Palladium catalyzed isomerization of alkenes: a pronounced influence of an *o*-phenol hydroxyl group†

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Received 14th April 2009, Accepted 6th May 2009
First published as an Advance Article on the web 8th June 2009
DOI: 10.1039/b907426k

A novel palladium catalyzed isomerization of alkenes has been found, where an *ortho*-phenol hydroxyl group has a pronounced influence on the isomerization.

Introduction

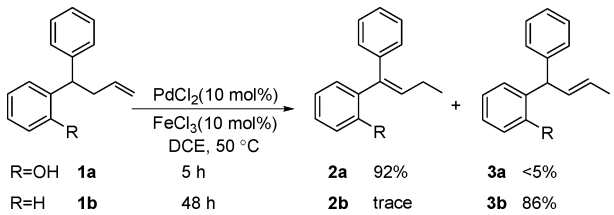
Isomerization of the functionalities of organic compounds provides efficient access to molecules that would otherwise be more complicated to synthesise,[1] and isomerization of organic compounds through the catalytic activity of transition metals has been used widely in organic transformations.[2] Examples of isomerizations are Brown's borane migration,[3] base-catalyzed alkyne migration,[4] transition-metal catalyzed transformation of allylic alcohols to ketones[1b,5] *etc.* Double-bond migration as one method of isomerization in allyl systems has been well recognized in organic synthesis. Ever since the isomerization of allylbenzene was first reported by Shimizu and Blum using a Natta-type catalyst[6a] and platinum complex catalyst,[6b] a wide array of complexes of transition metals, such as iron, nickel, cobalt, titanium, zirconium, ruthenium, rhodium and iridium, have been utilized for this purpose.[7] Base-catalyzed isomerizations of allylbenzene have also been reported.[8] However, isomerization of but-3-enylbenzene has rarely been reported. To the best of our knowledge, only one paper has reported the isomerization of but-3-enylbenzene using potassium tert-butoxide and hydroquinone as a catalyst at 350 °C, giving 68% yield.[9]

On the other hand, the apparent influence on the reaction rate or type caused by an *ortho*-substituent group has gained much attention in the organic community.[10–12] By virtue of an *ortho*-effect, some coupling reactions,[10] ring-closing reactions[11] of terminal alkenes and palladium-catalyzed aerobic dialkoxylation[12] can be accelerated and improved.

Results and discussion

Herein, we reported a novel and pronounced influence of an *o*-phenol hydroxyl group on the palladium-catalyzed isomerization of alkene (Scheme 1). Moreover, the products of the isomerization are potential precursors to many building blocks.[13]

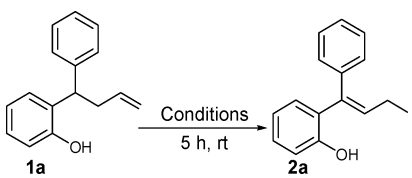
In an initial experiment, we discovered that 2-(1-phenylbut-3-enyl)phenol **1a** could be isomerized to 2-(1-phenylbut-1-enyl)phenol **2a** in the presence of a catalytic amount of $PdCl_2$.



Scheme 1 The influence of *o*-phenol hydroxyl group on the palladium–catalyzed isomerization of alkene.

However, **1b** cannot be isomerized to the corresponding **2b** under the same reaction conditions. This interesting phenomena drew our attention and various reaction conditions were investigated (Table 1). First, palladium sources were examined and $PdCl_2$ was most effective. Different solvents were also screened and 1,2-dichloroethane proved to be a better solvent (Table 1, entries 1, 4–7). Due to the observation of some palladium black in the system,[14] the co-oxidant was investigated and $FeCl_3$ gave the best result (Table 1, entries 8–11). After considerable experimentation, it was also found that the most suitable temperature is 50 °C (Table 1, entry 12). There was no evident difference when

Table 1 Screen of reaction conditions for the isomerization.[a]



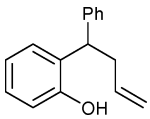
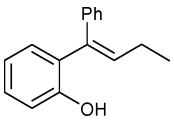
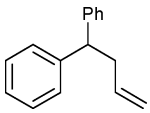
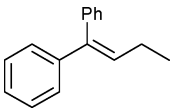
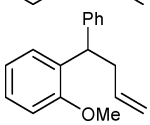
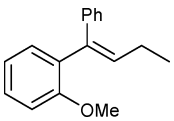
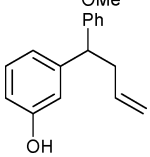
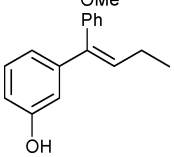
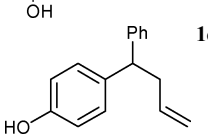
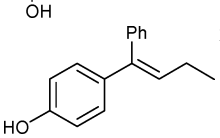
Entry	Catalyst (10 mol%)	Solvent	Yield (%)[b]
1	$PdCl_2$	DCE	37
2	$Pd(OAc)_2$	DCE	trace
3	$PdCl_2(CH_3CN)_2$	DCE	30
4	$PdCl_2$	MeOH	22
5	$PdCl_2$	Tol	29
6	$PdCl_2$	**DMSO**	0
7	$PdCl_2$	DMF	trace
8	$PdCl_2$+$FeCl_3$ (10 mol%)	DCE	69
9	$PdCl_2$+O_2 (1 atm)	DCE	44
10	$PdCl_2$+benzoquinone (1 equiv)	DCE	11
11	$PdCl_2$+$CuCl_2$ (10 mol%)	DCE	52
12[c]	$PdCl_2$+$FeCl_3$ (10 mol%)	DCE	92
13	$FeCl_3$ (10 mol%)	DCE	0

[a] Reaction conditions: 2-(1-phenylbut-3-enyl)phenol **1a** (0.5 mmol), catalyst palladium salt (10 mol%), DCE (1.5 mL), air, rt, 5 h. [b] Yield of isolated product. [c] 50 °C.

Hefei National Laboratory for Physical Science at Microscale, Joint-Lab of Green Synthetic Chemistry and Department of Chemistry, University of Science and Technology of China, Hefei, 230026, P. R. China. E-mail: zwang3@ustc.edu.cn; Fax: (+86) 551-360-3185; Tel: (+86) 551-360-3185

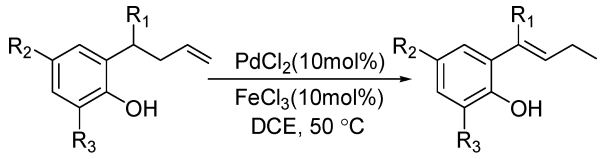
† Electronic supplementary information (ESI) available: Synthesis of substrates, characterisation data and NMR spectra of all compounds. See DOI: 10.1039/b907426k

Table 2 Control and additional experiments to clarify the existence of the pronounced influence caused by the *ortho*-phenol hydroxyl group[a]

Entry	Substrates	Products	Yield (%)[b]
1	 **1a**	 **2a**	92
2	 **1b**	 **2b**	trace (86)
3	 **1c**	 **2c**	trace (84)
4	 **1d**	 **2d**	trace (83)
5	 **1e**	 **2e**	trace (89)

[a] All reactions were carried out with **1** (0.5 mmol), $PdCl_2$ (10 mol%), $FeCl_3$ (10 mol%), DCE (1.5 mL), air, 50 °C, 5 h. [b] Yield of isolated product. ^1H NMR yield of **3b–3e** in parentheses.

Table 3 Scope of this accelerating effect caused by the *ortho*-phenol hydroxyl group.[a]



1a, 1f-1r **(*E*)-2a, 2f-2r**

Entry	R_1	R_2	R_3	T (°C)	t (h)	Yield (%)[b]
1	Ph	H	H	50	5	92
2	Ph	OMe	H	50	5	94
3	Ph	Cl	H	50	10	85
4	4-Me-Ph	H	H	50	5	88
5	4-Me-Ph	Br	H	50	5	83
6	Me	H	H	rt	6	79
7	Me	OMe	H	rt	6	82, 89[c]
8	Me	Br	H	rt	8	77[d]
9	Me	t-Bu	t-Bu	rt	4	95
10	H	H	H	rt	6	89
11	H	Br	H	50	8	88
12	H	t-Bu	t-Bu	rt	4	92
13	OH	H	H	rt	2	complex[e]
14	OMe	H	H	rt	2	complex[e]

[a] All reactions were carried out with **1** (0.5 mmol), $PdCl_2$ (10 mol%), $FeCl_3$ (10 mol%), DCE (1.5 mL), air. [b] Yield of isolated product. [c] When the reaction was performed at 50 °C for 3 h, an E/Z mixture with a ratio of 3:2 was obtained. [d] E/Z = 17:20 determined by ^1H NMR. [e] Unknown complex mixture.

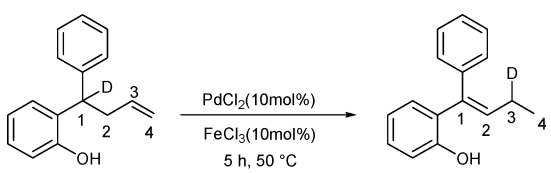
the reaction was performed in dry 1,2-dichloroethane or 1,2-dichloroethane without drying.

In order to clarify the pronounced influence caused by the *ortho*-phenol hydroxyl group, control and additional experiments were conducted (Table 2). As shown in Table 2, the reaction substrates **1b–1e** without an *ortho*-phenol hydroxyl group didn't give the desired products **2b–2e** and the main products were **3b–3e** (Table 2, entries 2–5). When **1b** was used as the reaction substrate, for example, the corresponding isomerization product **2b** was hardly obtained. Prolonging the reaction time to 48 h, only a trace of the desired product **2b** was detected by GC-MS (Table 2, entry 2) and **3b** was obtained as a main product (see the ^1H NMR spectra in the ESI†). As for substrates **1c–1e**, which bear 2-methoxy, 3-phenol hydroxyl group or 4-phenol hydroxyl group, similar results were observed. This indicated that the *ortho*-phenol hydroxyl group had a great influence on the isomerization.

In order to explore the scope of this *ortho*-effect from the *ortho*-phenol hydroxyl group, various 2-(but-3-enyl)phenol substrates were investigated under the optimized conditions (Table 3). In general, owing to the participation of the *ortho*-phenol hydroxyl group, all isomerizations of the different substrates in Table 3 were greatly facilitated. Furthermore, the electronic effect of the substitution on the phenol ring has an influence on the isomerization. When the phenol ring bears an electron-donating group, the reaction can be carried out in a faster rate with a higher yield (Table 3, entries 2, 7, 9, 12). In contrast, an electron-withdrawing group on the phenol rings retarded the isomerization, resulting in a longer reaction time with a lower yield (Table 3, entries 3, 5, 8, 11). Additionally, an aromatic substituent or a hydrogen atom on the benzylic position of **1** appeared beneficial for this transformation (Table 3, entries 1–5, 10–12). Nevertheless, hydroxyl group substitution or methoxy substitution on the benzylic position under the same conditions led to unknown complex mixtures (Table 3, entries 13–14).

Regarding the stereochemistry of the isomerization, in most cases only single diastereomers were determined from ^1H NMR spectra of the crude products. The (*E*)-geometry of **2a** was established *via* NOESY study. However, in the case of **1l** as the substrate at room temperature, we isolated an E/Z mixture with a ratio of 17:20 (Table 3, entry 8). Besides, when **1k** was subjected to the reaction at 50 °C, an E/Z mixture with a ratio of 3:2 was also obtained. In spite of the unclear reason for this stereochemistry, this difference implied that substituents on the phenol ring had a great influence on the transition state of the isomerization.

Afterwards, the reaction mechanism was investigated. At the outset, a deuterium labeling experiment was designed and performed (Scheme 2). When deuterium labeled substrate **1a-*d*** was subjected to the standard reaction conditions, it was found that deuterium was transferred from C-1 in **1a-*d*** to C-3 in **2a-*d*** exclusively. To probe further the mechanism of the accelerating effect of the *ortho*-phenol hydroxyl group, we next monitored the



1a-*d* **2a-*d***

Yield = 91%

Scheme 2 Deuterium labeling experiment of the isomerization.

reaction of **1a** and **1b** by ^{1}H NMR. ^{1}H NMR showed that **1a** was converted to the desired product **2a** in 86% NMR yield after 12 h, while substrate **1b** under the same conditions gave a trace of the desired product **2b** (Fig. 1). The NMR monitoring experiment strongly further demonstrated the existence of the pronounced influence caused by the *ortho*-phenol hydroxyl group. Owing to its participation, the reaction is greatly facilitated.

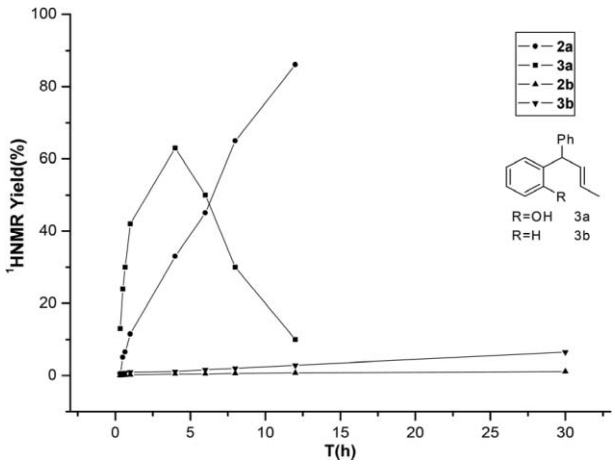
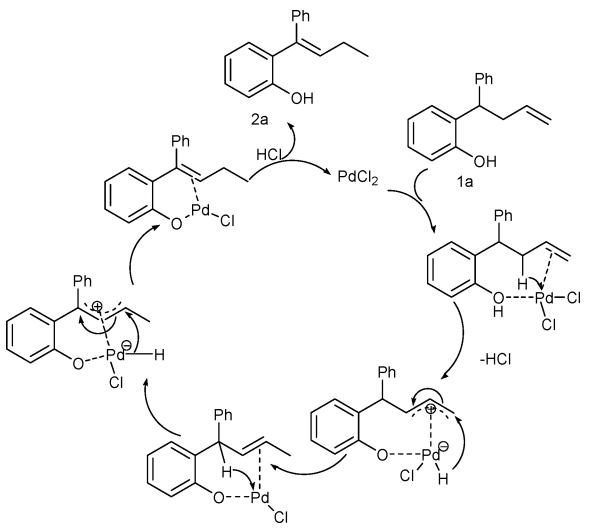


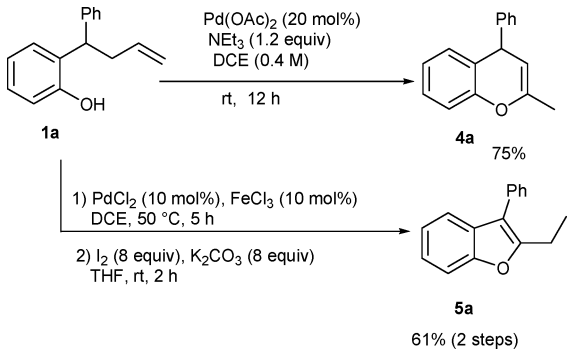
Fig. 1 Interval NMR experiment, conditions: substrates **1a** or **1b** (0.5 mmol), $PdCl_2$ (10 mol%), $CDCl_3$ (0.5 ml), in NMR tube, rt.

Based on the deuterium labeling and the NMR monitoring experiments, a plausible mechanism is proposed in Scheme 3: complexation of the $PdCl_2$ catalyst with the substrate followed by oxidative addition of the allyllic C–H bond[15] generates an allylpalladium hydride. This intermediate undergoes reductive elimination with transfer of the hydride to the allylic position. Afterwards, a similar tandem oxidative addition and reductive elimination process take places and gives the desired isomerization product. In this process, sequential 1,3-hydride alkyl to palladium migration is involved.



Scheme 3 Proposed mechanism for the palladium catalyzed isomerization accelerated by the *ortho*-phenol hydroxyl group.

Additionally, the isomerization developed can be used for the synthesis of benzofuran and benzopyran derivatives.[16] For instance, benzofuran and benzopyran could be obtained from the same substrate by this new isomerization and the traditional Wacker oxidation respectively (Scheme 4). When **1a** was a substrate under the traditional Wacker oxidation conditions, we got benzopyran **4a** in 75% yield after 12 h at room temperature in air. In contrast, the isomerization of the same substrate **1a** by $PdCl_2$ (Table 3, entry 1) and, after purification, subsequent I_2-catalyzed cyclization of the resulting 2-(1-phenylbut-1- enyl)phenol **2a** gave the desired benzofuran **5a** in 61% yield over the two steps.



Scheme 4 Synthesis of benzofuran and benzopyran derivatives.

Conclusions

In summary, we have found a novel palladium catalyzed isomerization of alkenes, where an *ortho*-phenol hydroxyl group has a pronounced *ortho*-effect on the isomerization. Also, the isomerization developed is very useful in the preparation of benzofuran and benzopyran derivatives. Investigations of the influence of other functional groups on the isomerization and the applications of the isomerization are currently in progress in our lab.

Experimental

IR (Perkin–Elmer, 2000FTIR), ^{1}H NMR ($CDCl_3$, 400 or 300 MHz), ^{13}C NMR ($CDCl_3$, 100 or 75 MHz) and MS–GC (HP 5890(II)/HP5972, EI. Analytical thin-layer chromatography (TLC) plates were commercially available. Solvents were reagent grade unless otherwise noted. All starting materials and reagents are commercially available and were used as received.

General procedure for the isomerization of alkene

$PdCl_2$ (8.8 mg, 0.05 mmol) and $FeCl_3$ (8.1 mg, 0.05 mmol) were added to a solution of **1a** (112.0 mg, 0.5 mmol) in 1,2-dichloroethane (1.5 mL). The resulting mixture was warmed to 50 °C for 5 h, then the mixture was extracted with CH_2Cl_2 twice. The combined organic extracts were dried over Na_2SO_4 and filtered. Solvents were evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using PE-EtOAc (20:1, v/v) as eluent to give **2a** as a yellow oil (103.0 mg, 92%).

(*E*)-2-(1-Phenylbut-1-enyl)phenol (2a). The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 7.26$–7.21 (m, 6 H), 7.04–6.90 (m, 3 H), 6.37 (t, $J = 7.5$ Hz, 1 H), 5.06

(s, 1 H), 2.05 (dq, $J_1 = 7.5$ Hz, $J_2 = 7.5$ Hz, 2 H), 1.02 (t, $J = 7.5$ Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 153.1, 140.5, 135.2, 135.1, 130.8, 129.3, 128.7, 127.7, 126.6, 125.8, 120.7, 115.5, 23.5, 14.2$; IR (KBr, cm^{-1}): $\nu = 3524, 2966, 2872, 1580, 1486, 1449, 1334, 1284, 1193, 1148, 1033, 910, 828, 755, 698$; HRMS calc. $C_{16}H_{16}O$ (M^+): 224.1201. Found: 224.1204.

Deuterium (*E*)-2-(1-phenylbut-1-enyl)phenol (2a-*d*). The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 7.28–7.23$ (m, 6 H), 7.02–6.94 (m, 3 H), 6.37 (t, $J = 7.5$ Hz, 1 H), 5.02 (s, 1 H), 2.05 (dq, $J_1 = 7.5$ Hz, $J_2 = 7.5$ Hz, 1 H), 1.03 (t, $J = 7.5$ Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 153.1, 140.5, 135.2, 135.1, 130.8, 129.3, 128.7, 127.7, 126.6, 125.8, 120.7, 115.5, 23.5, 14.2$; IR (KBr, cm^{-1}): $\nu = 3524, 2966, 2872, 1580, 1486, 1449, 1334, 1284, 1193, 1148, 1033, 910, 838, 755, 698$; HRMS calc. $C_{16}H_{15}DO$ (M^+): 225.1264. Found: 225.1258.

(*E*)-4-Methoxy-2-(1-phenylbut-1-enyl)phenol (2f). The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 7.35–7.12$ (m, 5 H), 6.91–6.80 (m, 2 H), 6.56 (s, 1 H), 6.36 (t, $J = 7.5$ Hz, 1 H), 4.73 (s, 1 H), 3.72 (s, 3 H), 2.06 (dq, $J_1 = 7.5$ Hz, $J_2 = 7.5$ Hz, 2 H), 1.03 (t, $J = 7.5$ Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 153.7, 147.2, 135.8, 134.9, 129.2, 128.6, 127.6, 126.5, 116.5, 116.0, 115.7, 115.4, 55.8, 23.4, 14.0$; IR (KBr, cm^{-1}): $\nu = 3528, 2964, 2872, 1596, 1491, 1446, 1360, 1274, 1212, 1145, 1039, 952, 852, 772, 697$; HRMS calc. $C_{17}H_{18}O_2$ (M^+): 254.1307. Found: 254.1302.

(*E*)-4-Chloro-2-(1-phenylbut-1-enyl)phenol (2g). The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 7.30–7.21$ (m, 6 H), 7.04–6.92 (m, 2 H), 6.40 (t, $J = 7.5$ Hz, 1 H), 5.07 (s, 1 H), 2.07 (dq, $J_1 = 7.5$ Hz, $J_2 = 7.5$ Hz, 2 H), 1.06 (t, $J = 7.5$ Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 152.2, 135.7, 133.4, 130.1, 129.1, 128.7, 127.8, 126.5, 116.7, 23.4, 13.9$; IR (KBr, cm^{-1}): $\nu = 3522, 2966, 2872, 1597, 1480, 1408, 1326, 1266, 1194, 1079, 943, 881, 764, 666$; HRMS calc. $C_{16}H_{15}ClO$ (M^+): 258.0811. Found: 258.0816.

(*E*)-2-(1-*p*-Tolylbut-1-enyl)phenol (2h). The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 7.24–6.92$ (m, 8 H), 6.34 (t, $J = 7.5$ Hz, 1 H), 5.04 (s, 1 H), 2.31 (s, 3 H), 2.04 (dq, $J_1 = 7.5$ Hz, $J_2 = 7.5$ Hz, 2 H), 1.01 (t, $J = 7.5$ Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 153.5, 138.2, 135.3, 134.0, 130.6, 130.4, 129.3, 129.1, 128.8, 126.4, 120.5, 120.3, 115.3, 23.3, 21.1, 14.0$; IR (KBr, cm^{-1}): $\nu = 3515, 2965, 2872, 1606, 1484, 1457, 1334, 1284, 1196, 1035, 932, 817, 754, 685$; HRMS calc. $C_{17}H_{18}O$ (M^+): 238.1358. Found: 238.1353.

(*E*)-4-Bromo-2-(1-*p*-tolylbut-1-enyl)phenol (2i). The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 7.37–7.33$ (m, 1 H), 7.16–7.08 (m, 5 H), 6.87 (d, $J = 5.7$ Hz, 1 H), 6.34 (t, $J = 7.5$ Hz 1 H), 5.01 (s, 1 H), 2.33 (s, 3 H), 2.04 (dq, $J_1 = 7.5$ Hz, $J_2 = 7.5$ Hz, 2 H), 1.03 (t, $J = 7.5$ Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 152.9, 138.1, 137.9, 134.9, 133.0, 132.0, 129.6, 129.5, 129.2, 126.5, 117.3, 112.3, 23.4, 21.2, 14.1$; IR (KBr, cm^{-1}): $\nu = 3516, 2965, 2871, 1569, 1476, 1412, 1325, 1264, 1195, 1074, 941, 817, 720, 611$; HRMS calc. $C_{17}H_{17}BrO$ (M^+): 316.0463. Found: 316.0469.

(*E*)-2-(Pent-2-en-2-yl)phenol (2j). The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 7.18–7.07$ (m, 2 H), 6.93–6.88 (m, 2 H), 5.64–5.52 (m, 2 H), 2.24 (dq, $J_1 = 7.5$ Hz, $J_2 = 7.5$ Hz, 2 H), 1.99 (s, 3 H), 1.07 (t, $J = 7.5$ Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 152.0, 133.5, 131.6, 131.1, 128.4, 128.2, 120.3, 115.4, 21.9, 17.9, 14.2$; IR (KBr, cm^{-1}): $\nu = 3512, 2965, 2873, 1578, 1487, 1448, 1340, 1282, 1222, 1182, 1037, 909, 828, 753$; GC-MS (EI) calc. $C_{11}H_{14}O$ (M^+): 162. Found: 162.

(*E*)-4-Methoxy-2-(pent-2-en-2-yl)phenol (2k). The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 6.86–6.82$ (m, 1 H), 6.75–6.71 (m, 1 H), 6.58 (d, $J = 7.5$ Hz, 1 H), 5.69 (t, $J = 7.5$ Hz, 1 H), 4.83 (s, 1 H), 3.76 (s, 3 H), 1.97 (s, 3 H), 1.85 (dq, $J_1 = 7.5$ Hz, $J_2 = 7.5$ Hz, 2 H), 0.92 (t, $J = 7.5$ Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 145.7, 133.4, 130.8, 115.5, 113.9, 113.8, 113.2, 112.4, 55.9, 25.1, 22.7, 14.2$; IR (KBr, cm^{-1}): $\nu = 3450, 2962, 2873, 1589, 1493, 1423, 1364, 1275, 1218, 1165, 1040, 856, 810, 762$; GC-MS (EI) calc. $C_{12}H_{16}O_2$ (M^+): 192. Found: 192.

(*E*)-4-Bromo-2-(pent-2-en-2-yl)phenol compound with (*Z*)-4-bromo-2-(pent-2-en-2-yl)phenol (17:20) (2l). The title mixture was a yellow oil (with a trace of byproducts from NMR). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 7.27–7.14$ (m, 2 H), 6.82–6.77 (m, 1 H), 5.22 (m, 0.38 H), 5.63 (s, 0.5 H), 5.55 (m, 0.51 H), 5.26 (s, 0.5 H), 2.28–2.18 (m, 1.11 H), 1.96 (s, 3 H), 1.88–1.80 (m, 0.95 H), 1.06 (t, $J = 7.5$ Hz, 1.64 H), 0.93 (t, $J = 7.5$ Hz, 1.19 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 151.5, 134.1, 134.0, 131.0, 130.8, 130.6, 117.0, 116.6, 24.7, 22.4, 21.6, 20.9, 14.0, 13.8$; IR (KBr, cm^{-1}): $\nu = 3511, 2965, 2874, 1594, 1481, 1403, 1376, 1265, 1210, 1175, 1044, 909, 816, 759, 734$; GC-MS(EI): two peaks and both are 240.

(*E*)-2,4-Di-*tert*-butyl-6-(pent-2-en-2-yl)phenol (2m). The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 7.19$ (d, $J = 2.7$ Hz, 1 H), 6.93 (d, $J = 2.7$ Hz, 1 H), 5.80 (s, 1 H), 5.05 (t, $J = 7.5$ Hz, 1 H), 2.23 (dq, $J_1 = 7.5$ Hz, $J_2 = 7.5$ Hz, 2 H), 2.00 (s, 3 H), 1.07 (t, $J = 7.5$ Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 148.1, 141.5, 135.0, 133.8, 133.5, 132.4, 122.6, 115.4, 35.3, 34.4, 31.8, 29.8, 21.9, 18.5, 14.2$; IR (KBr, cm^{-1}): $\nu = 3506, 2961, 2872, 1600, 1489, 1442, 1362, 1264, 1201, 1168, 1119, 1032, 909, 878, 817, 767, 648$; HRMS calc. $C_{19}H_{30}O$ (M^+): 274.2297. Found: 274.2295.

(*E*)-2-(But-1-enyl)phenol (2n). The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 7.30$ (d, $J = 7.5$ Hz, 1 H), 7.10–7.05 (m, 1 H), 6.89–6.84 (m, 1 H), 6.77 (d, $J = 8.1$ Hz, 1 H), 6.55 (d, $J = 15.9$ Hz, 1 H), 6.28–6.19 (m, 1 H), 5.10 (s, 1 H), 2.27–2.22 (m, 2 H), 1.09 (t, $J = 7.5$ Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 153.0, 135.3, 128.1, 127.9, 127.5, 123.2, 121.0, 115.8, 26.6, 13.8$; IR (KBr, cm^{-1}): $\nu = 3424, 2964, 2872, 1605, 1486, 1455, 1331, 1242, 1132, 1087, 971, 908, 879, 798, 750$; GC-MS (EI) calc. $C_{10}H_{12}O$ (M^+): 148. Found: 148.

(*E*)-4-Bromo-2-(but-1-enyl)phenol (2o). The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 8.13$ (s,1 H), 7.27–7.24 (m, 1 H), 7.04–7.03 (m, 1 H), 6.74 (d, $J = 8.4$ Hz, 1 H), 5.82–5.64 (m, 1 H), 5.09 (s, 1 H), 3.58–3.51 (m, 2 H), 1.24 (t, $J = 6.9$ Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 155.1, 133.7, 131.8, 130.8, 130.3, 118.9, 118.0, 111.7, 40.5, 13.9$; IR (KBr, cm^{-1}): $\nu = 3339, 2976, 2876, 1578, 1481, 1370, 1246, 1167, 1075, 993, 912, 819, 734$; HRMS calc. $C_{10}H_{11}BrO$ (M^+): 225.9993. Found: 225.9988.

(*E*)-2-(But-1-enyl)-4,6-di-*tert*-butylphenol (2p). The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.25 (d, J = 2.4 Hz, 1 H), 7.11 (d, J = 2.4 Hz, 1 H), 6.50 (d, J = 15.9 Hz, 1 H), 6.22–6.11 (m, 1 H), 5.25 (s, 1 H), 2.36–2.25 (m, 2 H), 1.46 (s, 9 H), 1.34 (s, 9 H), 1.16 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 150.0, 142.1, 137.3, 129.5, 124.0, 123.2, 122.8, 121.9, 31.7, 30.2, 30.0, 29.8, 26.6, 13.8; IR (KBr, cm^{-1}): v = 3355, 2960, 1599, 1468, 1368, 1217, 1061, 980, 910, 824, 737; HRMS calc. $C_{18}H_{28}O$ (M^+): 260.2140. Found: 260.2146.

(*E*)-3-(1-Phenylbut-2-enyl)phenol (3d). The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.30–7.10 (m, 6 H), 6.75 (d, J = 7.5 Hz, 7.5 Hz, 1 H), 6.65 (d, J = 6.3 Hz, 2 H), 5.92–5.84 (m, 1 H), 5.45–5.40 (m, 1 H), 5.19 (s, 1 H), 4.60 (d, J = 7.5 Hz, 1 H), 1.71 (d, J = 3.9 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 155.6, 146.2, 140.1, 132.9, 129.6, 128.6, 128.4, 127.1, 126.3, 121.0, 115.6, 113.2, 54.0, 18.0; IR (KBr, cm^{-1}): v = 3398, 3025, 1596, 1491, 1450, 1364, 1262, 1150, 1030, 970, 873, 779, 699; HRMS calc. $C_{16}H_{16}O$ (M^+): 224.1201. Found: 224.1208.

2-Methyl-4-phenyl-4*H*-chromene (4a). The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.31–7.14 (m, 5 H), 7.11–7.7.08 (m, 1 H), 6.94–6.89 (m, 2 H), 4.77 (d, J = 3.6 Hz, 1 H), 4.62 (d, J = 3.6 Hz, 1 H), 1.95 (s, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 147.3, 147.0, 129.9, 128.6, 128.3, 127.6, 126.5, 125.5, 123.2, 116.7, 116.4, 100.6, 41.0, 19.4; IR (KBr, cm^{-1}): v = 3426, 3027, 2921, 1699, 1584, 1486, 1453, 1382, 1320, 1229, 1168, 1105, 1075, 938, 836, 754, 700; HRMS calc. $C_{16}H_{14}O$ (M^+): 222.1045. Found: 222.1047.

2-Ethyl-3-phenylbenzofuran (5a). The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.91 (d, J = 2.5 Hz, 1 H), 7.79 (d, J = 2.5 Hz, 1 H), 7.50–7.47 (m, 3 H), 7.43–7.35 (m, 4 H), 2.90 (q, J = 7.5 Hz, 2 H), 1.37 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 158.0, 153.8, 139.7, 131.9, 128.9, 128.5, 127.8, 123.7, 122.7, 119.6, 116.7, 111.0, 20.4, 13.0; IR (KBr, cm^{-1}): v = 3423, 3061, 2975, 1618, 1590, 1497, 1424, 1378, 1310, 1244, 1191, 1155, 1076, 984, 908, 848, 733, 700; HRMS calc. $C_{16}H_{14}O$ (M^+): 222.1045. Found: 222.1055.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant no. 20628202 and 90813008) and support from the Chinese Academy of Sciences.

Notes and references

1 (*a*) T. Naota, H. Takaya and S.-I. Murahashi, *Chem. Rev.*, 1998, **98**, 2599–2660; (*b*) R. Uma, C. Crévisy and R. Grée, *Chem. Rev.*, 2003, **103**, 27–51; (*c*) N. Kuźnik and S. Krompiec, *Coordin. Chem. Rev.*, 2007, **251**, 222–233.

2 (*a*) L. Hintermanna and M. Schmitz, *Adv. Synth. Catal.*, 2008, **350**, 1469–1473; (*b*) T.-P. Loh, K.-T. Tan and Q.-Y. Hu, *Angew. Chem., Int. Ed.*, 2001, **40**, 2921–2922; (*c*) F. Gagosz, *Org. Lett.*, 2005, **7**, 4129–4132; (*d*) Y. Takada, S. Hayashi, K. Hirano, H. Yorimitsu and K. Oshima, *Org. Lett.*, 2006, **8**, 2515–2517; (*e*) K. R. Sawyer, E. A. Glascoe, J. F. Cahoon, J. P. Schlegel and C. B. Harris, *Organometallics.*, 2008, **27**, 4370–4379.

3 H. C. Brown and B. C. S. Rao, *J. Am. Chem. Soc.*, 1959, **81**, 6434–6437.

4 F. M. Menger, X. Y. Chen, S. Brocchini, H. P. Hopkins and D. Hamilton, *J. Am. Chem. Soc.*, 1993, **15**, 6600–6608.

5 (*a*) R. C. Drift, E. Bouwman and E. Drent, *J. Organomet. Chem.*, 2002, **650**, 1–24; (*b*) Shagufta, A. K. Srivastava and G. Panda, *Tetrahedron Lett.*, 2006, **47**, 1065–1070; (*c*) B. M. Trost and R. J. Kulawiec, *J. Am. Chem. Soc.*, 1993, **115**, 2027–2036 and references cited therein.

6 (*a*) A. Shimizu, T. Otsu and M. Imoto, *Bull. Chem. Soc. Jpn*, 1968, **41**, 953; (*b*) J. Blum and Y. Pickholtz, *Isr. J. Chem.*, 1969, **7**, 723.

7 (*a*) P. A. Tooley, L. W. Arndt and M. Y. Darensberg, *J. Am. Chem. Soc.*, 1985, **107**, 2422–2427; (*b*) H. Bricout, A. Mortreux and E. Monflier, *J. Organomet. Chem.*, 1998, **553**, 469–471; (*c*) N. Satyanarayana and M. Periasamy, *J. Organomet. Chem.*, 1987, **319**, 113–118; (*d*) C. Averbuj and M. S. Eisen, *J. Am. Chem. Soc.*, 1999, **121**, 8755–8759; (*e*) E. Shaviv, M. Botoshansky and M. S. Eisen, *J. Organomet. Chem.*, 2003, **683**, 165–180; (*f*) M. Arisawa, Y. Terada, M. Nakagawa and A. Nishida, *Angew. Chem., Int. Ed.*, 2002, **41**, 4732–4734; (*g*) T. C. Morrill and C. A. D'Souza, *Organometallics.*, 2003, **22**, 1626–1629; (*h*) I. R. Baxendale, A.-L. Lee and S. V. Ley, *Synlett*, 2002, 516–518.

8 H. Pines and W. M. Stalick, *Base-Catalyzed Reactions of Hydrocarbons and Related Compounds*, Academic Press Inc., New York, 1977.

9 M. Newcomb and R. S. Vieta, *J. Org. Chem.*, 1980, **45**, 4793–4795.

10 (*a*) Q. Cai, B. Zou and D. Ma, *Angew. Chem., Int. Ed.*, 2006, **45**, 1276–1279; (*b*) X. Xie, Y. Chen and D. Ma, *J. Am. Chem. Soc.*, 2006, **128**, 16050–16051; (*c*) D. Ma and Q. Cai, *Acc. Chem. Res.*, 2008, *DOI: 10.1021/ar8000298*; (*d*) K. C. Nicolaou, C. N. C. Boddy, S. Natarajan, T.-Y. Yue, H. Li, S. Brase and J. M. Ramanjulu, *J. Am. Chem. Soc.*, 1997, **119**, 3421–3422.

11 (*a*) T. Imahori, H. Ojima, Y. Yoshimura and H. Takahata, *Chem.–Eur. J.*, 2008, 10762–10771; (*b*) T. Imahori, H. Ojima, H. Tateyama, Y. Mihara and H. Takahata, *Tetrahedron Lett.*, 2008, **49**, 265–268; (*c*) R. M. Kanada, D. Itoh, M. Nagai, J. Niijima, N. Asai, Y. Mizui, S. Abe and Y. Kotake, *Angew. Chem., Int. Ed.*, 2007, **46**, 4350–4355; (*d*) G. S. Forman, A. E. McConnell, R. P. Tooze, W. J. Rensburg, W. H. Meyer, M. M. Kirk, C. L. Dwyer and D. W. Serfontein, *Organometallics.*, 2005, **24**, 4528–4542; (*e*) D. A. Clark, J. R. Clark and S. T. Diver, *Org. Lett.*, 2008, **10**, 2055–2058; (*f*) B. Schmidt and S. Nave, *Chem. Commun.*, 2006, 2489–2491.

12 M. J. Schultz and M. S. Sigman, *J. Am. Chem. Soc.*, 2006, **128**, 1460–1461.

13 (*a*) K. M. Gligorich, M. J. Schultz and M. S. Sigman, *J. Am. Chem. Soc.*, 2006, **128**, 2794–2795; (*b*) P. Laura, C. Massimiliano, P. Laura and L. Luigi, *Synth. Commun.*, 2006, **36**, 2203–2209; (*c*) D. J. Faulkner, *Nat. Prod. Rep.*, 2001, **18**, 1–49; (*d*) J. Dowdenand and J. Savović, *Chem. Commun.*, 2001, 37–38; (*e*) B. B. Snider, R. A. H. F. Hui and Y. S. Ku!karni, *J. Am. Chem. Soc.*, 1985, **107**, 2194–2196; (*f*) Y. Zhang and M. S. Sigman, *Org. Lett.*, 2006, **8**, 5557–5560.

14 Palladium blacks resulted from the side reaction of Wacker-type cyclizations.

15 (*a*) M. S. Chen and M. C. White, *J. Am. Chem. Soc.*, 2004, **126**, 1346–1347; (*b*) M. S. Chen, N. Prabagaran, N. A. Labenz and M. C. White, *J. Am. Chem. Soc.*, 2005, **127**, 6970–6971; (*c*) K. J. Fraunhoffer, N. Prabagaran, L. E. Sirois and M. C. White, *J. Am. Chem. Soc.*, 2006, **128**, 9032–9033; (*d*) J. H. Delcamp and M. C. White, *J. Am. Chem. Soc.*, 2006, **128**, 15076–15077; (*e*) K. J. Fraunhoffer and M. C. White, *J. Am. Chem. Soc.*, 2007, **129**, 7274–7276; (*f*) S. A. Reed and M. C. White, *J. Am. Chem. Soc.*, 2008, **130**, 3316–3318.

16 (*a*) J. M. Fan and Z. Y. Wang, *Chem. Commun.*, 2008, 5381–5383; (*b*) D. M. Schultz, J. A. Prescher, S. Kidd, D. M. Lewicka, D. E. Nicholsb and A. Monte, *Bioorg. Med. Chem.*, 2008, **16**, 6242–6251; (*c*) V. Fiandanese, D. Bottalico, G. Marchese and A. Punzi, *Tetrahedron.*, 2008, **64**, 53–60; (*d*) M. I. Naumov, S. A. Sutirin, A. S. Shavyrin, O. G. Ganina, I. P. Beletskaya, V. B. Rey, S. Combes, J. P. Finet and A. Y. Fedorov, *J. Org. Chem.*, 2007, **72**, 3293–3301; (*e*) M. Nagamochi, Y.-Q. Fang and M. Lautens, *Org. Lett.*, 2007, **9**, 2955–2958.

