Ligand-Free $PdCl_2$-Catalyzed Heck Reaction of Arylboronic Acids and Olefins under Reusable TBAB/H_2O Conditions

Bo-Xiao Tang,* Xiao-Niu Fang, Ren-Yun Kuang, Rong-Hua Hu, Ji-Wei Wang, Ping Li, Xiao-hang Li

School of Chemistry and Chemical Engineering, The Key Laboratory of Coordination Chemistry of Jiangxi Province, and Institute of Applied Chemistry, Jinggangshan University, Ji'an, 343009, P. R. of China
Fax +86(796)8110 676; E-mail: 520tangboxiao@163.com

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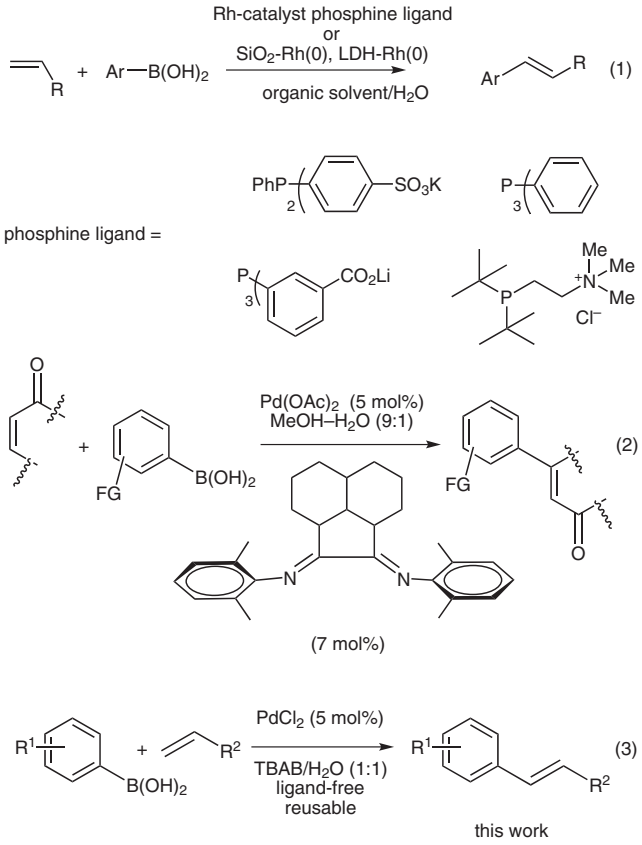
Abstract: A novel method was developed for Heck reaction of olefins and arylboronic acids using a ligand-free $PdCl_2$ catalyst to afford the coupling products with excellent regio- and stereoselectivity. It is noteworthy that the $PdCl_2/CuSO_4/K_2CO_3$/TBAB/H_2O system can be recovered and used for three cycles directly.

Key words: ligand-free, reusability, $PdCl_2$, Heck reaction, arylboronic acids

Transition-metal-catalyzed Heck reaction is an extremely powerful tool for C–C bond formation and has been widely utilized in the synthesis of valuable intermediates, biologically active agents, and functional organic materials.[1] Among them, Heck reaction of olefins and boron reagents has received considerable attention using various oxidant systems.[2] In recent years, Rh- and Pd-catalyzed Heck coupling reactions of arylboronic acids have been particularly attractive under organic solvent/H_2O conditions. Lautens,[3] Zou,[4] Michelet,[5] and their co-workers reported Rh-catalyzed Heck coupling of arylboronic acids with olefins in the presence of phosphine ligands. Similarly, SiO_2-Rh(0)- and LDH-Rh(0)-catalyzed Heck-type reactions of arylboronic acids were also reported by Trivedi et al. using a toluene–H_2O (5:1) system (Scheme 1, equation 1).[6] In 2011, Minnaard and co-workers reported that $Pd(OAc)_2$/BIAN ligand is an excellent catalyst for the base-free oxidative Heck reaction of arylboronic acids under MeOH–H_2O (9:1) conditions (Scheme 1, equation 2).[7]

From an economical as well as environmental point of view, it is highly desirable to design a ligand-free and green heterogeneous system for this elegant cross-coupling reaction. We have been engaged for a long time in a program devoted to reusable ionic liquid system.[8] Therefore, we aimed to develop an efficient green solvent system for Pd-catalyzed Heck reaction of arylboronic acids using a reusable procedure that is simple and easy to operate. Herein, we report a novel Heck-type cross-coupling reaction of olefins and arylboronic acids using a ligand-free palladium catalyst under reusable TBAB (*n*-Bu_4NBr)/H_2O conditions (Scheme 1, equation 3).

We began our investigation by studying the Heck-type coupling reaction of phenylboronic acid (**1a**) with *tert*-butyl acrylate (**2a**) in the presence of 5 mol% $PdCl_2$ as a catalyst under various reaction conditions (Table 1). As shown in Table 1, a range of aqueous media including TBAF (tetrabutylammonium fluoride)/H_2O, EMIB (1-ethyl-3-methyl imidazolium bromide)/H_2O, EMPB (1-ethyl-1-methyl piperidine bromide)/H_2O, and EPB (*N*-ethylpyridinium bromide)/H_2O were screened; however, the yields of the target product **3a** were all less than 30% (Table 1, entries 1–4). To our delight, the Heck-type reaction exhibited high catalytic activity in the presence of TBAB/H_2O (entry 5, the product **3a** is an *E*-alkene). Subsequently, a series of oxidants were evaluated, and $CuSO_4$ was found to provide higher yield than $Cu(OAc)_2$, TBHP, AgOAc, $CuCl_2$ (entries 5–9). Using 1.5 and 2.5 equivalents of $CuSO_4$, 73% and 29% yield of **3a** could be obtained, respectively (entries 10, 11). Product **3a** was



Scheme 1 Rh- and Pd-catalyzed Heck coupling reactions of arylboronic acids under organic solvent/H_2O conditions

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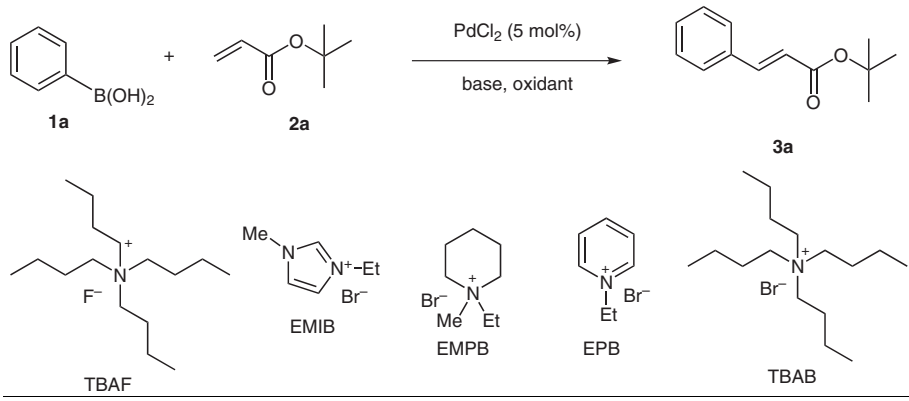
Table 1 Screening Conditions for Heck-Type Reaction between *tert*-Butyl Acrylate and Phenylboronic Acid[a]



Entry	Oxidant	Ionic liquid/H_2O	Base	Yield (%)[b]
1	$Cu(OAc)_2$	TBAF/H_2O	K_2CO_3	25
2	$Cu(OAc)_2$	EMIB/H_2O	K_2CO_3	<10
3	$Cu(OAc)_2$	EMPB/H_2O	K_2CO_3	28
4	$Cu(OAc)_2$	EPB/H_2O	K_2CO_3	26
5	$Cu(OAc)_2$	TBAB/H_2O	K_2CO_3	83
6[c]	TBHP	TBAB/H_2O	K_2CO_3	19
7	AgOAc	TBAB/H_2O	K_2CO_3	21
8	$CuCl_2$	TBAB/H_2O	K_2CO_3	79
9	$CuSO_4$	TBAB/H_2O	K_2CO_3	90
10[d]	$CuSO_4$	TBAB/H_2O	K_2CO_3	73
11[e]	$CuSO_4$	TBAB/H_2O	K_2CO_3	29
12[f]	$CuSO_4$	TBAB/H_2O	K_2CO_3	69
13[g]	$CuSO_4$	TBAB/H_2O	K_2CO_3	73
14[h]	$CuSO_4$	TBAB/H_2O	K_2CO_3	76
15	$CuSO_4$	TBAB/H_2O	KOAc	<10
16	$CuSO_4$	TBAB/H_2O	NaOH	<10
17	$CuSO_4$	TBAB/H_2O	Cs_2CO_3	80
18	$CuSO_4$	TBAB/H_2O	–	trace

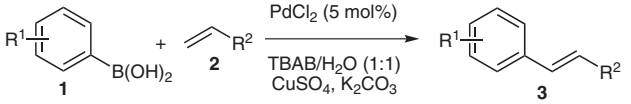
[a] Reaction conditions: **1a** (0.6 mmol), **2a** (0.4 mmol), $PdCl_2$ (5 mol%), oxidant (2 equiv), base (2 equiv), ionic liquid (0.5 g)/H_2O (0.5 g) = 1:1, 10 h, 85 °C, air.
[b] Isolated yield.
[c] TBHP = *tert*-butyl hydroperoxide.
[d] $CuSO_4$ (1.5 equiv).
[e] $CuSO_4$ (2.5 equiv).
[f] $CuSO_4$ (1.5 equiv), O_2.
[g] TBAB/H_2O = 7:3.
[h] TBAB/H_2O = 3:7.

obtained in 69% yield using 1.5 equivalents of $CuSO_4/O_2$ (entry 12). The ratio of TBAB and H_2O were then investigated; the target product **3a** could be isolated in 73% and 76% yield with a TBAB/H_2O ratio of 7:3 and 3:7, respectively (entries 13, 14). Finally, comparison of the different bases indicated that K_2CO_3 was superior to KOAc, NaOH, and Cs_2CO_3 (entries 9, 15–17). Only a trace amount of the target product **3a** was observed without base (entry 18).

The palladium-catalyzed coupling reaction of arylboronic acids **1** with olefins **2** were conducted under optimized conditions, and the results are summarized in Table 2. Various olefins with phenylboronic acid (**1a**) were trans-

formed into the corresponding products **3** ranging from 36–81% yields (Table 2, entries 1–5). Electronic effect of the substrates **2** seemed to have a distinction in the yields. For example, the yields of *n*-hexyl acrylate (**2c**) (81%) and acrylamide (**2d**) (66%) implied that there was discrimination between different electron-withdrawing functional groups (entries 2, 3). Allyl phenyl ether (**2e**) and styrene (**2f**) also affected the coupling reaction (entries 4, 5). All the alkenes afforded the target products exclusively with *E*-configuration.

Table 2 Ligand-Free $PdCl_2$-Catalyzed Heck-Type Reaction of Arylboronic Acids[a]



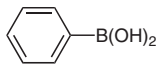
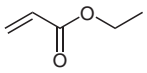
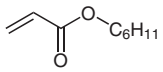
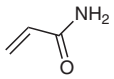
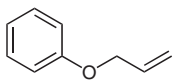
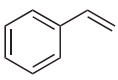
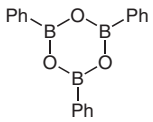
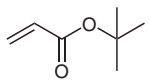
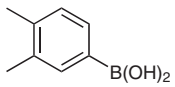
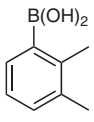
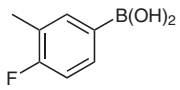
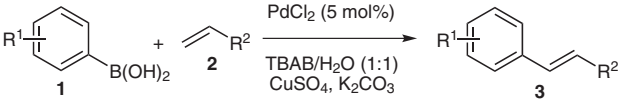
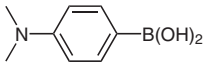
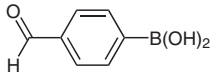
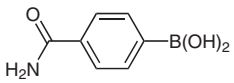
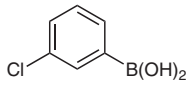
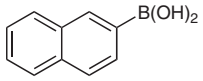
Entry	Arylboronic acid	Olefin	Time (h)	Product, yield (%)[b]
1	 **1a**	 **2b**	12	**3b**, 70
2	**1a**	 **2c**	10	**3c**, 81
3	**1a**	 **2d**	14	**3d**, 66
4	**1a**	 **2e**	20	**3e**, 36
5	**1a**	 **2f**	12	**3f**, 62
6[c]	 **1b**	 **2a**	10	**3a**, 85
7	 **1c**	**2a**	10	**3g**, 79
8	 **1d**	**2a**	10	**3h**, 69
9	 **1e**	**2a**	10	**3i**, 76

Table 2 Ligand-Free $PdCl_2$-Catalyzed Heck-Type Reaction of Arylboronic Acids[a] (continued)



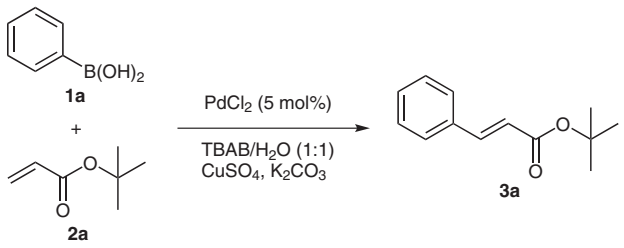
Entry	Arylboronic acid	Olefin	Time (h)	Product, yield (%)[b]
10	 **1f**	**2a**	10	**3j**, 79
11	 **1g**	**2a**	10	**3k**, 84
12	 **1h**	**2a**	10	**3l**, 65
13	 **1i**	**2a**	10	**3m**, 70
14	 **1j**	**2a**	10	**3n**, 58
15	 **1k**	**2a**	10	**3o**, 62

[a] Reaction conditions: **1** (0.6 mmol), **2** (0.4 mmol), $PdCl_2$ (5 mol%), $CuSO_4$ (0.8 mmol), K_2CO_3 (0.8 mmol), TBAB (0.5 g)/H_2O (0.5 g) = 1:1, air, 85 °C.
[b] Isolated yield.
[c] Amount of **1b** used: 0.2 mmol.

We were also pleased to observe that the Heck-type reaction of *tert*-butyl acrylate (**2a**) with various boron reagents proceeded well to give the target products in moderate to excellent yields under the standard conditions (Table 2, entries 6–15). Reaction of 2,4,6-triphenyl-1,3,5,2,4,6-trioxatriborinane (**1b**; 0.2 mmol) with **2a** provided the product in 85% yield (entry 6). A variety of arylboronic acids **1f**,**g**, having electron-donating groups on the aromatic ring were examined in the presence of TBAB/H_2O. The results demonstrated that several functional groups, such as dimethylamino and propoxy groups, were tolerated well under the standard conditions (entries 10, 11). Some *ortho*-substituted phenylboronic acids were also examined, and less amount of product was obtained in view of steric hindrance effect (entries 7, 8). Reactions with electron-deficient phenylboronic acids **1h**, **1i**, and **1j** also proceed smoothly (entries 12–14). When naphthalen-2-ylboronic acid (**1k**) was used, the desired product was obtained in 62% yield (entry 15). All the coupling products **3** were in the *E*-isomeric form.

Next the reusability of $PdCl_2/CuSO_4/K_2CO_3/TBAB/H_2O$ system in the Heck-type reaction of **1a** and **2a** was studied (Table 3). After initial coupling experimentation, the reaction mixture was extracted with hexane–ethyl acetate, and the $PdCl_2/CuSO_4/K_2CO_3/TBAB/H_2O$ system was then evaporated under vacuum and cooled. The recovered Heck-type reaction system was employed in the next run by charging with **1a** and **2a**. The results of three runs showed that the yield of the target product **3a** decreased significantly after each cycle (run 1, 89%; run 2, 72%; run 3, 61%).

Table 3 Reusability of $PdCl_2/CuSO_4/K_2CO_3/TBAB/H_2O$ System in the Heck-Type Reaction of Phenylboronic Acid (**1a**) with *tert*-Butyl Acrylate (**2a**)



Olefin	Arylboronic acid	Cycle	Time (h)	Yield (%)[a] of **3a**
		1[b]	10	89
1a	**2a**	2[c]	13	72
		3[c]	16	61

[a] Isolated yield.
[b] Reaction conditions: **1a** (0.6 mmol), **2a** (0.4 mmol), $PdCl_2$ (5 mol%), $CuSO_4$ (0.8 mmol), K_2CO_3 (0.8 mmol), TBAB (0.5 g)/H_2O (0.5 g) = 1:1, air, 85 °C.
[c] Amounts present: **1a** (0.6 mmol), **2a** (0.4 mmol).

In summary, we have developed a novel ligand-free $PdCl_2$-catalyzed method for Heck-type coupling of arylboronic acids under $TBAB/H_2O$ conditions. The scope of the catalytic system is well documented in the Heck-type reaction of various arylboronic acids and alkenes to afford the coupling products with excellent regio- and stereoselectivity. It is noteworthy that the $PdCl_2/CuSO_4/K_2CO_3/TBAB/H_2O$ system can be recovered and used for three cycles directly. Studies to broaden the scope of the catalytic system are currently underway.

Starting materials and other reagents were obtained from commercial suppliers and used without further purification. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz on a Bruker ARX400 spectrometer. Melting points were recorded in capillary tubes heated slowly in paraffin oil and are uncorrected. IR and LRMS data were recorded on a Thermo Nicolet AVATAR 370 and a Shimadzu GCMS-QP2010, respectively.

Heck-Type Reaction; *tert*-Butyl (*E*)-3-Phenylpropenoate (3a);[9a] Typical Procedure

To a Schlenk tube were added phenylboronic acid (**1a**; 73.2 mg, 0.6 mmol), *tert*-butyl acrylate (**2a**; 51.2 mg, 0.4 mmol), $PdCl_2$ (3.6 mg, 5 mol%), $CuSO_4$ (127.1 mg, 0.8 mmol), K_2CO_3 (110.4 mg, 0.8 mmol), TBAB (0.5 g), and H_2O (0.5 g). Then, the tube was charged with air, and the reaction mixture was stirred at 85 °C (oil bath temp) for 10 h until complete consumption of the starting material as monitored by TLC (hexane–EtOAc, 30:1). After completion of the reaction, the mixture was cooled to r.t., diluted with Et_2O (15 mL), washed with sat. NaCl solution (2 × 5 mL), dried over anhydrous Na_2SO_4 (2 g), and transferred to a round-bottom flask. The organic extract was concentrated under vacuum, and the resulting residue was purified by silica gel column chromatography (hexane–EtOAc) to afford the desired product **3a**; yield: 73.2 mg (90%); colorless oil.

IR (film): 1708, 1638, 1329, 1151 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 16.0 Hz, 1 H), 7.52–7.48 (m, 2 H), 7.38–7.34 (m, 3 H), 6.40 (d, *J* = 16.0 Hz, 1 H), 1.54 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 143.5, 134.5, 129.9, 128.7, 127.9, 120.0, 80.4, 28.1.

LRMS (EI, 70 eV): *m*/*z* (%) = 204 (M^+, 15), 147 (M^+ – *t*-Bu, 100).

Ethyl (*E*)-Cinnamate (3b)[9a]

Yield: 49.3 mg (70%); colorless oil.

IR (film): 1713, 1638, 1311, 1177 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 16.0 Hz, 1 H), 7.54–7.51 (m, 2 H), 7.39–7.36 (m, 3 H), 6.46 (d, *J* = 16.0 Hz, 1 H), 4.29 (q, *J* = 7.2 Hz, 2 H), 1.36 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 144.5, 134.3, 130.2, 128.8, 128.0, 118.1, 60.5, 14.3.

LRMS (EI, 70 eV): *m*/*z* (%) = 176 (M^+, 33), 131 ($M^+ – OC_2H_5$, 100).

Hexyl (*E*)-Cinnamate (3c)

Yield: 75.1 mg (81%); colorless oil.

IR (film): 1714, 1638, 1310, 1170 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 16.0 Hz, 1 H), 7.54–7.52 (m, 2 H), 7.39–7.37 (m, 3 H), 6.47 (d, *J* = 16.0 Hz, 1 H), 4.22 (t, *J* = 7.2 Hz, 2 H), 1.74–1.67 (m, 2 H), 1.42–1.31 (m, 6 H), 0.92–0.89 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 144.5, 134.3, 130.2, 128.8, 128.0, 118.1, 64.7, 31.4, 28.6, 25.6, 22.5, 14.0.

LRMS (EI, 70 eV): *m*/*z* (%) = 232 (M^+, 3), 131 ($M^+ – OC_6H_{13}$, 25), 117 (100).

(*E*)-Cinnamamide (3d)[2b]

Yield: 38.6 mg (66%); pale yellow solid; mp 132–133 °C.

IR (KBr): 3375, 3173, 1662, 1608, 1399 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 15.6 Hz, 1 H), 7.54–7.51 (m, 2 H), 7.39–7.38 (m, 3 H), 6.50 (d, *J* = 15.6 Hz, 1 H), 5.85 (br, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 142.5, 134.4, 130.0, 128.8, 127.9, 119.3.

LRMS (EI, 70 eV): *m*/*z* (%) = 147 (M^+, 46), 146 (M^+ – H, 100), 131 ($M^+ – NH_2$, 48).

(*E*)-1-(3-Phenoxyprop-1-enyl)benzene (3e)[9b]

Yield: 30.2 mg (36%); white solid; mp 61–62 °C.

IR (KBr): 3436, 1593, 1495, 1238 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.6 Hz, 2 H), 7.34–7.21 (m, 5 H), 6.97 (d, *J* = 8.4 Hz, 3 H), 6.74 (d, *J* = 16.0 Hz, 1 H), 6.45–6.40 (m, 1 H), 4.69 (d, *J* = 5.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 136.4, 132.9, 129.5, 128.5, 127.8, 126.5, 124.4, 120.8, 114.7, 68.4.

LRMS (EI, 70 eV): *m*/*z* (%) = 210 (M^+, 5), 117 ($M^+ – OC_6H_5$, 100).

(*E*)-1,2-Diphenylethene (3f)[9a]

Yield: 44.5 mg (62%); white solid; mp 122–123 °C.

IR (KBr): 3445, 1384, 765, 693 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 7.6 Hz, 4 H), 7.37 (t, *J* = 7.6 Hz, 4 H), 7.27 (d, *J* = 7.2 Hz, 2 H), 7.10 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.2, 128.6, 128.5, 127.6, 126.5.

LRMS (EI, 70 eV): *m*/*z* (%) = 180 (M^+, 100).

***tert*-Butyl (*E*)-3-(3,4-Dimethylphenyl)acrylate (3g)**
Yield: 73.3 mg (79%); colorless oil.

IR (film): 1705, 1635, 1322, 1151 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 16.0 Hz, 1 H), 7.28 (s, 1 H), 7.26 (d, *J* = 7.6 Hz, 1 H), 7.13 (d, *J* = 7.6 Hz, 1 H), 6.35 (d, *J* = 16.0 Hz, 1 H), 2.26 (s, 6 H), 1.53 (m, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 143.7, 139.0, 137.0, 132.2, 130.0, 129.1, 125.5, 118.7, 80.2, 28.1, 19.8, 19.7.

LRMS (EI, 70 eV): *m*/*z* (%) = 232 (M^+, 19), 176 (100).

***tert*-Butyl (*E*)-3-(2,3-Dimethylphenyl)acrylate (3h)**
Yield: 64.1 mg (69%); colorless oil.

IR (film): 1710, 1632, 1317, 1152 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 15.6 Hz, 1 H), 7.31 (d, *J* = 7.6 Hz, 1 H), 7.09 (d, *J* = 7.6 Hz, 1 H), 7.03 (t, *J* = 7.6 Hz, 1 H), 6.19 (d, *J* = 15.6 Hz, 1 H), 2.23 (s, 3 H), 2.22 (s, 3 H), 1.46 (m, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 142.2, 137.2, 135.9, 133.8, 131.2, 125.6, 124.3, 121.4, 80.4, 28.1, 20.6, 15.3.

LRMS (EI, 70 eV): *m*/*z* (%) = 232 (M^+, 23), 176 (100).

***tert*-Butyl (*E*)-3-(3-Fluoro-4-methylphenyl)acrylate (3i)**
Yield: 71.8 mg (76%); colorless oil.

IR (film): 1708, 1639, 1324, 1150 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 16.0 Hz, 1 H), 7.35–7.31 (m, 2 H), 7.02 (t, *J* = 8.8 Hz, 1 H), 6.30 (d, *J* = 16.0 Hz, 1 H), 2.28 (s, 3 H), 1.53 (m, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 163.5 (d, *J* = 247.9 Hz), 142.5, 131.1 (d, *J* = 5.6 Hz), 130.5 (d, *J* = 3.6 Hz), 127.2 (d, *J* = 8.6 Hz), 125.5 (d, *J* = 17.9 Hz), 119.5 (d, *J* = 2.2 Hz), 115.6 (d, *J* = 22.9 Hz), 80.4, 28.1, 14.5 (d, *J* = 3.5 Hz).

LRMS (EI, 70 eV): *m*/*z* (%) = 236 (M^+, 14), 180 (M^+ – *t*-Bu, 100).

***tert*-Butyl (*E*)-3-[4-(Dimethylamino)phenyl]acrylate(3j)**[2b]
Yield: 78.1 mg (79%); pale yellow solid; mp 80–82 °C.

IR (KBr): 1697, 1600, 1530, 1141 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 16.0 Hz, 1 H), 7.41 (d, *J* = 8.8 Hz, 2 H), 6.65 (d, *J* = 8.8 Hz, 2 H), 6.18 (d, *J* = 16.0 Hz, 1 H), 2.99 (s, 6 H), 1.53 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 151.4, 144.0, 129.5, 122.2, 114.3, 111.6, 79.7, 40.1, 28.2.

LRMS (EI, 70 eV): *m*/*z* (%) = 247 (M^+, 35), 191 (M^+ – *t*-Bu, 100).

***tert*-Butyl (*E*)-3-(4-Propoxyphenyl)acrylate (3k)**
Yield: 87.8 mg (84%); pale yellow solid; mp 62–64 °C.

IR (KBr): 1701, 1604, 1250, 1151 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 16.0 Hz, 1 H), 7.46 (d, *J* = 8.8 Hz, 2 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 6.26 (d, *J* = 16.0 Hz, 1 H), 3.96–3.91 (m, 2 H), 1.85–1.77 (m, 2 H), 1.53 (s, 9 H), 1.07–1.02 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 160.6, 143.3, 129.5, 127.6, 117.3, 114.6, 80.1, 69.5, 28.2, 22.4, 10.5.

LRMS (EI, 70 eV): *m*/*z* (%) = 262 (M^+, 24), 164 (100).

***tert*-Butyl (*E*)-3-(4-Formylphenyl)acrylate (3l)**
Yield: 60.3 mg (65%); pale yellow solid; mp 100–102 °C.

IR (KBr): 2717, 1703, 1638, 1151 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.03 (s, 1 H), 7.90 (d, *J* = 8.4 Hz, 2 H), 7.67 (d, *J* = 8.4 Hz, 2 H), 7.63 (d, *J* = 16.0 Hz, 1 H), 6.51 (d, *J* = 16.0 Hz, 1 H), 1.55 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.5, 165.7, 141.8, 140.4, 136.9, 130.1, 128.3, 123.4, 81.0, 28.1.

LRMS (EI, 70 eV): *m*/*z* (%) = 232 (M^+, 8), 176 (100).

***tert*-Butyl (*E*)-3-(4-Carbamoylphenyl)acrylate (3m)**
Yield: 69.2 mg (70%); pale yellow solid; mp 196–198 °C.

IR (KBr): 1679, 1621, 1387, 1157 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.4 Hz, 2 H), 7.61–7.54 (m, 3 H), 6.46 (d, *J* = 16.0 Hz, 1 H), 6.23 (br, 2 H), 1.54 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 166.8, 142.0, 138.1, 128.6, 128.1, 127.9, 122.3, 80.9, 28.1.

LRMS (EI, 70 eV): *m*/*z* (%) = 247 (M^+, 8), 175 (100).

***tert*-Butyl (*E*)-3-(3-Chlorophenyl)acrylate (3n)**
Yield: 55.3 mg (58%); colorless oil.

IR (film): 1709, 1639, 1319, 1152 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 16.0 Hz, 1 H), 7.83 (s, 1 H), 7.38–7.27 (m, 3 H), 6.39 (d, *J* = 16.0 Hz, 1 H), 1.53 (m, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 141.9, 136.5, 134.8, 130.1, 129.9, 127.7, 126.2, 121.6, 80.8, 28.2.

LRMS (EI, 70 eV): *m*/*z* (%) = 238 (M^+, 9), 240 (M^+ + 2, 3), 182 (M^+ – *t*-Bu, 100).

***tert*-Butyl (*E*)-3-(Naphthalen-2-yl)acrylate (3o)**
Yield: 63.2 mg (62%); pale yellow solid; mp 61–63 °C.

IR (KBr): 1706, 1636, 1366, 1145 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 19.2 Hz, 1 H), 7.74–7.68 (m, 3 H), 7.64 (s, 1 H), 7.57–7.54 (m, 1 H), 7.42–7.15 (m, 2 H), 6.42 (d, *J* = 16.0 Hz, 1 H), 1.47 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 143.7, 134.1, 133.3, 132.1, 129.7, 128.6, 128.5, 127.8, 127.1, 126.7, 123.6, 120.3, 80.6, 28.3.

LRMS (EI, 70 eV): *m*/*z* (%) = 254 (M^+, 23), 182 (100).

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