

Supporting Information

Sterically-constrained tripodal phosphorus-bridged *tris*-pyridyl ligands

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Representative NMR spectra for selected compounds

NMR spectra of $P(2\text{-py})_3$ (**1**)

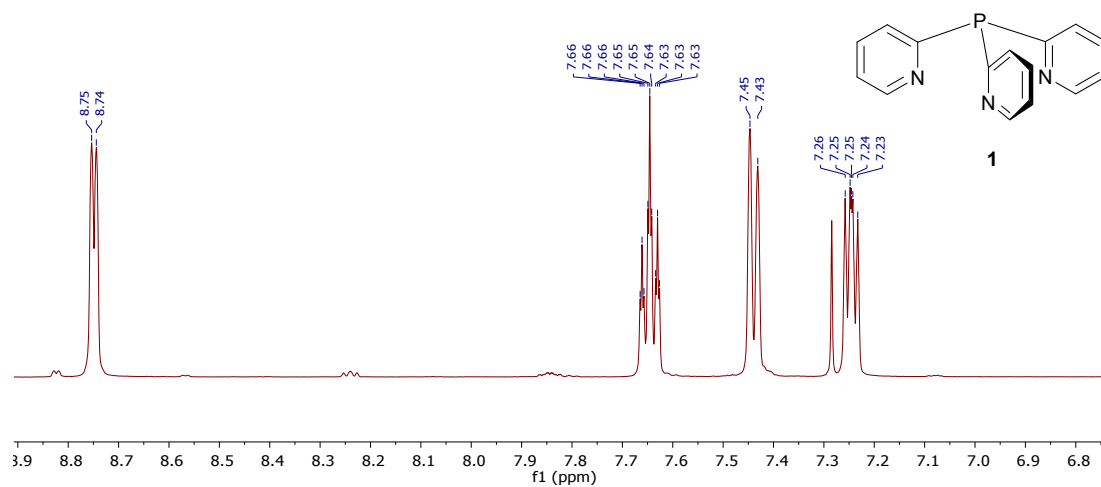


Figure S1: ^1H NMR (298 K, CDCl_3 , 500.20 MHz) spectrum of $P(2\text{-py})_3$ (**1**).

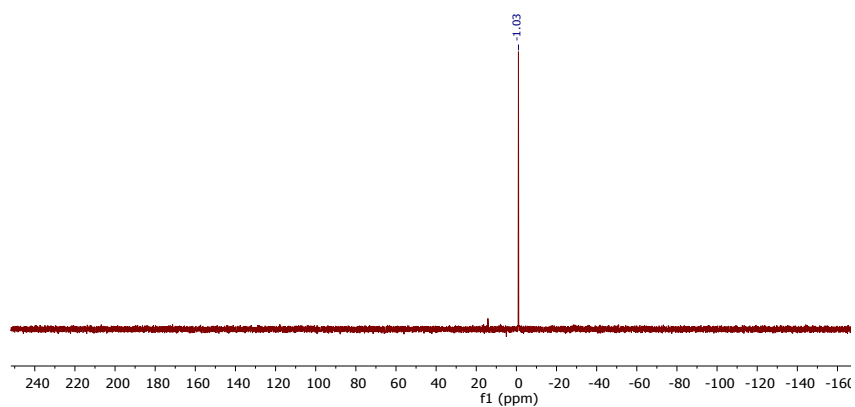


Figure S2: $^{31}\text{P}\{^1\text{H}\}$ NMR (298 K, CDCl_3 , 202.48 MHz) spectrum of $P(2\text{-py})_3$ (**1**).

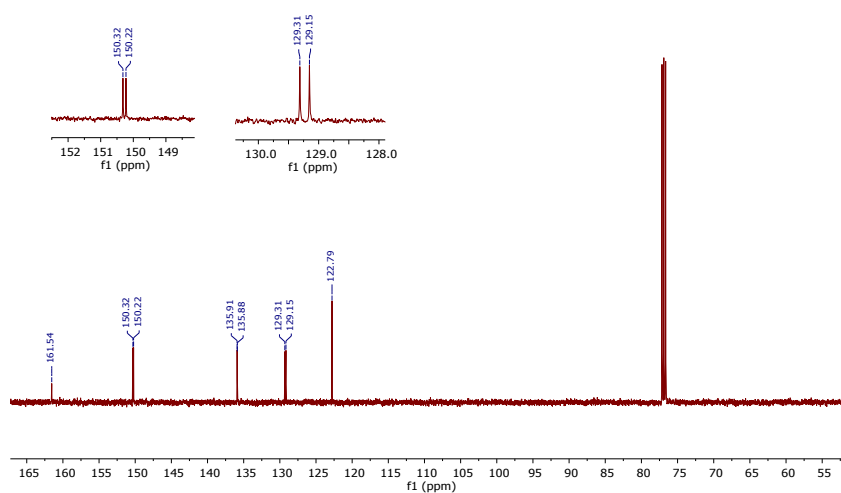


Figure S3: $^{13}\text{C}\{^1\text{H}\}$ NMR (298 K, CDCl_3 , 125.78 MHz) spectrum of $P(2\text{-py})_3$ (**1**).

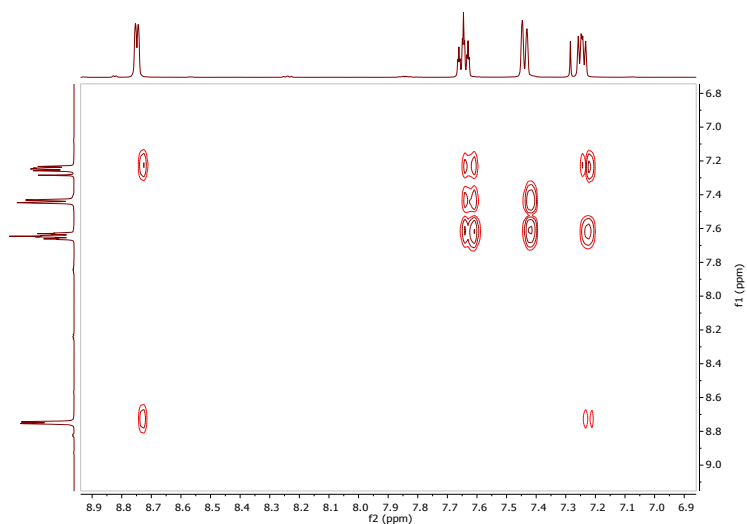


Figure S4: ^1H - ^1H COSY (298 K, CDCl_3 , 500.20 MHz) spectrum of $P(2\text{-py})_3$ (**1**).

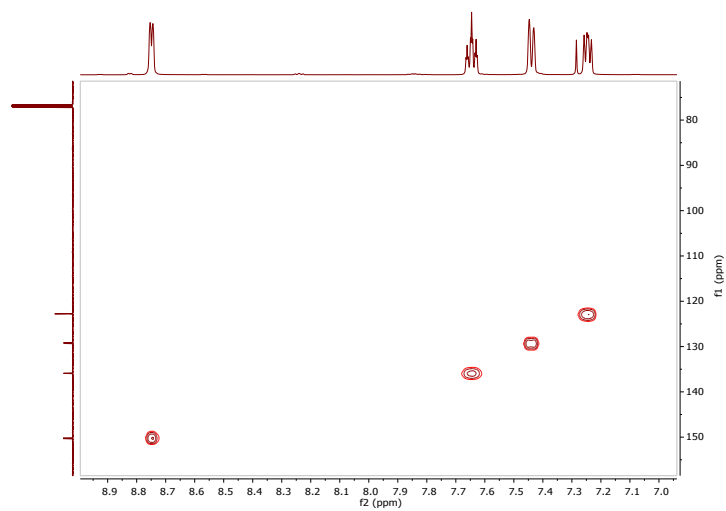


Figure S5: ^1H - ^{13}C HMQC (298 K, CDCl_3 , 500.20 MHz) spectrum of $P(2\text{-py})_3$ (**1**).

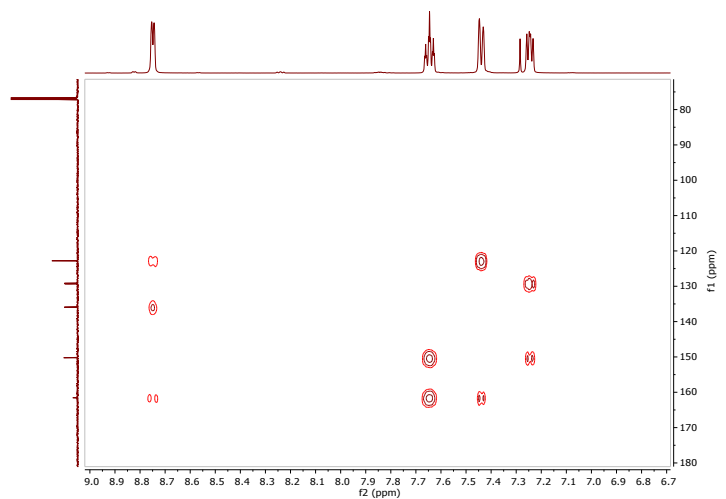


Figure S6: ^1H - ^{13}C HMBC (298 K, CDCl_3 , 500.20 MHz) spectrum of $P(2\text{-py})_3$ (**1**).

NMR spectra of P(6-Me-2-py)₃ (**2**)

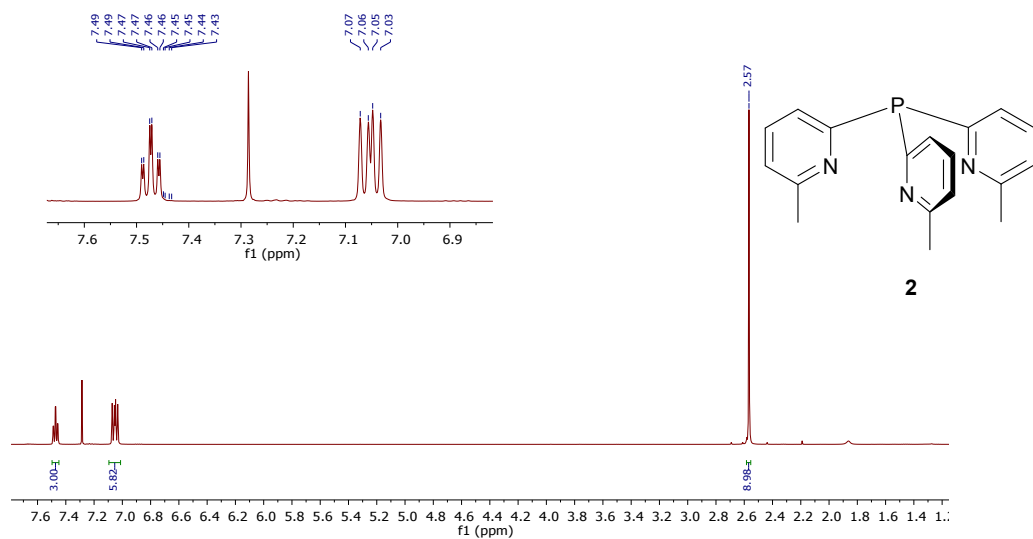


Figure S7: ¹H NMR (298 K, CDCl₃, 500.20 MHz) spectrum of P(6-Me-2-py)₃ (**2**).

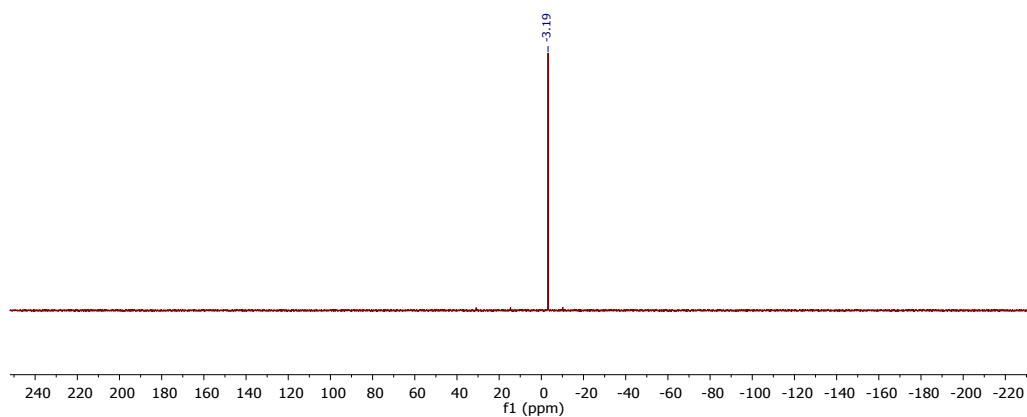


Figure S8: ³¹P{¹H} NMR (298 K, CDCl₃, 202.48 MHz) spectrum of P(6-Me-2-py)₃ (**2**).

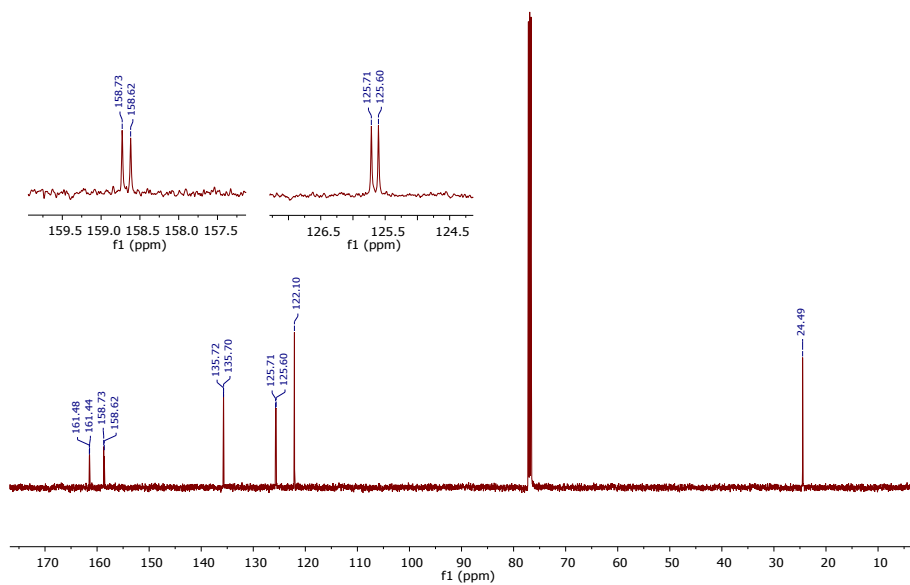


Figure S9: ¹³C{¹H} NMR (298 K, CDCl₃, 125.78 MHz) spectrum of P(6-Me-2-py)₃ (**2**).

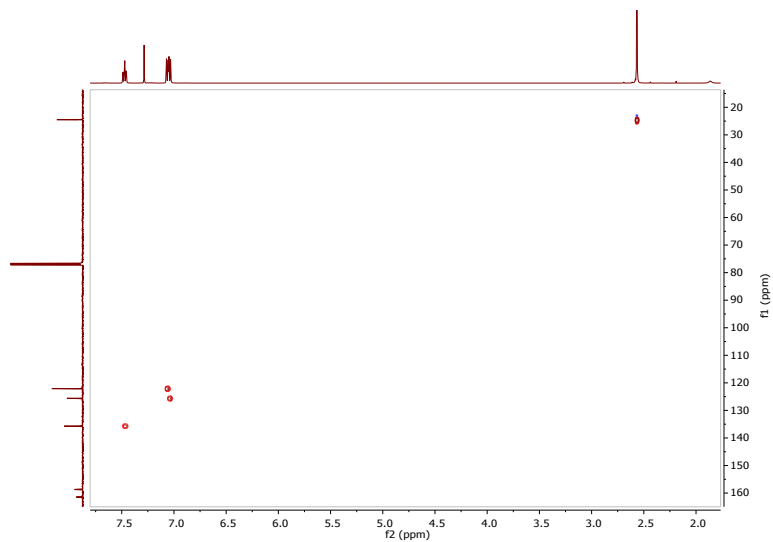


Figure S10: ^1H - ^{13}C HMQC (298 K, CDCl_3 , 500.20 MHz) spectrum of $\text{P}(6\text{-Me-2-py})_3$ (**2**).

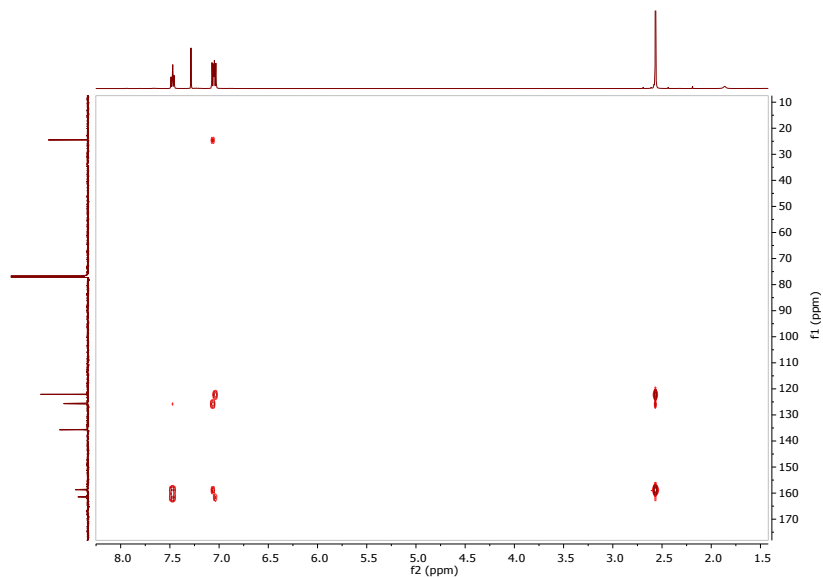


Figure S11: ^1H - ^{13}C HMBC (298 K, CDCl_3 , 500.20 MHz) spectrum of $\text{P}(6\text{-Me-2-py})_3$ (**2**).

NMR spectra of $\text{P}(6\text{-Br-2-py})_3$ (**3**)

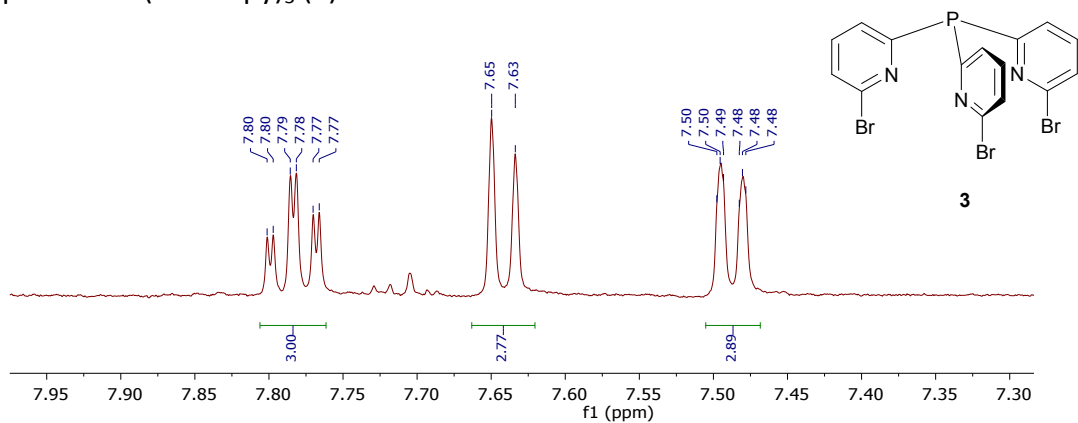


Figure S12: ^1H NMR (298 K, CD_3COCD_3 , 500.20 MHz) spectrum of $\text{P}(6\text{-Br-2-py})_3$ (**3**).

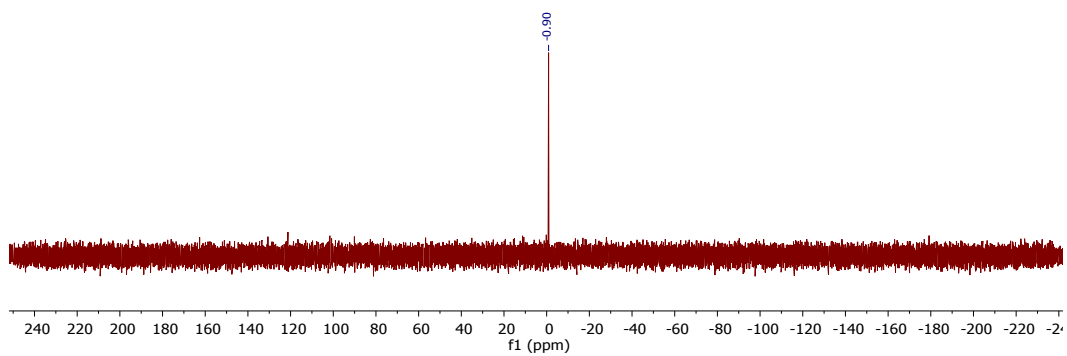


Figure S13: $^{31}\text{P}\{^1\text{H}\}$ NMR (298 K, CD_3COCD_3 , 202.48 MHz) spectrum of $\text{P}(6\text{-Br-2-py})_3$ (**3**).

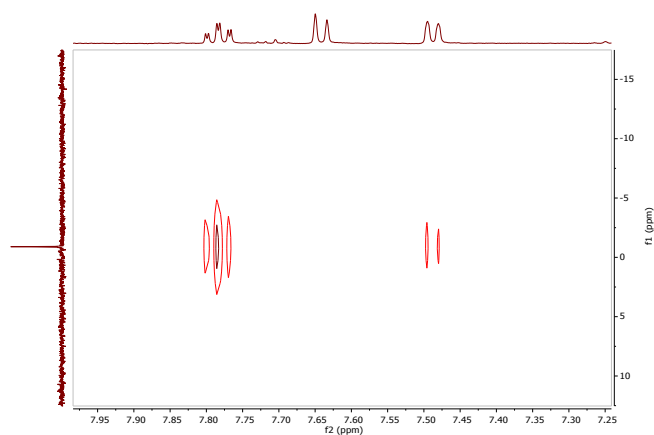


Figure S14: $^1\text{H-}^{31}\text{P}\{^1\text{H}\}$ HMQC (298 K, CD_3COCD_3 , 500.20 MHz) spectrum of $\text{P}(6\text{-Br-2-py})_3$ (**3**).

NMR spectra of $[\{\text{P}(2\text{-py})_3\}_2\text{Fe}](\text{OTf})_2$ (**4**)

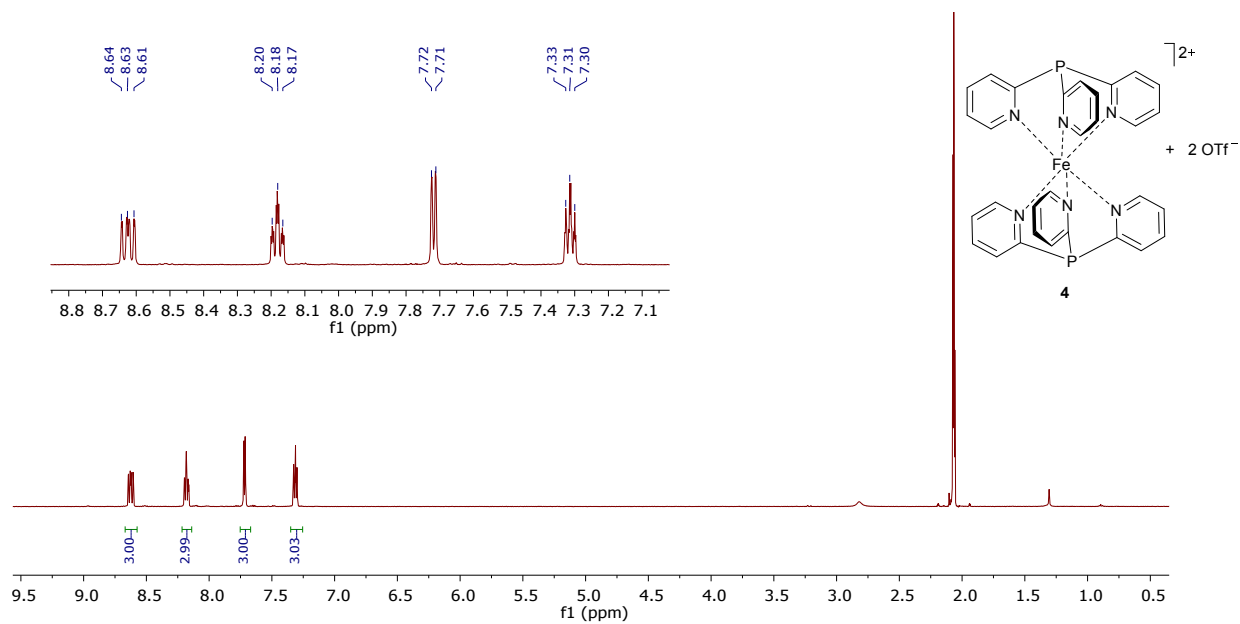


Figure S15: ^1H NMR (298 K, CD_3COCD_3 , 500.20 MHz) spectrum of $[\{\text{P}(2\text{-py})_3\}_2\text{Fe}](\text{OTf})_2$ (**4**).

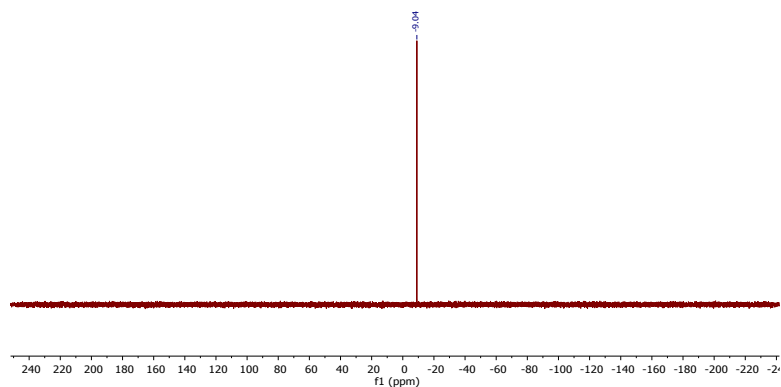


Figure S16: $^{31}\text{P}\{^1\text{H}\}$ NMR (298 K, CD_3COCD_3 , 202.48 MHz) spectrum of $[\{\text{P}(2\text{-py})_3\}_2\text{Fe}(\text{OTf})_2]$ (**4**).

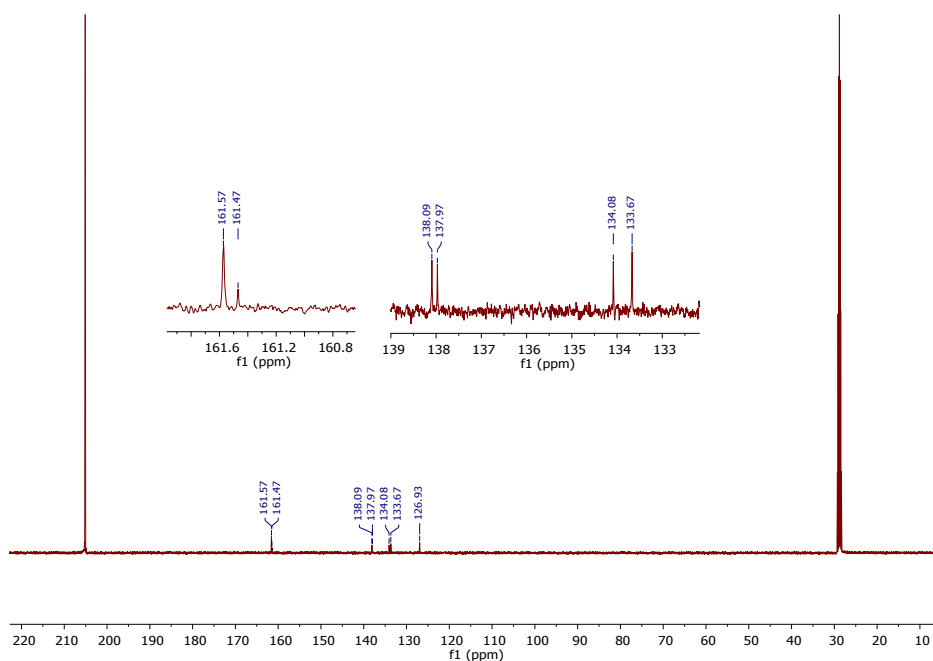


Figure S17: $^{13}\text{C}\{^1\text{H}\}$ NMR (298 K, CD_3COCD_3 , 125.78 MHz) spectrum of $[\{\text{P}(2\text{-py})_3\}_2\text{Fe}(\text{OTf})_2]$ (**4**).

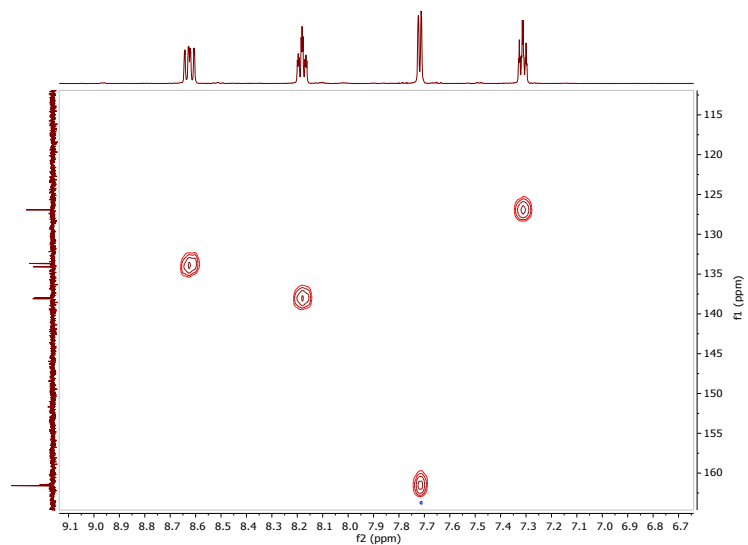


Figure S18: $^1\text{H}-^{13}\text{C}$ HMQC (298 K, CD_3COCD_3 , 500.20 MHz) spectrum of $[\{\text{P}(2\text{-py})_3\}_2\text{Fe}(\text{OTf})_2]$ (**4**).

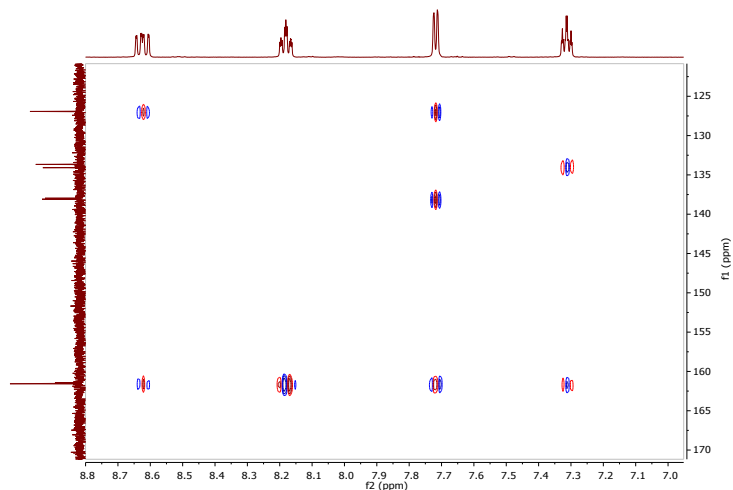


Figure S19: ^1H - ^{13}C HMBC (298 K, CD_3COCD_3 , 500.20 MHz) spectrum of $[\{\text{P}(2\text{-py})_3\}_2\text{Fe}](\text{OTf})_2$ (**4**).

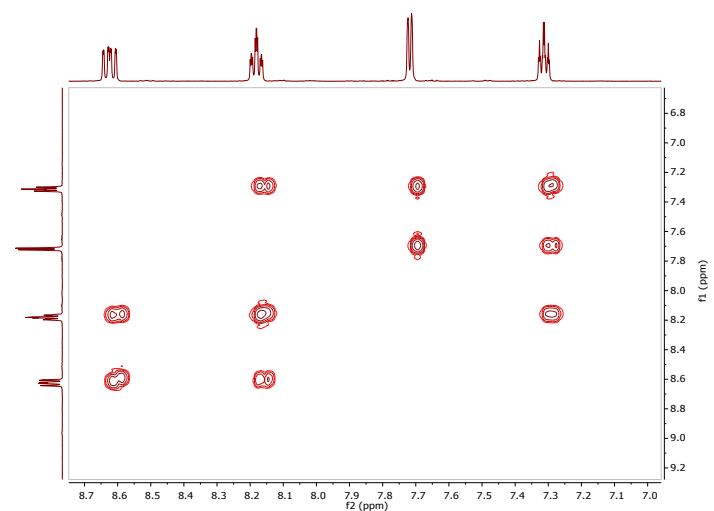


Figure S20: ^1H - ^1H COSY (298 K, CD_3COCD_3 , 500.20 MHz) spectrum of $[\{\text{P}(2\text{-py})_3\}_2\text{Fe}](\text{OTf})_2$ (**4**).

NMR spectra of $[(\text{MeCN})_3\text{Cu}\{\text{P}(6\text{-Me-2-py})_3\}\text{Cu}(\text{MeCN})](\text{PF}_6)_2$ (**7**)

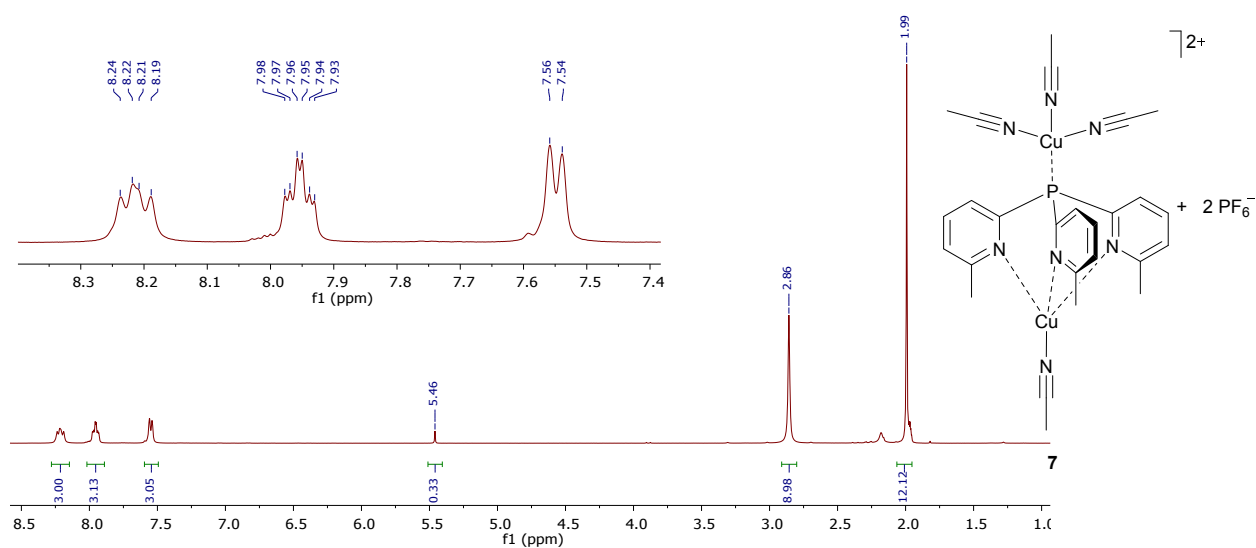


Figure S21: ^1H NMR (298 K, CD_3CN , 400.13 MHz) spectrum of $[(\text{MeCN})_3\text{Cu}\{\text{P}(6\text{-Me-2-py})_3\}\text{Cu}(\text{MeCN})](\text{PF}_6)_2$ (**7**).

Note: The acetonitrile solvent residual signal overlaps with the signal of the coordinated CH₃CN molecules at 1.99 ppm. Furthermore, the peak at 5.46 ppm arises from CH₂Cl₂.

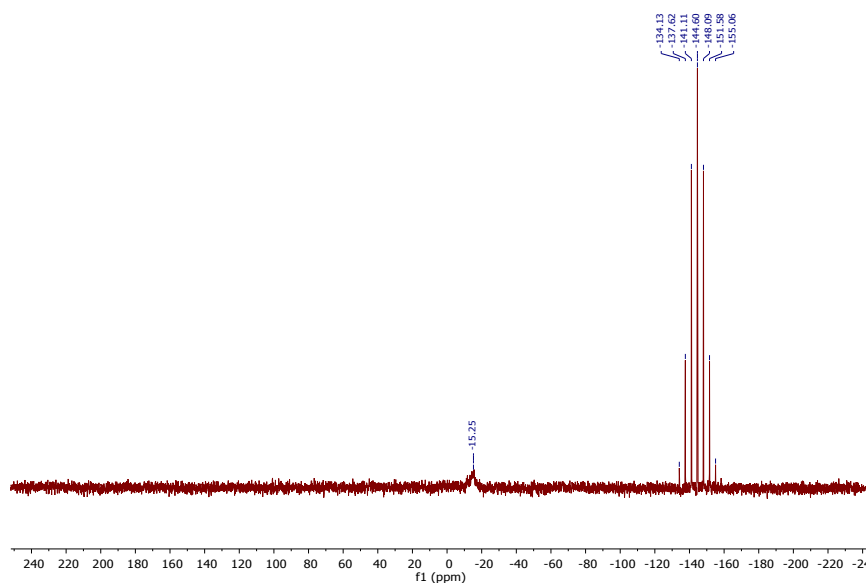


Figure S22: ³¹P{¹H} NMR (298 K, CD₃CN, 202.48 MHz) spectrum of [(MeCN)₃Cu{P(6-Me-2-py)₃}Cu(MeCN)](PF₆)₂ (**7**).

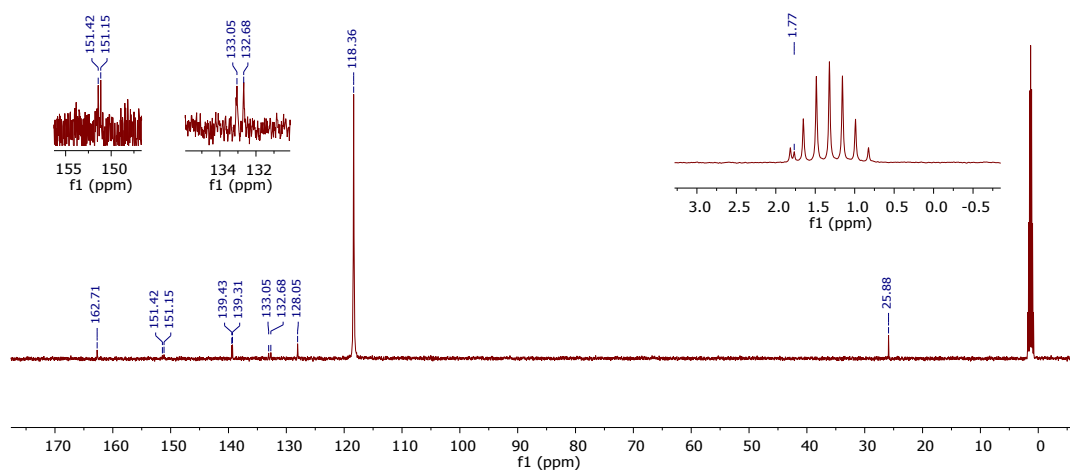


Figure S23: ¹³C{¹H} NMR (298 K, CD₃CN, 125.78 MHz) spectrum of [(MeCN)₃Cu{P(6-Me-2-py)₃}Cu(MeCN)](PF₆)₂ (**7**).

Note: The solvent residual peak of acetonitrile (septet at 1.32 ppm) overlaps with the signal of the coordinated CH₃CN molecules (1.77 ppm). The same observation was made for the second solvent residual peak of acetonitrile, which also overlaps with the signal of the coordinated CH₃CN molecules at 118.36 ppm.

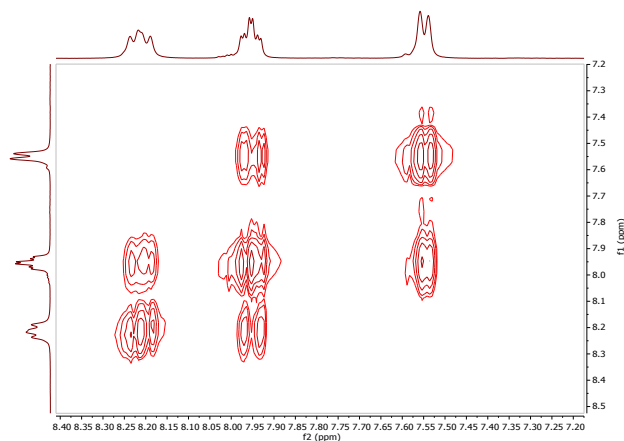


Figure S24: ¹H-¹H COSY (298 K, CD₃CN, 400.13 MHz) spectrum of [(MeCN)₃Cu{P(6-Me-2-py)₃}Cu(MeCN)](PF₆)₂ (**7**).

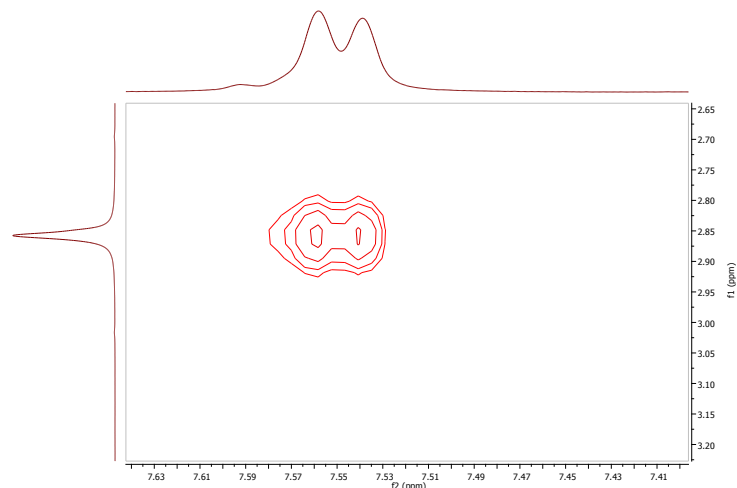


Figure S25: Section of the ^1H - ^1H NOESY (298 K, CD_3CN , 400.13 MHz) spectrum of $[(\text{MeCN})_3\text{CuP}(6\text{-Me-2-py})_3\text{Cu}(\text{MeCN})](\text{PF}_6)_2$ (**7**).

Note: The crosspeak between H(5) and the CH_3 group of the $\text{P}(6\text{-Me-2-py})_3$ ligand (**2**) in the ^1H - ^1H NOESY spectrum of **7** arises from intramolecular cross-relaxation of protons, which are in close spatial proximity. The observation of this crosspeak confirms the assignment of H(5). This was the only crosspeak observed between a pyridyl-H and the 6-CH_3 -group.

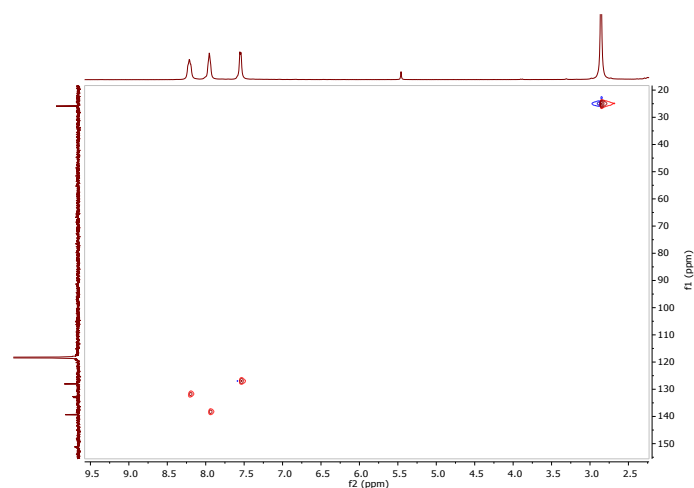


Figure S26: ^1H - ^{13}C HMQC (298 K, CD_3CN , 500.20 MHz) spectrum of $[(\text{MeCN})_3\text{CuP}(6\text{-Me-2-py})_3\text{Cu}(\text{MeCN})](\text{PF}_6)_2$ (**7**).

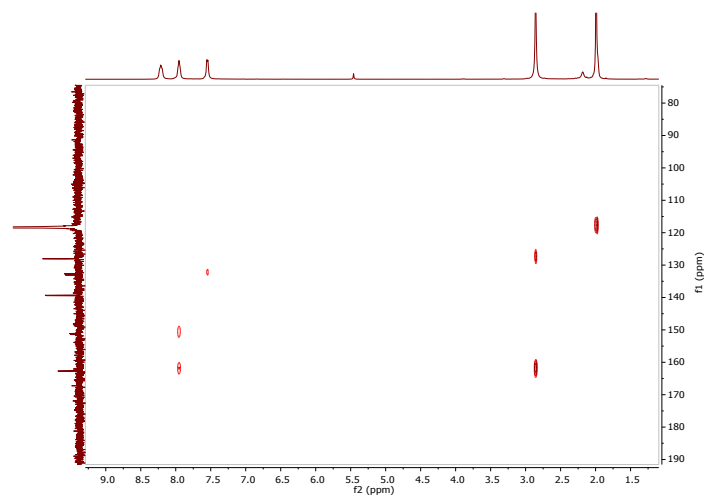


Figure S27: ^1H - ^{13}C HMBC (298 K, CD_3CN , 500.20 MHz) spectrum of $[(\text{MeCN})_3\text{CuP}(6\text{-Me-2-py})_3\text{Cu}(\text{MeCN})](\text{PF}_6)_2$ (**7**).

UV-visible spectroscopy

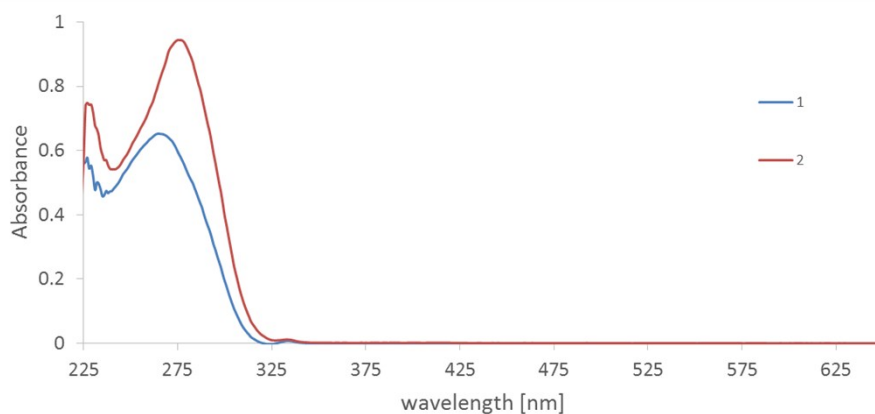


Figure S28: UV-visible spectra of the ligands **1** (blue) and **2** (red). Spectra were recorded in CH_2Cl_2 (both at a concentration of $5.0 \cdot 10^{-5} \text{ mol L}^{-1}$). Background solvent corrections were applied.

Table S1: Molar extinction coefficients calculated from UV-visible spectra (all at a concentration of $5.0 \cdot 10^{-5} \text{ mol L}^{-1}$)

Compound	Solvent	Wavelength λ [nm]	Absorbance	Molar extinction coefficient $\epsilon \left[\frac{\text{L}}{\text{cm} \cdot \text{mol}} \right]$
1	CH_2Cl_2	268.0	0.649	12976.5
2	CH_2Cl_2	281.0	0.905	18107.2
4	CH_2Cl_2	475.0	0.592	11834.3
		379.9	0.411	8227.6
		300.9	0.155	3091.5
		267.0	1.850	37003.1
4	MeOH	476.0	0.491	9816.5
		382.0	0.338	6751.2
		297.0	0.179	3579.5
		267.0	1.598	31915.5
5-toluene	CH_3CN	367.1	0.455	9102.5
		313.9	0.784	15682.3
		276.0	1.519	30379.6
6-2THF	MeOH	276.9	0.434	8685.3
7	CH_3CN	363.0	0.202	4036.6
		276.9	1.517	30344.8

Single-crystal X-ray crystallography

Table S2: Crystallographic parameters.

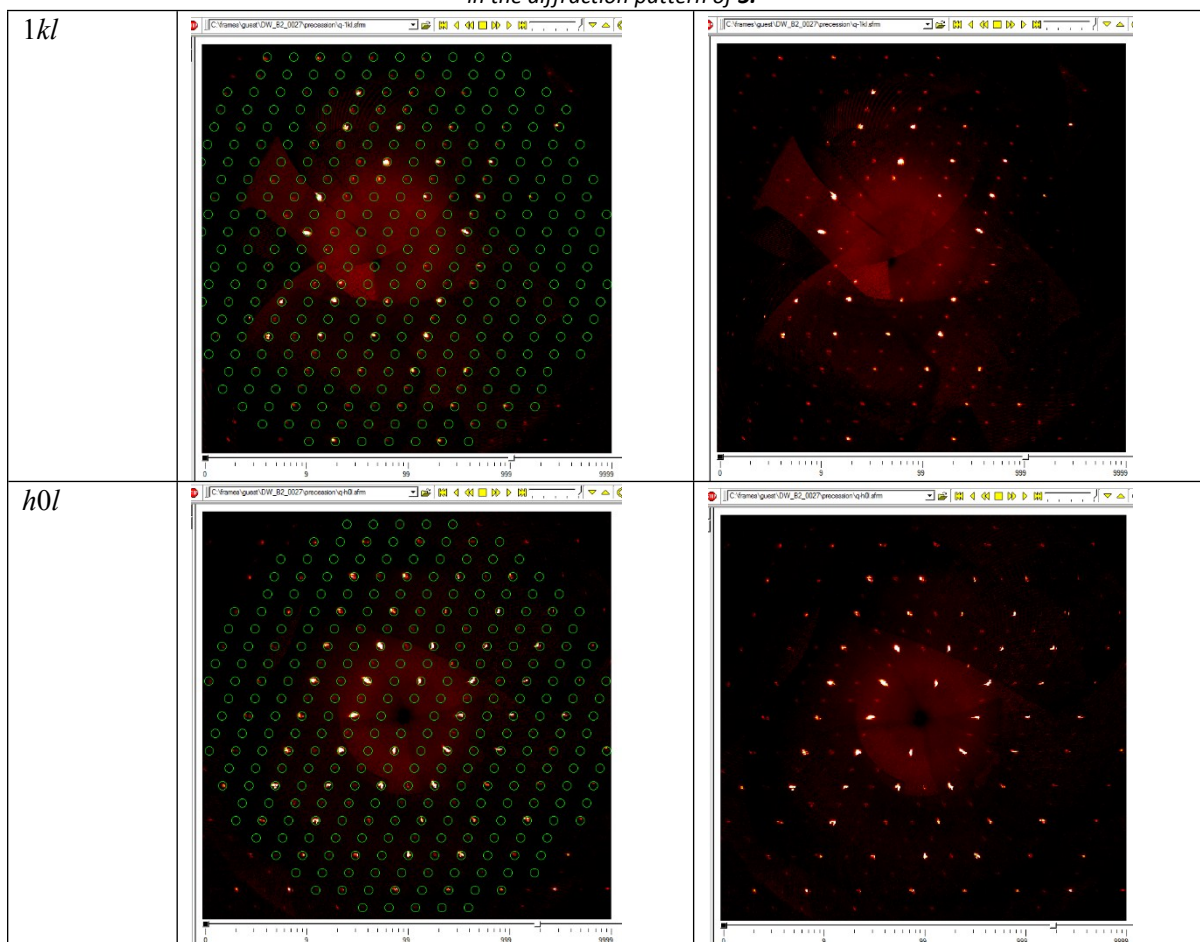
Compound reference	2	3	4	5.toluene	6.2THF	7
Chemical formula	$\text{C}_{18}\text{H}_{18}\text{N}_3\text{P}$	$\text{C}_{15}\text{H}_9\text{Br}_3\text{N}_3\text{P}$	$\text{C}_{30}\text{H}_{24}\text{FeN}_6\text{P}_2^{2+}$ ($\text{CF}_3\text{O}_3\text{S}^-$) ₂	$\text{C}_{18}\text{H}_{18}\text{Cl}_2\text{FeN}_3\text{P} \cdot \text{C}_7\text{H}_8$	$\text{C}_{19}\text{H}_{18}\text{ClF}_3\text{FeN}_3\text{O} \cdot \text{C}_4\text{H}_8\text{O}$	$\text{C}_{26}\text{H}_{30}\text{Cu}_2\text{N}_7\text{P}^{2+}(\text{PF}_6^-)_2$
Formula mass	307.32	501.95	884.48	526.21	619.80	888.56
Crystal system	trigonal	trigonal	monoclinic	triclinic	monoclinic	triclinic
a/Å	30.7488(8)	15.7876(6)	17.6327(9)	8.0155(3)	13.7879(4)	8.2686(5)
b/Å	30.7488(8)	15.7876(6)	20.0111(11)	10.7101(4)	8.6473(2)	14.9441(9)
c/Å	11.8199(4)	11.1637(5)	19.8093(10)	15.0458(6)	22.5638(6)	14.9496(8)
$\alpha/^\circ$	90	90	90	98.595(2)	90	78.976(2)
$\beta/^\circ$	90	90	91.836(2)	99.108(2)	95.0326(12)	80.942(2)
$\gamma/^\circ$	120	120	90	91.742(2)	90	84.159(2)
Unit cell volume/Å ³	9678.3(6)	2409.7(2)	6986.1(6)	1259.09(8)	2679.87(12)	1785.67(18)
Temperature/K	180(2)	180(2)	180(2)	180(2)	180(2)	180(2)
Space group	<i>R</i> 3c	<i>R</i> 3c	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> 2/ <i>c</i>	<i>P</i> -1

Z	24	6	8	2	4	2
Radiation type	CuK α	CuK α	CuK α	CuK α	CuK α	CuK α
Absorption coefficient, μ/mm^{-1}	1.495	10.247	6.234	7.489	7.225	3.598
No. of reflections measured	35814	7384	103989	14375	32629	45856
No. of independent reflections	3769	941	12364	4367	4745	6267
R_{int}	0.036	0.062	0.054	0.042	0.036	0.031
Final R1 values ($I > 2\sigma(I)$)	0.028	0.033	0.039	0.045	0.036	0.049
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.072	0.061	0.094	0.092	0.088	0.126
Final R1 values (all data)	0.031	0.039	0.052	0.059	0.042	0.054
Final $wR(F^2)$ values (all data)	0.074	0.062	0.102	0.098	0.094	0.130
Goodness of fit on F^2	1.05	1.09	1.02	1.06	1.07	1.03
Flack x determined using quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$	0.03(1)	-0.01(3)				

Note regarding the structures of **2** and **3**

The structures of **2** (methyl derivative) and **3** (bromo derivative) are very closely comparable. However, **2** appears to adopt a superstructure with a unit-cell volume four times that of **3**. While **3** contains only $\frac{1}{2}$ of a molecule in the asymmetric unit, **2** contains $1+\frac{1}{2}$. The structure of **2** contains local translations that amount to C -centring ($\frac{1}{2}, \frac{1}{2}, 0$) in the reported R -centred cell. If these translations are considered to be real, the structure can be described with a subcell essentially identical to **3**. However, reconstructed precession images show clearly that the additional diffraction peaks are present and that the supercell is appropriate (Figure S29). For **3**, there is no sign of any additional diffraction peaks to indicate a larger cell. Thus, we conclude that the supercell structure for **2** is genuine, at least for the crystal examined. Refining **2** in the smaller cell analogous to **3** does produce a satisfactory refinement, but with somewhat elongated displacement ellipsoids, especially for the methyl group (of which there is only one unique in that representation) (Figure S30).

Figure S29: Reconstructed precession images for **2**, showing the consistency between the diffraction pattern and the reported supercell description indicated by the predicted reflection positions (green circles). No such additional spots appear in the diffraction pattern of **3**.



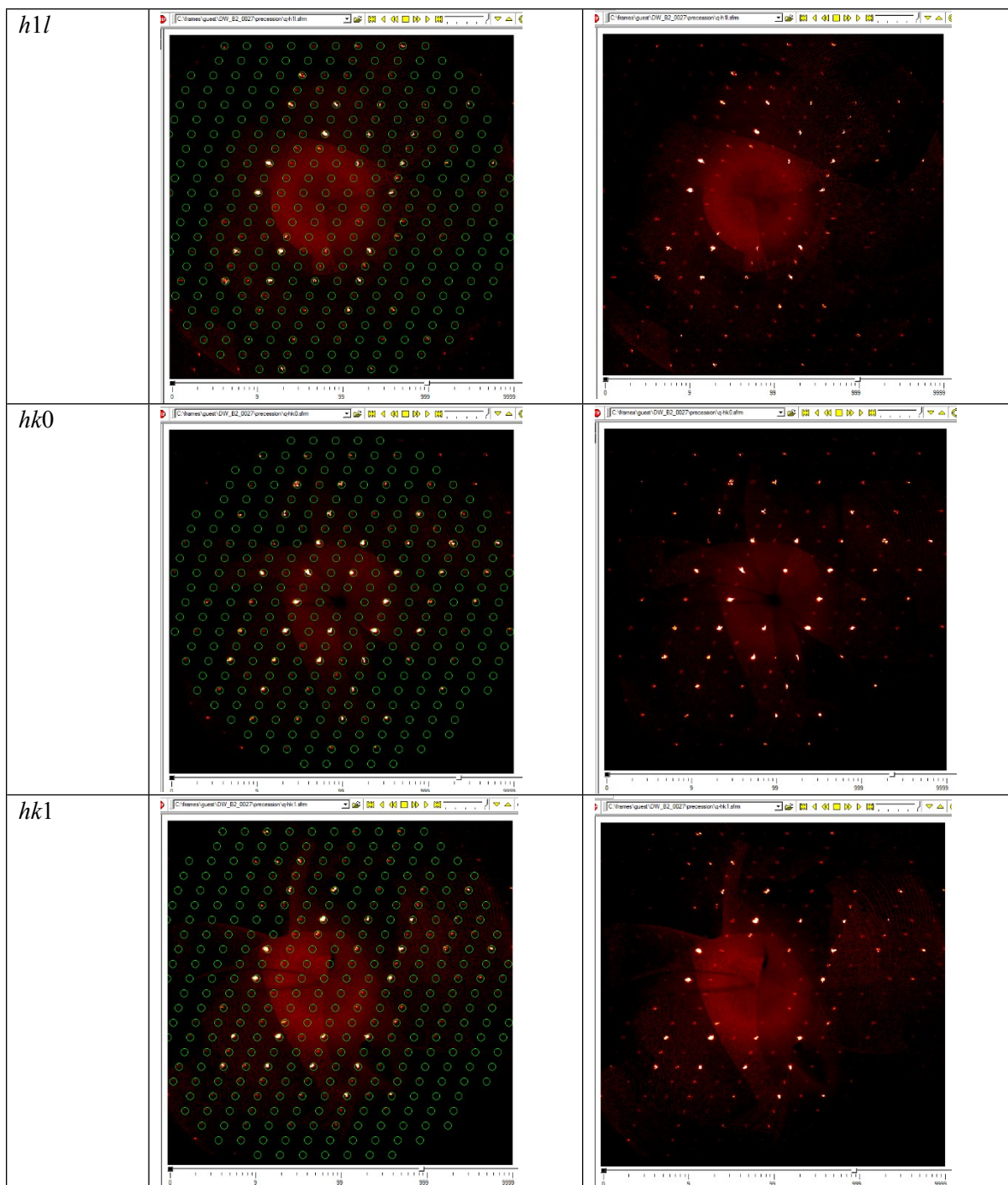


Figure S30. Displacement ellipsoid plot for the asymmetric unit of **2** in the subcell analogous to **3**.

