Electronic Supplementary Information

The isocyanide insertion across the Pd-C bond of allenyl and propargyl palladium complexes bearing phosphoquinoline as spectator ligand. The synthesis of a palladium complex bearing a coordinated cyclobutenyl fragment.

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1) NMR characterization of complex 4

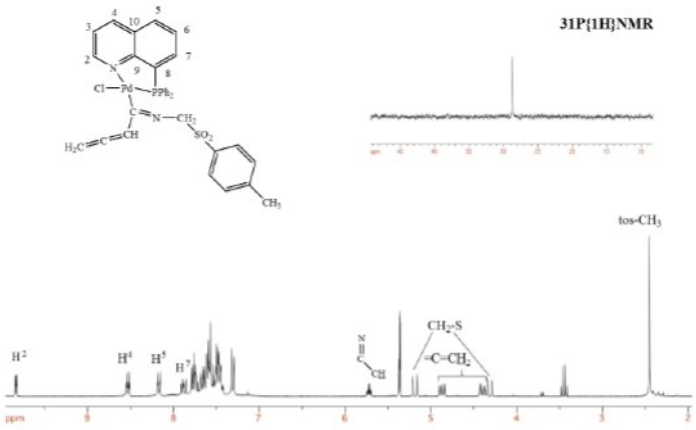


Fig. S1: ^{1}H and ^{31}P (top insert) NMR spectra of complex **4** in CD_2Cl_2 at 298K.

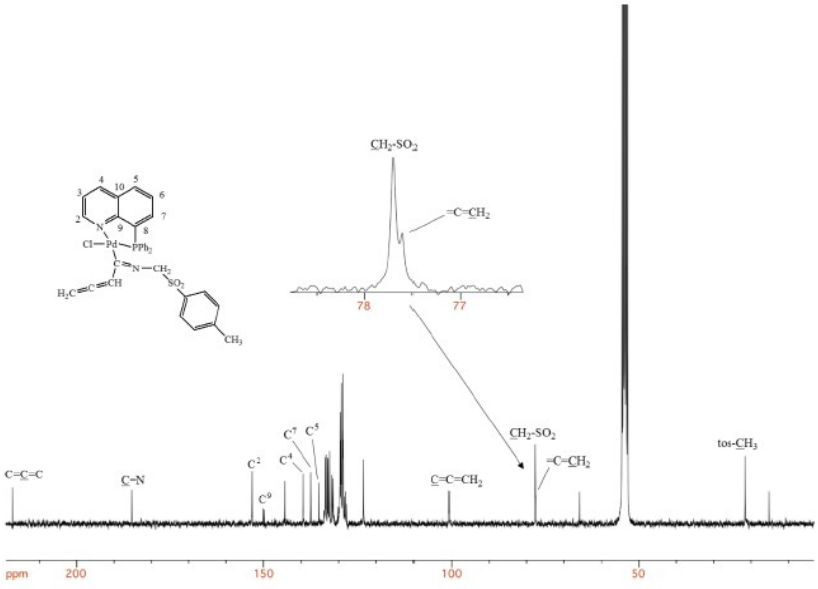


Fig.S2: $^{13}C\{H^{1}\}$ NMR spectrum of complex **4** in CD_2Cl_2 at 298K.

2) NMR characterization of complex 6

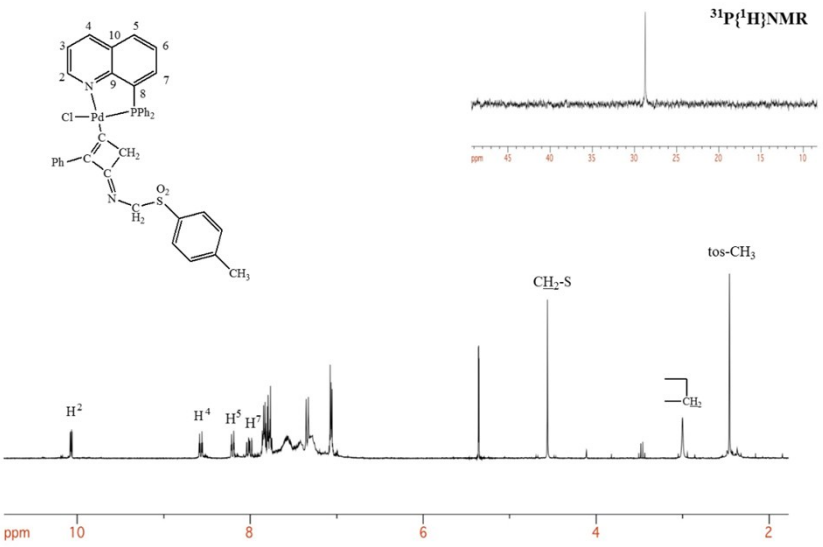


Fig. S3: ^{1}H and ^{31}P (top insert) NMR spectra of complex **6** in CD_2Cl_2 at 298K.

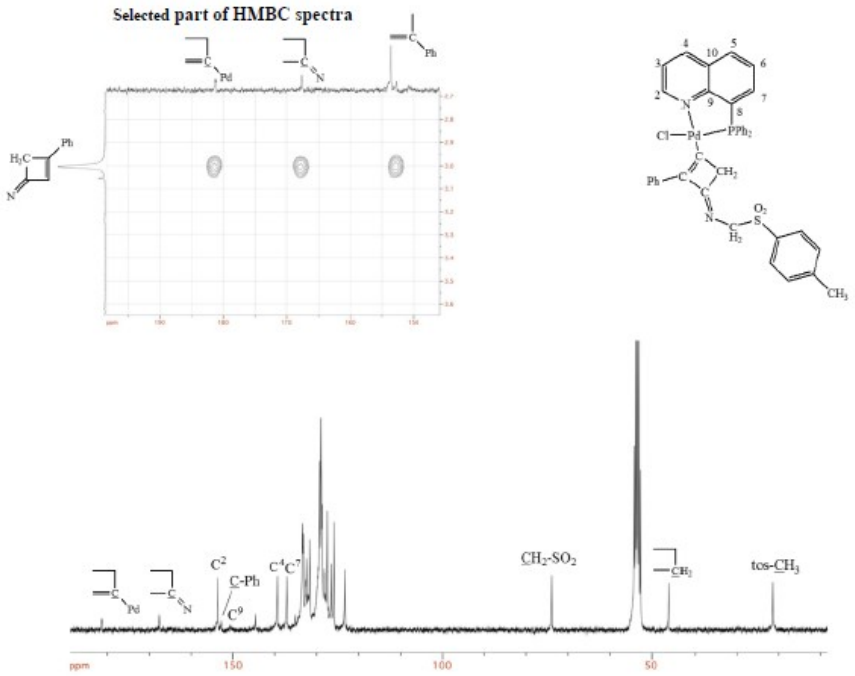


Fig. S4: $^{13}C\{H^{1}\}$ NMR spectrum of complex **6** in CD_2Cl_2 at 298K. Top insert: Selected part of the $^{1}H–^{13}C$ HMBC spectra showing the signals ascribable to the carbons of the cyclobutenyl fragment.

3) NMR study of the reaction: 6 + PhC≡CSn(Bu)$_3$ -> PPBTM + [Pd(DPPQ)(fn)] + ClSn(Bu)$_3$

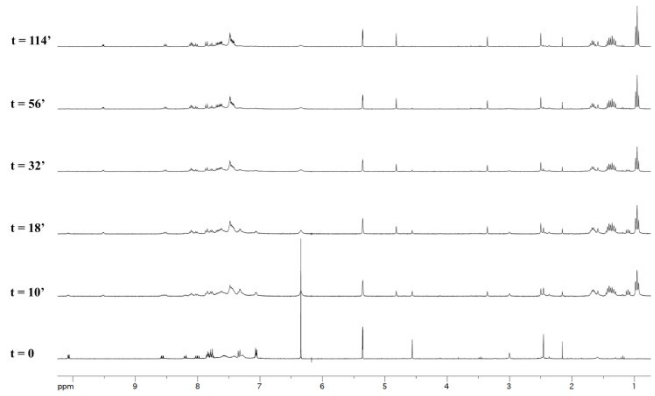


Fig. S5: ^{1}H NMR of the reaction **6** + PhC≡CSn(Bu)$_3$ -> PPBTM + [Pd(DPPQ)(fn)] + ClSn(Bu)$_3$ in CD_2Cl_2 at 298 K

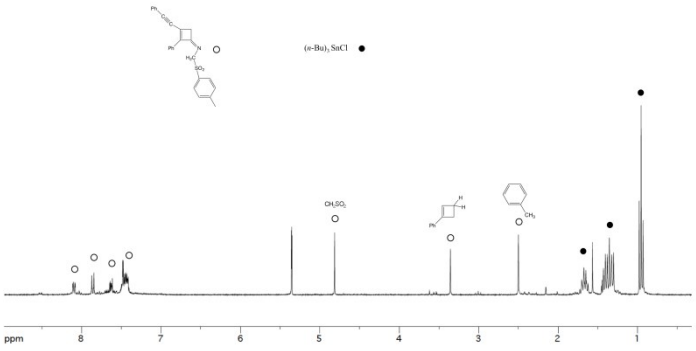


Fig. S6: ^{1}H NMR spectrum of the product of the reaction above reported (See Fig. S5) (CD_2Cl_2 at 298 K)

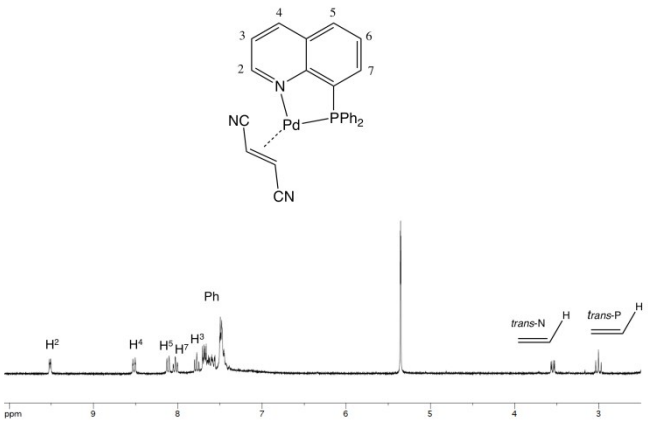


Fig. S7: ^{1}H NMR spectrum of the isolated complex [Pd(η^2–fn) (DPPQ)] (**7**) in CD_2Cl_2 at 298 K.

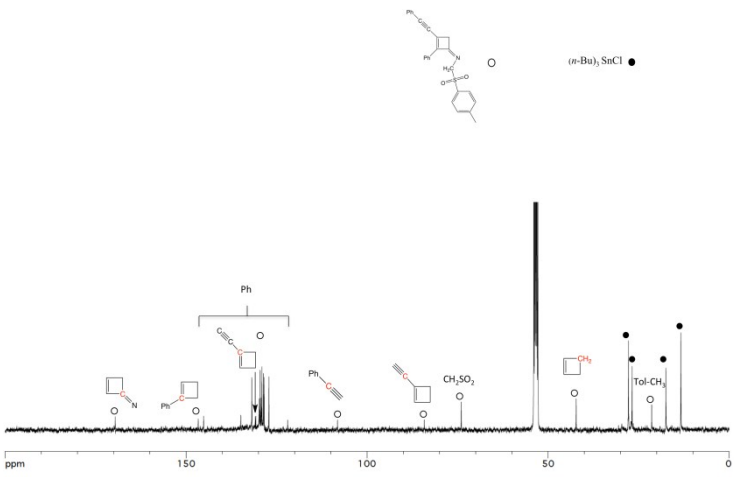


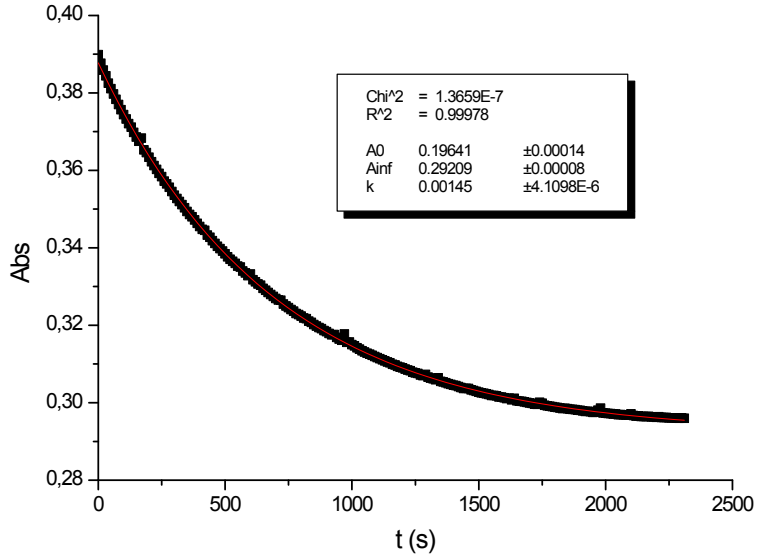
Fig. S8: ^{13}C NMR spectrum in CD_2Cl_2 at 298 K of the extracted products of the reaction above reported (See Fig. S5).

4) Summary of the kinetic studies

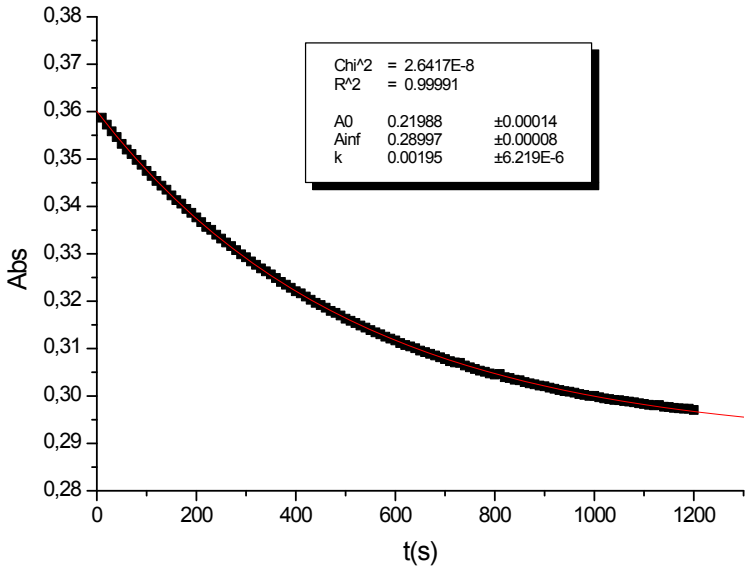
Absorbance *vs.* time and linear regression analysis

1+TosMic -> 4

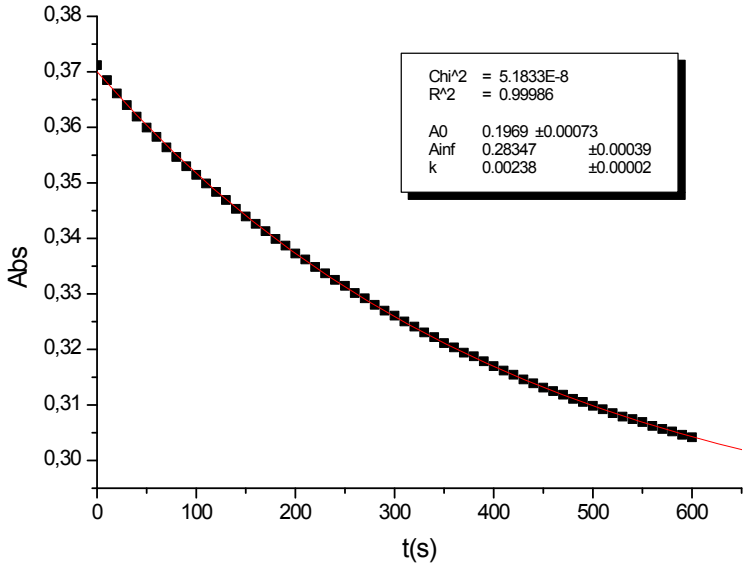
10 equivalents TosMic



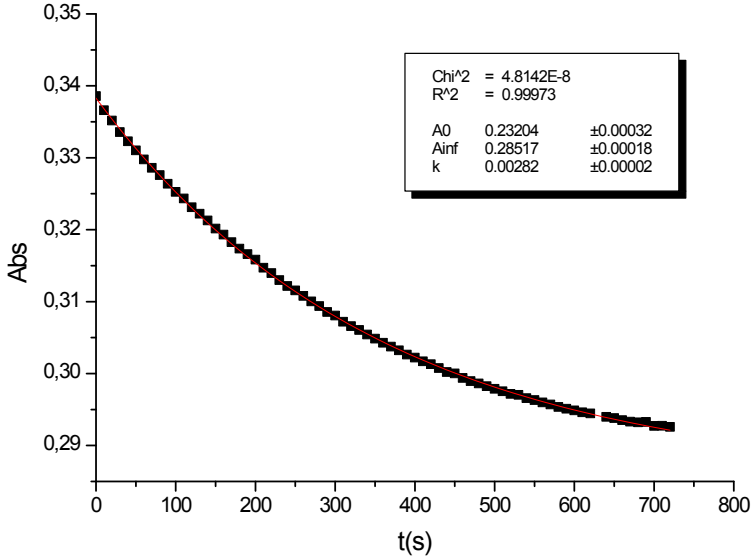
12.5 equivalents TosMic



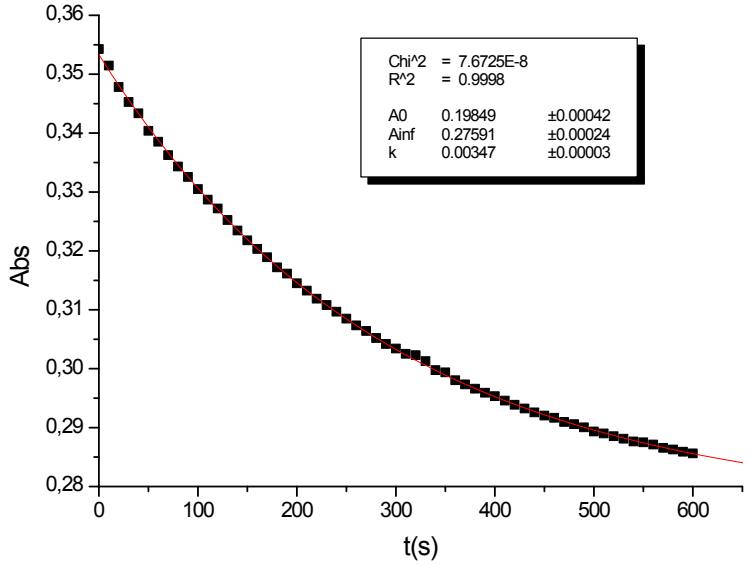
15 equivalents TosMic



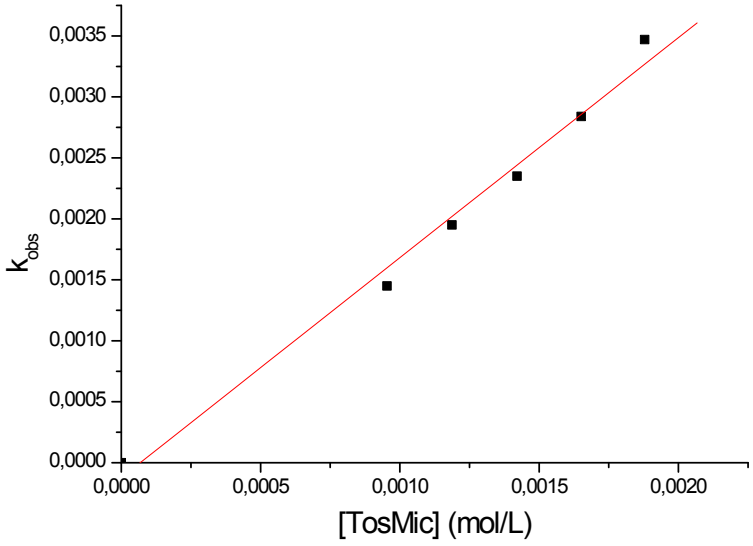
17.5 equivalents TosMic



20 equivalents TosMic



k_{obs} vs [TosMic]



Intercept	-1,2269E-4	1,3501E-4
K_eK_2	1,8043	0,1016

R	SD	N	P
0,99372	1,5112E-4	6	<0.0001

2 + 3 +TosMic -> 5

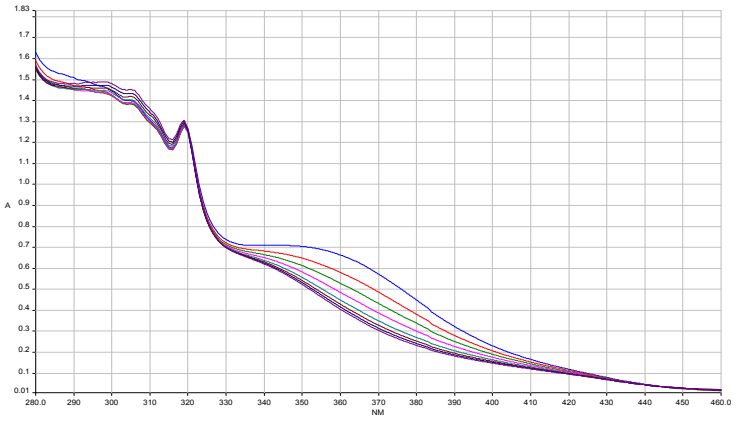
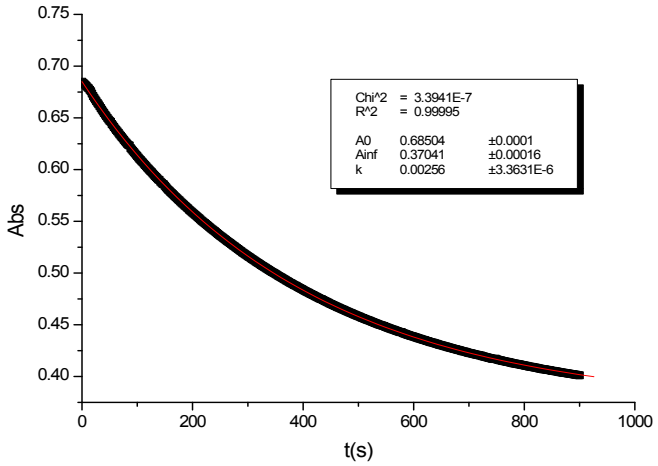
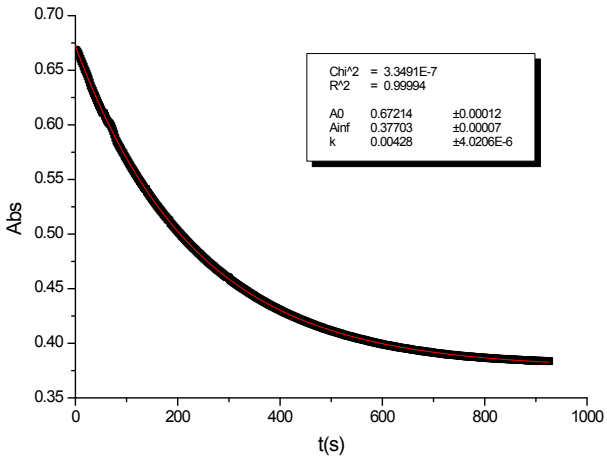


Fig. S9: Absorbance vs. wavelengths for the reaction 2 + 3 +TosMic -> 5

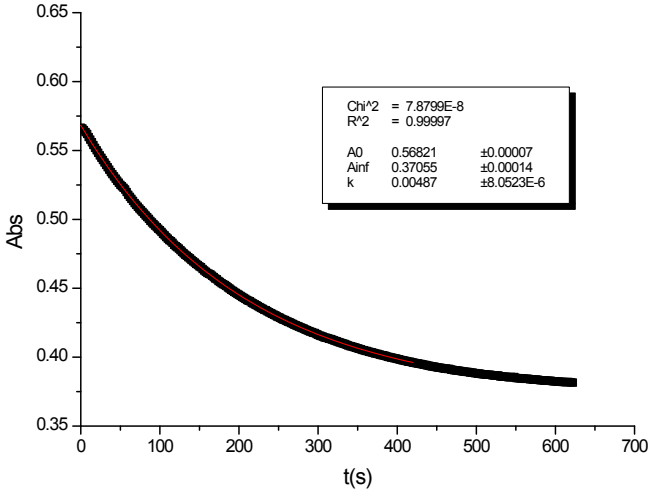
10 equivalents TosMic



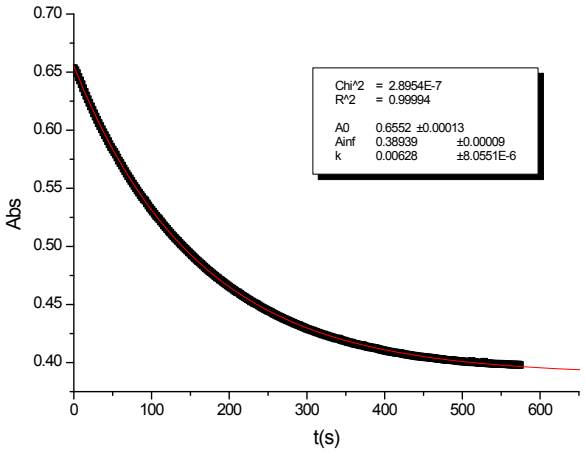
15 equivalents TosMic



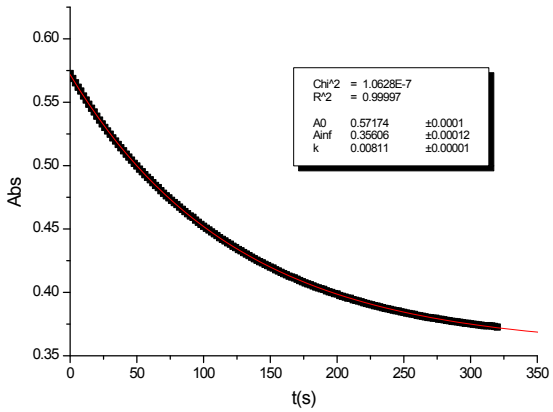
17.5 equivalents TosMic



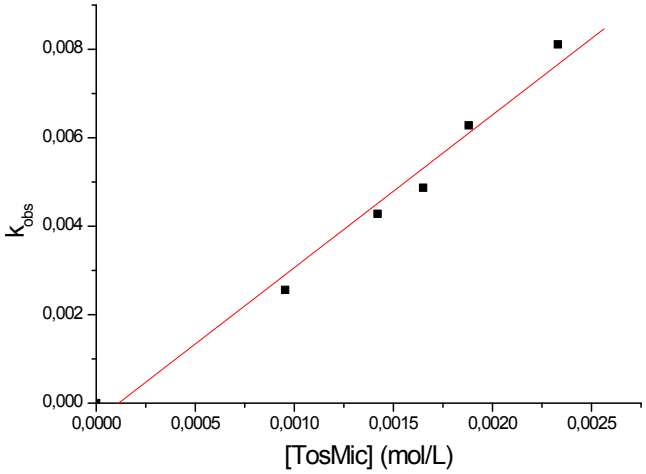
20 equivalents TosMic



25 equivalents TosMic



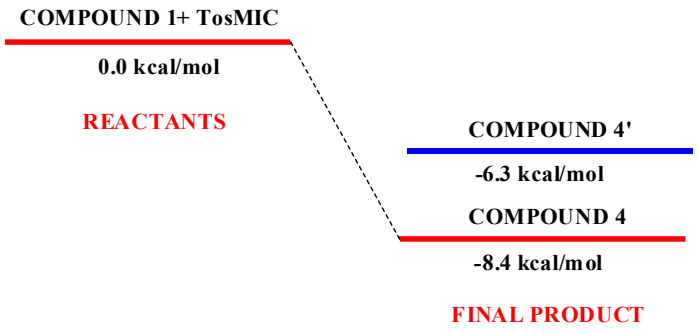
k_{obs} vs [TosMic]

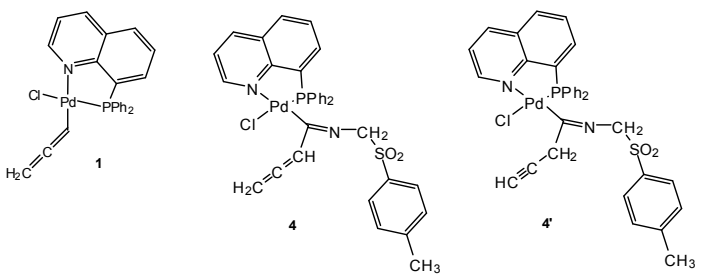


Parameter	Value	Error
intercept	-3,8949E-4	3,7244E-4
$K_T K_e k_2$	3,4536	0,2387

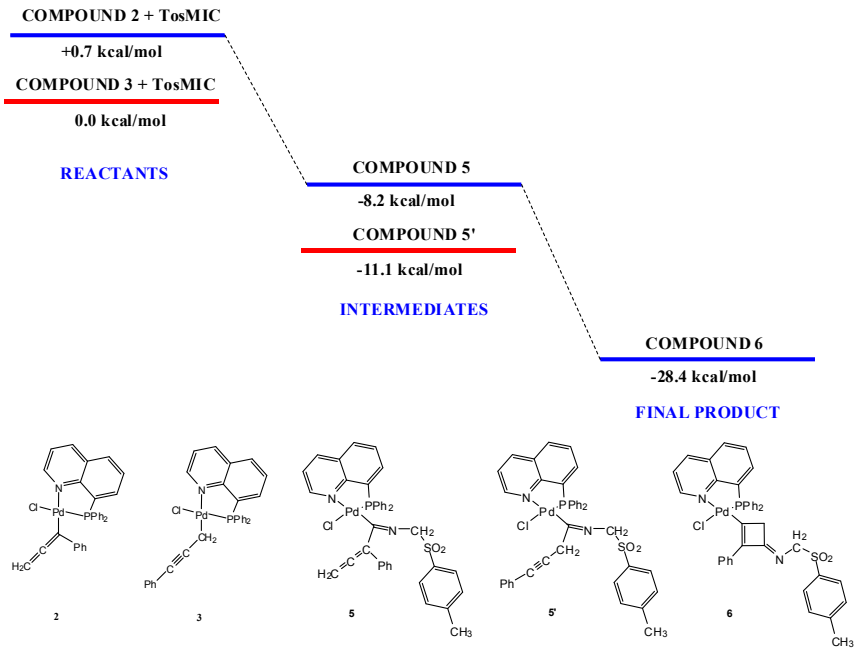
R	SD	N	P
0,99058	4,3436E-4	6	1,3257E-4

5) DFT schemes





Scheme S1: Computed **e**nergies for the involved species in the reaction between complexes **1** and the isocyanide TosMIC.



Scheme S2: Computed **e**nergies for the involved species in the reaction between the tautomers **2**, **3** and the isocyanide TosMIC.

6) Crystallographic data (Table S1 and S2)

Table S1. Crystallographic data.

Compound	**6**
Formula	$C_{39}H_{32}ClN_2O_2PPdS{\bullet}1.5(CH_2Cl_2)$
M	892.93
Space group	*C2*
Crystal system	Monoclinic
a/Å	18.6709(4)
b/Å	9.3853(3)

c/Å	23.9410(8)
β/°	106.914(2)
U/Å^3	4013.8(2)
Z	4
T/K	293(2)
D_c/g cm^{-3}	1.478
F(000)	1812
μ(Mo-Kα)/mm^{-1}	0.858
Measured Reflections	19027
Unique Reflections	10073
R_{int}	0.0474
Obs. Refl.ns [I≥2σ(I)]	8370
θ_{min}- θ_{max}/°	2.28 – 30.00
hkl ranges	-26,25;-13,12;-33,22
R(F^2) (Obs.Refl.ns)	0.0394
wR(F^2) (All Refl.ns)	0.0865
No. Variables	466
Goodness of fit	1.040
$\Delta\rho_{max}$; $\Delta\rho_{min}$ /e Å^{-3}	0.407; -0.703
CCDC Deposition N.	1509243

Table S2. Selected bond distances and angles (Å and degrees) .

Distances		**Angles**	
Pd1-Cl1	2.359(1)	Cl1-Pd1-P1	178.04(4)
Pd1-P1	2.210(1)	Cl1-Pd1-N1	93.6(1)
Pd1-N1	2.146(3)	Cl1-Pd1-C22	89.3(1)
Pd1-C22	1.977(4)	P1-Pd1-N1	84.6(1)

C22-C23	1.351(6)	P1-Pd1-C22	92.6(1)
C22-C24	1.533(7)	N1-Pd1-C22	176.1(2)
C23-C25	1.468(7)	C23-C22-C24	94.4(4)
C24-C25	1.530(9)	C22-C23-C25	92.3(4)
C25-N2	1.268(6)	C22-C24-C25	83.3(4)
		C23-C25-C24	90.0(3)