Synthesis of Functionalized Deuterioallylic Compounds

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Functionalized deuterioallylic compounds were efficiently prepared by reaction of the corresponding propargylic derivative with the Schwartz reagent followed by hydrolysis of the adduct with D_2O. The *Z*-3-deuterio-2-propenylstannane, prepared in pure form for the first time, is a useful reagent for the preparation of deuterioallylic compounds which cannot be synthesized by hydrozirconation of the corresponding derivatives.

Introduction

Although the chemistry of functionalized allylic compounds is one of the most efficient ways to form carbon−carbon bonds,[1] the synthesis of selectively labeled allylic derivatives bearing functionalized groups is still an interesting challenge. Such compounds are potential useful reagents to prepare other selectively labeled species or to precise the reactions pathways of reactions both with and without an allylic transposition.[1] Deuterioallylic alcohols are easily formed by reduction of the corresponding acrylaldehyde or acrylic esters,[2] no isomerization occurring even in the presence of strong Lewis bases. However, starting from these alcohols, approaches involving substitution reactions only led to mixtures of isomers of the expected product. These results were attributed to a low regioselectivity of the reaction or to the isomerization of the formed product.[3,4] The reduction of propargylic compounds is another general approach to the corresponding allylic systems,[5] but the presence of functional groups strongly limits the choice of the reducing agent. We now report an approach using as reagent the biscyclopentadienylchlorozirconium hydride **1** (the Schwartz reagent) followed by hydrolysis of the formed adduct by D_2O. The role played by the nature of the functional group of the alkynyl derivatives is clearly evidenced. Also described is the efficacy of the formed deuterioallylstannane in the preparation of deuterioallylic compounds which cannot be prepared by the hydrozirconation approach.

Results and Discussion

Several preparations of the Schwartz reagent have been reported.[6] A quite similar compound (**1′**) can be generated in situ starting from Cp_2ZrCl_2 and the superhydride.[7] Most of these approaches can be extended to the deuterio derivatives Cp_2ZrDCl **2** and Cp_2ZrDCl **2′**.[8]

The addition of Cp_2ZrHCl **1** on propargyl bromide **3** in a halogenated solvent followed by the addition of D_2O (method A) led to the (*E*)-1-deuterio-3-bromopropene **4a** in a 83% yield and with an isotopic purity higher than 97%. The product was easily isolated when 1,1,2,2-tetrachloroethane was used as solvent. Allyl bromide **4a** diluted in THF has also been prepared by the in situ generation of the zirconium hydride **1′** (method B) (yield: 86%, isot. pur. ≈ 94%). To prepare the (*E*)-1,2-dideuterio derivative **4b** diluted in THF, a similar reaction has been performed using compound **2′** as reagent (Scheme 1).

Starting from the *(tert*-butyldimethylsiloxy)prop-2-yn-1-ol **5** and the hydride **1′**, the (*E*)-(*tert*-butyldimethylsiloxy)-3-deuterio-2-propene **6a** was prepared in a 65% yield and with an isotopic purity higher than 96% (Scheme 1). The corresponding (*E*)-2,3-dideuterioderivative **6b** was prepared from compounds **5**, **2′**, and D_2O in a 64% yield (isot. pur. > 95%).[9]

Similarly, the propargyldimethylphenylsilane **7** reacted with Cp_2ZrHCl (**1** or **1′**) to give the corresponding adduct. The latter led to the *E*-deuterioallylsilane **8a** after addition of D_2O (yield: 93%, isot. pur. > 96%).[10] Using **2′**, then D_2O, the (*E*)-2,3-dideuteriopropenylsilane **8b** was obtained in a 95% yield (isot. pur. > 95%) (Scheme 1).

However the Schwartz reagent is not efficient with some functional groups. So, the propargylphosphonic acid diethyl ester **9** reacted with a stoichiometric or substoichiometric amount of the Schwartz reagent **1** to give, after hydrolysis, the corresponding 1-propynylphosphonic acid diethyl ester **10** in a good yield (82%) and only traces of the expected product, the 3-deuterio-2-propenylphos-

(1) Yamamoto, Y.; Asao, N.*Chem. Rev.* **1993**, *93*, 2207−2293.

(2) See for example: Casey, C. P.; Vosejpka, P. C.; Underiner, T. L.; Slough, G. A.; Gavney, J. A., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 6680−6688. Legoupy, S.; Crévisy, C.; Guillemin, J.-C.; Grée, R.; Toupet, L. *Chem.*−*Eur. J.* **1998**, *4*, 2155−2165.

(3) See for example: (a) Pasto, D. J.; Huang, N.-Z. *J. Org. Chem.* **1986**, *51*, 412−413. (b) Mazzanti, G.; Ruinaard, R.; Van Vliet, L. A.; Zani, P.; Bonini, B. F.; Zwanenburg, B. *Tetrahedron Lett.* **1992**, *33*, 6383−6386. (c) Hill, E. A.; Boyd, W. A.; Desai, H.; Darki, A.; Bivens, L. *J. Organomet. Chem.* **1996**, *514*, 1−11. (d) Capps, S. M.; Lloyd-Jones, G. C.; Murray, M.; Peakman, T. M.; Walsh, K. E. *Tetrahedron Lett.* **1998**, *39*, 2853−2856.

(4) Cadiot, P.; Matarasso-Tchiroukine, E. *C. R. Acad. Sci. C* **1972**, *274*, 2118−2120.

(5) See for example: McMichael, K. D. *J. Am. Chem. Soc.* **1967**, *89*, 2943−2947.

(6) Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 405−411. Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521−3531. Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895−3898. Buchwald, S. L.; La Maire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Org. Synth.* **1993**, *71*, 77−81. For a review on hydrozirconation see: Wipf, P.; Jahn, H. *Tetrahedron Rep.* **1996**, *52*, 12853−12910.

(7) Lipshutz, B. H.; Keil, R.; Ellsworth, E. L. *Tetrahedron Lett.* **1990**, *31*, 7257−7260.

(8) Zippi, E. M.; Andres, H.; Morimoto, H.; Williams, P. G. *Synth. Commun.* **1994**, *24*, 1037−1044.

(9) The preparation of a (*Z*)-deuteriosiloxypropene has recently been reported. Ridgway, B. H.; Woerpel, K. A. *J. Org. Chem.* **1998**, *63*, 458−460.

(10) The preparation of mixtures of (*E*) and (*Z*) isomers has already been reported. Fleming, I.; Langley, J. A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1421−1423.

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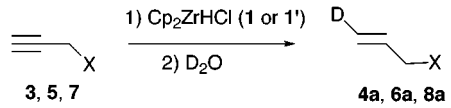
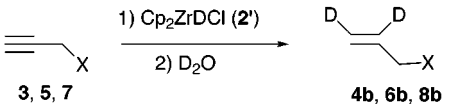
Scheme 1

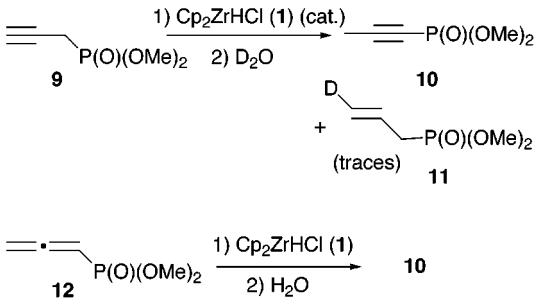


3, **4a**: X = Br; **5**, **6a**: X = OTBDMS; **7**, **8a**: X = $SiMe_2Ph$



3, **4b**: X = Br; **5**, **6b**: X = OTBDMS; **7**, **8b**: X = $SiMe_2Ph$

Scheme 2

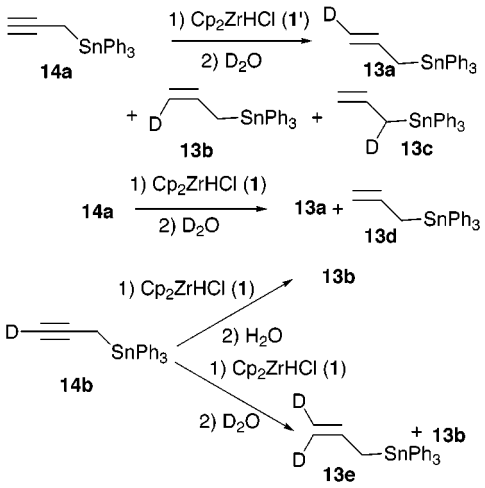


phonate **11** (Scheme 2). Compound **1** thus promoted the isomerization of propargylphosphonate **9** in the propynyl isomer **10**. This property was confirmed by the formation of phosphonate **10** starting from the allenylphosphonic acid diethyl ester **12** and small amounts of the Schwartz reagent **1**.

Some approaches have already been reported to prepare deuterioallylstannanes but have been limited by partial isomerization in the reaction mixture before isolation.[4] Using the Schwartz reagent and a propargylstannane, a selective hydrolysis of the Zr−C bond of the adduct should be easily performed, while the experimental conditions used with some other reagents (as boranes or stannanes for example) probably cannot prevent a partial or complete loss of the tin group in the allylic position.[11] However, starting from propargyltriphenylstannane **14a**[12] and Cp_2ZrHCl **1′** generated in situ, only a mixture of three isomers, **13a**−**c**, was obtained in a 1:1:2 ratio (Scheme 3). Using pure Schwartz reagent **1** and stannane **14a**, the subsequent addition of D_2O led to the 3-deuterio-2-propenyltriphenylstannane **13a** in a 95% yield, but the isotopic purity only rose to 86%. The presence of about 14% (or more) of the hydrogenated stannane **13d** cannot be avoided and is dependent on the presence of traces of impurities in the Schwartz reagent. The presence of the isomer **13c** has been excluded on the basis of the NMR spectra. Moreover we never observed any isomerization of stannane **13a** even after 2 h of stirring at RT in the presence of small amounts of compound **1** with or without water.

To prepare a pure sample of a deuterioallylstannane, a better approach was found starting from the 3-deuteriopropargyltriphenylstannane **14b**[13] and the Schwartz reagent **1**. After hydrolysis with H_2O, the (*Z*)-3-deuteriopropenyltriphenylstannane **13b** was obtained in a 95% yield and with a high isotopic purity (>97%). The 3,3-dideuteriopropenyltriphenylstannane **13e** was also prepared by this approach using D_2O in the hydrolysis step but with an isotopic purity never better than 80% (Scheme 3).

Scheme 3



Stannane **13b** is a very useful reagent for mechanistic studies and synthetic applications. It can be used to prepare various labeled allylic derivatives which cannot be synthesized via the approach reported above. Its addition to a weak, medium, or strong Lewis acid clearly showed the ability of such compounds to rearrange from one isomer to the other one: with a weak Lewis acid such as PBr_3 or $AsCl_3$ diluted in $CDCl_3$, only the kinetic products, the phosphane **15** (a potential precursor of an isomer of the deuterioallylphosphonate **11**) and the arsane **16a**, respectively, were isolated even when the reaction was performed at room temperature.[14] Arsane **16a** diluted in $CDCl_3$ very slowly rearranged at RT to give after some days a mixture of the isomers **16a** and (*Z*)- and (*E*)-**16b**. With tin tetrabromide (a moderatly strong Lewis acid) diluted in $CDCl_3$, only the kinetic product **17a** was observed by low temperature (−50 °C) NMR, while a mixture of isomers **17a** and (*Z*)- and (*E*)-**17b** was obtained at RT. At a temperature higher than −80 °C, the allyltrichlorostannane **18a** diluted in CD_2Cl_2 rearranged in a mixture of isomers **18a** and (*Z*)- and (*E*)-**18b**. With $SbCl_3$, a complex mixture containing the isomers **19a** and (*Z*)- and (*E*)-**19b** probably in a thermodynamic equilibrium was observed even when the reaction was performed and analyzed at −80 °C (Scheme 4).[14]

Allylstannanes are also very useful reagents in the preparation of homoallylic alcohols or amines.[1,15] It is well-known that the reaction pathway of the allylation of an electrophile by an allylic stannane in the presence

(11) . For a recent review on boron derivatives in organic chemistry see: Vaultier, M.; Carboni, B. Boron. In *Comprehensive Organometallic Chemistry II*, Vol. 11; Elsevier Science Ltd.: New York, 1995; Chapter 5, pp 191−276. Selective monodestannylation of distannane derivatives has already been reported for symmetric compounds: Bogoradovskii, E. T.; Cherkasov, V. N.; Zavgorodnii, V. S.; Rogozev, B. I.; Petrov, A. A. *J. Gen. Chem. USSR* **1980**, *50*, 1641−1649. Guillemin, J. C.; Lassalle, L.; Dréan, P.; Wlodarczak, G.; Demaison, J. *J. Am. Chem. Soc.* **1994**, *116*, 8930−8936.

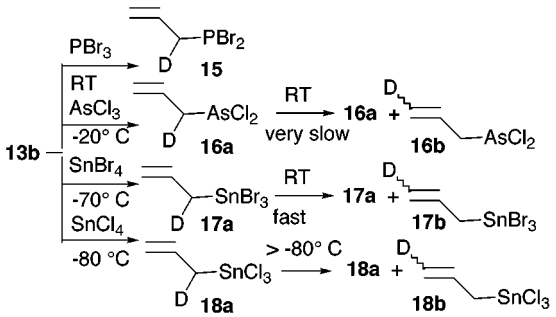
(12) Le Quan, M.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1965**, 45−47.

(13) The 1-deuteriopropargylbromide was prepared as reported. Ollis, W. D.; Sutherland, I. O.; Thebtaranonth, Y. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1981−1993. Compound **14b** was prepared starting from 1-deuteriopropargylbromide with the experimental procedure reported for **14a** (ref 12).

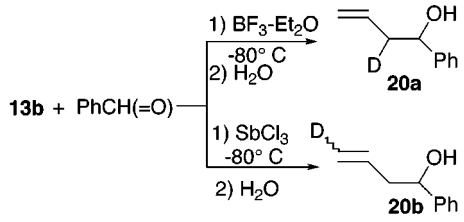
(14) Le Serre, S.; Guillemin, J.-C.; Karpati, T.; Soos, L.; Nyulászi, L.; Veszprémi, T. *J. Org. Chem.* **1998**, *63*, 59.

(15) *Tin in Organic Synthesis*; Pereyre, M., Quintard, J.-P., Rahm, A., Ed.; Butterworth & Co. (Publishers Ltd.): London, 1987; pp 130−256.

Scheme 4



Scheme 5



of a Lewis acid is dependent on this Lewis acid.[1,16] Thus, using BF_3-Et_2O as Lewis acid, stannane **13b**, and benzaldehyde, the reaction occurred at −78 °C without transmetalation[17] and mainly led to only one kind of regioisomer of the corresponding homoallylic alcohol, the *syn*- and *anti*-2-deuterio-1-phenylbut-3-en-1-ol **20a** (Scheme 5). The presence of *syn* and *anti* isomers has been evidenced by ^{2}H NMR spectroscopy. A 4:1 ratio has been observed and the structure of the major isomer, formed from the *Z*-derivative **13b**, is probably the *syn* compound by analogy with crotyl derivatives.[1] Using $SbCl_3$ as Lewis acid,[14] the isomers **20b** and **20a** were obtained in a 5:1 ratio when the reaction was performed at −78 °C. In this case, a redistribution reaction between stannane **13b** and $SbCl_3$ occurred and was quickly followed by the addition of the formed stibine **19a** on the electrophile before equilibrium between both isomers **19a** and **19b**. The reaction performed at −50 °C gave isomers **20a** and **20b** in a 6:4 ratio, showing that, at this temperature, the isomerization occurs faster than the allylation reaction of the electrophile. In these experiments using $SbCl_3$ as Lewis acid, the observed 1:1/*syn:anti* ratio is consistent with a reaction pathway involving a transmetalation reaction.[14,17] Competitions between isomerization and allylation have already been reported and are generally a consequence of some steric hindrance or complexation.[18] To our knowledge, this is the first example with deuterioallyl derivatives.

In conclusion, we have reported several efficient approaches to selectively prepare functionalized deuterioallylic derivatives. The Schwartz reagent is useful to synthesize such products in one step or via a reagent as an allylstannane.

Experimental Section

General Procedures. All manipulations were performed under an atmosphere of dry argon. Lithium triethylborohydride (Super-Hydride), Schwartz reagent **2**, and deuterium oxide (99.992%) were purchased from Aldrich and used as received. Lithium triethylborodeuteride (Super-Deuteride) was purchased from Fluka. The Schwartz reagent **1** and biscyclopentadienylzirconium dichloride were purchased from Strem. The isotopic purity was determined by ^{1}H and ^{13}C NMR spectroscopy. The prop-2-ynyltriphenylstannane **14a**[12] and the 1-deuteriopropargylbromide[13] have been prepared as reported.

General Procedure for Hydrozirconation Reaction Using Pure Schwartz Reagent 1 (Method A). In a dried Schlenck flask equipped with a stirring bar were introduced under argon the Schwartz reagent **1** (258 mg, 1 mmol) and THF (5 mL). The propargylic derivative (0.8 equiv) was then added, and the mixture was stirred at RT for 1 h. Pure D_2O (500 μL) was quickly added, and the mixture was stirred for 10 min. Diethyl ether (10 mL) was added, and the mixture was dried on $MgSO_4$. The product was purified by chromatography on alumina except compound **4a**, which was prepared in 1,1,2,2-tetrachloroethane and purified by trap-to-trap distillation.

General Procedure for Hydrozirconation Reaction Using the Schwartz Reagent Generated in Situ (Method B). In a dried Schlenck flask protected from the light by aluminum foil and equipped with a stirring bar were introduced under argon Cp_2ZrCl_2 (292 mg, 1 mmol) and THF (10 mL). $LiEt_3BH$ or $LiEt_3BD$ (1 equiv) was then slowly added, and the mixture was stirred for 45 min at RT. The propargylic derivative (1 equiv) was added, and the stirring was maintained for 1 h. Pure D_2O (500 μL) was quickly added, and the mixture was stirred for 30 min. Diethyl ether (10 mL) was added, and the mixture was dried on $MgSO_4$. The product was purified by chromatography on alumina. Compounds **8a** and **8b** have been prepared on gram-scale by this approach.

(*E*)-3-Bromo-1-deuterioprop-1-ene 4a. Yield: 83%, isot. pur. > 97% (method A); 86% (crude), isot. pur. ≈ 94% (method B). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (dtt, 1H, J = 15.6, 7.6, 1.4 ($^3J_{HDcis}$) Hz); 5.28 (d, 1H, J = 15.6 Hz); 3.92 (dd, 2H, J = 7.6, 0.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0; 118.8 ($^1J_{CD}$ = 24.0 Hz (t)), 32.7.

(*E*)-3-Bromo-1,2-dideuterioprop-1-ene 4b. Yield: 86%, isot. pur. > 94% (method B). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.28 (s, 1H); 3.92 (d, 2H, J = 0.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.0; 118.8 ($^1J_{CD}$ = 24.1 Hz (t)), 32.7.

(*E*)-1-(*tert*-Butyldimethylsiloxy)-3-deuterioprop-2-ene 6a. Yield: 65%, isot. pur. > 96% (method B). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.93 (dtt, 1H, J = 16.8, 4.7, 1.5 ($^3J_{HDcis}$) Hz); 5.25 (dt, 1H, J = 16.8, 2.0 Hz); 4.18 (dd, 2H, J = 4.7, 2.0 Hz); 0.91 (s, 9H); 0.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2, 113.6 ($^1J_{CD}$ = 23.9 Hz (t)), 64.0, 25.6, 18.3, −5.3. HRMS calcd for $C_9H_{19}DOSi$: 173.1349. Found: 173.134.

(*E*)-1-(*tert*-Butyldimethylsiloxy)-2,3-dideuterioprop-2-ene 6b. Yield: 64%, isot. pur. > 95% (method B). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.26 (t, 1H, $^2J_{HD}$ = 1.5 Hz, =C*H*D); 4.19 (s, 2H); 0.93 (s, 9H); 0.09 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.1 ($^1J_{CD}$ = 24.4 Hz (t)), 113.3 ($^1J_{CD}$ = 24.3 Hz (t)), 67.7, 25.6, 18.1, −5.4.

(*E*)-3-(Dimethylphenylsilyl)-1-deuterioprop-1-ene 8a. Yield: 93%, isot. pur. > 96% (method B). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.6 (m, 2H); 7.4 (m, 3H); 5.84 (dtt, 1H, J = 16.8, 8.2, 1.5 ($^3J_{HDcis}$) Hz); 4.96 (dt, 1H, J = 16.8, 1.5 Hz); 1.86 (dd, 2H, J = 8.2 Hz, 1.5 Hz); 0.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.6, 134.4, 133.6, 128.8, 127.7, 113.1 ($^1J_{CD}$ = 24.2 Hz (t)), 23.6, −3.5. HRMS calcd for $C_{11}H_{15}DSi$: 177.1084. Found: 177.111.

(*E*)-3-(Dimethylphenylsilyl)-1,2-dideuterioprop-1-ene 8b. Yield: 95%, isot. pur. > 95% (method B). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.6 (m, 2H); 7.4 (m, 3H); 4.93 (s, 1H); 1.84 (s, 2H); 0.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.6, 133.6 ($^1J_{CD}$ = 23.2 Hz), 129.0, 127.7, 113.0 ($^1J_{CD}$ = 24.1 Hz), 23.5, −3.5. HRMS calcd for $C_{11}H_{14}D_2Si$: 178.1147. Found: 178.115.

(*E*)-3-Deuterioprop-2-enylphosphonic Acid Dimethyl Ester 11. Yield ≈ 4% (crude). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.80 (dtd, 1H, J = 17.0, 7.3, 1.2 Hz); 5.24 (dtd, 1H, J = 17.0, 4.9, 1.5 Hz); 3.76 (d, 6H, J = 12.0 Hz); 2.64 (ddd, 2H, J = 22.1, 7.3, 1.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ: 26.1.

(16) Le Serre, S.; Guillemin, J.-C. *Organometallics* **1997**, *16*, 5844−5849.
(17) Denmark, S. E.; Wilson, T.; Willson, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 984−986.
(18) Depew, K. M.; Danishefsky, S. J.; Rosen, N.; Sepp-Lorenzino, L. *J. Am. Chem. Soc.* **1996**, *118*, 12463−12464. Hoffman, R. W.; Polachowski, A. *Chem.—Eur. J.* **1998**, *4*, 1724−1730.

3-Deuterio-2-propynyltriphenylstannane 14b. In a 250 mL three-necked flask equipped with a nitrogen inlet, a reflux condenser, and a stirring bar were introduced magnesium (1.2 g, 50 mmol) and diethyl ether (10 mL). A few drops of 1-deuteriopropargylbromide[13] were added, and the reaction was initiated by addition of few milligrams of $HgCl_2$. The 1-deuteriopropargylbromide (6.0 g, 50 mmol) diluted in diethyl ether (50 mL) was then added at a rate to maintain the reflux of the solvent. At the end of the addition, the mixture was stirred for 15 min, and the chlorotriphenylstannane (18 g, 46 mmol) diluted in THF (30 mL) was added. After 2 h of stirring under reflux, the cooled solution was poured in a saturated ammonium chloride solution. The reaction mixture was extracted with diethyl ether (2 × 50 mL), and the combined organic layers were dried over anhydrous $MgSO_4$. After removal of solvents in vacuo, crystallization in hexanes gave the 3-deuterioprop-2-ynyltriphenylstannane **14b** (9.5 g) in a 53% yield. Isot. pur. > 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (m, 6H); 7.52 (m, 9H); 2.37 (s, 2H, J_{SnH} = 63.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.3, 136.8, 129.3; 128.3, 82.6 (J_{CD} = 7.7 Hz); 67.6 (J_{CD} = 37.9 Hz); −1.8 (J_{SnC} = 324 Hz (d)). ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −121.7 (t, $^4J_{SnD}$ = 6.6 Hz). Anal. Calcd for $C_{21}H_{17}DSn$: C, 64.60; H, 4.91. Found: C, 64.36; H, 4.96. HRMS (LSIMS with cesium gun, positive mode, matrix: mNBA) *m/z*: calcd for $C_{21}H_{16}D^{120}Sn$ [M − H]$^+$ 390.0415; found 390.042.

(*E*)-3-Deuterioprop-2-enyltriphenylstannane 13a. This compound was prepared starting from prop-2-ynyltriphenylstannane **14a** (method A). Yield: 90%. Isot. pur. ≤ 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (m, 6H); 7.41 (m, 9H); 6.10 (m, 1H); 4.97 (d, 1H, J = 16.8 Hz); 2.45 (d, 2H, J = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.0, 137.7, 137.6, 129.7, 129.2, 112.8 ($^1J_{CD}$ = 23.9 Hz (t)), 18.4 ($^3J_{CD}$ = 2.0 Hz (t)). ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −120.7.

(*Z*)-3-Deuterioprop-2-enyltriphenylstannane 13b. This compound was prepared starting from 3-deuterioprop-2-ynyltriphenylstannane **14b** (method A with H_2O). Yield: 95%, isot. pur. > 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.6 (m, 6H); 7.3 (m, 9H); 6.10 (brd dt, 1H, J = 9.9, 8.4 Hz); 4.82 (d, 1H, J = 9.9 Hz); 2.45 (d, 2H, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.3, 137.0, 135.7, 129.0, 128.4, 112.1 ($^1J_{CD}$ = 23.5 Hz (t)), 17.7. ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −120.7 ($^4J_{SnD}$ = 3.0 Hz). Anal. Calcd for $C_{21}H_{19}DSn$: C, 64.27; H, 5.40. Found: C, 64.48; H, 5.27. HRMS (LSIMS with cesium gun, positive mode, matrix: mNBA) *m/z*: calcd for $C_{21}H_{18}D^{120}Sn$ [M − H]$^+$ 392.0572; found 392.057.

3,3-Dideuterioprop-2-enyltriphenylstannane 13e. This compound was prepared starting from 3-deuterioprop-2-ynyltriphenylstannane **14b** and D_2O (method A). Yield: 80%. Isot. pur. ≤ 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (m, 6H); 7.41 (m, 9H); 6.10 (t, 1H, J = 7.1 Hz); 2.45 (d, 2H, J = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.0, 137.7, 137.6, 129.7, 129.2, 112.8, 18.4. ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −120.7.

Reaction of Stannane 13d with Lewis Acids PBr_3, $AsCl_3$, $SnBr_4$, and $SnCl_4$. The reaction was performed in an NMR tube at low temperature. The stannane **13b** (0.5 mmol) diluted in CD_2Cl_2 or $CDCl_3$ (300 μL) was slowly added to the Lewis acid (1 equiv) diluted in the same solvent (300 μL) and cooled to −80 °C ($SnCl_4$), −50 °C ($SnBr_4$), −20 °C ($AsCl_3$), or RT (PBr_3). The NMR tube was shaken for a few seconds and directly introduced in the cooled NMR probe. Phosphane **15** and arsane **16a** have also been prepared on gram-scale in CH_2Cl_2 and purified by trap-to-trap distillation in vacuo.[14]

1-Deuterioprop-2-enyldibromophosphane 15. Yield: 63%. Isot. pur. > 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.89 (dddd, 1H, J = 19.8, 10.1, 6.5, 4.3 Hz); 5.38 (ddm, 1H, J = 10.2, 4.1 Hz); 5.33 (ddt, 1H, J = 19.8, 4.1, 1.2 Hz); 3.48 (ddt, 1H, J = 17.5, 6.5, 1.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ: 177.1. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 46.3 ($^1J_{CD}$ = 20.9 Hz (t)), 121.7, 129.1. HRMS *m/z* calcd for $C_3H_4Br_2DP$: 230.8559. Found: 230.855.

1-Deuterioprop-2-enyldichloroarsane 16a. Yield: 86%. Isot. pur. > 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.90 (ddd, 1H, J = 16.9, 10.2, 7.9 Hz); 5.30 (dd, 1H, J = 10.2, 1.2 Hz); 5.26 (dd, 1H, J = 16.9, 1.2 Hz); 3.19 (dt, 2H, J = 7.9, 1.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 128.0, 121.6, 48.4 ($^1J_{CD}$ = 21.6 Hz (t)). HRMS calcd for $C_3H_4AsCl_2D$: 186.9048. Found: 186.905.

1-Deuterioprop-2-enyltribromostannane 17a. Yield (crude): 73%. Isot. pur. > 95%. ^{1}H NMR (400 MHz, $CDCl_3$, −50 °C) δ: 5.97 (ddd, 1H, J = 16.3, 9.7, 7.9 Hz); 5.48 (d, 1H, J = 16.3 Hz); 5.45 (d, 1H, J = 9.7 Hz); 3.32 (dt, 1H, J = 7.9 Hz, J_{SnH} = 112.3 Hz (d)). ^{13}C NMR (100 MHz, $CDCl_3$, −50 °C) δ: 128.3, 121.3, 37.8 ($^1J_{CD}$ = 21.9 Hz (t)). ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −171.2.

1-Deuterioprop-2-enyltrichlorostannane 18a. Yield (crude): 70%. Isot. pur. > 93%. ^{1}H NMR (400 MHz, CD_2Cl_2, −80 °C) δ: 5.97 (ddd, 1H, J = 16.8, 10.0, 8.2 Hz); 5.45 (d, 1H, J = 16.8 Hz); 5.38 (d, 1H, J = 10.0 Hz); 3.26 (brd t, 1H, J = 8.2 Hz, J_{SnH} = 125.8 Hz (d)). ^{13}C NMR (100 MHz, CD_2Cl_2, −80 °C) δ: 127.6, 121.7, 37.2 ($^1J_{CD}$ = 22.0 Hz (t)). ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −25.7.

Reaction of Stannane 13d with Benzaldehyde in the Presence of a Lewis Acid. General Procedure. In a dried two-necked flask equipped with a stirring bar and a nitrogen inlet were introduced benzaldehyde (76 μL, 0.75 mmol) and CH_2Cl_2 (6 mL). The solution was cooled to −78 °C and the Lewis acid (1.2 mmol) was added. After 15 min of stirring, stannane **13b** (390 mg, 1 mmol) diluted in CH_2Cl_2 (3 mL) was slowly added, and the solution was stirred for 3 h at −78 °C. The mixture was then poured in a saturated solution of NH_4Cl. After a usual workup, the alcohol **20** was purified by chromatography on silica gel (diethyl ether/petroleum ether 1:9).

2-Deuterio-1-phenylbut-3-en-1-ol 20a. BF_3−Et_2O was used as Lewis acid. Yield: 64%. Isot. pur. > 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29 (m, 5H); 5.63 (ddd, 1H, J = 17.3, 9.7, 7.2 Hz); 5.11 (dd, 1H, J = 17.3, 1.5 Hz), 5.07 (dd, 1H, J = 9.7, 1.5 Hz), 4.52 (d, 1H, J = 7.6 Hz), 2.85 (s, 1H), 2.30 (dd, 1H, J = 7.6, 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.5, 135.1, 128.8, 127.9, 126.3, 118.9, 73.7, 44.0 ($^1J_{CD}$ = 20.2 Hz (t)).

4-Deuterio-1-phenylbut-3-en-1-ol 20b. $SbCl_3$ was used as Lewis acid. Yield: 78%. Isot. pur. > 81%. *Z*:*E*/45:55. (*Z*) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29 (m, 5H); 5.73 (dt, 1H, J = 8.3, 7.2 Hz); 5.07 (d, 1H, J = 8.3 Hz), 4.62 (d, 1H, J = 6.6 Hz), 4.52 (s, 1H), 2.45 (ddt, 1H, J = 7.2, 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.5, 135.1, 128.8, 127.9, 126.3, 118.8 ($^1J_{CD}$ = 23.7 Hz (t)), 44.1. (*E*) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29 (m, 5H); 5.73 (ddt, 1H, J = 17.8, 7.2 Hz); 5.11 (d, 1H, J = 17.8 Hz), 4.62 (d, 1H, J = 6.6 Hz), 4.52 (s, 1H), 2.45 (dd, 1H, J = 7.1, 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.5, 135.1, 128.8, 127.9, 126.3, 118.8 ($^1J_{CD}$ = 23.7 Hz (t)), 44.1.

Supporting Information Available: 400-MHz ^{1}H and 100-MHz ^{13}C NMR spectral data of arsanes **16b**,**c**, stannanes **17b**,**c**, **18b**,**c**. 400-MHz ^{1}H, 100-MHz ^{13}C, and 121-MHz ^{31}P NMR spectra of the phosphane **15**. 400-MHz ^{1}H and 100-MHz ^{13}C spectra of **6a**,**b**, **8a**,**b**, **13b**, **14b**, **16a**, **17a**, **18a**, **20b** and mixtures of isomers **16a**−**c**, **17a**−**c**, **18a**−**c**. 400-MHz ^{1}H, 46 MHz ^{2}D, and 100-MHz ^{13}C spectra of **20a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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