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Annelated P-containing heterocycles from aryl- and hetaryl-substituted phosphonium iodonium ylides with a methoxycarbonyl-group

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ABSTRACT

Hetaryl-substituted phosphonium–iodonium ylides with a methoxycarbonyl group as acceptor proved to be highly reactive toward various alkynes in comparison with triphenyl-substituted analogue. We were able to isolate annelated P-containing heterocycles—λ^5-phosphininothiophenes, λ^5-phosphininofurans, λ^5-phosphinolines, and rare polyaryl-substituted phosphonium salts, which can be traced back to three different rotamers of an intermediate adduct of the alkyne with the cation generated from the mixed ylide by removal of iodobenzene.

1. Introduction

Phosphorus-containing heterocycles are a less numerous and less accessible class of compounds in comparison with accessible nitrogen or sulfur heterocycles.[1] However, interest in this class of compound, especially toward the ones with an endocyclic P–C bond, has increased due to their recent use in wide variety of areas as model objects in fundamental research,[2] as ligands for new catalysts,[3] for modifying properties of materials[4] and as important building blocks for drug discovery[5].

Until recently λ^5-phosphinoline (Fig. 1) —the structural analogue of quinoline—was virtually inaccessible. There were only two known approaches to the synthesis of these heterocycles.[6]

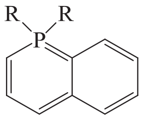
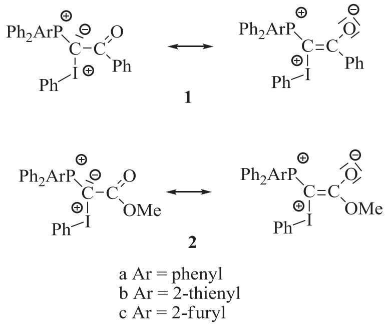


Fig. 1. λ^5-Phosphinoline is a structural analogue of quinoline.

Through the study of the properties of mixed ylides, we have opened new reactions to synthesize annelated P-containing compounds—interesting but virtually unexplored heterocyclic systems.

Recently we investigated the photochemical heterocyclization of mixed phosphonium–iodonium ylides of type **1** with a CC-triple bond[7] (Scheme 1). In this paper we summarize our results with the methoxycarbonyl group (**2** in Scheme 1) as acceptor unit. For the aryl substituent at the phosphorus atom we used phenyl, furyl or thienyl rings. It will be shown that there are remarkable differences in the reaction of **1** and **2** with alkynes.



Scheme 1. Structural representations of mixed ylides **1** and **2**.

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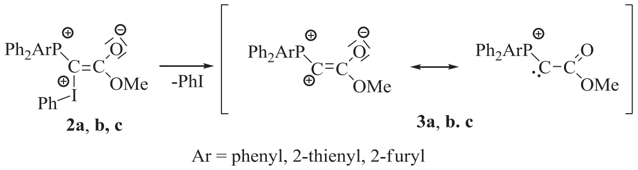
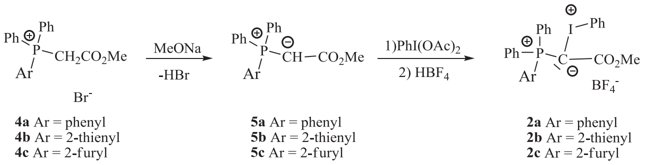
The higher reactivity of **2b**, **c** as compared to **2a** allows the generation of cation **3** (Scheme 2) at room temperature without irradiation. This in turn allowed us to trap various rotamers of **3** by reacting this species with alkynes.



Scheme 2. Generation of the intermediate **3** from **2**.

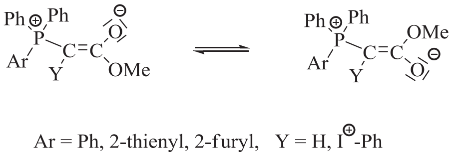
2. Results and discussion

The preparation of **2a** has been described earlier.[8] In Scheme 3 we summarize briefly the most important steps in the synthesis of the starting materials **2**.

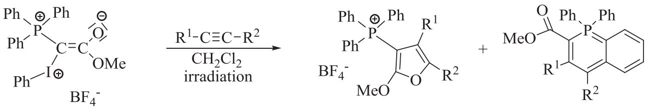


Scheme 3. Preparation of **2a**, **b**, **c** from the phosphonium salts **4a**, **b**, **c**.

The phosphoranes **5** were obtained quantitatively from the phosphonium salts **4**, respectively. The NMR spectroscopic data of **5** showed that there is a 1:1 mixture between the *Z*- and *E*-isomers as shown in Scheme 4.[8c]



Scheme 4. Equilibrium between *E*- and *Z*-isomers of **5** (Y=H) and **2** (Y=I$^+$–Ph).



2a

Alkyne	R^1	R^2	Furans		Phosphinoline	
6	H	Ph	-	-	**12**	75%
7	H	3-thienyl	-	-	**13**	50%
8	Ph	Ph	-	-	**14**	45%
9	H	n-C_8H_{17}	-	-	**15**	55%
10	H	*p*-MeO-C_6H_4	**16**	20%	**17**	50%
11	H	9-phenanthryl	**18**	65%	**19**	10%

Scheme 5. The reaction products and yields (%) of **2a** with alkynes **6**–**11**.

The phosphonium–iodonium ylides **2** (Scheme 3) were synthesized in high yields by oxidation of **5** with di(acetoxy)iodobenzene at 0 °C with further treatment of HBF_4. We found that the ylide **2b** is less stable than **2a**, and **2c** is less stable than **2b**; therefore **2b** has to be stored at 0 °C and **2c**—below 0 °C. For the three mixed ylides **2a**, **2b**, and **2c** we also observed an equilibrium between *E*- and *Z*-isomers by means of NMR studies.

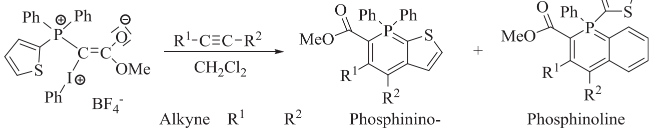
2.1. Reactions of 2a with alkynes

The reaction of ylide **2a** with alkynes took more time in comparison with ylide **1a**, it requires irradiation with a mercury lamp (366 nm) for 30–90 min.

The ylide **2a** chemoselectively interacted with alkynes **6**–**9** with the formation of λ^5-phosphinoline **12**–**15** with yields of 45–75%. The reaction of **2a** with alkynes **10**–**11** led to two heterocyclic systems—λ^5-phosphinoline **17**, **19**, and phosphonium substituted furans **16**, **18**. In the case of alkyne **10** the yield of phosphinoline was higher than the yield of furan, but this was opposite in the case of alkyne **11**. A similar situation was noted with ylide **1a**, but the product ratio was in favor of the furans in both cases.

2.2. Reactions of 2b with alkynes

The reaction of **2b** with terminal alkynes, such as phenylacetylene and 3-ethynylthiophene takes place in a few seconds without irradiation and even in the dark. Similarly, for 1-decyne, no light was necessary for the reaction with **2b**. This behavior contrasts with that of benzoyl substituted phosphonium ylides where irradiation was necessary. The reaction of **2b** with diphenylacetylene requires irradiation with a mercury lamp (366 nm) for 15 min. These results are summarized in Scheme 6. In all cases the thiophene ring and phenyl ring, respectively, are involved in the reaction, yielding to phosphininothiophenes (**20**, **22**, **24**, **26**) and phosphinolines (**21**, **23**, **25**, **27**).

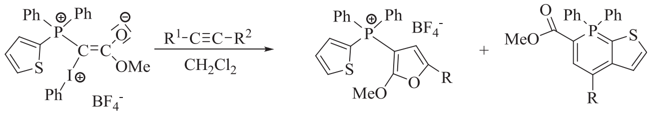


2b

Alkyne	R^1	R^2	Phosphinino-thiophene		Phosphinoline	
6	H	Ph	**20**	20%	**21**	20%
7	H	3-thienyl	**22**	20%	**23**	20%
8	Ph	Ph	**24**	40%	**25**	10%
9	H	n-C_8H_{17}	**26**	14*%	**27**	25%

Scheme 6. The reaction products and yields (%) of **2b** with alkynes **6**–**9**. In the case of diphenylacetylene irradiation was required. *Yield according to ^{31}P NMR spectroscopy of the reaction mixture.

The reaction of ylide **2b** with electron rich alkynes, such as 4-ethynylanisole and 9-ethynylphenanthrene also occurs very rapidly and no irradiation was necessary. The products obtained are summarized in Scheme 7. The main reaction products were the phosphonium substituted furans **28** and **30**. In the case of 4-ethynylanisole, the corresponding phosphininothiophene **29** could also be isolated as a minor product.



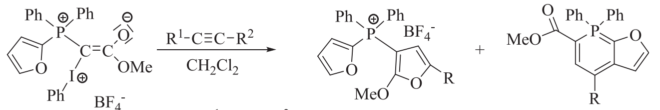
2b

Alkyne	R^1	R^2	Furans		Phosphinino-thiophene	
10	H	*p*-MeO-C_6H_4	**28**	35%	**29**	15%
11	H	9-phenanthryl	**30**	60%	-	-

Scheme 7. The reaction products and yields (%) of **2b** with alkynes **10**–**11**.

2.3. Reactions of 2c with alkynes

In Scheme 8 we have summarized the reaction between **2c** and alkynes **6**–**11**. Again these reactions proceed without irradiation and are complete within seconds. In the cases of alkynes **6**–**9** only phosphininofurans **31**–**34** were isolated. In the case of **34**, ^{31}P NMR measurements show a yield of 40% in solution, however, due to the low stability of the resulting phosphininofuran **34**, the isolated yield was only 10%. It is interesting to note that in the case of **2c** no phosphinolines were isolated.



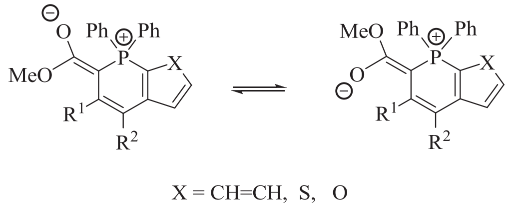
2c

Alkyne	R^1	R^2	Furans		Phosphinino-furans	
6	H	Ph	-	-	**31**	45%
7	H	3-thienyl	-	-	**32**	40%
8	Ph	Ph	-	-	**33**	40%
9	H	n-C_8H_{17}	-	-	**34**	10%
10	H	p-MeO-C_6H_4	**35**	15%	**36**	30%
11	H	9-phenanthryl	**37**	20%	**38**	30%

Scheme 8. The reaction products and yields (%) of **2c** with alkyne **6**–**11**.

The reaction of **2c** and the electron-rich alkynes 4-ethynylanisole and 9-ethynylphenanthrene lead to the formation of two heterocyclic systems: phosphininofurans (**36** and **38**) and phosphonium-substituted furans (**35** and **37**).

In the ^{31}P NMR spectrum the signals of the phosphinolines, phosphininothiophenes, phosphininofurans were observed as the superposition of two signals. This fact indicated the presence of a dynamic equilibrium between two geometric isomers of these heterocycles (Scheme 9).



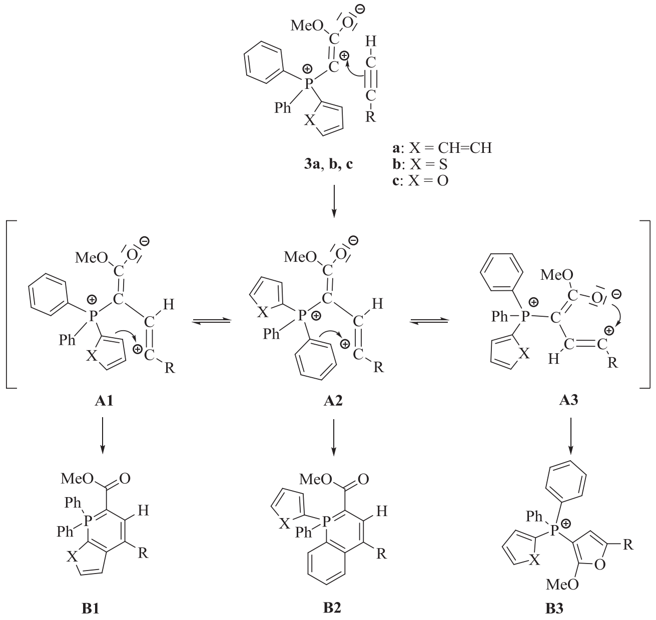
Scheme 9. A dynamic equilibrium between two geometric isomers.

All the studied processes were accompanied by the formation of the phosphonium salts having a signal in the ^{31}P NMR spectra at δ 14–15 ppm.[9]

2.4. Rationalization of products

Our rationale for the various products is shown in Scheme 10. This scheme is based on our previous preparative studies and on recent spectroscopic studies, which used steady state and time resolved methods to find transient species.[9b] These investigations suggest that in the first step, a cleaving of the C–I bond in **2a**, **b**, **c** occurs to produce the stabilized cations **3a**, **b**, **c**, respectively (cf. Scheme 2). In the case of **2a** irradiation was necessary, however, for **2b**, **c** the generation of the cation **3** occurs at room temperature without light. In the second step we assume the trapping of the vinylic cation **3** by the alkyne giving rise to cation **A** for which different conformers are likely, such as **A1**, **A2**, and **A3** (see Scheme 10). In case of ylide **2a** the products **B1** and **B2** are equal.

In the case of ylides **2b** and **2c**, the rotamers **A1** and **A2** provide four *ortho* positions from the two phenyl rings and only one from the thiophene or furan ring. Therefore we expect a ratio of the phosphinolines **B2** to the phosphininothiophenes or phosphininofuran (**B1**), respectively of 1:4. For the reaction of **2b** with phenylacetylene the ratio found was 1:1 (see Scheme 6). This indicates a preference of the thiophene over the phenyl ring for electrophilic substitution. In line with these arguments are the first ionization energies of thiophene=8.9 eV and benzene=9.3 eV. When we look at the reaction of **2b** with diphenylacetylene in Scheme 6 we find the anticipated ratio of 4:1. For steric reasons the reaction rate with diphenylacetylene is slowed down and thus the regioselectivity of the cations **A1** and **A2** is increased. The occurrence of products **B3** when electron rich substituents at the alkyne units are used (cf. Schemes 5, 7, and 8) can be traced back to a higher stability of the vinyl cation in the intermediate **A3**, which leads to **B3**.



Scheme 10. Plausible mechanism of formation of the products **B1**–**B3** from the rotamers **A1**–**A3**, which originate from **3a**–**c** and an alkyne.

3. Conclusions

Our studies reveal a considerable difference in the reactivity of the mixed ylides **1** and **2** toward alkynes. The higher reactivity of **2b** and **2c** allowed us to carry out reactions with various alkynes without irradiation. The results gave us evidence for the presence of three rotamers of the intermediate vinyl cation, which is generated from **3** and the alkyne. The reaction between **2** and alkynes provided us with new heterocycles, such as λ^5-phosphininothiophenes, λ^5-phosphininofurans, λ^5-phosphinolines, and rare polyaryl-substituted phosphonium salts.

4. Experimental section

4.1. General information

^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, and CD_3CN with Me_4Si as the internal standard. ^{1}H NMR spectra were measured at 400 MHz, ^{31}P NMR at 161 MHz, and ^{13}C NMR at 100 MHz. Chemical shifts (d) are reported in parts per million (ppm) and coupling constants (*J*) in Hertz. The IR spectra were measured in KBr or CCl_4. High resolution mass spectra (HRMS) were measured on a Bruker maXis instrument using electrospray ionization (ESI).[10] The measurements were done in a positive ion mode (interface capillary voltage—4500 V); mass range from *m*/*z* 50 to *m*/*z* 3000 Da; external calibration was done with Electrospray Calibrant Solution (Fluka). A syringe injection was used for solutions in acetonitrile, methanol, or water (flow rate 3 µL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. The progress of the reactions and the purity after chromatographic separation were monitored by TLC on silica gel 60 plates. Chromatographic separation was carried out on columns with silica gel 60.

4.2. General procedure for the synthesis of phosphonium salts 4b, 4c

Methyl bromoacetate (4.12 mmol) was added to a solution of phosphine (3.71 mmol) in dry acetonitrile (5 mL). A reaction mixture was stirred under reflux for 2 h, the precipitate was filtered, washed with diethyl ether (5 mL), and dried in vacuo to afford the corresponding product **2a** (**2c**).

*4.2.1. (2-Methoxy-2-oxoethyl)(diphenyl)thiophen-2-ylphosphonium bromide (**4b**).* White solid, 80% yield. [Found: C, 54.18; H, 4.32; S, 7.67. $C_{19}H_{18}BrO_2PS$ requires C, 54.17; H, 4.31; S, 7.61%]; Mp: 177–179 °C; ν_{max} (KBr) 1720, 1470, 780–700 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 8.20 (1H, ddd, *J* 4.8, 1.0 Hz, α-*H* thienyl), 8.03 (1H, ddd, *J* 8.1, 3.8, 1.0 Hz, β-H thienyl), 7.95–7.89 (4H, m, arom.), 7.86–7.82 (2H, m, arom.), 7.72–7.67 (4H, m, arom.), 7.46 (1H, m, β-*H* thienyl), 5.53 (2H, d, *J* 13.4 Hz, CH_2), 3.67 (3H, s, OCH_3); δ_C (100.6 MHz, $CDCl_3$) 164.9 (s, *C*=O), 143.4 (d, *J* 9.5 Hz, β-*C* thienyl), 140.0 (s, α-*C* thienyl), 135.1 (s, arom.), 133.3 (d, *J* 11.7 Hz, arom.), 130.2 (d, *J* 16.1 Hz, β-*C* thienyl), 130.0 (d, *J* 13.9 Hz, arom.), 118.5 (d, *J* 90.8 Hz, arom.), 115.2 (d, *J* 105.4 Hz, α-*C* thienyl), 53.2 (s, OCH_3), 34.0 (d, *J* 60.7 Hz, CH_2); δ_P (161 MHz, CD_2Cl_2) 14.93.

*4.2.2. Furan-2-yl(2-methoxy-2-oxoethyl)diphenylphosphonium bromide (**4c**).* White solid, 84% yield. [Found: C, 56.11; H, 4.47. $C_{19}H_{18}BrO_3P$ requires C, 56.32; H, 4.48%]; Mp: 187–189 °C; ν_{max} (KBr) 1760, 1480, 790–700 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 8.07–8.06 (1H, m, α-*H* fur), 7.99–7.93 (4H, m, arom.), 7.85–7.79 (3H, m, arom.), 7.71–7.66 (4H, m, arom.), 6.81 (1H, ddd, *J* 3.8, 3.7, 1.8 Hz, β-*H* fur), 5.51 (2H, d, *J* 13.9 Hz, CH_2), 3.65 (3H, s, OCH_3); δ_C (100.6 MHz, $CDCl_3$) 164.5 (s, *C*=O), 152.8 (d, *J* 7.3 Hz, α-*C* fur), 135.4 (s, arom.), 133.7 (d, *J* 11.7 Hz, arom.), 132.7 (d, *J* 132.5 Hz, α-*C* fur), 131.1 (d, *J* 19.8 Hz, β-*C* fur), 130.1 (d, *J* 13.9 Hz, arom.), 116.6 (d, *J* 94.4 Hz, arom.), 113.1 (d, *J* 9.5 Hz, β-*C* fur), 53.4 (s, OCH_3), 32.1 (d, *J* 60.7 Hz, CH_2); δ_P (161 MHz, $CDCl_3$) 8.74.

4.3. General procedure for the synthesis of phosphoranes 5b, 5c

A solution of sodium methoxide (3.18 mmol) in dry methanol (1 mL) was added gradually to a solution of phosphonium salt **4b** (**4c**) (3.10 mmol) in dry methanol (10 mL), at 0–5 °C. The mixture was stirred for 2 h, then it was evaporated in vacuo, and the residue was dissolved in methylene chloride (10 mL). The precipitate of sodium bromide was separated from the solution of ylide **5b** (**5c**) by filtration, washed on the filter with methylene chloride (2×5 mL). The residue was evaporated in vacuo, and the resulted oil was triturated with diethyl ether. The precipitate was separated by filtration, washed with ether (10 mL), and dried in vacuo to give the corresponding product **5b** (**5c**). The ylide **5c** was then used without further purification.

*4.3.1. Methyl [diphenyl(thiophen-2-yl)-λ^5-phosphanylidene]acetate (**5b**).* White solid, 74% yield. [Found: C, 66.82; H, 5.14; S, 9.15. $C_{19}H_{17}O_2PS$ requires C, 67.04; H, 5.03; S, 9.42%]; Mp: 157–179 °C; ν_{max} (KBr) 1620, 1470, 1440, 770–710 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.72 (1H, dd, *J* 4.2 Hz, α-*H* thienyl), 7.67 (4H, dd, *J* 13.0, 7.7 Hz, arom.), 7.56–7.53 (2H, m, arom.), 7.47–7.43 (5H, m, arom.), 7.16–7.15 (1H, m, arom.), 3.56 (3H, br s, OCH_3), 2.99 (1H, br s, C*H*); δ_C (100.6 MHz, $CDCl_3$) 171.3 (br s, *C*=O), 137.7 (d, *J* 6.6 Hz, β-*C* thienyl), 134.2 (d, *J* 2.9 Hz, α-*C* thienyl), 132.3 (d, *J* 11.0 Hz, arom.), 132.0 (s, arom.), 128.5 (d, *J* 12.4 Hz, arom.), 128.0 (d, *J* 13.9 Hz, β-*C* thienyl), 128.0 (d, *J* 98.8 Hz, arom.), 49.5 (s, OCH_3), 30.8 (d, *J* 131.7 Hz, *C*H); δ_P (161 MHz, CD_2Cl_2) 10.44, 9.28.

*4.3.2. Methyl [furan-2-yl(diphenyl)-λ^5-phosphanylidene]acetate (**5c**).* White solid, 70% yield. δ_H (400 MHz, CD_2Cl_2) 7.79 (1H, br s, α-*H* fur), 7.75–7.68 (4H, m, arom.), 7.60–7.57 (2H, m, arom.), 7.51–7.47 (4H, m, arom.), 7.19 (1H, br s, β-*H* fur), 6.60–6.59 (1H, m, β-*H* fur), 3.51, 3.30 (3H, 2 br s, OCH_3), 2.78, 2.47 (1H, 2 d, *J* 23.2 Hz, C*H*); δ_P (161 MHz, CD_2Cl_2) 4.70, 3.51.

4.4. General procedure for the synthesis of phosphonium–iodonium ylides 2b, 2c

A solution of diacetoxyiodobenzene (1.30 mmol) in methanol (3 mL) was added to the solution of ylide **3** (1.30 mmol) in methanol (2 mL) at 0–5 °C, then a solution of HBF_4 (40%, 1.30 mmol) was added at 0–5 °C. The mixture was stirred for 1 h, then diethyl ether (5 mL) was added, and stirred for 1 h. The precipitate was filtered, washed with diethyl ether (10 mL), and dried in vacuo to give the corresponding product **4**.

*4.4.1. [Diphenyl(thiophen-2-yl)phosphonio](methoxycarbonyl)(phenyliodonio)methanide tetrafluoroborate (**2b**).* White solid, 85% yield. [Found: C, 47.69; H, 3.42; S, 4.79. $C_{25}H_{21}BF_4IO_2PS$ requires C, 47.65; H, 3.36; S, 5.09%]; Mp: 210–212 °C; ν_{max} (KBr) 1610, 1470, 1440, 1300, 1120–1040, 750 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 8.00 (1H, ddd, *J* 4.8, 4.5, 0.9 Hz, α-*H* thienyl), 7.77–7.73 (2H, m, arom.), 7.63–7.51 (12H, m, arom.), 7.43 (2H, t, *J* 7.7 Hz, arom.), 7.33 (1H, m, β-*H* thienyl), 3.62 (3H, br s, OCH_3); δ_C (100.6 MHz, CD_3CN) 168.7 (d, *J* 14.6 Hz, *C*=O), 142.4 (d, *J* 10.3 Hz, β-*C* thienyl), 139.4 (d, *J* 4.4 Hz, α-*C* thienyl), 135.5 (s, arom.), 134.7 (d, *J* 11.0 Hz, arom.), 134.2 (s, arom.), 133.4 (s, arom.), 132.8 (s, arom.), 130.9 (d, *J* 13.7 Hz, arom.), 130.9 (d, *J* 13.7 Hz, β-*C* thienyl), 125.5 (d, *J* 98.1 Hz, arom.), 124.7 (d, *J* 90.0 Hz, α-*C* thienyl), 119.2 (s, arom.), 53.6 (s, OCH_3); δ_P (161 MHz, CD_2Cl_2) 22.39.

*4.4.2. [Furan-2-yl(diphenyl)phosphonio](methoxycarbonyl)(phenyliodonio)methanide tetrafluoroborate (**2c**).* White solid, 74% yield. [Found: C, 48.44; H, 3.51. $C_{25}H_{21}BF_4IO_3P$ requires C, 48.81; H, 3.60%]; Mp: 159–160 °C; ν_{max} (KBr) 1610, 1470, 1450, 1300, 1100–1040, 750 cm^{-1}; δ_H (400 MHz, CD_3CN) 8.04–8.03 (1H, m, α-*H* fur), 7.80–7.75 (2H, m, arom.), 7.67–7.57 (11H, m, arom.), 7.48 (2H, t, *J* 7.2 Hz, arom.), 7.12–7.11 (1H, m, β-*H* fur), 6.74–6.73 (1H, m, β-*H* fur), 3.57 (3H, br s, OCH_3); δ_C (100.6 MHz, CD_3CN) 168.4 (d, *J* 14.6 Hz, *C*=O), 153.3 (d, *J* 7.3 Hz, α-*C* fur), 140.1 (d, *J* 132.5 Hz, α-H fur), 135.6 (s, arom.), 134.6 (d, *J* 11.0 Hz, arom.), 134.1 (s, arom.), 133.4 (s, arom.), 132.9 (s, arom.), 130.9 (d, *J* 13.9 Hz, arom.), 129.7 (d, *J* 19.8 Hz, β-*C* fur), 124.1 (d, *J* 100.3 Hz, arom.), 119.0 (s, arom.), 113.6 (d, *J* 9.5 Hz, β-*C* fur), 53.6 (s, OCH_3); δ_P (161 MHz, CD_2Cl_2) 16.19.

4.5. General procedure for the reaction of ylides 2a, 2b, and 2c with alkynes

The alkyne (0.60 mmol) was added to a solution of ylide **2** (0.3 mmol) in anhydrous methylene chloride (2 mL). The progress of the reaction was monitored by TLC. After the end of the reaction, the mixture was concentrated in vacuo. The residue was dissolved in a minimum of CH_2Cl_2 and chromatographed on silica gel. To elute the residual alkynes and PhI, benzene was used; the corresponding phosphinoline was eluted by using a CH_2Cl_2, and the furans were eluted by using a CH_2Cl_2/MeOH mixture in a ratio of 100:1 and CH_2Cl_2/CH_3CN mixture in a ratio of 5:1.

*4.5.1. Methyl 1,1,4-triphenyl-1λ^5-phosphinoline-2-carboxylate (**12**).* Yellow oil, 75% yield (reaction with UV irradiation with a mercury lamp (366 nm) for 30 min). ν_{max} (liquid film) 1635, 1577, 1436, 767–692 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.06 (4H, dd, *J* 8.2, 11.7 Hz, arom.), 7.61–7.51 (6H, m, arom.), 7.49–7.28 (9H, m, arom.), 7.06 (1H, dd, *J* 7.1, 7.1 Hz, arom.), 3.60 (3H, br s, OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 168.7 (d, *J* 10.2 Hz, *C*=O), 143.4 (s, arom.), 142.2 (d, *J* 4.7 Hz, arom.), 133.7 (d, *J* 10.9 Hz, arom.), 133.7 (d, *J* 7.8 Hz, arom.), 133.4 (br s, arom.), 132.3 (d, *J* 3.1 Hz, arom.), 131.8 (d, *J* 1.6 Hz, arom.), 130.6 (s, arom.), 129.1 (d, *J* 13.2 Hz, arom.), 128.8 (s, arom.), 126.3 (s, arom.), 125.6 (d, *J* 7.8 Hz, arom.), 123.8 (d, *J* 11.7 Hz, arom.), 50.8 (br s, OCH_3); δ_P (161 MHz, CD_2Cl_2) 5.47; HRMS (EI): M^+, found 434.1420. $C_{29}H_{23}O_2P$ requires 434.1430.

*4.5.2. Methyl 1,1-diphenyl-4-thiophen-3-yl-1λ^5-phosphinoline-2-carboxylate (**13**).* Yellow oil, 50% yield (reaction with UV irradiation with a mercury lamp (366 nm) for 30 min). ν_{max} (liquid film) 1637, 1575, 1437, 788–744 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.73 (4H, dd, *J* 7.8, 12.5 Hz, arom.), 7.60–7.41 (9H, m, arom.), 7.38–7.34 (2H, m, arom.), 7.20 (1H, dd, *J* 3.1, 1.2 Hz, arom.), 7.16 (1H, dd, *J* 4.7, 1.2 Hz, arom.), 7.08–7.04 (1H, m, arom.), 3.57 (3H, br s, OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 168.6 (br s, *C*=O), 143.8, 142.3 (two s, arom.), 133.7 (d, *J* 10.2 Hz, arom.), 132.3, 131.9, 130.4 (all s, arom.), 129.1 (d, *J* 12.5 Hz, arom.), 125.5 (d, *J* 8.1 Hz, arom.), 125.1 (s, arom.), 123.8 (d, *J* 12.4 Hz, arom.), 122.1 (s, arom.), 50.7 (br s, OCH_3); δ_P (161 MHz, CD_2Cl_2) 5.53; HRMS (EI): M$^+$, found 440.0989. $C_{27}H_{21}O_2PS$ requires 440.0994.

*4.5.3. Methyl 1,1,3,4-tetraphenyl-1λ^5-phosphinoline-2-carboxylate (**14**).* Yellow oil, 45% yield (reaction with UV irradiation with a mercury lamp (366 nm) for 90 min). ν_{max} (liquid film) 1627, 1427, 784–759 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.82 (4H, ddd, *J* 13.0, 8.3, 1.6, arom.), 7.63–7.54 (6H, m, arom.), 7.36 (1H, ddd, *J* 12.9, 7.8, 1.3, arom.), 7.27–7.24 (1H, m, arom.), 7.14–6.94 (11H, m, arom.), 6.91 (1H, dd, *J* 8.2, 5.3, arom.), 2.97 (3H, s, OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 167.6 (d, *J* 12.4, *C*=O), 144.5 (d, *J* 10.2, arom.), 143.7 (d, *J* 2.9, arom.), 142.8 (d, *J* 5.1, arom.), 141.9, 133.66 (two s, arom.), 133.6 (d, *J* 11.0, arom.), 132.8 (d, *J* 7.3, arom.), 132.1, 131.7, 130.4 (all s, arom.), 129.8 (d, *J* 92.2, arom.), 129.1 (d, *J* 12.4, arom.), 120.0 (s, arom.), 126.9 (d, *J* 8.1, arom.), 126.8, 125.9, 125.4 (all s, arom.), 124.0 (d, *J* 11.7, arom.), 118.3 (d, *J* 8.1, arom.), 110.6 (d, *J* 88.6, arom.), 55.8 (d, *J* 109.0, *C*-COOMe), 49.7 (s, OCH_3); δ_P (161 MHz, CD_2Cl_2) 9.35; HRMS (EI): M$^+$, found 510.1728. $C_{35}H_{27}O_2P$ requires 510.1743.

*4.5.4. Methyl 4-octyl-1,1-diphenyl-1λ^5-phosphinoline-2-carboxylate (**15**).* Yellow oil, 55% yield (reaction with UV irradiation with a mercury lamp (366 nm) for 60 min). ν_{max} (liquid film) 2925, 1666, 1635, 1579, 1434, 786–744 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.69–7.64 (4H, m, arom.), 7.56–7.37 (9H, m, arom.), 7.24 (1H, d, *J* 29.4, *C*H), 7.06–7.02 (1H, m, arom.), 3.60, 3.39 (3H, two br s, OCH_3), 2.57 (2H, t, *J* 7.5, CH_2), 1.64–1.55 (2H, m, CH_2), 1.41–1.30 (10H, m, 5CH_2), 0.90 (3H, t, *J* 7.1, CH_3); δ_C (100.6 MHz, CD_2Cl_2) 168.7 (d, *J* 13.9, *C*=O), 142.5 (d, *J* 4.4, arom.), 133.9 (d, *J* 8.1, arom.), 133.7 (d, *J* 11.0, arom.), 132.1 (d, *J* 2.2, arom.), 132.0 (s, arom.), 130.4 (br s, *C*H), 129.0 (d, *J* 13.2, arom.), 123.6 (d, *J* 8.1, arom.), 123.3 (d, *J* 12.4, arom.), 111.7 (br s, arom.), 103.5 (d, *J* 101.7, arom.), 50.63, 50.14 (two br.s, OCH_3), 34.8, 32.5, 30.6, 30.3, 30.2, 30.0, 23.3 (all s, 7CH_2), 14.5 (s, CH_3); δ_P (161 MHz, CD_2Cl_2) 6.50, 6.01; HRMS (EI): M$^+$, found 470.2356. $C_{31}H_{35}O_2P$ requires 470.2369.

*4.5.5. [2-Methoxy-5-(4-methoxyphenyl)furan-3-yl](triphenyl)phosphonium tetrafluoroborate (**16**).* Colorless oil, 20% yield (reaction with UV irradiation with a mercury lamp (366 nm) for 30 min). ν_{max} (liquid film) 1470, 1070, 730 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.91–7.87 (3H, m, arom.), 7.77–7.72 (6H, m, arom.), 7.66 (6H, dd, *J* 7.3, 13.5 Hz, arom.), 7.53 (2H, d, *J* 9.0 Hz, arom.), 6.96 (2H, d, *J* 9.0 Hz, arom.), 6.33 (1H, d, *J* 2.6 Hz, *C*H), 4.05 (3H, s, OCH_3), 3.83 (3H, s, OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 165.4 (d, *J* 13.7 Hz, *C*–Ph–OMe), 160.6 (s, arom.), 148.5 (d, *J* 13.7 Hz, MeO–*C*–O), 135.9 (d, *J* 2.9 Hz, arom.), 134.4 (d, *J* 10.8 Hz, arom.), 130.9 (d, *J* 13.7 Hz, arom.), 125.5 (s, arom.), 121.4 (s, arom.), 119.2 (d, *J* 94.3 Hz, arom.), 115.0 (s, arom.), 105.6 (d, *J* 10.1 Hz, Ph_3P^+C–*C*H), 73.9 (d, *J* 121.6 Hz, Ph_3P^+*C*), 59.6 (s, OCH_3), 55.9 (s, OCH_3); δ_P (161 MHz, CD_2Cl_2) 12.25; HRMS (EI): M$^+$, found 465.1623. $C_{30}H_{26}O_3P$ requires 465.1614.

*4.5.6. Methyl 4-(4-methoxyphenyl)-1,1-diphenyl-1λ^5-phosphinoline-2-carboxylate (**17**).* Yellow oil, 50% yield (reaction with UV irradiation with a mercury lamp (366 nm) for 30 min). ν_{max} (liquid film) 1640, 1580, 1470, 750–730 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.76–7.71 (4H, m, arom.), 7.59–7.50 (6H, m, arom.), 7.46–7.29 (4H, m, arom.), 7.30 (2H, d, *J* 8.7 Hz, arom.), 7.04 (1H, dd, *J* 7.5, 7.5 Hz, arom.), 6.94 (2H, d, *J* 8.7 Hz, arom.), 3.84 (3H, s, PhOCH_3), 3.56 (3H, br s, C(O)OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 168.7 (d, *J* 12.9 Hz, *C*=O), 158.6 (s, arom.), 142.6 (d, *J* 5.2 Hz, arom.), 135.8 (s, arom.), 133.7 (d, *J* 10.4 Hz, arom.), 133.7 (d, *J* 7.8 Hz, arom.), 132.3 (d, *J* 2.6 Hz, arom.), 131.7 (s, arom.), 129.1 (d, *J* 12.9 Hz, arom.), 125.7 (d, *J* 7.8 Hz, arom.), 123.7 (d, *J* 12.9 Hz, arom.), 114.2 (s, arom.), 55.8 (s, Ph-OCH_3), 50.6 (br s, C(O)OCH_3); δ_P (161 MHz, CD_2Cl_2) 5.63; HRMS (EI): M$^+$, found 464.1543. $C_{30}H_{25}O_3P$ requires 464.1536.

*4.5.7. (2-Methoxy-5-phenanthren-9-ylfuran-3-yl)(triphenyl)-phosphonium tetrafluoroborate (**18**).* Colorless oil, 65% yield (reaction with UV irradiation with a mercury lamp (366 nm) for 60 min). ν_{max} (liquid film) 1590, 1470, 1070, 750–720 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 8.80 (1H, d, *J* 7.8 Hz, arom.), 8.72 (1H, d, *J* 8.4 Hz, arom.), 8.23 (1H, dd, *J* 8.2, 1.4 Hz, arom.), 8.03 (1H, s, arom.), 7.98 (1H, d, *J* 8.0 Hz, arom.), 7.94–7.90 (3H, m, arom.), 7.81–7.64 (16H, m, arom.), 6.61 (1H, d, *J* 2.6 Hz, CH), 4.14 (3H, s, OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 166.1 (d, *J* 13.2 Hz, O–*C*–Phntr), 147.8 (d, *J* 13.9 Hz, MeO–*C*–O), 136.0 (s, arom.), 134.4 (d, *J* 11.0 Hz, arom.), 131.35, 131.23 (two s, arom.), 130.9 (d, *J* 13.9 Hz, arom.), 129.6, 129.4, 129.2, 129.0, 128.5, 127.9, 127.7, 125.9, 124.9, 123.9, 123.1 (all s, arom.), 119.1 (d, *J* 94.4 Hz, arom.), 112.3 (d, *J* 10.2 Hz, Ph_3P^+C–*C*H), 73.9 (d, *J* 121.5 Hz, Ph_3P^+*C*), 59.8 (s, OCH_3); δ_P (161 MHz, CD_2Cl_2) 12.50; HRMS (EI): M$^+$, found 535.1824. $C_{37}H_{28}O_2P$ requires 535.1821.

*4.5.8. Methyl 4-(phenanthren-9-yl)-1,1-diphenyl-1λ^5-phosphinoline-2-carboxylate (**19**).* Yellow oil, 10% yield (reaction with UV irradiation with a mercury lamp (366 nm) for 90 min). ν_{max} (liquid film) 1666, 1637, 1573, 1436, 786–763 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 8.77 (2H, t, *J* 9.0, arom.), 7.92–7.78 (7H, m, arom.), 7.70–7.44 (12H, m, arom.), 7.16–7.12 (1H, m, arom.), 7.03–6.99 (1H, m, arom.), 6.83 (1H, dd, *J* 8.1, 5.7, arom.), 3.53 (3H, br s, OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 168.8 (d, *J* 13.2, *C*=O), 143.1 (d, *J* 3.7, arom.), 139.7 (s, arom.), 134.0 (d, *J* 11.0, arom.), 133.7 (d, *J* 11.0, arom.), 133.5 (d, *J* 9.5, arom.), 133.0, 132.4, 131.8, 131.1, 130.5, 129.4 (all s, arom.), 129.3 (d, *J* 13.2, arom.), 129.1 (d, *J* 12.4, arom.), 129.0, 128.0, 127.2, 127.0, 126.8 (all s, arom.), 126.4 (d, *J* 7.3, arom.), 123.7 (d, *J* 12.4, arom.), 123.4, 123.0 (two s, arom.), 50.70 (br s, OCH_3); δ_P (161 MHz, CD_2Cl_2) 8.01; HRMS (EI): M$^+$, found 534.1728. $C_{37}H_{27}O_2P$ requires 534.1743.

*4.5.9. Methyl 4,7,7-triphenyl-7λ^5-phosphinino[2,3-b]thiophene-6-carboxylate (**20**).* Yellow oil, 20% yield. ν_{max} (liquid film) 1641, 1479, 1437, 797–758 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.69 (4H, dd, *J* 13.4, 7.0 Hz, arom.), 7.58–7.48 (8H, m, arom.), 7.44 (1H, d, *J* 32.1 Hz, *C*H), 7.38 (2H, m, arom.), 7.26 (1H, tt, *J* 7.3, 1.3 Hz, arom.), 7.03–6.98 (2H, m, α,β-*H* thienyl), 3.56 (3H, br s, OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 169.1 (d, *J* 15.3 Hz, *C*=O), 154.6 (d, *J* 8.5 Hz, arom.), 142.9 (s, arom.), 133.4 (d, *J* 11.7 Hz, arom.), 132.4 (br s, *C*H=C–Ph), 132.3 (d, *J* 2.7 Hz, arom.), 129.1 (d, *J* 13.0 Hz, arom.), 129.0 (s, arom.), 128.7 (s, arom.), 128.6 (d, *J* 13.0 Hz, β-*C* thienyl), 128.1 (d, *J* 99.2 Hz, arom.), 126.7 (s, arom.), 121.3 (d, *J* 17.1 Hz, α-*C* thienyl), 111.9 (br s, CH=*C*–Ph), 104.5 (d, *J* 100.1 Hz, arom.), 61.7 (d, *J* 110.4 Hz, *C*1), 50.9 (d, *J* 2.7 Hz, OCH_3); δ_P (161 MHz, CD_2Cl_2) 2.94; HRMS (EI): M$^+$, found 440.0995. $C_{27}H_{21}O_2PS$ requires 440.0994.

*4.5.10. Methyl 1,4-diphenyl-1-thiophen-2-yl-1λ^5-phosphinoline-2-carboxylate (**21**).* Yellow oil, 20% yield. ν_{max} (liquid film) 1664, 1458, 1435, 767–705 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.84 (1H, ddd, *J* 5.0, 5.0, 1.1 Hz, β-*H* thienyl), 7.79 (2H, dd, *J* 14.0, 7.0 Hz, arom.), 7.58–7.47 (5H, m, arom.), 7.41–7.25 (8H, m, arom.), 7.22 (1H, ddd, *J* 5.0, 3.6, 1.7 Hz, β-*H* thienyl), 7.09–7.04 (1H, m, arom.), 3.55 (3H, br s, OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 168.7 (d, *J* 14.8 Hz, *C*=O), 143.3 (s, arom.), 142.1 (d, *J* 5.8 Hz, arom.), 138.4 (d, *J* 19.3 Hz, β-*C* thienyl), 135.7 (d, *J* 4.9 Hz, β-*C* thienyl), 133.9 (d, *J* 8.1 Hz, α-*C* thienyl), 133.3 (d, *J* 11.2 Hz, arom.), 133.0 (br s, *C*H=C–Ph), 132.5 (d, *J* 3.1 Hz, arom.), 132.0 (d, *J* 1.8 Hz, arom.), 130.7 (s, arom.), 129.1 (d, *J* 13.5 Hz, arom.), 128.8 (s, arom.), 128.8 (d, *J* 13.9 Hz, arom.), 128.1 (d, *J* 95.1 Hz, arom.), 127.9 (d, *J* 87.1 Hz, arom.), 126.4 (s, arom.), 125.8 (d, *J* 8.5 Hz, arom.), 123.8 (d, *J* 12.6 Hz, arom.), 115.8 (br s, CH=*C*–Ph), 109.8 (d, *J*

91.6 Hz, arom.), 50.7 (br s, OC*H*$_3$); δ_P (161 MHz, CD_2Cl_2) −1.36; HRMS (EI): M$^+$, found 440.0988. $C_{27}H_{21}O_2PS$ requires 440.0994.

*4.5.11. Methyl 7,7-diphenyl-4-thiophen-3-yl-7λ^5-phosphinino[2,3-b]thiophene-6-carboxylate (**22**).* Yellow oil, 20% yield. ν_{max} (liquid film) 1655, 1477, 1427, 784–707 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.68 (4H, dd, *J* 13.6, 7.0 Hz, arom.), 7.60–7.49 (8H, m, arom.), 7.38–7.33 (2H, m, arom.), 7.07 (1H, dd, *J* 5.5, 3.1 Hz, α-*H* thienyl), 7.01 (1H, dd, *J* 5.5, 3.7 Hz, β-*H* thienyl), 3.57 (3H, br s, OC*H*$_3$); δ_C (100.6 MHz, CD_2Cl_2) 169.0 (d, *J* 9.9 Hz, *C*═O), 154.4 (d, *J* 8.5 Hz, arom.), 143.3 (s, arom.), 133.4 (d, *J* 11.7 Hz, arom.), 132.3 (d, *J* 3.1 Hz, arom.), 132.2 (br s, *C*H═C thienyl), 129.1 (d, *J* 103.7 Hz, arom.), 129.1 (d, *J* 13.0 Hz, arom.), 128.6 (d, *J* 13.0 Hz, β-*C* thienyl), 128.6 (s, arom.), 125.6 (s, arom.), 121.5 (d, *J* 17.5 Hz, α-*C* thienyl), 120.0 (s, arom.), 106.8 (br s, CH═*C* thienyl), 104.4 (d, *J* 97.4 Hz, arom.), 50.9 (d, *J* 4.0 Hz, O*C*H$_3$); δ_P (161 MHz, CD_2Cl_2) 4.85; HRMS (EI): M$^+$, found 446.0550. $C_{25}H_{19}O_2PS_2$ requires 446.0559.

*4.5.12. Methyl 1-phenyl-1-thiophen-2-yl-4-thiophen-3-yl-1λ^5-phosphinoline-2-carboxylate (**23**).* Yellow oil, 20% yield. ν_{max} (liquid film) 1664, 1458, 1435, 779–717 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.83 (1H, ddd, *J* 5.0, 5.0, 0.9 Hz, β-*H* thienyl), 7.77 (2H, dd, *J* 14.2, 7.2 Hz, arom.), 7.59–7.43 (6H, m, arom.), 7.38 (1H, d, *J* 30.5 Hz, C*H*), 7.39–7.34 (2H, m, arom.), 7.21 (1H, ddd, *J* 5.1, 3.7, 1.9 Hz, β-*H* thienyl), 7.18 (1H, dd, *J* 2.9, 1.3 Hz, arom.), 7.13 (1H, dd, *J* 4.8, 1.3 Hz, arom.), 7.10–7.05 (1H, m, arom.), 3.55 (3H, br s, OC*H*$_3$); δ_C (100.6 MHz, CD_2Cl_2) 168.6 (br s, *C*═O), 143.8 (s, arom.), 142.2 (d, *J* 5.4 Hz, arom.), 138.5 (d, *J* 10.3 Hz, β-*C* thienyl), 135.7 (d, *J* 4.5 Hz, β-*C* thienyl), 133.9 (d, *J* 8.1 Hz, α-*C* thienyl), 133.3 (d, *J* 11.7 Hz, arom.), 133.2 (br s, *C*H═C thienyl), 132.6 (d, *J* 3.1 Hz, arom.), 132.2 (d, *J* 1.8 Hz, arom.), 130.5 (s, arom.), 129.1 (d, *J* 13.5 Hz, arom.), 128.8 (d, *J* 14.4 Hz, arom.), 128.0 (d, *J* 98.3 Hz, arom.), 127.8 (d, *J* 87.5 Hz, arom.), 125.7 (d, *J* 8.1 Hz, arom.), 125.2 (s, arom.), 123.8 (d, *J* 12.6 Hz, arom.), 122.3 (s, arom.), 110.2 (br s, CH═*C* thienyl), 108.7 (d, *J* 91.1 Hz, arom.), 50.8 (d, *J* 4.1 Hz, O*C*H$_3$); δ_P (161 MHz, CD_2Cl_2) 0.58; HRMS (EI): M$^+$, found 446.0554. $C_{25}H_{19}O_2PS_2$ requires 446.0559.

*4.5.13. Methyl 4,5,7,7-tetraphenyl-7λ^5-phosphinino[2,3-b]thiophene-6-carboxylate (**24**).* Yellow oil, 40% yield (reaction with UV irradiation with a mercury lamp (366 nm)). ν_{max} (liquid film) 1682, 1466, 1427, 760–700 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.80 (4H, ddd, *J* 13.6, 7.3, 1.7 Hz, arom.), 7.59–7.53 (6H, m, arom.), 7.14–6.97 (12H, m, arom.), 3.07 (3H, s, OC*H*$_3$); δ_C (100.6 MHz, CD_2Cl_2) 169.3 (d, *J* 12.6 Hz, *C*═O), 157.7 (d, *J* 9.4 Hz, arom.), 144.4 (d, *J* 12.1 Hz, arom.), 143.7 (d, *J* 7.6 Hz, *C*—Ph), 143.2 (s, arom.), 134.3 (d, *J* 11.2 Hz, arom.), 133.6 (s, arom.), 133.0 (d, *J* 2.7 Hz, arom.), 131.6 (d, *J* 94.7 Hz, arom.), 131.5 (s, arom.), 130.0 (d, *J* 13.0 Hz, arom.), 129.5 (d, *J* 11.7 Hz, β-*C* thienyl), 129.2 (s, arom.), 128.0 (s, arom.), 127.6 (s, arom.), 126.9 (s, arom.), 123.5 (d, *J* 16.6 Hz, α-*C* thienyl), 114.8 (d, *J* 6.7 Hz, *C*—Ph), 106.1 (d, *J* 94.2 Hz, arom.), 61.2 (d, *J* 112.2 Hz, *C*1), 51.0 (s, O*C*H$_3$); δ_P (161 MHz, CD_2Cl_2) 4.79; HRMS (EI): M$^+$, found 516.1301. $C_{33}H_{25}O_2PS$ requires 516.1307.

*4.5.14. Methyl 1,3,4-triphenyl-1-thiophen-2-yl-1λ^5-phosphinoline-2-carboxylate (**25**).* Yellow oil, 10% yield (reaction with UV irradiation with a mercury lamp (366 nm)). ν_{max} (liquid film) 1674, 1456, 1427, 758–700 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.90–7.84 (3H, m, arom.), 7.60–7.53 (3H, m, arom.), 7.50 (1H, ddd, *J* 7.6, 3.6, 0.9 Hz, arom.), 7.42 (1H, ddd, *J* 13.6, 7.8, 0.9 Hz, arom.), 7.29–7.25 (2H, m, arom.), 7.13–6.95 (11H, m, arom.), 6.90–6.87 (1H, m, arom.), 3.04 (3H, s, OC*H*$_3$); δ_C (100.6 MHz, CD_2Cl_2) 167.6 (d, *J* 11.2 Hz, *C*═O), 144.3 (d, *J* 11.7 Hz, arom.), 143.6 (d, *J* 8.5 Hz, *C*—Ph), 142.8 (d, *J* 5.8 Hz, arom.), 141.9 (s, arom.), 138.3 (d, *J* 9.9 Hz, β-*C* thienyl), 135.5 (d, *J* 4.0 Hz, β-*C* thienyl), 133.7 (s, arom.), 133.1 (d, *J* 7.6 Hz, α-*C* thienyl), 133.0 (d, *J* 11.2 Hz, arom.), 132.3 (d, *J* 2.2 Hz, arom.), 132.0 (d, *J* 97.8 Hz, arom.), 131.9 (s, arom.), 131.2 (d, *J* 96.0 Hz, arom.), 129.1 (d, *J* 13.5 Hz, arom.), 128.7 (d, *J* 14.4 Hz, arom.), 128.0 (s, arom.), 127.1 (d, *J* 8.5 Hz, arom.), 126.8 (s, arom.), 126.0 (s, arom.), 125.5 (s, arom.), 123.9 (d, *J* 12.6 Hz, arom.), 118.1 (d, *J* 8.5 Hz, *C*—Ph), 110.6 (d, *J* 91.1 Hz, arom.), 58.3 (d, *J* 112.2 Hz, *C*1), 49.9 (s, O*C*H$_3$); δ_P (161 MHz, CD_2Cl_2) 0.62; HRMS (EI): M$^+$, found 516.1299. $C_{33}H_{25}O_2PS$ requires 516.1307.

*4.5.15. Methyl 4-octyl-1-phenyl-1-thiophen-2-yl-1λ^5-phosphinoline-2-carboxylate (**27**).* Yellow oil, 25% yield. ν_{max} (liquid film) 2926, 2854, 1635, 1462, 1433, 787–692 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.81 (1H, ddd, *J* 4.7, 4.7, 0.8 Hz, β-*H* thienyl), 7.73 (2H, dd, *J* 13.9, 7.5 Hz, arom.), 7.57–7.45 (7H, m, arom.), 7.20 (1H, d, *J* 30.8 Hz, C*H*), 7.19 (1H, ddd, *J* 5.1, 3.7, 1.9 Hz, β-*H* thienyl), 7.09–7.04 (1H, m, arom.), 3.59 (3H, br s, OC*H*$_3$), 2.59–2.54 (2H, m, C*H*$_2$), 1.63–1.55 (2H, m, C*H*$_2$), 1.41–1.30 (10H, m, 5C*H*$_2$), 0.90 (3H, t, *J* 6.7 Hz, C*H*$_3$); δ_C (100.6 MHz, CD_2Cl_2) 168.6 (br s, *C*═O), 142.3 (d, *J* 5.4 Hz, arom.), 138.0 (d, *J* 10.3 Hz, β-*C* thienyl), 135.4 (d, *J* 4.5 Hz, β-*C* thienyl), 134.1 (d, *J* 8.1 Hz, α-*C* thienyl), 133.3 (d, *J* 11.2 Hz, arom.), 132.4 (d, *J* 2.7 Hz, arom.), 132.2 (d, *J* 1.3 Hz, arom.), 131.4 (d, *J* 109.1 Hz, arom.), 130.3 (br s, *C*H═C–C_8H_{17}), 129.6 (d, *J* 98.3 Hz, arom.), 129.0 (d, *J* 13.5 Hz, arom.), 128.7 (d, *J* 14.4 Hz, arom.), 124.0 (d, *J* 8.5 Hz, arom.), 123.3 (d, *J* 13.0 Hz, arom.), 112.1 (br s, CH═*C*–C_8H_{17}), 110.6 (d, *J* 88.9 Hz, arom.), 64.0 (d, *J* 124.3 Hz, *C*1), 50.6 (d, *J* 8.5 Hz, O*C*H$_3$), 34.7, 32.5, 30.7, 30.3, 30.2, 30.0, 23.3 (all s, 5*C*H$_2$), 14.5 (s, *C*H$_3$); δ_P (161 MHz, CD_2Cl_2) −0.46, −1.32; HRMS (EI): M$^+$, found 476.1928. $C_{29}H_{33}O_2PS$ requires 476.1933.

*4.5.16. [2-Methoxy-5-(4-methoxyphenyl)furan-3-yl](diphenyl)thiophen-2-ylphosphonium tetrafluoroborate (**28**).* Colorless oil, 35% yield. ν_{max} (liquid film) 1441, 1057, 795–708 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 8.23 (1H, ddd, *J* 4.8, 4.8, 1.1 Hz, α-*H* thienyl), 7.92–7.87 (2H, m, arom.), 7.77–7.67 (9H, m, arom.), 7.54–7.50 (1H, m, β-*H* thienyl), 7.52 (2H, d, *J* 8.3 Hz, arom.), 6.96 (2H, d, *J* 9.0 Hz, arom.), 6.35 (1H, d, *J* 3.0 Hz, β-*H* fur), 4.08 (3H, s, OC*H*$_3$), 3.83 (3H, s, OC*H*$_3$); δ_C (100.6 MHz, CD_2Cl_2) 165.4 (d, *J* 14.4 Hz, α-*C* fur), 160.7 (s, arom.), 148.6 (d, *J* 14.4 Hz, α-*C* fur), 142.8 (d, *J* 11.2 Hz, α-*C* thienyl), 140.4 (d, *J* 5.1 Hz, β-*C* thienyl), 136.2 (d, *J* 3.1 Hz, arom.), 133.9 (d, *J* 12.1 Hz, arom.), 131.1 (d, *J* 16.0 Hz, β-*C* thienyl), 130.9 (d, *J* 13.9 Hz, arom.), 125.6 (s, arom.), 121.4 (s, arom.), 120.0 (d, *J* 97.8 Hz, arom.), 118.2 (d, *J* 110.9 Hz, α-*C* thienyl), 115.0 (s, arom.), 105.3 (d, *J* 10.8 Hz, β-*C* fur), 74.6 (d, *J* 126.1 Hz, β-*C* fur), 59.7 (s, O*C*H$_3$), 56.0 (s, O*C*H$_3$); δ_P (161 MHz, CD_2Cl_2) 5.49; HRMS (EI): M$^+$, found 471.1172. $C_{28}H_{24}O_3PS$ requires 471.1178.

*4.5.17. Methyl 4-(4-methoxyphenyl)-7,7-diphenyl-7λ^5-phosphinino[2,3-b]thiophene-6-carboxylate (**29**).* Red oil, 15% yield. ν_{max} (liquid film) 1639, 1479, 1436, 761–708 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.69 (4H, dd, *J* 13.2, 6.9 Hz, arom.), 7.57–7.48 (6H, m, arom.), 7.48–7.44 (2H, m, arom.), 7.36 (1H, d, *J* 31.8 Hz, C*H*), 7.03–6.99 (2H, m, α,β-*H* thienyl), 6.94–6.91 (2H, m, arom.), 3.84 (3H, s, OC*H*$_3$), 3.56 (3H, br s, COOC*H*$_3$); δ_C (100.6 MHz, CD_2Cl_2) 169.1 (br s, *C*═O), 158.7 (s, arom.), 155.2 (d, *J* 8.1 Hz, arom.), 135.4 (s, arom.), 133.4 (br s, *C*H═C–C_6H_{14}–*p*OMe), 133.4 (d, *J* 11.2 Hz, arom.), 132.2 (d, *J* 102.3 Hz, arom.), 132.2 (d, *J* 2.7 Hz, arom.), 129.9 (s, arom.), 129.0 (d, *J* 13.0 Hz, arom.), 128.7 (d, *J* 12.1 Hz, β-*C* thienyl), 121.3 (d, *J* 17.1 Hz, α-*C* thienyl), 114.3 (s, arom.), 111.6 (br s, CH═*C*–C_6H_4–*p*OMe), 104.5 (d, *J* 95.6 Hz, arom.), 55.8 (s, O*C*H$_3$), 50.8 (br s, COO*C*H$_3$); δ_P (161 MHz, CD_2Cl_2) 2.91; HRMS (EI): M$^+$, found 470.1092. $C_{28}H_{23}O_3PS$ requires 470.1100.

*4.5.18. (2-Methoxy-5-phenanthren-9-ylfuran-3-yl)(diphenyl)thiophen-2-ylphosphonium tetrafluoroborate (**30**).* Colorless oil, 60% yield. ν_{max} (liquid film) 1439, 1057, 750–691 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 8.80–8.78 (1H, m, arom.), 8.71 (1H, d, *J* 8.4 Hz, arom.), 8.28 (1H, ddd, *J* 5.0, 5.0, 1.1 Hz, α-*H* thienyl), 8.26–8.24 (1H, m, arom.), 8.05 (1H, s, arom.), 7.99 (1H, dd, *J* 7.8, 1.3 Hz, arom.), 7.95–7.90 (2H, m, arom.), 7.82–7.77 (10H, m, arom.), 7.76–7.70 (3H, m, arom.), 7.68–7.64 (1H, m, arom.), 7.55 (1H, ddd, *J* 4.8, 3.7, 2.2 Hz, β-*H* thienyl), 6.64 (1H,d, *J* 2.8 Hz, β-*H* fur), 4.16 (3H, s, OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 166.1 (d, *J* 13.9 Hz, α-C fur), 147.8 (d, *J* 14.4 Hz, α-*C* fur), 142.9 (d, *J* 11.2 Hz, α-*C* thienyl), 140.5 (d, *J* 5.8 Hz, β-*C* thienyl), 136.2 (d, *J* 3.1 Hz, arom.), 134.0 (d, *J* 11.7 Hz, arom.), 131.4 (s, arom.), 131.2 (d, *J* 15.7 Hz, β-*C* thienyl), 131.0 (d, *J* 13.9 Hz, arom.), 129.7 (s, arom.), 129.4 (s, arom.), 129.2 (s, arom.), 128.5 (s, arom.), 127.9 (s, arom.), 127.9 (s, arom.), 127.7 (s, arom.), 125.9 (s, arom.), 124.9 (s, arom.), 123.9 (s, arom.), 123.1 (s, arom.), 120.0 (d, *J* 97.8 Hz, arom.), 118.1 (d, *J* 110.9 Hz, α-*C* thienyl), 112.0 (d, *J* 10.3 Hz, β-*C* fur), 74.6 (d, *J* 125.7 Hz, β-*C* fur), 59.9 (s, OCH_3); δ_P (161 MHz, CD_2Cl_2) 5.56; HRMS (EI): M^+, found 541.1380. $C_{35}H_{26}O_2PS$ requires 541.1386.

*4.5.19. Methyl 4,7,7-triphenyl-7λ^5-phosphinino[2,3-b]furan-6-carboxylate (**31**).* Yellow oil, 45% yield. ν_{max} (liquid film) 1643, 1483, 1439, 760–694 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.69 (4H, dd, *J* 12.9, 6.5 Hz, arom.), 7.59 (1H, d, *J* 34.7 Hz, C*H*), 7.61–7.49 (8H, m, arom.), 7.43 (1H, dd, *J* 2.3, 2.3 Hz, α-*H* fur), 7.39–7.34 (2H, m, arom.), 7.20 (1H, tt, *J* 7.5, 1.3 Hz, arom.), 6.50 (1H, dd, *J* 2.3, 2.3 Hz, β-*H* fur), 3.59 (3H, br s, OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 169.1 (br s, C=O), 162.6 (d, *J* 13.5 Hz, CH=*C*-Ph), 141.6 (d, *J* 13.9 Hz, α-*C* fur), 139.0 (s, arom.), 134.3 (br s, *C*H=C–Ph), 133.2 (d, *J* 11.7 Hz, arom.), 132.3 (d, *J* 3.1 Hz, arom.), 130.2 (d, *J* 98.5 Hz, arom.), 129.1 (d, *J* 13.0 Hz, arom.), 128.7 (s, arom.), 128.0 (s, arom.), 125.9 (s, arom.), 110.8 (d, *J* 8.1 Hz, β-*C* fur), 105.4 (br s, arom.), 89.4 (d, *J* 110.0 Hz, arom.), 50.9 (s, OCH_3); δ_P (161 MHz, CD_2Cl_2) 4.50; HRMS (EI): M^+, found 424.1219. $C_{27}H_{21}O_3P$ requires 424.1223.

*4.5.20. Methyl 7,7-diphenyl-4-thiophen-3-yl-7λ^5-phosphinino[2,3-b]furan-6-carboxylate (**32**).* Yellow oil, 40% yield. ν_{max} (liquid film) 1645, 1485, 1440, 800–710 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.84 (1H, d, *J* 34.1 Hz, C*H*), 7.67 (4H, dd, *J* 13.7, 7.2 Hz, arom.), 7.57–7.47 (8H, m, arom.), 7.44 (1H, dd, *J* 5.1, 1.4 Hz, α-*H* thienyl), 7.32 (1H, dd, *J* 5.0, 3.0 Hz, β-*H* thienyl), 6.49 (1H, dd, *J* 2.3, 2.3 Hz, β-*H* fur), 3.60 (3H, br s, OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 168.9 (d, *J* 12.6 Hz, *C*=O), 162.4 (d, *J* 13.0 Hz, CH=*C* thienyl), 141.7 (d, *J* 13.9 Hz, α-*C* fur), 138.9 (s, arom.), 133.3 (br s, *C*H=C thienyl), 133.2 (d, *J* 11.7 Hz, arom.), 132.3 (d, *J* 2.7 Hz, arom.), 129.9 (d, *J* 113.1 Hz, arom.), 129.1 (d, *J* 13.0 Hz, arom.), 127.3 (s, arom.), 124.9 (s, arom.), 117.9 (s, arom.), 110.8 (d, *J* 7.6 Hz, β-*C* fur), 100.9 (d, *J* 2.2 Hz, arom.), 89.5 (d, *J* 109.9 Hz, arom.), 62.0 (d, *J* 116.2 Hz, *C*1), 51.0 (s, OCH_3); δ_P (161 MHz, CD_2Cl_2) 4.08; HRMS (EI): M^+, found 430.0787. $C_{25}H_{19}O_3PS$ requires 430.0787.

*4.5.21. Methyl 4,5,7,7-tetraphenyl-7λ^5-phosphinino[2,3-b]furan-6-carboxylate (**33**).* Yellow oil, 40% yield. ν_{max} (liquid film) 1695, 1600, 760–690 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.78 (4H, ddd, *J* 13.7, 7.5, 1.6 Hz, arom.), 7.58–7.52 (6H, m, arom.), 7.30 (1H, dd, *J* 2.2, 2.2 Hz, α-*H* fur), 7.11–7.01 (10H, m, arom.), 6.45 (1H, dd, *J* 2.2, 2.2 Hz, β-*H* fur), 3.07 (3H, s, OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 168.3 (d, *J* 12.6 Hz, *C*=O), 162.6 (d, *J* 14.8 Hz, *C*–Ph), 145.2 (d, *J* 9.4 Hz, *C*–Ph), 143.0 (d, *J* 13.0 Hz, arom.), 141.9 (d, *J* 13.5 Hz, α-*C* fur), 138.0 (s, arom.), 133.2 (d, *J* 11.2 Hz, arom.), 132.9 (s, arom.), 132.0 (d, *J* 2.2 Hz, arom.), 130.7 (d, *J* 97.4 Hz, arom.), 130.6 (s, arom.), 129.0 (d, *J* 13.0 Hz, arom.), 127.7 (s, arom.), 127.0 (s, arom.), 126.0 (s, arom.), 110.7 (d, *J* 7.2 Hz, β-*C* fur), 108.0 (d, *J* 1.8 Hz, arom.), 90.2 (d, *J* 107.7 Hz, arom.), 60.3 (d, *J* 113.1 Hz, *C*1), 50.1 (s, OCH_3); δ_P (161 MHz, CD_2Cl_2) 7.06; HRMS (EI): M^+, found 500.1522. $C_{35}H_{26}O_3P$ requires 500.1536.

*4.5.22. Methyl 4-octyl-7,7-diphenyl-7λ^5-phosphinino[2,3-b]furan-6-carboxylate (**34**).* Yellow oil, 10% yield. ν_{max} (liquid film) 2925, 2854, 1635, 1497, 1437, 789–692 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.62 (4H, dd, *J* 12.3, 7.0 Hz, arom.), 7.55–7.45 (6H, m, arom.), 7.40 (1H, dd, *J* 2.3, 2.3 Hz, α-*H* fur), 7.20 (1H, d, *J* 33.9 Hz, C*H*), 6.42 (1H, dd, *J* 2.2, 2.2 Hz, β-*H* fur), 3.55 (3H, br s, OCH_3), 2.46 (2H, t, *J* 7.3 Hz, CH_2), 1.62–1.54 (2H, m, CH_2), 1.34–1.29 (10H, m, 5CH_2), 0.89 (3H, t, *J* 7.2 Hz, CH_3); δ_C (100.6 MHz, CD_2Cl_2) 169.0 (br s, *C*=O), 164.5 (d, *J* 13.5 Hz, CH=*C*–C_8H_{17}), 141.6 (d, *J* 13.9 Hz, α-*C* fur), 133.1 (d, *J* 11.2 Hz, arom.), 132.0 (d, *J* 2.2 Hz, arom.), 131.1 (br s, *C*H=C–C_8H_{17}), 129.9 (d, *J* 124.3 Hz, arom.), 128.9 (d, *J* 13.0 Hz, arom.), 110.8 (d, *J* 7.6 Hz, β-*C* fur), 104.5 (br s, arom.), 88.6 (d, *J* 115.3 Hz, arom.), 50.6 (br s, OCH_3), 32.5, 31.0, 30.9, 30.1, 30.1, 29.9, 23.3 (all s, 5CH_2), 14.5 (s, CH_3); δ_P (161 MHz, CD_2Cl_2) 6.88; HRMS (EI): M^+, found 460.2152. $C_{29}H_{33}O_3P$ requires 460.2162.

*4.5.23. Furan-2-yl[2-methoxy-5-(4-methoxyphenyl)furan-3-yl]diphenylphosphonium tetrafluoroborate (**35**).* Colorless oil, 15% yield. ν_{max} (liquid film) 1440, 1070, 750–700 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 8.13 (1H, ddd, *J* 2.7, 1.7, 0.8 Hz, α-*H* fur), 7.90–7.88 (2H, m, arom.), 7.76–7.74 (5H, m, arom.), 7.72–7.69 (3H, m, arom.), 7.53 (2H, d, *J* 9.0 Hz, arom.), 7.29 (1H, ddd, *J* 3.7, 2.0, 0.6 Hz, β-*H* fur), 6.96 (2H, d, *J* 9.0 Hz, arom.), 6.84 (1H, ddd, *J* 3.7, 1.9, 1.9 Hz, β-*H* fur), 6.38 (1H,d, *J* 3.1 Hz, β-*H* fur), 4.05 (3H, s, OCH_3), 3.83 (3H, s, OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 165.9 (d, *J* 14.8 Hz, α-*C* fur), 160.7 (s, arom.), 154.1 (d, *J* 8.1 Hz, α-*C* fur), 148.8 (d, *J* 14.4 Hz, α-*C* fur), 136.3 (d, *J* 3.1 Hz, arom.), 134.9 (d, *J* 136.9 Hz, α-*C* fur), 134.0 (d, *J* 12.1 Hz, arom.), 131.0 (d, *J* 13.9 Hz, arom.), 130.7 (d, *J* 21.1 Hz, β-*C* fur), 125.6 (s, arom.), 121.4 (s, arom.), 118.3 (d, *J* 98.7 Hz, arom.), 115.0 (s, arom.), 113.4 (d, *J* 9.4 Hz, β-*C* fur), 104.8 (d, *J* 10.8 Hz, β-*C* fur), 72.0 (d, *J* 127.9 Hz, β-*C* fur), 59.7 (s, OCH_3), 56.0 (s, OCH_3); δ_P (161 MHz, CD_2Cl_2) −1.11; HRMS (EI): M^+, found 455.1411. $C_{28}H_{24}O_4P$ requires 455.1407.

*4.5.24. Methyl 4-(4-methoxyphenyl)-7,7-diphenyl-7λ^5-phosphinino[2,3-b]furan-6-carboxylate (**36**).* Yellow oil, 30% yield. ν_{max} (liquid film) 1645, 1470, 1450, 800–730 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 7.68 (4H, dd, *J* 13.4, 7.2 Hz, arom.), 7.57 (1H, d, *J* 32.2 Hz, C*H*), 7.56–7.49 (6H, m, arom.), 7.50 (2H, d, *J* 8.7 Hz, arom.), 7.42 (1H, dd, *J* 2.5, 2.5 Hz, α-*H* fur), 6.91 (2H, d, *J* 8.7 Hz, arom.), 6.49 (1H, dd, *J* 2.2, 2.2 Hz, β-*H* fur), 3.82 (3H, s, OCH_3), 3.58 (3H, br s, COOCH_3); δ_C (100.6 MHz, CD_2Cl_2) 169.1 (br s, *C*=O), 162.8 (d, *J* 13.5 Hz, CH=*C*–C_6H_4–*p*OMe), 158.4 (s, arom.), 141.6 (d, *J* 13.9 Hz, α-*C* fur), 133.2 (br s, *C*H=C–C_6H_4–*p*OMe), 133.2 (d, *J* 11.2 Hz, arom.), 132.2 (d, *J* 2.7 Hz, arom.), 131.5 (s, arom.), 129.2 (s, arom.), 129.0 (d, *J* 13.5 Hz, arom.), 114.1 (s, arom.), 110.8 (d, *J* 7.6 Hz, β-*C* fur), 105.2 (br s, arom.), 89.4 (d, *J* 118.5 Hz, arom.), 55.8 (s, OCH_3), 50.9 (s, $COOCH_3$); δ_P (161 MHz, CD_2Cl_2) 4.47; HRMS (EI): M^+, found 454.1324. $C_{28}H_{23}O_4P$ requires 454.1328.

*4.5.25. Furan-2-yl(2-methoxy-5-phenanthren-9-ylfuran-3-yl)diphenylphosphonium tetrafluoroborate (**37**).* Colorless oil, 20% yield. ν_{max} (liquid film) 1439, 1084, 750–690 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 8.81 (1H, dd, *J* 8.1, 0.8 Hz, arom.), 8.73 (1H, d, *J* 8.3 Hz, arom.), 8.23 (1H, dd, *J* 8.1, 1.4 Hz, arom.), 8.17–8.16 (1H, m, α-*H* fur), 8.04 (1H, s, arom.), 7.98 (1H, dd, *J* 7.6, 0.8 Hz, arom.), 7.95–7.90 (2H, m, arom.), 7.83–7.65 (12H, m, arom.), 7.37–7.36 (1H, m, β-*H* fur), 6.88 (1H, ddd, *J* 3.4, 1.7, 1.7 Hz, β-*H* fur), 6.66 (1H,d, *J* 3.0 Hz, β-*H* fur), 4.13 (3H, s, OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 166.6 (d, *J* 14.4 Hz, α-*C* fur), 154.2 (d, *J* 8.1 Hz, α-*C* fur), 148.1 (d, *J* 14.8 Hz, α-*C* fur), 136.4 (d, *J* 2.7 Hz, arom.), 134.9 (d, *J* 136.9 Hz, α-*C* fur), 134.1 (d, *J* 12.1 Hz, arom.), 131.4 (d, *J* 8.5 Hz, β-*C* fur), 131.1 (d, *J* 13.9 Hz, arom.), 130.8 (s, arom.), 129.7 (s, arom.), 129.4 (s, arom.), 129.3 (s, arom.), 128.6 (s, arom.), 128.0 (s, arom.), 127.8 (s, arom.), 125.9 (s, arom.), 124.9 (s, arom.), 124.0 (s, arom.), 123.2 (s, arom.), 118.3 (d, *J* 98.7 Hz, arom.), 113.5 (d, *J* 9.4 Hz, β-*C* fur), 111.7 (d, *J* 10.8 Hz, β-*C* fur), 72.1 (d, *J* 127.9 Hz, β-*C* fur), 60.0 (s, OCH_3); δ_P (161 MHz, CD_2Cl_2) −1.01; HRMS (EI): M^+, found 525.1611. $C_{35}H_{26}O_3P$ requires 525.1614.

*4.5.26. Methyl 4-phenanthren-9-yl-7,7-diphenyl-7λ^5-phosphinino[2,3-b]furan-6-carboxylate (**38**).* Yellow oil, 30% yield. ν_{max} (liquid film) 1643, 1477, 1433, 766–690 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 8.77 (1H, d, *J* 8.3 Hz, arom.), 8.73 (1H, d, *J* 8.1 Hz, arom.), 7.90 (1H, dd, *J*

7.8, 1.6 Hz, arom.), 7.87 (1H, dd, *J* 8.3, 1.1 Hz, arom.), 7.80–7.51 (16H, m, arom.), 7.26 (1H, dd, *J* 2.3, 2.3 Hz, α-*H* fur), 6.52 (1H, dd, *J* 2.4, 2.2 Hz, β-*H* fur), 3.58 (3H, br s, OCH_3); δ_C (100.6 MHz, CD_2Cl_2) 169.0 (br s, *C*=O), 163.3 (d, *J* 13.9 Hz, CH=*C*–Phenantryl), 142.0 (d, *J* 13.9 Hz, α-*C* fur), 135.7 (s, arom.), 135.4 (br s, *C*H=C–Phenantryl), 133.3 (d, *J* 11.2 Hz, arom.), 133.0 (s, arom.), 132.7 (s, arom.), 132.3 (d, *J* 3.1 Hz, arom.), 131.6 (d, *J* 95.6 Hz, arom.), 131.1 (s, arom.), 130.5 (s, arom.), 129.1 (d, *J* 13.5 Hz, arom.), 129.0 (s, arom.), 128.7 (s, arom.), 127.8 (s, arom.), 127.2 (s, arom.), 126.8 (s, arom.), 126.8 (s, arom.), 123.3 (s, arom.), 123.1 (s, arom.), 110.8 (d, *J* 7.6 Hz, β-*C* fur), 103.6 (d, *J* 4.5 Hz, arom.), 88.8 (d, *J* 116.7 Hz, arom.), 61.5 (d, *J* 122.1 Hz, *C*1), 50.9 (br s, OCH_3); δ_P (161 MHz, CD_2Cl_2) 5.19; HRMS (EI): M^+, found 524.1531. $C_{35}H_{25}O_3P$ requires 524.1536.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.06.066.

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