Electronic supplementary information (ESI)

Synthesis of water-soluble palladium(II) complexes with N-heterocyclic carbene chelate ligands and their use in the aerobic oxidation of 1-phenylethanol

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1. ^{1}H and ^{13}C{^{1}H} NMR spectra for bis-carbene complexes 4–6

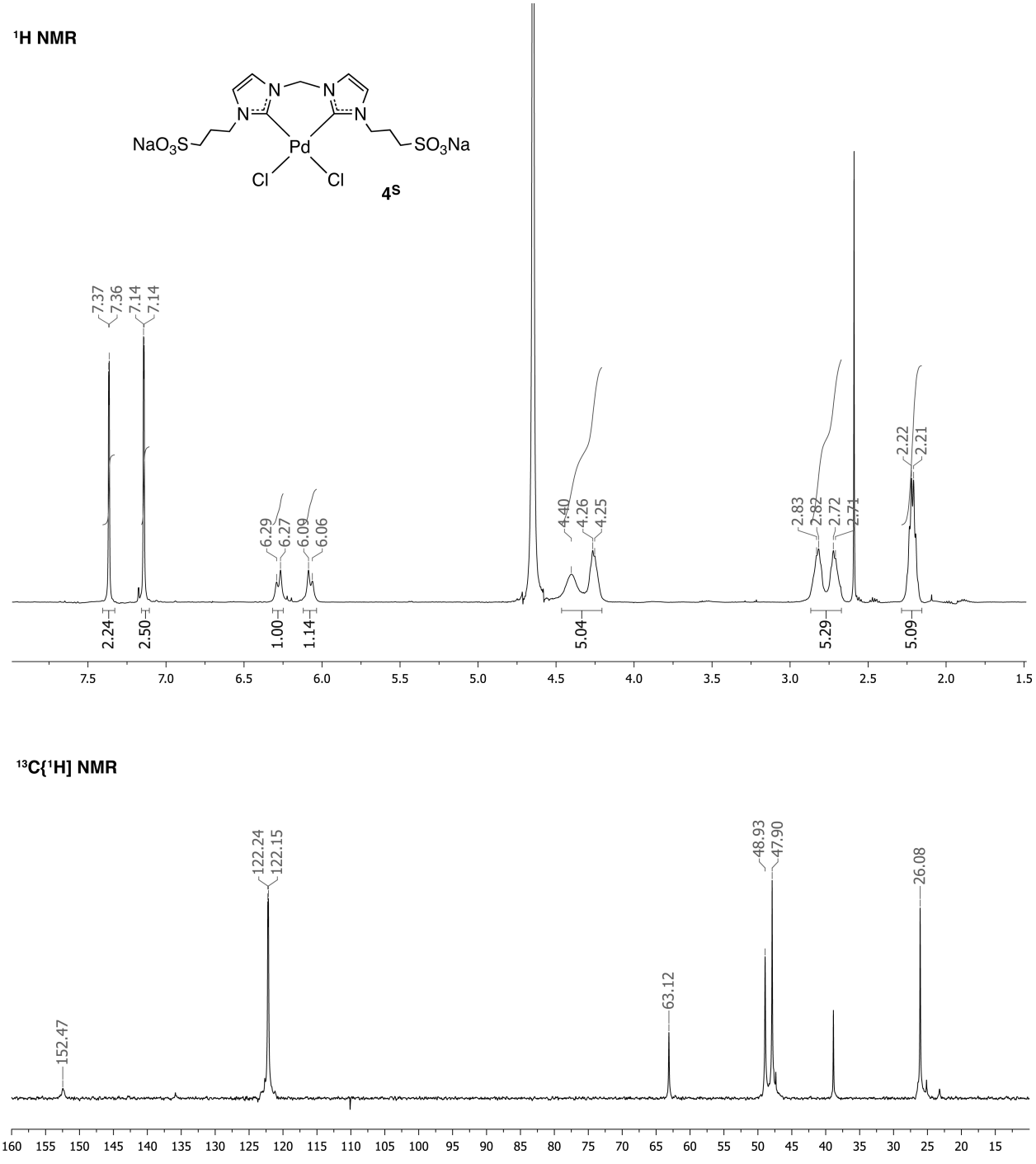

Fig. S1 ^{1}H and ^{13}C{^{1}H} NMR spectra for **4^{S}** in D_2O.

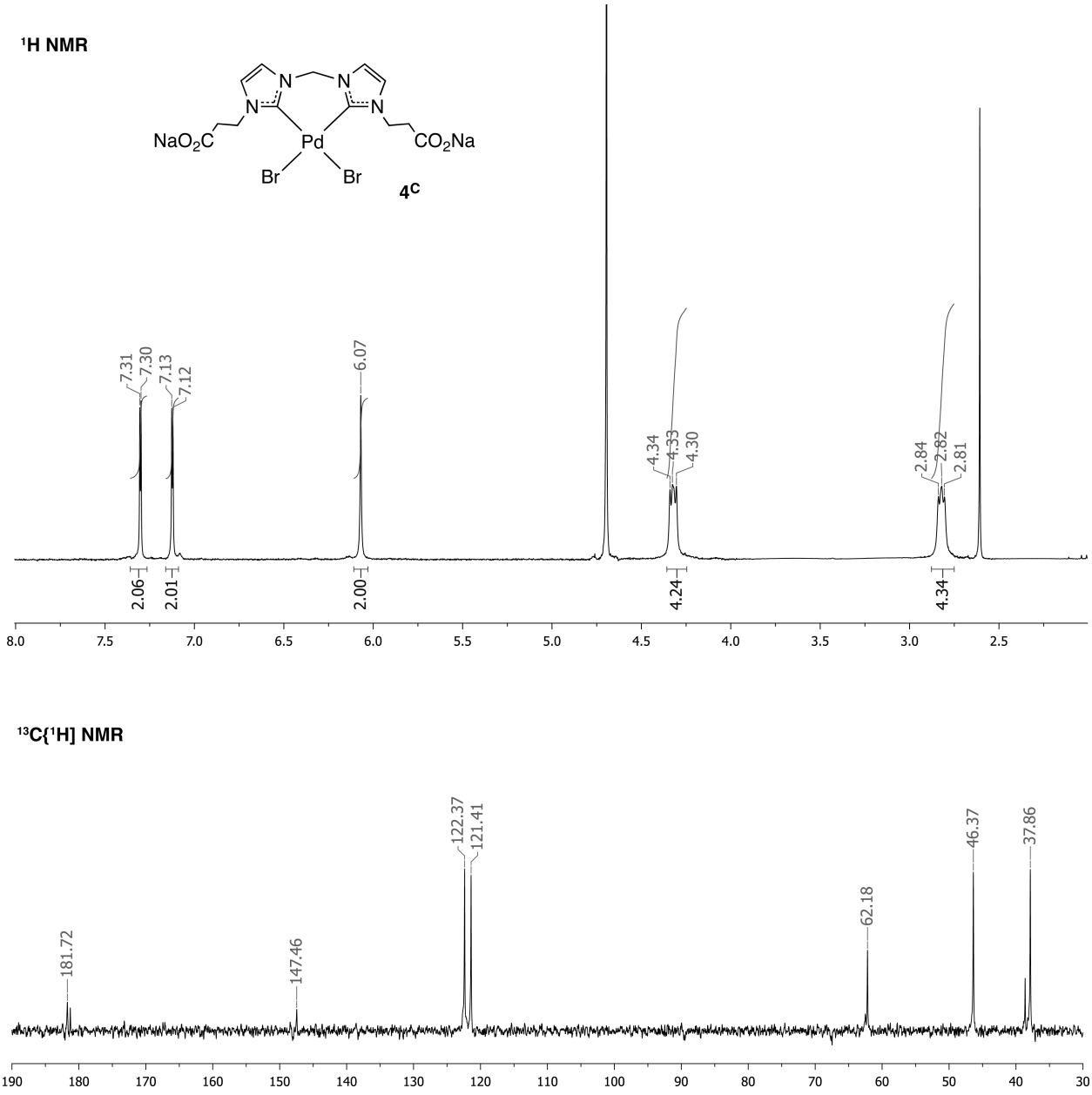

Fig. S2 ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for **4**^{C} in D_2O.

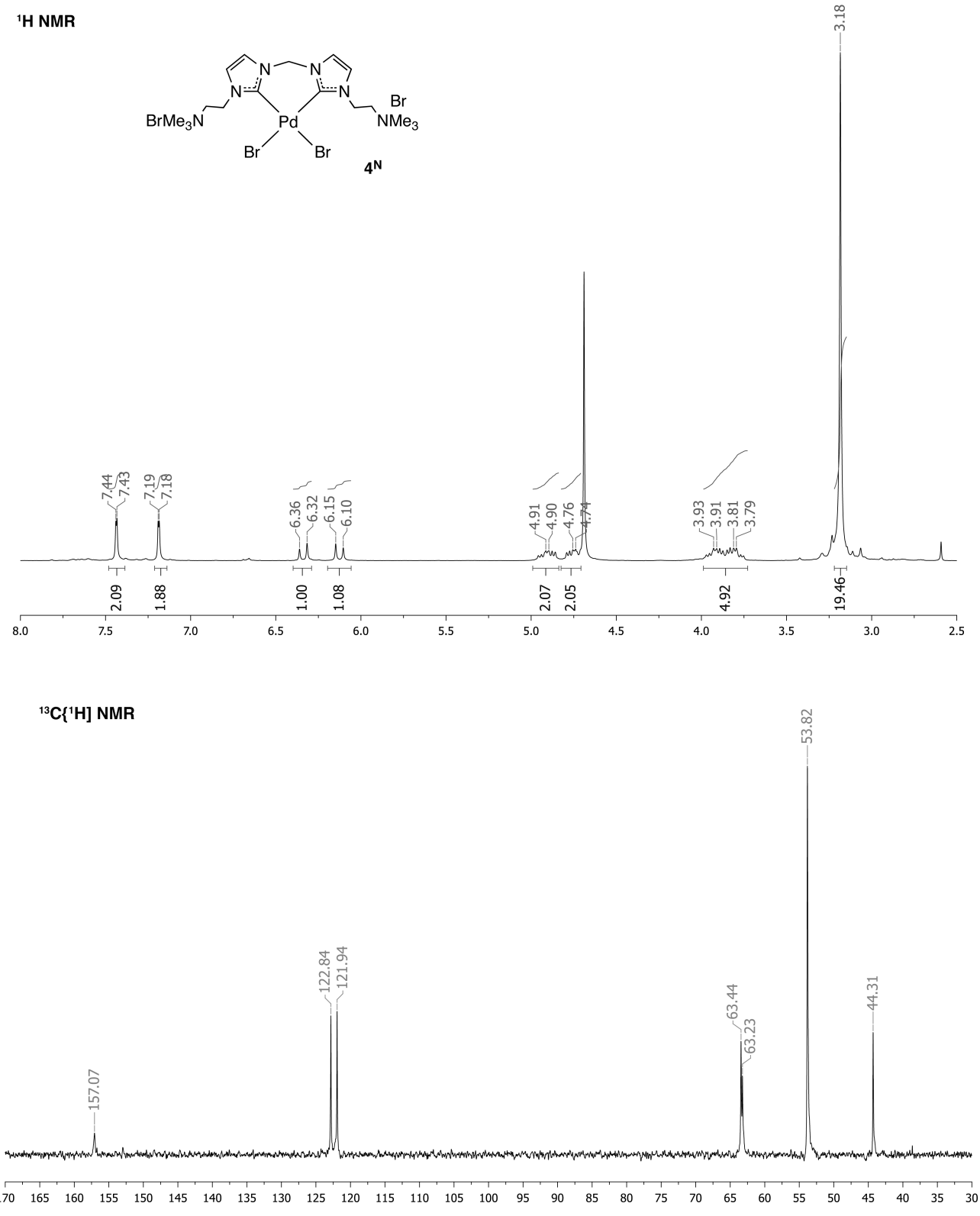

Fig. S3 ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for $\mathbf{4^N}$ in D_2O.

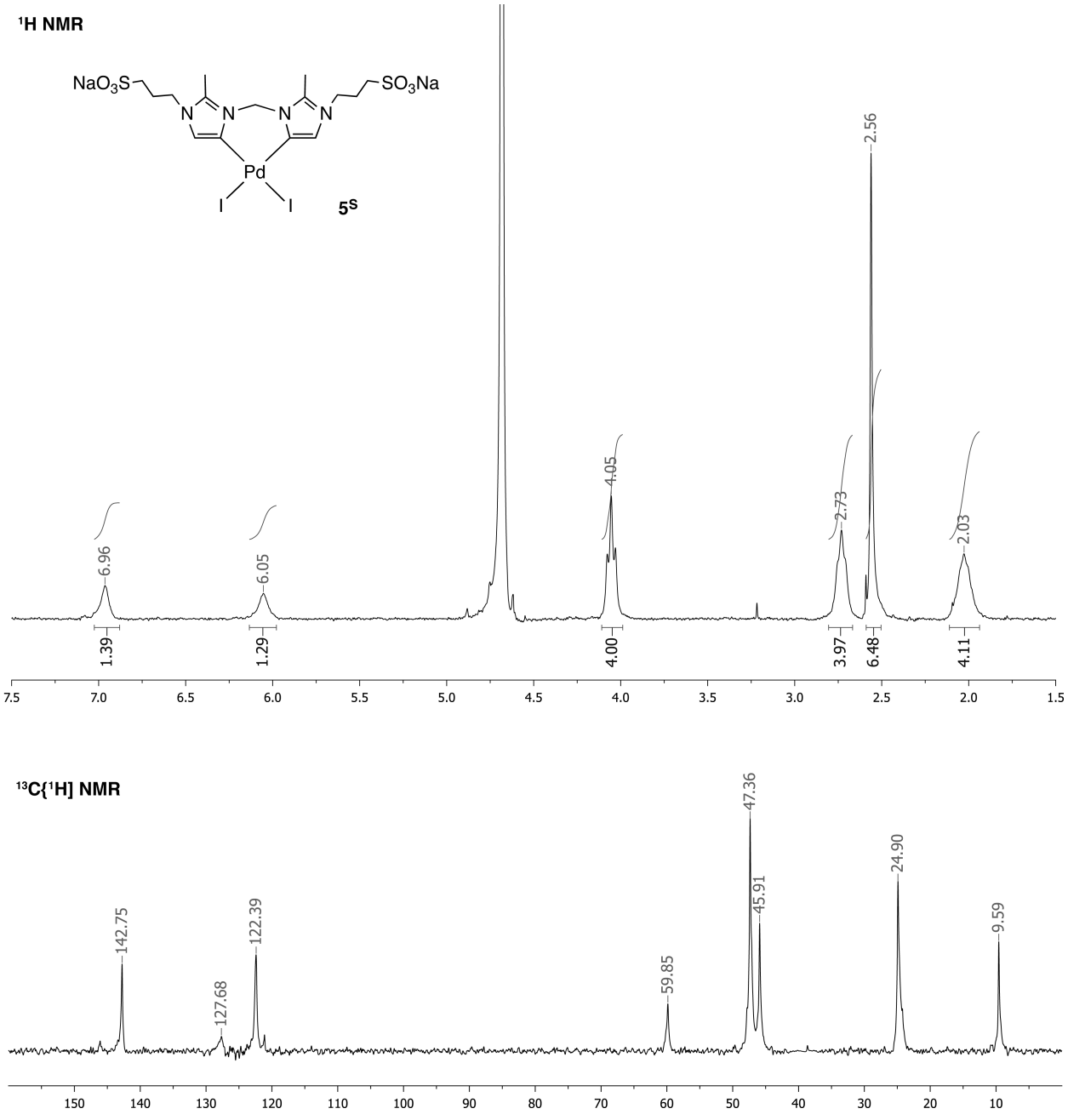

Fig. S4 ^{1}H and ^{13}C{^{1}H} NMR spectra for **5^{S}** in dmso-d_6.

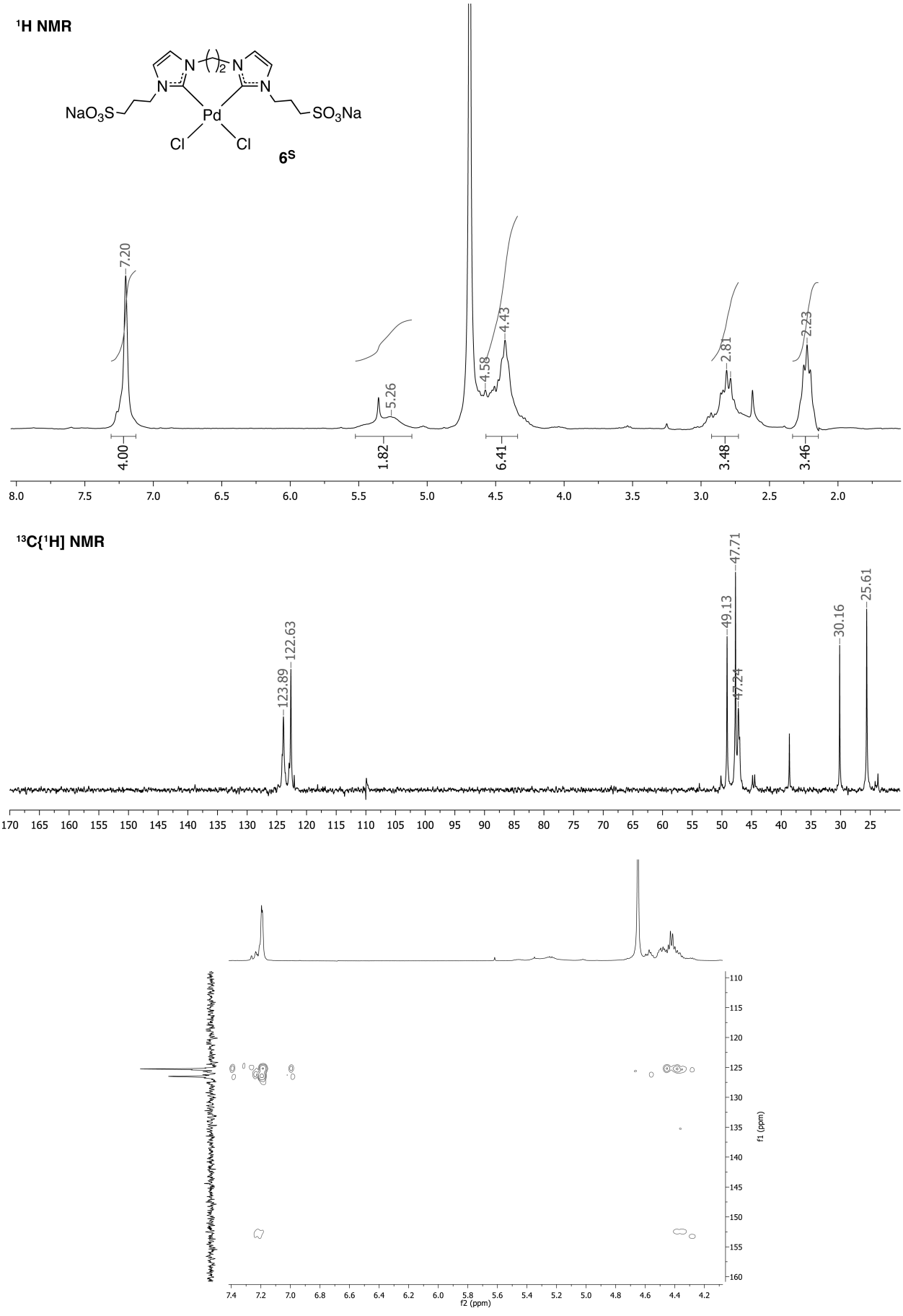

Fig. S5 ^{1}H, $^{13}C\{^{1}H\}$ and $^{1}H,^{13}C$-HMBC NMR spectra for **6^{S}** in D_2O.

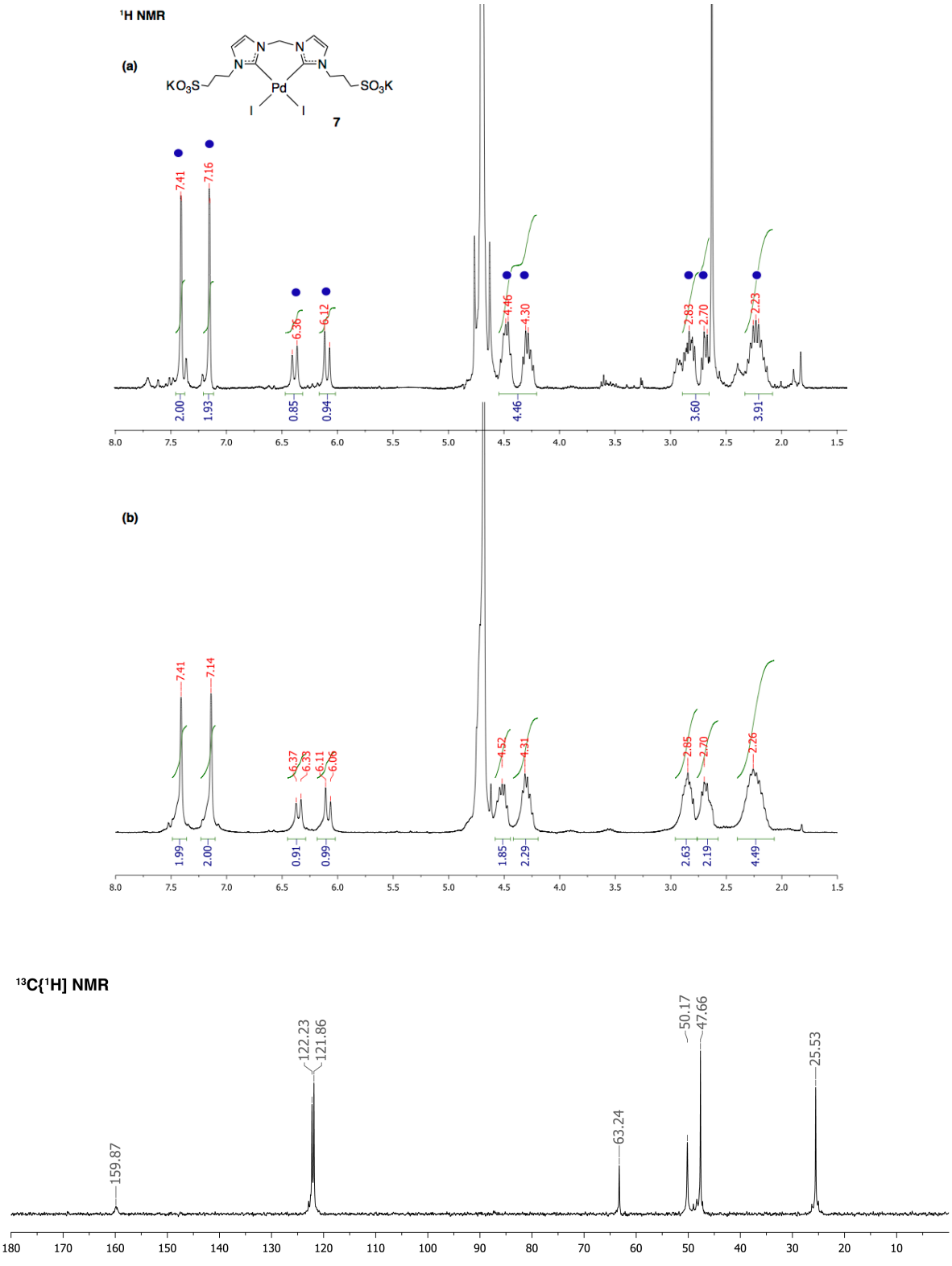

Fig. S6 ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for **7** in D_2O. (a) ^{1}H NMR spectrum of a sample of **7** obtained from $Pd(OAc)_2$. (b) ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of a sample of **7** obtained by dissolving dichlorido $\mathbf{4}^{S}$ in an excess of KI. The excess of KI was used to slow down the transformation of **7** into **8** that is observed in D_2O, permitting the accumulation of the ^{13}C NMR spectra without evolution of the sample.

2. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for tetrakis-carbene complexes 8 and 9

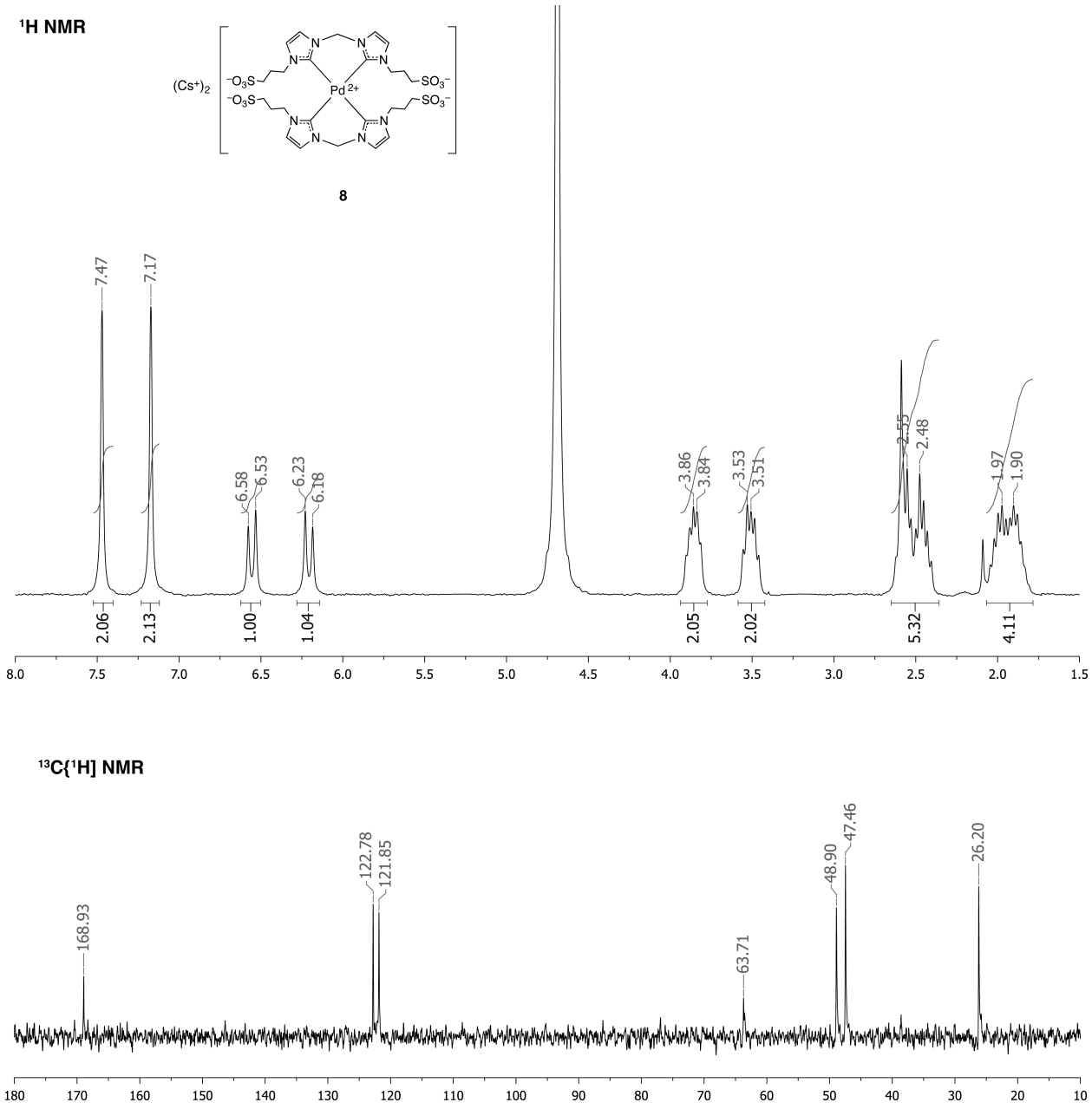

Fig. S7 ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for **8** in D_2O.

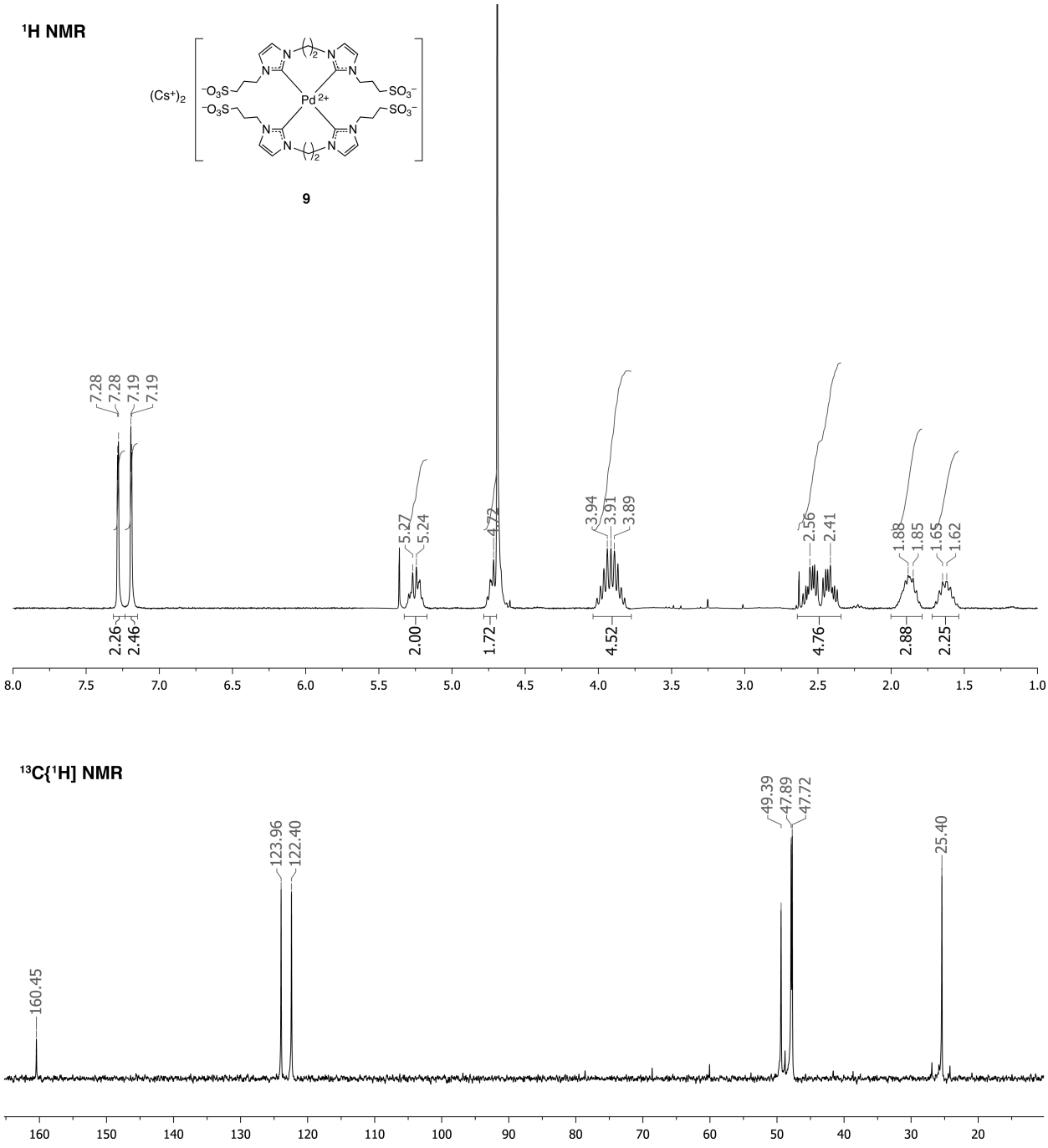

Fig. S8 ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for **9** in D_2O.

3. Crystallographic data for compounds 4^S-PPh_4 and 8

A summary of crystal data, data collection, and refinement parameters for the structural analysis is given in Table S1.

Table S1 Crystallographic data for compounds $\mathbf{4^S\text{-}PPh_4}$ and **8**.

	$\mathbf{4^S\text{-}PPh_4}$•$5H_2O$	$\mathbf{8}$•$^1/_6CsCl$•$^1/_3HCl$•$4H_2O$
empirical formula	$C_{61}H_{68}Cl_2N_4O_{11}P_2PdS_2$	$C_{78}H_{133}Cl_{1.5}Cs_{6.5}N_{24}O_{47}Pd_3S_{12}$
formula weight	1336.55	3780.10
crystal size (mm)	0.41 × 0.34 × 0.21	0.4 × 0.06 × 0.06
color / habit	colorless / prism	colorless / prism
temperature (K)	200(2)	200(2)
wavelength (Å)	0.71073	0.71073
crystal system	triclinic	triclinic
space group	*P*-1	*P*-1
a (Å)	13.305(4)	14.0002(13)
b (Å)	14.001(7)	14.4399(11)
c (Å)	17.266(10)	16.3759(15)
α (deg)	84.02(3)	96.682(7)
β(deg)	76.24(3)	100.591(7)
γ (deg)	80.48(3)	99.196(8)
volume ($Å^3$)	3074(3)	3175.9(5)
Z	2	1
calcd density (g/cm^3)	1.444	1.977
μ (mm^{-1})	0.571	2.577
F(000)	1384	1860
θ range (deg)	3.12 to 26.50	3.00 to 26.00
limiting indices (*h*, *k*, *l*)	–16/16, –17/17, –21/21	–16/17, –17/17, –20/20
no. of reflns collected	23595	21407
no. of reflns unique / R_{int}	12571 / 0.0442	12363 / 0.0644
no. of reflns observed [$I > 2\sigma(I)$]	7933	7048
completeness to θ	98.6%	99.1%
absorption correction	multi-scan	multi-scan
max. and min. transmission	0.823 and 0.731	0.802 and 0.614
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data / restraints / parameters	12571 / 0 / 773	12363 / 0 / 805
goodness of fit on F^2	0.971	0.962
*R*1 / *wR*2 [$I > 2\sigma(I)$][a]	0.0467 / 0.1052	0.0607 / 0.1461
*R*1 / *wR*2 (all data)	0.0968 / 0.1213	0.1232 / 0.1734
largest diff. peak and hole ($e/Å^3$)	0.896 and –0.627	2.039 and –2.119

[a] $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; $wR2 = \{[\Sigma w(F_o^2-F_c^2)]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

4. TEM images

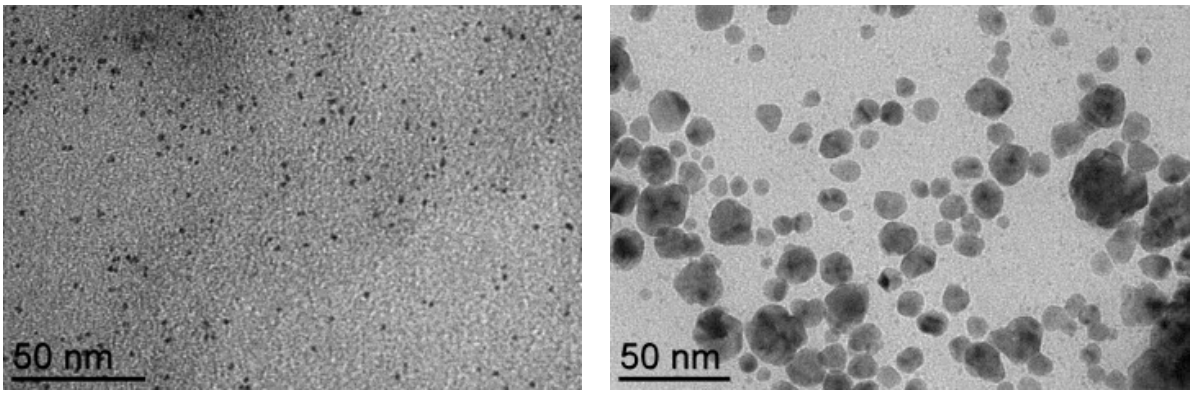

Fig. S9 Transmission electron microscopy images of the aqueous phase in the oxidation of 1-phenylethanol catalyzed by $\mathbf{4}^{S}$, after 4 hours of reaction. The sample for TEM was prepared by evaporation of 1 drop of the aqueous solution, on a holey copper grid covered by amorphous carbon.