Electronic Supplementary Information

Toward eco-friendly protocols: insights into direct arylation polymerizations under aerobic conditions in anisole

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Fig. S1. ³¹P NMR spectra (recorded in CDCl₃) of P(*o*-Anisyl)₃ dispersed in anisole before and after a thermal treatment at 110 °C for 24 h in air. The comparison clearly evidences the formation of a new species (the phosphine-oxide) immediately after the phosphine dissolution in anisole under aerobic conditions. The protection exerted by the anisole vapours against the oxygen dissolution in the solvent during the thermal treatment avoids the complete oxidation of the pristine ligand, as described in the manuscript.

Entry	Palladium source	Yield (%) ^a	M _n (Da) ^b	M _w (Da) ^b	Đb
1	Pd ₂ dba ₃	42	4500	6800	1.5
2	$Pd(AcO)_2$	58	5100	7000	1.4
3	Pd(PivO) ₂	53	5000	7900	1.6

Table S1. Molecular weights and yield of P1 synthesized by using different palladium precatalysts.

^aMeasured after polymer precipitation in methanol, Soxhlet washing with methanol, acetone and hexane, Soxhlet extraction with chloroform, and reprecipitation in methanol. ^bNumber-average molecular weights (M_n), weight-average molecular weights (M_w) and dispersity (Đ) as determined by GPC (PS standards, THF).



Fig. S2. ¹H NMR spectrum of P1 (entry 5) recorded in C₂D₂Cl₄.



Fig. S3. ¹H NMR spectrum of P2 recorded in $C_2D_2Cl_4$.



Fig. S4. ¹H NMR spectrum of P3 recorded in C₂D₂Cl₄.



Fig. S5. ¹H NMR spectrum of P4 recorded in C₂D₂Cl₄.



Fig. S6. PL spectrum of P1 recorded in chloroform.



Fig. S7. ¹H NMR spectrum of P5 recorded in CDCl₃.



Fig. S8. ¹H NMR spectrum of P6 recorded in CDCl₃.



Fig. S9. ¹H NMR spectrum of P8 recorded in $C_2D_2Cl_4$.