

Electronic Supporting Information

Phys. Chem. Chem. Phys.

Thermal behaviour and electrochemical properties of bis(trifluoromethanesulfonyl)amide and dodecatungstosilicate viologen dimers

**Marcella Bonchio,^a Mauro Carraro,^b Girolamo Casella,^b Valerio Causin,^b Federico Rastrelli,^b and
Giacomo Saielli^{a*}**

TGA traces

DSC traces of mixtures.

IR spectra

¹³C CP-MAS spectra (aliphatic region) of 8BP8(Tf₂N)₂, 7BP10(Tf₂N)₂ and (9BP9)₂SiW₁₂O₄₀

Synthetic details

¹H and ¹³C solution NMR spectra of bistriflimide dimers 2BPnBP2(Tf₂N)₄.

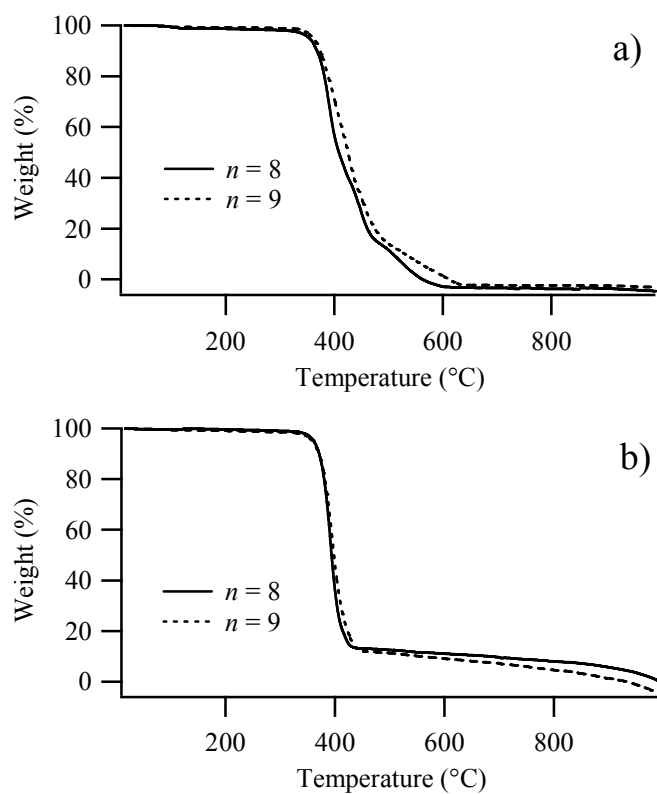


Figure 1. Thermogravimetric curve of the dimers with $n = 8$ and 9 , in a) air and b) nitrogen atmosphere.

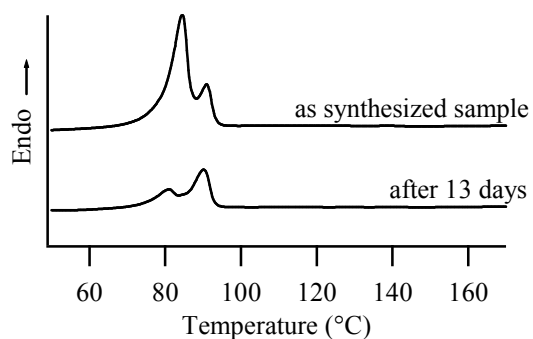


Figure 2. DSC traces of the first heating steps of the sample with $n = 9$, as synthesized and 13 days after melting. During the cooling ramp which followed the first melting no crystallization occurred and the subsequent heating DSC ramp was featureless.

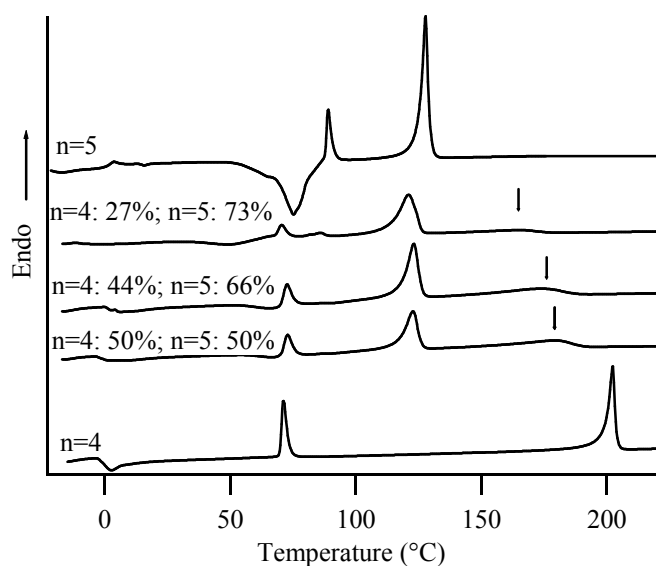


Figure 3. DSC traces of the second heating step of dimers with $n = 4$ and $n = 5$, and of mixtures of these two compounds. Arrows are added to show the shift and the intensity decrease of the second melting peak of the $n = 4$ dimer.

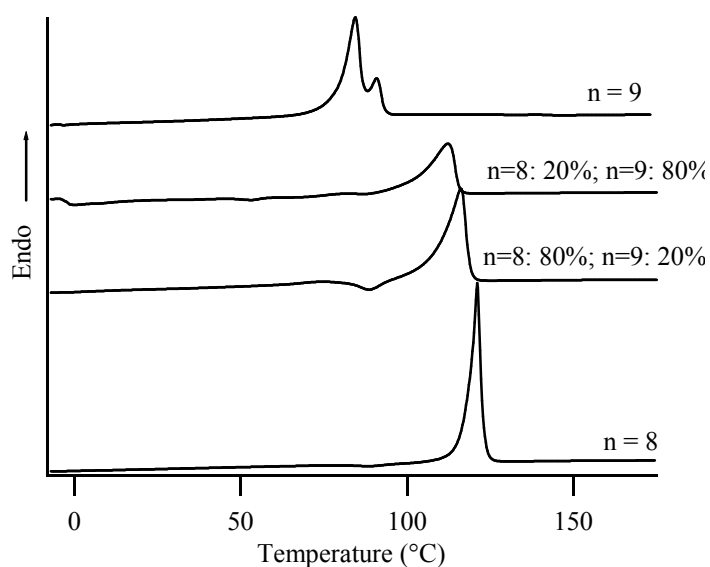


Figure 4. DSC traces of the second heating step of dimers with $n = 8$ and $n = 9$, and of mixtures of these two compounds.

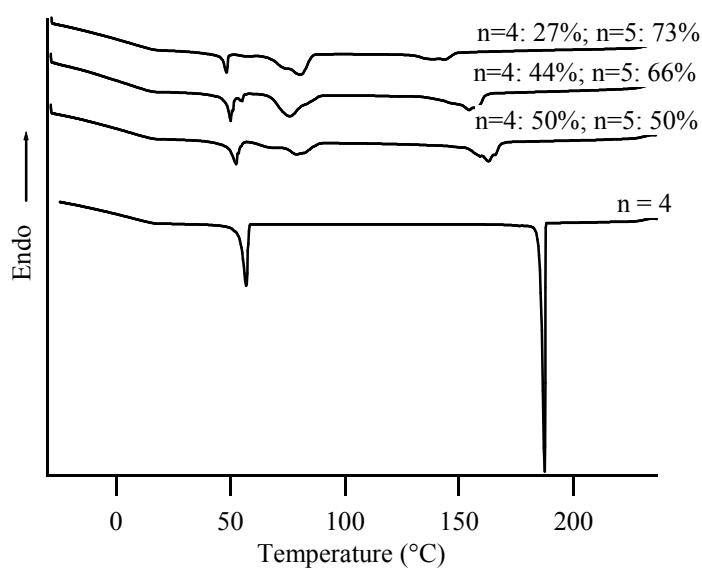


Figure 5. DSC traces of the first cooling step of dimers with $n = 4$ and $n = 5$, and of mixtures of these two compounds.

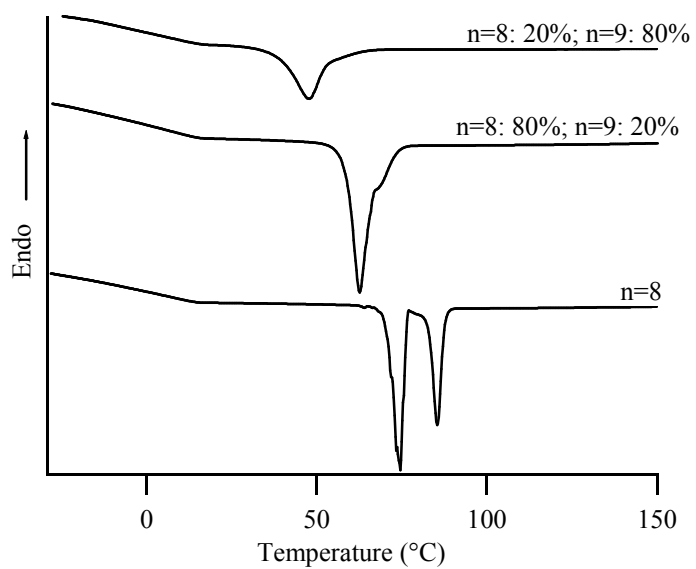


Figure 6. DSC traces of the first cooling step of dimers with $n = 8$ and $n = 9$, and of mixtures of these two compounds.

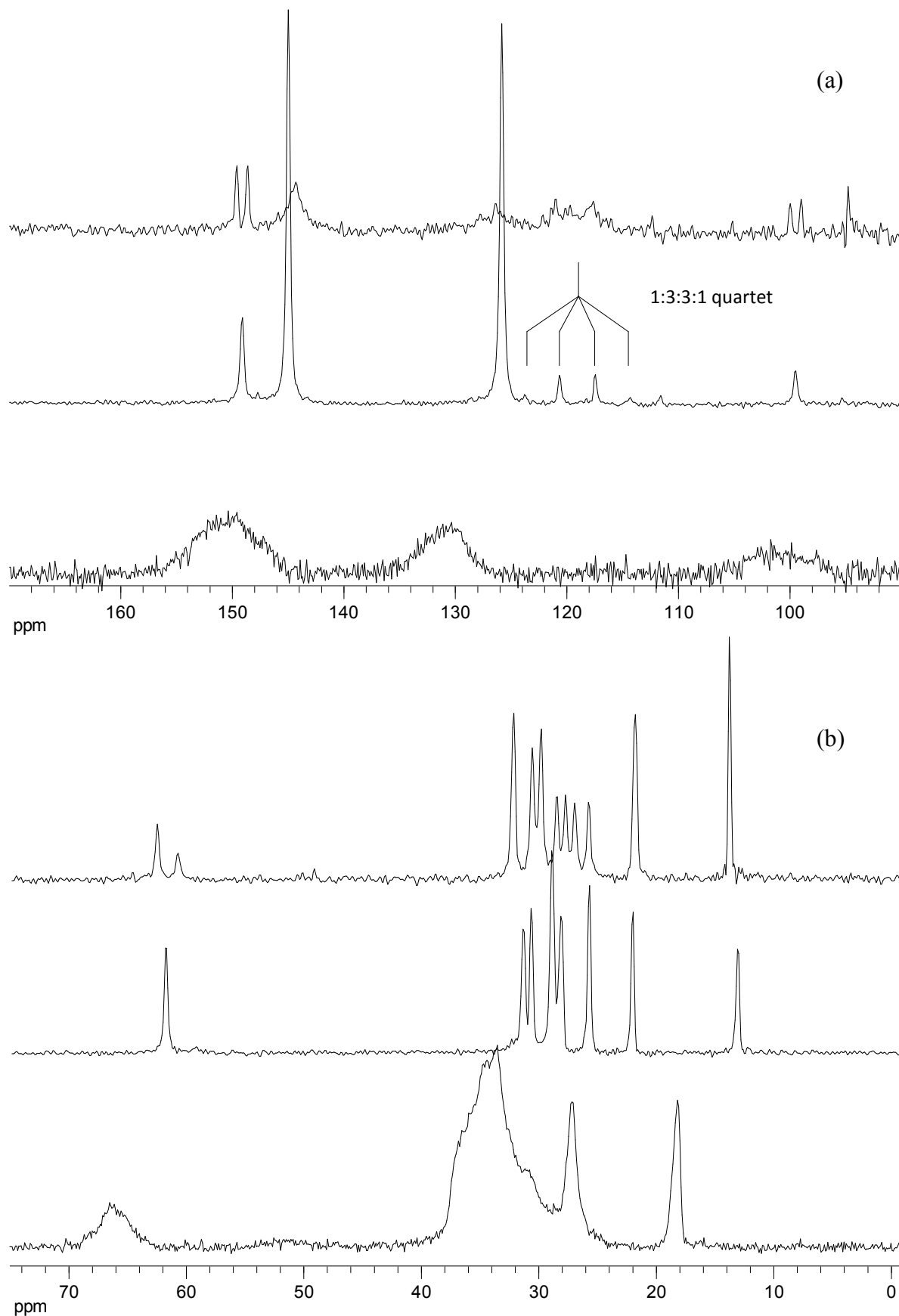


Figure 7. (a) Aromatic and (b) aliphatic region of the room temperature ^{13}C CP-MAS spectra (100 MHz, SR 5 kHz) of (top) $8\text{BP}8(\text{Tf}_2\text{N})_2$, (middle) $7\text{BP}10(\text{Tf}_2\text{N})_2$ and (bottom) $(9\text{BP}9)_2\text{SiW}_{12}\text{O}_{40}$. It is noteworthy that the top trace shows more resonances than the expected eight ones (one for each carbon of the octyl chain) due to the splitting of most of the signals in two, indicating two non-equivalent positions in the unit cell. The middle trace, in contrast, shows less resonances than the expected seventeen ones, in the aliphatic region, because of the overlap due to the larger width of the lines and the suppression of any solid-state splitting. Finally, the bottom trace shown a very large overlap of the resonances of the aliphatic carbons from C2 to C7; larger, though resolved resonance of the mobile final methylene and methyl of the alkyl chain and very large resonances of the $-\text{CH}_2-\text{N}(\text{bipy})$ at about 66 ppm and of the aromatic signals.

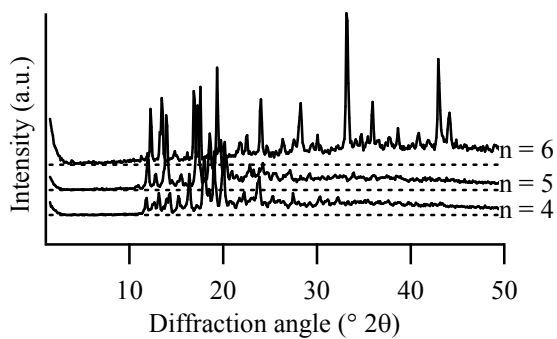


Fig. 8 WAXD traces of the dimers with $n = 4, 6$ and 7 . The dotted lines show horizontal baselines intended to show the presence of an amorphous halo due to the disordered distribution of the bistriflimide anion.

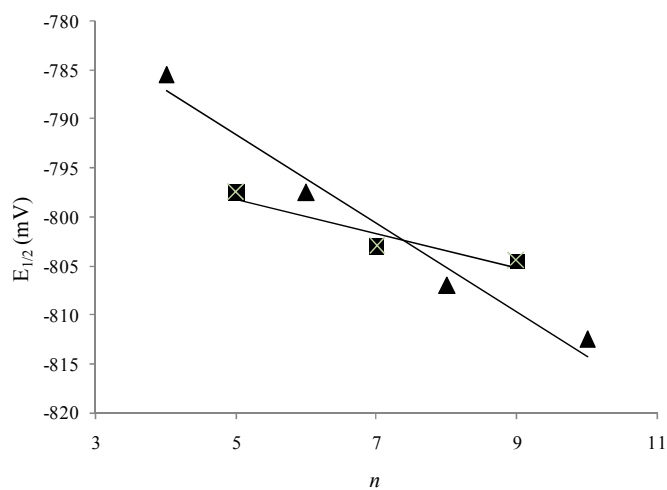
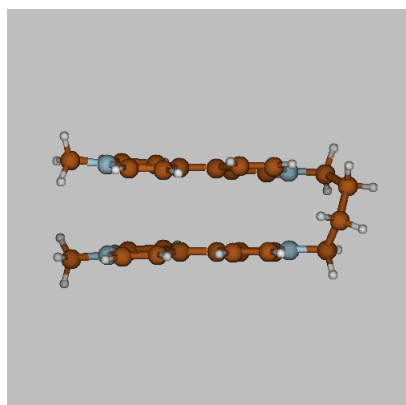
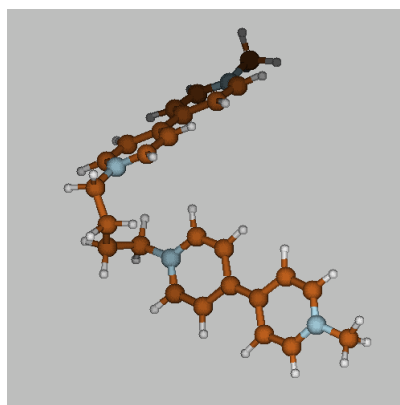


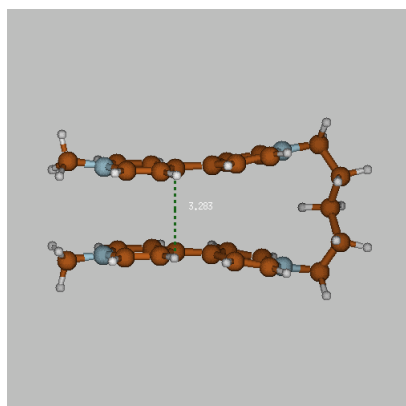
Figure 9. $E_{1/2}(1)$ values obtained from cyclic voltammetry (vs Ag/Ag^+) for the reduction of dimeric viologens, in DMF containing 0.1 M Bu_4NClO_4 .



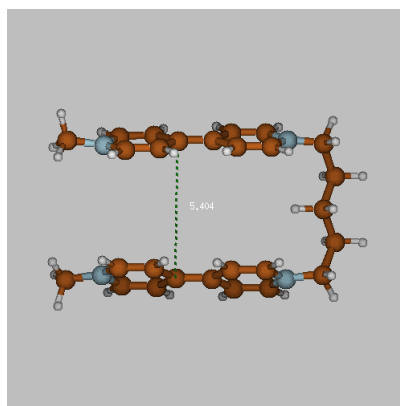
1BP4BP1 a)



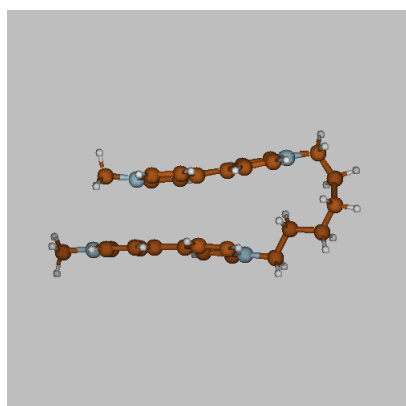
1BP4BP1 b)



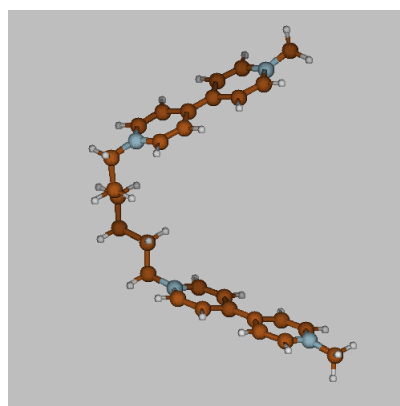
1BP5BP1 a)



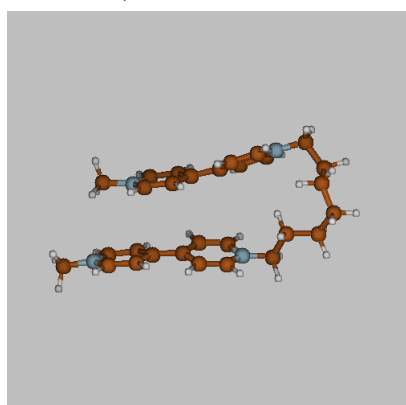
1BP5BP1 b)



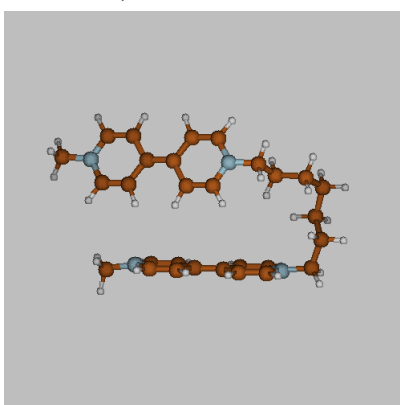
1BP6BP1 a)



1BP6BP1 b)



1BP7BP1 a)

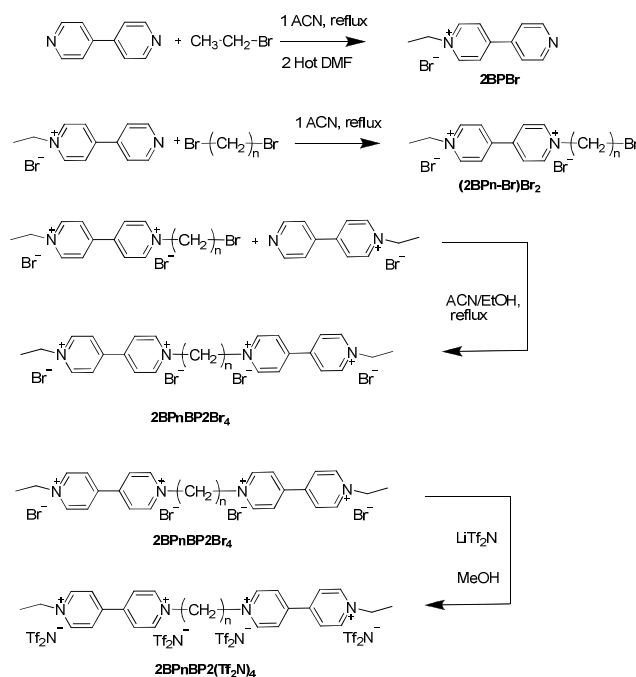


1BP7BP1 b)

Figure 10. Optimized structures (PBE0/6-31+G*, PCM, solvent=N,N-dimethylformamide; no imaginary frequencies found) of model system dimers (from top to bottom) 1BP4BP1, 1BP5BP1, 1BP6BP1 and 1BP7BP1. **a)** and **b)** are the singlet state with total charge +2, where formally each viologen unit is a radical cation, and the neutral, fully reduced species optimized starting from the corresponding optimized structure **a)**.

Synthesis

The synthetic protocol, see Scheme 1, consists in five main steps: *i*) the synthesis of the monoethylated bromide, **2BPBr**; *ii*) the synthesis of the monomeric unit, $(2BPn-Br)Br_2$; *iii*) the synthesis of the viologen dimer bromide, $2BPnBP2Br_4$; *iv*) the metathesis with lithium bistriflimide to give the final salt, $2BPnBP2(Tf_2N)_4$; *v*) a final metathesis with dodecatungstosilicic acid yields the dodecatungstosilicate salt. The various steps are summarized in Scheme 1. For selected samples, $n = 4, 5$ and 6 , an additional metathesis step with dodecatungstosilicic acid, $H_4SiW_{12}O_{40}$, in methanol was carried out.



Scheme 1. Synthesis of the bistriflimide viologen dimers. For $n = 4, 5$ and 6 an additional metathesis step with $H_4SiW_{12}O_{40}$ in MeOH affords the dodecatungstosilicic salt.

1-ethyl-4-(pyridin-4-yl)pyridinium bromide (**2BPBr**).

According to Ref. 1, 15 g of 4,4'-bipyridine (96 mmol) were dissolved in 150 mL of ACN; 7.5 mL of 1-bromoethane (100 mmol) were added and the solution was heated with an oil bath at 81 °C for 24 h. After cooling, the yellow precipitate was filtered and suspended in 300 mL of hot DMF. The mono-alkylated product dissolved in the DMF while the yellow, insoluble di-alkylated salt was separated by filtration. Ether was then added to the cooled solution to precipitate the white/pale yellow mono-alkylated salt. Yield 70%. Purity was checked by ^1H NMR revealing less than 0.5 % mol of dialkylated product (See Figure 11 in ESI). ^1H NMR (D_2O , 200 MHz): $\delta = 9.04$ (d, $J=7.2$ Hz, 2H); 8.83 (d, $J=1.7$ Hz, 2H); 8.45 (d, $J=6.6$ Hz, 2H); 7.96 (d, $J=1.7$ Hz, 2H); 4.76 (q, $J=7.51$ Hz, signal partially overlapped with HDO); 1.74 (t, $J=7.1$ Hz, 3H) ppm.

1',1''-(alkane-1,n-diyl)bis(1-ethyl-4,4'-bipyridinium) tetrabromide (alkane = butane to decane) **2BPnBP2Br₄**

500 mg of **2BPBr** were allowed to reflux in 40 mL of acetonitrile at 70 °C with the appropriate amount of α,ω -dibromo alkane ($\text{Br-(CH}_2\text{)}_n\text{-Br}$, with $n=4$ to 10, stoichiometric ratio 1:20) and after about 1 hour a yellow precipitate was formed; the system was left to react for 24 hours. The precipitate, **1-(n-bromoalkyl)-1'-ethyl-4,4'-bipyridinium bromide** (alkyl = $-\text{C}_4\text{H}_9$ to $\text{C}_{10}\text{H}_{21}$) [$(2BPn-Br)Br_2$], was filtered, washed with cold acetone and dried under *vacuum* in presence of P_4O_{10} with yield 85-95%. Furthermore, 300-500 mg of $(2BPn-Br)Br_2$ and an excess of **2BPBr** (stoichiometric ratio 1:5) were solubilised in 30 mL of ACN/EtOH (10:1) mixture and refluxed for 48 h. The yellow precipitate was filtered, washed with cold acetone and dried under *vacuum* in presence of P_4O_{10} . Yield 85-90%. **2BP4BP2Br₄**: ^1H NMR (D_2O , 200 MHz): δ 9.14 (sb, 8H); 8.60 (sb, 8H); 4.80 (partially overlapped with HDO); 2.26 (m, 4H); 1.70 (t, $J=7.3$ Hz, 6H) ppm. **2BP5BP2Br₄**: ^1H NMR (D_2O , 200 MHz): δ 9.13 (d, $J=6.7$ Hz, 8H); 8.55 (d, $J=6.6$ Hz, 8H); 4.77 (partially overlapped with HDO); 2.19 (m, 4H); 1.69 (t, $J=7.3$ Hz, 6H) 1.58 (m, 2H) ppm; **2BP6BP2Br₄**: ^1H

NMR (D₂O, 200 MHz): δ 9.17 (d, J = 6.8 Hz, 4H); δ 9.13 (d, J = 6.8 Hz, 4H); 8.57 (d, J = 6.6 Hz, 8H); 4.79 (overlapped with HDO); 2.16 (m, 4H); 1.73 (t, J = 7.31 Hz, 6H); 1.53 (m, 4H) ppm;
2BP7BP2Br₄: ¹H NMR (D₂O, 200 MHz): δ 9.11 (t, J=6.8 Hz, 8H); 8.54 (d, J = 6.6 Hz, 8H); 4.73 (partially overlapped with HDO); 2.09 (m, 4H); 1.70 (t, J = 7.3 Hz; 6) 1.45 (m, 6H) ppm;
2BP8BP2Br₄: ¹H NMR (D₂O, 200 MHz): δ 9.14 (d, J = 6.5 Hz, 2H); 9.11 (d, J=6.5 Hz, 2H); 4.76 (partially overlapped with HDO); 2.10 (tb, J = 6.2 Hz, 4H) 1.71 (t, J = 7.4 Hz, 6H) 1.40 (sb, 8H).;
2BP9BP2Br₄: ¹H NMR (D₂O, 200 MHz): δ 9.12 (t, J = 6.5 Hz, 8H); 8.53 (d, J = 6.5 Hz, 8H); 4.73 (partially overlapped with HDO); 2.07 (sb, 4H); 1.70 (t, J = 7.3 Hz, 6H) 1.37 (sb, 10H) ppm;
2BP10BP2Br₄: ¹H NMR (D₂O, 200 MHz): δ 9.12 (t, J = 6.5 Hz, 8H); 8.53 (d, J = 6.5 Hz, 8H); 4.73 (q, J = 7.3 Hz, partially overlapped with HDO); 2.08 (sb, 4H); 1.69 (t, J = 7.3 Hz, 6H); 1.32 (sb, 12H).

1',1''-(alkane-1,n-diyl)bis(1-ethyl-4,4'-bipyridinium) tetra[bis(trifluoromethanesulfanyl)amide] (alkane = butane to decane) 2BPnBP2(Tf₂N)₄

500 mg of **2BPnBP2Br₄** and an excess of LiTf₂N were dissolved in 30 mL of methanol (stoichiometric ratio 1:5) and left to react for 3 h at room temperature. From the obtained solution, the methanol was removed by rotavapor and 20 mL of water were added. A white precipitate was formed which was filtered and washed several times with water until tests with a 0.5 N solution of AgNO₃ showed the absence of bromide. The product was then dried under *vacuum* in presence of P₄O₁₀.

2BP4BP2(Tf₂N)₄: ¹H NMR (MeOD, 300 MHz) δ 9.25 (d, J = 6.77 Hz, 4H) 9.19 (d, J = 6.77 Hz, 4H); 8.61 (d, J = 5.6 Hz, 8H); 4.77 (q, J = 7.37 Hz, signal partially overlapped with HDO); 2.25 (sb, 4H); 1.72 (t, J = 7.3 Hz, 6H) ppm. ¹³C NMR (MeOD, 75 MHz) δ 151.8; 151.3; 147.1; 146.9; 128.6; 128.3; 121.3 (q, ¹J(¹³C, ¹⁹F) = 321.1 Hz); 62.4; 58.8; 28.8; 16.6 ppm. ESI-MS: *m/z* = 1266 [M⁺], 493 [M²⁺], 235.3 [M³⁺].

2BP5BP2(Tf₂N)₄: ¹H NMR (MeOD, 200 MHz) δ 9.24 (d, J = 6.9 Hz, 4H); 9.20 (d, J = 6.9 Hz, 4H); 8.62 (b, 8H); 4.78 (q, J = 7.37 Hz, partially overlapped with HDO); 2.20 (m J = 7.6 Hz, 4H); 1.72 (t, J=7.3 Hz, 6H); 1.61 (m,2H) ppm. ¹³C NMR (MeOD, 100 MHz) δ 151.6; 151.4; 147.0; 146.8; 128.5; 128.4; 121.1 (q, ¹J(¹³C, ¹⁹F) = 321.1 Hz); 62.9; 58.8; 31.8; 23.7; 16.6 ppm. ESI-MS: *m/z* = 500 [M²⁺], 240 [M³⁺]. Elemental analysis, C₃₇H₃₆F₂₄N₈O₁₆S₈: found C 28.9 %, H 2.2% N 6.9% S 16.9% ; calcd C 28.5%, H 2.3 %, N 7.2%, S 16.4%.

2BP6BP2(Tf₂N)₄: ¹H NMR (MeOD, 400 MHz) δ 9.23 (d, J = 6.7 Hz , 4H); 9.19 (d, J = 6.7 Hz, 4H); 8.60 (d, J = 5.8 Hz, 8H); 4.75 (q, J = 7.3 Hz, 4H); 4.8 (q, J = 7.10 Hz, 4); 2.12 (sb, 4H); 1.71 (t, J = 7.3 Hz, 6H); 1.54 (sb, 4H) ppm. ¹³C NMR (MeOD, 100 MHz) δ 151.5; 151.4; 147.0; 146.8; 128.4; 128.3; 121.1 (q, ¹J(¹³C, ¹⁹F) = 321.1 Hz); 63.2; 58.8; 32.1; 26.5; 16.6 ppm. ESI-MS: *m/z* = 507 [M²⁺], 245 [M³⁺].

2BP7BP2(Tf₂N)₄: ¹H NMR (MeOD, 300 MHz) δ 9.24 (d, J = 6.7 Hz , 4H) 9.19 (d, J = 6.7 Hz, 4H) 8.60 (d, J = 5.9 Hz, 8H) 4.76 (t, J = 7.3 Hz) 4.73 (t, J = 7.2 HZ) 2.10 (sb, 4H); 1.72 (t, J = 7.3 Hz, 6); 1.49 (sb, 6H) ppm. ¹³C NMR (MeOD, 75 MHz) δ 147.0; 128.3; 63.3; 58.8; 32.2; 29.6; 26.8; 16.7 ppm. ESI-MS: *m/z* = 1308 [M⁺], 514 [M²⁺], 249.3 [M³⁺].

2BP8BP2(Tf₂N)₄: ¹H NMR (MeOD, 300 MHz) δ 9.23 (t, J = 5.4 Hz, 8H); 8.61 (d, J = 5.7 Hz, 8H); 4.77 (b); 4.73 (b); 2.10 (sb, 4H); 1.72 (tb, J = 7.1 Hz, 6H); 1.46 (sb, 8H) ppm. ¹³C NMR (MeOD, 75 MHz) δ 151.4; 147.0; 128.3; 121.2 (q, ¹J(¹³C, ¹⁹F) = 321.2 Hz); 63.3; 58.8; 32.4; 29.7; 26.9; 16.7 ppm. ESI-MS: *m/z* = 1322 [M⁺], 521 [M²⁺], 254 [M³⁺].

2BP9BP2(Tf₂N)₄: ¹H NMR (MeOD, 300 MHz) δ 9.21 (t, J = 7.0 Hz, 4H); 9.18 (t, J = 7.0 Hz, 4H); 8.58 (d, J = 6.7 Hz, 8H); 4.76 (t, J = 7.3 Hz); 4.71 (t, J = 7.4 Hz) 2.09 (sb, 4H); 1.72 (t, J = 7.1 Hz, 6H); 1.42 (sb, 10H) ppm. ¹³C NMR (MeOD, 75 MHz) δ 151.4; 147.0; 146.8; 128.33, 128.31; 121.2 (q, ¹J(¹³C, ¹⁹F) = 321.1 Hz); 63.4; 58.8; 32.3; 29.9; 29.8; 27.0; 16.6 ppm. ESI-MS: *m/z* = 1336 [M⁺], 528 [M²⁺], 258.7 [M³⁺].

2BP10BP2(Tf₂N)₄: ¹H NMR (MeOD, 200 MHz) δ 9.23 (d, J = 7.1 Hz, 4H); 9.20 (d, J = 7.1 Hz, 4H); 8.61 (d, J = 6.5 Hz, 8H); 4.76 (t, J = 7.2 Hz, 4H); 4.72 (t, J = 7.2 Hz, 4H); 2.08 (t, J = 7.3 Hz, 4H); 1.72 (t, J = 7.3 Hz, 6H); 1.40 (mb,12H) ppm. ¹³C NMR (MeOD, 75 MHz) δ 151.4; 147.0; 146.8; 128.33; 128.31; 121.2 (q, ¹J(¹³C, ¹⁹F) = 321.2 Hz); 63.4; 58.8; 32.5; 30.2; 30.0; 27.1; 16.7 ppm. ESI-MS: *m/z* = 1350 [M⁺], 535 [M²⁺], 263.7 [M³⁺].

bis(1,1'-nonyl-4,4'-bipyridinium) dodecatungstosilicate, (9BP9)₂SiW₁₂O₄₀

114 mg (0.20 mmol) of bis (1,1'-nonyl-4,4'-bipyridinium) dibromide and 300 mg of H₄SiO₄₀W₁₂ (0.10 mmol) were separately dissolved in 8 mL of MeOH. After the two solution were mixed, a white precipitate was suddenly formed. The white solid was filtered, washed several times with MeOH and dried under *vacuum* in presence of P₄O₁₀.

1',1''-(alkane-1,n-diyl)bis(1-ethyl-4,4'-bipyridinium) dodecatungstosilicate (alkane = butane to hexane) 2BPnBP2SiW₁₂O₄₀

250 mg of 2BPnBP2(Tf₂N)₄ [n=4-6], were dissolved in 8 mL MeOH. The solution was added with 8 mL of a solution containing the corresponding stoichiometric amount of H₄SiW₁₂O₄₀ (1:1). After the mixing, a white precipitate was suddenly formed for all the three viologen solutions. The white solid was filtered, washed several times with MeOH and dried under *vacuum* in presence of P₄O₁₀. The solid was insoluble in several solvents: benzene, toluene, chloroform, dichloromethane, acetone, acetonitrile, DMSO, water, thus preventing any characterization by standard spectroscopic techniques. Solid State NMR data are discussed in the Results and Discussion Section.

2BP5BP2SiW₁₂O₄₀: Elemental analysis, C₂₈H₃₄N₄SiW₁₂O₄₀: found C 10.3%, H 0.9%, N 1.8%; calcd C 10.2%, H 1.0%, N 1.7%.

1.M. F. Pepitone, G. G. Jernigan, J. S. Melinger, O. -. Kim *Org. Lett.*, 2007, **9**, 801-804.

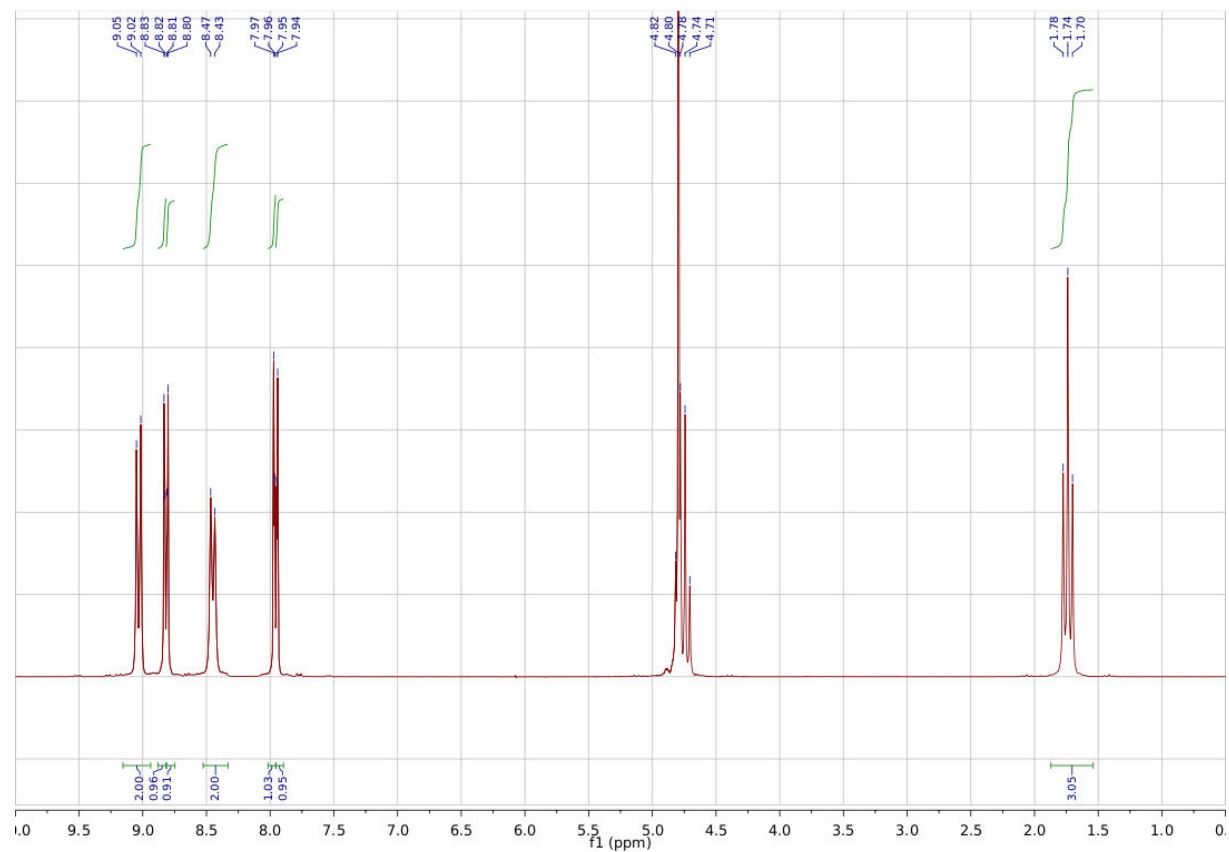


Figure 11. ^1H NMR spectrum of 2BPBr (200 MHz; D_2O).

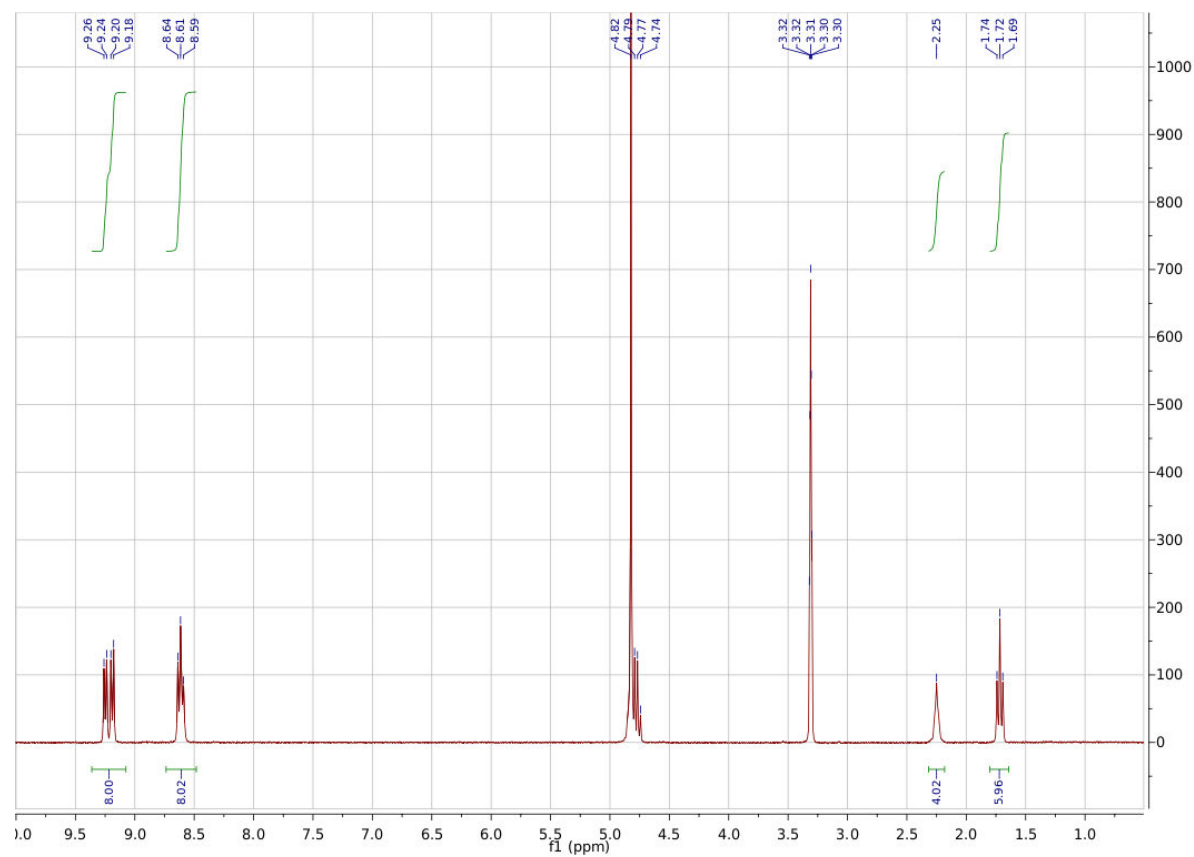


Figure 12. ^1H NMR spectrum of 2BP4BP2(Tf_2N) $_4$ (300 MHz; MeOD).

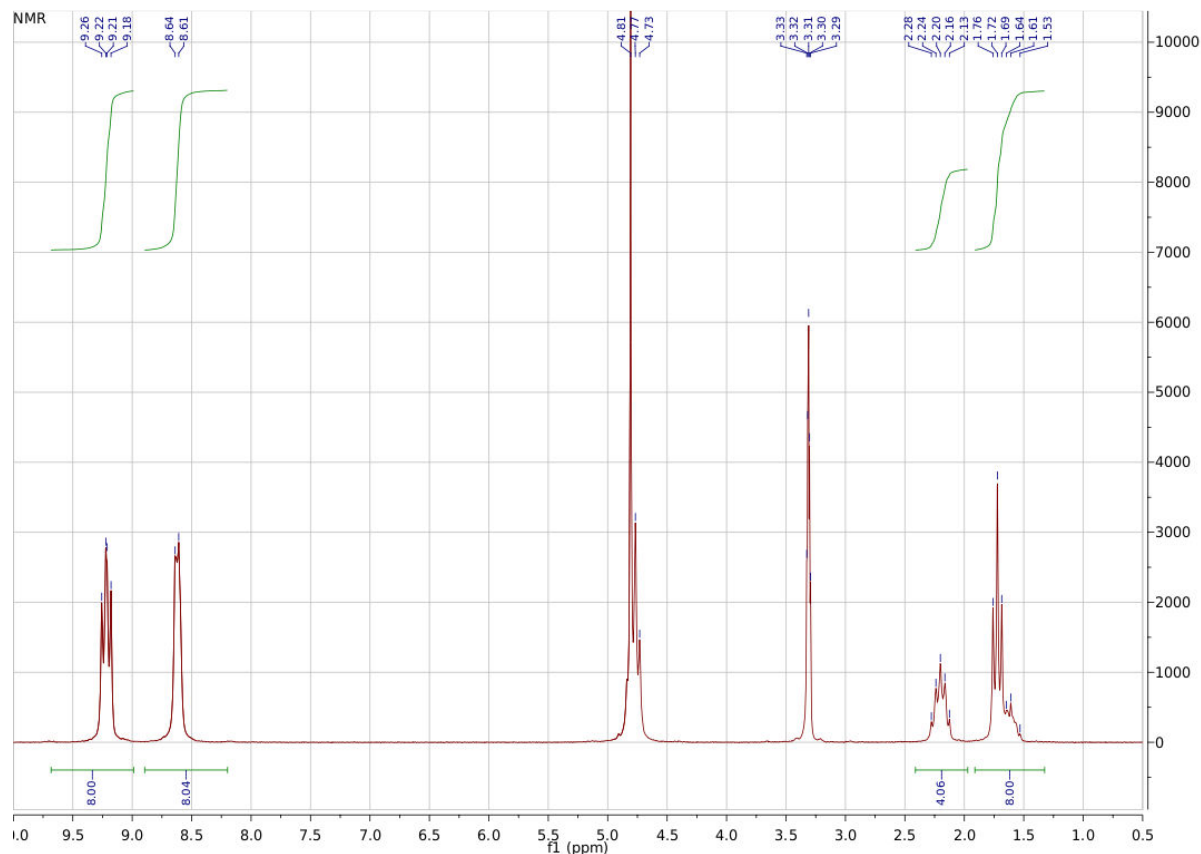


Figure 13. ^1H NMR spectrum of $2\text{BP}5\text{BP}2(\text{Tf}_2\text{N})_4$ (200 MHz; MeOD).

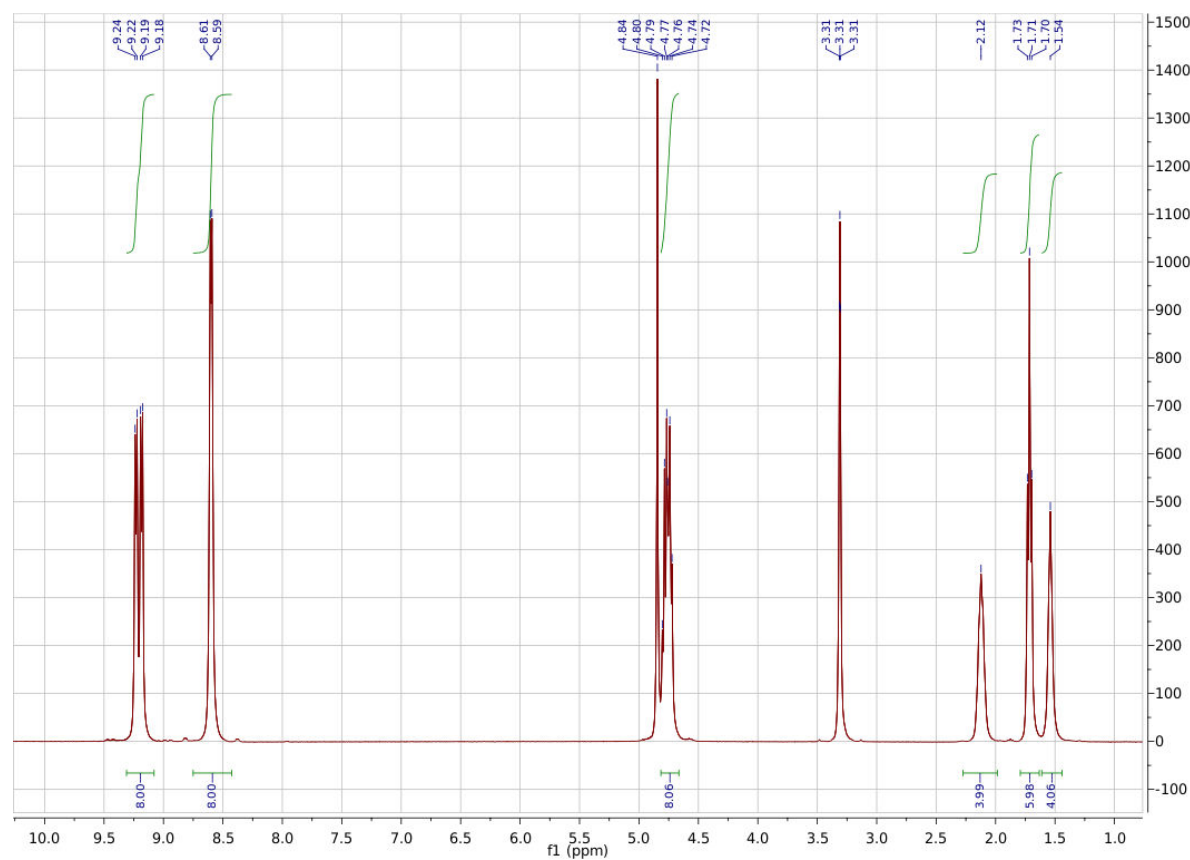


Figure 14. ^1H NMR spectrum of $2\text{BP}6\text{BP}2(\text{Tf}_2\text{N})_4$ (400 MHz; MeOD).

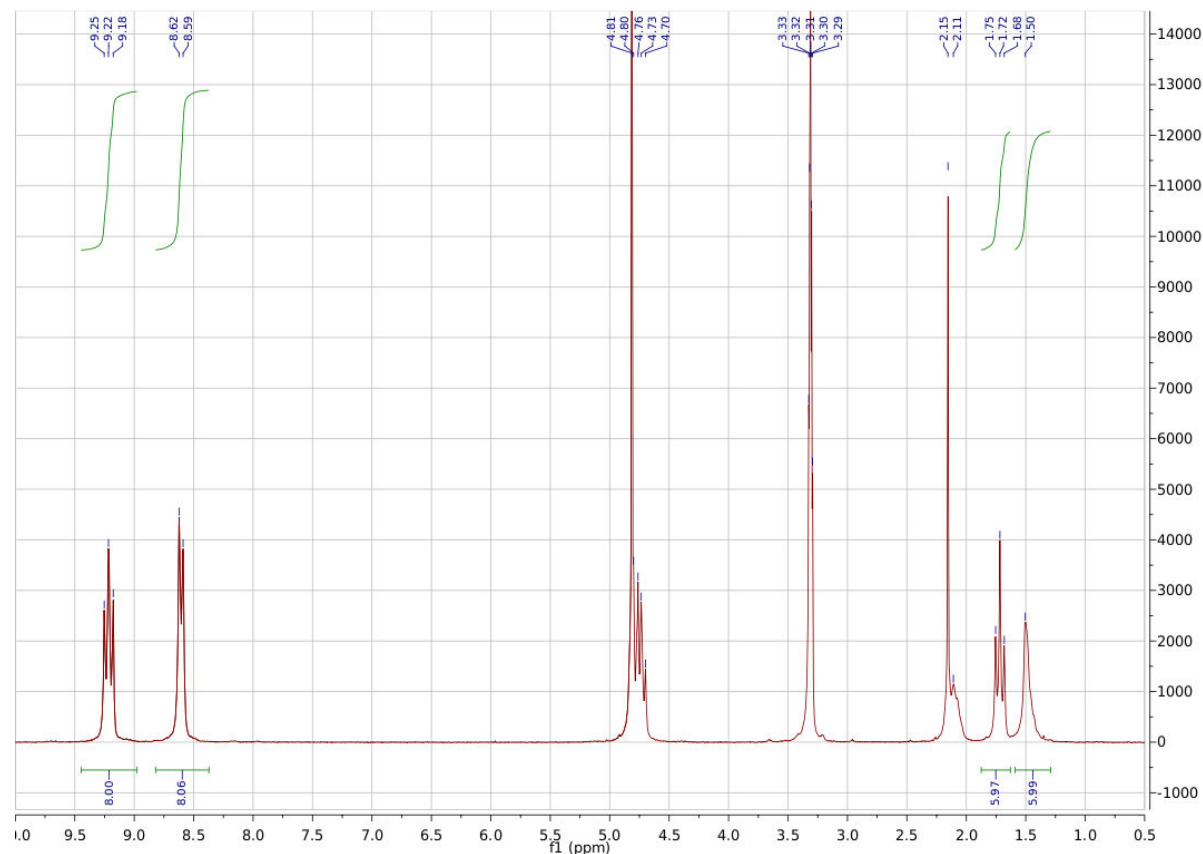


Figure 15. ^1H NMR spectrum of $2\text{BP}7\text{BP}2(\text{Tf}_2\text{N})_4$ (200 MHz; MeOD).

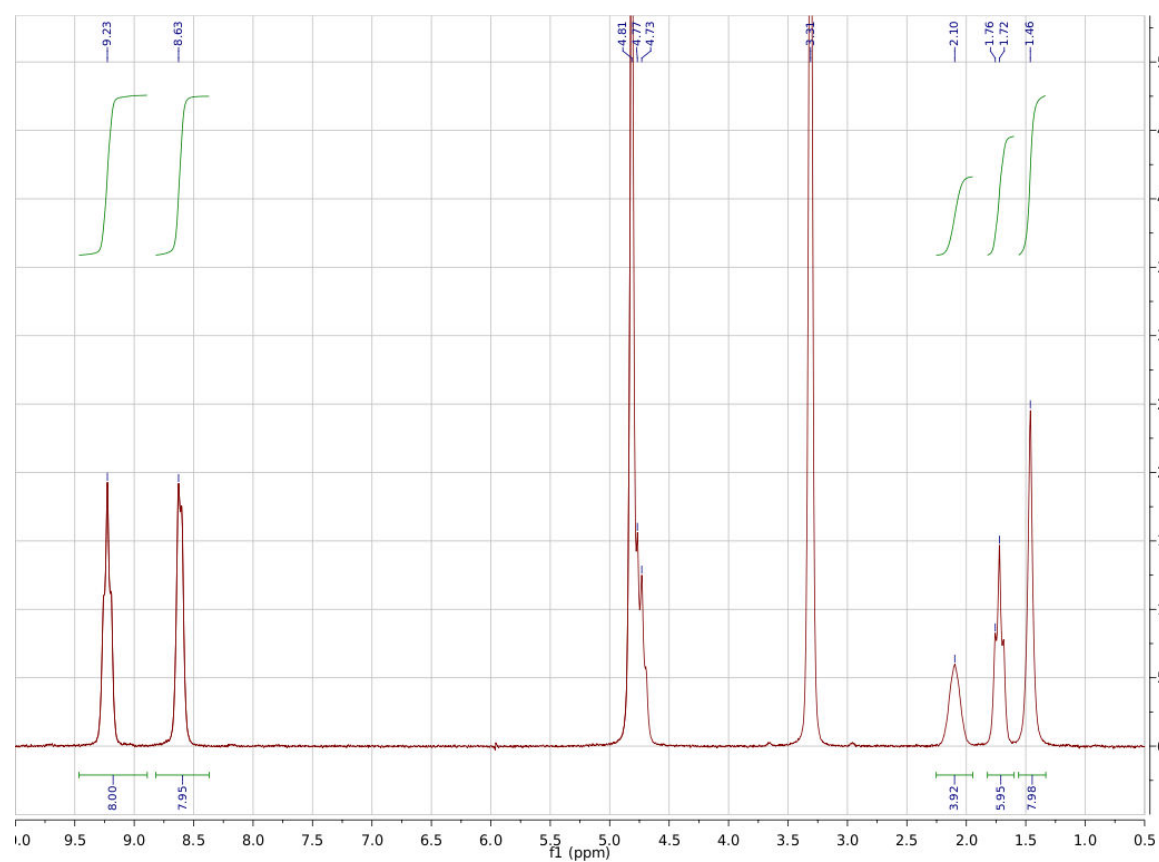


Figure 16. ^1H NMR spectrum of $2\text{BP}8\text{BP}2(\text{Tf}_2\text{N})_4$ (200 MHz; MeOD).

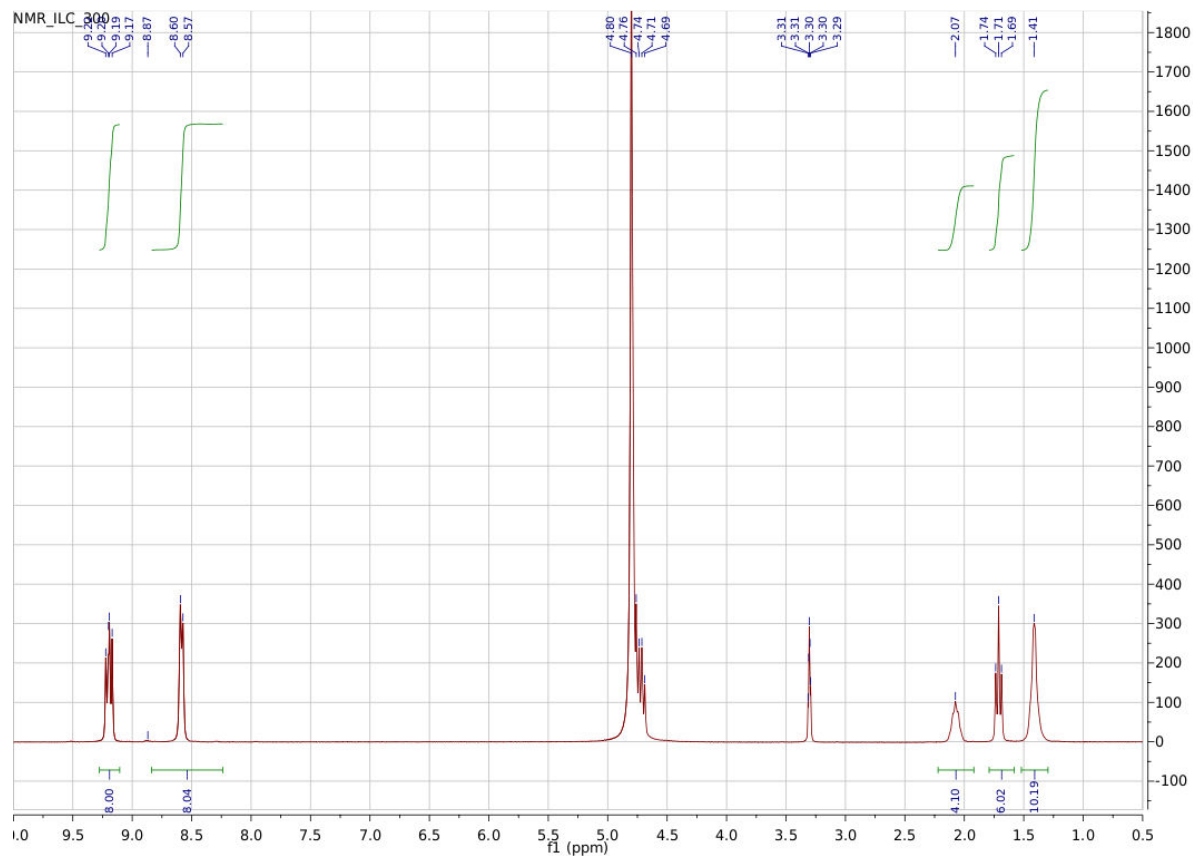


Figure 17. ^1H NMR spectrum of $2\text{BP}9\text{BP}2(\text{Tf}_2\text{N})_4$ (300 MHz; MeOD).

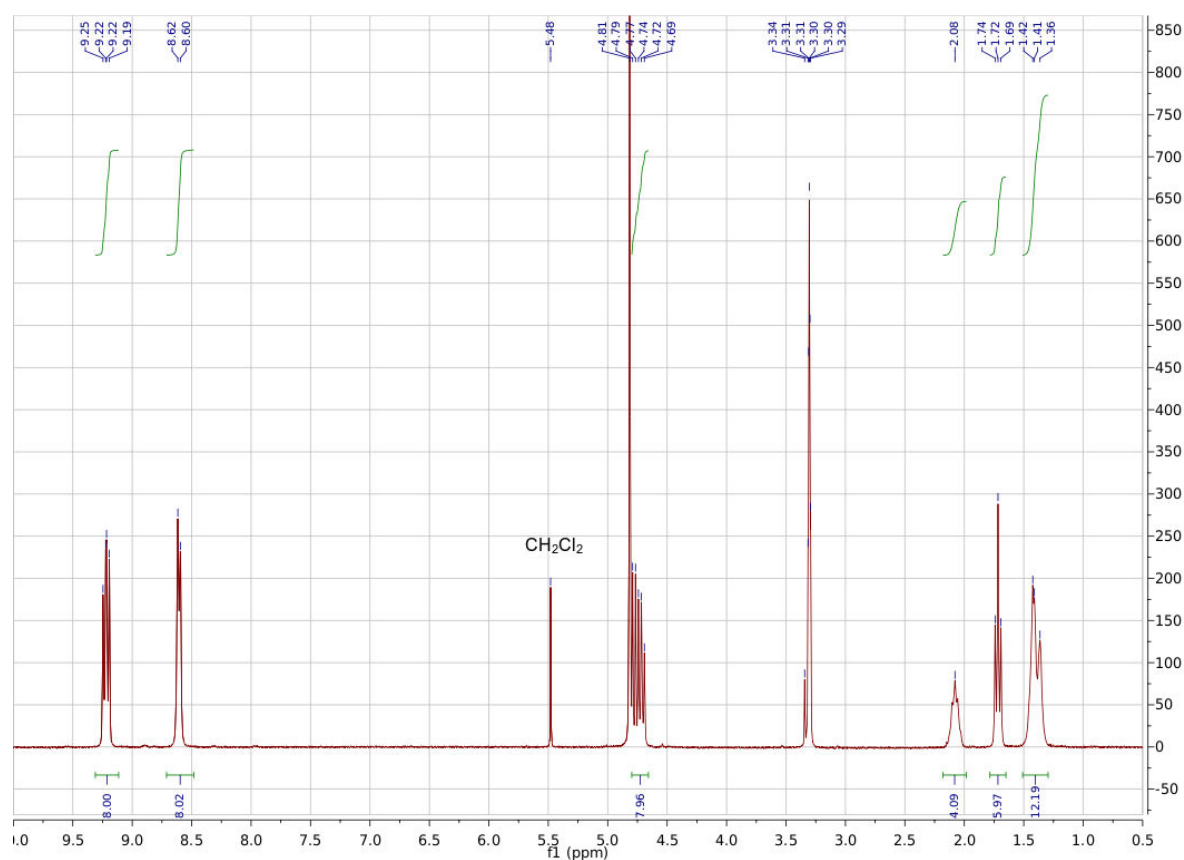


Figure 18. ^1H NMR spectrum of $2\text{BP}10\text{BP}2(\text{Tf}_2\text{N})_4$ (300 MHz; MeOD).

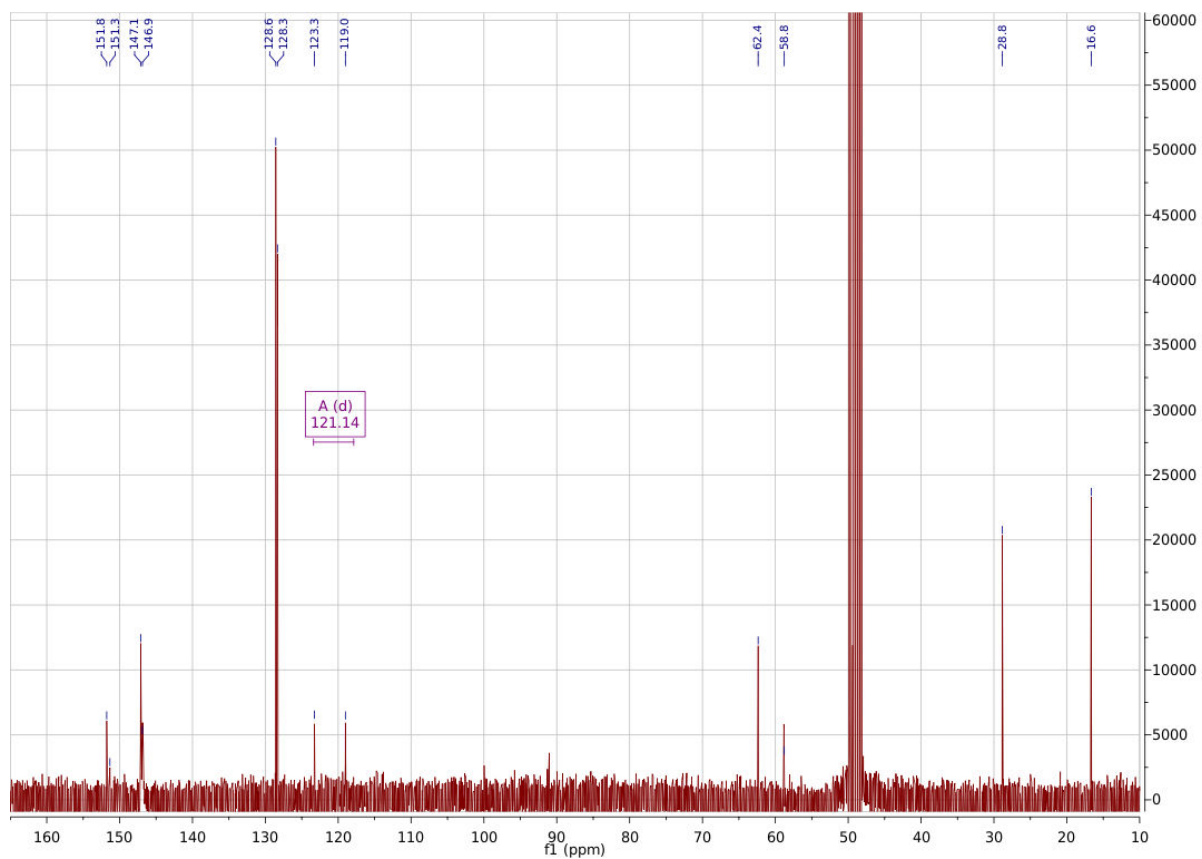


Figure 19. ^{13}C NMR spectrum of $2\text{BP4BP2}(\text{Tf}_2\text{N})_4$ (75 MHz; MeOD).

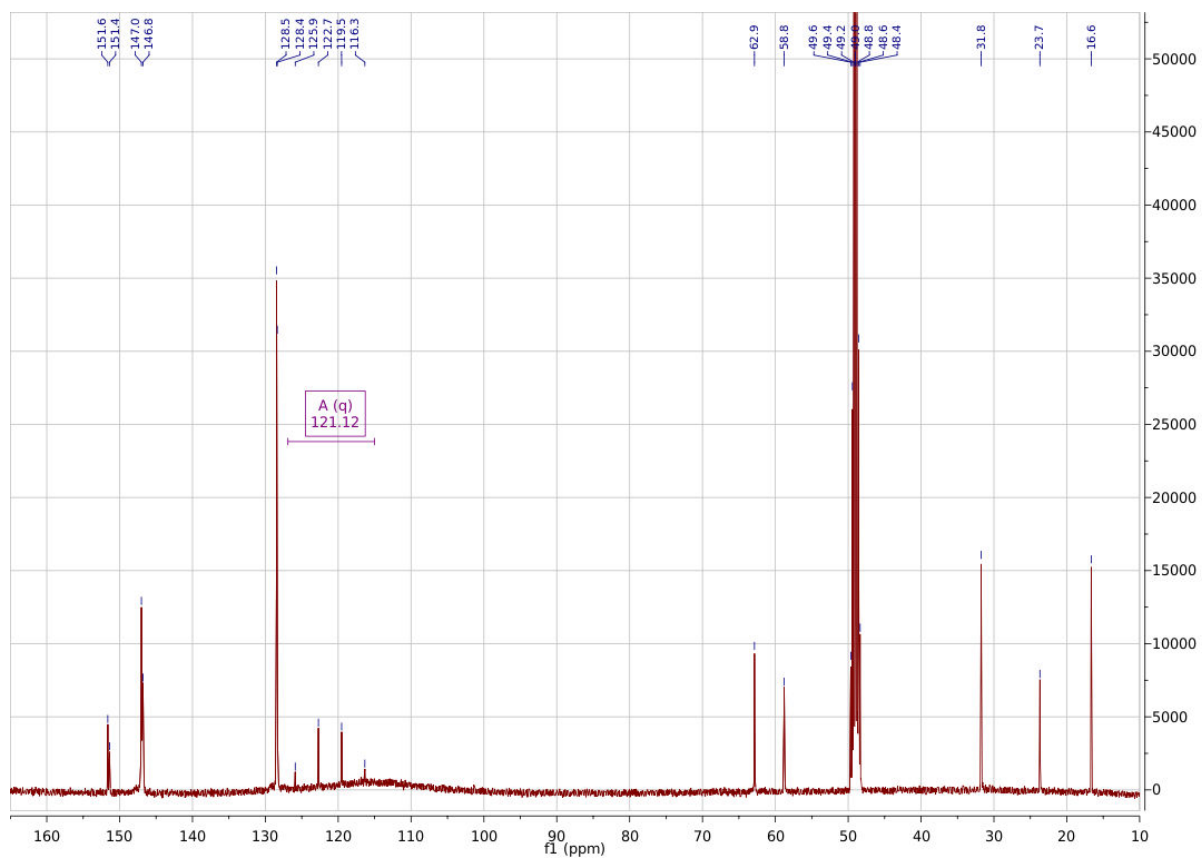


Figure 20. ^{13}C NMR spectrum of $2\text{BP5BP2}(\text{Tf}_2\text{N})_4$ (100 MHz; MeOD).

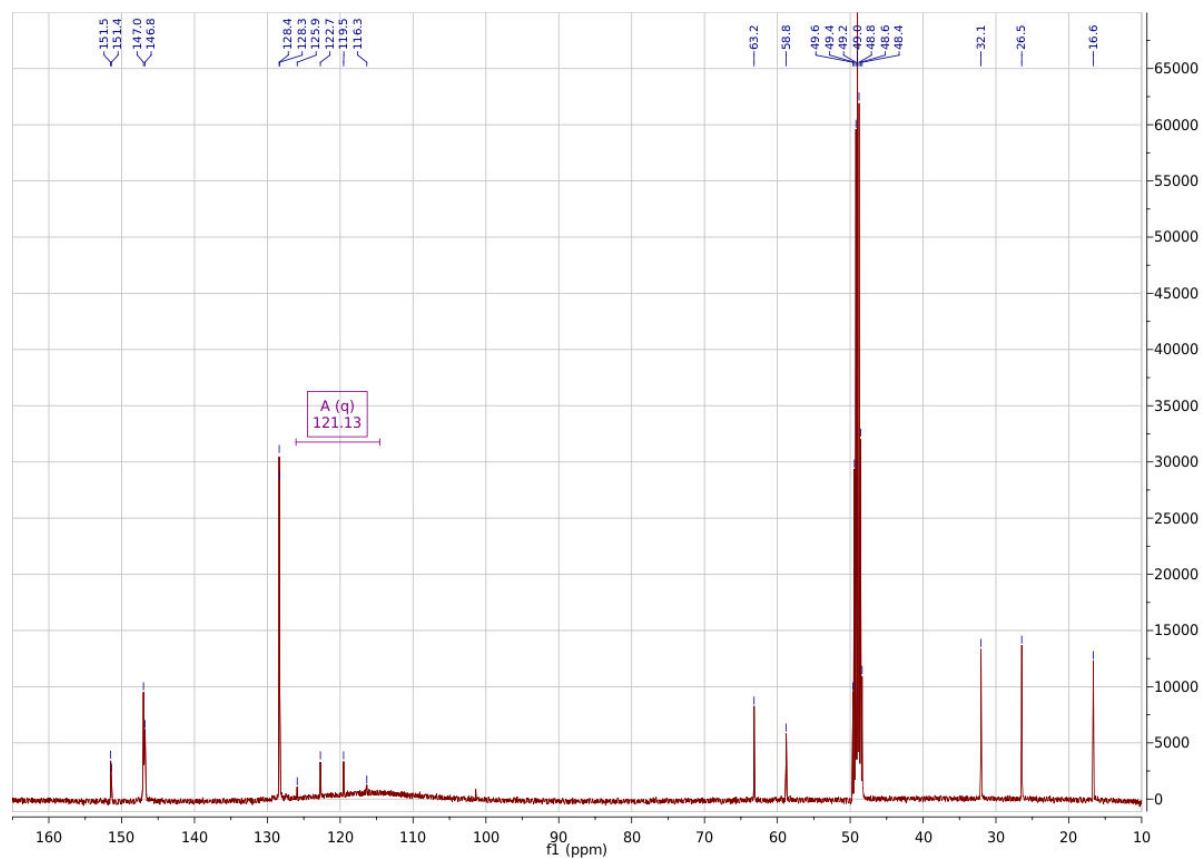


Figure 21. ^{13}C NMR spectrum of 2BP6BP2(Tf₂N)₄ (100 MHz; MeOD).

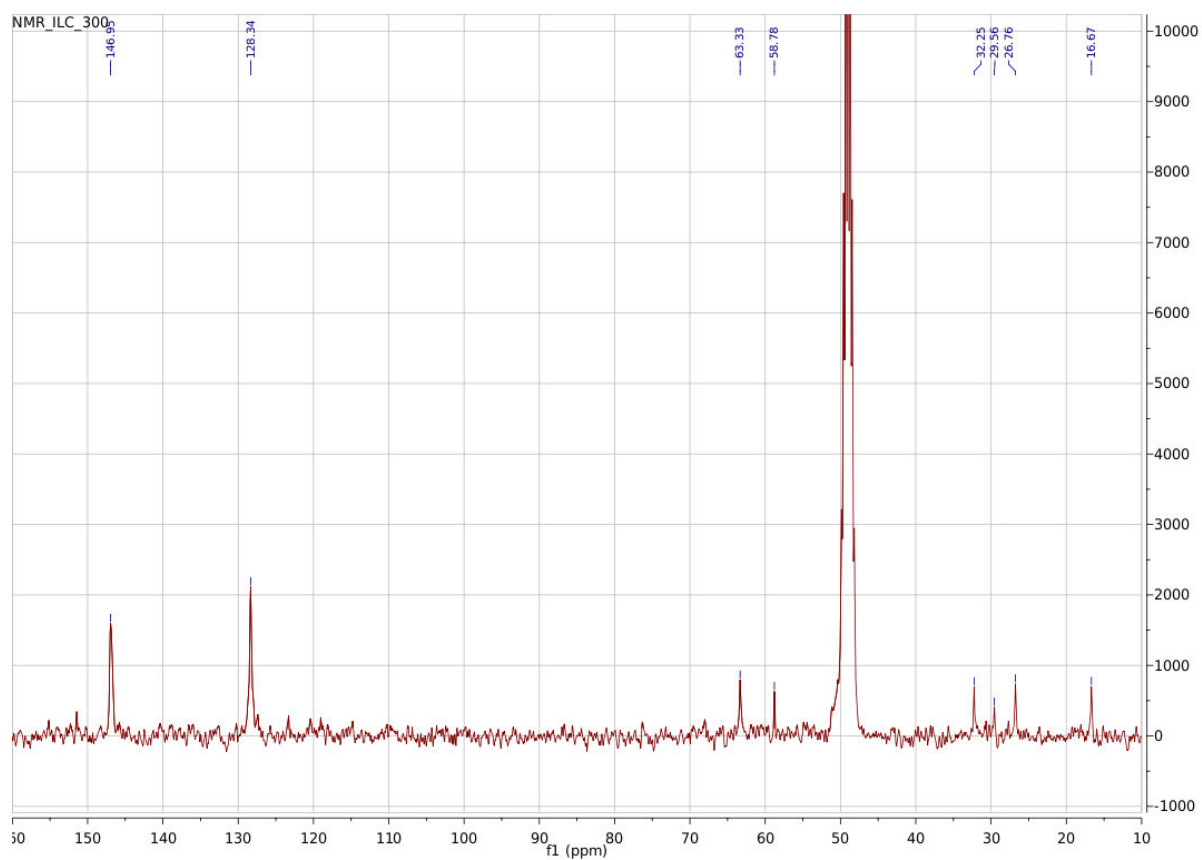


Figure 22. ^{13}C NMR spectrum of 2BP7BP2(Tf₂N)₄ (75 MHz; MeOD).

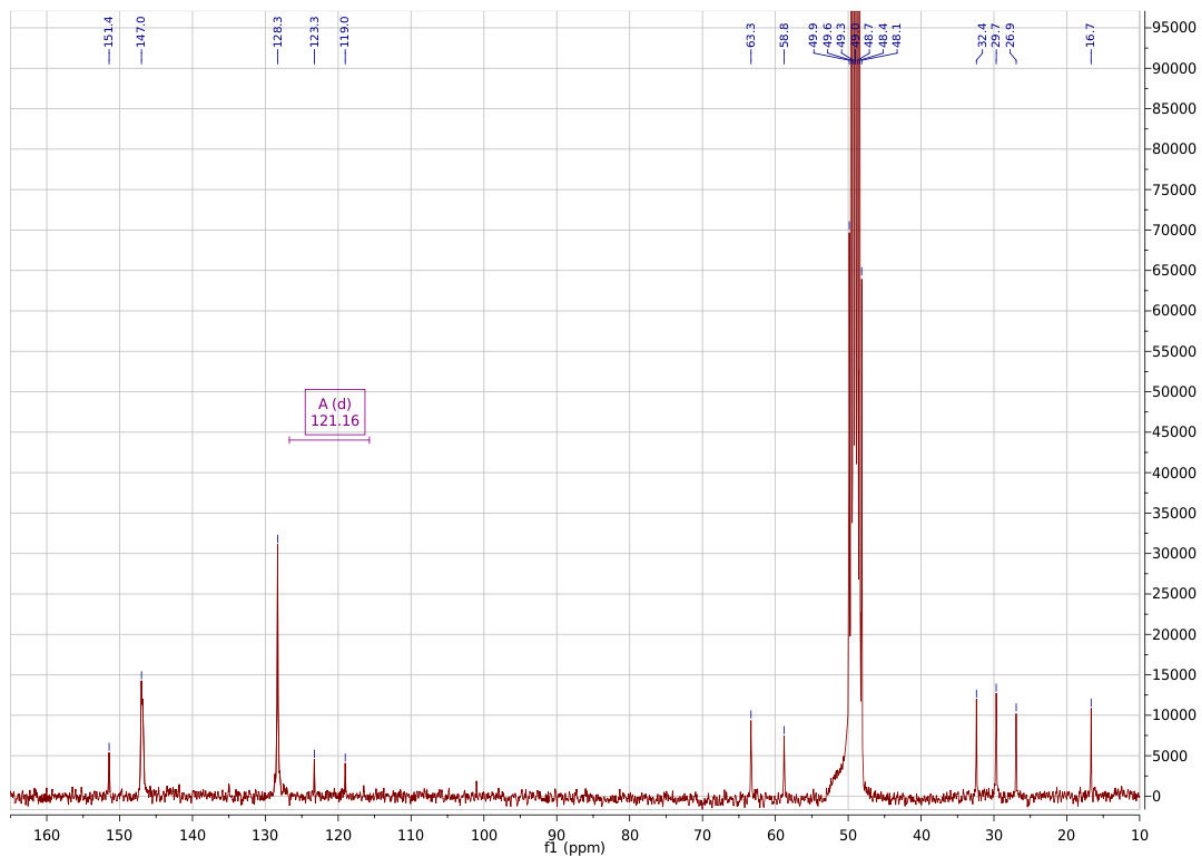


Figure 23. ^{13}C NMR spectrum of 2BP8BP2(Tf₂N)₄ (75 MHz; MeOD).

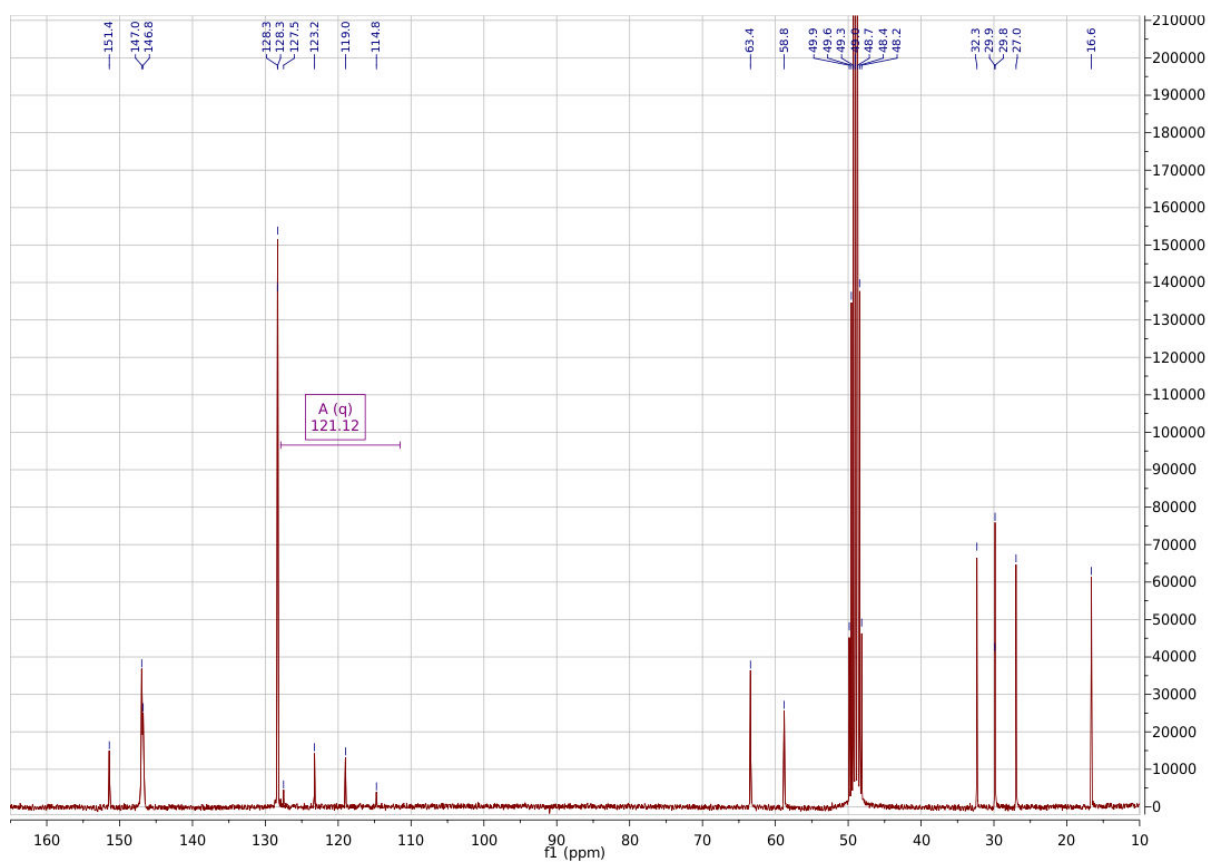


Figure 24. ^{13}C NMR spectrum of 2BP9BP2(Tf₂N)₄ (75 MHz; MeOD).

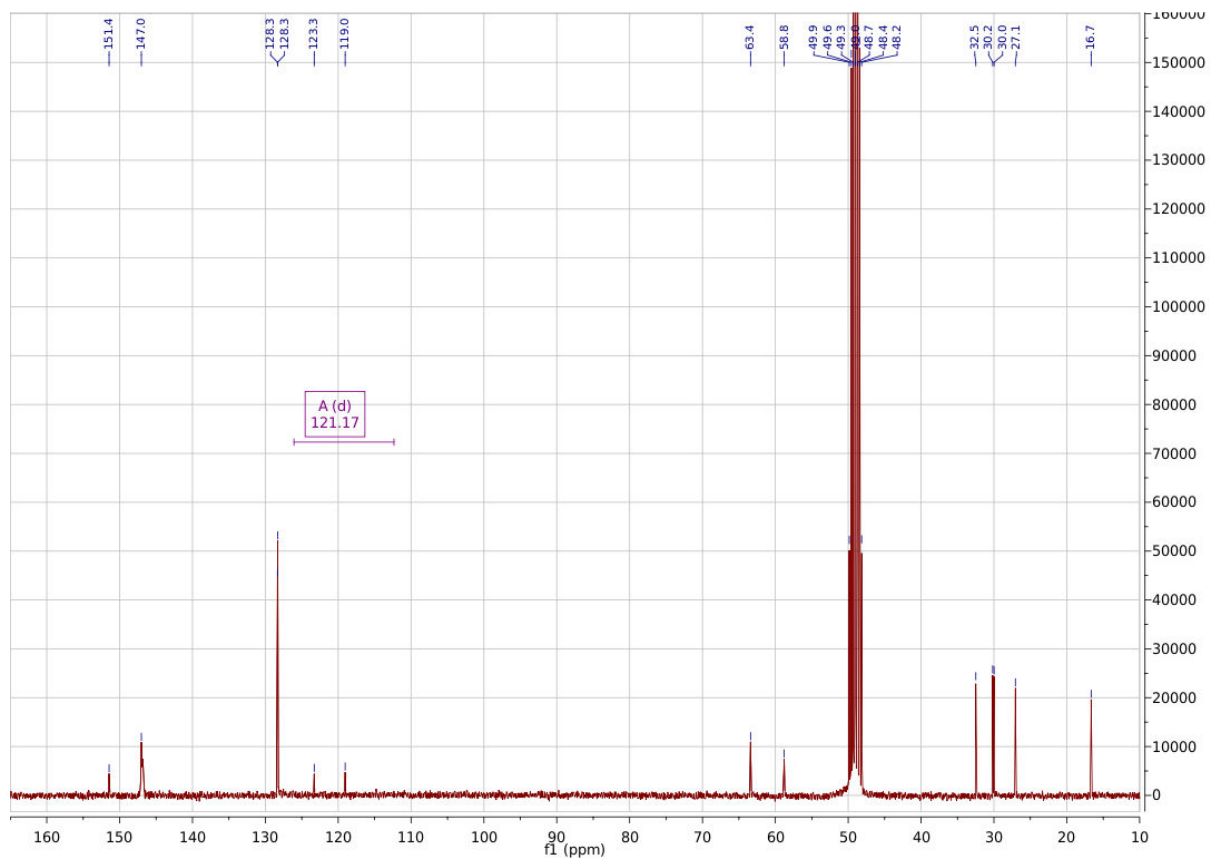


Figure 25. ^{13}C NMR spectrum of 2BP10BP2(Tf₂N)₄ (75 MHz; MeOD).