Oxidative coupling of tetraalkynyltin with aldehydes leading to alkynyl ketones

Andrey S. Levashov, Nicolai A. Aksenov, Inna V. Aksenova and Valeriy V. Konshin

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 alcohulates, 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 indenes,7–12 thiazoles,13 1,5-benzodiazepines,14 spirocyclic products15 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 R₃SnC≡CR’ were successfully used in this reaction as reactive acetylene species. The reaction with aldehydes occurs in the presence of InCl₃,20 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 trialkynyl reagents suffer from some drawbacks such as a high E-factor23 (which is defined as the mass ratio of the waste to desired product) and high toxicity of the R₃Sn 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 Cl₃SnC≡CR’, which was generated in situ from 1-alkynes and the SnCl₄–Bu₄N 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(sp²)–Sn and C(sp³)–Sn reagents; however, the E-factor still remains too high.

Recently, we have developed two convenient methods for the preparation of tetraalkynyltin compounds (RC≡C)₄Sn, by a reaction of 1-alkynes either with SnCl₄ in the presence of anhydrous ZnCl₂ and Et₂NH,25,26 or with tin tetra(N,N-diethylcarbamate) in the presence of anhydrous ZnCl₂.27 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 compounds32–36 and with aly halides under Stille-type conditions.37

Tetraalkynyltin compounds, as well as other C(sp³)-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≡C)₄Sn seemed to be good compounds to be used as a source of soft acetylene nucleophiles RC≡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...
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 alcohols by a second molecule of an aldehyde 2 (Scheme 3), by analogy with oxidative addition of alkenes to aldehydes in the presence of InBr$_3^{18}$ or ZnI$_2^{19}$.

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≡C)Sn 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.

When aromatic aldehydes were allowed to react with (Ph–C≡C)Sn 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$_3$N) 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>
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<tr>
<th>Ratio 1a : 2a</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Time, h</th>
<th>Yield of 4ac, %</th>
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$^a$ Yields were determined by GC–MS. Unless otherwise stated, the reaction conditions were as follows: (Ph–C≡C)Sn 1a (0.123 mmol), PhCHO 2c (0.492 mmol), a catalyst (0.05 mmol) and a solvent (0.5 mL) at 60 °C. $^b$ An eight-fold excess of benzaldehyde 2c (0.814 mmol) was used. $^c$ Triethylamine (0.25 mmol) was added.
When the amount of SnCl₄ 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≡C]₂Sn 1a and PhCHO 2c were taken in a 1:4 ratio, PhCHO was fully converted to acetylenic ketone and PhCH₂OH after 1–3 h at 60 °C. Meanwhile, the reaction of [Ph–C≡C]₂Sn 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≡C–C(O)Ph 4ac were achieved (Table 3). The reaction between [Ph–C≡C]₂Sn 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 alcohols. 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 alkylation 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 InBr₃ and Et₃N.39 Finally, the best yields (up to quantitative) of model ketone R–C–C(O)–thienyl-2 were achieved when the reaction was carried out in toluene at 60 °C using ZnCl₂ 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 z,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.

We have to note that under the given conditions the reaction of (Ar–C≡C)₂Sn with either 4-NO₂C₆H₄CHO 2f, thiophene-2-carbaldehyde 2m or 5-nitrothiophene-2-carbaldehyde 2n is

### Table 3: The effects of the reaction conditions on the yields of ketone 4ac in the reaction of (Ph–C≡C)₂ClSn 1a with PhCHO 2c

<table>
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<th>Ratio 1a:2c</th>
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<th>Catalyst</th>
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*Isolated yields are given. Unless otherwise stated, the reaction conditions were as follows: (Ph–C≡C)₂Sn 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). A acetone (36 µL, 0.492 mmol) was added. B 2 mL of DCE were used. C Triethylamine (0.05 mmol) was added.
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 ZnCl2. The crystalline structure of the previously unreported alkenyl 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-economic method for the preparation of α,β-alkynyl ketones starting from aldehydes and easily available tetaalkynyltin by a sequence involving a nucleophilic addition of a tin acetylide to aldehyde following by the Oppenauer-type oxidation of tin propargyl alcolholates 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.1H, 13C, and 119Sn NMR spectra were recorded on a JEOL ECA 400 instrument at operating frequencies 399.78, 100.52 respectively, in CDCl3 (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 HCl solution) and on a Bruker Vertex 70 instrument in ATR (attenuated total reflection) mode. Mass spectra (El, 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, KMnO4–H2SO4 solution or UV-light. The use of a sorbent modified with 3-aminopropyltriethoxysilane (1.14 mmol g−1 of NH2 groups) resulted in a much better separation of the desired acetylenic ketones and interfering by-products on a column.

The starting tetaalkynyltin 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 portion-wise to a stirred suspension of 4-HOC6H4CHO (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 PhCl(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 NaHCO3 and water. For purification benzoate 2l was reprepitated from acetone with water. Yield 12.0 g (65%, purity by GCMS 100%). White crystalline solid, m.p. 89.5–90.2 °C. 1H NMR (400 MHz, CDCl3) δ 7.41 (d, J = 8.7 Hz, 2H, Ar), 7.51–7.55 (m, 2H, Ar), 7.64–7.68 (m, 1H, Ar), 7.97 (d, J = 8.7 Hz, 2H, Ar), 8.19–8.21 (m, 2H, Ar). 13C NMR (100 MHz, CDCl3) δ 122.5, 128.7, 128.9, 130.2, 131.3, 134.0, 155.6, 164.5, 191.0. IR (KBr, cm−1) νmax 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, El, 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 portion-wise to a stirred suspension of 4-HOC6H4CHO (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 Bu4NBr (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 NaHCO3 and water. For purification product 2j was reprepitated 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. 1H NMR (400 MHz, CDCl3) δ 3.17 (s, 9H, Me), 7.40 (d, J = 8.7 Hz, 2H, Ar), 7.55 (d, J = 8.3 Hz, 2H, Ar), 7.96 (d, J = 8.7 Hz, 2H, Ar), 8.13 (d, J = 8.7 Hz, 2H, Ar), 10.02 (s, 1H, CHO). 13C NMR (100 MHz, CDCl3) δ 131.1, 35.3, 122.6, 125.7, 126.1, 130.2, 131.0, 132.6, 134.0, 155.9, 158.0, 164.5, 190.9. IR (KBr, cm−1) νmax 2966.4, 2904.7, 2740.7 (C–H, C–C), 1731.0, 1705.0, 1606.6, 1594.1. MS (m/z, El, 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 teta[phenylethyl]tinyltin 1a with aliphatic aldehydes 2a,b (the model reaction, Scheme 2 and Table 1)

A 2 mL scalable Wheaton vial was charged with 0.04 mmol of Lewis acid (ZnCl2, SnCl4 or InCl3), 0.102 mmol of (PhC≡C)2Sn 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 NH4Cl).

Preparative procedure for the synthesis of 1.3-diphenylprop-2-yn-1-one (4ac)

A 2 mL sealed Wheaton vial was charged with 10.4 mg (0.076 mmol) of anhydrous ZnCl2, PhMe (0.8 mL), 100 mg (0.191 mmol) tetra(phenylethyl)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 HCCl3 and purified using column chromatography (eluent – PhMe). The yield was 154.6 mg (98%), light yellow oil, m.p. 110.5–111.5 °C.

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

Acetylene ketone 4-NO2C6H4C(O)-C=C-Ph 4af was prepared according to a similar procedure to that for 4ac, using 6.7 mg (0.05 mmol) of anhydrous ZnCl2, toluene (0.5 mL), 64.4 mg (0.123 mmol) of (PhC=CH)2Sn 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).

1H NMR (400 MHz, CDCl3) δ 7.44–7.48 (m, 2H, Ar), 7.52–7.56 (m, 1H, Ar), 7.71 (d, J = 8.7 Hz, 2H, Ar), 3.85–4.10 (m, 4H, Ar); 13C NMR (100 MHz, CDCl3) δ 86.6, 95.4, 119.4, 123.9, 128.9, 130.4, 131.5, 133.3, 141.1, 150.9, 179.5. IR (KBr, cm–1) νmax 3113.0, 3048.4, 2193.9 (C=C), 1646.1 (C=O), 1593.1 (NO2 st as), 1516.0, 1343.4, 1321.2 (NO2 st sy). MS (m/z, EI, 70 eV) (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)

Acetylene ketone 4-MeOC6H4C(O)-C=C-Ph 4ag was prepared according to a similar procedure to that for 4ac, using 10.4 mg (0.076 mmol) of anhydrous ZnCl2, PhMe (0.8 mL), 100 mg (0.191 mmol) of (PhC=CH)2Sn 1a and 182 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).

1H NMR (400 MHz, CDCl3) δ 3.90 (s, 3H, OMe), 6.99 (d, J = 8.7 Hz, 2H, Ar), 7.39–7.49 (m, 3H, Ar), 7.67 (d, J = 8.7 Hz, 2H, Ar), 8.19 (d, J = 8.7 Hz, 2H, Ar); 13C NMR (100 MHz, CDCl3) δ 86.6, 86.9, 92.3, 113.9, 120.4, 128.7, 130.4, 130.6. 132.0, 130.6, 164.5, 176.7. IR (KBr, cm–1) νmax 3117.1, 2957.7, 2847.8, 2195.9 (C=C), 1629.9 (C=O), 1599.9, 1594.1, 1570.0. MS (m/z, EI, 70 eV) (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)

Acetylene ketone 2,3-(MeO)2C6H3C(O)-C=C-Ph 4ah was prepared according to a similar procedure to that for 4ac, using 6.7 mg (0.05 mmol) of anhydrous ZnCl2, PhMe (0.5 mL), 64.4 mg (0.123 mmol) of (PhC=CH)2Sn 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–H2O).

1H NMR (400 MHz, CDCl3) δ 7.47–7.53 (m, 3H, Ar), 7.70 (d, J = 7.8 Hz, 2H, Ar), 7.79 (d, J = 8.2 Hz, 2H, Ar), 8.32 (d, J = 8.2 Hz, 2H, Ar); 13C NMR (100 MHz, CDCl3) δ 86.6, 94.5, 119.7, 123.6 (q, 3JCF = 237.1 Hz), 125.7 (q, 3JCF = 3.8 Hz), 128.8, 129.8, 131.2, 133.2, 135.2 (q, 3JCF = 23.6 Hz), 139.5, 176.7. IR (KBr, cm–1) νmax 3059.9, 2202.6 (C=C), 1643.3 (C=O). MS (m/z, EI, 70 eV) (rel (%)): 274 (M+, 43), 246 (40), 129 (100), 98 (13), 75 (19).

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

Acetylene ketone 4-BrC6H4C=C-C(O)C6H4Br-4 4be was prepared according to a similar procedure to that for 4ac, using 6.7 mg (0.05 mmol) of anhydrous ZnCl2, toluene (0.5 mL), 71.3 mg (0.123 mmol) of (MeC6H4C≡CH)2Sn 1b and 182 mg (0.984 mmol) of 4-bromomethylacetylene 2e. The yield was 125.1 mg (85%), light yellow solid, m.p. 110.5–111.5 °C (from EtOH).

1H NMR (400 MHz, CDCl3) δ 2.41 (s, 3H, CH3), 2.73 (d, J = 7.8 Hz, 2H, Ar), 7.58 (d, J = 7.8 Hz, 2H, Ar), 7.65 (d, J = 8.7 Hz, 2H, Ar), 8.07 (d, J = 8.7 Hz, 2H, Ar); 13C NMR (100 MHz, CDCl3) 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) νmax 3085.0, 3030.0, 2914.3, 2855.5, 2194.9 (C=C), 1636.5 (C=O), 1603.7, 1583.5, 1569.0. MS (m/z, EI, 70 eV) (rel (%)): 300 (M+, 88 Br), 27, 398 (M+, 78 Br), 26, 272 (28, Br), 270 (28, Br), 190 (10), 189 (19), 143 (100), 115 (16), 95 (18), 89 (16), 75 (15), 63 (11), 50 (9).
2.41 (s, 3H, CH$_3$), 7.23 (d, 3H, Ar), 7.38 (d, 3H, Ar), 8.14 (d, $\delta$ = 8.7 Hz, 2H, Ar), 8.18 (d, $\delta$ = 8.7 Hz, 2H, Ar); $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 86.8, 93.4, 120.1, 121.1, 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$^{-1}$) $\nu_{max}$ 3063.3, 2959.2, 2918.6, 2897.4, 2919.4 (C=C), 1660.5 (C=C), 1628.1 (C=C), 1599.2, 1556.7, 1506.6. MS ($m/z$, El, 70 eV) ($I_{rel}$ (%)): 316([M]+), 28, 301, 143 (26), 115 (7).

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

Acetylenic ketone Ph-C≡C-C(=O)C$_6$H$_4$C≡C-Ph 4aI was prepared according to a similar procedure to that for 4ac, using 6.7 mg (0.05 mmol) of anhydrous ZnCl$_2$, toluene (0.5 mL), 64.4 mg (0.123 mmol) of (PhC≡C)Sn 1a and 203 mg (0.984 mmol) of 4-(phenylethynyl)benzaldehyde 2I. 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$_3$) $\delta$ 7.35–7.39 (m, 3H, Ar), 7.41–7.51 (m, 3H, Ar), 7.55–7.57 (m, 2H, Ar), 7.65 (d, $\delta$ = 8.7 Hz, 2H, Ar), 7.69 (d, $\delta$ = 8.7 Hz, 2H, Ar), 8.20 (d, $\delta$ = 8.7 Hz, 2H, Ar); $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 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. IR (KBr, cm$^{-1}$) $\nu_{max}$ 3080.7, 3055.6, 3034.3, 2201.1 (C=C), 2164.4 (C=C), 1628.1 (C=O), 1603.0, 1556.7. MS ($m/z$, El, 70 eV) ($I_{rel}$ (%)): 306([M]+), 95, 278 (100), 276 (23), 176 (15), 139 (31), 129 (80), 101 (11), 75 (15).

1-Phenyl-2-(phenylethynyl)prop-2-yn-1-one (4am)

Acetylenic ketone Ph–C≡C-C(=O)C$_6$H$_4$S–2 4am was prepared according to a similar procedure to that for 4ac, using 10.4 mg (0.067 mmol) of anhydrous ZnCl$_2$, toluene (0.8 mL), 100 mg (0.191 mmol) of (PhC≡C)Sn 1a and 143 $\mu$L (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$_3$) $\delta$ 7.10–7.12 (m, 1H, Ar), 7.32–7.43 (m, 3H, Ar), 7.59 (d, $\delta$ = 8.2 Hz, 2H, Ar), 7.65 (d, $\delta$ = 4.6 Hz, 1H, Ar), 7.94 (d, $\delta$ = 3.7 Hz, 1H, Ar); $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 86.4, 91.7, 119.9, 128.3, 128.7, 130.8, 133.0, 135.0, 135.2, 144.9, 167.9. IR (KBr, cm$^{-1}$) $\nu_{max}$ 3074.9, 2206.8 (C=C), 1612.7 (C=O), 1595.3, 1579.9, 1516.2. MS ($m/z$, El, 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).

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

Acetylenic ketone 5-NO$_2$C$_6$H$_4$SC(O)–C≡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≡C)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 HCl2C, with freezing).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43–7.56 (m, 3H, Ar), 7.68 (d, $\delta$ = 8.2 Hz, 2H, Ar), 7.86 (d, $\delta$ = 4.1 Hz, 1H, Ar), 7.93 (d, $\delta$ = 4.1 Hz, 1H, Ar); $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 85.6, 95.2, 118.9, 128.2, 130.1, 131.9, 133.3, 148.0, 156.8, 161.9. IR (KBr, cm$^{-1}$) $\nu_{max}$ 3107.7, 3092.3, 3065.3, 2193.3 (C=C), 1618.5, 1610.8, 1593.4, 1535.5, 1512.4. MS ($m/z$, El, 70 eV) ($I_{rel}$ (%)): 257 (M$^+$, 51), 229 (20), 199 (10), 139 (32), 29 (100), 101 (14), 75 (22), 51 (11).

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

Acetylenic ketone 4ClC$_6$H$_4$C≡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
of PhCHO

105.5–106.5

4aj

Single crystals of ketone 

CH₂CH₂CH₂CH₂–C≡C–(O)Ph 4dc

were prepared according to a similar procedure to that for 4ac, using 10.4 mg (0.076 mmol) of anhydrous ZnCl₂, toluene (0.8 mL), 84.7 mg (0.191 mmol) of (PhC≡C)₂Sn 1a and 155 mg (1.53 mmol) of PhCHO 2c. The yield was 38.9 mg (27%), light yellow oil. "H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 8.2 Hz, 2H, Ar), 7.58–7.61 (m, 1H, Ar), 8.14 (d, J = 3.9 Hz, 2H, Ar); 13C NMR (100 MHz, CDCl₃) δ 135.2, 139.2, 140.0, 146.4, 150.7, 159.7, 159.9, 174.4, 191.0 (m/z, EI, 70 eV) (rel (%)): 242 [M⁺] Cl, 239, 212 (100), 210 (100), 198 (31), 186 (31), 178 (51), 166 (51), 154 (29), 138 (27), 126 (27), 92 (23), 80 (23). IR (liquid film, cm⁻¹) νmax 3063.3, 2959.1, 2932.1, 2874.3, 2237.7, 2201.0, 1764.4, 1597.2, 1579.9. MS (EI, 70 eV) (rel (%)): 166 (M⁺, 7), 153 (13), 157 (43), 144 (100), 129 (27), 115 (57), 109 (27), 105 (95), 79 (40), 77 (33), 66 (32), 53 (26), 51 (39). X-ray studies of 4-(3-phenylprop-2-ynyl)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, Atlas2s diffractometer at 100 K. Using Olex2, the structure was solved with the ShelXT refm structure solution program using Intrinsic Phasing and refined by the least squares technique using the ShelXL refinement package. Crystals of compound 4aj are triclinic, C₆₂H₈₂O₈ (M = 382.43), space group P̅1 (No 2), a = 6.7125(3) Å, b = 9.9947(3) Å, c = 15.6535(3) Å, α = 88.19(2)°, β = 87.315(2)°, γ = 103.50(6)°, V = 1035.50(6) Å³, Z = 2, T = 100.00(10) K, μ(CuKα) = 0.630 mm⁻¹, Dcalc = 1.227 g cm⁻³, 19353 reflections were collected (8964 ≤ 2θ ≤ 147.682°), of which 4133 were unique (Rint = 0.0373, Rsigma = 0.0216). The final probability factors were: R1 = 0.0374 (I > 2σ(I)), wR2 = 0.1038 (all reflections). The full crystallographic data have been deposited at the Cambridge Crystallographic Data Center as deposit CCDC 1543712.†

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Notes and references

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