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Supplementary Material

A one-pot synthesis of oligo(arylene–ethynylene)-molecular wires and their use in the further verification of molecular circuit laws

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Molecular Structures

The structure of 2,5-bis((trimethylsilyl)ethynyl)thiophene**, 1** (**Figure S1**) was determined by single crystal X-ray diffraction from crystals grown in hexane. The structures of compounds **2** and **3** have already been determined and reported elsewhere by others,[1] giving us the opportunity to calculate the aromaticity from the structural parameters of the central units in each member of this series. The alkyne moieties exhibit linear geometries and average C≡C bond length of 1.206(2) Å which is consistent with the analogous bond lengths in **2** and **3**.

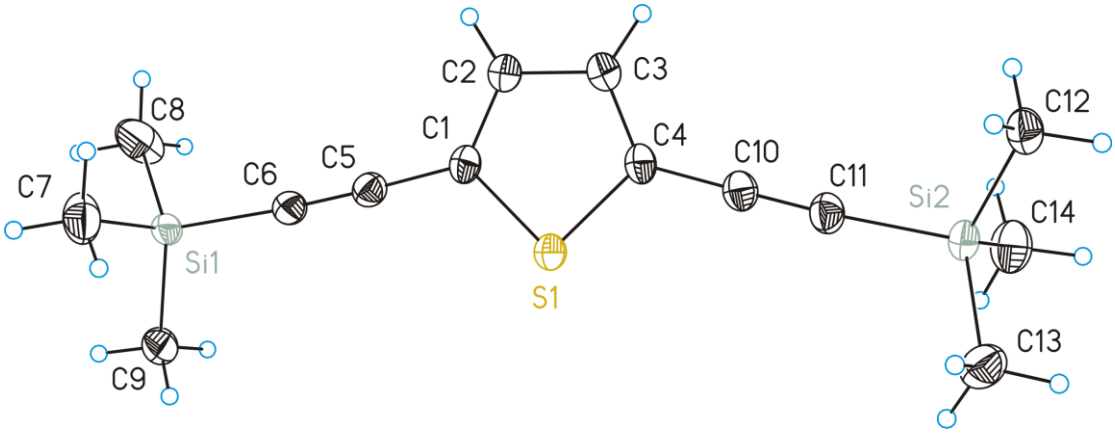

Figure S1: ORTEP drawing (50% probability level) of the molecular structure of **1** with its atom-numbering scheme. All hydrogen atoms except from the thiophene hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (◦): C1–C5 1.432(2), C4–C10 1.421(2); C5–C6 1.204(2), C10–C11 1.206(2); C6–Si1 1.844(1), C11–Si2 1.843(1); C2–C8–C9 179.6(5), C1–C5–C6 178.1(1), C4–C10–C11 178.6(2); C5–C6–Si1 176.6(1), C10–C11–Si2 176.7(1).

Similarly the crystallographically determined structures of the compounds **7a** and **7b** have also been reported,[2] with the structure of **7c** (**Figure S2**) being determined in this work from the single crystals grown by slow diffusion of CH_2Cl_2/MeOH. In the solid state **7c** adopts an essentially linear structure with the central phenyl ring sitting on an inversion center. The central anthracene ring canted by 29.10(4)° and 29.47(4)° with respect to the two terminal phenyl rings. The central anthracene ring in the crystal packing does not follow any usual $\pi - \pi$ stacking. The S···S distances of **7a**,[2] **7b**[2] and **7c** are 20.092(4), 20.051(3), 20.026(2) Å, respectively.

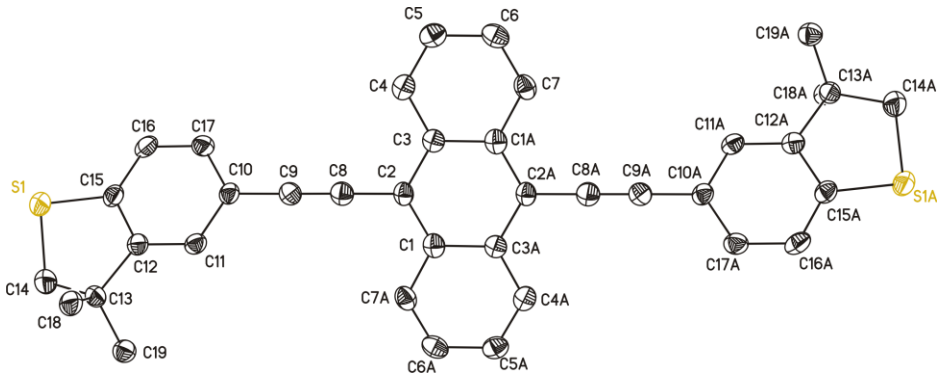

Figure S2: ORTEP drawing (50% probability level) of the molecular structure of **7c** with its atom-numbering scheme. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å), angles (◦) and plane (*p*) intersections (◦): C2–C8 1.429(6), C8–C9 1.206(6), C9–C10 1.433(6), C15–S11.761(4), S1-C14 1.829(5), S1···S1A 20.026(2), C2–C8–C9 179.6(5), C8–C9–C10 176.5(5), C15–S1–C14 90.8(2), *p*(C_6H_3)···*p*A(C_6H_3) 000(2), p(C_6H_3)···p($C_{14}H_8$) 29.8(1). Symmetry operation for generating equivalent atoms: (A) 1–x, 1–y, –z.

Table S1. Crystal structure and refinement details

	1	**7c**
CCDC Number	2107811	2107812
Empirical formula	$C_{14}H_{20}SSi_2$	$C_{38}H_{30}S_2$
Formula weight	276.54	550.74
Temperature/K	100.6(10)	99.9(6)
Crystal system	monoclinic	*orthorhombic*
Space group	$P2_1/n$	*Pbca*
a/Å	9.74570(10)	8.3436(4)
b/Å	10.56570(10)	36.111(2)
c/Å	16.15090(10)	9.2528(3)
α/°	90	90
β/°	93.5480(10)	90
γ/°	90	90
V/Å^3	1659.87(3)	2787.8(2)
Z	4	4
ρ_{calc} g/cm^3	1.107	1.312
μ/mm^{-1}	2.936	1.919
F(000)	592	1160
Crystal size/mm^3	0.257×0.192×0.107	0.123×0.099×0.067
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.01 to 151.194	4.894 to 151.986
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -20 ≤ l ≤ 18	-9 ≤ h ≤ 10, -45 ≤ k ≤ 42, -10 ≤ l ≤ 11
Reflections collected	49381	19295
Independent reflections	3414 [R_{int} = 0.0463, R_{sigma} = 0.0167]	2857 [R_{int} = 0.1105, R_{sigma} = 0.0592]
Data/restraints /parameters	3414/0/160	2857/0/183
Goodness-of-fit on F^2	1.082	1.17
Final R indexes [$I \geq 2\sigma$ (I)]	R_1 = 0.0305, wR_2 = 0.0805	R_1 = 0.0968, wR_2 = 0.2200
Final R indexes [all data]	R_1 = 0.0323, wR_2 = 0.0821	R_1 = 0.1089, wR_2 = 0.2264
Largest diff. peak/hole / e Å^{-3}	0.25/-0.33	0.75/-0.44

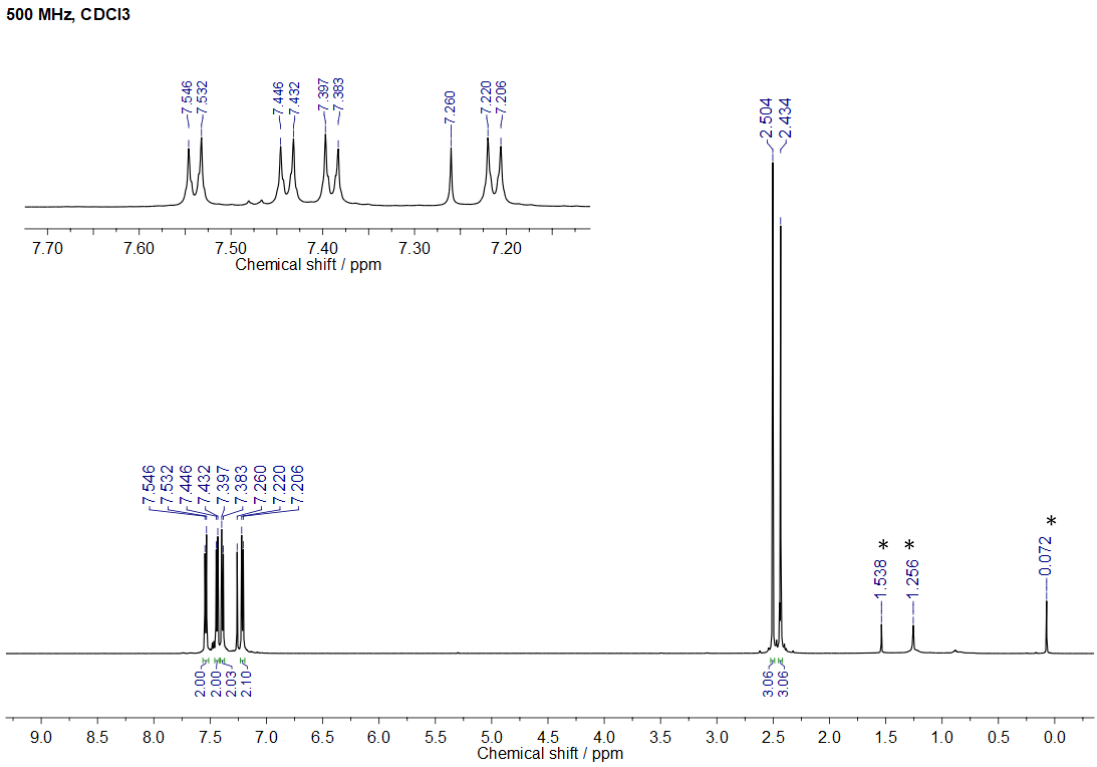

Figure S3: ^{1}H NMR spectrum of **A** recorded in $CDCl_3$. * impurity

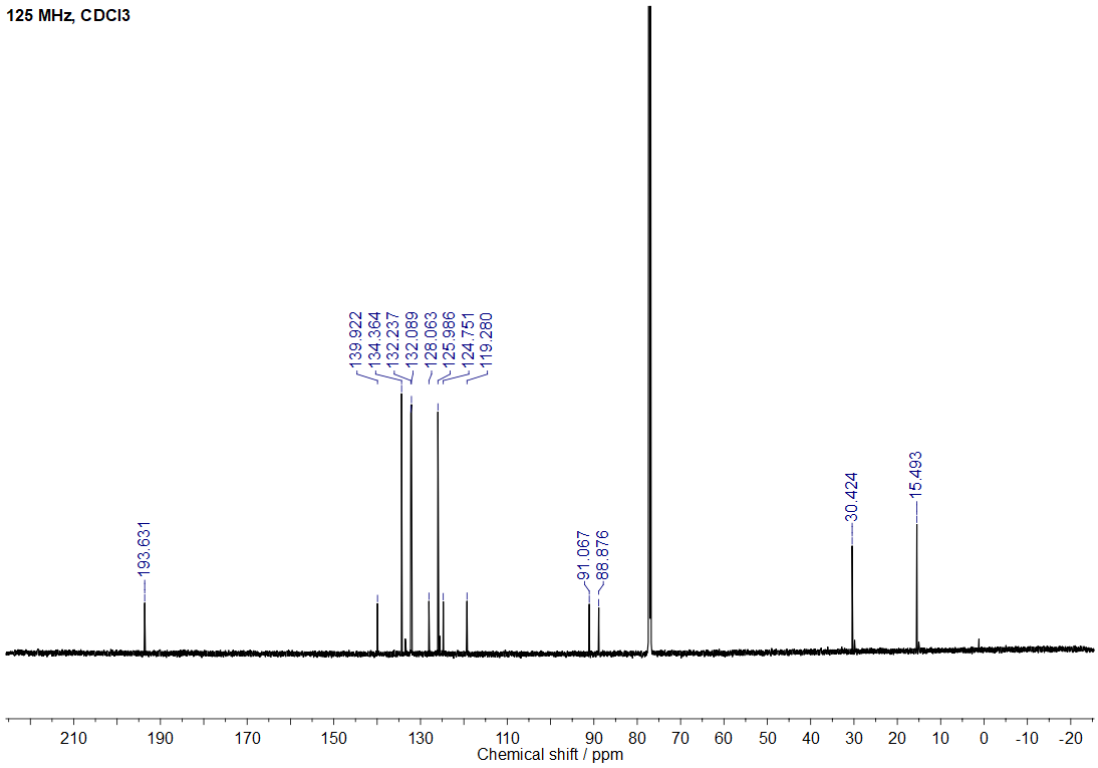

Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum of **A** recorded in $CDCl_3$.

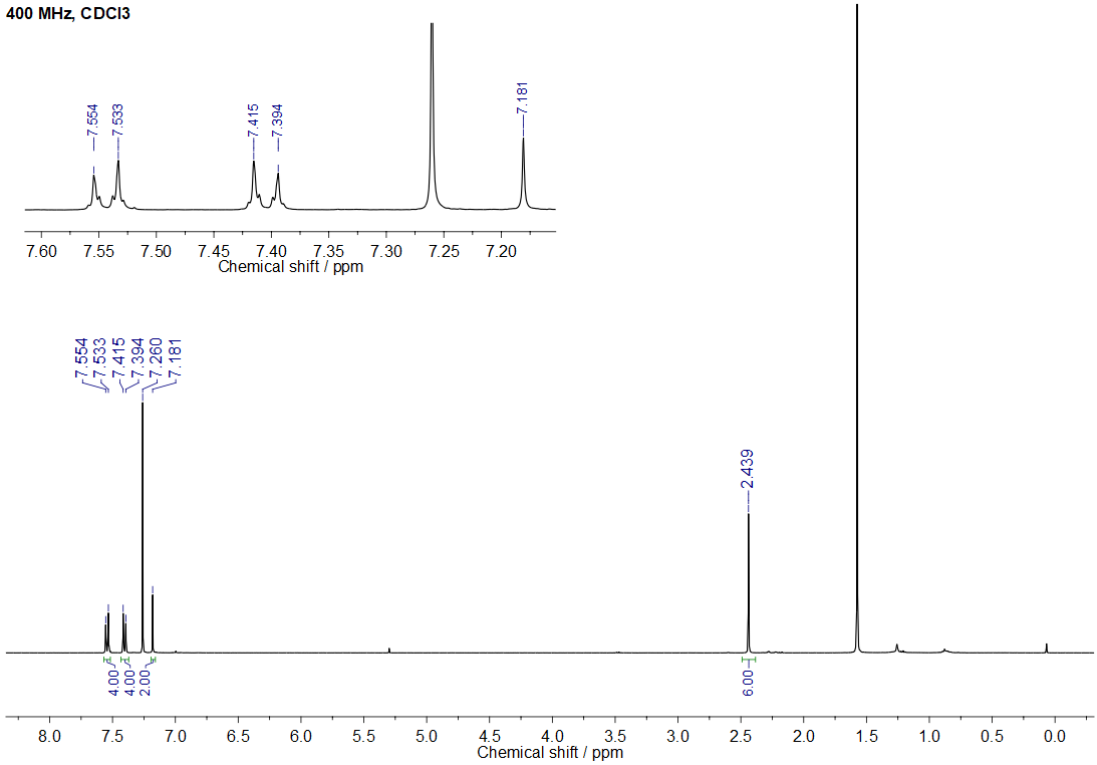

Figure S5: ^{1}H NMR spectrum of **5a** recorded in $CDCl_3$.

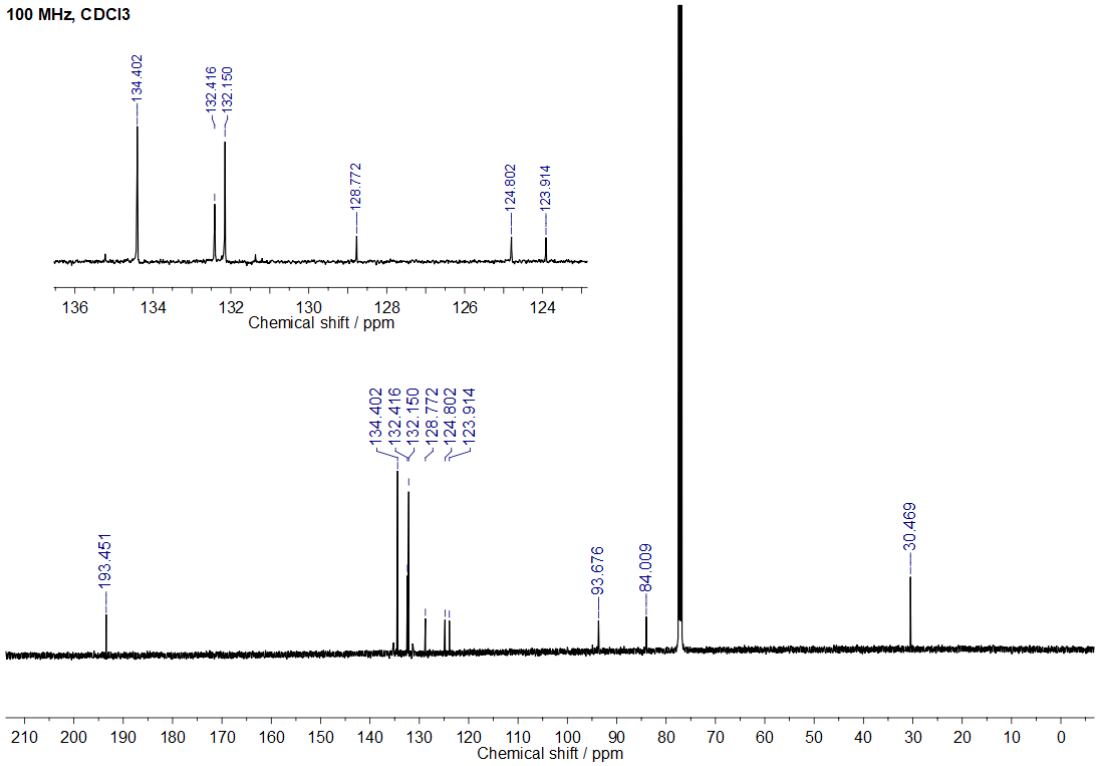

Figure S6: ^{13}C{^{1}H} NMR spectrum of **5a** recorded in $CDCl_3$.

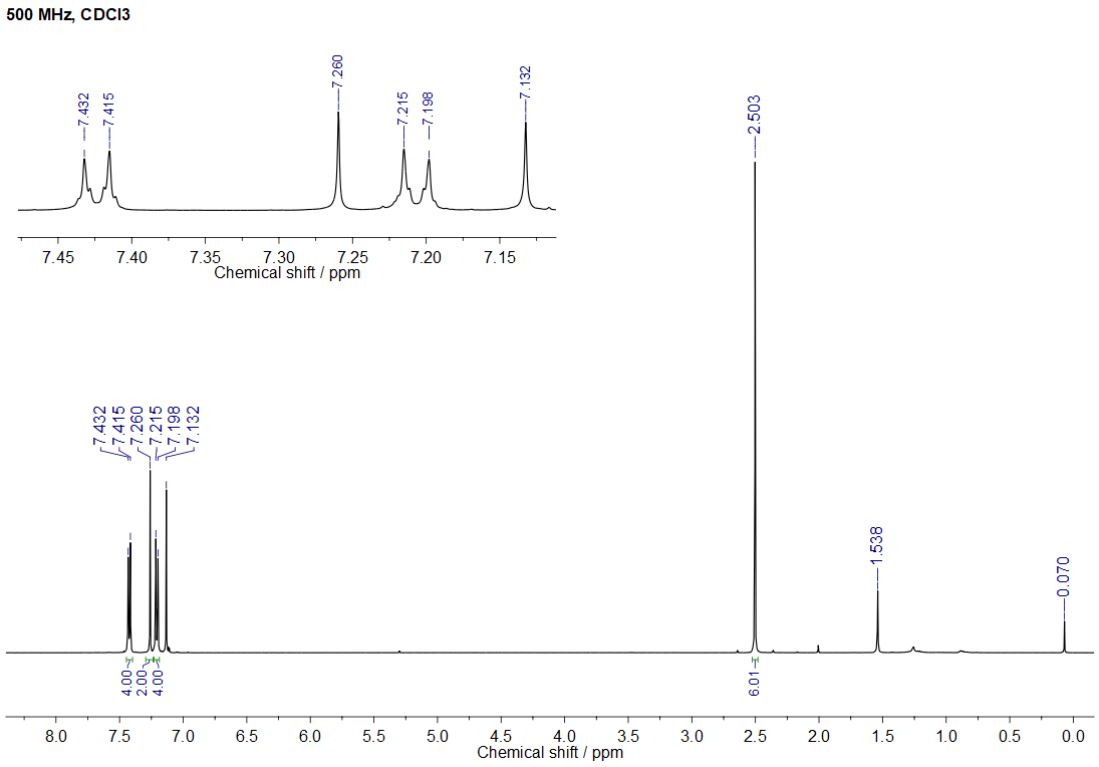

Figure S7: ^{1}H NMR spectrum of **5b** recorded in $CDCl_3$.

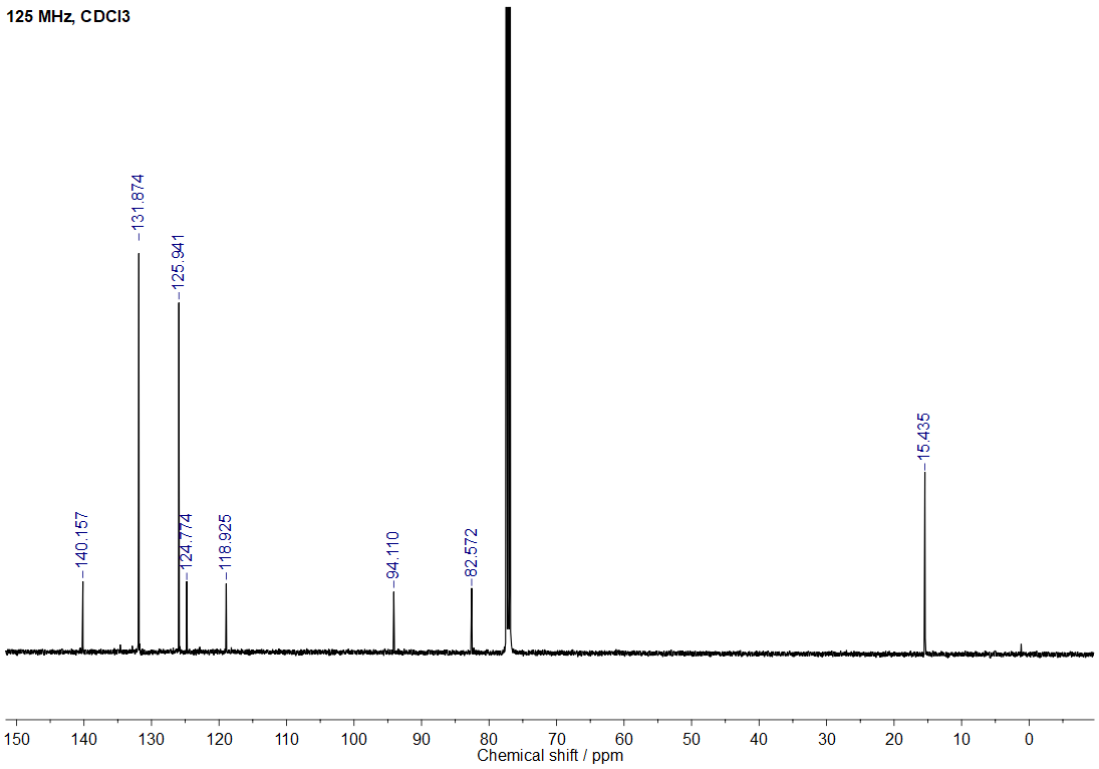

Figure S8: $^{13}C\{^{1}H\}$ spectrum of **5b** recorded in $CDCl_3$.

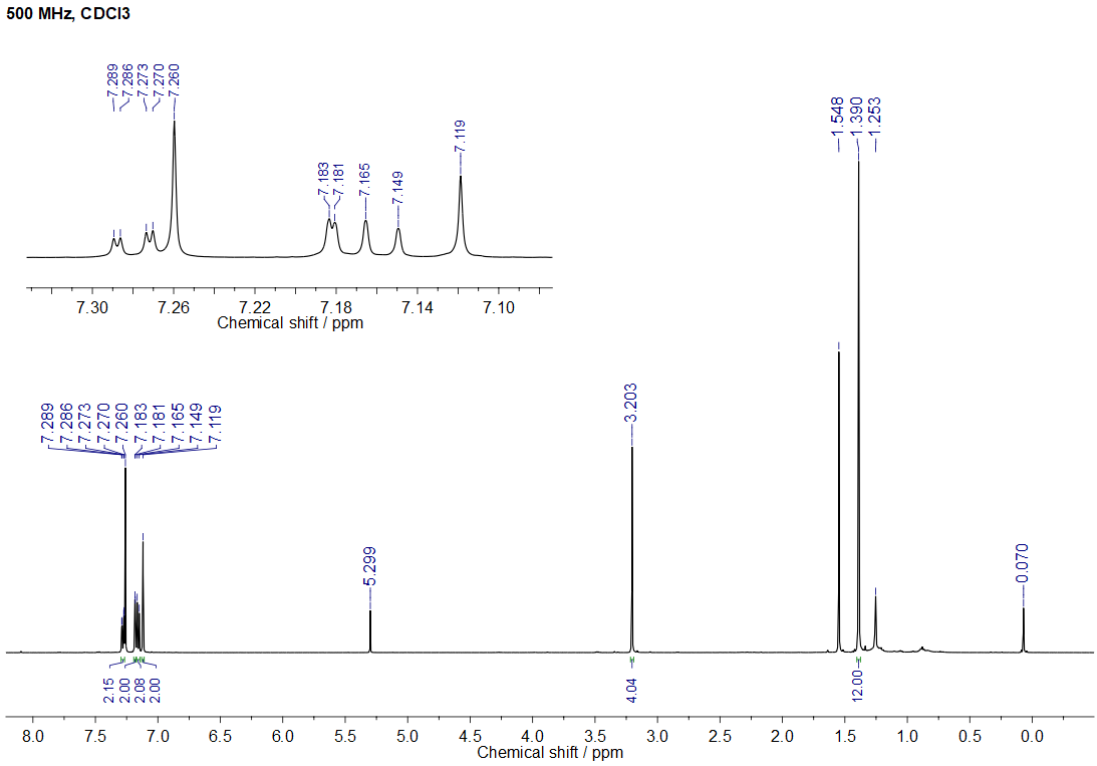

Figure S9: ^{1}H NMR spectrum of **5c** recorded in $CDCl_3$.

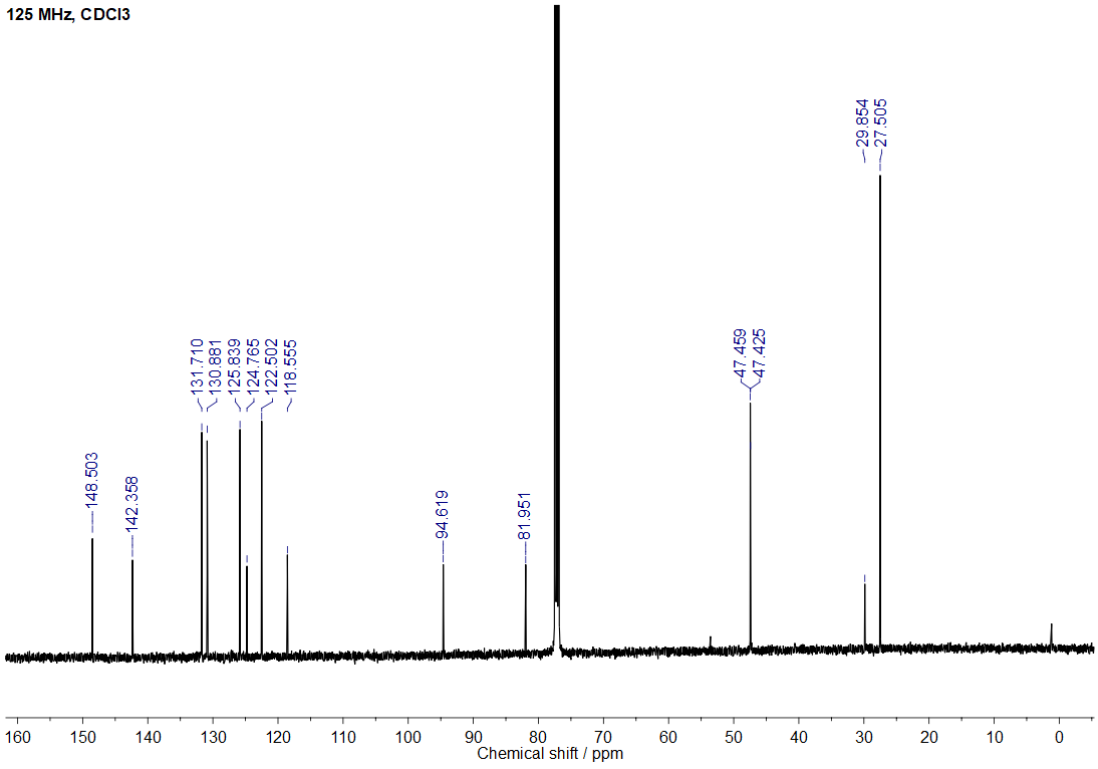

Figure S10: ^{13}C NMR spectrum of **5c** recorded in $CDCl_3$.

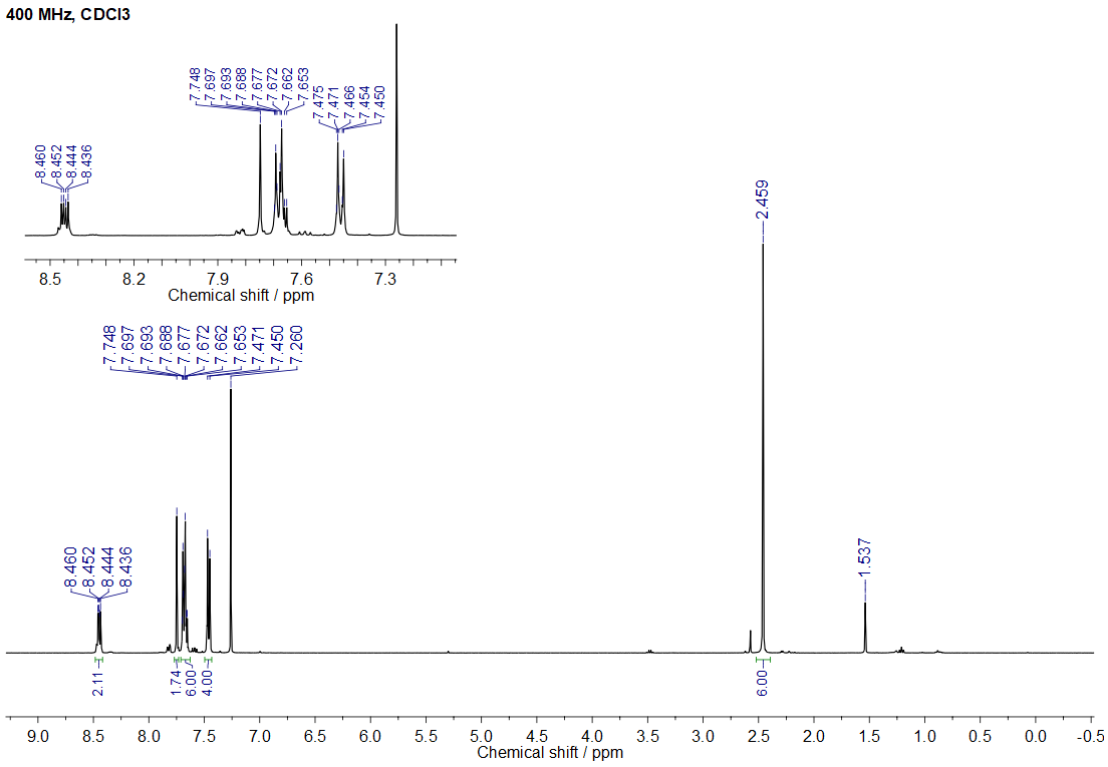

Figure S11: ^{1}H NMR spectrum of **6a** recorded in $CDCl_3$.

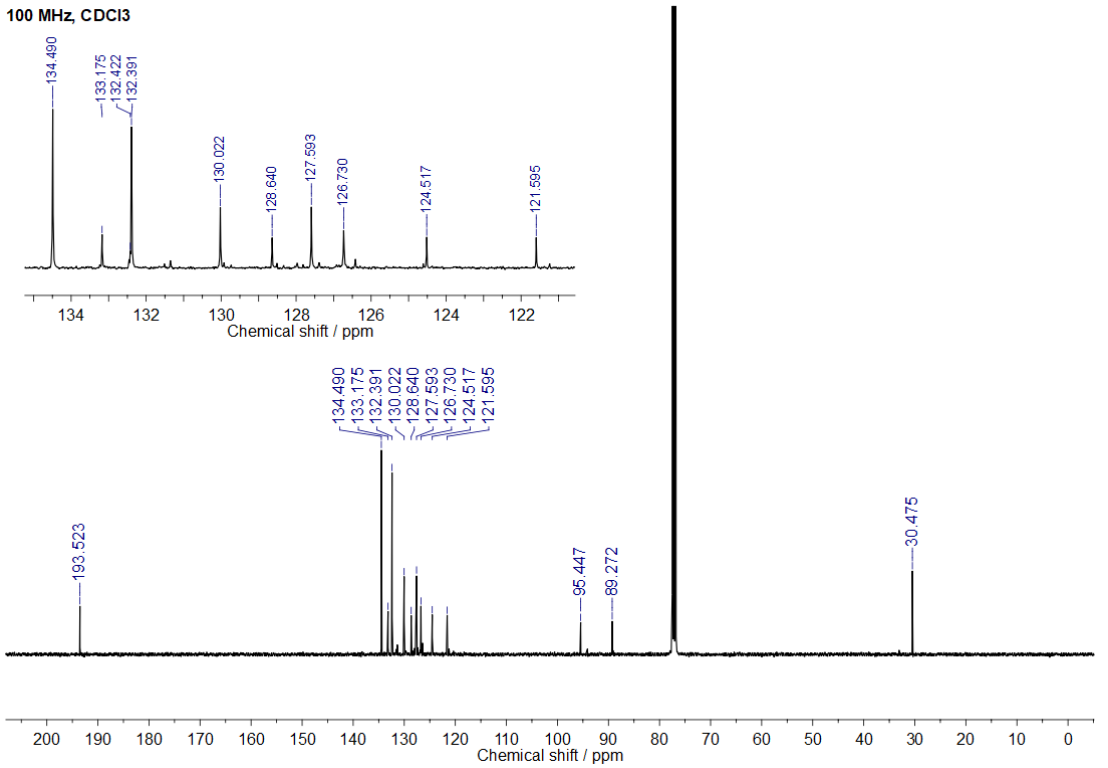

Figure S12: ^{13}C{^{1}H} NMR spectrum of **6a** recorded in $CDCl_3$.

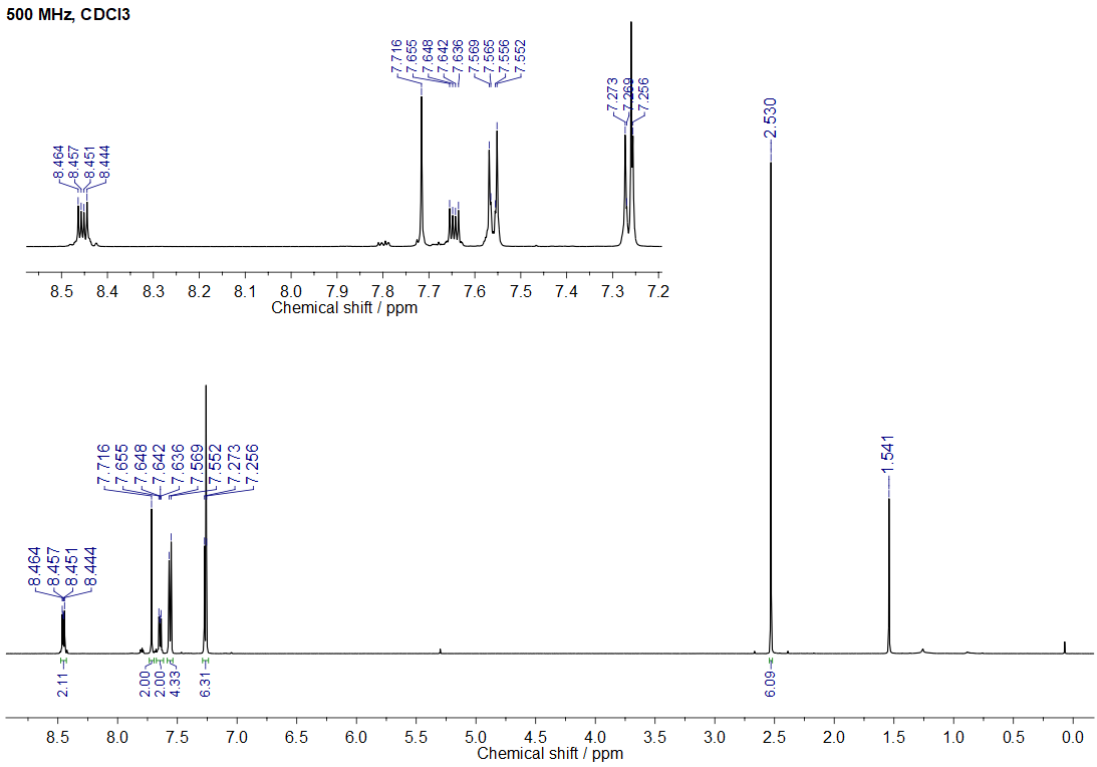

Figure S13: ^{1}H NMR spectrum of **6b** recorded in $CDCl_3$.

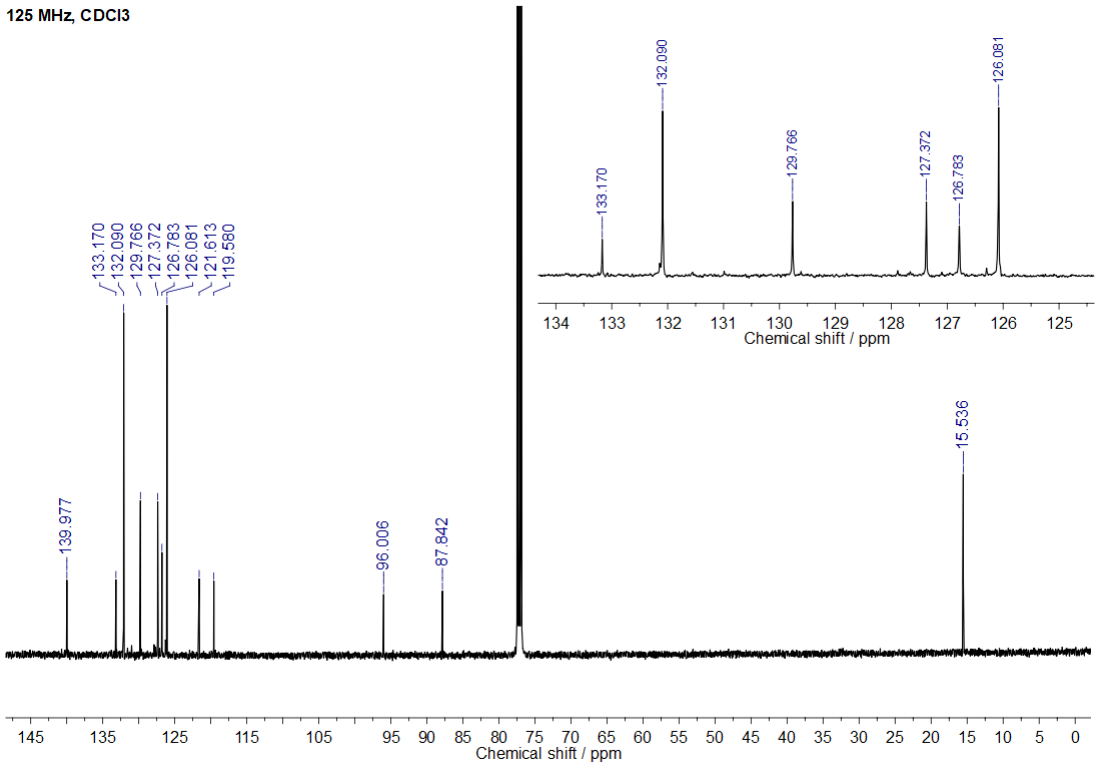

Figure S14: $^{13}C\{^{1}H\}$ spectrum of **6b** recorded in $CDCl_3$.

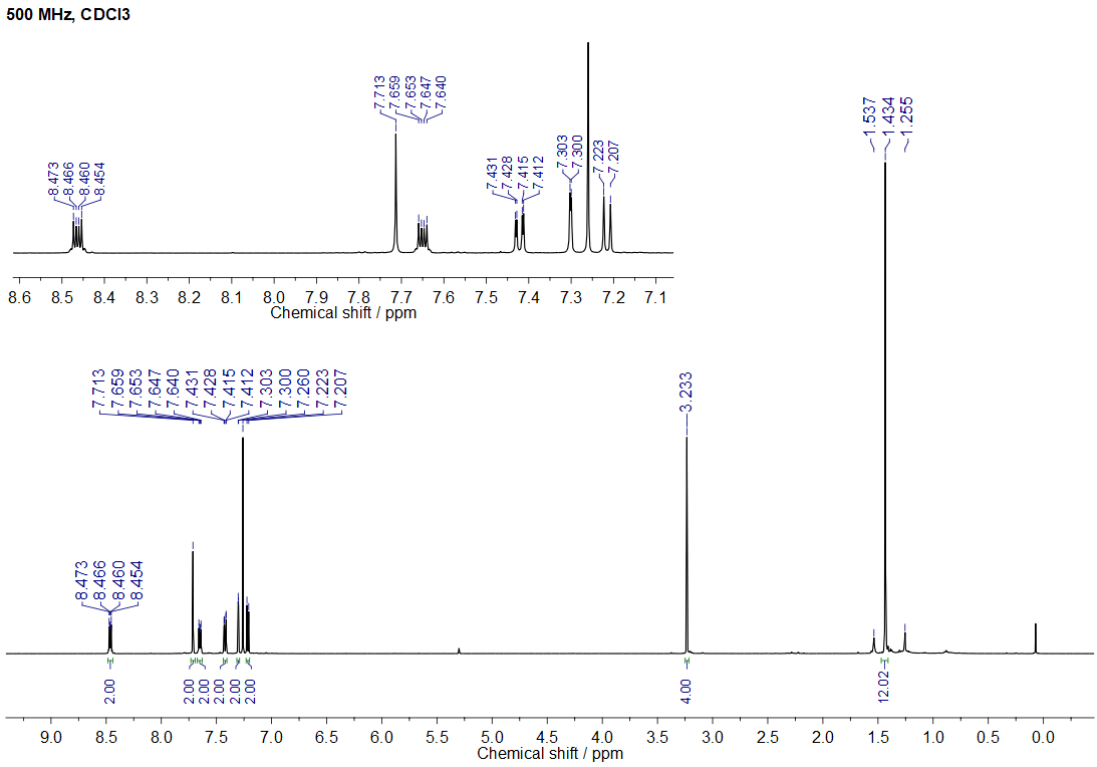

Figure S15: ^{1}H NMR recorded spectrum of **6c** in $CDCl_3$.

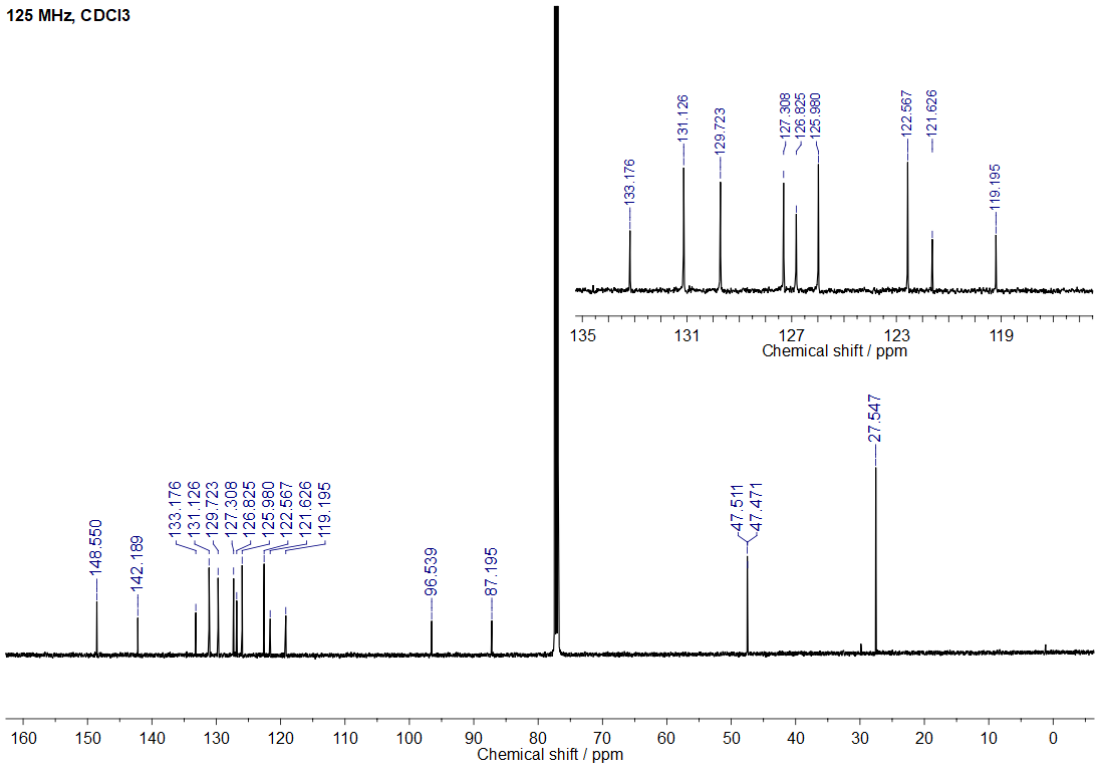

Figure S16: $^{13}C\{^{1}H\}$ spectrum of **6c** recorded in $CDCl_3$.

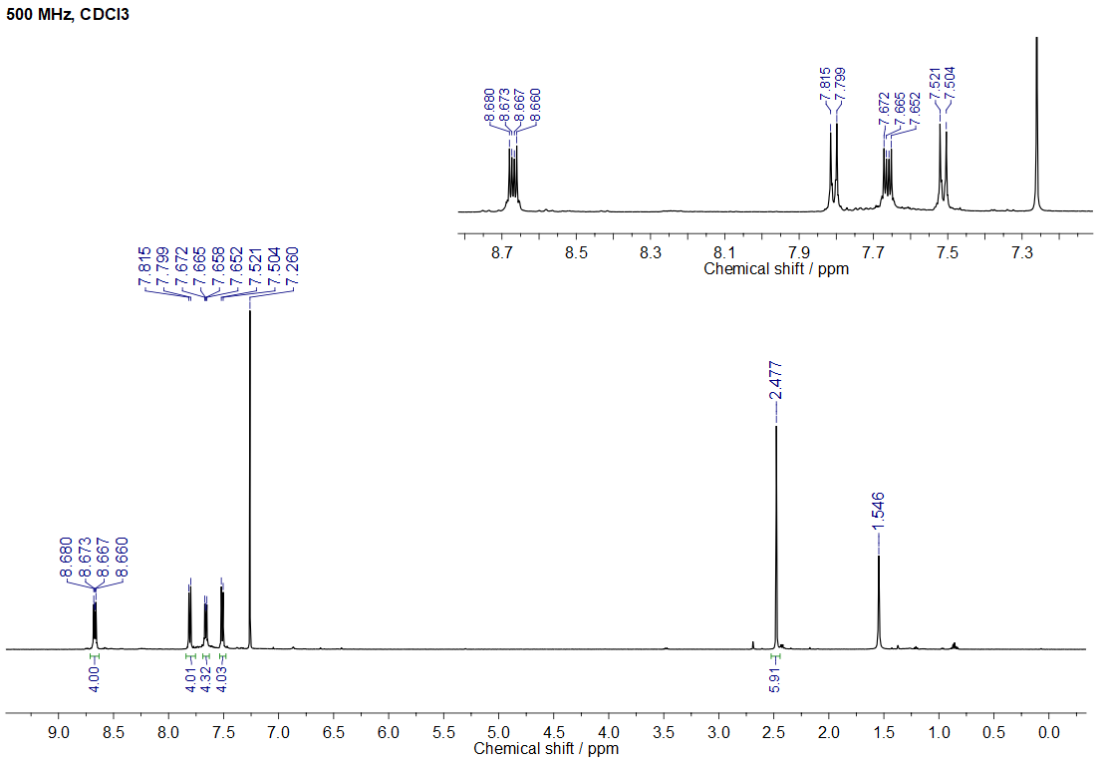

Figure S17: ^{1}H NMR spectrum of **7a** recorded in $CDCl_3$.

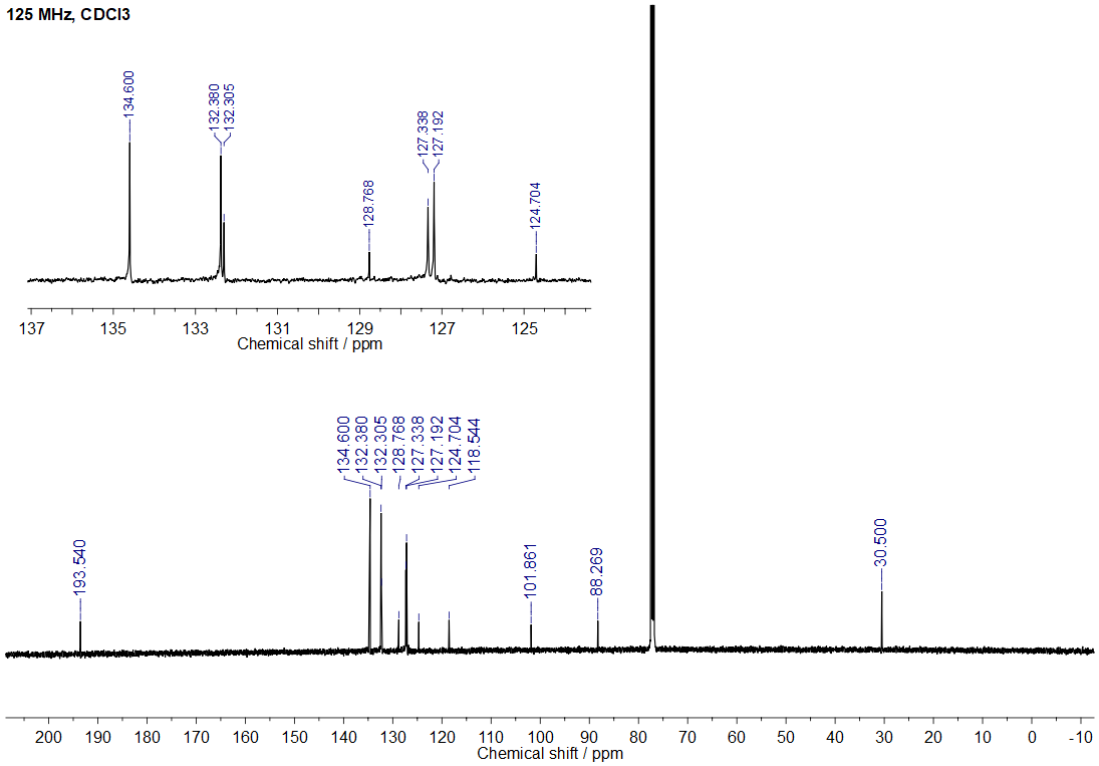

Figure S18: $^{13}C\{^{1}H\}$ spectrum of **7a** recorded in $CDCl_3$.

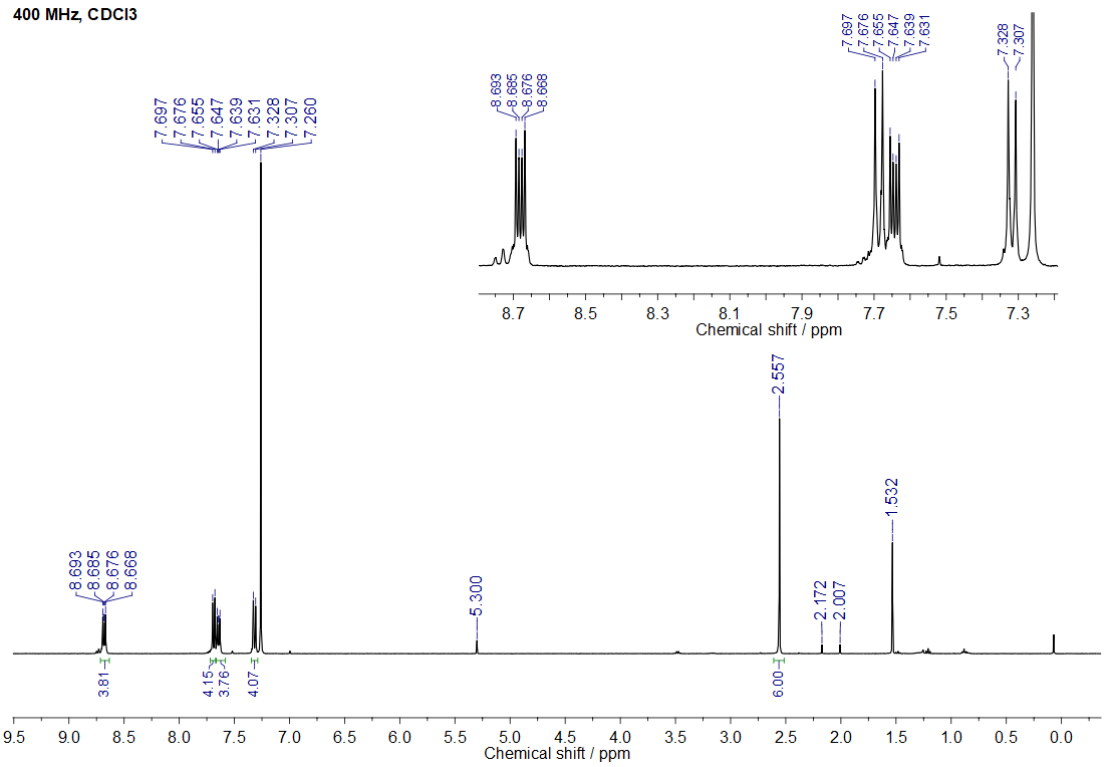

Figure S19: ^{1}H NMR spectrum of **7b** recorded in $CDCl_3$.

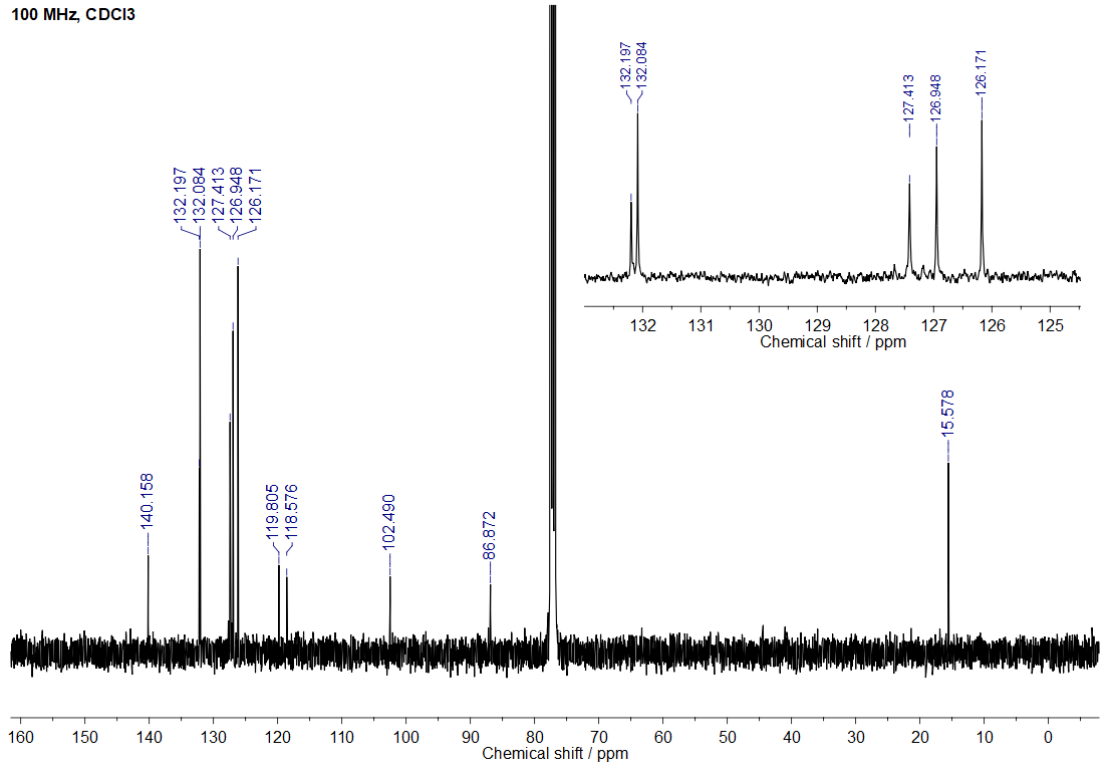

Figure S20: $^{13}C\{^{1}H\}$ spectrum of **7b** recorded in $CDCl_3$.

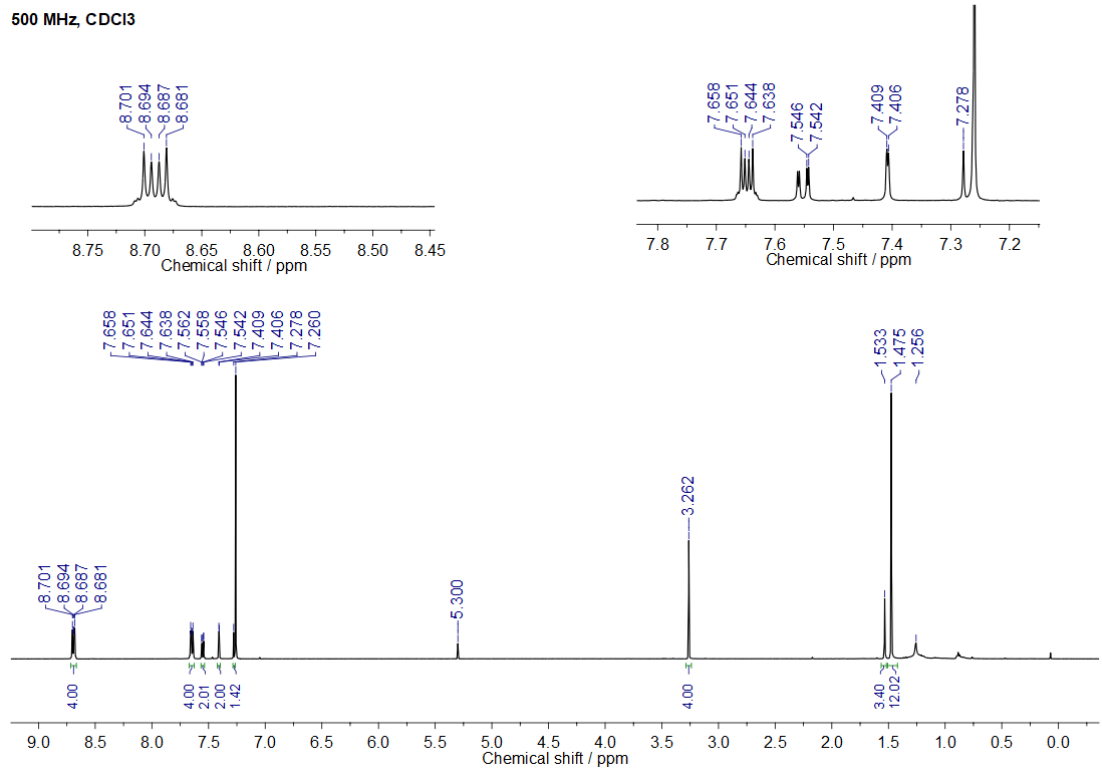

Figure S21: ^{1}H NMR spectrum of **7c** recorded in $CDCl_3$.

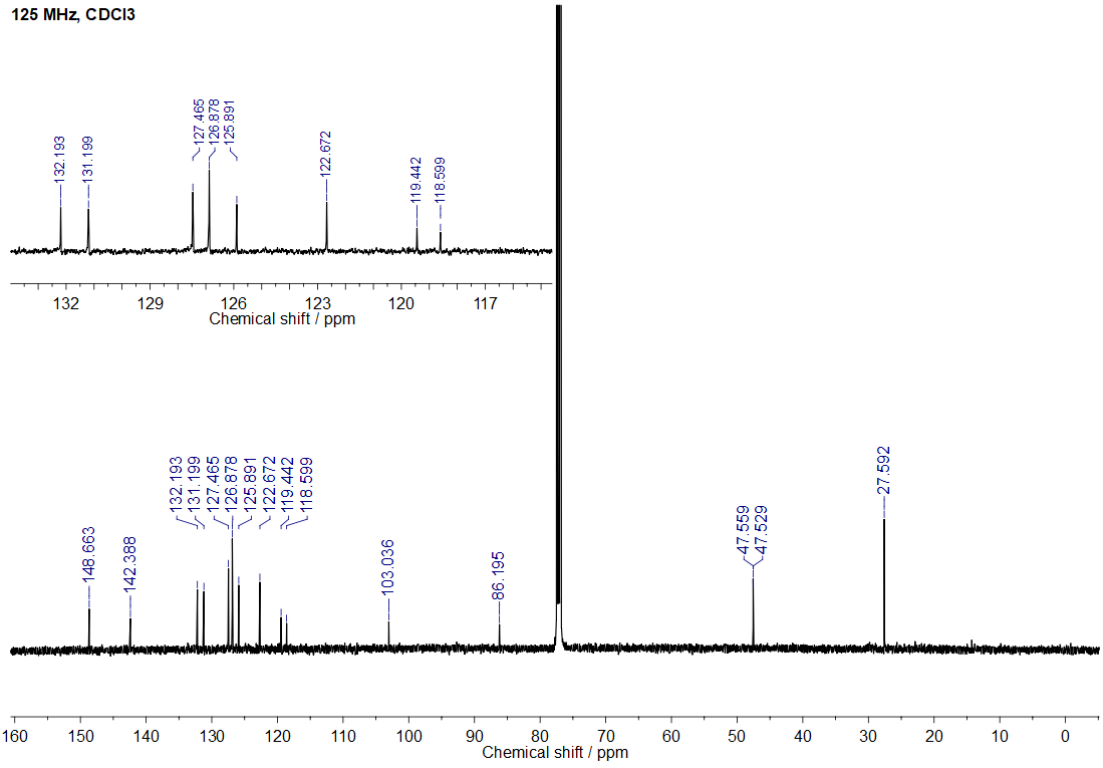

Figure S22: $^{13}C\{^{1}H\}$ spectrum of **7c** recorded in $CDCl_3$.

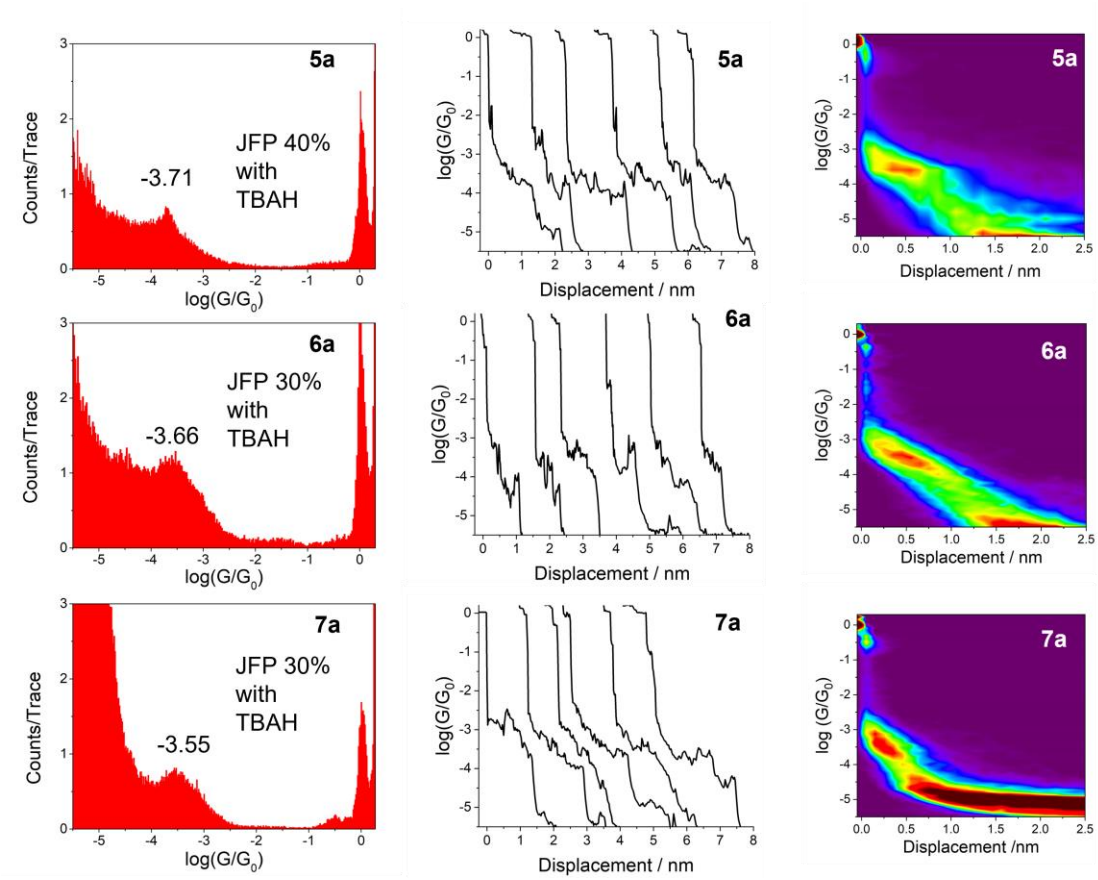

Figure S23. Representative conductance ($log\left(^{G}/_{G_0}\right)$) vs electrode displacement curves, conductance histograms, and 2D conductance – relative displacement histograms from compounds **5a**, **6a** and **7a** in xylene solution containing tetrabutylammonium hydroxide (0.1 M solution in THF, 10 equivalents).

References:

1. Khan, M. S.; Al-Mandhary, M. R. A.; Al-Suti, M. K.; Al-Battashi, F. R.; Al-Saadi, S.; Ahrens, B.; Bjernemose, J. K.; Mahon, M. F.; Raithby, P. R.; Younus, M.; Chawdhury, N.; Köhler, A.; Marseglia, E. A.; Tedesco, E.; Feeder, N.; Teat, S. J., Synthesis, characterisation and optical spectroscopy of platinum(ii) di-ynes and poly-ynes incorporating condensed aromatic spacers in the backbone. *Dalton Trans.* **2004,** (15), 2377-2385.
2. Wang, X.; Bennett, T. L.; Ismael, A.; Wilkinson, L. A.; Hamill, J.; White, A. J.; Grace, I. M.; Kolosov, O. V.; Albrecht, T.; Robinson, B. J., Scale-up of room-temperature constructive quantum interference from single molecules to self-assembled molecular-electronic films. *J. Am. Chem. Soc.* **2020,** *142* (19), 8555-8560.