Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis and Redox Chemistry of Pd(II) Complexes of a Pincer Verdazyl Ligand

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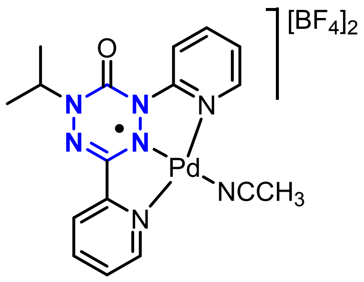

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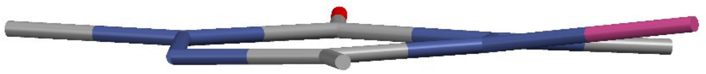

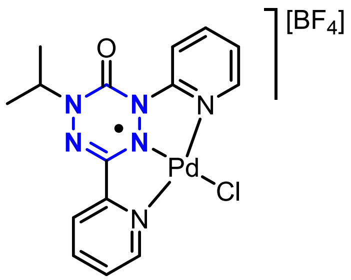

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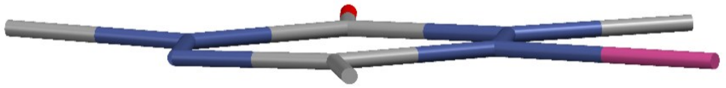

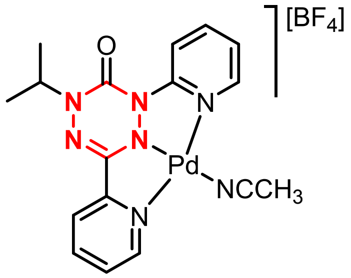

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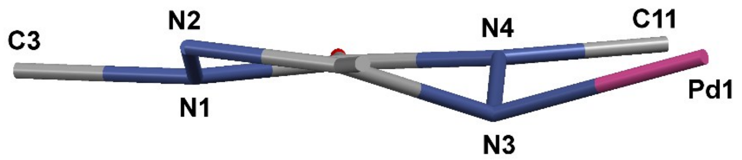

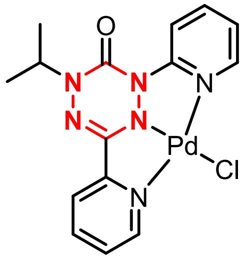

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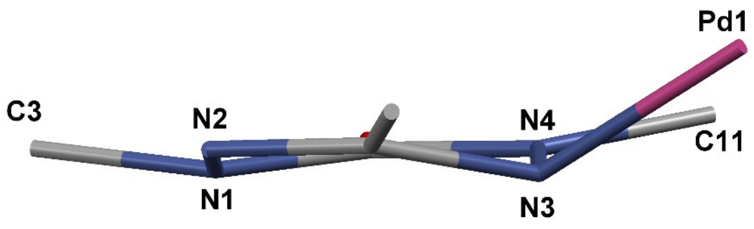

Figure S1: Side-on perspectives of the verdazyl ring in the X-ray structures of verdazyl-palladium complexes

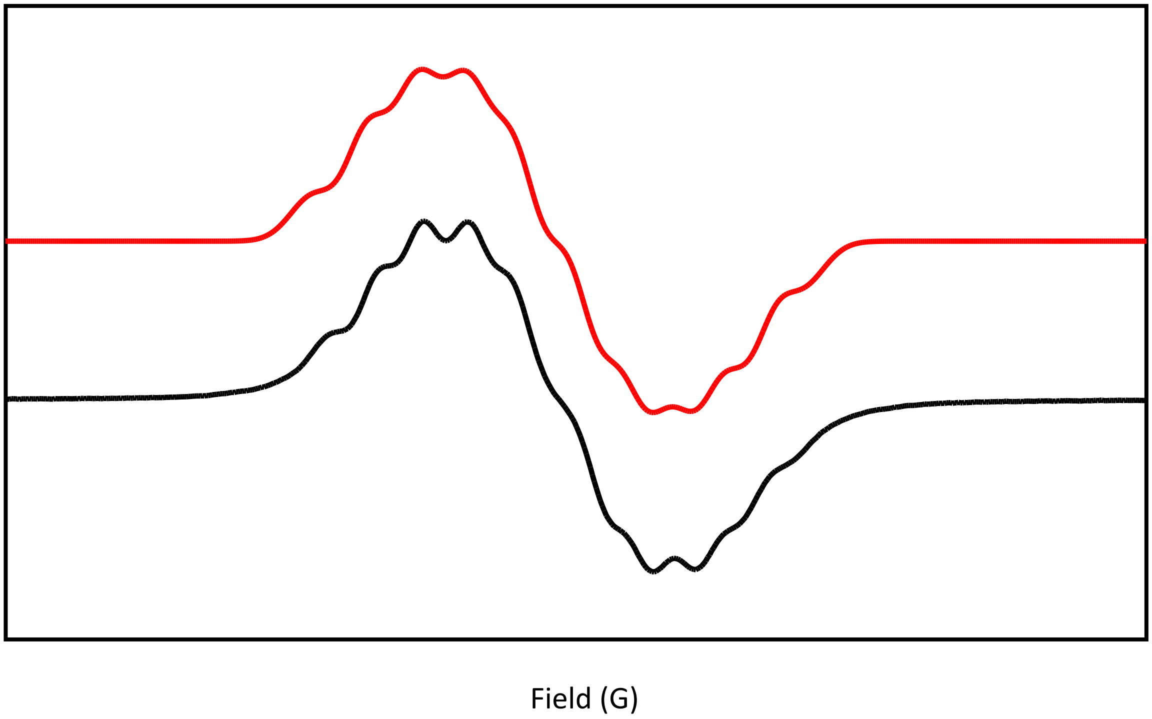

Figure S2: EPR spectrum of radical/chloro complex **12** in acetonitrile (black trace) and the corresponding simulated spectrum (red trace)

Table S1: EPR Parameters for **12** and **6**. Hyperfine coupling constants are given in G.

	12	**6**
Frequency (GHz)	9.8819	9.8780
g	2.0039	2.0033
a(N)	4.7	4.4
a(N)	5.8	5.2
a(N)	6.1	5.7
a(N)	8.4	8.0

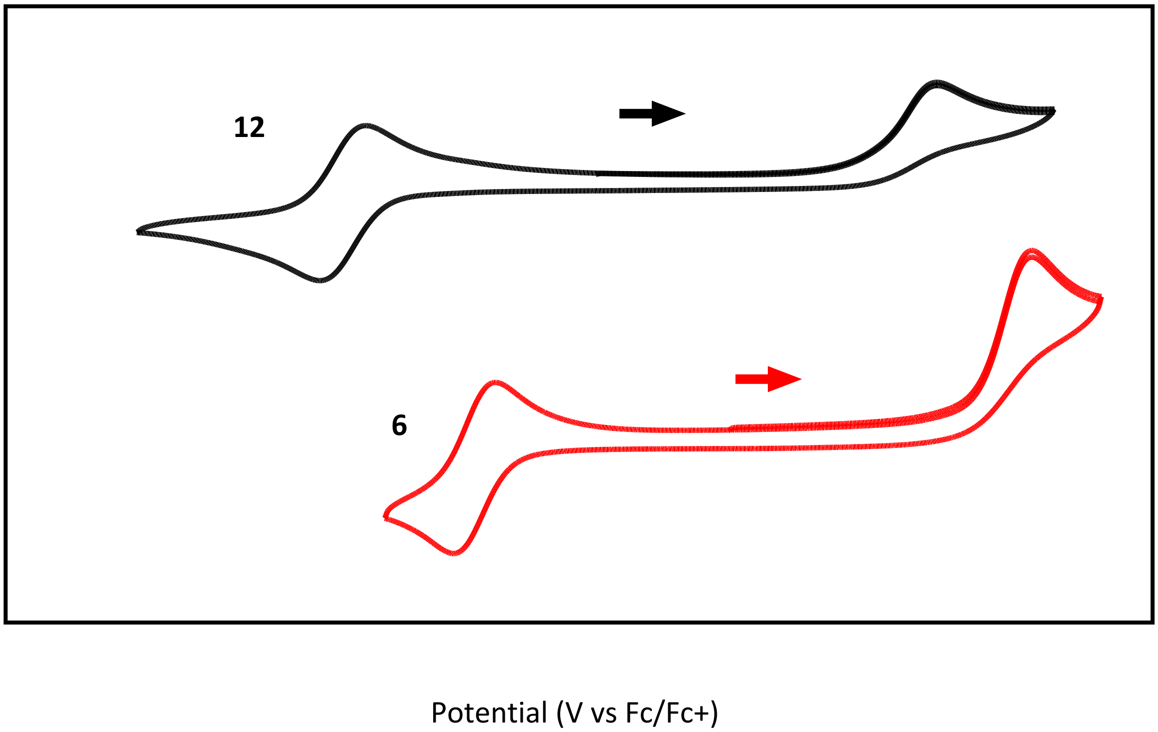

Figure S3: Cyclic voltammogram of radical/acetonitrile complex **6** (red trace) and radical/chloro complex **12** (black trace). The scan range was selected to only include redox events at potentials greater than -0.5 V vs Fc/Fc^{+}. The vertical axis is current and the arrows show both the direction and starting point for each scan. Both CVs were recorded as 1 mM solutions in acetonitrile at a scan rate of 100 mV/s (both solutions contain 0.1 M Bu_4NBF_4 as electrolyte).

Table S2: Electrochemical parameters for free radical **5,** acetonitrile complexes **6** and **10**, and chloro complexes **12** and **9**. Potentials are in V vs Fc/Fc^{+} and the CVs are in acetonitrile.

	E^{o}_{red}	E^{o}_{ox}
5	-0.84	+0.43
6	+0.42	+1.39[b]
10	+0.43[a]	+1.41[b]
12	+0.19	+1.23[b]
9	+0.19[a]	+1.23[b]

[a] 1st oxidation potential (**9** and **10** contain reduced verdazyl ligands)

[b] Irreversible process, anodic peak potential given

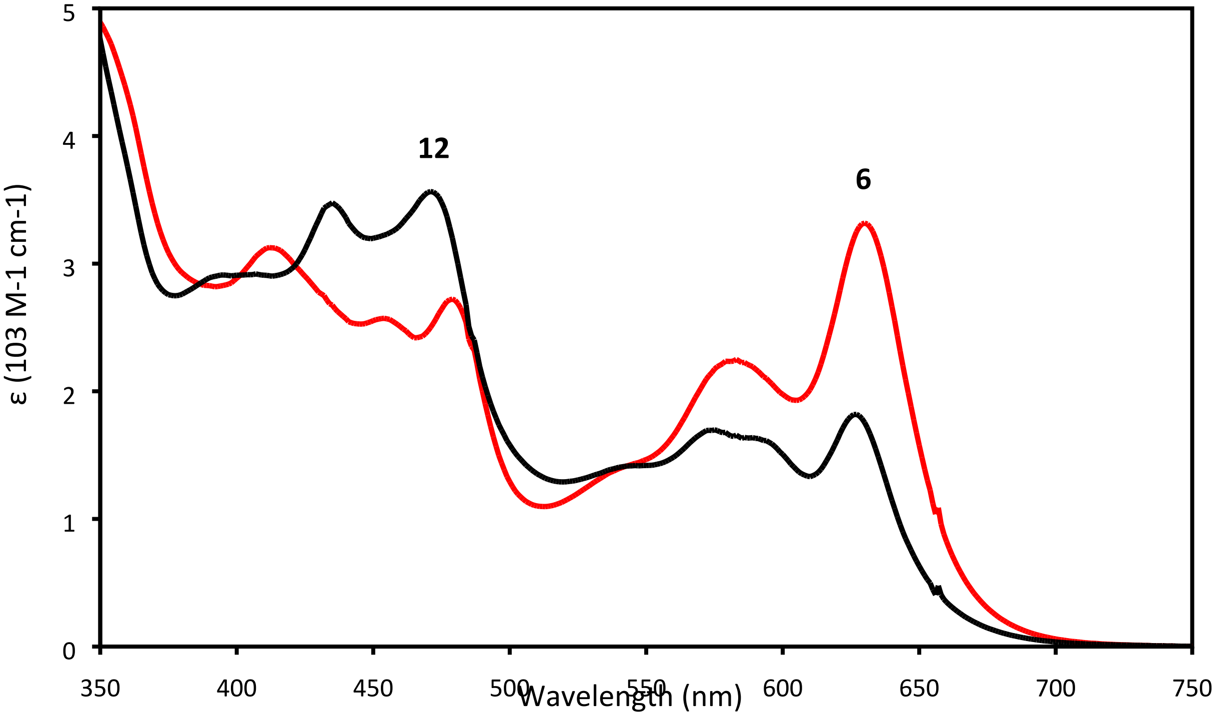

Figure S4: Electronic spectrum of radical/chloro complex **12** (black line) and radical/acetonitrile complex **6** (red line) in acetonitrile.

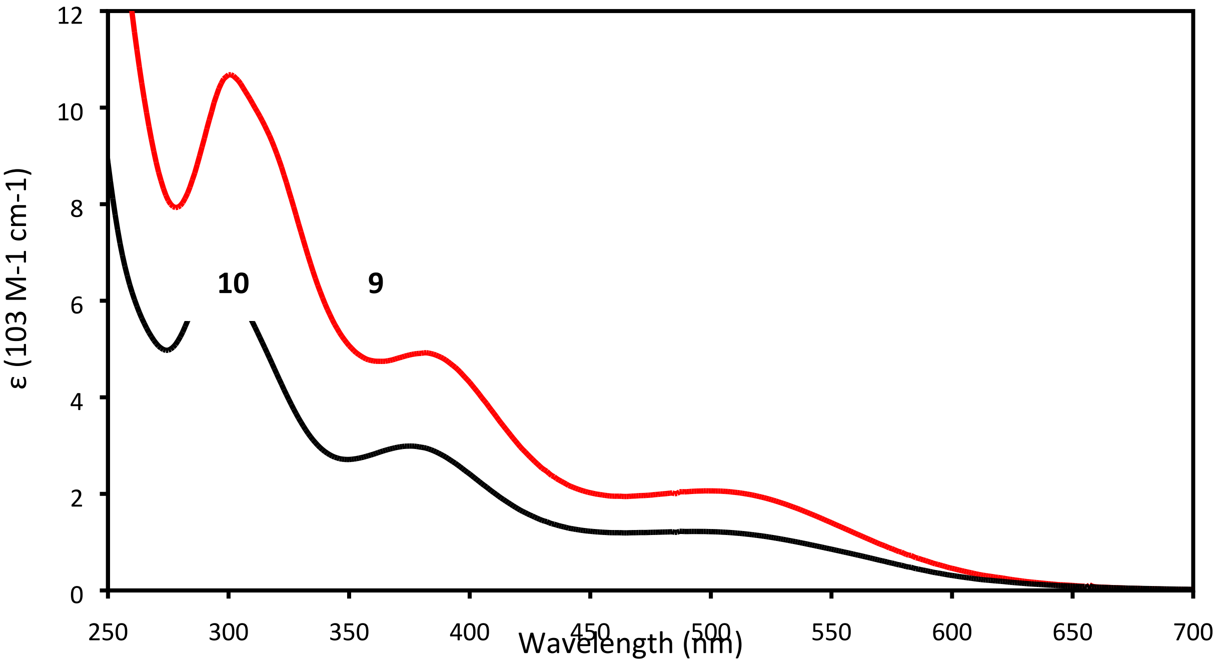

Figure S5: Electronic spectra of verdazyl-anion/acetonitrile complex **10** (black line) and verdazyl-anion/chloro complex **9** (red line) in acetonitrile.

Table S3: Crystallographic parameters for **6** and **9**

	6	**9**
Empirical formula	$C_{17}H_{18}B_2N_7OF_8Pd$	$C_{15}H_{15}ClN_6OPd$
Formula weight	616.40	437.18
Temperature/K	90	90
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a/Å	7.9377(11)	8.7021(4)
b/Å	11.1851(16)	17.8213(9)
c/Å	12.3025(18)	10.2618(5)
α/°	81.951(2)	90
β/°	83.335(2)	96.0610(10)
γ/°	85.737(2)	90
Volume/$Å^3$	1072.3(3)	1582.53(13)
Z	2	4
$\rho_{calc}g/cm^3$	1.909	1.835
μ/mm^{-1}	0.963	1.357
F(000)	610.0	872.0
Crystal size/mm^3	0.16 × 0.1 × 0.02	0.15 × 0.1 × 0.09
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.362 to 55.956	4.572 to 60.178
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16	-12 ≤ h ≤ 12, -25 ≤ k ≤ 24, -14 ≤ l ≤ 12
Reflections collected	17152	19349
Independent reflections	5165 [R_{int} = 0.0346, R_{sigma} = 0.0349]	4631 [R_{int} = 0.0387, R_{sigma} = 0.0332]
Data/restraints/parameters	5165/0/328	4631/0/219
Goodness-of-fit on F^2	1.068	0.927
Final R indexes [I>=2σ (I)]	R_1 = 0.0381, wR_2 = 0.0910	R_1 = 0.0284, wR_2 = 0.0640
Final R indexes [all data]	R_1 = 0.0485, wR_2 = 0.0962	R_1 = 0.0398, wR_2 = 0.0689
Largest diff. peak/hole / e $Å^{-3}$	1.98/-0.88	1.78/-0.45
CCDB #	1916347	1916348

$R_1 = \Sigma(|F_0|-|F_c|)/\Sigma|F_0|$, $wR_2 = [\Sigma w(|F_0|-|F_c|)^2/\Sigma w(|F_0|)^2]^{1/2}$

Table S4: Crystallographic parameters for **10** and **12**

	10	**12**
Empirical formula	$C_{17}H_{18}BF_4N_7OPd$	$C_{15}H_{15}BClF_4N_6OPd$
Formula weight	529.59	523.99
Temperature/K	90	90
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/n$
a/Å	7.0857(4)	8.6741(4)
b/Å	14.7257(9)	15.7852(8)
c/Å	21.1621(13)	14.5177(7)
α/°	82.339(3)	90
β/°	82.935(3)	100.721(3)
γ/°	77.558(3)	90
Volume/Å^3	2126.8(2)	1953.10(16)
Z	4	4
ρ_{calc}g/cm^3	1.654	1.782
μ/mm^{-1}	0.931	1.143
F(000)	1056.0	1036.0
Crystal size/mm^3	0.3 × 0.08 × 0.04	0.6 × 0.04 × 0.02
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.08 to 55.898	5.092 to 60.12
Index ranges	$-9 \le h \le 9$, $-19 \le k \le 19$, $0 \le l \le 27$	$-12 \le h \le 11$, $-21 \le k \le 22$, $-20 \le l \le 20$
Reflections collected	14498	24257
Independent reflections	14498 [R_{int} = ?, R_{sigma} = 0.0298]	5692 [R_{int} = 0.0492, R_{sigma} = 0.0450]
Data/restraints/parameters	14498/0/566	5692/0/264
Goodness-of-fit on F^2	1.064	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0552, wR_2 = 0.1295	R_1 = 0.0390, wR_2 = 0.0901
Final R indexes [all data]	R_1 = 0.0636, wR_2 = 0.1331	R_1 = 0.0533, wR_2 = 0.0958
Largest diff. peak/hole / e Å^{-3}	1.03/-0.89	1.04/-0.55
CCDB#	1916349	1916350

$R_1 = \Sigma (|F_0|-|F_c|)/\Sigma|F_0|$, $wR_2 = [\Sigma w(|F_0|-|F_c|)^2/\Sigma w(|F_0|)^2]^{1/2}$

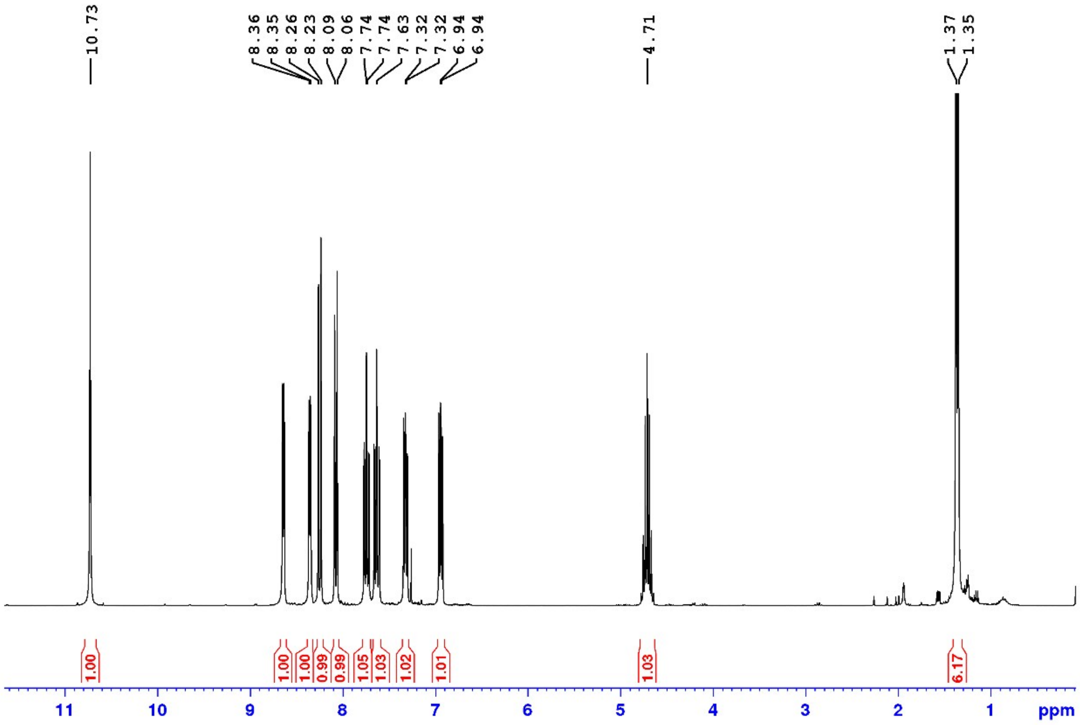

Figure S6: ^{1}H NMR spectrum of **7** in $CDCl_3$.

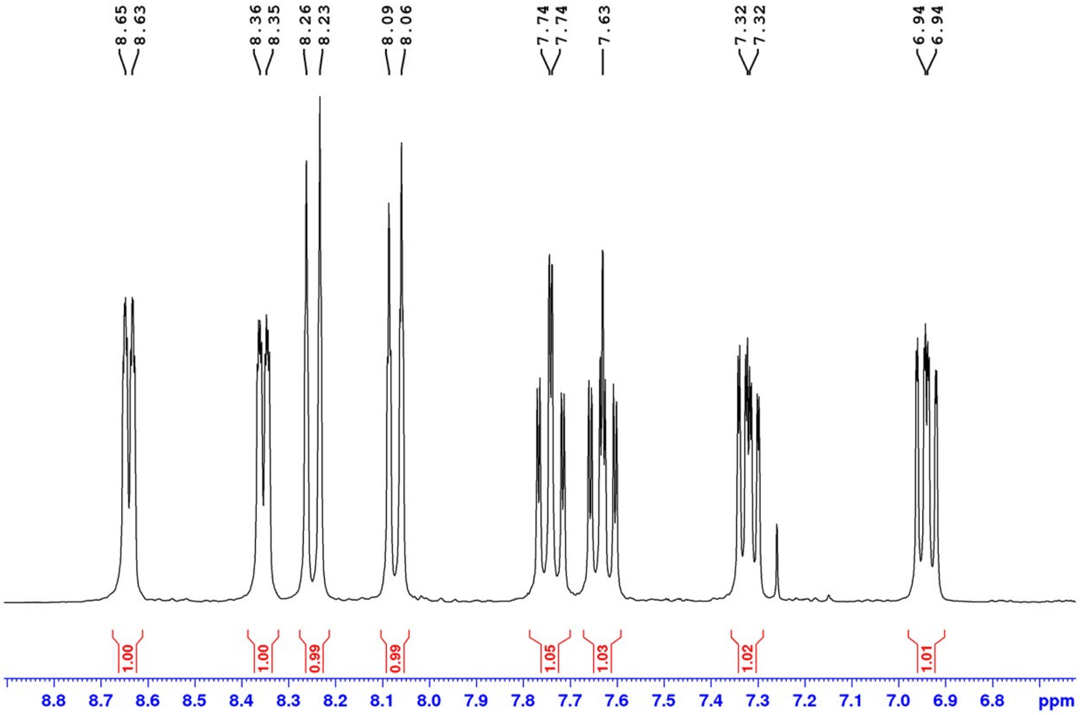

Figure S7: Expanded aromatic region of the ^{1}H NMR spectrum of **7** (6.7-8.9 ppm). The peak at 7.26 is from the NMR solvent.

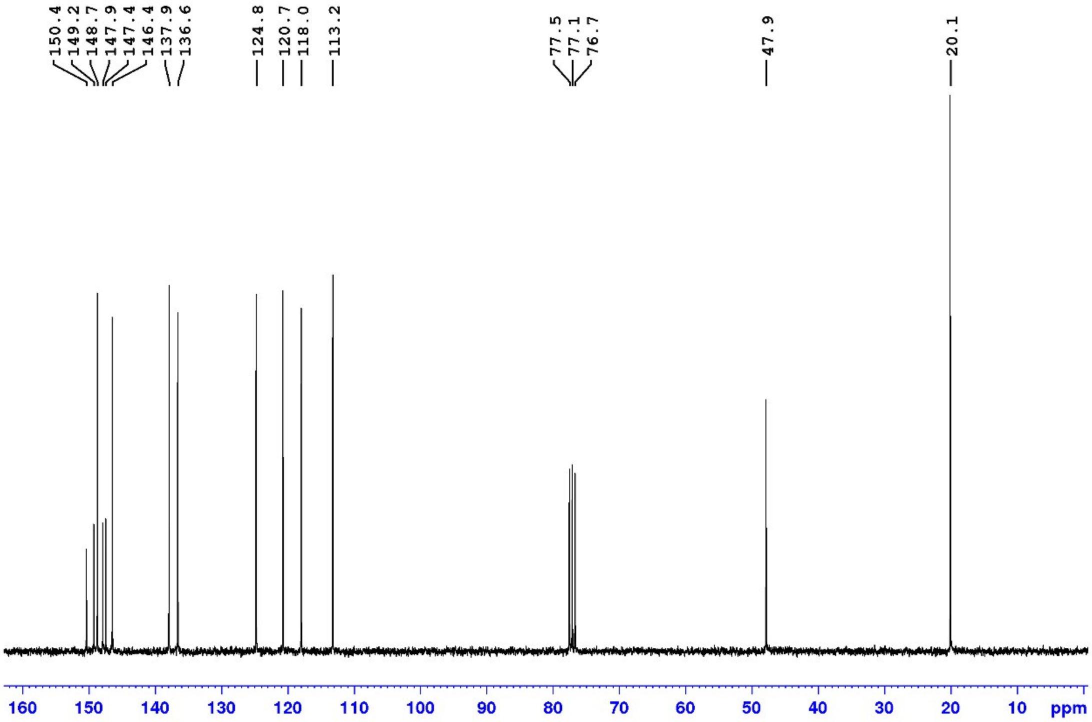

Figure S8: $^{13}C\{^1H\}$ NMR spectrum of **7** in $CDCl_3$. The triplet at 77 ppm is from the NMR solvent.

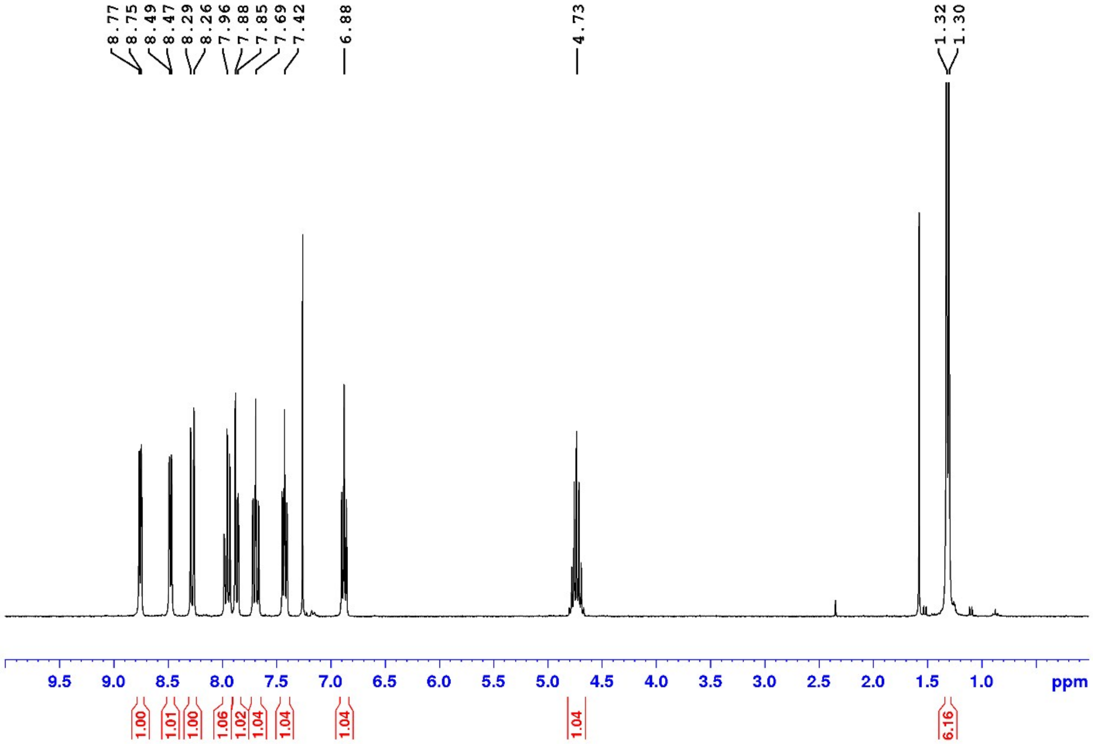

Figure S9: ^{1}H NMR spectrum of **9** in $CDCl_3$. The peak at 7.3 ppm is from the NMR solvent and the peak at 1.5 ppm is from residual water.

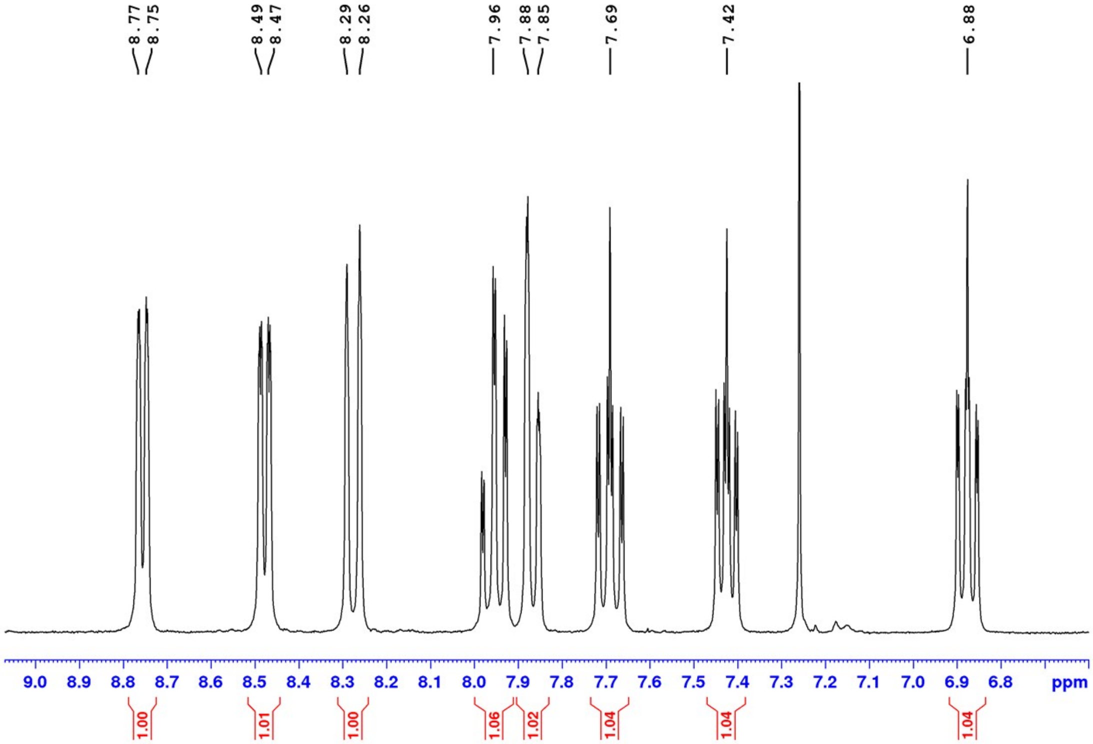

Figure S10: Expanded aromatic region of the ^{1}H NMR spectrum of **9** (6.7-9.1 ppm). The peak at 7.26 is from the NMR solvent.

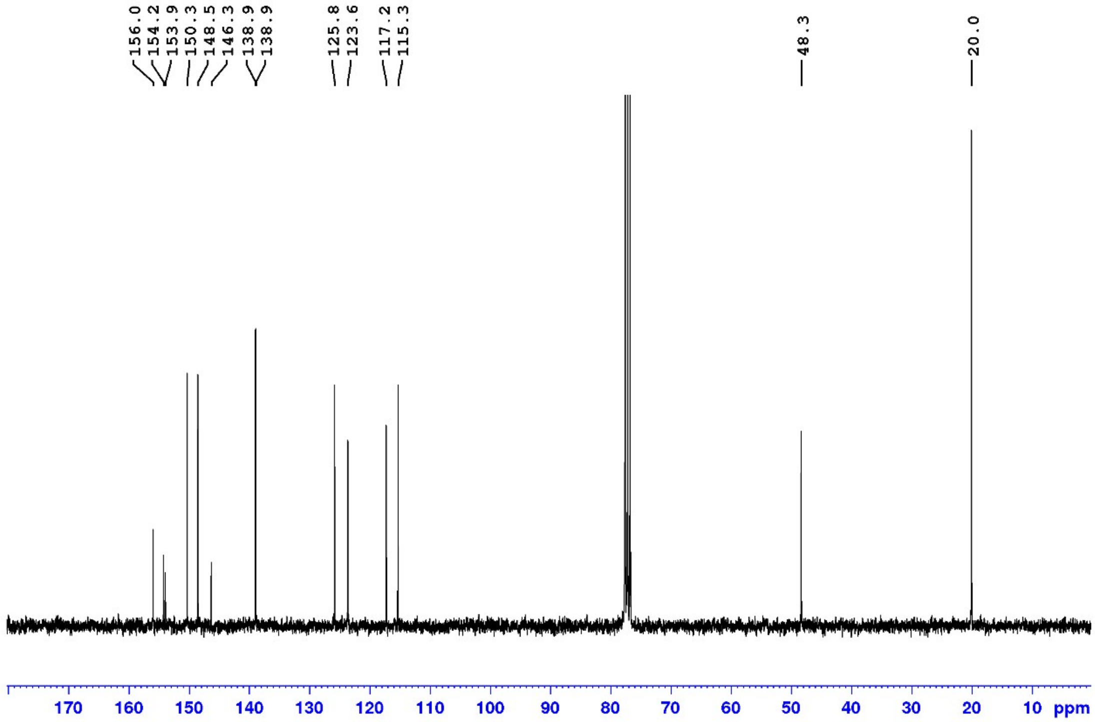

Figure S11: $^{13}C\{^1H\}$ NMR spectrum of **9** in $CDCl_3$. The triplet at 77 ppm is from the NMR solvent.

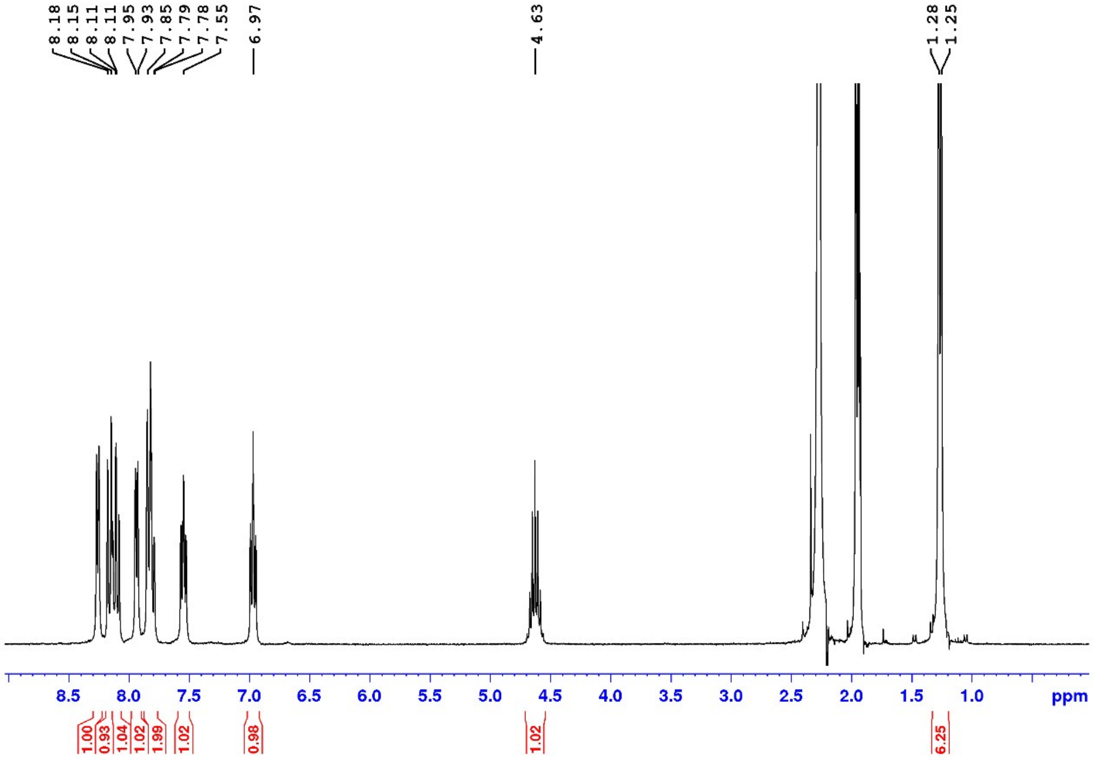

Figure S12: ^{1}H NMR spectrum of **10** in CD_3CN. The peak at 1.9 ppm is from the NMR solvent and the peak at 2.3 ppm is from residual water.

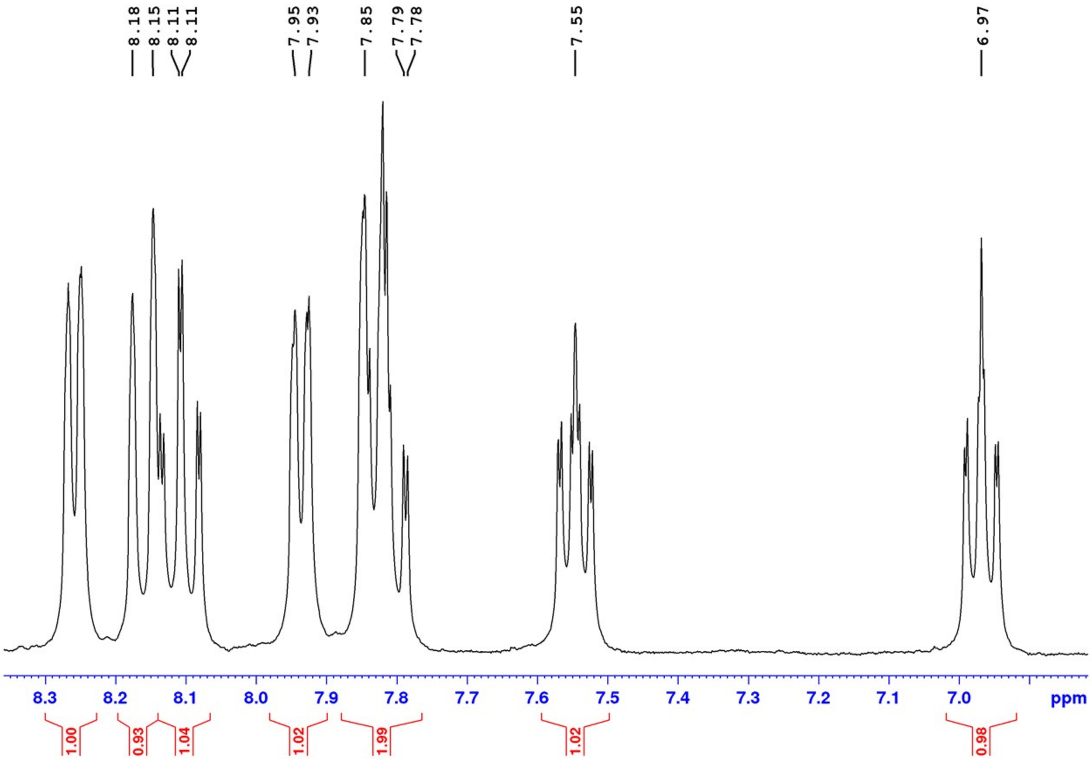

Figure S13: Expanded aromatic region of the ^{1}H NMR spectrum of **10** (6.9-8.3 ppm).

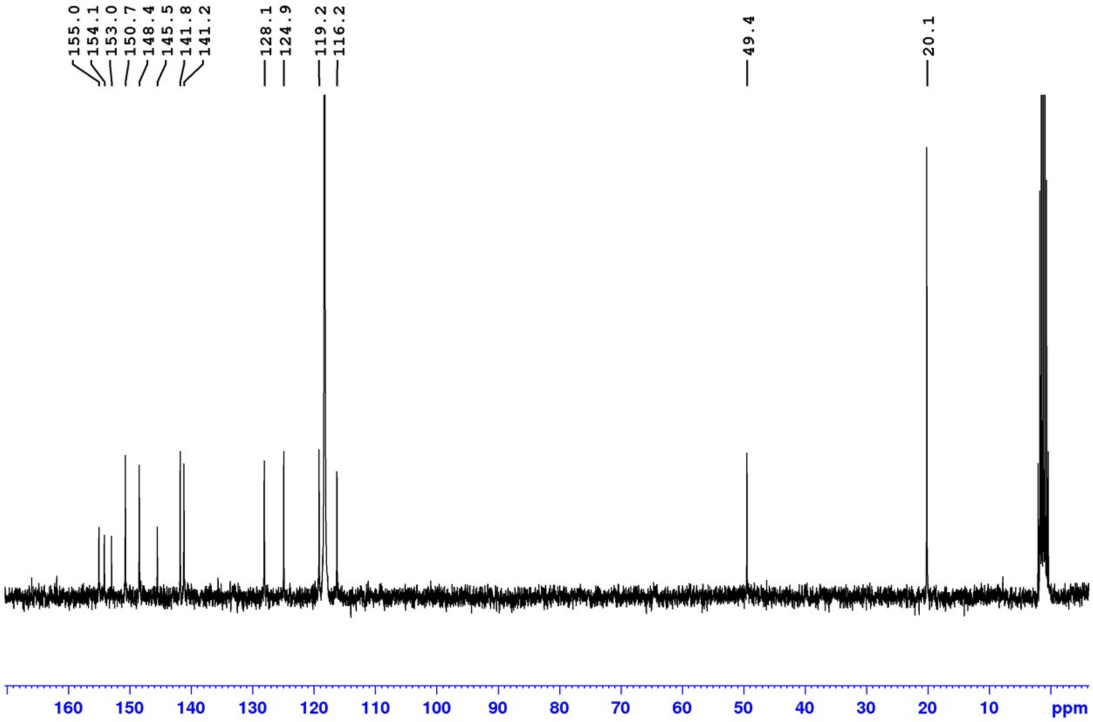

Figure S14: $^{13}C\{^1H\}$ NMR spectrum of **10** in CD_3CN. The peaks at 1 and 118 ppm are from the NMR solvent.