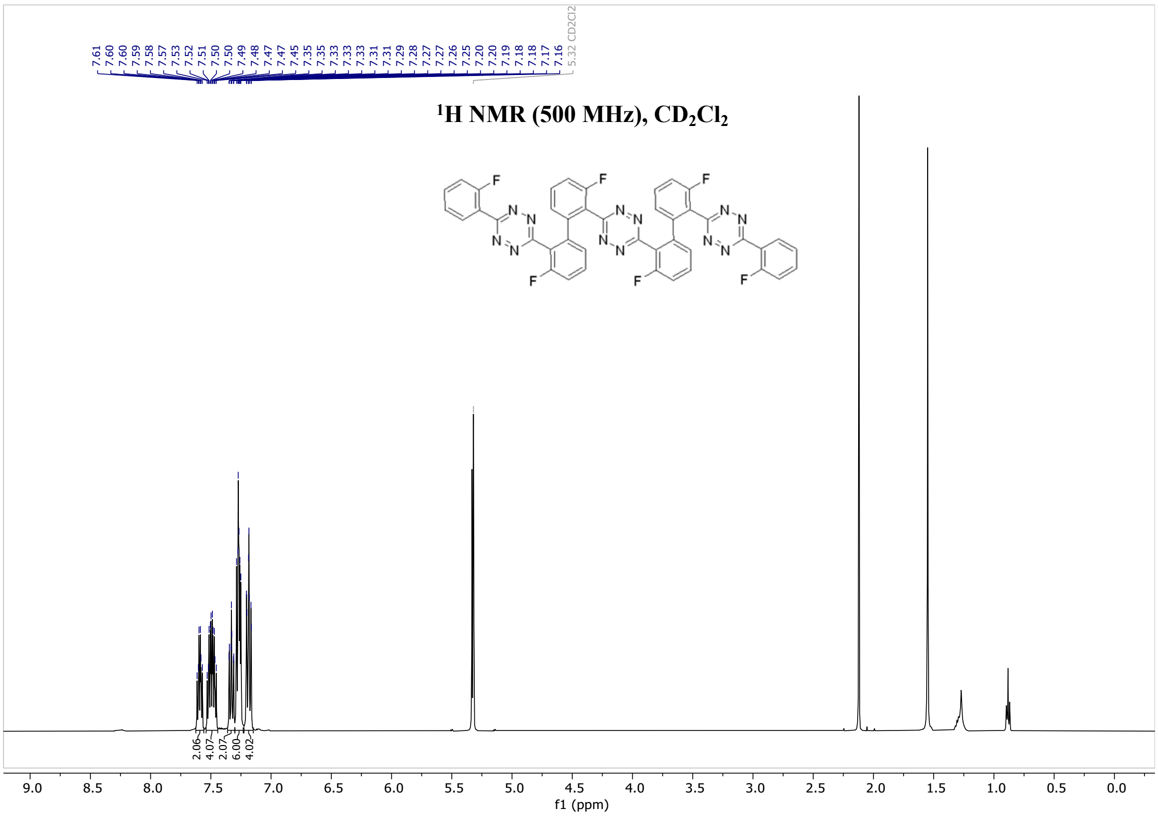


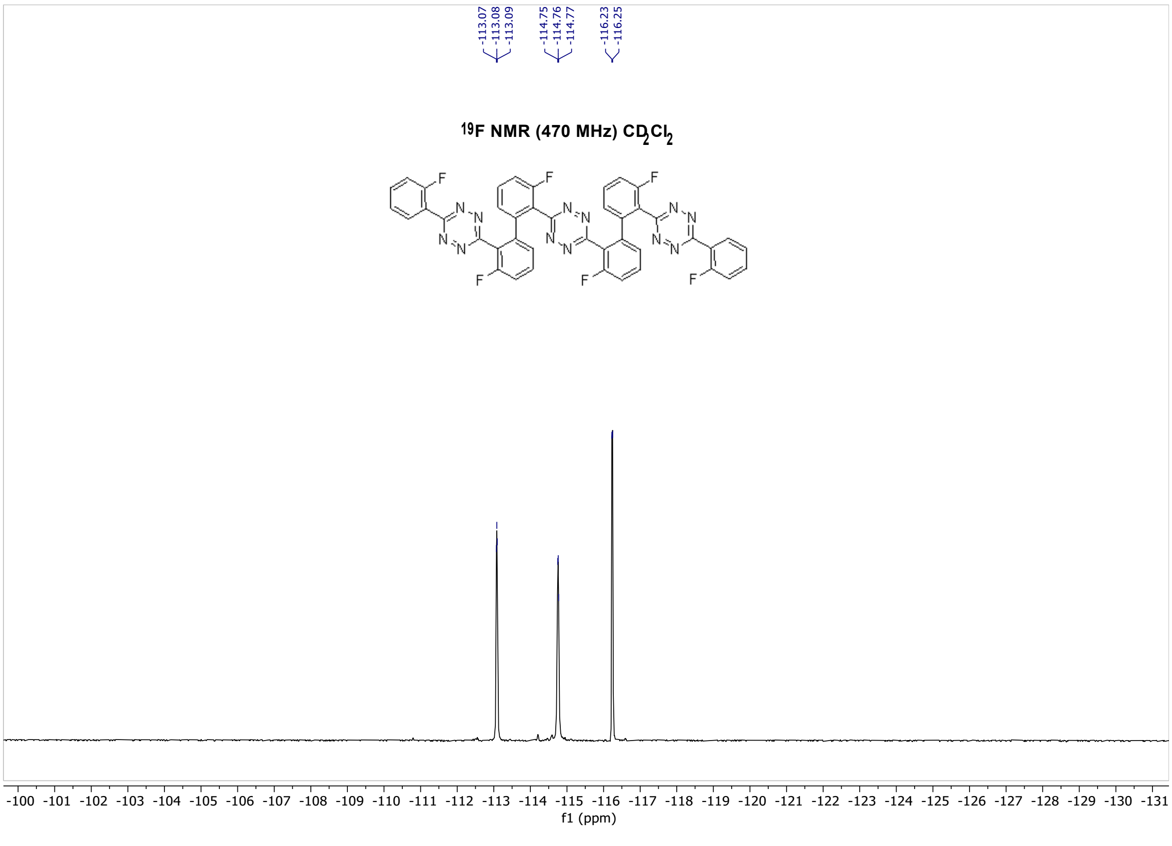
^{13}C NMR (126 MHz), CD_2Cl_2

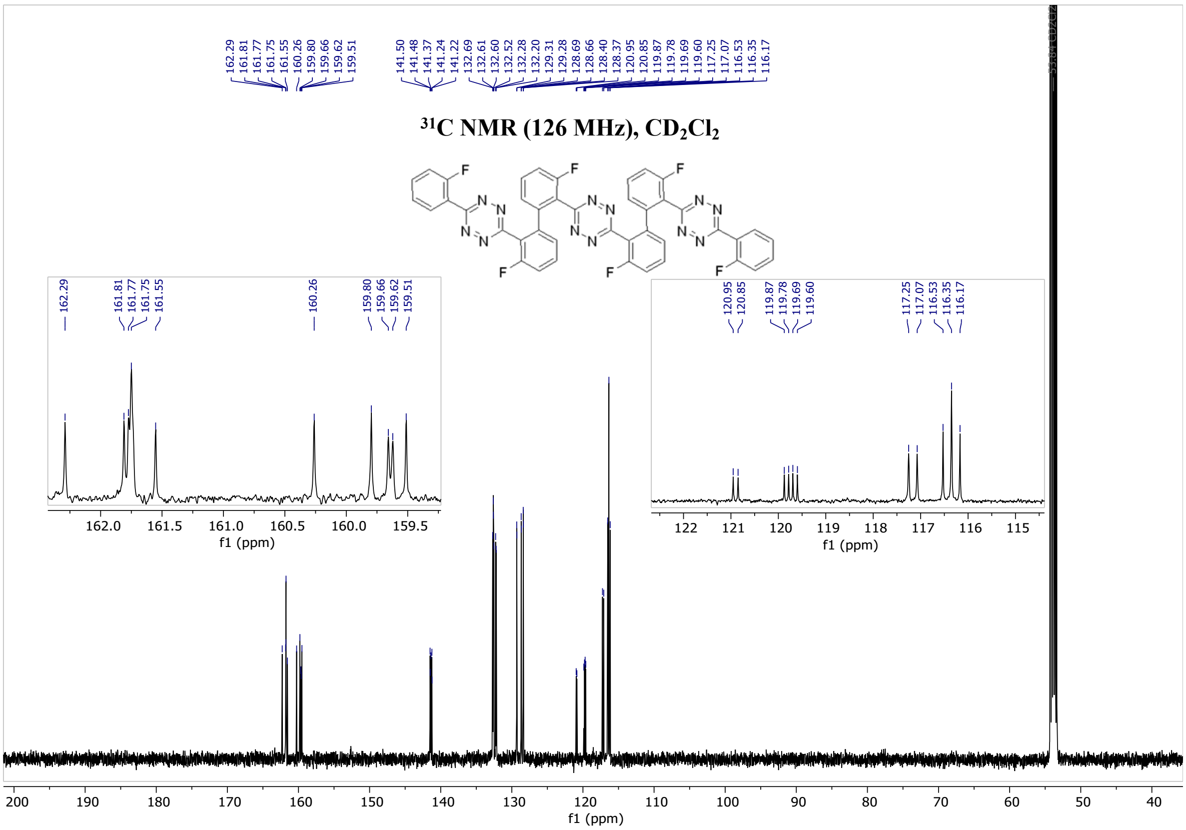


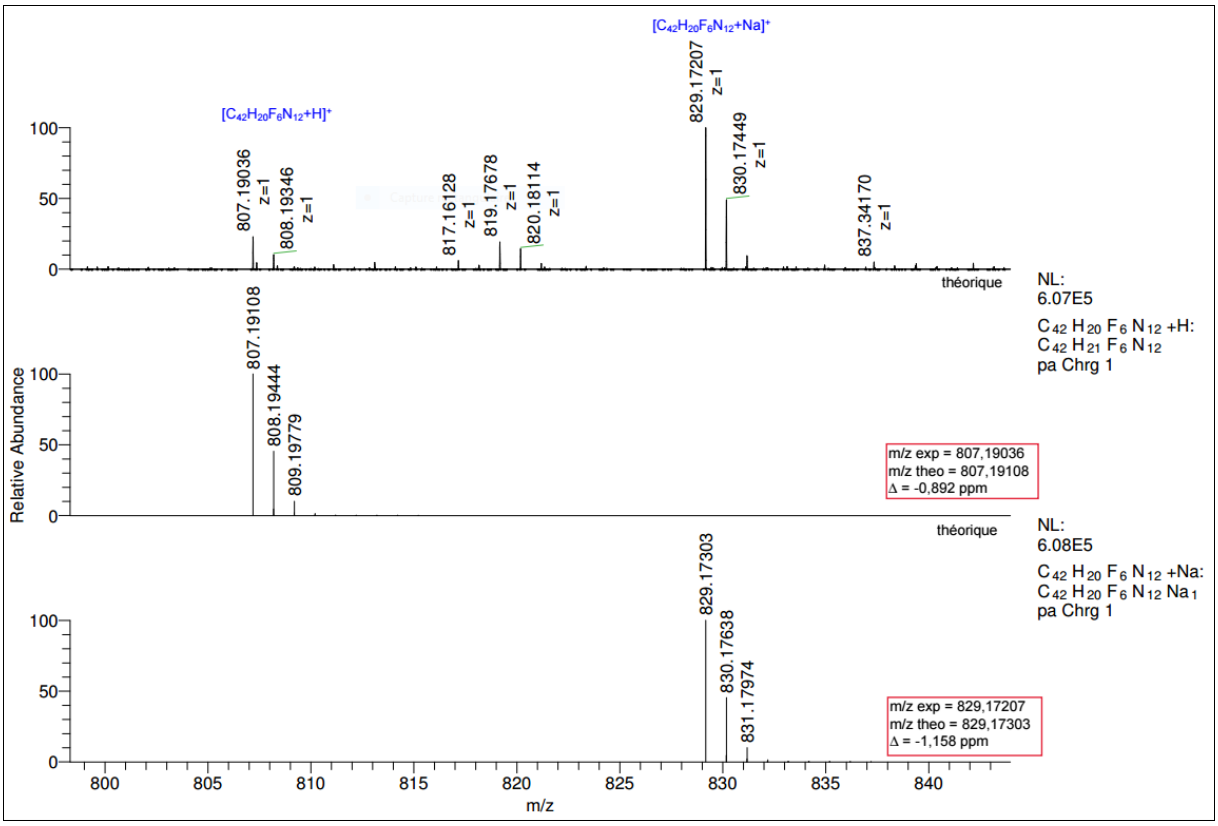


3,6"bis[2,2'-fluorophenyl]-3'6,3"6'-[bis(2,2'-fluorophenyl)-(1,1',1",1"'-biphenyl)-2,2',2",2"'-diyl]-1,2,4,5-tetrazine (5b")

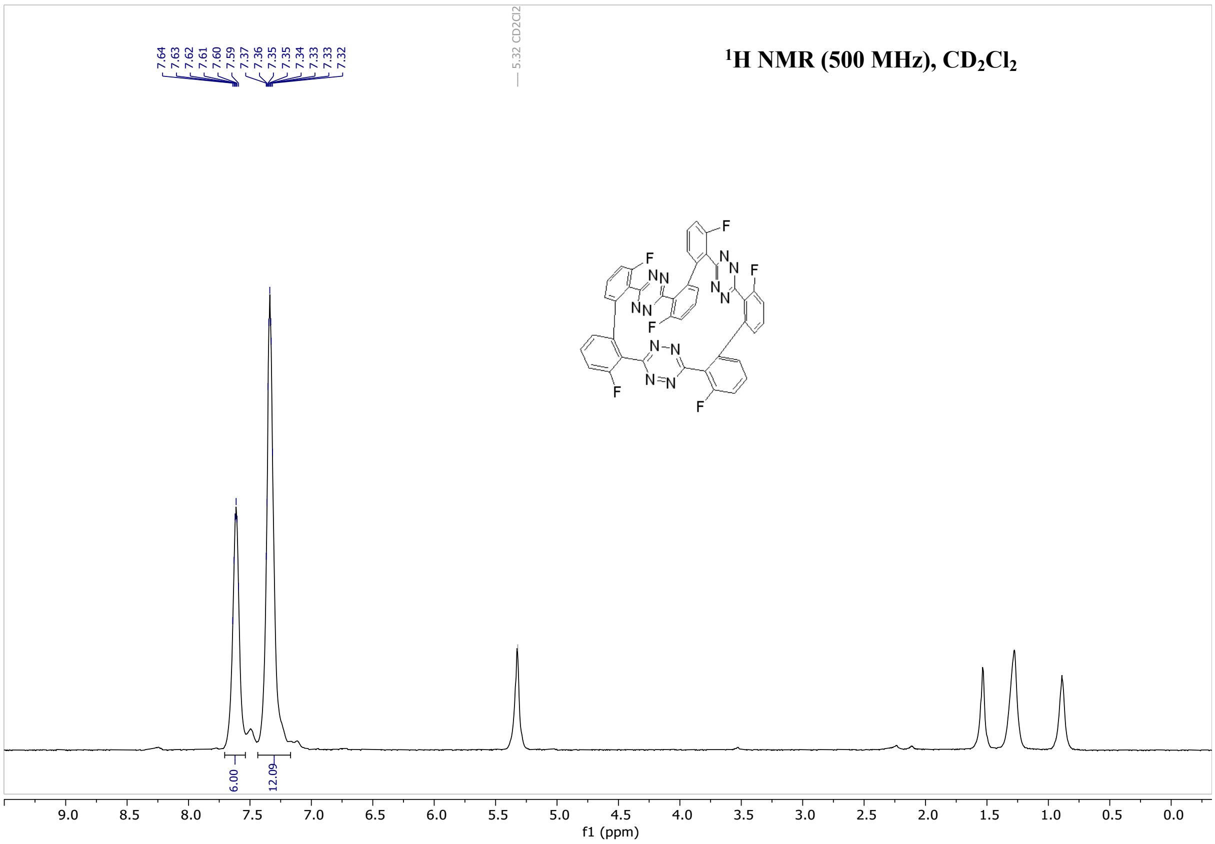




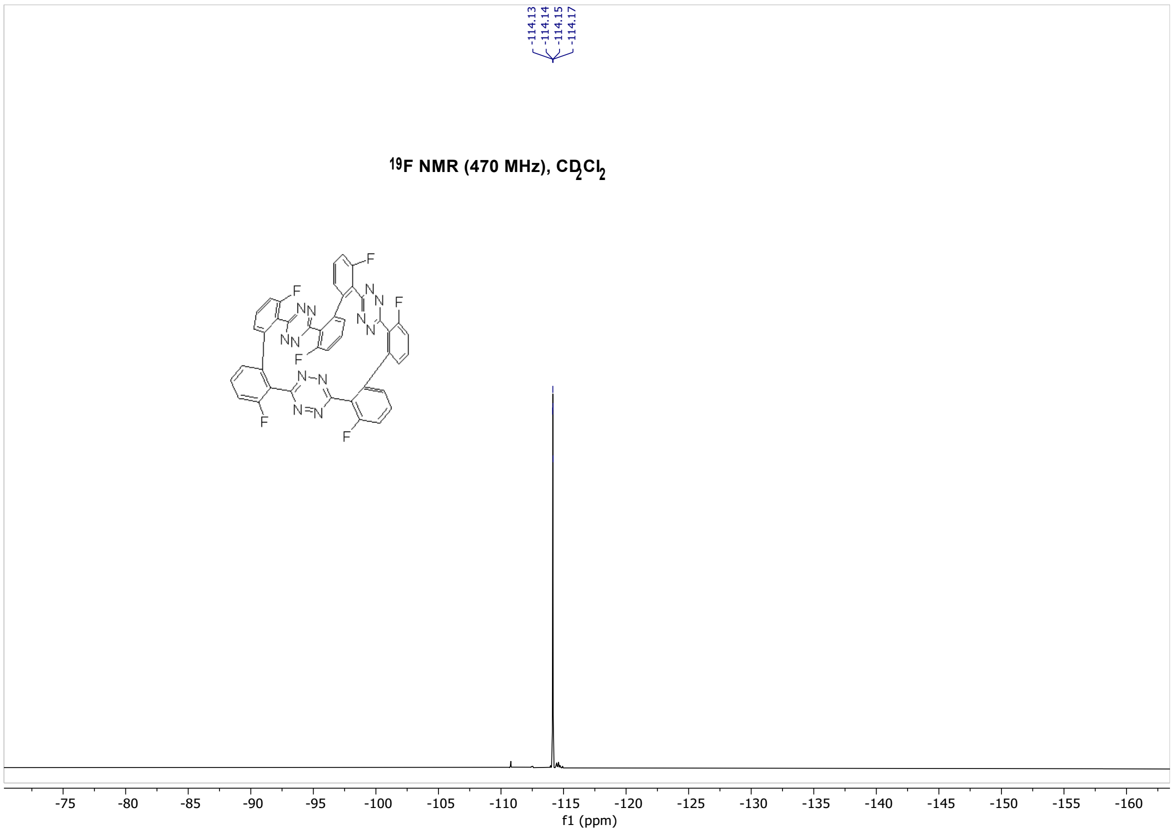




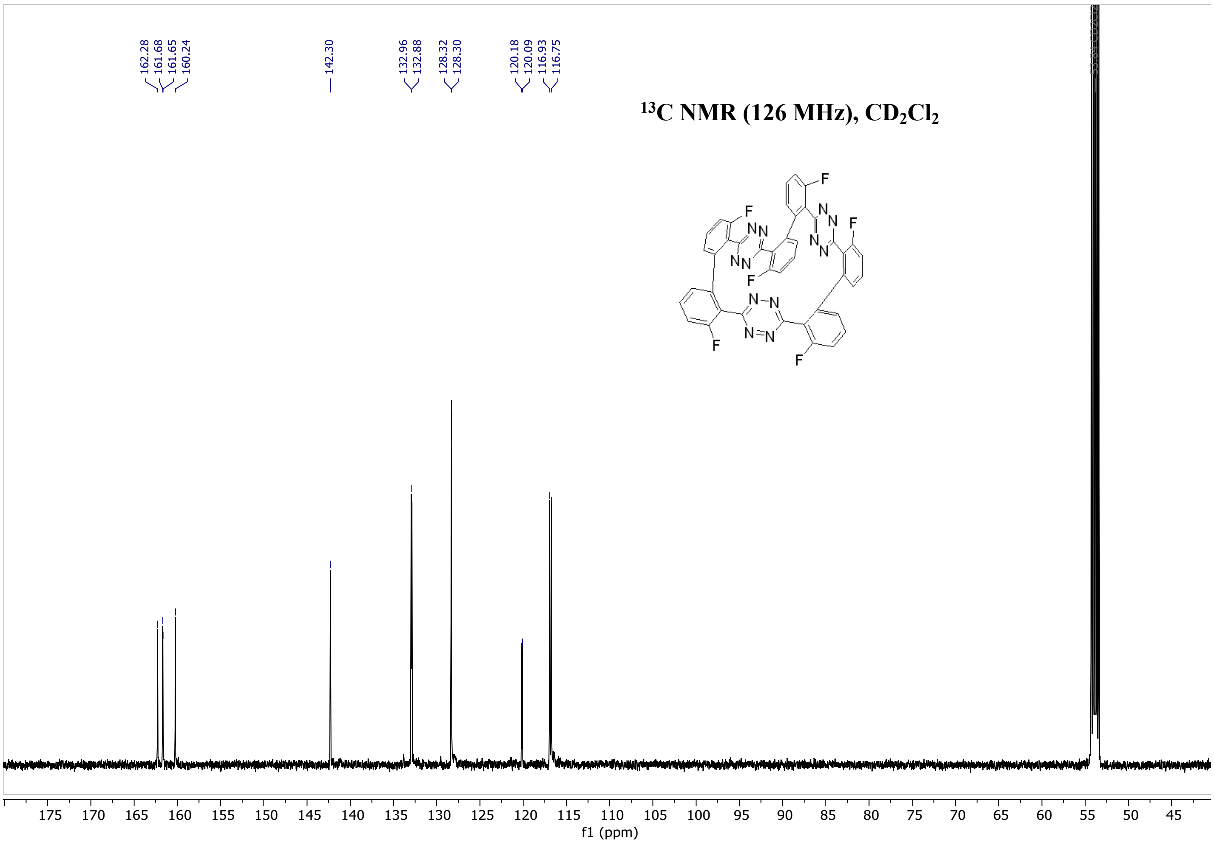
3',6,3",6',3,6"-[bis(2,2'-fluorophenyl)-(1,1',1",1"',1"",1""'-biphenyl)-2,2',2",2"',2"",2""'-diyl]-1,2,4,5-tetrazine (6b)

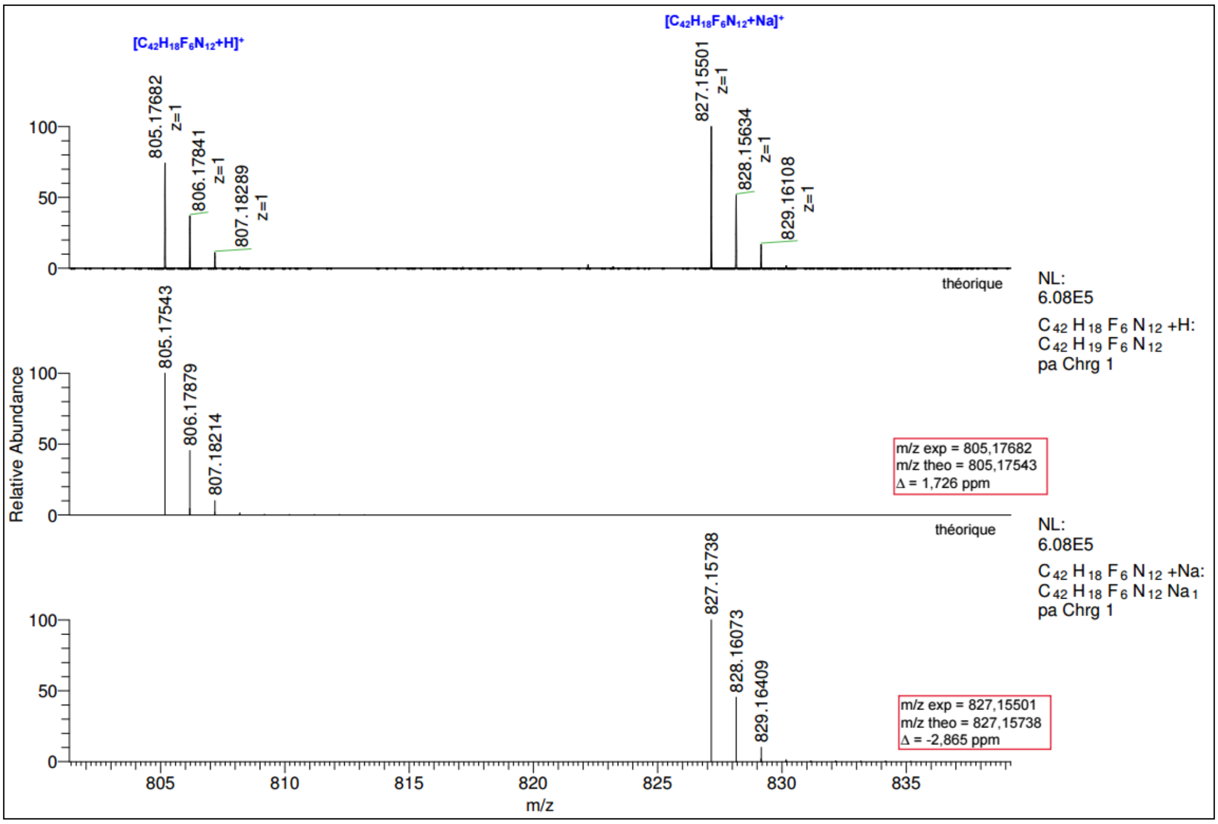


7.64
7.63
7.62
7.61
7.60
7.59
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.32
5.32 CD2Cl2
¹H NMR (500 MHz), CD₂Cl₂
6.00
12.09
f1 (ppm)



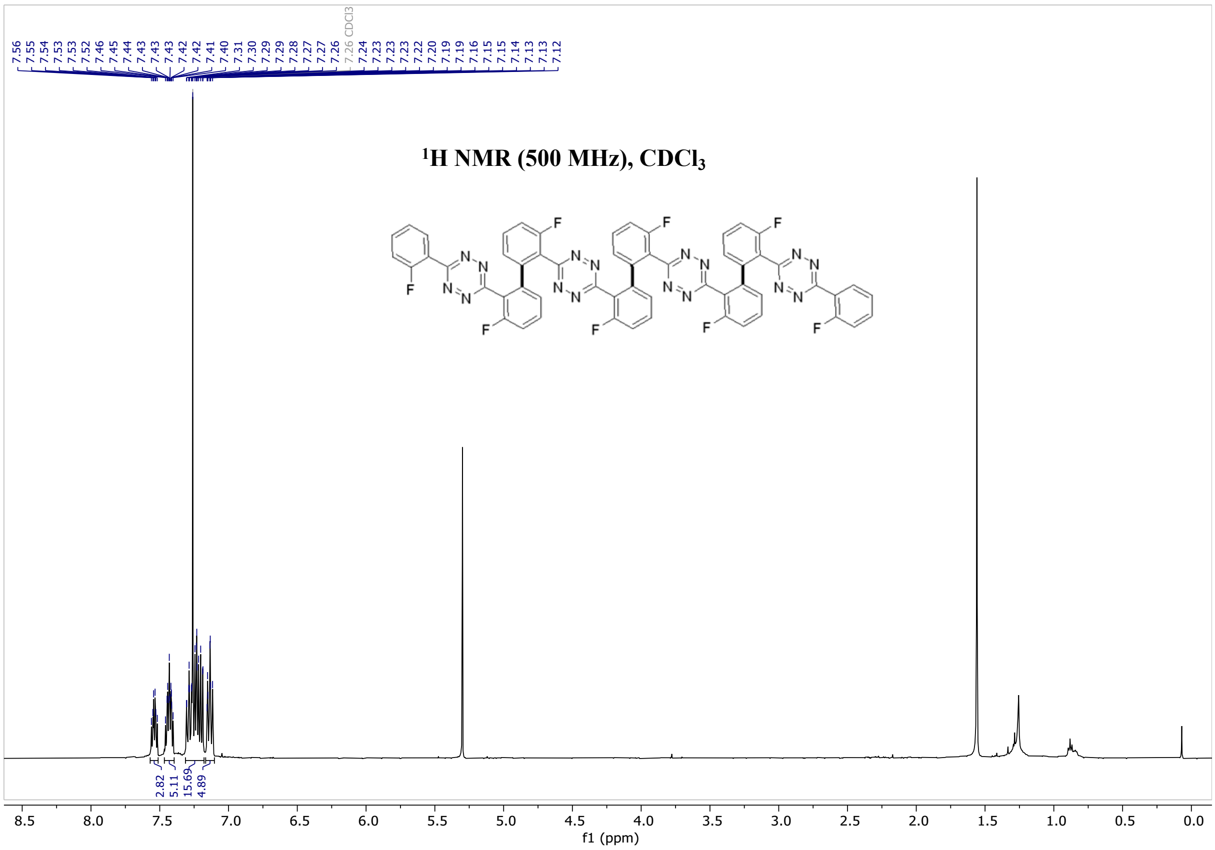
-114.13
-114.14
-114.15
-114.17
¹⁹F NMR (470 MHz), CD₂Cl₂
f1 (ppm)



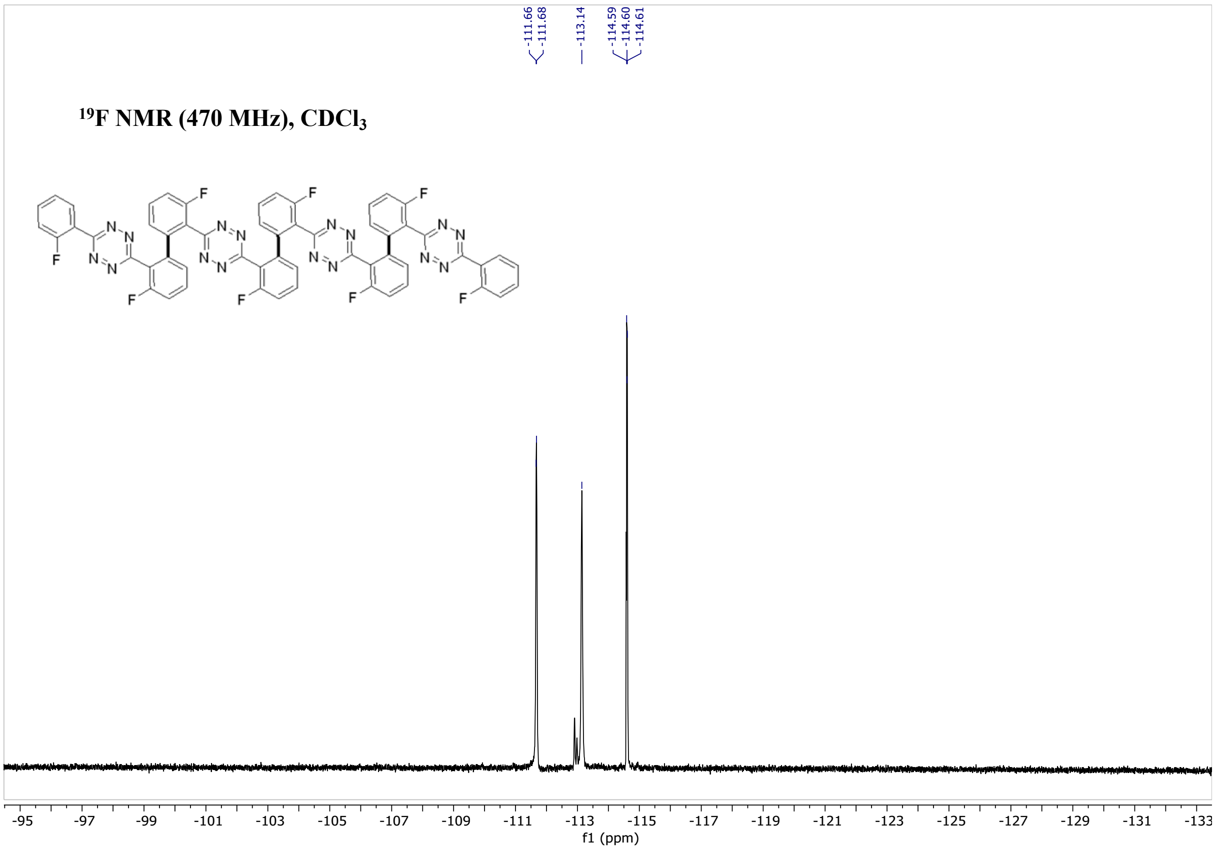


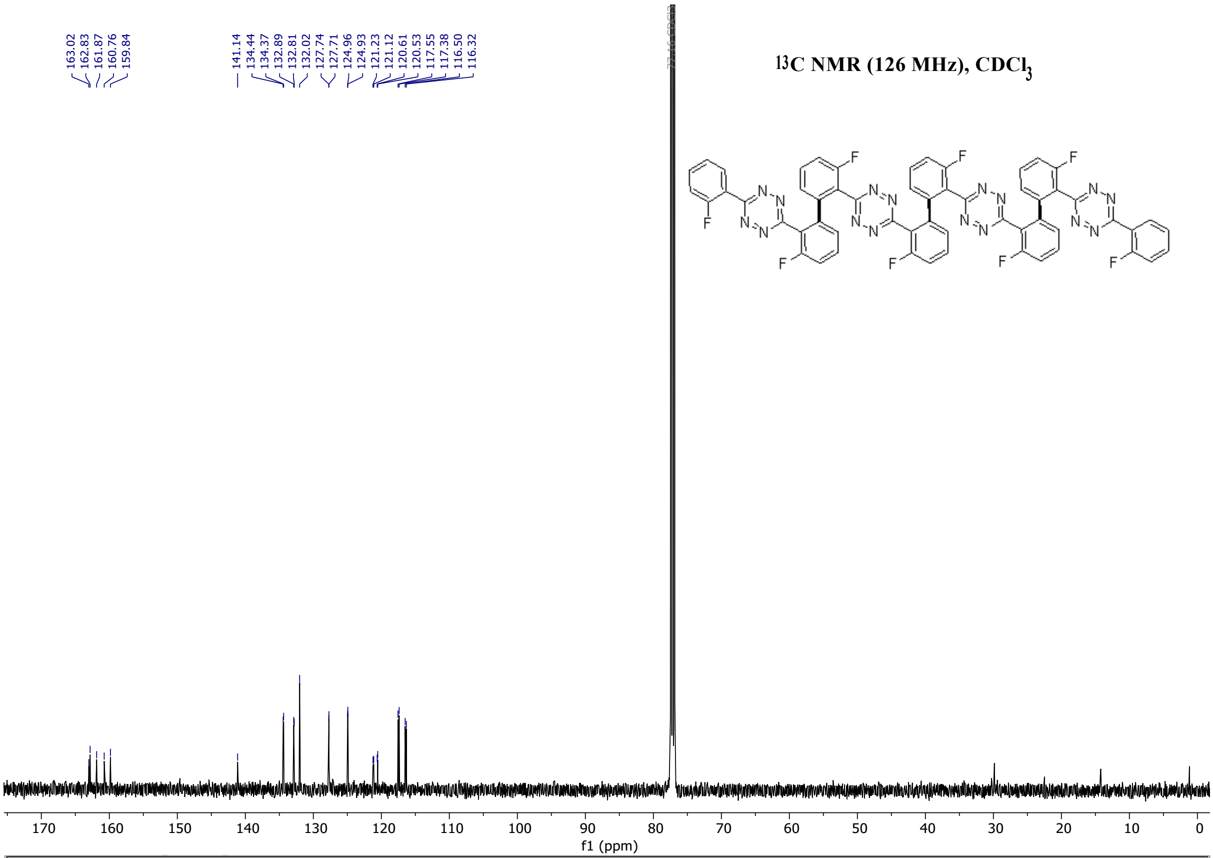
3,6''-bis[2,2'-fluorophenyl]-3',6,3'',6',3''',6''-[bis(2,2'-fluorophenyl)-(1,1',1'',1''',1'''',1''''')-biphenyl)-2,2',2'',2''',2'''',2'''''-diyl]-1,2,4,5-tetrazine (7b'')

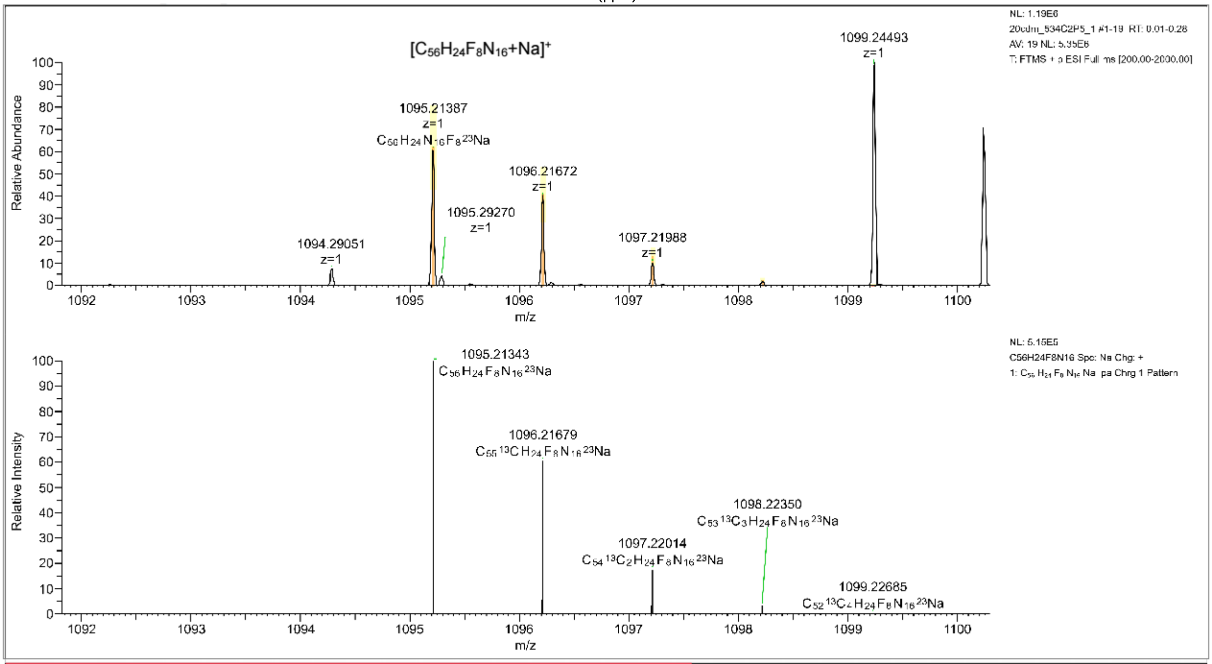
^1H NMR (500 MHz), $CDCl_3$



^{19}F NMR (470 MHz), $CDCl_3$

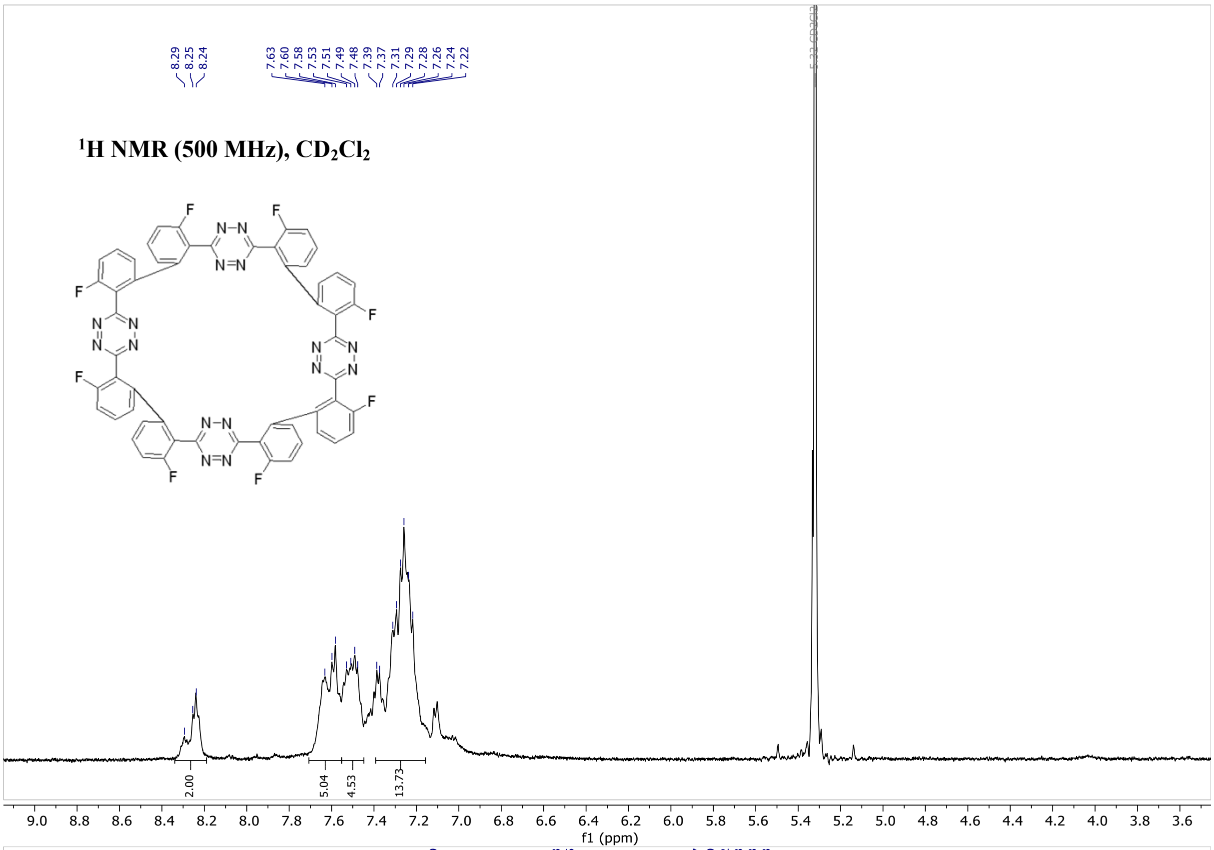




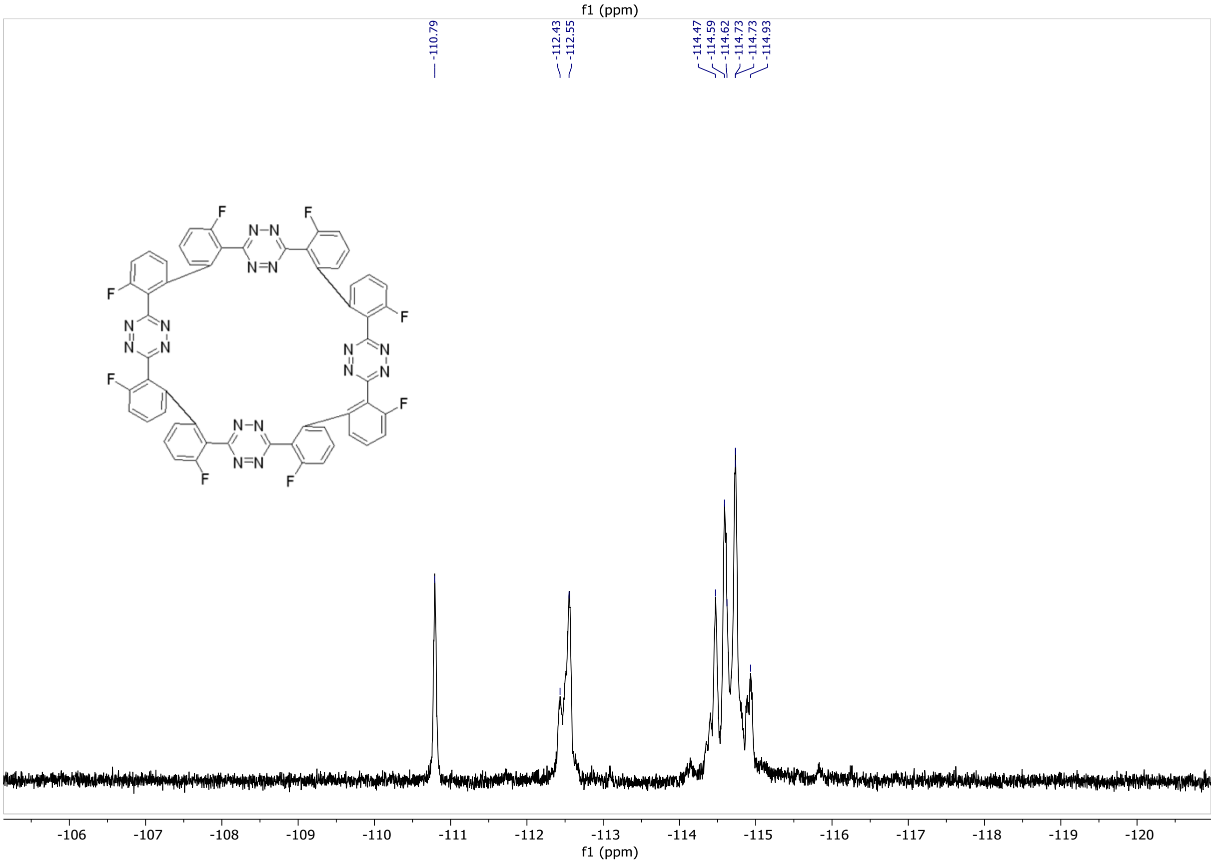


Display Formula	Peak Mass	Theo. mass	Delta [ppm]	RDB	Pattern Cov. [%]	MSMS Matched Fragments
$C_{56}H_{24}N_{16}F_8{}^{23}Na$	1095.21387	1095.21343	0.40	48.50	0	(Collection)

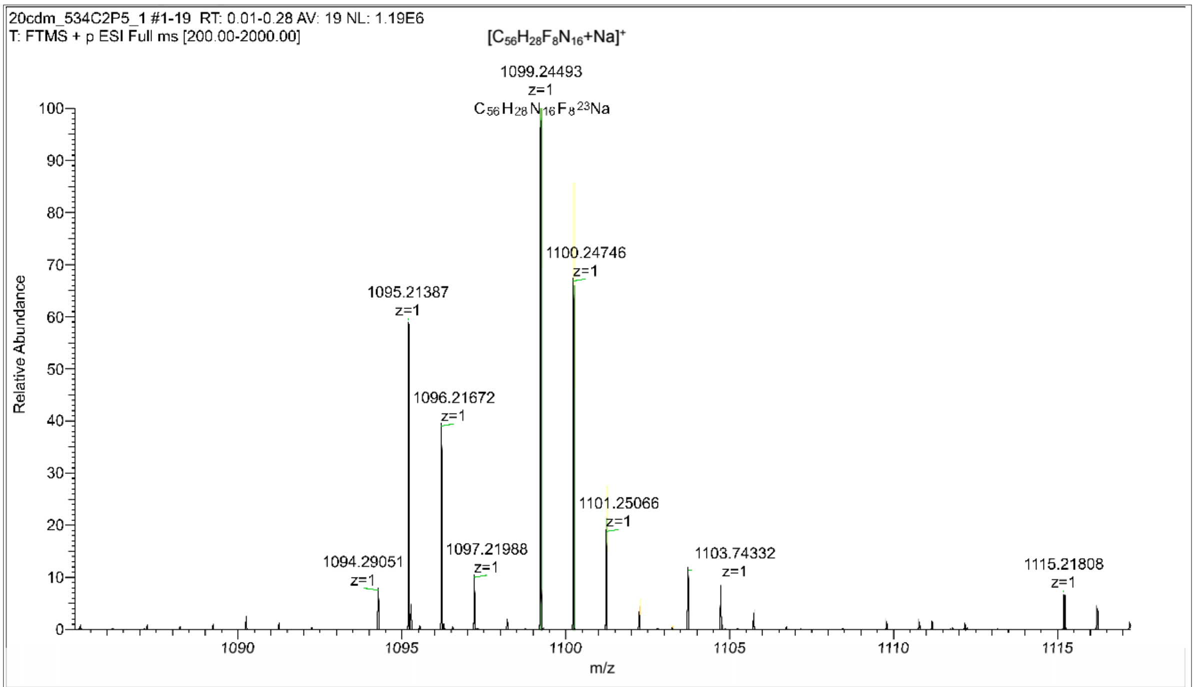
3',6,3'',6',3''',6'',3,6'''-[bis(2,2'-fluorophenyl)-(1,1',1'',1''',1'''',1''''',1'''''',1''''''')-biphenyl)-2,2',2'',2''',2'''',2''''',2'''''',2'''''''-diyl]-1,2,4,5-tetrazine (8b)



8.29
8.25
8.24
7.63
7.60
7.58
7.53
7.51
7.49
7.48
7.39
7.37
7.31
7.29
7.28
7.26
7.24
7.22
5.32 CD2Cl2
¹H NMR (500 MHz), CD₂Cl₂
2.00
5.04
4.53
13.73
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
f1 (ppm)



-110.79
-112.43
-112.55
-114.47
-114.59
-114.62
-114.73
-114.73
-114.93
-106
-107
-108
-109
-110
-111
-112
-113
-114
-115
-116
-117
-118
-119
-120
f1 (ppm)



Display Formula	Peak Mass	Theo. mass	Delta [ppm]	RDB	Pattern Cov. [%]	MSMS Matched Fragments
$C_{56}H_{28}N_{16}F_8{}^{23}Na$	1099.24493	1099.24473	0.18	46.50	97.24	(Collection)