SUPPLEMENTARY INFORMATION

Ionic liquid crystals based on viologen dimers: tuning the mesomorphism by varying the conformational freedom of the ionic layer.

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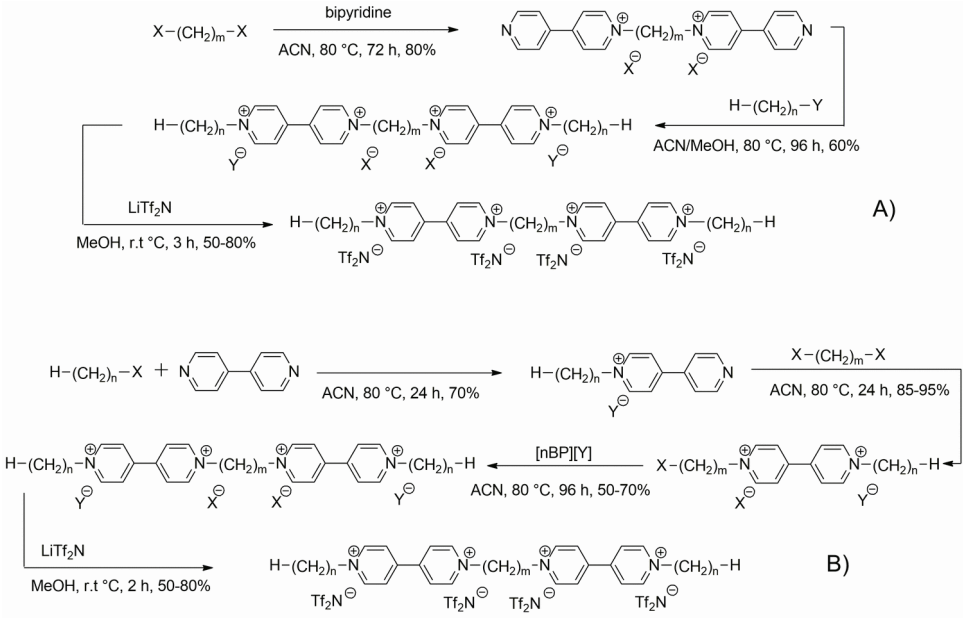
SYNTHESES

Two synthetic protocols have been used, named A and B. Throughout the ESI we use the notation nBPmBPn (BP meaning bipyridinium) for the molecules labelled **n.m.n** in the main text.



Scheme 1: Syntethic protocols. [nBP][Y] is the monoalkylated obtained from the first step in protocol B.

Protocol A:

i) Synthesis of the central core [BPmBP]Br_2 (m= 3,4); ii) synthesis of the viologen dimers halides [nBPmBPn]X_4 (n =10,11,12,16; m= 3,4 ; X = Br, I); iii) metathesis with lithium bistriflimide to obtain the salt [nBPmBPn]$(Tf_2N)_4$.

Procedure:

i) *Synthesis of the central cores [BP3BP]Br2 and [BP4BP]Br2*: 500 mmol of dibromoethane or dibromopropane were left to reflux for 72 hrs in 40mL of ACN (80 °C) with an excess of bipyridine (ratio 1:10). A yellow precipitate was formed. The suspension was cooled at 4 ° C for 1 hr and then filtered with Gooch 4 filter, washed with cold acetone and dried under vacuum in presence of $CaCl_2$ for at least two weeks.Yield:80%.

iii) *Synthesis of the viologen dimer halides nBPmBPn:* 1 mole of [BPmBP]Br_2 (m=3,4) was letf to reflux in 20 mL of ACN (80 °C) with a large excess (ratio 1:20) of the corresponding haloalkanes: $C_{10}H_{21}Br$, $C_{11}H_{23}I$, $C_{12}H_{25}I$, $C_{16}H_{33}Br$. After about 1 hr a yellow or red/orange, (depending on the halide), solid began to precipitate. After 24 hrs MeOH was added drop-wise until a clear solution was formed; the solution was then left to react for 72 hrs and finally cooled to room temperature and kept at 4°C for 2 hrs. The precipitate formed was washed with cold acetone (0°C) and recrystallized with a 7% (v/v) solution of methanol in ACN at 40 °C.**Yield:60%.**

iv) *Metathesis with lithium bistriflimide:* 300-500 mg of the viologen dimer halide salt and an excess of $LiTf_2N$ (stoichiometric ratio 1:5) were dissolved in the minimum amount of methanol and left to react for 3 hrs at room temperature under stirring. The volume of the solution was reduced under vacuum, removing ca. 1/3 of methanol, and then water was added until a white precipitate was formed. The suspension was left to react for 2 hrs and cooled at 4 °C. The precipitate was then filtered and washed several times with water until tests with a 0.5 M solution of $AgNO_3$ showed the absence of halide ions. The product was then dried under vacuum in the presence of $CaCl_2$ for at least two weeks.Yield:50%-80%.

[10BP4BP10](Tf$_2$N)$_4$: **^{1}H NMR** (MeOD, 500 MHz) δ 9.23 (d, J = 6.4 Hz, 4H); 9.18 (d, J = 6.4 Hz, 4H); 8.63 (d, J = 6.4 Hz, 4H); 8.60 (d, J = 6.5 Hz, 4H); 4.83 (signal partially overlapped to HDO); 4.72 (t, J = 7.5 Hz, 4H); 2.24 (4H); 2.07 (m, 4H); 1.41 (m. 8H); 1.28 (20H); 0.89 (t, J = 6.9 Hz, 6H); **^{13}C NMR** (126 MHz, MeOD) δ 151.72, 151.32, 147.06, 128.57, 128.31, 121.1 (q, $^1J(^{13}C,^{19}F)$ = 321.1 Hz), 63.38, 62.34, 33.01, 32.54, 30.58, 30.46, 30.38, 30.12, 28.84, 27.17, 23.71, 14.41.**Elemental Analysis**, $C_{52}H_{66}F_{24}N_8O_{16}S_8$: found C 34.87 %, H 3.52 %, N 6.02 %, S 14.41 % ; calcd C 35.25 %, H 3.76 %, N 6.32 %, S 14.48 %. **ESI-MS**: *m/z*=1490 $[10BP4BP10(Tf_2N)_3]^+$; *m/z*=605 $[10BP4BP10(Tf_2N)_2]^{2+}$.

[11BP4BP11](Tf$_2$N)$_4$: **^{1}H NMR** (MeOD, 500 MHz) δ 9.23 (d, J = 6.9 Hz, 4H); 9.18 (d, J = 6.9 Hz, 4H); 8.62 (d, J = 6.7 Hz, 4H); 8.59 (d, J = 6.7 Hz, 4H); 4.83 (signal partially overlapped to HDO); 4.72 (t, J = 7.5 Hz, 4H); 2.24 (4H); 2.07 (m, 4H); 1.41 (m. 8H); 1.28 (24H); 0.89 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (126 MHz, MeOD) δ 151.71, 151.32, 147.05, 128.56, 121.1 (q, $^1J(^{13}C,^{19}F)$ = 321.1 Hz) , 63.38, 62.34, 33.04, 32.53, 30.66, 30.62, 30.45, 30.41, 30.11, 28.83, 27.16, 23.71, 14.41. **Elemental Analysis**, $C_{54}H_{70}F_{24}N_8O_{16}S_8$: found C 35.69 %, H 3.74 %, N 5.97 %, S 14.37 % ; calcd C 36.04 %, H 3.92 %, N 6.23 %, S 14.25 %. **ESI-MS**: *m/z*=1518 $[10BP4BP10(Tf_2N)_3]^+$; *m/z*=605 $[10BP4BP10(Tf_2N)_2]^{2+}$.

[16BP3BP16](Tf$_2$N)$_4$: **^{1}H NMR** (MeOD, 500 MHz) δ 9.65 (d, J = 6.0 Hz, 8H); 9.09 (d, J = 6.4 Hz, 4H); 9.02 (d, J = 6.3 Hz, 4H); 5.36 (d, J = 7.5 Hz, 4H); 5.13 (t, J = 7.5 Hz, 4H); 2.48 (m, 4H); 1.82 (8H); 1.72-1.68 (42H); 1.29 (t, J = 6.8 Hz, 6H); **^{13}C NMR** (126 MHz, MeOD) δ 152.17, 151.21, 147.27, 147.08, 128.73, 128.36, 121.1 (q, $^1J(^{13}C,^{19}F)$ = 321.1 Hz) , 63.42, 59.60, 33.50, 33.07, 32.55, 30.77, 30.75, 30.72, 30.63, 30.47, 30.13, 27.21, 23.73, 14.43. **Elemental Analysis**, $C_{63}H_{88}F_{24}N_8O_{16}S_8$: found C 38.87 %, H 4.39 %, N 5.62 %, S 13.27 % ; calcd C 39.29 %, H 4.61 %, N 5.82 %, S 13.32 %. **ESI-MS**: *m/z*=1644 $[16BP3BP16(Tf_2N)_3]^+$; *m/z*=682 $[16BP3BP16(Tf_2N)_2]^{2+}$.

Protocol B:

i) Synthesis of the monoalkylated halides nBPBr (n=8,10,11,12,14,16) ; ii) synthesis of the viologen, [nBPm]X_2 (X= Br , I; m = 3,4,5,6,7,8); iii) synthesis of the viologen dimers halides [nBPmBPn]X_4 (n =12, 14, 16; m= 3,4,5,6,7,8 ; X = Br, I); iv) metathesis with lithium bistriflimide to obtain the salt [nBPmBPn](Tf$_2$N)$_2$.

Procedure:

i) S*ynthesis of the monoalkylated halide:* According to ref.[M. F. Pepitone, G. G. Jernigan, J. S. Melinger, O. -. Kim Org. Lett., 2007, 9, 801-804], 5 g of 4,4'-bipyridine (32 mmol) were dissolved in 150 mL of ACN with the same stoichiometric amount (32 mmol) of the corresponding haloalkane. The solution was heated with an oil bath at 80 °C for 24 h. After cooling, the yellow precipitate was filtered and suspended in 300 mL of hot DMF. The monoalkylated product dissolved in the DMF while the yellow, insoluble dialkylated salt was separated by filtration. Ether was then added to the cooled solution to precipitate the white/pale yellow monoalkylated salt. Yield 70%.

ii) S*ynthesis of the viologen*: 500 mg of nBPX (X=Br,I) were allowed to reflux in 40 mL of acetonitrile at 80 °C with the appropriate amount of dibromoalkane (stoichiometric ratio 1:20) and after almost 1 hour a yellow precipitate was formed; the system was left to react for 24 hours. The obtained precipitate was filtered, washed with cold acetone and dried under vacuum in presence of $CaCl_2$. Yield 85-95%.

iii) *Synthesis of the viologen dimer halides [nBPmBPn]X (X=Br,I):* 0.5 mole of [nBPmX]X was letf to reflux in 20 mL of ACN (80 °C) with an excess (ratio 1:5) of the corresponding monoalkylated halide nBPX. In some cases, once the sample reached 80 °C, a light suspension was formed: then methanol was added dropwise until a solution was formed. The solutions were refluxed for 96 hrs and then cool down at room temperature and stored at 4°C for 2 hrs. The precipitates were filtered and recrystallized with acetonitrile/methanol mixture (7%-10% in methanol) and, finally, washed with cold acetone and dried under vacuum in presence of $CaCl_2$ for two weeks. Yield 50%-70%.

iv) *Metathesis with lithium bistriflimide:* The procedure was the same as described for Protocol A.Yield 70%-80%

[12BP4BP12](Tf$_2$N)$_4$: **^{1}H NMR** (MeOD, 500 MHz) δ 9.23 (d, J = 6.7 Hz, 4H); 9.18 (d, J = 6.7 Hz, 4H); 8.62 (d, J = 6.9 Hz, 4H); 8.59 (d, J = 6.7 Hz, 4H); 4.82 (signal partially overlapped to HDO); 4.72 (t, J = 7.4 Hz, 4H); 2.24 (4H); 2.07 (m, 4H); 1.41 (m. 8H); 2.24 (8H); 1.28 (28H); 0.89 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (126 MHz, MeOD) δ 151.72, 151.32, 147.06, 128.57, 128.32, 121.1 (q, $^1J(^{13}C,^{19}F)$ = 321.1 Hz), 117.29, 63.38, 62.34, 33.05, 32.54, 30.71, 30.62, 30.46, 30.12, 28.84, 27.17, 23.72, 14.42. **Elemental Analysis**, $C_{56}H_{74}F_{24}N_8O_{16}S_8$: found C 36.79 %, H 4.20 %, N 6.18 %, S

14.42 % ; calcd C 36.80 %, H 4.08 %, N 6.13 %, S 14.04 %.**ESI-MS**: *m/z*=1546 [12BP4BP12(Tf_2N)$_3$]$^+$; *m/z*=634 [12BP4BP12(Tf_2N)$_2$]$^{2+}$;.*m/z*=329 [12BP4BP12(Tf_2N)]$^{3+}$.

[12BP5BP12](Tf_2N)$_4$: ^{1}H NMR (MeOD, 400 MHz) δ 9.24 (d, J = 6.5 Hz, 4H); 9.20 (d, J = 6.5 Hz, 4H); 8.62 (d, J = 6.9 Hz, 4H); 8.59 (d, J = 6.7 Hz, 4H); 4.77 (t, J = 7.4 Hz, 4H); 4.73 (t, J = 7.4 Hz, 4H); 2.24 (4H); 2.07 (m, 4H); 1.41 (m. 8H); 1.28 (28H); 0.89 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (101 MHz, MeOD) δ 151.57, 151.35, 146.98, 128.43, 128.29, 121.1 (q, $^1J(^{13}C,^{19}F)$ = 321.1 Hz), 63.35, 62.84, 33.01, 32.51, 31.76, 30.66, 30.58, 30.41, 30.08, 27.15, 23.68, 14.37. **Elemental Analysis**, $C_{57}H_{76}F_{24}N_8O_{16}S_8$: found C 36.79 %, H 4.02 %, N 6.06 %, S 14.42 % ; calcd C 37.17 %, H 4.16 %, N 6.08 %, S 13.93 %. **ESI-MS**: *m/z*=1560 [12BP5BP12(Tf_2N)$_3$]$^+$; *m/z*=640 [12BP5BP12(Tf_2N)$_2$]$^{2+}$.

[12BP6BP12](Tf_2N)$_4$: ^{1}H NMR (MeOD, 400 MHz) δ 9.23 (d, J = 6.0 Hz, 4H); 9.20 (d, J = 6.0 Hz, 4H); 8.61 (8H); 4.77 (t, J = 7.9 Hz, 4H); 4.73 (t, J = 7.8 Hz, 4H); 2.09 (broad, 8H); 1.54 (4H); 1.42 (8H); 1.29 (b, 28H); 0.89 (t, J = 6.9 Hz, 6H); **^{13}C NMR** (101 MHz, MeOD) δ 151.49, 151.41, 147.02, 128.38, 128.30, 121.1 (q, $^1J(^{13}C,^{19}F)$ = 321.1 Hz), 63.38, 63.20, 33.05, 32.55, 32.10, 30.70, 30.62, 30.46, 30.12, 27.19, 26.52, 23.71, 14.41.**Elemental Analysis**, $C_{58}H_{78}F_{24}N_8O_{16}S_8$: found C 37.31 %, H 4.42 %, N 5.95 %, S 13.92 % ; calcd C 37.54 %, H 4.24 %, N 6.04 %, S 13.82 %.

[12BP7BP12](Tf_2N)$_4$: ^{1}H NMR (MeOD, 500 MHz) δ 9.22 (d, J = 6.8 Hz, 4H); 9.19 (d, J = 6.8 Hz, 4H); 8.64 (d, J = 6.7 Hz, 4H); 8.62 (d, J = 6.9 Hz, 4H);4.77 (t, J = 7.4 Hz, 4H); 4.73 (t, J = 7.4 Hz, 4H); 2.2 (m, 4H); 2.09 (m, 4H); 1.61 (m, 2H); 1.42 (m, 4H); 1.29 (32H); 0.89 (t, J =6.9 Hz, 6H); **^{13}C NMR** (126 MHz, MeOD) δ 151.43, 146.97, 128.34, 121.1 (q, $^1J(^{13}C,^{19}F)$ = 321.1 Hz), 63.35, 33.06, 32.56, 32.23, 30.71, 30.63, 30.46, 30.12, 29.55, 27.19, 26.72, 23.72, 14.42. **Elemental Analysis**, $C_{59}H_{80}F_{24}N_8O_{16}S_8$: found C 37.66 %, H 4.35 %, N 6.09 %, S 13.75 % ; calcd C 37.90 %, H 4.31 %, N 5.99 %, S 13.72 %. **ESI-MS**: *m/z*=1588 [12BP7BP12(Tf_2N)$_3$]$^+$; *m/z*=654 [12BP7BP12(Tf_2N)$_2$]$^{2+}$; *m/z*=325 [12BP7BP12(Tf_2N)]$^{3+}$

[12BP8BP12](Tf_2N)$_4$: ^{1}H NMR (MeOD, 500 MHz) δ 9.22 (d, J = 6.8 Hz, 4H); 9.19 (d, J = 6.8 Hz, 4H); 8.60 (d, J = 6.7 Hz, 8H); 4.73 (t, J = 7.4 Hz, 4H); 4.72 (t, J = 7.8 Hz, 4H); 2.09 (broad, 8H); 1.45 (m. 8H); 1.42 (8H); 1.32-1.29 (28H); 0.89 (t, J =6.9 Hz, 6H); **^{13}C NMR** (126 MHz, MeOD) δ 151.41, 146.97, 128.32, 121.1 (q, $^1J(^{13}C,^{19}F)$ = 321.1 Hz) , 63.36, 33.04, 32.54, 32.37, 30.70, 30.61, 30.45, 30.11, 29.64, 27.18, 26.88, 23.71, 14.42. **Elemental Analysis**, $C_{60}H_{82}F_{24}N_8O_{16}S_8$: found C 38.31 %, H 4.29 %, N 5.88 %, S 14.24 % ; calcd C 38.25 %, H 4.39 %, N 5.95 %, S 13.62 %.

[14BP3BP14](Tf_2N)$_4$: ^{1}H NMR (MeOD, 500 MHz) δ 9.35 (d, J = 6.8 Hz, 4H); 9.2 (d, J = 6.8 Hz, 4H); 8.71 (d, J = 6.8 Hz, 4H); 8.66 (d, J = 6.6 Hz, 4H); 5.01(t, J = 7.7 Hz, 4H); 4.74 (d, J = 7.6 Hz, 4H); 2.95 (m, 2H); 2.09 (m, 4H);1.42 (8H); 1.32-1.28 (36H); 0.89 (t, J =6.9 Hz, 6H); **^{13}C NMR** (MeOD, 126 MHz): δ 152.01, 151.27, 147.37, 147.08, 128.69, 128.37, 121.1 (q, $^1J(^{13}C,^{19}F)$ = 321.1 Hz), 63.39, 59.53, 33.53, 33.07, 32.57, 30.78, 30.75, 30.72, 30.64, 30.49, 30.46, 30.15, 27.23, 23.73, 14.42. **Elemental Analysis**, $C_{59}H_{80}F_{24}N_8O_{16}S_8$: found C 38.33 %, H 4.64 %, N 5.75 %, S 13.24 % ; calcd C 37.90 %, H 4.31 %, N 5.99 %, S 13.72 %. **ESI-MS**: *m/z*=1588 [14BP3BP14(Tf_2N)$_3$]$^+$; *m/z*=654 [14BP3BP14(Tf_2N)$_2$]$^{2+}$.

[14BP4BP14](Tf_2N)$_4$: ^{1}H NMR (MeOD, 500 MHz) δ 9.24 (d, J = 6.9 Hz, 4H); 9.19 (d, J = 6.9 Hz, 4H); 8.63 (d, J = 6.8 Hz, 8H); 8.60 (d, J = 6.8 Hz, 8H); 4.83 (partially overlapped to HDO); 4.72 (t, J = 7.6 Hz, 4H); 2.24 (4H); 2.07 (m, 4H); 1.41 (m. 8H); 1.28 (36H); 0.90 (t, J =7.0 Hz, 6H); **^{13}C NMR** (126 MHz, MeOD) δ 151.72, 151.32, 147.07, 128.57, 128.31, 121.1 (q, $^1J(^{13}C,^{19}F)$ = 321.1 Hz) , 63.38, 62.34, 33.07, 32.55, 30.78, 30.74, 30.72, 30.63, 30.47, 30.13, 28.84, 27.18, 23.73, 14.43. **Elemental Analysis**, $C_{60}H_{82}F_{24}N_8O_{16}S_8$: found C 38.43 %, H 4.69 %, N 5.90 %, S 13.67 % ; calcd C 38.25 %, H 4.39 %, N 5.95 %, S 13.62 %. **ESI-MS**: *m/z*=1603 [14BP4BP14(Tf_2N)$_3$]$^+$; *m/z*=662 [14BP3BP14(Tf_2N)$_2$]$^{2+}$.

[14BP5BP14](Tf_2N)$_4$: ^{1}H NMR (MeOD, 400 MHz) δ 9.24 (d, J = 6.8 Hz, 4H); 9.29 (d, J = 6.8 Hz, 4H); 8.64-8.62 (two doublets partially overlapped, J = 6.3 HZ; J =n.d.,8H); 4.77 (t, J = 7.6 Hz, 4H); 4.72 (t, J = 7.6 Hz, 4H); 2.20 (m, 4H); 2.08 (m, 4H); 1.60 (b, 2H); 1.42 (8H)1.29 (36H); 0.89 (t, J =7.0 Hz, 6H); **^{13}C NMR** (MeOD, 101MHz) δ 151.60, 151.38, 147.02, 128.46, 128.32, 121.1 (q, $^1J(^{13}C,^{19}F)$ = 321.1 Hz), 63.38, 62.87, 33.06, 32.57, 31.81, 30.78, 30.63, 30.47, 30.13, 27.20, 23.72, 14.42.
Elemental Analysis, $C_{61}H_{84}F_{24}N_8O_{16}S_8$: found C 39.24 %, H 4.30 %, N 6.02 %, S 13.93 % ; calcd C 38.60 %, H 4.46 %, N 5.90 %, S 13.52 %. **ESI-MS**: *m/z*=1616.5 [14BP5BP14(Tf_2N)$_3$]$^+$; *m/z*=668.2 [14BP5BP14(Tf_2N)$_2$]$^{2+}$; *m/z*=352.3 [14BP6BP14(Tf_2N)]$^{3+}$.

[14BP6BP14](Tf_2N)$_4$: ^{1}H NMR (MeOD, 500 MHz) δ 9.22 (d, J = 6.8 Hz, 4H); 9.19 (d, J = 6.8 Hz, 4H); 8.61- 8.60 (two doublets partially overlapped, 8H); 4.74 - 4.72 (two triplets partially overlapped, 8H); 2.10 (m, 8H); 1.53 (b, 4H); 1.41 (8H); 1.29 (36H); 0.90 (t, J =7.0 Hz, 6H); **^{13}C NMR** (126 MHz, MeOD) δ 151.47, 146.99, 128.38, 121.1 (q, $^1J(^{13}C,^{19}F)$ = 321.1 Hz), 63.36, 63.18, 33.06, 32.55, 32.08, 30.78, 30.74, 30.71, 30.62, 30.46, 30.12, 27.18, 26.48, 23.72, 14.42. **Elemental Analysis**, $C_{62}H_{86}F_{24}N_8O_{16}S_8$: found C 38.56 %, H 4.43 %, N 5.80 %, S 13.55 % ; calcd C 38.95 %, H 4.53 %, N 5.86 %, S 13.42 %. **ESI-MS**: *m/z*=1630.5 [14BP6BP14(Tf_2N)$_3$]$^+$; *m/z*=675.2 [14BP6BP14(Tf_2N)$_2$]$^{2+}$; *m/z*=357.0 [14BP6BP14(Tf_2N)]$^{3+}$.

[16BP4BP16](Tf_2N)$_4$: ^{1}H NMR (MeOD, 500 MHz) δ 9.24 (d, J = 6.9 Hz, 4H); 9.19 (d, J = 6.9 Hz, 4H); 8.63 (d, J = 6.8 Hz, 8H); 8.60 (d, J = 6.7 Hz, 8H); 4.83 (partially overlapped to HDO); 4.72 (t, J = 7.6 Hz, 4H); 2.24 (4H); 2.07 (m, 4H); 1.41 (m. 8H); 1.28 (44H); 0.90 (t, J =7.0 Hz, 6H); **^{13}C NMR** (126 MHz, MeOD) δ 151.72, 151.31, 147.07, 128.57, 128.31, 121.1 (q, $^1J(^{13}C,^{19}F)$ = 321.1 Hz), 63.38, 62.34, 33.07, 32.55, 30.78, 30.75, 30.72, 30.64, 30.47, 30.14, 28.84, 27.19, 23.73, 14.43. **Elemental Analysis**, $C_{64}H_{90}F_{24}N_8O_{16}S_8$: found C 39.18 %, H 4.71 %, N 5.48 %, S 13.14 % ; calcd C 39.62 %, H 4.68 %, N 5.78 %, S 13.22 %. **ESI-MS**: *m/z*=1658 [16BP4BP16(Tf_2N)$_3$]$^+$; *m/z*=689 [16BP4BP16(Tf_2N)$_2$]$^{2+}$. We also observed two intense peaks in the ESI-MS spectrum at m/z = 1630 and 675, corresponding to a monocationic and dicationic species, respectively (as inferred from the spacing of the isotope peaks), that could not be assigned.

[16BP5BP16](Tf$_2$N)$_4$: ^{1}H NMR (MeOD, 500 MHz) δ 9.24 (d, J = 6.9 Hz, 4H); 9.20 (d, J = 6.8 Hz, 4H); 8.64 (m, J =6.9 Hz, 4H); 8.62 (d, J = 6.8 Hz, 4H); 4.77 (t, J = 7.4 Hz, 4H); 4.73 (t, J = 7.5 Hz, 4H); 2.20 (m, 4H); 2.08 (m, 4H); 1.61 (m, 2H); 1.42 (8H); 1.32 - 1.28 (44H); 0.90 (t, J =6.9Hz, 6H); **^{13}C NMR** (126 MHz, MeOD) δ 151.59, 151.37, 147.01, 128.46, 128.32,121.1 (q, $^1J(^{13}C,^{19}F)$ = 321.1 Hz) , 63.38, 62.87, 33.05, 32.55, 31.78, 30.76, 30.73, 30.70, 30.62, 30.45, 30.12, 27.19, 23.71, 14.41: **Elemental Analysis**, $C_{65}H_{92}F_{24}N_8O_{16}S_8$: found C 38.22 %, H 4.69 %, N 5.25 %, S 12.57 % ; calcd C 39.95 %, H 4.75 %, N 5.73 %, S 13.13 %. **ESI-MS**: *m/z*=1673.8 $[16BP5BP16(Tf_2N)_3]^+$; *m/z*=696.8 $[16BP5BP16(Tf_2N)_2]^{2+}$; *m/z*=371.2 $[16BP5BP16(Tf_2N)]^{3+}$.

[16BP6BP16](Tf$_2$N)$_4$: ^{1}H NMR (MeOD, 500 MHz) δ 9.22 (d, J = 6.7 Hz, 4H); 9.19 (d, J = 6.7 Hz, 4H); 8.60 (m, 8H); 8.60 (d, J = 6.7 Hz, 8H); 4.74 (t, J = 7.4 Hz, 4H); 4.72 (t, J = 7.5 Hz, 4H); 2.09 (m, 8H); 2.09 (m, 4H); 1.53 (b, 4H); 1.42 (8H); 1.28 (32H); 0.90 (t, J =6.9Hz, 6H); **^{13}C NMR** (126 MHz, MeOD) δ 151.47, 151.39, 146.99, 128.38, 128.30,121.1 (q, $^1J(^{13}C,^{19}F)$ = 321.1 Hz) , 63.36, 63.19, 33.07, 32.55, 32.08, 30.78, 30.75, 30.71, 30.12, 27.18, 26.48, 23.73, 14.43: **Elemental Analysis**, $C_{66}H_{94}F_{24}N_8O_{16}S_8$: found C 38.19 %, H 4.74 %, N 5.13 %, S 12.70 % ; calcd C 40.28 %, H 4.81 %, N 5.69 %, S 13.03 %. **ESI-MS**: *m/z*=1686 $[16BP6BP16(Tf_2N)_3]^+$; *m/z*=703 $[16BP6BP16(Tf_2N)_2]^{2+}$; *m/z*=375 $[16BP6BP16(Tf_2N)]^{3+}$.

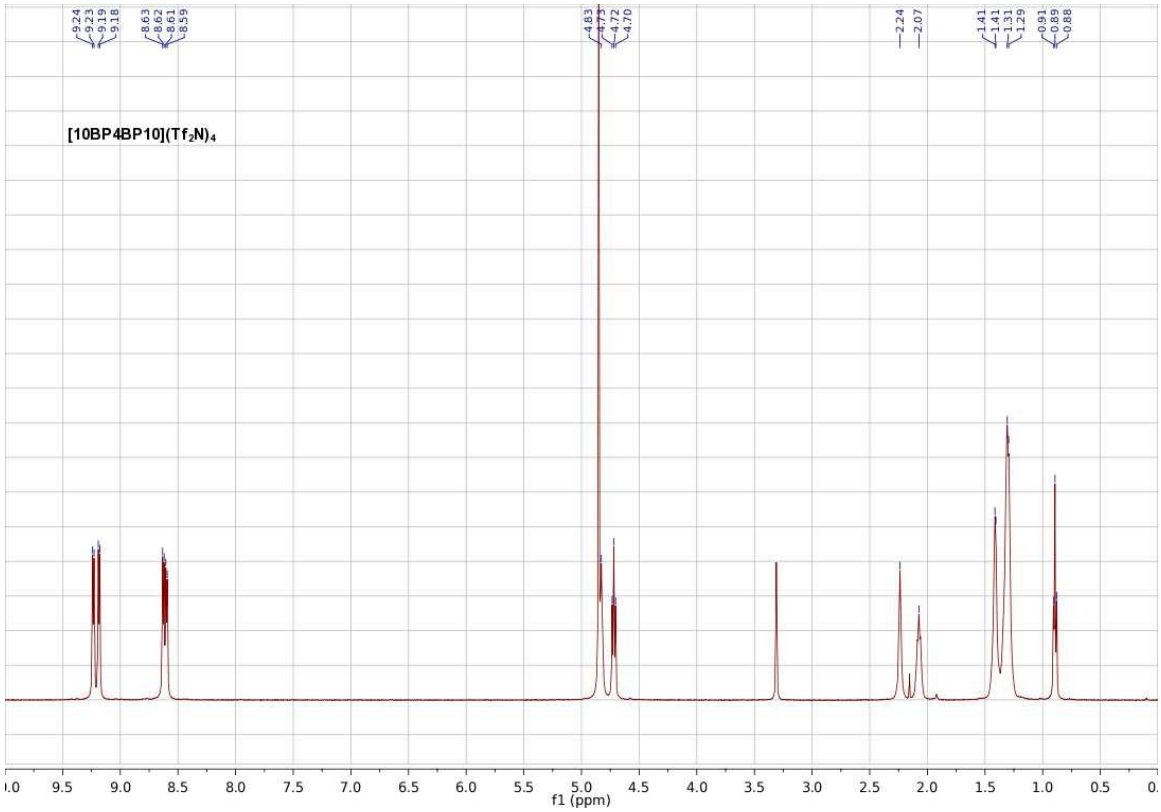


Fig S1: ^{1}H NMR (MeOD, 500 MHz) of [10BP4BP10](Tf$_2$N)$_4$

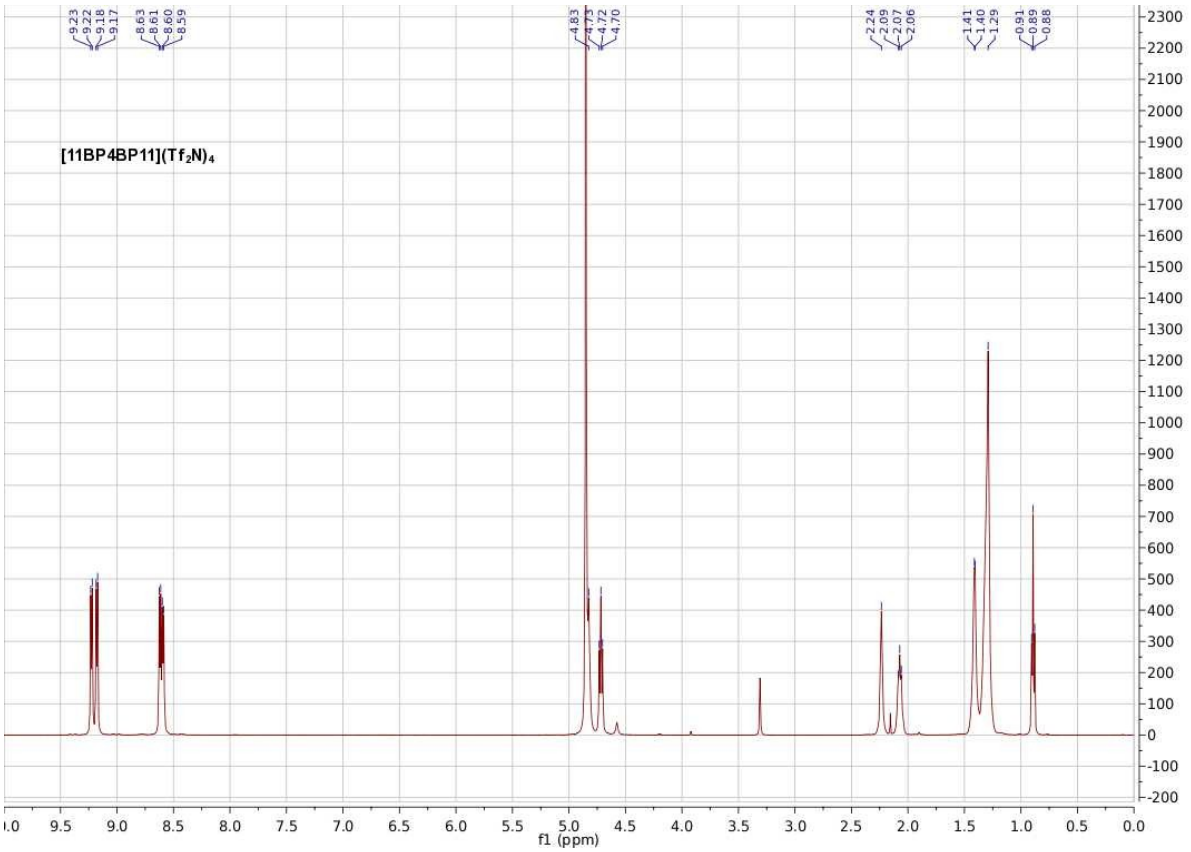


Fig S2: ^{1}H NMR (MeOD, 500 MHz) of [11BP4BP11](Tf$_2$N)$_4$

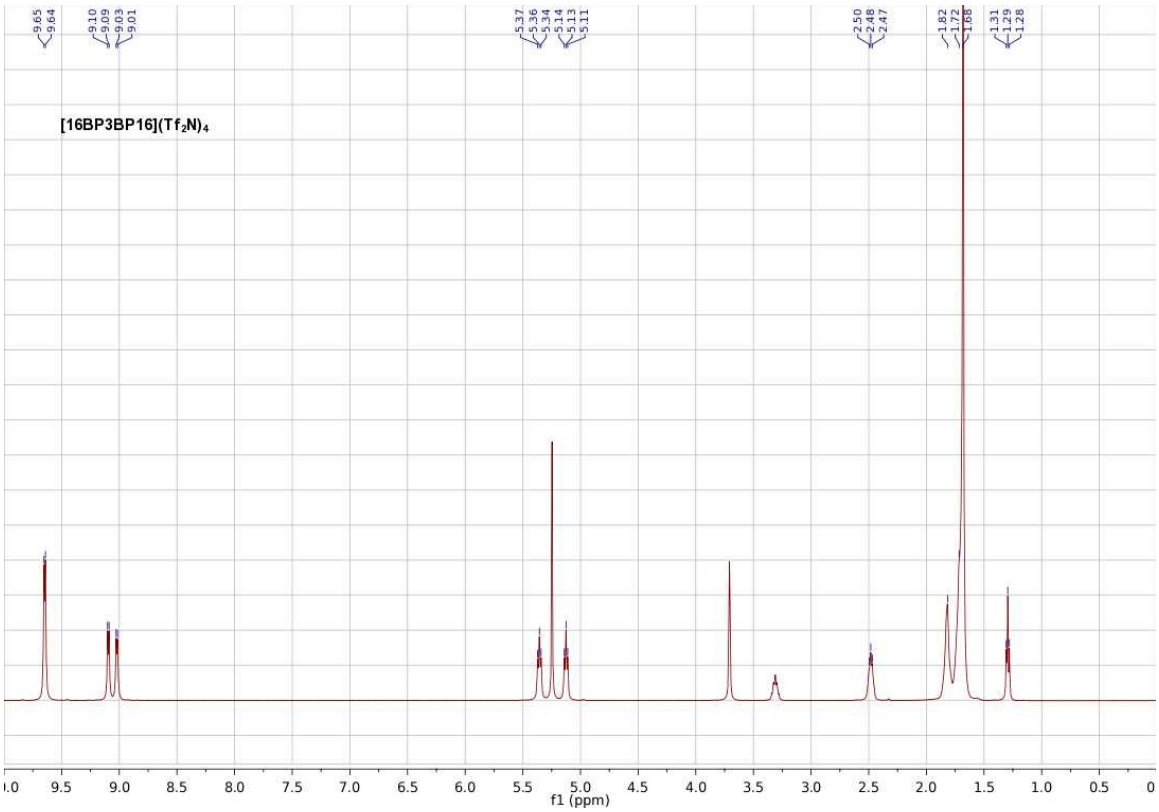


Fig S3: ^{1}H NMR (MeOD, 500 MHz) of [16BP3BP16](Tf$_2$N)$_4$

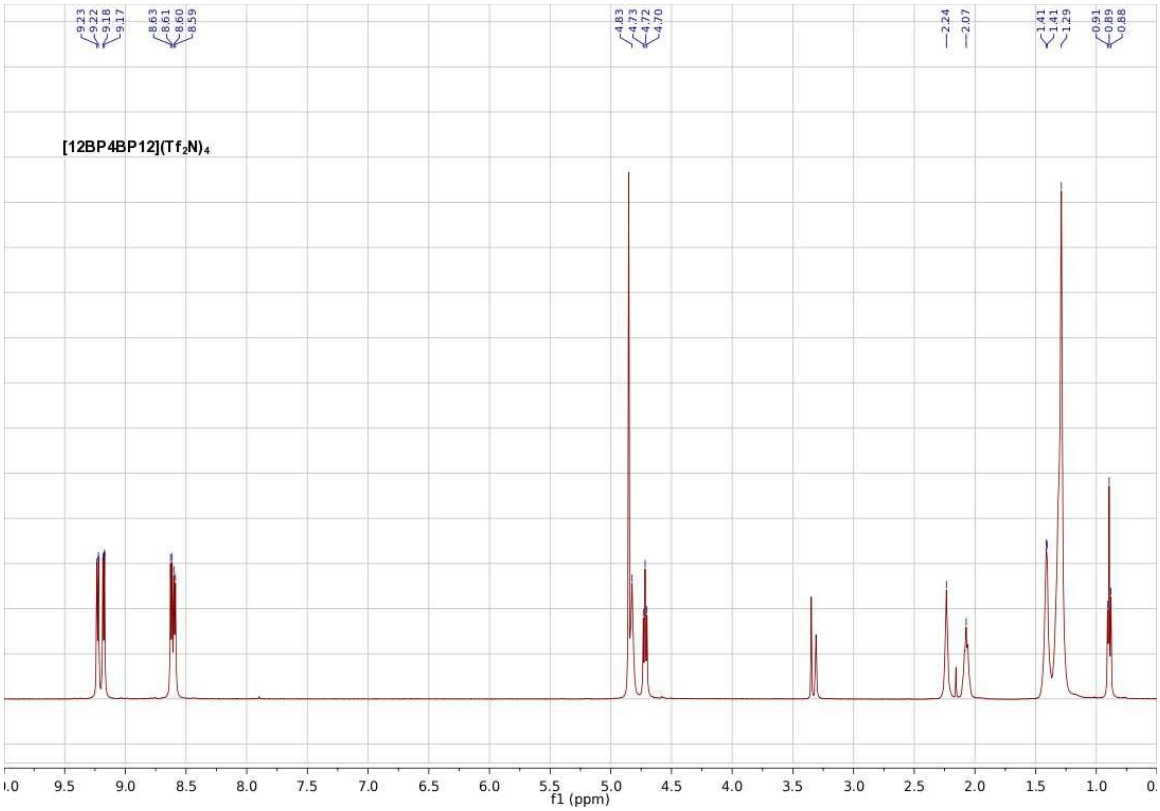


Fig S4: ^{1}H NMR (MeOD, 500 MHz) of [12BP4BP12](Tf$_2$N)$_4$

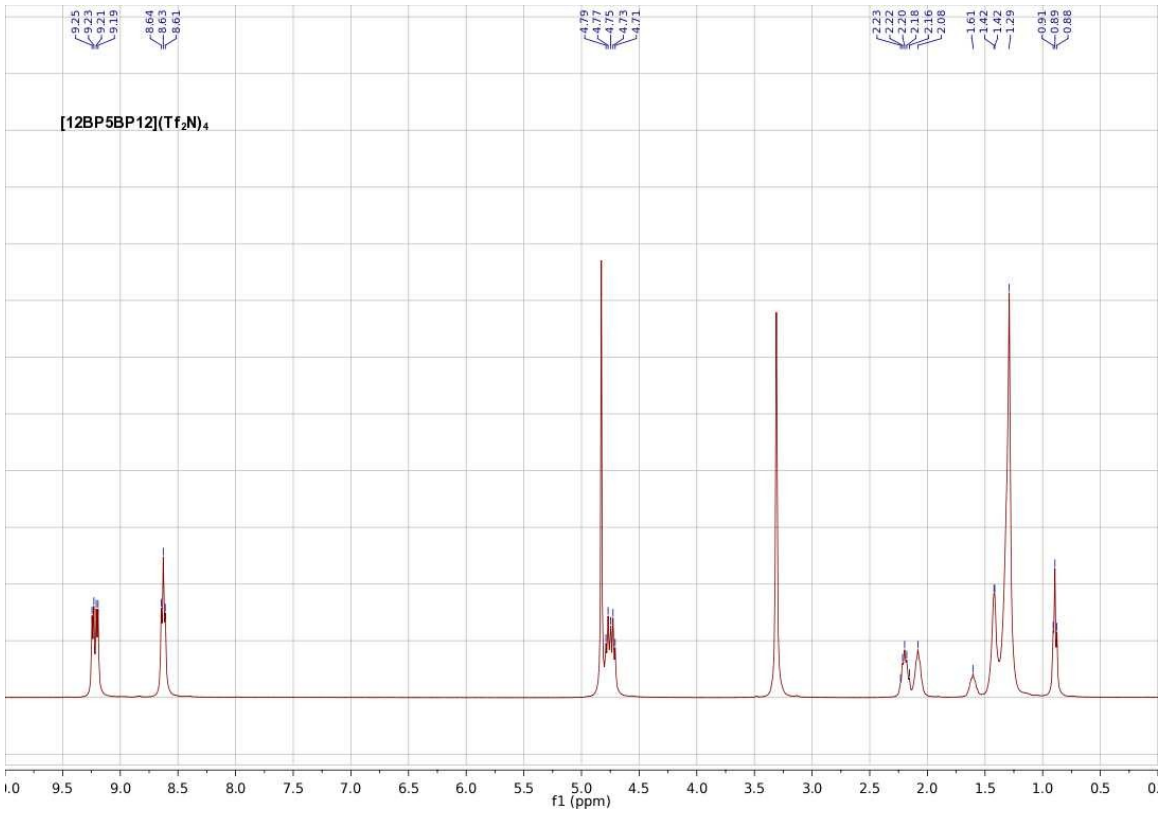


Fig S5: ^{1}H NMR (MeOD, 400 MHz) of [12BP5BP12](Tf$_2$N)$_4$

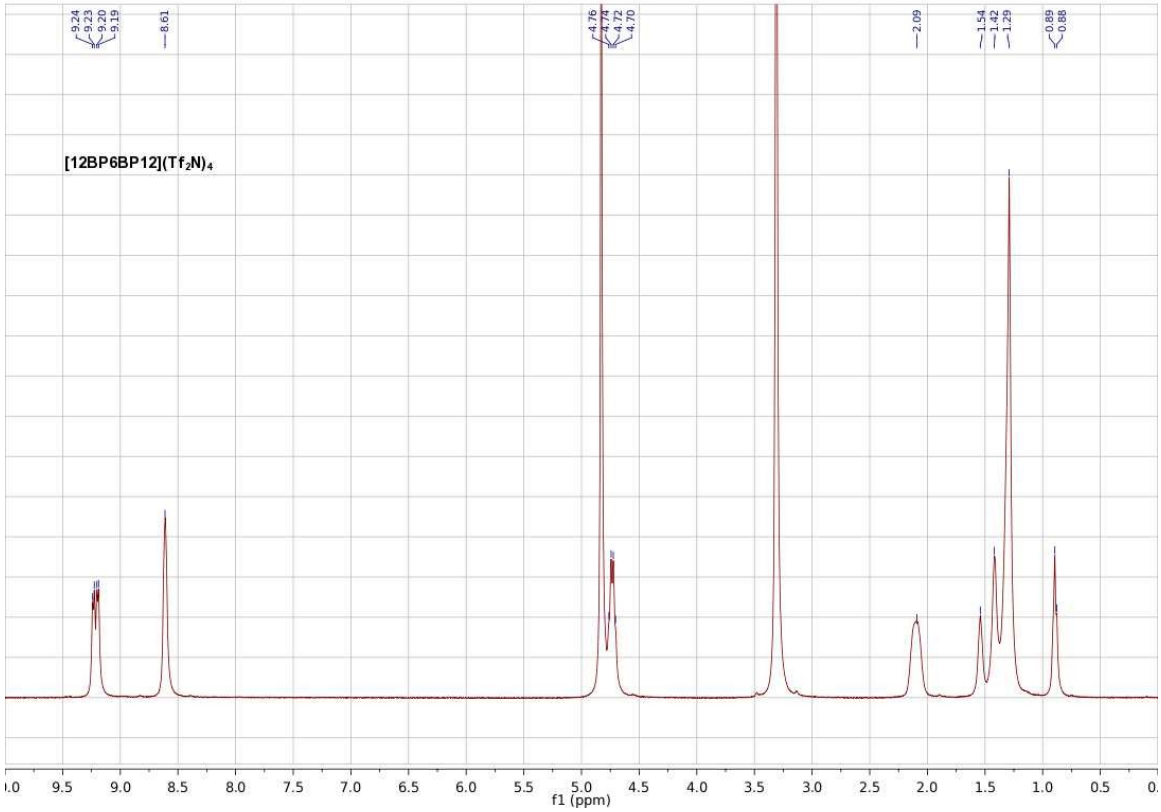


Fig S6: ^{1}H NMR (MeOD, 400 MHz) of [12BP6BP12](Tf$_2$N)$_4$

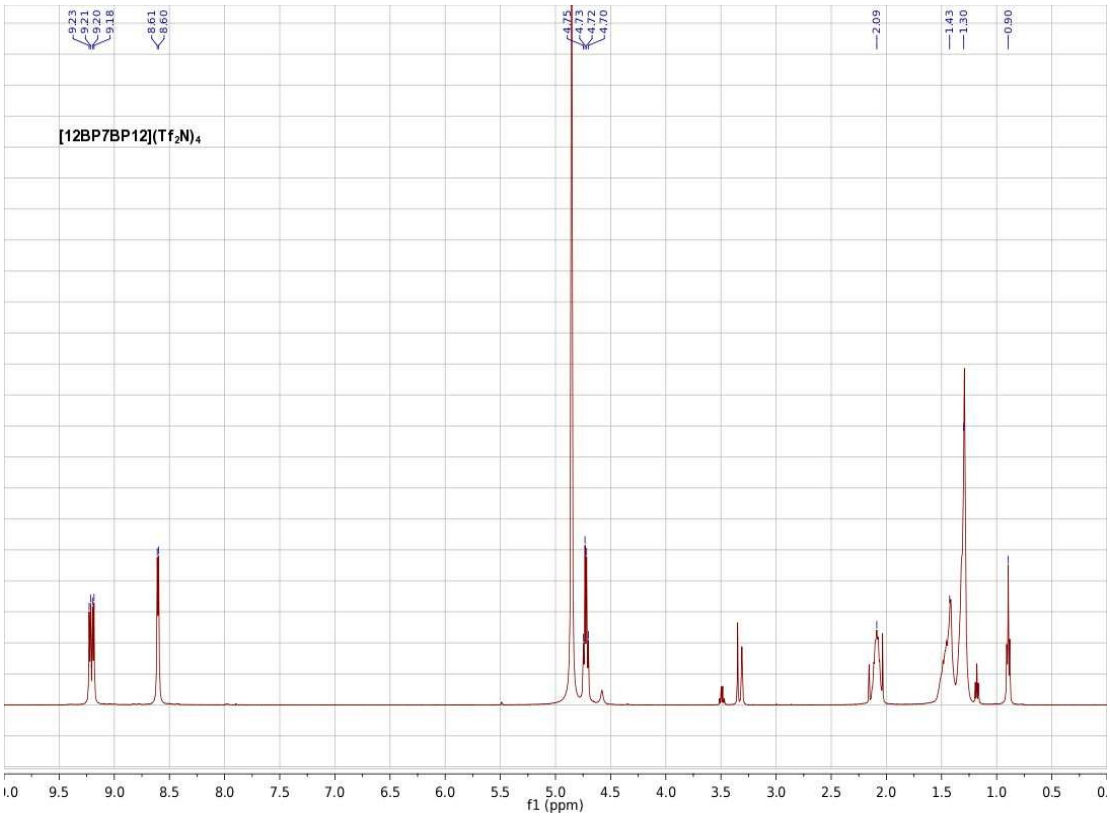


Fig S7: ^{1}H NMR (MeOD, 500 MHz) of [12BP7BP12](Tf$_2$N)$_4$

Fig S8: ^{1}H NMR (MeOD, 500 MHz) of [12BP8BP12](Tf$_2$N)$_4$

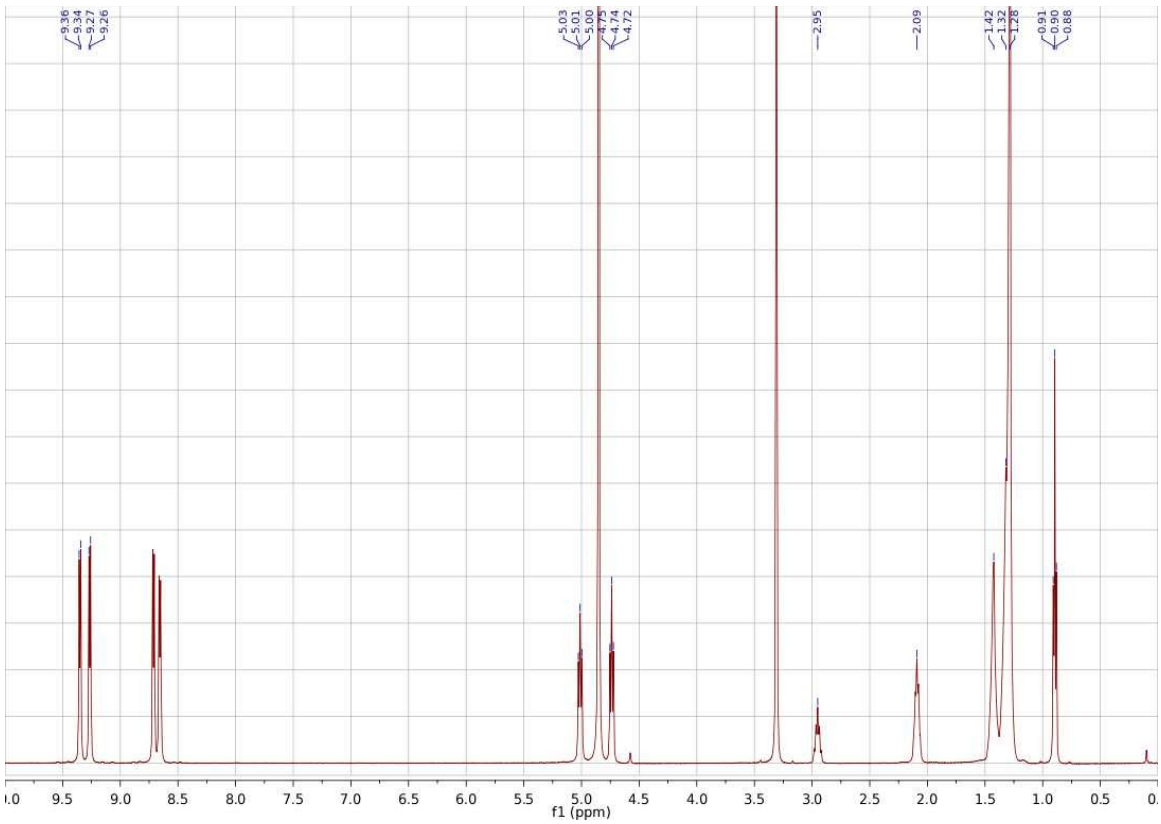


Fig S9: ^{1}H NMR (MeOD, 500 MHz) of [14BP3BP14](Tf$_2$N)$_4$

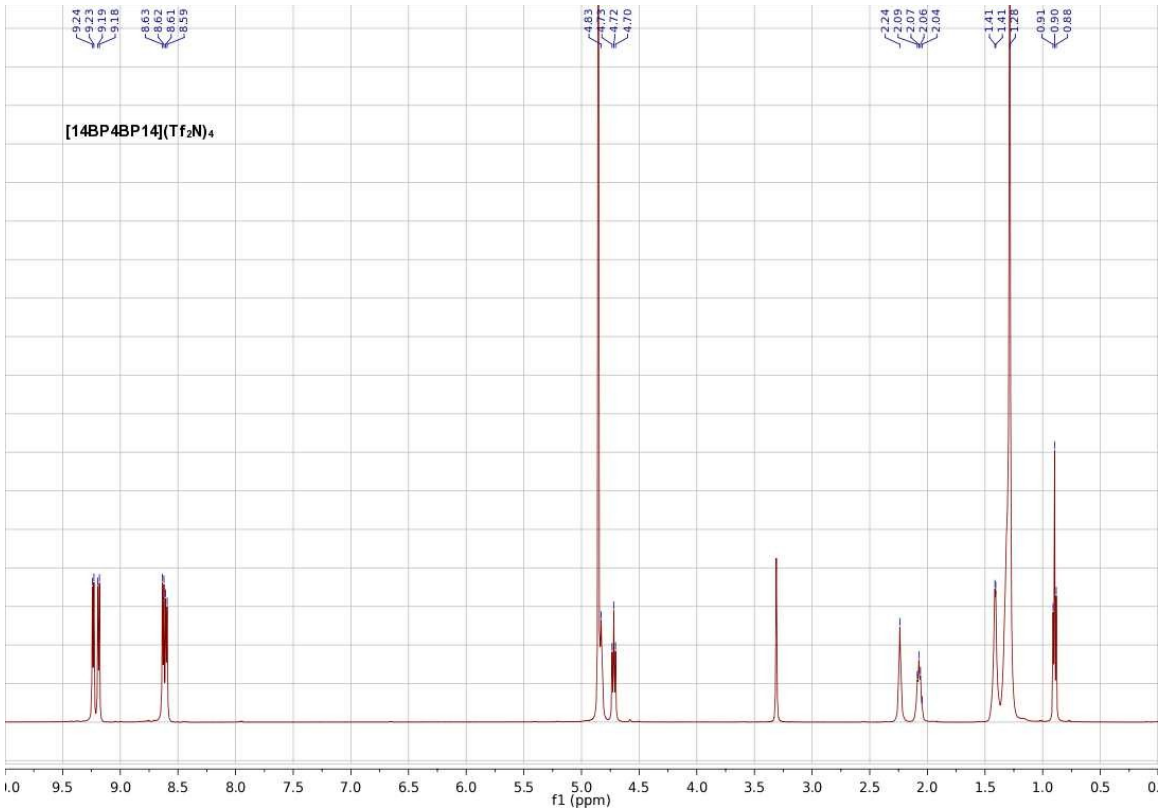


Fig S10: ^{1}H NMR (MeOD, 500 MHz) of [14BP4BP14](Tf$_2$N)$_4$

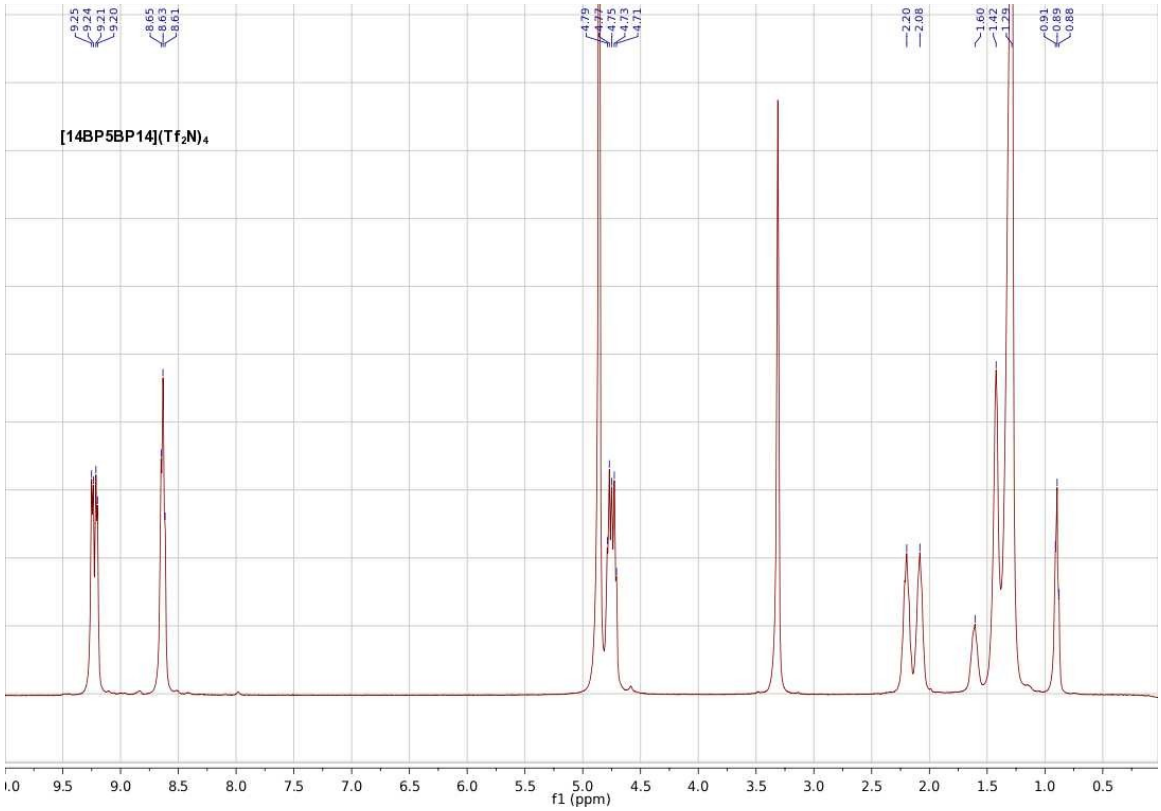


Fig S11: ^{1}H NMR (MeOD, 400 MHz) of [14BP5BP14](Tf$_2$N)$_4$

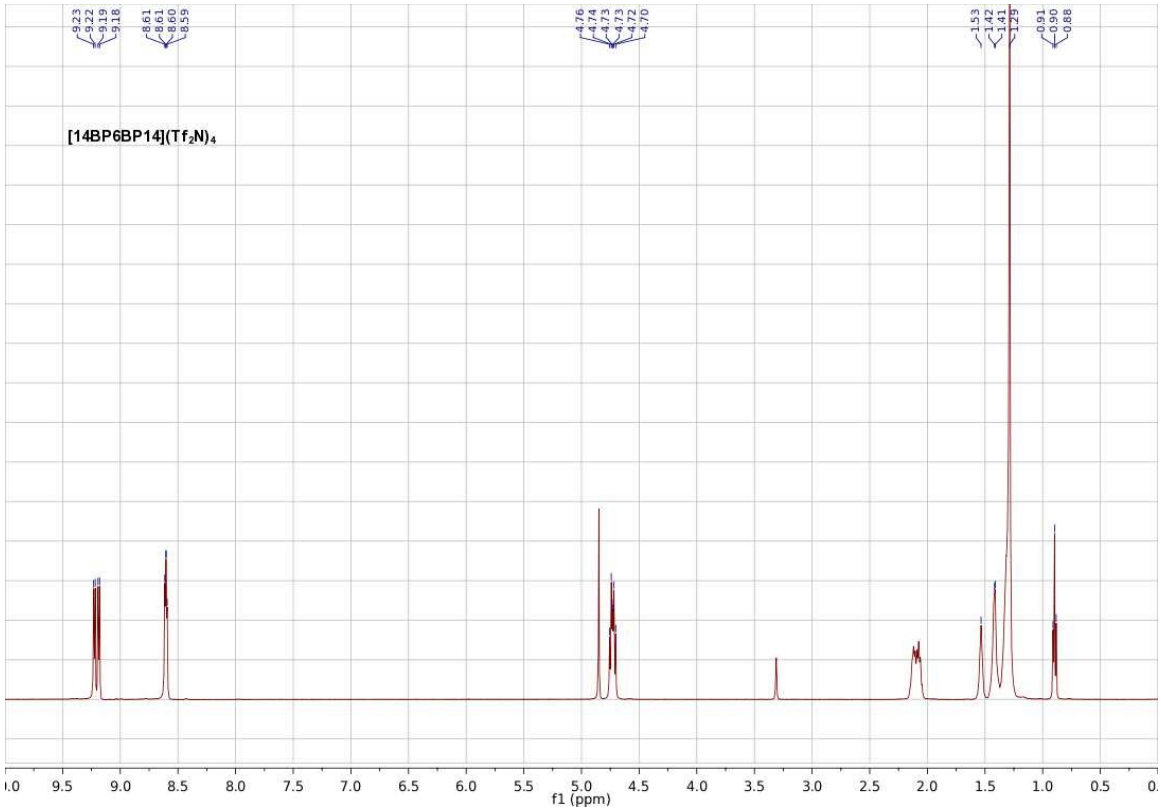


Fig S12: ^{1}H NMR (MeOD, 500 MHz) of [14BP6BP14](Tf$_2$N)$_4$

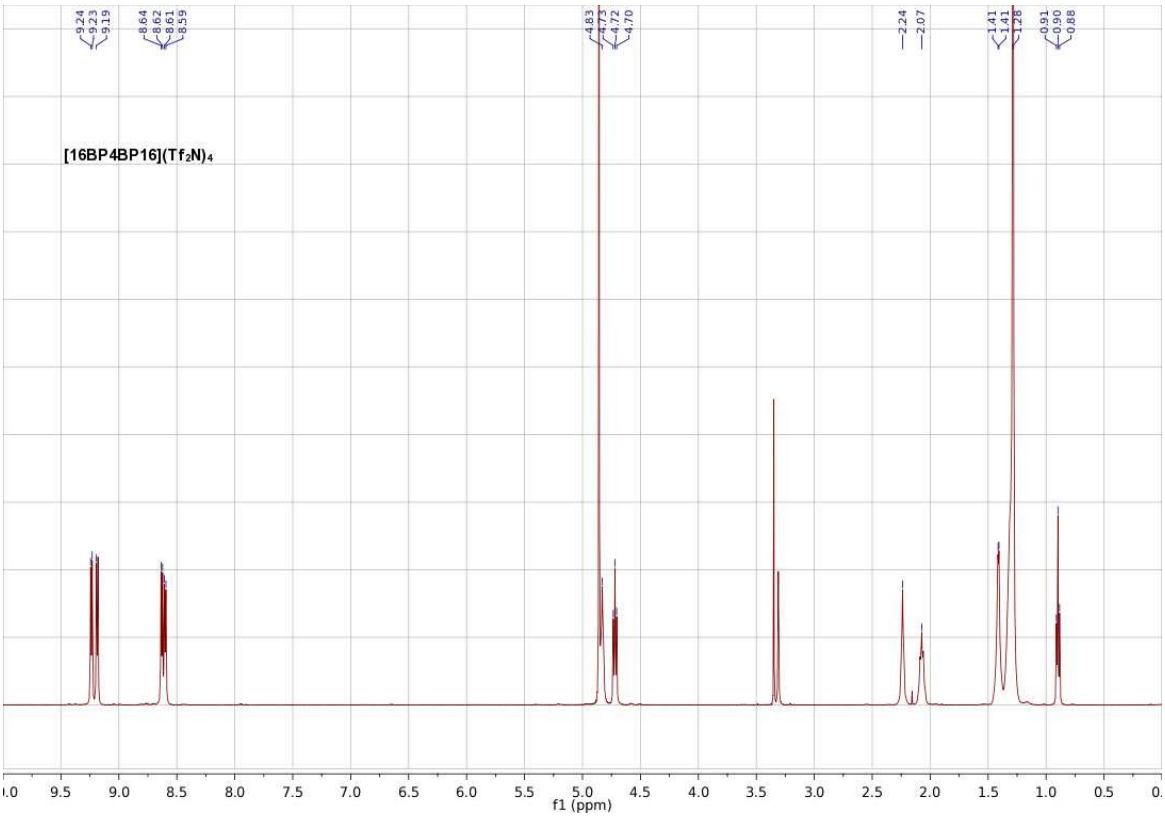


Fig S13: ^{1}H NMR (MeOD, 500 MHz) of [16BP4BP16](Tf$_2$N)$_4$

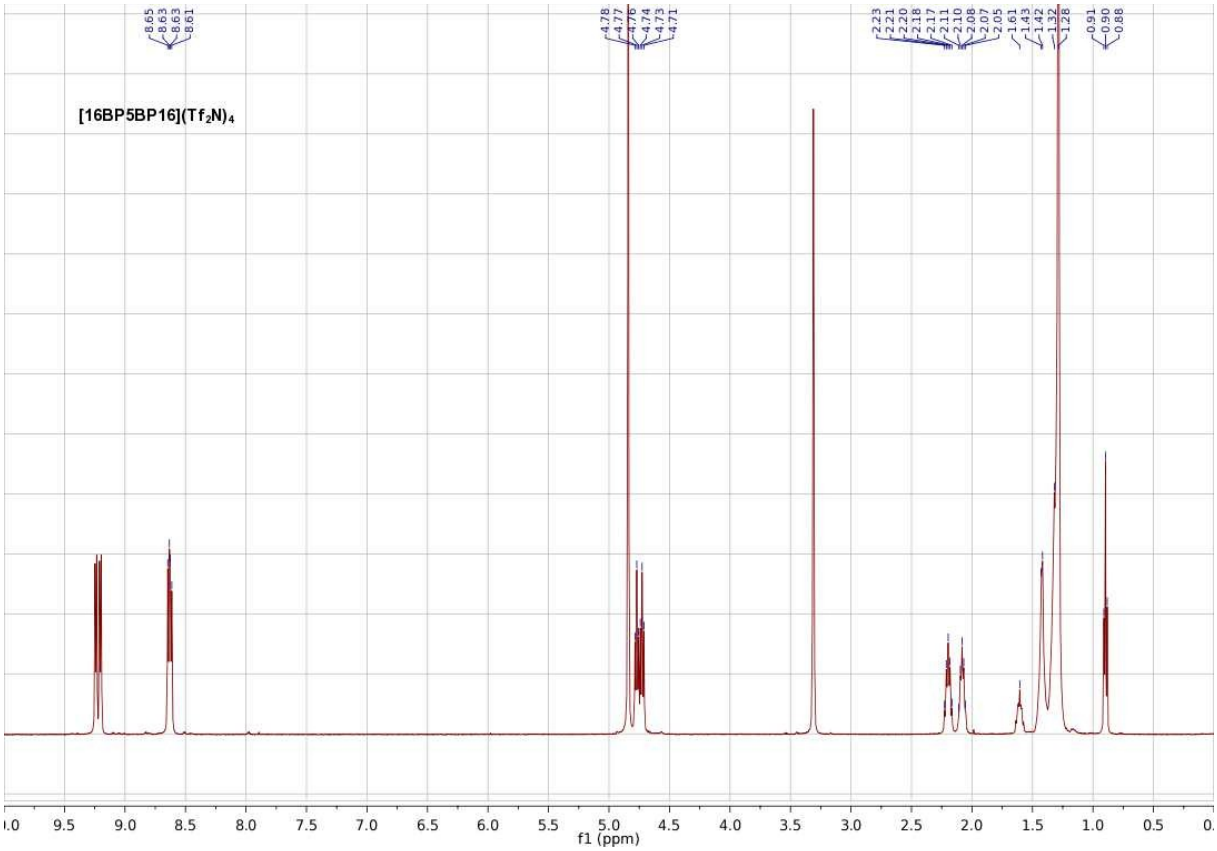


Fig S14: ^{1}H NMR (MeOD, 500 MHz) of [16BP5BP16](Tf$_2$N)$_4$

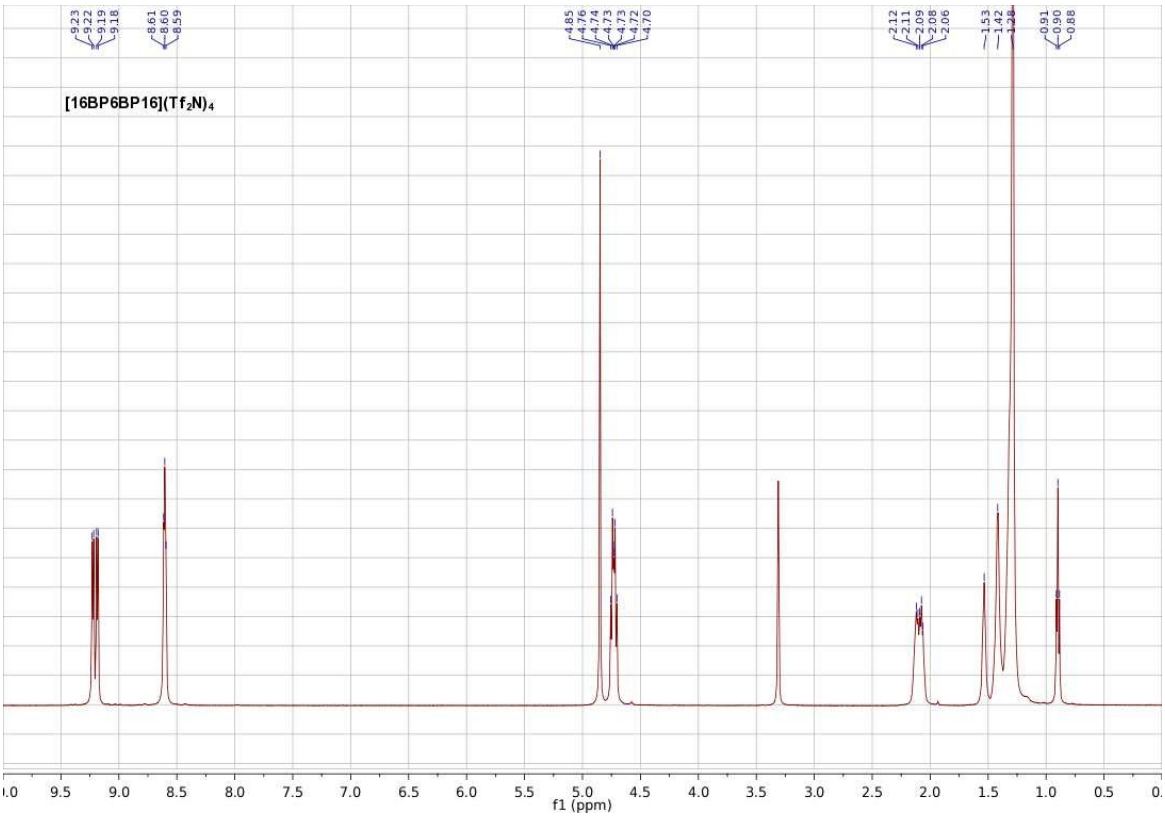


Fig S15: ^{1}H NMR (MeOD, 500 MHz) of [16BP6BP16](Tf$_2$N)$_4$

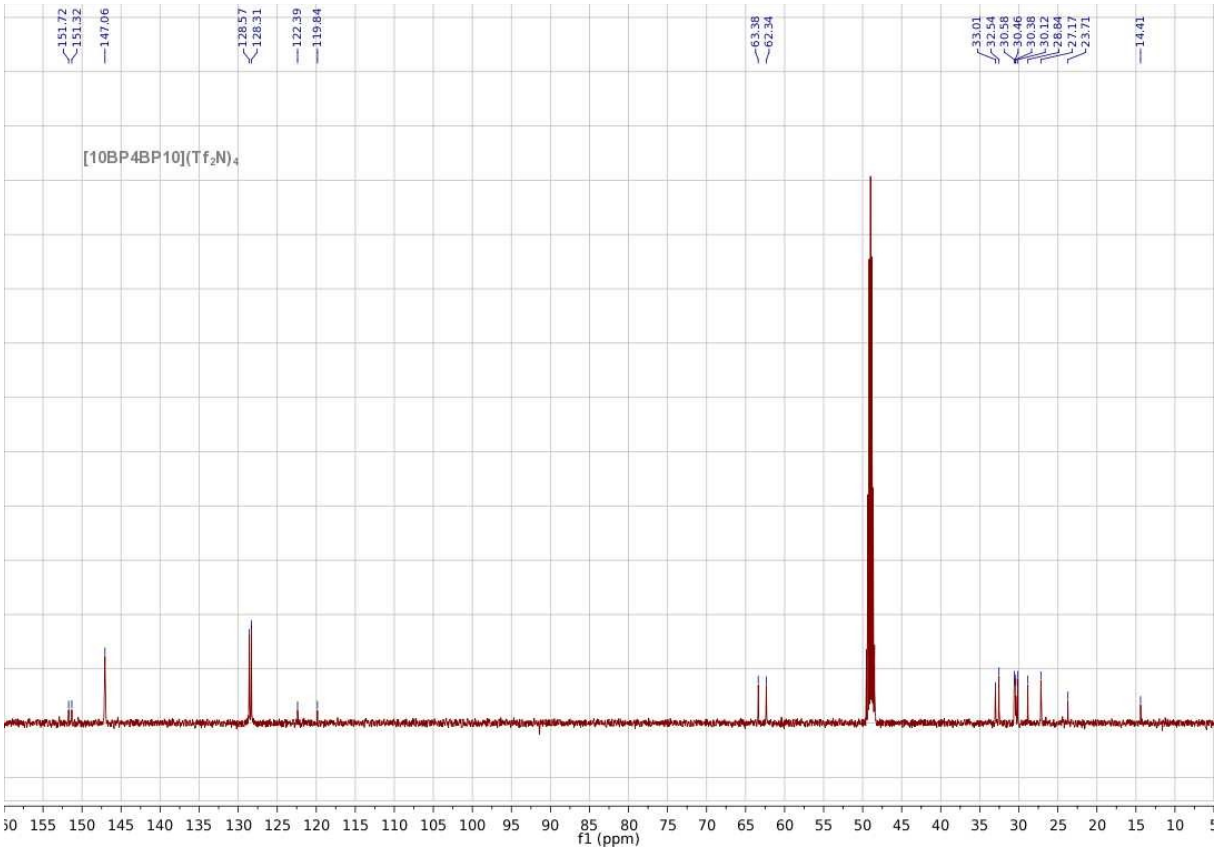


Fig S16: ^{13}C NMR (MeOD, 126 MHz) of [10BP4BP10](Tf$_2$N)$_4$

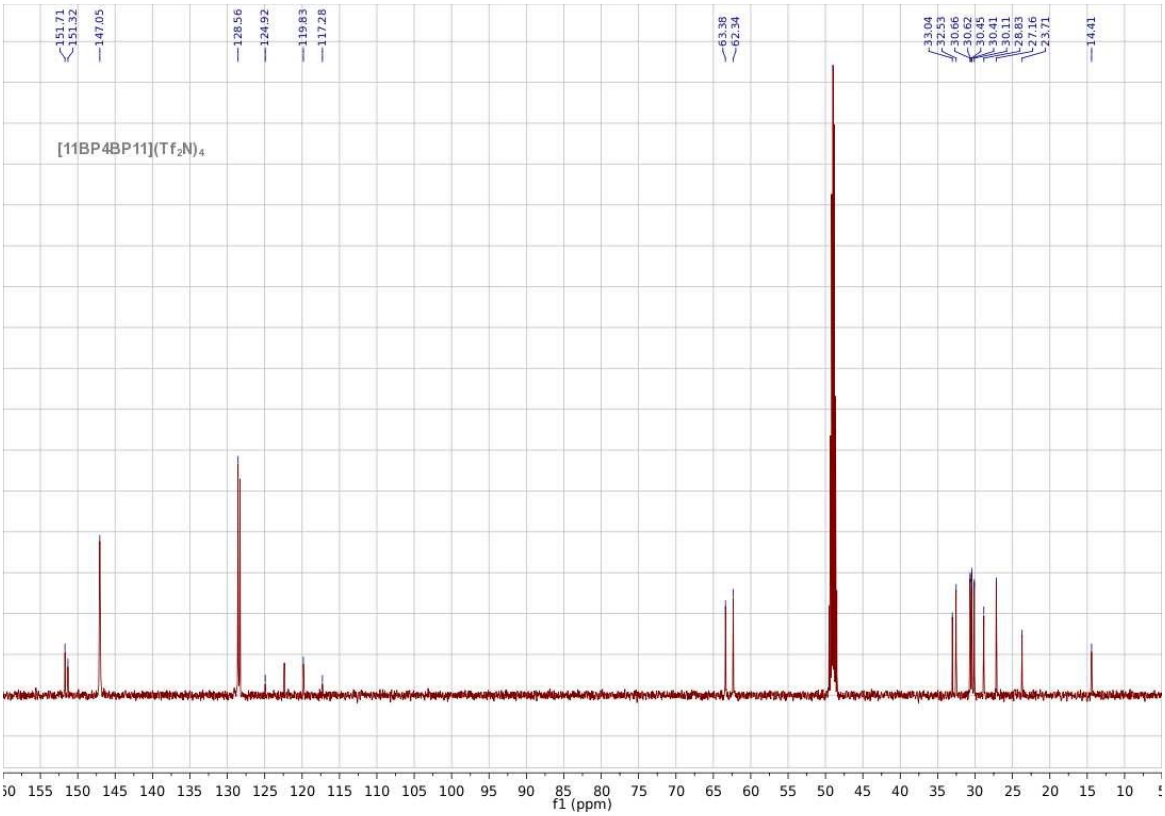


Fig S17: ^{13}C NMR (MeOD, 126 MHz) of [11BP4BP11](Tf$_2$N)$_4$

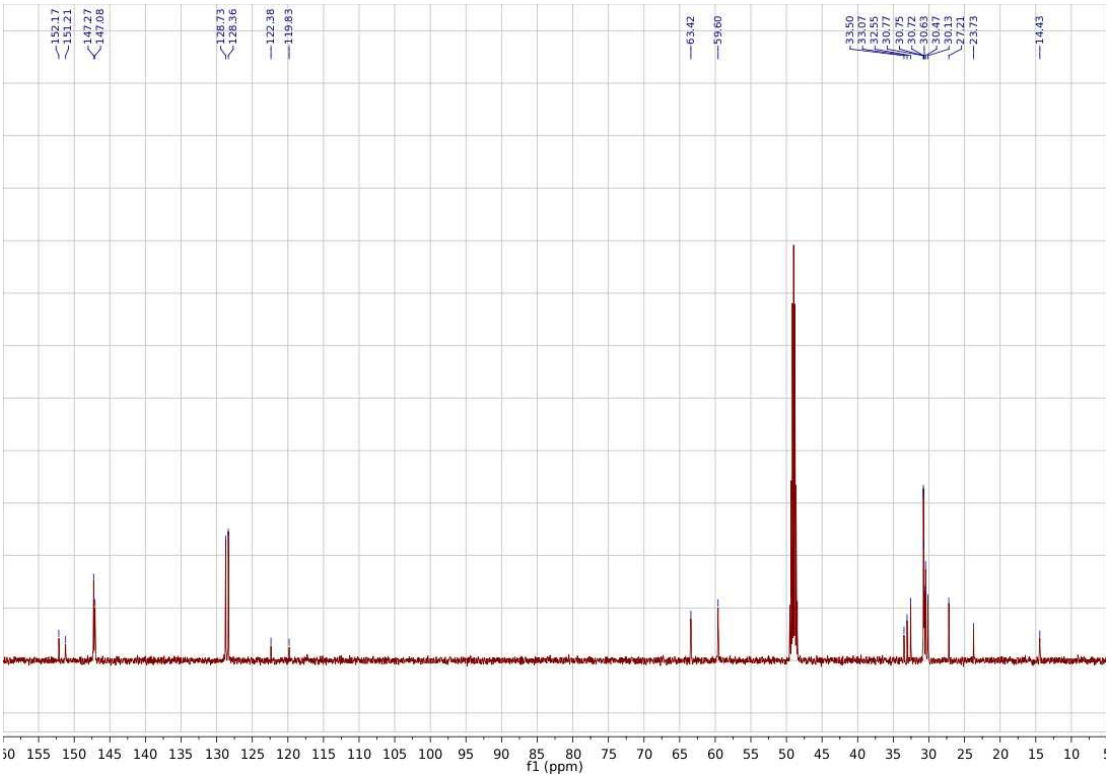


Fig S18: ^{13}C NMR (MeOD, 126 MHz) of [16BP3BP16](Tf$_2$N)$_4$

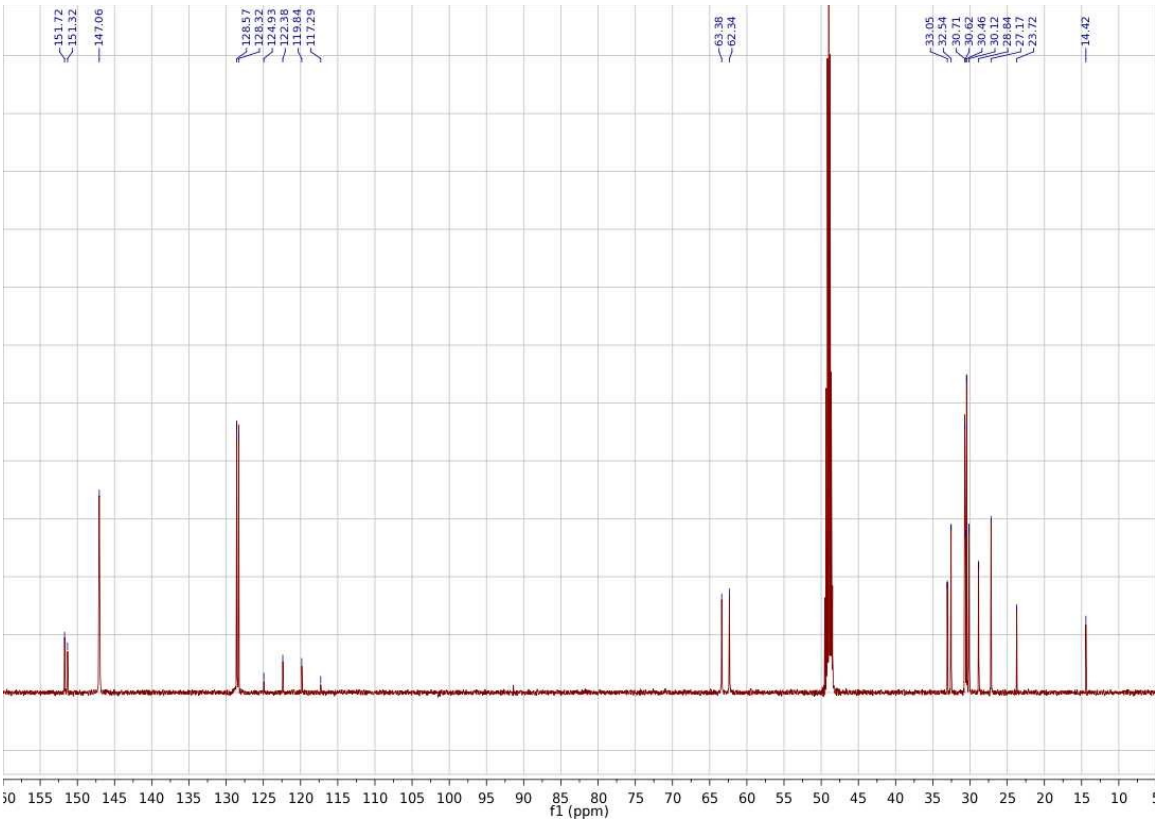


Fig S19: ^{13}C NMR (MeOD, 126 MHz) of [12BP4BP12](Tf$_2$N)$_4$

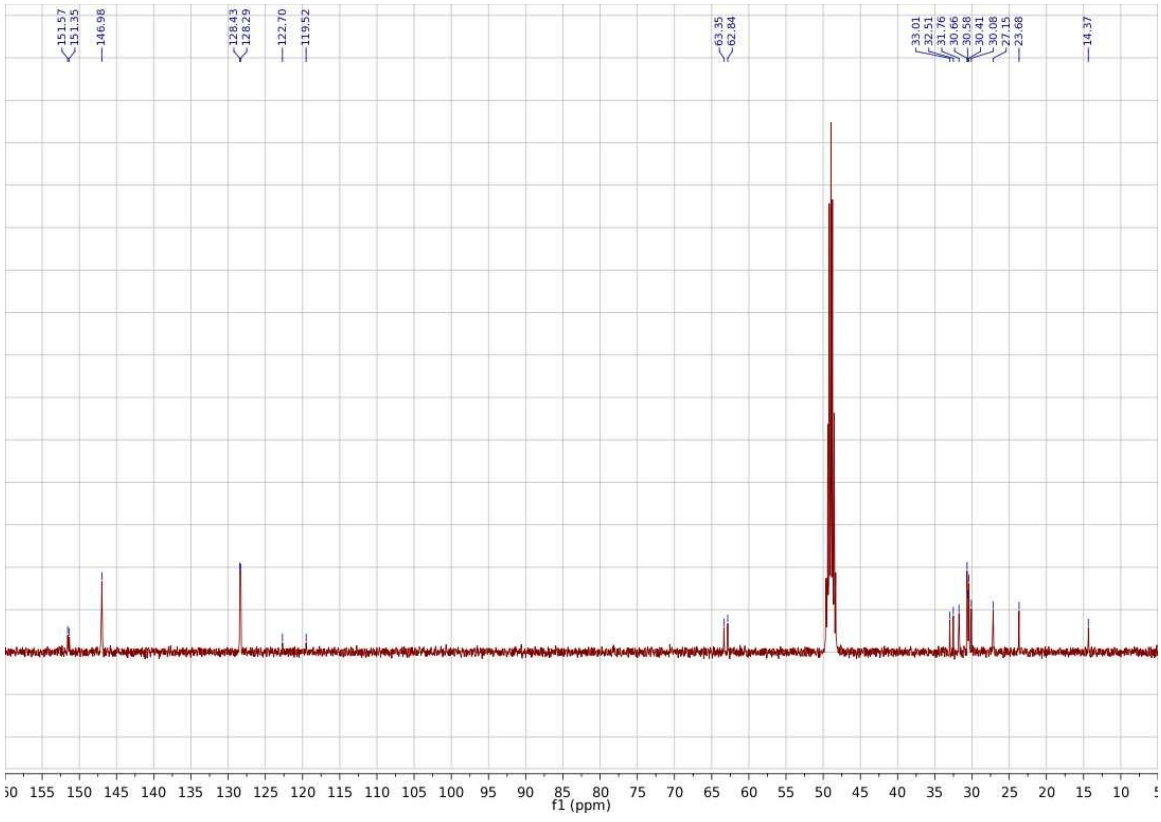


Fig S20: ^{13}C NMR (MeOD, 101 MHz) of [12BP5BP12](Tf$_2$N)$_4$

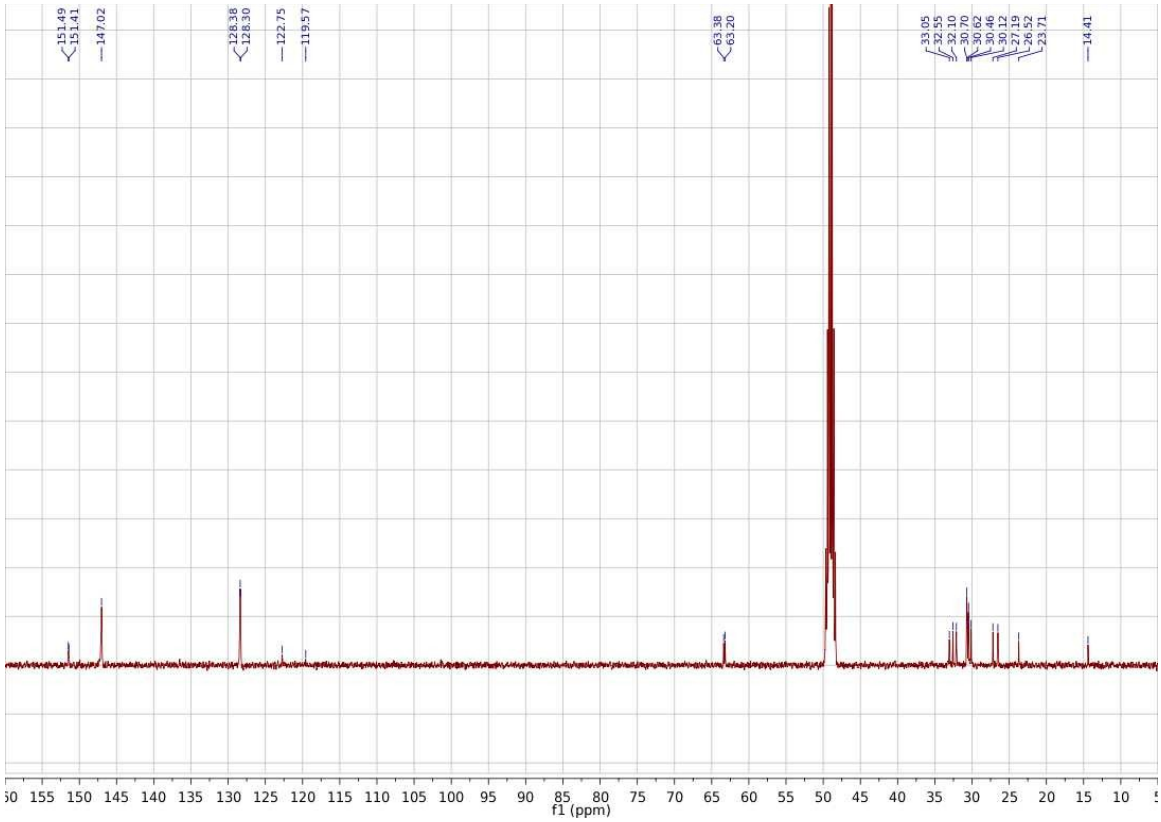


Fig S21: ^{13}C NMR (MeOD, 101 MHz) of [12BP6BP12](Tf$_2$N)$_4$

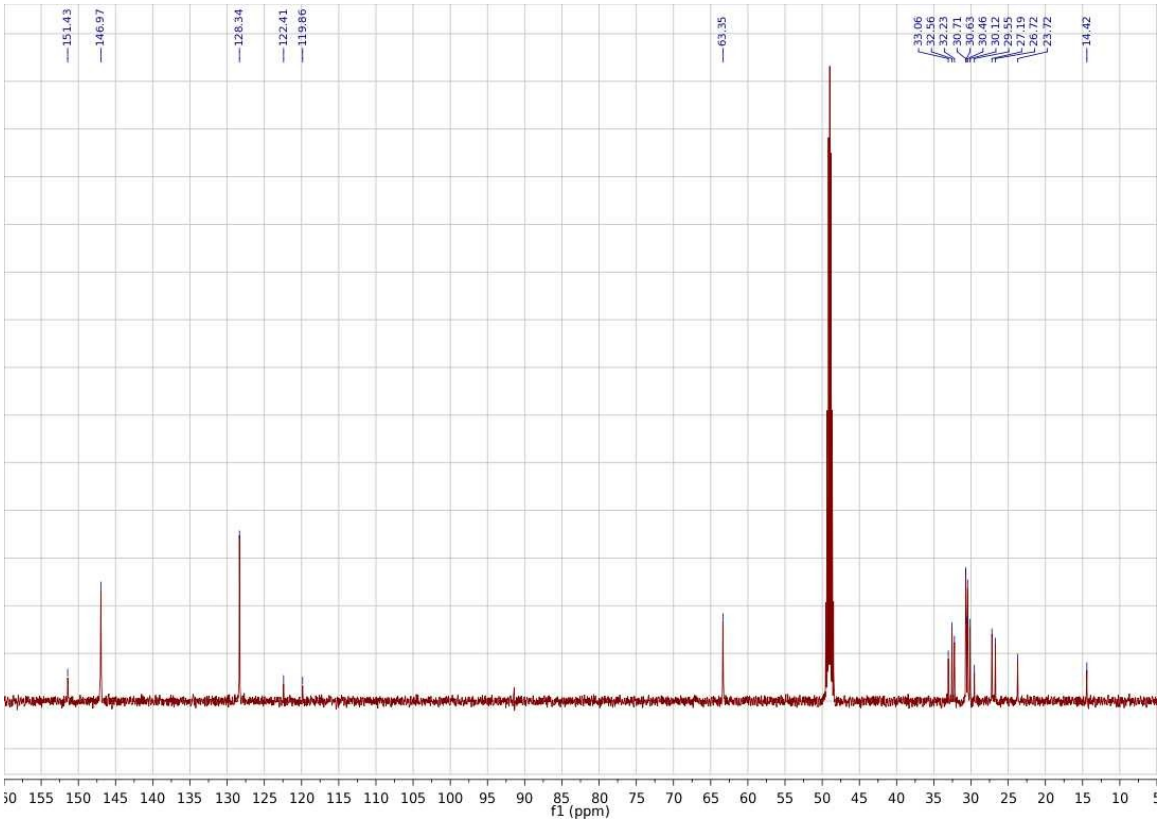


Fig S22: ^{13}C NMR (MeOD, 126 MHz) of [12BP7BP12](Tf$_2$N)$_4$

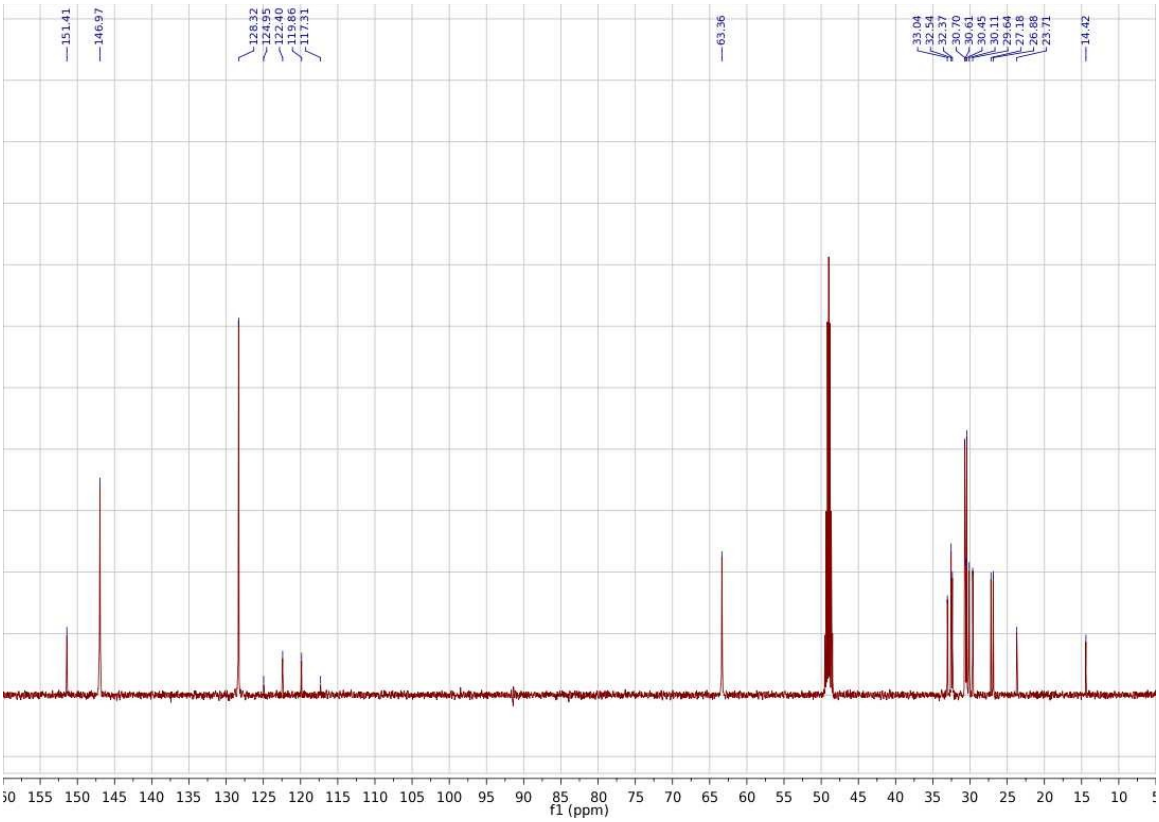


Fig S23: ^{13}C NMR (MeOD, 126 MHz) of [12BP8BP12](Tf$_2$N)$_4$

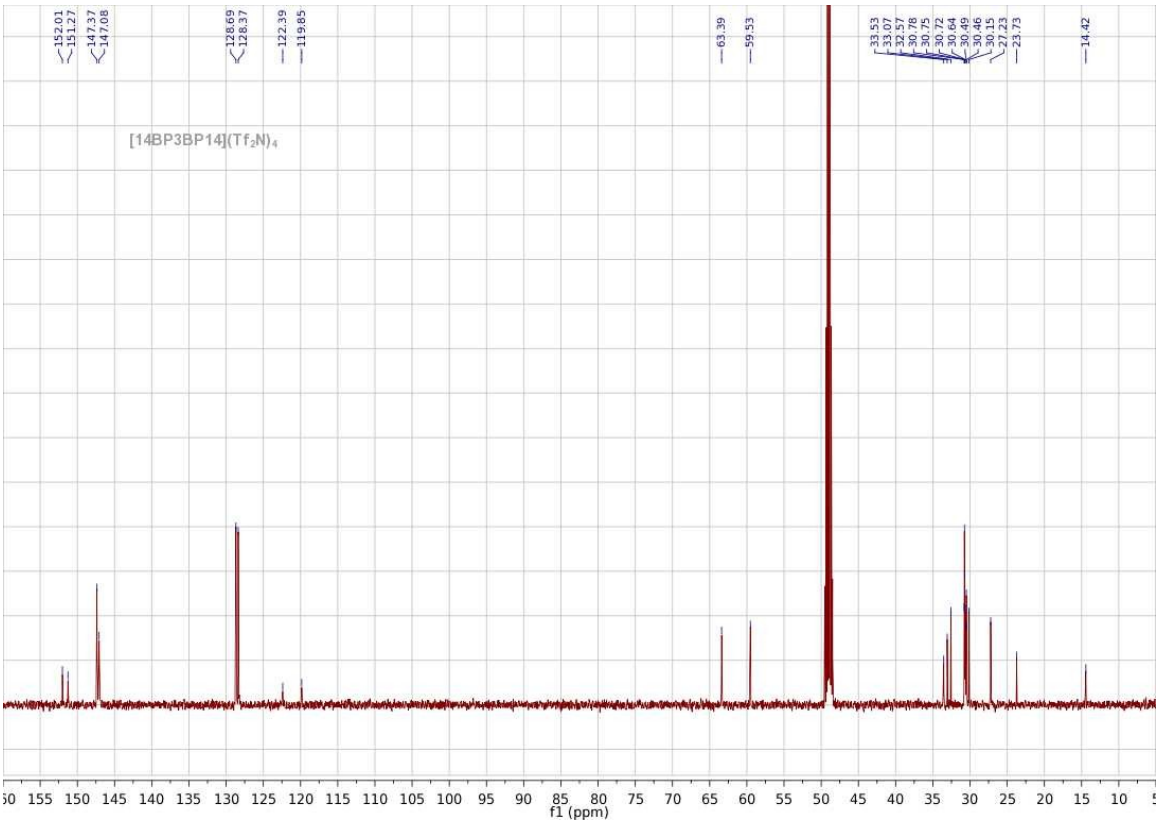


Fig S24: ^{13}C NMR (MeOD, 126 MHz) of [14BP3BP14](Tf$_2$N)$_4$

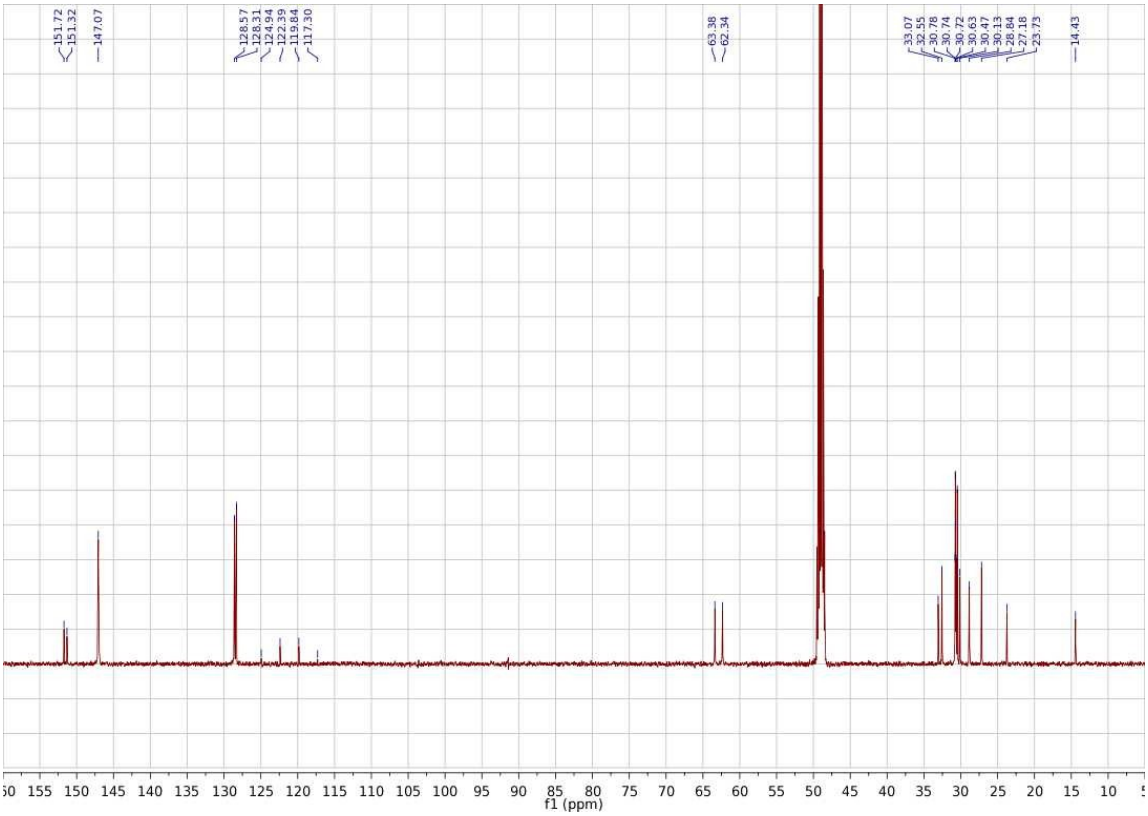


Fig S25: ^{13}C NMR (MeOD, 126 MHz) of [14BP4BP14](Tf$_2$N)$_4$

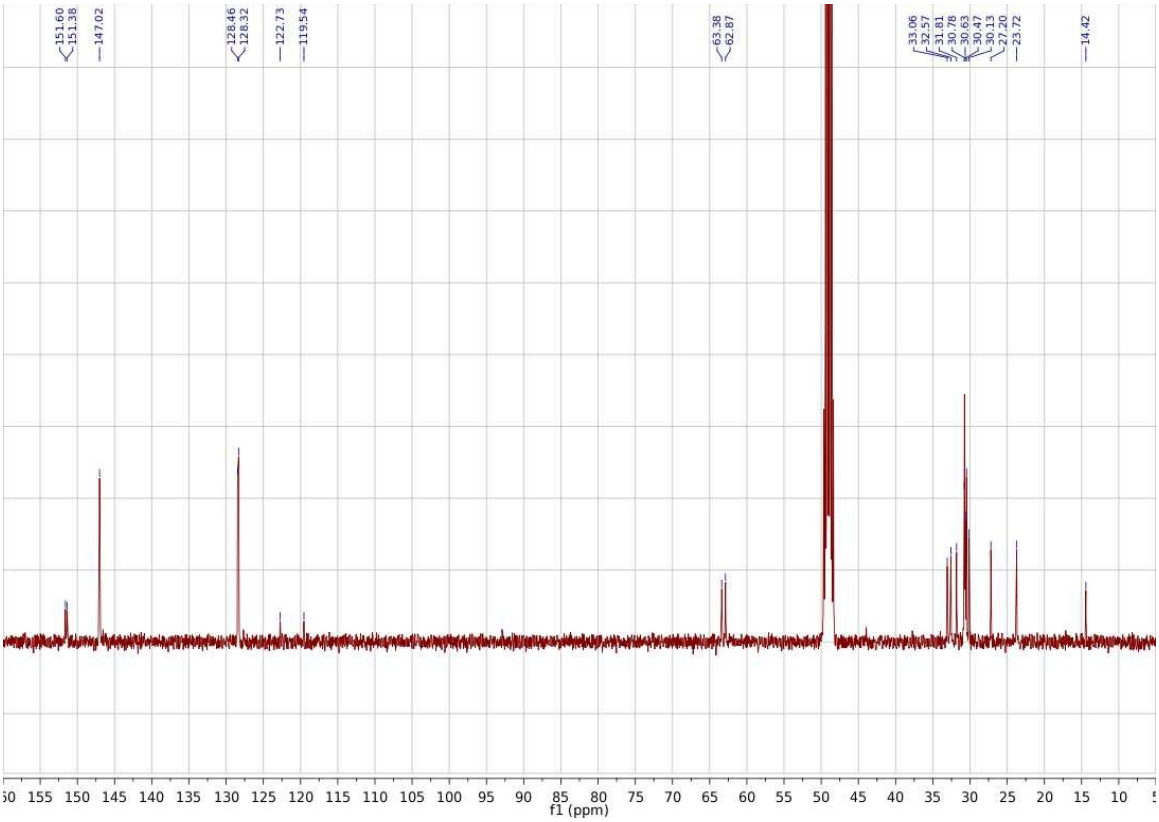


Fig S26: ^{13}C NMR (MeOD, 126 MHz) of [14BP5BP14](Tf$_2$N)$_4$

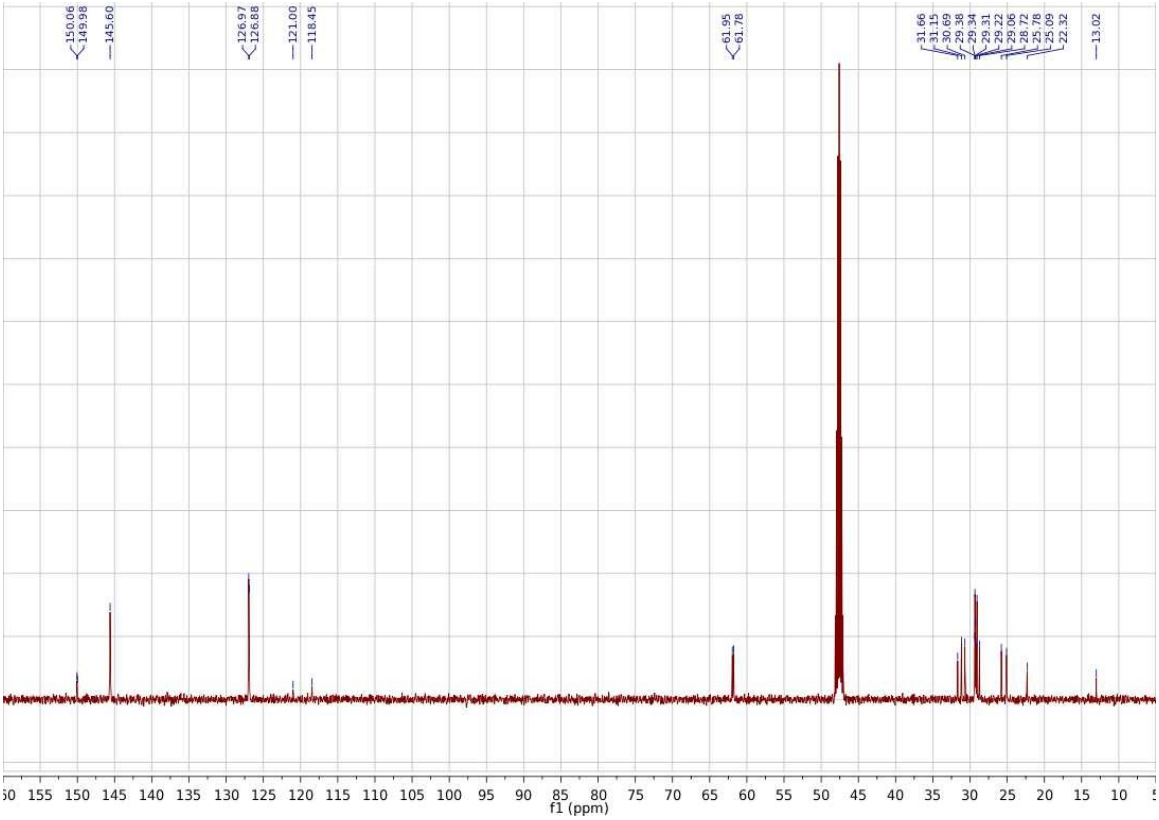


Fig S27: ^{13}C NMR (MeOD, 126 MHz) of [14BP6BP14](Tf$_2$N)$_4$

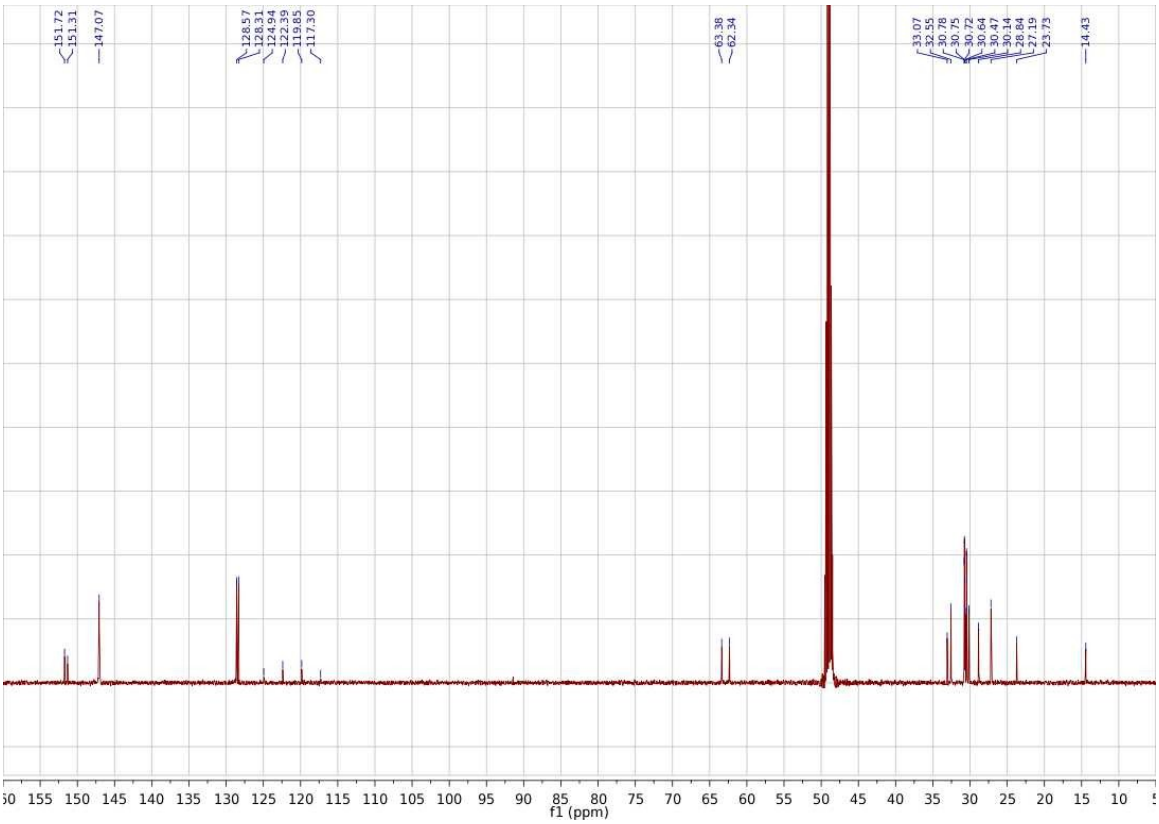


Fig S28: ^{13}C NMR (MeOD, 126 MHz) of [16BP4BP16](Tf$_2$N)$_4$

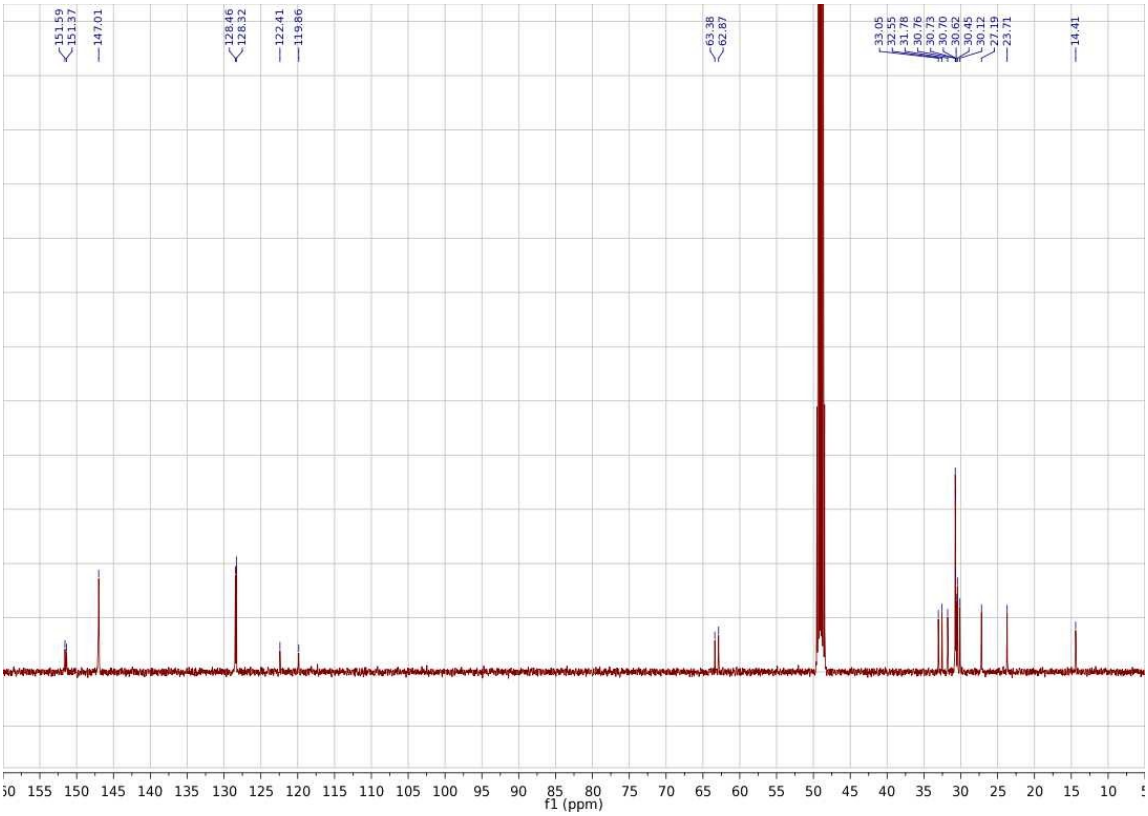


Fig S29: ^{13}C NMR (MeOD, 126 MHz) of [16BP5BP16](Tf$_2$N)$_4$

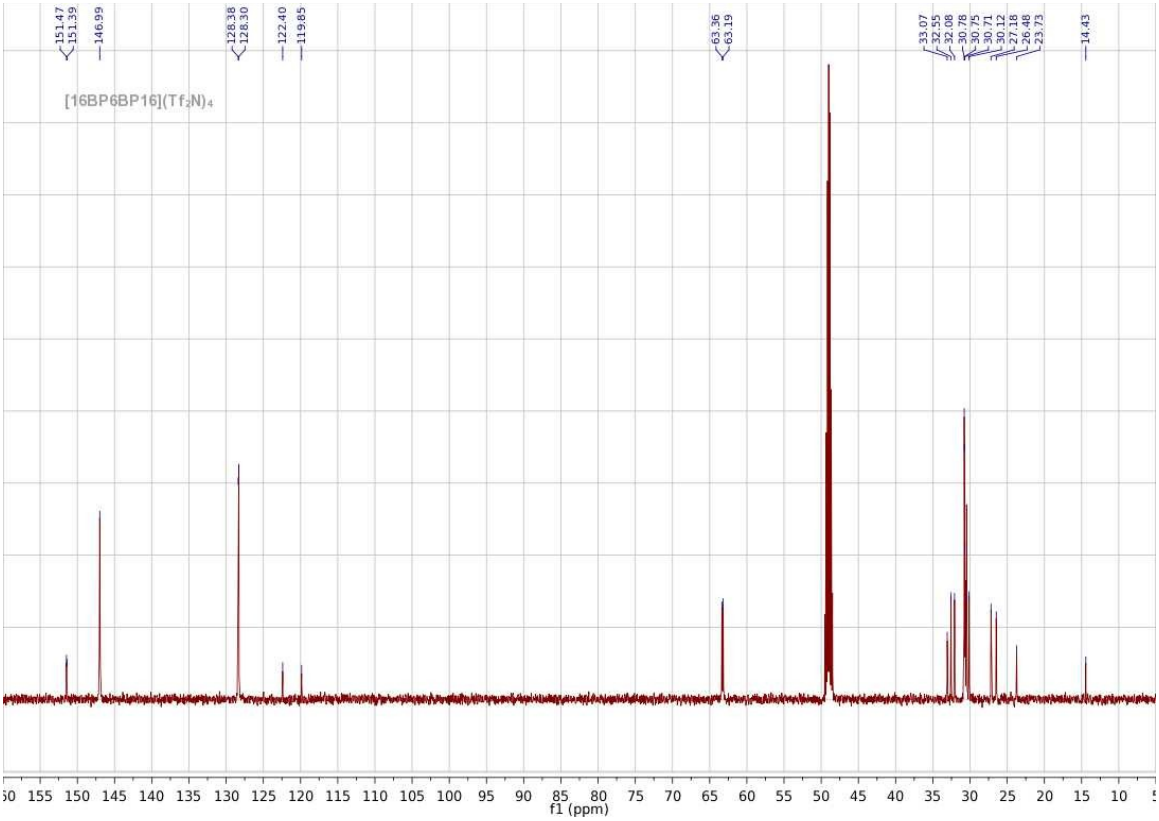


Fig S30: ^{13}C NMR (MeOD, 126 MHz) of [16BP6BP16](Tf$_2$N)$_4$

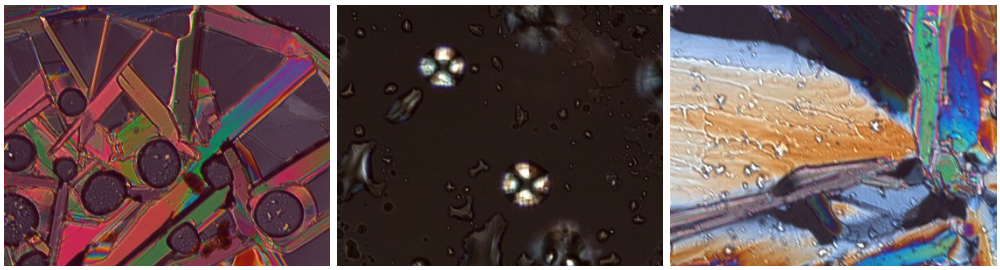


Fig S31:Textures of the SmX phase on cooling from the melt of: a) 8.8.8 at 145 °C; b) 10.4.10 at 130 °C; 12.6.12 at 170 °C observed under crossed-polarizers.

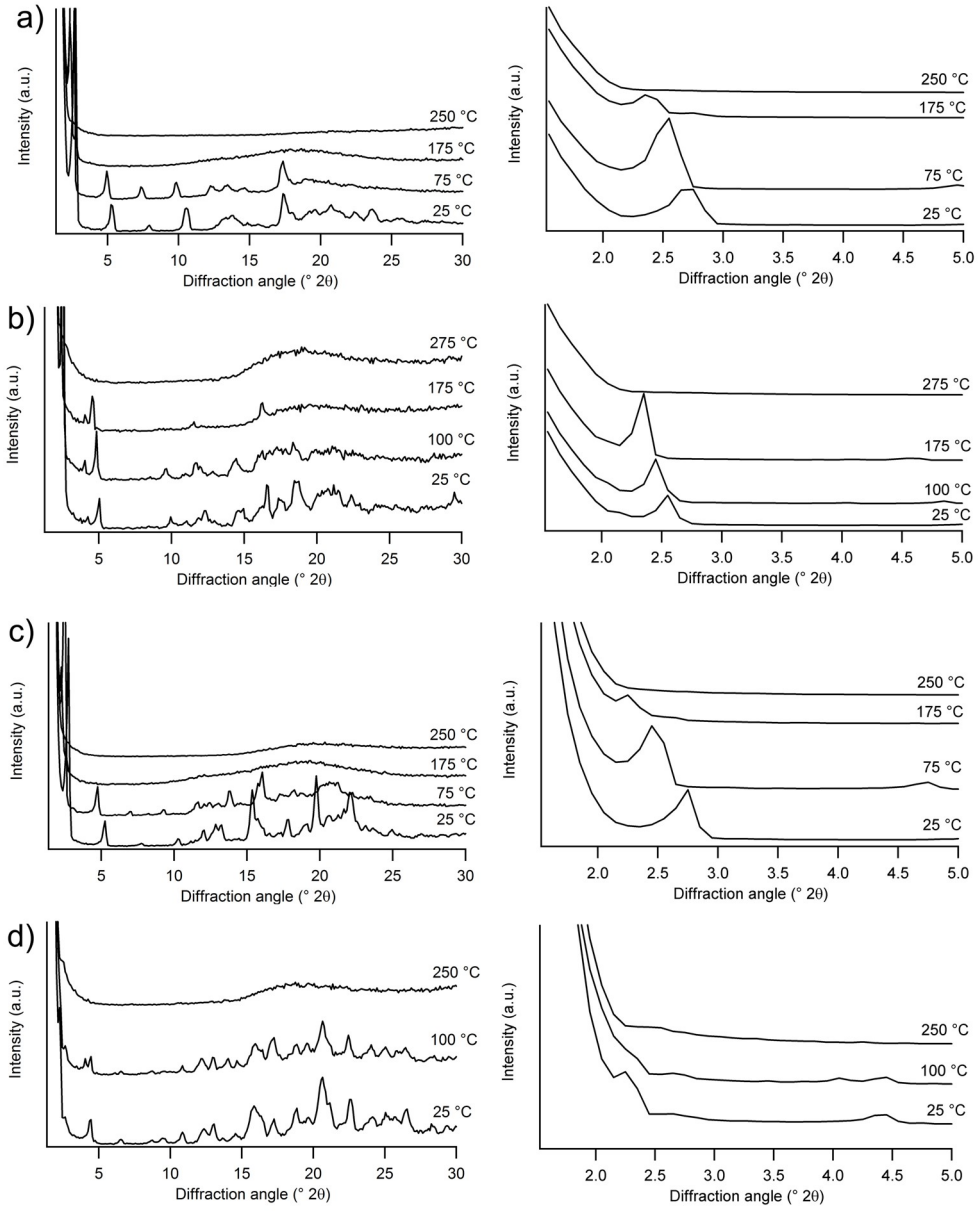


Figure S32: (Left panels) XRD patterns of samples a) 16.3.16, b) 16.4.16 c) 16.5.16 d) 16.6.16, acquired at the indicated temperatures.

(Right panels) Zoom of the low-angle region of the XRD patterns of samples a) 16.3.16, b) 16.4.16 c) 16.5.16 d) 16.6.16, acquired at the indicated temperatures. Note that the y scale hase been arbitrarily rescaled to fit the trace.

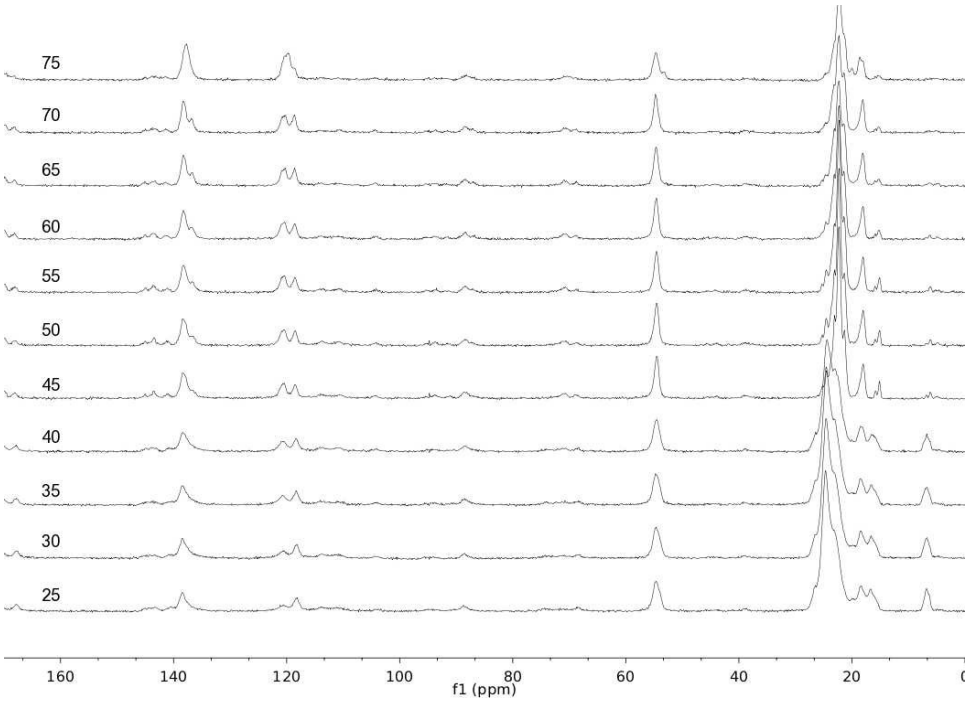


Fig S33: ^{13}C variable temperature (°C) MAS NMR (100 MHz, 5 kHz MAS) of [16BP4BP16](Tf$_2$N)$_4$

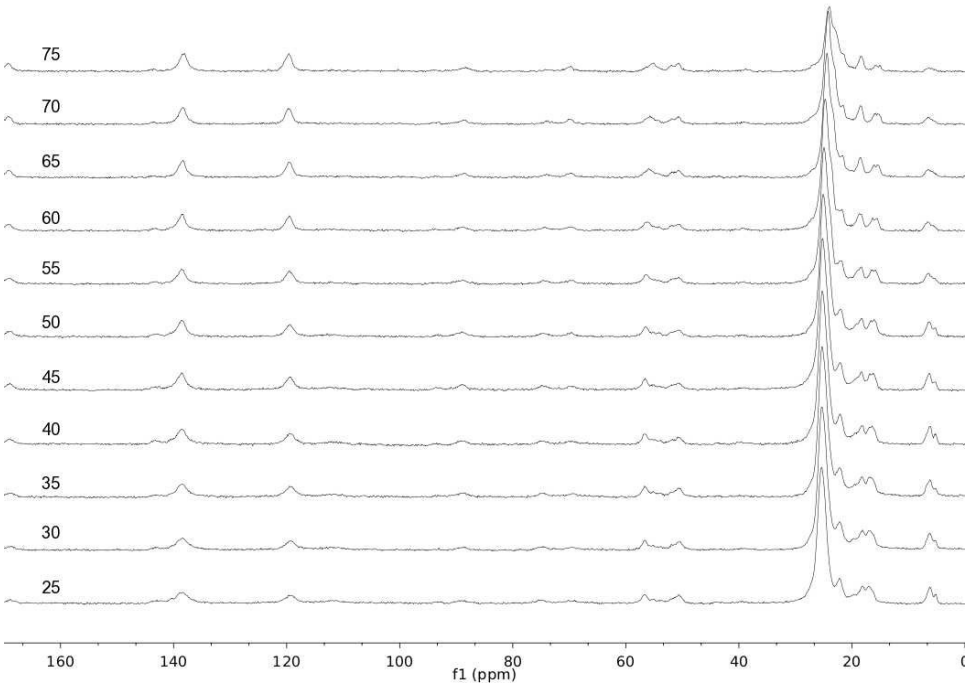


Fig S34: ^{13}C variable temperature (°C) MAS NMR (100 MHz, 5 kHz MAS) of [16BP3BP16](Tf$_2$N)$_4$

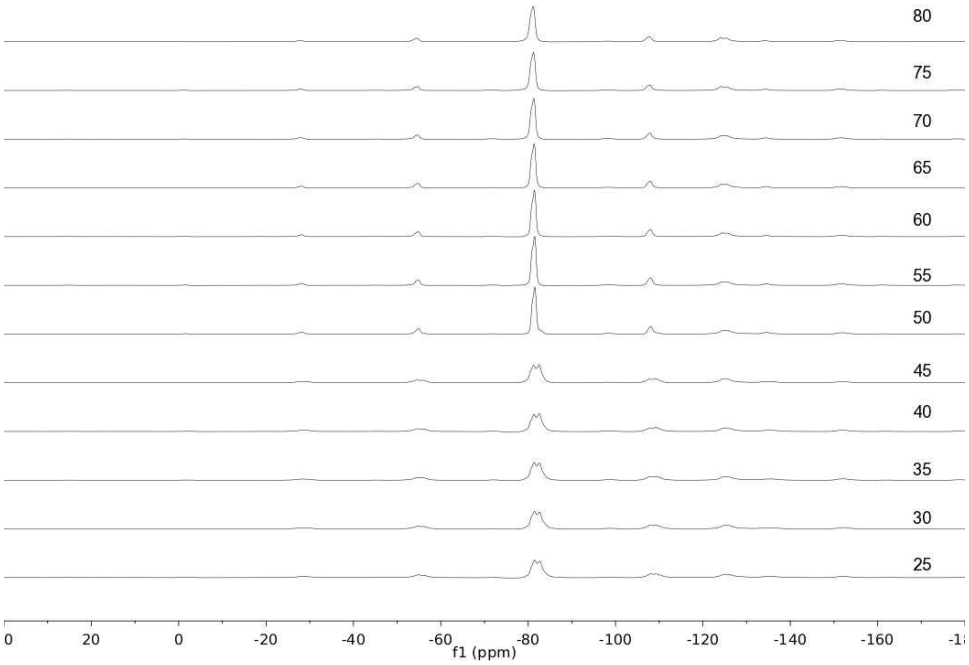


Fig S35: ^{19}F variable temperature (°C) MAS NMR (376 MHz, 10 kHz MAS) of [16BP6BP16](Tf$_2$N)$_4$

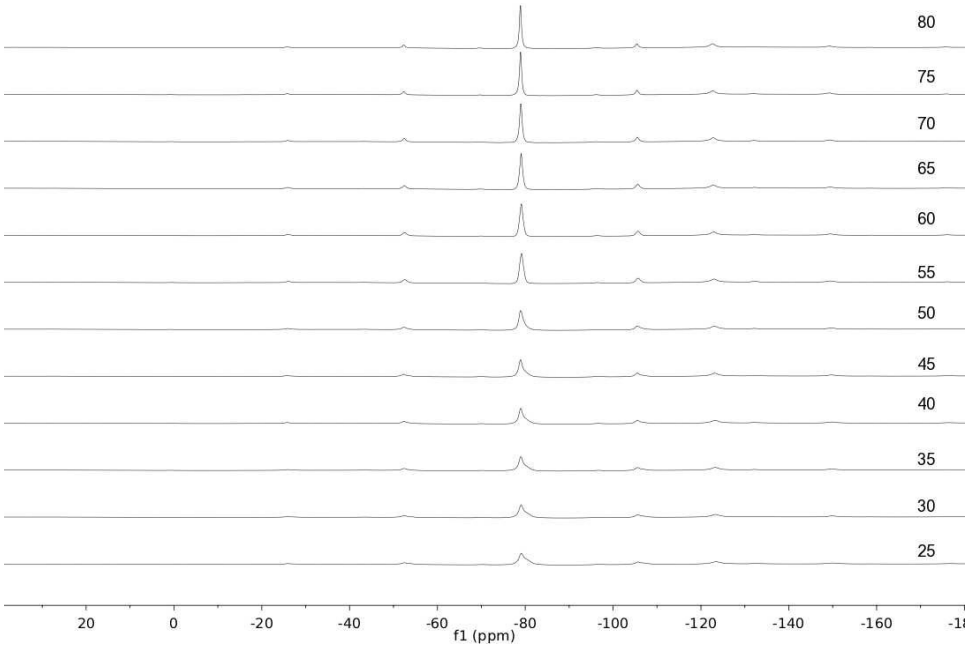


Fig S36: ^{19}F variable temperature (°C) MAS NMR (376 MHz, 10 kHz MAS) of [16BP5BP16](Tf$_2$N)$_4$

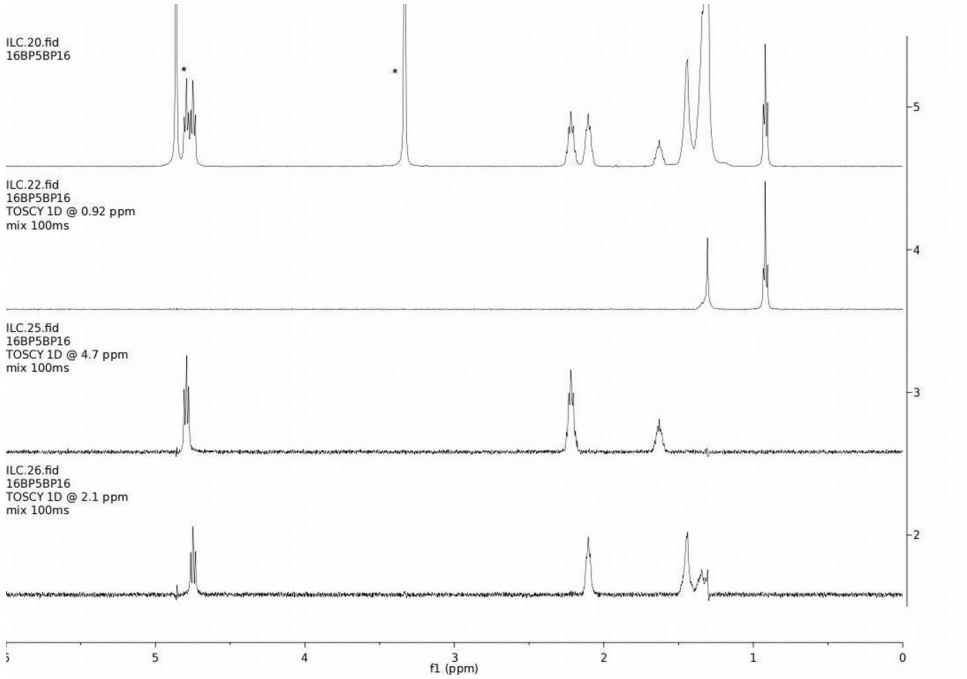


Fig S37: TOCSY (500.13 MHz) of [16BP5BP16](Tf$_2$N)$_4$.

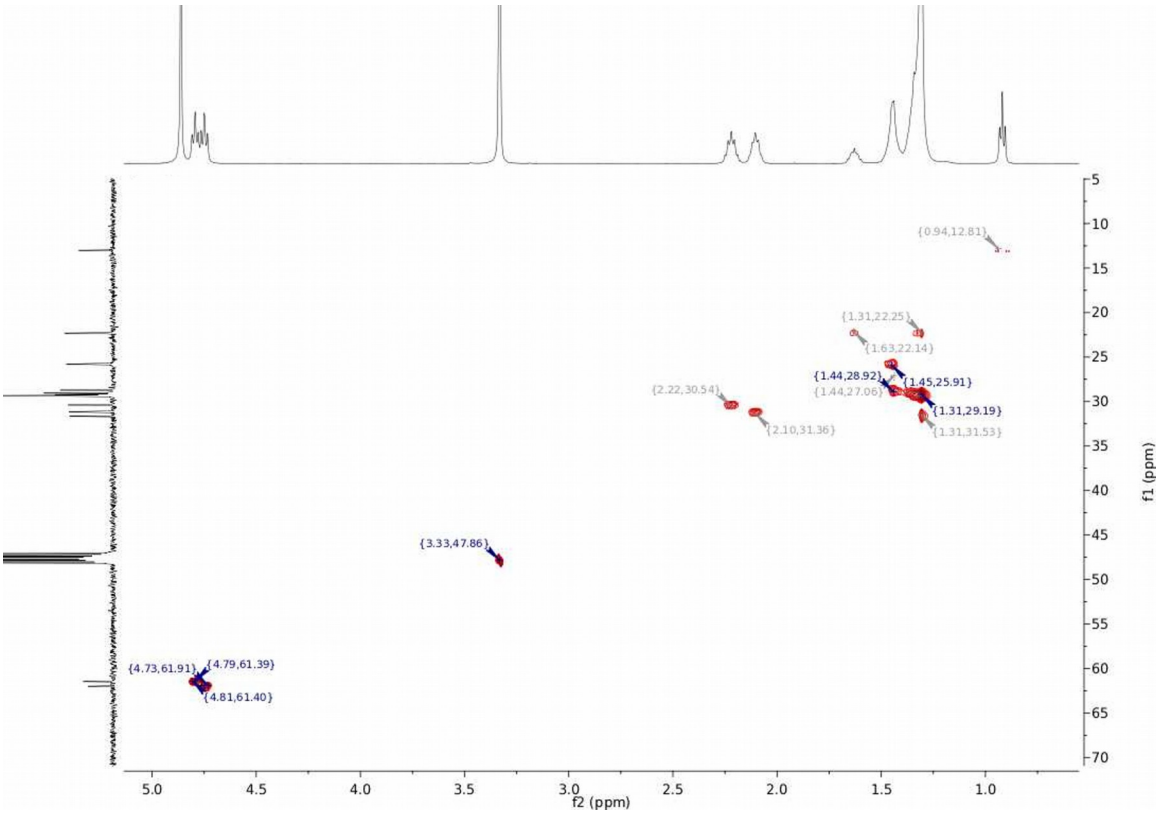


Fig S38:^{1}H-^{13}C HSQC (500.13; 125.77 MHz) of [16BP5BP16](Tf$_2$N)$_4$.