Supplementary Information

Triazaphosphaadamantane- Functionalized Terpyridine Metal Complexes: Cyclohexane Oxidation in Homogeneous and Carbon-Supported Catalysis

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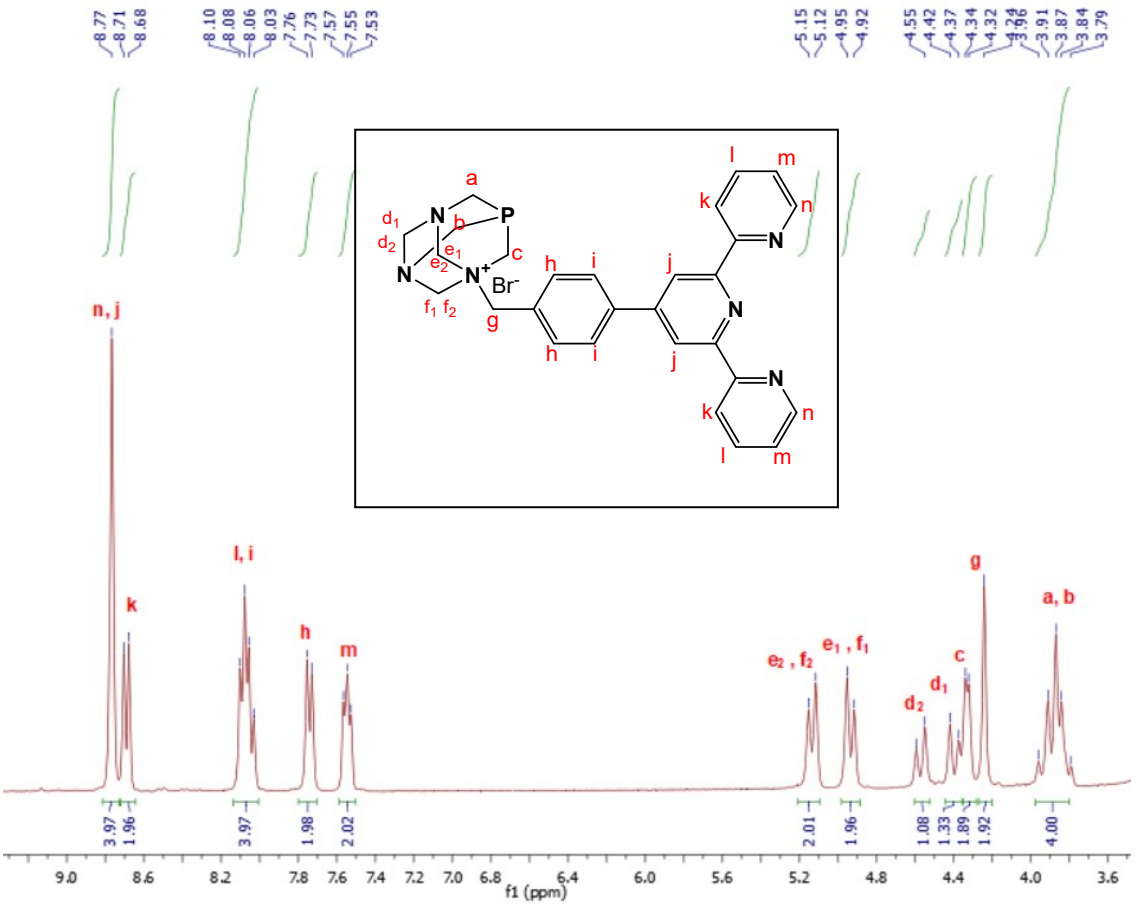

Figure S1. ^{1}H NMR spectrum of (*p*-tpy-C_6H_4-CH_2-PTA)Br (PTA-Bztpy bromide) in DMSO-d_6 (300 MHz).

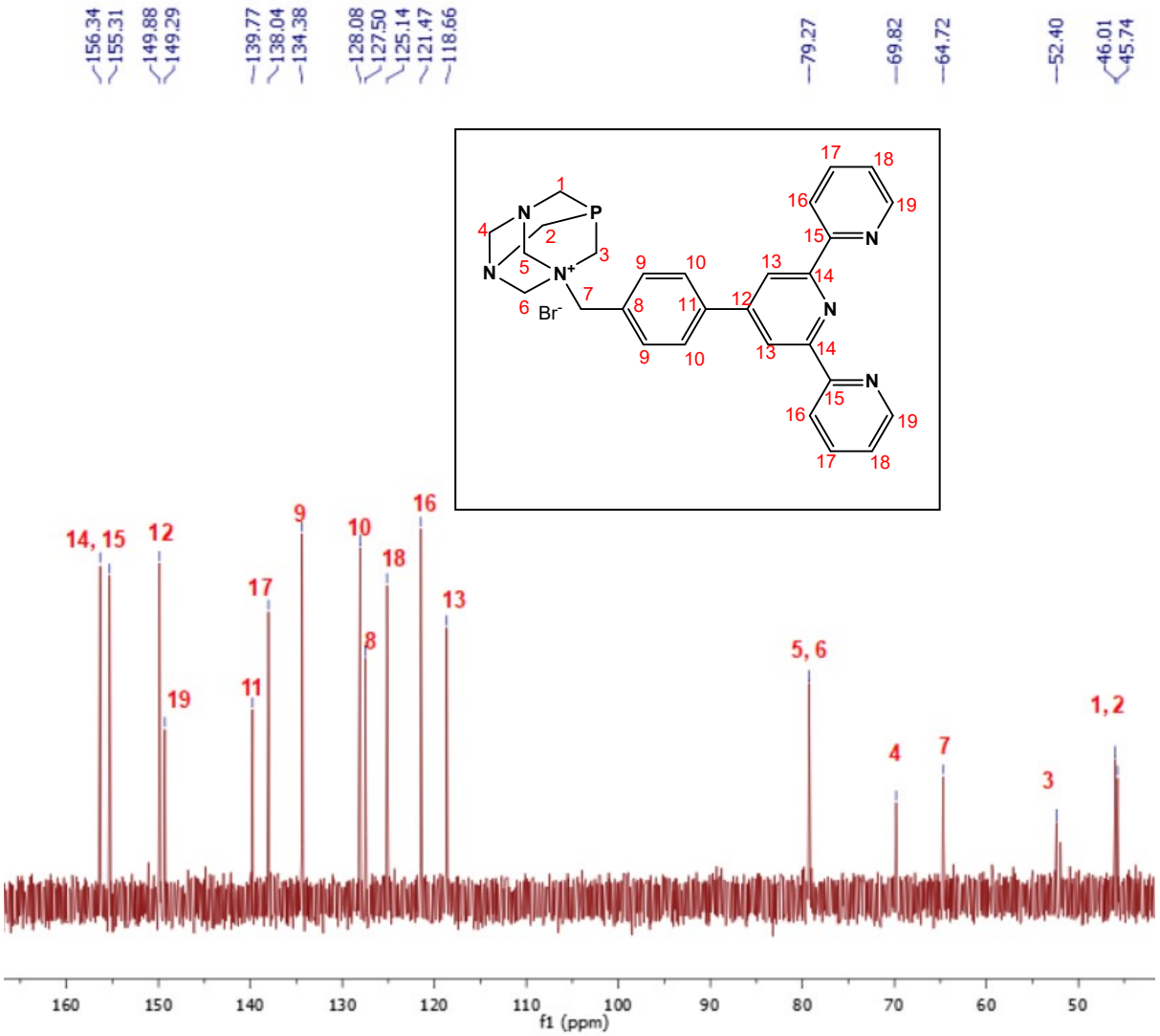

Figure S2. ^{13}C NMR spectrum of (*p*-tpy-C_6H_4-CH_2-PTA)Br (PTA-Bztpy bromide) in DMSO-d_6 (300 MHz).

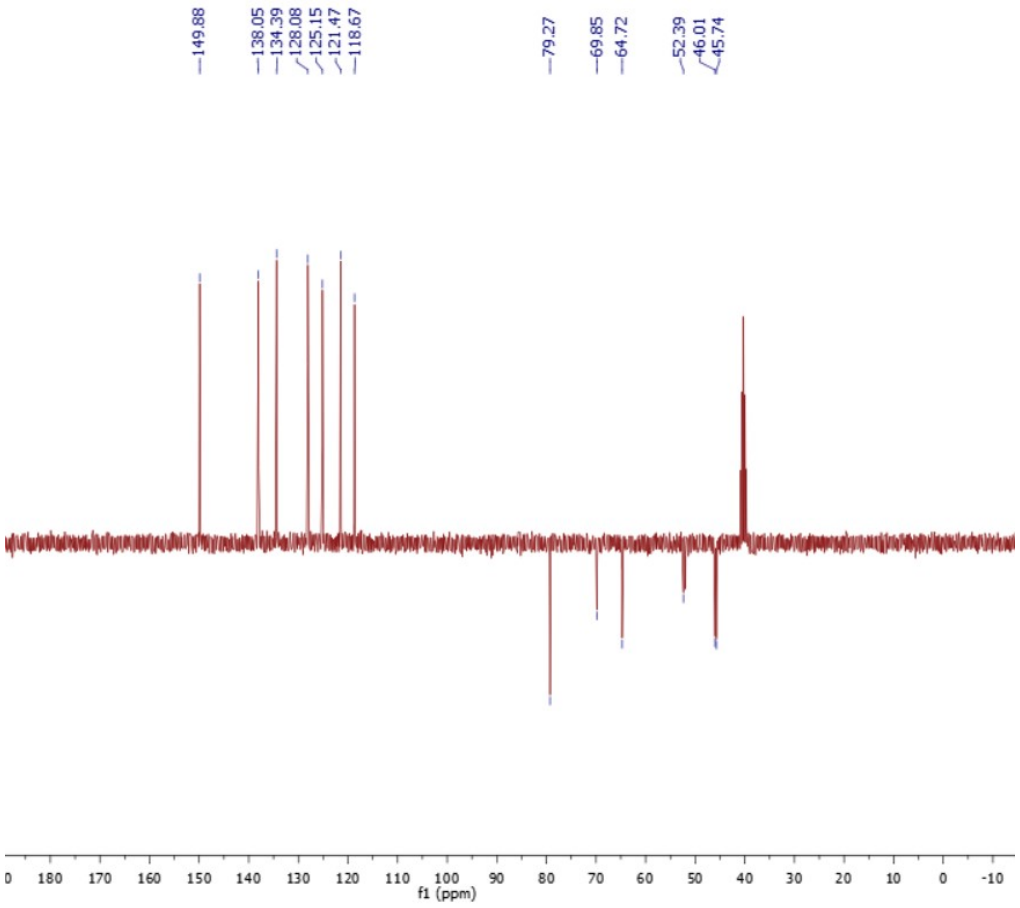

Figure S3. DEPT NMR spectrum of (*p*-tpy-C_6H_4-CH_2-PTA)Br (PTA-Bztpy bromide) in DMSO-d_6 (300 MHz).

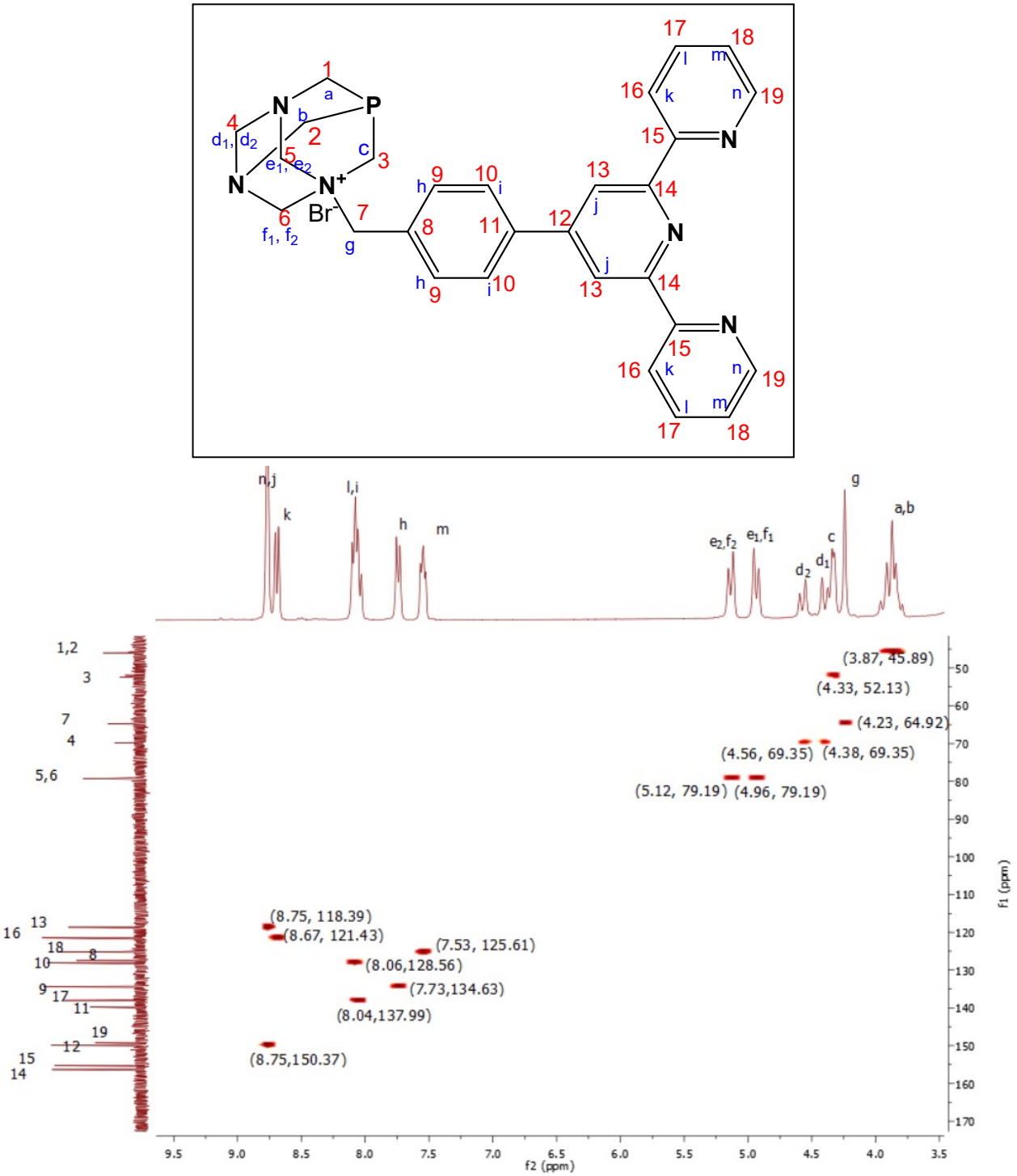

Figure S4. HSQC spectrum of (*p*-tpy-C_6H_4-CH_2-PTA)Br (PTA-Bztpy bromide) in DMSO-d_6 (300 MHz).

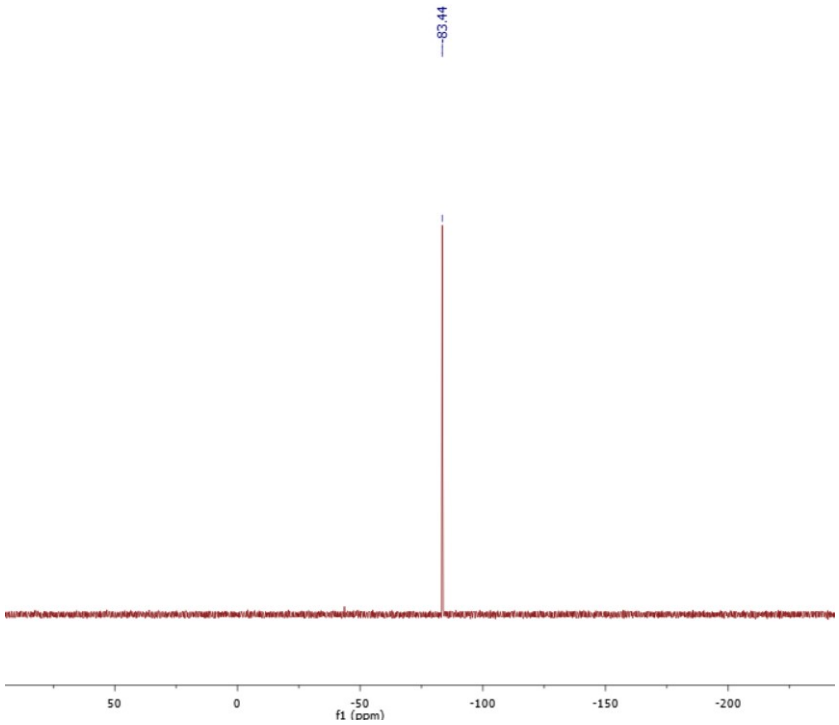

Figure S5. ^{31}P NMR spectrum of (*p*-tpy-C_6H_4-CH_2-PTA)Br (PTA-Bztpy bromide) in DMSO-d_6 (300 MHz).

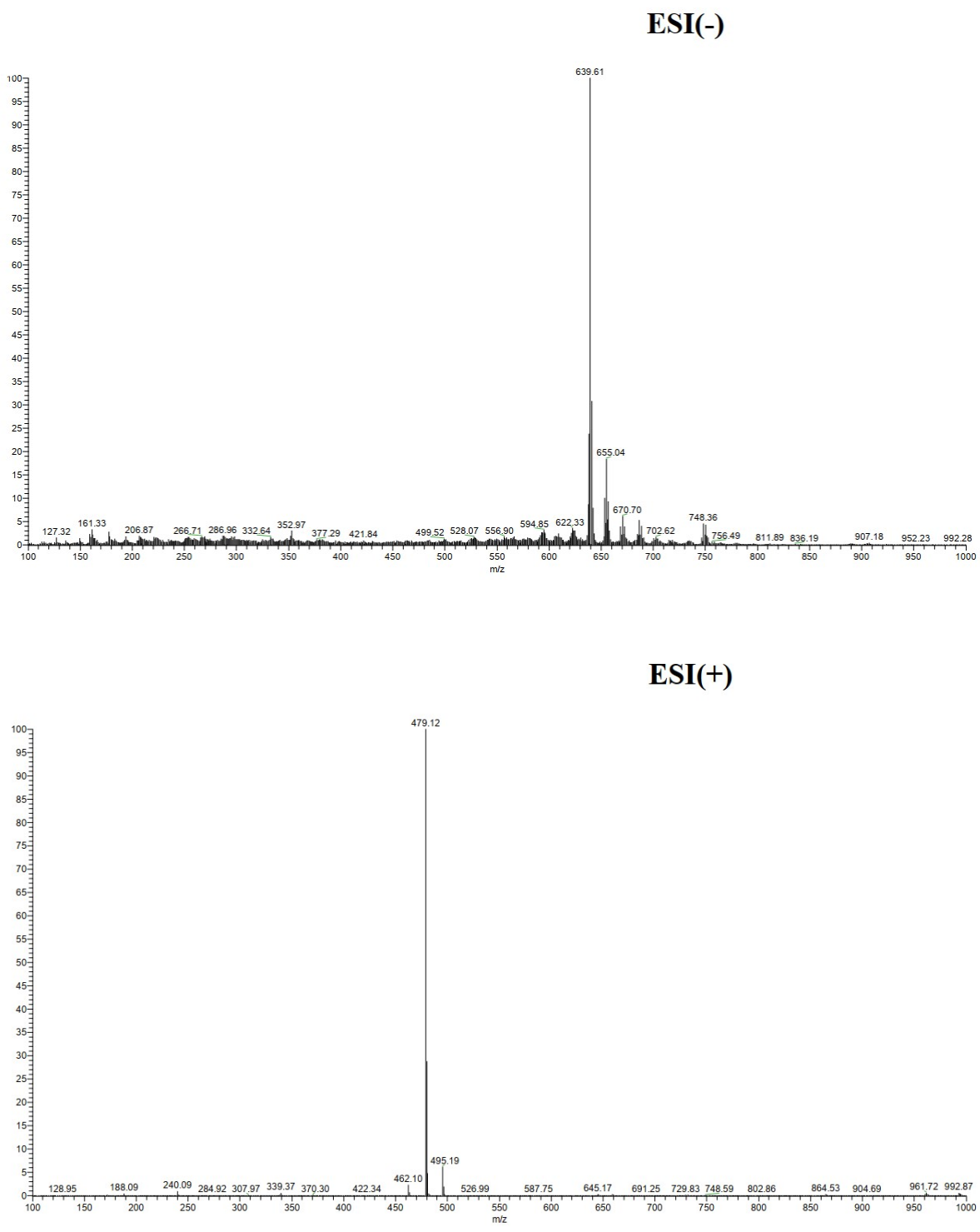

Figure S6. ESI-MS spectra of (*p*-tpy-C_6H_4-CH_2-PTA)Br (PTA-Bztpy bromide)

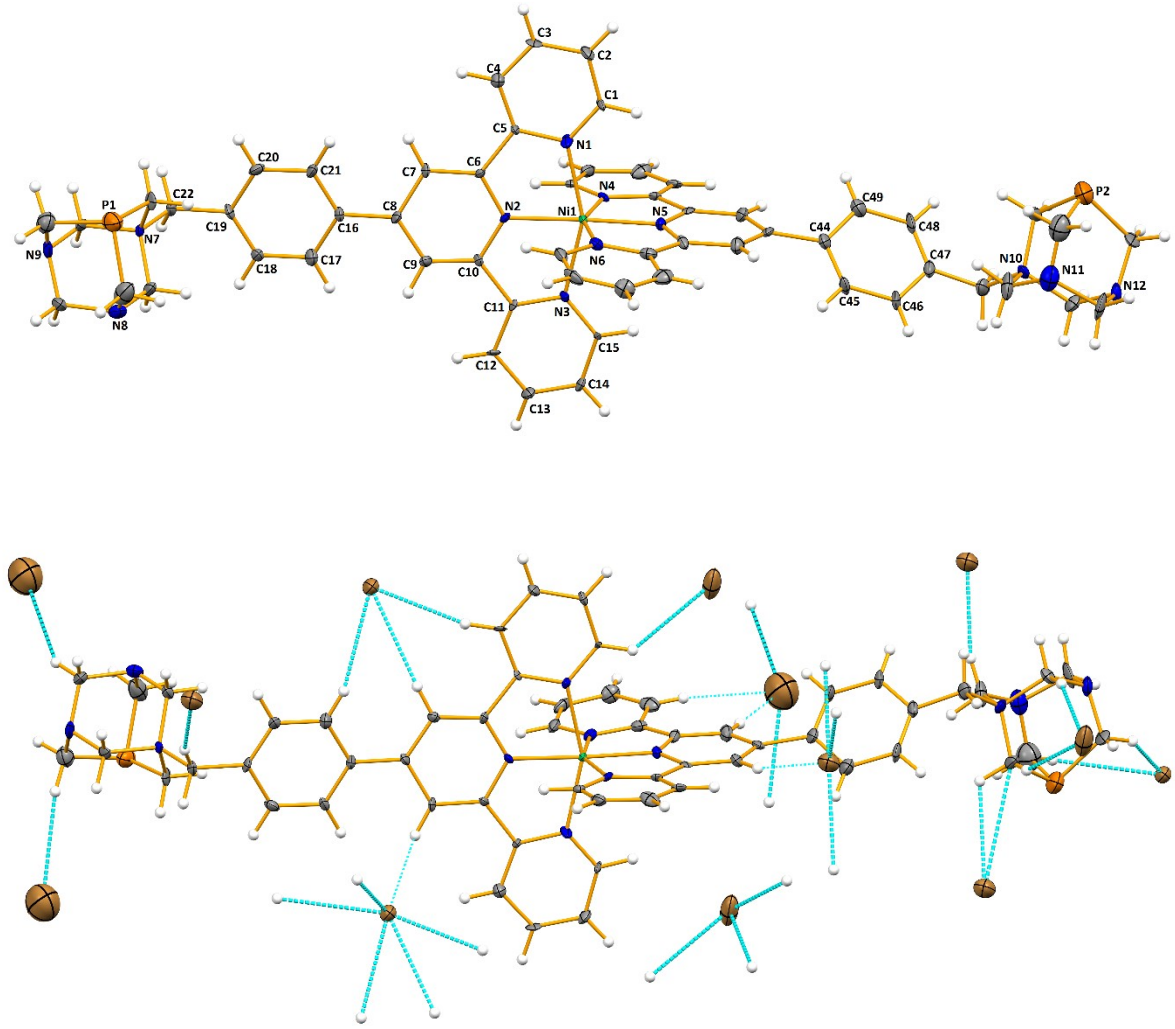

Figure S7. Crystal structure of complex **2**. Top: ellipsoid plot (drawn at 30% probability level) with partial atom labelling scheme; bromide counter anions were omitted for clarity. Bottom: extensive H···Br interactions (represented in dashed cyan colour)

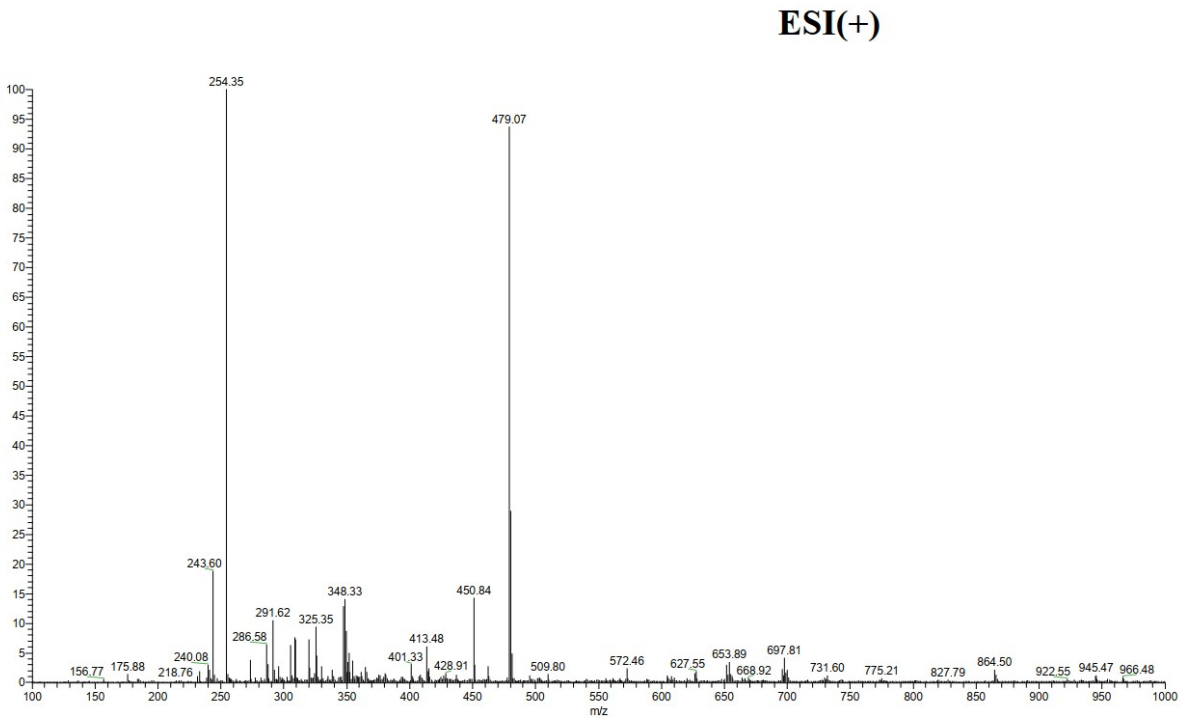

Figure S8. ESI(+)MS spectrum of complex **1**.

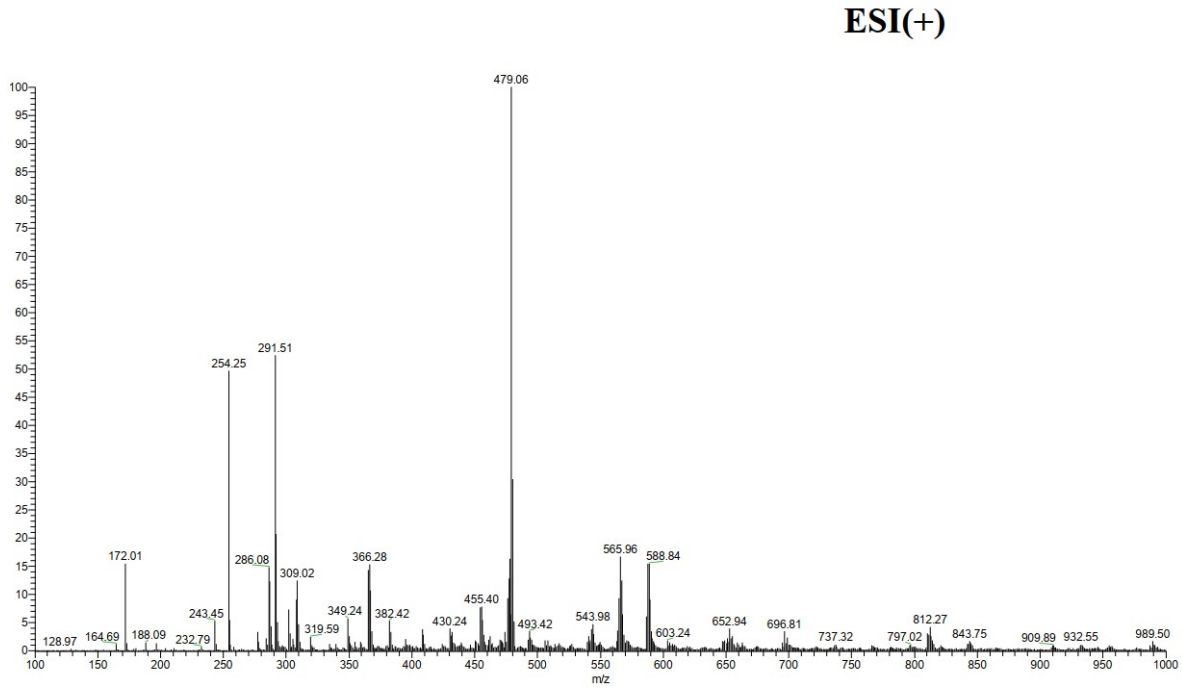

Figure S9. ESI(+)MS spectrum of complex **2**.

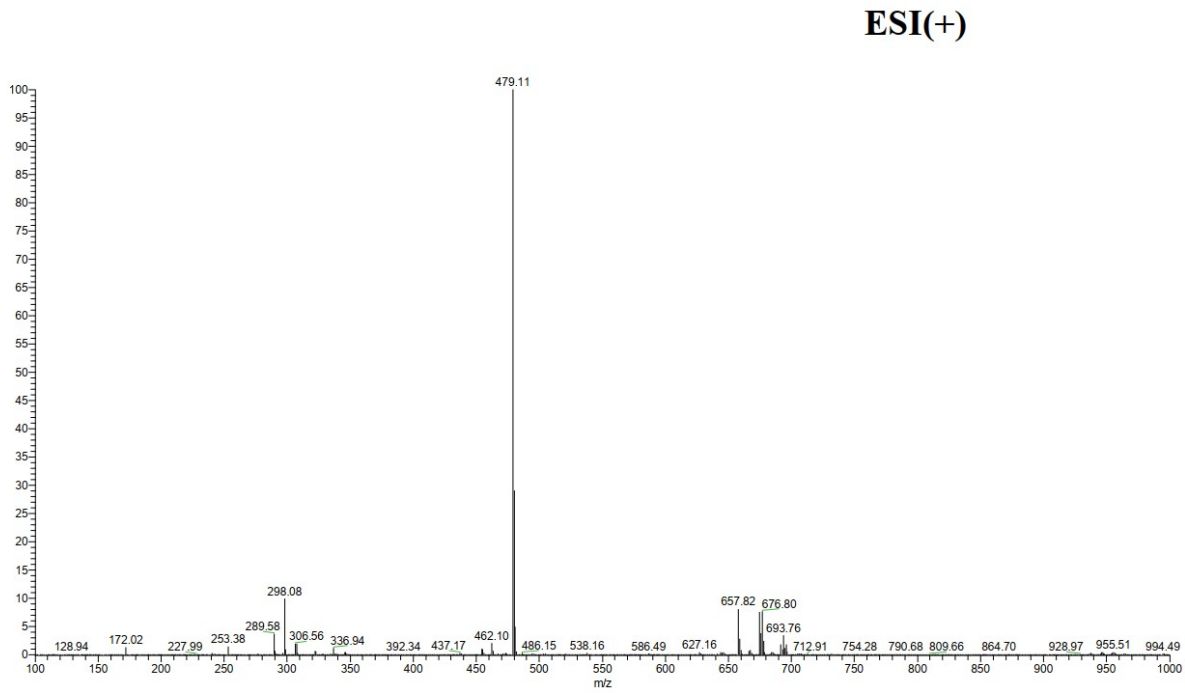

Figure S10. ESI(+)MS spectrum of complex **3**.

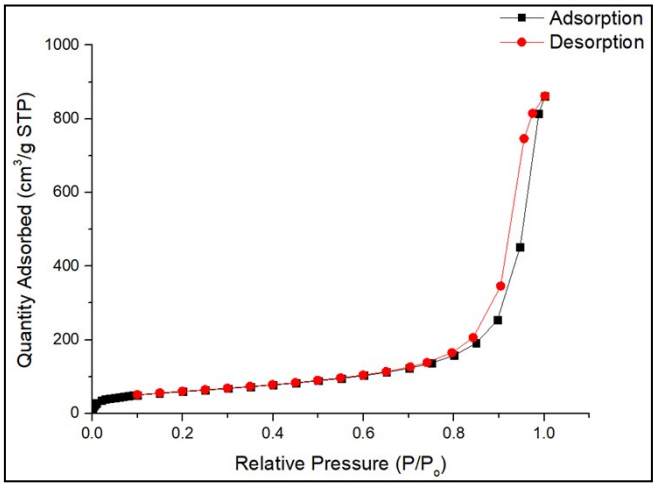

Figure S11. N_2 adsorption-desorption isotherm (77 K) of **3**-CNT-ox-Na.

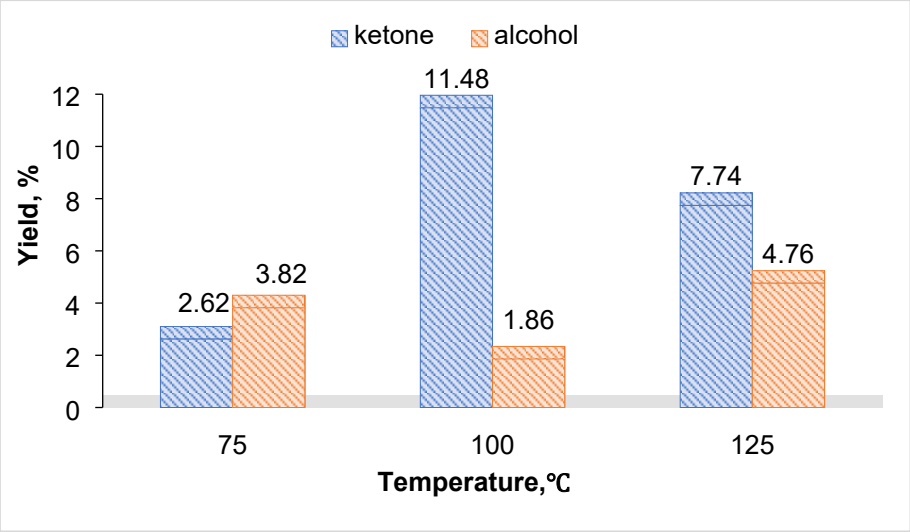

Figure S12. Effect of reaction temperature in the KA oil yield using complex **3** (3 mol % relative to the substrate) as catalyst. Reaction conditions: cyclohexane (*5*.0 mmol), 70% aqueous TBHP (10 mmol), 2 h, MW (30 W), 2 mL MeCN.

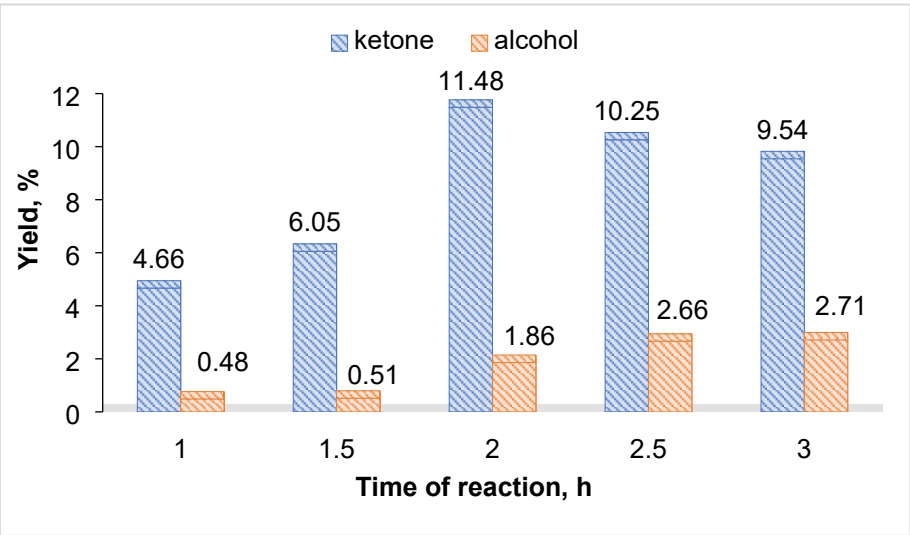

Figure S13. Effect of reaction time in the KA oil yield using complex **3** (3 mol % relative to the substrate) catalyst. Reaction conditions: cyclohexane (*5*.0 mmol), 70% aqueous TBHP (10 mmol), MW (30 W, 100°C), 2 mL MeCN.

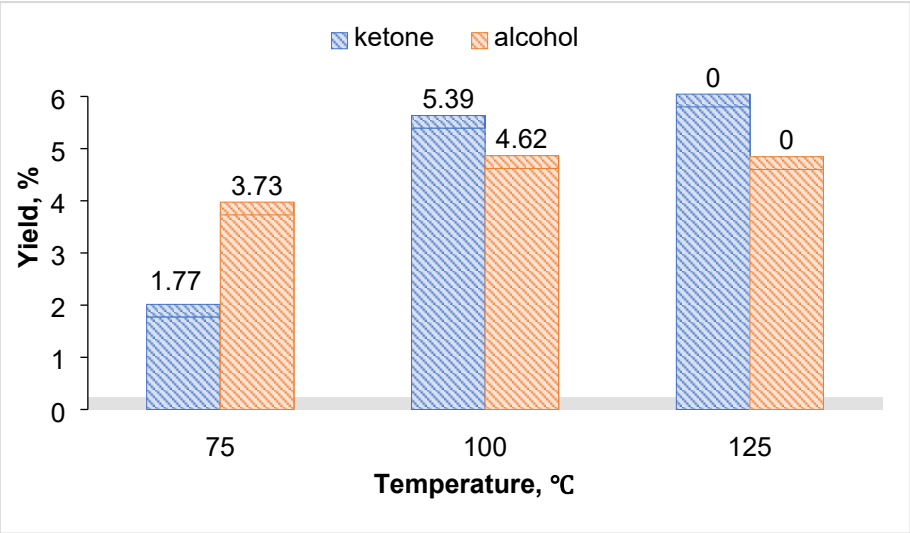

Figure S14. Effect of temperature in the KA oil yield . Reaction conditions: **3**-CNT-ox-Na as catalyst (0.5 mol % relative to substrate), cyclohexane (5.0 mmol), 70% aqueous TBHP (10 mmol), 2 h, MW (30 W), 2 mL MeCN.

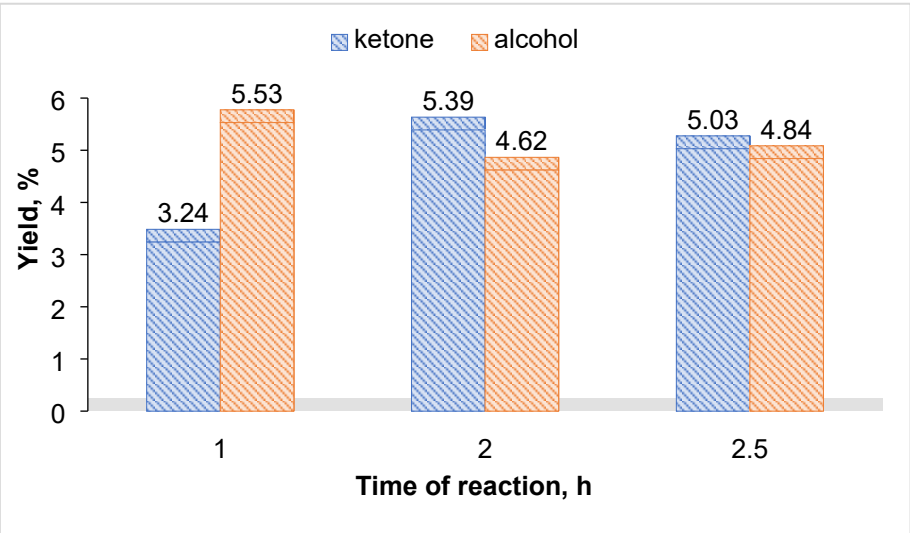

Figure S15. Effect of reaction time in the KA oil yield using **3**-CNT-ox-Na as catalyst (0.5 mol % relative to the substrate). Reaction conditions: cyclohexane (5.0 mmol), 70% aqueous TBHP (10 mmol), MW (30 W, 100°C), 2 mL MeCN.

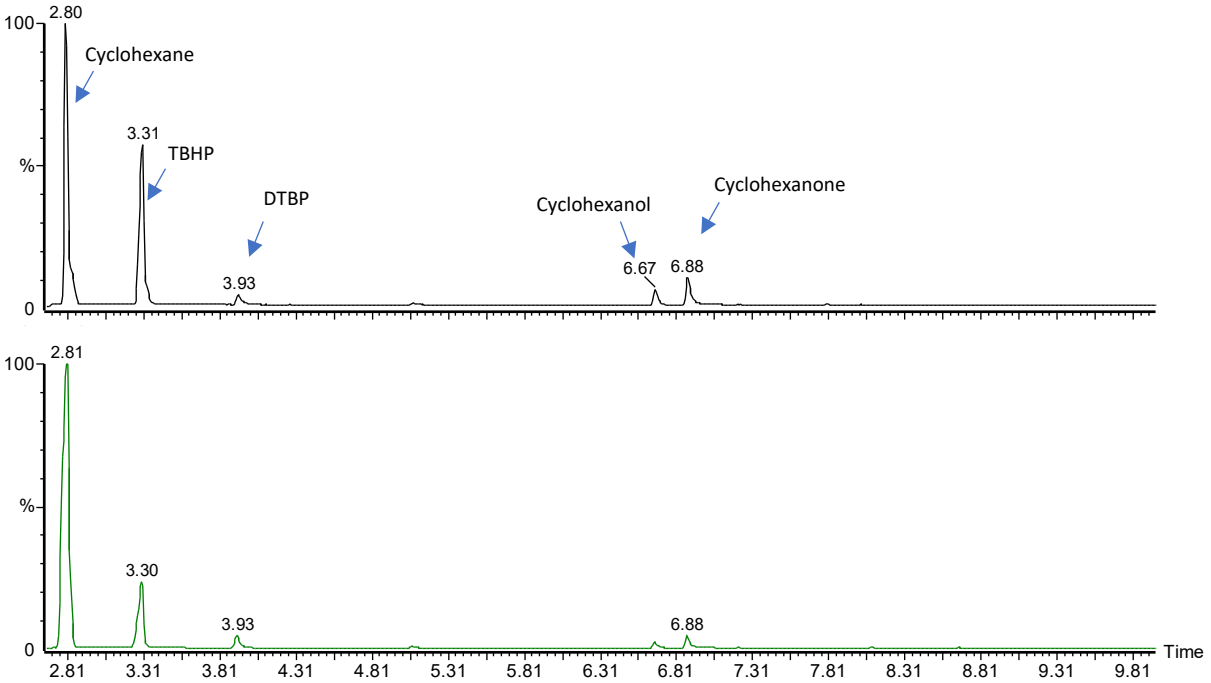

Figure S16. Chromatograms obtained at the end of cyclohexane oxidation reaction for: **3**-CNT-ox-Na (top) and homogeneous complex **3** (bottom).

Table S1. Crystal data and structure refinement details for complex **2**.

Formula	$C_{56}H_{56}Br_4N_{12}NiP_2$
Mol.wt	1337.41
Cryst. Syst.	Triclinic
Space group	P-1
Temperature *(K)*	150(2)
a (Å)	8.7950(3)
b (Å)	16.3840(5)
c (Å)	22.2853(7)
α, °	88.312 (2)
β, °	80.934(3)
γ, °	85.706(3)
V (Å^3)	3161.7(3)
Z	2
D_{calc} (g/cm^3)	1.405
F000	1348
μ(mm^{-1})	2.9229
Refl. measured	365649

Independent refl.	12654
Refl.with I > 2σ(I)	5318
No. parameters	676
Rint	0.1287
R(F) (I $\geq$ 2)	0.3370
wR (F^2) (all data)	0.4089
GOF (F^2)	1.145

Table S2. Characterization of supports by N_2 adsorption analysis at -196 ℃.

Carbon support	S_{BET}, $m^2\,g^{-1}$	**Pore volume,** $cm^3\,g^{-1}$	**Pore size,** nm
AC	866	0.45	5.2
AC-ox	724	0.31	4.6
AC-ox-Na	477	0.18	4.7
CNT	302	2.85	30.3
CNT-ox	301	1.62	19.0
CNT-ox-Na	261	1.21	16.5

Table S3. Amount of Manganese (% wt) loaded onto the carbon supports used in this study.[a]

Carbon material	**Mn** (wt %)
AC	0.07
AC-ox	2.85
AC-ox-Na	3.76
CNT	2.88
CNT-ox	0.78
CNT-ox-Na	2.91

[a] Results obtained from ICP-AES analysis.

Table S4. Selected data of the KA oil yield before and after PPh_3 treatment.

Catalyst	Solvent	Before PPh_3 treatment				After PPh_3 treatment			
		Yield (%)[b]			K/A	Yield (%)[b]			K/A
		K	**A**	**Total**		**K**	**A**	**Total**	
3-CNT-ox-Na	MeCN:H_2O(3:1v/v)	15.2	5.7	20.9	2.7	13.8	11.4	25.2	1.2
3-CNT-ox-Na	MeCN:H_2O(1:1v/v)	15.0	8.4	23.4	1.8	16.1	13.6	29.6	1.2

[a] Reaction conditions: cyclohexane (*5*.0 mmol), 70% aqueous TBHP (10 mmol), CH_3NO_2 (100 µL), 0.5 mol % catalyst, 2 h, MW (30 W), 100 °C, 2 mL solvent. [b] Molar yields based on substrate determined by GC analysis, i.e., moles of products (K + A) per 100 mol of cyclohexane; K= cyclohexanone, A= cyclohexanol. [c] Ratio between the molar concentrations of K and A

Table S5. Selected data on KA oil yield and corresponding selectivity values.

Catalyst	**Solvent**	**Yield, %** [b]			**Selectivity, %** [c]	
		K	**A**	**Total**	**K**	**A**
3 (Mn)	MeCN	11.48	1.86	13.34	86.1	13.9
3 (Mn)	MeCN: acetone (1:1v/v)	5.00	3.23	8.23	60.8	39.2
3 (Mn)	MeCN:H_2O(1:1v/v)	11.75	9.32	21.07	55.8	44.2
3-CNT-ox-Na [d]	MeCN	5.39	4.62	10.01	53.8	46.2
3-CNT-ox-Na [d]	MeCN: acetone (1:1v/v)	5.56	4.69	10.3	54.2	45.8
3-CNT-ox-Na [d]	MeCN:H_2O(1:1v/v)	16.06	13.6	29.6	54.2	45.8

[a] Reaction conditions: cyclohexane (*5*.0 mmol), 70% aqueous TBHP (10 mmol), CH_3NO_2 (100 µL), 100°C, MW (2 h, 30 W), 3 mol % catalyst loading, 2 mL solvent. [b] Molar yields based on substrate determined by GC analysis (after PPh_3 treatment), i.e., moles of products (K + A) per 100 mol of cyclohexane; K= cyclohexanone, A= cyclohexanol. [c] Moles of desired product per mol of converted cyclohexane. [d] 0.5 mol % catalyst loading.