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Photochemical Synthesis of Phosphinolines from Phosphonium−Iodonium Ylides

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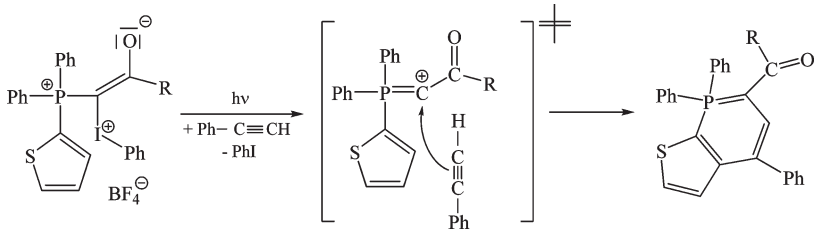

We describe three different series of experiments which were undertaken to test our hypothesis that during irradiation of phosphonium−iodonium ylides (**1a**, **1b**) an electrophilic carbene is generated. By opposing the assumed intermediate to monosubstituted alkynes, we observed in the case of electron-rich substituents at the triple bond a domination of a 1,3-dipolar cycloaddition of the intermediate with the triple bond to yield furans. In the case of electron poorer substituents, the formation of phosphinolines prevails. A second series of experiments was carried out with mixed ylides in which one phenyl ring at the triarylphosphonium group was replaced by a thienyl group. In this case, we observe only an intramolecular reaction with the thienyl ring to yield the phosphinolines **21**−**23**. In a third test, we replaced in the mixed ylides **1a**, **1b** the COR group by a CN substituent. This modification leads to phosphinolines only and avoids a 1,3-dipolar cycloaddition.

Introduction

Highly reactive species, such as carbenes,[1] 1,3-dipoles,[2] or ylides,[3] to name only a few, are of great significance in organic synthesis. Special interest has arisen lately for the mixed phosphonium−iodonium ylides (**1**) which are readily available.[4] Research on these species indicates[5] that their electronic ground state may be circumscribed by resonance structures *a*−*d* as shown in Scheme 1 for **1a**. The significant contribution of the highly polar resonance structure *d* to the ground state rationalizes very well the observed reactivity of **1a** (see Scheme 2). This reagent can be O-alkylated, O-acylated, and O-silylated.[6] The reaction of **1a** or **1b** with nucleophiles such as halogen anions or alkyl- or aryl-sulfides replaces the phenyl−iodonium substituent from **1**.[6b,7]

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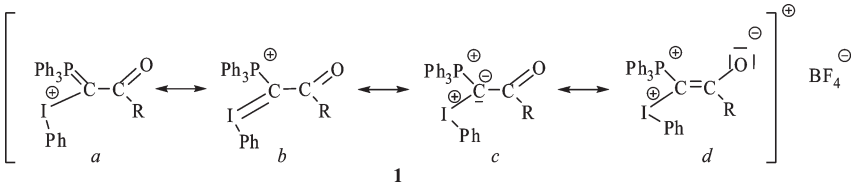
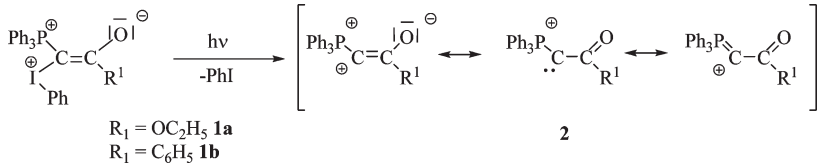
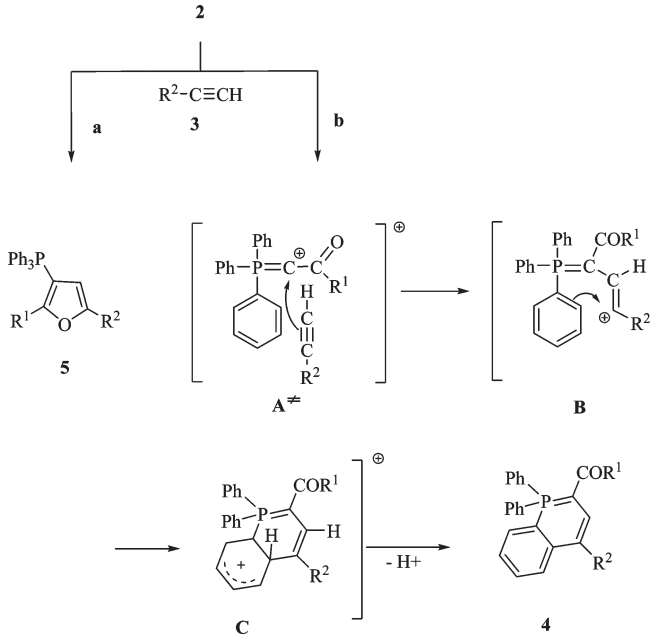
SCHEME 1. Resonance Structures (*a*−*d*) of Ylide 1



SCHEME 2. Generation of 2 by Photolysis of 1



SCHEME 3. Reaction of 2 with Alkyne 3[a]



[a]Path **a** yields furan **5**. Path **b** yields the intermediates **B** and **C** via the transition state **A** to **4**.

Recently, we discovered a new reaction path of mixed ylides by irradiation of **1** in presence of triple bonds. Irradiation of **1a** or **1b** with nitriles as solvents yielded oxazoles.[8] The reaction with a monosubstituted alkyne, **3**, is shown in Schemes 2 and 3 as an example.[8] In this sequence, it is assumed that the irradiation of **1** yields the short-lived intermediate **2**. The highly electrophilic species **2** reacts with the alkyne **3** via the intermediates **B** and **C** to **4**.[9] As a side product, **2** reacts via a 1,3-dipolar cycloaddition with **3** to the furan **5**. On the basis of theses schemes, we expect that the stabilization of the vinylic cation **B** by electron-rich substituents R^2 should favor the production of **4**. Furthermore, the nucleophilicity of the aryl ring at the phosphorus in **B** should favor the formation of **4**. In this paper, we will present our results by reacting various electron-rich alkynes with **1** and by using a mixed ylide in which one aryl ring in the triphenylphosphonium group is replaced by a more nucleophilic thiophen ring.

Results and Discussion

Preparation of Starting Materials. The preparation of the phosphonium−iodonium ylides **1d** and **1e** commenced with the synthesis of the phosphonium salts **8d** and **8e** from bromoacetophenone (**6**) and 2-thienyldiphenylphosphane (**7d**) and 3-thienyldiphenylphosphane (**7e**). The synthesis was carried out in acetonitrile (MeCN) (Scheme 4).

The phosphonium salts **8d** and **8e** were converted to the ylides **9d** and **9e** by treatment with sodium methoxide in dry methanol between 0 and 5 °C (Scheme 5). By treatment of **9d** and **9e** with diacetoxyiodobenzene followed by HBF_4, the desired mixed ylides **1d** and **1e** were isolated in 80−85% yield as tetrafluoroborates.

Reaction of 1b with Alkynes. The irradiation of the ylide **1b** with four different acetylenes (**10**−**13**) yielded a mixture of the phosphinolines (**14**−**17**) and furans (**18**−**21**) as summarized in Scheme 6.

These data show a decrease of the yield of the phosphinolines and an increase of the yield of furans with increasing the π-system of the substituent at the alkyne. To rationalize the result just discussed, we assume two competing reaction paths: (**a**) a 1,3-dipolar cycloaddition of the intermediate **2** and the alkyne **3** as described in the left part of Scheme 3, and (**b**) an electrophilic attack of the alkyne to the intermediate with subsequent cycloaddition as described in the right part of Scheme 3 by the sequence **B**−**C**−**4**. If the positive charge at the vinylic carbon of **B** is strongly localized, the formation of **4** competes successfully with the 1,3-dipolar cycloaddition to **5**. However, if the positive charge at the vinylic carbon of **B** is delocalized by an extended π-system, the 1,3-dipolar cycloaddition prevails.

A second test for the proposed mechanism in Scheme 3 is the reaction with the ylides **1d** and **1e**. These ylides provide two different aryl groups at the positively charged phosphorus center: two phenyl rings and only one thienyl ring. The latter is electron richer than the phenyl ring as shown by the first ionization energies (thiophene, 8.87 eV;[10] benzene,

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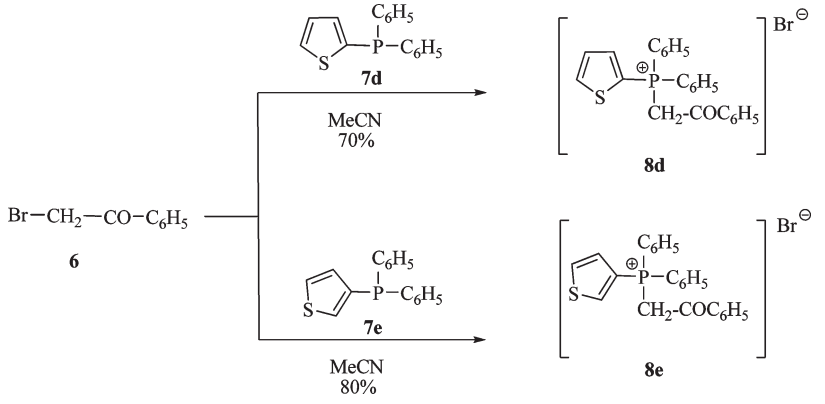
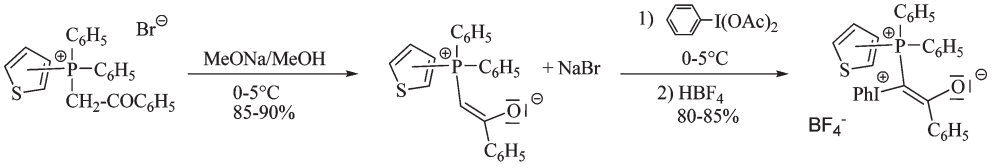
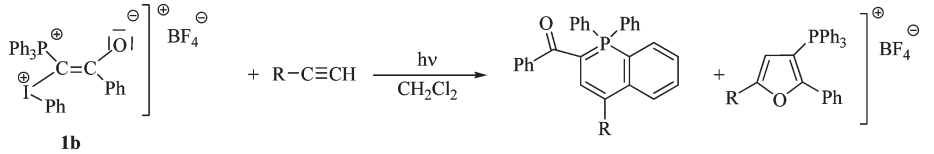
SCHEME 4. Preparation of the Thienyl−Phenylphosphonium Salts 8d and 8e

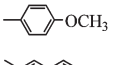
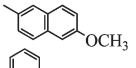


SCHEME 5. Preparation of the Mixed Ylides 1d and 1e via the Ylides 9d and 9e, Respectively



SCHEME 6. Preparation of the Phospholines 14−17 and Furans 18−21 by Irradiation of 1b with the Alkynes 10−13



No.		No. Yield	No. Yield
10		**14** 60	**18** 7
11		**15** 40	**19** 30
12		**16** 10	**20** 60
13		**17** 5	**21** 80

9.24 eV[11]). Thus, we can expect for path **b** a preference of the reaction with the thiophene ring. In Scheme 7, we have summarized the experimental results.

When a solution of **1d** and phenyl acetylene was irradiated in CH_2Cl_2, we obtained **22** in 30% yield. When **1e** was treated in the same way, a mixture of **23** and **24** was isolated as red oil in 25% yield together. A reaction with the phenyl rings was not observed.

When the benzoyl substituent in **1b** or the carbonylethoxy substituent in **1a** is replaced by a CN group, we expect for the reaction with alkynes no 1,3-dipolar cycloadditions to furans. This was indeed the case. By using **1c** (Scheme 8) and the alkynes **3**, **10**, **11**, **25**, and **26**, we obtained phosphinolines **27**−**31**. The lower yields of cyano-substituted phosphinolines as compared to benzoyl-substituted is due to the formation of **32**. The reagent **1c** acts also as a base to abstract the hydrogen of the substituted phenyl ring. In the case of 1,1,4-triphenyl-1λ^5-phospholine-2-carbonitrile (**27**), we were able to study the molecular structure by means of the X-ray technique on single crystals. As shown before,[9] the 10-membered ring system is almost planar. Indeed, the calculation of puckering of 6-membered phosphinoline ring gave puckering amplitude 'S' = 0.394, polar angle θ = 61.62, S(2) = 0.347, ψ = 24.82, S(3) = 0.187[12] with ring conformation intermediate between screw-boat and boat. The bond lengths in the heterocyclic ring are P−C2 = 1.721 Å, C2−C3 = 1.432 Å, C3−C4 = 1.362 Å, and C4−C10 = 1.458 Å and these values are similar to those obtained for related phosphinolines.[9]

Conclusion

The yields of the phosphinolines **14**−**17** and the furans **18**−**21** vary considerably in the light-induced reaction of **1b** with monosubstituted alkynes (3-ethynylthiophene (**10**),

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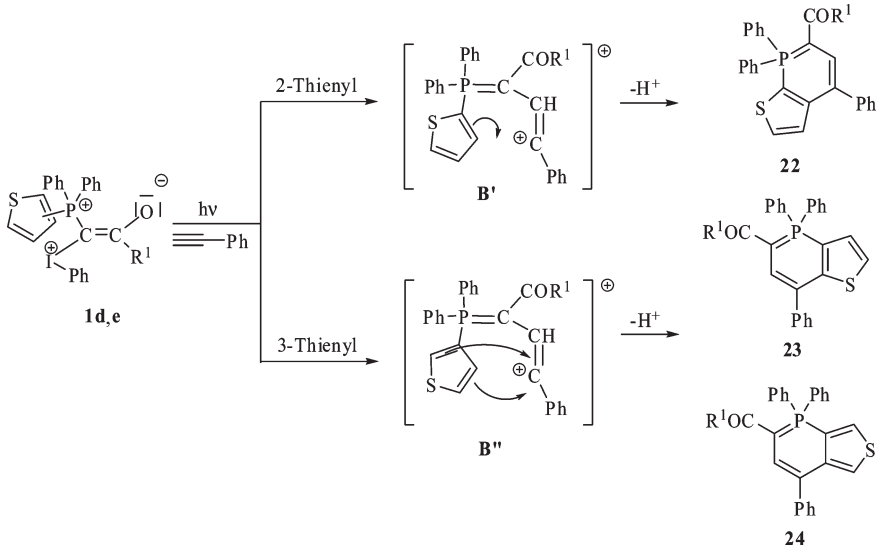
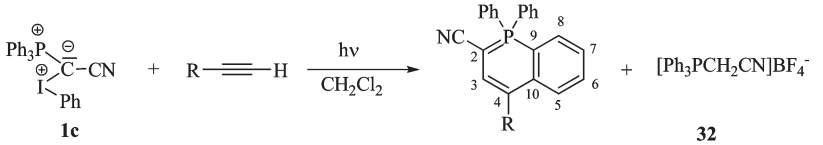
SCHEME 7. Light-Induced Reaction of 1d and 1e, Respectively, To Yield 22 and 23 + 24, Respectively



SCHEME 8. Light-Induced Reaction of lc with the Alkynes 3,10, 11, 25, and 26 To Yield the Phosphinolines 27−31 as well as 32



No.	R	No.	Yield%
3	C_6H_5	**27**	35
10	3-H_4C_4S	**28**	40
11	4-$MeOC_6H_4$	**29**	40
25	$\equiv(CH_2)_4-$	**30**	20
26	C_8H_{17}	**31**	15

p-methoxy-phenylacetylene (**11**), 2-ethinyl-6-methoxynaphthalene (**12**), and 9-ethynylphenanthrene (**13**)). The more extended the π-system at the alkyne unit was, the higher was the yield of the furans and the lower the yields of the phospholines. These trends could be ascribed to the electrophilicity of the intermediate vinylic cation at the former triple bond. The results summarized in Schemes 7 and 8 corroborate our picture of an electrophilic reaction of the aryl rings and that 1,3-dipolar cycloadditions are restricted to carbonyl substituents at the phosphonium−iodonium ylides.

Experimental Section

General. The ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded in $CDCl_3$ and CD_2Cl_2 with Me_4Si as the internal standard. The IR spectra were measured in CCl_4. HRMS measurements: The FAB spectra were recorded in positive ion mode using acetonitrile alcohol as matrix. The mass spectra were obtained on a quadrupole mass spectrometer (EI, 70 eV, direct inlet). The progress of the reactions and the purity after chromatographic separation were monitored by TLC on silica gel 60 plates. Chromatographic separations were carried out on columns with silica gel 60.

General Procedure for Preparation of Phosphonium Salts (8 d, 8e). Bromoacetophenone 1.48 g (7.43 mmol) was dissolved in 8 mL of dry acetonitrile, and 2.00 g (7.43 mmol) of thienyldiphenylphosphine was added. The mixture was stirred for 30 min, the precipitate was filtered, washed with acetonitrile (3 × 5 mL) and diethyl ether (5 mL), and dried at room temperature.

(2-Oxo-2-phenylethyl)(diphenyl)2-thienylphosphonium Bromide (8d.. Yield: 2.43 g (70%). Mp: 209−210 °C. ^{1}H NMR ($CDCl_3$), δ: 6.33 (d, 2H, J = 12.3 Hz); 7.36 (ddd, 1H, J = 4.8 Hz, J = 3.9 Hz, J = 2.2 Hz); 7.55−7.59 (m, 1H); 7.60−7.65 (m, 4H); 7.70−7.75 (m, 2H); 7.91−7.97 (m, 4H); 7.99 (ddd, 1H, J = 3.9 Hz, J = 1.1 Hz, J = 8.1 Hz); 8.07 (dt, 1H, J = 4.8 Hz, J = 1.1 Hz); 8.34−8.36 (m, 2H). ^{13}C NMR ($CDCl_3$), δ: 38.7 (d, CH_2, $^1J_{CP}$ = 64.9 Hz); 116.0 (d, arom., $^1J_{CP}$ = 105.1 Hz); 119.1 (d, arom., $^1J_{CP}$ = 92.8 Hz); 128.2 (s, arom.); 129.0 (s, arom.); 129.36 (d, arom., $^3J_{CP}$ = 18.2 Hz); 129.39 (d, arom., $^3J_{CP}$ = 13.6 Hz); 132.8 (d, arom., $^2J_{CP}$ = 11.4 Hz); 134.27 (s, arom.); 134.29 (d, arom., $^4J_{CP}$ = 3.0 Hz); 134.4 (d, arom., $^3J_{CP}$ = 5.9 Hz); 139.7 (d, arom., $^2J_{CP}$ = 4.7 Hz); 142.9 (d, arom., $^3J_{CP}$ = 11.0 Hz); 191.8 (d, C=O, $^2J_{CP}$ = 5.9 Hz). ^{31}P NMR ($CDCl_3$), δ: 16.54. IR, $\tilde{\nu}$/cm^{-1}: 1660 (C=O), 730−760, 1470 (Ar). Anal. Calcd for $C_{24}H_{20}BrOPS$: C, 61.68; H, 4.31. Found: 61.48; H, 4.49.

(2-Oxo-2-phenylethyl)(diphenyl)3-thienylphosphonium Bromide (8e). Yield: 2.78 g (80%). Mp: 188−190 °C. ^{1}H NMR ($CDCl_3$), δ: 6.06 (d, 2H, J = 13.0 Hz); 7.44−7.49 (m, 3H);

7.61−7.65 (m, 5H); 7.75−7.83 (m, 7H); 8.09 (d, 2H, J = 7.5 Hz); 8.32 (dd, 1H, J = 1.5 Hz, J = 8.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 36.1 (d, CH_2, $^1J_{CP}$ = 63.4 Hz); 116.3 (d, arom., $^1J_{CP}$ = 95.2 Hz); 118.4 (d, arom., $^1J_{CP}$ = 91.1 Hz); 127.6 (s, arom.); 128.11 (s, arom.); 128.7 (d, arom., $^3J_{CP}$ = 13.2 Hz); 129.2 (d, arom., $^2J_{CP}$ = 16.5 Hz); 129.3 (d, arom., $^2J_{CP}$ = 16.1 Hz); 132.2 (d, arom., $^2J_{CP}$ = 11.1 Hz); 133.5 (s, arom.); 133.5 (d, arom., $^4J_{CP}$ = 2.0 Hz); 134.1 (d, arom., $^3J_{CP}$ = 6.0 Hz); 140.2 (d, arom., $^3J_{CP}$ = 15.3 Hz); 190.9 (d, C=O, $^2J_{CP}$ = 5.4 Hz). ^{31}P NMR ($CDCl_3$), δ: 13.82. IR, $\tilde{\nu}$/cm^{-1}: 1660 (C=O), 730−760, 1470 (Ar). Anal. Calcd for $C_{24}H_{20}BrOPS$: C, 61.68; H, 4.31. Found: C, 61.52; H, 4.25.

General Procedure for Preparation of Phosphoranes (9 d, 9e). A solution of 240 mg of sodium methylate (44 mmol) in 2 mL of dry methanol was added gradually to a solution of 43 mmol phosphonium salt (**8**) in 10 mL of dry methanol, at 0−5 °C. The mixture was stirred for 1 h, then it was evaporated in vacuum and the residue was dissolved in 20 mL of methylene chloride. The precipitate of sodium bromide was separated from the solution of ylides (**9**) by filtration, washed on the filter with methylene chloride (3 × 10 mL.). The residue was evaporated in vacuum.

2-[Diphenyl(2-thienyl)phosphoranylidene]-1-phenylethanone (9d). Yield: 1.48 g (90%). Mp: 201 °C. ^{1}H NMR ($CDCl_3$), δ: 4.51 (d, 1H, J = 23.8 Hz); 7.15−7.18 (m, 1H); 7.36−7.37 (m, 3H); 7.46−7.51 (m, 5H); 7.56−7.59 (m, 2H); 7.71−7.76 (m, 5H); 7.98−8.00 (m, 1H). ^{13}C NMR ($CDCl_3$), δ: 51.6 (d, CH, $^1J_{CP}$ = 116.1 Hz); 126.9 (s, arom.); 127.5 (d, arom., $^1J_{CP}$ = 95.4 Hz); 127.70 (s, arom.); 127.73 (d, arom., $^1J_{CP}$ = 101.8 Hz); 127.8 (d, arom., $^3J_{CP}$ = 14.0 Hz); 128.8 (d, arom., $^3J_{CP}$ = 12.7 Hz); 129.4 (s, arom.); 132.2 (d, arom., $^4J_{CP}$ = 2.5 Hz); 132.7 (d, arom., $^2J_{CP}$ = 10.6 Hz); 134.6 (d, arom., $^2J_{CP}$ = 4.7 Hz); 138.2 (d, arom., $^3J_{CP}$ = 10.2 Hz); 140.7 (d, arom., $^3J_{CP}$ = 14.0 Hz); 185.1 (d, C=O, $^2J_{CP}$ = 2.1 Hz). ^{31}P NMR ($CDCl_3$), δ: 9.34. IR, $\tilde{\nu}$/cm^{-1}: 1590 (C=O), 730−760, 1470 (Ar). Anal. Calcd for $C_{24}H_{19}OPS$: C, 74.59; H, 4.96; S, 8.30. Found: C, 74.41; H, 5.10; S, 7.96.

2-[Diphenyl(3-thienyl)phosphoranylidene]-1-phenylethanone (9e). Yield: 1.40 g (85%). Mp: 173 °C. ^{1}H NMR ($CDCl_3$), δ: 4.35 (br.s, 1H); 7.25−7.27 (m, 3H); 7.31−7.33 (m, 1H); 7.36−7.40 (m, 5H); 7.45−7.49 (m, 2H); 7.59−7.64 (m, 4H); 7.79 (dd, 1H, J = 8.3 Hz, J = 1.7 Hz); 7.87−7.89 (m, 1H). ^{13}C NMR ($CDCl_3$), δ: 50.9 (d, CH, $^1J_{CP}$ = 114.0 Hz); 127.0 (s, arom.); 127.4 (d, arom., $^2J_{CP}$ = 14.9 Hz); 127.5 (d, arom., $^1J_{CP}$ = 92.8 Hz); 127.8 (s, arom.); 128.1 (d, arom., $^1J_{CP}$ = 109.2 Hz); 129.0 (d, arom., $^3J_{CP}$ = 12.5 Hz); 129.4 (s, arom.); 131.0 (d, arom., $^2J_{CP}$ = 15.2 Hz); 132.2 (d, arom., $^4J_{CP}$ = 2.4 Hz); 132.8 (d, arom., $^2J_{CP}$ = 10.8 Hz); 136.4 (d, arom., $^3J_{CP}$ = 14.4 Hz); 141.2 (d, arom., $^3J_{CP}$ = 14.5 Hz); 185.1 (d, C=O, $^2J_{CP}$ = 3.2 Hz). ^{31}P NMR ($CDCl_3$), δ: 8.35. IR, $\tilde{\nu}$/cm^{-1}: 1590 (C=O), 730−760, 1470 (Ar). Anal. Calcd for $C_{24}H_{19}OPS$: C, 74.59; H, 4.96. Found: C, 74.63; H, 4.90.

General Procedure for Preparation of Phosphonium−Iodonium Ylides (1d, 1e). A solution of 3 mmol of diacetoxyiodobenzene in 8 mL of methanol was added to the solution of 3 mmol ylides (**9**) in 5 mL of methanol at 0−5 °C, then 3 mmol of a solution of HBF_4 (40%) was added at 0−5 °C. The mixture was stirred for 1 h, then 10 mL of diethyl ether was added and stirred for 1 h. The precipitate was filtered and washed with diethyl ether.

1-[Diphenyl(2-thienyl)phosphonio]-2-oxo-2-phenyl-1-(phenyliodonio)ethanide Tetrafluoroborate (1d). Yield: 1.40 g (80%). Mp: 157 °C. ^{1}H NMR (CD_3CN), δ: 7.24 (d, 2H, J = 7.6 Hz); 7.34−7.41 (m, 3H); 7.49−7.61 (m, 15H); 7.76−7.77 (m, 2H); 8.09−8.11 (m, 3H). ^{13}C NMR (CD_3CN), δ: 124.0 (s, arom.); 124.4 (d, arom., $^1J_{CP}$ = 109.0 Hz); 125.0 (d, arom., $^1J_{CP}$ = 97.3 Hz); 128.8 (s, arom.); 129.9 (s, arom.); 130.6 (d, arom., $^3J_{CP}$ = 15.4) Hz; 131.0 (d, arom., $^3J_{CP}$ = 13.9 Hz); 132.0 (s, arom.); 133.1 (s, arom.); 133.6 (s, arom.); 134.0 (s, arom.); 134.7 (d, arom., $^2J_{CP}$ = 10.3 Hz); 135.5 (s, arom.); 139.6 (d, arom., $^2J_{CP}$ = 4.4 Hz); 140.7 (d, arom., $^3J_{CP}$ = 7.3 Hz); 141.9 (d, arom., $^3J_{CP}$ = 11.0 Hz); 193.3 (d, C=O, $^2J_{CP}$ = 5.9 Hz). ^{31}P NMR (CD_3CN), δ: 20.07. IR, $\tilde{\nu}$/cm^{-1}: 1600 (C=O), 1150 (BF_4^-), 730−760, 1470 (Ar). Anal. Calcd for $C_{30}H_{23}BF_4IOPS$: C, 53.28; H, 3.43; S, 4.74. Found: C, 53.28; H, 3.60; S, 4.57.

1-[Diphenyl(3-thienyl)phosphonio]-2-oxo-2-phenyl-1-(phenyliodonio)ethanide Tetrafluoroborate (1e). Yield: 1.49 g (85%). Mp: 145 °C. ^{1}H NMR (CD_3CN), δ: 7.23−7.25 (m, 2H); 7.28−7.30 (m, 1H); 7.38−7.42 (m, 2H); 7.48−7.53 (m, 3H); 7.60−7.65 (m, 11H); 7.75−7.76 (m, 3H); 7.97 (d, 1H, J = 7.3 Hz). ^{13}C NMR (CD_3CN), δ: 121.9 (s, arom.); 124.3 (d, arom., $^1J_{CP}$ = 99.5 Hz); 124.9 (d, arom., $^1J_{CP}$ = 95.9 Hz); 128.8 (s, arom.); 128.9 (s, arom.); 130.9 (d, arom., $^3J_{CP}$ = 13.2 Hz); 131.2 (d, arom., $^2J_{CP}$ = 6.1 Hz); 131.8 (s, arom.); 132.0 (d, arom., $^2J_{CP}$ = 5.3 Hz); 133.1 (s, arom.); 133.5 (s, arom.); 133.8 (s, arom.); 134.6 (d, arom., $^2J_{CP}$ = 11.0 Hz); 135.3 (s, arom.); 140.8 (d, arom., $^3J_{CP}$ = 7.3 Hz); 141.5 (d, arom., $^3J_{CP}$ = 14.6 Hz); 193.1 (d, C=O, $^2J_{CP}$ = 4.4 Hz). ^{31}P NMR (CD_3CN), δ: 18.55. IR, $\tilde{\nu}$/cm^{-1}: 1600 (C=O), 1150 (BF_4^-), 730−760, 1470 (Ar). Anal. Calcd for $C_{30}H_{23}BF_4IOPS$: C, 53.28; H, 3.43. Found: C, 53.61; H, 3.53.

General Procedure for the Reaction of Ylide (1b)[5a,b] with Alkynes. The alkyne was added to a solution of ylide (**1b**) (0.3 mmol) in anhydrous methylene chloride. The mixture was irradiated in a quartz flask with a mercury lamp (366 nm) source under 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. To elute the residual alkynes and PhI, benzene was used; the corresponding phosphinoline was eluted by using a CH_2Cl_2/MeOH mixture in a ratio of 200:1, and the furans were eluted by using a CH_2Cl_2/MeOH mixture in a ratio of 100:1.

[1,1-Diphenyl-4-(3-thienyl)-1λ^5-phosphinolin-2-yl](phenyl)methanone (14). Yield: 88 mg (60%), red oil. ^{1}H NMR (CD_2Cl_2), δ: 7.00 (dd, 1H, J = 5.0 Hz, J = 1.3 Hz); 7.05 (dd, 1H, J = 2.9 Hz, J = 1.5 Hz); 7.09 (d, 1H, J = 31.8 Hz); 7.22 (dd, 1H, J = 5.0 Hz, J = 3.1 Hz); 7.28−7.32 (m, 5H); 7.34−7.44 (m, 6H); 7.46−7.48 (m, 2H.); 7.50−7.53 (m, 2H); 7.72−7.78 (m, 4H). ^{13}C NMR (CD_2Cl_2), δ: 75.5 (d, C1, $^1J_{CP}$ = 100.8 Hz); 112.4 (d, arom., $^1J_{CP}$ = 94.0 Hz); 112.8 (d, CH=C, $^3J_{CP}$ = 9.6 Hz); 123.3 (s, arom.); 125.6 (d, arom., $^3J_{CP}$ = 11.7 Hz); 126.4 (s, arom.); 126.9 (d, arom., $^2J_{CP}$ = 7.6 Hz); 128.7 (d, arom., $^1J_{CP}$ = 93.6 Hz); 129.5 (s, arom.); 130.2 (d, arom., $^3J_{CP}$ = 13.2 Hz); 130.2 (s, arom.); 131.1 (s, arom.); 131.3 (s, arom.), 133.2 (d, arom., $^4J_{CP}$ = 2.0 Hz); 133.4 (d, arom., $^4J_{CP}$ = 3.3 Hz); 134.9 (d, CH, $^2J_{CP}$ = 6.8 Hz); 134.9 (d, arom., $^2J_{CP}$ = 11.3 Hz); 135.03 (d, arom., $^3J_{CP}$ = 8.4 Hz); 142.20 (d, arom., $^3J_{CP}$ = 9.7 Hz); 143.13 (d, arom., $^2J_{CP}$ = 4.8 Hz); 144.8 (s, arom.); 191.0 (d, CO, $^2J_{CP}$ = 5.6 Hz). ^{31}P NMR (CD_2Cl_2), δ: 4.89. IR, $\tilde{\nu}$/cm^{-1}: 1580 (C=O), 1520 (C=C), 720−750, 1470 (Ar). MS, m/z: 486 $[M]^+$, 409 $[M - C_6H_5]^+$, 381 $[M - PhCO]^+$, 183 $[Ph_2P - 2H]^+$. HRMS calcd for $C_{32}H_{23}OPS$ (M^+) m/z 486.1207, found 486.1202.

[4-(6-Methoxy-2-naphthyl)-1,1-diphenyl-1λ^5-phosphinolin-2-yl](phenyl)methanone (16). Yield: 16 mg (10%), red oil. ^{1}H NMR (CD_2Cl_2), δ: 3.92 (s, 3H); 7.13 (dd, 2H., J = 8.7 Hz, J = 2.5 Hz); 7.18 (d, 1H, J = 2.3 Hz); 7.22 (d, 1H, J = 31.6 Hz); 7.34−7.47 (m, 7H); 7.52−7.62 (m, 6H); 7.64−7.67 (m, 2H); 7.70−7.74 (m, 3H); 7.87−7.93 (m, 4H). ^{13}C NMR (CD_2Cl_2), δ: 55.9 (s, OCH_3); 74.6 (d, C1, $^1J_{CP}$ = 100.8 Hz); 106.3 (s, arom.); 111.5 (d, arom., $^1J_{CP}$ = 85.9 Hz); 117.4 (d, CH=C, $^3J_{CP}$ = 10.0 Hz); 119.2 (s, arom.); 124.6 (d, arom., $^3J_{CP}$ = 11.7 Hz); 126.2 (d, arom., $^2J_{CP}$ = 7.6 Hz); 127.0 (s, arom.); 127.8 (d, arom., $^1J_{CP}$ = 93.6 Hz); 128.4 (s, arom.); 128.5 (s, arom.); 129.2 (d, arom., $^3J_{CP}$ = 12.9 Hz); 129.3 (s, arom.); 129.7 (s, arom.); 129.9 (s, arom.); 130.0 (s, arom.); 132.1 (d, arom., $^4J_{CP}$ = 1.6 Hz); 132.4 (d, arom., $^4J_{CP}$ = 3.2 Hz); 133.8 (s, arom.); 133.95 (d, arom., $^2J_{CP}$ = 11.2 Hz); 134.04 (d, arom., $^3J_{CP}$ = 7.6 Hz); 134.1 (d, CH, $^2J_{CP}$ = 7.6 Hz); 138.7 (s, arom.); 141.2 (d, arom., $^3J_{CP}$ = 10.0 Hz); 142.3 (d, arom., $^2J_{CP}$ = 4.8 Hz); 158.1 (s, arom.); 190.0 (d, CO, $^2J_{CP}$ = 6.0 Hz). ^{31}P NMR (CD_2Cl_2), δ: 5.01. IR, $\tilde{\nu}$/cm^{-1}: 1580 (C=O), 1520 (C=C),

730−750, 1460 (Ar). MS, *m/z*: 560 $[M]^+$, 545 $[M - Me]^+$, 183 $[Ph_2P - 2H]^+$, 105 $[PhC(O)]^+$, 77 $[Ph]^+$. HRMS calcd for $C_{39}H_{29}O_2P$ (M^+) *m/z* 560.1905, found 560.1900.

[4-(9-Phenanthryl)-1,1-diphenyl-1λ^5-phosphinolin-2-yl](phenyl)methanone (17). Yield: 8 mg (5%), red oil. ^{1}H NMR (CD_2Cl_2), δ: 6.84 (dd, 1H, *J* = 8.1 Hz, *J* = 5.3 Hz); 7.05−7.10 (m, 1H); 7.16−7.20 (m, 1H); 7.26 (d, 1H, *J* = 31.9 Hz); 7.28−7.30 (m, 2H); 7.44−7.50 (m, 2H); 7.57−7.68 (m, 12H); 7.76 (s, 1H); 7.80 (dd, 1H, *J* = 8.3 Hz, *J* = 1.0 Hz); 7.89 (dd, 1H, *J* = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz); 7.93−8.00 (m, 4H); 8.74 (dd, 2H, *J* = 8.1 Hz, *J* = 10.4 Hz). ^{13}C NMR (CD_2Cl_2), δ: 74.6 (d, C1, $^1J_{CP}$ = 100.3 Hz); 111.1 (d, arom., $^1J_{CP}$ = 84.8 Hz); 114.8 (d, CH═C, $^3J_{CP}$ = 10.4 Hz); 123.1 (s, arom.); 123.4 (s, arom.); 124.5 (d, arom., $^3J_{CP}$ = 11.6 Hz); 126.7 (d, arom., $^2J_{CP}$ = 7.6 Hz); 126.92 (s, arom.); 126.94 (s, arom.); 127.0 (s, arom.); 127.3 (s, arom.); 127.6 (d, arom., $^1J_{CP}$ = 94.8 Hz); 127.9 (s, arom.); 128.0 (d, arom., $^1J_{CP}$ = 93.6 Hz); 129.5 (s, arom.); 128.4 (s, arom.); 129.1 (d, arom., $^3J_{CP}$ = 12.5 Hz); 129.2 (s, arom.); 129.25 (s, arom.); 129.29 (s, arom.); 129.31 (d, arom., $^3J_{CP}$ = 12.5 Hz); 131.2 (s, arom.); 132.1 (d, arom., $^4J_{CP}$ = 1.6 Hz); 132.4 (d, arom., $^4J_{CP}$ = 3.3 Hz); 132.5 (d, arom., $^4J_{CP}$ = 2.8 Hz); 132.9 (s, arom.); 133.4 (s, arom.); 133.9 (s, CH, $^2J_{CP}$ = 7.2 Hz); 133.98 (d, arom., $^2J_{CP}$ = 10.9 Hz); 134.02 (d, arom., $^2J_{CP}$ = 10.9 Hz); 134.3 (d, arom., $^3J_{CP}$ = 7.6 Hz); 139.6 (s, arom.); 141.1 (d, arom., $^3J_{CP}$ = 10.0 Hz); 142.9 (d, arom., $^2J_{CP}$ = 4.8 Hz); 190.0 (s, CO). ^{31}P NMR (CD_2Cl_2), δ: 5.42. IR, $\tilde{\nu}$/cm^{-1}: 1580 (C═O), 1510 (C═C), 720−750, 1460 (Ar). MS, *m/z*: 580 $[M]^+$, 490 $[M - PhC(O) + H]^+$, 183 $[Ph_2P - 2H]^+$, 105 $[PhC(O)]^+$, 77 $[Ph]^+$. HRMS calcd for $C_{42}H_{29}OP$ (M^+) m/z 580.1956, found 580.1951.

Triphenyl[2-phenyl-5-(3-thienyl)-3-furyl]phosphonium Tetrafluoroborate (18). Yield: 12 mg (7%), colorless oil. ^{1}H NMR ($CDCl_3$), δ: 6.60 (d, 1H, *J* = 3.8 Hz); 7.08 (t, 2H, arom., *J* = 7.4 Hz); 7.18 (d, 2H, *J* = 7.2 Hz); 7.23 (t, 1H, *J* = 7.4 Hz); 7.40 (d, 2H, *J* = 2.1 Hz); 7.67−7.75 (m, 13H); 7.78−7.83 (m, 3H). ^{13}C NMR ($CDCl_3$), δ: 98.4 (d, Ph_3P^+C, $^1J_{CP}$ = 109.8 Hz); 109.2 (d, CH, $^2J_{CP}$ = 11.9 Hz); 117.6 (d, arom., $^1J_{CP}$ = 92.8 Hz); 122.7 (s, arom.); 124.8 (s, arom.); 127.4 (s, arom.); 128.1 (s, arom.); 128.5 (s, arom.); 129.5 (s, arom.); 130.5 (s, arom.); 130.7 (s, arom., $^3J_{CP}$ = 13.6 Hz); 134.1 (d, arom., $^2J_{CP}$ = 11.1 Hz); 135.6 (d, arom., $^4J_{CP}$ = 3.0 Hz); 153.4 (d, C-The, $^3J_{CP}$ = 14.9 Hz); 161.3 (d, Ph-C-O, $^2J_{CP}$ = 17.0 Hz). ^{31}P NMR ($CDCl_3$), δ: 14.20. IR, $\tilde{\nu}$/cm^{-1}: 1120 (BF_4^-), 730−760, 1470 (Ar). MS, *m/z*: 486 $[M - BF_4 - 1]^+$, 410 $[M - BF_4 - C_6H_5]^+$. HRMS calcd for $C_{32}H_{24}OPS$ (M^+) m/z 487.1280, found 487.1280.

[5-(6-Methoxy-2-naphthyl)-2-phenyl-3-furyl](triphenyl)phosphonium Tetrafluoroborate (20). Yield: 116 mg (60%), colorless oil. ^{1}H NMR ($CDCl_3$), δ: 3.93 (s, 3H); 6.76 (d, 1H, *J* = 3.9 Hz); 7.09−7.14 (m, 3H); 7.16 (dd, 1H, *J* = 8.9 Hz, *J* = 2.5 Hz); 7.23 (s, 1H); 7.24 (d, 2H, *J* = 8.1 Hz); 7.68−7.78 (m, 14H); 7.79−7.84 (m, 4H); 8.19 (s, 1H). ^{13}C NMR ($CDCl_3$), δ: 55.4 (s, OCH_3); 98.6 (d, Ph_3P^+C, $^1J_{CP}$ = 109.4 Hz); 106.0 (s, arom.); 109.1 (d, CH, $^2J_{CP}$ = 11.9 Hz); 117.6 (d, arom., $^1J_{CP}$ = 92.4 Hz); 119.8 (s, arom.); 122.6 (s, arom.); 123.1 (s, arom.); 123.9 (s, arom.); 127.5 (s, arom.); 127.8 (s, arom.); 128.1 (s, arom.); 128.57 (s, arom.); 128.64 (s, arom.); 130.1 (s, arom.); 130.5 (s, arom.); 130.7 (d, arom., $^3J_{CP}$ = 13.1 Hz); 134.1 (d, arom., $^2J_{CP}$ = 10.6 Hz); 135.0 (s, arom.); 135.7 (d, arom., $^4J_{CP}$ = 3.0 Hz); 156.9 (d, C-Naph, $^3J_{CP}$ = 14.4 Hz); 158.7 (s, arom.); 161.7 (d, Ph-C-O, $^2J_{CP}$ = 17.4 Hz). ^{31}P NMR ($CDCl_3$), δ: 14.25. IR, $\tilde{\nu}$/cm^{-1}: 1070 (BF_4^-), 730−760, 1470 (Ar). MS, *m/z*: 561 $[M - BF_4]^+$, 484 $[M - BF_4 - C_6H_5]^+$. HRMS calcd for $C_{39}H_{30}O_2P$ (M^+) m/z 561.1978, found 561.1978.

[5-(9-Phenanthryl)-2-phenyl-3-furyl](triphenyl)phosphonium Tetrafluoroborate (21). Yield: 160 mg (80%), colorless oil. ^{1}H NMR (CD_2Cl_2), δ: 6.82 (d, 1H, *J* = 3.7 Hz); 7.16 (t, 2H, *J* = 8.1 Hz); 7.29−7.34 (m, 2H); 7.66−7.91 (m, 20H); 8.02 (dd, 1H, *J* = 7.8 Hz, *J* = 1.3 Hz); 8.17 (s, 1H); 8.33 (dd, 1H, *J* = 7.9 Hz, *J* = 1.4 Hz); 8.73 (d, 1H, *J* = 8.1 Hz); 8.82 (dd, 1H, *J* = 8.1 Hz, *J* = 1.4 Hz). ^{13}C NMR (CD_2Cl_2), δ: 98.8 (d, Ph_3P^+C, $^1J_{CP}$ = 109.6 Hz); 114.6 (d, CH, $^2J_{CP}$ = 11.7 Hz); 118.2 (d, arom., $^1J_{CP}$ = 92.8 Hz); 123.2 (s, arom.); 123.9 (s, arom.); 124.9 (s, arom.); 125.9 (s, arom.); 127.8 (s, arom.); 127.95 (s, arom.); 128.01 (s, arom.); 128.8 (s, arom.); 129.2 (s, arom.); 129.3 (s, arom.); 129.8 (s, arom.); 130.0 (s, arom.); 131.2 (s, arom., $^3J_{CP}$ = 13.3 Hz); 131.30 (s, arom.); 131.32 (s, arom.); 131.4 (s, arom.); 134.7 (d, arom., $^2J_{CP}$ = 10.8 Hz); 136.3 (d, arom., $^4J_{CP}$ = 2.8 Hz); 156.8 (d, C-Phntr, $^3J_{CP}$ = 13.4 Hz); 163.4 (d, Ph-C-O, $^2J_{CP}$ = 16.9 Hz). ^{31}P NMR (CD_2Cl_2), δ: 16.32. IR, $\tilde{\nu}$/cm^{-1}: 1070 (BF_4^-), 730−760, 1470 (Ar). MS, *m/z*: 581 $[M - BF_4]^+$, 504 $[M - BF_4 - C_6H_5]^+$. HRMS calcd for $C_{42}H_{30}OP$ (M^+) m/z 581.2029, found 581.2029.

General Procedure for the Reaction of Ylides (1e, 1d) with Phenylacetylene. The ylides (0.3 mmol) were added gradually to a solution of phenylacetylene in anhydrous dichloromethane. The reactions were irradiated in a quartz flask with a mercury lamp (366 nm) source under argon atmosphere. The progress of the reaction was monitored by TLC. After the end of the reaction, the mixtures were concentrated in vacuo. The residue was dissolved in a minimum of CH_2Cl_2 and chromatographed on silica gel. To elute phenylacetylene and PhI, benzene was used; the corresponding phosphininothiophene was eluted by using a CH_2Cl_2/MeOH mixture in a ratio of 200:1.

Phenyl(4,7,7-triphenyl-7λ^5-phosphinino[2,3-*b*]thiophen-6-yl)methanone (22). Yield: 44 mg (30%), red oil. ^{1}H NMR (CD_2Cl_2), δ: 7.04 (dd, 1H, *J* = 5.3 Hz, *J* = 3.6 Hz); 7.10 (dd, 1H, *J* = 5.3 Hz, *J* = 2.8 Hz); 7.17 (d, 1H, *J* = 34.0 Hz); 7.24−7.28 (m, 1H); 7.34−7.38 (m, 2H); 7.40−7.43 (m, 3H); 7.50−7.60 (m, 8H); 7.62−7.64 (m, 2H); 7.82−7.87 (m, 4H). ^{13}C NMR (CD_2Cl_2), δ: 78.5 (d, C1, $^1J_{CP}$ = 103.4 Hz); 107.0 (d, arom., $^1J_{CP}$ = 90.8 Hz); 113.5 (d, CH═C, $^3J_{CP}$ = 8.1 Hz); 122.1 (d, α-Thio-arom., $^3J_{CP}$ = 16.5 Hz); 127.1 (s, arom.); 128.1 (d, arom., $^1J_{CP}$ = 98.8 Hz); 128.6 (s, arom.); 128.8 (s, arom.); 129.05 (s, arom.); 129.06 (d, arom., $^3J_{CP}$ = 13.3 Hz); 129.09 (s, arom.); 129.2 (d, β-Thio-arom., $^3J_{CP}$ = 11.1 Hz); 130.2 (s, arom.); 132.2 (d, CH, $^2J_{CP}$ = 7.6 Hz); 132.3 (d, arom., $^4J_{CP}$ = 3.2 Hz); 133.6 (d, arom., $^2J_{CP}$ = 11.2 Hz); 141.2 (d, arom., $^3J_{CP}$ = 9.3 Hz); 142.8 (s, arom.); 154.2 (d, arom., $^2J_{CP}$ = 8.0 Hz); 191.5 (d, CO, $^2J_{CP}$ = 5.6 Hz) ^{31}P NMR (CD_2Cl_2), δ: 1.97. MS, *m/z*: 486 $[M]^+$, 409 $[M - C_6H_5]^+$, 381 $[M - PhCO]^+$, 183 $[Ph_2P - 2H]^+$. HRMS calcd for $C_{32}H_{23}OPS$ (M^+) *m/z* 486.1207, found 486.1202.

Phenyl(4,4,7-triphenyl-4λ^5-phosphinino[3,2-*b*]thiophen-5-yl)methanone (23) and Phenyl(1,1,4-triphenyl-1λ^5-phosphinino[2,3-*c*]-thiophen-2-yl)methanone (24). Yield: 36 mg (25%), red oil. ^{1}H NMR (CD_2Cl_2), δ: 7.03 (dd, 1H, arom., $^3J_{HH}$ = 5.3 Hz, $^3J_{HP}$ = 3.6 Hz); 7.10 (dd, 1H, arom., $^3J_{HH}$ = 5.3 Hz, $^4J_{HP}$ = 2.7 Hz); 7.15 (d, 1H, CH, $^3J_{PH}$ = 33.9 Hz); 7.17 (d, 1H, CH, $^3J_{PH}$ = 34.7 Hz); 7.22 (dd, 1H, arom., $^4J_{HH}$ = 5.1 Hz, $^3J_{HP}$ = 4.3 Hz); 7.23−7.26 (m, 2H, arom.); 7.33−7.41 (m, 12H, arom.); 7.50−7.54 (m, 10H, arom.); 7.56−7.59 (m, 4H, arom); 7.60−7.64 (m, 4H, arom); 7.68 (dd, 1H, arom., $^4J_{HH}$ = 5.1, $^4J_{HP}$ = 2.7); 7.81−7.86 (m, 8H, arom.). ^{13}C NMR (CD_2Cl_2), δ: 75.5 (d, C1, $^1J_{CP}$ = 103.9 Hz); 78.5 (d, C1, $^1J_{CP}$ = 103.1 Hz); 115.6 (d, CH═C, $^3J_{CP}$ = 7.5 Hz); 122.1 (d, Thio-arom., $^3J_{CP}$ = 16.6 Hz); 126.4 (s, arom.); 126.95 (d, Thio-arom., $^2J_{CP}$ = 9.7 Hz); 127.03 (s, arom.); 127.5 (d, arom., $^1J_{CP}$ = 99.5 Hz); 128.0 (d, arom., $^1J_{CP}$ = 95.6 Hz); 128.6 (s, arom.); 128.8 (s, arom.); 128.9 (d, arom., $^3J_{CP}$ = 13.8 Hz); 128.97 (s, arom.); 129.04 (d, arom., $^3J_{CP}$ = 13.3 Hz); 129.06 (s, arom.); 129.14 (d, Thio-arom., $^2J_{CP}$ = 10.8 Hz); 129.3 (s, arom.); 130.1 (s, arom.); 130.2 (s, arom.); 132.2 (d, CH, $^2J_{CP}$ = 7.7 Hz); 132.26 (d, arom., $^4J_{CP}$ = 3.0 Hz); 132.32 (d, arom., $^4J_{CP}$ = 3.3 Hz); 133.60 (d, arom., $^2J_{CP}$ = 11.3 Hz); 133.61 (d, arom., $^2J_{CP}$ = 11.9 Hz); 133.8 (d, CH, $^2J_{CP}$ = 6.6 Hz); 141.0 (d, arom., $^3J_{CP}$ = 9.4 Hz); 141.1 (d, arom., $^3J_{CP}$ = 9.1 Hz); 143.2 (d, arom., $^4J_{CP}$ = 1.4 Hz); 142.8 (d, arom., $^4J_{CP}$ = 1.1 Hz); 150.7 (d, arom., $^2J_{CP}$ = 5.5 Hz); 191.6 (s, CO); 192.9 (s, CO). ^{31}P NMR (CD_2Cl_2), δ: −0.08 (**23**), 0.42 (**24**). MS, *m/z*: 486 $[M]^+$, 409 $[M - C_6H_5]^+$, 381 $[M - PhCO]^+$, 183 $[Ph_2P - 2H]^+$. HRMS calcd for $C_{32}H_{23}OPS$ (M^+) m/z 486.1207, found 486.1202.

General Procedure for the Reaction of Ylide 1c with Alkynes. The alkyne was added to a solution of the ylide **1c** (0.3 mmol) in

anhydrous methylene chloride. The solution was irradiated in a quartz flask with a mercury lamp (366 nm) under argon atmosphere. The course of the reaction was monitored by TLC. After the end of the reaction, the solvent was removed in vacuum. The residue was resolved 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 CH_2Cl_2/MeOH mixture in a ratio of 200:1.

1,1,4-Triphenyl-1λ^5-phosphinoline-2-carbonitrile (27). Yield: 42 mg (35%), yellow oil. This oil was dissolved in a minimum of CH_2Cl_2 and subsequent addition of diethyl ether to this solution resulted in crystallization of phosphinoline **27** as red crystal, mp 263−264 °C. ^{1}H NMR ($CDCl_3$), δ: 6.85 (d, 1H, J = 26.0 Hz); 7.02−7.08 (m, 1H); 7.15−7.21 (m, 1H); 7.23−7.38 (m, 7H); 7.43−7.55 (m, 6H); 7.56−7.65 (m, 4H). ^{13}C NMR ($CDCl_3$), δ: 31.9 (d, C1, $^1J_{CP}$ = 119.1 Hz); 104.8 (d, arom., $^1J_{CP}$ = 93.4 Hz); 116.9 (d, CN, $^2J_{CP}$ = 9.4 Hz); 123.9 (d, arom., $^3J_{CP}$ = 12.7 Hz); 124.3 (d, CHCPh,, $^3J_{CP}$ = 12.2 Hz); 125.7 (d, arom., $^3J_{CP}$ = 8.3 Hz); 126.1 (s, arom.); 127.5 (d, arom., $^1J_{CP}$ = 89.6 Hz); 128.5 (s, arom.); 129.3 (d, arom., $^3J_{CP}$ = 12.7 Hz); 130.0 (s, arom.); 131.7 (d, arom., $^2J_{CP}$ = 5.3 Hz); 131.8 (d, arom., $^4J_{CP}$ = 1.7 Hz); 132.8 (d, arom., $^4J_{CP}$ = 3.1 Hz); 132.9 (d, arom., $^2J_{CP}$ = 10.7 Hz); 133.3 (d, CH, $^2J_{CP}$ = 4.2 Hz); 140.8 (d, arom., $^2J_{CP}$ = 5.5 Hz); 141.9 (d, arom., $^4J_{CP}$ = 1.1 Hz) ^{31}P NMR ($CDCl_3$), δ: 9.39. IR, $\tilde{\nu}$/cm^{-1}: 2170 (CN), 1560 (C=C), 720−750, 1470 (Ar). MS, m/z: 401 $[M]^+$, 324 $[M - C_6H_5]^+$, 183 $[Ph_2P - 2H]^+$. HRMS calcd for $C_{28}H_{20}NP$ (M^+) m/z 401.1333, found 401.1328.

1,1-Diphenyl-4-(3-thienyl)-1λ^5-phosphinoline-2-carbonitrile (28). Yield: 48 mg (40%), yellow oil. ^{1}H NMR ($CDCl_3$), δ: 6.93 (d, 1H, J = 26.1 Hz); 7.01 (dd, 1H, J = 5.0 Hz, J = 1.1 Hz); 7.03−7.08 (m, 2H); 7.25 (dd, 1H, J = 5.0 Hz, J = 3.0 Hz); 7.30−7.38 (m, 2H); 7.41−7.50 (m, 5H); 7.52−7.55 (m, 2H); 7.58−7.63 (m, 4H). ^{13}C NMR ($CDCl_3$), δ: 32.0 (d, C1, $^1J_{CP}$ = 118.4 Hz); 104.8 (d, arom., $^1J_{CP}$ = 92.7 Hz); 111.2 (d, CN, $^2J_{CP}$ = 9.2 Hz); 121.8 (s, arom.); 123.9 (d, arom., $^3J_{CP}$ = 12.9 Hz); 124.1 (d, CH=C, $^3J_{CP}$ = 11.7 Hz); 124.9 (s, arom.); 125.6 (d, arom., $^3J_{CP}$ = 9.5 Hz); 127.6 (d, arom., $^1J_{CP}$ = 90.0 Hz); 129.4 (d, arom., $^3J_{CP}$ = 12.8 Hz); 129.7 (s, arom.); 131.8 (d, arom., $^2J_{CP}$ = 8.8 Hz); 131.9 (d, arom., $^4J_{CP}$ = 1.6 Hz); 132.8 (d, arom., $^4J_{CP}$ = 3.2 Hz); 132.9 (d, arom., $^2J_{CP}$ = 10.5 Hz); 133.5 (d, CH, $^2J_{CP}$ = 4.0 Hz); 141.0 (d, arom., $^2J_{CP}$ = 4.8 Hz); 142.4 (s, arom.). ^{31}P NMR ($CDCl_3$), δ: 9.49. IR, $\tilde{\nu}$/cm^{-1}: 2180 (CN), 1570 (C=C), 720−750, 1460 (Ar). MS, m/z: 407 $[M]^+$, 330 $[M - C_6H_5]^+$, 183 $[Ph_2P - 2H]^+$. HRMS calcd for $C_{26}H_{18}NPS$ (M^+) m/z 407.0898, found 407.0892.

4-(4-Methoxyphenyl)-1,1-diphenyl-1λ^5-phosphinoline-2-carbonitrile (29). Yield: 52 mg (40%), yellow oil. ^{1}H NMR (CD_2Cl_2), δ: 3.74 (s, 3H); 6.76 (d, 1H, J = 26.0 Hz); 6.83 (dd, 2H, J = 8.8 Hz, J = 2.2 Hz); 7.03−7.07 (m, 1H); 7.33−7.39 (m, 1H); 7.15 (dd, 2H, J = 8.8 Hz, J = 2.2 Hz); 7.28−7.30 (m, 2H); 7.48−7.52 (m, 4H); 7.54−7.63 (m, 6H). ^{13}C NMR (CD_2Cl_2), δ: 32.0 (d, C1, $^1J_{CP}$ = 117.7 Hz); 56.8 (s, OCH_3); 106.3 (d, arom., $^1J_{CP}$ = 93.2 Hz); 115.4 (s, arom.); 117.7 (d, CN, $^2J_{CP}$ = 9.6 Hz); 125.4 (d, arom., $^3J_{CP}$ = 12.9 Hz); 125.6 (d, CH=C, $^3J_{CP}$ = 12.1 Hz); 127.1 (d, arom., $^3J_{CP}$ = 8.4 Hz); 129.3 (d, arom., $^1J_{CP}$ = 90.4 Hz); 130.9 (d, arom., $^3J_{CP}$ = 12.9 Hz); 132.6 (s, arom.); 133.3 (d, arom., $^4J_{CP}$ = 1.6 Hz); 133.4 (d, arom., $^2J_{CP}$ = 8.8 Hz); 134.3 (d, arom., $^2J_{CP}$ = 10.8 Hz); 134.38 (d, CH, $^2J_{CP}$ = 5.4 Hz); 134.39 (d, arom., $^4J_{CP}$ = 3.2 Hz); 136.0 (s, arom.); 142.7 (d, arom., $^2J_{CP}$ = 5.7 Hz); 159.8 (s, arom.). ^{31}P NMR (CD_2Cl_2), δ: 11.49. IR, $\tilde{\nu}$/cm^{-1}: 2175 (CN), 1570 (C=C), 720−750, 1460 (Ar). MS, m/z: 431 $[M]^+$, 416 $[M - CH_3]^+$, 354 $[M - C_6H_5]^+$, 183 $[Ph_2P - 2H]^+$. HRMS calcd for $C_{29}H_{22}NOP$ (M^+) m/z 431.1439, found 431.1434.

4-Hex-5-yn-1-yl-1,1-diphenyl-1λ^5-phosphinoline-2-carbonitrile (30). Yield: 24 mg (20%), yellow oil. ^{1}H NMR ($CDCl_3$), δ: 1.45−1.53 (m, 2H); 1.55−1.62 (m, 2H); 1.85 (t, 1H, J = 2.8 Hz); 2.12 (dt, 2H, J = 6.9 Hz, J = 2.8 Hz); 2.47 (t, 2H, J = 7.6 Hz); 6.69 (d, 1H, J = 26.0 Hz); 7.03−7.07 (m, 1H); 7.30−7.35 (m, 1H); 7.40−7.47 (m, 6H); 7.49−7.50 (m, 1H); 7.51−7.57 (m, 5H). ^{13}C NMR ($CDCl_3$), δ: 18.4, 28.3, 28.8, 33.4 (all s, CH_2); 29.9 (d, C1, $^1J_{CP}$ = 119.2 Hz); 68.4 (s, C≡CH); 84.6 (s, C≡CH); 105.6 (d, arom., $^1J_{CP}$ = 93.1 Hz); 112.3 (d, CN, $^2J_{CP}$ = 9.3 Hz); 123.4 (d, arom., $^3J_{CP}$ = 12.8 Hz); 123.6 (d, arom., $^3J_{CP}$ = 8.9 Hz); 124.8 (d, CH=C, $^3J_{CP}$ = 11.6 Hz); 127.9 (d, arom., $^1J_{CP}$ = 89.2 Hz); 129.2 (d, arom., $^3J_{CP}$ = 12.5 Hz); 130.9 (d, CH, $^2J_{CP}$ = 4.0 Hz); 131.9 (d, arom., $^4J_{CP}$ = 2.0 Hz); 132.0 (d, arom., $^2J_{CP}$ = 8.8 Hz); 132.6 (d, arom., $^4J_{CP}$ = 3.3 Hz); 132.8 (d, arom., $^2J_{CP}$ = 10.4 Hz); 140.7 (d, arom., $^2J_{CP}$ = 5.6 Hz). ^{31}P NMR ($CDCl_3$), δ: 10.31. IR, $\tilde{\nu}$/cm^{-1}: 2170 (CN), 1580 (C=C), 730−750, 1470 (Ar), 3260 (≡C−H). MS, m/z: 405 $[M]^+$, 338 $[M - (CH_2)_3C{\equiv}CH]^+$, 183 $[Ph_2P - 2H]^+$. HRMS calcd for $C_{28}H_{24}NP$ (M^+) m/z 405.1646, found 405.1641.

4-Octyl-1,1-diphenyl-1λ^5-phosphinoline-2-carbonitrile (31). Yield: 20 mg (15%), yellow oil. ^{1}H NMR ($CDCl_3$), δ: 0.80 (t, 3H); 1.12−1.22 (m, 12H); 1.43−1.47 (m, 2H); 6.68 (d, 1H, J = 26.0 Hz); 7.03−7.06 (m, 1H); 7.29−7.35 (m, 1H); 7.42−7.46 (m, 6H); 7.49−7.57 (m, 6H). ^{13}C NMR ($CDCl_3$), δ: 14.2 (s, CH_3), 22.8, 29.4, 29.60, 29.62, 29.8, 32.0, 33.9 (all s, CH_2); 30.1 (d, C1, $^1J_{CP}$ = 119.7 Hz); 104.6 (d, arom., $^1J_{CP}$ = 90.8 Hz); 113.0 (d, CN, $^2J_{CP}$ = 8.8 Hz); 123.3 (d, arom., $^3J_{CP}$ = 12.9 Hz); 123.7 (d, arom., $^3J_{CP}$ = 8.8 Hz); 124.9 (d, CH = C, $^3J_{CP}$ = 12.1 Hz); 128.0 (d, arom., $^1J_{CP}$ = 89.1 Hz); 129.2 (d, arom., $^3J_{CP}$ = 12.9 Hz); 130.7 (d, CH, $^2J_{CP}$ = 3.6 Hz); 131.9 (d, arom., $^4J_{CP}$ = 1.6 Hz); 132.0 (d, arom., $^2J_{CP}$ = 8.4 Hz); 132.6 (d, arom., $^4J_{CP}$ = 2.8 Hz); 132.8 (d, arom., $^2J_{CP}$ = 10.8 Hz); 140.8 (d, arom., $^2J_{CP}$ = 6.0 Hz). ^{31}P NMR ($CDCl_3$), δ: 10.34. IR, $\tilde{\nu}$/cm^{-1}: 2170 (CN), 1580 (C=C), 720−750, 1470 (Ar). MS, m/z: 437 $[M]^+$, 338 $[M - C_7H_{15}]^+$, 183 $[Ph_2P - 2H]^+$. HRMS calcd for $C_{30}H_{32}NP$ (M^+) m/z 437.2272, found 437.2267.

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Supporting Information Available: ^{1}H, ^{31}P, ^{13}C NMR spectra of the new compounds **1**, **8**, **9**, **14**, **16**−**18**, **20**−**24**, **27**−**31**, X-ray analysis of the molecular structure of **27** and a table of the most relevant distances as well as CIF files of compound **27**. This material is available free of charge via the Internet at http://pubs.acs.org.