Electronic Supporting Information

Experimental and Kinetic Modelling Study of NC Palladacycle Mechanosynthesis

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1. EXPERIMENTAL PROCEDURES

1.1 General Procedures: Structures for complexes provided in the main text and with the NMR spectra, vide infra. All reagents including 2-aminobiphenyl (2-HABP), *N*,*N*-dimethylbenzylamine (HDMBA), *N*-ethyl-*N*-methylbenzylamine (HEMBA) and benzo[*h*]quinoline (Hbzq) were purchased from commercial sources and used without further purification. Proton NMR spectra were recorded on a JEOL-ECS 400 MHz spectrometer in $CDCl_3$ (**2**, **3** and **5**) or DMSO-d_6 (**1** and **4**). The $CDCl_3$ was stored over activated alumina to remove trace acid in the solution. Spectra were recorded at room temperature. Elemental analysis was performed by Atlantic Microlabs, Norcross, GA, USA. Mechanochemical reactions were performed in a SPEX 8000M Mixer Mill with a leminscate oscillation and 1725 revolutions per minute motor speed using a 5-mL Teflon® grinding vial with two 6.35-mm diameter stainless steel balls. Where noted, the reaction mixtures from multiple milling vials were combined for more rapid purification. Except in some trials for the preparation of **5**, syntheses were quantitative based on ^{1}H NMR spectroscopy. Yields given are isolated amounts, but percent yield has been calculated to account for mass loss due to sampling. Reaction times below are longer than those required for full conversion according to kinetic studies to ensure that complete conversion is achieved. Characterization information is provided for new compounds. Analysis of known compounds agreed with previously published results for $[Pd(2\text{-}ABP)Cl]_2$ (**1**),[1] $[Pd(2\text{-}ABP)OAc]_2$ (**2**),[1] $[Pd(DMBA)Cl]_2$ (**3**),[2] and $[Pd(bzq)OAc]_2$ (**5**).[3]

1.2 Synthesis of $[Pd(2\text{-}ABP)Cl]_2$ (1): A 66.5 mg (0.296 mmol) sample of palladium acetate was placed in the milling vial with 50.1 mg (0.296 mmol) 2-aminobiphenyl (2-HABP), 50.5 mg (0.864 mmol) sodium chloride, 83.6 μL methanol, and two steel balls and milled for 200 min. Pinkish-tan solid was removed from the vial and dissolved in ~20 mL hot methanol. Tan colored product precipitated from the methanol upon addition of 20 mL DI water. Solid was collected by vacuum filtration, dried under vacuum, and further dried in a desiccator with P_2O_5. Yield: 90.8 mg (97.0%).

1.3 Synthesis of $[Pd(2\text{-}ABP)OAc]_2$ (2): A 93.8 mg (0.418 mmol) sample of palladium acetate was placed in the milling vial with 45.5 mg (0.127 mmol) 2-aminobiphenyl (2-HABP), 83.6 μL methanol, and two steel balls and milled for 60 min. The orange paste was removed from the vial and dissolved in ~30 mL chloroform. A small amount of dark solid was filtered off using Celite® due to the very fine nature of the powder. Solvent was removed from the orange filtrate by rotary-evaporation and the resulting dark orange solid was dried in the desiccator with P_2O_5. Yield: 71.7 mg (90.1%).

1.4 Synthesis of [Pd(DMBA)Cl]$_2$ (3): A 66.7 mg (0.376 mmol) sample of palladium chloride was placed in the milling vial with 238.7 mg (2.252 mmol) sodium carbonate, 195.4 μL methanol and two steel balls. A 55.0 μL (0.366 mmol) sample of *N*,*N*-dimethylbenzylamine (HDMBA) was added, and the mixture was milled for 40 min. The reaction mixture was washed from the vial with ~20 mL chloroform. The initially dark undissolved solid is removed via filtration, and the desired product is isolated from the filtrate by rotary-evaporation. The resulting product is a pale-yellow solid. Yield: 89.4 mg (90.0%).

1.3 Synthesis of [Pd(EMBA)Cl]$_2$ (4): A 61.0 mg (0.344 mmol) sample of palladium chloride was placed in the milling vial with 215.4 mg (2.032 mmol) sodium carbonate, 30.0 μL methanol and two steel balls. A 48.4 μL (0.305 mmol) sample of *N*-ethyl-*N*-methylbenzylamine (HEMBA) was added, and the mixture was milled for 180 min. The reaction mixture was washed from the vial with ~20 mL chloroform. The initially dark undissolved solid is removed via filtration, and the desired product is isolated from the filtrate by rotary-evaporation. The resulting product is a pale-yellow solid. Yield: 86.0 mg (97.3%). IR (ATR, cm^{-1}): 1575 (m), 1441 (s), 1041 (m), 1024 (m), 987 (m), 939 (m), 790 (m), 740 (vs). ^{1}H NMR (DMSO-d_6, δ): 7.62 (*d*, 2H, *J*=8.0 Hz, ArH^6), 7.03 (*m*, 4H, ArH^{3,5}), 6.92 (*t*, 2H, *J*=7.6 Hz, ArH^4), 4.20 (*d*, 2H, *J*= 14 Hz, CH$_{2a}$), 3.89 (*d*, 2H, *J*=14 Hz, CH$_{2b}$), 3.01 (*m*, 2H, C**H**$_{2a}$CH$_3$), 2.76 (*s*, 6H, CH$_3$), 2.59 (*m*, 2H, C**H**$_{2b}$CH$_3$), 1.41 (*t*, 6H, *J*=7.6 Hz, CH$_2$C**H**$_3$) ppm. ^{13}C NMR (DMSO-d_6, δ): 148.9 (ArH^{1,2}), 132.4 (ArH^6), 125.1 (ArH^5), 124.9 (ArH^4), 122.0 (ArH^3), 68.8 (CH$_2$), 56.5 (**C**H$_2$CH$_3$), 49.8 (CH$_3$), 12.9 (CH$_2$**C**H$_3$). Anal. Calcd for C$_{20}$H$_{28}$N$_2$Pd$_2$Cl$_2$: C, 41.40; H, 4.87; N, 4.83. Found: C, 41.57; H, 5.02; N, 4.80.

1.6 Synthesis of [Pd(bzq)OAc]$_2$ (5): A 68.7 mg (0.306 mmol) sample of palladium acetate was placed in the milling vial with 50.3 mg (0.281 mmol) benzo[*h*]quinoline (Hbzq), 178.3 mg (1.682 mmol) sodium acetate, and two steel balls and milled for 200 min. The yellow solid was removed from the vial and suspended in ~30 mL chloroform. Undissolved solid was removed by filtration, and solvent was removed from the yellow filtrate by rotary-evaporation. The resulting yellow solid was dried in a desiccator with P_2O_5. Yield: 80.8 mg (83.6%).

2. CALCULATION OF EVIDENCE RATIOS

Our group has previously described the calculation and use of evidence ratios when modeling mechanochemical synthesis of transition metal complexes.[4] The method was taken from Finney's and Finke's demonstrating the similarities of the Johnson-Mehl-Avrami-Yerofeev-Kolmogrov (JMAYK) and Finke-Watzky (FW) models.[5] PSI-Plot version 8.81 was utilized to carry out fitting to each of the models and determine the residual sum of squares (*SS*) for each calculation as well as the number of data points (*N*). The number of parameters in the model (*K*) is two for both the JMAYK (Equation 1) and FW models (Equation 2). The parameters are *k* and *n* for the JMAYK model and k_1 and k'_2 for the FW models. The first order model has only one parameter (*k*, Equation 3). Akaike's Information Criteria ($AICc_i$) are calculated for each model from *SS*, *K*, and *N* according to Equation 4. *AICc* values estimate prediction error and can be used to examine the relative merit of models. Unlike R^2 values, *AICc* values and *ER*s account for variability in the number of parameters in different models. By determining the difference in $AICc_i$ values between each model and the lowest $AICc_i$ value for all models compared ($\Delta AICc_i$), the Akaike weight for each model can be determined according to Equation 5. *ER* are then calculated. Here two comparisons were made, the FW model was compared to the JMAYK model (Equation 6), and the FW model was compared to the first order model (Equation 7). Using the measures for statistical significance noted by Finney and Finke,[5] $ER \geq 10^4$ show the FW model would be preferred. $ER \leq 10^{-4}$ would show preference for the comparison model. *ER* between those limits demonstrate that the two models are statistically equivalent.

$$\alpha = 1 - e^{-(kt)^n} \tag{1}$$

$$\alpha = 1 - \frac{k_1 + k'_2}{k'_2 + k_1 e^{(k_1 + k'_2)t}} \tag{2}$$

$$\alpha = 1 - e^{-kt} \tag{3}$$

$$AICc_i = N ln\left(\frac{SS}{N}\right) + 2K + \frac{2K(K+1)}{N-K-1} \tag{4}$$

$$w = \frac{e^{-\frac{\Delta AICc_i}{2}}}{\sum_{r=1}^{R} e^{-\frac{\Delta AICc_r}{2}}} \tag{5}$$

$$ER = \frac{w_{FW}}{w_{JMAYK}} \tag{6}$$

$$ER = \frac{w_{FW}}{w_{First\ Order}} \tag{7}$$

3. REACTION PARAMETERS FOR KINETIC STUDIES AND KINETIC RESULTS

Table S-1. Synthetic conditions for various experiments and results of modeling. The standard methodology for determining kinetic data involves averaging the results from three reactions, with each reaction sampled at multiple times. Where sampling was shown to affect conversion, the results of numerous reactions each sampled once (i.e. single-sample) were used to determine conversion vs time plots.

Compound	Pd salt	Amine	LAG Solvent	Other	Sampling
$[Pd(2\text{-}ABP)Cl]_2$ (**1**)	68.3±0.2 mg $Pd(OAc)_2$	50.1±0.3 mg	48.2 μL DMSO-d_6 (η=0.3)	45.1±0.6 mg NaCl	multi
	72±7 mg $Pd(OAc)_2$	50.0±0.6 mg	195.4 μL MeOH (η=1.2)	47±4 mg NaCl	multi
$[Pd(2\text{-}ABP)OAc]_2$ (**2**)	94±1 mg $Pd(OAc)_2$	47.3±0.5 mg	83.6 μL DMSO-d_6 (η=0.3)	none	multi
	110±13 mg $Pd(OAc)_2$	47.6±0.6 mg	83.6 μL MeOH (η=0.5)	none	multi
	95±3 mg $Pd(OAc)_2$	47±1 mg	83.6 μL MeOH (η=0.6)	none	single
	92.4±2 mg $Pd(OAc)_2$	47±2 mg	83.6μL MeOH (η=0.6)	none	single[†]
$[Pd(DMBA)Cl]_2$ (**3**)	66.9±0.8 mg $PdCl_2$	55.0 μL	none*	237±4 mg Na_2CO_3	multi
	67.4±0.8 mg $PdCl_2$	55.0 μL	21.4 μL DMSO-d_6 (η=0.3)*	240±2 mg Na_2CO_3	multi
	67.5±0.8 mg $PdCl_2$	55.0 μL	21.4 μL MeOH (η=0.3)*	241±6 mg Na_2CO_3	single
	67.7±0.9 mg $PdCl_2$	55.0 μL	214 μL MeOH (η=0.9)*	240±5 mg Na_2CO_3	single
$[Pd(EMBA)Cl]_2$ (**4**)	62±3 mg $PdCl_2$	48.4 μL	none*	215±2 mg Na_2CO_3	multi
	60.2±0.7 mg $PdCl_2$	48.4 μL	30.0 μL DMSO-d_6 (η=0.3)*	215±2 mg Na_2CO_3	multi
	61±1 mg $PdCl_2$	48.4 μL [e]	195.4 μL MeOH (η=0.9)*	217.2±0.7 mg Na_2CO_3	multi
$[Pd(bzq)OAc]_2$ (**5**)	69.9±0.2 mg $Pd(OAc)_2$	49.9±0.9 mg	none	149±2 mg Na_2CO_3	multi
	69.6±0.7 mg $Pd(OAc)_2$	50.4±0.3 mg	none	none	multi
	70.±1 mg $Pd(OAc)_2$	50.1±0.6 mg	35.6 μL DMSO-d_6 (η=0.3)	none	multi
	69.6±0.8 mg $Pd(OAc)_2$	50.1±0.6 mg	63.0 μL MeOH (η=0.5)	none	multi
	83.7±0.7 mg $Pd(OAc)_2$	50.2±0.2 mg	66.4 μL MeOH (η=0.5)	none	multi

* When liquid reagents are used in mechanosynthesis, such as in the case of some of the amines used here, there is some controversy as to whether these should be termed "neat" or "LAG" reactions. Here, such reactions will be termed "neat" because no excess liquid reagent is utilized. However, when LAG reagent is added the total volume of all liquids is used in η=μL liquid/μg solid. [†]These reactions were sampled only once, but were manually stirred at intervals to mimic the affects of sampling without the loss of material.

Table S-2. Kinetic results.[a] Unless noted, data obtained from the average of three trials each sampled multiple times. Due to the liquid amine, neat reactions for **3** and **4** have η=0.2. See Section 2 for calculation of Evidence Ratios (*ER*).

Reaction[a] η	Model Parameters JMAYK	FW	1st Order	*ER* (FW/JMAYK)	ER (FW/first order)
1d η=0.3	k=0.0053 n=1.6761 R^2=0.9645	k_1=0.0016 k'_2=0.0123 R^2=0.9487	k=0.0033 R^2=0.8843	0.2743	2.3249
1m η=1.2	k=0.0406 n=0.7059 R^2=0.9785	k_1=0.0604 k'_2=-0.0471 R^2=0.9812	k=0.0367 R^2=0.9577	1.7454	1.0829×10^{1}
2m η=0.6	k=0.1216 n=2.0990 R^2=0.9718	k_1=0.0261 k'_2=0.3764 R^2=0.9722	k=0.1316 R^2=0.9587	0.0431	4.8692×10^{5}
2m[c] η=0.6	k=0.0769 n=3.4791 R^2=0.9752	k_1=0.0032 k'_2=0.4169 R^2=0.9787	k=0.0795 R^2=0.8379	1.5768	4.2460×10^{1}
2m[d] η=0.6	k=0.1258 n=1.3724 R^2=0.9718	k_1=0.0749 k'_2=0.1537 R^2=0.9722	k=0.1355 R^2=0.9587	1.0400	3.1688×10^{-1}
2d η=0.3	k=0.0221 n=0.9143 R^2=0.9867	k_1=0.0245 k'_2=-0.0063 R^2=0.9862	k=0.0218 R^2=0.9850	0.8653	1.8124×10^{-1}
3n[b] η=0.2	k=0.0053 n=4.7774 R^2=0.9974	k_1=5.7×10^{-5} k'_2=0.0377 R^2=0.9982	k=0.0047 R^2=0.7068	3.5605	1.5624×10^{11}
3d[b] η=0.3	k=0.0190 n=1.4553 R^2=0.9901	k_1=0.0098 k'_2=0.0287 R^2=0.9906	k=0.0203 R^2=0.9746	1.3098	1.6911×10^{1}
3m[bc] η=0.3	k=0.0604 n=2.1654 R^2=0.9564	k_1=0.0113 k'_2=0.1997 R^2=0.9641	k=0.0623 R^2=0.8655	1.9614	1.3707×10^{1}
3m[bc] η=0.9	k=0.1013 n=2.2436 R^2=0.9971	k_1=0.0156 k'_2=0.3681 R^2=0.9971	k=0.1071 R^2=0.9106	1.0099	2.2969×10^{4}
4n[b] η=0.2	k=0.0067 n=2.8907 R^2=0.9773	k_1=0.0005 k'_2=0.0311 R^2=0.9981	k=0.0070 R^2=0.8621	9.8734	2.7719×10^{12}
4d[b] η=0.3	k=0.0120 n=1.0617 R^2=0.9776	k_1=0.0107 k'_2=0.0034 R^2=0.9781	k=0.0122 R^2=0.9768	1.1030	2.7729×10^{-1}
4m[b] η=0.9	k=0.0291 n=1.6344 R^2=0.9981	k_1=0.0111 k'_2=0.0611 R^2=0.9987	k=0.0290 R^2=0.9696	4.6759	9.5789×10^{3}
5n[b] η=0	k=0.0051 n=1.1626 R^2=0.9934	k_1=0.0038 k'_2=0.0035 R^2=0.9936	k=0.0049 R^2=0.9855	1.1865	1.8178×10^{2}
5n η=0	k=0.0137 n=1.0547 R^2=0.9943	k_1=0.0129 k'_2=0.0022 R^2=0.9940	k=0.0138 R^2=0.9938	0.7948	3.0621×10^{-1}
5d η=0.3	k=1.2352 n=0.2743 R^2=0.9980	k_1=0.6684 k'_2=-0.6885 R^2=0.9991	k=0.1757 R^2=0.9807	53.0126	9.0895×10^{5}
5e η=0.5	k=0.0426 n=0.7837 R^2=0.9822	k_1=0.0634 k'_2=-0.0492 R^2=0.9864	k=0.0437 R^2=0.9771	2.8659	1.3219
5m η=0.5	k=0.0406 n=0.7059 R^2=0.9785	k_1=0.0604 k'_2=-0.0471 R^2=0.9812	k=0.0367 R^2=0.9577	2.5992	2.3813×10^{1}

[a]Reactions labelled with product number and the conditions; **n** (neat), or **d** (dimethyl sulfoxide-d_6), **m** (methanol), or **e** (ethanol) LAG. [b]Na_2CO_3 was used as base. [c]Reaction mixtures sampled only once, and data are three experiments averaged for each data point. [d]Experiments were carried out as in the previous footnote, but the reaction mixtures were manually stirred at intervals in addition to milling.

4. SPECTRA

4.1 Overview: Stacked spectra are shown for all kinetic data in Figures 2-4 and corresponding data series are noted. The first figure for each compound also includes a spectrum for the amine reactant. Amine and product resonances used in the determination of conversion fraction (α) are also marked in this first figure of each series. In the stacked spectra, the view has been selected to best show changes in composition over time. Full ^{1}H NMR spectra for all products are provided in Section 4.7 along with ^{13}C NMR and IR spectra for the new compound [Pd(EMBA)Cl]$_2$ (**4**).

4.2. [Pd(2-ADP)Cl]$_2$ (1):

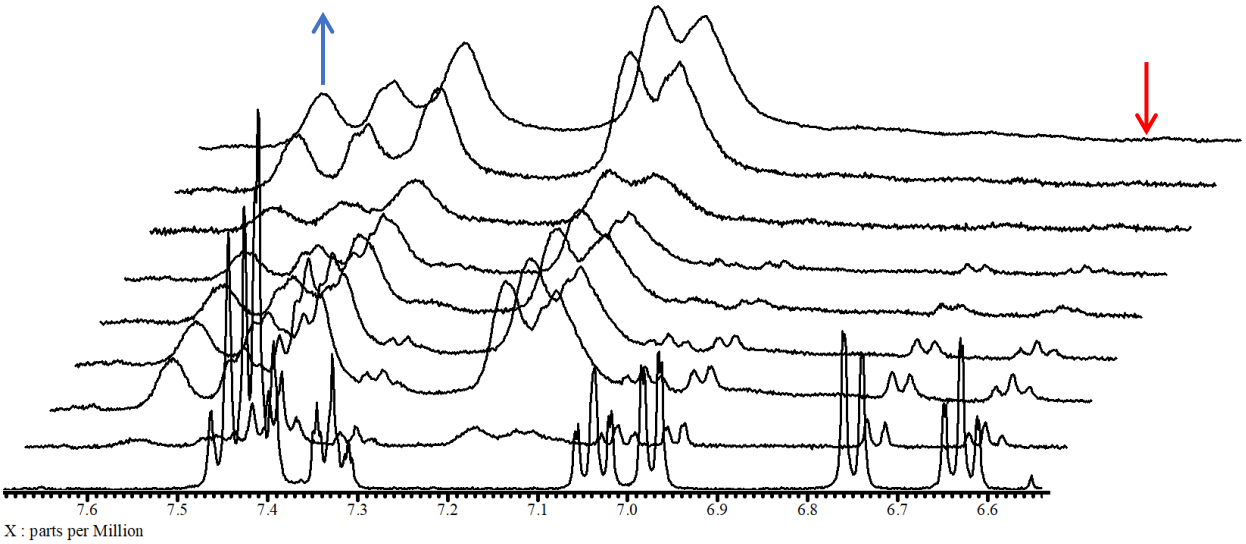


Figure S-1. Section of ^{1}H NMR spectra in DMSO-d_6 of 2-aminobiphenyl (H2-ADP, bottom) and the reaction mixture for the η=1.2 MeOH LAG mechanosynthesis of [Pd(2-ADP)Cl]$_2$ (**1**) at 15 minute intervals until 120 minutes (top). All samples were taken from a single reaction mixture (rja-4-44) and correspond to a portion of the average values in Figure 2, **1** ■. Resonances of H2-ADP (↓) and **1** (↑) used for determination of conversion fraction (α) marked.

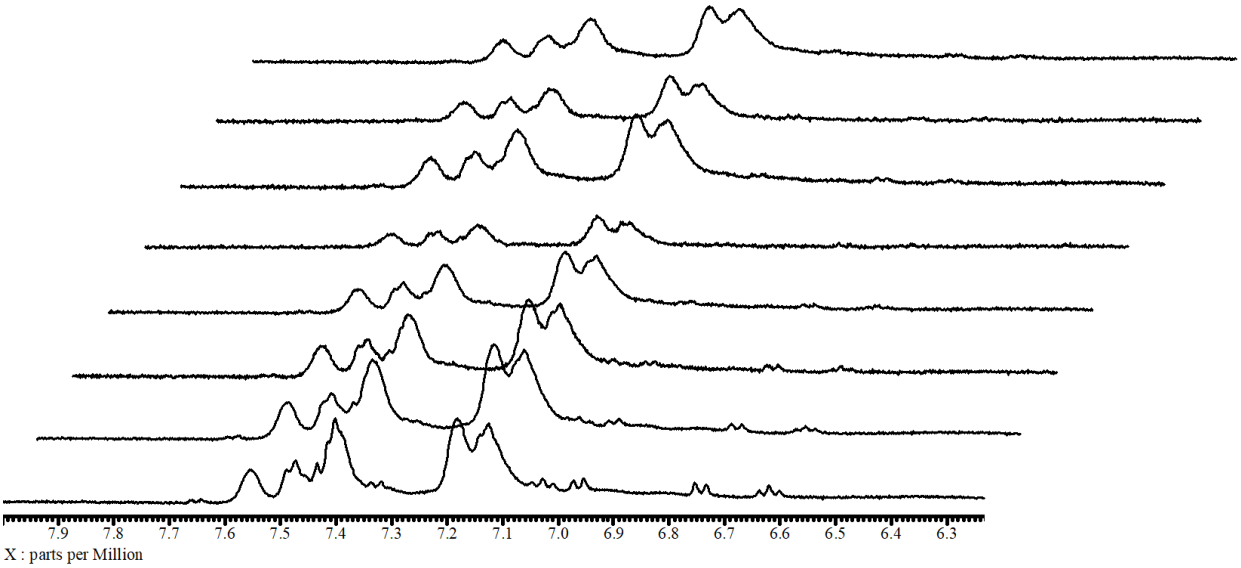


Figure S-2. Section of ^{1}H NMR spectra in DMSO-d_6 of the reaction mixture for the η=1.2 MeOH LAG mechanosynthesis of [Pd(2-ADP)Cl]$_2$ (**1**) at 15 minute intervals until 135 minutes (top). All samples were taken from a single reaction mixture (rja-4-45a) and correspond to a portion of the average values in Figure 2, **1** ■.

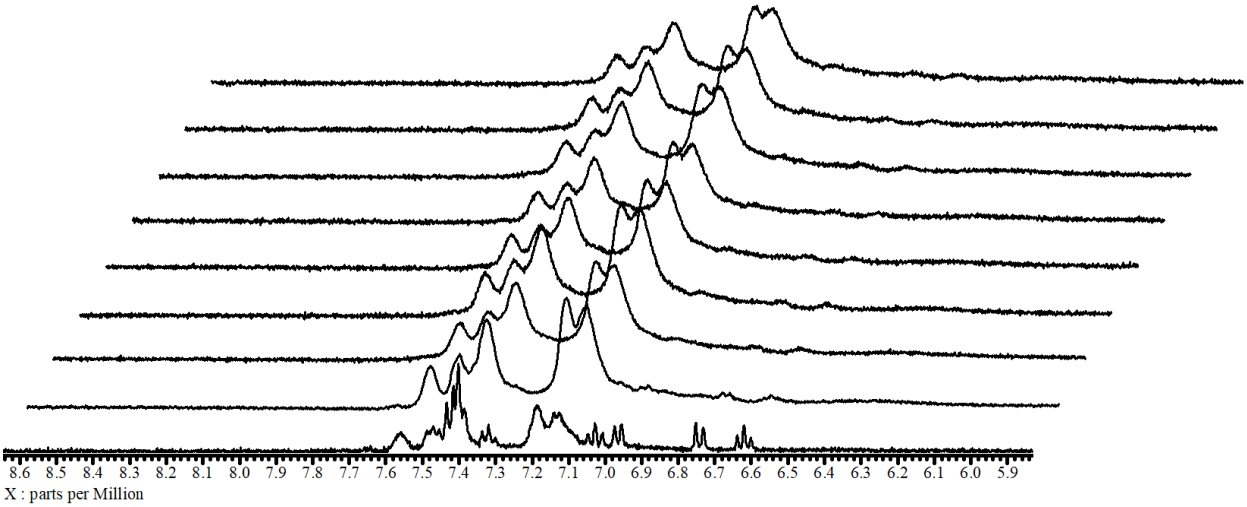


Figure S-3. Section of ^{1}H NMR spectra in DMSO-d_6 of the reaction mixture for the η=1.2 MeOH LAG mechanosynthesis of [Pd(2-ADP)Cl]$_2$ (**1**) at 15 minute intervals until 135 minutes (top). All samples were taken from a single reaction mixture (rja-4-45b) and correspond to a portion of the average values in Figure 2, **1** ■.

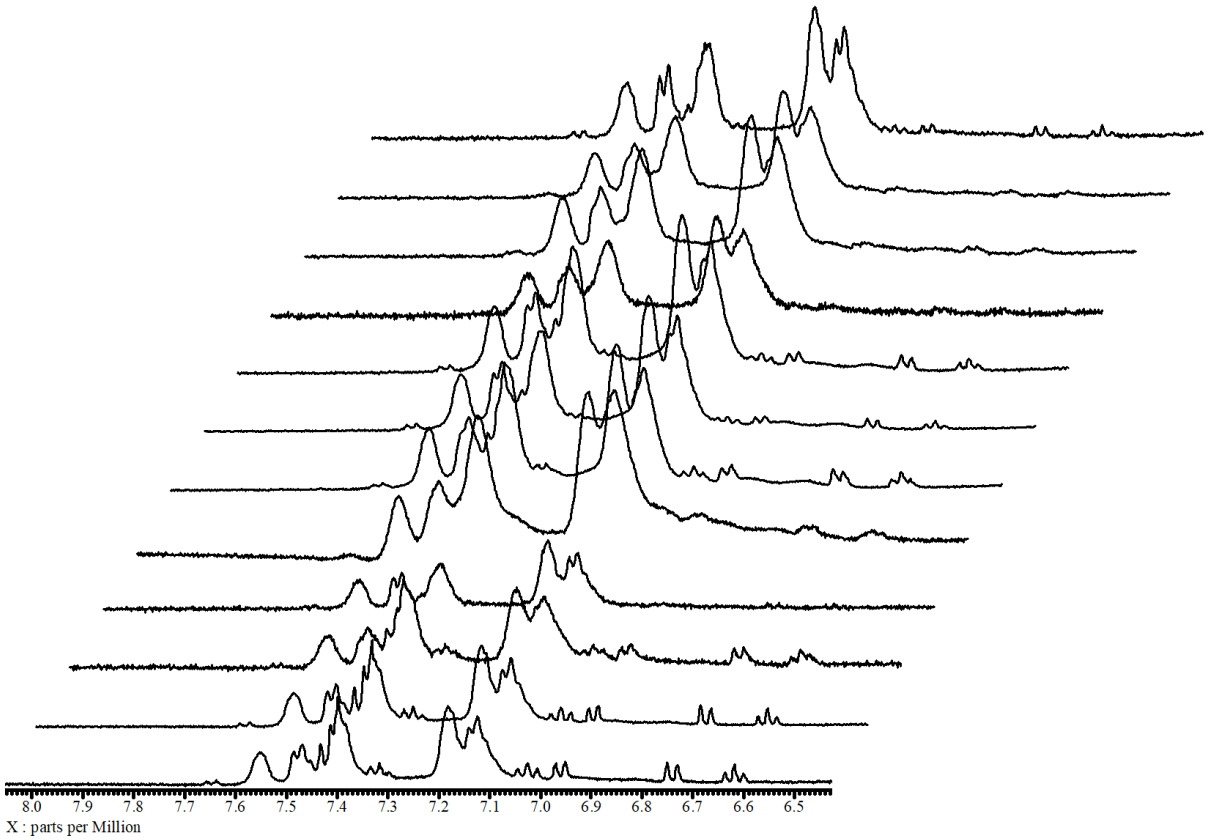


Figure S-4. Section of ^{1}H NMR spectra in DMSO-d_6 of the reaction mixture for the η=1.2 MeOH LAG mechanosynthesis of [Pd(2-ADP)Cl]$_2$ (**1**) at 30, 30, 30, 60, 90, 90, 90, 120, 120 and 120 minutes (top). Each spectrum is from a different reaction (bottom to top: jh-1-11a, jh-1-14a, jh-1-20/21d, jh-1-11b, jh-1-14b, jh-1-16b, jh-1-14c, jh-1-16c, jh-1-19b, jh-1-14d, jh-1-20/21a, and jh-1-20/21c). These data correspond to the average values in Figure 2, **1**□.

4.3. [Pd(2-ADP)OAc]$_2$ (2):

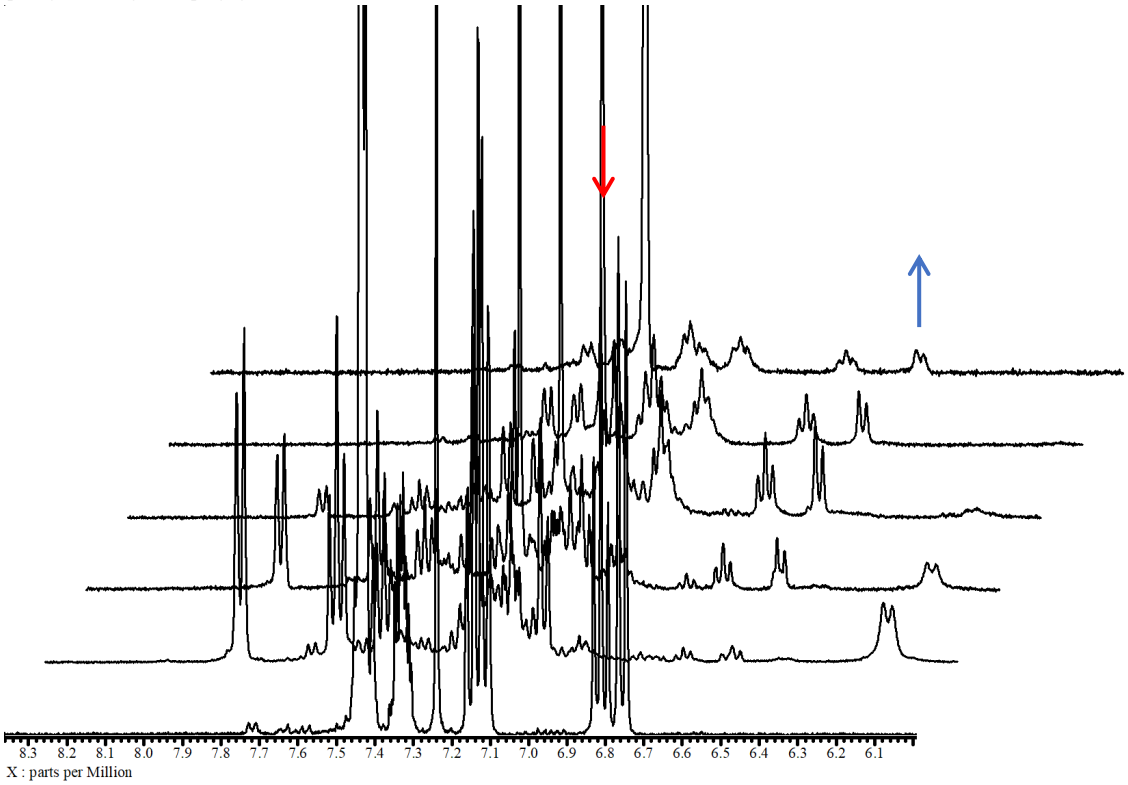


Figure S-5. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=1.2 MeOH LAG mechanosynthesis of [Pd(2-ADP)OAc]$_2$ (**2**) at 5, 10, 15, 20 and 30 minutes (top). Each spectrum is from a different reaction (bottom to top: jbs-1-25a, jbs-125b, jbs-1-25c, ta-1-28d, and rja-4-74a). These data correspond to a portion of the average values in Figure 2, **2**. Resonances of H2-ADP (↓) and **2** (↑) used for determination of conversion fraction (α) marked.

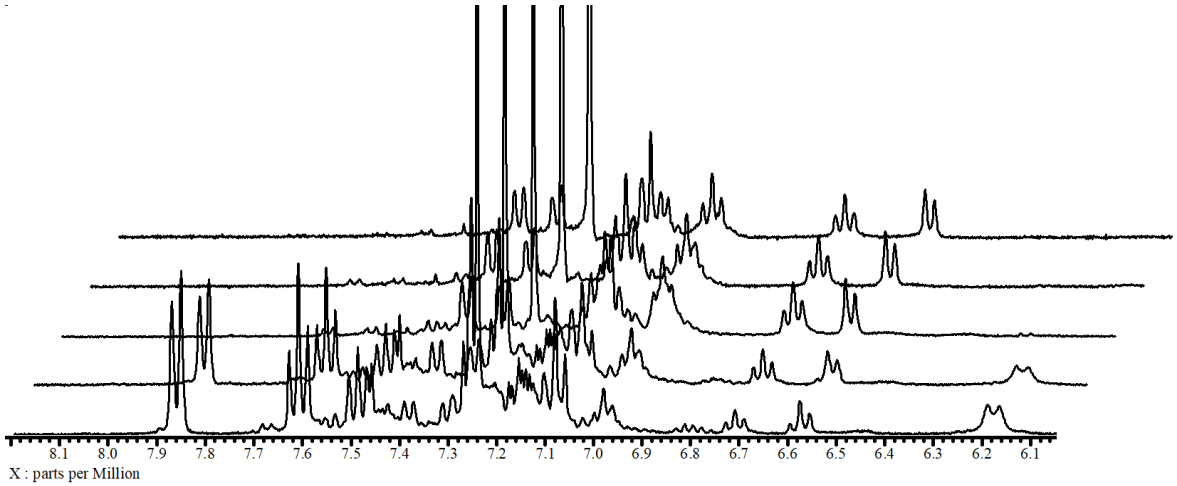


Figure S-6. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for 2-aminobiphenyl (H2-ADP, bottom) and the η=1.2 MeOH LAG mechanosynthesis of [Pd(2-ADP)OAc]$_2$ (**2**) at 5, 10, 15, 20 and 30 minutes (top). Each reaction mixture spectrum is from a different reaction (bottom to top: jbs-1-26a, jbs-1-26b, ta-1-28c, jbs-1-26d, and rja-4-74b). These data correspond to a portion of the average values in Figure 2, **2**.

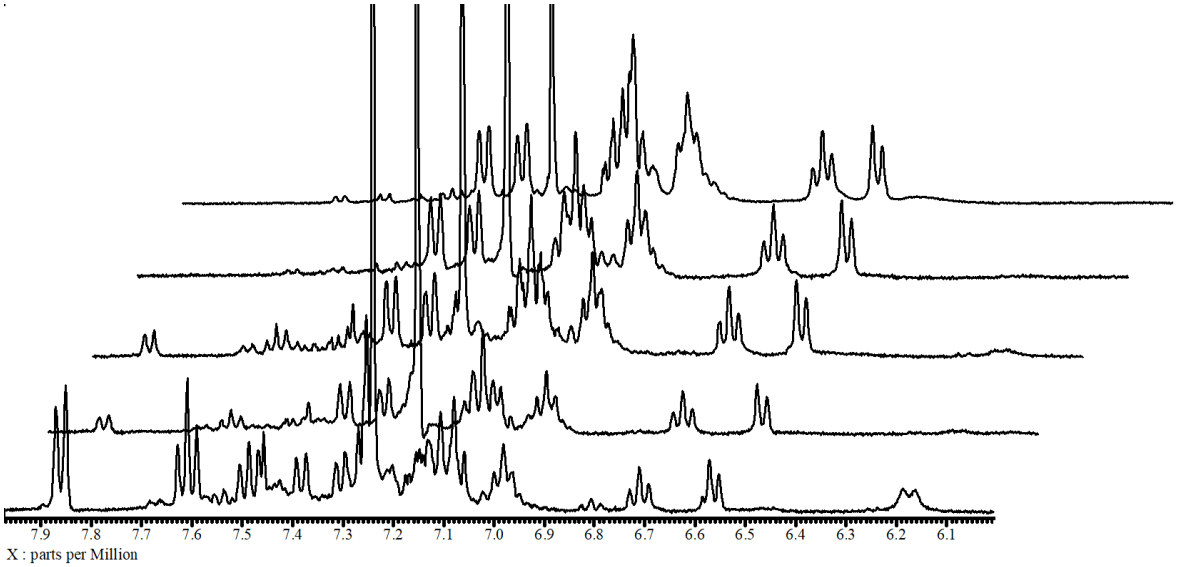


Figure S-7. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for 2-aminobiphenyl (H2-ADP, bottom) and the η=1.2 MeOH LAG mechanosynthesis of $[Pd(2\text{-}ADP)OAc]_2$ (**2**) at 5, 10, 15, 20 and 30 minutes (top). Each spectrum is from a different reaction (bottom to top: rja-4-74c, ta-1-28b, jbs-1-26c, rja-4-74d, and rja-4-74e). These data correspond to a portion of the average values in Figure 2, **2**□.

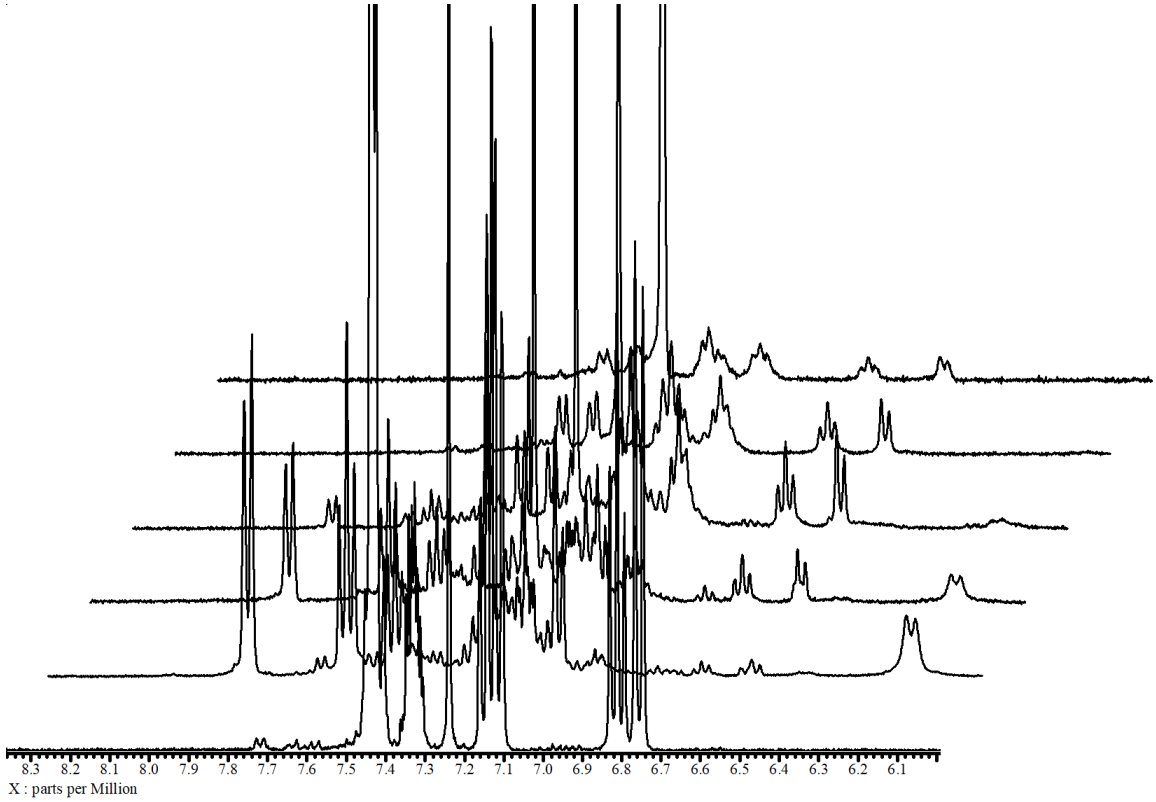


Figure S-8. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.3 DMSO-d_6 LAG mechanosynthesis of $[Pd(2\text{-}ADP)OAc]_2$ (**2**) at 20 minute intervals until 120 minutes (top). All samples were taken from a single reaction mixture (rja-4-96a) and correspond to a portion of the average values in Figure 2, **2**●.

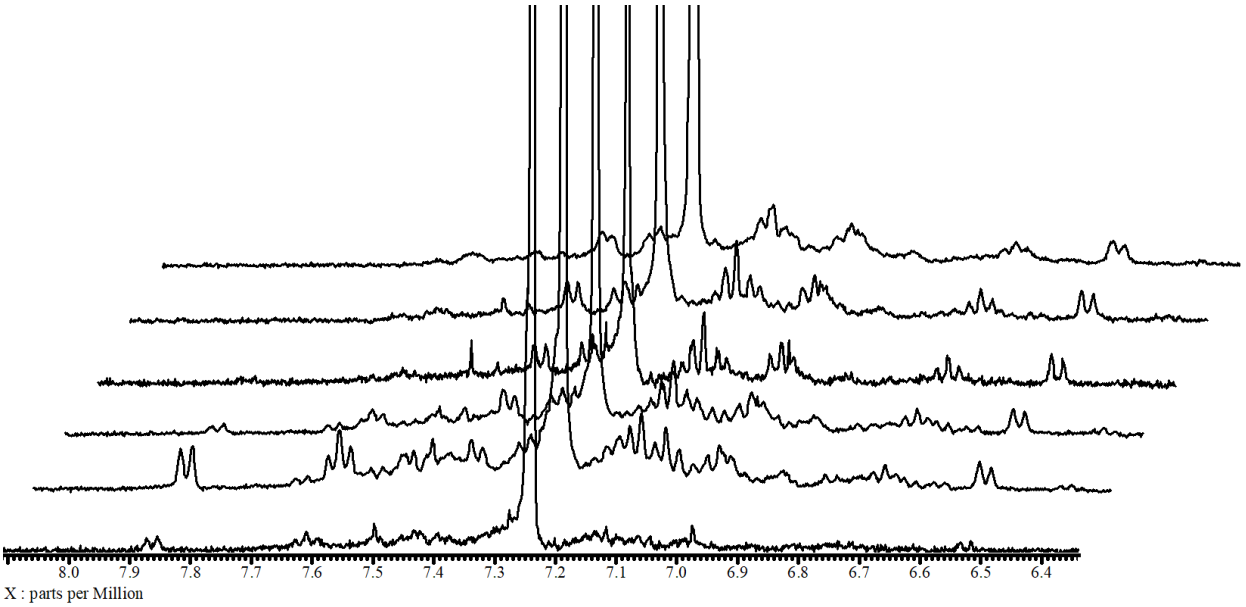


Figure S-9. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.3 DMSO-d_6 LAG mechanosynthesis of [Pd(2-ADP)OAc]$_2$ (**2**) at 20 minute intervals until 120 minutes (top). All samples were taken from a single reaction mixture (rja-4-96b) and correspond to a portion of the average values in Figure 2, **2**●.

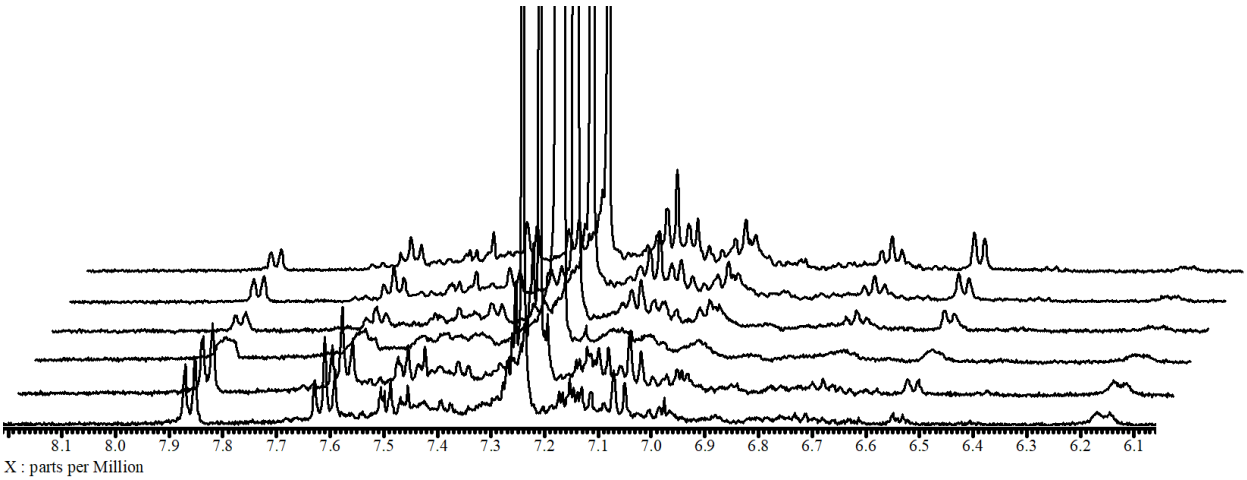


Figure S-10. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.3 DMSO-d_6 LAG mechanosynthesis of [Pd(2-ADP)OAc]$_2$ (**2**) at 20 minute intervals until 120 minutes (top). All samples were taken from a single reaction mixture (rja-4-96f) and correspond to a portion of the average values in Figure 2, **2**●.

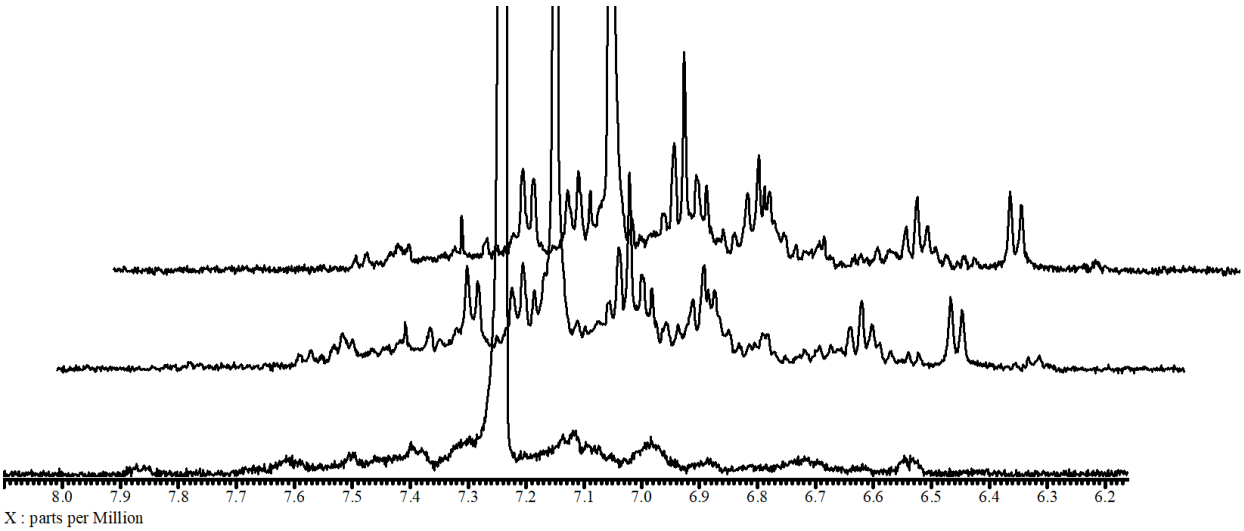


Figure S-11. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixtures for the η=0.3 DMSO-d_6 LAG mechanosynthesis of $[Pd(2\text{-}ADP)OAc]_2$ (**2**) at 40, 80, and 120 minutes (top). Each spectrum is from a different reaction (bottom to top: rja-4-96c, rja-4-96g, and rja-4-96d). These data correspond to a portion of the average values in Figure 2, **2**○.

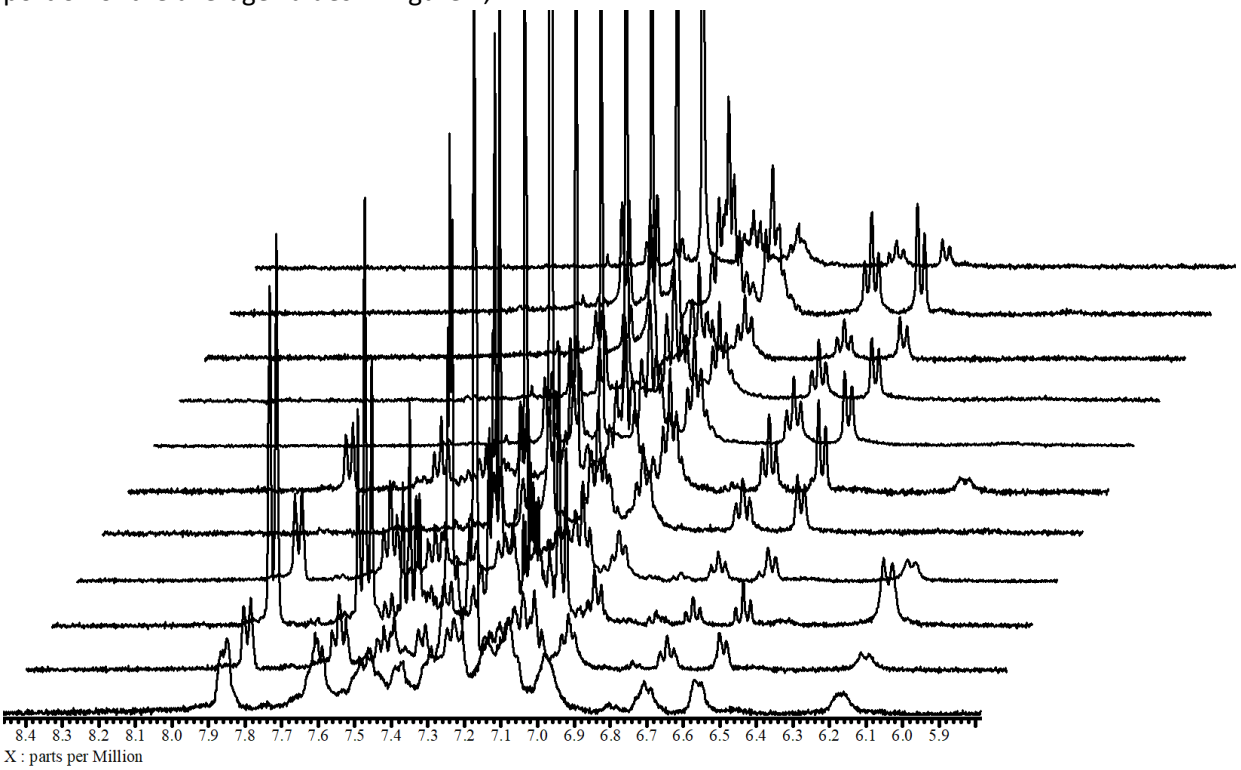


Figure S-12. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.6 MeOH LAG mechanosynthesis of $[Pd(2\text{-}ADP)OAc]_2$ (**2**). The experiments were carried out to determine if hand-mixing during sampling was affecting conversion in the production of **2**. Reaction mixtures were mixed by hand every five minutes but only sampled at once. Spectra are shown for reactions sampled at 5, 5, 5, 10, 10, 10, 15, 15, 15, 20, and 30 minutes (top). Each spectrum is from a different reaction (bottom to top: tma-1-60d, tma-1-60b, tma-1-63, tma-1-57, tma-1-60a, tma-a-62, tma-1-58a, tkma-1-58b, tma-1-58c, tma-1-59a, and tma-1-59b). These data correspond to the average values in Figure 3, ×.

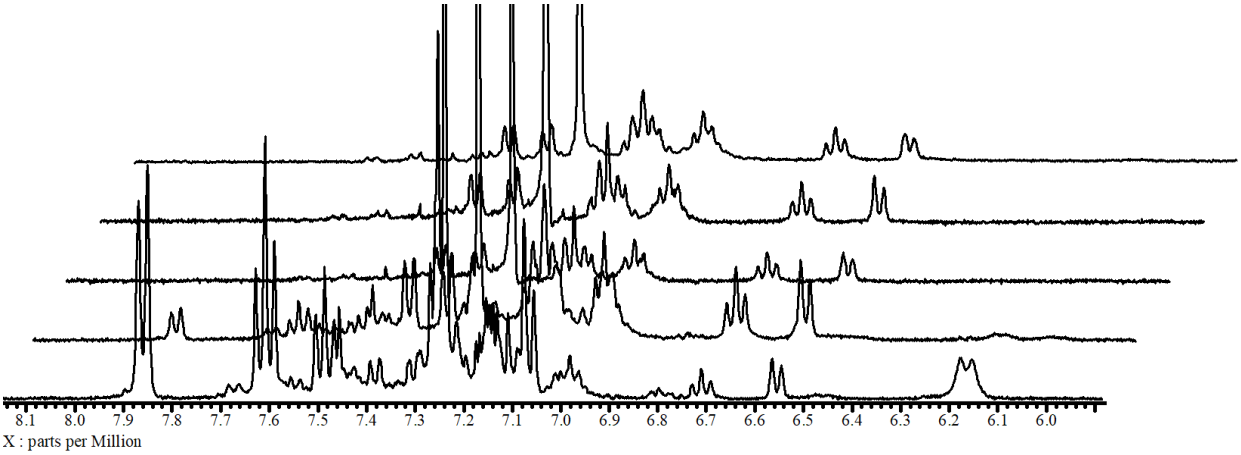


Figure S-13. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.6 MeOH LAG mechanosynthesis of $[Pd(2\text{-}ADP)OAc]_2$ (**2**) five minute intervals until 30 minutes (top). All samples were taken from a single reaction mixture (jbs-1-23) and correspond to a portion of the average values in Figure 3, ■.

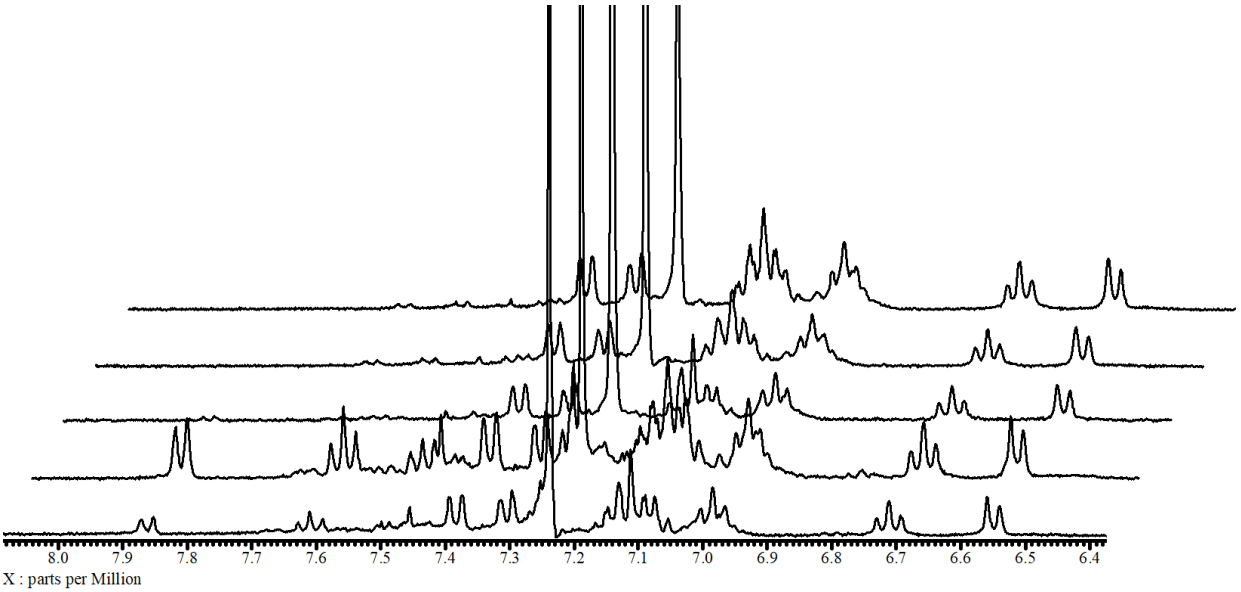


Figure S-14. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.6 MeOH LAG mechanosynthesis of $[Pd(2\text{-}ADP)OAc]_2$ (**2**) five minute intervals until 30 minutes (top). All samples were taken from a single reaction mixture (tma-1-25a) and correspond to a portion of the average values in Figure 3, ■.

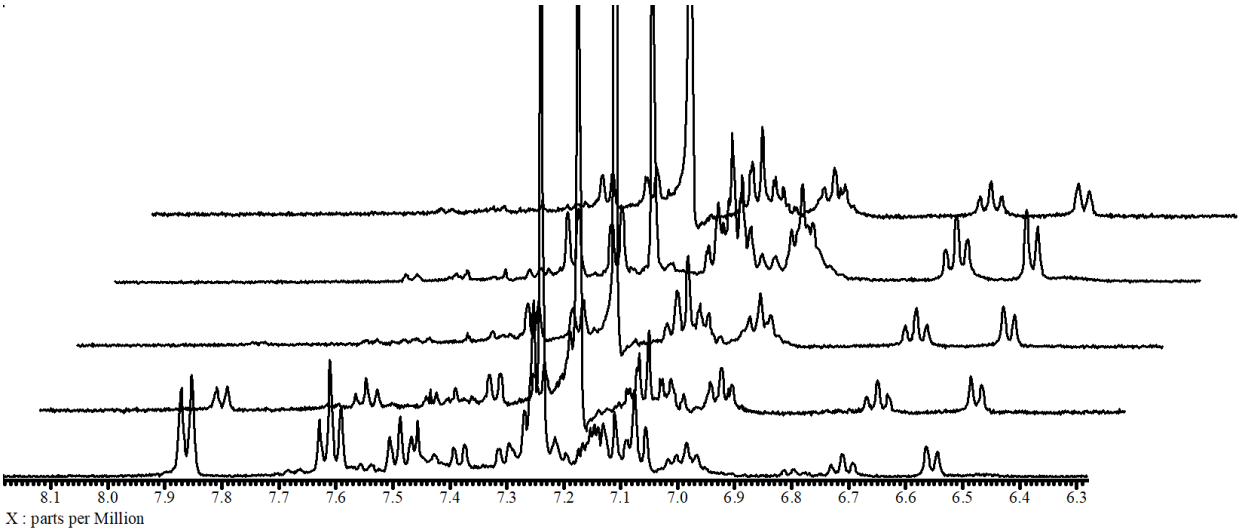


Figure S-15. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.6 MeOH LAG mechanosynthesis of $[Pd(2\text{-}ADP)OAc]_2$ (**2**) five minute intervals until 30 minutes (top). All samples were taken from a single reaction mixture (tma-1-25c) and correspond to a portion of the average values in Figure 3, ■.

4.3. $[Pd(DMBA)Cl]_2$ (3):

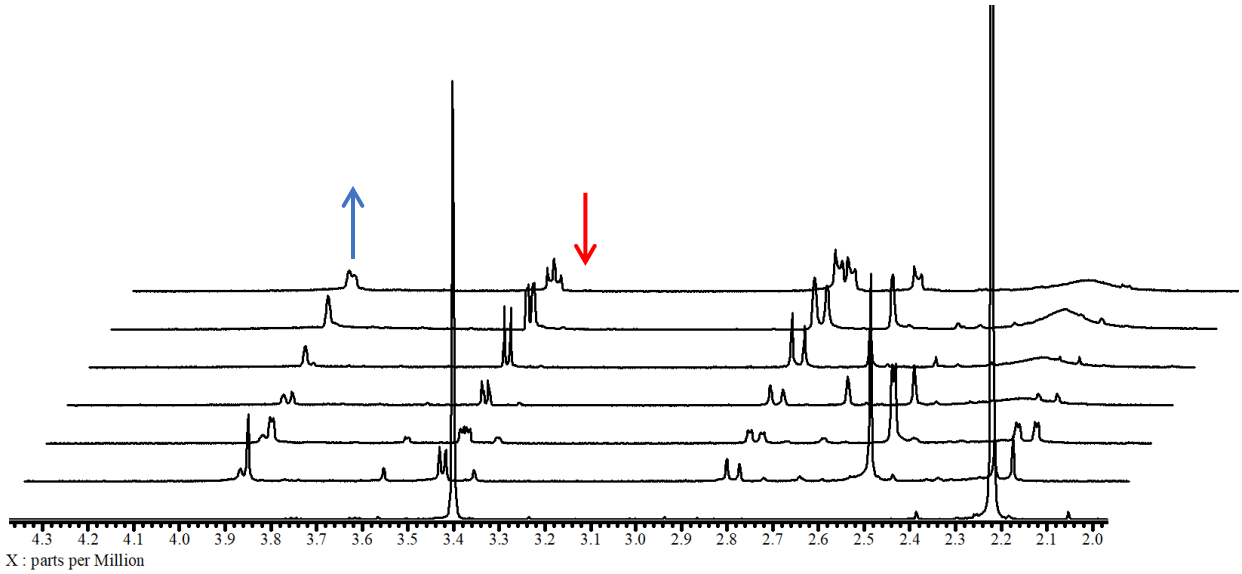


Figure S-16. Section of ^{1}H NMR spectra in $CDCl_3$ of *N*,*N*-dimethylbenzylamine (HDMBA, bottom) and the reaction mixtures for the η=0.3 methanol LAG mechanosynthesis of $[Pd(DMBA)Cl]_2$ (**3**) at five minute intervals of milling until 30 minutes (top). Each spectrum is from a different reaction (bottom to top: rja-4-94i, rja-4-91b, rja-4-93a, rja-4-93g, rja-4-94a, and rja-4-94d). These data correspond to a portion of the average values in Figure 2, **3**○. Resonances of HDMBA (↓) and **3** (↑) used for determination of conversion fraction (α) marked.

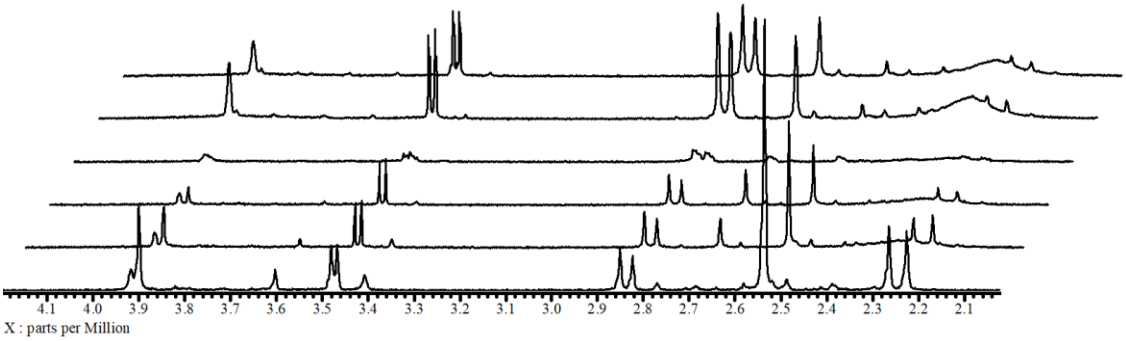


Figure S-17. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixtures for the η=0.3 methanol LAG mechanosynthesis of $[Pd(DMBA)Cl]_2$ (**3**) at five minute intervals of milling until 30 minutes (top). Each spectrum is from a different reaction (bottom to top: rja-4-94k, rja-4-92a, rja-4-93b, rja-4-93h, rja-4-94b, and rja-4-94c). These data correspond to a portion of the average values in Figure 2, **3**○.

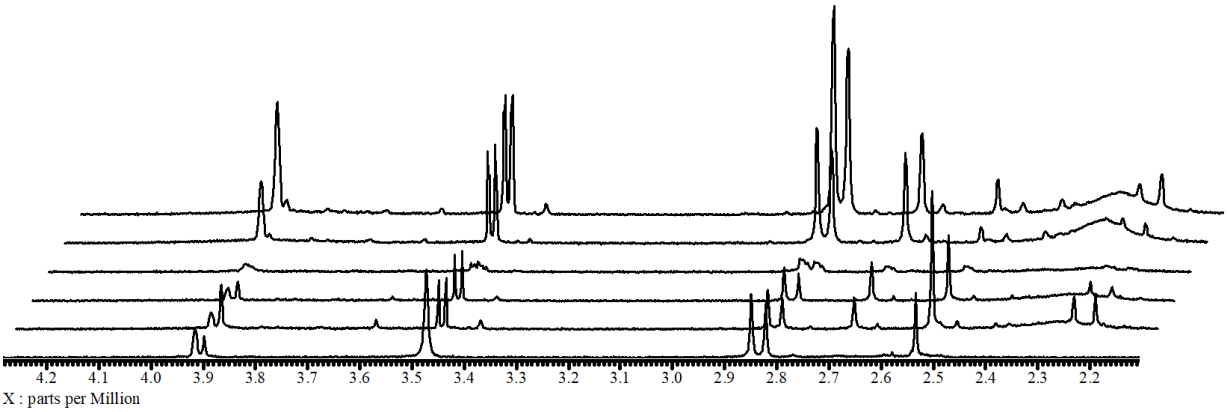


Figure S-18. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixtures for the η=0.3 methanol LAG mechanosynthesis of $[Pd(DMBA)Cl]_2$ (**3**) at five minute intervals of milling until 30 minutes (top). Each spectrum is from a different reaction (bottom to top: rja-4-94l, rja-4-92a, rja-4-93b, rja-4-93h, rja-4-94b, and rja-4-94f). These data correspond to a portion of the average values in Figure 2, **3**○.

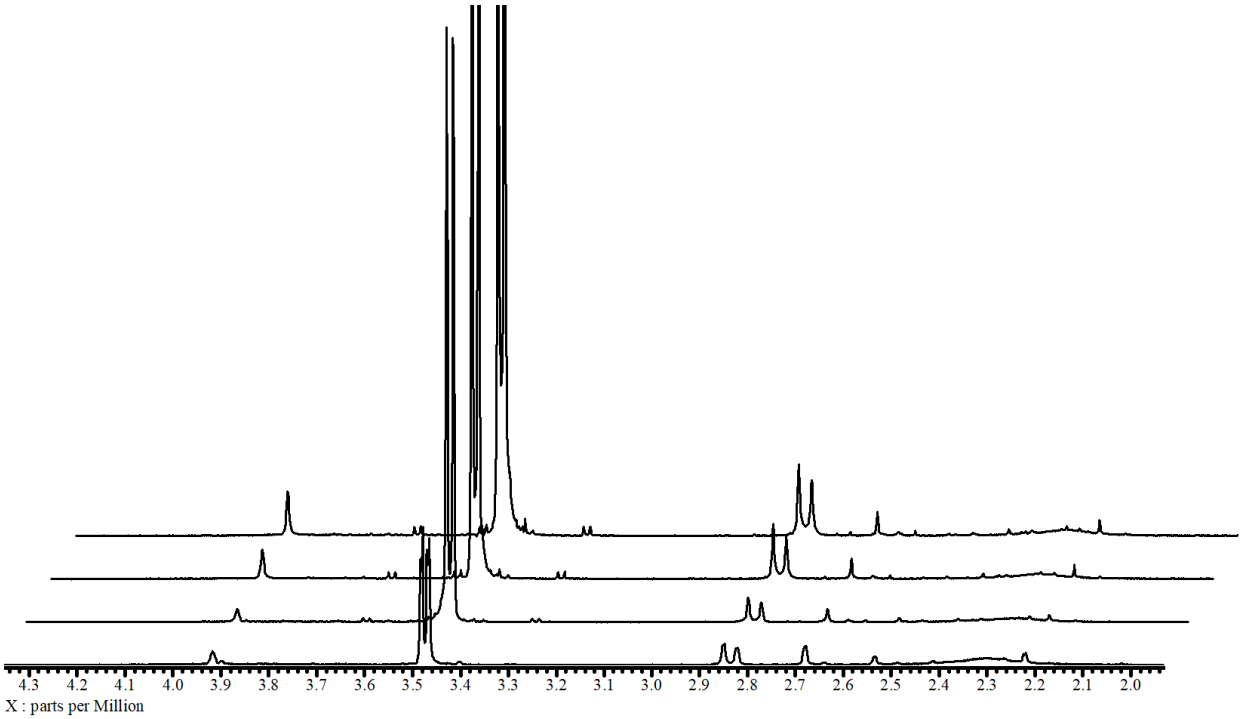


Figure S-19. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixtures for the η=0.9 methanol LAG mechanosynthesis of $[Pd(DMBA)Cl]_2$ (**3**) at 10, 15, and 20 minute intervals until 25 minutes (top). Each spectrum is from a different reaction (bottom to top: rja-4-91a, rja-4-93d, rja-4-93j, and rja-4-94g). These data correspond to a portion of the average values in Figure 2, **3**□.

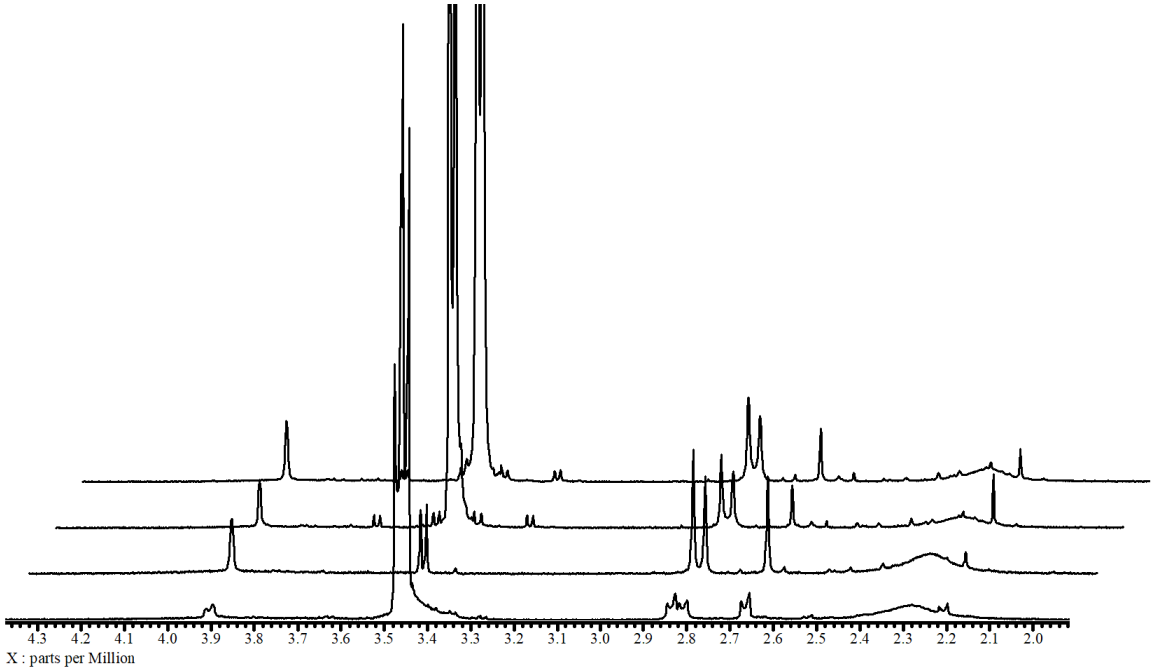


Figure S-20. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixtures for the η=0.9 methanol LAG mechanosynthesis of $[Pd(DMBA)Cl]_2$ (**3**) at 10, 15, and 20 minute intervals until 25 minutes (top). Each reaction mixture spectrum is from a different reaction (bottom to top: rja-4-92a, rja-4-93e, rja-4-93k, and rja-4-94h). These data correspond to a portion of the average values in Figure 2, **3**□.

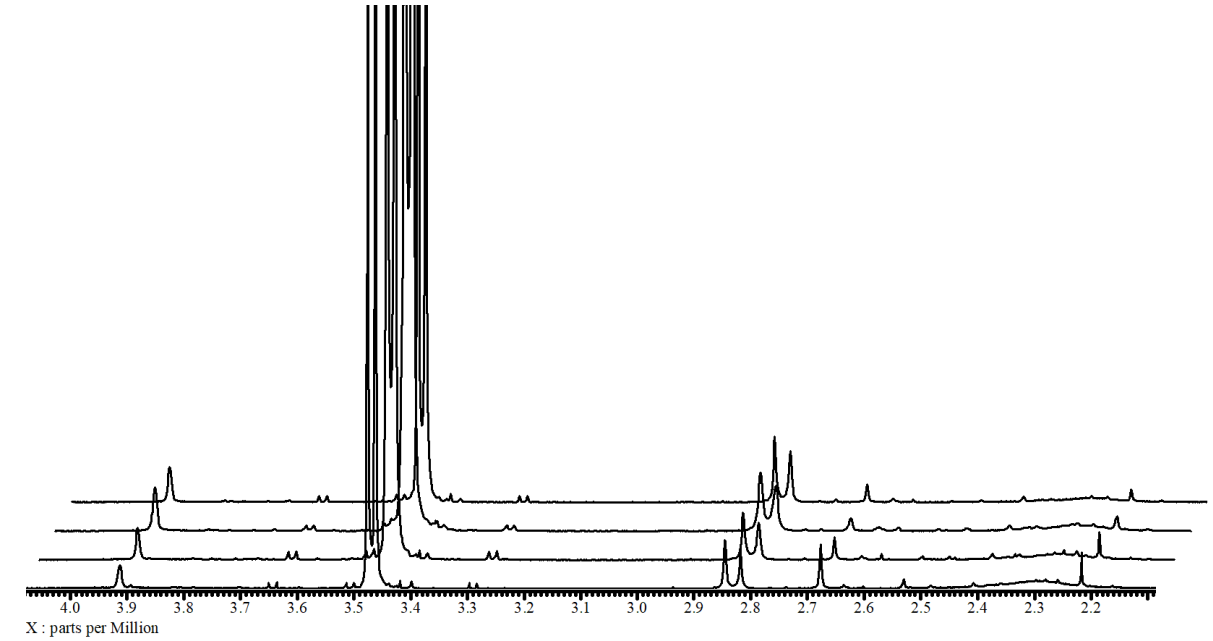


Figure S-21. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixtures for the η=0.9 methanol LAG mechanosynthesis of $[Pd(DMBA)Cl]_2$ (**3**) at 10, 15, and 20 minute intervals until 25 minutes (top). Each spectrum is from a different reaction (bottom to top: rja-4-92d, rja-4-93f, rja-4-93l, and rja-4-94i). These data correspond to a portion of the average values in Figure 2, **3**□.

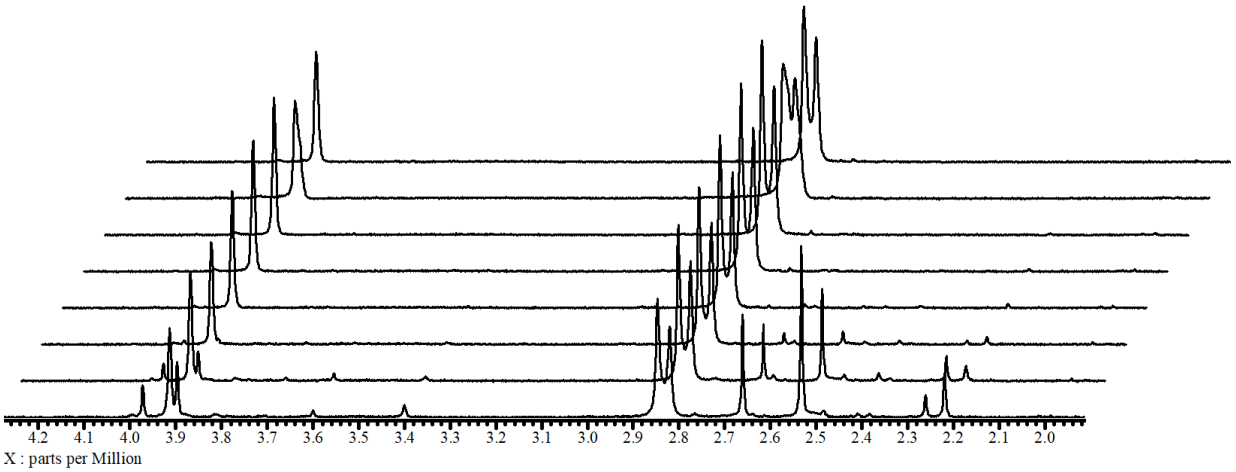


Figure S-22. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.3 DMSO-d_6 LAG mechanosynthesis of $[Pd(DMBA)Cl]_2$ (**3**) at 30 minute intervals until 240 minutes (top). All samples were taken from a single reaction mixture (rja-4-29a) and correspond to a portion of the average values in Figure 2, **3**●.

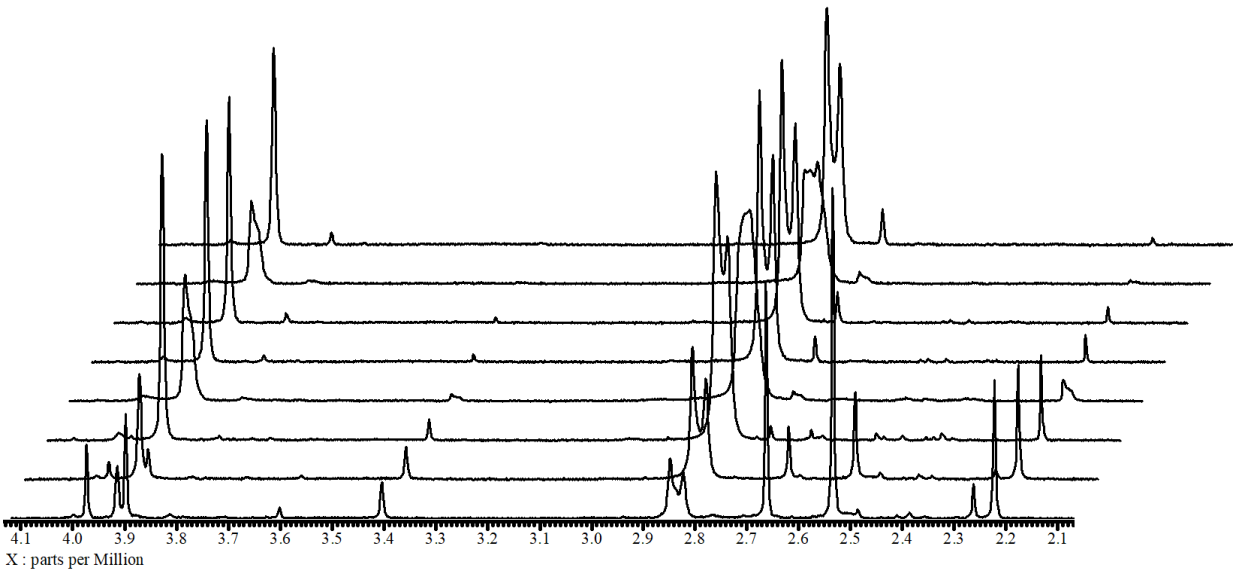


Figure S-23. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.3 DMSO-d_6 LAG mechanosynthesis of $[Pd(DMBA)Cl]_2$ (**3**) at 30 minute intervals until 240 minutes (top). All samples were taken from a single reaction mixture (rja-4-29b) and correspond to a portion of the average values in Figure 2, **3**●.

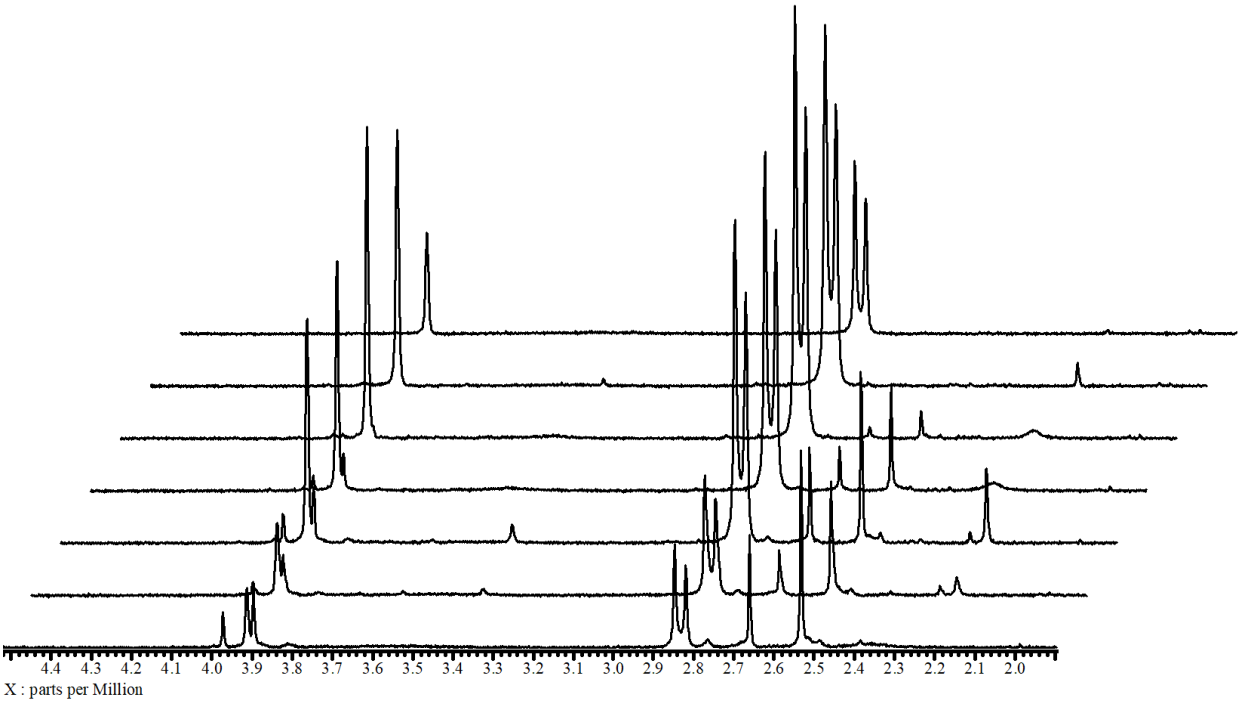


Figure S-24. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.3 DMSO-d_6 LAG mechanosynthesis of $[Pd(DMBA)Cl]_2$ (**3**) at 30 minute intervals until 240 minutes (top). All samples were taken from a single reaction mixture (rja-4-29c) and correspond to a portion of the average values in Figure 2, **3**●.

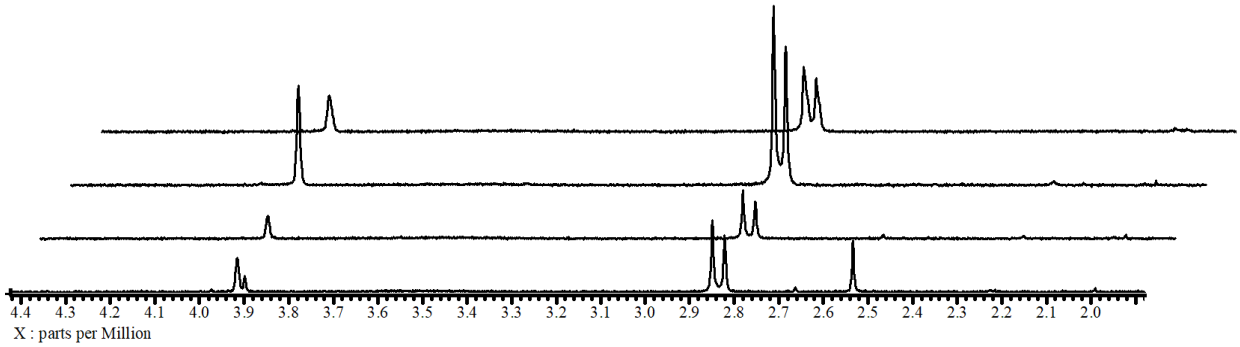


Figure S-25. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixtures for the η=0.3 DMSO-d_6 LAG mechanosynthesis of $[Pd(DMBA)Cl]_2$ (**3**) at minute 60 intervals until 240 minutes (top). Each spectrum is from a different reaction (bottom to top: jh-1-29, jh-1-30b, jh-1-30a, and jh-1-31). These data correspond to Figure 2, **3**○.

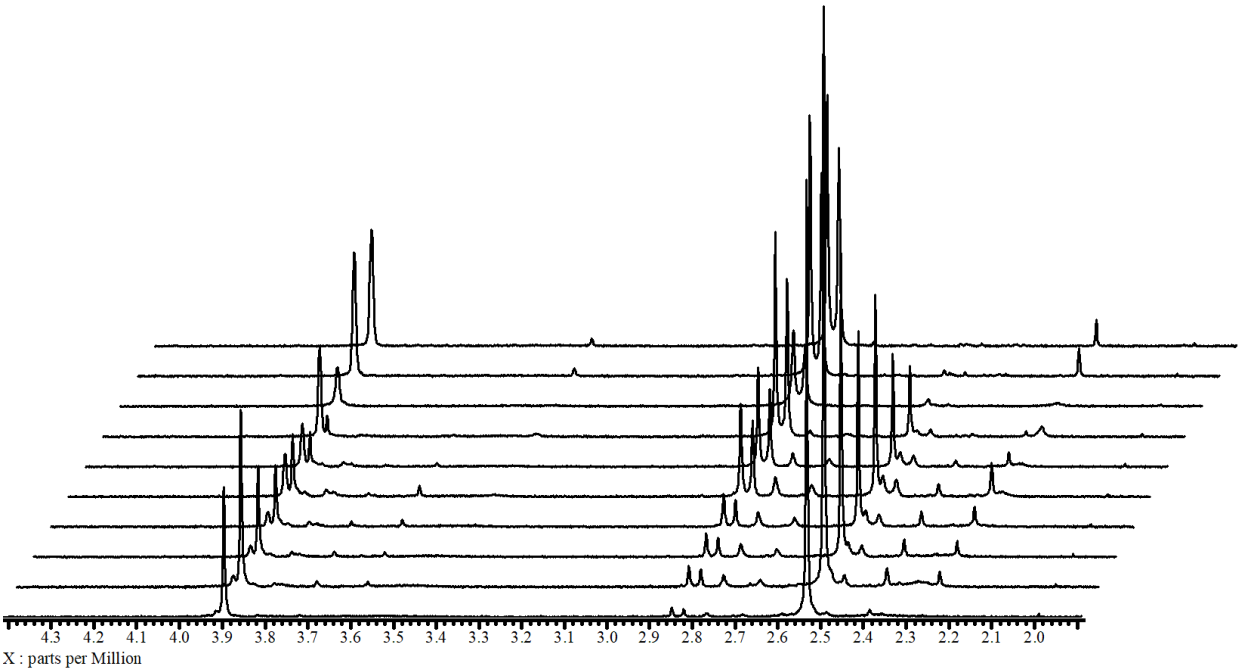


Figure S-26. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the neat mechanosynthesis of $[Pd(DMBA)Cl]_2$ (**3**) at 30 minute intervals until 300 minutes (top). All samples were taken from a single reaction mixture (rja-4-19) and correspond to a portion of the average values in Figure 2, **3**▲.

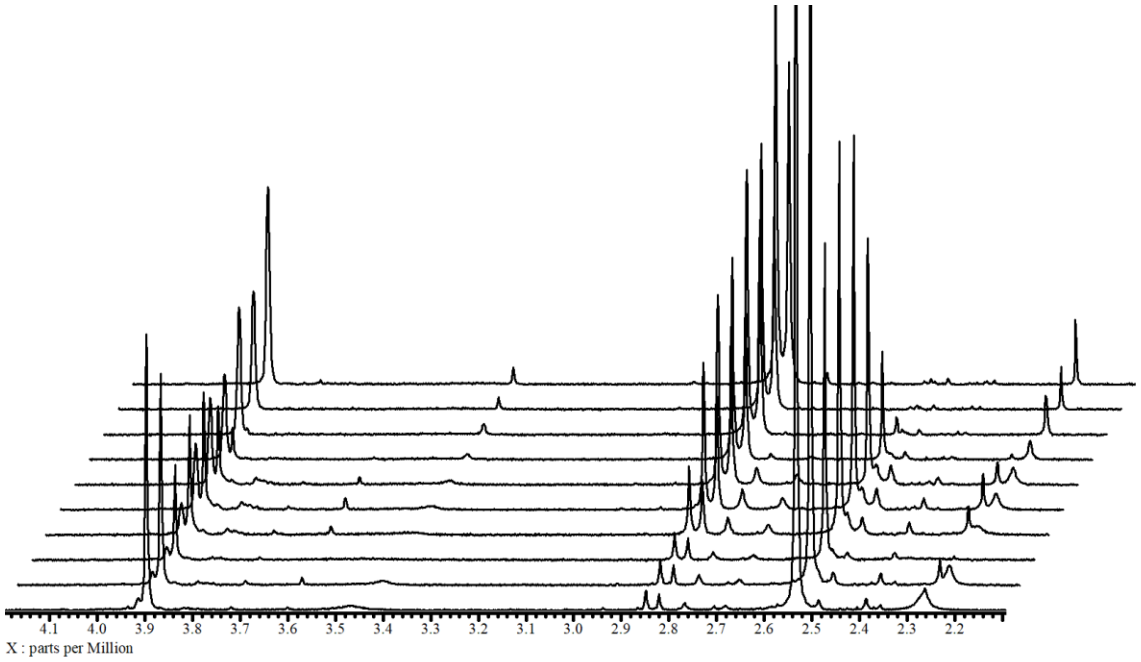


Figure S-27. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the neat mechanosynthesis of $[Pd(DMBA)Cl]_2$ (**3**) at 30 minute intervals until 300 minutes (top). All samples were taken from a single reaction mixture (rja-4-20) and correspond to a portion of the average values in Figure 2, **3**▲.

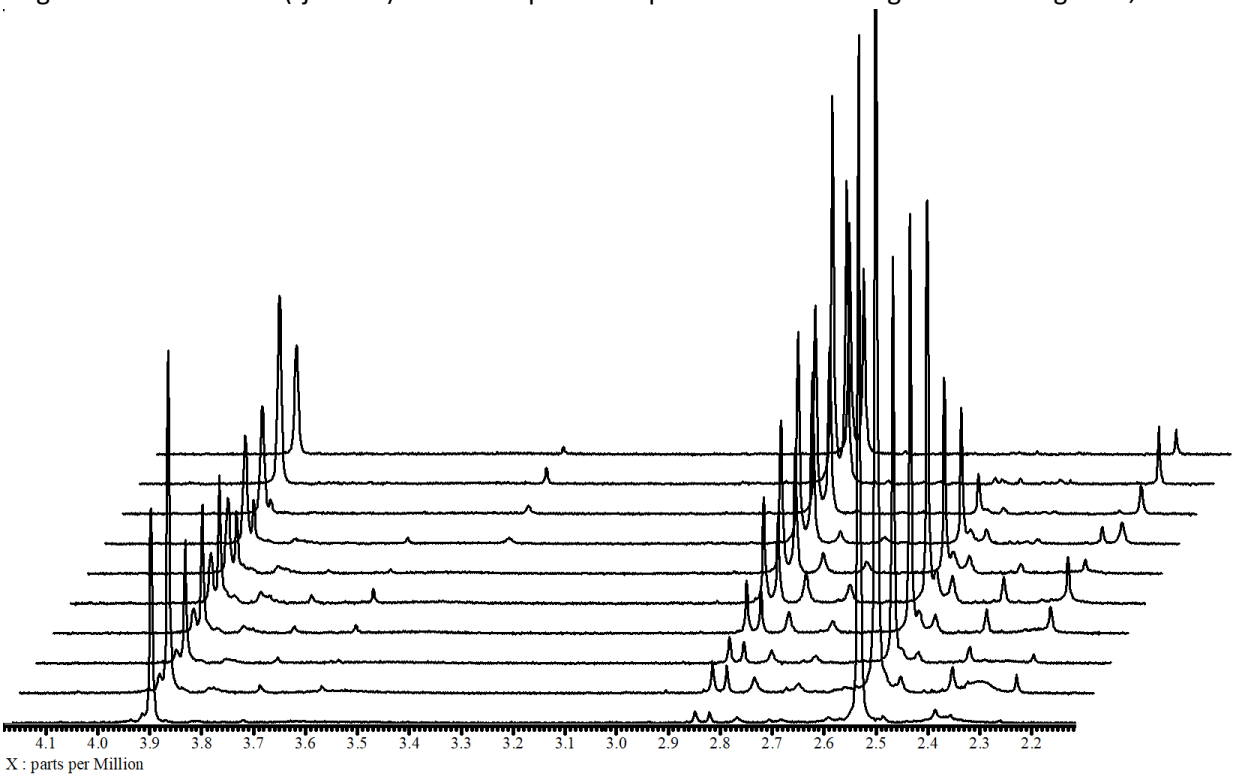


Figure S-28. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the neat mechanosynthesis of $[Pd(DMBA)Cl]_2$ (**3**) at 30 minute intervals until 300 minutes (top). All samples were taken from a single reaction mixture (rja-4-21) and correspond to a portion of the average values in Figure 2, **3**▲.

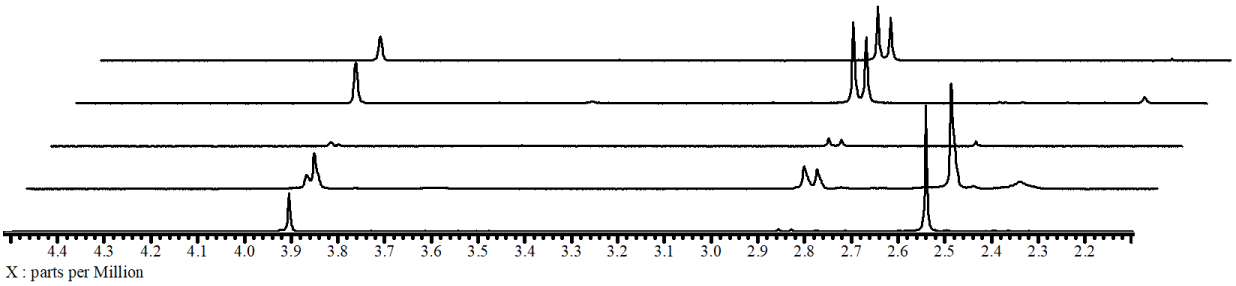


Figure S-29. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixtures for the neat mechanosynthesis of $[Pd(DMBA)Cl]_2$ (**3**) at minute 60 intervals until 300 minutes (top). Each spectrum is from a different reaction (bottom to top: ta-1-5, ta-1-5b, tma-1-5c, jh-1-22a, and jh-1-22b). These data correspond to Figure 2, **3**△.

4.4. $[Pd(EMBA)Cl]_2$ (4):

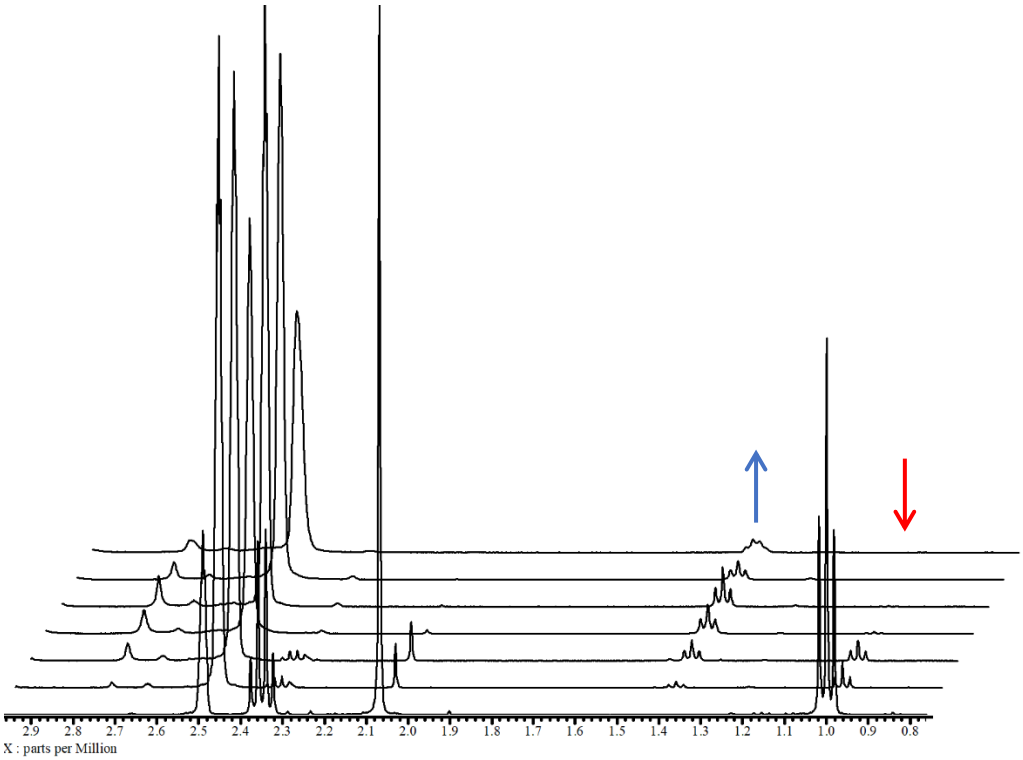


Figure S-30. Section of ^{1}H NMR spectra in DMSO-d_6 of *N*-ethyl-*N*-methylbenzylamine (HEMBA, bottom) and the reaction mixture for the η=0.9 MeOH LAG mechanosynthesis of $[Pd(EMBA)Cl]_2$ (**4**) at 15, 30, 60, 90, and 120 minutes until 150 minutes (top). All samples were taken from a single reaction mixture (rja-4-47a) and correspond to a portion of the average values in Figure 2, **4**■. Resonances of HEMBA (↓) and **4** (↑) used for determination of conversion fraction (α) marked.

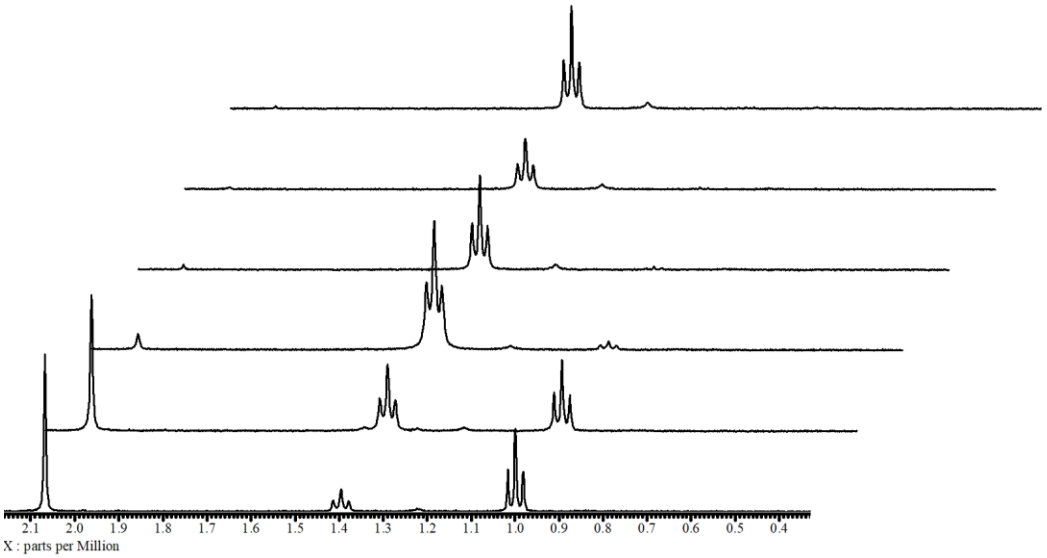


Figure S-31. Section of ^{1}H NMR spectra in DMSO-d_6 of the reaction mixture for the η=0.9 MeOH LAG mechanosynthesis of [Pd(EMBA)Cl]$_2$ (**4**) at 15, 30, 60, 90, and 120 minutes until 150 minutes (top). All samples were taken from a single reaction mixture (rja-4-47b) and correspond to a portion of the average values in Figure 2, **4** ■ .

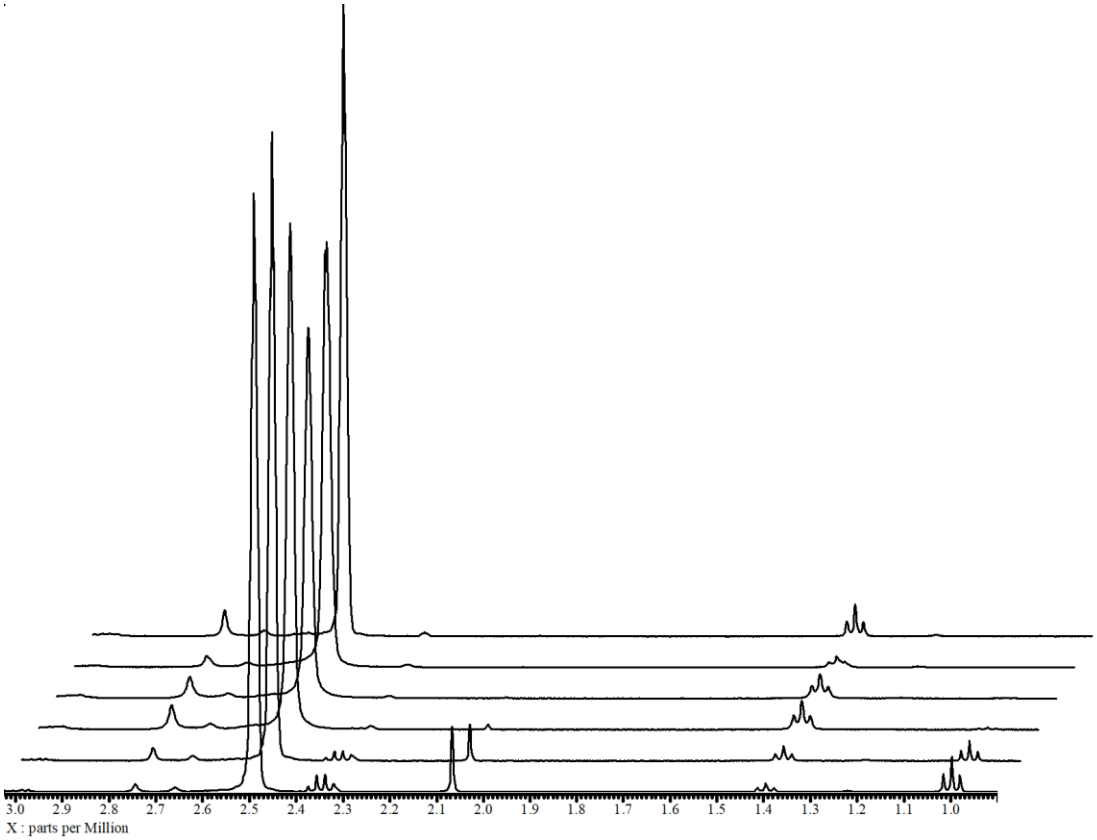


Figure S-32. Section of ^{1}H NMR spectra in DMSO-d_6 of the reaction mixture for the η=0.9 MeOH LAG mechanosynthesis of [Pd(EMBA)Cl]$_2$ (**4**) at 15, 30, 60, 90, and 120 minutes until 150 minutes (top). All samples were taken from a single reaction mixture (rja-4-47c) and correspond to a portion of the average values in Figure 2, **4** ■ .

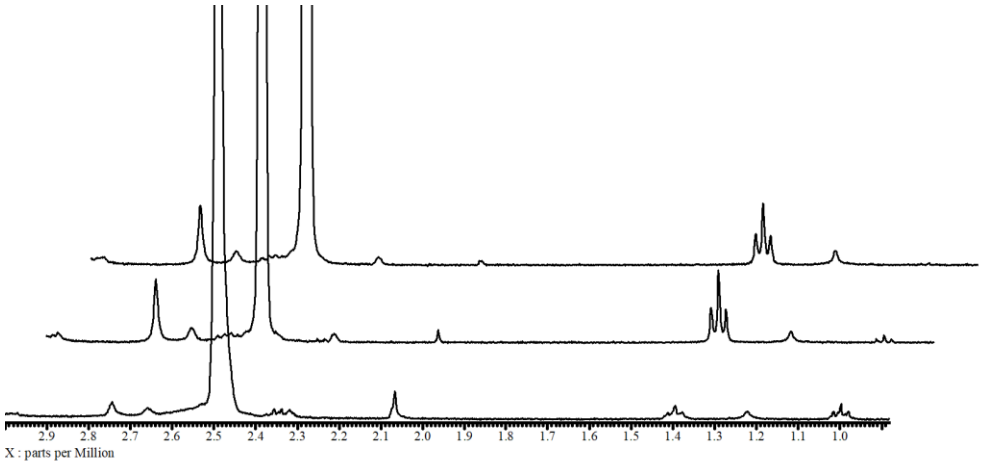


Figure S-33. Section of ^{1}H NMR spectra in DMSO-d_6 of the reaction mixtures for the η=0.9 MeOH LAG mechanosynthesis of [Pd(EMBA)Cl]$_2$ (**4**) at 30, 60, and 120 minutes (top). Each spectrum is from a different reaction (bottom to top: ta-1-9a, ta-1-9b, and ta-12a). These data correspond to Figure 2, **4**□.

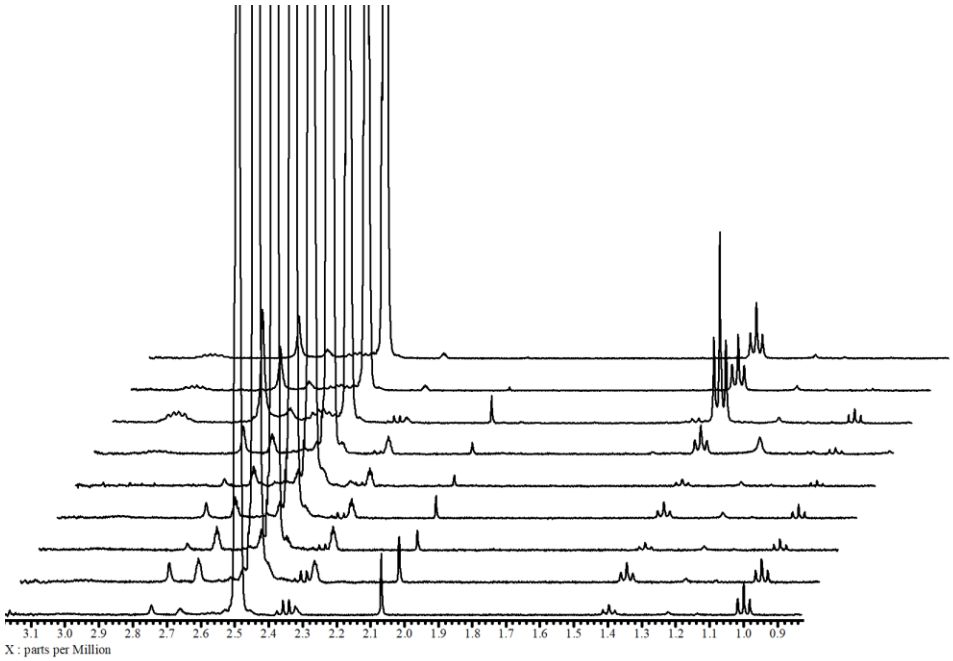


Figure S-34. Section of ^{1}H NMR spectra in DMSO-d_6 of the reaction mixture for the η=0.3 DMSO-d_6 LAG mechanosynthesis of [Pd(EMBA)Cl]$_2$ (**4**) at 30 minute intervals until 270 minutes (top). All samples were taken from a single reaction mixture (tma-1-50a) and correspond to a portion of the average values in Figure 2, **4**●.

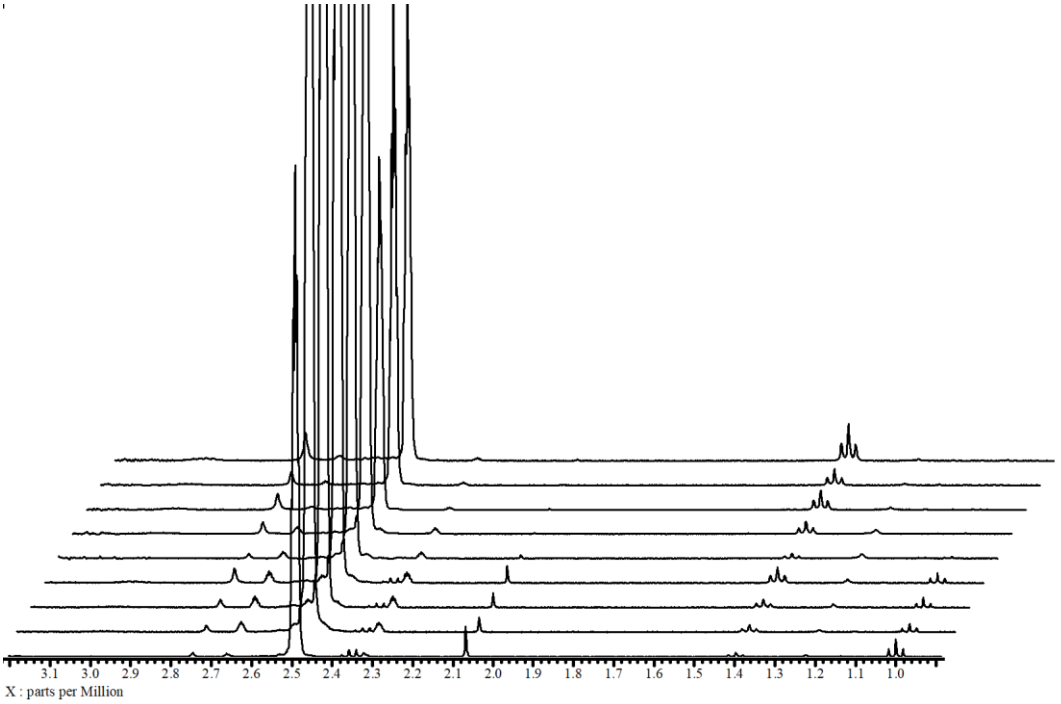


Figure S-35. Section of ^{1}H NMR spectra in DMSO-d_6 of the reaction mixture for the η=0.3 DMSO-d_6 LAG mechanosynthesis of [Pd(EMBA)Cl]$_2$ (**4**) at 30 minute intervals until 270 minutes (top). All samples were taken from a single reaction mixture (tma-1-50b) and correspond to a portion of the average values in Figure 2, **4**●.

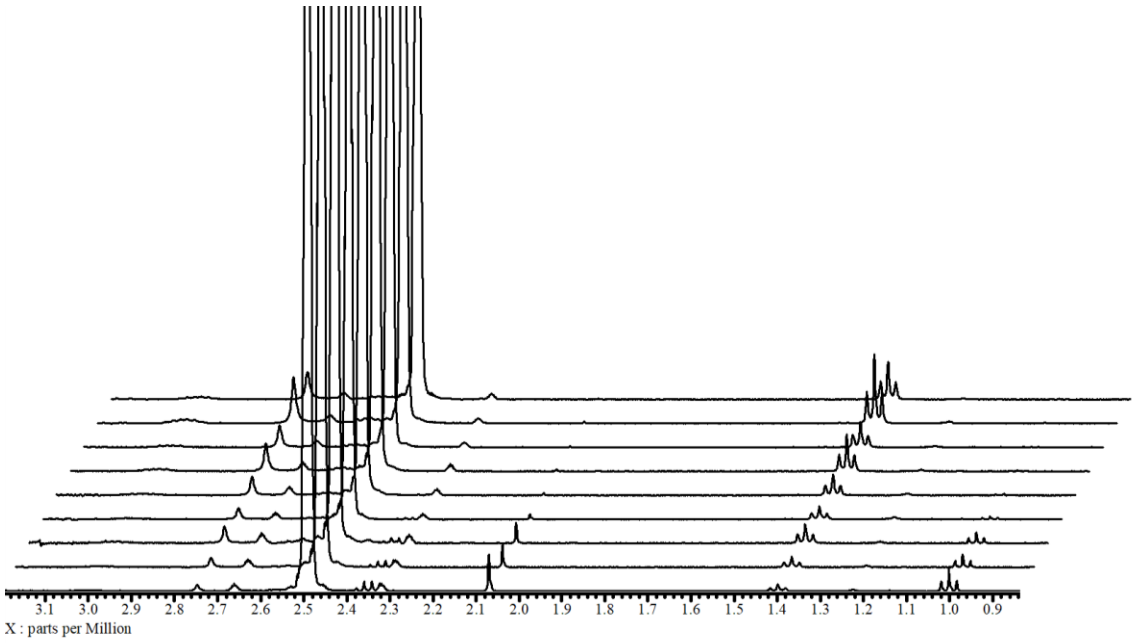


Figure S-36. Section of ^{1}H NMR spectra in DMSO-d_6 of the reaction mixture for the η=0.3 DMSO-d_6 LAG mechanosynthesis of [Pd(EMBA)Cl]$_2$ (**4**) at 30 minute intervals until 270 minutes (top). All samples were taken from a single reaction mixture (jbs-1-43) and correspond to a portion of the average values in Figure 2, **4**●.

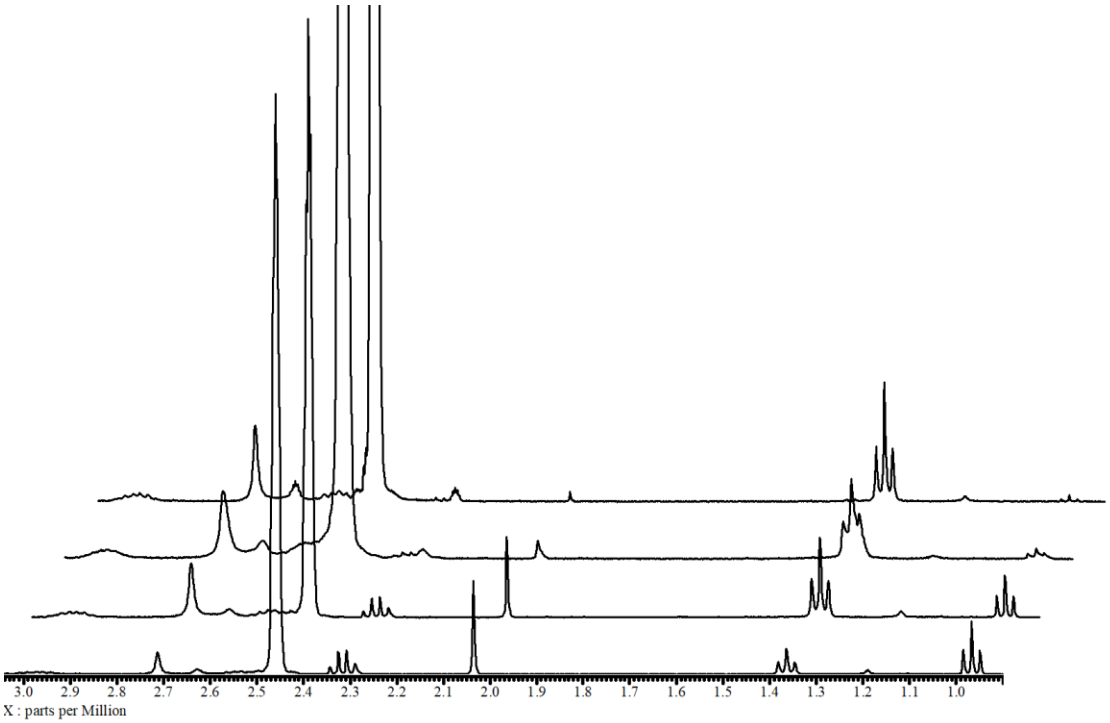


Figure S-37. Section of ^{1}H NMR spectra in DMSO-d_6 of the reaction mixtures for the η=0.3 DMSO-d_6 LAG mechanosynthesis of [Pd(EMBA)Cl]$_2$ (**4**) at 60, 120, and 180 minutes (top). Each reaction mixture spectrum is from a different reaction (bottom to top: rja-4-82a, rja-4-82b, rja-4-82c, and rja-4-82d). These data correspond to Figure 2, **4**○.

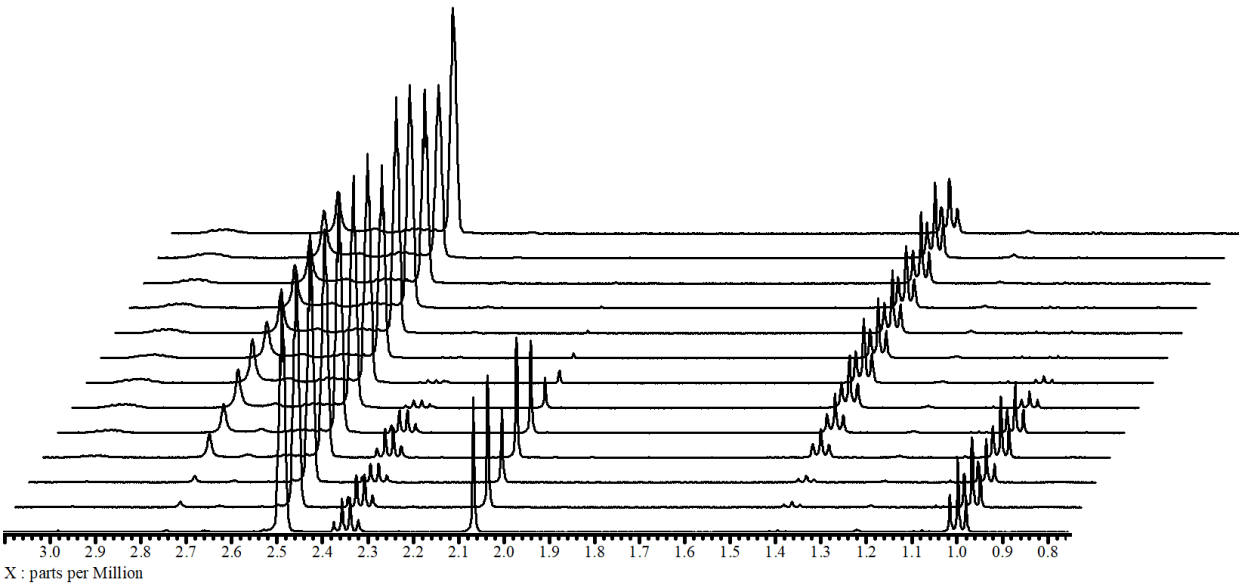


Figure S-38. Section of ^{1}H NMR spectra in DMSO-d_6 of the reaction mixture for the neat mechanosynthesis of [Pd(EMBA)Cl]$_2$ (**4**) at 30 minute intervals until 390 minutes (top). All samples were taken from a single reaction mixture (rja-4-42a) and correspond to a portion of the average values in Figure 2, **4**▲.

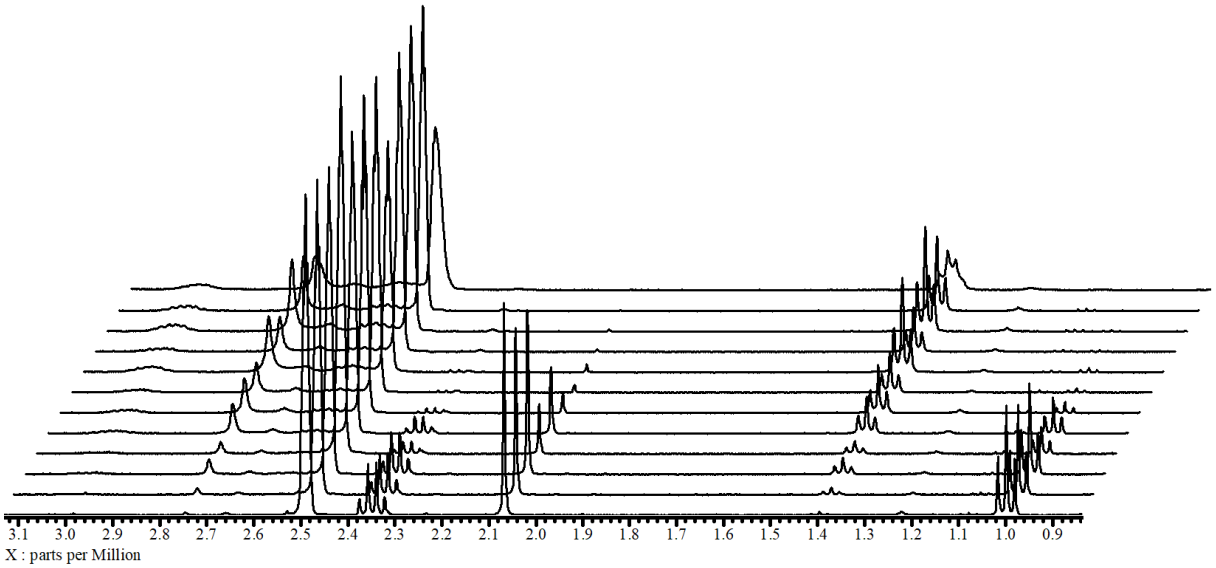


Figure S-39. Section of ^{1}H NMR spectra in DMSO-d_6 of the reaction mixture for the neat mechanosynthesis of [Pd(EMBA)Cl]$_2$ (**4**) at 30 minute intervals until 390 minutes (top). All samples were taken from a single reaction mixture (rja-4-42b) and correspond to a portion of the average values in Figure 2, **4**▲.

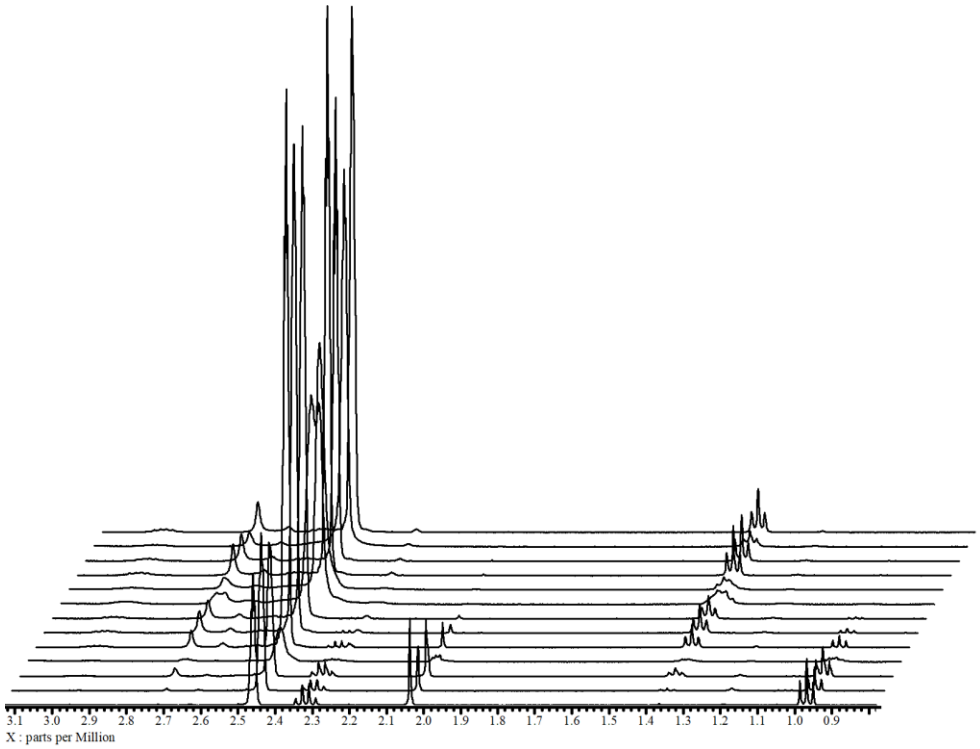


Figure S-40. Section of ^{1}H NMR spectra in DMSO-d_6 of the reaction mixture for the neat mechanosynthesis of [Pd(EMBA)Cl]$_2$ (**4**) at 30 minute intervals until 390 minutes (top). All samples were taken from a single reaction mixture (rja-4-43) and correspond to a portion of the average values in Figure 2, **4**▲.

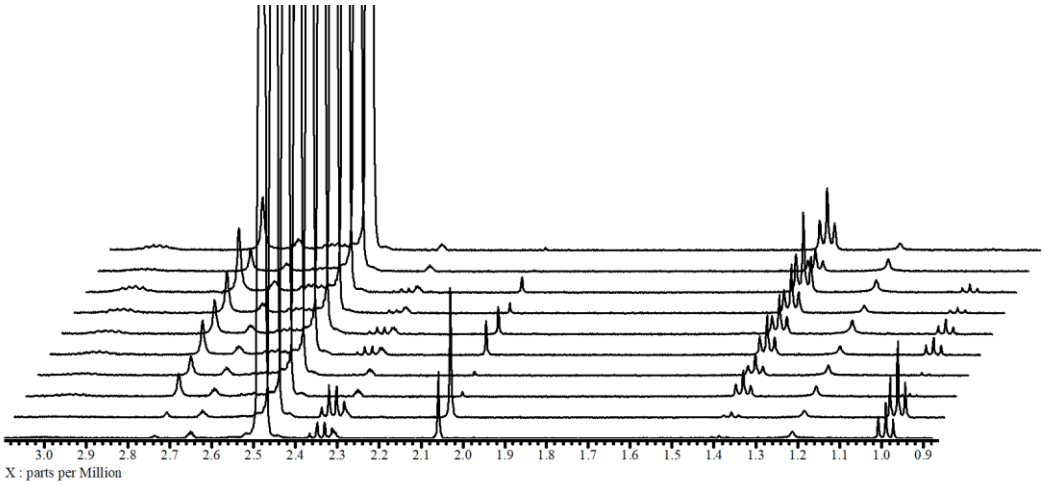


Figure S-41. Section of ^{1}H NMR spectra in DMSO-d_6 of the reaction mixtures for the neat mechanosynthesis of [Pd(EMBA)Cl]$_2$ (**4**) at 60 minute intervals to 300 minutes (top). Two spectra were collected from each reaction mixture, and each sampling time corresponds to a single reaction (bottom to top: jh-1-33b, jh-1-24a, ta-1-14a, jh-1-34b, and jh-1-35a) and correspond to Figure 2, **4**△.

4.6. [Pd(bzq)OAc]$_2$ (5):

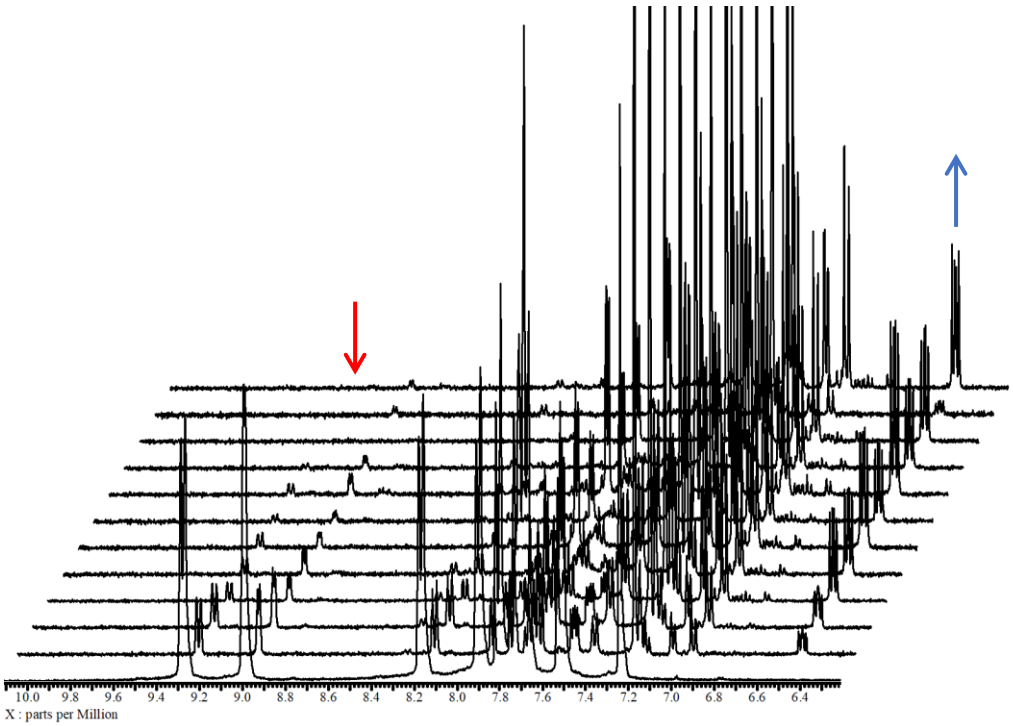


Figure S-42. Section of ^{1}H NMR spectra in $CDCl_3$ of benzo[h]qunioline (Hbzq, bottom) and the reaction mixture for the η=0.5 methanol LAG mechanosynthesis of [Pd(bzq)OAc]$_2$ (**5**) at 10 minute intervals until 120 minutes (top). All samples were taken from a single reaction mixture (rja-4-85) and correspond to a portion of the average values in Figure 2, **5**■. Resonances of Hbzq (↓) and **5** (↑) used for determination of conversion fraction (α) marked.

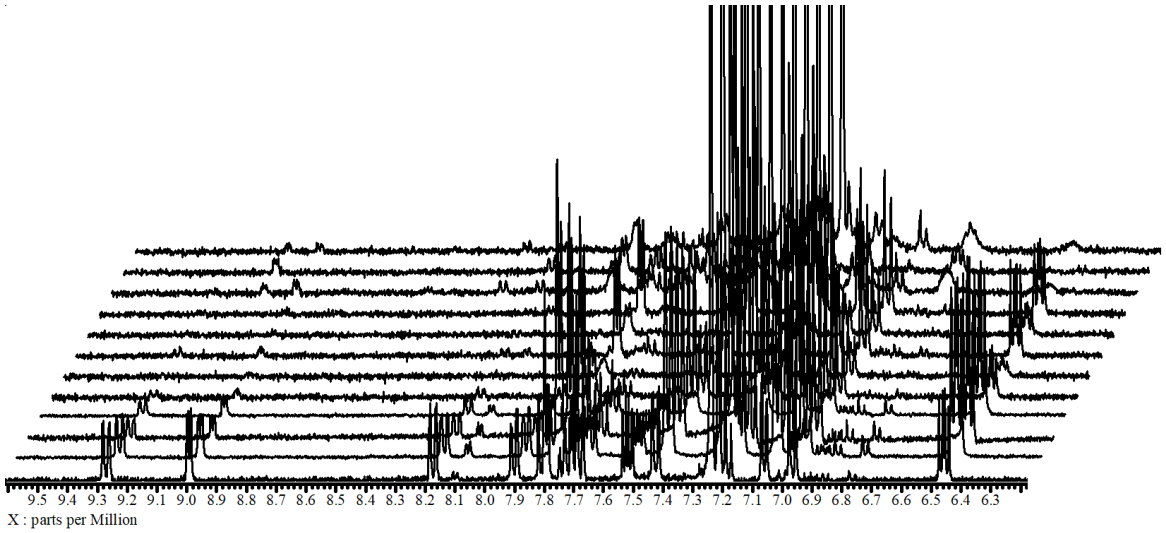


Figure S-43. Section of ^{1}H NMR spectra in $CDCl_3$ of benzo[h]qunioline (Hbzq, bottom) and the reaction mixture for the η=0.5 methanol LAG mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) at 10 minute intervals until 120 minutes (top). All samples were taken from a single reaction mixture (tma-1-51) and correspond to a portion of the average values in Figure 2, **5** ■.

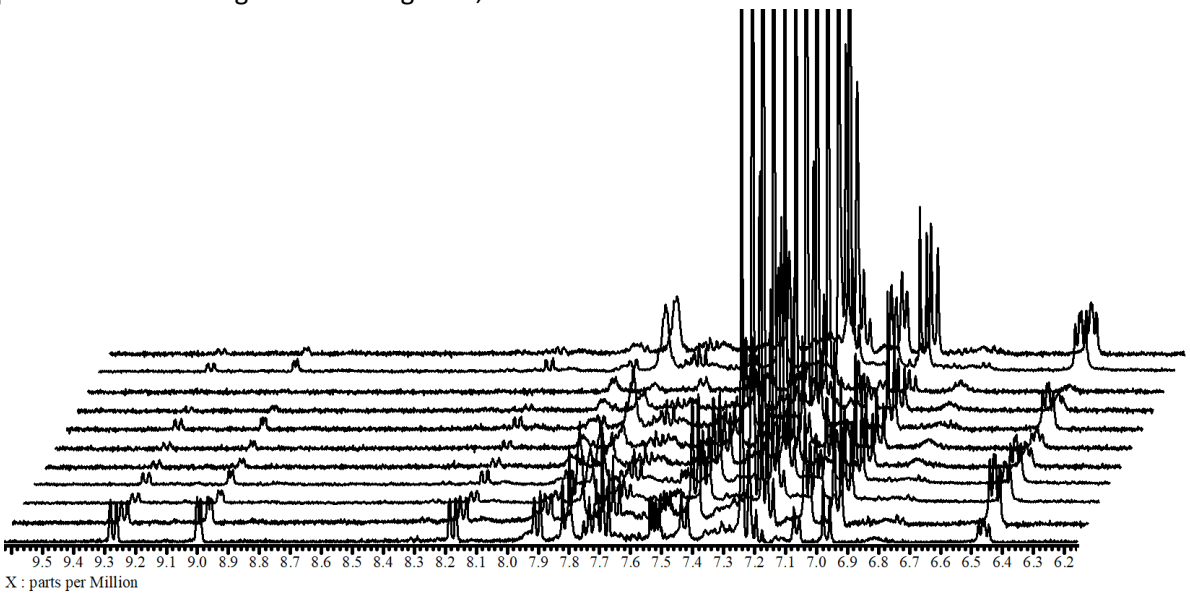


Figure S-44. Section of ^{1}H NMR spectra in $CDCl_3$ of benzo[h]quinoline (Hbzq, bottom) and the reaction mixture for the η=0.5 methanol LAG mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) at 10 minute intervals until 120 minutes (top). All samples were taken from a single reaction mixture (tma-1-52) and correspond to a portion of the average values in Figure 2, **5** ■.

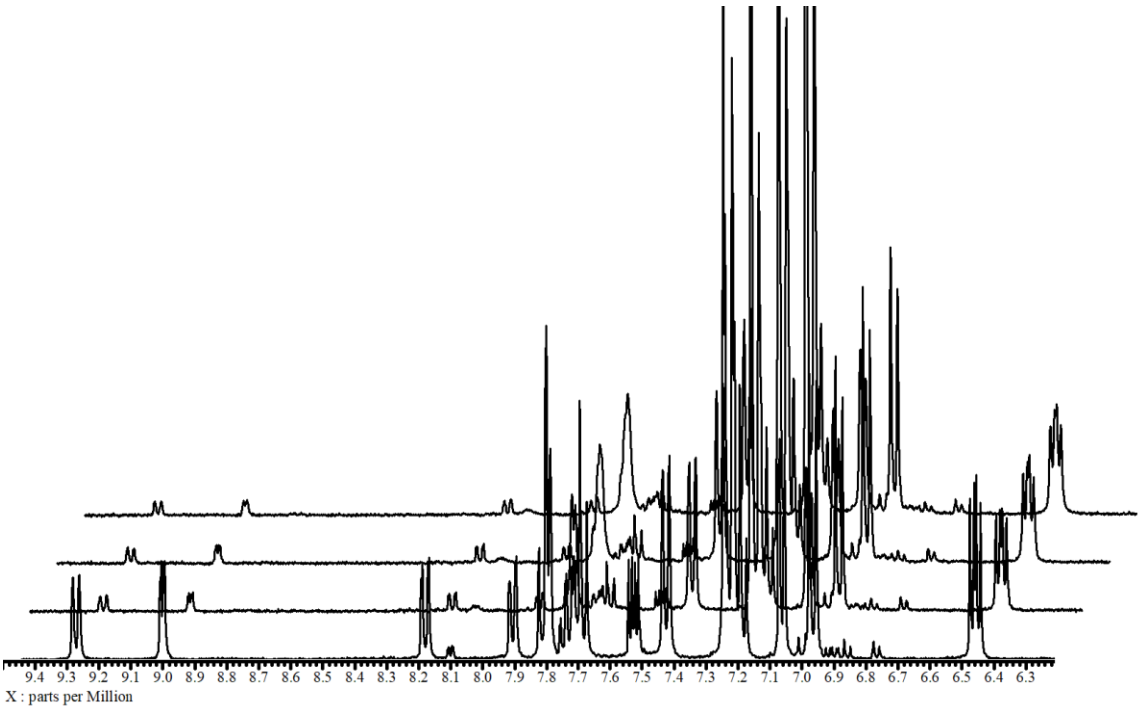


Figure S-45. Section of ^{1}H NMR spectra in $CDCl_3$ of benzo[h]quinoline (Hbzq, bottom) and the reaction mixture for the η=0.5 methanol LAG mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) at 20, 40, 80, and 120 minutes (top). Each spectrum is from a different reaction (bottom to top: ta-1-9a, ta-1-9b, and ta-12a). These data correspond to Figure 2, **5**□.

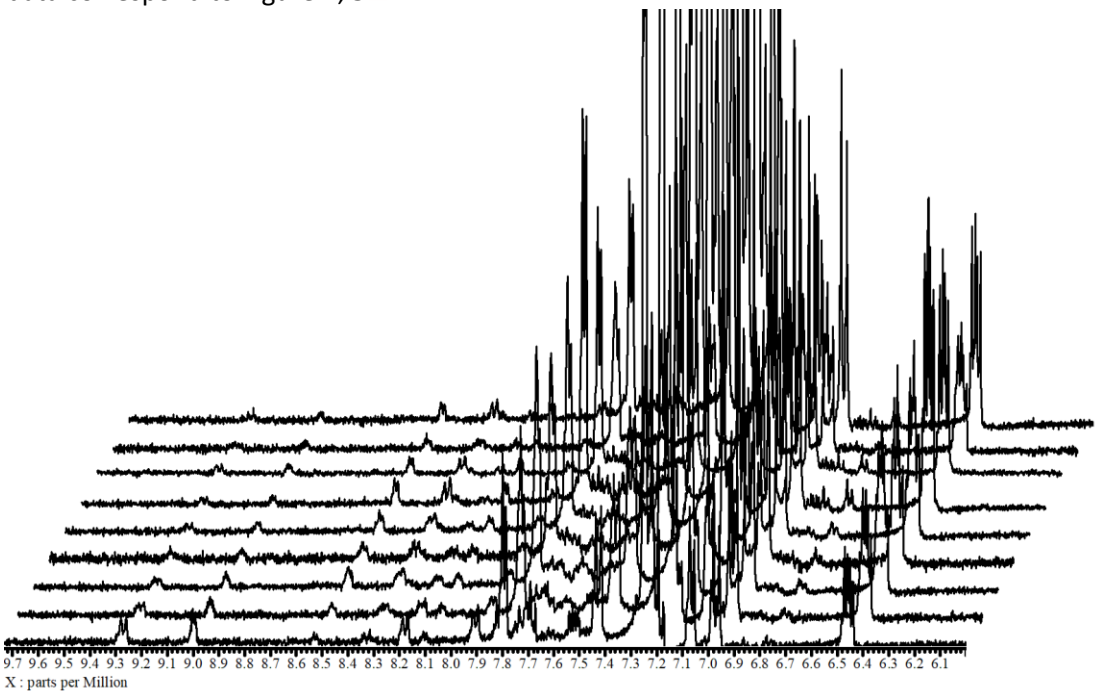


Figure S-46. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.3 DMSO-d_6 LAG mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) at 10 minute intervals until 90 minutes (top). All samples were taken from a single reaction mixture (rja-4-100) and correspond to a portion of the average values in Figure 2, **5**●.

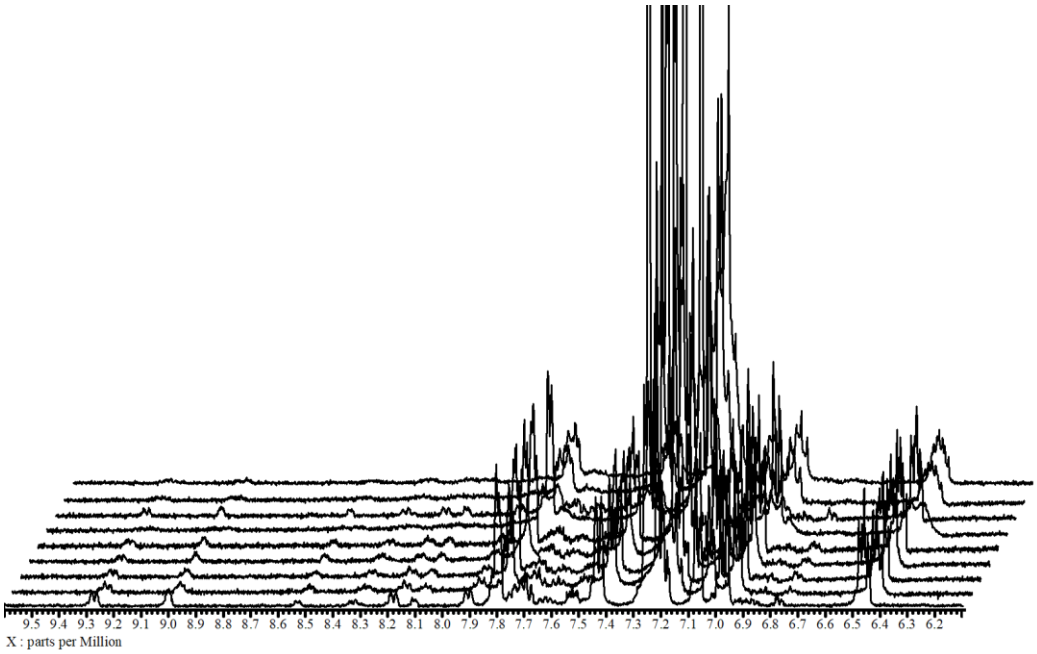


Figure S-47. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.3 DMSO-d_6 LAG mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) at 10 minute intervals until 90 minutes (top). All samples were taken from a single reaction mixture (tma-1-86) and correspond to a portion of the average values in Figure 2, **5●**.

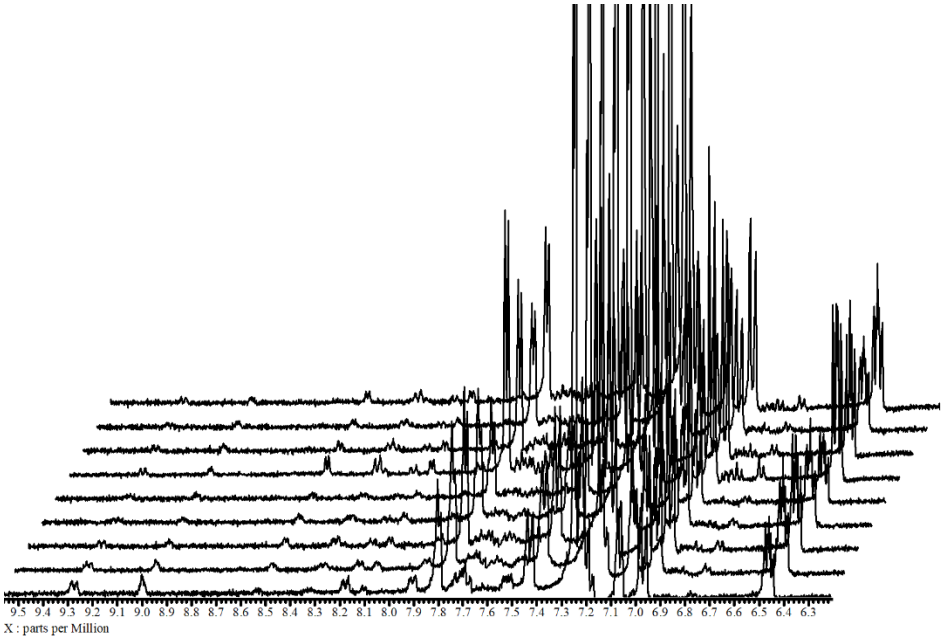


Figure S-48. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.3 DMSO-d_6 LAG mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) at 10 minute intervals until 90 minutes (top). All samples were taken from a single reaction mixture (rja-4-101a) and correspond to a portion of the average values in Figure 2, **5●**.

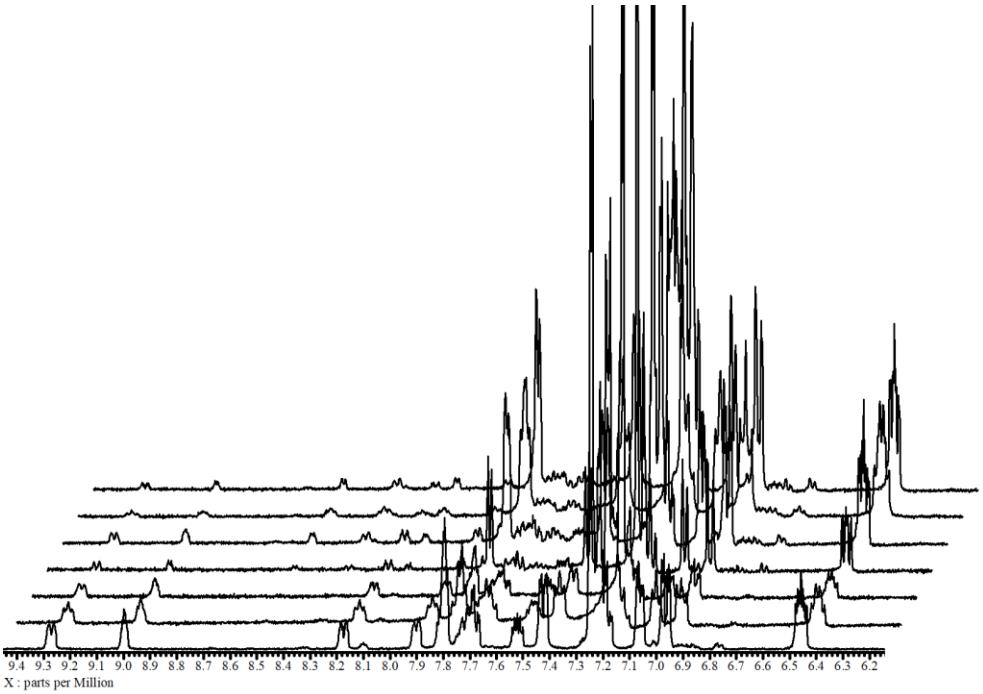


Figure S-49. Section of ^{1}H NMR spectra in $CDCl_3$ of benzo[h]quinoline (Hbzq, bottom) and the reaction mixture for the η=0.3 DMSO-d_6 LAG mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) at 2.5, 2.5, 5, 5, 20, 40, and 60 minutes (top). Each spectrum is from a different reaction (bottom to top: tma-1-88, tma-1-89a, rja-4-101, tma-1-89b, tma-1-87a, tma-1-87b, and tma-1-87c). These data correspond to Figure 2, **5**○.

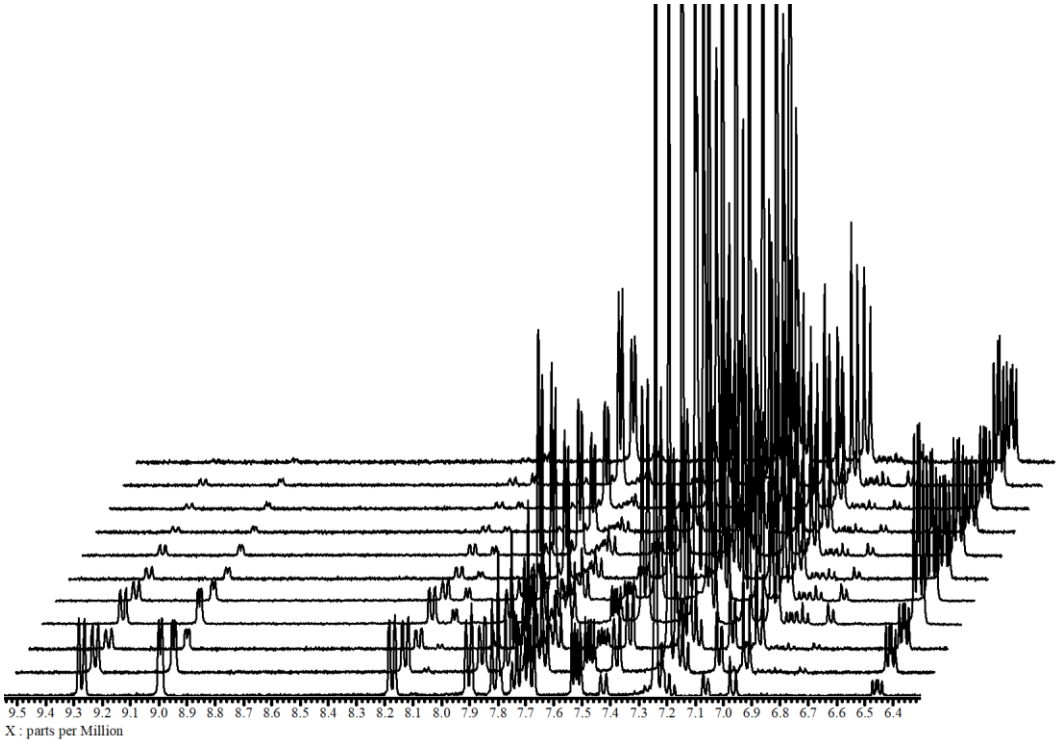


Figure S-50. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the neat mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) at 30 minute intervals until 330 minutes (top). All samples were taken from a single reaction mixture (rja-4-60a) and correspond to a portion of the average values in Figure 2, **5**▲.

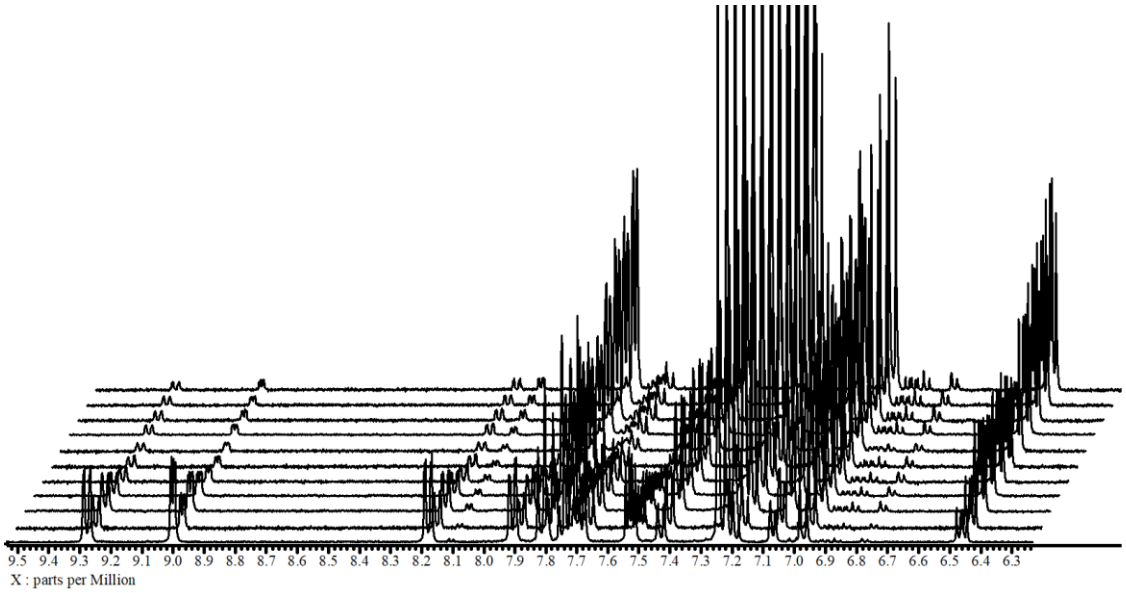


Figure S-51. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the neat mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) at 30 minute intervals until 330 minutes (top). All samples were taken from a single reaction mixture (rja-4-62a) and correspond to a portion of the average values in Figure 2, **5**▲.

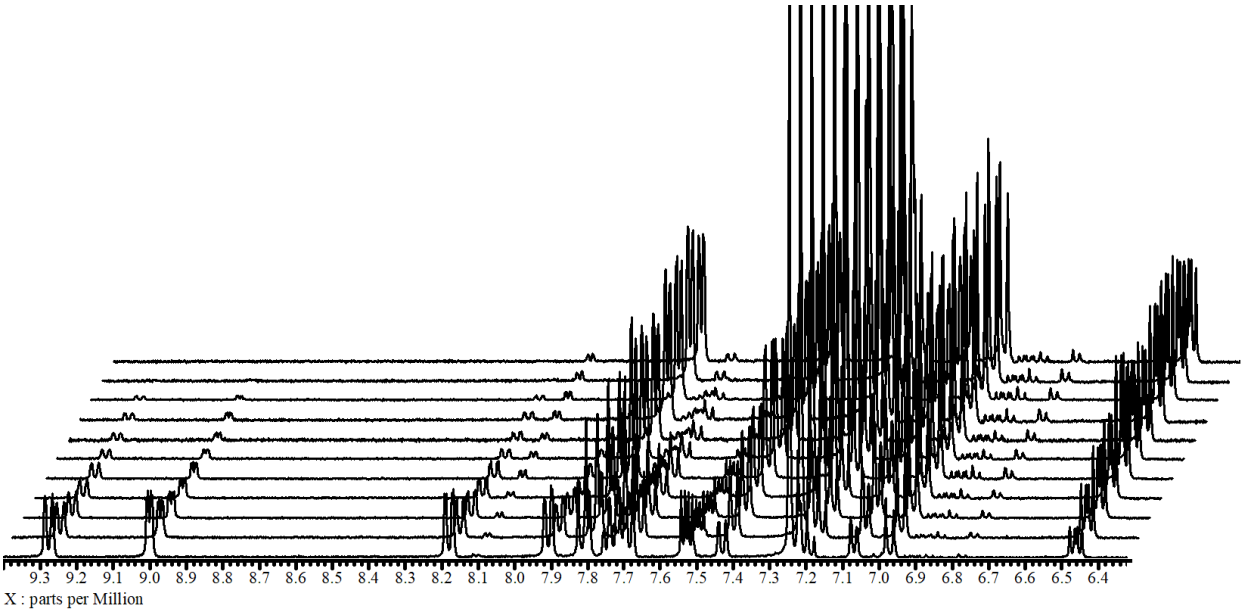


Figure S-52. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the neat mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) at 30 minute intervals until 330 minutes (top). All samples were taken from a single reaction mixture (rja-4-62b) and correspond to a portion of the average values in Figure 2, **5**▲.

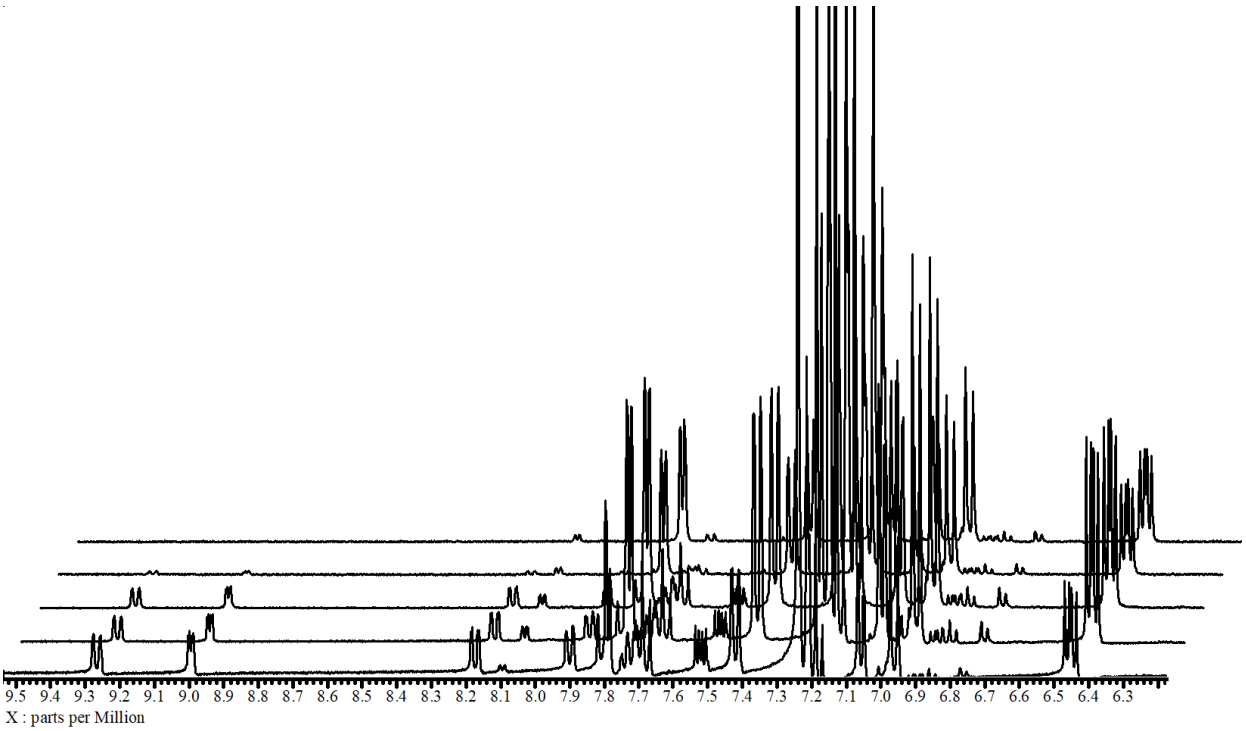


Figure S-53. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixtures for the neat mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) at 60, 120, 180, 240 and 300 minutes (top). Each reaction mixture spectrum is from a different reaction (bottom to top: rja-4-59c, rja-4-59d, rja-4-59e, rja-4-62d, and rja-4-62f). These data correspond to Figure 2, **5**△.

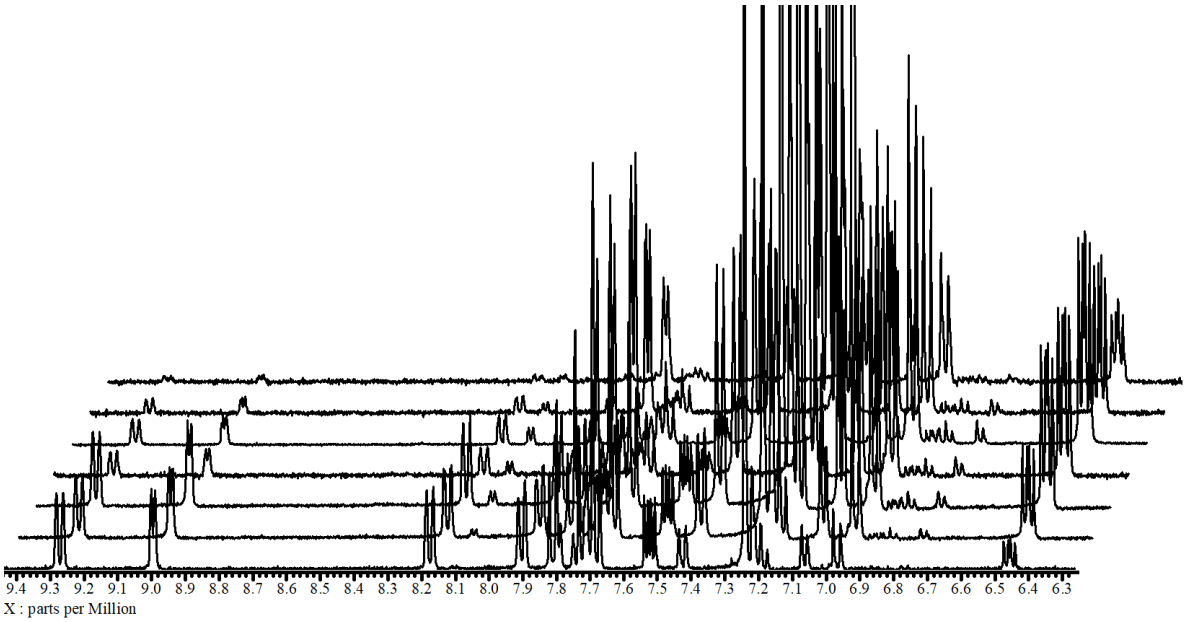


Figure S-54. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.5 EtOH LAG mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) at 10, 20, 30, 60, 90, 120, and 150 minutes until 330 minutes (top). All samples were taken from a single reaction mixture (jh-1-75a) and correspond to a portion of the average values in Figure 4, ◆.

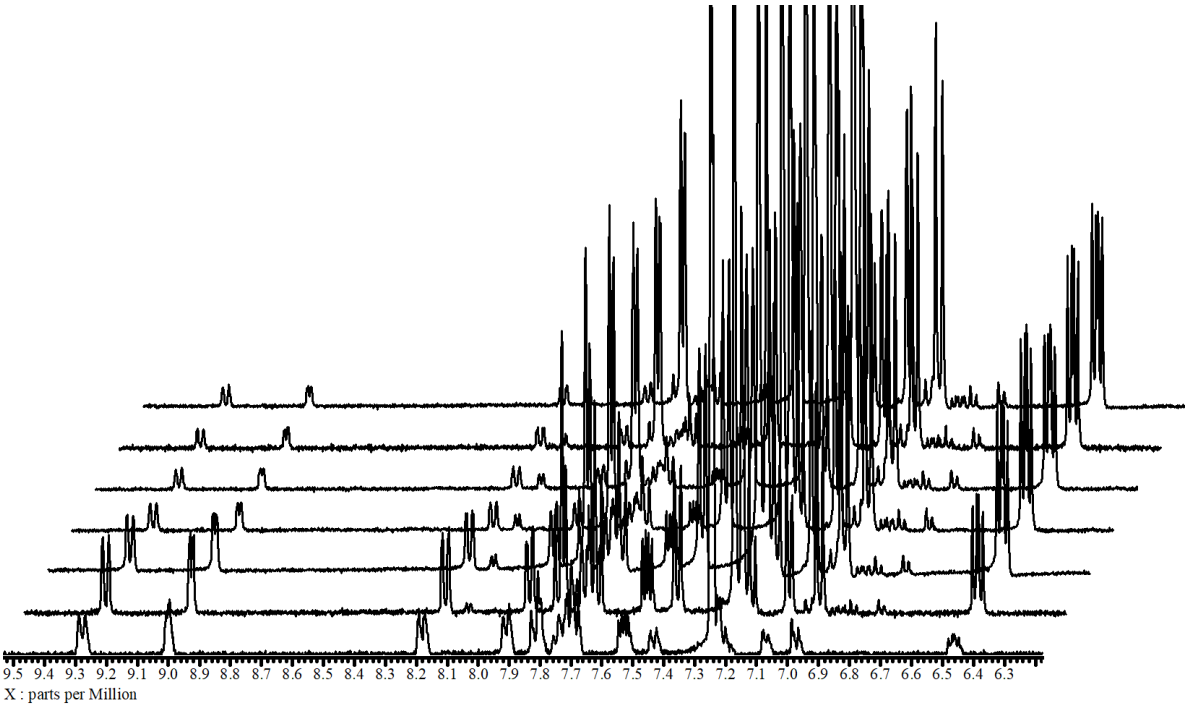


Figure S-55. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.5 EtOH LAG mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) at 10, 20, 30, 60, 90, 120, and 150 minutes until 330 minutes (top). All samples were taken from a single reaction mixture (jh-1-75b) and correspond to a portion of the average values in Figure 4, ◆.

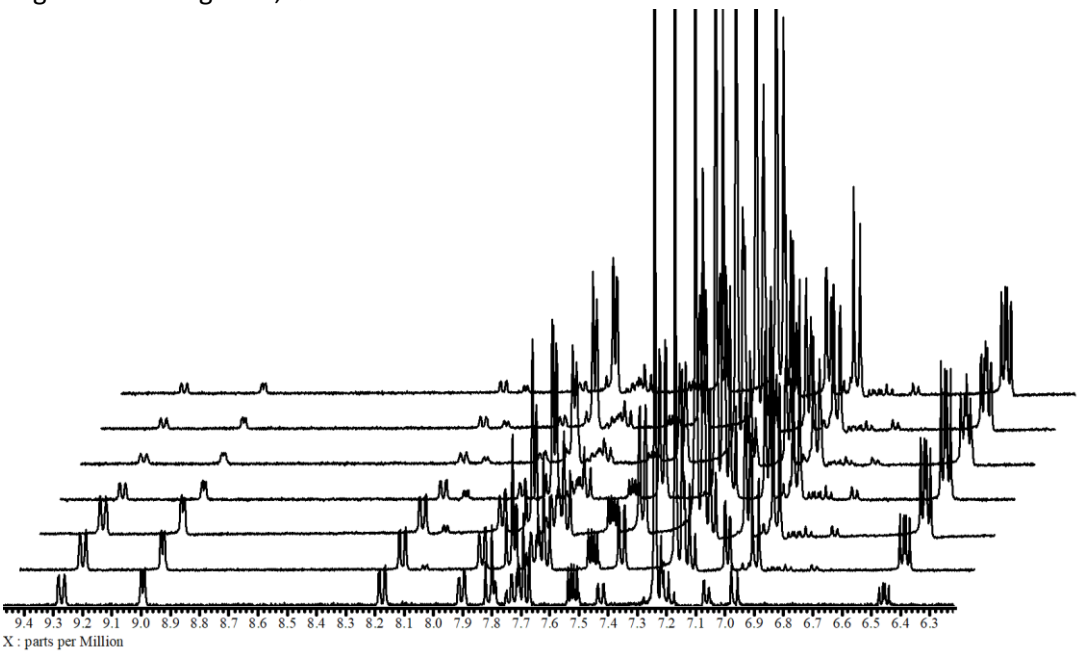


Figure S-56. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the η=0.5 EtOH LAG mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) at 10, 20, 30, 60, 90, 120, and 150 minutes until 330 minutes (top). All samples were taken from a single reaction mixture (jh-1-75c) and correspond to a portion of the average values in Figure 4, ◆.

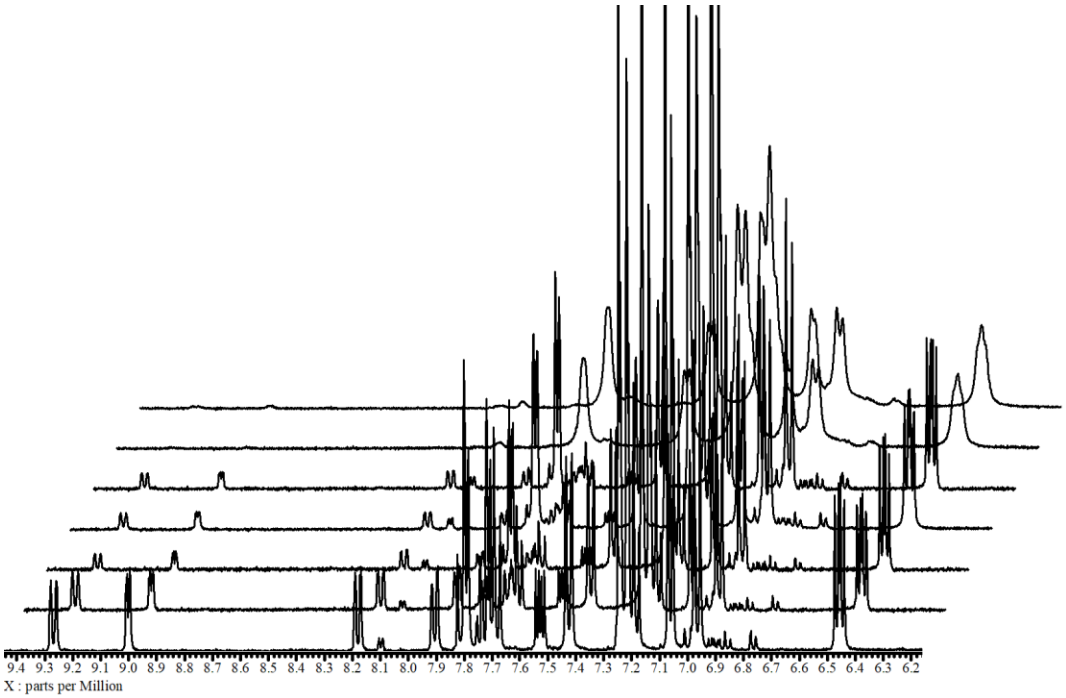


Figure S-57. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixtures for the η=0.5 EtOH LAG mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) at 30, 60, 90, 120, 150, 180, and 210 minutes (top). Each reaction mixture spectrum is from a different reaction (bottom to top: jh-1-65a, jh-1-65b, jh-1-64a, jh-1-63b, jh-1-63a, jh-1-62b, and jh-1-62a). These data correspond to Figure 4, ◇.

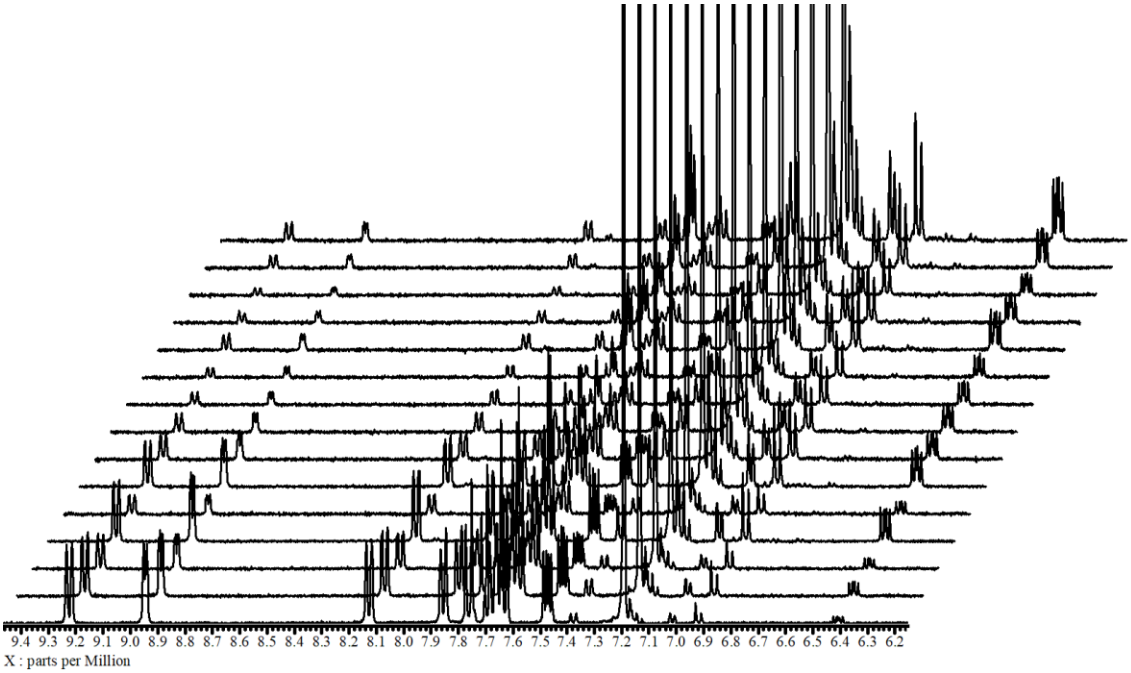


Figure S-58. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the neat mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) with the addition of Na_2CO_3 at 20 minute intervals until 300 minutes (top). All samples were taken from a single reaction mixture (rja-4-56) and correspond to a portion of the average values in Figure 4, ■.

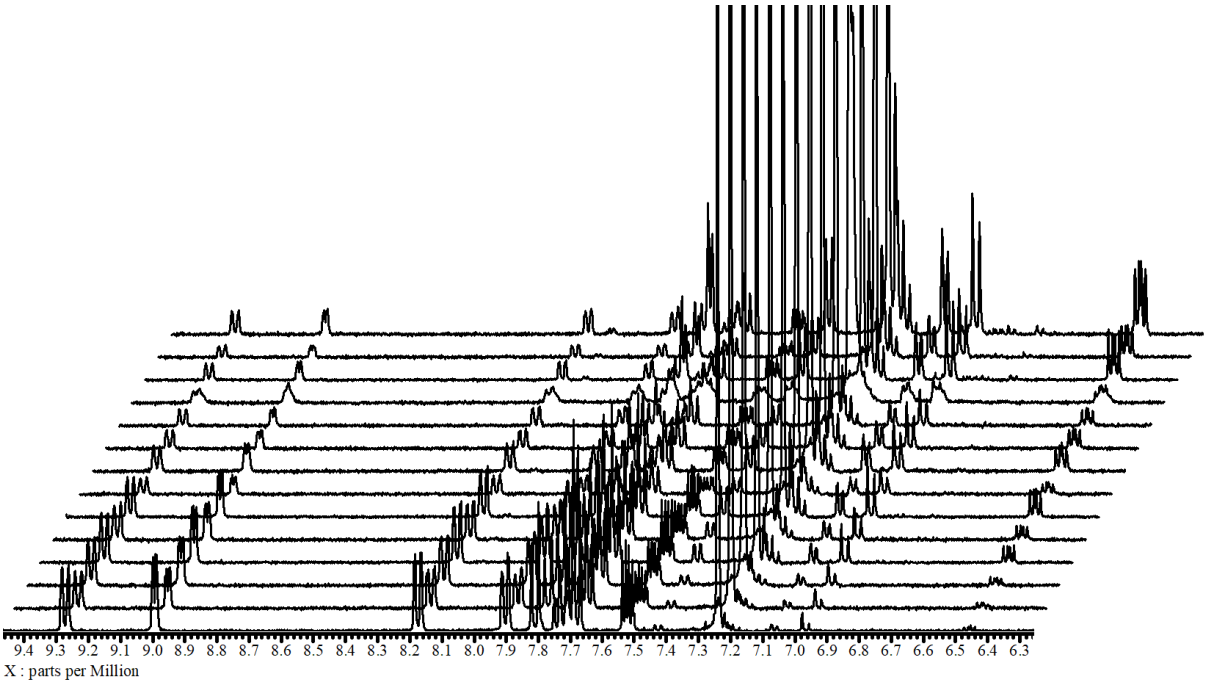


Figure S-59. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the neat mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) with the addition of Na_2CO_3 at 20 minute intervals until 300 minutes (top). All samples were taken from a single reaction mixture (rja-4-57a) and correspond to a portion of the average values in Figure 4, ■.

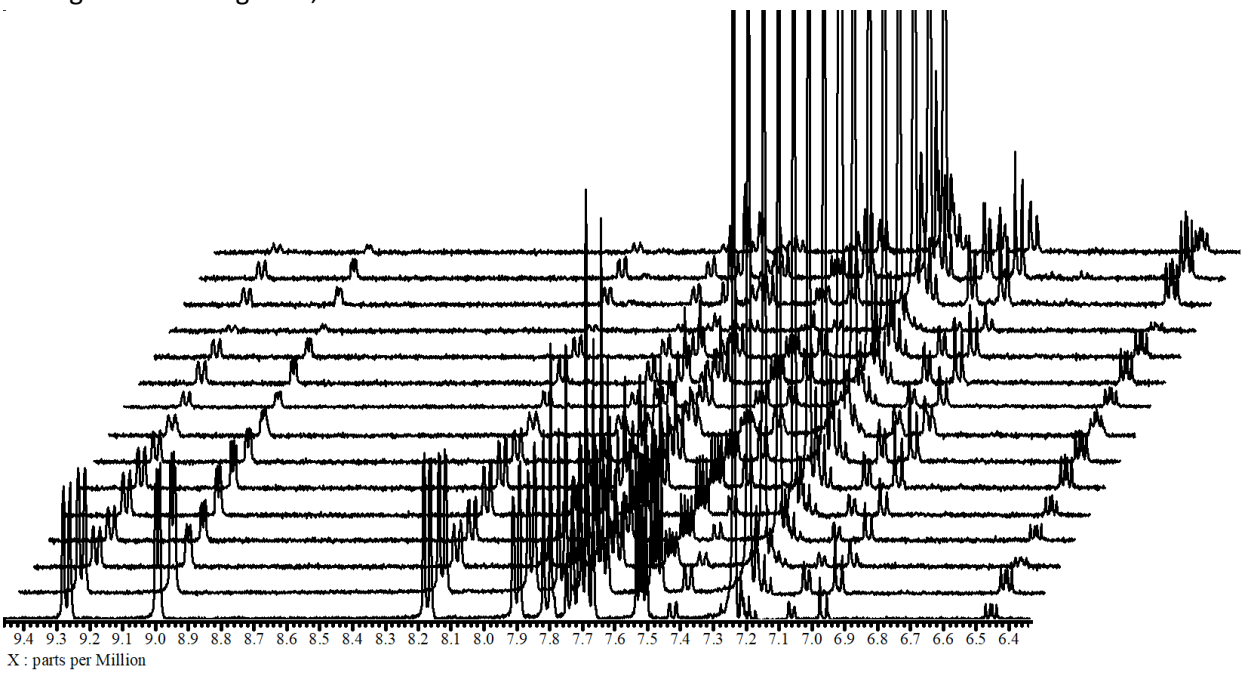


Figure S-60. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture for the neat mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) with the addition of Na_2CO_3 at 20 minute intervals until 300 minutes (top). All samples were taken from a single reaction mixture (rja-4-57b) and correspond to a portion of the average values in Figure 4, ■.

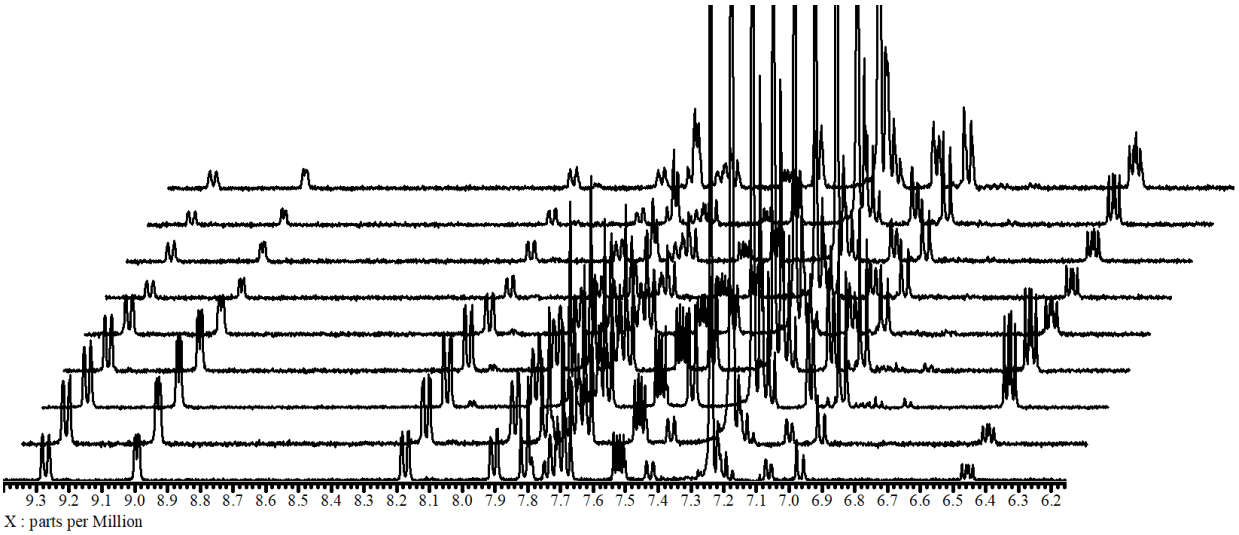
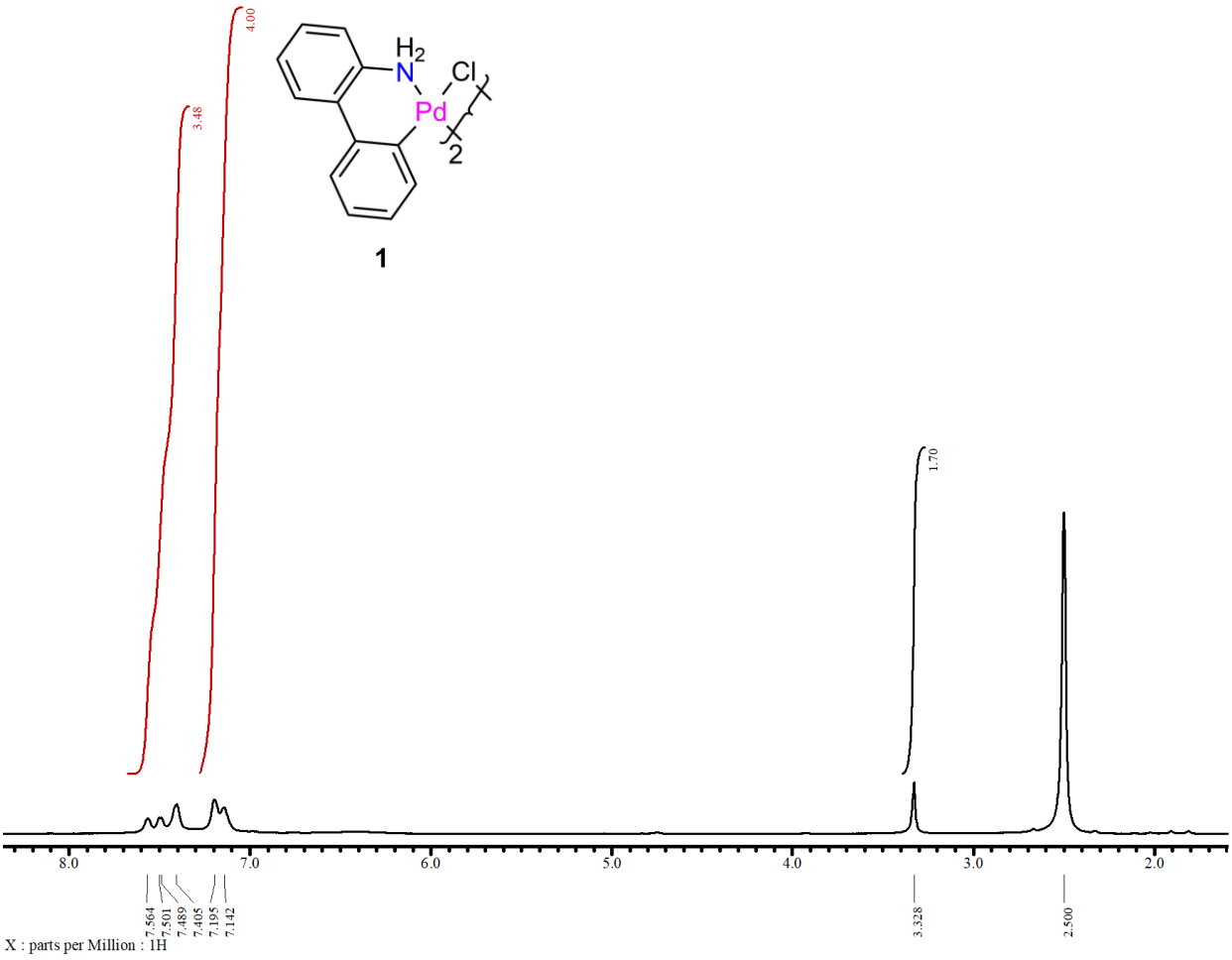


Figure S-61. Section of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixtures for the neat mechanosynthesis of $[Pd(bzq)OAc]_2$ (**5**) with the addition of Na_2CO_3 at 60, 60, 120, 120, 120, 180, 180, 240, and 240 minutes (top). Each spectrum is from a different reaction (bottom to top: rja-4-58a, rja-4-61a, rja-4-59b, rja-4-63a, rja-4-63d, rja-4-63b, rja-4-63e, rja-4-62e, and rja-4-63c). These data correspond to Figure 4, .

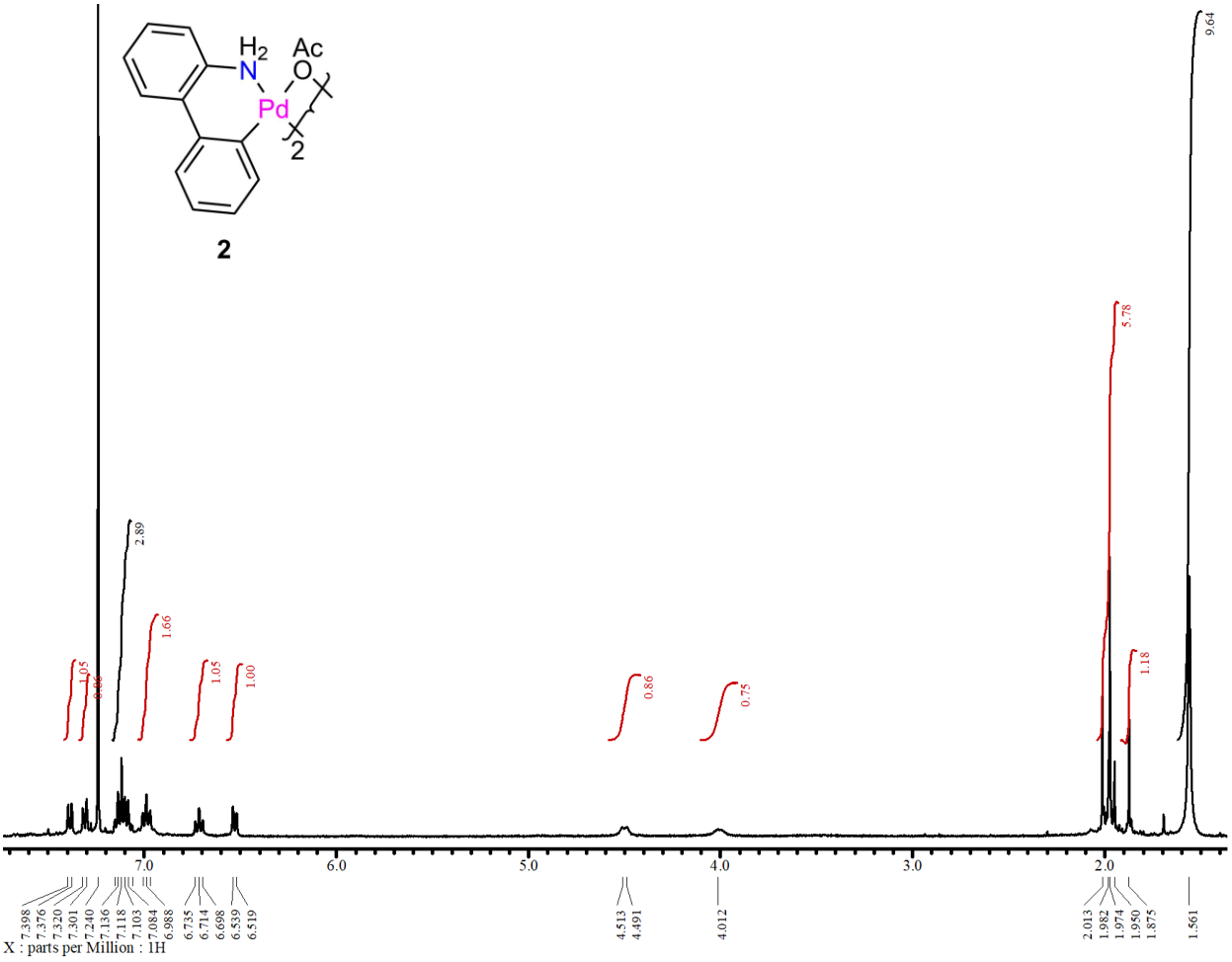
4.7. Product Spectra

4.7.1 $[Pd(2\text{-}ADP)Cl]_2$ (1)

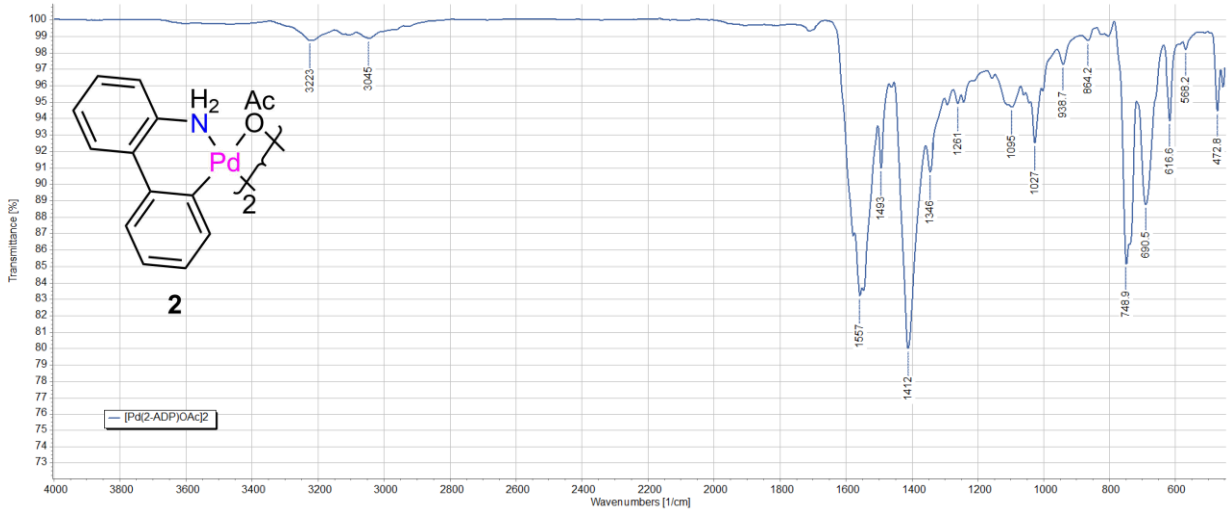


4.7.2 $[Pd(2\text{-}ADP)OAc]_2$ (2)

^{1}H NMR Spectrum ($CDCl_3$):

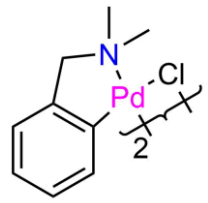


IR Spectrum (ATR):



4.7.3 $[Pd(DMBA)Cl]_2$ (3)

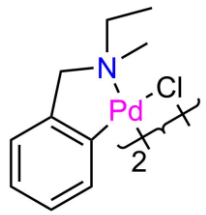
^1H NMR Spectrum (CD_2Cl_2)



3

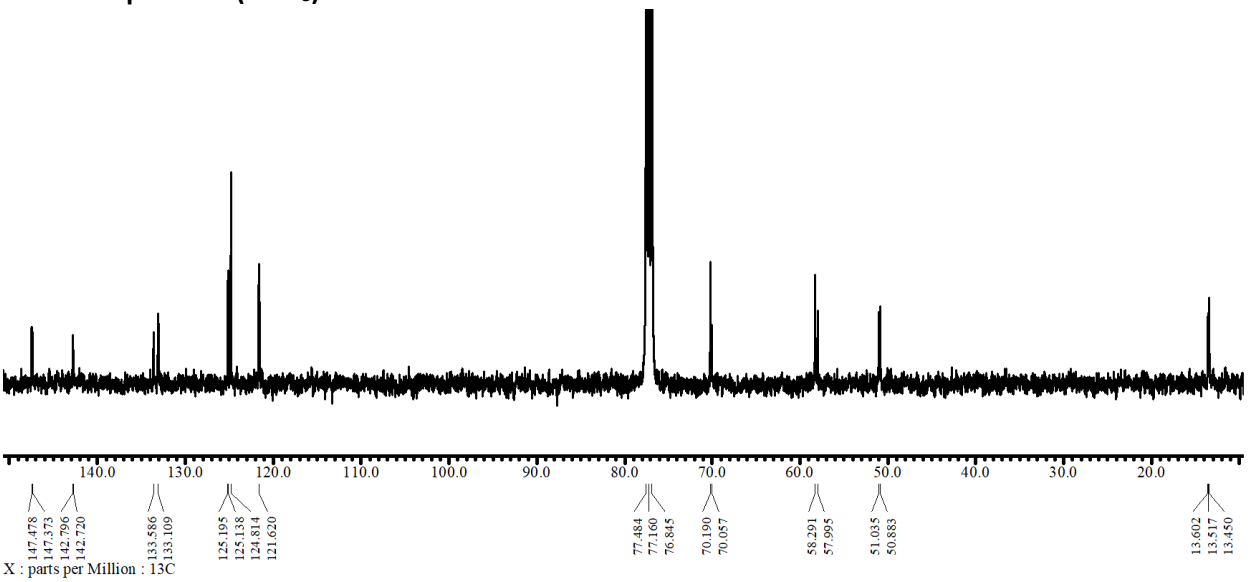
4.7.4 $[Pd(EMBA)Cl]_2$ (4)

^{1}H NMR Spectrum ($CDCl_3$)

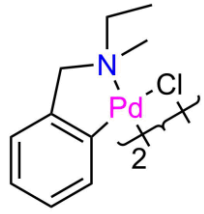


4

^{13}C NMR Spectrum ($CDCl_3$)

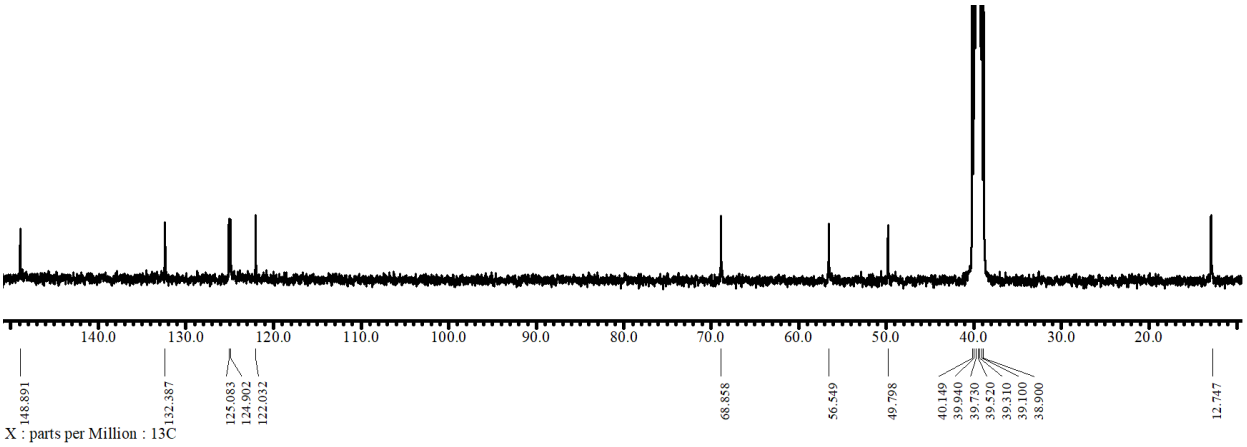


^{1}H NMR Spectrum (DMSO-d_6)

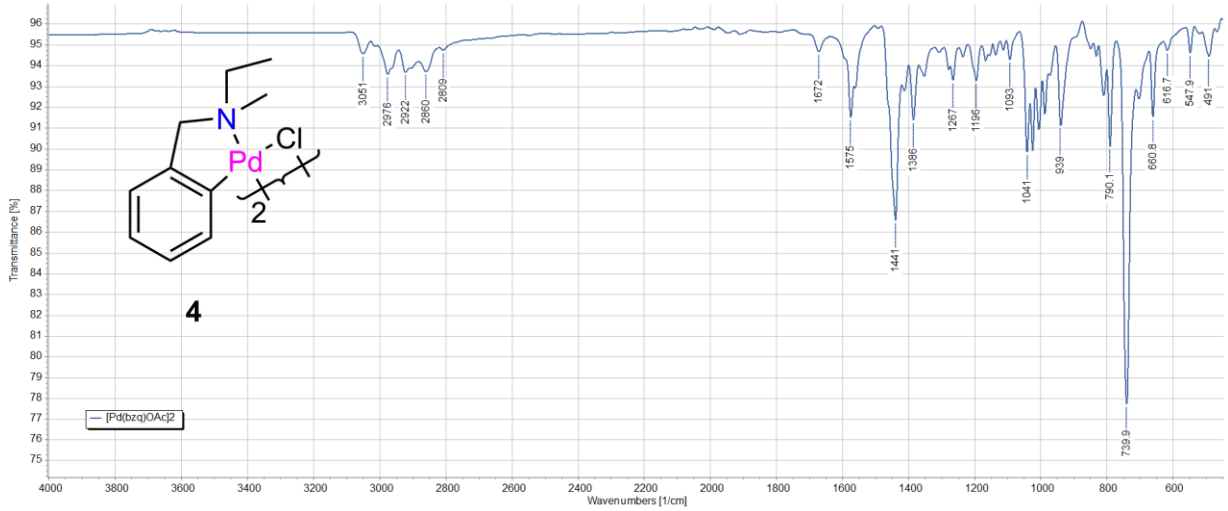


4

^{13}C NMR Spectrum (DMSO-d_6)



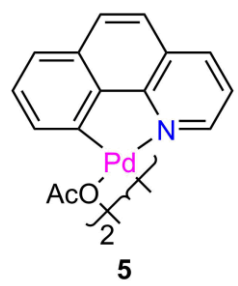
IR spectrum (ATR):



4

4.7.5 $[Pd(bzq)OAc]_2$ (5)

^{1}H NMR Spectrum (CD_2Cl_2)



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