Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Synthetic Routes to a Coordinatively Unsaturated Ruthenium Complex Supported by a Tripodal, Protic bis(N-heterocyclic Carbene) Phosphine Ligand

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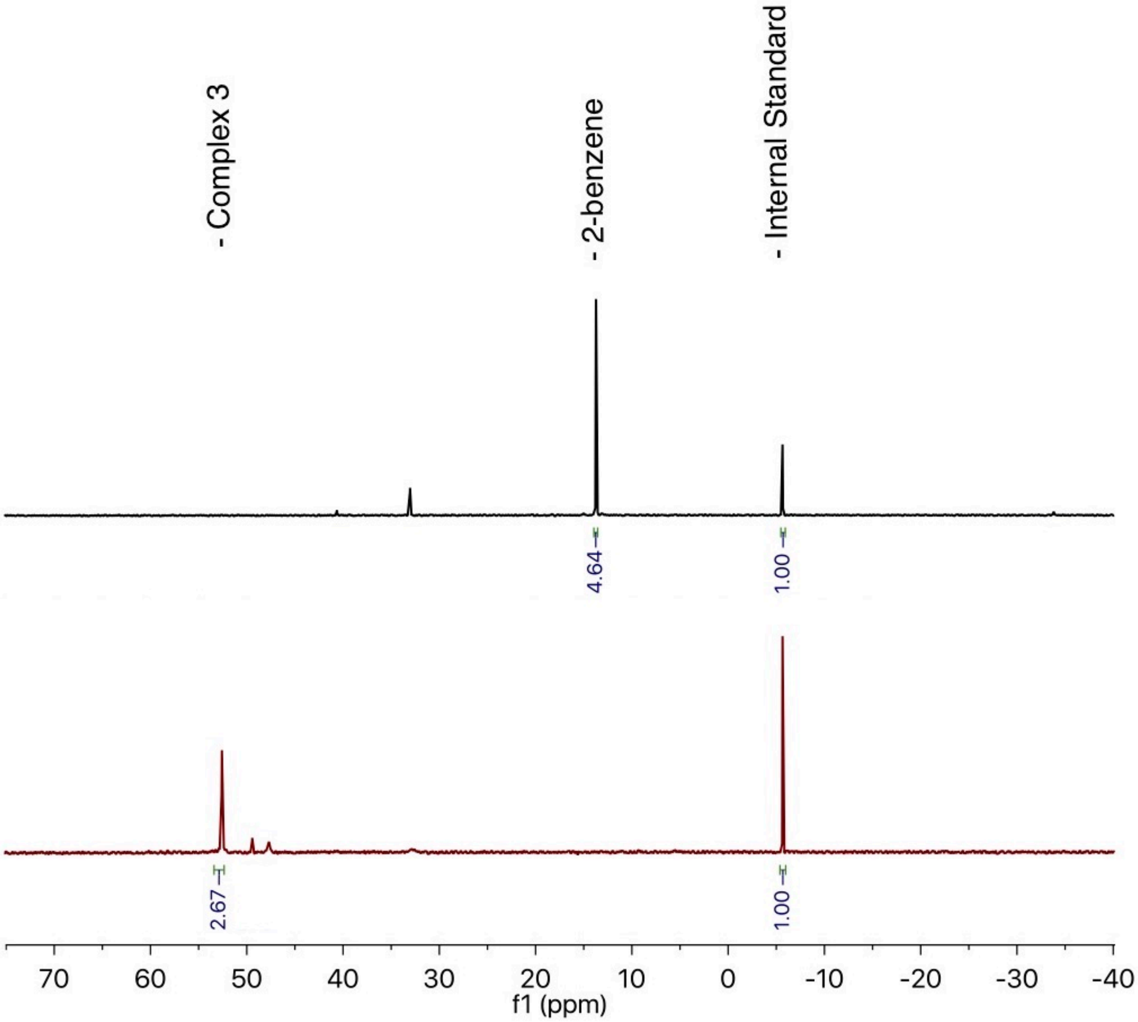

Figure S1. $^{31}P\{^1H\}$ NMR (299 K, 121.49 MHz) of **2-benzene** in NMP with a triphenyl phosphine internal standard in a capillary (top), heated at 170 °C for 45 minutes yielding complex **3** (bottom).

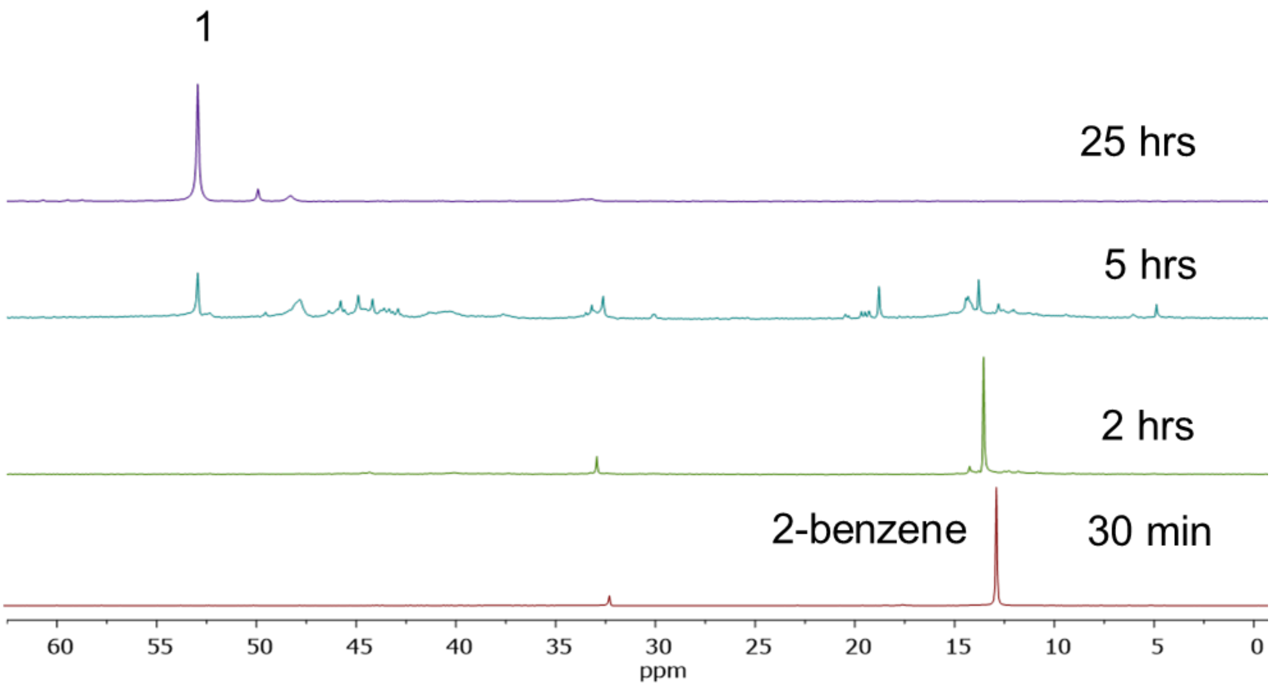

Figure S2. ^{31}P{^{1}H} NMR (298 K, 700 MHz) of **2-benzene** heated at 140 °C over time in NMP.

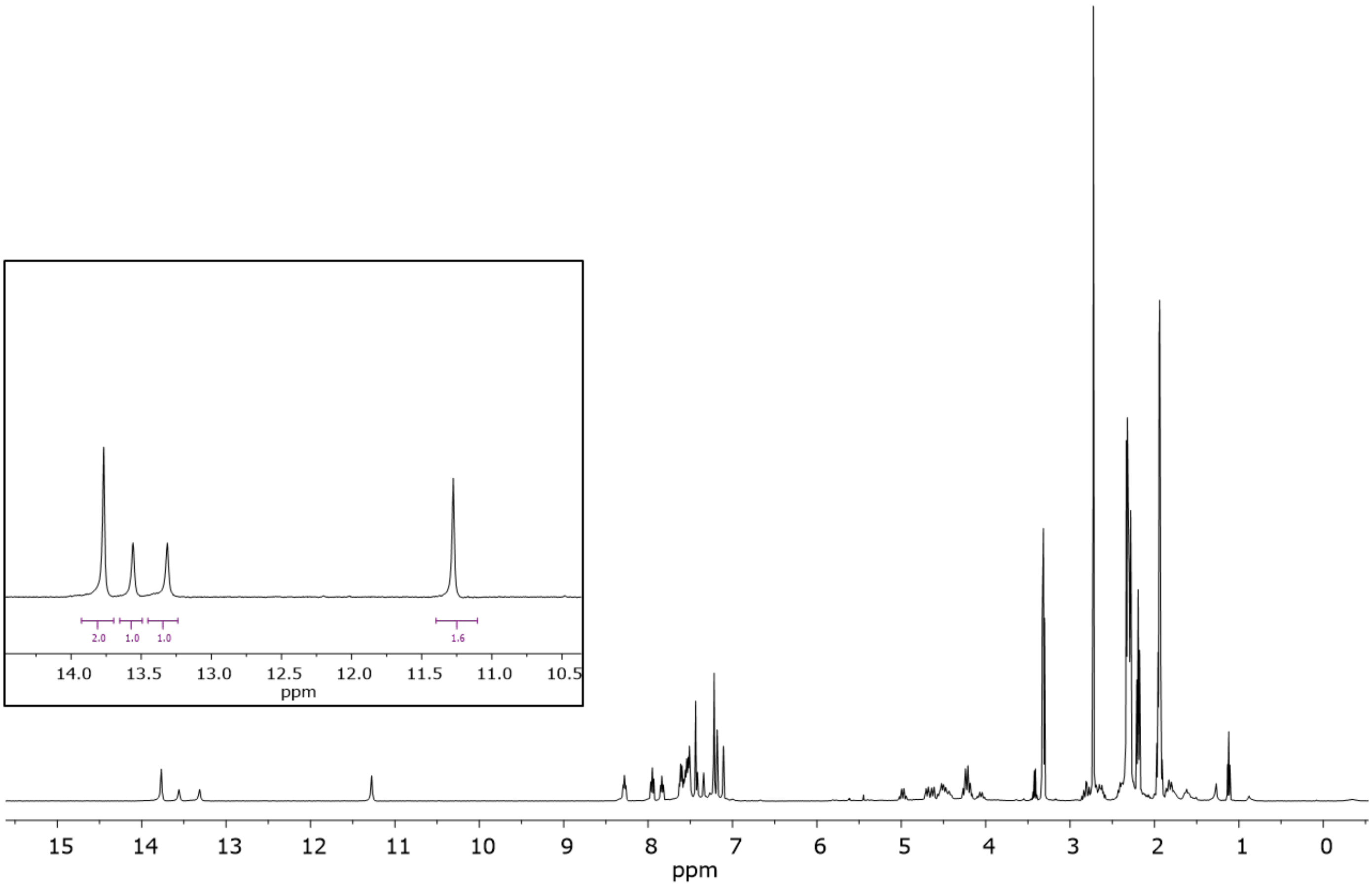

Figure S3. ^{1}H NMR (298 K, 499.72 MHz) of **3** in CD_3CN.

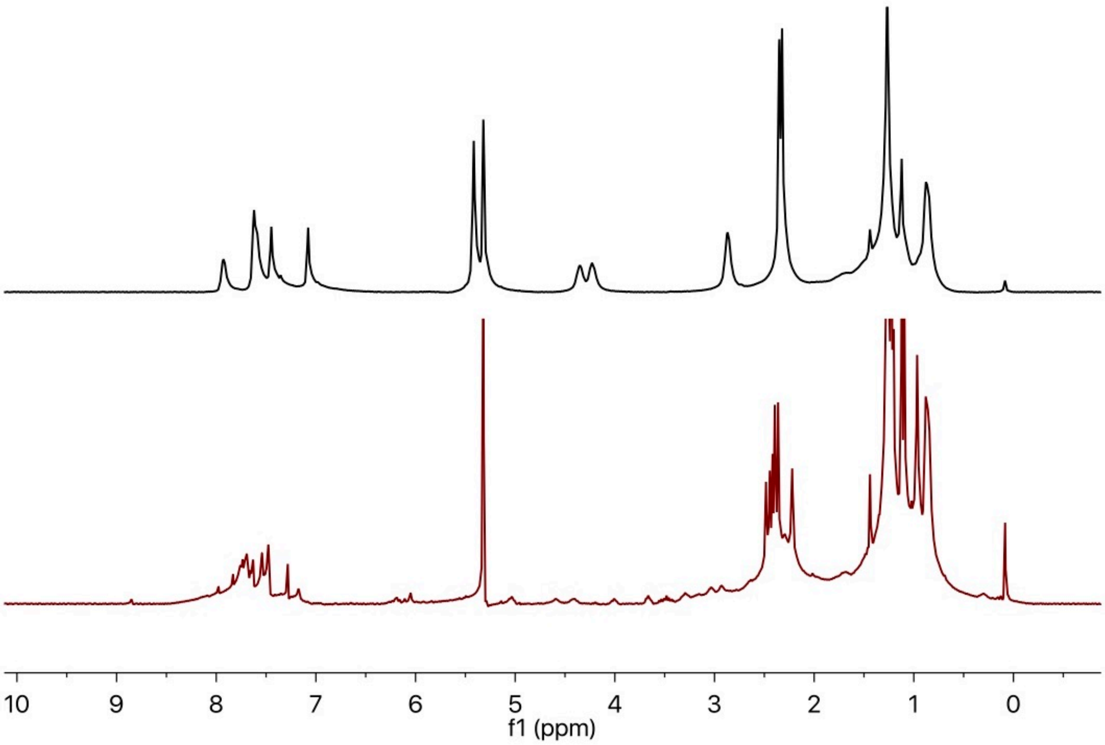

Figure S4. ^{1}H NMR (298 K, 499.7 MHz) in CD_2Cl_2 of **2-benzene** (top) and **2-benzene** with the addition of KOtBu after filtering (bottom).

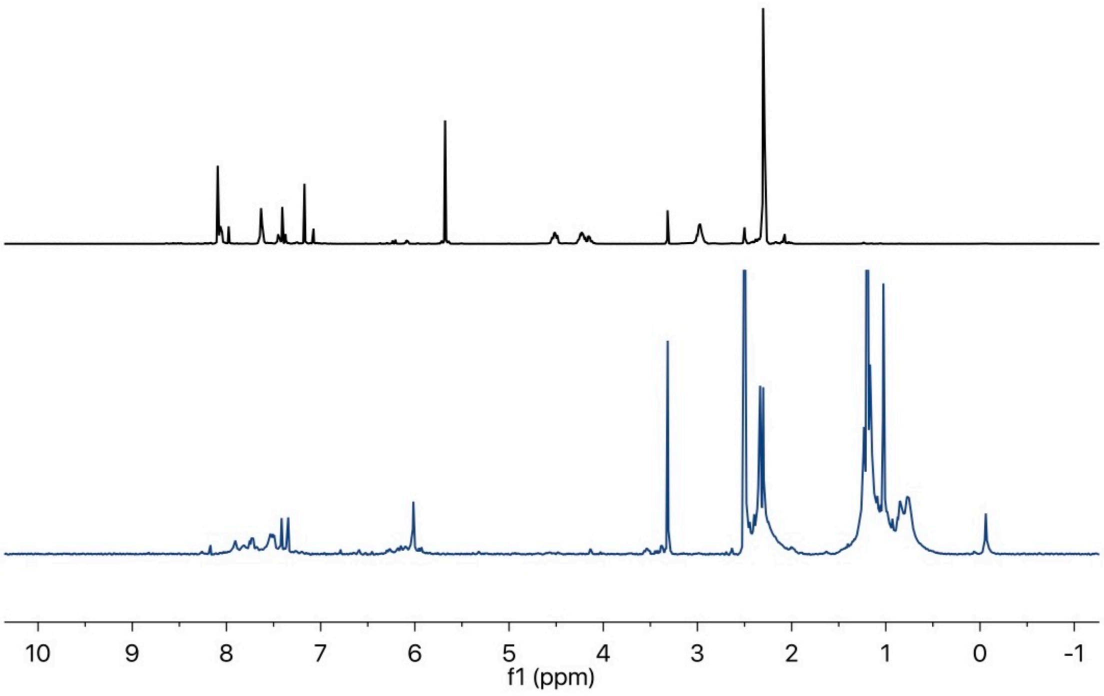

Figure S5. ^{1}H NMR (298 K, 499.7 MHz) in DMSO-d_6 of **2-benzene** (top) and **2-benzene** with the addition of KOtBu, followed by the addition of NH_4PF_6, filtered, concentrated, and redissolved in DMSO-d_6 (bottom).

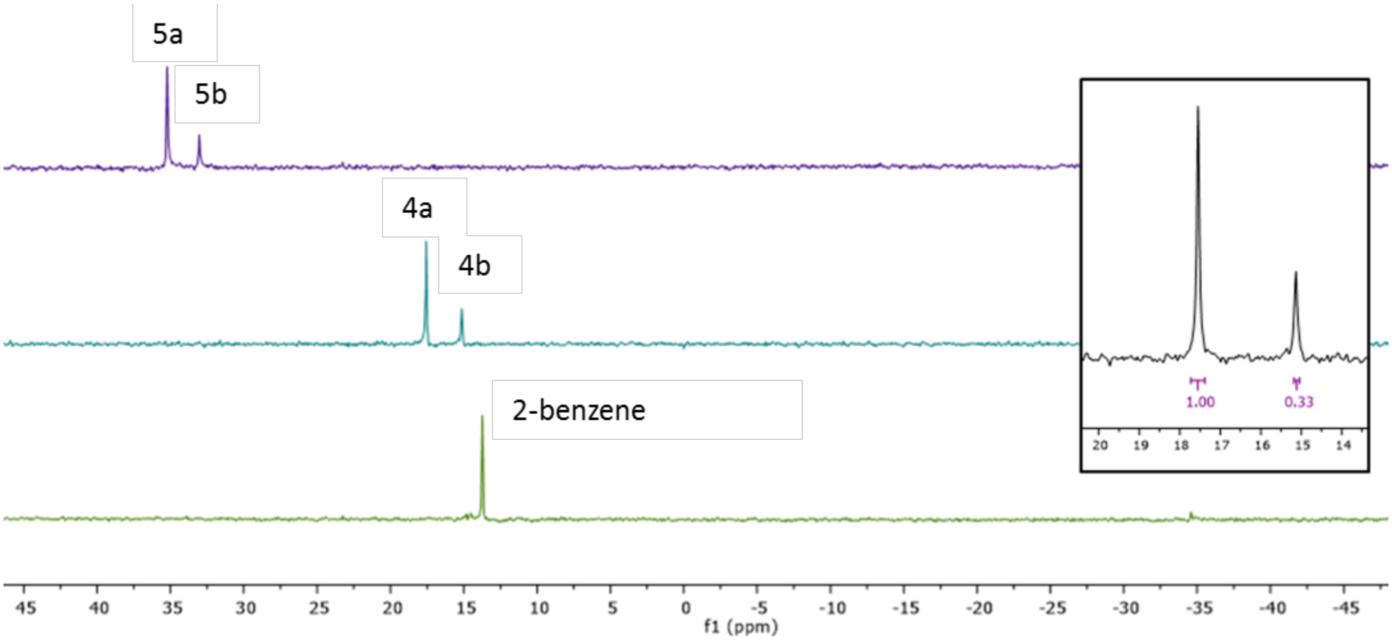

Figure S6. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (298 K, 700 MHz) spectra of 2, 4a, 4b, 5a, and 5b. DMSO-d$_6$.

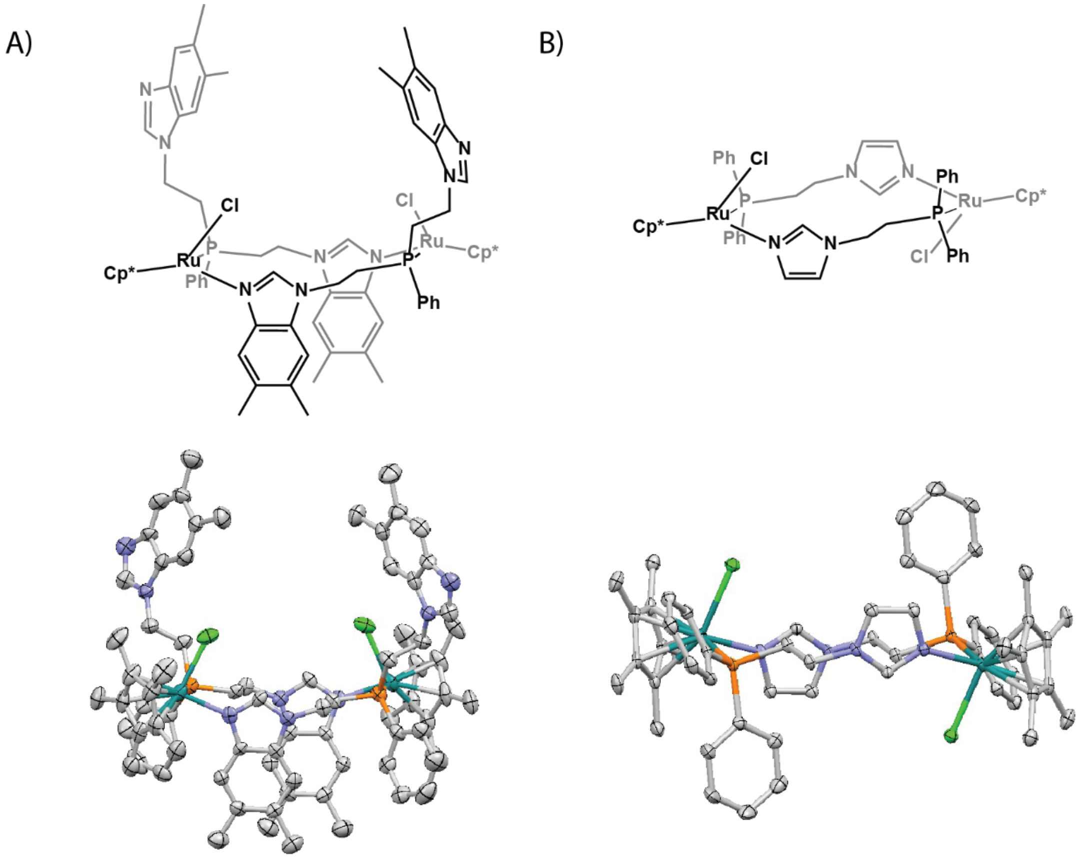

Figure S7. a) Crystal structure and ChemDraw model of [Cp*Ru(PNHC$_2$P^{Ph})Cl]$_2$, which show C$_2$ symmetry around the center of the molecule. b) Crystal structure and ChemDraw model of [Cp*Ru(PNHCP^{Ph2})Cl]$_2$ from unpublished work by Flowers and Lin, this molecule contains only a twofold improper inversion axis.

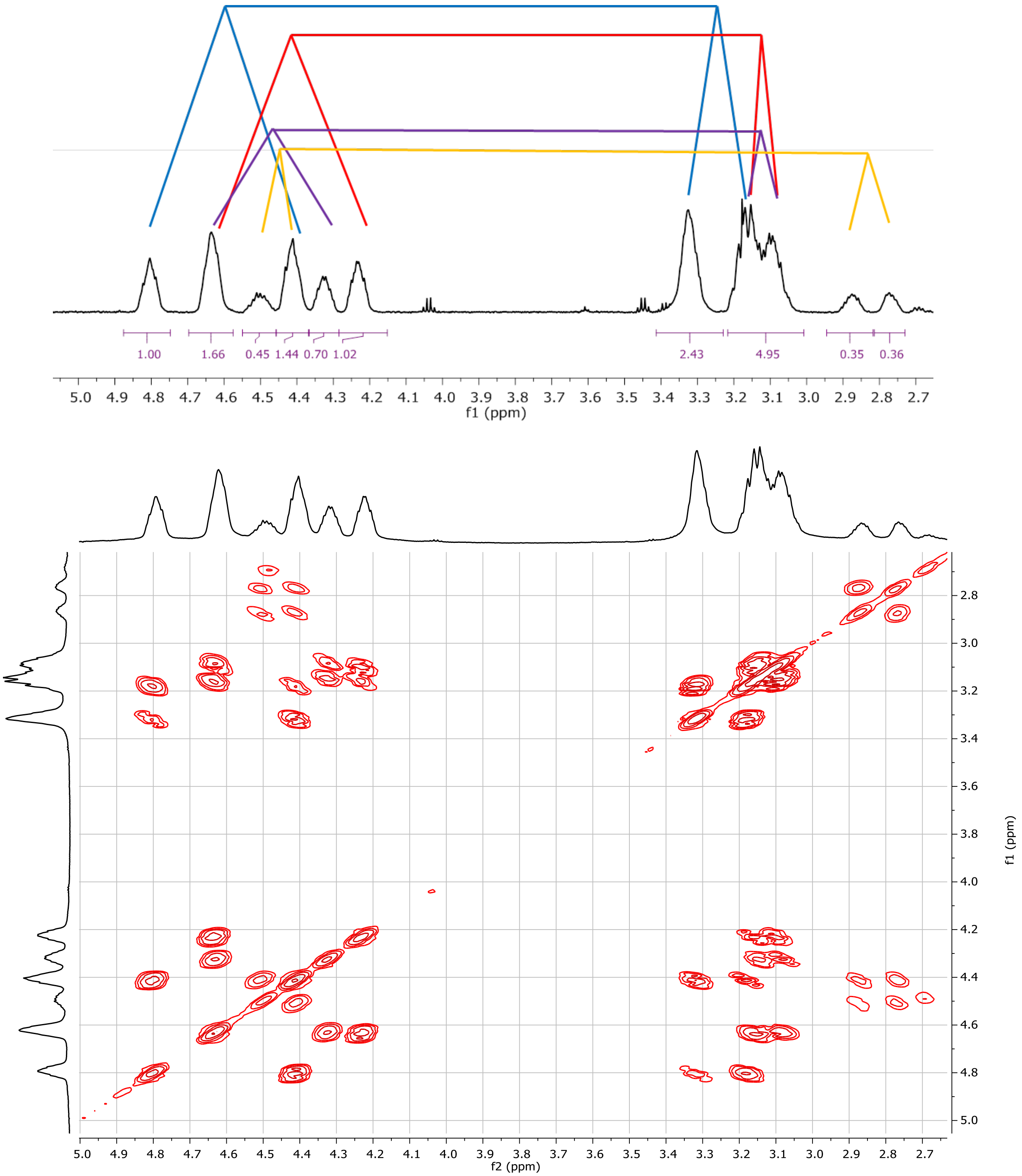

Figure S8. Top) ^{1}H NMR (DMSO-d$_6$, 298 K, 700 MHz) spectrum of the ethylene linker region of **5a** and **5b**. Bottom) COSY NMR spectrum of the ethyl linker region of **5a** and **5b**.

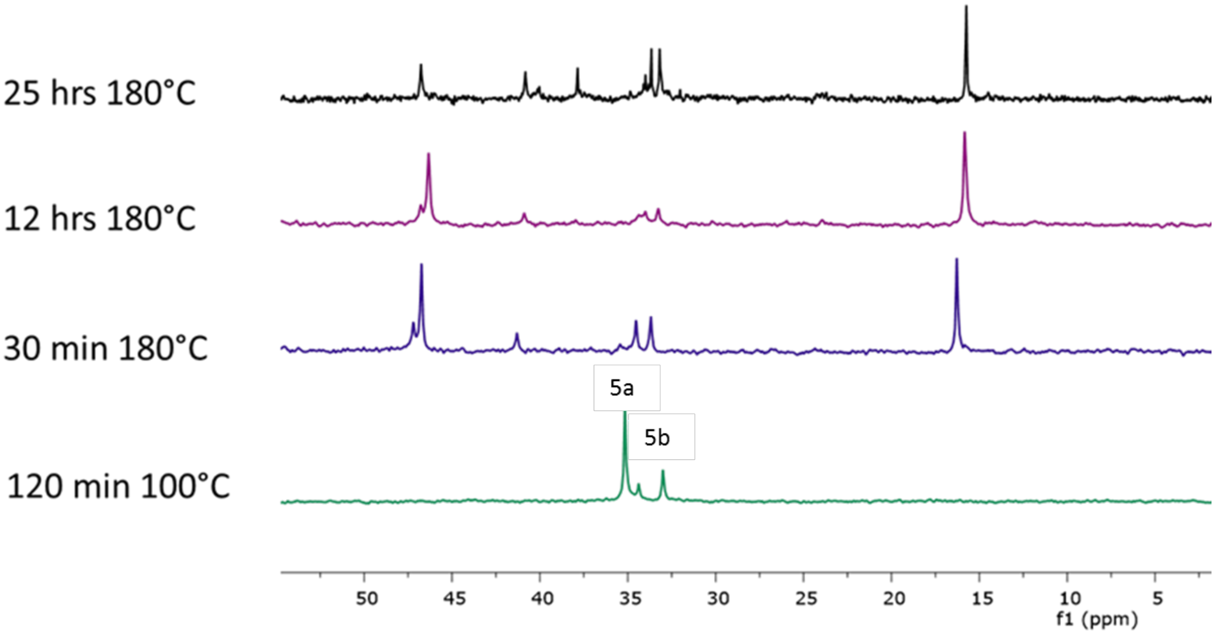

Figure S9. ^{1}H NMR (DMSO-d$_6$, 500 MHz) heating a mixture of **5a** and **5b** at 100 °C followed by 180 °C at different time points.

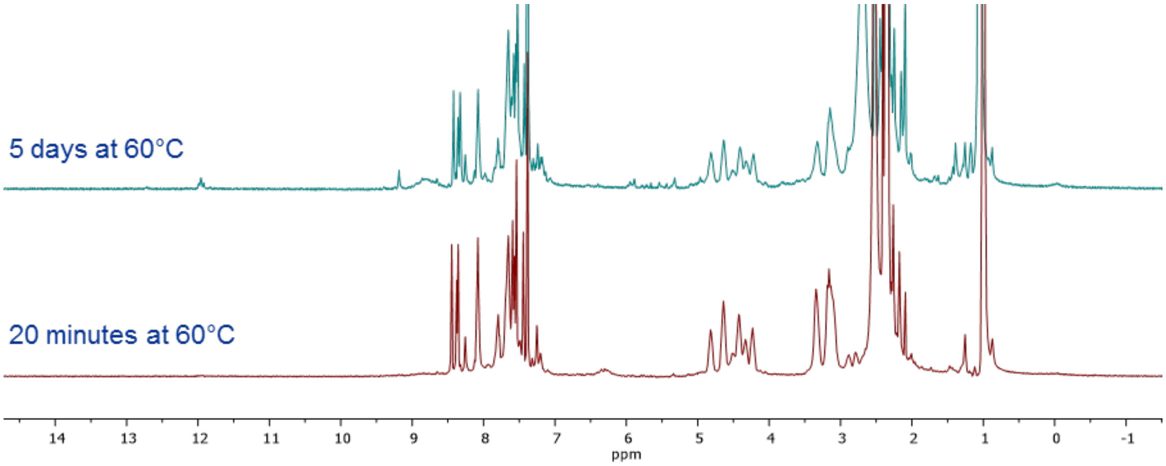

Figure S10. ^{1}H NMR (DMSO-d^6, 700 MHz, 298 K) of complexes **5a** and **5b** heated with triethyamine at 60 °C for 20 minutes (bottom) and 5 days (top).

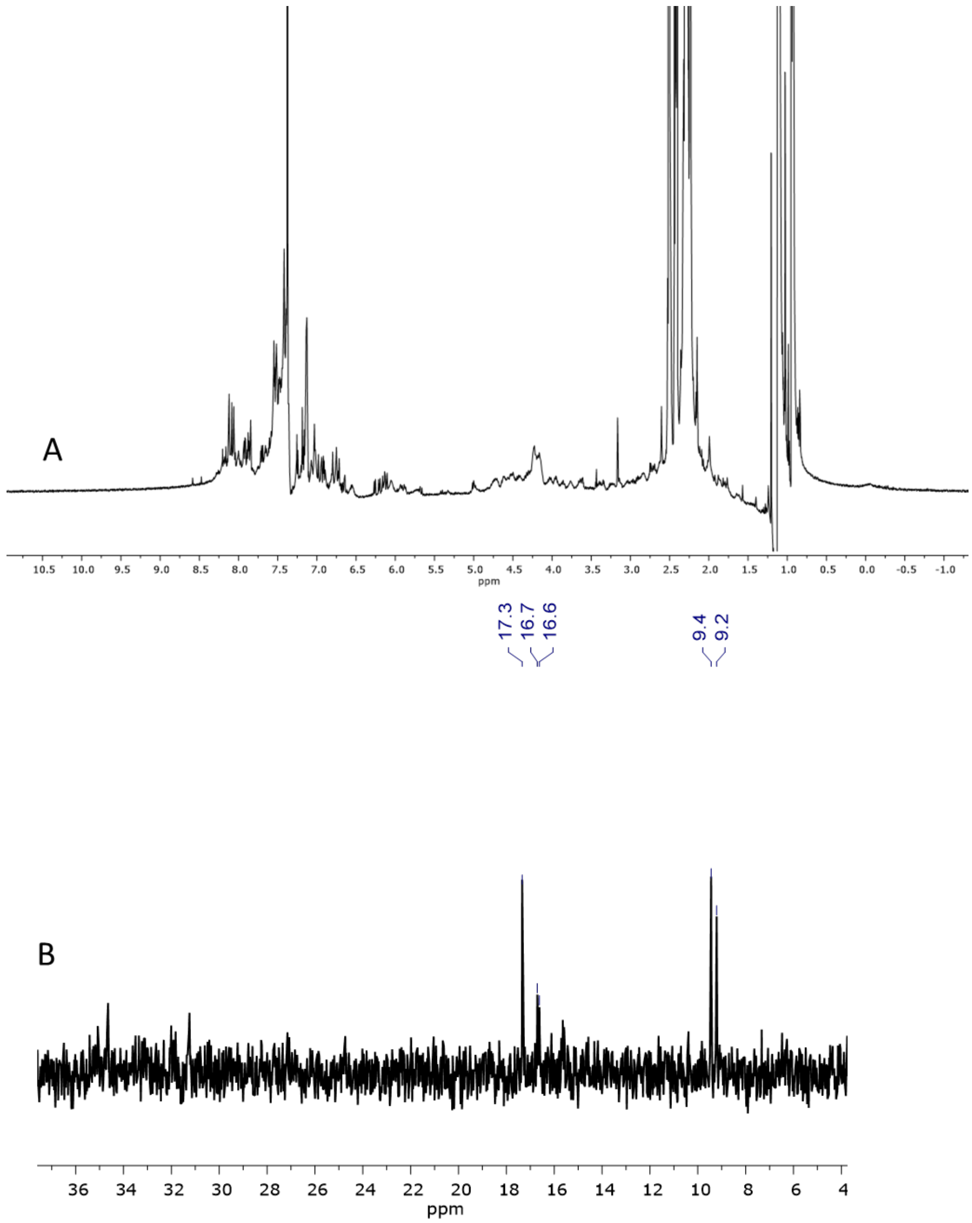

Figure S11. ^{1}H NMR (**A**, 700 MHz) and ^{31}P{^{1}H} NMR (**B,** 283.4 MHz) of **5a** and **5b** with addition of two equivalents of KOtBu to in DMSO-d$_6$ at 298 K.

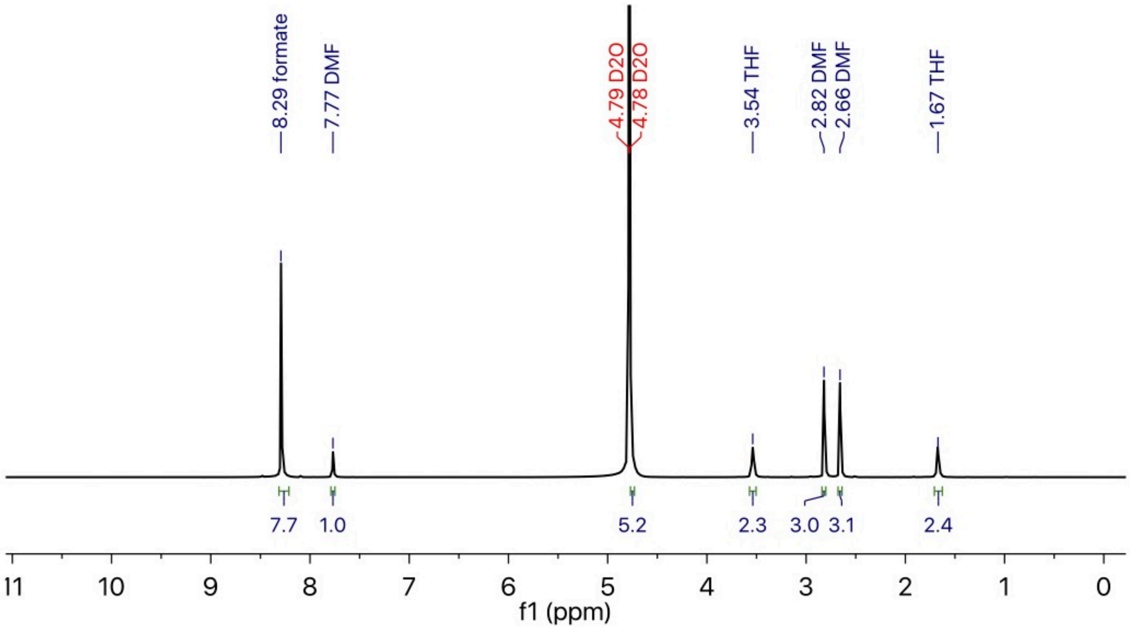

Figure S12. ^{1}H NMR analysis of formate production under catalytic CO_2 hydrogenation conditions, using **1** as a catalyst. ^{1}H NMR (298 K, 499.7 MHz) of precipitate dissolved in D_2O and with dimethylformamide (DMF) added as an internal standard.

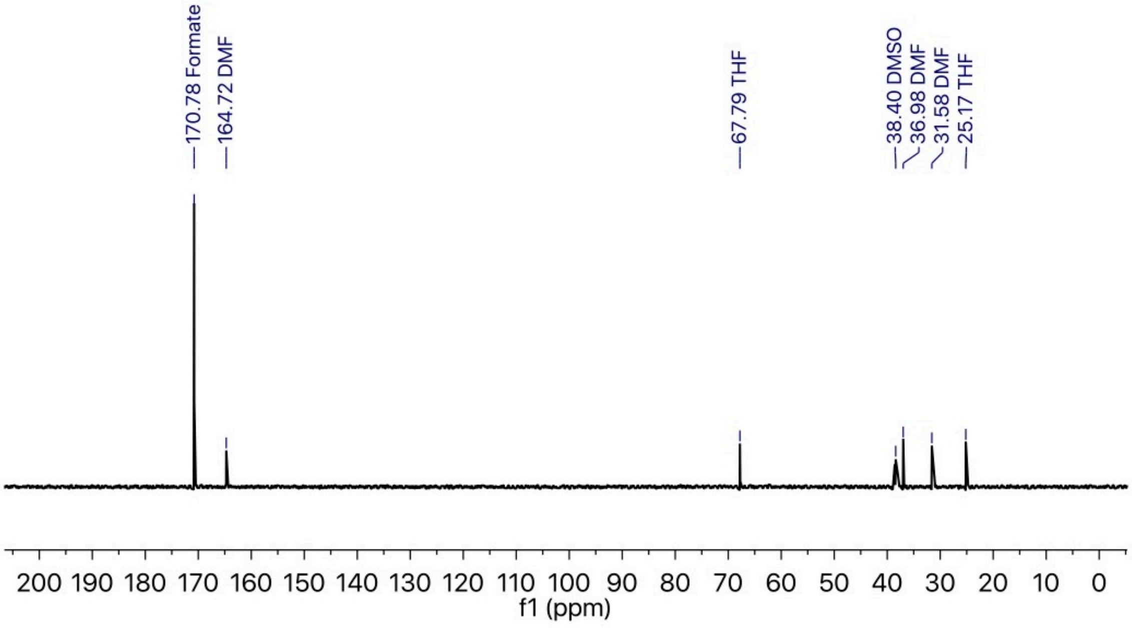

Figure S13. ^{13}C NMR (298 K, 125.7 MHz) of precipitate dissolved in D_2O, with DMF added as an internal standard.

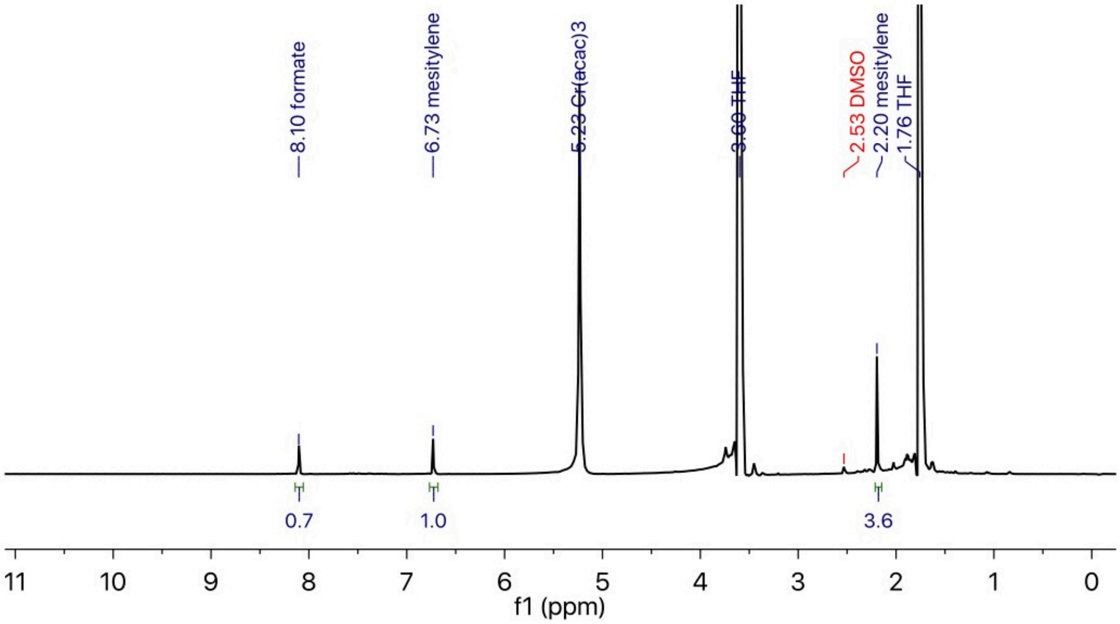

Figure S14. ^{1}H NMR analysis of formate production under catalytic CO_2 hydrogenation conditions, using **1** as a catalyst. ^{1}H NMR (298 K, 499.7 MHz) of crude solution, diluted with DMSO-d^{6} and with mesitylene added as an internal standard taken.

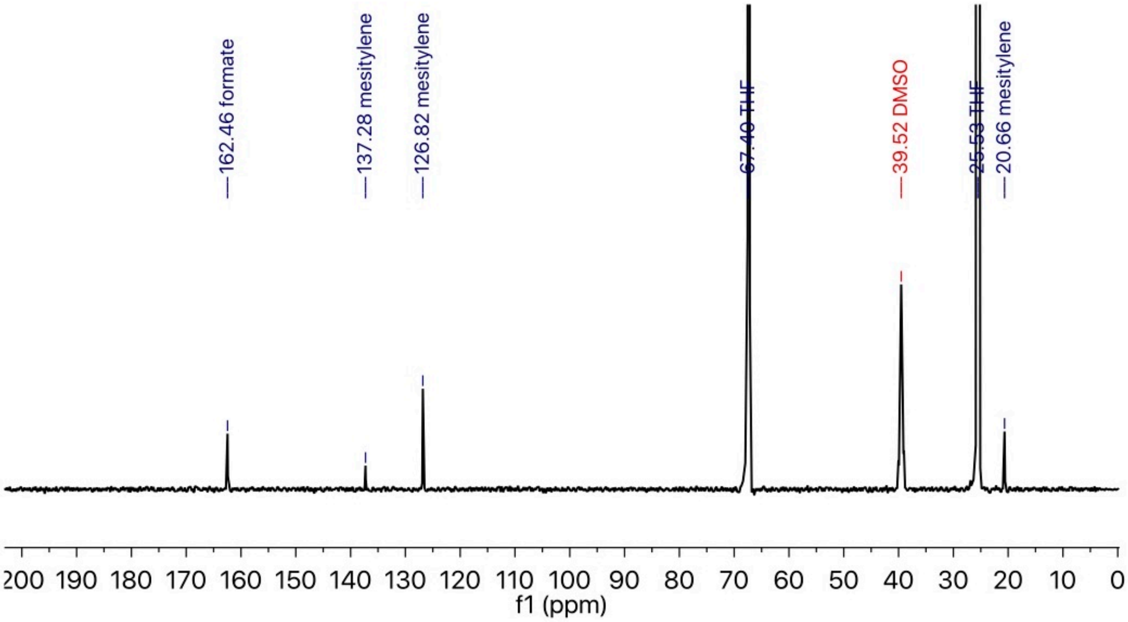

Figure S15. ^{13}C NMR (299 K, 125.7 MHz) of crude solution diluted with DMSO-d_6, with mesitylene added as an internal standard.

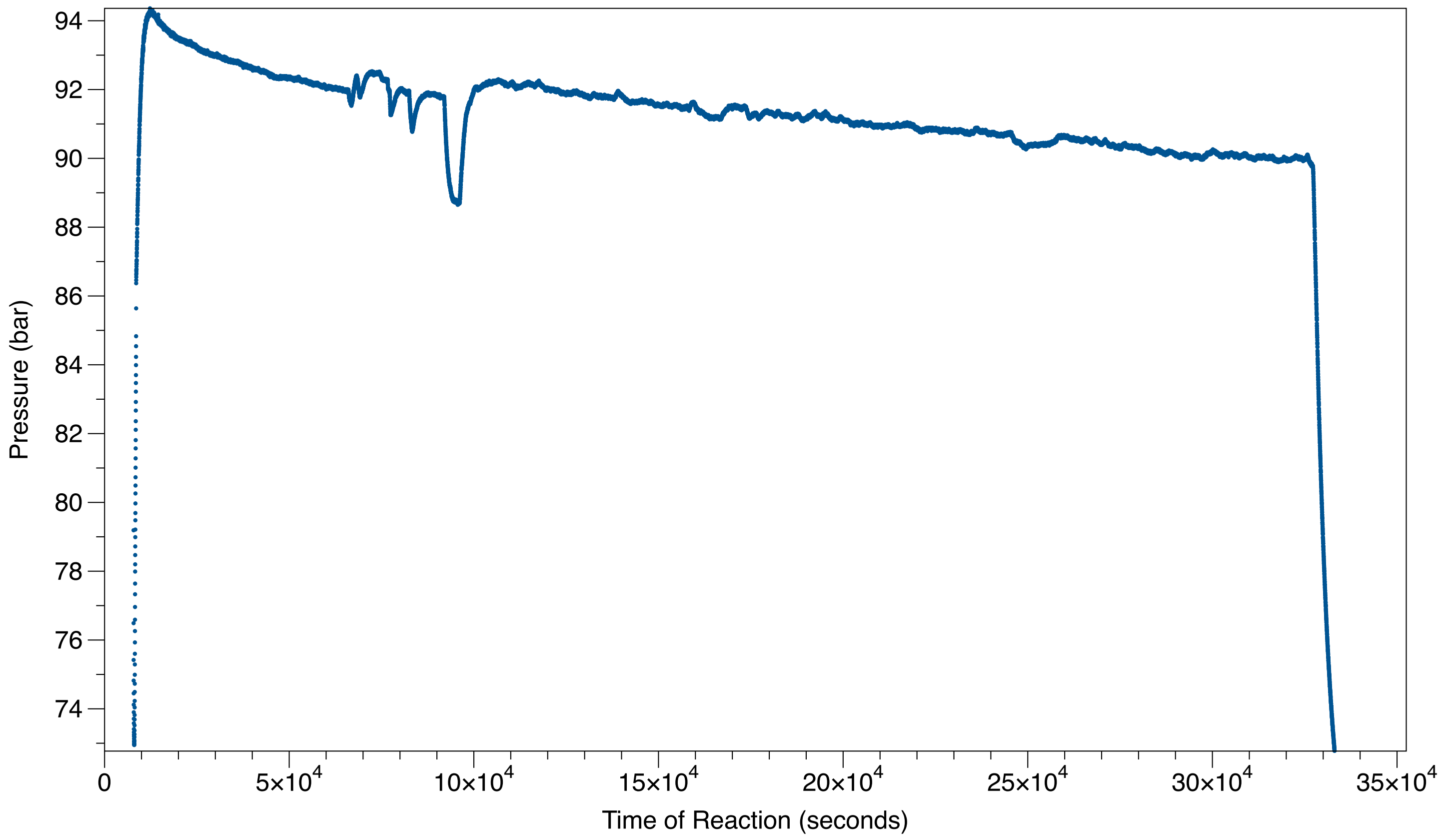

Figure S16. Pressure of Parr system vessel over the course of the reaction, shown in seconds. Unusual pressure spikes and dips between $6x10^4$ and $11x10^4$ seconds were consistent across multiple reactors on the Parr system manifold.

Additional NMR Spectra

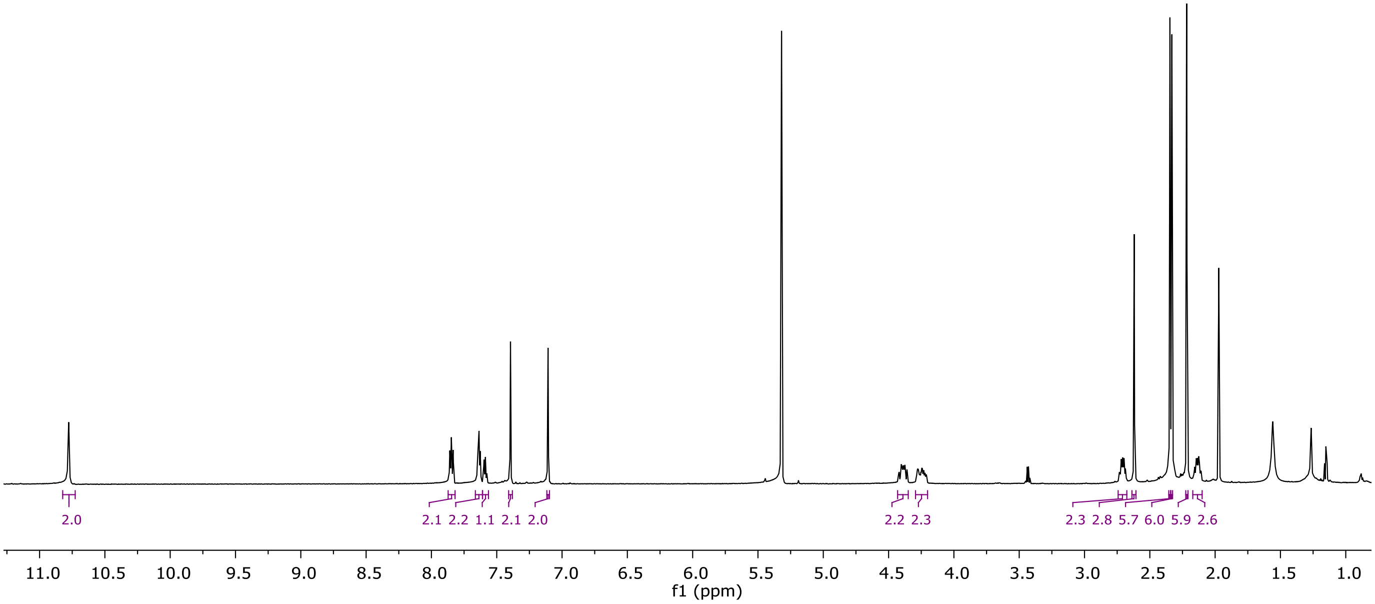

Figure S17. ^{1}H NMR (298 K, 499.7 MHz) of **1** in CD_2Cl_2.

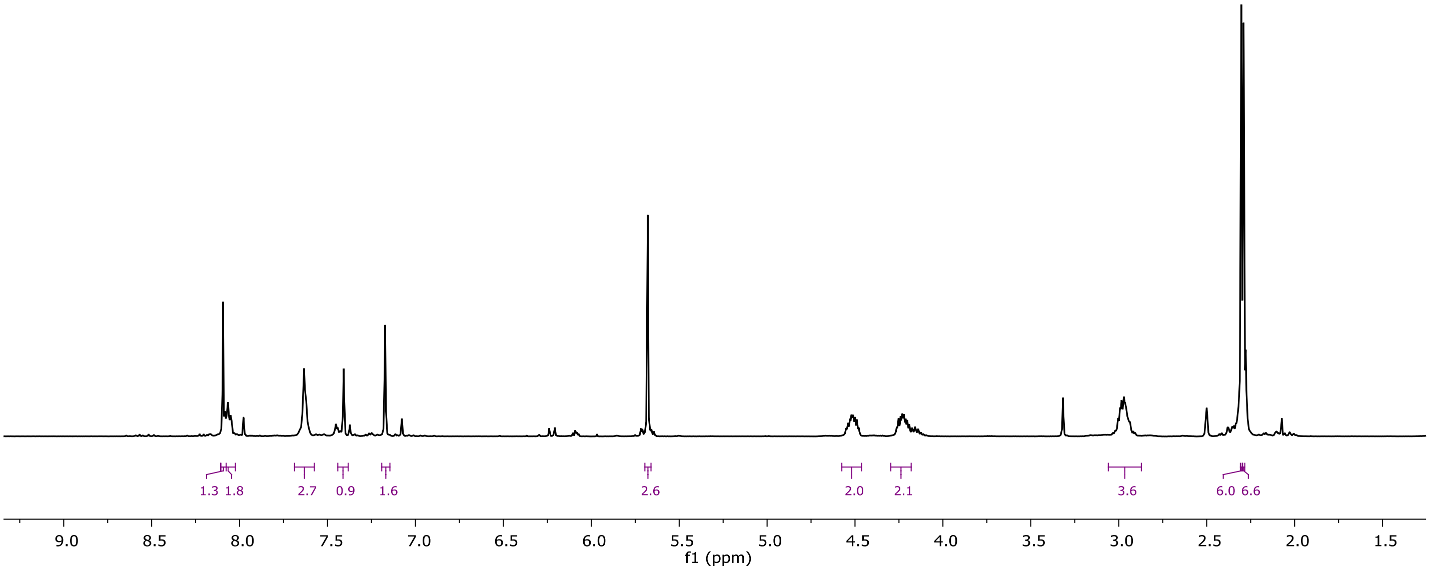

Figure S18. ^{1}H NMR (298 K, 499.72 MHz) of **2-benzene** in DMSO-d_6.

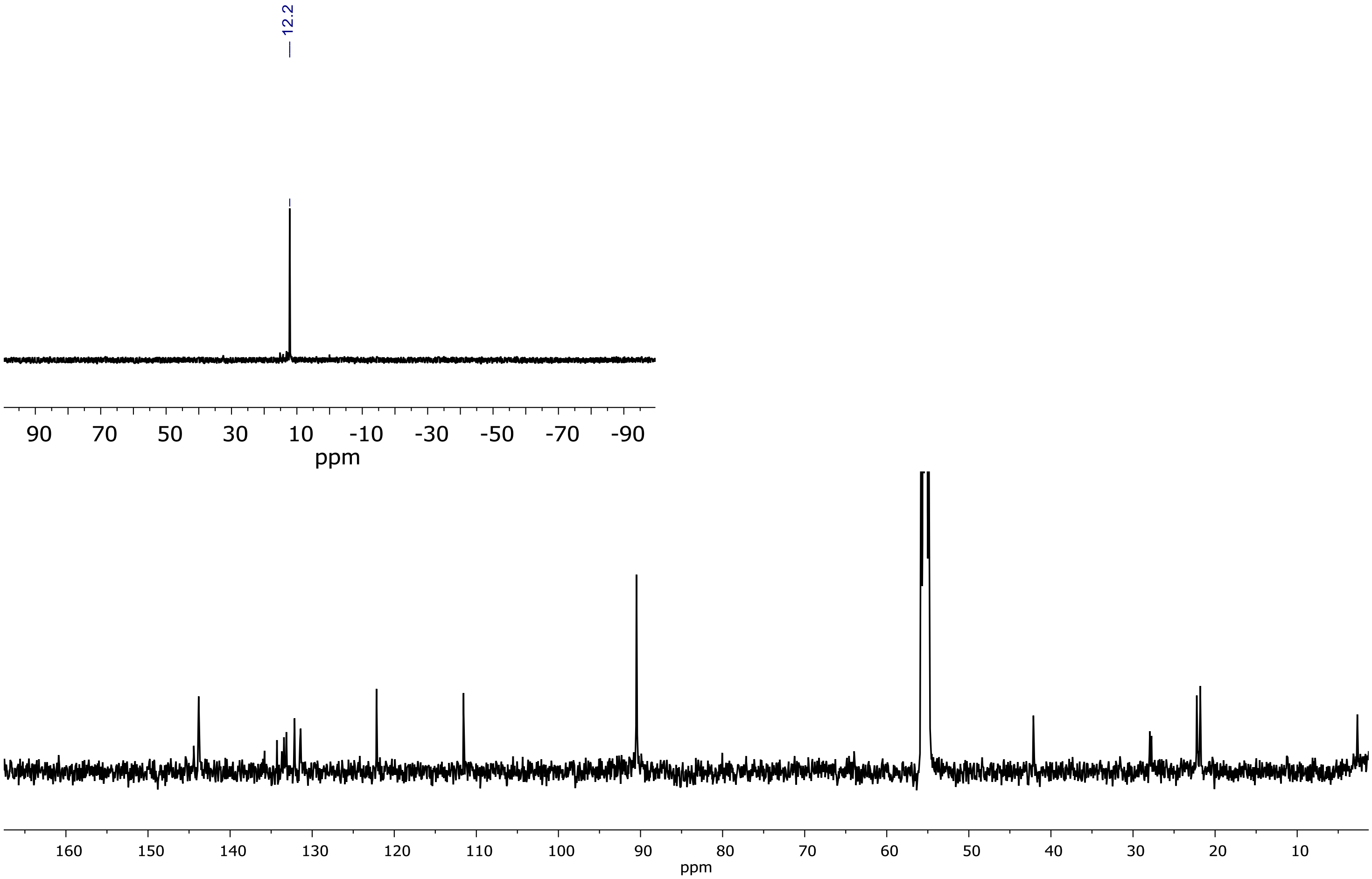

Figure S19. Top) ^{31}P NMR (298 K, 202.29 MHz) of **2-benzene** in DMSO-d$_6$. Bottom) ^{13}C NMR (298 K, 125.77 MHz) of **2-benzene** in DMSO-d$_6$.

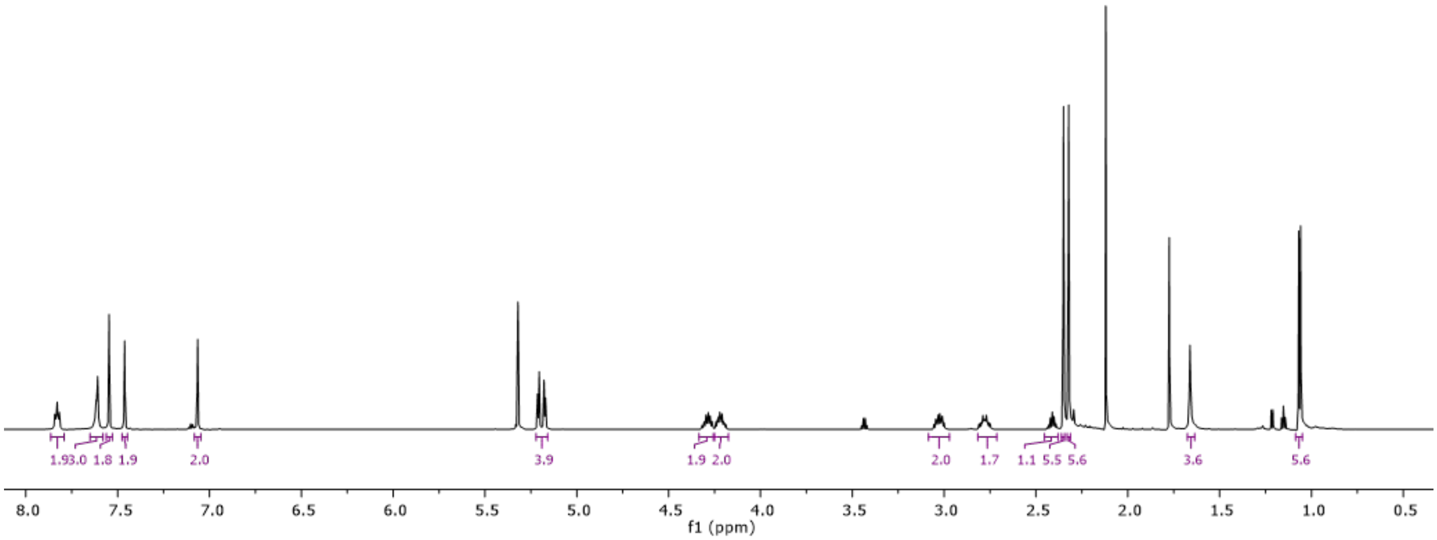

Figure S20. ^{1}H NMR (298 K, 700.07 MHz) of **2-cymene** in DMSO-d$_6$.

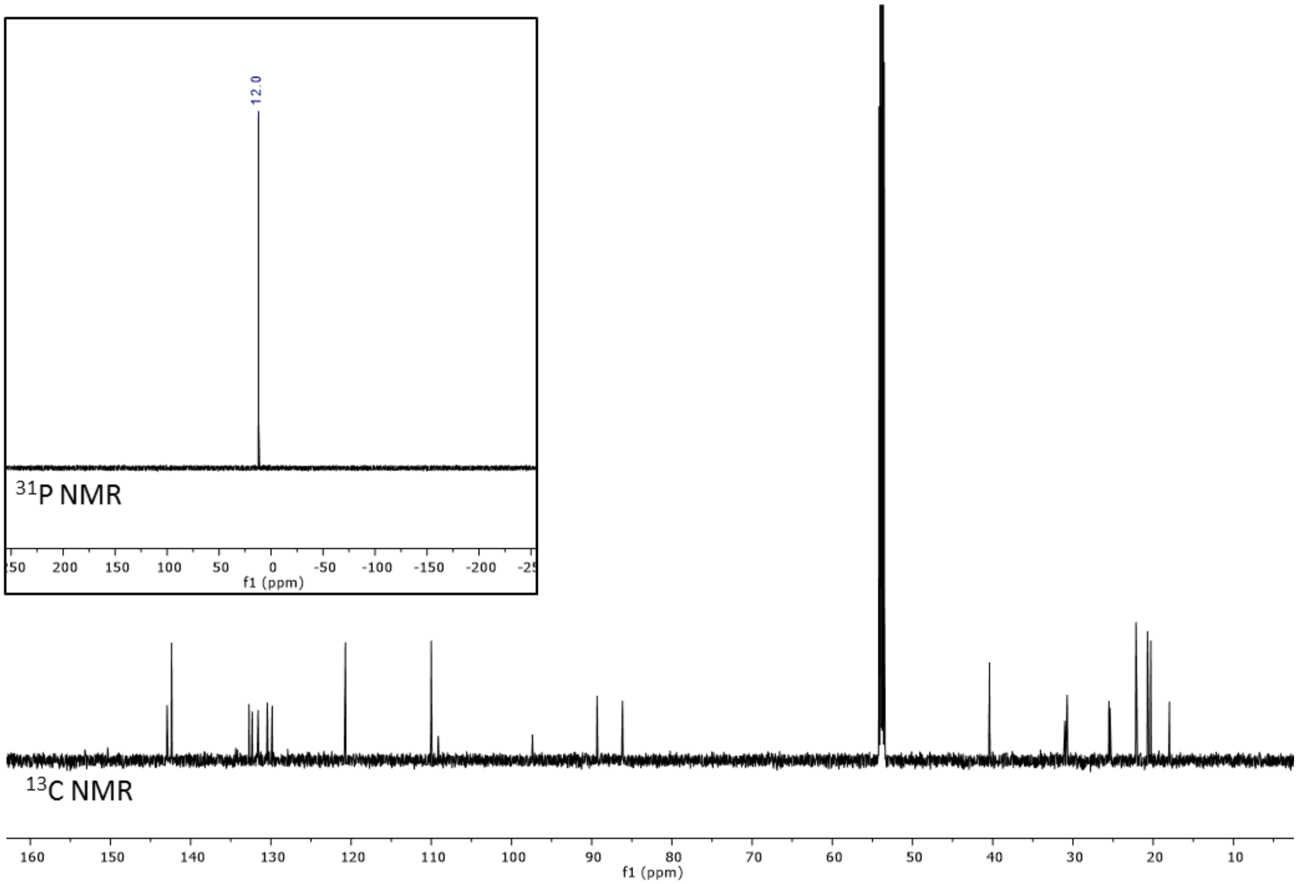

Figure S21. ^{31}P NMR (298 K, 283.39 MHz) of **2-cymene** in DMSO-d$_6$, and ^{13}C NMR (298 K , 176.05 MHz) of **2-cymene** in DMSO-d$_6$.

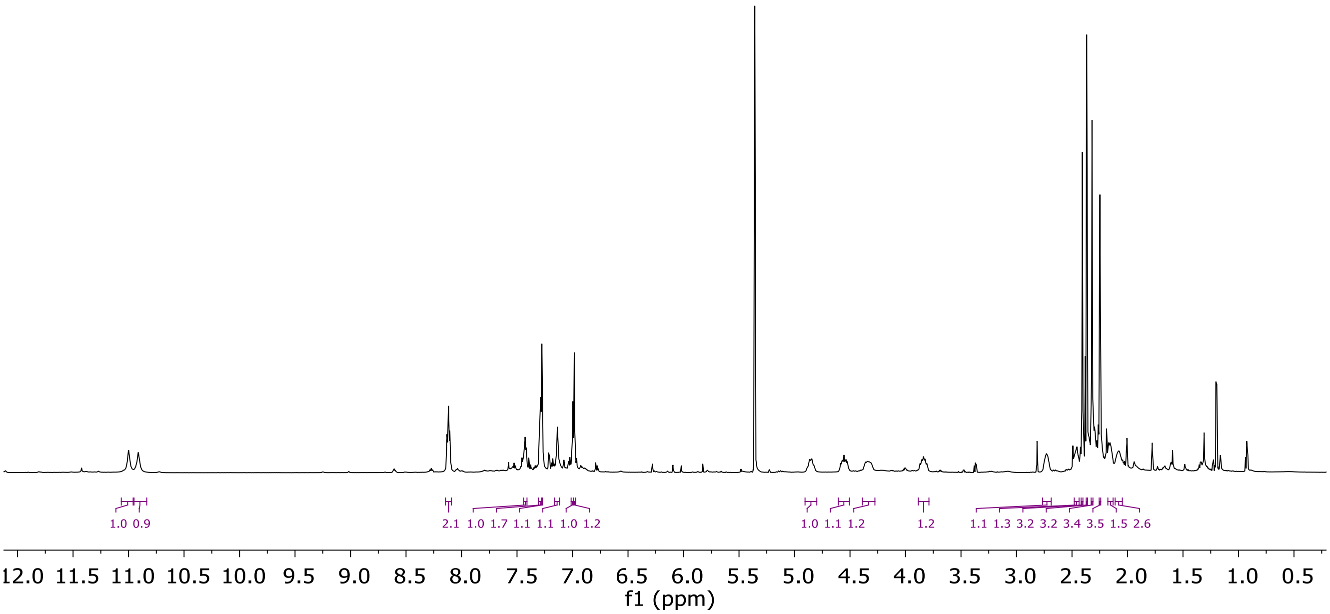

Figure S22. ^{1}H NMR (298 K, 700 MHz) of **3** in CD$_2$Cl$_2$.

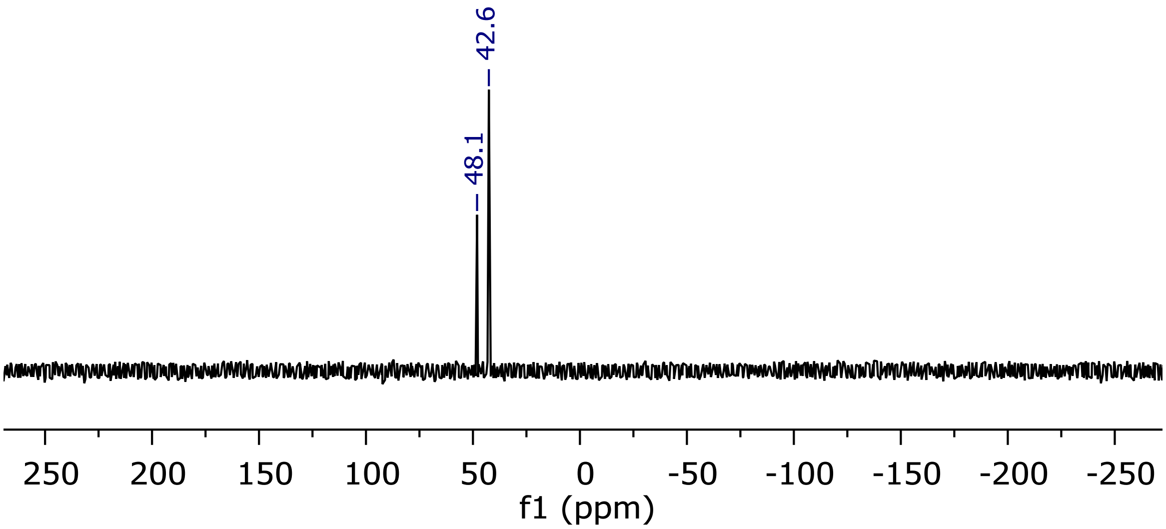

Figure S23. ^{31}P NMR (298 K, 283.39 MHz) of **3** in CD_3CN.

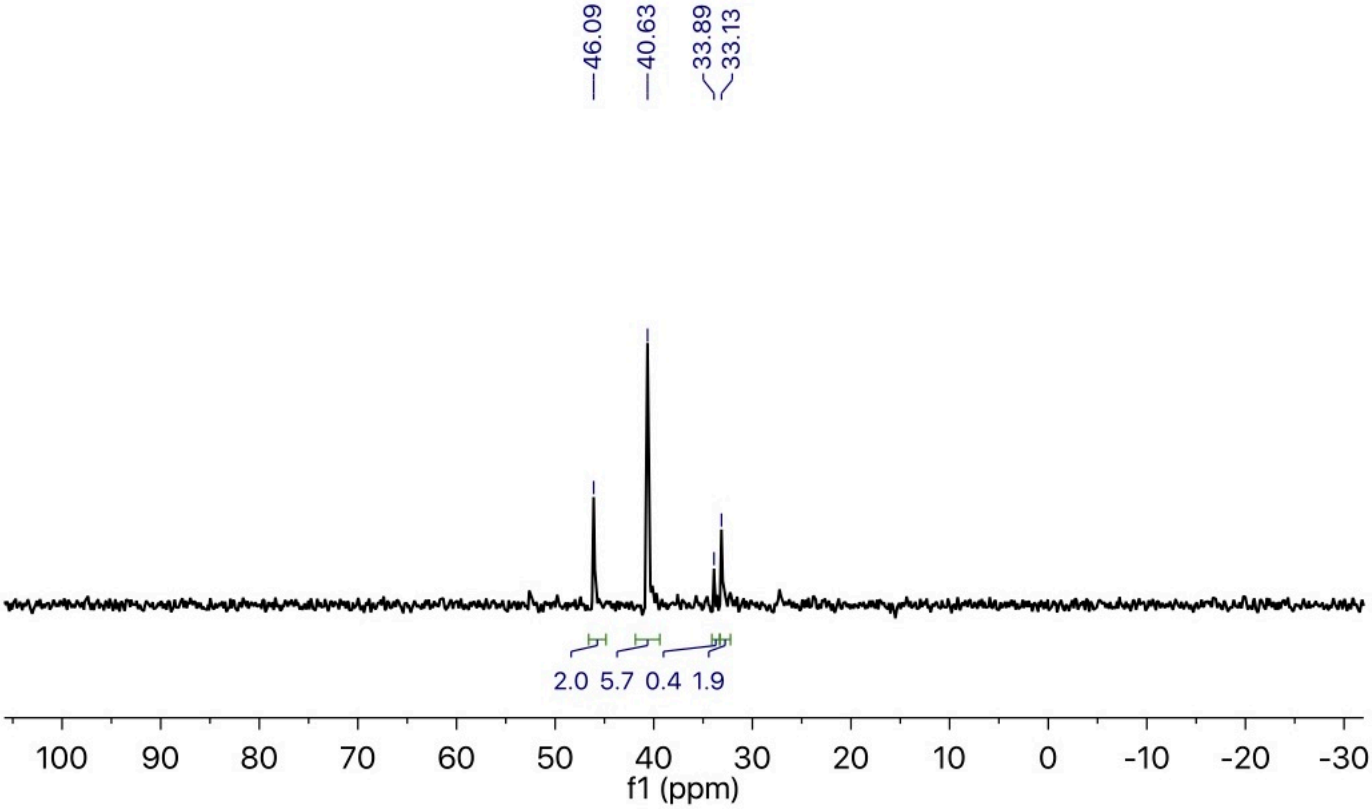

Figure S24. ^{31}P NMR (298 K, 202.29 MHz) of **3** in DMSO-d_6.

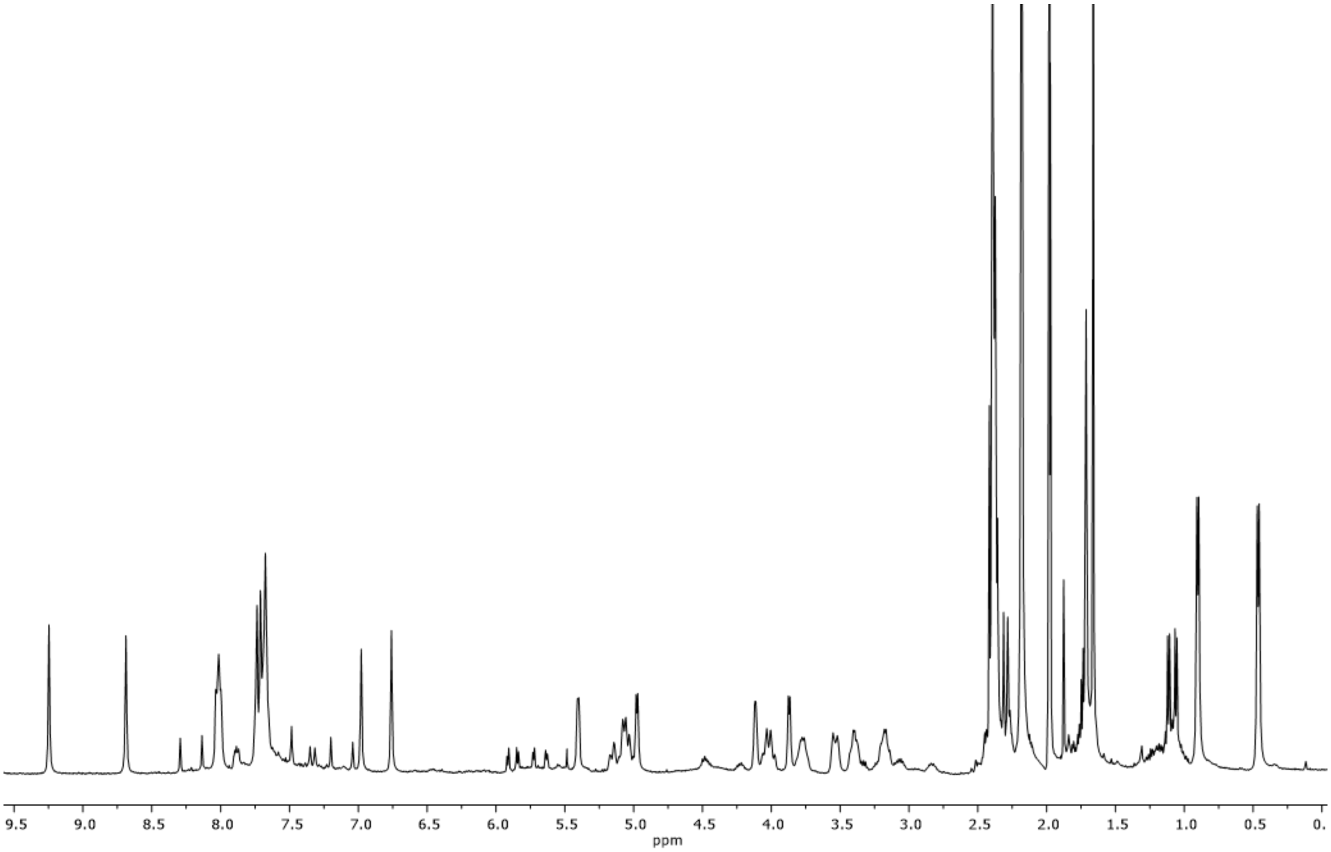

Figure S25. ^{1}H NMR (298 K, 500 MHz) in CD_3CN **4a-cymene** and **4b-cymene**.

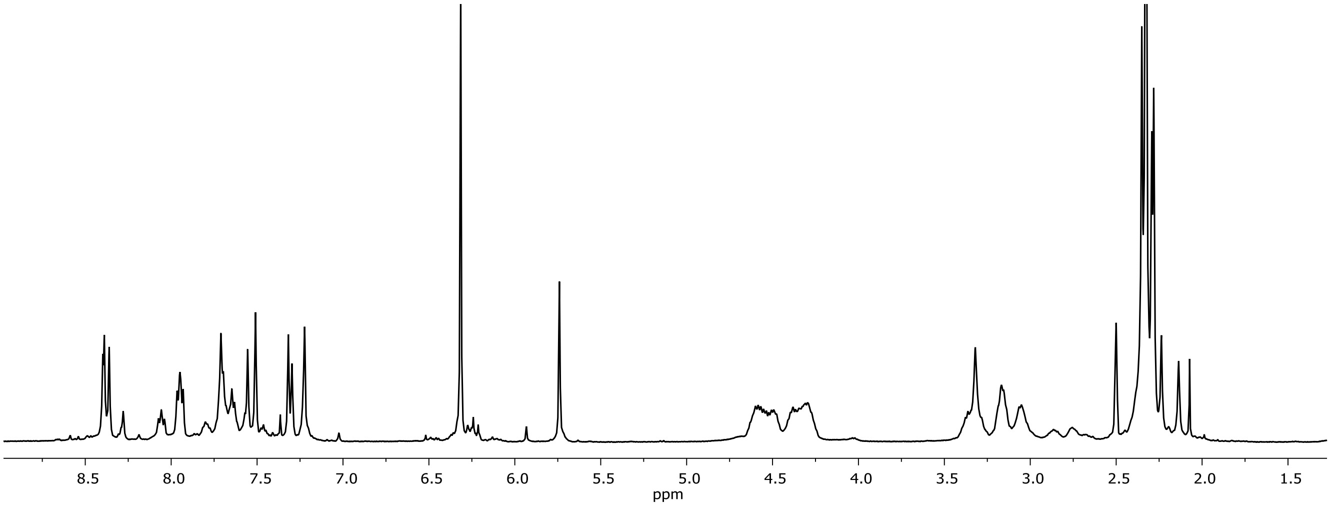

Figure S26. ^{1}H NMR (298 K, 700 MHz) **4a-benzene** and **4b-benzene** DMSO-d^6.

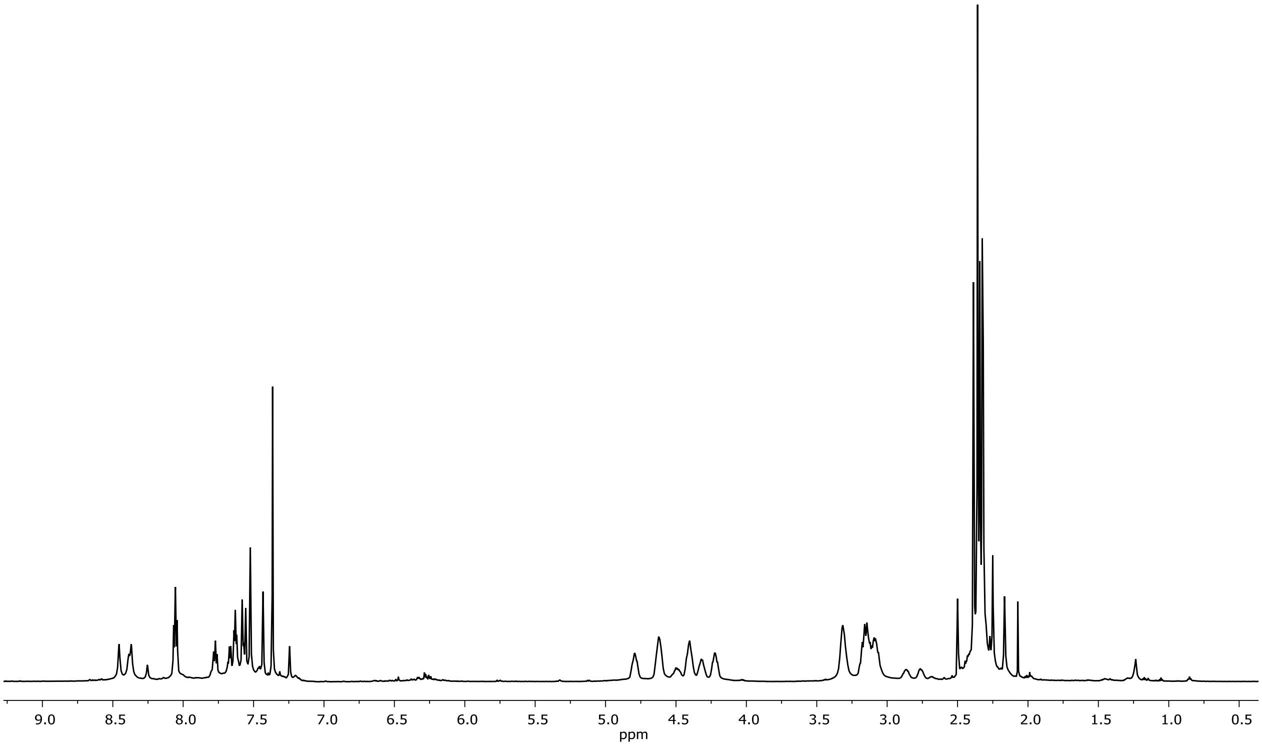

Figure S27. ^{1}H NMR (298 K, 700 MHz) **5a** and **5b** in DMSO-d_6.

T1 Experimental Details

A variable delay time list was created with time ranging from 1 to 31 seconds on second intervals. Experiments were run on standard solutions of sodium formate and DMF in D_2O (fig. S29) and of formic acid and mesitylene in DMSO-d_6 (fig. S30). Peak graphs were then created for the formate peaks and the internal standard peaks, and the data were fit with MestreNova's "Three Parameter Exponential Fit" function (eq. 1), where by comparison with equation 2,[1] we see $G = 1/T_1$.

$$B + Fe^{-xG} \qquad \text{eq. 1}$$

$$\Delta n(t) = \Delta n_{eq}[1 - \exp\left(-\frac{t}{T_1}\right)] \qquad \text{eq. 2}$$

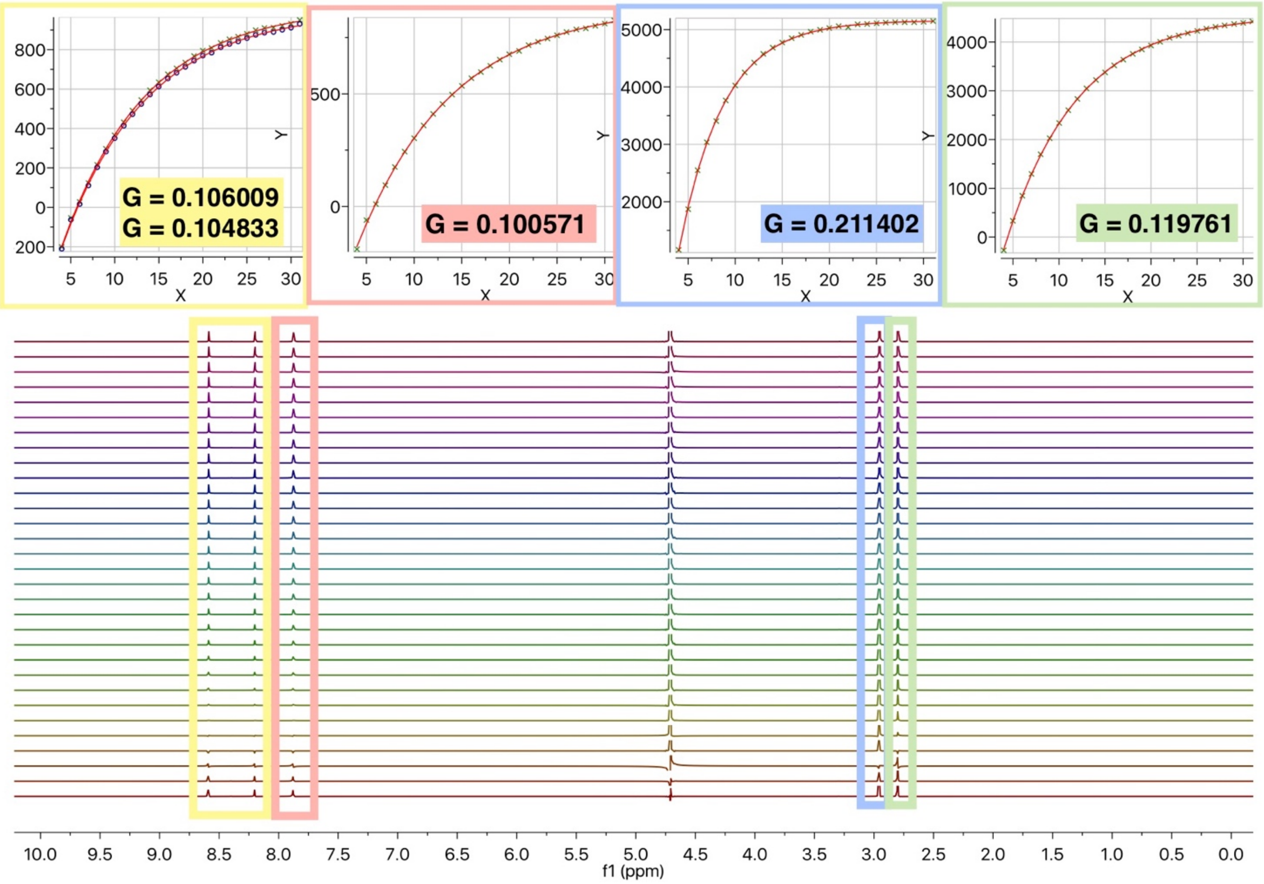

Figure S28. ^{1}H NMR (298 K, 499.7 MHz) of ^{13}C-labeled formic acid (yellow) and DMF (pink, blue, and green) in D_2O. Variable delay time list from 4 to 31 seconds.

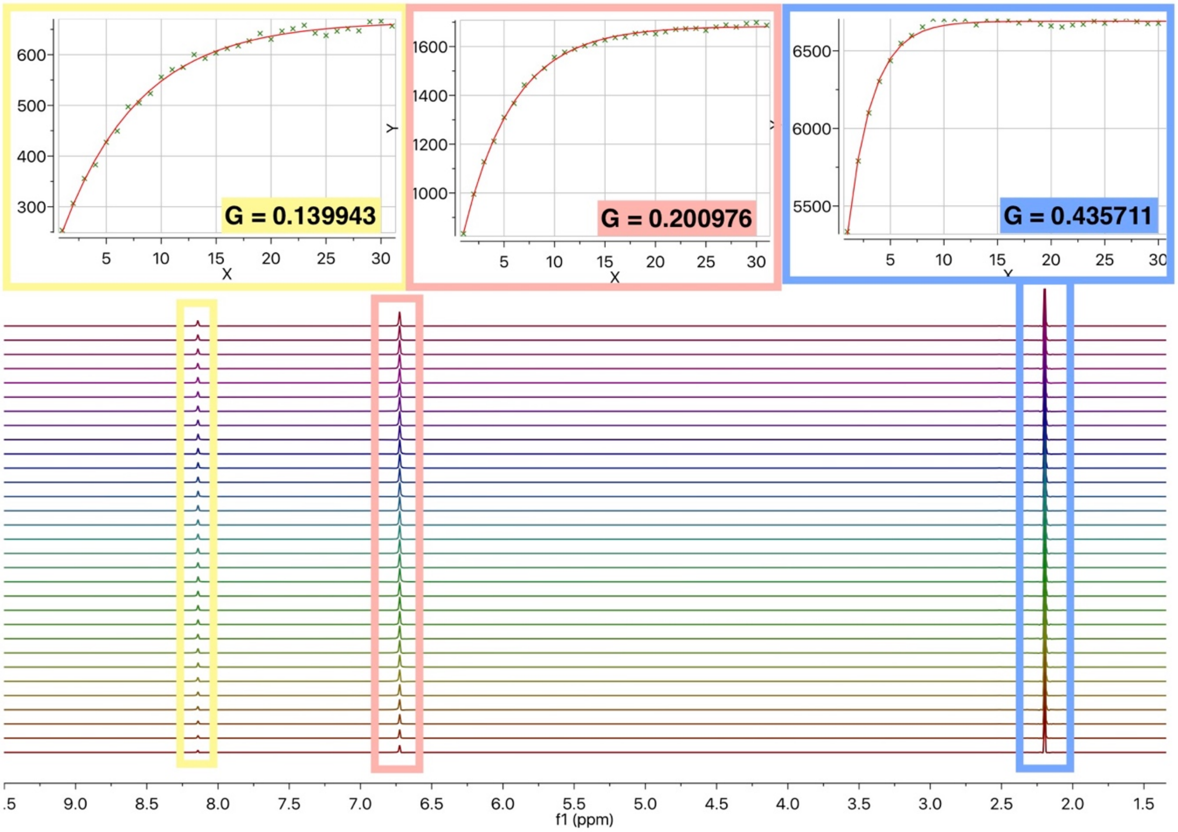

Figure S29. ^{1}H NMR (298 K, 499.7 MHz) of formic acid (yellow) and mesitylene (pink and blue) in DMSO-d_6. Variable delay time list from 1 to 31 seconds.

Table S1: Crystallographic data for the structure of complex **1**.

Identification code : CCDC	1570917	
Empirical formula	C40 H49 B2 F8 N10 P Ru	
Formula weight	975.55	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 13.1696(6) Å	a= 90°.
	b = 17.1948(8) Å	b= 94.836(3)°.
	c = 20.3695(10) Å	g = 90°.
Volume	4596.2(4) Å^3	
Z	4	
Density (calculated)	1.410 Mg/m^3	
Absorption coefficient	0.449 mm^{-1}	
F(000)	2000	
Crystal size	0.28 x 0.24 x 0.06 mm^3	
Theta range for data collection	1.55 to 26.50°.	
Index ranges	-16<=h<=16, -21<=k<=21, -25<=l<=25	
Reflections collected	202195	
Independent reflections	9538 [R(int) = 0.0425]	
Completeness to theta = 26.50°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9735 and 0.8845	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9485 / 0 / 569	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0413, wR2 = 0.1043	
R indices (all data)	R1 = 0.0518, wR2 = 0.1135	
Largest diff. peak and hole	1.284 and -0.837 e.Å^{-3}	

Table S2: Crystallographic data for the structure of **2-benzene**.

Identification code: CCDC	1570916	
Empirical formula	C34 H37 Cl2 N4 P Ru	
Formula weight	704.62	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R -3	
Unit cell dimensions	a = 33.798(4) Å	a= 90°.
	b = 33.798(4) Å	b= 90°.
	c = 19.6172(17) Å	g = 120°.
Volume	19407(4) Å^3	
Z	18	
Density (calculated)	1.085 Mg/m^3	
Absorption coefficient	0.547 mm^{-1}	
F(000)	6516	
Crystal size	0.09 x 0.05 x 0.03 mm^3	
Theta range for data collection	1.25 to 25.43°.	
Index ranges	-40<=h<=40, -40<=k<=40, -23<=l<=23	
Reflections collected	71162	
Independent reflections	7953 [R(int) = 0.1708]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9838 and 0.9524	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7953 / 0 / 383	
Goodness-of-fit on F^2	0.964	
Final R indices [I>2sigma(I)]	R1 = 0.0662, wR2 = 0.1379	
R indices (all data)	R1 = 0.1388, wR2 = 0.1581	
Largest diff. peak and hole	0.470 and -0.463 e.Å^{-3}	

Table S3. Crystallographic data for the structure of complex **3-DMSO**.

Identification code: CCDC	1570915	
Empirical formula	C66 H92 Cl4 N8 O5 P2 Ru2 S5	
Formula weight	1643.65	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2/n	
Unit cell dimensions	a = 13.445(5) Å	a= 90.000(5)°.
	b = 10.038(5) Å	b= 95.679(5)°.
	c = 27.511(5) Å	g = 90.000(5)°.
Volume	3695(2) Å^3	
Z	2	
Density (calculated)	1.477 Mg/m^3	
Absorption coefficient	0.791 mm^{-1}	
F(000)	1700	
Crystal size	0.05 x 0.09 x 0.105 mm^3	
Theta range for data collection	1.488 to 27.752°.	
Index ranges	-16<=h<=17, -12<=k<=12, -33<=l<=33	
Reflections collected	49234	
Independent reflections	7838 [R(int) = 0.1776]	
Completeness to theta = 25.000°	99.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7838 / 0 / 430	
Goodness-of-fit on F^2	0.968	
Final R indices [I>2sigma(I)]	R1 = 0.0666, wR2 = 0.1420	
R indices (all data)	R1 = 0.1762, wR2 = 0.1904	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.322 and -2.111 e.Å^{-3}	

References

1. Hore, P.J.; Spin Relaxation. In *Nuclear Magnetic Resonance*, Compton, R. G. Oxford Chemistry Primers; Oxford University Press: Oxford, 1995; pp 56-71.