NJC

PAPER

Check for updates

Cite this: New J. Chem., 2017, 41, 8297

Received 25th April 2017, Accepted 30th June 2017

DOI: 10.1039/c7nj01376k

rsc.li/njc

Oxidative coupling of tetraalkynyltin with aldehydes leading to alkynyl ketones[†]

Andrey S. Levashov, ^(b)*^a Nicolai A. Aksenov, ^(b)*^c Inna V. Aksenova ^(b)*^b and Valeriy V. Konshin ^(b)*^a

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 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 InCl₃²⁰ 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*-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 $Cl_3SnC \equiv CR'$, which was generated in situ from 1-alkynes and the SnCl₄-Bu₃N 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



Scheme 1 Some applications of alkynyl ketones.

 $C(sp^2)$ -Sn and $C(sp^3)$ -Sn reagents; however, the *E*-factor still remains too high.

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



View Article Online

^a Department of Organic Chemistry & Technologies, Kuban State University, 149 Stavropolskaya str., 350040 Krasnodar, Russian Federation.

E-mail: aslevashov@mail.ru

^b Department of Chemistry, North Caucasus Federal University, 1a Pushkin str., 355009 Stavropol, Russian Federation

^c Peoples Friendship University Russia, 6 Miklukho Maklaya St, Moscow 117198, Russia

[†] Electronic supplementary information (ESI) available: Spectral data. CCDC 1543712. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7nj01376k

14.5

3.2

1.8

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 $(Ph-C \equiv C)_4$ 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 1,2dichloroethane and an aliphatic aldehyde was used in excess,



Scheme 2 The reaction of tetraalkynyltin with aliphatic aldehydes



* = alkynyl or alkoxy

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

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

Table 1 The effects of solvents, catalysts and reaction time on the ratio of

products **3aa**: **4aa** in the reaction of $(Ph-C \equiv C)_4$ Sn **1a** with hexanal **2a**^a

^{*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 eightfold excess of hexanal **2a** (0.814 mmol) was used.

SnCL

DCE

1:8

5

2

5

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 $(Ph-C \equiv C)_4 Sn$ **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 (Et₃N) 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 SnCl₄ and ZnCl₂.

They were chosen as Lewis acids due to the successful application in similar reactions with aliphatic aldehydes. It was found that the use of SnCl₄ provides a faster reaction, but also causes some resinification and hence is less efficient.

Table 2The effects of solvents, catalysts, reaction time and the ratio ofthe starting reagents on the yield of ketone Ph-C \equiv C-C(O)Ph **4ac** in thereaction 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	1	87
		4	3	99
1:4	DCE	ZnCl ₂	1	77
		2	3	100
1:4	DCE	ZnCl ₂	1	80
		$Et_3N^{\tilde{c}}$		(10% 3ac)
$1:8^{b}$	DCE	SnCl ₄	1	13
		4	3	11
			5	69
1:4	PhMe	SnCL	3	98
1:4	PhMe	ZnCl ₂	1	100
$1:8^{b}$	PhMe	SnCl	-	49
1.0		~	3	86

^{*a*} Yields were determined by GC-MS. Unless otherwise stated, the reaction conditions were as follows: $(Ph-C \equiv C)_4$ Sn 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.

This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence. Open Access Article. Published on 30 June 2017. Downloaded on 8/23/2025 6:05:21 AM.

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 $(Ph-C \equiv C)_4$ Sn 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 $(Ph-C \equiv C)_4$ Sn 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 $(Ph-C \equiv C)_4$ Sn 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 Oppenauertype 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 InBr₃ and Et₃N.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 ZnCl₂ as a Lewis acid catalyst (Table 3).

All the reactions were conducted at 60 $^{\circ}$ 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.

We have to note that under the given conditions the reaction of $(Ar-C \equiv C)_4$ Sn with either 4-NO₂C₆H₄CHO 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

Table 3The effects of the reaction conditions on the yields of ketone4acin the reaction of $(Ph-C \equiv C)_4$ Sn 1a with PhCHO 2c ^a					
Ratio 1a:2c	Solvent	Catalyst	$T,^{\circ}C$	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	ZnCla	60	2	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	60	5	56
		Et_3N^d			
1:8	DCE	ZnCl ₂	60	5	83
		Et_3N^d			
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: $(Ph-C \equiv C)_4 Sn$ **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.

Tetraalkynyltin 1	Aldehyde 2	Product		Yield, ^a %
1a	2c	Ph-C=C-C(O)Ph	4ac	98
1a	2d	$4\text{-}CF_3C_6H_4C(O)\text{-}C\equiv C\text{-}Ph$	4ad	97
1b	2e	$4-MeC_6H_4-C \equiv C-$	4be	85
		$C(O)C_6H_4Br-4$		
1a	2f	$4-NO_2C_6H_4C(O)-C\equiv C-Ph$	4af	50^b
1a	2g	4 -MeOC ₆ H ₄ C(O)-C \equiv C-Ph	4ag	55
1a	2h	$2,3-(MeO)_2C_6H_3C(O)-C \equiv C-$	4ah	66
		Ph		
1a	2i	$4\text{-BzOC}_6\text{H}_4\text{C}(\text{O})\text{-C}\equiv\text{C}\text{-Ph}$	4ai	83
1a	2j	4-(t-Bu C ₆ H ₄ CO ₂)C ₆ H ₄ C(O)-	4aj	79
		C≡C-Ph		
1b	2k	$4-MeC_6H_4C\equiv C-$	4bk	80
		$C(O)C_6H_4C \equiv C-SiMe_3$		
1b	2 c	$4-MeC_6H_4-C \equiv C-C(O)Ph$	4bc	57
1a	21	$Ph-C \equiv C-C(O)C_6H_4C \equiv CPh$	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-	4an	47^b
		Ph		
1b	20	$5-NO_2C_4H_2OC(O)-C\equiv C-$	4bo	0^b
		C ₆ H ₄ Me-4		
1c	2c	$4\text{-ClC}_6H_4C\equiv C\text{-}C(O)Ph$	4cc	48
1d	2 c	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 ZnCl₂. 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 atomeconomical 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. 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 $400-4200 \text{ cm}^{-1}$ (KBr or HCCl₃ 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, KMnO₄-H₂SO₄ 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 NH₂ 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 21 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-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 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 NaHCO₃ 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. ¹H 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, ${}^{3}I$ = 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}) 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-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 reprecipitated from acetone with water. Yield was 5.0 g (87%, purity by GCMS - 98%). The further recrystallization from EtOH gave pure 2i (purity by GCMS - 100%) as white crystalline solid, m.p. 88.3–88.8 °C. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100 MHz, CDCl₃) 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) $\nu_{\rm max}$ 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 (ZnCl₂, SnCl₄ or InCl₃), 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-2yn-1-one (4ac)

A 2 mL sealable Wheaton vial was charged with 10.4 mg (0.076 mmol) of anhydrous ZnCl₂, PhMe (0.8 mL), 100 mg (0.191 mmol) tetra(phenylethynyl)tin **1a** and 155 μ L (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 of ketone Ph–C \equiv C–C(O)Ph **4ac** was 154.6 mg (98%), light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.39–7.53 (m, 5H, Ar), 7.60–7.69 (m, 3H, Ar), 8.22 (d, *J* = 7.3 Hz, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃) 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 \equiv 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-CF₃C₆H₄C(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 ZnCl₂, 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–H₂O). ¹H NMR (400 MHz, CDCl₃) δ 7.42–7.53 (m, 3H, Ar), 7.70 (d, ³*J* = 8.7 Hz, 2H, Ar), 7.79 (d, ³*J* = 8.2 Hz, 2H, Ar), 8.32 (d, ³*J* = 8.2 Hz, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃) δ 86.6, 94.5, 119.7, 123.6 (q, ¹*J*_{C-F} = 273.1 Hz), 125.7 (q, ³*J*_{C-F} = 3.8 Hz), 128.8, 129.8, 131.2, 133.2, 135.2 (q, ²*J*_{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-MeC₆H₄-C \equiv 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 \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). ¹H NMR (400 MHz, CDCl₃) δ 2.41 (s, 3H, CH₃), 7.23 (d, ³*J* = 7.8 Hz, 2H, Ar), 7.58 (d, ³*J* = 7.8 Hz, 2H, Ar), 7.65 (d, ³*J* = 8.7 Hz, 2H, Ar) 8.07 (d, ³*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) ν_{max} 3085.0, 3030.0, 2914.3, 2855.5, 2194.9 (C \equiv C), 1636.5 (C \longrightarrow O), 1603.7, 1583.5, 1569.0. MS (*m*/*z*, EI, 70 eV) (*I*_{rel} (%)): 300([M⁺, 8¹Br], 27), 398([M⁺, ⁷⁹Br], 26), 272 (28, ⁸¹Br), 270 (28, ⁷⁹Br), 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-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=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). ¹H NMR (400 MHz, CDCl₃) 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); 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, 175.9. IR (KBr, cm⁻¹) ν_{max} 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) (*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-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), 100.0 mg (0.191 mmol) of (PhC = 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). ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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=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)₂C₆H₃C(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 ZnCl₂, 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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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)OC₆H₄C(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 ZnCl₂, 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). ¹H NMR (400 MHz, CDCl₃) 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). $^{13}\mathrm{C}$ NMR (100 MHz, CDCl₃) 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 $^{-1}$) ν_{max} 3063.8, 2197.8 (C=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*-BuC₆H₄CO₂)C₆H₄C(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 ZnCl₂, toluene (0.5 mL), 64.4 mg (0.123 mmol) of (PhC \equiv C)₄Sn **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 HCCl₃-hexane). ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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) ν_{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-MeC₆H₄C \equiv C–C(O)C₆H₄C \equiv C–SiMe₃ **4bk** 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 \equiv C)₄Sn **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). ¹H NMR (400 MHz, CDCl₃) δ 0.28 (s, 9H, Me₃Si), 2.41 (s, 3H, CH₃), 7.23 (d, ³*J* = 8.2 Hz, 2H, Ar), 7.57–7.59 (m, 4H, Ar), 8.14 (d, ³*J* = 8.2 Hz, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃) 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) ν_{max} 3063.3, 2959.2, 2918.6, 2897.4, 2191.4 (C \equiv C), 2160.5 (C \equiv C), 1628.1 (C \equiv 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-MeC₆H₄-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 ZnCl₂, toluene (0.8 mL), 110.6 mg (0.191 mmol) of (MeC₆H₄C \equiv C)₄Sn **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). ¹H NMR (400 MHz, CDCl₃) δ 2.40 (s, 3H, Me), 7.22 (d, ³*J* = 7.8 Hz, 2H, Ar), 7.49-7.52 (m, 2H, Ar), 7.57-7.63 (m, 3H, Ar), 8.21 (d, ³*J* = 8.2 Hz, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃) 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) ν_{max} 3059.9, 3031.0, 2187.2 (C \equiv C), 1626.9 (C \equiv 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=C-C(O)C₆H₄C=C-Ph **4al** 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=C)₄Sn **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). ¹H NMR (400 MHz, CDCl₃) 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), 100 MHz, CDCl₃) 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) ν_{max} 3080.7, 3055.6, 3034.4, 2201.1 (C=C), 2164.4 (C=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=C-C(O)C₄H₃S-2 **4am** was prepared according to a similar procedure to that for **4ac**, using 10.4 mg (0.076 mmol) of anhydrous ZnCl₂, toluene (0.8 mL), 100 mg (0.191 mmol) of (PhC=C)₄Sn **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). ¹H NMR (400 MHz, CDCl₃) δ 7.10–7.12 (m, 1H, Ar), 7.32–7.43 (m, 3H, Ar), 7.59 (d, ³*J* = 8.2 Hz, 2H, Ar), 7.65 (d, ³*J* = 4.6 Hz, 1H, Ar), 7.94 (d, ³*J* = 3.7 Hz, 1H, Ar); ¹³C NMR (100 MHz, CDCl₃) 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) ν_{max} 3074.9, 2206.8 (C=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-NO₂C₄H₂SC(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 ZnCl₂, toluene (0.8 mL), 100 mg (0.191 mmol) of (PhC=C)₄Sn **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 HCCl₃, with freezing). ¹H NMR (400 MHz, CDCl₃) δ 7.43–7.56 (m, 3H, Ar), 7.68 (d, ³*J* = 8.2 Hz, 2H, Ar), 7.86 (d, ³*J* = 4.1 Hz, 1H, Ar), 7.93 (d, ³*J* = 4,1 Hz, 1H, Ar); ¹³C NMR (100 MHz, CDCl₃) 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) ν_{max} 3107.7, 3092.3, 3065.3, 2193.3 (C=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 $4\text{-ClC}_6\text{H}_4\text{C}\equiv\text{C}\text{-C}(\text{O})\text{Ph}$ **4cc** 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), 81.3 mg

(0.123 mmol) of (4-ClC₆H₄C \equiv C)₄Sn **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). ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, ³*J* = 8.7 Hz, 2H, Ar), 7.49–7.53 (m, 2H, Ar), 7.59–7.65 (m, 3H, Ar), 8.19 (d, ³*J* = 8.2 Hz, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃) 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) ν_{max} 3082.6, 3053.7, 2922.5, 2203.0 (C \equiv C), 2164.4 (C \equiv C), 1632.0 (C \equiv O), 1616.5, 1599.2, 1589.5, 1579.9. MS (*m*/*z*, EI, 70 eV) (*I*_{rel} (%)): 242[[M⁺] ³⁷Cl, 24), 240 ([M⁺] ³⁵Cl, 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 $CH_3CH_2CH_2CH_2-C \equiv C-C(O)Ph$ **4dc** was prepared according to a similar procedure to that for **4ac**, using 10.4 mg (0.076 mmol) of anhydrous ZnCl₂, toluene (0.8 mL), 84.7 mg (0.191 mmol) of $(PhC \equiv C)_4$ Sn **1a** and 155 µL (1.53 mmol) of PhCHO **2c**. The yield was 38.9 mg (27%), light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 0.97 (t, J = 7.3 Hz, 3H, CH₃), 1.46–1.56 (m, 2H, CH₂), 1.63–1.71 (m, 2H, CH₂), 2.51 (t, J = 7.3 Hz, 2H, CH₂), 7.46–7.49 (m, 2H, Ar), 7.58–7.61 (m, 1H, Ar), 8.14 (d, ³J = 8.2 Hz, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃) 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) ν_{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 ShelXT⁴² structure solution program using Intrinsic Phasing and refined by the least squares technique using the ShelXL⁴³ refinement package. Crystals of compound 4aj are triclinic, $C_{26}H_{22}O_3$ (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, $\alpha = 88.139(2)^{\circ}$, $\beta = 87.315(2)^{\circ}$, $\gamma = 80.902(3)^{\circ}$, V =1035.50(6) Å³, Z = 2, T = 100.00(10) K, μ (CuK α) = 0.630 mm⁻¹, $D_{\text{calc}} = 1.227 \text{ g cm}^{-3}$, 19 353 reflections were collected (8.964° \leq $2\theta \leq 147.682^{\circ}$), of which 4133 were unique ($R_{\rm int} = 0.0373$, $R_{\text{sigma}} = 0.0216$). The final probability factors were: $R_1 = 0.0374$ $(I > 2\sigma(I))$, wR₂ = 0.1038 (all reflections). The full crystallographic data have been placed at the Cambridge Crystallographic Data Center as deposit CCDC 1543712.†

Acknowledgements

This publication was financially supported by the Russian Ministry of Education and Science (project no. 4.4892.2017/8.9). N. A. A. and I. V. A. are grateful for financial support from the Russian Ministry of Education and Science (State Assignment to Higher Education Institutions, project no. 4.5547.2017/64 and agreement no. 02.A03.21.0008). This work was performed with the use of equipment of the Research and Educational Centrum "Diagnostics of the structure and properties of nanomaterials".

Notes and references

- D. A. Bulanov, I. A. Novokshonova, V. V. Novokshonov, I. A. Ushakov and I. V. Sterkhova, *Synth. Commun.*, 2017, 47, 335–343.
- 2 R. Harigae, K. Moriyama and H. Togo, *J. Org. Chem.*, 2014, 79, 2049–2058.
- 3 M. Jonušis, L. Šteinys, R. Bukšnaitienė and I. Čikotienė, Synthesis, 2016, A-1.
- 4 M. Yoshida, K. Saito, Y. Fujino and T. Doi, *Tetrahedron*, 2014, **70**, 3452–3458.
- 5 T. Ponpandian, S. Muthusubramanian and S. Rajagopal, *Eur. J. Inorg. Chem.*, 2013, 3974–3977.
- 6 J. Shao, X. Huang, X. Hong, B. Liu and B. Xu, *Synthesis*, 2012, 1798–1808.
- 7 J. Zhou, G. L. Zhang, J. P. Zou and W. Zhang, *Eur. J. Inorg. Chem.*, 2011, 3412–3415.
- 8 C. Pan, B. Huang, W. Hu, X. Feng and J. T. Yu, *J. Org. Chem.*, 2016, **81**, 2087–2093.
- 9 Y.-K. Song, P.-C. Qian, F. Chen, C.-L. Deng and X.-G. Zhang, *Tetrahedron*, 2016, **72**, 7589–7593.
- 10 A. V Vasilyev, S. Walspurger, M. Haouas, J. Sommer, P. Pale and A. P. Rudenko, *Org. Biomol. Chem.*, 2004, 2, 3483–3489.
- 11 A. V. Vasil'ev, S. Walspurger, P. Pale, J. Sommer, M. Haouas and A. P. Rudenko, *Russ. J. Org. Chem.*, 2004, **40**, 1769–1778.
- 12 A. V. Vasilyev, S. Walspurger, P. Pale and J. Sommer, *Tetrahedron Lett.*, 2004, 45, 3379–3381.
- T. E. Glotova, M. Y. Dvorko, A. I. Albanov, O. N. Kazheva,
 G. V. Shilov and O. A. D'yachenko, *Russ. J. Org. Chem.*, 2008,
 44, 1532–1537.
- 14 L. Yin and L. Wang, Tetrahedron Lett., 2016, 57, 5935-5940.
- 15 A. K. Clarke, M. J. James, P. O. Brien, R. J. K. Taylor and W. P. Unsworth, *Angew. Chem.*, *Int. Ed.*, 2016, 55, 13798–13802.
- 16 B. Schmidt, M. Riemer and U. Schilde, *Eur. J. Inorg. Chem.*, 2015, 7602–7611.
- 17 S. Ushijima, S. Dohi, K. Moriyama and H. Togo, *Tetrahedron*, 2012, 68, 1436–1442.
- 18 R. Livingston, L. R. Cox, S. Odermatt and F. Diederich, *Helv. Chim. Acta*, 2002, 85, 3052–3077.
- 19 T.-T. Jong and S.-J. Leu, J. Chem. Soc., Perkin Trans. 1, 1990, 423.
- 20 M. Yasuda, T. Miyai, I. Shibata, A. Baba, R. Nomura and H. Matsuda, *Tetrahedron Lett.*, 1995, **36**, 9497–9500.
- 21 D. A. Evans, D. P. Halstead and B. D. Allison, *Tetrahedron Lett.*, 1999, 40, 4461–4462.
- 22 E. J. Corey and K. A. Cimprich, *J. Am. Chem. Soc.*, 1994, **116**, 3151–3152.
- 23 R. A. Sheldon, Green Chem., 2007, 9, 1273-1283.
- 24 M. Yamaguchi, A. Hayashi and M. Hirama, *Chem. Lett.*, 1992, 2479–2482.

- 25 A. S. Levashov, A. A. Andreev and V. V. Konshin, *Tetrahedron Lett.*, 2015, 56, 1870–1872.
- 26 A. A. Andreev, A. S. Levashov and N. V. Komarov, RU2317993, 2008.
- 27 A. S. Levashov, A. A. Andreev, D. S. Buryi and V. V. Konshin, *Russ. Chem. Bull.*, 2014, **63**, 775–776.
- 28 H. Hartmann and W. Eschenbach, *Naturwissenschaften*, 1959, **46**, 321.
- 29 M. Lahcini, P. M. Castro, M. Kalmi and M. Leskela, Organometallics, 2004, 20, 4547–4549.
- 30 M. A. Brook, B. Ramacher, C. Dallaire, H. K. Gupta, D. Ulbrich and R. Ruffolo, *Inorg. Chim. Acta*, 1996, **250**, 49–57.
- 31 P. Jaumier, B. Jousseaume and M. Lahcini, Angew. Chem., Int. Ed., 1999, 38, 402–404.
- 32 B. Wrackmeyer and G. Kehr, *J. Organomet. Chem.*, 1995, **501**, 87–93.
- 33 B. Wrackmeyer, G. Kehr, A. Sebald and J. Kümmerlen, *Chem. Ber.*, 1992, **125**, 1597–1603.
- 34 B. Wrackmeyer, G. Kehr and B. Roland, *Chem. Ber.*, 1992, 125, 643–650.

- 35 B. Wrackmeyer, G. Kehr and R. Boese, *Angew. Chem.*, 1991, 103, 1374–1376.
- 36 B. Wrackmeyer and G. Kehr, *Polyhedron*, 1991, **10**, 1497–1506.
- 37 A. S. Levashov, D. S. Buryi, O. V. Goncharova, V. V. Konshin,
 V. V. Dotsenko and A. A. Andreev, *New J. Chem.*, 2017, 41, 2910–2918.
- 38 Y. Ogiwara, M. Kubota, K. Kurogi, T. Konakahara and N. Sakai, *Chem. - Eur. J.*, 2015, **21**, 18598–18600.
- 39 J. Yuan, J. Wang, G. Zhang, C. Liu, X. Qi and Y. Lan, *Chem. Commun.*, 2015, **51**, 576–579.
- 40 W. Armarego and C. Chai, *Purification of Laboratory Chemicals*, ElsevierScience, Oxford, 2003, p. 608.
- 41 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, 42, 339–341.
- 42 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Adv., 2015, A71, 3-8.
- 43 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, C71, 3–8.