

Supplementary Information

Unique *syndio*-selectivity in CO/styrene copolymerization reaction by palladium complexes with 2-(2'-oxazoliny)-1,10-phenanthrolines

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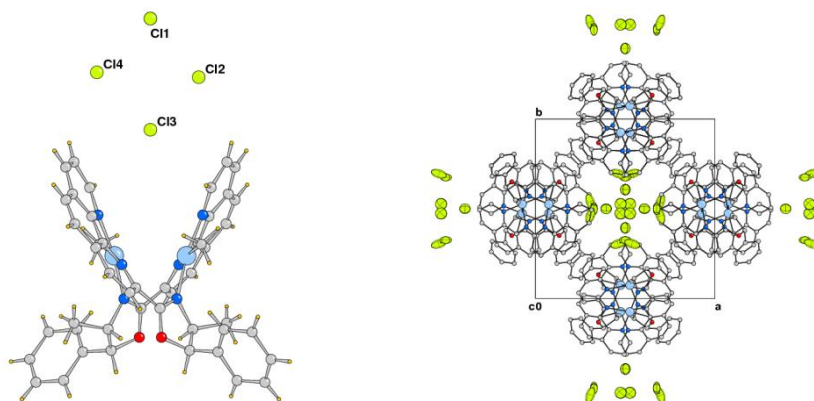
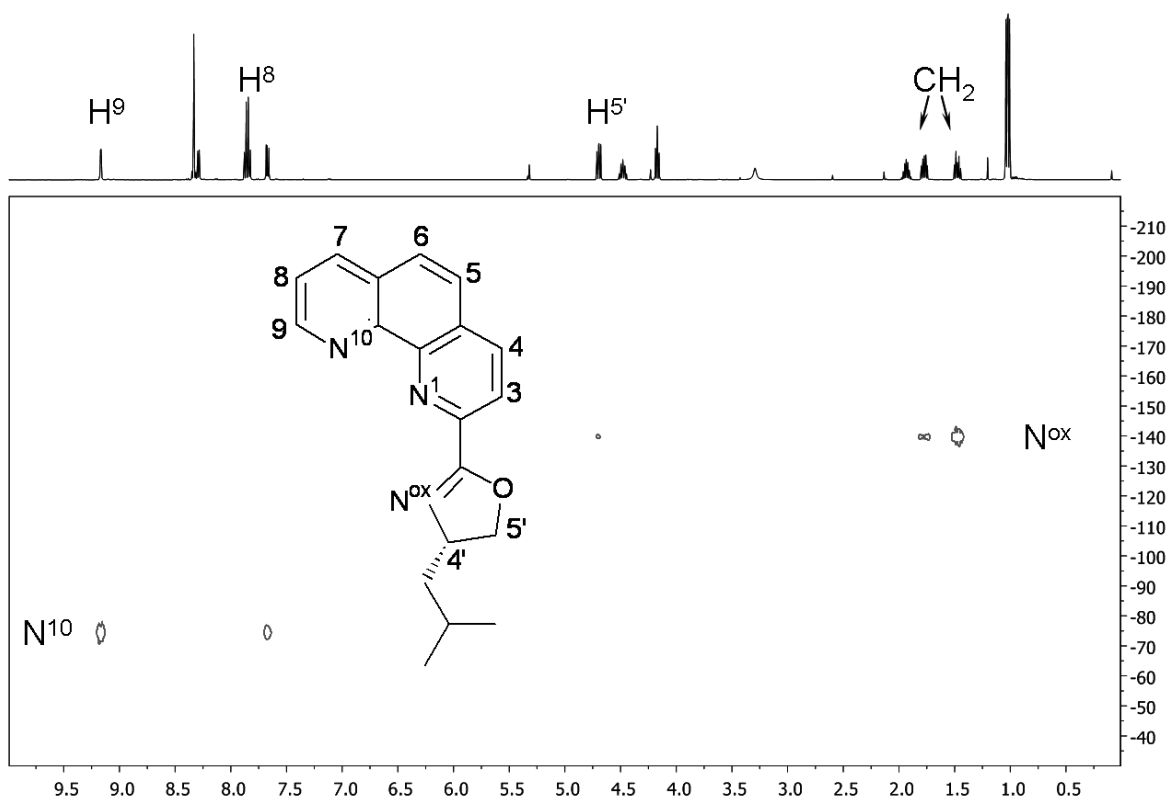
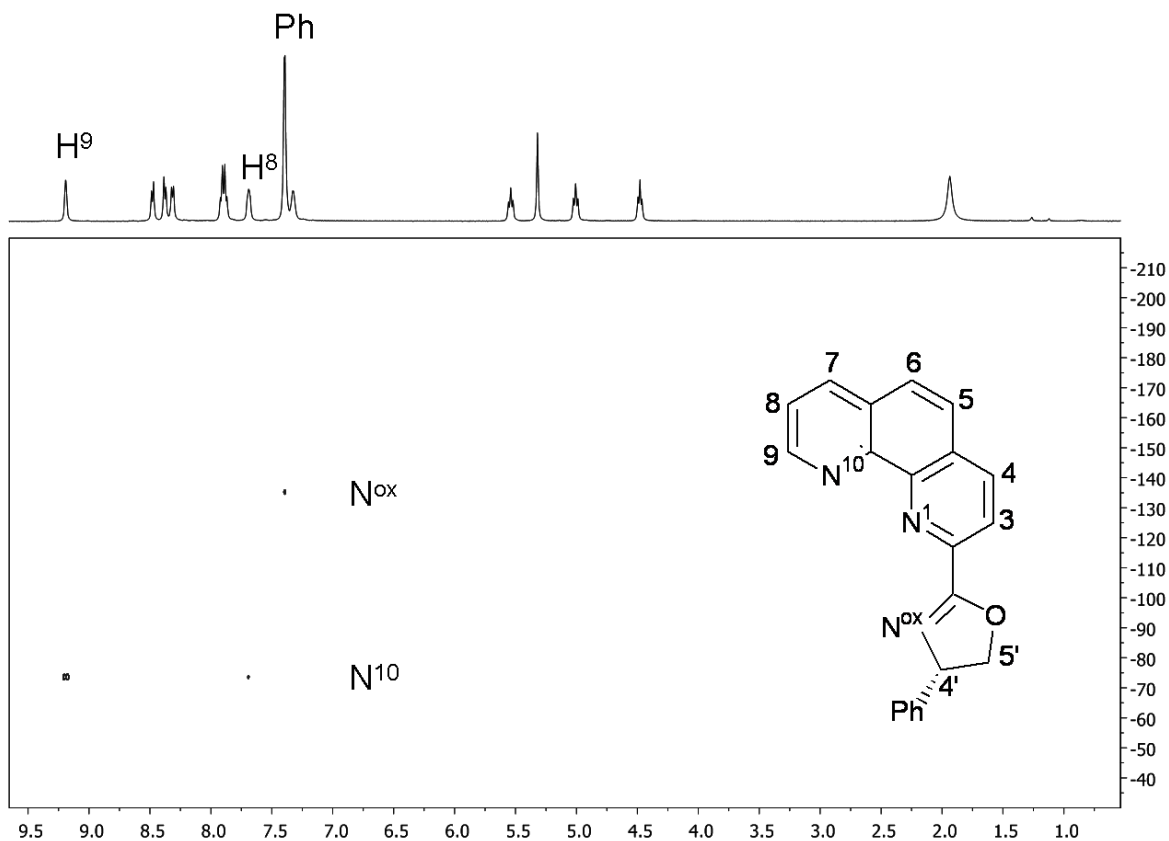


Figure S1. (a) Molecular structure of **3a** (chloride anions at half occupancy). (b) Crystal packing of compound **3a** viewed down axis *c*. Selected bond lengths [\AA] and angles [$^\circ$]: Pd-N(1) 2.154(18), Pd-N(2) 2.006(16), Pd-N(3') 2.013(16), Pd-C(23) 1.942(17), N(1)-Pd-N(2) 78.5(8), N(1)-Pd-N(3') 101.8(7), N(2)-Pd-N(3') 171.7(6), N(1)-Pd-C(23) 168.9(8), N(2)-Pd-C(23) 93.1(9), N(3')-Pd-C(23) 85.5(8); non-bonding Pd---Pd' interaction 3.039(4). Primed atoms at $y, x, -z+1/3$.

Data collection of **3a** was performed by using a Bruker Kappa CCD imaging plate mounted on a Nonius FR591 rotating anode ($\lambda = 1.5418\text{\AA}$). Due to the small number of data C atoms (with the exception of the coordinated methyl group) were isotropically refined. The chlorides were found disordered over two positions at half occupancy. A void of 464.5\AA^3 was detected in the unit cell and the Squeeze program (P.v.d. Sluis, A.L. Spek, Acta Crystallogr., Sect A 1990, 46, 194-201) was applied to remove the contributions of possible disordered solvent.

Crystal data of 3a: $\text{C}_{46}\text{H}_{40}\text{Cl}_2\text{N}_6\text{O}_2\text{Pd}_2$, $M = 992.54$, tetragonal, space group $P 4_122$ (No. 95), $a = 16.527(3)$, $c = 17.005(5) \text{\AA}$, $V = 4644.8(18) \text{\AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.419 \text{ g/cm}^3$, $\mu(\text{Cu-K}\alpha) = 7.638 \text{ mm}^{-1}$, $F(000) = 2000$. Final $R = 0.0636$, $wR2 = 0.1433$, $S = 1.109$ for 169 parameters and 28058 reflections, 2988 unique [$R(\text{int}) = 0.0535$], of which 1222 with $I > 2\sigma(I)$. Flack parameter = 0.09(5). Max positive and negative peaks in ΔF map 0.966, $-0.550 \text{ e \AA}^{-3}$.



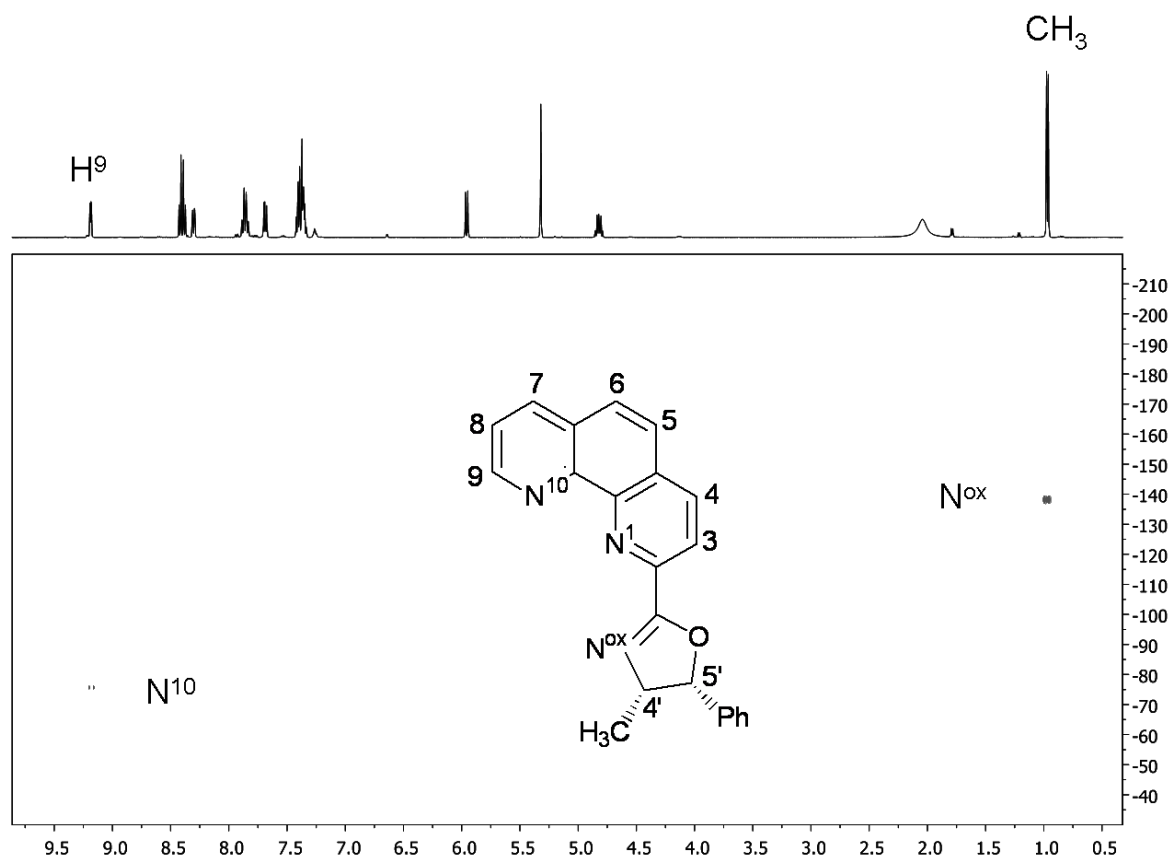


Figure S4. $\{^1\text{H}, ^{15}\text{N}\}$ -HMBC NMR spectrum of **3**, in CD_2Cl_2 at room temperature.

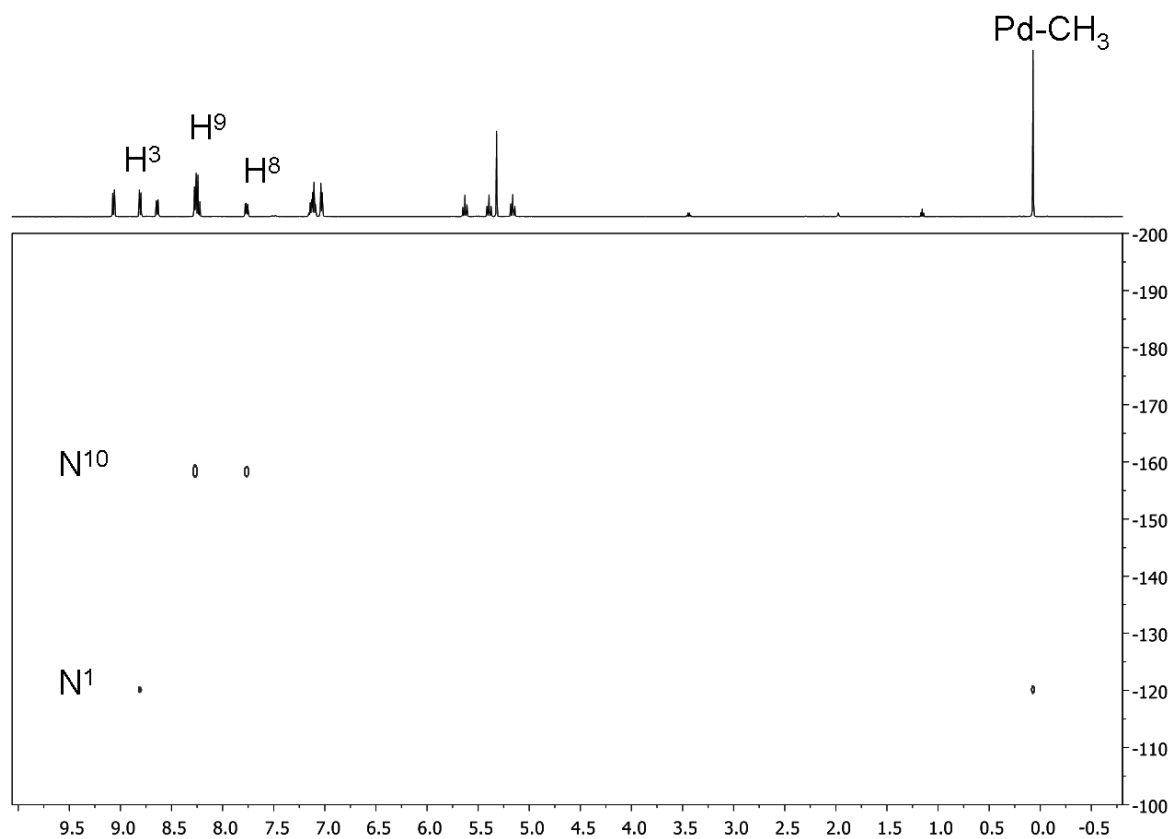


Figure S5. $\{^1\text{H}, ^{15}\text{N}\}$ -HMBC NMR spectrum of **1b**, in CD_2Cl_2 at room temperature.

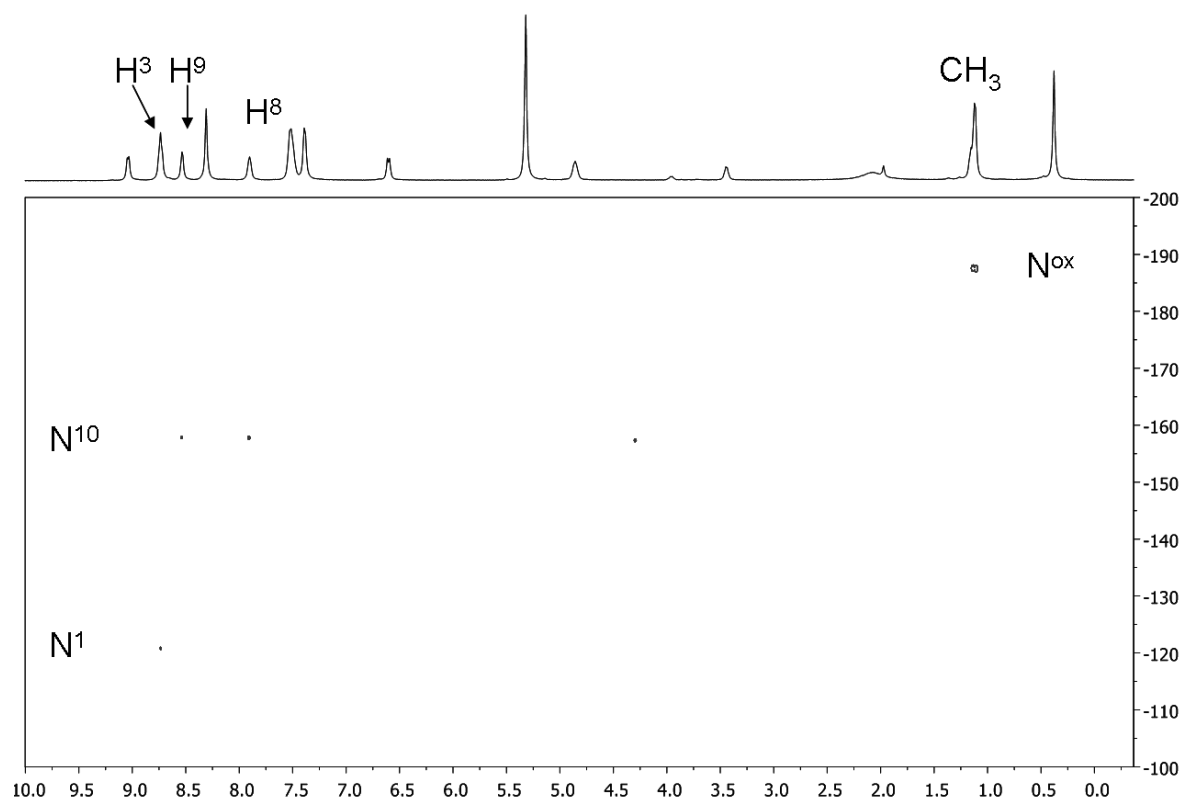


Figure S6. $\{^1\text{H}, ^{15}\text{N}\}$ -HMBC NMR spectrum of **3b**, in CD_2Cl_2 at room temperature.

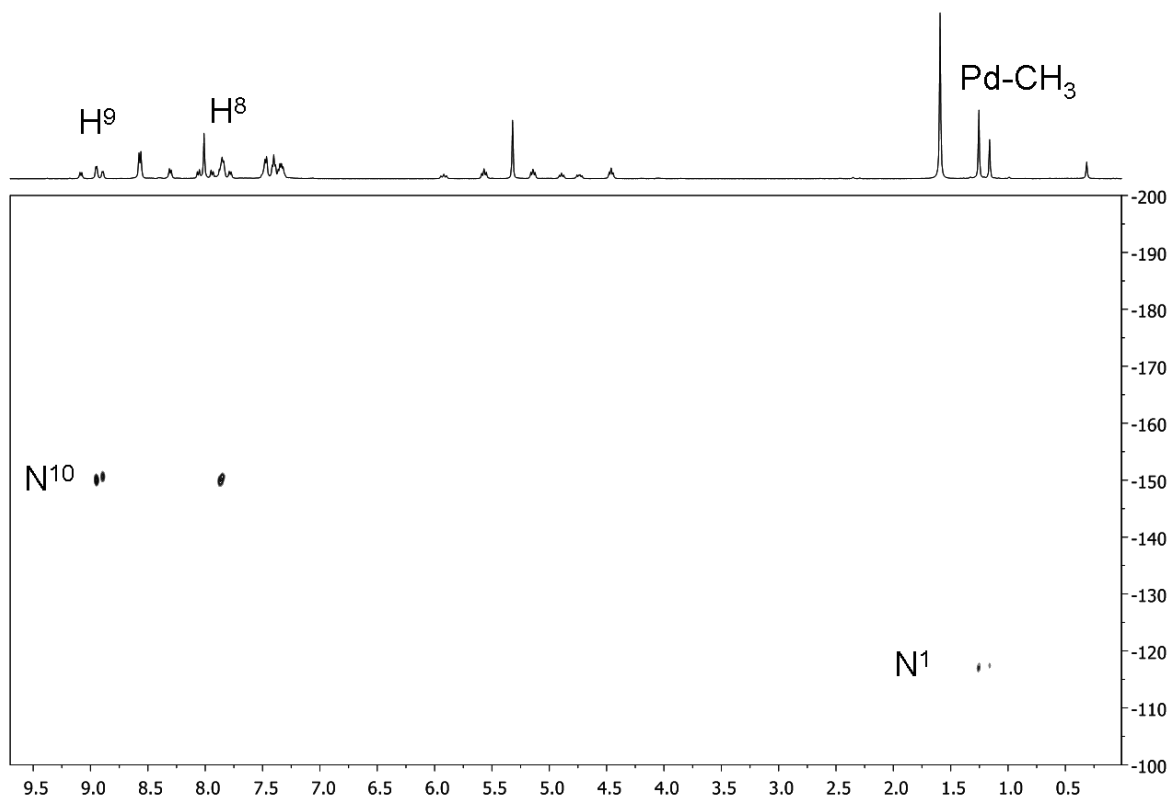


Figure S7. $\{^1\text{H}, ^{15}\text{N}\}$ -HMBC NMR spectrum of **1a**, in CD_2Cl_2 at room temperature.

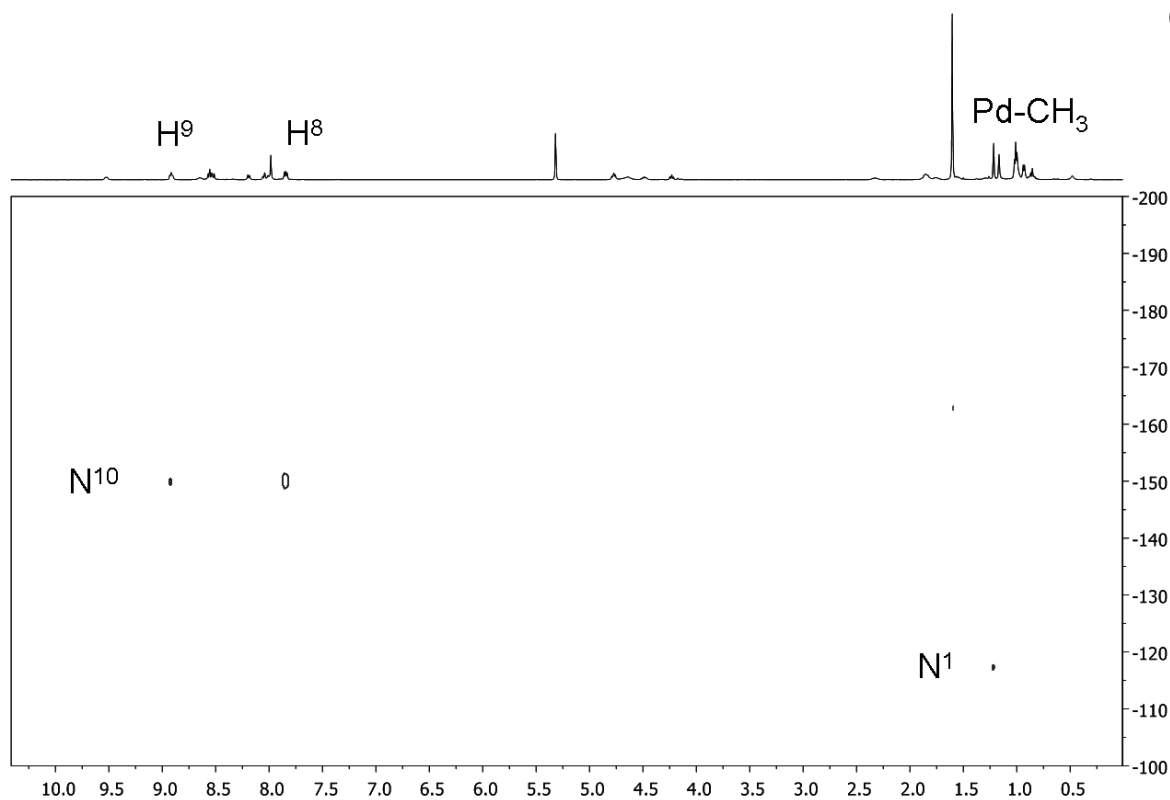


Figure S8. $\{^1\text{H}, ^{15}\text{N}\}$ -HMBC NMR spectrum of **2a**, in CD_2Cl_2 at room temperature.

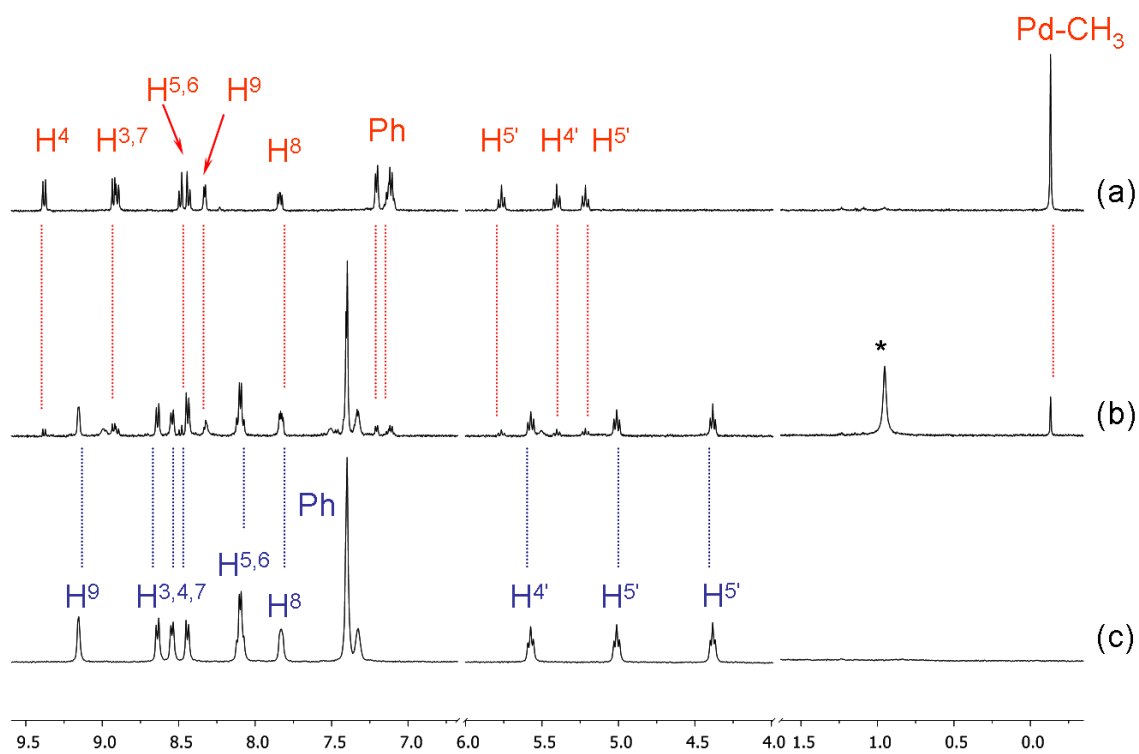


Figure S9. ^1H NMR spectra in dms0-d_6 at room temperature of: (a) **1b**; (b) **1a**; (c) **1**; (*) signal of $[\text{Pd}(\text{CH}_3)\text{Cl}(\text{dms0-d}_6)_2]$.

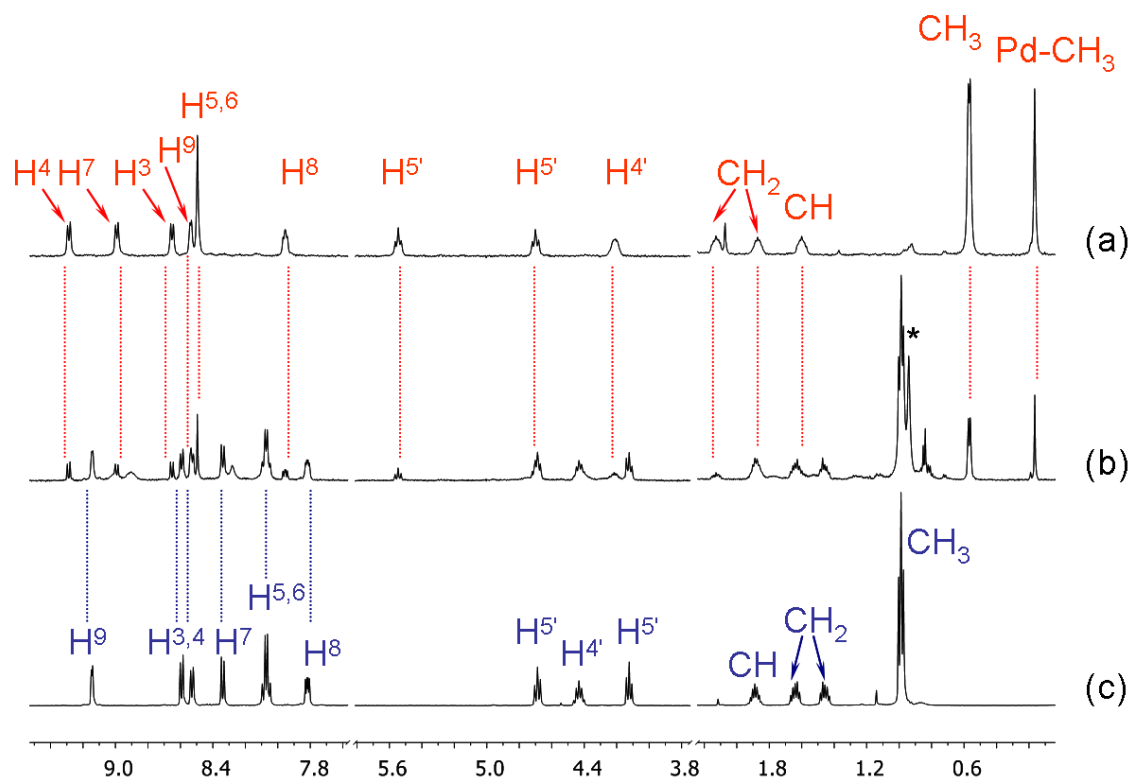


Figure S10. ^1H NMR spectra in dms0-d_6 at room temperature of: (a) **2b**; (b) **2a**; (c) **2**; (*) signal of $[\text{Pd}(\text{CH}_3)\text{Cl}(\text{dms0-d}_6)_2]$.

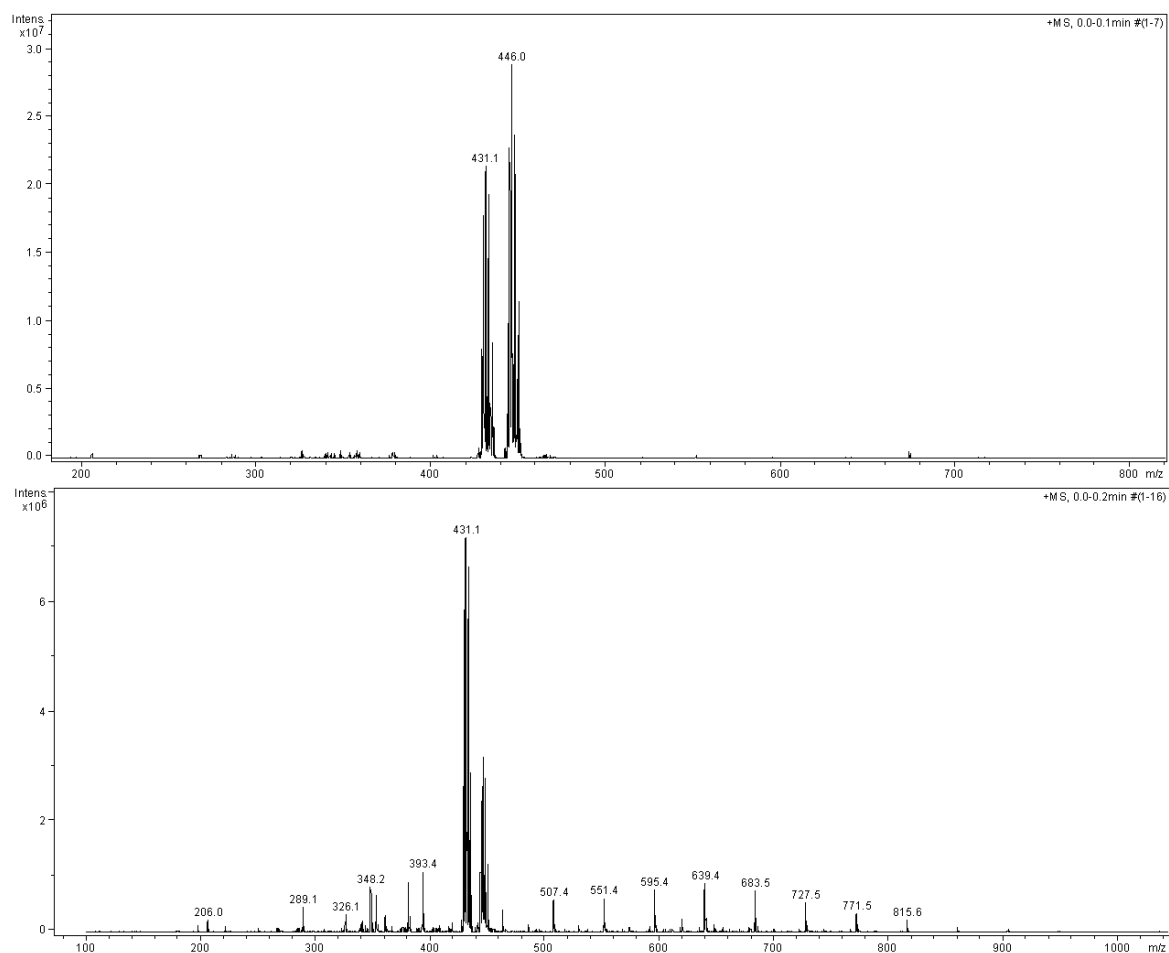


Figure S11. ESI-MS of: **1a** (up); **1b** (bottom).

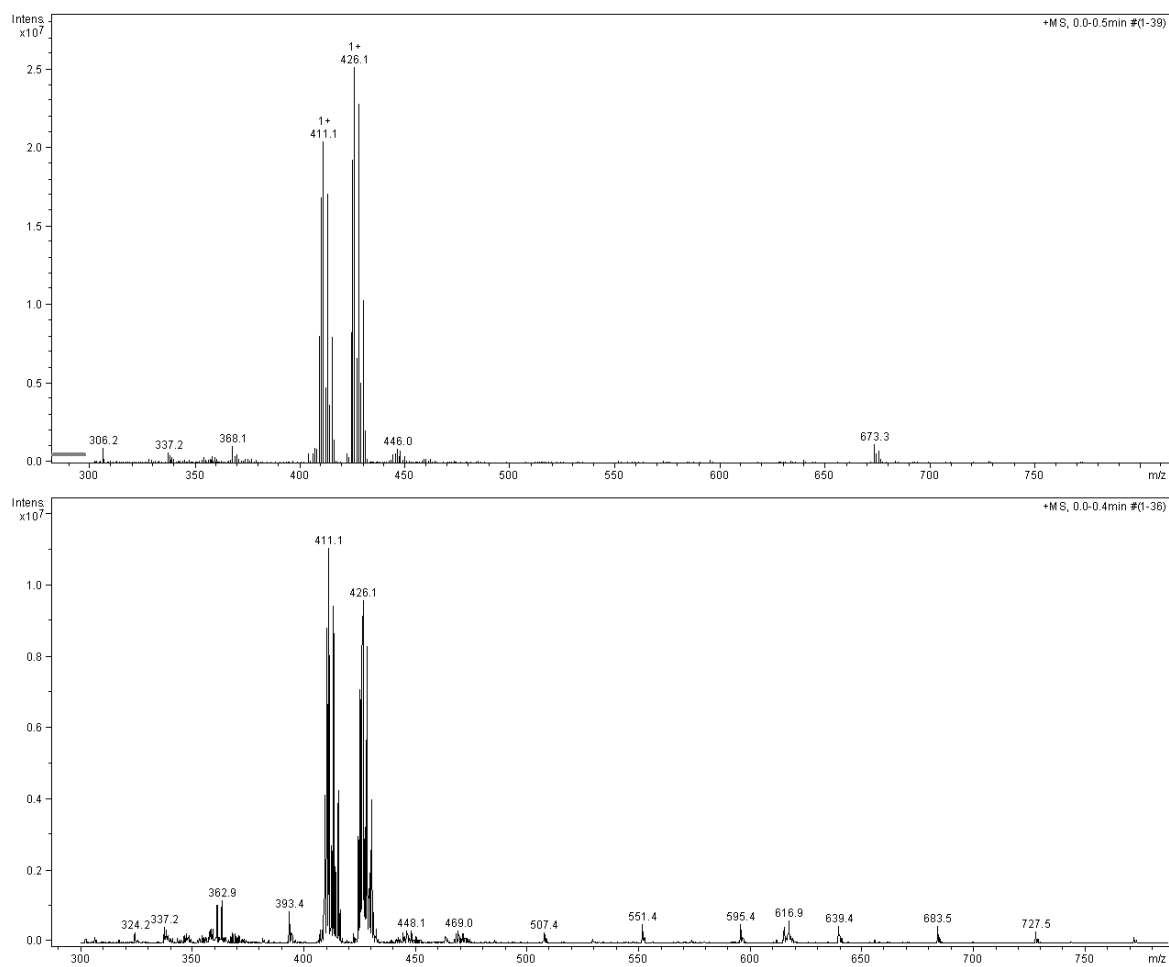


Figure S12. ESI-MS of: **2a** (up); **2b** (bottom).

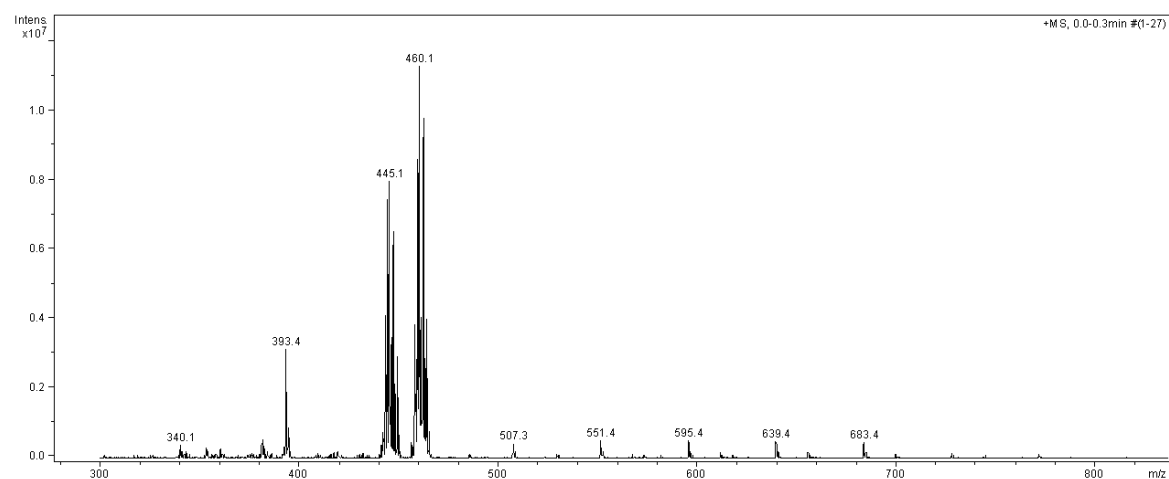
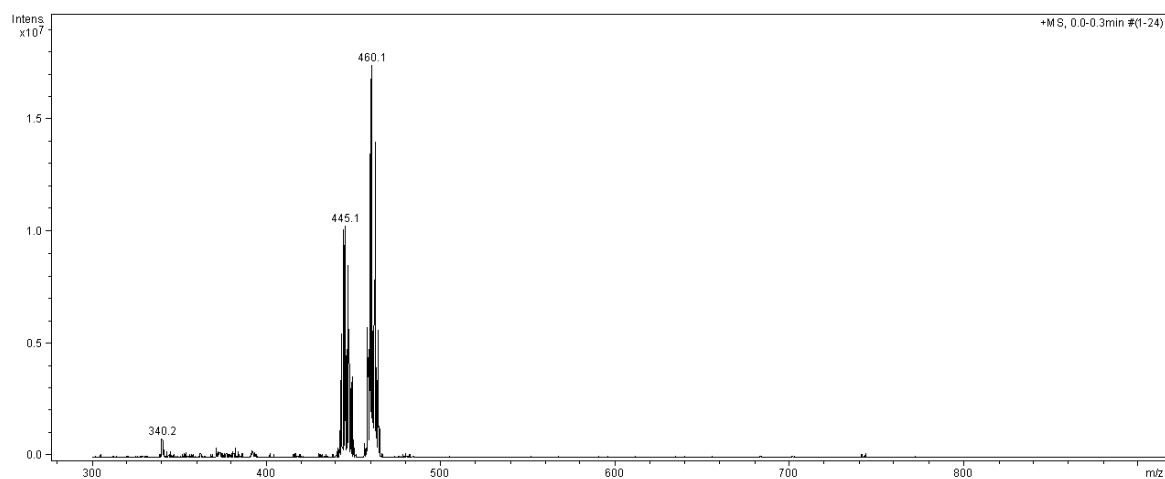


Figure S13. ESI-MS of: **3a** (up); **3b** (bottom).

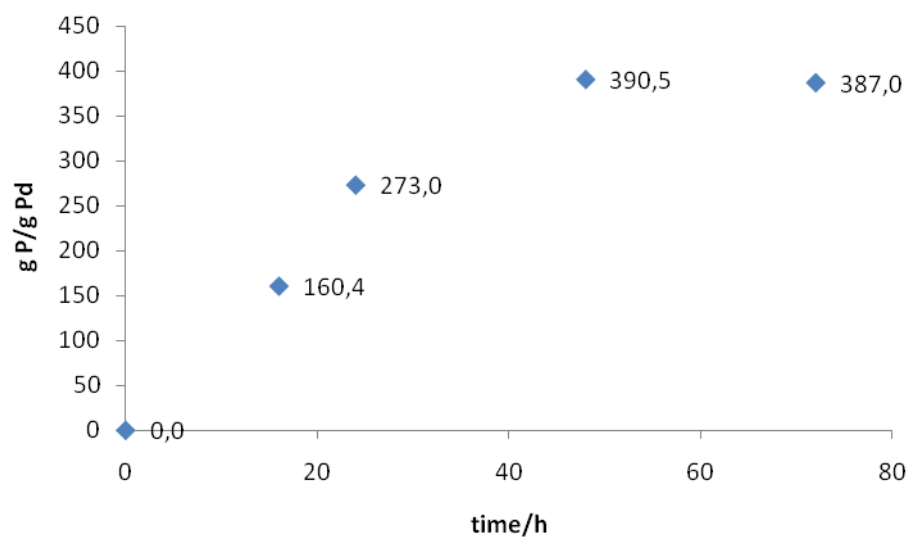


Figure S14. CO/styrene oligomerization: effect of reaction time.

Precatalyst: [$\{\text{Pd}(\text{CH}_3)(\mathbf{3})\}_2[\text{PF}_6]_2$] **3b**

Reaction conditions: $n_{\text{Pd}} = 1.27 \times 10^{-5}$ mol, styrene V = 10 mL, TFE V = 20 mL, $P_{\text{CO}} = 1$ bar, $T = 303$ K, $[\text{BQ}]/[\text{Pd}] = 40$, $[\text{styrene}]/[\text{Pd}] = 6800$. g P/g Pd = grams of product per gram of palladium.