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Supporting Information

An Extremely Highly Recoverable Clay-Supported Pd Nanoparticle Catalyst for Solvent-Free Heck–Mizoroki Reactions

Alejandro V. Martínez, Alejandro Leal-Duaso, José I. García and José A. Mayoral*

Content

1. Gas chromatography analyses of the Heck coupling reactions

1.1. Heck coupling reaction of iodobenzene with n-*butyl acrylate*

FID from Hewlett–Packard 6890-II, Agilent J&W GC Columns HP-5: 30 m ×0.25 mm × 0.25 μm; helium as carrier gas. 20 psi; injector temperature: 230 °C; detector temperature: 250 °C; oven program: 70 °C (1 min), 20°C min^{-1} to 250 °C (7,5 min); retention times: *n*-butyl acrylate: 1.8 min, *n*-decane: 2.5 min, iodobenzene: 2.8 min, *n*-butyl cinnamate: 7.1 min.

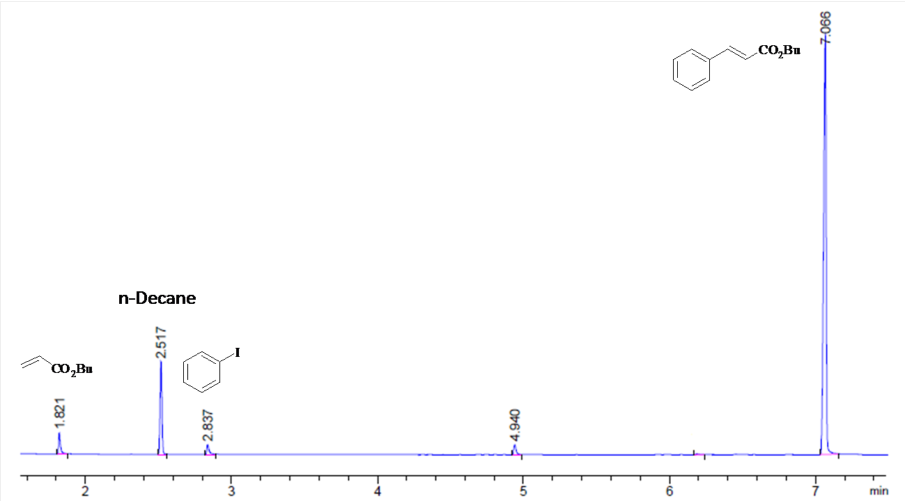

Fig. S1. *Typical CG chromatogram for the Heck coupling reaction of iodobenzene with butyl acrylate*

In order to determine the Heck coupling yield *n*-decane is used as internal standard. The following equation was used to calculate the reaction conversion and yield, obtained from previous calibration experiments:

$$Yield(\%) = 1.163 \cdot \frac{decane\ mmol \cdot cinnamate\ area}{iodobenzene\ mmol \cdot decane\ area} \cdot 100$$

$$Conversion(\%) = \left(1 - 0.593 \cdot \frac{decane\ mmol \cdot iodobenzene\ area}{iodobenzene\ mmol \cdot decane\ area}\right) \cdot 100$$

1.2. Heck coupling reaction of iodobenzene with styrene.

FID from Hewlett–Packard 6890-II, Agilent J&W GC Columns HP-5: 30 m ×0.25 mm × 0.25 µm; helium as carrier gas. 20 psi; injector temperature: 230 °C; detector temperature: 250 °C; oven program: 70 °C (1 min), 20°C min^{-1} to 250 °C (7,5 min); retention times: styrene: 1.8 min, *n*-decane: 2.5 min, iodobenzene: 2.8 min, 1,1-diphenylethylene: 6.1 min, (*E*)-stilbene: 7.3.

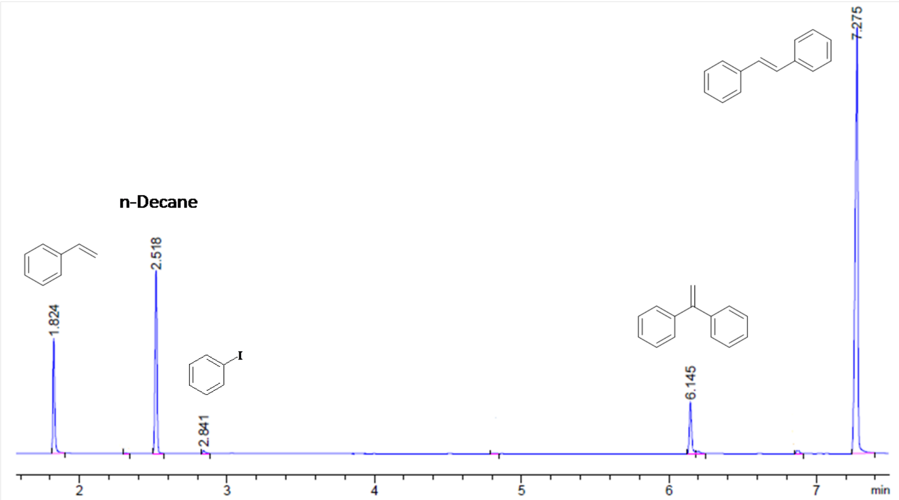

Fig. S2. *Typical CG chromatogram for the Heck coupling reaction of iodobenzene with butyl acrylate*

In order to determine the Heck coupling yield *n*-decane is used as internal standard. The following equation was used to calculate the reaction conversion and yield, obtained from previous calibration experiments:

$$Yield(\%) = 1.443 \cdot \frac{decane\ mmol \cdot styrene\ area}{iodobenzene\ mmol \cdot decane\ area} \cdot 100$$

$$Conversion(\%) = \left(1 - 0.593 \cdot \frac{decane\ mmol \cdot iodobenzene\ area}{iodobenzene\ mmol \cdot decane\ area}\right) \cdot 100$$

1.3. Heck coupling reaction of iodobenzene with (E)-4-methoxystyrene.

FID from Hewlett–Packard 6890-II, Agilent J&W GC Columns HP-5: 30 m ×0.25 mm × 0.25 μm; helium as carrier gas. 20 psi; injector temperature: 230 °C; detector temperature: 250 °C; oven program: 70 °C (1 min), 20°C min^{-1} to 250 °C (7,5 min); retention times: *n*-decane: 2.5 min, iodobenzene: 2.8 min, (*E*)-4-methoxystyrene: 3.7 min, 1-methoxy-4-(1-phenylvinyl)benzene: 7.7 min, (*E*)-4-methoxystilbene: 8.7.

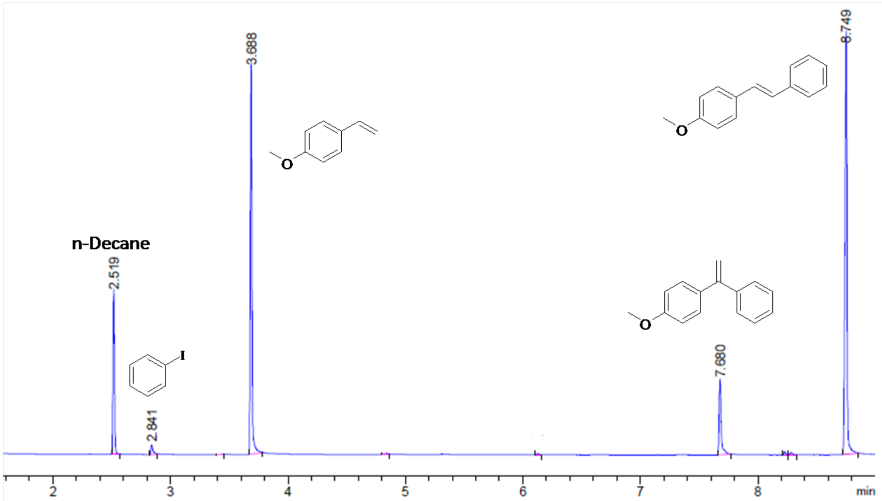

Fig. S3. *Typical CG chromatogram for the Heck coupling reaction of iodobenzene with (E)-4-methoxystyrene*

In order to determine the Heck coupling yield *n*-decane is used as internal standard. The following equation was used to calculate the reaction conversion and yield, obtained from previous calibration experiments:

$$Yield(\%) = 1.213 \cdot \frac{decane\ mmol \cdot (E) - 4 - \text{methoxystilbene}\ area}{iodobenzene\ mmol \cdot decane\ area} \cdot 100$$

$$Conversion(\%) = \left(1 - 0.593 \cdot \frac{decane\ mmol \cdot iodobenzene\ area}{iodobenzene\ mmol \cdot decane\ area}\right) \cdot 100$$

1.4. Heck coupling reaction of iodobenzene with (E)-4-chlorostyrene.

FID from Hewlett–Packard 6890-II, Agilent J&W GC Columns HP-5: 30 m ×0.25 mm × 0.25 µm; helium as carrier gas. 20 psi; injector temperature: 230 °C; detector temperature: 250 °C; oven program: 70 °C (1 min), 20°C min^{-1} to 250 °C (7,5 min); retention times: *n*-decane: 2.5 min, iodobenzene: 2.8 min, (*E*)-4-chlorostyrene: 3.1 min, 1-chloro-4-(1-phenylvinyl)benzene: 7.2 min, (*E*)-4-chlorostilbene: 8.4.

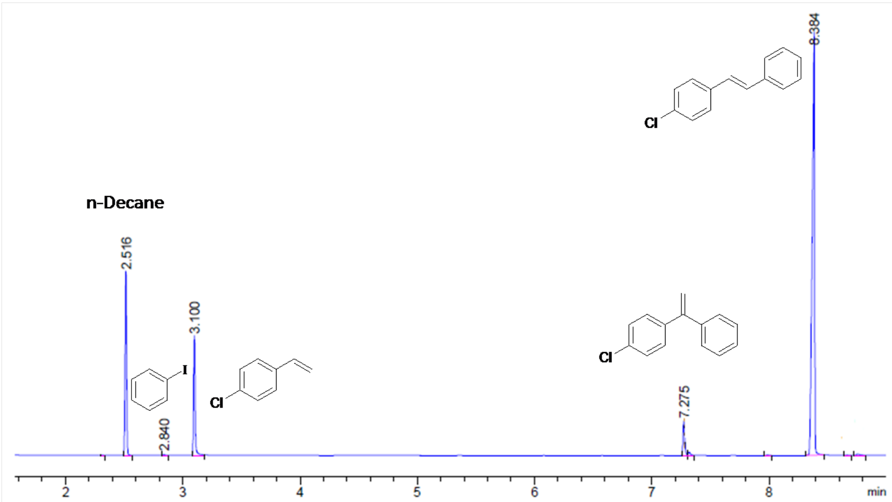

Fig. S4. *Typical CG chromatogram for the Heck coupling reaction of iodobenzene with (E)-4-chlorostyrene*

In order to determine the Heck coupling yield *n*-decane is used as internal standard. The following equation was used to calculate the reaction conversion and yield, obtained from previous calibration experiments:

$$Yield(\%) = 1.444 \cdot \frac{decane\ mmol \cdot (E) - 4 - \text{chlorostilbene}\ area}{iodobenzene\ mmol \cdot decane\ area} \cdot 100$$

$$Conversion(\%) = \left(1 - 0.593 \cdot \frac{decane\ mmol \cdot iodobenzene\ area}{iodobenzene\ mmol \cdot decane\ area}\right) \cdot 100$$

2. RMN analysis

2.1. RMN analysis of (*E*)-Butyl cinnamate

2.1.1. ^{1}H-RMN.

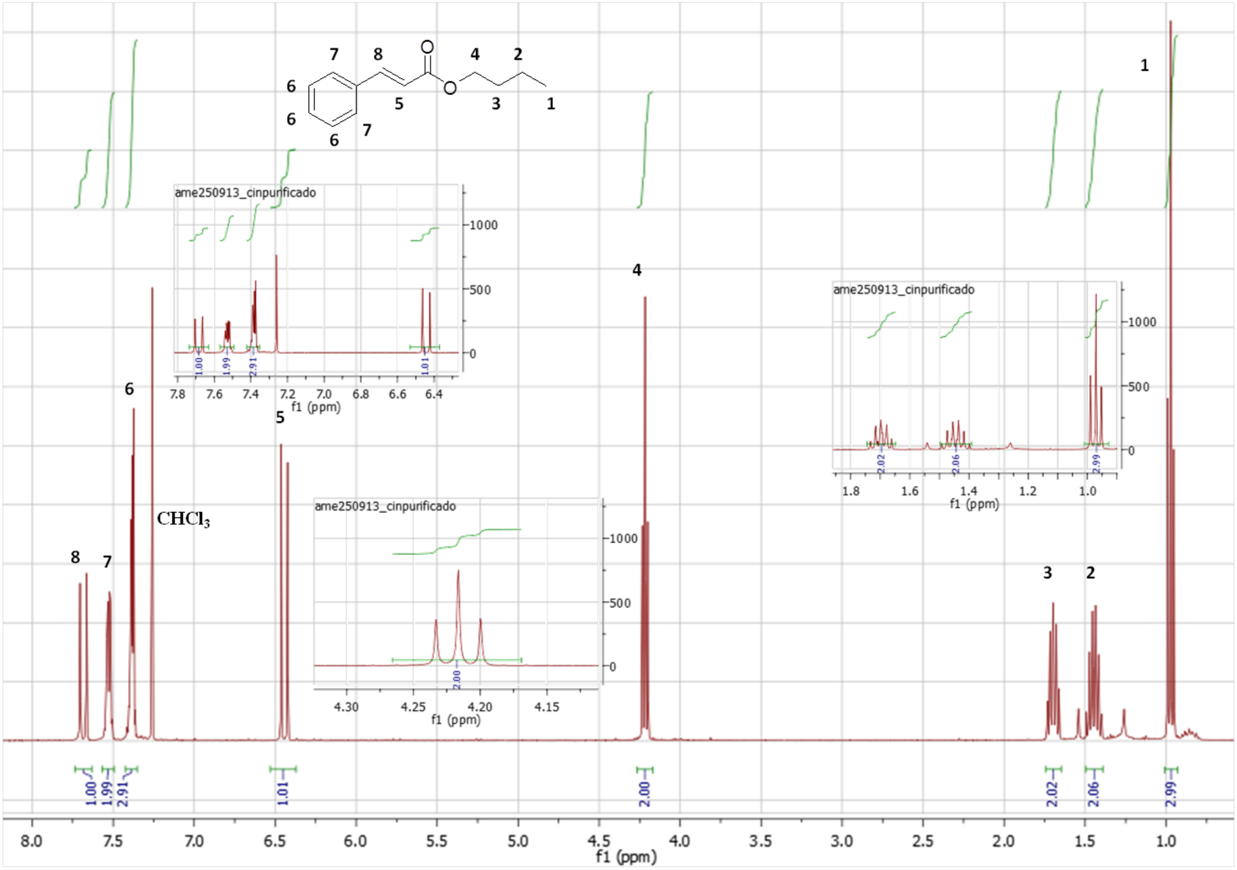

Fig. S5. *^{1}H-RMN of* n-*butyl cinnamate*

2.1.2. ^{13}C-RMN(APT).

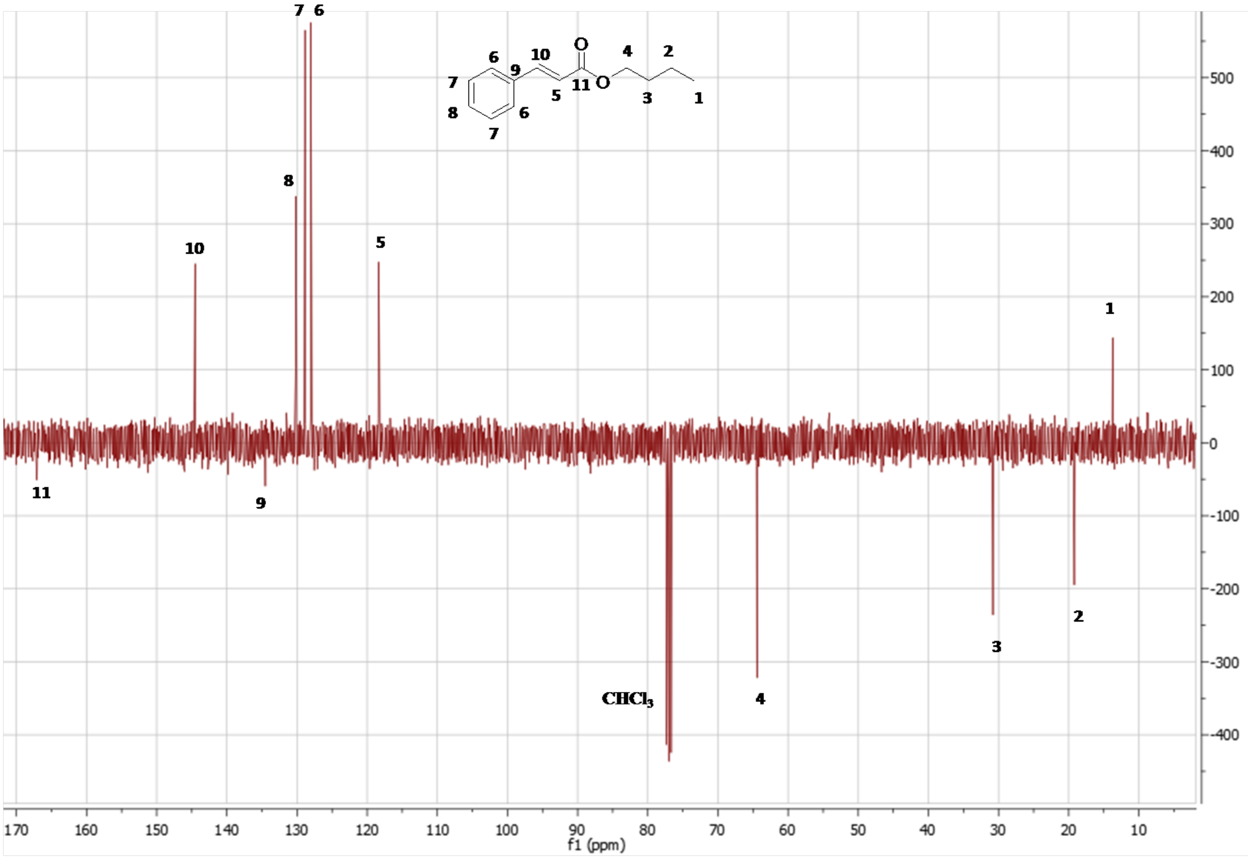

Fig. S6. *^{13}C-RMN(APT) of* n-*butyl cinnamate*

2.1.3. HSQC.

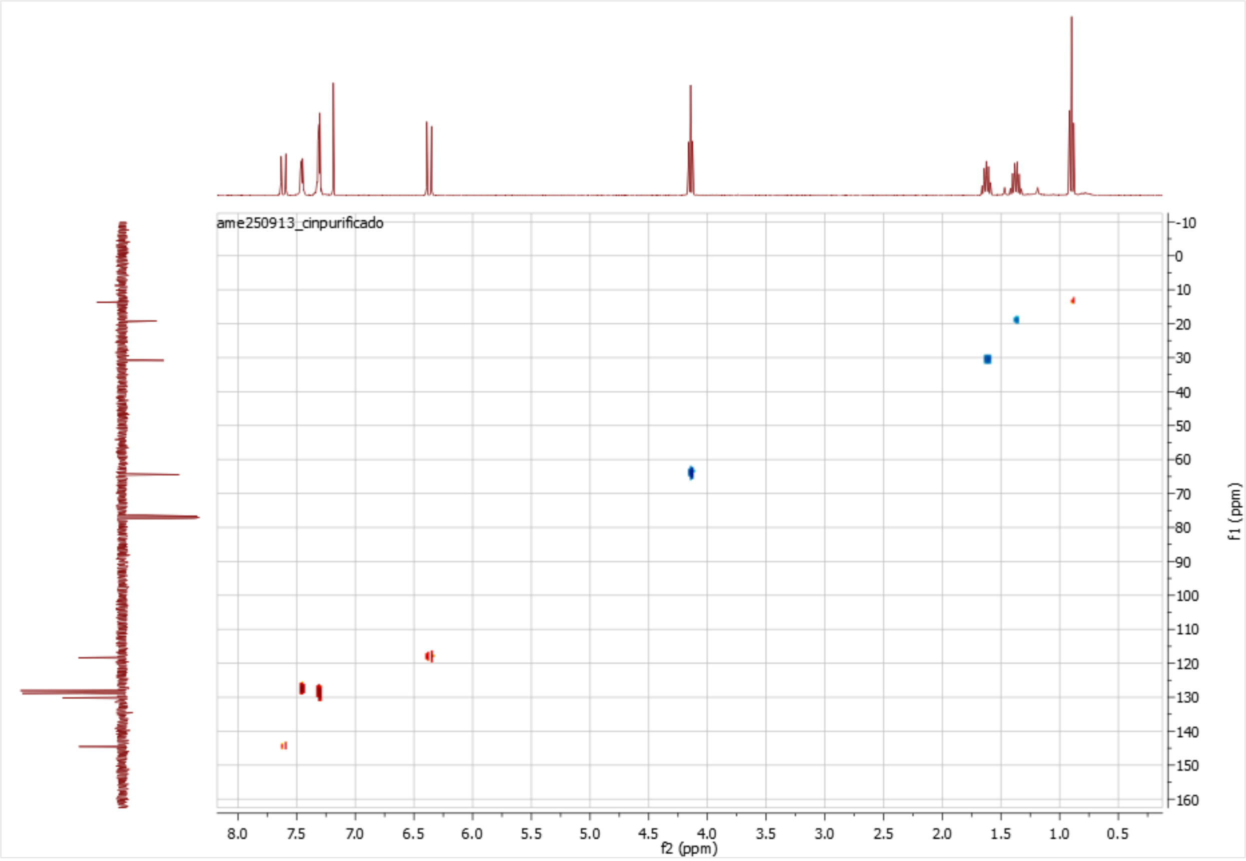

Fig. S7. *HSQC [^{1}H-^{13}C(APT)]of n-butyl cinnamate*

2.2. RMN analysis of stilbene

2.2.1. ¹H-RMN.

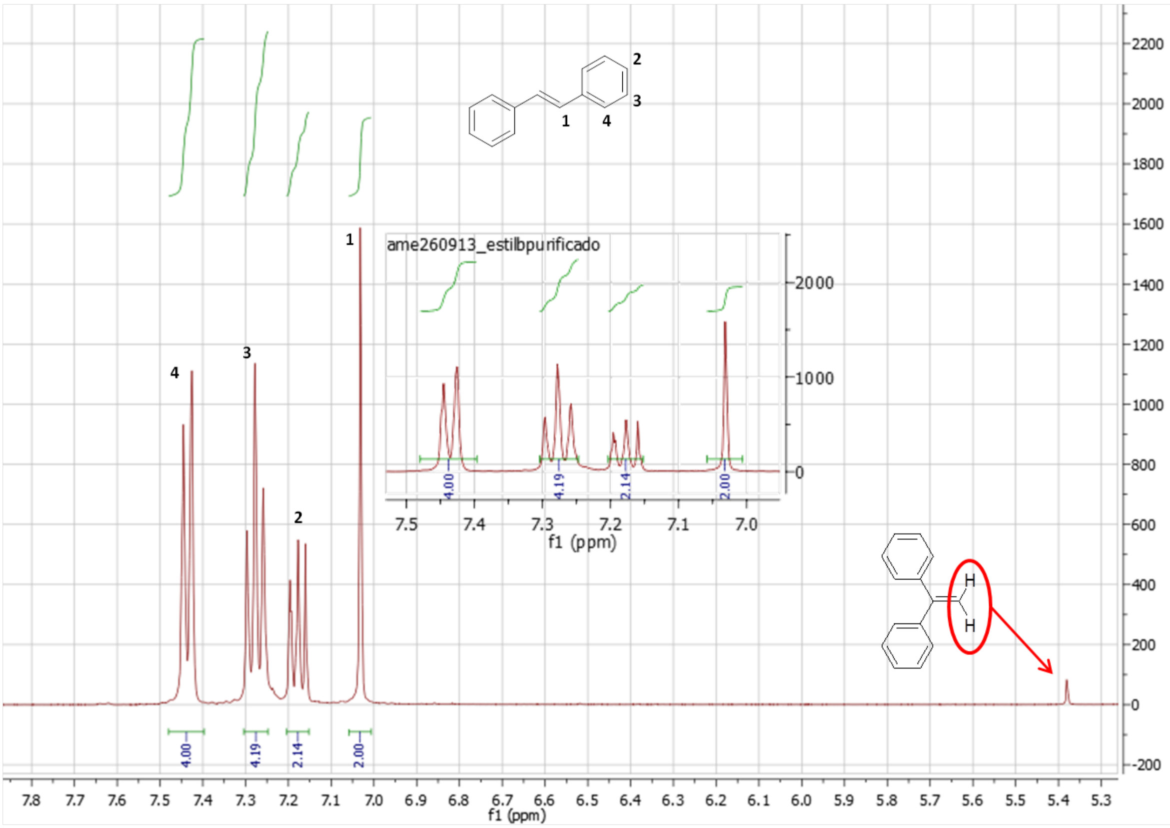

Fig. S8. *¹H-RMN of stilbene*

2.2.2. ^{13}C-RMN(APT).

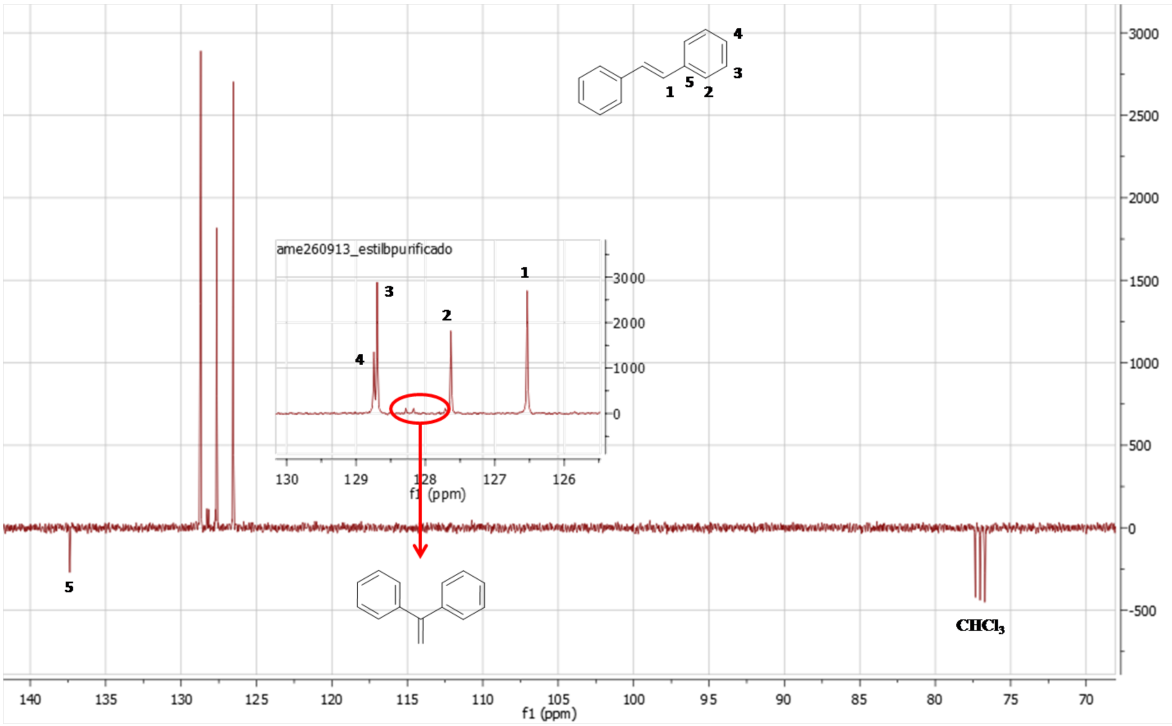

Fig. S9. *^{13}C-RMN(APT) of stilbene*

2.2.3. HSQC.

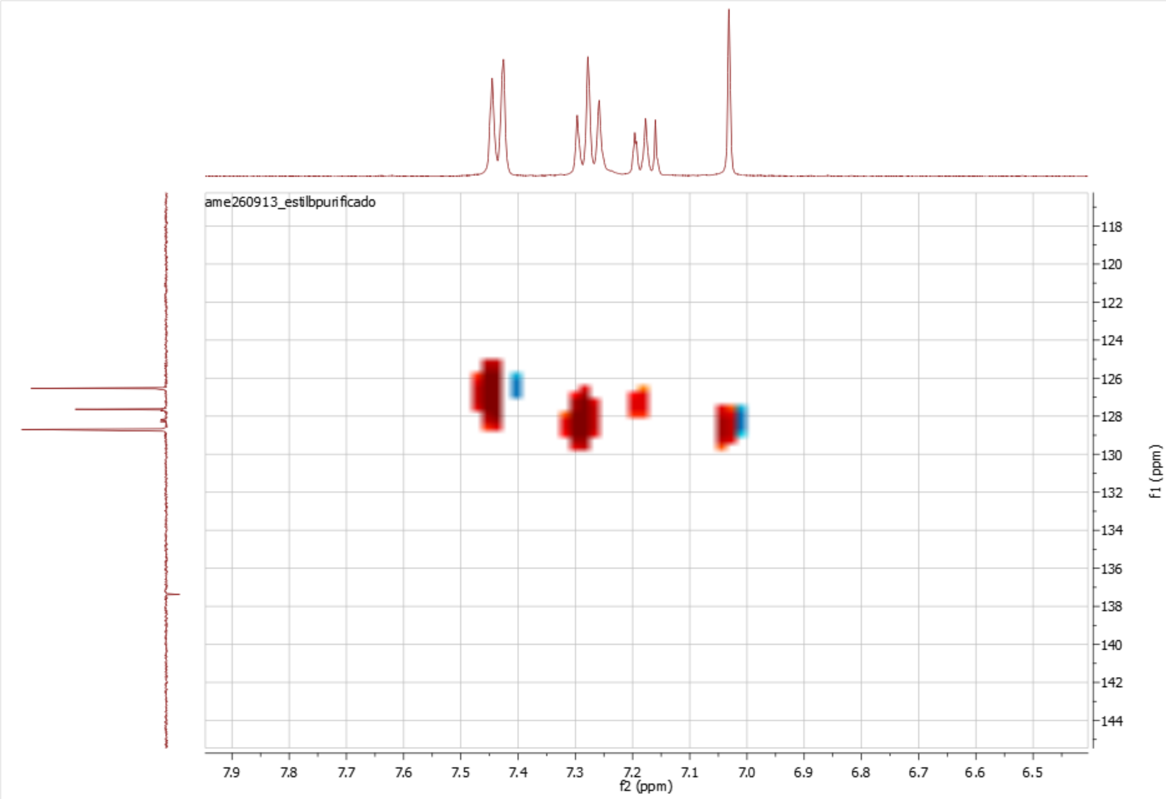

Fig. S10. *HSQC [^{1}H-^{13}C(APT)] of stilbene*

2.3. RMN analysis of (*E*)-4-methoxystilbene

2.3.1. [1]H-RMN.

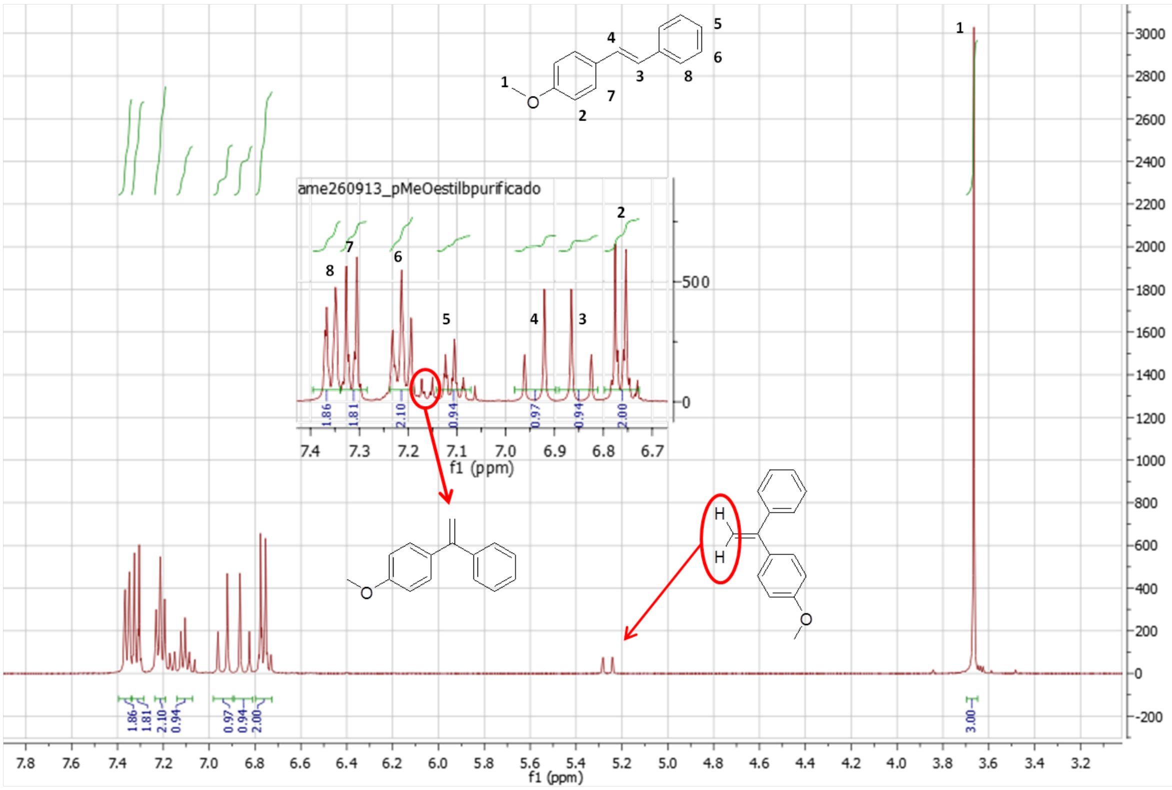

Fig. S11. *[1]H-RMN of (E)-4-methoxystilbene*

2.3.2. ¹³C-RMN(APT).

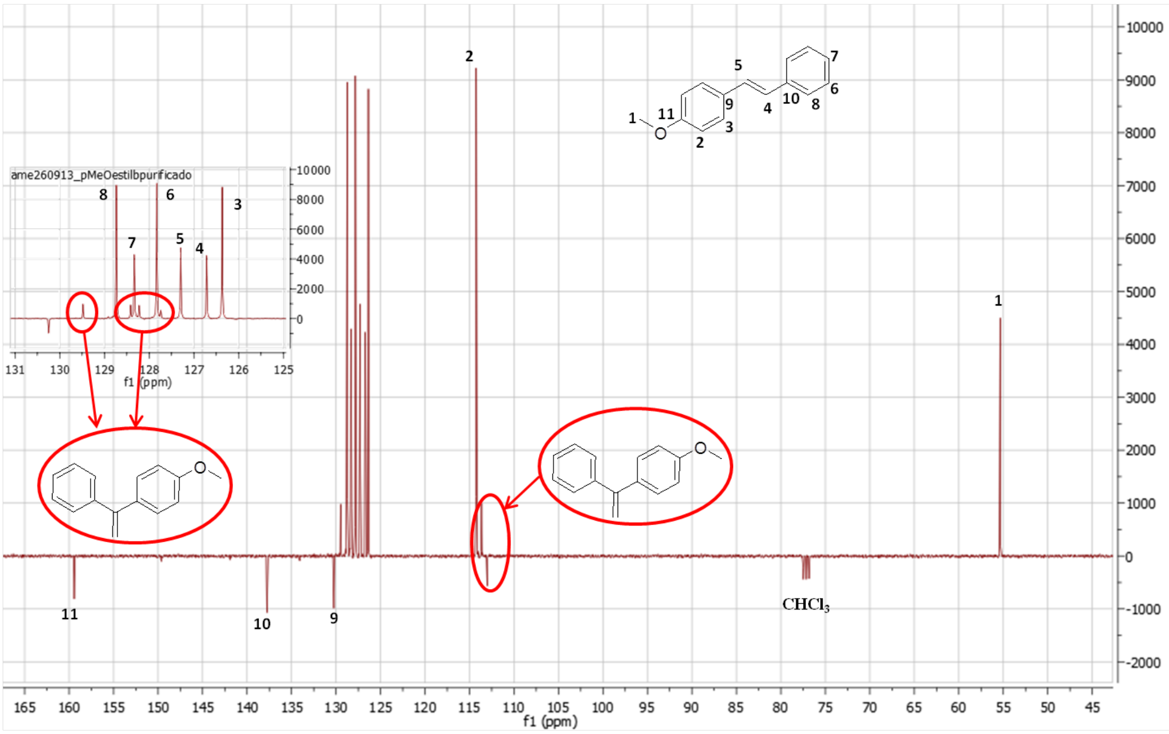

Fig. S12. *¹³C-RMN(APT) of (E)-4-methoxystilbene*

2.3.3. HSQC.

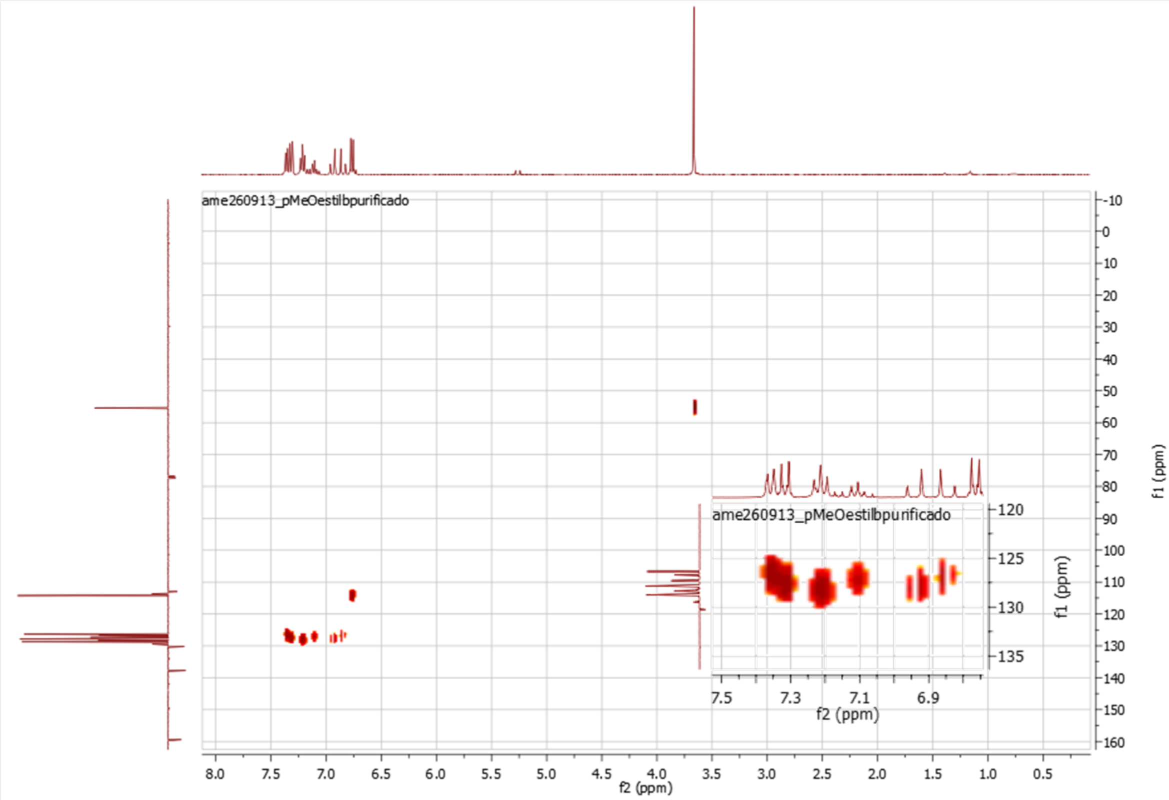

Fig. S13. *HSQC [^{1}H-^{13}C(APT)] of (E)-4-methoxystilbene*

2.4. RMN analysis of (*E*)-4-chlorostilbene

2.4.1. ^{1}H-RMN.

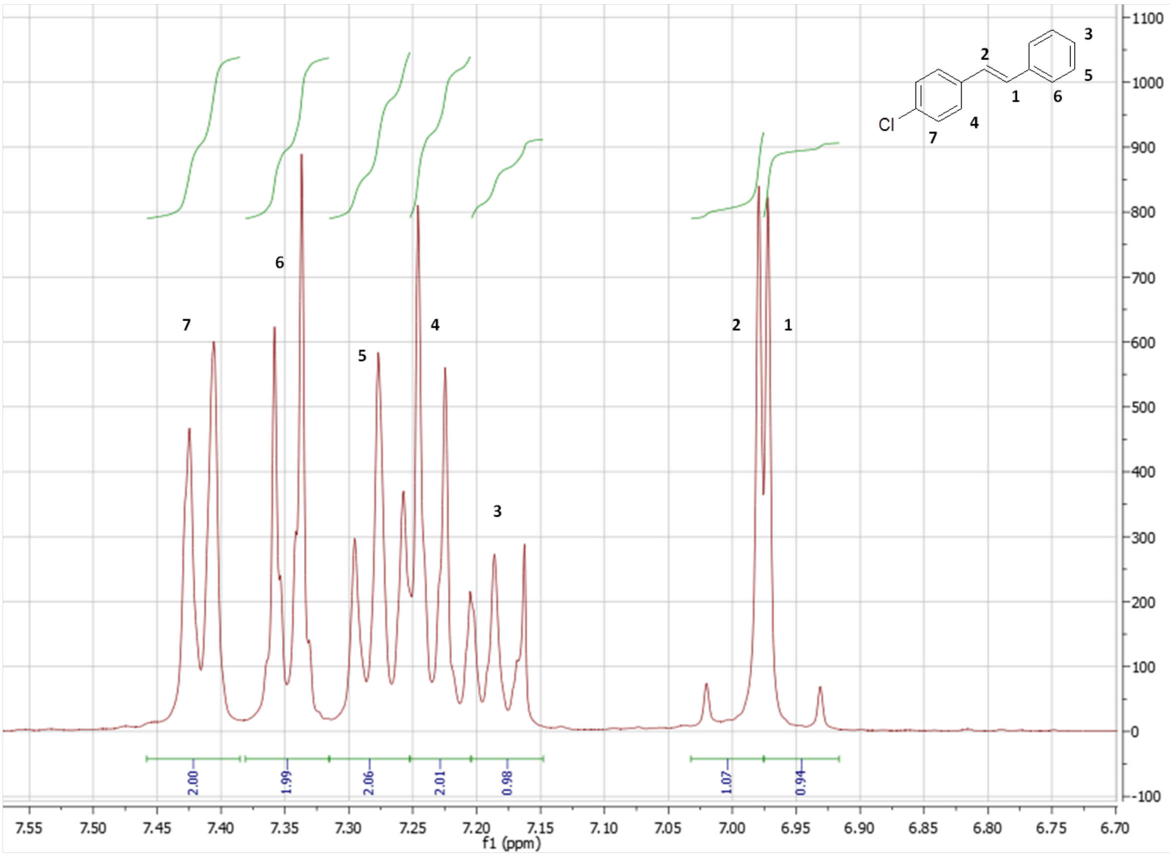

Fig. S14. *^{1}H-RMN of (E)-4-chlorostilbene*

2.4.2. ^{13}C-RMN(APT).

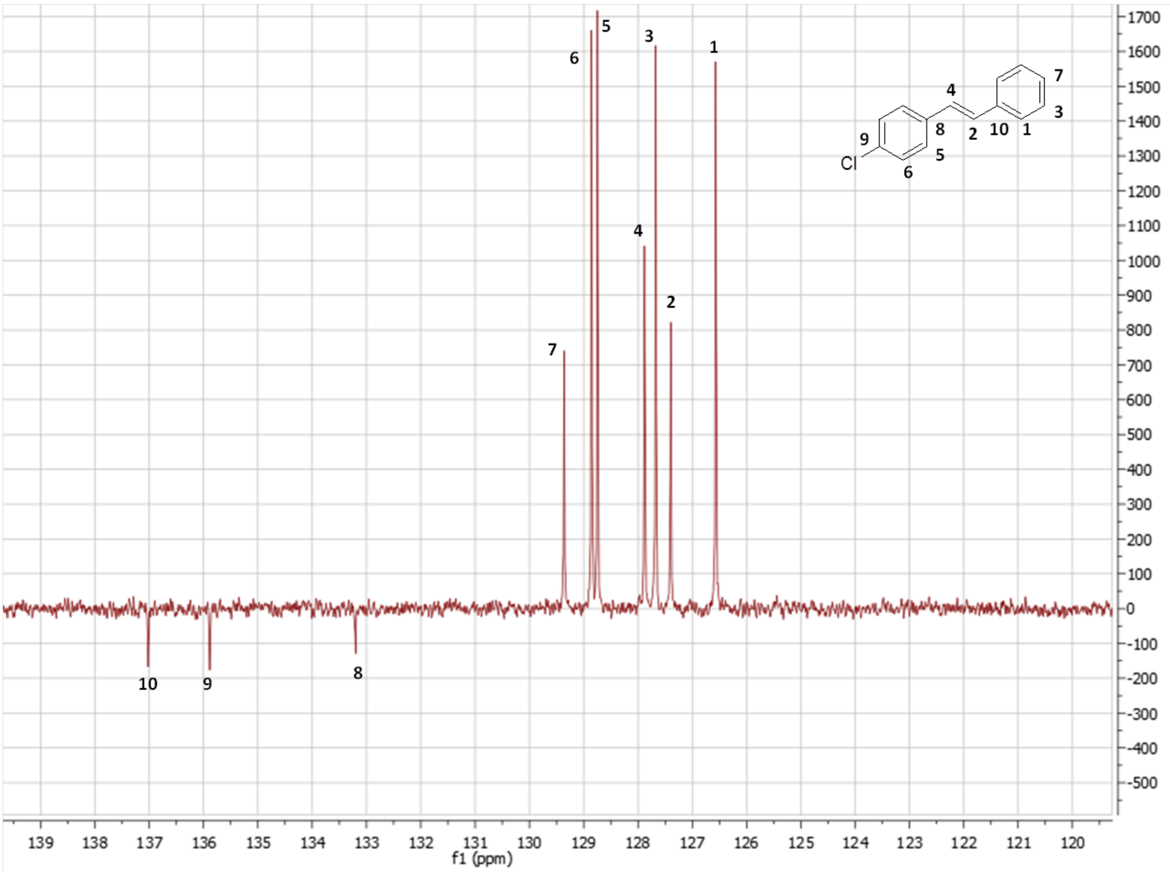

Fig. S15. *^{13}C-RMN(APT) of (E)-4-chlorostilbene*

2.4.3. HSQC.

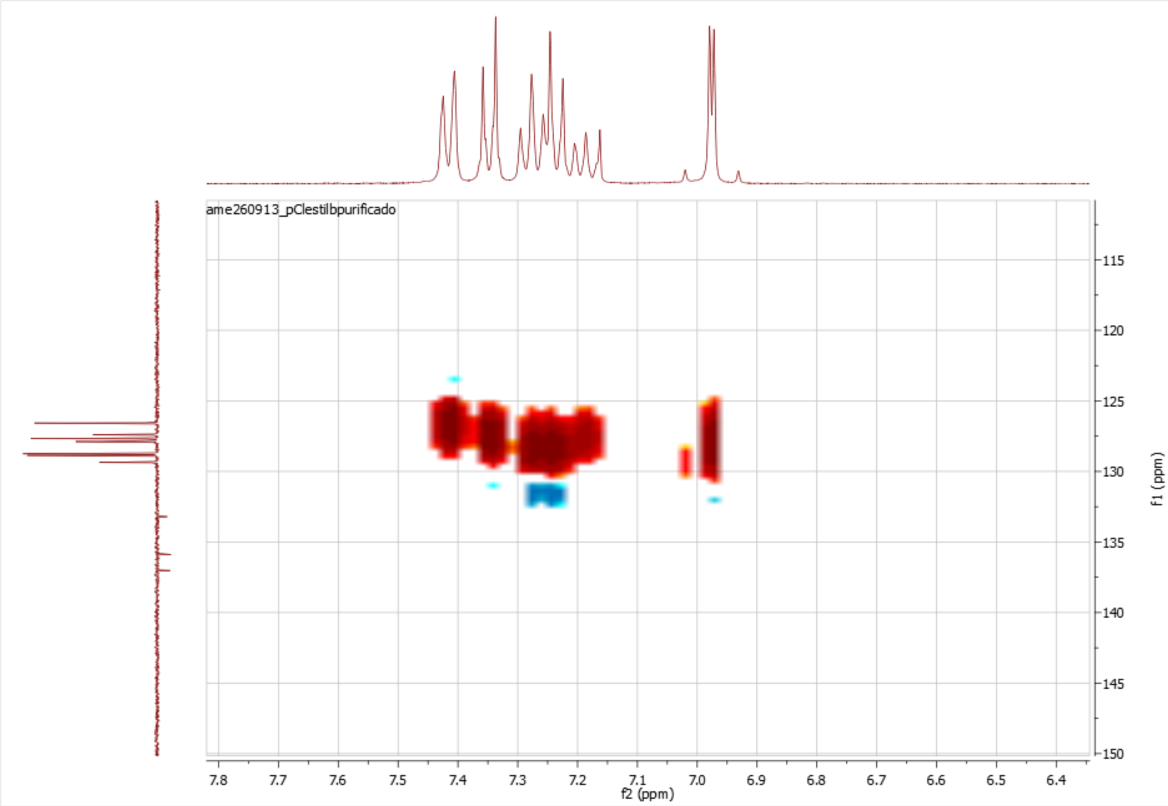

Fig. S16. *HSQC [^{1}H-^{13}C(APT)] of (E)-4-chlorostilbene*

3. TEM analysis of the Catalytic Systems

3.1. TEM analysis of the catalyst before use

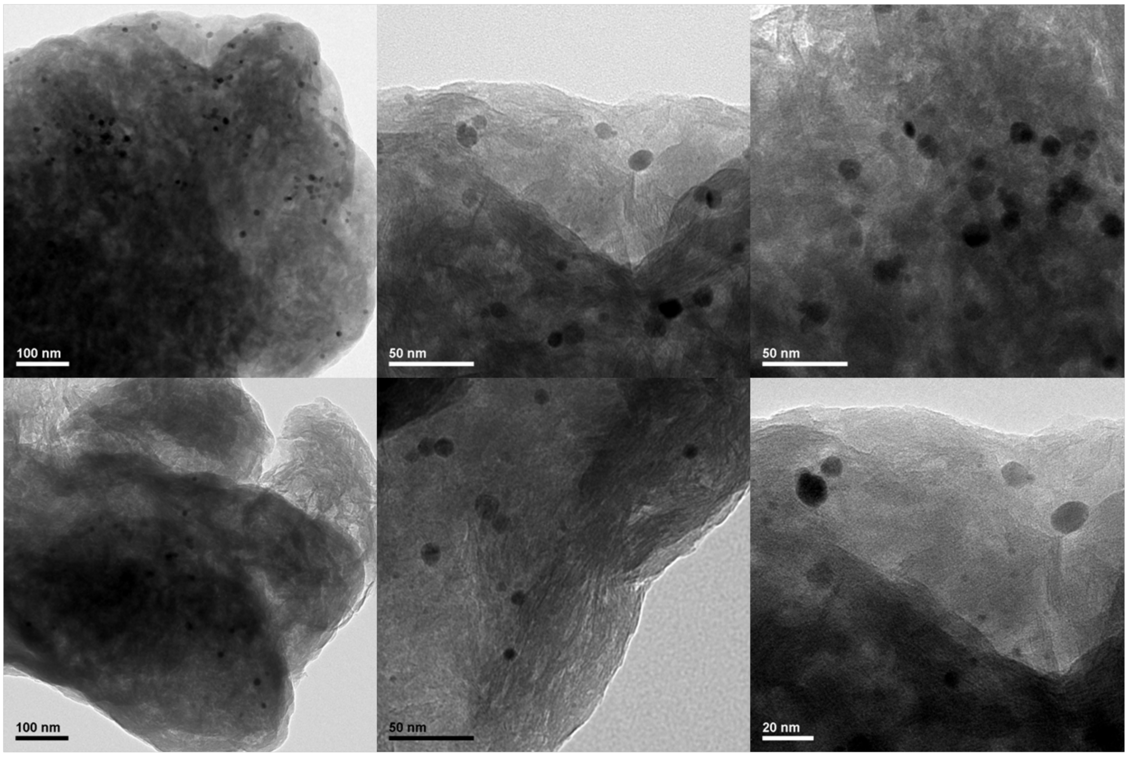

Fig. S17. *TEM micrographs of the catalyst before use*

3.2. TEM analysis of the used catalyst

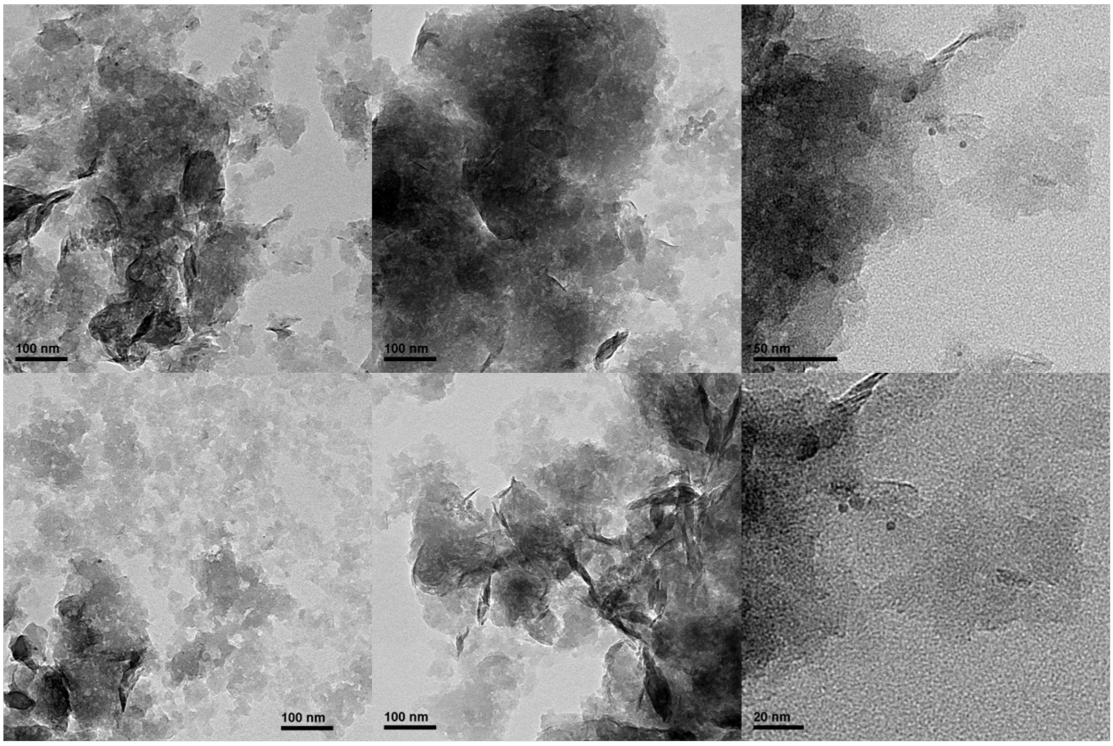

Fig. S18. *TEM micrographs of the used catalyst*

3.3. Size distribution of the supported nanoparticles after catalyst use

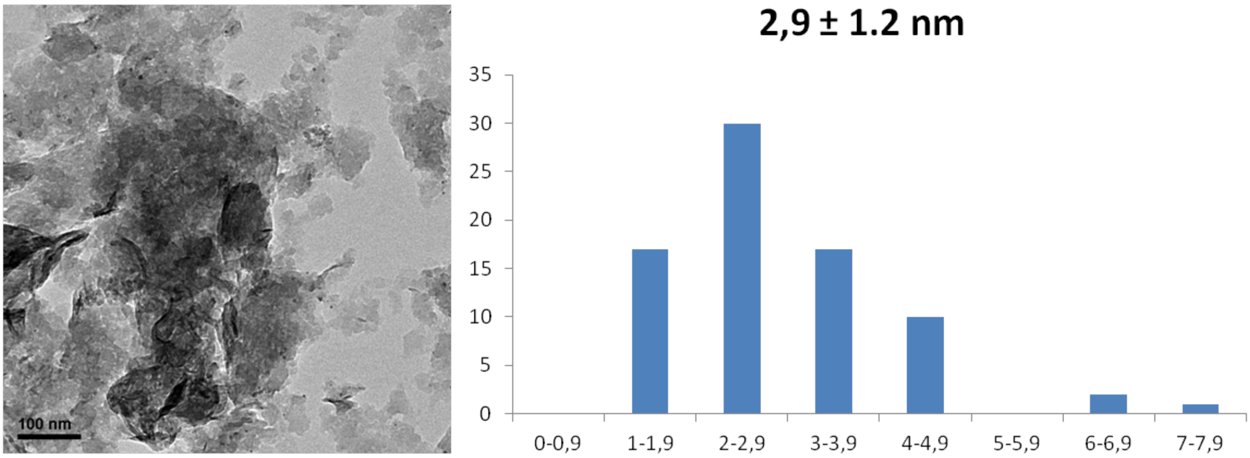

Fig. S19. *Size distribution of the supported nanoparticles after catalyst use*

4. FESEM analysis of the catalytic Systems

4.1. Catalyst before use

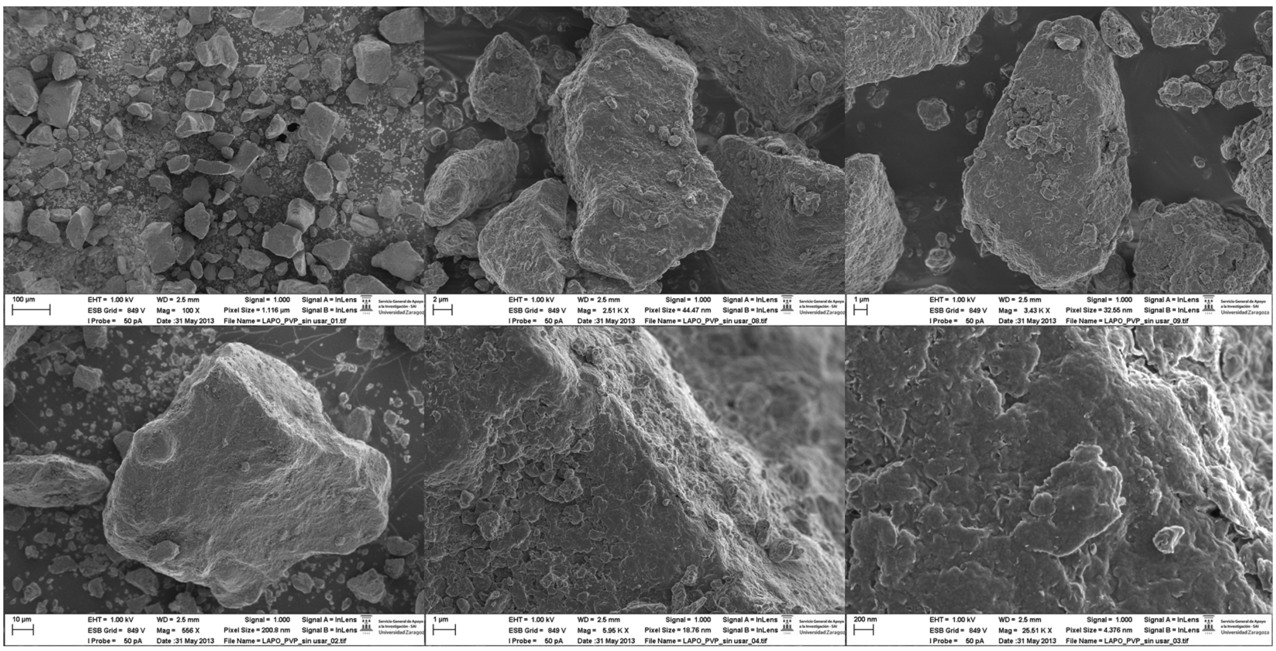

Fig. S20. *FESEM micrographs of the catalyst before use*

4.2. Used catalyst

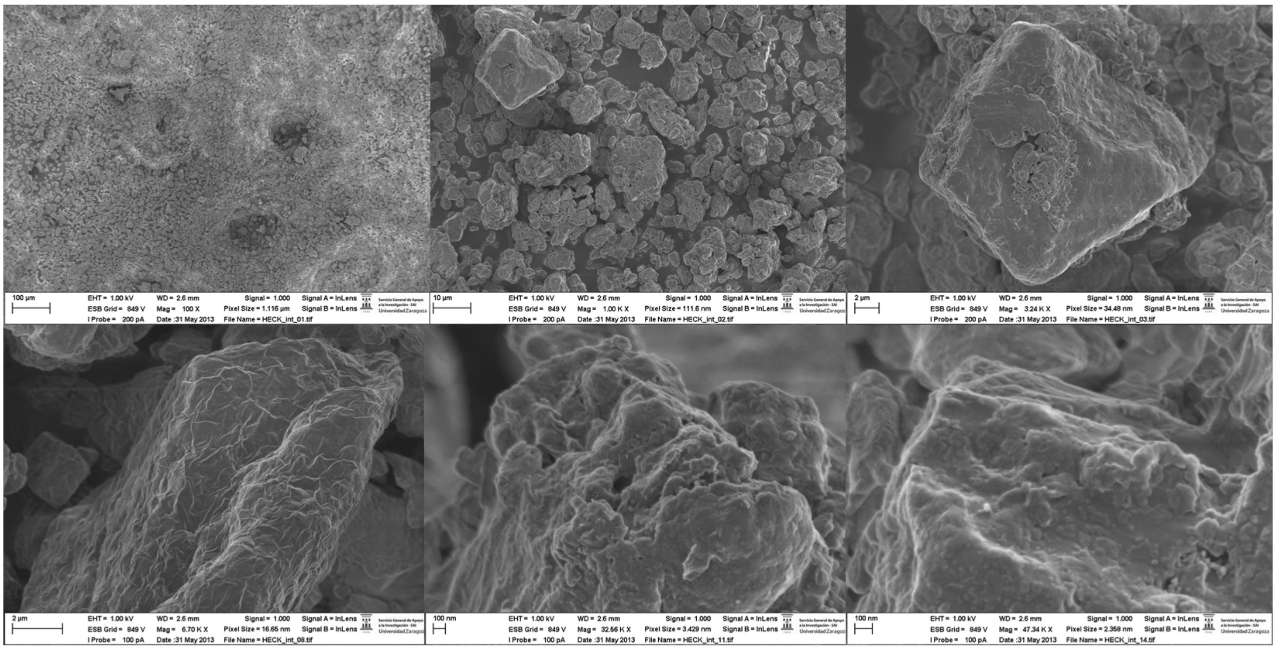

Fig. S21. *FESEM micrographs of the used catalyst*

5. ICP analyses of the catalytic systems

Table S1

ICP analyses of the fresh and recycled catalysts, used in the reaction between iodobenzene and several alkenes.[a]

Alkene	Run	Pd (mg g^{-1})	Mg (mg g^{-1})	Pd/Mg ratio (x 10^3)	Pd leaching (%)[b]	Pd leaching (%)[c]
butyl acrylate	0	0.3050	165.0	1.848	—	—
	1	0.2778	162,6	1.709	8.9	7.6
	2	0.2765	163,5	1.691	9.4	8.5
	3	0.2724	163.1	1.670	10.7	9.7
	50	0.2458	162.9	1.509	19.4	18.4
	75	0.2372	164.5	1.442	22.2	22.0
styrene	0	0.2428	168.3	1.443	—	—
styrene	12	0.1231	162.9	0.756	49.3	47.6
p-Cl-styrene	22	0.1438	165.5	0.869	40.8	39.8
p-MeO-styrene	18	0.1226	161.5	0.759	49.5	47.4

[a] All the catalyst samples were calcined at 550 ºC under air prior analyses. Pd analyses carried out with ICP-MS and Mg analyses with ICP-OES.
[b] Calculated from the absolute Pd content.
[c] Calculated from the Pd/Mg ratio.

6. Complete results of recycling experiments

6.1. Heck coupling reaction of iodobenzene with n*-butyl acrylate.*

Table S2

Heck coupling reaction of iodobenzene with n-butyl acrylate *catalyzed with* Pd-PVP@laponite.

	SAMPLE 1			SAMPLE 2		
Run	Conversion (%)	Yield (%)	Isolated Yield (%)	Conversion (%)	Yield (%)	Isolated Yield (%)
1	89	88	81	100	100	98
2	90	90	82	98	98	98
3	100	100	99	100	100	99
4	100	100	98	99	99	90
5	100	100	94	100	100	94
6	100	100	93	100	100	96
7	100	100	91	100	100	99
8	100	100	99	100	100	85
9	100	100	96	100	100	80
10	100	100	94	94	94	91
11	100	100	93	100	100	99
12	100	100	92	100	100	99
13	100	100	91	100	100	90
14	98	97	88	100	100	84
15	99	99	98	100	100	96
16	98	98	95	100	100	100
17	100	100	95	98	98	96
18	100	100	94	96	91	90
19	99	99	90	100	100	100
20	92	92	92	95	95	98
21	96	96	92	95	95	91
22	98	98	95	82	84	95
23	100	100	95	94	94	98
24	91	90	85	95	95	99
25	96	96	94	91	91	97
26	98	97	90	100	100	100
27	100	100	91	100	100	90
28	92	91	84	78	89	99
29	96	95	87	80	84	99
30	94	93	86	98	98	79
31	94	94	86			
32	92	92	91			
33	92	91	88			
34	92	91	84			
35	78	75	67			
36	99	99	79			
37	93	93	88			
38	84	82	75			
39	98	98	97			
40	94	94	92			
41	78	77	73			
42	95	94	89			
43	98	98	80			
44	96	96	94			
45	64	62	57			
46	91	91	90			
47	81	80	75			
48	74	72	68			
49	84	84	85			
50	86	85	80			

Table S3

Heck coupling reaction of iodobenzene with *n*-butyl acrylate after the first calcination of the Pd-PVP@laponite catalyst.

Run	Conversion (%)	Yield (%)	Isolated Yield (%)
1	100	100	91
2	98	96	94
3	96	96	95
4	100	100	100
5	90	89	76
6	97	97	95
7	100	100	97
8	15	14	14

Table S4

Heck coupling reaction of iodobenzene with *n*-butyl acrylate after the second calcination of the Pd-PVP@laponite catalyst.

Run	Conversion (%)	Yield (%)	Isolated Yield (%)
1	100	100	99
2	100	100	93
3	99	99	96
4	99	99	99
5	100	100	81
6	100	100	74
7	5	1	1

Table S5

Heck coupling reaction of iodobenzene with *n*-butyl acrylate after the third calcination of the Pd-PVP@laponite catalyst.

Run	Conversion (%)	Yield (%)	Isolated Yield (%)
1	100	100	81
2	89	88	82
3	100	100	96
4	100	100	96
5	100	100	100
6	100	100	100
7	100	100	92
8	100	100	42
9	97	81	42
10	50	49	47

6.2. Heck coupling reaction of iodobenzene with styrene.

Table S6

Heck coupling reaction of iodobenzene with styrene catalyzed with Pd-PVP@laponite.

Run	Conversion (%)	Yield (%)	Isolated Yield (%)	Selectivity (%)
1	100	100	66	92
2	100	100	91	90
3	98	98	97	90
4	100	100	99	90
5	99	98	99	91
6	99	98	89	92
7	100	100	100	92
8	98	98	100	92
9	91	89	82	93
10	91	88	71	92
11	97	97	100	93
12	24	33	39	97
13	22	22	23	93
14	4	12	14	92
15	3	7	8	89

6.3. Heck coupling reaction of iodobenzene with 4-methoxystyrene.

Table S7

Heck coupling reaction of iodobenzene with 4-methoxystyrene catalyzed with Pd-PVP@laponite.

Run	Conversion (%)	Yield (%)	Isolated Yield (%)	Selectivity (%)
1	99	98	59	89
2	100	100	60	87
3	91	90	79	89
4	99	99	94	88
5	95	96	100	90
6	99	99	78	90
7	80	83	90	93
8	93	92	75	92
9	57	52	42	94
10	35	25	20	90

6.4. Heck coupling reaction of iodobenzene with 4-chlorostyrene.

Table S8

Heck coupling reaction of iodobenzene with 4-chlorostyrene catalyzed with Pd-PVP@laponite.

Run	Conversion (%)	Yield (%)	Isolated Yield (%)	Selectivity (%)
1	75	73	63	95
2	100	100	87	93
3	100	100	89	94
4	100	100	91	92
5	100	100	92	94
6	100	100	91	94
7	100	100	92	94
8	99	99	92	94
9	100	100	91	94
10	100	100	90	94
11	100	100	96	94
12	100	100	93	95
13	95	95	89	95
14	100	100	92	94
15	100	100	95	94
16	100	100	79	94
17	100	100	100	95
18	98	98	91	95
19	91	92	92	95
20	40	44	45	94
21	3	17	19	94