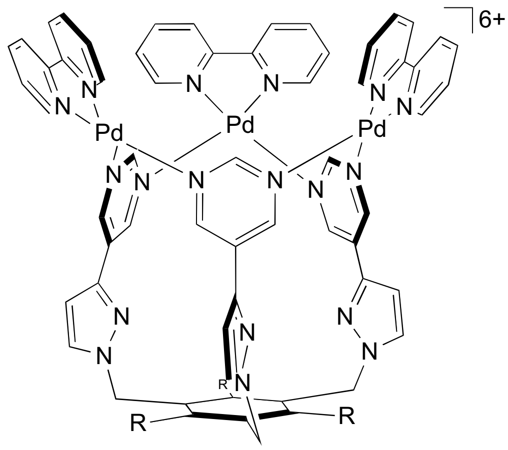
Supplementary Material

The $[Pd(bipy)]^{2+}$ "merry-go-round": insights into the lability of the Pd–N bond

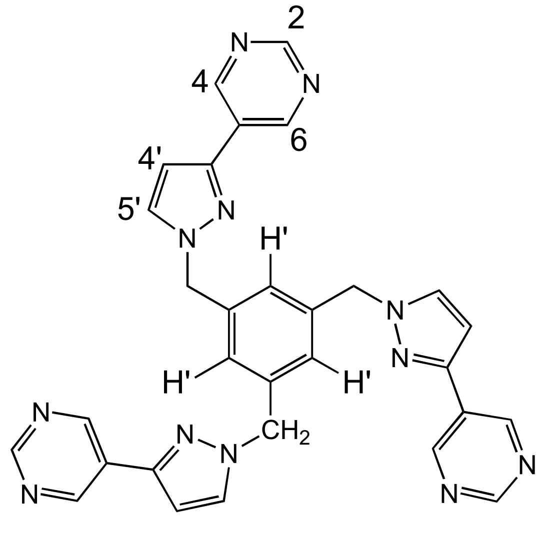
Partha Pratim Mukhopadhyay,[a] Jean-Claude Chambron,*[a] and Roland Graff[b]

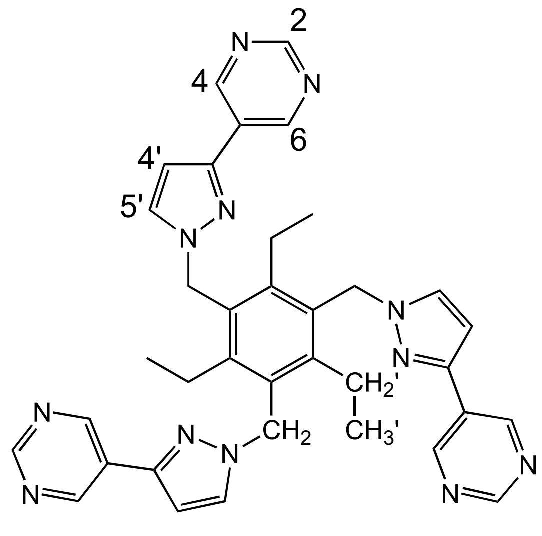
Table of Contents

[a] ICMUB (UMR n° 5260 of the CNRS), Université de Bourgogne, 9 avenue Alain Savary, BP 47870, 21078 Dijon, France
Tel: +33 (0) 380 39 61 16
Fax: +33 (0) 380 39 61 17
E-mail: Jean-Claude.Chambron@u-bourgogne.fr
[b] Institut de Chimie (UMR n° 7177 of the CNRS), Université de Strasbourg, 1 rue Blaise Pascal, BP 296R8, 67008 Strasbourg, France

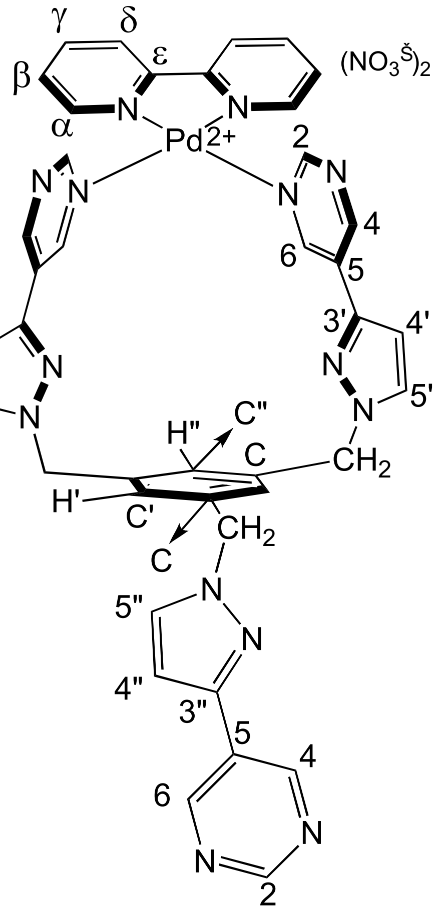


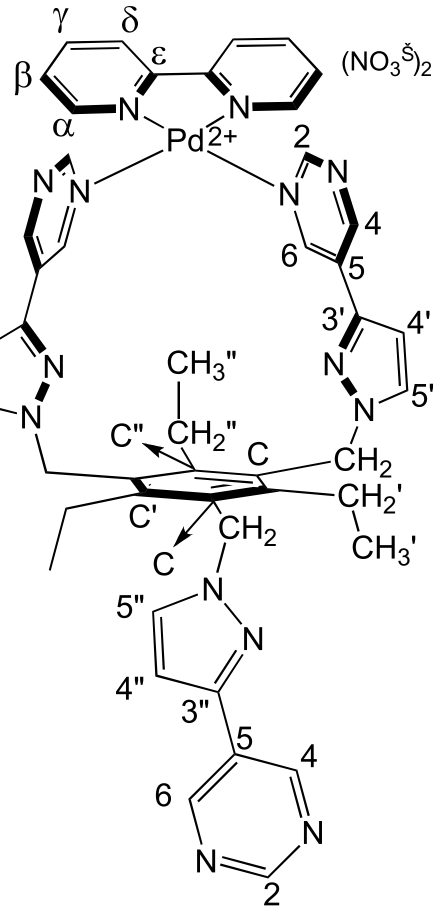
Scheme S1. The target metallo-organic macrotricycles $[Pd_3(bipy)_3(\mathbf{1})]^{2+}$ and $[Pd_3(bipy)_3(\mathbf{2})]^{2+}$.





1 **2**





$[Pd(\mathbf{1})(bipy)](NO_3)_2$ $[Pd(\mathbf{2})(bipy)](NO_3)_2$

Scheme S2. Structural formulae of tripod ligands **1** and **2**, and their $[Pd(bipy)]^{2+}$ complexes.

Table S1. ^{1}H NMR data and calculated $\Delta\delta$ between [Pd(**1**)(bipy)]$(NO_3)_2$ and [Pd(**2**)(bipy)]$(NO_3)_2$ and their relevant precursors, [Pd(bipy)]$(NO_3)_2$, and the free ligands **1** and **2**.[a]

Compound / Proton	2	2°	4	4°	6	6°	4'	4''	5'	5''	H'	H''	α	β	γ	δ	CH_2	CH_2°	CH_2'	CH_2''	CH_3'	CH_3''
[Pd(bipy)]$(NO_3)_2$													8.28	7.83	8.45	8.61						
1	9.07	9.07	9.06	9.06	9.06	9.06	6.88	6.88	7.94	7.94	7.08	7.08					5.40	5.40				
[Pd(**1**)(bipy)]$(NO_3)_2$	9.78	9.12	9.40	9.16	10.06	9.16	7.02	6.97	8.14	7.99	7.47	7.71	7.84	7.69	8.52	8.79	5.37	5.38				
$\Delta\delta$	0.71	0.05	0.34	0.10	1.00	0.10	0.14	0.09	0.20	0.05	0.39	0.63	–0.44	–0.14	0.07	0.18	–0.03	–0.02				
2	9.10	9.10	9.14	9.14	9.14	9.14	6.92	6.92	7.62	7.62							5.51	5.51	2.86	2.86	0.92	0.92
[Pd(**2**)(bipy)]$(NO_3)_2$	9.84	9.08	9.39	9.03	9.96	9.03	7.04	6.87	8.36	7.73			7.55	7.69	8.51	8.80	5.55	5.36	2.98	4.18	0.78	1.33
$\Delta\delta$	0.74	–0.02	0.25	–0.11	0.82	–0.11	0.12	–0.05	0.74	0.11			–0.73	–0.14	0.06	0.19	0.04	–0.15	0.12	1.32	–0.14	0.41

[a] d^6-dmso, 298 K, 600 MHz.

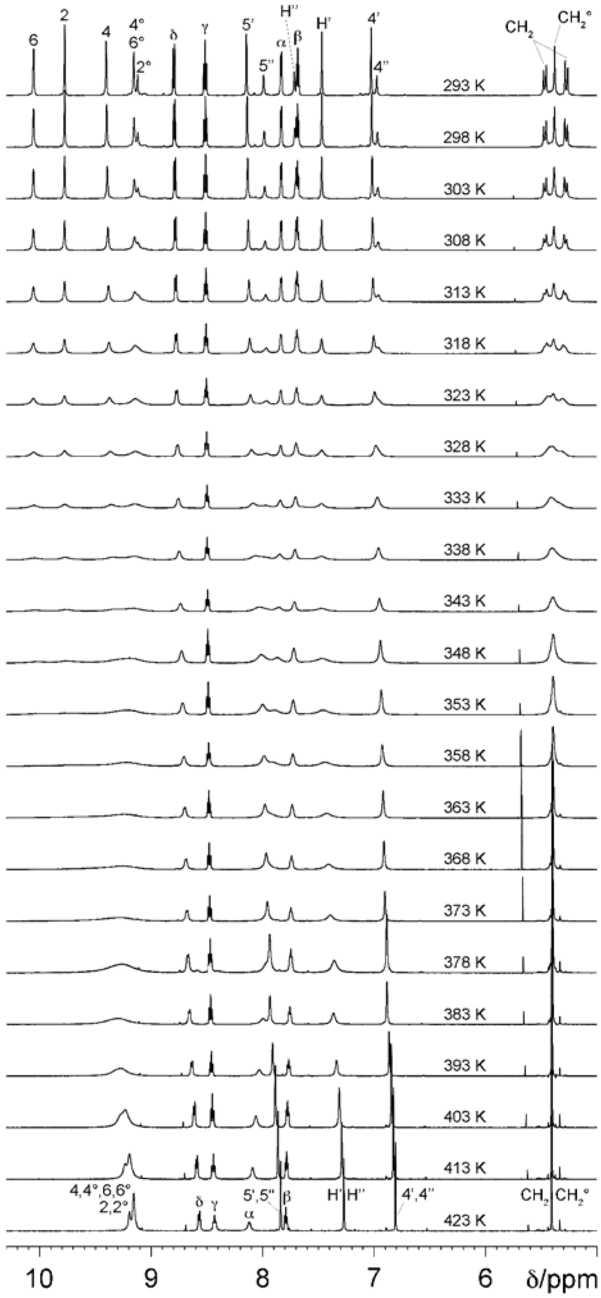


Figure S1. Sequence of variable temperature ^{1}H NMR spectra of $[Pd(\mathbf{1})(bipy)](NO_3)_2$ in d^6-dmso.

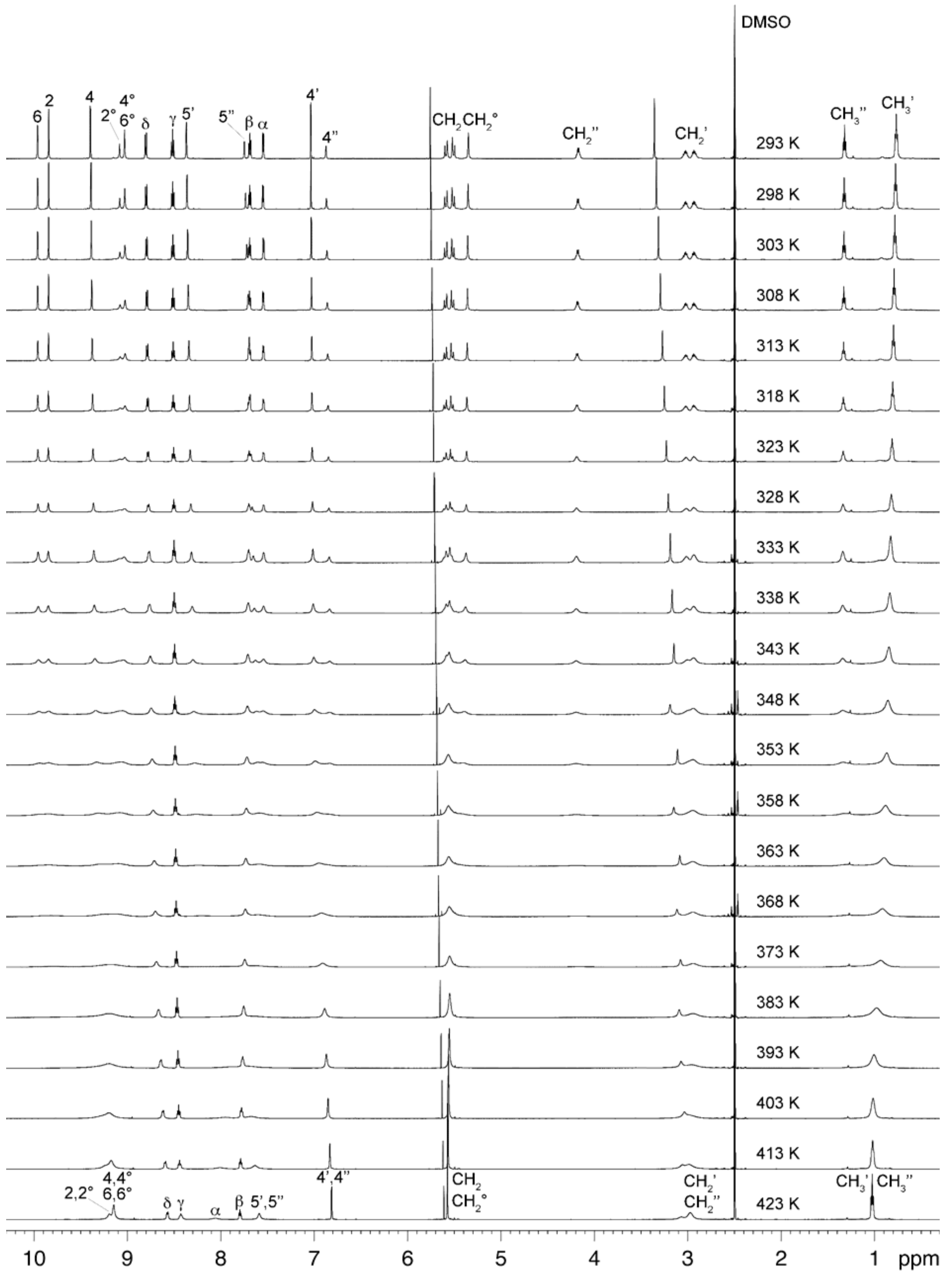


Figure S2. Sequence of variable temperature ^{1}H NMR spectra of [Pd(**2**)(bipy)](NO_3)$_2$ in d^6-dmso.

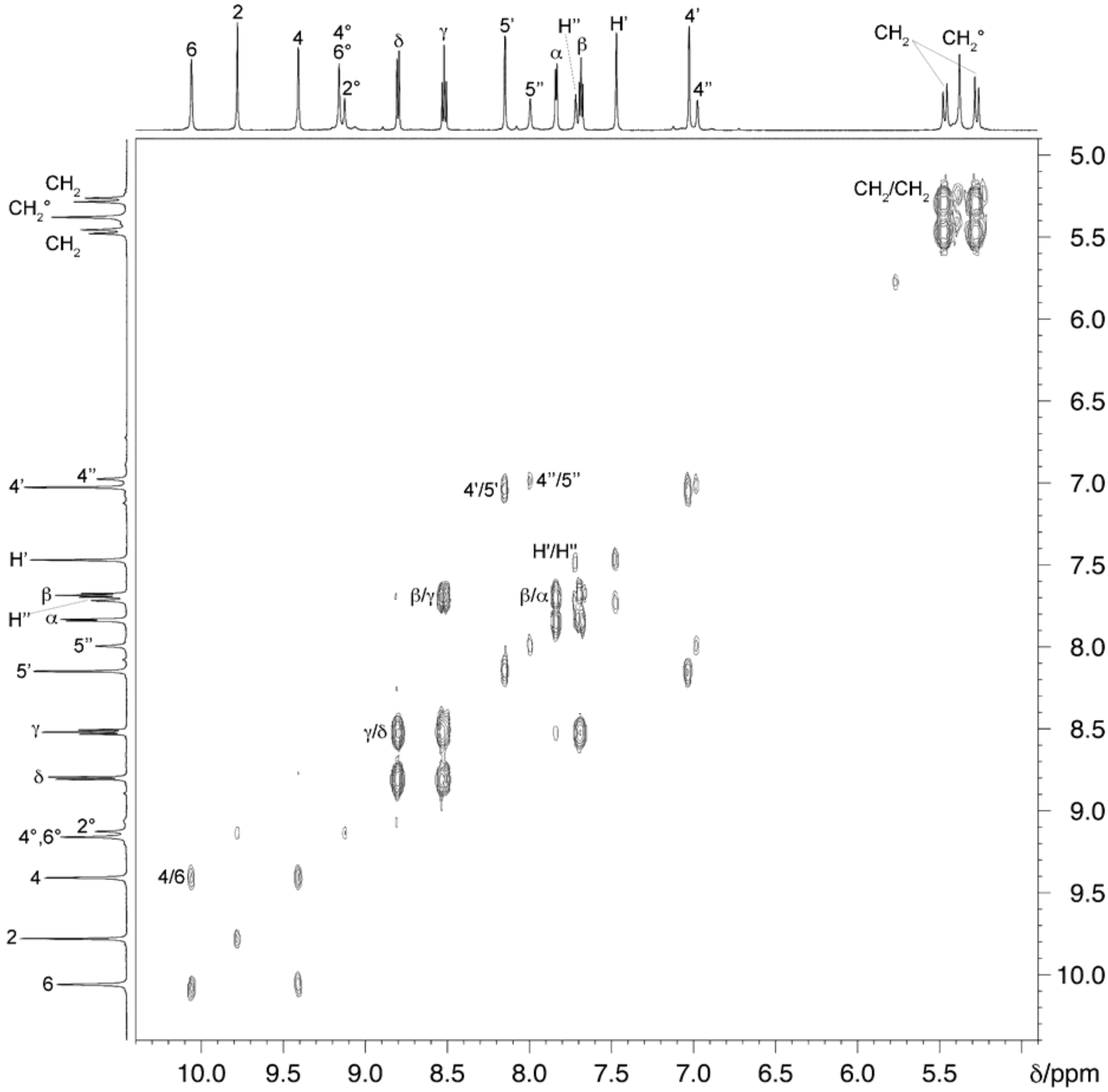


Figure S3. $^1H/^1H$ 2D NMR COSY map of $[Pd(\mathbf{1})(bipy)](NO_3)_2$ in d^6-dmso (600 MHz, 298 K).

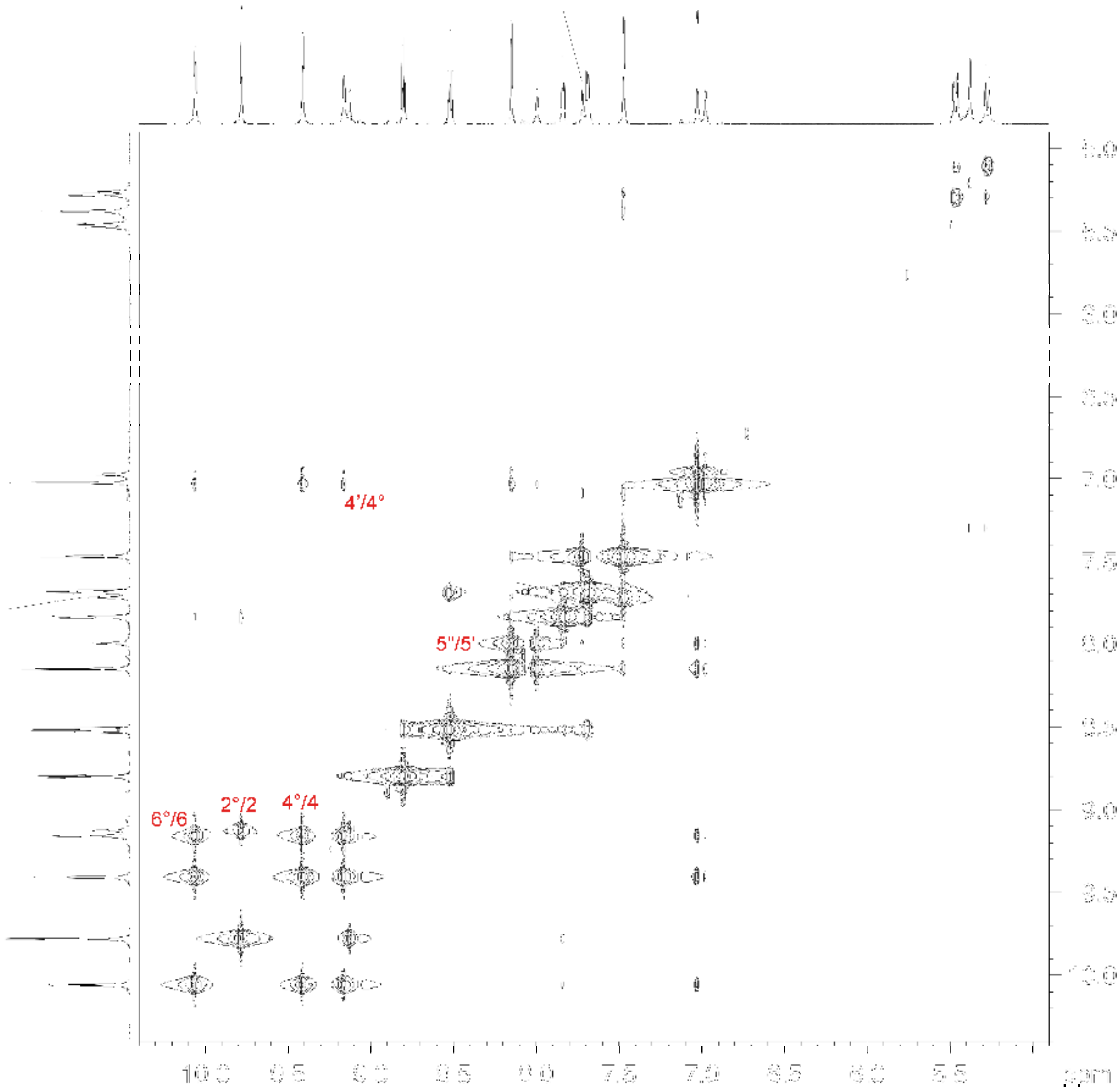


Figure S4. ^{1}H/^{1}H 2D NMR ROESY map of [Pd(**1**)(bipy)](NO_3)$_2$ in d^{6}-dmso (600 MHz, 293 K).

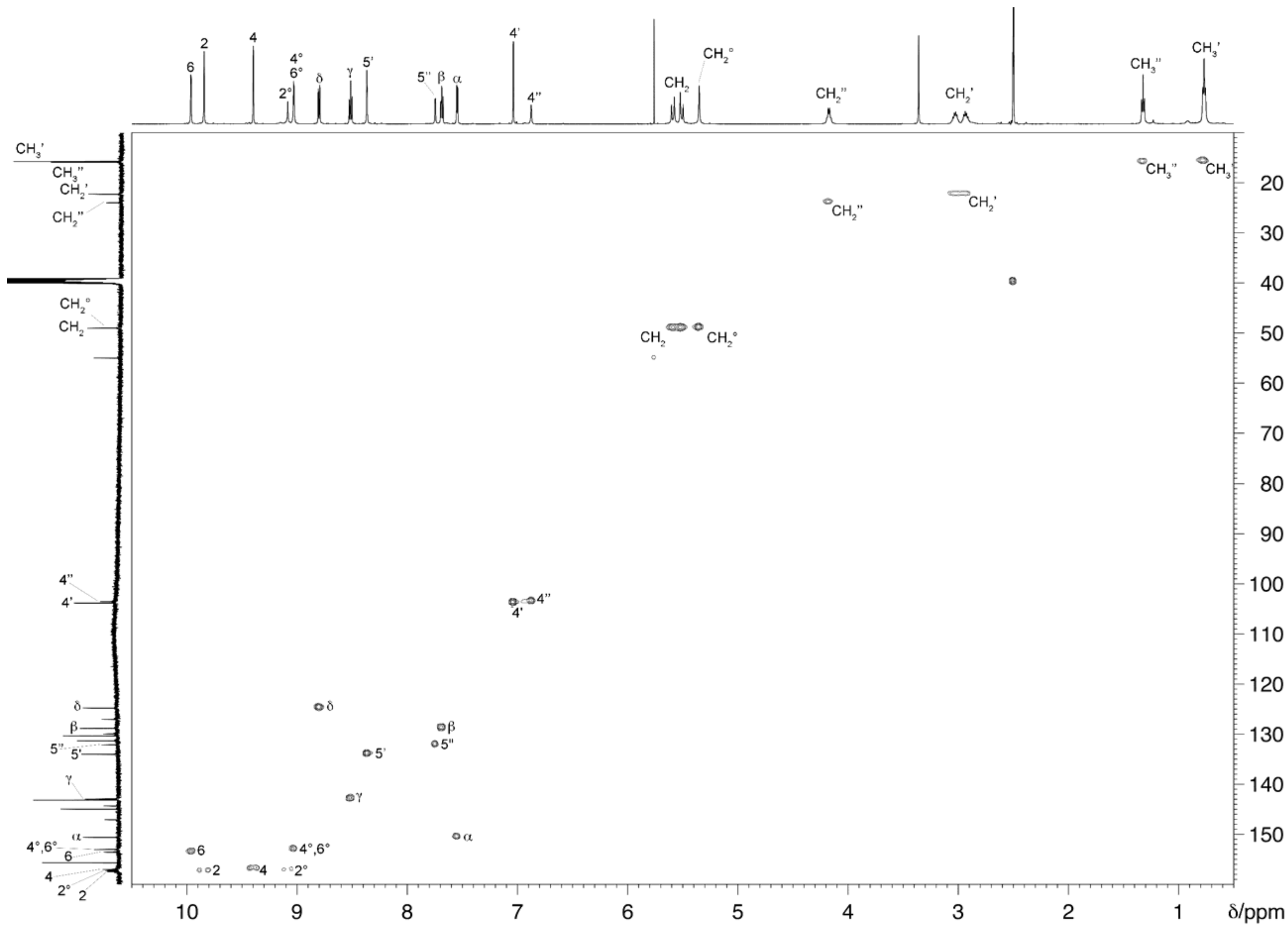


Figure S5. $^{13}C/^{1}H$ 2D NMR HSQC map of $[Pd(\mathbf{2})(bipy)](NO_3)_2$ in d^6-dmso (600 MHz, 293 K).

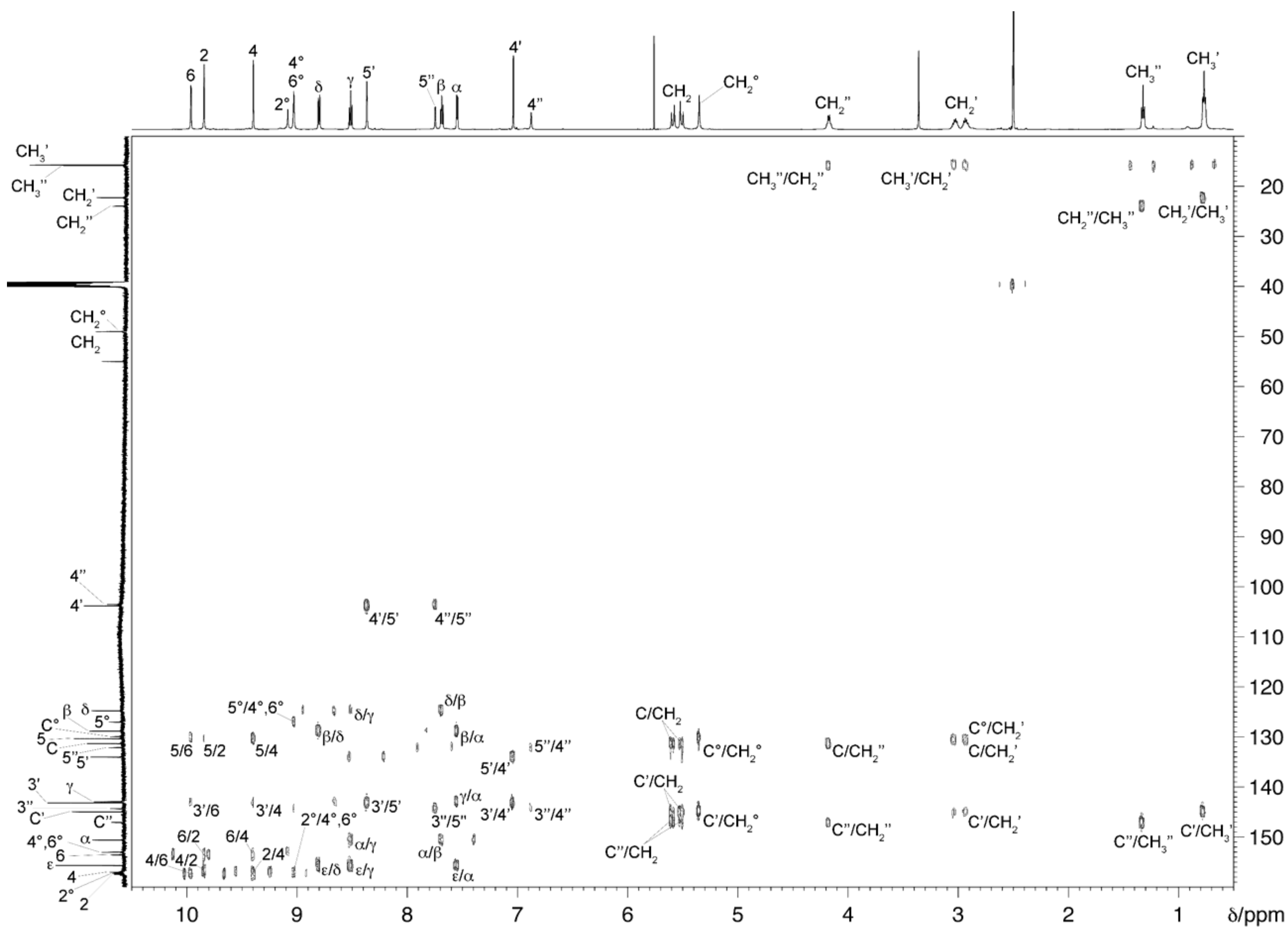


Figure S6. $^{13}C/^{1}H$ 2D NMR HMBC map of $[Pd(\mathbf{2})(bipy)](NO_3)_2$ in d^6-dmso (600 MHz, 298 K).

Table 3. Calculated errors of the free energies of activation.[a]

Compound	Probe protons	T_c/K	$\Delta\tilde{\nu}$/Hz	k_c/s^{-1}	$\Delta G^{\ddagger}$/kJmol^{-1}	$\sigma(T_c)$	$\sigma(\Delta\nu)$	$\sigma(k_c)$	$\partial(\Delta G)/\partial(T_c)$	$\partial(\Delta G)/\partial(\Delta\nu)$	$\partial(\Delta G)/\partial(k_c)$	$\sigma(\Delta G^{\ddagger})$
[Pd(**1**)(bipy)]$^{2+}$	4',4"	323	30	66.64	68.0	5.00	5.00	11.11	218.98	–89.51	–40.30	1.18
	5',5"	338	90	199.93	68.2	5.00	5.00	11.11	210.22	–31.22	–14.06	1.06
	H',H" and 4,4°	343	150	333.22	67.8	5.00	5.00	11.11	206.10	–19.01	–8.56	1.03
	2,2°	358	395	877.47	68.1	5.00	5.00	11.11	198.40	–7.54	–3.39	0.99
	6,6°	363	540	1199.58	68.1	5.00	5.00	11.11	195.92	–5.59	–2.52	0.98
[Pd(**2**)(bipy)]$^{2+}$	4',4"	358	100	222.14	72.1	5.00	5.00	11.11	209.83	–29.76	–13.40	1.06
	CH_2,CH_2°	358	120	266.57	71.6	5.00	5.00	11.11	208.31	–24.80	–11.17	1.05
	CH_3',CH_3"	373	330	733.08	71.6	5.00	5.00	11.11	200.24	–9.40	–4.23	1.00
	CH_2',CH_2"	383	715	1588.33	71.1	5.00	5.00	11.11	194.03	–4.45	–2.00	0.97

[a] $\sigma(\Delta G) = \sqrt{\{[\partial(\Delta G)/\partial(T_c)]^2\sigma^2(T_c) + [\partial(\Delta G)/\partial(\Delta\nu)]^2\sigma^2(\Delta\nu) + 2[\partial(\Delta G)/\partial(T_c)][\partial(\Delta G)/\partial(\Delta\nu)]\mathrm{cov}(T_c, \Delta\nu)\}}$. It is assumed that $\mathrm{cov}(T_c, \Delta\nu) = 0$, as T_c and $\Delta\nu$ are determined independently, see: P. Gans, Data Fitting in the Chemical Sciences, John Wiley & Sons Ltd, Chichester, England, 1992.