Carbon–arsine and carbon–antimony bonds activation of $AsPh_3$ and $SbPh_3$ at dimanganese and dirhenium centers in bimetallic clusters

Md. Jobayer Ahmed[a,b], Md. Sohag Hasan[a], Md. Atikul Islam [c], Md. Enamul Haque [c], Md. Abdullah Al Mamun[a], Joyanta K. Saha[c], Vladimir N. Nesterov[d], Shariff E. Kabir[a,c,*], Jagodish C. Sarker[b,*]

[a] *Department of Chemistry, Jahangirnagar University, Savar, Dhaka 1342, Bangladesh*

[b] *Department of Chemistry, Mawlana Bhashani Science & Technology University, Santosh, Tangail 1902, Bangladesh*

[c] *Department of Chemistry, Jagannath University, Dhaka 1100, Bangladesh*

[d] *Department of Chemistry, University of North Texas, 1155 Union Circle, Box 305070, Denton, TX, 76203, USA*

*Corresponding author, Email: jagodish@chem.jnu.ac.bd; skabir_ju@yahoo.com

Electronic Supplementary Information (ESI)

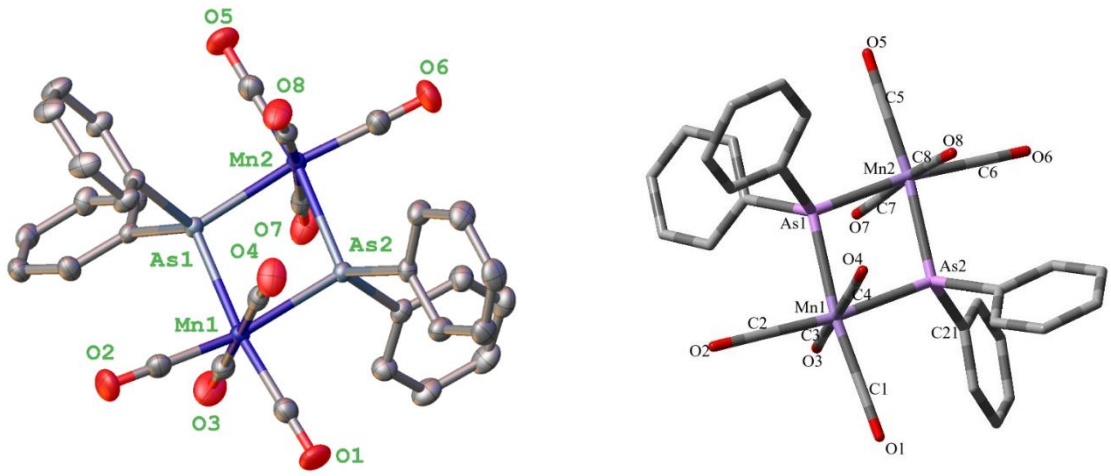

Fig. S1 Molecular structure of $[Mn_2(CO)_8(\mu\text{-}AsPh_2)_2]$ (**2**) showing 50% probability atomic displacement ellipsoids (left) and the DFT optimized structure (right). Ring hydrogen atoms are omitted for clarity.

Table S1. Comparative bond lengths (Å) and angles (°) from XRD and DFT data for **2**

	Bond length	Experimental	Reported	DFT	Bond Angle	Experimental	Reported	DFT
Compound **2**	As(1)–Mn(1)	2.4678(4)	2.4685(7)	2.485	Mn(2)–As(1)–Mn(1),	102.371(13)	102.23(2)	101.47
	As(2)–Mn(1)	2.4772(4)	2.4773(7)	2.485	Mn(2)–As(2)–Mn(1),	101.818(13)	101.73(2)	101.47
	As(1)–Mn(2)	2.4627(4)	2.4719(7)	2.485	As(1)–Mn(1)–As(2),	77.698(11)	77.99(2)	78.50
	As(2)–Mn(2)	2.4725(4)	2.4803(7)	2.485	As(1)–Mn(2)–As(2),	77.880(11)	77.87(2)	78.50
	Mn(1)–C(1)	1.831(2)	1.847(5)	1.799	C(1)–Mn(1)–As(1),	170.71(8)	83.8(2)	172.20
	Mn(1)–C(2)	1.820(2)	1.826(5)	1.799	C(2)–Mn(1)–As(1)	94.00(7)	94.5(2)	94.08
	Mn(1)–C(3)	1.849(2)	1.827(5)	1.838	C(3)–Mn(1)–As(1)	85.62(7)	171.3(2)	89.78
	Mn(1)–C(4)	1.854(2)	1.832(5)	1.837	C(1)–Mn(1)–As(2)	93.57(7)	93.2(2)	94.18
	Mn(2)–C(5)	1.823(2)	1.847(5)	1.799	C(7)–Mn(2)–As(1)	90.11(7)	93.9(2)	83.33
	Mn(2)–C(6)	1.823(2)	1.824(5)	1.799	C(5)–Mn(2)–As(2)	171.47(8)	95.2(2)	172.20
	Mn(2)–C(7)	1.842(2)	1.824(5)	1.838	C(6)–Mn(2)–As(2)	94.51(7)	93.6(2)	94.08
	Mn(2)–C(8)	1.848(2)	1.843(5)	1.837	C(7)–Mn(2)–As(2)	82.48(7)	170.1(2)	89.80
	As(2)–C(21)	1.9575(19)	1.968(4)	1.975	C(2)–Mn(1)–As(2)	170.02(7)	171.7(2)	172.02
	O(4)–C(4)	1.138(3)	1.138(6)	1.140	C(21)–As(2)–Mn(1)	111.65(6)	112.3(1)	113.70
	O(5)–C(5)	1.142(3)	1.123(6)	1.145	C(21)–As(2)–Mn(2)	115.90(6)	117.8(1)	113.70

Table S2. Crystal data and structure refinement details for compound **2**

Compound	**2**
CCDC	2493936
Empirical formula	$C_{32}H_{20}As_2Mn_2O_8$
Formula weight	792.20
Temperature (K)	150.00(10)
Wavelength (Å)	1.54184
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	12.11220(10)
b (Å)	16.39860(10)
c (Å)	15.7643(2)
α(°)	90
β (°)	102.2130(10)
γ (°)	90
Volume (Å^3)	3060.29(5)
Z	4
Density (calculated) (Mg/m^3)	1.719
Absorption coefficient (mm^{-1})	9.555
F(000)	1568.0
Crystal size (mm^3)	0.055 × 0.045 × 0.02
2Θ range for data collection (°)	7.874 to 160.72
Index ranges	$-15 \leq h \leq 15$ $-20 \leq k \leq 13$ $-20 \leq l \leq 19$
Reflections collected	33313
Independent reflections [R_{int}]	6586 [R_{int} = 0.0306]
Data / restraints / parameters	6586/0/398
Goodness of fit on F^2	1.064
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0276 wR_2 = 0.0712
R indices (all data)	R_1 = 0.0304 wR_2 = 0.0728
Largest diff. peak and hole (eÅ^{-3})	0.42 and -0.45

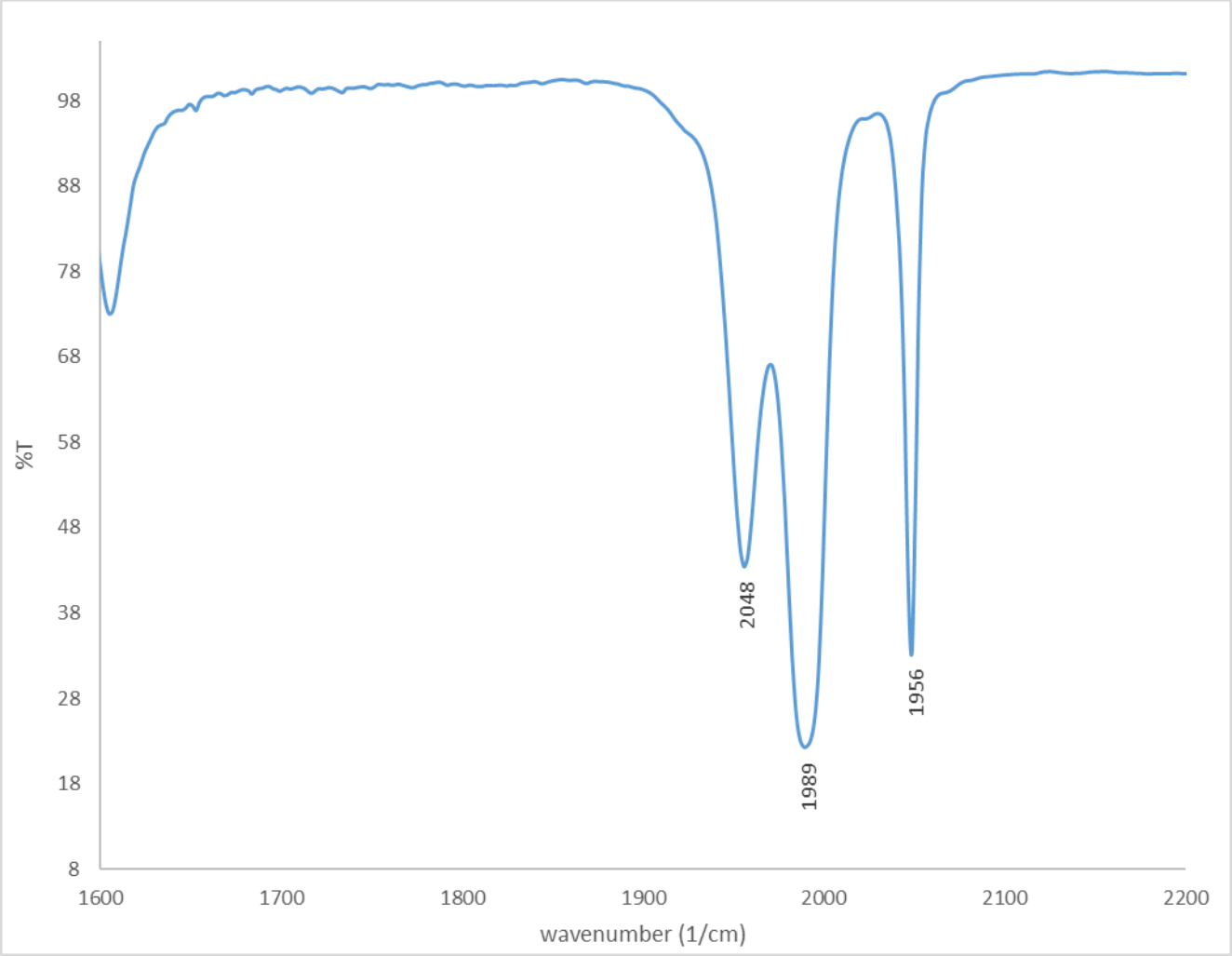

Fig. S2 IR spectrum of compound [(μ-H)(Mn_2(CO)$_7$(μ-$AsPh_2$)($AsPh_3$)] (**1**)

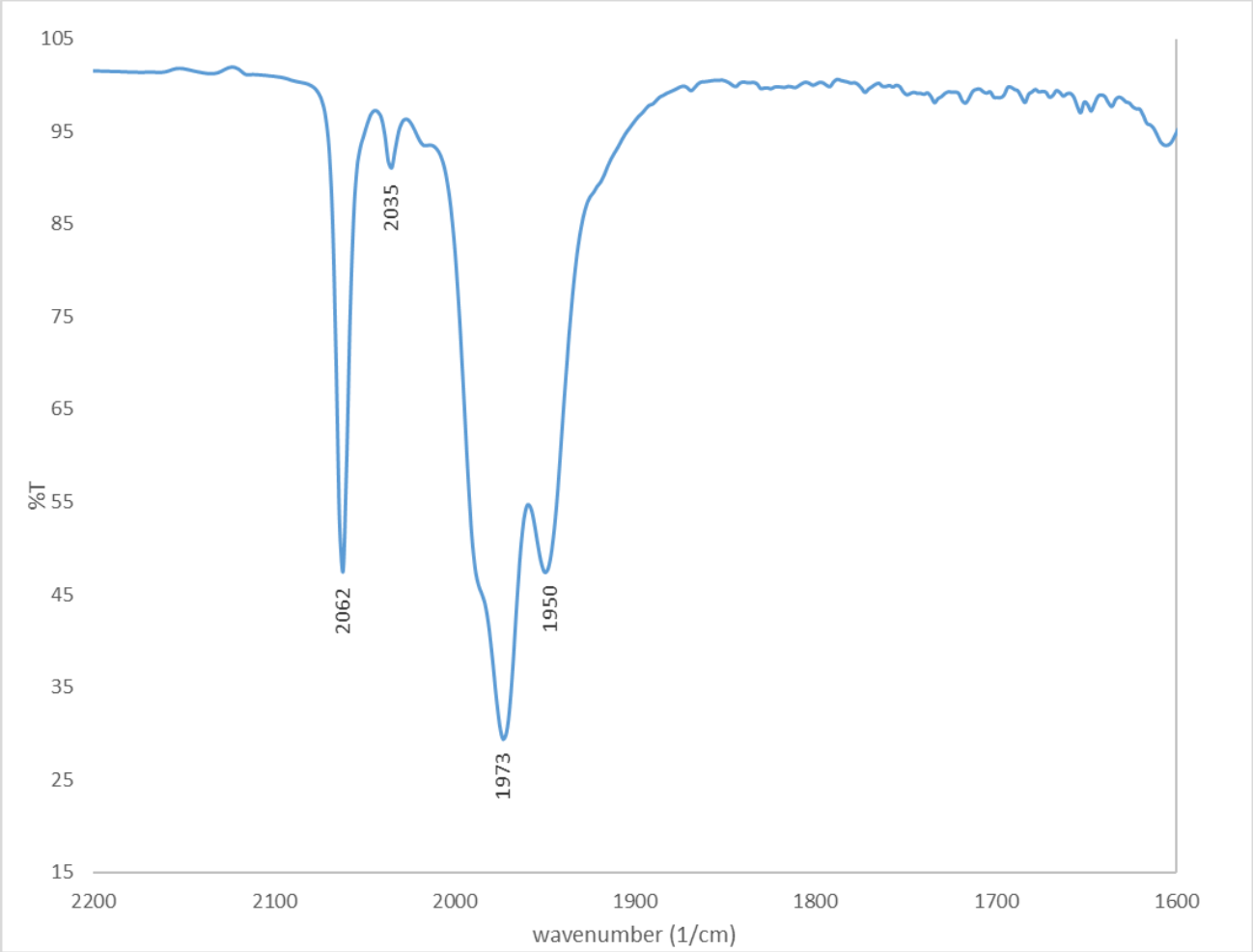

Fig. S3 IR spectrum of compound $[Mn_2(CO)_8(\mu\text{-}SbPh_2)_2]$ (**3**)

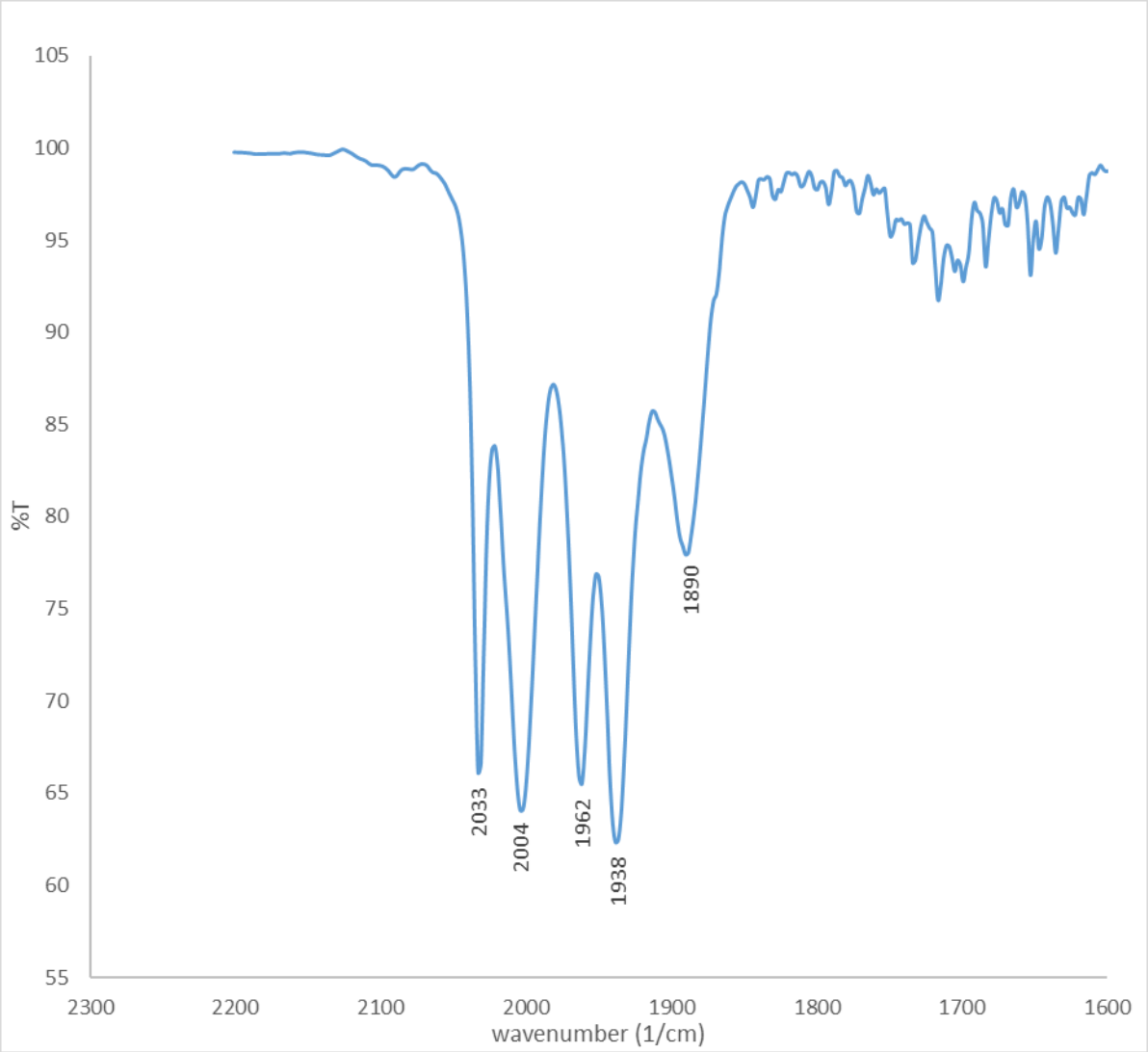

Fig. S4 IR spectrum of compound $[Re_2(CO)_5(\sigma\text{-}Ph)(\mu\text{-}MeCO_2)(\mu\text{-}AsPh_2)_2]$ (**5**)

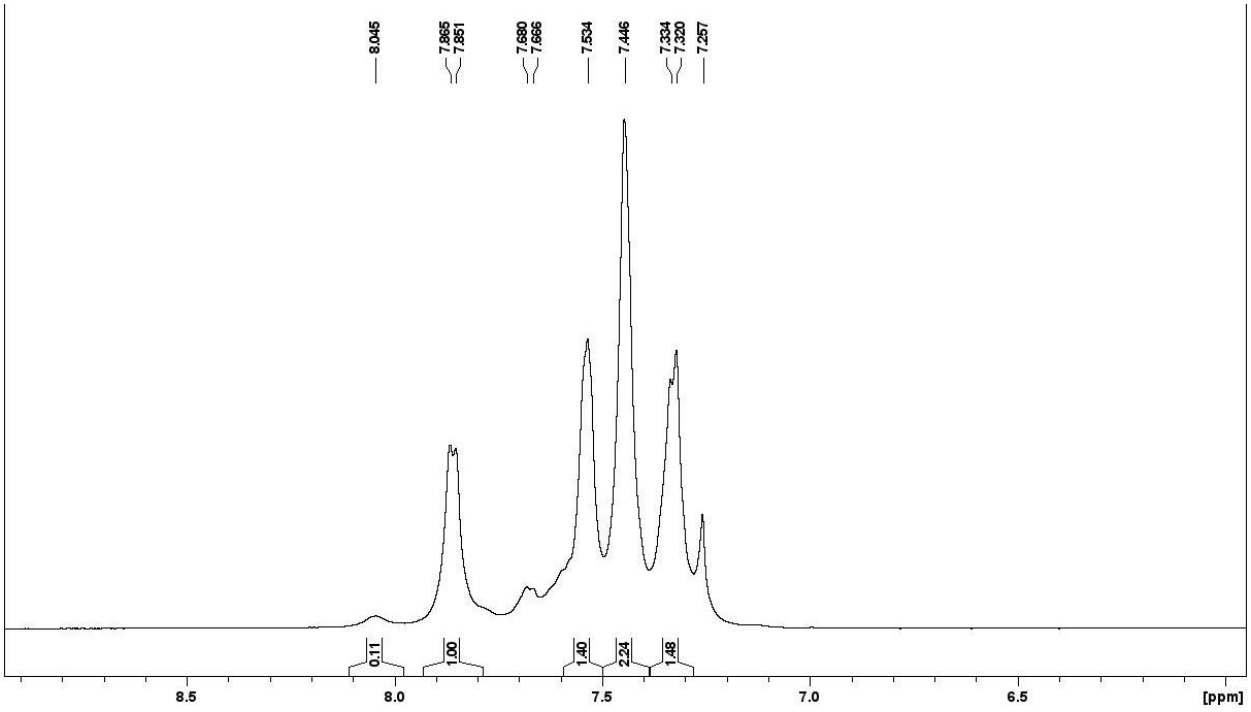

Fig. S5 Aromatic region of the ^{1}H NMR of [(μ-H)($Mn_2(CO)_7$(μ-$AsPh_2$)($AsPh_3$)] (**1**)

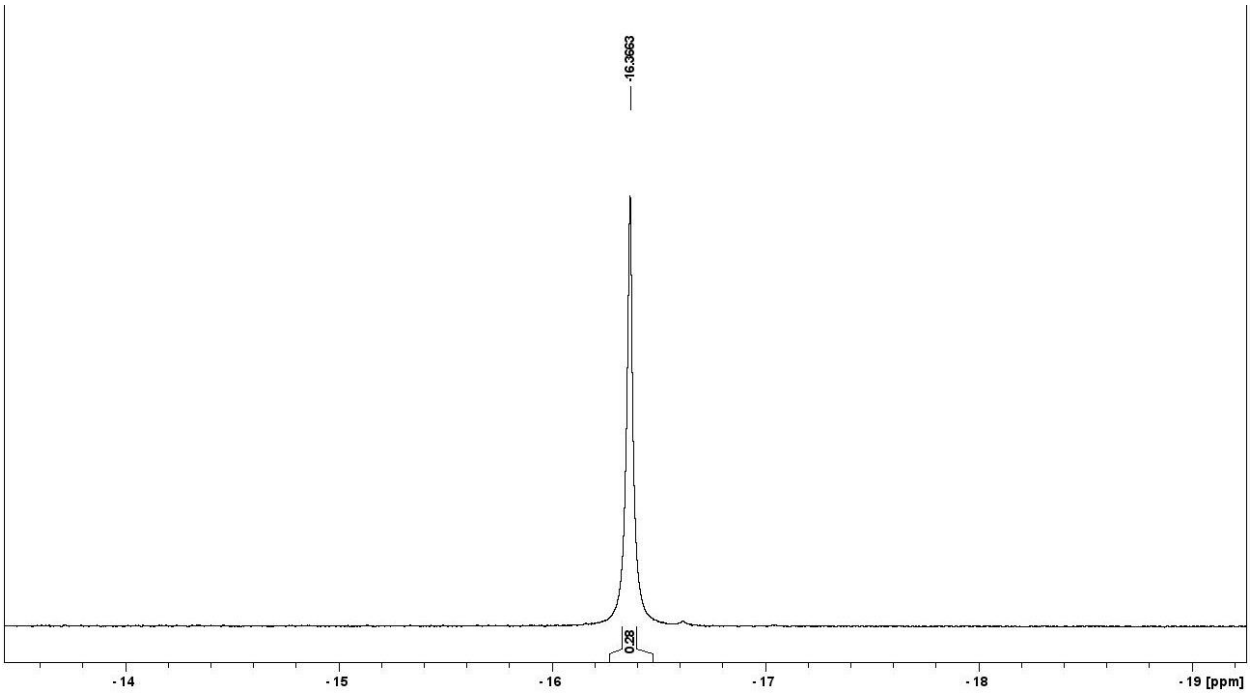

Fig. S6 Hydride region of the ^{1}H NMR of compound [(μ-H)($Mn_2(CO)_7$(μ-$AsPh_2$)($AsPh_3$)] (**1**)

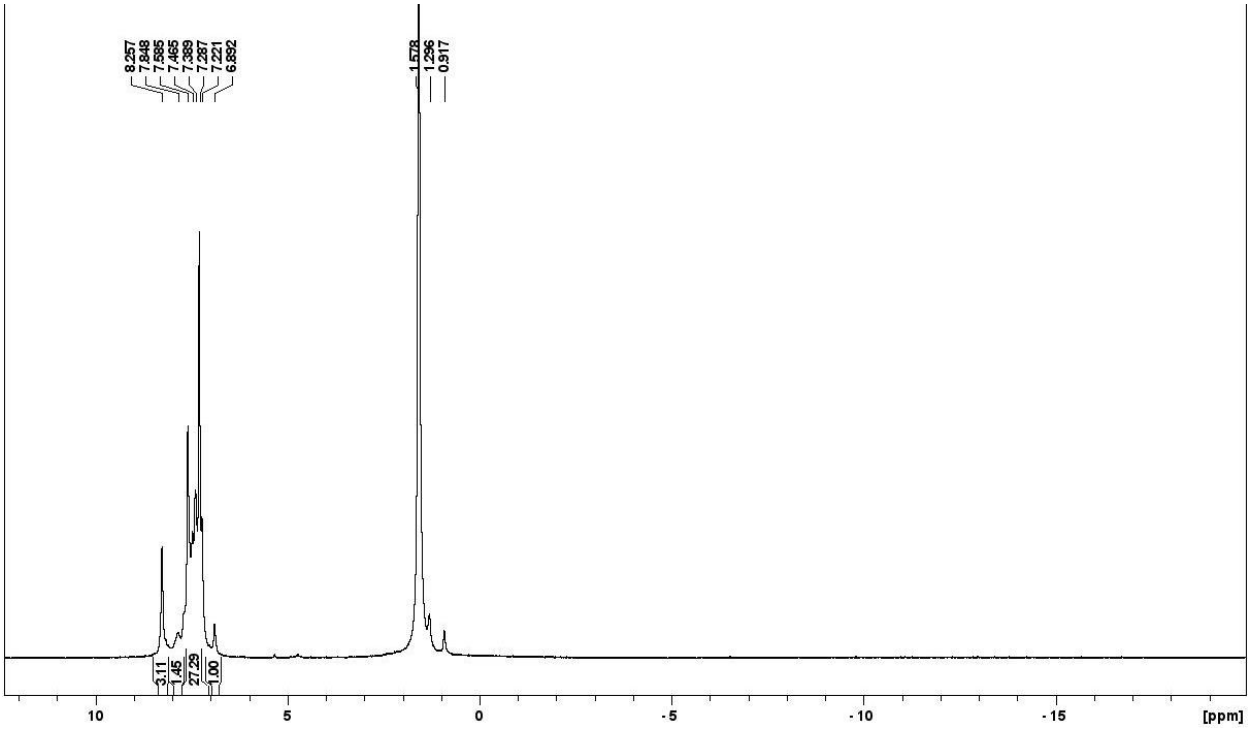

Fig. S7 ^{1}H NMR of compound $[Mn_2(CO)_8(\mu\text{-}SbPh_2)_2]$ (**3**)

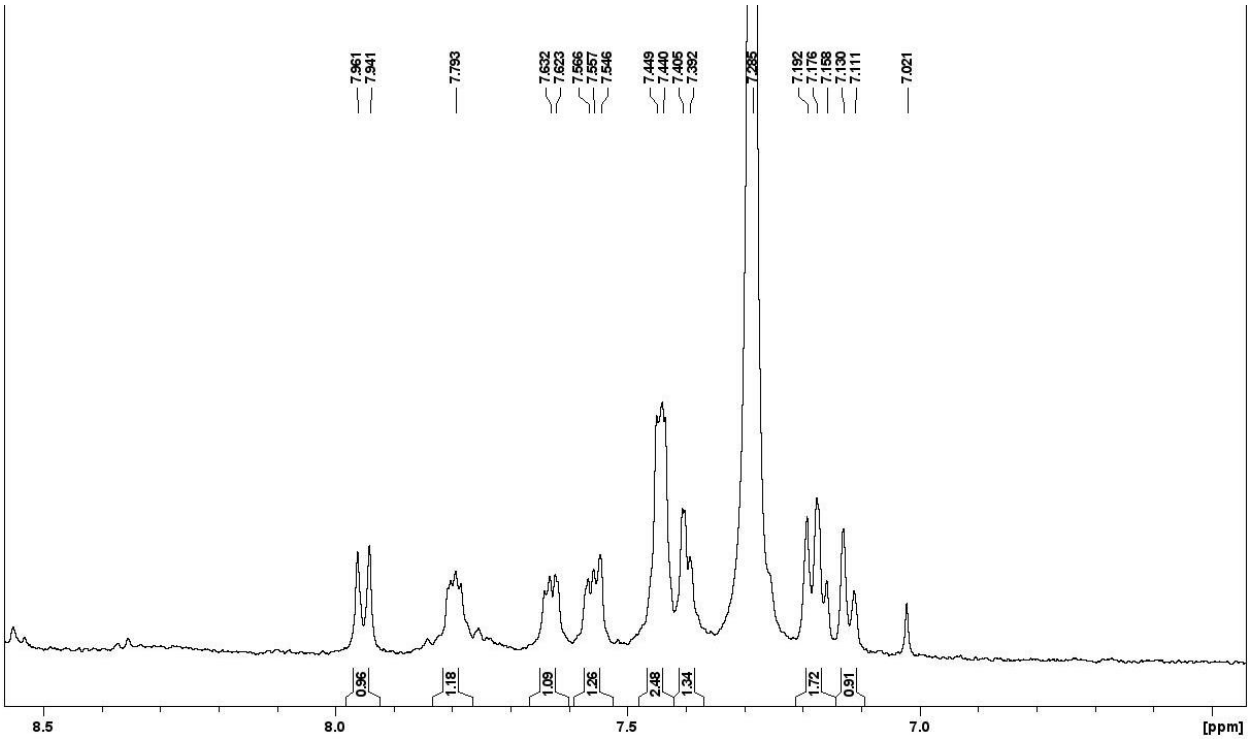

Fig. S8 Aromatic region of the ^{1}H NMR of compound $[Re_2(CO)_5(\sigma\text{-}Ph)(\mu\text{-}MeCO_2)(\mu\text{-}AsPh_2)_2]$ (**5**)