An Efficient Access to (Z)-Vinyltin Acetals *via* Titanation of the Corresponding Alkynyltins

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Received 1 April 1997

Abstract : Titanation of alkynyltin acetals has been exploited to obtain the corresponding (*Z*)-disubstituted vinyltins and γ-hydroxy trisubstituted vinyltins, as a single geometrical isomer.

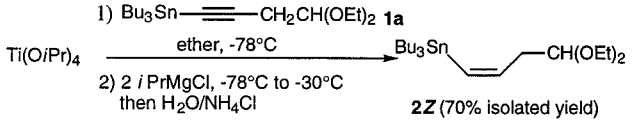
While vinyltins have been widely used in modern organic synthesis,[1] no general method is known to achieve their synthesis in a regio- and stereospecific fashion. Under standard experimental conditions (AIBN, 80°C), the hydrostannation of 1-alkynes usually affords the (*Z*) and (*E*) isomers as a thermodynamic mixture eventually polluted with the branched regioisomer when an oxygen or a nitrogen containing group is borne by the propargylic carbon.[2] Using this method, the obtention of nearly pure (*E*)-vinyltins (thermodynamic products) reflects the great difference in the stability of the (*E*) and (*Z*) isomers as observed when R=SiR'$_3$ or SnBu$_3$[3,4] and new routes have been proposed to obtain kinetically the (*E*) isomers using hydrometallation,[5] carbometallation[6] and stannylmetallation[7,8] of alkynes as well as rearrangement reactions.[8,9] However, starting from alkynes, while stereochemistry is easily controlled (*syn* addition), the regiochemistry appears to be highly dependent on the substrates and on the experimental conditions. For instance, we have had to optimize these parameters for stannylmetallation reactions in order to obtain cleanly di- and trisubstituted (*E*)-vinyltins bearing an acetal function on the propargylic or homopropargylic position.[10]

On the other hand, when disubstituted (*Z*)-vinyltins are desired, their obtention by hydrostannation of alkynes is much more tedious because it requires a control of the temperature in the initiation step in order to avoid their isomerization into the more stable (*E*)-vinyltins and in practice, just a few papers describe the synthesis of (*Z*)-vinyltins according to this way.[11] An alternative route using carbometallation[12] or stannylmetallation[13,14] of acetylene has been also used but suffer from a lack of generality, a limitation which is also encountered when ate-complexes, eventually formed *in situ*, are allowed to react on propargyl alcohol[12] or on alkynes,[15] an isomerization being possible when alkynylsilanes or alkynylstannanes have been employed.[16]

As we needed vinyltins bearing an acetal function in a *syn* relationship compared to the tributylstannyl group for our research program, we decided to submit the corresponding alkynyltins **1a-e**, readily obtained by quenching the appropriate alkynyllithiums with tributyltin chloride[4,17] to a titanation reaction taking into account recent results reported by Sato[18] and related to the reaction of alkynes and alkynylsilanes with Ti(O*i*Pr)$_4$ / *i*PrMgCl. This choice was justified by the fact that the monohydrogenation of alkynyltins is hard to control and that hydrogenolysis of the Sn-C$_{sp2}$ bond has been previously observed.[19] Furthermore, although it is efficient in obtaining (*Z*)-vinyltins, the hydrozirconation of alkynyltins using expensive Cp$_2$ZrHCl has been scarcely used.[17]

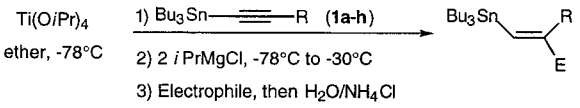
In our case the weakness of the Sn-C$_{sp}$ bond might be a problem and indeed, the order for the addition of the reagents appears to be crucial. Test experiments were done starting from 1-tributylstannyl-4,4-diethoxybut-1-yne (**1a**) allowing the following observations :

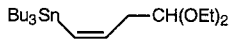
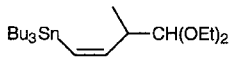
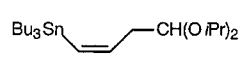
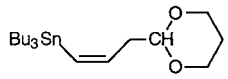
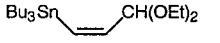
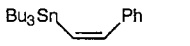
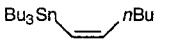
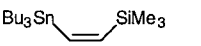
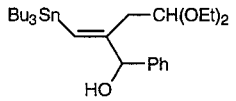
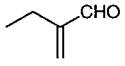
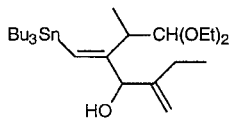
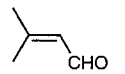
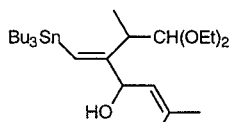
1) Addition of *i*PrMgCl (2eq) in ether to Ti(O*i*Pr)$_4$ at -78°C followed by addition of **1a** afforded 4,4-diethoxybut-1-yne and tributyltin chloride after hydrolysis with H$_2$O / NH$_4$Cl.
2) Addition of Ti(O*i*Pr)$_4$ to **1a** (ether, -78¡C) followed by addition of *i*PrMgCl (2eq) from -78°C to -30°C afforded (*Z*)-1-tributylstannyl-4,4-diethoxybut-1-ene (**2Z**) in 35% yield after hydrolysis with H$_2$O / NH$_4$Cl.
3) Addition of **1a** to Ti(O*i*Pr)$_4$ (ether, -78°C) followed by addition of *i*PrMgCl (2eq) from -78°C to -30°C before hydrolysis (H$_2$O / NH$_4$Cl, -30°C) afforded **2Z** in 70% yield (Scheme 1).



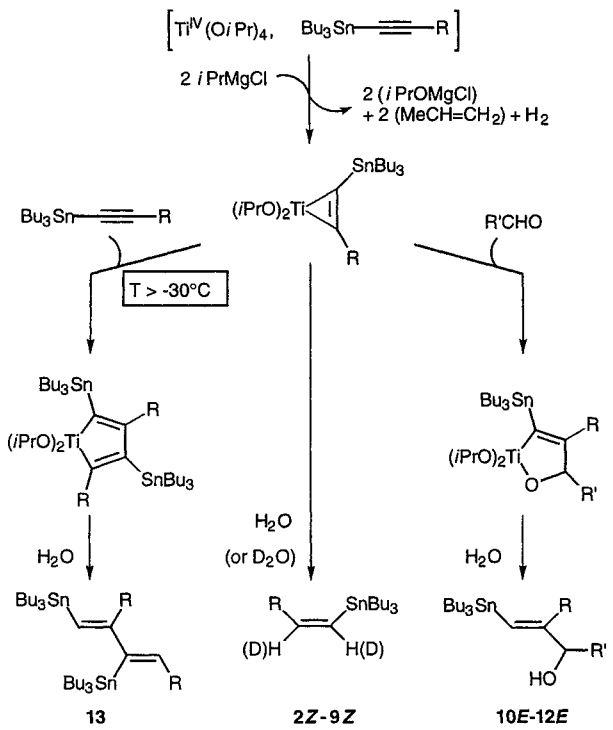
Scheme 1

Table I. Synthesis of (Z)-Vinyltins by Titanation of Alkynyltins

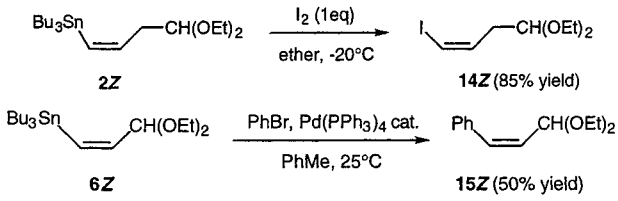


Entry	Electrophile	Adduct[a]		Yield[%][b]
1	H_2O, -30°C		**2Z**	70 (80)
2	"		**3Z**	65 (74)
3	"		**4Z**	63 (85)
4	"		**5Z**	68 (90)
5	"		**6Z**	70 (100)
6	H_2O, -50°C		**7Z**	39
7	"		**8Z**	(20)
8			**9Z**	(10)
9	PhCHO -30°C		**10*E***	40
10			**11*E***	60 15/85[c]
11			**12*E***	53 20/80[c]

[a] Physicochemical data are in agreement with the above mentioned structures.[24] [b] Isolated, chromatographically pure materials. Values in brackets are conversion rates (%). [c] Diastereoisomeric ratio.



Scheme 2



Scheme 3

As a consequence, the results presented in Table I were obtained using experimental conditions presented in the last attempt.[20] It should be noticed that increasing the temperature to -20°C (Scheme 2) induced a decrease in the yield of **2Z** with concomitant formation of insertion products like **13** (dimeric product).[21]

Whatever the nature of the substituents at the acetal function or its propargylic or homopropargylic position, satisfactory yields were obtained in pure disubstituted (*Z*)-vinyltins (entries 1-5). Furthermore, it should be noticed that treatment with deuterium oxide at the end of the reaction involving **1a** afforded exclusively (*Z*)-1,2-di-deutero-1-tributylstannyl-4,4-diethoxybut-1-ene as vinyltin of type **2**.

Unfortunately attempts of extension to alkynes like phenylacetylene, hex-1-yne or trimethylsilylacetylene afforded only moderate to low yields of the expected (*Z*)-vinyltins after hydrolysis (entries 6-8). Finally, regio- and stereoselective synthesis of trisubstituted vinyltins was attempted from homopropargylic acetals. While substitution reactions with methyl iodide or dimethylsulfate failed,[22] the addition to aldehydes affords regio- and stereospecifically the expected vinyltins with an *E* configuration (due to the modification of priority of the β substituents, *cf* entries 9-11).

Obviously, the presence of alkoxy groups (acetal function) on the propargylic or on the homopropargylic position appears to be highly favourable for the obtention of the desired reaction (chelation of titanium by oxygen), in agreement with the results already observed with alkynes and alkynylsilanes.[23] To avoid the transmetallation of the Sn-C_{sp} bond, isopropylmagnesium chloride must be added to the alkynyltin/Ti(O*i*Pr)$_4$ mixture in order to have always an excess of these reagents compared to *i*PrMgCl. The yellow color observed during the addition of *i*PrMgCl might be explained by the formation of the ate-complex [*i*PrTi(O*i*Pr)$_4$]$^-$MgCl$^+$ able to decompose to give a titanium hydride and subsequently (*i*PrO)$_2$Ti^{II} able to complex the alkyne and to give the observed reactions.

The vinyltin acetals so obtained[24] react as classical vinyltins towards iododestannylation and in cross coupling reactions with retention of the configuration[8] (Scheme 3).

In conclusion, even if not general enough, this new method to achieve regio- and stereocontrolled synthesis of vinyltin acetals appears to be very efficient to reach cleanly (*Z*)-disubstituted vinyltins and also γ-hydroxy trisubstituted vinyltins. Due to its reverse stereoselectivity it complements efficiently the stannylmetallation route.[10]

Acknowledgments : The authors are grateful to Chemetall g.m.b.h., Continentale Parker, Schering and Rhône-Poulenc Companies for the gift of organometallic starting materials, to the "GIS Medicaments" and to the "Conseil Gnancial support (V.L.).

References and notes

1. *Comprehensive Organic Synthesis*; Trost, B.M. and Fleming, I. Ed.; Pergamon Press, Oxford, 1991, Vol.4, p.865. Pereyre, M.; Quintard, J.P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths, London, 1987, p.127. Mitchell, T.N. *Synthesis* **1992**, 803.
2. Jung, M.E.; Light, L.A. *Tetrahedron Lett.* **1982**, *23*, 3851. Parrain, J.L.; Duchêne, A.; Quintard, J. P. *J. Chem. Soc., Perkin Trans I* **1990**, 187. Corriu, R.J.P.; Geng, B.; Moreau, J.J.E. *Bull. Soc. Chim. Fr.* **1993**, *130*, 273.
3. Corey, E.J.; Wollenberg, R.H. *J. Am. Chem. Soc.* **1974**, *96*, 5581. Cunico, R.F.; Clayton, F.J. *J. Org. Chem.* **1976**, *41*, 1480. Seyferth, D.; Vick, S.C. *J. Organomet. Chem.* **1978**, *144*, 1. Jones, T.K.; Denmark, S.E. *Helv. Chim. Acta* **1983**, *66*, 2397.
4. Bottaro, J.C.; Hanson, R.N.; Seitz, D.E. *J. Org. Chem.* **1981**, *46*, 5221.
5. Miyake, H.; Yamamura, K. *Chem. Lett.* **1989**, 981. Zhang, H.X.; Guibé, F.; Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1857. Fryzuk, M.D.; Bates, G.S.; Stone, C. *Tetrahedron Lett.* **1986**, *27*, 1537. Groh, B.L. *Tetrahedron Lett.* **1991**, *32*, 7647. Fagan, P.J.; Nugent, W.A.; Calabrese, J.C. *J. Am. Chem. Soc.* **1994**, *116*, 1880. Kim, S.; Kim, K.H. *Tetrahedron Lett.* **1995**, *36*, 3725.
6. Bellina, F.; Carpita, A.; Fontana, E.A.; Rossi, R. *Tetrahedron* **1994**, *50*, 5189.
7. Piers, E.; Chong, J.M.; Morton, H.E. *Tetrahedron Lett.* **1981**, *22* 4905. Matsubara, S.; Hibino, J.I.; Morizawa, Y.; Oshima, K.; Nozaki, H. *J. Organomet. Chem.* **1985**, *285*, 163. Piers, E.; Chong, J.M.; Morton, H.E. *Tetrahedon* **1989**, *45*, 363. Magriotis, P.A.; Doyle, T.J.; Kim, K.D. *Tetrahedron Lett.* **1990**, *31*, 2541. Capella, L.; Degl'Innocenti, A.; Mordini, A.; Reginato, G.; Ricci, A.; Seconi, G. *Synthesis* **1991**, 1201. Casarini, A.; Jousseaume, B.; Lazzari, D.; Porciatti, E.; Reginato, G.; Ricci, A.; Seconi, G. *Synlett* **1992**, 981. Barbero, A.; Cuadrado, P.; Fleming, I.; Gonzalez, A.M.; Pulido, F.J. *J. Chem. Soc., Chem. Commun.* **1992**, 351. Cabezas, J.A.; Oehlschlager, A.C. *Synthesis* **1994**, 432. Aksela, R.; Oehlschlager, A.C. *Tetrahedon* **1991**, *47*, 1163. Uenishi, J.I.; Kawakama, R.; Tanio, A.; Wakabayashi, S. *J. Chem. Soc., Chem. Commun.* **1993**, 1438.
8. Le Menez, P.; Fargeas, V.; Berque, I.; Poisson, J.; Ardisson, J.; Lallemand, J.Y.; Pancrazi, A. *J. Org. Chem.* **1995**, *60*, 3592. Fargeas, V.; Le Menez, P.; Berque, I.; Ardisson, J.; Pancrazi, A. *Tetrahedron* **1996**, *52*, 6613.
9. Hooz, J.; Mortimer, R. *Tetrahedon Lett.* **1976**, 805.

10. Beaudet, I.; Parrain, J.L.; Quintard, J.P. *Tetrahedron Lett.* **1991**, *32*, 6333. Beaudet, I.; Launay, V.; Parrain, J.L.; Quintard, J.P. *Tetrahedron Lett.* **1995**, *36*, 389. *Cf* also Marek, I.; Alexakis, A.; Normant, J.F. *Tetrahedron Lett.* **1991**, *32*, 6337.
11. Tolstikov, G.A.; Miftakhov, M.S.; Danilova, N.A.; Vel'Der, Y.A.L. *Synthesis* **1986**, 496. Lhermitte, F.; Carboni, B. *Synlett* **1996**, 377.
12. Corey, E.J.; Eckrich, T.M. *Tetrahedron Lett.* **1984**, *25*, 2419.
13. Westmijze, H.; Ruitenberg, K.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1982**, *23*, 2797. Magriotis, P.A.; Scott, M.E.; Kim, K.D. *Tetrahedron Lett.* **1991**, *32*, 6085. Pereira, O.Z.; Chan, T.H. *J. Org. Chem.* **1996**, *61*, 5406.
14. Barbero, A.; Cuadrado, P.; Fleming, I.; Gonzalez, A.M.; Pulido, F.J.; Rubio, R. *J. Chem. Soc., Perkin Trans I* **1993**, 1657.
15. Asao, N.; Liu, J.X.; Sudoh, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4568.
16. Lautens, M.; Delanghe, P.H.M.; Goh, B.J.; Zhang, C.H. *J. Org. Chem.* **1995**, *60*, 4213.
17. Lipshutz, B.H.; Keil, R.; Barton, J.C. *Tetrahedron Lett.* **1992**, *33*, 5861.
18. Harada, K.; Urabe, H.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 3203. Takayanagi, Y.; Yamashita, K.; Yoshida, Y.; Sato, F. *J. Chem. Soc., Chem. Commun.* **1996**, 1725.
19. Lautens, M.; Zhang, C.H.; Goh, B.J.; Crudden, C.M.; Jonhson, M.J.A. *J. Org. Chem.* **1994**, *59*, 6208.
20. Even obtained twice with several alkynyltins, we have no valuable explanation for the improved yields observed in attempts 3 compared to attempts 2.
Typical procedure for the preparation of **2Z** *:* to a stirred solution of $Ti(OiPr)_4$ (1.6mL, 5.5mmol) in dry ether (10mL) at -78°C was added dropwise a crude solution of **1a** (5mmol) obtained according to Lipshutz.[17] After 5 min, a solution of *i*PrMgCl (3.7mL, 3M in ether) was added and the yellow mixture was warmed to -30°C over 3 h. The resulting black solution was quenched with NH_4Cl / H_2O and after usual workup, the residue was chromatographed on Lichroprep^R RP-18 (Merck), eluting with MeCN/CH_2Cl_2 (90/10) to afford 1.51g (70% yield) of **2Z** as a single isomer : *^{1}H-NMR (CDCl$_3$; 200MHz)* δ : 0.89 (9H, t, ^{3}J = 7), 0.92 (6H, m), 1.21 (6H, t, ^{3}J = 7), 1.22-1.59 (12H, m), 2.37 (2H, ddd, ^{3}J = 5.8, ^{4}J = 1.1, ^{3}J = 6.9, ^{4}J$_{SnH}$ = 10.1), 3.51 (2H, qd, ^{3}J = 7, ^{2}J = -9.4), 3.66 (2H, qd, ^{3}J = 7, ^{2}J = -9.4), 4.49 (1H, t, ^{3}J = 5.8), 5.95 (1H, dt, ^{3}J = 12.7, ^{4}J = 1.1, ^{2}J$_{SnH}$ = 68.4 and 70.8), 6.51 (1H, dt, ^{3}J = 12.7, ^{3}J = 6.9, ^{3}J$_{SnH}$ = 135.5 and 141). *^{13}C-NMR (CDCl$_3$; 50.32Hz)* δ : 10.2 (3C, ^{1}J$_{SnC}$ = 324.6 and 339.9), 13.7 (3C), 15.3 (2C), 27.3 (3C, ^{3}J$_{SnC}$ = 54.5 and 57.2), 29.2 (3C, ^{2}J$_{SnC}$ = 20.6), 41.2 (1C, ^{3}J$_{SnC}$ = 36.6), 61.3 (2C), 102.8 (1C), 131.3 (1C, ^{1}J$_{SnC}$ = 361.6 and 378.8), 143.4 (1C). *^{119}Sn-NMR (CDCl$_3$; 149.21MHz)* δ : -62.1. MS m/z (relative intensity) : organotin fragments for ^{120}Sn : 377 (3), 333 (19), 331 (100), 275 (6), 217 (5), 179 (12), 177 (8), 165 (20), 121 (15) ; organic fragments : 103 (7), 75 (11), 47 (23), 29 (16). *IR (liquid film)* : 2958, 2928, 2872, 2857, 1599, 1465, 1420, 1375, 1261, 1124, 1063, 1036, 691. *Anal.* : C = 55.64 (th = 55.27), H = 9.92 (th = 9.75).
21. In a related area, 1,2-bis(methylene)cyclopentanes have been obtained from 1,6-diynes, *cf* Urabe, H.; Hata, T.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 4261. Meaningful data for compound **13** : *^{1}H-NMR (200MHz, CDCl$_3$)* : δ : 0.89-1.61 (66H, m), 2.38 (2H, dd, ^{3}J$_{1H}$ = 5.8, ^{3}J$_{1H}$ = 7.0), 2.42 (2H, d, ^{3}J$_{1H}$ = 5.8), 3.36- 3.74 (8H, qd, ^{3}J$_{3H}$ = 7.0, ^{2}J$_{1H}$ = -9.4), 4.49 (1H, t, ^{3}J$_{2H}$ = 5.8), 4.53 (1H, t, ^{3}J$_{2H}$ = 5.8), 5.31 (1H, s, ^{2}J$_{SnH}$ = 65.8 and 69.1), 6.03 (1H, t, ^{3}J$_{2H}$ = 7.0, ^{3}J$_{SnH}$ = 124.5 and 130.0). *MS m/z (relative intensity)* : organotin fragments for ^{120}Sn : 807 (4), 761 (10), 715 (14), 473 (3), 427 (55), 381 (28), 369 (11), 291 (38), 279 (26), 277 (18), 235 (72), 179 (100), 177 (91), 165 (33), 121 (23) ; organic fragments : 103 (51), 75 (38), 57 (16), 47 (42), 41 (19), 29 (57).
22. The alkyltrialkoxytitanium reagents are usually unreactive in S_N2 type reactions. See Reetz, M.T. *Organometallics in Synthesis*; Schlosser, M. Ed.; Wiley, 1994, Chap. 3, p.195.
23. Yamashita, K.; Sato, F. *Tetrahedron Lett.* **1996**, *37*, 7275.
24. Meaningful data for compounds **3Z-6Z** and **10E-12E** (**7Z**, **8Z**, **9Z** have been already described[25,14]). The configuration was assigned on the basis of the values of $^3J_{HH}$[(26)], $^3J_{SnH}$[(25)] and $^3J_{SnC}$[(27)] accross the double bond. *^{1}H-NMR (200MHz, CDCl$_3$)* : **3Z** : 2.24 (1H, m, ^{3}J$_{1H}$ = 5.5, ^{3}J$_{3H}$ = 6.7, ^{3}J$_{1H}$ = 9.6), 4.27 (1H, d, ^{3}J$_{1H}$ = 5.5), 5.82 (1H, d, ^{3}J$_{1H}$ = 12.6, ^{2}J$_{SnH}$ = 67.8 and 71.1), 6.40 (1H, dd, ^{3}J$_{1H}$ = 12.6, ^{3}J$_{1H}$ = 9.6, ^{3}J$_{SnH}$ = 137.0 and 143.7). **4Z** : 2.34 (2H, ddd, ^{3}J$_{1H}$ = 5.7, ^{4}J$_{1H}$ = 1.2, ^{3}J$_{1H}$ = 6.9, ^{4}J$_{SnH}$ = 10.0), 4.55 (1H, t, ^{3}J$_{2H}$ = 5.7), 5.92 (1H, td, ^{3}J$_{1H}$ = 12.7, ^{4}J$_{2H}$ = 1.2, ^{2}J$_{SnH}$ = 69.6 and 72.3), 6.51 (1H, td, ^{3}J$_{1H}$ = 12.7, ^{3}J$_{2H}$ = 6.9, ^{3}J$_{SnH}$ = 136.6 and 142.8). **5Z** : 2.35 (2H, ddd, ^{3}J$_{1H}$ = 7.0, ^{4}J$_{1H}$ = 1.2, ^{3}J$_{1H}$ = 5.2, ^{4}J$_{SnH}$ = 10.0), 4.55 (1H, t, ^{3}J$_{2H}$ = 5.2), 5.99 (1H, td, ^{3}J$_{1H}$ = 12.7, ^{4}J$_{2H}$ = 1.2, ^{2}J$_{SnH}$ = 67.6 and 70.5), 6.54 (1H, td, ^{3}J$_{1H}$ = 12.7, ^{3}J$_{2H}$ = 7.0, ^{3}J$_{SnH}$ = 133.7 and 140.0). **6Z** : 4.83 (1H, dd, ^{3}J$_{1H}$ = 5.0, ^{4}J$_{1H}$ = 1.1, ^{4}J$_{SnH}$ = 8.5), 6.20 (1H, dd, ^{3}J$_{1H}$ = 13.4, ^{4}J$_{1H}$ = 1.1, ^{2}J$_{SnH}$ = 60.1 and 63.2), 6.51 (1H, dd, ^{3}J$_{1H}$ = 13.4, ^{3}J$_{1H}$ = 5.0, ^{3}J$_{SnH}$ = 128.8 and 134.6). **10E** : 2.21 (1H, dd, ^{3}J$_{1H}$ = 4.5, ^{2}J$_{1H}$ = -13.8), 2.41 (1H, dd, ^{3}J$_{1H}$ = 7.2, ^{2}J$_{1H}$ = -13.8), 4.51 (1H, dd, ^{3}J$_{1H}$ = 7.2, ^{3}J$_{1H}$ = 4.5), 5.29 (1H, bd, ^{3}J$_{1H}$ = 2.7), 6.15 (1H, s, ^{2}J$_{SnH}$ = 58.9). **11E** *major* : 2.52 (1H, qd, ^{3}J$_{3H}$ = 7.2, ^{3}J$_{1H}$ = 7.8), 4.59 (1H, bd, ^{3}J$_{1H}$ = 4.7), 5.89 (1H, s, ^{2}J$_{SnH}$ = 58.1). **11E** *minor* : 2.60 (1H, qd, ^{3}J$_{3H}$ = 7.3, ^{3}J$_{1H}$ = 8.0), 4.47 (1H, bs), 5.92 (1H, s, ^{2}J$_{SnH}$ = 54.1 and 56.3). **12E** *major* : 4.44 (1H, d, ^{3}J$_{1H}$ = 7.9), 4.93 (1H, dd, ^{3}J$_{1H}$ = 8.6, ^{3}J$_{1H}$ = 2.7), 6.00 (1H, s, ^{2}J$_{SnH}$ = 57.6). **12E** *minor* : 4.53 (1H, d, ^{3}J$_{1H}$ = 6.5), 4.89 (1H, bd, ^{3}J$_{1H}$ = 8.4), 6.07 (1H, s, ^{2}J$_{SnH}$ = 56.6). *^{13}C-NMR (50.32Hz, CDCl$_3$)* : **3Z** : 45.5 (^{3}J$_{SnC}$ = 34.7), 106.0 (^{4}J$_{SnC}$ = 6.1), 128.2 (^{1}J$_{SnC}$ = 367.7 and 385.3), 150.3. **4Z** : 42.8 (^{3}J$_{SnC}$ = 36.2), 100.1 (^{4}J$_{SnC}$ = 6.9), 130.7 (^{1}J$_{SnC}$ = 365.1 and 382.6), 144.1 (^{2}J$_{SnC}$ = 9.9). **5Z** : 42.4 (^{3}J$_{SnC}$ = 36.2), 102.0 (^{4}J$_{SnC}$ = 6.9), 131.9 (^{1}J$_{SnC}$ = 358.6 and 376.1), 142.4. **6Z** : 102.3 (^{3}J$_{SnC}$ = 31.3), 134.2 (^{1}J$_{SnC}$ = 351.0 and 367.7), 144.7 (^{2}J$_{SnC}$ = 6.5). **10E** : 38.3 (^{3}J$_{SnC}$ = 26.3 and 29.1), 80.2 (^{3}J$_{SnC}$ = 54.8 and 60.4), 103.6, 129.7 (^{1}J$_{SnC}$ = 347.2 and 364.3), 154.4. **11E** *major* : 46.7 (^{3}J$_{SnC}$ = 31.3), 78.0 (^{3}J$_{SnC}$ = 54.9), 104.6, 128.6 (^{1}J$_{SnC}$ = 365.5 and 381.5), 152.3, 159.1. **11E** *minor* : 43.8 (^{3}J$_{SnC}$ = 31.3), 75.9 (^{3}J$_{SnC}$ = 54.9), 105.3, 128.9 (^{1}J$_{SnC}$ = 365.5 and 381.5), 151.1, 158.7. **12E** *major* : 46.4 (^{3}J$_{SnC}$ = 32.0), 70.8 (^{3}J$_{SnC}$ = 55.7), 104.5, 125.2 (^{1}J$_{SnC}$ = 375.0 and 392.2), 161.2. **12E** *minor* : 45.9, 69.5, 105.4, 126.5, 161.4. *^{119}Sn-NMR (149.31MHz, CDCl$_3$)* : in each case, a single signal was observed (absence of signal related to the other geometrical isomer near -51ppm) : **3Z** : -61.9 ; **4Z** : -62.4 ; **5Z** : -62.0 ; **6Z** : -61.2 ; **10E** : -59.9 ; **11E** *major* : -60.9 ; **11E** *minor* : -61.1 ; **12E** *major* : -60.5 ; **12E** *minor* : -60.6.
25. Leusink, A.J.; Budding, H.A.; Marsman, J.W. *J. Organomet. Chem.* **1967**, *9*, 285. Quintard, J.P.; Degueil-Castaing, M.; Dumartin, G.; Barbe, B.; Petraud, M. *J. Organomet. Chem.* **1982**, *234*, 27.
26. Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11.
27. Ardisson, J.; Férézou, J. P.; Li, Y.; Liu, W.; Pancrazi, A. *Bull. Soc. Chim. Fr.* **1992**, *129*, 401.
28. Meaningful data for compound **14Z** (**15Z** has been already described[29]) : *^{1}H-NMR (C$_6$D$_6$; 200MHz)* δ: 2.49 (2H, m, ^{3}J$_{1H}$ = 5.6, ^{3}J$_{1H}$ = 6.3, ^{4}J$_{1H}$ = 1.2), 4.41 (1H, t, ^{3}J$_{2H}$ = 5.6), 5.98 (1H, td, ^{3}J$_{1H}$ = 7.4, ^{4}J$_{2H}$ = 1.2), 6.08 (1H, td, ^{3}J$_{1H}$ = 7.4, ^{3}J$_{2H}$ = 6.3). *^{13}C-NMR (C$_6$D$_6$; 50.32Hz)* δ : 39.9, 84.0, 101.1, 137.1.
29. Beaudet, I.; Duchêne, A.; Parrain, J. L. Quintard, J. P. *J. Organomet. Chem.* **1992**, *427*, 201.