Paper

Regioselective Synthesis of 2-Acylbutadienes from β , γ -Unsaturated Ketones

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²⁻Acylbutadienes: promising reagents for further synthetic applications

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Abstract 2-Acylbuta-1,3-dienes have been synthesized regioselectively from aromatic and heteroaromatic β , γ -unsaturated ketones (readily accessible via base-catalyzed addition of ketones to acetylenes) and aldehydes. The reaction smoothly proceeds with piperidine (10 mol%)/acetic acid (10 mol%) catalytic pair in boiling toluene to provide synthetically attractive polyconjugated electron-deficient dienes in up to 94% yield.

Key words condensation, C–C bond formation, unsaturated ketones, aldehydes, conjugated dienes

The search for straightforward and efficient methods of carbon–carbon bond formation, especially those based on the principles of pot-atom-step-economy (PASE paradigm),¹ is among the main challenges of modern organic chemistry. In this context, the base-catalyzed addition of ketones to alkynes to afford β , γ -unsaturated ketones has recently been discovered (Scheme 1).² Due to inexpensive starting materials and easy-to-handle catalytic systems (alkali metal hydroxides or alkoxides in DMSO), this exclusively *E*-stereoselective reaction has rapidly become an indispensable tool for the synthesis of a broad range of carboand heterocycles.³



Over the past decade, carbon nucleophiles derived from β , γ -unsaturated ketones (allyl ketones) have been extensively studied in vinylogous reactions with diverse π -electrophiles,⁴ namely carbonyl compounds,⁵ imines,⁶ activated alkenes⁷ and alkynes.⁸ It is noteworthy that these studies are focused on regio-, diastereo-, and enantioselective syntheses of aldol-type products and mainly concern the reactivity of allyl ketones with free α , β , γ -positions (R² = R³ = H, Scheme 1). However, as far as we know, the only report presented to date has been when an aldol-type product, prepared from allyl ketone and ethyl glyoxalate in the presence of lithium diisopropylamide, was subsequently treated with methanesulfonyl chloride to form the corresponding diene system.⁹

Encouraged by this fact, we have initiated developing a regio- and/or stereoselective approach to synthetically attractive polyconjugated electron-deficient dienes in which for the first time the condensation of now readily available β , γ -unsaturated ketones as active methylene compounds with aldehydes was utilized (Scheme 2).



Scheme 2 Possible products of the reaction between β , γ -unsaturated ketones and aldehydes

We envisioned that acidity of methylene group in the α position of β , γ -unsaturated ketones should be high enough to ensure deprotonation under the action of a weak organic base, for example, an amine. Indeed, when a mixture of (*E*)-1,4-diphenyl-3-buten-1-one (**1a**), 4-nitrobenzaldehyde

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(2a), and piperidine (10 mol%) was refluxed in toluene for 3 hours, that is under Knoevenagel condensation conditions,¹⁰ we observed formation of the desired diene **3aa** (Table 1, entry 3). The condensation reaction turned out to be α -regioselective but afforded a mixture of *E*- and *Z*-isomers relative to newly formed C=C bond, while the existing C=C bond of ketone **1a** remained in the *E*-configuration.

Given that acidic additives facilitate the Knoevenagel condensation by increasing the electrophilicity of the aldehyde group,¹⁰ we easily achieved full conversion of the

starting aldehyde **2a** by the introduction of acetic acid (10 mol%, Table 1, entry 4) in the reaction mixture. Another issue to be addressed was stereoselectivity of the reaction. Although changing the catalyst and additive loadings (entries 1–14) and nature (entries 15–23) had an impact on E/Z-stereoselectivity of the model reaction, we finally failed to carry out this condensation in a stereoselective mode. Since it is well known that the stereoselectivity of the condensation reactions is governed by steric effects¹⁰ and, if necessary, the *E*- and *Z*-isomers could be separated (see be-

Table 1 Condensation of β , γ -Unsaturated Ketone **1a** with 4-Nitrobenzaldehyde (**2a**)^a

2a

Ph Ph		0
1a	Catalyst (X mol%) Additive (X mol%)	Ph
+ 0-N-0	PhMe, 110–115 °C	NC
°₂.		(<i>E.E</i>)-3aa



Entry	Catalyst (mol%)	Additive (mol%)	Time (h)	Ratio of 2a /(<i>E</i> , <i>E</i>)- 3aa /(<i>Z</i> , <i>E</i>)- 3aa ^b
1	-	_	3	100:0:0
2	-	AcOH (10)	3	100:0:0
3	piperidine (10)	-	3	40:32:28
4	piperidine (10)	AcOH (10)	3	0:55:45
5	piperidine (10)	AcOH (50)	3	0:50:50
6	piperidine (10)	AcOH (100)	3	0:65:35
7	piperidine (10)	AcOH (200)	3	15:73:12
8	piperidine (10)	AcOH (100)	1.5	29:57:14
9	piperidine (10)	AcOH (100)	6	0:55:45
10	piperidine (1)	AcOH (100)	3	50:43:7
11	piperidine (5)	AcOH (100)	3	10:75:15
12	piperidine (50)	AcOH (10)	3	0:35:65
13	piperidine (50)	AcOH (50)	3	0:35:65
14	piperidine (100)	AcOH (10)	3	0:35:65
15	pyrrolidine (10)	AcOH (100)	3	3:73:24
16	morpholine (10)	AcOH (100)	3	47:40:13
17	$PhCH_2NH_2$ (10)	AcOH (100)	3	68:22:10
18	PhNH ₂ (10)	AcOH (100)	3	_c
19	β-alanine (10)	AcOH (100)	3	72:22:6
20	ϵ -aminocaproic acid (10)	AcOH (100)	3	71:21:8
21	L-proline (10)	AcOH (100)	3	100:0:0
22	<i>t</i> -BuOK (10)	AcOH (100)	3	88:6:6
23	piperidine (10)	TFA (100)	3	65:32:3
24	piperidine (10)	TsOH·H ₂ O (100)	3	100:0:0 ^c
25	piperidine (10)	HCO ₂ H (100)	3	50:44:6

^a Reaction conditions: ketone **1a** (0.6 mmol), aldehyde **2a** (0.5 mmol), toluene (2 mL), 110–115 °C (oil bath).

^b According to ¹H NMR spectra of crude.

^c Intensive tar formation.

low), we have turned our attention to the examination of the reaction tolerance toward a set of β , γ -unsaturated ketones **1** and aldehydes **2** (Table 2).

As follows from Table 2, most of the β , γ -unsaturated ketones **1** readily react with 4-nitrobenzaldehyde **2a**, providing the condensation products as a mixture of isomers in 62–94% total yields. The presence of electron-donating groups at the carbonyl function of ketones **1** impedes the reaction; thus, the yield of diene **3ea** (derived from 4-methoxyphenyl-substituted β , γ -unsaturated ketone **1e**) was only 64% (in comparison with 88% yield of **3aa**), while *tert*butyl-substituted ketone **1h** gave even no traces of the desired product **3ha** after 8 hours (¹H NMR).

As mentioned above, the *E*- and *Z*-isomers can be separated that was exemplified by isolation of *E*- and *Z*-isomers of diene **3da** in a pure state in 23% and 59% yield, respectively (Scheme 3). Heating of pure samples of *E*- and *Z*-isomers of **3da** under the condensation reaction conditions [piperidine (10 mol%), acetic acid (10 mol%), toluene, 110– Due to the lower electrophilicity of the starting aldehydes **2b–h** compared to 4-nitrobenzaldehyde (**2a**), condensation of aromatic and heteroaromatic aldehydes **2b–g** with model β , γ -unsaturated ketone **1a** was less effective, and cyclohexanecarboxaldehyde (**2h**), a representative of alkyl aldehydes, was completely inert in the studied reaction. It should be noted that in all cases the starting ketone **1a** was entirely consumed, while aldehydes **2** were still detected in the crude (¹H NMR), that indicates the tendency of β , γ -unsaturated ketones **1** to participate in diverse side reactions (e.g., base-catalyzed autocondensation followed by a cascade formation of terphenyls).¹¹

Unfortunately, all attempts to prepare diene **3aa** in a one-pot manner, starting from acetophenone and phenyl-acetylene with the subsequent trapping of the enolate in-



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^a Reaction conditions: ketone **1** (0.6 mmol), aldehyde **2** (0.5 mmol), piperidine (5 μL, 10 mol%), AcOH (3 μL, 10 mol%), toluene (2 mL), 110–115 °C (oil bath). ^b Isolated yields after column chromatography (silica gel, eluent hexane/Et₂O, with gradient from 9:1 to 0:1).

e Reaction time was 3 h for 3aa, 3ba, 3ca, 3ja, 3ka, 3ab, 3ac, 3ad, 3ae, 3af, 4 h for 3ga, 3ia, 3la, 3ag, 5 h for 3da, 3ea, 3fa, and 8 h for 3ha, 3ah.

^d Ratios of isomers were determined by ¹H NMR spectra of the crude.

^e Stereochemistry was not determined due to intensive tar formation.



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termediate with 4-nitrobenzaldehyde (**2a**) (similar to the recently reported alkylation of β , γ -unsaturated ketones)¹² were unsuccessful. This is apparently caused by solvent effects since the first stage requires the use of DMSO as a solvent, while the condensation reaction in DMSO under standard conditions (Table 1, entry 4) turned out to be ineffective.

The structures of all synthesized dienes **3**, including the configurational assignment and the location of the substituents, were unambiguously proven by ¹H, ¹³C, and 2D (NO-ESY, 1H-13C HSQC, 1H-13C HMBC) NMR spectroscopy. For example, in the 2D NOESY spectra of **3aa** (Figure 1), crosspeaks were observed between the signals of proton at the C^{1'} and protons at the *ortho*-position of the benzoyl moiety for E.E-isomer of **3aa**, while for Z.E-isomer of **3aa** crosspeaks between the signals of proton at the C^{1'} and protons at the C^3 and C^4 were detected. The cross-peaks between the signals of olefinic protons at the C³ and C⁴ and protons at the ortho-position of phenyl moiety of 3aa and the values of vicinal ${}^{3}J_{H-3,H-4}$ (ca. 16 Hz) corresponds to the *E*-configuration of C³–C⁴ double bond. Additionally, the configuration of $C^{1'}-C^2$ double bond was confirmed by the values of vicinal ${}^{3}J_{C-1/H-1'}$ equal to 6.7 Hz and 10.3 Hz for E,E- and Z,E-isomers of 3aa, respectively.



Figure 1 Cross-peaks in the NOESY (solid lines) and HMBC (dashed lines) spectra of diene **3aa**

It is relevant to note here that 2-acylbutadienes are less accessible compounds in comparison with well-explored 1acylbutadienes.¹³ The first synthesis of a simple 2-acylbutadiene, namely 4-methyl-3-methylenepent-4-en-2-one, was reported in 1962.¹⁴ Later studies revealed a low stability of simple 2-acylbutadienes and their tendency to undergo a spontaneous dimerization,¹⁵ which in some cases was reduced by trapping of dienes with carbonyliron complexes.¹⁶ Several known approaches to more stable substituted 2-acylbutadienes are based on the reactions of lithium-,¹⁷ zinc-¹⁸ or tin-organic¹⁹ substrates with carboxylic acid derivatives and rhodium-catalyzed carbonylative arylation of allenols with arylboronic acids.²⁰ Therefore, a successful employment of readily available β , γ -unsaturated ketones (adducts of ketones with alkynes)² as active methylene compounds in the condensation with aldehydes contributes considerably to the accessibility of synthetically attractive 2-acylbutadienes.

In summary, we have successfully implemented the condensation of β , γ -unsaturated ketones with aldehydes, which proved to be an effective regioselective approach to polyconjugated electron-deficient dienes (2-acylbuta-dienes) based on the use of simple and cheap starting materials and catalytic system. Taking into account the rich chemistry of dienes,²¹ here synthesized butadienes, additionally activated by the presence of an electron-withdrawing acyl group, represent promising reactive reagents for further synthetic applications.

All chemicals and solvents were purchased from commercial sources. Toluene and piperidine were distilled over Na, and AcOH was distilled with Ac₂O in order to remove any H₂O. Starting β , γ -unsaturated ketones 1 were prepared according to the literature method.² TLC was carried out on Merck silica gel 60 F₂₅₄ pre-coated aluminum foil sheets and were visualized by UV light (254 nm). Column chromatography was carried out using slurry packed Sigma Aldrich silica gel (SiO₂), 70–230 mesh, pore size 60 Å. NMR spectra were recorded from solutions in CDCl₃ on Bruker DPX-400 and AV-400 spectrometers (400.1 MHz for ¹H and 100.6 MHz for ¹³C). Chemical shifts (δ) are quoted in parts per million (ppm). The residual solvent peak, δ_H 7.26 and δ_{c} 77.10 was used as a reference. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations are used for denoting multiplicity. Signals were assigned through analysis of 2D COSY, NO-ESY, HMBC, and HSQC experiments if required. High-resolution mass spectra were recorded from MeCN solution with 0.1% HFBA on HPLC Agilent 1200/Agilent 6210 TOF instrument equipped with an electrospray ionization (ESI) source. Melting points (uncorrected) were measured on a digital melting point apparatus Electrothermal IA 9200.

Synthesis of New Starting $\beta,\gamma\text{-}Unsaturated$ Ketones 1; General Procedure

A mixture of ketone (4.0 mmol), acetylene (4.0 mmol), and *t*-BuOK (449 mg, 4.0 mmol) in DMSO (10 mL) was stirred at 100 °C for 30 min. The reaction mixture after cooling to r.t. was diluted with H₂O (10 mL), neutralized with aq NH₄Cl, and extracted with Et₂O (4 × 10 mL). The combined organic extracts were washed with H₂O (3 × 5 mL) and

dried (MgSO₄). After removal of the solvent, the residue was purified by column chromatography (silica gel, eluent: hexane/Et₂O with gradient from 1:0 to 0:1) to afford the desired β , γ -unsaturated ketone **1**.

(E)-1-(4-Chlorophenyl)-4-phenylbut-3-en-1-one (1d)

Following the general procedure, **1d** was prepared from 4-chloroace-tophenone (618 mg, 4.0 mmol) and phenylacetylene (408 mg, 4.0 mmol); white solid; yield: 360 mg (35%); mp 122–124 °C.

¹H NMR (400.1 MHz, CDCl₃): δ = 7.95 (d, *J* = 8.6 Hz, 2 H, ArH), 7.46 (d, *J* = 8.6 Hz, 2 H, ArH), 7.39–7.37 (m, 2 H, C₆H₅), 7.33–7.29 (m, 2 H, C₆H₅), 7.25–7.21 (m, 1 H, C₆H₅), 6.57–6.41 (m, 2 H, CH=CH), 3.89–3.88 (m, 2 H, CH₂).

 $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CDCl_3): δ = 196.8, 139.8, 136.9, 135.0, 133.9, 129.8, 129.1, 128.6, 127.7, 126.4, 122.2, 42.8.

HRMS (ESI-TOF): m/z calcd for $[C_{16}H_{13}CIO + H]^*$: 257.0733; found: 257.0767.

(E)-1-(4-Methoxyphenyl)-4-phenylbut-3-en-1-one (1e)

Following the general procedure, **1e** was prepared from 4-methoxy-acetophenone (600 mg, 4.0 mmol) and phenylacetylene (408 mg, 4.0 mmol); white solid; yield: 425 mg (42%); mp 96–97 $^{\circ}$ C.

¹H NMR (400.1 MHz, CDCl₃): δ = 7.92 (d, J = 8.2 Hz, 2 H, ArH), 7.40–7.38 (m, 2 H, C₆H₅), 7.32–7.26 (m, 2 H, C₆H₅, 2 H, ArH), 7.24–7.20 (m, 1 H, C₆H₅), 6.57–6.44 (m, 2 H, CH=CH), 3.90–3.88 (m, 2 H, CH₂), 2.42 (s, 3 H, OCH₃).

 $^{13}C\{^1H\}$ NMR (100.6 MHz, CDCl_3): δ = 197.7, 144.1, 137.1, 134.3, 133.5, 129.4, 128.6, 128.5, 127.5, 126.4, 122.9, 42.7, 21.7.

HRMS (ESI-TOF): m/z calcd for $[C_{17}H_{16}O_2 + H]^+$: 253.1229; found: 253.1245.

(E)-4-([1,1'-Biphenyl]-4-yl)-1-phenylbut-3-en-1-one (1i)

Following the general procedure, **1i** was prepared from acetophenone (480 mg, 4.0 mmol) and 4-ethynyl-1,1'-biphenyl (713 mg, 4.0 mmol); white solid; yield: 480 mg (40%); mp 147–149 °C.

 ^1H NMR (400.1 MHz, CDCl_3): δ = 8.04–8.02 (m, 2 H, C_6H_5), 7.61–7.55 (m, 5 H, C_6H_5), 7.52–7.42 (m, 6 H, C_6H_5), 7.36–7.32 (m, 1 H, ArH), 6.62–6.49 (m, 2 H, CH=CH), 3.95–3.94 (m, 2 H, CH_2).

 $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CDCl₃): δ = 198.0, 140.8, 140.3, 136.7, 136.1, 133.3, 133.2, 128.9, 128.8, 128.4, 127.4, 127.3, 127.0, 126.8, 122.8, 42.8.

HRMS (ESI-TOF): m/z calcd for $[C_{22}H_{18}O + H]^+$: 299.1436; found: 299.1454.

(E)-4-(3-Fluorophenyl)-1-phenylbut-3-en-1-one (1j)

Following the general procedure, **1j** was prepared from acetophenone (480 mg, 4.0 mmol) and 3-fluorophenylacetylene (480 mg, 4.0 mmol); white solid; yield: 384 mg (40%); mp 94–96 °C.

¹H NMR (400.1 MHz, CDCl₃): δ = 8.02–7.99 (m, 2 H, C₆H₅), 7.61–7.57 (m, 1 H, C₆H₅), 7.51–7.47 (m, 2 H, C₆H₅), 7.29–7.23 (m, 1 H, ArH), 7.16–7.14 (m, 1 H, ArH), 7.11–7.07 (m, 1 H, ArH), 6.94–6.89 (m, 1 H, ArH), 6.52–6.50 (m, 2 H, CH=CH), 3.93–3.92 (m, 2 H, CH₂).

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ = 197.7, 163.1 (*J* = 245.1 Hz), 139.4 (*J* = 7.7 Hz), 136.5, 133.4, 132.5 (*J* = 2.5 Hz), 130.0 (*J* = 8.4 Hz), 128.8, 128.3, 124.1, 122.2 (*J* = 2.7 Hz), 114.3 (*J* = 21.4 Hz), 112.8 (*J* = 21.8 Hz), 42.5.

HRMS (ESI-TOF): m/z calcd for $[C_{16}H_{13}FO + H]^+$: 241.1029; found: 241.1022.

(E)-4-(3-Methoxyphenyl)-1-phenylbut-3-en-1-one (1k)

Following the general procedure, **1k** was prepared from acetophenone (480 mg, 4.0 mmol) and 3-methoxyphenylacetylene (529 mg, 4.0 mmol); white solid; yield: 360 mg (36%); mp 83–85 °C.

¹H NMR (400.1 MHz, CDCl₃): δ = 8.02–8.00 (m, 2 H, C₆H₅), 7.61–7.56 (m, 1 H, C₆H₅), 7.51–7.47 (m, 2 H, C₆H₅), 7.24–7.20 (m, 1 H, ArH), 6.99–6.97 (m, 1 H, ArH), 6.93–6.92 (m, 1 H, ArH), 6.80–6.77 (m, 1 H, ArH), 6.53 (d, ${}^{3}J$ = 16.1 Hz, 1 H, CH=CH), 6.48 (dt, ${}^{3}J$ = 5.5 Hz, ${}^{3}J$ = 16.1 Hz, 1 H, CH=CH), 3.92 (d, ${}^{3}J$ = 5.5 Hz, 2 H, CH₂), 3.81 (s, 3 H, OCH₃).

 $^{13}C{^1H}$ NMR (100.6 MHz, CDCl₃): δ = 198.0, 159.8, 138.5, 136.6, 133.5, 133.3, 129.6, 128.7, 128.4, 123.0, 119.1, 113.3, 111.5, 55.3, 42.7.

HRMS (ESI-TOF): m/z calcd for $[C_{17}H_{16}O_2 + H]^+$ 253.1229; found: 253.1235.

(E)-1-Phenyl-4-(thiophen-3-yl)but-3-en-1-one (11)

Following the general procedure, **11** was prepared from acetophenone (480 mg, 4.0 mmol) and 3-ethynylthiophene (432 mg, 4.0 mmol); white solid; yield: 384 mg (42%); mp 97–99 °C.

¹H NMR (400.1 MHz, CDCl₃): δ = 8.01–7.99 (m, 2 H, C₆H₅), 7.60–7.56 (m, 1 H, C₆H₅), 7.50–7.46 (m, 2 H, C₆H₅), 7.26–7.22 (m, 2 H, thienyl), 7.13 (s, 1 H, thienyl), 6.57 (d, ³*J* = 16.4 Hz, 1 H, CH=CH), 6.32 (dt, ³*J* = 6.9, 16.4 Hz, 1 H, CH=CH), 3.88 (d, ³*J* = 6.9 Hz, 2 H, CH₂).

 $^{13}C{^1H}$ NMR (100.6 MHz, CDCl₃): δ = 198.0, 139.7, 136.8, 133.3, 128.8, 128.4, 127.9, 126.0, 125.1, 122.5, 121.8, 42.7.

HRMS (ESI-TOF): m/z calcd for $[C_{14}H_{12}OS + H]^+$: 229.0687; found: 229.0686.

2-Acylbuta-1,3-dienes 3; General Procedure

A mixture of ketone **1** (0.6 mmol), aldehyde **2** (0.5 mmol), piperidine (5 μ L, 0.05 mmol) and AcOH (3 μ L, 0.05 mmol) in toluene (2 mL) was stirred at 110–115 °C (oil bath) for 3–8 h. After cooling to r.t., toluene was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, eluent hexane/Et₂O, with gradient from 9:1 to 0:1) to afford the desired 2-acylbuta-1,3-diene **3**.

(3E)-2-(4-Nitrobenzylidene)-1,4-diphenylbut-3-en-1-one (3aa)

Following the general procedure, **3aa** was prepared from (*E*)-1,4-diphenylbut-3-en-1-one (**1a**; 133 mg, 0.6 mmol) and 4-nitrobenzaldehyde (**2a**; 76 mg, 0.5 mmol); yellow solid; yield: 157 mg (88%); E:Z = 55:45.

¹H NMR (400.1 MHz, CDCl₃): δ (*E*-isomer) = 8.30 (d, *J* = 8.7 Hz, 2 H, ArH), 8.03–8.01 (m, 2 H, C₆H₅), 7.62 (d, *J* = 8.7 Hz, 2 H, ArH), 7.57–7.26 (m, 8 H, C₆H₅), 7.24 (d, *J* = 16.5 Hz, 1 H, CH=CH), 6.82 (d, *J* = 16.5 Hz, 1 H, CH=CH), 6.76 (s, 1 H, CH=); δ (*Z*-isomer) = 8.03–8.01 (m, 2 H, C₆H₅, 2 H, ArH), 7.57–7.26 (m, 10 H, C₆H₅), 7.08 (d, *J* = 16.5 Hz, 1 H, CH=CH), 6.90 (s, 1 H, CH=), 6.47 (d, *J* = 16.5 Hz, 1 H, CH=CH).

 $^{13}C{^1H}$ NMR (100.6 MHz, CDCl₃): δ (*E*-isomer) = 197.0, 147.0, 142.1, 142.1, 137.0, 136.5, 136.2, 133.7, 130.3, 130.1, 130.1, 128.7, 128.7, 128.7, 126.9, 123.8, 121.5; δ (*Z*-isomer) = 198.6, 146.7, 144.0, 141.7, 136.2, 135.5, 134.7, 134.6, 129.5, 129.2, 129.1, 129.1, 128.8, 128.8, 128.5, 126.9, 123.8.

HRMS (ESI-TOF): m/z calcd for $[C_{23}H_{17}NO_3 + H]^*$: 356.1286; found: 356.1315.

(3E)-1-([1,1'-Biphenyl]-4-yl)-2-(4-nitrobenzylidene)-4-phenylbut-3-en-1-one (3ba)

Following the general procedure, **3ba** was prepared from (*E*)-1-([1,1'-biphenyl]-4-yl)-4-phenylbut-3-en-1-one (**1b**; 179 mg, 0.6 mmol) and 4-nitrobenzaldehyde (**2a**; 76 mg, 0.5 mmol); yellow solid; yield: 170 mg (79%); E/Z = 40:60.

¹H NMR (400.1 MHz, CDCl₃): δ (*E*-isomer) = 8.31 (d, *J* = 8.6 Hz, 2 H, ArH), 8.11–8.03 (m, 2 H, ArH), 7.73 (d, *J* = 8.6 Hz, 2 H, ArH), 7.66–7.64 (m, 1 H, ArH), 7.50–7.26 (m, 11 H, C₆H₅, 1 H, CH=CH), 6.85 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.79 (s, 1 H, CH=); δ (*Z*-isomer) = 8.11–8.03 (m, 4 H, ArH), 7.66–7.64 (m, 3 H, ArH), 7.59–7.58 (m, 2 H, ArH), 7.50–7.26 (m, 9 H, ArH), 7.11 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.92 (s, 1 H, CH=), 6.50 (d, *J* = 16.4 Hz, 1 H, CH=CH).

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ (*E*-isomer) = 196.7, 147.1, 146.4, 142.3, 142.2, 139.6, 137.0, 136.2, 135.1, 129.3, 129.1, 129.0, 128.8, 128.8, 128.7, 128.7, 128.5, 127.3, 127.3, 127.0, 121.5; δ (*Z*-isomer) = 198.2, 147.2, 146.6, 144.0, 141.7, 139.4, 136.1, 134.6, 134.1, 130.8, 130.4, 130.1, 129.2, 129.0, 129.0, 128.8, 128.5, 127.7, 127.3, 126.8, 123.8.

HRMS (ESI-TOF): m/z calcd for $[C_{29}H_{21}NO_3 + H]^*$: 432.1600; found: 432.1603.

(3*E*)-1-(4-Fluorophenyl)-2-(4-nitrobenzylidene)-4-phenylbut-3en-1-one (3ca)

Following the general procedure, **3ca** was prepared from (*E*)-1-(4-fluorophenyl)-4-phenylbut-3-en-1-one (**1c**; 144 mg, 0.6 mmol) and 4-nitrobenzaldehyde (**2a**; 76 mg, 0.5 mmol); yellow solid; yield: 154 mg (82%); E/Z = 50:50.

¹H NMR (400.1 MHz, CDCl₃): δ (*E*-isomer) = 8.30 (d, *J* = 8.8 Hz, 2 H, ArH), 8.07–8.03 (m, 2 H, ArH), 7.62 (d, *J* = 8.8 Hz, 2 H, ArH), 7.35–7.28 (m, 5 H, C₆H₅), 7.20 (d, *J* = 16.7 Hz, 1 H, CH=CH), 7.20–7.16 (m, 2 H, ArH), 6.78 (d, *J* = 16.7 Hz, 1 H, CH=CH), 6.75 (s, 1 H, CH=); δ (*Z*-isomer) = 8.06–8.02 (m, 4 H, ArH), 7.39–7.27 (m, 7 H, ArH, C₆H₅), 7.12–7.08 (m, 2 H, ArH), 7.07 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.90 (s, 1 H, CH=), 6.45 (d, *J* = 16.4 Hz, 1 H, CH=CH).

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ (*E*-isomer) = 195.7, 166.2 (d, J = 256.5 Hz), 147.3, 142.2, 142.2, 137.3, 136.2, 132.9 (d, J = 9.5 Hz), 132.9 (d, J = 3.0 Hz), 130.4, 130.1, 129.0, 128.9, 127.0, 124.0, 121.4, 116.1 (d, J = 22.1 Hz); δ (*Z*-isomer) = 197.1, 166.6 (d, J = 257.7 Hz), 146.8, 143.7, 141.6, 136.1, 134.7, 132.3 (d, J = 9.7 Hz), 132.0 (d, J = 2.8 Hz), 129.2, 129.1, 128.9, 128.8, 128.3, 126.9, 123.9, 116.5 (d, J = 22.1 Hz).

HRMS (ESI-TOF): m/z calcd for $[C_{23}H_{16}FNO_3 + H]^+$: 374.1192; found: 374.1217.

(3*E*)-1-(4-Chlorophenyl)-2-(4-nitrobenzylidene)-4-phenylbut-3en-1-one (3da)

Following the general procedure, **3da** was prepared from (*E*)-1-(4-chlorophenyl)-4-phenylbut-3-en-1-one (**1d**; 154 mg, 0.6 mmol) and 4-nitrobenzaldehyde (**2a**; 76 mg, 0.5 mmol). After toluene evaporation, the residue was treated with cold Et_2O (2 mL) to afford the pure *Z*-isomer of **3da**; yellow solid; yield: 115 mg (59%); mp 196–198 °C. Et_2O mother solution was evaporated, and the obtained residue was purified by column chromatography (silica gel, eluent hexane/ Et_2O , with gradient from 9:1 to 0:1) to give the pure *E*-isomer of **3da**; yellow solid; yield: 44 mg (23%); mp 114–116 °C.

¹H NMR (400.1 MHz, CDCl₃): δ (*E*-isomer) = 8.29 (d, *J* = 8.8 Hz, 2 H, ArH), 7.96 (d, *J* = 8.4 Hz, 2 H, ArH), 7.62 (d, *J* = 8.8 Hz, 2 H, ArH), 7.48 (d, *J* = 8.4 Hz, 2 H, ArH), 7.36–7.28 (m, 5 H, C₆H₅), 7.24 (d, *J* = 17.0 Hz, 1

H, CH=CH), 6.78 (d, J = 17.0 Hz, 1 H, CH=CH), 6.76 (s, 1 H, CH=); δ (*Z*-isomer) = 8.04 (d, J = 8.8 Hz, 2 H, ArH), 7.95 (d, J = 8.4 Hz, 2 H, ArH), 7.41–7.27 (m, 9 H, ArH, C₆H₅), 7.07 (d, J = 16.4 Hz, 1 H, CH=CH), 6.90 (s, 1 H, CH=), 6.44 (d, J = 16.4 Hz, 1 H, CH=CH).

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ (*E*-isomer) = 195.9, 147.3, 142.1, 142.0, 140.3, 137.3, 136.1, 134.9, 131.6, 130.5, 130.4, 129.1, 129.0, 128.9, 127.0, 123.9, 121.3; δ (*Z*-isomer) = 197.4, 147.0, 143.6, 141.6, 141.3, 136.1, 134.9, 133.9, 130.9, 129.6, 129.3, 129.2, 128.9, 128.9, 128.2, 126.9, 124.0.

HRMS (ESI-TOF): m/z calcd for $[C_{23}H_{16}CINO_3 + H]^+$: 390.0897; found: 390.0932.

(3E)-1-(4-Methoxyphenyl)-2-(4-nitrobenzylidene)-4-phenylbut-3-en-1-one (3ea)

Following the general procedure, **3ea** was prepared from (*E*)-1-(4-methoxyphenyl)-4-phenylbut-3-en-1-one (**1e**; 151 mg, 0.6 mmol) and 4-nitrobenzaldehyde (**2a**; 76 mg, 0.5 mmol); yellow solid; yield: 123 mg (64%); E/Z = 40:60.

¹H NMR (400.1 MHz, CDCl₃): δ (*E*-isomer) = 8.29 (d, *J* = 8.6 Hz, 2 H, ArH), 7.92 (d, *J* = 8.0 Hz, 2 H, ArH), 7.62 (d, *J* = 8.6 Hz, 2 H, ArH), 7.33–7.26 (m, 5 H, C₆H₅, 2 H, ArH), 7.24 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.80 (d, *J* = 16.7 Hz, 1 H, CH=CH), 6.73 (s, 1 H, CH=), 2.44 (s, 3 H, OCH₃); δ (*Z*-isomer) = 8.01 (d, *J* = 8.8 Hz, 2 H, ArH), 7.92 (d, *J* = 8.2 Hz, 2 H, ArH), 7.39–7.37 (m, 2 H, ArH, 2 H, C₆H₅), 7.33–7.22 (m, 2 H, ArH, 3 H, C₆H₅), 7.08 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.87 (s, 1 H, CH=), 6.47 (d, *J* = 16.4 Hz, 1 H, CH=CH), 2.38 (s, 3 H, OCH₃).

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ (*E*-isomer) = 196.9, 147.2, 144.9, 142.7, 142.5, 137.1, 136.4, 134.0, 130.4, 130.4, 129.8, 129.5, 128.9, 128.8, 127.0, 123.9, 121.7, 21.9; δ (*Z*-isomer) = 198.2, 146.7, 145.8, 144.3, 141.9, 136.3, 134.7, 133.2, 129.9, 129.7, 129.2, 128.8, 128.8, 128.7, 128.6, 126.9, 123.8, 21.9.

HRMS (ESI-TOF): m/z calcd for $[C_{24}H_{19}NO_4 + H]^+$: 386.1392; found: 386.1406.

(3E)-1-(Naphthalen-2-yl)-2-(4-nitrobenzylidene)-4-phenylbut-3en-1-one (3fa)

Following the general procedure, **3fa** was prepared from (*E*)-1-(naph-thalen-2-yl)-4-phenylbut-3-en-1-one (**1f**; 163 mg, 0.6 mmol) and 4-nitrobenzaldehyde (**2a**; 76 mg, 0.5 mmol); yellow solid; yield: 166 mg (82%); E/Z = 50:50.

¹H NMR (400.1 MHz, CDCl₃): δ (*E*-isomer) = 8.50 (s, 1 H, naphthyl), 8.32 (d, *J* = 8.6 Hz, 2 H, ArH), 8.14–8.09 (m, 1 H, naphthyl), 8.00–7.85 (m, 4 H, C₆H₅, naphthyl), 7.66 (d, *J* = 8.6 Hz, 2 H, ArH), 7.64–7.50 (m, 3 H, C₆H₅, naphthyl), 7.42–7.26 (m, 3 H, C₆H₅, naphthyl, 1 H, CH=CH), 6.86 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.82 (s, 1 H, CH=); δ (*Z*-isomer) = 8.48 (s, 1 H, naphthyl), 8.14–8.09 (m, 1 H, naphthyl), 8.00–7.85 (m, 5 H, ArH, C₆H₅, naphthyl), 7.64–7.50 (m, 2 H, C₆H₅, naphthyl), 7.42–7.26 (m, 7 H, C₆H₅, naphthyl), 7.16 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.96 (s, 1 H, CH=), 6.51 (d, *J* = 16.4 Hz, 1 H, CH=CH).

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ (*E*-isomer) = 197.2, 147.3, 142.6, 142.4, 137.2, 136.3, 136.0, 133.9, 132.7, 132.5, 130.5, 130.3, 129.8, 129.3, 129.1, 128.9, 128.8, 128.0, 127.1, 127.1, 125.1, 124.0, 121.7; δ (*Z*-isomer) = 198.7, 146.8, 144.3, 141.8, 136.4, 136.2, 134.9, 133.0, 132.7, 132.5, 129.9, 129.4, 129.3, 129.3, 129.2, 128.8, 128.8, 128.7, 128.0, 127.1, 126.9, 124.0, 123.9.

HRMS (ESI-TOF): m/z calcd for $[C_{27}H_{19}NO_3 + H]^+$: 406.1443; found: 406.1465.

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(3E)-2-(4-Nitrobenzylidene)-4-phenyl-1-(thiophen-2-yl)but-3-en-1-one (3ga)

Following the general procedure, **3ga** was prepared from (*E*)-4-phe-nyl-1-(thiophen-2-yl)but-3-en-1-one (**1g**; 137 mg, 0.6 mmol) and 4-nitrobenzaldehyde (**2a**; 76 mg, 0.5 mmol); yellow solid; yield: 164 mg (91%); *E*/*Z* = 35:65.

¹H NMR (400.1 MHz, CDCl₃): δ (*E*-isomer) = 8.29 (d, *J* = 8.8 Hz, 2 H, ArH), 7.80–7.79 (m, 1 H, thienyl), 7.77–7.76 (m, 1 H, thienyl), 7.62 (d, *J* = 8.8 Hz, 2 H, ArH), 7.46–7.27 (m, 5 H, C₆H₅), 7.20 (d, *J* = 16.4 Hz, 1 H, CH=CH), 7.18–7.16 (m, 1 H, thienyl), 6.91 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.90 (s, 1 H, CH=); δ (*Z*-isomer) = 8.05 (d, *J* = 8.8 Hz, 2 H, ArH), 7.70–7.69 (m, 1 H, thienyl), 7.63–7.61 (m, 1 H, thienyl), 7.46–7.27 (m, 5 H, C₆H₅, 2 H, ArH), 7.05 (d, *J* = 16.4 Hz, 1 H, CH=CH), 7.03–7.01 (m, 1 H, thienyl), 6.97 (s, 1 H, CH=), 6.62 (d, *J* = 16.4 Hz, 1 H, CH=CH).

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ (*E*-isomer) = 188.9, 147.3, 143.7, 142.2, 142.0, 137.1, 136.3, 135.6, 135.4, 130.4, 129.3, 128.9, 128.8, 128.5, 127.1, 123.9, 121.1; δ (*Z*-isomer) = 190.3, 146.8, 143.8, 143.2, 141.7, 136.2, 136.2, 135.4, 134.6, 130.1, 129.1, 128.9, 128.8, 126.9, 123.9, 128.1.

HRMS (ESI-TOF): m/z calcd for $[C_{21}H_{15}NO_3S + H]^+$: 362.0851; found: 362.0855.

(3E)-4-([1,1'-Biphenyl]-4-yl)-2-(4-nitrobenzylidene)-1-phenylbut-3-en-1-one (3ia)

Following the general procedure, **3ia** was prepared from (*E*)-4-([1,1'-biphenyl]-4-yl)-1-phenylbut-3-en-1-one (**1i**; 179 mg, 0.6 mmol) and 4-nitrobenzaldehyde (**2a**; 76 mg, 0.5 mmol); yellow solid; yield: 202 mg (94%); E/Z = 50:50.

¹H NMR (400.1 MHz, $CDCI_3$): δ (*E*-isomer) = 8.31 (d, *J* = 8.7 Hz, 2 H, ArH), 8.05–8.01 (m, 2 H, C_6H_5), 7.65–7.32 (m, 14 H, ArH), 7.30 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.87 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.78 (s, 1 H, CH=); δ (*Z*-isomer) = 8.05–8.01 (m, 2 H, C_6H_5 , 2 H, ArH), 7.65–7.32 (m, 14 H, C_6H_5), 7.13 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.92 (s, 1 H, CH=), 6.51 (d, *J* = 16.4 Hz, 1 H, CH=CH).

 $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CDCl₃): δ (*E*-isomer) = 197.2, 147.2, 142.4, 142.3, 141.7, 140.3, 136.7, 136.6, 135.3, 133.8, 130.4, 130.2, 129.3, 129.2, 128.9, 128.9, 128.8, 127.2, 127.0, 124.0, 121.5; δ (*Z*-isomer) = 198.7, 146.8, 144.1, 141.8, 141.5, 140.4, 135.6, 135.2, 134.6, 134.3, 130.3, 129.6, 129.1, 128.5, 127.7, 127.7, 127.5, 127.5, 127.4, 127.0, 123.9.

HRMS (ESI-TOF): m/z calcd for $[C_{29}H_{21}NO_3 + H]^+$: 432.1600; found: 432.1637.

(3E)-4-(3-Fluorophenyl)-2-(4-nitrobenzylidene)-1-phenylbut-3en-1-one (3ja)

Following the general procedure, **3ja** was prepared from (*E*)-4-(3-fluorophenyl)-1-phenylbut-3-en-1-one (**1j**; 144 mg, 0.6 mmol) and 4-nitrobenzaldehyde (**2a**; 76 mg, 0.5 mmol); yellow solid; yield: 171 mg (92%); E/Z = 30:70.

¹H NMR (400.1 MHz, CDCl₃): δ (*E*-isomer) = 8.30 (d, *J* = 8.8 Hz, 2 H, ArH), 8.02–7.99 (m, 2 H, C₆H₅), 7.65–7.56 (m, 4 H, ArH), 7.29–7.23 (m, 2 H, ArH), 7.22 (d, *J* = 16.4 Hz, 1 H, CH=CH), 7.12–7.02 (m, 2 H, ArH), 6.97–6.92 (m, 1 H, ArH), 6.81 (s, 1 H, CH=), 6.80 (d, *J* = 16.4 Hz, 1 H, CH=CH); δ (*Z*-isomer) = 8.02–7.99 (m, 2 H, C₆H₅, 2 H, ArH), 7.53–7.49 (m, 1 H, C₆H₅), 7.45–7.42 (m, 2 H, C₆H₅), 7.37 (d, *J* = 8.8 Hz, 2 H, ArH), 7.29–7.23 (m, 1 H, ArH), 7.12–7.02 (m, 2 H, ArH), 7.07 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.97–6.92 (m, 1 H, ArH), 6.92 (s, 1 H, CH=), 6.41 (d, *J* = 16.4 Hz, 1 H, CH=CH).

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ (*E*-isomer) = 196.9, 163.1 (d, J = 246.1 Hz), 147.3, 142.0, 141.7, 138.6 (d, J = 7.7 Hz), 136.4, 135.7 (d, J = 2.7 Hz), 133.9, 131.4, 130.4, 130.3, 130.2, 129.7, 123.9, 122.9 (d, J = 2.7 Hz), 122.7, 115.6 (d, J = 21.4 Hz), 113.3 (d, J = 21.9 Hz); δ (*Z*-isomer) = 198.4, 163.1 (d, J = 246.1 Hz), 146.8, 143.5, 141.5, 138.5 (d, J = 7.7 Hz), 135.3, 134.7, 133.2 (d, J = 2.8 Hz), 130.4, 130.2, 130.0, 129.5, 129.3, 129.2, 128.8, 123.8, 115.5 (d, J = 21.4 Hz), 113.0 (d, J = 22.0 Hz).

HRMS (ESI-TOF): m/z calcd for $[C_{23}H_{16}FNO_3 + H]^+$: 374.1192; found: 374.1216.

(3*E*)-4-(3-Methoxyphenyl)-2-(4-nitrobenzylidene)-1-phenylbut-3-en-1-one (3ka)

Following the general procedure, **3ka** was prepared from (*E*)-4-(3-methoxyphenyl)-1-phenylbut-3-en-1-one (**1k**; 151 mg, 0.6 mmol) and 4-nitrobenzaldehyde (**2a**; 76 mg, 0.5 mmol); yellow solid; yield: 167 mg (87%); *E*:*Z* = 35:65.

¹H NMR (400.1 MHz, CDCl₃): δ (*E*-isomer) = 8.28 (d, *J* = 8.7 Hz, 2 H, ArH), 8.03–7.98 (m, 2 H, C₆H₅), 7.61 (d, *J* = 8.7 Hz, 2 H, ArH), 7.59–7.55 (m, 1 H, C₆H₅), 7.52–7.41 (m, 2 H, C₆H₅), 7.24–7.20 (m, 1 H, ArH, 1 H, CH=CH), 6.99–6.95 (m, 1 H, ArH), 6.90–6.80 (m, 2 H, ArH), 6.79 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.76 (s, 1 H, CH=), 3.77 (s, 3 H, OCH₃); δ (*Z*-isomer) = 8.03–7.98 (m, 2 H, C₆H₅, 2 H, ArH), 7.59–7.55 (m, 1 H, C₆H₅), 7.52–7.48 (m, 1 H, ArH), 7.45–7.41 (m, 2 H, C₆H₅), 7.36 (d, *J* = 8.8 Hz, 2 H, ArH), 7.26–7.20 (m, 1 H, ArH), 7.08 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.99–6.95 (m, 1 H, ArH), 6.90 (s, 1 H, CH=), 6.84–6.80 (m, 1 H, ArH), 6.43 (d, *J* = 16.4 Hz, 1 H, CH=CH), 3.79 (s, 3 H, OCH₃).

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ (*E*-isomer) = 197.13, 147.15, 146.67, 142.19, 142.16, 137.68, 136.97, 136.47, 133.79, 130.46, 129.80, 129.19, 129.19, 128.77, 123.88, 121.82, 119.42, 114.25, 112.62, 55.27; δ (*Z*-isomer) = 198.65, 159.87, 143.91, 141.67, 137.55, 135.43, 134.59, 134.54, 130.39, 130.19, 129.74, 129.53, 129.22, 129.13, 128.75, 123.82, 119.47, 114.52, 111.99, 55.27.

HRMS (ESI-TOF): m/z calcd for $[C_{24}H_{19}NO_4 + H]^+$: 386.1392; found: 386.1400.

(3E)-2-(4-Nitrobenzylidene)-1-phenyl-4-(thiophen-3-yl)but-3-en-1-one (3la)

Following the general procedure, **3la** was prepared from (*E*)-1-phe-nyl-4-(thiophen-3-yl)but-3-en-1-one (**1l**; 137 mg, 0.6 mmol) and 4-nitrobenzaldehyde (**2a**; 76 mg, 0.5 mmol); yellow solid; yield: 112 mg (62%); E/Z = 50:50.

¹H NMR (400.1 MHz, CDCl₃): δ (*E*-isomer) = 8.29 (d, *J* = 8.7 Hz, 2 H, ArH), 8.02–8.00 (m, 2 H, C₆H₅), 7.62–7.55 (m, 1 H, C₆H₅, 2 H, ArH), 7.53–7.49 (m, 2 H, C₆H₅), 7.31–7.26 (m, 2 H, thienyl), 7.21–7.19 (m, 1 H, thienyl), 7.08 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.83 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.72 (s, 1 H, CH=); δ (*Z*-isomer) = 8.02–8.00 (m, 2 H, C₆H₅), 7.35 (d, *J* = 8.8 Hz, 2 H, ArH), 7.31–7.26 (m, 2 H, thienyl), 7.21–7.19 (m, 1 H, thienyl), 6.92 (d, *J* = 16.3 Hz, 1 H, CH=CH), 6.85 (s, 1 H, CH=), 6.47 (d, *J* = 16.4 Hz, 1 H, CH=CH).

 $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CDCl₃): δ (*E*-isomer) = 197.2, 147.2, 142.4, 142.4, 139.3, 136.6, 133.8, 131.2, 130.4, 130.2, 129.8, 129.2, 128.8, 126.8, 125.0, 124.0, 121.5; δ (*Z*-isomer) = 198.7, 146.7, 144.2, 141.8, 139.2, 135.5, 134.6, 129.6, 129.6, 129.2, 129.2, 128.8, 128.5, 126.7, 124.7, 124.6, 123.9.

HRMS (ESI-TOF): m/z calcd for $[C_{21}H_{15}NO_3S + H]^+$: 362.0851; found: 362.0864.

(3E)-2-Benzylidene-1,4-diphenylbut-3-en-1-one (3ab)

Following the general procedure, **3ab** was prepared from (*E*)-1,4-diphenylbut-3-en-1-one (**1a**; 133 mg, 0.6 mmol) and benzaldehyde (**2b**; 53 mg, 0.5 mmol); yellow oil; yield: 82 mg (53%); E/Z = 70:30.

¹H NMR (400.1 MHz, CDCl₃): δ (*E*-isomer) = 8.05–8.03 (m, 2 H, C₆H₅), 7.61–7.57 (m, 1 H, C₆H₅), 7.51–7.13 (m, 12 H, C₆H₅, 1 H, CH=CH), 6.88 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.86 (s, 1 H, CH=); δ (*Z*-isomer) = 8.08–8.06 (m, 2 H, C₆H₅), 7.51–7.13 (m, 13 H, C₆H₅), 7.09 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.82 (s, 1 H, CH=), 6.39 (d, *J* = 16.4 Hz, 1 H, CH=CH).

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ (*E*-isomer) = 198.0, 138.9, 137.3, 137.0, 135.6, 134.9, 134.7, 133.2, 130.2, 129.9, 128.8, 128.7, 128.6, 128.5, 128.5, 126.8, 122.8; δ (*Z*-isomer) = 199.6, 140.0, 136.7, 135.9, 135.2, 134.0, 132.2, 131.9, 129.6, 129.3, 128.9, 128.6, 128.4, 128.2, 128.0, 128.0, 126.5.

HRMS (ESI-TOF): m/z calcd for $[C_{23}H_{18}O + H]^+$: 311.1436; found: 311.1449.

(3E)-2-(4-Chlorobenzylidene)-1,4-diphenylbut-3-en-1-one (3ac)

Following the general procedure, **3ac** was prepared from (*E*)-1,4-diphenylbut-3-en-1-one (**1a**; 133 mg, 0.6 mmol) and 4-chlorobenzaldehyde (**2c**; 70 mg, 0.5 mmol); pale yellow solid; yield: 128 mg (74%); E/Z = 50:50.

¹H NMR (400.1 MHz, CDCl₃): δ (*E*-isomer) = 8.03–7.99 (m, 2 H, Ph), 7.60–7.23 (m, 12 H, C₆H₅, 1 H, CH=CH), 6.80 (d, *J* = 16.2 Hz, 1 H, CH=CH), 6.76 (s, 1 H, CH=); δ (*Z*-isomer) = 8.03–7.99 (m, 2 H, C₆H₅), 7.60–7.23 (m, 8 H, C₆H₅), 7.17 (d, *J* = 8.7 Hz, 2 H, ArH), 7.13 (d, *J* = 8.7 Hz, 2 H, ArH), 7.05 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.82 (s, 1 H, CH=), 6.37 (d, *J* = 16.4 Hz, 1 H, CH=CH).

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ (mixture of isomers) = 199.4, 197.8, 140.7, 139.6, 137.1, 136.8, 136.6, 135.8, 135.5, 134.4, 134.3, 134.1, 133.9, 133.8, 133.4, 133.0, 132.5, 131.1, 130.6, 130.2, 130.0, 129.6, 129.0, 128.9, 128.8, 128.8, 128.7, 128.6, 128.4, 128.2, 126.8, 126.6, 122.3.

HRMS (ESI-TOF): m/z calcd for $[C_{23}H_{17}CIO + H]^+$: 345.1046; found: 345.1049.

(3E)-2-(4-(Dimethylamino)benzylidene)-1,4-diphenylbut-3-en-1one (3ad)

Following the general procedure, **3ad** was prepared from (*E*)-1,4-diphenylbut-3-en-1-one (**1a**; 133 mg, 0.6 mmol) and 4-(dimethylamino)benzaldehyde (**2d**; 75 mg, 0.5 mmol); orange solid; yield: 34 mg (19%); predominantly *Z*-isomer.

¹H NMR (400.1 MHz, CDCl₃): δ (*Z*-isomer) = 8.09-8.07 (m, 2 H, C₆H₅), 7.53–7.50 (m, 1 H, C₆H₅), 7.42–7.39 (m, 2 H, C₆H₅), 7.34–7.32 (m, 2 H, C₆H₅), 7.28–7.24 (m, 2 H, C₆H₅), 7.18–7.17 (m, 1 H, C₆H₅), 7.12 (d, *J* = 8.6 Hz, 2 H, ArH), 7.04 (d, *J* = 16.4 Hz, 1 H, CH=CH), 6.78 (s, 1 H, CH=), 6.48 (d, *J* = 8.6 Hz, 2 H, ArH), 6.22 (d, *J* = 16.4 Hz, 1 H, CH=CH), 2.87 (s, 6 H, CH₃).

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ (*Z*-isomer) = 200.6, 150.0, 137.3, 136.3, 135.4, 133.8, 132.9, 130.4, 130.2, 129.7, 129.2, 128.9, 128.6, 127.4, 126.3, 123.2, 111.9, 40.1.

HRMS (ESI-TOF): m/z calcd for $[C_{25}H_{23}NO + H]^+$: 354.1857; found: 354.1876.

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(3E)-2-[(1H-Pyrrol-2-yl)methylene]-1,4-diphenylbut-3-en-1-one (3af)

Following the general procedure, **3af** was prepared from (*E*)-1,4-diphenylbut-3-en-1-one (**1a**; 133 mg, 0.6 mmol) and 1*H*-pyrrole-2-carbaldehyde (**2f**; 48 mg, 0.5 mmol); orange oil; yield: 47 mg (31%); predominantly *Z*-isomer.

¹H NMR (400.1 MHz, CDCl₃): δ (*Z*-isomer) = 9.26 (br s, 1 H, NH), 8.04–8.03 (m, 2 H, C₆H₅), 7.59–7.55 (m, 1 H, C₆H₅), 7.47–7.44 (m, 2 H, C₆H₅), 7.29–7.26 (m, 4 H, C₆H₅), 7.22–7.18 (m, 1 H, C₆H₅), 7.00 (d, *J* = 16.3 Hz, 1 H, CH=CH), 6.86 (s, 1 H, CH=), 6.79–6.77 (m, 1 H, pyridyl), 6.41–6.38 (m, 1 H, pyridyl), 6.25 (d, *J* = 16.3 Hz, 1 H, CH=CH), 6.22–6.20 (m, 1 H, pyridyl).

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ (*Z*-isomer) = 200.6, 137.2, 137.1, 133.8, 131.9, 130.1, 129.9, 129.6, 128.8, 128.8, 128.7, 127.6, 126.2, 124.9, 121.9, 115.8, 110.5.

HRMS (ESI-TOF): m/z calcd for $[C_{21}H_{17}NO + H]^+$: 300.1388; found: 300.1421.

(3E)-2-(Furan-2-ylmethylene)-1,4-diphenylbut-3-en-1-one (3ag)

Following the general procedure, **3ag** was prepared from (*E*)-1,4-diphenylbut-3-en-1-one (**1a**; 133 mg, 0.6 mmol) and furfural (**2g**; 48 mg, 0.5 mmol); brown oil; yield: 98 mg (65%); E/Z = 65:35.

¹H NMR (400.1 MHz, CDCl₃): δ (*E*-isomer) = 7.97–7.95 (m, 2 H, C₆H₅), 7.91 (d, *J* = 16.5 Hz, 1 H, CH=CH), 7.63 (d, *J* = 1.8 Hz, 1 H, furyl), 7.59–7.55 (m, 1 H, C₆H₅), 7.49–7.43 (m, 4 H, C₆H₅), 7.34–7.29 (m, 2 H, C₆H₅), 7.23–7.21 (m, 1 H, C₆H₅), 6.83 (d, *J* = 16.5 Hz, 1 H, CH=CH), 6.59 (d, *J* = 3.4 Hz, 1 H, furyl), 6.53 (dd, *J* = 1.8, 3.4 Hz, 1 H, furyl), 6.50 (s, 1 H, CH=); δ (*Z*-isomer) = 8.07–8.06 (m, 2 H, C₆H₅), 7.59–7.55 (m, 1 H, C₆H₅), 7.49–7.43 (m, 2 H, C₆H₅), 7.36–7.34 (m, 4 H, C₆H₅), 7.29–7.26 (m, 1 H, C₆H₅), 7.19 (d, *J* = 1.8 Hz, 1 H, furyl), 7.00 (d, *J* = 16.3 Hz, 1 H, CH=CH), 6.64 (s, 1 H, CH=), 6.33 (d, *J* = 16.3 Hz, 1 H, CH=CH), 6.30 (d, *J* = 3.5 Hz, 1 H, furyl), 6.28 (dd, *J* = 1.8, 3.5 Hz, 1 H, furyl).

 $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CDCl₃): δ (*E*-isomer) = 197.7, 152.1, 144.5, 137.8, 137.3, 135.4, 135.0, 133.1, 130.1, 128.7, 128.6, 128.2, 126.9, 123.6, 121.5, 115.1, 112.3; δ (*Z*-isomer) = 198.6, 151.0, 143.7, 137.4, 136.8, 136.4, 133.7, 132.1, 129.5, 128.8, 128.7, 128.4, 128.1, 126.6, 118.6, 111.9, 111.9.

HRMS (ESI-TOF): m/z calcd for $[C_{21}H_{16}O_2 + H]^*$: 301.1229; found: 301.1194.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690003.

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