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Direct Olefination of Benzaldehydes into 1,3-diarylpropenes via Copper-Catalyzed Heterodomino Knoevenagel-Decarboxylation-Csp^3-H Activation Sequence

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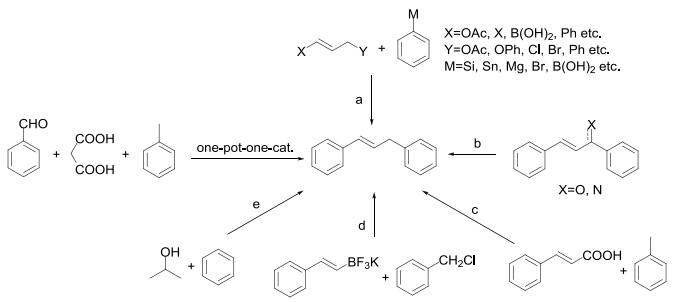
Copper-catalyzed direct olefination of benzaldehydes into 1,3-diarylpropenes by a novel domino Knoevenagel-decarboxylation-Csp^3-H activation sequence is reported. This method provides a concise and effective route toward the synthesis of unsymmetrical 1,3-diarylpropenes derivatives.

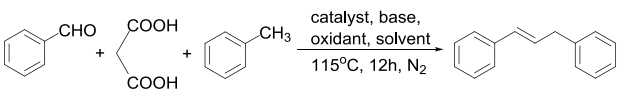
Introduction

In recent two decades, there is 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 generated waste.[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.



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

Table 1. Optimization of 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 (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.

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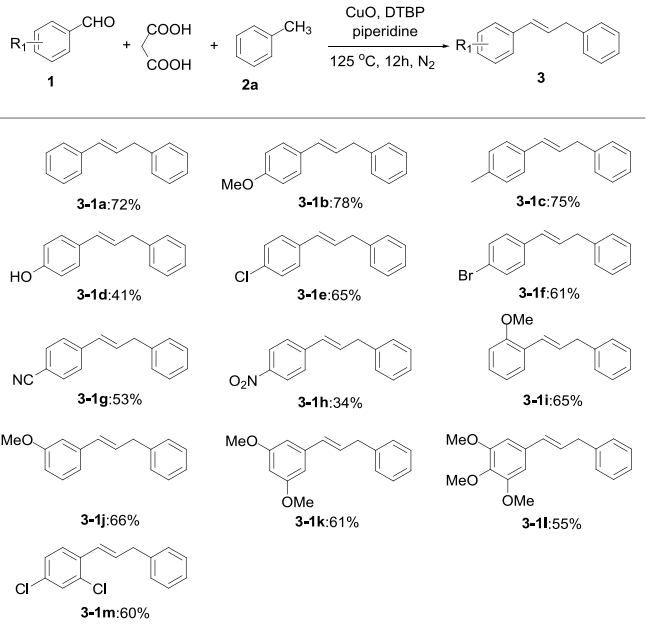
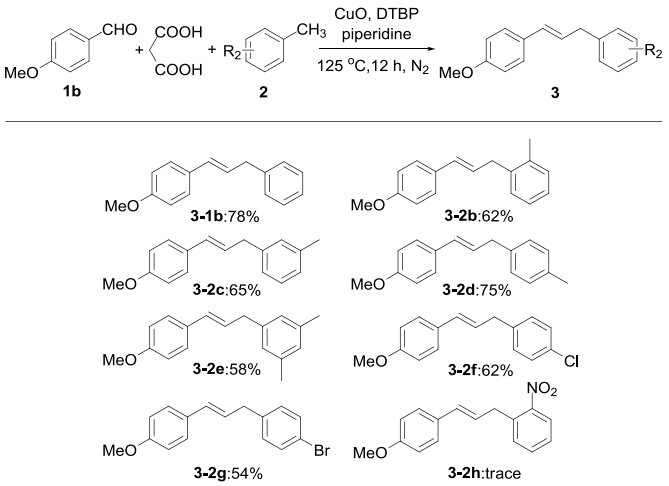
Table 2. Substrate Scope of the copper-catalyzed domino reaction of different benzaldehydes **1** with **2a**[a, b]



[a] Catalytic conditions: benzaldehydes (**1**) (0.3 mmol), malonic (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 benzaldehyde **1a** with **2**[a, b]



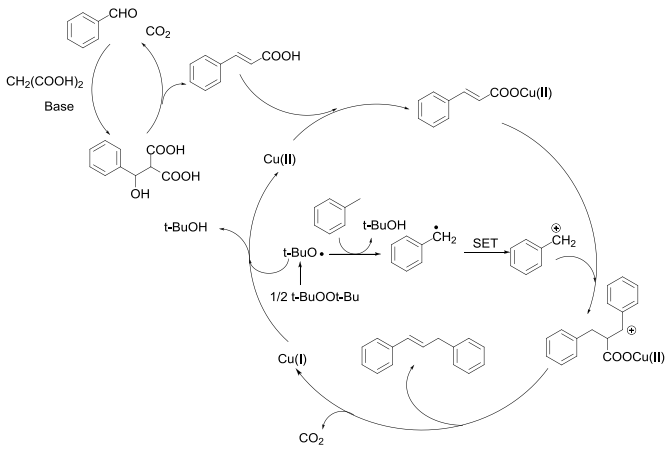
[a] Catalytic conditions: benzaldehyde (**1b**) (0.3 mmol), malonic (0.5 mmol), benzylic hydrocarbons (**2**) (2 mL), piperidine (0.2 mmol), CuO (20 mol%), DTBP (4 equiv.), 125 °C, 12 h, N_2 atmosphere. [b] Isolated yields based on benzaldehyde.

Furthermore, 1,3-diarylpropenes are often known as privileged structures or key intermediates in the synthesis of natural products and the development of biologically active compounds.[5] Traditionally, the 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 the disadvantages such as the 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**).

Results and discussion

We initiated 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 dramatical decrease in yield (entries 4-5). Modifying the quantity of oxidant, base, catalyst and time also 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 target product was detected below the boiling point of toluene (entry **12**) and a good result in 77% GC yield was achieved at 125 °C (entry **13**). However, when the reaction was conducted in air atmosphere, the yield decreased to 49% (entry **14**). A control experiment showed that the domino reaction was poor efficient when the reaction was carried out in absence of 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 observed to afford exclusively 1,3-diarylpropenes in moderate-to-good yields (**3-1a**-**3-1h**). Obviously, an electron-



Scheme 2. Proposed Mechanism

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

Substituent 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%

donating group at the *para*-position, such as the methoxy substituent in **3-1b**, afforded higher yield compared with an electron-withdrawing group, such as a cyano group substituent in **3-1g**. Para-substituted benzaldehydes (**3-1b**) gave an superior product yield 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 group (**3-1k**, **3-1l** and **3-1m**) would decrease 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**).

Considering the effects of electronic parameters on the reaction, it was found that the yield was 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 benzaldehyde and *m*,*m*,*p*-tri-methoxyl benzaldehyde, which might be dominated by the other factors such as hydrogen bonds and steric hindrance. However, 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 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 condition. CuO was purchased from Aladdin-reagent with high purity (99.5%). All reagents were used as supplied without further purified and dried. 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 BrukerAvance 400 MHz NMR spectrometer using d_6-DMSO as solvent and tetramethylsilane as internal standard (s = singlet, d = doublet, t = triplet, m = multiplet). MS analyses were performed on Agilent 5975 GC-MS instrument (EI). HRMS analyses were performed on Waters Micromass GCT instrument (EI).

General procedures for Copper-catalyzed allylation of benzaldehydes

Malonic (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), piperidine(20 μl, 0.2 mmol) were added at room temperature. The reaction vessel was purged with N_2 for three times. The mixture was stirred at 125 ℃ 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 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 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 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 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 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 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 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 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 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 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 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 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 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 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 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 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 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 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 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.

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Notes and references

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11 For a more detailed condition screening table, see the Supporting Information.

