Supporting Information

mer-$M(CO)_3(PNP)^{0/+}$ Pincer Complexes (M = W(0) or Re(I); PNP = 4,5-Bis(diphenylphosphino)acridine): Synthesis, Spectroscopy and Anti-Kasha Emission

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Table S1 Crystal data of **1**·$2CH_2Cl_2$ and **2**·$1.5CH_2Cl_2$·$1/2H_2O$

Compounds	**1**·$2CH_2Cl_2$	**2**·$1.5CH_2Cl_2$·$1/2H_2O$
Empirical formula	$C_{42}H_{31}Cl_4NO_3P_2W$	$C_{41.50}H_{31}Cl_4NO_{3.50}P_2Re$
Formula weight	985.27	989.61
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions		
a(Å)	9.4778(6)	11.8019(6)
b(Å)	18.2165(12)	17.4795(8)
c(Å)	21.7061(14)	19.5354(10)
α(°)	90	92.227(2)
β(°)	90.038(3)	91.695(2)
γ(°)	90	109.672(2)
Volume (Å^3)	3747.6(4)	3788.0(3)
Z	4	4
Calculated density (g cm^{-3})	1.671	1.735
Absorption coefficient (mm^{-1})	3.423	3.62
F(000)	1860	1952
Crystal size (mm^3)	0.27 × 0.18 × 0.16	0.28 × 0.07 × 0.07
□ range for data collection (°)	2.6 to 28.3	2.5 to 28.5
Index ranges	-12 ≤h≤ 12, -24 ≤k≤ 24, -28 ≤l≤ 28	-15 ≤h≤ 15, -23 ≤k≤ 23, 0 ≤l≤ 26
Reflections collected	91202	19284
Independent reflections [R(int)]	9311 0.0407	19284 0.058
Max. and min. transmission	0.7457 and 0.5065	0.746 and 0.608
Data/restraints/parameters	9311/ 0 /478	19284/ 104 / 981
Goodness-of-fit	1.233	07
Final R indices [I>2σ(I)]	$R1$= 0.0359 $wR2$= 0.0840	$R1$= 0.0648 $wR2$= 0.125
Largest diff. peak and hole (e.Å^{-3})	1.53 and −2.08	2.88 and −2.99

Table S2. Selected bond lenghts (Å) and angles (deg) in **1**·$2CH_2Cl_2$ and **2**·$1.5CH_2Cl_2$·$1/2H_2O$

1		**2**	
W(1)-P(1)	2.401(1)	Re(1)-P(1)	2.374(2)
W(1)-P(2)	2.415(1)	Re(1)-P(2)	2.381(2)
W(1)-N(1)	2.280(4)	Re(1)-N(1)	2.217(8)
W(1)-C(14)	2.027(5)	Re(1)-C(14)	1.987(12)
W(1)-C(16)	2.020(5)	Re(1)-C(15)	1.969(11)
W(1)-C(15)	1.950(5)	Re(1)-C(16)	1.914(9)
P(1)-W(1)-P(2)	156.62(4)	P(1)-Re(1)-P(2)	161.49(9)
N(1)-W(1)-P(1)	79.2(1)	N(1)-Re(1)-P(1)	80.9(2)
N(1)-W(1)-P(2)	79.0(1)	N(1)-Re(1)-P(2)	80.5(2)
C(14)-W-C(16)	169.2(2)	C(14)-Re(1)-C(15)	174.8(4)
C(14)-W-C(15)	83.1(2)	C(15)-Re(1)-C(16)	87.9(4)

Table S3 Selected bond lenghts (Å) and angles (°) of the other independent molecule in the crystal of **2**.	
Re(2)-P(3)	2.375(2)
Re(2)-P(4)	2.373(2)
Re(2)-N(2)	2.214(8)
Re(2)-C(30)	1.973(11)
Re(2)-C(31)	1.963(12)
Re(2)-C(32)	1.930(10)
P(3)-Re(2)-P(4)	161.49(9)
N(2)-Re(2)-P(3)	80.3(2)
N(2)-Re(2)-P(4)	80.9(2)
C(30)-Re(2)-C(31)	172.3(4)
C(30)-Re(2)-C(32)	86.5(4)
P(3)-Re(2)-C(31)	92.2(3)
P(3)-Re(2)-C(32)	99.8(3)
N(2)-Re(2)-C(32)	174.8(4)
N(2)-Re(2)-C(30)	88.3(4)

Table S4. Experimental and calculated frequency of CO vibrations

Complexes	Experimental /calculated frequencies of vibrational modes (cm^{-1})		
	$A_1(1)$	B_1	$A_1(2)$
1	1950/ 1938	1845/ 1862	1815/ 1849
2	2075/ 2026	1970/ 1950	1916/ 1934

Table S5. B3PW91/(6-31G(d) + SDD) calculated compositions of frontier orbitals of **1** and **2** with the major contributors highlighted in bold (CO_{ax} and CO_{eq} stand for axial and equatorial CO, respectively).

Orbital	Contribution					
	Metal		P	CO_{eq}	CO_{ax}	Acridine
	p	*d*				
			1			
L+2	1.1	0.1	1.9	0.1	2.1	**70.3**
L+1	0.1	0.2	0.3	0.0	0.2	**95.2**
L	0.1	0.5	1.1	0.4	0.4	**95.7**
H	2.6	**61.0**	5.7	**21.7**	1.4	3.9
H-1	0.0	**53.1**	1.3	**12.5**	24.1	8.2
H-2	0.0	**59.2**	5.9	0.1	**24.6**	0.9
H-3	0.1	3.1	0.8	0.4	0.9	**82.1**
			2			
L+2	**10.6**	0.2	5.3	0.5	**69.7**	0.0
L+1	**15.5**	3.2	2.6	0.0	**71.9**	3.3
L	0.0	0.2	1.0	0.3	0.2	**96.7**
H	2.9	**49.7**	7.8	**15.5**	0.8	1.3
H-1	0.0	**16.3**	1.3	3.5	5.0	**66.4**
H-2	0.4	**43.6**	4.1	0.3	**11.2**	5.4
H-3	0.9	**29.9**	8.7	1.9	3.4	6.7
H-4	0.0	**31.1**	0.2	5.4	8.8	**11.7**

Table S6. Calculated energies and major components of selected electronic transitions for **1** and **2** (intense transitions are in bold).

1				**2**			
Transition	λ(nm)	Oscillator strength		Transition	λ(nm)	Oscillator strength	
H-2 → L (100%)	757	0.0032	d_{yz}→π*(acridine)	**H-1 → L (98%)**	**422**	**0.1287**	d_{xz}→π*(acridine) π→π*(acridine)
H-1 → L (99%)	**731**	**0.0427**	**d_{xz}→π***(acridine)	H-2 → L (98%)	412	0.0029	d_{yz}→π*(acridine)
H → L+3 (85%) H → L+6 (12%)	435	0.0108	d_{xy}→π*(CO_{ax})	H–7 → L (94%)	343	0.0249	π(Ph)→π*(acridine)
H-3 → L (96%)	**397**	**0.0873**	**π →π***(acridine)$_i$	H–10 → L (91%) H–7 → L (5%)	335	0.0144	π(Ph)→π*(acridine)
H→ L+4 (6%) H→ L+5 (49%) H→ L+6 (35%)	377	0.0167	d_{xy}→π*(CO_{ax})	**H–12 → L (77%) H–1 → L+3 (18%)**	**318**	**0.1092**	**π→π***(acridine)
H-2 → L+6 (65%) H-2 → L+3 (11%)	**326**	**0.0816**	**d_{yz}→π*(CO_{ax})**				

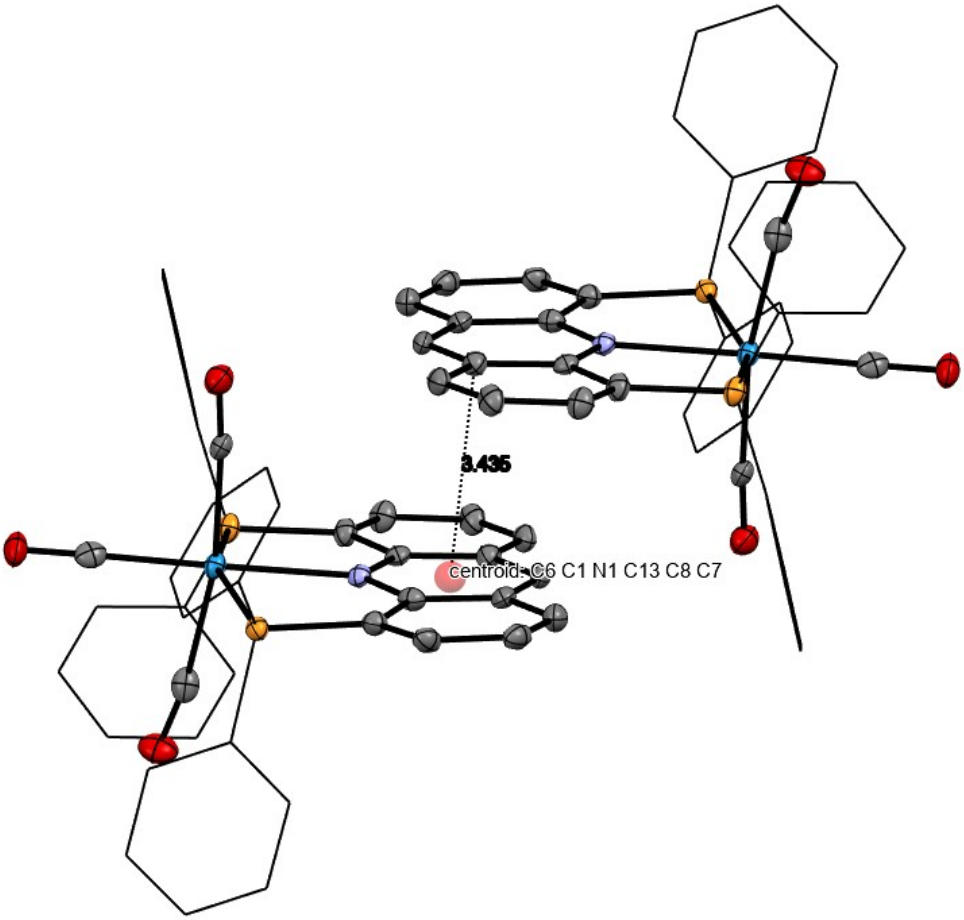

Figure S1. Stacking of molecules of **1** in crystal.

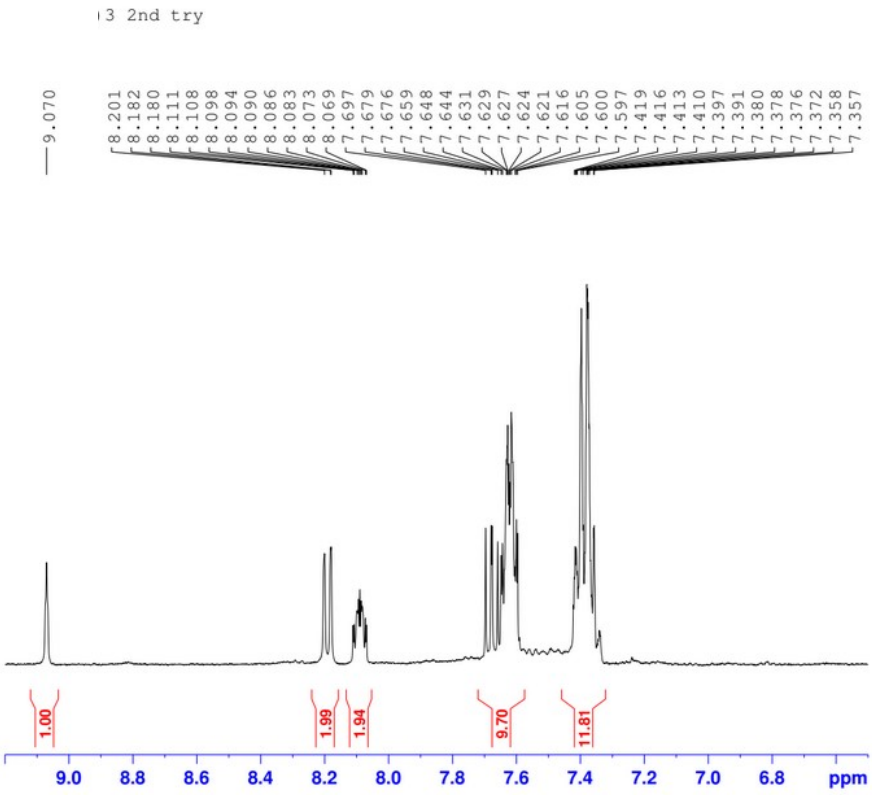

Figure S2a. ^{1}H NMR spectrum of **1** in CD_2Cl_2 (400 MHz)

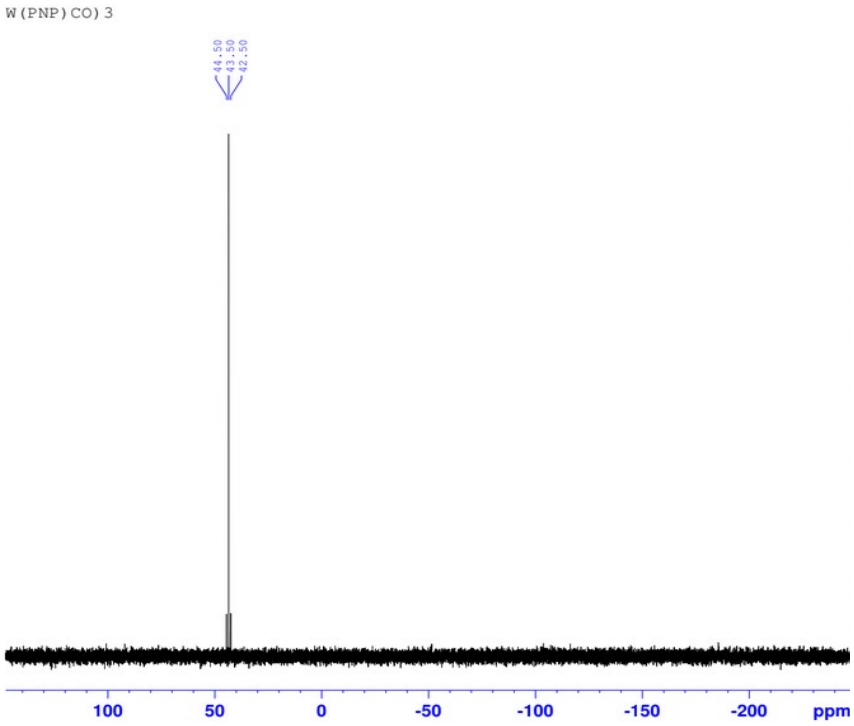

Figure S2b. $^{31}P\{^{1}H\}$ NMR spectrum of **1** in CD_2Cl_2 (162 MHz)

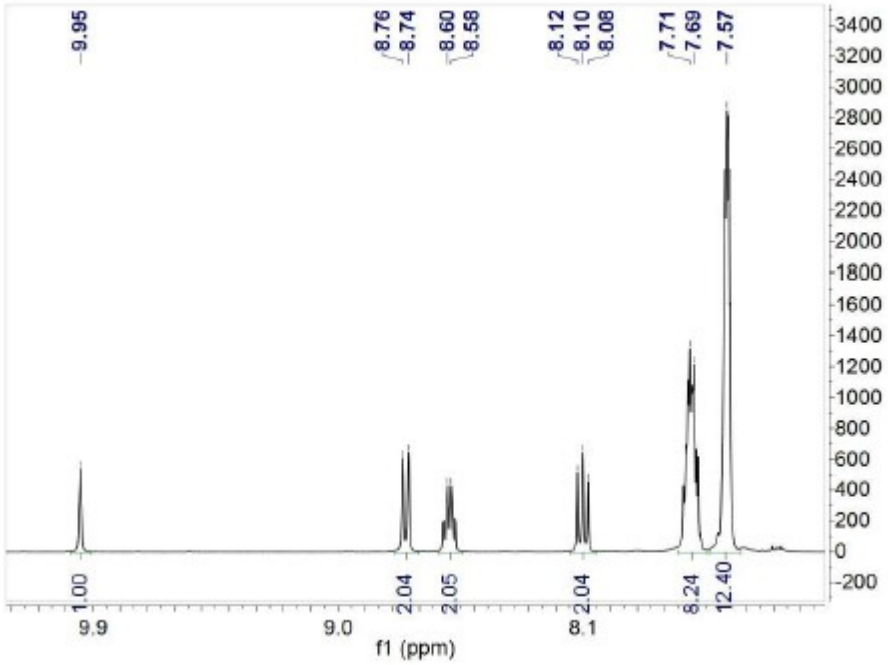

Figure S3a. ^{1}H NMR spectrum of **2** in CD_2Cl_2 (400 MHz)

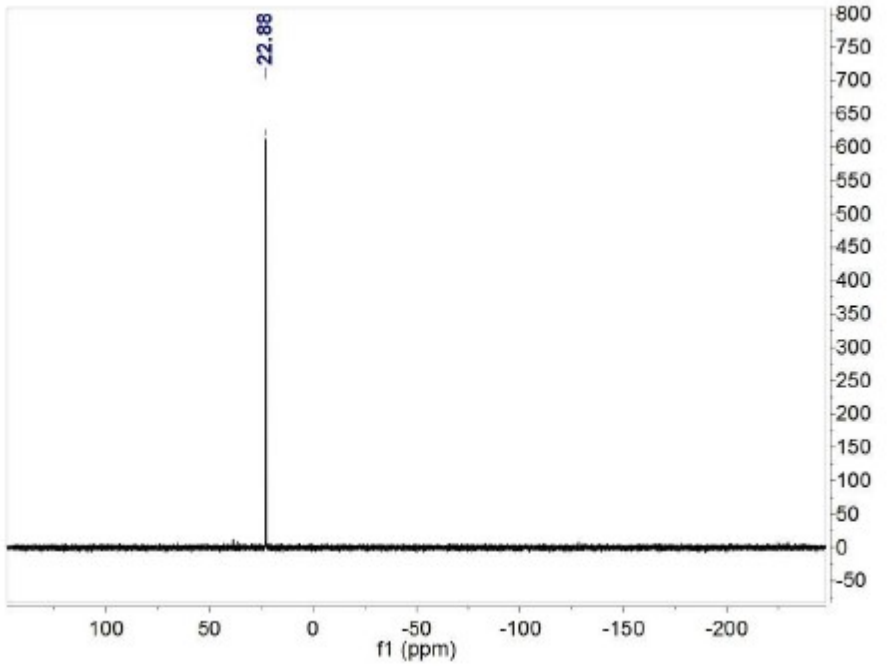

Figure S3b. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in CD_2Cl_2 (162 MHz)

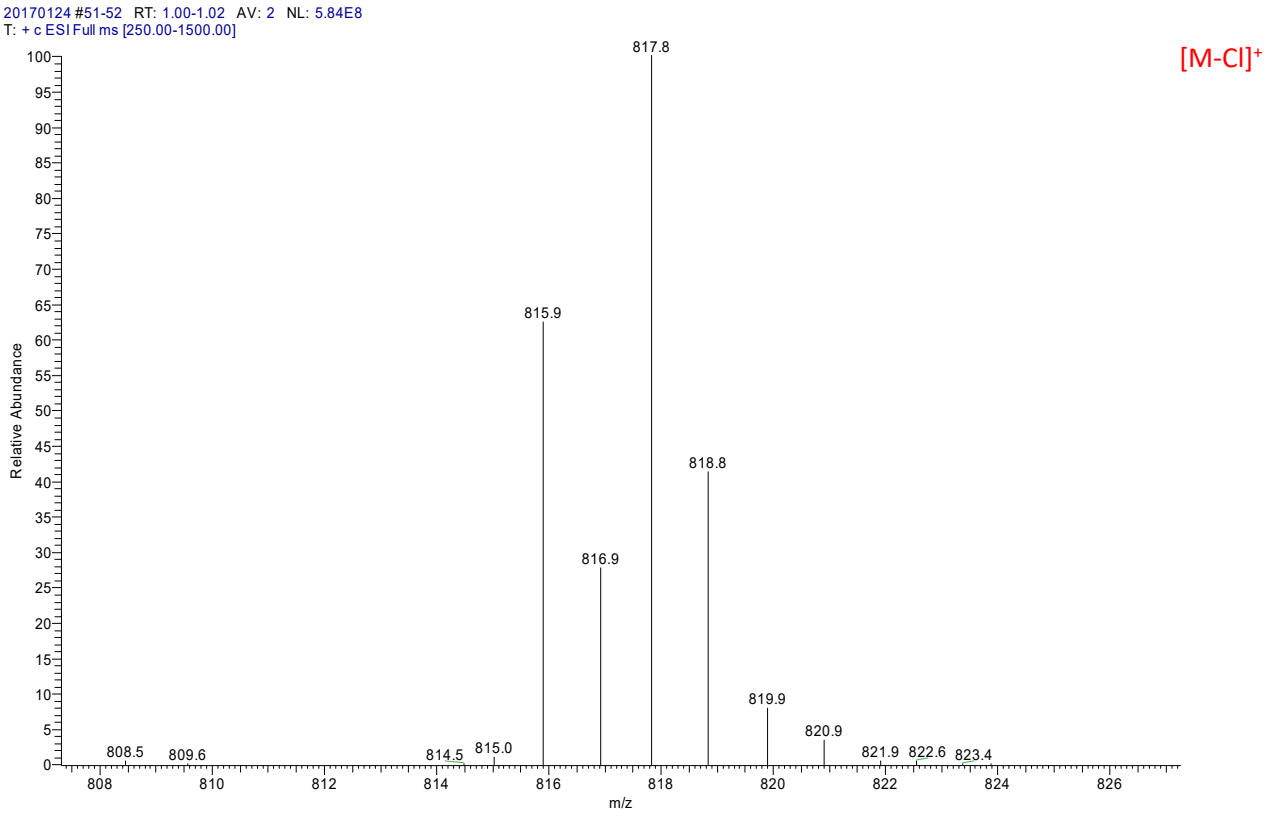

Figure S4. ESI-MS of **2**.

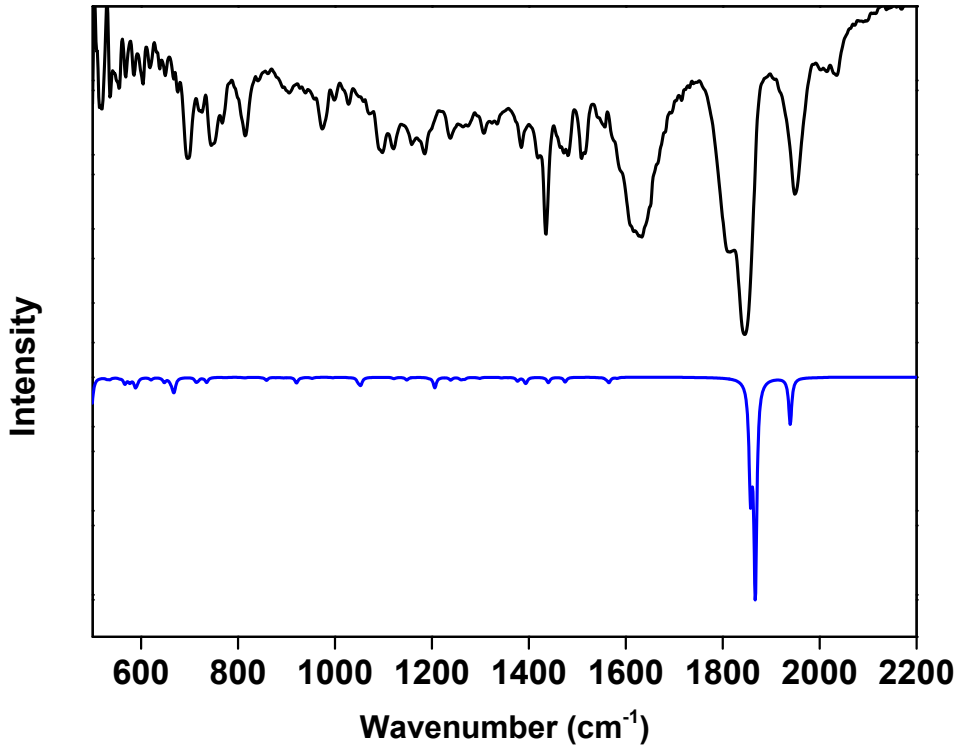

Figure S5a. Experimental (black) and DFT-calculated (Blue) IR spectra for **1** (B3PW91/LANL2DZ+6-31G(d); 0.94)

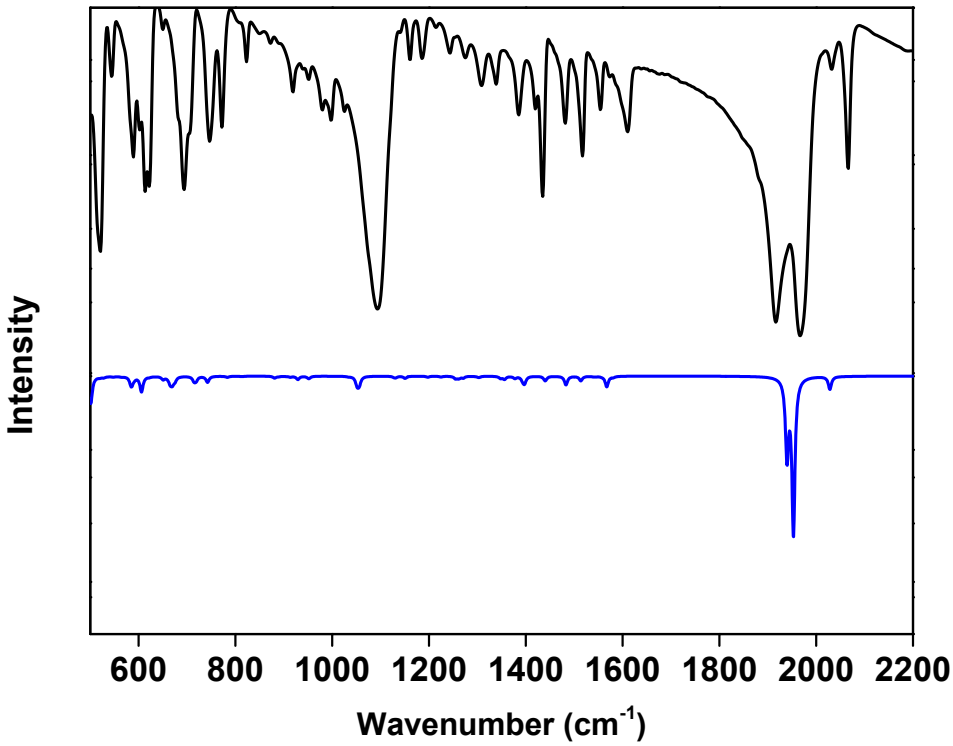

Figure S5b. Experimental (black) and DFT-calculated (blue) IR spectra for **2** (B3PW91/LANL2DZ+6-31G(d); 0.94)