Tetrahedron 65 (2009) 3404–3408

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Palladium(II) and palladium(0)-cocatalyzed ring opening and oxidation reactions of 2-(arylmethylene)cyclopropylcarbinols

Min Shi *, Guo-Qiang Tian, Jia Li

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, China

ARTICLE INFO

Article history:
Received 5 January 2009
Received in revised form 17 February 2009
Accepted 17 February 2009
Available online 21 February 2009

Keywords:
Palladium(II) and palladium(0)
2-(Arylmethylene)cyclopropylcarbinols
(2*E*,4*E*)-5-Arylpenta-2,4-dienals
Ring opening and oxidation reactions
Triethylamine
Triphenylphosphine

ABSTRACT

In the presence of Pd(II) acetate and triethylamine as well as triphenylphosphine, 2-(arylmethylene)cyclopropylcarbinols **1** underwent ring opening and oxidation reactions smoothly to deliver (2*E*,4*E*)-5-arylpenta-2,4-dienals **2** in toluene at 60 °C in moderate to good yields under ambient atmosphere. Mechanisms involved with an in situ generated Pd(0) species from Pd(II) and Et_3N or PPh_3 catalyzed isomerization of **1** to provide (*E*,*E*)-5-arylpenta-2,4-dien-1-ols **3** and following a Pd(II) catalyzed aerobic oxidation of **3** have been proposed on the basis of control and deuterium labeling experiments.

1. Introduction

Methylenecyclopropanes (MCPs) are highly strained and readily accessible compounds that can serve as useful building blocks for a variety of transformations in the presence of metal catalysts, Lewis acids or Brønsted acids under mild conditions.[1] 2-(Arylmethylene)cyclopropylcarbinols **1** are a new kind of MCPs bearing an additional hydroxymethyl group,[2] and as demonstrated by our group, can undergo a variety of transformations triggered by the nucleophilic hydroxyl group under milder conditions.[3] In view of this point, we hypothesized that the tethered hydroxyl group in **1** might undergo an oxidation reaction along with a ring-opening process in the presence of a transitional metal catalyst. Herein, we wish to report the palladium(II) and palladium(0)-cocatalyzed ring opening and oxidation reactions of 2-(arylmethylene)cyclopropylcarbinols **1** in the presence of triphenylphosphine and triethylamine to furnish (2*E*,4*E*)-5-arylpenta-2,4-dienals **2** in moderate to good yields under ambient atmosphere.

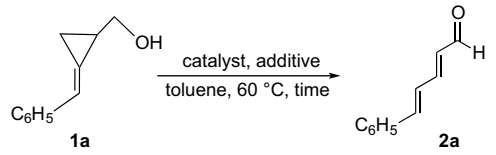
2. Results and discussion

The initial examination was performed by use of (*E*)-[2-(benzylidene)cyclopropyl]methanol **1a** (0.3 mmol) as the substrate upon treatment with $Pd(OAc)_2$ (0.03 mmol) and Et_3N at 60 °C in toluene, and we found that the starting materials **1a** disappeared rapidly and (2*E*,4*E*)-5-phenylpenta-2,4-dienal **2a** was obtained in 43% yield within 5.0 h under argon atmosphere (Table 1, entry 1). In the absence of Et_3N or using $PdCl_2$ as the catalyst, none of **2a** was formed under identical conditions (Table 1, entries 2 and 3). Using PPh_3 (0.18 mmol) as the ligand afforded **2a** in 42% yield within 5.0 h even in the absence of Et_3N under argon atmosphere (Table 1, entry 4). $Pd(PPh_3)_4$ [palladium(0)] did not promote this reaction and the coexistence of PPh_3 and Et_3N with $Pd(OAc)_2$ did not improve the yield of **2a** under the standard conditions (Table 1, entries 5 and 6). It should be noted that under oxygen atmosphere, no reaction occurred whether using $Pd(OAc)_2/PPh_3$ as the catalyst or even in the presence of Et_3N (Table 1, entries 7 and 8). Using $Pd(OAc)_2/PPh_3$ as the catalyst and $CuCl_2$ as the additive under oxygen atmosphere, no reaction occurred either (Table 1, entry 9). Other additives such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), Cs_2CO_3, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) did not produce **2a** under the standard conditions (Table 1, entries 10–14). When the reaction was carried out under ambient atmosphere (open to air), to our delight, we found that **2a** was obtained in 57% yield within 9.0 h using $Pd(OAc)_2$ as the catalyst in the presence of PPh_3 and Et_3N (Table 1, entry 15). Under this reaction conditions, we also examined various ligands for palladium acetate such as $AsPPh_3$, N-heterocyclic carbene (NHC) as well as pyridine in the presence of Et_3N and the results of these experiments are shown in entries 16–19. Only in the presence of pyridine, **2a** was formed in 38% yield. Using $Pd(OAc)_2$ as the catalyst under ambient atmosphere, we also examined a variety of additives such as $CuCl_2$, benzoquinone, 1,4-naphthoquinone, and iodosobenzene diacetate

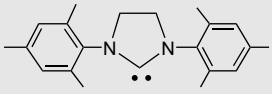
* Corresponding author. Fax: +86 21 64166128.
E-mail address: mshi@mail.sioc.ac.cn (M. Shi).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.02.028

Table 1
Optimization of the reaction conditions



1a **2a**

Entry[a]	Catalyst	Additive	Time (h)	Yield[b] (%)
				2a
1[c]	$Pd(OAc)_2$	Et_3N	4	43
2[c]	$Pd(OAc)_2$	—	11	—
3[c]	$PdCl_2$	Et_3N	12	—
4[c]	$Pd(OAc)_2/PPh_3$	—	5	42
5[c]	$Pd(PPh_3)_4/PPh_3$	—	24	—
6[c]	$Pd(OAc)_2/PPh_3$	Et_3N	6	42
7[d]	$Pd(OAc)_2/PPh_3$	—	7	—
8[d]	$Pd(OAc)_2/PPh_3$	Et_3N	30	—
9[d]	$Pd(OAc)_2/PPh_3$	$CuCl_2\cdot 2H_2O$	30	—
10[c]	$Pd(OAc)_2/PPh_3$	DBU	24	—
11[c]	$Pd(OAc)_2/PPh_3$	Cs_2CO_3	24	—
12[c]	$Pd(OAc)_2/PPh_3$	^tBuOK	24	—
13[c]	$Pd(OAc)_2/PPh_3$	AcONa	24	—
14[c]	$Pd(OAc)_2$	TMEDA	24	—
15[e]	***$Pd(OAc)_2/PPh_3$***	***Et_3N***	***9***	***57***
16[e]	$Pd(OAc)_2/AsPh_3$	Et_3N	10	—
17[e]	$Pd(OAc)_2$/NHC	Et_3N	19	—
				
18[e]	$Pd(OAc)_2$/Pyr	Et_3N	10	38
19[e]	$Pd(OAc)_2/PPh_3$	$CuCl_2\cdot 2H_2O$	30	—
20[e]	$Pd(OAc)_2$	BQ	11	—
21[e]	$Pd(OAc)_2$	1,4-NQ	11	—
22[e]	$Pd(OAc)_2/PPh_3$	$PhI(OAc)_2$	6	—
23[e]	$Pd(dba)_3/PPh_3$	Et_3N	6	—

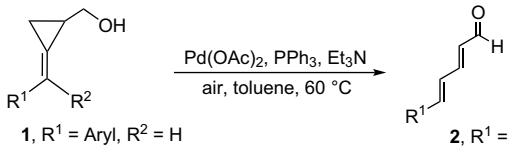
[a] All reactions were carried out with **1a** (0.30 mmol), catalyst (0.03 mmol), ligand (0.18 mmol), and additive (0.30 mmol, if needed) in l.0 mL of toluene at 60 °C.
[b] Isolated yields.
[c] The reactions were carried out under argon atmosphere and the dissolved oxygen in THF acted as an oxidant.
[d] The reactions were carried out under oxygen atmosphere.
[e] The reactions were carried out under ambient atmosphere.

in this reaction and found that none of the formation of **2a** could be identified (Table 1, entries 19–22). Using $Pd_2(dba)_3$ as the catalyst and PPh_3 as the ligand, no reaction occurred in the presence of Et_3N (Table 1, entry 23). In other solvents such as 1,2-dichloroethane, acetonitrile or tetrahydrofuran (THF), the reaction outcome is not as good as that carried out in toluene to give **2a** in <30% yields.

With these optimal conditions being identified, we next examined the scope of this transformation. Substrates **1** whether bearing electron-donating groups or electron-withdrawing groups on the benzene ring underwent this ring opening and oxidation reaction smoothly to provide the corresponding (2*E*,4*E*)-5-arylpenta-2,4-dienals **2** in moderate to good yields (Table 2, entries 1, 3–9). Only in the case of (*E*)-[2-(4-bromobenzylidene)cyclopropyl]methanol **1c**, none of the formation of the corresponding (2*E*,4*E*)-5-arylpenta-2,4-dienal **2** could be identified, presumably due to that the Pd(0) catalyst will promote an oxidative addition of bromobenzene moiety in **1c** and subsequently quench the active species in this process (Table 2, entry 2). Moreover, using (*Z*)-[2-(benzylidene)cyclopropyl]methanol (*Z*)-**1a** as the substrate did not deliver the same product under the standard conditions, presumably due to the steric hindrance (Table 2, entry 10).

To clarify the role of hydroxymethyl group in this transformation, a control experiment using deuterated MCP d_1-**1a** as the substrate was carried out under the standard conditions, and

Table 2
Palladium-catalyzed ring opening and oxidation of 2-(arylmethylene)-cyclopropylcarbinols **1**

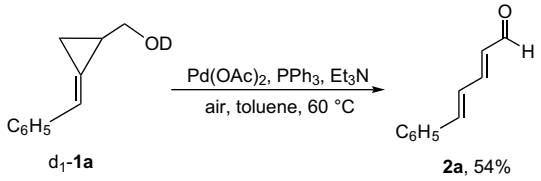


1, R^1 = Aryl, R^2 = H **2**, R^1 = Aryl

Entry[a]	R^1/R^2	Time (h)	Yield[b] (%)
			2
1	4-ClC_6H_4/H, **1b**	6	**2b**, 58
2	4-BrC_6H_4/H, **1c**	10	—
3	4-FC_6H_4/H, **1d**	7	**2d**, 42
4	3-$BnOC_6H_4$/H, **1e**	3	**2e**, 64
5	3-MeC_6H_4/H, **1f**	8	**2f**, 62
6	3,4,5-$(MeO)_3C_6H_2$/H, **1g**	3	**2g**, 67
7	2,5-$(MeO)_2C_6H_3$/H, **1h**	3	**2h**, 64
8	4-$MeOC_6H_4$/H, **1i**	3	**2i**, 65
9	4-MeC_6H_4/H, **1j**	6	**2j**, 57
10	H/C_6H_5, *Z*-**1a**	8	—

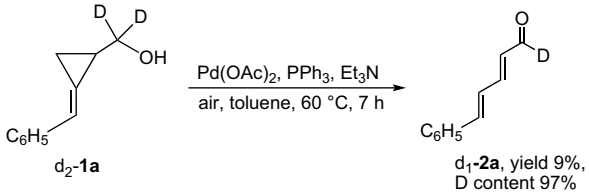
[a] All reactions were carried out with **1** (0.30 mmol), $Pd(OAc)_2$ (0.03 mmol), PPh_3 (0.18 mmol), and Et_3N (0.30 mmol) in l.0 mL of toluene under air atmosphere.
[b] Isolated yields.

we found that the corresponding product **2a** was obtained in 54% yield (Scheme 1). This result clearly suggested that the proton in hydroxyl group did not affect the reaction in this process. To learn more mechanistic insight on the hydroxymethyl group, we next carried out the deuterium labeling experiment by use of MCP d_2-**1a** as the substrate as shown in Scheme 2 under the standard reaction conditions. It was found that the reaction became sluggish to afford the corresponding d_1-**2a** in 9% yield with 97% D content (k_H/k_D=7.0), indicating that the oxidation of the methylene proton in MCPs **1** should be the rate-determining step.



d_1-**1a** **2a**, 54%

Scheme 1. Deuterium labeling experiment.

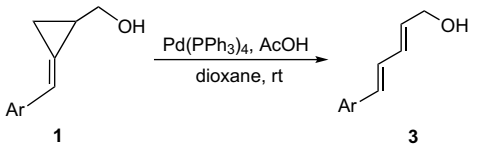


d_2-**1a** d_1-**2a**, yield 9%, D content 97%

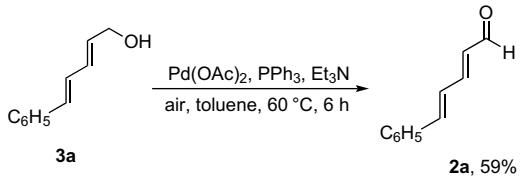
Scheme 2. Deuterium labeling experiment.

On the basis of above deuterium labeling experiment, we envisaged that product **2** might be produced via the oxidation of the in situ generated (*E*,*E*)-5-arylpenta-2,4-dien-1-ol **3** by air in the presence of Pd(II) catalyst. To determine the reaction pathway, we directly prepared the authentic sample (*E*,*E*)-5-phenylpenta-2,4-dien-1-ol **3a** using our previously reported Pd(0)-catalyzed isomerization of 2-(arylmethylene)cyclopropylcarbinol **1** in the presence of AcOH as shown in Scheme 3.[4] We confirmed that **3a** can be indeed transformed to **2a** under the standard reaction

conditions in 59% yield, suggesting that compound **3** should be the reaction intermediate (Scheme 4).

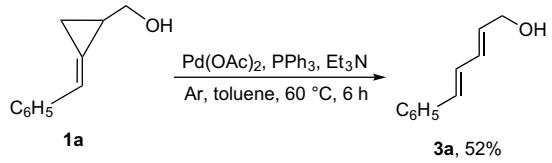


Scheme 3. Pd(0)-catalyzed isomerization of 2-(arylmethylene)cyclopropylcarbinol **1** in the presence of AcOH.



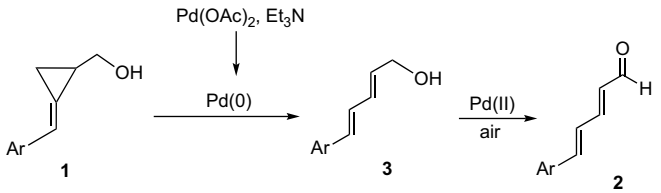
Scheme 4. Oxidation of dienol **3a** in the presence of $Pd(OAc)_2$ and air.

Next, we carried out the reaction of **1a** under rigorously deoxygenative condition by purging the dissolved molecular oxygen in toluene through bubbling with argon and replacing the reaction vessel with argon atmosphere under the standard reaction conditions. It was found that **3a** was obtained in 52% yield, indicating that **3a** is indeed formed during the reaction process (Scheme 5).



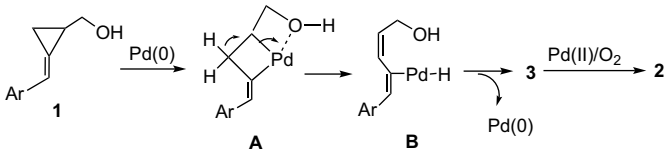
Scheme 5. Reactions of 2-(phenylmethylene)cyclopropylcarbinol **1a** in the presence of $Pd(OAc)_2$ under rigorously deoxygenative conditions.

On the basis of above control experiments, we can conclude that the formation of **2** proceeds through an in situ generated Pd(0) species from Pd(II) and Et_3N or PPh_3[5] catalyzed isomerization of MCP **1** to provide (*E*,*E*)-5-arylpenta-2,4-dien-1-ol **3** and following a Pd(II) catalyzed aerobic oxidation of **3** to furnish the final product **2** (Scheme 6).[6] Under oxygen atmosphere, Pd(0) species is hardly to be produced and therefore, the initial ring-opening process does not proceed at all. Furthermore, using Pd(0) as the catalyst, Pd(II) species should be in a low concentration in the reaction system, rendering that the oxidation of the formed 2,4-dien-1-ol **3** is impossible. Using $Pd(OAc)_2$ as the catalyst in the presence of Et_3N and PPh_3 under ambient atmosphere, Pd(0) can initiate the isomerization of **1** to give **3** and Pd(II) can catalyze the aerobic oxidation of **3** to produce **2**.



Scheme 6. Proposed process for the transformation of 2-(arylmethylene)-cyclopropylcarbinols **1** to dienals **2**.

The mechanism for the formation of **3** is shown in Scheme 7 on the basis of control and deuterium labeling experiments. Intermediate **A** is first formed from **1** and Pd(0), which gives intermediate **B** through anti-β-hydrogen elimination.[7] Reductive elimination of **B** produces **3** and regenerates Pd(0) species.



Scheme 7. Proposed mechanism for transformation of 2-(arylmethylene)-cyclopropylcarbinols **1** to dienals **2**.

The structure of products **2** was determined by ^1H, ^{13}C NMR spectroscopic data, MS, and HRMS analytic data as well as microanalyses. Moreover, their structures were unambiguously determined by X-ray diffraction of product **2g** and its CIF data have been summarized in Supplementary data (Fig. 1).[8]

In conclusion, we have developed a fairly efficient method for the ring opening and oxidation of 2-(arylmethylene)cyclopropylcarbinols **1** catalyzed by palladium(II) acetate in the presence of triethylamine as well as triphenylphosphine. Substrates whether bearing electron-donating groups or electron-withdrawing groups on the benzene ring undergo this transformation smoothly to provide (2*E*,4*E*)-5-arylpenta-2,4-dienals **2** in moderate to good yields under mild conditions. Mechanisms involved with an in situ generated Pd(0) species from Pd(II) and Et_3N or PPh_3 catalyzed isomerization of **1** to provide (*E*,*E*)-5-arylpenta-2,4-dien-1-ols **3** and following a Pd(II) catalyzed aerobic oxidation of **3** have been proposed on the basis of control and deuterium labeling experiments. Efforts are in progress to elucidate further mechanistic details of these reactions and to understand their scope and limitations.

3. Experimental section

3.1. General remarks

Melting point instrument is uncorrected. ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J*-values are in hertz. Mass spectra were recorded with a HP-5989 instrument. Dichloromethane was distilled from CaH_2 under Ar atmosphere. Some of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All of the reactions were monitored by TLC plates coated with Huanghai GF_{254} silica gel. Flash column chromatography was carried out using 200–300 mesh silica gel at increased pressure.

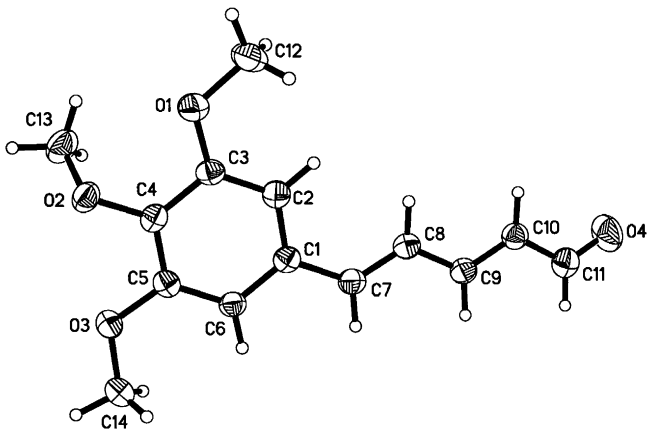


Figure 1. ORTEP drawing of **2g**.

3.2. General procedure for the preparation of products 2

Compound **1** (0.30 mmol), $Pd(OAc)_2$ (0.030 mmol), and PPh_3 (0.18 mmol) were weighed into an oven-dried Schlenk tube, which was charged with 1.0 mL of toluene. The reaction mixture was then stirred under ambient atmosphere. Then, 0.30 mmol of triethylamine (Et_3N) was added into the reaction mixture by a syringe. The mixtures were stirred and heated to 60 °C. After completion of the transformations monitored by TLC plates, the reaction mixture was directly transferred to silica gel column and eluted with mixtures of petroleum ether and ethyl acetate to afford the corresponding product **2**.

3.2.1. (2E,4E)-5-Phenylpenta-2,4-dienal

Product **2a**: R^1=C_6H_5; a yellow liquid; IR (film): ν 3339, 3028, 2822, 2741, 1954, 1674, 1619, 1591, 1492, 1449, 1417, 1389, 1266, 1200, 1153, 1117, 1012, 986, 880, 845, 737, 560 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 6.28 (dd, J=15.0, 8.1 Hz, 1H), 7.01–7.03 (m, 2H), 7.24–7.42 (m, 1H), 7.35–7.53 (m, 5H, ArH), 9.63 (d, J=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 126.0, 127.4, 128.8, 129.6, 131.4, 135.4, 142.3, 152.0, 193.5; MS (EI) m/z (%): 158 (M^+, 51.64), 130 (36.67), 129 (00.00), 128 (63.03), 115 (29.76), 77 (25.31), 51 (30.63); HRMS (EI) Calcd for $C_{11}H_{10}O$ 158.0732, found 158.0739.

3.2.2. (2E,4E)-5-(4-Chlorophenyl)penta-2,4-dienal

Product **2b**: R^1=4-ClC_6H_4; a yellow solid; mp 140–142 °C; IR (film): ν 3032, 2926, 2829, 2744, 1897, 1675, 1622, 1588, 1490, 1408, 1299, 1275, 1200, 1154, 1114, 1088, 1012, 989, 885, 836, 692, 583 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 6.28 (dd, J=15.0, 7.8 Hz, 1H), 6.97–6.99 (m, 2H), 7.21–7.30 (m, 1H), 7.34–7.37 (m, 2H, ArH), 7.43–7.45 (m, 2H, ArH), 9.63 (d, J=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 16.6, 128.5, 129.0, 131.8, 134.0, 135.2, 140.6, 151.4, 193.3; MS (EI) m/z (%): 192 (M^+, 41.40), 157 (30.03), 129 (100.00), 128 (65.36), 127 (46.14), 75 (18.56), 51 (22.82); HRMS (EI) Calcd for $C_{11}H_9ClO$ 192.0342, found 192.0348.

3.2.3. (2E,4E)-5-(4-Fluorophenyl)penta-2,4-dienal

Product **2d**: R^1=4-FC_6H_4; a yellow solid; mp 81–83 °C; IR (film): ν 3382, 3037, 2848, 2767, 1943, 1897, 1678, 1621, 1591, 1509, 1467, 1418, 1399, 1266, 1233, 1197, 1155, 1122, 1015, 989, 896, 841, 738, 552 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 6.27 (dd, J=15.3, 7.8 Hz, 1H), 6.87–7.97 (m, 2H), 7.02–7.11 (m, 2H, ArH), 7.22–7.30 (m, 1H), 7.47–7.52 (m, 2H, ArH), 9.62 (d, J=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 115.9, 116.1, 125.9 (d, J=2.2 Hz), 129.2 (d, J=8.7 Hz), 131.6 (d, J=16.0 Hz), 140.9 (d, J=2.2 Hz), 151.8, 163.4 (d, J=249.6 Hz), 193.5; MS (EI) m/z (%): 176 (M^+, 100.00), 175 (31.52), 148 (53.95), 147 (93.48), 146 (61.57), 133 (44.99), 127 (38.34), 75 (27.62), 51 (26.34); HRMS (EI) Calcd for $C_{11}H_9FO$ 176.0637, found 176.0627.

3.2.4. (2E,4E)-5-(3-(Benzyloxy)phenyl)penta-2,4-dienal

Product **2e**: R^1=3-$BnOC_6H_4$; a yellow liquid; IR (film): ν 3064, 3032, 2928, 2872, 1682, 1618, 1582, 1488, 1448, 1382, 1291, 1265, 1160, 1026, 989, 780, 738, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 5.80 (s, 2H, $PhCH_2O$), 6.26 (dd, J=15.3, 8.1 Hz, 1H), 6.96 (d, J=5.4 Hz, 2H), 7.10–7.45 (m, 10H), 9.60 (d, J=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 70.0, 113.5, 116.1, 120.5, 126.4, 127.4, 128.1, 128.6, 129.9, 131.6, 136.6, 136.9, 142.2, 152.0, 159.1, 193.6; MS (EI) m/z (%): 264 (M^+, 2.05), 149 (6.35), 92 (8.98), 91 (100.00), 65 (18.18), 57 (6.52), 51 (4.82), 43 (5.20), 41 (5.16); HRMS (EI) Calcd for $C_{18}H_{16}O_2$ 264.1150, found 264.1140.

3.2.5. (2E,4E)-5-m-Tolylpenta-2,4-dienal

Product **2f**: R^1=3-$CH_3C_6H_4$; a yellow liquid; IR (film): ν 3026, 2922, 2855, 2737, 1856, 1674, 1619, 1485, 1455, 1416, 1380, 1266, 1154, 1119, 1011, 986, 874, 779, 737, 570 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.38 (s, 3H, CH_3), 6.26 (dd, J=15.6, 7.8 Hz, 1H), 6.99–7.01 (m, 2H), 7.16–7.18 (m, 1H), 7.23–7.32 (m, 4H, ArH), 9.62 (d, J=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 21.2, 124.7, 125.9, 128.0, 128.7, 130.4, 131.3, 135.4, 138.4, 152.1, 193.5; MS (EI) m/z (%): 172 (M^+, 36.98), 157 (12.82), 143 (32.90), 129 (100.00), 128 (83.34), 115 (35.17), 91 (22.70), 65 (28.01), 63 (28.01), 51 (32.88); HRMS (EI) Calcd for $C_{12}H_{12}O$ 172.0888, found 172.0890.

3.2.6. (2E,4E)-5-(3,4,5-Trimethoxyphenyl)penta-2,4-dienal

Product **2g**: R^1=3,4,5-$(CH_3O)_3C_6H_2$; a yellow solid; mp 119–121 °C; IR (film): ν 2999, 2939, 2925, 2828, 2745, 2722, 1946, 1671, 1615, 1578, 1504, 1467, 1420, 1392, 1339, 1246, 1207, 1149, 1123, 1006, 988, 882, 843, 734, 574 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 3.89 (s, 3H, CH_3O), 3.92 (s, 6H, CH_3O), 6.28 (dd, J=15.0, 8.1 Hz, 1H), 6.74 (s, 2H, ArH), 6.87–6.99 (m, 2H), 7.18–7.31 (m, 1H), 9.63 (d, J=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 55.9, 60.7, 104.4, 125.4, 130.98, 131.02, 139.4, 142.2, 151.9, 153.2, 193.4; MS (EI) m/z (%): 248 (M^+, 100.00), 233 (41.19), 219 (55.60), 188 (52.87), 145 (26.44), 115 (21.97), 91 (18.57), 65 (15.28). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.54; H, 6.47.

3.2.7. (2E,4E)-5-(2,5-Dimethoxyphenyl)penta-2,4-dienal

Product **2h**: R^1=2,5-$(CH_3O)_2FC_6H_3$; a yellow solid; mp 73–75 °C; IR (film): ν 3001, 2944, 2835, 1676, 1612, 1493, 1466, 1428, 1293, 1227, 1180, 1156, 1123, 1046, 1021, 988, 804, 717 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 3.80 (s, 3H, CH_3O), 3.84 (s, 3H, CH_3O), 6.23 (dd, J=15.0, 7.8 Hz, 1H), 6.82–6.90 (m, 2H), 6.96–7.07 (m, 2H), 7.25 (d, J=15.0 Hz, 1H), 7.35 (d, J=15.6 Hz, 1H), 9.58 (d, J=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 55.6, 56.0, 112.1, 112.2, 116.3, 125.0, 126.7, 131.0, 137.4, 152.1, 153.1, 153.4, 193.7; MS (EI) m/z (%): 218 (M^+, 100.00), 189 (34.71), 159 (47.82), 144 (49.41), 115 (69.02), 91 (33.51), 77 (45.12), 55 (40.00); HRMS (EI) Calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0935.

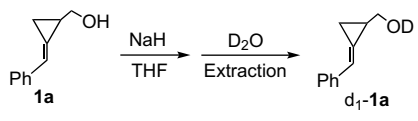
3.2.8. (2E,4E)-5-(4-Methoxyphenyl)penta-2,4-dienal

Product **2i**: R^1=4-$CH_3OC_6H_4$; a yellow solid; mp 80–82 °C; IR (film): ν 3053, 3034, 2979, 2845, 2753, 1895, 1670, 1622, 1511, 1462, 1423, 1402, 1256, 1197, 1177, 1154, 1113, 1017, 990, 839, 808, 737, 560 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 3.85 (s, 3H, CH_{3O}), 6.24 (dd, J=15.0, 8.1 Hz, 1H), 6.84–7.01 (m, 3H), 7.22–7.31 (m, 2H, ArH), 7.44–7.48 (m, 2H, ArH), 9.60 (d, J=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 55.2, 114.2, 123.9, 128.2, 129.0, 130.3, 142.2, 152.7, 160.8, 193.5; MS (EI) m/z (%): 188 (M^+, 100.00), 159 (41.60), 144 (44.96), 129 (29.94), 117 (25.12), 115 (51.39), 91 (24.80), 63 (22.37), 51 (18.46); HRMS (EI) Calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0834.

3.2.9. (2E,4E)-5-p-Tolylpenta-2,4-dienal

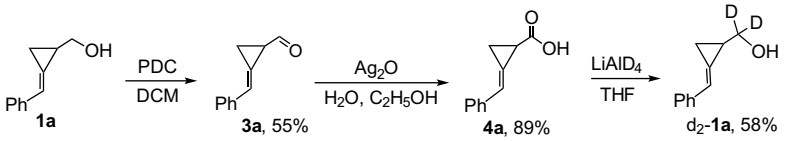
Product **2j**: R^1=4-$CH_3C_6H_4$; a yellow solid; mp 96–98 °C; IR (film): ν 3050, 3006, 2981, 2847, 2767, 1915, 1667, 1618, 1512, 1453, 1420, 1398, 1266, 1198, 1184, 1155, 1122, 1018, 994, 836, 810, 738, 552 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.38 (s, 3H, CH_3), 6.25 (dd, J=15.3, 8.1 Hz, 1H), 6.91–7.04 (m, 2H), 7.19 (d, J=7.8 Hz, 2H, ArH), 7.23–7.31 (m, 1H), 7.41 (d, J=7.8 Hz, 2H, ArH), 9.61 (d, J=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 21.3, 125.1, 127.4, 129.5, 130.9, 132.7, 139.9, 142.5, 152.4, 193.5; MS (EI) m/z (%): 172 (M^+, 55.44), 157 (17.10), 143 (30.89), 129 (100.00), 128 (83.60), 127 (25.60), 115 (33.57), 91 (14.09), 77 (13.58), 65 (13.82), 51 (14.69); HRMS (EI) Calcd for $C_{11}H_{12}O$ 172.0888, found 172.0887.

3.2.10. Synthesis of d_1-**1a**



Compound d_1-**1a**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.76–0.88 (m, 1H), 1.55–1.63 (m, 1H), 1.77–1.83 (m, 1H), 3.49 (dd, J=7.2, 11.1 Hz, 1H), 3.60 (dd, J=6.3, 11.1 Hz, 1H), 6.75 (d, J=1.5 Hz, 1H), 7.12–7.17 (m, 1H, ArH), 7.24 (d, J=7.2 Hz, 2H, ArH), 7.45 (d, J=7.2 Hz, 2H, ArH).

*3.2.11. Synthesis of d_2-**1a***



3.2.12. (E)-2-Benzylidenecyclopropanecarboxylic acid

Compound **4a**: a colorless solid; mp 133–135 °C; IR (film): ν 3054, 3028, 2920, 2843, 1681, 1448, 1369, 337, 1235, 1019, 940, 909, 867, 772, 739, 690, 666 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.96–2.02 (m, 1H), 2.15–2.18 (m, 1H), 2.33–2.35 (m, 1H), 6.84 (s, 1H), 7.22–7.27 (m, 1H, ArH), 7.33–7.36 (m, 2H, ArH), 7.49 (d, J=7.2 Hz, 2H, ArH), 11.34 (br s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.4, 15.9, 120.1, 122.6, 127.1, 127.7, 136.3, 179.1; MS (EI) m/z (%):174 (M^+, 14.38), 130 (15.39), 119 (100.009), 128 (64.65), 127 (21.78), 115 (21.66), 91 (24.28), 44 (62.77), 43 (27.44); HRMS Calcd for $C_{11}H_{10}O$ 174.0681, found 174.0686.

Compound d_1-**2a**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 6.27 (d, J=14.7 Hz, 1H), 7.00–7.02 (m, 2H), 7.23–7.32 (m, 2H), 7.35–7.42 (m, 3H, ArH), 7.50–7.53 (m, 2H, ArH).

Acknowledgements

We thank the Shanghai Municipal Committee of Science and Technology (06XD14005, 08dj1400100-2), National Basic Research Program of China (973)-2009CB825300, and the National Natural Science Foundation of China (20872162, 20672127, 20821002, and 20732008).

Supplementary data

The spectroscopic data (^{1}H, ^{13}C spectroscopic data), HRMS of the compounds shown in Tables 1 and 2 and the X-ray crystal data of **2g** along with the detailed description of experimental procedures are included in the Supplementary data. This material is available free of charge via the Internet at Website. Supplementary data associated with this article can be found in the online version at, doi:10.1016/j.tet.2009.02.028.

References and notes

1. For reviews, see: (a) Binger, P.; Büch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77–151; (b) Goti, A.; Cordero, F. M.; Brandi, A. *Top. Curr. Chem.* **1996**, *178*, 1–91; (c) Brandi, A.; Cicchi, S.; Cordero, F. M.; Goti, A. *Chem. Rev.* **2003**, *103*, 1213–1270; (d) Nakamura, E.; Yamago, S. *Acc. Chem. Res.* **2002**, *35*, 867–877; (e) Nakamura, I.; Yamamoto, Y. *Adv. Synth. Catal.* **2002**, *344*, 111–129; (f) Rubin, M.; Rubina, M.; Gevorgyan, V. *Chem. Rev.* **2007**, *107*, 3117–3179; (g) Shao, L.-X.; Shi, M. *Curr. Org. Chem.* **2007**, *11*, 1135–1153.
2. For the preparation of 2-(arylmethylene)cyclopropylcarbinols. See: (a) Turcant, A.; Corre, L. M. *Tetrahedron Lett.* **1976**, *17*, 1277–1280; (b) Corre, L. M.; Hercouet, A.; Bessieres, B. *J. Org. Chem.* **1994**, *59*, 5483–5484.
3. (a) Tian, G.-Q.; Shi, M. *Org. Lett.* **2007**, *9*, 2405–2408; (b) Tian, G.-Q.; Shi, M. *Org. Lett.* **2007**, *9*, 4917–4920; (c) Shao, L.-X.; Qi, M.-H.; Shi, M. *Tetrahedron Lett.* **2008**, *49*, 165–168; (d) Shi, M.; Tian, G.-Q. *Tetrahedron Lett.* **2006**, *47*, 8059–8062; (e) Tian, G.-Q.; Li, J.; Shi, M. *J. Org. Chem.* **2008**, *73*, 673–677; (f) Tian, G.-Q.; Yuan, Z.-L.; Zhu, Z.-B.; Shi, M. *Chem. Commun.* **2008**, 2668–2670; (g) Qi, M.-H.; Shao, L.-X.; Shi, M. *Synthesis* **2007**, 3567–3573; (h) Shi, M.; Jiang, M.; Liu, L.-P. *Org. Biomol. Chem.* **2007**, *5*, 438–440.
4. Shi, M.; Wang, B.-Y.; Shao, L.-X. *Synlett* **2007**, 909–912.
5. For the generation of Pd(0) species form Pd(II) complex in the presence of PPh_3 or Et_3N. (a) Bates, R. W.; Boonsombat, J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 654–656; (b) Batey, R. A.; Shen, M.; Lough, A. J. *Org. Lett.* **2002**, *4*, 1411–1414; (c) Hegedus, L. S.; Allen, G. F.; Waterman, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 2674–2676.
6. For the oxidation of allylic alcohol with Pd(II) in the presence of oxygen. Peterson, K. P.; Larock, R. C. *J. Org. Chem.* **1998**, *63*, 3185–3189.
7. Liu, G.; Stahl, S. S. *J. Am. Chem. Soc.* **2007**, *129*, 6328–6335 and references therein.
8. The crystal data of **2g** have been deposited in CCDC with number 281635. Empirical formula: $C_{14}H_{16}O_4$; formula weight: 248.27; crystal color, habit: colorless, prismatic; crystal dimensions: 0.517×0.505×0.397 mm; crystal system: monoclinic; lattice type: primitive; lattice parameters: a=10.869(2) Å, b=14.124(3) Å, c=17.504(3) Å, α=90°, β=103.901(3)°, γ=90°, V=2608.5(9) Å^3; space group: $P2(1)/c$; Z=8; D_{calcd}=1.264 g/cm^3; F_{000}=1056; diffractometer: Rigaku AFC7R; residuals: R; wR: 0.0660, 0.1582.