EurJIC
European Journal of Inorganic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

Title: A very simple synthesis of annelated lambda-3 and lambda-5 phosphanaphthalenes

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To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201700011

Link to VoR: http://dx.doi.org/10.1002/ejic.201700011

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A Very Simple Synthesis of Annelated λ^3- and λ^5-Phosphanaphthalenes

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Ortho-phosphino-benzonitriles (or thieno, pyridinoanalogs) react with dimethyl acetylene dicarboxylate between – 78 °C and room temperature to give annelatedλ^5-phosphanaphthalenes. Interesting variations of the fluorescence properties are observed when the R substituents at P are alkyl or aryl. When R = *t*-Bu, the thermolysis of the product affords the corresponding trivalent phosphanaphthalene.

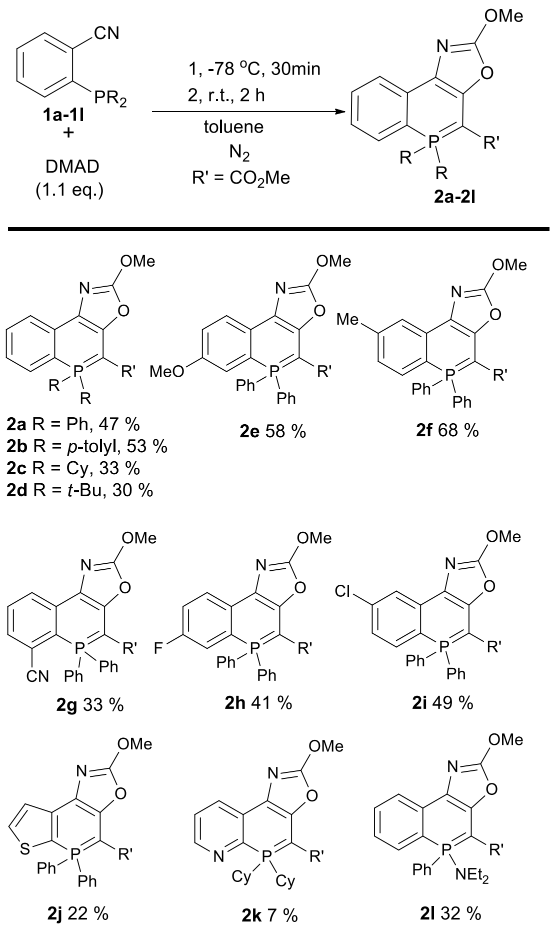
Introduction

Phosphorus containing π-conjugated systems are currently receiving special attention, owing to their potential applications in materials, such as liquid crystals[1], organogels[2], fibers[3], probes[4], sensors[4], n-type organic semiconductors[5], light-emitting diodes (OLEDs/PLEDs)[6] and photovoltaic cells[7].Compared with the well-known five-membered arene-fused phospholes[6], the research with the annelated six-membered phosphacycles is restricted by the lack of synthetic methods. Very recently, Matveeva's group developed a photochemical heterocyclization of mixed phosphonium–iodoniumylids with acetylenes to give annelated λ^5-phosphinines[8]. Romero-Nieto's group described a new non-catalyzed synthetic protocol to prepare phosphaphenalenes[9]. Here, we would like to report a facile method to synthesize a new type of functional six-membered phosphanaphthalenes (phosphinolines) from tertiary phosphines and dimethyl acetylenedicarboxylate (DMAD).

Phosphine catalyzed or mediated Michael addition is a powerful tool in modern organic synthesis[10]. Nucleophilic attacks of the phosphorus atom on electron-deficient multiple bonds create reactive zwitterionic carbenoid species, which emerged as versatile intermediates for various transformations. Some of these reactions provided a direct access to stable phosphorus-ylids containing conjugated heterocycles[11]. This led us to investigate the intramolecular nucleophilic reactivity between this type of zwitterionic carbenoid species and the cyanide group.

Results and discussion

After optimization of the reaction conditions (temperature, solvent), 2-diphenylphosphinobenzonitrile**1a** was reacted with DMAD at -78 °C in anhydrous toluene for 30 min (Scheme 1). Then, the reaction mixture was stirred at r.t. and monitored by ^{31}P NMR spectroscopy. The reaction was quite clean and a new product was isolated with a ^{31}P resonance at 13.2 ppm. Its structure was established by crystallographic analysis. It appeared that this reaction provides a facile access to annelated six-membered phosphacycle**2a** from readily accessible starting materials. Various α-phosphino benzonitriles reacted smoothly with DMAD to give the annelated phosphacycles. Both aryl-, alkyl- and even amino-substituted phosphines could be used (**2a**-**2d, 2l**). α-Phosphinobenzonitriles substituted by electron donating groups gavehigher yields (**2e**-**f**) than those with electron withdrawing groups, such as CN (**2g**), F (**2h**) and Cl (**2i**). Hetero-arene fused phosphacyclescould also be obtained using this new method (**2j**-**k**). It is interesting to note that all the solutions of alkyl-substituted phosphacycles (**2c**, **2d**, and **2k**) could be excited by UV light and yields yellow emission, whereas this phenomenon was not observed with all the aryl-substituted derivatives (Figure 1).



Scheme 1 Reactions of α-phosphinobenzonitriles with DMAD

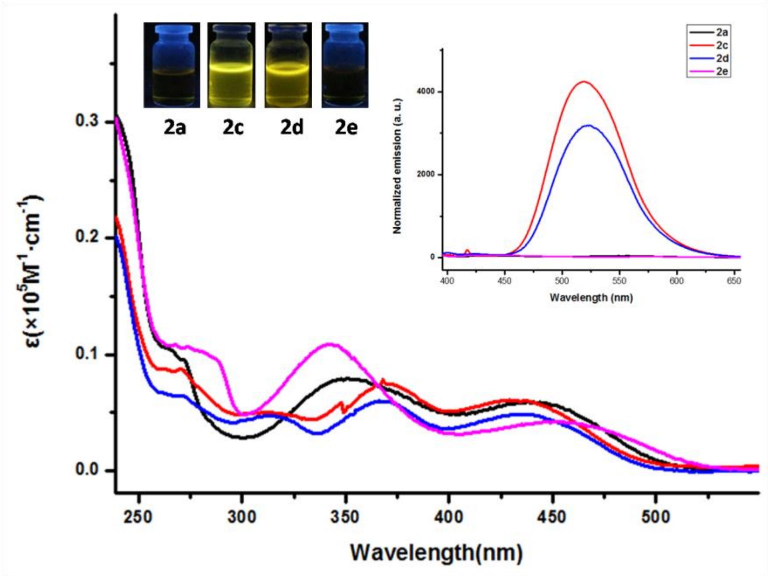


Figure 1UV-vis absorption and fluorescence spectra (inset) of **2a**, **2c**, **2d** and **2e** in CH_2Cl_2(10^{-5} M) at r.t.Photographs of **2a**, **2c**, **2d** and **2e** under irradiation with black light at 365 nm areshown in the inset.

Crystallographic studies were carried out on **2a** and **2c** (Figures 2 and 3). The intracyclic C(5)-P(1) bond lengths are 1.753(3) Å (**2a**) and 1.763(2) Å (**2c**), respectively, which are consistent with their ylidic structure[12]. The phosphorus ring of **2c** is nearly planar (∠C5-P1-C9-C14 = 3.07°) whereas the ring of **2a** is significantly distorted (∠C5-P1-C9-C14 = 26.31°). This suggests a higher electronic delocalization within the phosphorus ring of **2c** when compared to **2a**.

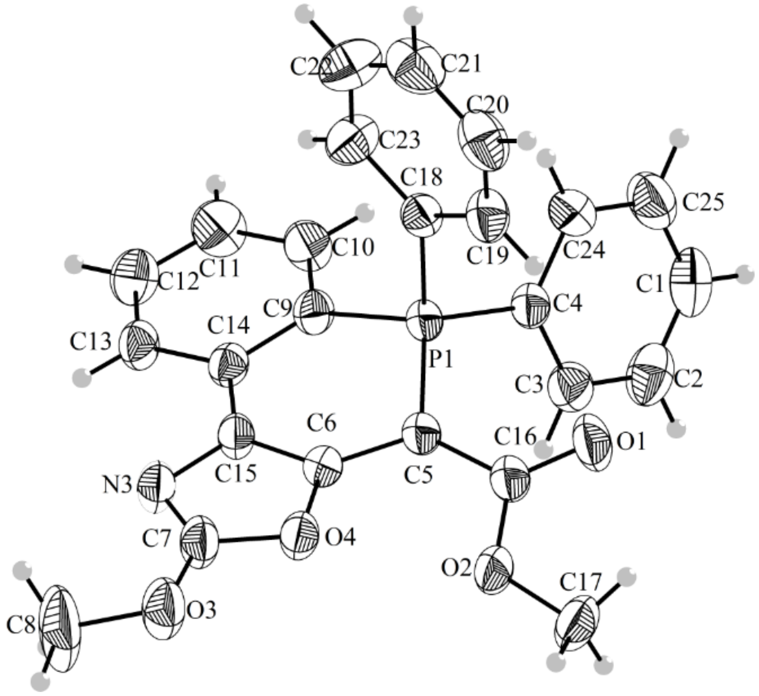


Figure 2 ORTEP drawing of **2a** (50% thermal ellipsoids). Main distances (Å) and angles (deg.): P1-C5 1.753(3), P1-C4 1.796(3), P1-C9 1.803(3), P1-C18 1.823(3), C5-C6 1.425(4), C6-C15 1.372(4), C14-C15 1.450(4), C9-C14 1.417(4); C4-P1-C9 109.34(14), C4-P1-C18 107.50(13),C5-P1-C4 113.67(14), C5-P1-C9 107.58(13), C5-P1-C18 112.30(13), C9-P1-C18 106.17(13); C5-P1-C9-C14 = 26.31°.

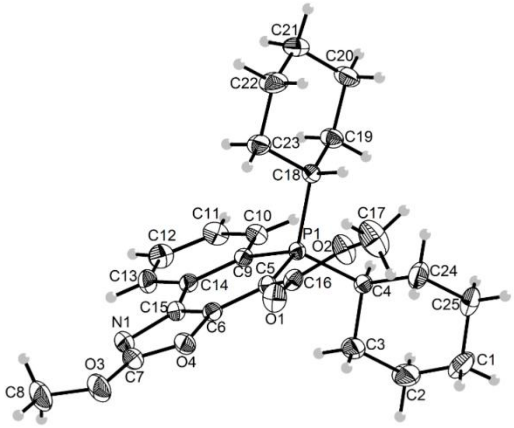
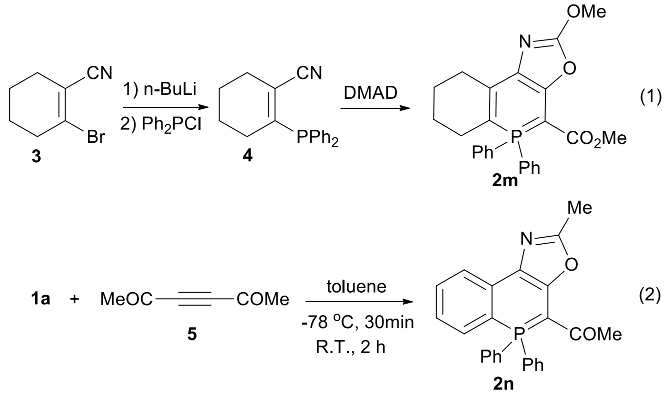


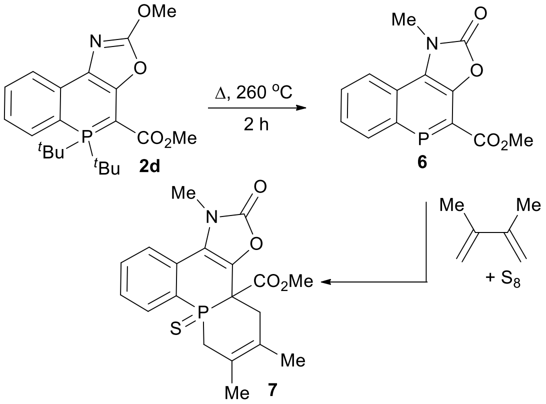
Figure 3 ORTEP drawing of **2c**(50% thermal ellipsoids). Main distances (Å) and angles (deg.): P1-C5 1.762(2), P1-C4 1.8273(19), P1-C9 1.806(2), P1-C18 1.837(2), C5-C6 1.421(3), C6-C15 1.356(3), C14-C15 1.433(3), C9-C14 1.414(3); C4-P1-C9 105.65(9), C4-P1-C18 108.50(10), C5-P1-C4 115.34(9), C5-P1-C9 106.52(10), C5-P1-C18 111.66(10), C9-P1-C18 108.83(9); C5-P1-C9-C14 = 3.07°.



Scheme 2 Synthesis of annelatedphosphinined

From a purely synthetic standpoint, this method appears to be quite general. Indeed it is possible to extend its use to the synthesis of annelatedphosphinines (Scheme 2).

In another vein, when the substituents at phosphorus are *t*-Bu (**2d**), it is possible to convert a λ5- into a λ3-phosphanaphthalene by thermolysis (Scheme 3).



Scheme 3 Synthesis of a λ3-phosphanaphthalene

The phosphanaphthalene **6** has been detected by ^{31}P MNR (^{31}P 190 ppm), but, due to its high reactivity, we trapped it by reaction with 2,3-dimethylbutadiene and sulfur (compound **7**) as shown in Scheme 3. Compound **7** has been characterized by X-ray crystal structure analysis (Figure 4).

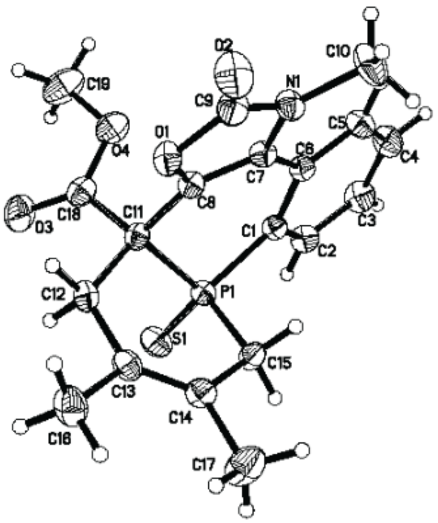
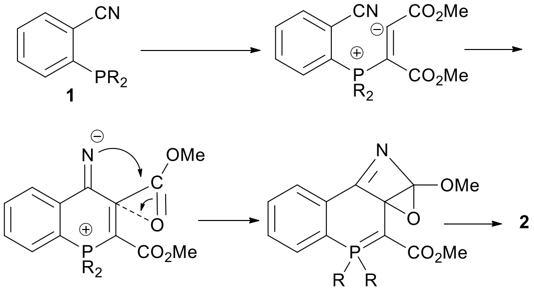


Figure 4 ORTEP drawing of **7** (30% thermal ellipsoids). Main distances (Å) and angles (deg.): P1-C1 1.811(2), P1-C11 1.852(2), P1-C15 1.814(3), P1-S1 1.9421(9), C1-C6 1.411(3), C6-C7 1.466(3), C7-C8 1.340(3), C8-C11 1.496(3); C1-P1-C11 105.13(11), C1-P1-C15 104.44(12), C1-P1-S1 113.85(8), C11-P1-S1 114.96(8), C15-P1-C11 100.73(11), C15-P1-S1 116.17(10).



Scheme 4 Proposed mechanism

On the basis of the known reaction of phosphines and DMAD, we propose the following mechanism (Scheme 4) involving a sequence of nucleophilic addition of phosphines **1** to DMAD to form zwitterionic intermediates, followed by an intramolecular cascade nucleophilic attack of CN^- on the carbonyl groups.

Conclusion

In conclusion, we have developed a very simple one-step synthesis of annelated λ^5-phosphanaphthalenes whose fluorescence properties vary with the substitution at phosphorus. Further studies will describe more in depth the optoelectronic properties of this new class of conjugated materials. The same scheme can also afford annelated phosphinines and trivalent phosphanaphthalenes.

Experimental section

All reactions were performed under nitrogen using solvents dried by standard methods. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker 300 and 400 MHz spectrometer. Chemical shifts are expressed in ppm from internal TMS (^1H and ^{13}C). All coupling constants (*J* values) are reported in hertz (Hz). HRMS spectra were obtained on a Water Q-Tof Premier MS. Element analytic data were obtained on a Thermo Electron Corporation flash EA 1112 element spectrometer. Silica gel (230-400 mesh) was used for the chromatographic separations. The UV-VIS spectra were recorded on a Varian Cary 5000 UV-Vis-NIR Spectrophotometer at room temperature. The emission spectra were recorded on a HITACHI F-4600 Fluorescence Spectrophotometer at room temperature. **2a**: λ_{abs}^{max}= 351 nm (ε = 7916 mol^{-1} L cm^{-1}), **2c**: λ_{abs}^{max} = 368 nm (ε = 7835 mol^{-1} L cm^{-1}), **2d**: λ_{abs}^{max} = 366 nm (ε = 6009 mol^{-1} L cm^{-1}), **2e**: λ_{abs}^{max} = 342 nm (ε = 10865 mol^{-1} L cm^{-1}). **1g**, **1j, 1m** and **1n** were prepared according to literature methods. Ph(Et$_2$N)PCl was made by the reaction of PhPCl$_2$ with HNEt$_2$ in anhydrous Et$_2$O. Commercially available reagents were used without further purification.

Synthesis of the starting phosphines

*Procedure A for the Synthesis of Compounds **1a**-**1b**, **1e**-**1f**, **1h**-**1j**:*

To a solution of *ortho*-bromoaryl nitriles or 2-bromothiophen-3-carbonitrile (15 mmol) in anhydrous THF (60 mL) (for **1a**, **1b** , **1e** and **1f**) or Et$_2$O (60 mL) (for **1j**) or THF/Et$_2$O (30 /30 mL) (for **1h** and **1i**), kept in an oven-dried 100 mL-Schlenk flask under an atmosphere of dry nitrogen, was added dropwise a 1.6 M solution of *n*-BuLi in hexane (9.4 mL, 15 mmol) at –78 °C over a period of 5 min. After stirring at –78 ^{o}C for 1 h, Ar$_2$PCl (15 mmol) in anhydrous THF (10 mL) was added dropwise. The mixture was kept at –78 ^{o}C for 1 h and then warmed to room temperature. After 1h, the reaction was monitored by ^{31}P NMR spectroscopy. The mixture was diluted with diethyl ether, the organic phase washed with water, brine and dried over anhydrous MgSO$_4$. The solvents were removed under reduced pressure to give a crude product, which was purified by column chromatography on silica gel (petroleum ether/ dichloromethane).

*Procedure B for the Synthesis of Compound **1g**:*

To a solution of 1,3-dicyanobenzene (2.56 g, 20 mmol) in anhydrous THF (50 mL), kept in an oven-dried 100 mL-Schlenk flask under an atmosphere of dry nitrogen, was added dropwise LDA (22 mmol) (which was prepared by the reaction of *n*-BuLi and HN(*i*-Pr)$_2$) in THF at –78 ^{o}C over a period of 10 min. After stirring at –78 ^{o}C for 1 h, Ph$_2$PCl (4.42 g, 20 mmol) in anhydrous THF (10 mL) was added dropwise. The mixture was kept at –78 ^{o}C for 1 h and then warmed to room temperature. After 1h, the reaction was monitored by ^{31}P NMR spectroscopy. The mixture was diluted with diethyl ether, the organic phase washed with water, brine and dried over anhydrous MgSO$_4$. The solvents were removed under reduced pressure to give a crude product, which was purified by column chromatography on silica gel (petroleum ether/ dichloromethane).

*Procedure C for the Synthesis of Compounds **1c(O)**-**1d(O)**, **1k(O)**-**1l(O)**:*

To a solution of 2-bromobenzonitrile or 2-bromopyridine-3-carbonitrile (9.6 mmol) in anhydrous THF (40 mL) (for **1c**, **1d**, and **1l**) or THF/Et$_2$O (20/20 mL) (for **1k**), kept in an oven-dried 100 mL-Schlenk flask under an atmosphere of dry nitrogen, was added dropwise a 1.6 M solution of *n*-BuLi in hexane (6.0 mL, 9.6 mmol) at –78 ^{o}C over a period of 5 min. After stirring at –78 ^{o}C for 1 h, RR’PCl (9.6 mmol) in anhydrous THF (10 mL) was added dropwise. The mixture was kept at –78 ^{o}C for 1 h and then warmed to room temperature. After 3 h, the reaction was monitored by ^{31}P NMR spectroscopy. The solvents were removed under reduced pressure and dichloromethane was added to the reaction mixture. After the residue was dissolved, the mixture was filtered to remove salt. H$_2$O$_2$ (ca. 30 %, a few drops) was added to the filtrate while stirring. After 10 min, the mixture was diluted with dichloromethane, the organic phase washed with water, brine and dried over anhydrous MgSO$_4$. The solvents were removed under reduced pressure to give a crude product, which was purified by column chromatography on silica gel (petroleum ether/ diethyl ether).

*Procedure D for the Synthesis of the Compound **1m(O)**:*

To a solution of 1-bromocyclohexene-2-carbonitrile (1190 mg, 6.4 mmol) in anhydrous THF/Et$_2$O (20/20 mL), kept in an oven-dried 100 mL-Schlenk flask under an atmosphere of dry nitrogen, was added dropwise a 1.6 M solution of *n*-BuLi in hexane (4.0 mL, 6.4 mmol) at –78 ^{o}C over a period of 5 min. After stirring at –78 ^{o}C for 1 h, Ph$_2$PCl (1412 mg, 6.4 mmol) in anhydrous THF (10 mL) was added dropwise. The mixture was kept at –78 ^{o}C for 1 h and then warmed to room temperature. After 3 h, the reaction was monitored by ^{31}P NMR spectroscopy. The solvents were removed under reduced pressure and dichloromethane was added to the reaction mixture. After the residue was dissolved, the mixture was filtered to remove salt. H_2O_2 (ca. 30 %, a few drops) was added to the filtrate while stirring. After 10 min, the mixture was diluted with dichloromethane, the organic phase washed with water, brine and dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure to give a crude product, which was purified by column chromatography on silica gel (petroleum ether/ diethyl ether).

*Phosphine **1a***

White solid, 3.28 g, 76 % yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ -8.3 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.06-7.10 (m, 1H), 7.27-7.51 (m, 12H), 7.70-7.74 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 117.66 (d, J_{CP} = 3.8 Hz, CN), 117.93 (d, J_{CP} = 33.0 Hz, C), 128.88 (d, J_{CP} = 7.5 Hz, 4CH), 128.93 (s, CH), 129.48 (s, 2CH), 132.47 (s, CH), 133.45 (s, CH), 133.76 (d, J_{CP} = 4.5 Hz, CH), 134.05 (d, J_{CP} = 20.3 Hz, 4CH), 134.70 (d, J_{CP} = 10.5 Hz, 2C), 143.03 (d, J_{CP} = 20.3 Hz, C). HRMS: m/z calcd. for $C_{19}H_{15}NP$ [M+H]$^+$: 288.0942; found : 288.0945.

*Phosphine **1b***

White solid, 2.93 g, 62 % yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ -10.7 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.38 (s, 6H, 2Me), 7.04-7.08 (m, 1H), 7.19-7.27 (m, 8H), 7.37-7.50 (m, 2H), 7.68-7.72 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 21.42 (s, 2CH$_3$), 117.62 (d, J_{CP} = 32.3 Hz, C), 117.74(d, J_{CP} = 3.8 Hz, CN), 128.64 (s, CH), 129.67 (d, J_{CP} = 7.5 Hz, 4CH), 131.27 (d, J_{CP} = 8.3 Hz, 2C), 132.34 (s, CH), 133.20 (s, CH), 133.69 (d, J_{CP} = 4.5 Hz, CH), 134.07 (d, J_{CP} = 21.0 Hz, 4CH), 139.50 (s, 2C), 143.82 (d, J_{CP} = 19.5 Hz, C). HRMS: m/z calcd for $C_{21}H_{19}NP$ [M+H]$^+$: 316.1255; found : 316.1259.

*Phosphine oxide**1c(O)***

White solid, 2.39 g, 79% yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ 46.4 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.08-1.52 (m, 12H), 1.64-1.84 (m, 6H), 2.07-2.11 (m, 2H), 2.34-2.44 (m, 2H), 7.60 (t, J = 7.8 Hz, 1H), 7.71-7.79 (m, 2H), 8.16-8.22 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 25.48 (d, J_{CP} = 3.8 Hz, 2CH$_2$), 25.65 (d, J_{CP} = 0.8 Hz, 2CH$_2$), 25.98 (d, J_{CP} = 3.8 Hz, 2CH$_2$), 26.07 (s, CH$_2$), 26.22 (d, J_{CP} = 3.0 Hz, 2CH$_2$), 26.38 (s, CH$_2$), 36.19 (d, J_{CP} = 66.0 Hz, 2CH), 112.74 (d, J_{CP} = 6.0 Hz, C), 118.72 (d, J_{CP} = 3.0 Hz, CN), 131.30 (d, J_{CP} = 2.3 Hz, CH), 132.64 (d, J_{CP} = 9.0 Hz, CH), 134.24 (d, J_{CP} = 6.8 Hz, CH), 135.39 (d, J_{CP} = 72.8 Hz, C), 135.52 (d, J_{CP} = 4.5 Hz, CH). HRMS: m/z calcd for $C_{19}H_{27}NOP$ [M+H]$^+$: 316.1830; found : 316.1829.

*Phosphine oxide **1d(O)***

^{31}P NMR (121 MHz, CDCl$_3$): δ 53.7 ppm. HRMS: m/z calcd for $C_{15}H_{23}NOP$ [M+H]$^+$: 264.1517; found : 264.1516.

*Phosphine **1e***

White solid, 2.53 g, 53 % yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ-7.9 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.69 (s, 3H, MeO), 6.52 (t, J = 3.0 Hz, 1H), 6.90 (dd, J = 2.4, 8.4 Hz, 1H), 7.27-7.41 (m, 10H), 7.66 (dd, J = 3.3, 8.7 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 55.4 (s, CH$_3$O), 109.3 (d, J_{CP} = 31.5 Hz, C), 113.9 (s, CH), 118.03 (d, J_{CP} = 3.8 Hz, CN), 119.7 (s, CH), 128.9 (d, J_{CP} = 7.5 Hz, 4CH), 129.5 (s, 2CH), 134.1 (d, J_{CP} = 20.3 Hz, 4CH), 134.5 (d, J_{CP} = 10.5 Hz, 2C), 135.6 (d, J_{CP} = 5.3 Hz, CH), 145.2 (d, J_{CP} = 20.3 Hz, C), 162.4 (s. C). HRMS: m/z calcd for $C_{20}H_{17}NOP$ [M+H]$^+$: 318.1048; found : 318.1049.

*Phosphine **1f***

White solid, 3.96 g, 88 % yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ-9.9 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.39 (s, 3H, Me), 6.97 (d, J = 7.8 Hz, 1H), 7.27-7.39 (m, 11H), 7.54 (s, H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 20.97 (s, CH$_3$), 117.87 (d, J_{CP} = 4.5 Hz, CN), 117.96 (d, J_{CP} = 33.8 Hz, C), 128.80 (d, J_{CP} = 7.5 Hz, 4CH), 129.32 (s, 2CH), 133.50 (s, CH), 133.62 (s, CH), 133.91 (d, J_{CP} = 20.3 Hz, 4CH), 134.21 (d, J_{CP} = 4.5 Hz, CH), 135.07 (d, J_{CP} = 10.5 Hz, 2C), 139.25 (d, J_{CP} = 18.0 Hz, C), 139.48 (s. C). HRMS: m/z calcd for $C_{20}H_{17}NP$ [M+H]$^+$: 302.1099; found : 302.1101.

*Phosphine **1g***

White solid, 4.50 g, 72% yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ -2.4 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.43-7.53 (m, 10H), 7.60 (t, J = 7.8 Hz, 1H), 7.91 (dd, J = 1.2, 7.8 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 116.14 (d, J_{CP} = 2.3 Hz, 2CN), 120.58 (d, J_{CP} = 19.5 Hz, 2C), 129.10 (d, J_{CP} = 6.8 Hz, 4CH), 130.01 (s, 2CH), 130.18 (s, CH), 132.25 (d, J_{CP} = 9.8 Hz, 2C), 133.62 (d, J_{CP} = 20.3 Hz, 4CH), 138.50 (d, J_{CP} = 2.3 Hz, 2CH), 145.73 (d, J_{CP} = 35.3 Hz, C). HRMS: m/z calcd for $C_{20}H_{14}N_2P$ [M+H]$^+$: 313.0895; found : 313.0891.

*Phosphine **1h***

White solid, 2.25 g, 49 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ -9.6 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.70-6.75 (m, 1H), 7.07-7.14 (m, 1H), 7.31-7.44 (m, 10H), 7.70-7.75 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 113.64 (dd, J = 3.0, 30.8 Hz, C), 116.49 (d, J= 22.5 Hz, CH), 116.92 (d, J = 3.0 Hz, CN), 120.57 (d, J= 22.5 Hz, CH), 129.08 (d, J= 7.5 Hz, 4CH), 129.86 (s, 2CH), 133.83 (d, J= 9.8 Hz, 2C), 134.12 (d, J= 20.3 Hz, 4CH), 136.15 (dd, J = 4.5, 9.0 Hz, CH), 147.58 (dd, J = 6.0, 23.3 Hz, C), 164.71 (d, J= 257.3 Hz, C). HRMS: m/z calcd for $C_{19}H_{14}FNP$ [M+H]$^+$: 306.0848; found : 306.0845.

*Phosphine **1i***

White solid, 2.70 g, 56 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ-9.4 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.02 (dd, J = 2.7, 8.4 Hz, 1H), 7.27-7.48 (m, 11H), 7.70 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 116.39 (d, J_{CP} = 3.0 Hz, CN), 119.26 (d, J_{CP} = 34.5 Hz, C), 129.03 (d, J_{CP} = 7.5 Hz, 4CH), 129.72 (s, 2CH), 132.82 (s, CH), 133.30 (d, J_{CP} = 4.5 Hz, CH), 134.02 (d, J_{CP} = 20.3 Hz, 4CH), 134.15 (s, C), 134.73 (d, J_{CP} = 67.5 Hz, 2C), 134.79 (s, CH), 141.85 (d, J_{CP} = 21.8 Hz, C). HRMS: m/z calcd for $C_{19}H_{14}ClNP$ [M+H]$^+$: 322.0552; found : 322.0554.

*Phosphine **1j***

Yellow solid, 3.39 g, 77% yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ -20.9 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.43 (m, 11H), 7.55-7.57 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 114. 69 (d, J_{CP} = 1.5 Hz, CN), 117.46 (d, J_{CP} = 27.8 Hz, C), 128.84 (d, J_{CP} = 7.5 Hz, 4CH), 129.77 (s, 2CH), 130.88 (d, J_{CP} = 3.0 Hz, CH), 131.97 (s, CH), 133.35 (d, J_{CP} = 20.3 Hz, 4CH), 135.25 (d, J_{CP} = 9.0 Hz, 2C), 151.57 (d, J_{CP} = 39.8 Hz, C). HRMS: m/z calcd for $C_{17}H_{13}NPS$ [M+H]$^+$: 294.0506; found : 294.0511.

*Phosphine oxide**1k(O)***

White solid, 2.43 g, 80% yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ 51.1 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10-1.47 (m, 14H), 1.64-1.73 (m, 3H), 1.81-1.83 (m, 1H), 2.12-2.16 (m, 2H), 2.28-2.40 (m, 2H), 7.54-7.59 (m, 1H), 8.12-8.16 (m, 1H), 8.89-8.91 (m, 1H);^{13}C NMR (75 MHz, $CDCl_3$): δ 24.59 (d, J_{CP} = 3.0 Hz, $2CH_2$), 25.27 (d, J_{CP} = 3.8 Hz, $2CH_2$), 25.65 (s, $2CH_2$), 26.10 (s, $2CH_2$), 26.27 (s, $2CH_2$), 35.32 (d, J_{CP} = 66.0 Hz, 2CH), 115.66 (s, CN), 115.85 (d, J_{CP} = 12.0 Hz, C), 124.52 (d, J_{CP} = 3.0 Hz, CH), 142.21 (d, J_{CP} = 5.3 Hz, CH), 151.67 (d, J_{CP} = 15.8 Hz, CH), 157.91 (d, J_{CP} = 102.8 Hz, C). HRMS: m/z calcd for $C_{18}H_{26}N_2OP$ [M+H]$^+$: 317.1816; found : 317.1815.

*Phosphine oxide**1l(O)***

White solid, 2.4 g, 84% yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ 26.2 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.07 (t, J = 6.9 Hz, 6H), 3.02-3.12 (m, 4H), 7.32-7.59 (m, 5H), 7.67-7.71 (m, 1H), 7.85-7.93 (m, 2H), 8.06-8.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.60 (d, J_{CP} = 3.8 Hz, $2CH_3$), 39.49 (d, J_{CP} = 3.0 Hz, $2CH_2$), 114.37 (d, J_{CP} = 4.5 Hz, C), 118.23 (d, J_{CP} = 4.5 Hz, CN), 128.59 (d, J_{CP} = 12.8 Hz, 2CH), 130.84 (d, J_{CP} = 130.5 Hz, C), 131.66 (d, J_{CP} = 2.3 Hz, CH), 132.19 (d, J_{CP} = 2.3 Hz, CH), 132.20 (d, J_{CP} = 9.8 Hz, 2CH),132.52(d, J_{CP} = 11.3 Hz, CH), 135.15 (d, J_{CP} = 8.3 Hz, CH), 135.68 (d, J_{CP} = 8.3 Hz, CH), 136.59 (d, J_{CP} = 122.3 Hz, C). HRMS: m/z calcd for $C_{17}H_{20}N_2OP$ [M+H]$^+$: 299.1313; found : 299.1313.

*Phosphine oxide**1m(O)***

White solid, 1.57 g, 80 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ 27.0 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.63-1.65 (m, 4H), 2.28-2.31 (m, 2H), 2.41-2.43 (m, 2H), 7.44-7.58 (m, 6H), 7.67-7.74 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.93 (s, CH_2), 21.08 (d, J_{CP} = 7.5 Hz, CH_2), 27.99 (d, J_{CP} = 7.5 Hz, CH_2), 31.14 (d, J_{CP} = 9.0 Hz, CH_2), 116.58 (d, J_{CP} = 10.5 Hz, CN), 122.75 (s, C), 128.79 (d, J_{CP} = 12.8 Hz, 4CH), 130.35 (d, J_{CP} = 104.3 Hz, 2C), 131.94 (d, J_{CP} = 9.8 Hz, 4CH), 132.65 (d, J_{CP} = 3.0 Hz, 2CH), 148.91 (d, J_{CP} = 87.0 Hz, C). HRMS: m/z calcd for $C_{19}H_{19}NOP$ [M+H]$^+$: 308.1204; found : 308.1202.

*Procedure E for the Synthesis of Compounds **2a-2b, 2e-2f, 2g-2j**:*

To a solution of phosphines **(1a-1b, 1e-1f, 1g-1j)** (1 mmol) in anhydrous toluene (20 mL) was added DMAD (136 μl, 1.1 mmol) at –78 °C under N_2 atmosphere. The mixture was kept at –78 °C for 30 min and then warmed to room temperature. After 2h, the ^{31}P NMR spectrum showed that the reaction was completed. The solvents were removed under reduced pressure to give a crude product, which was purified by column chromatography on silica gel (dichloromethane/ diethyl ether).

*Procedure F for the Synthesis of Compounds **2c**-**2d**, **2k**-**2l**:*

To a solution of 2-bromobenzonitrile or 2-bromopyridine-3-carbonitrile (3.2 mmol) in anhydrous THF (30 mL) (for **2c**, **2d**, and **2l**) or THF/Et_2O (15/15 mL) (for **2k**), kept in an oven-dried 50 mL-Schlenk flask under an atmosphere of dry nitrogen, was added dropwise a 1.6 M solution of *n*-BuLi in hexane (2.0 mL, 3.2 mmol) at –78 ^{o}C over a period of 5 min. After stirring at –78 ^{o}C for 1 h, RR' PCl (3.2 mmol, except for *t*-Bu_2PCl 1.6 mmol) was added dropwise. The mixture was kept at –78 ^{o}C for 1 h and then warmed to room temperature. After 3 h, the ^{31}P NMR spectrum showed that the reaction was completed. The solvents were removed under reduced pressure and toluene was added to the reaction mixture. After the residue was dissolved, the mixture was filtered under an atmosphere of dry nitrogen to remove the inorganic salt. At –78 ^{o}C DMAD (431 μl, 3.5 mmol) was added to the filtrate while stirring. After 30 min, the mixture was warmed to room temperature. After 2 h, the reaction was complete according to the ^{31}P NMR spectrum. Then the solvents were removed under reduced pressure to give a crude product, which was purified by column chromatography on silica gel (dichloromethane / diethyl ether).

*Procedure G for the Synthesis of the Compound **2m**:*

To a solution of 1-bromocyclohexene-2-carbonitrile (1190 mg, 6.4 mmol) in anhydrous THF/Et_2O (20/20 mL), kept in an oven-dried 100 mL-Schlenk flask under an atmosphere of dry nitrogen, was added dropwise a 1.6 M solution of *n*-BuLi in hexane (4.0 mL, 6.4 mmol) at –78 ^{o}C over a period of 5 min. After stirring at –78 ^{o}C for 1 h, Ph_2PCl (1412 mg, 6.4 mmol) was added dropwise. The mixture was kept at –78 ^{o}C for 1 h and then warmed to room temperature. After 3 h, the ^{31}P NMR spectrum showed that the reaction was completed. The solvents were removed under reduced pressure and toluene was added to the reaction mixture. After the residue was dissolved, DMAD (788 μl, 6.4 mmol) was added to the mixture at –78 ^{o}C while stirring. After 30 min, the mixture was warmed to room temperature. After 2 h, the reaction was complete according to the ^{31}P NMR spectrum. Then the solvents were removed under reduced pressure to give a crude product, which was purified by column chromatography on silica gel (dichloromethane / diethyl ether).

*Procedure H for the Synthesis of the Compound **2n**:*

To a solution of phosphine **1a** (288 mg, 1 mmol) in anhydrous toluene (20 mL) was added the alkyne (121 mg, 1.1 mmol) at –78 ^{o}C under N_2 atmosphere. The mixture was kept at –78 ^{o}C for 30 min and then warmed to room temperature. After 2h, the ^{31}P NMR spectrum showed that the reaction was complete. The solvents were removed under reduced pressure to give a crude product, which was purified by column chromatography on silica gel (dichloromethane/ diethyl ether).

*Phosphanaphthalene**2a***

Yellow solid, 200 mg, 47 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ 13.2 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.61 (br s, 3H, OMe), 4.12 (s, 3H, OMe), 6.98-7.03 (m, 1H), 7.24-7.31 (m, 1H), 7.45-7.56 (m, 7H), 7.68-7.84 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 45.54 (d, J_{CP} = 119.3 Hz, P=C), 50.45 (s, CH_3, OMe), 57.84 (s, CH_3, OMe), 108.28 (d, J_{CP} = 88.5 Hz, C), 116.24 (d, J_{CP} = 7.5 Hz, C), 121.32 (d, J_{CP} = 8.3 Hz, CH), 123.03 (d, J_{CP} = 12.8 Hz, CH), 127.38 (d, J_{CP} = 92.3 Hz, 2C), 128.63 (d, J_{CP} = 12.8 Hz, 4CH), 131.96 (d, J_{CP} = 3.0 Hz, 2CH), 132.22 (d, J_{CP} = 2.3 Hz, CH), 132.68 (d, J_{CP} = 8.3 Hz, CH), 133.13 (d, J_{CP} = 11.3 Hz, 4CH), 136.35 (d, J_{CP} = 6.0 Hz, C), 145.73 (d, J_{CP} = 23.3 Hz, C), 159.25 (s, C), 166.01 (b, CO_2). HRMS calcd for $C_{25}H_{21}NO_4P$ $[M+H]^+$: 430.1203; found : 430.1196. Anal. Calcd for $C_{25}H_{20}NO_4P$: C 69.93, H 4.69, N 3.26; found: C 69.78, H 4.63, N 3.15.

*Phosphanaphthalene**2b***

Yellow solid, 244 mg, 53 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ 12.7 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 6H, 2Me), 3.60 (br s, 3H, OMe), 4.10 (s, 3H, OMe), 6.95-7.00 (m, 1H), 7.23-7.29 (m, 5H), 7.44 (m, 1H), 7.59 (dd, *J* = 8.4, 13.2 Hz, 4H), 7.79 (dd, *J* = 4.5, 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.55 (d, J_{CP} = 0.8 Hz, $2CH_3$), 45.91 (d, J_{CP} = 120.8 Hz, P=C), 50.40 (br s, CH_3, OMe), 57.78 (s, CH_3, OMe), 109.00 (d, J_{CP} = 91.5 Hz, C), 116.13 (s, C), 121.19 (d, J_{CP} = 7.5 Hz, CH), 122.92 (d, J_{CP} = 12.8 Hz, CH), 124.25 (d, J_{CP} = 96.0 Hz, 2C), 129.40 (d, J_{CP} = 13.5 Hz, 4CH), 132.06 (s, CH), 132.65 (d, J_{CP} = 8.3 Hz, CH), 133.15 (d, J_{CP} = 11.3 Hz, 4CH), 136.26 (d, J_{CP} = 6.0 Hz, 2C), 142.57 (d, J_{CP} = 3.0 Hz, C), 145.88 (d, J_{CP} = 24.8 Hz, C), 159.19 (s, C), 165.89 (b, CO_2). HRMS calcd for $C_{27}H_{25}NO_4P$ $[M+H]^+$: 458.1516; found : 458.1509.

*Phosphanaphthalene**2c***

Yellow solid, 470 mg, 33 % yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ 27.2 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.13-1.54 (m, 10H), 1.66-1.77 (m, 8H), 2.03 (m, 2H), 2.83 (d, J = 11.1 Hz, 2H), 3.74 (s, CH$_3$, OMe), 4.06 (s, CH$_3$, OMe), 7.02 (m, 1H), 7.45-7.53 (m, 2H), 7.67 (m, 1H);^{13}C NMR (75 MHz, CDCl$_3$): δ 25.81 (s, 2CH$_2$), 26.67 (d, J_{CP} = 3.0 Hz, 2CH$_2$), 26.85 (d, J_{CP} = 3.0 Hz, 2CH$_2$), 27.04 (d, J_{CP} = 3.0 Hz, 2CH$_2$), 27.54 (d, J_{CP} =2.3 Hz, 2CH$_2$), 36.1 (d, J_{CP} =51.0 Hz, 2CH), 41.19 (d, J_{CP} =108.8 Hz, P=C), 50.43 (s, CH$_3$, OMe), 57.62 (s, CH$_3$, OMe), 106.80 (d, J_{CP} = 76.5 Hz, C), 115.14 (d, J_{CP} = 3.8 Hz, C), 121.27 (d, J_{CP} = 6.8 Hz, CH), 122.14 (d, J_{CP} = 11.3 Hz, CH), 130.90 (d, J_{CP} = 8.3 Hz, CH), 132.14 (s, CH), 138.23 (s, C), 146.76 (d, J_{CP} = 18.0 Hz, C), 158.70 (s, C), 166.82 (b, CO$_2$). HRMS calcd for $C_{25}H_{33}NO_4P$ [M+H]$^+$: 442.2142; found : 442.2125. Anal. Calcd for $C_{25}H_{32}NO_4P$: C 68.01, H 7.31, N 3.17; found: C 67.85, H 7.32, N 3.10.

*Phosphanaphthalene**2d***

Yellow solid, 374 mg, 30 % yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ 40.1 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.45 (d, J = 15.6 Hz, 18H, 6CH$_3$), 3.75 (s, 3H, OMe), 4.07 (s, 3H, OMe), 6.96 (t, J = 6.9 Hz, 1H), 7.40-7.45 (m, 1H), 7.71-7.77 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 29.36 (d, J_{CP} = 2.3 Hz, 6 CH$_3$), 42.96 (d, J_{CP} = 40.5 Hz, 2C), 46.32 (d, J_{CP} = 102.8 Hz, P=C), 50.53 (s, CH$_3$, OMe), 57.57 (s, CH$_3$, OMe), 107.76 (d, J_{CP} = 70.5 Hz, C), 115.14 (s, C), 120.58 (d, J_{CP} = 11.3 Hz, CH), 121.59 (d, J_{CP} = 6.8 Hz, CH), 131.79 (s, CH), 134.09 (d, J_{CP} = 7.5 Hz, CH), 138.17 (s, C), 147.43 (d, J_{CP} = 18.0 Hz, C), 158.64 (s, C), 167.67 (d, J_{CP} = 14.3 Hz, CO$_2$). HRMS calcd for $C_{21}H_{29}NO_4P$ [M+H]$^+$: 390.1829; found : 390.1809. Anal. Calcd for $C_{21}H_{28}NO_4P$: C 64.77, H 7.25, N 3.60; found: C 64.89, H 7.45, N 3.33.

*Phosphanaphthalene**2e***

Red solid, 265 mg, 58 % yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ 13.5 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.61 (br s, 3 H, OMe), 3.68 (s, 3H, Ph-OMe), 4.11 (s, 3H, OMe), 6.75 (dd, J = 2.7, 13.8 Hz, 1H), 7.12 (d, J = 9.0 Hz, 1H), 7.38-7.61 (m, 6H), 7.69-7.76 (m, 5H);^{13}C NMR (101 MHz, CDCl$_3$): δ 44.46 (d, J_{CP} = 122.2 Hz, P=C), 50.37 (s, CH$_3$, OMe), 55.48 (s, CH$_3$, Ph-OMe), 57.75 (s, CH$_3$, OMe), 109.50 (d, J_{CP} = 88.9 Hz, C), 116.26 (s, C), 116.81 (d, J_{CP} = 9.1 Hz, CH), 119.35 (s, CH), 123.12 (d, J_{CP} = 9.1 Hz, CH), 127.24 (d, J_{CP} = 93.9 Hz, 2C), 128.62 (d, J_{CP} = 12.1 Hz, 4CH), 130.42 (s, C), 131.95 (d, J_{CP} = 2.0 Hz, 2CH), 133.10 (d, J_{CP} = 11.1 Hz, 4CH), 143.79 (d, J_{CP} = 24.2 Hz, C), 155.59 (d, J_{CP} = 14.1 Hz, C), 159.22 (s, C), 166.00 (b, CO$_2$). HRMS calcd for $C_{26}H_{23}NO_5P$ [M+H]$^+$: 460.1308; found : 460.1297. Anal. Calcd for $C_{26}H_{22}NO_5P$: C 67.97, H 4.83, N 3.05; found: C 67.91, H 4.97, N 2.88.

*Phosphanaphthalene**2f***

Yellow solid, 300 mg, 68 % yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ 13.1 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.39 (s, 3H, Me), 3.61 (br s, 3H, OMe), 4.12 (s, 3H, OMe), 6.85 (td, J = 1.8, 8.1 Hz, 1H), 7.17 (dd, J = 8.1, 12.6 Hz, 1H), 7.44-7.57 (m, 6H), 7.63-7.75 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 21.72 (s, CH$_3$), 45.57 (d, J_{CP} = 114.0 Hz, P=C), 50.42 (s, CH$_3$, OMe), 57.81 (s, CH$_3$, OMe), 105.46 (d, J_{CP} = 92.3 Hz, C), 116.14 (d, J_{CP} = 7.5 Hz, C), 121.40 (d, J_{CP} = 8.3 Hz, CH), 124.53 (d, J_{CP} = 12.8 Hz, CH), 127.58 (d, J_{CP} = 95.3 Hz, 2C), 128.59 (d, J_{CP} = 12.8 Hz, 4CH), 131.89 (d, J_{CP} = 3.8 Hz, 2CH), 132.68 (d, J_{CP} = 9.0 Hz, CH), 133.14 (d, J_{CP} = 10.5 Hz, 4CH), 136.32 (d, J_{CP} = 6.8 Hz, C), 142.98 (d, J_{CP} = 2.3 Hz, C), 145.80 (d, J_{CP} = 21.8 Hz, C), 159.25 (s, C), 166.13 (b, CO$_2$). HRMS calcd for $C_{26}H_{23}NO_4P$ [M+H]$^+$: 444.1359; found : 444.1353.

*Phosphanaphthalene**2g***

Red solid, 150 mg,33% yield). ^{31}P NMR (121 MHz, CDCl$_3$): δ 13.6 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.55 (br s, 3H, OMe), 4.13 (s, 3H, OMe), 7.33-7.36 (m, 1H), 7.48-7.63 (m, 7H), 7.89-7.96 (m, 4H), 8.07-8.11 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 48.86 (d, J_{CP} = 121.5 Hz, P=C), 50.61 (br s, CH$_3$, OMe), 58.00 (s, CH$_3$, OMe), 107.21 (d, J_{CP} = 87.8 Hz, C), 115.32 (d, J_{CP} = 6.0 Hz, C), 115.57 (d, J_{CP} = 5.3 Hz, C), 117.51 (d, J_{CP} = 6.0 Hz, C), 126.14 (d, J_{CP} = 93.0 Hz, 2C), 126.22 (d, J_{CP} = 6.8 Hz, CH), 128.75 (d, J_{CP} = 13.5 Hz, 4CH), 130.75 (d, J_{CP} = 8.3 Hz, CH), 131.50 (d, J_{CP} = 1.5 Hz, CH), 132.57 (d, J_{CP} = 3.0 Hz, 2CH), 133.64 (d, J_{CP} = 11.3 Hz, 4CH), 137.44 (d, J_{CP} = 4.5 Hz, C), 147.21 (d, J_{CP} = 21.8 Hz, C), 159.28 (s, C), 165.32 (b, CO$_2$). HRMS calcd for $C_{26}H_{20}N_2O_4P$ [M+H]$^+$: 455.1155; found : 455.1155

*Phosphanaphthalene**2h***

Yellow solid, 184 mg, 41 % yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ 13.6 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.60 (br s, 3H, OMe), 4.11 (s, 3H, OMe), 6.90-6.98 (m, 1H), 7.18-7.27 (m, 1H), 7.48-7.85 (m, 11H)； ^{13}C NMR (75 MHz, CDCl$_3$): δ 44.67 (d, J_{CP} = 120.8 Hz, P=C), 50.51 (s, CH$_3$, OMe), 57.84 (s, CH$_3$, OMe), 109.39 (d, J_{CP} = 88.5 Hz, C), 115.82 (s, C), 118.02 (dd, J = 9.8, 23.5 Hz, CH), 120.52 (dd, J = 2.3, 22.5 Hz, CH), 123.56 (dd, J = 7.5, 9.8 Hz, CH), 126.83 (d, J_{CP} = 94.5 Hz, 2C), 128.78 (d, J_{CP} = 13.5 Hz, 4CH), 132.21 (d, J_{CP} = 3.0 Hz, 2CH), 133.07 (d, J_{CP} = 11.3 Hz, 4CH), 144.94 (d, J_{CP} = 21.8 Hz, C), 158.60 (dd, J = 16.5, 243.8 Hz, C), 159.29 (s, C), 165.85 (b, CO$_2$). One carbon is missing. HRMS: m/z calcd for $C_{25}H_{20}FNO_4P$ [M+H]$^+$: 448.1114; found : 448.1113.

*Phosphanaphthalene**2i***

Yellow solid, 225 mg, 49 % yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ 13.4 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.60 (br s, 3H, OMe), 4.11 (s, 3H, OMe), 6.94 (dt, J = 2.1, 8.4 Hz, 1H), 7.14-7.21 (m, 1H), 7.46-7.58 (m, 6H), 7.66-7.80 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 46.09 (d, J_{CP} = 120.0 Hz, P=C), 50.58 (s, CH$_3$, OMe), 57.95 (s, CH$_3$, OMe), 106.15 (d, J_{CP} = 91.5 Hz, C), 115.53 (d, J_{CP} = 5.3 Hz, C), 120.77 (d, J_{CP} = 9.0 Hz, CH), 123.06 (d, J_{CP} = 12.8 Hz, CH), 127.05 (d, J_{CP} = 93.8 Hz, 2C), 128.77 (d, J_{CP} = 12.8 Hz, 4CH), 138.20 (d, J_{CP} = 3.0 Hz, 2CH), 133.07 (d, J_{CP} = 10.5 Hz, 4CH), 134.08 (d, J_{CP} = 9.0 Hz, CH), 137.54 (d, J_{CP} = 6.8 Hz, C), 139.12 (d, J_{CP} = 3.0 Hz, C), 146.88 (d, J_{CP} = 23.3 Hz, C), 159.31 (s, C), 165.72 (b, CO$_2$). HRMS calcd for C$_{25}$H$_{20}$ClNO$_4$P [M+H]$^+$: 464.0813; found : 464.0806.

*Thienophosphinine**2j***

Yellow solid, 96 mg, 22 % yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ 10.3 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.64 (br s, 3H, OMe), 4.12 (s, 3H, OMe), 7.44-7.55 (m, 7H), 7.67-7.74 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 46.20 (d, J_{CP} = 125.3 Hz, P=C), 50.65 (s, CH$_3$, OMe), 57.87 (s, CH$_3$, OMe), 99.40 (d, J_{CP} = 102.0 Hz, C), 115.32 (d, J_{CP} = 3.8 Hz, C), 122.93 (d, J_{CP} = 10.5 Hz, CH), 127.23 (d, J_{CP} = 96.0 Hz, 2C), 128.38 (d, J_{CP} = 13.5 Hz, 4CH), 131.87 (d, J_{CP} = 3.0 Hz, 2CH), 132.84 (d, J_{CP} = 11.3 Hz, 4CH), 135.24 (d, J_{CP} = 6.8 Hz, CH), 144.65 (d, J_{CP} = 6.8 Hz, C), 146.71 (d, J_{CP} = 24.0 Hz, C), 159.00 (s, C), 166.49 (b, CO$_2$). HRMS calcd for C$_{23}$H$_{19}$NO$_4$PS [M+H]$^+$: 436.0767; found : 436.0769.

*Phosphaquinoline**2k***

Yellow solid, 95 mg, 7 % yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ 24.9 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.13-1.42 (m, 9H), 1.65-1.77 (m, 9H), 2.04 (m, 2H), 2.97 (d, J_{HP} = 11.4 Hz, 2H), 3.76 (s, 3H, OMe), 4.06 (s, 3H, OMe), 7.25-7.29 (m, 1H), 7.82-7.86 (m, 1H), 8.30 (d, J= 3.9 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 25.82 (d, J_{CP} = 0.8 Hz, 2CH$_2$), 26.64 (s, 2CH$_2$), 26.67 (d, J_{CP} = 22.5 Hz, 2CH$_2$), 26.69 (s, 2CH$_2$), 27.34 (d, J_{CP} = 2.3 Hz, 2CH$_2$), 35.25 (d, J_{CP} = 51.0 Hz, 2CH), 43.08 (d, J_{CP} = 104.3 Hz, P=C), 50.48 (s, CH$_3$, OMe), 57.68 (s, CH$_3$, OMe), 112.78 (s, C), 125.54 (d, J_{CP} = 2.3 Hz, CH), 126.95 (d, J_{CP} = 6.0 Hz, CH), 133.01 (d, J_{CP} = 105.0 Hz, C), 135.68 (d, J_{CP} = 13.5 Hz, C), 144.19 (d, J_{CP} = 17.3 Hz, CH), 147.75 (d, J_{CP} = 18.8 Hz, C), 159.03 (s, C), 166.89 (s, CO$_2$). HRMS calcd for C$_{24}$H$_{32}$N$_2$O$_4$P [M+H]$^+$: 443.2094; found : 443.1833. Anal. Calcd for C$_{24}$H$_{31}$N$_2$O$_4$P: C 65.14, H 7.06, N 6.33; found: C 64.76, H 7.21, N 6.52.

*Phosphanaphthalene**2l***

Yellow solid, 435 mg, 32 % yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ 35.0 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.02 (t, J = 7.2 Hz, 6H, 2CH$_3$), 3.00-3.17 (m, 4H, 2CH$_2$), 3.65 (s, 3H, OMe), 4.12 (s, 3H, OMe), 7.03-7.09 (m, 1H), 7.44-7.50 (m, 4H), 7.53-7.59 (m, 1H), 7.75-7.84 (m, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): δ13.30 (d, J_{CP} = 4.5 Hz, 2CH$_3$), 39.99 (d, J_{CP} = 3.8 Hz, 2CH$_2$), 50.31 (s, CH$_3$, OMe), 52.69 (d, J_{CP} = 123.8 Hz, P=C), 57.76 (s, CH$_3$, OMe), 111.47 (d, J_{CP} = 105.8 Hz, C), 116.16 (d, J_{CP} = 6.8 Hz, C), 121.39 (d, J_{CP} = 9.0 Hz, CH), 122.52 (d, J_{CP} = 12.0 Hz, CH), 127.62 (d, J_{CP} = 124.5 Hz, C), 128.54 (d, J_{CP} = 13.5 Hz, 2CH), 131.20 (d, J_{CP} = 6.8 Hz, CH), 131.67 (d, J_{CP} = 4.5 Hz, CH), 131.68 (s, CH), 132.93 (d, J_{CP} = 10.5 Hz, 2CH), 135.74 (d, J_{CP} = 7.5 Hz, C), 146.11 (d, J_{CP} = 24.0 Hz, C), 159.31 (s, C), 166.36 (d, J_{CP} = 6.8 Hz, CO$_2$). HRMS calcd for C$_{23}$H$_{26}$N$_2$O$_4$P [M+H]$^+$: 425.1625; found : 425.1621.

*Phosphinine**2m***

Yellow solid, 860 mg, 31 % yield. ^{31}P NMR (121 MHz, CDCl$_3$): δ 14.8 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.67-1.74 (m, CH2, 4H), 1.94-1.96 (m, CH2, 2H), 2.77-2.79 (m, CH2, 2H), 3.55 (s, 3H, OMe), 4.04 (s, 3H, OMe), 7.45-7.54 (m, 6H), 7.64-7.72 (m, 4H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 21.73 (s, CH$_2$), 22.83 (d, J_{CP} = 9.0 Hz, CH$_2$), 24.72 (d, J_{CP} = 9.0 Hz, CH$_2$), 27.06 (d, J_{CP} = 10.5 Hz, CH$_2$), 49.21 (d, J_{CP} = 115.5 Hz, P=C), 50.36 (s, CH$_3$, OMe), 57.70 (s, CH$_3$, OMe), 91.89 (d, J_{CP} = 86.3 Hz, C), 117.60 (d, J_{CP} = 11.3 Hz, C), 125.62 (d, J_{CP} = 92.3 Hz, 2C), 128.29 (d, J_{CP} = 12.8 Hz, 4CH), 131.29 (d, J_{CP} = 3.0 Hz, 2CH), 133.07 (d, J_{CP} = 10.5 Hz, 4CH), 145.77 (d, J_{CP} = 4.5 Hz, C), 147.19 (d, J_{CP} = 23.3 Hz, C), 158.18 (s, C), 165.97 (b, CO$_2$). HRMS calcd for C$_{25}$H$_{25}$NO$_4$P [M+H]$^+$: 434.1516; found : 434.1478. Anal. Calcd for C$_{25}$H$_{24}$NO$_4$P: C 69.28, H 5.58, N 3.23; found: C 68.93, H 5.64, N 2.96.

*Phosphanaphthalene**2n***

Yellow solid, 131 mg, 33 % yield). ^{31}P NMR (121 MHz, CDCl$_3$): δ 9.5 ppm; ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.48 (s, 3H, Me), 2.55 (s, 3H, Me), 7.04 (t, J= 7.2 Hz, 1H), 7.26-7.32 (m, 1H), 7.44-7.52 (m, 7H), 7.72-7.79 (m, 4H), 7.93(dd, J= 4.2, 7.8 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 14.11 (s, CH$_3$), 28.35 (d, J_{CP} = 9.0 Hz, OMe), 64.32 (d, J_{CP} = 110.3 Hz, P=C), 110.37 (d, J_{CP} = 84.8 Hz, C), 118.22 (d, J_{CP} = 5.3 Hz, C), 121.67 (d, J_{CP} = 8.3 Hz, CH), 123.73 (d, J_{CP} = 12.8 Hz, CH), 126.56 (d, J_{CP} = 95.3 Hz, 2C), 128.57 (d, J_{CP} = 13.5 Hz, 4CH), 131.77 (d, J_{CP} = 3.0 Hz, 2CH), 132.27 (d, J_{CP} = 1.5 Hz, CH), 133.12 (d, J_{CP} = 11.3 Hz, 4CH), 133.20 (d, J_{CP} = 8.3 Hz, CH), 136.46 (d, J_{CP} = 6.0 Hz, C), 148.96 (d, J_{CP} = 25.5 Hz, C), 155.87 (s, C), 188.56 (s, CO). HRMS calcd for $C_{25}H_{21}NO_2P$ [M+H]$^+$: 398.1304; found : 398.1304. Anal. Calcd for $C_{25}H_{20}NO_2P$: C 75.56, H 5.07, N 3.52; found: C 75.92, H 5.12, N 3.39.

*Tervalentphosphanaphthalene**6** and its cycloadduct**7***

The compound **2d** (500 mg, 1.28 mmol) was heated at 260 ºC in anhydrous toluene for 2h. After the disappearance of **2d** (monitored by ^{31}P NMR), 2,3-dimethyl-1,3-butadiene (260 μl, 2.2 mmol) was added and the mixture was stirred for another 1 h at room temperature . Then S_8 was added, the reaction mixture was stirred for another 2 h at 60 ºC. After evaporation of the solvent, the crude mixture was chromatographed on silica gel with petroleum ether/ethyl acetate (4:1) as eluent to give **7** (Yellow solid, 120 mg, 24 % yield). ^{31}P NMR (121 MHz, $CDCl_3$): δ 34.6 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.64 (s, CH_3), 1.77 (s, CH_3), 2.54 (t, J= 16.5 Hz, 1H), 2.90-3.05 (m, 2H), 3.28-3.37 (m, 1H), 3.56(s, 3H), 3.62(s, 3H), 7.47-7.51 (m, 1H), 7.58-7.60 (m, 2H), 8.16-8.23 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.47 (d, J_{CP} = 1.5 Hz, Me), 21.19 (d, J_{CP} = 11.3 Hz, Me), 31.27 (d, J_{CP} = 3.8 Hz, CH_2), 31.86 (s, Me), 39.2 (d, J_{CP} = 53.3 Hz, CH_2), 47.2 (d, J_{CP} = 44.3 Hz, C), 53.43 (s, OMe), 120.68 (d, J_{CP} = 6.8 Hz, C), 121.90 (d, J_{CP} = 7.5 Hz, CH), 124.00 (d, J_{CP} = 9.8 Hz, C), 125.93 (d, J_{CP} = 10.5 Hz, C), 126.70 (d, J_{CP} = 75.8 Hz, C), 126.97 (d, J_{CP} = 3.8 Hz, C), 128.81 (d, J_{CP} = 13.5 Hz, CH), 132.59 (d, J_{CP} = 3.0 Hz, CH), 133.34 (s, C), 133.90 (d, J_{CP} = 10.5 Hz, CH), 155.12 (s, C),166.86 (d, J_{CP} = 5.3 Hz, C). HRMS calcd for $C_{19}H_{21}NO_4PS$ [M+H]$^+$: 390.0923; found : 390.0932. Anal. Calcd for $C_{25}H_{20}NO_4P$: C 69.93, H 4.69, N 3.26; found: C 69.779, H 4.625, N 3.149. Anal. Calcd for $C_{19}H_{20}NO_4PS$: C 58.60, H 5.18, N 3.60; found: C 58.46, H 5.31, N 3.39.

Supplementary information available:

X-ray data for **2a**: CCDC no 1450169, **2c**: CCDC no 1471158 and **7**: CCDC no 1511014.
UV-vis absorption and fluorescence spectra of **2a**-**2e** and NMR spectra of all compounds.

Acknowledgements

This work was supported by the National Natural Science Foundation (21672193, 21272218), Specialized Research Fund for the Doctoral Program of Higher Education (20134101110004) and Zhengzhou University of China.

References

1 (a) X. He, J.-B. Lin, W. H. Kan, S. Trudel and T. Baumgartner, *Org. Lett.*,2014, **16**, 1366-1369; (b) X. He, J.-B. Lin, W. H. Kan, P. Dong, S. Trudel and T. Baumgartner, *Adv. Funct. Mater.*,2014, **24**, 897-906; (c) Y. Ren, W. H. Kan, M. A. Henderson, P. G. Bomben, C. P. Berlinguette, V. Thangadurai and T. Baumgartner, *J. Am. Chem. Soc.*,2011, **133**, 17014-17026; (d) L.-J. Qian, J.-G. Zhi, B. Tong, J.-B. Shi, F. Yang and Y.-P. Dong, *Polymer*,2009, **50**, 4813-4820; (e) M. Yang, L. Chen, C.-S. Zhao, H.-Z. Huang, J.-S. Wang and Y.-Z. Wang, *Polym. Adv. Technol.*,2009, **20**, 378-383; (f) E. Duran, D. Velasco, F. Lopez-Calahorra and H. Finkelmann, *Mol. Cryst. Liq. Cryst.*, 2002, **381**, 43-57.

2C. Romero-Nieto, M. Marcos, S. Merino, J. Barbera, T. Baumgartner and J. Rodriguez-Lopez, *Adv. Funct. Mater.*, 2011, **21**, 4088-4099.

3 Y. Ren, F. Biegger and T. Baumgartner, *J. Phys. Chem. C*,2013, **117**, 4748-4758.

4 P. Gong, K. Ye, J. Sun, P. Chen, P. Xue, H. Yang and R. Lu,*RSC Adv.*, 2015, **5**, 94990-94996.

5 (a) T. Umeyama and H. Imahori, *J. Mater. Chem. A*, 2014, **2**, 11545-11560; (b) Y. Dienes, M. Eggenstein, T. Karpati, T. C. Sutherland, L. Nyulaszi and T. Baumgartner, *Chem. Eur. J.*, 2008, **14**, 9878-9889.

6 (a) D. Joly, P.-A. Bouit and M. Hissler, *J. Mater. Chem. C*, 2016, **4**, 3686-3698; (b) J. Crassous and R. Réau, *Dalton Trans.*,2008, 6865-6876; (c) H. C. Su, O. Fadhel, C. J. Yang, T. Y. Cho, C. Fave, M. Hissler, C. C. Wu and R. Réau, *J. Am. Chem. Soc.*,2006, **128**, 983-995; (d) M. G. Hobbs and T. Baumgartner, *Eur. J. Inorg. Chem.*, 2007, 3611-3628; (e) M. Hissler, P. W. Dyer and R. Réau, *Coord. Chem. Rev.*, 2003, **244**, 1-44.

7 Y. Matano, Y. Hayashi, H. Nakano and H. Imahori, *Heteroat. Chem.*,2014, **25**, 533-547.

8 E. D. Matveeva, D. S. Vinogradov, T. A. Podrugina, T. D. Nekipelova, A. V. Mironov, R. Gleiter and N. S. Zefirov, *Eur. J. Org. Chem.*,2015, 7324-7333.

9 C. Romero-Nieto, A. López-Andarias, C. Egler-Lucas, F. Gebert, J.-P. Neus and O. Pilgram, *Angew. Chem. Int. Ed.*,2015, **54**, 15872-15875.

10 X. Y. Lu, C. M. Zhang and Z. R. Xu, *Acc. Chem. Res.*,2001, **34**, 535-544.

10.1002/ejic.201700011

11 (a) Y. Nishimura, Y. Kawamura, Y. Watanabe and M. Hayashi, *J. Org. Chem.*,2010, **75**, 3875-3877; (b) J. Li, Y. Li, I. Purushothaman, S. De, B. Li, H. Zhu, P. Parameswaran, Q. Ye and W. Liu, *Organometallics*, 2015, **34**, 4209-4217.

12 J. J. Daly, *J. Chem. Soc. A*,1970, 1832-1836.