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In-situ Generated Palladium on Aluminum Phosphate as Catalytic System for the Preparation of β,β-Diarylated Olefins by Matsuda-Heck Reaction

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KEYWORDS Palladium on Aluminum phosphate, bisarylation, Matsuda-Heck reaction, Design of experiments

ABSTRACT *In-situ* generated palladium on aluminum phosphate provides a novel and active catalytic system for the preparation of β,β-diarylated olefins using the Matsuda-Heck-reaction. The reaction conditions of this catalytic protocol were optimized by a Response-Surface- model.

Introduction

Due to the high reactivity of aryldiazonium salts the Matsuda-Heck reaction[1,2] is an important tool for the arylation of olefinic substrates.[3-6] Especially, for the synthesis of difficult accessible synthetic targets like bis-arylated derivatives the Matsuda-Heck reaction seems to be very auspicious.

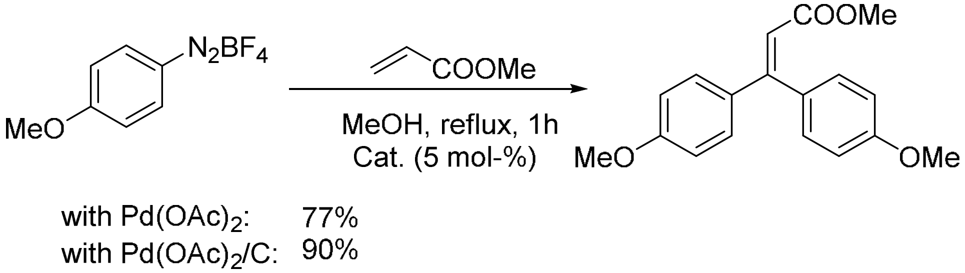
Stimulated by the seminal work of Correia *et al*[7,8]. and motivated by our own investigations regarding the development of improved catalytic systems[9] we were interested in the synthesis of bis-arylated olefinic substances. Despite the good to excellent yields in the synthesis of symmetrical β,β-diarylated acrylates using Correia's protocol the synthetic approach suffers from the utilization of high catalyst concentrations up to 7 mol-% and elevated temperatures up to 60 °C.[7] Furthermore, only the bisarylation using electron-rich aryldiazonium salts as electrophiles was reported.

In the light of an industrial utilization of this synthetic access towards β,β-diarylated olefins the development of a more efficient protocol concerning low catalyst-concentrations, lower reaction temperatures on the one hand and a broader scope of usable olefins on the other hand is tempting.

In previous investigations it could be stated that supported Pd-catalysts and the utilized supporting material show a tremendous impact on the reaction rates and yields of the Matsuda-Heck reaction.[9,10]

Even for the synthesis of β,β-diarylated acrylates Correia and co-workers could show improved results by the utilization of $Pd(OAc)_2/C$ as catalyst (**Scheme 1**).[7]

Scheme 1. Diarylation of methyl acrylate using Correia protocol[7]



In the course of our investigations of novel and more active catalysts for the Matsuda-Heck reaction[9] we want to present a new catalytic system $Pd(OAc)_2/AlPO_4$. Despite of the low price and its use as antacid in medicine it is interesting to notice that the utilization of aluminum phosphate as supporting material for catalysts is scarce[11]. The new catalytic system was prepared by a prereduction of $Pd(OAc)_2$ by methanol in the presence of methyl acrylate and aluminum phosphate before starting the Matsuda-Heck reaction. Investigations using scanning electron microscopy (SEM) indicated the formation of Pd-species immobilized on aluminum phosphate (Figure 1).

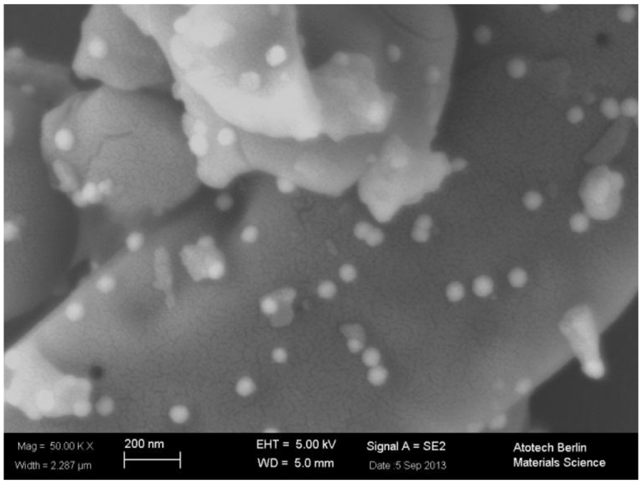
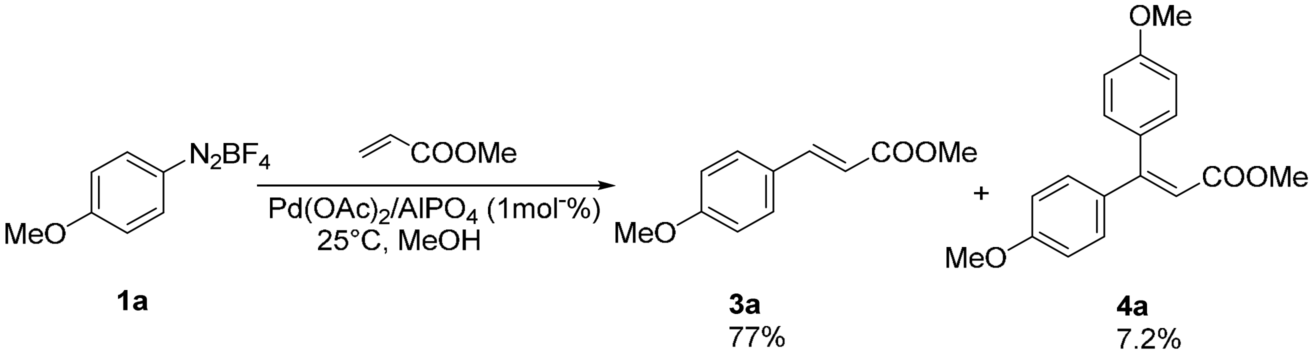


Figure 1. SEM image of Pd-species immobilzed on $AlPO_4$

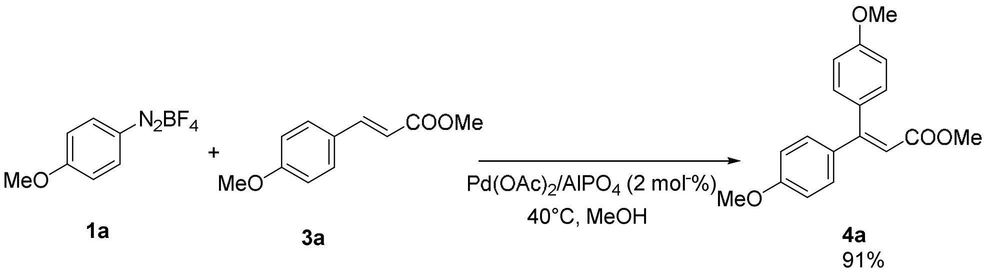
Having this new catalytic system in our hands we applied the new catalyst in a Matsuda-Heck reaction using methyl acrylate as olefine. During the reaction of 4-methoxy-benzenediazonium tertrafluoroborate with methyl acrylate on 10 mmol scale we could detect significant amounts of bis-arylated product 4a (Scheme 2):

Scheme 2. Reaction of 4-methoxy-benzenediazonium tertrafluoroborate with methyl acrylate



Whereas similar results could be obtained by the utilization of $Pd(OAc)_2/C$ as catalyst the $Pd(OAc)_2/AlPO_4$-system distinguished itself by significant higher reaction rates (1.49 mmol*mL^{-1*}*h^{-1} vs. 0.67 mmol*mL^{-1}*h^{-1}). In previous investigations we could demonstrate that especially for difficult synthetic targets the utilization of highly active catalytic systems is favourable.[9,10] However, compared with our quite recently described $Pd(OAc)_2/Al_2O_3$-catalyst[9] the formation of bis-arylated product is pronounced in face of similar catalytic activity. Encouraged by these findings we successfully conducted the arylation of *E*-methyl-3-(4-methoxyphenyl)-acrylate in excellent yields using the new catalytic system (Scheme 3).

Scheme 3. Arylation of *E*-methyl-3-(4-methoxyphenyl)acrylate



While Correia *et al.* obtained quite similar resulst by applying 5 mol-% and 60 °C reaction temperature[7] the new catalyst pleasingly gave slightly better results by using 2 mol-% palladium-concentration and 40 °C. Anyway, it had to be revealed that no significant reaction took place at ambient temperature.

Based on these results we set out to apply this novel catalytic system on the optimized and simple synthesis of β,β-diarylated olefins using different aryldiazonium salts and alkenes.

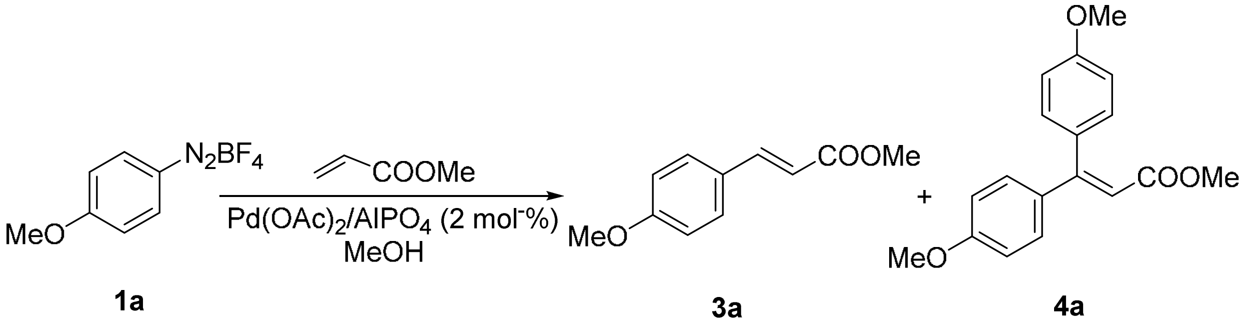
Results and discussion

Optimization of reaction conditions. For the optimization of the bisarylation we used the design of experiments (DoE) method. Despite of the usefulness it has to be stated that the utilization of DoE-methods for the optimization of Matsuda-Heck reactions is quite rare in literature.[12-14]

As a model reaction we examined the β,β-diarylation of methyl acrylate with 4-methoxybenzenediazonium tetrafluoroborate **1a**. At the beginning of this study we considered the reaction temperature, the catalyst loading on the supporting material $AlPO_4$, the prereduction time of the palladium acetate and the quantity of the utilized aryldiazonium salt as variables that might have an impact on the outcome of the reaction.

As DoE-method we chose a Response-Surface-model that is frequently used for the development and optimization of processes and products in industry (see Supporting Information).[15] Due to our prior results shown in Scheme 3 the reaction should be optimized for 2 mol-% $Pd(OAc)_2$ and a maximum reaction temperature of 40 °C. All reactions were conducted under isothermic conditions using the lab automation system EasyMax™ of Mettler-Toledo. For obtaining the most reactive Pd(0) on $AlPO_4$ catalyst the pre-catalyst $Pd(OAc)_2$ was reduced at the beginning of the reaction at 25 °C for a dedicated time before starting the Matsuda-Heck reaction. The set of experiments is outlined in **Table 1**.

Table 1. Set of experiments for the DoE and results



entry	T_R	W_{Pd} [%]	T_R [min]'	n_{DZS} [mmol]	3a [area-%][a]	4a [area-%][a]
1	32.5	1.5	60	20	15	68
2	32.5	1.0	45	21	9	82
3	40	0.5	45	22	-	11
4	32.5	1.0	45	21	11	81
5	40	0.5	60	21	-	85

6	32.5	0.5	60	22	8	79
7	32.5	1.0	30	22	2	88
8	25	1.0	60	21	17	77
9	32.5	1.0	45	21	5	81
10	25	0.5	60	20	14	72
11	25	1.5	45	22	7	80
12	40	1.5	60	22	3	86
13	40	0.5	30	20	16	75
14	40	1.0	45	20	10	76
15	25	1.0	30	20	11	71
16	32.5	1.0	45	21	3	83
17	32.5	0.5	45	21	5	90
18	25	*0.5*	30	22	6	87
19	45	1.5	30	21	2	93

[a] area-% HPLC

All reactions were run over 3.5h under the mentioned conditions. After separation of the catalyst, quenching with water and extraction with methylene chloride the reaction mixtures were analyzed by HPLC to provide the product distributions. According to table 1 the highest quantity of bis-arylated product in the set of experiments is obtained by using a catalyst loading of 1.5 wt.-% palladium and 21 mmol diazonium salt at 40 °C (entry 19). For finding the optimized process conditions all the results were evaluated by the JMP™-9.0-software. In figure 2 the significance of the synthetic parameter based on probabilities of errors is presented.

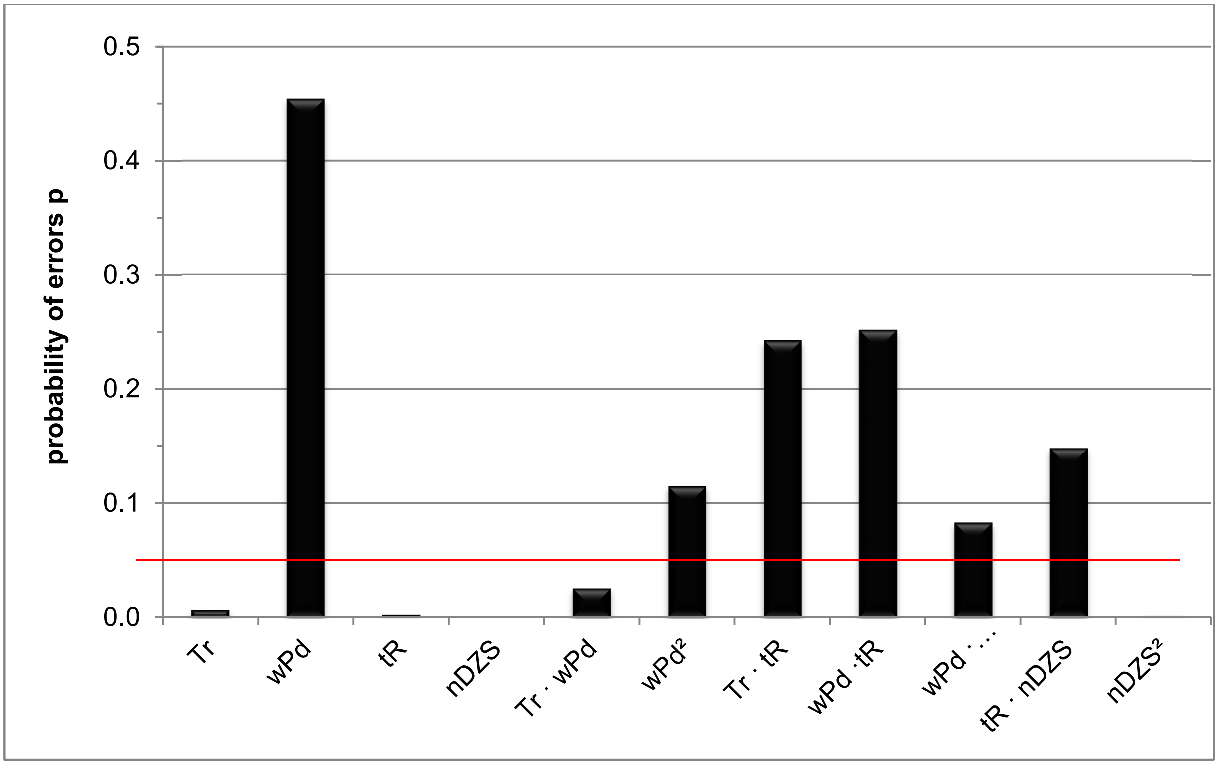


Figure 2. Significance of synthetic parameter

Referred to our DoE based on a Response-Surface model a reaction parameter has a significant impact if the probability of error is $p \leq 0.05$ in the t-test. According to figure 2 it is obvious that the yield of obtained bis-arylated methyl acrylate is significantly influenced by the reaction temperature T_R, the prereduction time t_R, the molar quantity of diazonium salt n_{DZS}, the squared molar quantity of diazonium salt n_{DZS}^2 and the interaction between the reaction temperature and the palladium loading T_R*w_{Pd}. The error probability of the interaction between the molar quantity of the diazonium salt and the palladium loading $w_{Pd}*n_{DZS}$ is 0.083. Therefore, a significant impact can not be excluded. Thereby, these parameter may influence the process in a positive or negative way. The impact of the parameter is shown in **Figure 3.**

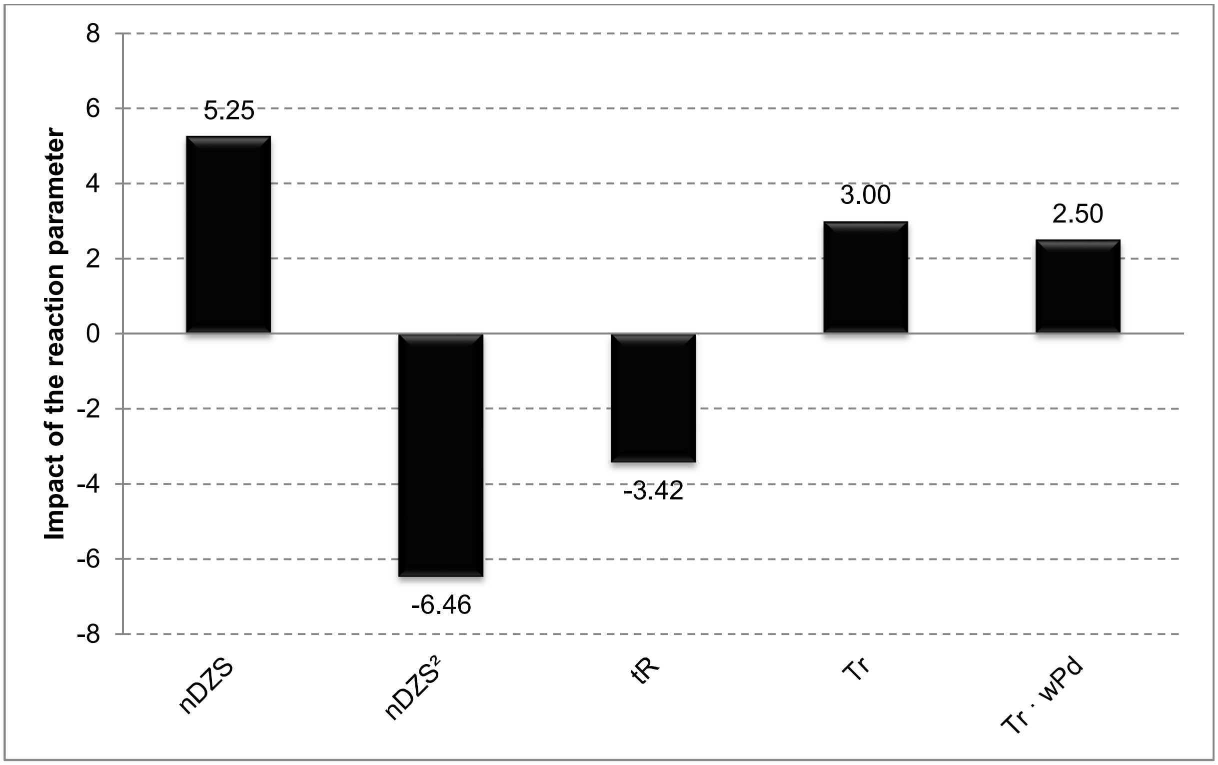


Figure 3. Impact of the reaction parameter

Figure 3 clearly indicates that the molar quantity of the utilized diazonium salt has the most positive influence concerning the yield of the bis-arylated product **4a**. On the other hand an excessive usage of diazonium salt has a negative impact on the outcome and is illustrated by the negative value of the squared molar quantity of diazonium salt (n_{DZS}^2). One reason might be that the molarity exerts an effect on the mass transport of the reactants in the reaction mixture. Thus, Felpin *et al.* reported a negative outcome in the Matsuda-Heck reaction utilizing high molar quantities of diazonium salts[6e]. Furthermore, an extended prereduction time has a negative impact on the formation of bis-arylated product **4a**. In precedent investigations we could demonstrate that prolonged prereduction times decrease the activity of the catalyst.[9] Therefore, the oxidative addition in the catalytic cycle and consequently the formation of bis-arylated product are hampered. In addition the reaction temperature and the interaction of the reaction temperature with the palladium loading on $AlPO_4$ have a positive impact on the obtained yield of product **4a**. Besides the classical kinetic effects this might be explained by a direct influence of the temperature on the nature and consequently catalytic activity of the formed Pd(0)-clusters and their dissolution behaviour in the catalytic cycle. This is in accordance with precedent observations described by Schmidt *et al.*[16]. A comparison of the reaction velocities at 30 °C and 40 °C clearly indicates that a higher reaction rate is obtained at 40 °C (3.719 $mmol*mL^{-1}*h^{-1}$ vs 1.476 $mmol*mL^{-1}*h^{-1}$) which is favourable to the formation of the bis-arylated product and is in line with the observed product distribution as depicted in table 1. Hence, a higher reaction temperature led to an improved product ratio between mono-arylated and bis-arylated products that faciliates the product isolation and purification.

The influence of the combination of the two reaction parameters on the yield of bis-arylated product can be scrutinized by means of interactions shown in figure 4.

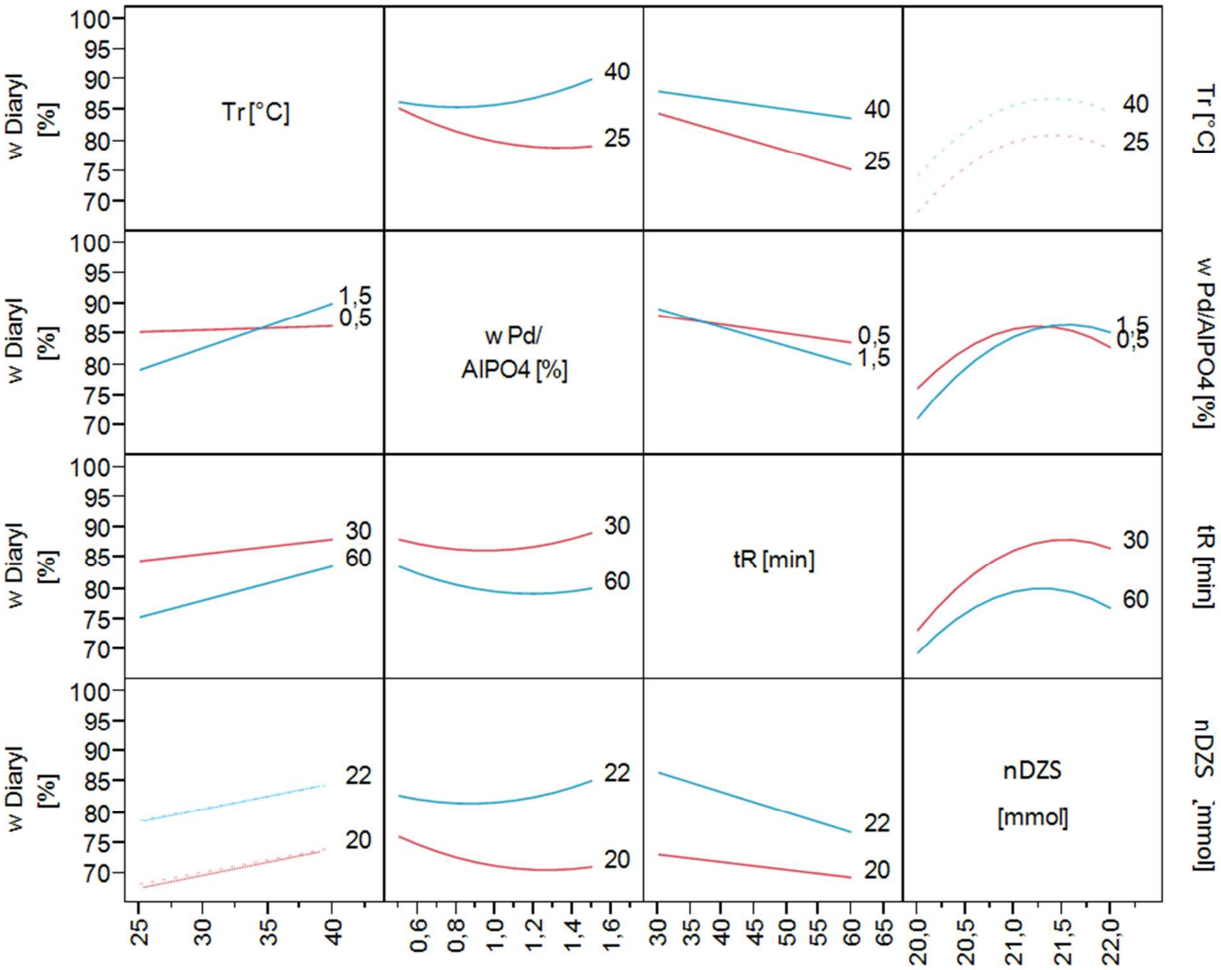


Figure 4. Analysis of the interaction of the reaction parameters

The depicted set of diagrams in which the yield of bis-arylated product is presented as a function of the interactions between two process variables. Thus, the twelve diagramed interactions are a result of the four chosen process parameters reaction temperature T_R, palladium loading w_{Pd}, the prereduction time t_R and the molar quantity of the utilized diazonium salt n_{DZS}. In this study only the interaction between the reaction temperature and the catalyst loading had a significant impact on the yield of the bis-arylated product **4a** (red labeled diagram in **Figure 4**). The diagram shows two graphs. The blue graph displays the proportional dependency on the yield of bis-arylated product as a function of the reaction temperature and catralyst loading of $Pd(OAc)_2/AlPO_4$ ($w_{Pd)}$)

of 1.5%. The red graph displays the outcome as a function of a catalyst loading of 0.5%. Whereas the red graph clearly indicates a horizontal linear slope the blue graph displays a significant ascending slope. The interception point of both graphs is located at a reaction temperature of 35 °C. Hence, a obtained yield of 86% at a reaction temperature does not depend on the catalyst loading. On the opposite the yield is diminished by 6% using 1.5% compared to 0.5% catalyst loading at 40 °C. By the means of an analysis of prediction the values of the parameter concerning the maxima and minima or defined target value can be determined. In figure 5 the influence of the target values reaction temperature (T_R), the prereduction period (t_R), and the molar quantity of diazonium salt (n_{DZS}) in the light of a desirability of 1 for a yield of bis-arylated product of 95.0 ± 4.7% are shown.

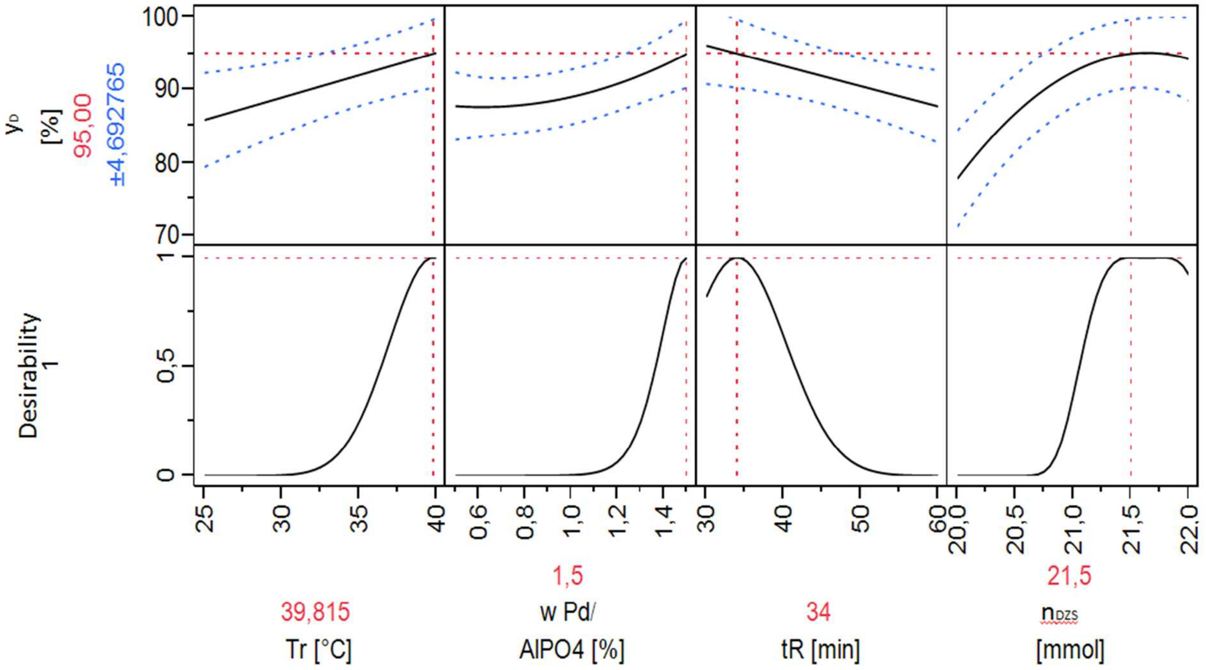
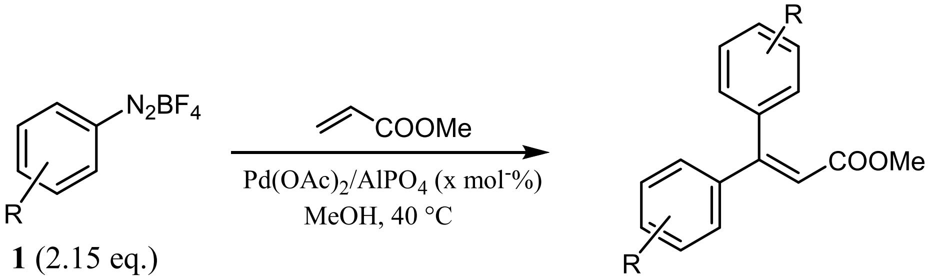


Figure 5. Prediction for the optimized reaction parameters

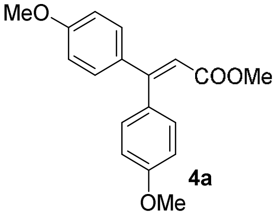
According to **Figure 5** the best results should be obtained by using an isothermic reaction temperature of 40° C, a catalyst loading of 1.5 wt.-%, a prereduction time of 34 minutes and a molar quantity of 21.5 mmol. A control test utilizing these optimized conditions gave an outcome of 91.5% in HPLC and 89% isolated yield of bis-arylated product **4a** and consequently is on the one hand in a good agreement with the prediction and on the other hand comparable to the results reported by Correia *et al*.[7]

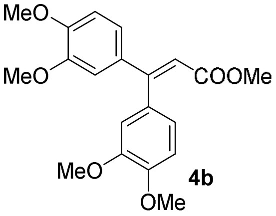
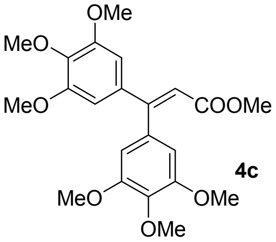
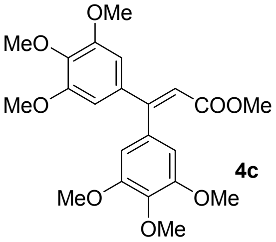
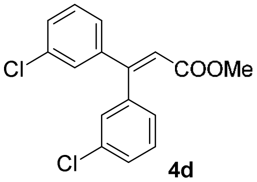
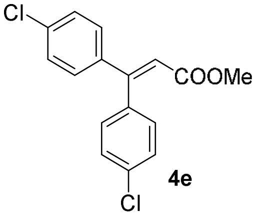
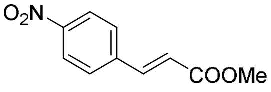
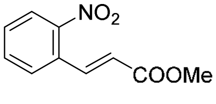
Scope of the catalytic system. These optimized reaction conditions were explored with various aryldiazonium salts and methyl acrylate (**Table 2**).

Table 2. Preparation of ββ-diarylated methyl acrylates



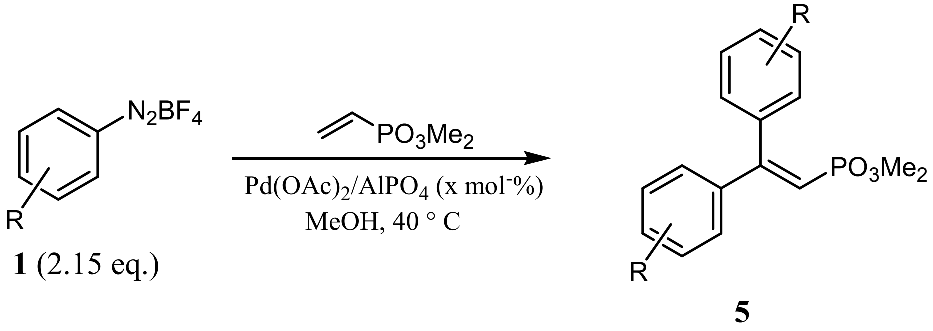
4

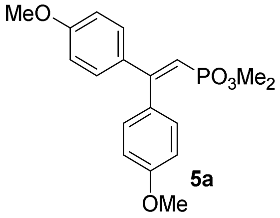
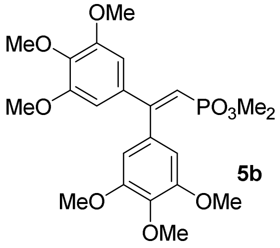
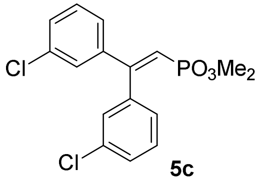
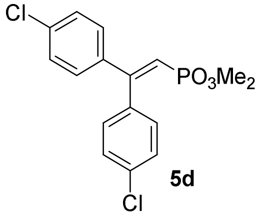
entry	R	Cat. [mol-%]	Product	Yield [%]
1	4-OMe	2	 **4a**	89

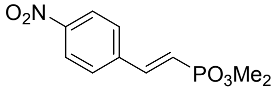
2	3,4-$(OMe)_2$	2	 **4b**	78
3	3,4,5-$(OMe)_3$	2	 **4c**	35
4	3,4,5-$(OMe)_3$	4	 **4c**	64
5	3-Cl	2	 **4d**	76
6	4-Cl	2	 **4e**	41
7	4-NO_2	2	 **3f**	91
8	2-NO_2	2	 **3g**	91

With exception of the nitro-derivatives all bis-arylated products were obtained in moderate to good yields. The diarylation of the nitro substituted aryldiazonium salts provided only monoarylated Heck products in excellent yields due to the modest solubility of the nitro cinnamic esters (entries 7 and 8, Table 2). However, we were pleased that the diarylation of deactivated diazonium salts was successful. Thus, to our best knowledge the first preparation of symmetrical diarylacrylates bearing chloro-functionalities by a Matsuda-Heck-reaction was easily accessible. Strikingly the 3-chloro-benzenediazonium tetrafluoroborate provided a better yield compared to its regioisomer (entries 5 and 6, Table 2). In the case of the highly substituted 3,4,5-trimethoxy-benzenediazonium tetrafluoroborate an increase of the catalyst concentration for obtaining a reasonable yield was necessary (entries 3 and 4, Table 2). However, it has to be pointed out that the new catalytic system $Pd(OAc)_2/AlPO_4$ distinguishes itself by a higher reactivity and enables benign diarylations of acrylates *via* Matsuda-Heck-coupling. This is well reflected in lower catalyst concentrations and temperatures. Encouraged by our findings utilizing our novel catalytic system we prospected to alternative olefins. In a precedent publication one of us described the utilization vinyl phosphonic esters in the Matsuda-Heck reaction.[17] Synthetic protocols towards the synthesis of bis-arylated vinylphosphonates are scarce in literature and all procedures have moderate yields and a limited range of accessible substrates.[18-23] Quite recently Tsai *et* al. reported the first synthesis of bis-arylated vinylphosphonates *via* Heck reaction using aryl iodides as electrophiles.[24] Keeping in mind that the phosphonic ester moiety represents a functional group that is isosteric to ester functionalities in medicinal chemistry the synthesis of bis-arylated vinylphosphonates should be an auspicious target. The synthetic applicability of our new catalytic procedure using the Matsuda-Heck reaction could be extended to the facile synthesis of these compounds for the first time (**Table 3**).

Table 3. Preparation of ββ-diarylated vinylphosphonates



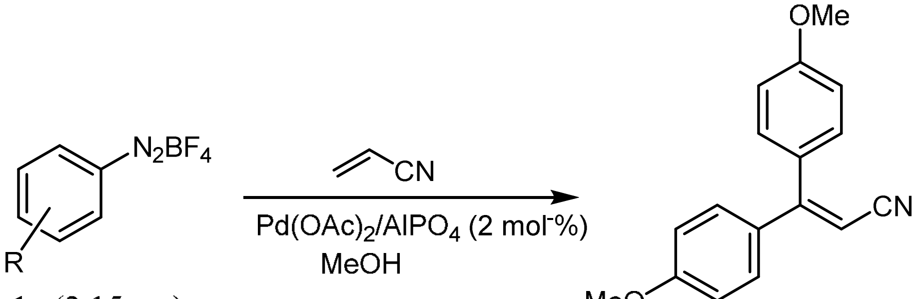
entry	R	Cat. [mol-%]	Product	Yield [%]
1	4-OMe	2	 **5a**	74
2	3,4,5-(OMe)$_3$	4	 **5b**	89
3	3-Cl	2	 **5c**	81
4	4-Cl	2	 **5d**	68

5	4-NO_2	2	 **6e**	95

As depicted in **Table 3** the diarylated vinylphosponates could be obtained in good yields.

It has to be pointed out that strikingly better results employing dimethylvinylphosphonate were obtained in the case of the highly substituted 3,4,5-trimethoxy-benzenediazonium and the chlorinated benzenediazonium salts compared to the analogues acrylate derivatives (entries 2-4, Table 3 vs. entries 4-6, Table 2). Similar to our prior findings utilizing methyl acrylate only monosubstituted Heck product could be obtained in the case of nitro substituted diazonium salt (entry 5, Table 3). Compared to the protocol published quite recently by Tsai *et al.* using aryl iodides[24] in the Mizoroki-Heck reaction this procedure distinguishes itself by lower reaction temperatures, lower palladium loadings and shorter reaction times. Furthermore, the presented method is characterized by its simplicity, the broader scope of substrates and the higher yields compared to the classical procedures described in literature. Besides methyl acrylate and vinyldimethylphosphonic ester, a preliminary study with acrylonitrile was also carried out (**Scheme 4**).

Scheme 4. β,β-Diarylation of acrylnitrile using 4-methoxy-benzenediazonium tetrafluoroborate



1a (2.15 eq.)

7

with T = 40°C: 42%
with T = 50°C: 57%
with T = 60°C: 53%

As depicted in Scheme 4, acrylonitrile could also be applied in the above-mentioned procedure. However, for obtaining a reasonable yield the utilization of 50°C as reaction temperature seems to be beneficial.

Conclusion

In summary, we have first presented a novel catalytic system consisting of palladium immobilized on aluminum phosphate that can be used for the preparation of β,β-diarylated olefins on gram-scale *via* Matsuda-Heck-reaction. The utilization of aluminum phosphate as supporting material for catalyst in cross coupling was not reported so far and represents another additional example for a target-oriented tuning of catalysts in the Matsuda-Heck reaction. The presented approach distinguishes itself by benign reaction conditions combined with high catalytic activity and short reaction times. The efficiency of the new protocol could be elaborated and validated by a Response-Surface-model. Besides an optimized procedure this study provides valuable indications concerning the most important reaction parameter in the Matsuda-Heck-reaction.

Experimental Section

General methods. NMR spectra were recorded on Varian ECX 500 and V300b Varian Mercury spectrometers. Chemical shifts in proton and carbon NMR spectra are reported in ppm relative to the TMS peak at 0.00 ppm or relative to $CDCl_3$ peak at 77.0 ppm, coupling constants (J) in Hz. Infrared (IR) spectra were recorded as neat samples in ATR mode using a Spectrum One (Perkin-Elmer) spectrometer. Mass spectra were recorded on Bruker micrOTOF-QII. Yields refer to isolated material determined to be pure by NMR-spectroscopy, mass spectrometry, and thin layer chromatography (TLC), unless specified otherwise in the text. Flash chromatography

(FC): Merck Silica Gel 60 (240-400 Mesh) and Merck Aluminium oxide 90 active neutral (70-230 Mesh). Melting points were recorded using a Büchi Melting point apparatus M-560. The scanning electron microscopy (SEM) image has been recorded with a Zeiss Gemini 1550 microscope. The catalyst was dispersed onto a carbon adhesive tape. Diazonium salts used in this study were all known and prepared as described in the literature, see Ref. 10. Solvents and chemicals were purchased from VWR or Aldrich and used as received. Dimethylvinylphosphonate was pruchased from BASF SE.

The statistical design of experiment was carried out with the Software JMP® 9.0 (SAS Institute Inc.) (see Supporting Information).

General Procedure for Synthesis of β,β-diarylated methyl acrylates 4a-e.

In a 100mL EasyMax™ reactor, equipped with a reflux condenser and a magnetc stirrer bar, 0.2 mmol palladium acetate (45 mg), 11.4 mmol (1.39 g) aluminum phosphate and 10 mmol (870 mg) methyl acrylate were dispersed in 68 mL methanol. The mixture was stirred (350 rpm) for 34 minutes at 25°C (isothermic conditions). After this pre-reduction of palladium actetate 21.5 mmol of aryldiazonium salt were added and the reaction mixture was heated to 40 °C within 1 min. Reaction development was monitored by heat flow control and gas evolution. When reaction was finalized, reaction mixture was filtrated through celite, poured into ice-water and the water phase was extracted with methylene chloride (3x50 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure. The obtained residues were purified by flash chromatography to obtain the desired product.

Methyl-3,3-bis(4-methoxyphenyl)-acrylate **(4a).** The product was purified by flash chromatography with cyclohexane/ethyl acetate (9:1 and 8:2) as eluent to give the desired product: 89%, 2.65 g (rose solid); m$_P$: 59.0 °C; ^{1}H NMR (500 MHz, CDCl$_3$, ppm) δ 7.24 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.16 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.92 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.85 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.24 (s, 1H), 3.85 (s, 3H); 3.82 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$, ppm) δ 166.70, 160.74, 159.64, 156.82, 133.75, 131.03, 130.80, 129.96, 114.19, 113.65, 113.16, 55.28, 55,13, 51.06; IR: 2959, 1722, 1604, 1511, 1246, 1172, 1162, 1152, 1029, 828; ESI-MS m/z (Intensity): 299 [MH$^+$] (22), 267 (100).

Methyl-3,3-bis(3,4-dimethoxyphenyl)-acrylate **(4b).** The product was purified by flash chromatography with cyclohexane/ethyl acetate (9:1 and 8:2) as eluent to give the desired product: 78%, 2.79 g (orange viscous oil); ^{1}H NMR (500 MHz, CDCl$_3$, ppm) δ 6.91 – 6.79 (m, 5H), 6.73 (d, $^3J_{HH}$ = 1.9 Hz,, 1H), 6.25 (s, 1H), 3.93 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H); 3.63 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$, ppm) δ 166.66, 156.67, 150.37, 149.10, 148.62, 148.22, 133.77, 131.15, 122.37, 122.09, 114.60, 112.73, 111.14, 110.55, 110.27, 55.89, 55,86, 55.74, 51.16; IR: 2947, 2837, 2376, 2281, 2038, 1719, 1514, 1253, 1216, 1142, 1129, 1024, 859, 811, 766; ESI-MS m/z (Intensity): 259 [MH$^+$] (61), 327 (100).

Methyl-3,3-bis(3,4,5-trimethoxyphenyl)-acrylate **(4c).** For the preparation of **4c** 4 mol-% Pd(OAc)$_2$ were used. The product was purified by flash chromatography with cyclohexane/ethyl acetate (9:1 and 8:2) as eluent to give the desired product: 64%, 2.65 g (white); m$_P$: 100.4°C; ^{1}H NMR (500 MHz, CDCl$_3$, ppm) δ 6.53 (s, 2H), 6.45 (s, 2H), 6.27 (s, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.82 (s, 3H), 3.79 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$, ppm) δ 166.44, 156.35, 152.91, 152.67, 139.48, 138.12, 136.12, 133.77, 116.21 106.82, 60.92, 56.18, 51.33; IR:

2952, 2839, 2376, 1696, 1583, 1505, 1421, 1339, 1287, 1248, 1125, 1005, 980, 818; ESI-MS m/z (Intensity): 419 [MH$^+$] (34), 387 (100); HR-MS (ESI): m/z = 419.1698 [MH$^+$], calcd. for $C_{22}H_{26}O_8$: 419.17067.

Methyl-3,3-bis(3-chlorphenyl)-acrylate **(4d).** The product was purified by flash chromatography with cyclohexane/ethyl acetate (9:1 and 8:2) as eluent to give the desired product: 76%, 2.33 g (colorless viscous liquid); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.40 - 7.24 (m, 5H), 7.18 (s, 1H), 7.14 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.10 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 6.36 (s, 1H), 3.63 (s, 3H), 3.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 165.71, 153.82, 141.93, 139.82, 134.66, 134.07, 129.78, 129.67, 129.34, 128.98, 128.60, 128.12, 127.28, 126.37, 118.66, 51.51; IR: 2959, 1726, 1564, 1261, 1162, 1162, 878, 789, 702; ESI-MS m/z (Intensity): 307 [MH$^+$] (45), 275 (100); HR-MS (ESI): m/z = 307.03124 [MH$^+$], calcd. for $C_{16}H_{12}Cl_2O_2$: 307.02934.

Methyl-3,3-bis(4-chlorphenyl)-acrylate **(4e).** The product was purified by flash chromatography with cyclohexane/ethyl acetate (9:1 and 8:2) as eluent to give the desired product: 41%, 1.25 g (white solid); m_P: 118.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.37 (d, $^3J_{HH}$ = 8.5 Hz,, 2H), 7.31 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.20 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.13 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.34 (s, 1H), 3.63 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 165.98, 154.56, 138.85, 136.66, 135.88, 134.55, 130.54, 129.52, 128.75, 128.34, 117.52, 51.43; IR: 2957, 1717, 1623, 1490, 1263, 1159, 1089, 1014, 834; ESI-MS m/z (Intensity): 307 [MH$^+$] (45), 275 (100); HR-MS (ESI): m/z = 307.03144 [MH$^+$], calcd. for $C_{16}H_{12}Cl_2O_2$: 307.02934.

Methyl-3-(2-nitrophenyl)-acrylate **(3f).** The product was obtained as yellow solid: 91%, 1.88 g; m_P: 72.5 °C (lit.m_p 71 – 73 °C)[25.]; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.12 (d, $^3J_{HH}$ = 15.8 Hz, 1H), 8.04 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.64 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.57

– 7.53 (m, 1H), 6.37 (d, $^3J_{HH}$ = 15.8 Hz, 1H), 6.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 165.17, 147.31, 139.12, 132.49, 129.54, 129.29, 128.10, 123.89, 121.86, 50.99; IR: 2956, 1718, 1520, 1345, 1332, 1292, 1208, 1196, 1180, 975, 756; ESI-MS m/z (Intensity): 208 [MH^+] (19), 176 (100).

Methyl-3-(4-nitrophenyl)-acrylate **(3g).** The product was obtained as yellow solid: 91%, 1.88 g; m_P: 136-137 °C (lit m_p.: 137.8-138.8 °C)[26.]; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.25 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.70 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.67 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.57 – 7.53 (m, 1H), 6.57 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 3.63 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 166.44, 148.49, 141.88, 140.45, 128.51, 123.90, 122.06, 52.31; IR: 2957, 1722, 1510, 1343, 1314, 1193, 1172, 847, 706; ESI-MS m/z (Intensity): 207 [M] (18), 176 (100).

General Procedure for Synthesis of β,β-diarylated dimethyl vinylphosphonates 5a-d.

In a 100mL EasyMax™ reactor, equipped with a reflux condenser and a magnetc stirrer bar, 0.2 mmol palladium acetate (45 mg), 11.4 mmol (1.39 g) aluminum phosphate and 10 mmol (1.36 g) dimethylvinylphosphonate were dispersed in 68 mL methanol. The mixture was stirred (350 rpm) for 34 minutes at 25 °C (isothermic conditions). After this pre-reduction of palladium actetate 21.5 mmol of aryldiazonium salt were added and the reaction mixture was heated to 40 °C within 1 min. Reaction development was monitored by heat flow control and gas evolution. When reaction was finalized, reaction mixture was filtrated through celite, poured into ice-water and the water phase was extracted with methylene chloride (3x50 mL). The combined organic phases were dried over anhydrous

$MgSO_4$ and then concentrated under reduced pressure. The obtained residues were purified by flash chromatography to obtain the desired product.

Dimethyl-(2,2-bis(4-methoxyphenyl)vinyl)-phosphonate (**5a**). The product was purified by flash chromatography with methylene chloride/ethyl acetate (9:1 and 8:2) as eluent to give the desired product: 74%, 2.56 g (yellow viscous liquid); ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.32 (d, $^3J_{HH}$ = 9.0 Hz,, 2H), 7.23 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.92 (d, $^3J_{HH}$ = 8.5 Hz; 2H), 6.84 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 5.99 (d, $^3J_{HP}$ = 15.7 Hz, 1H), 3.85 (s, 3H); 3.82 (s, 3H), 3.53 (s, 3H), 3.51 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 160.76, 160.28, 160.04, 134.20, 134.02, 131.34, 129.81, 113.60, 113.17, 111.02, 109.46, 55.26, 52,04; ^{31}P NMR (202 MHz, $CDCl_3$, ppm) δ 21.20; IR: 3667, 2965, 1606, 1510, 1248, 1175, 1028, 861, 834, 817, 800; ESI-MS m/z (Intensity): 349 [MH^+] (100); HR-MS (ESI): m/z = 349.12111 [MH^+], calcd. for $C_{18}H_{21}O_5P$: 349.12056.

Dimethyl-(2,2-bis(3,4,5-trimethoxyphenyl)vinyl)-phosphonate (**5b**). For the preparation of **5b** 4 mol-% $Pd(OAc)_2$ were used. The product was purified by flash chromatography with methylene chloride/ethyl acetate (9:1 and 8:2) as eluent to give the desired product: 89%, 4.17 g (brownish solid); m_P: 93.4 °C; ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 6.71 (s, 2H), 6.53 (s, 2H), 6.04 (d, $^3J_{HP}$ = 15.4 Hz, 1H), 3.91 (s, 12H); 3.89 (s, 3H), 3.87 (s, 6H), 3.81 (s, 6H), 3.56 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 160.58, 152.85, 152.52, 139.50, 138.52, 136.62, 136.44, 133.80, 113.51, 111.96, 107.41, 105.92, 60.87, 56.22, 52.20; ^{31}P NMR (121 MHz, $CDCl_3$, ppm) δ 20.65; IR: 2955, 2843, 1582, 1572, 1505, 1360, 1242, 1121, 849, 794; ESI-MS m/z (Intensity): 468 [M^+] (100); HR-MS (ESI): m/z = 469.16286 [MH^+], calcd. for $C_{22}H_{29}O_9P$: 469.16282.

Dimethyl-(2,2-bis(3-chlorphenyl)vinyl)-phosphonate **(5c).** The product was purified by flash chromatography with methylene chloride/ethyl acetate (9:1 and 8:2) as eluent to give the desired product: 81%, 2.89 g (yellow liquid); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.44 – 7.24 (m, 7H), 7.13 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.20 (d, $^3J_{HP}$ = 14.5 Hz, 1H), 3.57 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 157.46, 142.42, 142.25, 134.60, 134.00, 129.73, 129.69, 129.37, 129.09, 127.97, 127.77, 127.77, 127.75, 126.22, 116.88, 115.34, 55.26; ^{31}P NMR (202 MHz, $CDCl_3$, ppm) δ 18.54; IR: 2952, 2849, 1562, 1251, 1053, 1029, 859, 824, 790, 691; ESI-MS m/z (Intensity): 358 [MH$^+$] (67), 356 (100); HR-MS (ESI): m/z = 357.02191 [MH$^+$], calcd. for $C_{16}H_{15}Cl_2O_3P$: 357.02149.

Dimethyl-(2,2-bis(4-chlorphenyl)vinyl)-phosphonate **(5d).** The product was purified by flash chromatography with methylene chloride/ethyl acetate (9:1 and 8:2) as eluent to give the desired product: 68%, 2.43 g (yellow liquid); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.38 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.30 (d, $^3J_{HH}$ = 2.1 Hz, 2H), 7.29 (d, $^3J_{HH}$ = 2.1 Hz; 2H), 7.18 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.14 (d, $^3J_{HP}$ = 14.6 Hz, 1H), 3.55 (s, 3H); 3.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 158.12, 139.35, 139.17, 136.68, 136.62, 135.91, 135.10, 130.95, 129.36, 128.69, 128.29, 115.40, 113.86, 52.23; ^{31}P NMR (202 MHz, $CDCl_3$, ppm) δ 19.09; IR: 3668, 2969, 1588, 1491,, 1251, 1090, 1053, 1030, 1014, 926, 862, 825, 761; ESI-MS m/z (Intensity): 358 [MH$^+$] (70), 356 (100); HR-MS (ESI): m/z = 357.02232 [MH$^+$], calcd. for $C_{16}H_{15}Cl_2O_3P$: 357.02149.

Dimethyl-3-(4-nitrophenyl)vinyl phosphonate **(6e).** The product was obtained as yellow solid: 95%, 2.45 g; m_P: 109.9 °C (lit[28]: 97-100 °C); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.26 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.66 (d, $^3J_{HH}$ = 8.5 Hz 2H), 7.59 (d, $^3J_{HH}$ = 17.6 Hz, 1H), 7.54 (d, $^3J_{HH}$ = 17.6 Hz, 1H), 6.37 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 7.59 – 7.52 (m, 2H), 6.41 (t, $^3J_{HH}$ = 17.6 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$, ppm) δ 148.55, 146.33, 140.57, 128.34, 124.14, 118.71, 117.10, 52.66, 52.62; ^{31}P NMR (202 MHz, CDCl$_3$, ppm) δ 20.65; IR: 3073, 2956, 2849, 1514, 1345, 1246, 1043, 1019, 995, 853, 832, 766, 743; ESI-MS m/z (Intensity): 258 [M$^+$] (100).

3,3-Bis(4-methoxyphenyl)acrylnitrile **(7).** In a 100mL EasyMax™ reactor, equipped with a reflux condenser and a magnetc stirrer bar, 0.2 mmol palladium acetate (45 mg), 11.4 mmol (1.39 g) aluminum phosphate and 10 mmol (870 mg) acrylonitrile were dispersed in 68 mL methanol. The mixture was stirred (350 rpm) for 34 minutes at 25 °C (isothermic conditions). After this prereduction of palladium actetate 21.5 mmol of aryldiazonium salt were added and the reaction mixture was heated to 50 °C within 1 min. Reaction development was monitored by heat flow control and gas evolution. When reaction was finalized, reaction mixture was filtrated through celite, poured into ice-water and the water phase was extracted with methylene chloride (3x50 mL). The combined organic phases were dried over anhydrous MgSO$_4$ and then concentrated under reduced pressure. The product was purified by flash chromatography with methylene chloride/ethyl acetate (9:1 and 8:2) as eluent to give the desired product: 57%, 1.51 g m$_P$: 109.3 °C (lit mp: 105-108 °C)[27]; ^{1}H NMR (500 MHz, CDCl$_3$, ppm) δ 7.40 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.24 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.95 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.88 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 5:54 (s, 1H), 3.85 (s, 3H); 3.83 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$, ppm) δ 162.21, 161.36, 160.87, 131.55, 131.19, 130.97, 130.06, 129.43, 118.68, 113.88, 113.75, 91:41, 55,33, 55.26; IR: 3041, 2202, 1601, 1584, 1514, 1253, 1176, 1028, 838, 806; HR-MS (ESI): m/z = 266.11803 [MH$^+$], calcd. for $C_{17}H_{16}NO_2$: 266.11818.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and analytical data for isolated products.

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