**SUPPORTING INFORMATION**

**Complementary TEM experiments**

For a better understanding of the local influence of Pd NPs on their surrounding porosity, a detailed analysis of the general aspect of the carbon matrix above and below the Pd particles is shown in Figure SI1. The slices presented in Figures SI1a and SI1c show clearly that before and after several nm thickness from the NPs (Figure SI1b), the general aspect of the C support is the same as in areas containing no Pd particles. It confirms that the particles are surrounded by large voids within the C support with local distortion of the worm-like mesoporous framework around them.

![Figure SI1](image)

(a) (b) (c)

Figure SI1. Representative slices details extracted from the reconstructed volume of Pd@MC X3 sample to evidence the influence of metallic Pd nanoparticles on the porosity: a) slice at thickness $e_0 - 32$ nm; b) slice of reference at thickness $e_0$ and b) slice at thickness $e_0 + 44$ nm. The scale in the three slices is 100 nm.
Figure SI2: N$_2$ adsorption/desorption isotherms measured at 77K on (a) tanin-derived carbon samples and, (b) Pd@MC Xi samples. The figure evidences the variability of the synthesis and the negligible influence of Pd$^{2+}$ traces on the pore size distribution.
$^1$H and $^{13}$C-NMR Spectra of Biaryls 1a-i

1-(4-Biphenylyl)ethanone (1a): Elution with AcOEt / cyclohexane 5:95 as eluant afforded 1a as a white solid (195 mg, 98% yield). $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 2.65 (s, 3H), 7.45 (m, 3H), 7.64 (d, $^3$J(H,H) = 7.0 Hz, 2H), 7.70 (d, $^3$J(H,H) = 6.7 Hz, 2H), 8.05 (d, $^3$J(H,H) = 6.7 Hz, 2H).[1] $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ (ppm): 26.6, 127.2, 128.0, 128.8, 135.8, 139.8, 145.7, 197.7.

4-Methoxybiphenyl (1b): Elution with AcOEt / cyclohexane 5:95 afforded 1b as a white solid (177 mg, 96% yield). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm): 3.88 (s, 3H), 7.01 (d, $^3$J(H,H) = 8.8 Hz, 2H), 7.33 (t, $^3$J(H,H) = 7.3 Hz, 1H), 7.44 (m, 2H), 7.58 (m, 4H).[3] $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ (ppm): 55.3, 114.2, 126.7, 128.1, 133.7, 140.8, 159.1.

4-Methylbiphenyl (1c): Elution with AcOEt / cyclohexane 1:99 afforded 1c as a white solid (160 mg, 95% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 2.30 (s, 3H), 7.17 (m, 3H), 7.33 (t, $^3$J(H,H) = 7.6 Hz, 2H), 7.40 (d, $^3$J(H,H) = 8.4 Hz, 2H), 7.49 (d, $^3$J(H,H) = 8.4 Hz, 2H).[3] $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 21.1, 127.0, 129.3, 129.5, 137.0, 138.4, 141.2.

3-Methylbiphenyl (1d): Elution with AcOEt / cyclohexane 1:99 afforded 1d as a colorless oil (165 mg, 98% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 2.45 (s, 3H), 7.20 (m, 3H), 7.33 (t, $^3$J(H,H) = 7.6 Hz, 2H), 7.40 (d, $^3$J(H,H) = 8.4 Hz, 2H).[3] $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ (ppm): 21.5, 124.2, 127.2, 127.6, 128.7, 138.3, 141.2, 178.3.

2-Methylbiphenyl (1e): Elution with AcOEt / cyclohexane 1:99 afforded 1e as a yellowish oil (166 mg, 99% yield). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm): 2.19 (s, 3H), 7.16 (m, 4H), 7.26 (m, 3H), 7.32 (m, 2H).[3] $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ (ppm): 20.5, 125.7, 126.7, 126.8, 128.0, 129.1, 129.2, 130.1, 130.3, 135.3, 141.9.

2-Isopropylbiphenyl (2d): Elution with Et$_2$O / Cyclohexane 1 : 99 afforded 137 mg (70% yield) of a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 1.07 (d, $^3$J(H,H) = 6.9 Hz, 6H), 2.97 (hept, $^3$J(H,H) = 6.9 Hz, 1H), 7.15 (m, 9H).[29] $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 24.3, 29.3, 125.3, 125.5, 126.7, 127.6, 127.9, 129.3, 141.0, 142.1, 146.3.

1-(4-(4'-Methyl)biphenylyl)ethanone (1g): Elution with AcOEt / cyclohexane 5:95 afforded 1g as a white solid (203 mg, 97% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 2.30 (s, 3H), 2.52 (s, 3H), 7.17 (d,
3J(H,H) = 8.1 Hz, 2H), 7.42 (d, 3J(H,H) = 8.1 Hz, 2H), 7.56 (d, 3J(H,H) = 8.3 Hz, 2H), 7.90 (d, 3J(H,H) = 8.3 Hz, 2H).[2] 13C NMR (100 MHz, CDCl3) δ (ppm): 21.0, 26.5, 126.8, 126.9, 128.8, 129.6, 136.8, 137.6, 145.6, 197.6.

1-(4-(2'-Methyl)biphenylyl)ethanone (1h): Elution with AcOEt / cyclohexane 5:95 afforded 1h as a colorless oil (196 mg, 93% yield). 1H NMR (300 MHz, CDCl3) δ (ppm): 2.29 (s, 3H), 2.65 (s, 3H), 7.26 (m, 4H), 7.44 (d, 3J(H,H) = 8.5 Hz, 2H), 8.03 (d, 3J(H,H) = 8.5 Hz, 2H).[5] 13C NMR (100 MHz, CDCl3) δ (ppm): 20.2, 26.5, 125.8, 127.8, 128.1, 129.2, 129.3, 130.4, 134.9, 140.6, 146.8, 197.6.

1-(4-(4'-Methoxy)biphenylyl)ethanone (1i): Elution with AcOEt / cyclohexane 5:95 afforded 1i as a white solid (210 mg, 93% yield). 1H NMR (300 MHz, CDCl3) δ (ppm): 2.62 (s, 3H), 3.86 (s, 3H), 7.00 (d, 3J(H,H) = 8.8 Hz, 2H), 7.58 (d, 3J(H,H) = 8.8 Hz, 2H), 7.64 (d, 3J(H,H) = 8.3 Hz, 2H), 8.00 (d, 3J(H,H) = 8.3 Hz, 2H).[5] 13C NMR (100 MHz, CDCl3) δ (ppm): 26.5, 55.3, 114.3, 126.5, 128.3, 128.9, 132.1, 135.2, 145.2, 159.8, 197.6.
Compound 1a

$^1$H-NMR, 400 MHz, CDCl$_3$
Compound 1a

$^{13}$C-NMR, 75 MHz, CDCl$_3$
Compound 1b

$^1$H-NMR, 300 MHz, CDCl$_3$
Compound 1c

$^1$H-NMR, 400 MHz, CDCl$_3$
Compound 1d

$^1$H-NMR, 300 MHz, CDCl$_3$
Compound 1d

$^{13}$C-NMR, 75 MHz, CDCl$_3$
Compound 1e

$^1$H-NMR, 300 MHz, CDCl$_3$
Compound 1e

$^{13}$C-NMR, 75 MHz, CDCl$_3$
Compound 1f

$^1$H-NMR, 300 MHz, CDCl$_3$
Compound 1f
$^1$H-NMR, 300 MHz, CDCl$_3$
Compound 1g

$^1$H-NMR, 400 MHz, CDCl$_3$
Compound 1g

$^{13}$C-NMR, 100 MHz, CDCl$_3$
Compound 1h

$^1$H-NMR, 300 MHz, CDCl$_3$
Compound 1h

$^{13}$C-NMR, 75 MHz, CDCl$_3$
Compound 1i

$^1$H-NMR, 300 MHz, CDCl$_3$