Redox-active multinuclear Pd(II) complexes with bis- and tris-mesoionic carbenes

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Supporting Information

General Procedures.

All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques or in a glove box. Glassware was oven dried at 130 °C. Solvents were distilled by standard procedures prior to use. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker AC 250 spectrometer or a Jeol ECS 400 spectrometer. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard. All coupling constants are expressed in Hertz and only given for $^{1}H,^{1}H$ couplings unless mentioned otherwise. Mass spectra were obtained with Agilent 6210 ESI-TOF. Compound 1-ethyl-3-methyl-4-phenyl-1,2,3-triazolium Iodide **1**,[1] bistriazolium salt **3**[2], 1,3,5-tris(1-imidazolyl)benzene[3] were prepared as described in the literature. $PdCl_2$ was purchased from commercial sources and were used as received without further purification.

Compound [2].

To a mixture of 1-ethyl-3-Methyl-4-phenyl-1,2,3-triazolium Iodide salt **1**[1] (0.045 g, 0.143 mmol), K_2CO_3 (0.045 g, 0.326 mmol), $PdCl_2$ (0.054 g, 0.169 mmol) and KI (excess) was added pyridine (3 mL). The resulting suspension was stirred for 24 h at 84 °C. The pyridine was removed in *vacuo* and the crude mixture was extracted with dichloromethane (15 mL). The solvent was removed and the yellow residue was loaded onto a silica gel column. Elution with a hexane:ethyl acetate (6:4, v:v) mixture gave compound [**2**] as a yellow solid. Yield: 0.070 g (0.112 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.92−8.90 (m, 2H, H_{Py}), 7.92−7.90 (m,

2H, H_{Ar}), 7.68−7.63 (m, 1H, H_{Py}), 7.58−7.49 (m, 3H, H_{Ar}), 7.25−7.22 (m, 2H, H_{Py}), 4.90 (q, ^3J = 7.3 Hz, 2H, N−CH_2), 3.95 (s, 3H, N−CH_3), 1.79 (t, ^3J = 7.3 Hz, 3H, N−CH_2−CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 153.9 (C_{Py}), 143.7 (C_{trz}−Ar), 137.4 (C_{Py}), 132.9 (C_{trz}−Pd), 130.6 (C_{Ar}−H), 130.0 (C_{Ar}−H), 128.8 (C_{Ar}−C_{trz}), 124.3 (C_{Py}), 51.5 (N−CH_2), 37.5 (N−CH_3), 14.5 (N−CH_2−CH_3) ppm. HRMS (ESI, positive ions): *m/z* = 419.9181 (calcd for [[**2**]–I–Py]$^+$ 419.9194). Anal. Calcd. for [**2**]: C, 30.67; H, 2.90; N, 8.94. Found: C, 30.88; H, 2.99; N, 8.98.

Compound [4].

Compound [**4**] was prepared as described for [**2**] starting from bistriazolium salt **3**[2] (0.020 g, 0.036 mmol), K_2CO_3 (0.015 g, 0.109 mmol), $PdCl_2$ (0.015 g, 0.085 mmol) and KI (excess) in pyridine (3 mL). The compound was purified by silica gel column. Elution with a dichloromethane:methanol (9.6:0.4, v:v) mixture gave [**4**] as yellow solid. Yield: 0.036 g (0.031 mmol, 86%).^1H NMR (400 MHz, $CDCl_3$): δ = 8.93−8.92 (m, 4H, H_{Py}), 8.21 (s, 4H, H_{Ar}), 7.63−7.60 (m, 2H, H_{Py}), 7.24−7.21 (m, 4H, H_{Py}), 4.95 (q, ^3J = 7.4 Hz, 4H, N−CH_2), 4.10 (s, 6H, N−CH_3), 1.85 (t, ^3J = 7.4 Hz, 6H, N−CH_2−CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 153.9 (C_{Py}), 142.9 (C_{trz}−Ar), 137.3 (C_{Py}), 130.9 (C_{Ar}−H), 129.2 (C_{Ar}−C_{trz}), 128.3 (C_{trz}−Pd), 124.4 (C_{Py}), 51.6 (N−CH_2), 37.8 (N−CH_3), 14.5 (N−CH_2−CH_3) ppm. HRMS (ESI, positive ions): *m/z* = 1089.7935 (calcd for [[**4**]–I+CH_3CN]$^+$ 1089.8080). Anal. Calcd. for [**4**]: C, 26.58; H, 2.57; N, 9.54. Found: C, 26.94; H, 2.77; N, 9.67.

Compound 5.

1,3,5-Tris[(trimethylsilyl)ethynyl]benzene (0.732 g, 1.99 mmol), $CuSO_4{\cdot}5H_2O$(0.300 g, 1.20 mmol), sodium ascorbate (0.580 g, 2.93 mmol), ethyl iodide (1.2 g, 7.69 mmol), sodium azide (0.792 g, 12.2 mmol) and K_2CO_3 (0.830 g, 6.0 mmol) were suspended in H_2O:DMF (10 mL, 8:2, v:v) mixture. To this mixture was added 3 pipette of pyridine. The resulting suspension was stirred at ambient temperature for 72 h. The reaction mixture was then quenched with aqueous Na_2EDTA/NH_4OH solution and extracted with dichloromethane. The organic part was dried over $MgSO_4$. Removal of the solvent gave a white crude product which was further washed several times with diethyl ether. Yield: 0.613 g (1.69 mmol, 85%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (s, 3H, H_{Ar}), 7.94 (s, 3H, H_{trz}), 4.43 (q, ^3J = 7.6 Hz, 6H, N−CH_2), 1.56 (t, ^3J = 7.6 Hz, 9H, N−CH_2−CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 147.2 (C_{trz}−Ar), 131.9 (C_{Ar}−C_{trz}), 122.2 (C_{Ar}−H), 119.8 (C_{trz}−H), 45.5 (N−CH_2), 15.6 (N−CH_2−CH_3) ppm. HRMS (ESI, positive

ions): *m/z* = 364.2014 (calcd for $[C_{18}H_{21}N_9+H]^+$ 364.1998). Anal. Calcd. for **5**: C, 59.48; H, 5.82; N, 34.69. Found: C, 59.80; H, 5.86; N, 34.02.

Compound 6.

DMF (5 mL) was added to a mixture of tristriazole **5** (0.150 g, 0.413 mmol) and CH_3I (excess), The resulting solution was heated to 98 °C for 48 h. The reaction mixture was cooled to ambient temperature and to this was added diethyl ether (20 mL). The yellow coloured solid was filtered off and washed with excess amount of diethyl ether. Yield: 0.300 g (0.380 mmol, 92%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.27 (s, 3H, H_{trz}), 8.33 (s, 3H, H_{Ar}), 4.73 (q, ^3J = 8.0 Hz, 6H, N−CH_2), 4.36 (s, 9 H, N−CH_3), 1.58 (t, ^3J = 8.0 Hz, 9H, N−CH_2−CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ = 140.6 (C_{trz}−Ar), 133.5 (C_{Ar}−H), 130.1 (C_{trz}−H), 125.4 (C_{Ar}−C_{trz}), 49.7 (N−CH_2), 40.0 (N−CH_3), 14.8 (N−CH_2−CH_3) ppm. MS (ESI, positive ions): *m/z* = 662.0719 (calcd for $[\mathbf{6}-I]^+$ 662.0714). Anal. Calcd. for **6**: C, 31.96; H, 3.83; N, 15.98. Found: C, 32.00; H, 3.93; N, 15.96.

Compound [7].

The same synthetic procedure was employed as for [**2**] from tristriazolium salt (0.030 g, 0.038 mmol), $PdCl_2$ (0.024 g, 0.136 mmol), K_2CO_3 (0.024 g, 0.174 mmol) and KI (excess) in pyridine (3 mL). The crude solid was purification by column chromatography (silica gel) using dichloromethane:methanol (9.9:0.1, v:v) gave [**7**] as a yellow solid. Yield: 0.040 g, (0.023 mmol, 60.5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.06−8.95 (m, 6H, H_{Py}), 8.95 (s, 3H, H_{Ar}), 7.70−7.65 (m, 3H, H_{Py}), 7.26−7.23 (m, 6H, H_{Py}), 4.96 (q, ^3J = 7.4 Hz, 6H, N−CH_2), 4.36 (s, 9H, N−CH_3), 1.81 (t, ^3J = 7.4 Hz, 9H, N−CH_2−CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 154.5 (C_{Py}), 142.1 (C_{trz}−Ar), 137.6 (C_{Py}), 133.4 (C_{trz}−Pd), 132.3 (C_{Ar}−H), 128.5 (C_{Ar}−C_{trz}), 124.5 (C_{Py}), 51.9 (N−CH_2), 39.8 (N−CH_3), 14.4 (N−CH_2−CH_3) ppm. HRMS (ESI, positive ions): *m/z* = 1359. 4620 (calcd for $[[\mathbf{7}]-I-3Py]^+$ 1359.4741). Anal. Calcd. for [**7**]·$CHCl_3$: C, 24.11; H, 2.35; N, 9.12. Found: C, 24.12; H, 2.51; N, 9.24.

Compound 8.

DMF (5 mL) was added to a mixture of 1,3,5-tris(1-imidazolyl)benzene[3] (0.080 g, 0.290 mmol)

and CH_3I (excess), The resulting solution was heated to 98 °C for 48 h. The reaction mixture was cooled to ambient temperature and to this was added diethyl ether (20 mL). The yellow coloured solid was filtered off and washed with excess amount of diethyl ether. Yield: 0.200 g (0.269 mmol, 93%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.07 (s, br, 3H, N−CH−N), 8.60 (s, 3H, H_{Ar}), 8.49−8.48 (m, 3H, $H_{imidazole}$), 8.20 (m, 3H, $H_{imidazole}$), 4.36 (q, ^3J = 7.5 Hz, 6H, N−CH_2), 1.55 (t, ^3J = 7.5 Hz, 9H, N−CH_2−CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ = 136.9 (N−CH−N), 136.3 (C_{Ar}−$N_{imizalole}$), 124.3 ($C_{imidazole}$), 121.6 ($C_{imidazole}$), 116.7 (C_{Ar}−H), 45.9 (N−CH_2), 15.3 (N−CH_2−CH_3) ppm. HRMS (ESI, positive ions): *m/z* = 617.0376 (calcd for [**8**−I]$^+$ 617.0387). Anal. Calcd. for **8**·2H_2O: C, 32.33; H, 4.01; N, 10.77. Found: C, 32.44; H, 3.89; N, 10.62.

Compound [9].

The complex [**9**] was prepared by following the same synthetic procedure as [**2**] starting from trisimidazolium salt **6** (0.035 g, 0.047 mmol), K_2CO_3 (0.026 g, 0.188 mmol), $PdCl_2$ (0.027 g, 0.152 mmol) and KI (excess) in pyridine (5 mL). The crude solid was loaded onto a silica gel column and eluted with dichloromethane:methanol (9.9:0.1, v:v) to give [**9**] as a yellow solid. Yield: 0.057 g (0.034 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.68 (s, 3H, H_{Ar}), 9.0−8.98 (m, 6H, H_{Py}), 7.75 (d, ^3J = 2.0 Hz, 3H, $H_{imidazole}$), 7.69−7.65 (m, 3H, H_{Py}), 7.26−7.23 (m, 6H, H_{Py}), 7.15 (d, ^3J = 2.0 Hz, 3H, $H_{imidazole}$), 4.71 (q, ^3J = 7.4 Hz, 6H, N−CH_2), 1.67 (t, ^3J = 7.4 Hz, 9H, N−CH_2−CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 154.4 (C_{Py}), 147.9 (C_{NHC}−Pd), 140.5 (C_{Ar}−$N_{imidazole}$), 137.6 (C_{Py}), 124.5 (C_{Py}), 123.7 ($C_{imidazole}$), 122.0 ($C_{imidazole}$), 119.8 (C_{Ar}−H), 47.8 (N−CH_2), 14.8 (N−CH_2−CH_3) ppm. HRMS (ESI, positive ions): *m/z* = 1314.4324 (calcd for [[**7**]–I–3Py]$^+$ 1314.4415). Anal. Calcd. for [**9**]·CH_2Cl_2: C, 25.20; H, 2.34; N, 7.15. Found: C, 25.21; H, 2.77; N, 6.98.

X-ray Crystallography.

Single crystals suitable for X-ray diffraction studies were obtained for the complexes [**4**], [**7**] and [**9**] by slow evaporation of the solvents from concentrated dichloromethane:chloroform mixture. X-ray diffraction data were collected at T = 140 K with a Bruker Kappa Apex 2 duo or a Bruker Smart AXS diffractometer equipped with a rotation anode using graphite-monochromated Mo-

Kα radiation (λ = 0.71073 Å).). The strategy for the data collection was evaluated by using the CrysAlisPro CCD or Smart software. The data were collected by the standard 'phi-omega scan techniques', and were scaled and reduced using CrysAlisPro RED software or Saint+ software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on F^2.[3] Crystallographic details are given in Table S1.

CCDC 1019285, 1019286 and 1021276 contain the cif files of complexes [**4**]·2$CHCl_3$, [**7**]·$CHCl_3$ and [**9**] respectively. These data can be obtained free of charge from www.ccdc.cam.ac.uk/data_requests/cif.

Table S1. Selected bond lengths in Å

	[**4**]·2CHCl$_3$	[**7**]·CHCl$_3$	[**9**]
Chemical formula	$C_{28}H_{22}Cl_6I_4N_8Pd_2$	$C_{37}H_{43}N_{12}Cl_3I_6Pd_3$	$C_{36}H_{39}I_6N_9Pd_3$
M_r	1403.64	1842.78	1678.36
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*C2/c*	*P*-1	*P2(1)/C*
a (Å)	15.427(5)	9.6689(16),	15.1846(8)
b (Å)	11.389(4)	13.324(2),	12.8825(6)
c (Å)	24.293(8)	22.043(4)	24.7885(13)
α (°)	90.00	80.049(3)	90.00
β (°)	91.044(7)	80.289(3)	99.168(2)
γ (°)	90.00	71.545(4)	90.00
V (Å^3)	4264(3)	2633.3(8)	4787.1(4)
Z	6	2	4
Densitiy (g cm^{-3})	2.187	2.324	2.329
F(000)	2608	1712	3096
Radiation Type	Mo K_α	Mo K_α	Mo K_α
μ (mm^{-1})	4.146	4.723	5.020
Crystal size	0.27 x 0.18 x 0.07	0.525x 0.18 x 0.09	0.13 x 0.06 x 0.04
Meas. Refl.	17194	28786	68856
Indep. Refl.	3796	9326	14606
Obsvd. [$I > 2\sigma(I)$] refl.	3199	7809	11936
R_{int}	0.0810	0.0249	0.0350
R [$F^2 > 2\sigma(F^2)$]	0.0521	0.0708	0.0278
wR(F^2)	0.1309	0.1598	0.0504
S	1.203	1.202	1.037
$\Delta\rho_{max}$ (e Å^{-3})	2.222	3.806	1.755
$\Delta\rho_{min}$ (e Å^{-3})	-1.288	-2.518	-1.174

Table S2. Selected bond lengths in Å

Atoms	[4]	[7]	[9]
Pd1 – I1	2.6032(12)	2.5993(8)	2.6170(3)
Pd1 – I2	2.6250(12)	2.6057(8)	2.5998(3)
Pd2 – I3	-	2.6159(8)	2.6032(3)
Pd2 – I4	-	2.5995(8)	2.6160(3)
Pd3 – I5	-	2.5868(6)	2.600(1)
Pd3 – I6	-	2.5899(7)	2.6086(3)
Pd1– N3	-	-	2.105(2)
Pd1– N4	2.111(8)	2.112(4)	-
Pd2– N8	-	2.082(4)	-
Pd2– N6	-	-	2.100(3)
Pd3– N9	-	-	2.090(2)
Pd3– N12	-	2.109(4)	-
Pd1 – C1	1.967(10)	1.951(5)	1.962(3)
Pd2 – C14	-	1.950(5)	1.963(3)
N1 – N2	1.334(11)	1.337(6)	-
N2 – N3	1.325(11)	1.310(6)	-
N5 – N6	-	1.314(7)	-
N6 – N7	-	1.312(7)	-
N9 – N10	-	1.325(7)	-
N10 – N11	-	1.321(6)	-
N1 – C1	1.373(12)	1.342(7)	1.359(4)
N2 – C1	-	-	1.344(4)
N3 – C2	1.371(12)	1.380(6)	-
N4 – C14	-	-	1.362(4)
N5 – C14	-	-	1.340(4)
N5 – C15	-	1.358(6)	-
N7 – C14	-	1.370(7)	-
N7 – C27	-	-	1.361(4)
N9 – C27	-	1.339(8)	-
N11 – C28	-	1.359(7)	-
C1 – C2	1.367(14)	1.387(6)	-
C27 – C28	-	1.339(8)	-
C14 – C15	-	1.376(7)	-

Table S3. Selected bond angles in °

Atoms	[4]	[7]	[9]
I1 – Pd1 – I2	173.48(3)	171.98(2)	174.06(1)
I3 – Pd2 – I4	92.7(2)	172.78(2)	172.19(1)
I5 – Pd3 – I6	-	175.35(2)	172.54(3)
I1 – Pd1 – N4	-	92.2(2)	-
I4 – Pd2 – N8	-	92.6(2)	-
I6 – Pd3 – N12	-	92.7(2)	-
I1 – Pd1 – N3	88.0(3)	-	91.94(7)
I4 – Pd2 – N6	-	-	93.45(7)
I6 – Pd3 – N9	-	-	92.53(7)
I2 – Pd1 – C1	-	84.8(2)	87.64(8)
I3 – Pd2 – C14	-	90.6(2)	85.53(8)
I5 – Pd3 – C27	-	88.3(2)	90.01(9)
N3 – Pd1 – C1	-	-	177.32(11)
N6 – Pd2 – C14	-	-	174.66(11)
N9 – Pd3 – C27	-	-	173.84(11)
N4 – Pd1 – C1	178.8(3)	178.6(2)	-
N8 – Pd2 – C14	-	175.4(2)	-
N12 – Pd3 – C27	-	176.2(2)	-
C1 – C1 – N1	103.2(8)	102.9(4)	-
C15 – C14 – N7	-	102.6(5)	-
C28 – C27 – N9	-	102.6(5)	-
N1 – C1 – N2	-	-	105.5(2)
N4 – C14 – N5	-	-	105.2(3)
N7 – C27 – N8	-	-	105.5(2)

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3. *SHELXS-97*, *SHELXL-97* and G. M. Sheldrick, *Acta Crystallogr., Sect. A* 2008, **64**, 112−122.

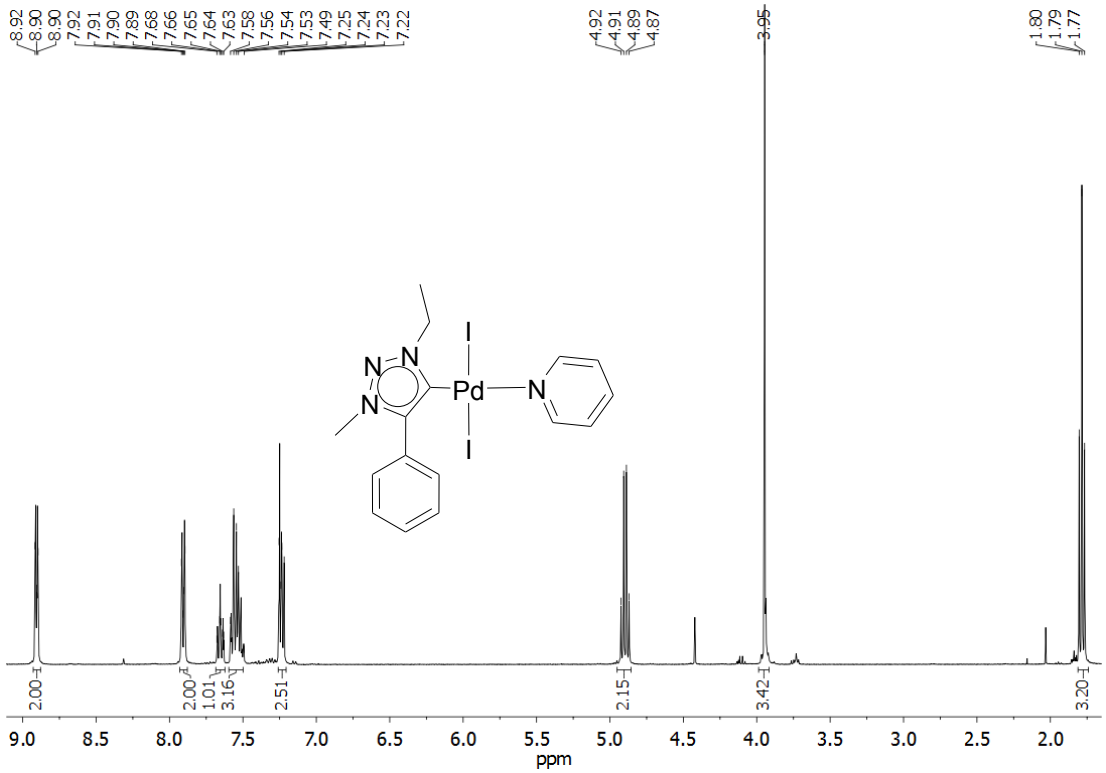

Figure S1. ^{1}H NMR spectrum of [**2**] in $CDCl_3$.

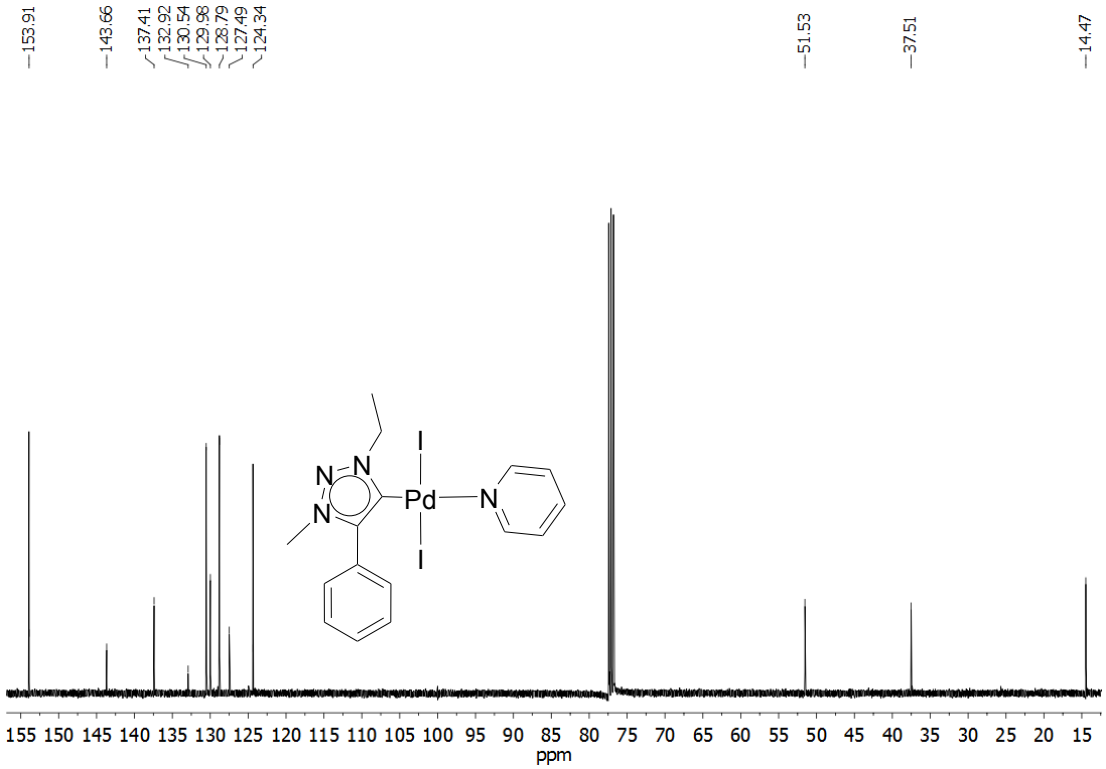

Figure S2. ^{13}C{^{1}H} NMR spectrum of [**2**] in $CDCl_3$.

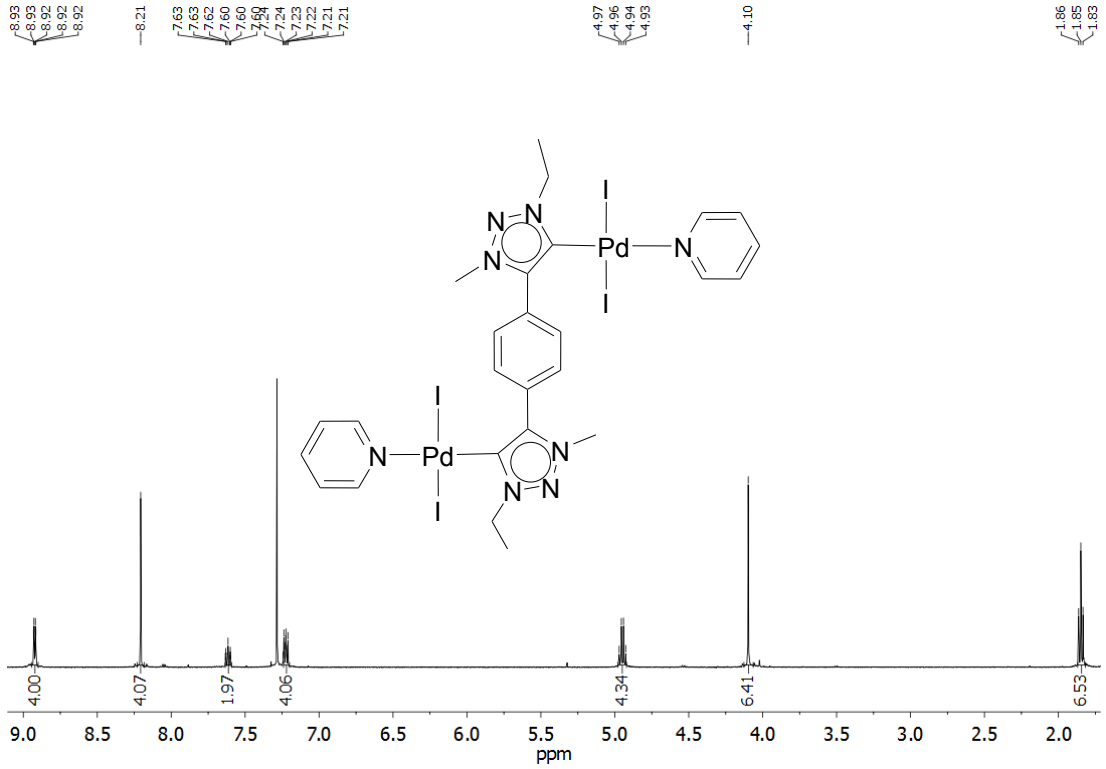

Figure S3. ^{1}H NMR spectrum of [**4**] in $CDCl_3$.

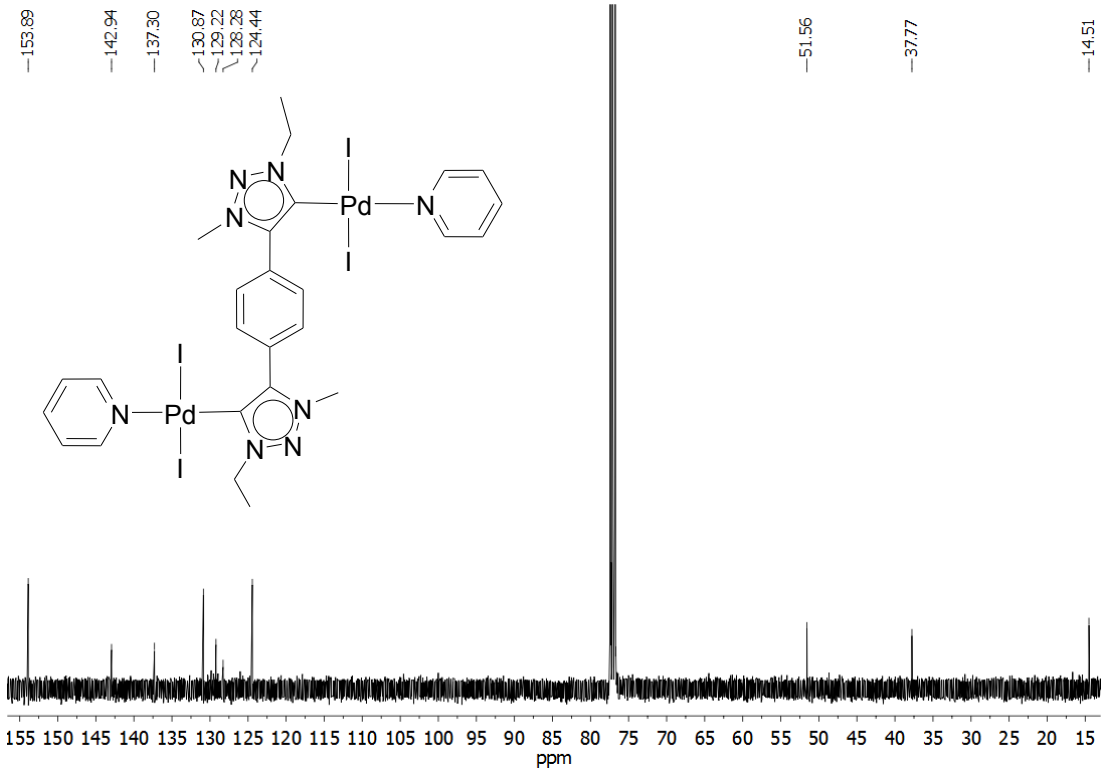

Figure S4. ^{13}C{^{1}H} NMR spectrum of [**4**] in $CDCl_3$.

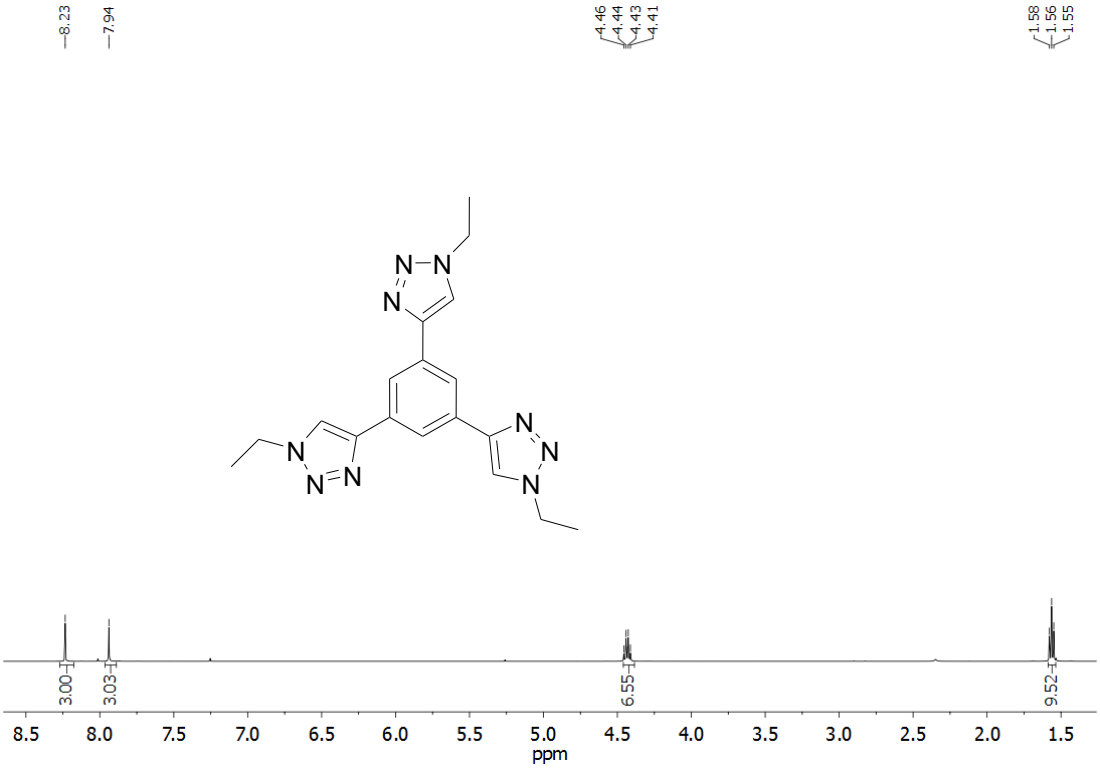

Figure S5. ^{1}H NMR spectrum of tristriazole **5** in $CDCl_3$.

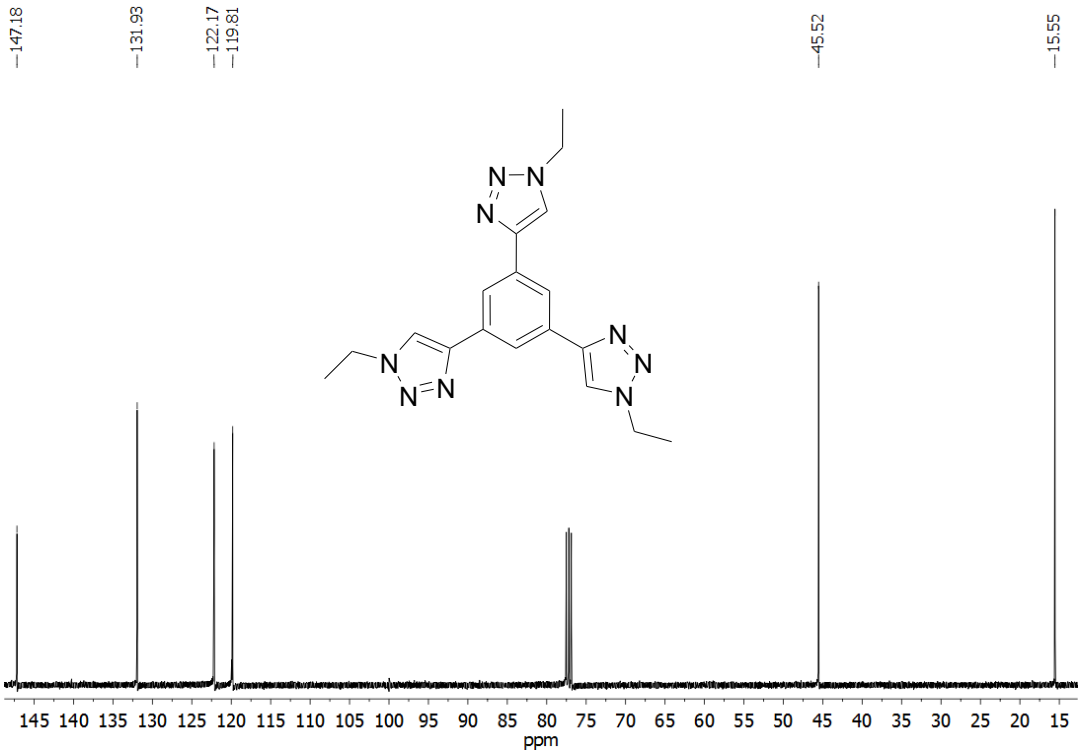

Figure S6. ^{13}C{^{1}H} NMR spectrum of tristriazole **5** in $CDCl_3$.

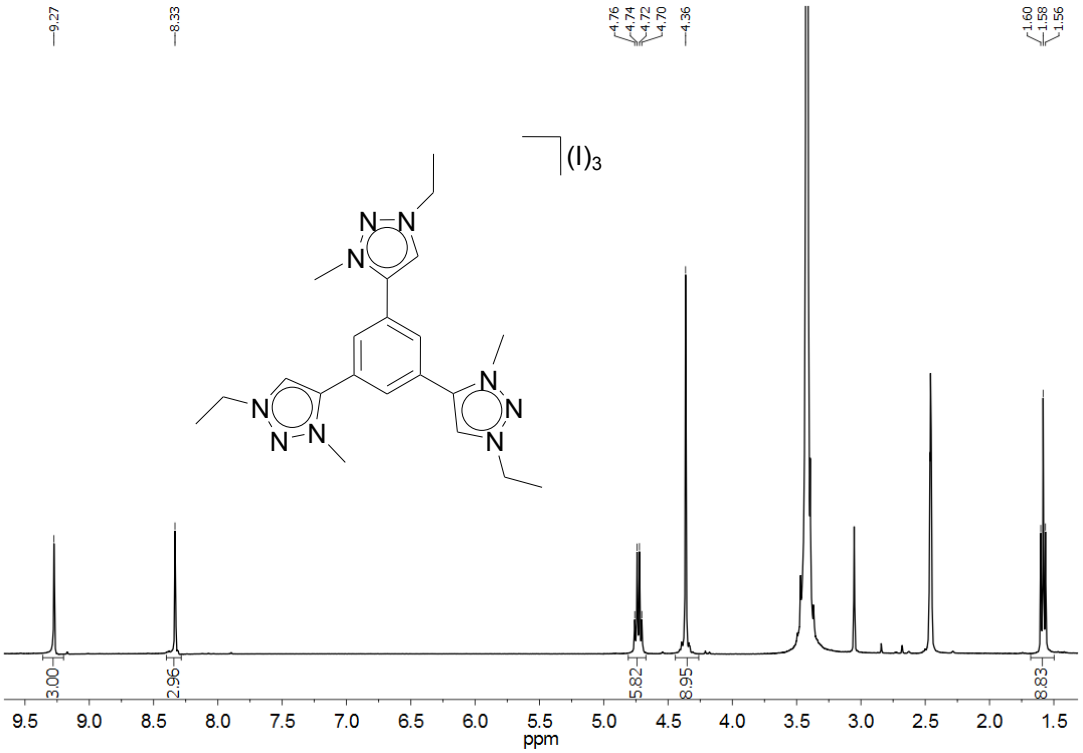

Figure S7. ^{1}H NMR spectrum of **6** in DMSO-d_6.

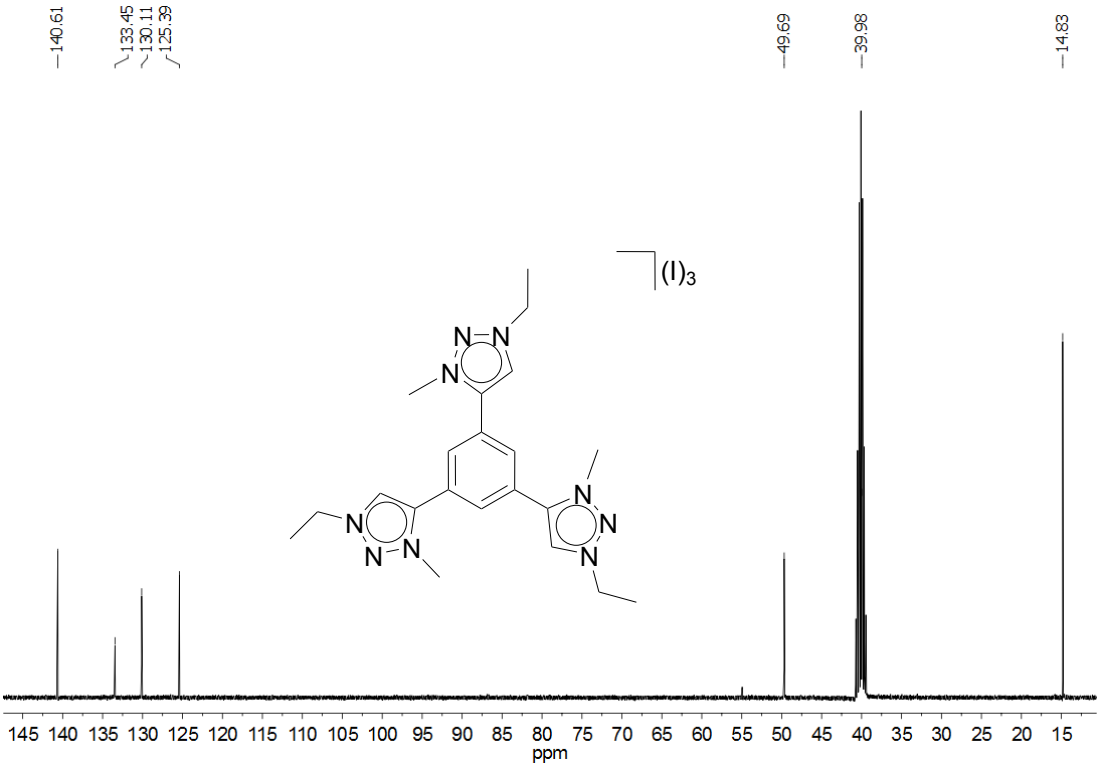

Figure S8. ^{13}C{^{1}H} NMR spectrum of **6** in DMSO-d_6.

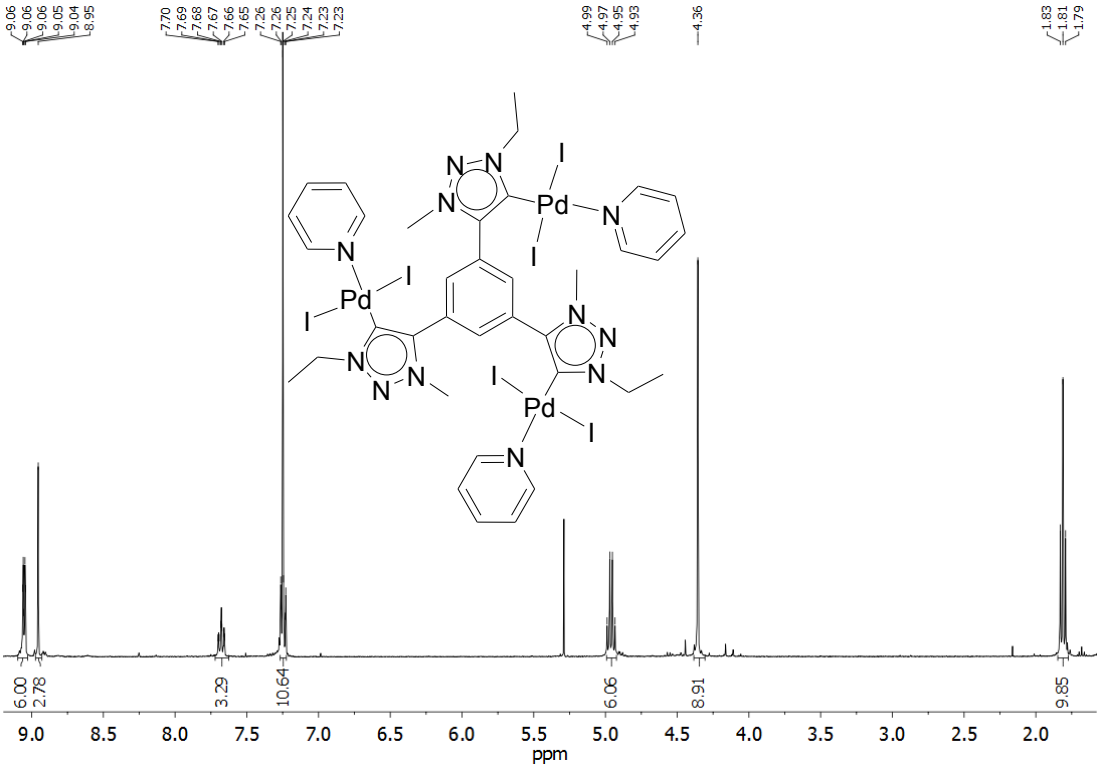

Figure S9. ^{1}H NMR spectrum of [**7**] in $CDCl_3$.

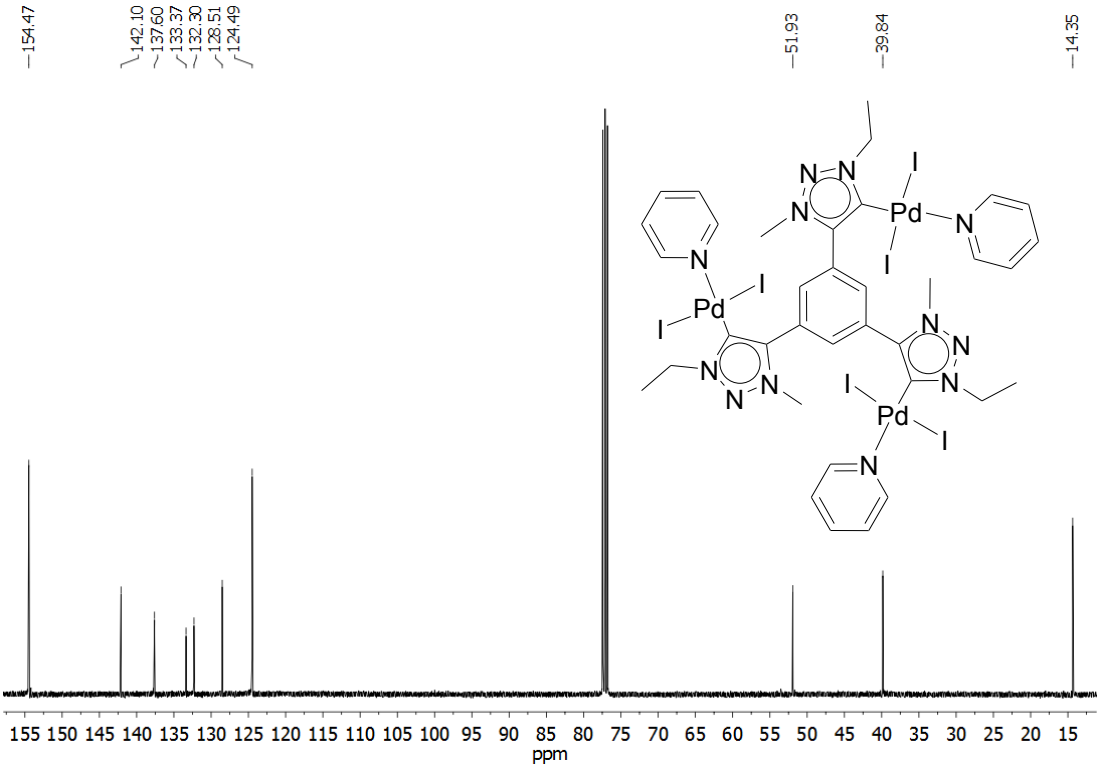

Figure S10. ^{13}C{^{1}H} NMR spectrum of [**7**] in $CDCl_3$.

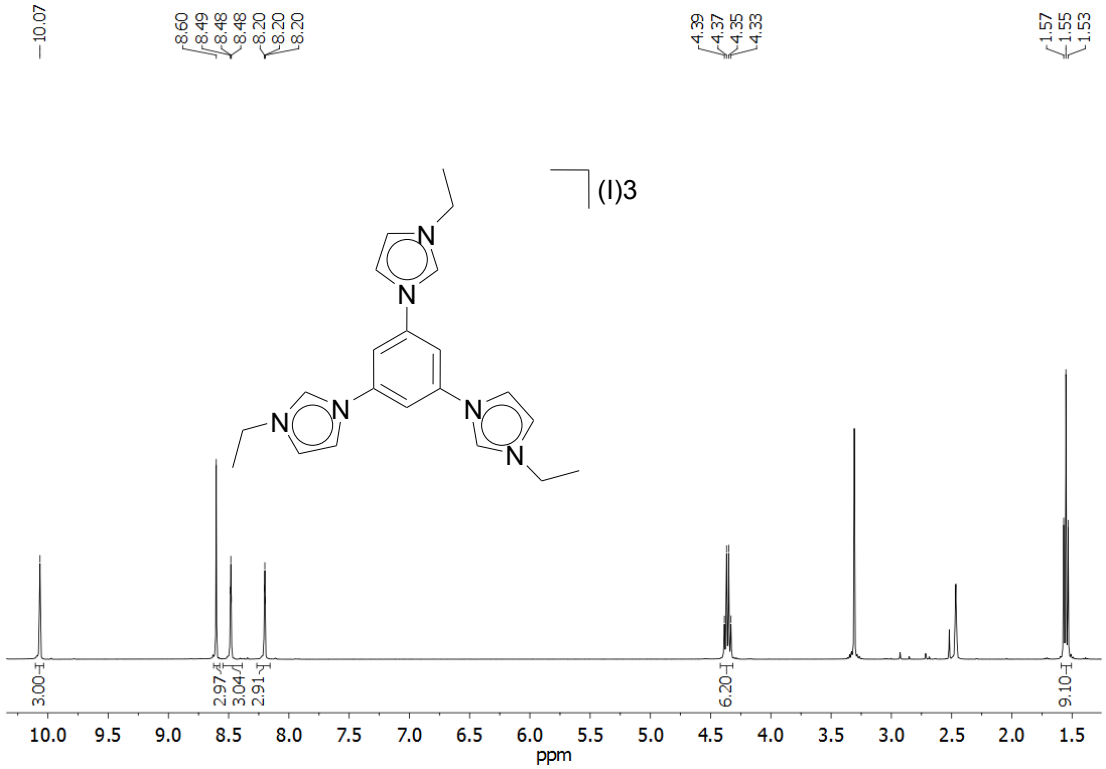

Figure S11. ^{1}H NMR spectrum of **8** in DMSO-d_3.

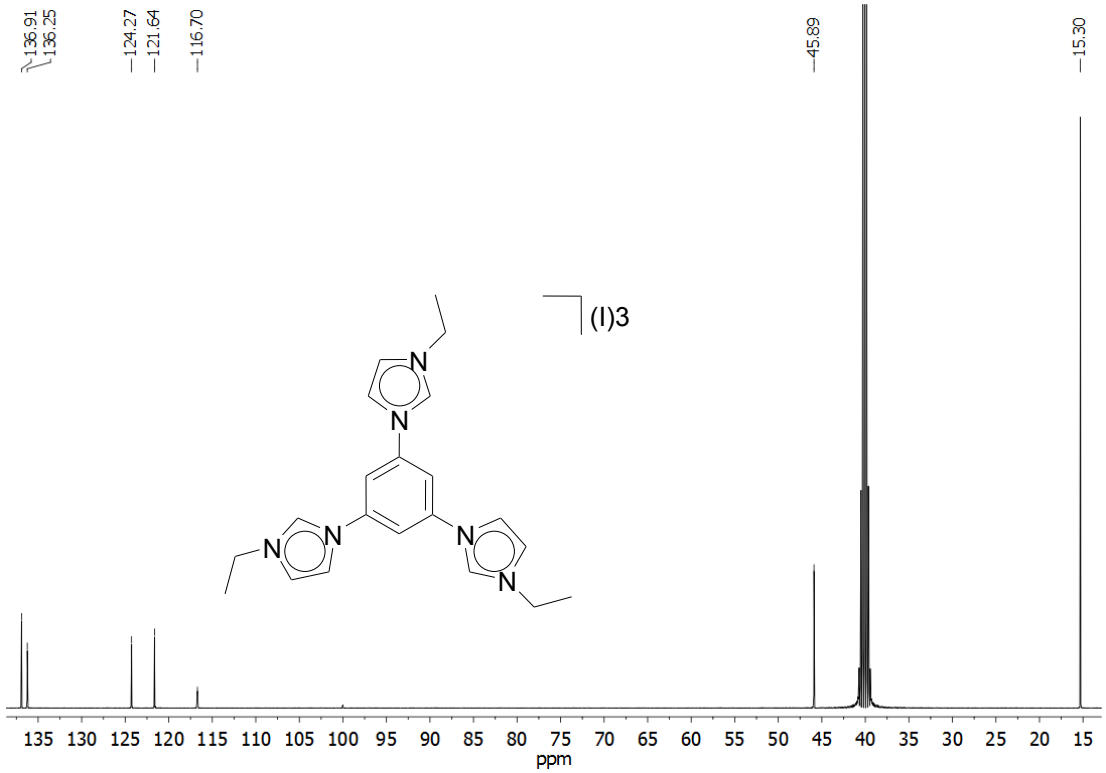

Figure S12. ^{13}C{^{1}H} NMR spectrum of **8** in DMSO-d_6.

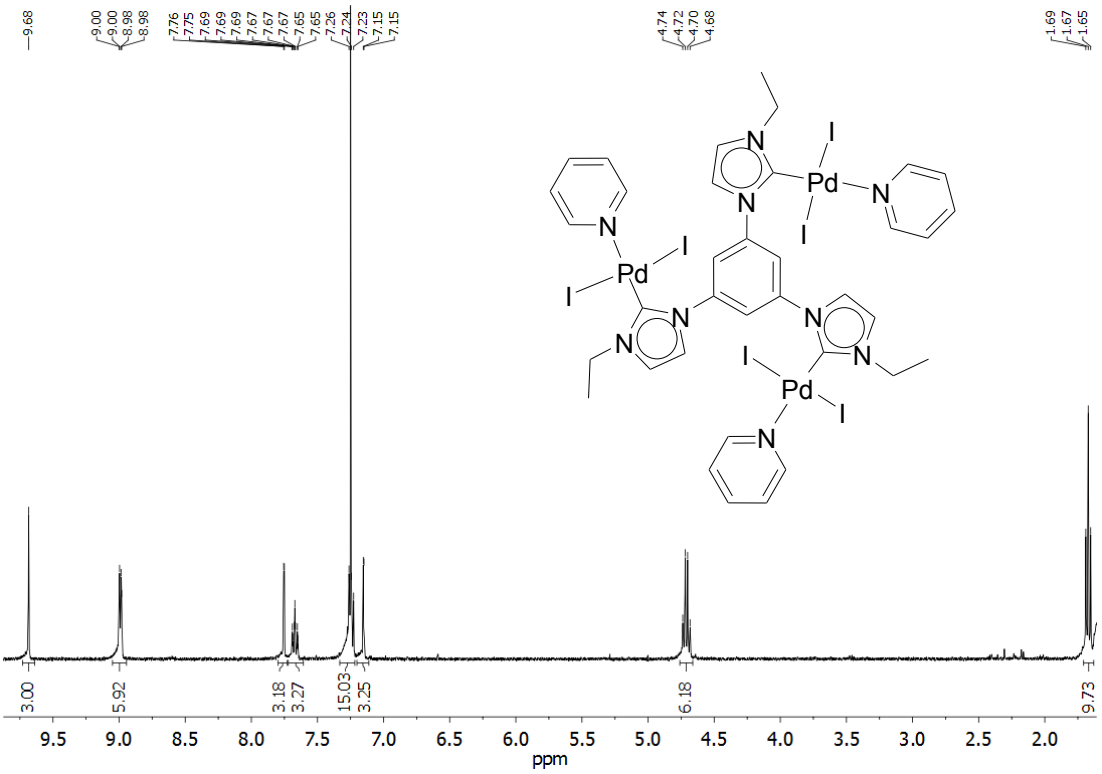

Figure S13. ^{1}H NMR spectrum of [**9**] in $CDCl_3$.

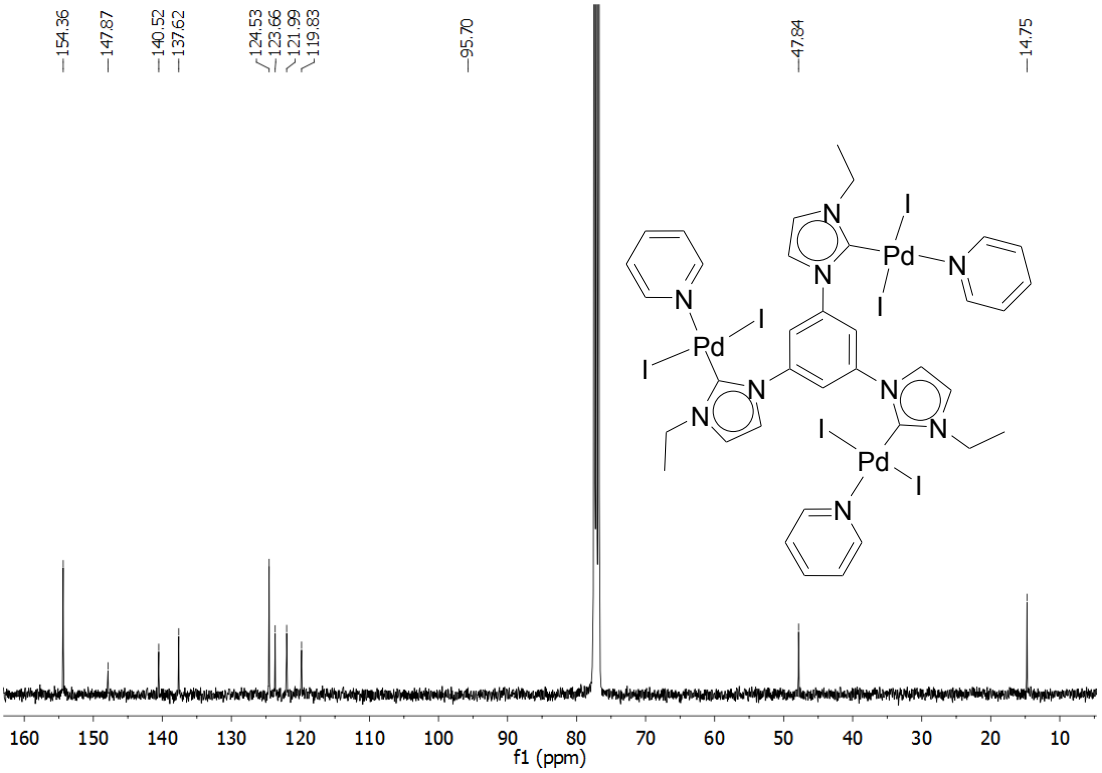

Figure S14. ^{13}C{^{1}H} NMR spectrum of [**9**] in $CDCl_3$.

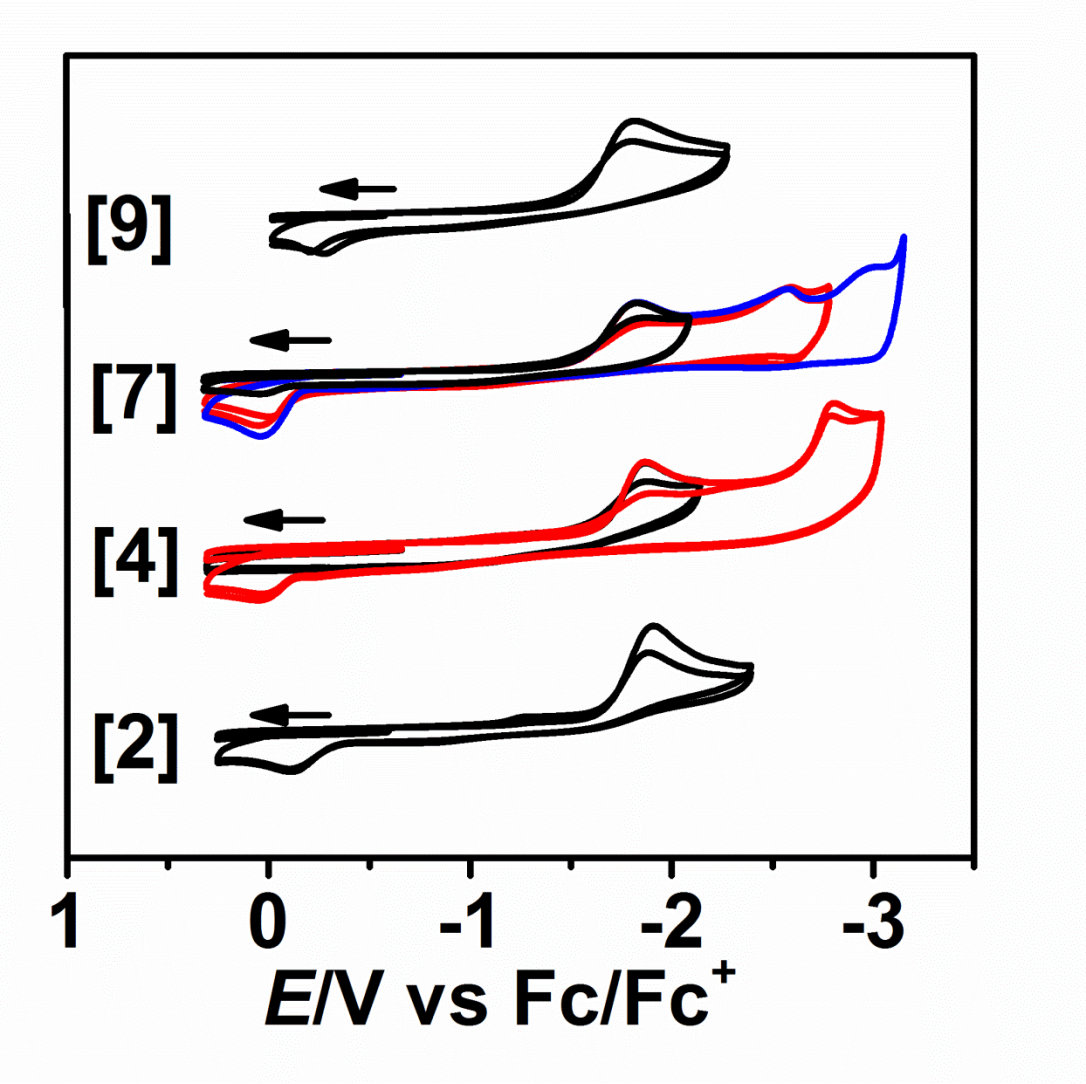

Figure S15. Cyclic voltammograms of the complexes in DMF / 0.1 M Bu_4NPF_6 at 295 K. Scan rate 250 mV / s. Fc/Fc^+ was used as an internal standard.

Table S4 Electrochemical data from cyclic voltammetry[a]

Complex	E^{red1} / V[b]	E^{ox1} / V[c]	E^{red2} / V[b]	E^{red3} / V[b]
[**2**]	-1.91	-0.11	-	-
[**4**]	-1.87	0.02	-2.80	-
[**7**]	-1.83	0.04	-2.59	-3.03
[**9**]	-1.80	-0.21	-	-

[a]Potentials from cyclic voltammetric measurements in DMF 0.1 M Bu_4NPF_6 at 298 K, scan rate 250 mV s^{-1}, ferrocene/ferrocenium was used as an internal standard. [b]Cathodic peak potential for irreversible reduction. [c]Anodic peak potential for irreversible oxidation.