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Strategies for the synthesis of bi- and triarylic materials starting from commercially available phenols

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Abstract

A series of arylstannanes have been synthesized, through an $S_{RN}1$ mechanism, in good to excellent yields (74–99%) by the photostimulated reaction of trimethyl stannyl ion with substrates supporting different nucleofugal groups. The arylstannanes thus obtained were suitable intermediates for Stille cross-coupling reactions leading to asymmetric bi- and triaryl compounds in acceptable global yields. An attractive feature of this route is that simple commercially available benzenediols, chloro- and methoxy phenols might be useful starting substrates, leading the latter to higher global yields of products in fewer steps. The strategies proposed open a broad synthetic tool.

Keywords: SRN1; Stille reaction; Arylstannanes; Biphenyls; Terphenyls

1. Introduction

Pd-catalyzed cross-coupling reaction has become a very important tool in organic synthesis [1]. Among others, Pd-catalyzed cross-coupling of organotin compounds with carbon electrophiles (the Stille reaction) has been a versatile method for C–C bond formation [2]. In connection with the synthetic importance of these reactions, we are interested in searching new routes to aryl- and vinylstannanes. Thus, application of $S_{RN}1$ reactions [3] to the synthesis of aryl- [4] and vinylstannanes [5] is currently in progress in our laboratory. This alternative route to the synthesis of organostannanes avoids the use of Grignard reagents or organolithium compounds. Recently [4c,4d,4e], we have demonstrated that a triorganostannyl group (Me_3Sn– and Ph_3Sn–) can, with interposition of one additional step, be introduced in place of a phenolic hydroxy group. Specifically, phenols are converted into their diethyl aryl phosphate esters (ArDEP) which on reaction with sodium triorganostannides (Me_3SnNa or Ph_3SnNa) in liquid ammonia afford aryltriorganostannanes by the $S_{RN}1$ mechanism in good to excellent yields (50–100%). It should be noted that, under similar conditions, substrates containing two leaving groups (Cl and DEP) also afford the related disubstitution product in high yield [4d].

Because of their interesting properties, there is a growing interest in the synthesis of valuable bi- and triaryls. Herein we report the synthesis of some trimethylstannyl derivatives and their potential appliance to the construction of mixed bi- and triarylic materials. The organic synthetic strategy proposed is based on the successive selective substitution of suitable leaving groups with trimethyltin anion followed by Pd-catalyzed cross-coupling reactions. An attractive feature of this approach is that simple commercially available derivatives such as benzenediols, chloro- and methoxy phenols might be useful starting substrates.

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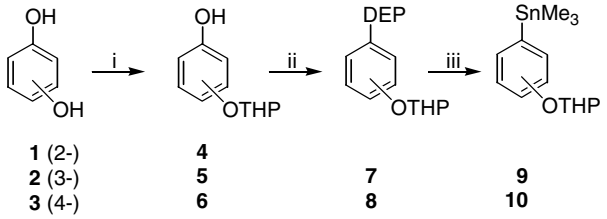
2. Results and discussion

We initiated our investigations employing 1,2-, 1,3- and 1,4-benzenediols as starting materials. The introduction of the first trimethylstannyl group in the aromatic moiety, i.e., the synthesis of the corresponding mono trimethylstannyl derivatives from these substrates, was carried out as is sketched in Scheme 1.

We decided to use tetrahydropyranyl as protecting group taking into account that the hydroxyl group may be easily regenerated under mild conditions. Desymmetrization of benzenediols was carried out with one equivalent of DHP [6a] (step i) affording, in all cases, the desired mono-ether in 30–40% yield, together with starting material (10–30%) and the related di-ether (20–30%). It should be mentioned that each component of the obtained mixtures could be isolated, quantitatively, by column chromatography on silica gel. In the second step (step ii) it was observed that meanwhile the reaction of **5** and **6** with diethyl phosphite led to the corresponding diethyl aryl phosphates **7** and **8** in very good yields (85% and 88%, respectively), the reaction of **4** with diethyl phosphite did not give the desired product (probably because of steric factors) and a complex mixture was obtained. Finally, the photostimulated reaction of **7** and **8** with trimethylstannyl sodium (**11**) (step iii) led, after 4 h, to trimethyl(3-tetrahydro-*2H*-2-pyranyloxyphenyl)stannane (**9**, 84%) and trimethyl(4-tetrahydro-*2H*-2-pyranyloxyphenyl)stannane (**10**, 82%), respectively (Table 1, entries 1 and 2). Thus, the mono-stannylated products **9** and **10** were both obtained in 25% overall yield from **2** and **3**. The low yields obtained were essentially owed to the desymmetrization reaction of benzenediols where substantial starting material was lost.

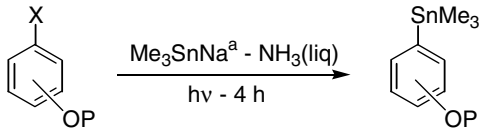
Taking into account that Cl is also a good nucleofugal group in $S_{RN}1$ reactions [4d], we considered of interest to carry out the synthesis of the mono-trimethylstannyl derivatives from commercially available chlorophenols. The route of synthesis is sketched in Scheme 2.

In order to compare the yields of these reactions, we used again tetrahydropyranyl as protecting group. The tetrahydropyranyl ethers **14** and **15** were obtained in 90% and 92% yield from **12** to **13**, respectively [6b].



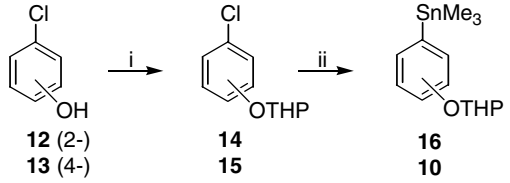
Scheme 1. Reagents and conditions (i) DHP, $AlCl_3$. (ii) $HPO(OEt)^3$, NEt^3, CCl_4 (iii) Me_3SnNa, NH_3(liq.), hν.

Table 1
Synthesis of arylstannanes by the photostimulated reaction of ArDEP with **11**



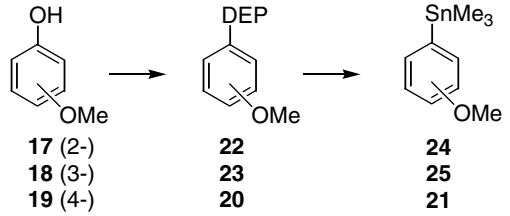
Entry	X[b]	OP[c]	Product and yield (%)[d]
1	DEP	3-OTHP	**9**; 84
2	DEP	4-OTHP	**10**; 82
3	Cl	2-OTHP	**16**; 85
4	Cl	4-OTHP	**10**; 85
5	DEP	4-OMe	**21**; 81[e]
6	DEP	2-OMe	**24**; 74
7	DEP	3-OMe	**25**; 90

[a] Substrate/Me_3 SnNa = 1:1.2.
[b] DEP = $OP(O)(OEt)_2$.
[c] THP = tetrahydropyranyl.
[d] Isolated yield of pure products.
[e] Ref. [4d].



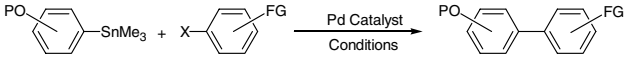
Scheme 2. Reagents and conditions (i) DHP, p-TsOH. (ii) Me_3SnNa, NH_3(liq.), hν.

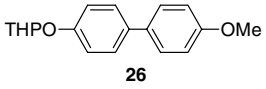
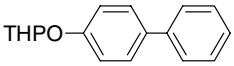
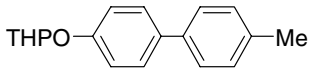
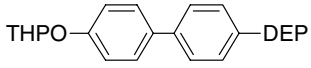
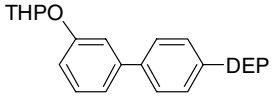
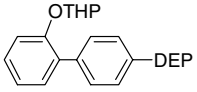
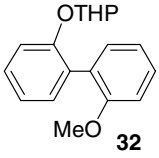
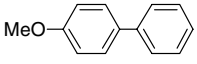
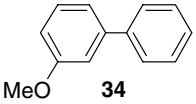
The subsequent photostimulated reaction of **14** and **15** with **11** in liquid ammonia rendered the trimethylstannyl derivatives in excellent yields. Thus, trimethyl(2-tetrahydro-*2H*-2-pyranyloxyphenyl)stannane (**16**) and its isomer **10** were both obtained in 85% yield (Table 1, entries 3 and 4). The overall yields of **16** and **10**, from **12** and **13**, were 77% and 78%, respectively; i.e., they were three times higher compared with those obtained from benzenediols. Since the low yields obtained from benezenediols as starting materials were owed to the desymmetrization reaction, we thought that this problem could be solved synthesizing the trimethylstannyl derivatives from commercially available desymmetrized dihydroxyphenols such as 2- (**17**), 3- (**18**) and 4-methoxy phenol (**19**), as is sketched in Scheme 3. We have previously proved that the diethyl phosphate ester **20**, derived



Scheme 3.

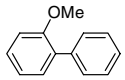
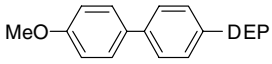
Table 2
Biphenyl substrates obtained by Pd-catalyzed cross-coupling reactions of arylstannanes with haloarenes



Entry	OP (No.)	X	FG	Pd Catalyst (mol%)[a]	Conditions			Product (No.)	Yield (%)[b,c]
					Solvent	Temp (°C)	Time (h)		
1	4-OTHP, **10**	I	4-OMe	$PdCl_2(PPh_3)_2$(2)	DMF	80	3	 **26**	50(5)
2	**10**	Br	–	”	”	”	3	 **27**	81
3	**10**	I	4-Me	”	”	”	24	 **28**	35(26)
4	**10**	Br	4-DEP	”	”	”	3	 **29**	70(18)
5	3-OTHP, **9**	Br	”	”	”	”	48	 **30**	4
6	**9**	”	”	$Pd(PPh_3)_4$(5)	Toluene	110	20	30	60(14)
7	2-OTHP, **16**	”	”	$PdCl_2$ $(PPh_3)_2$(2)	DMF	80	48	 **31**	5
8	**16**	”	”	$Pd(PPh_3)_4$(5)	Toluene	110	20	31	35(19)
9	**16**	–	2-OMe	$PdCl_2(PPh_3)_2$(20)[d]	DMF	80	48	 **32**	25(14)
10	4-OMe, **21**	”	–	$PdCl_2(PPh_3)_2$(2)	DMF	80	20	 **33**	75
11	3-OMe, **25**	”	–	$Pd(PPh_3)_4$(2)	Toluene	110	20	 **34**	65

(*continued on next page*)

Table 2 (*continued*)

Entry	OP (No.)	X	FG	Pd Catalyst (mol%)[a]	Conditions			Product (No.)	Yield (%)[b,c]
					Solvent	Temp (°C)	Time (h)		
12	**25**	”	–	$PdCI_2(PPh_3)_2$(2)	DMF	80	20	34	87
13	2-OMe, **24**	”	–	$PdCI_2(PPh_3)_2$(2)	DMF	80	20	 **35**	73
14	**21**	Br	4-DEP	$Pd(PPh_3)_4$(2)	Toluene	110	48	 **36**	73

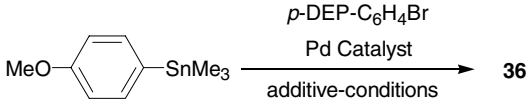
[a] With respect to arylstannane.
[b] Isolated yield of pure products.
[c] Yields in brackets refer to corresponding deprotected hydroxy compound obtained together with the cross-coupling product.
[d] With addition of CuI (1.25 equiv.), CsF (13.8 equiv.) and BHT (a crystal).

from **19**, reacted with **11** in liquid ammonia, yielding trimethyl(4-methoxyphenyl)stannane (**21**) in 81% yield [4d] (Table 1, entry 5). In the same way, the photostimulated reaction of **11** with *O*,*O*-diethyl *O*-2-methoxyphenyl phosphate (**22**) and *O*,*O*-diethyl *O*-3-methoxyphenyl phosphate (**23**), synthesized in 78% and 89% yield from the corresponding phenols **17** and **18**, led to the desired trimethylstannyl derivatives **24** [7] and **25** [7] in 74% and 90% yield, respectively. Thus, **21**, **24** and **25** were obtained in very good overall yields (71%, 58% and 80%, respectively) from economic commercially available substrates.

With the aim of determining the feasibility of the synthetic strategy proposed, we carried out a series of Stille cross-coupling reactions with the arylstannanes obtained in order to synthesize a series of biaryls. As seen from Tables 2 and 3, the choice of the appropriate catalytic system is very important for the success of the reaction.

First, we carried out the reactions between tetrahydropyranyl ethers **9**, **10** and **16** and aryl halides. The results obtained are summarized in Table 2. The coupling reaction of **10** with 4-iodoanisol in the presence of $Cl_2Pd(PPh_3)_2$ (2%) in DMF at 80 °C for 3 h, led to 4′-methoxybiphenyl-4-yl tetrahydro-*2H*-2-pyranyl ether (**26**) in 50% yield together with the corresponding deprotected hydroxy compound (5%) (entry 1). Under a similar catalytic protocol, biphenyl-4-yl tetrahydro-*2H*-2-pyranyl ether (**27**) and 4′-methylbiphenyl-4-yl tetrahydro-*2H*-2-pyranyl ether (**28**) were obtained from **10** by reaction with either bromobenzene or 4-iodotoluene in 81% (3 h) and 35% (24 h) yield, respectively (en-

Table 3
Different catalytic protocols for the synthesis of **36** from **21**



21

Pd catalyst (mol%)[a]	Ratio 21:ArBr	Additive (mol%)[a]	Solvent and conditions	Yield 33 (%)[b]
$PdCI_2(PPh_3)_2$ (**2**)	1.1:1	None	DMF 80 °C, 48 h	36[c]
$PdCI_2(PPh_3)_2$ (**5**)	1.3:1	CuI(10)	DMF r.t., 20 h	40[c]
$Pd_2(dba)_3$(2.8)$AsPh_3$(23)	1:1.2	CuI(57)	DMF 70 °C, 21 h	–[d]
$Pd(PPh_3)_4$ (**5**)	1:1.2	None	Toluene 110 °C, 48 h	60
$Pd(PPh_3)_4$ (**2**)	1:1.2	None	Toluene 110 °C, 48 h	73

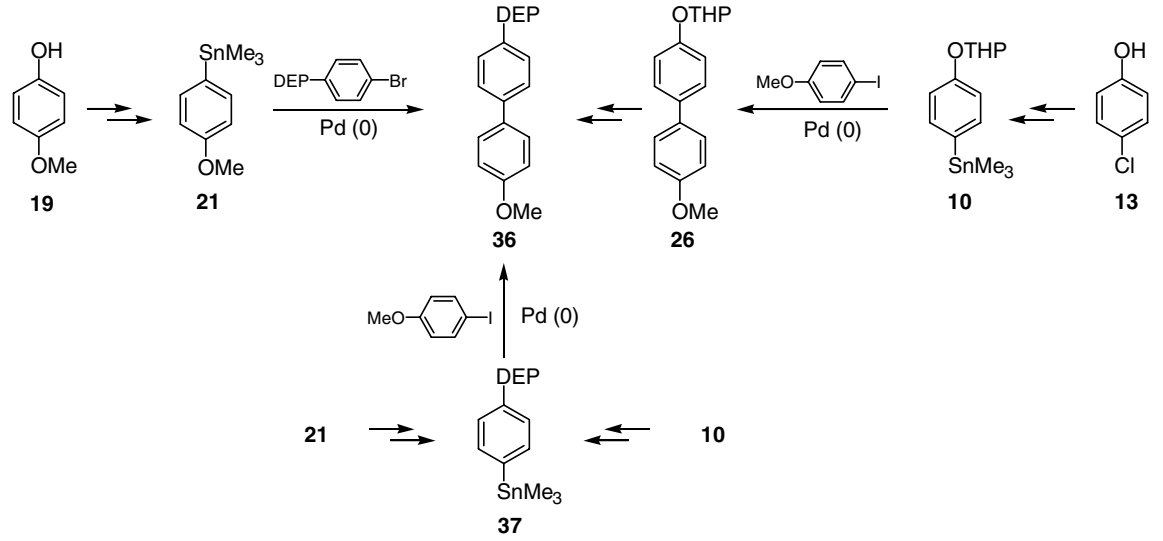
[a] With respect to the minor reagent.
[b] Isolated yield of pure products.
[c] Together with homocoupling and ‘‘scrambling’’products.
[d] Complex mixture.

tries 2 and 3). It should be emphasized that compound **28** was also obtained together with a significant amount (26%) of the related deprotected hydroxy compound. The cross-coupling reaction of **10** with *O*,*O*-diethyl *O*-4-bromophenyl phosphate yielded the desired product, i.e., *O*,*O*-diethyl *O*-4′-tetrahydro-*2H*-2-pyranyloxybiphenyl-4-yl phosphate (**29**) (70%) together with the corresponding deprotected hydroxy compound in 18% yield (entry 4).

On the other hand, the same catalytic protocol proved to be inefficient in the reaction between compound **9** and *O*,*O*-diethyl *O*-4-bromophenyl phosphate. An analogous result was obtained in the reaction carried out with compound **16**. In both cases, the desired cross-coupling products were detected in very low yields (ca. 5%) (entries 5 and 7). These coupling reactions worked better in presence of a catalytic amount of $Pd(PPh_3)_4$ (5%) in refluxing toluene. Thus, compounds **9** and **16** reacted with *O*,*O*-diethyl *O*-4-bromophenyl phosphate providing *O*,*O*-diethyl *O*-3′-tetrahydro-*2H*-2-pyranyloxybiphenyl-4-yl phosphate (**30**) (20 h) and *O*,*O*-diethyl *O*-2′-tetrahydro-*2H*-2-pyranyloxybiphenyl-4-yl phosphate (**31**) (20 h) in 60% and 35% yield, respectively (entries 6 and 8). In both cases the deprotected hydroxy compounds were also detected (14% and 19%, respectively). Typical byproducts found (CG/MS) in these reactions are the biaryls derived from homocoupling of the stannane and Ar–Ph derived from phenyl transfer from the ligand, which makes difficult the purification of the desired compounds. The reaction of **16** with 2-iodoanisol, in the presence of $Cl_2Pd(PPh_3)_2$ (20%), CuI, CsF and in DMF (80 °C, 48 h) [8], led to the expected cross-coupling product 2′-methoxybiphenyl-2-yl tetrahydro-*2H*-2-pyranyl ether (**32**) in 25% yield together with the corresponding deprotected compound (14%) (entry 9). As it is known, steric hindrance of the coupling position by *ortho* substituents usually has a negative effect on the yield. All the results obtained showed that the partial deprotection of the hydroxy group took place under the employed catalytic protocols.

We also carried out the cross-coupling reactions of (2-) (**24**), (3-) (**25**) and (4-methoxyphenyl)trimethylstannane (**21**) with different aryl halides. The best results obtained are summarized in Table 2. In our initial experiments, $Cl_2Pd(PPh_3)_2$ (2%) in DMF at 80 °C, proved to be an efficient protocol for the cross-coupling reaction of **21**, **24** and **25** with bromobenzene leading to biaryls **33**–**35** [9] in good yields (entries 10–13). Nevertheless, the same catalytic protocol proved to be inefficient in the cross-coupling reaction of **21** with *O*,*O*-diethyl *O*-4-bromophenyl phosphate. Thus, this reaction yielded only 36% of *O*,*O*-diethyl *O*-4′-methoxybiphenyl-4-yl phosphate (**36**) together with large amounts of undesired homocoupling and "scrambling" products (CG/MS). When we carried out the reaction under similar conditions but in the presence of Cu(I) [10], the yield of **36** was slightly increased (40%). In order to minimize the "scrambling" product we used $Pd_2(dba)_3$, CuI and $AsPh_3$ in DMF [11] as catalytic protocol. Unfortunately, under these conditions we could not detect the presence of biaryl **36** and a complex mixture was obtained. These coupling reactions worked better in the presence of catalytic amounts of $Pd(PPh_3)_4$ (5% and 2%) in refluxing toluene (48 h). Under these conditions, product **36** was obtained in 60% and 73% yields, respectively. These results are summarized in Table 3.

It should be mentioned that compound **36** could also be synthesized from compound **26** by deprotection of the hydroxy group and generation of the phosphate ester. The global yields of both synthetic procedures were 52% from 4-methoxyphenol (**19**) (three steps: 71% in the two first and 73% in the last one) and 28% from 4-chlo-



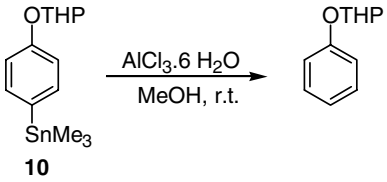
Scheme 4.

rophenol (**13**) (five steps: 78% in the two first, 50% in the third one and 72% in the two last steps) (Scheme 4).

Another route to compound **36** is also shown in Scheme 4. In order to propose different synthetic approaches, we considered that it would be interesting to synthesize aryltin compounds containing a DEP group, such as **37**, to be used as starting substrates in cross-coupling reactions.

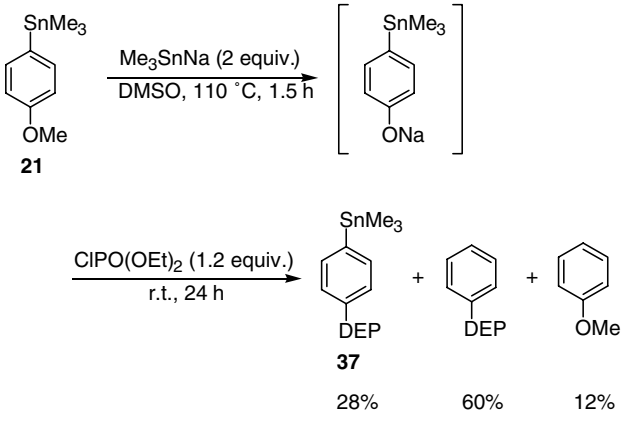
In principle, either compounds **10** or **21** might be used as starting materials for the synthesis of **37** by deprotection of the ether function and generation of DEP.

Unfortunately, under deprotection conditions [6], compound **10** led only to phenyl tetrahydro-*2H*-2-pyranyl ether due to aryl-tin bond cleavage (Eq. (1))



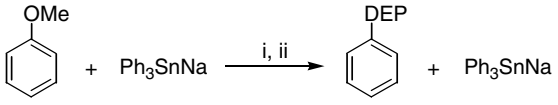
10 (1)

On the other hand, the reaction using compound **21** as starting substrate implies the cleavage of an aryl methyl ether. With this purpose, extremely harsh conditions such as BBr_3 or refluxing MeMgI [12] could not be applied to compound **21** because they would also lead to aryl-tin bond cleavage. Taking into account that aryl methyl ethers are susceptible to attack by powerful nucleophiles in dipolar aprotic solvents [12] we considered that it would be possible to cleave the methyl–oxygen bond with trimethyl tin anion in DMSO. Furthermore, the phenoxide ion thus obtained would be trapped with diethyl chloro phosphate [$ClOPO(OEt)_2$] yielding the aryl diethyl phosphate **37** in a "one-pot" reaction from compound **21**. We employed trimethyltin anion as nucleophile in order to minimize probable secondary reactions between the nucleophile and the aryl-tin bond of the substrate.



21 **37** (2)

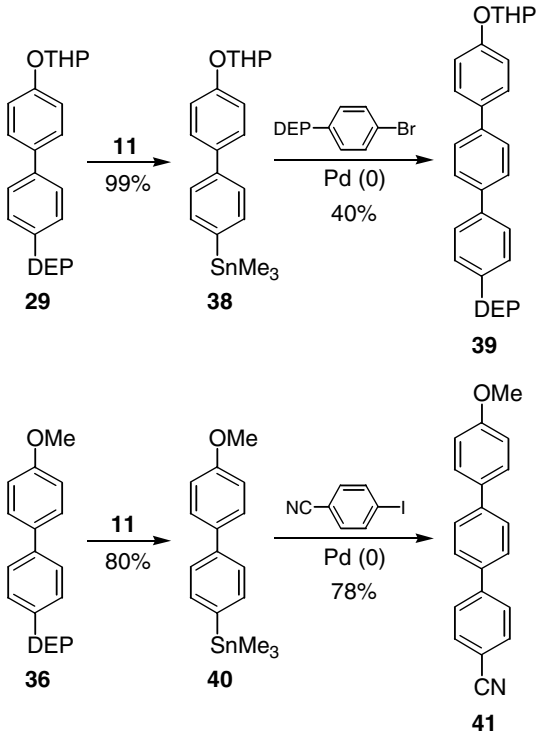
We carried out a series of reactions between **21** and **11** in DMSO. In an effort to improve the yield of **37**, the reaction conditions were varied with respect to **21**/**11**/$ClOPO(OEt)_2$ ratios as well as reaction times. Unfortunately, under the conditions studied, the aryl-tin bond is also partially cleaved and compound **37** was obtained in low yield together with some amounts of anisol and *O*,*O*-diethyl *O*-phenyl phosphate. In Eq. (2) are shown the conditions which led to higher yields of **37**. Although it is possible to purify compound **37** by column chromatography on silicagel, the low reaction yield prevented us to consider the strategy proposed in Scheme 4 as a good alternative. Similar reactions were carried out with isomers **24** and **25**, leading to analogous results. Nevertheless, the presence of *O*,*O*-diethyl *O*-phenyl phosphate in the reaction mixtures indicates that, under the reaction conditions studied, it is possible to cleave the methyl–oxygen bond and to generate the corresponding phosphate ester. Based on this observation we carried out a series of reactions with anisol and triphenyltin anion (Ph_3SnNa) in DMSO, in order to find the best reaction conditions for the synthesis of diethyl aryl phosphates from anisols in a "one-pot" reaction. We used Ph_3SnNa instead of **11** with the aim of recovering the tetraorganotin formed. We found that the reaction of anisol, Ph_3SnNa and $ClOPO(OEt)_2$ in 1/2/2.4 ratio in DMSO, led to the desired phenyl diethyl phosphate ester in quantitative yield (Eq. (3)).



Reagents and conditions i) DMSO, 110 °, 12 h. ii) $ClPO(OEt)_2$, r.t., 24 h (3)

It should be mentioned that both, the phosphate ester and the triphenylmethylstannane generated in the reaction were recovered, quantitatively, from the mixture by column chromatography on silicagel. These reaction conditions were used forward.

The biaryls resumed in Table 2 could be suitable starting materials for the synthesis of triaryl compounds. For instance, compounds supporting a DEP group, such as **29**–**31** and **36**, may be excellent starting substrates to generate the corresponding trimethyltin derivatives which, by posterior coupling reactions with the appropriate aryl halide, would lead to the expected triaryl material [13]. In Scheme 5 are shown two of such reactions. The photostimulated reaction of **29** with **11** yielded the corresponding trimethyltin derivative **38** (99%). The subsequent coupling reaction of **38** with *O*,*O*-diethyl *O*-4-bromophenyl phosphate led to the desired triaryl compound 4-(diethoxyphosphinyl)oxy-4″-tetrahydro-*2H*-2-pyranyloxy-[1,1′;4′,1″]terphenyl (**39**, 40%). On the other hand, the photostimulated reaction of **36** and **11** led to trimethyl(4′-methoxybiphenyl-4-yl)stannane (**40**) in 80% yield. The coupling reaction of



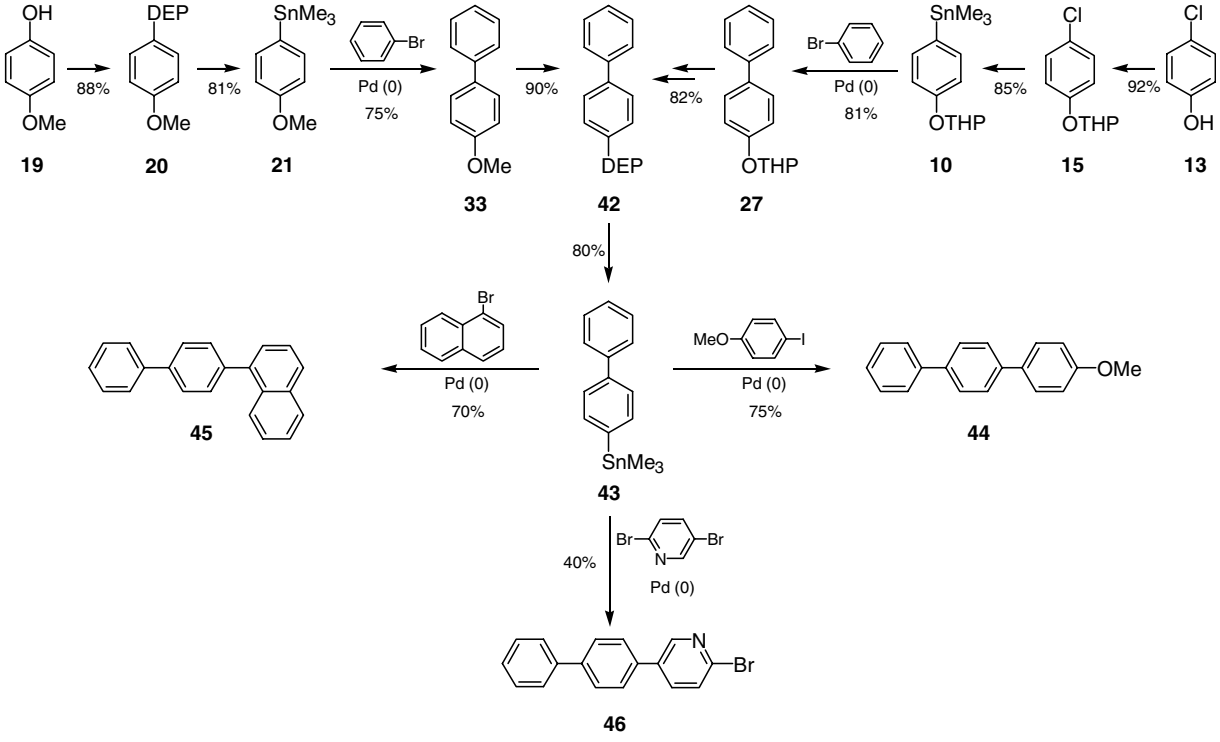
Scheme 5.

40 with 4-iodobenzonitrile gave 4-methoxy-4″-cyano [1,1′;4′,1″]terphenyl (**41**, 78%).

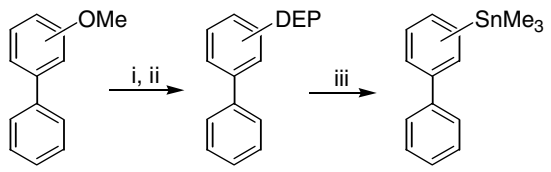
Alternatively, biaryl compounds **27**, **28** and **32**–**35** may also be suitable starting materials for the synthesis of triaryls. In order to prove the feasibility of our proposal and to compare results, we carried out a series of reactions with compounds **27** and **33** as starting materials as is sketched in Scheme 6.

Whereas compound **27** is an example of DHP as protecting group, compound **33** is an example of Me as protecting group. The deprotection and generation of the diethyl aryl phosphate ester **42** implies two sequential steps from **27**, with a global yield of 82%. On the other hand, **42** (90%) is obtained from **33** through the ''one-pot'' reaction mentioned above (see Section 3). The posterior photostimulated reaction of **42** with **11** yielded compound **43** (80%) [4d]. Therefore, the global yield of **43** was 72% (two steps) and 64% (three steps) starting from **33** and **27**, respectively. The coupling reaction of **43** with 4-iodoanisol, 1-bromonaphthalene and 2,5-dibromopyridine yielded the corresponding triaryl compounds, i.e., 4-methoxy-[1,1′; 4′, 1″]terphenyl (**44**, 75%) [14], 1-(biphenyl-4-yl)naphtalene (**45**, 70%), and 5-(biphenyl-4-yl)-2-bromopyridine (**46**, 40%). As shown in Scheme 6, these reactions illustrate the successive selective replacement of two substituents supported by an aryl substrate (compounds **13** and **19**).

Similar reaction schemes could be carried out starting from compounds **28**, **32**, **34** and **35**. It should be mentioned that we have proved that compounds **34** and **35** yielded the corresponding phosphate esters **47** (85%) and **48** (75%) [15] through a ''one-pot'' reaction, and that the photostimulated reaction of both esters with **11** in liquid ammonia led to the trimethyltin derivatives **49** [16]



Scheme 6.



34 (3-) **35** (2-) **47** **48** **49** **50**

Reagents and conditions i) Ph_3SnNa, DMSO. ii) $ClPO(OEt)_2$. iii) Me_3SnNa, NH_3(liq.), hν

Scheme 7.

and **50** [17] in good yields (75% and 78%, respectively). The global yield of stannanes **49** and **50** starting from **34** and **35** were 64% and 58%, respectively (Scheme 7).

The present results show the utility of readily accessible substances such benzenediols, chlorophenols and methoxyphenols for preparing asymmetric bi- and triaryl compounds. All the reactions involved – $S_{RN}1$ and Pd cross-coupling reactions – are regioselective, therefore it would be possible to synthesize tailored bi- and triarylic materials by choosing appropriately substituted aromatic moieties. The strategies proposed open a broad synthetic tool. The results obtained demonstrate that commercially available desymmetrized dihydroxybenzenes **17**–**19** are the best starting materials. They lead to higher global yields of the expected products in a fewer number of steps.

We have also proved that it is possible to introduce a trimethylstannyl group in an aryl moiety in place of a methoxy group, with interposition of one additional step. Thus, in a "one-pot" reaction a series of anisols have been converted to the corresponding arylDEP esters with high yields (75–90%). In a second step, the substitution reaction led to the corresponding stannylated substrate in excellent yields. It should be emphasized that an aryl-tin bond is highly reactive towards diverse electrophiles [18]. Therefore, an arylmethyl ether should be considered as a potential substrate for the introduction of diverse electrophiles in an aromatic moiety, opening important synthetic routes to different reaction schemes. Further work is in progress to study the scope of this reaction.

3. Experimental

3.1. General methods

Irradiation was conducted in a reactor made of Pyrex, equipped with four 250 W UV lamps emitting maximally at 350 nm (Philips Model HPT, water-refrigerated). NMR spectra were recorded on a Bruker ARX 300 (300.1 MHz for ^1H, 75.5 MHz for ^{13}C, 111.9 MHz for ^{119}Sn) using $CDCl_3$ as solvent (except where it is otherwise stated) and $SiMe_4$ or $SnMe_4$ as internal reference. Mass spectra were obtained by use of a GC/MS HP 6890. Infrared spectra were recorded on a Nicolet–Nexus FTIR. Most of the reagents and catalyst were commercially available. Diethyl aryl phosphate esters were prepared by the method of Kenner [19] and characterized by IR [20] and NMR spectroscopy. All manipulations were performed under nitrogen or argon. The solvents used were dried and distilled in accordance with standard procedures.

3.2. Photostimulated reaction of *O,O*-diethyl *O*-3-tetrahydro-2*H*-2-pyranyloxyphenyl phosphate (**7**) with Me_3SnNa (**11**) in liquid ammonia

The reactions were performed by following the same procedure in all cases. Into a 250-mL two-necked round-bottomed flask, equipped with a coldfinger condenser charged with acetone-liquid nitrogen, a nitrogen inlet and magnetic stirrer, were condensed 220 mL of sodium-dried ammonia. Me_3SnCl (1.10 mmol) was dissolved and sodium metal (2.53 mg atom) was added until the blue color persisted for at least 5 min. When the blue color disappeared, **7** (1.00 mmol) was added and the resulting solution was then irradiated with stirring for 4 h. The reaction was quenched by adding NH_4Cl in excess, and the ammonia was allowed to evaporate. The residue was treated with water and then extracted with diethyl ether. Ether extracts were washed with brine and dried over $MgSO_4$. Removal of the solvent left 0.286 g (0.841 mmol) of trimethyl(3-tetrahydro-2*H*-2-pyranyloxyphenyl)stannane (**9**) (84% yield, colorless oil). The product could be used for the coupling reaction without further purification, although the attempted purification by column chromatography on silica gel was unsuccessful due to decomposition. ^1H NMR ($CDCl_3$): δ 7.25–6.87 (m, 4H), 4.87 (m, 1H), 3.79 (m, 1H), 3.44 (m, 1H), 2.03–1.40 (m, 6H), 0.35 (s, $^2J_{HSn}$ = 55.3/53.0 Hz, 9H, $SnMe_3$); ^{13}C NMR: δ 157.11 (C_{aryl}), 143.99 ($^2J_{CSn}$ = 39.2 Hz, CH_{aryl}), 129.38 ($^1J_{CSn}$ = no, C_{aryl}), 129.29 (CH_{aryl}), 124.33 ($^3J_{CSn}$ = 29.7 Hz, CH_{aryl}), 116.51 ($^2J_{CSn}$ = 42.1 Hz, CH_{aryl}), 95.06 (CH), 63.29 (CH_2), 31.10 (CH_2), 25.87 (CH_2), 20.14 (CH_2), −9.17 ($^1J_{CSn}$ = 356.9/338.2 Hz, $SnCH_3$); ^{119}Sn NMR: δ −28.82; MS (*m*/*z*, relative intensity): 342 (1, M^+), 327 (3, $M^+ - 15$), 258 (11), 243 (100), 227 (2), 212 (16), 165 (8); HRMS (EI): *m*/*z* Calc. for $C_{14}H_{22}O_2Sn$ (M^+): 340.9261. Found: 340.9258.

3.3. Trimethyl(4-tetrahydro-2*H*-2-pyranyloxyphenyl)stannane (**10**)

The procedure described for compound **9** was followed using *O*,*O*-diethyl *O*-4-tetrahydro-2*H*-2-pyra-

nyloxyphenyl phosphate (**8**) (1.00 mmol) to give product **10** (0.280 g, 0.823 mmol, 82%) as a colorless oil. The product was used for the coupling reaction without further purification. ^{1}H NMR: δ 7.23 (d, $^3J_{HH}$ = 8.6 Hz, $^3J_{HSn}$ = 42.9 Hz, 2H), 6.89 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 5.27 (m, 1H), 3.86 (m, 1H), 3.54 (m, 1H), 2.03–1.34 (m, 6H), 0.09 (s, $^2J_{HSn}$ = 55.1/52.8 Hz, 9H, $SnMe_3$); ^{13}C NMR: δ 157.82 (C_{aryl}), 137.26 ($^3J_{CSn}$ = 40.5 Hz, CH_{aryl}), 134.02 ($^1J_{CSn}$ = no, C_{aryl}), 116.87 ($^2J_{CSn}$ = 48.7 Hz, CH_{aryl}), 96.51 (CH), 62.38 (CH_2), 30.79 (CH_2), 25.66 (CH_2), 19.19 (CH_2), −9.08 ($^1J_{CSn}$ = 350.9/335.7 Hz, $SnCH_3$); ^{119}Sn NMR: −30.43; MS (*m*/*z*, relative intensity): 342 (1, M^+), 327 (4, $M^+ - 15$), 258 (7), 243 (100), 227 (5), 212 (12), 165 (5); HRMS (EI): *m*/*z* Calc. for $C_{14}H_{22}O_2Sn$ (M^+): 340.9261. Found: 340.9267.

3.4. Trimethyl(2-tetrahydro-2H-2-pyranyloxyphenyl)stannane (16)

The procedure described for compound **9** was followed using 2-chlorophenyl tetrahydro-*2H* -2-pyranyl ether (**14**) (1.00 mmol) to give product **16** (0.290 g, 0.85 mmol, 85%) as a colorless oil. The product was used for the coupling reaction without further purification.^{1}H NMR: δ 7.54–7.25 (m, 4H), 5.51 (m, 1H), 3.93 (m, 1H), 3.66 (m, 1H), 2.12–1.58 (m, 6H), 0.35 (s, $^2J_{HSn}$ = 56.1/54.7 Hz, 9H, $SnMe_3$); ^{13}C NMR: δ 161.93 (C_{aryl}), 136.69 ($^3J_{CSn}$ = 26.4 Hz, CH_{aryl}), 130.55 (CH_{aryl}), 130.53 ($^1J_{CSn}$ = no, C_{aryl}), 122.00 ($^2J_{CSn}$ = 45.8 Hz, CH_{aryl}), 112.86 ($^3J_{CSn}$ = 22.3 Hz, CH_{aryl}), 96.20 (CH), 62.02 (CH_2), 30.76 (CH_2), 25.64 (CH_2), 19.02 (CH_2), −8.58 ($^1J_{CSn}$ = 360.3/344.5 Hz, $SnCH_3$); ^{119}Sn NMR: δ −31.77; MS (*m*/*z*, relative intensity): 342 (1, M^+), 327 (10, $M^+ - 15$), 258 (4), 243 (100), 227 (4), 212 (17), 165 (4); HRMS (EI): *m*/*z* Calc. for $C_{14}H_{22}O_2Sn$ (M^+): 340.9261. Found: 340.9256.

3.5. Trimethyl(4′-tetrahydro-2H-2-pyranyloxybiphenyl-4-yl)stannane (38)

The procedure described for compound **9** was followed using *O*,*O*-diethyl *O*-4′-tetrahydro-*2H*-2-pyranyloxybiphenyl-4-yl phosphate (**29**) (1.00 mmol). Crystallization from cold Et_2O gave 0.408 g (0.98 mmol, 98%) of product **38** as a white solid. M.p. 64–66 °C; ^{1}H NMR: δ 6.99–7.58 (m, 8H), 5.38 (m, 1H), 3.86 (m, 1H), 3.54 (m, 1H), 2.05–1.43 (m, 6H), 0.23 (s, $^2J_{HSn}$ = 54.9/53.0 Hz, 9H, $SnCH_3$); ^{13}C NMR: 157.07 (C_{aryl}), 141.22 (C_{aryl}), 140.72, ($^1J_{CSn}$ = no, C_{aryl}), 136.65 ($^3J_{CSn}$ = 36.9 Hz, CH_{aryl}), 135.05 (C_{aryl}), 128.50 (CH_{aryl}), 126.87 ($^2J_{CSn}$ = 46.9 Hz, CH_{aryl}), 117.14 (CH_{aryl}), 96.79 (CH), 62.48 (CH_2), 30.80 (CH_2), 25.66 (CH_2), 19.21 (CH_2), −9.10 ($^1J_{CSn}$ = 351.5/335.1 Hz, $SnCH_3$); ^{119}Sn NMR: δ −25.29; MS (*m*/*z*, relative intensity): 418 (1, M^+); 403 (2, $M^+ - 15$); 334 (8); 319 (100); 303 (1); 289 (32). HRMS (EI): *m*/*z* Calc. for $C_{20}H_{26}O_2Sn$ (M^+): 417.0234. Found: 417.0229.

3.6. Trimethyl(4′-methoxybiphenyl-4-yl)stannane (40)

The procedure described for compound **9** was followed using *O*,*O*-diethyl *O*-4′-methoxybiphenyl-4-yl phosphate (**33**) (1.00 mmol). Purification by column chromatography on silica gel (eluent: hexane:EtOAc, 8:2) gave 0.279 g (0.80 mmol, 80%) of product **40** as a white solid. M.p. 78–80 °C; ^{1}H NMR: δ 7.54–6.81 (m, 8H), 3.72 (s, 3H), 0.23 (s, $^2J_{HSn}$ = 55.2/53.9 Hz, 9H, $SnCH_3$), ^{13}C NMR: δ 159.67 (C_{aryl}), 141.32 (C_{aryl}), 140.68 ($^1J_{CSn}$ = 463.6/442.5 Hz, C_{aryl}), 136.69 ($^3J_{CSn}$ = 36.4 Hz, CH_{aryl}), 134.26 (C_{aryl}), 128.59 (CH_{aryl}), 126.84 ($^2J_{CSn}$ = 45.7 Hz, CH_{aryl}), 114.70 (CH_{aryl}), 55.75 (CH_3), −9.09 ($^1J_{CSn}$ = 350.9/335.7 Hz, $SnCH_3$); ^{119}Sn NMR: δ −27.10; MS (*m*/*z*, relative intensity): 348 (11, M^+), 333 (100, M − 15), 303 (37), 286 (5), 258 (6); HRMS (EI): *m*/*z* Calc. for $C_{16}H_{20}OSn$ (M^+): 346.9332. Found: 346.9347.

3.7. Cross-coupling reaction of trimethyl(3-methoxyphenyl)stannane (25) with PhBr catalyzed by $PdCl_2(PPh_3)_2$: General procedure A

A two-necked, 50 mL round-bottomed flask fitted with a reflux condenser, nitrogen inlet, magnetic stirrer and rubber septum, was charged with a mixture of bromobenzene (1.20 mmol) and $PdCl_2(PPh_3)_2$ (2 mol%) suspended in dry DMF (20 mL). **25** (1.00 mmol) was added dropwise via syringe and the mixture was stirred at 80 °C (oil bath) for 20 h (monitoring the disappearance of the stannane by TLC). After the resulting black precipitates were filtered through a silical gel pad, water (50 mL) was added and then the solution was extracted with ethyl ether (3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by dry column vacum chromatography (DCVC) [21] on silica gel (hexane:EtOAc, 9:1–6:4) to give 0.160 g (0.869 mmol, 87%) of 3-methoxybiphenyl (**34**) as a colorless oil. ^{1}H NMR: δ 7.50–7.43 (m, 2H), 7.34–7.26 (m, 2H), 7.25–7.17 (m, 2H), 7.10–6.99 (m, 2H); 6.77 (m, 1H), 3.71 (s, 3H); ^{13}C NMR: δ 160.51 (C_{aryl}), 143.27 (C_{aryl}), 141.63 (C_{aryl}), 130.22 (CH_{aryl}), 129.21 (CH_{aryl}), 127.88 (CH_{aryl}), 127.67 (CH_{aryl}), 120.16 (CH_{aryl}), 113.45 (CH_{aryl}), 113.20 (CH_{aryl}), 55.72 (CH_3) [9].

3.8. Cross-coupling reaction of 25 with PhBr catalyzed by $Pd(PPh_3)_4$: General procedure B

A two-necked, 50 mL round-bottomed flask fitted with a reflux condenser, a nitrogen inlet, a magnetic stirrer and rubber septum, was charged with a mixture of

bromobenzene (1.20 mmol) and $Pd(PPh_3)_4$ (2 mol%) suspended in dry toluene (20 mL). 25 (1.00 mmol) was added dropwise via syringe and the mixture was heated to 110 °C (oil bath) for 20 h. The reaction mixture was diluted with dietyl ether and then was filtered through a silical gel pad. The organic solution was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by DCVC on silica gel (eluent: hexane:EtOAc, 9:1–6:4) to give 0.118 g (0.65 mmol, 65%) of **34**.

3.9. 4′-Methoxybiphenyl-4-yl tetrahydro-2H-2-pyranyl ether (*26*)

General procedure A was followed to prepare the title compound by reaction of **10** (1.00 mmol) with 4-iodoanisol (1.20 mmol). The crude product was purified by column chromatography (eluent: hexane:EtOAc, 8:2) to give **26** (0.142 g, 0.501 mmol, 50%) as a white solid. M.p. 91–93 °C; ^{1}H NMR: δ 7.50–7.28 (m, 4H), 7.09–6.81 (m, 4H), 5.37 (m, 1H), 3.87 (m, 1H), 3.76 (s, 3H), 3.60–3.46 (m, 1H), 2.04–1.46 (m, 6H); ^{13}C NMR: δ 159.11 (C_{aryl}), 156.56 (C_{aryl}), 134.79 (C_{aryl}), 134.75 (C_{aryl}), 128.19 (CH_{aryl}), 128.06 (CH_{aryl}), 117.13 (CH_{aryl}), 114.54 (CH_{aryl}), 96.81 (CH), 62.47 (CH_2), 55.74 (CH_3), 30.79 (CH_2), 25.64 (CH_2), 19.21 (CH_2); MS (*m*/*z*, relative intensity): 284 (1, M^+), 200 (100, M^+-84), 185 (53), 157 (31), 128 (15), 102 (4); HRMS (EI): *m*/*z* Calc. for $C_{18}H_{20}O_3$ (M^+): 284.3536. Found: 284.3529.

3.10. 4′-Methylbiphenyl-4-yl tetrahydro-2H-2-pyranyl ether (*28*)

General procedure A was followed to prepare the title compound by reaction of **10** (1.00 mmol) with 4-iodotoluene (1.20 mmol). The crude product was purified by DCVC (eluent: hexane:EtOAc, 9:1) to give **28** (0.094 g, 0.35 mmol, 35%) as a white solid. M.p. 89–90 °C; ^{1}H NMR: δ 7.85–7.31 (m, 8H), 5.70 (m, 1H), 4.18 (m, 1H), 3.86 (m,1H), 2.62 (s, 3H), 2.38–1.85 (m, 6H); ^{13}C NMR: δ 160.99 (C_{aryl}), 136.79 (C_{aryl}), 135.01 (C_{aryl}), 129.81 (CH_{aryl}), 128.29 (CH_{aryl}), 127.04 (CH_{aryl}), 117.08 (CH_{aryl}), 96.79 (CH), 62.46 (CH_2), 30.77 (CH_2), 25.63 (CH_2), 21.46 (CH_3), 19.19 (CH_2); MS (*m*/*z*, relative intensity): 268 (1, M^+), 184 (100, M^+-84), 165 (4), 152 (4), 139 (2), 128 (3); HRMS (EI): *m*/*z* Calc. for $C_{18}H_{20}O_2$ (M^+): 268.3542. Found: 268.3539.

3.11. O,O-Diethyl O-4′-tetrahydro-2H-2-pyranyloxybiphenyl-4-yl phosphate (*29*)

General procedure A was followed to prepare the title compound by reaction of **10** (1.00 mmol) with *O*-*O*-diethyl *O*-4-bromophenyl phosphate (1.20 mmol). The crude product was purified by DCVC (eluent: hexane:EtOAc, 7:3) to give **29** (0.284 g, 0.70 mmol, 70%) as a pale yellow liquid. ^{1}H NMR: δ 7.52–6.99 (m, 8H), 5.38 (m, 1H), 4.16 (m, 4H), 3.85 (m, 1H), 3.55 (m, 1H), 2.08–1.46 (m, 6H), 1.28 (dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 0.9 Hz, 6H); ^{13}C NMR: δ 157.05 (C_{aryl}), 150.36 ($^2J_{CP}$ = 7.0 Hz, C_{aryl}), 138.22 (C_{aryl}), 134.05 (C_{aryl}), 128.35 (CH_{aryl}), 128.35 (CH_{aryl}), 120.57 ($^3J_{CP}$ = 4.7 Hz, CH_{aryl}); 117.18 (CH_{aryl}), 96.79 (CH), 64.99 ($^2J_{CP}$ = 6.5 Hz, CH_2), 62.45 (CH_2), 30.75 (CH_2), 25.61 (CH_2), 19.16 (CH_2); 16.50 ($^3J_{CP}$ = 6.5 Hz, CH_3); HRMS (EI): *m*/*z* Calc. for $C_{21}H_{27}O_6P$ (M^+): 406.4124. Found: 406.4126.

3.12. O,O-Diethyl O-3′-tetrahydro-2H-2-pyranyloxybiphenyl-4-yl phosphate (*30*)

General procedure B with the adjustment of 5 mol% of $Pd(PPh_3)_4$, was followed to prepare the title compound by reaction of **9** (1.00 mmol) with *O*,*O*-diethyl *O*-4-bromophenyl phosphate (1.20 mmol). The crude product was purified by DCVC (eluent: hexane:EtOAc, 7:3) to give **30** (0.244 g, 0.60 mmol, 60%) as an orange oil. ^{1}H NMR: δ 7.52–6.74 (m, 8H), 5.33 (m, 1H), 4.15 (m, 4H), 3.82 (m, 1H), 3.54 (m, 1H), 1.97–1.44 (m, 6H), 1.28 (dt, $^3J_{HH}$ = 6.1 Hz, $^4J_{HP}$ = 0.9 Hz, 6H), ^{13}C NMR: δ 158.54 (C_{aryl}), 151.92 ($^2J_{CP}$ = 7.0 Hz, C_{aryl}), 128.78 (C_{aryl}), 120.79 (C_{aryl}), 133.06 (CH_{aryl}), 130.27 (CH_{aryl}), 113.46 (CH_{aryl}), 122.22 (CH_{aryl}), 122.16 (CH_{aryl}), 109.20 ($^3J_{CP}$ = 5.3 Hz, CH_{aryl}), 96.95 (CH), 64.92 ($^2J_{CP}$ = 5.9 Hz, CH_2), 62.40 (CH_2), 30.66 (CH_2), 25.53 (CH_2), 19.06 (CH_2), 16.46 ($^3J_{CP}$ = 6.4 Hz, CH_3); HRMS (EI): *m*/*z* Calc. for $C_{21}H_{27}O_6P$ (M^+): 406.4124. Found: 406.4122.

3.13. O,O-Diethyl O-2′-tetrahydro-2H-2-pyranyloxybiphenyl-4-yl phosphate (*31*)

General procedure B with the adjustment of 5 mol% of $Pd(PPh_3)_4$, was followed to prepare **31** by reaction of **16** (1.00 mmol) with *O*,*O*-diethyl *O*-4-bromophenyl phosphate (1.20 mmol). The title compound could be isolated by DCVC (eluent: hexane:EtOAc, 6:4), as an orange liquid, contaminated by starting diethyl phosphate ester. (0.142 g, 0.35 mmol, 35%). ^{1}H NMR: δ 7.57–6.94 (m, 8H), 5.34 (m, 1H), 4.17 (m, 4H), 3.71 (m, 1H), 3.52 (m, 1H), 1.85–1.41 (m, 6H), 1.30 (dt, $^3J_{HH}$ = 6.5 Hz, $^4J_{HP}$ = 1.0 Hz, 6H); ^{13}C NMR: δ 154.24 (C_{aryl}); 150.12 ($^2J_{CP}$ = 7.0 Hz, C_{aryl}), 135.90 (C_{aryl}); 131.24 (CH_{aryl}); 130.05 (C_{aryl}); 129.06 (CH_{aryl}); 122.32 (CH_{aryl}); 122.20 ($^3J_{CP}$ = 5.3 Hz, CH_{aryl}), 120.38 ($^4J_{CP}$ = 4.7 Hz, CH_{aryl}), 116.24 (CH_{aryl}); 97.13 (CH), 64.89 ($^2J_{CP}$ = 5.9 Hz, CH_2), 62.22 (CH_2), 30.66 (CH_2), 25.59 (CH_2), 18.91 (CH_2), 16.46 ($^3J_{CP}$ = 6.55 Hz, CH_3);

HRMS (EI): *m/z* Calc. for $C_{21}H_{27}O_6P$ (M^+): 406.4124. Found: 406.4126.

3.14. 2′-Methoxybiphenyl-2-yl tetrahydro-2H-2-pyranyl ether (**32**)

General procedure A was followed with the adjustment of 20 mol% of $Cl_2Pd(PPh_3)_2$. In addition 1.25 equiv of CuI, 13.8 equiv of CsF and a crystal of 2,6-di-*tert*-butyl-4-methylphenol was added to DMF solution of 2-iodoanisol (1.20 mmol) to prepare the title compound from **16** (1.00 mmol). The crude product was purified by preparative TLC (eluent: hexane:EtOAc, 8:2) to give **32** (0.071 g, 0.25 mmol, 25%) as a pale yellow liquid. ^{1}H NMR: δ 7.34–6.84 (m, 8 H), 5.29 (m, 1H), 3.69 (s, 3H), 3.76 (m, 1H), 3.46 (m, 1H), 1.64–1.32 (m, 6H); ^{13}C NMR: δ 156.00 (C_{aryl}), 154.11 (C_{aryl}), 132.87 (CH_{aryl}), 131.68 (CH_{aryl}), 129.71 (CH_{aryl}), 129.62 (CH_{aryl}), 127.51 (C_{aryl}), 126.61 (C_{aryl}), 122.58 (CH_{aryl}), 121.34 (CH_{aryl}), 117.76 (CH_{aryl}), 112.08 (CH_{aryl}), 95.09 (CH), 63.30 (CH_2), 56.61 (CH_3), 30.07 (CH_2), 25,86 (CH_2), 20.13 (CH_2); MS (*m/z*, relative intensity): 284 (1, M^+), 200 (100, M^+-84), 185 (23), 169 (36), 157 (18), 139 (23), 128 (38), 115 (15); HRMS (EI): *m/z* Calc. for $C_{18}H_{20}O_3$ (M^+): 284.3534. Found: 284.3531.

3.15. O,O-Diethyl O-4′-methoxybiphenyl-4-yl phosphate (**36**)

General procedure B was followed to prepare the title compound by reaction of **21** (1.00 mmol) with *O*,*O*-diethyl *O*-4-bromophenyl phosphate (1.20 mmol). The crude product was purified by DCVC (eluent: hexane:EtOAc, 7:3) to give **36** (0.245 g, 0.73 mmol, 73%) as a pale yellow liquid. ^{1}H NMR: δ 7.59–7.46 (m, 4H), 7.35–7.24 (m, 2H), 7.06–6.95 (m, 2H), 4.34–4.19 (m, 4H), 3.86 (s, 3H), 1.39 (dt, $^3J_{HH}$ = 7.0, $^4J_{HP}$ = 0.9, 6H); ^{13}C NMR: δ 159.61 (C_{aryl}), 150.21 ($^2J_{CP}$ = 7.0 Hz, C_{aryl}), 138.16 (C_{aryl}), 133.21 (C_{aryl}), 128.39 (CH_{aryl}), 128.27 (CH_{aryl}), 120.59 ($^3J_{CP}$ = 4.7 Hz, CH_{aryl}), 114.67 (CH_{aryl}), 64.97 ($^2J_{CP}$ = 5.8 Hz, CH_2), 55.72 (CH_3), 16.48 ($^3J_{CP}$ = 6.4 Hz, CH_3); HRMS (EI): *m/z* Calc. for $C_{17}H_{21}O_5P$ (M^+): 336.3221. Found: 336.3219.

3.16. 4-Diethoxyphosphinyl)oxy-4″-tetrahydro-2H-2-pyranyloxy-[1,1′;4′,1″]terphenyl (**39**)

General procedure A was followed to prepare the title compound by reaction of **38** (1.00 mmol) with *O*,*O*-diethyl *O*-4-bromophenyl phosphate (1.20 mmol). The crude product was purified by DCVC (eluent: hexane:EtOAc, 6:4) to give **39** (0.193 g, 0.401 mmol, 40%) as a white solid. M.p. 109–110 °C; ^{1}H NMR: δ 7.62–7.02 (m, 12H), 5.41 (m, 1H), 4.27–4.11 (m, 4H), 3.88 (m, 1H), 3.58 (m, 1H), 2.06–1.46 (m, 6H), 1.31 (dt, $^3J_{HH}$ = 7.0 Hz; $^4J_{HP}$ = 0.9 Hz, 6 H); ^{13}C NMR: δ 157.19 (C_{aryl}), 150.67 ($^2J_{CP}$ = 7.0 Hz, C_{aryl}), 140.29 (C_{aryl}), 138.95 (C_{aryl}), 138.10 (C_{aryl}), 134.41 (C_{aryl}), 128.58 (CH_{aryl}), 128.35 (CH_{aryl}), 127.67 (CH_{aryl}), 127.53 (CH_{aryl}), 120.68 ($^3J_{CP}$ = 4.7 Hz, CH_{aryl}), 117.25 (CH_{aryl}), 96.87 (CH), 65.00 ($^2J_{CP}$ = 6.5 Hz, CH_2), 62.46 (CH_2), 30.78 (CH_2), 25.62 (CH_2), 19.18 (CH_2), 16.49 ($^3J_{CP}$ = 7.0 Hz, CH_3); HRMS (EI): *m/z* Calc. for $C_{27}H_{31}O_6P$ (M^+): 482.5101. Found: 482.5112.

3.17. 4-Methoxy-4″-cyano-[1,1′;4′,1″]terphenyl (**41**)

General procedure A was followed to prepare the title compound by reaction of **40** (1.00 mmol) with 4-iodobenzonitrile (1.20 mmol). The crude product was purified by DCVC (eluent: hexane:EtOAc, 7:3) to give **41** (0.222 g, 0.779 mmol, 78%) as a white solid. M.p. 212–214 °C; ^{1}H NMR (DMSO-d_6): δ 7.83–7.74 (m, 4H), 7.68–7.57 (m, 4H), 7.56–7.49 (m, 2H), 6.94–6.85 (m, 2H), 3.65 (s, 3H); ^{13}C NMR: δ 159.61 (C_{aryl}), 144.52 (C_{aryl}), 140.49 (C_{aryl}), 136.74 (C_{aryl}), 131.93 (C_{aryl}), 133.21 (CH_{aryl}), 128.42 (CH_{aryl}), 128.14 (CH_{aryl}), 127.65 (CH_{aryl}), 127.14 (CH_{aryl}), 119.23 (CN), 114.86 (CH_{aryl}), 110.28 (C_{aryl}), 55.59 (CH_3); MS (*m/z*, relative intensity): 285 (100, M^+), 270 (30, $M^+ - 15$), 242 (23), 214 (5), 190 (2), 163 (1), 142 (7), 115 (4), 94 (2), 63 (2); HRMS (EI): *m/z* Calc. for $C_{20}H_{15}NO$ (M^+): 285.3441. Found: 285.3439.

3.18. 1-Biphenyl-4-yl)naphthalene (**45**)

General procedure A with the adjustment of 5 mol% of $Cl_2Pd(PPh_3)_2$ was followed to prepare the title compound by reaction of **43** (1.00 mmol) with 1-bromonaphthalene (1.20 mmol). The crude product was purified by DCVC (eluent: hexane:EtOAc, 9:1) to give **45** (0.196 g, 0.703 mmol, 70%) as a white solid. M.p. 139–41 °C; ^{1}H NMR: δ 7.95–7.13 (m); ^{13}C NMR: δ 141.28 (C_{aryl}), 140.55 (C_{aryl}), 140.29 (C_{aryl}), 140.20 (C_{aryl}), 134.30 (C_{aryl}), 132.08 (C_{aryl}), 130.89 (CH_{aryl}), 129.24 (CH_{aryl}), 128.71 (CH_{aryl}), 128.11 (CH_{aryl}), 127.76 (CH_{aryl}), 127.54 (CH_{aryl}), 127.39 (CH_{aryl}), 127.34 (CH_{aryl}), 126.47 (CH_{aryl}), 126.44 (CH_{aryl}), 126.20 (CH_{aryl}), 125.80 (CH_{aryl}); MS (*m/z*, relative intensity): 280 (100, M^+), 202 (20), 138 (7), 98 (2), 77 (3), 51 (2); HRMS (EI): *m/z* Calc. for $C_{22}H_{16}$(M^+): 280.3682. Found: 280.3687.

3.19. 5-Biphenyl-4-yl)-2-bromopyridine (**46**)

General procedure B was followed to prepare the title compound by reaction of **43** (1.00 mmol) with 2,5-dibromopyridine (1.20 mmol). Crystallization from cold Et_2O gave 0.124 g (0.405 mmol, 40%) of compound **46** as a pale yellow solid. m.p. >300 °C; ^{1}H NMR (DMSO-d_6): δ 9.09–8.99 (m, 1 H); 8.58–8.21 (m, 4 H);

8.93–8.11 (m, 4H); 7.79–7.59 (m, 3H); ^{13}C NMR: δ 154.77 (C_{aryl}), 150.60 (CH_{aryl}), 141.44 (C_{aryl}), 140.13 (CH_{aryl}), 139.74 (C_{aryl}), 136.84 (C_{aryl}), 129.38 (CH_{aryl}), 128.18 (CH_{aryl}), 127.46 (CH_{aryl}), 127.43 (CH_{aryl}), 127.03 (CH_{aryl}), 122.31 (CH_{aryl}), 119.48 (C_{aryl}); HRMS (EI): *m/z* Calc. for $C_{17}H_{12}BrN$ (M^+): 310.1935. Found: 310.1929.

3.20. Synthesis of O,O-Diethyl O-biphenyl-4-yl phosphate (**42**) by demethylation of **34** with Ph_3SnNa followed by phosphorylation in a one-pot-type reaction

In a two-necked, 50 mL round-bottomed flask, Ph_3SnNa (2.00 mmol) was prepared in liquid ammonia (20 mL) starting from Ph_3SnCl (2.2 mmol) and Na (5.57 mg atom). Then, dry DMSO (10 mL) was added and the ammonia was allowed to evaporate. The cold-finger condenser was replaced by a reflux condenser and 35 (1.00 mmol) was added. The solution was stirred at 110 °C (oil bath) for 12 h. Diethyl chlorophosphate (2.4 mmol) was added at room temperature and the resulting solution was stirred for 24 h. The reaction was quenched by addition of 10 mL of water and then extracted with ethyl ether (3×20 mL). The ether fractions were washed with brine, dried (MgSO4) and concentrated under reduced pressure to give a crude orange–yellow liquid. The title product was purified by DCVC on silica gel (hexane:ethyl acetate, 6:4) yielding 0.260 g (0.85 mmol, 85%) of **42** as a pale yellow liquid. Spectroscopic characteristics are in agreement with those of an authentic sample prepared by a known procedure [19]. Ph_3SnMe eluted with hexane (0.764 g, 2.09 mmol).

3.21. O,O-Diethyl O-4-trimethylstannylphenyl phosphate (**37**)

The synthesis of the title compound was carried out according to a similar procedure starting from **21** using Me_3SnNa (**11**) instead Ph_3SnNa as deprotecting reagent. The mixture of **11** and **21** in DMSO was heated at 110 °C for 90 min. The crude product was purified by preparative TLC (eluent: hexane:EtOAc, 6:4) to yield 0.110 g (0.281 mmol, 28%) of **37** as a pale yellow liquid; ^{1}H NMR: δ 7.44 (d, $^3J_{HH} = 8.4$ Hz, 2H), 7.19 (d, $^3J_{HH} = 8.4$ Hz, 2H), 4.21 (m, 4H), 1.35 (dt, $^3J_{HH} = 7.1$ Hz; $^4J_{HP} = 1.1$ Hz, 6H), 0.28 (s, $^2J_{HSn} = 55.5/53.2$ Hz, 9H, $SnMe_3$); ^{13}C NMR: δ 151.56 ($^2J_{CP} = 7.0$ Hz, C_{aryl}),138.72 (CH_{aryl}), 137.40 ($^2J_{CSn} = 40.0$ Hz, CH_{aryl}), 120.05 ($^3J_{CSn} = 45.8$ Hz, $^3J_{CP} = 4.5$ Hz, C_{aryl}), 64.90 ($^2J_{CP} = 5.9$ Hz, CH_2), 16.45 ($^3J_{CP} = 7.0$ Hz, CH_3), −9.15 ($^1J_{CSn} = 353.5/338.0$ Hz, $SnCH_3$); MS (*m/z*, relative intensity): 394 (9, M^+), 379 (100, M − 15), 349 (16), 321 (12), 293 (9), 275 (3), 243 (7), 213 (11), 183 (8), 165 (12), 135 (16), 109 (11), 8 (20), 65 (4); HRMS (EI): *m/z* Calc. for $C_{13}H_{23}O_4PSn$ (M^+): 392.8953. Found: 392.8949.

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