Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

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

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1. RMN SPECTRA

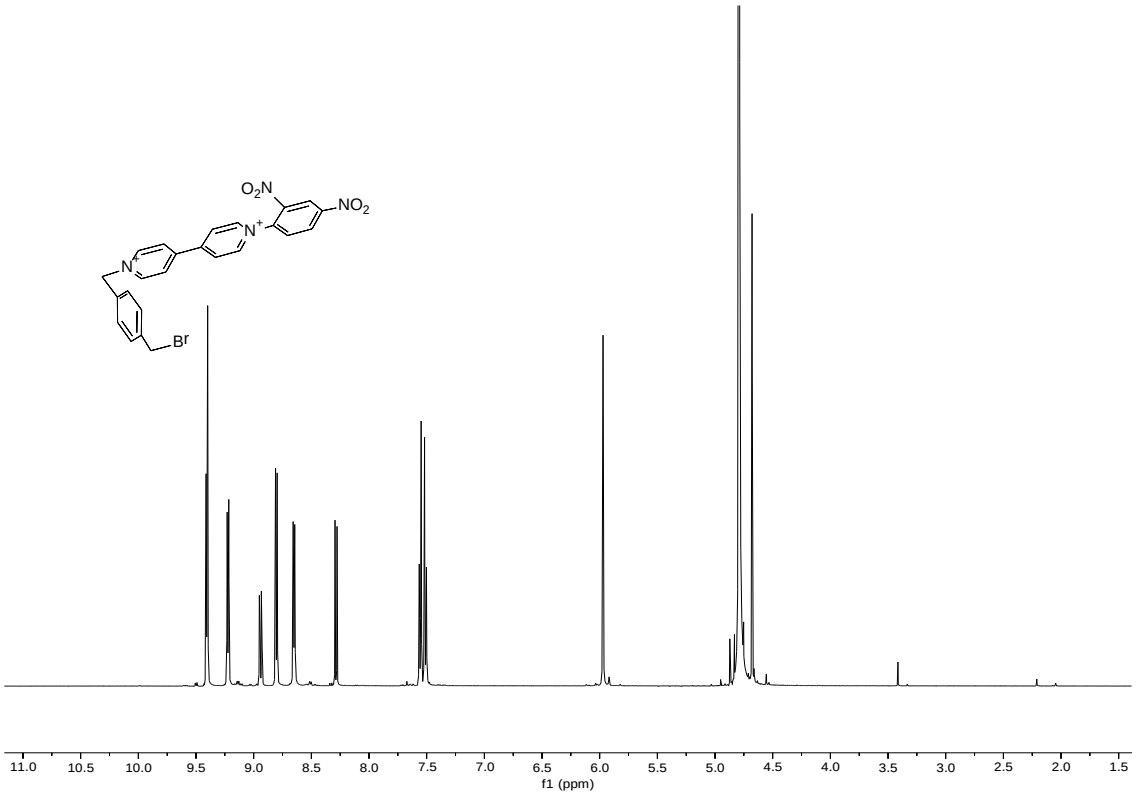


Figure S 1: ^{1}H RMN (500MHz, D_2O) spectrum of **6·Cl·Br.**

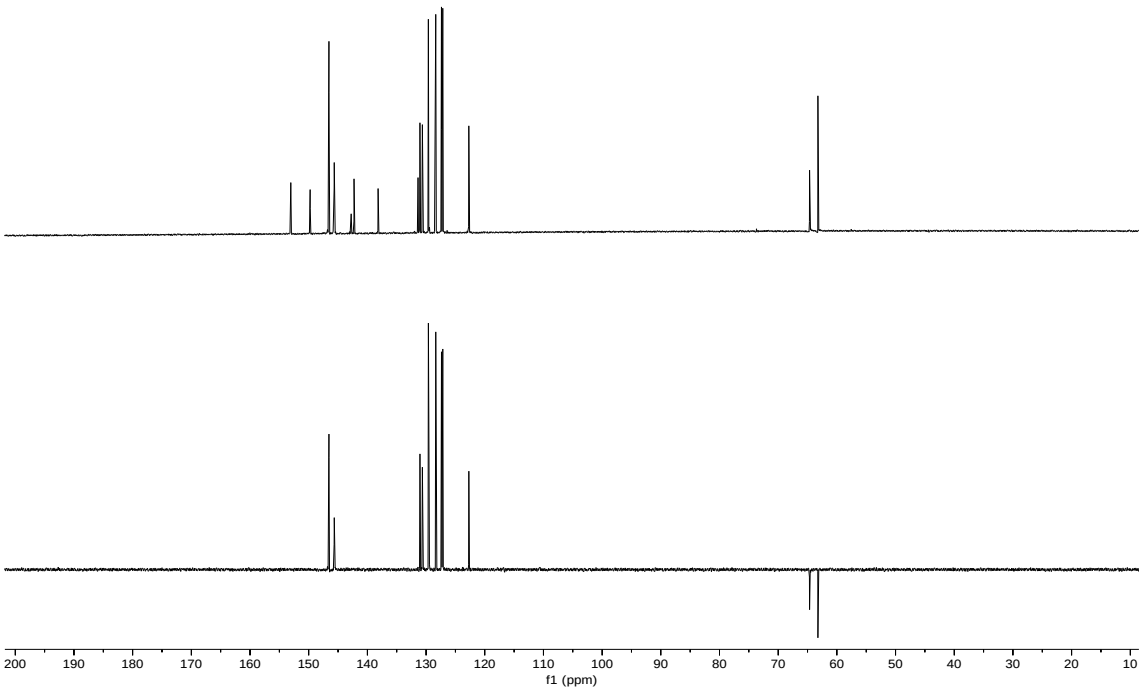


Figure S 2: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **6·Cl·Br.**

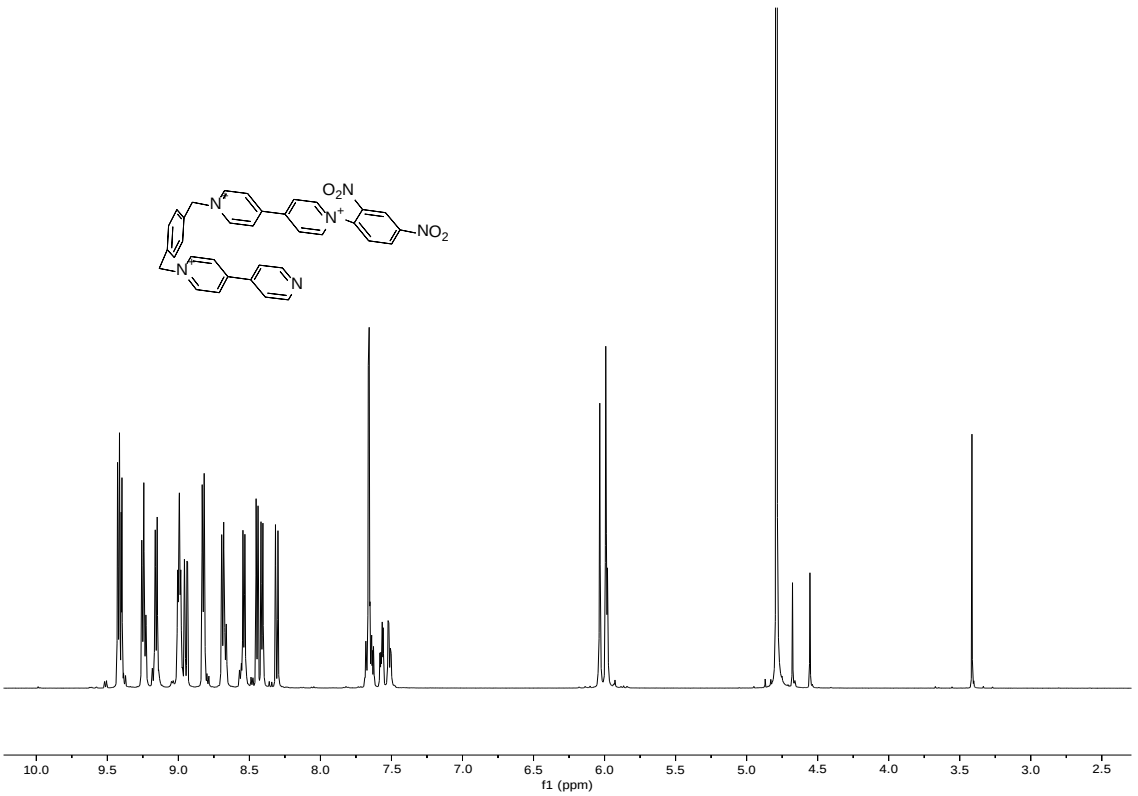


Figure S 3: ^{1}H RMN (500MHz, D_2O) spectrum of **7·Cl·2Br.**

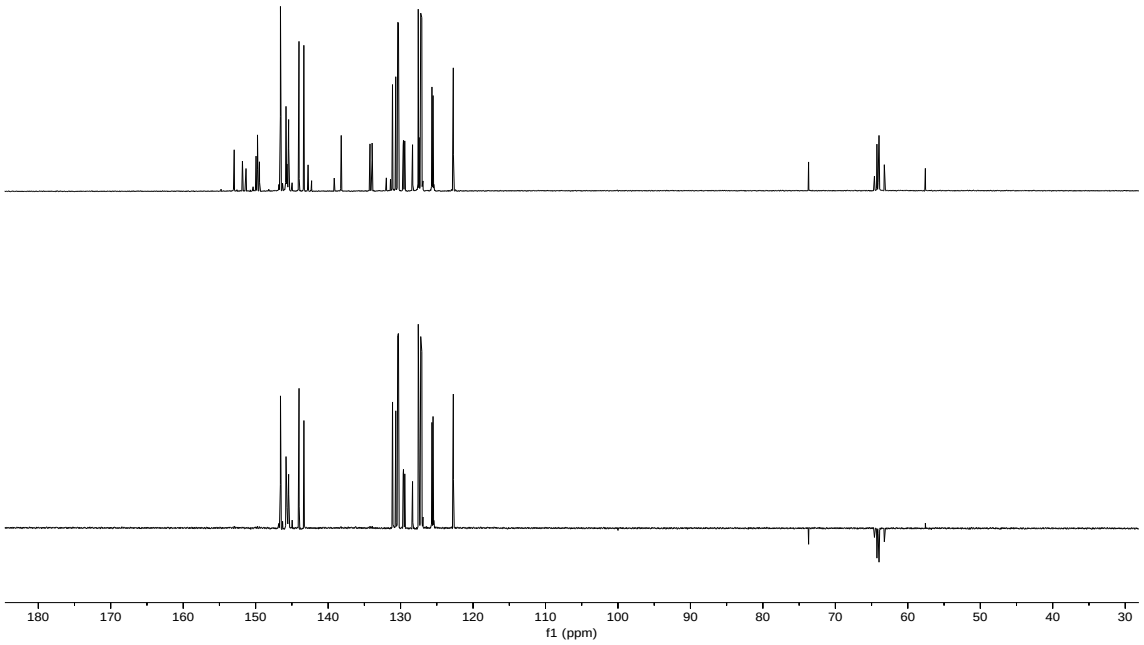


Figure S 4: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **7·Cl·2Br**.

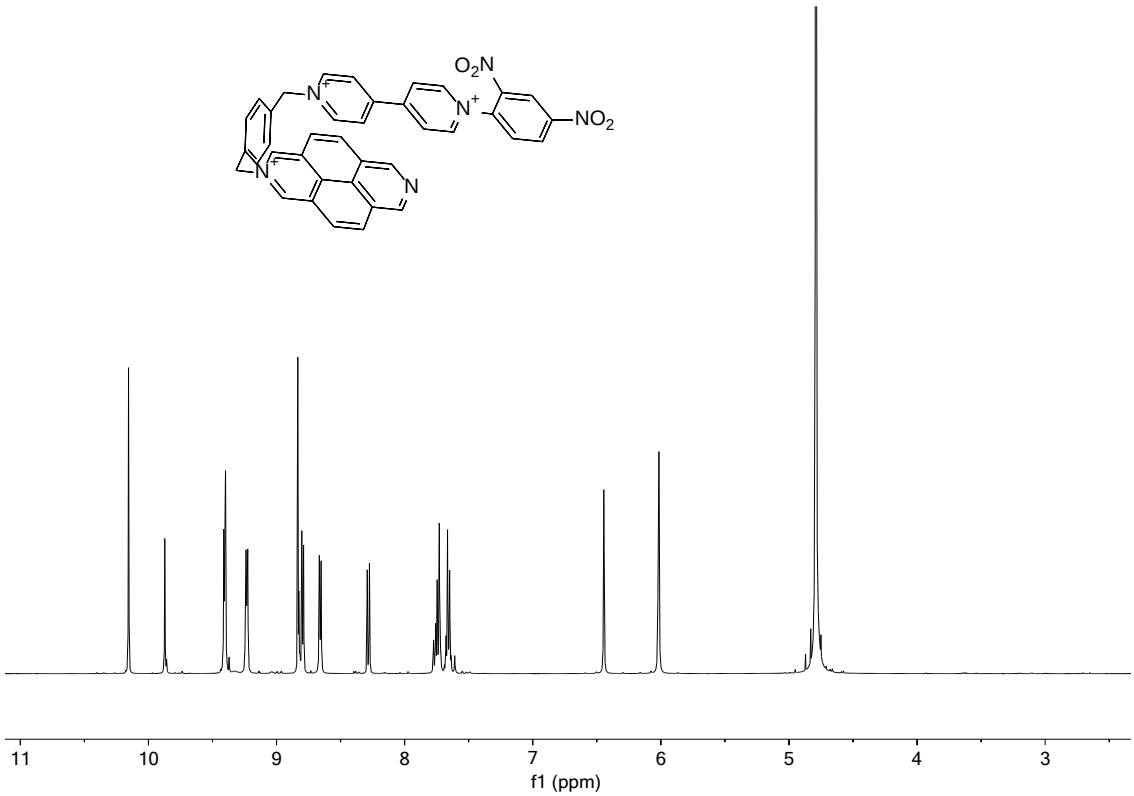


Figure S 5: ^{1}H RMN (500MHz, D_2O) spectrum of **12·Cl·2Br.**

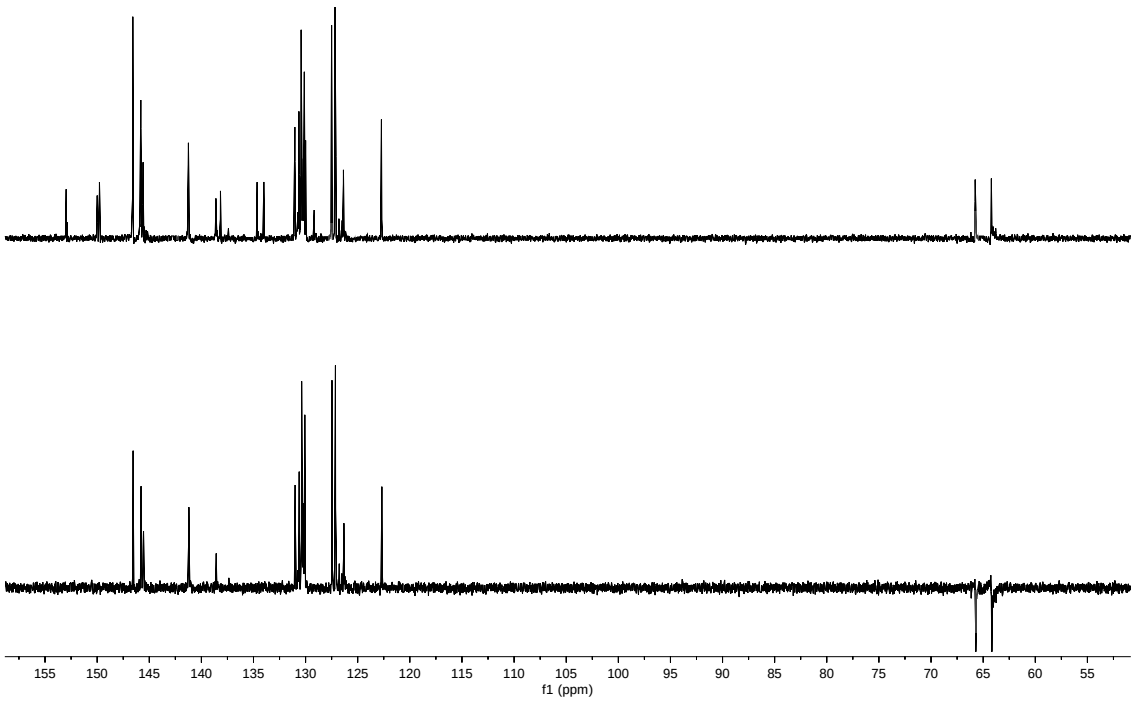


Figure S 6: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **12·Cl·2Br.**

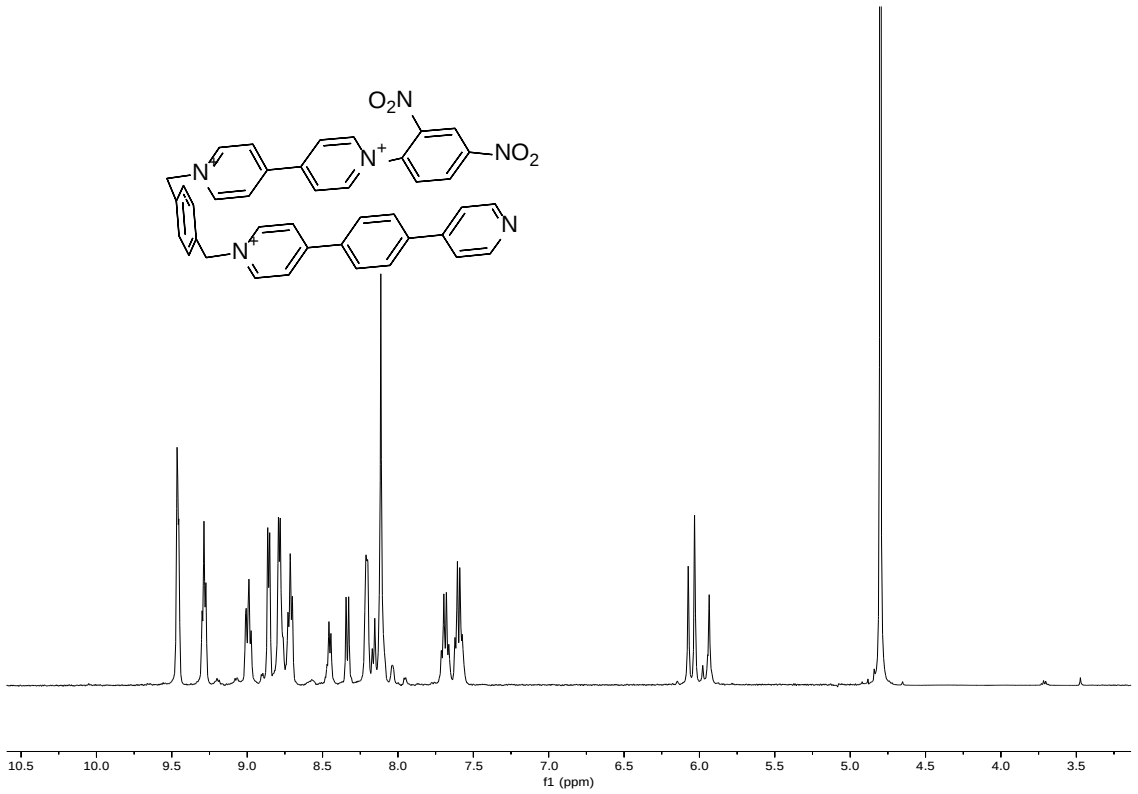


Figure S 7: ^{1}H RMN (500MHz, D_2O) spectrum of **13·Cl·2Br.**

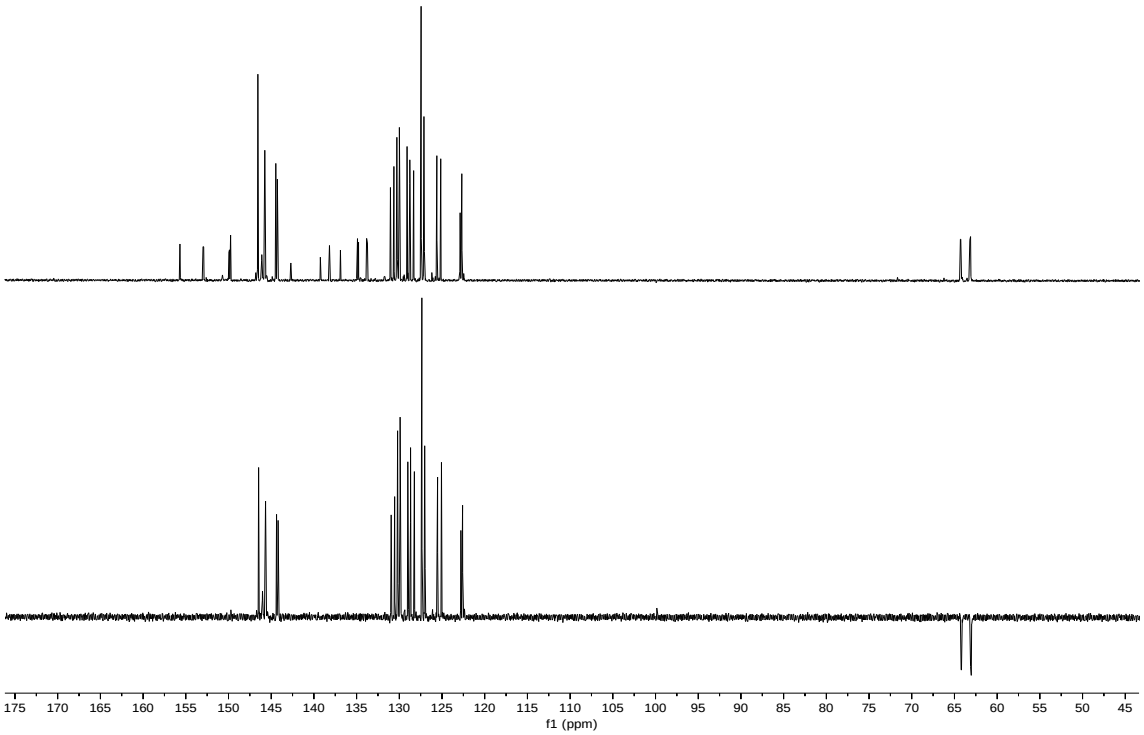


Figure S 8: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **13·Cl·2Br.**

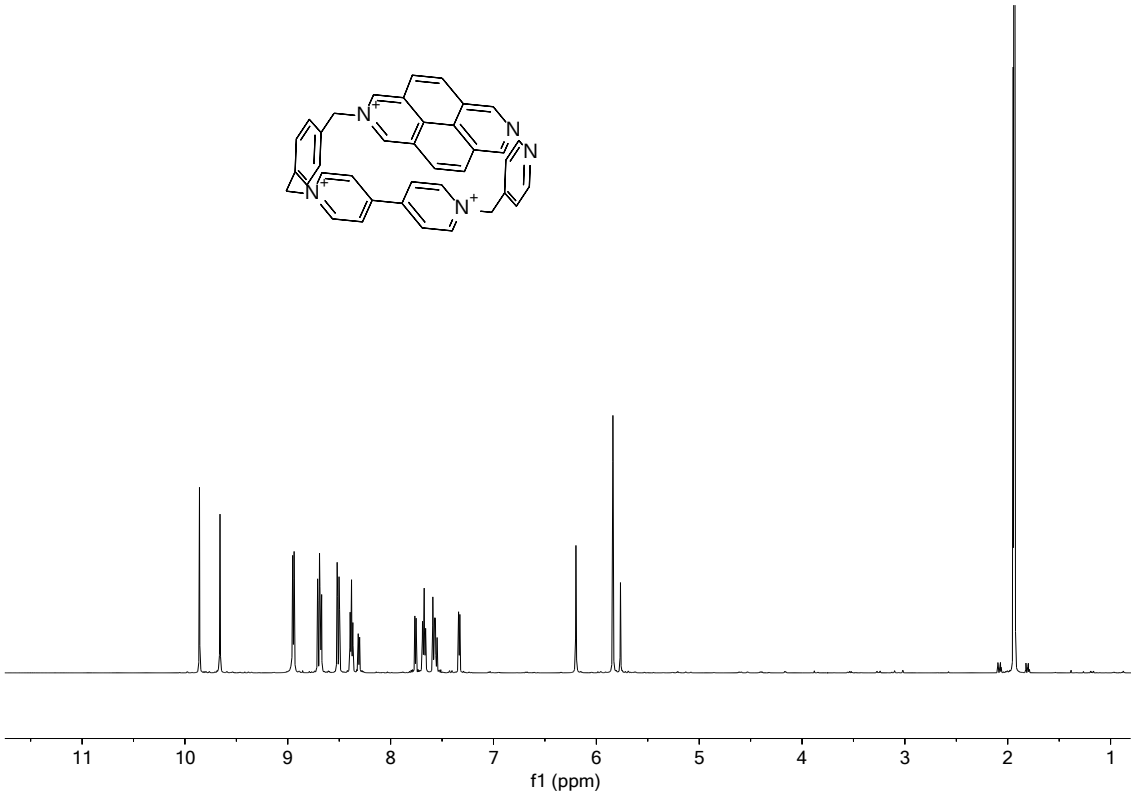


Figure S 9: ^{1}H RMN (500MHz, CD_3CN) spectrum of **L4·3PF$_6$**.

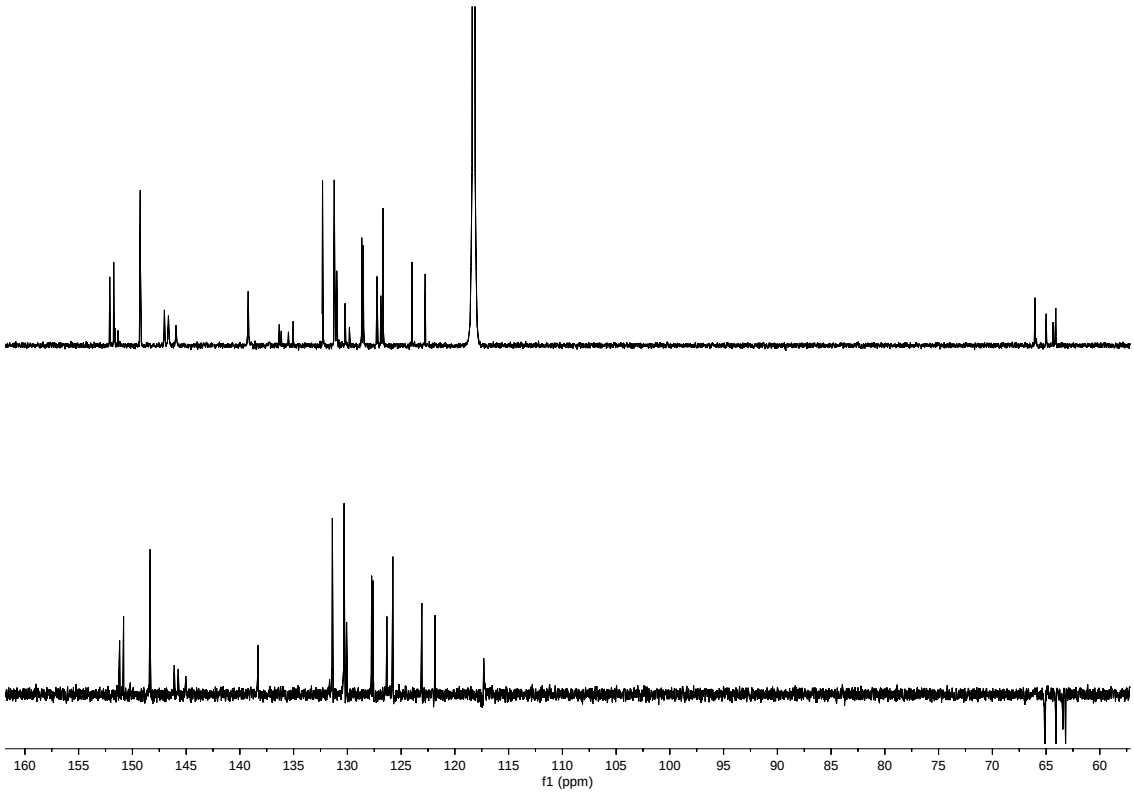


Figure S 10: ^{13}C and DEPT NMR (125 MHz, CD_3CN) spectrum of **L4·3PF$_6$.**

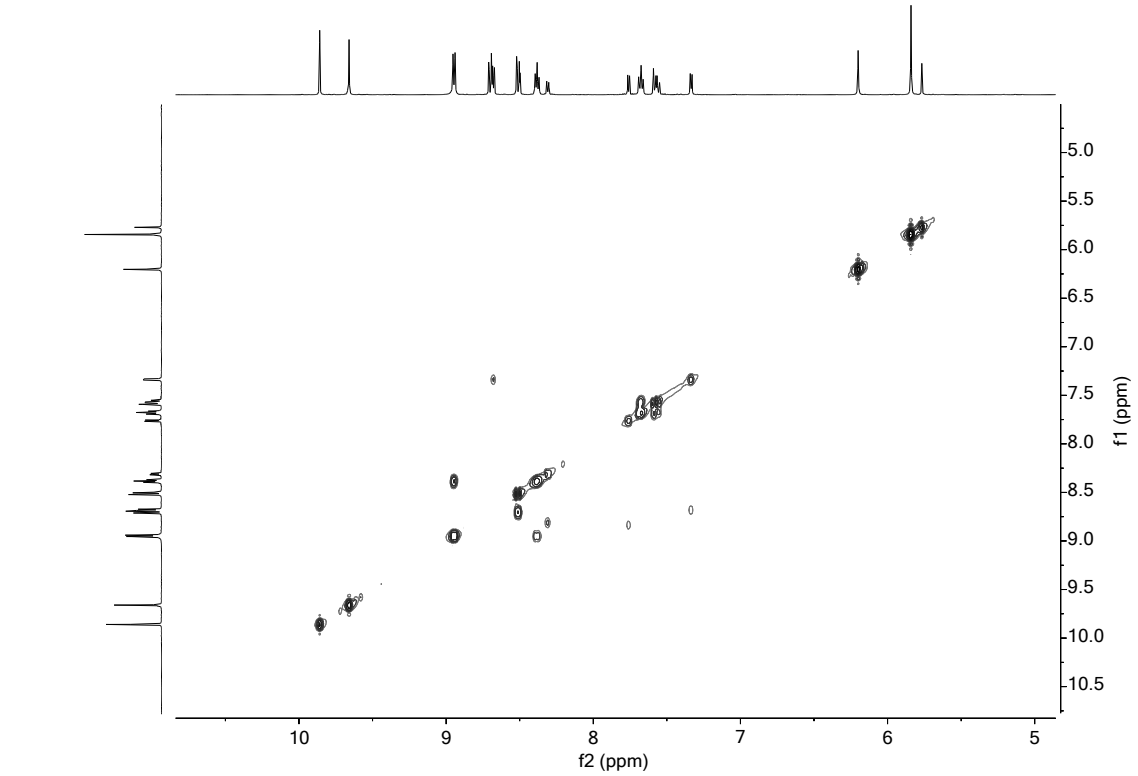


Figure S 11: COSY (500MHz, CD_3CN) spectrum of **L4·3PF$_6$.**

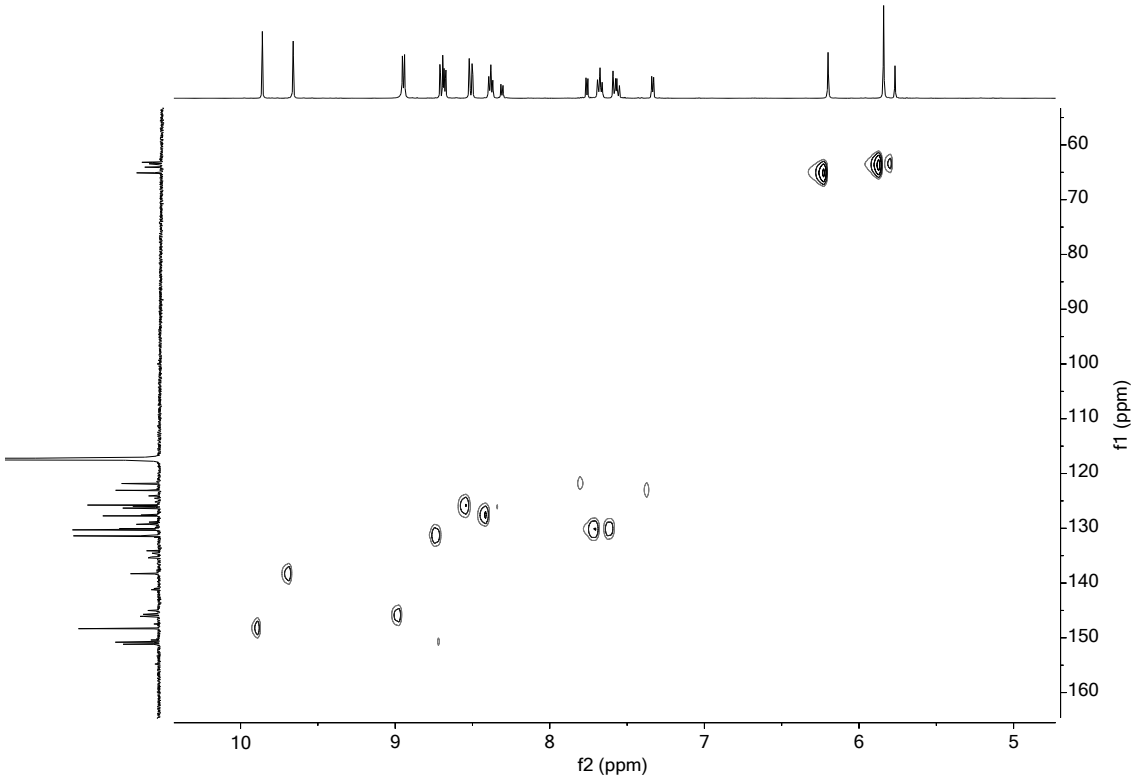


Figure S 12: HSQC (125 and 500MHz, CD_3CN) spectrum of **L4·3PF$_6$.**

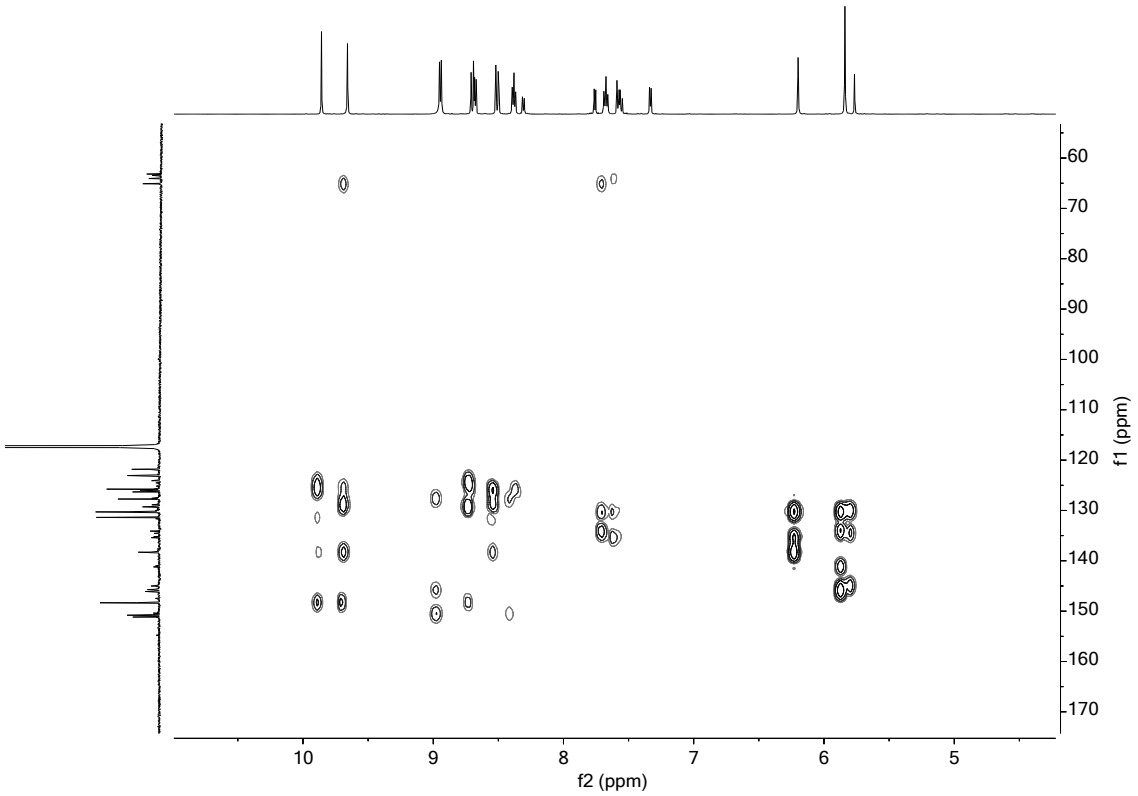


Figure S 13: HMBC (125 and 500MHz, CD_3CN) spectrum of **L4·3PF$_6$.**

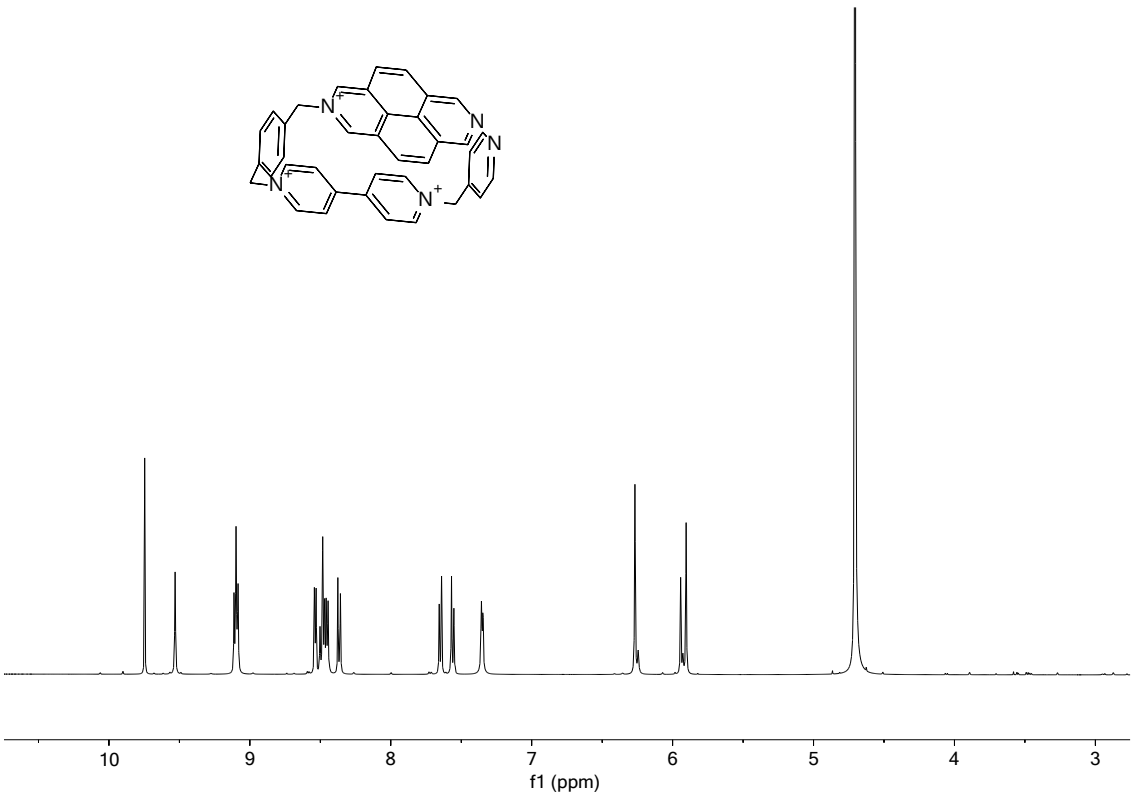


Figure S 14: ^{1}H RMN (500MHz, D_2O) spectrum of **L4·3NO$_3$.**

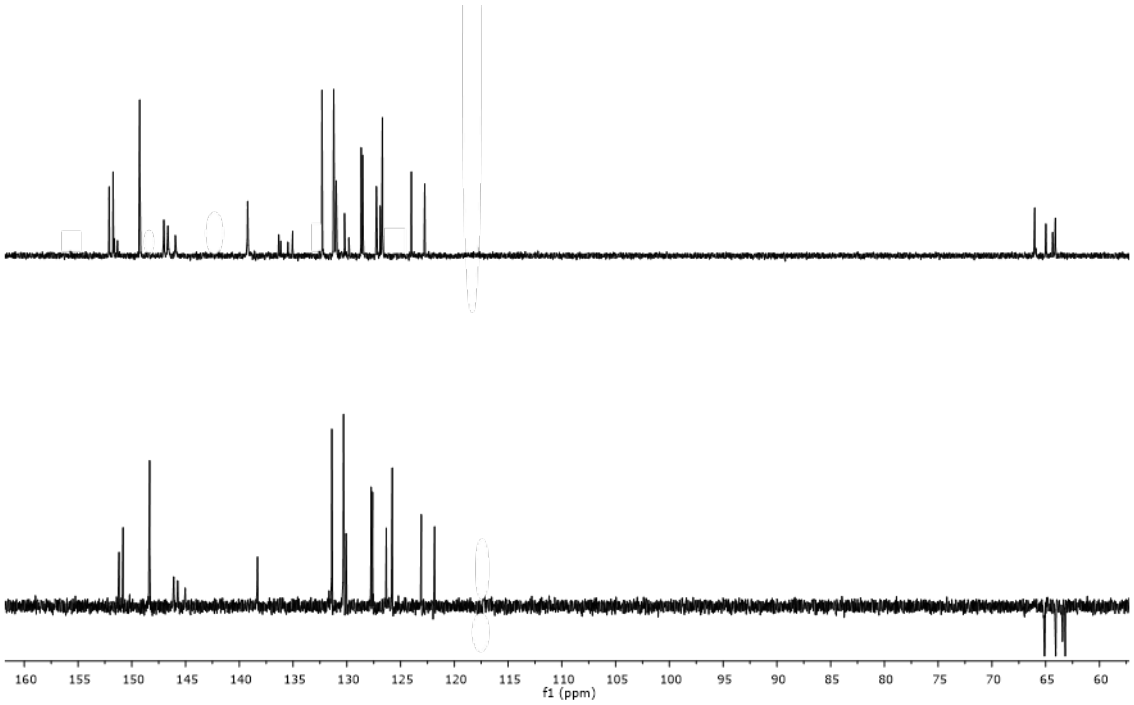


Figure S 15: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **L4·NO$_3$.**

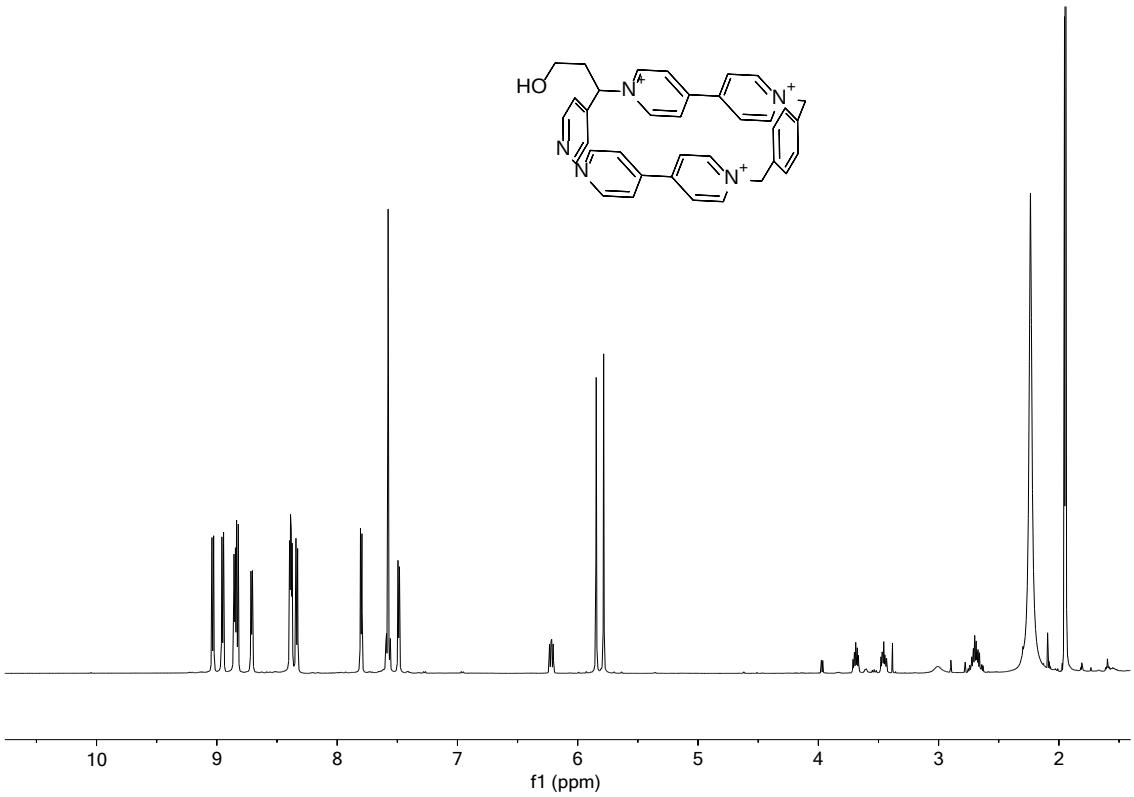
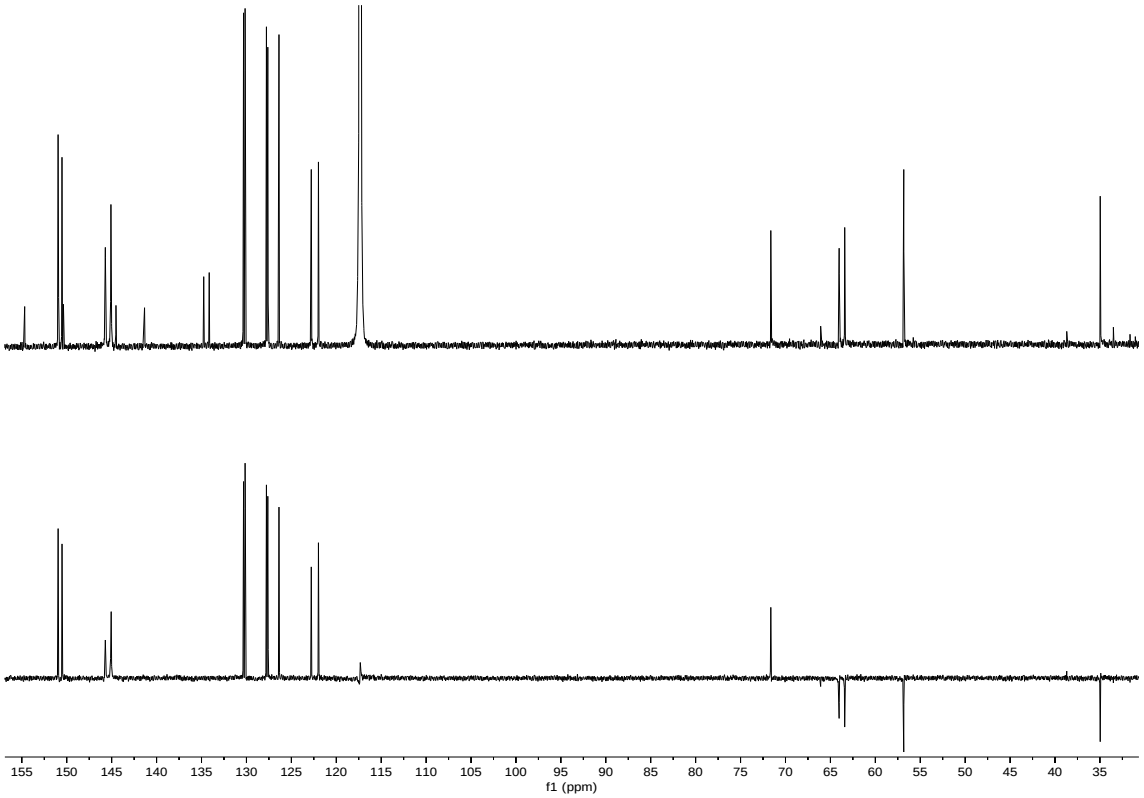


Figure S 16: ^{1}H RMN (500MHz, CD_3CN) spectrum of **L5·3PF$_6$.**



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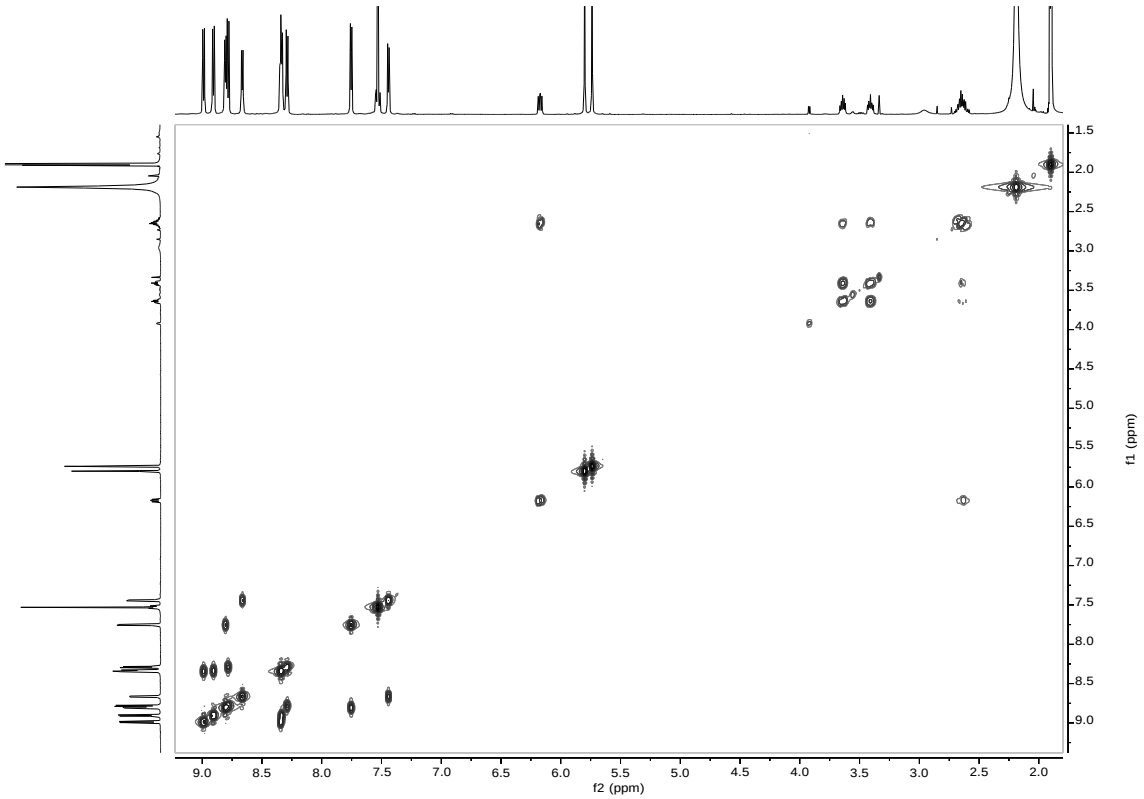

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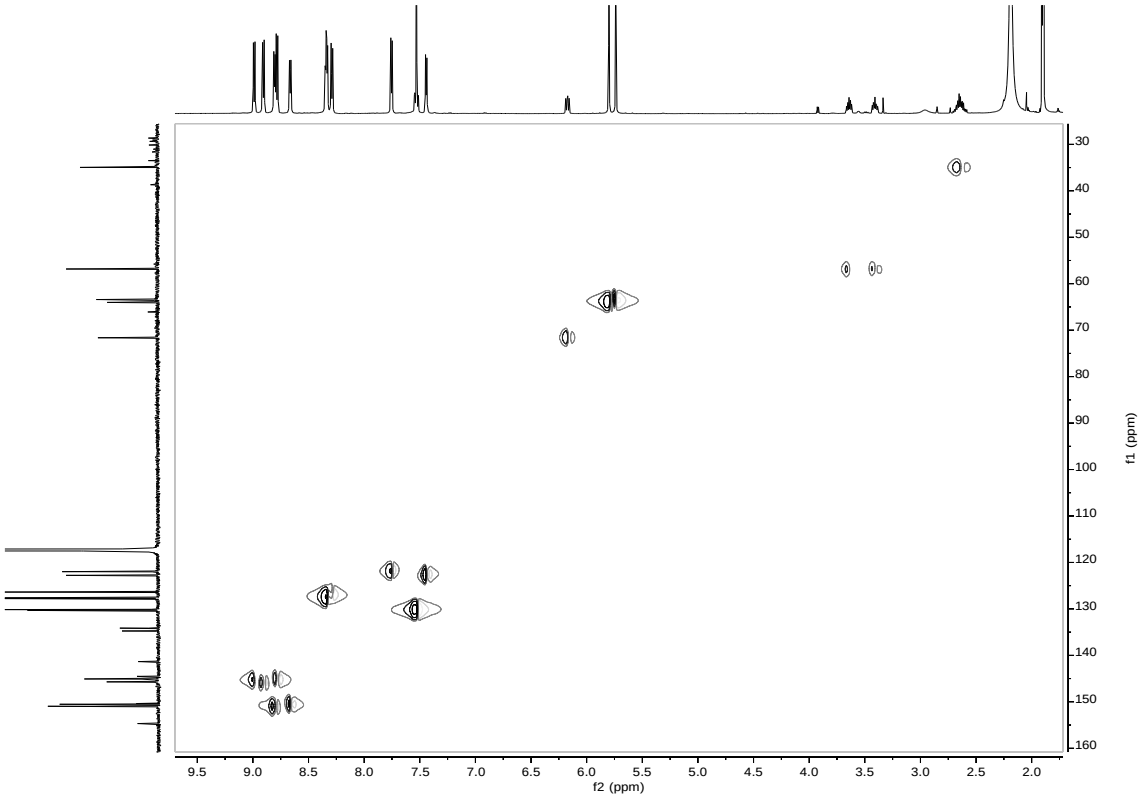

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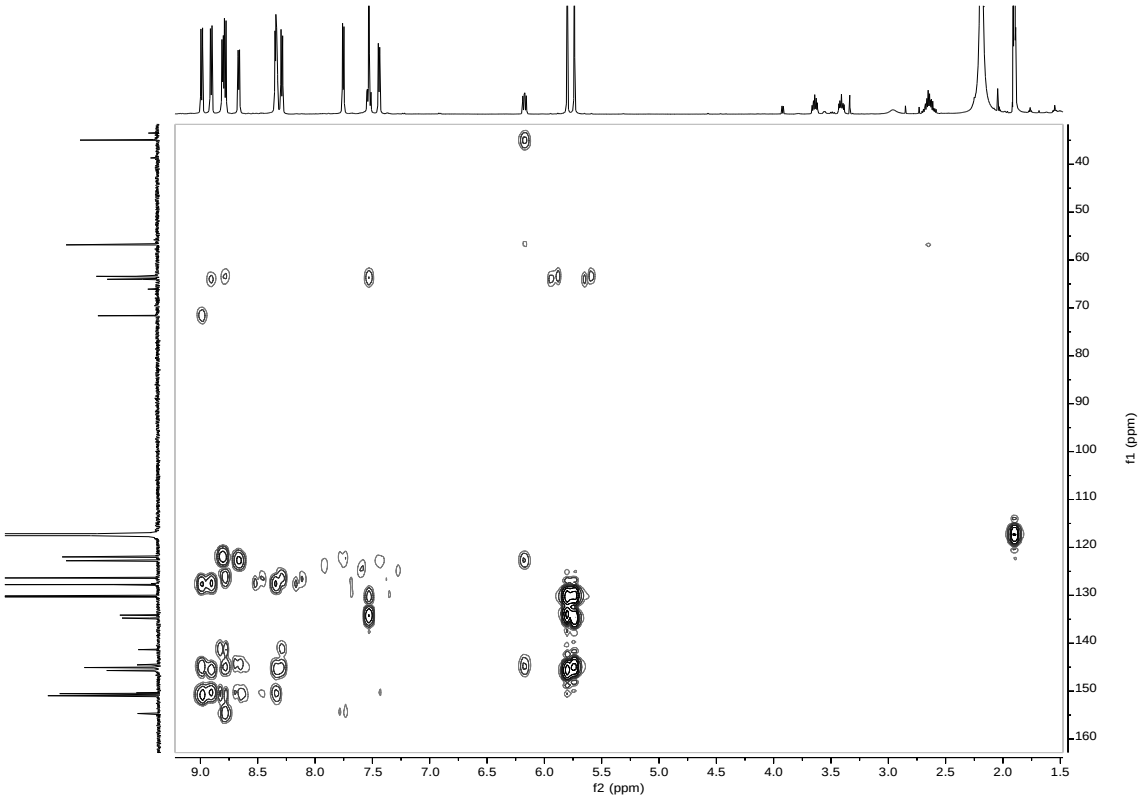


Figure S 20: HMBC (125 and 500MHz, CD_3CN) spectrum of **L5·3PF$_6$.**

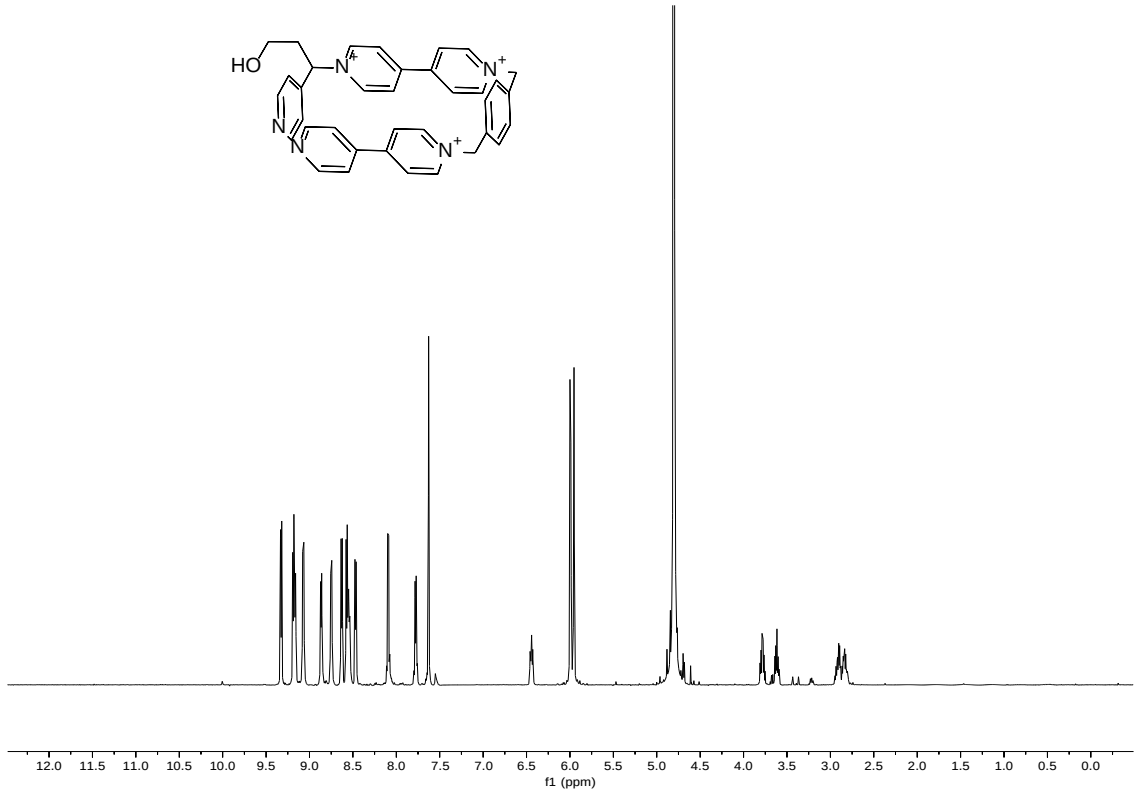


Figure S 21: ^{1}H RMN (500MHz, D_2O) spectrum of **L5·3NO$_3$.**

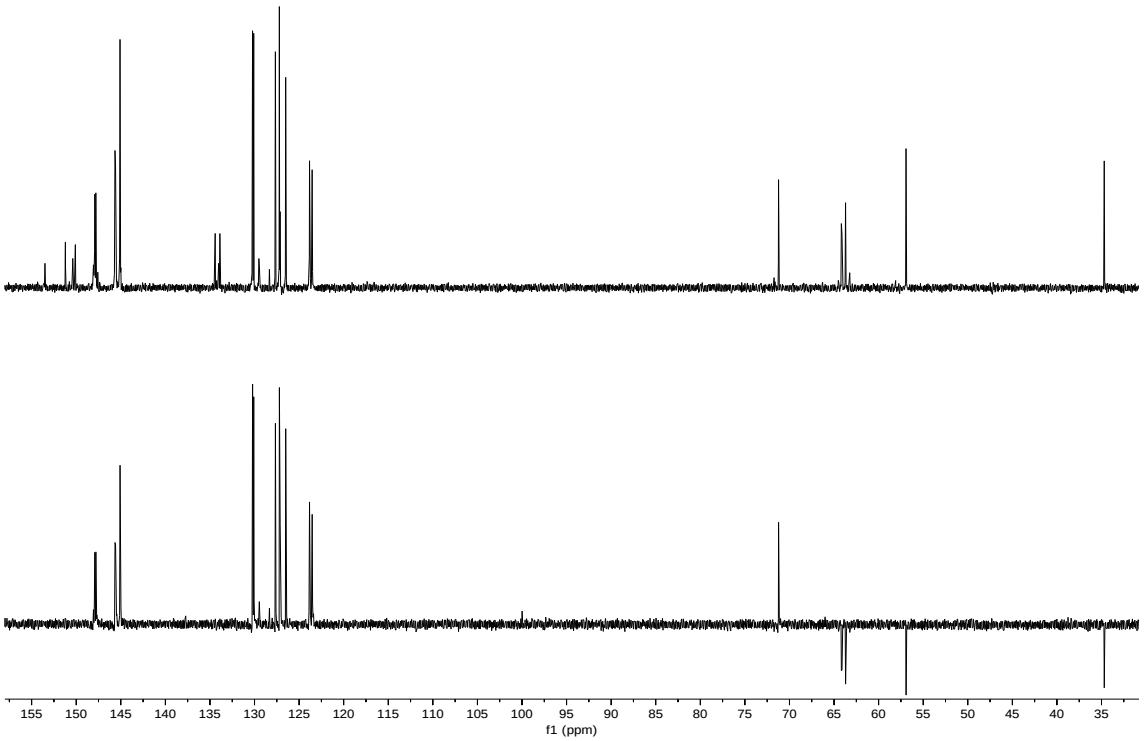


Figure S 22: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **L5·3NO$_3$.**

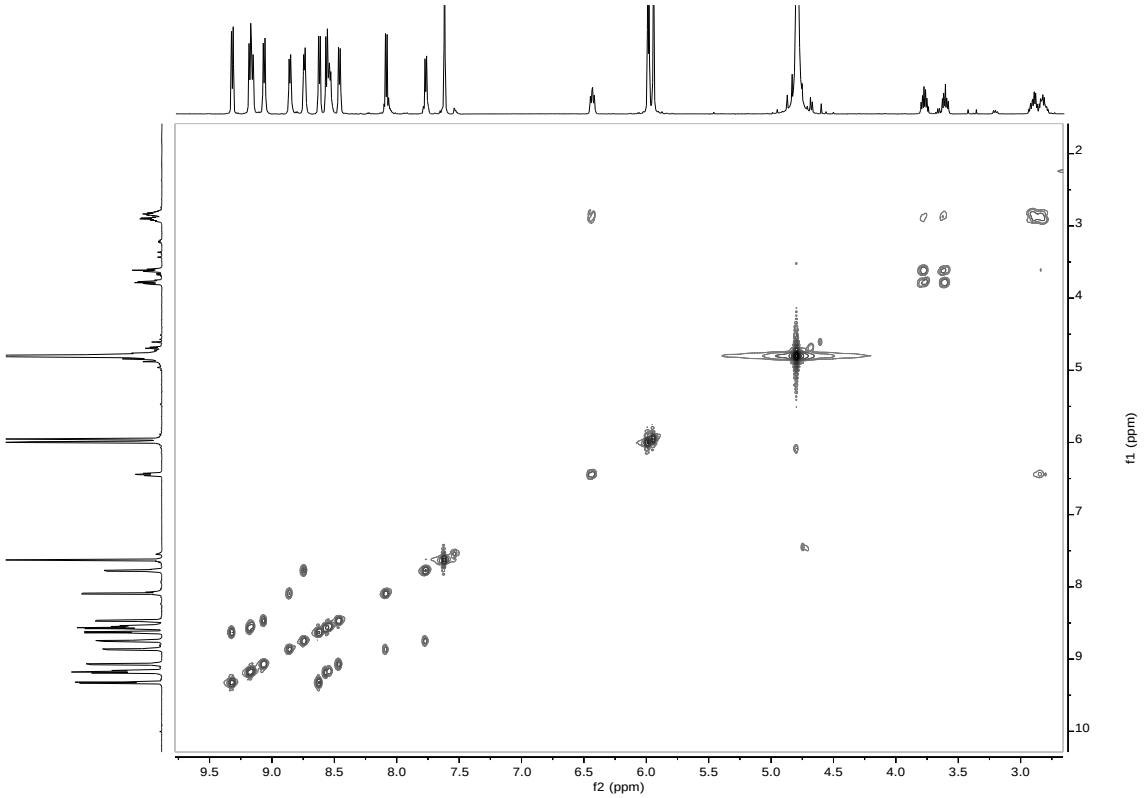


Figure S 23: COSY (500MHz, D_2O) spectrum of **L5·3NO$_3$.**

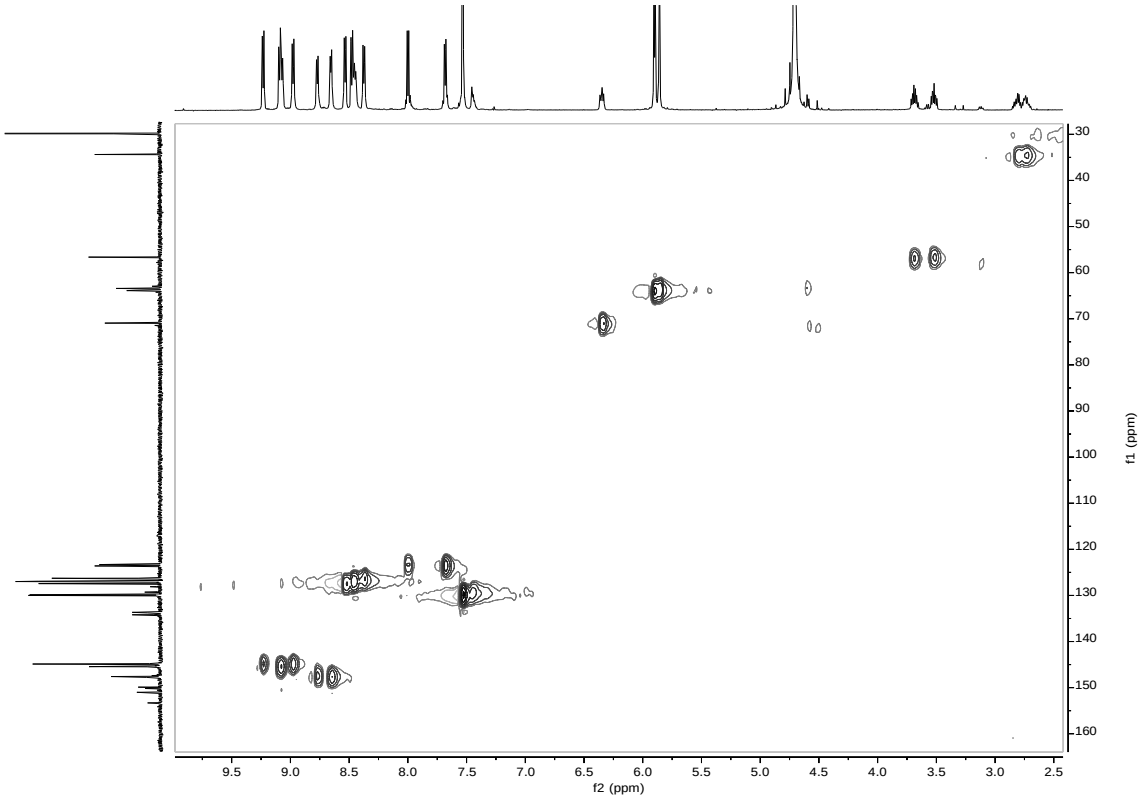


Figure S 24: HSQC (125 and 500MHz, D_2O) spectrum of **L5·3NO$_3$.**

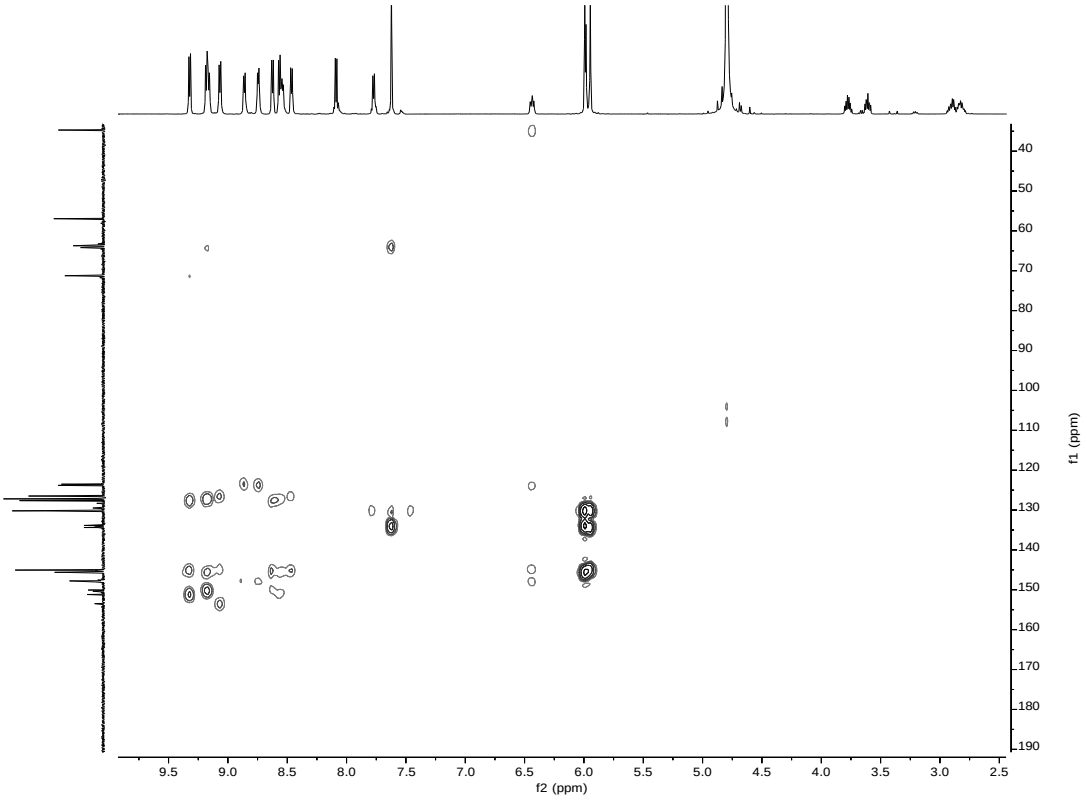


Figure S 25: HMBC (125 and 500MHz, D_2O) spectrum of **L5·3NO$_3$**

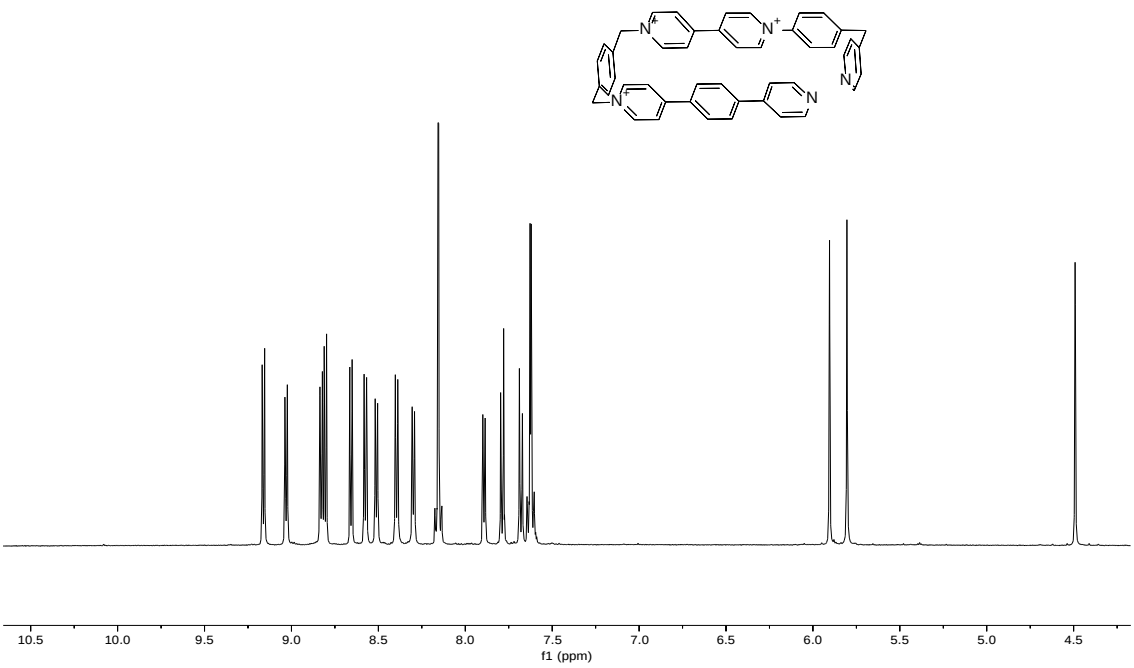
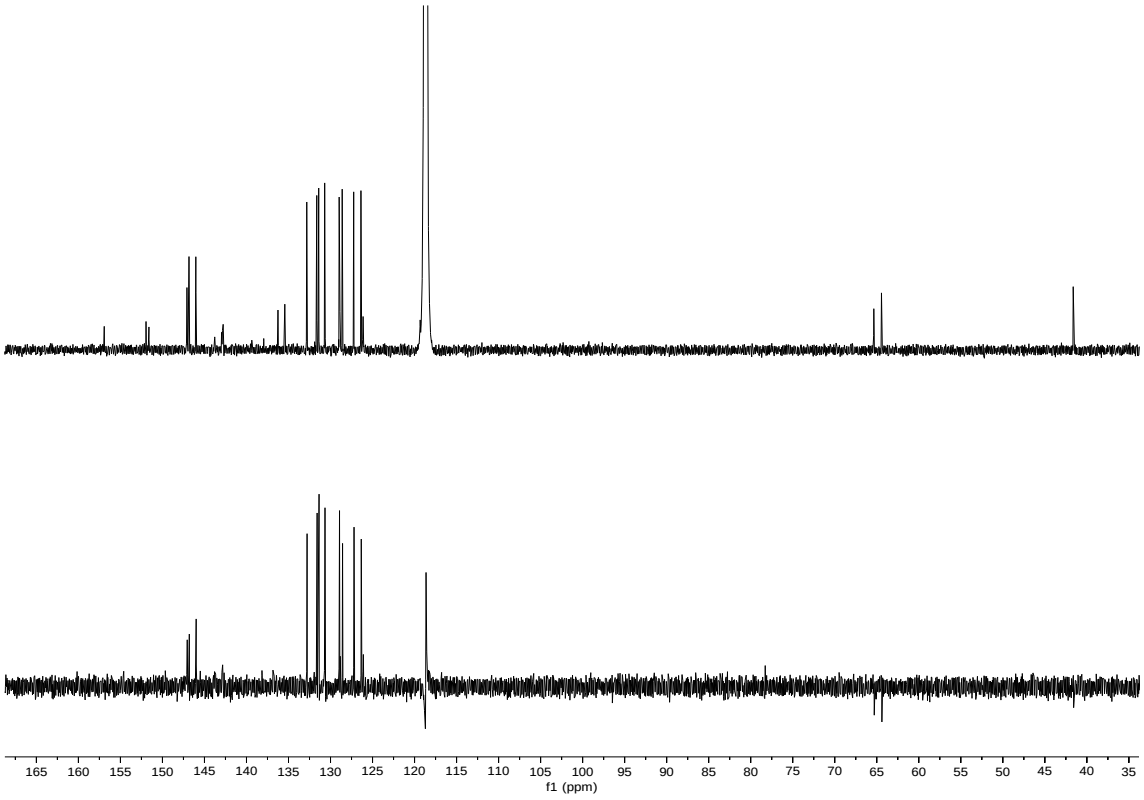


Figure S 26: ^{1}H RMN (500MHz, CD_3CN) spectrum of **L6·3PF$_6$.**



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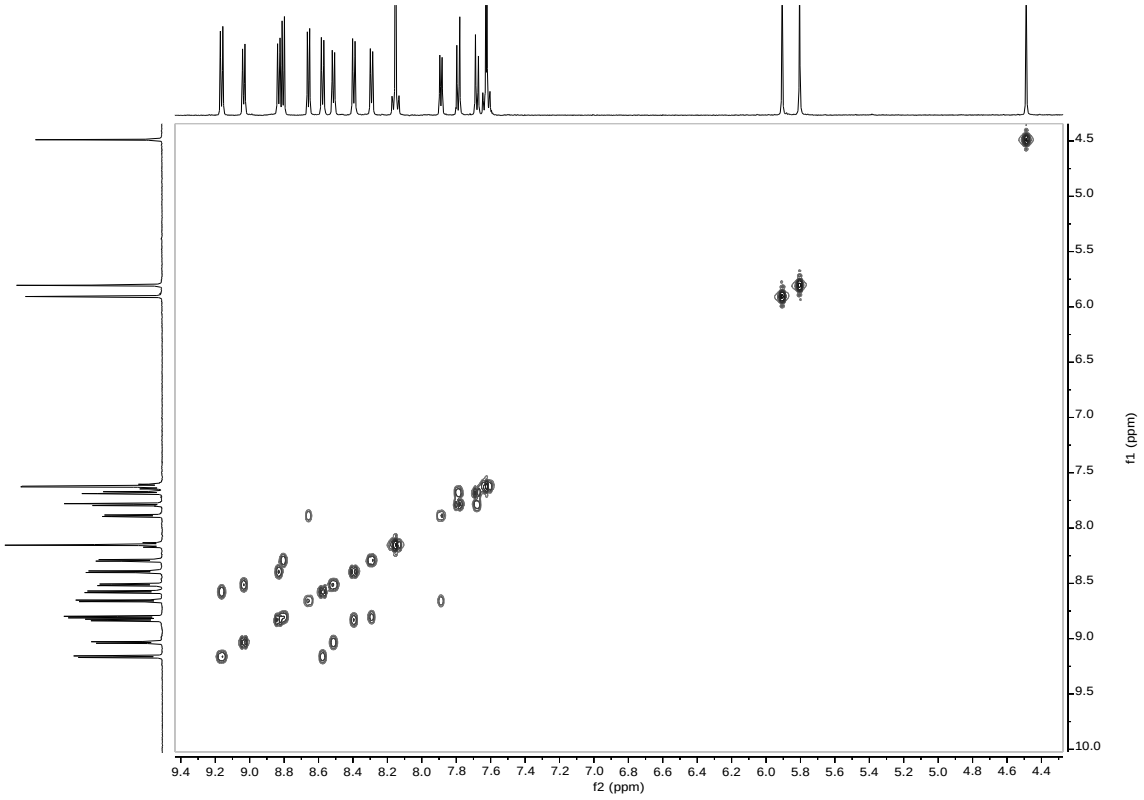

Figure S 28: COSY (500MHz, CD_3CN) spectrum of **L6·3PF$_6$.**

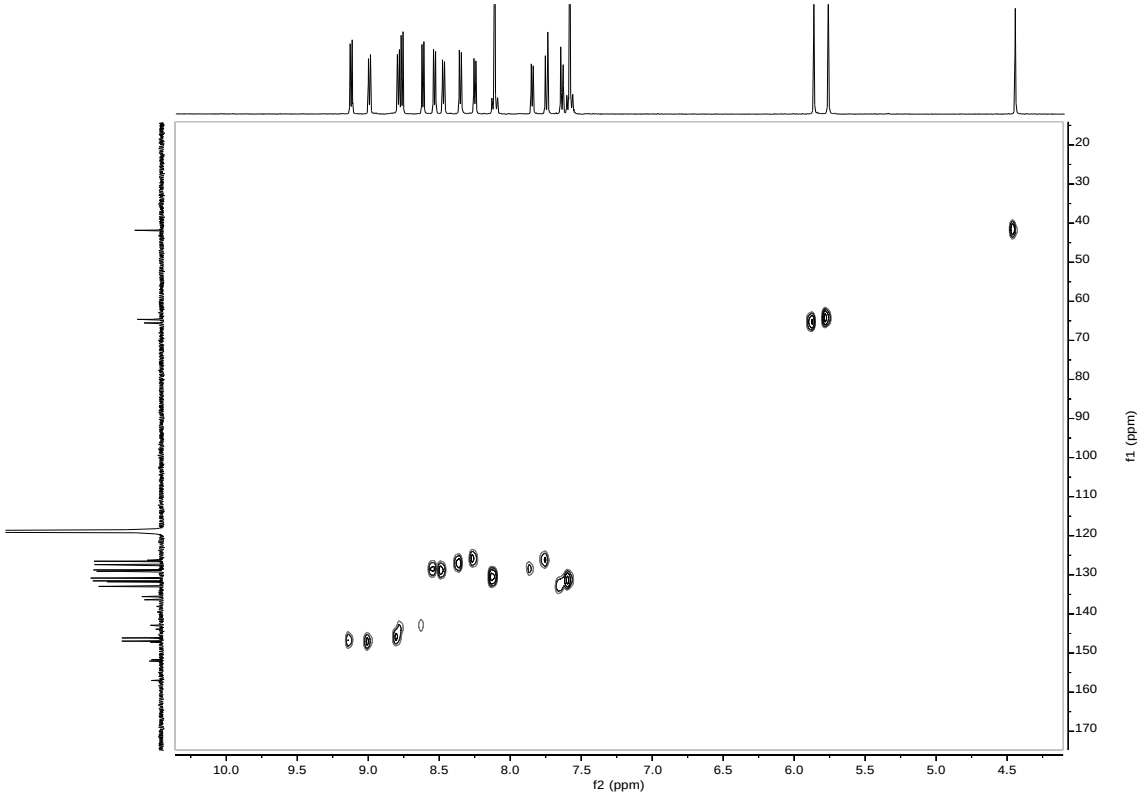

Figure S 29: HSQC (125 and 500MHz, CD_3CN) spectrum of **L6·3PF$_6$.**

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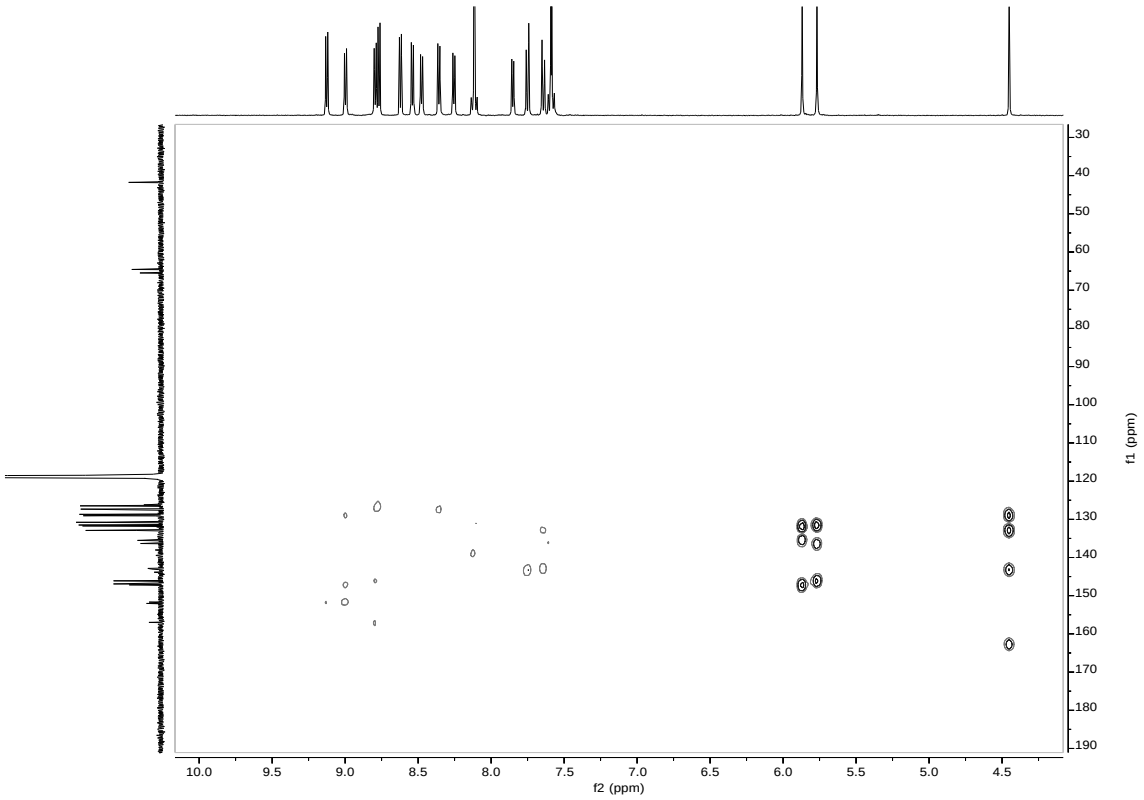


Figure S 30: HMBC (125 and 500MHz, CD_3CN) spectrum of **L6·3PF$_6$.**

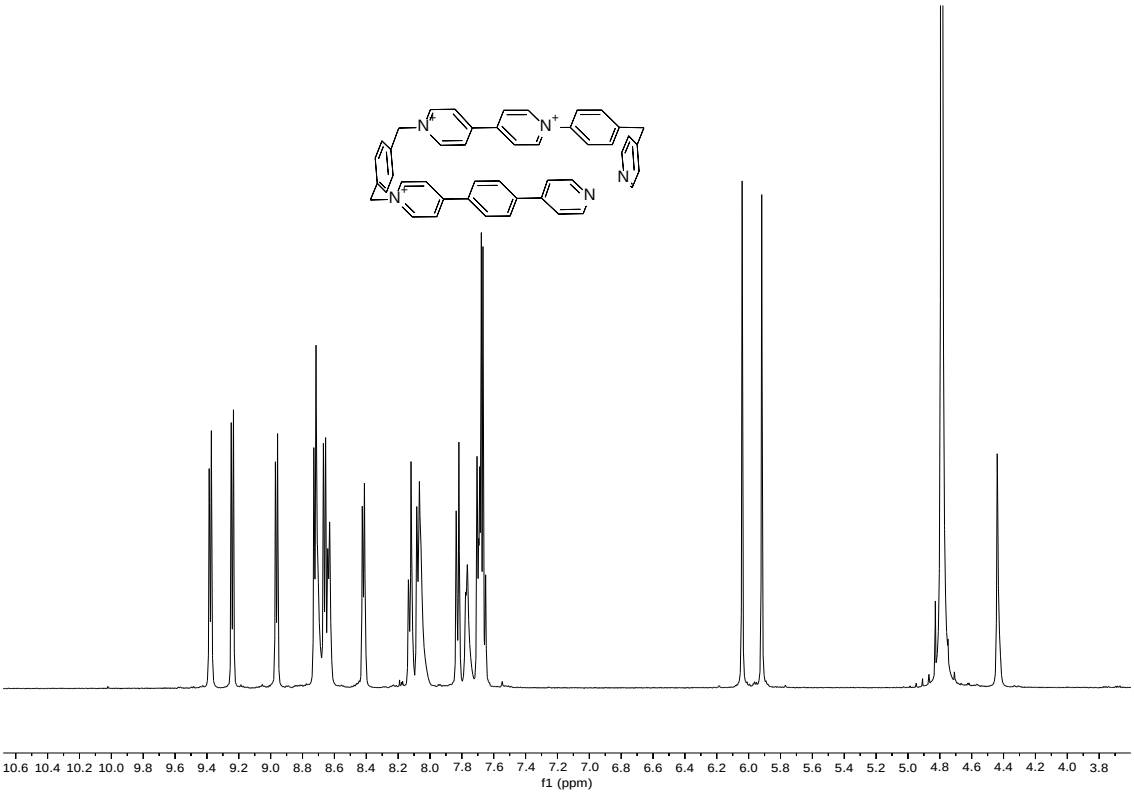


Figure S 31: ^{1}H RMN (500MHz, D_2O) spectrum of **L6·3NO$_3$.**

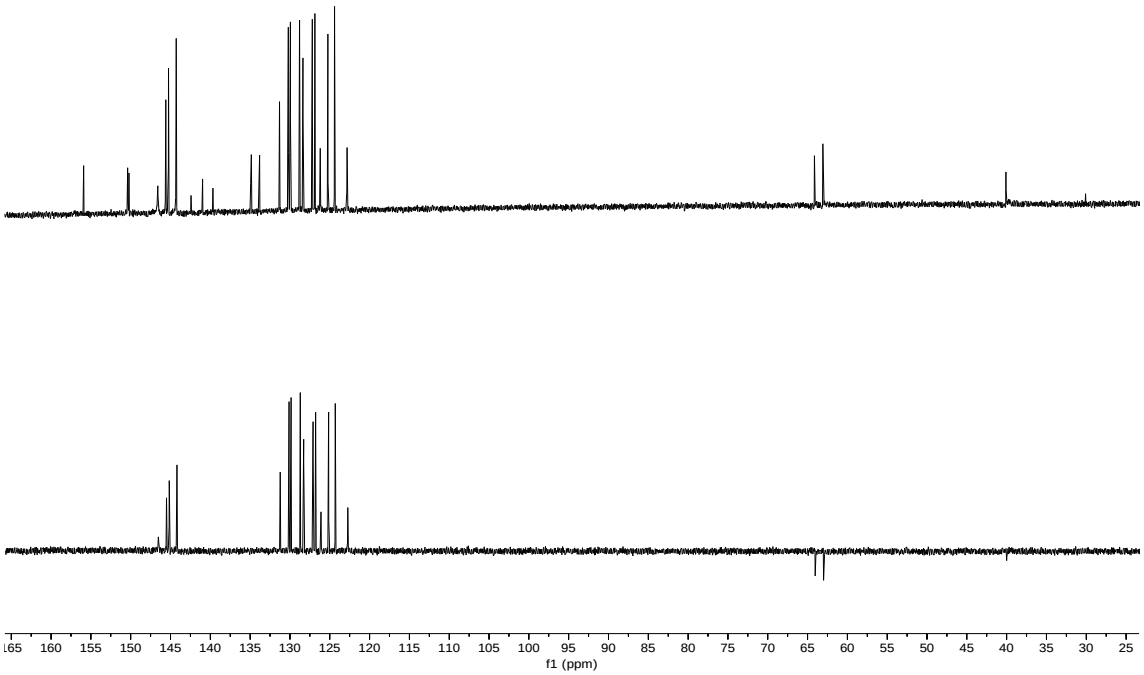


Figure S 32: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **L6·3NO$_3$.**

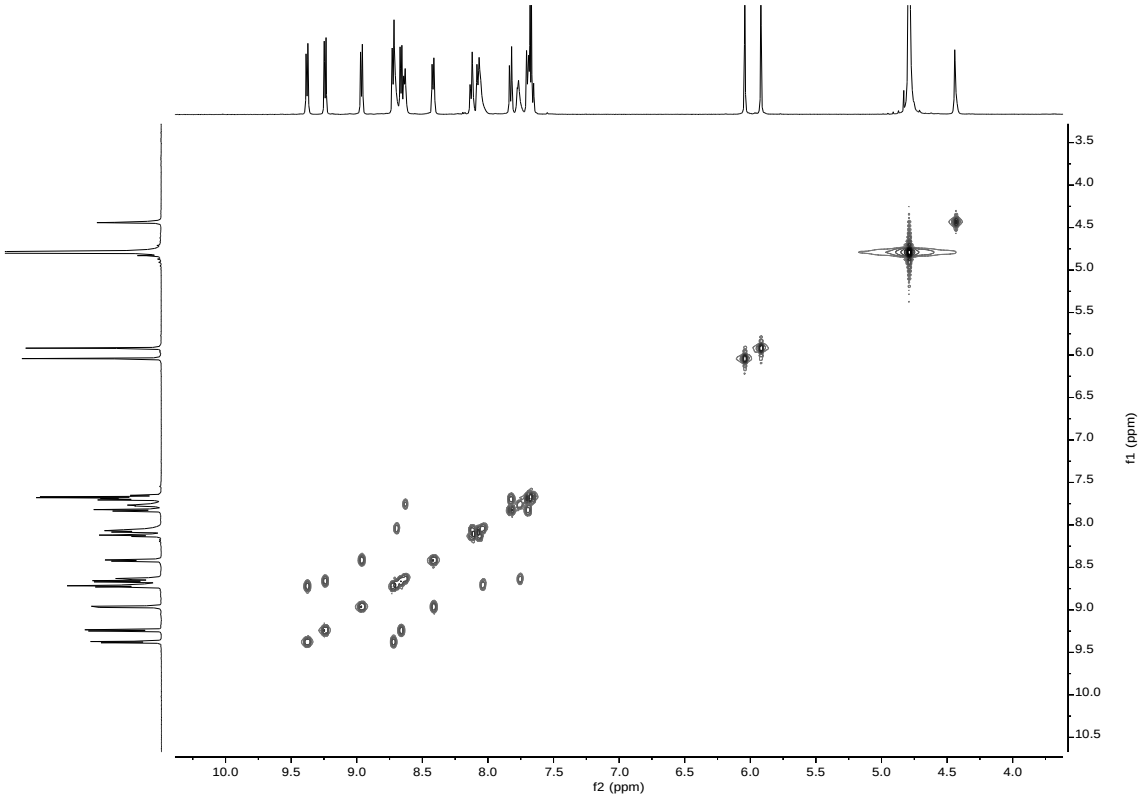


Figure S 33: COSY (500MHz, D_2O) spectrum of **L6·3NO$_3$.**

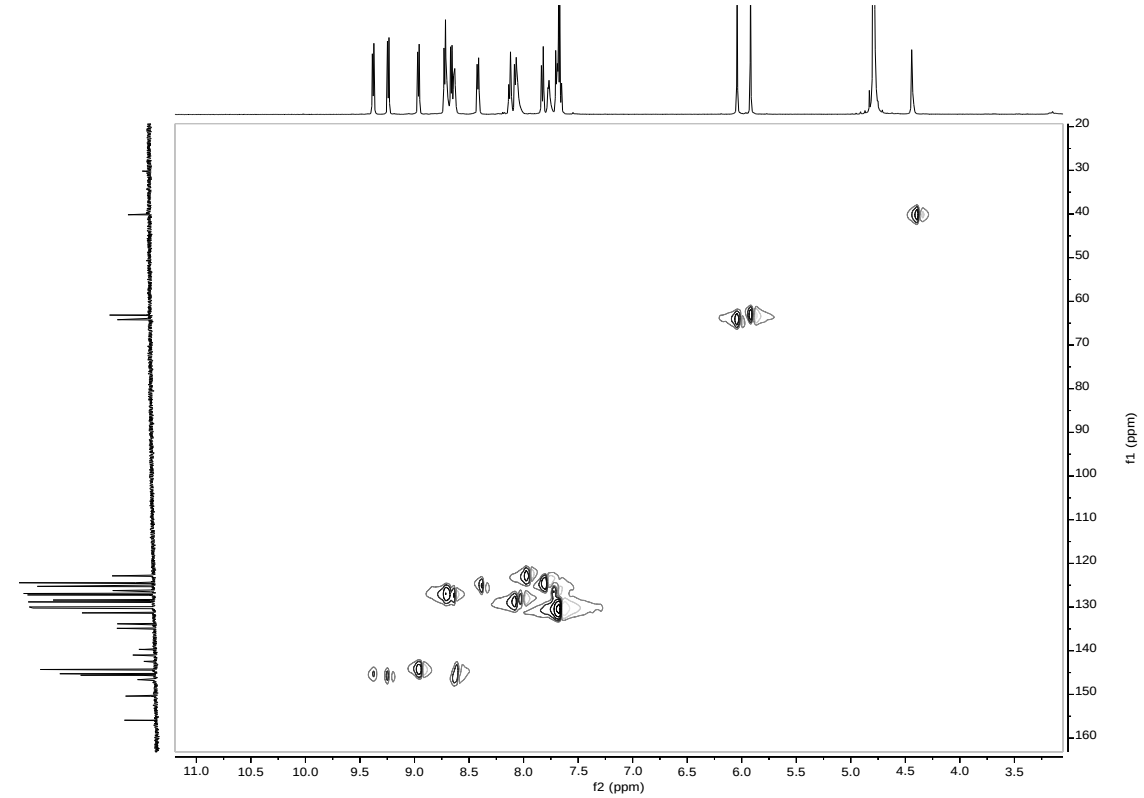
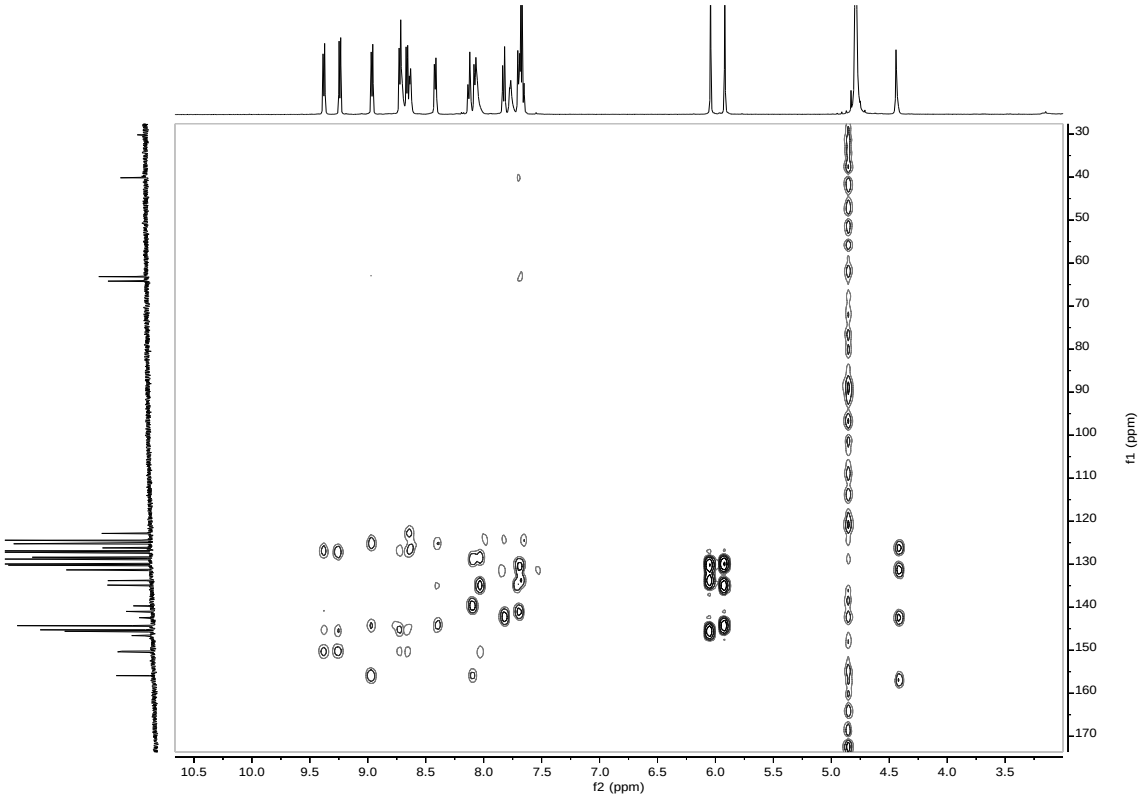


Figure S 34: HSQC (125 and 500MHz, D_2O) spectrum of **L6.3NO$_3$.**



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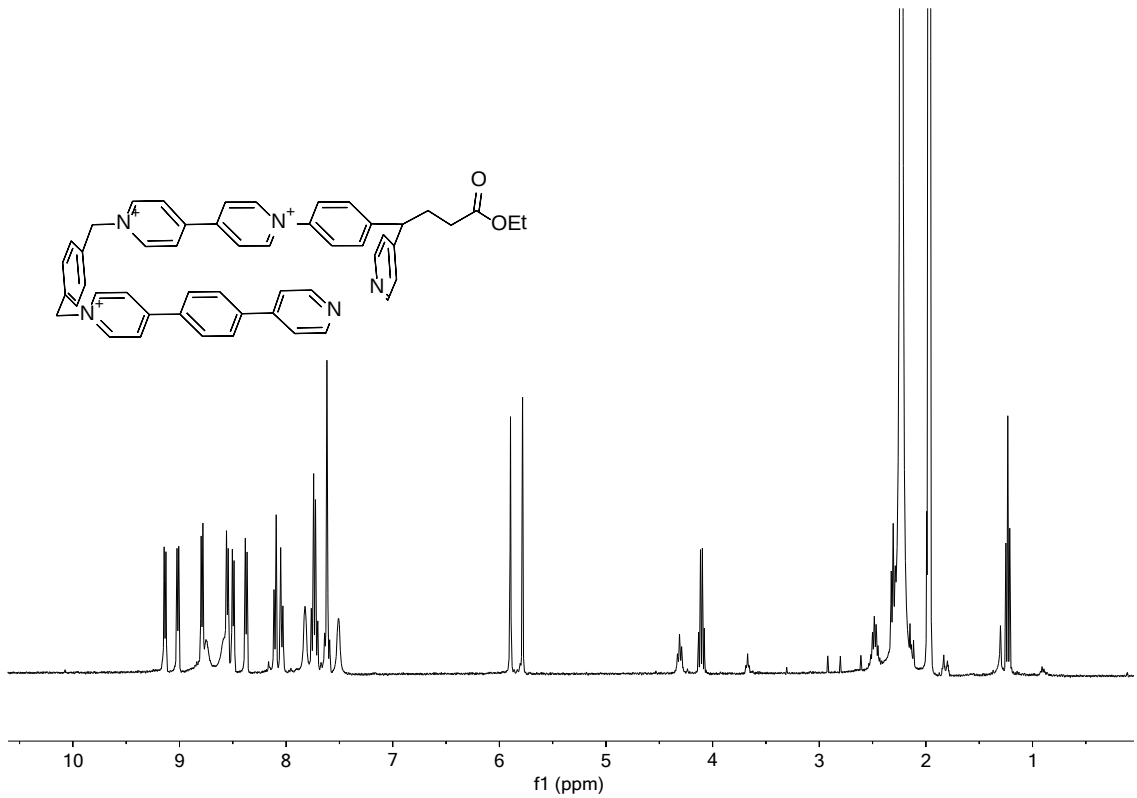


Figure S 36: ^{1}H RMN (500MHz, CD_3CN) spectrum of **L7·3PF$_6$.**

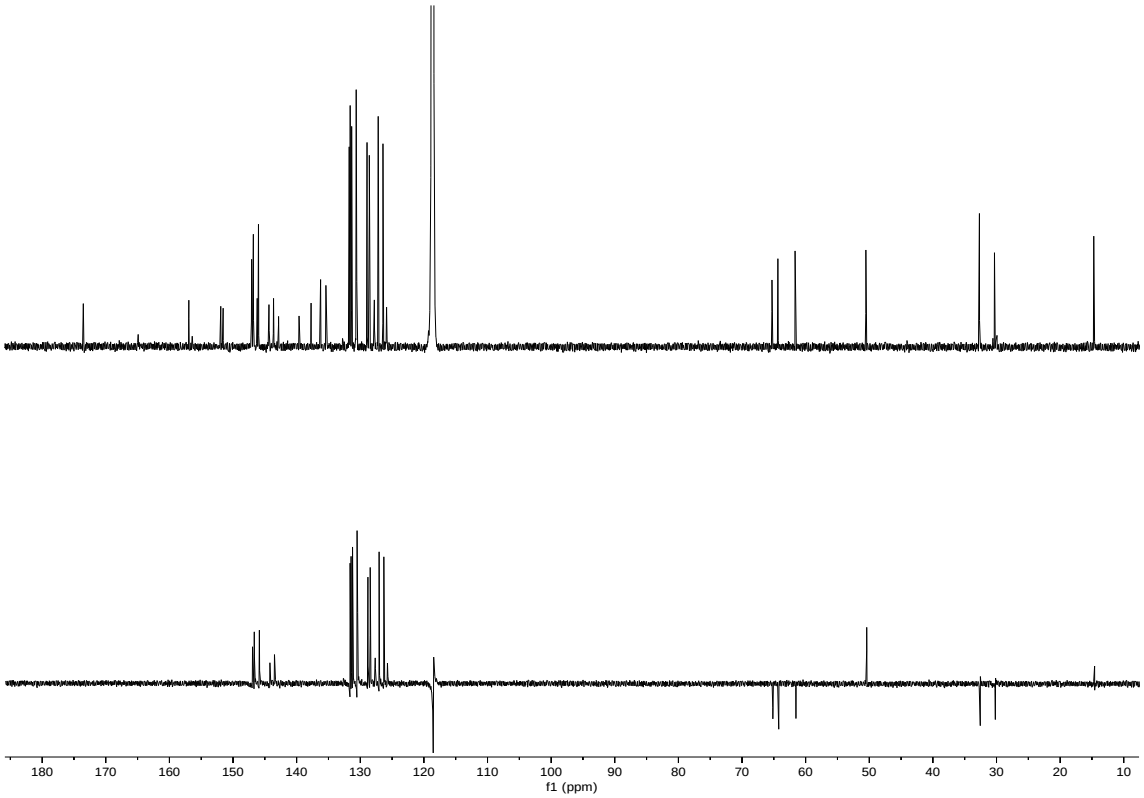


Figure S 37: ^{13}C and DEPT NMR (125 MHz, CD_3CN) spectrum of **L7·3PF$_6$.**

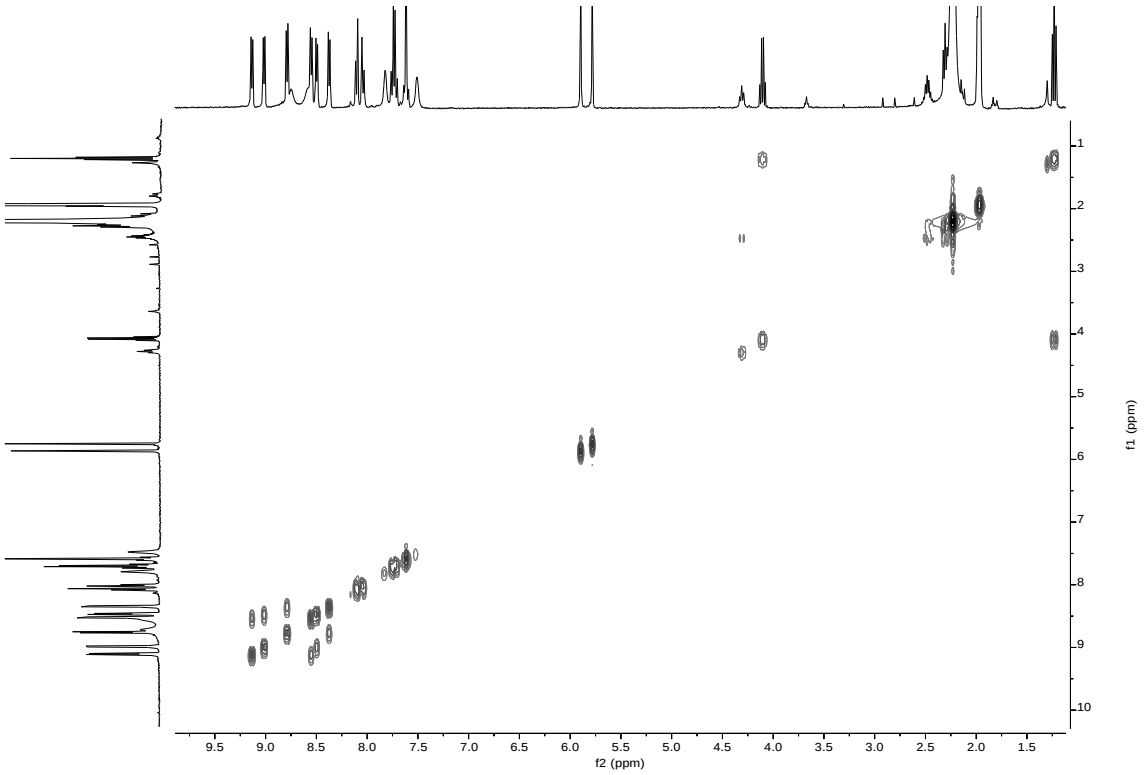


Figure S 38: COSY (500MHz, CD_3CN) spectrum of **L7·3PF$_6$.**

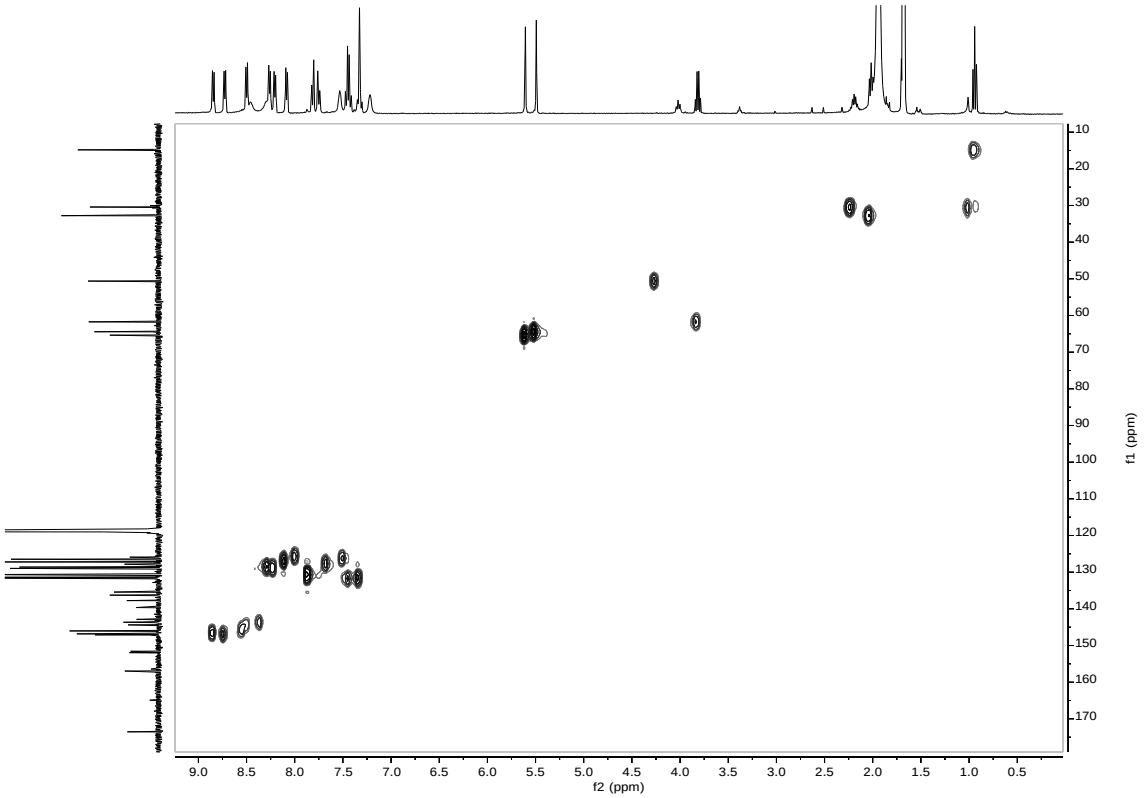
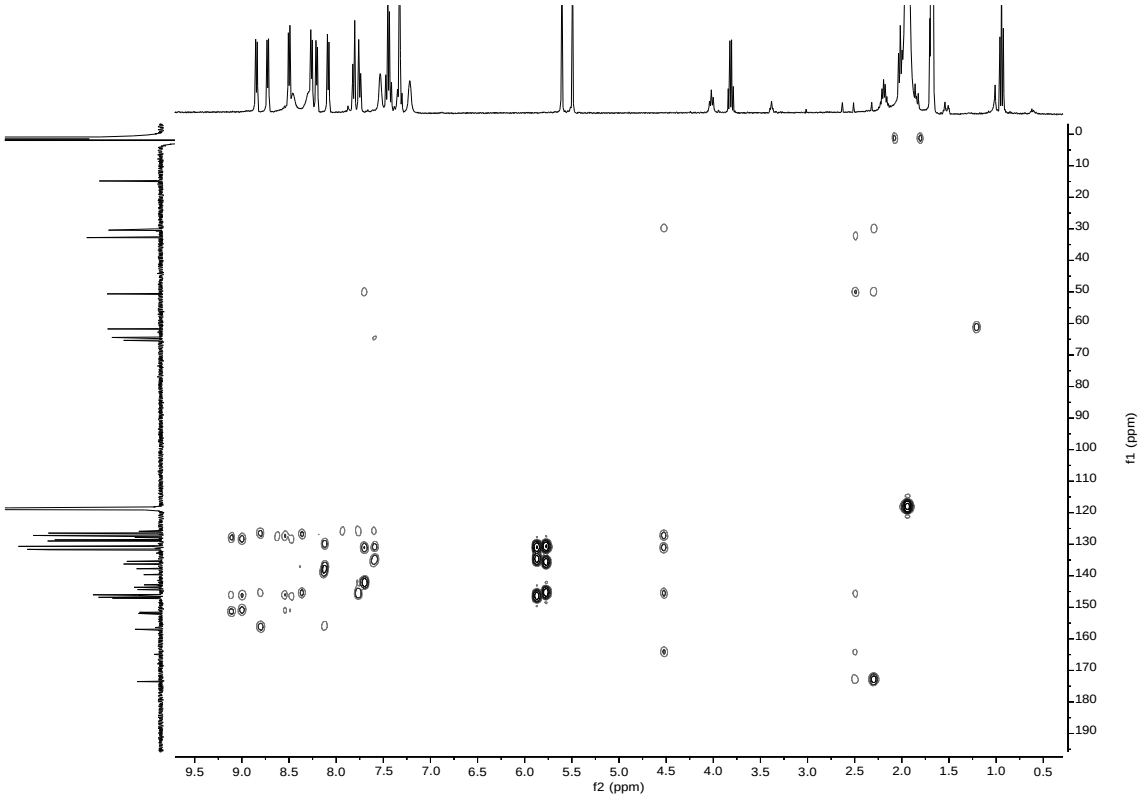


Figure S 39: HSQC (125 and 500MHz, CD_3CN) spectrum of **L7·3PF$_6$.**



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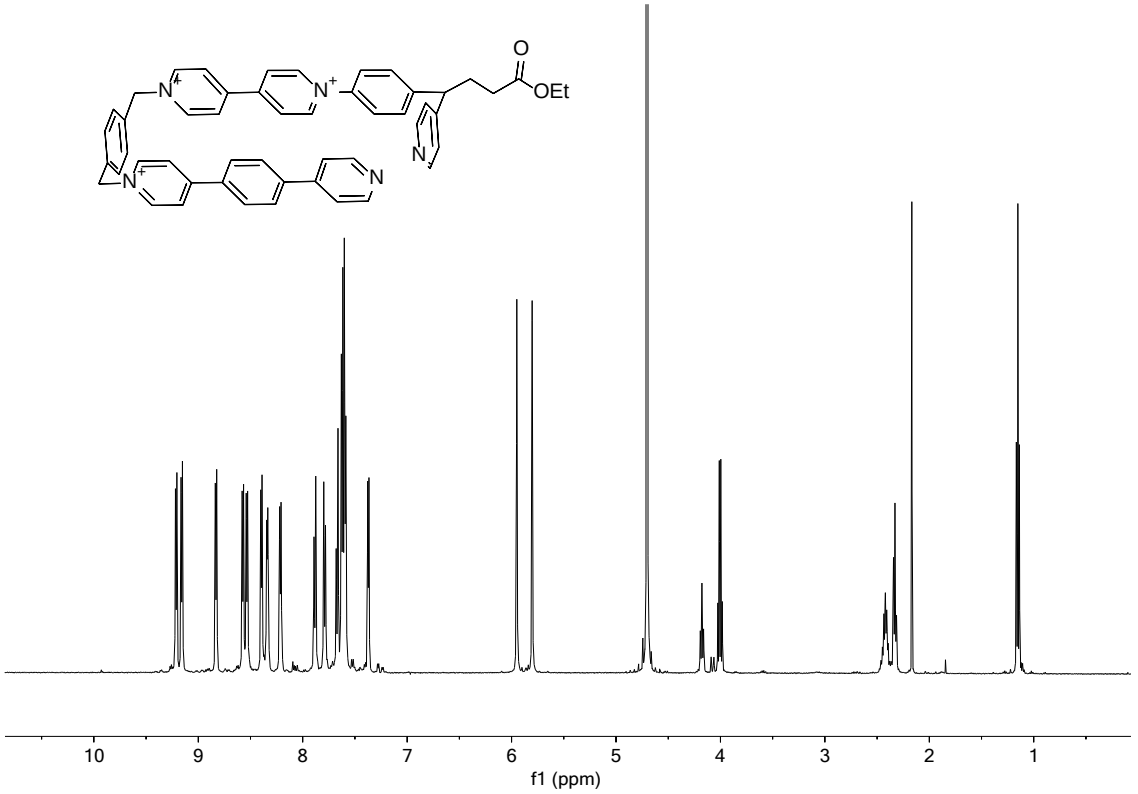

Figure S 41: ^{1}H RMN (500MHz, D_2O) spectrum of **L7·3NO$_3$.**

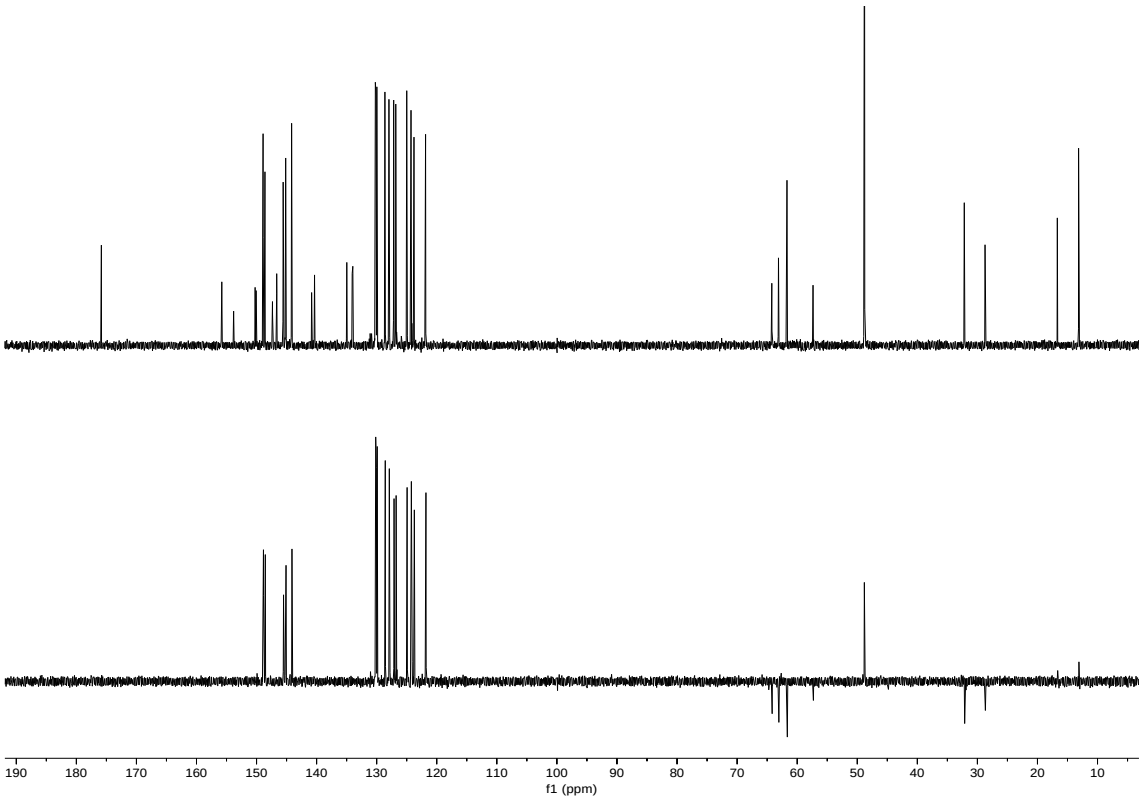

Figure S 42: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **L7·3NO$_3$.**

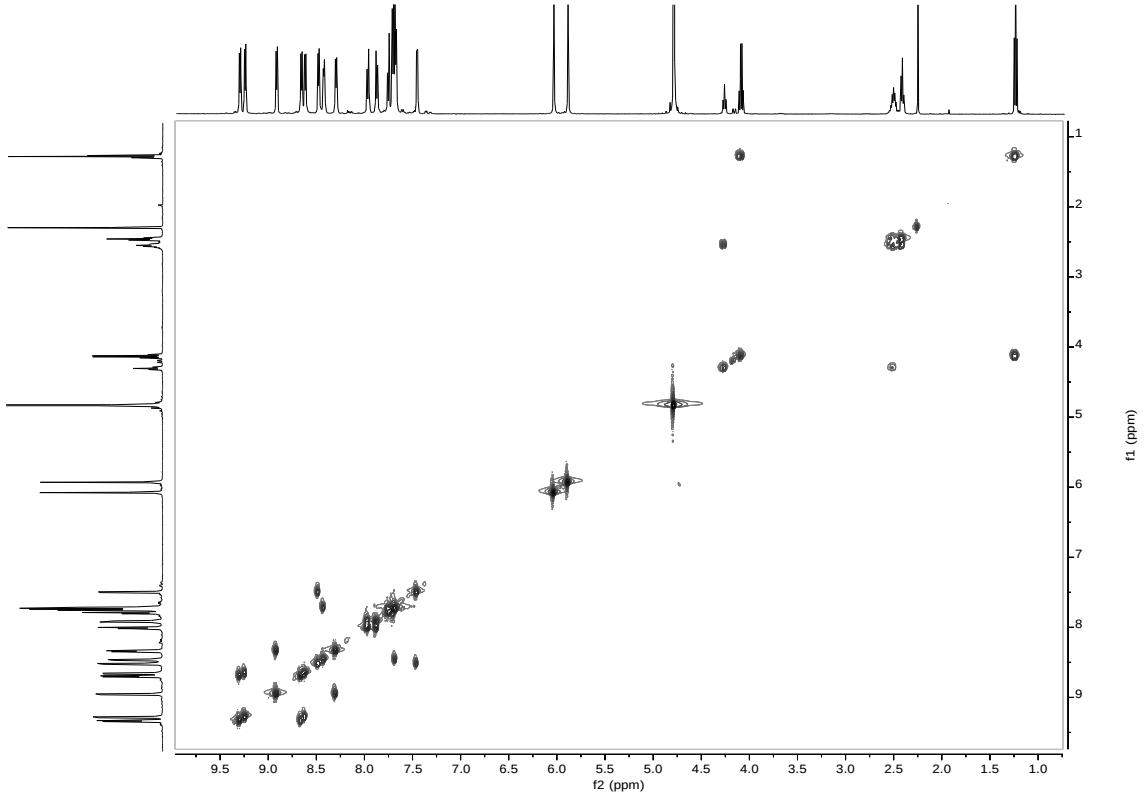

Figure S 43: COSY (500MHz, D_2O) spectrum of **L7·3NO$_3$.**

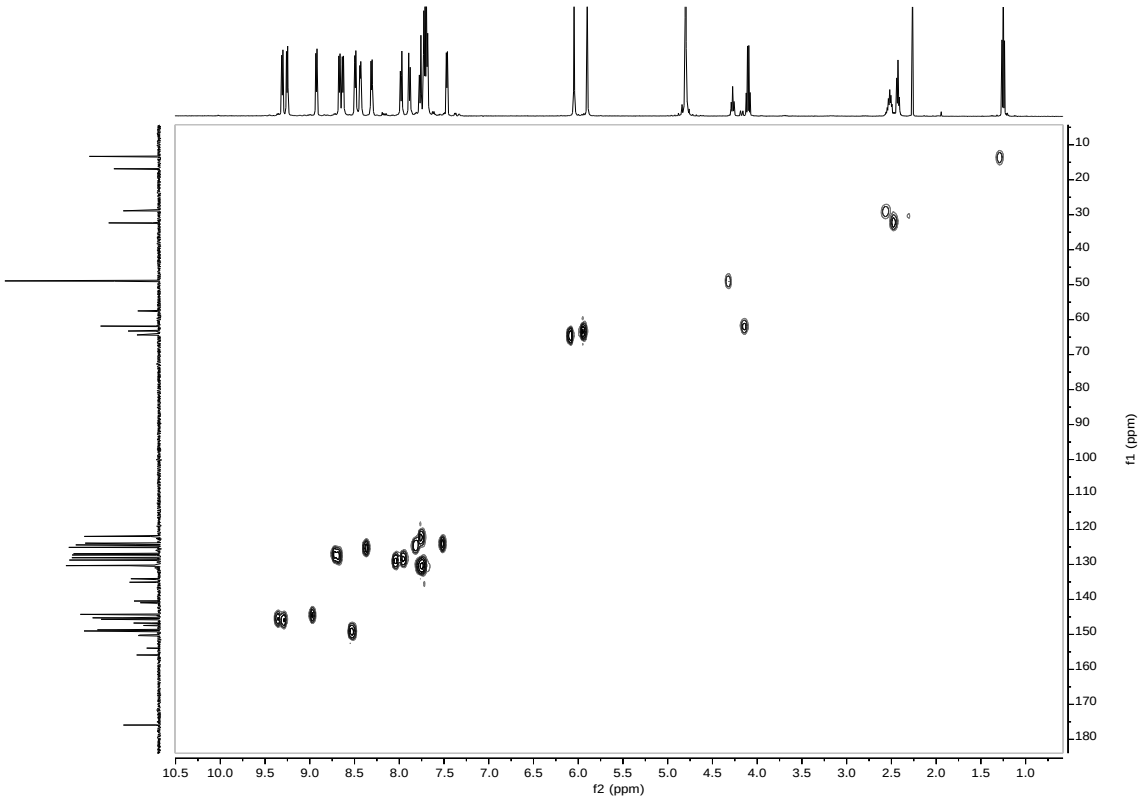

Figure S 44: HSQC (125 and 500MHz, D_2O) spectrum of **L7·3NO$_3$.**

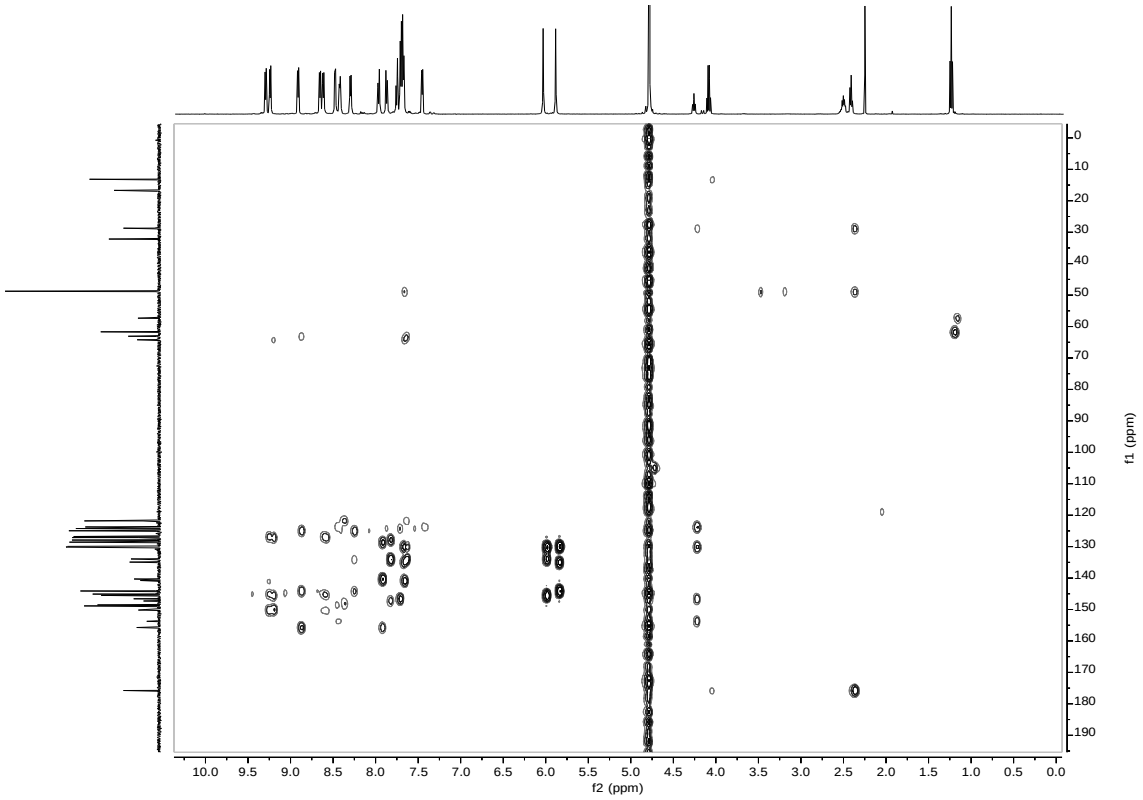

Figure S 45: HMBC (125 and 500MHz, D_2O) spectrum of **L7·3NO$_3$.**

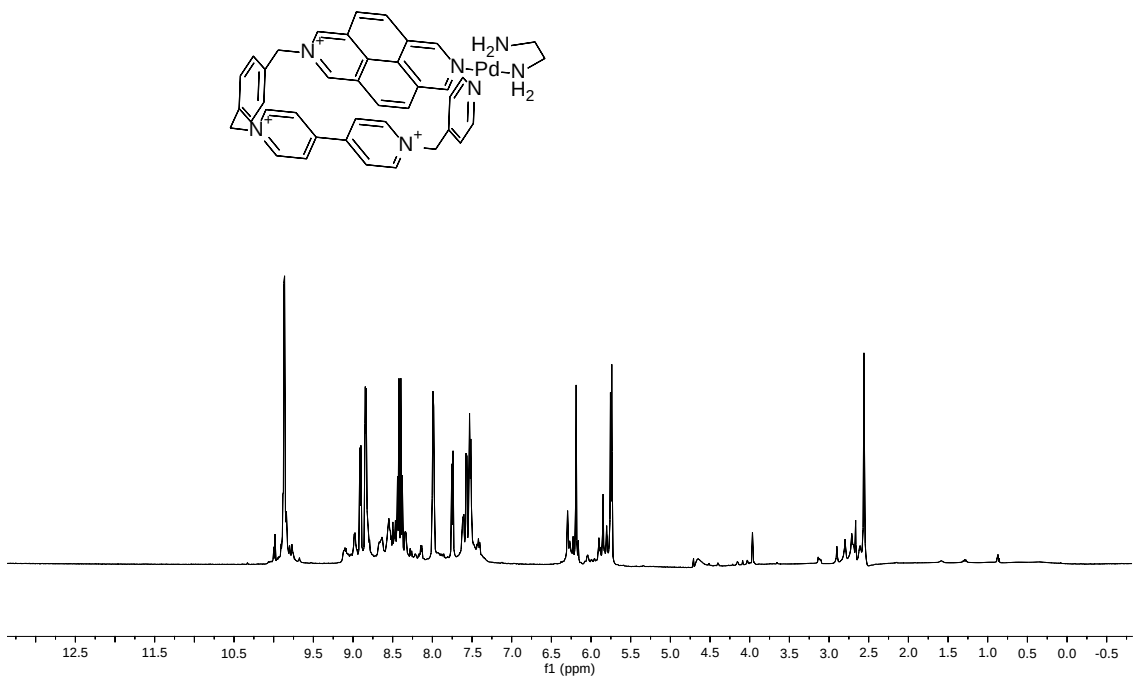

Figure S 46: ^{1}H RMN (500MHz, D_2O) spectrum of **M4a·5NO$_3$.**

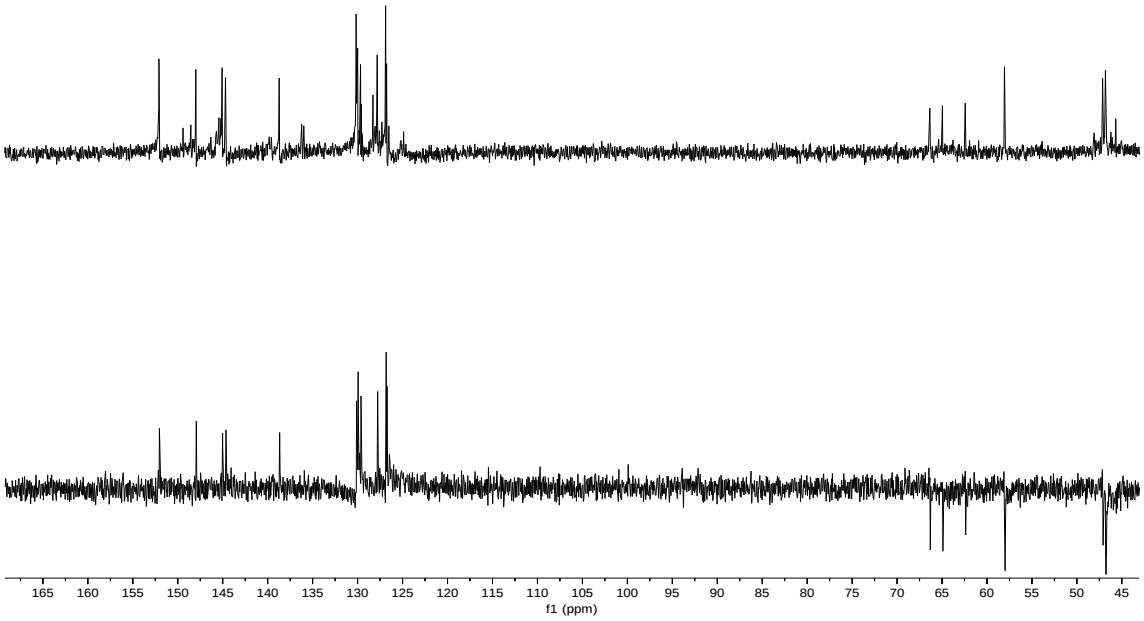

Figure S 47: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **M4a·5NO$_3$.**

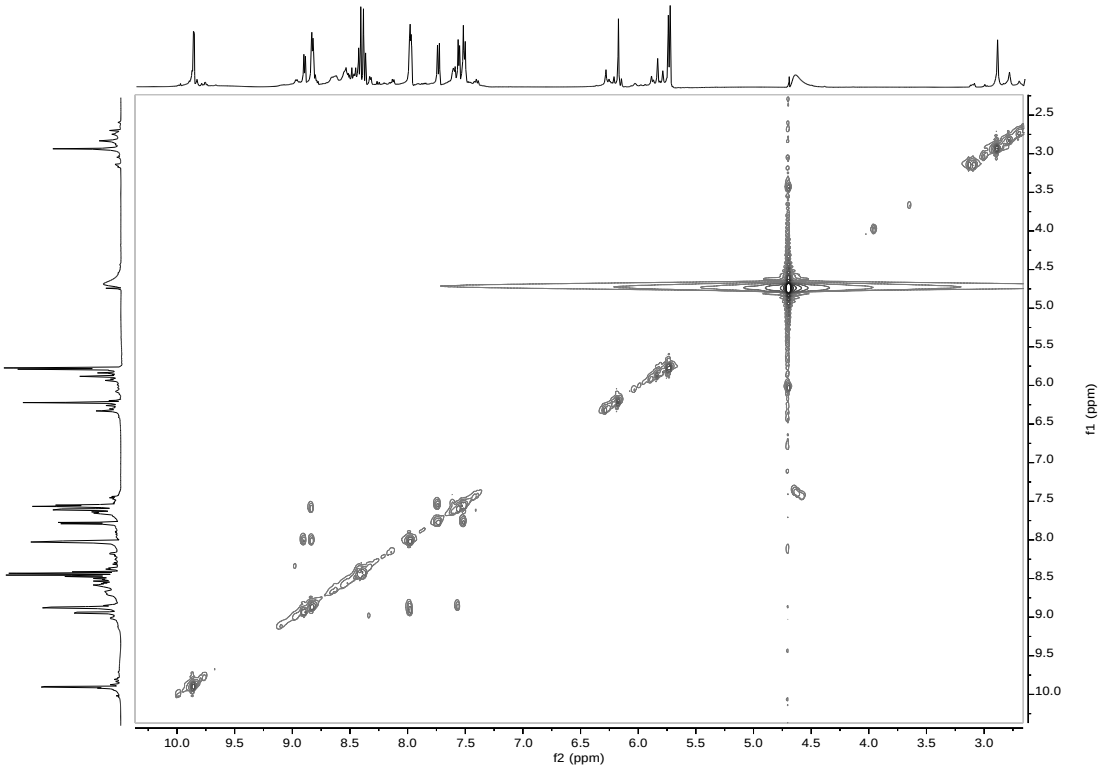

Figure S 48: COSY (500MHz, D_2O) spectrum of **M4a·5NO$_3$.**

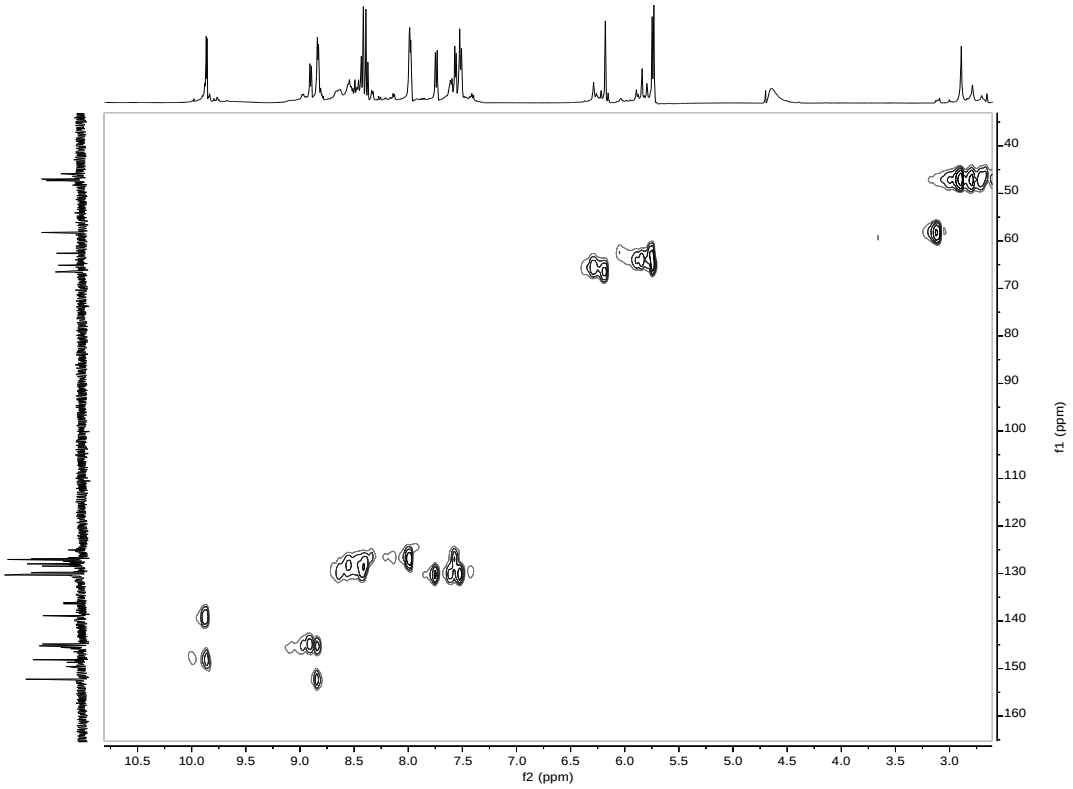

Figure S 49: HSQC (125 and 500MHz, D_2O) spectrum of **M4a·5NO$_3$.**

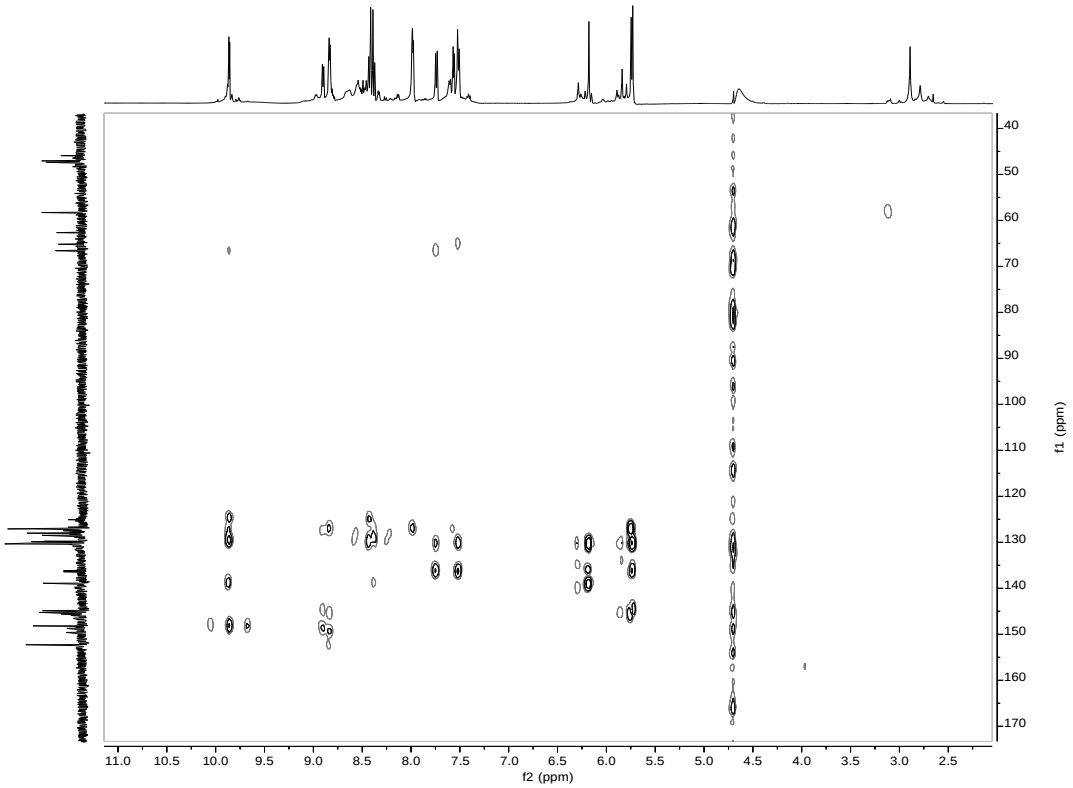

Figure S 50: HMBC (125 and 500MHz, D_2O) spectrum of **M4a.5NO$_3$.**

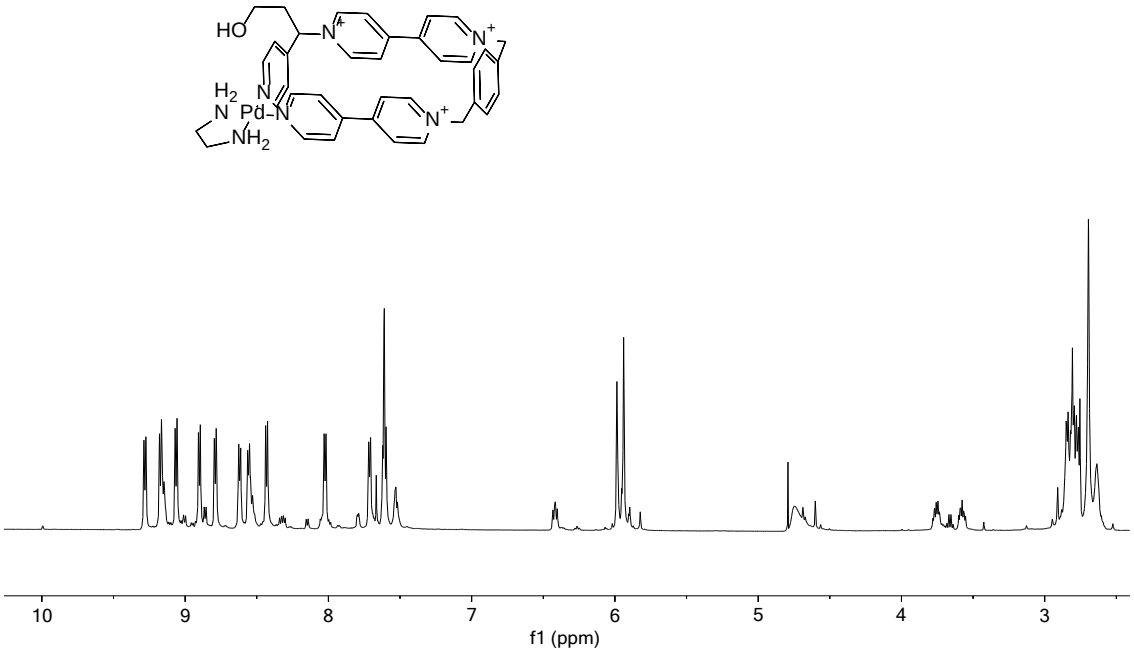

Figure S 51: ^{1}H RMN (500MHz, D_2O) spectrum of **M5a·5NO$_3$.**

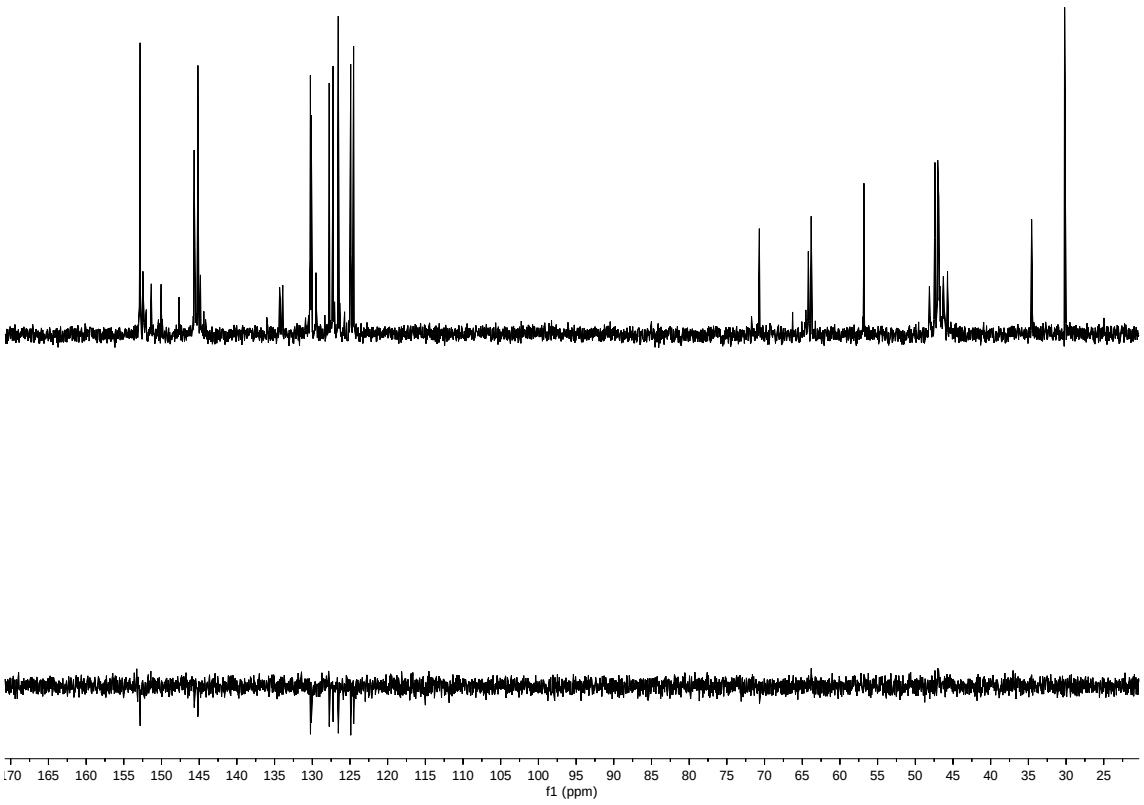

Figure S 52: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **M5a·5NO$_3$.**

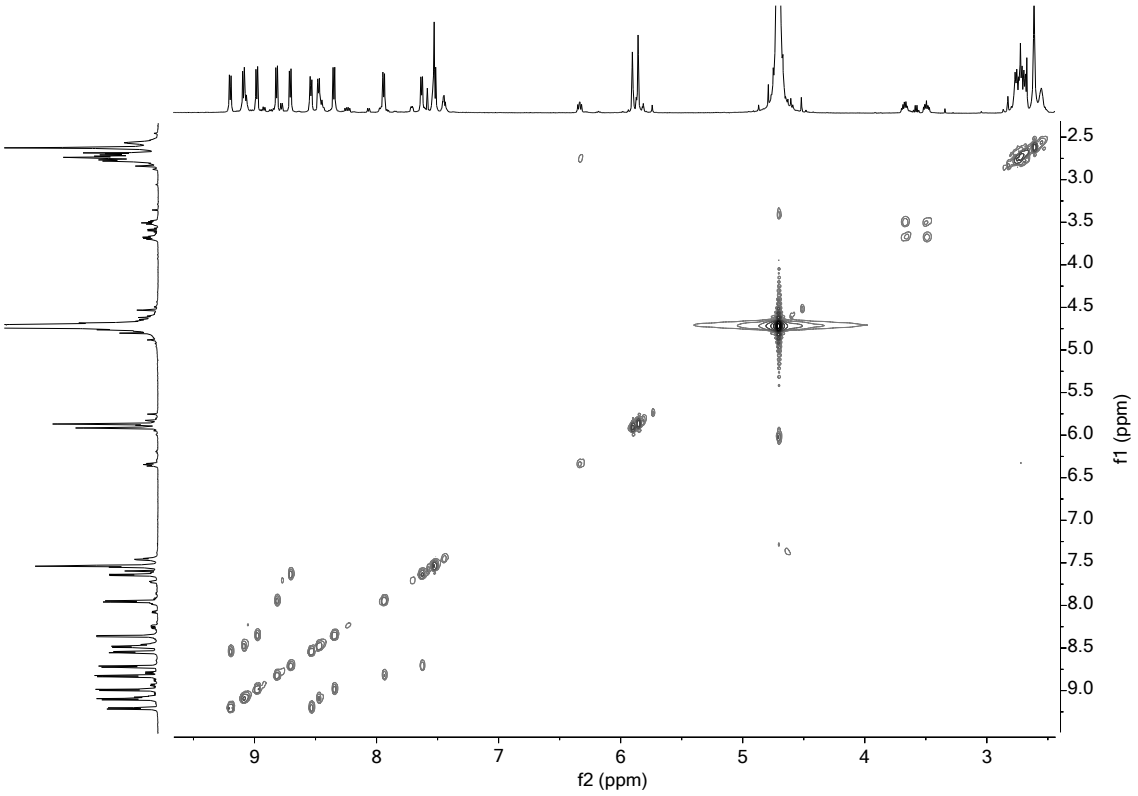

Figure S 53: COSY (500MHz, D_2O) spectrum of **M5a·5NO$_3$.**

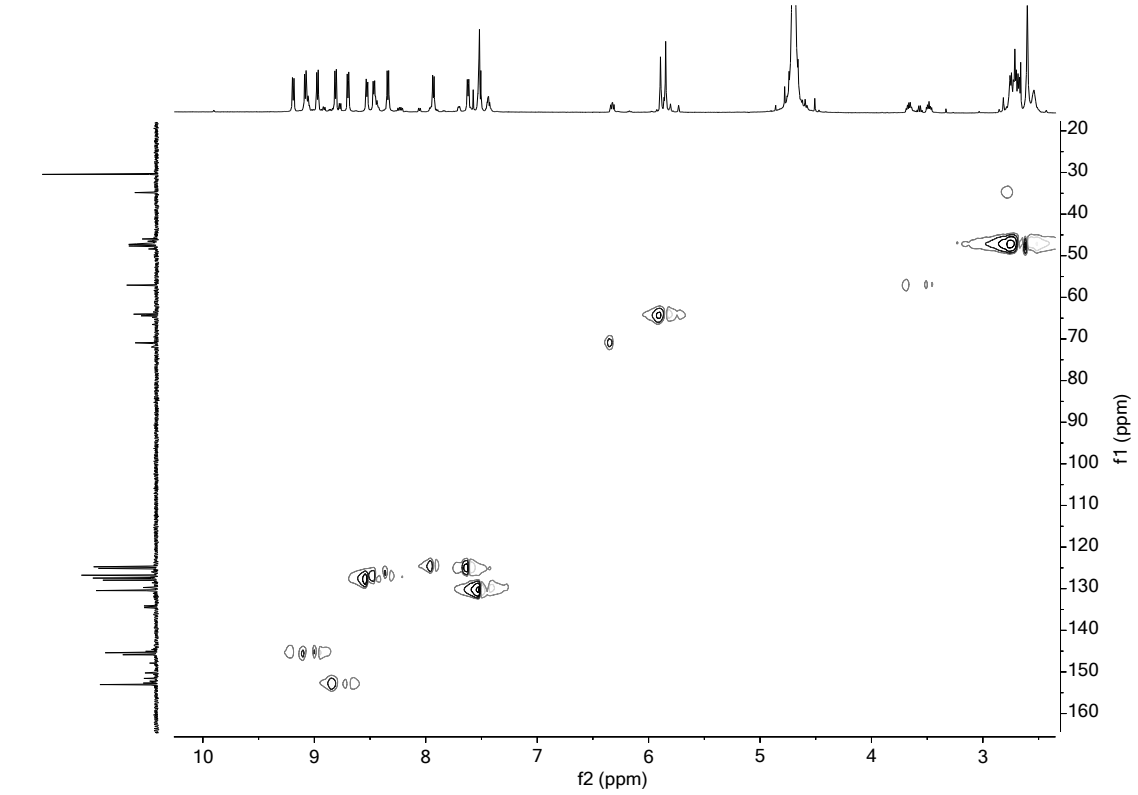

Figure S 54: HSQC (125 and 500MHz, D_2O) spectrum of **M5a·5NO$_3$.**

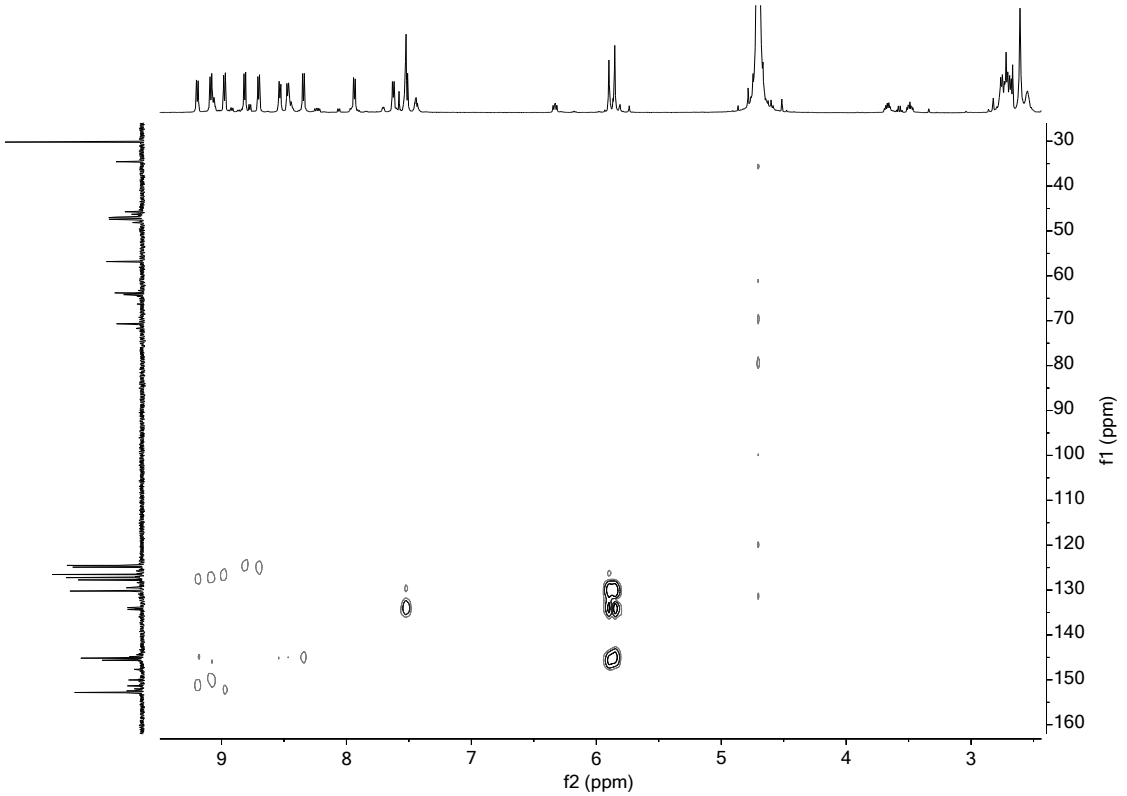

Figure S 55: HMBC (125 and 500MHz, D_2O) spectrum of **M5a·5NO$_3$.**

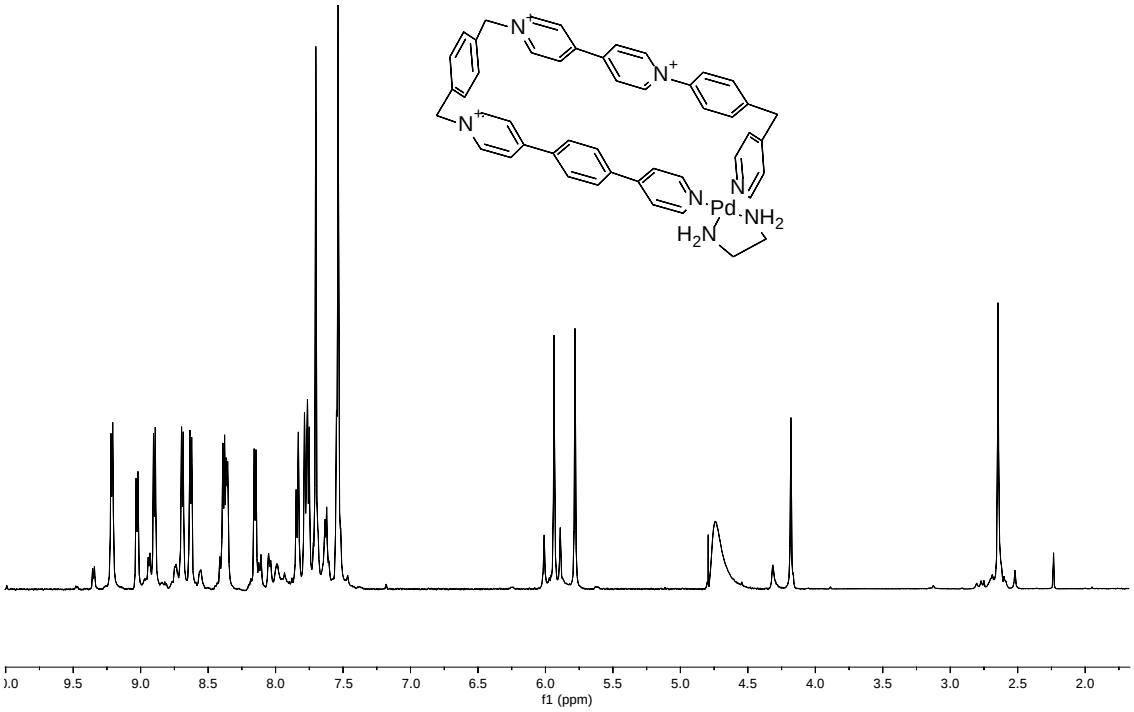

Figure S 56: ^{1}H RMN (500MHz, D_2O) spectrum of **M6a·5NO$_3$.**

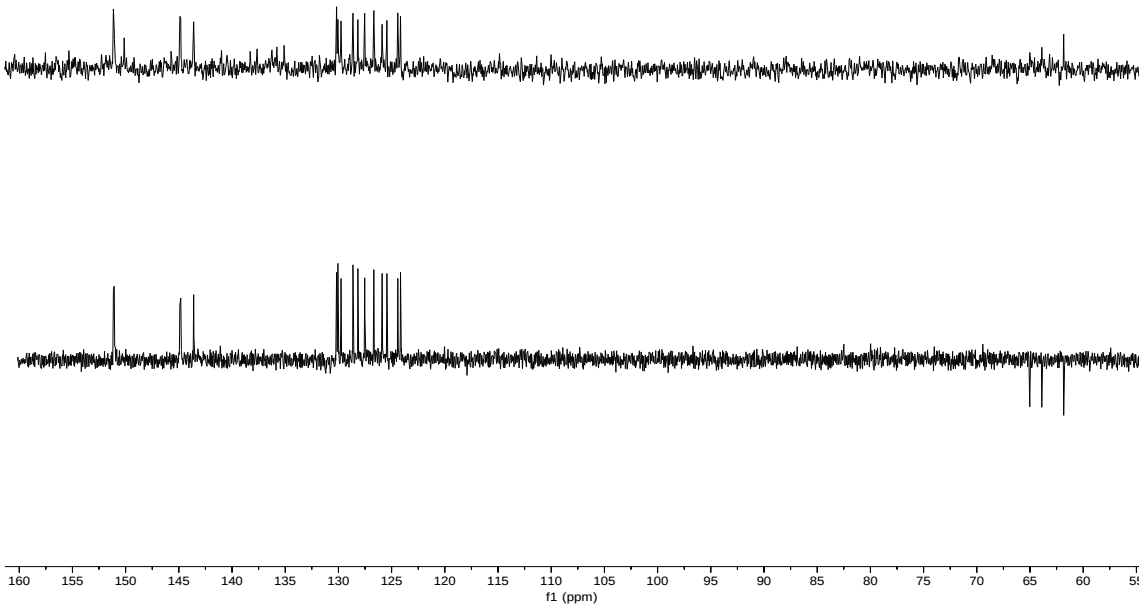

Figure S 57: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **M6a·5NO$_3$.**

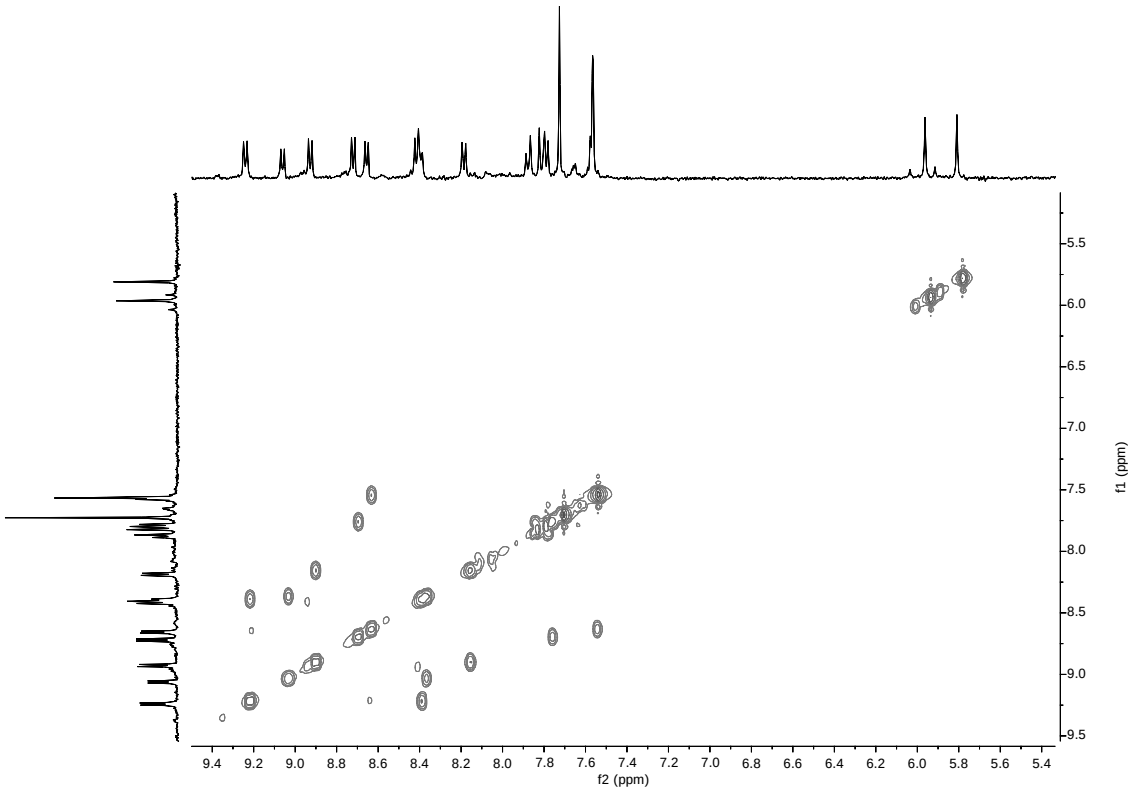

Figure S 58: COSY (500MHz, D_2O) spectrum of **M6a·5NO$_3$.**

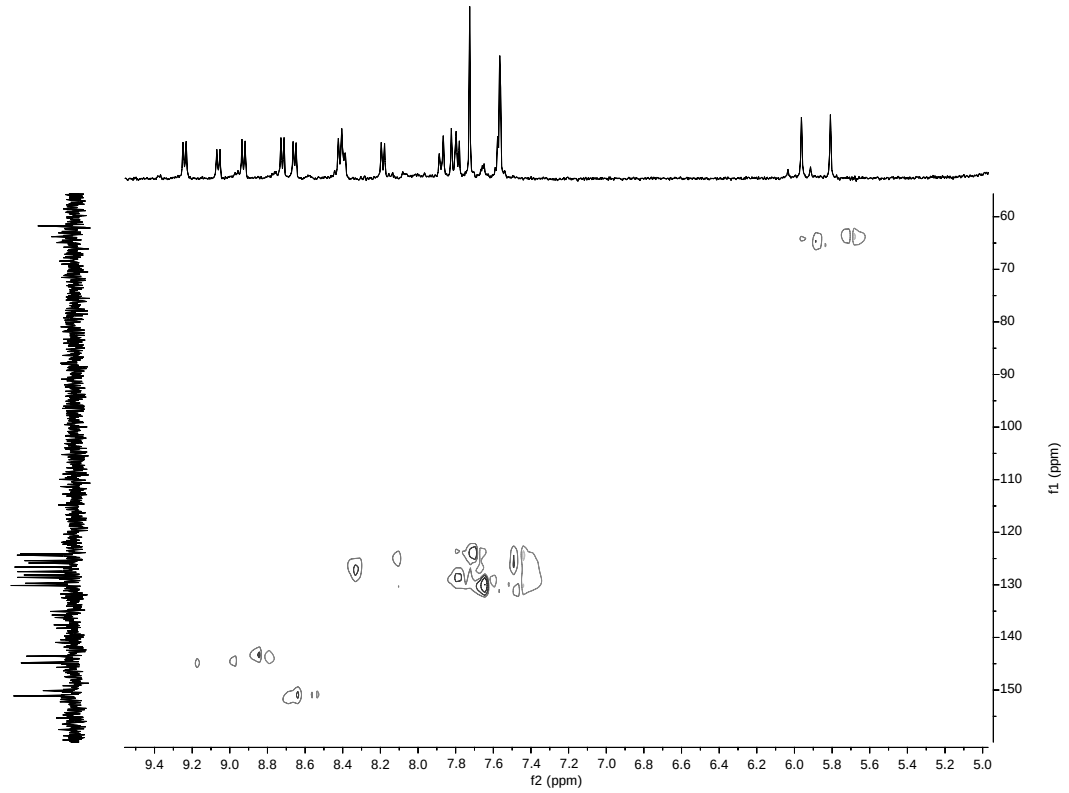

Figure S 59: HSQC (125 and 500MHz, D_2O) spectrum of **M6a·5NO$_3$.**

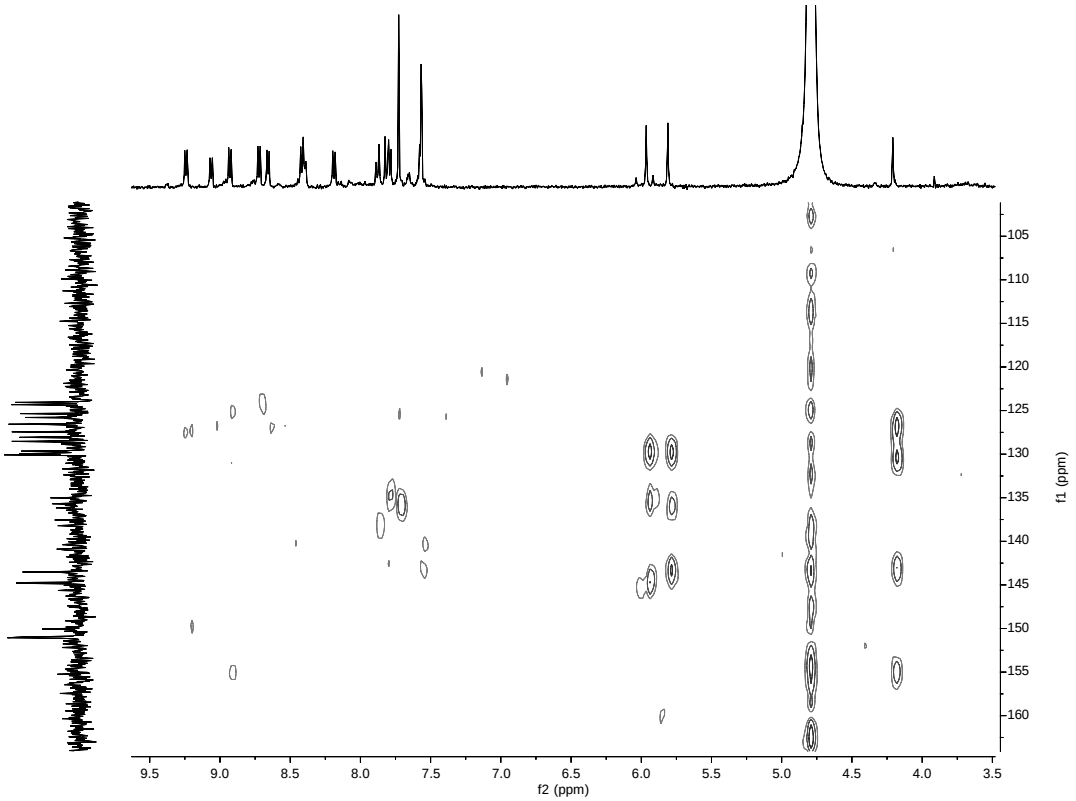

Figure S 60: HMBC (125 and 500MHz, D_2O) spectrum of **M6a·5NO$_3$.**

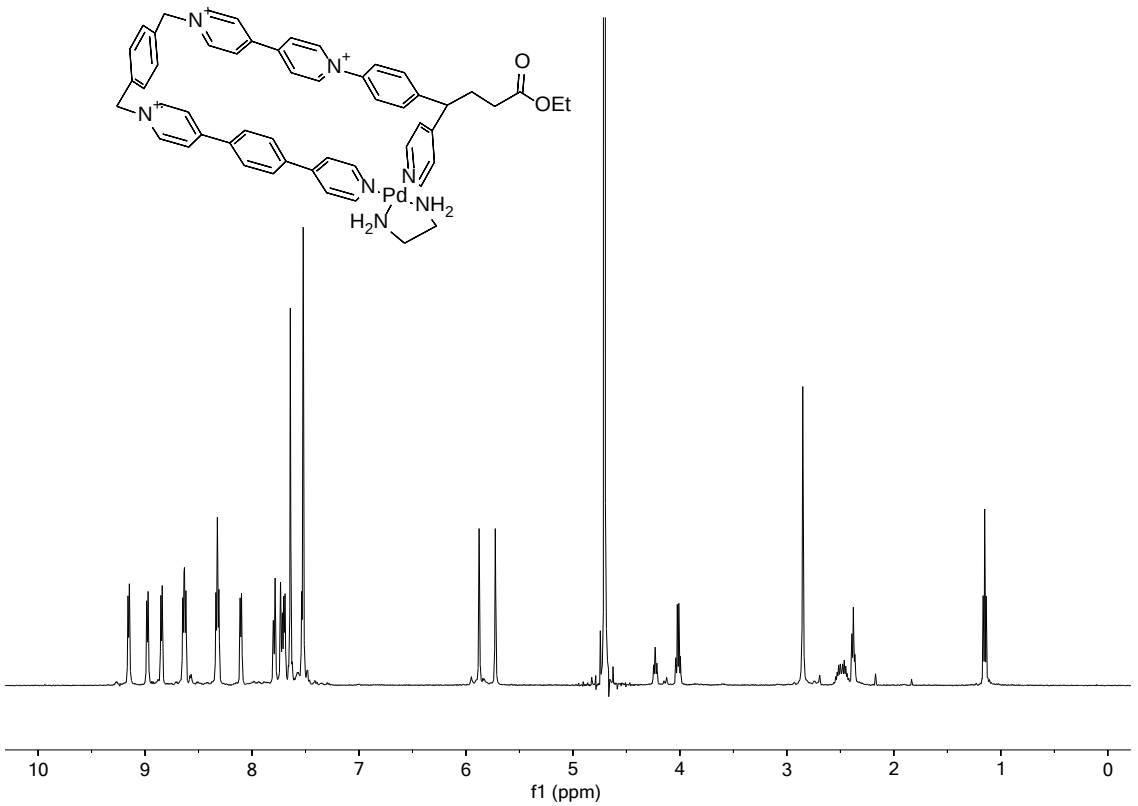

Figure S 61: ^{1}H RMN (500MHz, D_2O) spectrum of **M7a·5NO$_3$.**

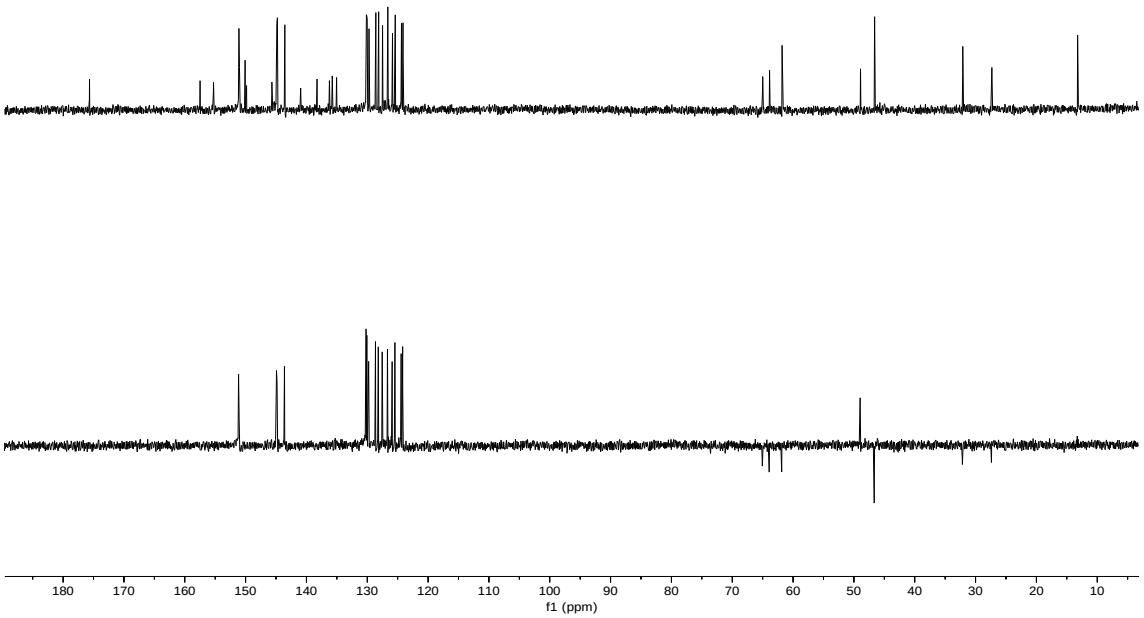

Figure S 62: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **M7a·5NO$_3$.**

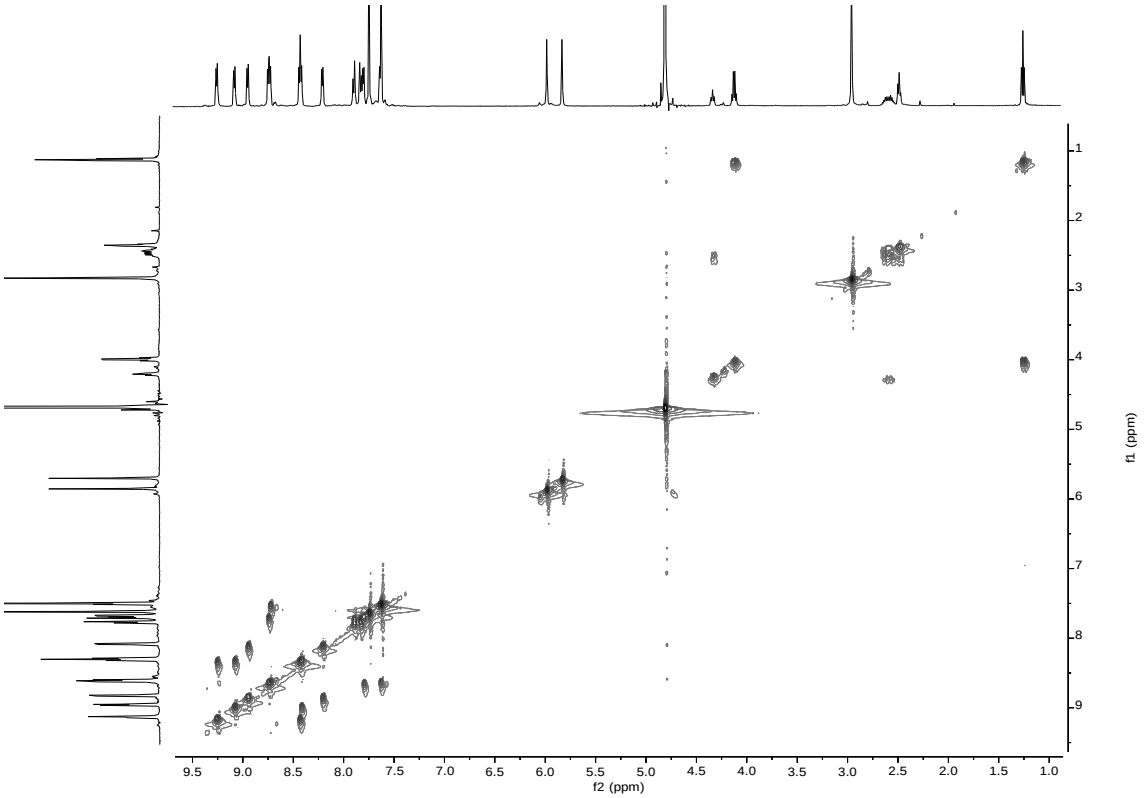

Figure S 63: COSY (500MHz, D_2O) spectrum of **M7a·5NO$_3$.**

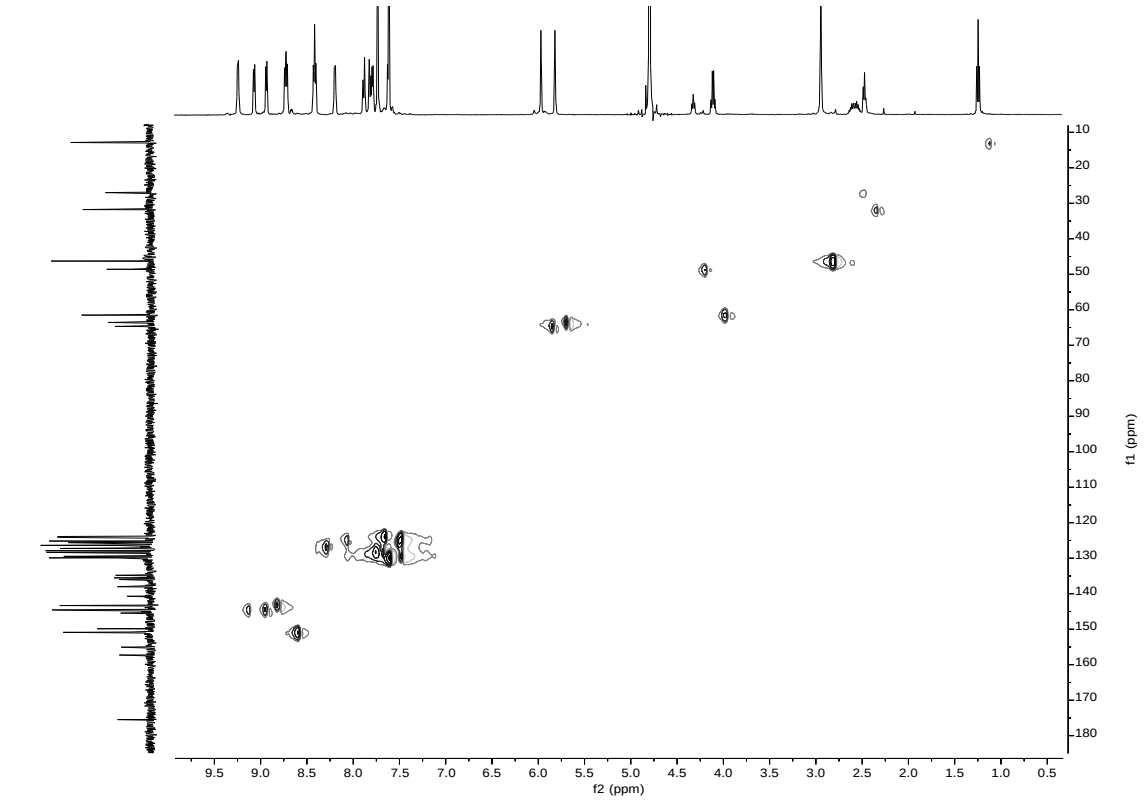

Figure S 64: HSQC (125 and 500MHz, D_2O) spectrum of **M7a·5NO$_3$.**

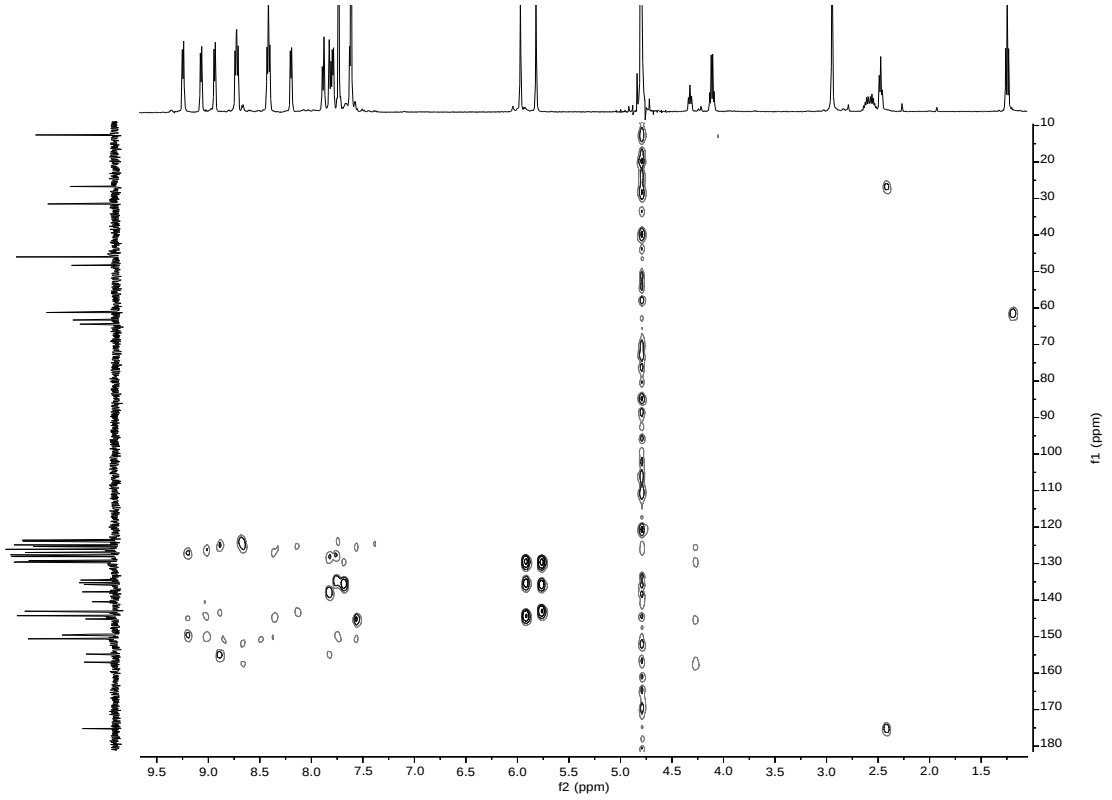

Figure S 65: HMBC (125 and 500MHz, D_2O) spectrum of **M7a·5NO$_3$.**

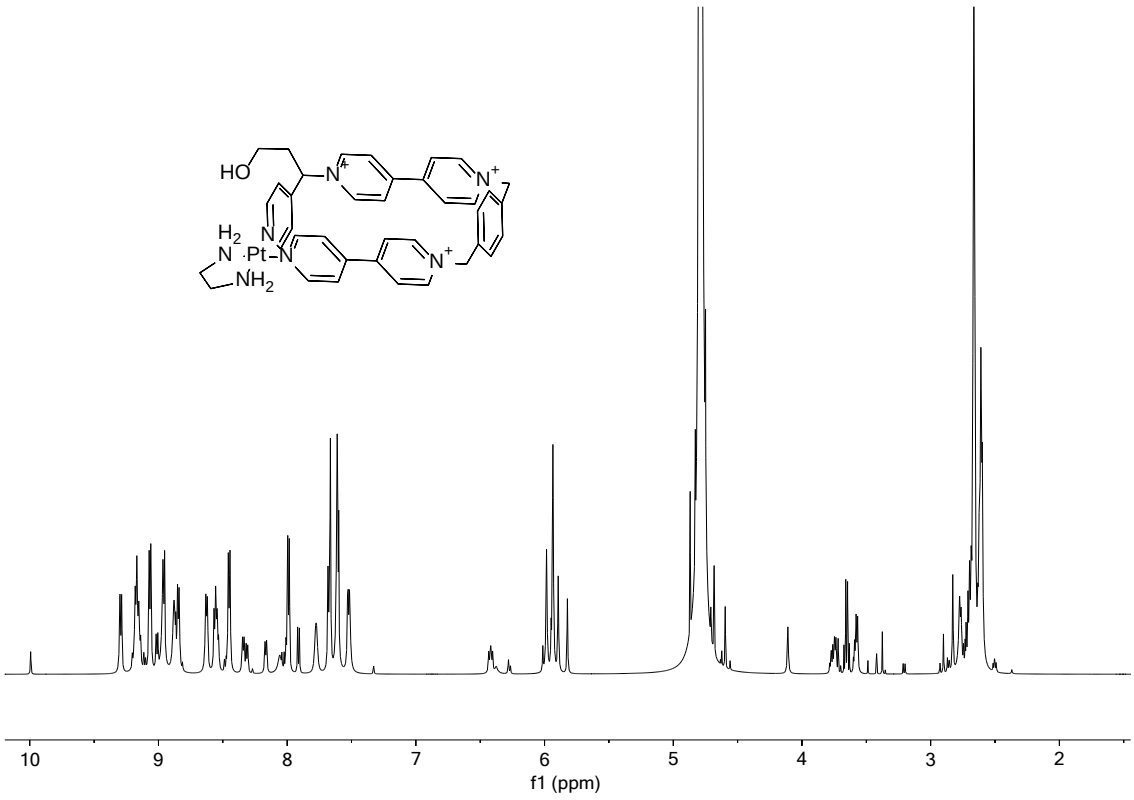

Figure S 66: ^{1}H RMN (500MHz, D_2O) spectrum of **M5b·5NO$_3$.**

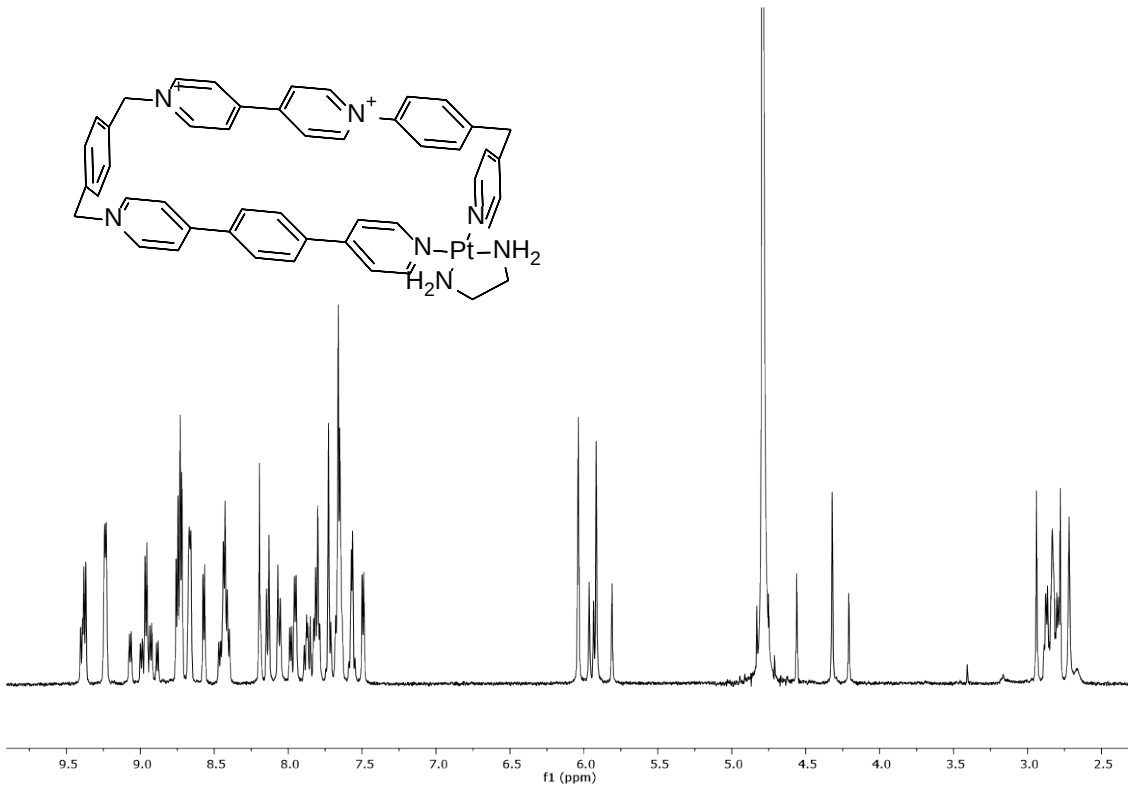

Figure S 67: ^{1}H RMN (500MHz, D_2O) spectrum of **M6b·5NO$_3$.**

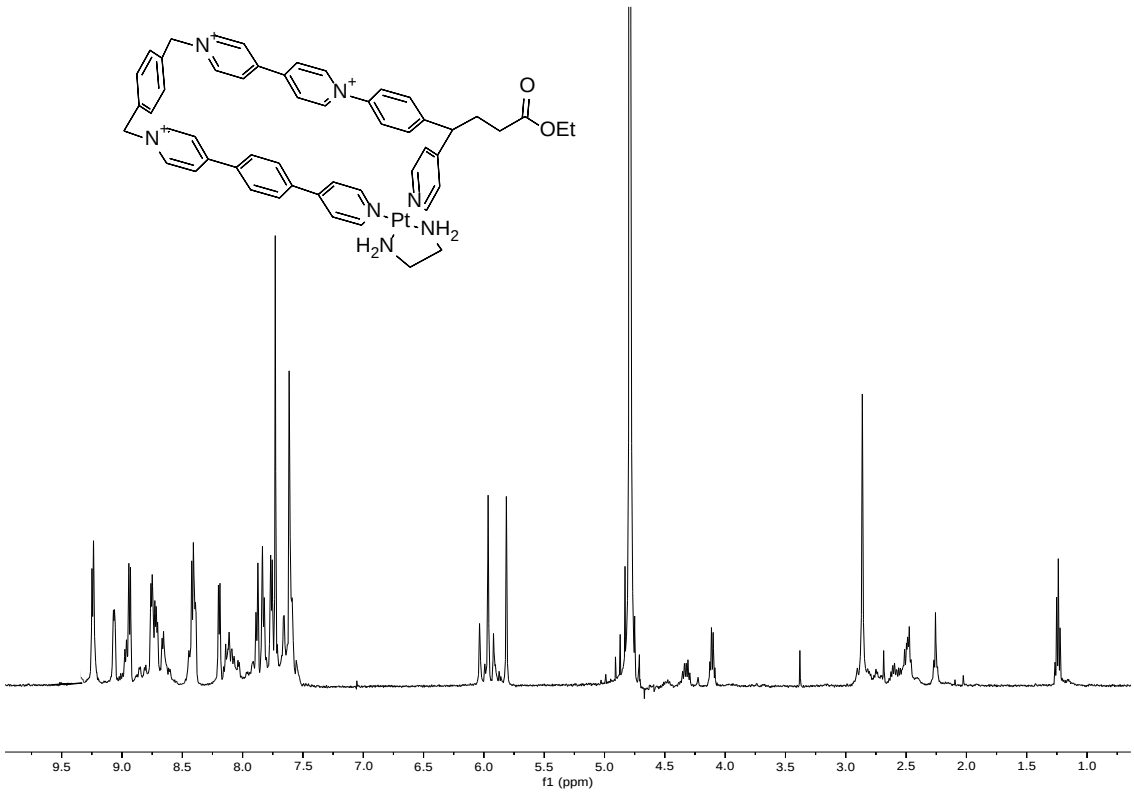

Figure S 68: ^{1}H RMN (500MHz, D_2O) spectrum of **M7b·5NO$_3$.**

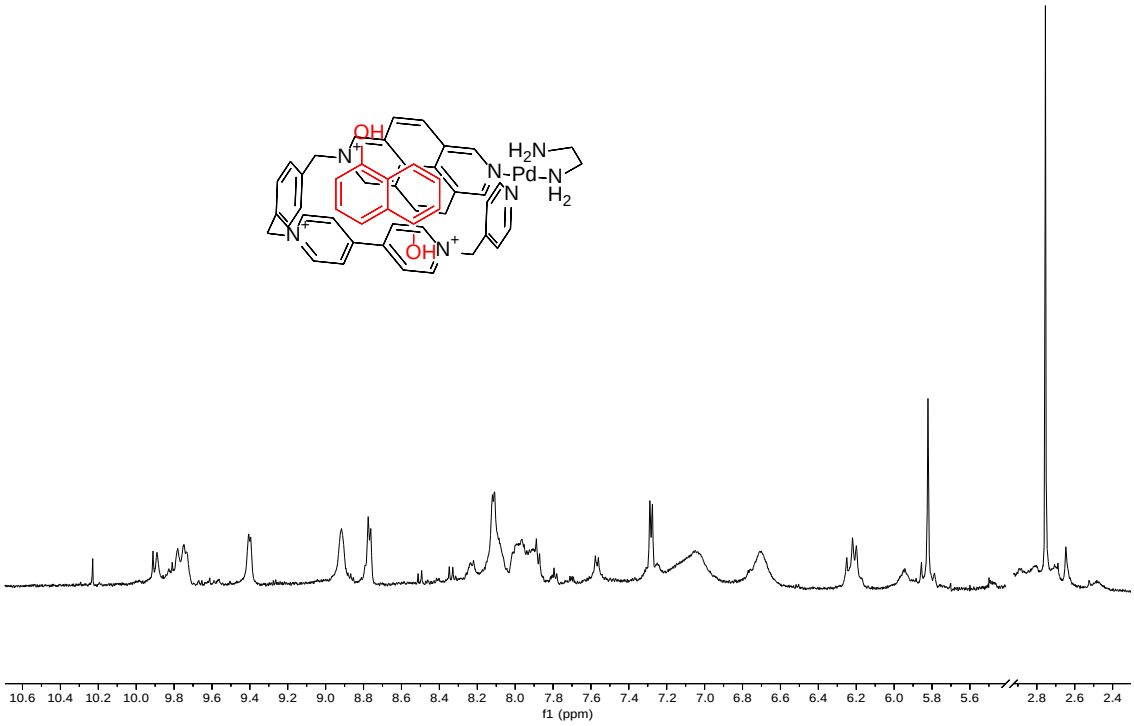

Figure S 69: ^{1}H RMN (400MHz, D_2O) spectrum of **M4a·5NO$_3$·**and **1,5DHN**.

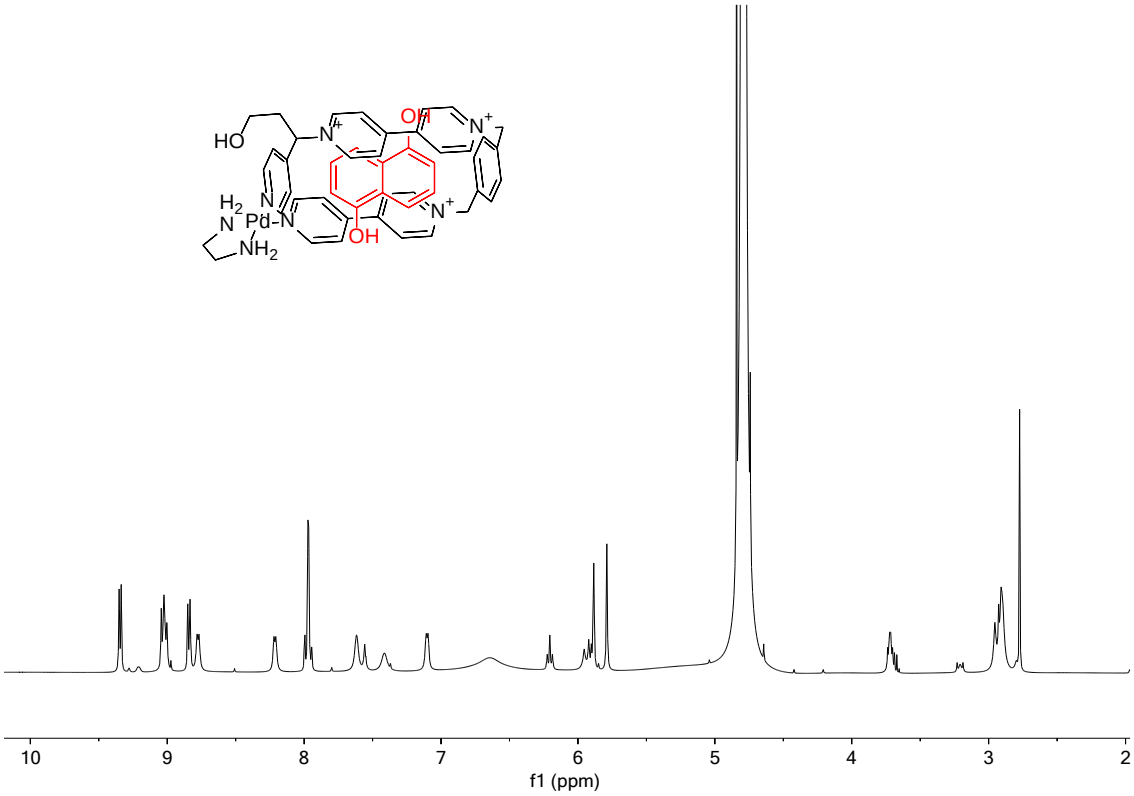

Figure S 70: ^{1}H RMN (400MHz, D_2O) spectrum of **M5a·5NO$_3$·**and **1,5DHN**.

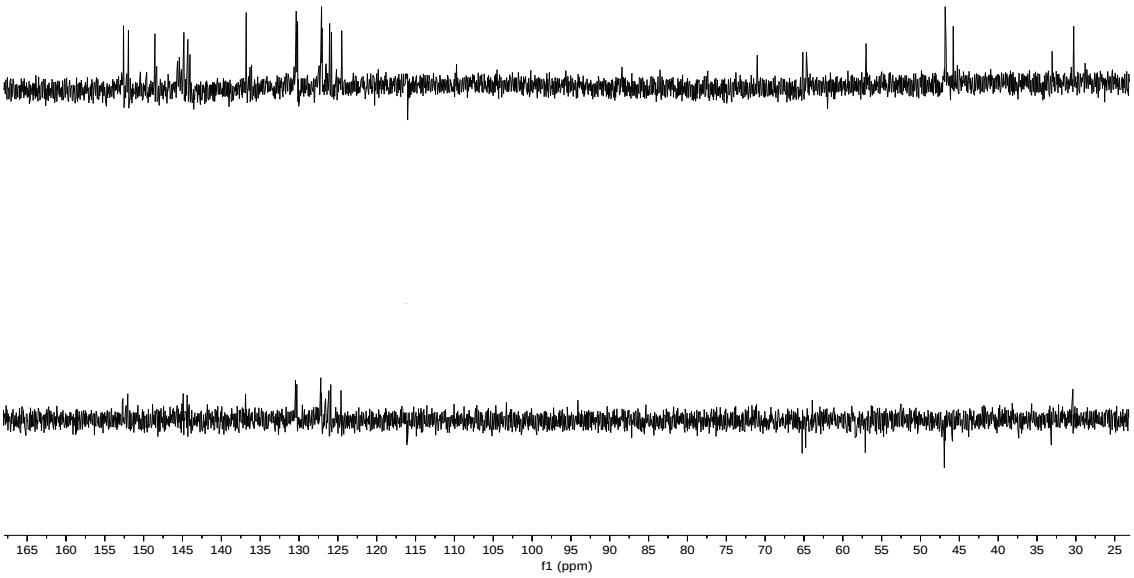

Figure S 71: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **M5a·5NO$_3$·**and **1,5DHN**.

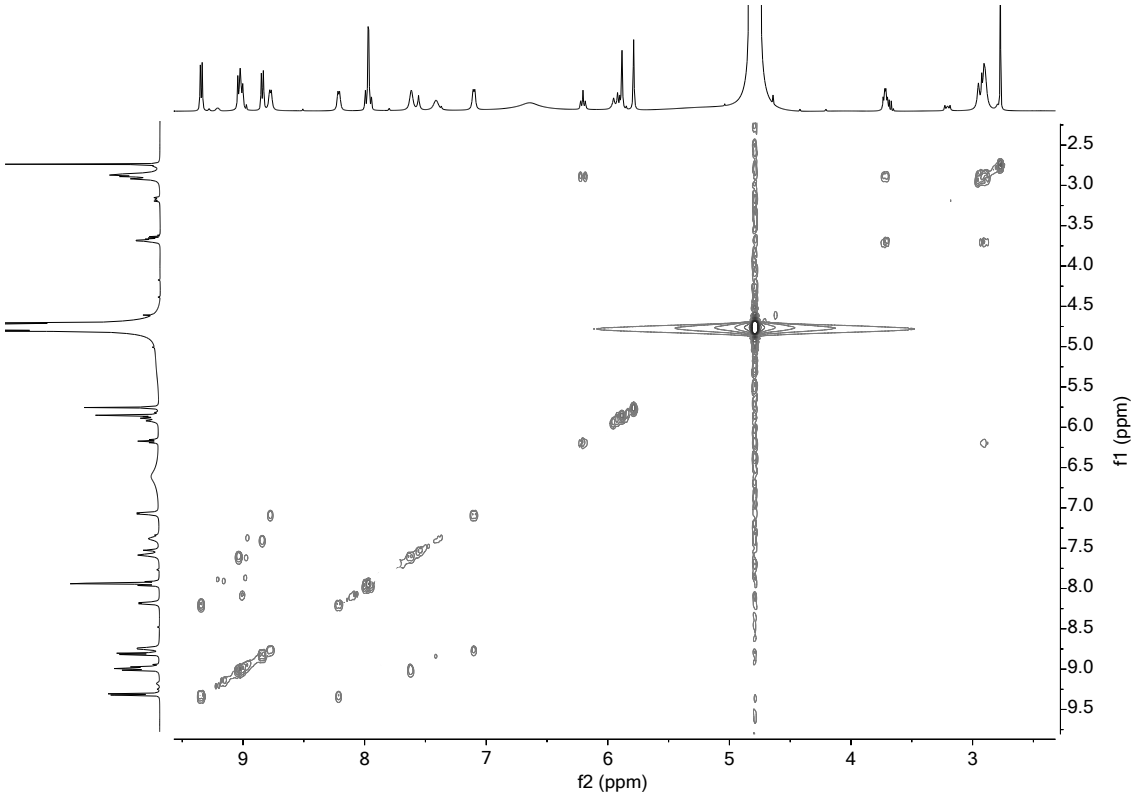

Figure S 72: COSY (400MHz, D_2O) spectrum of **M5a·5NO$_3$·**and **1,5DHN**.

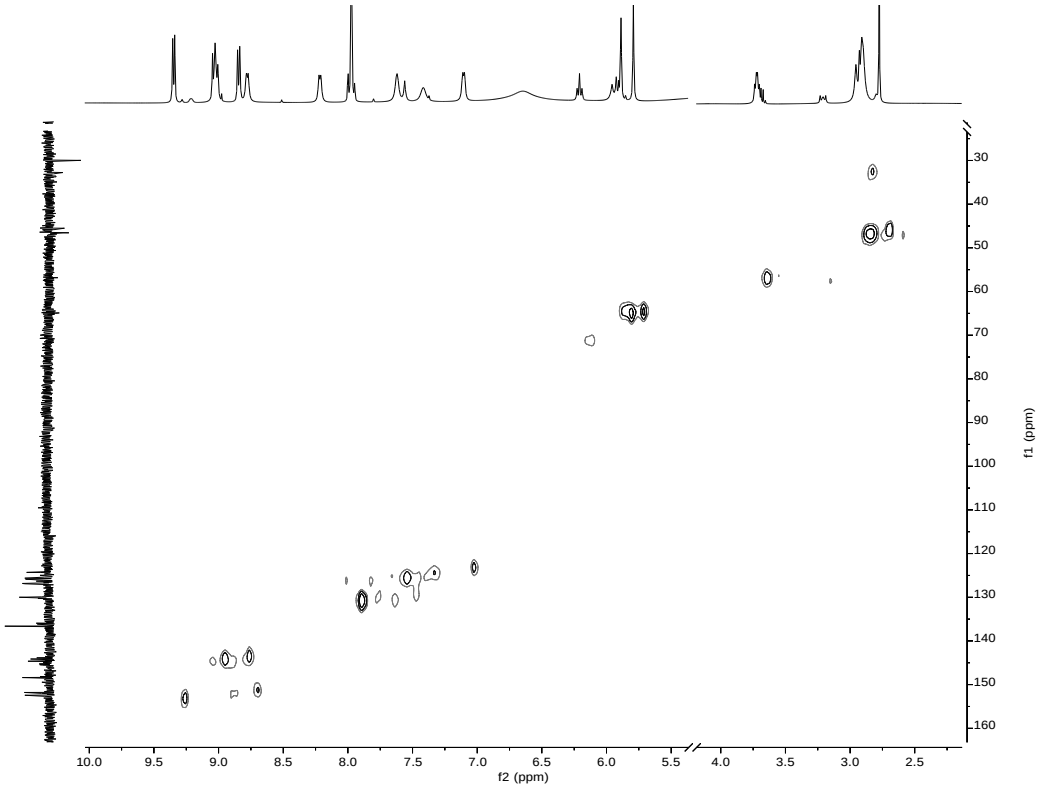

Figure S 73: HSQC (125 and 400MHz, D_2O) spectrum of **M5a·5NO$_3$·**and **1,5DHN**.

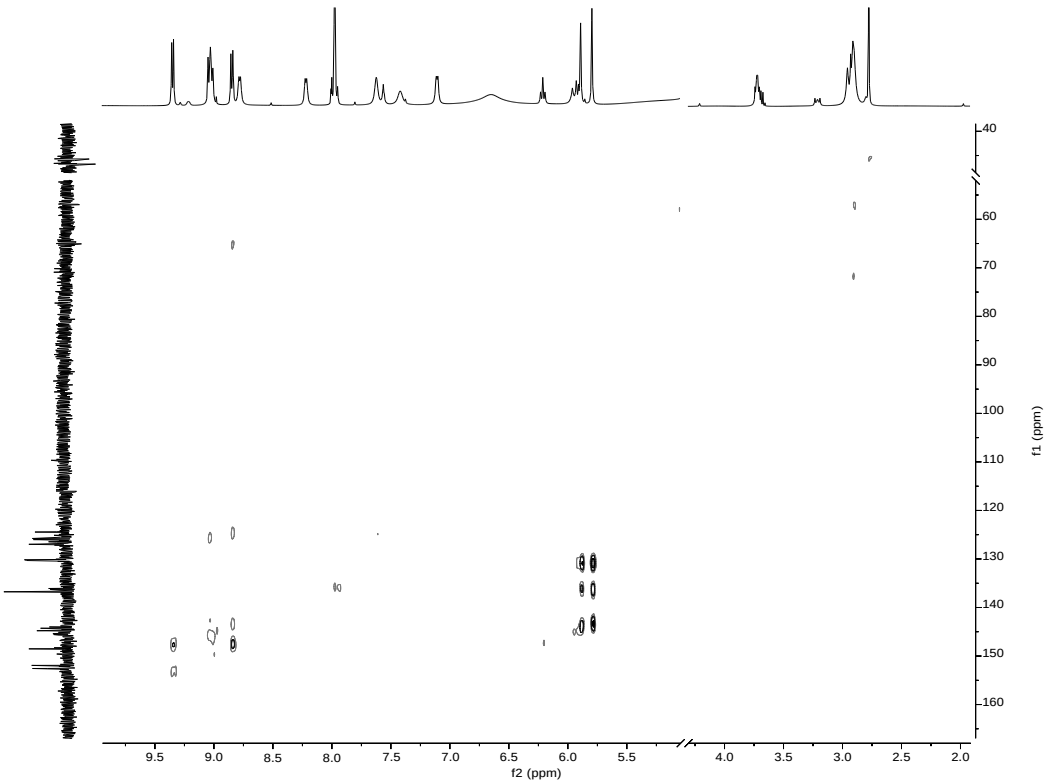

Figure S 74: HMBC (125 and 400MHz, D_2O) spectrum of **M5a·5NO$_3$·**and **1,5DHN**.

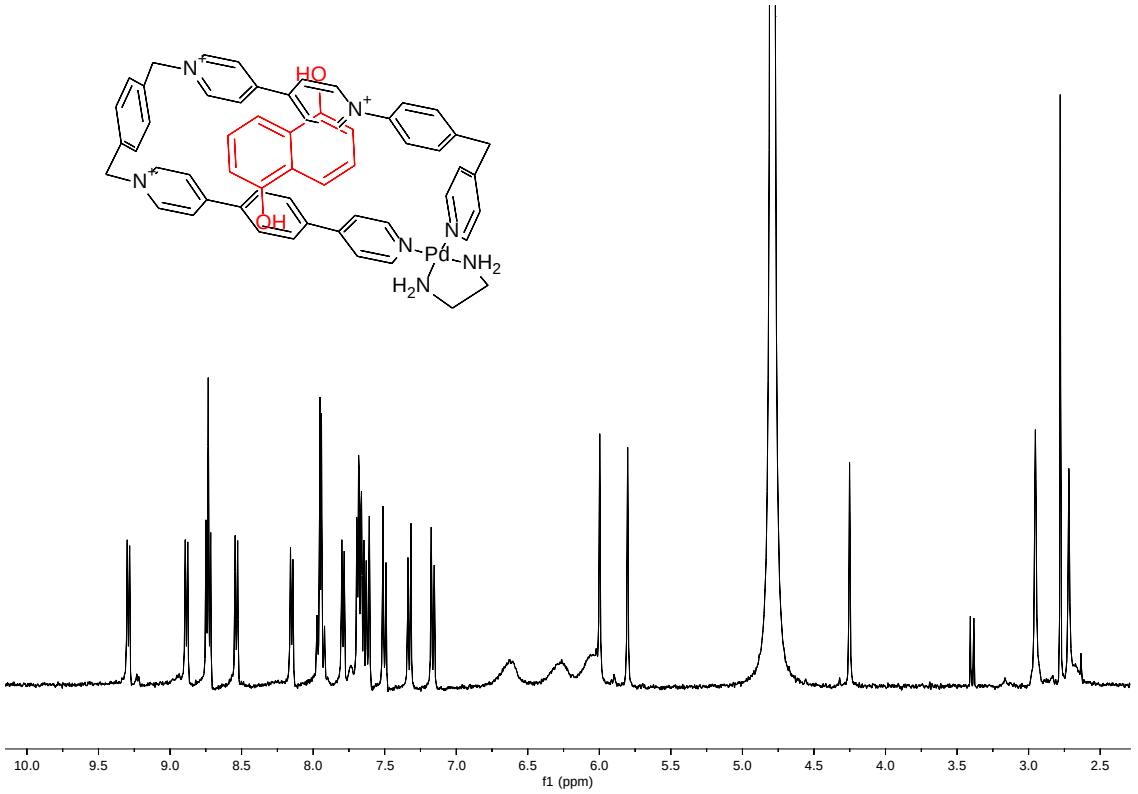

Figure S 75: ^{1}H RMN (500MHz, D_2O) spectrum of **M6a·5NO$_3$**·and **1,5DHN**.

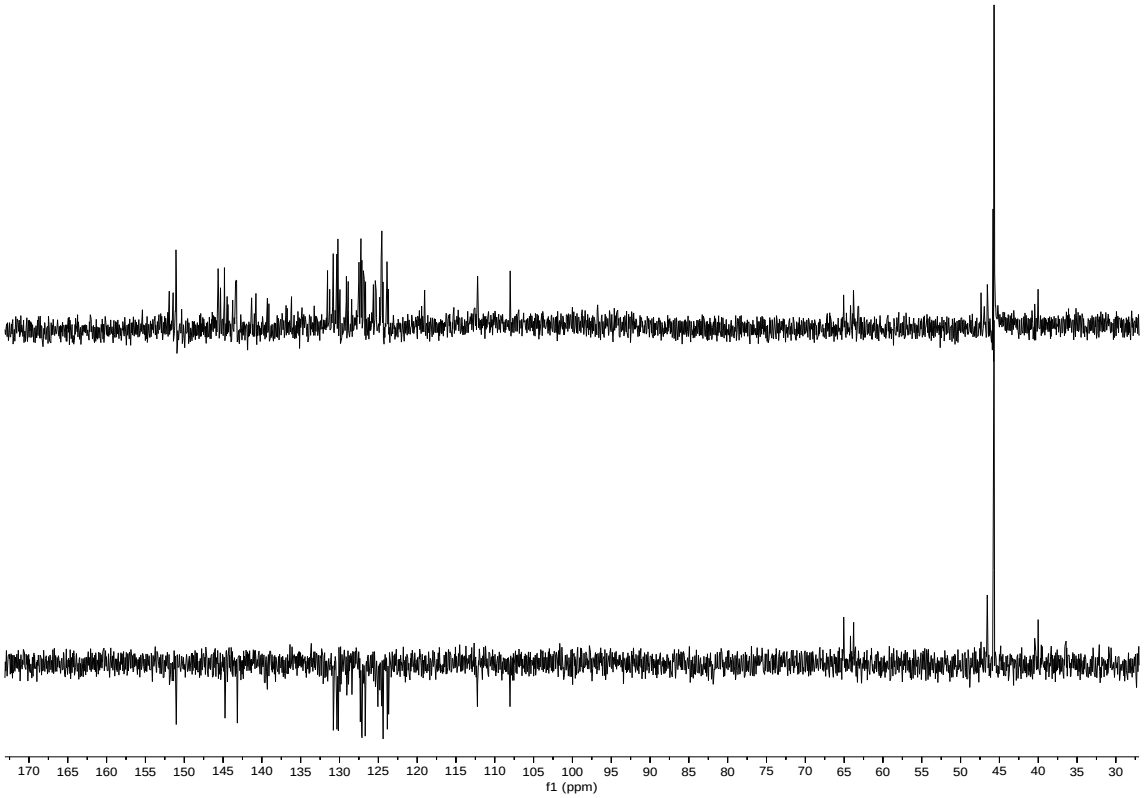

Figure S 76: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **M6a·5NO$_3$**·and **1,5DHN**.

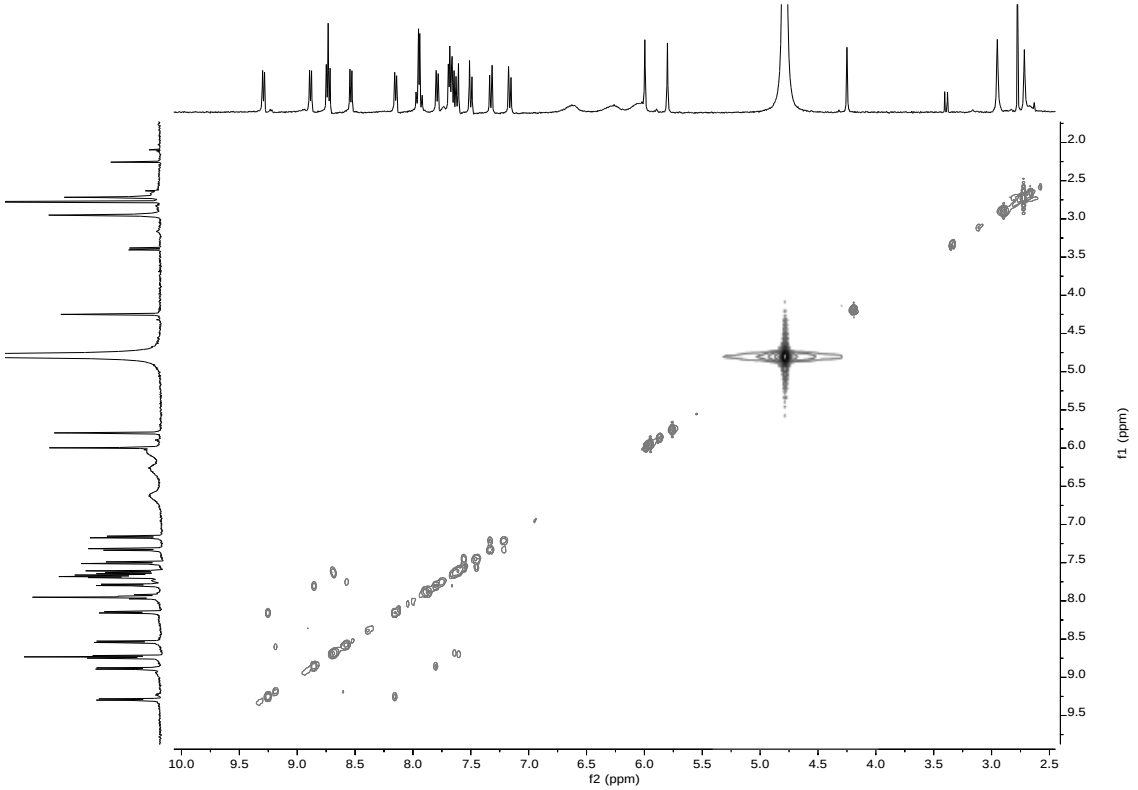

Figure S 77: COSY (500MHz, D_2O) spectrum of **M6a·5NO$_3$·**and **1,5DHN**.

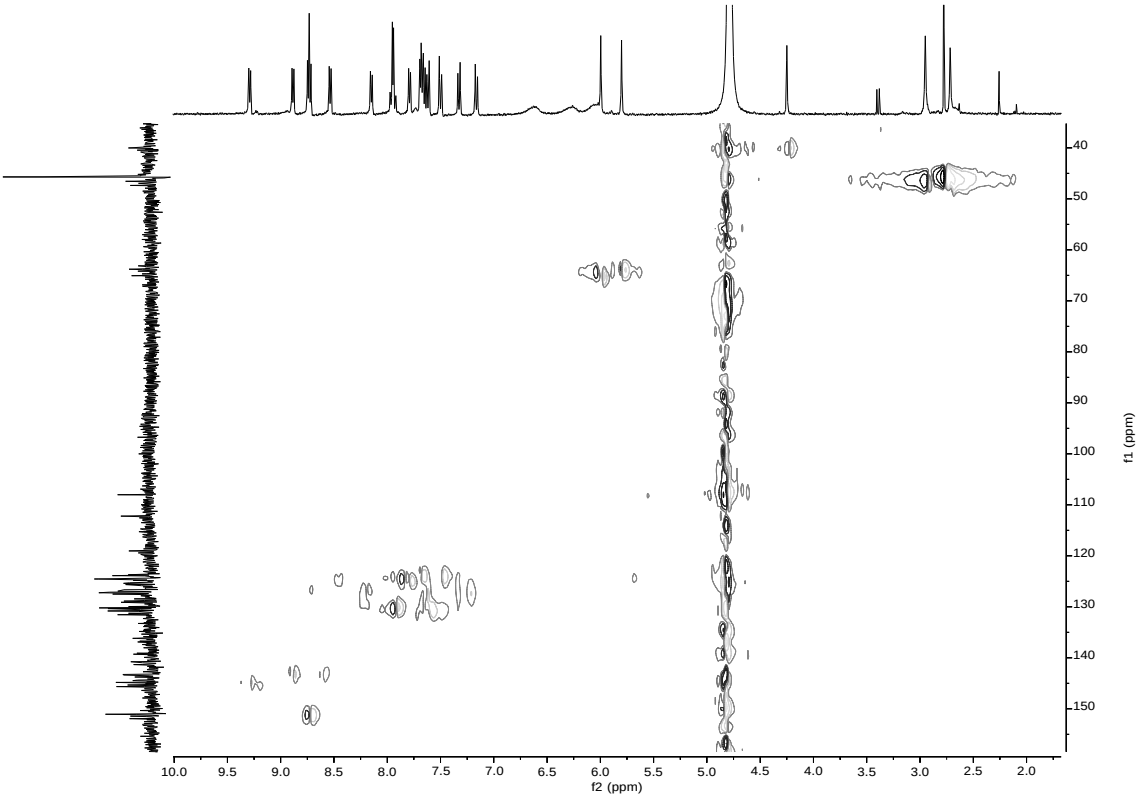

Figure S 78: HSQC (125 and 500MHz, D_2O) spectrum of **M6a·5NO$_3$·**and **1,5DHN**.

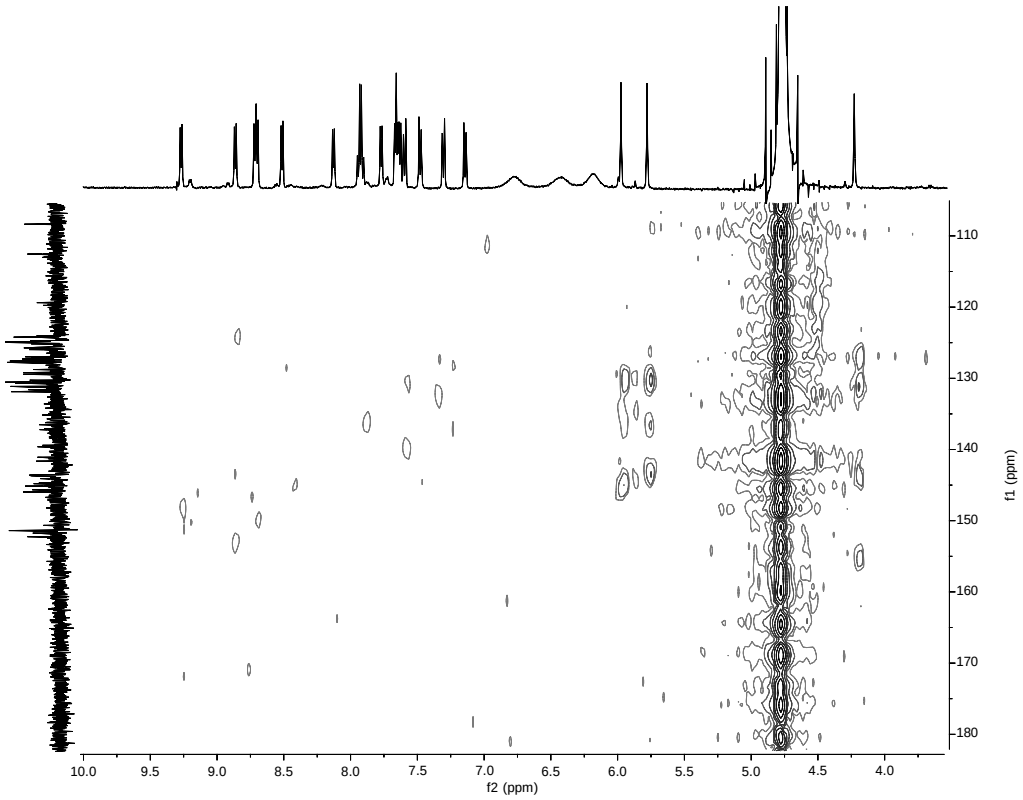

Figure S 79: HMBC (125 and 500MHz, D_2O) spectrum of **M6a·5NO$_3$·**and **1,5DHN**.

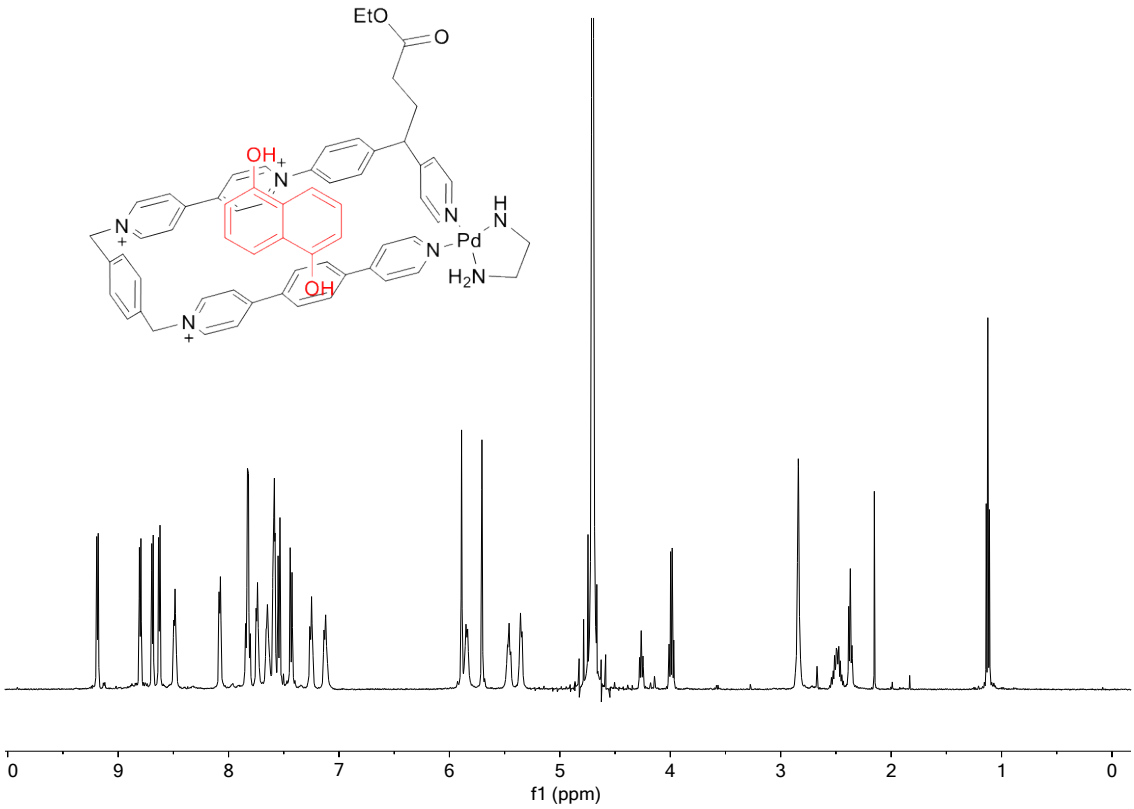

Figure S 80: ^{1}H RMN (500MHz, D_2O) spectrum of **M7a·5NO$_3$·**and **1,5DHN**.

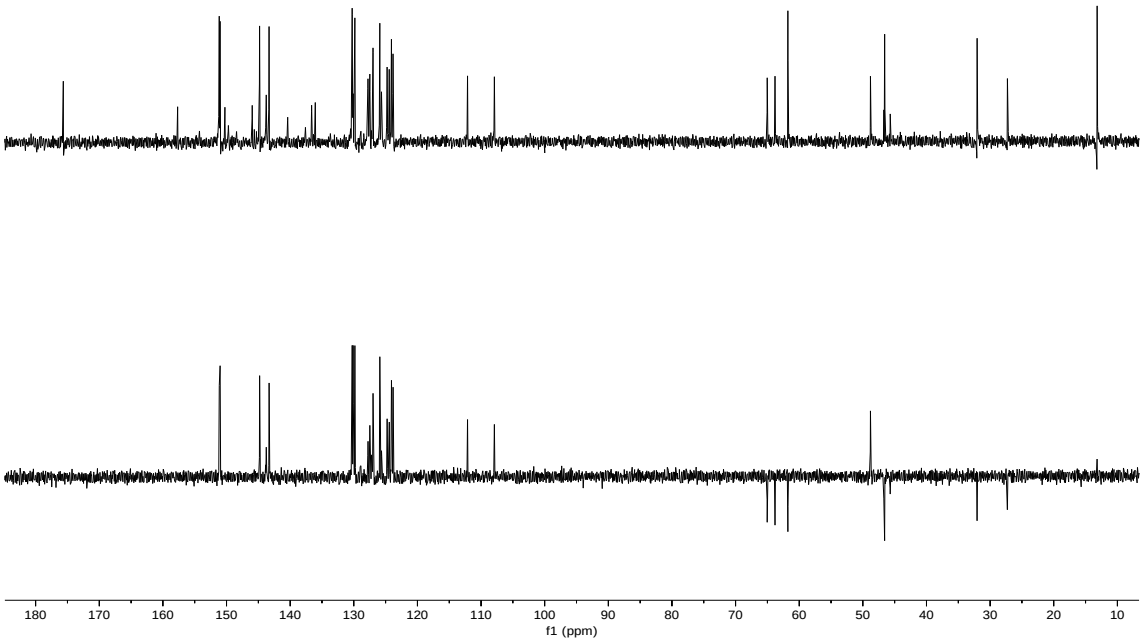

Figure S 81: ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **M7a·5NO$_3$·**and **1,5DHN**.

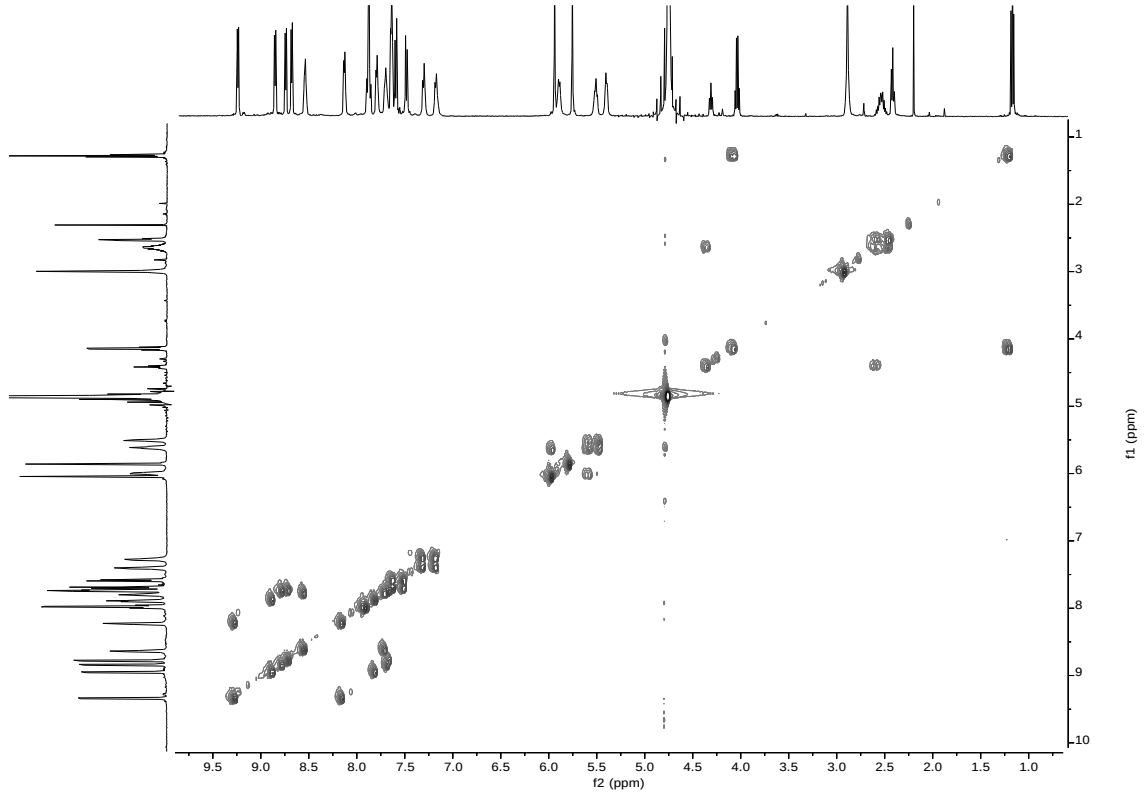

Figure S 82: COSY (500MHz, D_2O) spectrum of **M7a·5NO$_3$·**and **1,5DHN**.

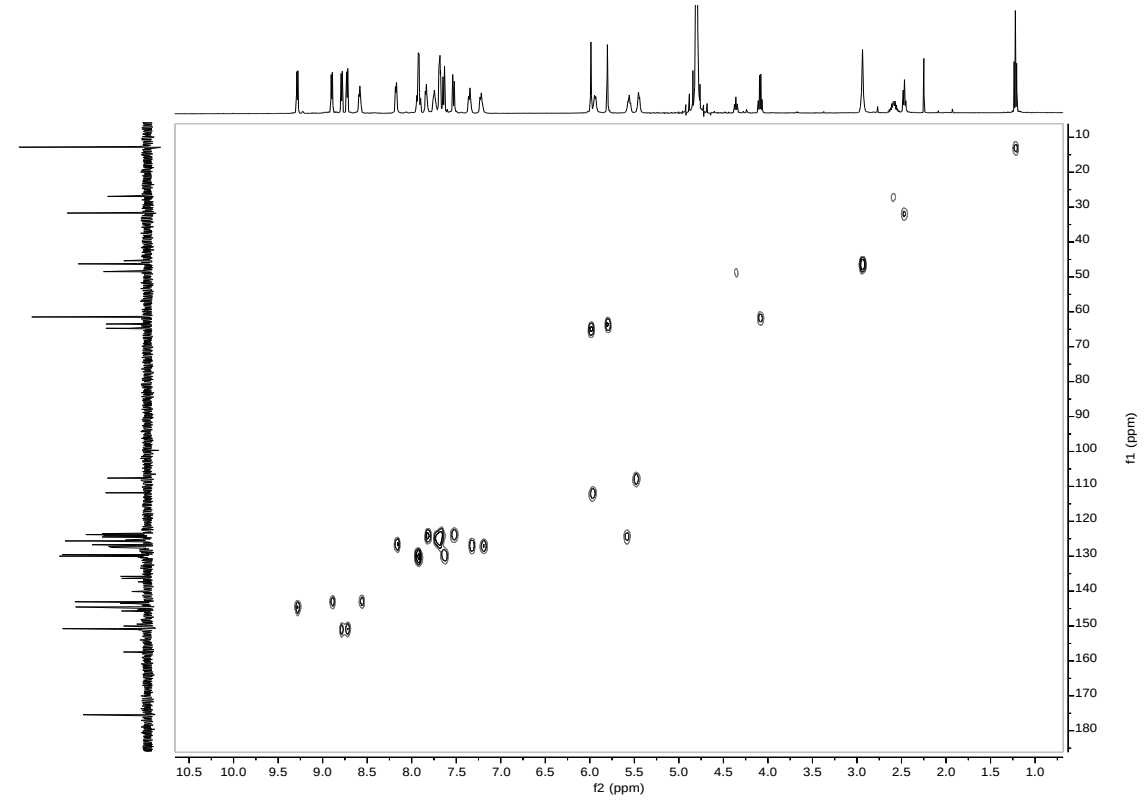

Figure S 83: HSQC (125 and 500MHz, D_2O) spectrum of **M7a·5NO$_3$·**and **1,5DHN**.

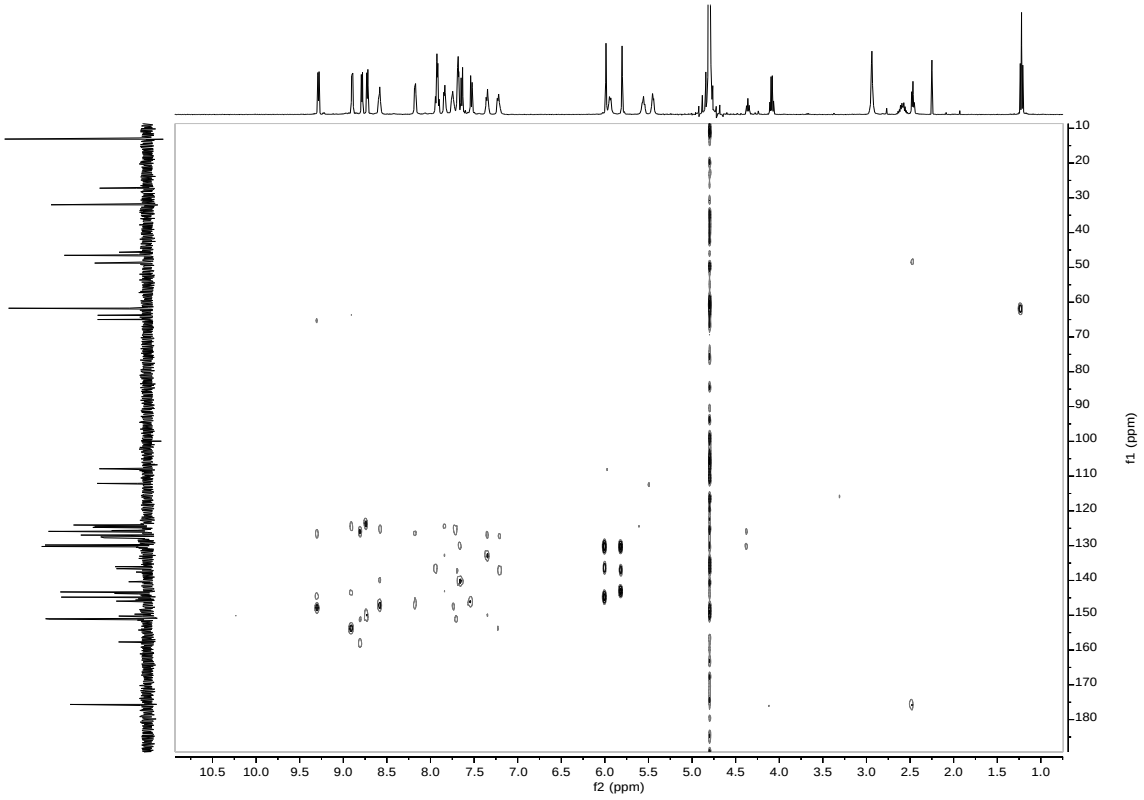

Figure S 84: HMBC (125 and 500MHz, D_2O) spectrum of **M7a·5NO$_3$·**and **1,5DHN**.

2. EXTRA FIGURES

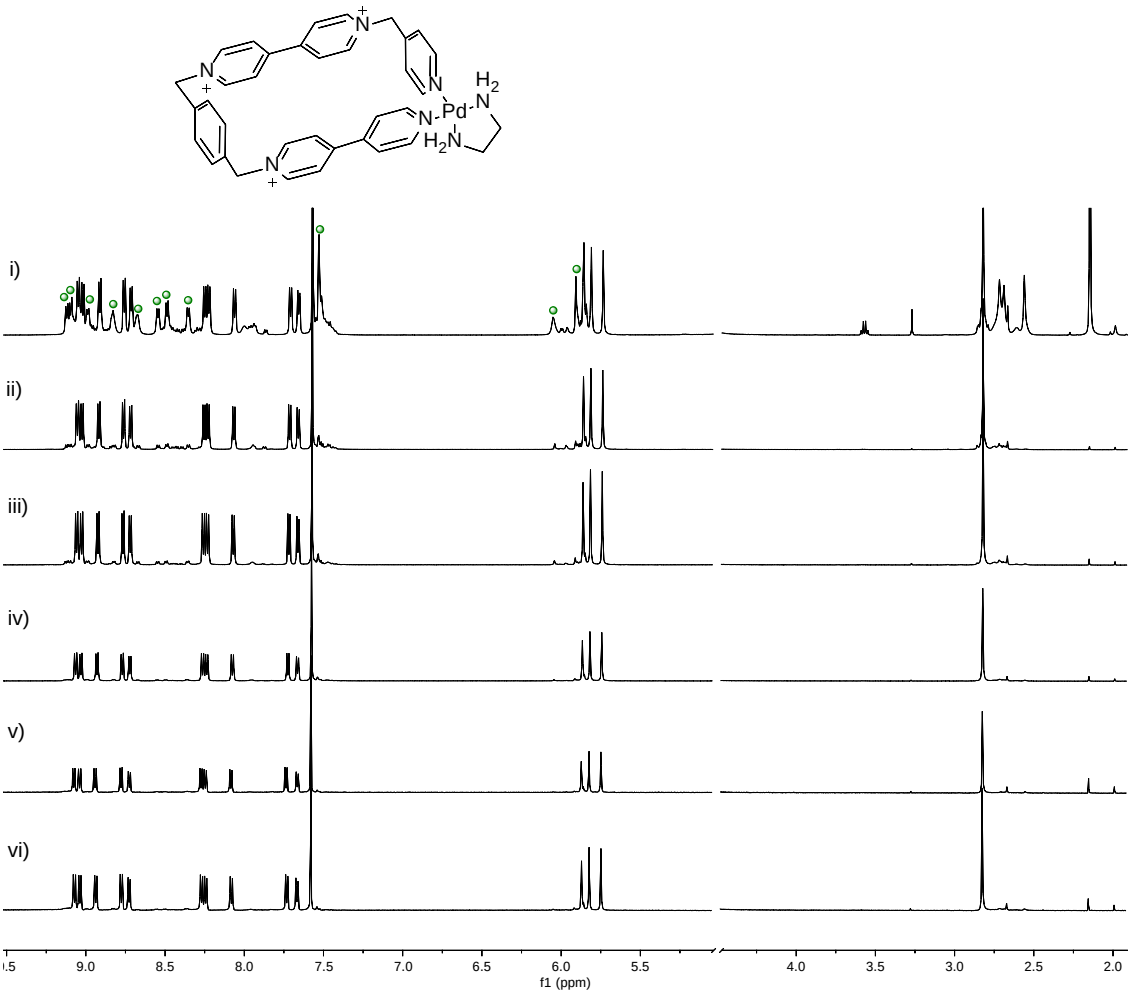

Figure S 85: Partial ^{1}H NMR (D_2O, 500 MHz) spectra of a solution of **L1·3NO$_3$** and (en)Pd(NO_3)$_2$ at different concentrations: (i) 15 mM (ii) 10 mM (iii) 5 mM (iv) 2,5 mM, v)1.25, vi) 0.75.

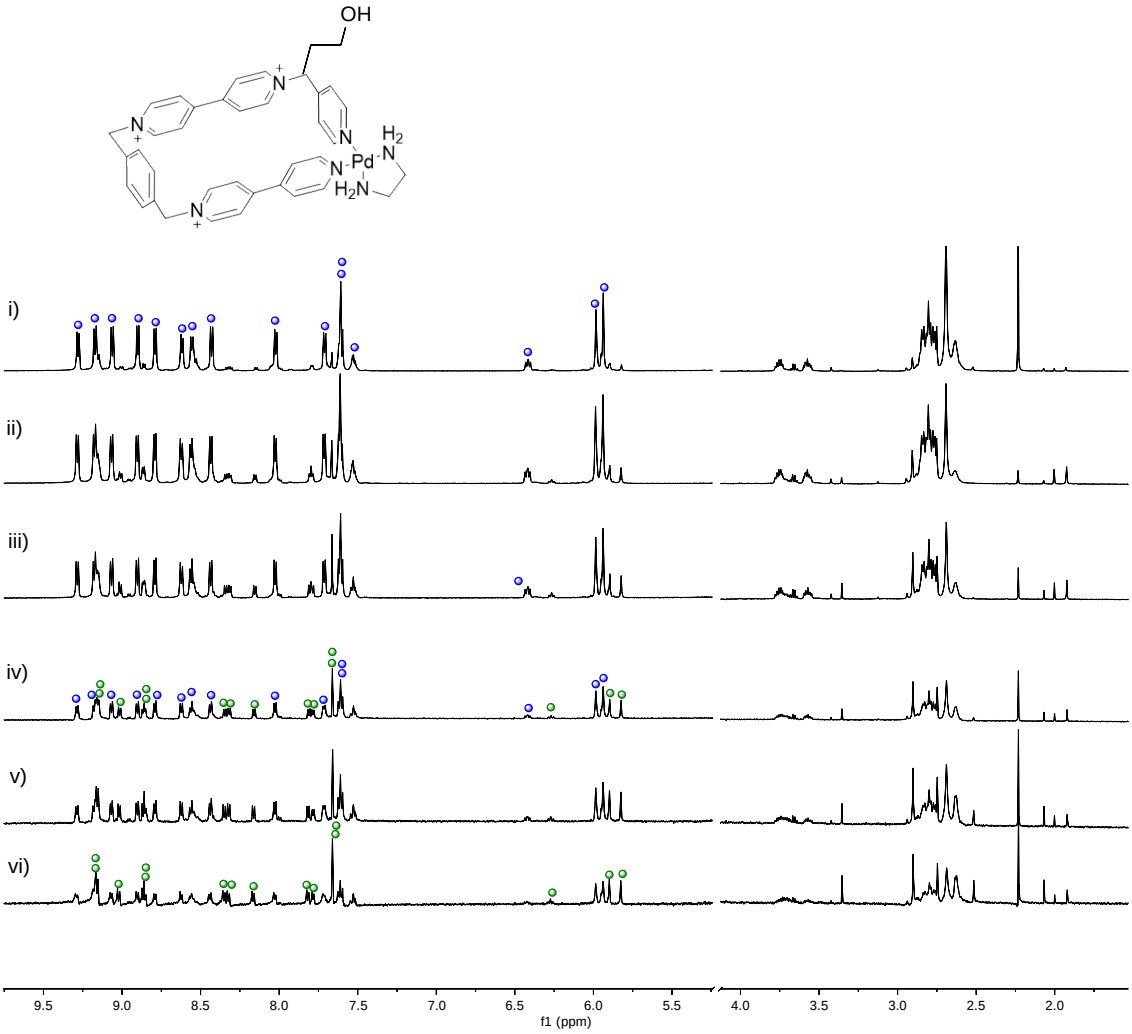

Figure S 86: Partial ^{1}H NMR (D_2O, 500 MHz) spectra of a solution of **L5·3NO$_3$** and (en)Pd(NO_3)$_2$ at different concentrations: (i) 5 mM (ii) 2.5 mM (iii) 1.25 mM (iv) 0.75 mM, v) 0.375, vi) 0.1.

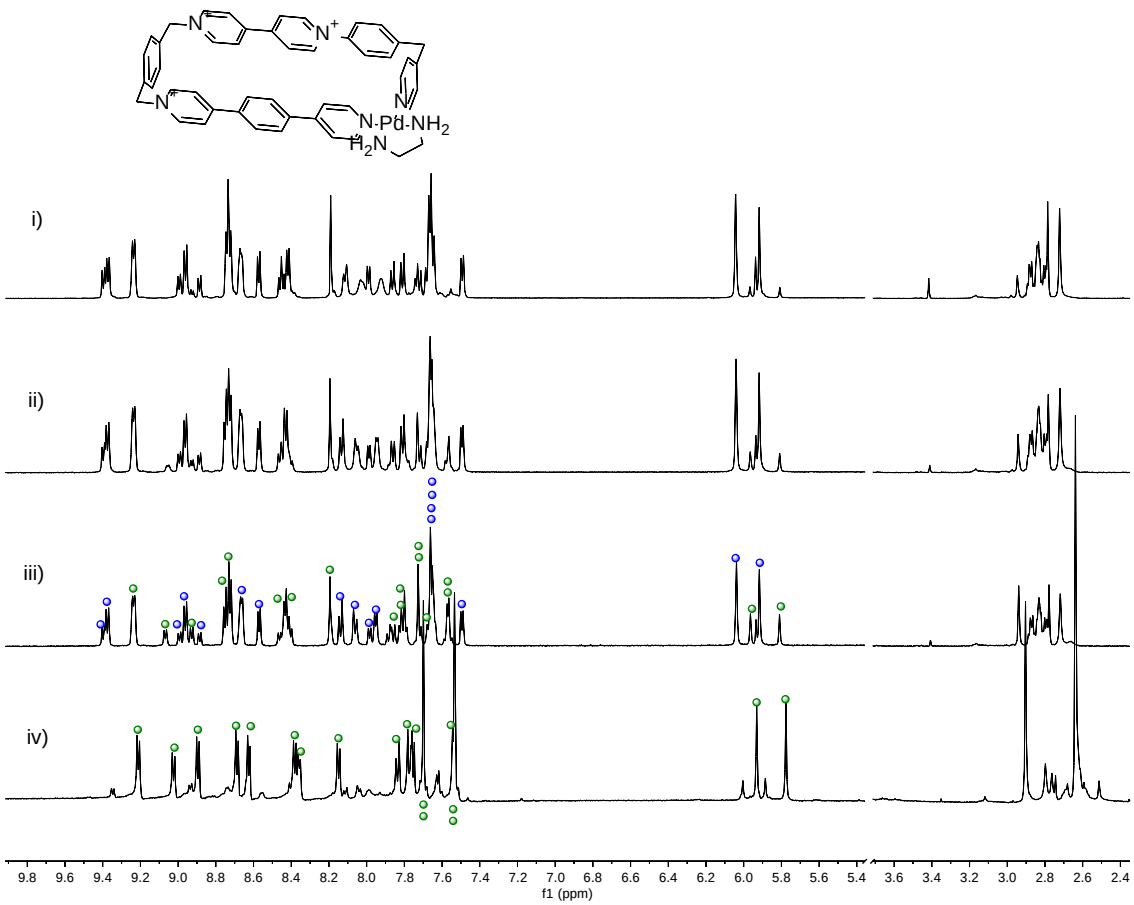

Figure S 87: Partial ^{1}H NMR (D_2O, 500 MHz) spectra of a solution of **L6·3NO$_3$** and (en)Pd(NO_3)$_2$ at different concentrations: (i) 15 mM (ii) 10 mM (iii) 7.5 mM (iv) 5 mM.

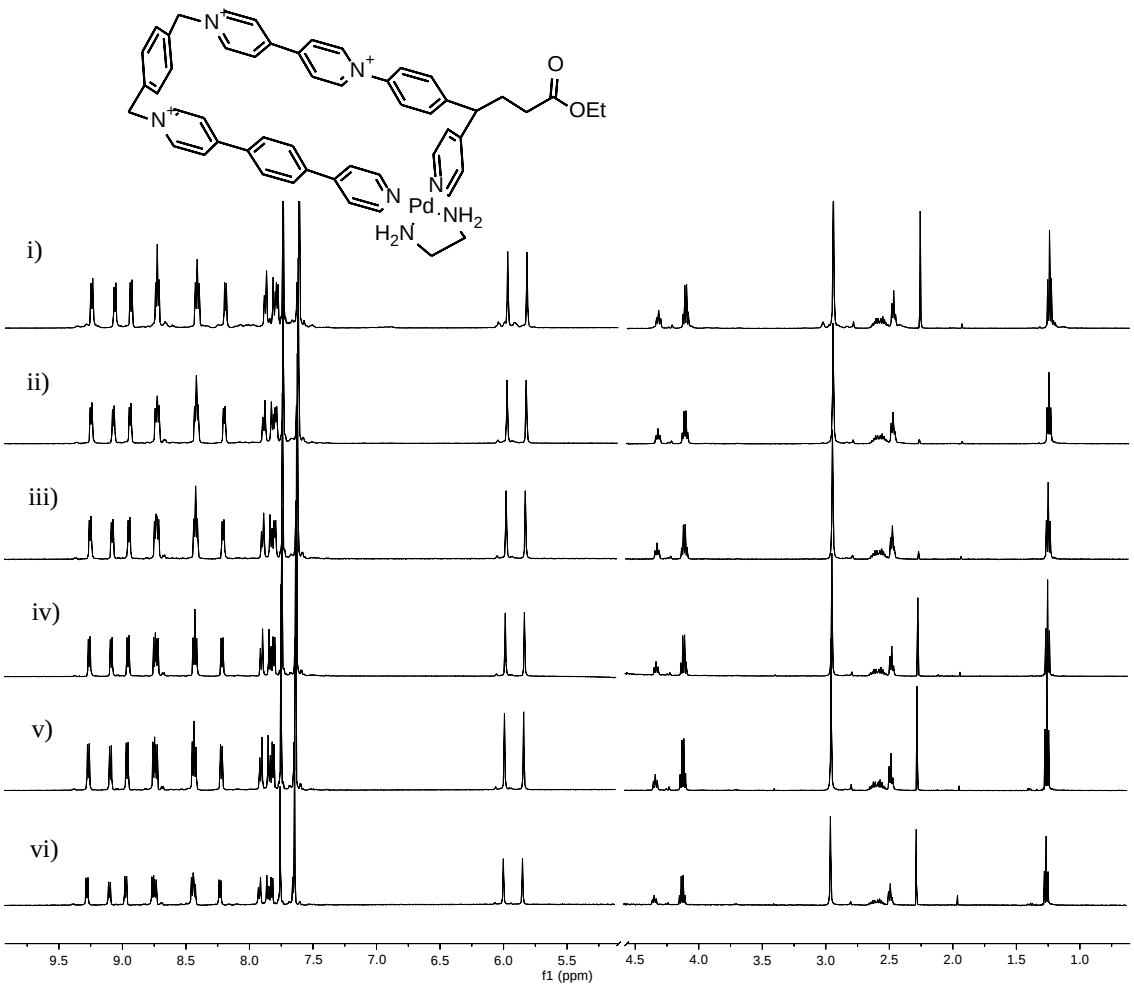

Figure S 88: Partial ^{1}H NMR (D_2O, 500 MHz) spectra of a solution of **L7·3NO$_3$** and (en)Pd(NO_3)$_2$ at different concentrations: (i) 15 mM (ii) 5 mM (iii) 2,5 mM (iv) 1,25 mM (v) 0,75 mM (vi) 0,375 mM.

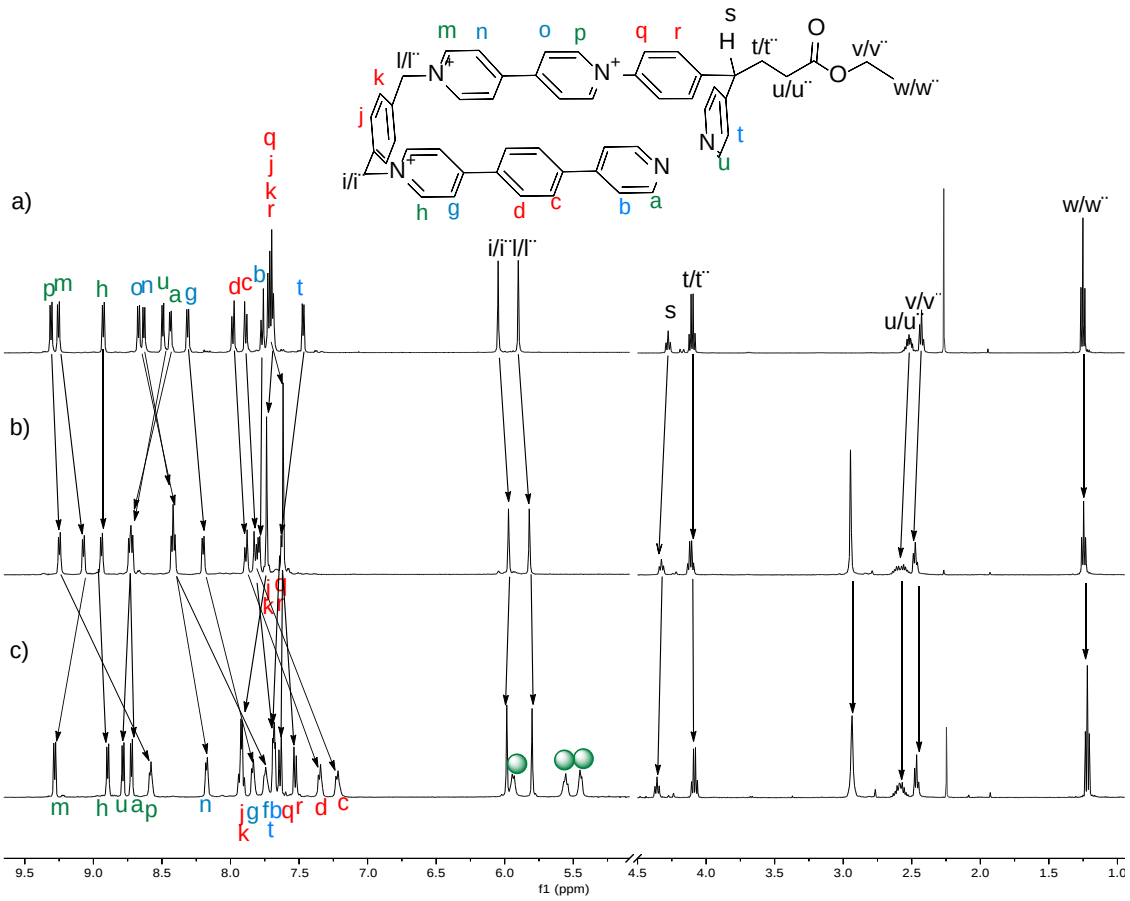

Figure S 89: Partial ^{1}H NMR (D_2O, 500MHz) spectra of: top, ligand **L7·3NO$_3$**; down metallacycle **M4a** and inclusion complex **M7a·5NO$_3$**·and **1,5DHN.**

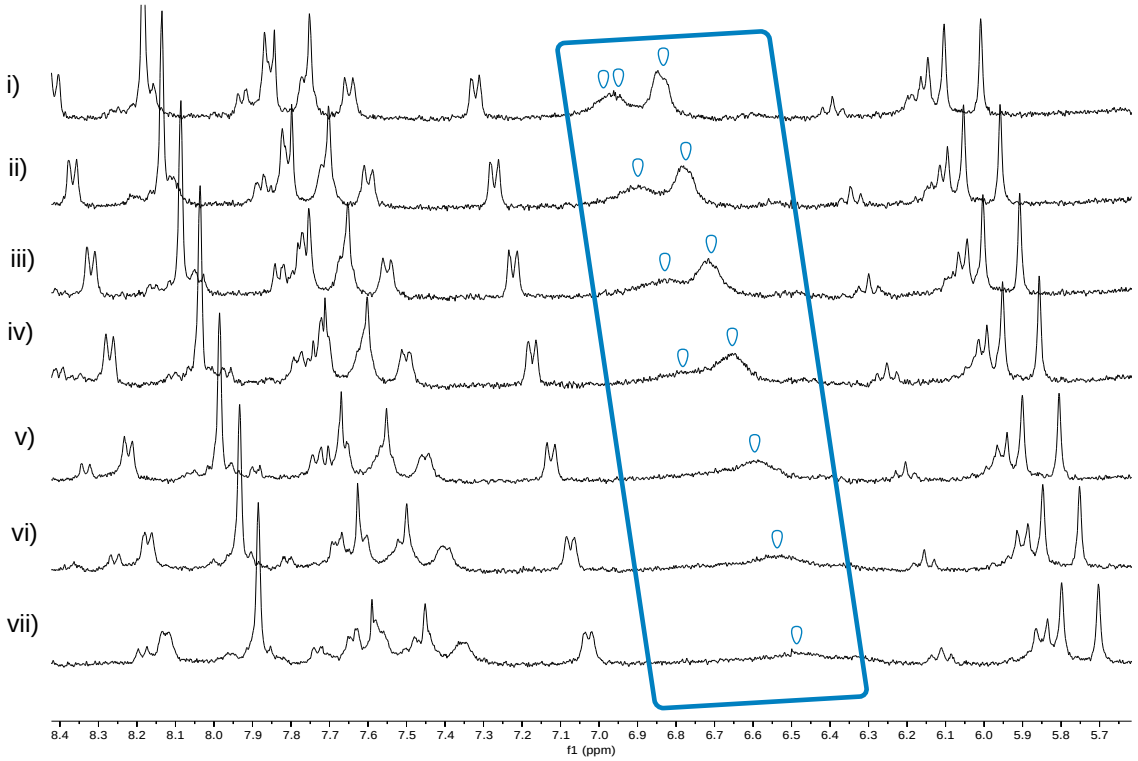

Figura S 90: Partial ^{1}H NMR (D_2O, 300MHz) spectra of **M5a·5NO$_3$**·and **1,5DHN** at different temperatures i) 333K; ii) 328K; iii) 323K; iv) 318K; v) 313K; vi) 308K; vii) 298K.