Synthesis Y.-l. Zheng et al. Paper

Palladium-Catalyzed Synthesis of β,β-Diaryl α,β-Unsaturated Ketones

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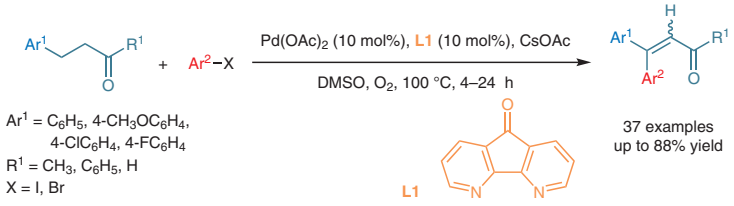

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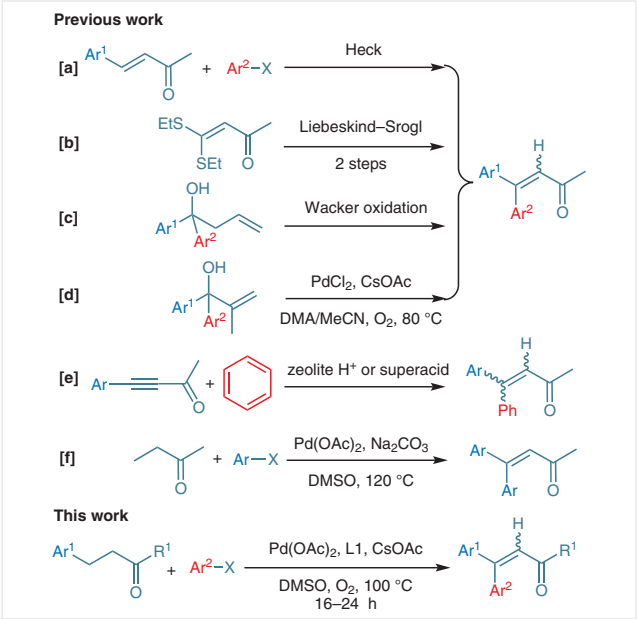
Abstract We herein describe a versatile palladium-catalyzed synthesis of β,β-diaryl α,β-unsaturated ketones. A broad range of aryl halides react with β-arylbutanones to afford biologically useful, symmetrical and unsymmetrical ketones. The use of 4,5-diazafluoren-9-one and oxygen makes this one-pot reaction more applicable. A plausible mechanism involving palladium-catalyzed oxidative Heck-type cross-coupling is also proposed.

Key words ketones, palladium, 4,5-diazafluoren-9-one, oxidation, cross-coupling

β,β-Diaryl α,β-unsaturated carbonyl compounds represent an important organic class with potential utility for forming various biologically useful molecules.[1] Recently, methods for carbonyl compound synthesis have been widely explored,[2] with approaches particularly suitable for β,β-diaryl α,β-unsaturated ketone synthesis rather less so. Since β,β-diaryl α,β-unsaturated ketones are stable and useful, broadening synthetic methods for their preparation is necessary.

Existing approaches for β,β-diaryl α,β-unsaturated ketone synthesis are limited, particularly when wide variations of aryl groups are desired. Heck arylation of α,β-unsaturated ketones is a major route to synthesize β,β-diaryl α,β-unsaturated ketones (Scheme 1, a).[3] α-Oxo ketene dithioacetals give the desired products, via oxo-directing Liebeskind–Srogl cross-coupling, after two steps (Scheme 1, b).[4] Procedures such as diaryl-substituted tertiary alcohol OH-directed Wacker oxidation–elimination (Scheme 1, c)[5] and oxidative palladium-catalyzed rearrangement (Scheme 1, d)[6] have also been reported. Arylacetylenes react with benzene under acidic zeolite or superacid conditions, affording a subclass of β,β-diaryl α,β-unsaturated ketones with one phenyl motif (Scheme 1, e).[7] However, the strict substrate restriction cannot be ignored. In 2014, Cheng and co-workers reported a palladium-catalyzed dehydrogenative β,β-diarylation method for the synthesis of symmetrical β,β-diaryl α,β-unsaturated ketones (Scheme 1, f).[8] While this method is convenient, the synthesis of unsymmetrical products is limited.

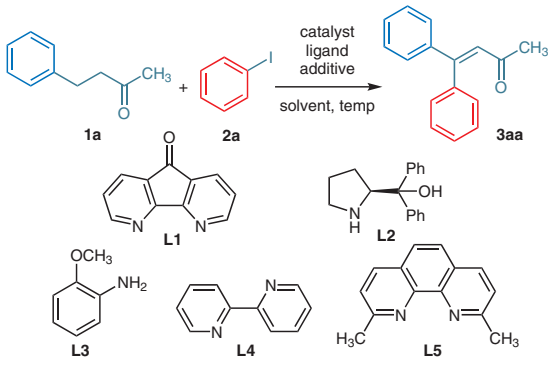


Scheme 1 Strategies for β,β-diaryl α,β-unsaturated ketones synthesis

Considering the biological importance of β,β-diaryl α,β-unsaturated ketones and synthetic difficulties, developing a convenient method for both symmetrical and unsymmetrical ketones continues to be valuable while challenging.

Herein, we report a novel palladium-catalyzed oxidative and Heck-type cross-coupling reaction to efficiently synthesize β,β-diaryl α,β-unsaturated ketones.

Table 1 Optimization of the Reaction Conditions[a]



Entry	Catalyst[b]	Additive (equiv)[c]	Ligand (mol%)[d]	Solvent (mL)[e]	Yield (%)[f]
1	$Pd(OAc)_2$	Ag_2CO_3 (1.5)	–	HOAc (2)	trace
2	$Pd(OAc)_2$	Na_2CO_3 (2.0)	–	DMSO (2)	18
3	$Pd(OAc)_2$	Na_2CO_3 (4.0)	–	DMSO (2)	25
4	$Pd(OAc)_2$	NaOAc (4.0)	–	DMSO (2)	27
5	$Pd(OAc)_2$	KOAc (4.0)	–	DMSO (2)	25
6	$Pd(OAc)_2$	CsOAc (4.0)	–	DMSO (2)	30
7	$Pd(OAc)_2$	AgOAc (4.0)	–	DMSO (2)	trace
8	$Pd(OAc)_2$	CsOAc (4.0)	–	DMSO (2)	37
9	$Pd(OAc)_2$	CsOAc (4.0)	–	DMF (2)	24
10	$Pd(OAc)_2$	CsOAc (4.0)	–	1,4-dioxane (2)	trace
11	$Pd(OAc)_2$	CsOAc (4.0)	–	toluene (2)	trace
12	$Pd(OAc)_2$	CsOAc (4.0)	–	*n*-BuOH (2)	trace
13	$Pd(OAc)_2$	CsOAc (4.0)	–	DMSO/H_2O (9:1, 2)	29
14	$Pd(OAc)_2$	CsOAc (4.0)	–	DMSO (1)	38
15	$Pd(OAc)_2$	CsOAc (4.0)	–	DMSO (0.5)	45
16	$Pd(OAc)_2$	CsOAc (4.0)	–	DMSO (0.2)	40
17	$Pd(TFA)_2$	CsOAc (4.0)	–	DMSO (0.5)	41
18	$PdCl_2$	CsOAc (4.0)	–	DMSO (0.5)	34
19	$Pd(PPh_3)_4$	CsOAc (4.0)	–	DMSO (0.5)	29
20	$Pd(OAc)_2$	CsOAc (4.0)	L1 (10)	DMSO (0.5)	50
21	$Pd(OAc)_2$	CsOAc (4.0)	L2 (20)	DMSO (0.5)	47
22	$Pd(OAc)_2$	CsOAc (4.0)	L3 (20)	DMSO (0.5)	41
23	$Pd(OAc)_2$	CsOAc (4.0)	L4 (10)	DMSO (0.5)	13
24	$Pd(OAc)_2$	CsOAc (4.0)	L5 (10)	DMSO (0.5)	40
25[g]	$Pd(OAc)_2$	CsOAc (4.0)	–	DMSO (0.5)	41
26[h]	$Pd(OAc)_2$	CsOAc (4.0)	–	DMSO (0.5)	49
27[h]	$Pd(OAc)_2$	CsOAc (4.0)	L1 (10)	DMSO (0.5)	56
28[h,i]	**$Pd(OAc)_2$**	**CsOAc (4.0)**	**L1 (10)**	**DMSO (0.5)**	**66**
29[h,j]	$Pd(OAc)_2$	CsOAc (4.0)	L1 (10)	DMSO (0.5)	62

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.25 mmol, entries 1–7; 1.75 mmol, entries 8–29), stirred at 120 °C (entries 1–27), sealed 10 mL tube, 24 h.
[b] Catalyst loading: 10 mol%.
[c] 0.75 mmol (entry 1); 1 mmol (entry 2); 2 mmol (entries 3–29).
[d] L1 (10 mol%), L2 (20 mol%), L3 (20 mol%), L4 (10 mol%), L5 (10 mol%).
[e] 2 mL (entries 1–13); 1 mL (entry 14); 0.5 mL (entries 15, 17–29); 0.2 mL (entry 16).
[f] Yield of isolated product, based on **1a**.
[g] The mixture was purged with argon.
[h] The mixture was purged with O_2.
[i] Reaction at 100 °C for 16 h.
[j] Reaction at 80 °C for 24 h.

Utilizing stable and readily available β-arylbutanones and aryl halides, various symmetrical and unsymmetrical β,β-diaryl α,β-unsaturated ketones were obtained, including electron-withdrawing aryl products. Furthermore, the method is also convenient for β,β-diaryl α,β-unsaturated aldehyde synthesis. However, this method fails to give relevant dehydrogenative β-arylation products from β-alkylated ketones. Such an unsuccessful result was also reported by Cheng and co-workers.[8] We assume reaction at the methylene site in β-alkylated ketones is more difficult than that in β-aryl ketones or at the terminal methyl group.

We started our investigation by using benzylacetone (**1a**) and iodobenzene (**2a**) as model substrates. Based on our previously reported work with aldehydes[2b] the reaction was initially performed in the presence of $Pd(OAc)_2$ and Ag_2CO_3 in HOAc at 120 °C for 24 hours (Table 1, entry 1). Unfortunately, only a trace amount of the desired product **3aa** was afforded. We hypothesized that the poor reactivity of ketone **1a** might relate to the higher pK_a of the α-C–H bond compared to aldehydes. We assumed that a basic environment may be superior for ketones. Inspired by Cheng's work,[8] we carried out the reaction of **1a** (0.5 mmol) and **2a** (1.25 mmol) using $Pd(OAc)_2$ (10 mol%) and Na_2CO_3 (1 mmol) in DMSO (2 mL) at 120 °C for 24 hours (Table 1, entry 2), and **3aa** was only obtained in 18% yield. To increase the yield, we set out to optimize the reaction conditions. Firstly, we doubled the amount of Na_2CO_3 (2 mmol), and the yield increased to 25% (Table 1, entry 3). Then, various bases (Table 1, entries 4–7) were screened, with CsOAc being the most effective (30% yield; Table 1, entry 6). Considering the low conversion rate of **1a**, as well as the homocoupled byproduct from **2a**,[9] we increased the amount of **2a** (3.5 equiv) which resulted in an elevated 37% yield (Table 1, entry 8). After further exploration, we found that DMSO was the most suitable solvent and 0.5 mL was the best solvent volume. Screening other palladium catalysts (Table 1, entries 17–19) did not provide a better result. To our delight,

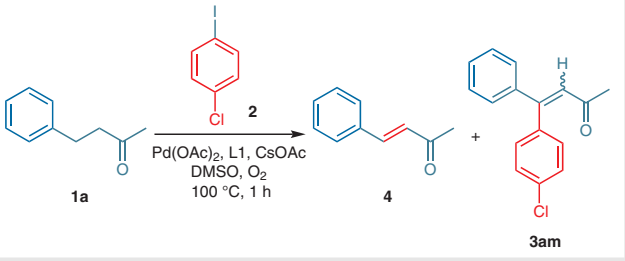
addition of 4,5-diazafluoren-9-one (L1, DAF) promoted $Pd(OAc)_2$ efficiency (50% yield; Table 1, entry 20),[10] especially under oxygen atmosphere (56% yield; Table 1, entry 27). Subsequently, different temperature conditions (Table 1, entries 27–29) were examined, and 100 °C for 16 hours turned out to give the highest yield (66%; Table 1, entry 28).

With the optimized conditions in hand, we further explored the scope and generality of the reaction. As shown in Table 2, this method was practical for β-arylbutanones **1a–d** and aryl iodides **2** to obtain the desired β,β-diaryl α,β-unsaturated ketones **3aa–dd** under the standardized conditions. The position of a substituent on the aryl iodide had a huge impact on the reaction outcome. If an *ortho*-substituted iodobenzene was employed, the yield decreased significantly because of steric effects (Table 2, **3ad** and **3al**). In comparison, *meta*-substituted iodobenzenes (Table 2, **3ac** and **3ak**) and *para*-substituted iodobenzenes (Table 2, **3ab** and **3aj**) still delivered the products in moderate yields. Electronic properties also influenced the results. An electron-donating group on the aryl iodide (Table 2, **3ab** and **3ac**) was more beneficial than an electron-withdrawing group (Table 2; **3aj**, **3ak**, **3am**, and **3an**). Furthermore, compounds with a terminal phenyl group resulted in 75–88% yield (Table 2, **3da–dd**), higher than the 59–71% yield for compounds with a terminal methyl group (Table 2; **3aa**, **3ab**, **3ah**, and **3aj**), which may be attributed to a reduction in the side reactions involving the terminal methyl group. Because of separation difficulty, unsymmetrical β,β-diaryl α,β-unsaturated ketones were obtained as a mixture of geometric isomers (see Table 2). The ratio of stereoisomers was calculated on the basis of NMR spectroscopy, and the *trans*/*cis* configuration of **3ag** (*E*/*Z* 1:0.1) was identified by comparison with reported spectroscopic data.[4]

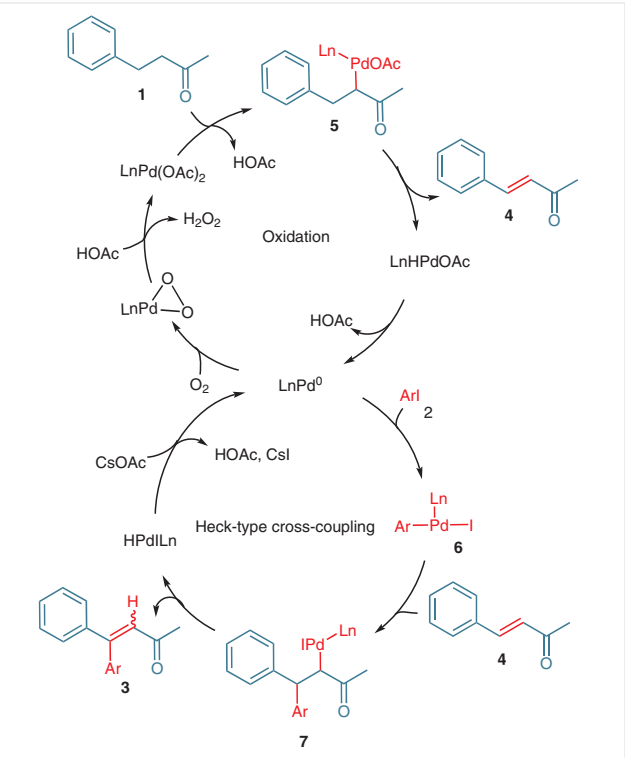
Notably, using aryl bromides to synthesize the β,β-diaryl α,β-unsaturated ketones (Table 3) was plausible, albeit with relatively lower yields than the corresponding aryl iodides. For *para*-methyl substitution the yield of the unseparated geometric isomers reached 52% (Table 3, **3ab**), while *para*-fluoro substitution resulted in 58% yield (Table 3, **3aj**).

The method was also convenient for the synthesis of β,β-diaryl α,β-unsaturated aldehydes (Table 4). The reaction time was shortened with comparable yields to the corresponding methyl ketones. Also, the predominant *trans*/*cis* configuration was consistent with the results under acidic conditions.[2b]

When we looked into the mechanism behind the reaction, we found that oxidized intermediate **4** (Scheme 2) was generated within 1 hour, as detected by ^1H NMR spectroscopy (see Supporting Information). Although the underlying mechanism remains to be elucidated, taking the experimental results obtained during optimization of the reaction conditions together with mechanisms suggested in earlier reports,[11] a plausible oxidative Heck-type cross-coupling mechanism for the formation of β,β-diaryl α,β-unsaturated ketones is proposed (Scheme 3).

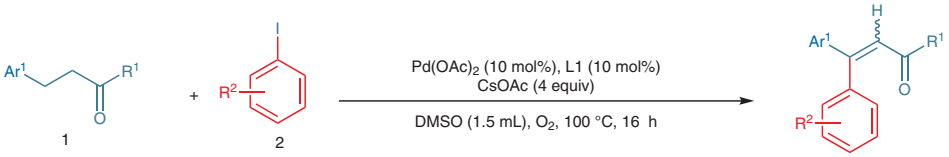


Scheme 2 Mechanism exploration. *Reagents and conditions*: **1a** (1.5 mmol), **2** (5.25 mmol), $Pd(OAc)_2$ (10 mol%), L1 (10 mol%), CsOAc (6.0 mmol), DMSO (1.5 mL), O_2 atmosphere, 100 °C, 1 h.

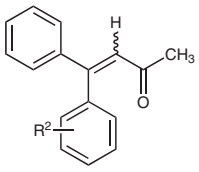
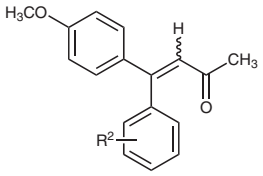
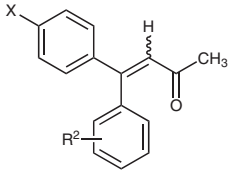
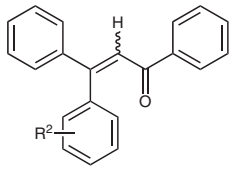


Scheme 3 Plausible mechanism

Table 2 Synthesis of β,β-Diaryl α,β-Unsaturated Ketones from β-Arylbutanones and Aryl Iodides[a]

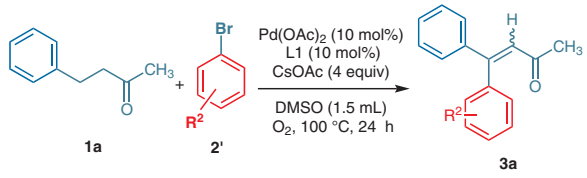


1a: $Ar^1 = C_6H_5$, $R^1 = CH_3$
1b: $Ar^1 = 4\text{-}CH_3OC_6H_4$, $R^1 = CH_3$
1c: $Ar^1 = 4\text{-}FC_6H_4$, $R^1 = CH_3$
1c': $Ar^1 = 4\text{-}ClC_6H_4$, $R^1 = CH_3$
1d: $Ar^1 = C_6H_5$, $R^1 = C_6H_5$

Entry	Compound		R^2	Yield (%)[b]	Ratio[c]
1		**3aa**	4-H	66	–
2		**3ab**	4-CH_3	71	1:0.9
3		**3ac**	3-CH_3	57	1:0.5
4		**3ad**	2-CH_3	trace	–
5		**3ae**	4-Et	55	1:0.3
6		**3af**	4-*i*-Pr	57	1:0.3
7		**3ag**	4-*t*-Bu	53	1:0.1 (*E*/*Z*)
8		**3ah**	4-OCH_3	59	1:0.6
9		**3ai**	3-OCH_3	57	1:0.3
10		**3aj**	4-F	60	1:0.7
11		**3ak**	3-F	42	1:0.3
12		**3al**	2-F	15	–
13		**3am**	4-Cl	38	1:0.2
14		**3an**	4-Br	26	1:0.1
15		**3ao**	3,5-$(CH_3)_2$	60	1:0.4
16		**3ap**	3,4-$(CH_3)_2$	78	1:0.7
17		**3ba**	4-CH_3	85	1:0.9
18		**3bb**	4-OCH_3	56	–
19		**3bc**	4-*t*-Bu	64	1:0.6
20		**3bd**	4-F	57	1:0.4
21		**3ca** (X = F)	4-CH_3	60	1:0.4
22		**3cb** (X = F)	4-Cl	24	1:0.3
23		**3c'a** (X = Cl)	4-CH_3	55	1:0.6
24		**3c'b** (X = Cl)	3-CH_3	50	1:0.3
25		**3da**	4-H	84	–
26		**3db**	4-CH_3	88	1:0.9
27		**3dc**	4-OCH_3	78	1:0.8
28		**3dd**	4-F	75	–

[a] Reaction conditions: **1** (1.5 mmol), **2** (5.25 mmol), $Pd(OAc)_2$ (10 mol%), L1 (10 mol%), CsOAc (6.0 mmol), DMSO (1.5 mL), stirred under O_2 atmosphere, 100 °C, 16 h.
[b] Yield of isolated product, based on **1**.
[c] Mixture of geometric isomers; ratio of major versus minor isomer calculated on the basis of NMR spectroscopic data.

Table 3 Synthesis of β,β-Diaryl α,β-Unsaturated Ketones from Benzylacetone and Aryl Bromides[a]

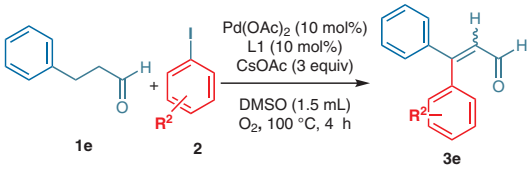


1a 2' 3a

Entry	Compound	R^2	Yield (%)[b]	Ratio[c]
1	**3aa**	4-H	33	–
2	**3ab**	4-CH_3	52	1:0.2
3	**3ac**	3-CH_3	34	1:1
4	**3aj**	4-F	58	1:0.1

[a] Reaction conditions: **1a** (1.5 mmol), **2'** (5.25 mmol), $Pd(OAc)_2$ (10 mol%), L1 (10 mol%), CsOAc (6.0 mmol), DMSO (1.5 mL), stirred under O_2 atmosphere, 100 °C, 24 h.
[b] Yield of isolated product, based on **1a**.
[c] Mixture of geometric isomers; ratio of major versus minor isomer calculated on the basis of NMR spectroscopic data.

Table 4 Synthesis of β,β-Diaryl α,β-Unsaturated Aldehydes from Benzenepropanal and Aryl Iodides[a]



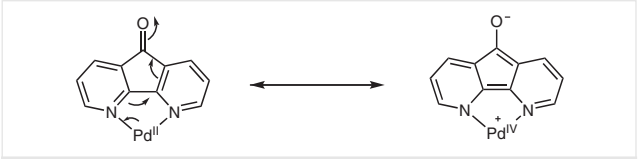
1e 2 3e

Entry	Compound	R^2	Yield (%)[b]	Ratio[c]
1	**3ea**	4-H	76	–
2	**3eb**	4-CH_3	75	1:0.5
3	**3ec**	3-CH_3	68	1:0.6
4	**3ed**	4-*t*-Bu	55	1:0.3
5	**3ee**	4-Cl	35	1:0.7

[a] Reaction conditions: **1e** (1.5 mmol), **2** (3.75 mmol), $Pd(OAc)_2$ (10 mol%), L1 (10 mol%), CsOAc (4.5 mmol), DMSO (1.5 mL), stirred under O_2 atmosphere, 100 °C, 4 h.
[b] Yield of isolated product, based on **1e**.
[c] Mixture of geometric isomers; ratio of major versus minor isomer calculated on the basis of NMR spectroscopic data.

The reaction is initiated by activation of the α-C–H bond, transforming **1** into intermediate **5**.[10a,12] Subsequent fast β-H elimination from **5** affords the enone product **4**[13] and a Pd^{II}–hydride intermediate. After loss of acetic acid, the Pd^0 can be oxidized by oxygen to regenerate the Pd^{II} catalyst.[14] Compound **4** undergoes a typical Heck reaction with aryl iodide **2**, catalyzed by palladium, to give the desired β,β-diaryl α,β-unsaturated ketone **3**.

In the catalytic cycle, DAF (L1) may have an influence on all steps, which allows for the development of a more reactive and robust catalyst. Also, by forming a complex with palladium, DAF may reduce the aggregation of Pd^0, decreasing palladium precipitation.[14d] Recently, Campbell and Stahl[15] and Le Bras and co-workers[16] proposed a Pd^{IV} resonance contribution via π-backbonding formed by Pd^{II} and DAF (Scheme 4). CsOAc is likely to serve as the OAc anion provider[13] and neutralizer, promoting the catalytic cycle. The process is sensitive to the nature of the solvent and the yields are highest in DMSO, which possibly contributes to the regeneration of the active catalytic species.[17]



Scheme 4 Pd^{IV} resonance contribution via π-backbonding

Compound **3aa** was obtained in 41% yield under argon atmosphere (Table 1, entry 25). In addition to our proposed mechanism, we assume that under oxygen-free conditions ArI[8,18] could form an Ar–Pd^{II}–I intermediate with palladium and then conduct the β-H elimination as well as regenerate active catalyst in the oxidation cycle, which may also function under oxygen atmosphere.

To summarize, we have developed a novel and efficient strategy for the one-pot synthesis of symmetrical and unsymmetrical β,β-diaryl α,β-unsaturated ketones and aldehydes. Through palladium catalysis with the help of the ligand 4,5-diazafluoren-9-one under oxygen atmosphere, this reaction was made more applicable and versatile. Overall, 32 β,β-diaryl α,β-unsaturated ketones and aldehydes were synthesized in up to 88% yield. Using aryl bromides instead of aryl iodides to synthesize the β,β-diaryl α,β-unsaturated ketones is also feasible. In addition, a plausible palladium-catalyzed oxidative Heck-type cross-coupling mechanism was proposed.

All commercially available reagents were used without further purification unless otherwise stated. Compounds were purified using a Smart Flash AI-580S system (Yamazen Co. Ltd.). ^1H and ^{13}C NMR spectra were recorded on Varian 400 MHz and Bruker 600 MHz spectrometers, respectively. Chemical shifts in ^1H NMR spectra are reported in parts per million (ppm) on the δ scale from an internal standard of TMS (0.00 ppm). Data are reported as follows: chemical shift (δ), multiplicity (standard abbreviations), coupling constant(s) in hertz (Hz), and integration. Chemical shifts in ^{13}C NMR spectra are reported in ppm from the central peak of TMS (0.0 ppm) on the δ scale. MS data were recorded on an Agilent Technologies 6120 quadrupole mass spectrometer. HRMS data were recorded on an AB Sciex 4000 quadrupole mass spectrometer.

β-Arylbutanones 1c and 1c'; General Procedure[19]

A mixture of pentane-2,4-dione (2 g, 20 mmol), a 4-substituted benzyl halide (20 mmol), and anhydrous K_2CO_3 (20 mmol) in MeOH (60 mL) was heated at reflux temperature for 16 h. The mixture was then cooled to room temperature, MeOH was removed under reduced pressure, and the resulting residue was partitioned between EtOAc (30 mL) and H_2O (30 mL). The organic layer was separated, and the aqueous layer was extracted further with EtOAc (3 × 30 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was then purified by column chromatography (silica gel; *n*-hexane/EtOAc) to afford the desired product.

4-(4-Fluorophenyl)butan-2-one (1c)[19]

Colourless oil; yield: 1.43 g (43%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19–7.05 (m, 2 H), 6.95 (t, *J* = 7.9 Hz, 2 H), 2.86 (t, *J* = 7.0 Hz, 2 H), 2.73 (t, *J* = 7.1 Hz, 2 H), 2.13 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 207.7, 161.5 (d, *J* = 234 Hz), 136.8 (d, *J* = 2 Hz), 129.8 (d, *J* = 8 Hz), 115.3 (d, *J* = 21 Hz), 45.2, 30.2, 29.0.

MS (ESI): *m*/*z* = 167.2 $[M + H]^+$.

4-(4-Chlorophenyl)butan-2-one (1c')[20]

Colourless oil; yield: 1.60 g (44%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 8.2 Hz, 2 H), 7.11 (d, *J* = 8.1 Hz, 2 H), 2.86 (t, *J* = 7.4 Hz, 2 H), 2.74 (t, *J* = 7.4 Hz, 2 H), 2.14 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 207.7, 139.6, 132.0, 129.9, 128.8, 45.1, 30.3, 29.2.

MS (ESI): *m*/*z* = 183.1 $[M + H]^+$.

β,β-Diaryl α,β-Unsaturated Ketones 3aa–dd (Table 2); General Procedure

A tube (30 mL) equipped with a magnetic stirring bar was charged with **1** (1.5 mmol), **2** (5.25 mmol), $Pd(OAc)_2$ (10 mol%), L1 (10 mol%), and CsOAc (6.0 mmol) in DMSO (1.5 mL), then the tube was sealed, purged with O_2, and the mixture was stirred at 100 °C for 16 h. At the end of the reaction, the mixture was partitioned between EtOAc (30 mL) and H_2O (30 mL). The organic layer was separated, and the aqueous layer was extracted further with EtOAc (3 × 30 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Then, the crude mixture was purified by column chromatography (silica gel; *n*-hexane/EtOAc) to afford the desired product.

4,4-Diphenylbut-3-en-2-one (3aa)[6,21]

Yellow oil; yield: 220 mg (66%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (dd, *J* = 5.0, 1.9 Hz, 3 H), 7.32 (m, *J* = 9.9, 8.2, 4.1 Hz, 5 H), 7.22 (dd, *J* = 6.4, 3.2 Hz, 2 H), 6.58 (s, 1 H), 1.88 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.3, 154.0, 140.8, 139.0, 129.6, 129.5, 128.8, 128.4, 127.7, 30.3.

MS (ESI): *m*/*z* = 223.1 $[M + H]^+$.

4-Phenyl-4-(*p*-tolyl)but-3-en-2-one (3ab)

Yellow oil; yield: 252 mg (71%); mixture of geometric isomers (~1:0.9).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.28 (m, 7.3 H), 7.23–7.09 (m, 9.8 H), 6.58 (s, 1 H, major CH), 6.54 (s, 0.9 H, minor CH), 2.41 (s, 2.7 H, minor CH_3), 2.36 (s, 3 H, major CH_3), 1.89 (s, 2.7 H, minor CH_3), 1.86 (s, 3 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.4, 200.2, 154.2, 154.1, 141.1, 139.8, 139.2, 138.9, 137.9, 136.0, 129.7, 129.6, 129.4, 129.2, 129.1, 128.7, 128.5, 128.4, 128.4, 127.6, 126.9, 30.3, 21.4, 21.3.

MS (ESI): *m*/*z* = 237.2 $[M + H]^+$.

4-Phenyl-4-(*m*-tolyl)but-3-en-2-one (3ac)

Yellow oil; yield: 202 mg (57%); mixture of geometric isomers (~1:0.5).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.39 (m, 3 H), 7.35–7.30 (m, 2.5 H), 7.25–7.12 (m, 5 H), 7.13 (s, 1 H), 7.08 (d, *J* = 7.3 Hz, 1 H), 7.03 (s, 1 H), 6.58 (s, 1 H, major CH), 6.57 (s, 0.5 H, minor CH), 2.36 (s, 1.5 H, minor CH_3), 2.32 (s, 3 H, major CH_3), 1.88 (s, 4.5 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.2, 200.0, 154.0, 140.7, 138.9, 138.8, 138.0, 137.9, 130.1, 130.0, 129.5, 129.4, 129.3, 128.8, 128.6, 128.3, 128.2, 127.6, 127.5, 126.6, 125.6, 30.2, 30.1, 21.2, 21.2.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{16}O$ $[M + H]^+$: 237.1274; found: 237.1268.

4-(4-Ethylphenyl)-4-phenylbut-3-en-2-one (3ae)

Yellow oil; yield: 205 mg (55%); mixture of geometric isomers (~1:0.3).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.29 (m, 4.6 H), 7.24–7.11 (m, 7.1 H), 6.59 (s, 1 H, major CH), 6.54 (s, 0.3 H, minor CH), 2.72–2.63 (m, 2.6 H), 1.88 (s, 0.9 H, minor CH_3), 1.86 (s, 3 H, major CH_3), 1.31–1.26 (m, 0.9 H, minor CH_3), 1.24 (t, *J* = 7.6 Hz, 3 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.4, 200.1, 154.3, 154.1, 146.2, 145.2, 141.2, 139.3, 138.2, 136.3, 129.9, 129.7, 129.5, 128.8, 128.6, 128.5, 128.5, 128.1, 128.0, 127.7, 127.1, 30.4, 30.3, 28.8, 28.7, 15.4.

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{18}O$ $[M + H]^+$: 251.1430; found: 251.1424.

4-(4-Isopropylphenyl)-4-phenylbut-3-en-2-one (3af)

Yellow oil; yield: 224 mg (57%); mixture of geometric isomers (~1:0.3).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.29 (m, 4.5 H), 7.25–7.12 (m, 7.2 H), 6.59 (s, 1 H, major CH), 6.54 (s, 0.3 H, minor CH), 2.99–2.87 (m, 1.3 H), 1.87 (d, *J* = 2.1 Hz, 0.9 H, minor CH_3), 1.86 (s, 3 H, major CH_3), 1.29 (d, *J* = 6.9 Hz, 1.8 H, minor CH_3), 1.24 (d, *J* = 6.9 Hz, 6 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.5, 200.1, 154.2, 154.1, 150.7, 149.8, 141.1, 139.2, 138.2, 136.2, 129.7, 129.6, 129.4, 128.7, 128.5, 128.4, 128.4, 128.4, 127.7, 127.0, 126.5, 126.4, 33.9, 33.9, 30.3, 30.2, 23.9, 23.8.

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{20}O$ $[M + H]^+$: 265.1587; found: 265.1579.

4-(4-(*tert*-Butyl)phenyl)-4-phenylbut-3-en-2-one (3ag)[4]

Yellow oil; yield: 221 mg (53%); mixture of geometric isomers (~1:0.1, *E*/*Z*).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.40 (m, 3 H), 7.36–7.21 (m, 6.6 H), 7.14 (d, *J* = 7.9 Hz, 0.3 H, *Z*-ArH), 6.60 (s, 1 H, *E*-CH), 6.54 (s, 0.1 H, *Z*-CH), 1.87 (s, 0.3 H, *Z*-CH_3), 1.86 (s, 3 H, *E*-CH_3), 1.36 (s, 0.9 H, *Z*-*t*Bu), 1.31 (s, 9 H, *E*-*t*Bu).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.5, 200.1, 154.2, 153.9, 152.9, 152.1, 141.1, 139.1, 137.7, 135.8, 129.6, 129.5, 129.4, 128.6, 128.5, 128.4, 128.1, 127.7, 127.0, 125.6, 125.4, 125.3, 34.7, 31.3, 31.2, 30.3, 30.2.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{22}O$ $[M + H]^+$: 279.1743; found: 279.1746.

4-(4-Methoxyphenyl)-4-phenylbut-3-en-2-one (3ah)

Yellow oil; yield: 222 mg (59%); mixture of geometric isomers (~1:0.6).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.28 (m, 6.2 H), 7.25–7.19 (m, 3.8 H), 7.15 (d, *J* = 8.4 Hz, 1.2 H, minor ArH), 6.93 (d, *J* = 8.4 Hz, 1.2 H, minor ArH), 6.85 (d, *J* = 8.6 Hz, 2 H, major ArH), 6.56 (s, 1 H, major CH), 6.50 (s, 0.6 H, minor CH), 3.86 (s, 1.8 H, minor OCH_3), 3.82 (s, 3 H, major OCH_3), 1.92 (s, 1.8 H, minor CH_3), 1.84 (s, 3 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.6, 200.1, 161.0, 160.4, 154.1, 154.0, 141.5, 139.4, 133.2, 131.5, 131.2, 130.0, 129.7, 129.5, 128.8, 128.8, 128.5, 128.5, 127.5, 126.1, 114.0, 114.0, 55.5, 55.4, 30.4.

MS (ESI): *m*/*z* = 253.2 $[M + H]^+$.

4-(3-Methoxyphenyl)-4-phenylbut-3-en-2-one (3ai)

Yellow oil; yield: 217 mg (57%); mixture of geometric isomers (~1:0.3).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.39 (m, 2.9 H), 7.36–7.30 (m, 2 H), 7.27–7.20 (m, 2.9 H), 6.96 (d, *J* = 8.2 Hz, 0.3 H, minor ArH), 6.89 (dd, *J* = 12.9, 8.1 Hz, 2 H), 6.85–6.79 (m, 1.3 H), 6.74 (s, 0.3 H, minor ArH), 6.61–6.55 (m, 1.3 H), 3.79 (s, 0.9 H, minor OCH_3), 3.77 (s, 3 H, major OCH_3), 1.91 (s, 0.9 H, minor CH_3), 1.87 (s, 3 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.4, 159.7, 159.7, 153.9, 153.7, 142.4, 140.6, 140.4, 139.0, 129.7, 129.7, 129.6, 129.5, 128.9, 128.5, 128.4, 128.0, 127.9, 122.2, 121.1, 115.2, 115.0, 114.4, 114.2, 55.4, 30.4, 30.3.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{16}O_2$ $[M + H]^+$: 253.1223; found: 253.1225.

4-(4-Fluorophenyl)-4-phenylbut-3-en-2-one (3aj)

Yellow oil; yield: 217 mg (60%); mixture of geometric isomers (~1:0.7).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.32 (m, 5.1 H), 7.31–7.26 (m, 3.4 H), 7.22–7.18 (m, 3.4 H), 7.10 (t, *J* = 8.6 Hz, 1.4 H, minor ArH), 7.02 (t, *J* = 8.6 Hz, 2 H, major ArH), 6.59 (s, 0.7 H, minor CH), 6.53 (s, 1 H, major CH), 1.97 (s, 2.1 H, minor CH_3), 1.87 (s, 3 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.0, 199.6, 163.6 (d, *J* = 251 Hz), 163.1 (d, *J* = 249 Hz), 152.9, 152.9, 140.9, 138.9, 137.0 (d, *J* = 2 Hz), 134.9 (d, *J* = 3 Hz), 131.6 (d, *J* = 8 Hz), 130.4 (d, *J* = 8 Hz), 129.7, 129.7, 129.1, 128.7, 128.6, 128.5, 127.6, 115.6, 115.5, 30.8, 30.4.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{13}FO$ $[M + H]^+$: 241.1023; found: 241.1016.

4-(3-Fluorophenyl)-4-phenylbut-3-en-2-one (3ak)

Yellow oil; yield: 150 mg (42%); mixture of geometric isomers (~1:0.3).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.28 (m, 5.8 H), 7.21 (d, *J* = 4.0 Hz, 2 H), 7.14–6.92 (m, 3.9 H), 6.61 (s, 0.3 H, minor CH), 6.57 (s, 1 H, major CH), 1.95 (s, 0.9 H, minor CH_3), 1.89 (s, 3 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.0, 199.3, 162.7 (d, *J* = 246 Hz), 162.7 (d, *J* = 248 Hz), 152.4, 152.3, 143.1 (d, *J* = 8 Hz), 141.1 (d, *J* = 8 Hz), 140.2, 138.4, 130.0 (d, *J* = 9 Hz), 129.9 (d, *J* = 9 Hz), 129.7, 129.5, 129.0, 128.6, 128.4, 128.3, 127.6, 125.4 (d, *J* = 2 Hz), 124.0 (d, *J* = 2 Hz), 116.6, 116.5, 116.3, 116.2, 115.7, 115.6, 115.4, 115.2, 30.6, 30.4.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{13}FO$ $[M + H]^+$: 241.1023; found: 241.1013.

4-(2-Fluorophenyl)-4-phenylbut-3-en-2-one (3al)

Yellow oil; yield: 54 mg (15%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.30 (m, 4 H), 7.25–7.20 (m, 2 H), 7.12–7.05 (m, 3 H), 6.51 (s, 1 H), 1.94 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.1, 159.6 (d, *J* = 252 Hz), 147.0, 138.3, 130.9, 130.8 (d, *J* = 5 Hz), 129.95 (d, *J* = 9 Hz), 128.6, 128.5, 128.4, 128.3, 127.8, 123.4, 123.4, 115.7, 115.6, 29.8.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{13}FO$ $[M + H]^+$: 241.1023; found: 241.1023.

4-(4-Chlorophenyl)-4-phenylbut-3-en-2-one (3am)

Yellow oil; yield: 145 mg (38%); mixture of geometric isomers (~1:0.2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.28 (m, 6.2 H), 7.24–7.14 (m, 4.6 H), 6.60 (s, 0.2 H, minor CH), 6.55 (s, 1 H, major CH), 2.00 (s, 0.6 H, minor CH_3), 1.88 (s, 3 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 199.8, 199.1, 152.5, 152.4, 140.3, 139.1, 138.3, 137.2, 135.4, 134.7, 130.8, 129.5, 129.5, 129.4, 128.9, 128.5, 128.4, 128.4, 128.2, 127.7, 127.2, 30.6, 30.2.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{13}ClO$ $[M + H]^+$: 257.0728; found: 257.0717.

4-(4-Bromophenyl)-4-phenylbut-3-en-2-one (3an)

Yellow oil; yield: 116 mg (26%); mixture of geometric isomers (~1:0.1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 7.0 Hz, 0.2 H, minor ArH), 7.46 (dd, *J* = 8.4, 1.1 Hz, 2 H, major ArH), 7.44–7.32 (m, 3.3 H), 7.28 (s, 0.2 H, minor ArH), 7.20 (dd, *J* = 5.4, 1.9 Hz, 2 H, major ArH), 7.16 (dd, *J* = 8.4, 1.1 Hz, 2 H, major ArH), 7.10 (d, *J* = 7.0 Hz, 0.2 H, minor ArH), 6.60 (s, 0.1 H, minor CH), 6.55 (s, 1 H, major CH), 2.00 (s, 0.3 H, minor CH_3), 1.88 (s, 3 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.0, 199.3, 152.7, 152.7, 140.6, 139.9, 138.6, 138.0, 131.8, 131.7, 131.4, 130.0, 129.8, 129.7, 129.1, 128.7, 128.7, 128.5, 128.0, 127.5, 124.1, 123.2, 30.9, 30.4.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{13}BrO$ $[M + H]^+$: 301.0223; found: 301.0212.

4-(3,5-Dimethylphenyl)-4-phenylbut-3-en-2-one (3ao)

Yellow oil; yield: 224 mg (60%); mixture of geometric isomers (~1:0.4).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.30 (m, 5.2 H), 7.23–7.20 (m, 1.8 H), 7.05 (s, 0.4 H, minor ArH), 7.00 (s, 1 H, major ArH), 6.90 (s, 2 H, major ArH), 6.83 (s, 0.8 H, minor ArH), 6.56 (s, 1 H, major CH), 6.52 (s, 0.4 H, minor CH), 2.32 (s, 2.4 H, minor CH_3), 2.27 (s, 6 H, major CH_3), 1.86 (2s, 4.2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.7, 200.3, 154.6, 154.5, 141.1, 141.0, 139.3, 139.0, 138.1, 138.1, 131.3, 130.6, 129.7, 129.5, 128.8, 128.5, 128.5, 127.9, 127.7, 127.5, 126.4, 30.4, 30.3, 21.4, 21.4.

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{18}O$ $[M + H]^+$: 251.1430; found: 251.1425.

4-(3,4-Dimethylphenyl)-4-phenylbut-3-en-2-one (3ap)

Yellow oil; yield: 292 mg (78%); mixture of geometric isomers (~1:0.7).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 4.6 Hz, 3.4 H), 7.32–7.29 (m, 3.4 H), 7.20 (d, *J* = 4.7 Hz, 2 H), 7.15 (d, *J* = 7.5 Hz, 0.7 H), 7.10–7.05 (m, 2 H), 6.96 (dd, *J* = 13.1, 8.5 Hz, 2.1 H), 6.58 (s, 1 H, major CH), 6.52 (s, 0.7 H, minor CH), 2.30 (s, 2.1 H, minor CH_3), 2.25 (s, 5.1 H, CH_3), 2.21 (s, 3 H, major CH_3), 1.88 (s, 2.1 H, minor CH_3), 1.84 (s, 3 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.6, 200.2, 154.5, 154.4, 141.3, 139.4, 138.6, 138.5, 137.6, 136.8, 136.6, 130.9, 129.9, 129.8, 129.8, 129.6, 129.5, 128.8, 128.7, 128.5, 127.7, 127.5, 127.0, 126.3, 30.4, 30.4, 20.0, 19.9, 19.8, 19.8.

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{18}O$ $[M + H]^+$: 251.1430; found: 251.1423.

4-(4-Methoxyphenyl)-4-(*p*-tolyl)but-3-en-2-one (3ba)

Yellow oil; yield: 338 mg (85%); mixture of geometric isomers (~1:0.9).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.18 (m, 5.8 H), 7.14 (d, *J* = 3.5 Hz, 1.8 H, minor ArH), 7.12 (d, *J* = 3.0 Hz, 1.8 H, minor ArH), 7.09 (d, *J* = 7.7 Hz, 2 H, major ArH), 6.92 (d, *J* = 8.4 Hz, 1.8 H, minor ArH), 6.84 (d, *J* = 8.7 Hz, 2 H, major ArH), 6.51 (s, 1 H, major CH), 6.49 (s, 0.9 H, minor CH), 3.84 (s, 2.7 H, minor OCH_3), 3.80 (s, 3 H, major OCH_3), 2.40 (s, 3 H, major CH_3), 2.35 (s, 2.7 H, minor CH_3), 1.89 (s, 2.7 H, minor CH_3), 1.85 (s, 3 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.5, 200.3, 161.0, 160.4, 154.3, 154.3, 139.8, 138.9, 138.6, 136.4, 133.5, 131.4, 131.4, 130.1, 129.8, 129.2, 128.7, 126.8, 126.0, 113.9, 113.9, 55.5, 55.4, 30.4, 21.5, 21.4.

MS (ESI): *m*/*z* = 267.2 $[M + H]^+$.

4,4-Bis(4-methoxyphenyl)but-3-en-2-one (3bb)[6]

Yellow oil; yield: 236 mg (56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8.5 Hz, 2 H), 7.14 (d, *J* = 8.2 Hz, 2 H), 6.93 (d, *J* = 8.3 Hz, 2 H), 6.85 (d, *J* = 8.5 Hz, 2 H), 6.47 (s, 1 H), 3.86 (s, 3 H), 3.82 (s, 3 H), 1.87 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.3, 160.9, 160.3, 154.0, 133.6, 131.3, 130.1, 125.8, 113.8, 55.4, 55.3, 30.2.

MS (ESI): *m*/*z* = 283.1 $[M + H]^+$.

4-(4-(*tert*-Butyl)phenyl)-4-(4-methoxyphenyl)but-3-en-2-one (3bc)

Yellow oil; yield: 297 mg (64%); mixture of geometric isomers (~1:0.6).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.9 Hz, 1.2 H, minor ArH), 7.35 (d, *J* = 7.8 Hz, 2 H, major ArH), 7.25 (t, *J* = 7.0 Hz, 3.2 H), 7.15 (t, *J* = 7.5 Hz, 3.2 H), 6.94 (d, *J* = 8.5 Hz, 2 H, major ArH), 6.86 (d, *J* = 8.6 Hz, 1.2 H, minor ArH), 6.52 (s, 1.6 H), 3.86 (s, 3 H, major OCH_3), 3.82 (s, 1.8 H, minor OCH_3), 1.89 (s, 3 H, major CH_3), 1.83 (s, 1.8 H, minor CH_3), 1.36 (s, 5.4 H, minor *t*Bu), 1.32 (s, 9 H, major *t*Bu).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.6, 200.5, 160.9, 160.3, 154.3, 154.1, 153.0, 152.2, 138.3, 136.2, 133.5, 131.4, 130.1, 129.6, 128.5, 126.9, 126.1, 125.5, 125.4, 113.9, 55.5, 55.4, 34.8, 31.5, 31.3, 30.4, 30.3.

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{24}O_2$ $[M + H]^+$: 309.1849; found: 309.1841.

4-(4-Fluorophenyl)-4-(4-methoxyphenyl)but-3-en-2-one (3bd)

Yellow oil; yield: 231 mg (57%); mixture of geometric isomers (~1:0.4).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.25 (m, 2.4 H), 7.24–7.18 (m, 1.4 H), 7.14–7.08 (m, 2.6 H), 7.02 (t, *J* = 7.7 Hz, 2 H), 6.94 (d, *J* = 7.7 Hz, 2 H), 6.86 (d, *J* = 7.9 Hz, 0.8 H, minor ArH), 6.56 (s, 0.4 H, minor CH), 6.45 (s, 1 H, major CH), 3.86 (s, 3 H, major OCH_3), 3.82 (s, 1.2 H, minor OCH_3), 1.93–1.90 (m, 4.2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.3, 199.4, 163.6 (d, *J* = 251 Hz), 163.0 (d, *J* = 249 Hz), 161.0, 160.4, 152.9, 152.9, 137.4 (d, *J* = 3 Hz), 135.1 (d, *J* = 2 Hz), 133.0, 131.5 (d, *J* = 7 Hz), 131.3, 130.9, 130.5 (d, *J* = 9 Hz), 129.9, 127.2, 125.7, 115.5, 115.5, 115.4, 115.3, 113.9, 55.4, 55.3, 30.6, 30.2.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{15}FO_2$ $[M + H]^+$: 271.1129; found: 271.1134.

4-(4-Fluorophenyl)-4-(*p*-tolyl)but-3-en-2-one (3ca)

Yellow oil; yield: 230 mg (60%); mixture of geometric isomers (~1:0.4).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (dd, *J* = 8.8, 5.5 Hz, 0.8 H, minor ArH), 7.24–7.06 (m, 9.6 H), 7.00 (t, *J* = 8.6 Hz, 0.8 H, minor ArH), 6.58 (s, 1 H, major CH), 6.49 (s, 0.4 H, minor CH), 2.41 (s, 1.2 H, minor CH_3), 2.36 (s, 3 H, major CH_3), 1.94 (s, 3 H, major CH_3), 1.89 (s, 1.2 H, minor CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.2, 199.5, 163.6 (d, *J* = 251 Hz), 163.1 (d, *J* = 249 Hz), 153.2, 153.1, 140.1, 139.2, 138.0, 137.3 (d, *J* = 2 Hz), 135.9, 135.1 (d, *J* = 3 Hz), 131.6 (d, *J* = 8 Hz), 130.6 (d, *J* = 9 Hz), 129.7, 129.4, 128.5, 127.5, 126.8, 115.6, 115.6, 115.5, 115.4, 30.7, 30.4, 21.5, 21.4.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{15}FO$ $[M + H]^+$: 255.1180; found: 255.1177.

4-(4-Chlorophenyl)-4-(4-fluorophenyl)but-3-en-2-one (3cb)

Yellow oil; yield: 99 mg (24%); mixture of geometric isomers (~1:0.3).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.2 Hz, 0.6 H, minor ArH), 7.31 (d, *J* = 8.5 Hz, 2 H, major ArH), 7.27 (d, *J* = 3.7 Hz, 0.3 H, minor ArH), 7.24–7.15 (m, 4.6 H), 7.11 (t, *J* = 8.7 Hz, 2.3 H), 7.03 (t, *J* = 8.5 Hz, 0.6 H, minor ArH), 6.55 (s, 1.3 H), 1.99 (s, 0.9 H, minor CH_3), 1.97 (s, 3 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 199.5, 199.2, 163.8 (d, *J* = 251 Hz), 163.3 (d, *J* = 251 Hz), 151.7, 151.7, 139.4, 137.3, 136.8 (d, *J* = 3 Hz), 135.9, 135.2, 134.5 (d, *J* = 3 Hz), 131.6 (d, *J* = 8 Hz), 131.1, 130.4 (d, *J* = 8 Hz), 129.8, 128.9, 127.8, 127.3, 115.9, 115.8, 115.7, 115.7, 30.9, 30.8.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{12}ClFO$ $[M + H]^+$: 275.0633; found: 275.0626.

4-(4-Chlorophenyl)-4-(*p*-tolyl)but-3-en-2-one (3c'a)

Yellow oil; yield: 224 mg (55%); mixture of geometric isomers (~1:0.6).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.1 Hz, 2 H, major ArH), 7.28 (d, *J* = 8.4 Hz, 1.2 H, minor ArH), 7.21 (d, *J* = 8.3 Hz, 2 H, major ArH), 7.19–7.11 (m, 6.4 H), 7.07 (d, *J* = 7.6 Hz, 1.2 H, minor ArH), 6.58 (s, 1 H, major CH), 6.49 (s, 0.6 H, minor CH), 2.40 (s, 1.8 H, minor CH_3), 2.35 (s, 3 H, major CH_3), 1.97 (s, 3 H, major CH_3), 1.88 (s, 1.8 H, minor CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 199.9, 198.9, 152.5, 152.5, 139.8, 139.4, 138.9, 137.4, 137.3, 135.3, 134.5, 130.8, 129.5, 129.4, 129.1, 128.4, 128.1, 127.5, 126.3, 30.6, 30.1, 21.2, 21.0.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{15}ClO$ [M + H]$^+$: 271.0884; found: 271.0880.

4-(4-Chlorophenyl)-4-(*m*-tolyl)but-3-en-2-one (3c'b)

Yellow oil; yield: 201 mg (50%); mixture of geometric isomers (~1:0.3).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 8.3 Hz, 2 H, major ArH), 7.29–7.25 (m, 0.6 H, minor ArH), 7.23–7.11 (m, 5.2 H), 7.07 (s, 1 H), 7.04 (d, *J* = 7.3 Hz, 1 H), 6.98 (s, 0.6 H), 6.57 (s, 1 H, major CH), 6.50 (s, 0.3 H, minor CH), 2.34 (s, 0.9 H, minor CH_3), 2.30 (s, 3 H, major CH_3), 1.96 (s, 3 H, major CH_3), 1.85 (s, 0.9 H, minor CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.2, 199.3, 152.9, 152.9, 140.7, 139.5, 138.6, 138.4, 138.3, 137.6, 135.6, 134.8, 131.1, 130.6, 130.2, 129.9, 129.8, 129.1, 128.8, 128.7, 128.6, 128.6, 128.0, 127.4, 126.9, 125.8, 30.9, 30.4, 21.5.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{15}ClO$ [M + H]$^+$: 271.0884; found: 271.0882.

1,3,3-Triphenylprop-2-en-1-one (3da)[22]

Yellow oil; yield: 358 mg (84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 7.4 Hz, 2 H), 7.45 (t, *J* = 7.3 Hz, 1 H), 7.40–7.33 (m, 7 H), 7.27–7.24 (m, 3 H), 7.21–7.16 (m, 2 H), 7.11 (s, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 192.5, 154.5, 141.2, 138.9, 138.1, 132.5, 129.6, 129.2, 128.6, 128.4, 128.3, 128.2, 127.9, 123.9.

MS (ESI): *m*/*z* = 285.1 [M + H]$^+$.

1,3-Diphenyl-3-(*p*-tolyl)prop-2-en-1-one (3db)[23]

Yellow solid; yield: 393 mg (88%); mp 106–108 °C; mixture of geometric isomers (~1:0.9).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (t, *J* = 8.8 Hz, 3.8 H), 7.35 (t, *J* = 7.0 Hz, 1.9 H), 7.30–7.20 (m, 7.9 H), 7.15 (t, *J* = 8.5 Hz, 5.4 H), 7.05 (d, *J* = 7.5 Hz, 3.8 H), 7.00 (s, 1 H), 6.98–6.93 (m, 4.7 H), 2.26 (s, 3 H, major CH_3), 2.20 (s, 2.7 H, minor CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 192.5, 192.4, 154.9, 154.8, 141.5, 139.5, 139.0, 138.4, 138.3, 138.2, 138.2, 135.9, 132.4, 132.4, 129.6, 129.1, 129.0, 128.6, 128.6, 128.5, 128.4, 128.2, 128.2, 128.2, 128.1, 127.8, 123.5, 122.9, 21.2, 21.1.

HRMS (ESI): *m*/*z* calcd for $C_{22}H_{18}O$ [M + H]$^+$: 299.1430; found: 299.1439.

3-(4-Methoxyphenyl)-1,3-diphenylprop-2-en-1-one (3dc)[23]

Yellow oil; yield: 369 mg (78%); mixture of geometric isomers (~1:0.8).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95–7.87 (m, 3.6 H), 7.47 (t, *J* = 7.3 Hz, 2 H), 7.39–7.27 (m, 12.4 H), 7.18 (d, *J* = 5.3 Hz, 2 H), 7.14–7.09 (m, 2.6 H), 7.01 (s, 0.8 H), 6.88 (d, *J* = 7.4 Hz, 2 H), 6.78 (d, *J* = 8.2 Hz, 1.6 H), 3.83 (s, 3 H, major OCH_3), 3.77 (s, 2.4 H, minor OCH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 192.8, 192.1, 160.7, 159.7, 154.8, 154.6, 141.8, 139.2, 138.5, 138.3, 133.6, 132.4, 132.3, 131.4, 131.1, 129.9, 129.6, 129.1, 128.7, 128.6, 128.5, 128.4, 128.2, 128.2, 128.2, 127.9, 123.3, 121.8, 113.7, 113.3, 55.2, 55.0.

HRMS (ESI): *m*/*z* calcd for $C_{22}H_{18}O_2$ [M + H]$^+$: 315.1380; found: 315.1380.

3-(4-Fluorophenyl)-1,3-diphenylprop-2-en-1-one (3dd)

Yellow oil; yield: 338 mg (75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (s, 2 H), 7.49 (d, *J* = 7.0 Hz, 1 H), 7.38 (s, 5 H), 7.27 (s, 2 H), 7.19–7.04 (m, 4 H), 6.97 (t, *J* = 8.5 Hz, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 191.5, 191.5, 162.5 (d, *J* = 251 Hz), 161.7 (d, *J* = 249 Hz), 152.7, 152.6, 140.2, 137.8, 137.1, 136.4 (d, *J* = 3 Hz), 133.9 (d, *J* = 3 Hz), 131.8, 131.7, 130.6 (d, *J* = 8 Hz), 129.4 (d, *J* = 8 Hz), 128.7, 128.5, 127.7, 127.7, 127.5, 127.5, 127.4, 127.4, 127.1, 123.1, 122.8, 114.5, 114.4, 114.2, 114.0.

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{15}FO$ [M + H]$^+$: 303.1180; found: 303.1182.

β,β-Diaryl α,β-Unsaturated Ketones 3a Using Aryl Bromides (Table 3); General Procedure

A tube (30 mL) equipped with a magnetic stirring bar was charged with benzylacetone (**1a**; 1.5 mmol), **2'** (5.25 mmol), $Pd(OAc)_2$ (10 mol%), L1 (10 mol%), and CsOAc (6.0 mmol) in DMSO (1.5 mL), then the tube was sealed, purged with O_2, and the mixture was stirred at 100 °C for 24 h. At the end of the reaction, the mixture was partitioned between EtOAc (30 mL) and H_2O (30 mL). The organic layer was separated, and the aqueous layer was extracted further with EtOAc (3 × 30 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Then, the crude mixture was purified by column chromatography (silica gel; *n*-hexane/EtOAc) to afford the desired product.

4-Phenyl-4-(*p*-tolyl)but-3-en-2-one (3ab)

Yellow oil; yield: 184 mg (52%); mixture of geometric isomers (~1:0.2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.29 (m, 4.2 H), 7.23–7.18 (m, 4.4 H), 7.15–7.09 (m, 2.2 H), 6.57 (s, 1 H, major CH), 6.54 (s, 0.2 H, minor CH), 2.41 (s, 0.6 H, minor CH_3), 2.36 (s, 3 H, major CH_3), 1.89 (s, 0.6 H, minor CH_3), 1.86 (s, 3 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.5, 200.2, 154.2, 154.1, 141.1, 139.8, 139.1, 138.9, 137.9, 136.0, 129.7, 129.6, 129.4, 129.2, 129.1, 128.7, 128.5, 128.4, 128.4, 127.6, 126.9, 30.3, 21.4, 21.3.

MS (ESI): *m*/*z* = 237.2 [M + H]$^+$.

4-Phenyl-4-(*m*-tolyl)but-3-en-2-one (3ac)

Yellow oil; yield: 120 mg (34%); mixture of geometric isomers (~1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.28 (m, 9 H), 7.25–7.17 (m, 5 H), 7.12 (s, 1 H), 7.07 (d, *J* = 7.4 Hz, 1 H), 7.02 (s, 2 H), 6.57 (s, 1 H), 6.55 (s, 1 H), 2.37 (s, 3 H), 2.32 (s, 3 H), 1.87 (s, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.5, 200.3, 154.2, 140.9, 140.8, 139.1, 138.9, 138.2, 138.1, 130.3, 130.1, 129.6, 129.6, 129.4, 129.0, 128.7, 128.6, 128.4, 128.3, 128.3, 127.8, 127.7, 127.6, 126.8, 125.7, 30.3, 30.2, 21.4, 21.4.

MS (ESI): *m*/*z* = 237.2 [M + H]$^+$.

4-(4-Fluorophenyl)-4-phenylbut-3-en-2-one (3aj)

Yellow oil; yield: 209 mg (58%); mixture of geometric isomers (~1:0.1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.39 (m, 3.1 H), 7.35 (d, *J* = 7.9 Hz, 0.2 H), 7.30–7.26 (m, 2.2 H), 7.23–7.18 (m, 2.2 H), 7.10 (t, *J* = 8.5 Hz, 0.2 H), 7.02 (t, *J* = 8.5 Hz, 2 H), 6.58 (s, 0.1 H), 6.53 (s, 1 H), 1.97 (s, 0.3 H), 1.87 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 200.0, 199.6, 163.5 (d, *J* = 251 Hz), 163.0 (d, *J* = 249 Hz), 152.9, 152.9, 140.7, 138.8, 136.9 (d, *J* = 1.51 Hz), 134.8 (d, *J* = 1.51 Hz), 131.5 (d, *J* = 7.55 Hz), 130.3 (d, *J* = 7.55 Hz), 129.6, 129.6, 128.8, 128.5, 128.5, 128.4, 127.5, 115.5, 115.4, 30.7, 30.3.

MS (ESI): *m*/*z* = 241.1 $[M + H]^+$.

β,β-Diaryl α,β-Unsaturated Aldehydes 3ea–ee (Table 4); General Procedure

A tube (30 mL) equipped with a magnetic stirring bar was charged with benzenepropanal (**1e**; 201 mg, 1.5 mmol), **2** (3.75 mmol), $Pd(OAc)_2$ (10 mol%), L1 (10 mol%), and CsOAc (4.5 mmol) in DMSO (1.5 mL), then the tube was sealed, purged with O_2, and the mixture was stirred at 100 °C for 4 h. At the end of the reaction, the mixture was partitioned between EtOAc (30 mL) and H_2O (30 mL). The organic layer was separated, and the aqueous layer was extracted further with EtOAc (3 × 30 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Then, the crude mixture was purified by column chromatography (silica gel; *n*-hexane/EtOAc) to afford the desired product.

3,3-Diphenylacrylaldehyde (3ea)

Yellow oil; yield: 237 mg (76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.53 (d, *J* = 8.0 Hz, 1 H), 7.49–7.35 (m, 8 H), 7.31 (d, *J* = 7.6 Hz, 2 H), 6.60 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 194.0, 162.7, 140.2, 137.1, 131.2, 131.0, 129.9, 129.1, 129.1, 128.8, 127.8.

MS (ESI): *m*/*z* = 209.1 $[M + H]^+$.

3-Phenyl-3-(*p*-tolyl)acrylaldehyde (3eb)

Yellow oil; yield: 249 mg (75%); mixture of geometric isomers (~1:0.5).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.43 (d, *J* = 8.0 Hz, 0.5 H, minor CHO), 9.38 (d, *J* = 8.0 Hz, 1 H, major CHO), 7.38–7.30 (m, 3.5 H), 7.27–7.23 (m, 2 H), 7.18 (d, *J* = 7.6 Hz, 2 H), 7.15–7.12 (m, 3 H), 7.07 (t, *J* = 6.7 Hz, 3 H), 6.47 (d, *J* = 8.0 Hz, 1 H, major CH), 6.44 (d, *J* = 8.0 Hz, 0.5 H, minor CH), 2.31 (s, 1.5 H, minor CH_3), 2.26 (s, 3 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 193.5, 162.4, 162.2, 140.9, 139.9, 139.6, 136.7, 133.6, 130.7, 130.6, 130.3, 129.2, 128.9, 128.6, 128.5, 128.4, 128.1, 127.0, 126.4, 21.2.

MS (ESI): *m*/*z* = 223.1 $[M + H]^+$.

3-Phenyl-3-(*m*-tolyl)acrylaldehyde (3ec)

Yellow oil; yield: 227 mg (68%); mixture of geometric isomers (~1:0.6).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.52 (dd, *J* = 7.9, 6.9 Hz, 1.6 H), 7.48–7.41 (m, 3.2 H), 7.38–7.35 (m, 2.6 H), 7.33–7.28 (m, 3.2 H), 7.27–7.22 (m, 2.2 H), 7.17 (s, 1 H), 7.15–7.09 (m, 2.2 H), 6.58 (dd, *J* = 8.0, 2.6 Hz, 1.6 H), 2.39 (s, 1.8 H, minor CH_3), 2.34 (s, 3 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 193.8, 193.7, 162.6, 162.6, 139.9, 139.9, 138.5, 138.2, 136.9, 136.8, 131.4, 131.4, 130.9, 130.6, 130.3, 129.5, 129.4, 128.8, 128.7, 128.6, 128.4, 128.3, 128.1, 127.4, 127.3, 126.1, 21.5, 21.5.

MS (ESI): *m*/*z* = 223.1 $[M + H]^+$.

3-(4-(*tert*-Butyl)phenyl)-3-phenylacrylaldehyde (3ed)

Yellow oil; yield: 217 mg (55%); mixture of geometric isomers (~1:0.3).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.55 (d, *J* = 7.9 Hz, 0.3 H, minor CHO), 9.50 (d, *J* = 7.9 Hz, 0.9 H, major CHO), 7.47–7.37 (m, 7.2 H), 7.31 (s, 3.9 H), 7.24 (d, *J* = 7.4 Hz, 0.6 H, minor ArH), 6.62 (d, *J* = 7.7 Hz, 1 H, major CH), 6.57 (d, *J* = 8.0 Hz, 0.3 H, minor CH), 1.37 (s, 2.7 H, minor CH_3), 1.33 (s, 9 H, major CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 193.8, 193.7, 162.5, 162.2, 154.2, 152.9, 140.0, 136.8, 136.6, 133.7, 130.7, 130.4, 129.3, 128.8, 128.6, 128.5, 128.3, 127.2, 126.6, 125.6, 125.2, 34.8, 31.3, 31.1.

MS (ESI): *m*/*z* = 265.2 $[M + H]^+$.

3-(4-Chlorophenyl)-3-phenylacrylaldehyde (3ee)

Yellow oil; yield: 126 mg (35%); mixture of geometric isomers (~1:0.7).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.52 (dd, *J* = 8.0, 5.3 Hz, 1.7 H), 7.50–7.43 (m, 5.1 H), 7.42–7.36 (m, 2.4 H), 7.35 (s, 2 H), 7.34–7.32 (m, 0.7 H), 7.30 (s, 2 H), 7.29–7.28 (m, 1.4 H), 7.27 (d, *J* = 2.7 Hz, 1 H), 7.26–7.24 (m, 0.7 H), 6.60 (d, *J* = 8.0 Hz, 0.7 H, minor CH), 6.58–6.55 (m, 1 H, major CH).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 193.3, 192.9, 160.9, 139.3, 138.2, 136.7, 136.2, 135.8, 135.1, 132.0, 130.7, 130.7, 129.9, 129.7, 128.9, 128.8, 128.7, 128.6, 128.5, 127.6, 127.4.

MS (ESI): *m*/*z* = 243.1 $[M + H]^+$.

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Supporting Information

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References

(1) (a) Welch, W. M.; Kraska, A. R.; Sarges, R.; Koe, B. K. *J. Med. Chem.* **1984**, *27*, 1508. (b) Murdoch, D.; McTavish, D. *Drugs* **1992**, *44*, 604. (c) Chen, G.; Xia, H.; Cai, Y.; Ma, D.; Yuan, J.; Yuan, C. *Bioorg. Med. Chem. Lett.* **2011**, *21*, 234. (d) Shen, Q.; Qian, Y.; Huang, X.; Xu, X.; Li, W.; Liu, J.; Fu, W. *ACS Med. Chem. Lett.* **2016**, *7*, 391. (e) Saku, O.; Ishida, H.; Atsumi, E.; Sugimoto, Y.; Kodaira, H.; Kato, Y.; Shirakura, S.; Nakasato, Y. *J. Med. Chem.* **2012**, *55*, 3436.

(2) (a) Tiwari, P. K.; Aidhen, I. S. *Eur. J. Org. Chem.* **2016**, 2637. (b) Xiao, L.; Zheng, Y.; Xie, Q.; Shao, L. *Eur. J. Org. Chem.* **2017**, 5880. (c) Zhu, Z. Q.; He, J. S.; Wang, H. J.; Huang, Z. Z. *J. Org. Chem.* **2015**, *80*, 9354. (d) Le Bras, J.; Muzart, J. *Adv. Synth. Catal.* **2018**, *360*, 2411.

(3) (a) Kondolff, I.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2003**, *44*, 8487. (b) Yokota, T.; Tani, M.; Sakaguchi, S.; Ishii, Y. *J. Am. Chem. Soc.* **2003**, *125*, 1476. (c) Tani, M.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **2004**, *69*, 1221. (d) Botella, L.; Nájera, C. *J. Org. Chem.* **2005**, *70*, 4360.

(4) Jin, W.; Du, W.; Yang, Q.; Yu, H.; Chen, J.; Yu, Z. *Org. Lett.* **2011**, *13*, 4272.

(5) Bethi, V.; Fernandes, R. A. *J. Org. Chem.* **2016**, *81*, 8577.
(6) Rosa, D.; Orellana, A. *Org. Lett.* **2011**, *13*, 3648.
(7) Ryabukhin, D. S.; Vasilyev, A. V. *Mendeleev Commun.* **2016**, *26*, 500.
(8) Gandeepan, P.; Rajamalli, P.; Cheng, C.-H. *ACS Catal.* **2014**, *4*, 4485.
(9) (a) Qi, C.; Sun, X.; Lu, C.; Yang, J.; Du, Y.; Wu, H.; Zhang, X.-M. *J. Organomet. Chem.* **2009**, *694*, 2912. (b) Wang, L.; Lu, W. *Org. Lett.* **2009**, *11*, 10792. (c) Hajipour, A. R.; Rafiee, F. *Synth. Commun.* **2013**, *43*, 1314. (d) Afsaneh, F.; Ayoob, B.; Balu, A. M.; Rafael, L. *Sci. Rep.* **2016**, *6*, 32719. (e) Lane, B. S.; Sames, D. *Org. Lett.* **2004**, *6*, 2897.
(10) (a) Diao, T.; Wadzinski, T. J.; Stahl, S. S. *Chem. Sci.* **2012**, *3*, 887. (b) Gao, W.; He, Z.; Qian, Y.; Zhao, J.; Huang, Y. *Chem. Sci.* **2012**, *3*, 883.
(11) (a) Shang, Y.; Jie, X.; Zhou, J.; Hu, P.; Huang, S.; Su, W. *Angew. Chem. Int. Ed.* **2013**, *52*, 1299. (b) Yip, K.-T.; Nimje, R. Y.; Leskinen, M. V.; Pihko, P. M. *Chem. Eur. J.* **2012**, *18*, 12590.
(12) Izawa, Y.; Pun, D.; Stahl, S. S. *Science* **2011**, *333*, 209.
(13) Muzart, J. *Eur. J. Org. Chem.* **2010**, 3779.
(14) (a) Konnick, M. M.; Stahl, S. S. *J. Am. Chem. Soc.* **2008**, *130*, 5753. (b) Decharin, N.; Popp, B. V.; Stahl, S. S. *J. Am. Chem. Soc.* **2011**, *133*, 13268. (c) Iosub, A. V.; Stahl, S. S. *ACS Catal.* **2016**, *6*, 8201. (d) Gligorich, K. M.; Sigman, M. S. *Angew. Chem. Int. Ed.* **2006**, *45*, 6612. (e) Muzart, J. *Chem. Asian J.* **2006**, *1*, 508. (f) Scheuermann, M. L.; Goldberg, K. I. *Chem. Eur. J.* **2014**, *20*, 14556.
(15) Campbell, A. N.; Stahl, S. S. *Acc. Chem. Res.* **2012**, *45*, 851.
(16) Vasseur, A.; Laugel, C.; Harakat, D.; Muzart, J.; Le Bras, J. *Eur. J. Org. Chem.* **2015**, 944.
(17) Larock, R. C.; Hightower, T. R. *J. Org. Chem.* **1993**, *58*, 5298.
(18) Tamaru, Y.; Yamamoto, Y.; Yamada, Y.; Yoshida, Z. I. *Tetrahedron Lett.* **1979**, 1401.
(19) Roman, G.; Riley, J. G.; Vlahakis, J. Z.; Kinobe, R. T.; Brien, J. F.; Nakatsu, K.; Szarek, W. A. *Bioorg. Med. Chem.* **2007**, *15*, 3225.
(20) Cao, J. J.; Zhou, F.; Zhou, J. *Angew. Chem. Int. Ed.* **2010**, *49*, 4976.
(21) Shchukin, A. O.; Vasilyev, A. V. *Appl. Catal., A* **2008**, *336*, 140.
(22) (a) Engel, D. A.; Dudley, G. B. *Org. Lett.* **2006**, *8*, 4027. (b) Uyanik, M.; Fukatsu, R.; Ishihara, K. *Org. Lett.* **2009**, *11*, 3470.
(23) Singh, G.; Purkayastha, M. L.; Ila, H.; Junjappa, H. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1289.