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Tetrahedron

Tetrahedron 63 (2007) 6210–6215

Rh(I)-catalyzed three-component reaction of 2,3-allenoates, organoboronic acids, and aldehydes. An efficient synthesis of α,β-unsaturated δ-lactones

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Received 23 January 2007; revised 2 March 2007; accepted 2 March 2007
Available online 7 March 2007

Abstract—α,β-Unsaturated δ-lactones were efficiently prepared by an Rh(I)-catalyzed three-component reaction of 2,3-allenoates, organoboronic acids, and aldehydes. The reaction may proceed via a sequential transmetalation, carbometalation of 2,3-allenoates, insertion of aldehydes, and lactonization process.

1. Introduction

α,β-Unsaturated δ-lactone is an important structural unit existing in many biologically important natural products such as jaborosalactones R, S, T,[1] physalolactone C,[2] goniothalamin,[3] forstriecin,[4] etc. On the other hand, allenes have recently shown unique reactivity and stereoselectivity due to the two mutually perpendicular π-orbitals.[5,6] Nowadays, metal-catalyzed reactions of allenes have become one of the powerful tools for the synthesis of the cyclic products and have been applied to the total synthesis of natural products.[7,8]

The carbometalation of allenes usually affords π-allylic intermediate.[9] It's well known that organorhodium intermediates may react easily with carbon–oxygen double bond.[10] Thus, we imagined that the carborhodiation of allenoates would afford π-allylic rhodium intermediate, which may react readily with aldehydes to afford alcohols. Lactonization of this hydroxyl ester may afford α,β-unsaturated δ-lactones. This method would allow for a one-pot selective construction of δ-lactones via a tandem three-component reaction, which would improve the efficiency of their synthesis as compared to the traditional methods.[11–18] Malinakova et al. reported the palladium-catalyzed three-component coupling of arylboronic acids with allenes and aldehydes.[19] In this paper, we wish to report the Rh-catalyzed three-component cyclization.

2. Results and discussion

As a first try, under nitrogen atmosphere, the reaction of methyl buta-2,3-dienoate **1**, phenylboronic acid **2a**, and benzaldehyde **3a** in the presence of $RhCl(PPh_3)_3$, cesium carbonate, and water was conducted at 60 °C overnight in THF to afford a 1:2.1 mixture of δ-lactone **4a** and 5-hydroxy-2-enoate **5a**,[20] which could not be separated by chromatography on silica gel (entry 1, Table 1). When 2.5 mol % PPh_3 was added to the reaction mixture, product **4a** was obtained with 33% isolated yield and the formation of acyclic product **5a** was not observed (entry 2, Table 1). In order to study the effect of PPh_3, $[RhCl(COD)]_2$ was used as the catalyst precursor together with KF.[21] With the **1**:**2a**:**3a** ratio being 2:1:4, the yield of **4a** reached 59% (entry 7, Table 1). Other inorganic fluoride salts failed to afford better results (entries 8–10, Table 1). Increasing the amount of PPh_3 from 10 mol % to 20 mol %, the yield was only 26% (entry 11, Table 1). Thus, the best ratio of Rh/PPh_3 is ∼1:2 to keep the catalytic reaction going. The reaction in dioxane at 80 °C afforded the product **4a** in <5% yield (entry 12, Table 1). The combination of $RhCl(PPh_3)_3$ with KF yielded **4a** in only 18% yield (entry 6, Table 1). If the reaction was conducted in the absence of H_2O, the reaction is rather poor (entry 5, Table 1).

With the reaction conditions presented in entry 7 of Table 1, other boronic acids and aldehydes were tested with the typical results being summarized in Table 2.

In all the cases, the α,β-unsaturated δ-lactones were isolated in moderate yields (42–55%). Halogen substituent on the

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Keywords: Rhodium; Allene; Synthesis; α,β-Unsaturated δ-lactone.

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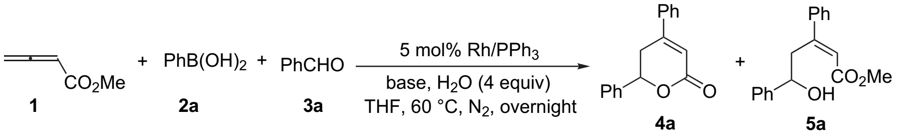
0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.03.021

Table 1. Optimization of the reaction conditions for Rh(I)-catalyzed three-component reaction of methyl 2,3-butadienoate, $PhB(OH)_2$, and PhCHO



Entry	Catalyst	PPh_3 (mol %)	**1**:**2a**:**3a** (molar ratio)	Base (equiv)	Yield of **4a**[d] (%)
1	$RhCl(PPh_3)_3$	—[a]	1:2:2	Cs_2CO_3 (0.5)	8[b]
2	$RhCl(PPh_3)_3$	2.5	1:2:2	Cs_2CO_3 (0.5)	33
3	$[RhCl(COD)]_2$	10	1:2:2	Cs_2CO_3 (2)	Trace
4	$[RhCl(COD)]_2$	10	1:2:2	KF (2)	31
5	$[RhCl(COD)]_2$	10	1:2:2	KF (2)	2[e,f]
6	$RhCl(PPh_3)_3$	—	2:1:4	KF (2)	18
7	$[RhCl(COD)]_2$	10	2:1:4	KF (2)	59
8	$[RhCl(COD)]_2$	10	2:1:4	LiF (2)	Trace
9	$[RhCl(COD)]_2$	10	2:1:4	NaF (2)	Trace
10	$[RhCl(COD)]_2$	10	2:1:4	CsF (2)	15
11	$[RhCl(COD)]_2$	20	2:1:4	KF (2)	26
12[c]	$[RhCl(COD)]_2$	10	2:1:4	KF (2)	<5

[a] Two equivalents of water were used.

[b] It was contaminated with 17% of **5a** (the ratio of **4a**:**5a** is 1:2.1).

[c] The reaction was conducted in dioxane at 80 °C.

[d] Isolated yield.

[e] The reaction was conducted in the absence of water.

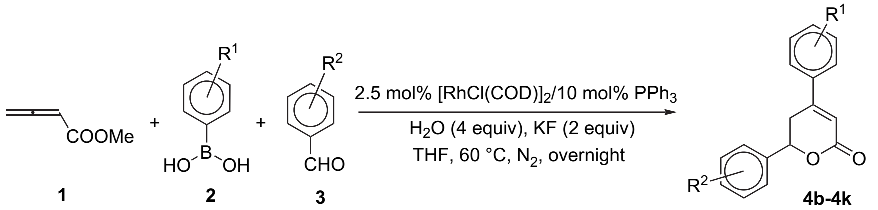
[f] It was contaminated with **5a** (20%).

aryl ring provides opportunity for the synthesis of new α,β-unsaturated δ-lactones via the related reactions of the C–X bond (entries 6–8). The structure of the lactone products was further established by the X-ray diffraction studies of **4c** (Fig. 1).[22] It should be noted that under the current reaction conditions the yields with aliphatic aldehydes are very low.

The chemical shifts of the non-aromatic protons H^a, H^b, H^c, and H^d of **4a**–**4k** are listed in Table 3. The olefinic proton H^a appears in the range of 6.37–6.48 in most cases as a singlet (**4a**, **4c**, **4e**, **4g**, **4h**, and **4k**). However, for compounds **4b**, **4d**, **4i**, and **4j**, it is a doublet while that of **4f** appears as a triplet due to the allylic coupling. The allylic proton (H^b and H^c) appears in the range of 2.83–3.23 mostly as multiplet (**4b**, **4d**, **4e**, **4f**, **4g**, **4h**, and **4j**). In compounds **4a**, **4c**, and **4k**, a doublet was observed due to the coupling from H^d. In **4i**, these two protons are not equal: they couple with each other, H^a, and/or H^d. The chemical shift of H^d is in the range of 5.45–5.93, which appears as triplet or doublet–doublet due to the coupling with H^b and H^c.

A plausible mechanism for the formation of **4** is illustrated in Scheme 1. Transmetalation of $ArB(OH)_2$ with the catalytically active rhodium hydroxide **I** (formed probably via

Table 2. The Rh-catalyzed reactions of methyl buta-2,3-dienoate, arylboronic acids, and aryl aldehydes[a]



Entry	Substrate **2**	Substrate **3**	Yield of **4**[c] (%)
	R^1	R^2	
1[d]	4-Me (**2b**)	H (**3a**)	50 (**4b**)
2[d]	3,5-Dimethyl (**2c**)	H (**3a**)	50 (**4c**)
3[b]	4-MeO (**2d**)	H (**3a**)	51 (**4d**)
4	3-MeO (**2e**)	H (**3a**)	45 (**4e**)
5	H (**2a**)	4-Me (**3f**)	55 (**4f**)
6[d]	H (**2a**)	4-Cl (**3g**)	49 (**4g**)
7	H (**2a**)	4-Br (**3h**)	50 (**4h**)
8[d]	H (**2a**)	2-Cl (**3i**)	51 (**4i**)
9[e]	H (**2a**)	4-MeO (**3j**)	54 (**4j**)
10	4-MeO (**2d**)	4-MeO (**3j**)	42 (**4k**)

[a] Reaction conditions: **1**/boronic acid **2**/aldehyde **3**=2:1:4, unless otherwise stated.

[b] CsF: 2 equiv.

[c] Isolated yield.

[d] Three equivalents of **1** were used.

[e] Four equivalents of **1** were applied.

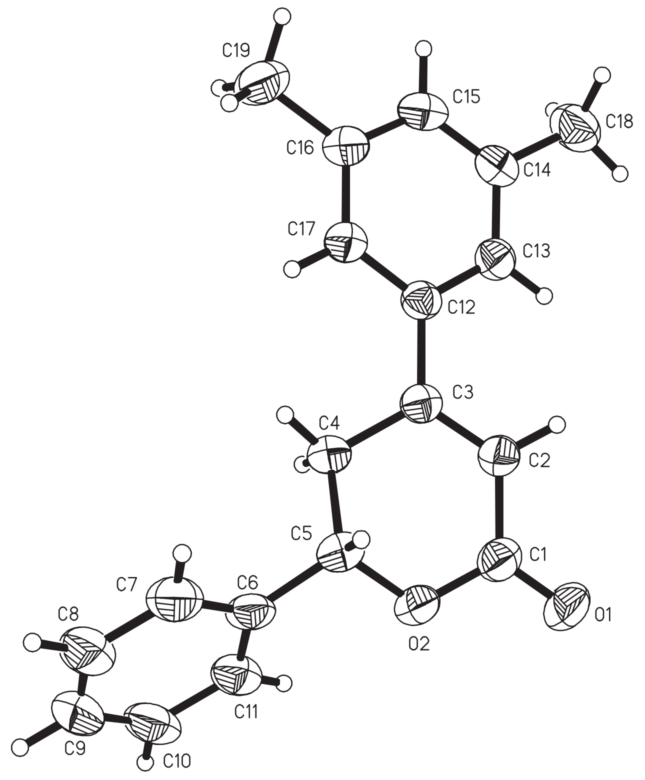
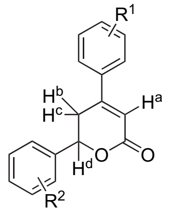


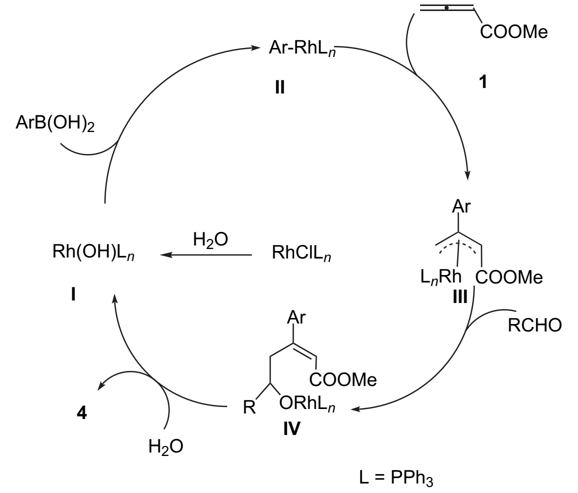
Figure 1. ORTEP drawing of **4c**.

the reaction of catalyst $RhClL_n$ with water[23]) may afford arylrhodium intermediate **II**; carborhodiation of methyl buta-2,3-dienoate **1** with **II** would form π-allyl rhodium intermediate **III**; further insertion of the carbon–oxygen double bond into the carbon–rhodium bond in **III** led to the formation of species **IV**; upon hydrolysis, it gave **4** and regenerated the catalytically active species **I**. It is believed that water helps the generation of the catalytically active species and the cyclization process.

Table 3. Non-aromatic ^{1}H NMR data of the products **4a**–**4k**



Product	Non-aromatic protons		
	H^a	H^b, H^c	H^d
4a	6.43 (s)	2.99 (d, J=7.7 Hz, 2H)	5.53 (t, J=7.7 Hz)
4b	6.44 (d, J=0.9 Hz)	3.04–2.99 (m, 2H)	5.53 (dd, J=9.0, 7.2 Hz)
4c	6.44 (s)	3.01 (d, J=8.1 Hz, 2H)	5.52 (t, J=8.1 Hz)
4d	6.40 (d, J=0.6 Hz)	3.03–2.96 (m, 2H)	5.52 (dd, J=9.9, 6.3 Hz)
4e	6.45 (s)	3.04–2.99 (m, 2H)	5.53 (dd, J=8.4, 7.2 Hz)
4f	6.47 (t, J=0.9 Hz)	3.06–3.00 (m, 2H)	5.51 (dd, J=9.6, 5.7 Hz)
4g	6.46 (s)	3.03–2.97 (m, 2H)	5.52 (dd, J=7.2, 6.3 Hz)
4h	6.46 (s)	3.03–2.98 (m, 2H)	5.51 (dd, J=9.6, 6.3 Hz)
4i	6.48 (d, J=2.4 Hz)	3.23 (dd, J=17.9, 3.5 Hz, 1H), 2.83 (ddd, J=17.9, 12.3, 2.4 Hz, 1H)	5.93 (dd, J=12.3, 3.5 Hz)
4j	6.45 (d, J=1.5 Hz)	3.05–2.98 (m, 2H)	5.49 (dd, J=10.8, 5.1 Hz)
4k	6.37 (s)	2.97 (d, J=7.0 Hz, 2H)	5.45 (t, J=8.0 Hz)



Scheme 1. Proposed catalytic cycle.

3. Conclusion

In summary, we have developed an efficient method to synthesize α,β-unsaturated δ-lactones via a Rh(I)-catalyzed three-component reaction. Further studies in this area including design of new catalysts and enantioselective reactions are being conducted in our laboratory.

4. Experimental

4.1. General experimental procedure for the synthesis of α,β-unsaturated δ-lactones (4a–4k)

Under an argon atmosphere, a mixture of organoboronic acid **2** (0.25 mmol), methyl 2,3-butadienoate **1** (0.5–1.0 mmol), aldehyde **3** (1.0 mmol), KF (0.5 mmol), $[RhCl(COD)]_2$ (2.5 mmol %), triphenylphosphine (10 mmol %), water (1.0 mmol), and anhydrous THF (3 mL) was stirred at 60 °C. The reaction was monitored by TLC. After complete consumption of starting material, the solvent was evaporated and the mixture was purified via flash chromatography on silica gel (petroleum ether/diethyl ether) to afford pure product.

4.1.1. 4,6-Diphenyl-5,6-dihydropyran-2-one (4a). The reaction of phenylboronic acid **2a** (31 mg, 0.25 mmol), methyl 2,3-butadienoate **1** (51 mg, 0.52 mmol), benzaldehyde **3a** (100 μL, 104 mg, 1.02 mmol), KF (29 mg, 0.50 mmol), $[RhCl(COD)]_2$ (3 mg, 0.006 mmol), PPh_3 (7 mg, 0.027 mmol), and H_2O (18 μL, 18 mg, 1.00 mmol) in 3 mL of anhydrous THF afforded **4a** (36 mg, 59%): solid, mp 91–93 °C (ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55–7.48 (m, 2H), 7.47–7.30 (m, 8H), 6.43 (s, 1H), 5.53 (t, J=7.7 Hz, 1H), 2.99 (d, J=7.7 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 165.3, 154.6, 138.5, 135.8, 130.7, 129.0, 128.7, 128.6, 126.1, 126.0, 114.9, 78.8, 34.1; MS (EI) *m/z* (%): 250 (M$^+$, 2.54), 144 (100); IR (KBr) ν (cm^{-1}): 1696, 1612, 1269, 1027. Anal. Calcd for $C_{17}H_{14}O_2$ (%): C, 81.58; H, 5.64. Found: C, 81.20; H, 5.92.

4.1.2. 6-Phenyl-4-(4-tolyl)-5,6-dihydropyran-2-one (4b). The reaction of 4-tolylboronic acid **2b** (33 mg, 0.24 mmol), methyl 2,3-butadienoate **1** (73 mg, 0.74 mmol), benzaldehyde **3a** (100 μL, 104 mg, 1.02 mmol), KF (30 mg, 0.52 mmol), $[RhCl(COD)]_2$ (3 mg, 0.006 mmol), PPh_3 (6 mg, 0.023 mmol), and H_2O (18 μL, 18 mg, 1.00 mmol) in 3 mL of anhydrous THF afforded **4b** (32 mg, 50%): solid, mp 90–91 °C (ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50–7.21 (m, 9H), 6.44 (d, J=0.9 Hz, 1H), 5.53 (dd, J=9.0, 7.2 Hz, 1H), 3.04–2.99 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 165.5, 154.5, 141.3, 138.6, 132.8, 129.7, 128.7, 128.6, 126.1, 125.9, 113.9, 78.7, 34.0, 21.3; MS (EI) *m/z* (%): 264 (M$^+$, 6.49), 158 (100); IR (KBr) ν (cm^{-1}): 1695, 1608, 1267, 1036, 1026. Anal. Calcd for $C_{18}H_{16}O_2$ (%): C, 81.79; H, 6.10. Found: C, 81.77; H, 6.08.

4.1.3. 4-(3′,5′-Dimethylphenyl)-6-phenyl-5,6-dihydropyran-2-one (4c). The reaction of 3,5-dimethylphenylboronic acid **2c** (37 mg, 0.25 mmol), methyl 2,3-butadienoate **1** (73 mg, 0.74 mmol), benzaldehyde **3a** (100 μL, 104 mg, 1.02 mmol), KF (30 mg, 0.52 mmol), $[RhCl(COD)]_2$ (3 mg, 0.006 mmol), PPh_3 (7 mg, 0.027 mmol), and H_2O (18 μL, 18 mg, 1.00 mmol) in 3 mL of anhydrous THF afforded **4c** (34 mg, 50%): solid, mp 123–125 °C (ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51–7.34 (m, 5H), 7.16 (s, 2H), 7.09 (s, 1H), 6.44 (s, 1H), 5.52 (t, J=8.1 Hz, 1H), 3.01 (d, J=8.1 Hz, 2H), 2.35 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 165.4, 154.9, 138.6, 138.57, 135.8, 132.4, 128.64, 128.57, 126.1, 123.8, 114.5, 78.8, 34.3, 21.3; MS (EI) *m/z* (%): 278 (M$^+$, 7.59), 172 (100); IR (KBr) ν (cm^{-1}) 1697, 1614, 1600, 1256, 1021. Anal. Calcd for $C_{19}H_{18}O_2$ (%): C, 81.99; H, 6.52. Found: C, 82.16; H, 6.67.

4.1.4. 4-(4′-Methoxyphenyl)-6-phenyl-5,6-dihydropyran-2-one (4d).[19b] The reaction of 4-methoxyphenylboronic acid **2d** (38 mg, 0.25 mmol), methyl 2,3-butadienoate **1** (75 mg, 0.74 mmol), benzaldehyde **3a** (100 μL, 104 mg, 1.02 mmol), CsF (75 mg, 0.49 mmol), $[RhCl(COD)]_2$ (3 mg, 0.006 mmol), PPh_3 (6 mg, 0.023 mmol), and H_2O (18 μL, 18 mg, 1.00 mmol) in 3 mL of anhydrous THF afforded **4d** (36 mg, 51%): solid, mp 112–114 °C (ether) [lit. 126–127 °C (ether)[19b]]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55–7.33 (m, 7H), 6.97–6.92 (m, 2H), 6.40 (d, J=0.6 Hz, 1H), 5.52 (dd, J=9.9, 6.3 Hz, 1H), 3.85 (s, 3H), 3.03–2.96 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 165.6, 161.7, 153.9, 138.6, 128.62, 128.55, 127.8, 127.6, 126.0, 114.3, 112.6, 78.6, 55.4, 33.9; MS (EI) *m/z* (%): 280 (M$^+$, 33.39), 174 (100); IR (KBr) ν (cm^{-1}): 1685, 1604, 1513, 1252, 1183, 1032. Anal. Calcd for $C_{18}H_{16}O_3$ (%): C, 77.12; H, 5.75. Found: C, 77.36; H, 5.64.

4.1.5. 4-(3′-Methoxyphenyl)-6-phenyl-5,6-dihydropyran-2-one (4e). The reaction of 3-methoxyphenylboronic acid **2e** (37 mg, 0.24 mmol), methyl 2,3-butadienoate **1** (52 mg, 0.53 mmol), benzaldehyde **3a** (100 μL, 104 mg, 1.02 mmol), KF (31 mg, 0.50 mmol), $[RhCl(COD)]_2$ (3 mg, 0.006 mmol), PPh_3 (7 mg, 0.027 mmol), and H_2O (18 μL, 18 mg, 1.00 mmol) in 3 mL of anhydrous THF afforded **4e** (31 mg, 45%): oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50–7.34 (m, 6H), 7.15–7.11 (m, 1H), 7.06–7.04 (m, 1H), 7.02–6.99 (m, 1H), 6.45 (s, 1H), 5.53 (dd, J=8.4, 7.2 Hz, 1H), 3.83 (s, 3H), 3.04–2.99 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 165.2, 159.9, 154.5, 138.5, 137.3, 130.0, 128.69, 128.65, 126.1, 118.4, 116.1, 115.2, 111.6, 78.8, 55.3, 34.2; MS (EI) *m/z* (%): 280 (M$^+$, 3.80), 84 (100); IR (neat) ν (cm^{-1}): 1712, 1617, 1598, 1578, 1266; HRMS calcd for $C_{18}H_{16}O_3$ [M$^+$] 280.1099. Found: 280.1094.

4.1.6. 4-Phenyl-6-(4-tolyl)-5,6-dihydropyran-2-one (4f). The reaction of phenylboronic acid **2a** (30 mg, 0.25 mmol), methyl 2,3-butadienoate **1** (53 mg, 0.54 mmol), 4-methylbenzaldehyde **3f** (118 μL, 120 mg, 1.00 mmol), KF (28 mg, 0.48 mmol), $[RhCl(COD)]_2$ (3 mg, 0.006 mmol), PPh_3 (6 mg, 0.023 mmol), and H_2O (18 μL, 18 mg, 1.00 mmol) in 3 mL of anhydrous THF afforded **4f** (36 mg, 55%): solid, mp 102–103 °C (ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58–7.53 (m, 2H), 7.48–7.42 (m, 3H), 7.37 (d, J=8.1 Hz, 2H), 7.27–7.20 (m, 2H), 6.47 (t, J=0.9 Hz, 1H), 5.51 (dd, J=9.6, 5.7 Hz, 1H), 3.06–3.00 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 165.3, 154.6, 138.5, 135.9, 135.5, 130.7, 129.3, 129.0, 126.0, 125.96, 114.9, 78.7, 34.0, 21.1; MS (EI) *m/z* (%): 264 (M$^+$, 1.98), 144 (100); IR (KBr) ν (cm^{-1}): 1711, 1613, 1266, 1082; HRMS calcd for [M$^+$] $C_{18}H_{16}O_2$, 264.1150. Found: 264.1141.

4.1.7. 6-(4′-Chlorophenyl)-4-phenyl-5,6-dihydropyran-2-one (4g). The reaction of phenylboronic acid **2a** (30 mg, 0.25 mmol), methyl 2,3-butadienoate **1** (75 mg, 0.77 mmol), 4-chlorobenzaldehyde **3g** (144 mg, 1.02 mmol), KF (30 mg, 0.52 mmol), $[RhCl(COD)]_2$ (3 mg, 0.006 mmol), PPh_3 (6 mg, 0.023 mmol), and H_2O (18 μL, 18 mg, 1.00 mmol) in 3 mL of anhydrous THF afforded **4g** (34 mg, 49%): solid, mp 116–117 °C (ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57–7.52 (m, 2H), 7.48–7.36 (m, 7H), 6.46 (s, 1H), 5.52 (dd, J=7.2, 6.3 Hz, 1H), 3.03–2.97 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 164.9, 154.4, 137.0, 135.6, 134.4, 130.8, 129.0, 128.9, 127.4, 126.0, 114.8, 78.0, 34.0; MS (EI) *m/z* (%): 286 (M$^+$ (^{37}Cl), 0.41), 284 (M$^+$ (^{35}Cl), 1.57), 144 (100); IR (KBr) ν (cm^{-1}): 1709, 1695, 1617, 1261, 1082. Anal. Calcd for $C_{17}H_{13}ClO_2$ (%): C, 71.71; H, 4.60. Found: C, 71.87; H, 4.55.

4.1.8. 6-(4-Bromophenyl)-4-phenyl-5,6-dihydropyran-2-one (4h). The reaction of phenylboronic acid **2a** (30 mg, 0.25 mmol), methyl 2,3-butadienoate **1** (50 mg, 0.51 mmol), 4-bromobenzaldehyde **3h** (184 mg, 0.99 mmol), KF (29 mg, 0.50 mmol), $[RhCl(COD)]_2$ (3 mg, 0.006 mmol), PPh_3 (7 mg, 0.027 mmol), and H_2O (18 μL, 18 mg, 1.00 mmol) in 3 mL of anhydrous THF afforded **4h** (40 mg, 50%): solid, mp 115–116 °C (ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58–7.51 (m, 4H), 7.48–7.41 (m, 3H), 7.39–7.33 (m, 2H), 6.46 (s, 1H), 5.51 (dd, J=9.6, 6.3 Hz, 1H), 3.03–2.98 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 165.0, 154.5, 137.5, 135.6, 131.8, 130.9, 129.0, 127.7, 126.0, 122.6, 114.9, 78.0, 34.0; MS (EI) *m/z* (%): 330 (M$^+$ (^{81}Br), 0.60), 328 (M$^+$ (^{79}Br), 0.79), 144 (100); IR (KBr) ν (cm^{-1}): 1708, 1616, 1488, 1260, 1080. Anal. Calcd for $C_{17}H_{13}BrO_2$ (%): C, 62.03; H, 3.98. Found: C, 61.98; H, 4.33.

4.1.9. 6-(2′-Chlorophenyl)-4-phenyl-5,6-dihydropyran-2-one (4i). The reaction of phenylboronic acid **2a** (30 mg, 0.25 mmol), methyl 2,3-butadienoate **1** (78 mg, 0.80 mmol), 2-chlorobenzaldehyde **3i** (112 μL, 140 mg, 1.00 mmol), KF (30 mg, 0.52 mmol), $[RhCl(COD)]_2$ (3 mg, 0.006 mmol), PPh_3 (6 mg, 0.023 mmol), and H_2O (18 μL, 18 mg, 1.00 mmol) in 3 mL of anhydrous THF afforded **4i** (36 mg, 51%): solid, mp 120–122 °C (ether); ^1H NMR (300 MHz, $CDCl_3$): δ 7.75–7.71 (m, 1H), 7.58–7.53 (m, 2H), 7.48–7.25 (m, 6H), 6.48 (d, J=2.4 Hz, 1H), 5.93 (dd, J=12.3, 3.5 Hz, 1H), 3.23 (dd, J=17.9, 3.5 Hz, 1H), 2.83 (ddd, J=17.9, 12.3, 2.4 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 165.1, 154.7, 136.3, 135.7, 131.3, 130.8, 129.6, 129.5, 129.0, 127.5, 127.45, 126.1, 114.7, 75.7, 32.6; MS (EI) *m/z* (%): 286 (M^+ (^{37}Cl), 0.54), 284 (M^+ (^{35}Cl), 1.33), 144 (100); IR (KBr) ν (cm^{-1}): 1705, 1619, 1263, 1024. Anal. Calcd for $C_{17}H_{13}ClO_2$ (%): C, 71.71; H, 4.60. Found: C, 71.86; H, 4.78.

4.1.10. 6-(4′-Methoxyphenyl)-4-phenyl-5,6-dihydropyran-2-one (4j). The reaction of phenylboronic acid **2a** (31 mg, 0.25 mmol), methyl 2,3-butadienoate **1** (98 mg, 1.00 mmol), 4-methoxybenzaldehyde **3j** (121 μL, 136 mg, 1.00 mmol), KF (28 mg, 0.48 mmol), $[RhCl(COD)]_2$ (3 mg, 0.006 mmol), PPh_3 (6 mg, 0.023 mmol), and H_2O (18 μL, 18 mg, 1.00 mmol) in 3 mL of anhydrous THF afforded **4j** (38 mg, 54%): solid, mp 94–95 °C (ether); ^1H NMR (300 MHz, $CDCl_3$): δ 7.58–7.52 (m, 2H), 7.48–7.36 (m, 5H), 6.97–6.91 (m, 2H,), 6.45 (d, J=1.5 Hz, 1H), 5.49 (dd, J=10.8, 5.1 Hz, 1H), 3.82 (s, 3H), 3.05–2.98 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 165.4, 159.8, 154.6, 135.9, 130.7, 130.5, 129.0, 127.6, 126.0, 114.9, 114.0, 78.6, 55.3, 34.0; MS (EI) *m/z* (%): 280 (M^+, 6.45), 144 (100); IR (KBr) ν (cm^{-1}): 1709, 1613, 1515, 1249, 1025. Anal. Calcd for $C_{18}H_{16}O_3$ (%): C, 77.12; H, 5.75. Found: C, 77.28; H, 5.91.

4.1.11. 4,6-Bis(4′-methoxyphenyl)-5,6-dihydropyran-2-one (4k).[19b] The reaction of 4-methoxyphenylboronic acid **2d** (38 mg, 0.25 mmol), methyl 2,3-butadienoate **1** (53 mg, 0.54 mmol), 4-methoxybenzaldehyde **3j** (120 μL, 136 mg, 1.00 mmol), KF (29 mg, 0.50 mmol), $[RhCl(COD)]_2$ (3 mg, 0.006 mmol), PPh_3 (7 mg, 0.027 mmol), and H_2O (18 μL, 18 mg, 1.00 mmol) in 3 mL of anhydrous THF afforded **4k** (32 mg, 42%): solid, mp 106–108 °C (ether) [lit. 116–118 °C (ether)[19b]]; ^1H NMR (300 MHz, $CDCl_3$): δ 7.52 (d, J=8.7 Hz, 2H), 7.39 (d, J=9 Hz, 2H), 6.97–6.90 (m, 4H), 6.37 (s, 1H), 5.45 (t, J=8.0 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.97 (d, J=7.0 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 161.7, 159.7, 154.0, 130.7, 127.9, 127.62, 127.60, 114.3, 114.0, 112.6, 78.5, 55.4, 55.3, 33.8; MS (EI) *m/z* (%): 310 (M^+, 6.27), 73 (100); IR (KBr) ν (cm^{-1}): 1697, 1600, 1517, 1247, 1186, 1031. Anal. Calcd for $C_{19}H_{18}O_4$ (%): C, 73.53; H, 5.85. Found: C, 73.72; H, 5.95.

4.2. Syhthesis of 4-(4′-methoxyphenyl)-6-phenyl-5,6-dihydropyran-2-one (4d) and methyl 5-hydroxy-3-(4-methoxyphenyl)-5-phenylpent-2(*E*)-enoate (5d)

The reaction of 4-methoxyphenylboronic acid **2d** (381 mg, 2.51 mmol), methyl 2,3-butadienoate **1** (125 mg, 1.28 mmol), benzaldehyde **3a** (250 μL, 265 mg, 2.50 mmol), $RhCl(PPh_3)_3$ (60 mg, 0.06 mmol), Cs_2CO_3 (200 mg, 0.61 mmol), H_2O (45 μL, 45 mg, 2.50 mmol) in 15 mL of anhydrous THF afforded white solid **4d** (45 mg, 13%) and colorless oil **5d** (72 mg, 19%). The data of **5d**: ^1H NMR (300 MHz, $CDCl_3$): δ 7.49–7.39 (m, 4H), 7.37–7.30 (m, 2H), 7.28–7.22 (m, 1H), 6.94–6.89 (m, 2H), 6.23 (s, 1H), 4.75 (dd, J=9.6, 3.0 Hz, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 3.69 (dd, J=13.5, 10.2 Hz, 1H), 3.19 (dd, J=13.5, 3.3 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 168.8, 160.7, 156.6, 145.0, 132.4, 128.35, 128.32, 127.3, 125.5, 117.4, 114.0, 73.6, 55.3, 51.7, 41.2; MS (EI) *m/z*: 312 (M^+, 0.40), 280 (12.30), 206 (100); IR (neat): ν (cm^{-1}): 1710, 1602, 1512, 1170; HRMS (MALDI/DHB): calcd for $C_{19}H_{20}O_4Na^+$ [$M+Na^+$] 335.1263. Found: 335.1254.

Acknowledgements

We thank the financial support from the National Natural Science Foundation of China (20429201) and the Chinese Academy of Sciences.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.03.021.

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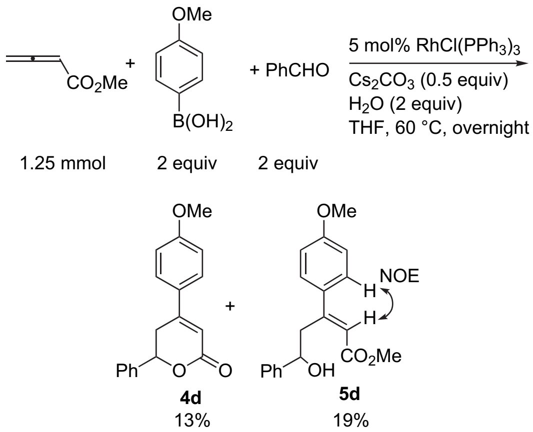

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