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An efficient palladium(II) catalyst for oxidative Heck-type reaction under base-free conditions

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ABSTRACT

An efficient catalytic system for the palladium-catalyzed oxidative Heck reaction between arylboronic acids and various alkenes has been developed. Using the bis(aminoalkoxy)palladium complex of *N*,*N*-dimethylethanolamine as a catalyst, a series of substituted alkenes were obtained in moderate to excellent yields under mild reaction conditions. This protocol could be tolerated to arylboronic acids containing electron-donating or withdrawing groups and a wide range of olefins, such as acrylate, allyl esters, allyl ethers and alkenylphosphonate. A plausible reaction mechanism of the oxidative Heck reaction was proposed.

1. Introduction

Substituted alkenes are ubiquitous structural motifs in natural products, pharmaceutical intermediates and organic materials.[1] One of the useful method for preparation of the substituted alkenes is the palladium(II)-catalyzed oxidative Heck reaction. During the past decade, this type of reaction has received much attention in synthetic chemistry for its ability to form carbon–carbon bonds with relatively mild reaction conditions and excellent chemoselectivity.[2] Especially, arylboronic acids as nucleophilic organometallic reagents are popularly used in organic synthesis because of their commercial availability, stability, low toxicity and easy removal of boron-derived byproducts.[3] Since the oxidative Heck reaction of arylboronic acids was discovered by Heck in 1975,[4] a considerable number of catalytic systems have been developed by Jung[5] and Larhed[6] et al. using $Pd(OAc)_2$ in the presence of oxidant, such as metal salt,[6a,7] quinone[6f,g] or oxygen.[5,6b–e] At the same time, a lot of bidentate nitrogenous[5b,6b,c,d,g] and phosphine ligands[6e,f] et al. were employed for optimizing the reaction conditions. Up to now, only a few premade palladium(II)-ligand complexes were used for the oxidative Heck reaction under base-free conditions,[8,9] for example, dimeric tridentate NHC–amidate–alkoxide palladium(II) complexes were successfully applied in the asymmetric oxidative Heck reactions.[9] Herein we will describe a base-free oxidative Heck-type reaction catalyzed by the palladium complex of *N*,*N*-dimethylethanolamine (Cat.I, Fig. 1), the catalytic activity of which was investigated in Sonogashira reaction in our previous report.[10] Furthermore, a possible reaction mechanism will be also proposed.

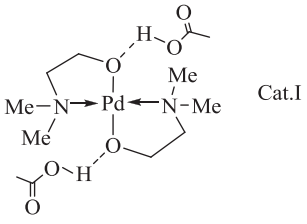

Fig. 1. The palladium complex of *N*,*N*-dimethylethanolamine (Cat.I).

2. Results and discussion

To begin our research, *n*-butyl acrylate **1a** and phenylboronic acid **2a** were chosen as model substrates. The feasibility of this reaction was tested in the presence of Cat.I under various reaction conditions. Among several oxidants screened benzoquinone (BQ) was found to be the best one for the oxidative Heck reaction (Table 1, entries 1–6). The polarity of the solvents greatly influenced the conversion of the reaction. The polar solvent DMF was the best choice for this reaction, and gave an excellent yield (93%, Table 1, entry 6). Less polar solvents, such as toluene could impede this process and lead to the formation of a trace amount of product (Table 1, entry 7). Interestingly, THF and mixed solvent DMSO/CH_3NO_2, respectively, gave comparative yields with DMF (Table 1,

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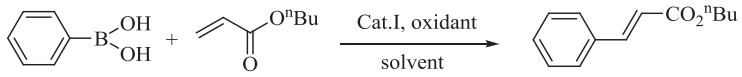
Table 1
Screening of reaction conditions for oxidative Heck reaction of *n*-butyl acrylate **1a** and phenylboronic acid **2a**[a]



2a **1a** **3a**

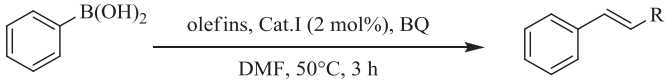
Entry	Oxidant	Solvent	*T* (°C)	Yield[b] (%)
1	O_2	DMF	50	11
2	Ag_2O	DMF	50	10
3	$Cu(OAc)_2$	DMF	50	5
4	AgOAc	DMF	50	45
5	$K_2S_2O_8$	DMF	50	76
6	BQ	DMF	50	93
7	BQ	Toluene	50	Trace
8	BQ	THF	50	84
9	BQ	Dioxane	50	48
10	BQ	CH_3NO_2	50	52
11	BQ	DMSO	50	85
12	BQ	DMSO/CH_3NO_2 (1:1)	50	91
13	BQ	DMF	80	95
14	BQ	DMF	30	87
15[c]	BQ	DMF	50	95
16[d]	BQ	DMF	50	51
17[e]	BQ	DMF	50	93

[a] Reaction conditions: *n*-butyl acrylate (0.5 mmol), phenylboronic acid (1.0 mmol), alkoxopalladium complex (2 mol %), oxidant (2 equiv), under N_2 in 1.5 mL solvent, 3 h.
[b] Isolated yield.
[c] 12 h.
[d] $Pd(OAc)_2$ (2 mol %) as a catalyst, 10 mol % *N*,*N*-dimethylethanolamine as a ligand.
[e] Under air.

entries 8 and 12). Increasing the reaction temperature to 80 °C or prolonging the reaction time to 12 h, there was little yield improvement (Table 1, entries 13 and 15). A significant drop of yield (87%) was observed by reducing the reaction temperature to 30 °C (Table 1, entry 14). To determine whether the precomposed complex was necessary, a large excess *N*,*N*-dimethylethanolamine was added as a ligand to the reaction catalyzed by $Pd(OAc)_2$ under the same conditions (Table 1, entry 16), however, the yield rapidly reduced to 51%. This result indicated that the premade complex has a higher catalytic activity than a corresponding premixed palladium–ligand system. Surprisingly, the reaction could proceed smoothly under air atmosphere to give the same yield comparing with that under nitrogen atmosphere (Table 1, entry 17).

Under the optimized conditions, the scope of the oxidative Heck reaction between phenylboronic acid and alkenes was examined. Various alkenes could be converted to (*E*)-isomers of phenyl substituted alkenes with a high regioselectivity. Electron-deficient acrylates, except for **1f**, which gave a low yield of 67% due to the steric effect (Table 2, entry 6), reacted smoothly to afford oxidative Heck products in high yields (Table 2, entries 1–5). At the same

Table 2
Cross-coupling reactions of various alkenes **1** with phenylboronic acid **2a** under the optimized conditions[a]



2a **3**

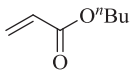
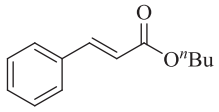
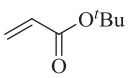
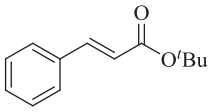
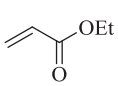
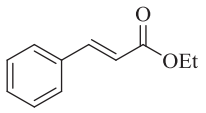
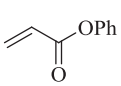
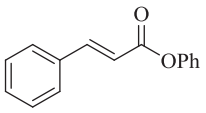
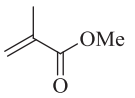
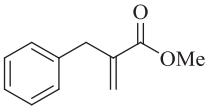
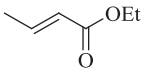
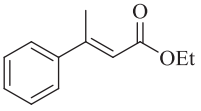
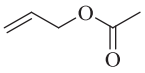
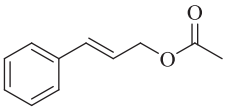
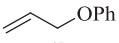
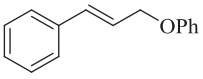
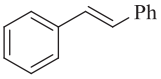
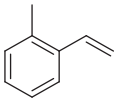
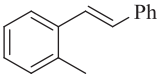
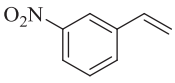
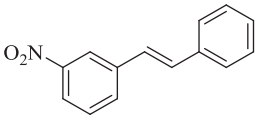
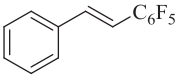
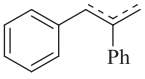
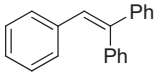
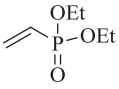
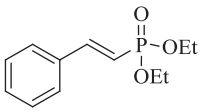
Entry	Olefin	Product	Yield[b] (%)
1	 **1a**	 **3aa**	93
2	 **1b**	 **3ba**	86
3	 **1c**	 **3ca**	97
4	 **1d**	 **3da**	95

Table 2 (*continued*)

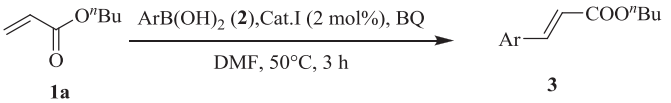
Entry	Olefin	Product	Yield[b] (%)
5	 **1e**	 **3ea**	82
6	 **1f**	 **3fa**	67
7	 **1g**	 **3ga**	72
8	 **1h**	 **3ha**	53
9	 **1i**	 **3ia**	87
10	 **1j**	 **3ja**	66
11	 **1k**	 **3ka**	83
12	 **1l**	 **3la**	93
13	 **1m**	 **3ma**	59(7:5)[c]
14	 **1n**	 **3na**	36
15	 **1o**	 **3oa**	98

[a] Reaction conditions: olefins (0.5 mmol), phenylboronic acid (1.0 mmol), alkoxopalladium complex (2 mol %), BQ (2 equiv), under air in 1.5 mL DMF, 3 h.
[b] Isolated yield.
[c] The ratio of Heck and migrated products was 7:5 by ^{1}H NMR analysis.

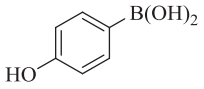
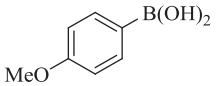
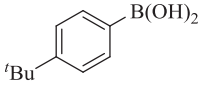
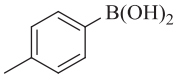
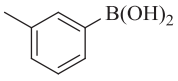
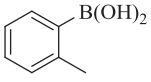
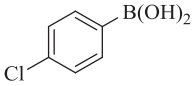
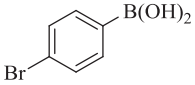
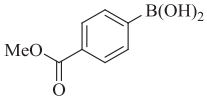
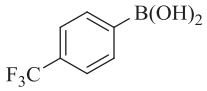
time, alkenes with stronger electron-withdrawing groups gave higher yields. Satisfyingly, the reaction of less active allyl ethers (**1g** and **1h**) with phenylboronic acid **2a** could also proceed smoothly under the same conditions to give the desired products in moderate yields (Table 2, entries 7 and 8). Furthermore, the oxidative procedure was also successfully extended to styrene derivatives (Table 2, entries 9–13). The product **3ja** was only obtained in a 66% yield because of the steric effect (Table 2, entry 10). Alkene **1l** containing pentafluorine group could give a yield of 93% (Table 2, entry 12). In addition, two isomers were obtained in the ratio of 7:5 from the reaction of the styrene derivative **1m** with phenylboronic acid **2a** owing to the formation of allyl palladium complexes (Table 2, entry 13). It was worth noting that diethylvinylphosphonate **1o** was tolerated and gave an excellent yield (Table 2, entry 15).

In order to further explore the universality of this catalytic system, a series of arylboronic acids were investigated under the given conditions. As shown in Table 3, this protocol was proven to be efficient for coupling *n*-butyl acrylate **1a** with various arylboronic acids bearing electron-donating or withdrawing groups and the corresponding coupling products were obtained in moderate to excellent yields. The reactions **1a** with arylboronic acids containing electron-withdrawing groups (Table 3, entries 7, 8 and 10) gave good yields, except of that with **2j** (Table 3, entry 9). Gratifyingly, halide groups (Cl and Br) were also tolerated and afforded the oxidative Heck-type compound in 87% and 93% yields without any Suzuki coupling and classical Heck coupling compounds. However, 2-methylphenylboronic acid **2g** only gave 23% yield, indicating that the steric hindrance on the arylboronic acid has a great effect on the reaction (Table 3, entry 6).

Table 3
Cross-coupling reactions of *n*-butyl acrylate **1a** with various arylboronic acids **2** under the optimized conditions[a]

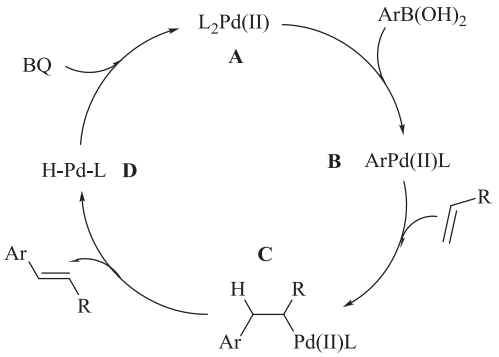


1a **3**

Entry	ArB(OH)$_2$	Yield[b] (%)
1	 **2b**	75
2	 **2c**	43
3	 **2d**	87
4	 **2e**	63
5	 **2f**	46
6	 **2g**	23
7	 **2h**	87
8	 **2i**	93
9	 **2j**	46
10	 **2k**	81

[a] Reaction conditions: olefins (0.5 mmol), arylboronic acid (1.0 mmol), alkoxopalladium complex (2 mol %), BQ (2 equiv), under air in 1.5 mL DMF, 3 h.
[b] Isolated yield.

Based on previous reports, a possible reaction mechanism for the oxidative Heck coupling reaction was proposed, as shown in Scheme 1. Initially, the palladium(II) complex **A** could react with phenylboronic acid to form the Pd^{II} intermediate **B**. Then the intermediate **B** is expected to be able to undergo the oxidative addition by the alkene to give the intermediate **C**. The process of β-H elimination gives the desired Heck cross-coupling product. Finally the hydride palladium complex **D** generated at the same time is oxidized to palladium(II) by the oxidant BQ to get back into the catalytic cycle.



Scheme 1. The proposed mechanism for oxidative Heck reaction.

3. Conclusions

In summary, an efficient catalyst was developed for the oxidative Heck reaction between arylboronic acids and various alkenes under base-free conditions in high regioselectivity. It was found that yields of alkenes and boronic acids containing electron-withdrawing groups were generally higher than those with electron-donating groups. The catalytic system could be also applied for diethylvinylphosphonate and give excellent yield of target product. A plausible reaction mechanism of the oxidative Heck reaction was proposed.

4. Experimental

4.1. General information

Unless otherwise noted, all reactions were carried out under air atmosphere and reagents were commercially available and used without further purification. Organic solvents have been purified prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as the solvent and TMS as an internal standard. Melting points were measured on a WC-1 microscopic apparatus and were uncorrected. All of the products were known and the purified compounds were identified by comparison of melting points, ^{1}H NMR, ^{13}C NMR spectra with the literature.

4.2. General procedure for palladium-catalyzed oxidative Heck reaction of alkene and arylboronic acid (Tables 2 and 3)

Under air atmosphere, a mixture of olefin (0.5 mmol), arylboronic acid (1.0 mmol), alkoxopalladium complex (4 mg, 2 mol %), oxidant (1.0 mmol) and DMF (1.5 mL) was stirred at 50 °C for 3 h. The reaction mixture was cooled to room temperature, and then directly purified by preparative thin layer chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to give desired compounds.

*4.2.1. (E)-Butyl 3-phenylpropenoate (**3aa**).*[8a] Yellow oil (93%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J=15.7 Hz, 1H), 7.53–7.51 (m, 2H), 7.38–7.25 (m, 3H), 6.44 (d, J=16.1 Hz, 1H), 4.20 (t, J=6.8 Hz, 2H), 1.69–1.62 (m, 2H), 1.46–1.39 (m, 2H), 0.96 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.13, 144.56, 134.49, 130.22, 128.89, 128.06, 118.31, 64.45, 30.79, 19.22, 13.78.

*4.2.2. (E)-tert-Butyl 3-phenylpropenoate (**3ba**).*[5b] Yellow oil (86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J=15.8 Hz, 1H), 7.51–7.50 (m, 2H), 7.37–7.35 (m, 3H), 6.37 (d, J=15.8 Hz, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.33, 143.54, 134.95, 129.95, 128.82, 127.96, 120.21, 80.50, 28.21.

*4.2.3. Ethyl (E)-3-phenyl-2-propenoate (**3ca**).*[11] Yellow oil (97%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J=16.0 Hz, 1H), 7.54–7.51 (m, 2H), 7.39–7.37 (m, 3H), 6.44 (d, J=16.0 Hz, 1H), 4.27 (q, J=7.1 Hz, 2H), 1.34 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.03, 144.60, 134.51, 130.23, 128.90, 128.07, 118.33, 60.52, 14.34.

*4.2.4. Phenyl (E)-3-phenyl-2-propenoate (**3da**).*[12] Yellow solid (95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J=16.1 Hz, 1H), 7.60–7.58 (m, 2H), 7.43–7.39 (m, 5H), 7.27–7.23 (m, 1H), 7.18–7.16 (m, 2H), 6.64 (d, J=16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.38, 150.80, 146.55, 134.18, 130.68, 129.43, 128.98, 128.29, 125.77, 121.62, 117.32.

*4.2.5. Methyl 2-benzylacrylate (**3ea**).*[25] Yellow oil (82%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.38 (m, 2H), 7.33–7.24 (m, 3H), 6.65 (d, J=15.8 Hz, 1H), 6.32–6.24 (m, 1H), 4.73–3.72 (m, 2H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.05, 65.12, 123.23, 126.66, 128.13, 128.62, 134.26, 136.26, 170.88.

*4.2.6. Ethyl (2E)-3-phenylbut-2-enoate (**3fa**).*[13] Yellow oil (67%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.46 (m, 2H), 7.40–7.25 (m, 3H), 6.14 (q, J=1.3 Hz, 1H), 4.22 (q, J=7.2 Hz, 2H), 2.58 (d, J=1.3 Hz, 3H), 1.32 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.92, 155.56, 142.24, 129.00, 128.51, 126.32, 117.18, 59.88, 17.97, 14.37.

*4.2.7. (E)-Cinnamyl acetate (**3ga**).*[8a] Yellow oil (72%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.38 (m, 2H), 7.34–7.30 (m, 2H), 7.27–7.25 (m, 1H), 6.65 (d, J=16.1 Hz, 1H), 6.32–6.26 (m, 1H), 4.73–4.71 (m, 2H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.88, 136.20, 134.23, 128.62, 128.09, 126.62, 123.17, 65.10, 21.03.

*4.2.8. (3-Phenylprop-2-enyl)oxy-benzene (**3ha**).*[14] White solid (53%); mp 66–67 °C (lit. 62–63 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.39 (m, 2H), 7.33–7.27 (m, 5H), 6.97–6.93 (m, 3H), 6.73 (d, J=15.7 Hz, 1H), 6.45–6.38 (m, 1H), 4.70–4.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.59, 136.43, 132.92, 129.44, 128.54, 127.84, 126.53, 124.50, 120.86, 114.76, 68.53.

*4.2.9. (E)-1,2-Diphenylethene (**3ia**).*[8a] White solid (87%); mp 123–124 °C (lit. 123–124 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J=8.2 Hz, 4H), 7.37–7.34 (m, 4H), 7.27–7.23 (m, 2H), 7.11 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.29, 128.64, 127.58, 126.47.

*4.2.10. (E)-2-Methylstilbene (**3ja**).*[8a] White solid (66%); mp 30 °C (lit. 31–32 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J=7.1 Hz, 1H), 7.52 (d, J=7.8 Hz, 2H), 7.38–7.31 (m, 3H), 7.28–7.17 (m, 4H), 6.99 (d, J=16.4 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.61, 136.33, 135.73, 130.32, 129.94, 128.61, 127.52, 127.47, 126.48, 126.13, 125.29, 19.84.

*4.2.11. (E)-3-Nitrostilbene (**3ka**).*[8a] Yellow solid (83%); mp 108–109 °C (lit. 106–107 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 8.08–8.06 (m, 1H), 7.77 (d, J=7.8 Hz, 1H), 7.53–7.48 (m, 3H), 7.39–7.35 (m, 2H), 7.31–7.28 (m, 1H), 7.19 (d, J=15.2 Hz, 1H), 7.11 (d, J=16.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.72, 139.14, 136.24, 132.21, 131.74, 129.52, 128.82, 128.50, 126.80, 126.07, 121.99, 120.86.

*4.2.12. (E)-1,2,3,4,5-Pentafluoro-6-styrylbenzene (**3la**).*[22] White solid (93%); mp 136–137 °C (lit. 134 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J=6.9 Hz, 2H), 7.45–7.30 (m, 4H), 6.97 (t, J=17.1 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ −142.74 (dd, J=21.4, 7.5 Hz), −156.53 (t, J=20.8 Hz, 1F), −162.95 (td, J=21.1, 7.5 Hz).

*4.2.13. (E)-1,2-Diphenylprop-1-ene and 2,3-diphenyl-1-propene (**3ma**).*[15,16] Mixture: white solid (59%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.49 (m, 2H), 7.42–7.39 (m, 2H), 7.36–7.32 (m, 6H), 7.28–7.27 (m, 1H), 7.24–7.15 (m, 7H), 6.82–6.80 (m, 1H), 5.47 (1H), 5.00–4.98 (m, 1H), 3.81 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.74, 148.67, 134.90, 134.68, 130.17, 128.78, 127.64, 114.83, 112.92, 62.77, 61.82, 16.36, 16.30.

*4.2.14. Triphenylethylene (**3na**).*[17] Yellow oil (36%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.27 (m, 8H), 7.22–7.19 (m, 2H), 7.12–7.09 (m, 3H), 7.03–7.01 (m, 2H), 6.98–6.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.31, 142.47, 140.24, 137.26, 130.27, 129.42, 128.50, 128.08, 128.04, 127.83, 127.48, 127.38, 127.28, 126.62.

*4.2.15. Diethyl (E)-2-phenyl-ethenylphosphonate (**3oa**).*[18] Yellow oil (98%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.46 (m, 3H), 7.39–7.38 (m, 3H), 6.26 (t, J=17.6 Hz, 1H), 4.17–4.09 (m, 4H), 1.38–1.34 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.74, 148.67, 134.90, 134.68, 130.17, 128.78, 127.64, 114.83, 112.92, 61.82, 62.77, 16.36, 16.30.

4.2.16. (E)-Butyl 3-(4-hydroxyphenyl)acrylate.[3b] Pale yellow solid (75%); mp 76–78 °C (lit. 74–76 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J=15.7 Hz, 1H), 7.44 (d, J=8.3 Hz, 2H), 6.88 (d, J=8.3 Hz, 2H), 6.32 (d, J=16.1 Hz, 1H), 4.23 (t, J=6.6 Hz, 2H), 1.75–1.67 (m, 2H), 1.51–1.41 (m, 2H), 0.98 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.40, 158.41, 145.04, 130.39, 127.45, 116.31, 115.83, 64.94, 31.17, 19.60, 14.14.

4.2.17. (E)-Butyl 3-(4-methoxyphenyl)acrylate.[3b] Yellow oil (43%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J=16.0 Hz, 1H), 7.50 (d, J=9.0 Hz, 2H), 6.92 (d, J=8.6 Hz, 2H), 6.63 (d, J=16.0 Hz, 1H), 4.22 (t,

J=6.9 Hz, 2H), 3.86 (s, 3H), 1.75–1.67 (m, 2H), 1.51–1.40 (m, 2H), 0.98 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.45, 161.34, 144.21, 129.69, 127.25, 115.81, 114.32, 64.27, 55.38, 30.84, 19.23, 13.77.

4.2.18. (E)-Butyl 3-(4-tert-butylphenyl)acrylate.[21] Yellow oil (87%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J*=15.8 Hz, 1H), 7.47 (d, *J*=8.3 Hz, 2H), 7.40 (d, *J*=8.5 Hz, 2H), 6.41 (d, *J*=16.1 Hz, 1H), 4.20 (t, *J*=6.7 Hz, 2H), 1.72–1.67 (m, 2H), 1.50–1.41 (m, 2H), 1.35 (s, 9H), 0.99 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.34, 153.76, 144.47, 131.73, 127.91, 125.86, 117.35, 64.38, 34.89, 31.17, 30.81, 19.23, 13.78.

4.2.19. (E)-Butyl 3-(4-methylphenyl)acrylate.[19] Yellow oil (63%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J*=16.0 Hz, 1H), 7.42 (d, *J*=7.8 Hz, 2H), 7.18 (d, *J*=7.8 Hz, 2H), 6.39 (d, *J*=16.0 Hz, 1H), 4.20 (t, *J*=6.7 Hz, 2H), 2.36 (s, 3H), 1.72–1.64 (m, 2H), 1.47–1.40 (m, 2H), 0.96 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.32, 144.56, 140.61, 131.77, 129.61, 128.05, 117.22, 64.35, 30.82, 21.46, 19.22, 13.77.

4.2.20. (E)-Butyl 3-(3-methylphenyl)acrylate.[20] Yellow oil (46%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J*=16.1 Hz, 1H), 7.34–7.25 (m, 3H), 7.19 (d, *J*=7.3 Hz, 1H), 6.43 (d, *J*=16.1 Hz, 1H), 4.21 (t, *J*=6.7 Hz, 2H), 2.37 (s, 3H), 1.73–1.65 (m, 2H), 1.47–1.41 (m, 2H), 0.97 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.22, 144.76, 138.55, 134.47, 131.07, 128.78, 118.10, 64.42, 30.82, 21.34, 19.24, 13.78.

4.2.21. (E)-Butyl 3-(2-methylphenyl)acrylate.[23] Yellow oil (23%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J*=15.8 Hz, 1H), 7.55 (d, *J*=7.3 Hz, 1H), 7.30–7.25 (m, 1H), 7.23–7.18 (m, 1H), 7.11–7.12 (m, 1H), 6.36 (d, *J*=15.8 Hz, 1H), 4.22 (t, *J*=6.7 Hz, 2H), 2.44 (s, 3H), 1.74–1.64 (m, 2H), 1.49–1.36 (m, 2H), 0.97 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.21, 142.27, 137.64, 133.45, 130.78, 129.96, 126.40, 126.33, 119.31, 64.44, 30.79, 19.81, 19.23, 13.78.

4.2.22. (E)-Butyl 3-(4-chlorophenyl)acrylate.[19] Pale yellow solid (87%); mp 35–36 °C (lit. 30–32 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J*=16.0 Hz, 1H), 7.45 (d, *J*=8.6 Hz, 2H), 7.35 (d, *J*=8.6 Hz, 2H), 6.41 (d, *J*=16.1 Hz, 1H), 4.21 (t, *J*=6.7 Hz, 2H), 1.73–1.65 (m, 2H), 1.49–1.39 (m, 2H), 0.96 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.85, 143.10, 136.13, 133.00, 129.22, 129.18, 118.93, 64.57, 30.78, 19.21, 13.76.

4.2.23. (E)-Butyl 3-(4-bromophenyl)acrylate.[21] Pale yellow solid (93%); mp 37 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J*=16.1 Hz, 1H), 7.52 (d, *J*=8.3 Hz, 2H), 7.39 (d, *J*=8.3 Hz, 2H), 6.43 (d, *J*=16.1 Hz, 1H), 4.21 (t, *J*=6.9 Hz, 2H), 1.73–1.65 (m, 2H), 1.49–1.39 (m, 2H), 0.96 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.22, 143.54, 133.81, 132.52, 129.81, 124.84, 119.43, 64.96, 31.15, 19.59, 14.13.

4.2.24. (E)-Methyl 4-(3-butoxy-3-oxoprop-1-en-1-yl)benzoate.[24] - White solid (46%); mp 55 °C (lit. 55–56 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J*=7.8 Hz, 2H), 7.69 (d, *J*=16.2 Hz, 1H), 7.59 (d, *J*=8.3 Hz, 2H), 6.52 (d, *J*=6.9 Hz, 1H), 4.22 (t, *J*=8 Hz, 2H), 3.93 (s, 3H), 1.74–1.66 (m, 2H), 1.48–1.41 (m, 2H), 0.97 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.66, 166.48, 143.14, 138.69, 131.31, 130.10, 127.91, 120.69, 64.69, 52.32, 30.73, 19.20, 13.77.

4.2.25. (E)-Butyl 3-(4-triflurophenyl)acrylate.[3b] Yellow oil (81%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.60 (m, 5H), 6.51 (d, *J*=16.0 Hz, 1H), 4.23 (t, *J*=6.7 Hz, 2H), 1.74–1.66 (m, 2H), 1.50–1.40 (m, 2H), 0.97 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.51, 142.67, 137.89, 132.22, 131.90, 131.57, 131.25, 128.17, 127.91, 125.88, 125.84, 125.20, 122.50, 120.92, 64.73, 30.75, 1920, 13.72.

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References and notes

1. (a) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897; (b) Mochida, S.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2010**, *12*, 5776; (c) Paek, S.-M. *Molecules* **2012**, *17*, 3348; (d) Ledwon, P.; Kuznik, W.; Lapkowski, M.; Majchrzak, M. *New J. Chem.* **2012**, *36*, 2347; (e) Greger, H. *J. Nat. Prod.* **2012**, *75*, 2261; (f) Robles, O.; Serna-Saldívar, S. O.; Gutiérrez-Uribe, J. A.; Romo, D. *Org. Lett.* **2012**, *14*, 1394; (g) Vamshikrishna, K.; Srihari, P. *Tetrahedron* **2012**, *68*, 1540.
2. (a) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009; (b) Jia, C.-G.; Piao, D.-G.; Oyamada, J.; Lu, W.-J.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, *287*, 1992; (c) Dounay, A. B.; Overman, L. E. *Chem. Rev.* **2003**, *103*, 2945; (d) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442; (e) Karimi, B.; Behzadnia, H.; Elhamifar, D.; Akhavan, P. F.; Esfahani, F. K.; Zamani, A. *Synthesis* **2010**, 1399; (f) Bras, J. L.; Muzart, J. *Chem. Rev.* **2011**, *111*, 1170; (g) Su, Y.-L.; Jiao, N. *Curr. Org. Chem.* **2011**, *15*, 3362.
3. (a) Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2003**, *680*, 3; (b) Lindh, J.; Enquist, P.-A.; Pilotti, Å.; Nilsson, P.; Larhed, M. *J. Org. Chem.* **2007**, *72*, 7957.
4. Dieck, H. A.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 1083.
5. (a) Jung, Y. C.; Mishra, R. K.; Yoon, C. H.; Jung, K. W. *Org. Lett.* **2003**, *5*, 2231; (b) Yoo, K. S.; Yoon, C. H.; Jung, K. W. *J. Am. Chem. Soc.* **2006**, *128*, 16384; (c) Yoo, K. S.; Park, C. P.; Yoon, C. H.; Sakaguchi, S.; O'Neill, J.; Jung, K. W. *Org. Lett.* **2007**, *9*, 3933.
6. (a) Andappan, M. M. S.; Nilsson, P.; Larhed, M. *Mol. Div.* **2003**, *7*, 97; (b) Andappan, M. M. S.; Nilsson, P.; Schenck, H.; Larhed, M. *J. Org. Chem.* **2004**, *69*, 5212; (c) Andappan, M. M. S.; Nilsson, P.; Larhed, M. *Chem. Commun.* **2004**, 218; (d) Enquist, P.-A.; Lindh, J.; Nilsson, P.; Larhed, M. *Green Chem.* **2006**, *8*, 338; (e) Lindh, J.; Sävmarker, J.; Nilsson, P.; Sjöberg, P. J. R.; Larhed, M. *Chem.—Eur. J.* **2009**, *15*, 4630; (f) Odell, L. R.; Lindh, J.; Gustafsson, T.; Larhed, M. *Eur. J. Org. Chem.* **2010**, 2270; (g) Nordqvist, A.; Björkelid, C.; Andaloussi, M.; Jansson, A. M.; Mowbray, S. L.; Karlén, A.; Larhed, M. *J. Org. Chem.* **2011**, *76*, 8986.
7. (a) Liu, Y.; Li, D.; Park, C.-M. *Angew. Chem., Int. Ed.* **2011**, *50*, 7333; (b) Inamoto, K.; Kawasaki, J.; Hiroya, K.; Kondo, Y.; Doi, T. *Chem. Commun.* **2012**, 4332; (c) Zhang, Y.-X.; Li, Z.-J.; Liu, Z.-Q. *Org. Lett.* **2012**, *14*, 226.
8. (a) Leng, Y.-T.; Yang, F.; Wei, K.; Wu, Y.-J. *Tetrahedron* **2010**, *66*, 1244; (b) Likhar, P. R.; Roy, M.; Roy, S.; Subhas, M. S.; Kantam, M. L.; Sreedhar, B. *Adv. Synth. Catal.* **2008**, *350*, 1968; (c) Delcamp, J. H.; Brucks, A. P.; White, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 11270.
9. (a) Sakaguchi, S.; Yoo, K. S.; O'Neill, J.; Lee, J. H.; Stewart, T.; Jung, K. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 9326; (b) Yoo, K. S.; O'Neill, J.; Sakaguchi, S.; Giles, R.; Lee, J. H.; Jung, K. W. *J. Org. Chem.* **2010**, *75*, 95.
10. Mi, X.; Huang, M.-M.; Feng, Y.-J.; Wu, Y.-J. *Synlett* **2012**, 1257.
11. Aggarwal, V. K.; Fulton, J. R.; Sheldon, C. G.; Vicente, J. *J. Am. Chem. Soc.* **2003**, *125*, 6034.
12. Zhang, L.-L.; Zhang, G.-Y.; Zhang, M.-L.; Cheng, J. *J. Org. Chem.* **2010**, *75*, 7472.
13. Paraskar, A. S.; Sudalai, A. *Tetrahedron* **2006**, *62*, 4907.
14. Trivedi, R.; Tunge, J. A. *Org. Lett.* **2009**, *11*, 5650.
15. Wu, S.; Ma, H.-C.; Jia, X.-J.; Zhong, Y.-M.; Lei, Z.-Q. *Tetrahedron* **2011**, *67*, 250.
16. Shono, T.; Kurashige, R.; Mukaiyama, R.; Tsubouchi, A.; Takeda, T. *Chem.—Eur. J.* **2007**, *13*, 4074.
17. Nunes, C. M.; Steffens, D.; Monteiro, A. L. *Synlett* **2007**, 103.
18. Lai, C.-B.; Xi, C.-J.; Chen, W.-X.; Hua, R.-M. *Tetrahedron* **2006**, *62*, 6295.
19. Zhang, W.; Qi, H.-L.; Li, L.-S.; Wang, X.; Chen, J.; Peng, K.-S.; Wang, Z.-H. *Green Chem.* **2009**, *11*, 1194.
20. Xie, G.-L.; Chellan, P.; Mao, J.-C.; Chibale, K.; Smith, G. S. *Adv. Synth. Catal.* **2010**, *352*, 1641.
21. Zhou, X.-Y.; Luo, J.-Y.; Liu, J.; Peng, S.-M.; Deng, G.-J. *Org. Lett.* **2011**, *13*, 1432.
22. Zhang, X.-G.; Fan, S.-L.; He, C.-Y.; Wan, X.-L.; Min, Q.-Q.; Yang, J.; Jiang, Z.-X. *J. Am. Chem. Soc.* **2010**, *132*, 4506.
23. Shi, M.; Qian, H.-X. *Tetrahedron* **2005**, *61*, 4949.
24. Xiong, Z.-C.; Wang, N.-D.; Dai, M.-J.; Li, A.; Chen, J.-H.; Yang, Z. *Org. Lett.* **2004**, *6*, 3337.
25. Nājera, C.; Mancheño, B.; Yus, M. *Tetrahedron Lett.* **1989**, *30*, 3837.