SUPPLIMENTARY DATA

Aerial oxygenation chemistry of *4*-TBC catalyzed by chloro bridged dinuclear copper(II) complexes of pyrazole based tridentate ligands – a relevance of Methane Monooxygenase(*p*MMO) behaviour

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Fig. S1. Cyclic voltammogram of **2** (1 mmol/L) in MeCN under pure N_2 atmosphere with a sweep rate of 50 mV s^{-1} at 25 ^{0}C with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. The CV for **2** is supplied as supporting information.

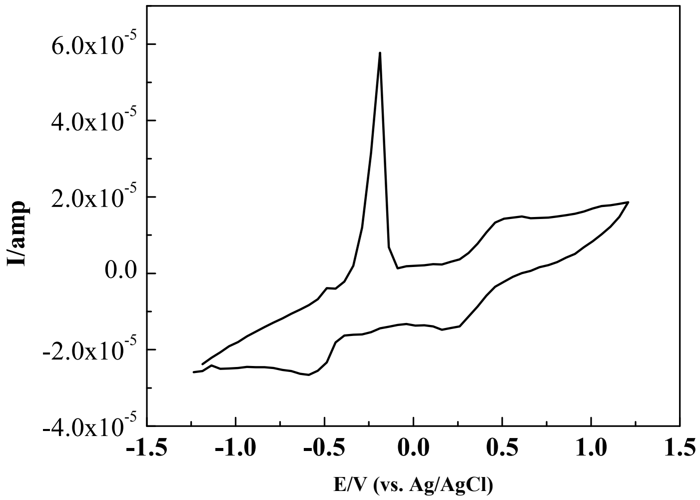


Fig S2(a) . TOF-MS-ES$^+$ spectrum of different species observed in the organic products.

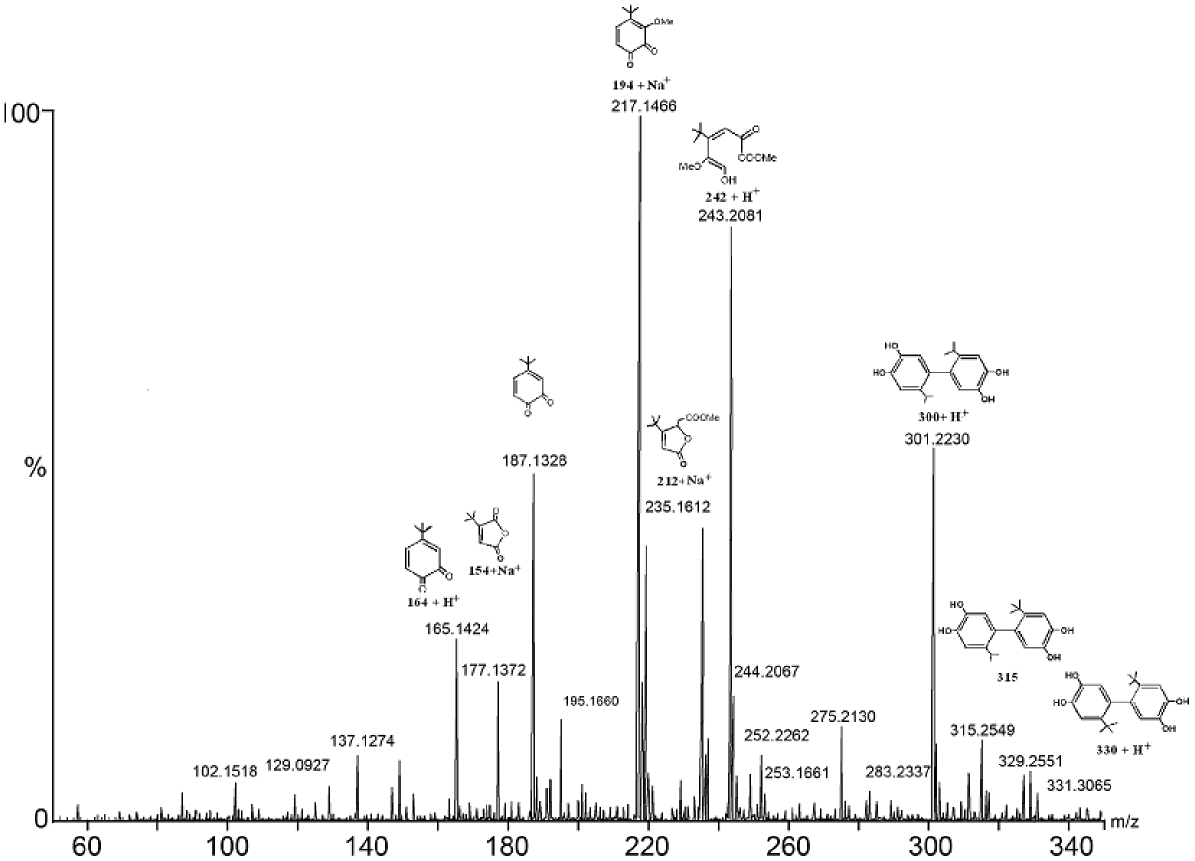
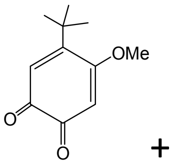
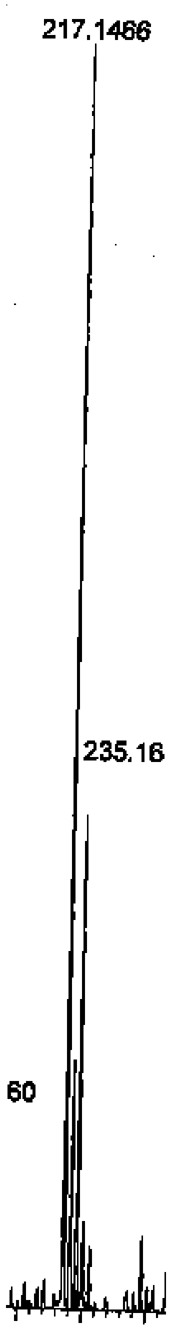


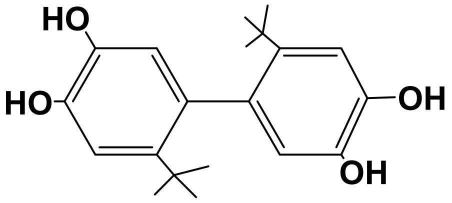
Fig S2(b) . Mass Spectra of different species observed in reaction mixtures.



+ Na^+ (ES^+-Mass)

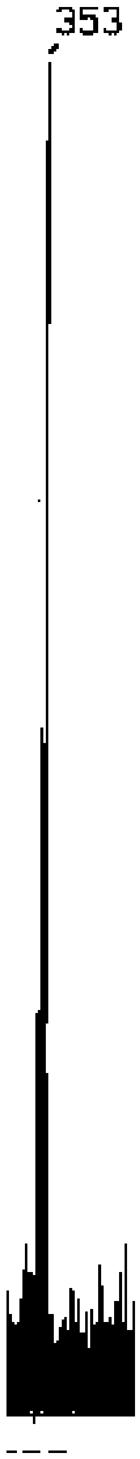
$[Cu(L^H)Cl]^+$ (FAB-Mass)

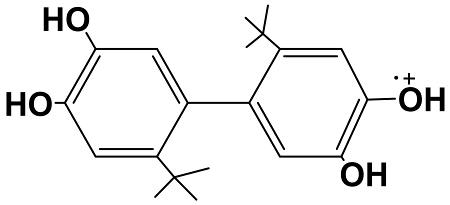




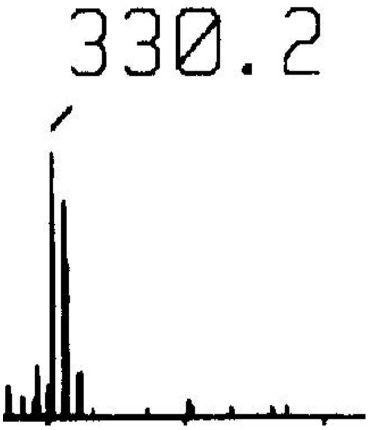
+ Na^+

(FAB-Mass)



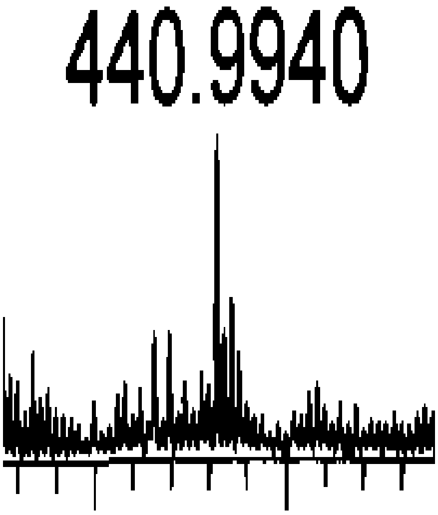


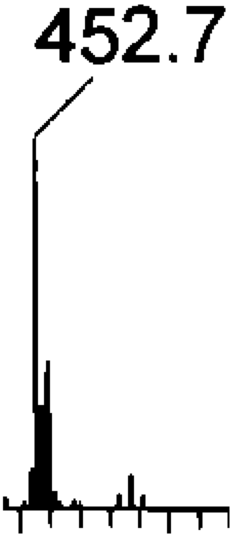
(FAB-Mass)



$[Cu(L^H)Cl(H_2O)]^+$

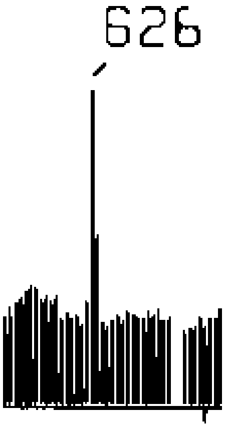
(ES^+-Mass)





$[Cu(L^H)Cl(MeOH)]^+$

(ES^+-Mass)

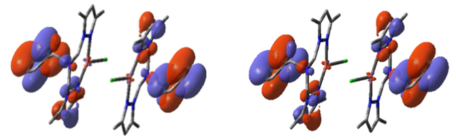


$[Cu(L^H)Cl(4\text{-}TBC\text{-}H)]$ + K^+

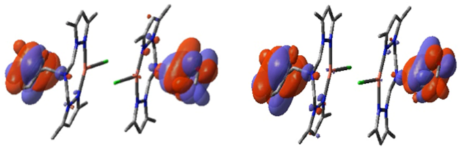
(FAB-Mass)

(FAB-Mass

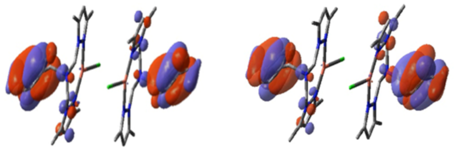
Fig. S3. Pairs of SOMOs for the triplet state of complexes **1**-**4**.



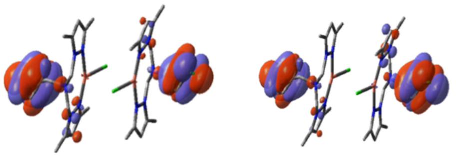
Complex 1



Complex 2



Complex 3



Complex 4

Fig. S4. Plot of k_i vs. [**1**] concentration for the oxidation of *4*-TBCH$_2$. Conditions are: [4-TBCH$_2$] = 1.5 mM; *T* =25^o C.

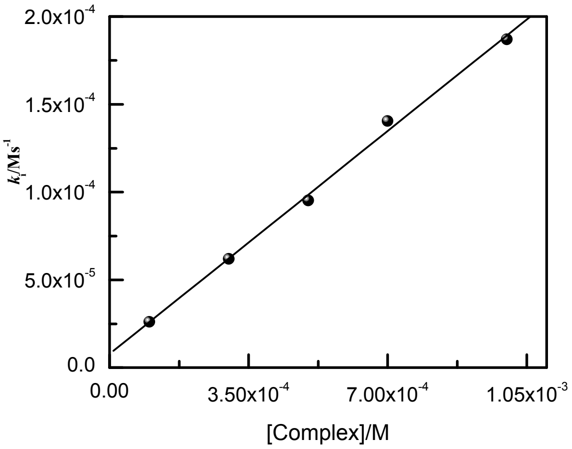
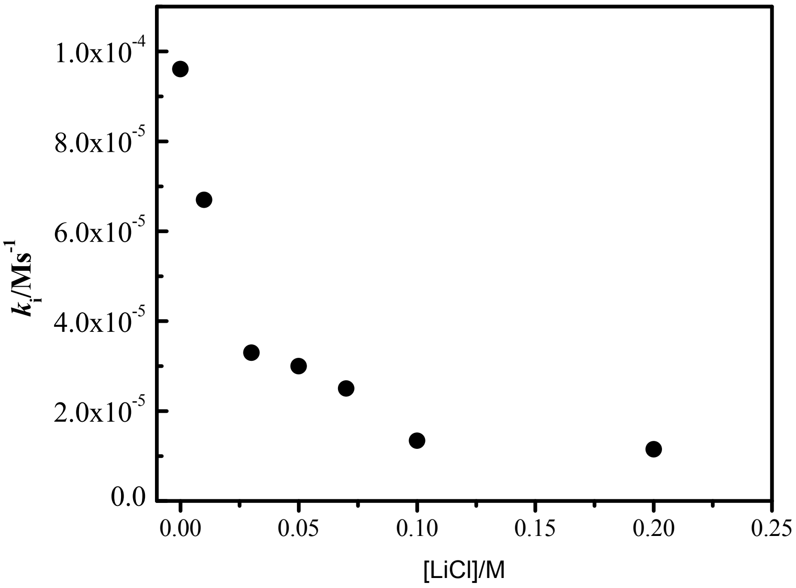


Fig. S5. Dependence of k_i on [Li$^+$] for the oxidation of *4*-TBCH$_2$ catalyzed by complex **1** in MeOH. Conditions are: [C] =0.50 mM; [*4*-TBCH$_2$] = 1.5 mM; Temp =25^o C.



SUP Figure 6. Time resolved spectra for the reaction between $[Cu_2(L^H)_2(Cl)_2]^{2+}$ and *3*,*5*-di-*tert* -butylcatechol in MeCN. Conditions: [C] = 0.50 mM, [*3*,*5*-$DTBCH_2$] = 1.0 mM, T= 32 ^{0}C.

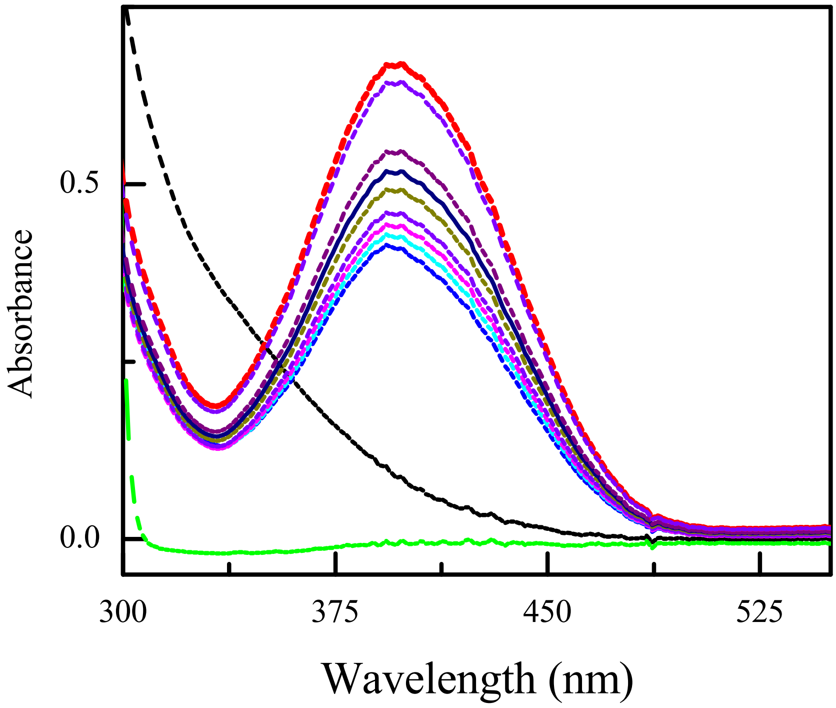


Table S1. Kinetic data for the catalytic oxidation of 4-TBC in MeOH. Conditions:[C] = 0.50 mM, temp. 25^{o} C

[4-TBC]/M	$10^5 k_i$/Ms^{-1} (**1**)	$10^5 k_i$/Ms^{-1} (**2**)	$10^5 k_i$/Ms^{-1} (**3**)
0.001	5.75e-005	1.01e-005	1.61e-005
0.0015	9.61e-005		
0.0025	1.41e-004	2.27e-005	3.43e-005
0.003	1.53e-004	2.56e-005	4.19e-005
0.004	1.93e-004	3.04e-005	4.79e-005
0.005	2.49e-004	3.65e-005	5.51e-005
0.007	2.91e-004	4.02e-005	6.57e-005
0.01	3.65e-004	4.61e-005	7.91e-005
0.02	5.21e-004	5.76e-005	9.71e-005
0.03	6.28e-004	5.97e-005	1.11e-004
0.04	6.63e-004	6.19e-005	1.17e-004
0.05	6.87e-004	6.24e-005	1.28e-004

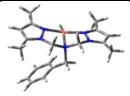
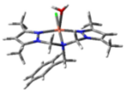
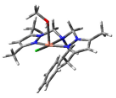
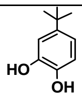
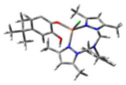
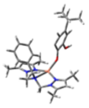
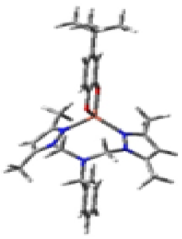
Table S2. Dependence of k_i on complex concentration for the catalytic oxidation of 4-TBC in MeOH. Conditions: [4-TBC] = 1.5 mM, temp. 25° C

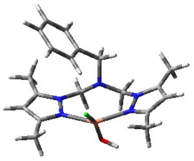
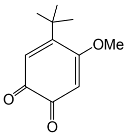
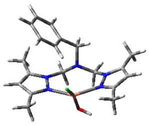
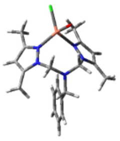
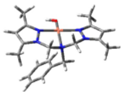
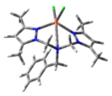
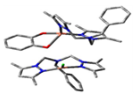
10^4 x $[Cu(L^H)Cl^+]$ /M	10^5 k_i/ Ms^{-1}
1.00	2.58
3.00	6.21
5.00	9.61
7.00	14.08
10.0	18.71

Table S3. Dependence of k_i on Cl^- ion concentration in MeOH for the catalytic oxidation of 4-TBC in MeOH. Conditions: [**1**] = 0.5 mM, [4-TBC] =1.5 mM , temp. 25° C.

[LiCl]/M	$10^5 k_i$/ Ms^{-1}
0.00	9.61
0.01	6.70
0.03	3.30
0.05	3.00
0.07	2.50
0.1	1.34

Table S4. Details of DFT calculations on different probable intermediates along with their stabilization energies.

Species	Energy (au) optimized at B3LYP/LanL2DZ/6-31+G(d)
$[Cu_2(\mu\text{-}Cl)_2(L^H)_2]^{2+}$	-2447.73013419
 **$[Cu(L^H)Cl]^+$** (Ia)	-1223.90435423
 $[Cu\ (L^H)\ Cl(H_2O)]^+$ (Ib)	-1300.36132313
 $[Cu\ (L^H)\ Cl(MeOH)]^+$ I(c)	-1339.66554927
 (II)	-540.00618563
 **$[Cu(L^H)(Cl)(4\text{-}TBC)]^+$ (III)**	-1763.51839105
 **$[Cu(L^H)(\ 4\text{-}\ HTBC)]^+$ (IIIa)**	-1747.59640434
	-1747.93806595

$[Cu(L^{H})(4\text{-}TBC)]$(IIIb)	
 **$[Cu(L^{H})(4\text{-}TBC)Cl]$(IIIc)**	-1747.93806595
 (VI)	-653.23071835
 **$[Cu(L^{H})(OH)Cl]$ (VII)**	-1299.93659345
 **$[Cu^{III}{=}O(L^{H})Cl]$ (VIII)**	-1299.2205793
 **$[Cu(L^{H})(OH)]^{+}$ (IX)**	-1284.75232177
 **$[Cu(L^{H})(Cl)_{2}]$ (X)**	-1223.90435423
 MPD’	-2815.42426956

Cl^-	-14.99863340
H_2O	-76.43522994
CH_3OH	-115.74060876
HCl	-15.53952509