JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Phosphonium-Iodonium Ylides with Heteroatomic Groups in the Synthesis of Annelated P-Containing Heterocycles

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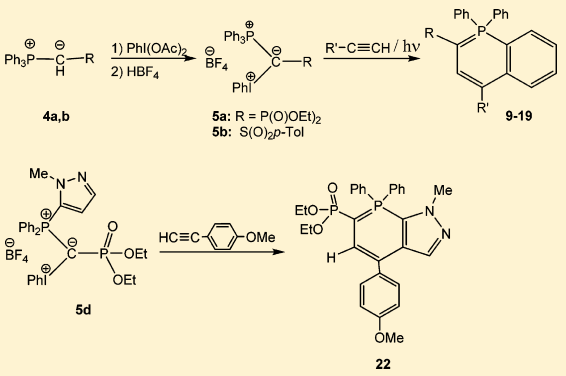
Supporting Information

ABSTRACT: The preparation and chemistry of novel sulfonyl- and phosphoryl-derived λ^3-iodanes are reported. These compounds with three different heteroatoms attached to a negatively charged C atom represent potentially useful reagents that combine in one molecule the synthetic advantages of a phosphonium ylide and an iodonium salt. Specifically, they can react with a number of acetylenes, leading to hitherto unknown sulfonyl- and phosphoryl-substituted phosphinolines, phosphininothiophenes, and a novel type of annelated P-containing heterocycle—phosphininopyrazole.



INTRODUCTION

Compounds with an endocyclic P−C bond, analogues of nitrogen or sulfur heterocycles,[1−3] are interesting due to their recent use in a wide variety of areas as model objects in fundamental research,[4,5] as ligands for new catalysts,[6,7] for modifying properties of materials,[8] and as important building blocks for drug discovery.[9,10]

Until recently λ^5-phosphinolines—the structural analogues of quinoline (Figure 1)—were virtually inaccessible. There were only two known approaches to the synthesis of these heterocycles.[11,12]

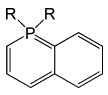


Figure 1. λ^5-Phosphinoline, a structural analogue of quinoline.

Through the investigation of the photochemical heterocyclization of mixed phosphonium-iodonium ylides **1** with compounds containing CN[13] and CC[14,15] triple bonds, we opened a new route to the relatively unknown annelated P-containing heterocycles **2** (Scheme 1).[16,17]

The benzoyl- and methoxycarbonyl-substituted ylides **1** reacted with triple bonds under UV irradiation (366 nm). The reactions of ylides **1** with CN triple bonds afforded only the triarylphosphonium-substituted oxazoles **3c**.[13] The reactions of ylides **1** with CC triple bonds led to mixturse of furans **3a,b** and annelated P-containing heterocycles **2a,b** mentioned above. In previous studies we have shown that the ratio of furans **3a,b** and heterocycles **2a,b** depended on the substituent R′ of the alkyne, and its variation allowed us to obtain furans **3a,b** or heterocycles **2a,b** selectively.[15]

In the present work we focused our attention on ylides **5** (Scheme 2), in which the stabilizing C(O)R group of the conventional phosphonium-iodonium ylides **1** is replaced by the heteroatomic moieties SO_2-*p*-Tol and $P(O)(OEt)_2$. We also introduced thienyl and pyrazolyl substituents on the phosphonium fragment of mixed ylides **5c,d** to obtain annelated P-containing heterocycles similar to **2b**.

RESULTS AND DISCUSSION

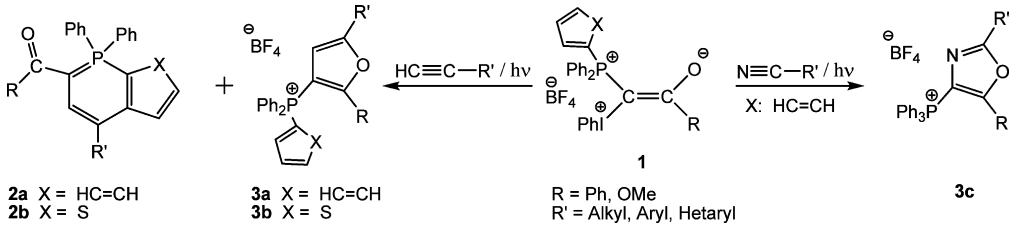
The phosphonium-iodonium ylides **5** (Scheme 2) were synthesized in high yields by oxidation of phosphoranes **4** with diacetoxyiodobenzene at 0 °C followed by treatment with HBF_4.

The ylides obtained belong to a class of mixed ylides stabilized by acceptor substituents. It should be noted that stability of the investigated ylides **5** depended not only on the stabilizer groups Z but also on the substituents in the phosphonium moiety. Thus, we found that the sulfonyl-substituted ylide **5a** is the most stable and can be stored at room temperature without decomposition for a long time (6 months). The phosphoryl-substituted ylide **5b** is less stable and requires storage at 0 °C. The heteroaryl-substituted ylides **5c,d**

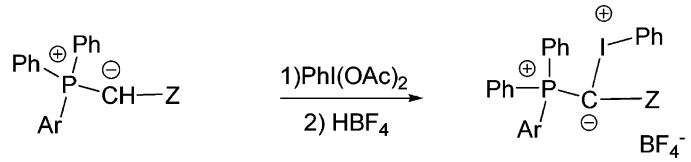
Received: July 12, 2013
Published: October 3, 2013

   dx.doi.org/10.1021/jo401514d | J. Org. Chem. 2013, 78, 11691−11697

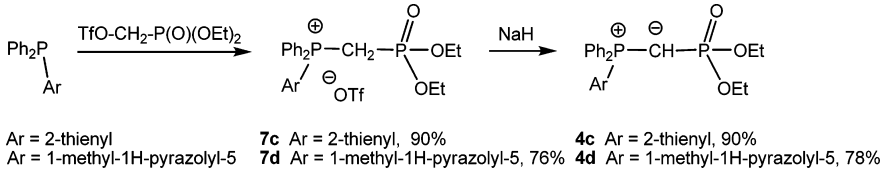
Scheme 1. Reaction of Ylides 1 with CN or CC Triple Bonds



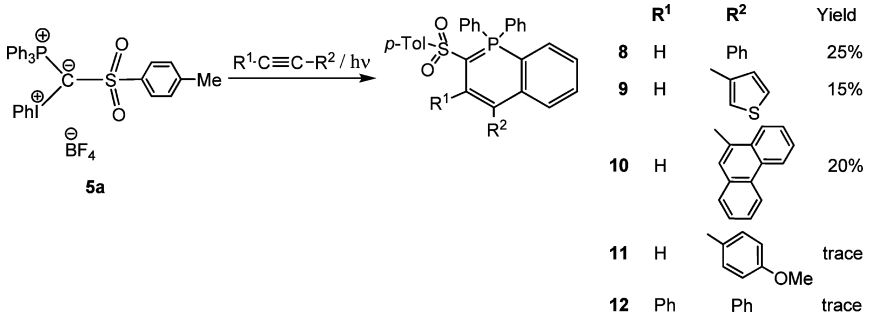
Scheme 2. Preparation of 5a–d from the Phosphoranes 4a–d



Scheme 3. Preparation of Phosphoranes 4c,d from the Phosphines 6c,d



Scheme 4. Reaction Products and Yields (%) of 5a with Alkynes



are less stable than **5b**; therefore, **5c,d** have to be stored below 0 °C.

The preparations of phosphoranes **4a,b** have been described earlier.[18,19] In Scheme 3 we summarize briefly the most important steps in the synthesis of new heteroaryl-substituted phosphoranes **4c,d**.

(Diethoxyphosphoryl)methyl triflate[19] reacted readily with aryldiphenylphosphines **6c,d** to give the phosphonium triflate salts **7c,d**, which in turn yield the phosphoranes **4c,d** after treatment with NaH (Scheme 3). Since phosphoranes **4c,d** are not stable, they were used in synthesis without further purification. The structures of the phosphoranes **4c,d** were confirmed by their ^{1}H and ^{31}P NMR spectral data.

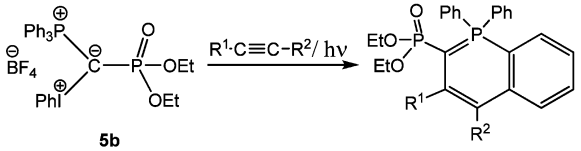
Reactions of 5 with Acetonitrile. We investigated the reaction of ylides **5** with acetonitrile under the conditions that the ylides **1** produce the triphenylphosphonium-substituted oxazoles **3c** (1,3-dipolar cycloaddition reaction (Scheme 1)).[13] Replacement of the C(O)R group of the ylides **1** by a SO_2-*p*-Tol or $P(O)(OEt)_2$ moiety (ylides **5**) makes the valence structure with a negative charge on the oxygen atom impossible. Thus, the 1,3-dipolar cycloadditions to five-membered heterocycles similar to **3c** should be suppressed. The only result of irradiation of acetonitrile solutions of ylides **5** was the formation of phosphonium salts $[Ph_2(Aryl)P^+\text{-}CH_2\text{-}Z]BF_4^-$.

At this point we mention that the irradiation of ylides **1** in aprotic solvents (e.g., $CHCl_3$, CH_2Cl_2) also affords the phosphonium salts $[Ph_2(Aryl)P^+\text{-}CH_2\text{–}C(O)R]BF_4^-$.[20,21] In other words, the introduction of a phosphoryl or sulfonyl group into the ylide structure prevents its reaction with acetonitrile. The latter plays only the role of an inert solvent for these particular ylides.

Reactions of 5a with Alkynes. The reaction time of sulfonyl-substituted ylide **5a** with alkynes is longer as compared to that for ylides **1**; it requires irradiation with a mercury lamp (366 nm) for 60–120 min. The long reaction time resulted in

dx.doi.org/10.1021/jo401514d | J. Org. Chem. 2013, 78, 11691–11697

Scheme 5. Reaction Products and Yields (%) of 5b with Alkynes



	R1	R2	Yield
13	H	Ph	60%
14	H	C_8H_{17}	75%
15	H	3-Thienyl	55%
16	H	4-Methoxyphenyl	50%
17	H	6-Methoxynaphthalen-2-yl	55%
18	H	9-Phenanthrenyl	65%
19	Ph	Ph	40%

lower yields of the target product, because in this case the rate of formation of the phosphonium salt $[Ph_3P^+\text{-}CH_2\text{-}P(O)(OEt)_2]BF_4^-$ prevails over the heterocyclization rate.

Ylide **5a** reacted with phenylacetylene, 3-thienylacetylene, and 9-phenantrylacetylene, affording the λ^5-phosphinolines **8**–**10** in yields of 15–25%. The reaction of **5a** with decyne-1, *p*-methoxyphenylacetylene, and diphenylacetylene took more than 3 h and led mainly to the formation of the phosphonium salt $[Ph_3P^+\text{-}CH_2\text{-}SO_2\text{-}p\text{-}Tol]BF_4^-$ (in the cases of *p*-methoxyphenylacetylene and diphenylacetylene it was possible to detect a trace amount of phosphinolines **11** and **12** (Scheme 4)).

Reactions of 5b with Alkynes. In strict contrast to the behavior of **5a**, the phosphoryl-substituted ylide **5b** was quite reactive in photochemical processes with alkynes, and these reactions led to λ^5-phosphinolines **13**–**19** in much higher yields (40–70% after column chromatography (Scheme 5)).

Unambiguous proof of the phosphinoline structures was possible by X-ray crystallography of **13**. Crystals of **13** ($C_{31}H_{30}P_2O_3$, M_r = 512.5) are monoclinic: space group $P2_1/c$, a = 9.170(2) Å, b = 12.496(2) Å, c = 23.338(3) Å, α = 90°, β = 94.7720(10)°, γ = 90°.

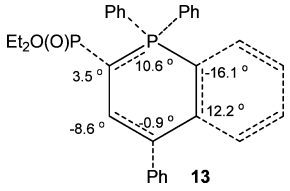


Figure 2. Torsion angles of the P-containing six-membered ring of λ^5-phosphinoline **13**.

The X-ray data obtained show that the P-containing six-membered ring of phosphinoline **13** is practically flat. Quantitative calculations of its conformation were carried out by using the Zefirov–Palyulin puckering coordinates and the computer program RICON[22] (S = 0.213, θ = 62.58273, ψ_2 = 21.94). These computations indicate that the conformation of this six-membered ring, containing the P atom, adopts an conformation intermediate between "screw" and "boat", but closer to "screw" (the determined torsion angles of the P-containing six-membered ring of λ^5-phosphinoline **13** are represented in Figure 2). The established C_1–P bond length in the six-membered ring of the phosphinoline **13** (1.724 Å) is almost equal to the length of the C_1–P bond in ylides. This result is indicative for a strong contribution of the ylidic valence structure of the phosphinoline **13.**

Reactions of 5c with Alkynes. The reaction of the thienyl-substituted ylide **5c** with terminal alkynes such as phenylacetylene and 3-ethynylthiophene takes place in a few seconds without irradiation. In these cases the thiophene ring was involved in the heterocyclization, yielding phosphininothiophenes **20** and **21** (Scheme 6). This result coincides with that of the benzoyl-substituted phosphonium ylide **1** (Scheme 1, X = S), for which the phosphininothiophenes **2b** were the only products.[15]

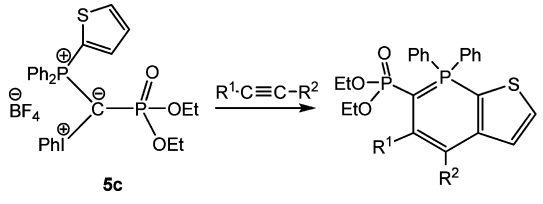
Similarly, for decyne-1, *p*-methoxyphenylacetylene, and 9-ethynylphenanthrene no light was necessary for the interaction with **5c**. However, in these cases the only product was the phosphonium salt $[Ph_2(thienyl)P^+\text{-}CH_2\text{-}P(O)(OEt)_2]BF_4^-$. The ylide **5c** did not form P-containing heterocycles with diphenylacetylene in daylight or under irradiation. Under these conditions the ylide **5c** decomposed to the same salt. This obviously shows that the rate of salt formation prevails over the heterocyclization rate for the alkynes mentioned above.

Reactions of 5d with Alkynes. The reaction of the pyrazolyl-substituted ylide **5d** with alkynes requires irradiation (366 nm). The reactions of **5d** with all of the investigated alkynes (phenylacetylene, 3-ethynylthiophene, *p*-methoxyphenylacetylene, 9-ethynylphenanthrene, 1-decyne, diphenylacetylene) led to the phosphonium salt $[Ph_2(Pyrazolyl)P^+\text{-}CH_2\text{-}P(O)(OEt)_2]BF_4^-$ as a major product. Only as a result of the interaction of **5d** with *p*-methoxyphenylacetylene could the heterocyclic products **22** and **23** be isolated (Scheme 7).

In this case the *N*-methylpyrazolyl ring and phenyl ring, respectively, are involved in the heterocyclization, yielding to a new annelated P-containing heterocycle—phosphininopyrazole **22**—and phosphinoline **23**. This behavior coincides with that of the methoxycarbonyl-substituted ylide **1** (Scheme 1, X = S), where phosphinolines were formed together with phosphininothiophenes.[17]

A plausible way of formation of the products **22** and **23** is shown in Scheme 8. This scheme is discussed in detail in our

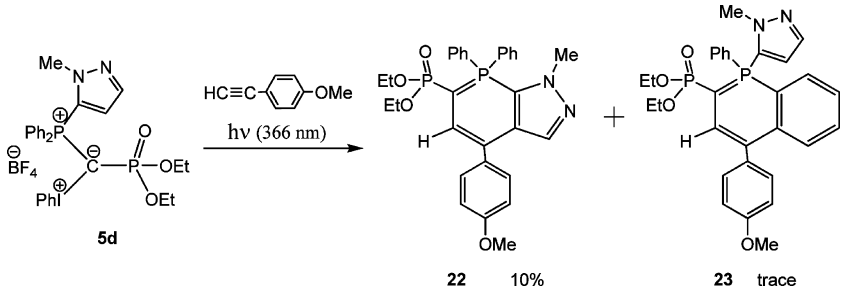
Scheme 6. Reaction Products and Yields (%) of 5c with Alkynes



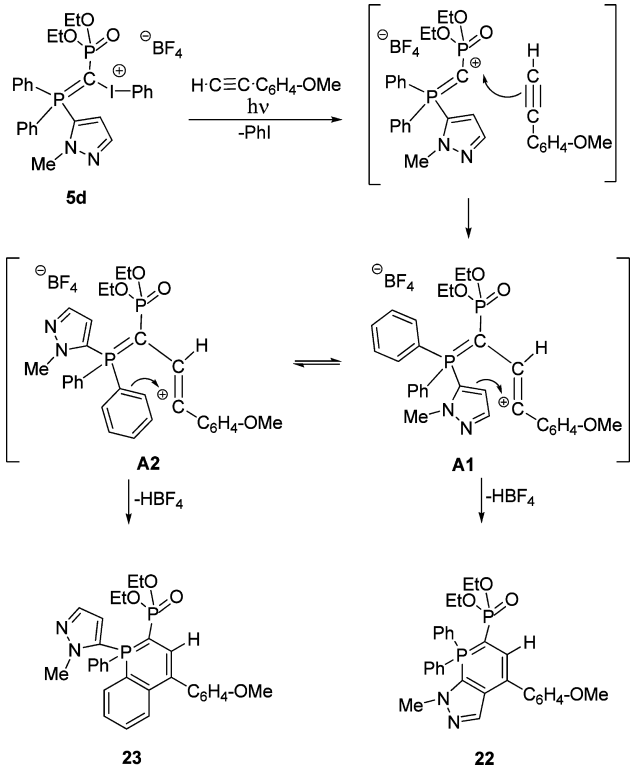
	R1	R2	Yield
20	H	Ph	15%
21	H	3-Thienyl	10%

dx.doi.org/10.1021/jo401514d | J. Org. Chem. 2013, 78, 11691–11697

Scheme 7. Reaction Products and Yields (%) of 5d with *p*-Methoxyphenylacetylene



Scheme 8. Plausible Mechanism of Formation of the Products 22 and 23 from Ylide 5d



previous investigations.[16,17] We assumed the trapping of the vinylic cation, which was produced by cleavage of the C–I bond in **5d**, by the alkyne gave rise to cation **A**, for which different conformers are likely such as **A1** and **A2**. Electrophilic substitution in the rotamers **A1** and **A2** led to products **22** and **23**, respectively. To the best of our knowledge this is the first example of such electrophilic alkylation of a pyrazole ring.

CONCLUSION

The preparation of novel types of phosphonium-iodonium ylides with phosphoryl and sulfonyl substituents in good yields was reported. These ylides contain three different heteroatomic groups attached to the ylidic C atom and differ qualitatively from previously known phosphonium-iodonium ylides. Photochemical heterocyclization of the obtained ylides with a number of acetylenes provided sulfonyl- and phosphoryl-substituted phosphinolines and phosphininothiophenes, as well as a novel type of annelated P-containing heterocycle—phosphininopyrazole.

It should be noted that the annelated P-containing heterocycle phosphininopyrazole can be obtained only from a phosphoryl-substituted phosphonium-iodonium ylide. This differs from the case for a phosphonium-iodonium ylide with a benzoyl substituent.[16]

Our investigation indicated that the yield of the annelated P-containing heterocycle was largely affected by the stabilizing group Z and heteroaryl substituents in the phosphonium moiety of the mixed ylides. The choice of substituents R′ of acetylene affected the yield to a lesser extent. Thus, replacement of $P(O)(OEt)_2$ by the SO_2-*p*-Tol group and introduction of heteroaryl substituents in the phosphonium moiety reduced the yield of the heterocycle an average of 40–50%, while variation of substituents R′ of acetylene changed the yield an average of 20%.

Thus, the present research significantly extended the structural types of annelated P-containing heterocycles.

EXPERIMENTAL SECTION

General Methods. The synthesis of {[(4-methylphenyl)sulfonyl]-methylidene}(triphenyl)-λ^5-phosphane (**4a**) and [(diethoxyphosphinyl)methylidene]triphenylphosphorane (**4b**) was carried out following literature procedures.[18,19] The ^{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. The IR spectra were measured in CCl_4. High-resolution mass spectra (HR MS) were measured using electrospray ionization (ESI) and the TOF mass analyzer.[23] The measurements were done in a positive ion mode (interface capillary voltage −4500 V), in a mass range from m/z 50 to 3000 Da; external calibration was done with electrospray calibrant solution. A syringe injection was used for solutions in acetonitrile or methanol (flow rate 3 μL/min). Nitrogen was applied as a dry gas; the 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.

General Procedure for the Synthesis of Phosphonium Salts 7c,d. To a stirred solution of phosphine **6c** (**6d**) (5.71 mmol) in anhydrous CH_2Cl_2 (9 mL) was added (diethoxyphosphinyl)methyl triflate (5.10 mmol) in anhydrous CH_2Cl_2 (3 mL) dropwise at 0 °C under argon. The mixture was warmed to room temperature and then stirred for 24 h. The solvent was removed in vacuo to about one-third volume, and the remaining oil was triturated with ether (10 mL). A white solid was formed and collected by filtration. After washing with ether (10 mL), the corresponding product **7c** (**7d**) was obtained.

*[(Diethoxyphosphoryl)methyl](diphenyl)thiophen-2-ylphosphonium Trifluoromethanesulfonate (**7c**).* Yield: 2.61 g (90%), white solid. Mp: 108–110 °C. ^{1}H NMR ($CDCl_3$): δ 1.09 (t, 6H, J = 7.0 Hz); 3.90–4.02 (m, 4H); 4.10 (dd, 2H, J = 16.6 Hz, J = 19.3 Hz); 7.39 (br. s, 1H); 7.62–7.64 (m, 4H); 7.74–7.82 (m, 6H); 8.07–8.12 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 15.8 (d, $^3J_{CP}$ = 6.6 Hz); 23.2 (dd, $^1J_{CP}$ = 54.2 Hz, $^1J_{CP}$ = 133.2 Hz); 63.5 (d, $^2J_{CP}$ = 6.6 Hz); 116.0 (d, $^1J_{CP}$ = 105.4 Hz); 119.1 (dd, $^1J_{CP}$ = 92.2 Hz, $^3J_{CP}$ = 2.9 Hz); 120.6 (q, $^1J_{CP}$ = 321.3 Hz); 129.9 (d, $^3J_{CP}$ = 13.2 Hz); 130.5 (d, $^3J_{CP}$ = 16.1 Hz); 133.5 (d, $^2J_{CP}$ = 11.0 Hz); 135.3 (s); 139.7 (d, $^3J_{CP}$ = 4.4 Hz); 143.5 (d, $^2J_{CP}$ =

dx.doi.org/10.1021/jo401514d | J. Org. Chem. 2013, 78, 11691–11697

11.0 Hz). ^{31}P NMR ($CDCl_3$): δ 14.15 (d, $^2J_{PP}$ = 9.9 Hz); 14.53 (d, $^2J_{PP}$ = 9.9 Hz). IR: ν/cm^{-1} 1270 (P═O), 1170 (SO_2), 1040 (P−O), 1470, 770−700 (Ar). Anal. Calcd for $C_{22}H_{25}F_3O_6P_2S_2$: C, 46.48; H, 4.43; S, 11.28. Found: C, 46.79; H, 4.41; S, 10.97.

*[(Diethoxyphosphoryl)methyl](diphenyl){1-methylpyrazol-5-yl}phosphonium Trifluoromethanesulfonate (**7d**).* Yield: 2.20 g (76%), white solid. Mp: 116 °C. ^{1}H NMR ($CDCl_3$): δ 1.19 (t, 6H, J = 7.1 Hz); 3.74 (s, 3H); 3.99−4.12 (m, 4H); 4.30 (dd, 2H, J = 20.0 Hz, J = 16.3 Hz); 6.96−6.97 (m, 1H); 7.46−7.49 (m, 1H); 7.70−7.75 (m, 5H); 7.82−7.86 (m, 2H); 7.92 (dd, 4H, J = 14.1 Hz, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ 15.8 (d, $^3J_{CP}$ = 5.9 Hz); 21.8 (dd, $^1J_{CP}$ = 133.9 Hz, $^1J_{CP}$ = 53.4 Hz); 40.5 (s); 63.8 (d, $^2J_{CP}$ = 6.6 Hz); 116.8 (d, $^1J_{CP}$ = 93.7 Hz); 120.1 (dd, $^1J_{CP}$ = 108.3 Hz, $^3J_{CP}$ = 2.9 Hz); 121.7 (d, $^2J_{CP}$ = 17.6 Hz); 130.4 (d, J_{CP} = 13.9 Hz); 133.5 (d, J_{CP} = 11.7 Hz); 135.7 (s); 139.8 (d, $^3J_{CP}$ = 16.1 Hz). ^{31}P NMR ($CDCl_3$): δ 6.69 (d, $^2J_{PP}$ = 10.4 Hz); 13.73 (d, $^2J_{PP}$ = 10.4 Hz). IR: ν/cm^{-1} 1277 (P═O), 1155 (SO_2), 1032 (P−O), 1443, 748−690 (Ar). Anal. Calcd for $C_{22}H_{27}F_3N_2O_6P_2S$: C, 46.65; H, 4.80; N, 4.95 S, 5.66. Found: C, 46.83; H, 4.95; N, 4.83, S, 5.73.

General Procedure for the Synthesis of Phosphoranes 4c,d. To a stirred suspension of NaH (10.0 mmol, washed with hexane) in anhydrous THF (16 mL) was added the phosphonium salt **7c** (**7d**) (4.00 mmol) in anhydrous THF (16 mL) at 0 °C under argon. The resulting mixture was stirred at 0 °C for 1 h. The solvent was then removed in vacuo and the residue extracted with anhydrous CH_2Cl_2 (20 mL). After concentration of the extracts, the corresponding product **4c** (**4d**) was obtained. Ylide **4c** (**4d**) was then used without further purification.

*Diethyl {[Diphenyl(thiophen-2-yl)-λ^5-phosphanylidene]methyl}phosphonate (**4c**).* Yield: 1.50 g (90%), pale yellow oil. ^{1}H NMR (CD_2Cl_2): δ 1.14 (t, 6H, J = 7.1 Hz); 1.28−1.31 (m, 1H); 3.80−3.88 (m, 4H); 7.19−7.22 (m, 1H); 7.43−7.49 (m, 4H); 7.53−7.57 (m, 3H); 7.71 (dd, 4H, J = 7.2 Hz, J = 12.6 Hz); 7.76−7.80 (m, 1H). ^{31}P NMR (CD_2Cl_2): δ 12.21 (d, $^2J_{PP}$ = 40.6 Hz); 32.84 (d, $^2J_{PP}$ = 40.6 Hz).

*Diethyl {[Diphenyl(1-methylpyrazol-5-yl)-λ^5-phosphanylidene]methyl}phosphonate (**4d**).* Yield: 1.30 g (78%), pale yellow oil. ^{1}H NMR (CD_2Cl_2): δ 1.14 (t, 6H, J = 7.1 Hz); 1.20−1.22 (m, 1H); 3.81−3.87(m, 4H); 3.89(s, 3H); 6.15−6.16(m, 1H); 7.48-7.73(m, 11H). ^{31}P NMR (CD_2Cl_2): δ 7.49 (d, $^2J_{PP}$ = 41.0 Hz); 34.19 (d, $^2J_{PP}$ = 41.0 Hz).

General Procedure for the Synthesis of Phosphonium-Iodonium Ylides 5a−d. A solution of 0.87 g (3 mmol) of diacetoxyiodobenzene in methanol (5 mL) was added to a solution of 3 mmol of ylide **4** in methanol (5 mL) at 0 °C. The mixture was stirred for 1 h at 0−5 °C, and then 3 mmol of a solution of HBF_4 (40%) was added. The mixture was stirred for 10 min, and then 20 mL of diethyl ether was added and this mixture stirred for 1 h. The precipitate was filtered and washed with diethyl ether (2 × 10 mL).

*[(4-Methylphenyl)sulfonyl](phenyliodonio)(triphenylphosphonio)methanide Tetrafluoroborate (**5a**).* Yield: 1.83 g (85%), white solid. Mp: 147 °C dec. ^{1}H NMR (CD_3CN): δ 2.42 (s, 3H); 7.23−7.28 (m, 4H); 7.43 (dd, 2H, J = 7.8 Hz, J = 7.9 Hz); 7.55−7.67 (m, 15H); 7.76−7.80 (m, 3H). ^{13}C NMR (CD_3CN): δ 21.9 (s); 37.3 (d, $^1J_{CP}$ = 95.8 Hz); 119.1 (d, $^3J_{CP}$ = 2.9 Hz); 124.2 (d, $^1J_{CP}$ = 94.5) Hz; 128.2 (s); 130.8 (d, $^3J_{CP}$ = 12.9 Hz); 130.9, 132.9, 133.8, 135.0 (all s); 135.6 (d, $^4J_{CP}$ = 2.9 Hz); 135.8 (d, $^2J_{CP}$ = 10.4 Hz); 142.6 (d, $^3J_{CP}$ = 1.2) Hz; 145.1 (s). ^{31}P NMR ($CDCl_3$): δ 28.65. IR: ν/cm^{-1} 1295−1284, 1132 (SO_2), 1081 (BF_4^-), 1439, 739 (Ar). Anal. Calcd for $C_{32}H_{27}BF_4IO_2PS$: C, 53.36; H, 3.78; S, 4.45. Found: C, 53.40; H, 3.94; S, 4.62. HRMS calcd for $C_{32}H_{27}IO_2PS$ (M^+) m/z 633.0509, found 633.0513.

*(Diethoxyphosphoryl)(phenyliodonio)(triphenylphosphonio)methanide Tetrafluoroborate (**5b**).* Yield: 1.60 g (75%), white solid. Mp: 173 °C dec. ^{1}H NMR($CDCl_3$): δ 1.18 (t, 6H, J = 7.1 Hz); 3.92−4.00 (m, 4H); 7.33 (dd, 2H, J = 7.8 Hz, J = 7.9 Hz); 7.49−7.57 (m, 7H); 7.61−7.70 (m, 11H). ^{13}C NMR (CD_3CN): δ 16.9 (d, $^3J_{CP}$ = 6.6 Hz); 63.8 (d, $^2J_{CP}$ = 5.8 Hz); 125.8 (d, $^1J_{CP}$ = 92.9 Hz); 130.7 (d, $^3J_{CP}$ = 12.4 Hz); 132.6, 133.5, 134.7, 135.0, 135.3 (all s); 135.6 (d, $^2J_{CP}$ = 10.2 Hz). ^{31}P NMR ($CDCl_3$): δ 22.66 (d, $^2J_{PP}$ = 49.5 Hz); 31.52 (d, $^2J_{PP}$ = 49.5 Hz). IR: ν/cm^{-1} 1210 (P═O), 1070 (BF_4^-), 760−780, 1440−1470 (Ar). Anal. Calcd for $C_{29}H_{30}BF_4IO_3P_2$: C, 49.60; H, 4.31. Found: C, 49.40; H, 4.37.

*(Diethoxyphosphoryl)[diphenyl(thiophen-2-yl)phosphonio](phenyliodonio)methanide Tetrafluoroborate (**5c**).* Yield: 1.38 g (65%), white solid. Mp: 173−175 °C dec. ^{1}H NMR (CD_2Cl_2): δ 1.15 (t, 6H, J = 6.8 Hz); 3.89−3.94 (m, 4H); 7.34−7.39 (m, 3H); 7.55−7.65 (m, 12H); 7.72 (t, 2H, J = 7.0 Hz); 7.99−8.01 (m, 1H). ^{13}C NMR (CD_2Cl_2): δ 16.5 (d, $^3J_{CP}$ = 7.3 Hz); 63.2 (d, $^2J_{CP}$ = 5.9 Hz); 117.6 (s); 125.4 (d, $^1J_{CP}$ = 106.1 Hz); 125.4 (d, $^1J_{CP}$ = 97.3 Hz); 129.9 (d, $^3J_{CP}$ = 13.9 Hz); 130.1 (d, $^3J_{CP}$ = 18.3 Hz); 131.7, 132.7, 133.6 (all s); 134.2 (d, $^2J_{CP}$ = 11.0 Hz); 134.7 (s); 138.1 (d, $^3J_{CP}$ = 4.4 Hz); 141.9 (d, $^2J_{CP}$ = 10.3 Hz). ^{31}P NMR (CD_2Cl_2): δ 21.93 (d, $^2J_{PP}$ = 47.6 Hz); 24.33 (d, $^2J_{PP}$ = 47.6 Hz). IR: ν/cm^{-1} 1210 (P═O), 1070−1030 (BF_4^-), 1470, 750 (Ar). Anal. Calcd for $C_{27}H_{28}BF_4IO_3P_2S$: C, 45.79; H, 3.98; S, 4.53. Found: C, 45.61; H, 4.03; S, 4.76.

*(Diethoxyphosphoryl)[diphenyl(1-methylpyrazol-5-yl)phosphonio](phenyliodonio)methanide Tetrafluoroborate (**5d**).* Yield: 1.14 g (54%), white solid. Mp: 178 °C dec. ^{1}H NMR (CD_3CN): δ 1.13 (t, 6H, $^3J_{HH}$ = 7.0 Hz); 3.40 (s, 3H), 3.84−3.92 (m, 4H); 6.70 (d, 1H, J = 2.1 Hz); 7.41 (t, 2H, J = 7.8 Hz); 7.56−7.67 (m, 12H); 7.76−7.80 (m, 2H). ^{13}C NMR (CD_3CN): δ 16.5 (d, $^3J_{CP}$ = 6.6 Hz); 41.3 (s); 63.6 (d, $^2J_{CP}$ = 5.9 Hz); 118.0 (s); 121.8 (d, $^2J_{CP}$ = 17.6 Hz); 124.6 (d, $^1J_{CP}$ = 98.0 Hz); 128.2 (d, $^1J_{CP}$ = 109.0 Hz); 130.8 (d, $^3J_{CP}$ = 13.0 Hz); 132.3, 133.4 (two s); 134.6 (d, $^2J_{CP}$ = 11.0 Hz); 134.9, 135.5 (two s); 140.3 (d, $^2J_{CP}$ = 15.4 Hz). ^{31}P NMR (CD_3CN): δ 16.92 (d, $^2J_{PP}$ = 49.0 Hz); 22.01 (d, $^2J_{PP}$ = 49.0 Hz). IR: ν/cm^{-1} 1200 (P═O), 1070−1032 (BF_4^-), 1440, 738 (Ar). Anal. Calcd for $C_{27}H_{30}BF_4IN_2O_3P_2$: C, 45.92; H, 4.28; N, 3.97. Found: C, 45.95; H, 4.48; N, 4.20.

General Procedure for the Reaction of Ylides 5 with Alkynes. The alkyne (0.6 mmol) was added to a solution of ylide **5** (0.2 mmol) in anhydrous acetonitrile. The mixture was irradiated in a quartz flask with a mercury lamp (366 nm) source under an argon atmosphere. 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. Benzene was used to elute the residual alkynes and PhI; the corresponding phosphinoline was eluted by using a CH_2Cl_2/MeOH mixture in a ratio of 200:1.

*2-[(4-Methylphenyl)sulfonyl]-1,1,4-triphenyl-1λ^5-phosphinoline (**8**).* Yield: 27 mg (25%), yellow oil. ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 3H); 6.95 (d, 2H, J = 8.2 Hz); 7.07 (d, 2H, J = 8.2 Hz); 7.25 (d, 1H, J = 25.8 Hz); 7.28−7.40 (m, 8H); 7.44−7.54 (m, 5H); 7.58−7.62 (m, 2H); 7.80 (dd, 4H, J = 13.5 Hz, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 21.2 (s); 62.1 (d, $^1J_{CP}$ = 111.2 Hz); 110.1 (d, $^1J_{CP}$ = 90.0 Hz); 123.9 (d, $^3J_{CP}$ = 12.4 Hz); 125.3 (d, $^3J_{CP}$ = 8.1 Hz); 125.5, 126.0 (two s); 127.4 (d, $^1J_{CP}$ = 92.2 Hz); 128.3 (s); 128.6 (d, $^3J_{CP}$ = 13.2 Hz); 128.8, 130.2, 131.4, 132.0 (all s); 132.3 (d, $^2J_{CP}$ = 8.8 Hz); 133.9 (d, $^2J_{CP}$ = 11.0 Hz); 140.9 (s); 141.1 (d, $^2J_{CP}$ = 4.4 Hz); 142.0, 143.7 (two s). ^{31}P NMR ($CDCl_3$): δ 4.38. IR: ν/cm^{-1} 1278, 1133 (SO_2), 1459, 735 (Ar). HRMS: calcd for $C_{34}H_{27}O_2PS$ (M^+) m/z 530.1464, found 530.1456.

*1,1-Diphenyl-4-(thiophen-3-yl)-1λ^5-phosphinolin-2-yl 4-Methylphenyl Sulfone (**9**).* Yield: 16 mg (15%), yellow oil. ^{1}H NMR ($CDCl_3$): δ 2.28 (s, 3H); 6.93 (d, 2H, J = 8.0 Hz); 7.04 (d, 2H, J = 8.0 Hz); 7.03−7.10 (m, 2H); 7.16 (d, 2H, J = 2.8 Hz); 7.29 (d, 1H, J = 25.9 Hz); 7.31−7.35 (m, 2H); 7.41−7.53 (m, 6H); 7.57−7.61 (m, 2H); 7.79 (dd, 4H, J = 13.3 Hz, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ 21.3 (s); 110.5 (d, $^3J_{CP}$ = 5.9 Hz); 122.0 (s); 123.9 (d, $^3J_{CP}$ = 12.4 Hz); 124.6 (s); 125.2 (d, $^3J_{CP}$ = 8.1 Hz); 125.5 (s); 127.4 (d, $^1J_{CP}$ = 93.7 Hz); 128.6 (d, $^3J_{CP}$ = 13.2 Hz); 128.8, 129.8 (two s); 131.4 (d, $^2J_{CP}$ = 5.1 Hz); 131.5, 132.1 (two s); 132.3 (d, $^2J_{CP}$ = 8.8 Hz); 133.9 (d, $^2J_{CP}$ = 11.0 Hz); 140.9, 141.4, 143.7 (all s). ^{31}P NMR ($CDCl_3$): δ 4.28. IR: ν/cm^{-1} 1281, 1132 (SO_2), 1460, 746−665 (Ar). HRMS: calcd for $C_{32}H_{25}O_2PS_2$ (M^+) m/z 536.1028, found 536.1025.

*2-[(4-Methylphenyl)sulfonyl]-4-(phenanthren-9-yl)-1,1-diphenyl-1λ^5-phosphinoline (**10**).* Yield: 25 mg (20%), yellow oil. ^{1}H NMR ($CDCl_3$): δ 2.31 (s, 3H); 6.84 (dd, 1H, J = 7.8 Hz, J = 5.9 Hz); 6.96 (d, 2H, J = 7.9 Hz); 7.03 (dd, 1H, J = 7.7 Hz, J = 6.2 Hz); 7.10 (d, 2H, J = 8.1 Hz); 7.09−7.14 (m, 1H); 7.38−7.41 (m, 3H); 7.43 (d, 1H, J = 25.9 Hz); 7.48−7.70 (m, 10H); 7.76 (s, 1H); 7.84−7.93 (m, 4H); 8.76

dx.doi.org/10.1021/jo401514d | J. Org. Chem. 2013, 78, 11691−11697

(dd, 2H, J = 8.1 Hz, J = 8.3 Hz). ^{13}C NMR ($CDCl_3$): δ 21.3 (s); 62.1 (d, $^1J_{CP}$ = 112.0 Hz); 109.7 (d, $^1J_{CP}$ = 90.0 Hz); 113.5 (d, $^3J_{CP}$ = 8.8 Hz); 122.5, 122.8 (two s); 123.8 (d, $^3J_{CP}$ = 12.4 Hz); 125.5 (s); 126.0 (d, $^3J_{CP}$ = 7.3 Hz); 126.2, 126.3, 126.6 (all s); 126.9 (d, $^1J_{CP}$ = 105.4 Hz); 127.3, 128.3, 128.5, 128.5, 128.7 (all s); 128.8 (d, $^3J_{CP}$ = 13.2 Hz); 128.8 (s); 128.9 (d, $^3J_{CP}$ = 13.2 Hz); 130.1, 130.6, 131.5 (all s); 132.0 (d, $^2J_{CP}$ = 9.5 Hz); 132.07 (s); 132.14 (s); 132.2 (d, $^2J_{CP}$ = 7.3 Hz); 132.8 (s); 133.6 (d, $^2J_{CP}$ = 11.0 Hz); 134.3 (d, $^2J_{CP}$ = 11.0 Hz); 138.2, 140.8 (two s); 141.9 (d, $^2J_{CP}$ = 5.1 Hz); 143.8 (s). ^{31}P NMR ($CDCl_3$): δ 4.80. IR: ν/cm^{-1} 1281, 1134 (SO_2), 1458, 746–692 (Ar). HRMS: calcd for $C_{42}H_{31}O_2PS$ (M^+) m/z 630.1777, found 630.1762.

*4-(4-Methoxyphenyl)-2-[(4-methylphenyl)sulfonyl]-1,1-diphenyl-1λ^5-phosphinoline (**11**).* Yield: 5 mg (less than 5%), yellow oil. ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 3H); 3.86 (s, 3H); 6.92 (d, 2H, J = 8.7 Hz); 6.96 (d, 2H, J = 8.0 Hz); 7.06–7.16 (m, 4H); 7.23 (d, 2H, J = 8.7 Hz); 7.31–7.36 (m, 2H); 7.43–7.53 (m, 5H); 7.57–7.61 (m, 2H); 7.81 (dd, 4H, J = 13.4 Hz, J = 7.3 Hz). ^{31}P NMR ($CDCl_3$): δ 4.36. HRMS: calcd for $C_{35}H_{29}O_3PS$ (M^+) m/z 560.1570, found 560.1567.

*2-[(4-Methylphenyl)sulfonyl]-1,1,3,4-tetraphenyl-1λ^5-phosphinoline (**12**).* Yield: 5 mg (less than 5%), yellow oil. ^{1}H NMR ($CDCl_3$): δ 2.21 (s, 3H); 6.44 (d, 2H, J = 8.0 Hz); 6.72 (d, 2H, J = 8.0 Hz); 6.71–6.80 (m, 5H); 6.84–6.88 (m, 3H); 6.94–6.98 (m, 1H); 7.00–7.05 (m, 3H); 7.18–7.22 (m, 1H); 7.47 (ddd, 1H, J = 13.3 Hz, J = 7.8 Hz, J = 1.2 Hz); 7.61–7.63 (m, 6H); 8.08 (ddd, 4H, J = 13.0 Hz, J = 7.0 Hz, J = 3.1 Hz). ^{31}P NMR ($CDCl_3$): δ 5.34. HRMS: calcd for $C_{40}H_{31}O_2PS$ (M^+) m/z 606.1777, found 606.1775.

*Diethyl (1,1,4-Triphenyl-1λ^5-phosphinolin-2-yl)phosphonate (**13**).* Yield: 62 mg (60%), yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.14 (t, 6H, J = 7.0 Hz); 3.76–3.86 (m, 4H); 6.99 (dd, 1H, J = 18.2 Hz, J = 31.3 Hz); 7.03–7.07 (m, 1H); 7.22–7.45 (m, 8H); 7.47–7.65 (m, 6H); 7.79–7.85 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 16.3 (d, $^3J_{CP}$ = 6.6 Hz); 40.5 (dd, $^1J_{CP}$ = 116.3 Hz, $^1J_{CP}$ = 217.3 Hz); 60.7 (d, $^2J_{CP}$ = 5.1 Hz); 107.4 (dd, $^1J_{CP}$ = 93.4 Hz, $^3J_{CP}$ = 9.1 Hz); 115.5 (dd, $^3J_{CP}$ = 13.2 Hz, $^3J_{CP}$ = 13.2 Hz); 123.2 (d, $^3J_{CP}$ = 12.4 Hz); 124.7 (d, $^3J_{CP}$ = 7.3 Hz); 125.5, 128.2 (two s); 129.4 (d, $^3J_{CP}$ = 12.4 Hz); 130.0 (d, $^1J_{CP}$ = 91.5 Hz); 130.1, 131.0, 131.7 (all s); 132.2 (d, $^2J_{CP}$ = 7.3 Hz); 133.4 (d, $^2J_{CP}$ = 10.2 Hz); 134.6 (d, $^2J_{CP}$ = 3.6 Hz); 141.3 (d, $^2J_{CP}$ = 4.4 Hz); 142.8 (s). ^{31}P NMR ($CDCl_3$): δ 9.39 (d, P_{cycle}, $^2J_{PP}$ = 50.5 Hz); 26.51 (d, -P(O)(OEt)$_2$, $^2J_{PP}$ = 50.5 Hz). IR: ν/cm^{-1} 1241 (P═O), 1027 (C–O), 1438, 782–694 (Ar). HRMS: calcd for $C_{31}H_{30}O_3P_2$ (M^+) m/z 512.1670, found 512.1665.

*Diethyl (4-Octyl-1,1-diphenyl-1λ^5-phosphinolin-2-yl)-phosphonate (**14**).* Yield: 77 mg (70%), yellow oil, crystallizing from CH_2Cl_2 with addition of Et_2O. Mp: 215–216 °C. ^{1}H NMR (CD_2Cl_2): δ 0.87 (t, 3H, J = 7.1 Hz); 1.12 (t, 6H, J = 7.0 Hz); 1.25–1.34 (m, 10H); 1.51–1.55 (m, 2H); 2.53 (t, 2H, J = 7.6 Hz); 3.68–3.78 (m, 4H); 6.68 (dd, 1H, J = 17.7 Hz, J = 31.4 Hz); 7.01–7.05 (m, 1H); 7.26 (dd, 1H, J = 13.5 Hz, J = 7.5 Hz); 7.42–7.56 (m, 8H); 7.68–7.74 (m, 4H). ^{13}C NMR (CD_2Cl_2): δ 14.5 (s); 16.6 (d, $^3J_{CP}$ = 7.3 Hz); 23.3, 30.0, 30.10, 30.13, 30.5, 32.5, 34.6 (all s); 61.0 (d, $^2J_{CP}$ = 5.1 Hz); 108.6 (d, $^1J_{CP}$ = 80.5 Hz); 111.7 (dd, $^3J_{CP}$ = 12.4 Hz, $^3J_{CP}$ = 13.2 Hz); 123.3 (d, $^3J_{CP}$ = 12.5 Hz); 123.3 (d, $^3J_{CP}$ = 7.3 Hz); 128.9 (d, $^3J_{CP}$ = 12.4 Hz); 131.1 (d, $^1J_{CP}$ = 90.8 Hz); 131.7, 132.0, 132.3 (all s); 133.0 (d, $^2J_{CP}$ = 8.0 Hz); 133.7 (s, $^2J_{CP}$ = 11.0 Hz); 141.8 (s, $^2J_{CP}$ = 5.1 Hz). ^{31}P NMR (CD_2Cl_2): δ 10.17 (d, P_{cycle}, $^2J_{PP}$ = 50.5 Hz); 26.77 (d, -P(O)(OEt)$_2$, $^2J_{PP}$ = 50.5 Hz). IR: ν/cm^{-1} 2854, 2925 (CH-alk), 1224 (P═O), 1029 (C–O), 1438, 732 (Ar). HRMS: calcd for $C_{33}H_{42}O_3P_2$ (M^+) m/z 548.2609, found 548.2604.

*Diethyl [1,1-Diphenyl-4-(thiophen-3-yl)-1λ^5-phosphinolin-2-yl]-phosphonate (**15**).* Yield: 57 mg (55%), yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.13 (t, 6H, ^3JH_H = 7.0 Hz); 3.75–3.85 (m, 4H); 7.06 (dd, 1H, J = 18.2 Hz, J = 31.3 Hz); 7.04–7.07 (m, 1H); 7.13–7.15 (m, 2H); 7.30–7.36 (m, 3H); 7.46–7.56 (m, 7H); 7.78–7.83 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 16.6 (d, $^3J_{CP}$ = 6.6 Hz); 61.2 (d, $^2J_{CP}$ = 5.9 Hz); 107.8 (dd, $^1J_{CP}$ = 90.2 Hz, $^3J_{CP}$ = 9.1 Hz); 121.7 (s); 123.8 (d, $^3J_{CP}$ = 12.4 Hz); 125.0 (d, $^3J_{CP}$ = 11.0 Hz); 125.1 (s); 129.0 (d, $^3J_{CP}$ = 12.4 Hz); 130.4 (s); 130.7 (d, $^1J_{CP}$ = 90.8 Hz); 131.8 (s); 132.3 (s); 132.9 (d, $^2J_{CP}$ = 8.1 Hz); 133.9 (d, $^2J_{CP}$ = 11.0 Hz); 135.2 (d, $^2J_{CP}$ = 2.1 Hz); 141.9 (d, $^2J_{CP}$ = 5.1 Hz); 143.9 (s). ^{31}P NMR ($CDCl_3$): δ 9.24 (d, P_{cycle}, $^2J_{PP}$ = 49.5 Hz); 26.42 (d, -P(O)(OEt)$_2$, $^2J_{PP}$ = 49.5 Hz). IR: ν/cm^{-1} 1238 (P═O), 1031 (C–O), 1455, 738 (Ar). HRMS: calcd for $C_{29}H_{28}O_3P_2S$ (M^+) m/z 518.1234, found 518.1236.

*Diethyl [4-(4-Methoxyphenyl)-1,1-diphenyl-1λ^5-phosphinolin-2-yl]phosphonate (**16**).* Yield: 52 mg (50%), yellow oil. ^{1}H NMR (CD_2Cl_2): δ 1.12 (t, 6H, J = 7.1 Hz); 3.72–3.80 (m, 4H); 3.83 (s, 3H); 6.82 (dd, 1H, J = 17.9 Hz, J = 31.5 Hz); 6.91 (d, 2H, J = 8.5 Hz); 7.04 (dd, 1H, J = 8.5 Hz, J = 8.5 Hz); 7.25 (d, 2H, J = 8.5 Hz); 7.27–7.36 (m, 3H); 7.50–7.59 (m, 6H); 7.79 (dd, 4H, J = 7.0 Hz, J = 13.1 Hz). ^{13}C NMR (CD_2Cl_2): δ 16.6 (d, $^3J_{CP}$ = 7.3 Hz); 41.6 (dd, $^1J_{CP}$ = 101.0 Hz, $^1J_{CP}$ = 207.8 Hz); 55.8 (s); 61.2 (d, $^2J_{CP}$ = 5.1 Hz); 107.8 (dd, $^1J_{CP}$ = 90.0 Hz, $^3J_{CP}$ = 9.5 Hz); 114.1 (s); 115.3 (dd, $^3J_{CP}$ = 13.2 Hz, $^3J_{CP}$ = 13.2 Hz); 123.2 (d, $^3J_{CP}$ = 12.4 Hz); 125.1 (d, $^3J_{CP}$ = 7.3 Hz); 129.0 (d, $^3J_{CP}$ = 12.4 Hz); 130.8 (d, $^1J_{CP}$ = 91.5 Hz); 131.6 (s); 132.2 (d, $^4J_{CP}$ = 2.2 Hz); 132.8 (d, $^2J_{CP}$ = 8.1 Hz); 133.8 (d, $^2J_{CP}$ = 11.0 Hz); 134.6 (s); 135.7 (s); 142.0 (d, $^2J_{CP}$ = 4.4 Hz); 158.4 (s). ^{31}P NMR (CD_2Cl_2): δ 11.34 (d, P_{cycle}, $^2J_{PP}$ = 50.5 Hz); 28.07 (d, -P(O)(OEt)$_2$, $^2J_{PP}$ = 50.5 Hz). IR: ν/cm^{-1} 1240 (P═O), 1029 (C–O), 1454, 786–746 (Ar). HRMS: calcd for $C_{32}H_{32}O_4P_2$ (M^+) m/z 542.1770, found 542.1773.

*Diethyl [4-(6-Methoxynaphthalen-2-yl)-1,1-diphenyl-1λ^5-phosphinolin-2-yl]phosphonate (**17**).* Yield: 59 mg (50%), yellow oil. ^{1}H NMR (CD_2Cl_2): δ 1.13 (t, 6H, J = 7.2 Hz); 3.73–3.84 (m, 4H); 3.93 (s, 3H); 6.99 (dd, 1H, J = 18.0 Hz, J = 31.4 Hz); 7.04–7.09 (m, 1H); 7.13 (dd, 1H, J = 9.0 Hz, J = 2.6 Hz); 7.19 (d, 1H, J = 2.6 Hz); 7.29–7.35 (m, 2H); 7.42 (ddd, 1H, J = 8.8 Hz, J = 5.9 Hz, J = 1.1 Hz); 7.47 (dd, 1H, J = 8.6 Hz, J = 1.7 Hz); 7.51–7.59 (m, 6H); 7.71–7.75 (m, 3H); 7.81 (ddd, 4H, J = 15.0 Hz, J = 8.6 Hz, J = 1.8 Hz). ^{13}C NMR (CD_2Cl_2): δ 16.6 (d, $^3J_{CP}$ = 6.8 Hz); 42.3 (dd, $^1J_{CP}$ = 100.8 Hz, $^1J_{CP}$ = 208.0 Hz); 55.8 (s); 61.2 (d, $^2J_{CP}$ = 5.4 Hz); 106.2 (s); 108.0 (dd, $^1J_{CP}$ = 90.3 Hz, $^3J_{CP}$ = 9.4 Hz); 115.7 (dd, $^3J_{CP}$ = 12.2 Hz, $^3J_{CP}$ = 14.0 Hz); 119.0 (s); 123.9 (dd, $^3J_{CP}$ = 12.2 Hz, $^5J_{CP}$ = 1.1 Hz); 125.2 (d, $^3J_{CP}$ = 7.6 Hz); 126.8, 128.1 (two s); 129.0 (d, $^3J_{CP}$ = 13.0 Hz); 129.6, 130.0, 130.2 (all s); 130.6 (dd, $^1J_{CP}$ = 91.4 Hz, $^3J_{CP}$ = 1.8 Hz); 131.6 (d, $^4J_{CP}$ = 1.8 Hz); 132.3 (d, $^4J_{CP}$ = 2.9 Hz); 132.8 (dd, $^2J_{CP}$ = 8.6 Hz, $^4J_{CP}$ = 2.9 Hz); 133.5 (s); 133.9 (d, $^2J_{CP}$ = 10.8 Hz); 135.3 (dd, $^2J_{CP}$ = 3.6 Hz, $^2J_{CP}$ = 1.1 Hz); 138.7 (s); 141.9 (dd, $^2J_{CP}$ = 5.4 Hz, $^4J_{CP}$ = 1.8 Hz); 157.9 (s). ^{31}P NMR (CD_2Cl_2): δ 9.23 (d, P_{cycle}, $^2J_{PP}$ = 50.5 Hz); 25.92 (d, P(O)(OEt)$_2$, $^2J_{PP}$ = 50.5 Hz). IR: ν/cm^{-1} 1203 (P═O), 1029 (C–O), 1454–1436 (Ar). HRMS: calcd for $C_{36}H_{34}O_4P_2$ (M^+) m/z 592.1927, found 592.1912.

*Diethyl [4-(Phenanthren-9-yl)-1,1-diphenyl-1λ^5-phosphinolin-2-yl]phosphonate (**18**).* Yield: 80 mg (65%), yellow oil. ^{1}H NMR (CD_2Cl_2): δ 1.07 (t, 3H, J = 7.1 Hz); 1.15 (t, 3H, J = 7.1 Hz); 3.70–3.86 (m, 4H); 6.80 (dd, 1H, J = 5.8 Hz, J = 8.0 Hz); 7.00–7.04 (m, 1H); 7.06 (dd, 1H, J = 17.7 Hz, J = 31.3 Hz);7.11–7.15 (m, 1H); 7.37 (ddd, 1H, J = 1.1 Hz, J = 7.8 Hz, J = 13.3 Hz); 7.42 (ddd, 1H, J = 0.9 Hz, J = 8.1 Hz, J = 8.1 Hz); 7.57–7.69 (m, 9H); 7.73 (dd, 1H, J = 0.8 Hz, J = 8.2 Hz); 7.78 (s, 1H); 7.86–7.93 (m, 5H); 8.75 (dd, 2H, J = 8.8 Hz, J = 9.0 Hz). ^{13}C NMR (CD_2Cl_2): δ 16.6 (d, $^3J_{CP}$ = 8.1 Hz); 16.7 (d, $^3J_{CP}$ = 8.1 Hz); 42.2 (dd, $^1J_{CP}$ = 101.0 Hz, $^1J_{CP}$ = 208.6 Hz); 61.2 (d, $^2J_{CP}$ = 5.1 Hz); 61.3 (d, $^2J_{CP}$ = 5.1 Hz); 107.5 (dd, $^1J_{CP}$ = 90.8 Hz, $^3J_{CP}$ = 9.5 Hz); 113.0 (dd, $^3J_{CP}$ = 13.2 Hz, $^3J_{CP}$ = 13.2 Hz); 123.0 (s); 123.4 (s); 123.7 (d, $^3J_{CP}$ = 12.4 Hz); 125.8 (d, $^3J_{CP}$ = 7.3 Hz); 126.7, 126.9, 127.2, 127.9 (all s); 129.0 (d, $^3J_{CP}$ = 16.8 Hz); 129.0 (d, $^3J_{CP}$ = 16.1 Hz); 129.2 (s); 130.1 (d, $^1J_{CP}$ = 94.4 Hz); 130.5 (s); 131.1 (d, $^1J_{CP}$ = 95.4 Hz); 131.2, 131.6, 132.3, 132.5 (all s); 132.6 (d, $^2J_{CP}$ = 8.1 Hz); 133.0 (s); 133.59 (s); 133.60 (d, $^2J_{CP}$ = 10.2 Hz); 134.3 (d, $^2J_{CP}$ = 11.0 Hz); 135.8 (d, CH, $^2J_{CP}$ = 2.2 Hz); 139.7 (s); 142.6 (d, $^2J_{CP}$ = 5.2 Hz). ^{31}P NMR ($CDCl_3$): δ 9.86 (d, P_{cycle}, $^2J_{PP}$ = 50.5 Hz); 26.38 (d, P(O)(OEt)$_2$, $^2J_{PP}$ = 50.5 Hz). IR: ν/cm^{-1} 1232 (P═O), 1020 (C–O), 1455, 765–728 (Ar). HRMS: calcd for $C_{39}H_{34}O_3P_2$ (M^+) m/z 612.1978, found 619.1970.

*Diethyl (1,1,3,4-Tetraphenyl-1λ^5-phosphinolin-2-yl)phosphonate (**19**).* Yield: 47 mg (40%), yellow oil. ^{1}H NMR (CD_2Cl_2): δ 0.90 (t, 6H, J = 7.1 Hz); 3.29–3.47 (m, 4H); 6.71 (dd, 1H, J = 6.4 Hz, J = 6.7 Hz); 6.93–7.02 (m, 7H); 7.05–7.10 (m, 4H); 7.18 (dd, 1H, J = 7.5 Hz, J = 7.9 Hz); 7.25 (dd, 1H, J = 7.8 Hz, J = 12.9 Hz); 7.52–7.59 (m, 6H); 7.93 (ddd, 4H, J = 2.3 Hz, J = 8.0 Hz, J = 13.0 Hz). ^{13}C NMR (CD_2Cl_2): δ 16.3 (d, $^3J_{CP}$ = 7.3 Hz); 42.8 (dd, $^1J_{CP}$ = 92.4 Hz, $^1J_{CP}$ = 204.2 Hz); 60.4 (d, $^2J_{CP}$ = 5.1 Hz); 109.5 (dd, $^1J_{CP}$ = 86.4 Hz, $^3J_{CP}$ =

dx.doi.org/10.1021/jo401514d | J. Org. Chem. 2013, 78, 11691–11697

9.5 Hz); 116.4 (dd, $^3J_{CP}$ = 12.4 Hz, $^3J_{CP}$ = 12.4 Hz); 123.5 (d, $^3J_{CP}$ = 11.7 Hz); 125.6 (s); 126.0 (s); 126.4 (d, $^3J_{CP}$ = 8.8 Hz); 126.4 (s); 128.0 (s); 128.7 (d, $^3J_{CP}$ = 12.4 Hz); 131.3 (s); 131.7 (s); 132.4 (d, $^1J_{CP}$ = 90.0 Hz); 132.8 (d, $^2J_{CP}$ = 8.8 Hz); 133.7 (s); 134.0 (d, $^2J_{CP}$ = 11.0 Hz); 142.4 (s); 142.7 (dd, $^3J_{CP}$ = 6.6 Hz, $^3J_{CP}$ = 13.9 Hz); 143.1 (d, $^2J_{CP}$ = 4.4 Hz); 145.0 (s). ^{31}P NMR (CD_2Cl_2): δ 10.73 (d, P_{cycle}, $^2J_{PP}$ = 49.5 Hz); 24.02 (d, -P(O)(OEt)$_2$, $^2J_{PP}$ = 49.5 Hz). IR: ν/cm^{-1} 1218 (P═O), 1025 (C−O), 1455, 696−804 (Ar). HRMS: calcd for $C_{37}H_{34}O_3P_2$ (M^+) m/z 588.1978, found 588.1979.

*Diethyl (4,7,7-Triphenyl-7λ^5-phosphinino[2,3-b]thiophen-6-yl)-phosphonate (**20**).* Yield: 16 mg (15%), yellow oil. ^{1}H NMR (CD_2Cl_2): δ 1.11 (t, 6H, J = 7.0 Hz); 3.70−3.80 (m, 4H); 6.92−7.02 (m, 2H); 6.95 (dd, J = 34.1 Hz, J = 18.2 Hz); 7.24 (tt, 1H, J = 7.4 Hz, J = 1.3 Hz); 7.34−7.39 (m, 2H); 7.48−7.58 (m, 8H); 7.73−7.80 (m, 4H). ^{13}C NMR (CD_2Cl_2): δ 16.6 (d, $^3J_{CP}$ = 6.6 Hz); 48.3 (dd, $^1J_{CP}$ = 201.6 Hz, $^1J_{CP}$ = 102.0 Hz); 61.3 (d, $^2J_{CP}$ = 5.5 Hz); 102.5 (d, $^1J_{CP}$ = 107.4 Hz); 111.7 (dd, $^3J_{CP}$ = 15.2 Hz, $^3J_{CP}$ = 10.1 Hz); 120.6 (d, $^3J_{CP}$ = 17.5 Hz); 126.5 (s); 128.3 (dd, $^3J_{CP}$ = 12.4 Hz, $^4J_{CP}$ = 3.9 Hz); 128.4 (s); 128.9 (d, $^3J_{CP}$ = 13.2 Hz); 129.0 (s); 131.5 (dd, $^1J_{CP}$ = 93.0 Hz, $^3J_{CP}$ = 2.0 Hz); 133.4 (d, J_{CP} = 11.3 Hz); 134.6 (dd, $^4J_{CP}$ = 4.7 Hz, $^4J_{CP}$ = 1.2 Hz); 142.9 (s); 153.9 (d, $^2J_{CP}$ = 8.6 Hz). ^{31}P NMR (CD_2Cl_2): δ 6.55 (d, $^2J_{PP}$ = 52.1 Hz); 25.71(d, $^2J_{PP}$ = 52.1 Hz). IR: ν/cm^{-1} 1242 (P═O), 1542, 806−752 (Ar). HRMS: calcd for $C_{29}H_{28}O_3P_2S$ (M^+) m/z 518.1234, found 518.1222.

*Diethyl [7,7-Diphenyl-4-(thiophen-3-yl)-7λ^5-phosphinino[2,3-b]-thiophen-6-yl]phosphonate (**21**).* Yield: 11 mg (10%); yellow oil. ^{1}H NMR (CD_2Cl_2): δ 1.10 (t, 6H, J = 7.0 Hz); 3.69−3.79 (m, 4H); 6.94 (dd, 1H, J = 5.4 Hz, J = 3.7 Hz); 7.04 (dd, 1H, J = 5.4 Hz, J = 3.0 Hz); 7.06 (dd, 1H, J = 34.0 Hz, J = 18.2 Hz); 7.30 (dd, 1H, J = 4.8 Hz, J = 1.5 Hz); 7.31−7.33 (m, 1H); 7.35 (dd, 1H, J = 4.8 Hz, J = 3.0 Hz); 7.48−7.58 (m, 6H); 7.72−7.79 (m, 4H). ^{13}C NMR (CD_2Cl_2): δ 16.6 (d, $^3J_{CP}$ = 6.6 Hz); 48.3 (dd, $^1J_{CP}$ = 207.0 Hz, $^1J_{CP}$ = 101.7 Hz); 61.3 (d, $^2J_{CP}$ = 5.1 Hz); 102.5 (dd, $^1J_{CP}$ = 96.6 Hz, $^3J_{CP}$ = 10.3 Hz); 106.8 (dd, $^3J_{CP}$ = 16.1 Hz, $^3J_{CP}$ = 11.0 Hz); 119.46 (s); 120.9 (d, $^3J_{CP}$ = 17.6 Hz); 125.5 (s); 128.3 (dd, α-thienyl, $^3J_{CP}$ = 13.4 Hz, $^5J_{CP}$ = 3.6 Hz); 128.4 (s); 129.0 (d, $^3J_{CP}$ = 13.2 Hz); 131.4 (d, $^1J_{CP}$ = 92.9 Hz); 132.2 (s); 133.5 (d, $^2J_{CP}$ = 11.7 Hz); 134.4 (d, $^2J_{CP}$ = 3.7 Hz); 143.3 (s); 153.8 (d,$^2J_{CP}$ = 8.8 Hz). ^{31}P NMR (CD_2Cl_2): δ 6.55(d, $^2J_{PP}$ = 52.0 Hz); 25.64 (d, $^2J_{PP}$ = 52.0 Hz). IR: ν/cm^{-1} 1243 (P═O), 1550, 815−700 (Ar). HRMS: calcd for $C_{27}H_{26}O_3P_2S_2$ (M^+) m/z 524.0799, found 524.0789.

*Diethyl [4-(4-Methoxyphenyl)-1-methyl-7,7-diphenyl-1H-7λ^5-phosphinino[2,3-c]pyrazol-6-yl]phosphonate (**22**).* Yield: 11 mg (10%), yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.08 (t, 6H, J = 6.9 Hz); 3.37 (s, 3H); 3.70−3.80 (m, 4H); 3.82 (s, 3H); 6.82 (dd, 1H, J = 35.6 Hz, J = 17.6 Hz); 6.87 (d, 2H, J = 6.3 Hz); 7.20 (d, 2H, J = 8.6 Hz); 7.43−7.49 (m, 7H); 7.77 (ddd, 4H, J = 14.1 Hz, J = 8.2 Hz, J = 1.6 Hz). ^{13}C NMR ($CDCl_3$): δ 16.2 (d, $^3J_{CP}$ = 6.9 Hz); 39.9 (s); 55.3 (s); 60.7 (d, $^2J_{PP}$ = 5.3 Hz); 113.4 (s); 126.7 (d, $^1J_{CP}$ = 93.1 Hz); 128.3 (d, $^2J_{CP}$ = 13.0 Hz); 131.2 (s); 131.5 (d, $^2J_{CP}$ = 3.1 Hz); 132.7 (d, $^3J_{CP}$ = 11.4 Hz); 152.2 (s); 153.2 (d, $^2J_{CP}$ = 10.7 Hz); 158.2 (s); 160.7 (s). ^{31}P NMR ($CDCl_3$): δ 3.73 (d,$^2J_{PP}$ = 54.5 Hz); 27.0 (d, $^2J_{PP}$ = 54.5 Hz). HRMS: calcd for $C_{30}H_{32}N_2O_4P_2$ (M^+) m/z 546.1832, found 546.1843.

*Diethyl [4-(4-Methoxyphenyl)-1-(1-methyl-1H-pyrazol-5-yl)-1-phenyl-1λ^5-phosphinolin-2-yl]phosphonate (**23**).* Yield: 5 mg (less than 5%), yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.13 (t, 6H, J = 7.0 Hz); 3.76−3.92 (m, 4H); 3.84 (s, 3H); 3.85 (s, 3H); 6.48 (dd, 1H, J = 1.9 Hz, J = 2.0 Hz); 6.92 (d, 2H, J = 8.2 Hz); 6.92 (dd, 1H, J = 35.6 Hz, J = 17.6 Hz); 7.07−7.11 (m, 1H); 7.26 (d, 2H, J = 8.0 Hz); 7.31−7.39 (m, 2H); 7.50−7.55(m, 3H); 7.57 (dd, 1H, J = 1.6 Hz, J = 2.0 Hz); 7.69 (dd, 1H, J = 12.5 Hz, J = 7.0 Hz); 7.88 (ddd, 2H, J = 13.7 Hz, J = 7.8 Hz, J = 1.6 Hz). ^{31}P NMR ($CDCl_3$): δ −6.85 (d, $^2J_{PP}$ = 48.0 Hz); 25.38 (d, $^2J_{PP}$ = 48.0 Hz). HRMS: calcd for $C_{30}H_{32}N_2O_4P_2$ (M^+) m/z 546.1832, found 546.1833.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and a CIF file giving ^{1}H, ^{31}P, and ^{13}C NMR spectra of the new compounds and an X-ray analysis of the molecular structure of **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Russian Foundation of Basic Research (Project 11-03-00641-a), the Grant of the President of the Russian Federation (NSh-6464.2012.3), and the Division of Chemistry and Materials Science of the Russian Academy of Sciences (OChNM-1 and OChNM-9) for financial support.

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