Supporting Information for

Degradation of the active species in the catalytic system $Pd(OAc)_2/NEt_3$

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1. *Characterization of $Pd(OAc)_2(HNEt_2)_2$*

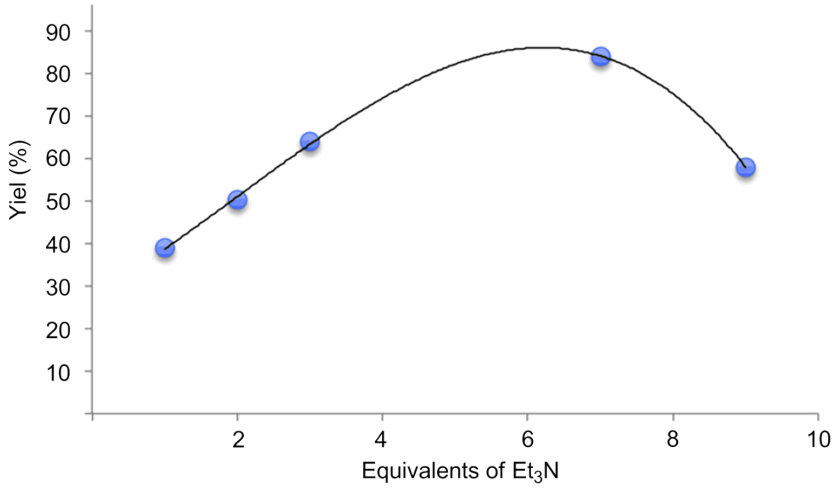


Fig. S1. Dependence of $Pd(OAc)_2(HNEt_2)_2$ yield with the used molar ratio (1:1, 1:2, 1:3, 1:7 and 1:9).

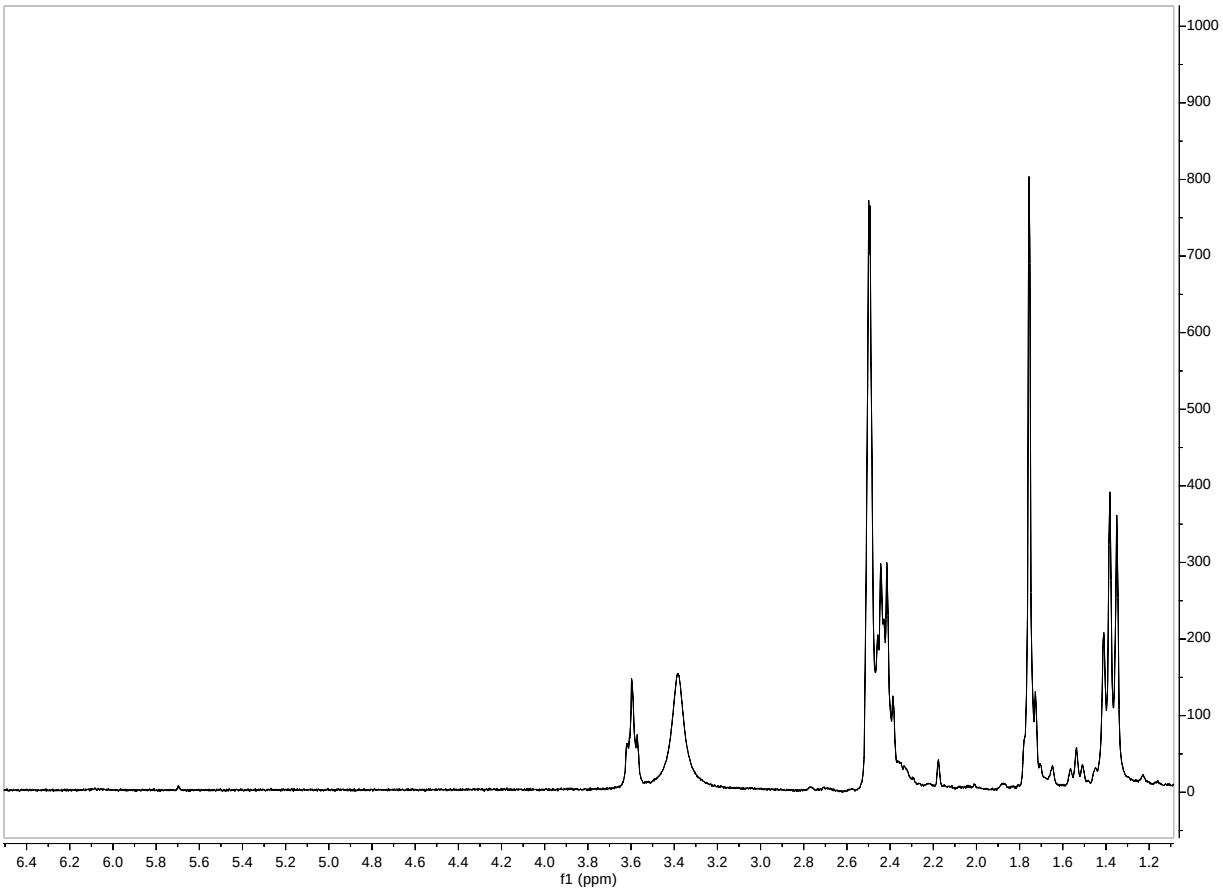


Fig. S2. ^{1}H NMR spectrum (in dmso-d_6) of an aliquot of the reaction crude previous to the hydrolysis

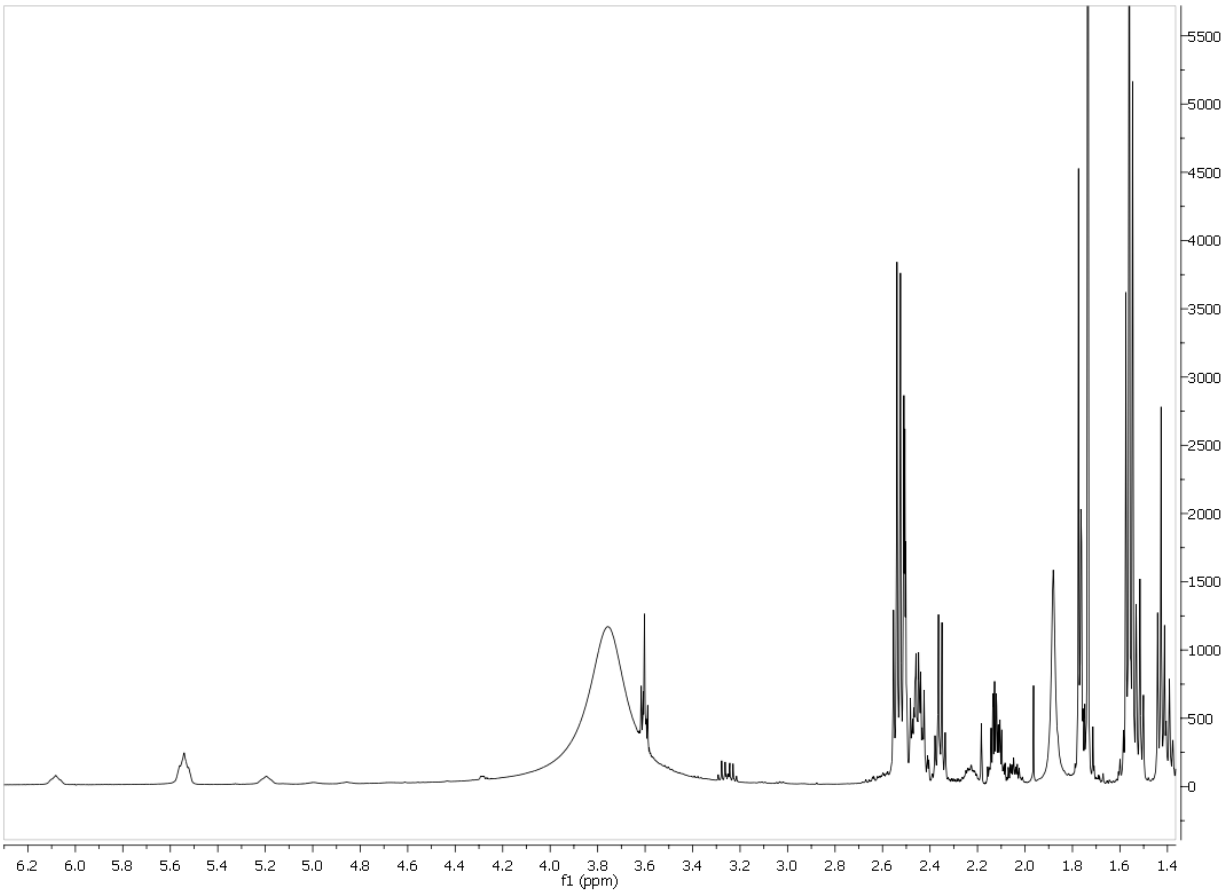


Fig. S3. ^{1}H NMR spectrum (in dmso-d_6) of an aliquot of the reaction crude after hydrolysis

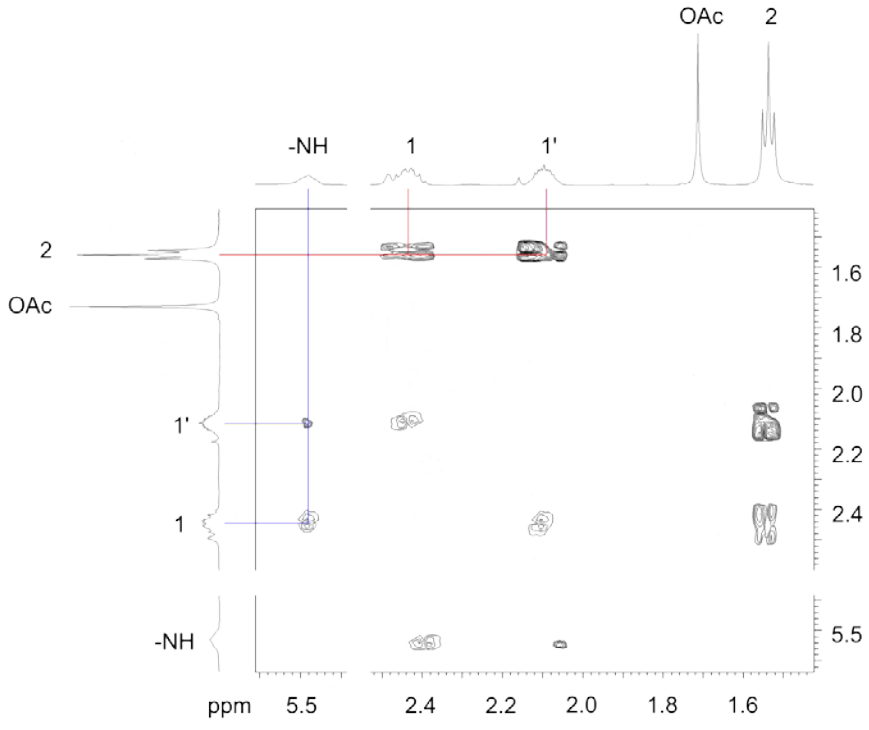


Fig. S4. COSY spectrum of $Pd(OAc)_2(HNEt_2)_2$

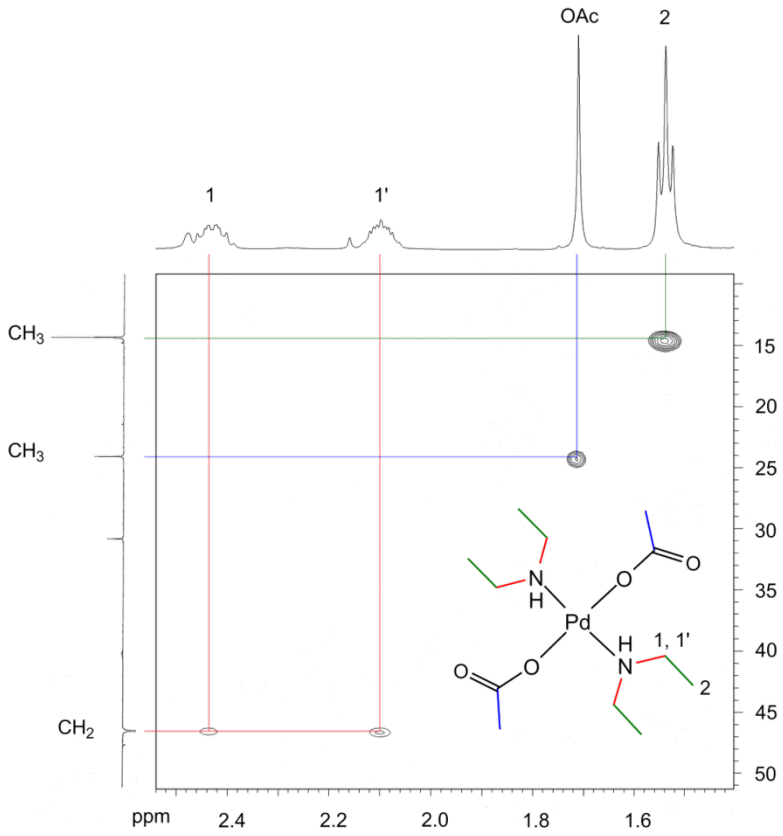


Fig. S5. HSQC spectrum of $Pd(OAc)_2(HNEt_2)_2$

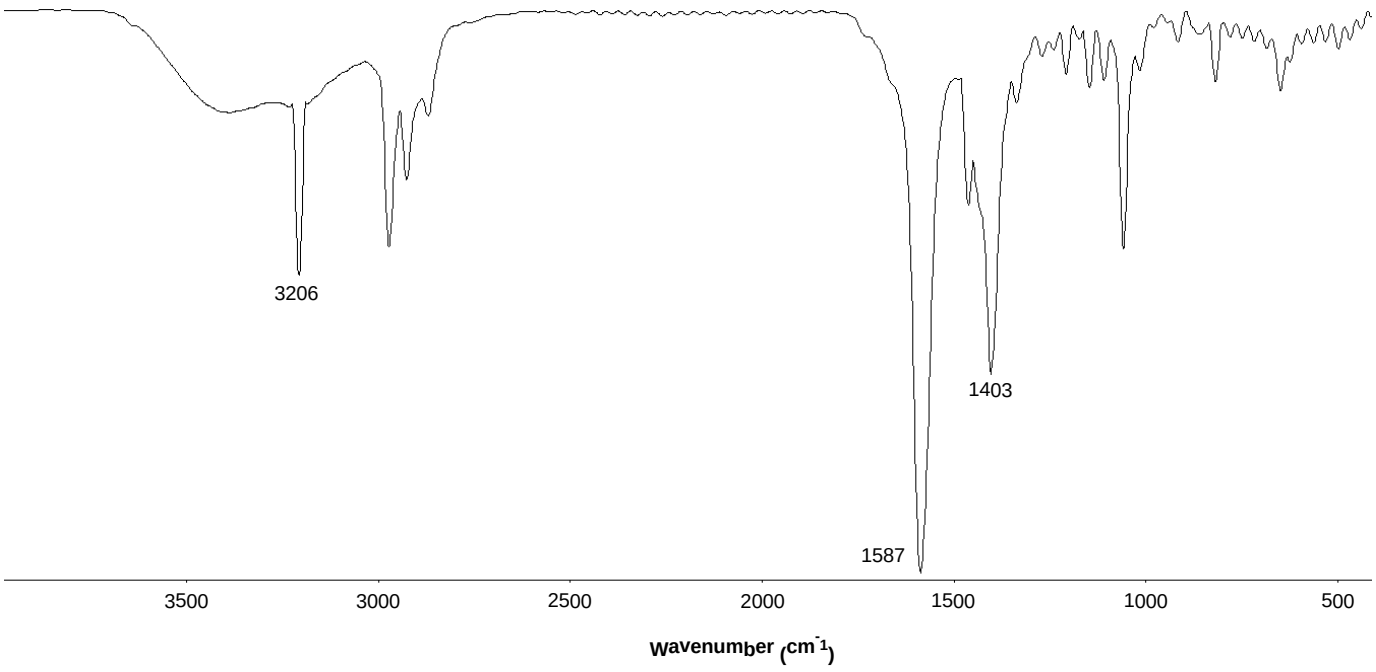


Fig. S6. IR spectrum of $Pd(OAc)_2(HNEt_2)_2$

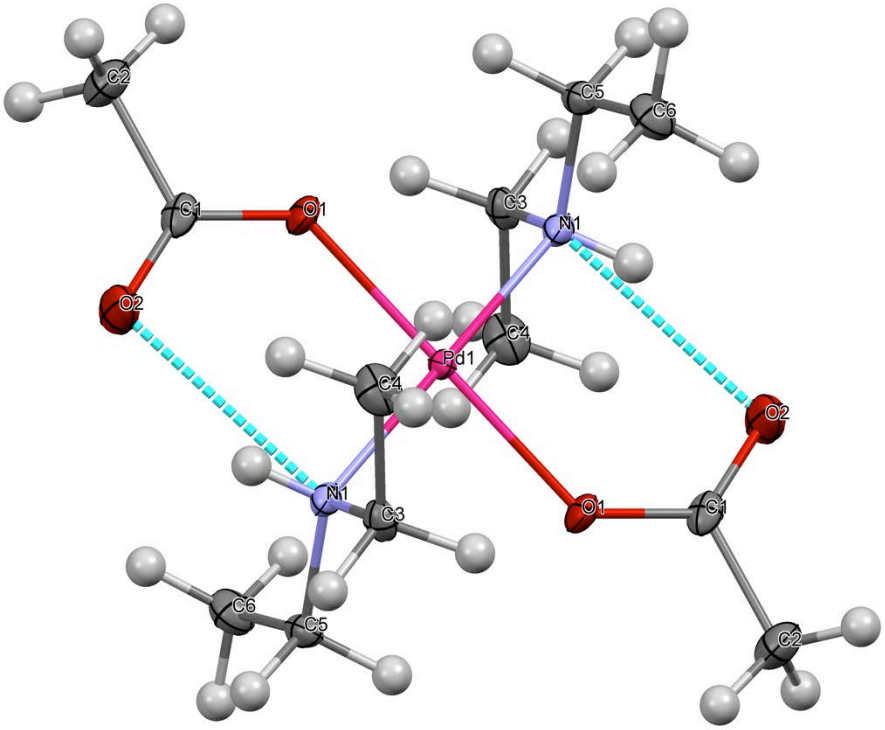


Fig. S7. Molecular structure of $Pd(OAc)_2(HNEt_2)_2$. Ellipsoids have been represented at 50% probability level. Intramolecular hydrogen bonds are shown as dotted lines.

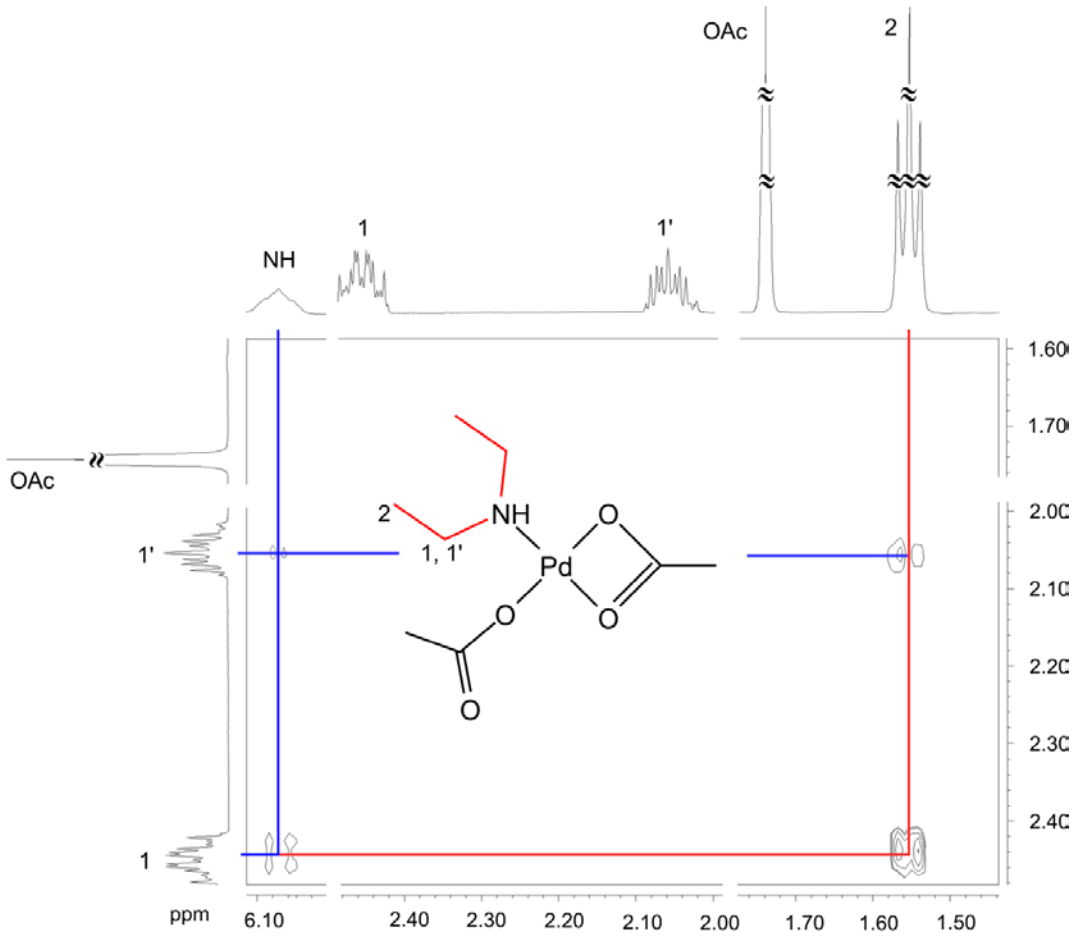


Fig. S8.COSY spectrum of $Pd(OAc)_2(HNEt_2)$

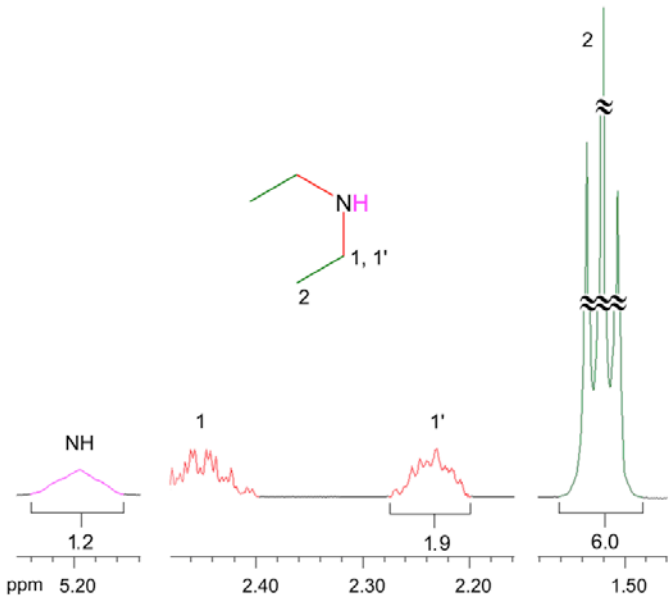


Fig. S9. ^{1}H NMR spectrum of $HNEt_2$ in dmso-d_6.

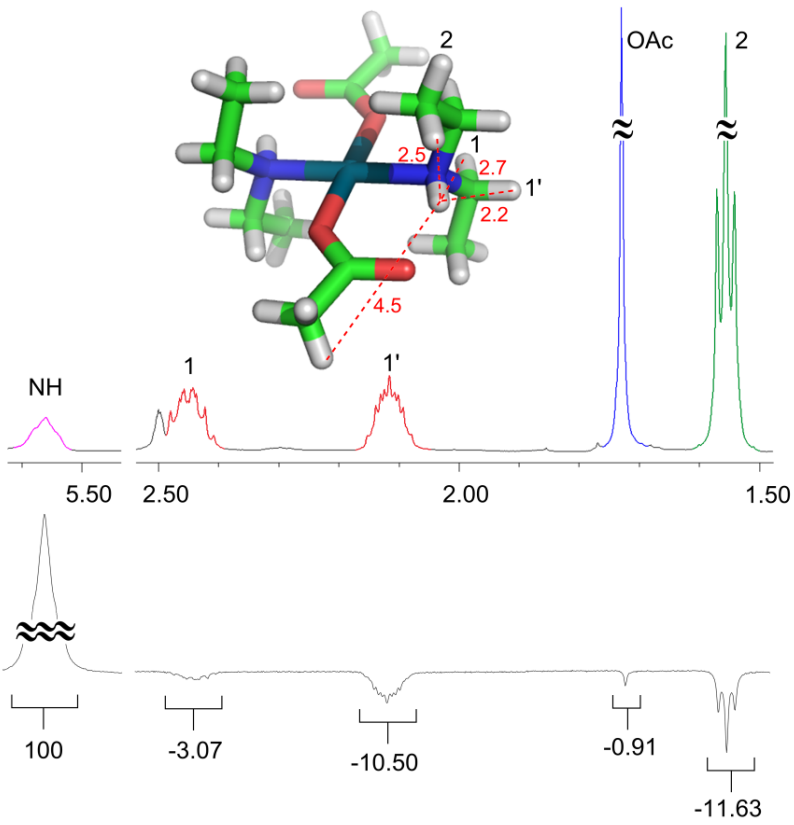


Fig. S10. 1D ^{1}H NMR spectrum (top) and selective 1D NOE spectrum (bottom) of $Pd(OAc)_2(HNEt_2)_2$ in dmso-d_6 (selective band centre: 5.56 ppm). H-H NOE interaction values have been placed under the peaks on the spectrum. The molecular structure of $Pd(OAc)_2(HNEt_2)_2$ with selected distances (in Å) demonstrates a good agreement between the molecular structure in solid state and in solution.

2. *Characterization of acetaldehyde derivatives*

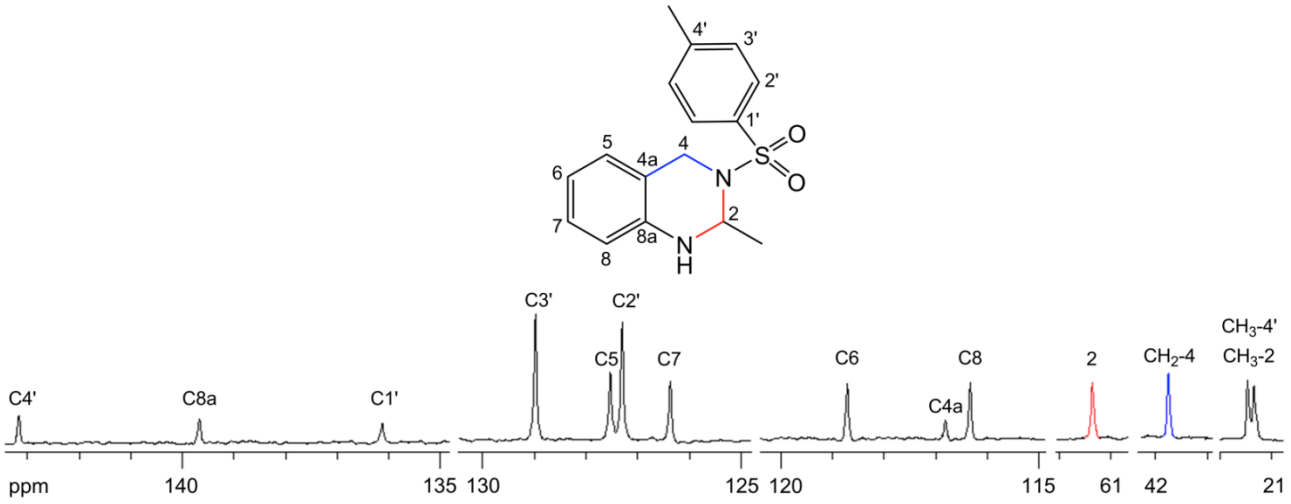


Fig. S11. ^{13}C NMR spectrum of 2-methyl-3-tosyl-1,2,3,4-tetrahydroquinazoline in chloroform-*d*.

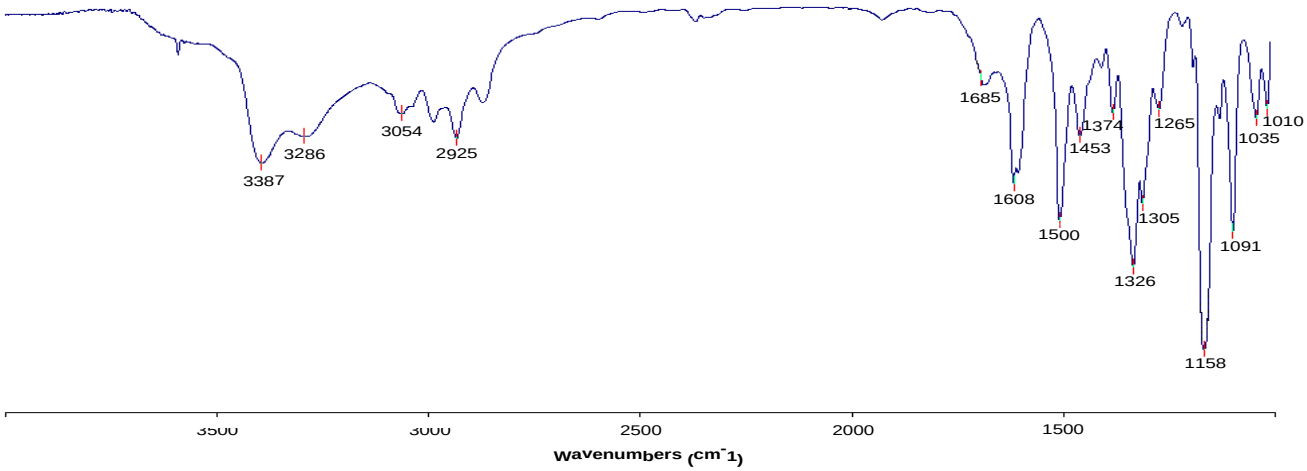


Fig. S12. IR spectrum of 2-methyl-3-tosyl-1,2,3,4-tetrahydroquinazoline.

Fig. S13 shows the calculated most stable conformer of 2-methyl-3-tosyl-1,2,3,4-tetrahydroquinazoline, which displays an anti-disposition of methyl and tosyl groups. This was obtained by geometry optimizations and energy calculations using the Gaussian 09W program package[1] at density functional theory (DFT) level by means of the B3LYP functional using the 6-31G** basis set, and using as starting point the crystallographic structure of 3-tosyl-1,2,3,4-tetrahydroquinazoline. First, the latter crystallographic structure was minimized at a DFT level. The two possible isomers were studied and their relative energies were compared. On the optimized geometries performed in vacuum a DFT minimization in THF solution by means of the polarizable continuum solvation model was carried out.[2] Harmonic frequencies were calculated at the same level of theory to characterize the stationary points and to determine the zero-point energies (ZPE). The results of the Gibbs free energy calculations in THF showed that the isomer with an anti-disposition of methyl and tosyl groups was 1.2 kcal mol-1 more stable than the syn isomer. These findings were further supported by NOE experiments. Saturation by a selective 180 degree pulse of methanetriyl H-2 (5.25 ppm) led to enhancement of the signals for the aromatic H-2´ (2.75%), the aminic H-1 (8.14%) and the methyl H-2 (6.37%).

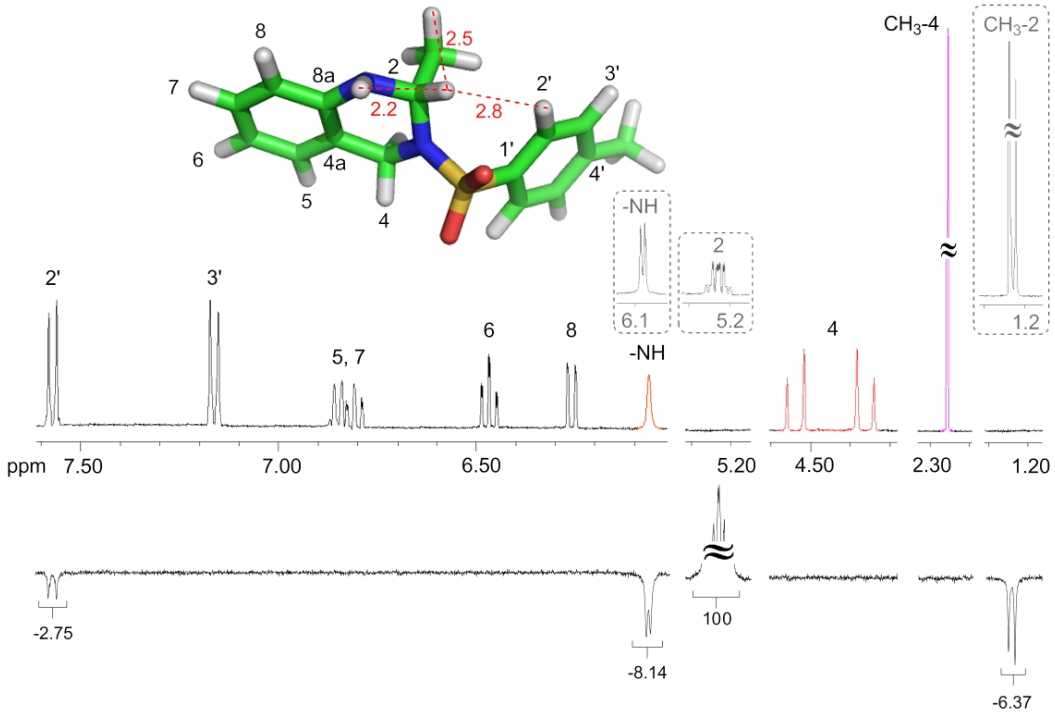


Fig. S13. DFT-calculated *anti* conformation of 2-methyl-3-tosyl-1,2,3,4-tetrahydroquinazoline, with selected distances (in Å) is shown (top). Selective 1D NOE spectrum (in dmso-d_6, selective band centre: 5.25 ppm) is also shown (bottom). H-H NOE interaction values have been placed under the peaks on the spectrum. Besides, the full assignment of ^{1}H NMR spectrum of tetradeuterated 2-methyl-3-tosyl-1,2,3,4-tetrahydroquinazoline (in dmso-d_6) is shown. The inset shows missing H-signals for deuterated carbons at 2-position (CD_3 and CD) as well as original multiplicity of the NH proton for easier comparison.

References

1. Gaussian 09, Revision A.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P.

Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

2 J. Tomasi, B. Mennucci, and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.

3. *Details of the theoretical studies on 2-methyl-3-tosyl-1,2,3,4-tetrahydroquinazoline*

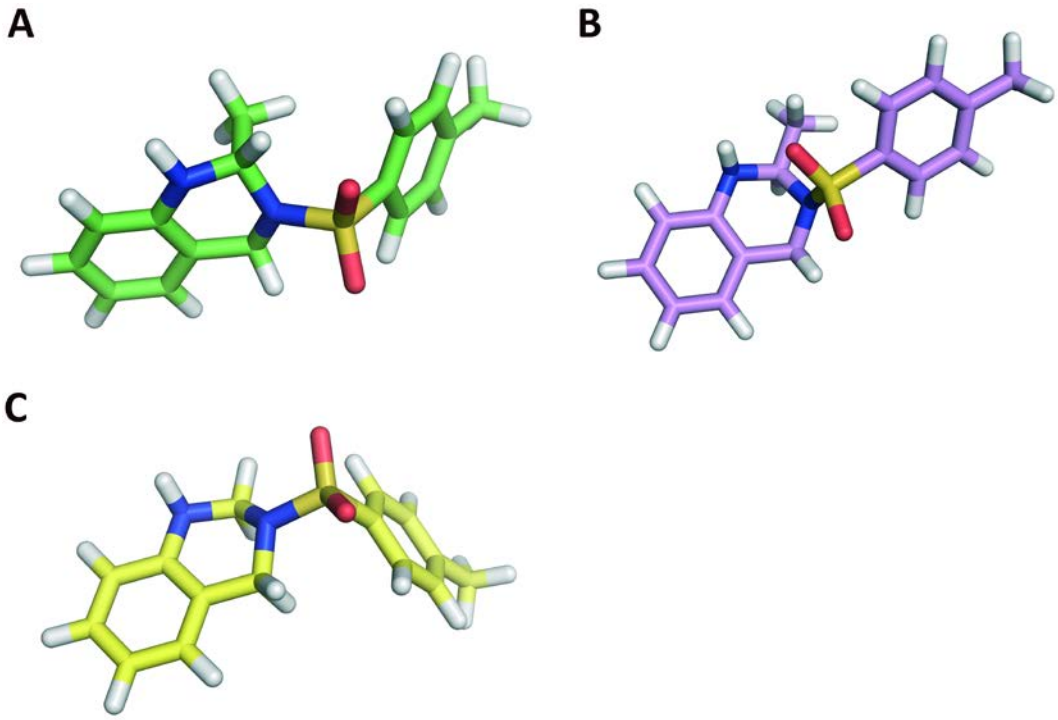


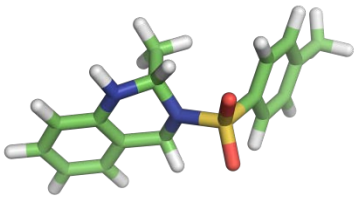
Figure S14. Sticks representation of the most stable conformations of 2-methyl-3-tosyl-1,2,3,4-tetrahydroquinazoline: (A) *anti*-disposition and (B) *syn*-disposition, and 3-tosyl-1,2,3,4-tetrahydroquinazoline (C) derived from the theoretical studies carried at DFT level and in THF solution.

Table S1. Enthalpy and free Gibbs energy (in Hartrees) calculated for the most stable conformers of 2-methyl-3-tosyl-1,2,3,4-tetrahydroquinazoline (*anti* and *syn*) and 3-tosyl-1,2,3,4-tetrahydroquinazoline using B3LYP/6-31G** in THF solution.

Ligand		H	G
2-methyl-3-tosyl-1,2,3,4-tetrahydroquinazoline	*anti*	−1278.355458	−1278.425311
	syn	−1278.354180	−1278.423390
3-tosyl-1,2,3,4-tetrahydroquinazoline		−1239.067361	−1239.134149

Energy details and coordinates for all the compounds studied:

A) *anti*-2-methyl-3-tosyl-1,2,3,4-tetrahydroquinazoline



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7	6	0.000720368	-0.000120547	-0.000095022
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36	1	0.000202760	0.000000384	0.000107814
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38	1	0.000373007	0.000077135	-0.001047013
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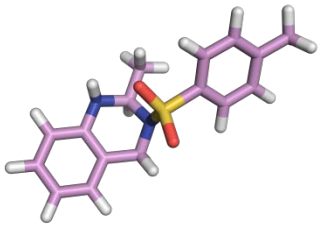
B) *syn*-2-methyl-3-tosyl-1,2,3,4-tetrahydroquinazoline



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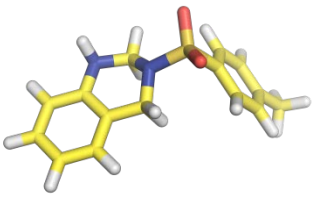
C) 3-tosyl-1,2,3,4-tetrahydroquinazoline



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4.Characterization of 2-tosylaminomethylaniline derivatives

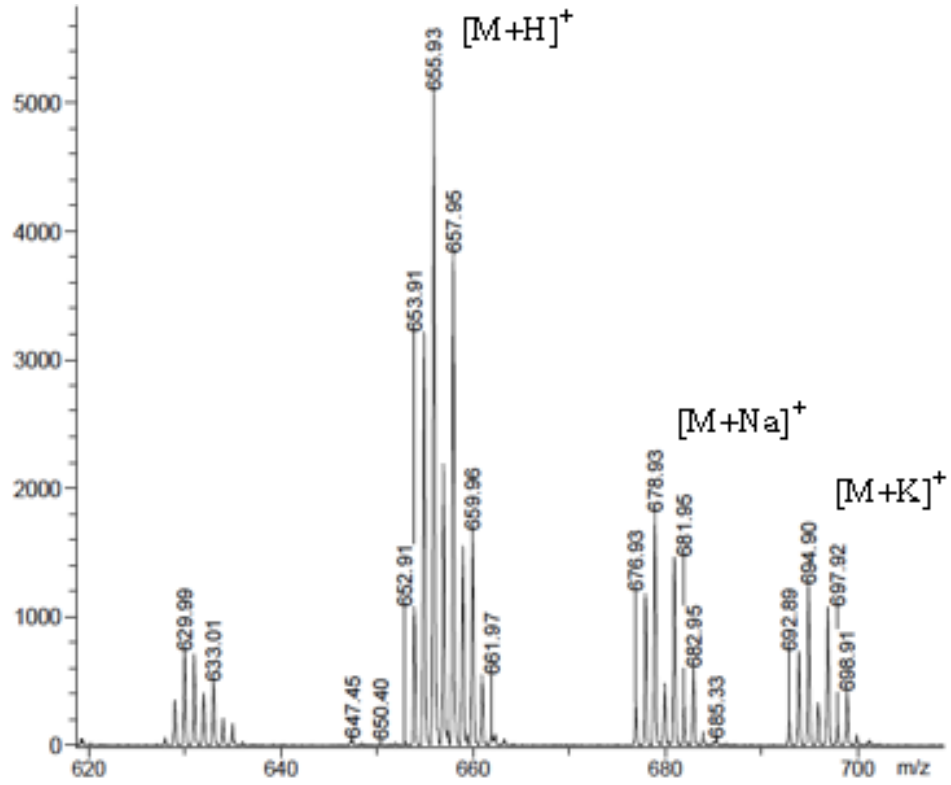

Fig. S15. Mass spectrum of Pd(A^{Ts})$_2$

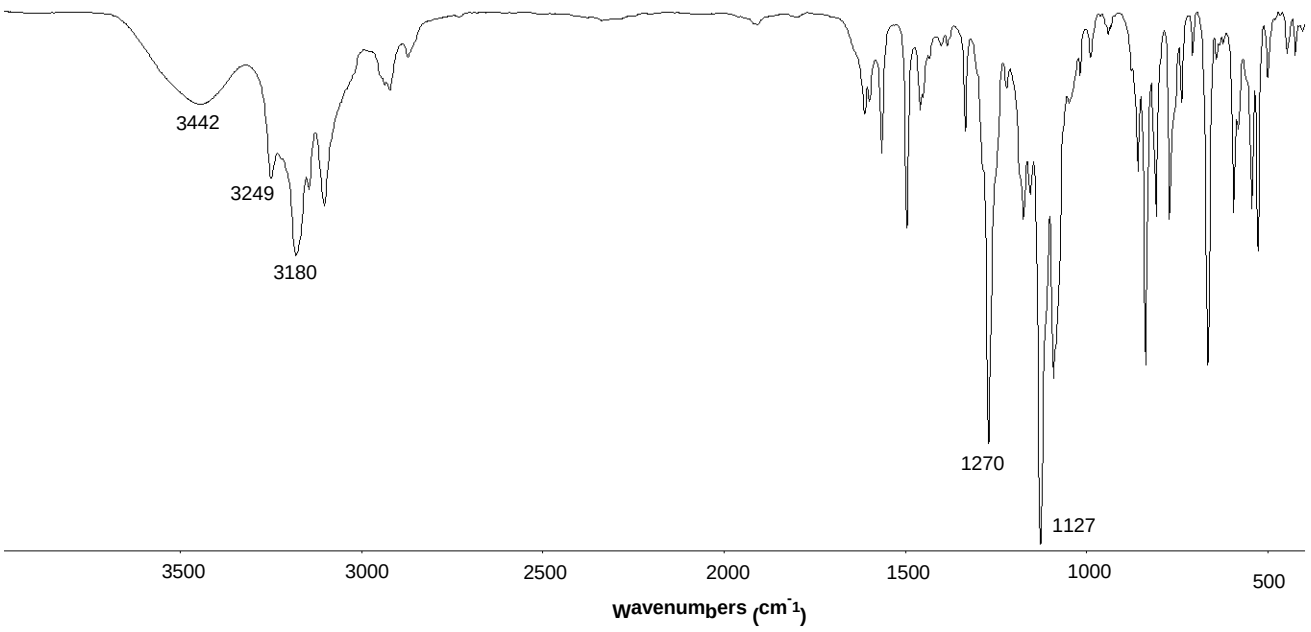

Fig. S16. IR spectrum of Pd(A^{Ts})$_2$.

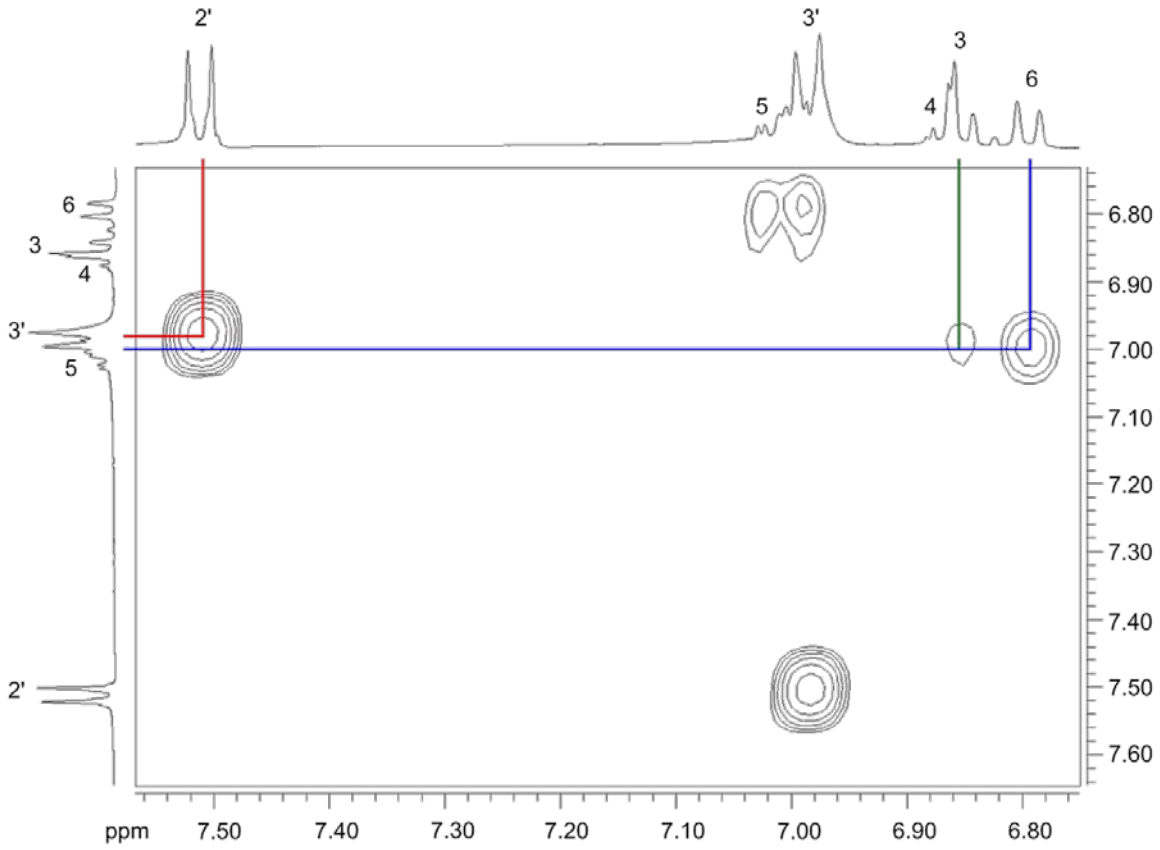

Fig. S17. COSY spectrum of Pd(A^{Ts})$_2$ in dmso-d_6.

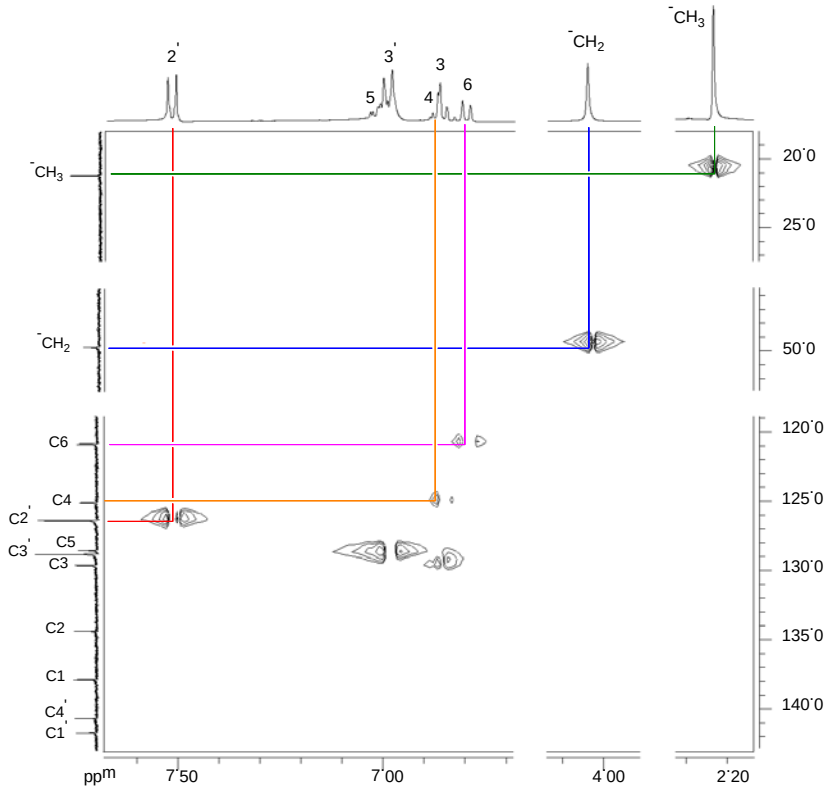

Fig. S18. HMQC spectrum of Pd(A^{Ts})$_2$ in dmso-d_6.

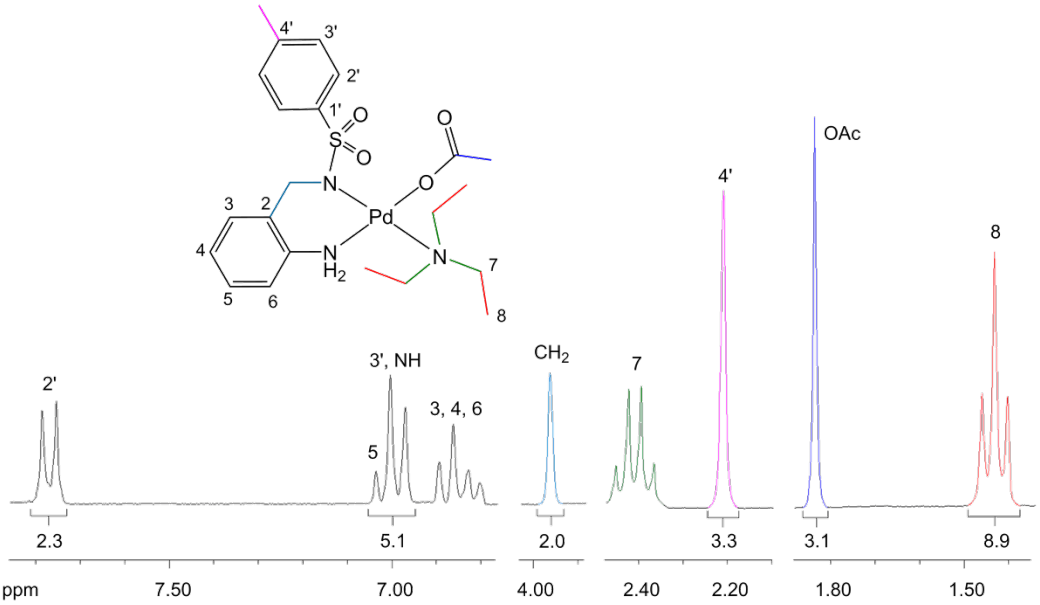

Fig. S19. ^{1}H NMR spectrum of Pd(OAc)(A^{Ts})(NEt_3) in dmso-d_6