

Practical Synthesis of Vinyl-Substituted *p*-Phenylenevinylene Oligomers and Their Triethoxysilyl Derivatives

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Abstract: Luminescent semiconducting organic compounds are widely used as active layers in electro-optical devices. Apart from conjugated polymers, monodisperse oligomers also represent attractive materials. The synthesis of stilbenoid oligomers with polymerizable end groups is presented. Oligo(phenylenevinylene)s with terminal vinyl groups **17–19** are prepared in good yields by Horner–Emmons olefinations or by the Heck reaction of

the iodo-substituted oligomers **15, 16** with compressed ethene. Triethoxysilyl groups can be linked via rigid 1,2-vinylene units to the chromophores **26–30**, either in the direct reaction of **14, 24** with silanes **21, 22** or by cross-metathesis of **17–19** with the vinylsilanes **21, 22** using Grubbs catalyst.

Keywords: cross metathesis; materials science; olefinations; oligomers; *p*-phenylenevinylene oligomers; silane

Introduction

The use of conjugated polymers in electro-optical devices has steadily increased since the first reports^[1] about light-emitting diodes with poly(*p*-phenylenevinylene) (PPV) as active layer. The properties, performance and processability of PPV and related materials have been tremendously improved since.^[2] Besides conjugated polymers, well-defined oligomers are attractive materials: they serve as model compounds for the polymers and are electronic materials in their own right.^[3] Oligomers can be prepared in high purity, with monodisperse chain lengths and free of structural defects. A broad variety of substituents can easily be introduced^[4] to alter the electrical and optical properties of the chromophore. Whereas the film forming capabilities of polymers are often excellent, amorphous films of most oligomers are metastable and tend to recrystallise. Flexible polymers with conjugated segments in the main chain^[5] or these units as side chains^[6] combine the advantages of both groups, monodisperse chromophores and high-quality films. To prepare flexible polymers with oligo(phenylenevinylene) (OPV) side chains, Greiner^[7] and Leising^[8] grafted vinylstilbene and bromostyrene on partially brominated polystyrene. Schrock^[9] used the ring-opening metathesis polymerisation of norbornenes with conjugated side chains. These polymers are suitable materials for single-layer light-emitting diodes. However, for the pre-

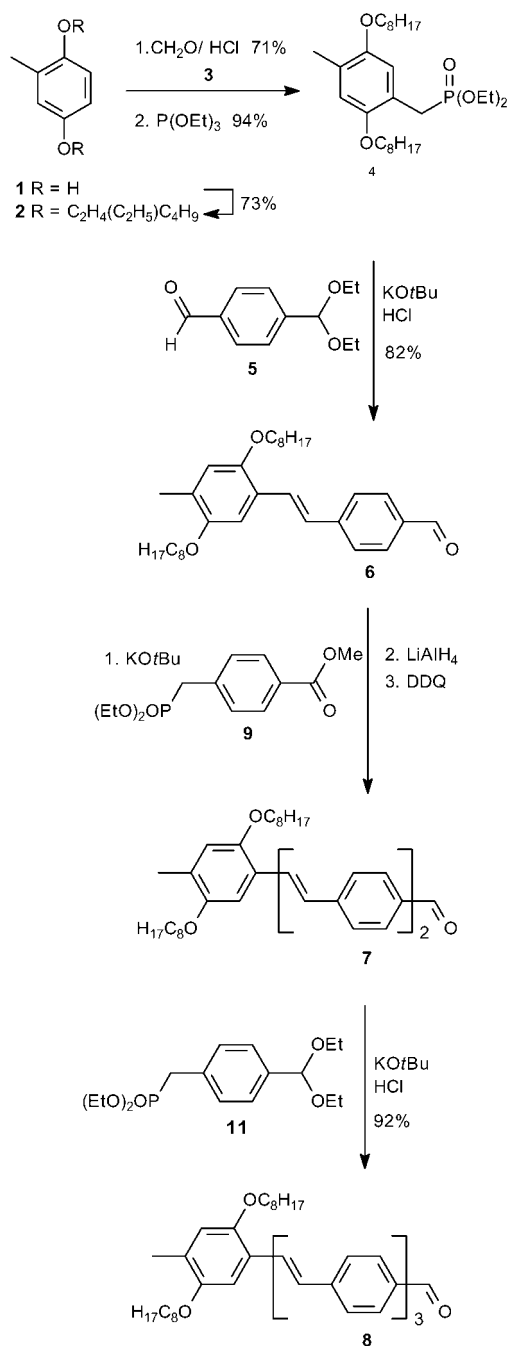
paration of multi-layer devices, which are coated from solution, one must ensure that the lower layers are not redissolved during the coating of subsequent layers. A successful route to achieve this goal is the casting of a soluble precursor and its thermal conversion to an insoluble polymer, as it is used for the preparation of non-substituted PPV. Electroluminescent materials with vinyl end groups or side chains^[10] are susceptible to thermal or photochemical cross-linking thus allowing the soluble and processable materials to be cured into insoluble layers.

In this paper, we describe a convenient route to monodisperse oligo(phenylenevinylene)s with terminal vinyl groups and the cross-metathesis of these compounds to chromophores with vinyltriethoxysilane end groups. The alkoxysilane group can be hydrolyzed and cross-linked to form polymeric networks^[11] or organic-inorganic hybrid materials, which can be used for coatings of glass surfaces or electro-optical devices.^[12]

Synthesis and Vinylation of Iodo-Substituted Oligo(phenylenevinylene)s

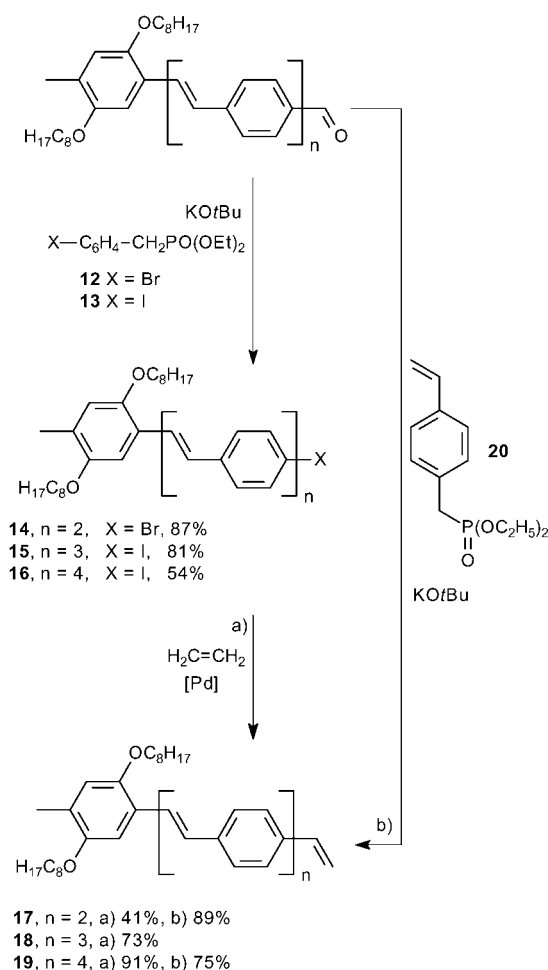
The PO-activated (Horner–Emmons) olefination of aromatic aldehydes with benzyl phosphonates is a versatile, convenient and high-yield route to stilbenes

and stilbenoid oligomers with (*E*)-configured double bonds. Small amounts of accompanying (*Z*)-stilbenes can be removed easily by chromatography, crystallization, or isomerization to the (*E*)-form. For the synthesis of the monodisperse oligo(phenylenevinylene)s (**17–19**, **27–30**) with a terminal reactive group (vinyl or trialkoxysilyl) and good solubility, a benzyl phosphonate with two branched alkoxy side chains **4** was prepared via alkylation of methylhydroquinone **1**, chloromethylation and subsequent Michaelis–Arbusov reaction. A Horner reaction with the



Scheme 1. Synthesis of OPV-aldehydes **6–8**.

monoprotected terephthal dialdehyde **5** led to stilbene aldehyde **6**, the key compound for the synthesis of **14–19**. For the extension of the conjugated system of the aldehyde **6**, two strategies were employed: the PO-activated olefination of **6** with phosphonate **9**^[13] carrying an ester group that was reduced to the alcohol **10** and reoxidized to an aldehyde **7**. The second approach is the olefination of this aldehyde **7** with synthon **11** followed by cleavage of the protecting group to yield aldehyde **8**. It is true that this route suffers from the lengthy preparation and purification of synthon **11**,^[14] but it is very convenient for small scale homologizations.



Scheme 2. Heck and Horner reactions to vinyl-substituted OPVs **17–19**.

a) $\text{Pd}(\text{OAc})_2$, $\text{P}(o\text{-tol})_3$, Et_3N , DMF, ethene (30 bar), 100–110 °C; b) KOtBu , THF, 18-crown-6.

The following conversions to the oligomers with bromine **14** or iodine **15**, **16** in the *p*-position of the terminal rings were performed with the 4-halophosphonates **12**,^[15] **13**, prepared from the corresponding benzyl bromides.^[16] The Heck coupling of ethene with bromoarenes to extended conjugated systems like the laser dye stilbene I has been investigated by

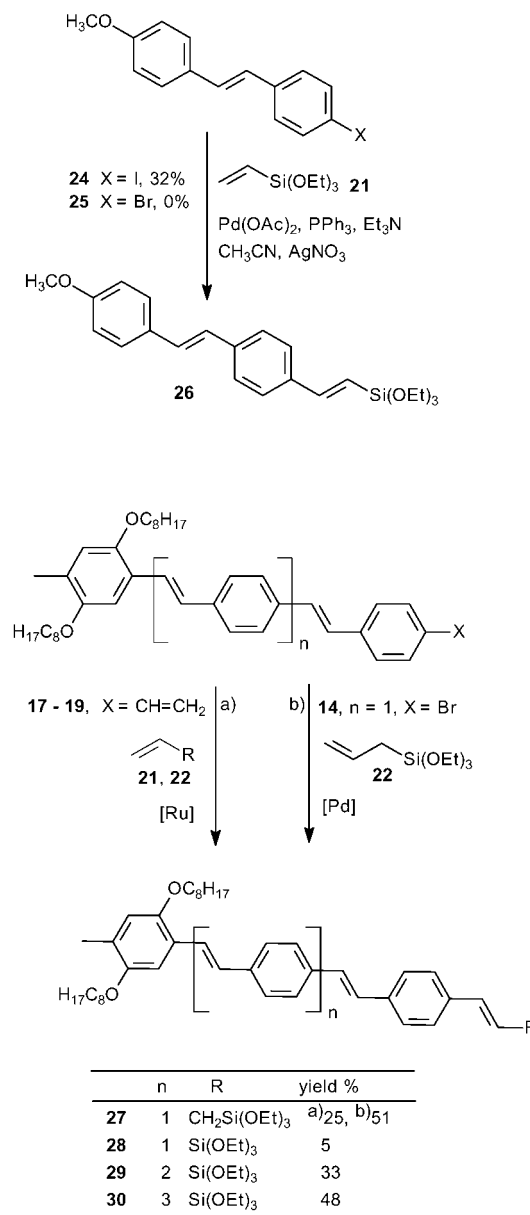
de Meijere;^[17] and a series of styrenes from substituted bromobenzenes and ethene was obtained by Heitz et al.^[18] Whereas electron-withdrawing groups activate the bromine atom in the Heck reaction,^[19] the reactivity of donor-substituted bromobenzenes is only poor. The rather low yield of 41% of **17** in the palladium-catalyzed vinylation of bromo-distyrylbenzene (DSB) **14** required vigorous conditions (140 °C, 5 d). When the Heck reaction of iodo-OPVs **15** and **16** was performed under a pressure of 30 bar ethene, the vinyl-substituted oligo(phenylenevinylene)s **18** and **19** were produced in good to excellent yields (73% and 91%, respectively) and no traces of the two-fold coupling products could be detected. A bypass to avoid the use of iodoarenes is opened when the vinylation step is performed on the phosphonate. More forcing conditions than used for the previous reactions had to be applied in the synthesis of 4-vinylbenzylphosphonate **20** (140 °C, 70 bar ethene) from **12**, which has already been prepared by Michaelis–Becker reaction of 4-chloromethyl styrene.^[20] The yields of vinyl-OPVs obtained via Horner olefination with **20** (**17**: 89%, **19**: 75%) are comparable to the two-step procedure with **13** and vinylation with ethene.

The Connection of Oligo(phenylenevinylene)s with Alkoxysilanes

Hallberg^[21] investigated the Heck reaction of iodoarenes with vinylsilanes, the arylethenylsilanes are produced in moderate yields provided that equimolar amounts of silver nitrate are present to immobilize the iodide. These conditions are also suitable for the conversion of iodo-substituted stilbenes like **24**. Triethoxyvinylsilane **21** could be coupled with **24**^[22] to yield **26** (32%) in the presence of AgNO₃, with **26** not being detected in an analogous reaction with the bromostilbene **25**.^[23] The Hallberg conditions are unsatisfactory in three aspects: moderate yield, the limitation to iodine-substituted OPVs, and, in particular, the need for equimolar amounts of silver salts.

Recently, the cross-metathesis of different alkenes with allylsilanes^[24] and alkoxyvinylsilanes^[25] with Schrock's^[26] molybdenum or Grubbs'^[27] ruthenium catalyst **23** were reported. These results and the now readily available vinyl-substituted OPVs (**17–19**) prompted us to study the synthesis of alkoxysilyl-substituted oligomers via cross-metathesis using Grubbs catalyst **23** [Cl₂(PCy₃)₂Ru=CHPh]. The reaction of the vinyl-distyrylbenzene **17** with triethoxyvinylsilane **22** was rather disappointing: only small amounts of **17** were consumed to yield **28** (5%) and the reaction could not be completed by removal of ethene in a gentle flow of dry and oxygen-free nitrogen, elevated

temperature, sonication, or additional catalyst. The yield increased significantly when the conjugated system was extended. From the homologous compound **18** the triethoxysilyl-OPV **30** was obtained in 33% yield and the yield increased to 48% in the transformation of **19** to **30**. No products derived from homocoupling in the metathesis reaction were observed.



Scheme 3. Synthesis of alkoxysilyl-substituted OPVs; a) cross-metathesis: [Cl₂(PCy₃)₂Ru=CHPh], benzene, ambient temperature; b) Pd(OAc)₂, P(*o*-tol)₃, Et₃N, DMF, 100 °C.

The homologization from **17** to **18** and **19** reduces the influence of the 2,5-dialkoxy-substituted terminal benzene ring on the electronic properties of the vinyl group on the opposite side of the conjugated system. In the same sequence, the yield improved consider-

ably. On the other hand, altering the electronic properties of the silicon-bound vinyl group by replacing an ethoxy group for methyl on the silane reduced the conversion dramatically, as it was observed with styrene;^[25] with diethoxymethylvinylsilane not even traces of the desired product were detected. Electronic decoupling of the vinyl group from the silane, as in the more flexible allylsilane **22**, increases the reactivity of the vinyl group in both metal-catalyzed reactions: a yield of 51% of the DSB-silane **27** was obtained via Heck reaction of the bromide **14** compared to 41% of **17** obtained by the reaction of **14** with ethene. The cross-metathesis of **17** too, benefited from the additional methylene group: the yield increased from 5% with silane **21** to 25% in the conversion of silane **22**.

In the isolated (by chromatography) compounds, the stereochemistry of the connecting 1,2-vinylene unit, generated via Heck reactions (**26**, **27**) or cross-metathesis (**27–30**) was found to be exclusively *E*, indicated by large vicinal coupling constants of 19–21 Hz. The vinyl-substituted OPVs (**17**, **18**, limited for **19**), as well as **26–30** with siloxane moieties are well soluble in common solvents, the intensively yellow compounds and their solutions being strongly fluorescent.

Conclusion

A stepwise synthesis of a series of vinyl-substituted oligo(phenylenevinylene)s **17–19** with solubilizing alkoxy side chains on the opposite side of the conjugated system is described. The vinyl group was introduced via palladium-catalyzed reaction of iodo-substituted OPVs with ethene or in a one-step procedure with vinylbenzyl phosphonate **20**. Access to OPVs with alkoxy-silane-substituted vinyl groups is possible by Heck reactions (**26**, **27**) and via cross metathesis of vinyl-substituted OPVs with triethoxyvinyl- and allylsilane (**27–30**). These highly fluorescent molecules, OPV chromophores rigidly connected to hydrolyzable alkoxy-silane moieties, are curable compounds that are interesting for electrical and optical applications.

Experimental Section

General Methods

IR spectra: in KBr, Beckman Acculab 4. NMR spectra: in CDCl₃, Bruker AC 200 and AM 400. Mass spectra: 70 eV, Varian MAT 711 (EI), MAT 95 (FD). Chemical shifts are reported in ppm and referenced to the solvent as internal standard. The elemental analyses were performed in the microanalytical laboratory of the Chemical Institute of the Johannes Gutenberg-Universität, Mainz, Germany, melting points: not corrected. Eluent mixtures are v/v. Chemicals were used as received, solvents dried according to standard proce-

dures and distilled. DMF was stirred with CaH₂ for 5 h at 120 °C, distilled in vacuum and stored over activated molecular sieves.

Diether 2

Methylhydroquinone **1** (124 g, 1.0 mol), K₂CO₃ (346 g, 2.5 mol), KI (5 g, 0.03 mol) and Aliquat 336 (5 g) were added to a solution of 2-ethylbromohexane (482 g, 2.5 mol) in dioxane (800 mL). The mixture was purged with nitrogen and heated and stirred under N₂ for 8 days. The mixture was cooled, the liquid phase transferred into a separatory funnel and the solids dissolved with water and added to the organic solution. Petroleum ether (500 mL) was added, the aqueous layer was separated and extracted with petroleum ether (2×200 mL). The combined organic layers were washed with water (3×250 mL), dried with CaCl₂, the solvents were evaporated and the product distilled in vacuum; bp 156–158 °C (0.04 mbar); yield: 254 g (73%), yellowish oil; IR (neat): $\tilde{\nu}$ = 3010, 2950, 2920, 2840, 1580, 1485, 1455, 1370, 1270, 1210, 1160, 1120, 1045, 860, 785 cm⁻¹; ¹H NMR (CDCl₃): δ = 0.87 (m, 12 H, CH₃), 1.20–1.55 (m, 16 H, CH₂), 1.70 (m, 2 H, β -CH), 2.18 (s, 3 H, CH₃), 5.77 (m, 4 H, OCH₂), 7.70 (m, 3 H, 3-H, 5-H, 6-H); ¹³C NMR (CDCl₃): δ = 11.1, 11.3, 14.1 (2 C), 16.4 (CH₃), 23.1 (2 C), 23.9, 24.1, 29.1, 29.2, 30.6, 30.8 (CH₂), 39.5, 39.7 (CH), 71.0, 71.1 (OCH₂), 111.5, 111.8 (C-5, C-6), 117.7 (C-3), 128.0 (C-2), 151.6, 153.1 (C-O); MS (EI): *m/z* = 348 (79) [M⁺], 256 (46) [M⁺ – C₈H₁₆], 124 (100) [M⁺ – 2 C₈H₁₆]; anal.: calcd. for C₂₅H₄₀O₂ (348.563): C 79.25%, H 11.57%; found: C 79.01%, H 11.23%.

Chloromethylbenzene 3

Paraformaldehyde (7.5 g, 0.25 mol) was added to a solution of diether **2** (70.0 g, 0.2 mol) and concentrated hydrochloric acid (50 mL) in dioxane (300 mL). The mixture was cooled with iced water and saturated with gaseous HCl. The saturated solution was slowly heated to a gentle reflux and kept at this temperature for 2 h. The cooled solution was diluted with water (1.5 L) and extracted with petroleum ether (4×200 mL). The combined organic layers were washed with water until the washings were neutral and dried with CaCl₂. The solvents were stripped off and the residue purified by chromatography on silica gel using petroleum ether (40–70) as an eluent; yield: 56.1 g (71%), colorless oil; IR (neat): $\tilde{\nu}$ = 3030, 2960, 2920, 2870, 1508, 1460, 1408, 1370, 1210, 1040, 860 cm⁻¹; ¹H NMR (CDCl₃): δ = 0.93 (m, 12 H, CH₃), 1.15–1.60 (m, 16 H, CH₂), 1.70 (m, 2 H, β -CH), 2.26 (s, 6 H, CH₃), 3.82 (2×d, 4 H, OCH₂), 4.62 (s, 2 H, CH₂Cl), 6.70, 6.81 (2×s, 2×1 H, 3-H, 6-H); ¹³C NMR (CDCl₃): δ = 11.2, 14.1, 16.3 (CH₃), 23.1, 24.0, 24.1, 29.1, 30.6, 30.7, 39.1, (CH, CH₂), 41.9 (CH₂Cl), 71.0, 71.2 (OCH₂), 113.4, 115.9 (C-3, C-6), 123.5, 128.7 (C-1, C-4), 150.6, 151.1 (C-2, C-5); MS (EI): *m/z* = 396 (61) Cl-pattern [M⁺], 284 (28) Cl-pattern [M⁺ – C₈H₁₆], 172 (100) Cl-pattern [M⁺ – 2 C₈H₁₆]; anal.: calcd. for C₂₄H₄₁ClO₂ (397.041): C 72.60%, H 10.41%; found: C 72.94%, H 10.68%.

Phosphonate 4

A mixture of triethyl phosphite (33 g, 0.2 mol) and benzyl chloride **3** (40 g, 0.1 mol) was stirred and heated in a round-

bottom flask equipped with a reflux condenser and bubble counter until the evolution of chloroethane started (ca. 160 °C). This temperature was held until the evolution of gas ceased and then raised to 180 °C for 30 min. Residual triethyl phosphite was removed by vacuum distillation and the product purified by chromatography on silica gel. Elution was performed with petroleum ether/ethyl acetate (10/1) first to separate some impurities and the product was eluted with ethyl acetate; yield: 47 g (94%), nearly colorless oil; IR (neat): $\tilde{\nu}$ = 2960, 2820, 2860, 1504, 1455, 1405, 1245, 1210, 1030, 960, 880 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.79–0.99 (m, 12 H, CH_3), 1.15–1.65 (m, 22 H, CH_2 , CH_3), 1.68 (m, 2 H, β -CH), 2.16 (s, 3 H, CH_3), 3.20 (d, J = 22.5 Hz, 2 H, CH_2P), 3.75 (d, J = 6.2 Hz, 4 H, OCH_2), 4.00 (qui, J = 7.5 Hz, 4 H, POCH_2), 6.66 (s, 1 H), 6.85 (s, 1 H); ^{13}C NMR (CDCl_3): δ = 11.2, 11.2, 14.0, 16.3 (CH_3), 16.4 (d, J = 6.4 Hz, CH_3), 23.1, 24.0, 24.1, 29.1, 30.6, 30.7 (CH_2), 25.0 (d, J = 139.0 Hz, $\text{CH}_2\text{-P}$), 39.7, 39.7 (β -CH), 61.8 (d, J = 7.4 Hz, OCH_2), 71.0, 71.3 (OCH_2), 114.3 (d, J = 4.8 Hz), 114.7 (d, J = 3.2 Hz) (C-3, C-6), 117.5 (d, J = 9.6 Hz), 126.2 (d, J = 4.1 Hz) (C-1, C-4), 150.4 (d, J = 7.9 Hz, C-2), 151.2 (C-5); MS (FD): m/z = 998 (7) [M_2^+], 499 (100) [M^+]; anal.: calcd. for $\text{C}_{28}\text{H}_{51}\text{O}_5\text{P}$ (498.675): C 67.44%, H 10.31%; found: C 67.62%, H 10.20%.

Aldehyde 6

KOtBu (11.2 g, 0.1 mol) was added to a nitrogen-purged solution of phosphonate 4 (25.0 g, 0.05 mol), 4-(diethoxymethyl)benzaldehyde 5 (10.5 g, 0.05 mol) and 18-crown-6 (250 mg) in anhydrous THF (150 mL). The mixture was stirred at room temperature for 4 h, 2 N hydrochloric acid was added until pH = 1 and the mixture was stirred for further 3 h. Water (250 mL) was added and the product was extracted with dichloromethane (3×70 mL). The combined organic solutions were washed with water and brine and dried with MgSO_4 . Purification by chromatography on silica gel with toluene as an eluent; yield: 19.5 g (82%), yellow oil; IR (neat): $\tilde{\nu}$ = 3030, 2950, 2910, 2860, 2725, 1690, 1590, 1501, 1458, 1405, 1375, 1301, 1202, 1162, 1035, 968, 856, 815 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.9 (m, 12 H, CH_3), 1.2–1.6 (m, 16 H, CH_2), 1.83 (m, 2 H, β -CH), 2.23 (s, 3 H, CH_3), 3.88 (d, J = 6.2 Hz, 4 H, OCH_2), 6.72 (s, 1 H), 7.01 (s, 1 H), 7.11 (d, J = 16.0 Hz, 1 H), 7.62 (d, J = 16.0 Hz, 1 H), 7.62 (d, J = 8.1 Hz, 2 H), 7.84 (d, J = 7.9 Hz, 2 H), 9.97 (s, 1 H, CHO); ^{13}C NMR (CDCl_3): δ = 11.3, 14.1, 16.6 (CH_3), 23.1, 24.1, 24.2, 29.2, 29.2, 30.8, 30.9 (CH_2), 39.7 (β -CH), 71.0, 71.9 (OCH_2), 109.0, 115.8 (C-3, C-6, Ph'), 126.2, 127.6 (CH, vin), 126.6, 130.2 (C-2, C-3, C-5, C-6, ph), 123.4, 129.1, 134.9, 144.5 (C_q), 151.1, 151.6 (C-O), 191.6 (CHO); MS (FD): m/z = 958 (49) [M_2^+], 479 (100) [M^+]; anal.: calcd. for $\text{C}_{32}\text{H}_{46}\text{O}_5$ (478.706): C 80.29%, H 9.69%; found: C 79.92%, H 9.88%.

Aldehyde 7

DDQ (2.2 g, 0.01 mol) was added to a solution of alcohol 10 (5.8 g, 0.01 mol) in dioxane (15 mL). The mixture was stirred for 18 h, filtered and concentrated. The residue was purified by chromatography on silica gel with toluene as an eluent; yield: 3.6 g (65%), greenish, yellow oil; IR (neat): $\tilde{\nu}$ = 2950, 2905, 2850, 1688, 1590, 1505, 1455, 1408, 1204, 1165, 1038, 968, 852, 822 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.90 (m, 12 H, CH_3), 1.20–1.60 (m, 16 H, CH_2), 1.73 (qui, 2 H,

β -CH), 2.23 (s, 3 H, CH_3), 3.87 (m, 4 H, OCH_2), 6.73 (s, 1 H, 3-H, Ph'), 7.03 (s, 1 H, 6-H, Ph'), 7.06 (d, J = 16.6 Hz, 1 H, vin), 7.12 (d, J = 16.1 Hz, 1 H, vin'), 7.26 (d, J = 16.3 Hz, 1 H, vin'), 7.51 (d, J = 16.6 Hz, 1 H, vin), 7.51 (s, 4 H, Ph'), 7.64 (d, J = 8.3 Hz, 2 H, 3-H, 5-H, Ph), 7.86 (d, J = 8.3 Hz, 2 H, 2-H, 6-H, Ph), 9.98 (s, 1 H, CHO); ^{13}C NMR (CDCl_3): δ = 11.3, 14.1, 16.5 (CH_3 , superimposed), 23.1 (2 C), 24.1, 24.2, 29.2, 29.2, 30.8, 30.9, 39.8, 39.8 (CH, CH_2), 71.0, 72.0 (OCH_2), 108.8, 115.8 (C-3, C-6, Ph), 126.7, 126.8, 127.3, 130.3 (CH, Ph, Ph'), 124.2, 124.5, 126.9, 128.2, 132.0, 135.2, 135.3, 138.7, 143.6 (CH vin, C_q , superimposed), 150.8, 151.6 (C-O), 191.6 (C-O); MS (FD): m/z = 581 (100) [M^+]; anal.: calcd. for $\text{C}_{40}\text{H}_{52}\text{O}_5$ (580.839): C 82.71%, H 9.02%; found: C 82.46%, H 8.83%.

Aldehyde 8

KOtBu (1.5 g, 13.0 mmol) was added to a nitrogen-purged solution of phosphonate 11 (2.2 g, 6.5 mmol), aldehyde 7 (3.8 g, 6.5 mmol) and 18-crown-6 (50 mg) in anhydrous THF (30 mL). The mixture was stirred at room temperature for 4 h, 2 N hydrochloric acid was added until pH = 1 and the mixture was stirred for further 2 h. Water (50 mL) was added and the product was extracted with dichloromethane (3×30 mL). The combined organic solutions were washed with water and brine and dried with MgSO_4 . Purification by chromatography on silica gel with toluene/petroleum ether (4/1); yield: 5.9 g (92%), yellow solid, mp 97 °C; IR (KBr): $\tilde{\nu}$ = 3012, 2950, 2910, 2850, 1689, 1580, 1503, 1457, 1405, 1204, 1164, 1037, 965, 852, 830, 788 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.85–1.00 (m, 12 H, CH_3), 1.17–1.64 (m, 16 H, CH_2), 1.78 (m, 2 H, β -CH), 2.23 (s, 3 H, CH_3), 3.87 (2 $\times$ d, 4 H, OCH_2), 6.71 (s, 1 H), 7.02 (s, 1 H), 7.06–7.22 (m, 4 H), 7.42–7.58 (m, 10 H), 7.64 (d, J = 8.0 Hz, 2 H), 7.88 (d, J = 8.0 Hz, 2 H), 9.98 (s, 1 H, CHO); ^{13}C NMR (CDCl_3): δ = 11.3, 14.1 (CH_3), 16.5 (CH_3), 23.1, 24.1, 29.2, 30.8, 30.9 (CH_2), 39.8 (CH), 71.0, 72.0 (OCH_2), 108.8, 115.8 (CH), 124.0, 124.3, 126.7, 126.9, 127.1, 127.5, 127.6, 128.0, 128.9, 130.3, 131.8, 135.3, 135.8, 136.0, 137.8, 137.9, 143.5 (CH, C_q , superimposed), 150.7, 151.6 (C-O), 191.6 (CHO); MS (FD): m/z = 683 (100) [M^+], 342 (2) [M^{2+}]; anal.: calcd. for $\text{C}_{48}\text{H}_{58}\text{O}_5$ (683.972): C 84.41%, H 8.56%; C 84.22%, H 8.52%.

Benzylic Alcohol 10

KOtBu (2.0 g, 18 mmol) was added to a nitrogen-purged solution of 4-methoxycarbonylbenzyl phosphonate 9^[15] (2.6 g, 9 mmol), aldehyde 6 (3.4 g, 9 mmol) and 18-crown-6 (80 mg) in anhydrous THF (50 mL). The mixture was stirred at room temperature for 4 h, and diluted with water (150 mL). The product was extracted with toluene (3×60 mL) and the combined organic layers were dried with MgSO_4 . The solvent was evaporated, the residue dissolved in anhydrous ether (60 mL) and added dropwise to a stirred and refluxing mixture of LiAlH_4 (0.6 g, 15.8 mmol) in anhydrous ether (20 mL). Heating and stirring were continued for 6 h, the mixture was cooled in ice and residual hydride was destroyed and dissolved with 2 N sulfuric acid. The organic layer was separated, the aqueous layer extracted with dichloromethane (2×30 mL) and the combined organic solutions were washed with brine until neutral, dried with Na_2SO_4 and concentrated. Purification by chromatography

on silica gel with petroleum ether/ether (6/1); yield: 3.9 g (74%), yellow, soft wax; IR (KBr): $\tilde{\nu}$ = 3490, 3020, 2960, 2920, 2860, 1510, 1492, 1460, 1408, 1380, 1200, 1040, 1012, 972, 840 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.95 (m, 12 H, CH_3), 1.20–1.65 (m, 16 H, CH_2), 1.68 (s, 1 H, OH), 1.77 (m, 2 H, β -CH), 2.24 (s, 3 H, CH_3), 3.88 (2 $\times$ d, 4 H, OCH_2), 4.69 (s, 2 H, CH_2Cl), 6.73 (s, 1 H, 3-H Ph'''), 7.08 (m, 4 H), 7.34 (d, 2 H), 7.49 (m, 8 H); ^{13}C NMR (CDCl_3): δ = 11.3, 14.1 (CH_3), 16.5, 23.1, 24.2, 24.2, 29.3, 30.8, 30.9, 39.8 (CH, CH_2 , CH_3), 65.2 (CH_2OH), 71.0, 72.0 (OCH_2), 108.8, 115.9 (C-3, C-6 Ph'''), 123.9, 124.4, 126.7 (4 C), 126.8 (2 C), 127.2, 127.4 (2 C), 127.8, 127.9, 128.5, 136.1, 137.0, 140.2 (CH, C_q), 150.7, 151.6 (C-2, C-5 Ph'''); MS (FD): m/z = 583 (100) [M^+]; anal.: calcd. for $\text{C}_{40}\text{H}_{54}\text{O}_5$ (582.855): C 82.43%, H 9.34%; found: C 82.35%, H 9.29%.

Phosphonate 11

A solution of 4-(diethoxymethyl)benzaldehyde **5** (36.5 g, 0.176 mol) in anhydrous ether (100 mL) was added dropwise during 30 min to a stirred, boiling mixture of LiAlH_4 (2.3 g, 0.060 mol) and ether (400 mL). Refluxing and stirring were continued for further 3.5 h, then a solution of NaOH (6.0 g, 0.15 mol) in water (12 mL) and methanol (13 mL) was added very cautiously dropwise to the stirred and boiling solution. After 30 min a saturated solution of NaCl in water was dropped into the still stirred and refluxing mixture until the organic layer separated from the inorganic compounds, stirring and heating were stopped in this moment. The mixture was cooled to room temperature, the organic layer was separated and the residual slurry was washed with ether (150 mL). The combined organic layers were thoroughly dried with MgSO_4 and the solvent was evaporated to yield 4-(diethoxymethyl)benzylic alcohol quantitatively. The alcohol (30 g, 0.140 mol) was added to a solution of triphenylphosphine (37.5 g, 0.14 mol) and *N*-ethyldicyclohexylamine in anhydrous CCl_4 (750 mL) and heated to reflux for 46 h. The cooled mixture was washed with water (400 mL) and a saturated solution of NaHCO_3 (2 $\times$ 200 mL) and dried with MgSO_4 . CCl_4 (700 mL) was distilled off and the residue was filtered, the precipitated triphenylphosphine oxide was washed thoroughly with petroleum ether. The combined organic solutions were concentrated and dried under vacuum to yield a dark brown oil. A sample of this oil (2.5 g) was mixed with triethyl phosphite (1.84 g, 11.1 mmol) and heated to 160 °C until the evolution of chloroethane had stopped. Purification by chromatography on basic alumina with ethyl acetate first, followed by silica gel using toluene/ethyl acetate (1/1) as an eluent; yield: 20% (over 3 steps), yellow oil; IR (neat): $\tilde{\nu}$ = 2960, 2880, 1600, 1510, 1445, 1380, 1365, 1240, 1150, 1040, 1020, 720, 690 cm^{-1} ; ^1H NMR (CDCl_3): δ = 1.16 (m, 12 H, CH_3), 3.08 (d, J = 21.8 Hz, 2 H, $\text{CH}_2\text{-P}$), 3.50 (m, 4 H, OCH_2), 3.95 (m, 4 H, OCH_2), 5.43 (s, 1 H, O-CH-O), 7.22 (d, 2 H), 7.34 (d, 2 H); ^{13}C NMR (CDCl_3): δ = 15.2 (CH_3), 16.3 (d, J = 6.1 Hz, CH_3), 33.5 (d, J = 136.8 Hz, $\text{CH}_2\text{-P}$), 60.9 (CH_2O), 62.1 (d, 6.4 Hz, OCH_2), 101.2 (O-C-O), 126.8 (d, J = 3.5 Hz, CH), 129.6 (d, J = 7.2 Hz, CH), 131.6 (d, J = 9.6 Hz, C-1), 137.8 (C_q); MS (FD): m/z = 331 (100) [M^+]; anal.: calcd. for $\text{C}_{16}\text{H}_{27}\text{O}_5\text{P}$ (330.356): C 58.17%, H 8.24%; found: C 57.91%, H 8.29%.

Iodophosphonate 12

A solution of 4-iodobenzyl bromide (23.8 g, 0.08 mol) in triethyl phosphite (33.2 g, 0.2 mol) was heated while stirring in a round-bottom flask equipped with a reflux condenser. The condenser was thermostated at 60 °C and connected to a distillation bridge. The reaction started at 140 °C and heating was continued until the evolution of bromoethane ceased. The temperature was raised to 160 °C for 30 min and residual triethyl phosphite was removed by vacuum distillation;^[16] yield: 27.7 g (98%), yellowish oil; IR (neat): $\tilde{\nu}$ = 2970, 2890, 1578, 1390, 1240, 1050, 1025, 960 cm^{-1} ; ^1H NMR (CDCl_3): δ = 1.25 (t, 6 H, CH_3), 3.05 (d, J = 21.5 Hz, 2 H, CH_2P), 4.00 (m, 4 H, OCH_2), 7.05 (dd, J = 8.2 Hz, J = 2.4 Hz, 2 H, 2-H, 6-H), 7.60 (d, J = 7.9 Hz, 2 H, 3-H, 5-H); ^{13}C NMR (CDCl_3): δ = 16.4 (d, J = 5.5 Hz, CH_3), 33.5 (d, J = 138.0 Hz, CH_2P), 62.2 (d, J = 6.0 Hz, OCH_2), 92.3 (C-4), 131.3 (d, J = 8.5 Hz, C-1), 131.8, 137.5 (C-2, C-3, C-5, C-6); MS (EI): m/z = 354 (54) [M^+], 326 (18) [$\text{M}^+ - \text{C}_2\text{H}_4$], 227 (29) [$\text{M}^+ - \text{I}$]; anal.: calcd.: for $\text{C}_{11}\text{H}_{16}\text{IO}_3\text{P}$ (354.121): C 37.31%, H 4.55%; found: C 37.69%, H 4.73%.

BromoOPV 14

KO^tBu (448 mg, 4 mmol) was added to a solution of aldehyde **6** (960 mg, 2 mmol) and phosphonate **12** (622 mg, 2 mmol) and 18-crown-6 (40 mg) in anhydrous THF (30 mL). The mixture was stirred at ambient temperature under nitrogen for 3.5 h, water (50 mL) was added and the product was isolated by extraction with chloroform (3 $\times$ 30 mL), washing of the pooled organic solutions with water, drying with MgSO_4 , evaporation of the solvent and chromatography on silica gel with petroleum ether/ethyl acetate as an eluent; yield: 1.1 g (87%), yellow solid, mp 65–67 °C; IR (KBr): $\tilde{\nu}$ = 2950, 2910, 2850, 1508, 1458, 1410, 1375, 1205, 1073, 1040, 1008, 958, 854, 822 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.85–1.00 (m, 12 H, CH_3), 1.24–1.67 (m, 16 H, CH_2), 1.77 (m, 2 H, β -CH), 2.23 (s, 3 H, CH_3), 3.88 (2 $\times$ d, 4 H, OCH_2), 7.73 (s, 1 H, 5-H, Ph'), 7.01–7.12 (m, 4 H), 7.30–7.52 (m, 9 H); ^{13}C NMR (CDCl_3): δ = 11.3, 14.1, 16.5 (CH_3), 23.1 (2 C), 24.1, 24.2, 29.2 (2 C), 30.7, 30.9, 39.7, 39.8 (CH, CH_2), 70.9, 71.9 (OCH_2), 108.7, 115.8, 121.2, 124.0, 124.2, 127.9, 135.7, 136.4, 138.0 (CH, C_q), 126.7, 126.9, 129.1, 131.8 (CH, Ph, Ph'), 150.7, 151.6 (C-O); MS (FD): m/z = 631 (100) Br-pattern [M^+]; anal.: calcd. for $\text{C}_{39}\text{H}_{51}\text{BrO}_2$ (631.725): C 74.15%, H 8.14%; found: C 74.17%, H 8.01%.

IodoOPV 15

Preparation from **7** (700 mg, 1.12 mmol) and **13** (396 mg, 1.12 mmol) according to the procedure described for **14**. Purification by recrystallization from chloroform/ethanol; yield: 54%, yellow solid, mp 145 °C; IR (KBr): $\tilde{\nu}$ = 2990, 2950, 2890, 1640, 1500, 1475, 1435, 1350, 1228, 1090, 1065, 1036, 990, 960, 875, 829 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.80–1.00 (m, 12 H, CH_3), 1.20–1.60 (m, 16 H, CH_2), 1.80 (m, 2 H, β -CH), 6.71 (s, 1 H, Ph'''), 2.23 (s, 3 H, CH_3), 3.88 (2 $\times$ d, 4 H, OCH_2), 6.95–7.15 (m, 6 H), 7.20–7.26 (m, 2 H), 7.42–7.53 (m, 9 H), 7.68 (d, J = 7.8 Hz, 2 H); ^{13}C NMR (CDCl_3): δ = 11.3, 14.1, 16.5 (CH_3), 23.1 (2 C), 24.1, 24.2, 29.2, 29.2, 30.8, 30.9 (CH_2), 39.7, 39.8 (β -CH), 71.0, 72.0 (OCH_2), 92.7 (C-I), 108.8, 115.9 (CH), 126.7 (2 C), 126.9 (2 $\times$ 2 C), 127.0 (2 C), 128.2 (2 C),

137.8 (2 C) (CH), 123.9, 124.3, 127.1, 127.3, 127.7, 127.9, 128.6, 129.1, 136.1, 136.2, 136.9, 137.2, 137.8 (CH vin, C_qar), 151.0, 152.9 (C–O); MS (FD): m/z = 781 (100) [M⁺]; anal.: calcd. for C₄₇H₅₇IO₂ (780.859): C 72.29%, H 7.36%; found: C 72.25%, H 7.51%.

IodoOPV 16

Preparation from aldehyde **8** (480 mg, 0.7 mmol) and phosphonate **13** (290 mg, 0.8 mmol) according to the procedure described for **14**. Purification by recrystallization from toluene; yield: 620 mg (89%), yellow solid, mp 270 °C; IR (KBr): $\tilde{\nu}$ = 3000, 2940, 2900, 2840, 1570, 1500, 1445, 1399, 1365, 1190, 1100, 1030, 958, 825 cm⁻¹; ¹H NMR (CDCl₃): δ = 0.82–1.00 (m, 12 H, CH₃), 1.20–1.62 (m, 16 H, CH₂), 1.80 (m, 2 H, β -CH₂), 2.23 (s, 3 H, CH₃), 3.88 (m, 4 H, OCH₂), 6.73 (s, 1 H), 7.00–7.15 (m, 8 H), 7.20–7.25 (m, 2 H), 7.42–7.58 (m, 13 H), 7.68 (d, J = 7.0 Hz, 2 H); MS (FD): m/z = 883 (100) [M⁺], 442 (14) [M²⁺]; anal.: calcd. for C₅₅H₆₅IO₂ (882.992): C 74.81%, H 7.19%; found: C 74.46%, H 7.28%.

VinylOPV 17

Preparation from **6** and **20** according to the procedure described for **14** in 89% yield. Via Heck reaction from **14** and ethene according to the procedure described for **18** using the two-fold amount of catalyst, and stirring for 5 d at 140 °C gave **17** in 41% yield. Purification by chromatography on silica gel using petroleum ether/ethyl acetate (10/1) as an eluent. Viscous yellow oil; IR (neat): $\tilde{\nu}$ = 2900, 2820, 1485, 1440, 1390, 1185, 1020, 950, 887, 840, 815 cm⁻¹; ¹H NMR (CDCl₃): δ = 0.80–0.98 (m, 12 H, CH₃), 1.23–1.64 (m, 16 H, CH₂), 1.73 (quin, 2 H, β -CH), 2.24 (s, 3 H, CH₃), 3.84 (2×d, 4 H, OCH₂), 5.23 (d, J = 11.2 Hz, 1 H, vin), 5.76 (d, J = 16.8 Hz, 1 H, vin), 6.70 (dd, J = 11.2 Hz, J = 17.0 Hz, 1 H, vin), 6.72 (s, 1 H, 3-H, Ph^{''}), 7.03 (s, 1 H, 6-H, Ph^{''}), 7.06 (d, J = 16.0 Hz, 1 H, vin), 7.10 (s, 2 H, vin), 7.36–7.53 (m, 9 H, Ph, Ph', vin); ¹³C NMR (CDCl₃): δ = 11.2, 14.0, 16.3 (CH₃), 23.0 (2 C), 24.1, 24.2, 29.1, 29.2, 30.7, 30.9 (CH₂), 39.7, 39.8 (CH), 71.0, 72.0 (OCH₂), 108.9, 113.5, 115.8 (C-3, C-6, Ph^{''}, CH₂ vin), 126.5 (2 C), 126.5 (2×2 C), 126.7 (2 C) (CH, Ph, Ph'), 123.9, 124.4, 127.1, 127.8, 127.8, 128.3, 136.1, 136.4, 137.0, 137.7 (CH, C_q), 150.7, 151.6 (C–O); MS (FD): m/z = 579 (100) [M⁺]; anal.: calcd. for C₄₁H₅₄O₂ (578.866): C 85.07%, H 9.40%; found: C 85.03%, H 9.37%.

VinylOPV 18

Pd(OAc)₂ (4.4 mg, 20 μ mol) and tri-*o*-tolylphosphine (12.0 mg, 40 μ mol) were added to a solution of OPV **15** (390 mg, 0.5 mmol) in a mixture of anhydrous DMF (30 mL) and triethylamine (0.5 g, 5 mmol). The mixture was placed in an autoclave (100 mL), purged with nitrogen, ethene was added (pressure 30 bar) and while stirring the temperature was brought to 100 °C for 8 h. The cooled mixture was diluted with water (100 mL), the product was extracted with chloroform (5×30 mL). The combined organic solutions were washed with water (2×100 mL) and brine (50 mL). After drying with MgSO₄, the solvent was evaporated and the residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate (20/1) as an eluent; yield: 250 mg (73%), yellow solid, mp 126 °C; IR (CDCl₃):

$\tilde{\nu}$ = 3008, 2960, 2920, 1580, 1505, 1418, 1215 cm⁻¹; ¹H NMR (CDCl₃): δ = 0.85–1.05 (m, 12 H, CH₃), 1.18–1.63 (m, 16 H, CH₂), 1.76 (quin, J = 5.5 Hz, 2 H, β -CH), 2.25 (s, 3 H, CH₃), 3.88 (2×d, 4 H, OCH₂), 5.25 (d, J = 11.2 Hz, 1 H, vin), 5.77 (d, J = 16.4 Hz, 1 H, vin), 6.71 (dd, J = 16.4 Hz, J = 11.2 Hz, 1 H, vin), 6.74 (s, 1 H, Ph^{'''}), 7.04 (s, 1 H, Ph^{'''}), 7.06–7.15 (m, 5 H, vin, Ar), 7.32–7.55 (m, 13 H); ¹³C NMR (CDCl₃): δ = 11.4, 14.2, 16.5 (CH₃), 21.0, 21.4, 24.2, 24.3, 29.2, 29.3, 30.8, 31.0 (CH₂), 39.8, 39.8 (β -CH), 71.0, 72.0 (OCH₂), 108.8, 113.8, 115.9 (C-3, C-6, Ph^{'''}, CH₂ vin), 126.2 (2 C), 126.9 (2 C), 128.7 (2 C), 130.6 (2 C), 130.2 (2 C), 133.1 (2 C) (CH, Ph, Ph', Ph^{'''}), 123.9, 124.4, 126.6, 126.7, 127.2, 127.8, 127.9, 128.3, 128.4, 134.4, 134.6, 136.3, 136.5, 137.0, 137.8 (CH, C_q), 150.7, 151.6 (C–O); MS (FD): m/z = 681 (100) [M⁺]; anal.: calcd. for C₄₉H₆₀O₂ (680.999): C 86.42%, H 8.88%; found: C 86.78%, H 8.55%.

VinylOPV 19

Synthesis via Heck reaction with ethene according to the procedure described for **18** in 91% yield, and also via Horner olefination of **8** with **20** according to the procedure described for **17** in 73% yield. Purification by chromatography on silica gel using petroleum ether/ethyl acetate (10/1) as an eluent; yellow solid, mp >190 °C; IR (KBr): $\tilde{\nu}$ = 3010, 2950, 2910, 2850, 1505, 1455, 1402, 1370, 1200, 1035, 965, 910, 840 cm⁻¹; ¹H NMR (CDCl₃): δ = 0.85–0.99 (m, 12 H, CH₃), 1.45–1.68 (m, 16 H, CH₂), 1.73 (m, 2 H, β -CH), 2.23 (s, 3 H, CH₃), 3.86 (t, J = 6.2 Hz, 4 H, OCH₂), 5.24 (d, J = 10.8 Hz, 1 H, vin), 5.76 (d, J = 18.2 Hz, 1 H, vin), 6.70 (dd, J = 10.8 Hz, J = 18.4 Hz, 1 H, vin), 6.72 (s, 1 H, Ph), 7.02 (s, 1 H, Ph), 7.06 (d, J = 16.4 Hz, 1 H, vin), 7.10 (m, 6 H), 7.39 (m, 2 H), 7.46–7.52 (m, 15 H); ¹³C NMR (CDCl₃): δ = 11.2, 14.0 (CH₃), 16.4 (CH₃), 23.0, 24.2, 24.2, 29.2, 29.2, 30.8, 30.9, (CH₂), 39.8 (CH), 71.1, 72.1 (OCH₂), 124.0, 126.6, 126.7, 126.8, 128.2, 128.4, 136.5, 136.7, 136.8, 151.8 (superimposed signals 125–127 ppm, some signals missing due to poor solubility); MS (FD): m/z = 783 (100) [M⁺]; anal.: calcd. for C₅₇H₆₆O₂ (783.133): C 87.42%, H 8.49%; found: C 87.09%, H 8.30%.

4-Vinylphosphonate 20

Pd(OAc)₂ (44 mg, 0.2 mmol) and tri-*o*-tolylphosphine (120 mg, 0.4 mmol) were added to a solution of phosphonate **12** (6.15 g, 0.02 mol) in a mixture of anhydrous DMF (30 mL) and triethylamine (10.0 g, 0.1 mol). The mixture was placed in an autoclave (100 mL), purged with nitrogen, ethene was added (pressure 50 bar) and while stirring the temperature was brought to 140 °C for 8 h (the pressure increased to 70 bar). The cooled mixture was diluted with water (100 mL), the product was extracted with chloroform (5×60 mL) and the combined organic solutions were washed with water (2×100 mL) and brine (50 mL). After drying with MgSO₄, the solvent was evaporated and the residue was purified by chromatography on silica gel using dichloromethane/ethyl acetate as an eluent; [²⁸] yield: 2.75 g (54%), yellowish oil; IR (neat): $\tilde{\nu}$ = 2960, 2870, 2850, 1611, 1497, 1435, 1395, 1235, 1175, 1045, 1015, 950, 845, 797, 772, 745, 680 cm⁻¹; ¹H NMR (CDCl₃): δ = 1.24 (t, J = 7.2 Hz, 6 H, CH₃), 3.11 (d, J = 22.0 Hz, 2 H, CH₂-P), 4.01 (quin, J = 7.0 Hz, 4 H, OCH₂), 5.22 (d, J = 10.8 Hz, 1 H, vin), 5.71 (d, J = 17.0 Hz, 1 H, vin), 6.68 (d, J = 10.8 Hz, J = 17 Hz, 1 H, vin), 7.23 (d, J = 8.2 Hz, 2 H, Ph),

7.35 (d, $J = 8.2$ Hz, 2 H, Ph); ^{13}C NMR (CDCl_3): $\delta = 16.4$ (d, $J = 6.4$ Hz, CH_3), 35.6 (d, $J = 136.8$ Hz, $\text{CH}_2\text{-P}$), 62.1 (d, $J = 7.2$ Hz, OCH_2), 113.7 (CH_2 , vin), 128.5 (CH), 129.9 (d, $J = 7.2$ Hz, CH), 132.9 (d, $J = 7.5$ Hz, C_q), 136.2 (C_q), 136.4 (CH, vin); MS (FD): $m/z = 255$ (100) [M^+].

Silane 26

Iodostilbene **24** (1.0 g, 3 mmol), $\text{Pd}(\text{OAc})_2$ (20 mg, 0.09 mmol), triphenylphosphine (47 mg, 0.18 mmol), and AgNO_3 (0.50 g, 3 mmol) were added to a solution of silane **21** (0.68 g, 3.6 mmol) and triethylamine (0.36 g, 3.6 mmol) in anhyd acetonitrile (20 mL). The mixture was transferred to an autoclave (100 mL), purged with nitrogen and stirred at 120°C for 19 h. The mixture was diluted with water (50 mL) and the product extracted with ethyl acetate (3×30 mL). The pooled organic solutions were washed with iced water, dried with MgSO_4 , and, after evaporation of the solvent, the residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate (10/1) as an eluent; yield: 0.38 g (32%), slightly yellow solid, mp 152°C ; IR (KBr): $\tilde{\nu} = 2970, 2890, 1600, 1510, 1388, 1260, 1180, 1100, 970, 850\text{ cm}^{-1}$; ^1H NMR (CDCl_3): $\delta = 1.26$ (t, $J = 6.9$ Hz, 9 H, CH_3), 3.83 (s, 3 H, OCH_3), 3.87 (q, $J = 7.0$ Hz, 6 H, OCH_2), 6.15 (d, 1 H, $J = 21.1$ Hz, 1 H, ethene-Si), 6.85 (d, $J = 8.0$ Hz, 2 H, 3-H, 5-H, Ph'), 9.92 (d, $J = 16.2$ Hz, 1 H, CH ethene, 7.10 (d, $J = 21.1$ Hz, 1 H, ethene-Si), 7.20 (d, 1 H ethene, 7.44 (m, 6 H); ^{13}C NMR (CDCl_3): $\delta = 18.3$ (CH_3), 55.3 (OCH_3), 58.6 (OCH_2), 114.2 (C-3, C-5 Ph'), 126.4, 127.2, 127.8 (3×2 C, CH, Ph, Ph'), 117.2, 126.0, 128.7 (CH), 130.1, 136.6, 138.2 (C_q), 148.7 (CH-CHSi), 159.5 (C-O); MS (FD): $m/z = 399$ (100) [M^+]; anal.: calcd. for $\text{C}_{25}\text{H}_{30}\text{O}_4\text{Si}$ (398.567): C 69.31%, H 7.59%; found: C 69.27%, H 7.55%.

Silane 27

Method a): $\text{Pd}(\text{OAc})_2$ (20 mg, 0.09 mmol) and tris-*o*-tolylphosphine (54 mg, 0.8 mmol) were added to a solution of bromo-DSB **14** (0.30 g, 0.47 mmol), silane **22** (0.10 g, 0.47 mmol) and triethylamine (0.24 g, 2.35 mmol) in anhydrous DMF (30 mL). The mixture was purged with N_2 and stirred under N_2 for 3 h at 120°C . Toluene (100 mL) was added, the mixture washed with iced water (3×70 mL) and dried with Na_2SO_4 . Evaporation of the solvent was followed by chromatography of the residue on silica gel with toluene/cyclohexane (10/1) to afford the product; yield: 0.18 g (51%), yellow oil.

Method b): Grubbs catalyst **23** (ca. 3 mg) was added to a solution of the vinyl-DSB **17** (0.23 g, 0.4 mmol) and silane **22** (0.40 g, 2 mmol) in anhydrous benzene (50 mL) and a gentle flow of dry and oxygen-free N_2 was passed through the solution for 6 h. The solvent was evaporated and the product isolated by chromatography; yield: 25%; IR (neat): $\tilde{\nu} = 3015, 2960, 2910, 2850, 1631, 1590, 1505, 1455, 1405, 1385, 1200, 1165, 1100, 1075, 1055, 960, 852, 785, 755, 730\text{ cm}^{-1}$; ^1H NMR (CDCl_3): $\delta = 0.88\text{--}0.94$ (m, 12 H, CH_3), 1.25 (t, $J = 6.9$ Hz, 9 H, CH_3), 1.28–1.58 (m, 16 H, CH_2), 1.74 (m, 2 H, $\beta\text{-CH}$), 1.81 (d, $J = 8.0$ Hz, 2 H, Si- CH_2), 3.22 (s, 3 H, CH_3), 3.85 (m, 10 H, OCH_2), 6.26 (dt, $J = 16.1$ Hz, $J = 8.0$ Hz, 1 H, vinyl), 6.34 (d, $J = 16.1$ Hz, 1 H, vin), 6.71 (s, 1 H, 3-H, Ph'), 7.00–7.09 (m, 4 H), 7.29 (m, 2 H, $J = 8.4$ Hz, 2 H), 7.42 (d, $J = 8.4$ Hz, 2 H), 7.45–7.50 (m, 7 H); ^{13}C NMR (CDCl_3): $\delta = 11.3, 14.1$ (CH_3),

16.5 (CH_3), 17.8 (Si- CH_2), 18.2 (CH_3), 23.1, 24.1, 24.2, 29.2, 29.2, 30.8, 30.9 (CH_2), 58.7 (OCH_2), 71.0, 72.0 (OCH_2), 108.8, 115.9 (C-3, C-6, Ph), 125.8, 124.3, 125.2, 126.0 (2 C), 126.6 (2×2 C), 126.7 (2 C), 127.2, 127.8, 128.0, 129.7, 135.7, 136.3, 137.6 (CH, C_q , 2 signals superimposed), 150.7, 151.6 (C-O); MS (FD): $m/z = 755$ (100) [M^+], 378 (4) [M^{2+}]; anal.: calcd. for $\text{C}_{48}\text{H}_{70}\text{O}_5\text{Si}$ (755.152): C 76.34%, H 9.34%; found: C 76.28%, H 9.46%.

Silane 28

Grubbs catalyst **23** (ca. 3 mg) was added to a solution of vinyl-DSB **17** (1.0 g, 1.72 mmol) and silane **21** (1.6 g 8.4 mmol) in anhydrous benzene (100 mL) in a round-bottom flask equipped with nitrogen inlet tube and a reflux condenser with bubble counter. A gentle flow of dry and oxygen-free nitrogen was bubbled through the solution for 20 h. The solution was concentrated and the product isolated by chromatography on silica gel with toluene/cyclohexane 10/1 as an eluent; yield: 60 mg (5%) of **28**, yellow oil, and 820 mg (82%) of unchanged **17**. **28**: IR (CDCl_3): $\tilde{\nu} = 2955, 2918, 2850, 1588, 1500, 1445, 1400, 1195, 1065\text{ cm}^{-1}$; ^1H NMR (CDCl_3): $\delta = 0.80\text{--}0.95$ (m, 12 H, CH_3), 1.30 (t, $J = 6.5$ Hz, 9 H, CH_3), 1.20–1.60 (m, 16 H, CH_2), 1.74 (qui, 2 H, $\beta\text{-CH}$), 2.22 (s, 3 H, CH_3), 3.81–3.93 (m, 10 H, OCH_2), 6.16 (d, $J = 19.0$ Hz, 1 H, Si-vin), 6.73 (s, 1 H, 3-H, Ph'), 7.02 (s, 1 H, 6-H, Ph'), 7.06 (d, $J = 16.2$ Hz, 1 H, vin), 7.11 (s, 2 H, vin), 7.20 (d, $J = 19.0$ Hz, 1 H, Si-vin), 7.49 (m, 9 H, Ph, Ph', vin); ^{13}C NMR (CDCl_3): $\delta = 11.3, 14.0, 16.4$ (CH_3), 18.3 (CH_3), 23.1, 24.2, 24.3, 29.2, 29.3, 30.8, 31.0 (CH_2), 39.8, 39.9 (CH), 58.6 (Si- OCH_2), 71.2, 72.1 (OCH_2), 108.8, 115.9, 117.5, 124.0, 126.7 (2 C), 126.9 (2 C), 127.1 (2), 127.2 (2 C), 127.7, 128.5, 128.9, 148.6 (CH), 124.5, 127.9, 136.1, 137.9, 138.0 (C_q), 150.8, 151.7 (C-O); MS (FD): $m/z = 741$ (100) [M^+], 371 (2) [M^{2+}]; anal.: calcd. for $\text{C}_{47}\text{H}_{68}\text{O}_5\text{Si}$ (741.125): C 76.17%, H 9.25%; found: C 76.07%, H 9.37%.

Silane 29

Preparation from **18** according to the procedure described for **28**. Yield: 33%, yellow, greenish oil; IR (CDCl_3): $\tilde{\nu} = 2955, 2918, 2850, 1588, 1500, 1445, 1400, 1195, 1065\text{ cm}^{-1}$; ^1H NMR (CDCl_3): $\delta = 0.80\text{--}1.00$ (m, 12 H, CH_3), 1.27 (t, $J = 6.5$ Hz, 9 H, CH_3), 1.20–1.60 (m, 16 H, CH_2), 1.74 (qui, 2 H, $\beta\text{-CH}$), 2.22 (s, 3 H, CH_3), 3.80–3.95 (m, 10 H, OCH_2), 6.16 (d, $J = 19.0$ Hz, 1 H, Si-vin), 6.72 (s, 1 H, 3-H, Ph'), 7.02 (s, 1 H, 6-H, Ph'), 7.11 (m, 6 H), 7.43–7.56 (m, 13 H, Ph, Ph', vin); ^{13}C NMR (CDCl_3): $\delta = 11.2, 13.9$ (CH_3), 16.3 (CH_3), 18.2 (CH_3), 22.9, 23.0, 24.1, 24.2, 29.2, 29.5, 30.8, 30.9 (CH_2), 39.7, 39.8 (CH), 58.5 (Si- OCH_2), 71.1, 72.1 (OCH_2), 109.0, 115.9, 117.7, 123.9, 126.6 (2 C), 126.7 (4 C), 126.8 (2 C), 127.1 (2 C), 127.2, 127.7, 127.9, 128.4, 128.6, 148.5 (CH), 124.4, 127.8, 128.8, 136.1, 136.5, 137.0, 137.8, 137.9 (C_q), 150.8, 151.8 (C-O) ($1 \times \text{CH}$ superimposed); MS (FD): $m/z = 844$ (100) [M^+], 422 (2) [M^{2+}]; anal. calcd. for $\text{C}_{55}\text{H}_{74}\text{O}_5\text{Si}$ (845.259): C 78.34%, H 8.85%; found: C 78.01%, H 8.64%.

Silane 30

Preparation from **19** according to the procedure described for **28**, due to the limited solubility of **19**, the flask was immersed into an ultrasonic cleaning bath. Yield: 48%, yellow

solid, mp 126 °C; IR (CDCl₃): $\tilde{\nu}$ = 2910, 2900, 2840, 1580, 1500, 1440, 1400, 1195, 1070 cm⁻¹; ¹H NMR (CDCl₃): δ = 0.80–1.00 (m, 12 H, CH₃), 1.29 (m, 9 H, CH₃), 1.20–1.65 (m, 16 H, CH₂), 1.75 (m, 2 H, β -CH₂), 2.22 (s, 3 H, CH₃), 3.85–3.92 (m, 10 H, OCH₂), 6.20 (d, J = 19.6 Hz, 1 H, vin), 6.73 (s, 1 H), 7.0–7.24 (m, 9 H), 7.38–7.57 (m, 15 H); ¹³C NMR (CDCl₃): δ = 11.3, 14.1 (CH₃), 16.5 (CH₃), 18.3 (CH₃), 23.1 (2 C), 24.1, 24.2, 29.7 (2 C), 30.8, 30.9 (CH₂), 39.7, 39.8 (CH), 58.7 (OCH₂), 71.0, 72.0 (OCH₂), 108.8, 115.8, 117.6, 123.9, 126.9–127.2 superimposed signals, 148.6 (CH) 124.3, 136.2, 136.6, 136.9, 137.8, 137.8, (C_q), 127.2, 127.8, 127.9, 128.1, 128.3, 128.4, 128.7, 130.5 (CH, C_q), 150.7, 151.6 (C–O); MS (FD): m/z = 946 (100) [M⁺], 473 (36) [M²⁺]; anal.: calcd. for C₆₃H₈₀O₅Si (945.392): C 80.04%, H 8.53%; found: C 80.02%, H 8.50%.

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