Tetraalkynylstannanes in the Stille cross coupling reaction: a new effective approach to arylalkynes\textsuperscript{†}

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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\textsuperscript{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.\textsuperscript{5} The Stille reaction has been thoroughly investigated and many advances have been made to expand both the scope and utility of this process.\textsuperscript{5,6} In contrast to other cross coupling reactions, the Stille reaction has often been found to be effective and relatively un demanding, allowing for harsher conditions, as the Stille reaction has often been found to be effective and relatively un demanding, allowing for harsher conditions, as organostannanes are relatively insensitive to moisture and oxygen.\textsuperscript{5} On the other hand, the use of organostannanes such as Bu\textsubscript{3}SnR raises problems with organotin contamination and waste. Both acute and long-term toxicities have been reported for many organotin reagents,\textsuperscript{7,8} and methods designed to limit or avoid the presence of organotin by-products in reaction products have been developed.\textsuperscript{9} In general, the toxicity of alkylstannanes decreases as the size of the alkyl groups increases (Me\textsubscript{3}SnX ≈ Et\textsubscript{2}SnX ≈ Bu\textsubscript{2}SnX ≈ Octyl\textsubscript{3}SnX) and the number of alkyl groups decreases (R\textsubscript{4}SnX > R\textsubscript{3}SnX\textsubscript{2} > R\textsubscript{2}SnX\textsubscript{3}).\textsuperscript{9} R\textsubscript{4}Sn may reveal enhanced delayed toxicity due to \textit{in vivo} transformation into R\textsubscript{3}SnX.\textsuperscript{10} However, the toxicity strongly depends on the nature of the organic group R.\textsuperscript{10} Due to the easy hydrolysis of the C(sp)–Sn bond, it is generally accepted that tetraalkynyltin compounds (RC≡C)\textsubscript{4}Sn are far less toxic than other organotin species having C(sp\textsuperscript{2})–Sn or C(sp\textsuperscript{3})–Sn bonds.

Another feature of tetraalkynylstannanes is their high atom economy. A practical disadvantage of the use of tin monofunctional reagents such as R–Sn(alkyl)\textsubscript{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)\textsubscript{4}Sn is reactive, tetraalkynyltin compounds may be compared with sodium acetylides with respect to low molecular weight and producing only inorganic Sn(0) 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.\textsuperscript{11} In other words, the \textit{E}-factor\textsuperscript{12} (which is defined as the mass ratio of waste to desired product) of the Stille reaction with R–Sn(alkyl)\textsubscript{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 tetraallylstannane with electrophilic substrates.\textsuperscript{13} Tetraallylstannane is a gentle nucleophile for allylation reactions and easily reacts with imines,\textsuperscript{14} aldehydes,\textsuperscript{15,16} phenacyl bromide,\textsuperscript{17} other ketones\textsuperscript{18} or carbon dioxide\textsuperscript{19} (Scheme 1). In contrast to allyltrimethylstannyl 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(CH\textsubscript{2}CH=CH\textsubscript{2})\textsubscript{4}.
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 SnCl₄ in the presence of anhydrous ZnCl₂ and diethylamine²⁰,²¹ 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 (RC≡CR)₄Sn as reagents (Scheme 3). Thus, the reactions with Grignard reagents were recognized as a convenient method of smooth transmetallation of tetraalkynylstannanes for the preparation of tri- and dialkynyltins.²³,²⁴ The organoboration of (RC≡CR)₄Sn with trialkylboranes led to the formation of 1,1₀-spirobistannoles.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 di- or trialkynylstannanes with iodovinyllic 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 C(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):

![Scheme 4](image-url)

Fig. 1. The scope of stannanes 1 and aryl halides 3 used.

![Scheme 5](image-url)

![Scheme 1](image-url)

Typical reactions of tetraallylstannane.

![Scheme 2](image-url)

Synthesis of tetraalkynylstannanes 1.

![Scheme 3](image-url)

The known reactions of tetraalkynylstannanes 1.
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(phenylethyl)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 reaction of tetraalkynylstannanes 1 with aryl halides 3 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 reaction of tetraalkynylstannanes 1 with aryl halides 3.

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

| Solvent | T (°C) | Yield of 4ad (%) | Yield of 5a (%) | Time’ (h) |
|---------|--------|-----------------|----------------|-----------|
| Et2O    | 35     | 0               | 5              | —         |
| THF     | 80     | —               | —              | —         |
| PhMe    | 100    | 55              | 10             | 7         |
| MeCN    | 85     | 89              | 6              | 5         |
| Dioxane | 100    | 84              | 2              | 3         |
| AcOEt   | 80     | 91              | 1              | 9         |
| AcOBu   | 125    | 98              | 2              | 1         |
| AcOBu   | 100    | 98              | 2              | 2         |
| Et3N    | 80     | —               | —              | —         |
| DMF     | 100    | —               | —              | —         |

* The reaction conditions were as follows: (PhC≡C)Sn 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). * Results were determined by GC-MS. * Reaction time when the highest yield was achieved.

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

| Amine | Time’ (h) | PhMe | Dioxane | Time’ (h) |
|-------|-----------|------|---------|-----------|
| Et3N  | 98        | 2    | 55      | 7         |
| EtN   | 85        | 5    | 27      | 5         |
| Bu3N  | 97        | 3    | 31      | 5         |
| DABCO | 68        | 2    | 87      | 0.5       |
| Morpholine | — | 54 | 7 | 86 |
| N-Methylmorpholine | 12.5 | 1 | — | — |
| Pyridine | — | — | — | 0 |
| Piperidine | 62 | 2 | 49 | 5 |
| [CH2]2(NH2)2 | 0 | 3 | — | — |
| PhCH2NH2 | 41 | 5 | 43 | 5 |
| Pr2NH | 99.5 | 1 | — | — |

* Yields were determined by GC-MS. * 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). * Reaction time when the highest yield was achieved.

Fig. 2 The kinetics of the reaction 1a + 3d → 4ad with different amounts of Et3N. The reaction conditions were as follows: (PhC≡C)Sn 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.
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 complex 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, when (PhC≡C)₅Sn 1a was added to 4-NO₂C₆H₄I 3d in pure Et₂N (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)₅Sn 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–C≡C)₅ 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 aryl halides 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 1a) 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](image-url) A possible mechanism for the reaction of tetraalkynylstannanes 1 with aryl halides 3.
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.⁴⁶ 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.

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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 EtO: hexane (10:1), MeOH: HClC\textsubscript{3} (1:10) or HClC\textsubscript{4}:Me\textsubscript{2}CO (10:1) mixtures as eluents. The spots were visualized with iodine vapors, K\textsubscript{2}MnO\textsubscript{4}–H\textsubscript{2}SO\textsubscript{4} solution or UV-light. The starting tetraalkynylstannanes 1a–g were obtained according to the reported methods\textsuperscript{20,21} the detailed procedures are given in the ESI.\textsuperscript{†}

**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 (PdCl\textsubscript{2}, Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, or Pd(PhCN)\textsubscript{2}Cl\textsubscript{2}) and 0.153 mmol of the amine additive (Et\textsubscript{3}NH, Et\textsubscript{3}N, Bu\textsubscript{4}N, DABCO, morpholine, etc.). Then the vial was flushed with a stream of dry argon, and subsequently a solution of 0.0382 mmol of (PhC\textsubscript{4}Sn\textsubscript{1})\textsubscript{2} 1a in a dry solvent (1 mL) and a solution of 0.153 mmol of 4-NO\textsubscript{2}C\textsubscript{6}H\textsubscript{4}J 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=CC=C)\textsubscript{2}Sn (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(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (36.6 mg, 0.052 mmol; 5 mol% vs. 3a) and (PhC=C=C)\textsubscript{2}Sn 1a (150 mg, 0.287 mmol). Then Pr\textsubscript{2}NH (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 (1 g, 1.14 mmol g\textsuperscript{–1} of NH\textsubscript{2} groups). Hexane was used as the eluent. The yield of 4ab was 81% (161.8 mg), white crystalline solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.35–7.38 (m, 3H, Ph), 7.49 (d, \(3J\) = 8.7 Hz, 2H, Ar), 7.50–7.53 (m, 2H, Ph); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 128.2, 128.3, 131.6. IR (KBr, cm\textsuperscript{–1}) \(\nu\)max 2922.5, 2851.1 (C–H, C–C), 2216.5 (C–C). MS (m/z, El, 70 eV) 258 (M\textsuperscript{+}\textsubscript{3}Br\textsuperscript{−}, 97.2), 256 (M\textsuperscript{+}\textsubscript{2}Br\textsuperscript{−}, 100), 177 [M–Br\textsuperscript{−}], 77 [Ph\textsuperscript{+}], 6.8).

**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. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.32–7.35 (m, 3H, Ph), 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); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 88.3, 90.5, 122.3, 122.5, 122.9, 128.4, 128.5, 131.60, 131.62, 133.0. IR (KBr, cm\textsuperscript{–1}) \(\nu\)max 3049.8, 2924.4, 2855 (C–H, C–C), 2216.4 (C=C), 1599.2 (C=C). MS (m/z, El, 70 eV) 256 (M\textsuperscript{+}\textsubscript{3}Br\textsuperscript{−}, 100), 177 [M–Br\textsuperscript{−}], 77 [Ph\textsuperscript{+}], 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. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 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); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 87.6, 94.7, 121.1, 123.6, 128.6, 129.3, 130.3, 131.9, 132.3, 147.0. IR (KBr, cm\textsuperscript{–1}) \(\nu\)max 2922.5, 2851 (C–H, C–C), 2216.5 (C=C), 1591.5 (C=C), 1436.5 (symm NO\textsubscript{2}). MS (m/z, El, 70 eV) 223 ([M\textsuperscript{+}], 100), 177 [M–NO\textsubscript{2}\textsuperscript{−}], 21.1, 77 [Ph\textsuperscript{+}], 8.8).

**2-Bromo-4-nitro-(phenylethynyl)benzene (4af).** A vial was charged with 2-bromo-1-iodo-4-nitrobenzene (3f) (102.5 mg, 0.331 mmol, Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (11.0 mg, 0.016 mmol; 5 mol% vs. 3f) and (PhC=C=C)\textsubscript{2}Sn 1a (90 mg, 0.172 mmol). Then Pr\textsubscript{2}NH (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, J = 8.2 Hz, 1H, H-6 Ar), 8.20 (dd, J = 8.2 Hz, J = 2.3 Hz, 1H, H-5 Ar), 8.48 (d, J = 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) νmax 3094.2, 3074.9 (C–H, C–C), 2218.4 (C≡C), 1319.5 (symm NO₂). MS (m/z, EI, 70 eV) 309 [M + Br], 301 [M + 7 Br], 257 [(M – NO₂)⁺, 81Br, 0.8], 225 [(M – NO₂ – Br)⁺, 90.3], 77 [(M – Br)⁺, 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 7.84–7.86 (2H, Ar), 7.35–7.37 (m, 2H, Ph), 7.56–7.59 (m, 2H, Ph), 7.60 (d, J = 8.2 Hz, 2H, Ar), 8.35 (d, J = 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, 129.5, 130.3, 132.1, 135.4, 191.4. IR (KBr, cm⁻¹) νmax 3049.3, 2845.8 (C–C, C–H), 1660.8 (C≡C), 1599.9 (C=O); 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 (3m) (151.4 mg, 0.761 mmol), Pd(PPh₃)₂Cl₂ (26.7 mg, 0.038 mmol; 5 mol% vs. 3m), (PhC≡C)₂Sn 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 diphenylidicyclopentadiene 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), 7.53–7.55 (m, 2H, Ph), 7.61 (d, J = 8.5 Hz, 2H, Ar), 7.93 (d, J = 8.5 Hz, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃) δ 26.6, 88.6, 92.7, 122.7, 128.2, 128.5, 128.8, 131.7, 131.8, 136.2, 197.3. IR (KBr, cm⁻¹) νmax 3061.4, 2997.7 (C–H, C–C), 1384.1 (C≡C), 1604.2 (C=O), 1803.0 (C=O); MS (m/z, EI, 70 eV) 220 [M⁺, 74.0], 87, 77 [(Ph⁺), 6.4].

1-Methyl-4-[4-nitrophenoxy]ethanol (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)₂Sn 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), eluted with hexane: hexane: PhMe 4:1 (after diphenylidicyclopentadiene 5a was eluted). Column fractions were analyzed by GCMS. The eluent was evaporated to give 243 mg (purity by GCMS – 87.3%) of benzene 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, J = 7.3 Hz, 3H, OCH₂CH₃), 4.42 (q, J = 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 (dd, J = 8.2 Hz, 1H, Ar), 7.97 (dd, J = 7.8 Hz, J = 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) νmax 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)₂Sn 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 7.37–7.39 (m, 3H, Ph), 7.54–7.57 (m, 2H, Ph), 7.67 (d, J = 8.2 Hz, 2H, Ar), 7.85 (d, J = 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, 129.5, 130.3, 132.1, 135.4, 191.4. IR (KBr, cm⁻¹) νmax 3049.3, 2845.8 (C–C, C–H), 1660.8 (C≡C), 1599.9 (C=O); MS (m/z, EI, 70 eV) 206 [M⁺, 100], 205 [M – H⁺, 71.4], 178 [(M – CO)⁺, 13.3], 77 [(Ph⁺), 5.9].
129.3, 130.5, 131.8, 132.2, 139.7, 146.9. IR (KBr, cm⁻¹) νmax 2922.5, 2847.3 (C–H, C–C), 2212.6 (C≡C), 1589.5 (C=C), 1342.6 (symm NO2). MS (m/z, El, 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≡C≡CSn 1 (181.7 mg, 0.275 mmol), PrNH (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 (1 g, 1.14 mmol g⁻¹ of NH2 groups), and subsequently eluted with hexane:HCCl3 9:1. Recrystallization from toluene yielded 160.9 mg (62%) of acetylene 4ed as a white crystalline solid. Another crop of (49.8 mg) was isolated from the mother liquor. The total yield was 210.7 mg (82%).

1H NMR (400 MHz, CDCl3) δ 7.04, 7.11, 8.15 (d, 3J = 7.3 Hz, 2H, Ar), 7.49 (d, 3J = 8.7 Hz, 2H, Ar), 8.05 (d, 3J = 8.7 Hz, 2H, Ar), 8.12 (d, 3J = 8.7 Hz, 2H, Ar); 13C NMR (100 MHz, CDCl3) δ 112.7, 129.3, 130.5, 131.8, 132.2, 139.7, 146.9. IR (KBr, cm⁻¹) νmax 3105.8, 2976.5, 2862.7 (C–H, C–C), 2220.3 (C≡C).

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

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