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Stereoselective access to functionalized β-γ unsaturated acids

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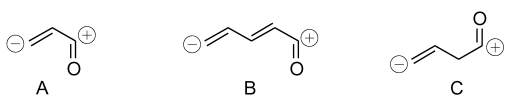
Abstract—Stereoselective synthesis of vinylstannanes bearing a carboxylic acid function was achieved from β-γ alkynoic acids via hydrostannation, stannylcupration or silastannation reactions. Regioselectivity is highly dependent on the nature of the stannylanions used and on protection of the carboxylic acid function. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

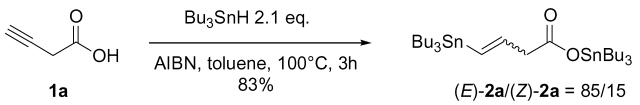
Vinyltin reagents have proved to be efficient tools for the transfer of a vinyl unit, with a high tolerance of numerous functions both on the substrate and on the reagent.[1] In this context, we have proposed numerous vinylstannanes and dienylstannanes bearing a conjugated non-protected carboxylic acid function, which is certainly one of the most often used functions in organic synthesis.[2] The most significant studies to date have focused on reagents able to transfer an 'umpolung' unit of d^3 type (vinyltins bearing acetal[3] or ester[4] functions) although some new vinyltin reagents such as those bearing an homoallylic acetal function have been described.[5] The most effective studies to date have focused on reagents able to transfer an acrylic or pentadienoic unit (A and B). To the best of our knowledge, the transfer of deconjugated butenoic acid has not been examined, although the synthon C is found in numerous natural products.



It would be valuable to offer new organotin reagents for the transfer of a four carbon chain bearing such a carboxylic acid function. We have previously described the synthesis and the reactivity of vinyltin bearing on homoallylic acetal which is a formal equivalent of C. Nevertheless, the main formation of conjugated enal during the acidic deprotection of acetal function prompted us to investigate another acylfunction equivalent. We report here the synthesis and the reactivity of tributylstannyl 4-tributylstannylbut-3-enoate.[6]

2. Results and discussions

The synthesis of vinyltin reagents was historically obtained through radical hydrostannation of alkynes.[7] However, this method was found to be limited because of its low selectivity, and numerous methods such as transition metal catalysed hydrostannation[8] have been proposed to resolve this problem. Among these, the stannylcupration reaction of alkynes generally offers good regio- and stereoselectivity.[9,10] Moreover, the intermediate vinyl copper can be alkylated, yielding trisubstituted vinylstannanes with fixed configuration.[11] Interestingly, the stannylcopper reagents were found to be inert towards hydroxy or NH amide functions at low temperature.[12] Another possibility is the addition of a bimetallic Si–Sn system[13] on alkynes,[14] although these reactions have been mostly achieved by the catalysis of palladium phosphine complexes.[15]



1a (*E*)-**2a**/(*Z*)-**2a** = 85/15

Scheme 1.

Keywords: hydrostannation; regioselectivity; iododestannylation.

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Table 1. Stannylmetallation of alk-3-ynoic acids

Entry	R	Σ	E	M	Tin reagent	**2**[a]/**3**	No.	Yield (%)[b]
1	H	H	H	Cu(Bu)Li, LiCN[c]	D	95/5	**2a/3a**	55 [d]
2	H	H	D	Cu(Bu)Li, LiCN[c]	D	95/5	**2b/3b**	53 [e]
3	H	H	H	$AlEt_2$, 15% CuCN[f]	A	20/80	**2a/3a**	28
4	H	H	H	MgMe, 15% CuCN[g]	B	70/30	**2a/3a**	35
5	H	H	H	$ZnSnBu_3$, [Pd][h] 5%	C	67/33	**2a/3a**	40
6	H	$SnBu_3$	H	Cu(Bu)Li, LiCN[c]	D	5/95	**2a/3a**	47
7	H	$SnBu_3$	H	MgMe, 15% CuCN[g]	B	30/70	**2a/3a**	53
8	Et	H	H	Cu(Bu)Li, LiCN[c]	D	90/10	**2c/3c**	40
9	H	H	Me	Cu(Bu)Li, LiCN[c]	D	98/2	**2d/3d**	55

[a] Only the *E* isomer is obtained.
[b] Yield ratio **2/3** determined by ^1H NMR.
[c] Isolated yield.
[d] The reaction was quenched with D_2O at −78°C.
[e] THF, −78°C, 1 h.
[f] THF, −30°C, 3 h.
[g] THF, 0°C, 2 h.
[h] [Pd]=$Pd(PPh_3)_4$.

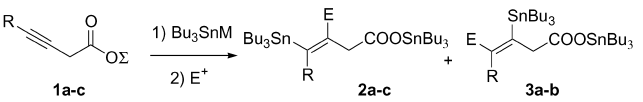
2.1. Hydrostannation of but-3-ynoic acid 1a

The required organotin precursor **2a** was easily obtained with 83% yield as a thermodynamic mixture (*E*)-**2a**/(*Z*)-**2a**=85/15 (Scheme 1) by radical hydrostannation of but-3-ynoic acid **1a** which was prepared via carbonatation of the corresponding allenylmagnesium bromide.[16]

2.2. Stannylmetallation of alk-3-ynoic acids

To improve the selectivity of this reaction, we studied the stannylmetallation of **1a** (results are consigned in Table 1). Numerous tin anion systems known to add to the triple bond were tested. When using $Bu_3SnAlEt_2$/CuCN A,[17] Bu_3-SnMgMe/CuCN B,[9b] $(Bu_3Sn)_2Zn/Pd(PPh_3)_4$ C,[9b] only low conversion rates into (*E*)-tributylstannyl 4-tributylstannyl-but-3-enoate **2a** were obtained. The best results were obtained with high order $Bu_3Sn(Bu)Cu(CN)Li_2$ cyanocuprate D (2.3 equiv.),[12d] which afford fair yields of the same isomer. As already observed,[12d] a clean *cis*-addition of stannylcuprate occurred and no Bu ligand was transferred to the triple bond.

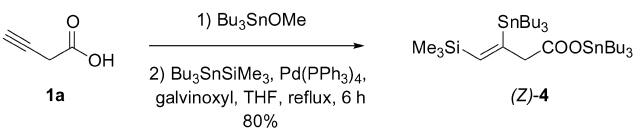
In order to acquire information regarding the influence of protection of the carboxylic acid function, tributylstannyl ester of but-3-ynoic acid **1b** (entry 6) was used in place of **1a** and was found to react with D with complete reverse regioselectivity in comparison to entry 1. Similarly, stannylanion B gave a 30/70 mixture in favour of internal vinylstannane **3a** (entry 7). Stannylcupration of hex-3-ynoic acid (entry 8) with D confirmed the regioselectivity of the addition. Finally, treatment of intermediate vinylcopper (entry 9) with methyl iodide led to trisubstituted vinylstannanes in fair yield but with an excellent regioselectivity. Concerning the factors governing the regioselectivity of the addition reaction, it is difficult to predict the trend of the addition which can be reversed by a slight change in the nature of both alkyne and stannyl reagents. Other tin anion reagents gave poor regioselectivity but with a reverse trend (entries 3–5) (Scheme 2). The results are recorded in Table 1.



Scheme 2.

2.3. Silastannation of but-3-ynoic acid 1a

The best results for stereospecific addition of (tributylstannyl)trimethylsilane on the tributylstannyl ester of but-3-ynoic acid derivatives was obtained using tetrakis(triphenylphosphine)palladium as catalyst, THF as the solvent, a small amount of galvinoxyl[18] and protection of the acidic function with a tributylstannyl group[19] (using acid **1a**, the reaction failed leaving the starting material unchanged). Under these experimental conditions, (*Z*)-tributylstannyl-3-tributylstannyl-4-trimethylsilylbut-3-enoate (*Z*)-**4** was isolated (80% yield) (Scheme 3).



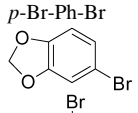
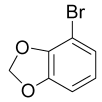
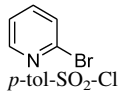
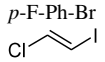
Scheme 3.

2.4. Reactivity of 2a and 4

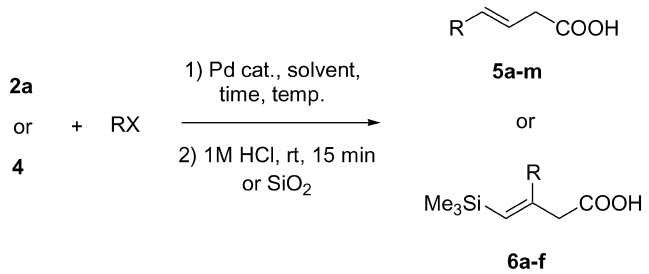
The reactivity of **2a** and (*Z*)-**4** was examined in the case of cross-coupling with organic halides under catalysis with palladium complexes.[20] In order to find optimal experimental conditions, various catalysts were tested and we found that tetrakis(triphenylphosphine)palladium was the most efficient for **2a** (entries 1–13). The substitution reaction of **4** appears to have a general character only if the aryl halide used exhibits an electron withdrawing group in its structure (entries 14–19). The results are reported in Table 2, (Scheme 4).

As seen in the results reported in Table 2, good yields were obtained with aryl or heteroaryl halides (entries 1–12). We observed that (*E*)-adduct reacted under our experimental

Table 2. Reactivity of **2a** and **4** with organic halides

Entry	Substrate	Organic halide	Catalyst	Yield (%)	No.
1	**2a**	Ph-I	A	72	**5a**
2	**2a**	*p*-F-Ph-Br	A	66	**5b**
3	**2a**	*p*-MeO-Ph-Br	A	55	**5c**
4	**2a**	*p*-Acetyl-Ph-Br	A	65	**5d**
5	**2a**	*p*-CHO-Ph-Br	A	65	**5e**
6	**2a**	*p*-CF_3-Ph-Br	A	73	**5f**
7	**2a**	*p*-Br-Ph-Br	A	75	**5g**
8	**2a**		A	88	**5h**
9	**2a**		A	55	**5i**
10	**2a**	*m*-CF_3-Ph-Br	A	74	**5j**
11	**2a**	*m*-Br-Ph-Br	A	78	**5k**[a]
12	**2a**		A	85	**5l**[b]
13	**2a**	*p*-tol-SO_2-Cl	B	83	**5m**
14	**4**	*o*-NO_2-Ph-I	A	68	**6a**
15	**4**	*p*-CHO-Ph-Br	A	50	**6b**
16	**4**	*m*-CF_3-Ph-Br	A	57	**6c**
17	**4**	*p*-F-Ph-Br	A	59	**6d**
18	**4**		C	63	**6e**
19	**4**	Ph-I	A	0	–

A=toluene, $Pd(PPh_3)_4$, 100°C, 12 h; B=THF, $Pd(PPh_3)_4$, 55°C, 12 h; C=DMF, $PdCl_2(MeCN)_2$, 50°C, 8 h.
[a] Only monosubstitution adduct is recovered.
[b] Isolated as a stannylester.

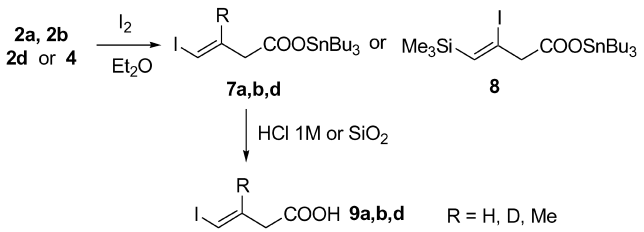


Scheme 4.

conditions (1.2 equiv. of vinyltin), thus revealing the great difference in reactivity between the two isomers. When the thermodynamic mixture of (*E*)-**2a**/(*Z*)-**2a**=85/15 was used for cross-coupling with organic halides, the crude mixture was found to contain a small amount of (*Z*)-**5** (<5%) which was eliminated during the crystallization purification process. In the particular case of 2-bromopyridine (entry 12, Table 1) the ratio *E*/*Z* of 5 L was 85/15. The temporary protection of the carboxylic acid function was removed by simple hydrolysis at room temperature with HCl/water 1 M or by stirring on silica gel. These results demonstrate the efficiency of **2a** to obtain the homocinnamyl skeleton cleanly and more generally to transfer the d^4 but-3-enoic acid synthon onto miscellaneous substrates.

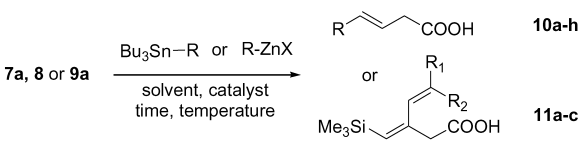
2.5. Iododestannylation and reactivity of 7, 8 and 9

In order to extend the potential of compounds **2a**,**b**,**d** and **4**, reverse cross-coupling reactions were investigated.[21] Iododestannylation of **2a**,**b**,**d** and **4** yielded the corresponding iodotributylstannylester **7a**,**b**,**d** and (*Z*)-tributylstannyl-3-iodo-4-trimethylsilylbut-3-enoate **8** in nearly quantitative amounts without isomerisation of the double bond. It is interesting to note that iodine treatment did not affect the tributyltincarboxylate function. Iodo vinylic acids **9a**,**b**,**d** were obtained by acidic hydrolysis (Scheme 5).



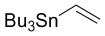
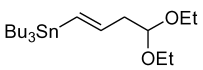
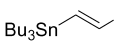
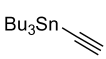
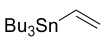
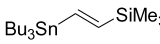
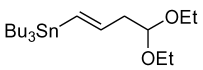
Scheme 5.

Using a similar procedure, **7a**, **9a** and **8** were cross-coupled with vinyltin reagents or organozinc reagents affording fair to good yields of **10a**–**h** and **11a**–**c** (Scheme 6, Table 3).



Scheme 6.

Table 3. Reactivity of **7a**, **8** and **9a** with vinyltin or organozinc reagents

Entry	Substrate	RM	Catalyst	Yield (%)	No.
1	**9a**		B	72	**10a**
2	**9a**		B	61	**10b**
3	**9a**		B	80	**10c**
4	**7a**		B	75	**10d**
5	**8**		A	71	**11a**
6	**8**		A	56	**11b**
7	**8**		A	65	**11c**
9	**9a**	MeZnBr	B	90	**10e**
10	**9a**	EtZnBr	B	92	**10f**
11	**9a**	BnZnBr	B	75	**10g**
12	**9a**	$MeOH_2C$—≡—ZnBr	B	79	**10h**

A=toluene, $Pd(PPh_3)_4$, 12 h; B=DMF, $PdCl_2(MeCN)_2$, 12 h.

The experimental conditions applied here are derived from the systematic study carried out on 3-iodobut-3-enoic acid[2a,d] and 3 equiv. of organozinc reagent were required to achieve complete conversion (entries 9–12). No isomerisation of the double bond was observed and no cyclisation, affording butenolides, occurred.

3. Conclusion

In summary, we investigated the hydrostannation, the stannylcupration and the silastannation reaction of homopropargylic acids, stereoselective synthesis of vinylstannanes bearing a carboxylic acid function was achieved. We, also, demonstrated that the regioselectivity is highly dependent on the nature of the stannylanions used and on protection of the carboxylic acid function.

4. Experimental

General Methods. ^{1}H NMR spectra were recorded at 200 or at 300 MHz using $CDCl_3$ as solvent. Results, reported using the residual proton resonance of $CDCl_3$ (δ_H=7.25 ppm) as the internal reference, were as follows (in order): chemical shift (δ in ppm relative to Me_4Si), multiplicity (s, d, t, m, b for singlet, doublet, triplet, multiplet, broad), coupling constants (J in Hz). ^{13}C NMR spectra were recorded at 50 or 75 MHz using $CDCl_3$ solvent peak at δ_C=77.0 ppm as the reference. Electron impact mass spectra were measured at 70 ev by GC-MS or direct introduction mode. The isotopic patterns are given for ^{120}Sn (isotopic values 33%) in organotin fragments; this means that the reported values (values in brackets) for organotin fragments were only roughly one third of the correct value, taking into account the 10 isotopes of tin compared with those of organic fragment. Raman spectra were recorded on a Bruker RFS 100, excitation with a laser Nd: YAG (1064 nm, 130 mW). Melting points were uncorrected. Standard column chromatography was performed on Merck silica gel (60 Å, 230–400 mesh silica gel) by flash column chromatography techniques. Analytical thin-layer chromatography (TLC) was conducted on Merck precoated silica gel 60 F_{254} Plate. All reactions were performed in oven-dried glassware under positive argon pressure, unless otherwise noted. Reaction mixtures were stirred magnetically. Ether was dried and freshly distilled from sodium/benzophenone. DMF was dried by distillation over calcium hydride prior to use. Tributyltin methoxide and tributyltin hydride were commercialy available (or prepared according to Refs. 22,23). Acid **1a** was prepared by a previously reported procedure.[16] Vinyltributylstannane was prepared from vinylmagnesium bromide and bistributyltin oxide.[24] (*E*)-1-Trimethylsilyl-2-*n*-tributylstannylethylene was prepared by hydrostannation of trimethylsilylacetylene.[25] (*E*)-β-Styryltributyltin was prepared by hydrostannation of phenylacetylene.[26] (*E*)-1-Tributylstannyl-4,4-diethoxybut-1-ene was obtained by stannylmetallation of the homopropargylic acetal using tributylstannylmethyl magnesium in the presence of cuprous cyanide.[27] Tributyltinacetylide was prepared from lithium acetylide, ethylenediamine complex and tributyltin chloride.[28] The preparation of tributylstannyl 4-tributylstannylbut-3-enoate (**2a**) was already described.[29]

4.1. Stannylmetallation of but-3-ynoic acid 1a

Tributylstannylcuprate was prepared according to the route described by Lipshutz et al.[12d] CuCN (1.8 g, 20 mmol) was suspended in freshly distilled THF (80 mL), cooled at −80°C and 25 mL of *n*-BuLi 1.6 M in hexane (40 mmol) were added dropwise at −80°C (green coloration until a homogeneous solution was obtained). The mixture was allowed to react for 15 min and then Bu_3SnH (10.9 mL, 40 mmol) was added dropwise (yellow coloration was obtained) at −80°C. After stirring for 15 min at −80°C, but-3-ynoic acid **1a** (0.68 g, 8 mmol) in THF (5 mL) was added slowly and allowed to react for 2 h at −80°C.

(a) The reaction mixture was then quenched with a saturated NH_4Cl or D_2O solution at −80°C and Et_2O was added. After filtration over Celite, the organic layer was separated, extracted with Et_2O, washed with brine and dried over $MgSO_4$. After evaporation of solvents, the crude products were used without further purification (entry 1).

(b) The vinylcopper intermediate was trapped by an excess of methyl iodide (30 mL) in the presence of HMPA (4 mL) at −80°C. The mixture was allowed to react at room temperature for 24 h. The reaction mixture was then quenched with a saturated NH_4Cl solution at 0°C and Et_2O was added. After filtration over Celite, the organic layer was separated, extracted with Et_2O, washed with brine and dried over $MgSO_4$. After evaporation of solvents, the crude product was used without further purification.

A similar procedure for the stannylmetallation of **1b** (the preparation of tributylstannylbut-3-ynoate (**1b**) was described[19]) was employed.

4.1.1. 3-Tributylstannylbut-3-enoic acid (3a′). (By purification of crude product **3a** on silica gel using PE/Et_2O=95/5, we only observed deprotection of stannyl ester into acid **3a′**.) IR: 3020, 1710, 1645, 1230. ^{1}H NMR (δ ppm): 0.85 (t, J=7.2 Hz, 9H), 0.88–1.05 (m, 6H), 1.20–1.60 (m, 12H), 3.24 (s, J_{Sn-H}=43 Hz, 2H), 5.24 (bs, J_{Sn-H}=56.7 Hz, 1H), 5.76 (bs, J_{Sn-H}=127 Hz, 1H), 11.60 (bs, 1H). ^{13}C NMR (δ ppm): 10.7 (J_{Sn-C}=344–328 Hz, 3C), 14.2 (3C), 27.9 (J_{Sn-C}=56 Hz, 3C), 29.6 (J_{Sn-C}=18.6 Hz, 3C), 44.5 (J_{Sn-C}=33.3 Hz), 129.6 (J_{Sn-C}=42.4 Hz), 147.9 (J_{Sn-C}=320 Hz), 179.2 (J_{Sn-C}=58 Hz). MS (70 eV, EI) *m*/*z*: 319 (M^+−57, 100), 291 (22), 275 (18), 235 (12), 205 (11), 179 (26), 177 (76), 121 (15), 57 (9), 41 (25), 39 (14).

4.1.2. (*E*)-Tributylstannyl 3-^{2}H-4-tributylstannylbut-3-enoate (2b). ^{1}H NMR (δ ppm): 0.80–1.70 (54H, m), 3.18 (2H, s), 5.72 (1H, s, J_{Sn-H}=65.5 Hz).

4.1.3. (*E*)-Tributylstannyl 3-methyl-4-tributylstannylbut-3-enoate (2d). ^{1}H NMR (δ ppm): 0.80–1.70 (m, 54H), 1.89 (s, 3H), 3.20 (s, 2H), 5.66 (s, J_{Sn-H}=65.5 Hz, 1H).

4.2. Silastannation of but-3-ynoic acid (1a)

A solution of (trimethylsilyl)tributylstannane (0.98 g, 2.7 mmol) in THF (1 mL) was added dropwise by syringe to a solution of **1b** tributylstannylbut-3-ynoate (1 g, 2.7 mmol), tetrakis(triphenylphosphine)palladium (62 mg, 2 mol%), and galvinoxyl (10 mg) in THF (50 mL) at room temperature. After stirring at 70°C for 6 h, the reaction mixture was filtered through a Celite pad and concentrated under vacuum. Silylstannane 4*Z* (1.58 g, 2.14 mmol, 80%) was purified by crystallization from Et_2O/hexane (5/95) to provide white needles (mp: 45°C).

4.2.1. (*Z*)-Tributylstannyl 3-tributylstannyl-4-trimethylsilyl-but-3-enoate (4). ^{1}H NMR (δ ppm): 0.14 (s, 9H), 0.93 (t, J=7.3 Hz, 18H), 1.22–1.65 (m, 36H), 3.32 (s, J_{Sn-H}=42 Hz, 2H), 6.44 (s, J_{Sn-H}=168 Hz, 1H). ^{13}C NMR (δ ppm): −0.7, 11.6 (J_{Sn-C}=318–330 Hz, 3C), 13.5 (6C), 16.3 (J_{Sn-C}=344–360 Hz, 3C), 26.9 (J_{Sn-C}=80 Hz, 3C), 27.5 (J_{Sn-C}=116 Hz, 3C), 27.7 (J_{Sn-C}=21 Hz, 3C), 29.1 (J_{Sn-C}=19 Hz, 3C), 52.4 (J_{Sn-C}=51 Hz), 146.2 (J_{Sn-C}=60 Hz), 158.6 (J_{Sn-C}=435 Hz), 171.4. MS (70 eV, EI) *m/z*: 681 (M^+−57, 62), 679 (74), 291 (15), 235 (58), 179 (94), 177 (100), 73 (41), 57 (57), 41 (80), 39 (25). ^{119}Sn (δ ppm): 107, 54.

4.3. Cross-coupling of 2a and 4 with organic halides: preparation of compounds 5 and 6

In a 50 mL flask are introduced toluene (20 mL), **2a** (7 mmol) or **7** (7 mmol), aryl bromide (5.8 mmol) and tetrakis(triphenylphosphine)palladium (3 mol%). The mixture is degased under vacuum and stirred overnight at 100°C. After cooling, the stannyl ester is hydrolysed with 10 mL of 1N HCl solution. After extraction with diethyl ether, the organic layer was treated with 1N NaOH solution. The aqueous layer was washed with ether then was acidified with 1N HCl solution and extracted with ether. After removal of the solvents under reduced pressure, compounds **5** or **6** were recovered from the crudes by crystallization from PE/Et_2O (95/5) or by column chromatography on silica gel with first EP/Et_2O 99/1 as eluent, then elution: PE/Et_2O 80/20.

4.3.1. (*E*)-4-Phenylbut-3-enoic acid (5a). Mp: 78–80°C. IR (KBr): 3433, 3059, 2955, 1701, 1655, 1493, 1417, 1300, 1223, 976, 746. RAMAN: 3062, 3028, 2952, 2890, 1661 (s), 1597 (s), 1279, 1210, 1000. ^{1}H NMR (δ ppm): 3.35 (dd, J=6.9, 1.2 Hz, 2H), 6.33 (dt, J=15.9, 6.9 Hz, 1H), 6.57 (dt, J=15.9, 1.2 Hz, 1H), 7.32–7.47 (m, 5H), 11.26 (bs, 1H). ^{13}C NMR (δ ppm): 38.1, 120.8, 126.4 (2C), 127.7, 128.4 (2C), 134.0, 136.6, 178.4. MS (70 eV, EI) *m/z*: 162 (M^+, 49), 118 (10), 117 (100), 116 (17), 115 (60), 91 (27), 45 (10), 39 (10). Anal. calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.11; H, 6.28.

4.3.2. (*E*)-4-(*p*-Fluorophenyl)but-3-enoic acid (5b). Mp: 101°C. IR (KBr): 3410, 3036, 2893, 1703, 1657, 1594, 1508, 1226, 976, 807. RAMAN: 3075, 2894, 1659, 1599, 1275, 1206, 999. ^{1}H NMR (δ ppm): 3.33 (dd, J=7.0, 1.1 Hz, 2H), 6.24 (dt, J=15.9, 7.0 Hz, 1H), 6.52 (dt, J=15.9, 1.1 Hz, 1H), 7.0–7.10 (m, 2H), 7.35–7.42 (m, 2H), 10.3 (bs, 1H). ^{13}C NMR (δ ppm): 37.9, 115.4 (J_{C-F}=21.6 Hz), 120.5, 127.8 (J_{C-F}=8 Hz), 130.0 (J_{C-F}=21.6 Hz), 132.8, 162.4 (J_{C-F}=247 Hz), 178.2. MS (70 eV, EI) *m/z*: 180 (M^+, 46), 136 (12), 135 (100), 134 (12), 133 (38), 115 (32), 109 (27), 83 (11), 57 (12), 45 (10). Anal. calcd for $C_{10}H_9FO_2$: C, 66.66; H, 5.03. Found: C, 66.71; H, 4.98.

4.3.3. (*E*)-4-(*p*-Methoxyphenyl)but-3-enoic acid (5c). Mp: 102°C. IR (KBr): 3443, 3036, 3016, 2951, 2835, 1709, 1655, 1606, 1512, 1290, 1242, 1176, 1032, 802. RAMAN: 1656, 1607, 1285, 1179, 756. ^{1}H NMR (δ ppm): 3.26 (dd, J=6.9, 1.1 Hz, 2H), 3.79 (s, 3H), 6.12 (dt, J=15.9, 6.9 Hz, 1H), 6.45 (dt, J=15.9, 1.1 Hz, 1H), 6.84 (d, J=8.5 Hz, 2H), 7.30 (d, J=8.5 Hz, 2H), 9.98 (bs, 1H). ^{13}C NMR (δ ppm): 38.0, 55.3, 114.0 (2C), 118.5, 127.5 (2C), 129.5, 133.4, 159.3, 178.2. MS (70 eV, EI) *m/z*: 192 (M^+, 100), 148 (10), 147 (96), 115 (14), 103 (10), 91 (16), 45 (13). Anal. calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.77; H, 6.34.

4.3.4. (*E*)-4-(*p*-Acetophenyl)but-3-enoic acid (5d). Mp: 132°C. IR (KBr): 3441, 3069, 2930, 2878, 1724, 1643, 1601, 1406, 1269, 1194, 969, 793. RAMAN: 3069, 2926, 1654, 1595, 1272, 1179, 1081. ^{1}H NMR (δ ppm): 2.63 (s, 3H), 3.37 (d, J=6.2 Hz, 2H), 6.46 (dt, J=16.0, 6.2 Hz, 1H), 6.61 (d, J=16.0 Hz, 1H), 7.48 (d, J=8.0 Hz, 2H), 7.94 (d, J=8.0 Hz, 2H), 8.80 (bs, 1H). ^{13}C NMR (δ ppm): 26.6, 38, 124, 133, 126.4 (2C), 128.8, (2C), 136, 141.3, 177, 198. MS (70 eV, EI) *m/z*: 204 (M^+, 38), 190 (12), 189 (100), 115 (33), 45 (10), 43 (46). Anal. calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.50; H, 5.95.

4.3.5. (*E*)-4-(*p*-Formylphenyl)but-3-enoic acid (5e). IR (KBr): 3437, 2978, 2845, 1722, 1678, 1653, 1601, 1398, 1313, 1180, 974, 852. RAMAN: 3069, 2916, 1653, 1601, 1219, 1170. ^{1}H NMR (δ ppm): 3.40 (d, J=6.0 Hz, 2H), 6.50 (dt, J=16.0, 6.0 Hz, 1H), 6.64 (d, J=16.0 Hz, 1H), 7.55–7.68 (m, 2H), 7.86–8.00 (m, 2H), 10 (s, 1H), 10.40 (s, 1H). ^{13}C NMR (δ ppm): 38, 124.8, 126.8 (2C), 130.2 (2C), 131.7, 131.9, 133, 177, 191.8. MS (70 eV, EI) *m/z*: 190 (M^+, 63), 148 (19), 145 (16), 118 (12), 117 (100), 116 (22), 115 (89), 91 (36), 89 (13), 77 (15), 65 (16), 63 (17), 51 (21), 45 (10), 39 (14). Anal. calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.51; H, 5.28.

4.3.6. (*E*)-4-(*p*-Trifluoromethylphenyl)but-3-enoic acid (5f). Mp: 58–60°C. IR (KBr): 3400–2500, 3047, 1708, 1598, 1428, 1325, 1284, 1232, 1122, 1066, 857, 808. RAMAN: 3067, 3022, 2934, 1662, 1610, 1279, 1213, 1183, 765. ^{1}H NMR (δ ppm): 3.38 (d, J=6.5 Hz, 2H), 6.43 (dt, J=16.0, 6.5 Hz, 1H), 6.60 (d, J=16.0 Hz, 1H), 7.47–7.64 (m, 4H), 8.34 (s, 1H). ^{13}C NMR (δ ppm): 38.3, 124, 124.6 (J_{C-F}=270 Hz), 126 (J_{C-F}=3.2 Hz, 2C), 126.9 (2C), 129.9 (J_{C-F}=32.2 Hz), 133.1, 140.5, 177.2. MS (70 eV, EI) *m/z*: 230 (M^+, 80), 211 (21), 188 (32), 186 (12), 185 (100), 165 (71), 164 (19), 145 (15), 133 (10), 117 (17), 116 (29), 115 50), 45 (17). Anal. calcd for $C_{11}H_9F_3O_2$: C, 57.40; H, 3.94. Found: C, 57.47; H, 3.98.

4.3.7. (*E*)-4-(*p*-Bromophenyl)but-3-enoic acid (5g). Mp: 110°C. IR (KBr): 3300–2400, 3048, 1718, 1602, 1487, 1423, 1302, 1219, 1072, 972, 790. RAMAN: 3059, 3022, 2926, 2889, 1661, 1603, 1583, 1272, 1208, 1073. ^{1}H NMR (δ ppm): 3.30 (d, J=6.5 Hz, 2H), 6.30 (dt, J=15.9, 6.5 Hz, 1H), 6.50 (d, J=15.9 Hz, 1H), 7.27 (d, J=8.4 Hz, 2H), 7.47 (d, J=8.5 Hz, 2H), 8.79 (s, 1H). ^{13}C NMR (δ ppm): 37.8, 121.5, 127.7 (2C), 131.5 (2C), 132.3, 132.7, 135.4, 177.5. MS (70 eV, EI) *m/z*: 242 (M^+, 36), 240 (35), 197 (19), 195 (20), 117 (13), 116 (100), 115 (54), 89 (10), 45 (10). Anal. calcd for $C_{10}H_9BrO_2$: C, 49.82; H, 3.76. Found: C, 49.77; H, 3.74.

4.3.8. (*E*)-4-[(8,9-Methylenedioxy)phenyl]but-3-enoic acid (5h). Mp: 115°C. IR (KBr): 3400–2500, 3018, 2903, 1689, 1604, 1498, 1430, 1257, 1230, 1179, 1100, 927, 782. RAMAN: 3073, 2897, 1654, 1617, 1603, 1448, 1284, 1198, 816. ^{1}H NMR (δ ppm): 3.30 (d, J=7.0 Hz, 2H), 6.00 (s, 2H), 6.14 (dt, J=15.8, 7.0 Hz, 1H), 6.46 (d, J=15.8 Hz, 1H),

6.76–6.86 (m, 2H), 6.96–7.00 (m, 1H), 8.55 (bs, 1H). ^{13}C NMR (δ ppm): 38.3, 101.5, 106, 108.7, 119.4, 121.4, 131.5, 133.9, 147.7, 148.4, 178.4. MS (70 eV, EI) *m/z*: 206 (M^+, 91), 161 (32), 132 (11), 131 (100), 104 (10), 103 (85), 102 (15), 77 (32), 51 (15), 45 (12). Anal. calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 64.07; H, 4.91.

4.3.9. (*E*)-4-[(6,7-Methylenedioxy)phenyl]but-3-enoic acid (5i). IR (KBr): 3018, 2960, 2920, 2714, 2609, 2553, 1711, 1655, 1547, 1452, 1288, 1250, 1221, 1060, 970, 939, 788, 761. ^{1}H NMR (δ ppm): 3.35 (d, J=4.8 Hz, 2H), 6.03 (s, 2H), 6.48–6.55 (m, 2H), 6.75–6.85 (m, 3H), 11.52 (bs, 1H). ^{13}C NMR (δ ppm): 38.4, 100.8, 107.4, 119, 120.6, 121.5 (3C), 123.8, 128.3, 144.5, 147.6 (2C), 177.9. MS (70 eV, EI) *m/z*: 206 (100), 161 (40), 132 (14), 131 (91), 104 (14), 103 (94), 102 (17), 78 (10), 77 (42), 76 (12), 75 (11), 63 (14), 51 (21), 50 (10), 45 (18). Anal. calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 64.11; H, 4.86.

4.3.10. (*E*)-4-(*m*-Trifluoromethylphenyl)but-3-enoic acid (5j). IR (KBr): 3038, 2926, 2854, 2737, 1709, 1593, 1419, 1402, 1332, 1228, 1167, 1120, 1070, 966, 792, 700. ^{1}H NMR (δ ppm): 3.37 (d, J=6.6 Hz, 2H), 6.40 (dt, J=16.0, 6.6 Hz, 1H), 6.60 (d, J=16.0 Hz, 1H), 7.42–7.60 (m, 3H), 7.66 (s, 1H), 9.57 (bs, 1H). ^{13}C NMR (δ ppm): 37.7, 122.8, 122.9, 123.9 (J_{C-F}=270 Hz), 124.2, 128.9, 129.3, 131.2 (J_{C-F}=32.2 Hz), 132.6, 137, 177.4. MS (70 eV, EI) *m/z*: 230 (M^+, 78), 211 (16), 188 (43), 186 (12), 185 (100), 165 (89), 145 (30), 117 (41), 116 (51), 115 (64), 39 (13). Anal. calcd for $C_{11}H_9F_3O_2$: C, 57.40; H, 3.94. Found: C, 57.43; H, 3.97.

4.3.11. (*E*)-4-(*m*-Bromophenyl)but-3-enoic acid (5k). IR: 3038, 2978, 2928, 2555, 1712, 1657, 1593, 1562, 1473, 1420, 1292, 1221, 1074, 964. ^{1}H NMR (δ ppm): 3.34 (d, J=6.5 Hz, 2H), 6.33 (dt, J=15.9, 6.5 Hz), 6.43 (d, J=15.9 Hz), 7.16–7.47 (m, 3H), 7.57 (s, 1H), 11.83 (bs, 1H). ^{13}C NMR (δ ppm): 37.8, 122.7, 122.4, 124.9, 129.2, 130, 130.5, 132.5, 138.7, 178.1. MS (70 eV, EI) *m/z*: 242 (M^+, 28), 240 (27), 198 (10), 197 (14), 195 (14), 117 (22), 116 (100), 115 (61), 89 (12), 63 (12), 45 (10), 39 (11). Anal. calcd for $C_{10}H_9BrO_2$: C, 49.82; H, 3.76. Found: C, 49.84; H, 3.81.

4.3.12. (*E*)-Tributylstannyl-4-[(2′-pyridynyl)]but-3-enoate (5l). IR: 2049, 2960–2850, 1655, 1587, 1469, 1375, 1286, 1153, 1078, 972, 910, 787–734. ^{1}H NMR (δ ppm): *E*-isomer: 0.76 (t, J=7.1 Hz, 9H), 0.98–1.58 (m, 18H), 3.26 (dd, J=7.0, 1.0 Hz, 2H), 6.54 (d, J=15.9 Hz, 1H), 6.77 (dt, J=15.9, 7.0 Hz, 1H), 7.06 (m, 1H), 7.29 (m, 1H), 7.55 (m, 1H), 8.48 (m, 1H); *Z*-isomer: 3.66 (dd, J=6.8, 1.3 Hz, 2H), 5.88 (dt, J=15.4, 1.3 Hz, 1H). ^{13}C NMR (δ ppm): *E*-isomer: 13.5 (3C), 16.4 (J_{Sn-C}=341–357 Hz, 3C), 26.9 (J_{Sn-C}=65.3 Hz, 3C), 27.7 (J_{Sn-C}=27 Hz, 3C), 38.7, 120.9, 121.9, 128.7, 132, 136.5, 149, 155.3, 175.8. *Z*-isomer: 40.6, 121, 124.6, 135.8, 144.2, 149.1. MS (70 eV, EI) *m/z*: 396 (M^+−57, 10), 352 (43), 238 (26), 177 (23), 121 (22), 120 (17), 119 (26), 118 (100), 117 (54), 65 (10), 57 (25), 52 (10), 51 (21), 45 (10), 41 (100), 39 (42).

4.3.13. (*E*)-4-(*p*-Toluenesulfonyl)but-3-enoic acid (5m). Mp: 164°C. IR (KBr): 3489, 2993, 2930, 1695, 1646, 1595, 1421, 1318, 1246, 1216, 1145, 1055, 982, 810. RAMAN: 3073, 3041, 2985, 2926, 1661, 1588, 1252, 1147, 757. ^{1}H NMR (δ ppm): 2.49 (s, 3H), 3.99 (dd, J=7.7, 0.9 Hz, 2H), 5.89 (dt, J=15.6, 0.9 Hz, 1H), 6.92 (dt, J=15.6, 7.7 Hz, 1H), 7.40 (d, J=8.0 Hz, 2H), 7.78 (d, J=8.0 Hz, 2H), 8.76 (bs, 1H). ^{13}C NMR (δ ppm): 21.7, 59.2, 128.3 (2C), 128.5, 130.1 (2C), 135.1, 135.9, 145.5, 169.8. MS (70 eV, EI) *m/z*: 240 (M^+, 1), 223 (13), 155 (21), 139 (10), 92 (10), 91 (100), 68 (91), 65 (33), 39 (20). Anal. calcd for $C_{11}H_{12}O_4S$: C, 54.99; H, 5.03. Found: C, 55.05; H, 5.08.

4.3.14. (*Z*)-4-Trimethylsilyl-3-(*o*-nitrophenyl)but-3-enoic acid (6a). IR: 3500–2800, 1710, 1615, 1600. ^{1}H NMR (δ ppm): −0.29 (s, 9H), 3.51 (s, 2H), 5.89 (s, 1H), 7.34–7.51 (m, 4H), 10.55 (bs, 1H). ^{13}C NMR (δ ppm): −0.9 (3C), 46.8, 124.4, 128.6, 129.1, 132.5, 132.9, 134.6, 137.4, 145.8, 177.4. MS (70 eV, EI) *m/z*: 206 (M^+−73, 10), 75 (17), 73 (100), 45 (27), 43 (11). Anal. calcd for $C_{13}H_{17}NO_4Si$: C, 55.89; H, 6.13; N, 5.01. Found: C, 55.95; H, 6.18; N, 5.12.

4.3.15. (*Z*)-4-Trimethylsilyl-3-(*p*-formylphenyl)but-3-enoic acid (6b). IR: 3400–2860, 1700, 1672, 1595, 1284, 1225. ^{1}H NMR (δ ppm): −0.25 (s, 9H), 3.45 (s, 2H), 5.86 (s, 1H), 7.34–7.38 (2H), 7.79–7.83 (2H), 9.98 (s, 1H), 10.3 (bs, 1H). ^{13}C NMR (δ ppm): −0.22 (3C), 47.6, 114.8, 129.3 (2C), 130 (2C), 136, 148.9, 149.2, 176.3, 192.4. MS (70 eV, EI) *m/z*: 218 (M^+−44, 18), 117 (10), 116 (100), 66 (22), 64 (11), 45 (22), 43 (11). Anal. calcd for $C_{14}H_{18}O_3Si$: C, 64.09; H, 6.91. Found: C, 64.15; H, 6.95.

4.3.16. (*Z*)-4-Trimethylsilyl-3-(*m*-trifluoromethylphenyl)but-3-enoic acid (6c). Mp: 134°C. IR (KBr): 3300–2800, 1710, 1603, 1438, 1400, 1333, 1214, 845. ^{1}H NMR (δ ppm): −0.17 (s, 9H), 2.87 (s, 2H) 5.89 (s, 1H), 7.40–7.54 (m, 4H), 11.2 (bs, 1H). ^{13}C NMR (δ ppm): 0.2, 47.9, 124.8 (q, J_{C-F}=4 Hz), 125.8 (q, J_{C-F}=4 Hz), 129.1, 131.1, 132.0, (q, J_{C-F}=32 Hz), 132.8 (q, J_{C-F}=272 Hz), 136.1, 143.7, 148.9, 177.9. MS (70 eV, EI) *m/z*: 302 (M^+, 62), 288 (13), 287 (88), 283 (11), 243 (35), 166 (100), 165 (18), 117 (10), 115 (18), 75 (15), 73 (99). Anal. calcd for $C_{14}H_{17}F_3O_2Si$: C, 55.61; H, 5.67. Found: C, 55.69; H, 5.62.

4.3.17. (*Z*)-4-Trimethylsilyl-3-(*p*-fluorophenyl)but-3-enoic acid (6d). IR: 3400–2800, 1675, 1602, 1214. ^{1}H NMR (δ ppm): −0.13 (s, 9H), 2.84 (s, 2H), 5.87 (s, 1H), 7.03–7.40 (m, 4H), 11.43 (bs, 1H). ^{13}C NMR (δ ppm): −0.64 (3C), 26.4, 112.9, 115.7, 116.1, 128.9, 129.1, 139.4, 163.6, 166.2, 172.9. MS (70 eV, EI) *m/z*: 252 (M^+, 4), 193 (17), 115 (100), 70 (12), 45 (12). Anal. calcd for $C_{13}H_{17}FO_2Si$: C, 61.87; H, 6.79. Found: C, 61.91; H, 6.85.

4.3.18. (*Z*)-5-Chloro-3-(2′-trimethylsilylethenyl)pent-4-enoic acid (6e). IR: 2970, 2930, 1720, 1635, 1590, 1260. ^{1}H NMR (δ ppm): 0.15 (s, 9H), 3.24 (s, 2H), 5.70 (s, 1H), 6.30 (d, J=13.5 Hz, 1H), 6.68 (d, J=13.5 Hz, 1H), 9.0 (bs, 1H). ^{13}C NMR (δ ppm): 0.7 (3C), 43.6, 121.6, 134.2, 138.5, 143.2, 177.5. MS (70 eV, EI) *m/z*: 205 (M^+−15, 36), 203 (100), 183 (19), 97 (14), 95 (50), 75 (53), 73 (14), 65 (13).

4.4. Iododestannylation

At 0°C, to vinylstannane **2a** (12 mmol) in freshly distilled Et_2O (30 mL) was added iodine (3.5 g, 14 mmol) in Et_2O

(35 mL). The mixture was stirred for 2 h at room temperature. Excess I_2 was eliminated by washing with a 0.5 M solution of sodium thiosulfate. The solution was then hydrolysed with 25 mL of a saturated solution of potassium fluoride and 25 mL of acetone in order to remove all the tributyltin salts formed. After vigourous stirring for 3 h, the reaction mixture was filtered and washed with water, the aqueous layer was acidified with 1 M HCl solution, extracted with Et_2O and washed with brine. After usual treatments, the crude acid **9a** (1.40 g, 6.6 mmol, 55%) was purified by crystallisation with PE/Et_2O (90/10).

4.4.1. (*E*)-4-Iodobut-3-enoic acid (9a). Mp: 56–58°C. IR (KBr): 3450, 3065, 3010, 2910, 1701, 1614, 1421, 1398, 1290, 1213, 952. RAMAN: 3042, 3024, 2912, 1614, 1421, 1398, 1290, 1213, 952. ^{1}H NMR (δ ppm): 3.14 (dd, J=7.1, 1.3 Hz, 2H), 6.30 (dt, J=14.6, 1.3 Hz, 1H), 6.60 (dt, J=14.6, 7.1 Hz, 1H), 10.36 (bs, 1H). ^{13}C NMR (δ ppm): 40.5, 79.7, 136.4, 176.3. MS (70 eV, EI) *m/z*: 212 (M^+, 11), 167 (24), 127 (15), 85 (100), 57 (13), 45 (11), 39 (44), 29 (21). Anal. calcd for $C_4H_5IO_2$: C, 22.66; H, 2.38. Found: C, 22.72; H, 2.45.

4.4.2. (*E*)-4-Iodo-3-^{2}H-but-3-enoic acid (9b). Mp: 55°C. IR (KBr): 3065, 2832, 2235, 1715, 1687, 1211, 952, 843. ^{1}H NMR (δ ppm): 3.17 (d, J=1.4 Hz, 2H), 6.35 (t, J=1.4 Hz, 1H), 10.5 (1H, bs). ^{13}C NMR (δ ppm): 40.1, 79.4 (t, J_{C-D}=28 Hz), 110.3, 175.5. MS (70 eV, EI) *m/z*: 213 (M^+, 8), 168 (12), 127 (13), 87 (10), 86 (100), 85 (24), 58 (13), 45 (22), 41 (20), 40 (68), 39 (49), 38 (13). Anal. calcd for $C_4H_4DIO_2$ C, 22.56; H, 2.84. Found: C, 22.59; H, 2.82.

4.4.3. 4-Iodo-3-methylbut-3-enoic acid (9d). IR: 3400, 3057, 2957, 2927, 1705, 1616, 1443, 1373, 1288. ^{1}H NMR (δ ppm): 1.99 (d, J=1.1 Hz, 3H), 3.28 (d, J=1.1 Hz, 2H), 6.25 (q, J=1.1 Hz, 1H), 8.05 (bs, 1H). ^{13}C NMR (δ ppm): 23.9, 43.7, 80.3, 139.5, 176.5. MS (70 eV, EI) *m/z*: 226 (M^+, 10), 99 (100), 81 (10), 71 (28), 54 (19), 53 (55), 45 (13), 43 (85), 41 (23), 39 (47). Anal. calcd for $C_5H_7IO_2$: C, 26.57; H, 3.12. Found: C, 26.62; H, 3.15.

4.5. Iododestannylation: preparation of stannyl iodobutenoate

At 0°C, to vinylstannane **2a** (12 mmol) in freshly distilled Et_2O (30 mL) was added iodine (3.5 g, 14 mmol) in Et_2O (35 mL). The mixture was stirred for 2 h at room temperature. Excess I_2 was eliminated by washing with a 0.5 M solution of sodium thiosulfate. The solution was then hydrolysed with 25 mL of a saturated solution of potassium fluoride and 25 mL of acetone in order to remove all the tributyltin salts formed. After vigourous stirring for 3 h, the reaction mixture was filtered over Celite, extracted with Et_2O and washed with brine. After usual treatments, the crude stannyl ester **7a** was purified by crystallisation with PE/Et_2O (90/10).

4.5.1. (*E*)-Tributylstannyl 4-iodobut-3-enoate (7a). Mp: 70°C. IR: 3028, 1583, 1216, 1151. ^{1}H NMR (δ ppm): 0.94 (t, J=7.2 Hz, 9H), 1.16–1.7 (m, 18H), 3.08 (d, J=7.3 Hz, 2H), 6.18 (d, J=14.5 Hz, 1H), 6.69 (dt, J=14.5, 7.3 Hz, 2H). ^{13}C NMR (δ ppm): 13.5 (3C), 16.4 (J_{Sn-C}=339–359 Hz, 3C), 26.9 (J_{Sn-C}=66.7 Hz, 3C), 27.6 (J_{Sn-C}=20.5 Hz, 3C), 41.4, 77.2, 139.4, 172.6. MS (70 eV, EI) *m/z*: 445 (M^+-57, 30), 361 (15), 305 (14), 291 (15), 247 (32), 177 (28), 121 (26), 97 (18), 85 (15), 57 (33), 55 (93), 41 (100), 40 (16), 39 (69).

4.5.2. (*Z*)-Tributylstannyl 3-iodo-4-trimethylsilylbut-3-enoate (8). Mp: 105°C. IR: 1591, 1566, 1241. ^{1}H NMR (δ ppm): 0.24 (s, 9H), 0.95 (t, J=7.1 Hz, 9H), 1.28–1.85 (m, 18H), 3.71 (d, J=1.0 Hz, 2H), 6.53 (t, J=1.0 Hz, 1H). ^{13}C NMR (δ ppm): −0.7, 14.2 (3C), 17.2 (J_{Sn-C}=339–357 Hz; 3C), 27.6 (J_{Sn-C}=65.3 Hz, 3C), 28.4 (J_{Sn-C}=20 Hz, 3C), 57.6, 111.2, 141, 177. MS (70 eV, EI) *m/z*: 517 (M^+-57, 8), 361 (100), 305 (45), 247 (31), 245 (23), 179 (15), 177 (27), 97 (17), 75 (18), 73 (67), 67 (15), 57 (31), 55 (10), 45 (27), 44 (13), 43 (20), 41 (59), 39 (23). ^{119}Sn (δ ppm): 121.

4.6. Stille coupling of 7a, 8 or 9a with vinyltin reagents

7a (5 mmol) diluted in DMF (5 mL) was added to a DMF soln of vinyltin reagent (5.5 mmol). At the end of the addition, dichlorobis(acetonitrile)palladium (II) (65 mg, 5 mol%) was added. The mixture was stirred for 6 h at 50°C then hydrolysed with a saturated solution of NH_4Cl. The organic layer was then treated with 1N NaOH solution at 0°C until the pH was >8. After washing with Et_2O, the aqueous layer was acidified with 1N HCl solution and extracted with Et_2O. The etheral solution was dried over $MgSO_4$. The solvent was removed and the crude products **10** or **11** were purified by column chromatography on silica gel first with PE/Et_2O 95/5 as eluent, then with EP/Et_2O 70/30.

4.6.1. (3*E*)-Hex-3,5-dienoic acid (10a). IR: 3088, 3022, 2966, 1713, 1653, 1604, 1417, 1292, 1221, 1005. ^{1}H NMR (δ ppm): 3.21 (d, J=7.1 Hz, 2H), 5.13 (dd, J=10.0, 1.5 Hz, 1H), 5.23 (dd, J=16.9, 1.5 Hz, 1H), 5.80 (dt, J=15.0, 7.1 Hz, 1H), 6.14–6.48 (m, 2H), 10.22 (bs, 1H). ^{13}C NMR (δ ppm): 37.6, 117.4, 124.6, 134.9, 136.2, 178.1. MS (70 eV, EI) *m/z*: 112 (M^+, 100), 83 (27), 67 (23), 66 (17), 65 (14), 55 (22), 53 (28), 45 (18), 39 (67). Anal. calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.31; H, 7.23.

4.6.2. (3*E*, 5*E*)-8,8-Diethoxyoct-3,5-dienoic acid (10b). IR: 3409, 3030, 2978, 2924, 1712, 1376, 1124, 1059, 985, 730. ^{1}H NMR (δ ppm): 1.16 (t, J=7.0 Hz, 6H), 2.39 (bt, J=6.3 Hz, 2H), 3.11 (d, J=6.7 Hz, 2H), 3.45–3.68 (qd, J=7.0, −9.4 Hz, 4H), 4.50 (t, J=5.6 Hz, 1H), 5.54–5.70 (m, 2H), 6.0–6.16 (m, 2H), 9.25 (bs, 1H). ^{13}C NMR (δ ppm): 15.2 (2C), 37.1, 37.6, 61.2 (2C), 102.3, 122.8, 128.6, 132, 134, 177. MS (70 eV, EI) *m/z*: 183 (M^+-45, 75), 125 (100), 117 (13), 111 (85), 83 (25), 45 (20), 39 (50). Anal. calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 63.18; H, 8.87.

4.6.3. (3*E*, 5*E*)-6-Phenylhex-3,5-dienoic acid (10c). IR: 3088, 3019, 2910, 1699, 1641, 1413, 1293, 994. ^{1}H NMR (δ ppm): 3.29 (d, J=7.1 Hz, 2H), 5.92 (dt, J=15.2, 7.1 Hz, 1H), 6.37 (dd, J=15.2, 10.2 Hz, 1H), 6.56 (d, J=15.6 Hz, 1H), 6.83 (dd, J=15.6, 10.2 Hz, 1H), 7.26–7.45 (m, 5H), 10.20 (bs, 1H). ^{13}C NMR (δ ppm): 37.7, 124.4, 126.3 (2C), 127.5, 128, 128.5 (2C), 132.4, 134.4, 159, 177. MS (70 eV, EI) *m/z*: 188 (M^+, 15), 143 (10), 129 (22), 128 (100), 115 (21), 91 (11), 65 (12), 51 (11), 45 (23), 39 (20).

4.6.4. (*E*)-Hex-3-en-5-ynoic acid (10d). IR: 3303, 3043,

2253, 2106, 1712, 1649, 1419, 1293, 1229, 1073, 1020, 748. ^{1}H NMR (δ ppm): 2.93 (s, 1H), 3.24 (d, J=7.0 Hz, 2H), 5.64 (d, J=16.0 Hz, 1H), 6.32 (dt, J=16.0, 7.0 Hz, 1H), 11.36 (bs, 1H). ^{13}C NMR (δ ppm): 37.6, 77.7, 81.1, 112.9, 136, 177. MS (70 eV, EI) m/z: 110 (M^+, 34), 71 (100), 68 (30), 66 (24), 65 (59), 63 (19), 62 (11), 60 (11), 57 (11), 45 (22), 44 (10), 43 (81), 42 (51), 41 (43), 40 (37), 39 (100), 38 (19), 37 (10). Anal. calcd for $C_6H_6O_2$: C, 65.45; H, 5.49. Found: C, 65.49; H, 5.53.

4.6.5. (*Z*)-Tributylstannyl-4-trimethylsilyl-3-vinylbut-3-enoate (11a). Mp: 84°C. IR: 3092, 1581, 1556, 1392, 1250, 869, 837. ^{1}H NMR (δ ppm): 0.19 (s, 9H), 0.94 (t, J=7.2 Hz, 9H), 1.23–1.83 (m, 18H), 3.32 (d, J=0.8 Hz, 2H), 5.18 (d, J=10.9 Hz, 1H), 5.33 (d, J=17.3 Hz, 1H), 5.72 (d, J=0.8 Hz, 1H), 6.65 (dd, J=17.3, 10.9 Hz, 1H). ^{13}C NMR (δ ppm): −0.7 (3C), 13.5 (3C), 16.3 (J_{Sn-C}=342–358 Hz, 3C), 26.9 (J_{Sn-C}=65 Hz, 3C), 27.7 (J_{Sn-C}=20 Hz, 3C), 42.8, 115, 134.8, 137, 147.6, 176.8. MS (70 eV, EI) m/z: 417 (M^+−57, 31), 373 (27), 291 (39), 249 (68), 235 (22), 193 (26), 179 (38), 177 (45), 135 (25), 133 (19), 123 (14), 121 (22), 79 (13), 75 (56), 73 (59), 61 (14), 59 (27), 57 (35), 56 (10), 55 (19), 45 (41), 44 (22), 43 (42), 41 (100), 39 (40).

4.6.6. (*Z*)-3-(2′-Trimethylsilylethenyl)-5-trimethylsilylpent-4-enoic acid (11b). Mp: 70°C. IR: 2956–2855, 1714, 1701, 1574, 1550, 1250, 850, 800. ^{1}H NMR (δ ppm): 0.07 (s, 9H), 0.14 (s, 9H), 3.29 (s, 2H), 5.72 (s, 1H), 5.96 (d, J=19.0 Hz, 1H), 6.80 (d, J=19.0 Hz, 1H), 9.50 (bs, 1H). ^{13}C NMR (δ ppm): −1.64 (3C), 0.22 (3C), 41.8, 131.1, 136.2, 136.7, 143.7, 178.2. MS (70 eV, EI) m/z: 256 (M^+, 4), 75 (17), 73 (100), 45 (12). Anal. calcd for $C_{12}H_{24}O_2Si_2$: C, 56.19; H, 9.43. Found: C, 56.25; H, 9.51.

4.6.7. (*Z*)-7,7-Diethoxy-3-(2′-trimethylsilylethenyl)hept-4-enoic acid (11c). IR: 2990, 2970, 2950, 1730, 1650, 1580. ^{1}H NMR (δ ppm): 0.18 (s, 9H), 0.93 (t, J=7.1 Hz, 6H), 2.48 (dd, J=5.9, 5.7 Hz, 2H), 3.30 (s, 2H), 3.57–3.68 (m, 4H), 4.54 (t, J=5.7 Hz, 1H), 5.61 (s, 1H), 5.80 (dt, J=15.7, 5.9 Hz, 1H), 6.46 (d, J=15.7 Hz, 1H), 9.0 (bs, 1H). ^{13}C NMR (δ ppm): 0.66 (3C), 15.7 (2C), 38.2, 43.0, 61.7 (2C), 96.3, 102.7, 127.2, 133.4, 177.5. MS (70 eV, EI) m/z: 255 (M^+−45, 18), 211 (14), 197 (35), 167 (10), 103 (100), 93 (20), 75 (97), 73 (50), 45 (23). Anal. calcd for $C_{15}H_{28}O_4Si$: C, 59.96; H, 9.39. Found: C, 59.91; H, 9.43.

4.7. Procedure for the substitution with organozinc reagents

Zinc bromide (7 g, 31 mmol) is added to an etheral solution of benzylmagnesium bromide, made from magnesium (0.729 g, 30 mmol) and benzylbromide (5.13 g, 32 mmol) in anhydrous ether (30 mL). The solution is stirred overnight at room temperature. THF (15 mL) and DMF (15 mL) are then added to the newly prepared organozinc until a homogeneous solution is obtained. Next, **9a** (10 mmol) diluted in DMF (5 mL) is added dropwise. At the end of the addition, dichlorobis(acetonitrile)palladium(II) (0.52 mg, 0.2 mmol) is added. The mixture is stirred for 12 h at 25°C then hydrolysed with a cold solution of hydrochloric acid (1N) and washed with a saturated solution of ammonium chloride. The organic phase is treated at 0°C with a solution of sodium hydroxide (1N). The aqueous solution obtained is acidified and extracted with diethyl ether. The solvent is removed and crude 10 g is purified using column chromatography on silica gel (PE/Et_2O: 70/30 as an eluent).

4.7.1. (3*E*)-Pent-3-enoic acid (10e). IR: 3038, 1714, 1294, 1223, 970, 912. ^{1}H NMR (δ ppm): 1.72 (bd, J=4.8 Hz, 3H), 3.08 (bd, J=5.7 Hz, 2H), 5.60 (m, 2H), 10.9 (bs, 1H). ^{13}C NMR (δ ppm): 17.7, 37.6, 121.8, 129.9, 178.6. MS (70 eV, EI) m/z: 100 (M^+, 53), 58 (13), 57 (10), 56 (15), 55 (100), 54 (22), 53 (17), 45 (16), 43 (16), 41 (30), 39 (39). Anal. calcd for $C_5H_8O_2$: C, 59.98; H, 8.05. Found: C, 60.05; H, 8.12.

4.7.2. (3*E*)-Hex-3-enoic acid (10f). IR: 3350, 3042, 2968, 2935, 1714, 1410, 1290, 1223, 968. ^{1}H NMR (δ ppm): 1.01 (t, J=7.4 Hz, 3H), 2.08 (m, J=7.4 Hz, 2H), 3.09 (dd, J=6.4, 0.8 Hz, 2H), 5.44–5.73 (m, 2H), 10.5 (bs, 1H). ^{13}C NMR (δ ppm): 13.8, 26, 38.3, 120.5, 137.4, 179.2. MS (70 eV, EI) m/z: 114 (M^+, 28), 73 (14), 69 (31), 68 (43), 67 (14), 60 (34), 57 (17), 55 (68), 54 (11), 53 (18), 45 (22), 43 (17), 42 (22), 41 (100), 40 (10), 39 (55). Anal. calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.18; H, 8.89.

4.7.3. (3*E*)-5-Phenylpent-3-enoic acid (10g). IR: 3450, 3088, 3063, 3028, 2880, 1709, 1664, 1600, 1580, 1207, 1022. ^{1}H NMR (δ ppm): 3.15 (d, J=6.2 Hz, 2H), 3.44 (d, J=6.4 Hz, 2H), 5.68 (dt, J=15.3, 6.4 Hz, 1H), 5.80 (dt, J=15.3, 6.2 Hz, 1H), 7.22–7.44 (m, 5H), 9.70 (bs, 1H). ^{13}C NMR (δ ppm): 37.5, 41.2, 123.8, 126.9, 129 (2C), 129.7 (2C), 137.4, 139.6, 177.1. MS (70 eV, EI) m/z: 176 (M^+, 73), 131 (82), 130 (25), 129 (32), 128 (14), 117 (37), 116 (57), 115 (66), 91 (100), 89 (13), 77 (10), 65 (35), 63 (15), 51 (17), 45 (26), 39 (24). Anal. calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.90; H, 6.89.

4.7.4. (3*E*)-7-Methoxyhept-2-en-3-ynoic acid (10h). IR: 3460, 2939, 2832, 2204, 1712, 1619, 1313, 1150. ^{1}H NMR (δ ppm): 3.21 (dd, J=7.2, 1.4 Hz, 2H), 3.42 (s, 3H), 4.26 (d, J=1.7 Hz, 2H), 5.68 (dd, J=15.9, 1.7 Hz, 1H), 6.25 (dd, J=15.9, 7.2 Hz, 1H), 10.5 (bs, 1H). ^{13}C NMR (δ ppm): 38.2, 57.8, 60.5, 83.1, 96.8, 124.5, 138.6, 176.8. MS (70 eV, EI) m/z: 154 (M^+, 18), 139 (100), 123 (21), 111 (83), 109 (20), 99 (15), 95 (20), 93 (33), 83 (52), 69 (18), 68 (22), 67 (43), 55 (12), 45 (30), 42 (22), 41 (39), 40 (10), 39 (55). Anal. calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.36; H, 6.58.

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