Organic & Biomolecular Chemistry

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2014, **12**, 3493

Direct olefination of benzaldehydes into 1,3-diarylpropenes *via* a copper-catalyzed heterodomino Knoevenagel-decarboxylation-Csp^3-H activation sequence†

Yaping Zhao, Lu Sun, Tieqiang Zeng, Jiayi Wang, Yanqing Peng and Gonghua Song*

Received 21st January 2014,
Accepted 26th March 2014

DOI: 10.1039/c4ob00155a

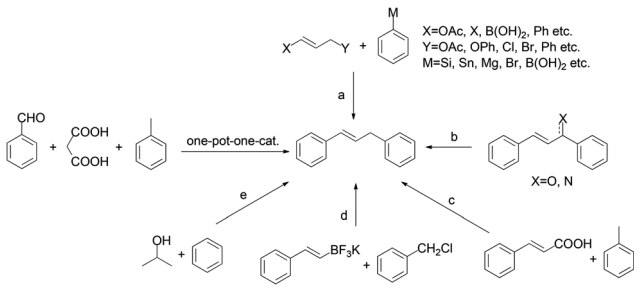
www.rsc.org/obc

Copper-catalyzed direct olefination of benzaldehydes into 1,3-diarylpropenes by a novel domino Knoevenagel-decarboxylation-Csp^3-H activation sequence is reported. This method provides a concise and effective route toward the synthesis of unsymmetrical 1,3-diarylpropene derivatives.

Introduction

In the last two decades, there has been increasing interest in the development of more efficient and environmentally friendly methods for chemical syntheses.[1] One of the related research areas is the development of sequential formation of multiple C–C bonds in one pot.[2] In general, these processes eliminate intermediate recovery steps, thereby considerably decreasing the amount of waste generated.[3] For the past few years, a number of notable domino sequence reactions involving decarboxylation have been developed using simpler substrates like benzaldehydes.[4] However, to the best of our knowledge, examples of utilizing benzaldehydes for one pot methylenation coupling into 1,3-diarylpropenes have not been explored.

Furthermore, 1,3-diarylpropenes are often known to be privileged structures or key intermediates in the synthesis of natural products and the development of biologically active compounds.[5] Traditionally, strategies toward the syntheses of 1,3-diarylpropenes include allylic arylation/alkenylation (Scheme 1, route a),[6] allylic selective defunctionalization (route b),[7] decarboxylation of cinnamic acids (route c),[8] cross-coupling reactions of potassium alkenyltrifluoroborates with benzyl halides (route d)[9] and alkylation of benzene (route e).[10] However, most of the above methods have to bear disadvantages such as limited substrates, multistep procedures and necessary prefunctionalization. Encouraged by the ecological and economic advantages of domino reactions, we wish to report herein the synthesis of unsymmetrical 1,3-diarylpropenes through a domino Knoevenagel-decarboxylation-Csp^3-H activation sequence (Scheme 1).



Scheme 1 Strategies toward syntheses of 1,3-diarylpropenes.

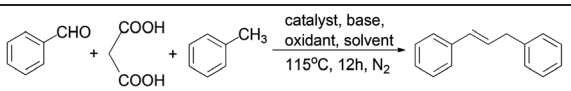
Results and discussion

We started our research by using benzaldehyde (**1a**) as the standard substrate. The combination of malonic acid, CuO, di-*t*-butyl peroxide (DTBP) and piperidine in toluene at 115 °C (oil bath temperature, unless otherwise noted) gave the desired product 1,3-diarylpropenes (**2a**) in 68% GC yield within 12 h (Table 1, entry 1). Other copper catalysts (entries 2 and 3), oxidants (entry 6), bases (entry 7), or solvents (entry 8) decreased the yield.[11] Employment of Fe_3O_4 or ferrocene resulted in a dramatic decrease in yield (entries 4 and 5). Modifying the quantity of oxidant, base, catalyst and time did not afford better results (entries 9–11 and 15).[11] Higher yields were obtained when the reaction was carried out at an elevated temperature. Particularly, trace amounts of the target product were detected below the boiling point of toluene (entry 12) and a good result in 77% GC yield was achieved at 125 °C

Shanghai Key Laboratory of Chemical Biology, Institute of Pesticides and Pharmaceuticals, East China University of Science and Technology, Shanghai 200237, P.R. China. E-mail: ghsong@ecust.edu.cn

†Electronic supplementary information (ESI) available: Detailed experimental procedures, characterization data, copies of ^{1}H-NMR and ^{13}C-NMR spectra. See DOI: 10.1039/c4ob00155a

Table 1 Optimization of the conditions for copper catalyzed domino olefination of benzaldehydes into 1,3-diarylpropenes[a]



Entry	Catalyst	Oxidant	Base	Solvent	Yield[b] (%)
1	CuO	DTBP	Piperidine	Toluene	68
2	$CuBr_2$	DTBP	Piperidine	Toluene	53
3	CuI	DTBP	Piperidine	Toluene	50
4	Fe_3O_4	DTBP	Piperidine	Toluene	30
5	Ferrocene	DTBP	Piperidine	Toluene	Trace
6	CuO	TBHP	Piperidine	Toluene	42
7	CuO	DTBP	DBU	Toluene	24
8	CuO	DTBP	Piperidine	DMSO	11
9[c]	CuO	DTBP	Piperidine	Toluene	69
10[d]	CuO	DTBP	Piperidine	Toluene	8
11[e]	CuO	DTBP	Piperidine	Toluene	33
12[f]	CuO	DTBP	Piperidine	Toluene	NR
13[g]	**CuO**	**DTBP**	**Piperidine**	**Toluene**	77
14[h]	CuO	DTBP	Piperidine	Toluene	49
15[i]	CuO	DTBP	Piperidine	Toluene	55
16	—	DTBP	Piperidine	Toluene	11

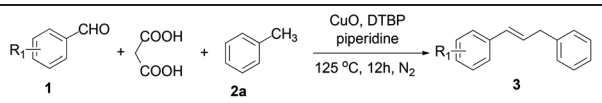
[a] Catalytic conditions: benzaldehyde (0.3 mmol), malonic acid (0.5 mmol), toluene (0.5 mmol), solvent (2 mL), base (0.2 mmol), catalyst (20 mol%), oxidant (4 equiv.), 115 °C, 12 h, N_2 atmosphere. [b] GC yields were given using dodecane as the internal standard. [c] The reaction was conducted within 24 h. [d] 0.1 mmol of piperidine was used. [e] 2 equiv. of DTBP was used. [f] The reaction was conducted at 105 °C under a N_2 atmosphere. [g] The reaction was conducted at 125 °C under a N_2 atmosphere. [h] The reaction was conducted at 125 °C under an air atmosphere. [i] 10 mol% of CuO was used.

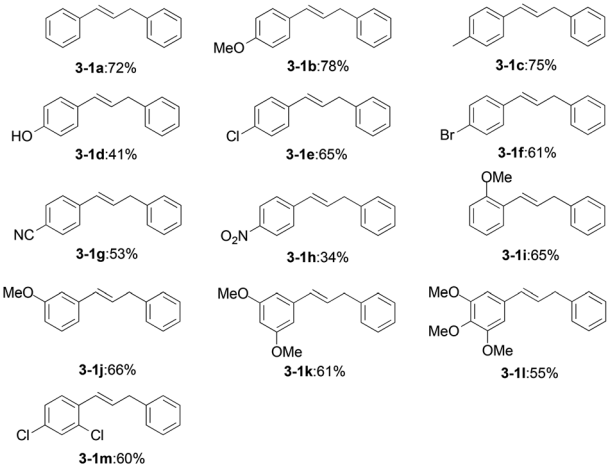
(entry 13). However, when the reaction was conducted under an air atmosphere, the yield decreased to 49% (entry 14). A control experiment showed that the domino reaction was poorly efficient when the reaction was carried out in the absence of a copper catalyst (entry 16).

Under the optimized reaction conditions, the allylation of a variety of benzaldehyde derivatives was examined. As shown in Table 2, benzaldehydes bearing a variety of substituents were found to afford exclusively 1,3-diarylpropenes in moderate to good yields (**3-1a–3-1h**). Obviously, an electron-donating group at the *para*-position, such as the methoxy substituent in **3-1b**, afforded a higher yield compared with an electron-withdrawing group, such as a cyano group substituent in **3-1g**. *para*-Substituted benzaldehydes (**3-1b**) gave a superior product yield compared to that of *ortho*- or *meta*-substituted benzaldehydes (**3-1i** and **3-1j**). The domino reaction with 4-nitrobenzaldehyde (**3-1h**) was also successful. OH-, Cl- and Br-substituted compounds (**3-1d**, **3-1e** and **3-1f**) were also well tolerated. It turned out that multiple substituent groups (**3-1k**, **3-1l** and **3-1m**) would decrease the reaction efficiency.

Subsequently, we surveyed the substrate scope of benzylic hydrocarbons (Table 3). All kinds of xylenes and mesitylene (**3-2b–3-2e**) offered the mono-coupling products in moderate yields. The toluenes substituted by electron-withdrawing groups (**3-2f**, **3-2g** and **3-2h**) were less reactive than xylenes (**3-2b** and **3-2d**).

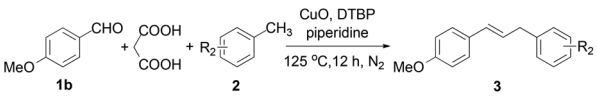
Table 2 Substrate scope of the copper-catalyzed domino reaction of different benzaldehydes **1** with **2a**[a,b]

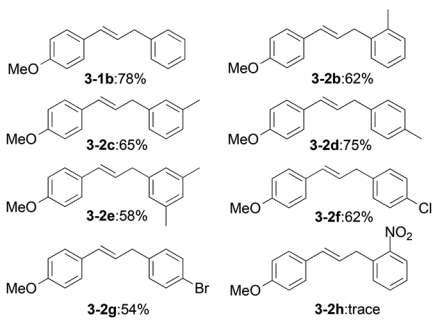




[a] Catalytic conditions: benzaldehydes (**1**) (0.3 mmol), malonic acid (0.5 mmol), toluene (**2a**) (2 mL), piperidine (0.2 mmol), CuO (20 mol %), DTBP (4 equiv.), 125 °C, 12 h, N_2 atmosphere. [b] Isolated yields based on benzaldehyde.

Table 3 Substrate scope of the copper-catalyzed domino reaction of 4-methoxybenzaldehyde (**1b**) with **2**[a,b]



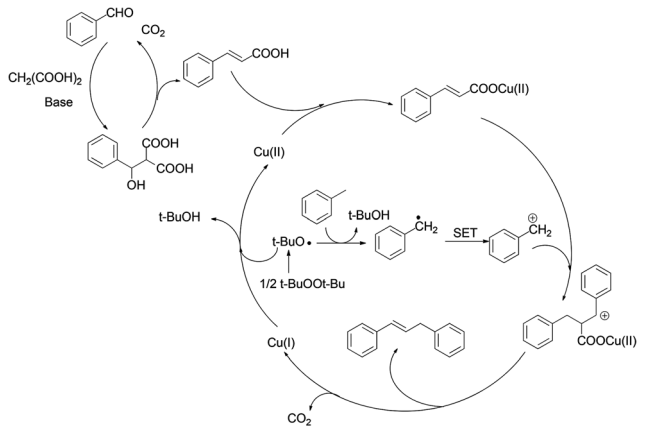


[a] Catalytic conditions: 4-methoxybenzaldehyde (**1b**) (0.3 mmol), malonic acid (0.5 mmol), benzylic hydrocarbons (**2**) (2 mL), piperidine (0.2 mmol), CuO (20 mol%), DTBP (4 equiv.), 125 °C, 12 h, N_2 atmosphere. [b] Isolated yields based on benzaldehyde.

Considering the effects of electronic parameters on the reaction, it was found that the yield roughly decreased with the increase of Hammett constant (σ) values of the substituents on benzaldehyde. For example, the yield of **3-1b** (p-CH_3O, σ_p = −0.27) is 78%, and the yield of **3-1g** (p-CN, σ_p = 0.66) is 53% as shown in Table 4. The exceptional substrates are p-hydroxyl

Table 4 Relationship between Hammett constant values (σ) of the substituents on benzaldehyde and domino reaction yields

Substituents on benzaldehyde	σ	Yield
p-OH	−0.37	41%
p-OCH3	−0.27	78%
p-CH3	−0.17	75%
m,*m*,*p*-tri-OCH3	−0.03	55%
p-H	0	72%
o-OCH3	0.04	65%
m-OCH3	0.12	66%
p-Cl	0.23	65%
p-Br	0.23	61%
m,*m*-di-OCH3	0.24	61%
o,*p*-di-Cl	0.63	60%
p-CN	0.66	53%
p-NO2	0.78	34%



Scheme 2 Proposed mechanism.

benzaldehyde and *m*,*m*,*p*-tri-methoxyl benzaldehyde, which might be dominated by other factors such as hydrogen bonds and steric hindrance. However, a similar approach for benzylic hydrocarbons is not applicable.

Based on previous observations and literature reports,[4h,8] we proposed a plausible catalytic cycle (Scheme 2). The reaction involves a domino anionic-metal catalyzed pathway,[2a,4h] wherein an incipient cinnamic acid (formed *in situ* from the K-D reaction) continuously undergoes copper catalyzed cross coupling and decarboxylation, leading to 1,3-diarylpropenes in one pot.[8]

Conclusions

In summary, we have developed the first copper-catalyzed one step direct olefination of benzaldehydes into 1,3-diarylpropenes *via* a novel domino Knoevenagel-decarboxylation-Csp^3-H activation sequence. The unsymmetrical 1,3-diarylpropenes were obtained in moderate to good yields. All of the substrates were economical, simple and readily available.

Experimental

General information

All reactions were carried out under an N_2 atmosphere. CuO was purchased from Aladdin-reagent with high purity (99.5%). All reagents were used as supplied without further purification and drying. Flash column chromatography was performed over silica gel (48–75 μm) and reactions were monitored by thin layer chromatography (TLC) using UV light (254 nm). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer using d_6-DMSO as a solvent and tetramethylsilane as an internal standard (s = singlet, d = doublet, t = triplet, m = multiplet). MS analyses were performed on an Agilent 5975 GC-MS instrument (EI). HRMS analyses were performed on a Waters Micromass GCT instrument (EI).

General procedures for copper-catalyzed allylation of benzaldehydes

Malonic acid (52 mg, 0.5 mmol) and CuO (4.8 mg, 0.06 mol) were added into a 10 mL Schlenk flask. Then toluene (2 mL), benzaldehyde (31 μl, 0.3 mmol), DTBP (120 μl, 1.2 mmol), and piperidine (20 μl, 0.2 mmol) were added at room temperature. The reaction vessel was purged with N_2 three times. The mixture was stirred at 125 °C for 12 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 and water. The organic phase was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether–ethyl acetate = 100 : 1) to afford the corresponding product.

(*E*)-1-1,3-Diphenylpropene (3-1a). Prepared according to the general procedure. A faint yellow liquid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.38–7.41 (m, 2H), 7.24–7.33 (m, 6H), 7.18–7.22 (m, 2H), 6.48 (d, J = 15.9 Hz, 1H), 6.46–6.38 (m, 1H), 3.52 (d, J = 5.8 Hz, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 140.52, 137.50, 130.99, 129.88, 129.02, 128.96, 128.92, 127.58, 126.53, 126.44, 39.06. GC/MS (*m*/*z*): $[M]^+$ calcd for $C_{15}H_{14}$, 194.1; found, 194.1. HRMS (EI^+) calcd for $C_{15}H_{14}$ $[M^+]$: 194.1095. Found: 194.1096.

(*E*)-1-(4-Methoxyphenyl)-3-phenylpropene (3-1b). Prepared according to the general procedure. A faint yellow liquid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.35–7.18 (m, 7H), 6.87 (d, J = 8.8 Hz, 2H), 6.42 (d, J = 15.8 Hz, 1H), 6.30–6.22 (m, 1H), 3.73 (s, 3H), 3.49 (d, J = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 158.97, 140.80, 130.46, 130.17, 128.91, 128.89, 127.63, 127.43, 126.46, 114.43, 55.51, 39.05. GC/MS (*m*/*z*): $[M]^+$ calcd for $C_{16}H_{16}O$, 224.1; found, 224.1. HRMS (EI^+) calcd for $C_{16}H_{16}O$ $[M^+]$: 224.1201. Found: 224.1202.

(*E*)-1-(4-Methyl)-3-phenylpropene (3-1c). Prepared according to the general procedure. A faint green solid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.33–7.18 (m, 7H), 7.11 (d, J = 7.9 Hz, 2H), 6.44 (d, J = 15.9 Hz, 1H), 6.39–6.32 (m, 1H), 3.50 (d, J = 6.4 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 140.65, 136.79, 134.73, 130.84, 129.59, 128.93, 128.90, 128.77, 126.49, 126.36, 39.06, 21.19. GC/MS (*m*/*z*): $[M]^+$ calcd

for $C_{16}H_{16}$, 208.1; found, 208.1. HRMS (EI^+) calcd for $C_{16}H_{16}$ [M^+]: 208.1252. Found: 208.1251.

(*E*)-4-(3-Phenylprop-1-enyl)phenol (3-1d). Prepared according to the general procedure. A faint yellow solid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 9.48 (s, 1H), 7.38 (s, 1H), 7.20 (d, J = 8.5 Hz, 3H), 6.75 (d, J = 8.5 Hz, 3H), 6.66 (dd, J = 17.7, 11.0 Hz, 1H), 5.78–5.55 (m, 2H), 5.07 (d, J = 11.2 Hz, 1H), 3.56 (dd, J = 15.9, 9.3 Hz, 1H), 3.11 (dd, J = 15.9, 8.1 Hz, 1H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 164.36, 162.50, 141.74, 136.89, 135.27, 132.84, 132.02, 127.58, 120.43, 116.28, 113.90, 89.25, 42.20. GC/MS (m/z): [M^+] calcd for $C_{15}H_{14}O$, 210.1; found, 210.1. HRMS (EI^+) calcd for $C_{15}H_{14}O$ [M^+]: 210.1045. Found: 210.1046.

(*E*)-1-(4-Chlorophenyl)-3-phenylpropene (3-1e). Prepared according to the general procedure. A faint yellow liquid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.43 (d, J = 8.6 Hz, 2H), 7.35–7.29 (m, 4H), 7.26–7.19 (m, 3H), 6.48–6.46 (m, 2H), 3.52 (d, J = 4.5 Hz, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 140.31, 136.46, 131.91, 130.97, 129.71, 128.96, 128.93, 128.14, 126.57, 39.01. GC/MS (m/z): [M^+] calcd for $C_{15}H_{13}Cl$, 228.1; found, 228.1. HRMS (EI^+) calcd for $C_{15}H_{13}Cl$ [M^+]: 228.0706. Found: 228.0706.

(*E*)-1-(4-Bromophenyl)-3-phenylpropene (3-1f). Prepared according to the general procedure. A colorless liquid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.48 (d, J = 8.5 Hz, 2H), 7.38–7.19 (m, 7H), 6.49–6.42 (m, 2H), 3.51 (d, J = 5.3 Hz, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 140.27, 136.81, 131.88, 131.08, 129.78, 128.97, 128.93, 128.49, 126.58, 120.44, 39.03. GC/MS (m/z): [M^+] calcd for $C_{15}H_{13}Br$, 272.0; found, 272.0. HRMS (EI^+) calcd for $C_{15}H_{13}Br$ [M^+]: 272.0201. Found: 272.0200.

(*E*)-4-(3-Phenylprop-1-enyl)benzonitrile (3-1g). Prepared according to the general procedure. A faint yellow liquid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.75 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.34–7.19 (m, 5H), 6.72–6.64 (m, 1H), 6.56 (d, J = 15.9 Hz, 1H), 3.56 (d, J = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 142.26, 139.92, 134.38, 132.98, 129.70, 129.02, 129.00, 128.98, 127.23, 126.68, 119.45, 109.73, 39.09. GC/MS (m/z): [M^+] calcd for $C_{16}H_{13}N$, 219.1; found, 219.1. HRMS (EI^+) calcd for $C_{16}H_{13}N$ [M^+]: 219.1048. Found: 219.1047.

(*E*)-4-(3-Phenylprop-1-enyl)nitrobenzene (3-1h). Prepared according to the general procedure. A yellow liquid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.13 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.37–7.15 (m, 6H), 6.73 (m, 1H), 6.60 (d, J = 15.9 Hz, 1H), 3.57 (d, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 151.26, 149.11, 144.52, 140.28, 134.03, 133.78, 133.73, 132.11, 131.45, 129.06, 43.92. GC/MS (m/z): [M^+] calcd for $C_{15}H_{13}NO_2$, 239.1; found, 239.1. HRMS (EI^+) calcd for $C_{15}H_{13}NO_2$ [M^+]: 239.0946. Found: 239.0949.

(*E*)-1-(2-Methoxyphenyl)-3-phenylpropene (3-1i). Prepared according to the general procedure. A faint yellow solid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.44 (dd, J = 7.6, 1.6 Hz, 1H), 7.32–7.18(m, 6H), 6.97 (d, J = 7.6 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H), 6.72 (d, J = 15.9 Hz, 1H), 6.42–6.34 (m, 1H), 3.78 (s, 3H), 3.52 (d, J = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 156.47, 140.73, 130.22, 128.93, 128.90, 128.79, 126.67, 126.47, 125.96, 125.57, 120.96, 111.70, 55.81, 39.37. GC/MS (m/z): [M^+] calcd for $C_{16}H_{16}O$, 224.1; found, 224.1. HRMS (EI^+) calcd for $C_{16}H_{16}O$ [M^+]: 224.1201. Found: 224.1202.

(*E*)-1-(3-Methoxyphenyl)-3-phenylpropene (3-1j). Prepared according to the general procedure. A faint yellow liquid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.34–7.29 (m, 2H), 7.27–7.19 (m, 4H), 6.98 (d, J = 8.3 Hz, 2H), 6.78 (dd, J = 9.4, 2.1 Hz, 1H), 6.46 (d, J = 4.2 Hz, 1H), 6.45–6.40 (m, 1H), 3.74 (s, 3H), 3.52 (d, J = 4.6 Hz, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 159.99, 140.48, 138.99, 130.93, 130.22, 130.01, 128.97, 128.92, 126.53, 118.99, 118.99, 113.46, 111.51, 55.44, 39.04. GC/MS (m/z): [M^+] calcd for $C_{16}H_{16}O$, 224.1; found, 224.1. HRMS (EI^+) calcd for $C_{16}H_{16}O$ [M^+]: 224.1201. Found: 224.1202.

(*E*)-1-(3,5-Dimethoxyphenyl)-3-phenylpropene (3-1k). Prepared according to the general procedure. A brown liquid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.34–7.29 (m, 2H), 7.26–7.19 (m, 3H), 6.58 (d, J = 2.1 Hz, 2H), 6.50–6.43 (m, 1H), 6.40 (d, J = 15.9 Hz, 1H), 6.37 (t, J = 2.1 Hz, 1H), 3.73 (s, 6H), 3.51 (d, J = 6.2 Hz, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 161.07, 140.44, 139.59, 131.03, 130.46, 128.99, 128.91, 128.82, 126.54, 104.42, 99.92, 55.58, 39.03. GC/MS (m/z): [M^+] calcd for $C_{17}H_{18}O_2$, 254.1; found, 254.1. HRMS (EI^+) calcd for $C_{17}H_{18}O_2$ [M^+]: 254.1307. Found: 254.1308.

(*E*)-1-(3,4,5-Trimethoxyphenyl)-3-phenylpropene (3-1l). Prepared according to the general procedure. A faint yellow liquid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.33–7.19 (m, 5H), 6.71 (s, 2H), 6.42–6.36 (m, 2H), 3.77 (s, 6H), 3.64 (s, 3H), 3.50 (d, J = 4.9 Hz, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 153.45, 140.58, 137.34, 133.28, 131.04, 129.30, 129.01, 128.91, 126.52, 103.80, 60.47, 56.25, 39.06. GC/MS (m/z): [M^+] calcd for $C_{18}H_{20}O_2$, 284.1; found, 284.1. HRMS (EI^+) calcd for $C_{18}H_{20}O_2$ [M^+]: 284.1412. Found: 284.1413.

(*E*)-1-(2,4-Chlorophenyl)-3-phenylpropene (3-1m). Prepared according to the general procedure. A colorless liquid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.67 (t, J = 7.0 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.37–7.29 (m, 3H), 7.28–7.19 (m, 3H), 6.77–6.67 (m, 1H), 6.59–6.47 (m, 1H), 3.57 (d, J = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 139.85, 134.46, 134.25, 132.62, 129.28, 129.01, 128.96, 128.58, 128.01, 126.66, 125.48, 39.15. GC/MS (m/z): [M^+] calcd for $C_{15}H_{12}Cl_2$, 262.0; found, 262.0. HRMS (EI^+) calcd for $C_{15}H_{12}Cl_2$ [M^+]: 262.0316. Found: 262.0320.

(*E*)-3-(2-Methylphenyl)-1-(4-methoxyphenyl)-propene (3-2b). Prepared according to the general procedure. A faint yellow liquid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.31 (d, J = 6.8 Hz, 2H), 7.19–7.10 (m, 4H), 6.85 (d, J = 9.7 Hz, 2H), 6.33 (d, J = 15.9 Hz, 1H), 6.26–6.18 (m, 1H), 3.72 (s, 3H), 3.46 (d, J = 6.4 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 163.70, 143.58, 141.08, 135.20, 135.07, 134.96, 134.16, 132.33, 131.38, 131.35, 131.21, 119.17, 60.25, 41.41, 24.21. GC/MS (m/z): [M^+] calcd for $C_{17}H_{18}O$, 238.1; found, 238.1. HRMS (EI^+) calcd for $C_{17}H_{18}O$ [M^+]: 238.1358. Found: 238.1359.

(*E*)-3-(3-Methylphenyl)-1-(4-methoxyphenyl)-propene (3-2c). Prepared according to the general procedure. A faint yellow liquid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.33 (d, J = 8.7 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 7.05–7.00 (m, 3H), 6.89–6.50 (m, 2H),

6.41 (d, J = 15.8 Hz, 1H), 6.28–6.20 (m, 1H), 3.73 (s, 3H), 3.45 (d, J = 6.9 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 158.97, 140.69, 137.92, 130.37, 130.19, 129.55, 128.77, 127.63, 127.49, 127.10, 125.99, 114.43, 55.51, 39.04, 21.45. GC/MS (m/z): $[M]^+$ calcd for $C_{17}H_{18}O$, 238.1; found, 238.1. HRMS (EI^+) calcd for $C_{17}H_{18}O$ $[M^+]$: 238.1358. Found: 238.1360.

(*E*)-3-(4-Methylphenyl)-1-(4-methoxyphenyl)-propene (3-2d). Prepared according to the general procedure. A faint yellow liquid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.33 (d, J = 8.7 Hz, 2H), 7.12 (s, 4H), 6.86 (d, J = 8.7 Hz, 2H), 6.39 (d, J = 15.8 Hz, 1H), 6.31–6.17 (m, 1H), 3.73 (s, 3H), 3.44 (d, J = 6.9 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 158.94, 137.65, 135.37, 130.24, 130.21, 129.45, 128.80, 127.67, 127.59, 114.43, 55.51, 38.63, 21.07. GC/MS (m/z): $[M]^+$ calcd for $C_{17}H_{18}O$, 238.1; found, 238.1. HRMS (EI^+) calcd for $C_{17}H_{18}O$ $[M^+]$: 238.1358. Found: 238.1359.

(*E*)-1-(4-Methoxyphenyl)-3-(3,5-dimethylphenyl)-propene (3-2e). Prepared according to the general procedure. A faint yellow liquid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.32 (d, J = 11.6 Hz, 2H), 6.85–6.82 (m, 5H), 6.40 (d, J = 15.8 Hz, 1H), 6.26–6.18 (m, 1H), 3.73 (s, 3H), 3.40 (d, J = 6.9 Hz, 2H), 2.23 (s, 6H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 163.70, 145.34, 142.51, 135.01, 134.96, 132.63, 132.37, 132.31, 131.43, 119.18, 60.27, 43.77, 26.10. GC/MS (m/z): $[M]^+$ calcd for $C_{18}H_{20}O$, 252.1; found, 252.1. HRMS (EI^+) calcd for $C_{18}H_{20}O$ $[M^+]$: 252.1514. Found: 252.1513.

(*E*)-1-(4-Methoxyphenyl)-3-(4-chlorophenyl)-propene (3-2f). Prepared according to the general procedure. A faint green liquid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.37–7.32 (m, 4H), 7.27 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.41 (d, J = 15.8 Hz, 1H), 6.28–6.20 (m, 1H), 3.74 (s, 3H), 3.48 (d, J = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 159.03, 139.86, 131.09, 130.83, 130.78, 130.06, 128.80, 127.68, 126.88, 114.44, 55.53, 38.21. GC/MS (m/z): $[M]^+$ calcd for $C_{16}H_{15}ClO$, 258.1; found, 258.1. HRMS (EI^+) calcd for $C_{16}H_{15}ClO$ $[M^+]$: 258.0811. Found: 258.0813.

(*E*)-3-(4-Bromophenyl)-1-(4-methoxyphenyl)-propene (3-2g). Prepared according to the general procedure. A faint yellow solid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.49 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.7 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.41 (d, J = 15.8 Hz, 1H), 6.28–6.20 (m, 1H), 3.74 (s, 3H), 3.47 (d, J = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 159.04, 140.30, 131.72, 131.20, 130.86, 130.05, 127.68, 126.80, 119.51, 114.44, 55.53, 38.27. GC/MS (m/z): $[M]^+$ calcd for $C_{16}H_{15}BrO$, 302.0; found, 302.0. HRMS (EI^+) calcd for $C_{16}H_{15}BrO$ $[M^+]$: 302.0306. Found: 302.0306.

Acknowledgements

The financial support for this study from the National Basic Research Program of China (973 Program) (grant 2010CB126101) is gratefully acknowledged.

Notes and references

1 P. T. Anastas and J. C. Warner, in *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, 1998.

2 For a seminal review on domino reactions, see: (*a*) L. F. Tietze, *Chem. Rev.*, 1996, **96**, 115; for representative examples; (*b*) S. W. Li and R. A. Batey, *Chem. Commun.*, 2007, **36**, 3759; (*c*) K. Alex, A. Tillack, N. Schwarz and M. Beller, *Angew. Chem., Int. Ed.*, 2008, **47**, 2304; (*d*) A. Trejos, A. Fardost, S. Yahiaoui and M. Larhed, *Chem. Commun.*, 2009, **48**, 7587; (*e*) D. M. Souza, F. Rominger and T. J. J. Muller, *Chem. Commun.*, 2006, **39**, 4096.

3 A. Bruggink, R. Schoevaart and T. Kieboom, *Org. Process Res. Dev.*, 2003, **7**, 622.

4 (*a*) M. Koichi and O. Hirofumi, *Chem. Commun.*, 2002, **22**, 2626; (*b*) P. Frederic, C. Sebastien, S. Morgane and D. Adam, *J. Org. Chem.*, 2008, **73**, 1975; (*c*) S. Amit, W. Roy, K. Naama and S. Doron, *J. Am. Chem. Soc.*, 2008, **130**, 5434; (*d*) X.-C. Huang, F. Wang, Y. Liang and J.-H. Li, *Org. Lett.*, 2009, **11**, 1139; (*e*) M. Liang, S. Cecilia, P. Chiara and W. Peter, *Tetrahedron Lett.*, 2009, **50**, 6810; (*f*) B. Alicia, H. Dacil and H. Rosendo, *Eur. J. Org. Chem.*, 2010, **20**, 3847; (*g*) P. B. S. Dawadi and L. Johan, *Synth. Commun.*, 2010, **40**, 2539; (*h*) S. Abhishek, S. Naina, K. Rakesh, S. Amit and A. K. Sinha, *Chem. Commun.*, 2010, **46**, 3283; (*i*) D. Zhao, C. Gao, X. Su, Y. He, J. You and Y. Xue, *Chem. Commun.*, 2010, **46**, 9049; (*j*) S. H. Kim, Y. M. Kim, H. S. Lee and J. N. Kim, *Tetrahedron Lett.*, 2010, **51**, 1592; (*k*) L. J. Cotterill, R. W. Harrington, C. William and M. J. Hall, *J. Org. Chem.*, 2010, **75**, 4604; (*l*) W. Xu and H. Fu, *J. Org. Chem.*, 2011, **76**, 3846; (*m*) A. Carlos, J.-O. Gonzalo, A. Alberto, J. H. Busto, J. M. Peregrina and M. M. Zurbano, *J. Org. Chem.*, 2011, **76**, 6990; (*n*) K.-P. Claire, D. M. Alba, O. Julie, P. Guillaume, M. Pedro and P. Giovanni, *J. Organomet. Chem.*, 2012, **714**, 53; (*o*) G. Steven, L. Frederic, P. Guillaume, W. Benoit, S. Mathieu, C. Yves, M. Andre and P. Giovanni, *Chem. Commun.*, 2012, **48**, 5889; (*p*) P. Thanasekaran and M. Shanmugam, *Tetrahedron Lett.*, 2012, **53**, 4248; (*q*) T. David, M.-A. Gabriela, C. Leandro and G.-T. Fernando, *Chem. – Eur. J.*, 2012, **18**, 3468; (*r*) W. Reina, K. Takashi, K. Robert, O. Hiromichi, U. Daisuke, Y. Shosuke and M. Kenji, *Tetrahedron Lett.*, 2013, **54**, 1921; (*s*) W. Xu, U. Kloeckner and B. J. Nachtsheim, *J. Org. Chem.*, 2013, **78**, 6065; (*t*) P. Svetlana, T. Tony, L. Vincent and J.-F. Briere, *Adv. Synth. Catal.*, 2013, **355**, 2513.

5 (*a*) B. Kramer and S. R. Waldvogel, *Angew. Chem., Int. Ed.*, 2004, **43**, 2446; (*b*) B. Kramer and S. R. Waldvogel, *Angew. Chem., Int. Ed.*, 2004, **116**, 2501; (*c*) J. C. Anderson, C. Headly, P. D. Stapleton and P. W. Taylor, *Tetrahedron*, 2005, **61**, 7703; (*d*) S. B. Wan, *Bioorg. Med. Chem.*, 2005, **13**, 2177; (*e*) C. R. Su, Y. C. Shen, P. C. Kuo, Y. L. Leu, A. G. Damu, Y. H. Wang and T. S. Wu, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 6155; (*f*) M. Belley, C. C. Chan, Y. Gareau, M. Gallant, H. Juteau, K. Houde, N. Lachance, M. Labelle,

N. Sawyer, N. Tremblay, S. Limontage, M. C. Carrière, D. Denis, G. M. Greig, D. Slipez, R. Gordon, N. Chauret, C. Lo, R. J. Zamboni and K. M. Metters, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 5639; (*g*) C. Ito, M. Itoigawa, T. Kanematsu, Y. Imamura, H. Tokuda, H. Nishino and H. Furukawa, *Eur. J. Med. Chem.*, 2007, **42**, 902; (*h*) K. N. Mewett, S. P. Fernandez, A. K. Pasricha, A. Pong, S. O. Devenish, D. E. Hibbs, M. Chebib, G. A. R. Johnston and J. R. Hanrahan, *Bioorg. Med. Chem.*, 2009, **17**, 7156; (*i*) K. Umehara, K. Nemoto, A. Matsushita, E. Terada, O. Monthakantirat, W. De-Eknamkul, T. Miyase, T. Warashina, M. Degawa and H. J. Noguchi, *Nat. Prod.*, 2009, **72**, 2163; (*j*) S. Cheenpracha, C. Karalai, C. Ponglimanont and A. J. Kanjana-Opas, *Nat. Prod.*, 2009, **72**, 1395; (*k*) F. M. Abdel Bar, M. A. Khanfar, A. Y. Elnagar, F. A. Badria, A. M. Zaghloul, K. F. Ahmad, P. W. Sylvester and K. A. El Sayed, *Bioorg. Med. Chem.*, 2010, **18**, 496; (*l*) M. Namara and M. Yvonne, *Bioorg. Med. Chem.*, 2011, **19**, 1328–1348; (*m*) J. C. Anderson, R. McCarthy, S. Paulin and P. W. Taylor, *Bioorg. Med. Chem. Lett.*, 2011, **21**, 6996; (*n*) M. Moriyasu, N. Nakatani, M. Ichimaru, Y. Nishiyama, A. Kato, S. G. Mathenge, F. D. Juma and P. B. C. Mutiso, *J. Nat. Med.*, 2011, **65**, 313.

6 (*a*) U. Yasuhiro, D. Hiroshi and H. Tamio, *J. Org. Chem.*, 1999, **64**, 3384; (*b*) C. Jordi, M. M. Marcial and P. Roser, *Eur. J. Org. Chem.*, 2000, **2**, 239; (*c*) R. Martin and A. Fürstner, *Angew. Chem., Int. Ed.*, 2004, **43**, 3955; (*d*) A. Fürstner, R. Martin, H. Krause, G. Seidel, R. Goddard and C. W. Lehmann, *J. Am. Chem. Soc.*, 2008, **130**, 8773; (*e*) M. Takashi, K. Kenji, S. Yoshiaki, S. Masami and F. Tsutomu, *Synlett*, 2008, **17**, 2711; (*f*) M. A. Y. Yoichi, W. Toshihiro, T. Kaoruand and U. Yasuhiro, *Chem. Commun.*, 2009, **37**, 5594; (*g*) M. Takashi, K. Taketo, A. Taichi, K. Tomoko, F. Tsutomu and S. Masami, *J. Org. Chem.*, 2009, **74**, 2321; (*h*) R. Ghosh, N. N. Adarsh and A. Sarkar, *J. Org. Chem.*, 2010, **75**, 5320; (*i*) A. M. Lauer, F. Mahmud and J. Wu, *J. Am. Chem. Soc.*, 2011, **133**, 9119; (*j*) B. Yao, Y. Liu, M. K. Wang, J. H. Li, R. Y. Tang, X. G. Zhang and C. L. Deng, *Adv. Synth. Catal.*, 2012, **354**, 1069; (*k*) C. Li, J. Xing, J. Zhao, P. Huynh, W. Zhang, P. Jiang and Y. J. Zhang, *Org. Lett.*, 2012, **14**, 390; (*l*) Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, *J. Am. Chem. Soc.*, 2012, **134**, 3190; (*m*) M. Takashi, K. Taketo, A. Taichi, K. Tomoko, F. Tsutomu and S. Masami, *Eur. J. Org. Chem.*, 2013, **8**, 1501.

7 (*a*) J. Wang, W. Huang, Z. Zhang, X. Xiang, R. Liu and X. Zhou, *J. Org. Chem.*, 2009, **74**, 3299; (*b*) B. L. Yang and S. K. Tian, *Chem. Commun.*, 2010, **46**, 6180; (*c*) G. G. K. S. N. Kumar and K. K. Laali, *Org. Biomol. Chem.*, 2012, **10**, 7347.

8 (*a*) H. Yang, P. Sun, Y. Zhu, H. Yan, L. Lu, X. Qu, T. Li and J. Mao, *Chem. Commun.*, 2012, **48**, 7847; (*b*) H. Yang, H. Yan, P. Sun, Y. Zhu, L. Lu, D. Liu, G. Rong and J. Mao, *Green Chem.*, 2013, **15**, 976.

9 E. Alacid and C. Nájera, *J. Org. Chem.*, 2009, **74**, 2321.

10 P. Makowski, R. Rothe, A. Thomas, M. Niederberger and F. Goettmann, *Green Chem.*, 2009, **11**, 34.

11 For a more detailed condition screening table, see the ESI.†

