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FULL PAPER

Benign Arylations of Dimethyl Itaconate *via* Heck-Matsuda Reaction Utilizing *in-situ* Generated Palladium on Aluminum Oxide

Lauryna Matelienė (née Dauksaitė),[a] Jan Knaup,[a] Frank von Horsten,[a] Xiaoting Gu,[b] and Heiko Brunner*[a]

Abstract: *In-situ* generated palladium on aluminum oxide provides an active and efficient catalytic system for the preparation of arylmethylidene succinates using the Heck-Matsuda reaction. Beside the monoarylation the first examples of the biarylation of these monomers will be described.

Introduction

Arylmethylidene succinates represent interesting building blocks for the preparation of synthetic targets and natural products. Thus, this class of substances were used as synthons for the preparation of γ-butyrolactones,[1] 1,4-diphenylbutadiene derivatives[2] and 2,3-butandioles.[3] Furthermore, they are excellent precursors of chiral benzyl succinates *via* asymmetric hydrogenation.[4]

Charlton *et al.* utilized the arylmethylidene succinates as key-building blocks for the synthesis of lignans such as Magnostinin and Cyclogalgravin.[5] Rama Devi and Rajaram used arylmethylidene succinates as intermediates for the synthesis of anthraquinone carboxylic acid- and coumarine acetic acid derivatives that are useful agents for the treatment of rheumatoid arthritis, osteoporosis and cancer.[6] Recently Shi and Pierce described the total synthesis of (+)-Plagiogyrin A using E-4-(allyloxy)-2-(4-allyloxy)benzylidene-4-oxobutanoic acid as key building block.[7]

The synthetic access to this important class of substances is frequently given by a classical Stobbe-condensation,[8] Wittig reaction[9] or Horner-Emmons reaction[10] Beside these reaction pathways McCombie and co-workers described a tri-n-butylphosphine mediated condensation reaction or aromatic and heteroraromatic aldehydes with diethyl fumarate or diethyl maleate.[11] Jiang *et al.* described a modification of this reaction type by using tris(4-anisyl)phosphine.[12] A disadvantage of classical condensation reactions due to possible aldol reactions is the inability to synthesize arylmethylidene succinates bearing carbonyl functionalities such as a keto group.

Wang *et al.* synthesized various dimethyl 2-arylidine succinates in moderate to reasonable yields *via* an unexpected reaction of dimethyl acetylenedicarboxylate with in situ generated arylketenes catalyzed by 1-methylimidazole.[13]

Next to the classical condensation reactions employing aromatic and heteroaromatic aldehydes the Mizoroki-Heck reaction using aromatic iodides and triflates was also successfully utilized for the preparation of arylmethylidene succinates.[6, 14] However, these reactions often had a long reaction time and had to be carried out at elevated reaction temperatures for obtaining the desired reaction products in moderate to good yields. Furthermore, the use of amines as bases and DMF as an ecologically problematic solvent was necessary. For exhibiting the efficiency of the synthesis of arylmethylidene succinates *via* Mizoroki-Heck reaction, Iyer et al. described very recently a ligand free catalytic system consisting of $Pd(OAc)_2$ and stoichiometric quantities of silver salts as sequestration agents for halides.[15] Despite the good results, the use of phosphines, bases and/or silver salts is indispensable for the synthetic protocols mentioned above. An additional disadvantage in the Heck reaction is the need for expensive iodides or triflates as electrophiles. Furthermore, halogenated arylidene succinates are not accessible *via* a classical Mizoroki-Heck reaction.

The Heck-Matsuda reaction, which has provided valuable services in organic synthesis over the past decades, opens up a way out of the limitations of the previous presentation methods described above.[16 – 25]

Due to the high reactivity of the aryldiazonium salts compared to the corresponding aryl halides, the above limitations can often be circumvented. The production of arylmethylidene succinates has hardly been described to date. Correia and Pastre have published

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only the preparation of two derivatives.[26] However, it is noteworthy that the reactions were carried out with a quite high palladium concentration of 10 mol-% and comparatively high reaction temperatures of 65°C in methanol. In this regard the development of a more efficient synthetic protocol is a rewarding target.[26]

Schmidt and colleagues recently described the successful arylation of itaconimides using the Heck-Matsuda reaction. With a catalyst concentration of 5 mol-% the synthesis of 3-arylmethylidene pyrrolidine-2,5-diones in good to very good yields was achieved.[27]

Thus, stimulated by these findings and based on our precedent results concerning the development and utilization of an *in-situ* generated palladium on aluminum oxide in gram-scale Matsuda-Heck reactions we wanted to apply this new catalytic system for the preparation of functionalized arylmethylidene succinates.[28]

Herein, we would like to report a synthetic protocol using the Heck-Matsuda reaction for a facile and benign synthesis of functionalized arylmethylidene succinates in the presence of an *in-situ* generated palladium on aluminum oxide as catalytic system.

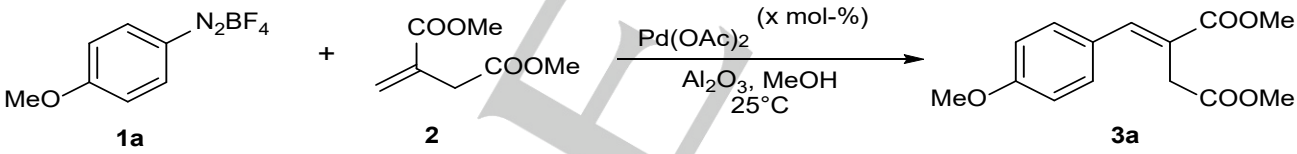
Results and Discussion

The conversion of 4-methoxybenzenediazonium tetrafluoroborate **1a** with dimethyl itaconate **2** was chosen as the starting point for our studies and reaction optimization. Based on our previous positive results with acrylates, the *in-situ* generated catalytic system was to be prepared by a pre-reduction of $Pd(OAc)_2$ in the presence of olefin and aluminum oxide 90 in methanol (1.9 wt.-% $Pd(OAc)_2$ on Al_2O_3).[28]

The objective of the optimization was to find and produce a suitable catalyst which would enable the conversion to the desired aryl-methylidene succinates in high yields with a low catalyst quantity at 25°C. In addition to the influence of the catalyst concentration and the ratio of reactants, the agitation speed should also be investigated. For this purpose, the corresponding optimization experiments are carried out at two different stirring speeds (200 and 350 rpm).

In addition to determining the yield, the reaction rate and the catalytic activity of the reaction system were investigated by measuring the gas quantity of the nitrogen released during the reaction (Table 1).

Table 1. Optimization of reaction conditions.



Entry[a]	Ratio **1a** vs **2**	Catalyst [mol %]	Agitation speed [rpm]	Pre-reduction	Conv- Rate [mmol mL^{-a} h^{-1}]	TOF [h^{-1}]	Yield [%]	Reference
1	1:1.5	1	200	60 min	0.247	74	60	This work
2	1:1.5	1	200	30 min	0.362	109	86	This work
3	1:1	1	200	30 min	0.310	93	89	This work
4	1:1	2	200	30 min	0.856	257	89	This work
5	1:1	1	350	30 min	0.255	76	97	This work
7	1:1	10	n.a.	no	n.a.	n.a.	86	Ref: [26]

[a] Reaction scale: 10 mmol diazonium salt in 30 mL MeOH

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As can be seen from Table 1, higher yields were obtained with a pre-reduction time of 30 minutes compared to 60 minutes (Entry 2 vs. Entry 1). This is also ultimately reflected in the course of the heat flow (Figure 1).

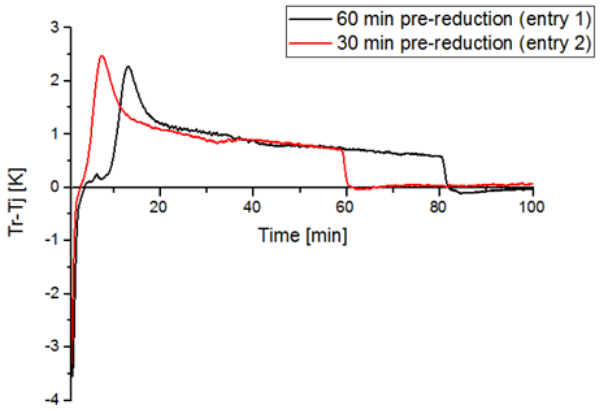


Figure 1. Impact of the pre-reduction time on the heat flow of the reaction.

Thus, the shorter pre-reduction time results in an earlier start of the reaction on the one hand (induction time 492 seconds after 30 minutes pre-reduction vs. 690 seconds after 60 minutes pre-reduction), and a higher exothermia, a higher reaction rate and thus a higher catalytic activity on the other hand (Figure 1; Entries 1 and 2, Table 1). Similar results concerning the impact of different pre-reduction times could be observed in the case of cinnamic ester derivatives.[28]

Another interesting effect is the ratio of diazonium salts to dimethyl itaconate. The investigations showed that, despite a lower reaction rate, somewhat better results were achieved in a ratio of 1:1, which is advantageous for a better atomic economy (Entry 2 vs. Entry 3, Table 1). Thus, the reaction products resulting from the reaction could be obtained in clean form without further column purification after filtration of the immobilized catalyst, quenching in water and extraction. In analogy to the results for cinnamic ester derivatives, only traces of palladium (< 10ppm) could be detected using ICP-MS after the isolation described above.(28)

An increase of the catalyst quantity to 2 mol-% led to a significant reaction acceleration and shortening of reaction time (34 minutes instead of 76 minutes in the case of 1 mol %) but no considerable improvement of yield (Table 1, Entry 4).

The effect of the agitation is noticeable. As can be seen from Table 1, increasing the stirring speed from 200 rpm to 350 rpm increased the yield to an excellent 97% on the one hand, but on the other hand a significant reduction in reaction speed and catalytic activity could be observed (Entry 5 vs. Entry 3, Table 1). The almost quantitative yield is bought with a longer reaction time (93 minutes at 350 rpm vs. 76 minutes at 200 rpm) and induction time (718 seconds at 350 rpm vs. 403 seconds at 200 rpm) of the reaction. This contrasts strikingly with the results of A. Schmidt *et al.* which, in the case of a Mizoroki-Heck reaction of bromobenzene with styrene using various palladium(II)-pre-catalysts and palladium on charcoal as well, showed that an increase in agitation speed is accompanied by an increase in the reaction rate and a shortening of the reaction time.[29]

For rationalizing these experimental findings we investigated on the one hand the particle size distribution using scanning transmission electron microscopy (STEM) in SEM (Figure 2) and on the other hand the immobilized palladium content by means of ICP-MS.

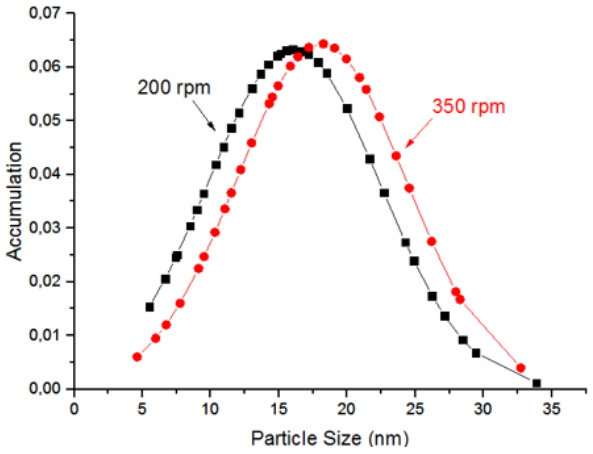


Figure 2. Particle size distribution of *in situ* generated palladium on aluminum oxide in dependence of the agitation speed.

As depicted in Figure 2, a slightly larger particle size distribution is obtained at higher agitation speed than at lower agitation speed. Another interesting aspect is the influence of the stirring speed on the content of immobilized palladium on the carrier material. In addition to the formation of smaller catalyst particles (Figure 2), a higher degree of immobilized palladium is obtained at a lower stirring speed (0.740% at 200 rpm vs. 0.680% at 350 rpm). Both the smaller particle size distribution and the larger supported palladium content explain to a certain extent the significantly

higher reaction rates obtained at the lower agitation speed despite the poorer mass transport. However, in contrast to previously used olefins such as methyl acrylate,[28] a higher yield is obtained despite the lower catalytic activity at the higher agitating speed, which to some extent might be explained by better mass transport. However, compared to the corresponding reaction of methyl acrylate, the dimethyl itaconate reacts much more slowly (0.255 mmol mL^{-1} h^{-1} vs 1.467 mmol mL^{-1} h^{-1}) under comparable reaction conditions despite a smaller particle size distribution (mean particle size 18.1 nm vs. 52.3 nm).[28] This might be explained by a stabilization of the Pd by the ester group in the Pd-complex, which occurs after the insertion step in the catalytic cycle. DFT calculations showed that complexation *via* carbonyl oxygen is 34.8 kJ/mol more stable than possible stabilization *via* the methoxy group of the ester functionality. (Figure 3)

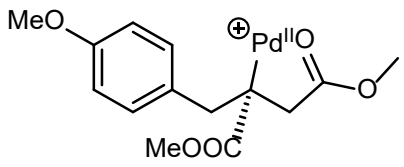


Figure 3. Pd^{II}-stabilization after syn insertion.

The stabilization might hamper the consecutive isomerization and therefor, the β-H-elimination. Similar complexations have recently been confirmed by Braga and colleagues in Heck-Matsuda reactions with allyl esters.[30]

Compared to the prior results published by Correia and Pastre (Entry 6, Table 1)[25] the presented synthetic protocol utilizing an *in-situ* generated palladium on aluminum oxide distinguishes itself by a higher yield and more benign reaction conditions.

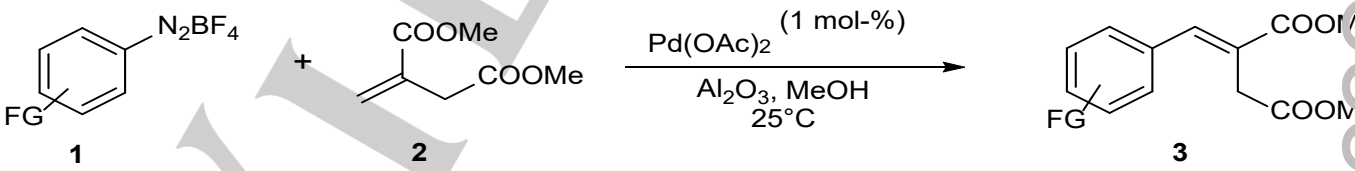
Having these optimized conditions for the Heck-Matsuda reaction in our hands, we explored the scope of the synthetic protocol with various diazonium salts (Table 2). As depicted in Table 2, with exception of the 4-nitrobenzenediazonium salt (Entry 13) and the 4-iodobenzenediazonium salt (Entry 7), all products are obtained in good to excellent yields.

In the case of the 4-nitro derivative, the moderate yield may be due to the poor solubility of the corresponding diazonium salt. However, doubling the amount of solvent did not improve the yield. Strikingly, in the case of the iodine derivative **3g** (Entry 7) only a moderate yield could be obtained in comparison to other halogenated representatives. Whereas double arylvinylation was also observed in the case of methyl acrylate in the 4-iodobenzenediazonium salt, this did not occur when dimethyl itaconate was used.[28] An extension of the reaction time from 720 minutes to 66 hours brought only a slight improvement of the yield. Instead, unreacted dimethyl itaconate could be recovered.

On the positive side, it should be noted that both halogenated aryl-methylidene succinates and arylmethylidene succinates with carbonyl functionalities could be obtained in excellent yields with the present synthesis protocol, which are not easily accessible by classical Heck reaction or Stobbe condensation.

Also the presence of a cyano group, which turned out to be problematic in the case of the production of the 4-cyanobenzalacetone by Heck-Matsuda reaction, was tolerated without any problems, so that the corresponding product **3l** could be obtained in excellent yields.[31] With the exception of some representatives, most reactions are completed within one hour.

Table 2. Optimization of reaction conditions.

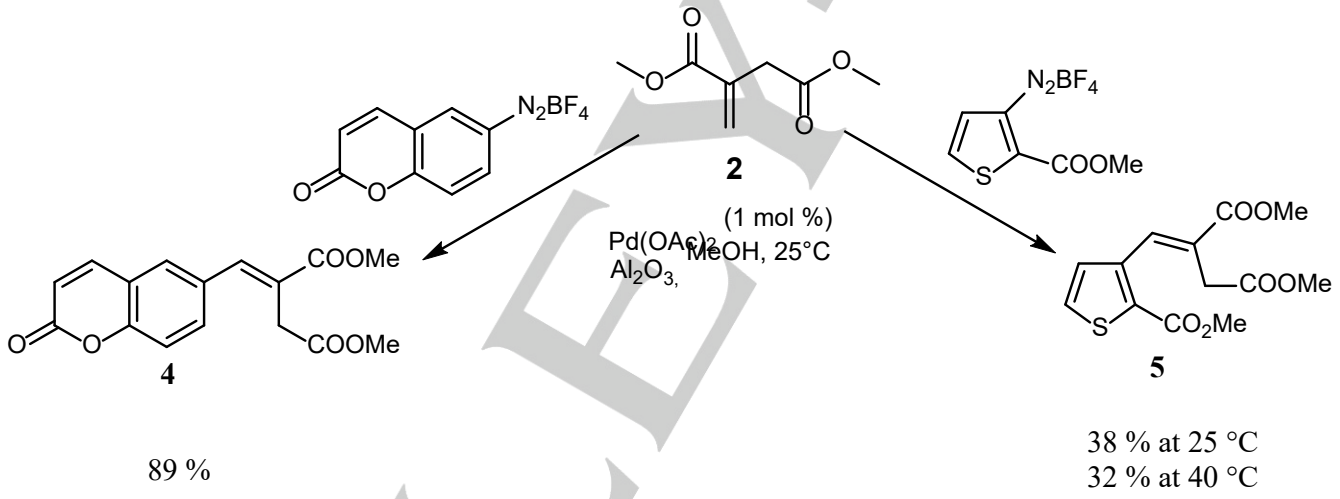


Entry[a]	FG	Product	Reaction time	Yield [%]
1	4-OMe	3a	93 minutes	97
2	3-OMe	3b	30 minutes	75
3	3,4,5-$(OMe)_3$	3c	35 minutes	89
4	4-Cl	3d	50 minutes	93
5	3-Cl	3e	40 minutes	84

6	4-F	3f	35 minutes	90
7	4-I	3g	720 minutes	53 (65)[b], [d]
8	4-Br	3h	30 minutes	89
9	2-COOMe	3i	105 minutes	80
10	4-COOMe	3j	50 minutes	84
11	4-COMe	3k	40 minutes	80
12	4-CN	3l	160 minutes	96
13	4-NO_2	3m	60 minutes	45 (47)[c]
14	H	3n	30 minutes	90

[a] Reaction scale: 10 mmol diazonium salt in 30 mL MeOH; 350 rpm. [b] 66 hours reaction time, [c] reaction in 60 mL MeOH, [d] 15% dimethyl itaconate recovered.

To demonstrate the further synthetic potential of our method, we investigated the monoarylation using heterocyclic diazonium salts. For this purpose 2-oxo-2H-chromene-6-diazonium tetrafluoroborate and 2-(methoxycarbonyl)-thiophene-3-diazonium tetrafluoroborate were reacted with dimethyl itaconate (Scheme 1).



Scheme 1. Heterocyclic Diazonium salts in the monoarylation of dimethyl itaconate

While in the case of the coumarine derivative an excellent yield could be obtained, the conversion of the 2-(methoxycarbonyl)-thiophene-3-diazonium tetrafluoroborate is more challenging. Neither at 25°C nor at 40°C high yields of the product **5** were obtained. In both cases, unreacted dimethyl itaconate (60% and 64%, respectively) could be recovered after completion of the reaction. The reason for this could be found in an intermolecular or intramolecular stabilization of the palladium after the oxidative addition or in a catalyst poisoning by the thiophene sulphur. Since in the literature the above mentioned diazonium salt was successfully converted by Raduán *et al.* with ethyl acrylate and by Brunner *et al.* with butanone in the Heck-Matsuda reaction, catalyst poisoning seems unlikely.[31, 32]

Due to the very good yield obtained with the benzene analogues 2-carboxymethylbenzenediazonium tetrafluoroborate **1i** (Table 2, Entry 9), a purely intramolecular stabilization of the cationic palladium species after oxidative addition can be substantially excluded.

However, DFT calculations indicate a more intermolecular stabilization of palladium after olefin insertion, which makes subsequent β-H-elimination significantly more difficult. (Figure 4)

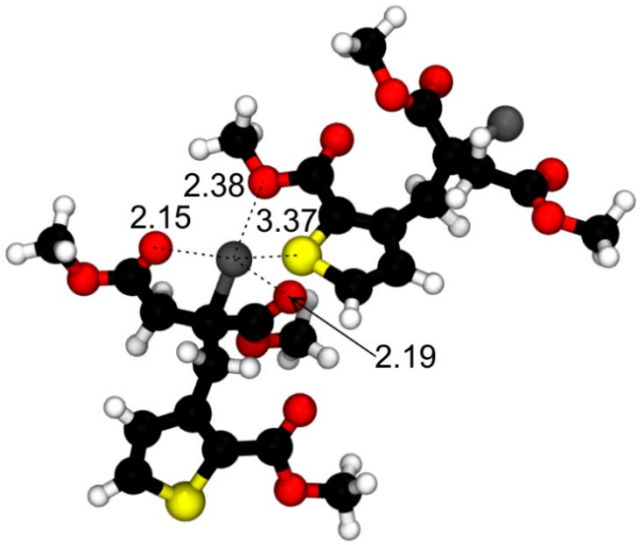


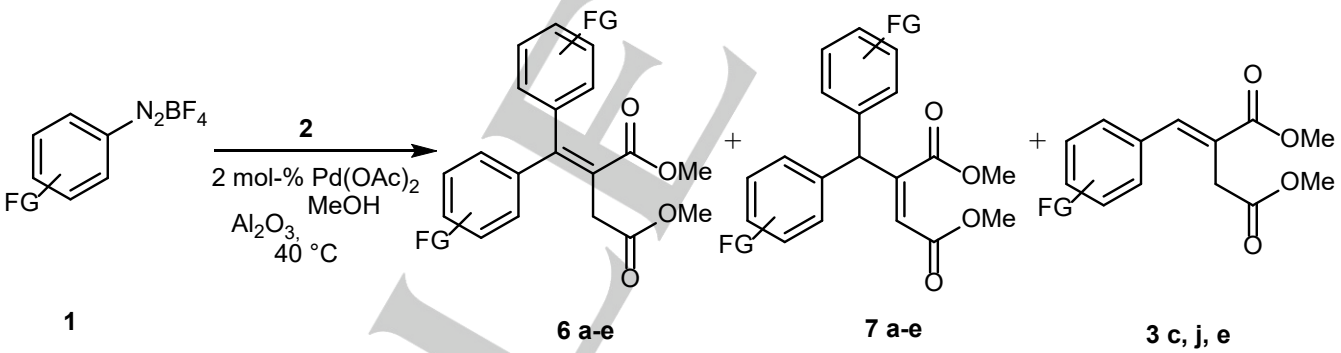
Figure 4. Proposed intermolecular interaction between Pd and thiophene moiety.

According to the DFT calculations, in addition to the stabilization of palladium by ester functionality described in Figure 3, further interaction with the carboxymethyl-thiophene moiety is likely and thus explains the moderate yields.

However, it should be pointed out, that in all cases the E-isomer was exclusively formed, confirmed by 2D NOESY or ROESY NMR.

Stimulated by the work of Correia and co-workers concerning the biarylation of acrylates and maleic anhydride[33-35], the iterative Heck-Matsuda couplings with itaconimides by B. Schmidt *et al.*[27] and encouraged by our studies regarding the β,β-diarylation of acrylates and vinylphosphonates[36] we decided to embark on the biarylation of dimethyl itaconate. In accordance with our previous reaction conditions regarding the β,β-diarylation of acrylates with palladium on aluminum phosphate as catalyst, we converted several diazonium salts (2.2 eq.) with dimethyl itaconate at 40°C and 2 mol-% catalyst.[36] In the context of this study both electron-rich and electron-poor aryldiazonium salts were investigated (Table 3).

Table 3. Diarylation of Dimethyl itaconate with various Aryldiazonium salts



Entry[a]	FG	Product **6** & **7**[b]	Product **3**[c]	Yield [%] **6** & **7**[c] (Ratio **6** : **7**)	Yield [%] **3**[c]
1	4-OMe	6a & 7a	-	93 (36:38)	-
2	2-OMe	6b & 7b	-	90 (73:27)	-
3	3,4,5-(OMe)$_3$	6c & 7c	3c	64 (13:87) 84 (17:83)[b]	31 8[b]
4	4-COOMe	6d & 7d	3j	37 (24:76) 33 (23:77)[b]	41 84[b]
5	4-Cl	6e & 7e	3e	84 (25:75)	10

[a] Reaction conditions: 2 mol-% $Pd(OAc)_2$; 40°C, 68mL MeOH, [b] Utilization of 5 mol-% catalyst, [c] Yields based on dimethyl itaconate used

As can be seen from Table 3, with exception of electron-poor 4-carboxymethyl-benzenediazonium tetrafluoroborate **1d** (Entry 4), biarylated products were obtained in good to excellent yields by using 2 mol-% catalyst. In the case of the electron-rich 4-methoxybenzenediazonium tetrafluoroborate (Entry 1) and the 2-methoxybenzenediazonium tetrafluoroborate (Entry 2), the diarylated products **6** and **7** have been produced in excellent yields, the formation of the regiosiomer **6** being preferred over the regioisomer **7**. In both cases, no monoarylated products could be isolated and detected. The 3,4,5-trimethoxy-benzenediazonium tetrafluoroborate, which exhibited inverse regioselectivity in comparison to the two methoxy derivatives mentioned above, was a special case and exception (Entry 3). Furthermore, a significant amount of monoarylated product **3c** could be isolated in this case with 31% (Entry 3). By increasing the catalyst quantity from 2 mol-% to 5 mol-%, a significant yield increase of the biarylated products **6** and **7** up to 84% could be achieved in the case of the 3,4,5-trimethoxybenzenediazonium salt.

However, in the case of the deactivated arenediazonium salts, it turned out that, as a rule, the formation of product **7** was strongly preferred compared to product **6** (Entries 4 and 5). Furthermore, significant quantities of monoarylated products were found for both 4-carboxymethylbenzenediazonium tetrafluoroborate and 4-chlorbenzenediazonium tetrafluoroborate (Entries 4 and 5) by using 2 mol-% catalyst. Whereas in the case of the chlorinated derivative with 84% a still very good yield of biarylated products could be obtained (Entry 5), this was only possible to a limited extent (37% yield) with the 4-carboxymethylbenzenediazonium salt (entry 4). Monoarylation clearly predominated with 41%. Furthermore, 9% methyl 4-methoxybenzoates could be isolated, which indicates an additional decomposition reaction of the diazonium salt by the solvent methanol. While in the case of the 3,4,5-trimethoxybenzenediazonium tetrafluoroborate a yield increase could be achieved by using larger catalyst amounts, this was not successful in the case of the 4-carboxymethylbenzenediazonium salt. By using 5 mol-% only the yield of monoarylated product **3e** could be increased (Entry 4).

Thus, with an increasing deactivation the formation of diarylated products is less favored. This effect could be rationalized by the reduced electron density of the intermediately formed arylmethylidene succinates, which have a decisive influence on the π-complex formation in the second arylation step (see supporting information). Given that we obtained significant amounts of monoarylated products from electron-poor arenediazonium salts, the nucleophilicity of the olefinic moiety of the monoarylated product is lower, which is detrimental to nucleophilic attack on the cationic palladium-aryl complex and thus to the formation of biarylated products.

Based on the available results, two different mechanistic paths are taken with the regard to β-H-elimination (see supporting information, p. 19). This type of double bond isomerization is a frequently observed phenomenon in 1,1-disubstituted alkenes. Thus, Correia and co-workers already observed a similar kind of isomerization in the Heck-Matsuda reaction of methyl methacrylate and 4-methoxybenzenediazonium salt, which gave a 1:1 ratio of constitutional isomers.[33] Furthermore, B. Schmidt and colleagues observed corresponding isomerizations during the iterative Heck-Matsuda coupling of itaconimide and discussed various migration mechanisms in this context.[27] In principle, the occurrence of the respective regioisomers should be explained by a respective kinetic or thermodynamic control. First orienting DFT calculations indicate that for both the electron-rich and the deactivated diazonium salts the products **6** are in all cases the thermodynamically favored products (see supporting information, page 6).

In the case of 2-methoxybenzenediazonium and 4-methoxybenzenediazonium salt, the energy differences of the optimized geometries of products **6** and **7** in favor of products **6** are greatest and are in good agreement with the experimental findings. In both cases, β-H-elimination is predominantly thermodynamically controlled. However, a different picture emerges strikingly with the deactivated diazonium salts and the 3,4,5-trimethoxybenzenediazonium salt. Although the products **6** should also be thermodynamically favored, in these cases the products **7** are predominantly retained, so that in these cases the β-H-elimination takes place in a kinetically controlled manner.

Conclusions

In summary, the monoarylation and biarylation of dimethyl itaconate *via* Heck-Matsuda reaction to obtain functionalized arylmethylidene succinates, biarylated succinates and maleates have been described. Depending on the stereoelectronic effects of the utilized diazonium salts the biarylation proceeded with different regioselectivities. The presented approach utilizing *in-situ* generated palladium on aluminum oxide distinguished itself by benign reaction conditions combined with low palladium loadings and paved the way to these important building blocks in

good to excellent yields. The elaboration of the optimized reaction conditions were supported by kinetic studies. The experimental results and outcome were explained and verified by DFT calculations.

Experimental Section

General methods. All reactions, unless otherwise specified, were performed in EasyMax 102 Advanced Synthesis Workstation from Mettler Toledo where 100 mL one-piece glass reactors were used. All solvents and reagents were purchased from commercial sources without further purification. NMR spectra were recorded on a Bruker Ascend™ 400 spectrometer. Chemical shifts were reported in parts per million (ppm) upfield to trimethylsilane as an internal standard. Multiplicity is presented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and coupling constant *J* in Hz. The assignment of the signals was carried out, where possible, employing 2D NMR techniques (^{1}H-^{1}H ROESY). Product distribution, were specified, was determined by advanced NMR plugin 'Simple Mixture Analysis' (SMA) from Mestrelab Research.

Purification of organic compounds was carried out by flash chromatography with PuriFlash® 450 Interchim equipment using 30 µm silica gel. Eluents for the column were mixtures of ethyl acetate/cyclohexane.

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer with ATR (germanium crystal).

The STEM analysis was performed by an FEI Helios NanoLab 650 Dual Beam System FIB with the state-of-the-art Elstar® electron column. Samples were prepared by dispersing the powder samples in hexane and three suspensions were dipped on Au-coated-holey-carbon Cu TEM grids. SEM analysis and imaging was operated by Field emission scanning microscopy (FESEM) and energy dispersive X-ray analysis (EDX).

Nitrogen gas evolution measurements for the studies of kinetic aspects of the Matsuda-Heck reaction were performed with Drum-Type Gas Meter TG05/7 from Dr.-Ing. Ritter Apparatebau GmbH & Co. KG. HPLC analysis of product composition was carried out on the system Smart Line Knauer Eurospher 100-5 via a C-18, 4 x 250 mm column with water/acetonitrile gradient. For the detection UV detector 2600 at 354 nm was used. HPLC-MS conditions for high resolution mass spectrometry: Bruker Micro TOF II equipment with Agilent 1260 pump, poroshell 120; C18, 2.7 µm column and ESI-TOF MS detector. Used eluent was mixtures of water/acetonitrile.

Palladium content on inorganic support and its traces in the final products was determined by inductively coupled plasma-optical emission spectrometer (ICP-OES) Varian 720-ES with custom-designed CCD detector.

Diazonium salts used in this study were all known and prepared as described in the literature, see Ref. 37. Solvents and chemicals were purchased from VWR or Aldrich and used as received.

Computational Methods. Molecular structures and energies were calculated using density functional theory (DFT)[38, 39] employing the B3-LYP exchange correlation functional[40] with D3 dispersion corrections[41], as implemented in the Turbomole Code Version 6.6.[42] The valence electrons ware described using linear combination of atomic orbitals (LCAO) in a triple-zeta basis set (def2-TZVP basis from the Turbomole library). The self-consistent solution of the Kohn-Sham equations was cycled until the change in energy between two cycles fell below 10E-6 Hartree. Cartesian atomic coordinates were optimized until the maximum force coordinate was less than 10E-4 Hartree/Bohr. Representations of 3D molecular structures were prepared using VMD.[43]

General procedure for preparation of immobilized Pd-NPs on alumina:

To a solution of aluminium oxide (1.389 g; 13.62 mmol) and palladium(II) acetate (45 mg; 0.2 mmol) in methanol (68 mL); olefin (10.0 mmol) was added and reaction mixture was stirred at 25 °C for 30 min. Afterwards, it was filtrated through fritted glass funnel and collected powder was washed with diethyl ether (2x25 mL) and dried without heating under reduced pressure for 30 min.

General procedure for the Matsuda-Heck monoarylation of dimethyl itaconate (3a-p):

To a solution of aluminium oxide (561 mg; 5.5 mmol) and palladium(II) acetate (22 mg; 0.1 mmol) in methanol (30 mL), dimethyl itaconate (1.582 g; 10.0 mmol, 1 eq.) was added and reaction mixture was stirred at 25 °C. After 30 min of preconditioning, diazonium salt (10.0 mmol, 1 eq.) was added and reaction development was monitored by heat flow control and gas evolution. Afterwards, reaction mixture was filtrated through celite, poured into ice-water and the water phase was extracted with diethyl ether (3x50 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure to obtain desired products.

Dimethyl (*E*)-2-(4-methoxybenzylidene) succinate 3a.[15] Pale yellow oil (2.51 g, 95 %); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (s, 1H), 7.33 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.82 (s, 3H), 3.74 (s, 3H), 3.58 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.7, 168.0, 160.2, 141.8, 130.9, 127.3, 123.7, 114.1, 55.3, 52.2, 52.1, 33.5; HRMS (ESI TOF): calcd for $C_{14}H_{17}O_5$ $[M+H]^+$ 265.1078, found 265.1074.

Dimethyl (*E*)-2-(3-methoxybenzylidene) succinate 3b.[44] Yellow oil (1.976 g, 75 %); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1H), 7.31 (td, *J* = 7.5, 1.3 Hz, 1H), 6.95-6.88 (m, 3H), 3.83 (s, 3H), 3.81 (s, 3H), 3.73 (s, 3H), 3.55 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.6, 167.8, 159.6, 142.1, 136.2, 129.7, 126.1, 121.4, 114.8, 114.2, 55.3, 52.3, 52.2, 33.6; HRMS (ESI-TOF): calcd for $C_{14}H_{17}O_5$ $[M+H]^+$ 265.1078, found 265.1085.

Dimethyl (*E*)-2-(3,4,5-trimethoxybenzylidene) succinate 3c.[2] Yellow oil (2.90 g, 89 %); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (s, 1H), 6.63 (s, 2H), 3.88 (s, 3H), 3.85 (s, 6H), 3.84 (s, 3H), 3.74 (s, 3H), 3.59 (s, 2H); ^{13}C

NMR (101 MHz, $CDCl_3$): δ = 171.7, 167.7, 153.2, 142.3, 138.7, 130.3, 125.1, 106.3, 60.9, 56.1, 52.2, 33.7; HRMS (ESI-TOF): calcd for $C_{16}H_{21}O_7$ $[M+H]^+$ 325.1289, found 325.1297.

Dimethyl (*E*)-2-(4-chlorobenzylidene) succinate 3d.[12, 13]- Yellow oil (2.49 g, 93 %); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.84 (s, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 3.83 (s, 3H), 3.74 (s, 3H), 3.51 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.4, 167.5, 140.9, 135.0, 133.3, 130.3, 128.9, 126.5, 52.4, 52.3, 33.4; HRMS (ESI-TOF): calcd for $C_{13}H_{14}ClO_4$ $[M+H]^+$ 269.0582, found 269.0569.

Dimethyl (*E*)-2-(3-chlorobenzylidene) succinate 3e.[12, 13] Pale yellow oil (2.26 g, 84 %); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.83 (s, 1H), 7.33 (d, *J* = 4.7 Hz, 3H), 7.22 (ddt, *J* = 4.8, 3.0, 0.8 Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 3.51 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.2, 167.4, 140.5, 136.6, 134.6, 128.9, 128.9, 127.2, 126.9, 52.4, 52.2, 33.4; HRMS (ESI-TOF): calcd for $C_{13}H_{14}ClO_4$ $[M+H]^+$ 269.0582, found 269.0543

Dimethyl (*E*)-2-(4-fluorobenzylidene) succinate 3f.[12, 13] Yellow oil (2.28 g, 90 %); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 1H), 7.38 – 7.31 (m, 2H), 7.09 (t, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 3.74 (s, 3H), 3.52 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.5, 167.7, 164.2, 161.7, 141.1, 131.0, 130.9, 125.8, 115.9, 115.7, 52.3, 52.3, 33.4; HRMS (ESI-TOF): calcd for $C_{13}H_{14}FO_4$ $[M+H]^+$ 253.0878, found 253.0848.

Dimethyl (*E*)-2-(4-iodobenzylidene) succinate 3g.[12] Yellow oil (2.35 g, 65 %); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 3.83 (s, 3H), 3.73 (s, 3H), 3.50 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.3, 167.5, 141.0, 137.8, 134.3, 130.6, 126.6, 95.1, 52.4, 52.2, 33.4; HRMS (ESI-TOF): calcd for $C_{13}H_{14}IO_4$ $[M+H]^+$ 360.9939, found 360.9933.

Dimethyl (*E*)-2-(4-bromobenzylidene) succinate 3h.[12] Reddish oil (2.78 g, 89 %); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, 1H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 3.83 (s, 3H), 3.73 (s, 3H), 3.50 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.3, 167.5, 140.8, 133.7, 131.9, 130.5, 126.5, 123.2, 52.3, 52.2, 33.4; HRMS (ESI-TOF): calcd for $C_{13}H_{14}BrO_4$ $[M+H]^+$ 313.0077, found 313.0069.

Dimethyl (*E*)-2-(2-methoxycarbonylbenzylidene) succinate 3i. Yellow oil (2.35 g, 80 %); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 0.9 Hz, 1H), 8.06 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.55 (td, *J* = 7.6, 1.4 Hz, 1H), 7.47 — 7.41 (m, 1H), 7.35 (ddt, *J* = 7.7, 1.4, 0.6 Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 3.71 (s, 3H), 3.30 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.8, 167.5, 166.7, 143.2, 137.0, 132.5, 130.9, 129.6, 128.9, 128.6, 125.2, 52.3, 52.3, 52.1, 33.5; HRMS (ESI-TOF): calcd for $C_{15}H_{17}O_6$ $[M+H]^+$ 293.1027, found 293.1016.

Dimethyl (*E*)-2-(4-methoxycarbonylbenzylidene) succinate 3j.[2] Greenish solid (2.45 g, 84 %); mp: 64-65 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.3 Hz, 2H), 7.91 (s, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 3.93 (s, 3H), 3.84 (s, 3H), 3.74 (s, 3H), 3.51 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.2, 167.3, 166.4, 140.9, 139.3, 130.3, 129.8, 128.8, 127.5, 52.4, 52.2, 33.4; HRMS (ESI-TOF): calcd for $C_{15}H_{17}O_6$ $[M+H]^+$ 293.1027, found 293.0992.

Dimethyl (*E*)-2-(4-acetylbenzylidene) succinate 3k. Yellow oil (2.22 g, 80 %); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.4 Hz, 2H), 7.91 (s, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 3.85 (s, 3H), 3.74 (s, 3H), 3.52 (s, 2H), 2.62 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.3, 171.2, 167.3, 140.8, 139.5, 137.0, 129.1, 128.6, 127.7, 52.4, 52.3, 33.4, 26.6; IR (Neat): ν_{max} = 3003, 2954, 1737, 1714, 1684, 1604, 1436, 1264, 1205, 1173, 1095, 774 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{15}H_{17}O_5$ $[M+H]^+$ 277.1078, found 277.1054.

Dimethyl (*E*)-2-(4-cyanobenzylidene) succinate 3l. Yellow oil (2.49 g, 96 %); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 3.85 (s, 3H), 3.75 (s, 3H), 3.48 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.0, 167.0, 139.9, 139.5, 132.4, 129.4, 128.5, 118.3, 112.4, 52.5, 52.4, 33.4; IR (Neat): ν_{max} = 2924, 2229, 1737, 1716, 1436, 1269, 1207, 1174, 1095, 848, 775 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{14}H_{14}NO_4$ $[M+H]^+$ 260.0925, found 260.0921.

Dimethyl (*E*)-2-(4-nitrobenzylidene) succinate 3m.[13] Yellow solid (1.25 g, 45 %); mp: 110 °C (Lit.: 111-112 °C) [13]; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 8.7 Hz, 2H), 7.92 (s, 1H), 7.52 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H), 3.76 (s, 3H), 3.49 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.9, 166.9, 147.7, 141.4, 139.5, 129.7, 129.0, 123.9, 52.6, 52.4, 33.4; HRMS (ESI-TOF): calcd for $C_{13}H_{14}NO_6$ $[M+H]^+$ 280.0823, found 280.0801

Dimethyl (*E*)-2-benzylidene succinate 3n.[13] Yellow oil (2.11 g, 90 %); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (s, 1H), 7.44 – 7.31 (m, 5H), 3.83 (s, 3H), 3.73 (s, 3H), 3.55 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.6, 167.8, 142.2, 134.9, 129.0, 128.9, 128.7, 125.9, 52.3, 52.2, 33.5; HRMS (ESI-TOF): calcd for $C_{13}H_{15}O_4$ $[M+H]^+$ 235.0972, found 235.0981.

Dimethyl (*E*)-2-(2-oxo-2*H*-chromen-6-yl)methylene) succinate 4. White solid (2.71 g, 89 %); mp: 100-101 °C; ^1H NMR (400 MHz, MeOD): δ = 7.96 (dd, *J* = 9.6, 0.7 Hz, 1H), 7.90 (s, 1H), 7.67 (d, *J* = 2.1 Hz, 1H), 7.61 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 6.47 (d, *J* = 9.6 Hz, 1H), 3.82 (s, 3H), 3.72 (s, 3H), 3.56 (d, *J* = 0.7 Hz, 2H); ^{13}C NMR (101 MHz, MeOD): δ = 171.8, 167.6, 160.8, 154.0, 143.8, 139.9, 132.3, 131.4, 128.7, 126.8, 119.1, 116.7, 116.5, 51.5, 51.3, 32.8 (C-4); IR (Neat): ν_{max} = 2947, 1720, 1701, 1623, 1434, 1201, 1181, 1173, 1134, 1091, 906, 830 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{16}H_{15}O_6$ $[M+H]^+$ 303.0870, found 303.0850.

Dimethyl (*E*)-2-((2-methoxycarbonyl) thiophen-3-yl)methylene) succinate 5. The precipitate formed in ice-water was filtrated and dried by lyophilization to obtain beige solid (1.13 g, 38 %); mp: 82-83 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 7.52 (d, *J* = 5.0 Hz, 1H), 7.15 (d, *J* = 5.0 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.72 (s, 3H), 3.45 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.3, 167.4, 162.1, 141.5, 135.8, 131.0, 130.5, 129.3, 126.9, 52.4, 52.3, 52.2, 33.9; IR (Neat): ν_{max} = 3104, 2962, 1706, 1437, 1284, 1237, 1207, 1104, 787 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{13}H_{15}O_6S$ $[M+H]^+$ 299.0591, found 299.0593.

General procedure for the Matsuda-Heck biarylation of dimethyl itaconate (6a-e and 7a-e):

To a solution of aluminium oxide (1.39 g; 13.62 mmol) and palladium(II)acetate (45 mg; 0.2 mmol) in methanol (68 mL), dimethyl itaconate (1.582 g; 10.0 mmol, 1 eq.) was added and reaction mixture was stirred at 25 °C. After 30 min of pre-conditioning, temperature was increased to 40 °C and diazonium salt (21.5 mmol, 2.15 eq.) was added. The reaction development was monitored by heat flow control and gas evolution. Afterwards, reaction mixture was filtrated through celite, poured into ice-water and the water phase was extracted with dichloromethane (3x50 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. All crude products were purified by column chromatography. In cases where mixtures of constitutional isomers were isolated, percentage ratio was determined by SMA analysis from ^{1}H NMR.

Dimethyl 2-(bis(4-methoxyphenyl)methylene) succinate 6a.
Purification by column chromatography (EtOAc/CycHex 15:85) gave yellow oil (2.136 g, 58%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 3.71 (s, 3H), 3.51 (s, 3H), 3.49 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.0, 170.5, 159.7, 159.5, 151.5, 134.7, 133.2, 130.9, 130.4, 122.8, 113.7, 113.3, 55.3, 55.2, 52.1, 51.7, 38.5; IR (Neat): ν_{max} = 2952, 2839, 1737, 1703, 1605, 1509, 1247, 1172, 1031, 834 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{21}H_{23}O_6$ $[M+H]^+$ 371.1496, found 371.1492.

Dimethyl 2-(bis(4-methoxyphenyl)methyl) maleate 7a. Purification by column chromatography (EtOAc/CycHex 15:85) gave yellow oil (1.309, 35%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (d, *J* = 8.6 Hz, 4H), 6.84 (d, *J* = 8.7 Hz, 4H), 5.53 (d, *J* = 1.8 Hz), 5.16 (d, *J* = 2.0 Hz, 1H), 3.78 (s, 6H), 3.70 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.7, 165.9, 158.7, 152.1, 131.4, 130.2, 123.6, 114.0, 55.2, 53.4, 52.4, 51.9; IR (Neat): ν_{max} = 2952, 2838, 1726, 1609, 1510, 1248, 1172, 1032, 832 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{21}H_{23}O_6$ $[M+H]^+$ 371.1496, found 371.1506.

Dimethyl 2-(bis(2-methoxyphenyl)methylene) succinate 6b.
Purification by column chromatography (EtOAc/CycHex 15:85) gave yellow oil (2.434 g, 66%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.16 (m, 2H, Ar-H), 7.03 (d, *J* = 7.4 Hz, 2H, Ar-H), 6.92 – 6.79 (m, 4H, Ar-H), 3.73 – 3.68 (s, 6H), 3.67 (s, 3H), 3.49 (s, 3H), 3.43 – 3.26 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.7, 169.0, 156.2, 156.0, 143.6, 131.2, 130.3, 129.9, 129.6, 129.3, 128.7, 127.0, 120.4, 120.2, 110.9, 110.8, 55.6, 55.3, 51.8, 51.4, 37.4; IR (Neat): ν_{max} = 3008, 2952, 2843, 1736, 1723, 1644, 1491, 1258, 1246, 1024, 758, 753 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{21}H_{23}O_6$ $[M+H]^+$ 371.1496, found 371.1494.

Dimethyl 2-(bis(2-methoxyphenyl)methyl) maleate 7b. Purification by column chromatography (EtOAc/CycHex 15:85) gave colourless oil (0.900 g, 24%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (td, *J* = 7.9, 1.8 Hz, 2H), 7.02 (dd, *J* = 7.5, 1.7 Hz, 2H), 6.91 – 6.84 (m, 4H), 5.97 (d, *J* = 1.7 Hz, 1H), 5.49 (d, *J* = 1.7 Hz, 1H), 3.76 (s, 6H), 3.69 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.6, 166.1, 157.1, 151.2, 129.9, 128.3, 127.7, 122.5, 120.2, 110.8, 55.7, 52.3, 51.8, 41.5; IR (Neat): ν_{max} = 2950, 2837, 1739, 1711, 1596, 1490, 1434, 1258, 1160, 1025, 753 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{21}H_{23}O_6$ $[M+H]^+$ 371.1496, found 371.1490.

Dimethyl 2-(bis(3,4,5-trimethoxyphenyl)methylene) succinate 6c and Dimethyl 2-(bis(3,4,5-trimethoxyphenyl)methyl) maleate 7c.
Synthesis according the general procedure but utilization of 5 mol-% catalyst. Purification by column chromatography (EtOAc/CycHex 25:75) gave yellow solid (4.13 g, 84 %) as a mixture of constitutional isomers with a percentage ratio of 13:87 (6c:7c); IR (Neat): ν_{max} = 2950, 2839, 1736, 1588, 1505, 1242, 1120, 1007 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{25}H_{31}O_{10}$ $[M+H]^+$ 491.1919, found 491.1921.

Dimethyl 2-(bis(3,4,5-trimethoxyphenyl)methylene) succinate 6c
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.36 (s, 4H, H-9), 3.89 (s, 3H), 3.87 (s, 3H), 3.78 (s, 12H), 3.72 (s, 3H), 3.53 (s, 3H), 3.50 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.7, 170.5, 153.0, 152.8, 150.9, 137.2, 134.5, 124.5, 106.6, 106.2, 60.9, 56.2, 52.1, 52.0, 38.5.

Dimethyl 2-(bis(3,4,5-trimethoxyphenyl)methyl) maleate 7c.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.40 (s, 4H, H-9), 5.60 (d, *J* = 1.8 Hz, 1H, H-4), 5.15 (d, *J* = 2.0 Hz, 1H, H-7), 3.84 (s, 6H, H-12), 3.80 (s, 12H, H-13), 3.74 (s, 3H, H-6), 3.70 (s, 3H, H-1); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.5, 165.8, 153.3, 150.9, 137.2, 134.5, 124.4, 106.4, 60.9, 56.2, 55.2, 52.6, 52.1.

Dimethyl 2-(bis(4-(methoxycarbonyl)phenyl)methylene) succinate 6d and Dimethyl 2-(bis(4-(methoxycarbonyl)phenyl)methyl) maleate 7d.
Purification by column chromatography (EtOAc/CycHex 15:85) gave pale yellow oil (1.56 g, 37 %) as a mixture of constitutional isomers with a percentage ratio of 24:76 (6d:7d); IR (Neat): ν_{max} = 3001, 2953, 1721, 1608, 1435, 1278, 1194, 1172, 1106, 1020, 712 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{23}H_{23}O_8$ $[M+H]^+$ 427.1395, found 427.1393.

Dimethyl 2-(bis(4-(methoxycarbonyl)phenyl)methylene) succinate 6d:
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.5 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 3.92 (s, 6H), 3.72 (s, 3H), 3.49 (s, 3H), 3.44 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.1, 168.9, 166.4, 149.9, 145.8, 144.3, 129.9, 129.6, 129.4, 129.0, 128.5, 126.7, 52.3, 52.1, 52.0, 37.8.

Dimethyl 2-(bis(4-(methoxycarbonyl)phenyl)methyl) maleate 7d
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.4 Hz, 4H), 7.26 (d, *J* = 8.2 Hz, 4H), 5.54 (d, *J* = 1.7 Hz, 1H), 5.37 (d, *J* = 1.7 Hz, 1H), 3.91 (s, 6H), 3.72 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.8, 166.6, 165.4, 149.0, 143.6, 130.1, 129.6, 129.3, 125.4, 54.5, 52.6, 52.2, 52.1.

Dimethyl 2-(bis(4-chlorophenyl)methylene) succinate 6e and Dimethyl 2-(bis(4-chlorophenyl)methyl) maleate 7e.

Purification by column chromatography (EtOAc/CycHex 10:90) gave colourless oil (3.18 g, 84 %) as a mixture of constitutional isomers with a percentage ratio of 25:75 (6e:7e); IR (Neat): ν_{max} = 3001, 2952, 1728, 1649, 1490, 1435, 1264, 1199, 1170, 1090, 1015, 829 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{19}H_{17}Cl_2O_4$ $[M+H]^+$ 379.0506, found 379.0495.

Dimethyl 2-(bis(4-chlorophenyl)methylene) succinate 6e

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 3.72 (s, 3H), 3.52 (s, 3H), 3.44 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.3, 169.3, 149.5, 139.9, 138.4, 134.7, 134.2, 130.5, 130.0, 128.9, 128.3, 125.7, 52.2, 51.9, 38.0.

Dimethyl 2-(bis(4-chlorophenyl)methyl) maleate 7e

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.5 Hz, 4H), 7.10 (d, *J* = 8.5 Hz, 4H), 5.53 (d, *J* = 1.7 Hz, 1H), 5.22 (d, *J* = 1.7 Hz, 1H), 3.72 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.0, 165.5, 149.8, 137.2, 133.6, 130.5, 129.0, 124.9, 53.4, 52.6, 52.1.

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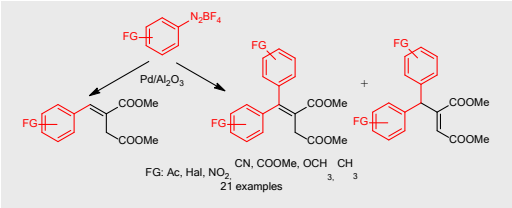

In-situ generated palladium on aluminium oxide provides an active and efficient catalytic system for the preparation of arylmethylidene succinates using the Heck-Matsuda reaction. Beside the monoarylation the first examples of the biarylation of this monomer will be described.

Arylmethylidene succinates*

Lauryna Matelienė (née Dauksaitė), Jan Knaup, Frank von Horsten, Xiaoting Gu, and Heiko Brunner*

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Benign Arylations of Dimethyl Itaconate via Heck-Matsuda Reaction Utilizing in-situ Generated Palladium on Aluminum Oxide