Electronic Supplementary Material (ESI) for Dalton Transactions.

Palladium(II) complexes with electron-poor, 4,5-disubstituted diimidazol-2-ylidene ligands: synthesis, characterization and catalytic activity.

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Supporting Information

Additional X-ray crystallographic details pp. S2-S4

NMR spectra of the compounds pp. S5-S20

Structure Determination

Preliminary examination and data collection were carried out on a NONIUS κ-CCD diffraction system equipped with an Oxford Cryosystems cooler at the window of a fine-focus sealed tube using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).

The reflections were merged and corrected from Lorentz, polarization and decay effects. An absorption correction was applied using SADABS.[1] The structures were solved by a combination of direct methods[2,3] with the aid of difference Fourier synthesis and were refined against all data using SHELXL-97.[4] Hydrogen atoms were assigned to calculated positions and then refined using the SHELXL-97 riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme. Details of the structure determinations are given in the Supporting Information. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography. All calculations were performed with the programs COLLECT,[5] DIRAX,[6] EVALCCD,[7] SIR92,[2] SIR97,[3]SHELXLE,[8]SADABS,[1] the SHELXL-97 package,[4] and ENCIFER.[9] Images of the solid state structures were generated with ORTEP-3.[10]

References

(1) Sheldrick, G. M. *SADABS*, Version 2.10; University of Goettingen, Goettingen, Germany, 2002.

(2) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.***1994**, 27, 435.

(3) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.***1999**, 32, 115-119.

(4) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.***2008**, A64, 112-122.

(5) Hooft, R. W. W.*Data Collection Software for Nonius-Kappa CCD*, Nonius B.V.: Delft, The Netherlands, 2001.

(6) Duisenberg, A. J. M. *J. Appl. Crystallogr.***1992**, 25, 92-96.

(7) Duisenberg, A. J. M.; Kroon-Batenburg, L. M. J.; Schreurs, A. M. M. *J. Appl. Crystallogr.***2003**, 36, 220-229.

(8) Huebschle, C. B.; Sheldrick, G. M.; Dittrich, B. *J. Appl.Crystallogr.***2011**, 44, 1281-1284.

(9) Allen, F. H.; Johnson, O.; Shields, G. P.; Smith, B. R.; Towler, M. *J. Appl. Crystallogr.***2004**, 37, 335-338.

(10) Farrugia, L. J. *J. Appl. Crystallogr.***2012**, *45*, 849-854.

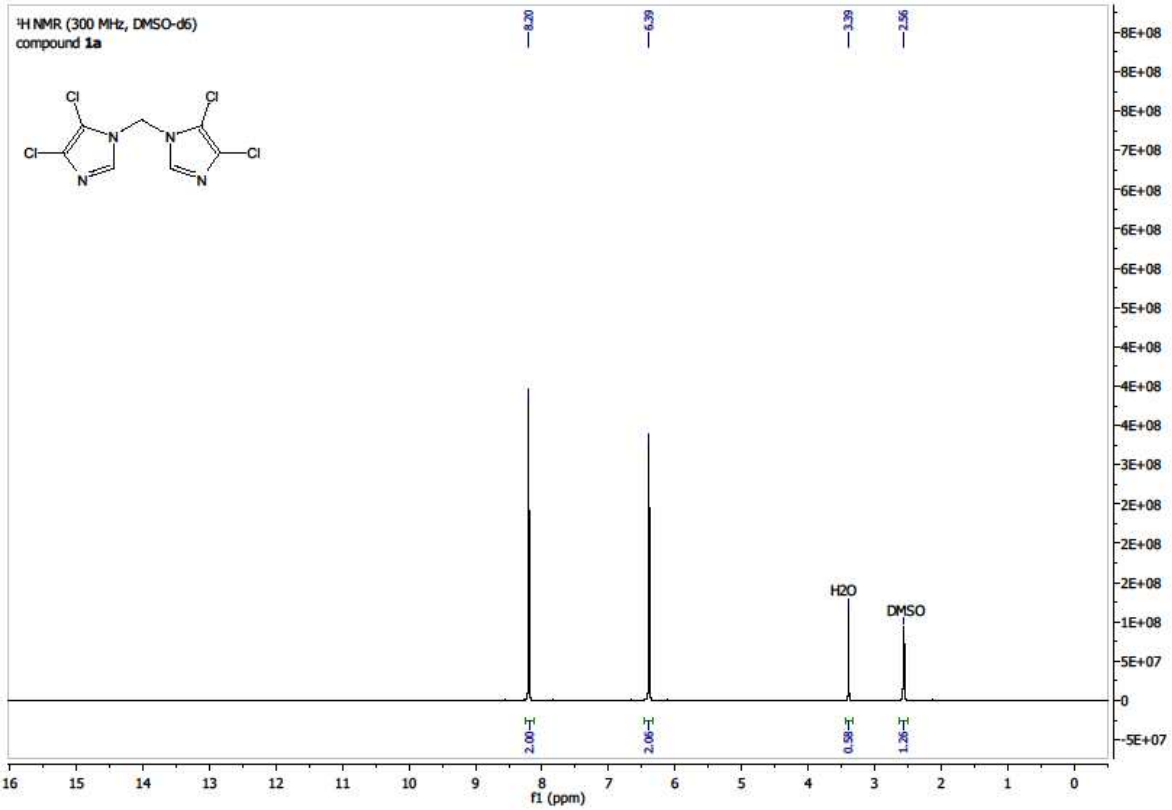
Table S1. Crystallographic Data for Compounds **3a** and **3b**.

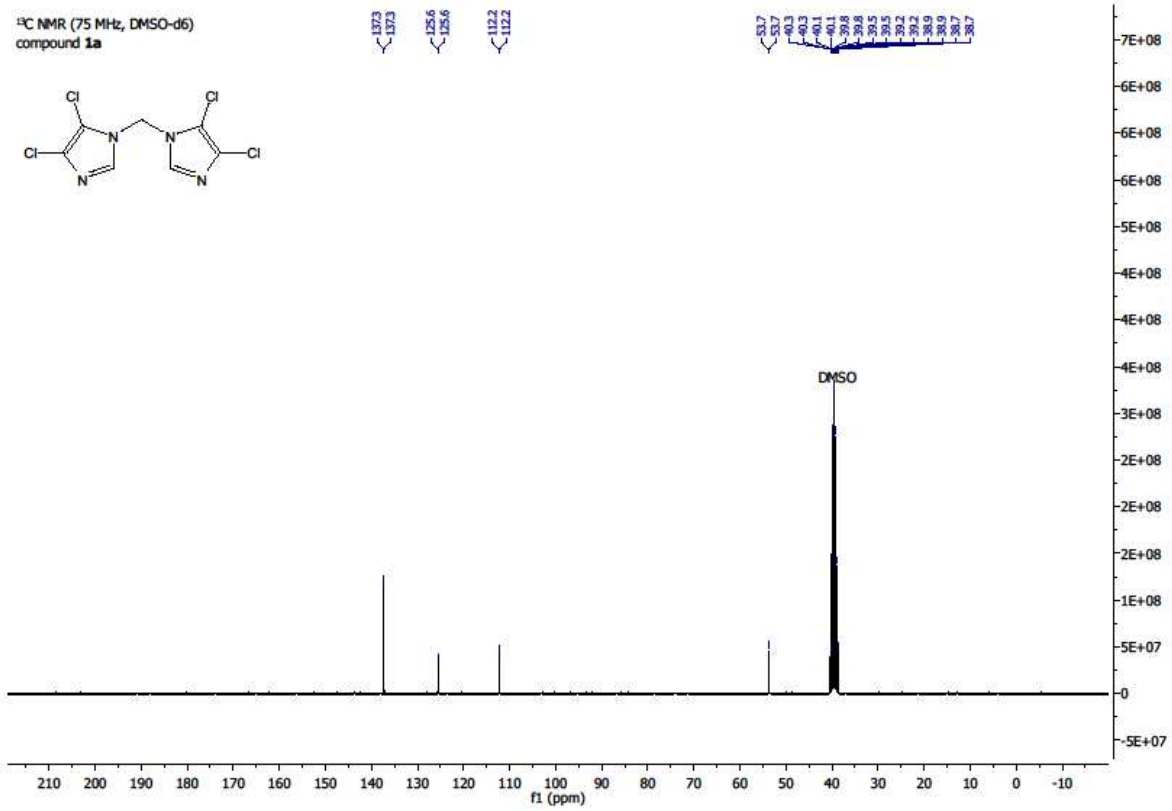
	3a		**3b**	
empirical formula	$C_{29}H_{27}Br_6Cl_{12}N_{13}Pd_3$		$C_{17}H_{26}Br_2Cl_4N_6O_2Pd$	
formula weight	1781.70		754.46	
temperature (K)	198(2)		198(2)	
wavelength (Å)	0.71073		0.71073	
crystal system	orthorhombic		triclinic	
space group	*P*bca		*P*-1	
unit cell dimensions (in Å and °)	a = 19.767(5)	α = 90	a = 8.0460(14)	α = 72.144(9)
	b = 15.478(10)	β = 90	b = 11.572(2)	β= 89.760(14)
	c = 34.001(9)	γ = 90	c = 15.7320(13)	γ = 74.103(15)
volume (in $Å^3$)	10403(8)		1336.0(4)	
Z	8		2	
density (g/cm^3, calculated)	2.275		1.875	
absorptioncoeff. (mm^{-1})	6.292		4.112	
F(000)	6752		740	
crystal size (mm)	0.48 x 0.18 x 0.17		0.73 x 0.53 x 0.38	
θ range for data collection (°)	2.06 to 23.25		2.64 to 26.40	
index ranges	-21 ≤*h*≤ 21		-9≤*h*≤ 10	
	-17≤*k*≤ 17		-14≤*k*≤ 13	
	-37≤*l*≤ 37		-19≤*l*≤ 18	
reflections collected	177002		13850	
independent reflections	7462[*R*(int) = 0.1558]		4963 [*R*(int) = 0.0242]	
absorption correction	semi-empirical from equivalents		semi-empirical from equivalents	
refinement method	full-matrix least-squares on F^2		full-matrix least-squares on F^2	
data/restraints/parameters	7462/0/575		4963/0/295	
goodness of fit on F^2	1.077		1.159	
final R indices [$I>2\sigma(I)$]	*R*1 = 0.0423, w*R*2 = 0.1044		*R*1 = 0.0341, w*R*2 = 0.0746	
R indices (all data)	*R*1 = 0.0849, w*R*2 = 0.1297		*R*1 = 0.0585, w*R*2 = 0.0809	
largest diff. peak and hole ($e \cdot A^{-3}$)	01134 and -1.119		0.590 and -0.521	

Table S2. Crystallographic Data for Compounds **3c** and **3e**.

	3c		**3e**	
empirical formula	$C_{16}H_{14}Br_2Cl_4N_4Pd$		$C_{15}H_{12}Br_2N_8Pd$	
formula weight	670.33		570.55	
temperature (K)	198(2)		198(2)	
wavelength (Å)	0.71073		0.71073	
crystal system	orthorhomic		tetragonal	
space group	*P*nma		*I*41cd	
unit cell dimensions (in Å and °)	a = 13.430(3)	α = 90	a = 23.913(3)	α = 90
	b = 18.758(2)	β = 90	b = 23.913(3)	β = 90
	c = 8.310(6)	γ = 90	c = 13.699(3)	γ = 90
volume (in $Å^3$)	2093.5(16)		7833.5(16)	
Z	4		16	
density (g/cm^3, calculated)	2.127		1.935	
absorptioncoeff. (mm^{-1})	5.225		5.044	
F(000)	1288		4384	
crystal size (mm)	0.53 x 0.36 x 0.24		0.25x 0.22 x 0.22	
θ range for data collection (°)	2.17 to 23.25		3.21 to 25.20	
index ranges	$-16 \leq h \leq 16$		$-28 \leq h \leq 28$	
	$-23 \leq k \leq 23$		$-28 \leq k \leq 28$	
	$-10 \leq l \leq 10$		$-16 \leq l \leq 16$	
reflections collected	43521		72663	
independent reflections	2215 [*R*(int) = 0.0669]		3514 [*R*(int) = 0.0793]	
absorption correction	semi-empirical from equivalents		semi-empirical from equivalents	
refinement method	full-matrix least-squares on F^2		full-matrix least-squares on F^2	
data/restraints/parameters	2215/0/125		3514/1/237	
goodness of fit on F^2	1.084		1.056	
final R indices [$I>2\sigma(I)$]	*R*1 = 0.0299, w*R*2 = 0.0608		*R*1 = 0.0331, w*R*2 = 0.0736	
R indices (all data)	*R*1 = 0.0472, w*R*2 = 0.0659		*R*1 = 0.0394, w*R*2 = 0.0764	
largest diff. peak and hole ($e \cdot A^{-3}$)	0.621 and -0.643		0.625 and -0.355	

1a

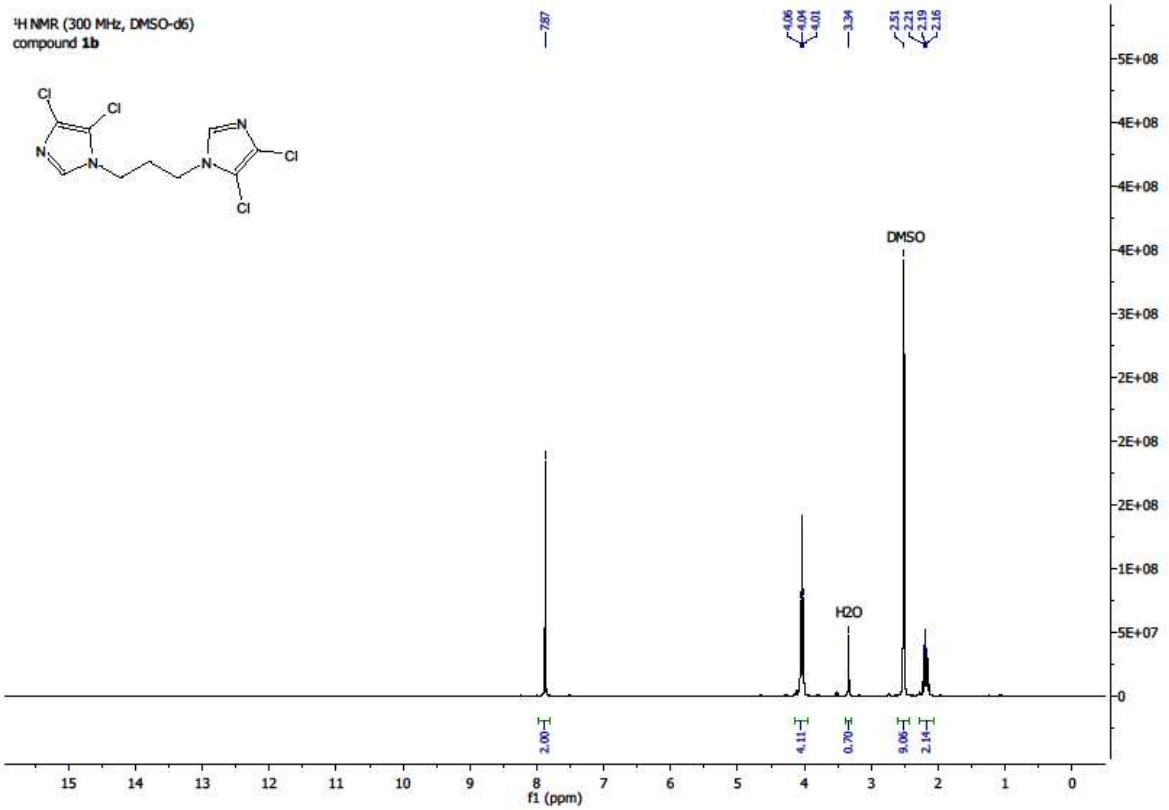


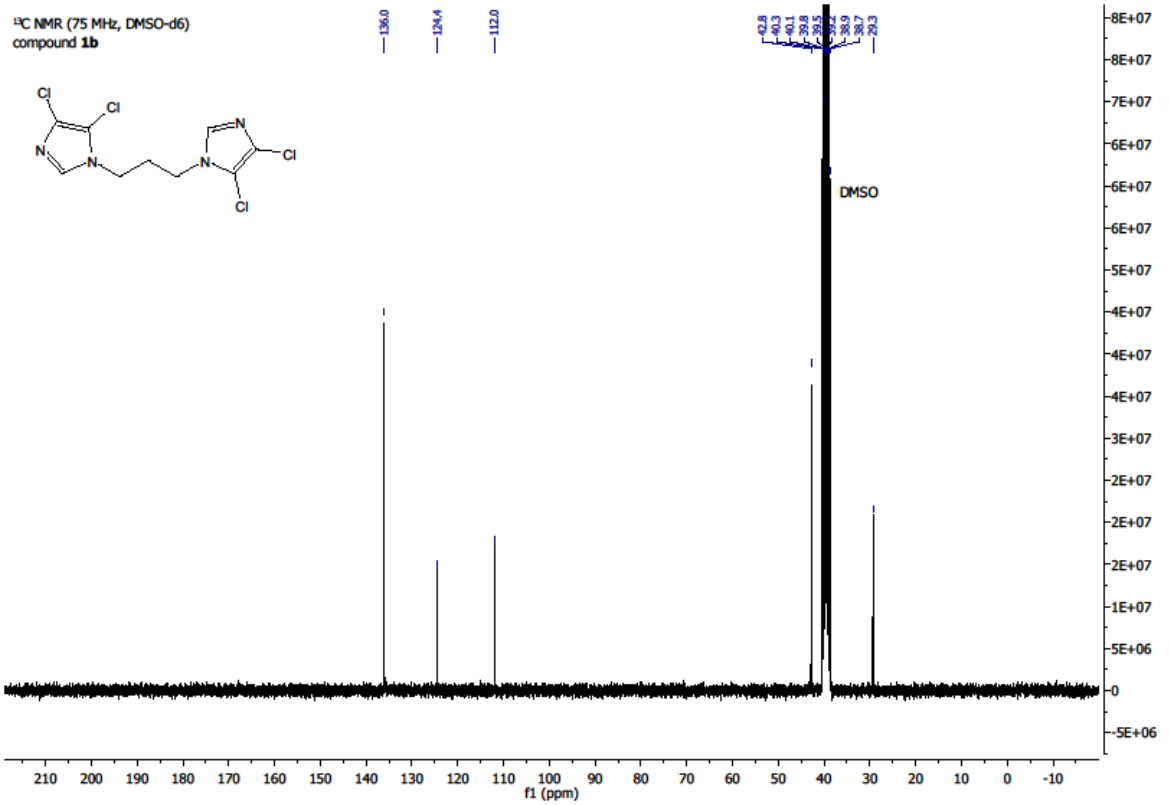


^{1}H-NMR (300 MHz, DMSO-d6) δ 8.20 (s, 2H), 6.39 (s, 2H).

^{13}C NMR (75 MHz, DMSO) δ 137.3 (s), 125.57 (s), 112.2 (s), 53.8 (s).

1b

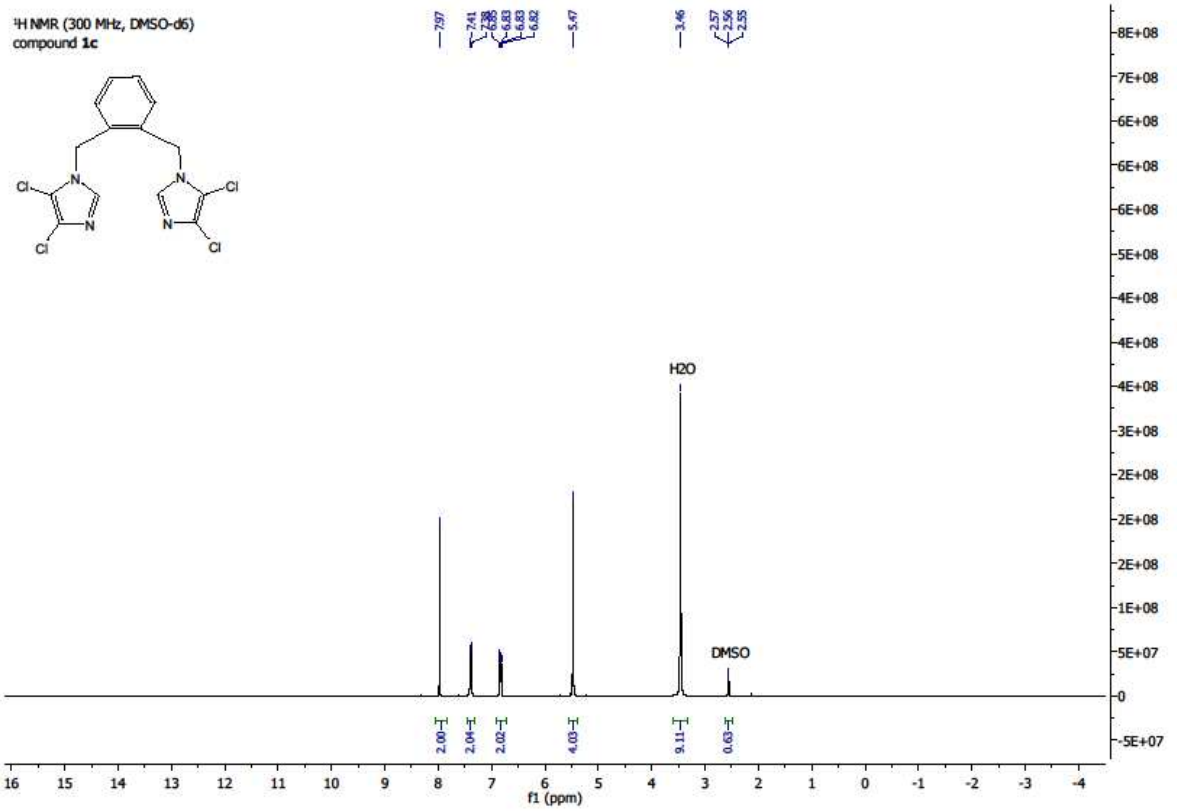


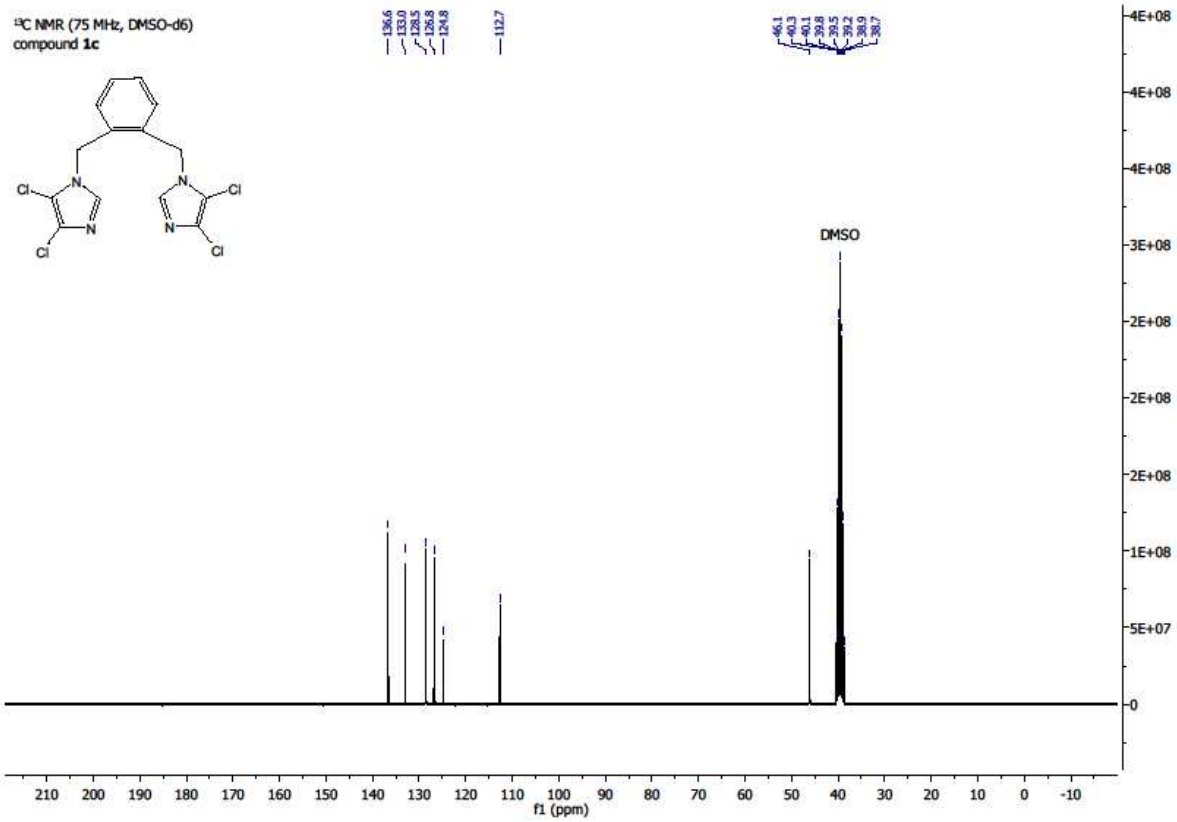


^{1}H-NMR (300 MHz, DMSO) δ 7.87 (s, 2H), 4.04 (t, *J* = 7.2 Hz, 4H), 2.29 (t, *J* = 7.2 Hz, 2H).

^{13}C-NMR (75 MHz, DMSO) δ 136.0 (s), 124.4 (s), 112.0 (s), 42.8 (s), 29.3 (s).

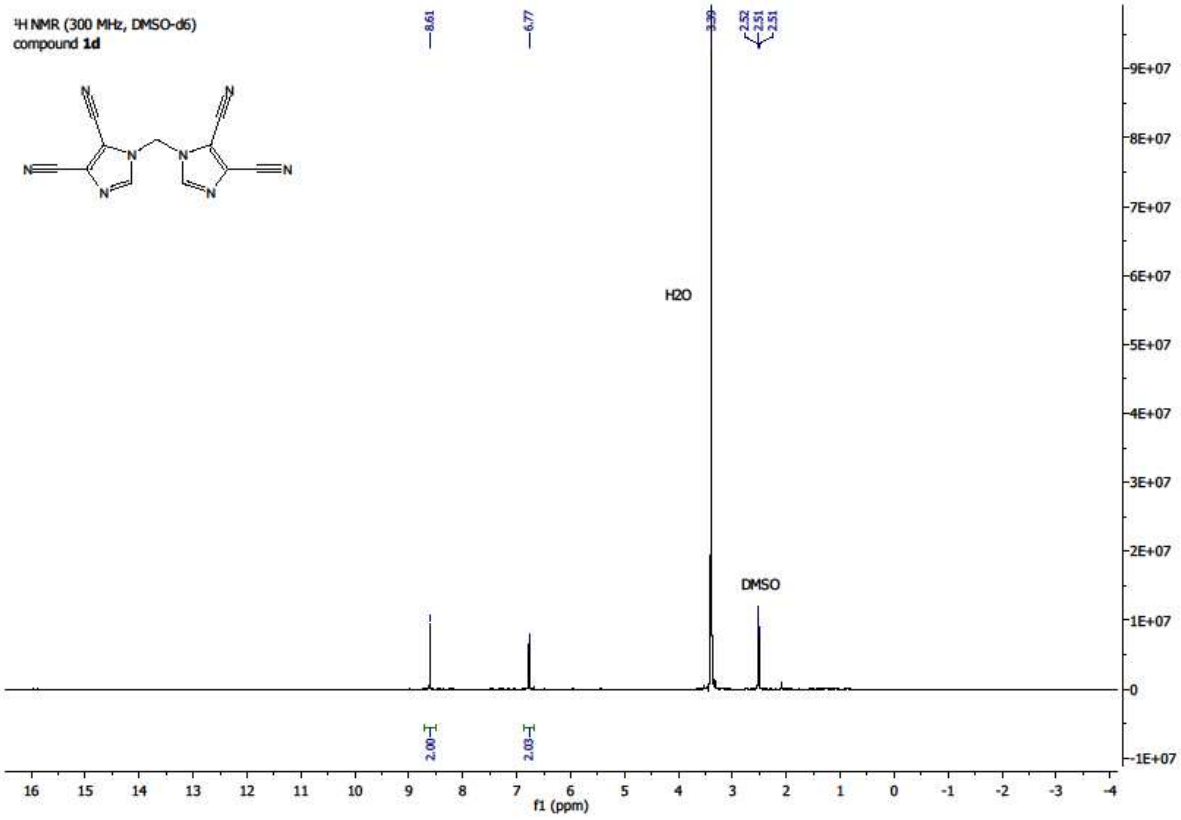
1c

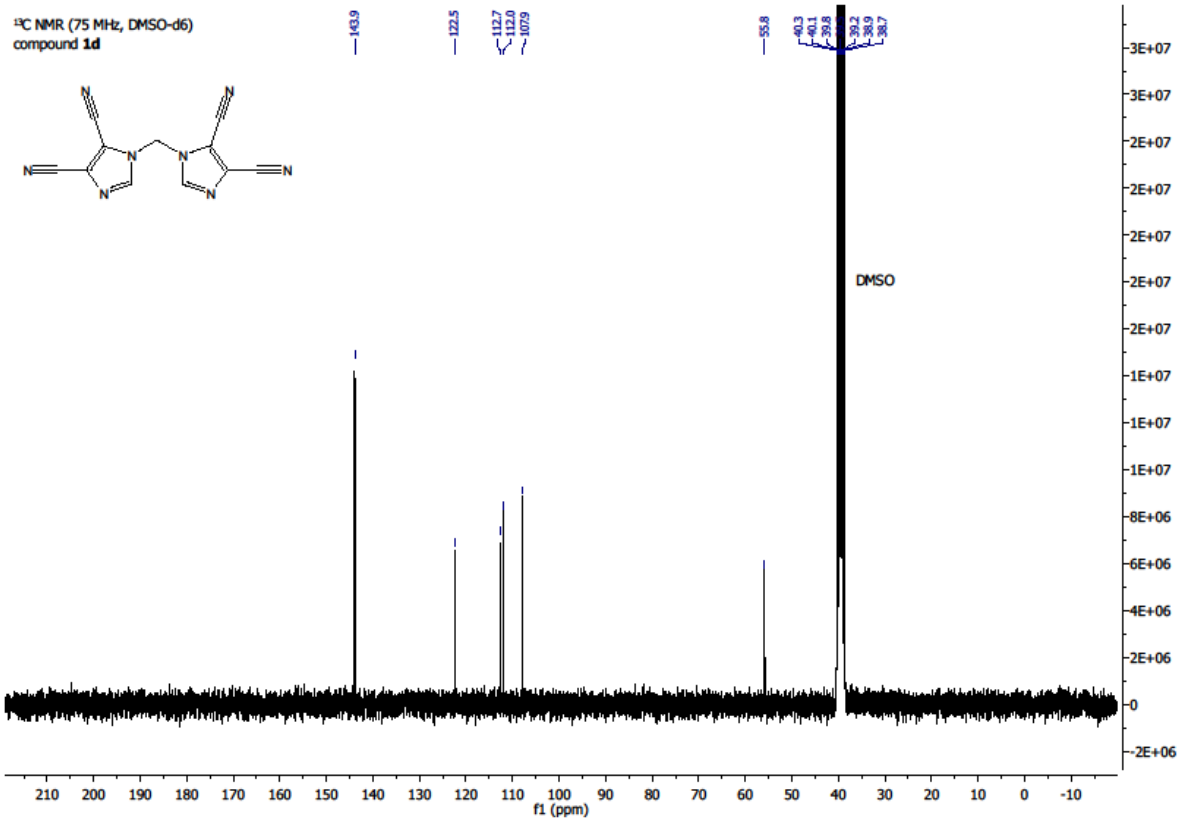




^{1}H-NMR (300 MHz, DMF) δ 7.97 (s, 2H), 7.39 (dd, *J* = 5.7, 3.4 Hz, 2H), 6.83 (dd, *J* = 5.6, 3.4 Hz, 2H), 5.47 (s, 4H).
^{13}C-NMR (75 MHz, DMSO) δ 136.6 (s), 133.0(s), 128.52 (s), 126.8 (s), 124.8 (s), 112.7 (s), 46.1 (s).

1d

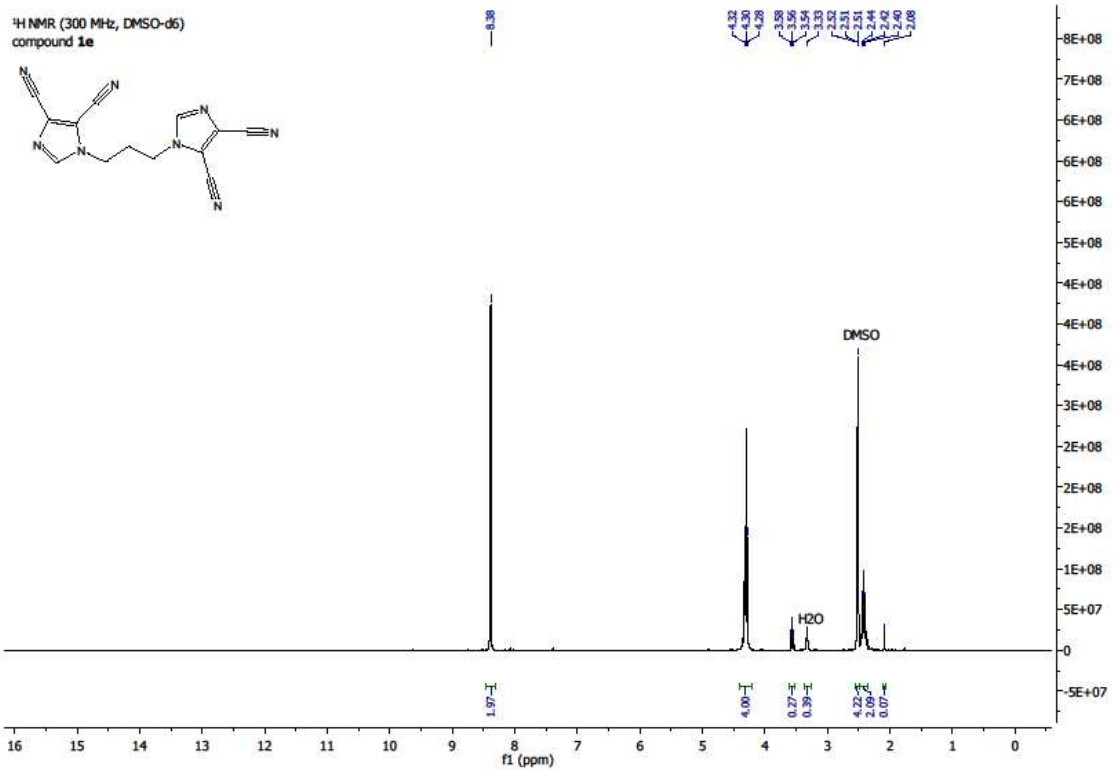


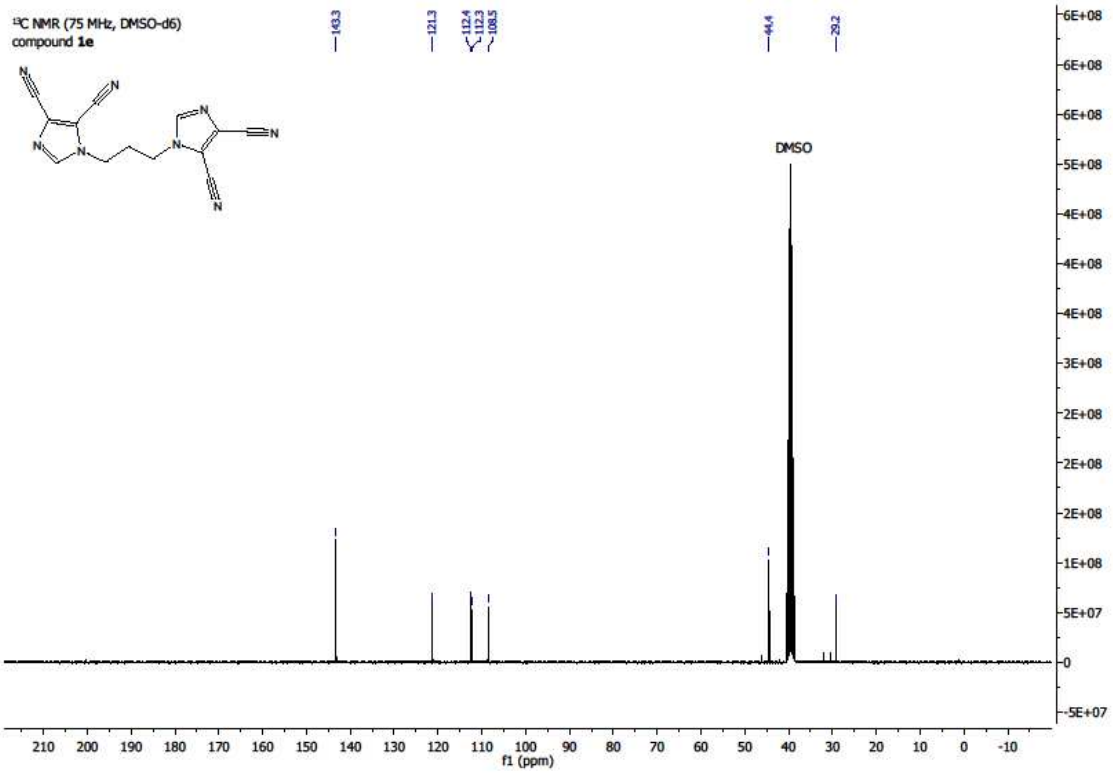


[1]H-NMR (300 MHz, DMSO) δ 8.61 (s, 2H), 6.77 (s, 2H).

[13]C-NMR (75 MHz, DMSO) δ 143.9 (s), 122.5 (s), 112.7 (s), 112.0 (s), 107.9 (s), 55.8 (s).

1e

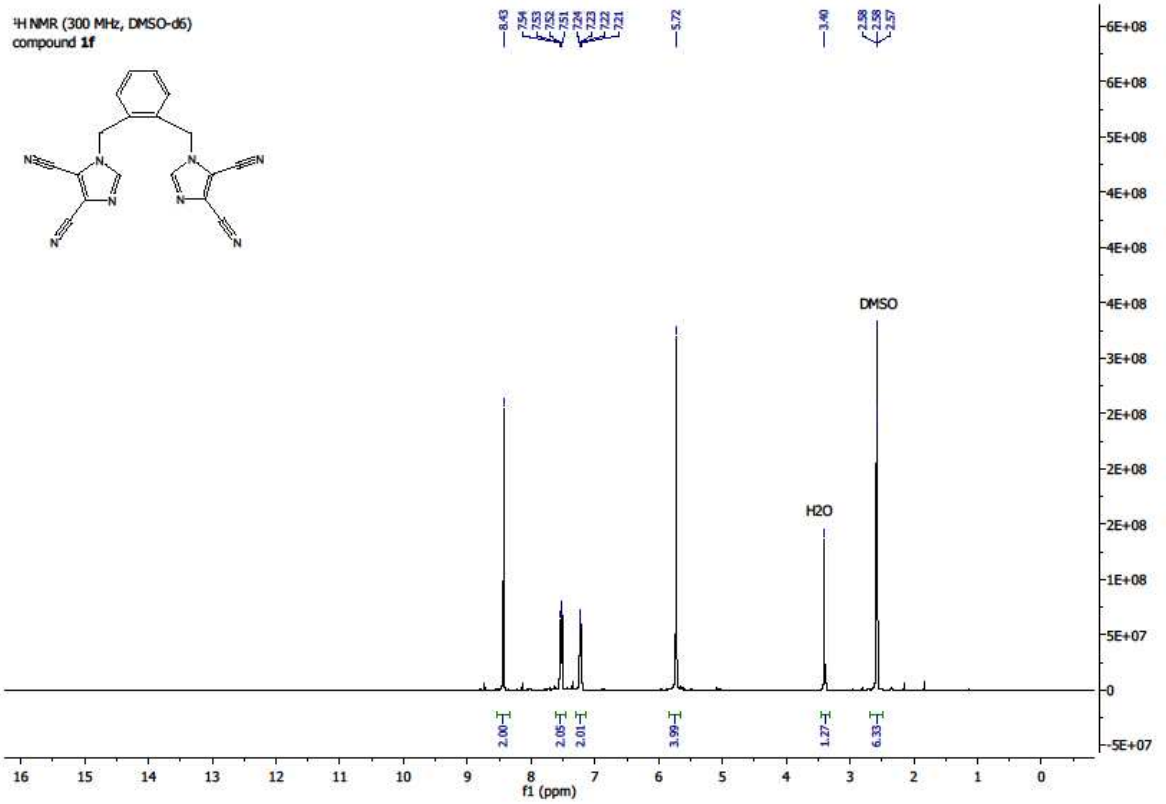


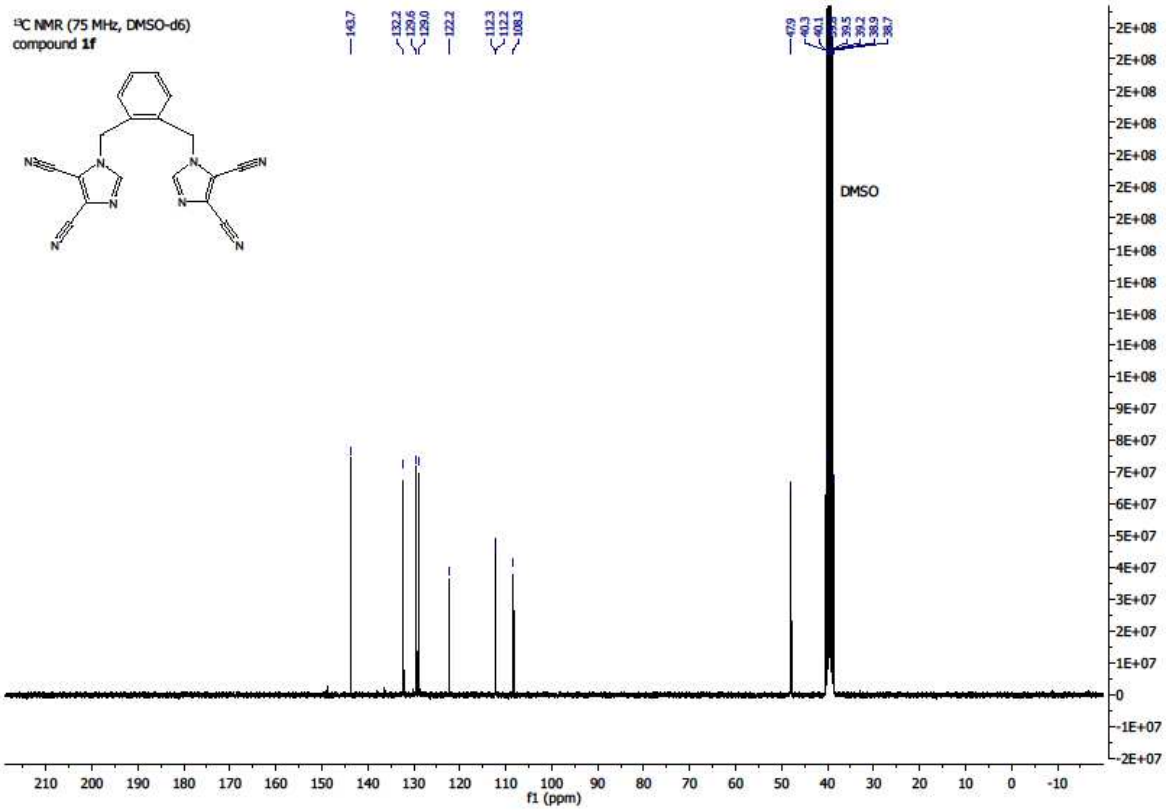


^{1}H-NMR (300 MHz, DMSO) δ 8.38 (s, 2H), 4.30 (t, *J* = 7.1 Hz, 4H), 2.48 – 2.33 (m, 2H).

^{13}C-NMR (75 MHz, DMSO) δ 143.3 (s), 121.3 (s), 112.4(s), 112,3(s), 108.5 (s), 44.4 (s), 29.2 (s).

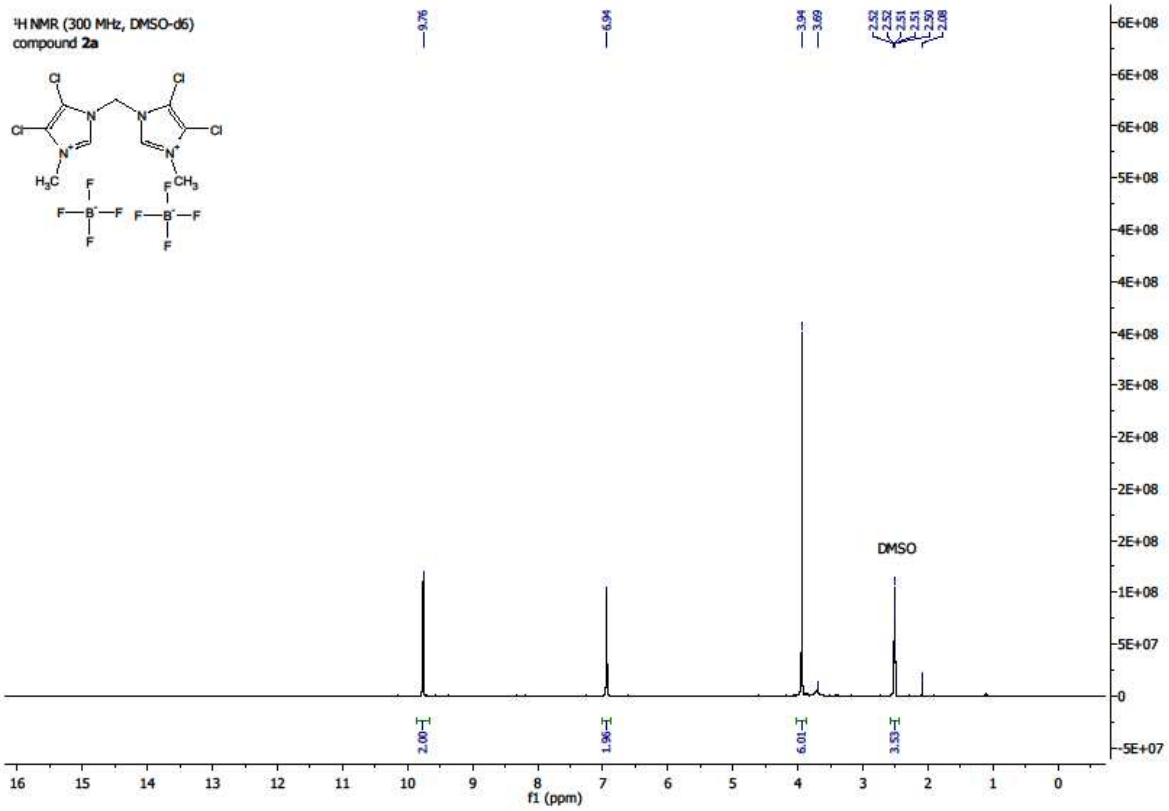
1f

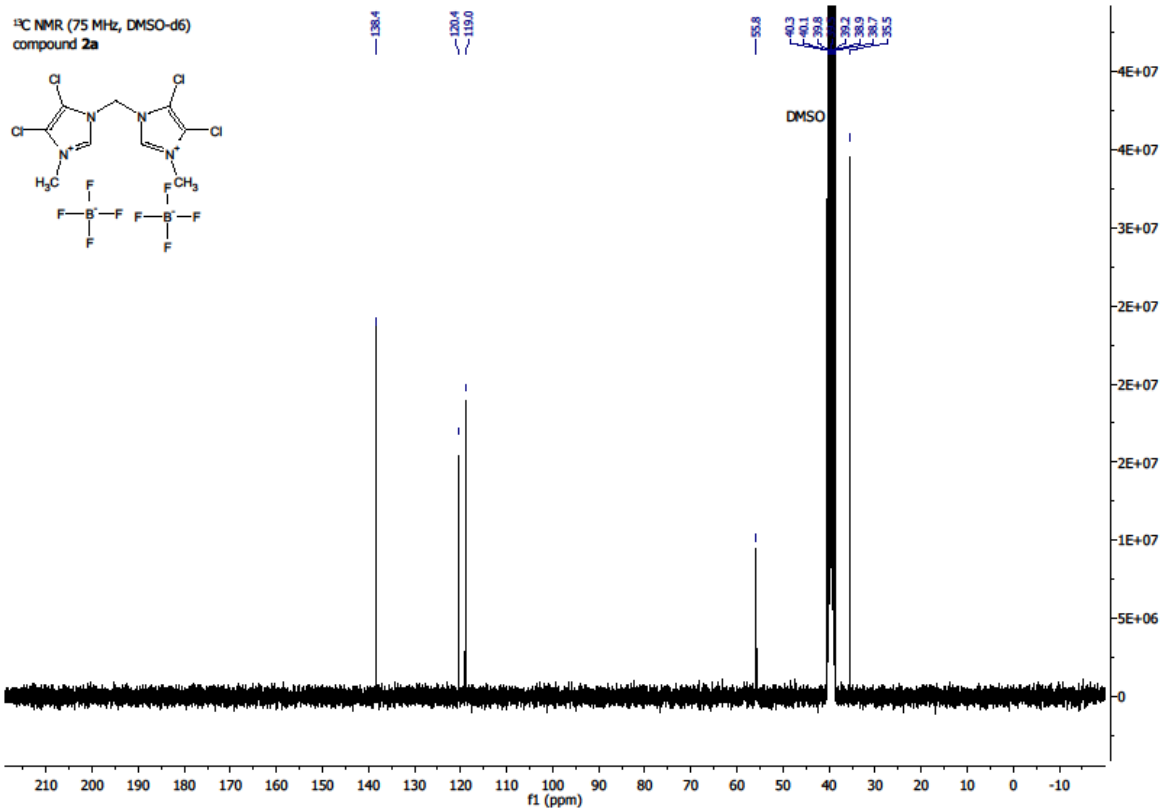




^{1}H-NMR (300 MHz, DMSO) δ 8.43 (s, 2H), 7.53 (dd, *J* = 5.7, 3.3 Hz, 2H), 7.22 (dd, *J* = 5.6, 3.4 Hz, 2H), 5.72 (s, 4H).
^{13}C-NMR (75 MHz, DMSO) δ 143.7 (s), 132.23 (s), 129.6 (s), 129.0 (s), 122.20 (s), 112.3 (s),112,2 (s), 108.3 (s), 47.9 (s).

2a


¹H NMR (300 MHz, DMSO-d6)
compound 2a
9.76
6.94
3.94
3.69
2.52
2.51
2.50
2.08
DMSO
2.00
1.96
6.01
3.53
f1 (ppm)


¹³C NMR (75 MHz, DMSO-d6)
compound 2a
138.4
120.4
119.0
55.8
40.3
40.1
39.8
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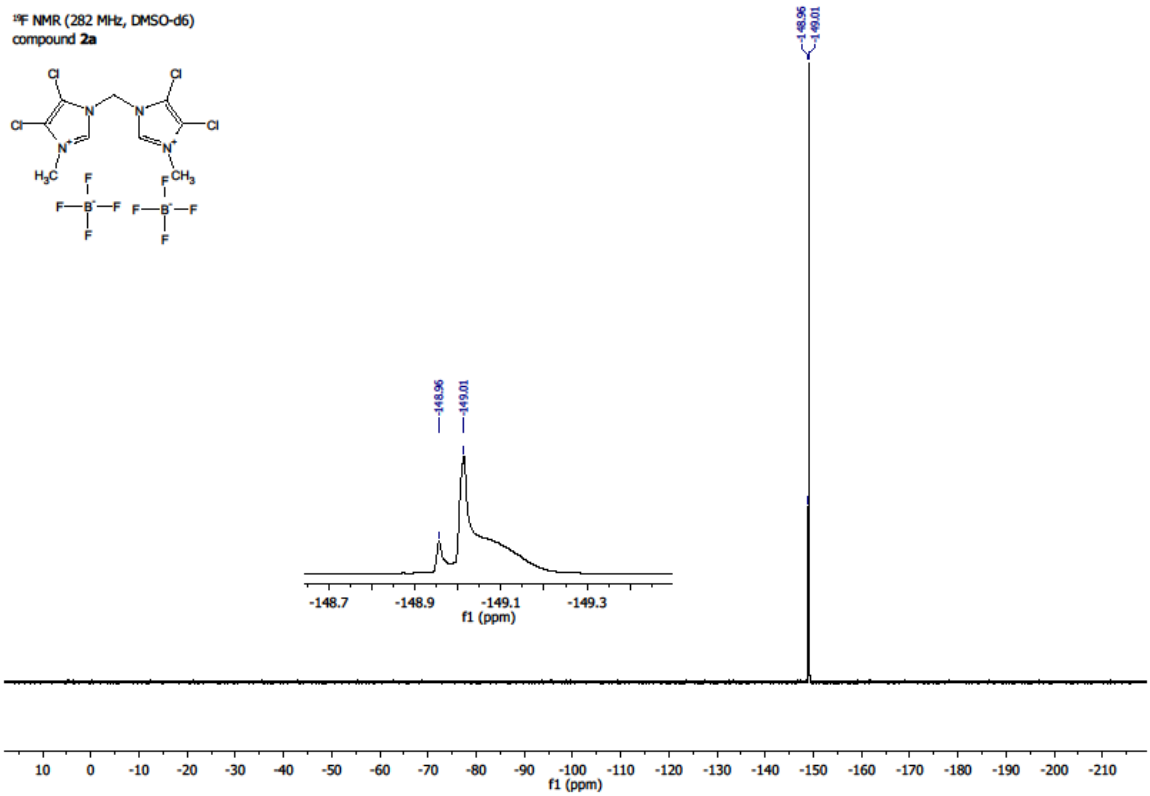
38.9
38.7
35.5
DMSO
f1 (ppm)

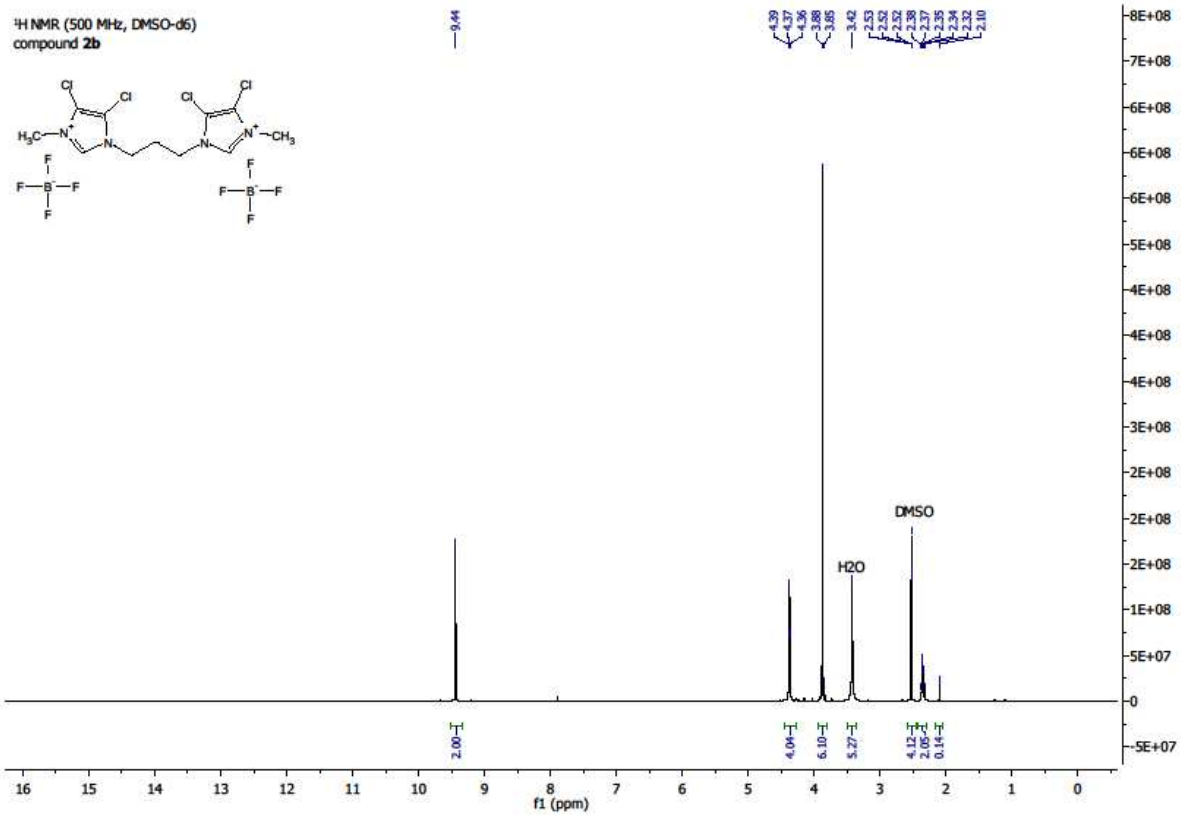


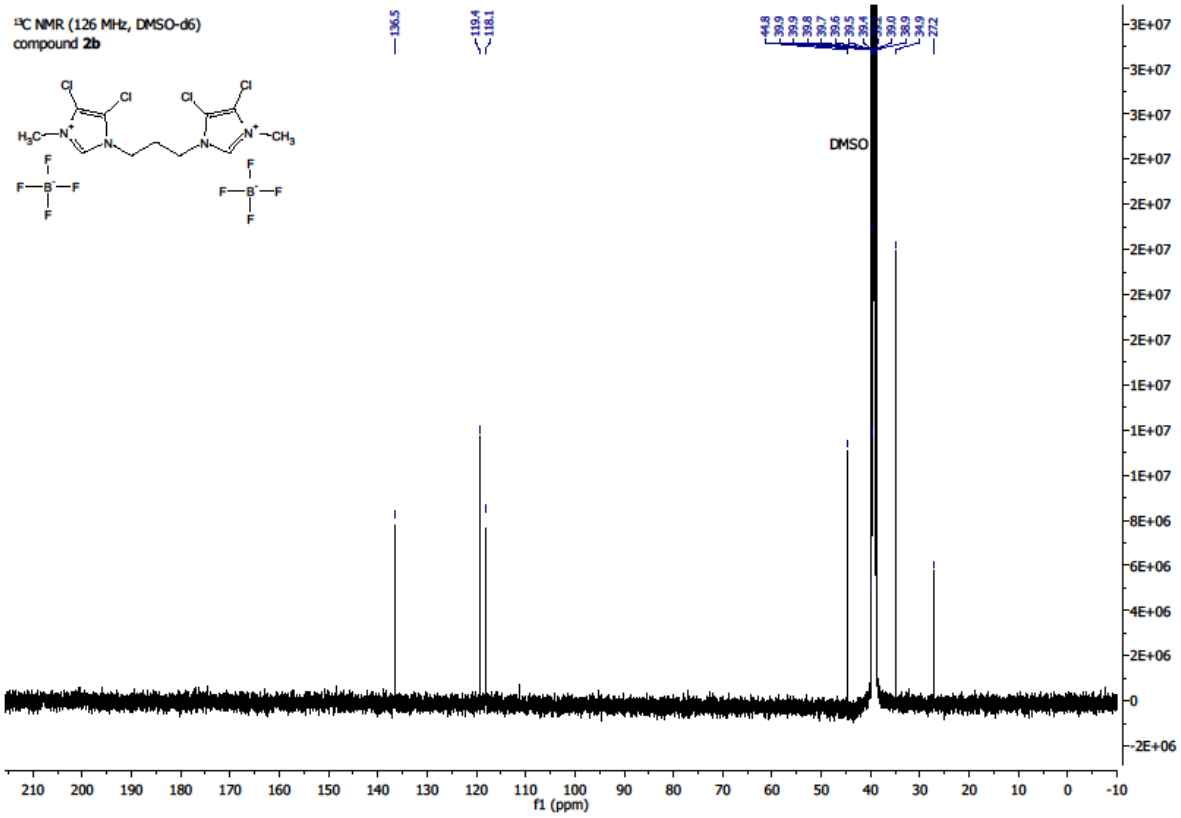
^{1}H-NMR (300 MHz, DMSO) δ 9.76 (s, 2H), 6.94 (s, 2H), 3.94 (s, 6H).

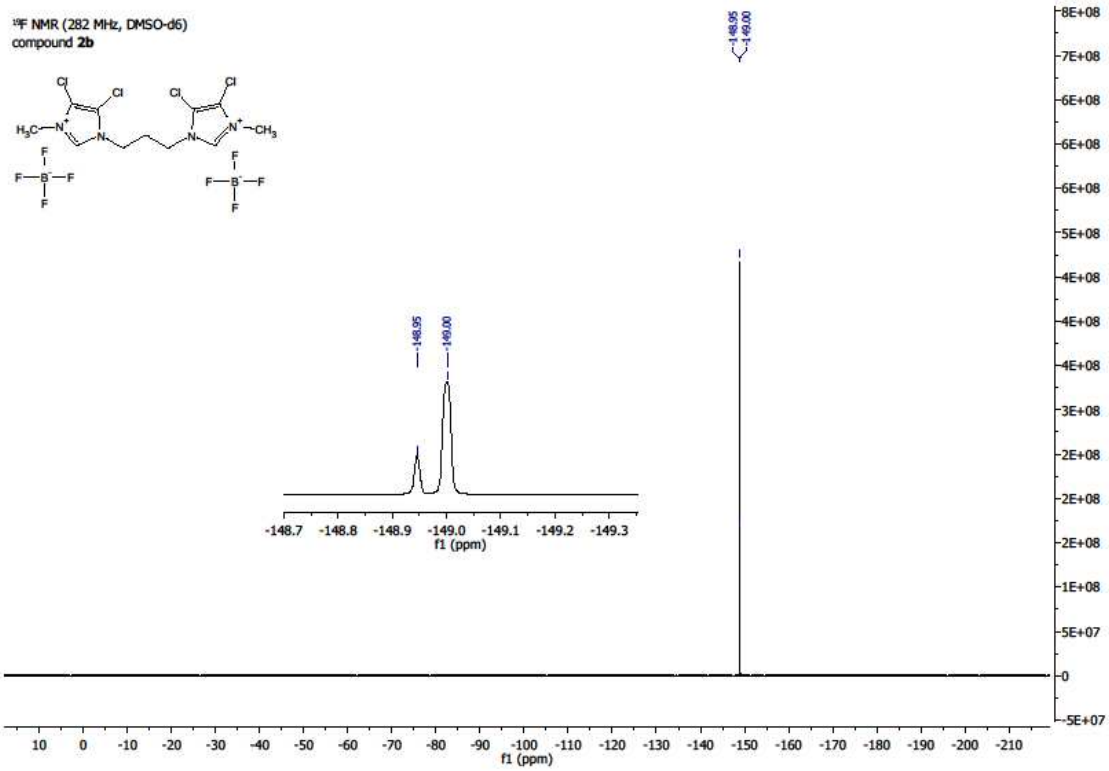
^{13}C- NMR (75 MHz, DMSO) δ 138.5 (s), 120.4 (s), 119.0 (s), 55.8 (s), 35.5 (s).

^{19}F-NMR (282 MHz, DMSO) δ -148.96(s), -149.01(s).

2b


¹H NMR (500 MHz, DMSO-d6)
compound 2b
DMSO
H2O
f1 (ppm)


¹³C NMR (126 MHz, DMSO-d6)
compound 2b
DMSO
f1 (ppm)

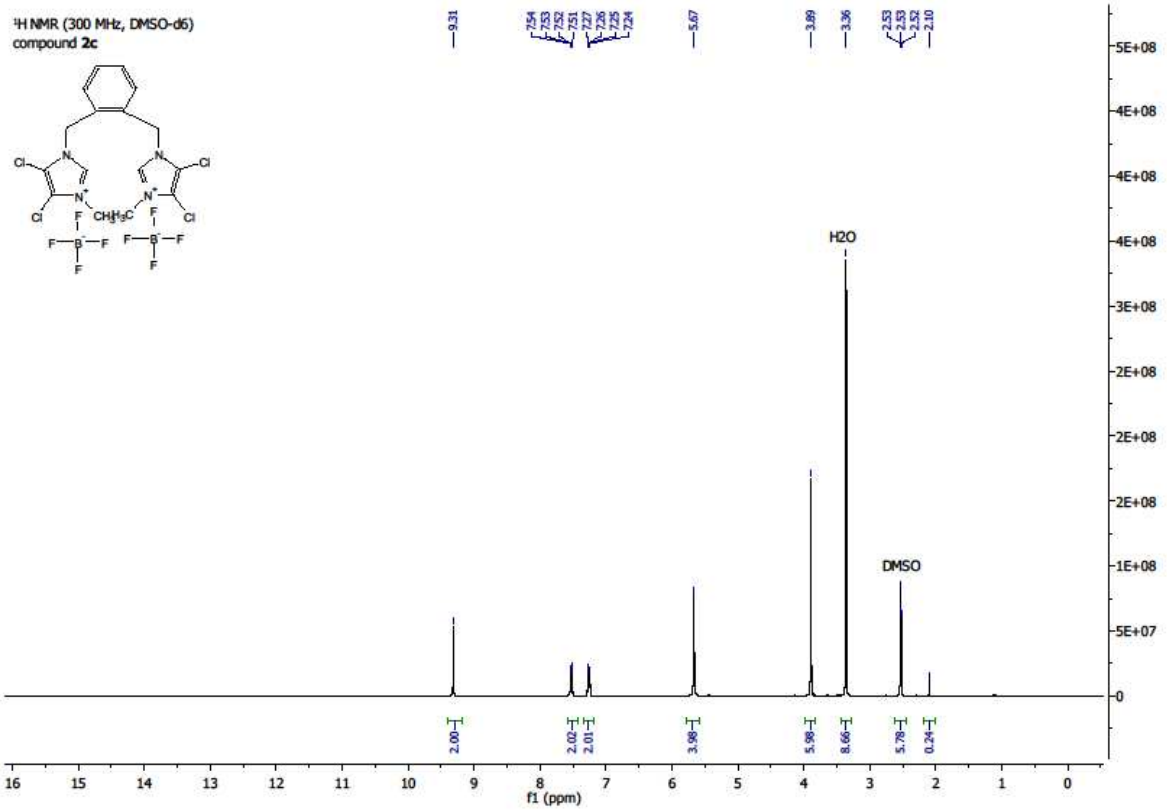


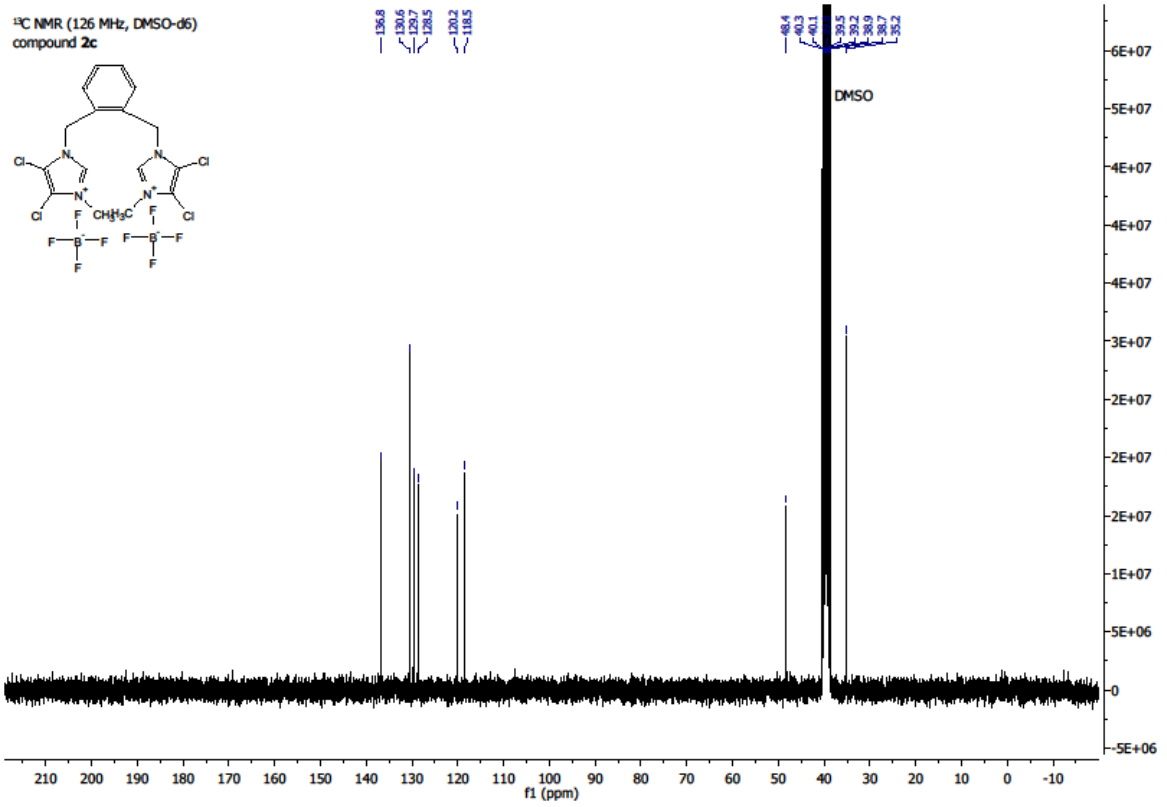
^{1}H-NMR (500 MHz, DMSO) δ 9.44 (s, 2H), 4.37 (t, *J* = 7.2 Hz, 4H), 3.86 (s, 6H), 2.42 – 2.29 (m, 2H).

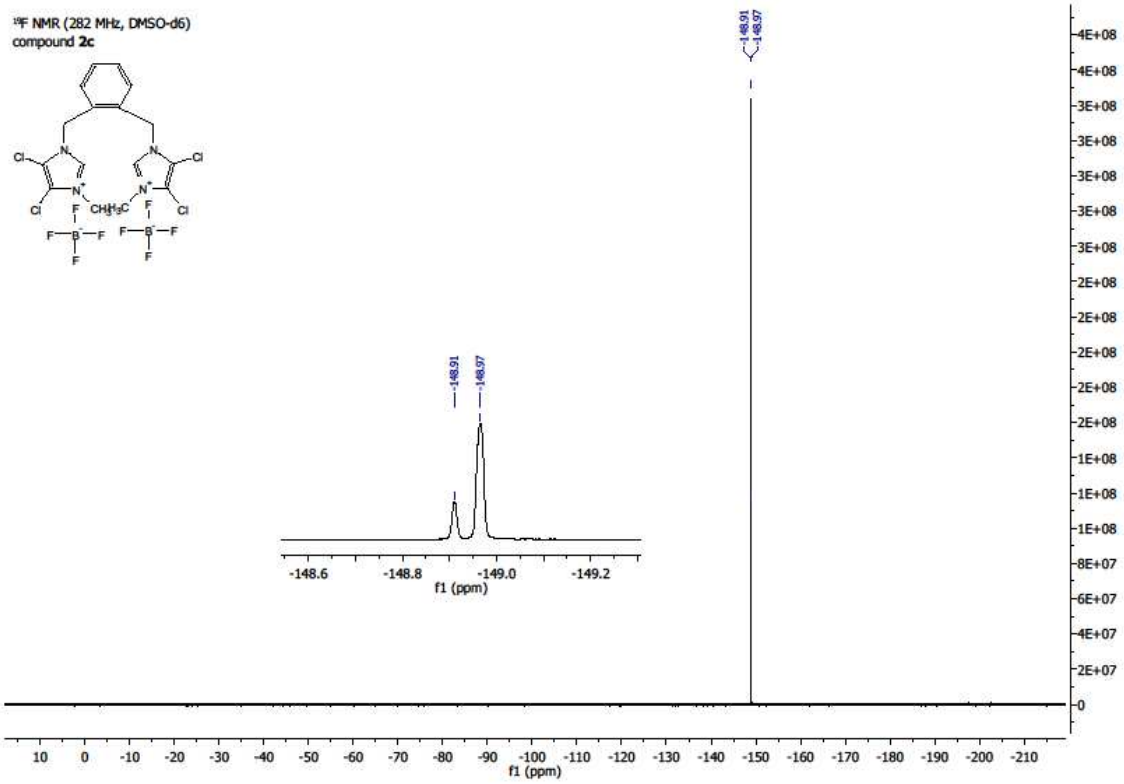
^{13}C-NMR (126 MHz, DMSO) δ 136.5 (s), 119.4 (s), 118.1 (s), 44.8 (s), 34.9 (s), 27.2 (s).

^{19}F-NMR (282 MHz, DMSO) δ -148.95(s), -149.00(s).

2c


¹H NMR (300 MHz, DMSO-d6)
compound 2c
9.31
7.54
7.53
7.52
7.51
7.27
7.26
7.25
7.24
5.67
3.89
3.36
2.53
2.53
2.52
2.10
H2O
DMSO
2.00
2.02
2.01
3.98
5.98
8.66
5.78
0.24
f1 (ppm)


¹³C NMR (126 MHz, DMSO-d6)
compound 2c
136.8
130.6
129.7
128.5
120.2
118.5
48.4
40.3
40.1
39.5
39.2
38.9
38.7
35.2
DMSO
f1 (ppm)

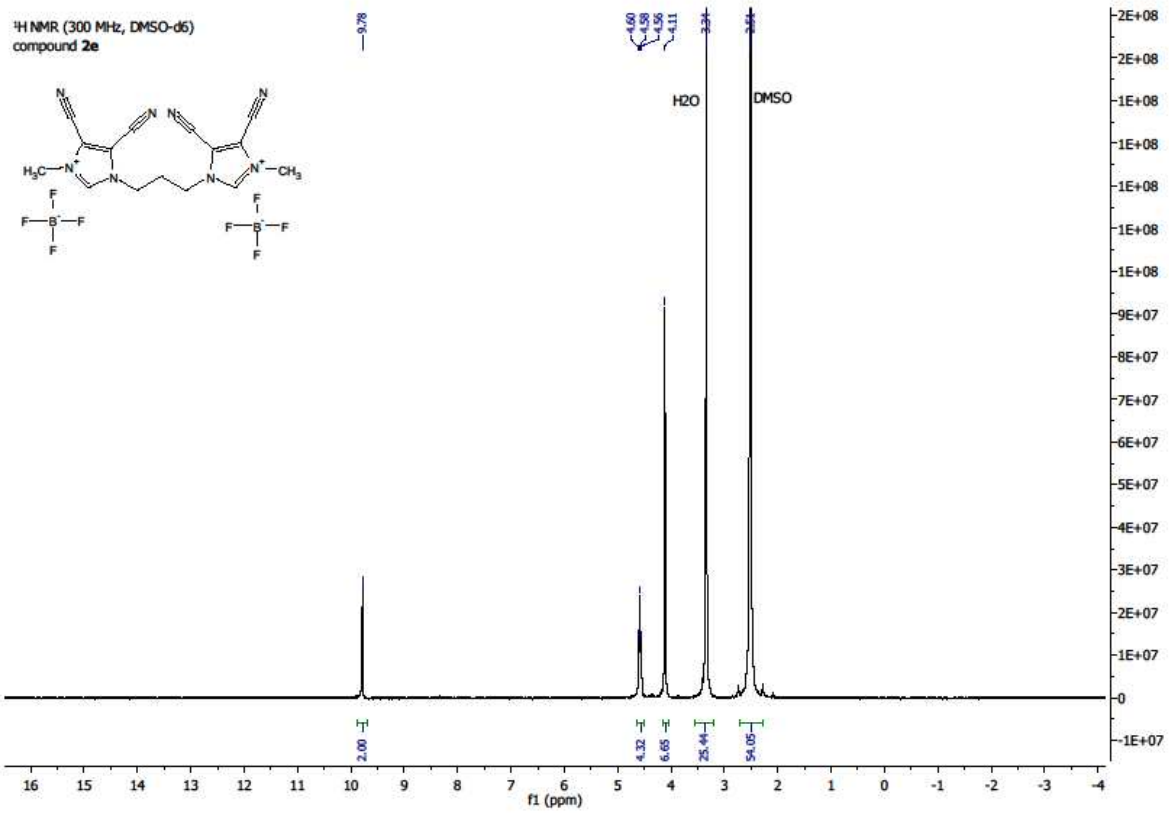


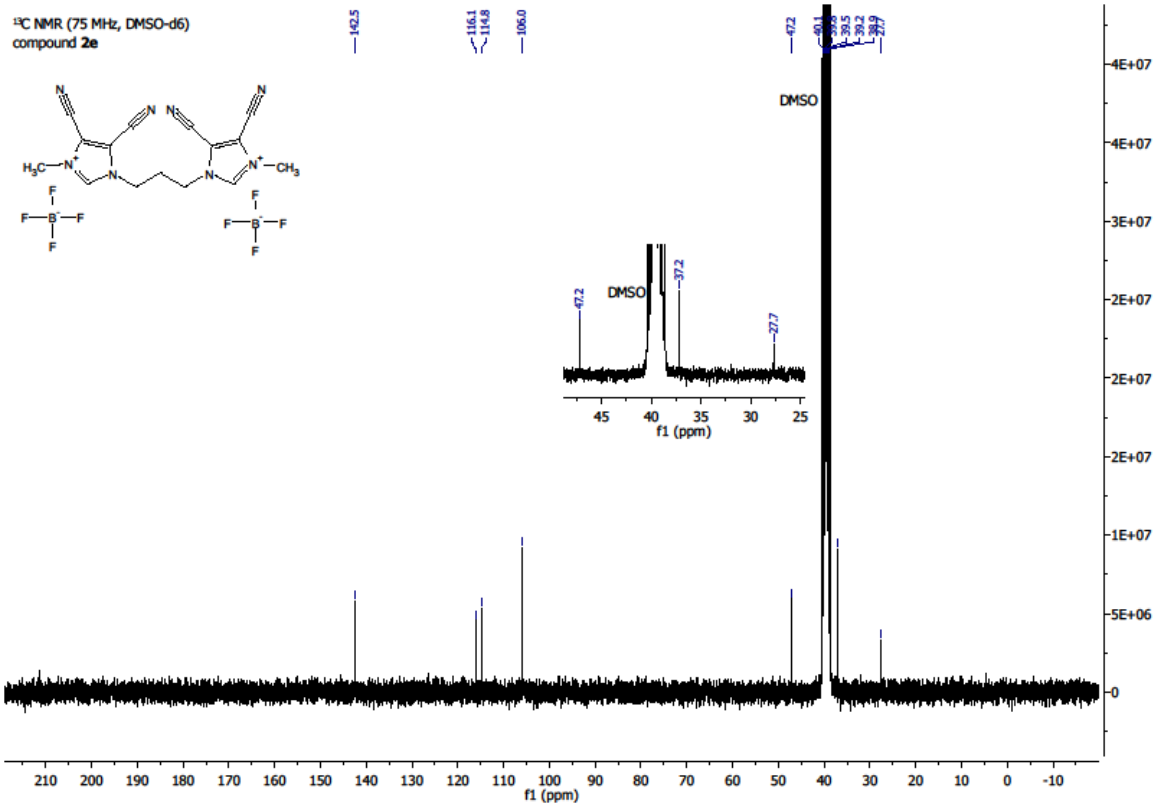
^{1}H-NMR (300 MHz, DMSO) δ 9.31 (s, 2H), 7.53 (dd, *J* = 5.7, 3.3 Hz, 2H), 7.26 (dd, *J* = 5.6, 3.4 Hz, 2H), 5.67 (s, 4H), 3.89 (s, 6H).

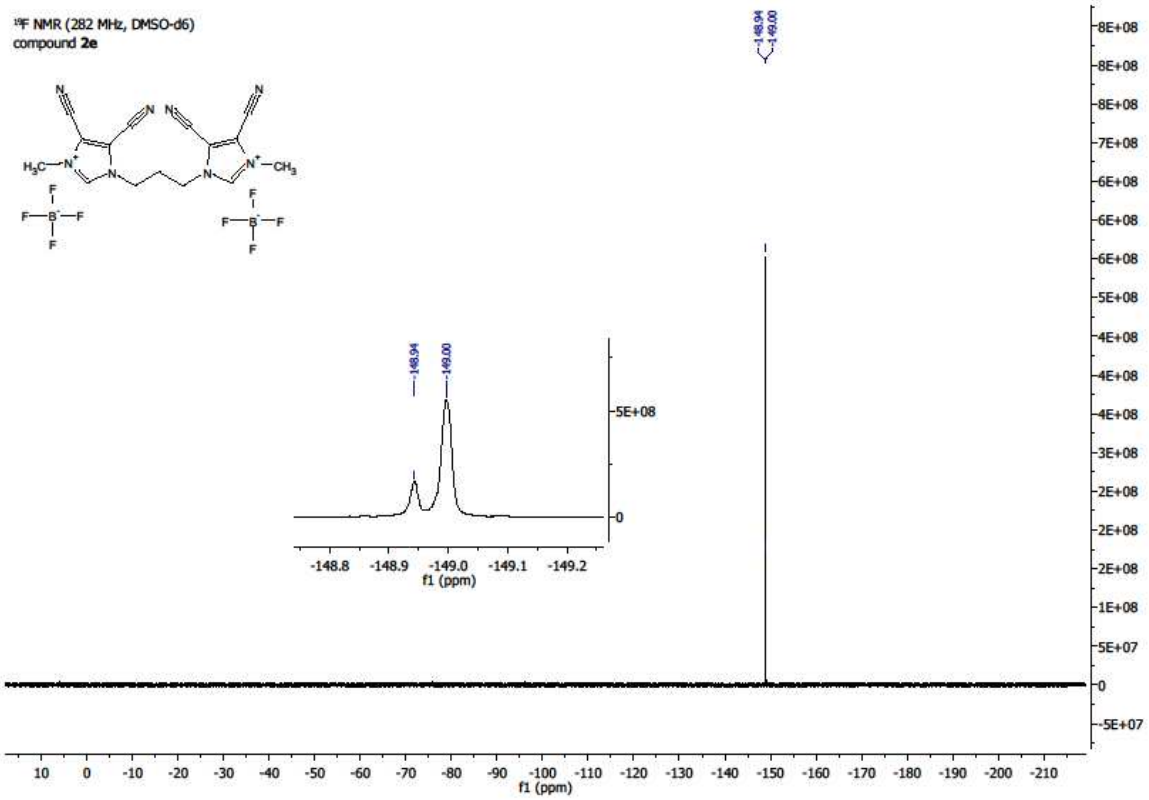
^{13}C-NMR (75 MHz, DMSO) δ 136.8 (s), 130.62 (s), 129.7 (s), 128.5 (s), 120.2 (s), 118.5 (s), 48.4 (s), 35.2 (s).

^{19}F-NMR (282 MHz, DMSO) δ -148.91(s), -148.97(s).

2e


¹H NMR (300 MHz, DMSO-d6)
compound 2e
H2O
DMSO
f1 (ppm)


¹³C NMR (75 MHz, DMSO-d6)
compound 2e
DMSO
DMSO
f1 (ppm)
f1 (ppm)

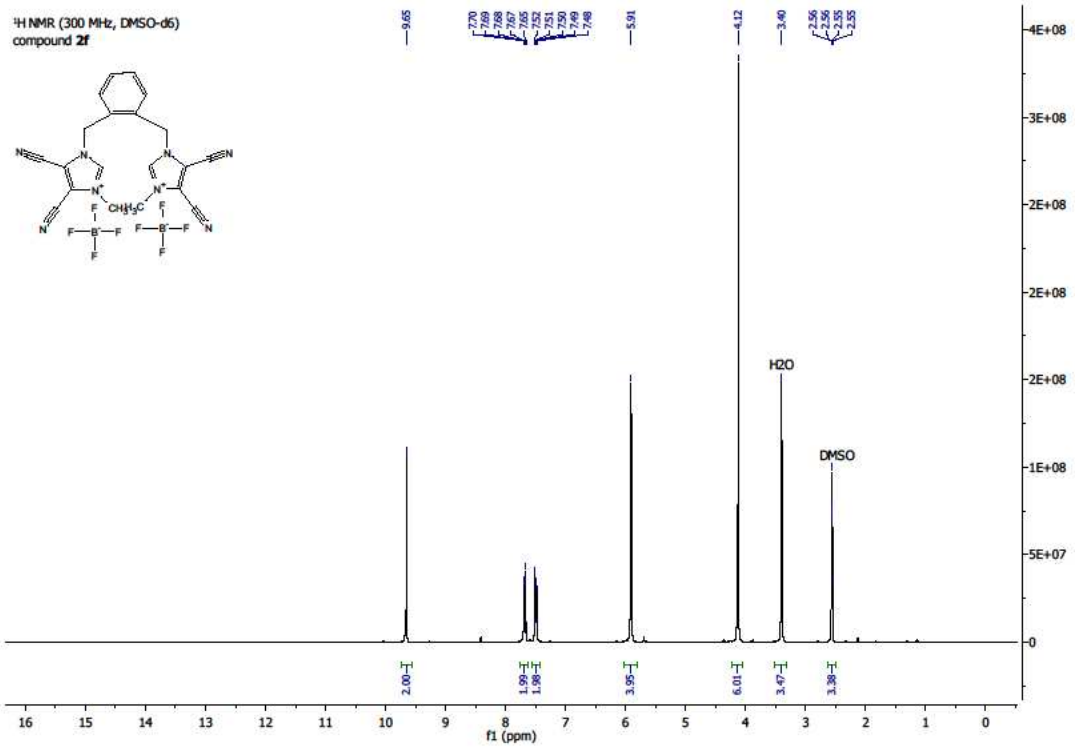


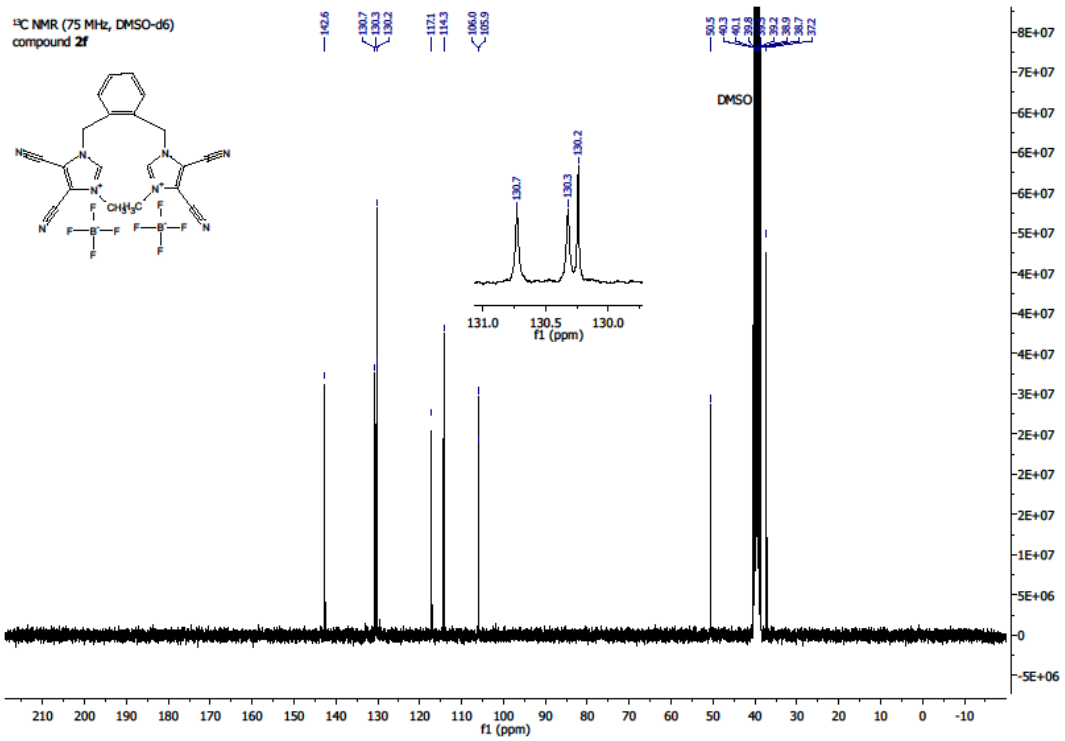
^{1}H-NMR (300 MHz, DMSO) δ 9.78 (s, 2H), 4.58 (t, *J* = 7.1 Hz, 4H), 4.11 (s, 6H).

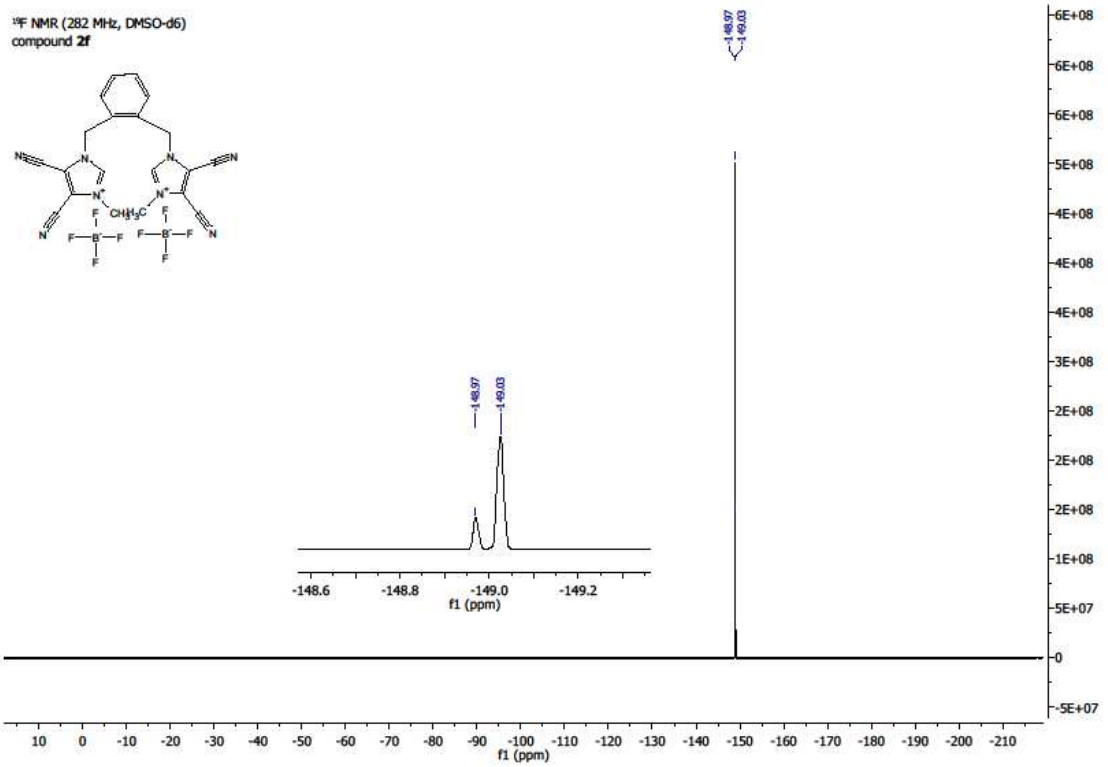
^{13}C-NMR (75 MHz, DMSO) δ 142.5 (s), 116.1 (s), 114.8 (s), 106.0 (s), 47.2 (s), 37.2 (s), 27.7 (s).

^{19}F NMR (282 MHz, DMSO) δ -148.94(s), -149.00(s).

2f


¹H NMR (300 MHz, DMSO-d6)
compound 2f
9.65
7.70
7.69
7.68
7.67
7.66
7.52
7.51
7.50
7.49
7.48
5.91
4.12
3.40
2.56
2.56
2.55
2.55
H2O
DMSO
2.00
1.99
1.98
3.95
6.01
3.47
3.38
f1 (ppm)


¹³C NMR (75 MHz, DMSO-d6)
compound 2f
142.6
130.7
130.3
130.2
117.1
114.3
106.0
105.9
40.5
40.3
40.1
39.9
39.7
39.5
39.2
38.9
38.7
37.2
DMSO
130.7
130.3
130.2
131.0
130.5
130.0
f1 (ppm)
f1 (ppm)

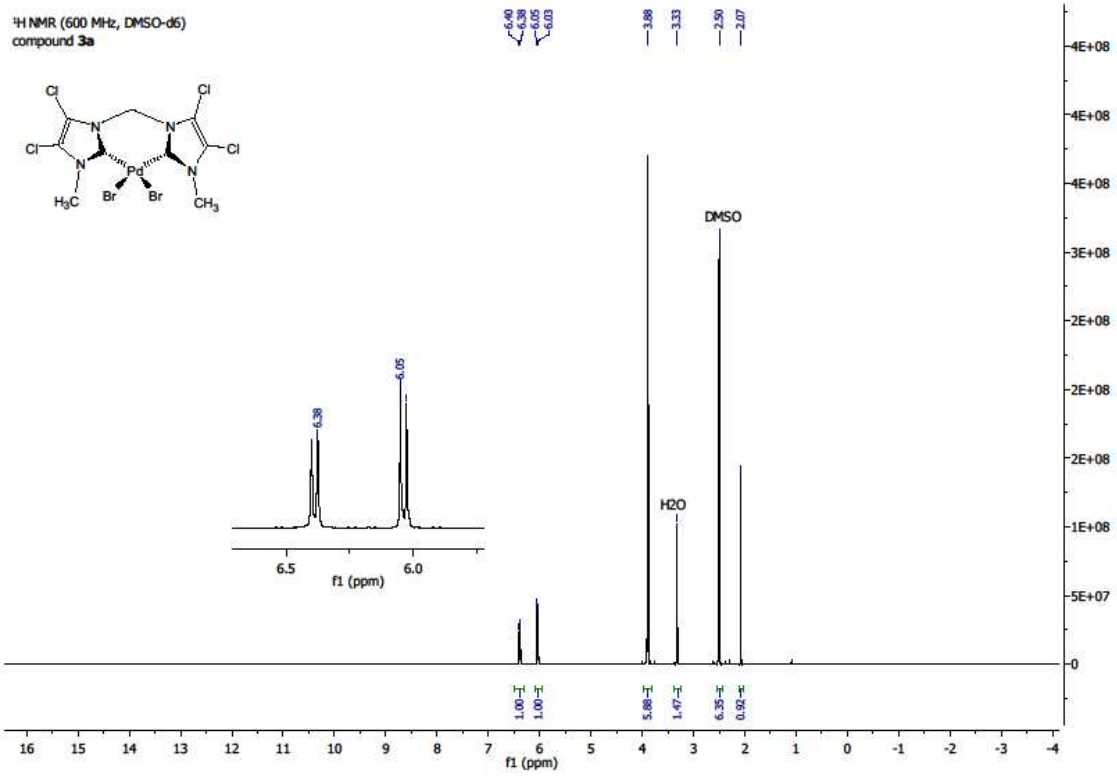


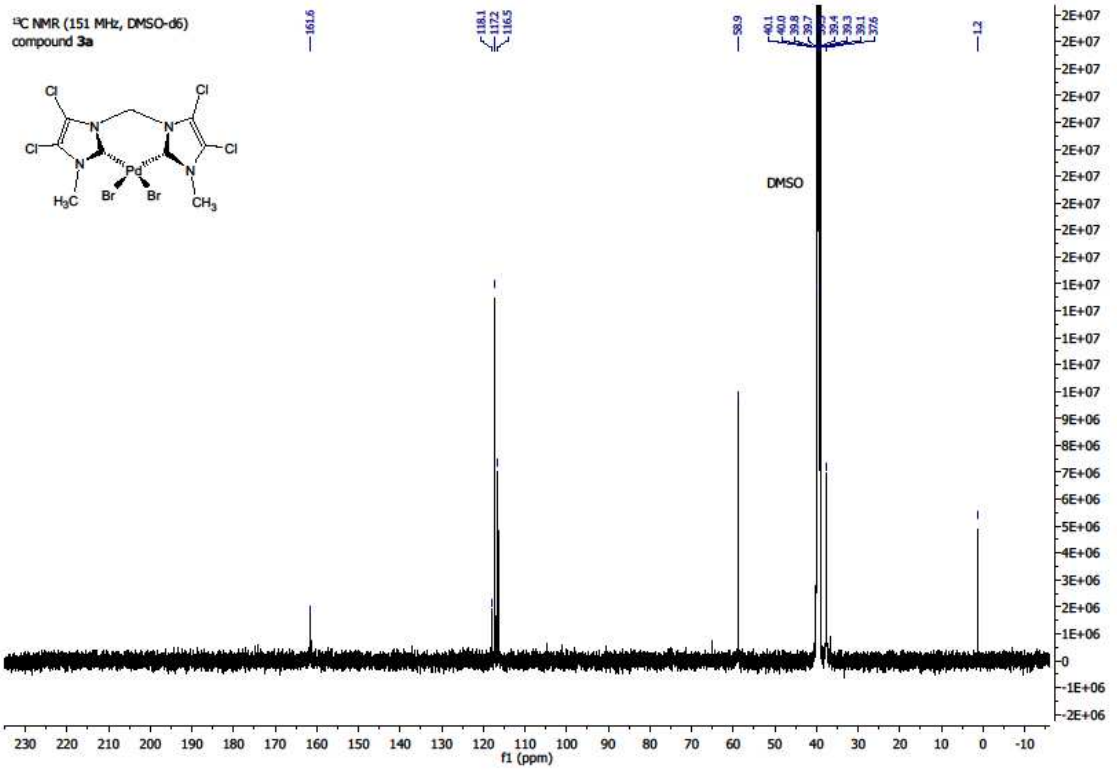
^{1}H-NMR (300 MHz, DMSO) δ 9.65 (s, 2H), 7.68 (dt, *J* = 7.4, 3.7 Hz, 2H), 7.57 – 7.42 (m, 2H), 5.91 (s, 4H), 4.12 (s, 6H).

^{13}C-NMR (75 MHz, DMSO) δ 142.6 (s), 130.7 (s), 130.3 (s), 130.2 (s), 117.1 (s), 114.3 (s), 106.0 (s), 105.9 (s), 50.5 (s), 37.2 (s).

^{19}F-NMR (282 MHz, DMSO) δ -148.97(s), -149.03(s).

3a

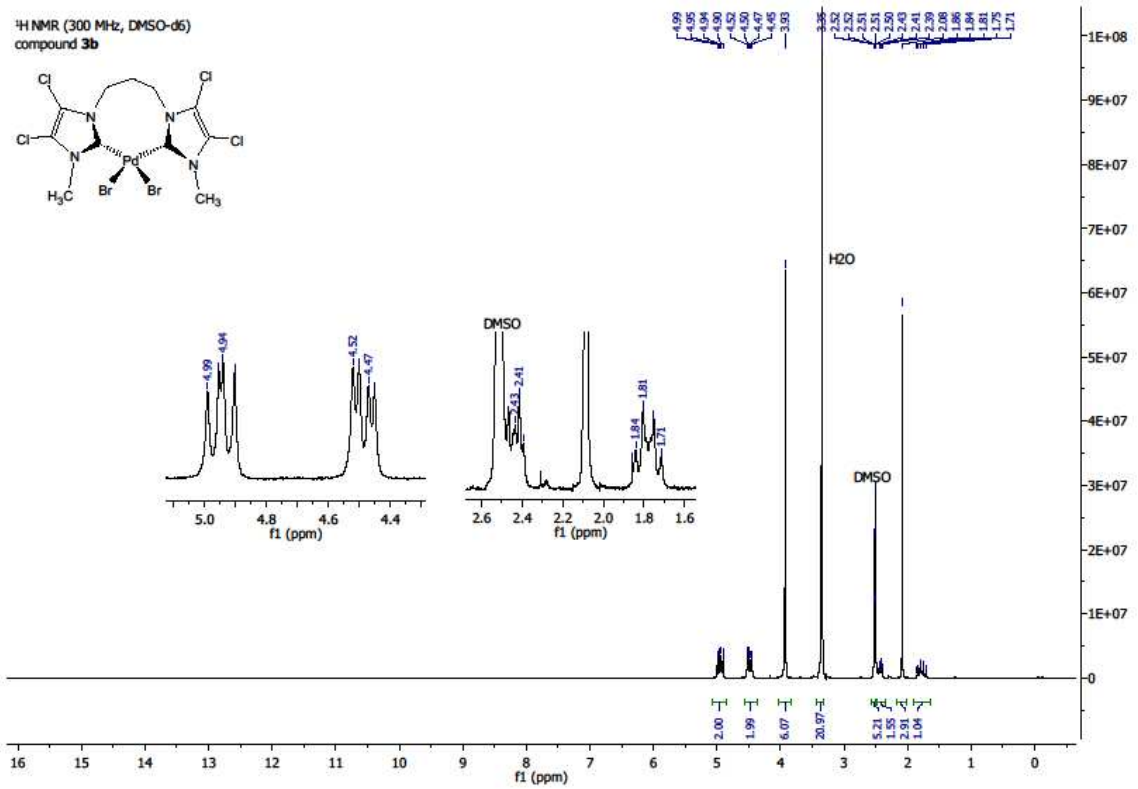


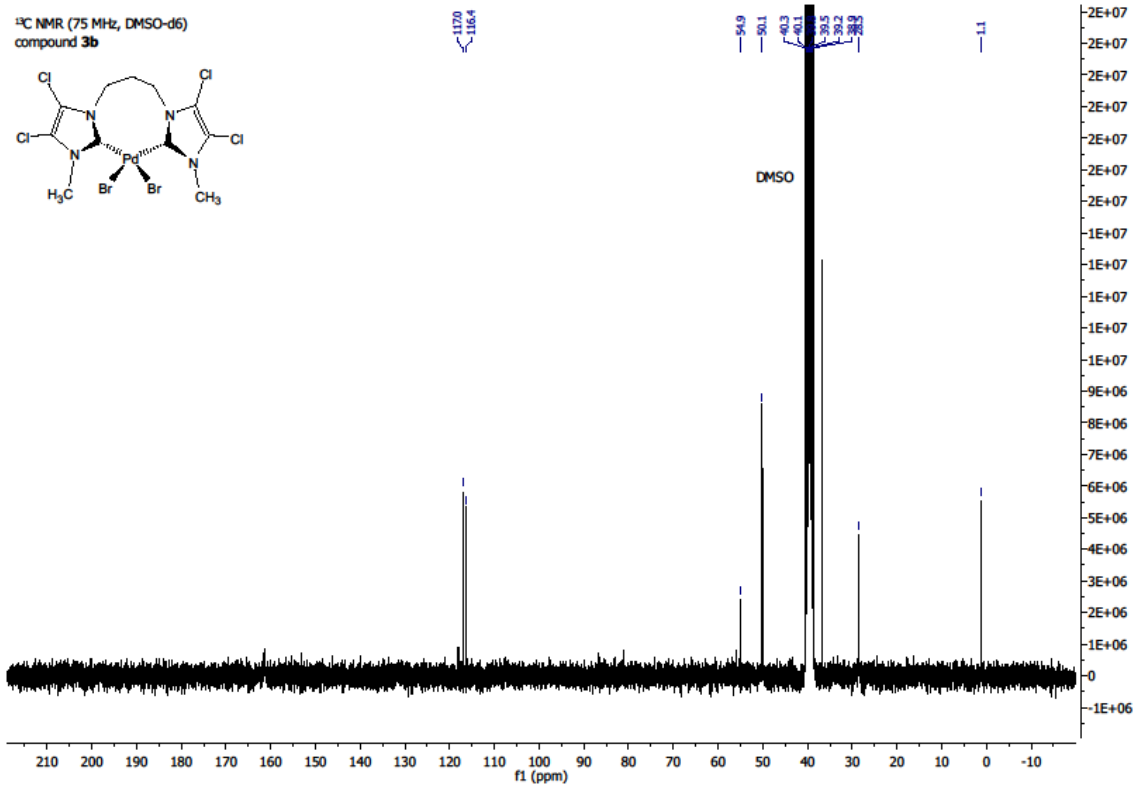


^{1}H-NMR (600 MHz, DMSO) δ 6.39 (d, *J* = 14.4 Hz, 1H), 6.04 (d, *J* = 14.4 Hz, 1H), 3.88 (s, 6H).

^{13}C-NMR (151 MHz, DMSO) δ 161.6 (s), 117.2 (s), 116.5 (s), 58.9 (s), 37.6 (s).

3b

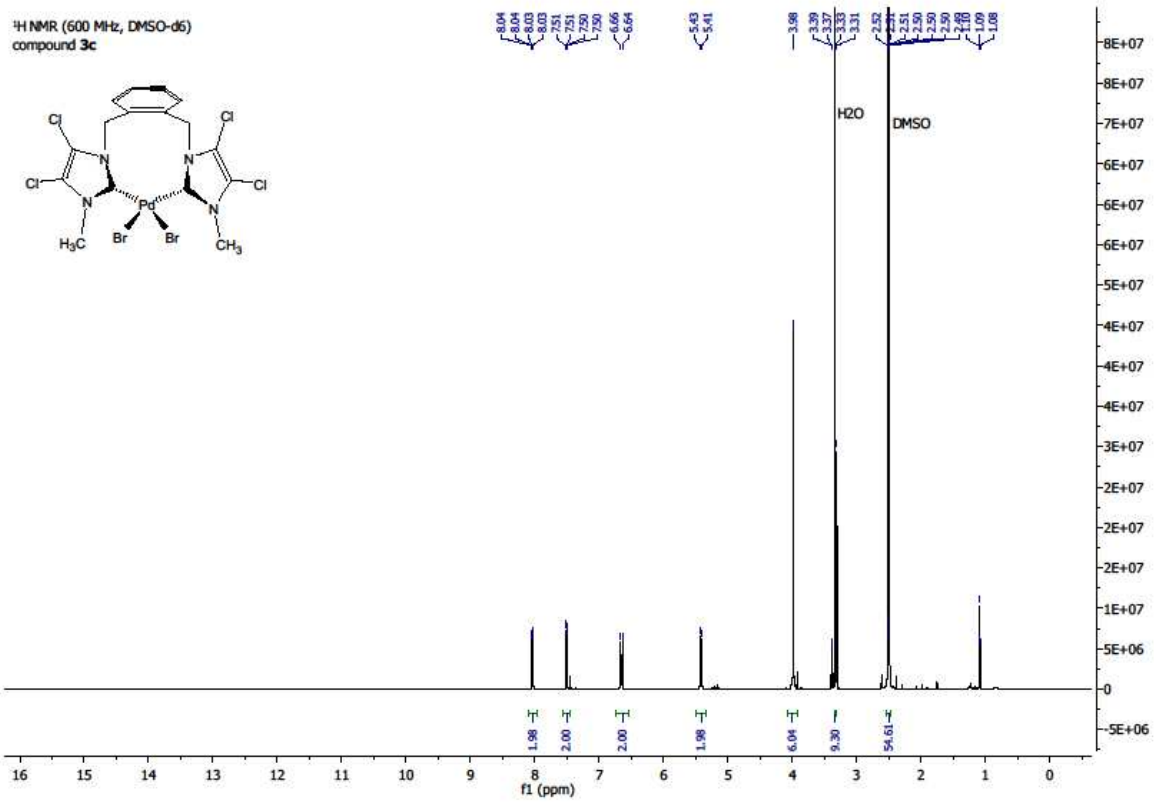


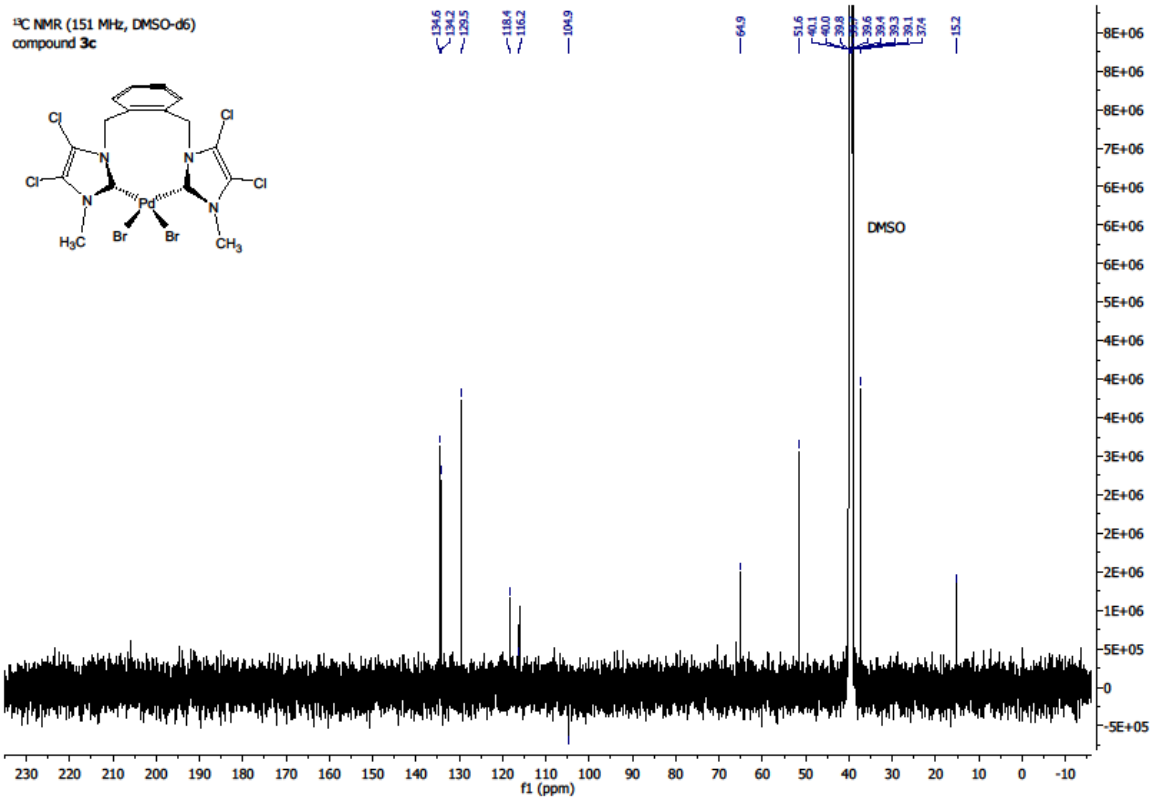


^{1}H-NMR (300 MHz, DMSO) δ 4.95 (dd, *J* = 15.1, 11.1 Hz, 2H), 4.49 (dd, *J* = 15.0, 5.8 Hz, 2H), 3.93 (s, 6H), 2.41 (t, *J* = 6.1 Hz, 1H), 1.88 – 1.65 (m, 1H).

^{13}C-NMR (75 MHz, DMSO) δ 117.0(s), 116.4 (s), 54.9 (s), 50.1 (s), 36.8 (s), 28.5 (s).

3c

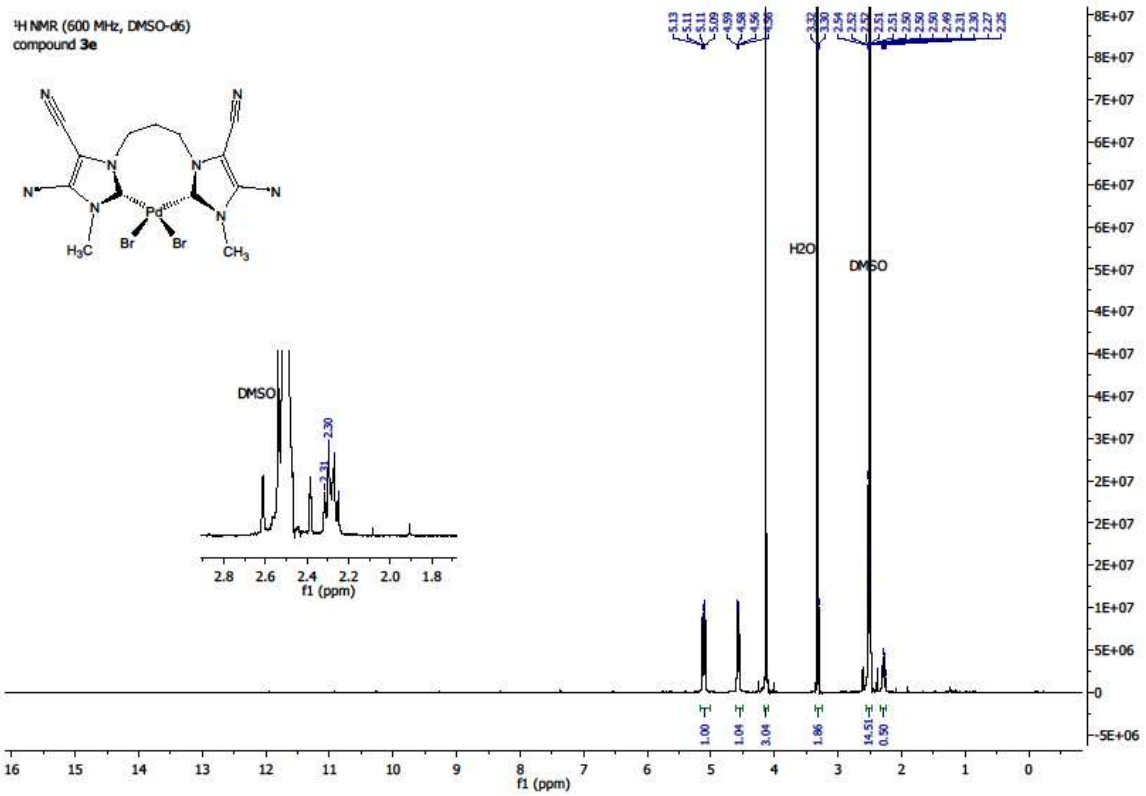


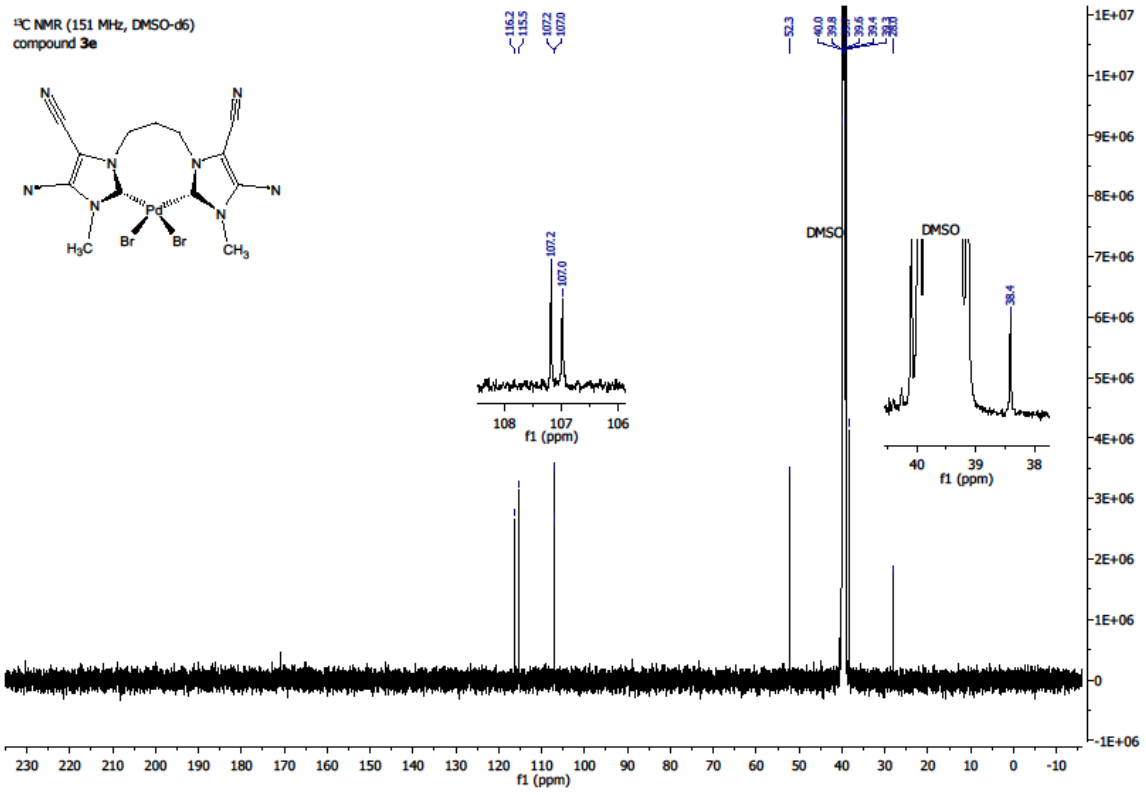


^{1}H-NMR (600 MHz, DMSO) δ 8.04 (dd, *J* = 5.7, 3.5 Hz, 2H), 7.50 (dd, *J* = 5.7, 3.4 Hz, 2H), 6.65 (d, *J* = 15.2 Hz, 2H), 5.42 (d, *J* = 15.3 Hz, 2H), 3.98 (s, 6H).

^{13}C-NMR (151 MHz, DMSO) δ 134.6 (s), 134.2 (s), 118.4 (s), 116.2 (s), 65.0(s), 51.6 (s), 37.4 (s).

3e

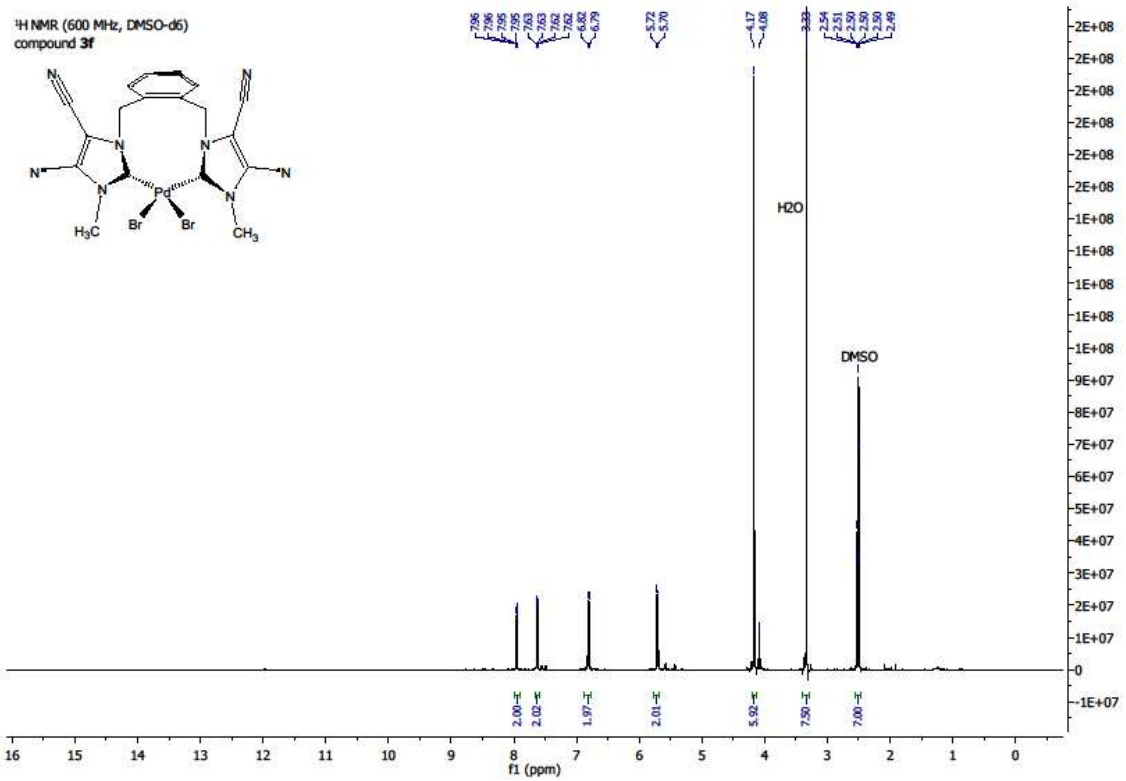


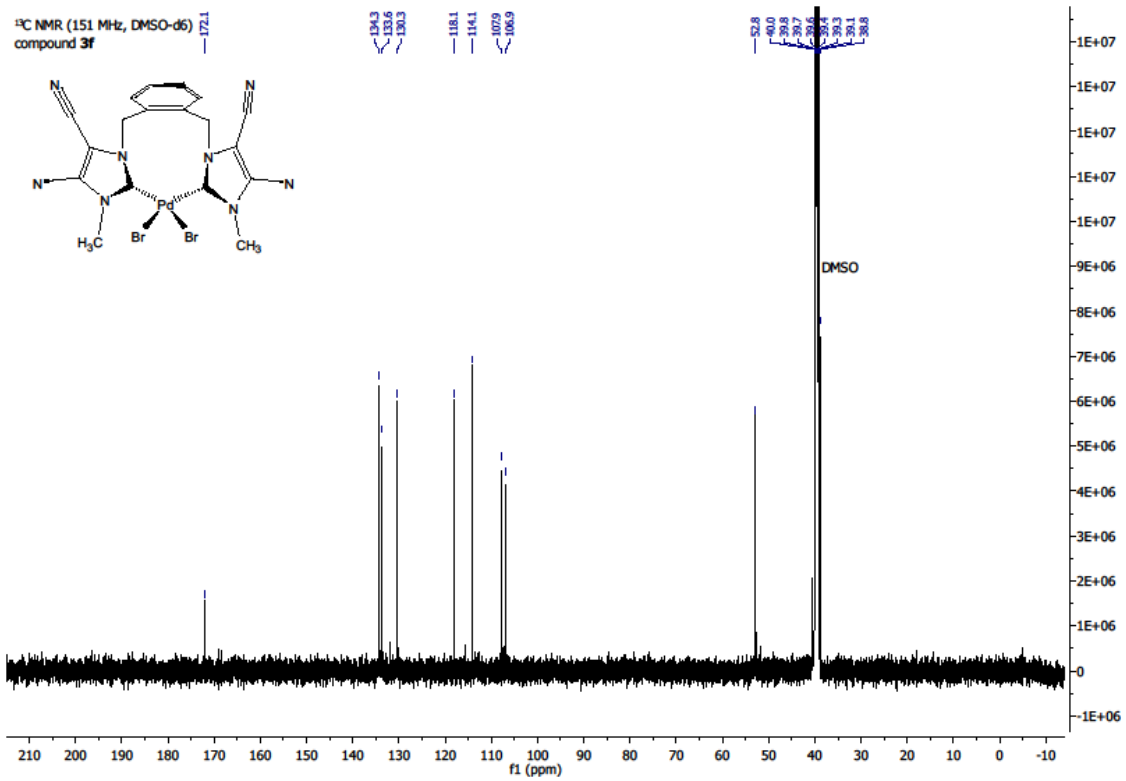


^{1}H-NMR (600 MHz, DMSO) δ 5.11 (dd, *J* = 15.2, 11.5 Hz, 2H), 4.57 (dd, *J* = 15.0, 5.8 Hz, 2H), 4.13 (s, 6H), 2.28 (dd, *J* = 27.2, 11.4 Hz, 1H).

^{13}C-NMR (151 MHz, DMSO) δ 116.2 (s), 115.5 (s), 107.2(s), 107,0 (s), 52.3 (s), 38.4 (s), 28.0 (s).

3f





^{1}H-NMR (600 MHz, DMSO) δ 7.95 (dd, *J* = 5.7, 3.5 Hz, 2H), 7.63 (dd, *J* = 5.7, 3.4 Hz, 2H), 6.81 (d, *J* = 15.2 Hz, 2H), 5.71 (d, *J* = 15.3 Hz, 2H), 4.17 (s, 6H).

^{13}C-NMR (151 MHz, DMSO) δ 172.1 (s), 134.3 (s), 133.6 (s), 130.3 (s), 118.1 (s), 114.1 (s), 107.9 (s), 106.9 (s), 52.8 (s).