

Synthesis of non-symmetric viologen-containing ditopic ligands and their Pd(II)/Pt(II)-directed self-assembly

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1. RMN SPECTRA

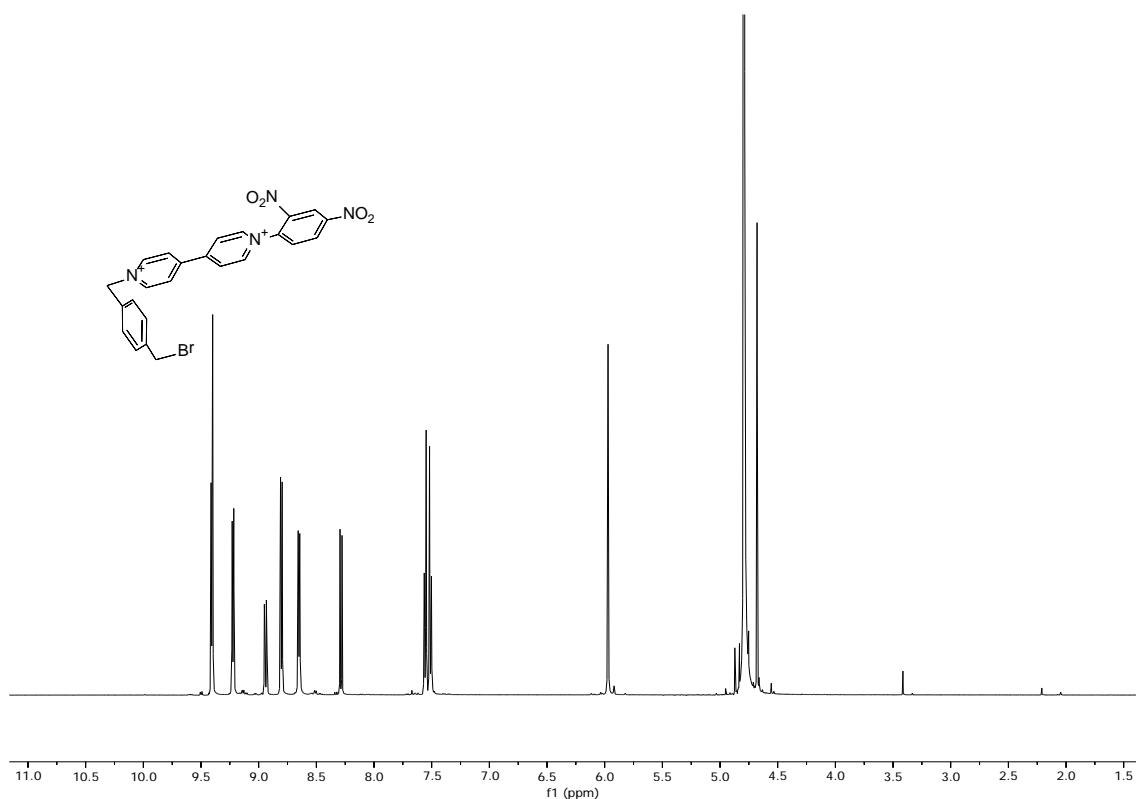


Figure S 1: ¹H RMN (500MHz, D₂O) spectrum of **6·ClBr**.

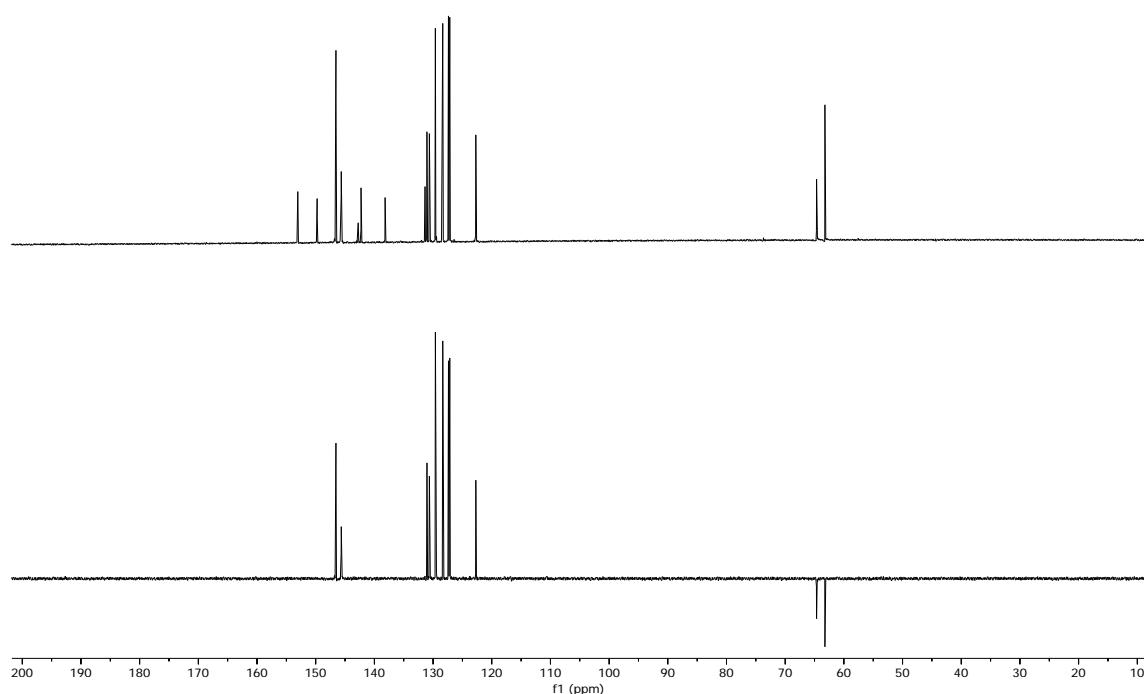


Figure S 2: ¹³C and DEPT NMR (125 MHz, D₂O) spectrum of **6·ClBr**.

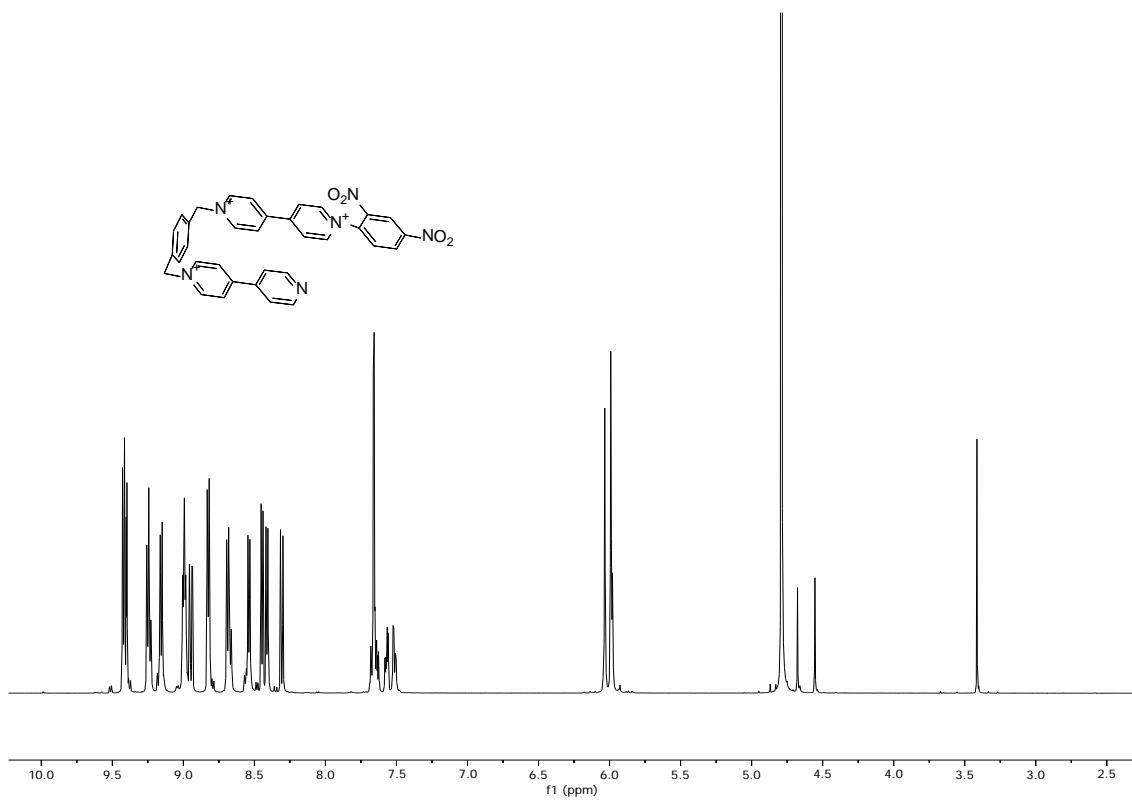


Figure S 3: ^1H RMN (500MHz, D_2O) spectrum of **7·Cl·2Br**.

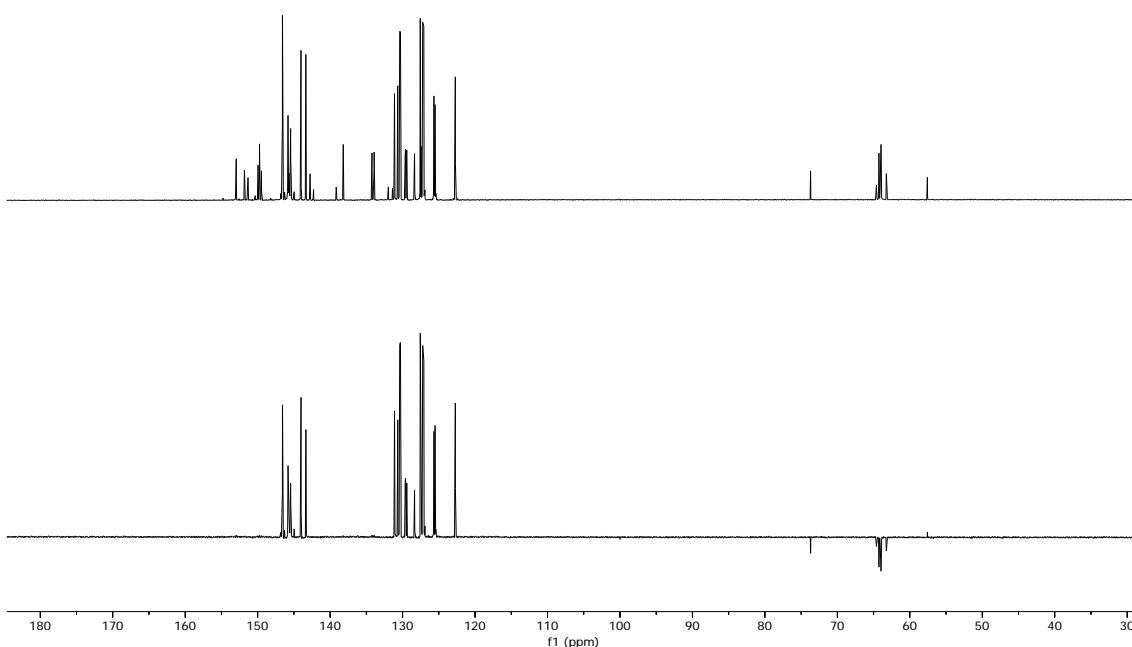


Figure S 4: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **7·Cl·2Br**.

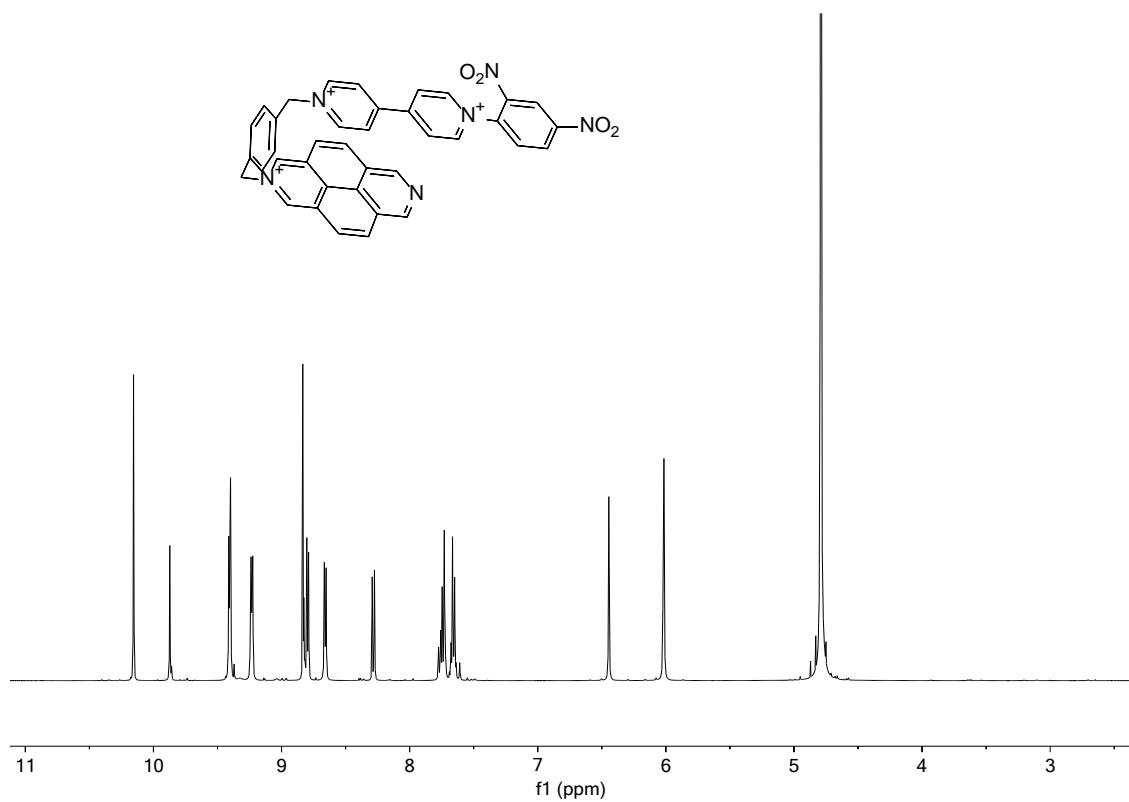


Figure S 5: ¹H RMN (500MHz, D₂O) spectrum of **12·Cl₂Br**.

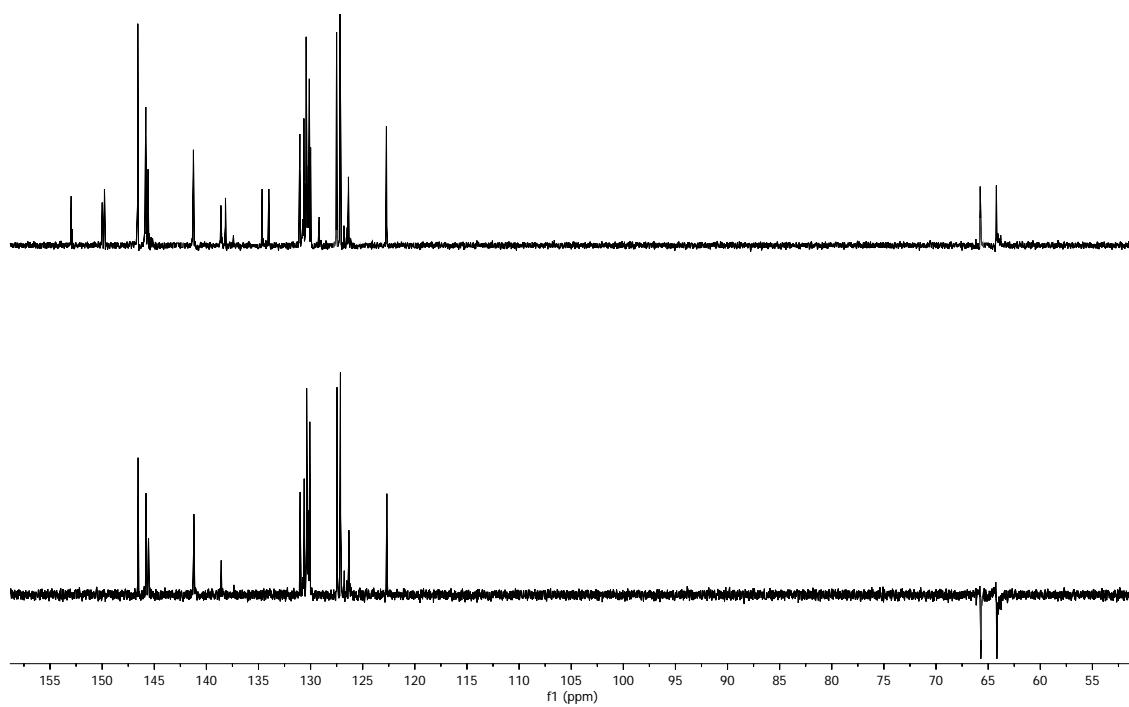


Figure S 6: ¹³C and DEPT NMR (125 MHz, D₂O) spectrum of **12·Cl₂Br**.

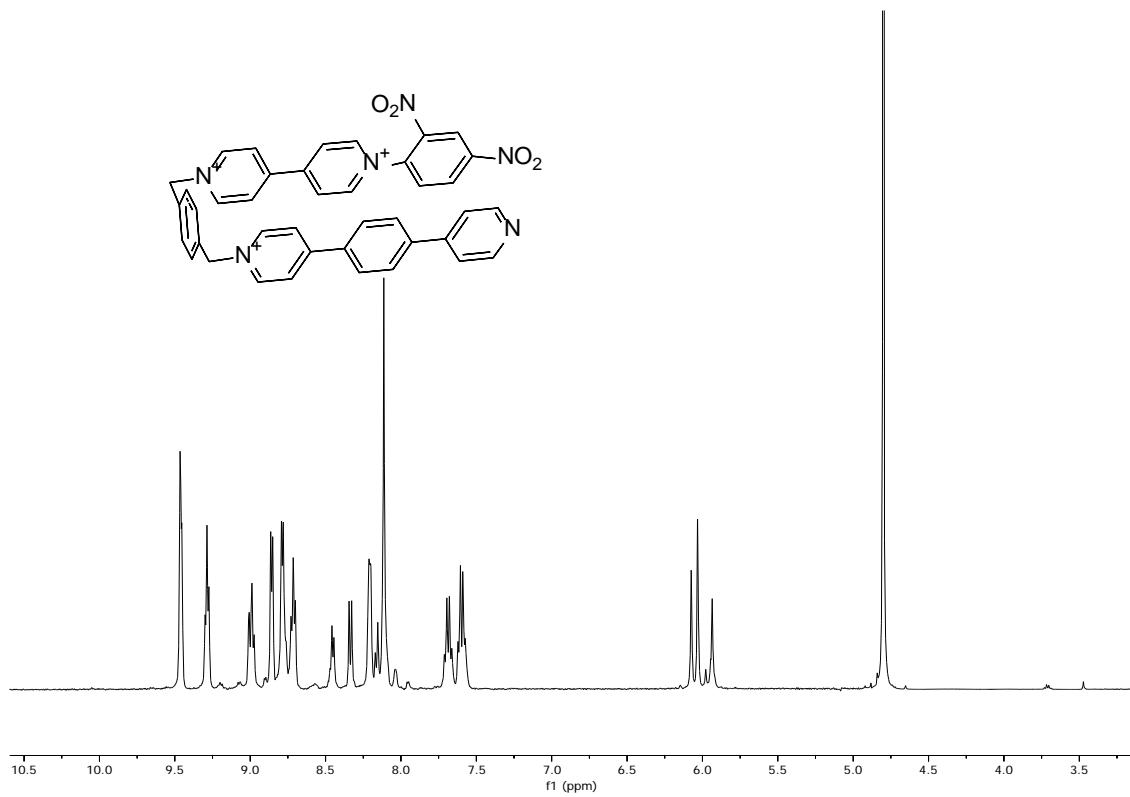


Figure S 7: ¹H RMN (500MHz, D₂O) spectrum of **13·Cl·2Br**.

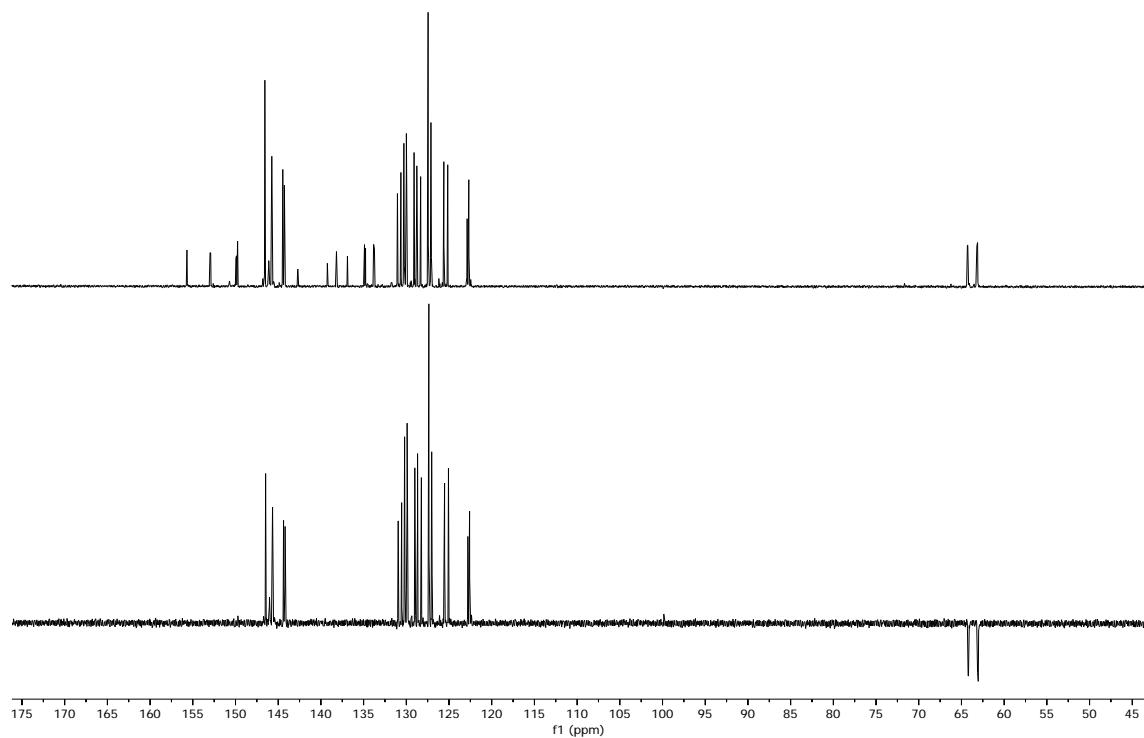


Figure S 8: ¹³C and DEPT NMR (125 MHz, D₂O) spectrum of **13·Cl·2Br**.

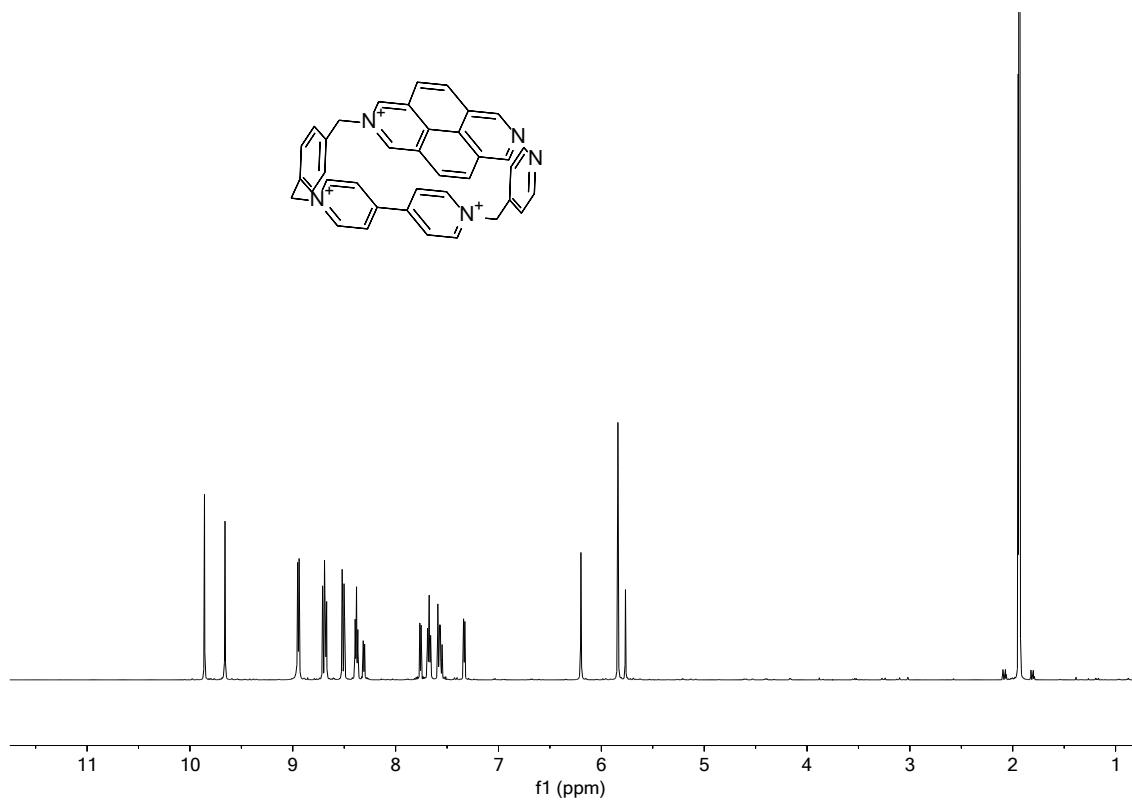


Figure S 9: ^1H RMN (500MHz, CD_3CN) spectrum of $\mathbf{L4}\cdot\mathbf{3PF}_6$.

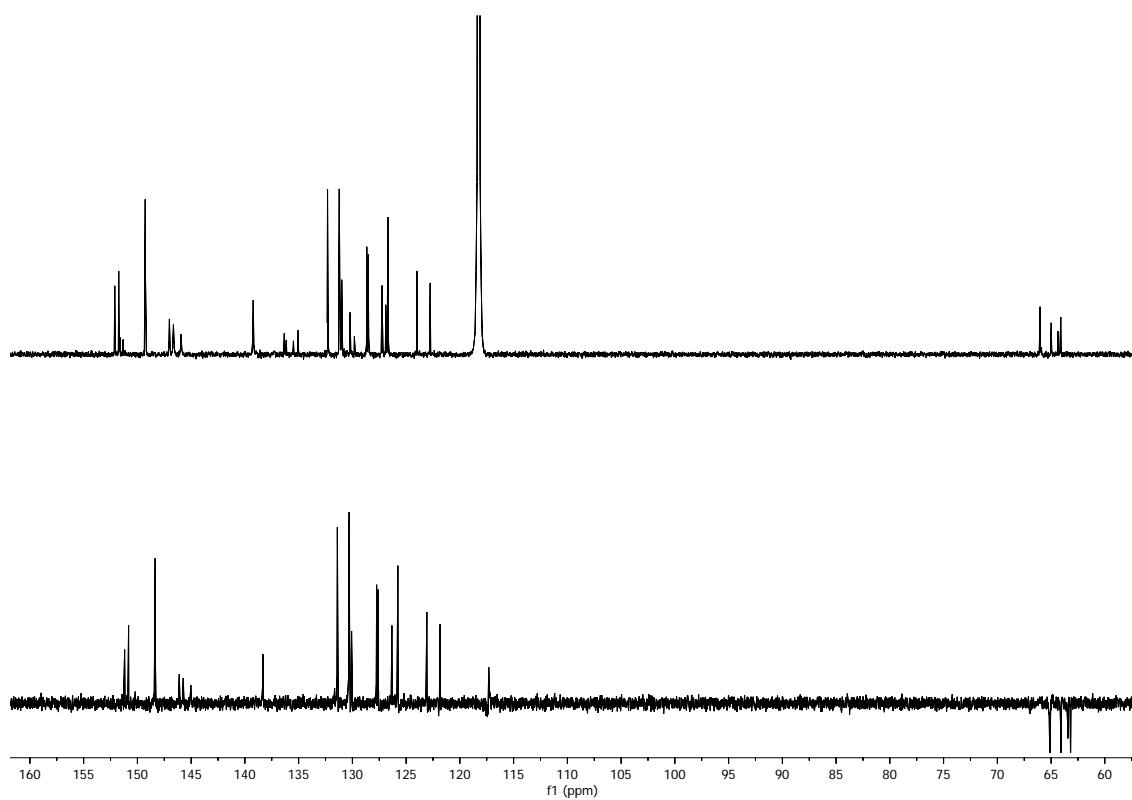


Figure S 10: ^{13}C and DEPT NMR (125 MHz, CD_3CN) spectrum of $\mathbf{L4}\cdot\mathbf{3PF}_6$.

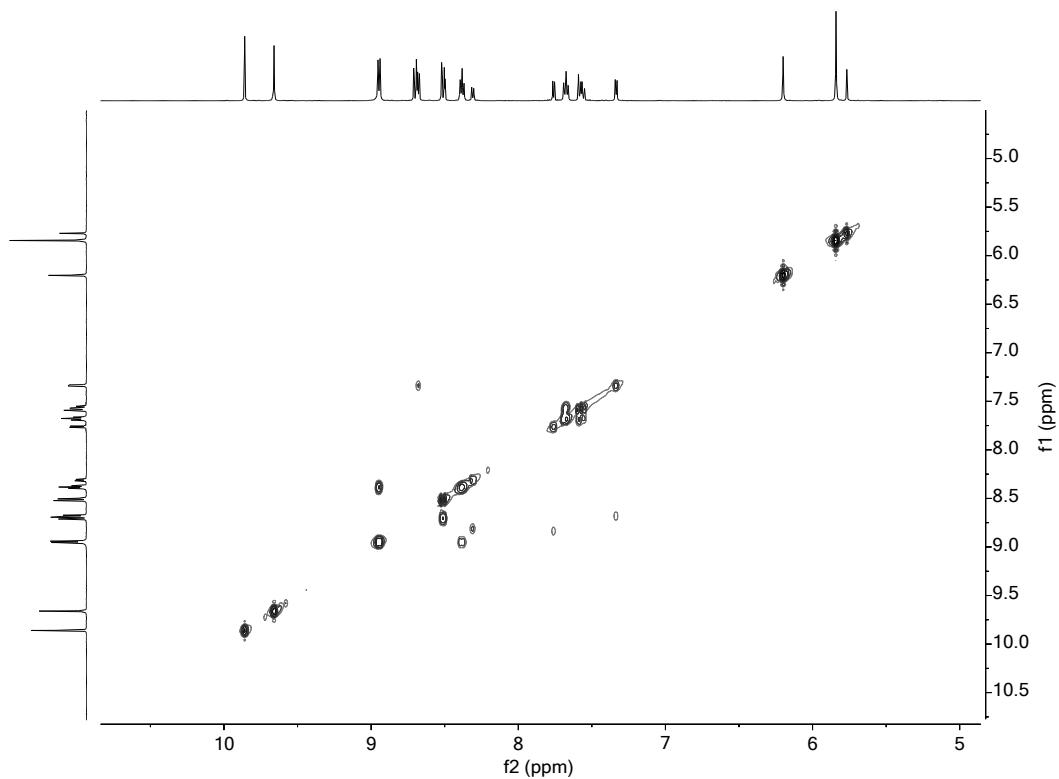


Figure S 11: COSY (500MHz, CD₃CN) spectrum of **L4·3PF₆**.

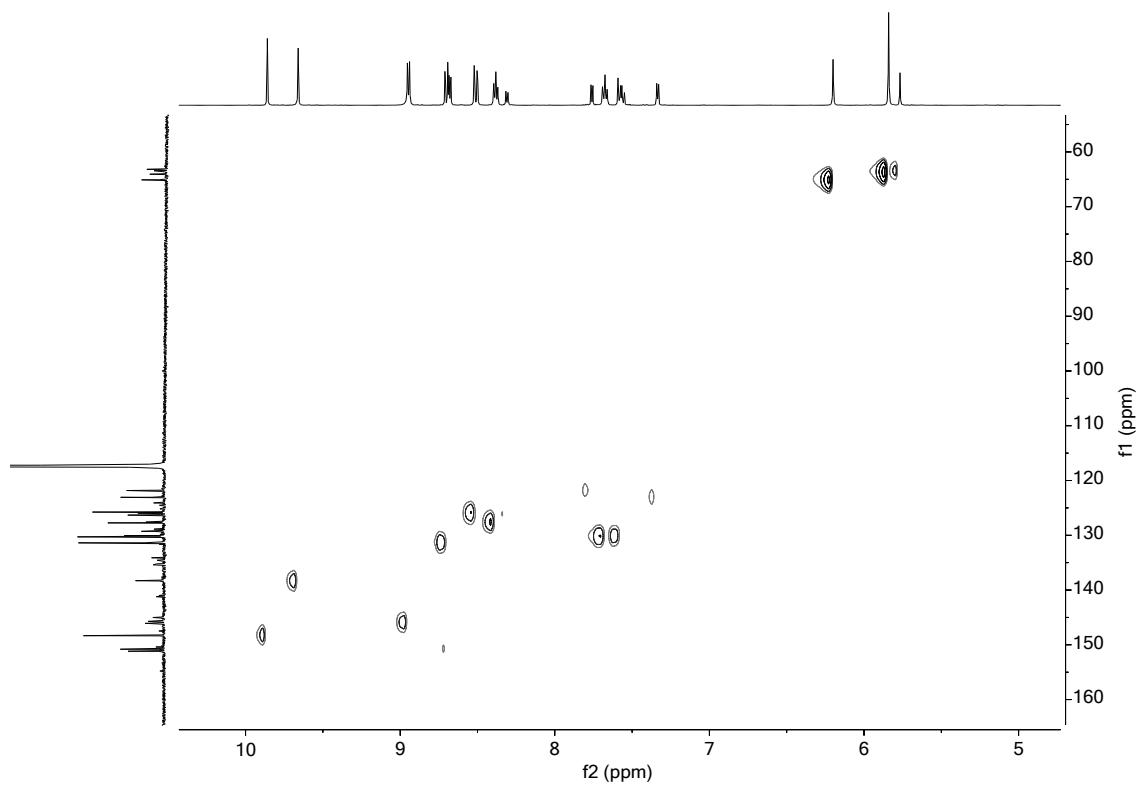


Figure S 12: HSQC (125 and 500MHz, CD₃CN) spectrum of **L4·3PF₆**.

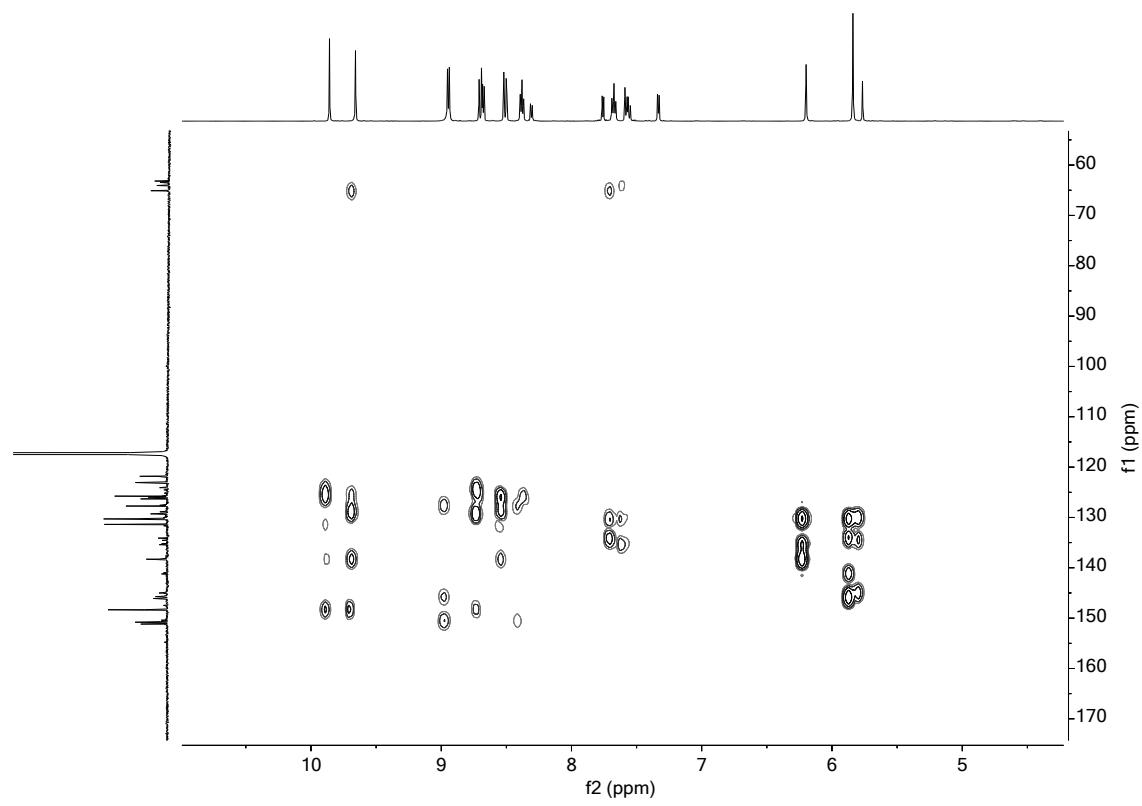


Figure S 13: HMBC (125 and 500MHz, CD₃CN) spectrum of **L4·3PF₆**.

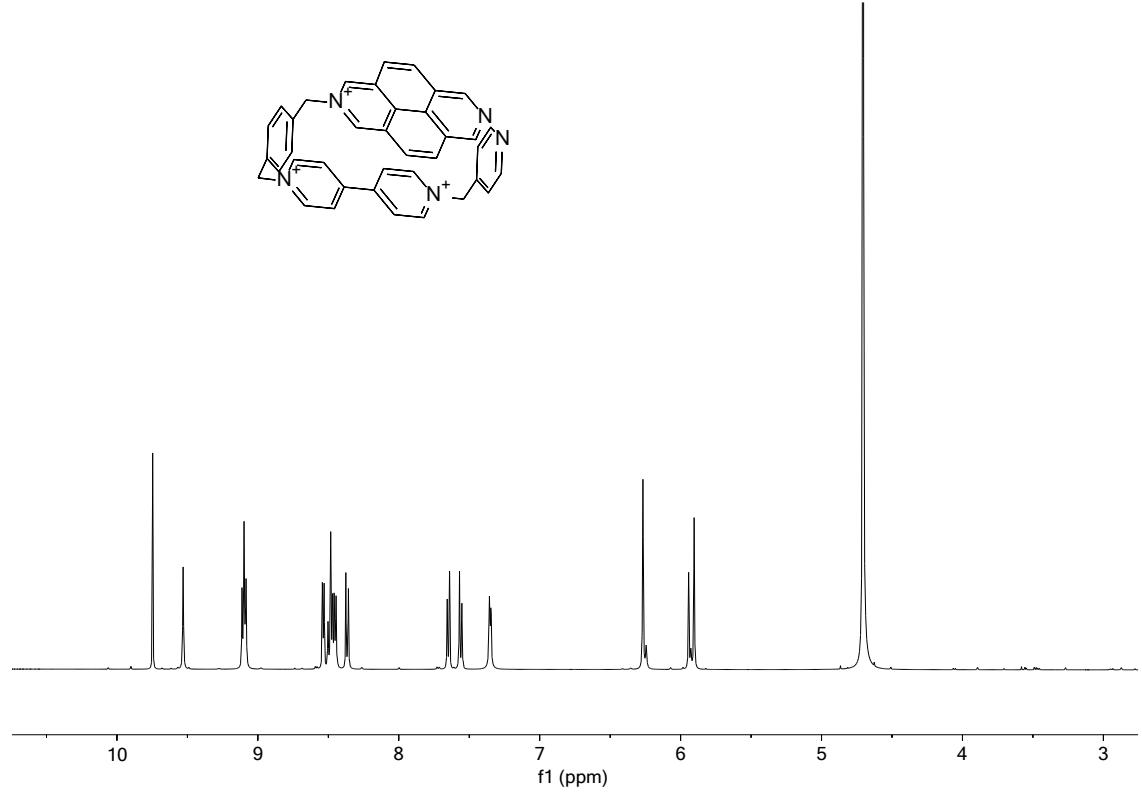


Figure S 14: ¹H RMN (500MHz, D₂O) spectrum of **L4·3NO₃**.

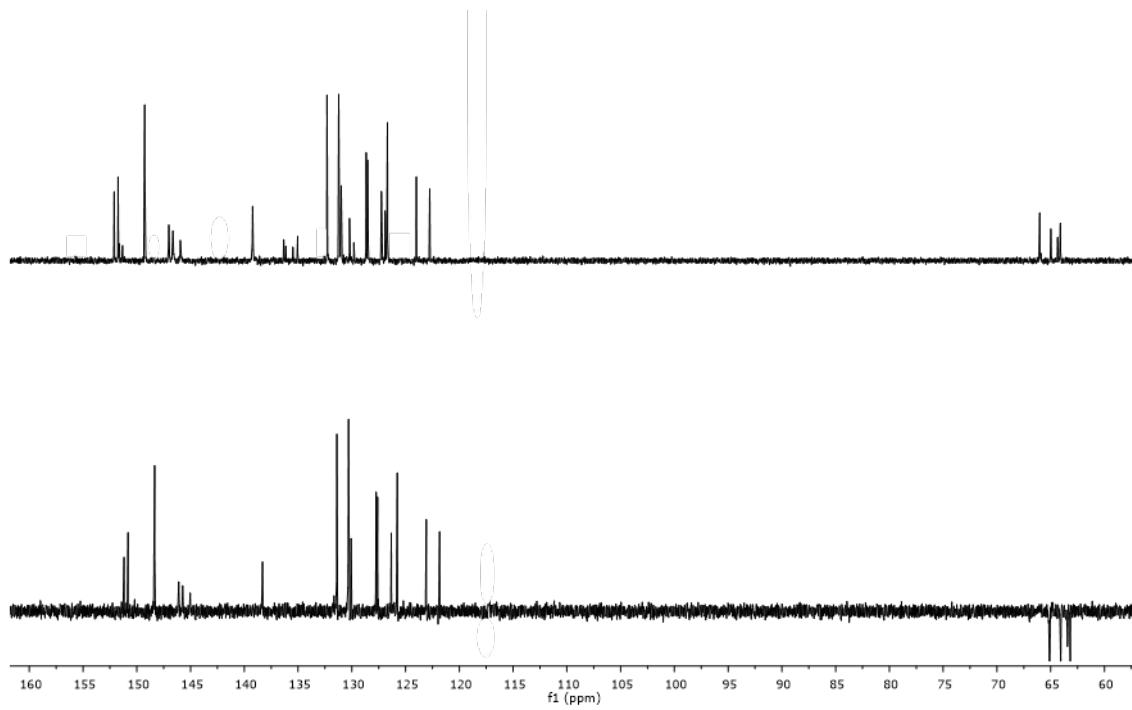


Figure S 15: ¹³C and DEPT NMR (125 MHz, D₂O) spectrum of **L4·NO₃**.

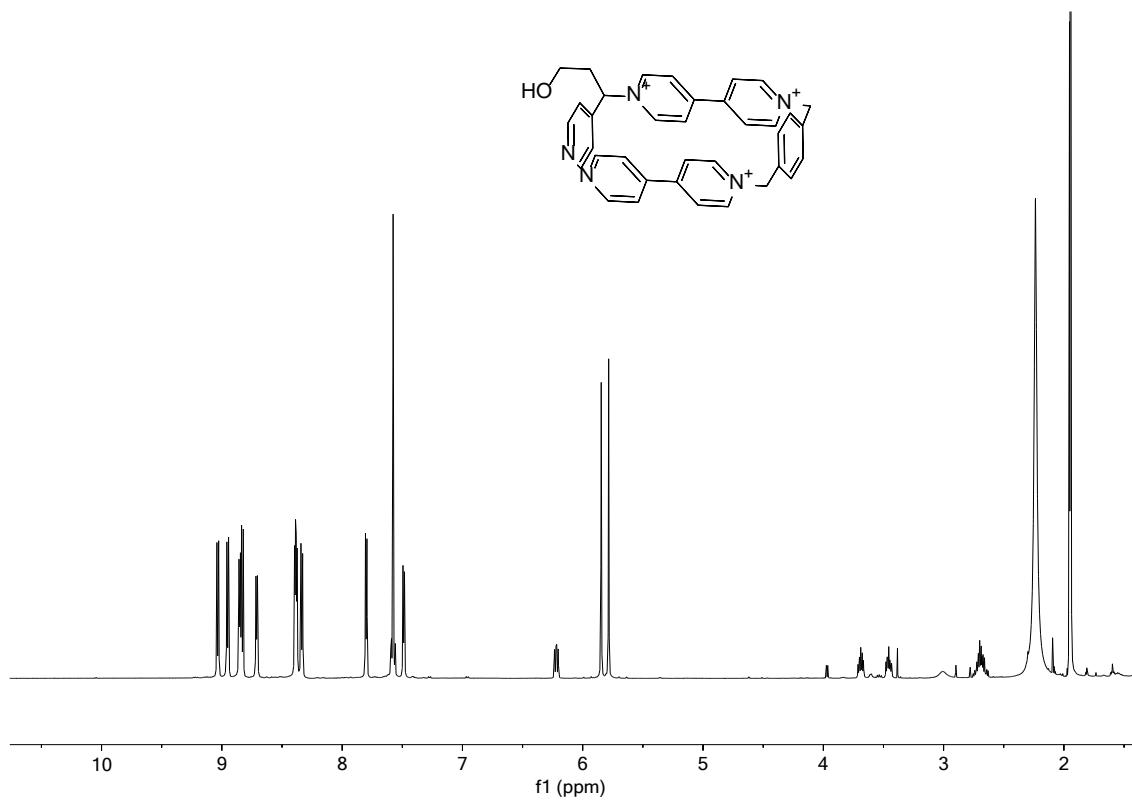


Figure S 16: ¹H RMN (500MHz, CD₃CN) spectrum of **L5·3PF₆**.

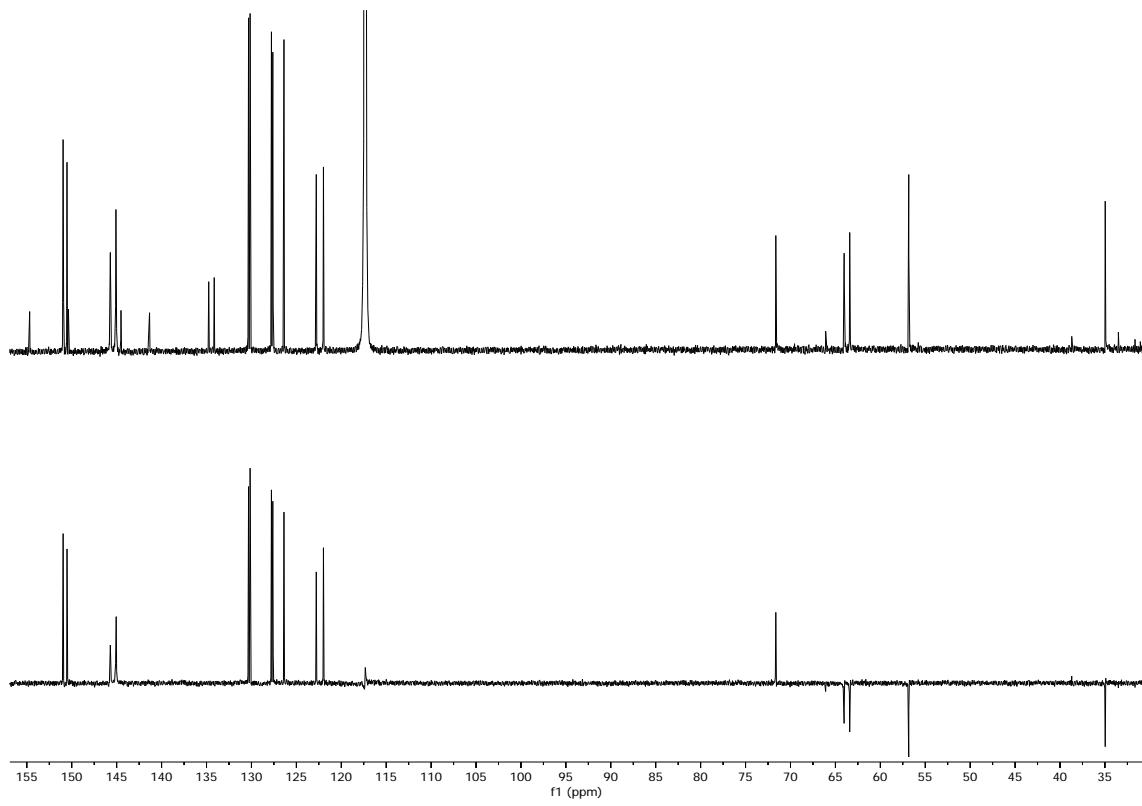


Figure S 17: ^{13}C and DEPT NMR (125 MHz, CD_3CN) spectrum of **L5·3PF₆**.

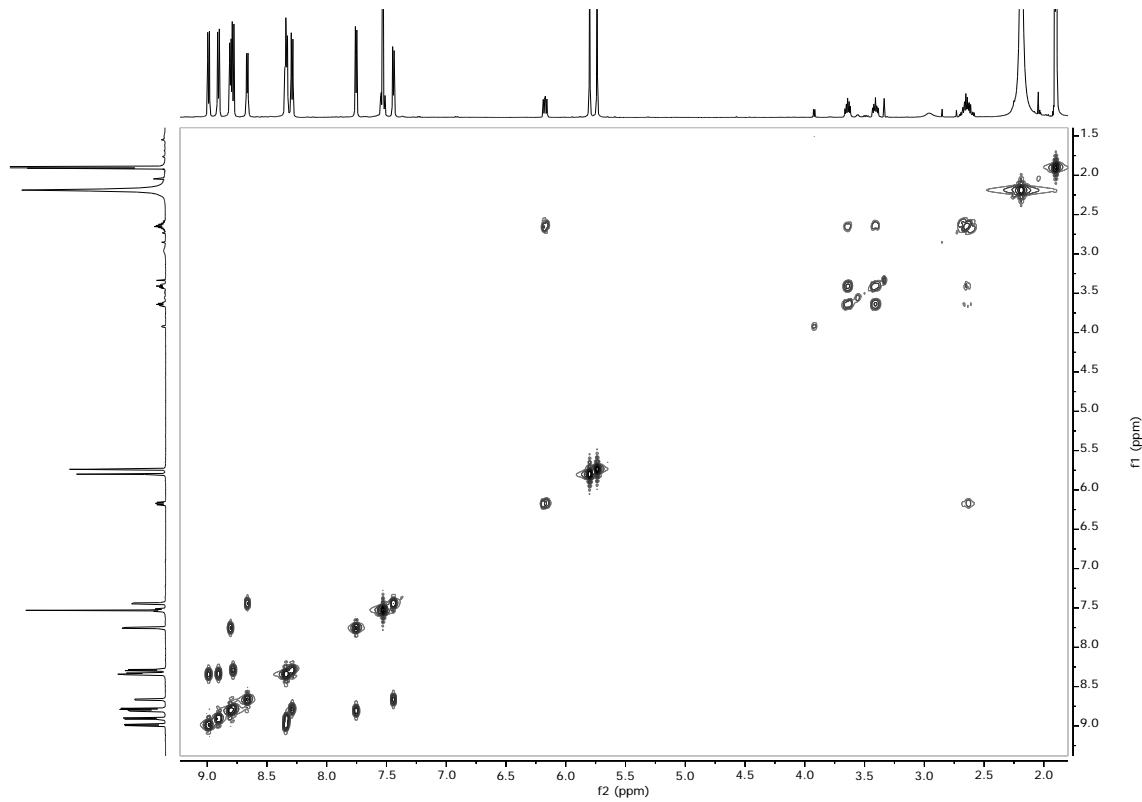


Figure S 18: COSY (500MHz, CD_3CN) spectrum of **L5·3PF₆**.

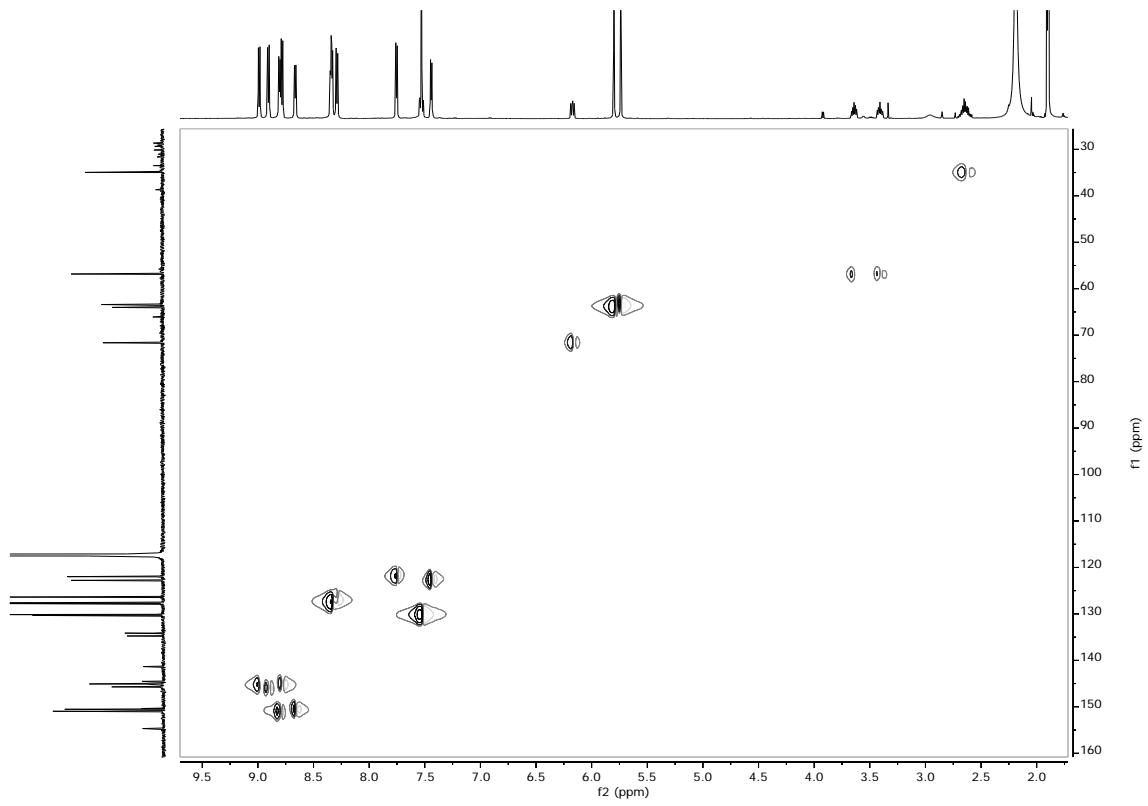


Figure S 19: HSQC (500 and 125MHz, CD_3CN) spectrum of **L5·3PF₆**.

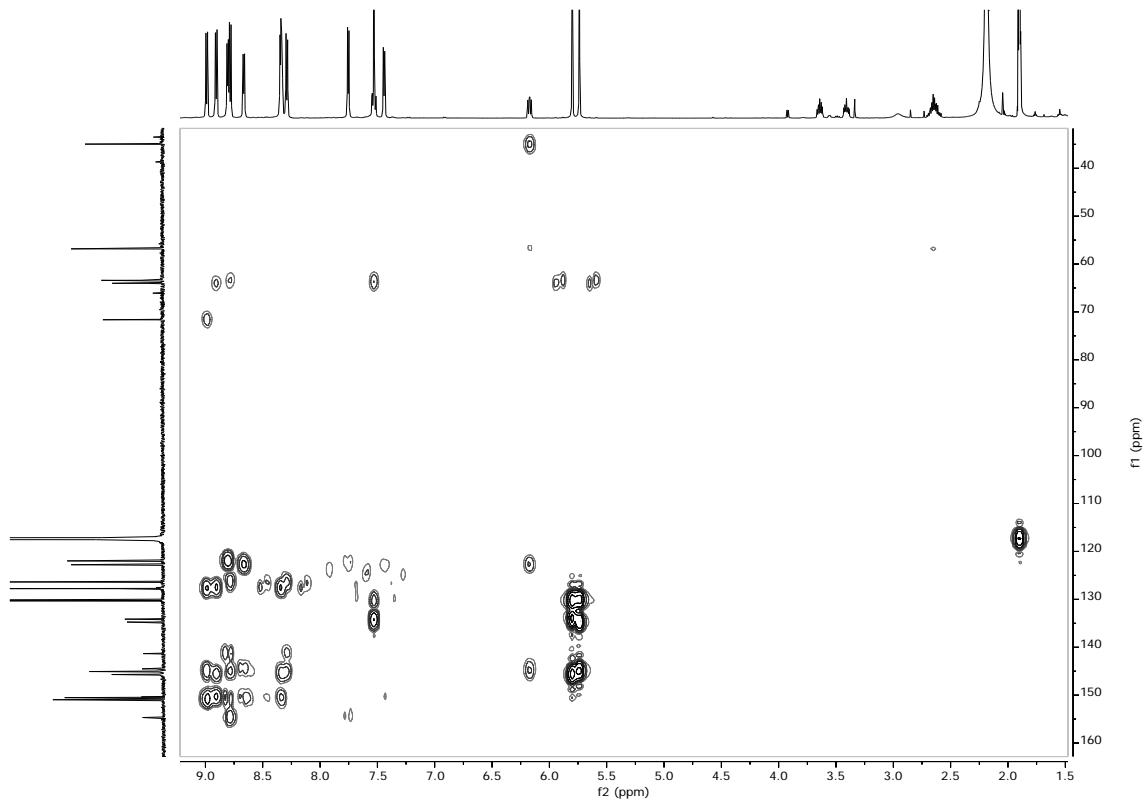


Figure S 20: HMBC (125 and 500MHz, CD_3CN) spectrum of **L5·3PF₆**.

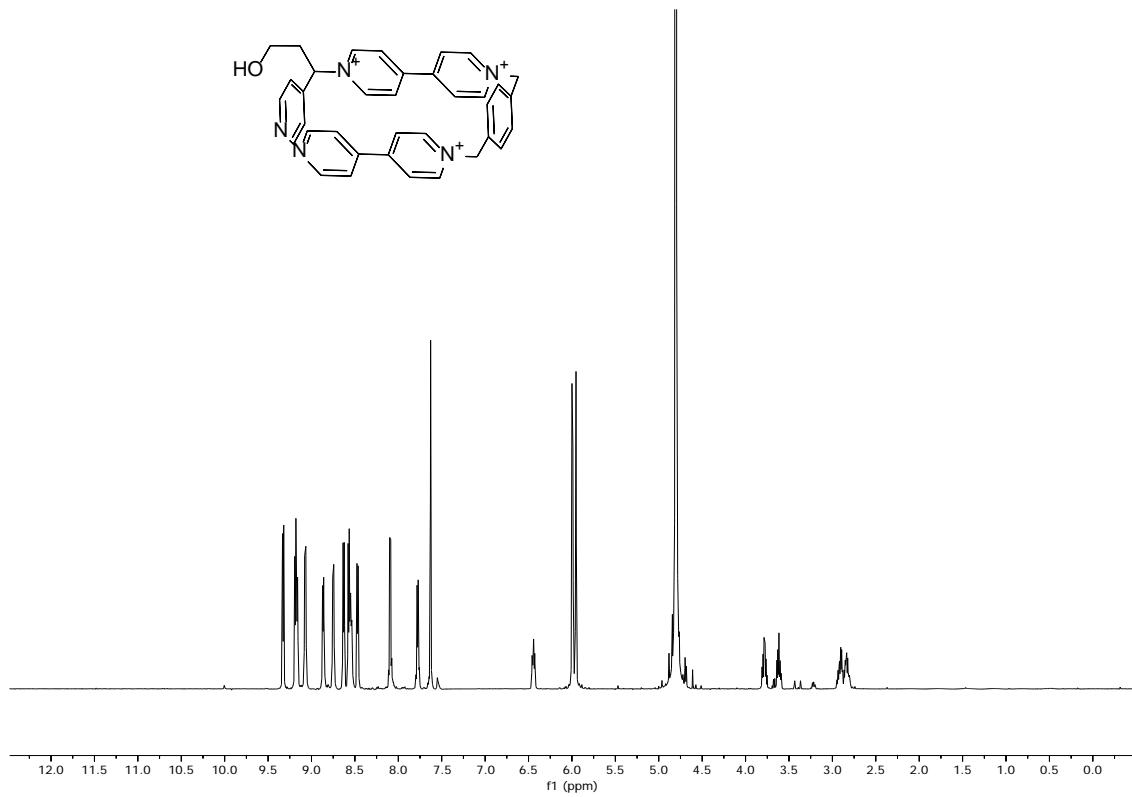


Figure S 21: ^1H RMN (500MHz, D_2O) spectrum of $\text{L5}'\text{3NO}_3$.

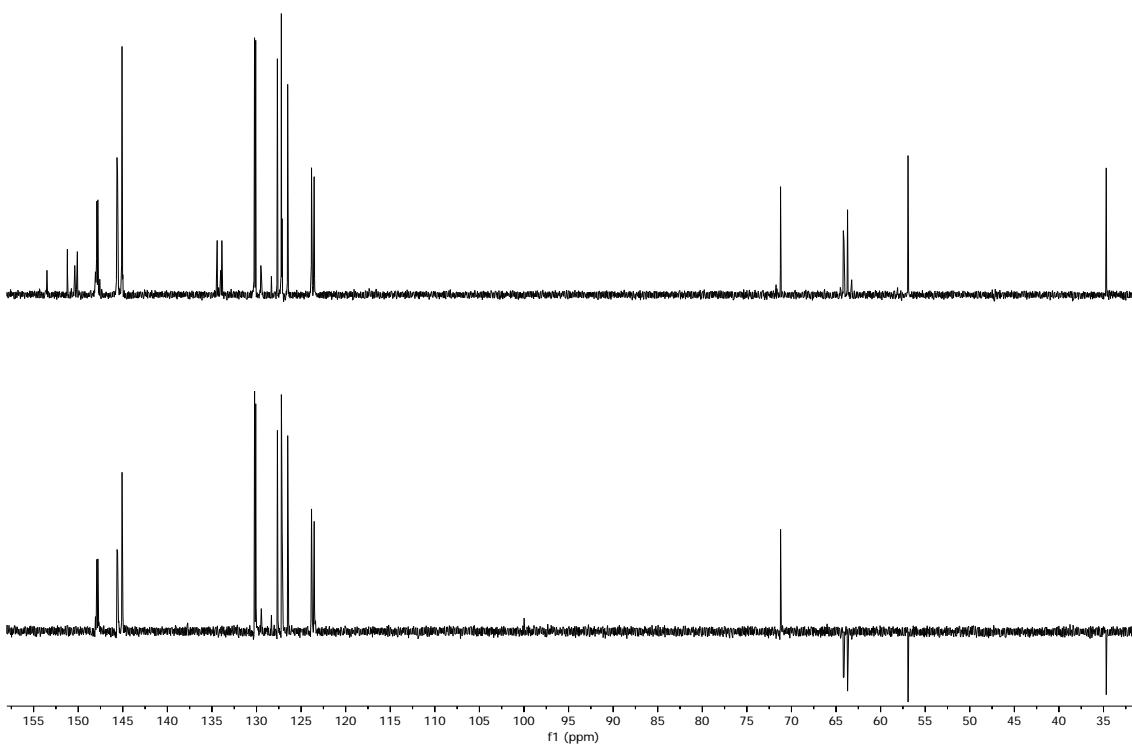


Figure S 22: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of $\text{L5}'\text{3NO}_3$.

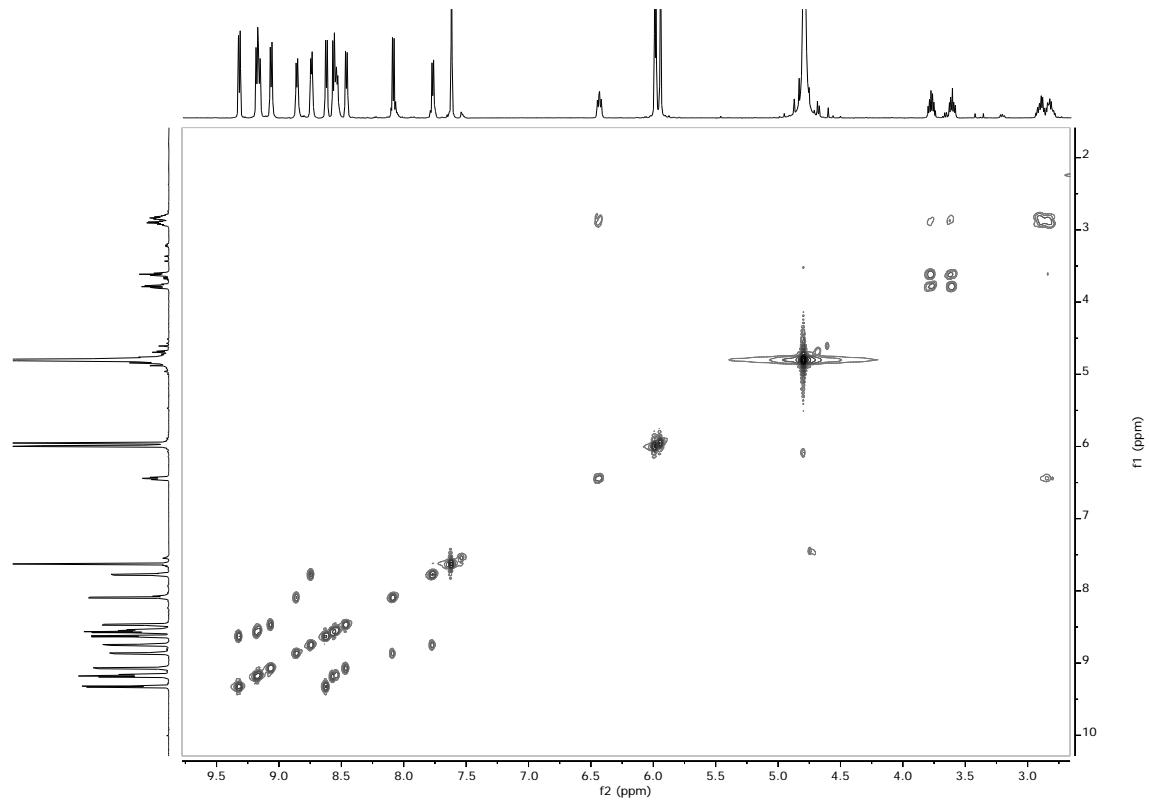


Figure S 23: COSY (500MHz, D₂O) spectrum of L5·3NO₃.

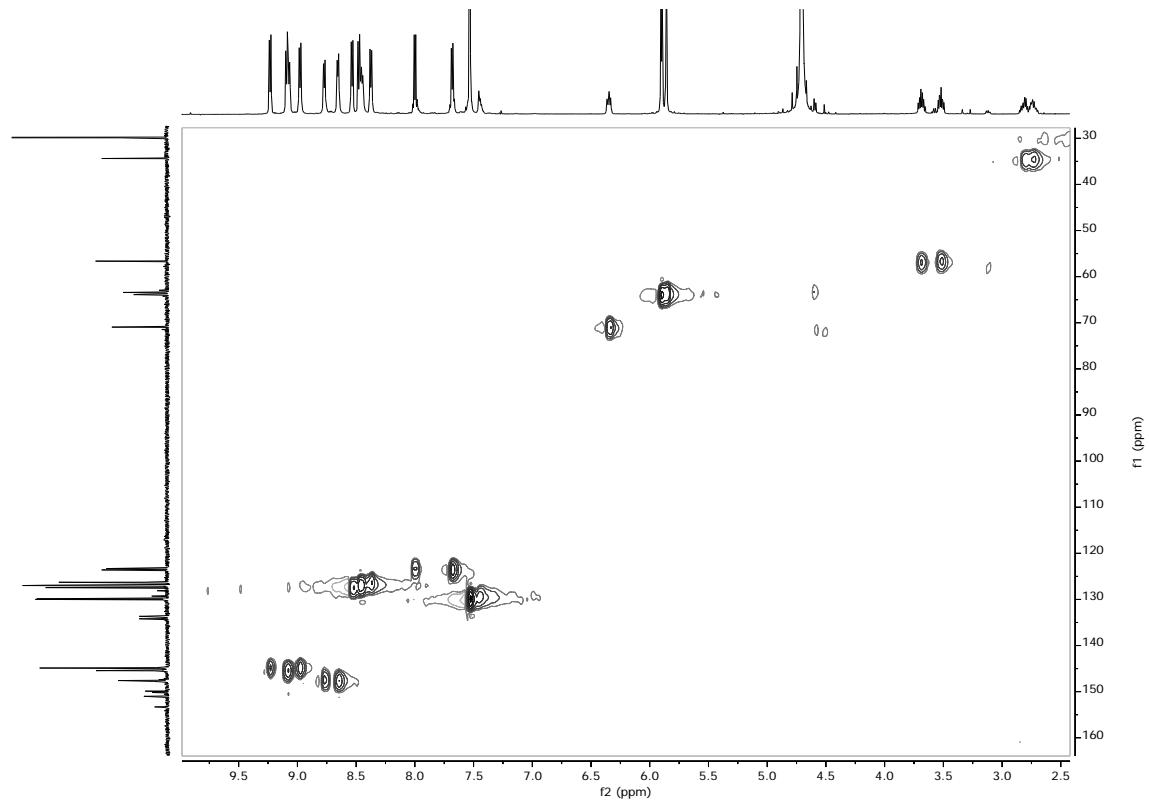


Figure S 24: HSQC (125 and 500MHz, D₂O) spectrum of L5·3NO₃.

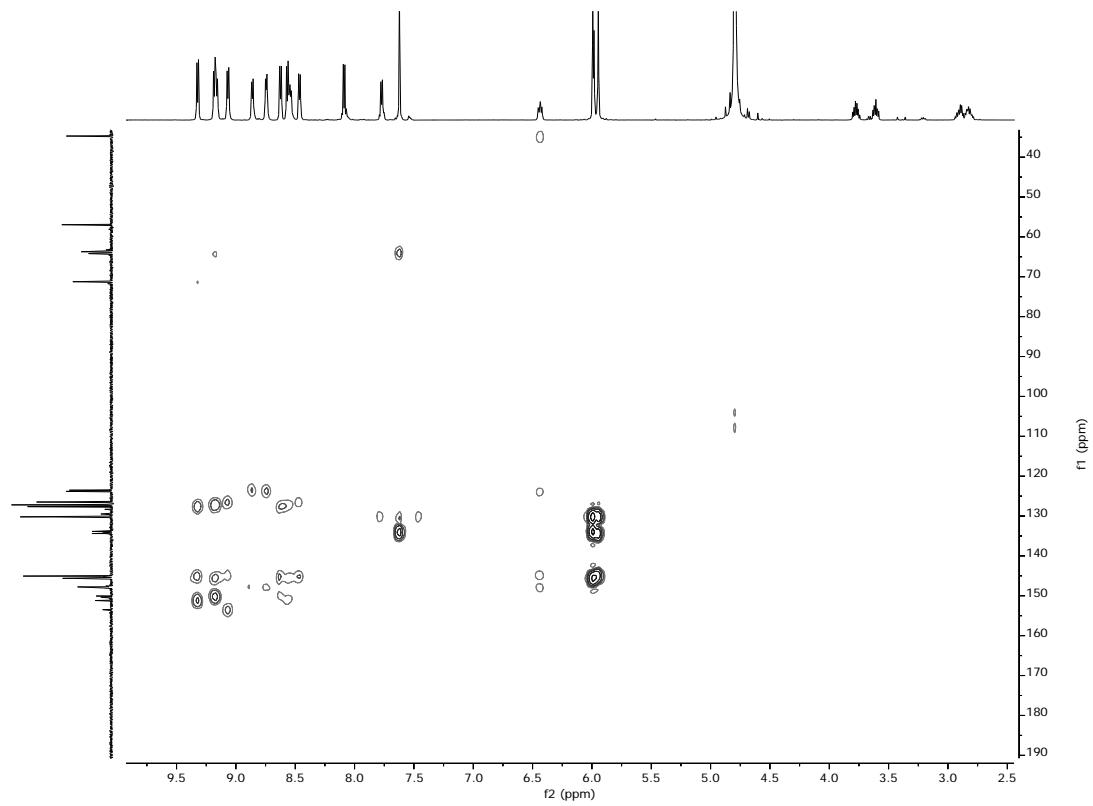


Figure S 25: HMBC (125 and 500MHz, D₂O) spectrum of **L5·3NO₃**

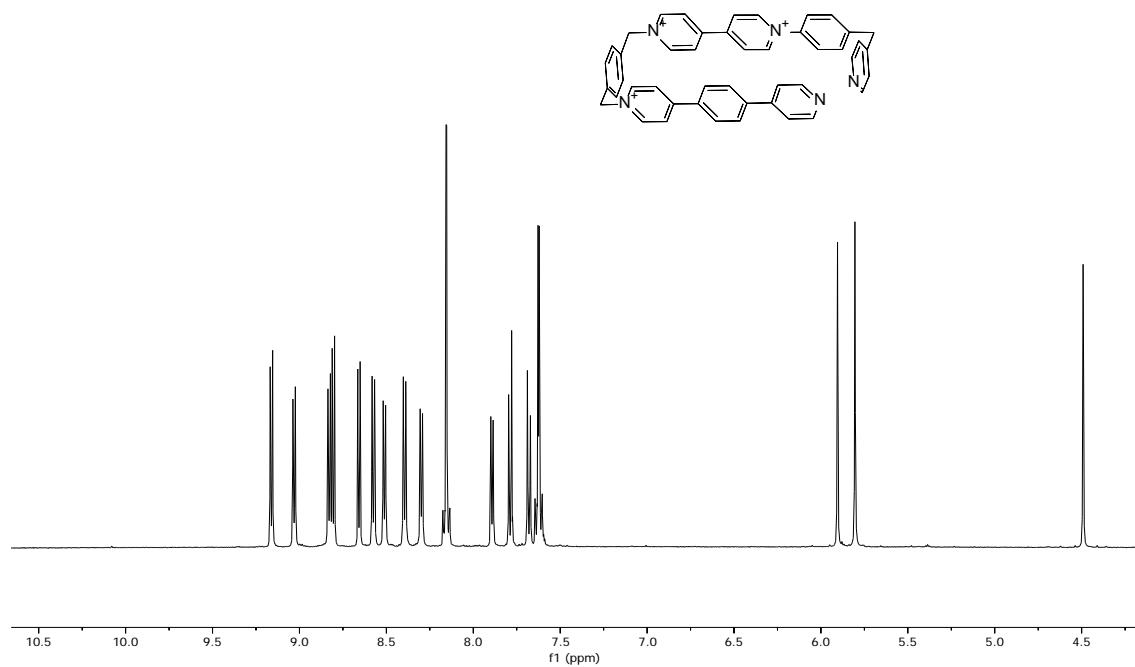


Figure S 26: ¹H RMN (500MHz, CD₃CN) spectrum of **L6·3PF₆**.

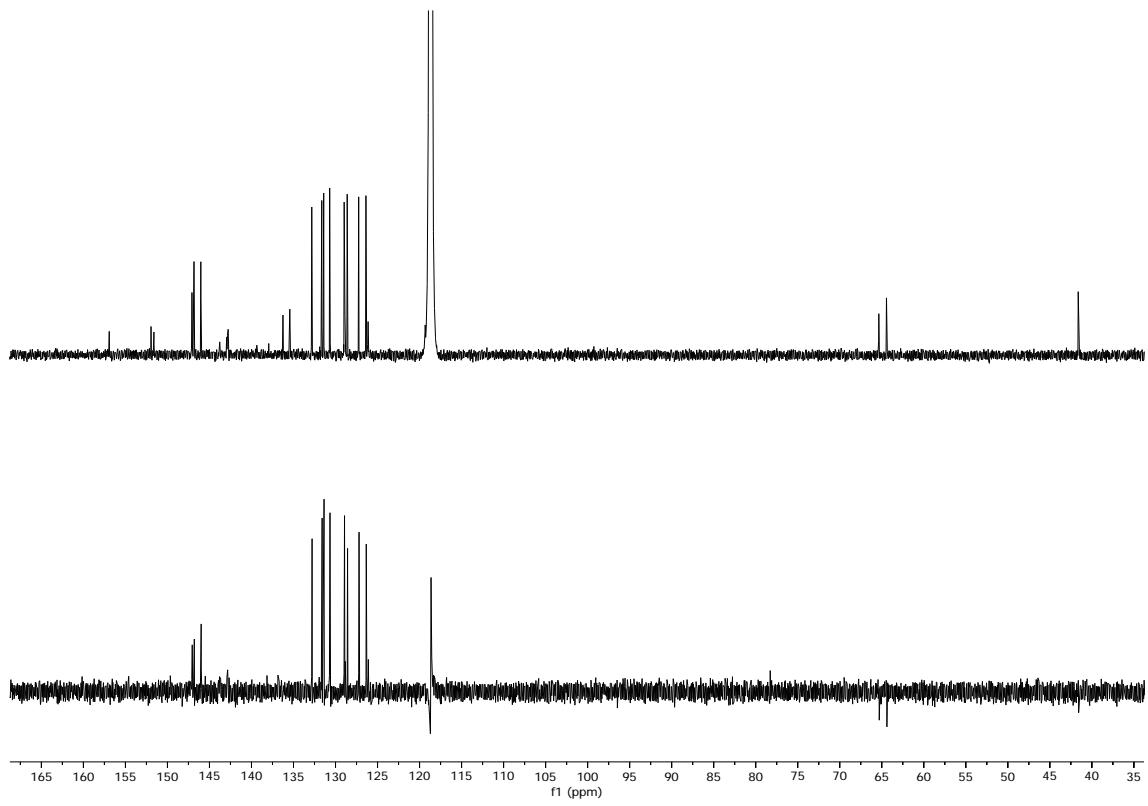


Figure S 27: ¹H RMN (500MHz, CD₃CN) spectrum of **L6·3PF₆**.

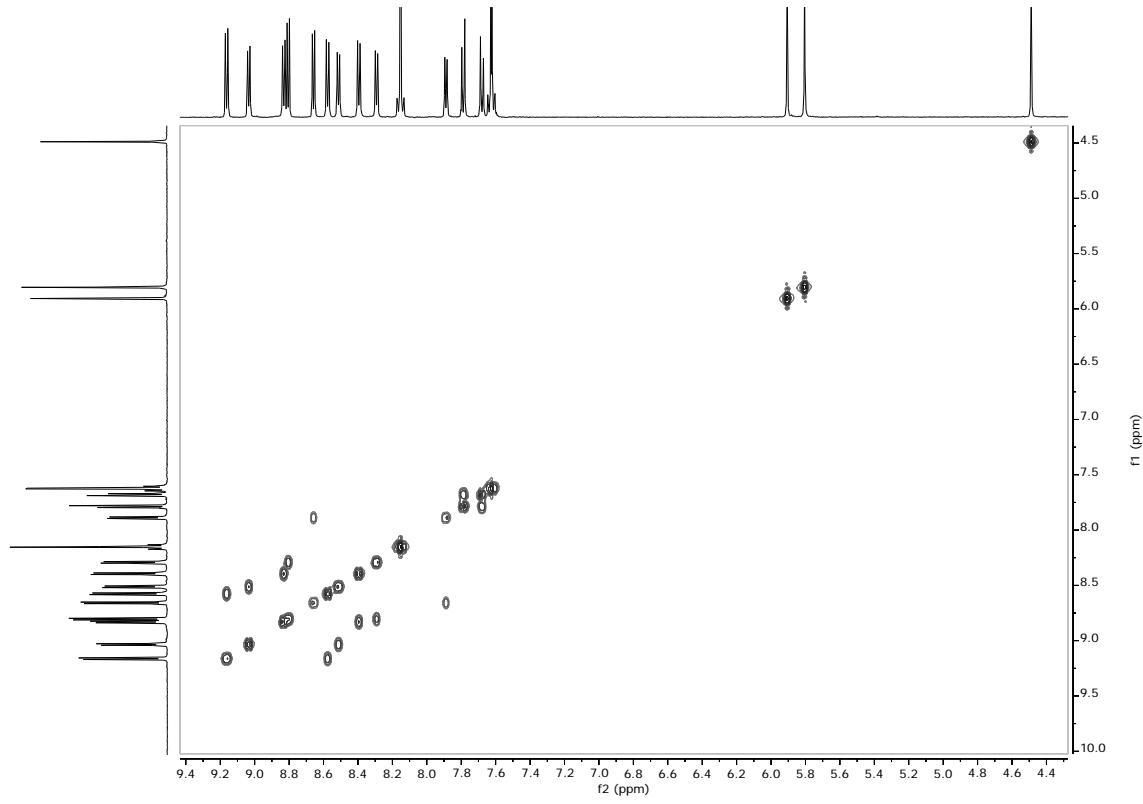


Figure S 28: COSY (500MHz, CD₃CN) spectrum of **L6·3PF₆**.

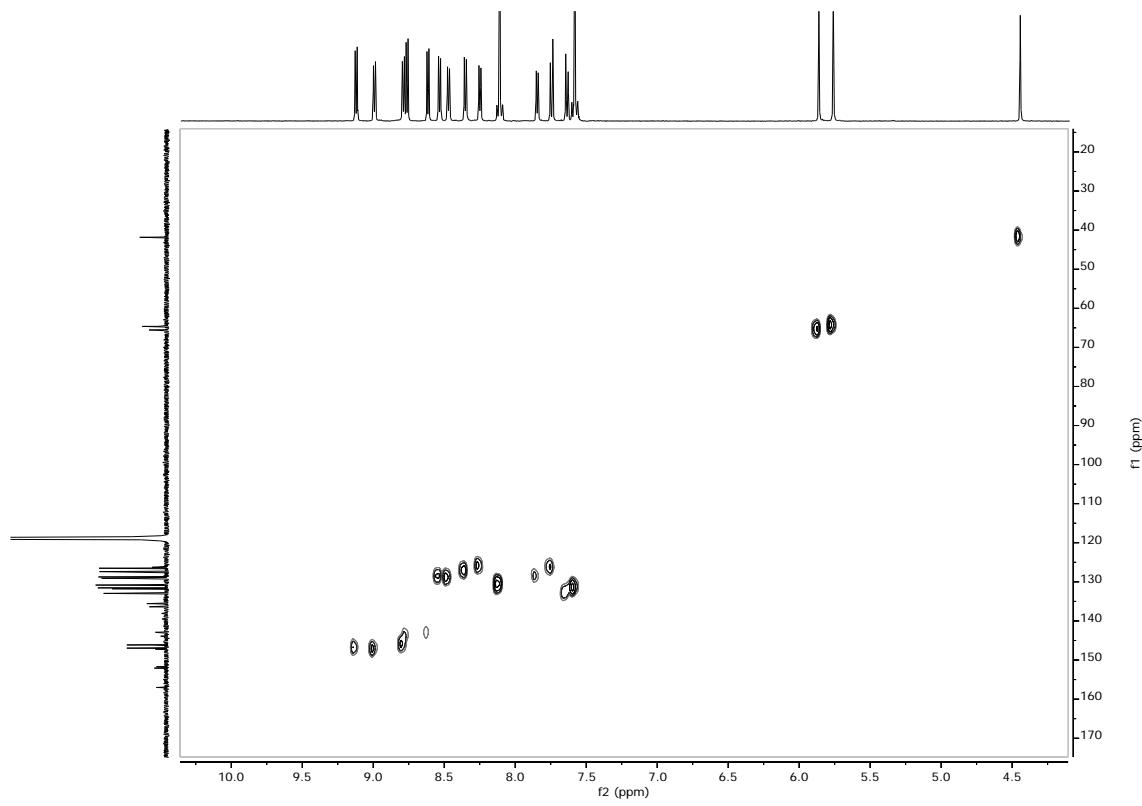


Figure S 29: HSQC (125 and 500MHz, CD_3CN) spectrum of **L6·3PF₆**.

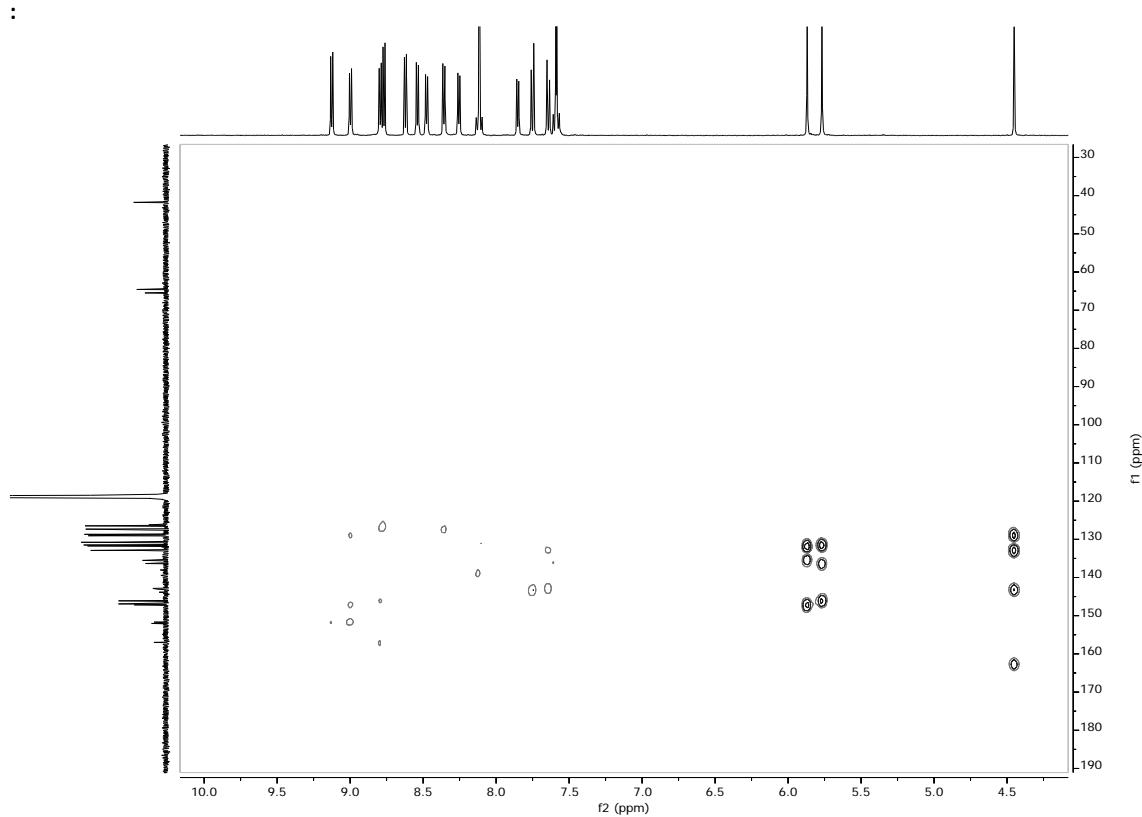


Figure S 30: HMBC (125 and 500MHz, CD_3CN) spectrum of **L6·3PF₆**.

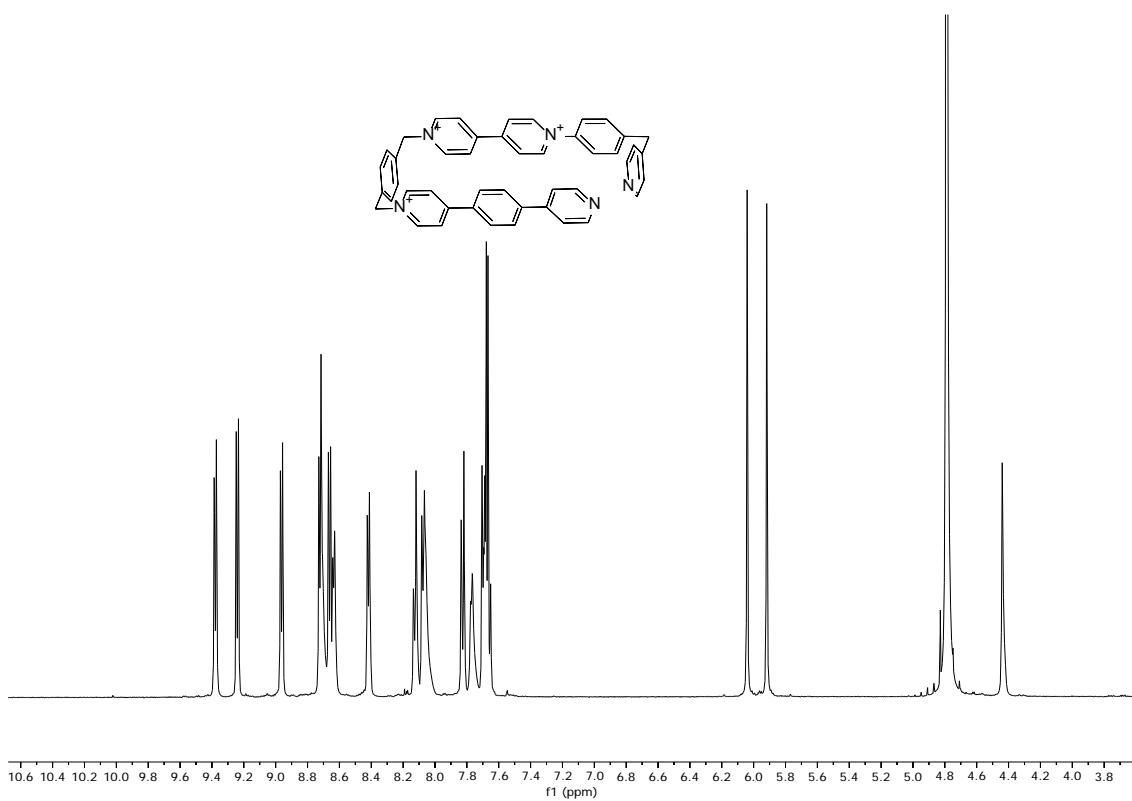


Figure S 31: ^1H RMN (500MHz, D_2O) spectrum of $\text{L6}\cdot 3\text{NO}_3$.

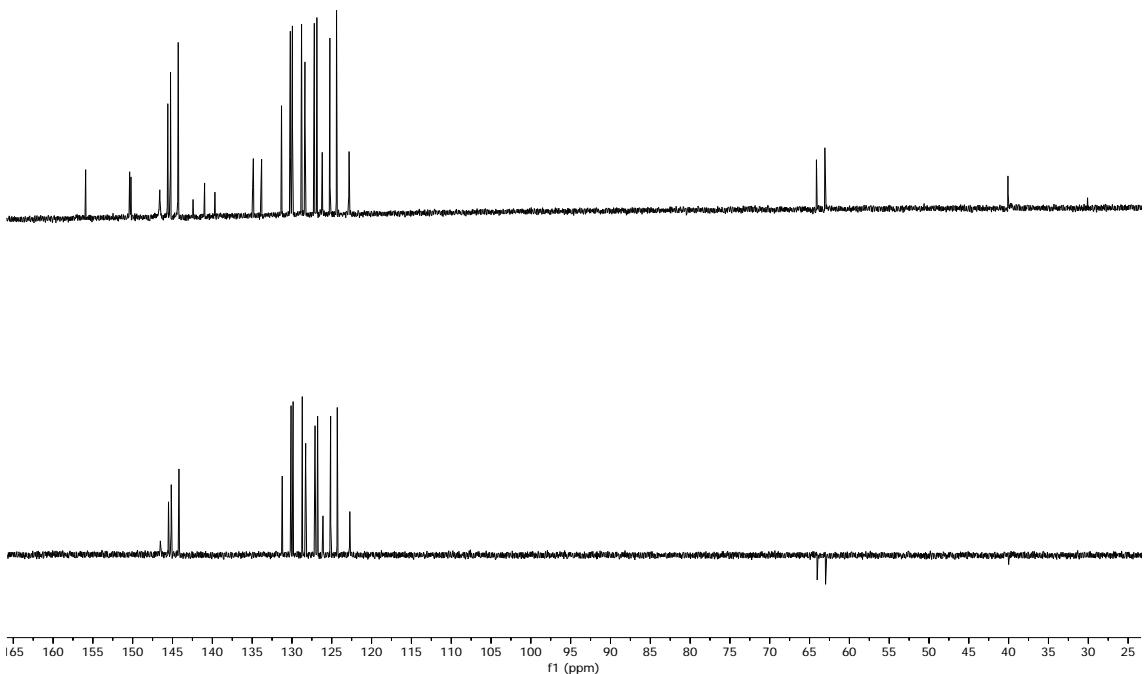


Figure S 32: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of $\text{L6}\cdot 3\text{NO}_3$.

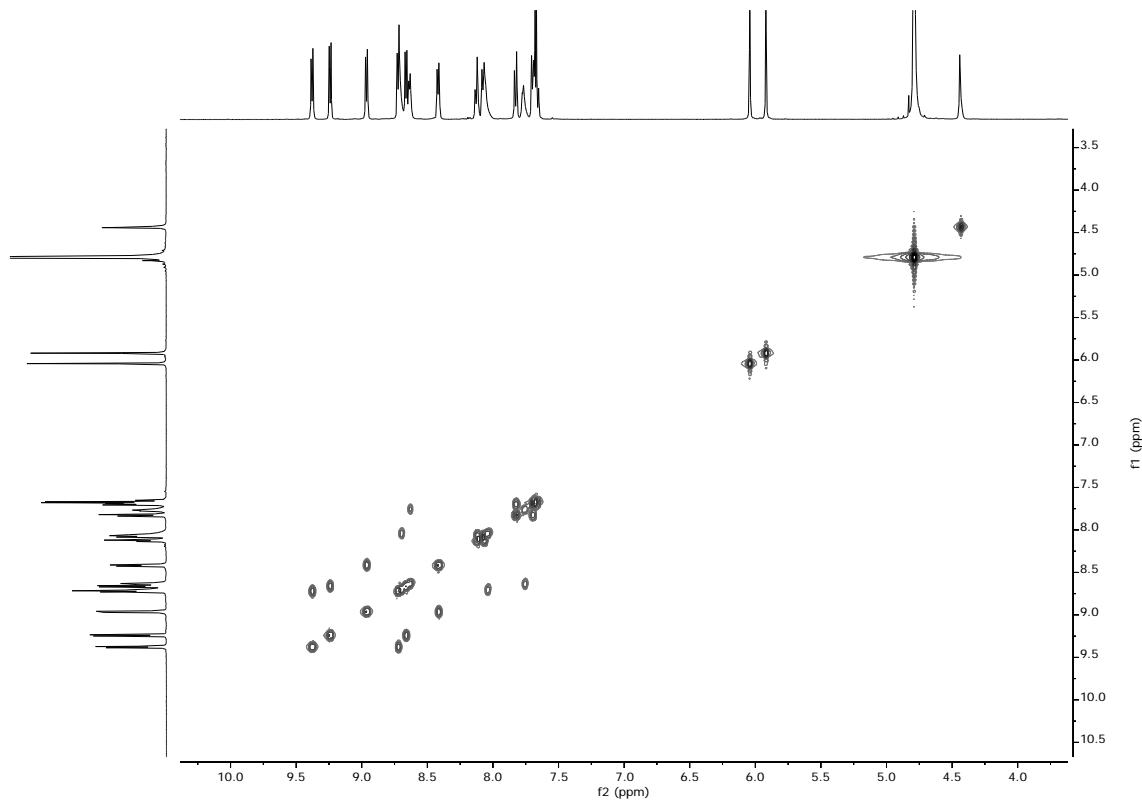


Figure S 33: COSY (500MHz, D₂O) spectrum of **L6·3NO₃**.

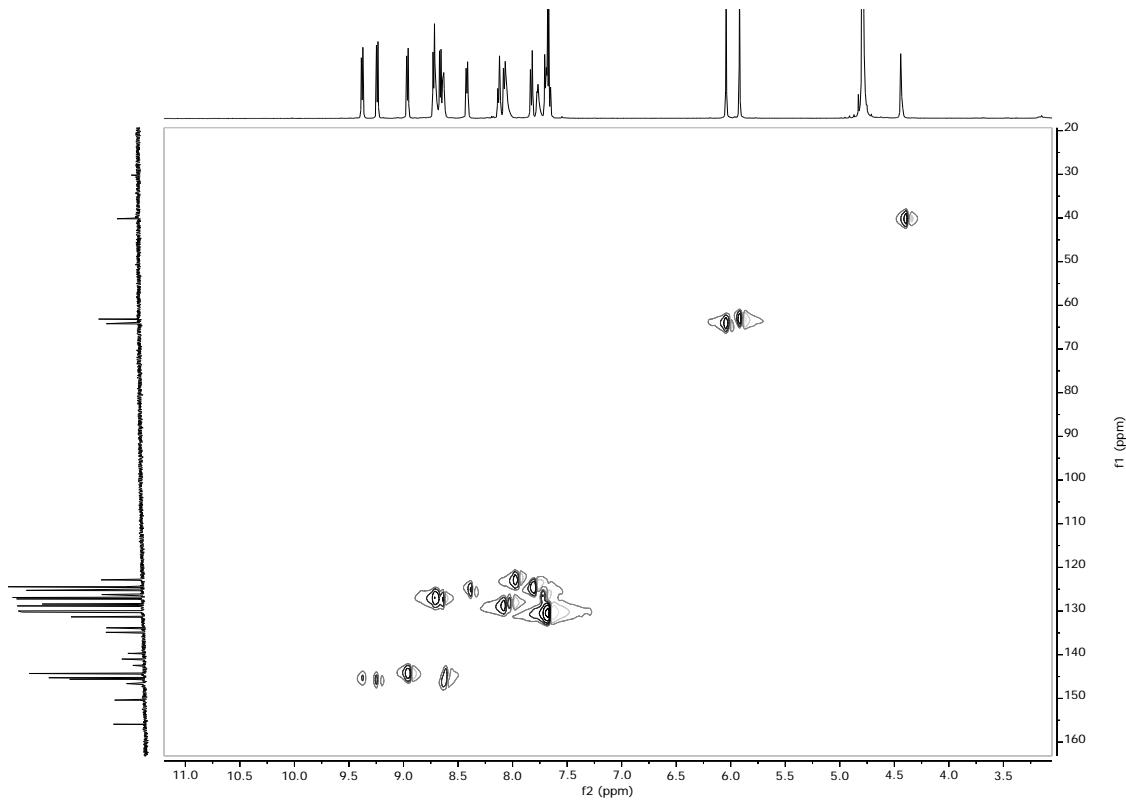


Figure S 34: HSQC (125 and 500MHz, D₂O) spectrum of **L6·3NO₃**.

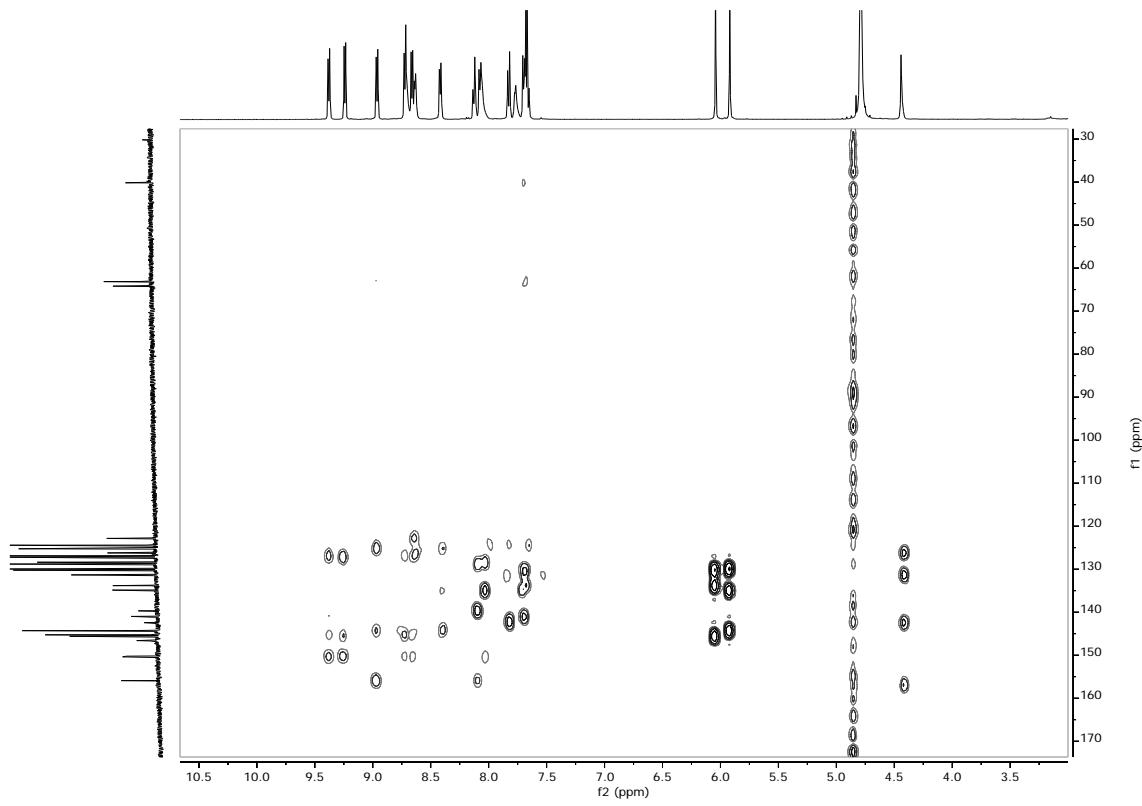


Figure S 35: HMBC (125 and 500MHz, D₂O) spectrum of L6·3NO₃.

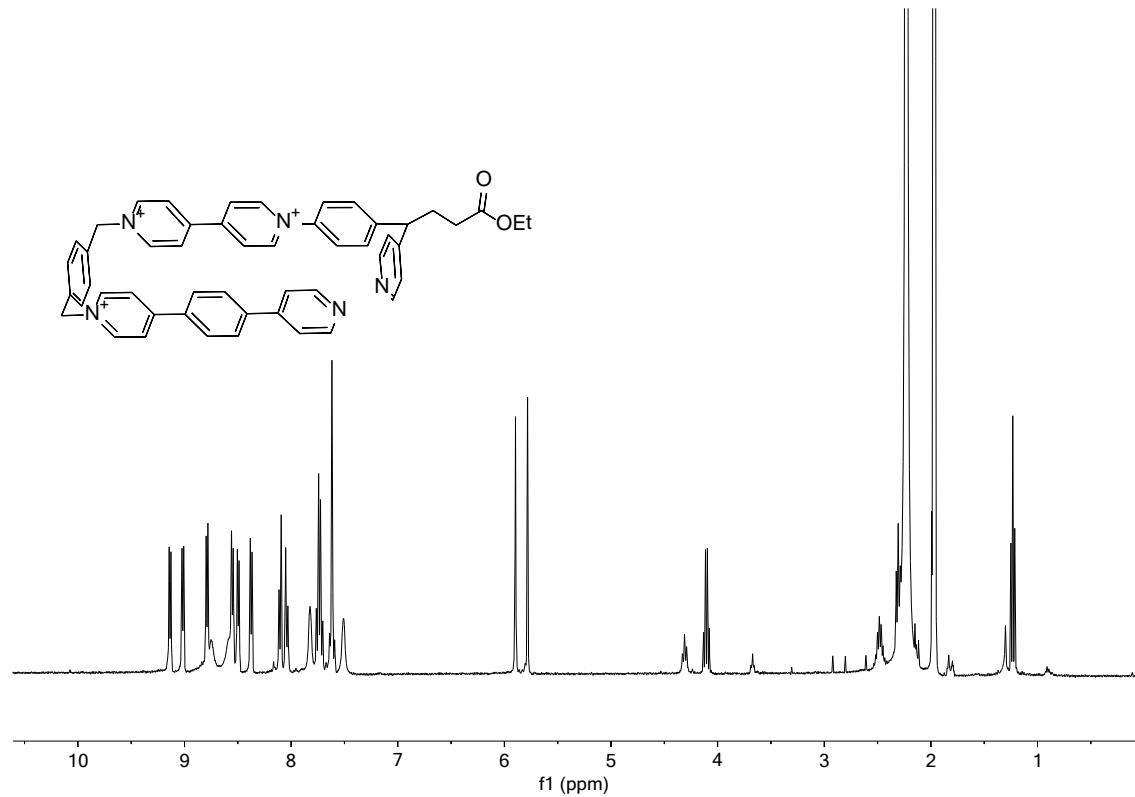


Figure S 36: ^1H RMN (500MHz, CD_3CN) spectrum of L7·3PF₆.

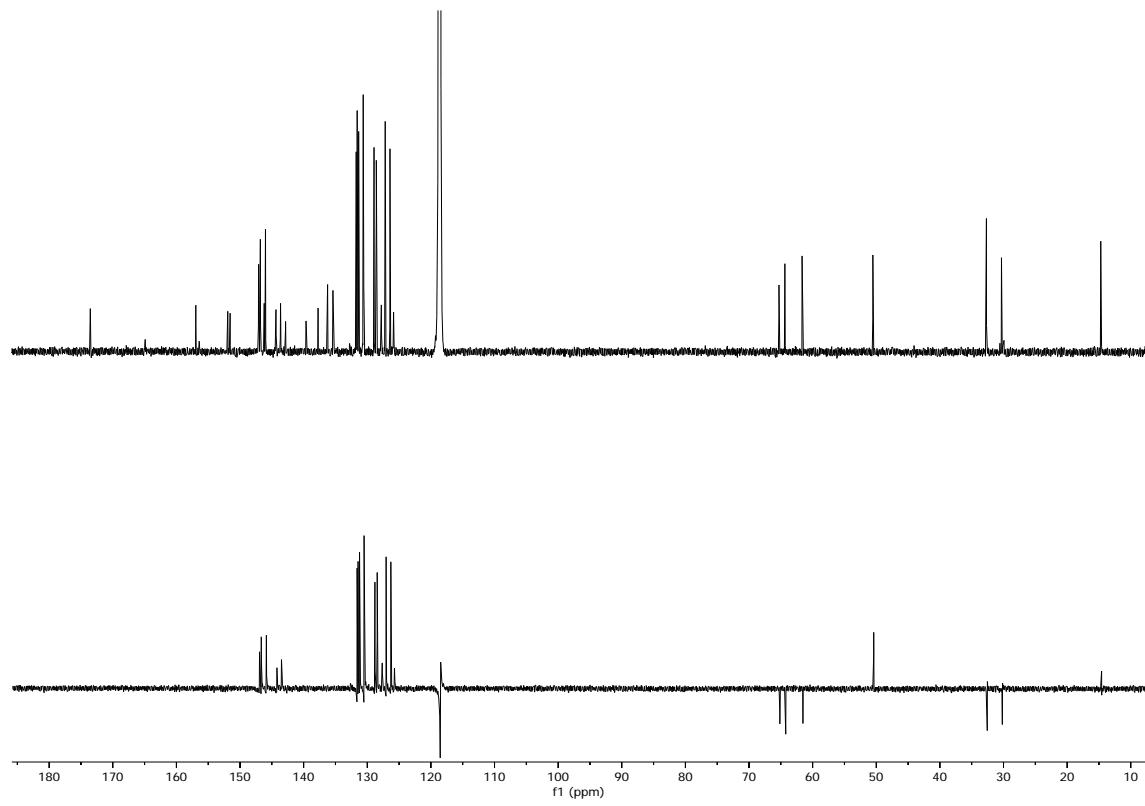


Figure S 37: ^{13}C and DEPT NMR (125 MHz, CD_3CN) spectrum of **L7·3PF₆**.

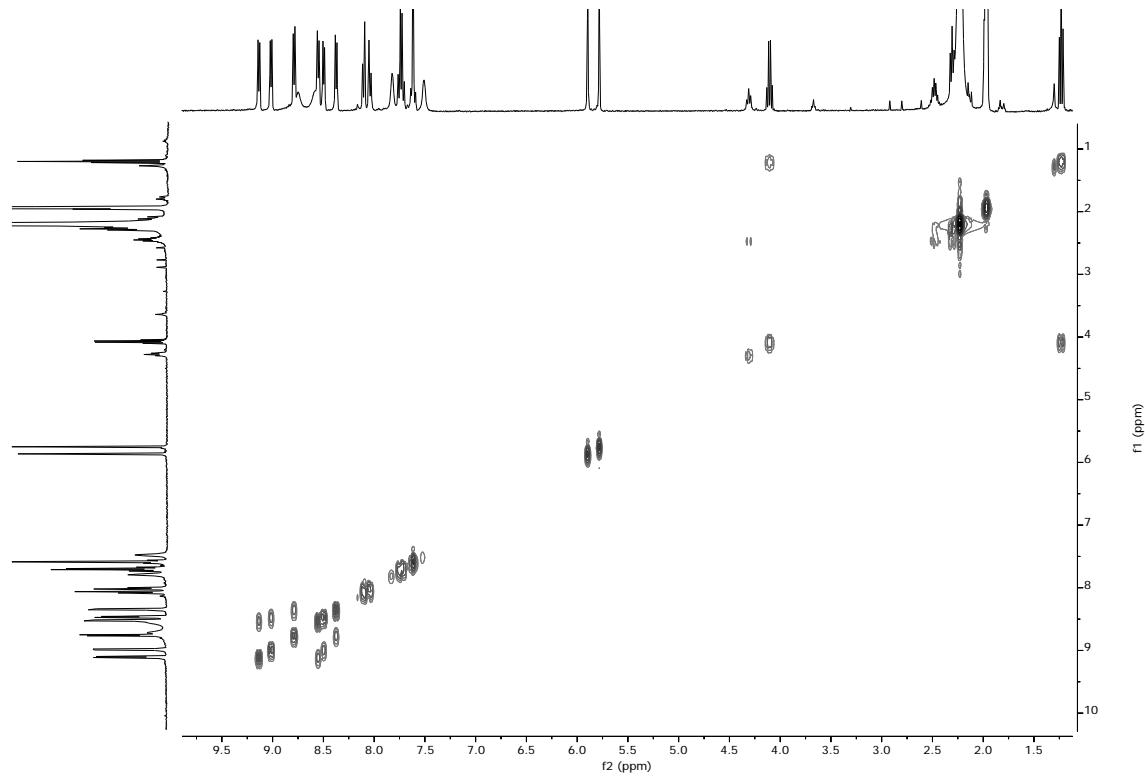


Figure S 38: COSY (500MHz, CD_3CN) spectrum of **L7·3PF₆**.

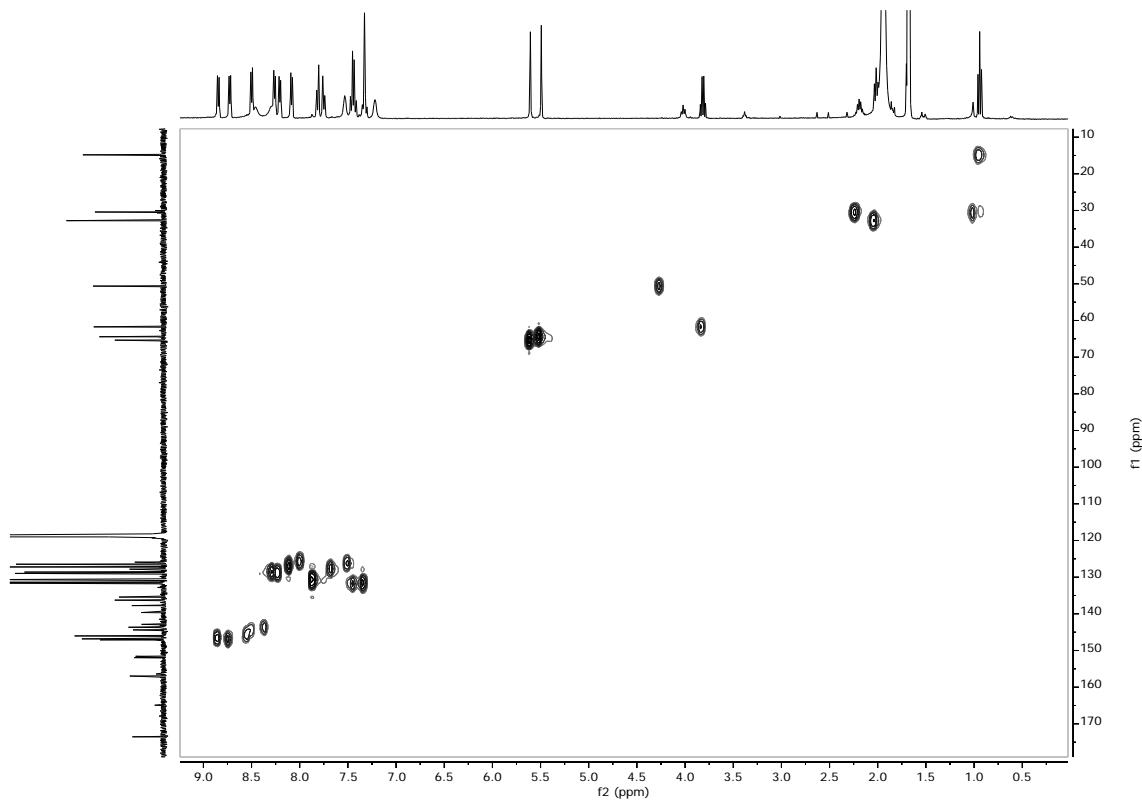


Figure S 39: HSQC (125 and 500MHz, CD_3CN) spectrum of $\mathbf{L7}\cdot\mathbf{3PF}_6$.

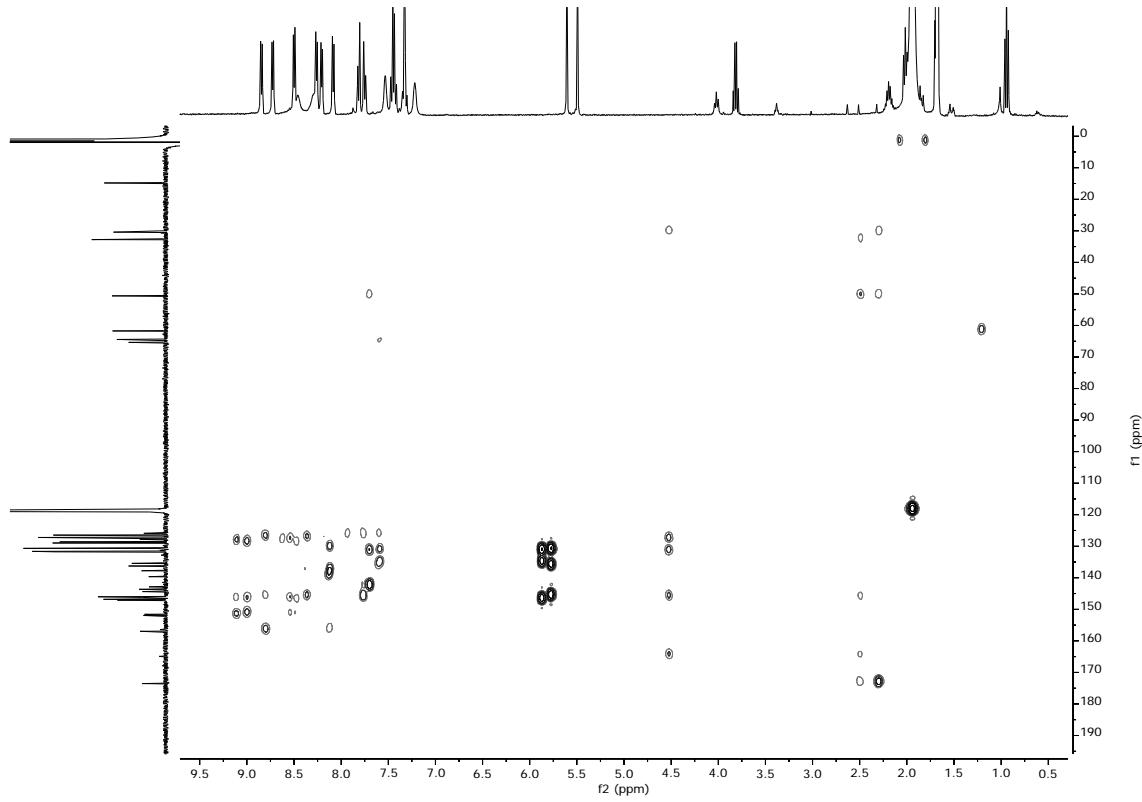


Figure S 40: HMBC (125 and 500MHz, CD_3CN) spectrum of $\mathbf{L7}\cdot\mathbf{3PF}_6$.

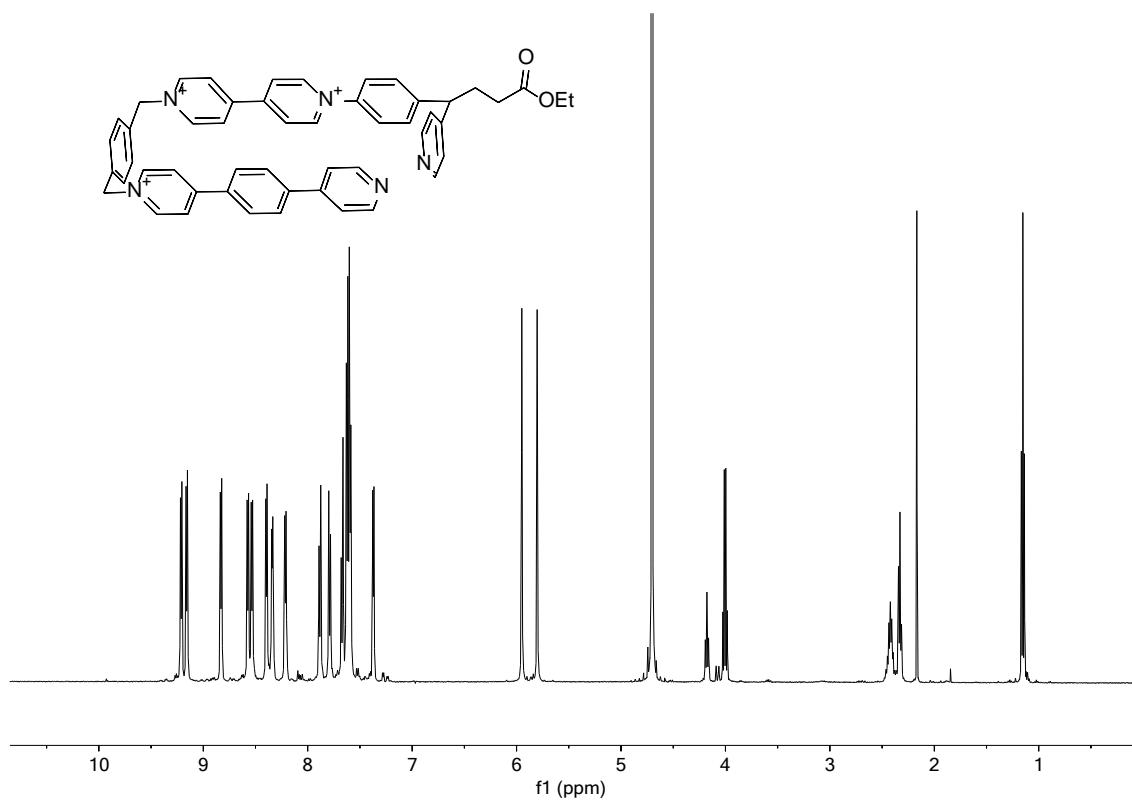


Figure S 41: ¹H RMN (500MHz, D₂O) spectrum of L73NO₃.

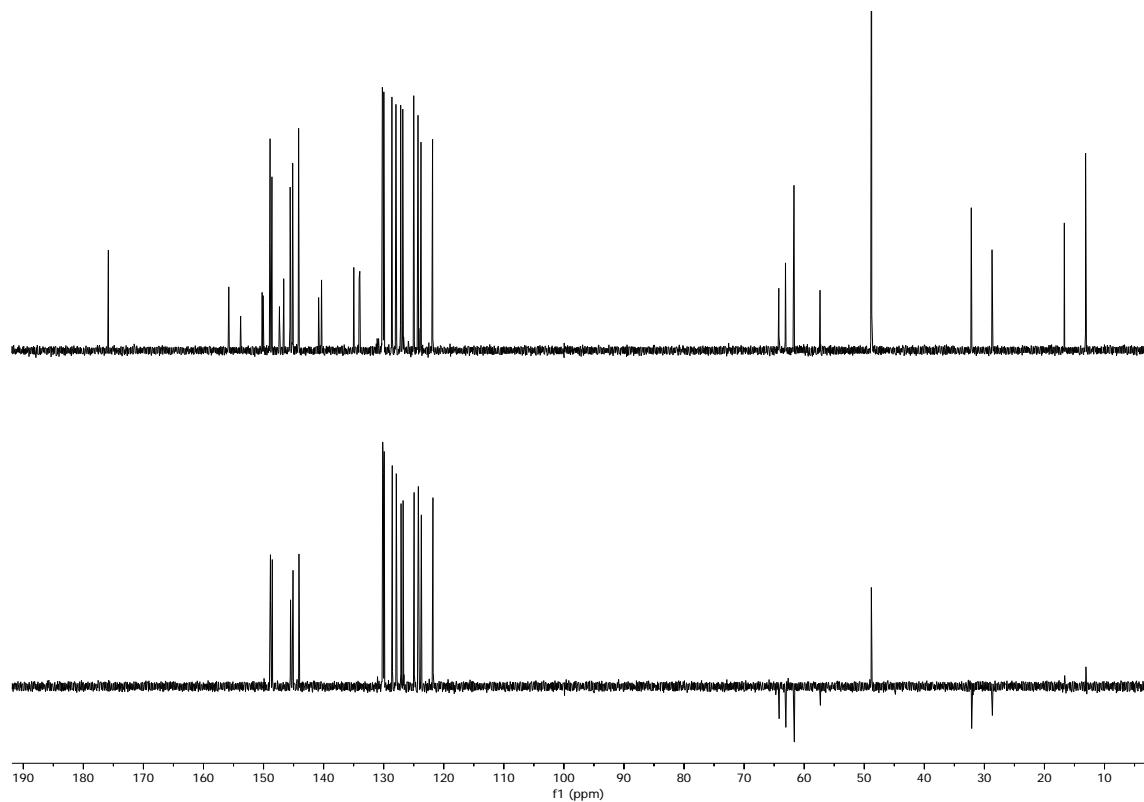


Figure S 42: ¹³C and DEPT NMR (125 MHz, D₂O) spectrum of L73NO₃.

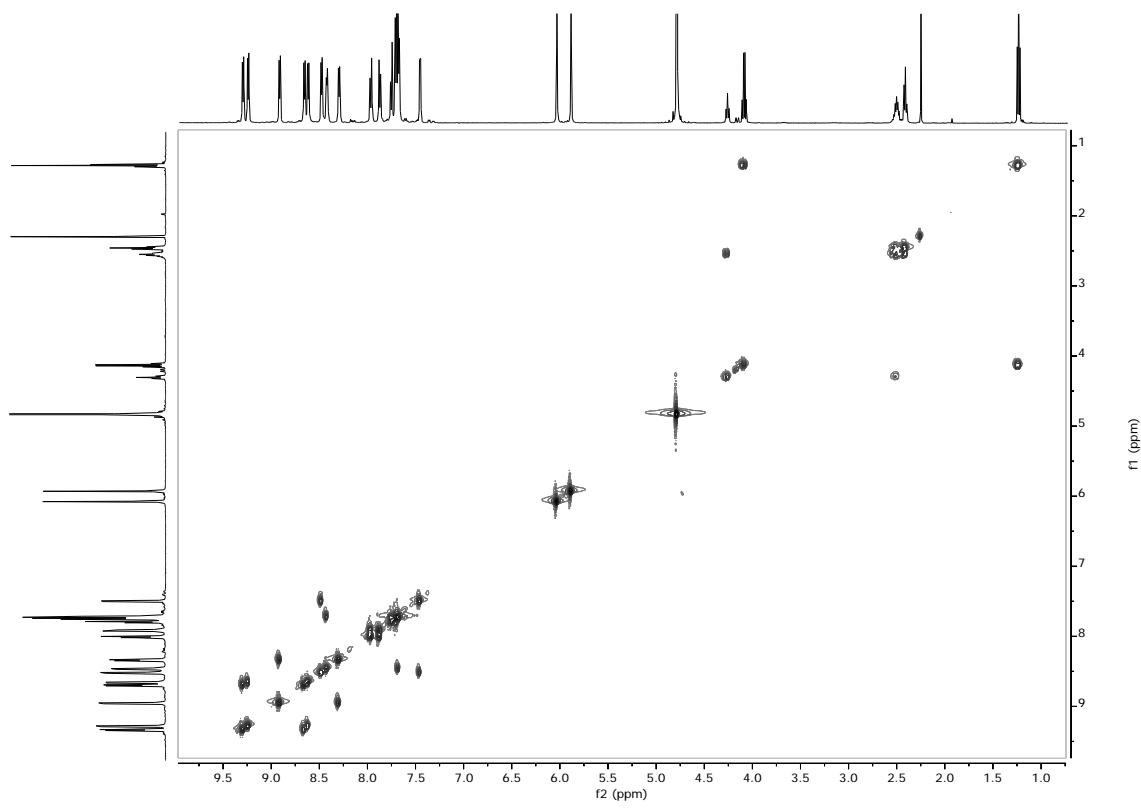


Figure S 43: COSY (500MHz, D₂O) spectrum of L7'3NO₃.

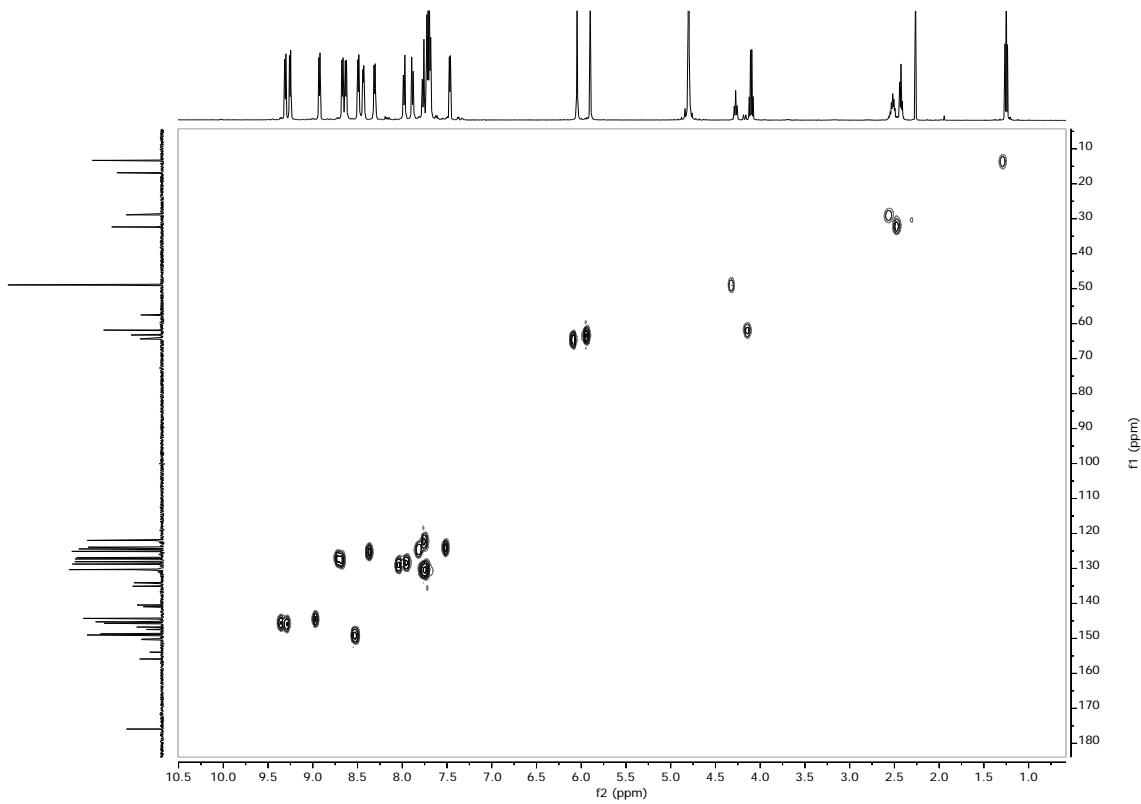


Figure S 44: HSQC (125 and 500MHz, D₂O) spectrum of L7'3NO₃.

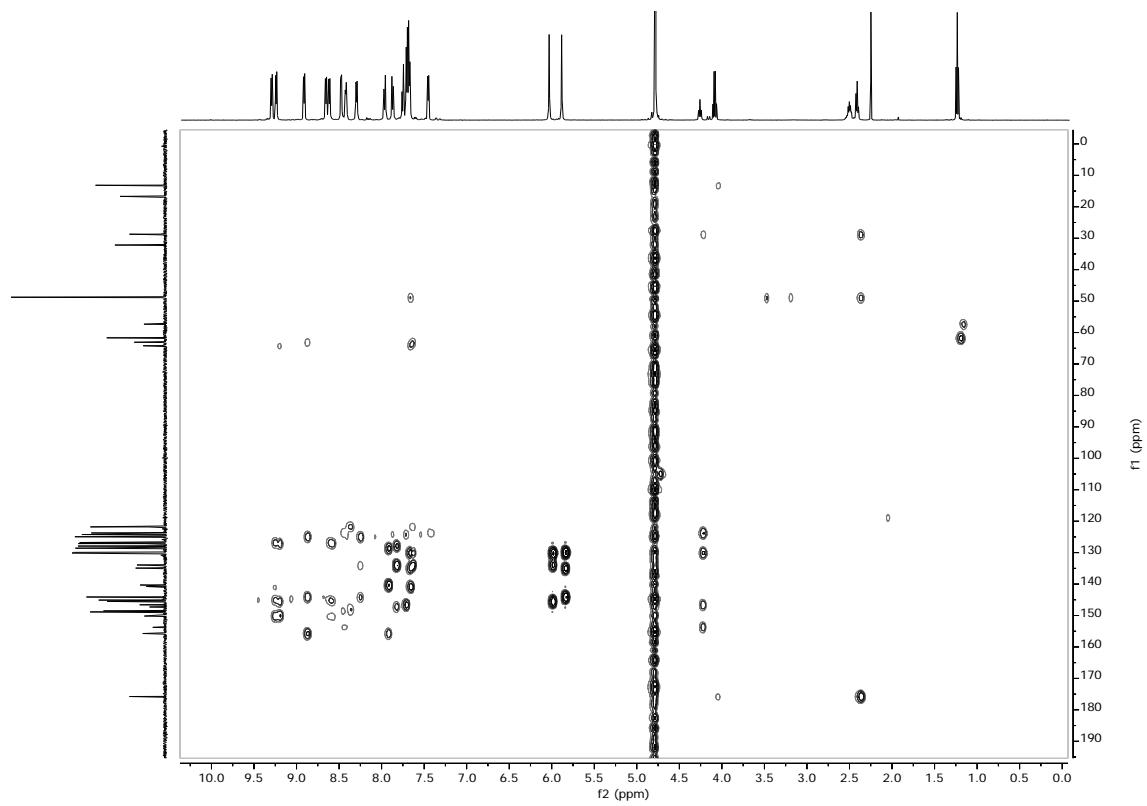


Figure S 45: HMBC (125 and 500MHz, D₂O) spectrum of L7·3NO₃.

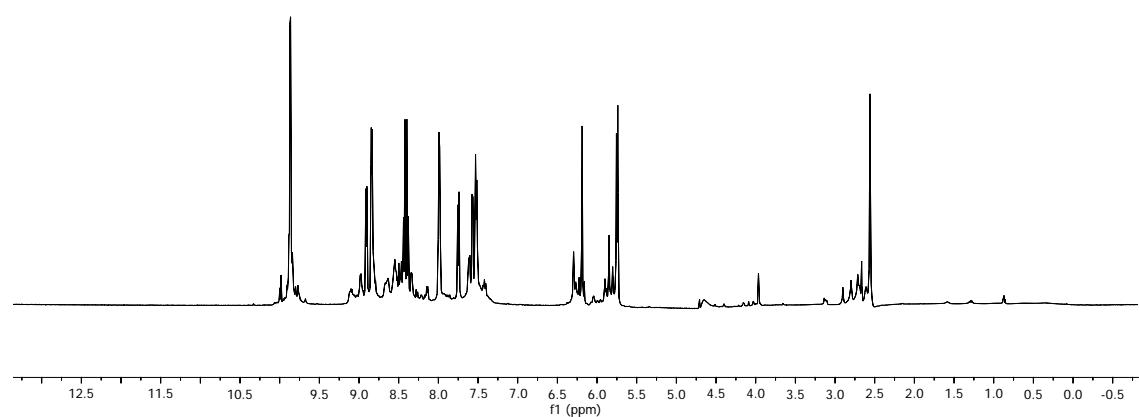
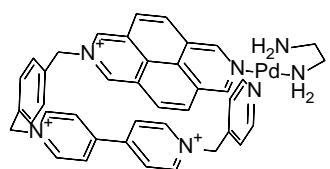


Figure S 46: ¹H RMN (500MHz, D₂O) spectrum of M4a·5NO₃.

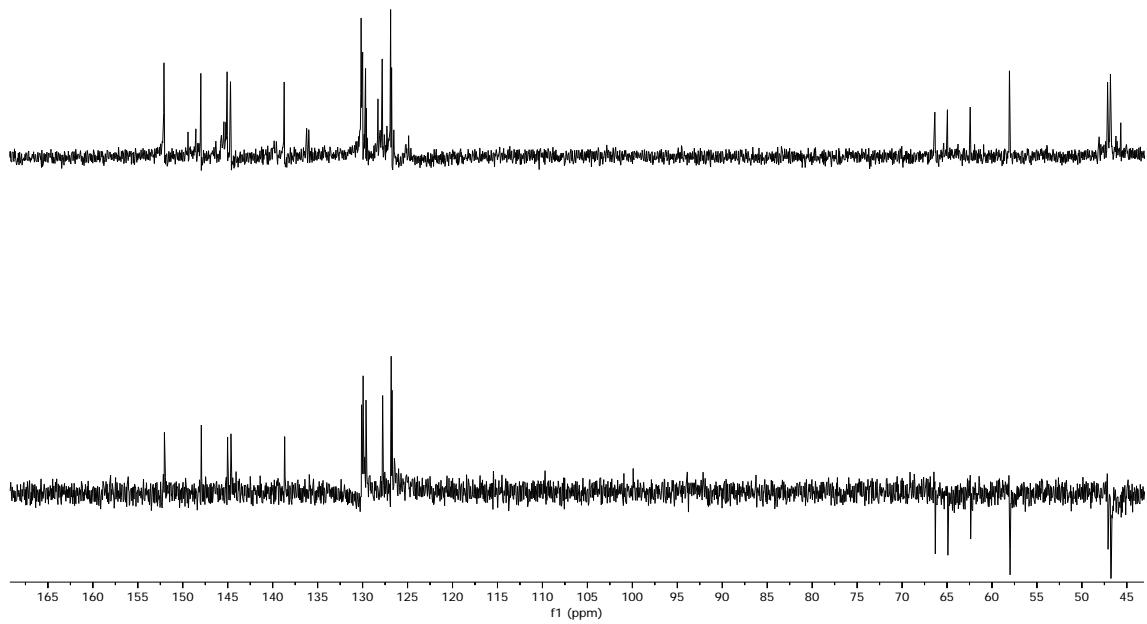


Figure S 47: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of $\text{M4a}\cdot\text{5NO}_3$.

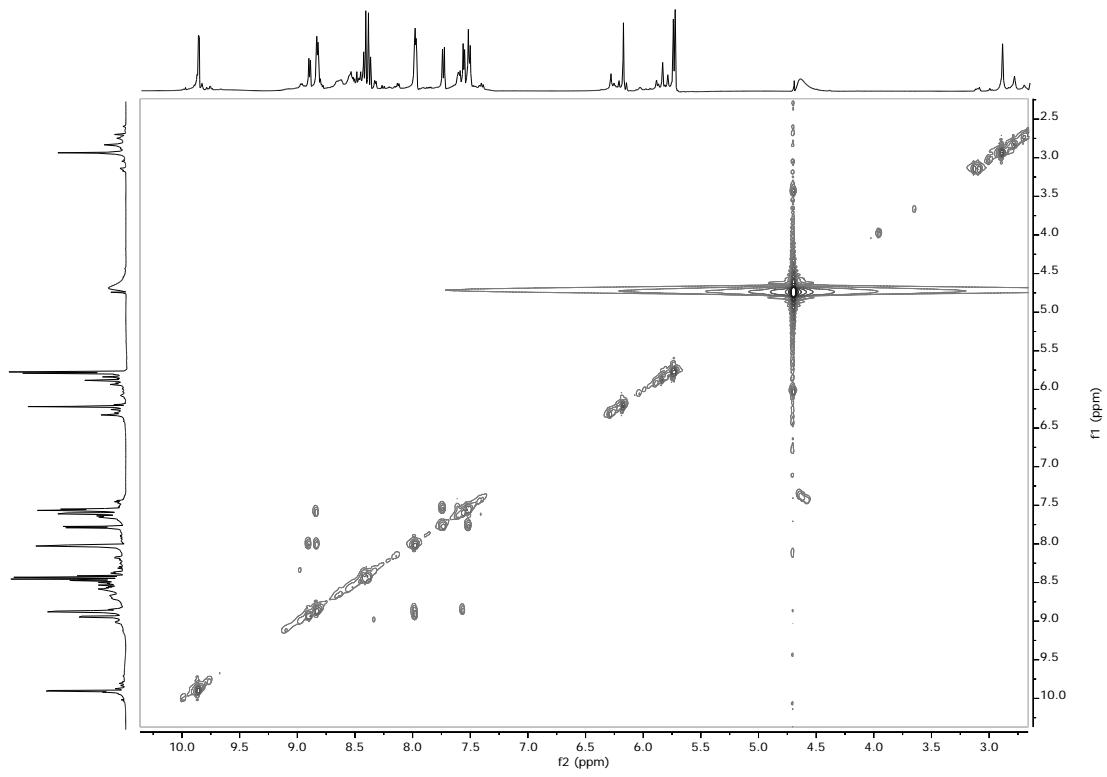


Figure S 48: COSY (500MHz, D_2O) spectrum of $\text{M4a}\cdot\text{5NO}_3$.

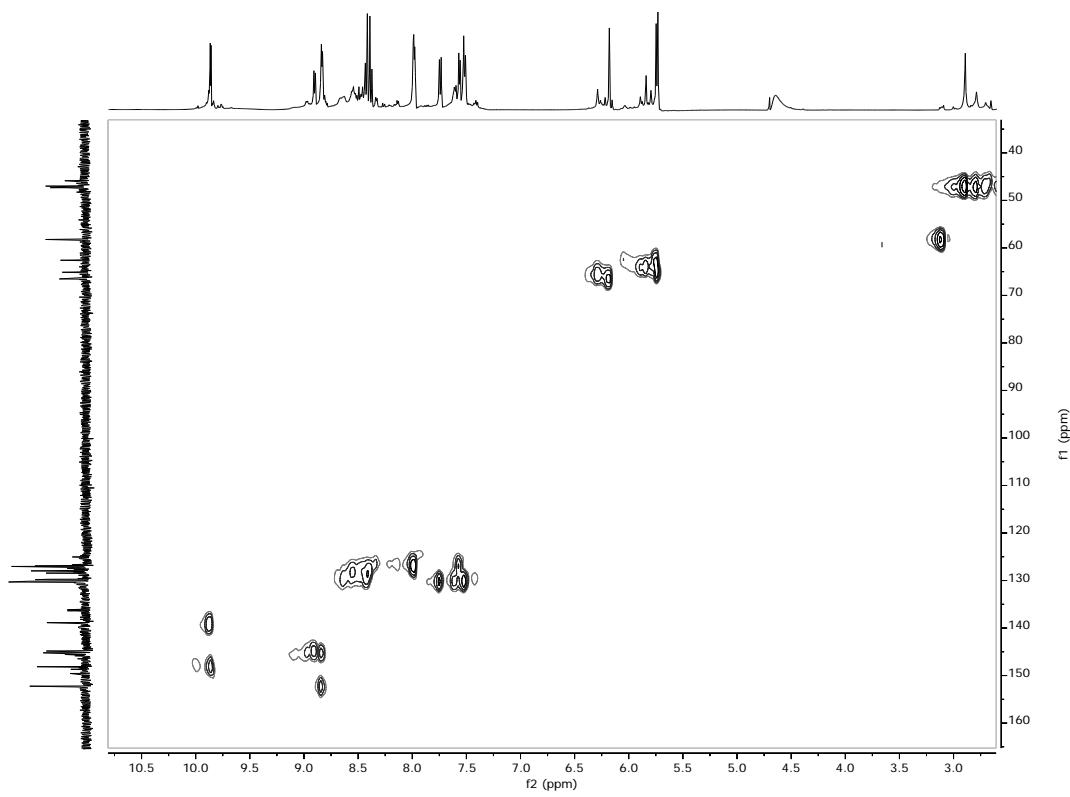


Figure S 49: HSQC (125 and 500MHz, D₂O) spectrum of **M4a·5NO₃**.

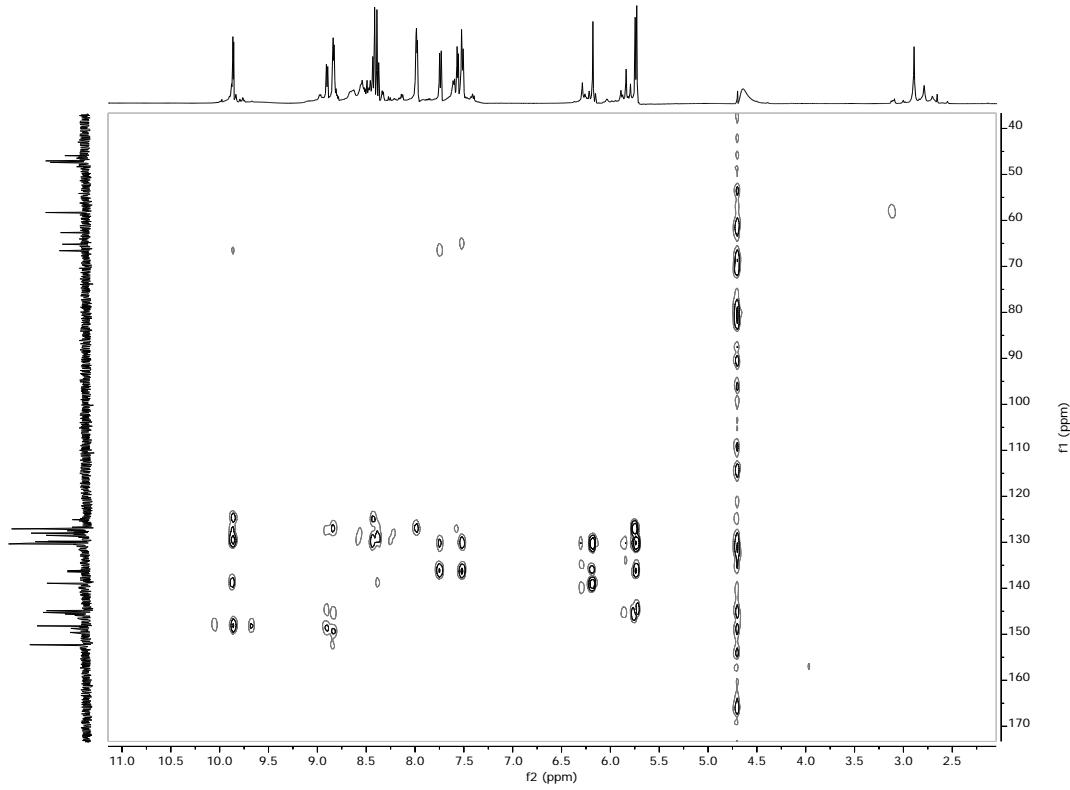


Figure S 50: HMBC (125 and 500MHz, D₂O) spectrum of **M4a·5NO₃**.

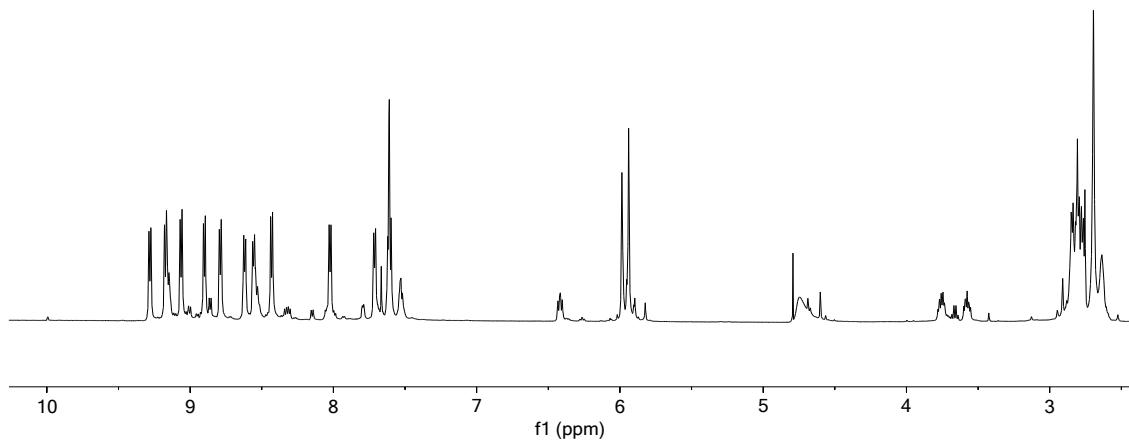
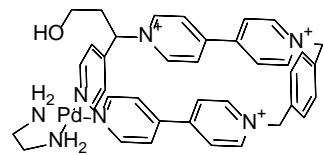


Figure S 51: ^1H RMN (500MHz, D_2O) spectrum of $\text{M5a}\cdot\text{5NO}_3$.

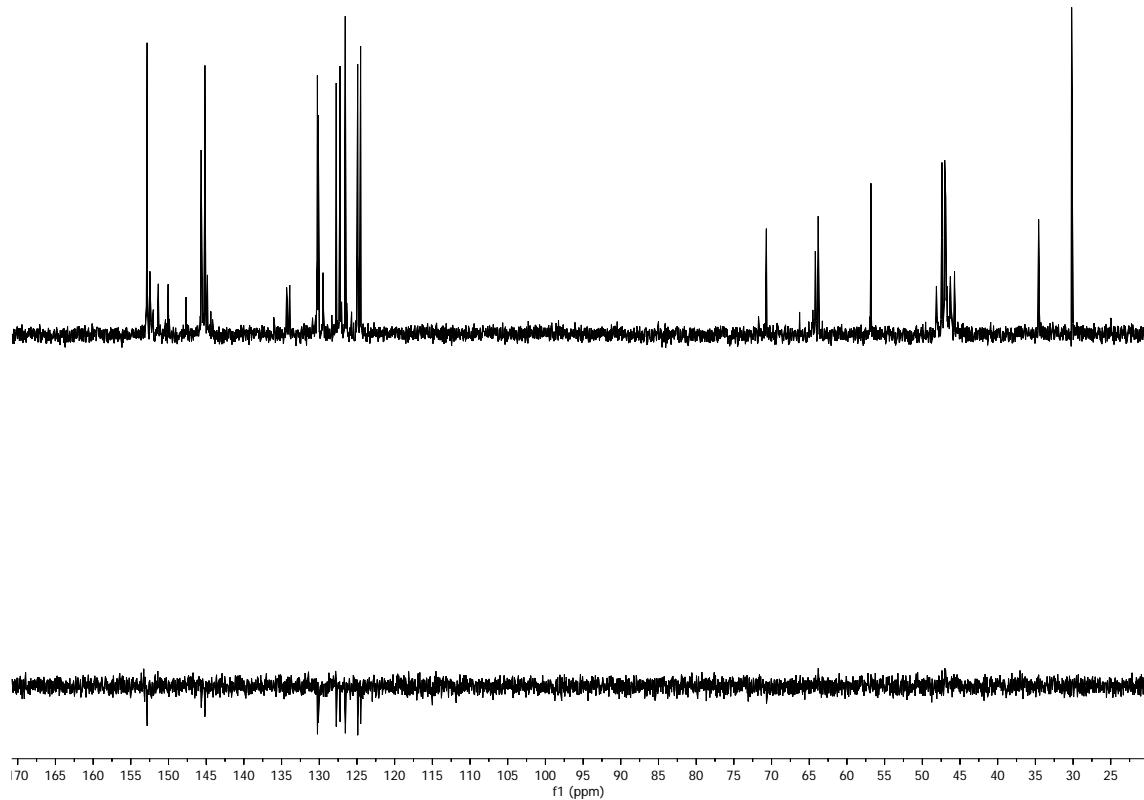


Figure S 52: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of $\text{M5a}\cdot\text{5NO}_3$.

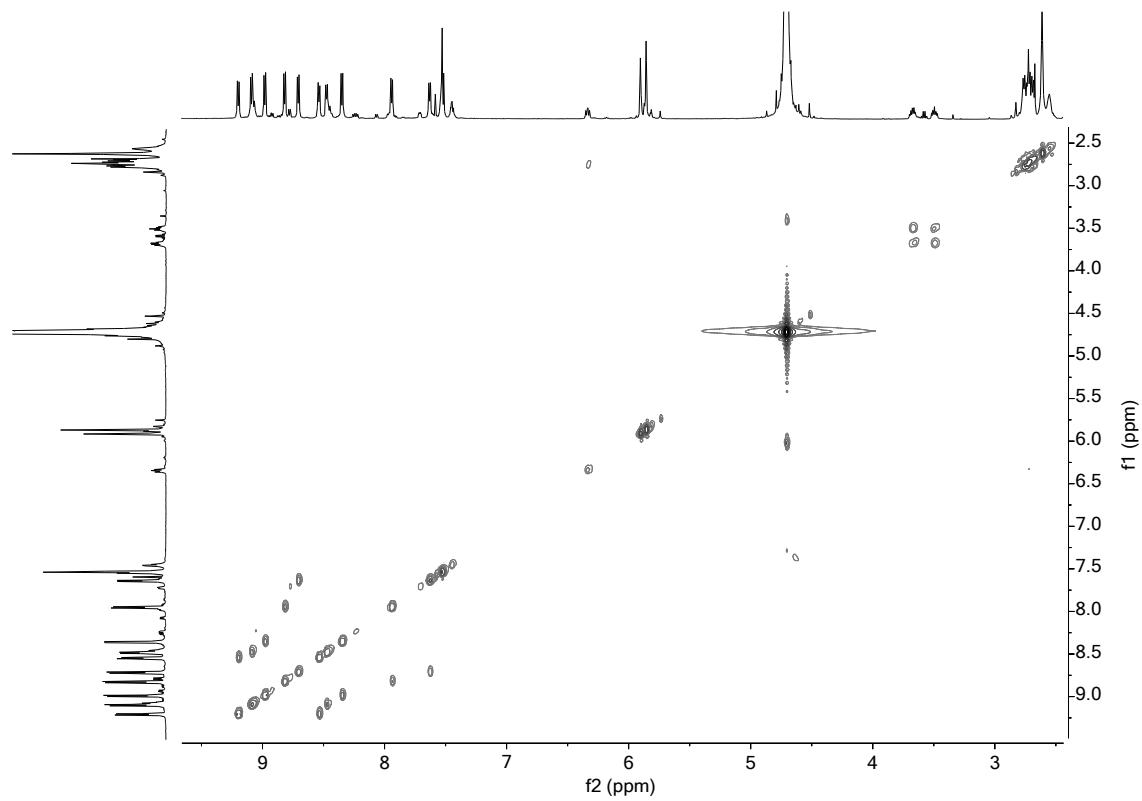


Figure S 53: COSY (500MHz, D₂O) spectrum of **M5a·5NO₃**.

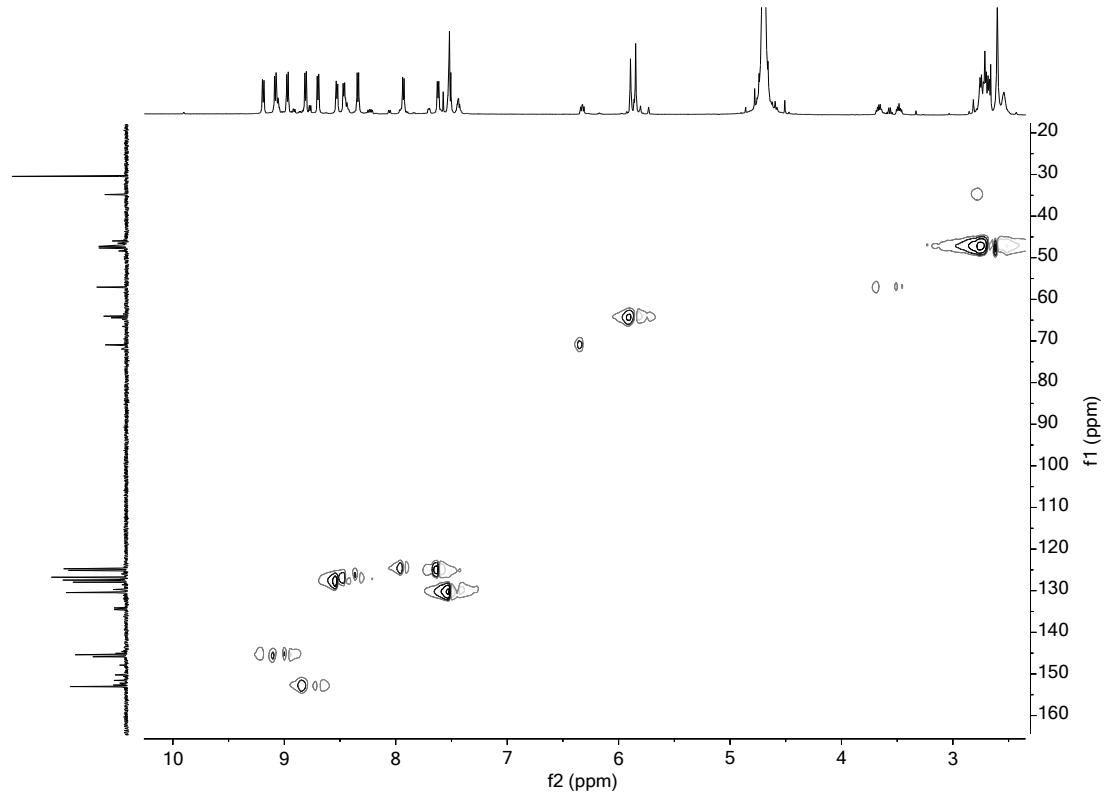


Figure S 54: HSQC (125 and 500MHz, D₂O) spectrum of **M5a·5NO₃**.

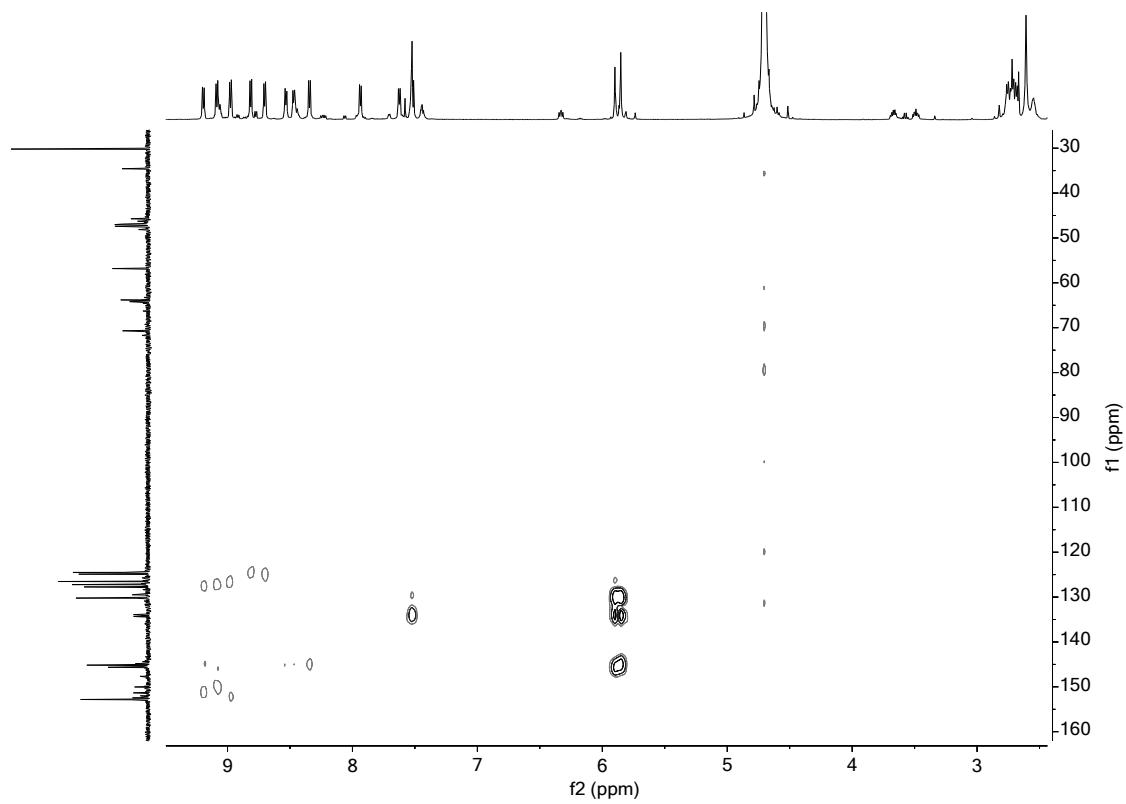


Figure S 55: HMBC (125 and 500MHz, D₂O) spectrum of **M5a·5NO₃**.

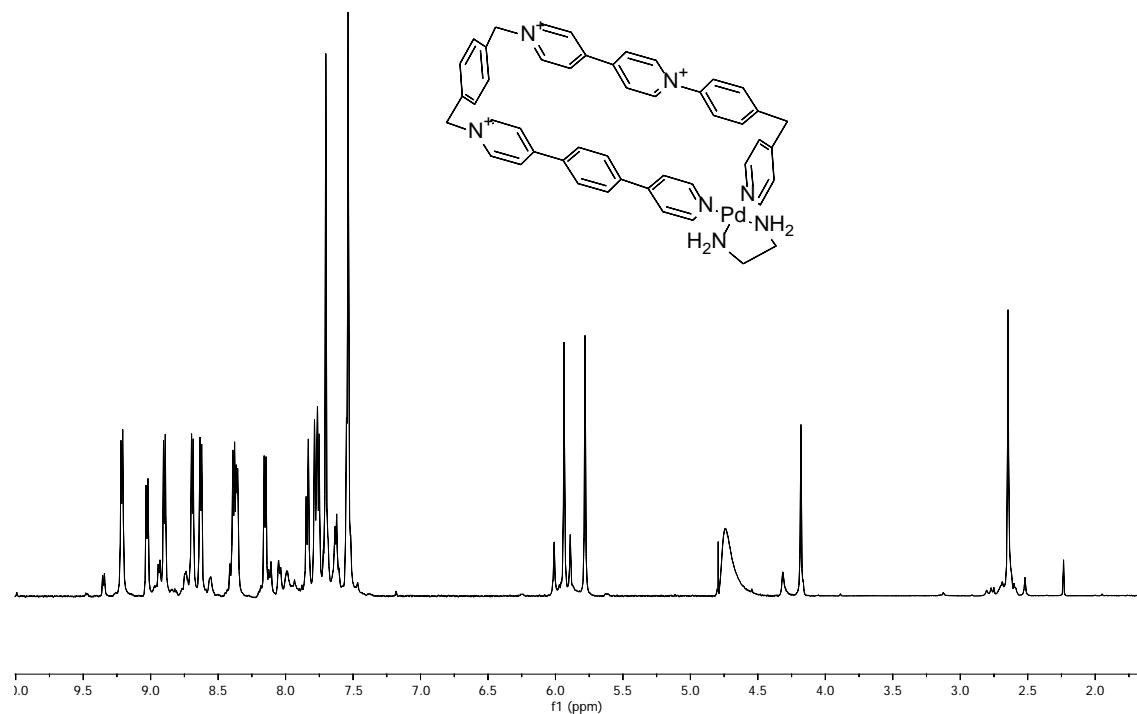


Figure S 56: ¹H RMN (500MHz, D₂O) spectrum of **M6a·5NO₃**.

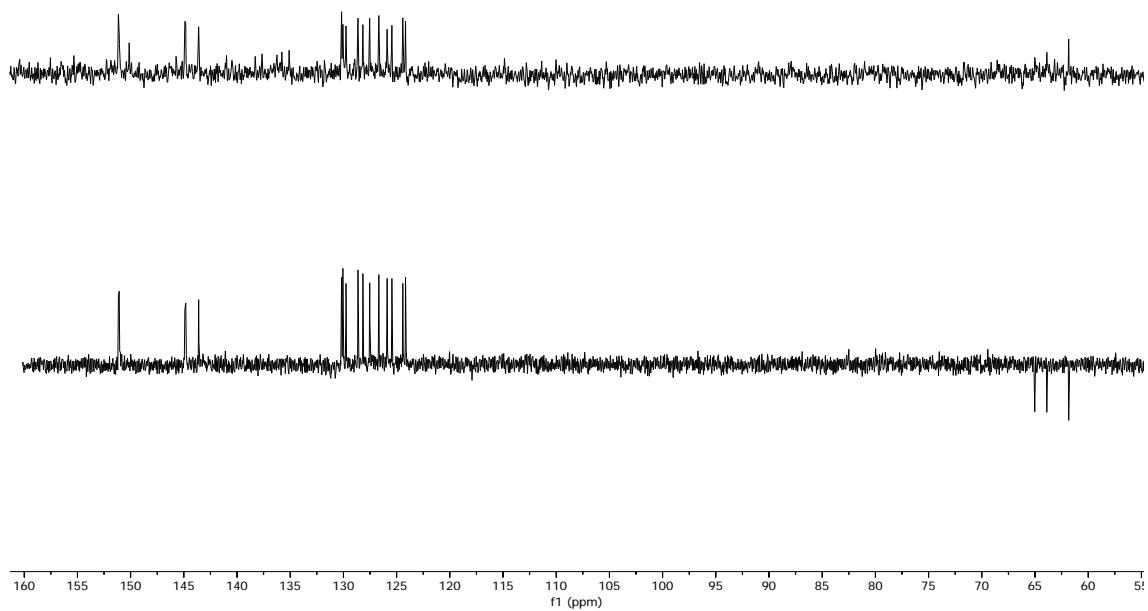


Figure S 57: ¹³C and DEPT NMR (125 MHz, D₂O) spectrum of M6a·5NO₃.

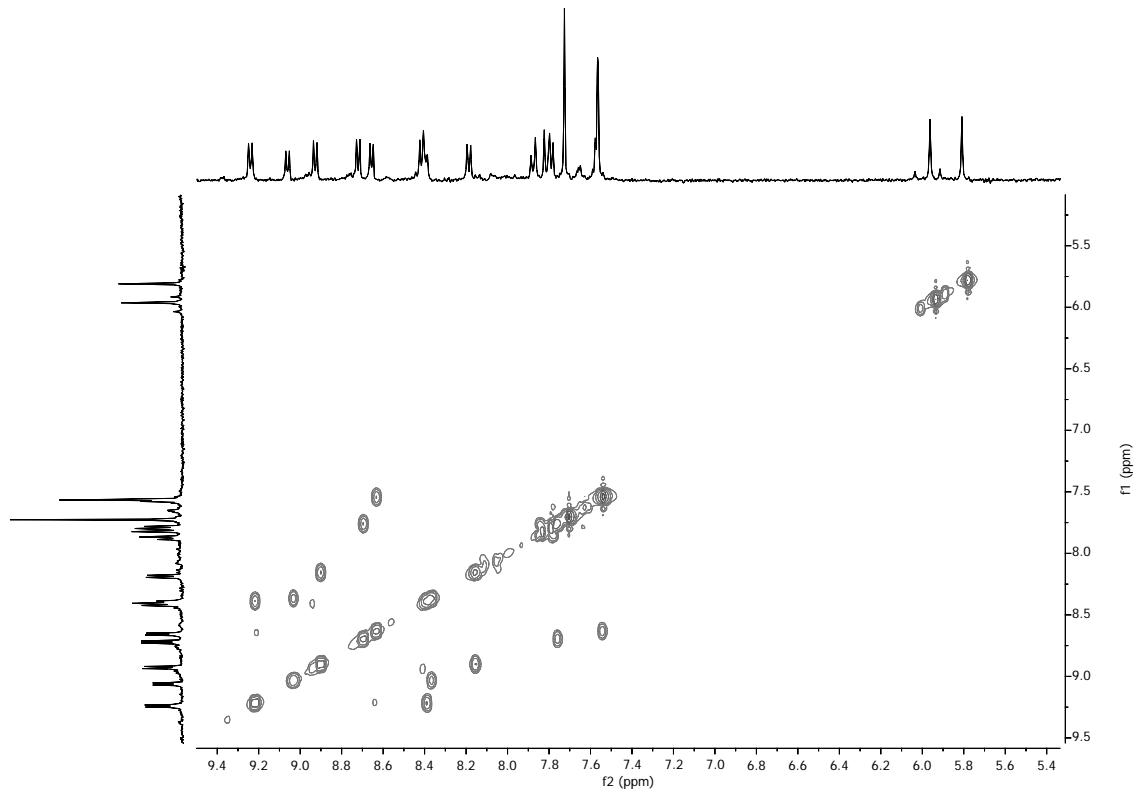


Figure S 58: COSY (500MHz, D₂O) spectrum of M6a·5NO₃.

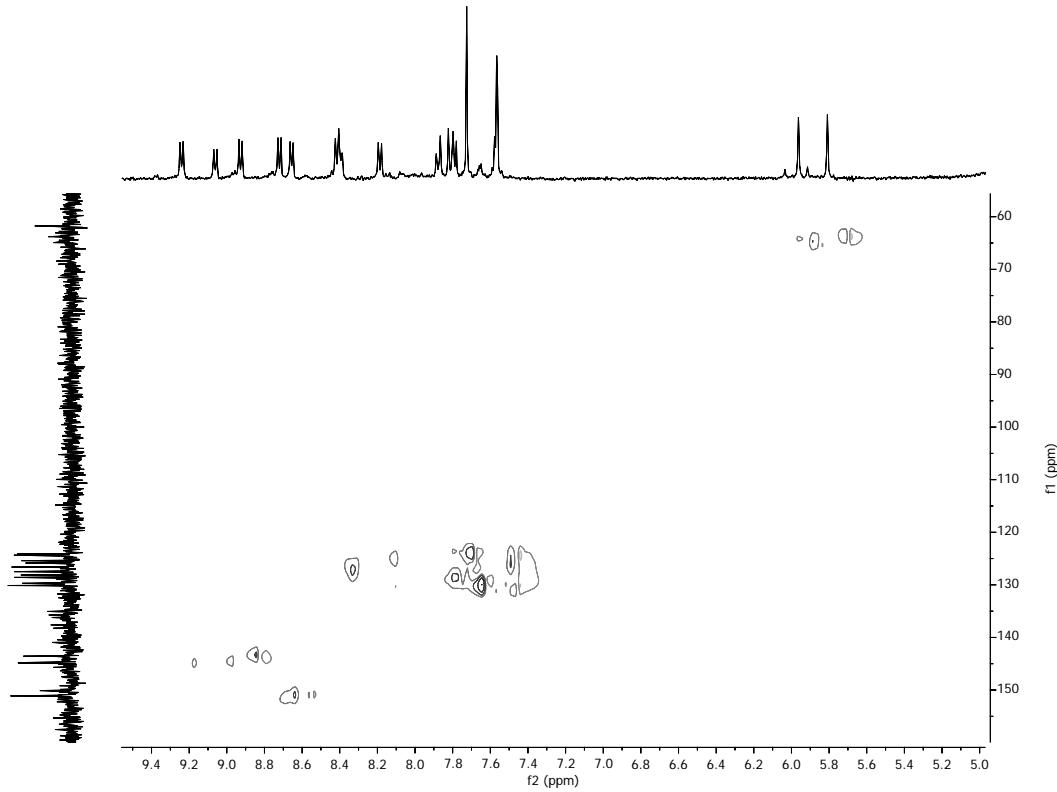


Figure S 59: HSQC (125 and 500MHz, D₂O) spectrum of **M6a·5NO₃**.

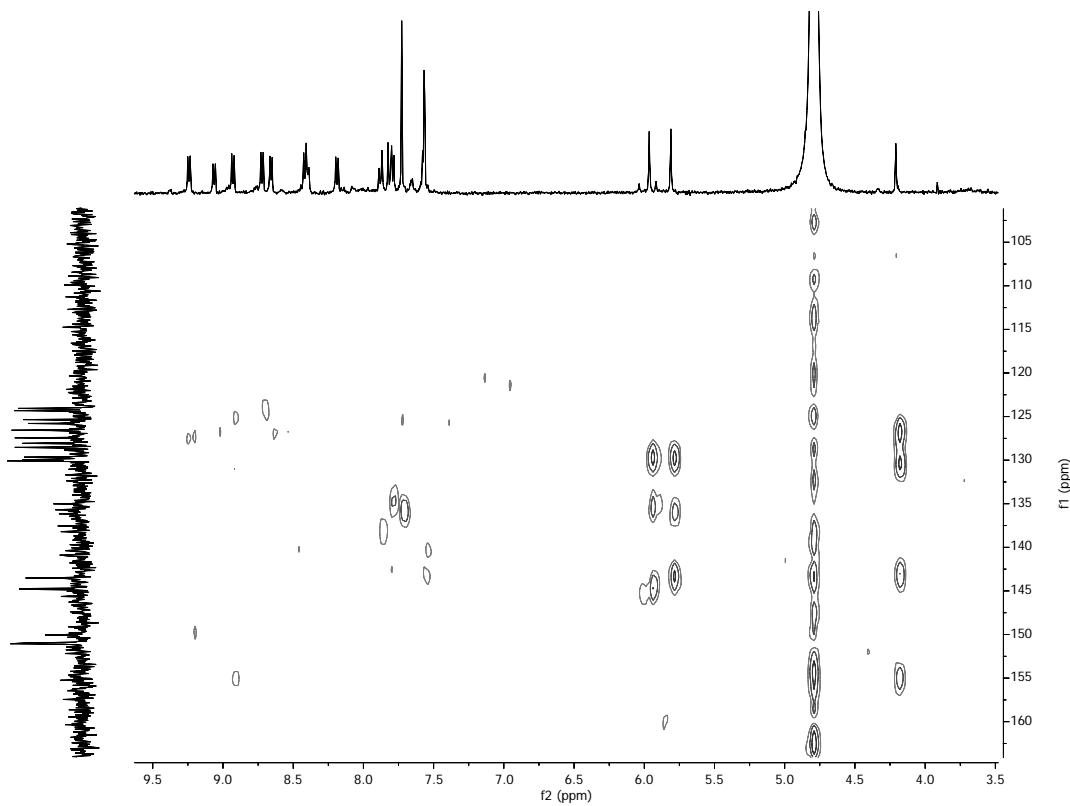


Figure S 60: HMBC (125 and 500MHz, D₂O) spectrum of **M6a·5NO₃**.

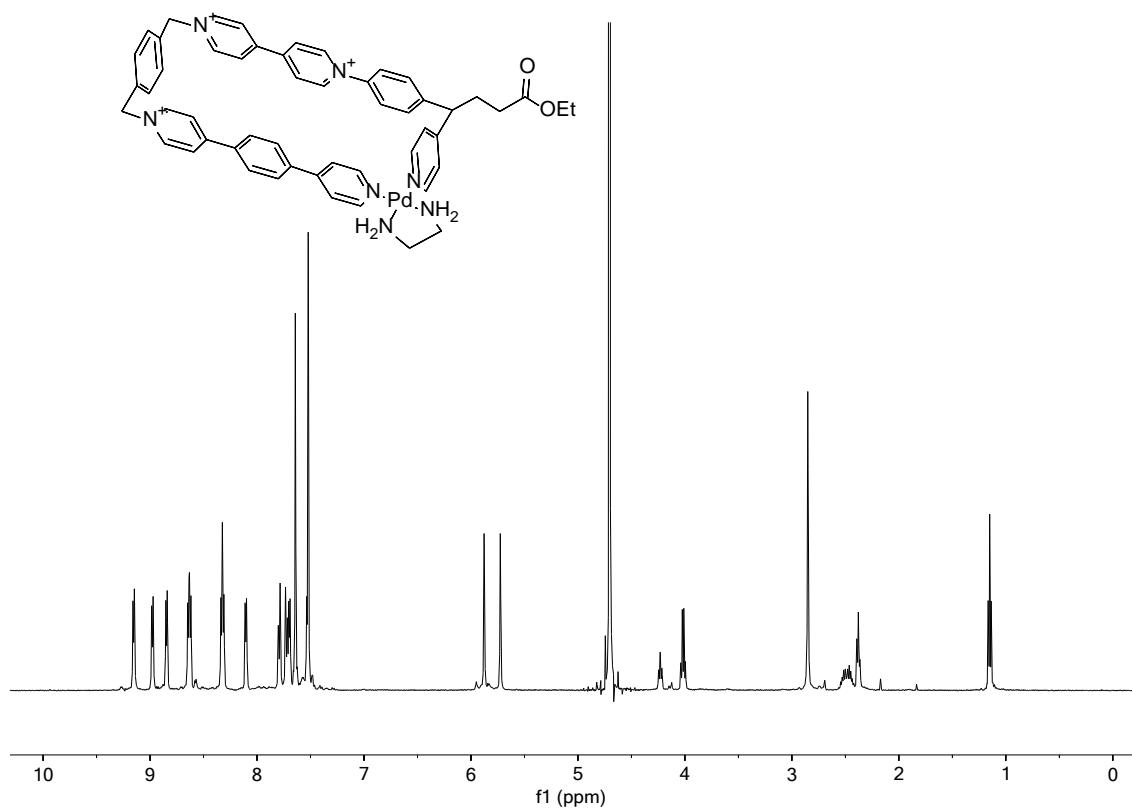


Figure S 61: ^1H RMN (500MHz, D_2O) spectrum of $\text{M7a}\cdot\text{5NO}_3$.

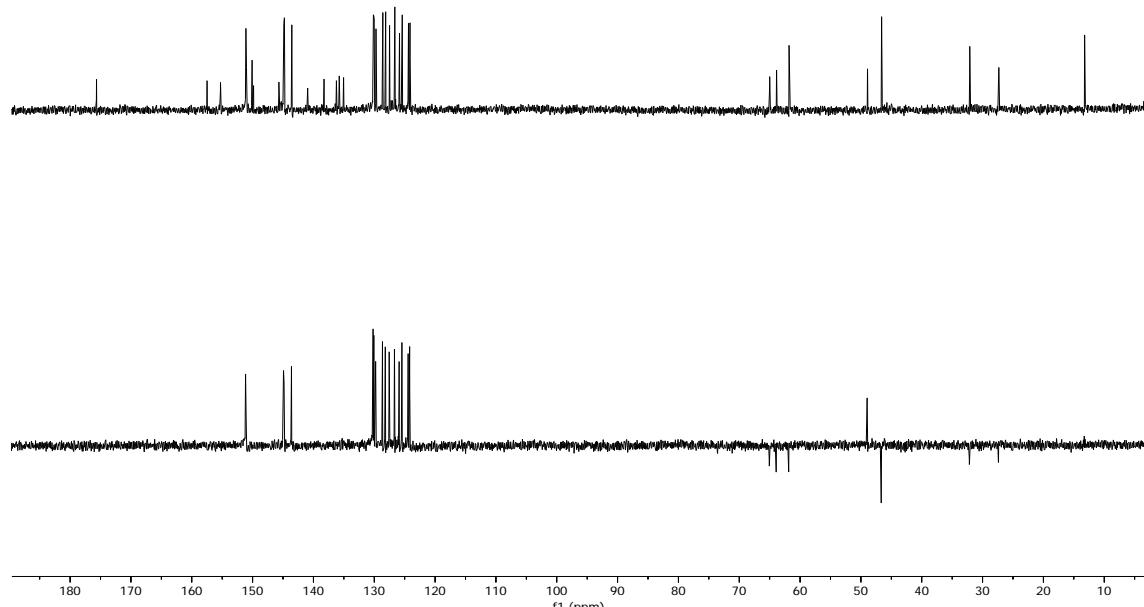


Figure S 62: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of $\text{M7a}\cdot\text{5NO}_3$.

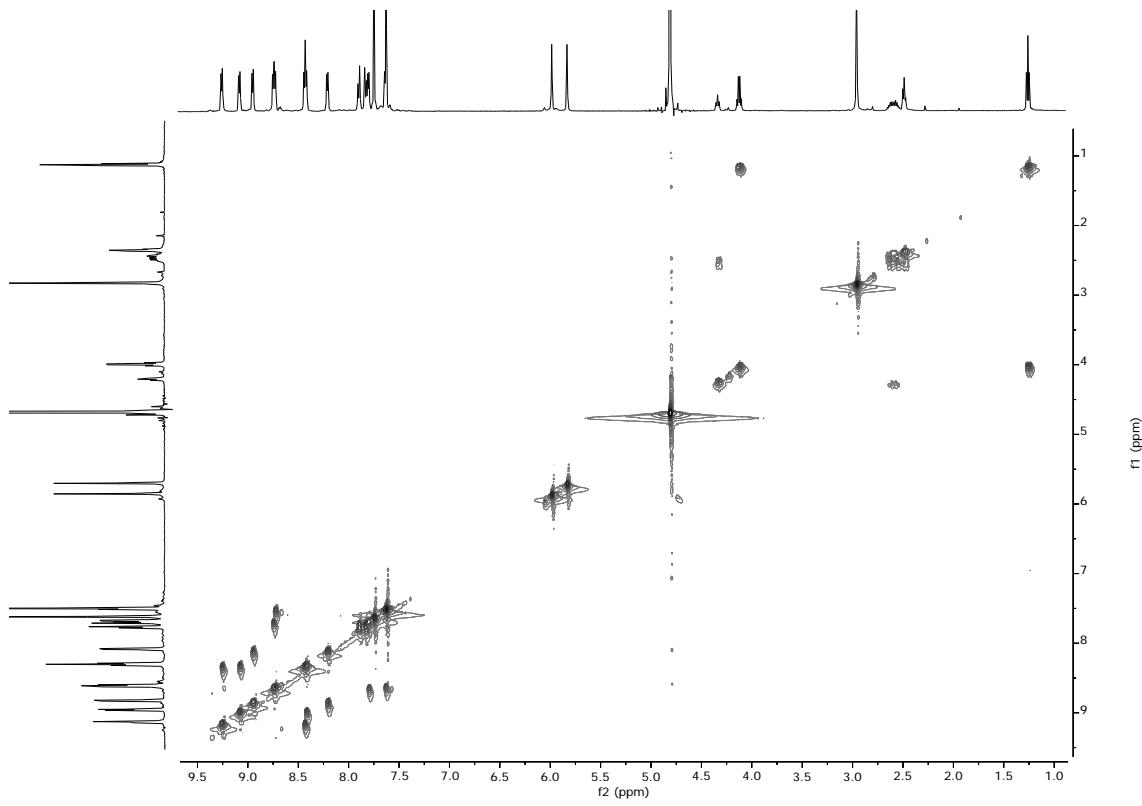


Figure S 63: COSY (500MHz, D₂O) spectrum of M7a·5NO₃.

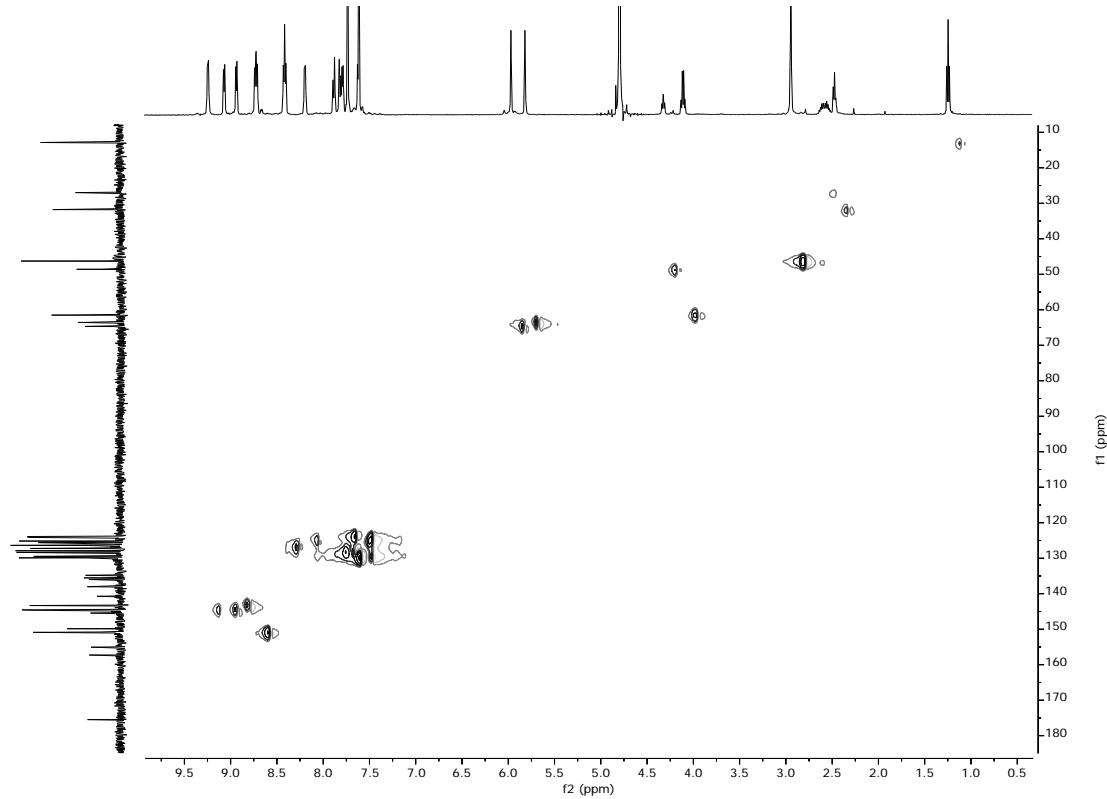


Figure S 64: HSQC (125 and 500MHz, D₂O) spectrum of M7a·5NO₃.

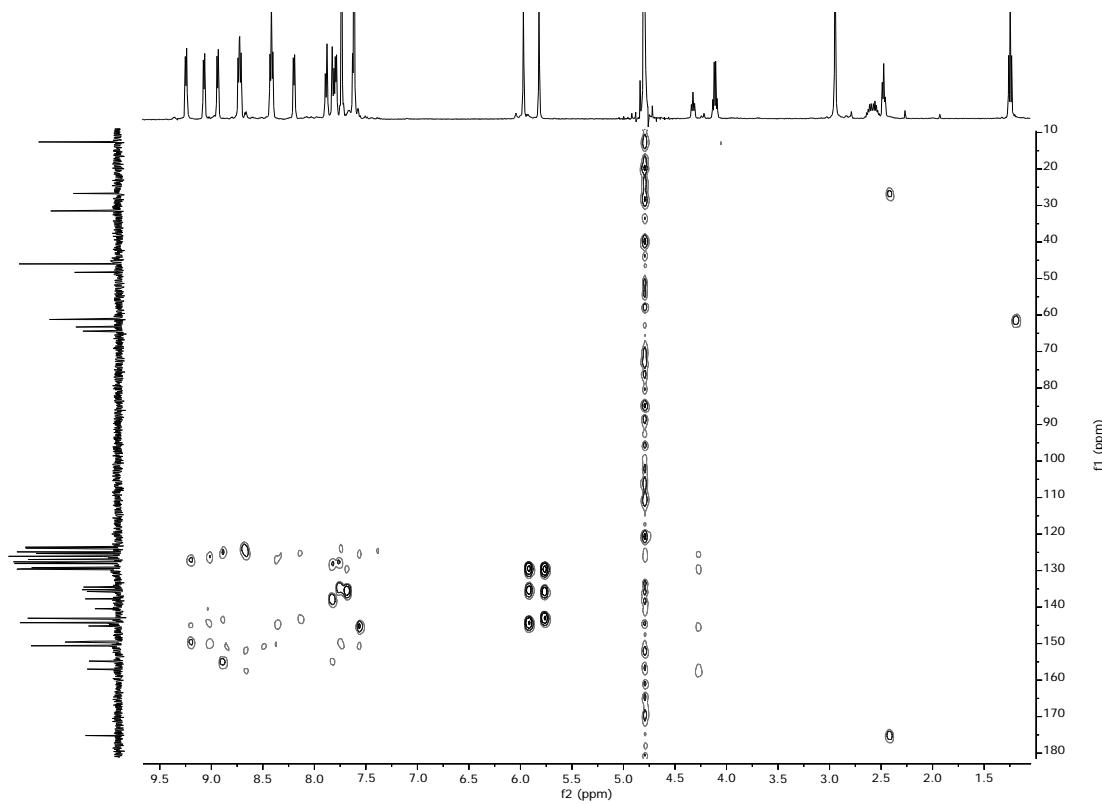


Figure S 65: HMBC (125 and 500MHz, D₂O) spectrum of M7a·5NO₃.

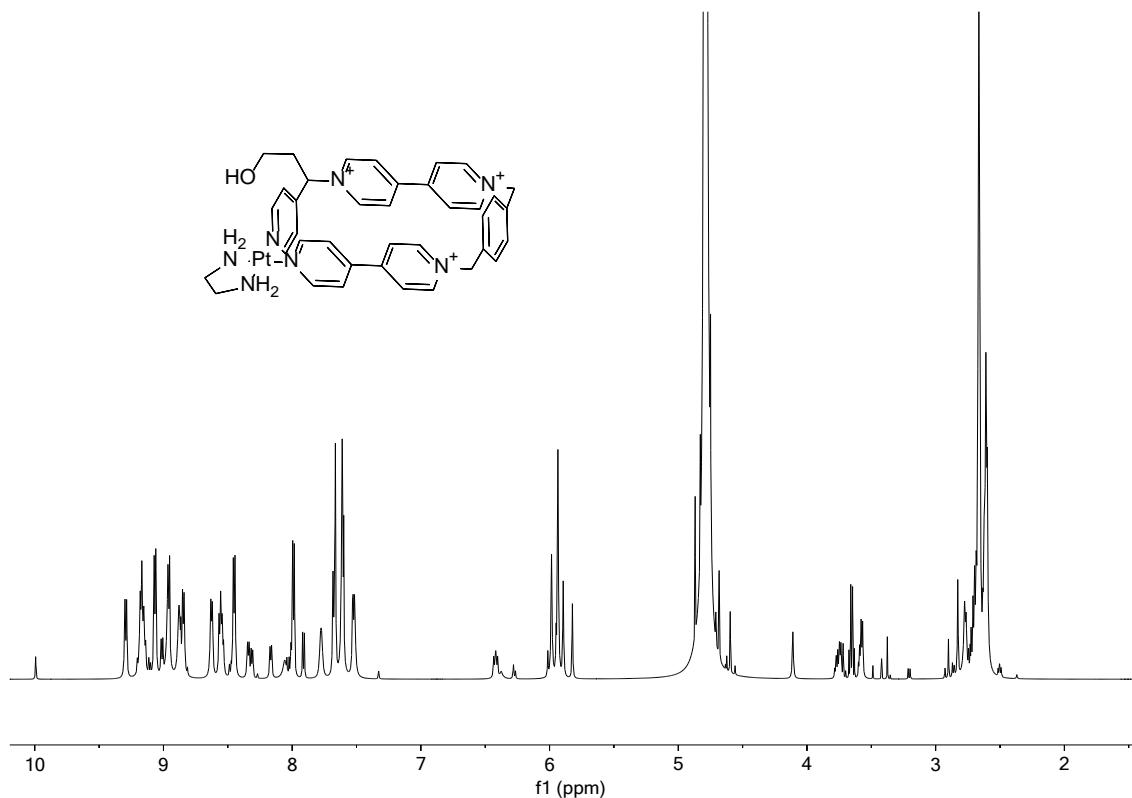


Figure S 66: ¹H RMN (500MHz, D₂O) spectrum of M5b·5NO₃.

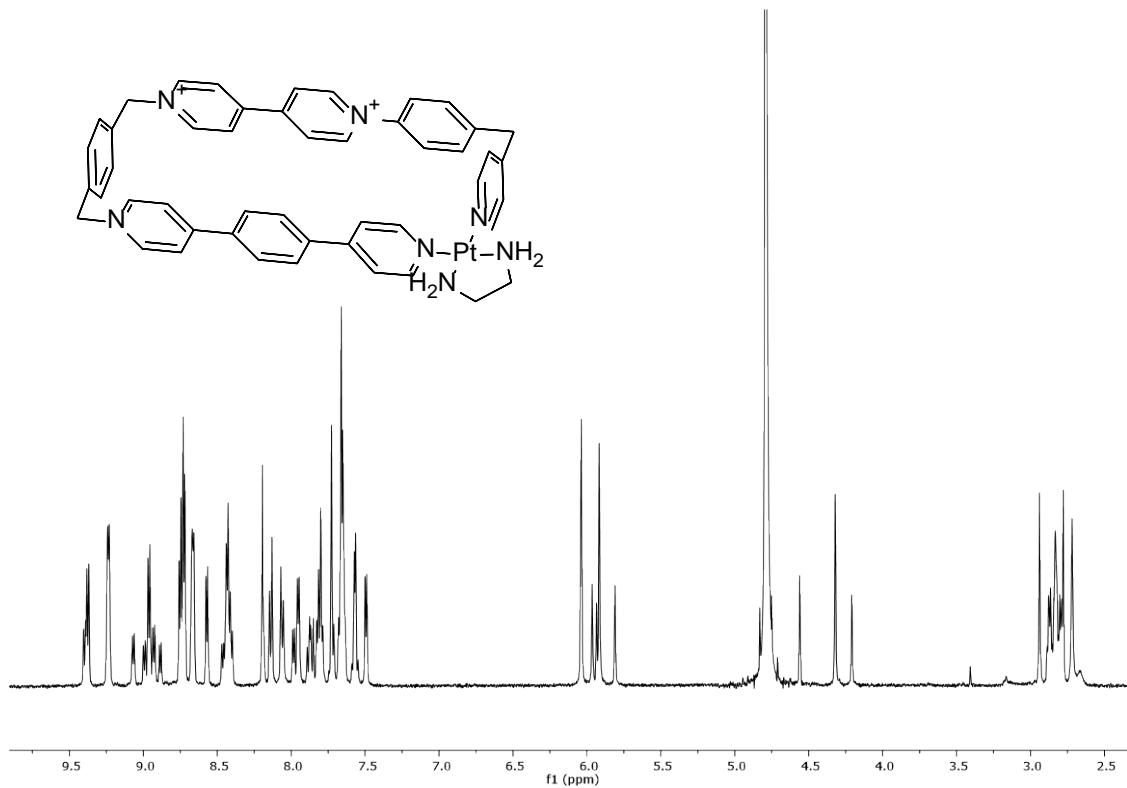


Figure S 67: ¹H RMN (500MHz, D₂O) spectrum of **M6b**·5NO₃.

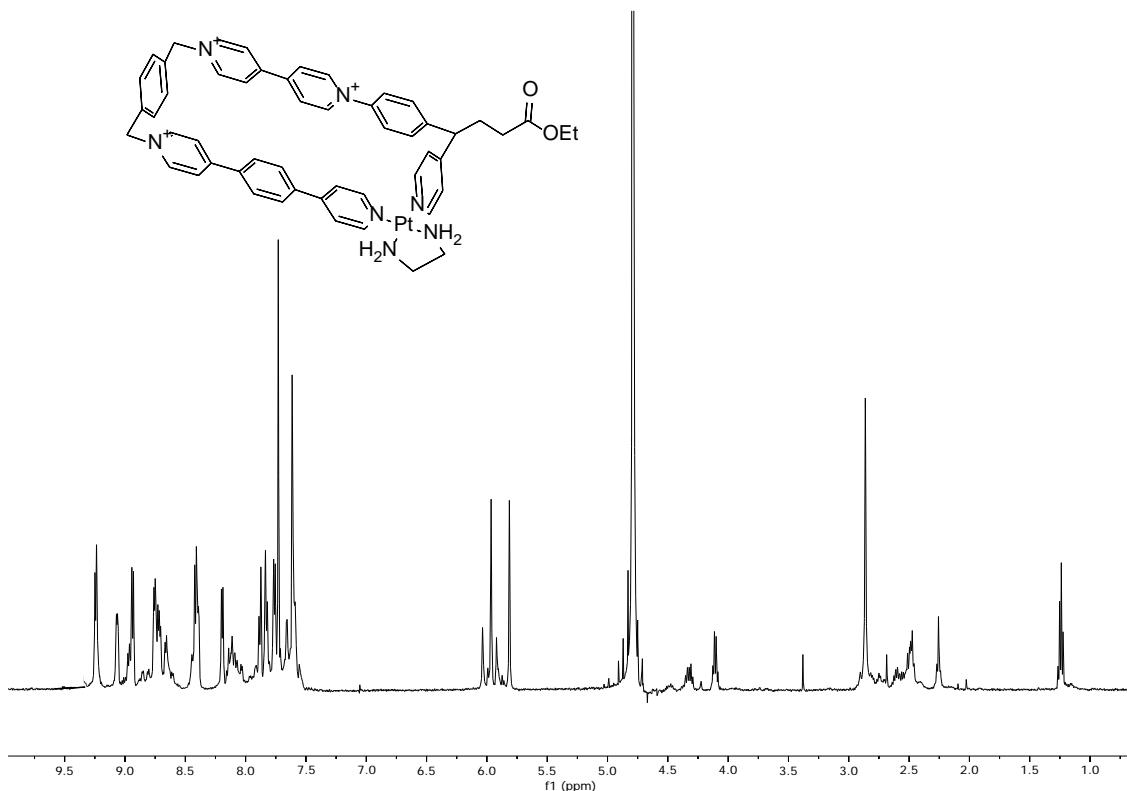


Figure S 68: ¹H RMN (500MHz, D₂O) spectrum of **M7b**·5NO₃.

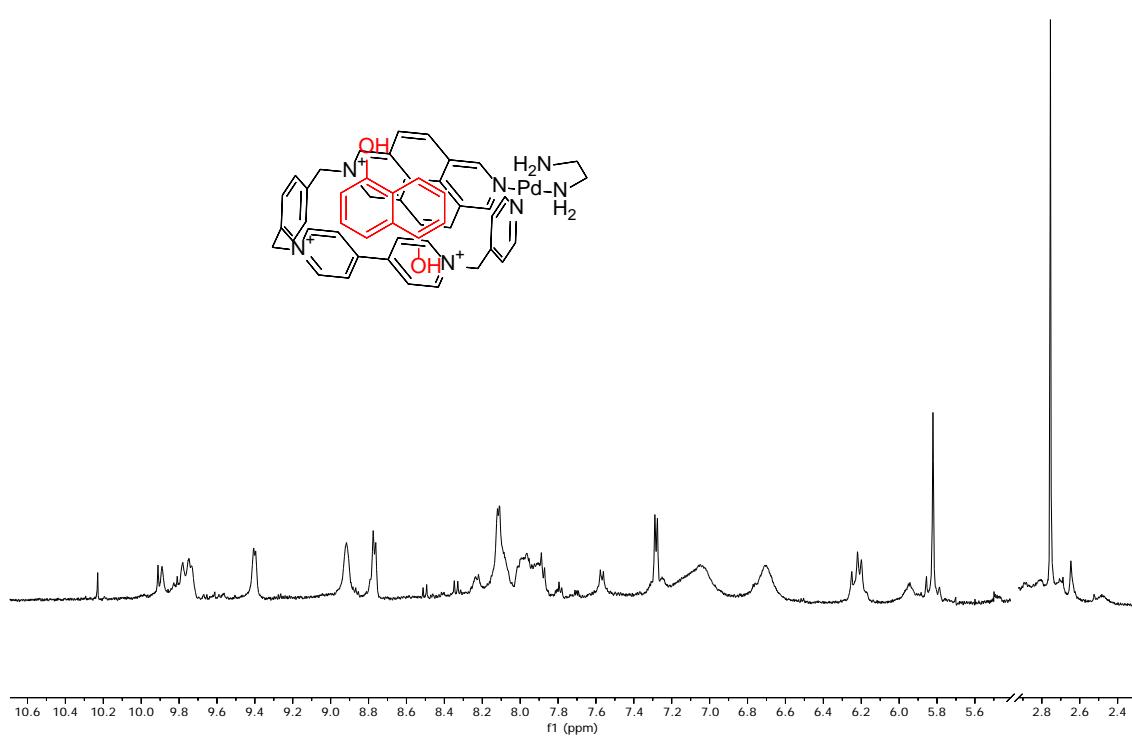


Figure S 69: ¹H RMN (400MHz, D₂O) spectrum of **M4a·5NO₃** and **1,5DHN**.

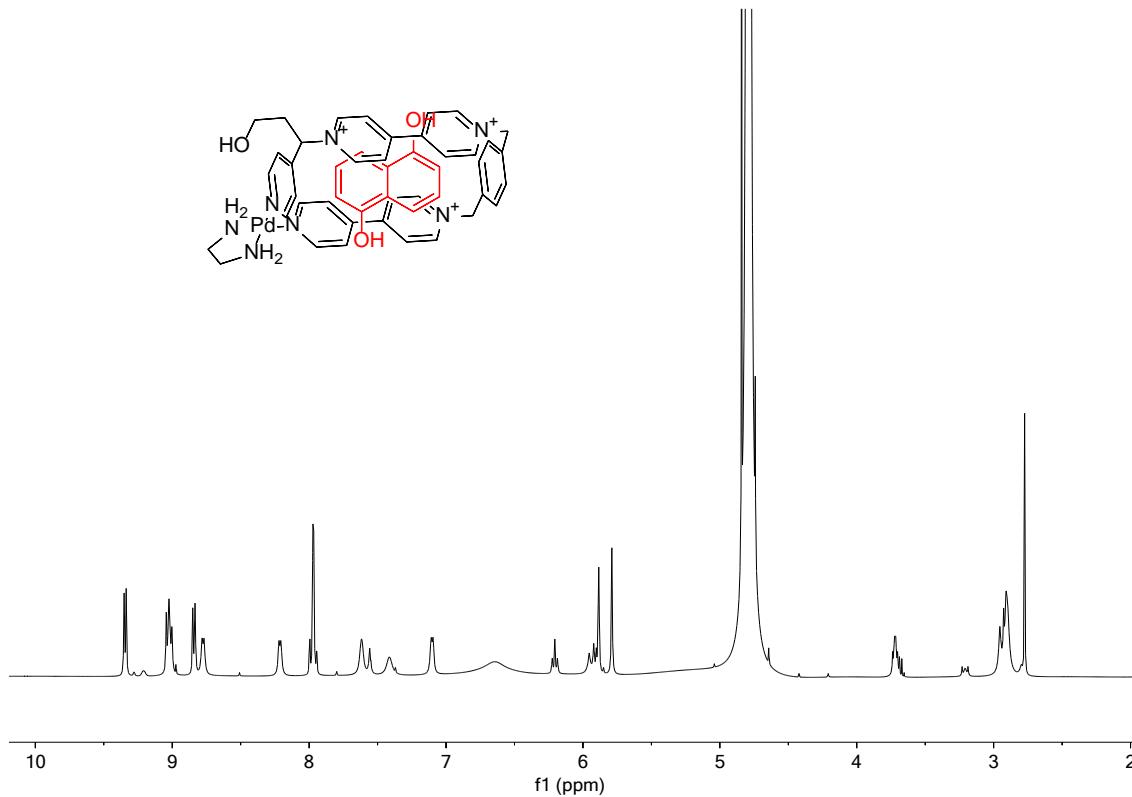


Figure S 70: ¹H RMN (400MHz, D₂O) spectrum of **M5a·5NO₃** and **1,5DHN**.

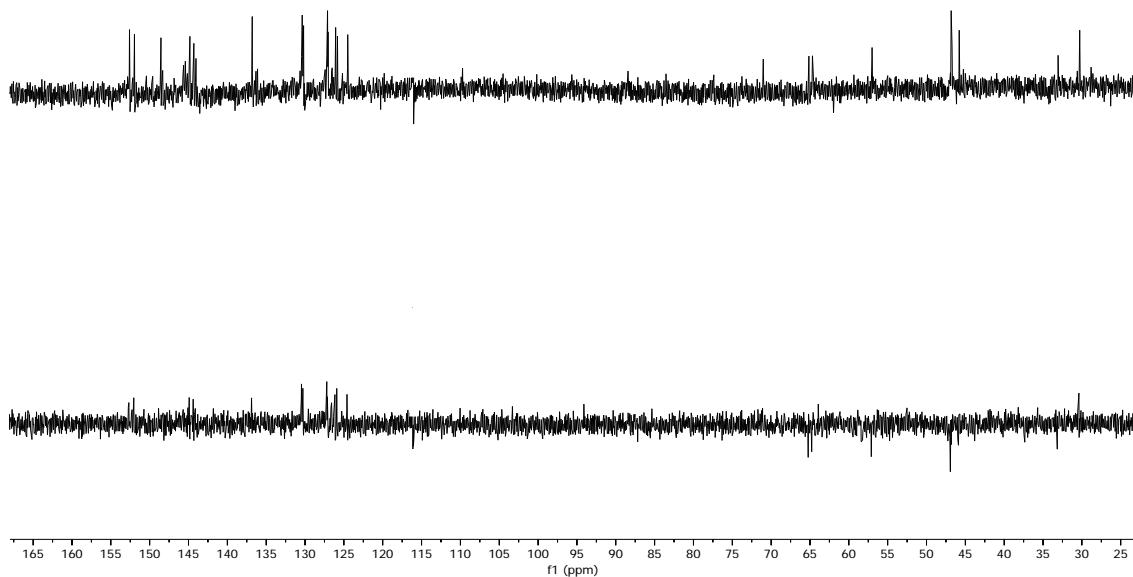


Figure S 71: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of $\text{M5a}\cdot 5\text{NO}_3$ and $1,5\text{DHN}$.

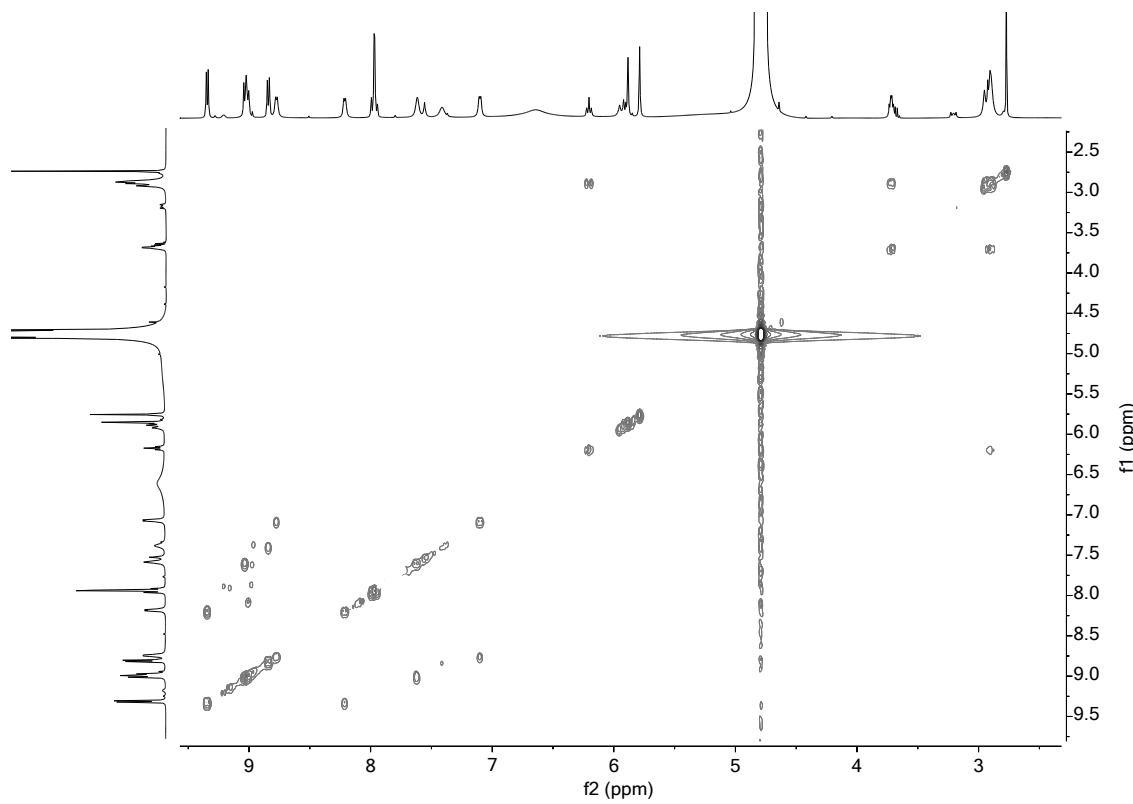


Figure S 72: COSY (400MHz, D_2O) spectrum of $\text{M5a}\cdot 5\text{NO}_3$ and $1,5\text{DHN}$.

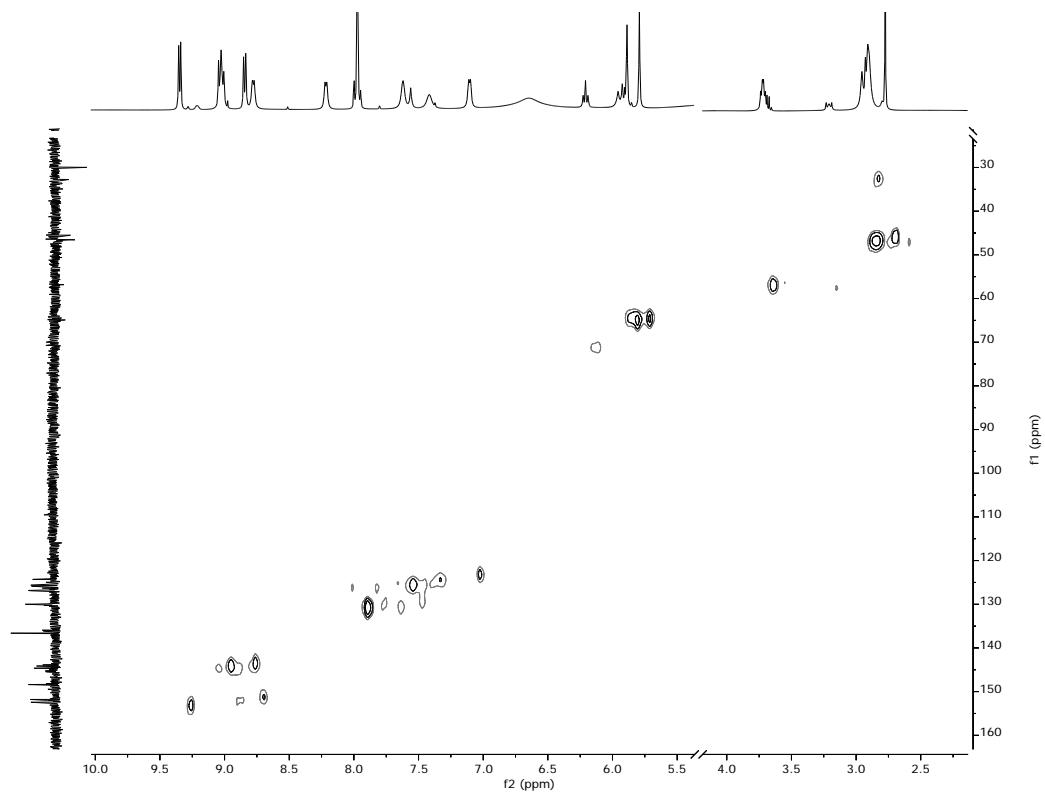


Figure S 73: HSQC (125 and 400MHz, D₂O) spectrum of **M5a·5NO₃** and **1,5DHN**.

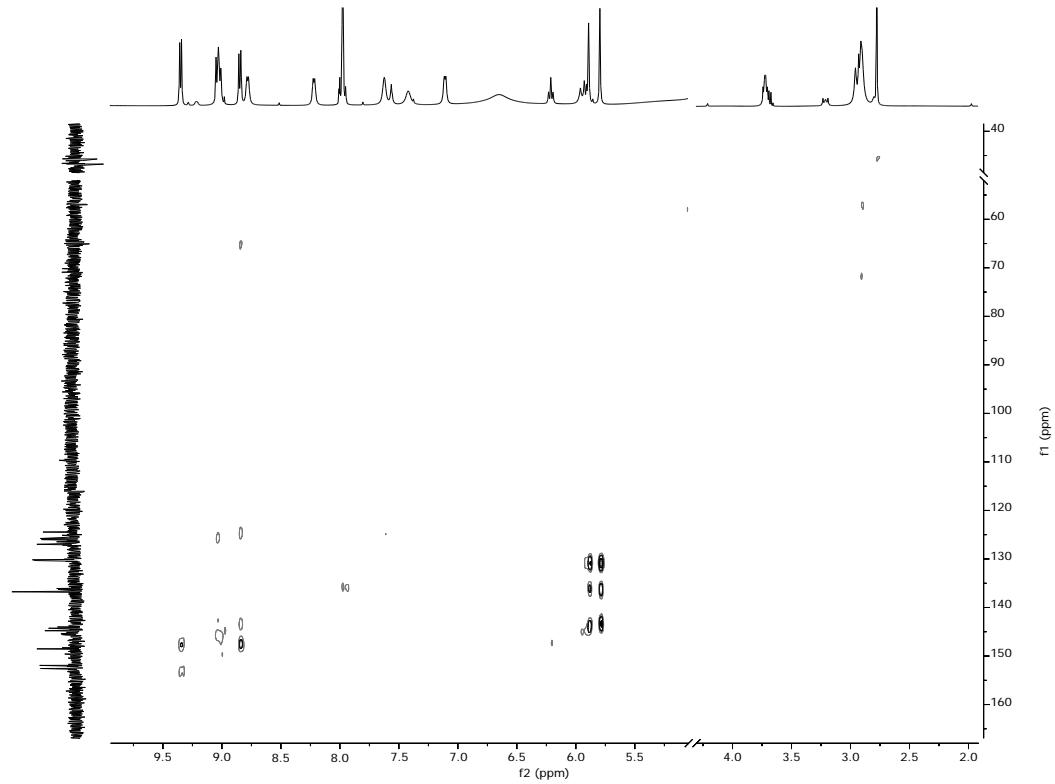


Figure S 74: HMBC (125 and 400MHz, D₂O) spectrum of **M5a·5NO₃** and **1,5DHN**.

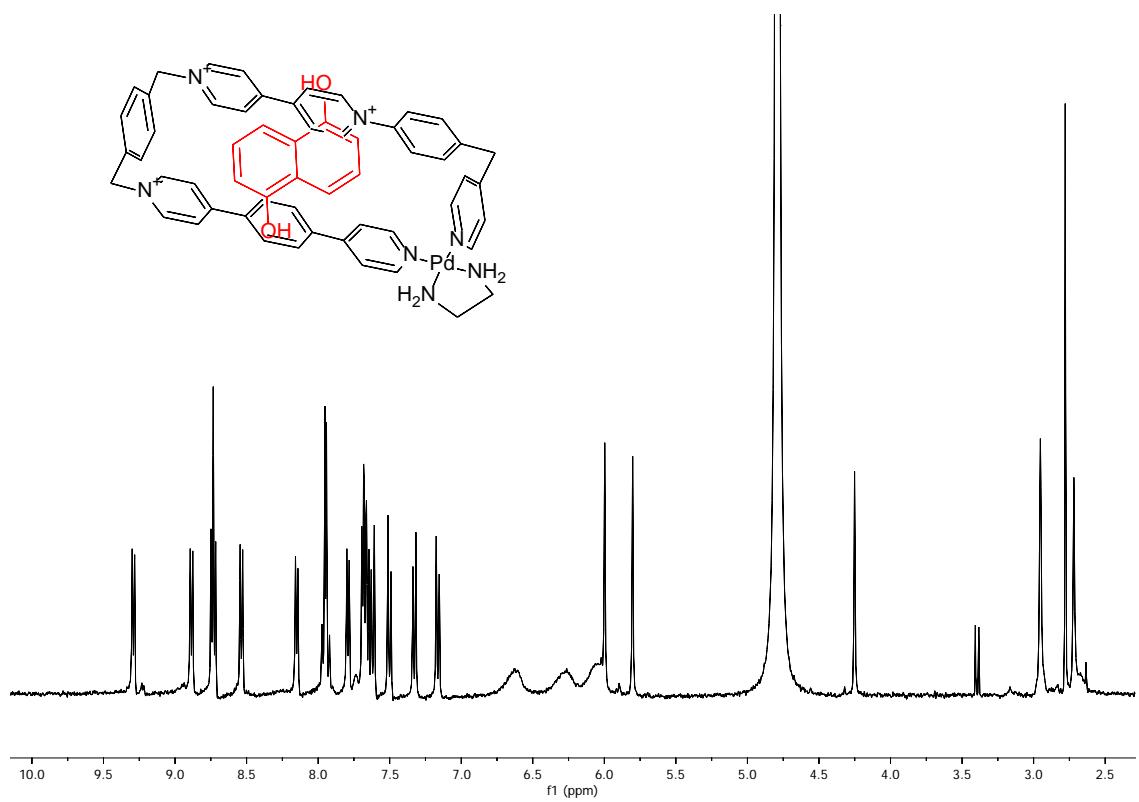


Figure S 75: ¹H RMN (500MHz, D₂O) spectrum of **M6a**⁺·**5NO**₃⁻ and **1,5DHN**.

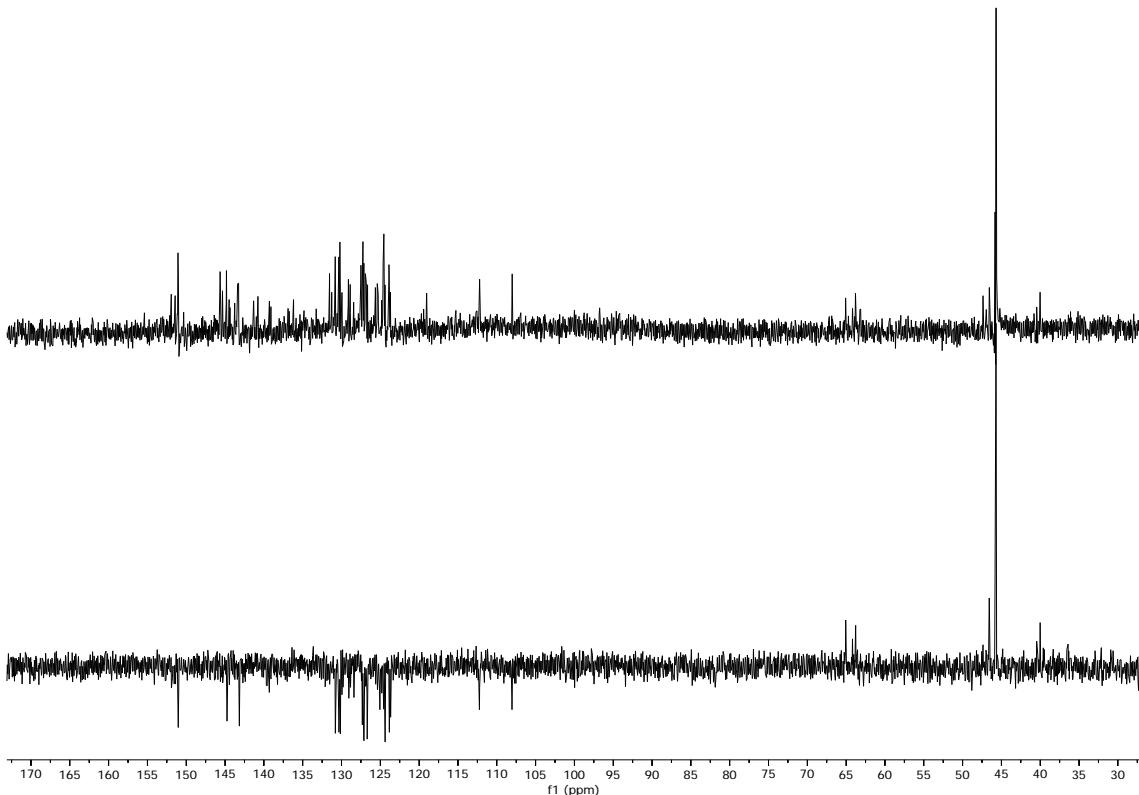


Figure S 76: ¹³C and DEPT NMR (125 MHz, D₂O) spectrum of **M6a**⁺·**5NO**₃⁻ and **1,5DHN**.

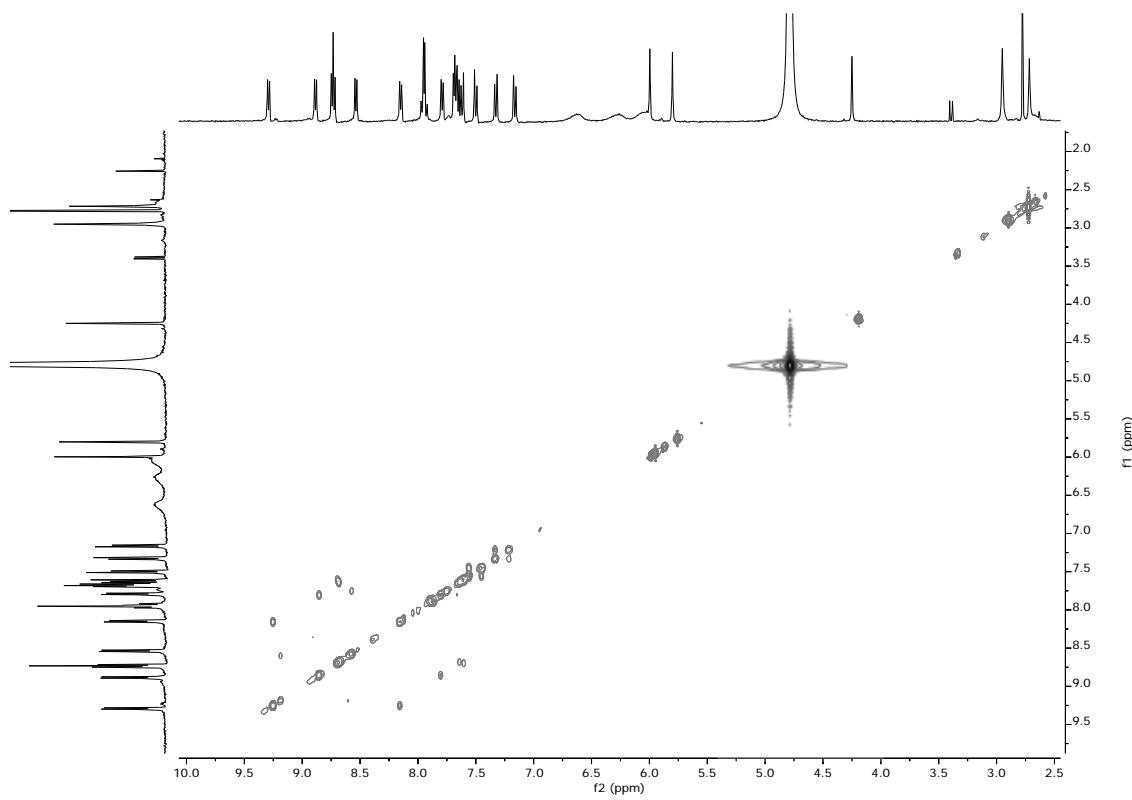


Figure S 77: COSY (500MHz, D₂O) spectrum of **M6a·5NO₃** and **1,5DHN**.

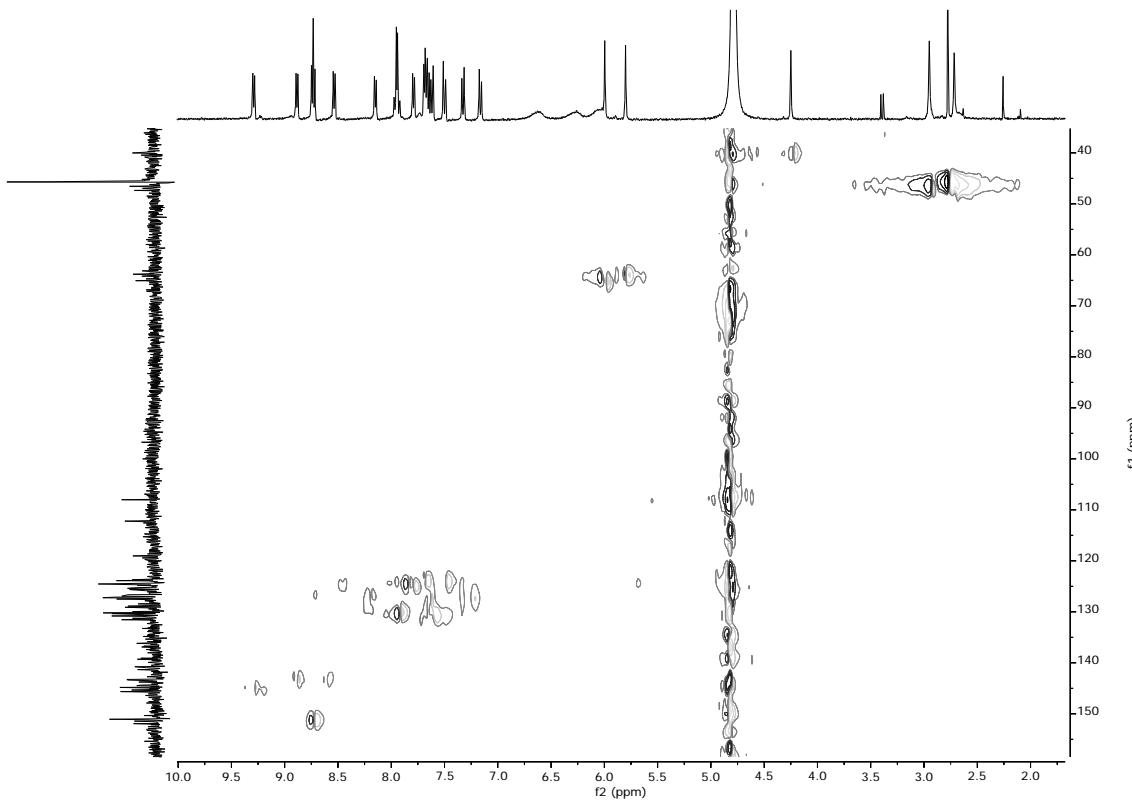


Figure S 78: HSQC (125 and 500MHz, D₂O) spectrum of **M6a·5NO₃** and **1,5DHN**.

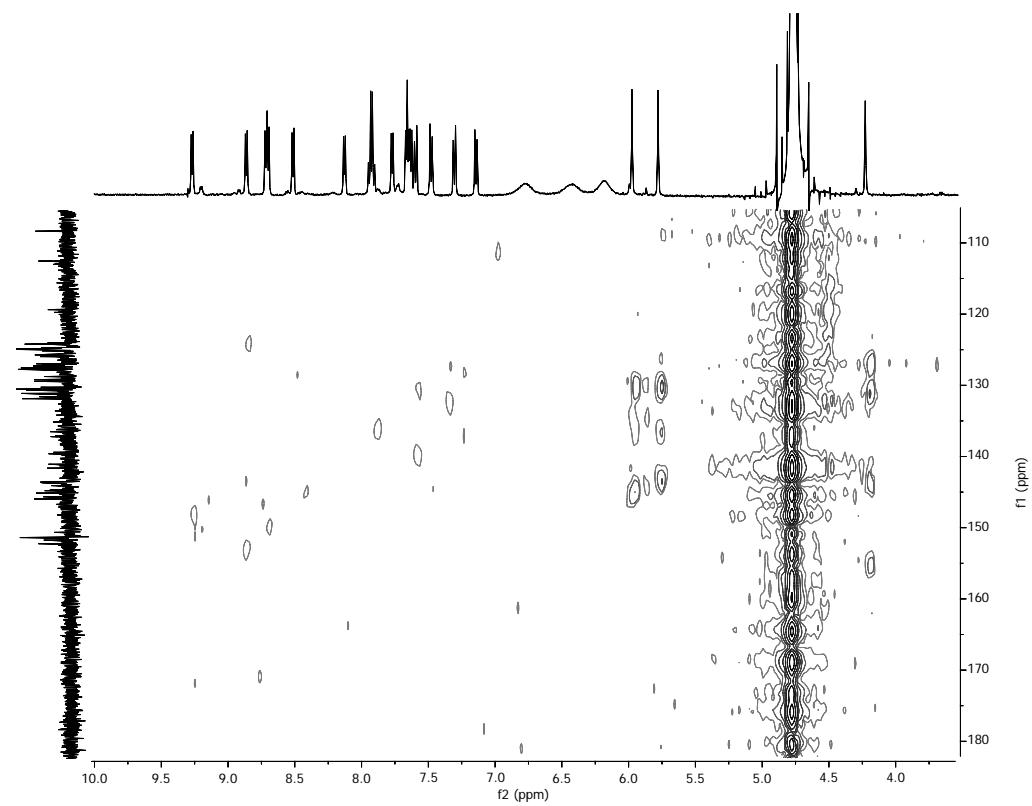


Figure S 79: HMBC (125 and 500MHz, D₂O) spectrum of M6a·5NO₃⁻ and 1,5DHN.

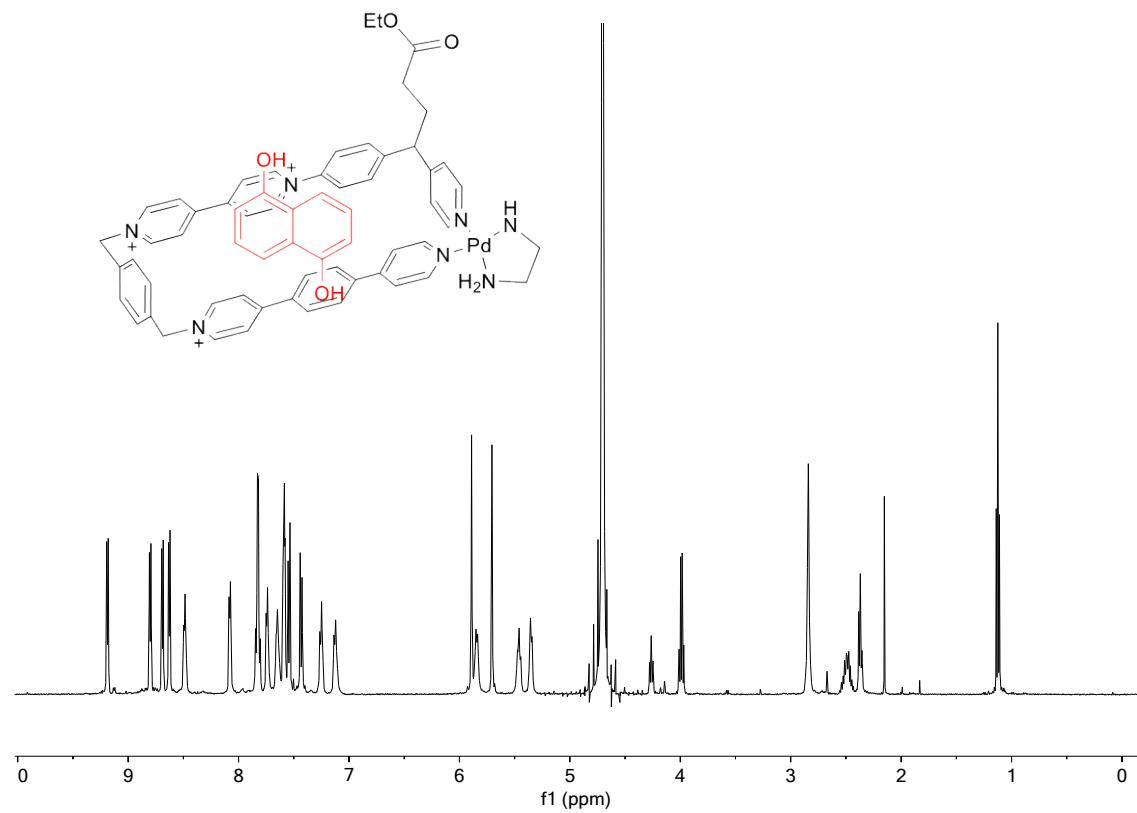


Figure S 80: ¹H RMN (500MHz, D₂O) spectrum of M7a·5NO₃⁻ and 1,5DHN.

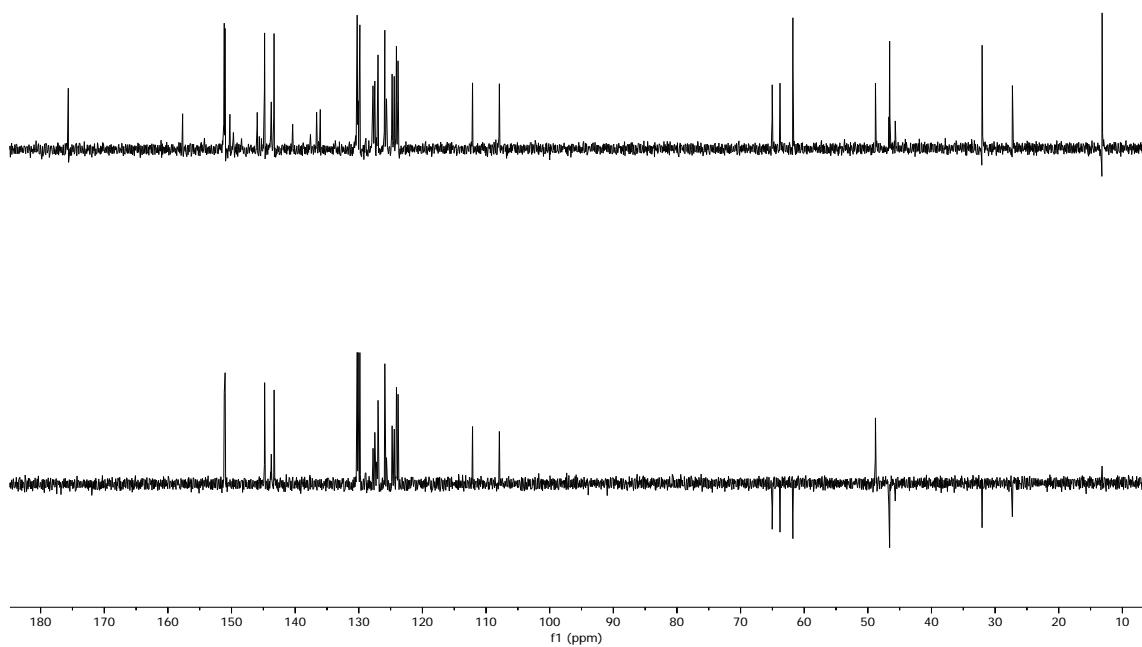


Figure S 81: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of $\text{M7a}\cdot\text{5NO}_3$ and 1,5DHN .

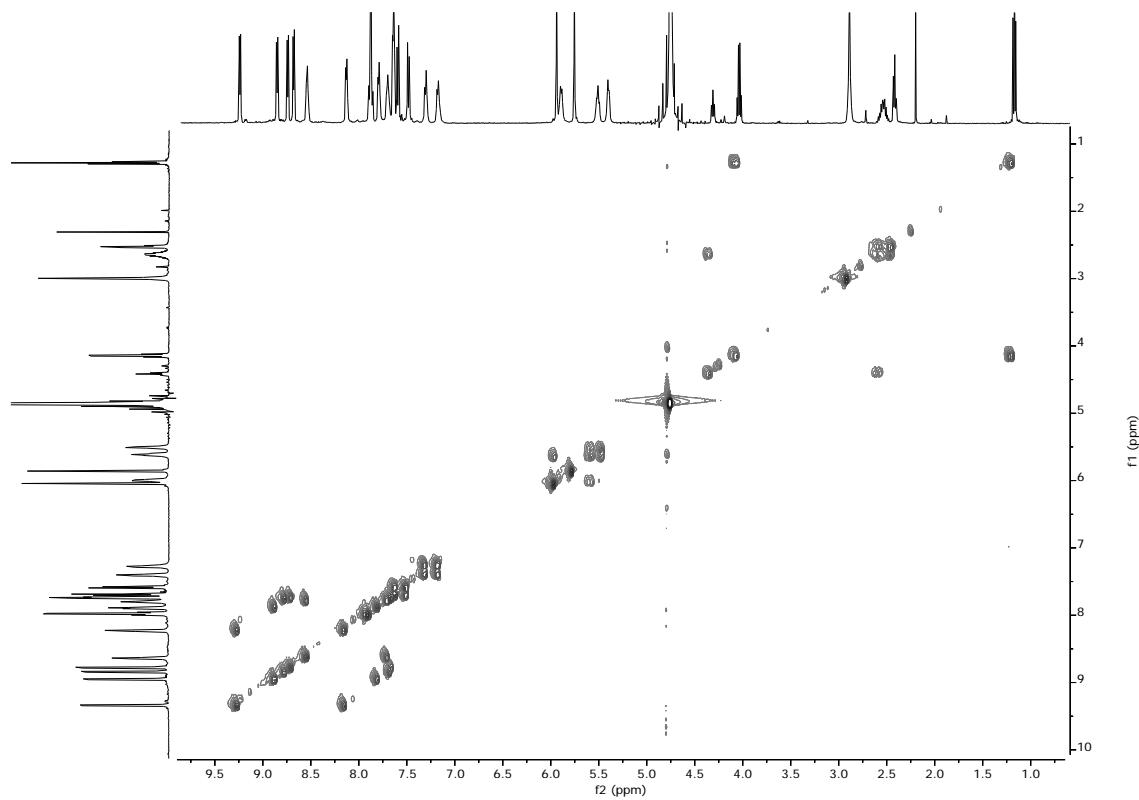


Figure S 82: COSY (500MHz, D_2O) spectrum of $\text{M7a}\cdot\text{5NO}_3$ and 1,5DHN .

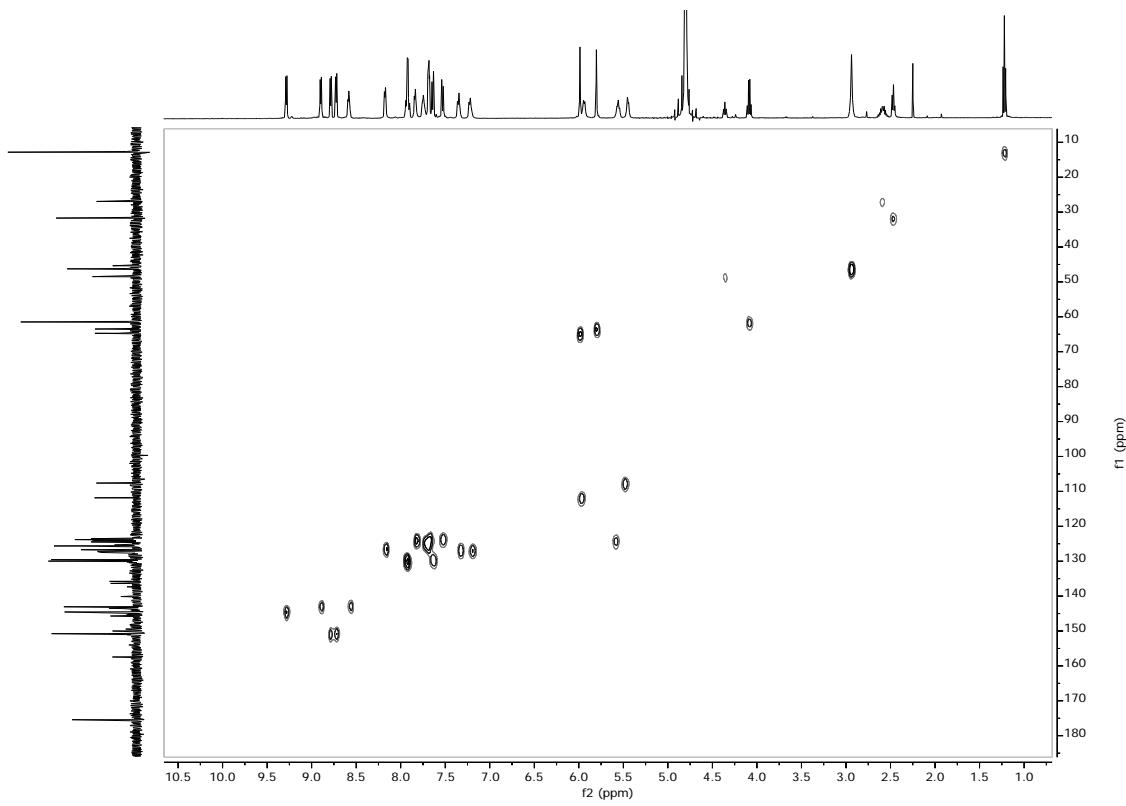


Figure S 83: HSQC (125 and 500MHz, D₂O) spectrum of **M7a·5NO₃·** and **1,5DHN**.

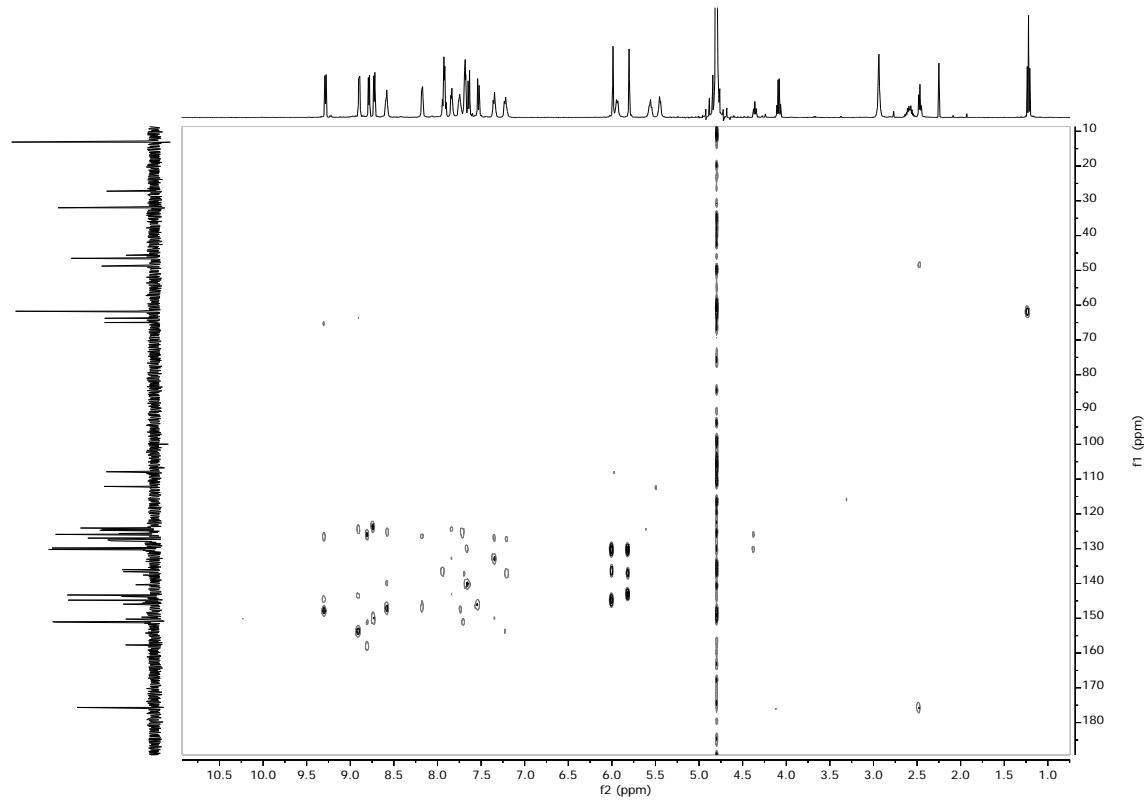


Figure S 84: HMBC (125 and 500MHz, D₂O) spectrum of **M7a·5NO₃·** and **1,5DHN**.

2. EXTRA FIGURES

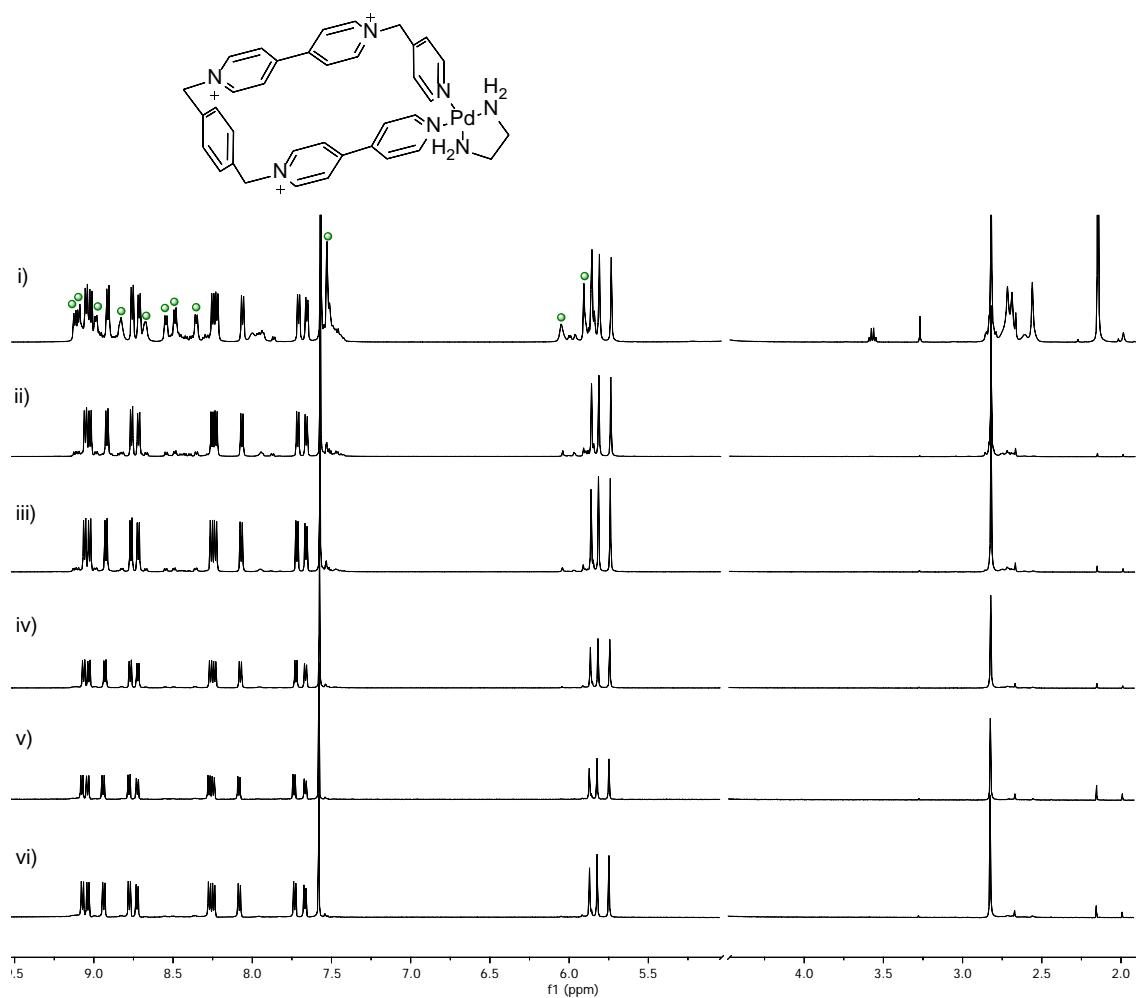


Figure S 85: Partial ^1H NMR (D_2O , 500 MHz) spectra of a solution of **L1**· 3NO_3^- and (en)Pd(NO_3^-)₂ at different concentrations: (i) 15 mM (ii) 10 mM (iii) 5 mM (iv) 2.5 mM, v) 1.25, vi) 0.75.

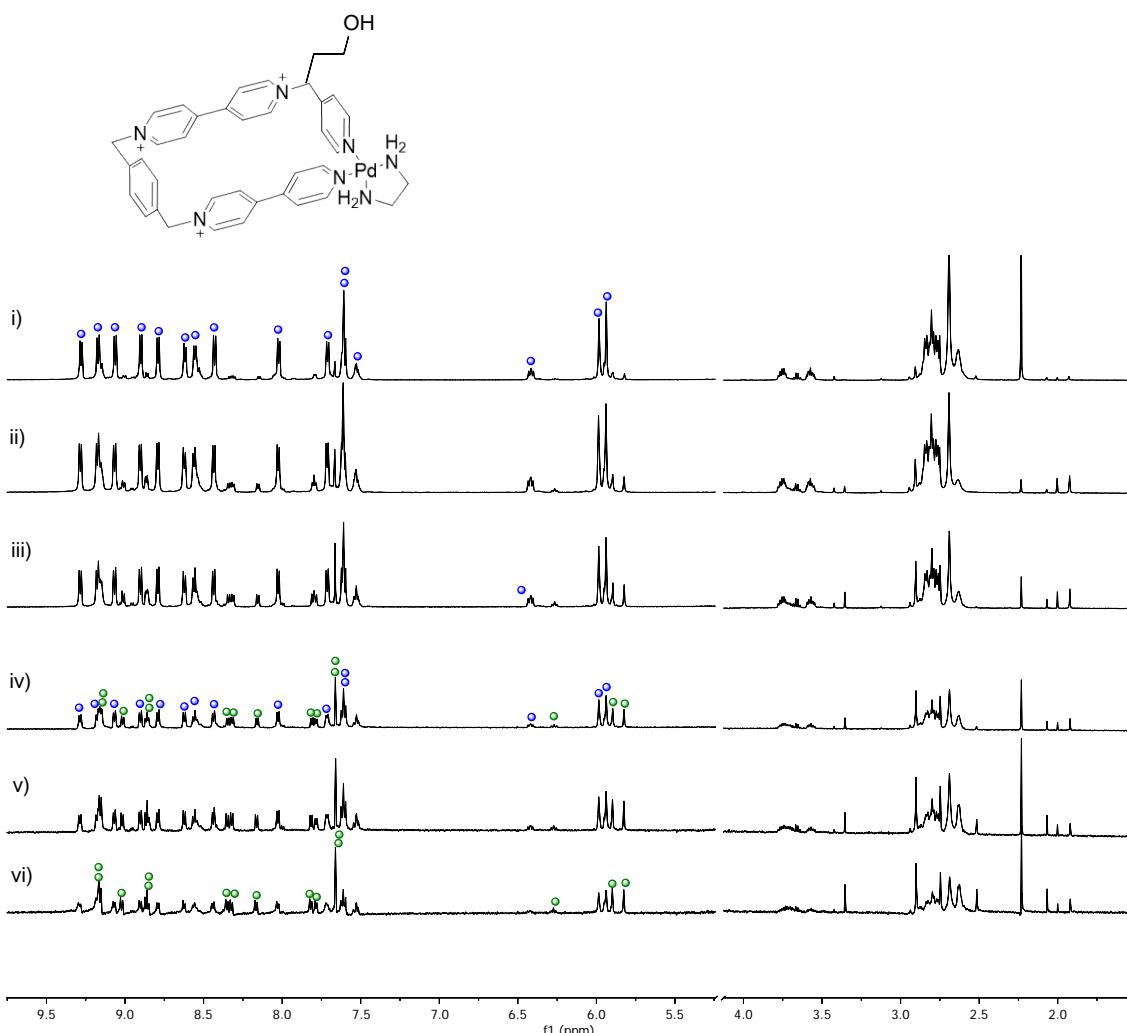


Figure S 86: Partial ^1H NMR (D_2O , 500 MHz) spectra of a solution of $\text{L5}\cdot\text{3NO}_3$ and $(\text{en})\text{Pd}(\text{NO}_3)_2$ at different concentrations: (i) 5 mM (ii) 2.5 mM (iii) 1.25 mM (iv) 0.75 mM, v) 0.375, vi) 0.1.

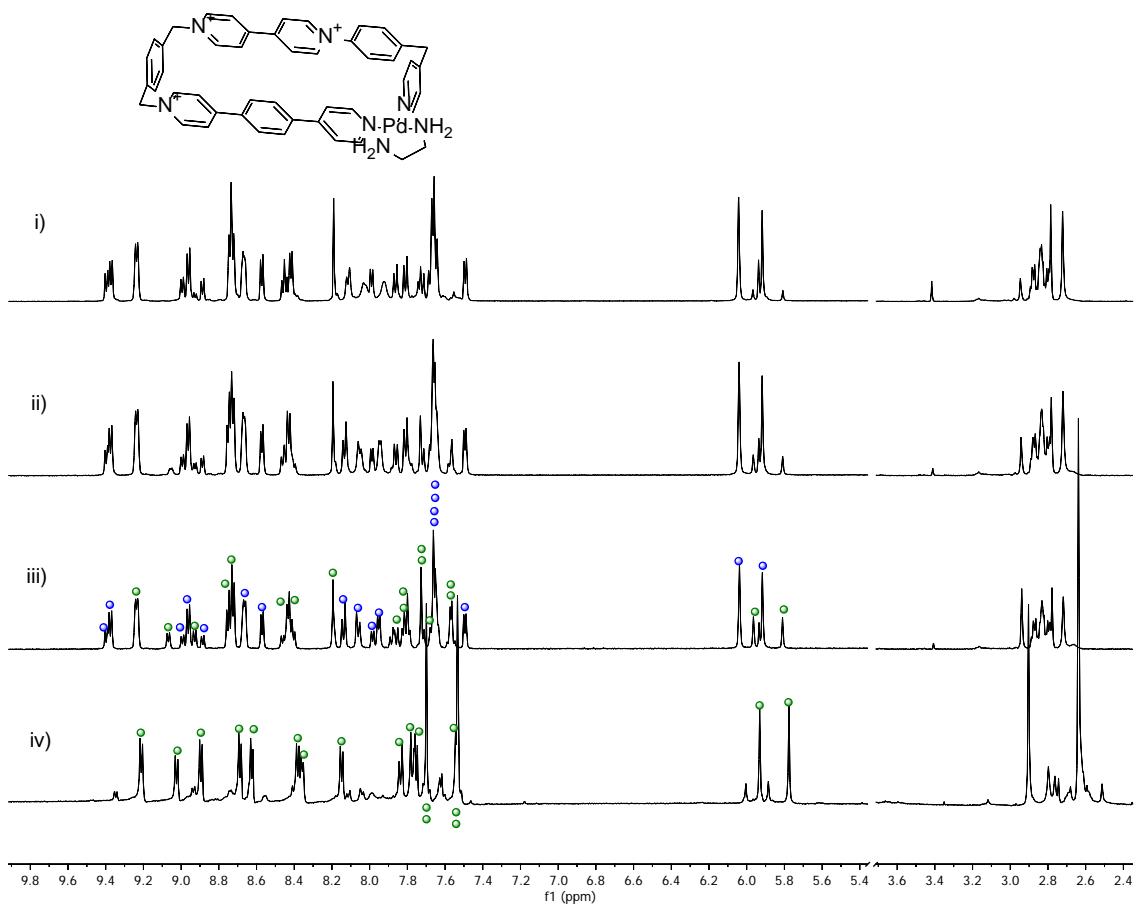


Figure S 87: Partial ^1H NMR (D_2O , 500 MHz) spectra of a solution of **L6·3NO₃** and (en)Pd(NO₃)₂ at different concentrations: (i) 15 mM (ii) 10 mM (iii) 7.5 mM (iv) 5 mM.

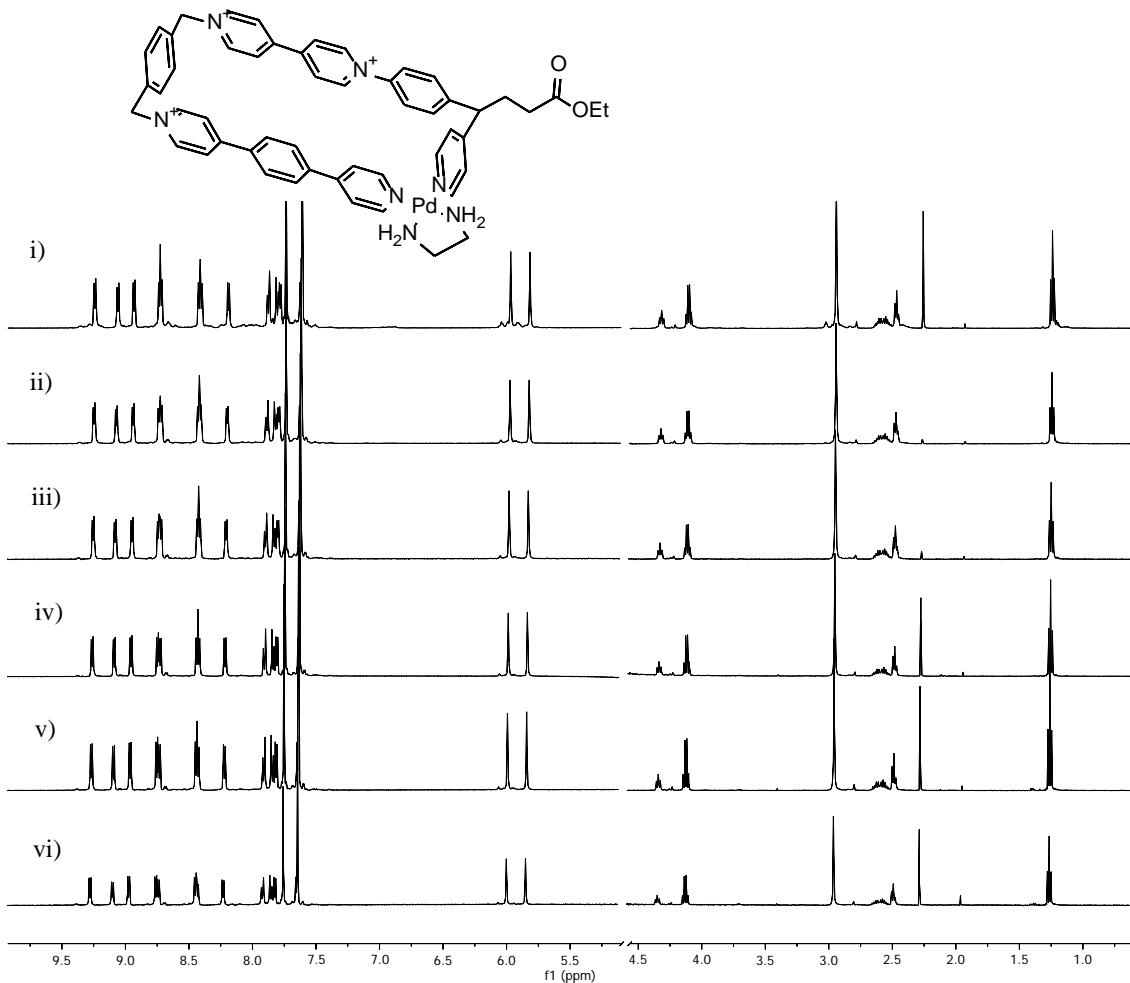


Figure S 88: Partial ¹H NMR (D_2O , 500 MHz) spectra of a solution of **L7·3NO₃** and (en)Pd(NO₃)₂ at different concentrations: (i) 15 mM (ii) 5 mM (iii) 2,5 mM (iv) 1,25 mM (v) 0,75 mM (vi) 0,375 mM.

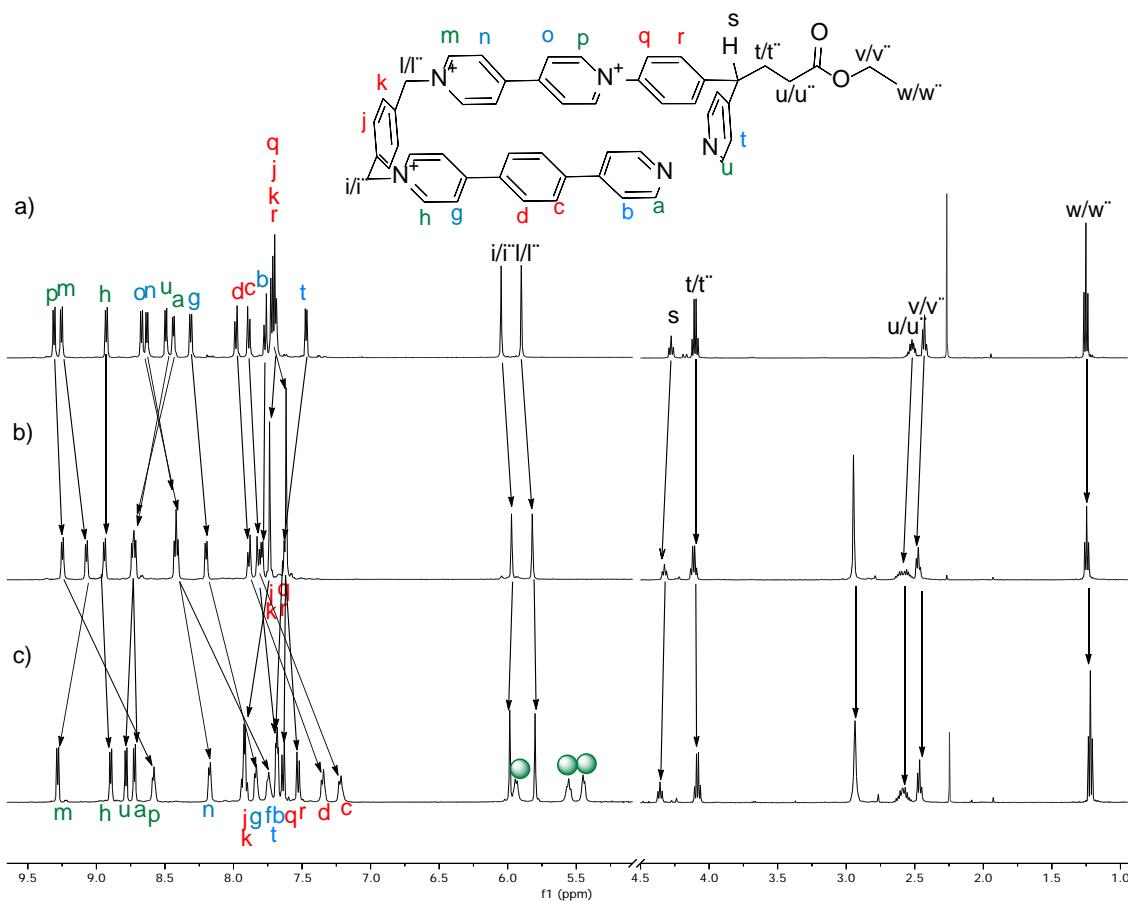


Figure S 89: Partial ¹H NMR (D_2O , 500MHz) spectra of: top, ligand **L7**·**3NO**₃; down metallacycle **M4a** and inclusion complex **M7a**·**5NO**₃·**1,5DHN**.

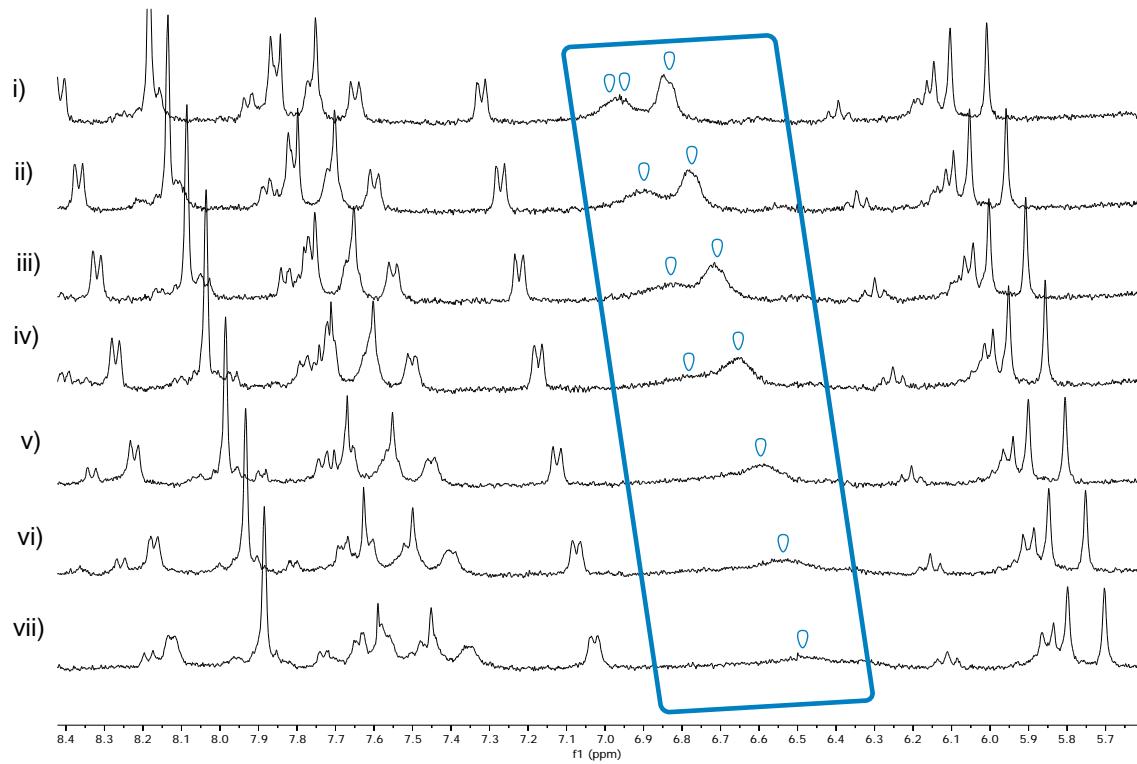


Figura S 90: Partial ¹H NMR (D_2O , 300MHz) spectra of **M5a·5NO₃** and **1,5DHN** at different temperatures i) 333K; ii) 328K; iii) 323K; iv) 318K; v) 313K; vi) 308K; vii) 298K.