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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 Bu_3SnR 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 ($Me_3SnX \sim Et_3SnX \gg Bu_3SnX \gg Octyl_3SnX$) and the number of alkyl groups decreases ($R_3SnX > R_2SnX_2 > RSnX_3$);[9] R_4Sn may reveal enhanced delayed toxicity due to *in vivo* transformation into R_3SnX.[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 $(RC{\equiv}C)_4Sn$ are far less toxic than other organotin species having C(sp^2)–Sn or C(sp^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)$_3$ (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 $(RC{\equiv}C)_4Sn$ 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*-factor[12] (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 tetraallylstannane with electrophilic substrates.[13] Tetraallylstannane is a gentle nucleophile for allylation reactions and easily reacts with imines,[14] aldehydes,[15,16] phenacyl bromide,[17] other ketones[18] or carbon dioxide[19] (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 $Sn(CH_2CH{=}CH_2)_4$.

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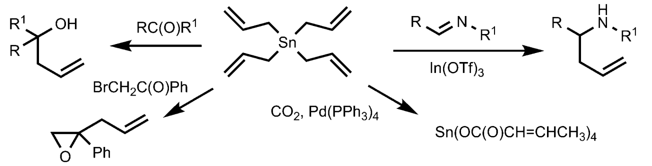
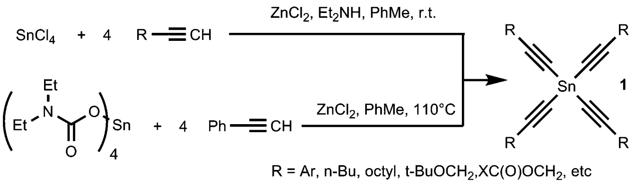


Scheme 1 Typical reactions of tetraallylstannane.

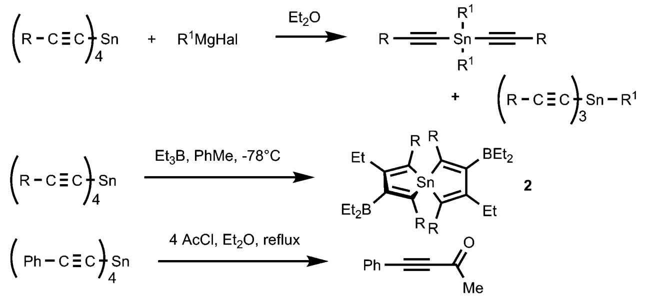


Scheme 2 Synthesis of tetraalkynylstannanes **1**.

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 $(RC{\equiv}C)_4Sn$ 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 $(RC{\equiv}C)_4Sn$ 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 reported[31] the Stille cross coupling reaction of di- or trialkynylstannanes with iodovinylic 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**.

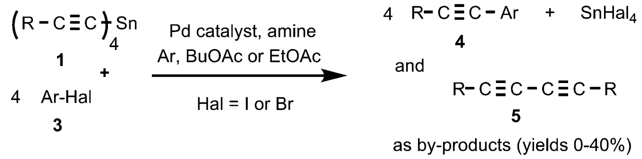


Scheme 3 The known reactions of tetraalkynylstannanes **1**.

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**.

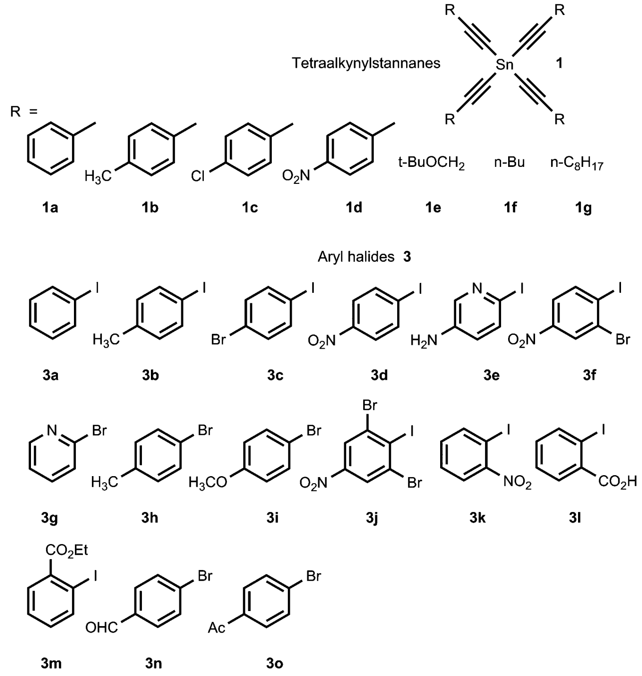
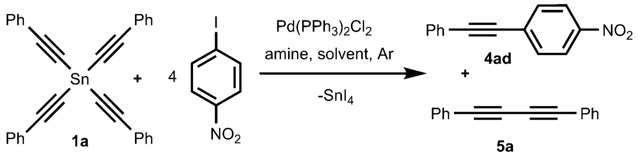


Fig. 1 The scope of stannanes **1** and aryl halides **3** used.



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]

		Et_2NH			Et_3N			DABCO		
Solvent	*T* (°C)	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_2O	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_3N	80	—	—	—	96	4	2.5	—	—	—
DMF	100	—	—	—	89	9	2.5	—	—	—

[a] The reaction conditions were as follows: $(PhC{\equiv}C)_4Sn$ **1a** (20 mg, 0.038 mmol), $4\text{-}NO_2C_6H_4I$ **3d** (0.153 mmol), $Pd(PPh_3)_2Cl_2$ (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 $Pd(PPh_3)_2Cl_2$ 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 Et_3N as solvents in the temperature range of 80–125 °C, while the use of less polar (dioxane, PhMe) and low-boiling (Et_2O) 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 Et_3N, Bu_3N, DABCO, and especially with Et_2NH and Pr_2NH. 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. Et_2NH (the yield of **4ad** reached only 66% after 5 h in EtOAc at 80 °C), and quite rapidly when the amount of Et_2NH was increased.

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

	The yield of aryl acetylene **4ad**[a,b] (%)					
Amine	AcOBu	Time[c] (h)	PhMe	Time[c] (h)	Dioxane	Time[c] (h)
Et_2NH	98	2	55	7	84	3
Et_3N	85	5	27	5	44	2
Bu_3N	97	3	31	5	87	3
DABCO	68	2	87	0.5	78	0.5
Isophorone diamine	—	—	54	7	86	9
Morpholine	—	—	—	—	54	1
N-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	—	—	—	—
$PhCH_2NH_2$	41	5	43	5	56	5
$(PhCH_2)_2NH$	—	—	11	3	26	5
Pr_2NH	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), $Pd(PPh_3)_2Cl_2$ (5 mol% *vs.* **3d**), amine (0.153 mmol) and solvent (2 mL) at 100 °C. [c] Reaction time when the highest yield was achieved.

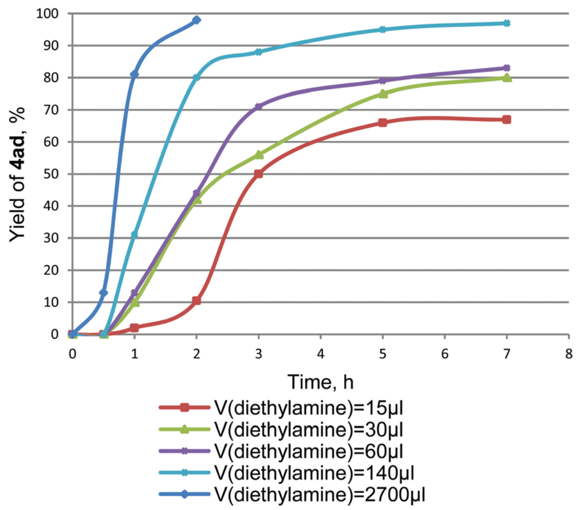


Fig. 2 The kinetics of the reaction **1a** + **3d** → **4ad** with different amounts of Et_2NH. The reaction conditions were as follows: $(PhC{\equiv}C)_4Sn$ **1a** (20 mg, 0.038 mmol), $4\text{-}NO_2C_6H_4I$ **3d** (0.153 mmol), $Pd(PPh_3)_2Cl_2$ as the catalyst (5 mol% with respect to **3d**), AcOEt (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_2NH	900	1 : 57	96.4	1.5	6
Pr_2NH	21	1 : 1	99.5	0.5	1
Pr_2NH	105	1 : 5	99.2	0.8	1
Pr_2NH	210	1 : 10	98.8	1.2	1
Pr_2NH	840	1 : 40	98.9	1.1	1
Pr_2NH	900	1 : 43	99.0	1.0	1
Pr_2NH	1000	1 : 47	98.3	1.7	1
Bu_3N	36	1 : 1	75.7	2.0	4
Bu_3N	182	1 : 5	99.5	0.5	1
Bu_3N	640	1 : 10	99.5	0.5	1
Bu_3N	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), $Pd(PPh_3)_2Cl_2$ (5 mol% with respect to **3d**), BuOAc, 100 °C, total volume solvent + amine = 1000 μL. [b] Yields were determined by GC-MS. [c] TMEDA = $Me_2NCH_2CH_2NMe_2$. [d] Reaction time when the maximum yield was achieved.

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

	The yield of $4\text{-}NO_2C_6H_4C{\equiv}CPh$ **4ad**[b] (%)					
Amine	$PdCl_2$	Time[c] (h)	$Pd(PhCN)_2Cl_2$	Time[c] (h)	$Pd(PPh_3)_2Cl_2$	Time[c] (h)
Et_2NH	13	7	7	5	98	2
Et_3N	72	3	71	2	89	7
Bu_3N	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.

The use of a large excess of Et_2NH under the same conditions produced tolane **4ad** in almost quantitative yields after 2 h (Fig. 2).

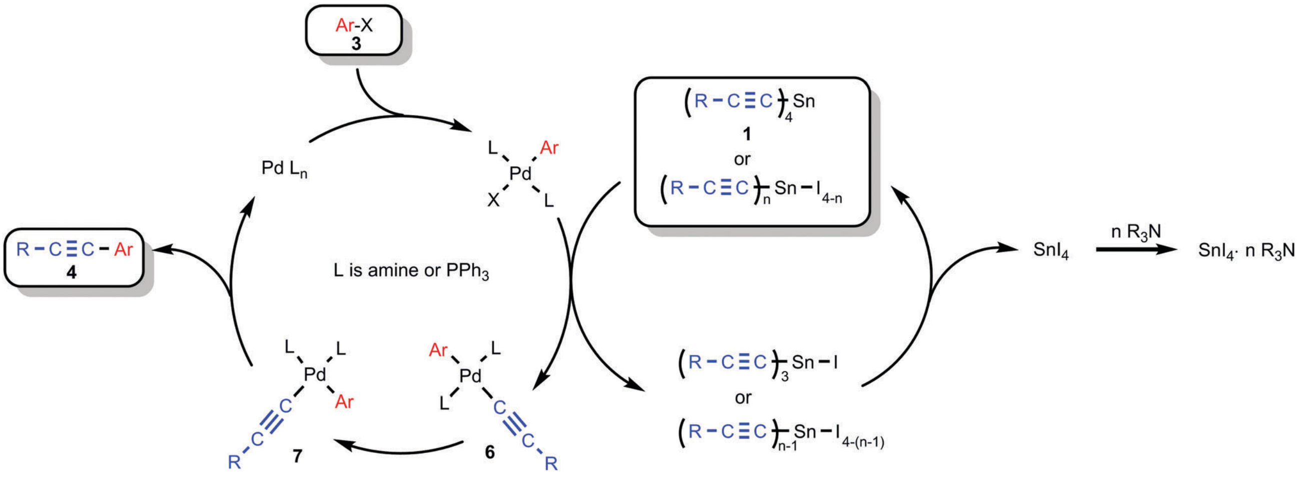
To optimize the conditions, we studied the effect of excessive amounts of different amines on the kinetics of the reaction. It was found that other amines were also as effective as Et_2NH when they were used in high excess. The results are summarized in Table 3.

We have to admit that the mechanistic picture of the Stille reaction is rather complex[35] 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 alkynylpalladium 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 $(PhC{\equiv}C)_4Sn$ **1a** was added to $4\text{-}NO_2C_6H_4I$ **3d** in pure Et_3N (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 $(PhC{\equiv}C)_4Sn$ **1a** was treated with a 4-fold excess of $CuBr_2$ (THF, 0.5 h, 25 °C), the oxidative Glaser-type coupling product $(Ph–C{\equiv}C–)_2$ **5a** was formed in a good yield. The first success came with the use of Pd catalysts, especially $Pd(PPh_3)_2Cl_2$. 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 $Pd(PPh_3)_2Cl_2$ and PPh_3 (5 mol% and 20 mol% with respect to **3d**, respectively), while $Pd(PPh_3)_2Cl_2$ with no PPh_3 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% $Pd(PPh_3)_2Cl_2$, and an excess (4-fold or more with respect to stannane **1**) of an amine additive – Et_2NH, Pr_2NH, DABCO or Bu_3N), 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)$_4$Sn **1a** under the optimized conditions[a]

Aryl Halides **3**	Solvent	Time[b] (h)	Amine	Yield of **4**
Ph–I **3a**	DMF	2.5	Et_3N	87
4-MeC_6H_4I **3b**	DMF	5	Et_3N	95
4-MeC_6H_4I **3b**	BuOAc	9	Et_2NH	54
4-$NO_2C_6H_4I$ **3d**	DMF	2.5	Et_3N	89
4-$NO_2C_6H_4I$ **3d**	BuOAc	6	Et_2NH	98
4-$NO_2C_6H_4I$ **3d**	BuOAc	1	Pr_2NH	99.5
4-$NO_2C_6H_4I$ **3d**	BuOAc	3	Bu_3N	97
4-MeC_6H_4Br **3h**	BuOAc	9	Et_2NH	11
4-$MeOC_6H_4Br$ **3i**	BuOAc	5	Et_2NH	7
4-$MeOC_6H_4Br$ **3i**	BuOAc	3	DABCO	15
2-$NO_2C_6H_4I$ **3k**	BuOAc	10	Et_2NH	83
2-$IC_6H_4CO_2H$ **3l**	BuOAc	5	Et_2NH	0
2-$IC_6H_4CO_2H$ **3l**	Et_3N	4	Et_3N	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), $Pd(PPh_3)_2Cl_2$ (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 in good yields. The analogs of (PhC≡C)$_4$Sn **1a**, *i.e.*, tetraalkynylstannanes **1b–g**, reacted with 4-$NO_2C_6H_4I$ **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.

Table 6 The reactivity of different tetraalkynylstannanes **1** towards 4-$NO_2C_6H_4I$ **3d** under the optimized conditions[a]

Tetraalkynylstannanes **1**	Time[b] (h)	Amine	Yields of **4** (%)
(PhC≡C)$_4$Sn **1a**	2	Et_2NH	98
(*t*-$BuOCH_2C$≡C)$_4$Sn **1e**	1	DABCO	74
(*t*-$BuOCH_2C$≡C)$_4$Sn **1e**	2	Et_2NH	33
(*n*-$C_8H_{18}CH_2C$≡C)$_4$Sn **1g**	7	Et_2NH	50
(*n*-$C_8H_{18}CH_2C$≡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), $Pd(PPh_3)_2Cl_2$ (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.

Conclusions

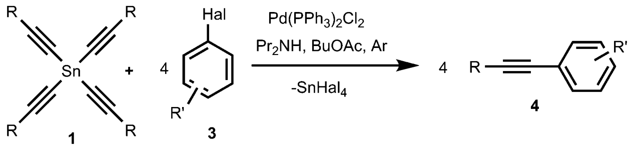
In conclusion, we have developed an effective synthetic protocol based on the Stille cross coupling reaction of easily available tetraalkynylstannanes with aryl halides. The reported method provides atom-economical access to aryl acetylenes and diaryl acetylenes (tolanes) which are valuable reagents 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, ^{13}C, and ^{119}Sn NMR spectra were recorded on a JEOL ECA 400 instrument at operating frequencies of 399.78, 100.52 and 149.08 MHz respectively, in $CDCl_3$ (Aldrich) with reference to TMS or to the residual signals of a solvent (with $SnMe_4$ as a standard for ^{119}Sn 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 $HCCl_3$ solution) and on a Bruker Vertex 70 instrument in ATR (attenuated total reflection) mode.

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_6H_4I **3b**	4-MeC_6H_4C≡CPh **4ab**	81
(PhC≡C)$_4$Sn **1a**	4-BrC_6H_4I **3c**	4-BrC_6H_4C≡CPh **4ac**	80
(PhC≡C)$_4$Sn **1a**	4-$NO_2C_6H_4I$ **3d**	4-$NO_2C_6H_4C$≡CPh **4ad**	93
(PhC≡C)$_4$Sn **1a**	2-Br-4-$NO_2C_6H_3I$ **3f**	2-Br-4-$NO_2C_6H_3C$≡CPh **4af**	40[b]
(PhC≡C)$_4$Sn **1a**	2-$NO_2C_6H_4I$ **3k**	2-$NO_2C_6H_4C$≡CPh **4ak**	88
(PhC≡C)$_4$Sn **1a**	2-$EtO_2CC_6H_4I$ **3m**	2-$EtO_2CC_6H_4C$≡CPh **4am**	81
(PhC≡C)$_4$Sn **1a**	4-BrC_6H_4CHO **3n**	PhC≡CC_6H_4CHO **4an**	82
(PhC≡C)$_4$Sn **1a**	4-$BrC_6H_4C(O)Me$ **3o**	PhC≡$CC_6H_4C(O)Me$ **4ao**	65
(4-MeC_6H_4C≡C)$_4$Sn **1b**	4-$NO_2C_6H_4I$ **3d**	4-MeC_6H_4C≡$CC_6H_4NO_2$ **4bd**	91
(4-ClC_6H_4C≡C)$_4$Sn **1c**	4-$NO_2C_6H_4I$ **3d**	4-ClC_6H_4C≡$CC_6H_4NO_2$ **4cd**	82
(*t*-$BuOCH_2C$≡C)$_4$Sn **1e**	4-$NO_2C_6H_4I$ **3d**	*t*-$BuOCH_2C$≡$CC_6H_4NO_2$ **4ed**	49
(*n*-BuC≡C)$_4$Sn **1f**	4-$NO_2C_6H_4I$ **3d**	*n*-BuC≡$CC_6H_4NO_2$ **4fd**	47

[a] Isolated yields are given. [b] When 2-Br-4-$NO_2C_6H_3I$ **3f** and (PhC≡C)$_4$Sn **1a** were added in a 2 : 1 ratio, acetylene **4af** was obtained in 81% yield.

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 Et_2O : hexane (10 : 1), MeOH : $HCCl_3$ (1 : 10) or $HCCl_3$: Me_2CO (10 : 1) mixtures as eluents. The spots were visualized with iodine vapors, $KMnO_4$–H_2SO_4 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 ($PdCl_2$, $Pd(PPh_3)_2Cl_2$, or $Pd(PhCN)_2Cl_2$) and 0.153 mmol of the amine additive (Et_2NH, Et_3N, Bu_3N, DABCO, morpholine, *etc.*). Then the vial was flushed with a stream of dry argon, and subsequently a solution of 0.0382 mmol of $(PhC{\equiv}C)_4Sn$ **1a** in a dry solvent (1 mL) and a solution of 0.153 mmol of 4-$NO_2C_6H_4I$ 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 $(PhC{\equiv}C)_4Sn$ (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), $Pd(PPh_3)_2Cl_2$ (36.6 mg, 0.052 mmol; 5 mol% *vs.* **3a**) and $(PhC{\equiv}C)_4Sn$ **1a** (150 mg, 0.287 mmol). Then Pr_2NH (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 NH_2 groups; the use of the modified silica gel allowed us to remove easily the by-product SnI_4, 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, $CDCl_3$) δ 7.33–7.73 (m, 6H, Ph), 7.52–7.54 (m, 4H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) 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 ($[M - C_2H_2]^+$, 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), $Pd(PPh_3)_2Cl_2$ (36.6 mg, 0.052 mmol; 5 mol% *vs.* **3b**) and $(PhC{\equiv}C)_4Sn$ **1a** (150 mg, 0.287 mmol). Then Pr_2NH (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 NH_2 groups). Hexane was used as the eluent. The yield of **4ab** was 81% (161.8 mg), white crystalline solid. ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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^{+} ^{81}Br], 97.2), 256 ([M^{+} ^{79}Br], 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, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 NO_2). MS (*m*/*z*, EI, 70 eV) 223 ([M^+], 100), 177 ($[M - NO_2]^+$, 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), $Pd(PPh_3)_2Cl_2$ (11.0 mg, 0.016 mmol; 5 mol% *vs.* **3f**) and $(PhC{\equiv}C)_4Sn$ **1a** (90 mg, 0.172 mmol). Then Pr_2NH (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 NH_2 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, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 ($C\equiv C$), 1583.8 (C=C), 1340.7 (symm NO_2). MS (*m*/*z*, EI, 70 eV) 303 ([M^+ ^{81}Br], 59.4), 301 ([M^+ ^{79}Br], 60.2), 257 ([$(M-NO_2)^+$, ^{81}Br], 0.8), 255 ([$(M-NO_2)^+$, ^{79}Br], 0.9), 176 (([$M-NO_2-Br$])$^+$, 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, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 ($C\equiv C$), 1339.5 (symm NO_2). MS (*m*/*z*, EI, 70 eV) 223 ([M^+], 5.2), 177 ([$M-NO_2$]$^+$, 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-$IC_6H_4C(O)OEt$ (**3m**) (287.9 mg, 1.043 mmol), $Pd(PPh_3)_2Cl_2$ (36.6 mg, 0.052 mmol; 5 mol% *vs.* **3m**) and $(PhC\equiv C)_4Sn$ **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 NH_2 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, $CDCl_3$) δ 1.40 (t, ^3J = 7.3 Hz, 3H, $OCH_2C\underline{H}_3$), 4.42 (q, ^3J = 7.3 Hz, 2H, $OC\underline{H}_2CH_3$), 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 ($C\equiv C$), 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-BrC_6H_4CHO (**3n**) (193 mg, 1.043 mmol), $Pd(PPh_3)_2Cl_2$ (36.6 mg, 0.052 mmol; 5 mol% *vs.* **3n**), $(PhC\equiv C)_4Sn$ **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, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 ($C\equiv C$), 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-$BrC_6H_4C(O)CH_3$ (**3o**) (151.4 mg, 0.761 mmol), $Pd(PPh_3)_2Cl_2$ (26.7 mg, 0.038 mmol; 5 mol% *vs.* **3o**), $(PhC\equiv C)_4Sn$ **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, $CDCl_3$) δ 2.61 (s, 3H, $COCH_3$), 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 ($C\equiv C$), 1680.2 (C=O), 1603.0 (C=C). MS (*m*/*z*, EI, 70 eV) 220 ([M^+], 72.5), 205 ([$M-CH_3$]$^+$, 100), 177 ([$M-COCH_3$]$^+$, 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), $Pd(PPh_3)_2Cl_2$ (25.1 mg, 0.036 mmol; 5 mol% *vs.* **3d**), $(4\text{-}MeC_6H_4C\equiv C)_4Sn$ **1b** (114.1 mg, 0.197 mmol), Pr_2NH (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 NH_2 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 tolane **4bd** was 155.2 mg (91%). ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H, CH_3), 7.18 (d, ^3J = 7.8 Hz, 2H, 4-MeC_6H_4), 7.44 (d, ^3J = 7.8 Hz, 2H, 4-MeC_6H_4), 7.63 (d, ^3J = 9.2 Hz, 2H, 4-$NO_2C_6H_4$), 8.19 (d, ^3J = 9.2 Hz, 2H, 4-$NO_2C_6H_4$); ^{13}C NMR (100 MHz, $CDCl_3$) 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}) $\nu_{\max}$ 2922.5, 2847.3 (C–H, C–C), 2212.6 (C$\equiv$C), 1589.5 (C$=$C), 1342.6 (symm NO$_2$). MS (*m*/*z*, EI, 70 eV) 237 ([M$^+$], 100), 191 ([M − NO$_2$]$^+$, 13.6), 176 ([M − Me − NO$_2$]$^+$, 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(PPh$_3$)$_2$Cl$_2$ (35.1 mg, 0.05 mmol; 5 mol% *vs.* **3d**), (4-ClC$_6$H$_4$C$\equiv$C)$_4$Sn **1c** (181.7 mg, 0.275 mmol), Pr$_2$NH (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 NH$_2$ groups), and subsequently eluted with hexane, hexane : HCCl$_3$ 9 : 1, hexane : HCCl$_3$ 3 : 2 and hexane : HCCl$_3$ 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%). ^{1}H NMR (400 MHz, CDCl$_3$) 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); ^{13}C NMR (100 MHz, CDCl$_3$) 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}) $\nu_{\max}$ 3092.3, 2926.4, 2851.1 (C–H, C–C), 2210.7 (C$\equiv$C), 1587.6 (C$=$C), 1346.5 (symm NO$_2$). MS (*m*/*z*, EI, 70 eV) 259 ([M$^+$] ^{37}Cl, 32.7), 257 ([M$^+$] ^{35}Cl, 100), 213 ([M − NO$_2$]$^+$ ^{37}Cl, 2.8), 211 ([M − NO$_2$]$^+$ ^{35}Cl, 9.5), 176 ([M − Cl − NO$_2$]$^+$, 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(PPh$_3$)$_2$Cl$_2$ (40.8 mg, 0.058 mmol; 5 mol% *vs.* **3d**), (*t*-BuOCH$_2$C$\equiv$C)$_4$Sn **1e** (180 mg, 0.32 mmol), Pr$_2$NH (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 NH$_2$ groups), and subsequently eluted with hexane and hexane : HCCl$_3$ 9 : 1. The yield of acetylene **4ed** was 132 mg (49%), yellow crystalline solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.30 (s, 9H, *t*Bu), 4.34 (s, 2H, OCH$_2$), 7.57 (d, ^3J = 9.2 Hz, 2H, Ar), 8.16 (d, ^3J = 9.2 Hz, 2H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$) δ 27.5, 51.0, 74.8, 83.0, 92.7, 123.5, 130.0, 132.4, 147.1. IR (KBr, cm^{-1}) $\nu_{\max}$ 3105.8, 2976.5, 2862.7 (C–H, C–C), 2220.3 (C$\equiv$C), 1593.4 (C$=$C), 1342.6 (symm NO$_2$). MS (*m*/*z*, EI, 70 eV) 233 ([M$^+$], 0.3), 218 ([M − CH$_3$]$^+$, 10.4), 160 ([M − *t*BuO]$^+$, 100), 57 ([*t*Bu]$^+$, 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(PPh$_3$)$_2$Cl$_2$ (35.1 mg, 0.05 mmol; 5 mol% *vs.* **3d**), (CH$_3$CH$_2$CH$_2$CH$_2$C$\equiv$C)$_4$Sn **1f** (121.9 mg, 0.275 mmol), Pr$_2$NH (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 NH$_2$ 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. ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.96 (t, ^3J = 7.3 Hz, 3H, Me), 1.44–1.53 (m, 2H, CH$_2$), 1.58–1.65 (m, 2H, CH$_2$), 2.45 (t, ^3J = 6.9 Hz, 2H, CH$_2$C$\equiv$), 7.51 (d, ^3J = 8.7 Hz, 2H, Ar), 8.15 (d, ^3J = 8.7 Hz, 2H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$) 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}) $\nu_{\max}$ 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 NO$_2$). MS (*m*/*z*, EI, 70 eV) 203 ([M$^+$], 39.9), 188 ([M − CH$_3$]$^+$, 58.3), 174 ([M − CH$_2$CH$_3$]$^+$, 6.6), 157 ([M − NO$_2$]$^+$, 17.9).

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

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