Elongated phosphoranes by C–C coupling of haloaroylmethylidenetriphenylphosphoranes: synthesis and applications

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Haloaroylmethylidenephosphoranes **3** can be subjected to Pd(0) mediated C–C coupling reactions to yield diaryl-, arylhetaryl-, dihetaryl, arylethenylaryl/hetaryl- and arylethynylaryl/hetaryl-carbonylmethylidenephosphoranes **4**–**9**. *Suzuki–Kumada reactions* can also be run in a one-step procedure from (haloaroylmethyl)triphenylphosphonium bromides **2**. Compounds **4**–**9** are air-stable phosphoranes which undergo formal Wittig-olefination reactions with aldehydes **10** under benzoic acid catalysis. C–C coupling reaction and Wittig olefination can also be performed in a one-step procedure. Preliminary experiments have been performed to carry out the synthesis on a solid support. Applications to the chain elongation and functionalisation of the chain terminus in a C-7 substituted estra-1,3,5(10)-triene **14** and a C-16 substituted estra-1,3,5(10),6-tetraene **12** are shown.

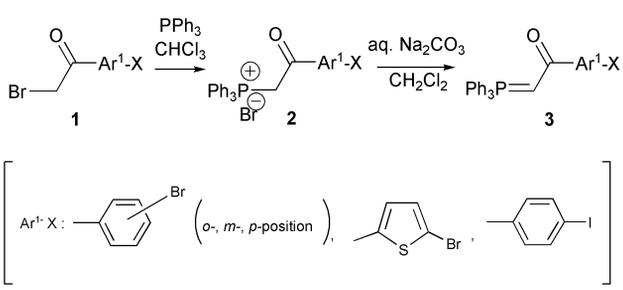
Introduction

The Wittig olefination is a well-established reaction.[1] After its discovery[2] in 1949–1954[3] it developed very quickly into an important implement in the tool-kit of the organic synthetic chemist. The preparations of phosphoranes as reagents for the Wittig olefination are manifold.[4] Early in the development of new Wittig reagents interest focussed on phosphoranes in which the ylene P=C bond is in conjugation with either a carbonyl[5] or a cyano[6] group. These phosphoranes show little basicity, tolerate oxygen and can usually be stored as solids over a long period of time. Furthermore, they discriminate between carbaldehydes and ketones, reacting readily with aldehydes, but only with very reactive ketones.[7] In the following the synthesis, physical properties and reactivity in Wittig-olefination reactions of these phosphoranes are discussed.[8]

Results and discussion

I. Synthesis

Haloaroylmethylidenetriphenylphosphoranes **3** (Scheme 1) are easily synthesized by reacting haloaryl halomethyl ketones **1** with triphenylphosphine to yield the respective aroylmethyltriphenylphosphonium halides **2**,[5] which in turn can be converted to the phosphoranes **3** by base-catalysed dehydrohalogenation (usually by employing an aq. Na_2CO_3 solution).[9] For the most part the haloaryl halomethyl ketones **1** are commercially available. Where they are not, the haloaryl methyl ketones were brominated with bromine in acetic acid. The haloaryl methyl ketones possess low solubility in acetic acid and it was found to be very beneficial to carry out the bromination of a suspension of the starting material in acetic acid under ultrasonication. The progress of the reaction could be monitored optically by the disappearance of color, ending in many cases with totally colorless material which could be filtered and used without any further purification.



Scheme 1 Synthesis of haloaroylmethylidenetriphenylphosphoranes.

a. C–C bond formation under Suzuki–Kumada conditions. The aroylmethylidenephosphoranes are known to exhibit a certain stability in slightly basic media. It is for this reason that it was deemed possible to transform the haloaroylmethylidenephosphoranes into aryl/hetarylaroylphosphoranes, when using the mild reaction conditions of the Suzuki–Kumada cross-coupling reaction.[13,14] The haloaroylmethylidenephosphoranes undergo the coupling reaction with a number of arylboronic acids, upon using [$Pd(PPh_3)_4$, 2 M aq. Na_2CO_3, DME], [$Pd(PPh_3)_4$, CsF, DME] or [K_3PO_4–DMF] (Tables 1 and 2).[15,16] Most of the arylboronic acids are commercially available, **4m**–**p** were prepared.[17,18]

During the coupling reaction a small amount of phosphorane is hydrolysed to give the corresponding disubstituted biphenyls and triphenylphosphine.[19] The amount of hydrolysed phosphorane depends not only on the reaction time, but also on the substituent(s) of the phosphorane, *i.e.* on the initially used aryl/hetarylboronic acid. Thus, preliminary studies of the electrochemical oxidation of the phosphoranes have also shown that the electrochemical potential at which electrons are transferred from the phosphoranes is dependent on the nature of the substituent on the phenyl group. For the most part, a linear relationship could be found between the oxidation potential at which the phosphorane is oxidized and the Hammett

† Corresponding author for the X-ray crystal structure.

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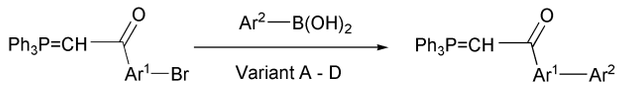
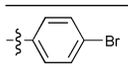
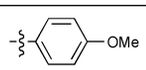
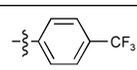
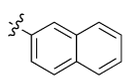
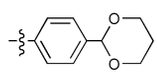
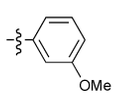
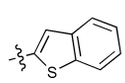
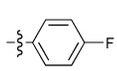
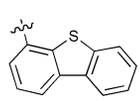
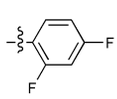
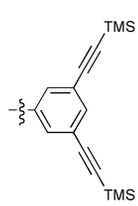
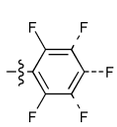
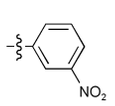
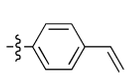
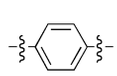
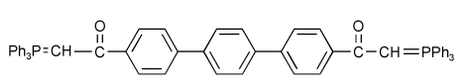
Table 1 Suzuki coupling of *p*-bromobenzoylmethylidenetriphenylphosphorane under various conditions



3 **4**

–Ar¹–Br	–Ar²	Variant[a]	Yield (%)		–Ar¹–Br	–Ar²	Variant[a]	Yield (%)	
 **3a**		A	64	**4a**			A	60	**4k**
		B	89				A	90	**4l**
		C	62						
		A	65	**4b**			B	36	**4m**
		D[b]	91						
		A	89	**4c**			A	98	**4n**
		A	68	**4d**			A	85	**4o**
		A	66	**4e**			A	16	**4p**
		A	—	**4f/g**[c]					
		A	94	**4h**			A	55	**4q**
		A	70	**4i**			A	65	**4r**[d]
		A	58	**4j**					

[a] A: $Pd(PPh_3)_4$, 2 M aq. Na_2CO_3, DME, 3–11 h, 75 °C; B: $Pd(PPh_3)_4$, CsF, DME, 3 h, 75 °C; C: $Pd(Pd(PPh_3)_4$, K_3PO_4, dry DMF, 4 h, 100 °C; D: $Pd(OAc)_2$, $NaHCO_3$, Bu_4NCl, chloroform, 72 h, rt. Note: for methods B and C the corresponding boronic acid trimethylene glycol esters were used. [b] For Suzuki-type coupling under PTC conditions, see ref. 22. [c] Denotes results for both 2,6-difluorophenylboronic acid and pentafluorophenylboronic acid. [d] Bis-coupling compound.

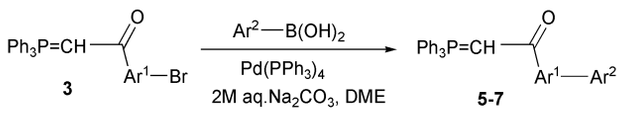


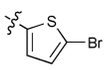
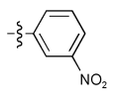
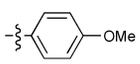
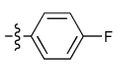
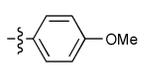
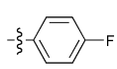
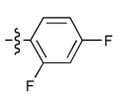
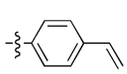
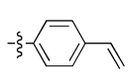
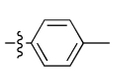
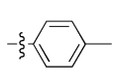
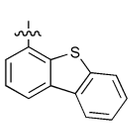
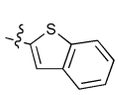
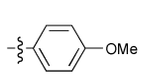
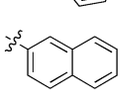
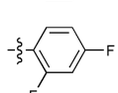
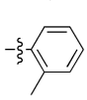
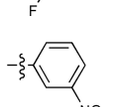
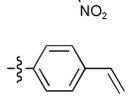
parameter of the benzoyl substituent.[20] In certain cases, as for thienylbenzoylmethylidenetriphenylphosphorane, this relation is more complex, and does not follow the electron-donating/electron-withdrawing character of the substituent.[20] Nevertheless, the phosphoranes are by far the major products in the Suzuki–Kumada coupling. They can be purified easily either by precipitation or by column chromatography on silica gel and subsequent recrystallization. The system [$Pd(PPh_3)_4$, CsF, DME] gives slightly better yields in a number of cases. The system [Na_2CO_3–DME] is environmentally more viable and cheaper, and it was thus used most of all. It is possible to carry out Suzuki–Kumada coupling reactions with haloaroylmethylidenephosphoranes using phase-transfer conditions (PTC). These conditions resemble the conditions used by Jeffery[21,22] (see below) in Heck reactions. Palladium acetate is used as the Pd catalyst, $NaHCO_3$ as the base and tetrabutylammonium chloride as the phase-transfer catalyst. The reactions can be carried out in chloroform. They are carried out at rt, however, the reaction time tends to be long (72 h). At rt only the iodoarylmethylidenephosphoranes give good results in the Suzuki–Kumada coupling under PTC conditions.

Interestingly, both pentafluoro- as well as 2,5-difluorophenylboronic acids do not undergo the coupling reaction under the conditions tried. It may be that the boronic acids hydrolyse too quickly in these cases—it is known that fluoro substituents accelerate the hydrolysis.[23] On the other hand, both the *p*- and the *o*-monofluorophenylboronic acids give the coupling products in acceptable yields.

As the aroylmethylidenephosphoranes themselves are prepared under base-induced elimination of 'HBr' from the corresponding aroyltriphenylphosphonium bromides, it only seemed expedient to subject the aroyltriphenylphosphonium bromides themselves to the C–C bond-forming reaction under Suzuki–Kumada conditions. Indeed, when this reaction was carried out, the phosphoranes **4** could be isolated in good yield (Table 3). Here, elimination to the phosphoranes and the C–C bond-forming reaction take place as a one-pot procedure. As the phosphonium salts are somewhat more stable than the

Table 2 Suzuki coupling of haloaroylmethylidenetriphenylphosphoranes



–Ar[1]–Br	–Ar[2]	Yield (%)		–Ar[1]–Br	–Ar[2]	Yield (%)	
 **3b**		62	**5a**	**3b**		89	**5m**
3b		72	**5b**	 **3c**		94	**6a**
3b		57	**5c**	**3c**		65	**6b**
3b		78	**5d**	**3c**		95	**6c**
3b		78	**5e**	**3c**		55	**6d**
3b		95	**5f**	**3c**		72	**6e**
3b		55	**5g**	**3c**		55	**6f**
3b		66	**5h**	 **3d**		81	**7a**
3b		49	**5i**	**3d**		95	**7b**
3b		75	**5j**	**3d**		82	**7c**
3b		56	**5k**	**3d**		89	**7d**
3b		13	**5l**	**3d**		70	**7e**

corresponding phosphoranes and can be stored over long periods of time, the use of the phosphonium salts as starting materials in the coupling reactions is a viable alternative to the reactions presented above.

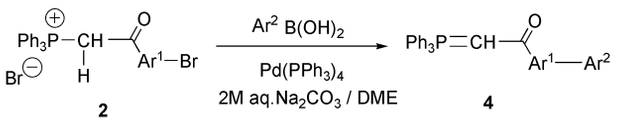
b. C–C bond formation under Heck conditions. Although the Heck reaction is a well-studied transformation in organic chemistry, to our knowledge no example of a Heck reaction with phosphoranes to yield substituted phosphoranes[24] has been described in the literature.

Here, we have subjected both the *p*-bromobenzoylmethylidenetriphenylphosphorane (**3a**) and the corresponding iodo-substituted **3e** to Heck reactions under a number of conditions. Under the classical conditions, **3a** gives the Heck reaction products, *e.g.* **8a**–**c** in only mediocre yields. Better yields are achieved using conditions employed formerly by Jeffery. In this case the reaction is run in a-two phase system (solid–liquid) with a tetraalkylammonium salt as phase-transfer catalyst. The reaction is run at rt and no triphenylphosphine is added as ligand, which would help stabilize the transient palladium(0) species. While Jeffery[21] uses tetrabutylammonium chloride as phase-transfer catalyst, other ammonium salts serve equally well. In our case benzyltrimethylammonium chloride was used. Although the reaction is run at rt, the reaction time tends to be long. Not all the reactions have been monitored with respect to reaction time, however, as an example, the reaction between **3e** and acrylonitrile is not complete after 42 h. After 60 h most of the systems tried show virtually no more starting material. Exceptions are methyl vinyl ketone and vinylpyridine. Vinylpyridine could not be reacted under these conditions. Methyl vinyl ketone could be reacted; the products, however, could not be isolated (Table 4).

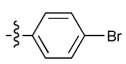
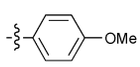
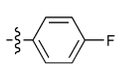
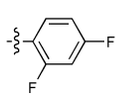
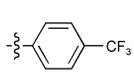
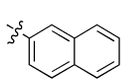
Interestingly, under the same conditions the reaction of *p*-bromobenzoylmethylidenetriphenylphosphorane (**3a**) with acrylonitrile does not proceed and the reaction under Jeffery conditions seems to be limited to an iodo-substituted coupling partner.

c. C–C bond formation by Pd(0)-catalysed ethynylation. *p*-Iodophenylcarbonylmethylidenetriphenylphosphorane (**3e**)

Table 3 Suzuki coupling of haloaroylmethylidenetriphenylphosphoranes



2 4

–Ar¹–Br	–Ar²	Yield (%)	Yield (%)[a] from phosphorane
 **2a**		64 (**4b**)	65
		49 (**4a**)	64
		62 (**4d**)	68
		74 (**4e**)	66
		42 (**4j**)	58
		54 (**4k**)	60
		55 (**4l**)	90

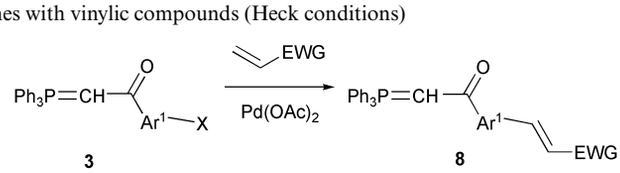
[a] These yields are given for comparison. Partly, they can also be found in Table 1.

was successfully reacted with substituted phenylacetylenes and thienylacetylene. The *p*-substituted phenylacetylenes themselves were prepared in the usual manner by reaction of the *p*-substituted bromoarenes with trimethylsilylacetylene [$(Ph_3P)_2PdCl_2$, CuI, *i*-Pr_2NH, toluene] with subsequent desilylation (1 M KOH, MeOH). *p*-Ethynylbenzamide was obtained by partial hydrolysis of *p*-ethynylbenzonitrile [$(n\text{-}C_4H_9)N^+HSO_4^-$, 30 w% aq. H_2O_2, CH_2Cl_2–20 w% aq. NaOH, 20–25 °C, PTC conditions).[25] The ethynylation reactions of the *p*-iodobenzoylmethylidenetriphenylphosphorane (**3e**) itself were carried out with the typical $Pd(PPh_3)_4$–CuI catalyst system in toluene (see Table 5). The yields of the reactions were found to be dependent on the *p*-substituent of the phenylacetylene. Thus, while in the reaction of *p*-nitrophenylacetylene the coupling product **9c** could be obtained in an almost quantitative yield, the corresponding *p*-amido-substituted product **9d** was only obtained in a mediocre yield. The outcome with certain substrates, such as with the thienyl derivative **9e** or with *p*-cyanophenylacetylene, product **9b**, was found to be strongly dependent on the reaction time. Thus, *p*-cyanophenylacetylene gave the product in 98% yield after 3 h, while **9b** was only obtained in 50% yield after 13 h.

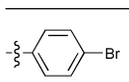
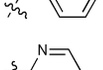
II. Properties

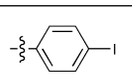
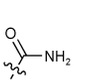
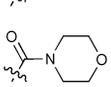
a. Spectroscopic data. The carbon NMR spectra of all the conjugated phosphoranes that have been prepared by Suzuki coupling show the methylidene ylide carbon at about δ 50 ppm.[26,27] The value of the chemical shift of this carbon is not affected greatly by the substituent on the benzoyl or thienoyl units. The UV spectra of compounds **3a**, **4a**, **4n**, **5b**, **5c**, **5h**, and **5m** were taken. The samples were measured at a concentration of 2×10^{-5} M in 99.5% ethanol (0.5% H_2O) and in CH_2Cl_2. In the latter series, a number of single 'core' benzoylmethylidenetriphosphoranes were also included. In general, the coupled products, *e.g.* **4a** and **4n**, show a bathochromic shift and a hyperchromic effect. The thienoylmethylidenephos-

Table 4 Cross-coupling of phosphoranes with vinylic compounds (Heck conditions)



3 8

–Ar¹–X	–EWG	Variant[a]	Yield (%)	
 **3a**		A	6	**8a**
3a		A	18	**8b**
3a		A	38	**8c**
3a		A	—	
3a		A	—	
3a		A	—	

–Ar¹–X	–EWG	Variant[a]	Yield (%)	
 **3e**		A	45	**8a**
		B[b]	75	**8a**
3e		A	25	**8b**
		C	55	**8b**
3e		A	—	
3e		A	—	
		C	64	**8d**
3e		C	96	**8c**

[a] A: PPh_3, Et_3N, DMF, 15–24 h, 100 °C; B: $NaHCO_3$, Bu_4NCl, chloroform; 72 h, rt; C: $NaHCO_3$, $[PhCH_2N(CH_3)_3]Cl$, chloroform, 40–60 h, rt. [b] For Heck reaction under PTC conditions, also see ref. 21.

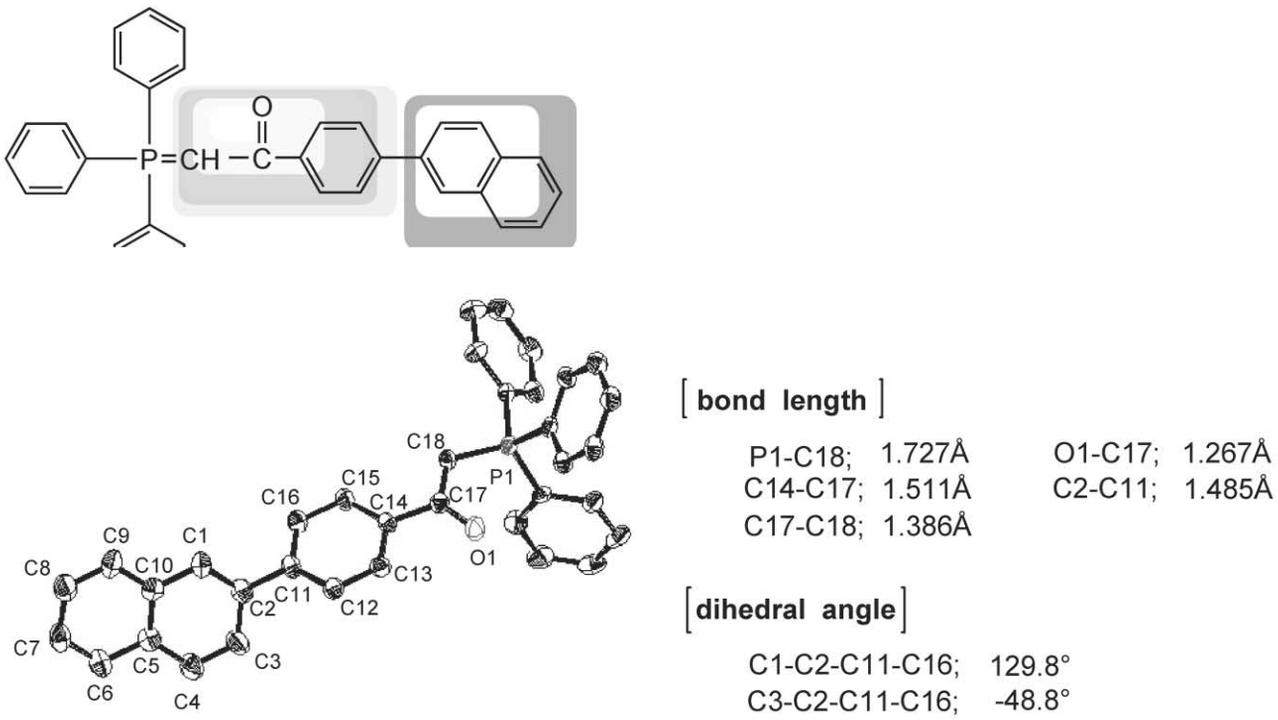
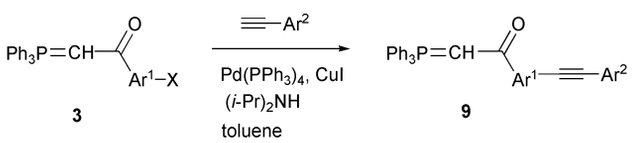
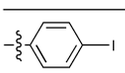
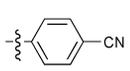
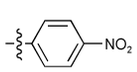
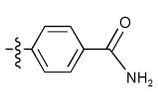
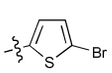
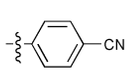


Fig. 1 Representation of the X-ray crystal structure of 4-(2′-naphthyl)benzoylmethylidenetriphenylphosphorane.

Table 5 Cross-coupling of phosphoranes with arylacetylenes



3 **9**

–Ar¹–X	–Ar²	Yield (%)		Time/h
 **3e**		4	**9a**	13
3e		5	**9b**	13
		9	**9b**	3
3e		9	**9c**	13
3e		13	**9d**	13
 **3b**		46	**9e**	4

phoranes show a shift of the absorption maximum to longer wavelengths when compared to the corresponding benzoylmethylidenephosphoranes, *e.g.* **5b** *vs.* **4a**. Typical absorption maxima ($\lambda_{max[solvent]}$/nm, log ε) are as follows: **3a** ($322_{[EtOH]}$, 4.05); **4a** ($328_{[EtOH]}$, 4.30); **4n** ($342_{[EtOH]}$, 4.45); **5b** ($356_{[EtOH]}$, 4.44); **5c** ($350_{[EtOH]}$, 4.37); **5h** ($357_{[EtOH]}$, 4.15); **5m** ($353_{[EtOH]}$, 4.33).

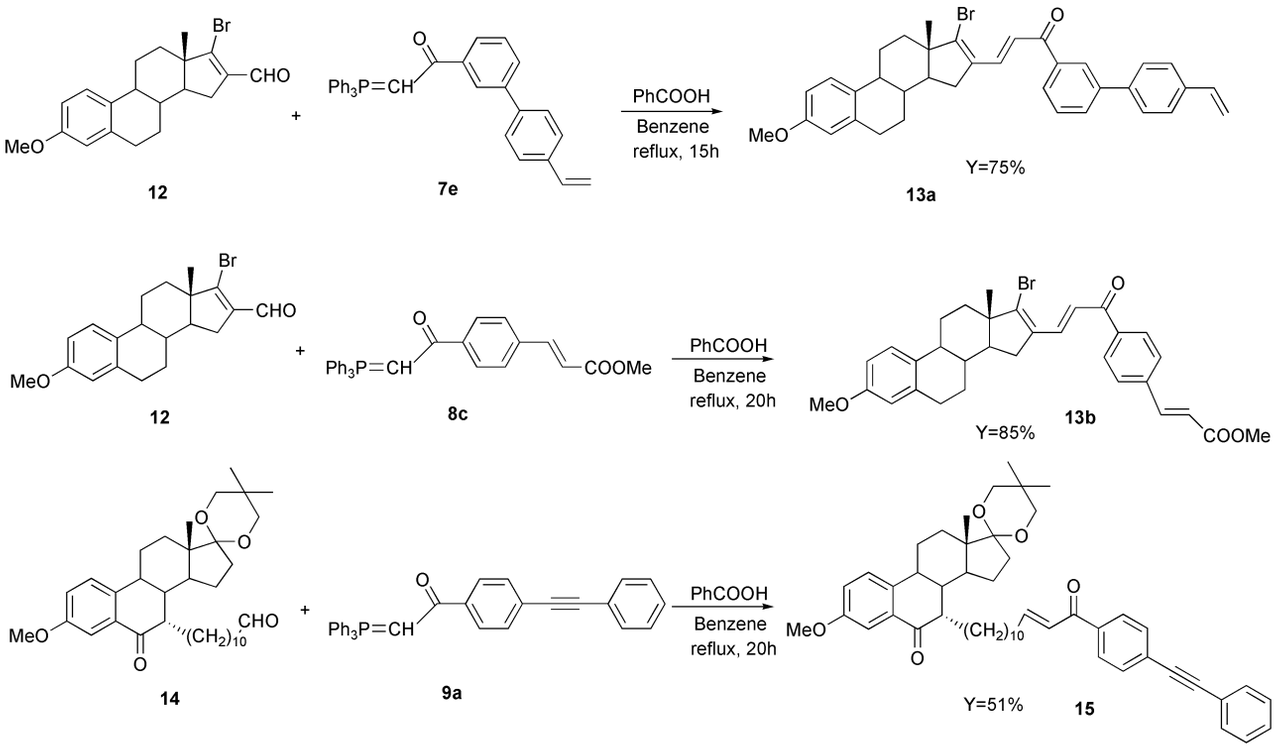
As in the case of the unsubstituted benzoylmethylidenetriphenylphosphorane, the elongated phosphoranes reported here can be best described in terms of their structure as being ylides (rather than ylenes). This can be seen from their UV spectra, their ^{13}C NMR spectra (*vide supra*), and the X-ray crystal structure of **4l** (*vide infra*). Also, when analysed by electrocyclovoltammetry, the compounds show no reduction peak typical for a carbonyl group.[20]

b. Structural properties. A single-crystal X-ray structural analysis was carried out with compound **4l** (Fig. 1). The X-ray crystal structure of benzoylmethylidenetriphenylphosphorane is known in the literature.[28] In **4l** the bond length P1–C18 is 1.726 Å. This is slightly longer than the bond in benzoylmethylidenetriphenylphosphorane itself at 1.71 Å. As the value for the bond length of a typical PC double bond is taken to be around 1.67 Å and that of a typical PC single bond to be around 1.87 Å, the bond in **4l** has more character of a PC double bond rather than a PC single bond. However, the single bond character increases slightly with the added aryl group. The X-ray study of **4l** also reveals that the naphtho group is not in conjugation with the phenylene unit. This, however, is most likely due to better packing in the crystal. The dihedral angle C1–C2–C11–C16 measures 129.9°.

c. Cytotoxic behavior. Compounds **4a**, **4e**, **4h**, **4j**, **5b**, **5c**, **5m**, and **7d** were subjected to a three-cell line (NCI-H460 [Lung], MCF7 [Breast], SF-268 [CNS]), one-dose anticancer assay.[29] Of these compounds only **5b** and **5c** were found to be inactive. Compounds **4a**, **4e**, **4h**, **4j**, **5m**, and **7d** were then subjected to an *in vitro* anti-tumour screen comprising 60 human tumour cell lines. The compounds showed moderate but not selective activity towards a number of cancer cell types. As there is a slow hydrolysis of the compounds in slightly acidic aqueous media, it still needed to be ascertained what role the hydrolysis products, *e.g.*, the acetyl-substituted biaryls, play in the cytotoxicity of the phosphoranes. Acetyl-substituted biaryls have been known to have physiological activity, but have been patented mainly in the area of blood anti-coagulents. Initial electroanalytical experiments on the oxidizability of the phosphoranes, however, do not show any relationship between the sensitivity of the phosphoranes towards oxidation and their cytotoxic activity.

III. Wittig-olefination reaction of the phosphoranes

For the most part, conjugated phosphoranes such as those described above are quite unreactive towards ketones. Few



Scheme 2 Acid-catalysed Wittig olefination of estrone derivatives with elongated phosphoranes.

examples of ketones are known that are sufficiently reactive for the olefination reaction with the phosphoranes to proceed.[30,31] Aldehydes, however, readily react with the phosphoranes.

Here, both arenecarbaldehyde (*p*-tolualdehyde and *m*-nitrobenzaldehyde) as well as alkanecarbaldehydes (*n*-butanal) have been used as the aldehyde component. Two steroidal substrates, **12**[32] and **14**, have also been used. Both are estranes, one (**12**)[32] with a formyl substituent at C-16, the other (**14**) with a formyl group as the terminal functionality of a chain substituting the estrane at C-7α. The latter has been synthesized as an intermediate to C-7α-substituted estra-1,3,5(10)-trienes and to C-7-substituted estra-1,3,5(10),6-tetraenes[33–35] as novel ligands for the estrogen receptor ERα. This research is closely connected to the development of radiodiagnostics and of drug delivery systems for estrogen-positive breast cancer.[33–36]

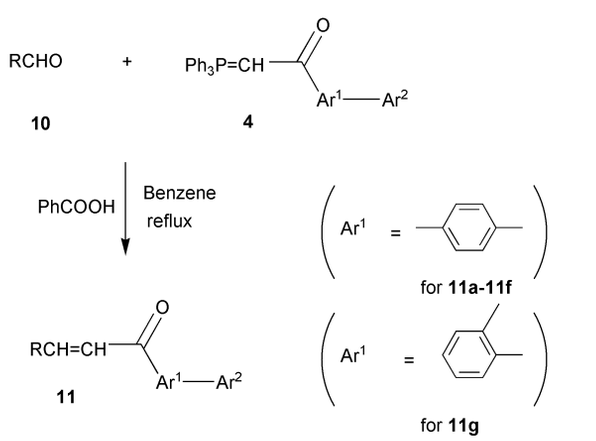
All of the substrates could be reacted with the elongated phosphoranes used, as shown in Table 6 and in Scheme 2. It has been found that it is advantageous to carry out the Wittig reactions under acid catalysis.[37,38] Here, benzoic acid has been used. The major products obtained and those isolated are (*E*)-isomers.

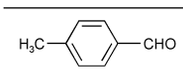
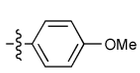
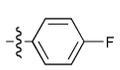
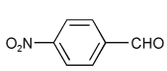
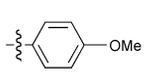
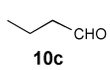
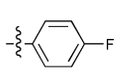
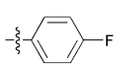
In our endeavour to develop one-pot procedures, which are more time- and cost-effective while limiting excessive production of waste materials, we looked at the possibility of running the Suzuki–Kumada coupling concurrently with the Wittig olefination.[31] Here, the products were obtained in good yields (Scheme 3). It must be pointed out that two equivalents of arylboronic acid were used. Where the carbaldehyde substrates also carried an interchangeable halo functionality a mixture of products was obtained, as the Suzuki–Kumada coupling also took place on the carbaldehyde component to give doubly-coupled products. The separation of products such as these is difficult to achieve. Where product mixtures are obtained it is often advisable to follow the step-wise sequence to facilitate work-up.

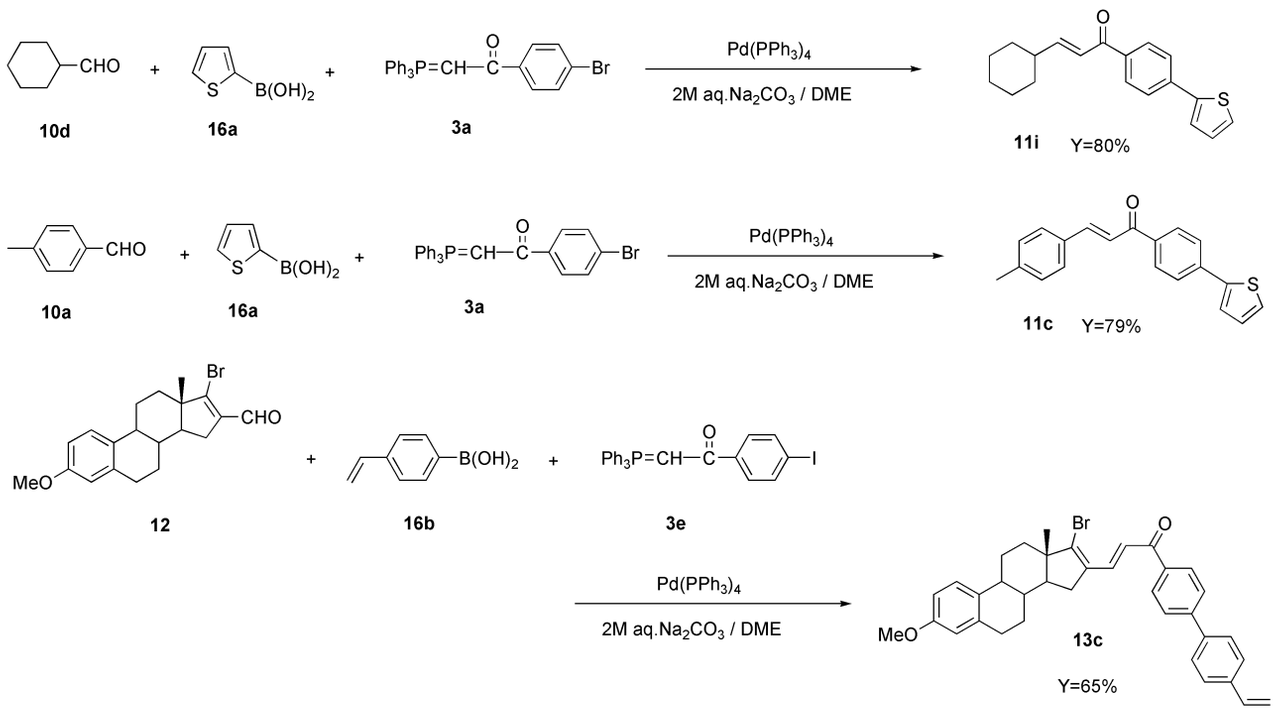
IV. Synthesis on solid support[39]

Wittig olefinations using phosphoranes derived from triphenylphosphine-polystyrene have been described in the literature. The preparation of the individual phosphoranes varies depending

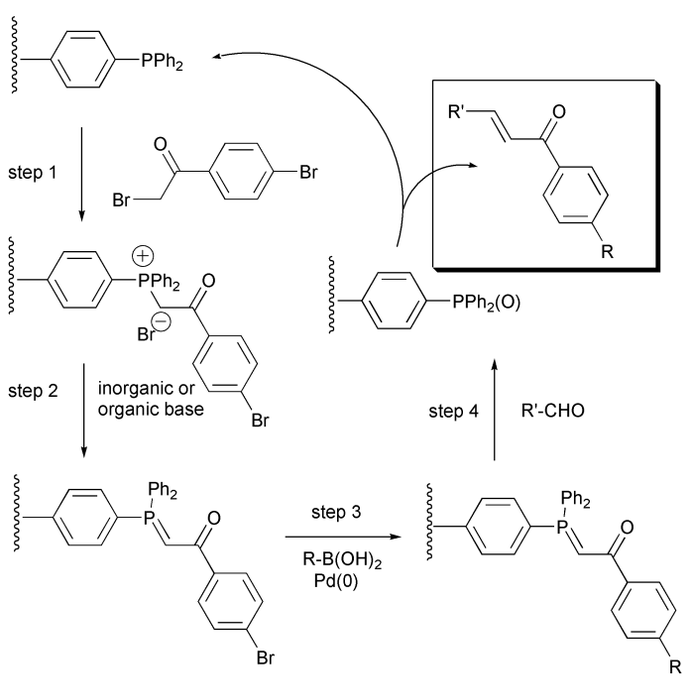
Table 6 Acid-catalysed Wittig olefination with elongated phosphoranes



RCHO	–Ar²	Yield (%)	
 **10a**		98	**11a**
10a		98	**11b**
10a		98	**11c**
10a		90	**11d**
 **10b**		97	**11e**
 **10c**		50	**11f**
10a		45	**11g**



Scheme 3 Suzuki coupling–Wittig olefination as a one-pot/three-component reaction.



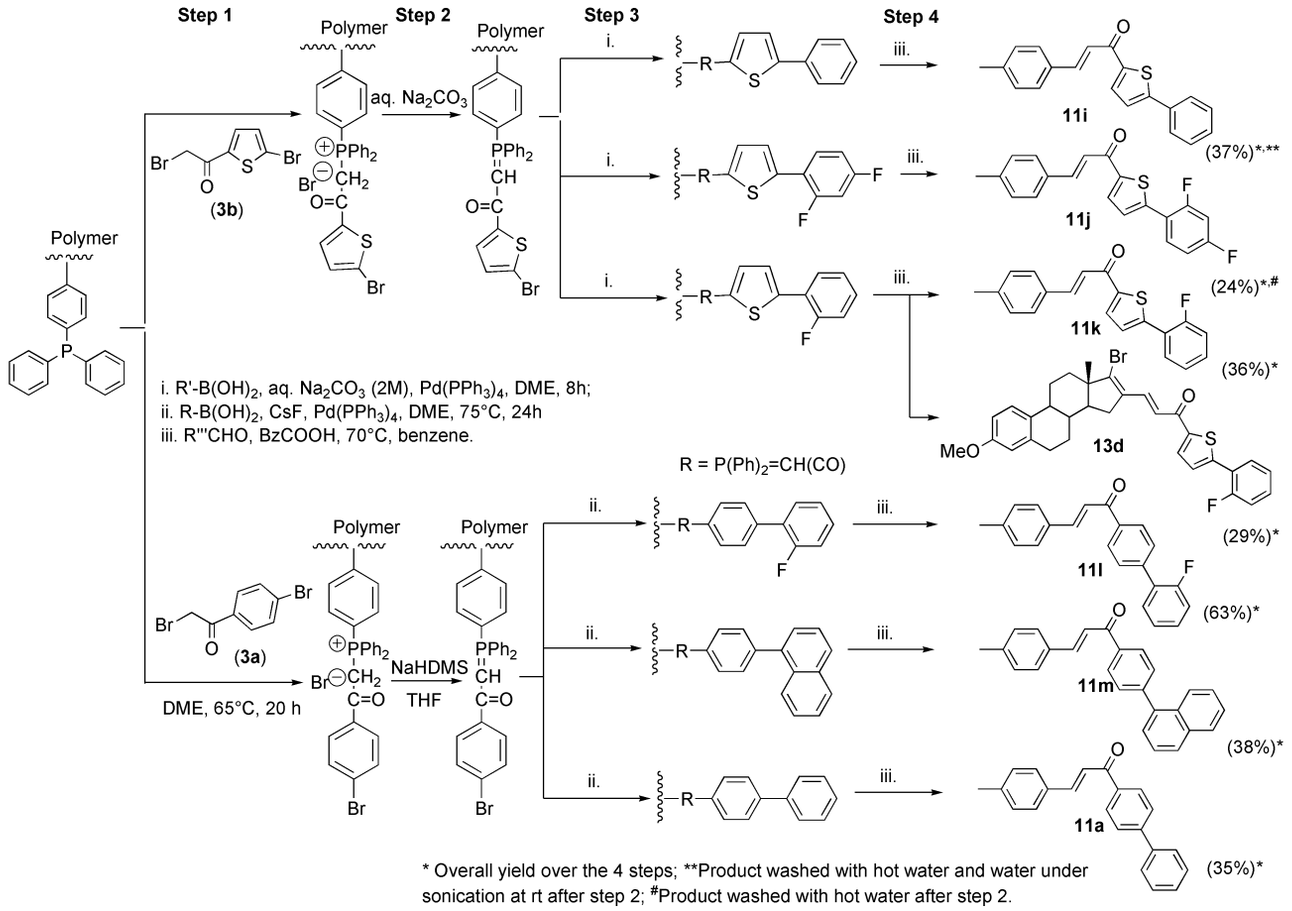
Scheme 4 Phosphorane synthesis and Wittig reaction were carried out successfully with a number of boronic acids on a solid support [(*p*-styryldiphenylphosphine) polymer]. The problems of efficient recycling of the ensuing phosphine oxide polymer and cleansing of the polymer from palladium after the coupling reactions still need to be solved.

on the nature and the stability of phosphorane synthesized (Scheme 4). In the case described here, the corresponding halo-substituted α-bromoacetoarenone, such as *p*-bromophenacyl bromide, could be reacted with *p*-poly(styryldiphenylphosphine)[40] in DME (65 °C, 20 h). The ensuing phosphonium bromide was dehydrobrominated to the phosphorane using either aq. 7 w% Na_2CO_3 (1 h, rt) or sodium hexamethyldisilazane in THF (4 h, rt). While for the preparation of poly(*p*-bromobenzoylmethylidenediphenylstyrylphosphine) either Na_2CO_3 or preferably sodium hexamethyldisilazane could be used, the synthesis of the bromothienyl analog did not proceed with sodium hexadimethyldisilazane.

The phosphoranes bound to the solid support were subjected to Suzuki–Kumada coupling[41] reactions with a number of arylboronic acids. Again, for the thienoylmethylidenephosphoranes, the reaction conditions [$Pd(PPh_3)_4$, aq. Na_2CO_3, DME] were different from those used for the bromobenzoylphosphorane [$Pd(PPh_3)_4$, CsF, DME] and gave better results.

The resulting phosphoranes were reacted with *p*-tolualdehyde (**10a**) in refluxing benzene in the presence of a catalytic amount of benzoic acid. The resulting alkene leaves the solid support, with triphenylphosphine oxide remaining on the support. The reaction mixture was analysed after termination of the reaction by ^1H NMR spectroscopy. Thereafter, it was separated by column chromatography or by preparative thin layer chromatography and the coupled phosphoranes were isolated as pure substances.

Reactions were also carried out with 17-bromo-16-formyl-



Scheme 5

3-methoxyestra-1,3,5(10),16-tetraene (**12**). Representative reactions are shown in Scheme 5.

After each synthetic step on the support, the support was analysed by IR spectroscopy. Very clear and significant changes in the IR bands could be observed after every step and within the 'finger-print' region a clear identification of the polymer-bound phosphoranes could be made, as the absorption frequencies closely resembled those of the monomeric phosphoranes synthesized in solution and isolated in substance: polymer-bound phosphorane *vs. monomeric phosphorane* [*p*-biphenylcarbonylmethylidenetriphenylphosphorane (**4b**), measured as KBr pellets] 1564 (*1567*), 1491 (*1481*), 1437 (*1436*), 1384 (*1388*), 1109 (*1102*), 884 (*880*), 749 (*746*), 687 (*693*) cm^{-1}.

Elemental analyses were carried out after every step for representative samples. The elemental analysis of the commercial triphenylphosphine-polystyrene showed the loading of the phosphine to be 1.6 mmol g^{-1} reagent. Analyses of the support/supported material after the preparation of the phosphonium bromide, which includes a thorough washing of the solid support with THF and dichloromethane at the end of the reaction, showed this first step to be a very clean reaction. The second step, which is the actual preparation of the phosphorane that is to be elongated subsequently by C–C coupling and consists of the dehydrobromination of the corresponding phosphonium salt, leaves impurities on the solid support, probably due to salt inclusion. Different methods of washing the support after the reaction were tested at this stage: a) rinsing with water at rt; b) washing with hot water (50 °C), c) treating the support with water under sonication in an Kaijo Denki Cleaning Bath 100 (for 1 h at rt). Good results were obtained with method c); in certain cases the results achieved by method a) were comparable.

After the Wittig reaction, an appreciable amount of phosphine oxide is formed on the solid support. Initial experiments have been carried out to recycle the solid support reagent as triphenylphosphine-polystyrene, which entails a reduction step of triphenylphosphine oxide to triphenylphosphine. An added difficulty in the recycling process comes from the fact that the Suzuki coupling leaves palladium adsorbed to the solid support. A number of methods are known for the reduction of triphenylphosphine oxide to triphenylphosphine. Thus, monomeric triphenylphosphine oxide in solution can be reduced by $LiAlH_4$–$CeCl_3$,[42a] by trichlorosilane (Cl_3SiH)[42b] as well as with a hydrocarbon/carbon reductant[42c] at high temperatures. Here, preliminary experiments have been carried out with $LiAlH_4$–$CeCl_3$. For this experiment triphenylphosphine-polystyrene was treated with MCPBA and oxidized to triphenylphosphine oxide polystyrene. With this in hand, it could be shown both by IR spectrocopy of the product and by repeating the first step (preparation of the phosphonium salt) of the sequence described above that $LiAlH_4$–$CeCl_3$ also reduces polymer-bound triphenylphosphine oxide. However, the purity of the reduced product obtained still needs to be improved.

Experimental

General

Melting points were measured on a Yanaco microscopic hot-stage and are uncorrected. Infrared spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM machines. ^1H and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer. The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). Mass spectra were measured with a JMS-01-SG-2 spectrometer (EI, 70 eV). Column chromatography was carried out on Wakogel 300. All experiments were purged with argon at the start. Ether = diethyl ether.

Commercially available triphenylphosphine-polystyrene

(100–200 mesh, loading: 1.2 mmol triphenylphosphine g^{-1} reagent, Novabiochem) was used. The preparative procedures for 17-bromo-16-formyl-3-methoxyestra-1,3,5(10),16-tetraene (**12**) and **14** have been described earlier.

The preparations of 4-(*m*-nitrophenyl)benzoylmethylidenetriphenylphosphorane **4h** from **3a**, of 4-(2′,4′-difluorophenyl)-benzoylmethylidenetriphenylphosphorane **4e** from **2a**, and of 1-(*p*-phenylbenzoyl)-2-(*p*-tolyl)ethene **11a** by Wittig olefination from **4b** and **10a** have been reported previously.

o-Bromophenylcarbonylmethylidenetriphenylphosphorane (3c)

To a stirred solution of triphenylphosphine (2.19 g, 8.35 mmol) in chloroform (5 mL) was added dropwise (*o*-bromo)bromoacetylbenzene (2.11 g, 7.50 mmol) in chloroform (5 mL). The solution, which warmed slightly upon addition, was stirred at rt for 10 h. Thereafter the mixture was poured into dry ether (100 mL) and filtered. The filter cake, which is hygroscopic, was transferred quickly into a mixture of 10 w% aq. Na_2CO_3 (30 mL) and CH_2Cl_2 (10 mL). The resulting two-phase solution was stirred at rt for 10 h. Thereafter, the organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (ether) to give **3c** (1.0 g, 29%) as colorless plates, mp 175–176 °C (Found: C, 68.06; H, 4.38. $C_{26}H_{20}BrOP$ requires C, 67.99; H, 4.39%). ν_{max} (KBr)/cm^{-1} 3050, 2920, 1530, 1392, 1108, 747, 717, 692, 520, 508; δ_H (270 MHz, $CDCl_3$) 4.04 (1H, d, $^2J_{P-H}$ 24.7 Hz), 7.11 (1H, m), 7.26 (1H, m), 7.45–7.60 (11H, m), 7.72–7.81 (6H, m); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 54.93 ($^1J_{C=P}$ 104.9 Hz), 119.87 (C_{quat}), 126.56 (C_{quat}, $^1J_{C-P}$ 90.2 Hz), 126.74 (CH, 2C), 128.88 (CH, J_{C-P} 12.2 Hz), 129.24 (CH), 132.19 (CH, J_{C-P} 3.6 Hz), 132.87 (CH), 133.22 (CH, 10.9 Hz), 145.43 (C_{quat}, J_{C-P} 15.8 Hz), 186.76 (J_{C-P} 3.7 Hz, C=O, C_{quat}); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 461 ($^{81}BrMH^+$, 100%), 459 ($^{79}BrMH^+$, 100), 303 (47); MS (70 eV) *m*/*z* 460 ($^{81}BrM^+$, 50%), 458 ($^{79}BrM^+$, 50); HRMS found: 460.0403; calcd. for $C_{26}H_{20}O^{81}BrP$: 460.0418; found: 458.0439; calcd. for $C_{26}H_{20}O^{79}BrP$: 458.0435.

p-Iodophenylcarbonylmethylidenetriphenylphosphorane (3e)

(*p*-Bromoacetyl)iodobenzene (3.01 g, 9.26 mmol) and triphenylphosphine (2.70 g, 10.31 mmol) in chloroform (15 mL) were reacted as above to give hygroscopic *p*-iodobenzoylmethyltriphenylphosphonium bromide, which, after filtration, was immediately transferred to a second flask where it was reacted with aq. 10 w% Na_2CO_3 (37 mL). After the reaction mixture had been extracted with chloroform, dried and concentrated *in vacuo*, the residue was subjected to column chromatography on silica gel (ether⟶ether–chloroform 1 : 1) to give **3e** (1.88 g, 40%); R_f 0.42 (ether); mp 217–218 °C (ether) (Found: C, 61.19; H, 4.02. $C_{26}H_{20}OPI$ requires C, 61.68; H, 3.98%). ν_{max} (KBr)/cm^{-1} 3052, 1576, 1513, 1482, 1436, 1399, 1376, 1177, 1105, 1070, 1004, 885, 742, 691; δ_H (270 MHz, $CDCl_3$) 4.39 (1H, d, $^2J_{P-H}$ 23.8 Hz), 7.43–7.50 (6H, m), 7.54–7.58 (3H, m), 7.66–7.74 (10H, m); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 51.20 ($^1J_{C=P}$ 112.1 Hz), 95.83 (C_{quat}), 126.73 (C_{quat}, $^1J_{C-P}$ 91.3 Hz), 128.82 (CH), 128.91 (CH, J_{C-P} 12.2 Hz), 132.16 (CH, J_{C-P} 4.1 Hz), 133.10 (CH, J_{C-P} 10.9 Hz), 136.80 (CH), 140.70 (C_{quat}, J_{C-P} 14.6 Hz), 183.60 (C_{quat}, J_{C-P} 3.7 Hz, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 507 (MH^+, 100%), 303 (28); HRMS found: 507.0374; calcd. for $C_{26}H_{21}OPI$: 507.0375 (MH^+).

4′-Methoxybiphenyl-4-ylcarbonylmethylidenetriphenylphosphorane (4a)—general procedure A

Method 1. A mixture of *p*-bromobenzoylmethylidenephosphorane (**3a**) (448 mg, 0.97 mmol), *p*-methoxyphenylboronic acid (297 mg, 1.95 mmol) and tetrakis(triphenylphosphine)palladium(0) (27 mg, 2.3 × 10^{-2} mmol) in 1,2-dimethoxyethane (DME) (5 mL) and 2 M aq. Na_2CO_3 (3.7 mL) was heated at 75 °C for 5 h. Thereafter the cooled solution was diluted with water (10 mL) and extracted with ether (10 mL) and chloroform (2 × 15 mL). The combined organic phase was washed with water, dried over $MgSO_4$ and concentrated *in vacuo*. Addition of ether (15 mL) to the residue led to precipitation of **4a** (304 mg, 64%) as a colorless powder, mp 231 °C (ether) (Found: C, 81.50; H, 5.66. $C_{33}H_{27}O_2P$ requires C, 81.46; H, 5.59%). ν_{max} (KBr)/cm^{-1} 3050, 1604, 1580, 1563, 1505, 1481, 1438, 1384, 1253, 1181, 1103, 882, 837, 744, 717, 690; δ_H (270 MHz, $CDCl_3$) 3.84 (3H, s, OCH_3), 4.47 (1H, d, $^2J_{H-P}$ 24.4 Hz), 6.97 (2H, d, ^3J 8.9 Hz), 8.02 (2H, d, ^3J 8.2 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 50.65 (CH, $^1J_{C=P}$ 112 Hz), 55.34, 114.14 (CH), 126.02 (CH), 127.10 (C_{quat}, J_{C-P} 91.5 Hz), 127.40 (CH), 128.16 (CH), 128.87 (CH, J_{C-P} 12.2 Hz), 132.04 (CH, J_{C-P} 2.4 Hz), 133.17 (CH, J_{C-P} 9.8 Hz), 133.55 (C_{quat}), 139.48 (C_{quat}, J_{C-P} 14.6 Hz), 141.63 (C_{quat}), 159.17 (C_{quat}), 184.42 (C=O, $^2J_{C-P}$ 3.6 Hz); MS (70 eV) *m*/*z* 486 (M^+, 100%), 457 (M^+ − CHO, 21), 303 ([M^+ − *p*-MeO-Ph-Ph], 70); HRMS found: 486.1748; calcd. for $C_{33}H_{27}O_2P$: 486.1749.

Method 2. A mixture of **3a** (153 mg, 0.33 mmol), *p*-methoxyphenylboronic acid (100 mg, 0.66 mmol), caesium fluoride (200 mg, 1.32 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0 × 10^{-3} mmol) in DME (4 mL) was held at reflux for 3 h. The cooled solution was diluted with water (10 mL) and extracted with chloroform (3 × 10 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography on silica gel [eluant: ether⟶ether–ethyl acetate (1 : 10)] gave **4a** (142 mg, 89%).

Method 3. A mixture of **3a** (153 mg, 0.33 mmol), *p*-methoxyphenylboronic acid trimethyleneglycol ester (127 mg, 0.66 mmol), $Pd(PPh_3)_4$ (10 mg, 9.0 × 10^{-3} mmol), dry K_3PO_4 (212 mg, 1.00 mmol) in dry DMF (5 mL) was held at 100 °C for 4 h. Thereafter, the cooled mixture was poured into water (75 mL) and extracted with chloroform (3 × 20 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (ether) to give **4a** (100 mg, 62%).

Biphenyl-4-ylcarbonylmethylidenetriphenylphosphorane (4b)

Method A. A mixture of **3a** (448 mg, 0.97 mmol), phenylboronic acid (238 mg, 1.95 mmol), $Pd(PPh_3)_4$ (27 mg, 2.3 × 10^{-2} mmol) in DME (5 mL) and 2 M aq. Na_2CO_3 (3.7 mL) was reacted as above (procedure A). After concentration of the organic phase *in vacuo*, the residue was subjected to chromatography on silica gel (eluant ether) to give **4b** (287 mg, 65%) as a colorless solid, mp 242–244 °C (ether) (Found: C, 84.31; H, 5.55. $C_{32}H_{25}OP$ requires C, 84.19; H, 5.52%). ν_{max} (KBr)/cm^{-1} 3028, 1567, 1509, 1481, 1436, 1408, 1388, 1102, 880, 746, 693; δ_H (270 MHz, $CDCl_3$) 2.40 (3H, s, CH_3), 3.87 (3H, s, OCH_3), 7.01 (2H, d, ^3J 8.6 Hz), 7.24 (2H, d, ^3J 9.2 Hz), 7.58–7.67 (6H, m), 7.69 (2H, d, ^3J 8.2 Hz), 7.83 (1H, d, ^3J 15.8 Hz), 8.09 (2H, d, ^3J 8.2 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 50.82 (CH, $^1J_{C=P}$ 112 Hz), 126.44 (CH), 127.15 (CH), 127.27 (CH), 127.42 (CH), 128.27 (C_{quat}, J_{C-P} 84 Hz), 128.74 (CH, J_{C-P} 7.3 Hz), 132.03 (CH), 132.07 (CH), 133.17 (CH, J_{C-P} 9.8 Hz), 140.07 (C_{quat}, J_{C-P} 14.6 Hz), 141.00 (C_{quat}), 142.03 (C_{quat}), 184.35 (C=O, $^2J_{C-P}$ 3.6 Hz); MS (70 eV) *m*/*z* 456 (M^+, 100%), 303 (Ph_3PCHCO^+, 72); HRMS found: 456.1640; calcd. for $C_{32}H_{25}OP$: 456.1643.

Method B (variant D). A mixture of **3a** (108 mg, 0.21[5] mmol), phenylboronic acid (53 mg, 0.43 mmol), $NaHCO_3$ (44 mg, 0.52 mmol), tetrabutylammonium chloride (71 mg, 0.25[5] mmol) and $Pd(OAc)_2$ (12 mg, 5.3 × 10^{-2} mmol) in chloroform (1.5 mL) was stirred for 72 h at rt. Thereafter water

(5 mL) was added and the mixture was extracted with chloroform (3 × 10 mL). The combined organic phase was washed with water (2 × 5 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give a residue, which was subjected to column chromatography on silica gel (ether) to give **4b** (88 mg, 91%).

p-(*m*-Methoxyphenyl)benzoylmethylidenetriphenylphosphorane (4c)

A mixture of **3a** (263 mg, 0.57 mmol), *m*-methoxyphenylboronic acid (148 mg, 0.97 mmol), $Pd(PPh_3)_4$ (21 mg, 1.7×10^{-2} mmol) in 2 M Na_2CO_3 (2.3 mL) and DME (3.5 mL) was held at reflux for 9 h. Thereafter the cooled reaction mixture was worked up according to procedure A. Column chromatography on silica gel (ether⟶ethyl acetate–ether 1 : 9) gave **4c** (246 mg, 89%) as a slightly yellow solid, mp 72–74 °C (ether); R_f 0.17 (ether–ethyl acetate 1 : 9) (Found: C, 81.31; H, 5.68. $C_{33}H_{27}O_2P$ requires: C, 81.46; H, 5.59%); ν_{max} (KBr)/cm^{-1} 3052, 2956, 1602, 1569, 1511, 1403, 1383, 1106, 884, 692; δ_H (270 MHz, $CDCl_3$, H–H-COSY) 3.86 (3H, s, OCH_3), 4.46 (1H, d, $^2J_{P-H}$ 24.4 Hz), 8.04 (2H, d, ^3J 8.6 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 50.81 ($^1J_{C-P}$ 110.8 Hz, CH), 55.33 (OCH_3), 112.79 (J_{C-P} 4.9 Hz, CH), 119.71 (CH), 126.56 (CH), 127.10 (C_{quat}, $^1J_{C-P}$ 91.3 Hz), 127.40 (CH), 128.89 (CH, J_{C-P} 12.1 Hz), 129.68 (CH), 132.05 (CH, J_{C-P} 2.4 Hz), 133.19 (CH, J_{C-P} 9.8 Hz), 140.16 (C_{quat}, J_{C-P} 14.6 Hz), 141.88 (C_{quat}), 142.57 (C_{quat}), 159.91 (C_{quat}), 184.35 ($^2J_{C-P}$ 3.6 Hz, C_{quat}); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 487 (MH^+, 100%). HRMS found: 487.1832; calcd. for $C_{33}H_{28}O_2P$: 487.1827 (MH^+).

4-(*p*-Fluorophenyl)benzoylmethylidenetriphenylphosphorane (4d)

A mixture of **3a** (153 mg, 0.33 mmol), *p*-fluorophenylboronic acid (93 mg, 0.65 mmol) and $Pd(PPh_3)_4$ (12.7 mg, 1.1×10^{-2} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 5 h. Work-up according to general procedure A and column chromatography on silica gel (eluant: ether) gave **4d** (106 mg, 68%) as a colorless solid, mp; R_f 0.21 (Found: C, 80.82; H, 5.17. $C_{32}H_{24}OFP$ requires C, 81.00; H, 5.10%); ν_{max} (KBr)/cm^{-1} 3032, 2924, 1599, 1510, 1401, 1385, 1103, 880, 827, 691, 522, 505; δ_H (270 MHz, $CDCl_3$) 4.47 (1H, d, $^3J_{P-H}$ 23.1 Hz), 7.11 (3H, t, ^3J 8.5 Hz), 7.44–7.60 (6H, m), 7.73–7.83 (12H, m), 8.04 (2H, d, ^3J 7.9 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 50.80 (+, CH, $^1J_{C-P}$ 112.3 Hz), 115.55 (+, CH, *J* 20.7 Hz), 126.34 (+, CH), 127.49 (+, CH), 128.28 (C_{quat}, J_{C-P} 70.7 Hz), 128.68 (+, CH), 132.07 (+, CH, J_{C-P} 2.4 Hz), 133.09 (+, CH, 12.1 Hz), 133.18 (+, CH, J_{C-P} 10.9 Hz), 137.18 (C_{quat}), 140.14 (C_{quat}, J_{C-P}, 14.6 Hz), 141.02 (C_{quat}), 162.49 (C_{quat}, J_{C-F} (−) 245 Hz), 184.25 (C_{quat}, C=O, $^2J_{C-P}$ 2.4 Hz); MS (70 eV) *m*/*z* 474 (M^+, 100%), 303 (Ph_3PCHCO^+, 66), 277 (85), 262 (41). HRMS found: 474.1552; calcd. for $C_{32}H_{24}OFP$: 474.1549.

4-(2,4-Difluorophenyl)benzoylmethylidenetriphenylphosphorane (4e)

A mixture of **3a** (153 mg, 0.33 mmol), 2,4-difluorophenylboronic acid (104 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 5 h. Work-up according to general procedure A and column chromatography on silica gel (ether) gave **4e** (108 mg, 66%) as colorless rhombic crystals, mp 190–192 °C (ether) (Found: C, 77.97; H, 4.75. $C_{32}H_{23}OF_2P$ requires C, 78.04; H, 4.71%); ν_{max} (KBr)/cm^{-1} 3052, 2924, 1598, 1573, 1514, 1492, 1481, 1436, 1401, 1385, 1103, 885, 846, 714; δ_H (270 MHz, $CDCl_3$) 4.48 (1H, d, $^2J_{P-H}$ 24.1 Hz), 6.92 (2H, m), 7.37–7.77 (18H, m), 8.04 (2H, d, ^3J 7.9 Hz); δ_C (67.8 MHz) 51.23 ($^1J_{C-P}$ 112.3 Hz), 104.33 ($^2J_{C-F}$ 25.6, $^2J_{C-F}$ 25.6 Hz), 111.48 ($^2J_{C-F}$ 20.7, $^4J_{C-F}$ 3.7 Hz), 127.02 (J_{C-P} 90.2 Hz), 127.13, 128.35 (J_{C-P} 2.4 Hz), 128.91 (J_{C-P} 12.1 Hz), 132.09, 133.28 (J_{C-P} 9.0 Hz), 133.45, 135.88, 140.61 (*J* 14.6 Hz), 159.21 ($^1J_{C-F}$ 169.7, $^3J_{C-F}$ 12.2 Hz), 162.89 ($^1J_{C-F}$ 166.3, $^3J_{C-F}$ 11.0 Hz), 184.25 ($^2J_{C-P}$ 2.4 Hz, C=O); MS (70 eV) *m*/*z* 492 (M^+, 100%), 463 (19), 303 (Ph_3PCHCO^+, 72). HRMS found: 492.1458; calcd. for $C_{32}H_{23}OF_2P$: 492.1455.

4-(*p*-Vinylphenyl)benzoylmethylidenetriphenylphosphorane (4i)

A mixture of **3a** (153 mg, 0.33 mmol), 4-vinylphenylboronic acid (97 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 5 h. Work-up according to general procedure A and column chromatography on silica gel (ether) gave **4i** (111 mg, 70%) as a pale yellow solid, R_f 0.29 (ether); mp 216–218 °C (ether) (Found: C, 84.02; H, 5.82. $C_{34}H_{27}OP{\cdot}0.25H_2O$ requires C, 83.84; H, 5.69%); ν_{max} (KBr)/cm^{-1} 1475, 1375, 1175, 1095, 880, 825, 740, 685; δ_H (270 MHz, $CDCl_3$) 4.46 (1H, br s), 5.26 (1H, d, $^3J_{cis}$ 10.8 Hz), 5.79 (1H, d, $^2J_{trans}$ 17.8 Hz), 6.75 (1H, dd, $^3J_{trans}$ 17.8, $^3J_{cis}$ 10.8 Hz), 7.46–7.77 (21H, m), 8.04 (2H, d, ^3J 8.3 Hz); δ_C NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 50.91 (CH, $^1J_{C-P}$ 112.3 Hz), 113.83 (−), 126.31 (CH), 126.59 (CH), 127.09 (C_{quat}, $^1J_{C-P}$ 90.3 Hz), 127.22 (CH), 127.45 (CH), 128.89 (CH, J_{C-P} 12.2 Hz), 132.07 (CH, J_{C-P} 2.5 Hz), 133.19 (CH, J_{C-P} 9.7 Hz), 136.46 (CH), 136.63 (C_{quat}), 140.18 (C_{quat}, J_{C-P} 14.6 Hz), 140.37 (C_{quat}), 141.53 (C_{quat}), 184.35 (C_{quat}, C=O, $^2J_{C-P}$ 3.6 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 483 (MH^+, 84%). HRMS found: 483.1877; calcd. for $C_{34}H_{28}OP$: 483.1878 (MH^+).

p-(2-Thienyl)benzoylmethylidenetriphenylphosphorane (4j)

A mixture of **3a** (448 mg, 0.97 mmol), 2-thienylboronic acid (250 mg, 1.95 mmol), $Pd(PPh_3)_4$ (27 mg, 2.3×10^{-2} mmol) in DME (5 mL) and 2 M aq. Na_2CO_3 (3.7 mL) was reacted as above (procedure A). After concentration of the organic phase *in vacuo*, the residue was subjected to column chromatography on silica gel (eluant ether) to give **3a** (starting material; 32%), R_f 0.31, and **4j** (264 mg, 58%), R_f 0.16, mp 199–201 °C (ether) (Found: C, 77.66; H, 5.08. $C_{30}H_{23}OPS$ requires C, 77.90; H, 5.01%); ν_{max} (KBr)/cm^{-1} 3052, 1604, 1572, 1510, 1480, 1435, 1410, 1390, 1102, 880, 716, 691; δ_H NMR (270 MHz, $CDCl_3$) 4.44 (1H, d, $^2J_{H-P}$ 24.1 Hz), 7.07 (1H, m, thienyl-H), 7.26 (1H, m, thienyl-H), 7.34 (1H, m, thienyl-H), 7.43–7.76 (17H, m), 7.97 (2H, d, ^3J 7.9 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 50.80 (CH, $^1J_{C-P}$ 112 Hz), 123.23 (CH), 124.90 (CH), 125.21 (CH), 127.54 (CH), 127.18 (C_{quat}, J_{C-P} 90.3 Hz), 128.01 (CH), 128.89 (CH, J_{C-P} 12.2 Hz), 132.07, (CH, J_{C-P} 2.5 Hz), 133.16 (CH, J_{C-P} 11.0 Hz), 135.16 (C_{quat}), 140.25 (C_{quat}, J_{C-P} 14.6 Hz), 144.38 (C_{quat}), 184.04 (C=O, $^2J_{C-P}$ 2.5 Hz); MS (70 eV) *m*/*z* 462 (M^+, 100%), 303 ([M^+ − Thienyl-Ph], 73); HRMS found: 462.1209; calcd. for $C_{30}H_{23}OPS$: 462.1207.

p-(*p*-Trifluoromethylphenyl)benzoylmethylidenetriphenylphosphorane (4k)

A mixture of **3a** (263 mg, 0.57 mmol), *p*-trifluoromethylphenylboronic acid (185 mg, 0.97 mmol), and $Pd(PPh_3)_4$ (20 mg, 1.7×10^{-2} mmol) in DME (3.5 mL) and 2 M aq. Na_2CO_3 (2.3 mL) were held at 75 °C for 9 h. Work-up according to procedure A and column chromatography on silica gel (ether⟶ether–ethyl acetate 9 : 1) gave **4k** (180 mg, 60%) as a pale yellow solid; mp 248–250 °C (ether) (Found: C, 75.27; H, 4.81.$C_{33}H_{24}OF_3P$ requires C, 75.57; H, 4.61%); ν_{max} (KBr)/cm^{-1} 3056, 2924, 1613, 1565, 1511, 1437, 1399, 1385, 1327, 1165, 1107, 1069, 885, 832, 750, 712; δ_H (270 MHz, $CDCl_3$) 4.50 (1H, br s), 7.44–7.78 (21H, m), 8.07 (2H, d, ^3J 8.2 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 51.21 (CH, $^1J_{C-P}$ 112.3 Hz), 125.67 (CH, *J* 3.7 Hz), 126.70 (CH), 126.99 (C_{quat}, $^1J_{C-P}$ 90.2 Hz), 127.42 (CH), 127.65 (CH), 128.95 (CH, J_{C-P} 12.1 Hz), 129.57 (C_{quat}, CF_3, $^1J_{C-F}$ (−)270 Hz), 129.80 (C_{quat}), 132.13 (CH, J_{C-P} 2.4 Hz), 133.18 (CH, J_{C-P} 11.0 Hz), 140.46 (C_{quat}), 141.07 (C_{quat}, J_{C-P} 14.7 Hz), 144.56 (C_{quat}), 184.03 (C_{quat}, C=O, $^2J_{C-P}$ 3.7 Hz); MS (FAB, 3-nitrobenzyl alcohol) 525 (MH^+, 100%), 307 (19). HRMS found: 525.1597; calcd. for $C_{33}H_{25}OF_3P$: 525.1595 (MH^+).

p-(2-Naphthyl)benzoylmethylidenetriphenylphosphorane (4l)

A mixture of **3a** (263 mg, 0.57 mmol), 2-naphthylboronic acid (167 mg, 0.97 mmol), and $Pd(PPh_3)_4$ (20 mg, 1.7×10^{-2} mmol) in DME (3.5 mL) and 2 M aq. Na_2CO_3 (2.3 mL) were held at 75 °C for 6 h. Work-up according to procedure A and column chromatography on silca gel (ether⟶ether–ethyl acetate 9 : 1) gave **4l** (261 mg, 90%) as pale yellow needles; mp 205-206 °C (ether); ν_{max} (KBr)/cm^{-1} 3052, 1569, 1517, 1381, 1105, 883, 747, 717, 693; δ_H (270 MHz, $CDCl_3$) 4.52 (1H, br s), 7.44–7.59 (11H, m), 7.70–7.79 (9H, m), 7.83–7.91 (3H, m), 8.11 (3H, m); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 50.87 (CH, $^1J_{C=P}$ 112.07 Hz), 125.60 (CH), 125.78 (CH), 125.89 (CH), 126.23 (CH), 126.77 (CH), 127.14 (C_{quat}, $^1J_{C-P}$ 91.3 Hz), 127.54 (CH), 127.63 (CH), 128.25 (CH), 128.33 (CH), 128.91 (CH, J_{C-P} 12.1 Hz), 132.07 (CH, J_{C-P} 2.4 Hz), 132.68 (C_{quat}), 133.20 (CH, J_{C-P} 9.8 Hz), 133.69 (C_{quat}), 138.36 (C_{quat}), 140.23 (C_{quat}, J_{C-P} 14.6 Hz), 141.92 (C_{quat}), 184.38 (C_{quat}, C=O, $^2J_{C-P}$ 2.4 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 507 (100%, MH$^+$); 303 (28). HRMS found: 507.1882; calcd. for $C_{36}H_{28}OP$: 507.1878 (MH$^+$, FAB).

4-[*p*-(1,3-Dioxan-2-yl)phenyl]benzoylmethylidenetriphenylphosphorane (4m)

A mixture of **3a** (153 mg, 0.33 mmol), *p*-(1,3-dioxan-2-yl)-phenylboronic acid (164 mg, 0.66 mmol), CsF (400 mg, 2.64 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (8 mL) were held at 75 °C for 3 h. The cooled solution was diluted with water (10 mL) and extracted with chloroform (3 × 10 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography on silica gel [eluant: ether⟶ether–ethyl acetate (1.5 : 10)] to give **4m** (64 mg, 36%) as a colorless crystalline solid, mp 120 °C; ν_{max} (KBr)/cm^{-1} 3050, 2964, 2846, 1582, 1565, 1511, 1482, 1436, 1386, 1148, 1102, 1005, 996, 879, 853, 823, 748, 718; δ_H (270 MHz, $CDCl_3$) 2.24 (2H, m), 4.02 (2H, m), 4.28 (2H, dd, ^2J 15.9, ^3J 4.9 Hz), 4.45 (1H, br s), 5.54 (1H, s), 7.45–7.77 (21H, m), 8.03 (2H, d, ^3J 7.9 Hz); δ_C NMR ($CDCl_3$, DEPT 90, DEPT 135) 26.31 (−), 51.19 (CH, $^1J_{C=P}$ 110.8 Hz), 67.82 (−), 101.96 (+, CH), 126.93 (CH, *J* 9.7 Hz), 127.47 (CH), 127.76 (C_{quat}, *J* 90.0 Hz), 127.89 (CH), 128.93 (CH, *J* 12.2 Hz), 129.33 (CH, *J* 12.2 Hz), 132.40 (C_{quat}, *J* 6.1 Hz), 132.58 (CH, *J* 9.7 Hz), 133.67 (CH, *J* 9.8 Hz), 138.33 (C_{quat}), 140.81 (C_{quat}, *J* 14.6 Hz), 142.11 (C_{quat}, *J* 18.3 Hz), 184.94 (C_{quat}, C=O, $^2J_{C-P}$ 2.4 Hz); MS (70 eV) *m*/*z* 277 (100%); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* (%) 543 (MH$^+$, 46). HRMS found: 543.2092; calcd. for $C_{36}H_{32}O_3P$: 543.2089 (MH$^+$).

4-(1-Benzothiophen-2-yl)benzoylmethylidenetriphenylphosphorane (4n)

A mixture of **3a** (153 mg, 0.33 mmol), 1-benzothiophen-2-ylboronic acid (150 mg, 0.84 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 10 h. Work-up according to general procedure A and column chromatography on silica gel (ether) gave **4n** (165 mg, 98%) as a colorless solid, mp 254–256 °C (ether) (Found: C, 79.21; H, 4.94. $C_{34}H_{26}OPS$ requires C, 79.51; H, 5.10%); ν_{max} (KBr)/cm^{-1} 3052, 1602, 1572, 1512, 1436, 1407, 1386, 1105, 881, 761, 745, 717, 691; δ_H (270 MHz, $CDCl_3$) 4.47 (1H, d, $^2J_{P-H}$ 24.1 Hz), 7.27–7.83 (22H, m), 8.03 (2H, d, ^3J 8.3 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 51.01 (CH, $^1J_{C=P}$ 112.5 Hz), 119.64 (CH), 122.24 (CH), 123.57 (CH), 124.31 (CH), 124.47 (CH), 125.84 (CH), 126.92 (C_{quat}, $^1J_{C-P}$ 92.6 Hz), 127.60 (CH), 128.57 (C_{quat}), 128.95 (CH, J_{C-P} 12.1 Hz), 133.12 (CH, br s), 133.19 (CH, J_{C-P} 9.8 Hz), 135.00 (C_{quat}), 139.58 (C_{quat}), 140.70 (C_{quat}), 144.13 (C_{quat}, br s), 183.72 (C_{quat}, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 513 (MH$^+$, 52%), 307 (42), 154 (100). HRMS found: 513.1446 (MH$^+$); calcd. for $C_{34}H_{26}OPS$: 513.1442.

4-(Dibenzo[*b*,*d*]thiophen-3-yl)benzoylmethylidenetriphenylphosphorane (4o)

A mixture of **3a** (153 mg, 0.33 mmol), dibenzothienylboronic acid (150 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) were held at 75 °C for 9 h. Work-up according to general procedure A and column chromatography on silica gel (ether) gave **4o** (158 mg, 85%) as a colorless solid; R_f 0.14 (ether); mp 267–269 °C (ether) (Found: C, 81.05; H, 4.84. $C_{38}H_{28}OPS$ requires C, 80.96; H, 5.00%); ν_{max} (KBr)/cm^{-1} 3054, 1571, 1518, 1480, 1438, 1411, 1386, 1105, 883, 746, 693; δ_H (270 MHz, $CDCl_3$) 4.52 (1H, d, $^2J_{P-H}$ 24.1 Hz), 7.47–7.59 (9H, m), 7.27–7.35 (13H, m), 7.73–8.05 (4H, m); δ_C (67.8 MHz, $CDCl_3$, DEPT 90,DEPT 135) 51.10 (CH, $^1J_{C=P}$ 112.07 Hz), 120.43 (CH), 121.69 (CH), 122.62 (CH), 124.31 (CH), 125.05 (CH), 126.73 (CH), 126.92 (CH), 127.46 (CH), 127.73 (CH), 127.05 (C_{quat}, $^1J_{C-P}$ 91.4 Hz), 128.92 (CH, J_{C-P} 13.4 Hz), 132.11 (CH, J_{C-P} 2.4 Hz), 133.20 (CH, J_{C-P} 18.3 Hz), 135.77 (C_{quat}), 136.21 (C_{quat}), 136.98 (C_{quat}), 138.63 (C_{quat}), 139.68 (C_{quat}), 140.92 (C_{quat}, J_{C-P} 15.9 Hz), 141.51 (C_{quat}), 184.30 (C_{quat}, J_{C-P} 3.7 Hz, C=O); MS (70 eV) *m*/*z* 563 (MH$^+$, 100%), 303 (36). HRMS found: 563.1597 (MH$^+$); calcd. for $C_{38}H_{28}OPS$: 563.1599.

4-[3,5-Bis(trimethylsilylethynyl)phenyl]benzoylcarbonylmethylidenetriphenylphosphorane (4p)

A mixture of **3a** (150 mg, 0.33 mmol), 3,5-bis(trimethylsilylethynyl)phenylboronic acid (314 mg, 1.0 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3.0 mL) and 2 M aq. Na_2CO_3 (1.2 mL) was held at 75 °C for 7 h. Work-up according to general procedure A and column chromatography on silica gel (ether) gave **4p** (34 mg, 16%) as a pale yellow oil; R_f 0.23 (ether); ν_{max} (neat)/cm^{-1} 3058, 2954, 2150, 1656, 1564, 1510, 1438, 1406, 1387, 1249, 1106, 881, 842, 690; δ_H (270 MHz, $CDCl_3$) 0.26 (9H, s, 3 CH_3), 0.28 (9H, s, 3 CH_3), 4.49 (1H, v br s), 7.49–7.76 (20H, m), 7.94 (2H, d, ^3J 7.9 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) −1.26 (+, 6 × CH_3), 51.49 (+, CH, $^1J_{C=P}$ 113.5 Hz), 94.60 (C_{quat}), 104.43 (C_{quat}), 122.80 (C_{quat}), 122.90 (C_{quat}), 123.85 (C_{quat}), 126.92 (C_{quat}, $^1J_{C-P}$ 91.4 Hz), 127.01 (+, CH), 128.98 (+, CH, J_{C-P} 12.2 Hz), 131.19 (+, CH), 132.20 (+, CH), 133.22 (+, CH, J_{C-P} 9.8 Hz), 135.27 (+, CH), 136.26 (+, CH), 141.13 (C_{quat}), 183.99 (C_{quat}, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 649 (MH$^+$, 100%), 303 (22), 275 (23). HRMS found: 649.2515; calcd. for $C_{42}H_{42}OSi_2P$: 649.2512 (MH$^+$).

p-(*o*-Tolyl)benzoylmethylidenetriphenylphosphorane (4q)

A mixture of **3a** (263 mg, 0.57 mmol), *o*-tolylboronic acid (132 mg, 0.97 mmol), $Pd(PPh_3)_4$ (20 mg, 1.7×10^{-2} mmol) in 2 M Na_2CO_3 (2.3 mL) and DME (3 mL) was held at reflux for 5 h. Thereafter the cooled reaction mixture was worked up according to procedure A. Column chromatography on silica gel (ether⟶ether–ethyl acetate 9 : 1) gave **4q** (147 mg, 55%) as colorless needles; mp 261–262 °C (ether) (Found: C, 83.96; H, 5.89. $C_{33}H_{27}OP$ requires C, 84.23; H, 5.79%); ν_{max} (KBr)/cm^{-1} 3056, 1578, 1513, 1481, 1438, 1408, 1386, 1105, 885, 750, 692; δ_H (270 MHz, $CDCl_3$) 2.27 (3H, s, CH_3), 4.47 (1H, d, $^2J_{P-H}$ 24.4 Hz), 7.24 (4H, m), 7.31 (2H, d, ^3J 8.1 Hz), 7.44–7.59 (9H, m), 7.70–7.78 (6H, m), 8.01 (2H, d, ^3J 8.3 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 20.49 (+, CH_3), 50.74 (+, CH, $^1J_{C=P}$ 112.1 Hz), 125.69 (CH), 126.72 (CH), 127.13 (C_{quat}, $^1J_{C-P}$ 90.1 Hz), 127.20 (CH), 128.68 (CH), 128.89 (CH, J_{C-P} 12.1 Hz), 129.74 (CH), 130.28 (CH), 132.06 (CH, J_{C-P} 2.4 Hz), 133.19 (CH, J_{C-P} 9.8 Hz), 135.42 (C_{quat}), 139.79 (C_{quat}, J_{C-P} 13.4 Hz), 141.88 (C_{quat}), 143.02 (C_{quat}), 184.66 (C_{quat}, C=O, $^2J_{C-P}$ 3.7 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 471 (MH$^+$, 100%); HRMS found: 471.1884; calcd. for $C_{33}H_{28}OP$: 471.1878.

1,4-Bis[(triphenylphosphoranylidene)acetyl]benzene (4r)

A mixture of **3a** (459 mg, 1.0 mmol), 1,4-phenylenediboronic acid (83 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (30 mg, 2.5×10^{-2} mmol)

in DME (4 mL) and 2 M aq. Na_2CO_3 (2 mL) was held at 75 °C for 11 h. Thereafter water (10 mL) was added to the cooled reaction mixture and the suspension was extracted with chloroform (3 × 10 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* until about 5 mL of solution remained. To this was added ether (20 mL). The precipitate formed was filtered, washed with ether (10 mL) and dried *in vacuo* to give **4r** (270 mg, 65%) as a greyish powder; ν_{max} (KBr)/cm^{-1} 3052, 1576, 1515, 1388, 885, 755, 718, 692; δ_H (270 MHz, $CDCl_3$) 4.49 (2H, br s), 7.44–7.77 (34H, m), 7.70 (4H, s), 8.06 (4H, d, ^3J 8.2 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 51.47 (CH, $^1J_{C=P}$ 112.07 Hz), 126.85 (CH), 127.91 (CH), 127.52 (C_{quat}, $^1J_{C-P}$ 91.4 Hz), 129.34 (CH, J_{C-P} 12.2 Hz), 132.52 (CH, J_{C-P} 13.4 Hz), 133.64 (CH, J_{C-P} 9.8 Hz), 140.39 (C_{quat}), 140.59 (C_{quat}, J_{C-P} 14.6 Hz), 142.01 (C_{quat}), 184.84 (C_{quat}, C=O, $^2J_{C-P}$ 3.7 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 835 (MH^+, 5%). HRMS found: 835.2893; calcd. for $C_{58}H_{45}O_2P_2$: 835.2895 (MH^+).

5-Phenyl-2-thienylcarbonylmethylidenetriphenylphosphorane (5a)

A mixture of **3b** (153 mg, 0.33 mmol), phenylboronic acid (80 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 11 h. Work-up according to general procedure A and column chromatography on silica gel (ether) gave **5a** (95 mg, 62%) as a yellow solid; mp 194–196 °C (ether) (Found: C, 77.60; H, 4.99. $C_{30}H_{23}OPS$ requires C, 77.91; H, 5.01%); ν_{max} (KBr)/cm^{-1} 3052, 1539, 1519, 1481, 1453, 1438, 1386, 1107, 870, 748, 732, 714, 691; δ_H (270 MHz, $CDCl_3$) 4.31 (1H, d, $^2J_{H-P}$ 22.8 Hz), 7.25 (2H, m), 7.33 (2H, m), 7.47–7.75 (18H, m); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 50.14 (+, CH, $^1J_{C=P}$ 113.7 Hz), 122.32 (+, CH), 125.96 (+, CH), 127.01 (+, CH), 127.23 (C_{quat}, $^1J_{C=P}$ 91.6 Hz), 127.49 (+, CH), 128.96 (+, CH, J_{C-P} 13.4 Hz), 132.16 (+, CH, J_{C-P} 2.4 Hz), 133.31 (+, CH, J_{C-P} 9.8 Hz), 134.98 (C_{quat}), 145.84 (C_{quat}), 147.88 (C_{quat}, J_{C-P} 18.3 Hz), 178.32 (C_{quat}, C=O, $^2J_{C-P}$ 3.7 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 463 (MH^+, 41%). HRMS found: 463.1278; calcd. for $C_{30}H_{24}OPS$: 463.1286.

5-(*p*-Methoxyphenyl)-2-thienylcarbonylmethylidenetriphenylphosphorane (5b)

A mixture of **3b** (154 mg, 0.33 mmol), *p*-methoxyphenylboronic acid (150 mg, 1.0 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 5 h. Work-up according to general procedure A and column chromatography on silica gel [eluant: ether⟶ethyl acetate–ether (1 : 10)] gave **5b** (117 mg, 72%) as a pale yellow solid, mp 205–207 °C (ether) (Found: C, 75.07; H, 5.26. $C_{31}H_{25}O_2PS{\cdot}0.25H_2O$ requires C, 74.91; H, 5.17%); ν_{max} (KBr)/cm^{-1} 3050, 2836, 1516, 1452, 1438, 1387, 1251, 1104, 730, 693, 505; δ_H (270 MHz, $CDCl_3$) 3.82 (3H, s, OCH_3), 4.23 (1H, ill-resolved d), 6.89 (2H, d, ^3J 8.9 Hz), 7.12 (1H, d, ^3J 3.6 Hz), 7.26–7.59 (12H, m), 7.67–7.76 (6H, m); δ_C (67.8 MHz, $CDCl_3$) 50.05 ($^1J_{C=P}$ 112.1 Hz), 55.33 (OCH_3), 114.23, 122.26, 126.27, 127.04, 127.64, 128.89 (J_{C-P} 12.2 Hz), 132.11, 133.18 (J_{C-P} 11.0 Hz), 145.76, 146.57 (J_{C-P} 18.2 Hz), 159.26, 178.26 ($^2J_{C-P}$ 3.7 Hz, C=O); MS (70 eV) *m*/*z* 492 (M^+, 100%), 303 (Ph_3PCHCO^+, 56), 291 (49), 262 (51), 232 (50), 183 (63). HRMS found: 493.1393; calcd. for $C_{31}H_{26}O_2PS$: 493.1391 (MH^+).

5-(*p*-Fluorophenyl)-2-thienylcarbonylmethylidenetriphenylphosphorane (5c)

A mixture of **3b** (154 mg, 0.33 mmol), *p*-fluorophenylboronic acid (93 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 5 h. The reaction mixture was poured into water and extracted with chloroform (3 × 30 mL). The organic phase was dried and concentrated *in vacuo*. The residue was recrystallized in ether to give **5c** (91 mg, 57%) as yellow crystals, mp 210–216 °C (Found C, 73.42; H, 5.12. $C_{30}H_{22}OSFP{\cdot}0.5H_2O$ requires C, 73.60; H, 4.73%); ν_{max} (KBr)/cm^{-1} 3045, 2900, 1500, 1430, 1370, 1217, 1155, 1095, 863, 840, 798, 685; δ_H (270 MHz, $CDCl_3$) 4.31 (1H, ill-resolved d), 7.04 (2H, dd, ^3J 8.9, ^3J 8.6 Hz), 7.15 (1H, d, ^3J 2.5 Hz), 7.26–7.75 (18H, m); δ_C (67.9 MHz, $CDCl_3$) 50.45 ($^1J_{C=P}$ 113.5 Hz), 123.27, 126.16, 128.96 (J_{C-P} 12.1 Hz), 132.20 (J 2.4 Hz), 133.21 (J_{C-P} 9.8 Hz), 144.61, 147.74 (J 17.1 Hz), 162.37 ($^1J_{C-F}$ 246.1 Hz), 178.02 ($^2J_{C-P}$ 4.9 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 481 (MH^+, 100%), 303 (Ph_3PCHCO^+, 20). HRMS found: 481.1190; calcd. for $C_{30}H_{23}OFPS$: 481.1191 (MH^+).

5-(2,4-Difluorophenyl)-2-thienylcarbonylmethylidenetriphenylphosphorane (5e)

A mixture of **3b** (77 mg, 0.17 mmol), 2,4-difluorophenylboronic acid (93 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 5 h. Work-up according to general procedure A and column chromatography on silica gel (ether) gave **5e** (64 mg, 78%) as a pale yellow solid, mp 202–203 °C (ether), R_f 0.38 (ether); ν_{max} (KBr)/cm^{-1} 3050, 1505, 1440, 1380, 1105, 880; δ_H (270 MHz, $CDCl_3$) 4.33 (1H, d, ^2J 22.1 Hz), 6.88 (2H, m), 7.32 (1H, d, ^3J 3.6 Hz), 7.46–7.75 (17H, m); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 50.61 (CH, $^1J_{C=P}$ 113.4 Hz), 104.60 (CH, J_{C-F} 25.6, J_{C-F} 25.6 Hz), 111.73 (CH, J_{C-F} 20.7, J_{C-F} 3.6 Hz), 126.42 (C_{quat}) 126.50 (CH), 126.63 (CH), 126.80 (C_{quat}, $^1J_{C-P}$ 91.6 Hz), 128.96 (CH, J_{C-P} 12.2 Hz), 129.68 (CH, J 9.7, J 4.8 Hz), 132.22 (CH, J_{C-P} 2.5 Hz), 133.21 (CH, J_{C-P} 9.8 Hz), 137.57 (C_{quat}), 148.36 (C_{quat}, J 20.7 Hz), 158.75 (C_{quat}, J_{C-F} 183.8, J_{C-F} 12.1 Hz), 162.41 (C_{quat}, $^1J_{C-F}$ 182.3, $^3J_{C-F}$ 12.1 Hz), 177.89 (C_{quat}, $^2J_{C-P}$ 4.9 Hz, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 499 (MH^+, 100%), 303 (Ph_3PCHCO^+, 24). HRMS found: 499.1093; calcd. for $C_{30}H_{22}OF_2PS$: 499.1097.

5-(*p*-Vinylphenyl)-2-thienylcarbonylmethylidenetriphenylphosphorane (5f)

A mixture of **3b** (69 mg, 0.15 mmol), *p*-vinylphenylboronic acid (44 mg, 0.29 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (1.5 mL) and 2 M aq. Na_2CO_3 (0.6 mL) was held at 75 °C for 5 h. Work-up according to general procedure A and column chromatography on silica gel [ether⟶ethyl acetate–ether (1 : 4)] gave **5f** (69 mg, 95%) as a yellow solid, mp 221–223 °C (ether); ν_{max} (KBr)/cm^{-1} 3050, 1509, 1450, 1436, 1387, 1105, 874, 692, 505; δ_H (270 MHz, $CDCl_3$) 4.32 (1H, br s), 5.24 (1H, d, ^3J 10.9 Hz), 5.75 (1H, d, ^3J 17.5 Hz), 6.71 (1H, dd, ^3J 17.5, ^3J 10.9 Hz), 7.25 (1H, m), 7.38–7.60 (16H, m), 7.69 (2H, d, ^3J 7.9 Hz), 7.74 (2H, d, ^3J 7.6 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 50.34 (CH, $^1J_{C=P}$ 113.3 Hz), 113.75 (−, CH_2), 122.27 (CH), 125.89 (CH), 126.68 (CH), 127.01 (C_{quat}, $^1J_{C-P}$ 91.4 Hz), 127.04 (CH), 128.93 (CH, J_{C-P} 12.2 Hz), 132.15 (CH, J_{C-P} 2.4 Hz), 133.23 (CH, J_{C-P} 10.9 Hz), 134.27 (C_{quat}), 136.41 (CH), 136.85 (C_{quat}), 145.43 (C_{quat}), 147.49 (C_{quat}, J_{C-P} 17.7 Hz), 178.13 (C_{quat}, $^2J_{C-P}$ 3.7 Hz, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 489 (MH^+, 100%), 303 (40). HRMS found: 489.1449; calcd. for $C_{32}H_{26}OPS$: 489.1442 (MH^+).

5-(Dibenzo[*b*,*d*]thiophen-3-yl)-2-thienylcarbonylmethylidenetriphenylphosphorane (5h)

A mixture of **3b** (153 mg, 0.33 mmol), dibenzothienylboronic acid (150 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 12 h. Work-up according to general procedure A and column chromatography on silica gel (ether) gave **5h** (124 mg, 66%) as a yellow solid (Found: C, 75.95; H, 4.57. $C_{36}H_{25}OPS_2$ requires C, 76.03; H, 4.43%); ν_{max} (KBr)/cm^{-1} 3056, 1539, 1516, 1480, 1461, 1436, 1382, 1106, 885, 745, 732, 714;

δ_H (270 MHz, $CDCl_3$) 4.36 (1H, d, $^2J_{P-H}$ 22.8 Hz), 7.42–7.79 (22H, m), 7.87 (1H, m), 8.09 (1H, d, ^3J 9.0 Hz), 8.16 (1H, m); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 50.65 (+, CH, $^1J_{C-P}$ 113.3 Hz), 120.59 (+, CH), 121.65 (+, CH), 122.61 (+, CH), 124.44 (+, CH), 124.92 (+, CH), 125.88 (+, CH), 126.41 (+, CH), 126.70 (+, CH), 126.82 (C_{quat}, $^1J_{C-P}$ 91.3 Hz), 126.85 (+, CH), 128.93 (+, CH, J_{C-P} 12.2 Hz), 130.22 (C_{quat}), 132.17 (+, CH, J_{C-P} 3.7 Hz), 133.20 (+, CH, J_{C-P} 10.9 Hz), 135.54 (C_{quat}), 136.57 (C_{quat}), 137.52 (C_{quat}), 139.57 (C_{quat}), 143.79 (C_{quat}), 148.35 (C_{quat}, J_{C-P} 18.2 Hz), 177.96 (C_{quat}, $^2J_{C-P}$ 3.6 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 569 (MH^+, 100%), 303 (50). HMRS found: 569.1171; calcd. for $C_{36}H_{26}OPS_2$: 569.1163 (MH^+).

5-(1-Benzothiophen-2-yl)-2-thienylcarbonylmethylidenetriphenylphosphorane (5i)

A mixture of **3b** (153 mg, 0.33 mmol), 1-benzothiophen-2-ylboronic acid (120 mg, 0.67 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 9 h. Work-up according to general procedure A and column chromatography on silica gel (ether) gave **5i** (84 mg, 49%) as a yellow solid; R_f 0.14 (ether); mp 222–225 °C (ether) (Found: C, 74.02; H, 4.55. $C_{32}H_{23}OPS_2$ requires C, 74.07; H, 4.47%); ν_{max} (KBr)/cm^{-1} 3052, 1524, 1508, 1435, 1388, 1105, 871, 744, 731, 714, 692; δ_H (270 MHz, $CDCl_3$) 4.31 (1H, d, $^2J_{H-P}$ 22.8 Hz), 7.20 (1H, d, ^3J 3.6 Hz), 7.23–7.75 (21H, m); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 50.72 (+, CH, $^1J_{C-P}$ 113.3 Hz), 119.69 (+, CH), 122.05 (+, CH), 123.40 (+, CH), 124.37 (+, CH), 124.56 (+, CH), 125.19 (+, CH), 126.65 (+, CH), 126.71 (C_{quat}, $^1J_{C-P}$ 91.3 Hz), 128.93 (+, CH, J_{C-P} 12.2 Hz), 132.22 (+, CH), 133.15 (+, CH, J_{C-P} 9.7 Hz), 137.77 (C_{quat}), 138.62 (C_{quat}), 139.19 (C_{quat}), 140.40 (C_{quat}), 148.53 (C_{quat}, J_{C-P} 18.3 Hz), 177.60 (C_{quat}, C=O, $^2J_{C-P}$ 3.7 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 519 (MH^+, 28%). HRMS found: 519.1004; calcd. for $C_{32}H_{24}OPS_2$: 519.1006 (MH^+).

5-(2-Naphthyl)-2-thienylcarbonylmethylidenetriphenylphosphorane (5j)

A mixture of **3b** (153 mg, 0.33 mmol), 2-naphthylboronic acid (114 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 12 h. Work-up according to general procedure A and column chromatography on silica gel (ether) gave **5j** (122 mg, 72%) as a yellow solid; mp 248–249 °C (ether); R_f 0.12 (ether) (Found: C, 79.46; H, 5.05. $C_{34}H_{25}OPS$ requires C, 79.66; H, 4.90%); ν_{max} (KBr)/cm^{-1} 3050, 1542, 1511, 1476, 1438, 1381, 1147, 1105, 1080, 871, 853, 813, 732, 716, 692; δ_H (270 MHz, $CDCl_3$) 4.31 (1H, d, $^2J_{H-P}$ 23.1 Hz), 7.36 (1H, d, ^3J 3.9 Hz), 7.40–7.83 (25H, m), 8.06 (1H, s); δ_C ($CDCl_3$, 67.8 MHz, DEPT 90, DEPT 135) 50.12 (C_{quat}, $^1J_{C=P}$ 113.4 Hz), 123.68 (+, CH), 124.24 (+, CH), 124.40 (+, CH), 125.89 (+, CH), 126.45 (+, CH), 127.12 (+, CH), 127.16 (C_{quat}, $^1J_{C-P}$ 96.5 Hz), 127.69 (+, CH), 128.12 (+, CH), 128.44 (+, CH), 128.93 (+, CH, J_{C-P} 12.2 Hz), 132.13 (+, CH, J_{C-P} 2.4 Hz), 132.34 (C_{quat}), 132.92 (C_{quat}), 133.28 (+, CH J_{C-P} 9.8 Hz), 133.78 (C_{quat}), 145.79 (C_{quat}), 148.01 (C_{quat}, J_{C-P} 17.1 Hz), 178.24 (C_{quat}, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 513 (MH^+, 100%), 303 (36). HRMS found: 513.1439; calcd. for $C_{34}H_{26}OPS$: 513.1442 (MH^+).

5-(*o*-Tolyl)-2-thienylcarbonylmethylidenetriphenylphosphorane (5k)

A mixture of **3b** (153 mg, 0.33 mmol), *o*-tolylboronic acid (88 mg, 0.65 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 6h. Work-up according to general procedure A and column chromatography on silica gel (ether) gave **5k** (88 mg, 56%) as a pale yellow solid; mp 172 °C (ether); ν_{max} (KBr)/cm^{-1} 3058, 1539, 1517, 1483, 1455, 1436, 1394, 1246, 1181, 1106, 1037, 866, 747, 734, 718; δ_H (270 MHz, $CDCl_3$) 1.75 (3H, s, CH_3), 4.31 (1H, d, $^2J_{P-H}$ 23.1 Hz), 6.98 (1H, d, ^3J 4.0 Hz), 7.19–7.76 (20H, m); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 21.08 (+, CH_3), 50.23 (+, CH, $^1J_{C=P}$ 113.5 Hz), 125.84 (+, CH), 126.13 (+, CH), 126.74 (+, CH), 126.87 (C_{quat}, $^1J_{C-P}$ 91.5 Hz), 127.69 (+, CH), 128.66 (C_{quat}), 128.91 (+, CH, J_{C-P} 12.2 Hz), 130.28 (+, CH), 130.69 (+, CH), 132.13 (+, CH, J_{C-P} 2.4 Hz), 133.17 (+, CH, J_{C-P} 9.8 Hz), 136.05 (C_{quat}), 144.83 (C_{quat}), 147.90 (C_{quat}, J 17.1 Hz), 178.29 (C_{quat}, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 477 (MH^+, 28%). HRMS found: 477.1440; calcd. for $C_{31}H_{26}OPS$: 477.1442.

(2,2′-Bithiophen-5-yl)carbonylmethylidenetriphenylphosphorane (5l)

A mixture of **3b** (153 mg, 0.33 mmol), 2-thienylboronic acid (84 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 5 h. Work-up according to general procedure A and column chromatography on silica gel [ether⟶ethyl acetate–ether (1 : 4)] gave **5l** (20 mg, 13%) as a yellow solid, mp 193–194 °C (ether), R_f 0.14 (ether) (Found: C, 71.65; H, 4.63. $C_{28}H_{21}OS_2P$ requires C, 71.77; H, 4.52%); ν_{max} (KBr)/cm^{-1} 3080, 1527, 1517, 1443, 1395, 1115, 875, 815, 740, 700; δ_H (270 MHz, $CDCl_3$) 4.28 (1H, d, $^2J_{H-P}$ 22.8 Hz), 7.00 (1H, m), 7.09 (1H, d, ^3J 4.0 Hz), 7.18 (2H, m), 7.41–7.75 (16H, m); δ_C (67.8 MHz, $CDCl_3$) 51.35 ($^1J_{C=P}$ 113.4 Hz), 124.69, 124.76, 127.60, 127.75 ($^1J_{C-P}$ 91.4 Hz), 128.70, 129.85 (J_{C-P} 12.3 Hz), 133.08 ($^4J_{C-P}$ 2.4 Hz), 134.11 (J_{C-P} 9.8 Hz), 138.92, 139.75, 148.09 ($^3J_{C-P}$ 18.3 Hz), 178.79 ($^2J_{C-P}$ 3.7 Hz, C=O); MS (70 eV) *m*/*z* 468 (M^+, 100%), 303 (Ph_3PCHCO^+, 66), 183 (74). HRMS found: 469.0850; calcd. for $C_{28}H_{22}OPS_2$: 469.0850 (MH^+, FAB).

5-(*m*-Nitrophenyl)-2-thienylcarbonylmethylidenetriphenylphosphorane (5m)

A mixture of **3b** (154 mg, 0.33 mmol), *m*-nitrophenylboronic acid (110 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 5 h. Work-up according to general procedure A and column chromatography on silica gel gave **5m** (150 mg, 89%) as a yellow solid, mp 203–207 °C (ether) (Found: C, 70.54; H, 4.47; N, 2.82. $C_{30}H_{22}O_3NPS$ requires C, 71.00; H, 4.37; N, 2.76%); ν_{max} (KBr)/cm^{-1} 3050, 1512, 1375, 1340, 1095, 870; δ_H (270 MHz, $CDCl_3$) 4.35 (1H, d, $^2J_{P-H}$ 18.1 Hz), 7.36 (1H, d, ^3J 2.0 Hz), 7.47–7.91 (18H, m), 8.10 (1H, dd, J 8.3, J 2.0 Hz), 8.46 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 51.04 ($J_{C=P}$ 113.3 Hz), 120.25, 121.80, 124.91, 126.62 ($^1J_{C-P}$ 91.3 Hz), 127.01, 129.00 (J 12.1 Hz), 129.79, 131.39, 132.29 (J 2.4 Hz), 133.18 (J 10.9 Hz), 136.50, 142.41, 148.77, 177.39 (C=O); MS (FAB, 3-nitrobenzyl alcohol) 508 (MH^+, 40%), 307 (73), 303 (12). HRMS found: 508.1134; calcd. for $C_{30}H_{23}O_3NPS$: 508.1136 (MH^+).

1,4-Bis{5-[(triphenylphosphoranylidene)acetyl]-2-thienyl}benzene (5n)

A mixture of **3b** (240 mg, 0.51 mmol), 1,4-phenylenediboronic acid (44 mg, 0.27 mmol) and $Pd(PPh_3)_4$ (25 mg, 2.2×10^{-2} mmol) in DME (3.5 mL) and 2 M aq. Na_2CO_3 (2 mL) was held at 75 °C for 5 h. Thereafter water (5 mL) was added to the cooled mixture and it was extracted with chloroform (3 × 10 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated *in vacuo* to give a residue, which was taken up with ether (15 mL). The precipitate formed was filtered and washed generously with ether and subsequently dried to give **5n** (80 mg, 35%) as a light yellow solid, mp 270–275 °C (decomp., ether); ν_{max} (KBr)/cm^{-1} 3054, 1544, 1522, 1501, 1480, 1436, 1386, 1103, 879, 731; δ_H (270 MHz, $CDCl_3$) 4.32 (2H, d, $^2J_{P-H}$ 22.4 Hz), 7.46–7.76 (34H, m), 7.61 (4H, s); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 847 (MH^+, 1.4%). HRMS found: 847.2020; calcd. for $C_{54}H_{41}O_2P_2S_2$: 847.2023 (MH^+).

2-Phenylbenzoylmethylidenetriphenylphosphorane (6a)

A mixture of **3c** (153 mg, 0.33 mmol), phenylboronic acid (100 mg, 0.65 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 10 h. Work-up according to general procedure A and column chromatography on silica gel (eluant: ether–chloroform 2 : 1) gave **6a** (142 mg, 94%) as a colorless oil; ν_{max} (KBr)/cm^{-1} 3054, 2924, 1525, 1481, 1437, 1388, 1187, 1107, 746, 719, 693; δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 56.47 ($^1J_{C-P}$ 106.0 Hz, CH), 126.76 (CH), 127.26 (CH), 127.19 (C_{quat}, $^1J_{C-P}$ 90.2 Hz), 128.20 (*J* 11.0 Hz, CH), 128.64 (CH), 128.86 (CH), 129.15 (*J* 12.3 Hz, CH), 129.94 (CH), 130.33 (CH), 132.43 (*J* 2.4 Hz, CH), 132.61 (CH), 133.58 (*J* 9.7 Hz, CH), 140.23 (C_{quat}), 143.18 (C_{quat}), 144.37 (J_{C-P} 15.9 Hz, C_{quat}), 188.72 (J_{C-P} 3.7 Hz, C_{quat}, C=O); MS (FAB) *m*/*z* 457 (MH^+, 100%), 303 (24), 279 (37). HRMS (FAB) found: 457.1717 (MH^+); calcd. for $C_{32}H_{26}OP$: 457.1721.

2-(*p*-Methoxyphenyl)benzoylmethylidenetriphenylphosphorane (6b)

A mixture of **3c** (153 mg, 0.33 mmol), *p*-methoxyphenylboronic acid (100 mg, 0.66 mmol), $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in 2 M Na_2CO_3 (1.3 mL) and DME (3 mL) was held at reflux for 8 h. Thereafter the cooled reaction mixture was worked up acccording to procedure A. Column chromatography on silica gel (ether) gave **6b** (104 mg, 65%) as a colorless slow-moving oil. ν_{max} (neat)/cm^{-1} 1517, 1438, 1387, 1182, 1117, 720, 695; δ_H(270 MHz, $CDCl_3$) 3.58 (1H, d, $^2J_{P-H}$ 25.4 Hz), 3.73 (3H, s, OCH_3), 6.72 (2H, d, ^3J 8.6 Hz), 7.18–7.21 (3H, m), 7.31–7.51 (12H, m), 7.56–7.63 (6H, m); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 55.24 (OCH_3), 158.40 (C_{quat}); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 487 (MH^+, 100%), 303 (21), 279 (89). HRMS (FAB) found: 487.1830 (MH^+); calcd. for $C_{33}H_{28}O_2P$: 487.1827.

2-(*p*-Fluorophenyl)benzoylmethylidenetriphenylphosphorane (6c)

A mixture of **3c** (153 mg, 0.33 mmol), *p*-fluorophenylboronic acid (93 mg, 0.65 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was reacted at 75 °C for 6 h. Work-up according to general procedure A and column chromatography on silica gel (eluant: ether–chloroform 2 : 1) gave **6c** (149 mg, 95%) as a colorless oil; ν_{max} (neat)/cm^{-1} 3054, 2972, 1512, 1482, 1437, 1387, 1189, 1117, 750, 720, 694; δ_H (270 MHz, $CDCl_3$) 3.66 (1H, d, $^1J_{C-P}$ 25.4 Hz), 6.93 (2H, dd, ^3J 8.6, ^3J 8.9 Hz), 7.28–7.81 (21H, m); δ_C (67.8 MHz, DEPT 90, DEPT 135) 55.75 ($^1J_{C-P}$ 106.0 Hz), 114.40 (+, *J* 20.7 Hz), 126.72 (C_{quat}, $^1J_{C-P}$ 90.2 Hz), 126.88 (CH), 129.79 (CH), 132.03 (CH, *J* 4.9 Hz), 133.10 (CH, *J* 9.7 Hz), 138.63 (C_{quat}), 144.16 (C_{quat}, *J* 15.9 Hz), 188.38 (C_{quat}, *J* 3.7 Hz, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 475 (MH^+, 100%), 303 (24), 279 (91). HRMS found: 475.1624 (MH^+); calcd. for $C_{32}H_{25}OFP$: 475.1627.

2-(*o*-Fluorophenyl)benzoylmethylidenetriphenylphosphorane (6d)

A mixture of **3c** (263 mg, 0.57 mmol), *o*-fluorophenylboronic acid (136 mg, 0.97 mmol) and $Pd(PPh_3)_4$ (28 mg, 2.4×10^{-2} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (2.3 mL) was held at 75 °C for 6 h. Work-up according to procedure A and column chromatography on silica gel (ether⟶ethyl acetate–ether 1 : 9) gave **6d** (149 mg, 55%) as colorless needles (Found: C, 81.13; H, 5.18. $C_{32}H_{24}OFP$ requires C, 81.00; H, 5.10%); ν_{max} (KBr)/cm^{-1} 3048, 1581, 1510, 1481, 1450, 1436, 1408, 1385, 1190, 1103, 881, 756, 747, 715, 691; δ_H (270 MHz, $CDCl_3$) 4.48 (1H, d, $^2J_{P-H}$ 24.4 Hz), 7.09–7.31 (4H, m), 7.43–7.60 (11H, m), 7.69–7.78 (6H, m), 8.05 (2H, d, ^3J 8.8 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 50.92 (CH, $^1J_{C-P}$ 112.3 Hz), 116.07 (CH, $^2J_{C-F}$ 23.2 Hz), 124.28 (CH, *J* 3.7 Hz), 127.04 (CH), 127.08 (C_{quat}, $^1J_{C-P}$ 90.1 Hz), 128.44 (CH), 128.48 (CH), 128.89 (CH, J_{C-P} 12.2 Hz), 130.77 (CH, *J* 3.7 Hz), 132.07 (CH, J_{C-P} 2.5 Hz), 133.19 (CH, J_{C-P} 9.7 Hz), 136.71 (C_{quat}), 140.50 (C_{quat}, *J* 14.6 Hz), 159.83 (C_{quat}, $^1J_{C-F}$ (−)247.8 Hz), 184.33 (C_{quat}, C=O, $^2J_{C-P}$ 2.4 Hz); MS (70 eV) *m*/*z* 474 (M^+, 82%), 303 (61), 277 (60), 183 (100). HRMS found: 474.1547; calcd. for $C_{32}H_{24}OFP$: 474.1549.

2-(*p*-Vinylphenyl)benzoylmethylidenetriphenylphosphorane (6e)

A mixture of **3c** (153 mg, 0.33 mmol), 4-vinylphenylboronic acid (97 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 5 h. Work-up according to general procedure A and column chromatography on silica gel (ether) gave **6e** (115 mg, 72%) as a colorless solid; ν_{max} (neat)/cm^{-1} 3054, 1525, 1437, 1387, 1195, 1117, 746, 720, 694; δ_H (270 MHz, $CDCl_3$) 3.63 (1H, d, $^2J_{P-H}$ 24.6 Hz), 5.24 (1H, d, ^3J 11.5 Hz), 5.74 (1H, d, ^3J 17.1 Hz), 6.75 (1H, dd, ^3J 11.5, ^3J 17.1 Hz), 7.27–7.75 (23H, m); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 56.81 (CH, J_{C-P} 106.0 Hz), 113.98 (−), 126.43 (CH), 127.47 (C_{quat}, $^1J_{C-P}$ 90.2 Hz), 127.69 (CH), 128.66 (CH), 129.00 (CH), 129.33 (CH, J_{C-P} 12.2 Hz), 129.61 (CH), 130.49 (CH), 132.89 (CH, J_{C-P} 11.0 Hz), 133.95 (CH, J_{C-P} 11.0 Hz), 136.47 (C_{quat}), 137.70 (CH), 140.26 (C_{quat}), 143.19 (C_{quat}), 144.82 (C_{quat}, J_{C-P} 15.8 Hz), 189.00 (C_{quat}, J_{C-P} 2.4 Hz, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 483 (MH^+, 100%), 303 (36), 279 (55). HRMS found: 483.1879 (MH^+); calcd. for $C_{34}H_{28}OP$: 483.1878.

3-Phenylbenzoylmethylidenetriphenylphosphorane (7a)

A mixture of **3d** (76 mg, 0.17 mmol), phenylboronic acid (63 mg, 0.51 mmol), $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (1.5 mL) and 2 M Na_2CO_3 (0.6 mL) was reacted at 75 °C for 7 h. Column chromatography on silica gel (ether) gave **7a** as a colorless, crystalline solid (63 mg, 81%); mp 216–218 °C (ether) (Found: C, 84.25; H, 5.56. $C_{32}H_{25}OP$ requires C, 84.19; H, 5.52%); ν_{max} (KBr)/cm^{-1} 3052, 2922, 1522, 1376, 1105, 886, 731, 691; δ_H (270 MHz, $CDCl_3$) 4.45 (1H, d, ill-resolved), 7.28–7.77 (22H, m), 7.94 (1H, d, ^3J 7.9 Hz), 8.21 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 50.98 (CH, $^1J_{C-P}$ 112.3 Hz), 125.84 (CH), 125.97 (CH), 127.06 (CH), 127.16 (C_{quat}, $^1J_{C-P}$ 91.4 Hz), 127.31 (CH), 128.07 (CH), 128.18 (CH), 128.59 (CH), 128.88 (CH, J_{C-P} 12.2 Hz), 132.05 (CH, J_{C-P} 3.6 Hz), 133.20 (CH, J_{C-P} 9.7 Hz), 140.75 (C_{quat}), 141.49 (C_{quat}), 141.94 (C_{quat}, J_{C-P} 14.6 Hz), 184.83 (C_{quat}, C=O, $^2J_{C-P}$ 3.5 Hz); MS (70 eV) *m*/*z* 456 (M^+, 100%), 303 (Ph_3PCHCO^+, 95), 277 (39), 183 (51), 149 (82). HRMS found: 456.1646; calcd. for $C_{32}H_{25}OP$: 456.1643.

3-(*p*-Methoxyphenyl)benzoylmethylidenetriphenylphosphorane (7b)

A mixture of **3d** (153 mg, 0.33 mmol), *p*-methoxyphenylboronic acid (100 mg, 0.66 mmol), $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in 2 M Na_2CO_3 (1.3 mL) and DME (3 mL) was held at reflux for 5 h. Thereafter the cooled reaction mixture was worked up acccording to procedure A. Column chromatography on silica gel (ether) gave **7b** (152 mg, 95%) as colorless needles, mp 136–138 °C (ether); ν_{max} (KBr)/cm^{-1} 3054, 1609, 1513, 1438, 1375, 1246, 1107, 693; δ_H (270 MHz, $CDCl_3$) 3.84 (3H, s, OCH_3), 4.47 (1H, d, $^2J_{P-H}$ 24.4 Hz), 6.95 (2H, d, ^3J 7.9 Hz), 7.37–7.61 (15H, m), 7.71 (2H, d, ^3J 8.2 Hz), 7.76 (2H, d, ^3J 7.9 Hz), 7.90 (1H, d, ^3J 7.6 Hz), 8.17 (1H, s); δ_C (67.9 MHz, $CDCl_3$, DEPT 90, DEPT 135) 50.8 (CH, $^1J_{C-P}$ 111.6 Hz), 55.35 (+, OCH_3), 114.12 (CH), 125.41 (CH), 127.27 ($^1J_{C-P}$ 91.3 Hz, C_{quat}), 127.65 (CH), 128.10 (CH), 128.30 (CH), 128.88 (CH, *J* 12.2 Hz), 132.02 (CH, *J* 2.4 Hz), 133.22 (CH, *J* 9.7 Hz), 134.11 (C_{quat}), 140.36 (C_{quat}), 141.81 (C_{quat}, *J* 16.2 Hz), 159.11 (C_{quat}), 185.01 (C_{quat}, C=O); MS (70 eV) *m*/*z* 486 (M^+, 97%), 303 (100), 277 (35), 183 (50). HRMS found: 486.1747; calcd. for $C_{33}H_{27}O_2P$: 486.1749.

3-(2,4-Difluorophenyl)benzoylmethylidenetriphenylphosphorane (7c)

A mixture of **3d** (153 mg, 0.33 mmol), 2,4-difluorophenylboronic acid (104 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 5 h. Work-up according to general procedure A and column chromatography on silica gel (ether) gave **7c** (134 mg, 82%) as a colorless solid; R_f 0.40; ν_{max} (KBr)/cm^{-1} 3048, 2924, 1620, 1597, 1526, 1506, 1481, 1438, 1377, 1103, 882, 868, 848, 754, 745; δ_H (270 MHz, $CDCl_3$) 4.46 (1H, br s), 6.89 (2H, m), 7.39–7.76 (18H, m), 7.96 (1H, d, ^3J 7.9 Hz), 8.08 (1H, s); MS (70 eV) *m*/*z* 492 (M^+, 100%), 303 (Ph_3PCHCO^+, 84), 262 (76), 183 (77); MS (70 eV) *m*/*z* (%) 492 (M^+, 100), 303 (Ph_3PCHCO^+, 84), 262 (76), 183 (77). HRMS found: 492.1456; calcd. for $C_{32}H_{23}OF_2P$: 492.1455.

3-(*m*-Nitrophenyl)benzoylmethylidenetriphenylphosphorane (7d)

A mixture of **3d** (153 mg, 0.33 mmol), *m*-nitrophenylboronic acid (110 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 5 h. Work-up according to general procedure A and column chromatography on silica gel (ether) gave **7d** (148 mg, 89%) as a pale yellow solid, mp 78–81 °C (ether–hexane 1 : 1) (Found: C, 76.31; H, 5.26; N, 2.62. $C_{32}H_{24}O_3NP$ requires C, 76.64; H, 4.82; N, 2.79%); ν_{max} (KBr)/cm^{-1} 3058, 2924, 1522, 1438, 1381, 1351, 1107, 909, 880, 731; δ_H (270 MHz, $CDCl_3$) 4.50 (1H, d, $^2J_{H-P}$ 23.1 Hz), 7.48–7.78 (18H, m), 8.01 (2H, m), 8.17 (1H, d, ^3J 6.9 Hz), 8.26 (1H, s), 8.51 (1H, s); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 51.88 (CH, $^1J_{C-P}$ 112.3 Hz), 122.14 (CH), 122.36 (CH), 126.18 (CH), 126.65 (CH), 127.65 (CH), 128.00 (C_{quat}), 128.39 (CH), 128.84 (CH), 129.38 (CH, J_{C-P} 12.2 Hz), 129.96 (CH), 132.59 (CH, J_{C-P} 2.4 Hz), 133.61 (CH, J_{C-P} 11.0 Hz), 138.65 (C_{quat}), 142.75 (C_{quat}, J_{C-P} 14.6 Hz), 143.56 (C_{quat}), 149.15 (C_{quat}), 184.47 ($^2J_{C-P}$ 2.4 Hz, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 502 (MH^+, 100%), 303 (Ph_3PCHCO^+, 45). HRMS found: 501.1492; calcd. for $C_{32}H_{24}O_3NP$: 501.1494.

3-(*p*-Vinylphenyl)benzoylmethylidenetriphenylphosphorane (7e)

A mixture of **3d** (153 mg, 0.33 mmol), 4-vinylphenylboronic acid (97 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (10 mg, 9.0×10^{-3} mmol) in DME (3 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 75 °C for 5 h. Work-up according to general procedure A and column chromatography on silica gel (ether) gave **7e** (112 mg, 70%) as a pale yellow solid (Found: C, 84.67; H, 5.75. $C_{34}H_{27}OP$ requires C, 84.62; H, 5.64%); ν_{max} (KBr)/cm^{-1} 3048, 2924, 2852, 1523, 1511, 1479, 1435, 1375, 1105, 888, 756, 729, 693; δ_H (270 MHz, $CDCl_3$) 4.48 (1H, d, $^2J_{P-H}$ 24.1 Hz), 5.25 (1H, d, ^3J 10.9 Hz), 5.77 (1H, d, ^3J 17.5 Hz), 6.74 (1H, dd, ^3J 10.9, ^3J 17.5 Hz), 7.39–7.65 (17H, m), 7.73 (2H, d, ^3J 7.9 Hz), 7.76 (2H, d, ^3J 7.9 Hz), 7.93 (1H, d, ^3J 7.6 Hz), 8.23 (1H, s); δ_C (67.9 MHz, $CDCl_3$, DEPT 90, DEPT 135) 50.88 (CH,J_{C-P} 108.8 Hz), 113.57 (−), 125.61 (CH), 126.04 (CH), 126.51 (CH), 127.17 (C_{quat}, $^1J_{C-P}$ 90.2 Hz), 127.35 (CH), 127.89 (CH), 128.16 (CH), 128.86 (CH, J_{C-P} 12.2 Hz), 132.02 (CH, J_{C-P} 2.4 Hz), 133.21 (CH, J_{C-P} 9.7 Hz), 136.49 (C_{quat}), 136.59 (CH), 140.25 (C_{quat}), 140.86 (C_{quat}), 142.01 (C_{quat}, J_{C-P} 14.6 Hz), 184.85 (C_{quat}, J_{C-P} 2.4 Hz, C=O); MS (70 eV) *m*/*z* 482 (M^+, 19%), 303 (25), 262 (50), 178 (57). HRMS found: 482.1801; calcd. for $C_{34}H_{27}OP$: 482.1800.

4′-Methoxybiphenyl-4-ylcarbonylmethylidenetriphenylphosphorane (4a)—general procedure B

A mixture of *p*-bromobenzoylmethylenephosphonium bromide **2a** (527 mg, 0.97 mmol), *p*-methoxyphenylboronic acid (297 mg, 1.95 mmol) and $Pd(PPh_3)_4$ (27 mg, 2.3×10^{-2} mmol) in DME (7 mL) and 2 M aq. Na_2CO_3 (4.7 mL) was heated for 5 h at 75 °C. After the reaction mixture had cooled, water (15 mL) was added and the mixture was extracted with ether (10 mL) and chloroform (2 × 15 mL). The combined organic phase was washed with water, dried over $MgSO_4$ and concentrated *in vacuo*. Ether (20 mL) was added to the residue and the precipitate formed was filtered off and washed with cold ether to give **4a** (233 mg, 49%).

Biphenyl-4-ylcarbonylmethylidenetriphenylphosphorane (4b)

A mixture of **2a** (527 mg, 0.97 mmol), phenylboronic acid (238 mg, 1.95 mmol) and $Pd(PPh_3)_4$ (27 mg, 2.3×10^{-2} mmol) in DME (5 mL) and 2 M aq. Na_2CO_3 (3.7 mL) was treated according to procedure B (5 h, 75 °C). Column chromatography on silica gel (ether) yielded **4b** (286 mg, 64%).

4-(*p*-Fluorophenyl)benzoylmethylidenetriphenylphosphorane (4d)

A mixture of **2a** (268 mg, 0.5 mmol), *p*-fluorophenylboronic acid (140 mg, 1.0 mmol) and $Pd(PPh_3)_4$ (12.5 mg, 1.1 mmol) in DME (2.5 mL) and 2 M aq. Na_2CO_3 (1.85 mL) was treated according to procedure B (5 h, 75 °C). Column chromatography on silica gel (ether⟶ether–ethyl acetate 95 : 5) gave **4d** (146 mg, 62%).

p-(2-Thienyl)benzoylmethylidenetriphenylphosphorane (4j)

A mixture of **2a** (527 mg, 0.97 mmol), 2-thienylboronic acid (250 mg, 1.95 mmol) and $Pd(PPh_3)_4$ (27 mg, 2.3×10^{-2} mmol) in DME (5 mL) and 2 M aq. Na_2CO_3 (3.7 mL) was treated according to procedure B (7 h, 75 °C). Column chromatography on silica gel (ether) yielded **4j** (190 mg, 42%).

4-(*p*-Trifluoromethylphenyl)benzoylmethylidenetriphenylphosphorane (4k)

A mixture of **2a** (527 mg, 0.97 mmol), *p*-trifluorophenylboronic acid (185 mg, 0.97 mmol) and $Pd(PPh_3)_4$ (27 mg, 2.3×10^{-2} mmol) in DME (7.0 mL) and 2 M aq. Na_2CO_3 (4.7 mL) was treated according to procedure B (12h, 75 °C). Column chromatography on silica gel (ether) gave **4k** (276 mg, 54%).

4-(2-Naphthyl)benzoylmethylidenetriphenylphosphorane (4l)

A mixture of **2a** (527 mg, 0.97 mmol), 2-naphthylboronic acid (166 mg, 0.97 mmol) and $Pd(PPh_3)_4$ (27 mg, 2.3×10^{-2} mmol) in DME (7.0 mL) and 2 M aq. Na_2CO_3 (4.7 mL) was treated according to procedure B (8 h, 75 °C). Column chromatography on silica gel (ether) gave **4l** (272 mg, 55%).

p-(2-Phenylethenyl)benzoylmethylidenephosphorane (8a)

Method A. A mixture of **3a** (500 mg, 1.09 mmol), styrene (0.19 mL, 170 mg, 1.64 mmol), triethylamine (0.18 mL, 132 mg, 1.31 mmol), palladium acetate (24 mg, 0.11 mmol) and triphenylphosphine (71 mg, 0.27 mmol) in *N*,*N*-dimethylformamide (2 mL) was heated at 100 °C for 24 h. Thereafter the cooled solution was diluted with water and extracted with dichloromethane. The organic phase was washed with water, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Chromatography on silica gel (eluant: ether) yielded **8a** (32 mg, 6%) as a pale yellow powder (ether), mp 208–210 °C (ether) (Found: C, 83.83; H, 5.69. $C_{34}H_{27}OP{\cdot}0.25H_2O$ requires C, 83.59; H, 5.56%); ν_{max} (KBr)/cm^{-1} 3050, 1519, 1481, 1437, 1410, 1387, 1103, 880, 746, 715, 693; δ_H (270 MHz, $CDCl_3$) 4.45 (d, 1H, $^2J_{H-P}$24.5 Hz), 7.14 (s, 2H), 7.32–7.76 (m, 22H), 7.96 (d, 2H, ^3J 8.6 Hz); δ_C (67.8 MHz, $CDCl_3$) 50.91 (CH, $^1J_{C-P}$ 112.1 Hz), 125.95 (+, CH), 126.52 (+, CH), 127.03 (C_{quat}, J_{C-P} 91.3 Hz), 127.35 (+, CH), 127.58 (+, CH), 128.55 (+, CH), 128.64 (+, CH), 128.84 (+, CH), 128.87 (+, CH, J_{C-P} 12.1 Hz), 132.06 (+, CH, J_{C-P} 2.4 Hz), 133.16 (CH, J_{C-P} 10.9 Hz), 137.37 (C_{quat}), 138.27 (C_{quat}), 140.50 (C_{quat}, J_{C-P} 14.6 Hz), 184.28 (C=O, C_{quat}, $^2J_{C-P}$ 2.4 Hz). MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 483 (MH^+, 51%). HRMS found: 483.1877; calcd. for $C_{34}H_{28}OP$: 483.1878 (MH^+).

Method B. A mixture of **3e** (273 mg, 0.54 mmol), styrene (0.1 mL, 84 mg, 0.81 mmol), triethylamine (0.09 mL, 65 mg, 0.65 mmol), palladium acetate (12 mg, 0.054 mmol) and triphenylphosphine (35 mg, 0.135 mmol) in *N*,*N*-dimethylformamide (1 mL) was heated at 100 °C for 2 h. Thereafter the cooled solution was diluted with water, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Chromatography on silica gel (eluant: ether–ethyl acetate 1 : 1) yielded **8a** (117 mg, 45%).

Method C. A mixture of **3e** (108 mg, 0.21[5] mmol), styrene (60 mg, 0.58 mmol), tetrabutylammonium chloride (71 mg, 0.25[5] mmol), $NaHCO_3$ (44 mg, 0.52 mmol), and palladium(II) acetate (18 mg, 0.08 mmol) in chloroform (1.5 mL) was stirred at rt for 72 h. Thereafter water (5 mL) was added and the mixture was extracted with chloroform (2 × 15 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography of the residue on silica gel (ether) gave **8a** (78 mg, 75%).

(*E*)-*p*-(2-Cyanoethenyl)benzoylmethylidenetriphenylphosphorane (8b)

Method 1. A mixture of *p*-bromobenzoylmethylidenetriphenylphosphorane (**3a**) (250 mg, 0.54 mmol), acrylonitrile (0.05 mL, 43 mg, 0.82 mmol), triethylamine (0.09 mL, 65 mg, 0.65 mmol), palladium acetate (12 mg, 0.054 mmol) and triphenylphosphine (35 mg, 0.135 mmol) in *N*,*N*-dimethylformamide (1 mL) was heated at 90 °C for 15 h. Thereafter the cooled solution was diluted with water and extracted with dichloromethane. The organic phase was washed with water, dried over magnesium sulfate and concentrated *in vacuo*. Chromatography on silica gel (eluant: ether–ethyl acetate 1 : 0–1 : 1) yielded **8b** (42 mg, 18%) as an orange powder (ether), mp 209–210 °C (ether) (Found: C, 80.28; H, 5.21; N, 3.21. $C_{29}H_{22}ONP{\cdot}0.25H_2O$ requires C, 79.89; H, 5.20; N, 3.21%); ν_{max} (KBr)/cm^{-1} 3008, 2212, 1614, 1573, 1495, 1478, 1436, 1412, 1394, 1310, 1211, 1179, 1105, 1071, 1014, 997, 972, 883, 824, 752, 715, 693; δ_H (270 MHz, $CDCl_3$) 4.38 (1H, d, $^2J_{H-P}$ 23.1 Hz), 5.81 (1H, d, *J* 16.7 Hz), 7.29–7.68 (18H, m), 7.91 (2H, d, ^3J 7.3 Hz); δ_C (67.8 MHz, $CDCl_3$) 52.09 (CH, $^1J_{C-P}$ 110.9 Hz), 96.10 (CH), 118.29 (CN), 126.59 (C_{quat}, $^1J_{C-P}$ 91.4 Hz), 126.92 (CH), 127.60 (CH), 128.93 (CH, J_{C-P} 12.2 Hz), 132.20 (CH, J_{C-P} 2.4 Hz), 133.08 (CH, J_{C-P} 9.8 Hz), 134.07 (C_{quat}), 143.92 (C_{quat}, J_{C-P} 14.6 Hz), 150.37 (CH), 183.12 (C=O, $^2J_{C-P}$ 3.7 Hz); MS (EI, 70 eV) *m*/*z* 431 (M^+, 100%), 402 (M^+ − CHO, 21), 303 ([M^+ − NC-CH=CH-Ph], 70); HRMS found: 432.1521; calcd. for $C_{29}H_{23}NOP$: 432.1517 (MH^+, FAB).

Method 2. A mixture of *p*-iodobenzoylmethylidenetriphenylphosphorane (**3e**) (273 mg, 0.54 mmol), acrylonitrile (0.05 mL, 43 mg, 0.82 mmol), triethylamine (0.09 mL, 65 mg, 0.65 mmol), palladium acetate (12 mg, 0.054 mmol) and triphenylphosphine (35 mg, 0.135 mmol) in *N*,*N*-dimethylformamide (1 mL) was heated at 90 °C for 15 h. Thereafter the cooled solution was diluted with water and extracted with dichloromethane. The organic phase was washed with water, dried over magnesium sulfate and concentrated *in vacuo*. Chromatography on silica gel (eluant: ether–ethyl acetate 1 : 1) yielded **8b** (58 mg, 25%) as an orange powder (ether).

Method 3. A mixture of *p*-iodobenzoylmethylidenetriphenylphosphorane (**3e**) (108 mg, 0.21 mmol), acrylonitrile (0.05 mL, 43 mg, 0.82 mmol), benzyltrimethylammonium chloride (40 mg, 0.22 mmol), solid $NaHCO_3$ (40 mg, 0.5 mmol), $Pd(OAc)_2$ (9.0 mg, 0.041 mmol) in DMF (1 mL) was stirred at rt for 60 h. Thereafter, the mixture was poured into water and extracted with $CHCl_3$ (3 × 15 mL). The organic phase was washed with water (3 × 10 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography of the residue on silica gel (ether) gave **8b** (50 mg, 55%).

p-(2-Methoxycarbonylethenyl)benzoylmethylidenephosphorane (8c)

Method A. A mixture of **3a** (500 mg, 1.09 mmol), methyl acrylate (0.15 mL, 141 mg, 1.64 mmol), triethylamine (0.18 mL, 132 mg, 1.31 mmol), palladium acetate (24 mg, 0.11 mmol) and triphenylphosphine (71 mg, 0.27 mmol) in *N*,*N*-dimethylformamide (2 mL) was heated at 100 °C for 24 h. Thereafter the cooled solution was diluted with water and extracted with dichloromethane. The organic phase was washed with water, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Chromatography on silica gel (eluant: chloroform–ethyl acetate 5 : 1–3 : 1) yielded **8c** (193 mg, 38%) as an orange powder (ether); mp 198–199 °C (ether) (Found: C, 76.69; H, 5.49. $C_{30}H_{25}0_3P{\cdot}0.25H_2O$ requires C, 76.82; H, 5.37%); ν_{max} (KBr)/cm^{-1} 3042, 1712, 1633, 1574, 1518, 1480, 1437, 1408, 1388, 1312, 1203, 1171, 1104, 881, 840, 747, 716, 694; δ_H (270 MHz, $CDCl_3$) 3.80 (3H, s, OCH_3), 4.45 (1H, d, $^1J_{H-P}$ 24.1 Hz), 6.46 (1H, d, ^3J 16.2 Hz, olef. H), 7.46–7.58 (11H, m), 7.60–7.75 (7H, m), 7.98 (2H, d, Ar-H); δ_C (67.8 MHz, DEPT 90, DEPT 135) 51.65 (+, $COOCH_3$), 51.70 (+, CH, $^1J_{C-P}$ 112.2 Hz), 117.79 (+, CH), 126.79 (C_{quat}, $^1J_{C-P}$ 90.1 Hz), 127.46 (+, CH), 127.64 (+, CH), 128.91 (+, CH, J_{C-P} 12.2 Hz), 132.15 (+, CH, J_{C-P} 2.4 Hz), 133.14 (+, CH, J_{C-P} 9.9 Hz), 135.11 (C_{quat}), 143.07 (C_{quat}, J_{C-P} 14.6 Hz), 144.69 (+, CH), 167.49 (C_{quat}, C=O, $COOCH_3$); MS (70 eV) *m*/*z* 464 (M^+, 100%), 435 (M^+ − CHO, 22), 303 (M^+ − CH_3COOCH=CHPh, 73). HRMS found: 464.1539; calcd. for $C_{30}H_{25}O_3P$: 464.1541.

Method B—general procedure D. A mixture of **3e** (166 mg, 0.33 mmol), methyl acrylate (57 mg, 0.66 mmol), solid $NaHCO_3$ (68 mg, 0.8 mmol), benzyltrimethylammonium chloride (61 mg, 0.33 mmol) and $Pd(OAc)_2$ (4.4 mg, 0.02 mmol) in dry DMF (1 mL) was stirred at rt and under an inert atmosphere for 60 h. Then water (5 mL) was added and the mixture was extracted with chloroform (3 × 10 mL). The organic phase was washed with water (3 × 10 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography (ether) to give **8c** (147 mg, 96%).

(*E*)-*p*-[2-(Morpholinocarbonyl)ethenyl]benzoylmethylidenetriphenylphosphorane (8d)

A mixture of **3e** (108 mg, 0.215 mmol), *N*-morpholinylacrylamide (75 mg, 0.53 mmol), solid $NaHCO_3$ (44 mg, 0.5 mmol), benzyltrimethylammonium chloride (40 mg, 0.22 mmol) and $Pd(OAc)_2$ (4.0 mg, 0.02 mmol) in dry DMF (1 mL) is treated according to procedure D (reaction time: 40 h). Chromatography on silica gel (eluant: ether–ethyl acetate) gives **8d** (71 mg, 64%) as an off-white solid; mp 236–238 °C (ether) (Found: C, 74.55; H, 5.86; N, 2.58. $C_{33}H_{30}O_3NP{\cdot}0.75H_2O$ requires C, 74.35; H, 5.95; N, 2.63%); ν_{max} (KBr)/cm^{-1} 3054, 2964, 2850, 1651, 1640, 1605, 1572, 1510, 1500, 1438, 1409, 1389, 1228, 1108, 883, 846, 748; δ_H (270 MHz, $CDCl_3$) 3.73 (8H, br s), 4.44 (1H, d, $^2J_{P-H}$ 24.1 Hz), 6.86 (1H, d, ^3J 15.2 Hz), 7.45–7.75 (18H, m), 7.96 (2H, d, ^3J 8.2 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 42.60 (−, very broad), 46.50 (−, very broad), 51.65 (+, CH, $^1J_{C-P}$ 112.3 Hz), 66.87 (−, 2C), 116.53 (+, CH), 126.82 (C_{quat}, $^1J_{C-P}$ 91.5 Hz), 127.35 (+, CH), 127.40 (+, CH), 128.91 (+, CH, J_{C-P} 12.2 Hz), 132.15 (+, CH, J_{C-P} 1.6 Hz), 133.14 (+, CH, J_{C-P} 9.7 Hz), 135.90 (C_{quat}), 142.82 (C_{quat}), 143.02 (+, CH), 165.64 (C_{quat}, $CONR_2$), 183.76 (C_{quat}, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 520 (MH^+, 15%), 307 (31), 154 (100). HRMS (FAB, 3-nitrobenzyl alcohol) found: 520.2045; calcd. for $C_{33}H_{31}O_3NP$: 520.2042 (MH^+).

p-(Phenylethynyl)benzoylmethylidenetriphenylphosphorane (9a)

In an oven-dried flask held under argon was placed *p*-iodobenzoylmethylidenetriphenylphosphorane (**3e**) (500 mg, 0.99 mmol), dry diisopropylamine (3 mL), dry toluene (1.9 mL) and $Pd(PPh_3)_4$ (34 mg, 2.9×10^{-2} mmol). The reaction mixture

was heated to 60 °C, and phenylacetylene (0.11 mL, 101 mg, 0.99 mmol) and CuI (4 mg, 2.1×10^{-2} mmol) were added. The reaction was stirred under argon at 60 °C for 13 h. The flask was allowed to cool to room temperature, and diethyl ether (25 mL) was added. The mixture was washed with water, and saturated aqueous NaCl and dried over magnesium sulfate. The solvent was concentrated *in vacuo*. Chromatography on silica gel (eluant: ether–ethyl acetate 1 : 1) yielded **9a** (209 mg, 44%) as yellow powder (ether), mp 222–223 °C (ether) (Found: C, 84.98; H, 5.24. $C_{34}H_{25}OP$ requires C, 85.21; H, 5.27%); ν_{max} (KBr)/cm^{-1} 3056, 1565, 1516, 1482, 1438, 1403, 1387, 1188, 1104, 1079, 1015, 998, 876, 853, 753, 718, 689; δ_H (270 MHz, $CDCl_3$) 4.44 (1H, d, $^2J_{H-P}$ 24.1 Hz), 7.28–7.83 (22H, m), 7.95 (d, 2H, ^3J 8.3 Hz); δ_C (67.8 MHz, $CDCl_3$) 51.38 (CH, $^1J_{C-P}$ 110.9 Hz), 89.77 (C_{quat}), 90.19 (C_{quat}), 123.32 (C_{quat}), 123.97 (C_{quat}), 126.85 (C_{quat}, $^1J_{C-P}$ 91.4 Hz), 126.92 (CH), 128.19 (CH), 128.30 (CH), 128.91 (CH, J_{C-P} 12.1 Hz), 131.07 (CH), 131.59 (C_{quat}), 132.13 (CH, J_{C-P} 2.4 Hz), 133.13 (CH, J_{C-P} 9.8 Hz), 140.95 (C_{quat}, J_{C-P} 14.6 Hz), 183.79 (C=O, $^2J_{C-P}$ 2.4 Hz); MS (EI, 70 eV) *m*/*z* 480 (M^+, 100%), 451 ($M^+ - CHO$, 25), 303 ([M^+ − Ph-C≡C-Ph], 74). HRMS (FAB, 3-nitrobenzyl alcohol) found: 481.1714 (MH^+); calcd. for $C_{34}H_{26}OP$: 481.1721.

p-(4-Cyanophenylethynyl)benzoylmethylidenetriphenylphosphorane (9b)

p-Iodobenzoylmethylidenetriphenylphosphorane (**3e**) (40 mg, 0.08 mmol), *p*-cyanophenylacetylene (10 mg, 0.08 mmol), $Pd(PPh_3)_4$ (3 mg, 2.4×10^{-6} mol, 3 mol%) and CuI (0.3 mg, 1.6×10^{-6} mol, 2 mol%) in dry diisopropylamine (0.24 mL) and dry toluene (0.15 mL) were reacted (13 h, 60 °C, argon) and worked up as described above. The reaction mixture was purified by TLC chromatography (ether⟶ether–ethyl acetate 1 : 1) to give **9b** (20 mg, 50%) as a pale yellow solid; mp 277–278 °C (ether); R_f 0.54 (ether–ethyl acetate 1 : 1); ν_{max} (KBr)/cm^{-1} 3050, 2220, 1603, 1565, 1507, 1436, 1404, 1385, 1107, 886, 690; δ_H (270 MHz, $CDCl_3$) 4.46 (1H, d, $^2J_{P-H}$ 23.1 Hz), 7.45–7.76 (21H, m), 7.97 (2H, d, ^3J 8.2 Hz); δ_C (67.8 MHz, DEPT 90, DEPT 135) 51.93 (CH, $^1J_{C-P}$ 88.52 (C_{quat}), 94.23 (C_{quat}), 111.32 (C_{quat}), 118.60 (C_{quat}), 122.84 (C_{quat}), 126.69 (C_{quat}, $^1J_{C-P}$ 91.4 Hz), 127.06 (CH), 128.33 (C_{quat}), 128.96 (CH, J_{C-P} 12.1 Hz), 131.34 (CH), 132.14 (CH, J_{C-P} 13.5 Hz), 132.19 (CH), 133.13 (CH, J_{C-P} 9.8 Hz), 141.78 (C_{quat}, J_{C-P} 14.6 Hz), 183.50 (C_{quat}, $^2J_{C-P}$ 2.4 Hz, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 506 (MH^+, 100%), 303 (29). HRMS (FAB, 3-nitrobenzyl alcohol) found: 506.1672 (MH^+); calcd. for $C_{35}H_{25}ONP$: 506.1674.

p-(4-Nitrophenylethynyl)benzoylmethylidenetriphenylphosphorane (9c)

p-Iodobenzoylmethylidenetriphenylphosphorane (**3e**) (500 mg, 0.99 mmol), *p*-nitrophenylacetylene (146 mg, 0.99 mmol), $Pd(PPh_3)_4$ (34 mg, 2.72×10^{-2} mmol, 3 mol%), CuI (4 mg, 2.13×10^{-2} mmol, 2 mol%) in dry diisoproylamine (3.0 mL) and dry toluene (1.9 mL) were reacted (13 h, 60 °C, argon). After the reaction had cooled to rt, chloroform (25 mL) was added, the mixture was washed with water (2 × 15 mL) and sat. aq. NaCl (1 × 15 mL). The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo*. The residue was washed with ether (20 mL) and yielded **9c** (518 mg, 99%) as a pale yellow powder; mp 258–259 °C (ether); R_f 0.18 (ether); ν_{max} (KBr)/cm^{-1} 3058, 2216, 1592, 1569, 1515, 1482, 1437, 1406, 1387, 1344, 1187, 1107, 1015, 877, 854, 824, 748, 718, 692; δ_H (270 MHz, $CDCl_3$) 4.46 (1H, d, $^2J_{H-P}$ 23.8 Hz), 7.45–7.76 (19H, m), 7.98 (2H, d, ^3J 8.6 Hz), 8.21 (2H, d, ^3J 8.6 Hz); δ_C NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 51.83 (CH, $^1J_{C-P}$ 110.9 Hz), 88.30 (C_{quat}), 95.17 (C_{quat}), 122.66 (C_{quat}), 123.59 (CH), 126.69 (C_{quat}, $^1J_{C-P}$ 91.3 Hz), 127.04 (CH), 128.91 (CH, J_{C-P} 12.2 Hz), 130.35 (C_{quat}), 131.36 (CH), 132.20 (CH), 132.78 (CH), 133.10 (CH, J_{C-P} 9.7 Hz), 141.97 (C_{quat}, J_{C-P} 15.8 Hz), 146.86 (C_{quat}), 183.43 (C_{quat}, C=O, $^2J_{C-P}$ 2.4 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 526 (MH^+, 46%). HRMS (FAB, 3-nitrobenzyl alcohol) found: 526.1577; calcd. for $C_{34}H_{25}O_3NP$: 526.1572 (MH^+).

p-(*p*-Amidophenylethynyl)benzoylmethylidenetriphenylphosphorane (9d)

A mixture of *p*-iodobenzoylmethylidenetriphenylphosphorane (**3e**) (100 mg, 0.2 mmol), dry isopropylamine (0.6 mL) and $Pd(PPh_3)_4$ (7 mg, 3mol%, 6.3 μmol) in dry toluene (0.4 mL) was heated at 60 °C under argon, and *p*-amidophenylacetylene (29 mg, 0.2 mmol) and CuI (0.3 mg, 2 mol%, 1.5 μmol) were added. The reaction mixture was stirred at 60 °C for 13 h. Then it was cooled to rt and ether (10 mL) was added. The mixture was washed with water (5 mL), sat. aq. NaCl solution (5 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated *in vacuo* and the residue was subjected to column chromatography on silica gel (ethyl acetate) to give **9d** (49 mg, 47%) as a pale yellow powder, mp 295–296 °C (ethyl acetate); R_f 0.11 (ethyl acetate); ν_{max} (KBr)/cm^{-1} 3300, 3166, 1737, 1680, 1609, 1564, 1437, 1238, 1108, 875, 750, 716, 691; δ_H (270 MHz, DMSO-d_6) 4.59 (1H, d, $^2J_{H-P}$ 24.1 Hz), 7.47–8.07 (25H, m); δ_C NMR (67.8 MHz, DMSO-d_6, DEPT 135, DEPT 90) 49.68 (CH, $^1J_{C-P}$ 111.3 Hz), 89.72 (C_{quat}), 91.25 (C_{quat}), 122.51 (C_{quat}), 124.90 (C_{quat}), 126.40 (C_{quat}, J_{C-P} 91.4 Hz), 126.88 (CH), 127.74 (CH), 128.96 (CH, J_{C-P} 12.2 Hz), 130.91 (CH), 131.14 (CH), 132.27 (CH), 132.69 (CH, J_{C-P} 11.0 Hz), 134.00 (C_{quat}), 140.91 (C_{quat}, J_{C-P} 14.6 Hz), 166.97 (C_{quat}, C=O), 181.47 (C_{quat}, C=O); MS (FAB, 3-nitrobenyzl alcohol) *m*/*z* 524 (MH^+, 64%); HRMS found: 524.1779; calcd. for $C_{35}H_{27}NO_2P$: 524.1777 (MH^+).

5-(4-Cyanophenylethynyl)-2-thienoylmethylidenetriphenylphosphorane (9e)

A mixture of 5-bromo-2-thienoylmethylidenetriphenylphosphorane (**3b**) (70 mg, 0.15 mmol), dry isopropylamine (0.5 mL) and $Pd(PPh_3)_4$ (5 mg, 4.5 mmol) was heated at 60 °C under argon, and *p*-cyanophenylacetylene (19 mg, 0.15 mmol) and CuI (0.6 mg, 3.0 mmol) were added. The reaction mixture was stirred at 60 °C for 4 h. Then it was cooled to rt and ether (10 mL) was added and the phases were separated. The organic phase was washed with sat. aq. NaCl (5 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated *in vacuo* and the residue was subjected to column chromatography on silica gel (ether) to give **9e** (35 mg, 46%) as yellow needles, mp 240–242 °C; R_f 0.18 (ether); ν_{max} (KBr)/cm^{-1} 3054, 2224, 2194, 1601, 1519, 1436, 1385, 1104, 867, 838, 744, 729; δ_H (270 MHz, $CDCl_3$) 4.30 (1H, d, $^2J_{H-P}$ 22.4 Hz), 7.22 (1H, d, ^3J 3.6 Hz), 7.41 (1H, d, ^3J 3.6 Hz), 7.45–7.74 (19H, m); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 51.52 (+, CH, $^1J_{C-P}$ 112.1 Hz), 88.16 (C_{quat}), 91.75 (C_{quat}), 111.32 (C_{quat}), 118.54 (C_{quat}), 123.02 (C_{quat}), 125.95 (+, CH), 126.52 (C_{quat}, $^1J_{C-P}$ 91.6 Hz), 128.05 (C_{quat}), 129.00 (+, CH, J_{C-P} 12.2 Hz), 131.73 (+, CH), 132.00 (+, CH), 132.32 (+, CH, J_{C-P} 2.4 Hz), 133.13 (+, CH, J_{C-P} 9.7 Hz), 133.40 (+, CH), 151.45 (C_{quat}, J 16.0 Hz), 176.70 (C_{quat}, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 512 (18%). HRMS found: 512.1240; calcd. for $C_{33}H_{23}ONPS$: 512.1238.

1-[*p*-(2-Thienyl)benzoyl]-2-(*p*-tolyl)ethene (11c)—general procedure C

A mixture of *p*-tolualdehyde (**10a**) (45 mg, 0.36 mmol), **4j** (102 mg, 0.22 mmol) and benzoic acid (5 mg, 4.0×10^{-2} mmol) in benzene (1.5 mL) were held at reflux for 11 h. After the reaction solution had cooled, the solvent was evaporated *in vacuo* and the residue was subjected to column chromatography on silica gel (eluant: hexane–$CHCl_3$ 1 : 1) to give **11c** (66 mg, 98%) as a colorless solid; R_f 0.25 (hexane–$CHCl_3$); mp 186 crystal to crystal transition 197 (hexane–ether) (Found: C, 77.63; H, 5.14. $C_{20}H_{16}OS \cdot 0.25\ H_2O$ requires C, 77.76; H, 5.38%); ν_{max} (KBr)/cm^{-1} 3042, 3014, 2914, 1655, 1606, 1334, 1229, 1184, 1034, 983,

810, 692 cm; δ_H (270 MHz, $CDCl_3$) 2.40 (3H, s, CH_3), 7.13 (1H, m), 7.23 (2H, d, ^3J 8.2 Hz), 7.37 (1H, m), 7.50 (2H, d, ^3J 15.5 Hz), 7.56 (2H, d, ^3J 8.2 Hz), 7.73 (2H, d, ^3J 8.3 Hz), 7.83 (1H, d, ^3J 15.5 Hz), 8.04 (2H, d, ^3J 8.3 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 21.56 (CH_3), 120.86 (CH), 124.56 (CH), 125.70 (CH, 2C), 126.39 (CH), 128.37 (CH), 128.51 (CH, 2C), 129.30 (CH, 2C), 132.20 (CH, 2C), 132.20 (C_{quat}), 136.98 (C_{quat}), 138.47 (C_{quat}), 141.13 (C_{quat}), 143.11 (C_{quat}), 144.88 (CH), 189.57 (C_{quat}, C=O); MS (70 eV) *m*/*z* 304 (M^+, 91%), 289 ($M^+ - CH_3$), 187 (25), 115 (100). HRMS found: 304.0917; calcd. for $C_{20}H_{16}OS$: 304.0922.

1-[*p*-(Methoxyphenyl)benzoyl]-2-(*p*-tolyl)ethene (11b)

A mixture of *p*-tolualdehyde (**10a**) (45 mg, 0.36 mmol), **4a** (107 mg, 0.22 mmol), benzoic acid (26 mg, 0.21 mmol) in benzene (2 mL) was held at reflux for 24 h. The reaction was worked up as described in procedure C to give **11b** (71 mg, 98%) as a mixture of (*E*)- and (*Z*)-isomers (*E*/*Z*). The (*E*)-isomer could be crystallized from ether to give pale yellow crystals, mp 211–213 °C (ether); ν_{max} (KBr)/cm^{-1} 3012, 2916, 2836, 1659, 1604, 1290, 1258, 1200, 1037, 827, 810; δ_H (270 MHz, $CDCl_3$, ^1H–^1H-COSY) 2.41 (3H, s, CH_3), 3.88 (3H, s, OCH_3), 7.01 (2H, d, ^3J 8.2 Hz), 7.24 (2H, d, ^3J 8.9 Hz), 7.53 (1H, d, ^3J 15.8 Hz), 7.55–7.73 (4H, m), 7.69 (2H, d, ^3J 7.9 Hz), 7.83 (1H, d, ^3J 15.8 Hz), 8.09 (2H, d, ^3J 7.9 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 21.56 (CH_3), 55.38 (OCH_3), 114.39 (CH), 121.00 (CH), 126.66 (CH), 128.44 (CH), 129.13 (CH), 129.70 (CH), 132.22 (C_{quat}), 132.36 (C_{quat}), 136.44 (C_{quat}), 141.04 (C_{quat}), 144.69 (CH), 145.03 (C_{quat}), 159.87 (C_{quat}), 189.95 (C_{quat}); MS (70 eV) *m*/*z* 328 (M^+, 100%); 313 ($M^+ - CH_3$, 33), 148 (42); HRMS found: 328.1463; calcd. for $C_{23}H_{20}O_2$: 328.1463.

1-[*p*-(*p*-Fluorophenyl)benzoyl]-2-(*p*-tolyl)ethene (11d)

A mixture of *p*-tolualdehyde (**10a**) (51 mg, 0.41 mmol), **4d** (102 mg, 0.22 mmol) and benzoic acid (6 mg, 4.85×10^{-2} mmol) were held at reflux for 12 h. The reaction was worked up as described in procedure C. Column chromatography on silica gel ($CHCl_3$–hexane 1 : 2) yielded **11d** (61 mg, 90%) as off-white needles; R_f 0.20 ($CHCl_3$–hexane 1 : 2); mp 209–210 °C (ether) (Found: C, 82.35; H, 5.45. $C_{22}H_{17}OF \cdot 0.25H_2O$ requires C, 82.35; H, 5.49%); ν_{max} (KBr)/cm^{-1} 3062, 2920, 1654, 1597, 1242, 1196, 812; δ_H (270 MHz, $CDCl_3$) 2.40 (3H, s, CH_3), 7.13–7.25 (4H, m), 7.49–7.64 (5H, m), 7.68 (2H, d, ^3J 8.2 Hz), 7.83 (1H, d, ^3J 15.8 Hz), 8.09 (2H, d, ^3J 8.2 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 21.55 (+, CH_3), 115.90 (+, CH, $^3J_{C-F}$ 21.8 Hz), 120.99 (+, CH), 127.10 (+, CH), 128.52 (+, CH), 128.94 (+, CH, J_{C-F} 8.5 Hz), 129.15 (+, CH), 129.74 (+, CH), 132.18 (C_{quat}), 136.13 (C_{quat}, J_{C-F} 3.7 Hz), 137.09 (C_{quat}), 141.15 (C_{quat}), 144.37 (C_{quat}), 144.96 (+, CH), 162.94 (C_{quat}, J_{C-F} (−)240 Hz), 189.95 (C_{quat}, C=O); MS (70 eV) *m*/*z* 316 (M^+, 100%), 301 ($M^+ - CH_3$, 85). HRMS found: 316.1264; calcd. for $C_{22}H_{17}OF$: 316.1263.

1-[*p*-(*p*-Methoxyphenyl)benzoyl]-2-(*p*-nitrophenyl)ethene (11e)

A mixture of *p*-nitrobenzaldehyde (**10b**) (61 mg, 0.40 mmol), **4a** (106 mg, 0.22 mmol) and benzoic acid (12 mg, 9.7×10^{-2} mmol) in benzene (2.0 mL) were held at reflux for 12 h. The reaction was worked up as described in procedure C. Column chromatography on silica gel ($CHCl_3$–hexane 2 : 1) yielded **11e** (77 mg, 97%) as a mixture of (*E*)- and (*Z*)-isomers. The (*E*)-isomer could be crystallized from ether to give **11e** as yellow crystals; mp 97 °C (ether); ν_{max} (KBr)/cm^{-1} 3080, 2962, 2836, 1656, 1597, 1518, 1494, 1345, 1318, 1292, 1257, 1198, 1029, 818; δ_H (270 MHz, $CDCl_3$, ^1H–^1H-COSY) 3.88 (3H, s, OCH_3), 7.02 (2H, d, ^3J 8.9 Hz), 7.61 (2H, d, ^3J 8.9 Hz), 7.66–7.88 (4H, m), 8.10 (2H, d, ^3J 8.6 Hz), 8.29 (2H, d, ^3J 8.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 55.40 (OCH_3), 114.47, 124.23, 125.70, 126.83, 128.41, 128.91, 129.27, 132.06, 135.60, 141.15, 141.24, 145.73, 160.07, 188.91; MS (70 eV) *m*/*z* 359 (64%), 211 (22), 153 (78). HRMS found: 359.1157; calcd. for $C_{22}H_{17}O_4N$: 359.1158.

1-[*o*-(*p*-Fluorophenyl)benzoyl]-2-(*p*-tolyl)ethene (11g)

A mixture of *p*-tolualdehyde (**10a**) (70 mg, 0.55 mmol), **6c** (164 mg, 0.34 mmol) and benzoic acid (30 mg, 0.25 mmol) in benzene (4 mL) was held at reflux for 24 h. The reaction mixture was concentrated *in vacuo* and directly subjected to column chromatography on silica gel (eluant: chloroform–hexane 1 : 2.5–1 : 2) to give **11g** (48 mg, 45%); ν_{max} (neat)/cm^{-1} 3058, 3026, 2922, 1665, 1601, 1513, 1326, 1223, 761; δ_H (270 MHz, $CDCl_3$) 2.33 (3H, s, CH_3), 6.55 (1H, d, ^3J 15.8 Hz), 7.04 (2H, m), 7.12 (2H, d, ^3J 8.5 Hz), 7.17 (2H, d, ^3J 8.5 Hz), 7.25–7.56 (6H, m), 7.35 (1H, d, ^3J 15.8 Hz), δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 21.49 (+, CH_3), 115.51 (+, CH, $^3J_{C-F}$ 20.7 Hz), 125.78 (+, CH), 127.49 (+, CH), 128.22 (+, CH), 128.35 (+, CH, J_{C-F} 17.0 Hz), 129.59 (+, CH), 130.15 (+, CH), 130.64 (+, CH), 130.76 (+, CH), 131.75 (C_{quat}), 136.52 (C_{quat}, J_{C-F} 3.7 Hz), 139.75 (C_{quat}), 139.85 (C_{quat}), 141.11 (C_{quat}), 144.54 (+, CH), 162.50 (C_{quat}, J_{C-F} (−)247 Hz), 196.56 (C_{quat}, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 317 (MH^+, 100%), 199 (F-Ph-Ph-CO^+, 41); EI (70 eV) *m*/*z* 316 (M^+, 100%), 301 ($M^+ - CH_3$, 76), 222 (M^+ − [F-Ph], 33), 207 ($M^+ - 15$, 44), 199 (17). HRMS found: 316.1261; calcd. for $C_{22}H_{17}OF$: 316.1263.

17-Bromo-3-methoxy-16-{[*m*-(4-vinylphenyl)benzoyl]ethenyl}-estra-1,3,5(10),16-tetraene (13a)

A mixture of **12** (41 mg, 0.11 mmol), **7e** (58 mg, 0.12 mmol) and benzoic acid (15 mg, 0.12 mmol) was held at reflux for 20 h. The cooled solution was concentrated *in vacuo* and the residue was subjected to column chromatography on silca gel (hexane–ether 3 : 1) to give **13a** (48 mg, 75%) as colorless plates, mp 201–203 °C (hexane–ether 3 : 1); ν_{max} (KBr)/cm^{-1} 2926, 2854, 1657, 1580, 1499, 1309, 1255, 1192, 1021, 906, 842, 801, 729; δ_H (270 MHz, $CDCl_3$) 0.94 (3H, s, CH_3), 1.45–2.38 (10H, m), 2.60 (1H, dd, ^2J 13.8, ^3J 6.6 Hz), 2.91 (2H, m), 3.78 (3H, s, OCH_3), 5.30 (1H, d, ^3J 11.2 Hz), 5.81 (1H, d, ^3J 17.4 Hz), 6.66 (1H, br s), 6.72 (1H, m), 6.77 (1H, dd, ^3J 11.2, ^3J 17.4 Hz), 6.97 (1H, d, *J* 15.4 Hz), 7.20 (1H, d, ^3J 8.7 Hz), 7.52 (2H, d, ^3J 8.6 Hz), 7.57 (1H, d, ^3J 7.6 Hz), 7.61 (2H, d, ^3J 8.6 Hz), 7.75 (1H, d, ^3J 15.4 Hz), 7.76 (1H, m), 7.91 (1H, d, ^3J 7.6 Hz), 8.16 (1H, s); δ_C (67.8 MHz, $CDCl_3$, DEPT 135, DEPT 90) 15.60 (+, CH_3), 26.18 (−), 27.31 (−), 29.58 (−), 31.27 (−), 34.71 (−), 37.56 (+, CH), 42.22 (+, CH), 51.19 (C_{quat}), 53.39 (+, CH), 55.22 (+, OCH_3), 111.53 (+, CH), 113.94 (+, CH), 114.32 (−), 124.33 (+, CH), 126.00 (+, CH), 126.79 (+, CH, 2C), 126.97 (+, CH), 127.36 (+, CH, 2C), 129.05 (+, CH), 131.16 (+, CH), 132.20 (C_{quat}), 136.28 (+, CH), 136.58 (C_{quat}), 137.14 (C_{quat}), 137.66 (C_{quat}), 138.77 (C_{quat}), 138.94 (+, CH), 139.64 (C_{quat}), 141.29 (C_{quat}), 146.20 (C_{quat}), 157.64 (C_{quat}), 190.85 (C_{quat}, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* 581 ([^{81}Br]MH^+, 8%), 579 ([^{79}Br]MH^+, 9). HRMS found: 579.1899; calcd. for $C_{36}H_{36}O_2{}^{79}Br$: 579.1899.

17-Bromo-3-methoxy-16-[2-(*p*-{4-[(*E*)-2-(methoxycarbonyl)-ethenyl]phenyl}benzoyl)ethenyl]estra-1,3,5(10),16-tetraene (13b)

A mixture of **12** (41 mg, 0.11 mmol), **8c** (52 mg, 0.11 mmol), and benzoic acid (15 mg, 0.12 mmol) in benzene (1.5 mL) was reacted at 80 °C for 20 h. Thereafter the solution was cooled and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (ether–hexane 1 : 1) to give **13b** (52 mg, 85%) as a colorless powder; mp 177–178 °C (ether–hexane 1 : 1); ν_{max} (KBr)/cm^{-1} 2926, 1717, 1656, 1604, 1585, 1499, 1308, 1280, 1211, 1171, 829; δ_H (270 MHz, $CDCl_3$) 0.94 (3H, s, CH_3), 1.40–2.43 (11H, m), 2.60 (1H, dd, ^2J 14.8, ^3J 6.6 Hz), 2.93 (2H, m), 3.79 (3H, s, OCH_3), 3.83 (3H, s, OCH_3), 6.65 (1H, d, ^4J 3.0 Hz), 6.73 (1H, dd, ^3J 7.9, ^4J 3.0 Hz), 6.93 (1H, d, ^3J 16.2 Hz), 7.23 (1H, d, ^3J 7.9 Hz), 7.63 (2H, d, ^3J 8.2 Hz), 7.73 (2H, d, ^3J 16.2 Hz), 7.97 (2H, d, ^3J 8.2 Hz); δ_C (67.8 MHz,

$CDCl_3$, DEPT 90, DEPT 135) 15.60 (+, CH_3), 26.18 (−), 27.31 (−), 29.58 (−), 31.25 (−), 34.72 (−), 37.57 (+, CH), 44.24 (+, CH), 51.25 (C_{quat}), 51.91 (+, OCH_3), 53.40 (+, CH), 55.24 (+, OCH_3), 111.52 (+, CH), 113.96 (+, CH), 120.18 (+, CH), 123.93 (+, CH), 126.02 (+, CH), 128.17 (+, CH, 2C), 129.04 (+, CH, 2C), 132.18 (C_{quat}), 136.55 (C_{quat}), 137.64 (C_{quat}), 138.34 (C_{quat}), 139.15 (+, CH), 139.30 (C_{quat}), 143.47 (+, CH), 146.61 (C_{quat}), 157.66 (C_{quat}), 167.01 (C_{quat}, C=O), 189.95 (C_{quat}, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m/z* 563 ([^{81}Br]MH^+, 11%), 561 ([^{79}Br]MH^+, 12). HRMS found: 561.1637; calcd. for $C_{32}H_{34}O_4{}^{79}Br$: 561.1640.

17-Bromo-3-methoxy-16-(2-{[*p*-(4-vinylphenyl)benzoyl]}-ethenyl)estra-1,3,5(10),16-tetraene (13c)

A mixture of **12** (30 mg, 0.08 mmol), phosphorane **4i** (37 mg, 0.08 mmol), benzoic acid (10 mg, 0.08 mmol) in benzene (2 mL) were heated at 80 °C for 20 h. Thereafter the cooled solution was concentrated *in vacuo* and the residue was subjected to column chromatography on silica gel (ether–hexane 1 : 4) to give **13c** (28 mg, 60%) as a colorless powder; mp 190–191 °C (ether–hexane 1 : 4); ν_{max} (KBr)/cm^{-1} 2924, 2852, 1657, 1605, 1589, 1498, 1304, 1278, 1038, 824; δ_H (270 MHz, $CDCl_3$, ^{1}H–^{1}H-COSY) 0.95 (3H, s, CH_3), 1.55–2.61 (11H, m), 2.93 (2H, m), 3.79 (3H, s, OCH_3), 5.32 (1H, d, ^3J 10.9 Hz), 5.83 (1H, d, ^3J 16.8 Hz), 6.66 (1H, br s), 6.73 (1H, dd, ^3J 16.8, ^3J 10.9 Hz), 7.00 (1H, d, ^3J 15.2 Hz), 7.22–7.32 (2H, m), 7.51 (2H, d, ^3J 8.6 Hz), 7.62 (2H, d, ^3J 8.6 Hz), 7.68 (2H, d, ^3J 8.6 Hz), 7.75 (1H, d, ^3J 15.2 Hz), 8.04 (2H, d, ^3J 8.6 Hz); δ_C (67.8 MHz, $CDCl_3$) 15.62 (+, CH_3), 26.20 (−), 27.33 (−), 29.60 (−), 31.28 (−), 34.73 (−), 37.57 (+, CH), 44.26 (+, CH), 51.19 (C_{quat}), 53.42 (+, CH), 55.24 (+, OCH_3), 111.53 (+, CH), 113.96 (+, CH), 114.57 (−), 124.22 (+, CH), 126.02 (+, CH), 126.83 (+, CH, 2C), 127.02 (+, CH, 2C), 127.40 (+, CH, 2C), 129.13 (+, CH, 2C), 132.24 (C_{quat}), 136.22 (+, CH), 136.60 (C_{quat}), 136.91 (C_{quat}), 137.57 (C_{quat}), 137.68 (C_{quat}), 138.63 (+, CH), 139.24 (C_{quat}), 144.94 (C_{quat}), 146.02 (C_{quat}), 157.64 (C_{quat}), 190.20 (C_{quat}, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m/z* 581 ([^{81}Br]MH^+, 0.6%), 579 ([^{79}Br]MH^+, 0.6). HRMS found: 579.1896; calcd. for $C_{36}H_{36}O_2{}^{79}Br$: 579.1899.

7α-[12-(Phenylethynylbenzoyl)dodec-11-enyl]-17,17-(2,2-dimethylpropane-1,3-diyldioxy)-3-*O*-methylestra-1,3,5(10)-triene (15)

To **14** (35 mg, 0.06 mmol) in benzene (1.5 mL) were added benzoic acid (20 mg, 0.16 mmol) and the phosphorane **9a** (91 mg, 0.18 mmol). The resulting reaction mixture was held at reflux for 15 h. Then, the solution was concentrated *in vacuo* and subjected to column chromatography on silica gel (toluene–ethyl acetate 15 : 1) to give **15** (24 mg, 51%) as a pale yellow oil; R_f 0.68; ν_{max} (KBr)/cm^{-1} 3014, 2926, 2854, 1674, 1606, 1493, 1464, 1288, 1215, 1105, 1035, 756; δ_H (270 MHz, $CDCl_3$) 0.74 (3H, s, CH_3), 0.83 (3H, s, CH_3), 1,17 (3H, s, CH_3), 1.23–1.74 (22H, m), 1.93–2.12 (3H, m), 2.25–2.48 (6H, m), 2.68–2.76 (1H, m), 3.37–3.50 (3H, m), 3.67 (1H, d, *J* 11.2 Hz), 3.84 (3H, s, OCH_3), 6.88 (1H, d, *J* 15.5 Hz), 7.04–7.38 (6H, m), 7.52–7.57 (3H, m), 7.62 (2H, d, ^3J 8.2 Hz), 7.92 (2H, d, ^3J 8.2 Hz); δ_C (67.9 MHz, $CDCl_3$, DEPT 90, DEPT 135) 17.80 (+, CH_3), 22.02 (+, CH_3), 22.27 (−), 22.52 (+, CH_3), 23.83 (−), 26.55 (−), 26.93 (−), 27.42 (−), 28.17 (−), 29.25 (−), 29.35 (−), 29.37 (−), 29.48 (−), 29.55 (−), 29.72 (−), 30.38 (−), 32.92 (−), 37.32 (+, CH), 42.81 (+, CH), 42.92 (+, CH), 47.36 (C_{quat}), 48.86 (+, CH), 55.45 (+, OCH_3), 70.75 (−), 72.61 (−), 88.75 (C_{quat}), 92.45 (C_{quat}), 108.38 (C_{quat}), 110.00 (+, CH), 121.38 (+, CH), 122.73 (C_{quat}), 125.55 (+, CH), 127.23 (+, CH), 127.66 (C_{quat}), 128.43 (+, CH), 128.51 (+, CH), 128.75 (+, CH), 131.65 (+, CH), 131.74 (+, CH), 132.31 (C_{quat}), 137.20 (C_{quat}), 139.03 (C_{quat}), 150.52 (+, CH), 158.07 (C_{quat}), 189.97 (C_{quat}), 201.42 (C_{quat}); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (754, M^+); HRMS (FAB) found 755.4672 (MH^+); calcd. for $C_{51}H_{63}O_5$: 755.4676.

1-[*p*-(2-Thienyl)benzoyl]-2-(*p*-tolyl)ethene (11c)—general procedure E

A mixture of *p*-tolualdehyde (80 mg, 0.66 mmol), **4j** (166 mg, 0.33 mmol), 2-thienylboronic acid (85 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (24 mg, 2.0×10^{-2} mmol) in DME (2.5 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was held at 85 °C for 24 h. After the reaction solution had cooled, water (5 mL) was added and the mixture was extracted with chloroform (3 × 10 mL). The organic phase was dried over anhydrous $MgSO_4$. Thereafter, the solvent was evaporated *in vacuo* and the residue was subjected to column chromatography on silica gel (eluant: hexane–$CHCl_3$ 1 : 1) to give **11c** (79 mg, 79%) after recrystallization from hexane–ether (3 : 1).

1-[*p*-(*p*-Fluorophenyl)benzoyl]-2-(*p*-tolyl)ethene (11d)

A mixture of *p*-tolualdehyde (**10a**) (80 mg, 0.66 mmol), **3a** (166 mg, 0.33 mmol), *p*-fluorophenylboronic acid (93 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (34 mg, 2.8×10^{-2} mmol) in DME (2.5 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was reacted according to general procedure E (reaction time: 24 h). Column chromatography on silica gel (hexane–$CHCl_3$ 3 : 2) and recrystallization in hexane furnished **11d** (73 mg, 70%).

1-[*p*-(2-Thienyl)benzoyl]-2-(*o*-nitrophenyl)ethene (11h)

A mixture of *p*-tolualdehyde (**10a**) (100 mg, 0.66 mmol), **3a** (166 mg, 0.33 mmol), 2-thienylboronic acid (85 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (24 mg, 2.0×10^{-2} mmol) in DME (2.5 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was reacted according to general procedure E (reaction time: 24 h). Column chromatography on silica gel (hexane–$CHCl_3$ 1 : 1) and recrystallization in hexane furnished **11h** (88 mg, 75%) as a yellow solid; mp 155–156 °C (hexane) (Found: C, 67.71; H, 3.96; N, 4.21. $C_{19}H_{13}NO_3S$ requires C, 68.05; H, 3.91; N, 4.18%); ν_{max} (KBr)/cm^{-1} 2924, 2852, 1652, 1604, 1520, 1339, 1292, 1223, 1187, 856, 815; δ_H (270 MHz, $CDCl_3$) 7.13 (1H, dd, ^3J 5.1, ^3J 3.9 Hz), 7.33 (1H, d, ^3J 15.8 Hz), 7.38 (1H, m), 7.46 (1H, d, ^3J 3.9 Hz), 7.58 (1H, m), 7.75 (2H, d, ^3J 7.9 Hz), 7.75 (2H, m), 8.05 (2H, d, ^3J 7.9 Hz), 8.07 (1H, m), 8.16 (1H, d, ^3J 15.8 Hz); δ_C NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 124.76 (+, CH), 125.03 (+, CH), 125.82 (+, CH, 2C), 126.61 (+, CH), 127.30 (+, CH), 128.41 (+, CH), 129.29 (+, CH), 129.67 (+, CH, 2C), 130.33 (+, CH), 131.40 (C_{quat}), 133.55 (+, CH), 135.80 (C_{quat}), 139.10 (C_{quat}), 140.07 (+, CH), 142.90 (C_{quat}), 145.35 (C_{quat}), 189.40 (C_{quat}, C=O); MS (70 eV) *m/z* 335 (M^+, 14%), 303 (9), 289 (35), 187 (95), 115 (100). HRMS found: 335.0614; calcd. for $C_{19}H_{13}O_3NS$: 335.0616.

1-[*p*-(2-Thienyl)benzoyl]-2-cyclohexylethene (11i)

A mixture of cyclohexanecarbaldehyde (**10d**) (74 mg, 0.66 mmol), **3a** (166 mg, 0.33 mmol), 2-thienylboronic acid (**16a**) (85 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (24 mg, 2.0×10^{-2} mmol) in DME (2.5 mL) and 2 M aq. Na_2CO_3 (1.3 mL) was reacted according to general procedure E (reaction time: 17 h). Column chromatography on silica gel (hexane–$CHCl_3$ 1 : 1) and recrystallization in hexane furnished **11i** (78 mg, 80%) as a pale yellow solid; mp 82–83 °C (hexane) (Found: C, 76.82; H, 6.88. $C_{19}H_{20}OS$ requires C, 76.99; H, 6.80%); ν_{max} (KBr)/cm^{-1} 2916, 2846, 1657, 1609, 1596, 1422, 815, 685; δ_H (270 MHz, $CDCl_3$) 1.16–1.43 (4H, m), 1.68–1.87 (6H, m), 2.27 (1H, m), 6.84 (1H, dd, ^3J 15.5, ^4J 1.3 Hz), 7.03 (1H, dd, ^3J 15.5, ^3J 6.6 Hz), 7.12 (1H, dd, ^3J 3.9, ^3J 5.0 Hz), 7.42 (1H, dd, ^3J 3.9, ^4J 1.0 Hz), 7.36 (1H, dd, ^3J 5.0, ^4J 1.0 Hz), 7.70 (2H, d, ^3J 8.6 Hz), 7.94 (2H, d, ^3J 8.6 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 25.77 (−), 25.98 (−), 31.90 (−), 41.09 (+, CH), 123.20 (+, CH), 124.49 (+, CH), 125.66 (+, CH, 2C), 126.32 (+, CH), 128.35 (+, CH), 129.36 (+, CH, 2C), 136.80 (C_{quat}), 138.36 (C_{quat}), 143.14 (C_{quat}), 154.84 (+, CH), 190.35 (C_{quat}, C=O); MS (70 eV)

m/z 296 (M^+, 58%), 187 (100), 115 (24). HRMS found: 296.1236; calcd. for $C_{19}H_{20}OS$: 296.1235.

Approach to the preparation of elongated phosphoranes and their coupling reactions on a solid support

Under argon a mixture of 2-bromo-5-acetylthiophene (**3b**) (1.14 g, 4.0 mmol) and TPPPS resin ‡ (0.5 g, 0.8 mmol) in DME (4 mL) was stirred at 60 °C for 6 h. Thereafter, the resin was filtered and diligently washed with THF and CH_2Cl_2 and dried *in vacuo* at rt.

Then under an inert atmosphere, the resin was added to distilled water (3 mL) and aq. 7w% Na_2CO_3 (3 mL) was added and the mixture was stirred for 3 h. The resin was washed thoroughly with warm water (50 °C), THF (100 mL) and CH_2Cl_2 (100 mL) and subsequently dried *in vacuo* at rt.

Under an inert atmosphere, the resin was suspended in DME (4 mL) at rt. Then, 2-fluoroboronic acid (420 mg, 3 mmol), 2 M aq. Na_2CO_3 (3 mL) and $Pd(PPh_3)_4$ (45 mg, 4×10^{-5} mol) were added and the resulting mixture was stirred at 75 °C for 8 h. Thereafter, the resin was isolated by filtration and was washed with distilled water (100 mL), THF (100 mL) and CH_2Cl_2 (100 mL) and dried *in vacuo* at rt.

The resin was suspended in benzene (5 mL) and steroidal aldehyde (1.2 mmol) and benzoic acid (10 mg, 8×10^{-5} mol) were added. The resulting mixture was stirred at 80 °C under argon for 20 h. The resin was filtered off and washed with THF (50 mL) and CH_2Cl_2 (50 mL). The combined filtrate was concentrated *in vacuo* and the residue was subjected to column chromatography on silica gel (toluene–ether 10 : 1) to give 17-bromo-3-methoxy-16-{(*E*)-2-[*p*-(*o*-fluorophenyl)-benzoyl]ethenyl}estra-1,3,5(10),16-tetraene (**13d**) (132 mg, 29%) as a pale yellow solid; R_f 0.72; mp 185–186 °C; ν_{max} (KBr)/cm^{-1} 2924, 1736, 1658, 1608, 1587, 1500, 1280, 1255, 1034, 820, 753; δ_H (270 MHz, $CDCl_3$) 0.94 (3H, s, CH_3), 1.43–2.45 (10H, m), 2.62 (1H, dd, ^2J 13.8, ^3J 6.6 Hz), 2.93 (2H, m), 3.79 (3H, s, OCH_3), 6.66 (1H, d, ^4J 2.9 Hz), 6.73 (1H, dd, ^3J 8.5, ^4J 2.9 Hz), 7.00 (1H, d, ^3J 15.5 Hz), 7.15–7.28 (3H, m), 7.36 (1H, m), 7.48 (1H, m), 7.70 (2H, m), 7.76 (1H, d, ^3J 15.5 Hz), 8.05 (2H, d, ^3J 8.2 Hz); δ_C (67.8 MHz, $CDCl_3$) 15.58, 26.17, 27.30, 29.58, 31.23, 34.68, 37.52, 44.21, 51.16, 53.35, 55.22, 111.50, 113.91, 116.30 ($^3J_{C-F}$ 21.8 Hz), 124.08, 124.55, 126.00, 128.62, 129.20, 129.79, 129.92, 130.63, 132.18, 136.57, 137.18, 137.66, 138.72, 140.20, 146.13, 157.59, 159.75 ($^1J_{C-F}$ (−)263 Hz), 190.22; MS (70 eV) *m/z* 572 ([^{81}Br]M^+, 18%), 570 ([^{79}Br]M^+, 16). HRMS found: 570.1572; calcd. for $C_{34}H_{32}O_2{}^{79}BrF$: 570.1570.

X-Ray crystal structure determination of 4l §

Crystal data. $C_{36}H_{27}OP$, M = 506.55. Crystal system: monoclinic, unit cell dimensions: a = 15.4024(9), b = 8.0545(4), c = 21.492(1) Å, β = 96.1(8)° V = 2651(2) Å^3, space group $P2_1/c$, Z= 4, D_c = 1.269 g cm^{-3}, colorless, platelet, crystal size 0.40 × 0.20 × 0.05 mm, μ(Mo-Kα) = 0.132 mm^{-1}.

Data collection and processing. Rigaku RAXIS-RAPID, Imaging Plate, graphite-monochromated Mo-Kα radiation; 6425 reflections were measured ($1.33 \leq \theta \leq 27.48°$, $0 \leq h \leq 20$, $0 \leq k \leq 10$, $-27 \leq l \leq 27$). 6007 unique [max, min. transmission factor = 0.9492, 0.9934], linear and approx. isotopic crystal decay, *ca.* 0.0% corrected during procedure, measurement temperature 183.2 K.

Structure analysis and refinement. The structure was solved by direct methods (SIR92).[43] Full-matrix least-squares refinement on F^2 with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with U_{iso} = 1.3 $U_{(bonded\ atoms)}$ was performed. The weighting scheme is $w = 1/[\sigma^2(F_o^2) + (0.0976\ P)^2 + 0.0000\ P]$, where $P = (F_o^2 + 2\ Fc^2)/3$. Final R and R_w values for 3186 reflections with $I > 3.00\ \sigma(I)$ are 0.0694, 0.1643 (refined on F^2). All calculations were performed on a Gateway GP7-7000 using SIR92,[43] Texsan,[44] Oscail[45] and SHELXL-97–2.[46]

‡ At the beginning of all the reaction sequences, the solid support was 'pre-swelled' in the solvent for 1 h before use.

§ CCDC reference number 182734. See http://www.rsc.org/suppdata/p1/b2/b202745n/ for crystallographic files in .cif or other electronic format.

Acknowledgements

The testing of compounds **4a**, **4e**, **4h**, **4j**, **5b**, **5c**, **5m**, and **7d** was performed by the Developmental Therapeutics Program, DCTD, NCI in Bethesda, Maryland, USA. The elemental analyses were carried out at the Center of Analysis, Kyushu University, Hakozaki Campus, Fukuoka.

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17 Compound **4m** was prepared from the *p*-formylphenylboronic acid and trimethylene glycol in refluxing benzene.
18 Compound **4p** was prepared from 1-bromo-3,5-bis(trimethylsilylethynyl)benzene, **4n** from bromo-1-benzothiophene and **4o** from dibenzothiophene by lithiation and reaction with trimethyl borate with subsequent acidic work-up.
19 Typical examples are: 4′-acetyl-4-methoxybiphenyl, colorless solid, mp 152 °C (lit. 153–154 °C[47a]): ν_{max} (neat)/cm^{-1} 2956, 2840, 1674, 1399, 1361, 1294, 1032, 1011, 816; δ_H (270 MHz, $CDCl_3$) 2.63 (3H, s, CH_3), 3.86 (3H, s, OCH_3), 7.00 (2H, d, ^3J 8.6 Hz), 7.57 (2H, d, ^3J 8.6 Hz), 7.64 (2H, d, ^3J 8.6 Hz), 8.01 (2H, d, ^3J 8.6 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 26.58 (+, CH_3), 55.36 (+, OCH_3), 114.41 (+, CH, 2C), 126.59 (+, CH, 2C), 128.36 (+, CH, 2C), 128.93 (+, CH, 2C), 132.25 (C_{quat}), 135.29 (C_{quat}), 145.37 (C_{quat}), 159.93 (Cquat), 197.70 (Cquat, C=O); MS (70 eV) *m/z* 226 (M^+, 78%), 211 ($M^+ - CH_3$, 100), 183 (10), 168 (14), 139 (19). HRMS: found: 226.0995; calcd. for $C_{15}H_{14}O_2$: 226.0994; 4′-acetyl-4-fluorobiphenyl, colorless solid, mp 88 °C (lit. 90 °C[47b]): ν_{max} (neat)/cm^{-1} 2926, 1681, 1604, 1395, 906, 819, 731; δ_H (270 MHz, $CDCl_3$) 2.64 (3H, s, $COCH_3$), 7.16 (2H, dd, ^3J 8.2, $^3J_{H-F}$ 8.5 Hz), 7.59 (2H, dd, ^3J 8.2, $^4J_{H-F}$ 5.3 Hz), 7.64 (2H, d, ^3J 8.2 Hz), 8.02 (2H, d, ^3J 8.2 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 26.63 (+, CH_3), 115.91 (+, CH, 2C, $^2J_{C-F}$ 20.8 Hz), 127.06 (+, CH, 2C), 128.97 (+, CH, 4C), 135.87 (C_{quat}, $^4J_{C-F}$ 2.5 Hz), 136.01 (C_{quat}), 144.74 (C_{quat}), 163.00 (C_{quat}, $^1J_{C-F}$ 247.8 Hz), 197.66 (C_{quat}, C=O); MS (70 eV)

m/z 214 (M^+, 48%), 199 (100), 170 (55). HRMS: found: 214.0793; calcd. for $C_{14}H_{11}OF$: 214.0794; 5-acetylbithiophene, pale yellow solid, mp 112 °C (lit. 113 °C;[47c] 108–111 °C[47d]); ν_{max} (KBr)/cm^{-1} 3080, 2924, 1651, 1448, 1359, 1310, 1278, 1034, 932, 835, 802, 716, 691; δ_H (270 MHz, $CDCl_3$) 2.55 (3H, s, CH_3), 7.06 (1H, dd, ^3J 3.9, ^3J 4.6 Hz), 7.17 (1H, d, ^3J 3.9 Hz), 7.33 (2H, m), 7.59 (1H, d, ^3J 3.9 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 26.53 (+, CH_3), 124.13 (+, CH), 125.62 (+, CH), 126.49 (+, CH), 128.23 (+, CH), 131.90 (C_{quat}), 132.10 (C_{quat}), 133.28 (+, CH), 142.44 (C_{quat}), 198.15 (C_{quat}, C=O); MS (70 eV) *m/z* 208 (M^+, 76%), 193 ($M^+ - CH_3$, 100). HRMS: found: 208.0017; calcd. for $C_{10}H_8OS_2$: 208.0017; *p*-acetylphenylbenzothiophene, ν_{max} (KBr)/cm^{-1} 2922, 2850, 1674, 1261, 819; δ_H (270 MHz, $CDCl_3$) 2.57 (3H, s, CH_3), 7.28 (2H, m), 7.61 (1H, s), 7.76 (2H, d, ^3J 8.6 Hz), 7.82 (2H, m), 7.95 (2H, d, ^3J 8.6 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 26.63 (+, CH_3), 121.17 (+, CH), 122.34 (+, CH), 123.97 (+, CH), 124.78 (+, CH), 125.00 (+, CH), 126.34 (+, CH), 129.07 (+, CH), 134.80 (C_{quat}), 136.01 (C_{quat}), 138.55 (C_{quat}), 139.80 (C_{quat}), 140.06 (C_{quat}), 197.30 (C_{quat}, C=O); MS (70 eV) *m/z* 252 (M^+, 100%), 237 ($M^+ - CH_3$, 92), 208 (36), 165 (29). HRMS: found; 252.0606; calcd. for $C_{16}H_{12}OS$: 252.0609.

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