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Tetraalkynylstannanes in the Stille cross coupling reaction: a new effective approach to arylalkynes†

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The Stille-type cross coupling reaction with tetraalkynylstannanes was studied in detail for the first time. The reaction provides a simple and effective route towards a variety of arylalkynes. The advantages and limitations of the proposed procedure are discussed.

Introduction

For almost forty years after the pioneering research of John K. Stille, the cross coupling reaction named after him of organic electrophiles with organostannanes has been recognized as a powerful tool for the formation of carbon–carbon bonds (see reviews^{1–5}). The organotin compounds useful in the Stille reaction are mild reagents that tolerate a variety of functional groups and are the reagents of choice for delicate cross coupling syntheses of complex functionalized molecules.⁵ The Stille reaction has been thoroughly investigated and many advances have been made to expand both the scope and utility of this process.^{5,6} In contrast to other cross coupling reactions, the Stille reaction has often been found to be effective and relatively undemanding, allowing for harsher conditions, as organostannanes are relatively insensitive to moisture and oxygen.⁵ On the other hand, the use of organostannanes such as Bu₃SnR raises problems with organotin contamination and waste. Both acute and long-term toxicities have been reported for many organotin reagents,^{7,8} and methods designed to limit or avoid the presence of organotin by-products in reaction products have been developed.⁹ In general, the toxicity of alkylstannanes decreases as the size of the alkyl groups increases (Me₃SnX ~ Et₃SnX >> Bu₃SnX >> Octyl₃SnX) and the number of alkyl groups decreases (R₃SnX > R₂SnX₂ > RSnX₃),⁹ R₄Sn may reveal enhanced delayed toxicity due to *in vivo*

transformation into R₃SnX.¹⁰ However, the toxicity strongly depends on the nature of the organic group R.¹⁰ Due to the easy hydrolysis of the C(sp)–Sn bond, it is generally accepted that tetraalkynyltin compounds (RC≡C)₄Sn are far less toxic than other organotin species having C(sp²)–Sn or C(sp³)–Sn bonds.

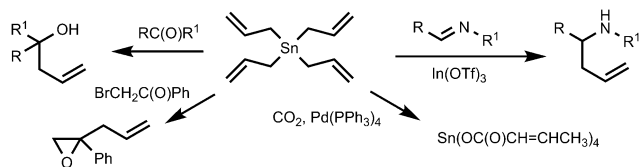
Another feature of tetraalkynylstannanes is their high atom economy. A practical disadvantage of the use of tin mono-functional reagents such as R–Sn(alkyl)₃ (R is aryl, vinyl or alkynyl) is that a reactant of a high molecular weight is used to introduce a hydrocarbon group of a (relatively) low molecular weight, at the same time producing bulky and highly toxic triorganotin waste. Since each of the four alkynyl fragments in (RC≡C)₄Sn is reactive, tetraalkynyltin compounds may be compared with sodium acetylides with respect to low molecular weight and producing only inorganic Sn(IV) waste of low toxicity. It is noteworthy that, generally, the reactions involving organostannanes (*e.g.*, classical Stille coupling or any other organotin-mediated process) are considered to be of a low atom economy, due to the loss of heavy and toxic tin-containing moieties.¹¹ In other words, the *E*-factor¹² (which is defined as the mass ratio of waste to desired product) of the Stille reaction with R–Sn(alkyl)₃ agents is much higher than that expected for coupling reactions with tetraalkynylstannanes, and the latter reactions could be considered as more environmentally benign. The advantages of the use of organotin compounds capable of transferring more than one organyl group are illustrated by the reactions of tetraalkylstannane with electrophilic substrates.¹³ Tetraalkylstannane is a gentle nucleophile for allylation reactions and easily reacts with imines,¹⁴ aldehydes,^{15,16} phenacyl bromide,¹⁷ other ketones¹⁸ or carbon dioxide¹⁹ (Scheme 1). In contrast to allyltrialkylstannyl reagents which transfer only one organyl moiety out of four groups on the tin atom, from two to four allyl residues can be utilized in the case of Sn(CH₂CH=CH₂)₄.

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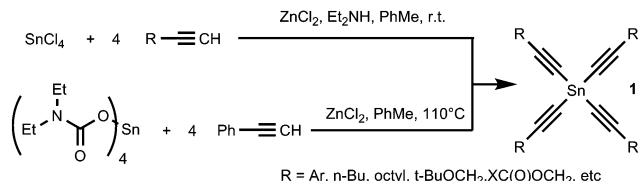
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† Electronic supplementary information (ESI) available: Spectral data. See DOI: 10.1039/c6nj03905g

‡ Deceased.



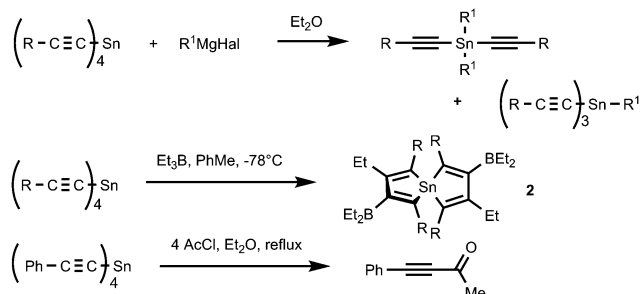
Scheme 1 Typical reactions of tetraalkynylstannane.

Scheme 2 Synthesis of tetraalkynylstannanes **1**.

The alkynyl fragment can be easily introduced onto a tin atom in different ways. Recently we have developed two convenient and effective methods of synthesis of tetraalkynylstannanes **1** (Scheme 2); the first is based on the direct reaction of terminal alkynes with SnCl_4 in the presence of anhydrous ZnCl_2 and diethylamine^{20,21} and the next is based on the reaction of tin tetra(*N,N*-diethylcarbamate) with phenylacetylene.²² Tetraalkynylstannanes **1** are oily or solid compounds that can be easily purified and isolated in good yields after column chromatography on a silanized silica. Also they are stable enough to be stored in a freezer for months.

While much is known about the mono-, di- and trialkynyl tin compounds, less is known about the chemistry of tetraalkynyltin compounds. Only a limited number of reactions are reported encompassing $(\text{RC}\equiv\text{C})_4\text{Sn}$ as reagents (Scheme 3). Thus, the reactions with Grignard reagents were recognized as a convenient method of smooth transmetalation of tetraalkynylstannanes for the preparation of tri- and dialkynyltins.^{23,24} The organoboration of $(\text{RC}\equiv\text{C})_4\text{Sn}$ with trialkylboranes led to the formation of 1,1'-spirobistannoles **2**.^{25–28} Tetra(phenylethynyl)-tin was reported to be an efficient catalyst of ring-opening polymerization of *L*-lactide to poly(*L*-lactide).²⁹ As expected for tetraalkynylstannanes **1**, they may also react with acyl chlorides (4 eq.) to afford alkynyl ketones.³⁰

To the best of our knowledge, Stille-type cross coupling reactions with tetraalkynylstannanes have not been described in the literature prior to the present work. Recently, French researchers reported³¹ the Stille cross coupling reaction of

Scheme 3 The known reactions of tetraalkynylstannanes **1**.

di- or trialkynylstannanes with iodovinyl acids/esters, first introducing a half or a third equivalent of di- or tri-functional organotin compounds. This is the only previous report on Stille cross coupling with multi-functional $\text{C}(\text{sp})$ -Sn organotin compounds. In this paper, we wish to report the first example of a Stille-type cross coupling reaction of aryl halides **3** with tetraalkynyltin compounds **1**.

Results and discussion

We found that tetraalkynylstannanes **1** easily react with a variety of aryl iodides and bromides under Stille conditions according to the following scheme (Scheme 4):

The tetraorganylstannanes **1** and aryl halides **3** used in the reaction are shown in Fig. 1. To prevent side reactions such as hydrolysis of stannanes **1** or oxidative couplings, the reactions

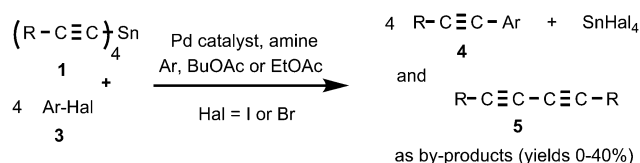
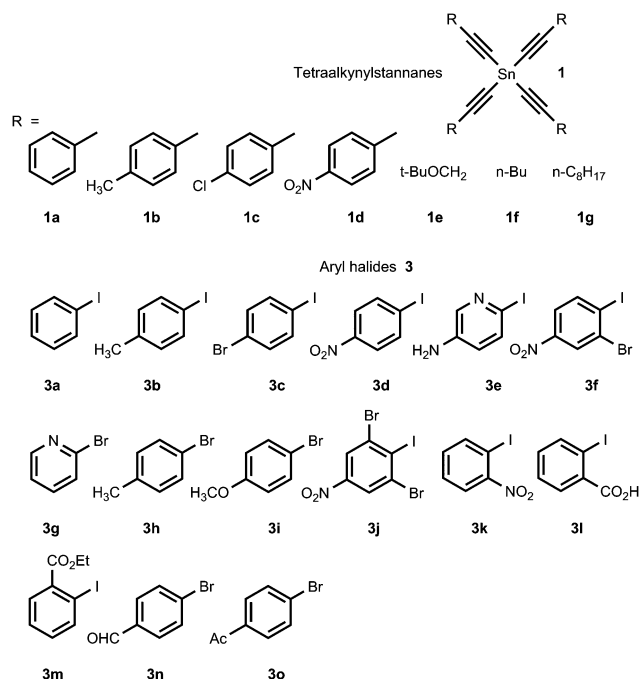
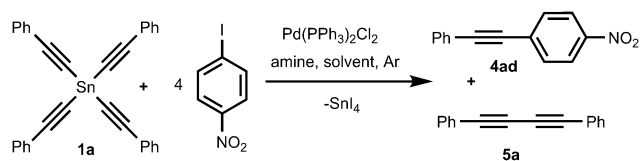
Scheme 4 The reaction of tetraalkynylstannanes **1** with aryl halides **3**.Fig. 1 The scope of stannanes **1** and aryl halides **3** used.Scheme 5 The model reaction of tetra(phenylethynyl)tin **1a** with *p*-nitroiodobenzene **3d**.

Table 1 The effect of solvents and amines on the yields of aryl acetylene **4ad** and the side product, diphenyl diacetylene **5a**^a

| Solvent | <i>T</i> (°C) | Et ₂ NH | | | Et ₃ N | | | DABCO | | |
|-------------------|---------------|--------------------------------------|-------------------------------------|-----------------------|--------------------------------------|-------------------------------------|-----------------------|--------------------------------------|-------------------------------------|-----------------------|
| | | Yield of 4ad ^b (%) | Yield of 5a ^b (%) | Time ^c (h) | Yield of 4ad ^b (%) | Yield of 5a ^b (%) | Time ^c (h) | Yield of 4ad ^b (%) | Yield of 5a ^b (%) | Time ^c (h) |
| Et ₂ O | 35 | 0 | 0 | 5 | 0 | 3 | 5 | 71 | 6 | 5 |
| THF | 80 | — | — | — | 20 | 22 | 5 | 50 | 6 | 1 |
| PhMe | 100 | 55 | 10 | 7 | 27 | 14 | 5 | 87 | 8 | 0.5 |
| MeCN | 85 | 89 | 6 | 5 | 68 | 13 | 5 | 63 | 6.5 | 5 |
| Dioxane | 100 | 84 | 2 | 3 | 44 | 6 | 2 | 78 | 8 | 5 |
| AcOEt | 80 | 91 | 1 | 9 | 87 | 4 | 2 | 87 | 4 | 0.5 |
| AcOBu | 125 | 98 | 2 | 1 | 98 | 2 | 2 | 87 | 5 | 2 |
| AcOBu | 100 | 98 | 2 | 2 | 85 | 2 | 5 | 86 | 5 | 2 |
| Et ₃ N | 80 | — | — | — | 96 | 4 | 2.5 | — | — | — |
| DMF | 100 | — | — | — | 89 | 9 | 2.5 | — | — | — |

^a The reaction conditions were as follows: (PhC≡C)₄Sn **1a** (20 mg, 0.038 mmol), 4-NO₂C₆H₄I **3d** (0.153 mmol), Pd(PPh₃)₂Cl₂ (5.4 mg, 0.0077 mmol; 5 mol% vs. **3d**), amine (0.15 mmol), and solvent (2 mL). ^b Yields were determined by GC-MS. ^c Reaction time when the highest yield was achieved.

should be conducted in an inert atmosphere (argon) wherein water and oxygen are excluded. Diaryl diacetylenes **5** are by-products probably derived from the Pd-mediated Glaser-type coupling reaction occurring in the presence of trace oxygen.

A number of attempts have been made to optimize the coupling reaction conditions. We found that a variety of factors may affect the reaction outcome, such as the nature and quantity of amine additive used, the nature of the Pd catalysts and solvents, the temperature and the reaction time. As a model reaction, we examined the coupling of tetra(phenylethynyl)tin **1a** with *p*-nitroiodobenzene **3d** under different conditions (Scheme 5). First, we examined the effect of different solvents and amine additives on the yields of the target aryl acetylene **4ad**, using Pd(PPh₃)₂Cl₂ as a catalyst. The selected results are summarized in Table 1; the complete set of data is given in ESI,[†] Table S1.

As can be seen, the best results were obtained with BuOAc, EtOAc, DMF and pure Et₃N as solvents in the temperature range of 80–125 °C, while the use of less polar (dioxane, PhMe) and low-boiling (Et₂O) solvents resulted in lower yields of the aryl acetylene **4ad** with increased amounts of the diacetylene by-product **5a**. Though only a few examples^{32–34} have been reported for the amine-promoted Stille reaction, we found that the presence of an amine additive is strongly required for the reaction of tetraalkynylstannanes **1** with aryl halides **3**. In the absence of an amine no reaction occurs, while even trace amounts give coupling products, albeit in low yields. The nature of the amine additive as well as its amount has a dramatic effect on the reaction course, as shown in Table 2. The best results were obtained with the strong bases such as Et₃N, Bu₃N, DABCO, and especially with Et₂NH and Pr₂NH. The application of benzylic amines, piperidine, morpholine and *N*-methylmorpholine lowered significantly the yield of **4ad**, whereas pyridine and ethylene diamine were found to be completely inactive. The full set of data on the amines used is given in ESI,[†] Table S1. The amine concentration was also important and strongly influenced the reaction rate. Thus, the reaction proceeded more slowly in the presence of 1 eq. Et₂NH (the yield of **4ad** reached only 66% after 5 h in EtOAc at 80 °C), and quite rapidly when the amount of Et₂NH was increased.

Table 2 Effects of the different amines and solvents on the yields of **4ad**

| Amine | The yield of aryl acetylene 4ad ^{a,b} (%) | | | | | |
|---|---|--------------------------|------|--------------------------|---------|--------------------------|
| | AcOBu | Time ^c (h) | PhMe | Time ^c (h) | Dioxane | Time ^c (h) |
| Et ₂ NH | 98 | 2 | 55 | 7 | 84 | 3 |
| Et ₃ N | 85 | 5 | 27 | 5 | 44 | 2 |
| Bu ₃ N | 97 | 3 | 31 | 5 | 87 | 3 |
| DABCO | 68 | 2 | 87 | 0.5 | 78 | 0.5 |
| Isophorone diamine | — | — | 54 | 7 | 86 | 9 |
| Morpholine | — | — | — | — | 54 | 1 |
| <i>N</i> -Methyl-morpholine | 12.5 | 1 | — | — | 73 | 2 |
| Pyridine | — | — | — | — | 0 | 3 |
| Piperidine | 62 | 2 | 49 | 5 | 55 | 2 |
| (CH ₂) ₂ (NH ₂) ₂ | 0 | 3 | — | — | — | — |
| PhCH ₂ NH ₂ | 41 | 5 | 43 | 5 | 56 | 5 |
| (PhCH ₂) ₂ NH | — | — | 11 | 3 | 26 | 5 |
| Pr ₂ NH | 99.5 | 1 | — | — | — | — |

^a Yields were determined by GC-MS. ^b The reaction conditions were as follows: **1a** (0.038 mmol), **3d** (0.153 mmol), Pd(PPh₃)₂Cl₂ (5 mol% vs. **3d**), amine (0.153 mmol) and solvent (2 mL) at 100 °C. ^c Reaction time when the highest yield was achieved.

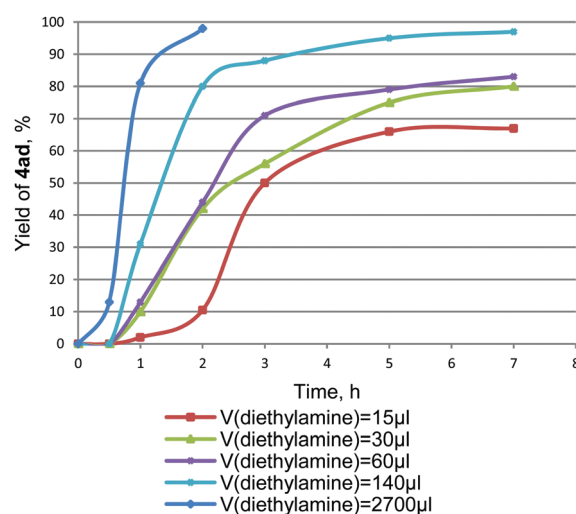


Fig. 2 The kinetics of the reaction **1a** + **3d** → **4ad** with different amounts of Et₂NH. The reaction conditions were as follows: (PhC≡C)₄Sn **1a** (20 mg, 0.038 mmol), 4-NO₂C₆H₄I **3d** (0.153 mmol), Pd(PPh₃)₂Cl₂ as the catalyst (5 mol% with respect to **3d**), AcOEt (2.0 mL), 80 °C.

Table 3 Effects of the amine additive and its amount on the reaction outcome^a

| Amine | Volume (μL) | Aryl iodide 3a:amine ratio | The yields ^b of | | |
|--------------------|-------------|-------------------------------|----------------------------|--------|-----------------------|
| | | | 4ad (%) | 5a (%) | Time ^d (h) |
| Et ₂ NH | 900 | 1:57 | 96.4 | 1.5 | 6 |
| Pr ₂ NH | 21 | 1:1 | 99.5 | 0.5 | 1 |
| Pr ₂ NH | 105 | 1:5 | 99.2 | 0.8 | 1 |
| Pr ₂ NH | 210 | 1:10 | 98.8 | 1.2 | 1 |
| Pr ₂ NH | 840 | 1:40 | 98.9 | 1.1 | 1 |
| Pr ₂ NH | 900 | 1:43 | 99.0 | 1.0 | 1 |
| Pr ₂ NH | 1000 | 1:47 | 98.3 | 1.7 | 1 |
| Bu ₃ N | 36 | 1:1 | 75.7 | 2.0 | 4 |
| Bu ₃ N | 182 | 1:5 | 99.5 | 0.5 | 1 |
| Bu ₃ N | 640 | 1:10 | 99.5 | 0.5 | 1 |
| Bu ₃ N | 900 | 1:25 | 83.7 | 9.2 | 4 |
| TMEDA ^c | 23 | 1:1 | 95.0 | 1.5 | 4 |
| TMEDA | 115 | 1:5 | 97.7 | 2.3 | 1 |
| TMEDA | 229 | 1:10 | 97.2 | 2.8 | 1 |
| TMEDA | 920 | 1:40 | 97.3 | 2.7 | 1 |
| TMEDA | 1000 | 1:43 | 94.0 | 6.0 | 1 |

^a Unless otherwise stated, the conditions were as follows: **1a** (0.038 mmol), **3d** (0.153 mmol), Pd(PPh₃)₂Cl₂ (5 mol% with respect to **3d**), BuOAc, 100 °C, total volume solvent + amine = 1000 μL. ^b Yields were determined by GC-MS. ^c TMEDA = Me₂NCH₂CH₂NMe₂. ^d Reaction time when the maximum yield was achieved.

The use of a large excess of Et₂NH under the same conditions produced tolane **4ad** in almost quantitative yields after 2 h (Fig. 2).

To optimize the conditions, we studied the effect of excessive amounts of different amines on the kinetics of the reaction. It was found that other amines were also as effective as Et₂NH when they were used in high excess. The results are summarized in Table 3.

We have to admit that the mechanistic picture of the Stille reaction is rather complex³⁵ and details cannot be specified with confidence, so the role of an amine and its amount still remains unclear and requires further investigation. We suggest that the reaction proceeds by way of formation of alkynyl-palladium complexes **6** and **7** according to Scheme 6.

The effect of different catalysts was studied to determine the best catalytic system. No reaction occurs without a catalyst: thus,

Table 4 Effects of the different catalysts on the yields of **4ad**^a

| Amine | The yield of 4-NO ₂ C ₆ H ₄ C≡CPh 4ad ^b (%) | | | | | |
|--------------------|--|-----------------------|---------------------------------------|-----------------------|--|-----------------------|
| | PdCl ₂ | Time ^c (h) | Pd(PhCN) ₂ Cl ₂ | Time ^c (h) | Pd(PPh ₃) ₂ Cl ₂ | Time ^c (h) |
| Et ₂ NH | 13 | 7 | 7 | 5 | 98 | 2 |
| Et ₃ N | 72 | 3 | 71 | 2 | 89 | 7 |
| Bu ₃ N | 60 | 7 | 50 | 5 | 97 | 3 |
| DABCO | 57 | 2 | 56 | 1 | 68 | 2 |

^a The reaction conditions were as follows: **1a** (0.038 mmol), **3d** (0.153 mmol), Pd catalyst (5 mol% with respect to **3d**), amine (0.153 mmol), BuOAc, 100 °C. ^b Yields were determined by GC-MS. ^c Reaction time when the maximum yield was achieved.

when (PhC≡C)₄Sn **1a** was added to 4-NO₂C₆H₄I **3d** in pure Et₃N (80 °C, 2 h), no conversion was observed.

However, when a catalytic amount of CuI was added under the same conditions, a trace amount of the coupling product was detected by GC-MS. It is noteworthy that when (PhC≡C)₄Sn **1a** was treated with a 4-fold excess of CuBr₂ (THF, 0.5 h, 25 °C), the oxidative Glaser-type coupling product (Ph-C≡C)₂ **5a** was formed in a good yield. The first success came with the use of Pd catalysts, especially Pd(PPh₃)₂Cl₂. To our surprise, the reaction was completely suppressed by the addition of an excess of phosphine ligand. Thus, no reaction between stannane **1a** and 1-iodo-4-nitrobenzene **3d** occurred in the presence of Pd(PPh₃)₂Cl₂ and PPh₃ (5 mol% and 20 mol% with respect to **3d**, respectively), while Pd(PPh₃)₂Cl₂ with no PPh₃ additive gave the best yields. The results using different Pd catalysts are summarized in Table 4.

Next, using an optimized protocol (BuOAc or DMF, 100 °C, 5 mol% Pd(PPh₃)₂Cl₂, and an excess (4-fold or more with respect to stannane **1**) of an amine additive – Et₂NH, Pr₂NH, DABCO or Bu₃N), we studied the reactivity of different tetraalkynylstannanes **1** and aryl halides **3**. As expected, aryl halides bearing electron-withdrawing groups showed the best reactivity and gave the highest yields of acetylenes **4**. Selected results are summarized in Table 5; the complete set of data is given in ESI,[†] Table S1.

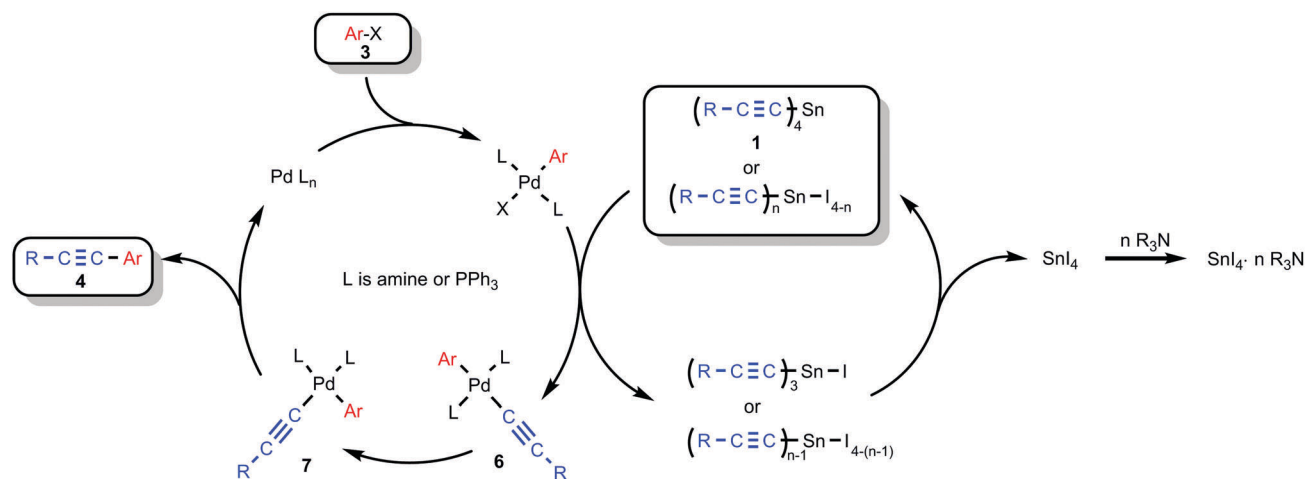
**Scheme 6** A possible mechanism for the reaction of tetraalkynylstannanes **1** with aryl halides **3**.

Table 5 The reactivity of different aryl halides **3** towards (PhC≡C)₄Sn **1a** under the optimized conditions^a

| Aryl Halides 3 | Solvent | Time ^b (h) | Amine | Yield of 4 |
|--|-------------------|-----------------------|--------------------|-------------------|
| Ph-I 3a | DMF | 2.5 | Et ₃ N | 87 |
| 4-MeC ₆ H ₄ I 3b | DMF | 5 | Et ₃ N | 95 |
| 4-MeC ₆ H ₄ I 3b | BuOAc | 9 | Et ₂ NH | 54 |
| 4-NO ₂ C ₆ H ₄ I 3d | DMF | 2.5 | Et ₃ N | 89 |
| 4-NO ₂ C ₆ H ₄ I 3d | BuOAc | 6 | Et ₂ NH | 98 |
| 4-NO ₂ C ₆ H ₄ I 3d | BuOAc | 1 | Pr ₂ NH | 99.5 |
| 4-NO ₂ C ₆ H ₄ I 3d | BuOAc | 3 | Bu ₃ N | 97 |
| 4-MeC ₆ H ₄ Br 3h | BuOAc | 9 | Et ₂ NH | 11 |
| 4-MeOC ₆ H ₄ Br 3i | BuOAc | 5 | Et ₂ NH | 7 |
| 4-MeOC ₆ H ₄ Br 3i | BuOAc | 3 | DABCO | 15 |
| 2-NO ₂ C ₆ H ₄ I 3k | BuOAc | 10 | Et ₂ NH | 83 |
| 2-IC ₆ H ₄ CO ₂ H 3l | BuOAc | 5 | Et ₂ NH | 0 |
| 2-IC ₆ H ₄ CO ₂ H 3l | Et ₃ N | 4 | Et ₃ N | 63 |

^a Yields were determined by GC-MS. Unless otherwise stated, the reaction conditions were as follows: **1a** (0.038 mmol), **3d** (0.153 mmol), Pd(PPh₃)₂Cl₂ (5 mol% with respect to **3d**), amine (0.153 mmol) and solvent (DMF or BuOAc, 2 mL) at 100 °C. ^b Reaction time when the maximum yield was achieved.

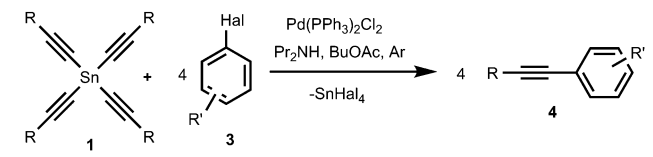
However, when the reaction was carried out using DMF as a solvent instead of BuOAc, the coupling products with aryl halides **3** bearing electron-donating substituents were obtained

Table 6 The reactivity of different tetraalkynylstannanes **1** towards 4-NO₂C₆H₄I **3d** under the optimized conditions^a

| Tetraalkynylstannanes 1 | Time ^b (h) | Amine | Yields of 4 (%) |
|---|-----------------------|--------------------|------------------------|
| (PhC≡C) ₄ Sn 1a | 2 | Et ₂ NH | 98 |
| (<i>t</i> -BuOCH ₂ C≡C) ₄ Sn 1e | 1 | DABCO | 74 |
| (<i>t</i> -BuOCH ₂ C≡C) ₄ Sn 1e | 2 | Et ₂ NH | 33 |
| (<i>n</i> -C ₈ H ₁₈ CH ₂ C≡C) ₄ Sn 1g | 7 | Et ₂ NH | 50 |
| (<i>n</i> -C ₈ H ₁₈ CH ₂ C≡C) ₄ Sn 1g | 5 | DABCO | 52 |

^a Yields were determined by GC-MS. The reaction conditions were as follows: **1** (0.038 mmol), **3d** (0.153 mmol), Pd(PPh₃)₂Cl₂ (5 mol% with respect to **3d**), amine (0.153 mmol), BuOAc (2 mL) at 100 °C. ^b Reaction time when the maximum yield was achieved.

Table 7 The preparative-scale synthesis of acetylenes **4**

|  | | | |
|--|--|---|------------------------|
| Tetraalkynyl stannane 1 | Aryl halide 3 | Product | Yield ^a (%) |
| (PhC≡C) ₄ Sn 1a | Ph-I 3a | PhC≡CPh 4aa | 78 |
| (PhC≡C) ₄ Sn 1a | 4-MeC ₆ H ₄ I 3b | 4-MeC ₆ H ₄ C≡CPh 4ab | 81 |
| (PhC≡C) ₄ Sn 1a | 4-BrC ₆ H ₄ I 3c | 4-BrC ₆ H ₄ C≡CPh 4ac | 80 |
| (PhC≡C) ₄ Sn 1a | 4-NO ₂ C ₆ H ₄ I 3d | 4-NO ₂ C ₆ H ₄ C≡CPh 4ad | 93 |
| (PhC≡C) ₄ Sn 1a | 2-Br-4-NO ₂ C ₆ H ₃ I 3f | 2-Br-4-NO ₂ C ₆ H ₃ C≡CPh 4af | 40 ^b |
| (PhC≡C) ₄ Sn 1a | 2-NO ₂ C ₆ H ₄ I 3k | 2-NO ₂ C ₆ H ₄ C≡CPh 4ak | 88 |
| (PhC≡C) ₄ Sn 1a | 2-EtO ₂ CC ₆ H ₄ I 3m | 2-EtO ₂ CC ₆ H ₄ C≡CPh 4am | 81 |
| (PhC≡C) ₄ Sn 1a | 4-BrC ₆ H ₄ CHO 3n | PhC≡CC ₆ H ₄ CHO 4an | 82 |
| (PhC≡C) ₄ Sn 1a | 4-BrC ₆ H ₄ C(O)Me 3o | PhC≡CC ₆ H ₄ C(O)Me 4ao | 65 |
| (4-MeC ₆ H ₄ C≡C) ₄ Sn 1b | 4-NO ₂ C ₆ H ₄ I 3d | 4-MeC ₆ H ₄ C≡CC ₆ H ₄ NO ₂ 4bd | 91 |
| (4-ClC ₆ H ₄ C≡C) ₄ Sn 1c | 4-NO ₂ C ₆ H ₄ I 3d | 4-ClC ₆ H ₄ C≡CC ₆ H ₄ NO ₂ 4cd | 82 |
| (<i>t</i> -BuOCH ₂ C≡C) ₄ Sn 1e | 4-NO ₂ C ₆ H ₄ I 3d | <i>t</i> -BuOCH ₂ C≡CC ₆ H ₄ NO ₂ 4ed | 49 |
| (<i>n</i> -BuC≡C) ₄ Sn 1f | 4-NO ₂ C ₆ H ₄ I 3d | <i>n</i> -BuC≡CC ₆ H ₄ NO ₂ 4fd | 47 |

^a Isolated yields are given. ^b When 2-Br-4-NO₂C₆H₃I **3f** and (PhC≡C)₄Sn **1a** were added in a 2 : 1 ratio, acetylene **4af** was obtained in 81% yield.

in good yields. The analogs of (PhC≡C)₄Sn **1a**, *i.e.*, tetraalkynylstannanes **1b–g**, reacted with 4-NO₂C₆H₄I **3d** to form the desired acetylenes **4bd–gd**, but the yields were generally lower than those obtained with **1a**. The selected results are presented in Table 6. Finally, the Stille coupling products **4** were obtained in 40–93% yields in preparative-scale experiments using conditions similar to those of the kinetic runs and the optimization protocols. The results are given in Table 7.

Conclusions

In conclusion, we have developed an effective synthetic protocol based on the Stille cross coupling reaction of easily available tetraalkynylstannanes with aryl halides. The reported method provides atom-economical access to aryl acetylenes and diaryl acetylenes (tolanes) which are valuable reagents for further transformations. The scope and limitations of the reaction were studied and the conditions were optimized.

Experimental

Materials and methods

Solvents and starting reagents were thoroughly dried and purified according to common procedures.³⁶ All reactions were carried out and the target compounds were isolated in an argon (99.993%) atmosphere. ¹H, ¹³C, and ¹¹⁹Sn NMR spectra were recorded on a JEOL ECA 400 instrument at operating frequencies of 399.78, 100.52 and 149.08 MHz respectively, in CDCl₃ (Aldrich) with reference to TMS or to the residual signals of a solvent (with SnMe₄ as a standard for ¹¹⁹Sn NMR). Chemical shifts are given in ppm; coupling constants are given in Hz. IR spectra were recorded on an InfraLUM FT-02 instrument in the range of 400–4200 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. The purity of the compounds was checked by TLC (Sorbfil A plates) with Et₂O:hexane (10:1), MeOH:HCCL₃ (1:10) or HCCL₃:Me₂CO (10:1) mixtures as eluents. The spots were visualized with iodine vapors, KMnO₄-H₂SO₄ solution or UV-light. The starting tetraalkynylstannanes **1a-g** were obtained according to the reported methods;^{20,21} the detailed procedures are given in the ESI.†

General procedure for the synthesis of 4-nitrotolane (1-nitro-4-(phenylethynyl)benzene) (4ad**) (the model reaction, Scheme 5, Tables 1, 2 and 4)**

A 5 mL sealable Wheaton vial was charged with 0.00765 mmol of Pd catalyst (PdCl₂, Pd(PPh₃)₂Cl₂, or Pd(PhCN)₂Cl₂) and 0.153 mmol of the amine additive (Et₂NH, Et₃N, Bu₃N, DABCO, morpholine, etc.). Then the vial was flushed with a stream of dry argon, and subsequently a solution of 0.0382 mmol of (PhC≡C)₄Sn **1a** in a dry solvent (1 mL) and a solution of 0.153 mmol of 4-NO₂C₆H₄I in a dry solvent (1 mL) were added through a syringe. The mixture was stirred for the indicated time, and the yield was determined by GC-MS.

Preparative procedure for the synthesis of tolane (diphenyl acetylene) (4aa**) from (PhC≡C)₄Sn (**1a**).** A dry 25 mL, two-necked, round-bottomed flask equipped with an argon gas inlet tube and a magnetic stirrer was flushed with argon and charged with iodobenzene **3a** (212.7 mg, 1.043 mmol), Pd(PPh₃)₂Cl₂ (36.6 mg, 0.052 mmol; 5 mol% vs. **3a**) and (PhC≡C)₄Sn **1a** (150 mg, 0.287 mmol). Then Pr₂NH (1.43 mL, 10.43 mmol) and dry BuOAc (6 mL) were added, the solution was degassed by freezing in liquid nitrogen and pumping under vacuum several times, and then it was flushed with argon. The reaction mixture was stirred at 100 °C for 5 h, then allowed to cool and quenched with EtOH (10 mL). The mixture was treated with 0.5 g of silica modified with 3-aminopropyltriethoxysilane, the solvent was removed on a rotary evaporator and the traces of BuOAc were removed *in vacuo*. The resulting mixture was purified by column chromatography over silica gel (2 g) with pure dry PhMe (50 mL). The eluent was evaporated, the residue was dissolved in *n*-hexane and purified by column chromatography on a mixture of silica gel (6 g) and silica gel modified with 3-aminopropyltriethoxysilane (1 g, 1.14 mmol g⁻¹ of NH₂ groups; the use of the modified silica gel allowed us to remove easily the by-product SnI₄, which appears to be hard to separate when a non-modified silica gel is used as sorbent). Hexane was used as the eluent. Column fractions were analyzed by GC-MS. The eluent was evaporated to give 152.3 mg of tolane **4aa** as a colorless crystalline solid (78%, purity by GCMS – 95.3%).

¹H NMR (400 MHz, CDCl₃) δ 7.33–7.73 (m, 6H, Ph), 7.52–7.54 (m, 4H, Ph); ¹³C NMR (100 MHz, CDCl₃) δ 89.4, 123.3, 128.2, 128.3, 131.6. IR (KBr, cm⁻¹) ν_{max} 3063, 2928 (C–H, C–C), 1599 (C=C). MS (*m/z*, EI, 70 eV) 178 ([M]⁺, 100), 152 ([M – C₂H₂]⁺, 17.6), 77 ([Ph]⁺, 3.3).

4-Methyltolane (1-methyl-4-(phenylethynyl)benzene) (4ab**).**

A dry 25 mL, two-necked, round-bottomed flask equipped with an argon gas inlet tube and a magnetic stirrer was flushed with argon and charged with 4-iodotoluene (**3b**) (227.4 mg, 1.043 mmol),

Pd(PPh₃)₂Cl₂ (36.6 mg, 0.052 mmol; 5 mol% vs. **3b**) and (PhC≡C)₄Sn **1a** (150 mg, 0.287 mmol). Then Pr₂NH (1.43 mL, 10.43 mmol) and dry BuOAc (6 mL) were added, the solution was degassed by freezing in liquid nitrogen and pumping under vacuum several times, and then it was flushed with argon. The reaction mixture was stirred at 100 °C for 5 h, then allowed to cool and quenched with EtOH (10 mL). The mixture was treated with 0.5 g of silica modified with 3-aminopropyltriethoxysilane, the solvent was removed on a rotary evaporator and the traces of BuOAc were removed *in vacuo*. The resulting mixture was purified by column chromatography on a mixture of silica gel (6 g) and silica gel modified with 3-aminopropyltriethoxysilane (1 g, 1.14 mmol g⁻¹ of NH₂ groups). Hexane was used as the eluent. The yield of **4ab** was 81% (161.8 mg), white crystalline solid. ¹H NMR (400 MHz, CDCl₃) δ 2.35 (s, 3H, Me), 7.114 (d, ³J = 8.0 Hz, 2H, Ar), 7.29–7.35 (m, 3H, Ph), 7.42 (d, ³J = 8.0 Hz, 2H, Ar), 7.50–7.53 (m, 2H, Ph); ¹³C NMR (100 MHz, CDCl₃) δ 21.5, 88.7, 89.6, 120.2, 123.5, 128.1, 128.3, 129.1, 131.6, 132.5, 138.4. IR (KBr, cm⁻¹) ν_{max} 2920.6, 2853.1 (C–H, C–C), 2214.6 (C≡C), 1595.3 (C=C). MS (*m/z*, EI, 70 eV) 192 ([M]⁺, 100), 115 ([M – Ph]⁺, 8.3), 77 ([Ph]⁺, 2.6).

4-Bromotolane (1-bromo-4-(phenylethynyl)benzene) (4ac**).**

4-Bromotolane (**4ac**) was prepared using a similar procedure to that for **4ab**, using 1-bromo-4-iodobenzene (**3c**) (295 mg, 1.043 mmol) instead of 4-iodotoluene (**3b**). The yield was 80% (214.4 mg), white crystalline solid. ¹H NMR (400 MHz, CDCl₃) δ 7.32–7.35 (m, 3H, Ar), 7.38 (d, ³J = 8.7 Hz, 2H, Ar), 7.47 (d, ³J = 8.7 Hz, 2H, Ar), 7.50–7.53 (m, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃) δ 88.3, 90.5, 122.3, 122.5, 122.9, 128.4, 128.5, 131.60, 131.62, 133.0. IR (KBr, cm⁻¹) ν_{max} 3049.8, 2924.4, 2855 (C–H, C–C), 2214.6 (C≡C), 1599.2 (C=C). MS (*m/z*, EI, 70 eV) 258 ([M⁺ ⁸¹Br], 97.2), 256 ([M⁺ ⁷⁹Br], 100), 177 ([M – Br]⁺, 13.6), 77 ([Ph]⁺, 6.8).

4-Nitrotolane (1-nitro-4-(phenylethynyl)benzene) (4ad**).**

4-Nitrotolane was prepared using a similar procedure to that for **4ab**, using 1-iodo-4-nitrobenzene (**3d**) (259.7 mg, 1.043 mmol) instead of 4-iodotoluene (**3b**). The reaction time was 1 h 40 min. The yield was 93% (216.5 mg), light yellow crystals. ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.39 (m, 3H, Ph), 7.54–7.56 (m, 2H, Ph), 7.65 (d, ³J = 8.7 Hz, 2H, Ar), 8.20 (d, ³J = 8.7 Hz, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃) δ 87.6, 94.7, 122.1, 123.6, 128.6, 129.3, 130.3, 131.9, 132.3, 147.0. IR (KBr, cm⁻¹) ν_{max} 2922.5, 2851.1 (C–H, C–C), 2216.5 (C≡C), 1591.5 (C=C), 1346.5 (symm NO₂). MS (*m/z*, EI, 70 eV) 223 ([M]⁺, 100), 177 ([M – NO₂]⁺, 21.1), 77 ([Ph]⁺, 8.8).

2-Bromo-4-nitro-1-(phenylethynyl)benzene (4af**).**

A vial was charged with 2-bromo-1-iodo-4-nitrobenzene (**3f**) (102.5 mg, 0.313 mmol), Pd(PPh₃)₂Cl₂ (11.0 mg, 0.016 mmol; 5 mol% vs. **3f**) and (PhC≡C)₄Sn **1a** (90 mg, 0.172 mmol). Then Pr₂NH (0.43 mL, 3.13 mmol) and dry BuOAc (1.8 mL) were added, the solution was degassed by freezing in liquid nitrogen and pumping under vacuum several times, and then the vial was flushed with argon. The reaction mixture was stirred at 100 °C for 4.5 h, then allowed to cool and quenched with EtOH (2 mL). The mixture was treated with 0.2 g of silica gel modified with 3-aminopropyltriethoxysilane, the solvent was removed on a rotary evaporator and the traces of BuOAc were removed *in vacuo*. The resulting mixture was purified by column chromatography on a mixture of silica gel (6 g) and

silica gel modified with 3-aminopropyltriethoxysilane (1 g, 1.14 mmol g⁻¹ of NH₂ groups), eluted with hexane, then hexane:PhMe 4:1. Column fractions were analyzed by GCMS. The eluent was evaporated to give 76 mg (81%) of acetylene **4af** as a yellow crystalline solid. In addition, the sample could be recrystallized from *n*-heptane. ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.42 (m, 3H, Ph), 7.59–7.61 (m, 2H, Ph), 7.68 (d, ³J = 8.2 Hz, 1H, H-6 Ar), 8.20 (dd, ³J = 8.2 Hz, ⁴J = 2.3 Hz, 1H, H-5 Ar), 8.48 (d, ⁴J = 2.3 Hz, 1H, H-3 Ar); ¹³C NMR (100 MHz, CDCl₃) δ 86.8, 99.5, 121.8, 122.1, 125.9, 127.6, 128.6, 129.7, 132.0, 132.1, 133.3, 146.9. IR (KBr, cm⁻¹) ν_{max} 3094.2, 3074.9 (C–H, C–C), 2218.4 (C≡C), 1583.8 (C=C), 1340.7 (symm NO₂). MS (*m/z*, EI, 70 eV) 303 ([M⁺ ⁸¹Br], 59.4), 301 ([M⁺ ⁷⁹Br], 60.2), 257 ([M – NO₂]⁺, ⁸¹Br, 0.8), 255 ([M – NO₂]⁺, ⁷⁹Br, 0.9), 176 ([M – NO₂ – Br]⁺, 100), 77 ([Ph]⁺, 1.6).

2-Nitrotolane (2-nitro-4-(phenylethynyl)benzene) (4ak). 2-Nitrotolane was prepared using a similar procedure to that for **4ab**, using 1-iodo-2-nitrobenzene (**3k**) (259.7 mg, 1.043 mmol) instead of 4-iodotoluene (**3b**). The reaction time was 3.5 h. The yield was 88% (205 mg), red oil. ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.38 (m, 3H, Ph), 7.42–7.46 (m, 1H, Ar), 7.56–7.60 (m, 3H, Ar), 7.70 (d, ³J = 7.8 Hz, 1H, Ar), 8.06 (d, ³J = 8.3 Hz, 1H, Ar); ¹³C NMR (100 MHz, CDCl₃) δ 84.8, 97.1, 118.7, 122.4, 124.7, 128.45, 128.54, 129.2, 132.0, 132.8, 134.6, 149.6. IR (neat, cm⁻¹) ν_{max} 3059.9 (C–C, C–H), 2219.0 (C≡C), 1339.5 (symm NO₂). MS (*m/z*, EI, 70 eV) 223 ([M⁺], 5.2), 177 ([M – NO₂]⁺, 3.8), 77 ([Ph]⁺, 89.0).

Ethyl 2-(phenylethynyl)benzoate (4am). A dry 25 mL, two-necked, round-bottomed flask equipped with an argon gas inlet tube and a magnetic stirrer was flushed with argon and charged with 2-IC₆H₄C(O)OEt (**3m**) (287.9 mg, 1.043 mmol), Pd(PPh₃)₂Cl₂ (36.6 mg, 0.052 mmol; 5 mol% vs. **3m**) and (PhC≡C)₄Sn **1a** (150 mg, 0.287 mmol). Then TMEDA (1.56 mL, 10.43 mmol) and dry BuOAc (6 mL) were added, the solution was degassed by freezing in liquid nitrogen and pumping under vacuum several times, and then it was flushed with argon. The reaction mixture was stirred at 100 °C for 5 h, then allowed to cool and quenched with EtOH (10 mL). The mixture was treated with 0.5 g of silica gel modified with 3-aminopropyltriethoxysilane, the solvent was removed on a rotary evaporator and the traces of BuOAc were removed *in vacuo*. The resulting mixture was purified by column chromatography on a mixture of silica gel (6 g) and silica gel modified with 3-aminopropyltriethoxysilane (1 g, 1.14 mmol g⁻¹ of NH₂ groups), eluted with hexane, then with hexane:PhMe 4:1 (after diphenyldiacetylene **5a** was eluted). Column fractions were analyzed by GCMS. The eluent was evaporated to give 243 mg (purity by GCMS – 87.3%) of benzoate **4am** as a yellow solid. The product was further purified with flash chromatography (2 g of silica gel, hexane). Yield 81%. ¹H NMR (400 MHz, CDCl₃) δ 1.40 (t, ³J = 7.3 Hz, 3H, OCH₂CH₃), 4.42 (q, ³J = 7.3 Hz, 2H, OCH₂CH₃), 7.34–7.39 (m, 4H, Ar), 7.46–7.50 (m, 1H, Ar), 7.56–7.58 (m, 2H, Ar), 7.64 (d, ³J = 8.2 Hz, 1H, Ar), 7.97 (dd, ³J = 7.8 Hz, ⁴J = 0.9 Hz, 1H, Ar); ¹³C NMR (100 MHz, CDCl₃) δ 14.4, 61.2, 88.3, 94.2, 123.4, 123.6, 127.9, 128.4, 128.5, 130.4, 131.5, 131.7, 132.3, 134.0, 166.4. IR (KBr, cm⁻¹) ν_{max} 3061.4, 2982.3 (C–H, C–C), 2218.4 (C≡C), 1726.5 (C=O). MS (*m/z*, EI, 70 eV) 250 ([M⁺], 94.4), 235 ([M – Me]⁺, 3.0), 222 ([M – CO]⁺, 100), 221

([M – Et]⁺, 29.7), 205 ([M – EtO]⁺, 36.0), 177 ([M – COOEt]⁺, 22.1), 77 ([Ph]⁺, 13.9).

4-(Phenylethynyl)benzaldehyde (4an). Aldehyde **4an** was prepared using a similar procedure to that for benzoate **4am**, using 4-BrC₆H₄CHO (**3n**) (193 mg, 1.043 mmol), Pd(PPh₃)₂Cl₂ (36.6 mg, 0.052 mmol; 5 mol% vs. **3n**), (PhC≡C)₄Sn **1a** (150 mg, 0.287 mmol), TMEDA (1.56 mL, 10.43 mmol) and dry BuOAc (6 mL). The reaction time was 3 h. The yield of crude aldehyde **4an** was 176 mg. For further purification, the sample was recrystallized from *n*-heptane. Yield 82%, beige crystalline solid. ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.38 (m, 3H, Ph), 7.54–7.57 (m, 2H, Ph), 7.67 (d, ³J = 8.2 Hz, 2H, Ar), 7.85 (d, ³J = 8.2 Hz, 2H, Ar), 10.00 (s, 1H, CHO); ¹³C NMR (100 MHz, CDCl₃) δ 88.5, 93.5, 122.5, 128.5, 129.0, 129.58, 129.60, 131.8, 132.1, 135.4, 191.4. IR (KBr, cm⁻¹) ν_{max} 3049.3, 2845.8 (C–C, C–H), 2216.1 (C≡C), 1697.3 (C=O), 1599.9 (C=C); MS (*m/z*, EI, 70 eV) 206 ([M⁺], 100), 205 ([M – H]⁺, 71.4), 178 ([M – CO]⁺, 13.3), 77 ([Ph]⁺, 5.9).

1-[4-(Phenylethynyl)phenyl]ethanone (4ao). Ketone **4ao** was prepared using a similar procedure to that for benzoate **4am**, using 4-BrC₆H₄C(O)CH₃ (**3o**) (151.4 mg, 0.761 mmol), Pd(PPh₃)₂Cl₂ (26.7 mg, 0.038 mmol; 5 mol% vs. **3o**), (PhC≡C)₄Sn **1a** (109.4 mg, 0.209 mmol), TMEDA (0.57 mL, 3.8 mmol) and dry BuOAc (4.5 mL). The product was purified by column chromatography on a silica gel (7 g), eluted with hexane, then hexane:PhMe 4:1 (after diphenyldiacetylene **5a** was eluted). The yield of crude ketone **4ao** was 129.3 mg (purity by GCMS – 84%). For further purification, the sample was recrystallized from *n*-heptane. Yield 65%, white crystalline solid. ¹H NMR (400 MHz, CDCl₃) δ 2.61 (s, 3H, COCH₃), 7.36–7.37 (m, 3H, Ph), 7.53–7.56 (m, 2H, Ph), 7.61 (d, ³J = 8.5 Hz, 2H, Ar), 7.93 (d, ³J = 8.5 Hz, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃) δ 26.6, 88.6, 92.7, 122.7, 128.2, 128.3, 128.5, 128.8, 131.7, 131.8, 136.2, 197.3. IR (KBr, cm⁻¹) ν_{max} 3061.4, 2997.7 (C–H, C–C), 2218.4 (C≡C), 1680.2 (C=O), 1603.0 (C=C). MS (*m/z*, EI, 70 eV) 220 ([M⁺], 72.5), 205 ([M – CH₃]⁺, 100), 177 ([M – COCH₃]⁺, 27.8), 77 ([Ph]⁺, 6.4).

1-Methyl-4-[(4-nitrophenyl)ethynyl]benzene (4bd). Acetylene **4bd** was prepared using a similar procedure to that for **4ab**, using 1-iodo-4-nitrobenzene (**3d**) (178.3 mg, 0.716 mmol), Pd(PPh₃)₂Cl₂ (25.1 mg, 0.036 mmol; 5 mol% vs. **3d**), (4-MeC₆H₄C≡C)₄Sn **1b** (114.1 mg, 0.197 mmol), Pr₂NH (0.98 mL, 7.16 mmol) and BuOAc (4.5 mL). The reaction time was 3.5 h. The resulting crude product was purified by column chromatography on a mixture of silica gel (6 g) and silica gel modified with 3-aminopropyltriethoxysilane (1 g, 1.14 mmol g⁻¹ of NH₂ groups), and subsequently eluted with hexane, hexane:EtOAc 9:1, hexane:EtOAc 4:1 and pure toluene. Recrystallization from toluene yielded 108.6 mg (63.9%) of acetylene **4bd** as a white crystalline solid. Another crop of product (49.1 mg, purity by GC-MS – 95%) was obtained from the mother liquor. The total yield of toluene **4bd** was 155.2 mg (91%). ¹H NMR (400 MHz, CDCl₃) δ 2.38 (s, 3H, CH₃), 7.18 (d, ³J = 7.8 Hz, 2H, 4-MeC₆H₄), 7.44 (d, ³J = 7.8 Hz, 2H, 4-MeC₆H₄), 7.63 (d, ³J = 9.2 Hz, 2H, 4-NO₂C₆H₄), 8.19 (d, ³J = 9.2 Hz, 2H, 4-NO₂C₆H₄); ¹³C NMR (100 MHz, CDCl₃) δ 21.6, 87.1, 95.1, 119.1, 123.6,

129.3, 130.5, 131.8, 132.2, 139.7, 146.9. IR (KBr, cm^{-1}) ν_{max} 2922.5, 2847.3 (C–H, C–C), 2212.6 (C \equiv C), 1589.5 (C=C), 1342.6 (symm NO₂). MS (m/z , EI, 70 eV) 237 ([M⁺], 100), 191 ([M – NO₂]⁺, 13.6), 176 ([M – Me – NO₂]⁺, 17.1).

1-Chloro-4-[(4-nitrophenyl)ethynyl]benzene (4cd). Acetylene **4cd** was prepared using a similar procedure to that for **4ab**, using 1-iodo-4-nitrobenzene (**3d**) (249 mg, 1.00 mmol), Pd(PPh₃)₂Cl₂ (35.1 mg, 0.05 mmol; 5 mol% vs. **3d**), (4-ClC₆H₄C \equiv C)₄Sn **1c** (181.7 mg, 0.275 mmol), Pr₂NH (1.37 mL, 10.0 mmol) and BuOAc (6 mL). The reaction time was 2.5 h. The resulting crude product was purified by column chromatography on a mixture of silica gel (6 g) and silica gel modified with 3-aminopropyltriethoxysilane (1 g, 1.14 mmol g^{−1} of NH₂ groups), and subsequently eluted with hexane, hexane:HCCL₃ 9:1, hexane:HCCL₃ 3:2 and hexane:HCCL₃ 1:1. Recrystallization from toluene yielded 160.9 mg (62%) of acetylene **4cd** as a white crystalline solid. Another crop of product (49.8 mg) was isolated from the mother liquor. The total yield was 210.7 mg (82%). ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, ³J = 8.2 Hz, 2H, Ar), 7.49 (d, ³J = 8.2 Hz, 2H, Ar), 7.65 (d, ³J = 8.7 Hz, 2H, Ar), 8.22 (d, ³J = 8.7 Hz, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃) δ 88.4, 93.4, 120.6, 123.7, 129.0, 129.9, 132.3, 133.1, 135.5, 147.2. IR (KBr, cm^{-1}) ν_{max} 3092.3, 2926.4, 2851.1 (C–H, C–C), 2210.7 (C \equiv C), 1587.6 (C=C), 1346.5 (symm NO₂). MS (m/z , EI, 70 eV) 259 ([M⁺]³⁷Cl, 32.7), 257 ([M⁺]³⁵Cl, 100), 213 ([M – NO₂]⁺³⁷Cl, 2.8), 211 ([M – NO₂]⁺³⁵Cl, 9.5), 176 ([M – Cl – NO₂]⁺, 82.7).

tert-Butyl 3-(4-nitrophenyl)prop-2-ynyl ether (4ed). Acetylene **4ed** was prepared using a similar procedure to that for **4ab**, using 1-iodo-4-nitrobenzene (**3d**) (289.8 mg, 1.164 mmol), Pd(PPh₃)₂Cl₂ (40.8 mg, 0.058 mmol; 5 mol% vs. **3d**), (t-BuOCH₂C \equiv C)₄Sn **1e** (180 mg, 0.32 mmol), Pr₂NH (1.6 mL, 11.64 mmol) and BuOAc (6 mL). The reaction time was 5.5 h. The resulting crude product was purified by column chromatography on a mixture of silica gel (6 g) and silica gel modified with 3-aminopropyltriethoxysilane (1 g, 1.14 mmol g^{−1} of NH₂ groups), and subsequently eluted with hexane and hexane:HCCL₃ 9:1. The yield of acetylene **4ed** was 132 mg (49%), yellow crystalline solid. ¹H NMR (400 MHz, CDCl₃) δ 1.30 (s, 9H, tBu), 4.34 (s, 2H, OCH₂), 7.57 (d, ³J = 9.2 Hz, 2H, Ar), 8.16 (d, ³J = 9.2 Hz, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃) δ 27.5, 51.0, 74.8, 83.0, 92.7, 123.5, 130.0, 132.4, 147.1. IR (KBr, cm^{-1}) ν_{max} 3105.8, 2976.5, 2862.7 (C–H, C–C), 2220.3 (C \equiv C), 1593.4 (C=C), 1342.6 (symm NO₂). MS (m/z , EI, 70 eV) 233 ([M⁺], 0.3), 218 ([M – CH₃]⁺, 10.4), 160 ([M – tBuO]⁺, 100), 57 ([tBu]⁺, 60.5).

1-Hex-1-ynyl-4-nitrobenzene (4fd). Acetylene **4fd** was prepared using a similar procedure to that for **4ab**, using 1-iodo-4-nitrobenzene (**3d**) (249.0 mg, 1.00 mmol), Pd(PPh₃)₂Cl₂ (35.1 mg, 0.05 mmol; 5 mol% vs. **3d**), (CH₃CH₂CH₂CH₂C \equiv C)₄Sn **1f** (121.9 mg, 0.275 mmol), Pr₂NH (1.37 mL, 10.0 mmol) and BuOAc (6 mL). The reaction time was 15 h. The resulting product was purified by column chromatography over a mixture of silica gel (6 g) and silica gel modified with 3-aminopropyltriethoxysilane (1 g, 1.14 mmol g^{−1} of NH₂ groups). Hexane was used as the eluent. The column fractions were concentrated, the unreacted 1-iodo-4-nitrobenzene (**3d**) was filtered off, and the crude product was again purified under

the same column chromatography conditions as previously to give 96.1 mg (47%) of acetylene **4fd** as a light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 0.96 (t, ³J = 7.3 Hz, 3H, Me), 1.44–1.53 (m, 2H, CH₂), 1.58–1.65 (m, 2H, CH₂), 2.45 (t, ³J = 6.9 Hz, 2H, CH₂C \equiv), 7.51 (d, ³J = 8.7 Hz, 2H, Ar), 8.15 (d, ³J = 8.7 Hz, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃) δ 13.6, 19.3, 22.0, 30.5, 79.3, 96.8, 123.5, 131.3, 132.3, 146.6. IR (KBr, cm^{-1}) ν_{max} 3107.7, 3080.7, 2957.2, 2932.2, 2872.4 (C–H, C–C), 2230.0 (C \equiv C), 1592.3 (C=C), 1342.6 (symm NO₂). MS (m/z , EI, 70 eV) 203 ([M⁺], 39.9), 188 ([M – CH₃]⁺, 58.3), 174 ([M – CH₂CH₃]⁺, 6.6), 157 ([M – NO₂]⁺, 17.9).

Further details on the experimental procedures and spectra are given in the ESI.†

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Notes and references

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