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Regioselective hydrostannation of highly hindered arylalkynes under *ortho*-directing effects

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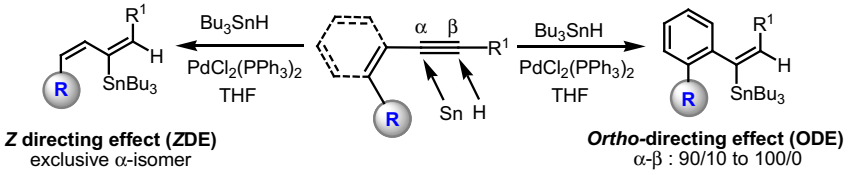
ABSTRACT

Palladium-catalyzed hydrostannation reactions of *ortho*-disubstituted arylalkynes were achieved with total stereo- and regio-selectivity in THF at room temperature. The regioselectivity was found to be under the control of the *ortho*-substituents (*ortho*-directing effects, ODE) and pure α-vinylstannanes are produced in good yields and as single isomers regardless of the substituents' nature. These hydrostannation α-products are precursors of choice for the preparation of stereo-defined triarylolefins.

1. Introduction

Organostannanes, and particularly vinylstannanes are of increasing importance as synthetic intermediates in organic chemistry due to the large number of carbon–carbon bond forming reactions available to these substrates.[1] As a result of their synthetic utility, considerable effort has been expended toward their preparation[2] and the addition of tributyltin hydride to alkynes remains the most simple and straightforward route to these vinylstannanes intermediates.[2c,d,3] The challenge in the hydrostannation of unsymmetrical alkynes is to directly produce vinylstannanes of high purity with a total regio- and stereo-selectivity because mixtures of vinyl stannanes are tedious to separate (destannylation, non-polar isomers,…). For palladium-catalyzed hydrostannation of alkynes, control of stereoselectivity is not a problem since the addition of tributyltin hydride proceeds in a *syn* manner (*cis*-addition).[2d,4] In contrast, the regiochemical control of this reaction appears to be dependent on steric,[2d,4,5] electronic,[2d] and chelating[2d,6] factors of the alkyne substituents. We previously described the regioselective palladium-catalyzed hydrostannation of conjugated alkynes. With (*Z*)-enyne[7] and (*Z*)-enediyne[8] substrates, the regioselectivity of the H–Sn bond addition was found to be totally controlled by the geometry of the double bond (Z-Directing Effect, ZDE) rather than the nature of its substituents (Cl, alkyl, aryl,…) to give exclusively α-vinylstannanes (Scheme 1). With *ortho* substituted internal[9] and terminal[10] arylalkyne derivatives, we demonstrated that an *ortho* substituent delivered the Bu_3Sn group on the carbon atom (C_α) whatever the electronic nature of the substituent, electron withdrawing or electron donating (e.g., CO_2R, COR, OR, Cl,…). This trend in α-regioselectivity was also observed with substrates having *ortho* non-chelating alkyl substituents (e.g., CH_3, ^{i}Pr,…), clearly indicating that coordinating factors were not at the origin of this remarkable



Scheme 1.

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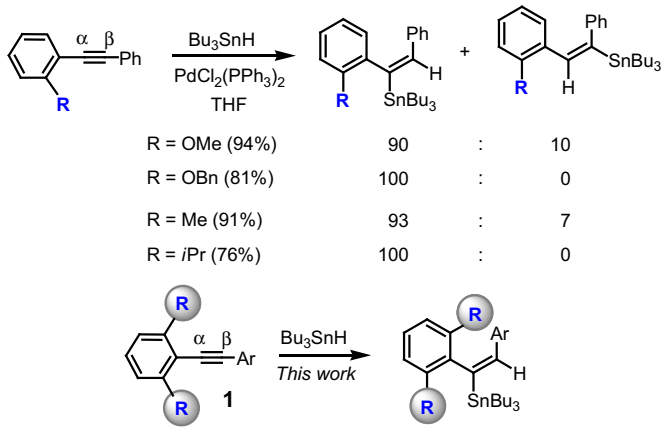
regioselectivity (Scheme 1). The results have been rationalized in terms of electronic polarization across the alkyne bond, induced by the *ortho* substituent whatever its electronic nature.[9b] Although at the moment, we did not succeed in correlating the α-selectivity observed with the triple bond polarization, this *ortho*-directing effect (ODE) has been successfully extended to control the regiochemistry of the platinum-catalyzed hydrosilylation of internal aliphatic arylalkynes as well as diarylalkynes.[11]

Although it was clearly established that the regioselectivity of the Pd-catalyzed hydrostannation of aliphatic alkynes is very sensitive to the steric hindrance,[2d,5a,b] we showed previously in the case of internal *ortho* substituted diarylalkynes[9b] that increasing steric hindrance of *ortho* substituent provides better α-regioselectivities (*anti* steric effects) as depicted in Scheme 2.



Scheme 2.

These findings clearly highlighted the role of steric hindrance of substituent in directing the α-addition of the metals to the more hindered alkyne carbon atom (C_α). To the best of our knowledge there has been no systematic study on metal-catalyzed hydrometallation of highly hindered arylalkynes **1** having *ortho*/*ortho*′ substituents. Herein, the results of these studies are reported using tributyltin hydride or triethylsilane in order to determine the impact of *ortho*/*ortho*′ substituents of **1** on the α-regioselectivity.

2. Results and discussion

At the beginning of this work, hindered *ortho*/*ortho*′-diarylalkynes **1** were prepared according to Sonogashira–Linstrumelle (SL) couplings[12] using $PdCl_2(PPh_3)_2$ (5 mol %), CuI (10 mol %), piperidine as the base in THF, in good to excellent yields. The hydrostannation of diarylalkynes **1** was conducted under standard conditions using $PdCl_2(PPh_3)_2$ (5 mol %) and Bu_3SnH (1.3 equiv) in THF. The results of this study are summarized in Table 1. In order to establish a baseline regioselectivity control, 1-(2-methoxyphenyl)-2-phenylacetylene **1a** bearing a single *ortho* MeO substituent was evaluated. Under the above conditions, **1a** was hydrostannylated to give a diastereomeric mixture of non-separable α and β vinylstannanes with an excellent but not total α-preference (entry 1, α-**1a**/β-**2a**: 90/10). For comparison, by switching the MeO substituent from the *ortho* to the *para* position on the aromatic, an equimolar isomeric α-**2**/β-**2** product distribution was obtained (data not shown). More interestingly, hydrostannation of *ortho*-disubstituted arylalkyne **1b**, **1c**, and **1d** bearing on the same aromatic nucleus two *ortho* electron-donating substituents was totally regioselective[13] furnishing α-vinylstannanes **2b**–**d** in good yields (entries 2–4). As expected for electronic considerations, hydrostannation of *ortho*/*ortho*′ disubstituted diarylalkynes **1e**–**g**, bearing a *para* MeO substituent on the second aromatic nucleus, furnished vinylstannanes **2e**–**g**, again with a total α-regioselectivity (entries 5–7). The example depicted in entry 8 with 'push–pull' diarylalkyne **1h** is particularly interesting. In this case, where ODE is opposed by a strong electronic effect (induced by the *para*-CN), the α-regioselectivity was less spectacular and β-vinylstannane was obtained as minor products together with α-adduct (entry 8, α-**2h**/β-**2h**: 81/19). By replacing the *ortho* and *ortho*′ electron-donating substituents with chlorine atoms, the α-regioselectivity is entirely governed by ODE rather than the *p*-CN induced polarization of the triple bond (entry 9). For substrate **1j**–**l**, ODE and electronic factors cooperate to give α-substituted vinylstannanes **2j**–**l** exclusively in good yields (entries 10–12). We next tested the *ortho*-directing effect on the distribution products with arylalkynol **1m**. It was found that hydrostannation of **1m** proceeded with an excellent α-regioselectivity in a nearly quantitative yield (entry 13, α-**2m**/β-**2m**: 95/5). As it was observed for diarylalkynes **1b**–**g**, **1i**–**l**, the hydrostannation of arylalkynols **1m** and **1n** bearing two substituents on the *ortho* position was totally regioselective and produced α-vinylstannanes **2m** and **2n** in good yields. The last example, described in entry 15 sums up this study. The two triple bonds of alkyne **1o** were successfully hydrostannylated with a total regioselectivity furnishing a single compound α,α-**2o** in an excellent isolated yield. In this case, if *ortho*-substituents are at the origin of the α-regioselectivity observed for the hydrostannation of the hindered alkyne, the exclusive α-stannylation of the alkynol moiety is not immediately clear.

The success of this *ortho*/*ortho*′-substituent regiocontrol prompted additional investigations with *ortho*-disubstituted terminal arylalkynes. The results of this study are abstracted in Scheme 3. Hydrostannation of electron-rich arylalkyne **1p** as well as electron deficient arylalkyne **1q** was achieved and again, a total regioselectivity was observed. In these cases, exclusive α-isomers **2p** and **2q** were produced in excellent yields (**2p**: 92%, **2q**: 98%).

Next, to examine the synthetic utility of α-vinylstannanes of type **2**, we first evaluated the Stille coupling of 4-iodoanisole with **2k** and **2o**. However, the coupling products **4a** and **4b** were not obtained in satisfactory yields. Therefore, a second synthetic approach involving an iododestannylation–Negishi sequence was explored (Scheme 4).[8b,9c] Thus, stereospecific iodo-destannylation of **2k** and **2o** with molecular iodine (1 equiv) in CH_2Cl_2 at 20 °C provided cleanly and rapidly the suitable electrophilic vinyl iodides **3a** and **3b** in quantitative yields. Further coupling with 4-methoxyarylzinc chloride in the presence of $PdCl_2(PPh_3)_2$ (5 mol %) furnished the triarylated ethylenic compounds **4a**,**b** with a total stereospecificity in good yields (Scheme 4).

Finally, we wanted to examine if this total α-selectivity could be successfully extended to the hydrosilylation of various *ortho*-disubstituted alkynes. Preliminary results are presented in Table 2. Reaction of *ortho*-disubstituted diarylalkyne **1b** with triethylsilane in THF in the presence of PtO_2 (5 mol %) at 70 °C for 1 h afforded regioselectively an inseparable 90/10 mixture of the vinylsilanes α-**3a** and α-**3b** in 90% yield (entry 1, Table 2). For comparison, the hydrosilylation of alkyne **1a** bearing a single MeO substituent on the *ortho* position (baseline control) afforded a mixture of α- and β-vinylsilanes but with a lower α-selectivity (α/β: 80/20).

A similar α-preference was also observed with alkyne **1e** bearing two MeO-substituents on the *ortho* and *ortho*′ position (97%, entry 2). As previously observed for the hydrostannation of **1j** (entry 10, Table 1), the hydrosilylation of **1j** bearing two chlorine atoms on the *ortho* positions was totally regioselective. Again, electronic factors, generated by the chlorine atoms, and ODE cooperate and the reaction produced a single α-vinylsilane **3c** in a nearly quantitative yield (98%, entry 3, Table 2).

3. Conclusion

In summary, we demonstrated that hydrostannation of hindered arylalkynes bearing on the same aromatic nucleus two *ortho*-

Table 1
Hydrostannation of highly hindered arylalkynes **1** under palladium catalysis

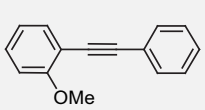
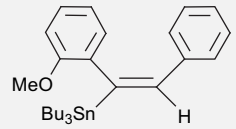
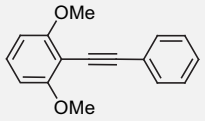
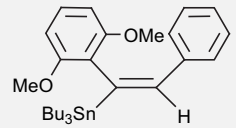
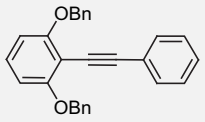
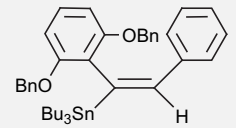
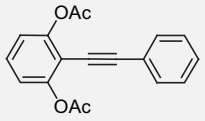
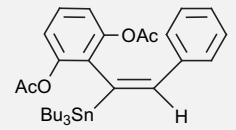
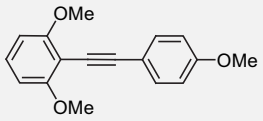
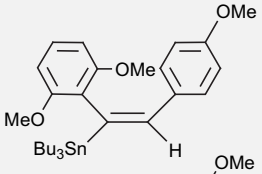
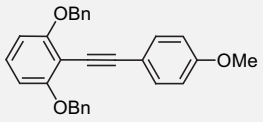
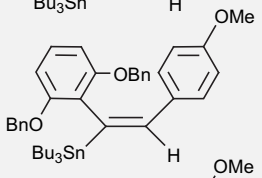
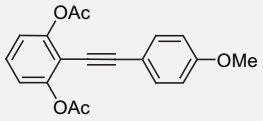
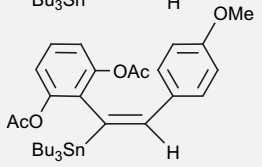
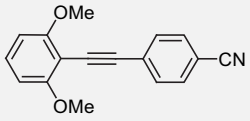
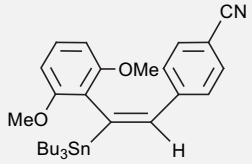
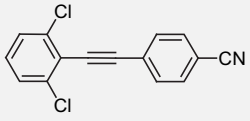
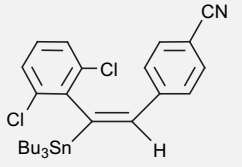
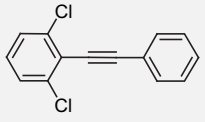
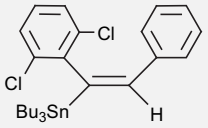
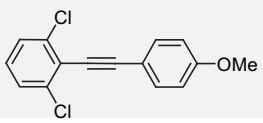
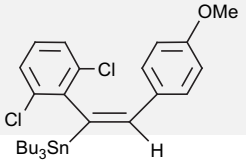
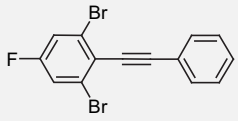
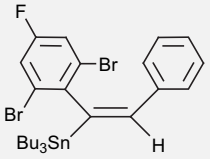
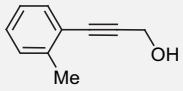
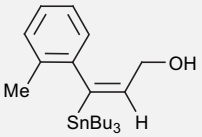
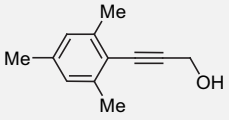
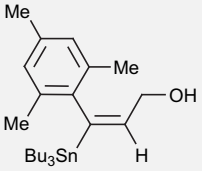
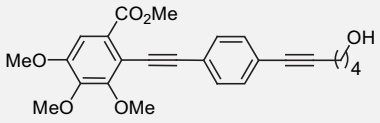
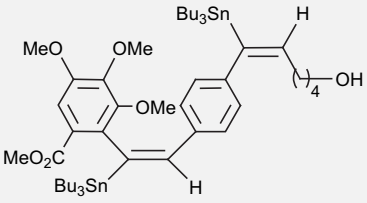
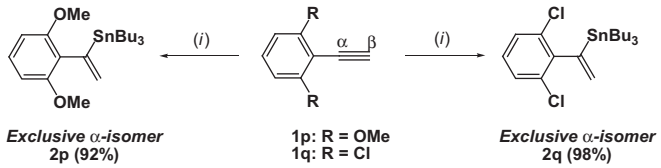
Entry	Alkyne **1**		α/β ratio[a]	Vinyl stannane **2**		Yield[b] (%)
1		**1a**	90/10		**2a**	94
2		**1b**	100/0		**2b**	86
3		**1c**	100/0		**2c**	90
4		**1d**	100/0		**2d**	65
5		**1e**	100/0		**2e**	71
6		**1f**	100/0		**2f**	55
7		**1g**	100/0		**2g**	70
8		**1h**	81/19		**2h**	86
9		**1i**	100/0		**2i**	88
10		**1j**	100/0		**2j**	98
11		**1k**	100/0		**2k**	98

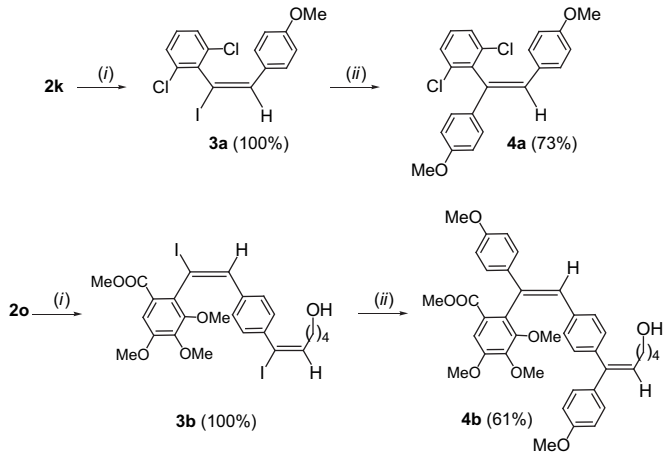
Table 1 (*continued*)

Entry	Alkyne **1**		α/β ratio[a]	Vinyl stannane **2**		Yield[b] (%)
12		**1l**	100/0		**2l**	48
13		**1m**	95/5		**2m**	97
14		**1n**	100/0		**2n**	81
15		**1o**	100/0 100/0		**2o**	91[c]

[a] Ratio was determined by ^{1}H NMR analysis.
[b] Yields were given for isolated products.
[c] Bu_3SnH (3.0 equiv) was used.

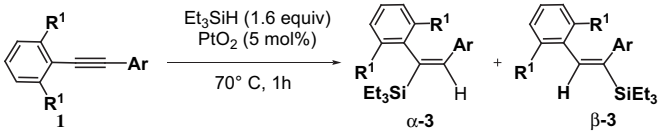


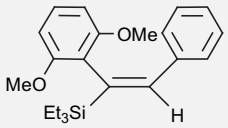
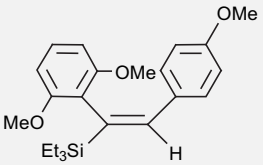
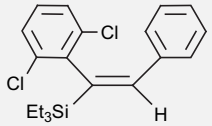
Scheme 3. Hydrostannation of terminal *ortho*/*ortho*′ disubstituted arylalkynes **1p** and **1q**. Reagents and conditions. (i) Bu_3SnH (1.3 equiv), $PdCl_2(PPh_3)_2$ (5 mol %), 20 °C, THF, 0.5 h.



Scheme 4. Iodo-destannylation of **2k** and **2o** followed by Negishi Cross-coupling reactions under palladium catalysis. Reagents and conditions. (i) I_2, CH_2Cl_2. (ii) 4-$MeOC_6H_4ZnCl$, $PdCl_2(PPh_3)_2$ 5 mol %, THF.

Table 2
Hydrosilylation of *ortho*-disubstituted arylalkynes **1**



Entry	Alkyne 1	Selectivity α/β[a]	Vinylsilane α-**3**		Yield[b] (%)
1	**1b**	90/10		α-**3a**	90
2	**1e**	92/8		α-**3b**	97
3	**1j**	100/0		α-**3c**	98

[a] Ratio was determined by ^{1}H NMR analysis.
[b] Yields were given for isolated products.

substituents give exclusively the α-vinylstannanes in good yields whatever the electronic nature and steric hindrance of substituents. Moreover, preliminary results indicate that the PtO_2-catalyzed hydrosilylation of these hindered alkynes was also highly regioselective. The factors governing this total α-selectivity would be close to those observed in the hydrostannation or hydrosilylation of

arylalkynes bearing on the *ortho* position a single substituent (ODE). This study shows that it is possible to predict the exclusive α-isomers formation even if the exact origin of this regioselectivity remains unclear.[9b,14] Interestingly, the products of the hydrostannation reaction can be efficiently used as versatile substrates in iododestannylation–Negishi sequences to afford stereo-defined triarylolefins of therapeutic interest.[15]

4. Experimental

4.1. General comments

All glasswares were oven-dried at 140 °C and all reactions were conducted under a nitrogen atmosphere. Solvents: cyclohexane, ethyl acetate (EtOAc), for chromatography were technical grade. Diethylether (Et_2O) and tetrahydrofuran (THF) were distilled under argon from sodium-benzophenone ketyl, piperidine, triethylamine from potassium hydroxide. $PdCl_2(PPh_3)_2$ and Bu_3SnH[16] were prepared following literature procedure. All new compounds were characterized by ^1H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis. ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ with a Bruker ARX 400 or Bruker Avance 300. ^1H chemical shifts are reported in ppm from an internal standard TMS or of residual chloroform (7.27 ppm). The following abbreviations are used: m (multiplet), s (singlet), br s (broad singlet), d (doublet), t (triplet) dd (doublet of doublet), q (quadruplet), sextet (sextuplet). ^{13}C chemical shifts are reported in parts per million from the central peak of deuteriochloroform (77.14). IR spectra were measured on a Bruker Vector 22 spectrophotometer (neat, cm^{-1}). Elemental analyses were performed with a Perkin–Elmer 240 analyzer. Analytical TLC was performed on Merck precoated silica gel 60 F-254 plates. Merck silica gel 60 (230–400 mesh) was used for column chromatography. The plates were visualized by either UV light (254 nm), or by a solution of phosphomolybdic acid in ethanol. Melting points (mp) were recorded on a Büchi B-450 apparatus and were uncorrected.

4.2. General procedure for the synthesis of diarylalkynes 1

4.2.1. Procedure for the synthesis of diarylalkynes (A). To a flame-dried flask under a nitrogen atmosphere were added $PdCl_2(PPh_3)_2$ (120 mg, 0.17 mmol), CuI (76 mg, 0.4 mmol), aryliodide (4.0 mmol), and piperidine (1.2 mL, 12.0 mmol) in THF (12 mL). To this solution was added dropwise 1-alkyne (6.0 mmol). After stirring at room temperature for 12 h, the mixture was diluted in Et_2O (25 mL), and then washed with a saturated NH_4Cl solution (20 mL). After extraction with Et_2O (25 mL) the combined organic layers were dried over $MgSO_4$. After concentration under reduced pressure, the residue was purified by column chromatography over silica gel, to yield the desired *ortho*-disubstituted alkyne **1**.

*4.2.2. 1,3-Bis(benzyloxy)-2-(phenylethynyl)benzene (**1c**).* White solid, mp: 106–108 °C. Yield (90%). R_f=0.23 (Et_2O/cyclohexane, 5/95, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 5.14 (4H, s), 6.54 (2H, d, *J*=8.4 Hz), 7.11 (1H, t, *J*=8.4 Hz), 7.15–7.54 (15H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 70.6 ($2CH_2$), 82.6 (C), 98.4 (C), 103.7 (C), 106.0 (2CH), 124.3 (C), 126.9 (4CH), 127.8 (2CH), 127.9 (CH), 128.3 (2CH), 128.5 (4CH), 129.6 (CH), 131.6 (2CH), 137.2 (2C), 160.6 (2C). IR (cm^{-1}, neat): 1582, 1474, 1446, 1375, 1261, 1116, 771, 732, 690. Anal. Calcd for $C_{28}H_{22}O_2$ (390.47): C 86.13, H 5.68, found C 85.91, H 5.70.

*4.2.3. 2-(Phenylethynyl)-1,3-phenylene diacetate (**1d**).* Brown solid, mp: 106–108 °C. Yield (65%). R_f=0.40 (Et_2O/cyclohexane, 30/70, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.37 (6H, s), 7.06 (2H, d, *J*=8.2 Hz), 7.40–7.32 (4H, m), 7.51–7.43 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.9 ($2CH_3$), 79.7 (C), 98.8 (C), 112.5 (C), 119.9 (2CH), 122.7 (C), 128.5 (2CH), 128.9 (CH), 129.2 (CH), 131.5 (2CH), 152.3 (2C), 168.5 (2C). IR (cm^{-1}, neat): 1761, 1494, 1457, 1371, 1182, 1026, 882, 758, 690. Anal. Calcd for $C_{18}H_{14}O_4$ (294.30): C 73.46, H 4.79, found C 73.74, H 4.65.

*4.2.4. 1,3-Dimethoxy-2-((4-methoxyphenyl)ethynyl)benzene (**1e**).* Brown solid, mp: 142–144 °C. Yield (71%). R_f=0.15 (Et_2O/cyclohexane, 10/90, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 3.82 (3H, s), 3.91 (6H, s), 6.56 (2H, d, *J*=8.4 Hz), 6.86 (2H, d, *J*=8.4 Hz), 7.24 (1H, t, *J*=8.4 Hz), 7.53 (2H, d, *J*=8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.3 (CH_3), 56.2 ($2CH_3$), 80.4 (C), 97.9 (C), 102.0 (C), 103.6 (2CH), 113.9 (2CH), 116.2 (C), 129.5 (CH), 133.2 (2CH), 159.4 (C), 161.3 (2C). IR (cm^{-1}, neat): 1579, 1513, 1472, 1252, 1103, 826, 778, 726. Anal. Calcd for $C_{17}H_{16}O_3$ (268.31): C 76.10, H 6.01, found C 76.25, H 5.84.

*4.2.5. (2-((4-Methoxyphenyl)ethynyl)-1,3-phenylene) bis(oxy)bis(methylene)dibenzene (**1f**).* Brown solid, mp: 89–91°C. Yield (55%). R_f=0.20 (Et_2O/cyclohexane, 5/95, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 3.84 (3H, s), 5.21 (4H, s), 6.61 (2H, d, *J*=8.3 Hz), 6.87 (2H, d, *J*=8.8 Hz), 7.17 (1H, t, *J*=8.3 Hz), 7.66–7.25 (12H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4 (CH_3), 70.7 ($2CH_2$), 81.1 (C), 98.4 (C), 104.1 (C), 106.1 (2CH), 114.0 (2CH), 116.6 (C), 127.0 (4CH), 127.8 (2CH), 128.5 (4CH), 129.2 (CH), 133.0 (2CH), 137.3 (2C), 159.4 (C), 160.4 (2C). IR (cm^{-1}, neat): 1574, 1509, 1449, 1378, 1247, 1087, 1028, 830, 780, 727, 692. Anal. Calcd for $C_{29}H_{24}O_3$ (420.50): C 82.83, H 5.75, found C 82.72, H 5.64.

*4.2.6. 2-((4-Methoxyphenyl)ethynyl)-1,3-phenylene diacetate (**1g**) (in this case TEA was used as base instead piperidine).* Brown solid, mp: 117–119 °C. Yield (85%). R_f=0.45 (Et_2O/cyclohexane, 30/70, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.36 (6H, s), 3.83 (3H, s), 6.88 (2H, d, *J*=8.8 Hz), 7.04 (2H, d, *J*=8.0 Hz), 7.35 (1H, t, *J*=8.0 Hz), 7.40 (2H, d, *J*=8.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.9 ($2CH_3$), 55.4 (CH_3), 78.4 (C), 99.0 (C), 112.8 (C), 114.2 (2CH), 114.8 (C), 119.9 (2CH), 128.8 (CH), 133.1 (2CH), 152.2 (2C), 160.2 (C), 168.6 (2C). IR (cm^{-1}, neat): 1756, 1515, 1458, 1374, 1190, 1029, 882, 836, 734. Anal. Calcd for $C_{19}H_{16}O_5$ (324.33): C 70.36, H 4.97, found C 70.01, H 4.75.

*4.2.7. 4-((2,6-Dimethoxyphenyl)ethynyl)benzonitrile (**1h**).* White solid, White solid, mp: 120–122 °C. Yield (88%). R_f=0.20 (Et_2O/cyclohexane, 5/95, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 3.92 (6H, s), 6.57 (2H, d, *J*=8.4 Hz), 7.27 (1H, t, *J*=8.4 Hz), 7.60 (2H, d, *J*=8.6 Hz), 7.65 (2H, d, *J*=8.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.2 ($2CH_3$), 87.0 (C), 96.2 (C), 100.7 (C), 103.6 (2CH), 111.0 (C), 118.8 (C), 129.1 (C), 130.9 (CH), 131.9 (2CH), 132.2 (2CH), 161.7 (2C). IR (cm^{-1}, neat): 2215, 1585, 1475, 1257, 1110, 834, 774, 725. Anal. Calcd for $C_{17}H_{13}NO_2$ (263.29): C 77.55, H 4.98, found C 77.13, H 4.70.

*4.2.8. 4-((2,6-Dichlorophenyl)ethynyl)benzonitrile (**1i**).* White solid, mp: 144–146 °C. Yield (90%). R_f=0.32 (Et_2O/cyclohexane, 5/95, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.22 (1H, t, *J*=8.8 Hz), 7.38 (2H, d, *J*=8.8 Hz), 7.66 (2H, d, *J*=8.7 Hz), 7.69 (2H, d, *J*=8.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 87.5 (C), 97.7 (C), 112.3 (C), 118.5 (C), 122.5 (C), 127.5 (C), 127.8 (2CH), 130.0 (CH), 132.2 (2CH), 132.4 (2CH), 137.6 (2C). IR (cm^{-1}, neat): 2229, 1550, 1504, 1425, 1192, 834, 778, 718. Anal. Calcd for $C_{15}H_7Cl_2N$ (272.13): C 66.20, H 2.59, found C 65.91, H 2.50.

*4.2.9. 1,3-Dichloro-2-(phenylethynyl)benzene (**1j**).* White solid, mp: 56–58 °C. Yield (75%). R_f=0.60 (Et_2O/cyclohexane, 2/98, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.95 (1H, dd, *J*=7.5, 1.2 Hz), 7.10–7.23 (5H, m), 7.35–7.45 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 83.6 (C), 100.0 (C), 122.7 (C), 123.5 (C), 127.6 (2CH), 128.5 (2CH), 129.0 (CH), 129.1 (CH), 132.0 (2CH), 137.3 (2C). IR (cm^{-1}, neat): 2220, 1553, 1493, 1443, 1428, 1189, 1101, 788, 766, 749, 716. Anal. Calcd for $C_{14}H_8Cl_2$ (247.12): C 68.04, H 3.26, found C 67.84, H 3.31.

*4.2.10. 1,3-Dichloro-2-((4-methoxyphenyl)ethynyl)benzene (**1k**).* White solid, mp: 71–73 °C. Yield (53%). R_f=0.34 (Et_2O/cyclohexane, 5/95, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 3.77 (3H, s), 6.83

(2H, d, J=8.8 Hz), 7.10 (1H, t, J=8.1 Hz), 7.26 (2H, d, J=8.1 Hz), 7.50 (2H, d, J=8.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4 (CH_3), 82.6 (C), 100.3 (C), 114.2 (2CH), 114.8 (C), 123.7 (C), 127.6 (2CH), 128.6 (CH), 133.5 (2CH), 137.0 (2C), 160.3 (C). IR (cm^{-1}, neat): 2195, 1604, 1509, 1429, 1248, 1024, 830, 716. Anal. Calcd for $C_{15}H_{10}Cl_2O$ (277.15): C 65.01, H 3.64, found C 64.88, H 3.54.

*4.2.11. 1,3-Dibromo-5-fluoro-2-(phenylethynyl)benzene (**1l**).* Brown oil. (55%). R_f=0.60 (Et_2O/cyclohexane, 5/95, SiO_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.20–7.33 (3H, m), 7.42–7.48 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 73.9 (C), 81.5 (C), 103.7 (d, J_{C-F}=3.7 Hz, C), 119.1 (d, J_{C-F}=24.0 Hz, 2CH), 121.7 (C), 129.2 (2CH), 131.3 (d, J_{C-F}=10.0 Hz, 2C,), 131.6 (CH), 132.5 (2CH), 161.9 (d, J_{C-F}=255.0 Hz, C). Anal. Calcd for $C_{14}H_7Br_2F$ (354.01): C 47.50, H 1.99, found C 47.02, H 1.98.

*4.2.12. Methyl 2-((4-(6-hydroxyhex-1-ynyl)phenyl)ethynyl)-3,4,5-tri-methoxybenzoate (**1o**).* Compound **1o** was prepared from methyl-2-iodo-3,4,5-tri-methoxybenzoate and 6-(4-ethynyl phenyl)hex-5-yn-1-ol (in this case heating to 80 °C was necessary). Yellow solid, mp: 118–120 °C. Yield (77%). R_f=0.43 (Et_2O/cyclohexane, 50/50, SiO_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.63 (4H, m), 2.37 (2H, t, J=6.4 Hz), 3.59 (2H, t, J=6.5 Hz), 3.79 (3H, s), 3.83 (3H, s), 3.86 (3H, s), 3.92 (3H, s), 7,24 (1H, s), 7.35 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 19.3 (CH_2), 25.0 (CH_2), 31.8 (CH_2), 52.2 (CH_3), 56.1 (CH_3), 61.1 (CH_3), 61.3 (CH_3), 62.1 (CH_2), 80.7 (C), 85.2 (C), 92.1 (C), 97.1 (C), 109.8 (C), 112.1 (C), 122.8 (C), 123.9 (C), 127.6 (C), 131.2 (2CH), 131.4 (2CH), 145.7 (C), 153.0 (C), 155.2 (C), 166.1 (CO). IR (cm^{-1}, neat): 3058, 2937, 1728, 1338, 1115. Anal. Calcd for $C_{25}H_{26}O_6$ (422.47): C 71.07, H 6.20, found C 69.95, H 6.32.

4.3. General procedure for the hydrostannation of alkynes (B)

Tributyltin hydride (11 mmol) was added dropwise at room temperature to a solution of $PdCl_2(PPh_3)_2$ (0.1 mmol) and alkyne **1** (10 mmol) in THF (15 mL). The dark brown reaction mixture was stirred for 30 min and tributyltin hydride (2 mmol) was added more on the crude mixture to complete the hydrostannation reaction. After stirring for 30 additional minutes, the solution was concentrated in vacuo. Purification by flash chromatography on silica gel gave the desired products.

*4.3.1. Hydrostannation of **1b**.*

*4.3.1.1. (E)-Tributyl(1-(2,6-dimethoxyphenyl)-2-phenylvinyl) stannane (**2b**).* Colorless oil (86%). R_f=0.75 (Et_2O/cyclohexane, 1/9 TEA 1%, SiO_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.73–0.83 (15H, m), 1.20 (6H, sextet, J=7.2 Hz), 1.32–1.44 (6H, m), 3.57 (6H, s), 6.43 (2H, d, J=8.3 Hz,), 6.64 (1H, s, J_{Sn-H}=67.0 Hz), 6.91–7.11 (6H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.6 ($3CH_2$), 13.9 ($3CH_3$), 27.5 ($3CH_2$), 29.1 ($3CH_2$), 55.7 ($2CH_3$), 104.0 (2CH), 122.4 (C), 126.4 (CH), 126.5 (CH), 127.9 (2CH), 128.1 (2CH), 139.2 (C), 139.4 (CH), 141.6 (C), 155.4 (2C). IR (cm^{-1}, neat): 2954, 2925, 2870, 2852, 1579, 1494, 1467, 1431, 1375, 1282, 1245, 1171, 1110, 1074, 961, 921, 865, 778, 756, 713. Anal. Calcd for $C_{28}H_{42}O_2Sn$ (529.34): C 63.53, H 8.00, found C 63.41, H 8.05.

*4.3.2. Hydrostannation of **1c**.*

*4.3.2.1. (E)-(1-(2,6-Bis(benzyloxy)phenyl)-2-phenylvinyl)tributyl-stannane (**2c**).* Colorless oil (90%). R_f=0.56 (Et_2O/cyclohexane, 5/95 TEA 1%, SiO_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.54–0.91 (15H, m), 1.10 (6H, sextet, J=7.4 Hz), 1.21–1.41 (6H, m), 4.82 (2H, d, J=12.4 Hz), 4.86 (2H, d, J=12.4 Hz), 6.43 (2H, d, J=8.3 Hz), 6.70 (1H, s, J_{Sn-H}=68.0 Hz), 6.85–7.25 (16H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.7 ($3CH_2$), 13.8 ($3CH_3$), 27.5 ($3CH_2$), 29.0 ($3CH_2$), 70.1 ($2CH_2$), 105.6 (2CH), 123.5 (C), 126.3 (CH), 126.4 (CH), 127.0 (4CH), 127.5 (2CH), 128.0 (2CH), 128.2 (2CH), 128.3 (4CH), 137.7 (2C), 139.3 (C), 139.5 (1CH), 142.0 (C), 154.5 (2C). IR (cm^{-1}, neat): 2954, 2921, 2870, 2852, 1580, 1496, 1449, 1418, 1377, 1246, 1229, 1201, 1177, 1155, 1096, 1074, 1029, 961, 922, 864, 843, 733, 693. Anal. Calcd for $C_{40}H_{50}O_2Sn$ (681.53): C 70.49, H 7.39, found C 70.10, H 7.50.

*4.3.3. Hydrostannation of **1d**.*

*4.3.3.1. (E)-2-(2-phenyl-1-(tributylstannyl)vinyl)-1,3-phenylene diacetate (**2d**).* Colorless oil (65%). R_f=0.60 (Et_2O/cyclohexane, 3/7 TEA 1%, SiO_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.63–1.10 (15H, m), 1.23 (6H, sextet, J=7.4 Hz), 1.33–1.58 (6H, m), 2.02 (6H, s), 6.66 (1H, s, J_{Sn-H}=61.4 Hz), 6.87 (2H, d, J=8.0 Hz), 6.98–7.21 (6H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.3 ($3CH_2$), 13.8 ($3CH_3$), 21.0 ($2CH_3$), 27.6 ($3CH_2$), 29.0 ($3CH_2$), 120.3(2CH), 126.2 (CH), 127.4 (CH), 128.2 (2CH), 128.3 (2CH), 131.8 (C), 137.6 (C), 139.3 (C), 142.0 (1CH), 146.9 (2C), 168.8 (2CO). IR (cm^{-1}, neat): 2956, 2921, 2851, 1767, 1493, 1455, 1366, 1184, 1156, 1074, 1025, 985, 962, 926, 881, 867. Anal. Calcd for $C_{30}H_{42}O_4Sn$ (585.36): C 61.56, H 7.23, found C 61.74, H 7.48.

*4.3.4. Hydrostannation of **1e**.*

*4.3.4.1. (E)-Tributyl(1-(2,6-dimethoxyphenyl)-2-(4-methoxyphenyl) vinyl)stannane (**2e**).* Colorless oil (71%). R_f=0.14 (Et_2O/cyclohexane, 2/98 TEA 1%, SiO_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.66–0.92 (15H, m), 1.20 (6H, sextet, J=7.3 Hz), 1.30–1.44 (6H, m), 3.57 (6H, s), 3.65 (3H, s), 6.44 (2H, d, J=8.3 Hz), 6.52–6.67 (3H, m), 6.93 (2H, d, J=8.8 Hz), 7.05 (1H, t, J=8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.6 ($3CH_2$), 13.9 ($3CH_3$), 27.5 ($3CH_2$), 29.1 ($3CH_2$), 55.3 (CH_3), 55.7 ($2CH_3$), 104.1 (2CH), 113.3 (2CH), 126.4 (CH), 129.4 (2CH), 132.3 (C), 138.6 (CH), 138.8 (C), 155.5 (2C), 158.2 (C), 177.1 (C). IR (cm^{-1}, neat): 2994, 2954, 2927, 2870, 2835, 1604, 1582, 1508, 1466, 1431, 1375, 1292, 1244, 1175 1109, 1036, 960, 896, 874, 823, 805, 781, 760, 732. Anal. Calcd for $C_{29}H_{44}O_3Sn$ (559.37): C 62.27, H 7.93, found C 62.00, H 8.18.

*4.3.5. Hydrostannation of **1f**.*

*4.3.5.1. (E)-(1-(2,6-Bis(benzyloxy)phenyl)-2-(4-methoxyphenyl)-vinyl)tributyl-stannane (**2f**).* Colorless oil (55%). R_f=0.37 (Et_2O/cyclohexane, 5/95 TEA 1%, SiO_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.70–0.92 (15H, m), 1.18 (6H, sextet, J=7.3 Hz), 1.29–1.49 (6H, m), 3.75 (3H, s), 4.94 (2H, d, J=12.7 Hz), 4.98 (2H, d, J=12.7 Hz), 6.53 (2H, d, J=8.3 Hz), 6.67 (2H, d, J=8.6 Hz), 6.73 (1H, s, J_{Sn-H}=67.0 Hz), 6.97–7.10 (3H, m), 7.17–7.38 (10H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 10.6 ($3CH_2$), 13.8 ($3CH_3$), 27.5 ($3CH_2$), 29.0 ($3CH_2$), 55.2 (CH_3), 70.1 ($2CH_2$), 105.8 (2CH), 113.4 (2CH), 123.8 (C), 126.2 (CH), 127.0 (4CH), 127.4 (2CH), 128.3 (4CH), 129.4 (2CH), 132.5 (C), 137.8 (2C), 138.8 (CH), 139.3 (C), 154.7 (2C), 158.2 (C). IR (cm^{-1}, neat): 2953, 2929, 2869, 2852, 2836, 1604, 1582, 1508, 1464, 1449, 1417, 1377, 1291, 1245, 1226, 1201, 1175, 1110, 1095, 1072, 1031, 959, 935, 901, 877, 862, 823, 784, 766. Anal. Calcd for $C_{41}H_{52}O_3Sn$ (711.56): C 69.21, H 7.37, found C 69.36, H 7.20.

*4.3.6. Hydrostannation of **1g**.*

*4.3.6.1. (E)-2-(2-(4-Methoxyphenyl)-1-(tributylstannyl)vinyl)-1,3-phenylene diacetate (**2g**).* Colorless oil (70%). R_f=0.52 (Et_2O/cyclohexane, 30/70 TEA 1%, SiO_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.64–1.00 (15H, m), 1.22 (6H, sextet, J=7.3 Hz), 1.34–1.49 (6H, m), 2.02 (6H, s), 3.65 (3H, s), 6.58 (1H, s, J_{Sn-H}=62.0 Hz), 6.61 (2H, d, J=8.8 Hz), 6.88 (2H, d, J=8.1 Hz), 6.96 (2H, d, J=8.8 Hz), 7.13 (1H, t, J=8.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.3 ($3CH_2$), 13.8 ($3CH_3$), 21.0 ($2CH_3$), 27.6 ($3CH_2$), 29.0 ($3CH_2$), 55.2 (CH_3), 113.5 (2CH), 120.3 (2CH), 126.0 (CH), 129.7 (2CH), 130.6 (C), 132.1 (C), 136.2 (C), 141.3 (CH), 147.2 (2C), 158.9 (C), 168.9 (2CO). IR (cm^{-1}, neat): 2955, 2929,

1767, 1604, 1509, 1454, 1419, 1367, 1293, 1250, 1191, 1177, 1157, 1113, 1074, 1026, 985, 959, 908, 878, 825, 802, 781. Anal. Calcd for $C_{31}H_{44}O_5Sn$ (615.39): C 60.50, H 7.21, found C 60.24, H 7.18.

4.3.7. Hydrostannation of ***1h****.*

*4.3.7.1. (E)-4-(2-(2,6-Dimethoxyphenyl)-2-(tributylstannyl)vinyl) benzonitrile (**2l**) (major α-isomer).* Colorless oil (86%). R_f=0.59 (Et_2O/cyclohexane, 30/70 TEA 1%, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.73–1.01 (15H, m), 1.27 (6H, sextet, J=7.4 Hz), 1.37–1.53 (6H, m), 3.61 (6H, s), 6.50 (2H, d, J=8.4 Hz), 6.72 (1H, s, $^3J_{Sn-H}$=66.0 Hz), 7.05–7.20 (3H, m), 7.37 (2H, d, J=8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.7 ($3CH_2$), 13.9 ($3CH_3$), 27.5 ($3CH_2$), 29.0 ($3CH_2$), 55.6 ($2CH_3$), 103.9 (2CH), 109.4 (C), 119.5 (CN), 121.2 (C), 127.3 (CH), 128.4 (2CH), 131.8 (2CH), 137.6 (CH), 143.5 (C), 147.8 (C), 155.0 (2C). IR (cm^{-1}, neat): 2957, 2925, 2893, 2870, 2853, 2836, 2226, 1730, 1714, 1600, 1582, 1494, 1468, 1431, 1376, 1290, 1246, 1208, 1173, 1155, 1111, 1075, 1039, 960, 901, 879, 862, 840, 820, 781, 757. Anal. Calcd for $C_{29}H_{41}NO_2Sn$ (554.35): C 62.83, H 7.45, found C 62.75, H 7.27.

4.3.8. Hydrostannation of ***1i****.*

*4.3.8.1. (E)-4-(2-(2,6-Dichlorophenyl)-2-(tributylstannyl)vinyl) benzonitrile (**2i**).* Colorless oil (88%). R_f=0.50 (Et_2O/cyclohexane, 5/95 TEA 1%, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.79 (9H, t, J=7.3 Hz), 0.86–1.00 (6H, m), 1.21 (6H, sextet, J=7.3 Hz), 1.33–1.48 (6H, m), 6.73 (1H, s, J_{Sn-H}=57.0 Hz), 6.92–7.08 (3H, m), 7.21 (2H, d, J=8.0 Hz), 7.36 (2H, d, J=8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.5 ($3CH_2$), 13.7 ($3CH_3$), 27.4 ($3CH_2$), 28.8 ($3CH_2$), 110.5 (C), 119.1 (CN), 127.3 (CH), 128.2 (2CH), 128.4 (2CH), 131.4 (2C), 132.2 (2CH), 138.5 (CH), 141.8 (C), 142.2 (C), 150.5 (C). IR (cm^{-1}, neat): 2955, 2930, 2871, 2851, 2227, 1602, 1553, 1502, 1462, 1426, 1405, 1377, 1339, 1253, 1187, 1148, 1088, 1071, 1017, 961, 903, 876, 824, 777, 729. Anal. Calcd for $C_{27}H_{35}Cl_2NSn$ (563.19): C 57.58, H 6.26, found C 57.41, H 6.03.

4.3.9. Hydrostannation of ***1j****.*

*4.3.9.1. (E)-Tributyl (1- (2,6-dichlorophenyl)-2-phenylvinyl) stannane (**2j**).* Colorless oil (98%). R_f=0.64 (Et_2O/cyclohexane, 2/98 TEA 1%, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.79 (9H, t, J=7.3 Hz), 0.85–1.01 (6H, m), 1.21 (6H, sextet, J=7.3 Hz), 1.32–1.47 (6H, m), 6.70 (1H, s, J_{Sn-H}=60.8 Hz), 6.88–7.14 (6H, m), 7.21 (2H, d, J=7.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.3 ($3CH_2$), 13.8 ($3CH_3$), 27.5 ($3CH_2$), 28.9 ($3CH_2$), 126.8 (CH), 127.3 (CH), 127.9 (2CH), 128.0 (2CH), 128.3 (2CH), 131.8 (2C), 138.0 (C), 140.3 (1CH), 142.8 (C), 144.8 (C). IR (cm^{-1}, neat): 2955, 2923, 2870, 2851, 1553, 1493, 1463, 1425, 1376, 1254, 1191, 1148, 1088, 1073, 1047, 1028, 1001, 960, 921, 893, 874, 774. Anal. Calcd for $C_{26}H_{36}Cl_2Sn$ (538.18): C 58.02, H 6.74, found C 58.37, H 6.77.

4.3.10. Hydrostannation of ***1k****.*

*4.3.10.1. (E)-Tributyl(1-(2,6-dichlorophenyl)-2-(4-methoxyphenyl)-vinyl)stannane (**2k**).* Colorless oil (98%). R_f=0.43 (Et_2O/cyclohexane, 5/95 TEA 1%, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.80 (9H, t, J=7.3 Hz), 0.84–0.95 (6H, m), 1.20 (6H, sextet, J=7.3 Hz), 1.33–1.53 (6H, m), 6.60 (2H, d, J=8.8 Hz), 3.66 (3H, s), 6.62 (1H, s, J_{Sn-H}=62.1.0 Hz), 6.84 (2H, d, J=8.8 Hz), 6.95 (1H, t, J=8.3 Hz), 7.21 (2H, d, J=8.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.3 ($3CH_2$), 13.8 ($3CH_3$), 27.5 ($3CH_2$), 28.9 ($3CH_2$), 55.3 ($1CH_3$), 113.8 (2CH), 126.7 (CH), 128.0 (2CH), 129.4 (2CH), 131.0 (C), 132.1 (2C), 139.7 (CH), 142.0 (C), 142.9 (C), 158.8 (C). IR (cm^{-1}, neat): 2955, 2925, 2870, 2852, 1603, 1552, 1508, 1462, 1426, 1376, 1340, 1292, 1249, 1176, 1148, 1112, 1088, 1072, 1036, 960, 879, 823. Anal. Calcd for $C_{27}H_{38}Cl_2OSn$ (568.21): C 57.07, H 6.74, found C 57.22, H 6.38.

4.3.11. Hydrostannation of ***1l****. 4.3.11.1. (E)-Tributyl(1-(2,6-dibromo-4-fluorophenyl)-2-phenylvin yl) stannane (**2l**).* Colorless oil (48%). R_f=0.50 (Et_2O/cyclohexane, 2/98 TEA 1%, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.54–0.86 (15H, m), 1.08–1.42 (12H, m), 6.29 (1H, s, J_{Sn-H}=66.0 Hz), 7.05–7.10 (1H, m), 7.18 (2H, t, J=6.9 Hz), 7.29 (2H, d, J=7.6 Hz), 7.37 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.0 ($3CH_2$), 13.7 ($3CH_3$), 27.5 ($3CH_2$), 29.0 ($3CH_2$), 103.7 (d, J_{C-F}=5.0 Hz, C), 119.1 (d, J_{C-F}=24.0 Hz, 2CH), 126.4 (C), 128.1 (2CH), 128.2 (2CH), 131.3 (d, J_{C-F}=10.0 Hz, 2C), 131.6 (CH), 140.1 (1C), 154.2 (CH), 161.9 (d, $^1J_{C-F}$=255.0 Hz, C). Anal. Calcd for $C_{26}H_{35}Br_2FSn$ (645.07): C 48.41, H 5.47, found C 48.60, H 5.33.

4.3.12. Hydrostannation of ***1n****.*

*4.3.12.1. (E)-3-Mesityl-3-(tributylstannyl)prop-2-en-1-ol (**2n**).* Colorless oil (81%). R_f=0.41 (AcOEt/cyclohexane, 5/95 TEA 1%, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.78–0.86 (9H, m), 1.16–1.44 (19H, m), 2.05 (6H, s), 2.23 (3H, s), 3.87 (2H, s), 5.98 (1H, t, J=5.6 Hz, J_{Sn-H}=63.0 Hz), 6.78 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.9 ($3CH_2$), 14.1 ($3CH_3$), 20.9 ($2CH_3$), 21.3 (CH_3), 27.8 ($3CH_2$), 29.2 ($3CH_2$), 61.8 (CH_2), 128.4 (2CH), 132.8 (C), 134.8 (C), 139.7 (C), 139.8 (2C), 148.4 (CH). IR (cm^{-1}, neat): 3340, 2950, 2930, 2840, 1460, 1370, 1010. Anal. Calcd for $C_{24}H_{42}OSn$ (465.30): C 61.95, H 9.10, found C 62.21, H 8.98.

4.3.13. Hydrostannation of ***1o****.*

*4.3.13.1. Methyl-2-((E)-2-(4-((E)-6-hydroxy-1-(tributyl stannyl) hex-1-enyl)phenyl)-1-(tributylstannyl)vinyl)-3,4,5 trimetho-xybenzoate (**2o**).* Yellow oil (91%). R_f=0.28 (AcOEt/cyclohexane, 30/70 TEA 1%, SiO_2). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.35 (30H, m), 1.23 (14H, m), 1.43 (14H, m), 1.97 (2H, q, J=7.0 Hz), 3.48 (2H, dd, J=5.5 Hz), 3.57 (3H, s), 3.65 (3H, s), 3.89 (3H, s), 3.90 (3H, s), 5.66 (1H, t, J=7.0 Hz, $^3J_{Sn-H}$=62.0 Hz), 6.61 (1H, s, J_{Sn-H}=66.0 Hz), 6.64 (2H, d, J=8.2 Hz), 6.81 (2H, d, J=8.2 Hz), 7.23 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.9 ($6CH_2$), 13.6 ($6CH_3$), 25.7 (CH_2), 26.9 (CH_2), 27.2 ($6CH_2$), 28.9 (6 $CH_{2'}$), 31.9 (CH_2), 51.7 (CH_3), 55.9 (CH_3), 60.6 (CH_3), 60.7 (CH_3), 62.4 (CH_2), 109.7 (CH), 122.5 (C), 126.7 (2CH), 127.9 (2CH), 134.7 (C), 135.4 (C), 137.2 (CH), 141.6 (CH), 143.4 (C), 144.8 (C), 145.3 (C), 146.1 (C), 148.9 (C), 150.8 (C), 167.7 (C). IR (cm^{-1}, neat): 2961, 2849, 1721, 1589, 1291, 1061. Anal. Calcd for $C_{49}H_{82}O_6Sn_2$ (1004.59): C 58.58, H 8.23, found C 58.39, H 8.50.

4.3.14. Hydrostannation of ***1p****.*

*4.3.14.1. Tributyl(1-(2,6-dimethoxyphenyl)vinyl)stannane (**2p**).* Colorless oil (92%). R_f=0.70 (AcOEt/cyclohexane, 5/95 TEA 1%, SiO_2). ^1H NMR (300 MHz, $CDCl_3$) δ 0.93–0.74 (15H, m), 1.62–1.09 (12H, m), 3.75 (6H, s), 5.63 (1H, d, J=3.3 Hz, J_{H-Sn}=64.3 Hz), 5.89 (1H, d, J=3.3 Hz, J_{H-Sn}=137.0 Hz), 6.52 (2H, t, J=8.5 Hz), 7.08 (1H, t, J=8.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.6 ($3CH_2$), 13.9 ($3CH_3$), 27.5 ($3CH_2$), 29.1 ($3CH_2$), 55.80 ($2CH_3$), 103.9 (2CH), 124.2 (C), 126.4 (CH), 129.0 (2C), 147.4 (C), 156.0 (C). IR (cm^{-1}, neat): 2957, 2928, 2870, 1585, 1468, 1433, 1247, 1115. Anal. Calcd for $C_{22}H_{38}O_2Sn$ (453.25): C 58.30, H 8.45, found C 58.34, H 8.42.

4.3.15. Hydrostannation of ***1q****.*

*4.3.15.1. Tributyl(1-(2,6-dichlorophenyl)vinyl)stannane (**2q**).* Colorless oil (98%). R_f=0.8 (cyclohexane, TEA 1%, SiO_2). ^1H NMR (300 MHz, $CDCl_3$) δ 1.03–0.74 (15H, m), 1.52–1.15 (12H, m), 5.69 (1H, d, J=2.5 Hz), 5.79 (1H, d, J=2.5 Hz), 7.01 (1H, t, J=8.0 Hz), 7.39–7.17 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.3 ($3CH_2$), 13.8 ($3CH_3$), 27.4 ($3CH_2$), 28.9 ($3CH_2$), 126.8 (CH), 127.8 (2CH), 130.1 (2C), 132.2 (C), 152.2 (C). IR (cm^{-1}, neat): 2955, 2922, 1555, 1425, 1192, 1075, 930, 774, 743, 688. Anal. Calcd for $C_{20}H_{32}Cl_2Sn$ (462.08): C 51.98, H 6.98, found C 51.95, H 6.94.

4.4. Typical procedure for iodination of *ortho-ortho′* vinylstannes (C)

To a flame-dried flask under a nitrogen atmosphere were added at 0°C vinyl stannane **2k** (1 equiv), dry CH_2Cl_2 (2 mL per mmol of substrate), sublimed finely divided I_2 (1.05 equiv), and the dark wine solution was vigorously stirred at room temperature until all of the substrate had been consumed (TLC). Saturated aqueous $Na_2S_2O_3$ was added to remove the excess of iodine followed by addition of a potassium fluoride aqueous solution. After stirring at room temperature for 1 h, the resulting white precipitate of tributyltin fluoride was removed by filtration and the filtrate was extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated (the crude vinyl iodide could be used in the further step without purification).

*4.4.1. (E)-1,3-Dichloro-2-(1-iodo-2-(4-methoxyphenyl)vinyl) benzene (**3a**).* Colorless oil (yield=98% after filtration through silica gel). R_f=0.50 (Et_2O/cyclohexane, 5/95 TEA 1%, SiO_2). ^1H NMR (300 MHz, $CDCl_3$): δ 3.65 (3H, s), 6.61 (2H, d, J=8.8 Hz), 6.75 (2H, d, J=8.8 Hz), 7.15 (1H, t, J=8.8 Hz), 7.28 (2H, d, J=8.5 Hz,), 7.39 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3 (CH_3), 86.5 (C), 114.0 (2CH), 128.7 (2CH), 129.1 (C), 129.6 (2CH), 130.0 (CH), 134.2 (2C), 139.6 (C), 143.9 (CH), 159.5 (C). IR (cm^{-1}, neat): 3077, 2955, 2837, 1602, 1574, 1554, 1509, 1459, 1428, 1355, 1308, 1294, 1260, 1179, 1169, 1151, 1114, 1092, 1034, 951, 935, 891, 878, 816, 780, 739, 679.

*4.4.2. Methyl 2-((E)-2-(4-((E)-6-hydroxy-1-iodohex-1-enyl)phenyl)-1-iodovinyl)-3,4,5-tri-methoxybenzoate (**3b**).* Following the above General procedure (C), using vinylstannane **2o** (1.3 g, 1.29 mmol), DCM (40 mL) as solvent, I_2 solution (2.2 equiv 723 mg, 2.85 mmol) in DCM (40 mL). The reaction was stirred at −40 °C for 4 h in the dark.

Yellow oil (yield=98% after filtration through silica gel). R_f=0.37 (AcOEt/cyclohexane, 20/80 TEA 1%, SiO_2). ^1H NMR (300 MHz, $CDCl_3$): δ 1.21 (4H, m), 1.76 (2H, q, J=7.4 Hz), 3.35 (2H, t, J=5.7 Hz), 3.61 (3H, s), 3.67 (3H, s), 3.69 (3H, s), 3.78 (3H, s), 6.21 (1H, t, J=7.4 Hz), 6.62 (2H, d, J=8.6 Hz), 6.85 (2H, d, J=8.7 Hz), 7.14 (1H, s), 7.29 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.9 (CH_2), 32.6 ($2CH_2$), 46.1 (CH_2), 51.3 (CH_3), 55.6 (CH_3), 59.9 (CH_3), 60.1 (CH_3), 60.2 (CH_2), 91.6 (C), 94.3 (C), 108.7 (CH), 123.9 (2 CH), 127.4 (C), 128.5 (C), 131.2 (2 CH), 136.8 (CH), 140.5 (CH), 145.9 (C), 150.1 (C), 153.2 (2C), 170.9 (C=O). IR (cm^{-1}, neat): 3406, 2937, 2857, 1725, 1585, 1489, 1451, 1431, 1393, 1333, 1255, 1223, 1194, 1171, 1116, 1052, 755.

4.5. Typical procedure for Negishi coupling between *ortho-ortho′* vinyl iodide and organozinc compounds (D)

To a solution of vinyl iodide **2**, $PdCl_2(PPh_3)_2$ (5 mol %) in THF was added at room temperature ArZnCl (2 equiv) prepared by transmetallation from the corresponding Grignard reagent (2 equiv) and anhydrous $ZnCl_2$ (2.1 equiv). The reaction was stirred at room temperature and monitored by TLC until complete consumption of starting materials (2–4 h). The reaction was hydrolyzed at 0°C with aqueous HCl (1 N), extracted with Et_2O, the organic extract was dried over $MgSO_4$, and the solvent was removed in vacuo.

*4.5.1. (Z)-4,4′-(1-(2,6-Dichlorophenyl)ethene-1,2-diyl)bis(methoxybenzene) (**4a**).* Colorless oil (yield=73%). R_f=0.29 (Et_2O/cyclohexane, 5/95, SiO_2). ^1H NMR (300 MHz, $CDCl_3$): δ 3.66 (3H, s), 3.73 (3H, s), 6.63 (2H, d, J=8.9 Hz), 6.79 (2H, d, J=8.9 Hz), 6.84 (2H, d, J=8.9 Hz), 6.99 (1H, s), 7.22–7.11 (3H, m), 7.31 (2H, d, J=7.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.3 (CH_3), 55.4 (CH_3), 113.8 (2CH), 114.1 (2CH), 127.2 (2CH), 128.6 (2CH), 128.6 (CH), 129.4 (CH), 129.7 (2CH), 129.8 (C), 132.8 (C), 133.9 (C), 135.7 (2C), 138.4 (C), 158.8 (C), 159.2 (C). IR (cm^{-1}, neat): 3001, 2955, 2932, 2900, 1606, 1573, 1555, 1511, 1462, 1441, 1427, 1366, 1302, 1288, 1256, 1241, 1175, 1153, 1113, 1090, 1031, 908, 850, 827, 783, 767, 754, 681. Anal. Calcd for $C_{22}H_{18}Cl_2O_2$ (385.28): C 68.58, H 4.71, found C 68.62, H 4.54.

*4.5.2. Methyl 2-((Z)-2-(4-((E)-6-hydroxy-1-(4-methoxyphenyl) hex-1-enyl)phenyl)-1-(4-methoxyphenyl)vinyl)-3,4,5-tri-methoxybenzoate (**4b**).* Following the above General procedure (D), using bromo (4-methoxyphenyl)zinc (6 equiv) in THF, $PdCl_2(PPh_3)_2$ (5%) and **3l** (1 equiv). The reaction was stirred at room temperature for 2 h in the dark.

Yellow oil (yield=61%). R_f=0.10 (AcOEt/cyclohexane, 30/70, SiO_2). ^1H NMR (400 MHz, $CDCl_3$): δ 1.44 (4H, m), 1.62 (2H, m), 2.01 (1H, br s, OH), 3.71 (2H, m), 3.76 (6H, s), 3.81 (3H, s), 3.91 (3H, s), 3.94 (3H, s), 3.97 (3H, s), 6.08 (1H, t, J=7.8 Hz), 6.87–6.91 (12H, m), 7.12 (1H, s), 7.23 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.9 (CH_2), 29.1 (CH_2), 31.9 (CH_2), 51.1 (CH_3), 59.9 (CH_3), 60.5 (CH_3), 60.7 (CH_3), 62.3 (CH_2), 109.4 (CH), 113.3 (2CH), 113.5 (2CH), 127.8 (2 CH), 127.5 (2 CH), 128.1 (2C), 129.4 (C), 135.3 (2CH), 135.5 (2CH), 135.8 (C), 136.4 (2C), 136.7 (C), 138.5 (C), 139.0 (CH), 140.9 (CH), 152.6 (C), 158.6 (2C), 158.8 (2C), 167.3 (C=O). IR (cm^{-1}, neat): 2940, 2250, 1726, 1510, 1335, 1115, 910, 730. Anal. Calcd for $C_{39}H_{42}O_8$ (638.75): C 73.33, H 6.63, found C 73.42, H 6.32.

4.6. General procedure for the hydrosilylation of alkynes (E)

In a sealed tube, PtO_2 (11.35 mg, 0.05 mmol) and alkyne (1 mmol) were placed under nitrogen atmosphere. Triethylsilane (0.24 mL, 1.5 mmol) was introduced via syringe and the mixture was stirred at 60 °C in an oil bath for 1 h in the absence of solvent. The residue was then purified by column chromatography over silica gel to yield the title adducts either as a single α-isomer **5** or as a mixture of inseparables **5α** and **5β**-isomers.

*4.6.1. (E)-(1-(2,6-Dimethoxyphenyl)-2-phenylvinyl)triethylsilane (α-**5a**).* Colorless oil (yield=90% after filtration through silica gel). R_f=0.70 (AcOEt/cyclohexane, 20/80, SiO_2). *Major α isomer*: ^1H NMR (300 MHz, $CDCl_3$) δ 0.61 (6H, q, J=6.1 Hz), 0.93 (9H, t, J=6.2 Hz), 3.63 (6H, s), 6.52 (2H, d, J=8.3 Hz), 6.85 (1H, s), 7.12–6.99 (5H, m), 7.16 (1H, t, J=8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 3.7 ($3CH_2$), 7.4 ($3CH_3$), 55.6 (2 CH_3), 104.0 (2 CH), 120.2 (C), 126.8 (CH), 127.1 (CH), 127.9 (2 CH), 128.5 (2 CH), 136.2 (C), 138.9 (C), 139.6 (CH), 156.5 (2C). IR (cm^{-1}, neat): 2950, 2875, 1583, 1468, 1431, 1246, 1110, 1006, 907, 781, 762, 649. Anal. Calcd for $C_{22}H_{30}O_2Si$ (354.56): C 74.53, H 8.53, found C 74.41, H 8.44.

*4.6.2. (E)-(1-(2,6-Dimethoxyphenyl)-2-(4-methoxyphenyl)vinyl) triethylsilane (α-**5b**).* Colorless oil (yield=97% after filtration through silica gel). R_f=0.65 (AcOEt/cyclohexane, 20/80, SiO_2). *Major α isomer*: ^1H NMR (300 MHz, $CDCl_3$) δ 0.58 (6H, q, J=7.8 Hz), 0.93 (9H, t, J=7.8 Hz), 3.65 (6H, s), 3.72 (3H, s), 6.54 (2H, d, J=8.3 Hz), 6.64 (2H, d, J=8.8 Hz), 6.78 (1H, s), 6.99 (2H, d, J=8.8 Hz), 7.16 (1H, t, J=8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 3.7 ($3CH_2$), 7.4 ($3CH_3$), 55.2 (CH_3), 55.6 (2 CH_3), 104.1 (2CH), 113.4 (2CH), 120.4 (C), 127.0 (CH), 129.8 (2CH), 131.9 (C), 133.5 (C), 138.8 (CH), 156.6 (2C), 158.5 (C). IR (cm^{-1}, neat): 2950, 1508, 1468, 1432, 1246, 1176, 1111, 1036, 1007, 905, 762, 727,696, 650. Anal. Calcd for $C_{23}H_{32}O_3Si$ (384.58): C 71.83, H 8.39, found C 71.49, H 8.32.

*4.6.3. (E)-(1-(2,6-Dichlorophenyl)-2-phenylvinyl)triethylsilane (α-**5c**).* Colorless oil (yield=98% after filtration through silica gel). R_f=0.40 (cyclohexane, SiO_2). ^1H NMR (300 MHz, $CDCl_3$) δ 0.72 (6H, q, J=6.1 Hz), 0.96 (9H, t, J=6.1 Hz), 7.18–6.88 (6H, m), 7.30–7.26 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 4.4 ($3CH_2$), 7.4 ($3CH_3$), 127.6 (CH), 127.7 (CH), 128.2 (CH), 128.3 (2CH), 133.4 (2C), 137.7 (C), 140.7 (C), 141.5 (2CH), 148.2 (C). IR (cm^{-1}, neat): 2954, 2875, 1426, 1009, 965,

937, 777, 765, 749, 730, 717, 688. Anal. Calcd for $C_{20}H_{24}Cl_2Si$ (363.40): C 66.10, H 6.66, found C 66.05, H 6.45.

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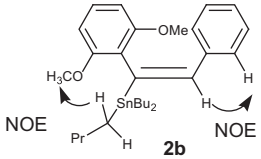
13. For diaryl derivatives, α isomers have been fully identified by NOESY experiments., e.g., for **2b**.



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