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Heck Cross-Coupling of Aryldiazonium Tetrafluoroborate with Acrylates Catalyzed by Palladium on Charcoal

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Abstract: A property-activity relationship study of various palladium supported on charcoal (Pd/C) catalysts has been undertaken for the Heck reaction of aryldiazonium tetrafluoroborate with acrylates. The optimized protocol enables the cross-coupling with a low loading of palladium at room temperature in technical grade methanol. Although the catalyst could not be recycled at this time, measurement of the palladium content by inductively coupled plasma mass spectrometry (ICP-MS) shows low palladium contamination of the solvent and product, rendering this method safer for the environment compared to homogeneous conditions.

Keywords: acrylates; aryldiazonium tetrafluoroborate salts; Heck reaction; palladium on charcoal; practical cross-coupling

Introduction

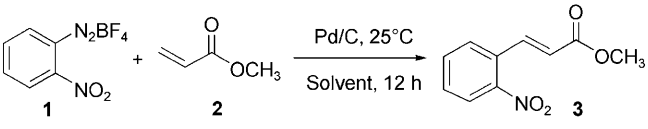
Palladium-catalyzed cross-coupling reactions have become a standard in both academic and industrial laboratories all over the world.[1] The Heck reaction is probably one of the most important methods for C–C bond formation that allows the coupling of aryl or vinyl halides with olefins. Since the pioneering studies from Mizoroki[2] and Heck[3] in the early 1970s, an impressive amount of work has been devoted to develop efficient systems.[1] On the other hand, aryldiazonium salts have been proposed as useful and highly reactive aryl halide substitutes for ligand-free Heck cross-coupling under mild conditions (room temperature to 60 °C).[4] However, ligand-free systems using aryldiazonium salts as electrophiles typically require a catalyst loading ranging from 1 to 10 mol% of unrecoverable homogeneous palladium complexes such as Pd(OAc)$_2$ or Pd$_2$(dba)$_3$.[5] Despite their synthetic advantages, heterogeneous palladium catalysts for such a cross-coupling have been much less explored.[6] The immobilization of palladium on a support allows its recovery by simple filtration and eventually its reuse for a further reaction.[7] However, supported palladium catalysts show usually lower activity, and the preparation of the support can be quite complex and tedious, resulting in a lack of practicability. Amongst the many supports used for palladium, activated charcoal is certainly one of the most convenient in terms of cost, inertness, safety and availability. As a consequence, the use of palladium supported on activated charcoal in a variety of cross-coupling reactions has found many applications.[8] In continuation of our program devoted to the development of easy to handle palladium-catalyzed reactions,[9] we present here our latest results on Pd/C-mediated reactions of aryldiazonium salts with acrylates. In this paper, we wish to establish a property-activity relationship of Pd/C catalysts in the context of the Heck reaction. Our studies show that fine tuning of properties of the Pd/C catalyst associated with the optimization of the reaction parameters allows the cross-coupling of aryldiazonium salts with acrylates at room temperature in technical grade methanol under ligand-free conditions. In addition, this extremely efficient procedure tolerates a low catalyst loading (up to 0.1 mol%). Although a related study has been described by Köhler et al. for the Pd/C-catalyzed Heck reaction of aryl bromides with styrene,[10] we report, herein, on the differences with aryldiazonium salts.

Results and Discussion

Optimization of Reaction Conditions

Initial studies focused on the establishment of a property-activity relationship of Pd/C on a cross-coupling reaction model. We used four different catalysts varying according to their oxidation degree [i.e., Pd(II)/C

Table 1. Optimization of the catalyst.

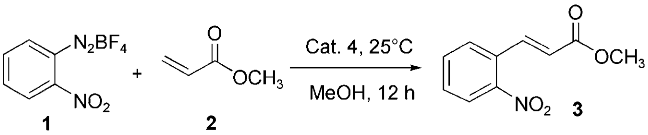


Entry	Catalyst type[a]	Catalyst loading	Solvent	Yield[b] [%]
1	Cat. 1	1 mol%	MeOH	29
2	Cat. 1	1 mol%	*i*-PrOH	<5
3	Cat. 2	1 mol%	MeOH	42
4	Cat. 2	1 mol%	*i*-PrOH	<5
5	Cat. 3	1 mol%	MeOH	53
6	Cat. 3	1 mol%	*i*-PrOH	<5
7	**Cat. 4**	**1 mol%**	**MeOH**	**78**
8	Cat. 4	1 mol%	*i*-PrOH	11

[a] Cat. 1: Pd(0)/$C_{uniform}$; Cat. 2: Pd(0)/$C_{eggshell}$; Cat. 3: Pd(II)/$C_{uniform}$; Cat. 4: Pd(II)/$C_{eggshell}$.

[b] Yields are an average of at least two runs.

Table 2. Optimization of the reaction conditions.



Entry	Equiv		Concentration Diazo [M]	Pd [mol%]	Yield[a] [%]
	1	2			
1	1	2	0.25	1	78
2	1.2	1	0.25	1	85
3	1.2	1	0.15	1	75
4	1.2	1	0.50	1	89
5	1.2	1	0.50	0.5	94
6	**1.2**	**1**	**0.50**	**0.1**	**93**

[a] Yields are an average of at least two runs.

or Pd(0)/C] as well as their distribution over charcoal (i.e., eggshell or uniform). They were selected at a constant loading of 5 wt% Pd and, for safety issues, with 50% water content.[11] In our initial studies, we examined the challenging reaction of 2-nitrobenzenediazonium tetrafluoroborate **1** with methyl acrylate **2** in the presence of 1 mol% of the four different Pd/C catalysts (Table 1). It was previously observed that 2-nitrobenzenediazonium tetrafluoroborate **1** was quite sensitive and prone to decomposition resulting in low yields of cross-coupled products.[12] This reactivity has been ascribed to the high redox potentials and a preference for homolytic dediazonization pathways. As expected for this model, dramatic differences were observed according to the catalyst and the solvent used. As a general observation, it is interesting to note that the cross-coupling in MeOH is much more efficiently conducted than in *i*-PrOH at 25 °C. This remark may be ruled out when conducting the cross-coupling at higher temperatures (50–60 °C), at which point MeOH leads to some decomposition of diazonium salts whereas *i*-PrOH showed some efficiency.[13] However, we considered the advantage of working at room temperature for practical and economic reasons. As a result, all reactions described here have been performed and optimized in MeOH.

Table 1 shows clearly that a high oxidation state was required (entries 1 *versus* 5 and 3 *versus* 7) while the eggshell distribution led to more active catalysts (entries 1 *versus* 3 and 5 *versus* 7). As a consequence Pd(II)/C catalyst with an eggshell distribution (Cat. 4) proved to have the greatest catalytic activity in our model reaction, giving a 78% yield of **3** under non-optimized reaction conditions. The high oxidation state of the Pd nanoparticles required for the cross-coupling is fully consistent with the usual homogeneous Heck reaction. On the other hand, the greatest activity of the catalysts having an eggshell distribution could be explained by a higher exposition of Pd nanoparticules (at the outer surface of the charcoal) toward the diazonium salt during the oxidative step. This result contrasts with those obtained by Köhler et al.[10] for the Heck reaction of aryl bromides with styrene at 140 °C where a Pd(II)/C catalyst with a uniform Pd impregnation displayed the higher catalytic activity. It is clearly understandable that the unique electronic properties of diazonium salts and low temperature (25 °C) can lead to substantial differences in the intimate mechanism of the reaction.

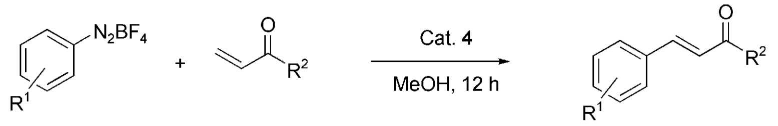
Next, as shown in Table 2, various parameters of the cross-coupling, including equivalents of reagents, concentration and catalyst loading were optimized. The best conditions found (entry 6), which required a slight excess of the diazonium salt **1** in a rather concentrated solution, permitted a low loading of Pd (0.1 mol%).

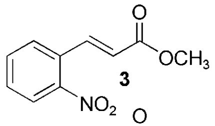
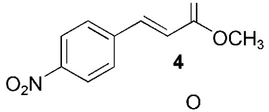
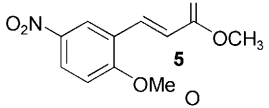
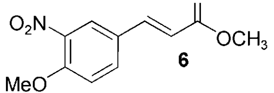
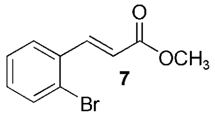
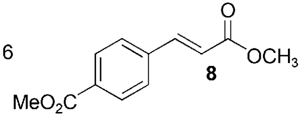
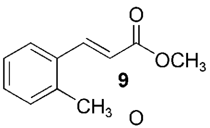
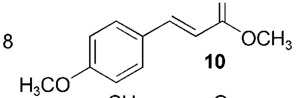
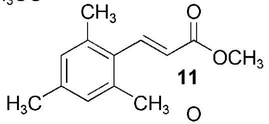
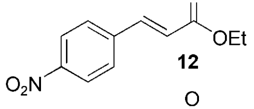
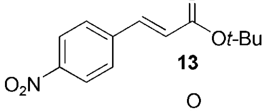
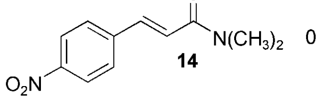
These results invoke two important remarks: (1) more concentrated solutions (> 0.5 M) are not recommended for reproducible stirring of crystalline reactants; (2) such a low loading is quite exceptional for ligand-free conditions at room temperature and, to the best of our knowledge, has only few precedents in the literature, albeit, with homogeneous catalysts.[14] One can note that the optimized conditions can be slightly adapted: for less reactive diazonium salts (electron-rich) or conditions requiring heating, an excess of the acrylate could be preferred.[15]

Scope of the Reaction

Encouraged by these promising results, we further explored the scope of this process with a variety of cross-coupling partners (Table 3). All aryldiazonium

Table 3. Scope of the cross-coupling.



Entry	Product	Pd [mol%]	Temp. [°C]	Base	Yield[a] [%]
1	 **3**	0.1	25	-	93
2	 **4**	0.1	25	-	93
3	 **5**	0.1	25	-	98
4	 **6**	0.1	25	-	98
5	 **7**	0.1	25	-	85
6	 **8**	0.1	25	-	92
7	 **9**	0.5	25	-	82
8	 **10**	0.5	45	$CaCO_3$	71
9	 **11**	1	45	$CaCO_3$	43
10	 **12**	0.1	25	$CaCO_3$	97
11	 **13**	0.1	25	$CaCO_3$	90
12	 **14**	0.5	45	$CaCO_3$	84

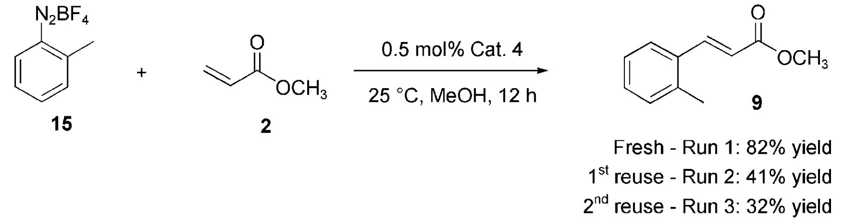
[a] Yields are an average of at least two runs.

tetrafluoroborate salts were easily accessible by reaction of the corresponding anilines with sodium nitrite and tetrafluoroboric acid.[16] Importantly, the prepared aryldiazonium tetrafluoroborate salts showed excellent stability over years when stored at −20 °C. Diazonium electrophiles compete favorably with less reactive and more expensive halogenated electrophiles as exemplified by reported industrial applications.[17]

Nitro-substituted diazonium salts reacted cleanly with methyl acrylate, contrasting with some literature precedents on a similar coupling.[12] A high level of chemoselectivity for the diazonium group was observed with the 2-bromobenzenediazonium tetrafluoroborate (entry 5). Indeed, no evidence for a competing electrophilic reactivity of the bromine atom was observed. While electron-poor diazonium salts reacted smoothly at 25 °C with loading as low as 0.1 mol% Pd, electron-rich substrates required higher Pd loading and eventually a moderate heating activation (entries 7–9). The use of $CaCO_3$ as an additive proved to be beneficial in terms of yields and kinetics for less reactive arenediazonium salts (entries 8 and 9). The base could enhance the rate of the reductive elimination step. Moreover, the choice of the base proved to be crucial since the use of Na_2CO_3 led to a rapid and complete decomposition of the diazonium salt. Although the reaction of mesityldiazonium salt with methyl acrylate (entry 9) proceeds in modest yield (43%), the coupling still remains valuable since it has been reported that this kind of cross-coupling has been quite problematic under homogeneous conditions.[18] Indeed, the mild conditions developed in this study (45 °C) contrast with literature precedents reporting the use of high pressure (4000 bar, 90 °C)[18a] or prolonged refluxing times (120–160 °C, 12 h).[18b] Finally, to avoid any unwanted transesterification processes with other acrylates (entries 10–12) it is recommended to use 0.5–0.6 equivalent of $CaCO_3$.

Since Pd/C could be easily separated from the reaction mixture by simple filtration, we examined its recyclability for the cross-coupling of 2-methylbenzenediazonium tetrafluoroborate **15** with methyl acrylate **2** (Scheme 1). Unfortunately, the recycled catalyst displayed a significant deactivation resulting in modest yields after the first reuse.

Investigations were conducted to determine the reason for this loss of activity. ICP-MS analysis was used to evaluate the amount of Pd leached into the



Scheme 1. Recycling tests.

solvent that did not redeposit on the charcoal at the end of the reaction. After 12 h of stirring the concentration of solubilized Pd was around 1.6 ppm, indicating that only 0.9% of the metal used for the reaction had leached into the solvent.[19] From this observation, we concluded that virtually all palladium still remained on the charcoal and the observed decrease in catalytic activity is not related to a lower loading of Pd on the charcoal. Additionally, the low concentration of palladium in the solution proved to be inactive in promoting a further reaction after separation of the catalyst by filtration.[20] Characterization of the fresh and the reused catalysts by transmission electron microscopy (TEM) showed that the deactivation could be correlated to the increase of the average of crystallite size from 20 nm to 60 nm (Figure 1). The change in nanoparticles size clearly indicated that palladium is leached from the support during the oxidative addition step and later re-precipitated onto the charcoal after the reductive elimination step as already observed by other groups.[10,21] However, the extremely mild conditions (25 °C) used in this study ruled out a temperature-induced leaching, indicating that oxidative addition of the diazonium salt could be responsible of the palladium desorption. Moreover, we mentioned in Table 1 that the use of Pd(II) precatalyst was critical for the success of the cross-coupling but, according to the widely accepted mechanism of the Heck reaction, the reused Pd/C catalyst should be reduced to its Pd(0) form. This point is fully consistent with the strong reactivity decrease observed with the reused catalyst. Studies aimed at its reactivation have not yet been carried out, but could be successful following the literature precedents.[22]

Conclusions

In summary, we have reported that a fine-tuning of the properties of Pd/C led to the establishment of a highly efficient protocol for the cross-coupling of aryldiazonium tetrafluoroborate with acrylates. The experimental simplicity associated with the mild conditions render the method highly competitive over existing procedures. Although the catalyst was not recyclable, ICP-MS analyses showed a low contamination of the products by palladium species. It is also expected that such a simple protocol represents an important advance toward sustainability.

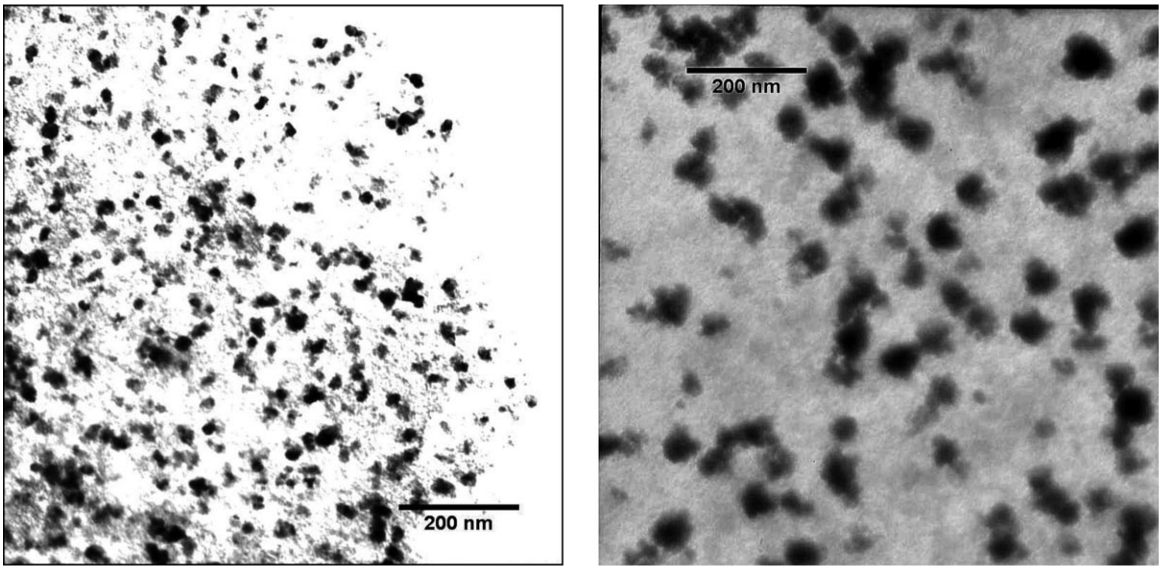


Figure 1. TEM images of the fresh catalyst (*left*) and the reused catalyst (*right*) at the same magnification.

Experimental Section

General Remarks

Chemical shifts from proton and carbon NMR spectra are reported in ppm relative to the $CDCl_3$ peak at 7.26 ppm (^1H) or 77.0 ppm (^{13}C). Infrared (IR) spectra were recorded as neat samples on NaCl plates or with KBr pellets. The transmission electron microscopy (TEM) images have been obtained with a Hitachi H-600 microscope. The catalysts were dispersed into methanol and samples of the solution have been taken and air-dried onto standard Formar/carbon-coated copper support grids. The micrographs of this work have been realised with the same magnification.

Yields refer to isolated material determined to be pure by NMR spectroscopy and thin layer chromatography (TLC), unless specified otherwise in the text. Diazonium salts used in this study were all known and prepared as described in the litterature. Pd/C catalysts were commercially available from Evonik industries AG. An eggshell distribution means that palladium nanoparticles are distributed close to the surface of the charcoal. A uniform distribution means that palladium nanoparticles are homogeneously dispersed on the charcoal.

General Procedure for the Heck Cross-Coupling Reaction

To a solution of diazonium salt (1–1.2 mmol) in MeOH (2.5 mL) were added acrylate (1–2 mmol) and 5% Pd(II)/$C_{eggshell}$ (0.1–1 mol%, see Table 2) at 25 °C. The resulting mixture was stirred for 12 h at 25–45 °C (see Table 2) and then concentrated under reduced pressure. The crude material was purified by flash chromatography to give the corresponding cross-coupled product.

(*E*)-Methyl 2-nitrocinnamate (3): This compound was prepared according to the general procedure, with diazonium salt (1.2 mmol), acrylate (1 mmol) and 5% Pd(II)/$C_{eggshell}$ (0.1 mol%) in MeOH (2.5 mL) at 25 °C. Purification by flash chromatography (70% CH_2Cl_2:petroleum ether) gave a yellow solid; mp 71–72 °C [Lit.[23] 71–72 °C]. IR (KBr): ν = 1637, 1719, 2953, 3024 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.80 (s, 3H), 6.34 (d, 1H, J = 15.9 Hz), 7.49–7.68 (m, 4H), 8.01 (d, 1H, J = 7.9 Hz), 8.08 (d, 1H, J = 15.9 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 51.9, 122.7, 124.8, 129.0, 130.3, 130.4, 133.5, 140.0, 148.2, 166.1; MS (EI): *m/z* = 207 (M), 176 (M−OCH_3).

(*E*)-Methyl 4-nitrocinnamate (4): This compound was prepared according to the general procedure, with diazonium salt (1.2 mmol), acrylate (1 mmol) and 5% Pd(II)/$C_{eggshell}$ (0.1 mol%) in MeOH (2.5 mL) at 25 °C. Purification by flash chromatography (60% CH_2Cl_2:petroleum ether) gave a white solid; mp 161 °C [Lit.[24] 161 °C]. IR (KBr); ν = 1638, 1721, 2958, 3041 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.84 (s, 3H), 6.56 (d, 1H, J = 16.2 Hz), 7.67 (d, 2H, J = 8.7 Hz), 7.72 (s, 1H, J = 15.8 Hz), 8.25 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 52.1, 122.0, 124.2, 128.6, 140.4, 141.9, 166.5; MS (EI): *m/z* = 207 (M), 176 (M−OCH_3).

(*E*)-Methyl 2-methoxy-5-nitrocinnamate (5): This compound was prepared according to the general procedure, with diazonium salt (1.2 mmol), acrylate (1 mmol) and 5% Pd(II)/$C_{eggshell}$ (0.1 mol%) in MeOH (2.5 mL) at 25 °C. Purification by flash chromatography (5% AcOEt:petroleum ether) gave a yellow solid; mp 164–165 °C [Lit.[25] 159–161 °C]. IR (KBr): ν = 1637, 1714, 2946, 3021 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.82 (s, 3H), 4.00 (s, 3H), 6.60 (d, 1H, J = 16.2 Hz), 6.99 (d, 1H, J = 9.2 Hz), 7.93 (d, 1H, J = 16.2 Hz), 8.25 (dd, 1H, J = 2.7, 9.2 Hz), 8.40 (d, 1H, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 51.8, 56.4, 111.0, 121.0, 124.0, 126.7, 137.6, 141.4, 162.4, 167.0; MS (EI): *m/z* = 237 (M), 206 (M−OCH_3).

(*E*)-Methyl 4-methoxy-3-nitrocinnamate (6): This compound was prepared according to the general procedure, with diazonium salt (1.2 mmol), acrylate (1 mmol) and 5% Pd(II)/$C_{eggshell}$ (0.1 mol%) in MeOH (2.5 mL) at 25 °C. Purification by flash chromatography (10% AcOEt:petroleum ether) gave a yellow solid; mp 128 °C [Lit.[26] 130–130.5 °C]. IR (KBr): ν = 1639, 1702, 2952, 2983, 3062 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.80 (s, 3H), 4.00 (s, 3H), 6.38 (d, 1H, J = 16.1 Hz), 7.11 (d, 1H, J = 8.5 Hz), 7.61 (d, 1H, J = 15.9 Hz), 7.68 (dd, 1H, J = 2.1, 8.8 Hz), 8.00 (d, 1H, J = 2.1 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 51.8, 56.7, 113.8, 118.4, 124.9, 127.0, 133.4, 141.7, 154.0, 166.8; MS (EI): *m/z* = 237 (M), 206 (M−OCH_3).

(*E*)-Methyl 2-bromocinnamate (7): This compound was prepared according to the general procedure, with diazonium salt (1.2 mmol), acrylate (1 mmol) and 5% Pd(II)/$C_{eggshell}$ (0.1 mol%) in MeOH (2.5 mL) at 25 °C. Purification by flash chromatography (5% AcOEt:petroleum ether) gave a colorless oil. IR (neat): ν = 1636, 1720 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ = 3.82 (s, 3H), 6.38 (d, 1H, J = 16.0 Hz), 7.17–7.36 (m, 2H), 7.57–7.63 (m, 2H), 8.05 (d, 1H, J = 15.9 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 51.8, 120.6, 125.3, 127.8, 127.7, 131.2, 133.4, 134.4, 143.1, 166.8; MS (EI): *m/z* = 240 (M, ^{79}Br), 242 (M, ^{81}Br), 161 (M−Br).

(*E*)-Methyl 4-methoxycarbonylcinnamate (8): This compound was prepared according to the general procedure, with diazonium salt (1.2 mmol), acrylate (1 mmol) and 5% Pd(II)/$C_{eggshell}$ (0.1 mol%) in MeOH (2.5 mL) at 25 °C. Purification by flash chromatography (15% AcOEt:petroleum ether) gave a white solid; mp 124 °C [Lit.[27] 122–123 °C]. IR (KBr): ν = 1641, 1720, 2958 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.81 (s, 3H), 3.92 (s, 3H), 6.51 (d, 1H, J = 15.9 Hz), 7.57 (d, 2H, J = 8.5 Hz), 7.70 (d, 1H, J = 16.1 Hz), 8.04 (d, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 51.8, 52.2, 120.1, 127.9, 130.0, 131.3, 138.5, 143.4, 166.4, 166.9; MS (EI): *m/z* = 220 (M), 189 (M−OCH_3).

(*E*)-Methyl 2-methylcinnamate (9): This compound was prepared according to the general procedure, with diazonium salt (1 mmol), acrylate (2 mmol) and 5% Pd(II)/$C_{eggshell}$ (0.5 mol%) in MeOH (2.5 mL) at 25 °C. Purification by flash chromatography (10% AcOEt:petroleum ether) gave a colorless oil. IR (neat): ν = 1634, 1718, 2950 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.44 (s, 3H), 3.81 (s, 3H), 6.36 (d, 1H, J = 15.9 Hz), 7.18–7.31 (m, 3H), 7.55 (d, 1H, J = 7.3 Hz), 7.99 (d, 1H, J = 15.9 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 51.8, 120.6, 125.3, 127.8, 127.7, 131.2, 133.4, 134.4, 143.1, 166.8; MS (EI): *m/z* = 176 (M), 145 (M−OCH_3).

(*E*)-Methyl 4-methoxycinnamate (10): This compound was prepared according to the general procedure, with diazonium salt (1 mmol), acrylate (2 mmol), $CaCO_3$ (0.5 mmol) and 5% Pd(II)/$C_{eggshell}$ (0.5 mol%) in MeOH (2.5 mL) at 45 °C. Purification by flash chromatography

(20% AcOEt:petroleum ether) gave a white solid; mp 87 °C [Lit.[28] 90 °C]. IR (KBr): ν = 1641, 1716, 2964 cm^{-1}; ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 3.79 (s, 3 H), 3.83 (s, 3 H), 6.31 (d, 1 H, J = 15.9 Hz), 6.90 (dm, 2 H, J = 8.8 Hz), 7.47 (dm, 1 H, J = 8.8 Hz), 7.65 (d, 1 H, J = 15.9 Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 51.8, 52.2, 120.1, 127.9, 130.0, 131.3, 138.5, 143.4, 166.4, 166.9; MS (EI): m/z = 192 (M), 161 (M−OCH$_3$).

(*E*)-Methyl 2,4,6-trimethylcinnamate (11): This compound was prepared according to the general procedure, with diazonium salt (1 mmol), acrylate (2 mmol), CaCO$_3$ (0.5 mmol) and 5% Pd(II)/C$_{\text{eggshell}}$ (1 mol%) in MeOH (2.5 mL) at 45 °C. Purification by flash chromatography (5% AcOEt:petroleum ether) gave a white solid; mp 50 °C. IR (KBr): ν = 1637, 1718, 2960, 2949 cm^{-1}; ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 2.29 (s, 3 H), 2.33 (s, 3 H), 3.82 (s, 3 H), 6.07 (d, 1 H, J = 16.5 Hz), 6.90 (s, 2 H), 7.86 (d, 1 H, J = 16.5 Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 21.0, 21.0, 51.6, 122.8, 129.1, 130.9, 136.8, 138.3, 143.4, 167.4; MS (EI): m/z = 204 (M), 189 (M−CH$_3$), 173 (M−2CH$_3$); HR-MS (electrospray): m/z = 227.1041, calcd. for C$_{13}$H$_{16}$O$_2$Na (M+Na$^+$): 227.1042.

(*E*)-Ethyl 4-nitrocinnamate (12): This compound was prepared according to the general procedure, with diazonium salt (1.2 mmol), acrylate (1 mmol), CaCO$_3$ (0.6 mmol) and 5% Pd(II)/C$_{\text{eggshell}}$ (0.1 mol%) in MeOH (2.5 mL) at 25 °C. Purification by flash chromatography (70% CH$_2$Cl$_2$:petroleum ether) gave a white solid; mp 138–139 °C [Lit.[5g] 138.5–139 °C]. IR (KBr): ν = 1645, 1713, 2938, 2984, 3080 cm^{-1}; ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 1.35 (t, 3 H, J = 7.0 Hz), 4.29 (q, 2 H, J = 7.3 Hz), 6.55 (d, 1 H, J = 16.1 Hz), 7.67 (d, 2 H, J = 8.8 Hz), 7.70 (d, 1 H, J = 15.9 Hz), 8.24 (d, 1 H, J = 8.8 Hz); ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 14.2, 61.0, 122.5, 124.1, 128.6, 140.5, 141.6, 148.4, 166.0; MS (EI): m/z 221 (M), 176 (M−OC$_2$H$_5$).

(*E*)-*t*-Butyl 4-nitrocinnamate (13): This compound was prepared according to the general procedure, with diazonium salt (1.2 mmol), acrylate (1 mmol), CaCO$_3$ (0.6 mmol) and 5% Pd(II)/C$_{\text{eggshell}}$ (0.1 mol%) in MeOH (2.5 mL) at 25 °C. Purification by flash chromatography (10% AcOEt:petroleum ether) gave a white solid; mp 149 °C [Lit.[29] 146–147 °C]. IR (KBr): ν = 1639, 1709, 2941, 2982, 3077 cm^{-1}; ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 1.54 (s, 3 H), 6.49 (d, 1 H, J = 15.8 Hz), 7.60 (d, 1 H, J = 15.2 Hz), 7.65 (d, 1 H, J = 8.5 Hz), 8.23 (d, 1 H, J = 8.8 Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 28.1, 124.1, 124.6, 128.5, 140.5, 140.9, 148.3, 165.2; MS (EI): m/z = 249 (M), 176 (M−OC$_4$H$_9$).

(*E*)-*N*,*N*-Dimethyl-3-(4-nitrophenyl)acrylamide (14): This compound was prepared according to the general procedure, with diazonium salt (1.2 mmol), acrylate (1 mmol), CaCO$_3$ (0.6 mmol) and 5% Pd(II)/C$_{\text{eggshell}}$ (0.5 mol%) in MeOH (2.5 mL) at 45 °C. Purification by flash chromatography (4% MeOH:CH$_2$Cl$_2$) gave a white solid; mp 174–175 °C [Lit.[30] 176–178 °C]. IR (KBr): ν = 1614, 1654, 2932, 3060 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 3.09 (s, 3 H), 3.20 (s, 3 H), 7.02 (d, 1 H, J = 15.4 Hz), 7.66 (d, 1 H, J = 8.6 Hz), 7.69 (d, 1 H, J = 15.9 Hz), 8.23 (d, 1 H, J = 8.9 Hz); ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 36.0, 37.4, 121.7, 124.1, 128.3, 139.5, 141.6, 148.0, 165.6; MS (EI): m/z = 220 (M), 176 [M−N(CH$_3$)$_2$].

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