

Supporting information

for

Chemically activated Spruce Organosolv Lignin as Carbocatalyst for Heterogeneous Oxidative Dehydrogenations in Liquid Phase

Anna Lenarda,^a Michele Melchionna,^b Santeri Aikonen,^a Tiziano Montini,^b Paolo Fornasiero,^b Tao Hu,^c Michael Hummel,^d and Juho Helaja^{*a}

^aDepartment of Chemistry, University of Helsinki, A. I. Virtasen aukio 1, P.O. Box 55, 00014 Helsinki, Finland; *juho.helaja@helsinki.fi

^bDepartment of Chemical and Pharmaceutical Sciences, INSTM, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy

^cResearch Unit of Sustainable Chemistry, University of Oulu, 90570 Oulu, Finland

^dDepartment of Bioproducts and Biosystems, Aalto University, Vuorimiehentie 1, 02150 Espoo, Finland

Contents

General remarks	2
Carbon BET analysis	4
Carbon material XPS measurements	6
Carbon material ICP-MS measurements	11
Temperature programmed desorption	11
THQ dehydrogenation kinetic monitoring under Ar	13
Electrochemical measurements	13
Indole substrates cyclic voltammetries	13
Carbon materials cyclic voltammetries	14
References	14

General remarks

Spruce organosolv lignin was received from the Lignocellulosic Biorefinery Pilot Plant, Fraunhofer CBP in Leuna, Germany. The received batch showed an average molar mass of M_n of 0.5 kg/mol and M_w of 5.89 kg/mol, lignin content of 97.1 %, 0.5 % carbohydrates, and 0.2 % ash as described earlier.¹ CHN analysis gave C: 66.79 %, H: 5.84 %, and N: 0.16 %. The OH-group characterization is summarized in Table S1.

All HPLC-grade solvents were used without further purification as obtained from the supplier (Honeywell, VWR, Merck, Sigma Aldrich). Distilled water was produced with an Aquatron AS4 (Bibby). All reagents were commercially available and used without further purification as obtained from the supplier. All oxidized active carbon species (oAC) were synthesized in our lab. Oxidized carbon nanotubes (oCNT) were prepared by HNO_3 oxidation.²

Table S1. Amount of different OH groups (mmol/g of lignin) in spruce organosolv lignin determined by ^{31}P NMR analysis.¹

Aliphatic	S + Gcond.	Gnc + H	Total Ph-OH	Total OH	COOH
1.91	1.33	1.98	3.51	5.42	0.18

S+Gcond.: syringyl + condensed guaiacyl; Gnc: non-condensed guaiacyl; H: *p*-hydroxyphenyl; COOH: carboxylic acid; Ph-OH: Gcond. + Gnc + H; Total OH: phenolic OH + aliphatic OH

Table S2. Carbonization of organosolv lignin with 1-3 mass equiv. KOH and thermal treatment 700 -900 °C under argon.

Entry	Sample name	T (°C)	Mass ratio (KOH:lignin)	Mass loss (%)	Received mass (mg)
1	LAC-1-800	800	1:1	73	550
2	LAC-2-800	800	2:1	72	565
3	LAC-3-800	800	3:1	78	447
4	LAC-1-700	700	1:1	47	1078
5	LAC-2-700	700	2:1	52	968
6	LAC-3-700	700	3:1	63	741
7	LAC-1-900	900	1:1	73	550
8	LAC-2-900	900	2:1	86	284
9	LAC-3-900	900	3:1	67	666

Table S3. Catalytic activity tests with lignin active carbons before nitric acid activation.

Entry	Sample name	T (°C)	Mass ratio (KOH:lignin)	Homocoupling yield (%)	THQ aromatization yield (%)
1	LAC-1-800	800	1:1	6	49
2	LAC-2-800	800	2:1	8	50
3	LAC-3-800	800	3:1	1	23
4	LAC-1-700	700	1:1	9	63
5	LAC-2-700	700	2:1	7	62

6	LAC-3-700	700	3:1	5	41
7	LAC-1-900	900	1:1	8	45
8	LAC-2-900	900	2:1	7	34
9	LAC-3-900	900	3:1	4	22

Table S4. Catalytic activity tests with lignin active carbons prepared with NaOH as base.

Entry	Sample name	T (°C)	Mass ratio (NaOH:lignin)	Homocoupling yield (%)	THQ aromatization yield (%)
1	NaLAC-2-700	700	2:1	59	58
2	NaLAC-3-700	700	3:1	59	53
3	NaLAC-2-800	800	2:1	59	58
4	NaLAC-3-800	800	3:1	58	52
5	NaLAC-2-600	600	2:1	58	63
6	NaLAC-1-700	700	1:1	6	48

Carbon BET analysis

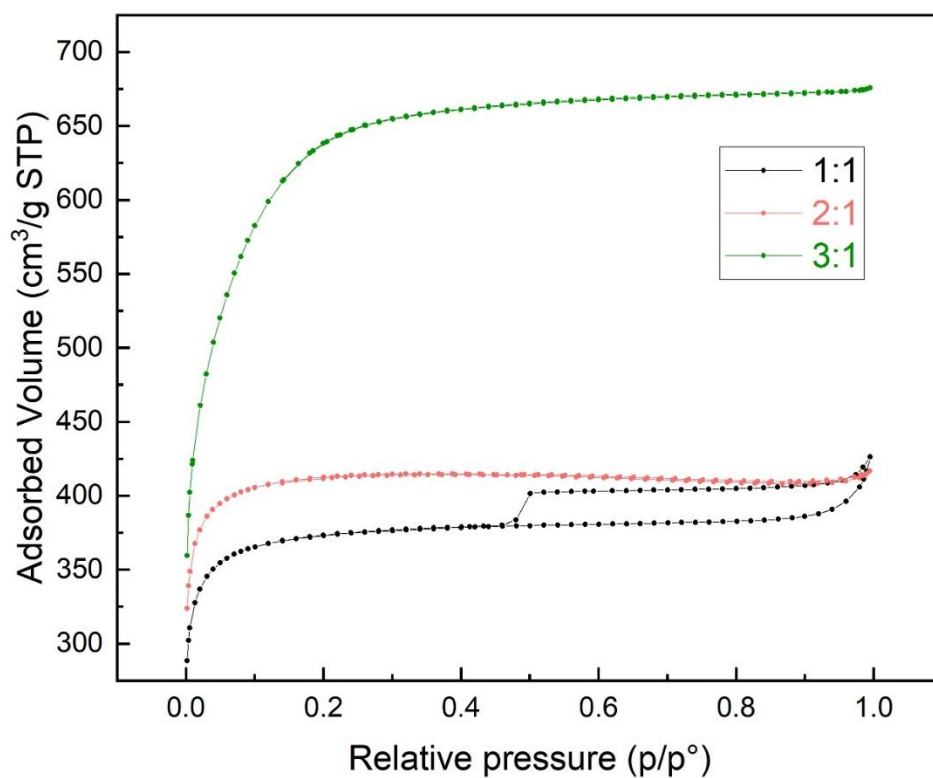


Figure S1. Adsorption-desorption isotherm of oLAC-1-700 (black), oLAC-2-700 (red) and oLAC-3-700 (green)

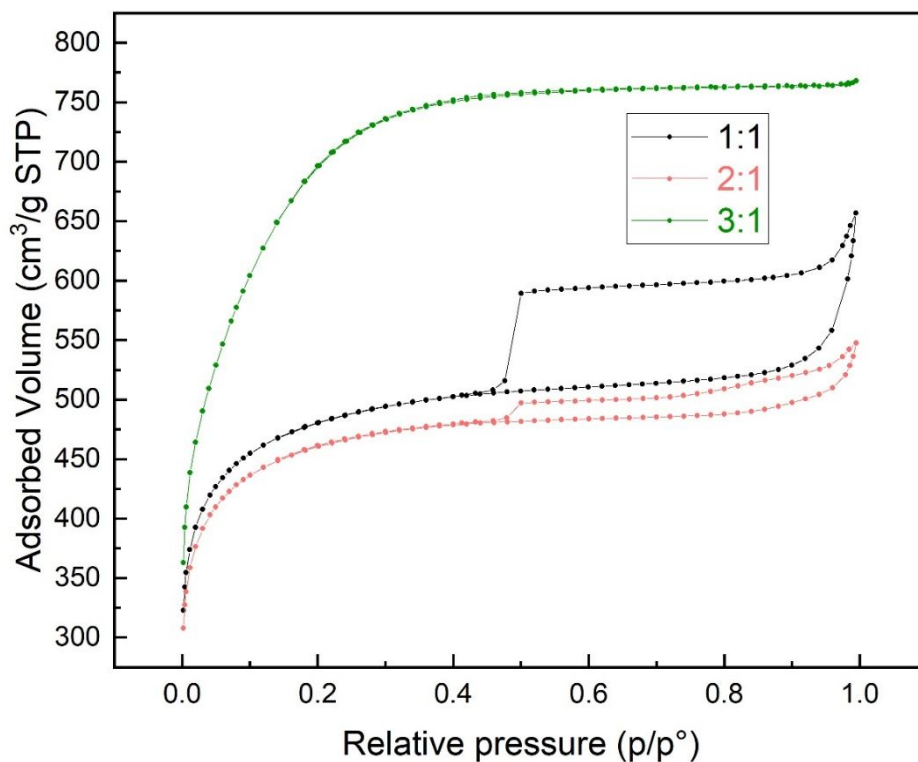


Figure S2. Adsorption-desorption isotherm of oLAC-1-800 (black), oLAC-2-800 (red) and oLAC-3-800 (green)

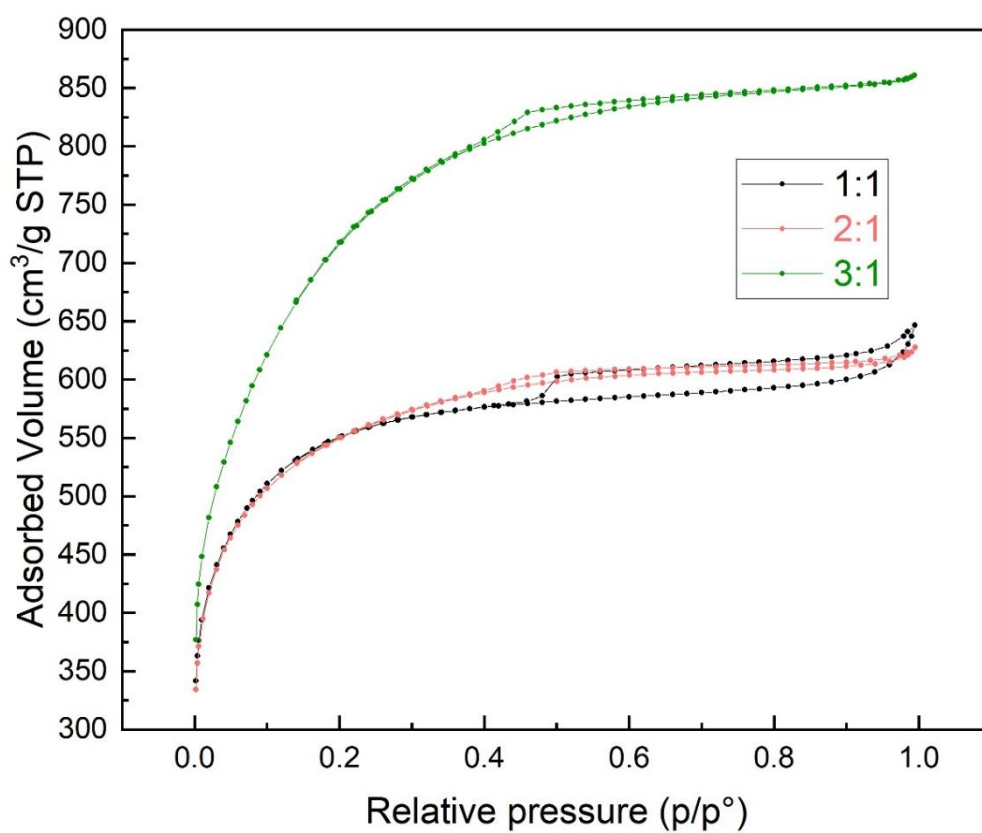


Figure S3. Adsorption-desorption isotherm of oLAC-1-900 (black), oLAC-2-900 (red) and oLAC-3-900 (green)

Carbon material XPS measurements

The X-ray Photoelectron Spectroscopy (XPS) analysis was performed by Thermo Fisher Scientific ESCALAB 250Xi XPS System at the Center of Microscopy and Nanotechnology, University of Oulu (Finland). The monochromatic AlK α radiation (1486.7 eV) operated at 20 mA and 15 kV. The powder samples were put in gold sample holder and O, C, N and Au were measured for all samples. The measurement data were analyzed by Avantage V5 program developed by Thermo Fisher Scientific. Charge compensation was used to determine the presented spectra and the binding energies (BE) were calibrated by the C1s peak position of 284.8 eV. The deconvolution of the peaks was carried out for C1s and O1s with Avantage program utilizing peak BE values for groups as reported for carbon materials by Figueiredo and Pereira.³

Table S5. Summary of C1s and O1s XPS deconvolutions

	LAC-1-700	LAC-2-700	LAC-3-700	LAC-1-800	LAC-2-800	LAC-3-800	LAC-1-900	LAC-2-900	LAC-3-900
C1s									
graphitic	25.37	28.28	26.82	28.99	29.95	24.24	28.91	24.87	24.86
aliphatic	32.22	28.83	29.39	34.01	30.22	32.07	34.85	38.32	40.23
C-O	3.59	4.83	4.16	4.14	4.18	5.4	3.63	3.51	3.44
C=O	6.42	7.59	6.45	7.21	6.43	7.18	6.63	6.08	7.5
O-C=O	4.21	4.18	3.33	4.38	3.72	3.22	3.92	2.97	3.37
π - π^*	12.16	10.06	10.72	11.04	14.16	11.72	11.83	11.21	12.67
O1s (total)	12.69	16.21	16.72	10.09	9.18	13.21	10	12.71	7.94
C-O	5.8	6.54	9.75	5.69	3.92	7.75	4.49	6.36	3.78
C=O	5.47	5.34	5.97	2.73	4.01	4.78	3.82	4.78	2.93
chemisorbed	1.42	4.33	1	1.67	1.25	0.68	1.69	1.57	1.23
	oLAC-1-700	oLAC-2-700	oLAC-3-700	oLAC-1-800	oLAC-2-800	oLAC-3-800	oLAC-1-900	oLAC-2-900	oLAC-3-900
C1s									
graphitic	26.56	29.07	27.07	28.23	20.47	25.15	19	27.59	22.3
aliphatic	31.11	27.52	32.74	31.29	39.58	36.05	43.02	34.94	38.32
C-O	5.64	4.37	3.86	4.05	3.09	3.85	2.34	3.46	3.48
C=O	6	8.48	7.74	7.98	8.27	8.24	7.97	7.09	8.9
O-C=O	4.07	4.76	4.46	5.24	4.88	4.44	4.09	4.09	4.26
π - π^*	8.92	10.17	10.33	9.9	11.24	11.38	12.14	10.36	12.06
O1s (total)	17.29	15.62	13.18	12.79	11.98	10.29	10.86	11.83	10.69
C-O	7.94	7.99	7.78	6.76	6.33	5.89	6.18	6.61	5.62
C=O	6.88	5.46	3.76	4.21	3.77	2.85	2.92	3.63	3.35
chemisorbed	2.47	2.17	1.64	1.82	1.88	1.55	1.76	1.59	1.72

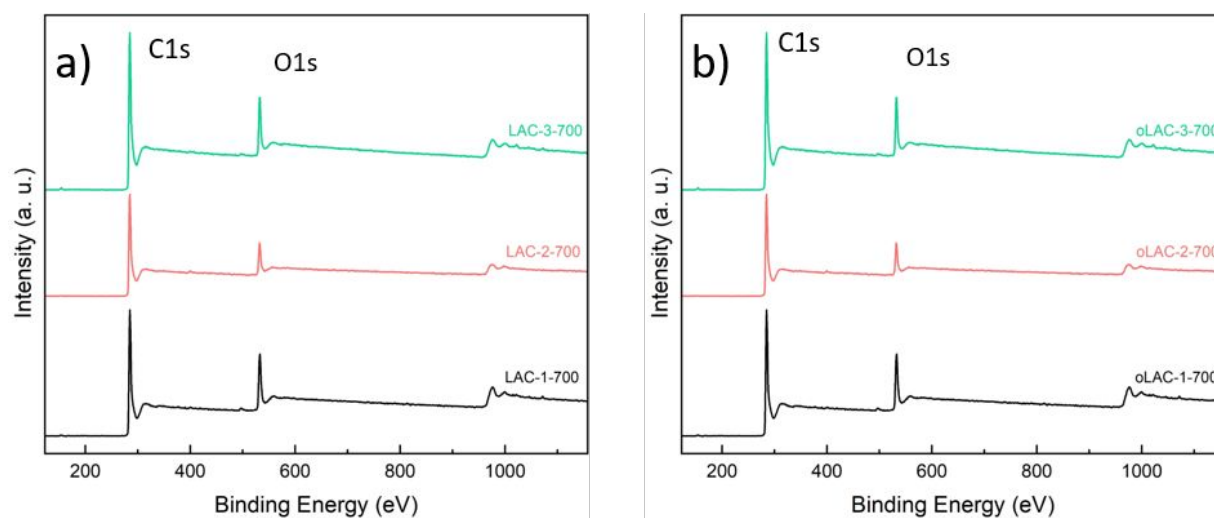


Figure S4. a) XPS survey spectrum of LAC-1-700 (black), LAC-2-700 (red) and LAC-3-700 (green) and b) XPS survey spectrum of oLAC-1-700 (black), oLAC-2-700 (red) and oLAC-3-700 (green)

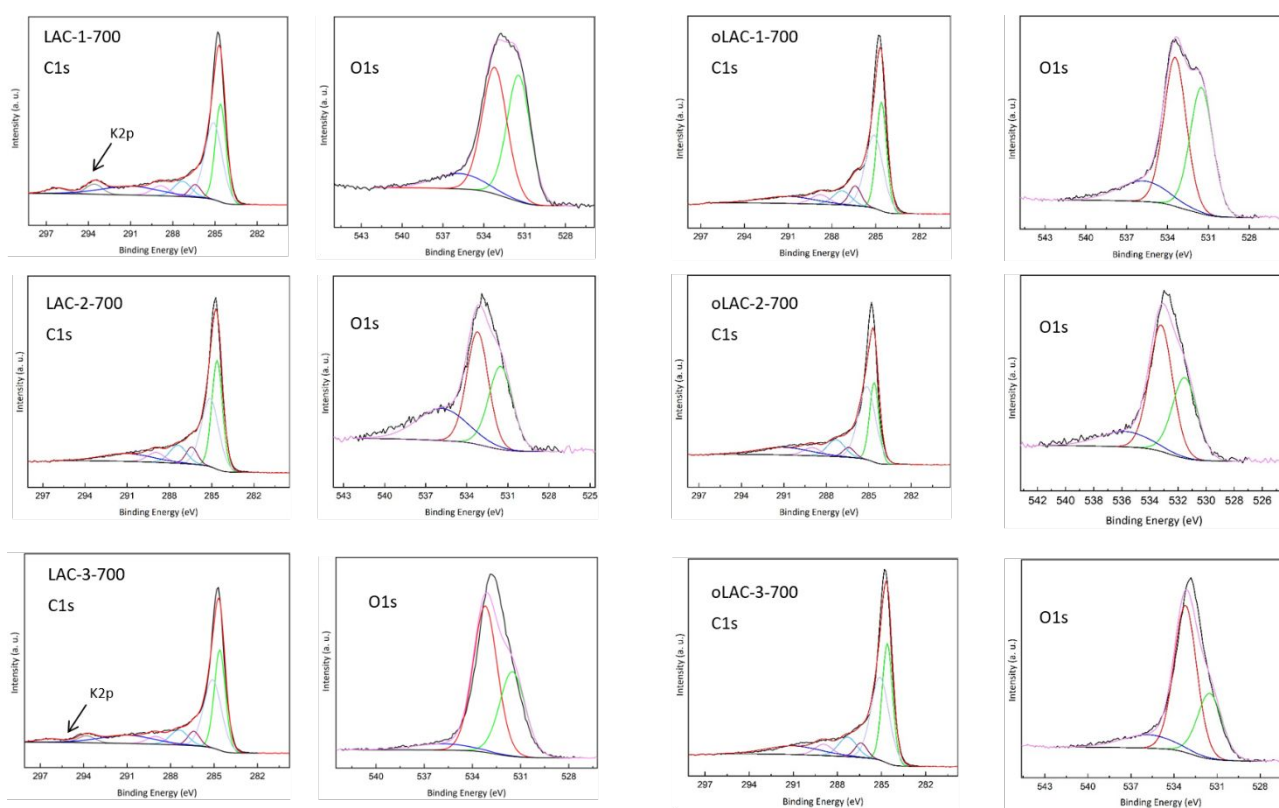


Figure S5. C1s and O1s deconvolutions of LAC-1-700, LAC-2-700, LAC-3-700, oLAC-1-700, oLAC-2-700 and oLAC-3-700.

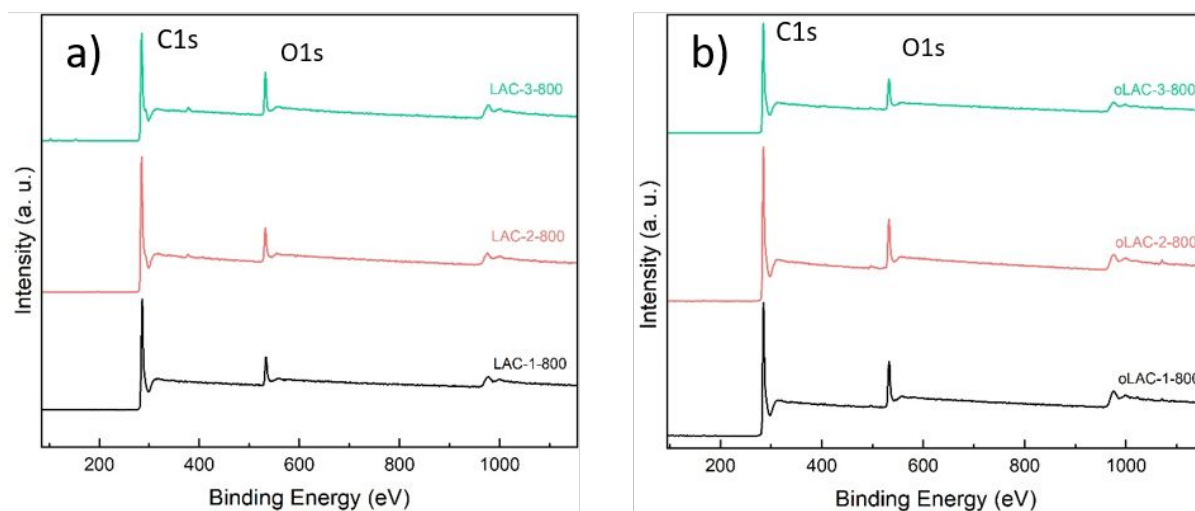


Figure S6. a) XPS survey spectrum of LAC-1-800 (black), LAC-2-800 (red) and LAC-3-800 (green) and b) XPS survey spectrum of oLAC-1-800 (black), oLAC-2-800 (red) and oLAC-3-800 (green)

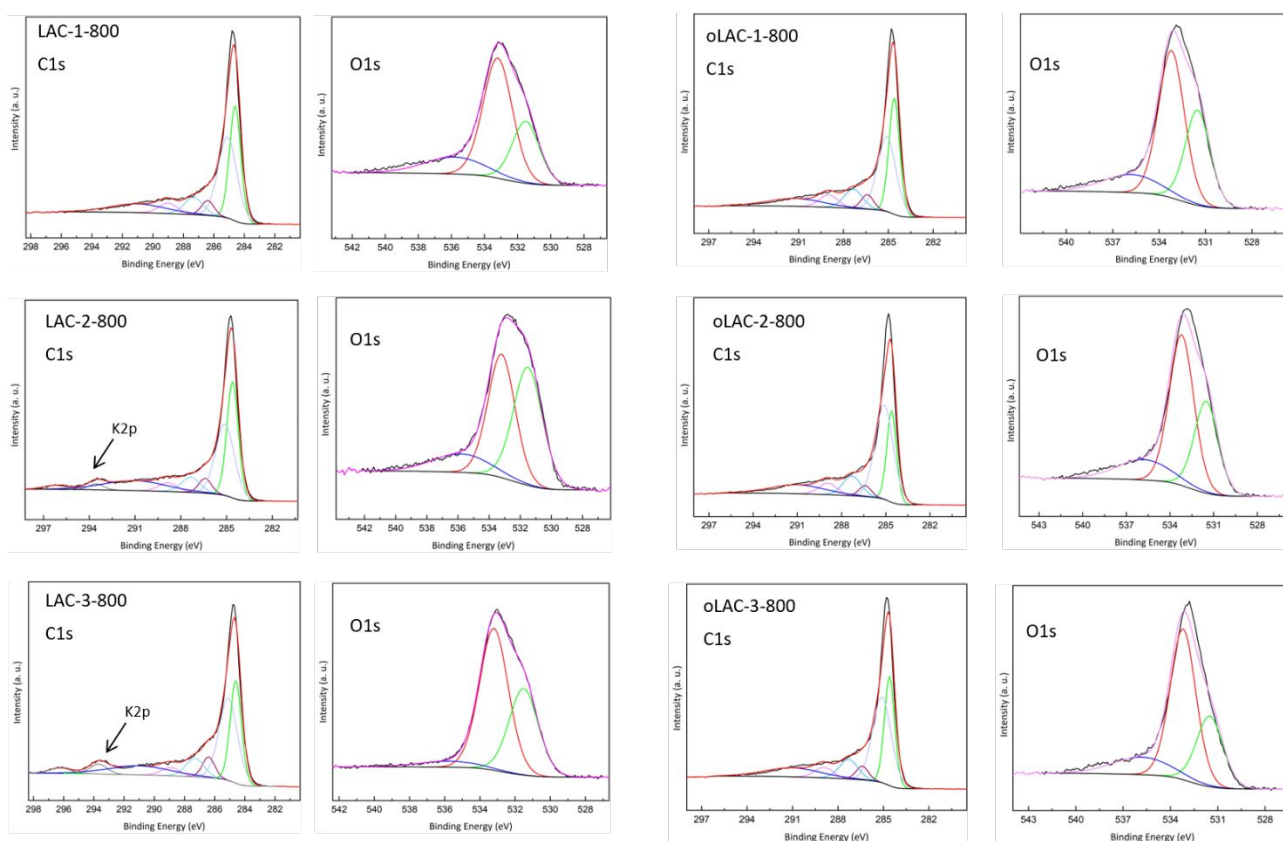


Figure S7. C1s and O1s deconvolutions of LAC-1-800, LAC-2-800, LAC-3-800, oLAC-1-800, oLAC-2-800 and oLAC-3-800

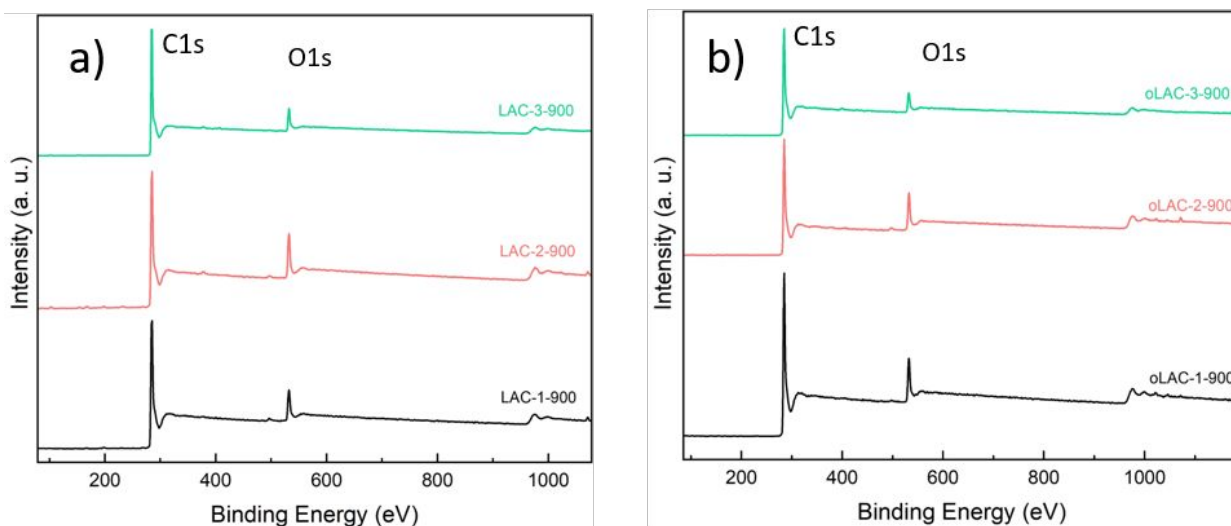


Figure S8. a) XPS survey spectrum of LAC-1-900 (black), LAC-2-900 (red) and LAC-3-900 (green) and b) XPS survey spectrum of oLAC-1-900 (black), oLAC-2-900 (red) and oLAC-3-900 (green)

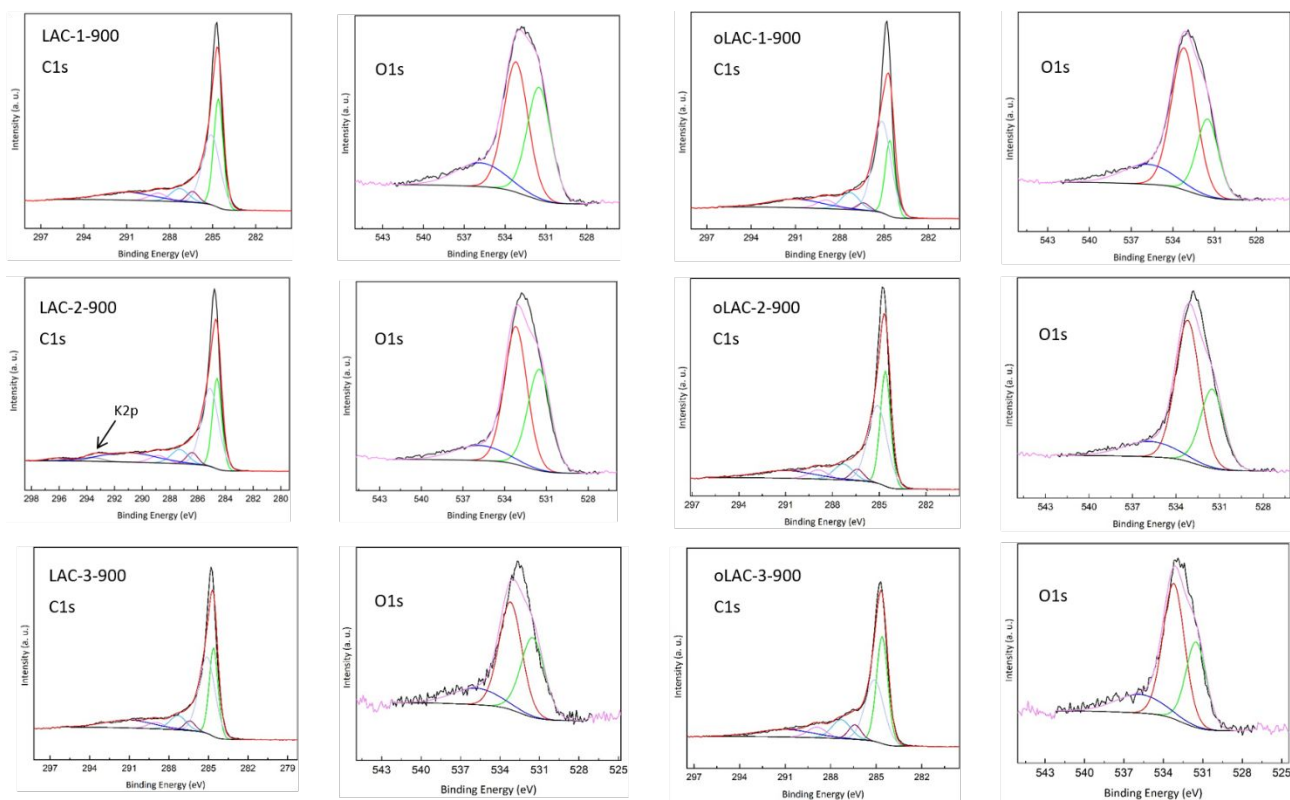


Figure S9. C1s and O1s deconvolutions of LAC-1-900, LAC-2-900, LAC-3-900, oLAC-1-900, oLAC-2-900 and oLAC-3-900

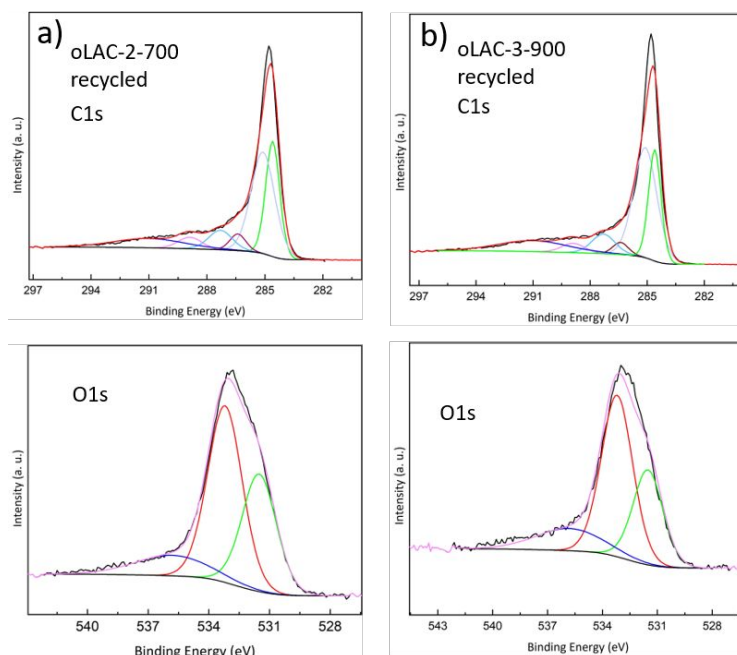


Figure S10. C1s and O1s deconvolutions of a) recycled oLAC-2-700 and b) recycled oLAC-3-900

Table S6. Summary of XPS deconvolutions for F-blocked XPS samples

Sample	C1s							O1s			F1s	N1s	
	graphite	aliphatic	CO	COO	COOO	plasmon	C-F	C-O	C=O	chemisor	F-C	N-N=C	NOO
oLAC-2-700F	16.74	31.79	3.88	7.37	3.79	7.43	2.81	4.6	3.08	1.24	14.59	2.69	
oLAC-3-900F	22.74	30.55	3.76	6.29	3.04	9.23	2.43	3.27	2.39	0.92	14.24	0.93	0.22

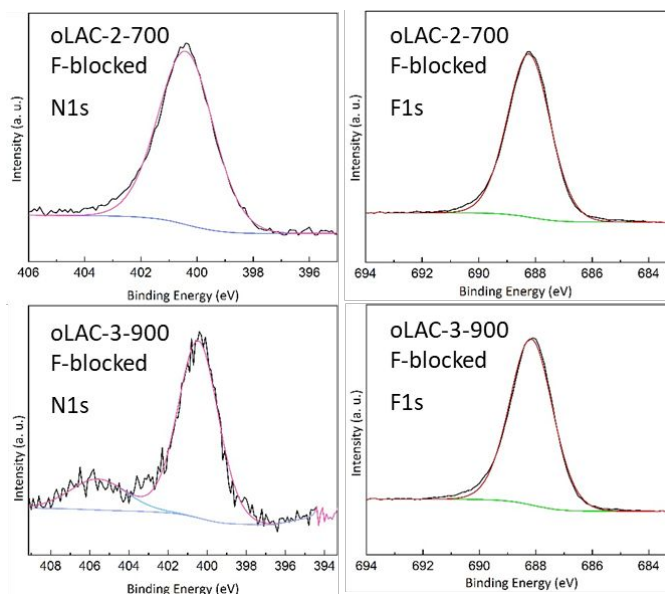


Figure S11. N1s and F1s deconvolutions of F-blocked oLAC-2-700 and F-blocked oLAC-3-900

Carbon material ICP-MS measurements

Sample	Al (mg/g)	K (mg/g)	Mg (mg/g)	Na (mg/g)	Mn (mg/g)	Fe (mg/g)	Co (mg/g)	Ni (mg/g)	Cu (mg/g)
oLAC-3-900	0.67 ± 0.04	0.62 ± 0.06	< 0.03	1.00 ± 0.01	< 0.005	< 0.05	< 0.002	< 0.005	< 0.005
oLAC-2-700	< 0.09	< 0.5	< 0.03	< 0.08	< 0.005	< 0.05	< 0.002	< 0.005	< 0.005

Table S7. ICP-MS determination of metal impurities

Temperature programmed desorption

Temperature-programmed desorption (TPD) of ammonia was conducted in a home-made flow apparatus using a mass spectrometer Hiden HPR20 as analyzer. In a typical TPD experiment, about 0.15 g of the sample was loaded in U-shaped quartz microreactor. To remove weakly adsorbed species, the sample was subjected to a cleaning treatment in Ar flow (50 mL min⁻¹) at 300 °C for 30 min. Afterwards, the sample was cooled at 110 °C under the inert gas flow. Saturation of the samples were performed at 110 °C for 60 min by flowing NH₃ (10%)/Ar (50 mL min⁻¹) or pure CO₂ (30 mL min⁻¹). After saturation, the sample was flushed in Ar flow at 110 °C for 1h to remove physically adsorbed molecules. The TPD profile for each sample was recorded by increasing the temperature with a heating rate of 10 °C min⁻¹ under flow of Ar (50 mL min⁻¹). The desorbed products were analyzed by means of a mass spectrometer operating in the electron impact mode with an ionization energy of 35 eV. The desorbed species were identified on the basis of the intensity of various mass fragments. In particular, the most interesting signal to follow was m/z = 17 for ammonia, m/z = 28 for CO and m/z = 44 for CO₂.

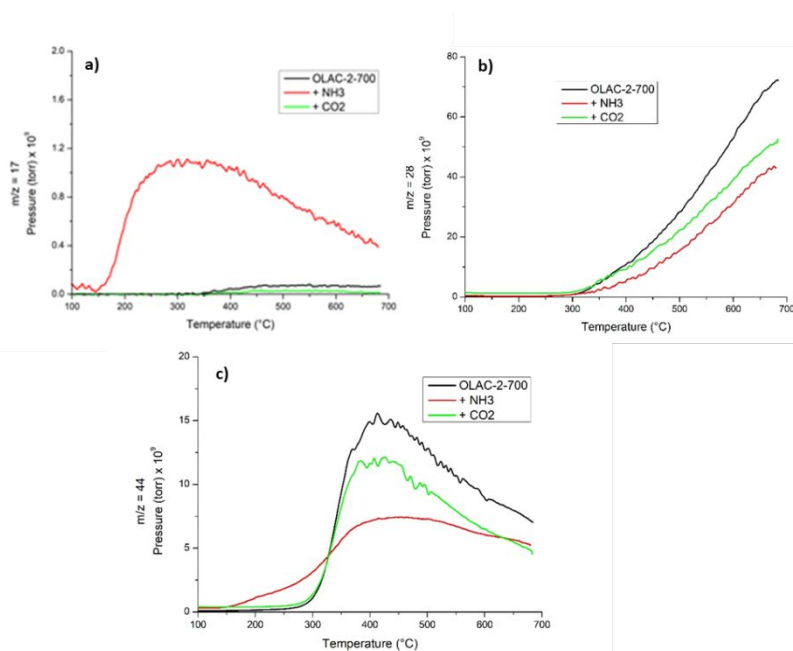


Figure S12. TPD desorption curve for a) NH_3 , b) CO and c) CO_2 for oLAC-2-700 pristine (black), after NH_3 saturation (red) and after CO_2 saturation (green)

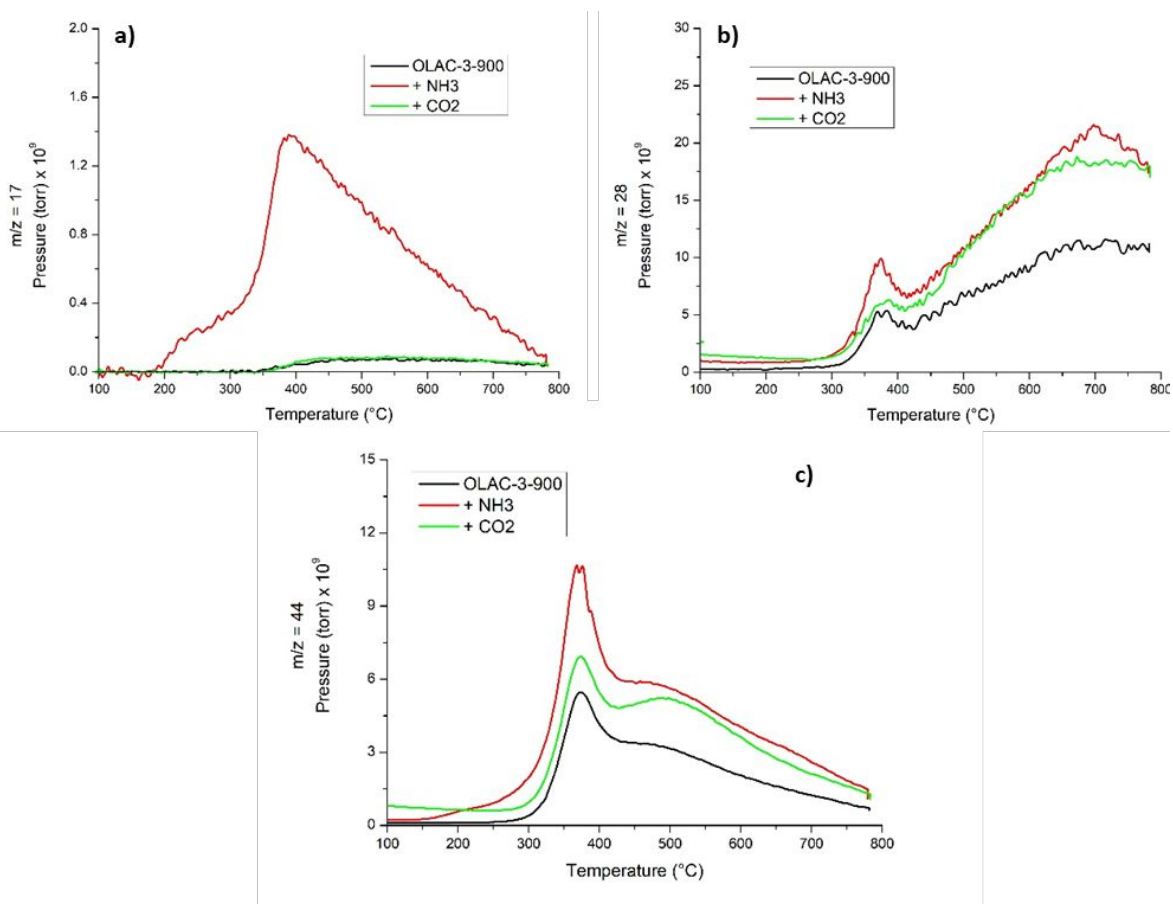


Figure S13. TPD desorption curve for a) NH_3 , b) CO and c) CO_2 for oLAC-3-900 pristine (black), after NH_3 saturation (red) and after CO_2 saturation (green)

THQ dehydrogenation kinetic monitoring under Ar

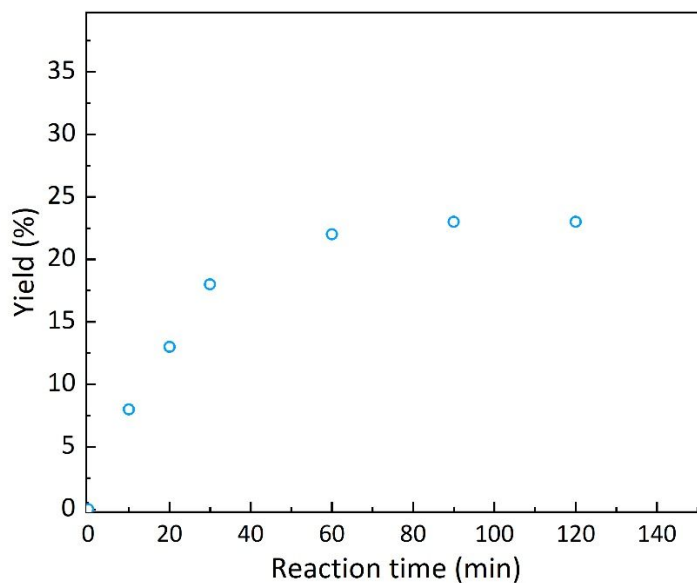


Figure S14. Reaction monitoring over time for the dehydrogenation of THQ using oLAC-2-700 as catalyst under Ar atmosphere

Electrochemical measurements

Indole substrates cyclic voltammtries

Electrochemical tests were performed at room temperature using an Interface 1000 electrochemical workstation (Gamry Instruments). The set-up cell used for the experiments was a three-electrode system consisting of a platinum coil as the counter electrode, a Pt wire as pseudo-reference electrode with Fc/Fc⁺ as an internal standard and a glassy carbon electrode as a working electrode. Oxidation potentials were estimated from the irreversible oxidation curves as E^{p/2} which, according to literature, is the value closest to E_{1/2} at the scan rate of 0.5 V/s.⁴

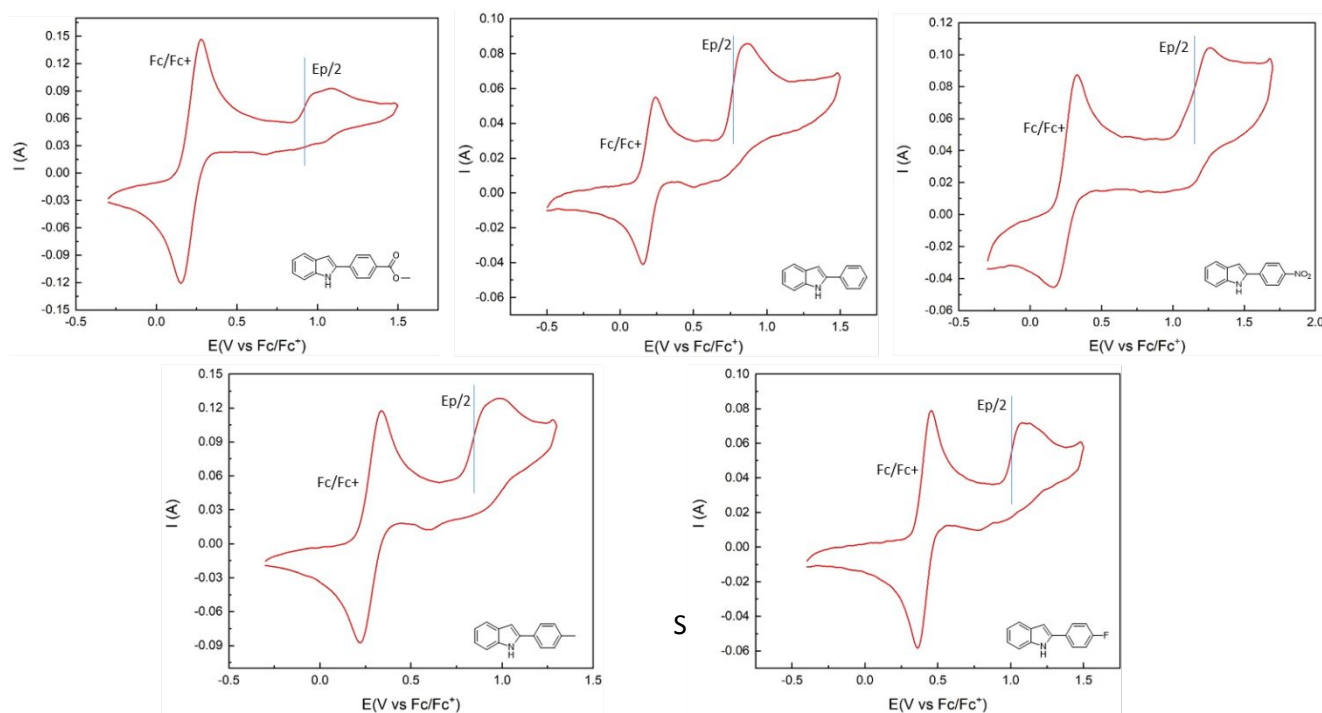


Figure S15. CV of differently substituted indoles in presence of ferrocene as internal standard using a glassy carbon electrode in a 0.10 M NBu_4PF_6 solution in acetonitrile under Ar. Scan rate: 0.5 V s^{-1} .

Carbon materials cyclic voltammetries

The catalyst ink was prepared by dispersing the powder into a water:isopropanol:Nafion mixture (5 mg catalyst, 20 μl di Nafion, 500 μl di water, 500 μl isopropanol), and then drop-casted onto a Toray paper. The electrochemical measurements were carried out at room temperature by using an Autolab potentiostat/galvanostat (Model 302N) and a RDE (Autolab), both equipped with a three-electrode cell under a stream of purified Ar gas. All potentials were measured with respect to Ag/AgCl electrode contained in a glass tube filled with the supporting electrolyte solution, separated from the solution by a Vycor frit and located close to the tip of the working electrode to minimize the ohmic drop. The counter electrode was a Pt wire directly dipped in the solution. The supporting electrolyte was composed of 0.5 M H_2SO_4 aqueous solution and the scan rate for the CV measurements was of 50 V sec^{-1} .

Examples of NMR spectra of reaction crude mixture for NMR yield calculation with internal standard (trimethoxybenzene)

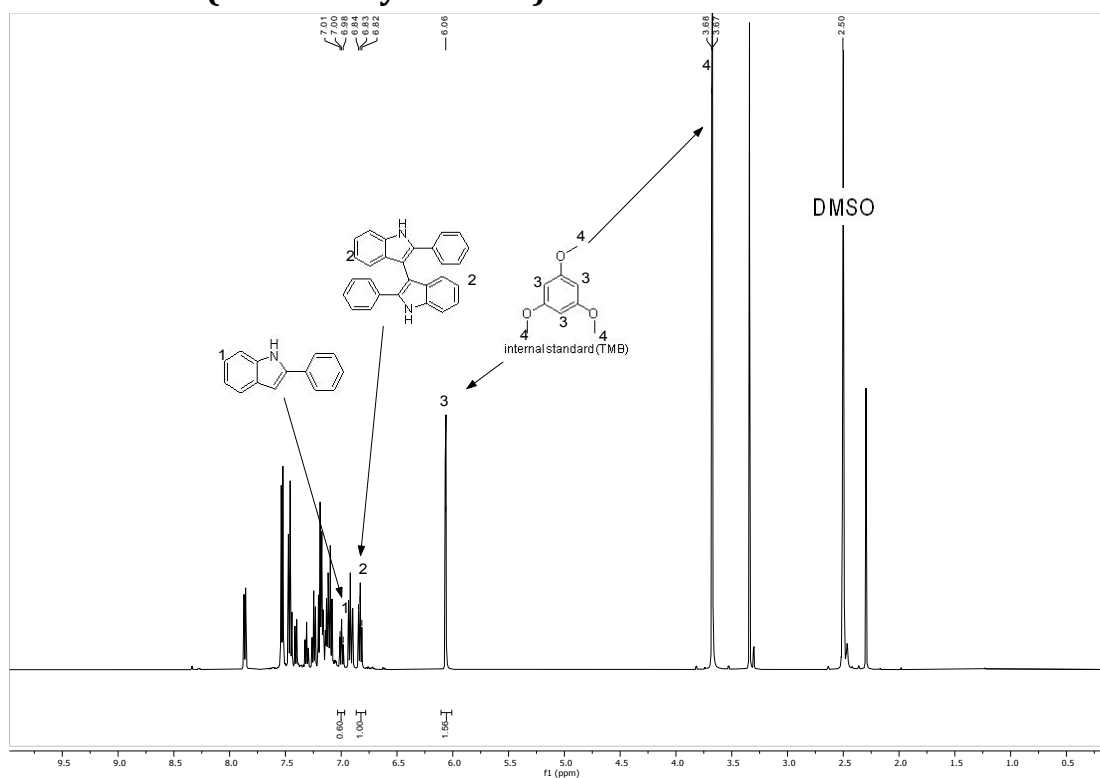


Figure S16. Homocoupling of 2-phenylindole

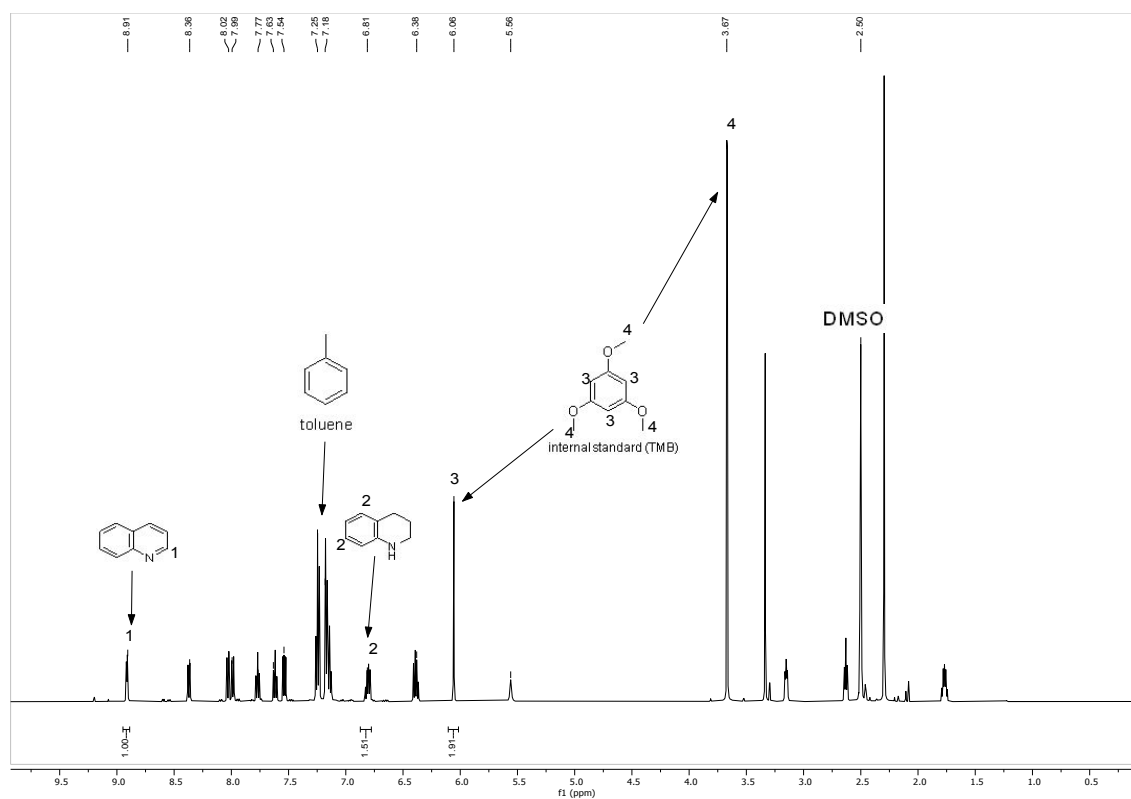


Figure S17. THQ dehydrogenation

References

- 1 Trogen, M.; Le, N.-D.; Sawada, D.; Guizani, C.; Lourençon, T. V.; Pitkänen, L.; Sixta, H.; Shah, R.; O'Neill, H.; Balakshin, M.; Byrne, N.; Hummel, M. Cellulose-lignin composite fibres as precursors for carbon fibres. Part 1 – Manufacturing and properties of precursor fibres. *Carbohydr. Polym.* **2021**, *252*, 117133. DOI: 10.1016/j.carbpol.2020.117133.
- 2 Wirtanen, T.; Mäkelä, M. K.; Sarfraz, J.; Ihalainen, P.; Hietala, S.; Melchionna, M.; Helaja, J. Carbocatalysed oxidative C_{sp^2} - C_{sp^2} homocouplings of benzo-fused heterocycles. *Adv. Synth. Catal.* **2015**, *357* (16-17), 3718-3726. DOI: 10.1002/adsc.201500664.
- 3 Figueiredo, J. L.; Pereira, M. F. R. The role of surface chemistry in catalysis with carbons. *Catal. Today* **2010**, *150* (1-2), 2-7. DOI: 10.1016/j.cattod.2009.04.010.
- 4 Espinoza, E. M.; Clark, J. A.; Soliman, J.; Derr, J. B.; Morales, M.; Vullev, V. I. Practical aspects of cyclic voltammetry: how to estimate reduction potentials when irreversibility prevails. *J. Electrochem. Soc.* **2019**, *166* (5), H3175-H3187. DOI: 10.1149/2.0241905jes.