DOI: 10.1002/ejoc.200800418

Synthesis of Stannylated Allyl- and Vinylphosphonates via Molybdenum-Catalyzed Hydrostannations

Nivedita Jena[a] and Uli Kazmaier*[a]

Keywords: Allylphosphonates / Cross couplings / Hydrostannations / Molybdenum / Vinylphosphonates

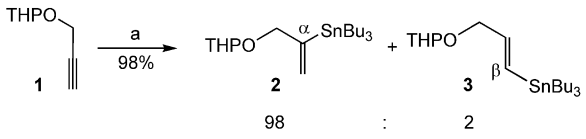
Syntheses of stannylated allyl and vinylphosphonates by molybdenum-catalyzed hydrostannation of the corresponding propargyl- and alkynylphosphonate derivatives proceed with high regioselectivities. The stannylated phosphonates obtained are versatile building blocks for further modifications, such as iodinations or cross coupling reactions.

Introduction

Functionalized unsaturated phosphonates are of great interest as key intermediates in the synthesis of complex molecules.[1] Vinylphosphonates can undergo Michael addition followed by a Horner–Wadsworth–Emmons (HWE) olefination[1a] and α-metallated derivatives can be coupled with a wide range of electrophiles.[1b] Allyl- and propargylphosphonates, easily obtained via Arbuzov reaction,[2] can be used for the synthesis of highly functionalized dienes[3] and enynes.[4] While α-metallated vinylphosphonates can be obtained from the corresponding vinylphosphonates by deprotonation with LDA[5] or via 1,4-addition of organometallics towards alkynylphosphonates,[6] the corresponding metallated allylphosphonates are by far less available. The most straightforward approach would be a hydrometallation, e.g. hydrostannation of propargylphosphonates. The resulting stannylated phosphonates would be interesting building blocks and suitable precursors for further modifications via Stille coupling.[7]

It is well known, that hydrostannations of acetylenes are induced either by radical initiators, Lewis acids or transistion metal catalysts.[8] The major drawbacks of these methods result from difficulties in controlling the regioselectivity of the tinhydride addition to unsymmetrical alkynes although the transistion metal catalyzed version has the advantage of a clean *cis* addition, based on the reaction mechanism.[9] In the case of terminal alkynes, hydrometallation in general gives rise to the terminal vinyl metal species.

Recently, our group has developed a new catalyst based on molybdenum.[10] $Mo(CO)_3(CN\mathit{t}Bu)_3$ ($MoBI_3$) was found to be an excellent catalyst for highly regio- and stereoselective hydrostannations of functionalized alkynes (**1**) (see Scheme 1) preferentially affording the α-stannylated products **2**.[11]



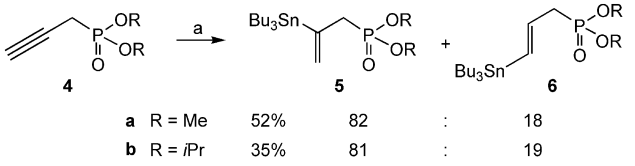
Scheme 1. Hydrostannation of alkyne **1**. Reaction conditions: a) Bu_3SnH (3 equiv.), hydroquinone (10 mol-%), $Mo(CO)_3(CN\mathit{t}Bu)_3$ (2 mol-%), THF, 60 °C, 4 h.

We now report on our investigations of $MoBI_3$-catalyzed hydrostannations of alkynyl and propargylphosphonates, leading to the corresponding phosphorylated vinyl stannanes and their subsequent modifications via Stille couplings.

Results and Discussion

We began our studies with the reactions of two propargylic phosphonates (**4a**,**b**) to see if the substituents on the phosphorus have any influence on the outcome of the hydrostannation (Scheme 2). As expected, an increase in the steric demand of the substituents decellerated the reaction, what resulted in longer reaction times (16 h vs. 6 h) and lower yields. The moderate yields observed for both propargylic substrates **4** may be attributed to the instability of these terminal alkynes as they are known to isomerize under these conditions (into mixture of allenes and 2-alkynes)[12a] which gives rise to other products or leads to decomposition.

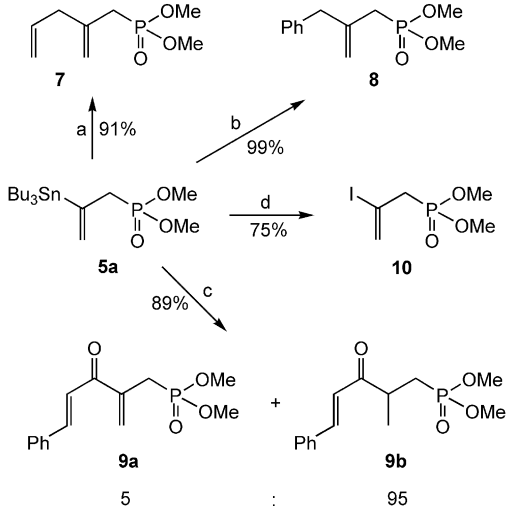
[a] Universität des Saarlandes, Institut für Organische Chemie, Universitaetscampus, Geb. C4.2, 66123 Saarbrücken
Fax: +49-6813022409
E-mail: u.kazmaier@mx.uni-saarland.de



Scheme 2. Hydrostannation of propargylic phosphonates **4**. Reaction conditions: Bu_3SnH (3 equiv.), hydroquinone (10 mol-%), $MoBI_3$ (2 mol-%), THF, 55 °C, (R = Me, 6 h; R = *i*Pr, 16 h).

The regioselectivities (ratio **5/6**) with these substrates were also lower than other terminal alkynes,[11] but still in the range of 80/20. Here, the influence of the substituents can be neglected.

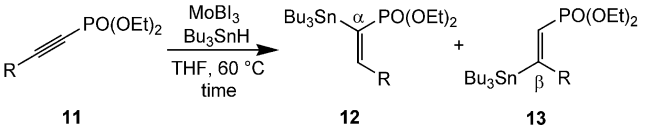
The regioisomeric products could easily be separated via flash chromatography. With pure stannylated phosphonates **5a** in hand, we subjected it to several cross coupling reactions (Scheme 3). Excellent yields were obtained with allyl and benzyl bromide furnishing products **7** and **8**. Surprisingly, coupling with cinnamoyl chloride resulted only in 5% of the expected coupling product **9a**, the major one was the reduced unsaturated ketone **9b** with an *E*/*Z*-ratio of 88:12. Obvoiously, the primarily formed dienone, which is the expected coupling product, undergoes reduction of the methylene group either by Bu_3SnH or a molybdenum hydride intermediate. Iodination of **5a** was a very clean reaction, and the iodide **10** obtained is an interesting substrate for further modification.



Scheme 3. Cross coupling reactions of stannated phosphonate **5a**. Reaction conditions: a) Allyl bromide, $[(allyl)PdCl]_2/PPh_3$, THF, 60 °C, 16 h; b) Benzyl bromide, $[(allyl)PdCl]_2/PPh_3$, PPh_3, THF, 60 °C, 16 h; c) cinnamoyl chloride, $[(allyl)PdCl]_2/PPh_3$, THF, 60 °C, 16 h; d) I_2, $CHCl_3$, room temperature, 1 h.

Next, we focused on the alkynylphosphonates **11**, where the electron-withdrawing group is directly located at the triple bond (Table 1). Our previous work showed, that electron-poor alkynes give better yields and regioselectivities in the $MoBI_3$-catalyzed hydrostannation step, and indeed, this was also true with these phosphonates.

Table 1. $MoBI_3$-catalyzed hydrostannations of alkynylphosphonates **11**.



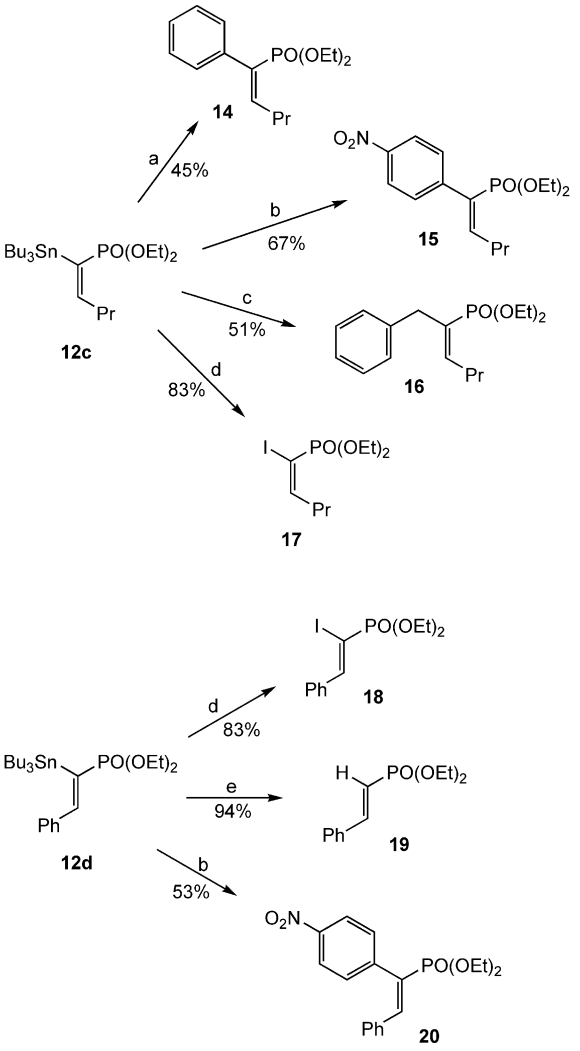
Entry	Alkyne	R	Time	% Yield[a]	**12/13**[b]
1	**11a**	H	12 h	57	92:8
2	**11b**	Me	8 h	67	>95(*E*):5
3	**11c**	Pr	12 h	61	>95(*E*):5
4	**11d**	Ph	6 h	74	93(*Z*):7
5	**11d**	Ph	15 h	77	93(*E*):7
6	**11e**	CH_2CH_2Ph	12 h	59	>95(*E*):5
7	**11f**	cyclohexyl	12 h	51	>95(*E*):5

[a] Isolated yields. [b] Determined by ^1H NMR and ^{31}P NMR spectra of crude reaction product.

The regioselectivities for the α-substituted products **12** were excellent with all substrates, independent on the substitution pattern of the triple bond.[13] The (*E*)-configured products were formed preferentially, except for the phenyl-substituted derivative, which gave rise to the (*Z*)-product (entry 4). This is not completely surprising, because phenylated alkynes often show a special reaction behaviour in hydrostannations.[14] It is worth mentioning, that both isomers could be synthesized by simply varying the reaction time. The α-(*Z*) derivative was formed preferentially within 6 h, while the α-(*E*) isomer was formed on heating the reaction mixture for 15 h. The isomers could be identified via their ^1H NMR and ^{31}P NMR spectra. The α-(*Z*) isomer showed a signal at δ = 26.2 ppm and α-(*E*) derivative gave a peak at δ = 21.6 ppm in the ^{31}P NMR spectroscopy. The (*Z*)-isomer showed a coupling of J_{P-H} = 33.2 Hz in the ^1H NMR spectrum, while the coupling constant for the α-(*E*) isomer was J_{P-H} = 62.4 Hz, which is in accordance with the large coupling constants typically observed for vinylic protons *trans* to phosphonate.[13]

To investigate the reaction behaviour of these stannylated vinylphosphonates, we subjected the (*E*)-configured stannane **12c** and the (*Z*)-configured isomer of **12d** also to cross coupling reactions (Scheme 4).

The Stille coupling of **12c** with iodobenzene gave the coupling product **14** with high regioselectivity and complete retention of the olefin geometry. Electron-withdrawing groups (such as NO_2) at the aromatic ring system increased the yield (**15**) compared to the unsubstituted iodobenzene. Benzyl bromide also reacted with complete retention of the olefin geometry (**16**). These coupling reactions were always accompanied by some protodestannylation. The formation of alkenes by this process was more tremendous in reactions with acyl halides, e.g. benzoyl chloride,[15] and when the reactions were conducted in polar solvent such as acetonitrile. Therefore, the yields in these cross couplings were moderate. In contrast, iodination of **12c** proceeded smoothly furnishing **17** in good yield.



Scheme 4. Cross coupling reaction of stannated vinylphosphonates. Reaction conditions: a) PhI, CuI, $Pd_2(dba)_3$ (2 mol-%), $P(fur)_3$ (15 mol-%), NMP, room temp., 16 h; b) *p*-NO_2-PhI, CuI, $Pd_2(dba)_3$ (2 mol-%), $P(fur)_3$ (15 mol-%), *N*-methylpyrrolidinone (NMP), room temp., 16 h; c) BnBr, $Pd_2(dba)_3$ (2 mol-%), $AsPh_3$ (15 mol-%), toluene, 90 °C, 15 h; d) I_2, $CHCl_3$, room temp. 1 h; e) PhCOCl, $[(allyl)PdCl]_2/PPh_3$, THF, 60 °C.

The same effects were observed with (*Z*)-configured **12d**. While the iodination furnished the expected product **18** in good yield as a single isomer, the coupling with benzoyl chloride in THF resulted mainly in protodestannylation, furnishing alkene **19** as the major product in high yields with complete retention of geometry. Stille reaction with *p*-nitroiodobenzene gave rise to **20**.

Conclusions

In conclusion, we have shown that molybdenum-catalyzed hydrostannations of propargyl and alkynylphosphonates gave rise to stannylated phosphonates. Palladium-catalyzed cross coupling reactions of these phosphonates with alkyl and aryl halides occur with clean retention of the olefin geometry. The unexpected outcome of coupling reactions with acyl halides such as benzoyl chloride (**19**) or cinnamoyl chloride (**9**) is subject of further investigations.

Experimental Section

General Remarks: All reactions were carried out in oven-dried glassware (100 °C) under argon. All solvents were dried before use. THF was distilled from $LiAlH_4$, NMP was dried with KOH, acetonitrile from calcium hydride. The products were purified by flash chromatography on silica gel. Mixtures of EtOAc and hexanes were generally used as eluents. TLC: commercially precoated Polygram® SIL-G/UV 254 plates. Visualization was accomplishhed with UV light, iodine and $KMnO_4$ solution. NMR spectra were recorded in $CDCl_3$ using a Bruker DRX 500 or a Bruker AV 400 NMR spectrometer. Selected signals in the NMR spectra for the minor isomers are extracted from the spectra of the isomeric mixture. CI-MS analyses were performed using a Finnigan MAT 95. Elemental analyses were carried out at the Department of Chemistry, Saarland University.

General Procedure for $MoBI_3$-Catalyzed Hydrostannations: In a oven dried Schlenk tube the corresponding phosphonoalkyne (1 mmol) and the catalyst $MoBI_3$ (8.6 mg, 20 μmol) were dissolved together with hydroquinone (10 mg) in dry THF (2 mL) under argon. The solution was heated to 55 °C for 10 min before Bu_3SnH (0.8 mL, 3 mmol) was added. The reaction mixture was stirred for 6–15 h based on the consumption of the starting material. After cooling to room temperature, the solvent was evaporated in vacuo and the crude product was purified by flash chromatography on silica gel using hexane/ethyl acetate mixtures containing 1% NEt_3.

Dimethyl [2-(Tributylstannyl)allyl]phosphonate (5a): Stannylated allylphosphonate **5a** was prepared from propargylphosphonate **4a** (148 mg, 1.0 mmol) in 6 h according to the general procedure for $MOBI_3$-catalyzed hydrostannations as a colourless oil (228 mg, 0.52 mmol, 52%). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.3 Hz, 9 H), 0.93–0.97 (m, 6 H), 1.28–1.37 (m, 6 H), 1.46–1.54 (m, 6 H), 2.80 (d, J = 22.2 Hz, 2 H), 3.73 (d, J = 10.8 Hz, 6 H), 5.35 (dd, J = 5.1, 2.3, Hz, 1 H), 5.89 (dd, J = 5.5, 2.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.0, 13.7, 27.4, 29.0, 36.2, 37.5, 52.4, 52.5, 130.8 (d, J = 13.9 Hz), 143.8 (d, J = 11.9 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.8 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –38.1 (d, J = 31.9 Hz) ppm. HRMS (CI) *m*/*z* calcd. for $C_{17}H_{38}O_3PSn$ $[M + H]^+$: 440.1502, found 440.1520; *m*/*z* calcd. for $C_{13}H_{29}O_3PSn$ $[M – Bu]^+$: 383.0798, found 383.0783.

Dimethyl [(3*E*)-3-(Tributylstannyl)allyl]phosphonate (6a): Stannane **6a** was obtained as the minor regioisomer in the hydrostannation of **4a**. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.87–0.94 (m, 15 H), 1.28–1.35 (m, 6 H), 2.71 (dd, J = 6.8, 1.3 Hz, 1 H), 2.76 (dd, J = 6.8, 1.3 Hz, 1 H), 3.73 (d, J = 10.8 Hz, 6 H), 5.84–5.93 (m, 1 H), 6.18 (ddt, J = 18.8, 4.5, 1.3 Hz, 1 H) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.5 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –49.5 (d, J = 24.2 Hz) ppm.

Diisopropyl [2-(Tributylstannyl)allyl]phosphonate (5b): Stannylated allylphosphonate **5b** was prepared from propargylphosphonate **4b** (204 mg, 1.0 mmol) in 16 h according to the general procedure for $MOBI_3$-catalyzed hydrostannations as a colourless oil (169 mg, 0.35 mmol, 35%). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.3 Hz, 9 H), 0.94–0.98 (m, 6 H), 1.28–1.36 (t, J = 6.2 Hz, 18 H), 1.47–1.54 (m, 6 H), 2.73 (d, J = 22.3 Hz, 2 H), 4.68 (sept, J = 6.2 Hz, 2 H), 5.31 (dd, J = 5.1, 2.4 Hz, 1 H), 5.86 (dd, J = 5.4, 2.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.2, 13.7,

24.0 (q, J = 7.5 Hz), 27.4, 29.0, 38.5, 39.9, 69.9 (d, J = 6.7 Hz), 130.2 (d, J = 14 Hz), 144.5 (d, J = 11.4 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$) : δ = 25.5 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ = –40.7 (d, J = 32.8 Hz) ppm. HRMS (CI) m/z calcd. for $C_{21}H_{46}O_3PSn$ $[M + H]^+$: 496.2128, found 496.2151. HRMS (CI) m/z calcd. for $C_{17}H_{37}O_3PSn$ $[M – Bu]^+$: 439.1424, found 439.1429.

Diisopropyl [(3*E*)-3-(Tributylstannyl)allyl]phosphonate (6b): Stannane **6b** was obtained as the minor regioisomer in the hydrostannation of **4b**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87–0.90 (m, 15 H), 1.26–1.33 (m, 18 H), 1.45–1.53 (m, 6 H), 2.66 (dd, J = 6.8, 1.2 Hz, 1 H), 2.71 (dd, J = 6.8, 1.2 Hz, 1 H), 4.68 (sept, J = 6.2 Hz, 2 H), 5.85–5.95 (m, 1 H), 6.12 (ddt, J = 18.8, 4.4, 1.2 Hz, 1 H) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 25.1 ppm. ^{119}Sn NMR (149 Hz, $CDCl_3$): δ = –49.8 (d, J = 23 Hz) ppm.

Dimethyl (2-Methylenepent-4-enyl)phosphonate (7): A mixture of dimethyl 2-[(tributylstannyl)allyl]phosphonate (**5a**) (123 mg, 0.28 mmol) and allyl bromide (84.6 mg, 0.70 mmol) was dissolved in dry THF (1 mL) in a Schlenk tube under argon. A solution of $[(allyl)PdCl]_2$ (1 mg, 2.8 μmol) and PPh_3 (3.3 mg, 0.12 mmol) in dry THF (1 mL) was added and the reaction mixture was warmed up to 55 °C overnight. The solution was cooled to room temperature, before a saturated aqueous solution of KF was added and mixture stirred vigorously for 2 h. The reaction mixture was extracted with diethyl ether and the precipitated tin fluoride was filtered. The residue obtained after evaporation was purified by flash chromatography to yield phosphonate **7** as a colourless oil (52 mg, 0.27 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.61 (d, J = 22.3 Hz, 2 H), 2.93 (d, J = 6.7 Hz, 2 H), 3.74 (d, J = 10.8 Hz, 6 H), 4.98–5.03 (m, 2 H), 5.07–5.12 (m, 2 H), 5.71–5.81 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.2 (d, J = 137.9 Hz), 41.2 (d, J = 3.4 Hz), 53.7 (d, J = 6.9 Hz), 115.8 (d, J = 11.6 Hz), 117.1, 135.4, 138.2 (d, J = 10.4 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.5 ppm. HRMS (CI) m/z calcd. for $C_8H_{16}O_3P$ $[M + H]^+$: 191.0837, found 191.0835.

Dimethyl (2-Benzylallyl)phosphonate 8: A mixture of dimethyl [2-(tributylstannyl)allyl]phosphonate (**5a**) (100 mg, 0.23 mmol) and benzyl bromide (94 mg, 0.55 mmol) was dissolved in dry THF (1 mL) in a Schlenk tube under argon. A solution of $[(allyl)PdCl]_2$ (1 mg, 2.8 μmol) and PPh_3 (3.3 mg, 0.12 mmol) in dry THF (1 mL) was added and the reaction mixture was warmed up to 55 °C overnight. The solution was cooled to room temperature, before a saturated aqueous solution of KF was added and the mixture was stirred vigorously for 2 h. The reaction mixture was extracted with diethyl ether and the precipitated tin fluoride was filtered. The residue obtained after evaporation was purified by flash chromatography to yield product **8** as a colourless oil (57 mg, 0.23 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.54 (dd, J = 22.2, 0.8 Hz, 2 H), 3.52 (s, 2 H), 3.75 (d, J = 10.9 Hz, 6 H), 5.01 (d, J = 5.4 Hz, 1 H), 5.07 (d, J = 5.4 Hz, 1 H), 7.20–7.24 (m, 3 H), 7.28–7.32 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.8 (d, J = 137.7 Hz), 43.3 (d, J = 3.4 Hz), 52.7 (d, J = 7.0 Hz), 116.6 (d, J = 11.6 Hz), 126.4, 128.4, 129.1, 138.7, 139.1 (d, J = 10.4 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.5 ppm. HRMS (CI) m/z calcd. for $C_{12}H_{18}O_3P$ $[M + H]^+$: 241.0993, found 241.1005.

Dimethyl (2-Methyl-3-oxo-5-phenylpent-4-enyl)phosphonate (9): A mixture of dimethyl [2-(tributylstannyl)allyl]phosphonate **5a** (200 mg, 0.46 mmol) and cinnamoyl chloride (184 mg, 1.1 mmol) was dissolved in dry THF (1 mL) in a Schlenk tube under argon. A solution of $[(allyl)PdCl]_2$ (2 mg, 5.6 μmol) and PPh_3 (3.3 mg, 0.12 mmol) in dry THF (1 mL) was added and the reaction mixture was warmed up to 55 °C overnight. The solution was cooled to room temperature, before a saturated aqueous solution of KF was added and the mixture stirred vigorously for 2 h. The reaction mixture was extracted with diethyl ether and the precipitated tin fluoride was filtered off. The residue obtained after evaporation was purified by flash chromatography to yield **9** as a colourless oil (112 mg, 0.40 mmol, 86%). (*E*)-**9**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (d, J = 7.1 Hz, 3 H), 1.80 (ddd, J = 15.6, 6.6, 2.2 Hz, 1 H), 2.39 (ddd, J = 15.6, 6.6, 2.2 Hz, 1 H), 3.26–3.34 (m, 1 H), 3.70 (dd, J = 10.9, 2.7 Hz, 6 H), 6.80 (d, J = 16.0 Hz, 1 H), 7.38–7.40 (m, 3 H), 7.55–7.57 (m, 2 H), 7.65 (d, J = 16.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 18.8 (d, J = 10.2 Hz), 27.1 (d, J = 141.4 Hz), 38.8 (d, J = 3.3 Hz), 52.3 (dd, J = 6.6, 3.1 Hz), 124.3, 128.4, 128.5, 128.9, 130.6, 134.4, 143.6, 201.1 (d, J = 10.3 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 33.1 ppm. Selected signal for minor isomer (*Z*)-**9**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (d, J = 7.1 Hz, 3 H), 1.67 (ddd, J = 15.6, 6.6, 2.2 Hz, 1 H), 2.3 (ddd, J = 15.6, 6.6, 2.2 Hz, 1 H), 2.80–2.93 (m, 1 H), 3.65 (dd, J = 10.9, 2.7 Hz, 6 H), 6.25 (d, J = 12.7 Hz, 1 H), 6.80 (d, J = 12.7 Hz, 1 H), 7.16–7.19 (m, 3 H), 7.24–7.28 (m, 2 H) ppm. HRMS (CI) m/z calcd. for $C_{14}H_{19}O_4P$ (mixture of isomers) $[M]^+$: 282.1021, found 282.1044.

Dimethyl (2-Iodoallyl)phosphonate (10): Iodine (62 mg, 0.24 mmol) dissolved in $CHCl_3$ (0.7 mL) was added to a solution of dimethyl [2-(tributylstannyl)allyl]phosphonate **5a** (100 mg, 0.23 mmol) in $CHCl_3$ (0.5 mL) at room temperature. After 1 h, saturated KF solution (1 mL) and ethyl acetate were added and the mixture was allowed to stir for 2 h. The organic layer was separated and dried with Na_2SO_4. After evaporation of the solvent, the crude product was purified by flash chromatography to yield **10** as yellow liquid (47 mg, 0.17 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.16 (dd, J = 21.5, 1.0 Hz, 2 H), 3.79 (d, J = 10.9 Hz, 6 H), 5.95 (dd, J = 5.1, 1.8 Hz, 1 H), 6.30 (dd, J = 5.3, 1.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.2 (d, J = 139.7 Hz), 53.1 (d, J = 6.7 Hz), 92.7 (d, J = 12.6 Hz), 131.4 (d, J = 10.7 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 25.6 ppm. HRMS (CI) m/z calcd. for $C_5H_{11}IO_3P$ $[M + H]^+$: 276.9490, found 276.9501. $C_5H_{10}IO_3P$ (276.01): calcd. C 21.76, H 3.65; found C 22.42, H 3.51.

Diethyl [1-(Tributylstannyl)vinyl]phosphonate (12a): Stannylated vinylphosphonate **12a** was prepared from **11a** (162 mg, 1.0 mmol) according to the general procedure for $MOBI_3$-catalyzed hydrostannations in 12 h as a colourless oil (258 mg, 0.57 mmol, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.3 Hz, 9 H), 1.09–1.04 (m, 6 H), 1.31 (t, J = 7.1 Hz, 6 H), 1.26–1.35 (m, 6 H), 1.47–1.55 (m, 6 H), 4.00–4.10 (m, 4 H), 6.25 (dd, J = 62.2, 3.3 Hz, 1 H), 6.90 (dd, J = 34.6, 3.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.2 (d, J = 1.2 Hz), 13.6, 16.4 (d, J = 6.0 Hz), 27.2, 28.7, 61.2 (d, J = 6.0 Hz), 142.7 (d, J = 130.7 Hz), 144.1 (d, J = 2.7 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.1 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –29.1 (d, J = 112 Hz) ppm. HRMS (CI) m/z calcd. for $C_{14}H_{31}O_3PSn$ $[M – Bu]^+$: 397.0955, found 397.0941.

Diethyl (*E*)-[1-(Tributylstannyl)prop-1-enyl]phosphonate (12b): Stannylated vinylphosphonate **12b** was prepared from **11b** (176 mg, 1.0 mmol) according to the general procedure for $MOBI_3$-catalyzed hydrostannations in 8 h as a colourless oil (313 mg, 0.67 mmol, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.3 Hz, 9 H), 0.95–0.99 (m, 6 H), 1.27–1.36 (m, 12 H), 1.46–1.54 (m, 6 H), 2.18 (dd, J = 6.8, 3.6 Hz, 3 H), 4.04 (quin, J = 7.2 Hz, 4 H), 6.66 (dq, J = 64.5, 6.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.6 (d, J = 1.1 Hz), 13.6, 16.4 (d, J = 6.5 Hz), 20.6 (d, J = 14.5 Hz), 27.3, 28.8, 60.8 (d, J = 5.7 Hz), 132.2 (d, J = 132.4 Hz), 156.8 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 22.9 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –20.8 (d, J = 127.4 Hz) ppm. HMRS (CI) m/z calcd. for $C_{19}H_{42}O_3PSn$ $[M + H]^+$: 468.1815, found

468.1768; *m/z* calcd. for $C_{15}H_{32}O_3PSn$ [M – Bu]$^+$: 411.1111, found 411.1089. $C_{19}H_{41}O_3PSn$ (467.19): calcd. C 48.84, H 8.85; found C 48.83, H 8.89.

Diethyl (*E*)-[1-(Tributylstannyl)pent-1-enyl]phosphonate (12c): Stannylated vinylphosphonate **12c** was prepared from **11c** (205 mg, 1.0 mmol) according to the general procedure for $MOBI_3$-catalyzed hydrostannations in 12 h as a colourless oil (302 mg, 0.61 mmol, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.3 Hz, 9 H), 0.93–0.97 (m, 9 H), 1.26–1.35 (t, J = 7.1 Hz, 14 H), 1.44–1.52 (m, 8 H), 2.56 (dq, J = 7.5, 3.3 Hz, 2 H), 4.01 (quin, J = 7.2 Hz, 4 H), 6.50 (dt, J = 64.2, 7.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.6 (d, J = 1.1 Hz), 13.6, 13.7, 16.4 (d, J = 6.6 Hz), 22.3, 27.3, 28.8, 36.1, 60.7 (d, J = 5.7 Hz), 130.6 (d, J = 233.4 Hz), 162.5 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 22.9 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –20.4 (d, J = 131.4 Hz) ppm. HRMS (CI) *m/z* calcd. for $C_{21}H_{45}O_3PSn$ [M]$^+$: 495.2058, found 495.2012. HRMS (CI) *m/z* calcd. for $C_{17}H_{36}O_3PSn$ [M – Bu]$^+$: 439.1424, found 439.1281. $C_{21}H_{45}O_3PSn$ (495.25): calcd. C 50.93, H 9.16; found C 51.11, H 9.10.

Diethyl (*E*)-[1-(Tributylstannyl)-2-phenylvinyl]phosphonate (*E*)-12d: Stannylated vinylphosphonate **(*E*)-12d** was prepared from **11d** (240 mg, 1.0 mmol) according to the general procedure for $MOBI_3$-catalyzed hydrostannations in 15 h as a colourless oil (408 mg, 0.77 mmol, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.3 Hz, 9 H), 1.06–1.10 (m, 6 H), 1.17 (t, J = 7.1 Hz, 6 H), 1.31–1.40 (m, 6 H), 1.53 (m, 6 H), 3.82–3.90 (m, 4 H), 7.28–7.36 (m, 3 H), 7.51 (d, J = 62.8 Hz, 1 H), 7.64–7.66 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.3, 13.7, 16.1 (d, J = 6.6 Hz), 27.3, 28.9, 61.1 (d, J = 6.6 Hz), 127.9, 128.6, 129.2, 134.4 (d, J = 135 Hz), 138.0 (d, J = 14.1 Hz), 156.0 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.9 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –10.5 (d, J = 114 Hz) ppm.

Diethyl (*Z*)-[1-(Tributylstannyl)-2-phenylvinyl]phosphonate (*Z*)-12d: Stannylated vinylphosphonate **(*Z*)-12d** was prepared from **11d** (240 mg, 1.0 mmol) according to the general procedure for $MOBI_3$-catalyzed hydrostannations in 6 h as a colourless oil. (387 mg, 0.73 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, J = 7.3 Hz, 9 H), 0.85–0.89 (m, 6 H), 1.18–1.28 (m, 6 H), 1.35 (t, J = 7.0 Hz, 6 H), 1.33–1.40 (m, 6 H), 4.09–4.13 (m, 4 H), 7.27–7.37 (m, 5 H), 8.40 (d, J = 33.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.0 (d, J = 1.9 Hz), 13.6, 16.4 (d, J = 6.6 Hz), 27.2, 28.8, 61.3 (d, J = 5.9 Hz), 127.6, 128.2, 128.6, 134.2, 134.5, 139.9 (d, J = 31.4 Hz), 158.4 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.2 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –40.6 (d, J = 104.0 Hz) ppm. HRMS (CI) *m/z* calcd. for $C_{24}H_{44}O_3PSn$ [M + H]$^+$: 530.1972, found 530.1966. $C_{24}H_{43}O_3PSn$ (529.27): calcd. C 54.46, H 8.19; found C 54.71, H 8.10.

Diethyl (*E*)-[1-(Tributylstannyl)-4-phenylbut-1-enyl]phosphonate (12e): Stannylated vinylphosphonate **12e** was prepared from **11e** (267 mg, 1.0 mmol) according to the general procedure for $MOBI_3$-catalyzed hydrostannations in 12 h as a colourless oil (330 mg, 0.59 mmol, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, J = 7.3 Hz, 9 H), 0.98–1.02 (m, 6 H), 1.33 (t, J = 7 Hz, 6 H), 1.35–1.40 (m, 6 H), 1.47–1.60 (m, 6 H), 2.83 (t, J = 7.3 Hz, 2 H), 2.99 (dq, J = 7.2, 3.2 Hz, 2 H), 3.97–4.06 (m, 6 H), 6.55 (dt, J = 64.4, 7.1 Hz, 1 H), 7.17–7.29 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.6, 13.6, 16.4 (d, J = 6.4 Hz), 27.3, 28.8, 35.3 (d, J = 1.9 Hz), 35.7 (d, J = 13.2 Hz), 60.1 (d, J = 5.7 Hz), 125.9, 128.3, 128.6, 131.9 (d, J = 133.5 Hz), 141.2, 161.1 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 22.7 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –19.9 (d, J = 128 Hz) ppm. HRMS (CI) *m/z* calcd. for $C_{26}H_{47}O_3PSn$ [M]$^+$: 557.2215, found 557.2206. $C_{26}H_{47}O_3PSn$ (557.32): calcd. C 56.03, H 8.50; found C 56.69, H 8.54.

Diethyl (*E*)-[1-(Tributylstannyl)-2-cyclohexylvinyl]phosphonate (12f): Stannylated vinylphosphonate **12f** was prepared from **11f** (245 mg, 1.0 mmol) according to the general procedure for $MOBI_3$-catalyzed hydrostannations in 12 h as a colourless oil (273 mg, 0.51 mmol, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.3 Hz, 9 H), 0.94–0.98 (m, 6 H), 1.01–1.72 (m, 28 H), 2.98–3.08 (m, 1 H), 4.02 (m, 4 H), 6.28 (dd, J = 64.8, 9.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.6 (d, J = 1.0 Hz), 13.7, 16.4 (d, J = 6.6 Hz), 25.3, 25.9, 27.3, 27.5, 28.8, 32.3 (d, J = 2.1 Hz), 42.8 (d, J = 12.4 Hz), 60.1 (d, J = 5.7 Hz), 127.0, 128.3 (d, J = 134.0 Hz), 167.6 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 23.1 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –20.0 (d, J = 134.4 Hz) ppm. HRMS (CI) *m/z* calcd. for $C_{20}H_{40}O_3PSn$ [M – Bu]$^+$: 479.1737, found 479.1751.

Diethyl (*Z*)-(1-Phenylpent-1-enyl)phosphonate (14): diethyl (*E*)-[1-(tributylstannyl)pent-1-enyl]phosphonate (**12c**) (247 mg, 0.5 mmol) and iodobenzene (92 mg, 0.45 mmol) were dissolved in dry *N*-methylpyrrolidinone (NMP) (3 mL). This solution was added to a solution of $Pd_2(dba)_3$ (8.2 mg, 9 μmol) and tri(2-furyl)phosphane (17 mg, 0.073 mmol) in dry NMP (1 mL) followed by addition of CuI (95 mg, 0.5 mmol). The reaction mixture was stirred at room temperature overnight. The reaction mixture was poured into 10% aqueous KF solution (5 mL) stirred vigourously for 20 min before it was filtered through celite. After evaporation of the solvent, the residue was purified by flash chromatography to yield **14** as yellow oil (57 mg, 0.20 mmol, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.4 Hz, 3 H), 1.24 (t, J = 7.1 Hz, 6 H), 1.44–1.48 (m, 2 H), 2.58 (dq, J = 7.5, 3.2 Hz, 2 H), 4.09–4.19 (m, 4 H), 6.46 (dt, J = 48.5, 7.7 Hz, 1 H), 7.24–7.34 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 16.2 (d, J = 6.6 Hz), 22.6 (d, J = 1.7 Hz), 32.5 (d, J = 5.9 Hz), 61.5 (d, J = 5.7 Hz), 127.1, 128.0, 128.4, 128.4, 131.4 (d, J = 175.8 Hz), 140.2 (d, J = 12.1 Hz), 152.6 (d, J = 11.3 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 16.5 ppm. HRMS (CI) *m/z* calcd. for $C_{15}H_{23}O_3P$ [M]$^+$: 282.1385, found 282.1368. $C_{15}H_{23}O_3P$ (282.32): calcd. C 63.82, H 8.21; found C 63.20, H 8.00.

Diethyl (*Z*)-[1-(4-Nitrophenyl)pent-1-enyl]phosphonate (15): A solution of diethyl (*E*)-[1-(tributylstannyl)pent-1-enyl]phosphonate (**12c**) (247 mg, 0.5 mmol) and *p*-Iodonitrobenzene (113 mg, 0.45 mmol) in dry NMP (3 mL) was added to a solution of $Pd_2(dba)_3$ (8.2 mg, 9 μmol) and tri-2-furyl phosphane (17 mg, 0.073 mmol) in dry NMP (1 mL), followed by the addition of CuI (95 mg, 0.5 mmol). The reaction mixture was stirred at room temperature overnight, before it was poured into 10% aqueous KF solution (5 mL). After vigorous stirring for 20 min the solution was filtered through celite, dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography to yield **15** as yellow oil (101 mg, 0.31 mol, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.4 Hz, 3 H), 1.36 (t, J = 7.1 Hz, 6 H), 1.44–1.48 (m, 2 H), 2.58 (dq, J = 7.9, 2.7 Hz, 2 H), 4.09–4.19 (m, 4 H), 6.45 (dt, J = 47.3, 8.0 Hz, 1 H), 7.50 (dd, J = 12.0, 4.0 Hz, 2 H), 8.16 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 16.2 (d, J = 6.4 Hz), 22.4 (d, J = 1.4 Hz), 32.6 (d, J = 5.7 Hz), 61.9 (d, J = 5.8 Hz), 123.3, 129.2, 129.2, 130.4 (d, J = 178.0 Hz), 147.5 (d, J = 12.4 Hz), 154.6 (d, J = 10.2 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 14.7 ppm. HRMS (CI) *m/z* calcd. for $C_{15}H_{22}NO_5P$ [M]$^+$: 327.1236, found 327.1250. $C_{15}H_{22}NO_5P$ (327.32): calcd. C 55.04, H 6.77, N 4.28; found C 55.03, H 6.68, N 4.43.

Diethyl (*Z*)-(1-Benzylpent-1-enyl)phosphonate (16): To a solution of diethyl (*E*)-[1-(tributylstannyl)pent-1-enyl]phosphonate (**12c**)

(247 mg, 0.5 mmol) in toluene (2 mL) benzyl bromide (214 mg, 1.25 mmol) was added at room temperature under argon. The catalyst solution was prepared in another Schlenk tube by stirring $Pd_2(dba)_3$ (11 mg, 0.0125 mmol) and triphenylarsane (80 mg, 0.1 mmol) in toluene (1 mL) for 15 min, before it was added to the stannane solution. The mixture was warmed up to 90 °C for 15 h. After cooling to room temperature, saturated KF solution (5 mL) was added and the mixture was stirred for 2 h, before diethyl ether was added. The aqueous layer was separated and the organic layer was washed with water. The combined organic layers were evaporated under reduced pressure and the residue obtained was dissolved in ethyl acetate. The insoluble tributyltin fluoride was filtered off, the solvent was removed and the crude product was purified by flash column chromatography giving rise to **16** in 51% yield (75 mg, 0.25 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, J = 7.4 Hz, 3 H), 1.14 (t, J = 7.1 Hz, 6 H), 1.32–1.41 (m, 2 H), 2.58 (dq, J = 7.5, 3.2 Hz, 2 H), 3.46 (d, J = 13.3 Hz, 2 H), 3.73–3.93 (m, 4 H), 6.10 (dt, J = 49.7, 7.7 Hz, 1 H), 7.09–7.22 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 16.2 (d, J = 6.6 Hz), 22.5 (d, J = 2.0 Hz), 32.1 (d, J = 6.6 Hz), 41.0 (d, J = 12.7 Hz), 61.1 (d, J = 5.6 Hz), 126.2, 128.2, 129.1, 128.4 (d, J = 173.1 Hz), 139.3 (d, J = 4.5 Hz), 149.9 (d, J = 12.5 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.8 ppm. HRMS (CI) m/z calcd. for $C_{16}H_{25}O_3P$ $[M]^+$: 296.1541, found 296.1526.

Diethyl (*E*)-(1-Iodopent-1-enyl)phosphonate (17): Iodine (142 mg, 0.55 mmol), dissolved in $CHCl_3$ (2 mL), was added to a solution of diethyl (*E*)-[1-(tributylstannyl)pent-1-enyl]phosphonate (**12c**) (247 mg, 0.5 mmol) in $CHCl_3$ (1 mL) at room temperature. After 1 h, saturated KF solution (4 mL) and ethyl acetate were added, and the suspension was allowed to stir for 2 h. After separation of the layers, the organic layer was separated and dried with Na_2SO_4. After evaporation of the solvent, the crude product was purified by flash chromatography to yield **17** as a yellow oil (136 mg, 0.41 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.9 (t, J = 7.4 Hz, 3 H), 1.36 (t, J = 7.1 Hz, 6 H), 1.44–1.48 (m, 2 H), 2.58 (dq, J = 7.9, 2.6 Hz, 2 H), 4.09–4.19 (m, 4 H), 7.31 (dt, J = 43.3, 8.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 16.2 (d, J = 6.7 Hz), 22.0 (d, J = 1.7 Hz), 35.7 (d, J = 4.6 Hz), 62.7 (d, J = 5.5 Hz), 82.7 (d, J = 186.3 Hz), 163.5 (d, J = 12.6 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 8.90 ppm. HRMS (CI) m/z calcd. for $C_9H_{18}IO_3P$ $[M]^+$: 332.0038, found 331.9999. $C_9H_{18}IO_3P$ (332.12): calcd. C 32.55, H 5.46; found C 32.63, H 5.18.

Diethyl (*Z*)-(1-Iodo-2-phenylvinyl)phosphonate (18): Iodine (53.2 mg, 0.206 mmol), dissolved in $CHCl_3$ (0.7 mL), was added to a solution of diethyl (*Z*)-[1-(tributylstannyl)-2-phenylvinyl]phosphonate (**12d**) (100 mg, 0.188 mmol) in $CHCl_3$ (0.5 mL) at room temperature. After 1 h, saturated KF solution (2 mL) and ethyl acetate were, and the suspension was allowed to stir for 2 h. After separation of the layers, the organic layer was separated and dried with Na_2SO_4. Evaporation of the solvent and purification of the crude product by flash chromatography yielded **18** (57 mg, 0.15 mmol, 83%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (t, J = 7.1 Hz, 6 H), 4.11–4.43 (m, 4 H), 7.40–7.43 (m, 3 H), 7.73–7.76 (m, 2 H), 8.11 (d, J = 18.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.2 (d, J = 6.6 Hz), 63.0 (d, J = 5.5 Hz), 86.0 (d, J = 189.1 Hz), 128.3, 129.0, 130.0, 135.7 (d, J = 19.2 Hz), 151.4 (d, J = 13.0 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.4 ppm. HRMS (CI) m/z calcd. for $C_{12}H_{16}IO_3P$ $[M]^+$: 365.9882, found 365.9734. $C_{12}H_{16}IO_3P$: calcd.: C 39.37, H 4.40; found C 39.88, H 4.39.

Diethyl (*E*)-(2-Phenylvinyl)phosphonate (19): To a solution of diethyl (*Z*)-[1-(tributylstannyl)-2-phenylvinyl]phosphonate (**12d**) (100 mg, 0.18 mmol) in THF (1 mL) benzoyl chloride (28 mg, 0.2 mmol) was added, followed by a THF solution (1 mL) of $[(allyl)PdCl]_2$ (1 mg, 0.002 mmol) and PPh_3 (2.2 mg, 0.08 mmol). The reaction mixture was warmed to 60 °C overnight. After cooling to room temperature, 10% KF solution was added and the mixture was stirred for 2 h. After separation of the layers, the aqueous phase was extracted with diethyl ether and the combined organic solvents were evaporated in vacuo. The residue was dissolved in ethyl acetate, and the precipitated tin fluoride was filtered. The residue obtained after evaporation of the solvent was purified by flash chromatography to yield **19** (43 mg, 0.17 mmol, 94%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.3 (t, J = 7.2 Hz, 6 H), 4.11–4.15 (m, 4 H), 6.25 (t, J = 17.6 Hz, 1 H), 7.36–7.38 (m, 3 H), 7.49 (d, J = 17.6, 4.4 Hz, 1 H), 7.45–7.51 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.1 (d, J = 6.5 Hz), 61.7 (d, J = 5.3 Hz), 116.7 (d, J = 191.4 Hz), 128.1, 129.3, 129.6, 135.3 (d, J = 8.7 Hz), 148.3 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.5 ppm. HRMS (CI) m/z calcd. $C_{12}H_{17}O_3P$ $[M]^+$: 240.0915, found 240.0921. $C_{12}H_{17}O_3P$ (240.24): calcd. C 59.99, H 7.13; found C 59.47, H 7.23.

Diethyl (*E*)-[1-(4-Nitrophenyl)-2-phenylvinyl]phosphonate (20): A mixture of diethyl (*Z*)-1-(tributylstannyl)-2-phenylvinylphosphonate (**12d**) (100 mg, 0.18 mmol) and *p*-iodo-nitrobenzene (41.58 mg, 0.167 mmol) was dissolved in dry NMP (1 mL) before it was added to a solution of $Pd_2(dba)_3$ (1 mg, 0.001 mmol) and tri-(2-furyl)phosphane (2 mg, 0.08 mmol) in dry NMP (1 mL) followed by addition of CuI (35.8 mg, 0.188 mmol) in the same solvent (2 mL). The reaction mixture was stirred at room temperature overnight and poured into 10% aqueous KF solution (3 mL). Stirring was continued for 20 min and the mixture was then filtered through celite. The filtrate was extracted twice with ether and the combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The residue obtained was purified by flash chromatography to yield **20** (36 mg, 0.1 mmol, 53%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (t, J = 7.3 Hz, 6 H), 4.16–4.11 (m, 4 H), 7.02 (d, J = 7.4 Hz, 2 H), 7.17–7.25 (m, 3 H), 7.46 (dd, J = 8.8, 1.8 Hz, 2 H), 7.71 (d, J = 24.4 Hz, 1 H), 8.21 (d, J = 8.9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.7 (d, J = 6.2 Hz), 62.8 (d, J = 5.9 Hz), 124.5 (d, J = 1.6 Hz), 128.8, 129.9, 130.5 (d, J = 1.0 Hz), 130.7, 130.8, 134.3 (d, J = 21.6 Hz), 143.5 (d, J = 8.1 Hz), 145.4 (d, J = 9.7 Hz), 147.8 (d, J = 2.4 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 16.4 ppm. HRMS (CI) m/z calcd. for $C_{18}H_{20}NO_5P$ $[M]^+$: 361.1079, found 361.1078. $C_{18}H_{20}NO_5P$: C 59.83, H 5.58, N 3.88; found C 60.25, H 5.62, N 3.77.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) and by the Fonds der Chemischen Industrie. N. J. thanks the Alexander von Humboldt Foundation for a postdoctoral fellowship.

[1] Reviews: a) T. Minami, J. Motoyoshiya, *Synthesis* **1992**, 333–349; b) T. Minami, T. Okauchi, R. Kouno, *Synthesis* **2001**, 349–357; c) M. Mikolajczyk, P. Balczewski, *Top. Curr. Chem.* **2003**, *223*, 161–214; d) M. R. Harnden, A. Parkin, M. J. Parrat, R. M. Perkins, *J. Med. Chem* **1993**, *36*, 1343–1355; e) S. Megati, S. Phadtare, J. Zemlicka, *J. Org. Chem.* **1992**, *57*, 2320–2327.

[2] Z. J. Lesnikowski, R. F. Schinazi, *J. Org. Chem.* **1993**, *58*, 6531–6534.

[3] a) Y. Wang, A. M. Arif, F. G. West, *J. Am. Chem. Soc.* **1999**, *121*, 876–877; b) A. B. Smith III, Q. Lin, G. R. Pettit, J.-C. Chapuis, J. M. Schmidt, *Bioorg. Med. Chem. Lett.* **1998**, *8*, 567–568; c) R. M. Garbaccio, S. J. Stachel, D. K. Baeschlin,

S. J. Danishefsky, *J. Am. Chem. Soc.* **2001**, *123*, 10903–10908; d) G. Zhou, Q.-Y. Hu, E. J. Corey, *Org. Lett.* **2003**, *5*, 3979–3982.

[4] a) B. Borhan, M. L. Souto, J. M. Um, B. Zhou, K. Nakanishi, *Chem. Eur. J.* **1999**, *5*, 1172–1175; b) Y. Fujimoto, J. Ishihara, S. Maki, N. Fujioka, T. Wang, T. Furuta, N. Fishkin, B. Borhan, N. Berova, K. Nakanishi, *Chem. Eur. J.* **2001**, *7*, 4198–4204; c) W. Adam, C. M. Ortega-Schulte, *J. Org. Chem.* **2003**, *68*, 1007–1011; d) A. K. Mandal, J. S. Schneekloth, K. Kuramochi, C. M. Crews, *Org. Lett.* **2006**, *8*, 427–430.

[5] a) F. M. Atta, R. Betz, B. Schmid, R. R. Schmidt, *Chem. Ber.* **1986**, *119*, 472–481; b) C. Santelli-Rouvier, L. Toupet, M. Santelli, *J. Org. Chem.* **1997**, *62*, 9039–9047.

[6] M. B. Marszak, M. Simalty, A. Seuleiman, *Tetrahedron Lett.* **1974**, *15*, 1905–1908.

[7] J. K. Stille, *Angew. Chem.* **1986**, *98*, 504–519; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508–523.

[8] a) A. J. Leusink, H. A. Budding, W. Drenth, *J. Organomet. Chem.* **1967**, *9*, 295–306; b) Y. Ichinose, H. Oda, K. Oshima, K. Utimoto, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3468–3470; c) K. Nozaki, K. Oshima, K. Utimoto, *J. Am. Chem. Soc.* **1987**, *109*, 2547–2549; d) H. X. Zhang, F. Guibe, G. Balavoine, *Tetrahedron Lett.* **1988**, *29*, 619–622; e) H. X. Zhang, F. Guibé, G. Balavoine, *J. Org. Chem.* **1990**, *55*, 1857–1867; f) N. Asao, N. Asao, J. X. Liu, T. Sudoh, Y. Yamamoto, *J. Chem. Soc., Chem. Commun.* **1995**, 2405–2406; g) N. Asao, Y. Matsukawa, Y. Yamamoto, *Chem. Commun.* **1996**, 1513–1514; h) N. Asao, J. X. Liu, T. Sudoh, Y. Yamamoto, *J. Org. Chem.* **1996**, *61*, 4568–4571.

[9] A comprehensive survey on palladium-catalyzed reactions can be found in J. L. Malleron, J. C Fiaud, J. Y. Legros, *Handbook of Palladium-Catalyzed Organic Reactions*, Academic Press, San Diego, **1997**.

[10] a) U. Kazmaier, D. Schauß, M. Pohlman, *Org. Lett.* **1999**, *1*, 1017–1019; b) U. Kazmaier, D. Schauß, M. Pohlman, S. Raddatz, *Synthesis* **2000**, 914–917; c) S. Braune, U. Kazmaier, *J. Organomet. Chem.* **2002**, *641*, 26–29; d) S. Braune, M. Pohlman, U. Kazmaier, *J. Org. Chem.* **2004**, *69*, 468–474; e) U. Kazmaier, M. Klein, *Chem. Commun.* **2005**, 501–503; f) U. Kazmaier, A. Wesquet, *Synlett* **2005**, 1271–1274.

[11] a) U. Kazmaier, M. Pohlman, D. Schauß, *Eur. J. Org. Chem.* **2000**, 2761–2766; b) A. O. Wesquet, S. Dörrenbächer, U. Kazmaier, *Synlett* **2006**, 1105–1109; c) U. Kazmaier, S. Dörrenbächer, A. Wesquet, S. Lucas, M. Kummeter, *Synthesis* **2007**, 320–326; d) H. Lin, U. Kazmaier, *Eur. J. Org. Chem.* **2007**, 2839–2843.

[12] a) M. Gordon, C. E. Griffin, *J. Org. Chem.* **1966**, *31*, 333–334; b) M. S. Chattha, A. M. Aguiar, *J. Org. Chem.* **1971**, *36*, 2719–2720; c) M. S. Chattha, A. M. Aguiar, *J. Org. Chem.* **1971**, *36*, 2720–2721.

[13] a) Z. C. Xiong, X. Huang, *J. Chem. Res.* **2003**, 372–373; b) X. Huang, Z. C. Xiong, *Synth. Commun.* **2003**, *33*, 2511–2517; c) Z. C. Xiong, L. L. Wu, X. Huang, *Chin. Chem. Lett.* **2004**, *15*, 35–36.

[14] R. Miao, S. Li, P. Chiu, *Tetrahedron* **2007**, *63*,6737–6740.

[15] a) Y. Wang, D. J. Burton, *Org. Lett.* **2006**, *8*, 1109–1111; b) J. C. Cochran, H. K. Phillips, S. Tom, A. R. Hurd, B. S. Bronk, *Organometallics* **1994**, *13*, 947–953.

Received: May 27, 2008

