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Oxidative coupling of tetraalkynyltin with aldehydes leading to alkynyl ketones†

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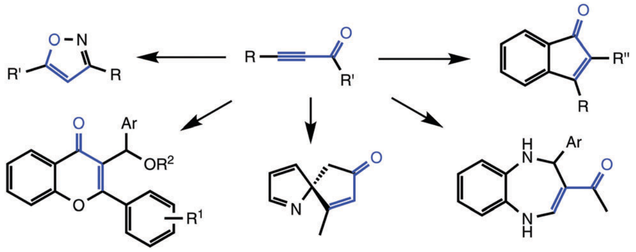
The reaction of tetraalkynyltin with aldehydes was studied for the first time. The reaction was shown to proceed as a tandem process of nucleophilic addition of tin acetylide to aldehyde followed by Oppenauer-type oxidation of produced tin alcoholates, and may be used as a convenient one-pot approach to acetylenic ketones. The advantages and limitations of the proposed method are discussed.

Introduction

α,β-Acetylenic ketones are valuable reagents for the synthesis of isoxazoles,[1,2] chromones,[3,4] triazoles,[5] quinolones,[6] indenones,[7–12] thiazoles,[13] 1,5-benzodiazepines,[14] spirocyclic products[15] *etc.* (Scheme 1). One of the most straightforward and useful methods to prepare alkynyl ketones is based on a two-step procedure including the reaction of metal acetylides with aldehydes followed by a subsequent oxidation of propargylic alcohols formed.[6,16–19]

Trialkyl(ethynyl)tin $R_3SnC{\equiv}CR'$ were successfully used in this reaction as reactive acetylene species. The reaction with aldehydes occurs in the presence of $InCl_3$,[20] and also in the presence of organoboron and organoaluminum catalysts, to give propargyl alcohols.[21,22] Although the results achieved with this method are usually good, all the procedures involving the use of trialkyltin reagents suffer from some drawbacks such as a high *E*-factor[23] (which is defined as the mass ratio of the waste to desired product) and high toxicity of the R_3Sn ballast moiety. As far as we know, the literature refers to only one example of the use of other ethynyltin compounds in the reaction with aldehydes; thus, alkynyltin trichloride $Cl_3SnC{\equiv}CR'$, which was generated *in situ* from 1-alkynes and the $SnCl_4$–Bu_3N system, was shown to react with aldehydes.[24] It should be noted that this approach is less dangerous and more environmentally friendly since it avoids the use of highly toxic $C(sp^2)$–Sn and $C(sp^3)$–Sn reagents; however, the *E*-factor still remains too high.



Scheme 1 Some applications of alkynyl ketones.

Recently, we have developed two convenient methods for the preparation of tetraalkynyltin compounds $(RC{\equiv}C)_4Sn$, by a reaction of 1-alkynes either with $SnCl_4$ in the presence of anhydrous $ZnCl_2$ and Et_2NH,[25,26] or with tin tetra(*N*,*N*-diethylcarbamate) in the presence of anhydrous $ZnCl_2$.[27] It is noteworthy that although tetraalkynyltin compounds were first prepared as early as the 1950s,[28] their synthetic potential was not sufficiently realized. There are only a few reports available on the reactions of tetraalkynyltin reagents with alcohols,[29] acids,[30] Grignard reagents,[31] organoboron compounds[32–36] and with aryl halides under Stille-type conditions.[37]

Tetraalkynyltin compounds, as well as other C(sp)–Sn species, were proved to be superior reagents in terms of toxicity and atom efficiency in comparison with alkyl- and alkenyltin reagents, and could be compared with sodium acetylides with respect to a low molecular weight and a low *E*-factor. Considering the low toxicity and atom economy, tetraalkynyltins $(RC{\equiv}C)_4Sn$ seemed to be good compounds to be used as a source of soft acetylide nucleophiles $RC{\equiv}C^-$. Based on this idea, we suggested that the reaction between tetraalkynyltin compounds and aldehydes would be a good starting point for preparation of propargylic alcohols and α,β-acetylenic ketones. To our knowledge, this

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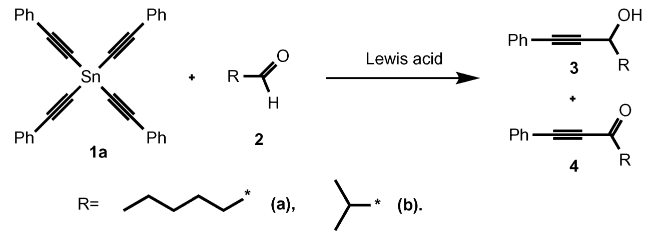
approach was not reported by any of the previous workers. It is the aim of the present paper to fill this gap.

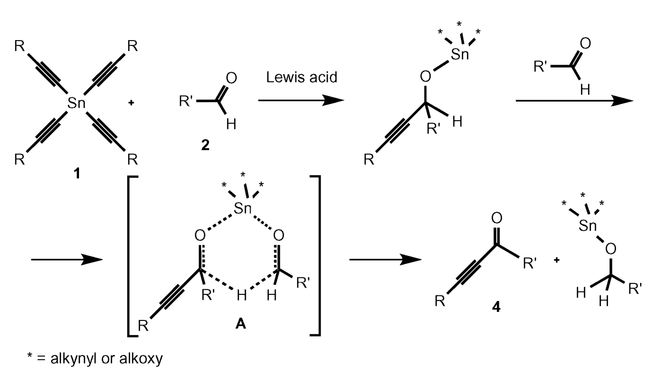
Results and discussion

When we studied the reaction of tetraalkynyltin **1** with aliphatic aldehydes **2**, we found that, besides the expected products of nucleophilic addition **3**, acetylenic ketones **4** were formed (Scheme 2). It was suggested that ketones **4** resulted from the Oppenauer-type oxidation of propargyl alcoholate by a second molecule of an aldehyde **2** (Scheme 3), by analogy with oxidative addition of alkynes to aldehydes in the presence of $InBr_3$[38] or ZnI_2.[39]

It was found that the reaction does not occur in the absence of Lewis acids as catalysts. The ratio of alcohols **3** and ketones **4** depends mostly on the ratio of the starting reagents and the nature of a solvent used. The effects of the different factors on the ratio of products **3aa**/**4aa** obtained by the reaction of $(Ph–C{\equiv}C)_4Sn$ **1a** with hexanal **2a** are summarized in Table 1. A similar picture was observed when tetraphenylethynyltin **1a** was reacted with isobutyraldehyde **2b**. The experimental data show that the oxidation rate strongly depends on the solvent polarity. Presumably, a more polar solvent favors the tin atom solvation that resulted in a decrease in complexation of tin atoms with propargyl alcohols and aldehydes **2** leading to the formation of an Oppenauer-type six membered transition state **A** (Scheme 3). As a result, the oxidation rate is decreased. It should also be noted that when tin tetrachloride was used as a catalyst in 1,2-dichloroethane and an aliphatic aldehyde was used in excess, side reactions occur and aldehyde self-condensation products were detected using GC–MS in the reaction mixture.



Scheme 2 The reaction of tetraalkynyltin with aliphatic aldehydes.



Scheme 3 The suggested mechanism of Oppenauer-type propargyl alcoholate oxidation.

Table 1 The effects of solvents, catalysts and reaction time on the ratio of products **3aa** : **4aa** in the reaction of $(Ph–C{\equiv}C)_4Sn$ **1a** with hexanal **2a**[a]

Ratio **1a** : **2a**	Solvent	Catalyst	Time, h	Ratio **3aa**/**4aa**
1 : 4	DCE[b]	—	2	No reaction
			5	Traces of **3aa**
1 : 4	DCE	$SnCl_4$	2	7.5
			5	2.7
1 : 4	Dioxane	$SnCl_4$	2	11.5
			5	7.1
1 : 4	THF	$ZnCl_2$	2	10.7
			5	7.1
1 : 4	THF	$InCl_3$	2	10.1
			5	14.5
1 : 8[c]	DCE	$SnCl_4$	2	3.2
			5	1.8

[a] The ratio of products **3aa** : **4aa** was determined using GC-MS. Unless otherwise stated, the reaction conditions were as follows: **1a** (0.102 mmol), **2a** (0.407 mmol), a catalyst (0.04 mmol) and a solvent (0.5 mL) at 60 °C. [b] Here and throughout the paper: DCE = 1,2-dichloroethane. [c] An eight-fold excess of hexanal **2a** (0.814 mmol) was used.

When aromatic aldehydes were allowed to react with $(Ph–C{\equiv}C)_4Sn$ **1a**, almost complete oxidation reaction occurs even if the ratio of the starting ethynyltin **1a** : aldehyde **2** was 1 : 4 (no aldehyde excess). Only the addition of an electron donating reagent (Et_3N) was required to slow down the oxidation and to give a mixture of alcohol **3** and ketone **4** (Table 2). To explore the effect of Lewis acid on the reaction, all the experiments were conducted with both $SnCl_4$ and $ZnCl_2$.

They were chosen as Lewis acids due to the successful application in similar reactions with aliphatic aldehydes. It was found that the use of $SnCl_4$ provides a faster reaction, but also causes some resinification and hence is less efficient.

Table 2 The effects of solvents, catalysts, reaction time and the ratio of the starting reagents on the yield of ketone $Ph–C{\equiv}C–C(O)Ph$ **4ac** in the reaction of tetraphenylethynyltin **1a** with PhCHO **2c**[a]

Ratio **1a** : **2c**	Solvent	Catalyst	Time, h	Yield of **4ac**, %
1 : 4	Dioxane	$ZnCl_2$	24	4
1 : 4	Dioxane	$SnCl_4$	5	2
1 : 4	DMF	$ZnCl_2$	24	1
1 : 4	DMF	$SnCl_4$	3	0
1 : 4	THF	$ZnCl_2$	3	7
1 : 4	DCE	$SnCl_4$	1	87
			3	99
1 : 4	DCE	$ZnCl_2$	1	77
			3	100
1 : 4	DCE	$ZnCl_2$ Et_3N[c]	1	80 (10% **3ac**)
1 : 8[b]	DCE	$SnCl_4$	1	13
			3	11
			5	69
1 : 4	PhMe	$SnCl_4$	3	98
1 : 4	PhMe	$ZnCl_2$	1	100
1 : 8[b]	PhMe	$SnCl_4$	1	49
			3	86

[a] Yields were determined by GC-MS. Unless otherwise stated, the reaction conditions were as follows: $(Ph–C{\equiv}C)_4Sn$ **1a** (0.123 mmol), PhCHO **2c** (0.492 mmol), a catalyst (0.05 mmol) and a solvent (0.5 mL), 60 °C. [b] An eight-fold excess of benzaldehyde **2c** (0.984 mmol) was used. [c] Triethylamine (0.25 mmol) was added.

When the amount of $SnCl_4$ was increased to 25 mol%, no significant acceleration of the reaction was observed while the yields of ketone products were a little bit lower (see the ESI† for details). The use of non-polar solvents (PhMe, DCE) resulted in good yields of products **4**. Thus, when $(Ph–C{\equiv}C)_4Sn$ **1a** and PhCHO **2c** were taken in a 1 : 4 ratio, PhCHO was fully converted to acetylenic ketone and $PhCH_2OH$ after 1–3 h at 60 °C. Meanwhile, the reaction of $(Ph–C{\equiv}C)_4Sn$ **1a** with aromatic aldehydes almost does not occur in polar aprotic solvents such as dioxane, THF, or DMF (Table 2), and the starting reagents were detected in the reaction mixture. Next, we run a series of detailed experiments to find an optimal temperature at which the highest preparative yields of the model compound $Ph–C{\equiv}C–C(O)Ph$ **4ac** were achieved (Table 3). The reaction between $(Ph–C{\equiv}C)_4Sn$ **1a** and PhCHO **2c** does not occur at room temperature. The temperature in the range of 40–60 °C was determined to be optimal for the reaction. A further increase in the temperature to 80 °C causes a decrease in yields of the target ketones **4** and also results in the formation of side products.

Then we tried to run the reaction in the presence of acetone as the possible oxidant/hydrogen acceptor for the Oppenauer-type oxidation of the intermediate tin alcoholates. However, the addition of acetone in 4-fold molar excess with regard to tetraphenylethynyltin **1a** gave no increase in the yield of ketone **4ac**. It is noteworthy that no Favorskii-type acetone alkynylation products were detected.

The yields of target ketones **4** strongly depend on the concentration of the starting compounds (Table 3). This fact is in a good agreement with the previously reported results of oxidative coupling of alkynes with aldehydes in the presence of $InBr_3$ and Et_3N.[39] Finally, the best yields (up to quantitative) of the model ketone $Ph–C{\equiv}C–C(O)Ph$ **4ac** were achieved when the reaction was carried out in toluene at 60 °C using $ZnCl_2$ as a Lewis acid catalyst (Table 3).

All the reactions were conducted at 60 °C in a dry solvent under an argon atmosphere to prevent the hydrolysis of tetraalkynyltin **1**. With an improved preparative protocol for the synthesis of ketones **4** in hand, we have prepared and isolated a series of α,β-acetylenic ketones **4**. Tetraalkynyltin **1** and aldehydes **2** used in the reaction are shown in Fig. 1. The preparative yields of ketones **4** are shown in Table 4. It is clear from the table that the best results were obtained with aldehydes bearing electron withdrawing groups.

Table 3 The effects of the reaction conditions on the yields of ketone **4ac** in the reaction of $(Ph–C{\equiv}C)_4Sn$ **1a** with PhCHO **2c**[a]

Ratio **1a** : **2c**	Solvent	Catalyst	T,°C	Time, h	Yield of **4ac**, %
1 : 4	DCE	$SnCl_4$	60	1.5	50
1 : 4[b]	PhMe	$ZnCl_2$	60	3	45
1 : 4[b]	DCE	$ZnCl_2$	60	2	50
1 : 8	DCE[c]	$ZnCl_2$	60	5	72
1 : 8	DCE	$ZnCl_2$	60	5	80
1 : 8	DCE[c]	$ZnCl_2$ Et_3N[d]	60	5	56
1 : 8	DCE	$ZnCl_2$ Et_3N[d]	60	5	83
1 : 8	DCE	$SnCl_4$	60	5	71
1 : 8	PhMe	$ZnCl_2$	60	5	98
1 : 8	PhMe	$ZnCl_2$	40	5	97
1 : 8	PhMe	$ZnCl_2$	80	5	88
1 : 8	PhMe	$ZnCl_2$	25	5	0

[a] Isolated yields are given. Unless otherwise stated, the reaction conditions were as follows: $(Ph–C{\equiv}C)_4Sn$ **1a** (0.123 mmol), PhCHO **2c** (0.492 mmol or 0.984 mmol, depending on the **1a** : **2c** ratio), catalyst (0.05 mmol), and solvent (0.5 mL). [b] Acetone (36 μL, 0.492 mmol) was added. [c] 2 mL of DCE were used. [d] Triethylamine (0.05 mmol) was added.

We have to note that under the given conditions the reaction of $(Ar–C{\equiv}C)_4Sn$ with either $4-NO_2C_6H_4CHO$ **2f**, thiophene-2-carbaldehyde **2m** or 5-nitrothiophene-2-carbaldehyde **2n** is

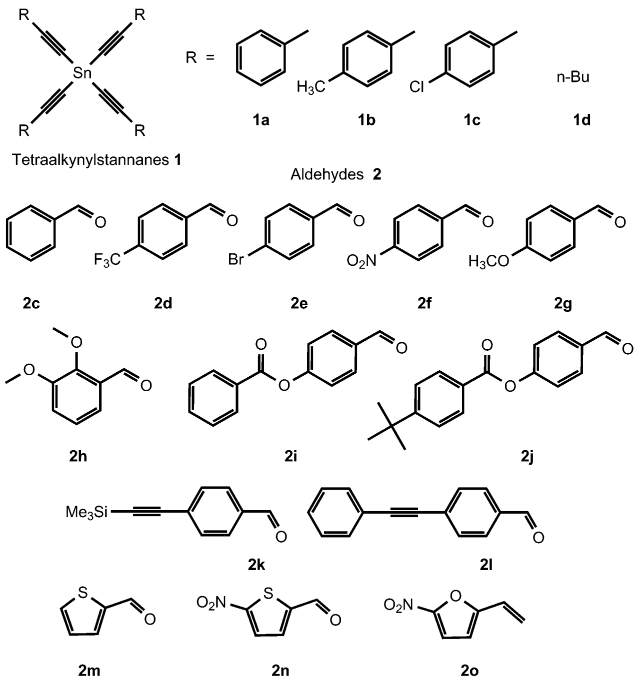


Fig. 1 The scope of tetraalkynyltin **1** and aldehydes **2** used.

Table 4 The preparative-scale synthesis of alkynyl ketones **4**

Tetraalkynyltin 1	Aldehyde 2	Product		Yield,[a] %
1a	**2c**	$Ph–C{\equiv}C–C(O)Ph$	**4ac**	98
1a	**2d**	$4-CF_3C_6H_4C(O)–C{\equiv}C–Ph$	**4ad**	97
1b	**2e**	$4-MeC_6H_4–C{\equiv}C–C(O)C_6H_4Br-4$	**4be**	85
1a	**2f**	$4-NO_2C_6H_4C(O)–C{\equiv}C–Ph$	**4af**	50[b]
1a	**2g**	$4-MeOC_6H_4C(O)–C{\equiv}C–Ph$	**4ag**	55
1a	**2h**	$2,3-(MeO)_2C_6H_3C(O)–C{\equiv}C–Ph$	**4ah**	66
1a	**2i**	$4-BzOC_6H_4C(O)–C{\equiv}C–Ph$	**4ai**	83
1a	**2j**	4-(t-Bu $C_6H_4CO_2)C_6H_4C(O)–C{\equiv}C–Ph$	**4aj**	79
1b	**2k**	$4-MeC_6H_4C{\equiv}C–C(O)C_6H_4C{\equiv}C–SiMe_3$	**4bk**	80
1b	**2c**	$4-MeC_6H_4–C{\equiv}C–C(O)Ph$	**4bc**	57
1a	**2l**	$Ph–C{\equiv}C–C(O)C_6H_4C{\equiv}CPh$	**4al**	90
1a	**2m**	$Ph–C{\equiv}C–C(O)$–thienyl-2	**4am**	30[b]
1a	**2n**	$5-NO_2$–thienyl–$C(O)–C{\equiv}C–Ph$	**4an**	47[b]
1b	**2o**	$5-NO_2C_4H_2OC(O)–C{\equiv}C–C_6H_4Me-4$	**4bo**	0[b]
1c	**2c**	$4-ClC_6H_4C{\equiv}C–C(O)Ph$	**4cc**	48
1d	**2c**	n-Bu–$C{\equiv}C–C(O)Ph$	**4dc**	27

[a] Isolated yields are given. [b] Resinification of the reaction mixture was observed.

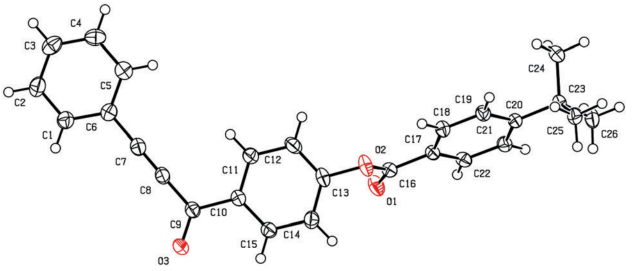


Fig. 2 The general view of 4-(3-phenylprop-2-ynoyl)phenyl 4-*tert*-butylbenzoate **4aj** in a crystal.

accompanied by formation of tarry products and resulted in much lower yields of target acetylene ketones **4**. The attempts to obtain ketone **4bo** starting from 5-nitrofurfural **2o** failed because of strong resinification probably due to complexation and side reactions of the aldehyde with $ZnCl_2$. The crystalline structure of the previously unreported alkynyl ketone **4aj** was studied using the X-ray diffraction technique (Fig. 2). Crystal data for compound **4aj** have been deposited (CCDC 1543712, http://www.ccdc.cam.ac.uk).†

Conclusions

In summary, we have developed a one-pot, mild and atom-economical method for the preparation of α,β-alkynyl ketones starting from aldehydes and easily available tetraalkynyltin by a sequence involving a nucleophilic addition of a tin acetylide to aldehyde following by the Oppenauer-type oxidation of tin propargyl alcoholates formed. The reaction conditions were optimized, the scope and limitations of the method were explored.

Experimental

Materials and methods

Solvents and starting reagents were thoroughly dried and purified according to common procedures.[40] All reactions were carried out in an argon (99.993%) atmosphere. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a JEOL ECA 400 instrument at operating frequencies 399.78, 100.52 respectively, in $CDCl_3$ (Aldrich) with reference to TMS or to the residual signals of a solvent. Chemical shifts are given in ppm, coupling constants are given in Hz. IR spectra were recorded on a InfraLUM FT-02 instrument in the range of 400–4200 cm^{-1} (KBr or $HCCl_3$ solution) and on a Bruker Vertex 70 instrument in ATR (attenuated total reflection) mode. Mass spectra (EI, 70 eV) were obtained on a Shimadzu GCMS-QP 2010 spectrometer. Melting points were measured in open capillaries on a Stuart SMP30 apparatus and are uncorrected. The purity of the compounds was checked by TLC (Sorbfil A plates) with toluene or a hexane : AcOEt (10 : 1) mixture as an eluent. The spots were visualized with iodine vapors, $KMnO_4$–H_2SO_4 solution or UV-light. The use of a sorbent consisting of 85% non-modified silica gel and 15% silica gel modified with 3-aminopropyltriethoxysilane (1.14 mmol g^{-1} of NH_2 groups) resulted in a much better separation of the desired acetylenic ketones and interfering by-products on a column.

The starting tetraalkynyltin **1a–d** were obtained according to the reported methods.[25,27] Aldehydes **2a–h**, **k**, **m–o** are commercially available (Aldrich). Aldehyde **2l** was prepared according to the known procedure.[37]

4-Formylphenyl benzoate (2i)

Sodium hydrocarbonate (16.0 g, 0.19 mol) was added portionwise to a stirred suspension of $4\text{-}HOC_6H_4CHO$ (10.0 g, 0.082 mol) in water (100 mL) at room temperature, and the mixture was stirred until the aldehyde is completely dissolved. The solution was cooled on an ice bath and PhC(O)Cl (9.8 mL, 0.085 mol) was added dropwise under vigorous stirring. After all the acyl chloride has been added, the ice bath is removed, and the reaction mixture is then allowed to warm to room temperature. Then the mixture was stirred for 1 h at 25 °C, the precipitated product was filtered off, washed with aqueous $NaHCO_3$ and water. For purification benzoate **2i** was reprecipitated from acetone with water. Yield 12.0 g (65%, purity by GCMS 100%). White crystalline solid, m.p. 89.5–90.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, ^{3}J = 8.7 Hz, 2H, Ar), 7.51–7.55 (m, 2H, Ar), 7.64–7.68 (m, 1H, Ar), 7.97 (d, ^{3}J = 8.7 Hz, 2H, Ar), 8.19–8.21 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.5, 128.7, 128.9, 130.2, 131.3, 134.0, 155.6, 164.5, 191.0. IR (KBr, cm^{-1}) ν_{max} 3097.5, 3070.5, 3053.2 (C–H, C–C), 2821.7, 2790.9, 2726.3 (C–H, CHO), 1734.9 (C=O, COO), 1696.3 (C=O, CHO), 1595.1. MS (*m*/*z*, EI, 70 eV) 226 ([M^+], 0.3), 105 (100), 77 (43), 51 (15).

4-Formylphenyl 4-*tert*-butylbenzoate (2j)

Sodium hydrocarbonate (4.0 g, 47.6 mmol) was added portionwise to a stirred suspension of $4\text{-}HOC_6H_4CHO$ (2.5 g, 20.5 mmol) in water (25 mL) at room temperature, and the mixture was stirred until the aldehyde becomes completely dissolved. The solution was cooled on an ice bath and 4-*tert*-butylbenzoyl chloride (4.13 g, 21 mmol) was added dropwise under vigorous stirring. Then THF (15 mL) and Bu_4NBr (0.1 g) were added, the mixture was stirred for 2 h at room temperature and left overnight. The precipitated solid was filtered off, washed with aqueous $NaHCO_3$ and water. For purification product **2j** was reprecipitated from acetone with water. Yield was 5.0 g (87%, purity by GCMS – 98%). The further recrystallization from EtOH gave pure **2j** (purity by GCMS – 100%) as white crystalline solid, m.p. 88.3–88.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 9H, Me), 7.40 (d, ^{3}J = 8.7 Hz, 2H, Ar), 7.55 (d, ^{3}J = 8.3 Hz, 2H, Ar), 7.96 (d, ^{3}J = 8.7 Hz, 2H, Ar), 8.13 (d, ^{3}J = 8.7 Hz, 2H, Ar), 10.02 (s, 1H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.1, 35.3, 122.6, 125.7, 126.1, 130.2, 131.2, 134.0, 155.9, 158.0, 164.5, 190.9. IR (KBr, cm^{-1}) ν_{max} 2966.4, 2904.7, 2740.7 (C–H, C–C), 1731.0, 1705.0, 1606.6, 1594.1. MS (*m*/*z*, EI, 70 eV) 282 ([M^+], 0.1), 267 (0.6), 161 (100), 146 (10.7), 133 (5.2), 118 (13.9), 91 (9.4).

General procedure for the reaction of tetra(phenylethynyl)tin 1a with aliphatic aldehydes 2a,b (the model reaction, Scheme 2 and Table 1)

A 2 mL sealable Wheaton vial was charged with 0.04 mmol of Lewis acid ($ZnCl_2$, $SnCl_4$ or $InCl_3$), 0.102 mmol of $(PhC{\equiv}C)_4Sn$ **1a** and 0.5 mL of a dry solvent. Then the vial was flushed with a stream of dry argon, and 0.407 mmol (or 0.814 mmol if the ratio **1a** : **2a** was set as 1 : 8) of aliphatics aldehydes **2a** or **2b** were added subsequently through a syringe. The mixture was stirred for the indicated time (Table 1). The progress of the reaction was monitored using GC-MS (before the analysis, samples taken at regular intervals were quenched with saturated aqueous NH_4Cl).

Preparative procedure for the synthesis of 1,3-diphenylprop-2-yn-1-one (4ac)

A 2 mL sealable Wheaton vial was charged with 10.4 mg (0.076 mmol) of anhydrous $ZnCl_2$, PhMe (0.8 mL), 100 mg (0.191 mmol) tetra(phenylethynyl)tin **1a** and 155 μL (1.53 mmol) of freshly distilled PhCHO **2c**. A reaction mixture was stirred at 60 °C for 5 h, then treated with 1 M aqueous HCl. The product was extracted with $HCCl_3$ and purified using column chromatography (eluent – PhMe). The yield of ketone Ph–C$\equiv$C–C(O)Ph **4ac** was 154.6 mg (98%), light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.53 (m, 5H, Ar), 7.60–7.69 (m, 3H, Ar), 8.22 (d, J = 7.3 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 86.8, 93.1, 120.1, 128.6, 128.7, 129.5, 130.8, 133.0, 134.1, 136.8, 177.9. IR (liquid film, cm^{-1}) ν_{max} 3099.9, 3082.6, 3059.5, 3034.4, 2199.1 (C$\equiv$C), 1641.6 (C=O), 1597.2, 1581.8. MS (m/z, EI, 70 eV) (I_{rel} (%)): 206 (M$^+$, 52), 178 (88), 152 (11), 129 (100), 101 (14), 89 (11), 77 (26), 76 (21), 75 (33), 51 (35).

3-Phenyl-1-[4-(trifluoromethyl)phenyl]prop-2-yn-1-one (4ad)

Acetylenic ketone 4-$CF_3C_6H_4$C(O)–C$\equiv$C–Ph **4ad** was prepared according to a similar procedure to that for **4ac**, using 6.7 mg (0.05 mmol) of anhydrous $ZnCl_2$, toluene (0.5 mL), 64.4 mg (0.123 mmol) of $(PhC{\equiv}C)_4Sn$ **1a** and 135 μL (0.984 mmol) of 4-(trifluoromethyl)-benzaldehyde **2d**. The yield was 130.7 mg (97%), light yellow solid, m.p. 73–74 °C (from EtOH–H_2O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.53 (m, 3H, Ar), 7.70 (d, ^3J = 8.7 Hz, 2H, Ar), 7.79 (d, ^3J = 8.2 Hz, 2H, Ar), 8.32 (d, ^3J = 8.2 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 86.6, 94.5, 119.7, 123.6 (q, $^1J_{C–F}$ = 273.1 Hz), 125.7 (q, $^3J_{C–F}$ = 3.8 Hz), 128.8, 129.8, 131.2, 133.2, 135.2 (q, $^2J_{C–F}$ = 23.6 Hz), 139.5, 176.7. IR (KBr, cm^{-1}) ν_{max} 3059.9, 2202.6 (C$\equiv$C), 1643.3 (C=O). MS (m/z, EI, 70 eV) (I_{rel} (%)): 274 (M$^+$, 43), 246 (40), 129 (100), 98 (13), 75 (19).

1-(4-Bromophenyl)-3-(4-methylphenyl)prop-2-yn-1-one (4be)

Acetylenic ketone 4-MeC_6H_4-C$\equiv$C–C(O)C_6H_4Br-4 **4be** was prepared according to a similar procedure to that for **4ac**, using 6.7 mg (0.05 mmol) of anhydrous $ZnCl_2$, toluene (0.5 mL), 71.3 mg (0.123 mmol) of $(MeC_6H_4C{\equiv}C)_4Sn$ **1b** and 182 mg (0.984 mmol) of 4-bromobenzaldehyde **2e**. The yield was 125.1 mg (85%), light yellow solid, m.p. 110.5–111.5 °C (from EtOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H, CH_3), 7.23 (d, ^3J = 7.8 Hz, 2H, Ar), 7.58 (d, ^3J = 7.8 Hz, 2H, Ar), 7.65 (d, ^3J = 8.7 Hz, 2H, Ar) 8.07 (d, ^3J = 8.7 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 86.5, 94.4, 116.8, 129.4, 129.6, 130.9, 131.9, 133.2, 135.8, 141.8, 176.9. IR (KBr, cm^{-1}) ν_{max} 3085.0, 3030.0, 2914.3, 2855.5, 2194.9 (C$\equiv$C), 1636.5 (C=O), 1603.7, 1583.5, 1569.0. MS (m/z, EI, 70 eV) (I_{rel} (%)): 300([M$^+$, 8^{1}Br], 27), 398([M$^+$, ^{79}Br], 26), 272 (28, ^{81}Br), 270 (28, ^{79}Br), 190 (10), 189 (19), 143 (100), 115 (16), 95 (18), 89 (16), 75 (15), 63 (11), 50 (9).

1-(4-Nitrophenyl)-3-phenylprop-2-yn-1-one (4af)

Acetylenic ketone 4-$NO_2C_6H_4$C(O)–C$\equiv$C–Ph **4af** was prepared according to a similar procedure to that for **4ac**, using 6.7 mg (0.05 mmol) of anhydrous $ZnCl_2$, toluene (0.5 mL), 64.4 mg (0.123 mmol) of $(PhC{\equiv}C)_4Sn$ **1a** and 149 mg (0.984 mmol) of 4-nitrobenzaldehyde **2f**. The yield was 61.8 mg (50%), light yellow solid, m.p. 160 °C (from toluene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.48 (m, 2H, Ar), 7.52–7.56 (m, 1H, Ar), 7.71 (d, ^3J = 8.7 Hz, 2H, Ar), 8.35–4.10 (m, 4H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 86.6, 95.4, 119.4, 123.9, 128.9, 130.4, 131.5, 133.3, 141.1, 150.9, 175.9. IR (KBr, cm^{-1}) ν_{max} 3113.0, 3048.4, 2193.9 (C$\equiv$C), 1646.1 (C=O), 1593.1 (NO_2 st as), 1516.0, 1343.4, 1321.2 (NO_2 st sy). MS (m/z, EI, 70 eV) (I_{rel} (%)): 251 (M$^+$, 33), 223 (13), 193 (7), 176 (11), 129 (100), 101 (10), 75 (23).

1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-one (4ag)

Acetylenic ketone 4-$MeOC_6H_4$C(O)–C$\equiv$C–Ph **4ag** was prepared according to a similar procedure to that for **4ac**, using 10.4 mg (0.076 mmol) of anhydrous $ZnCl_2$, PhMe (0.8 mL), 100.0 mg (0.191 mmol) of $(PhC{\equiv}C)_4Sn$ **1a** and 186.2 μL (1.53 mmol) of 4-methoxybenzaldehyde **2g**. The yield was 98.8 mg (55%), light yellow solid, m.p. 98–99 °C (from EtOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H, OMe), 6.99 (d, ^3J = 8.7 Hz, 2H, Ar), 7.39–7.49 (m, 3H, Ar), 7.67 (d, ^3J = 8.7 Hz, 2H, Ar), 8.19 (d, ^3J = 8.7 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 86.9, 92.3, 113.9, 120.4, 128.7, 130.4, 130.6. 132.0, 133.0, 164.5, 176.7. IR (KBr, cm^{-1}) ν_{max} 3111.7, 2957.7, 2847.8, 2195.9 (C$\equiv$C), 1626.9 (C=O), 1599.9, 1594.1, 1570.0. MS (m/z, EI, 70 eV) (I_{rel} (%)): 236 (M$^+$, 100), 208 (99), 193 (73), 165 (53), 129 (75), 104 (12), 101 (17), 92 (15), 75 (29), 63 (19), 51 (15).

1-(2,3-Dimethoxyphenyl)-3-phenylprop-2-yn-1-one (4ah)

Acetylenic ketone 2,3-$(MeO)_2C_6H_3$C(O)–C$\equiv$C–Ph **4ah** was prepared according to a similar procedure to that for **4ac**, using 6.7 mg (0.05 mmol) of anhydrous $ZnCl_2$, PhMe (0.5 mL), 64.4 mg (0.123 mmol) of $(PhC{\equiv}C)_4Sn$ **1a** and 164 mg (0.984 mmol) of 2,3-dimethoxybenzaldehyde **2h**. The yield was 86.4 mg (66%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H, OMe), 3.99 (s, 3H, OMe), 7.12–7.14 (m, 2H, Ar), 7.36–7.47 (m, 3H, Ar), 7.52–7.57 (m, 1H, Ar), 7.62–7.65 (m, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.1, 61.7, 89.5, 91.6, 117.1, 120.6, 122.3, 123.8, 128.6, 130.5, 132.1, 133.0, 149.8, 153.5, 176.9. IR (liquid film, cm^{-1}) ν_{max} 3063.3, 3003.5, 2937.9, 2837.6, 2203.0 (C$\equiv$C), 1645.5, 1624.3, 1593.4, 1577.9. MS (m/z, EI, 70 eV) (I_{rel} (%)): 266 (M$^+$, 26), 255 (14), 207 (25), 165 (25), 152 (36), 151 (29), 150 (22), 135 (14), 129 (100), 126 (24), 122 (79), 115 (23), 107 (18), 101 (23), 75 (50), 51 (48).

4-(3-Phenylprop-2-ynoyl)phenyl benzoate (4ai)

Acetylenic ketone 4-PhC(O)OC_6H_4C(O)–C$\equiv$C–Ph **4ai** was prepared according to a similar procedure to that for **4ac**, using 6.7 mg (0.05 mmol) of anhydrous $ZnCl_2$, PhMe (0.5 mL), 64.4 mg (0.123 mmol) of $(PhC{\equiv}C)_4Sn$ **1a** and 222.6 mg (0.984 mmol) of 4-formylphenyl benzoate **2i**. The yield was 133.3 mg (83%), white solid, m.p. 96.5–97.5 °C (from EtOH). ^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.38–7.44 (m, 4H, Ar), 7.47–7.55 (m, 3H, Ar), 7.64–7.71 (m, 3H, Ar), 8.20–8.22 (m, 2H, Ar), 8.29–8.32 (m, 2H, Ar). ^{13}C NMR (100 MHz, CDCl$_3$) δ 86.8, 93.4, 120.1, 122.1, 128.7, 129.0, 130.3, 130.9, 131.2, 133.1, 134.0, 134.6, 155.6, 164.5, 176.8. IR (KBr, cm^{-1}) $\nu_{\max}$ 3063.8, 2197.8 (C$\equiv$C), 1734.9 (C$=$O, COO), 1635.6 (C$=$O), 1597.9, 1585.4.

4-(3-Phenylprop-2-ynoyl)phenyl 4-*tert*-butylbenzoate (4aj)

Acetylenic ketone 4-(*t*-BuC$_6$H$_4$CO$_2$)C$_6$H$_4$C(O)–C$\equiv$C–Ph **4aj** was prepared according to a similar procedure to that for **4ac**, using 6.7 mg (0.05 mmol) of anhydrous ZnCl$_2$, toluene (0.5 mL), 64.4 mg (0.123 mmol) of (PhC$\equiv$C)$_4$Sn **1a** and 277.8 mg (0.984 mmol) of 4-formylphenyl 4-*tert*-butylbenzoate **2j**. The yield was 148.6 mg (79%), white solid, m.p. 140.8–141.2 °C (from HCCl$_3$–hexane). ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.37 (s, 9H, Me), 7.38 (d, ^3J = 8.7 Hz, 2H, Ar), 7.41–7.49 (m, 3H, Ar), 7.54 (d, ^3J = 8.7 Hz, 2H, Ar), 7.69 (d, ^3J = 8.2 Hz, 2H, Ar), 8.14 (d, ^3J = 8.7 Hz, 2H, Ar), 8.30 (d, ^3J = 8.7 Hz, 2H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$) δ 31.1, 35.2, 86.8, 93.3, 120.1, 122.1, 125.7, 126.2, 128.7, 130.2, 130.8, 131.2, 133.1, 134.5, 155.7, 157.9, 164.5, 176.8. IR (KBr, cm^{-1}) $\nu_{\max}$ 3059.5, 2961.1, 2905.1, 2866.6, 2201.0 (C$\equiv$C), 1734.9 (C$=$O, COO), 1630.1 (C$=$O), 1597.2, 1583.7.

3-(4-Tolyl)-1-{4-[(trimethylsilyl)ethynyl]phenyl}prop-2-yn-1-one (4bk)

Acetylenic ketone 4-MeC$_6$H$_4$C$\equiv$C–C(O)C$_6$H$_4$C$\equiv$C–SiMe$_3$ **4bk** was prepared according to a similar procedure to that for **4ac**, using 6.7 mg (0.05 mmol) of anhydrous ZnCl$_2$, toluene (0.5 mL), 71.3 mg (0.123 mmol) of (MeC$_6$H$_4$C$\equiv$C)$_4$Sn **1b** and 199 mg (0.984 mmol) of 4-[(trimethylsilyl)ethynyl]benzaldehyde **2k**. The yield was 124.3 mg (80%), light yellow solid. M.p. 142.5–144.0 °C (from hexane). ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.28 (s, 9H, Me$_3$Si), 2.41 (s, 3H, CH$_3$), 7.23 (d, ^3J = 8.2 Hz, 2H, Ar), 7.57–7.59 (m, 4H, Ar), 8.14 (d, ^3J = 8.2 Hz, 2H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$) δ 0.21, 21.8, 86.7, 94.3, 98.9, 104.0, 116.9, 128.8, 129.3, 129.5, 132.0, 133.1, 136.3, 141.7, 177.1. IR (KBr, cm^{-1}) $\nu_{\max}$ 3063.3, 2959.2, 2918.6, 2897.4, 2191.4 (C$\equiv$C), 2160.5 (C$\equiv$C), 1628.1 (C$=$O), 1599.2, 1556.7, 1506.6. MS (*m*/*z*, EI, 70 eV) (I_{rel} (%)): 316([M$^+$], 28), 301 (100), 143 (26), 115 (7).

3-(4-Methylphenyl)-1-phenylprop-2-yn-1-one (4bc)

Acetylenic ketone 4-MeC$_6$H$_4$–C$\equiv$C–C(O)Ph **4bc** was prepared according to a similar procedure to that for **4ac**, using 10.4 mg (0.076 mmol) of anhydrous ZnCl$_2$, toluene (0.8 mL), 110.6 mg (0.191 mmol) of (MeC$_6$H$_4$C$\equiv$C)$_4$Sn **1a** and 155.4 μL (1.53 mmol) of benzaldehyde **2c**. The yield was 96.0 mg (57%), light yellow solid, m.p. 58.3–59.2 °C (from hexane, with freezing). ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.40 (s, 3H, Me), 7.22 (d, ^3J = 7.8 Hz, 2H, Ar), 7.49–7.52 (m, 2H, Ar), 7.57–7.63 (m, 3H, Ar), 8.21 (d, ^3J = 8.2 Hz, 2H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$) δ 86.8, 93.8, 117.0, 128.6, 129.5, 129.6, 133.1, 134.0, 137.0, 141.6, 178.1. IR (KBr, cm^{-1}) $\nu_{\max}$ 3059.9, 3031.0, 2187.2 (C$\equiv$C), 1626.9 (C$=$O), 1603.7, 1598.9, 1578.7. MS (*m*/*z*, EI, 70 eV) (I_{rel} (%)): 220 (M$^+$, 65), 192 (60), 189 (14), 165 (11), 143 (100), 115 (19), 89 (17), 77 (18), 63 (12), 51 (16).

3-Phenyl-1-[4-(phenylethynyl)phenyl]prop-2-yn-1-one (4al)

Acetylenic ketone Ph–C$\equiv$C–C(O)C$_6$H$_4$C$\equiv$C–Ph **4al** was prepared according to a similar procedure to that for **4ac**, using 6.7 mg (0.05 mmol) of anhydrous ZnCl$_2$, toluene (0.5 mL), 64.4 mg (0.123 mmol) of (PhC$\equiv$C)$_4$Sn **1a** and 203 mg (0.984 mmol) of 4-(phenylethynyl)benzaldehyde **2l**. The yield was 135.2 mg (90%), light yellow solid, m.p. 104.9–105.2 °C (from heptane). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35–7.39 (m, 3H, Ar), 7.41–7.51 (m, 3H, Ar), 7.55–7.57 (m, 2H, Ar), 7.65 (d, ^3J = 8.7 Hz, 2H, Ar), 7.69 (d, ^3J = 8.7 Hz, 2H, Ar), 8.20 (d, ^3J = 8.7 Hz, 2H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$) δ 86.8, 88.7, 93.5, 120.0, 122.5, 128.4, 128.7, 128.9, 129.2, 129.5, 130.9, 131.7, 131.8, 133.1, 136.0. 177.0. IR (KBr, cm^{-1}) $\nu_{\max}$ 3080.7, 3055.6, 3034.4, 2201.1 (C$\equiv$C), 2164.4 (C$\equiv$C), 1628.1 (C$=$O), 1603.0, 1556.7. MS (*m*/*z*, EI, 70 eV) (I_{rel} (%)): 306([M$^+$], 95), 278 (100), 276 (23), 176 (15), 139 (31), 129 (80), 101 (11), 75 (15).

3-Phenyl-1-(2-thienyl)prop-2-yn-1-one (4am)

Acetylenic ketone Ph–C$\equiv$C–C(O)C$_4$H$_3$S-2 **4am** was prepared according to a similar procedure to that for **4ac**, using 10.4 mg (0.076 mmol) of anhydrous ZnCl$_2$, toluene (0.8 mL), 100 mg (0.191 mmol) of (PhC$\equiv$C)$_4$Sn **1a** and 143 μL (1.53 mmol) of thiophene-2-carbaldehyde **2m**. The product was extracted from a reaction mixture with boiling hexane. The yield was 48.5 mg (30%), light yellow solid, m.p. 57.0–57.6 °C (from hexane, with freezing). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.10–7.12 (m, 1H, Ar), 7.32–7.43 (m, 3H, Ar), 7.59 (d, ^3J = 8.2 Hz, 2H, Ar), 7.65 (d, ^3J = 4.6 Hz, 1H, Ar), 7.94 (d, ^3J = 3.7 Hz, 1H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$) δ 86.4, 91.7, 119.9, 128.3, 128.7, 130.8, 133.0, 135.0, 135.2, 144.9, 169.7. IR (KBr, cm^{-1}) $\nu_{\max}$ 3074.9, 2206.8 (C$\equiv$C), 1612.7 (C$=$O), 1595.3, 1579.9, 1516.2. MS (*m*/*z*, EI, 70 eV) (I_{rel} (%)): 212 (M$^+$, 71), 184 (100), 152 (23), 139 (23), 129 (77), 111 (11), 101(17), 92 (12), 75 (36), 51 (20).

1-(5-Nitro-2-thienyl)-3-phenylprop-2-yn-1-one (4an)

Acetylenic ketone 5-NO$_2$C$_4$H$_2$SC(O)–C$\equiv$C–Ph **4an** was prepared according to a similar procedure to that for **4ac**, using 10.4 mg (0.076 mmol) of anhydrous ZnCl$_2$, toluene (0.8 mL), 100 mg (0.191 mmol) of (PhC$\equiv$C)$_4$Sn **1a** and 212.8 mg (1.53 mmol) of 5-nitrothiophene-2-carbaldehyde **2n**. The product was extracted from a reaction mixture with boiling hexane. The yield was 93.1 mg (47%), yellow solid, m.p. 151.3–152.3 °C (from HCCl$_3$, with freezing). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43–7.56 (m, 3H, Ar), 7.68 (d, ^3J = 8.2 Hz, 2H, Ar), 7.86 (d, ^3J = 4.1 Hz, 1H, Ar), 7.93 (d, ^3J = 4,1 Hz, 1H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$) δ 85.6, 95.2, 118.9, 128.2, 128.9, 131.7, 131.9, 133.3, 148.0, 156.8, 169.1. IR (KBr, cm^{-1}) $\nu_{\max}$ 3107.7, 3092.3, 3065.3, 2193.3 (C$\equiv$C), 1618.5, 1610.8, 1593.4, 1535.5, 1512.4. MS (*m*/*z*, EI, 70 eV) (I_{rel} (%)): 257 (M$^+$, 51), 229 (20), 199 (10), 139 (32), 29 (100), 101 (14), 75 (22), 51 (11).

3-(4-Chlorophenyl)-1-phenylprop-2-yn-1-one (4cc)

Acetylenic ketone 4-ClC$_6$H$_4$C$\equiv$C–C(O)Ph **4cc** was prepared according to a similar procedure to that for **4ac**, using 6.7 mg (0.05 mmol) of anhydrous ZnCl$_2$, toluene (0.5 mL), 81.3 mg

(0.123 mmol) of $(4\text{-ClC}_6\text{H}_4\text{C}{\equiv}\text{C})_4\text{Sn}$ **1c** and 100 μL (0.984 mmol) of PhCHO **2c**. The yield was 56.4 mg (48%), light yellow solid, m.p. 105.5–106.5 °C (from hexane). ^{1}H NMR (400 MHz, CDCl_3) δ 7.40 (d, ^3J = 8.7 Hz, 2H, Ar), 7.49–7.53 (m, 2H, Ar), 7.59–7.65 (m, 3H, Ar), 8.19 (d, ^3J = 8.2 Hz, 2H, Ar); ^{13}C NMR (100 MHz, CDCl_3) δ 87.6, 91.6, 118.6, 128.7, 129.2, 129.6, 134.2, 136.8, 137.2, 177.8. IR (KBr, cm^{-1}) $\nu_{\max}$ 3082.6, 3053.7, 2922.5, 2203.0 ($\text{C}{\equiv}\text{C}$), 2164.4 ($\text{C}{\equiv}\text{C}$), 1632.0 ($\text{C}{=}\text{O}$), 1616.5, 1599.2, 1589.5, 1579.9. MS (m/z, EI, 70 eV) (I_{rel} (%)): 242([M$^+$] ^{37}Cl, 24), 240 ([M$^+$] ^{35}Cl, 75), 214 (32), 212 (100), 176 (33), 165 (31), 163 (100), 151 (12), 135 (11), 106 (20), 99 (39), 88 (16), 77 (33), 51 (29).

1-Phenylhept-2-yn-1-one (4dc)

Acetylenic ketone $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{–C}{\equiv}\text{C–C(O)Ph}$ **4dc** was prepared according to a similar procedure to that for **4ac**, using 10.4 mg (0.076 mmol) of anhydrous ZnCl_2, toluene (0.8 mL), 84.7 mg (0.191 mmol) of $(\text{PhC}{\equiv}\text{C})_4\text{Sn}$ **1a** and 155 μL (1.53 mmol) of PhCHO **2c**. The yield was 38.9 mg (27%), light yellow oil. ^{1}H NMR (400 MHz, CDCl_3) δ 0.97 (t, J = 7.3 Hz, 3H, CH_3), 1.46–1.56 (m, 2H, CH_2), 1.63–1.71 (m, 2H, CH_2), 2.51 (t, J = 7.3 Hz, 2H, CH_2), 7.46–7.49 (m, 2H, Ar), 7.58–7.61 (m, 1H, Ar), 8.14 (d, ^3J = 8.2 Hz, 2H, Ar); ^{13}C NMR (100 MHz, CDCl_3) δ 13.5, 18.9, 22.1, 29.9, 79.7, 96.8, 128.5, 129.6, 133.9, 137.0, 178.3. IR (liquid film, cm^{-1}) $\nu_{\max}$ 3063.3, 2959.1, 2932.1, 2874.3, 2237.7, 2201.0, 1645.5, 1597.2, 1579.9. MS (m/z, EI, 70 eV) (I_{rel} (%)): 186 (M$^+$, 7), 185 (13), 157 (43), 144 (100), 129 (27), 115 (57), 109 (27), 105 (95), 79 (40), 77(73), 66 (32), 53 (26), 51 (39).

X-ray studies of 4-(3-phenylprop-2-ynoyl)phenyl 4-*tert*-butylbenzoate (4aj)

Single crystals of ketone **4aj** were obtained by recrystallization from EtOH. X-ray diffraction studies were performed on an Agilent SuperNova, Dual, Cu at zero, AtlasS2 diffractometer at 100 K. Using Olex2,[41] the structure was solved with the ShelXT[42] structure solution program using Intrinsic Phasing and refined by the least squares technique using the ShelXL[43] refinement package. Crystals of compound **4aj** are triclinic, $\text{C}_{26}\text{H}_{22}\text{O}_3$ (M = 382.43), space group $P\bar{1}$ (No 2), a = 6.7125(3) Å, b = 9.9947(3) Å, c = 15.6535(3) Å, α = 88.139(2)°, β = 87.315(2)°, γ = 80.902(3)°, V = 1035.50(6) Å^3, Z = 2, T = 100.00(10) K, $\mu(\text{CuK}\alpha)$ = 0.630 mm^{-1}, D_{calc} = 1.227 g cm^{-3}, 19 353 reflections were collected (8.964° $\leq 2\theta \leq$ 147.682°), of which 4133 were unique (R_{int} = 0.0373, R_{sigma} = 0.0216). The final probability factors were: R_1 = 0.0374 ($I > 2\sigma(I)$), wR_2 = 0.1038 (all reflections). The full crystallographic data have been placed at the Cambridge Crystallographic Data Center as deposit CCDC 1543712.†

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