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Oxidative Heck Coupling of Allylic Amines with 2,2,6,6-Tetramethylpiperidine-*N*-oxyl (TEMPO) as Oxidant for the Preparation of Tetrasubstituted Alkenes

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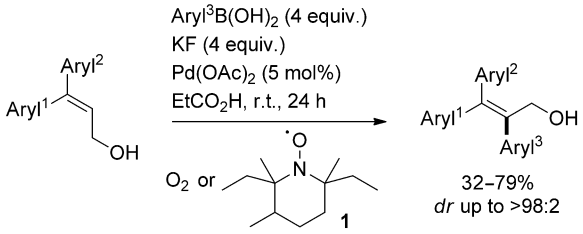
Abstract: The paper describes the oxidative Heck arylation of various allylic amines using arylboronic acids for the preparation of tetrasubstituted alkenes. As oxidant the commercially available 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) is used and coupling reactions occur under very mild conditions at room temperature. The densely substituted alkenes are formed in good to excellent yields with complete control of the diastereoselectivity. Substrate scope with respect to the allylic amine and the arylboronic acid is investigated.

Keywords: allylic amines; catalysis; cross coupling; nitroxides; palladium; 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO)

Introduction

The Heck reaction as one of the most valuable methods for C–C bond formation has been intensively used in organic synthesis.[1] In this Pd-catalyzed coupling reaction halides or pseudohalides are cross-coupled with olefins. In the oxidative version (oxidative Heck reaction) arylboronic acids are generally used as aryl-Pd sources and a stoichiometric external oxidant is necessary to run the catalytic process. Compared to the heavily investigated parent Heck reaction this oxidative variant is less well explored.[2,3] In general the oxidative process works under milder conditions and allows for the preparation of densely substituted olefins with high regio- and stereocontrol. Despite the great achievements in the field of transition metal-catalyzed cross-coupling chemistry, the synthesis of highly substituted alkenes is still a demanding task.[4]

We have recently[5] shown that the oxidative Heck coupling using either the 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical (TEMPO),[6,7] a related bulky nitroxide **1** or O_2 as external stoichiometric oxidants can be used for the synthesis of triaryl-substituted allylic alcohols under very mild conditions (Scheme 1). As a continuation of these investigations we report herein stereoselective Pd-catalyzed C–H arylations of protected allylic amines for the synthesis of tetrasubstituted alkenes. Notably, Boc-protected allylic amines



Scheme 1. Triaryl-substituted alkenes *via* oxidative Heck coupling of allylic alcohols.

were recently shown to be valuable substrates for regioselective oxidative Heck chemistry.[3j] In that paper the synthesis of trisubstituted alkenes was reported but examples on the successful preparation of tetrasubstituted olefins were not included. Moreover, results on the synthesis of tetrasubstituted alkenes were recently disclosed using the Fujiwara–Moritani variant of the oxidative Heck reaction.[8] However, in these transformations high reaction temperatures are necessary which makes the control of the stereoselectivity difficult to achieve. Moreover, the aryl-Pd source, which is an arene in those cases, has to be used in a large excess as a cosolvent.

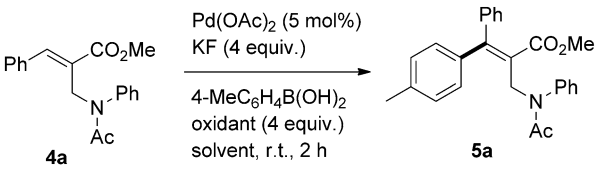
Results and Discussion

The allylic amines used in this study were readily prepared according to a literature procedure.[9] In the first step, four different aldehydes were reacted in a Morita–Baylis–Hillman reaction[10] with methyl acrylate to give the corresponding allylic alcohols **2a–d** in good yields (Scheme 2). Stereoselective bromination with $LiBr/H_2SO_4$ and subsequent amination with aniline afforded the allylic amines **3a–d** which were eventually N-acylated to provide substrates **4a–d** in good overall yields. To investigate the effect of the N-substituents, we also prepared the analogues **4e–j** and the effect of the ester moiety on the coupling reaction was addressed by including the nitrile congener **4k**, the aryl derivatives **4l–n** and the methyl compound **4o** into these studies (for their preparation see the Supporting Information).

Oxidative Heck arylation was optimized using substrate **4a** (R = Ph) in combination with *para*-tolylboronic acid as arene source. Oxidants and solvents were systematically varied. We were pleased to find that with TEMPO (4 equiv.) in the presence of KF (4 equiv.) in propionic acid at room temperature for 2 h, **5a** was obtained in near quantitative yield (Table 1, entry 1). Importantly, **5a** was formed with complete stereocontrol as checked by NMR spectroscopy. The relative configuration was unambiguously assigned by X-ray analysis (Figure 1).[11]

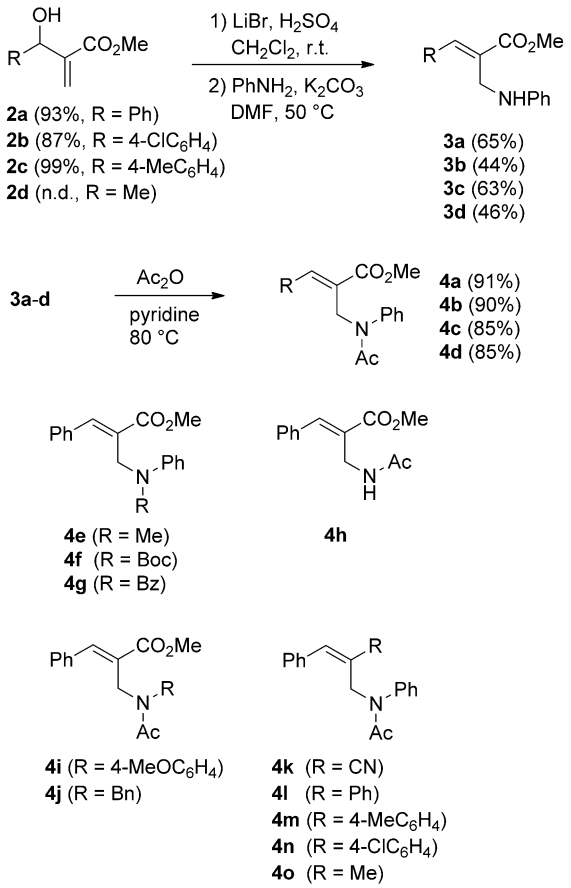
Efficient coupling was also achieved using O_2 as oxidant. However, the reaction was significantly slower and yield decreased (entry 2). Reducing the amount of KF and TEMPO led to slightly decreased yields

Table 1. Oxidative Heck coupling of **4a** with 4-$MeC_6H_4B(OH)_2$ (4 equiv.) under different conditions.



Entry	Oxidant	Solvent	Yield [%]
1	**TEMPO**	**propionic acid**	**97**
2	O_2	propionic acid	78[a]
3	TEMPO	propionic acid	84[b]
4	TEMPO	propionic acid	89[c]
5	**1**	propionic acid	51
6	1,4-benzoquinone	propionic acid	no reaction
7	$Cu(OAc)_2$	propionic acid	30
8	$PhI(OAc)_2$	propionic acid	traces
9	AgOAc	propionic acid	no reaction
10	TEMPO	CH_2Cl_2	no reaction
11	TEMPO	DMF	no reaction
12	TEMPO	MeOH	no reaction
13	TEMPO	acetic acid	14
14	TEMPO	butyric acid	73

[a] Reaction run for 24 h.
[b] With 3 equiv. TEMPO.
[c] With 3 equiv. KF.



Scheme 2. Preparation of allylic amine derivatives.

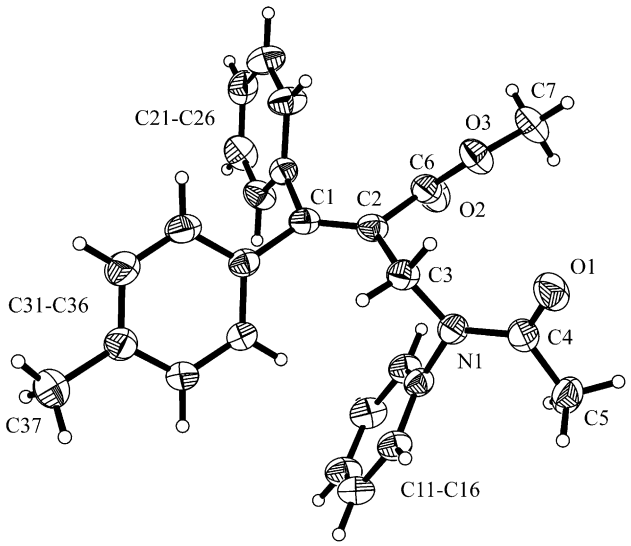
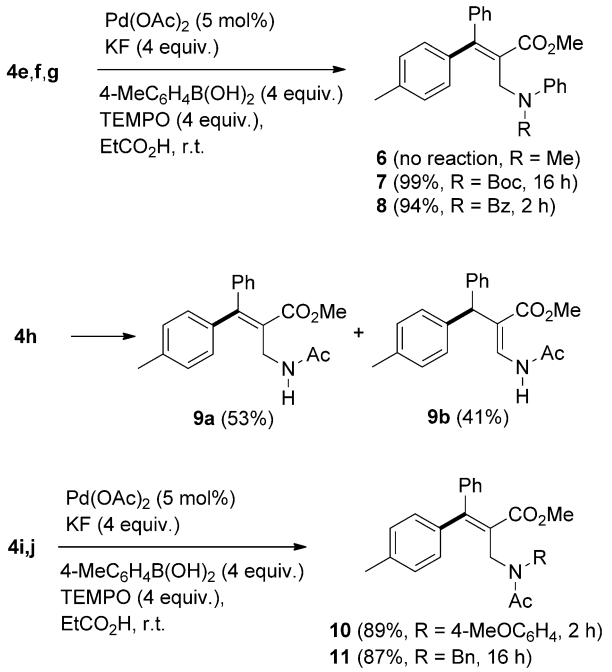


Figure 1. X-ray structure of **5a**.



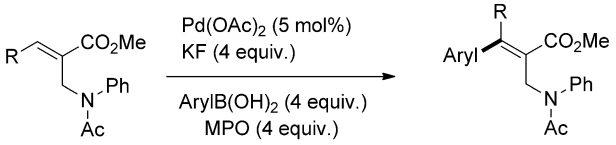
Scheme 3. Effect of the N-substituents on the Heck coupling.

(entries 3 and 4). Oxidant **1**, which performed very well in the oxidative arylation of densely substituted allylic alcohols (see Scheme 1),[5] provided **5a** in a moderate yield (entry 5) and no coupling occurred with benzoquinone as an oxidant (entry 6). $Cu(OAc)_2$ was also not a good oxidant (entry 7) and little or no reaction was observed with $PhI(OAc)_2$ or Ag(OAc), respectively (entries 8 and 9). The proper choice of the solvent is crucial since coupling to **5a** was not achieved in CH_2Cl_2, DMF and MeOH (entries 10–12). Interestingly, running the reaction in acetic or butyric acid as solvents afforded lower yields documenting the importance the solvent exerts on the coupling reaction (entries 13 and 14).

With the optimized conditions in hand we next investigated the effect of the N-substituents on the reaction outcome. The carbonyl moiety in the N-protecting group is important since with the N-methyl derivative **4e** coupling did not occur (Scheme 3). This assumption was further supported by the successful transformation of the Boc-protected allylic amine to tetrasubstituted alkene **7**. A quantitative yield was achieved; however, reaction time had to be increased to 16 h. The slightly decreased reactivity might be caused by steric effects. A very good result was also obtained with the Bz-protected substrate **4g** to give **8**, so proving the importance of the carbonyl-containing substituent on this coupling reaction. The N-phenyl group in **4a** was replaced by the 4-$MeOC_6H_4$ substituent, which can be cleaved under oxidative conditions, and reaction with *para*-tolylboronic acid under optimized conditions afforded alkene **10** in 89% isolated yield. Interestingly, derivative **4h** lacking the phenyl protecting group showed high reactivity. However, besides the targeted Heck coupling product **9a** (53%), the isomer **9b** was isolated as diastereoisomerically pure compound in 41% yield (relative configuration assigned by NOE experiments). The N-benzyl derivative **4j** showed slightly decreased reactivity compared to the N-phenyl compound **4a** and alkene **11** was obtained in 87% yield in 16 h.

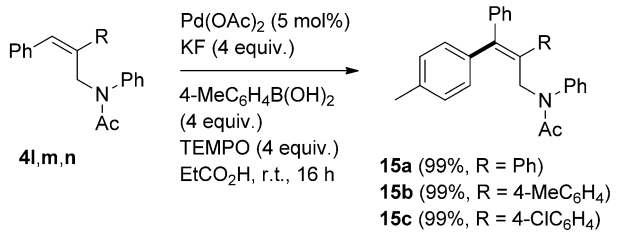
We then investigated the substrate scope with respect to the arylboronic acid component using alkene **4a** as substrate (Table 2). For all boronic acids studied the reaction occurred with complete stereocontrol and products **5b–i** were isolated as single diastereoisomers as evaluated by NMR spectroscopy. We noted good yields for arylboronic acids bearing electron-donating as well as electron-withdrawing substituents at the *para* position (entries 1–7). In general the electron-poorer boronic acids provided slightly better results. As expected the *meta*-tolylboronic acid worked well (entry 8) but no coupling was achieved with the *ortho*-tolyl derivative for steric reasons (entry 9). Side reactions in these couplings are the homocoupling of the arylboronic acid and the protodeborylation. The aryl group in the alkene substrate could be varied without affecting reactivity and products **12** and **13** were isolated in very good yields in the reaction with phenylboronic acid (entries 10 and 11). Importantly, substrate **4d** bearing the methyl group instead of an aryl substituent delivered the corresponding product **14** in excellent yield and selectivity showing that the

Table 2. Substrate scope.



Entry	Substrate	R	Aryl	Product	Yield [%]
1	**4a**	Ph	4-*t*-BuC_6H_4	**5b**	72
2	**4a**	Ph	4-$MeOC_6H_4$	**5c**	73
3	**4a**	Ph	4-PhC_6H_4	**5d**	79[a]
4	**4a**	Ph	4-AcC_6H_4	**5e**	69[a]
5	**4a**	Ph	4-ClC_6H_4	**5f**	85
6	**4a**	Ph	4-FC_6H_4	**5g**	96
7	**4a**	Ph	4-$CF_3C_6H_4$	**5h**	89
8	**4a**	Ph	3-MeC_6H_4	**5i**	82
9	**4a**	Ph	2-MeC_6H_4	**5j**	n.i.[b]
10	**4b**	4-ClC_6H_4	Ph	**12**	95
11	**4c**	4-MeC_6H_4	Ph	**13**	90
12	**4d**	Me	Ph	**14**	96

[a] Reaction for 16 h.
[b] n.i. = not identified.



Scheme 4. Oxidative Heck coupling on stilbene derivatives.

chemistry is not restricted to cinnamic acid derivatives (entry 12).

Finally, we studied the effect of the ester moiety on the coupling reaction and noted that the nitrile derivative **4k** (see Scheme 1) in the reaction with *para*-tolylboronic acid under optimized conditions did not provide the corresponding targeted Heck product. However, with the alkene **4l** carrying a phenyl group in place of the ester moiety, coupling worked with high yield and alkene **15a** was isolated in 99% yield (Scheme 4). As compared to ester **4a**, transformation was significantly slower and reaction time had to be extended to 16 h. In analogy, the other two stilbene derivatives **4m** and **4n** underwent oxidative Heck coupling to give **15b** and **15c** with perfect stereocontrol in quantitative yield. The relative configuration of **15c** was confirmed by X-ray analysis (Figure 2).[12] However, reaction with the methyl-substituted congener **4o** was not clean and different products which could not be separated were identified.[13]

Considering the importance of the acyl protecting group on the reaction outcome we suggest the following mechanism (Scheme 5) for the stereoselective oxidative Heck arylation. PdX_2 in propionic acid likely present as $(EtCO_2)_2Pd$ first,[14] then reacts with the arylboronic acid to give $EtCO_2PdAryl$. We assume that

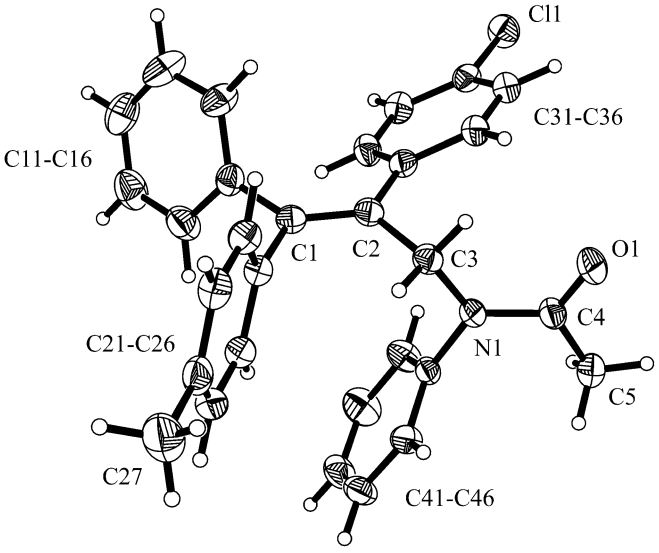
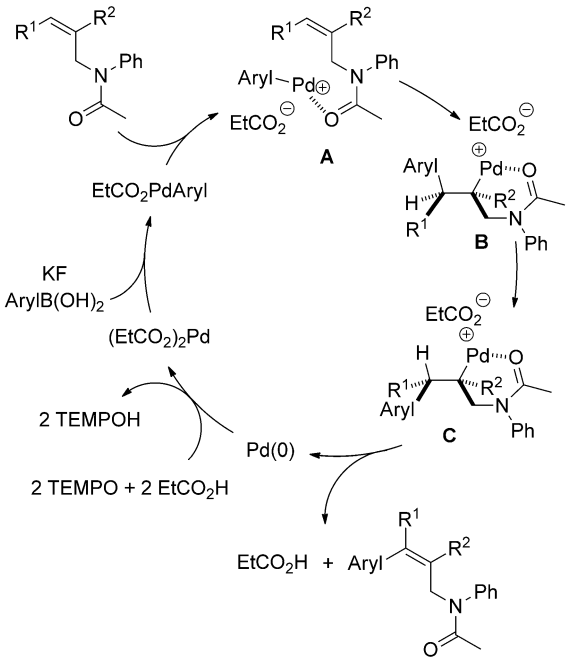


Figure 2. X-ray structure of **15c**.



Scheme 5. Suggested mechanism.

the Pd complex interacts in its dissociated cationic form ($^+$PdAryl) with the acyl protecting group to generate complex **A**. *syn*-Carbopalladation then provides **B** which after sigma bond rotation (least motion) undergoes β-H-elimination *via* conformer **C** to give the observed Heck product. The Pd(0) formed after α-elimination is eventually oxidized with TEMPO in the presence of propionic acid to regenerate the $(EtCO_2)_2Pd$ complex.

Conclusions

We reported the application of the oxidative Heck coupling for the arylation of densely substituted allylic amines which are readily prepared using known methods. Commercially available TEMPO was shown to be the ideal oxidant for these transformations which occur under very mild conditions with complete stereocontrol. Proper choice of the substituents at the N atom in the substrate allylic amines was shown to be important for successful Heck coupling. Best results were achieved using the N-acyl-N-phenyl derivatives.

Experimental Section

General Procedure (GP) for the Synthesis of Tetrasubstituted Olefins by Oxidative Heck Coupling

An arylboronic acid (1.0 mmol, 4.0 equiv.), potassium fluoride (58 mg, 1.0 mmol, 4.0 equiv.), $Pd(OAc)_2$ (2.8 mg,

12.5 mmol, 5 mol%), alkene **4** (0.25 mmol, 1.0 equiv.) and propionic acid (1.0 mL) were stirred at room temperature for 2 h or 16 h. Na_2CO_3 (aqueous saturated soluition, 5 mL) was added and the mixture was extracted with DCM (3× 10 mL). The combined organic layers were dried over $MgSO_4$ and the volatiles were removed under reduced pressure. The residue was purified by flash chromatography (FC).

(*E*)-Methyl 3-phenyl-2-[(*N*-phenylacetamido)methyl]-3-(*p*-tolyl)acrylate (5a): According to the GP with *p*-tolylboronic acid (135 mg, 1.0 mmol, 4.0 equiv.) and (*E*)-methyl 3-phenyl-2-[(*N*-phenylacetamido)methyl]acrylate **4a** (77 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 10/1) gave the desired product **5a** as a yellow oil; yierld: 97 mg (97%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.33–7.31 (m, 3H, CH_{arom}), 7.12–7.10 (m, 5H, CH_{arom}), 6.95–6.92 (m, 2H, CH_{arom}), 6.84 (d, *J* = 7.8 Hz, 2H, CH_{arom}), 6.35 (d, *J* = 7.8 Hz, 2H, CH_{arom}), 4.60 (s, 2H, CH_2), 3.43 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 1.73 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 170.3 (C), 169.8 (C), 148.9 (C), 142.0 (C), 141.4 (C), 137.5 (C), 136.3 (C), 129.5 (CH), 129.0 (CH), 128.7 (CH), 128.7 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.9 (C), 127.8 (CH), 51.7 (CH_3), 48.3 (CH_2), 22.6 (CH_3), 21.1 (CH_3); HR-MS (ESI): *m/z* = 422.1732, calcd. for $C_{26}H_{25}NO_3Na$ $[M+Na]^+$: 422.1727. IR (neat): ν = 2947 *w*, 1722 *s*, 1662 *s*, 1595 *m*, 1495 *m*, 1387 *m*, 1282 *m*, 1254 *m*, 1119 *s*, 699 *s* cm^{-1}.

(*E*)-Methyl 3-[4-(*tert*-butyl)phenyl]-3-phenyl-2-[(*N*-phenylacetamido)methyl]acrylate (5b): According to the GP with [4-(*tert*-butyl)phenyl]boronic acid (178 mg, 1.00 mmol, 4.00 equiv.) and (*E*)-methyl 3-phenyl-2-[(*N*-phenylacetamido)methyl]acrylate **4a** (77 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 10/1) gave the desired product **5b** as a yellow solid; yield: 80 mg (72%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.33–7.31 (m, 3H, CH_{arom}), 7.14–7.09 (m, 5H, CH_{arom}), 7.04 (d, *J* = 8.4 Hz, 2H, CH_{arom}), 6.97–6.94 (m, 2H, CH_{arom}), 6.41 (d, *J* = 8.4 Hz, 2H, CH_{arom}), 4.62 (s, 2H, CH_2), 3.44 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 1.19 (s, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 170.1 (C), 169.8 (C), 150.6 (C), 148.9 (C), 142.1 (C), 141.5 (C), 136.2 (C), 129.5 (CH), 129.0 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 128.0 (C), 127.9 (CH), 127.7 (CH), 124.8 (CH), 51.7 (CH_3), 48.2 (CH_2), 34.5 (C), 31.3 (CH_3), 22.7 (CH_3); HR-MS (ESI): *m/z* = 464.2196, calcd. for $C_{29}H_{31}NO_3Na$ $[M+Na]^+$: 464.2202;IR (neat): ν = 2958 *w*, 1723 *s*, 1663 *s*, 1495 *m*, 1389 *s*, 1355 *s*, 1257 *s*, 1123 *s* cm^{-1}.

(*E*)-Methyl 3-(4-methoxyphenyl)-3-phenyl-2-[(*N*-phenylacetamido)methyl]acrylate (5c): According to the GP with (4-methoxyphenyl)boronic acid (152 mg, 1.0 mmol, 4.0 equiv.) and (*E*)-methyl 3-phenyl-2-((*N*-phenylacetamido)methyl)acrylate **4a** (77 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 10/1) gave the desired product **5c** as a colorless oil; yield: 76 mg (73%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.33–7.31 (m, 3H, CH_{arom}), 7.13–7.12 (m, 5H, CH_{arom}), 6.94–6.91 (m, 2H, CH_{arom}), 6.58 (d, *J* = 8.5 Hz, 2H, CH_{arom}), 6.41 (d, *J* = 8.5 Hz, 2H, CH_{arom}), 4.64 (s, 2H, CH_2), 3.67 (s, 3H, CH_3), 3.42 (s, 3H, CH_3), 1.73 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 170.2 (C), 169.8 (C), 159.1 (C), 148.8 (C), 142.1 (C), 141.6 (C), 131.6 (C), 130.2 (CH), 129.5 (CH), 129.0 (CH), 128.3 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.7 (C), 113.4 (CH), 55.2 (CH_3), 51.7 (CH_3), 48.3 (CH_2), 22.7 (CH_3). HR-MS (ESI) *m/z* = 438.1676, calcd. for $C_{26}H_{25}NO_4Na$ $[M+Na]^+$: 438.1681; IR (neat): ν = 2948 *w*, 1721 *s*, 1661 *s*, 1606 *m*, 1495 *m*, 1388 *m*, 1283 *s*, 1246 *s*, 1119 *m*, 699 *s* cm^{-1}.

(*E*)-Methyl 3-[(1,1′-biphenyl)-4-yl]-3-phenyl-2-[(*N*-phenylacetamido)methyl]acrylate (5d): According to the GP with [1,1′-biphenyl]-4-ylboronic acid (198 mg, 1.0 mmol, 4.0 equiv.) and (*E*)-methyl 3-phenyl-2-[(*N*-phenylacetamido)methyl]acrylate **4a** (77 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 10/1) gave the desired product **5d** as a yellow oil;: yield: 92 mg (79%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.46–7.43 (m, 2H, CH_{arom}), 7.35–7.25 (m, 8H, CH_{arom}), 7.16–7.12 (m, 5H, CH_{arom}), 7.01–6.98 (m, 2H, CH_{arom}), 6.53 (d, *J* = 8.1 Hz, 2H, CH_{arom}), 4.64 (s, 2H, CH_2), 3.46 (s, 3H, CH_3), 1.74 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 170.3 (C), 169.7 (C), 148.3 (C), 142.1 (C), 141.1 (C), 140.5 (C), 140.4 (C), 138.2 (C), 129.6 (CH), 129.2 (CH), 129.1 (CH), 128.8 (CH), 128.4 (C), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.5 (CH), 127.0 (CH), 126.7 (CH), 51.9 (CH_3), 48.4 (CH_2), 22.6 (CH_3); HR-MS (ESI): *m/z* = 484.1883, calcd. for $C_{31}H_{27}NO_3Na$ $[M+Na]^+$: 484.1889; IR (neat): ν = 2949 *w*, 1713 *s*, 1661 *s*, 1595 *m*, 1494 *m*, 1389 *m*, 1283 *s*, 1256 *s*, 1120 *m*, 733 *s*, 697 *s* cm^{-1}.

(*E*)-Methyl 3-(4-acetylphenyl)-3-phenyl-2-[(*N*-phenylacetamido)methyl]acrylate (5e): According to the GP with 4-acetylbenzeneboronic acid (164 mg, 1.0 mmol, 4.0 equiv.) and (*E*)-methyl 3-phenyl-2-[(*N*-phenylacetamido)methyl]acrylate **4a** (77 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 5/1) gave the desired product **5e** as a white solid; yield: 74 mg (69%); mp 133 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K) δ 7.63 (d, *J* = 8.0 Hz, 2H, CH_{arom}), 7.36–7.35 (m, 3H, CH_{arom}), 7.16–7.11 (m, 5H, CH_{arom}), 6.97–6.94 (m, 2H, CH_{arom}), 6.57 (d, *J* = 7.8 Hz, 2H, CH_{arom}), 4.54 (s, 2H, CH_2), 3.48 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 1.73 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K) δ 197.4 (C), 170.2 (C), 169.2 (C), 146.9 (C), 144.0 (C), 142.0 (C), 140.2 (C), 136.2 (C), 129.7 (CH), 129.2 (C), 129.0 (CH), 129.0 (CH), 128.3 (CH), 128.2 (CH), 128.2 (CH), 128.1 (CH), 128.1 (CH), 51.9 (CH_3), 48.4 (CH_2), 26.5 (CH_3), 22.6 (CH_3); HR-MS (ESI): *m/z* = 450.1676, calcd. for $C_{27}H_{25}NO_4Na$ $[M+Na]^+$: 450.1681; IR (neat): ν = 2948 *w*, 1725 *s*, 1683 *s*, 1664 *s*, 1596 *m*, 1495 *m*, 1391 *m*, 1265 *s*, 1122 *m* cm^{-1}.

(*E*)-Methyl 3-(4-chlorophenyl)-3-phenyl-2-[(*N*-phenylacetamido)methyl]acrylate (5f): According to the GP with (4-chlorophenyl)boronic acid (156 mg, 1.0 mmol, 4.0 equiv.) and (*E*)-methyl 3-phenyl-2-[(*N*-phenylacetamido)methyl]acrylate **4a** (77 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 10/1) gave the desired product **5f** as a white solid; yield: 89 mg (85%); mp 142 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.46–7.42 (m, 3H, CH_{arom}), 7.29–7.22 (m, 5H, CH_{arom}), 7.12 (d, *J* = 8.3 Hz, 2H, CH_{arom}), 7.06–7.03 (m, 2H, CH_{arom}), 6.49 (d, *J* = 8.3 Hz, 2H, CH_{arom}), 4.66 (s, 2H, CH_2), 3.56 (s, 3H, CH_3), 1.84 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 170.3 (C), 169.4 (C), 147.0 (C), 142.0 (C), 140.6 (C), 137.6 (C), 133.7 (C), 130.1 (CH), 129.7 (CH), 129.0 (CH), 128.9 (C), 128.3 (CH), 128.2 (CH), 128.2 (CH), 128.1 (CH), 128.1 (CH), 51.9 (CH_3), 48.4 (CH_2), 22.6 (CH_3); HR-MS (ESI): *m/z* = 442.1180, calcd. for $C_{25}H_{22}ClNO_3Na$ $[M+Na]^+$: 442.1186; IR (neat): ν = 2949 *w*, 1722 *s*, 1661 *s*, 1494 *s*, 1390 *s*, 1278 *s*, 1253 *s*, 1122 *m* cm^{-1}.

(*E*)-Methyl 3-(4-fluorophenyl)-3-phenyl-2-[(*N*-phenylacetamido)methyl]acrylate (5g): According to the GP with (4-fluorophenyl)boronic acid (140 mg, 1.0 mmol, 4.0 equiv.)

and (*E*)-methyl 3-phenyl-2-[(*N*-phenylacetamido)methyl]-acrylate **4a** (77 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 10/1) gave the desired product **5g** as a yellow solid; yield: 97 mg (96%); mp 145 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.34–7.32 (m, 3H, CH_{arom}), 7.15–7.11 (m, 5H, CH_{arom}), 6.96–6.93 (m, 2H, CH_{arom}), 6.73 (t, *J* = 8.5 Hz, 2H, CH_{arom}), 6.46–6.41 (m, 2H, CH_{arom}), 4.57 (s, 2H, CH_2), 3.45 (s, 3H, CH_3), 1.73 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 170.3 (C), 169.5 (C), 162.2 (d, *J* = 247.5 Hz, C), 147.4 (C), 142.1 (C), 140.9 (C), 135.1 (d, *J* = 3.4 Hz, C), 130.5 (d, *J* = 8.5 Hz, CH), 129.6 (CH), 129.0 (CH), 128.6 (C), 128.2 (CH), 128.2 (CH), 128.1 (CH), 128.1 (CH), 115.1 (d, *J* = 21.5 Hz, CH), 51.9 (CH_3), 48.3 (CH_2), 22.6 (CH_3). HR-MS (ESI) *m/z* = 404.1662, calcd. for $C_{25}H_{22}FNO_3H$ $[M+H]^+$, found: 404.1565. IR (neat): ν = 2948 *w*, 1717 *s*, 1660 *s*, 1596 *m*, 1494 *m*, 1390 *s*, 1252 *s*, 1216 *s*, 1119 *s*, 700 *s* cm^{-1}.

(*E*)-Methyl 3-phenyl-2-[(*N*-phenylacetamido)methyl]-3-[4-(trifluoromethyl)phenyl]-acrylate (5h): According to the GP with [4-(trifluoromethyl)phenyl]boronic acid (190 mg, 1.0 mmol, 4.0 equiv.) and (*E*)-methyl 3-phenyl-2-((*N*-phenylacetamido)methyl)acrylate **4a** (77 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 10/1) gave the desired product **5h** as a yellow solid; yield: 101 mg (89%); mp 149 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.47–7.45 (m, 3H, CH_{arom}), 7.40 (d, *J* = 8.4 Hz, 2H, CH_{arom}), 7.29–7.21 (m, 5H, CH_{arom}), 7.09–7.05 (m, 2H, CH_{arom}), 6.69 (d, *J* = 8.1 Hz, 2H, CH_{arom}), 4.64 (s, 2H, CH_2), 3.59 (s, 3H, CH_3), 1.84 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 170.2 (C), 169.2 (C), 146.4 (C), 142.8 (C), 142.0 (C), 140.1 (C), 129.7 (q, *J* = 13.2 Hz, CH), 129.7 (CH), 129.4 (C), 129.0 (CH), 129.0 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.1 (CH), 125.0 (q, *J* = 3.6 Hz, CF_3), 122.6 (q, *J* = 216 Hz, C), 52.0 (CH_3), 48.3 (CH_2), 22.6 (CH_3); HR-MS (ESI): *m/z* = 476.1444, calcd. for $C_{26}H_{22}F_3NO_3Na$ $[M+Na]^+$: 476.1449; IR (neat): ν = 2950 *w*, 1728 *s*, 1667 *s*, 1496 *m*, 1324 *s*, 1390 *s*, 1252 *s*, 1216 *s*, 1119 *s*, 700 *s* cm^{-1}.

(*E*)-Methyl 3-phenyl-2-[(*N*-phenylacetamido)methyl]-3-(*meta*-tolyl)acrylate (5i): According to the GP with *meta*-tolylboronic acid (135 mg, 1.0 mmol, 4.0 equiv.) and (*E*)-methyl 3-phenyl-2-[(*N*-phenylacetamido)methyl]acrylate **4a** (77 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 10/1) gave the desired product **5i** as a colorless oil; yield: 82 mg (82%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.35–7.32 (m, 3H, CH_{arom}), 7.13–7.12 (m, 5H, CH_{arom}), 6.98–6.91 (m, 4H, CH_{arom}), 6.30 (d, *J* = 6.7 Hz, 1H, CH_{arom}), 6.16 (s, 1H, CH_{arom}), 4.58 (s, 2H, CH_2), 3.46 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 1.72 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 170.2 (C), 169.7 (C), 148.7 (C), 142.0 (C), 141.4 (C), 139.1 (C), 137.6 (C), 129.5 (CH), 129.1 (CH), 129.0 (CH), 128.4 (CH), 128.1 (CH), 128.1 (CH), 128.1 (C), 128.0 (CH), 127.9 (CH), 127.8 (CH), 125.7 (CH), 51.8 (CH_3), 48.2 (CH_2), 22.6 (CH_3), 21.3 (CH_3); HR-MS (ESI): *m/z* = 422.1727, calcd. for $C_{26}H_{25}NO_3Na$ $[M+Na]^+$: 422.1732; IR (neat): ν = 2948 *w*, 1723 *s*, 1662 *s*, 1595 *m*, 1495 *m*, 1387 *m*, 1286 *s*, 1261 *s*, 1119 *m* cm^{-1}.

(*E*)-Methyl 2-{[(*tert*-butoxycarbonyl)(phenyl)amino]-methyl}-3-phenyl-3-(*para*-tolyl)acrylate (7): According to the GP with *para*-tolylboronic acid (135 mg, 1.0 mmol, 4.0 equiv.) and (*E*)-methyl 2-{[(*tert*-butoxycarbonyl)-(phenyl)amino]methyl}-3-phenylacrylate **4f** (92 mg, 0.25 mmol, 1.0 equiv.) for 16 h. FC (pentane/Et_2O = 10/1) gave the desired product **7** as a yellow **oil;** yield: 113 mg (99%); **mp** 114 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.23 (t, *J* = 7.3 Hz, 2H, CH_{arom}), 7.15 (t, *J* = 7.3 Hz, 1H, CH_{arom}), 7.12–7.05 (m, 5H, CH_{arom}), 6.94–6.91 (m, 2H, CH_{arom}), 6.87 (d, *J* = 7.8 Hz, 2H, CH_{arom}), 6.45 (d, *J* = 7.8 Hz, 2H, CH_{arom}), 4.52 (s, 2H, CH_2), 3.41 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 1.31 (s, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 169.8 (C), 154.6 (C), 147.9 (C), 141.5 (C), 141.5 (C), 137.5 (C), 136.5 (C), 128.9 (CH), 128.9 (C), 128.8 (CH), 128.7 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 127.7 (CH), 125.6 (CH), 80.3 (C), 51.6 (CH_3), 49.8 (CH_2), 28.3 (CH_3), 21.2 (CH_3); HR-MS (ESI): *m/z* = 480.2145, calcd. for $C_{29}H_{31}NO_4Na$ $[M+Na]^+$: 480.2151; IR (neat): ν = 2948 *w*, 1698 *s*, 1384 *s*, 1303 *m*, 1255 *s*, 1165 *s*, 1119 *s* cm^{-1}.

(*E*)-Methyl 3-phenyl-2-[(*N*-phenylbenzamido)methyl]-3-(*para*-tolyl)acrylate (8): According to the GP with *para*-tolylboronic acid (135 mg, 1.0 mmol, 4.0 equiv.) and (*E*)-methyl 3-phenyl-2-((*N*-phenylbenzamido)methyl)acrylate **4g** (93 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 10/1) gave the desired product **8** as a yellow **oil**; yield: 109 mg (94%); **mp** 108 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.19–7.04 (m, 11H, CH_{arom}), 6.99–6.92 (m, 6H, CH_{arom}), 6.60 (d, *J* = 7.9 Hz, 2H, CH_{arom}), 4.81 (s, 2H, CH_2), 3.45 (s, 3H, CH_3), 2.23 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 170.7 (C), 169.8 (C), 148.6 (C), 142.6 (C), 141.5 (C), 137.6 (C), 136.5 (C), 136.2 (C), 129.4 (CH), 128.9 (CH), 128.9 (CH), 128.8 (CH), 128.8 (CH), 128.5 (CH), 128.4 (CH), 128.1 (C), 127.9 (CH), 127.8 (CH), 127.6 (CH), 126.9 (CH), 51.8 (CH_3), 49.7 (CH_2), 21.2 (CH_3); HR-MS (ESI): *m/z* = 484.1883, calcd. for $C_{31}H_{27}NO_3Na$ $[M+Na]^+$: 484.1889; IR (neat): ν = 2948 *w*, 1712 *s*, 1651 *s*, 1493 *m*, 1381 *m*, 1363 *m*, 1304 *m*, 1255 *m*, 1220 *s*, 1166 *s* cm^{-1}.

(*E*)-Methyl 2-(acetamidomethyl)-3-phenyl-3-(*para*-tolyl)-acrylate (9a) and (*Z*)-Methyl 3-acetamido-2-(phenyl(*p*-tolyl)methyl)-acrylate (9b): According to GP with *para*-tolylboronic acid (135 mg, 1.0 mmol, 4.0 equiv.) and (*E*)-methyl 2-(acetamidomethyl)-3-phenylacrylate 4 h (58 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 10/1) gave the desired product **9a** as a yellow solid (yield: 43 mg, 53%) along with **9b** as a yellow solid (yield: 33 mg, 41%).

9a: mp 90 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.20–7.18 (m, 3H, CH_{arom}), 7.09–7.00 (m, 6H, CH_{arom}), 5.99 (s, 1H, NH), 4.11 (d, *J* = 5.4 Hz, 2H, CH_2), 3.40 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 1.87 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 107.3 (C), 169.8 (C), 150.7 (C), 141.9 (C), 138.4 (C), 136.8 (C), 129.2 (CH), 129.1 (CH), 128.5 (CH), 128.0 (CH), 128.0 (CH), 127.7 (C), 51.7 (CH_3), 40.1 (CH_2), 23.2 (CH_3), 21.2 (CH_3); HR-MS (ESI): *m/z* = 346.1414, calcd. for $C_{20}H_{21}NO_3Na$ $[M+Na]^+$: 346.1419; IR (neat): ν = 2948 *w*, 1714 *s*, 1651 *s*, 1546 *s*, 1433 *m*, 1275 *s*, 1236 *s*, 1126 *s* cm^{-1}.

9b: mp 134 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 10.57 (d, *J* = 10.7 Hz, 1H, NH), 7.22–7.17 (m, 2H, CH_{arom}), 7.14–7.10 (m, 1H, CH_{arom}), 7.03–6.98 (m, 4H, CH_{arom}), 6.91–6.89 (m, 2H, CH_{arom}), 5.26 (s, 1H, CH), 3.56 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.03 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 169.6 (C), 167.9 (C), 142.5 (C), 139.1 (CH), 138.2 (C), 136.1 (C), 129.2 (CH), 128.9 (CH), 128.9 (CH), 128.4 (CH), 126.5 (CH), 112.2 (C), 51.7 (CH_3), 50.0 (CH), 23.7 (CH_3), 21.0 (CH_3); HR-MS (ESI): *m/z* = 346.1414, calcd. for $C_{20}H_{21}NO_3Na$ $[M+Na]^+$: 346.1419; IR (neat): ν = 2951 *w*, 1709 *m*, 1683 *s*, 1624 *s*, 1434 *m*, 1194 *s* cm^{-1}.

(*E*)-Methyl 2-{[*N*-(4-methoxyphenyl)acetamido]methyl}-3-phenyl-3-(*para*-tolyl)acrylate (10): According to the GP with *para*-tolylboronic acid (122 mg, 1.0 mmol, 4.0 equiv.) and (*E*)-methyl 2-{[*N*-(4-methoxyphenyl)acetamido]methyl}-3-phenylacrylate **4i** (85 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 10/1) gave the desired product **10** as a colorless oil; yield: 96 mg (89%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.22–7.20 (m, 3H, CH_{arom}), 7.12 (d, *J* = 8.0 Hz, 2H, CH_{arom}), 7.12–7.01 (m, 2H, CH_{arom}), 6.94–6.91 (m, 4H, CH_{arom}), 6.47 (d, *J* = 8.0 Hz, 2H, CH_{arom}), 4.65 (s, 2H, CH_2), 3.85 (s, 3H, CH_3), 3.52 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 1.80 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 170.7 (C), 169.8 (C), 159.2 (C), 148.8 (C), 141.4 (C), 137.4 (C), 136.4 (C), 134.7 (C), 130.0 (CH), 128.7 (CH), 128.7 (CH), 128.2 (CH), 128.0 (CH), 128.0 (C), 127.8 (CH), 114.5 (CH), 51.9 (CH_3), 48.3 (CH_2), 22.6 (CH_3), 21.2 (CH_3); HR-MS (ESI): *m/z* = 452.1832, calcd. for $C_{27}H_{27}NO_4Na$ $[M+Na]^+$: 452.1838; IR (neat): ν = 2947 *w*, 1723 *s*, 1661 *s*, 1510 *s*, 1247 *s*, 1121 *s* cm^{-1}.

(*E*)-Methyl 2-[(*N*-benzylacetamido)methyl]-3-phenyl-3-(*para*-tolyl)acrylate (11): According to the GP with *para*-tolylboronic acid (135 mg, 1.0 mmol, 4.0 equiv.) and (*E*)-methyl 2-((*N*-benzylacetamido)methyl)-3-phenylacrylate **4j** (80 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 10/1) gave the desired product **11** as a yellow oil; yield: 90 mg (87%). Two rotamers were obtained, the ratio of rotamer *a*:rotamer *b* = 1:1. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.29–7.27 (m, 6H, CH_{arom}), 7.18–7.15 (m, 3H, CH_{arom}), 7.08–7.02 (m, 4H, CH_{arom}), 6.94 (d, *J* = 7.8 Hz, 1H, CH_{arom}), 4.68 (s, 1H, CH_2), 4.57 (s, 1H, CH_2), 4.46 (s, 1H, CH_2), 4.30 (s, 1H, CH_2), 3.51 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.22 (s, 1.5H, CH_3), 2.12 (s, 1.5H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 171.3 (C), 169.9 (C), 169.4 (C), 149.1 (C), 148.0 (C), 141.6 (C), 141.1 (C), 138.1 (C), 137.7 (C), 137.2 (C), 136.7 (C), 136.4 (C), 136.1 (C), 129.2 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.7 (C), 128.6 (CH), 128.5 (CH), 128.5 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 127.4 (CH), 127.1 (CH), 124.6 (CH), 51.8 (CH_3), 51.8 (CH_3), 51.4 (CH_2), 48.2 (CH_2), 47.3 (CH_2), 45.7 (CH_2), 21.6 (CH_3), 21.2 (CH_3); HR-MS (ESI): *m/z* = 436.1883, calcd. for $C_{27}H_{27}NO_3Na$ $[M+Na]^+$: 436.1889; IR (neat): ν = 2947 *w*, 1717 *s*, 1649 *s*, 1416 *s*, 1256 *s*, 1114 *m*, 728 *s* cm^{-1}.

(*Z*)-Methyl 3-(4-chlorophenyl)-3-phenyl-2-[(*N*-phenylacetamido)methyl]acrylate (12): According to the GP with phenylboronic acid (122 mg, 1.0 mmol, 4.0 equiv.) and (*E*)-methyl 3-(4-chlorophenyl)-2-[(*N*-phenylacetamido)methyl]-acrylate **4b** (86 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 10/1) gave the desired product **12** as a colorless oil; yield: 95 mg (95%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.34–7.31 (m, 3H, CH_{arom}), 7.12–7.04 (m, 7H, CH_{arom}), 6.91–6.88 (m, 2H, CH_{arom}), 6.45–6.41 (m, 2H, CH_{arom}), 4.57 (s, 2H, CH_2), 3.50 (s, 3H, CH_3), 1.72 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 170.2 (C), 169.4 (C), 147.2 (C), 141.9 (C), 139.5 (C), 138.7 (C), 133.9 (C), 129.6 (CH), 129.6 (CH), 128.9 (CH), 128.7 (C), 128.6 (CH), 128.3 (CH), 128.2 (CH), 128.2 (CH), 127.9 (CH), 52.0 (CH_3), 48.2 (CH_2), 22.7 (CH_3); HR-MS (ESI): *m/z* = 442.1180, calcd. for $C_{25}H_{22}ClNO_3Na$ $[M+Na]^+$: 442.1186; IR (neat): ν = 2948 *w*, 1722 *s*, 1661 *s*, 1494 *s*, 1387 *s*, 1281 *s*, 1254 *s*, 1120 *s* cm^{-1}.

(*Z*)-Methyl 3-phenyl-2-[(*N*-phenylacetamido)methyl]-3-(*para*-tolyl)acrylate (13): According to the GP with phenylboronic acid (122 mg, 1.0 mmol, 4.0 equiv.) and (*E*)-methyl 2-[(*N*-phenylacetamido)methyl]-3-(*p*-tolyl)-acrylate **4c** (81 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 10/1) gave the desired product **13** as a colorless oil; yield: 95 mg (90%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.34–7.32 (m, 3H, CH_{arom}), 7.12–7.01 (m, 5H, CH_{arom}), 6.95 (d, *J* = 8.0 Hz, 2H, CH_{arom}), 6.85 (d, *J* = 8.0 Hz, 2H, CH_{arom}), 6.45–6.42 (m, 2H, CH_{arom}), 4.57 (s, 2H, CH_2), 3.50 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 1.74 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 170.3 (C), 169.8 (C), 148.7 (C), 142.0 (C), 139.4 (C), 138.2 (C), 137.8 (C), 129.5 (CH), 129.0 (CH), 128.7 (CH), 128.7 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.6 (C), 127.5 (CH), 51.9 (CH_3), 48.3 (CH_2), 22.6 (CH_3), 21.2 (CH_3); HR-MS (ESI): *m/z* = 422.1727, calcd. for $C_{26}H_{25}NO_3Na$ $[M+Na]^+$: 422.1732; IR (neat): ν = 2948 *w*, 1721 *s*, 1661 *s*, 1387 *s*, 1283 *s*, 1255 *s*, 1119 *s*, 699 *s* cm^{-1}.

(*E*)-Methyl 3-phenyl-2-[(*N*-phenylacetamido)methyl]-but-2-enoate (14): According to the GP with phenylboronic acid (122 mg, 1.00 mmol, 4.00 equiv.) and (*E*)-methyl 2-((*N*-phenylacetamido)methyl)but-2-enoate **4d** (62 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 10/1) gave the desired product **14** as a colorless oil; yield: 72 mg (96%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.30–7.28 (m, 3H, CH_{arom}), 7.09–7.01 (m, 3H, CH_{arom}), 6.95–6.92 (m, 2H, CH_{arom}), 6.41–6.38 (m, 2H, CH_{arom}), 4.39 (s, 2H, CH_2), 3.73 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 1.67 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 170.0 (C), 169.3 (C), 146.8 (C), 141.9 (C), 141.0 (C), 129.4 (CH), 128.8 (CH), 128.1 (CH), 127.9 (CH), 127.1 (CH), 126.8 (CH), 126.0 (C), 51.9 (CH_3), 47.5 (CH_2), 23.4 (CH_3), 22.6 (CH_3); HR-MS (ESI): *m/z* = 346.1414, calcd. for $C_{20}H_{21}NO_3Na$ $[M+Na]^+$: 346.1419; IR (neat): ν = 2948 *w*, 1712 *s*, 1656 *s*, 1495 *s*, 1391 *s*, 1304 *s*, 1283 *s*, 1255 *s*, 1062 *s* cm^{-1}.

(*Z*)-*N*-[2,3-Diphenyl-3-(*para*-tolyl)allyl]-*N*-phenylacetamide (15a): According to the GP with *para*-tolylboronic acid (122 mg, 1.0 mmol, 4.0 equiv.) and (*Z*)-*N*-(2,3-diphenylallyl)-*N*-phenylacetamide **4l** (82 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 40/1) gave the desired product **15a** as a colorless oil; yield: 100 mg (99%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.30–7.28 (m, 3H, CH_{arom}), 7.12–7.04 (m, 5H, CH_{arom}), 6.90–6.85 (m, 5H, CH_{arom}), 6.73–6.80 (m, 4H, CH_{arom}), 6.42 (d, *J* = 7.9 Hz, 2H, CH_{arom}), 4.83 (s, 2H, CH_2), 2.22 (s, 3H, CH_3), 1.50 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 170.2 (C), 143.0 (C), 142.6 (C), 142.2 (C), 139.5 (C), 139.0 (C), 136.3 (C), 135.9 (C), 130.6 (CH), 130.4 (CH), 129.3 (CH), 129.0 (CH), 128.9 (CH), 128.9 (CH), 128.0 (CH), 127.5 (CH), 127.5 (CH), 126.7 (CH), 126.1 (CH), 50.3 (CH_2), 22.6 (CH_3), 21.2 (CH_3); HR-MS (ESI): *m/z* = 440.1985, calcd. for $C_{30}H_{27}NONa$ $[M+Na]^+$: 440.1990; IR (neat): ν = 3022 *w*, 1656 *s*, 1494 *m*, 1388 *s*, 729 *s*, 698 *s* cm^{-1}.

(*Z*)-*N*-Phenyl-*N*-(3-phenyl-2,3-di-*para*-tolylallyl)acetamide (15b): According to the **GP** with *para*-tolylboronic acid (122 mg, 1.0 mmol, 4.0 equiv.) and (*Z*)-*N*-phenyl-*N*-[3-phenyl-2-(*p*-tolyl)allyl]acetamide **4m** (85 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 40/1) gave the desired product **15b** as a white solid; yield: 107 mg (99%); mp 124 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.31–7.29 (m, 3H, CH_{arom}), 7.01 (d, *J* = 8.1 Hz, 2H, CH_{arom}), 6.89–6.86 (m, 7H, CH_{arom}), 6.73–6.69 (m, 4H, CH_{arom}), 6.36 (d, *J* = 8.0 Hz, 2H, CH_{arom}), 4.80 (s, 2H, CH_2), 2.21 (s, 3H, CH_3),

2.19 (s, 3H, CH_3), 1.51 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 170.2 (C), 142.8 (C), 142.6 (C), 142.2 (C), 139.6 (C), 136.3 (C), 136.2 (C), 135.8 (C), 135.8 (C), 130.5 (CH), 130.3 (CH), 129.3 (CH), 129.1 (CH), 128.9 (CH), 128.8 (CH), 128.3 (CH), 128.0 (CH), 127.5 (CH), 126.0 (CH), 50.1 (CH_2), 22.7 (CH_3), 21.3 (CH_3), 21.2 (CH_3); HR-MS (ESI): *m/z* = 454.2141, calcd. for $C_{31}H_{29}NONa$ $[M+Na]^+$: 454.2147; IR (neat): ν = 3024 *w*, 1655 *s*, 1494 *m*, 1389 *s*, 729 *s* cm^{-1}.

(*Z*)-*N*-[2-(4-Chlorophenyl)-3-phenyl-3-(*para*-tolyl)allyl]-*N*-phenylacetamide (15c): According to the GP with *p*-tolylboronic acid (122 mg, 1.0 mmol, 4.0 equiv.) and (*Z*)-*N*-(2-(4-chlorophenyl)-3-phenylallyl)-*N*-phenylacetamide **4n** (90 mg, 0.25 mmol, 1.0 equiv.) for 2 h. FC (pentane/acetone = 40/1) gave the desired product **15c** as a white solid; yield: 111 mg (99%); mp 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.32–7.30 (m, 3H, CH_{arom}), 7.06–7.05 (m, 4H, CH_{arom}), 6.90–6.87 (m, 5H, CH_{arom}), 6.72–6.67 (m, 4H, CH_{arom}), 6.37 (d, *J* = 8.0 Hz, 2H, CH_{arom}), 4.81 (s, 2H, CH_2), 2.21 (s, 3H, CH_3), 1.52 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 170.3 (C), 143.8 (C), 142.2 (C), 142.0 (C), 139.2 (C), 137.5 (C), 136.5 (C), 134.7 (C), 132.5 (C), 132.0 (CH), 130.3 (CH), 129.4 (CH), 128.9 (CH), 128.9 (CH), 128.7 (CH), 128.2 (CH), 127.8 (CH), 127.7 (CH), 126.4 (CH), 50.0 (CH_2), 22.6 (CH_3), 21.2 (CH_3); HR-MS (ESI): *m/z* = 474.1595, calcd. for $C_{30}H_{26}NClONa$ $[M+Na]^+$: 474.1601; IR (neat): ν = 3024 *w*, 1655 *s*, 1494 *m*, 1389 *s*, 729 *s* cm^{-1}.

Supporting Information

Copies of the ^{1}H NMR and ^{13}C NMR spectra for all compounds and experimental procedures and physical data of the protected allylic amines **4a**–**4o** are available in the Supporting Information.

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[11] CCDC 961205 (**5a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] CCDC 967270 (**15c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[13] According to mass spectrometric analysis double arylation product was also formed. In the initial Heck reaction β-H- elimination can also occur at the methyl substituent under formation of the methylene which can then act as a substrate for a second arylation.
[14] In an NMR experiment we mixed $Pd(OAc)_2$ in propionic acid and observed the complete formation of $(EtCO_2)_2Pd$.

