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Tin(II) Chloride Mediated Coupling Reactions between Alkynes and Aldehydes

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Tin(II) chloride, which is insensitive to water and air, mediated the coupling reaction between alkynes and aldehydes as a Lewis acid in nitromethane to produce (*E*)-α,β-unsaturated ketones by a skeletal transformation in which one alkynic carbon atom changed into an oxo carbon atom accompanied by the cleavage of a C=O bond in the starting aldehydes. This coupling reaction was promoted by a catalytic amount of a primary or secondary alkanol. The coupling reaction between 1-deuterio-2-phenylethyne and benzaldehyde with BuOH afforded 1,3-diphenyl-2-deuterio-2-propenone (2-deuteriation: 94 % D), whereas the coupling reaction between phenylethyne and benzaldehyde with BuOD afforded 1,3-diphenyl-2-propenone (2-deuteriation: 0 % D). Because almost no exchange between hydrogen and deuterium at the 2-position of 1,3-diphenyl-2-propenone occurs in either of the reactions, the coupling reaction between alkynes and aldehydes with tin(II) chloride is presumed to proceed by nucleophilic addition of alkynes to aldehydes. The cleavage of the C–O single bond generated by the nucleophilic addition might be induced by the strong oxophilicity of tin.

Introduction

Carbon skeleton constructions with alkynes have made considerable progress since the reactions of directly activated alkynes were discovered, namely hydrometalation and carbometalation to alkynes,[1] terminal C–H bond activation of terminal alkynes,[2] and nucleophilic addition to alkynes,[3] which have been recognized as versatile methodologies because of their easy manipulation and high efficiency (atom economy). In comparison with the methodologies described above, the electrophilic addition to alkynes would be unsuitable for carbon skeleton construction because of the poor availability of carbon electrophiles. Nevertheless, the coupling reactions between alkynes and Lewis acid activated aldehydes provide one example of the addition of carbon electrophiles to alkynes. Such coupling reactions have been carried out with SbF_5,[4] $GaCl_3$,[5] $In(OTf)_3$,[5,6] $Yb(OTf)_3$,[7] $FeCl_3$,[8] or TMSOTf[9] as the Lewis acid, and form a remarkable methodology for the production of (*E*)-α,β-unsaturated ketones accompanied by skeletal transformation.[10–13] We have studied the possible applications of the relatively weak Lewis acid, tin(II) chloride, which is insensitive to water and air, in organic synthetic reactions, and found that it catalyzes the propargylic substitution of propargylic alcohols with carbon and nitrogen nucleophiles in nitromethane;[14] oxophilic tin(II) chloride cleaves the propargylic C–O bond leading to propargylic substitution. We envisioned that tin(II) chloride could be used to activate aldehydes and subsequently cleave the C=O bond, similarly to the Lewis acids described above in the coupling reactions between alkynes and Lewis acid activated aldehydes.

Results and Discussion

The coupling reactions between alkynes and aldehydes with tin(II) halides were investigated by using phenylethyne (**1a**) and benzaldehyde (**2a**) under various reaction conditions (Table 1). Tin(II) chloride mediated the coupling reaction in CH_3NO_2 at 80 °C for 24 h to afford (*E*)-1,3-diphenyl-2-propen-1-one (**3aa**) stereoselectively in 34 % yield (Entries 1 and 2). The addition of butanol (20 mol-% with respect to $SnCl_2$) promoted the coupling reaction at 80 °C for 3 h to give **3aa** in 71 % yield (Entry 5),[4b,6] which is the same yield as that obtained with 100 mol-% of butanol (Entry 7). The yield was lower at 70 °C and remained unchanged at 90 °C (Entries 4 and 6). The use of 20 mol-% $SnCl_2$ with respect to **1a** afforded **3aa** in 41 % yield (Entry 8). Increasing the amount of **2a** improved the yield (Entries 5 and 9–12), but increasing the amount of **1a** did not (Entries 12–14). $SnCl_2$ is a superior activating agent to $SnBr_2$ and SnI_2 (Entries 5, 16, and 17), and SnF_2 could not be used in the coupling reaction, because it is insoluble in CH_3NO_2 (Entry 15). Primary alcohols, such as methanol, ethanol, and propanol, and secondary alcohols, such as 2-butanol, can also be used to promote the coupling reaction (Entries 5 and 18–21). However, both *tert*-butyl alcohol and water inhibited the coupling reaction (Entries 22 and 24).

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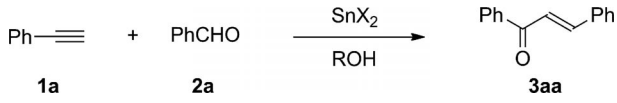
Table 1. Coupling reactions between **1a** and **2a**.



1a **2a** **3aa**

Entry	**1a** [mmol]	**2a** [mmol]	SnX_2/quantity [mmol]	ROH/quantity [mmol]	Solvent[a]	Temp. [°C]	Time [h][b]	Yield of **3aa** [%][c]
1	1.0	4.0	–	–	CH_3NO_2	80	24	–[d]
2	1.0	4.0	$SnCl_2$/1.0	–	CH_3NO_2	80	24	34
3	1.0	4.0	$SnCl_2$/1.0	BuOH/0.2	CH_3NO_2	r.t.	24	–[d]
4	1.0	4.0	$SnCl_2$/1.0	BuOH/0.2	CH_3NO_2	70	4	60
5	1.0	4.0	$SnCl_2$/1.0	BuOH/0.2	CH_3NO_2	80	3	71
6	1.0	4.0	$SnCl_2$/1.0	BuOH/0.2	CH_3NO_2	90	3	68
7	1.0	4.0	$SnCl_2$/1.0	BuOH/1.0	CH_3NO_2	80	3	70
8	1.0	4.0	$SnCl_2$/0.2	BuOH/0.1	CH_3NO_2	80	24	41
9	1.0	5.0	$SnCl_2$/1.0	BuOH/0.2	CH_3NO_2	80	3	68
10	1.0	3.0	$SnCl_2$/1.0	BuOH/0.2	CH_3NO_2	80	3	54
11	1.0	2.0	$SnCl_2$/1.0	BuOH/0.2	CH_3NO_2	80	3	48
12	1.0	1.0	$SnCl_2$/1.0	BuOH/0.2	CH_3NO_2	80	3	27
13	2.0	1.0	$SnCl_2$/1.0	BuOH/0.2	CH_3NO_2	80	3	27
14	3.0	1.0	$SnCl_2$/1.0	BuOH/0.2	CH_3NO_2	80	3	31
15	1.0	4.0	SnF_2/1.0	BuOH/0.2	CH_3NO_2	80	24	–[d]
16	1.0	4.0	$SnBr_2$/1.0	BuOH/0.2	CH_3NO_2	80	8	21
17	1.0	4.0	SnI_2/1.0	BuOH/0.2	CH_3NO_2	80	24	31
18	1.0	4.0	$SnCl_2$/1.0	MeOH/0.2	CH_3NO_2	80	3	65
19	1.0	4.0	$SnCl_2$/1.0	EtOH/0.2	CH_3NO_2	80	3	68
20	1.0	4.0	$SnCl_2$/1.0	PrOH/0.2	CH_3NO_2	80	3	65
21	1.0	4.0	$SnCl_2$/1.0	*s*BuOH/0.2	CH_3NO_2	80	3	65
22	1.0	4.0	$SnCl_2$/1.0	*t*BuOH/0.2	CH_3NO_2	80	24	–[d]
23	1.0	4.0	$SnCl_2$/1.0	PhOH/0.2	CH_3NO_2	80	3	20
24	1.0	4.0	$SnCl_2$/1.0	H_2O/1.0	CH_3NO_2	80	24	–[d]
25	1.0	4.0	$SnCl_2$/1.0	BuOH/0.2	CH_3CN	80	8	52
26	1.0	4.0	$SnCl_2$/1.0	BuOH/0.2	toluene	80	24	38
27	1.0	4.0	$SnCl_2$/1.0	BuOH/0.2	DCE	80	24	31
28	1.0	4.0	$SnCl_2$/1.0	BuOH/0.2	dioxane	80	24	–[d]
29	1.0	4.0	$SnCl_2$/1.0	BuOH/0.2	THF	reflux	24	–[d]

[a] 1 mL of solvent was used. [b] The reactions were discontinued after the specified times. [c] Isolated yields. [d] The reactions did not occur.

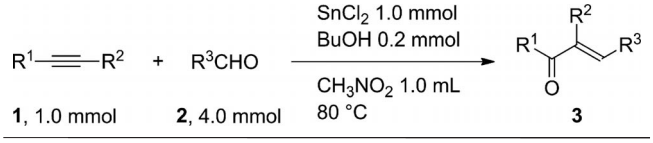
CH_3NO_2 is superior as solvent to CH_3CN, toluene, or DCE (Entries 5 and 25–27), and the coupling reaction failed with dioxane and THF (Entries 28 and 29).

The coupling reaction of phenylethyne (**1a**) with substituted benzaldehydes **2b**–**i** under the same conditions as those of Entry 5 in Table 1 afforded the corresponding (*E*)-α,β-unsaturated ketones stereoselectively (Entries 1–8 in Table 2). 4-Methoxybenzaldehyde (**2e**) was relatively unreactive (Entry 4), and the reaction with 4-nitrobenzaldehyde (**2i**) gave undetermined byproducts (Entry 8). The α-branched aliphatic aldehyde cyclohexanecarbaldehyde (**2j**) reacted with **1a** to produce (*E*)-3-cyclohexyl-1-phenyl-2-propen-1-one (**3aj**; Entry 9), whereas the straight-chain aliphatic aldehyde heptanal did not afford the corresponding coupling product. 4-Ethynyltoluene (**1b**) and 1-ethynyl-4-fluorobenzene (**1c**) exhibited almost the same reactivity as **1a** (Entries 10–12), whereas the straight-chain terminal alkyne 1-octyne (**1d**) was less reactive under the same conditions as those of Entry 5 in Table 1, the corresponding α,β-unsaturated ketone, (*E*)-1-phenyl-1-nonen-3-one (**3da**), being obtained in 15% yield (Entry 13). Internal alkynes, namely 1-phenyl-1-propyne (**1e**) and 1-phenyl-1-pentyne (**1f**) readily underwent the coupling reaction with **2a** to form 2-alkylated (*E*)-2-propen-1-one derivatives **3ea** and **3fa**, respectively, stereoselectively, accompanied by the same skeletal transformation as that of **1a** (Entries 14 and 15).[4b]

To confirm the skeletal transformation in the synthesis of the α,β-unsaturated ketone products, an X-ray diffraction study was performed on colorless crystals of **3bf** obtained by the slow diffusion of hexane into a chloroform solution (Entry 11). The ORTEP drawing of the molecular structure of **3bf** is shown in Figure 1. Thus, one alkynic carbon atom changes into an oxo carbon atom accompanied by the cleavage of the C=O bond in the starting aldehyde.

To investigate the reaction mechanism, deuteriation experiments were performed; the coupling reaction between 1-deuterio-2-phenylethyne (**1a**-*d*, 99% D) and **2a** with BuOH afforded **3aa**-*d* [2-deuteriation: 94% D; Equation (1)], whereas the coupling reaction between **1a** and **2a** with BuOD (97% D) afforded **3aa** [2-deuteriation: 0% D; Equation (2)]. In contrast to the coupling reaction with $In(OTf)_3$,[6] almost no exchange between hydrogen and deuterium at the 2-position of **3aa** occurred. It is known that π-acids, such as gold complexes, catalyze the nucleophilic addition of alcohols to alkynes to prepare enol ethers or ketones.[15] Thus, we investigated whether alkynes activated by tin(II) chloride, similarly to gold complexes, could be used to prepare enol ethers or ketones for application in

Table 2. Coupling reactions between alkynes **1** and aldehydes **2**.[a]



Entry	**1**: R^1, R^2	**2**: R^3	Time [h][b]	**3**, yield [%][c]
1	**1a**: Ph, H	**2b**: 2-ClC_6H_4	3	**3ab**, 70
2	**1a**: Ph, H	**2c**: 3-BrC_6H_4	3	**3ac**, 57
3	**1a**: Ph, H	**2d**: 4-MeC_6H_4	3	**3ad**, 77
4	**1a**: Ph, H	**2e**: 4-$MeOC_6H_4$	24	**3ae**, 32
5	**1a**: Ph, H	**2f**: 4-ClC_6H_4	3	**3af**, 60
6	**1a**: Ph, H	**2g**: 4-FC_6H_4	3	**3ag**, 54
7	**1a**: Ph, H	**2h**: 4-NCC_6H_4	3	**3ah**, 62
8	**1a**: Ph, H	**2i**: 4-$O_2NC_6H_4$	3	**3ai**, 38
9	**1a**: Ph, H	**2j**: *c*-C_6H_{11}	4	**3aj**, 48
10	**1b**: 4-MeC_6H_4, H	**2a**: Ph	3	**3ba**, 70
11	**1b**: 4-MeC_6H_4, H	**2f**: 4-ClC_6H_4	3	**3bf**, 58
12	**1c**: 4-FC_6H_4, H	**2a**: Ph	3	**3ca**, 68
13	**1d**: C_6H_{13}, H	**2a**: Ph	24	**3da**, 15
14	**1e**: Ph, Me	**2a**: Ph	3	**3ea**, 75[d]
15	**1f**: Ph, Pr	**2a**: Ph	5	**3fa**, 70

[a] The coupling reactions between **1** (1.0 mmol) and **2** (4.0 mmol) were performed with $SnCl_2$ (1.0 mmol) and BuOH (0.2 mmol) at 80 °C in CH_3NO_2 (1.0 mL). [b] The reactions were discontinued after the specified times. [c] Isolated yields of the (*E*) isomers. [d] The (*E*)/(*Z*) ratio was 93:7.

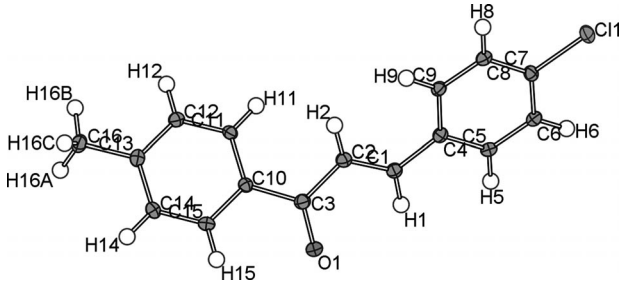
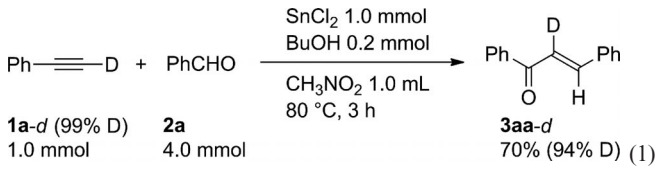


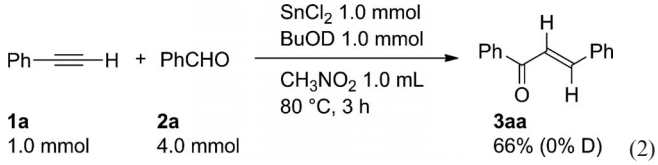
Figure 1. ORTEP drawing of the molecular structure of **3bf** with ellipsoids drawn at the 50% probability level.

aldol condensation reactions with aldehydes. The reaction of **1a** (1 mmol) and BuOH (1 mmol) with tin(II) chloride (1 mmol) at 80 °C for 24 h in CH_3NO_2 (1 mL) in the absence of **2a** followed by hydrolysis of the reaction mixture with aqueous HCl scarcely produced acetophenone. In the light of this result and the result of Entry 24 in Table 1, the coupling reaction between **1a** and **2a** is not considered to be a simple aldol condensation of **2a** with α-butoxystyrene or its hydrolysate, acetophenone, derived from **1a**.[12] If tin(II) chloride assisted nucleophilic addition of BuOH to **1a**, similarly to gold complexes, led to the preparation of α-butoxystyrene and subsequent aldol-type condensation with **2a**, the coupling reaction between **1a** and **2a** with BuOD would afford [D]**3aa** with a high 2-deuteriation rate.

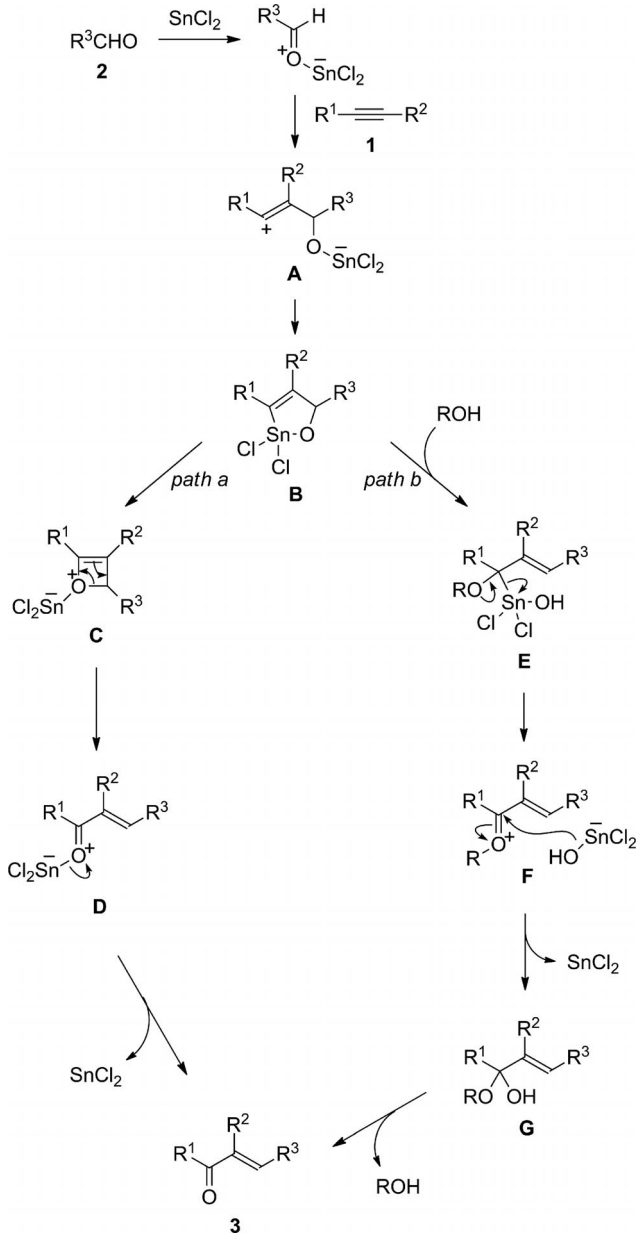
On the basis of these experimental results and the X-ray diffraction study, plausible mechanisms without ROH (*path a*) and with ROH (*path b*) are illustrated in Scheme 1. An aldehyde activated by coordination to $SnCl_2$ reacts by



(1)



(2)



Scheme 1. Plausible mechanisms without ROH (*path a*) and with ROH (*path b*).

electrophilic addition to an alkyne to generate zwitterion **A** and subsequently oxametallacyclopentene **B**, which is transformed into oxetene-like intermediate **C** in the absence of ROH (*path a*). The intermediate **C** undergoes ring-opening to form the relatively stable ketone–$SnCl_2$ adduct **D**, from which $SnCl_2$ is released to produce α,β-unsaturated ketone **3**. On the other hand, in the presence of ROH (*path b*), ROH undergoes S_N2' reaction with oxametallacyclopentene **B** with *O*-protonation to generate alcohol adduct **E**, from which dichlorohydroxystannate [$^-Sn(OH)Cl_2$] is eliminated to form oxycarbenium intermediate **F**. The formation of **B** and subsequent cleavage of the C–O bond might be quite rapid because of the strong oxophilicity of tin.[14,16] Next, the intermediate **F** reacts with the dichlorohydroxystannate to generate hemiacetal **G** and $SnCl_2$. Finally, ROH is released from hemiacetal **G** to produce α,β-unsaturated ketone **3**.

Conclusions

A weak Lewis acid, tin(II) chloride, which is insensitive to water and air, mediated the coupling reactions between alkynes and aldehydes to afford (*E*)-α,β-unsaturated ketones by a skeletal transformation in which one alkynic carbon atom changes into an oxo carbon atom accompanied by the cleavage of the C=O bond in the starting aldehydes. The coupling reaction is promoted by a catalytic amount of primary or secondary alkanol. Tin(II) chloride was the most effective mediator among all tin(II) halides for the coupling reaction. The coupling reaction between 1-deuterio-2-phenylethyne and benzaldehyde with BuOH afforded 1,3-diphenyl-2-deuterio-2-propenone (2-deuteriation: 94% D), whereas the coupling reaction between phenylethyne and benzaldehyde with BuOD afforded 1,3-diphenyl-2-propenone (2-deuteriation: 0% D). Because almost no exchange between hydrogen and deuterium at the 2-position of 1,3-diphenyl-2-propenone occurs in either reaction, the coupling reactions between alkynes and aldehydes with tin(II) chloride are presumed to proceed by nucleophilic addition of the alkynes to aldehydes. The cleavage of the C–O single bond generated by the nucleophilic addition might be induced by the strong oxophilicity of tin and has potential for further functionalization in organic synthetic reactions.

Experimental Section

General Methods: Tin(II) chloride (Wako first-grade, over 97%) was purchased from Wako Pure Chemical Industries and used after being dried at 120 °C under vacuum for 5 h. Phenylethyne (**1a**), 1-deuterio-2-phenylethyne (**1a**-*d*), and 1-ethynyl-4-fluorobenzene (**1c**) were purchased from Sigma–Aldrich. 1-Octyne (**1d**), 1-phenyl-1-propyne (**1e**), and 1-phenyl-1-pentyne (**1f**) were purchased from Kanto Chemical Co. [D]Butanol (BuOD, 97% D), 4-ethynyltoluene (**1b**), benzaldehyde (**2a**), 2-chlorobenzaldehyde (**2b**), 3-bromobenzaldehyde (**2c**), 4-cyanobenzaldehyde (**2h**), 4-fluorobenzaldehyde (**2g**), 4-methoxybenzaldehyde (**2e**), 4-methylbenzaldehyde (**2d**), 4-nitrobenzaldehyde (**2i**), and cyclohexanecarbaldehyde (**2j**) were purchased from Tokyo Chemical Industry Co. 4-Chlorobenzaldehyde (**2f**) was purchased from Wako Pure Chemical Industries. All purchased organic reagents were used as received. TLC analysis was carried out on silica gel plates (Merck 105735), and column chromatography on silica gel (Kanto Chemical Co., Inc. Cat. No. 37564). HPLC purification was performed with a Japan Analysis Industry LC-908 or LC-9201 instrument (JAIGEL-2 H, $CHCl_3$). NMR spectra were recorded with a JEOL ECX-300 spectrometer, and EI-MS data were recorded with a JEOL JMS-700 spectrometer.

Typical Reaction Procedure: Tin(II) chloride (1.0 mmol, 0.19 g) was added to a solution of phenylethyne (**1a**; 1.0 mmol, 0.10 g), benzaldehyde (**2a**; 4.0 mmol, 0.42 g), and butanol (0.2 mmol, 0.015 g) in nitromethane (1.0 mL). The mixture was stirred at 80 °C for 3 h, being monitored by TLC (Merck silica gel 60 F_{254}, 105735; hexane/EtOAc, 3:1) and then extracted with diethyl ether/dichloromethane (1:1, 150 mL). The extracted mixture was washed with water and a saturated solution of aqueous NaCl and then dried with anhydrous $MgSO_4$. After evaporation of the volatiles, purification by column chromatography (Kanto Chemical Co., silica gel 60, 37564; hexane/EtOAc, 8:1) and GPC (Japan Analytical Industry Co., LC-908, JAIGEL-2 H; $CHCl_3$) afforded 0.15 g (71%) of (*E*)-1,3-diphenyl-2-propen-1-one (**3aa**).

(*E*)-1,3-Diphenyl-2-propen-1-one (3aa):[6] ^1H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.63 (m, 9 H), 7.79 (d, J = 15.5 Hz, 1 H), 7.98–8.03 (m, 2 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 121.9, 128.27, 128.32, 128.4, 128.8, 130.4, 132.6, 134.7, 138.0, 144.6, 190.2 ppm. HRMS (EI): calcd. for $C_{15}H_{12}O$ 208.0888; found 208.0864.

(*E*)-2-Deuterio-1,3-diphenyl-2-propen-1-one (3aa-*d*): ^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.64 (m, 8 H), 7.79 (s, 1 H), 7.98–8.04 (m, 2 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 121.6 (J_{C-D} = 24 Hz), 128.3, 128.4, 128.5, 128.8, 130.4, 132.7, 134.7, 138.1, 144.6, 190.3 ppm.

(*E*)-3-(2-Chlorophenyl)-1-phenyl-2-propen-1-one (3ab): ^1H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.37 (m, 2 H), 7.41–7.55 (m, 4 H), 7.56–7.63 (m, 1 H), 7.71–7.78 (m, 1 H), 7.99–8.05 (m, 2 H), 8.18 (d, J = 15.8 Hz, 1 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 124.8, 127.1, 127.8, 128.60, 128.64, 130.3, 131.1, 132.9, 133.2, 135.5, 137.9, 140.6, 190.4 ppm. HRMS (EI): calcd. for $C_{15}H_{11}{}^{35}ClO$ 242.0498; found 242.0490.

(*E*)-3-(3-Bromophenyl)-1-phenyl-2-propen-1-one (3ac): ^1H NMR (300 MHz, $CDCl_3$): δ = 7.26 (t, J = 7.7 Hz, 1 H), 7.45–7.62 (m, 6 H), 7.70 (d, J = 15.8 Hz, 1 H), 7.76 (br., 1 H), 8.01 (d, J = 6.9 Hz, 2 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 122.96, 123.02, 127.1, 128.4, 128.6, 130.3, 130.7, 132.9, 133.1, 136.8, 137.7, 142.8, 189.8 ppm. HRMS (EI): calcd. for $C_{15}H_{11}{}^{79}BrO$ 285.9993; found 285.9972.

(*E*)-3-(4-Methylphenyl)-1-phenyl-2-propen-1-one (3ad): ^1H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 7.18 (d, J = 8.3 Hz, 2 H), 7.43–7.57 (m, 6 H), 7.78 (d, J = 15.8 Hz, 1 H), 7.97–8.02 (m, 2 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 21.4, 120.9, 128.30, 128.33, 128.4, 129.5, 131.0, 132.5, 138.2, 140.9, 144.7, 190.3 ppm. HRMS (EI): calcd. for $C_{16}H_{14}O$ 222.1045; found 222.1022.

(*E*)-3-(4-Methoxyphenyl)-1-phenyl-2-propen-1-one (3ae):[6] ^1H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 6.93 (d, J = 8.9 Hz, 2 H), 7.41 (d, J = 15.5 Hz, 1 H), 7.45–7.63 (m, 5 H), 7.79 (d, J = 15.5 Hz, 1 H), 7.98–8.03 (m, 2 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 55.4, 114.4, 119.7, 127.6, 128.4, 128.5, 130.2, 132.5, 138.5, 144.7, 161.6, 190.5 ppm. HRMS (EI): calcd. for $C_{16}H_{14}O_2$ 238.0994; found 238.0989.

(*E*)-3-(4-Chlorophenyl)-1-phenyl-2-propen-1-one (3af): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.36 (m, 2 H), 7.43–7.59 (m, 6 H), 7.72 (d, J = 15.8 Hz, 1 H), 7.97–8.02 (m, 2 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 122.2, 128.3, 128.5, 129.0, 129.4, 132.8, 133.2, 136.2, 137.8, 143.0, 189.9 ppm. HRMS (EI): calcd. for $C_{15}H_{11}{}^{35}ClO$ 242.0498; found 242.0490.

(*E*)-3-(4-Fluorophenyl)-1-phenyl-2-propen-1-one (3ag): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11 (t, J = 8.6 Hz, 2 H), 7.46 (d, J = 15.8 Hz, 1 H), 7.46–7.67 (m, 5 H), 7.78 (d, J = 15.8 Hz, 1 H), 8.02 (d, J = 7.9 Hz, 2 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 116.1 ($^2J_{C\text{-}F}$ = 22 Hz), 121.7, 128.4, 128.6, 130.3 ($^3J_{C\text{-}F}$ = 9 Hz), 131.1 ($^4J_{C\text{-}F}$ = 4 Hz), 132.8, 138.1, 143.5, 164.0 ($^1J_{C\text{-}F}$ = 251 Hz), 190.3 ppm. HRMS (EI): calcd. for $C_{15}H_{11}FO$ 226.0794; found 226.0784.

(*E*)-3-(4-Cyanophenyl)-1-phenyl-2-propen-1-one (3ah): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.53 (m, 2 H), 7.56–7.63 (m, 1 H), 7.58 (d, J = 15.8 Hz, 1 H), 7.68–7.70 (br., 4 H), 7.75 (d, J = 15.8 Hz, 1 H), 7.97–8.02 (m, 2 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 113.5, 118.4, 125.0, 128.6, 128.7, 128.8, 132.9, 133.3, 137.6, 139.2, 142.1, 189.7 ppm. HRMS (EI): calcd. for $C_{16}H_{11}NO$ 233.0841; found 233.0833.

(*E*)-3-(4-Nitrophenyl)-1-phenyl-2-propen-1-one (3ai): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.58 (m, 2 H), 7.60–7.69 (m, 2 H), 7.77–7.87 (m, 3 H), 8.02–8.07 (m, 2 H), 8.26–8.31 (m, 2 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 124.2, 125.7, 128.6, 128.8, 128.9, 133.4, 137.5, 141.0, 141.5, 148.5, 189.6 ppm. HRMS (EI): calcd. for $C_{15}H_{11}NO_3$ 253.0739; found 253.0740.

(*E*)-3-Cyclohexyl-1-phenyl-2-propen-1-one (3aj): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11–1.46 (m, 6 H), 1.57–1.89 (m, 4 H), 2.17–2.32 (m, 1 H), 6.82 (dd, J = 15.5, 1.3 Hz, 1 H), 7.01 (dd, J = 15.5, 6.5 Hz, 1 H), 7.41–7.49 (m, 2 H), 7.50–7.57 (m, 1 H), 7.89–7.95 (m, 2 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 25.7, 25.9, 31.8, 41.0, 123.3, 128.4, 128.5, 132.5, 138.1, 154.8, 191.2 ppm. HRMS (EI): calcd. for $C_{15}H_{18}O$ 214.1358; found 214.1333.

(*E*)-1-(4-Methylphenyl)-3-phenyl-2-propen-1-one (3ba):[6] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 7.24–7.7.30 (m, 2 H), 7.38–7.7.40 (m, 3 H), 7.53 (d, J = 15.5 Hz, 1 H), 7.61–7.63 (m, 2 H), 7.80 (d, J = 15.8 Hz, 1 H), 7.92–7.95 (m, 2 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 21.6, 121.9, 128.3, 128.6, 128.8, 129.2, 130.3, 134.9, 135.5, 143.5, 144.3, 189.8 ppm. HRMS (EI): calcd. for $C_{16}H_{14}O$ 222.1045; found 222.1044.

(*E*)-3-(4-Chlorophenyl)-1-(4-methylphenyl)-2-propen-1-one (3bf): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 3 H), 7.28 (d, J = 7.9 Hz, 2 H), 7.36 (d, J = 8.6 Hz, 2 H), 7.49 (d, J = 15.8 Hz, 1 H), 7.54 (d, J = 8.3 Hz, 2 H), 7.73 (d, J = 15.8 Hz, 1 H), 7.92 (d, J = 8.2 Hz, 2 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 21.6, 122.4, 128.6, 129.1, 129.3, 129.5, 133.4, 135.4, 136.2, 142.7, 143.7, 189.5 ppm. HRMS (EI): calcd. for $C_{16}H_{13}{}^{35}ClO$ 256.0655; found 256.0651.

(*E*)-1-(4-Fluorophenyl)-3-phenyl-2-propen-1-one (3ca): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11–7.20 (m, 2 H), 7.38–7.44 (m, 3 H), 7.49 (d, J = 15.8 Hz, 1 H), 7.58–7.67 (m, 2 H), 7.81 (d, J = 15.5 Hz, 1 H), 8.01–8.09 (m, 2 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 115.6 ($^2J_{C\text{-}F}$ = 22 Hz), 121.5, 128.4, 128.9, 130.6, 131.0 ($^3J_{C\text{-}F}$ = 10 Hz), 134.4 ($^4J_{C\text{-}F}$ = 3 Hz), 134.7, 144.9, 166.5 ($^1J_{C\text{-}F}$ = 255 Hz), 188.7 ppm. HRMS (EI): calcd. for $C_{15}H_{11}FO$ 226.0794; found 226.0775.

(*E*)-1-Phenyl-1-nonen-3-one (3da): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 6.9 Hz, 3 H), 1.25–1.42 (m, 6 H), 1.61–1.74 (m, 2 H), 2.67 (t, J = 7.4 Hz, 2 H), 6.75 (d, J = 16.1 Hz, 1 H), 7.37–7.42 (m, 3 H), 7.52–7.58 (m, 3 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 14.0, 22.5, 24.3, 29.0, 31.6, 41.0, 126.2, 128.2, 128.9, 130.4, 134.6, 142.3, 200.7 ppm. HRMS (EI): calcd. for $C_{15}H_{20}O$ 216.1514; found 216.1497.

(*E*)-2-Methyl-1,3-diphenyl-2-propen-1-one (3ea):[4b] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.15 (d, J = 1.7 Hz, 0.2 H), 2.26 (d, J = 1.4 Hz, 2.8 H), 7.17 (d, J = 1.4 Hz, 0.93 H), 7.26–7.54 (m, 8 H), 7.72–7.75 (m, 1.9 H), 7.86–7.89 (0.1 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 14.3, 128.0, 128.3, 128.4, 129.3, 129.5, 131.5, 135.6, 136.7, 138.3, 142.0, 199.2 ppm. HRMS (EI): calcd. for $C_{16}H_{14}O$ 222.1045; found 222.1022.

(*E*)-2-Propyl-1,3-diphenyl-2-propen-1-one (3fa): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (t, J = 7.2 Hz, 3 H), 1.53–1.67 (m, 2 H), 2.69–2.76 (m, 2 H), 7.06 (s, 1 H), 7.29–7.58 (m, 8 H), 7.77–7.82 (m, 2 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 14.3, 22.1, 29.7, 128.2, 128.4, 128.5, 129.1, 129.6, 131.9, 135.7, 138.6, 140.8, 142.2, 199.4 ppm. HRMS (EI): calcd. for $C_{18}H_{18}O$ 250.1358; found 250.1343.

X-ray Diffraction Analyses of 3bf: Single crystals were obtained by recrystallization by slow diffusion of hexane into a chloroform solution. A colorless crystal (0.30 × 0.15 × 0.03 mm) was mounted on a MicroMount™ (MiTeGen) and coated with liquid paraffin. All measurements were made with a Rigaku Mercury CCD area detector with graphite-monochromated Mo-K_α radiation at 93 K. The structure was solved by direct methods[17] and expanded by using Fourier techniques. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined by using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 2860 observed reflections and 164 variable parameters. All calculations were performed by using the CrystalStructure[18] crystallographic software package except for the refinement, which was performed by using SHELXL-97.[19] The crystallographic data are presented in Table S1 in the Supporting Information. CCDC-933560 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra and HRMS (EI) data of all compounds, X-ray crystallographic analysis of **3bf**.

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