JOC The Journal of Organic Chemistry

Note

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b02847 • Publication Date (Web): 17 Jan 2020

Just Accepted

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Facile Synthesis of Nitrogen-Containing Six-Membered Benzofuzed Phenophosphazinine Oxides and Studies of the Photophysical Properties

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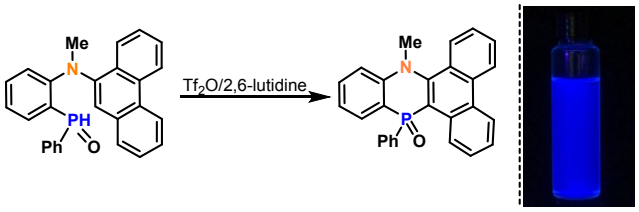
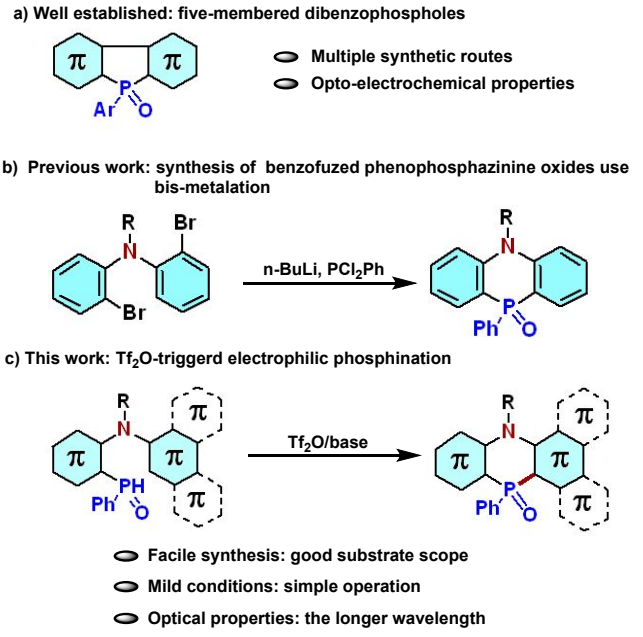
Supporting Information Placeholder



□**BS**□□□□□□ A facile synthesis of nitrogen-containing six-membered benzofuzed phosphacycles has been described. This cyclization reaction triggered by Tf_2O provides an expedient protocol of phosphacycles with simple operation at mild conditions. The preliminary photophysical studies of these novel materials reveal that the fluorescence intensity enhances with the molecular aggregation in the solid state and introduction of sterically bulky phenanthrene group into the phosphacycles allows significantly increase on the fluorescence quantum yield.

π-Conjugated molecular materials with fused aromatic rings, particularly dibenzophospholes have been the focus of considerable interest in the emerging area of organic electronics. They exhibit unique optical and electronic properties thus, have widespread applications in organic light-emitting diodes (OLEDs) and other devices.[1] Recently, several novel strategies have recently been developed for the synthesis of five-membered dibenzophospholes.[2-10] For instance, Kawashima group employed the Et_3B/O_2-mediated intramolecular radical cyclization of phosphine oxide.[3] This moiety can also be prepared through Pd-catalyzed P–H/C–X and P–H/C–H coupling strategies developed by Nozaki[4] and Takai group[5] independently. Meanwhile, C-P bond cleavage was recently applied to synthesize phosphacycles via palladium-catalysed C–P/C–H,[6] C–P/C–X[7] or C–P/C–P[8] couplings. More recently, Tobisu and co-workers elegantly utilized nickel catalysis to cleave two C–P bonds.[9] Unfortunately, the efficient synthesis of six-membered benzofuzed phosphacycles,[11,12] especially the nitrogen-containing phosphacycles still remains a significant synthetic challenge. The classic reaction of organometallic reagents with P–X to afford six-membered phosphacycles was extremely scarce (Scheme 1b),[12] because the incorporation of two aromatic halides in one molecular sometimes was synthetically difficult. Very recently, a bislithiation strategy of aryl bromide followed by trap with $PhPCl_2$ was reported by Samsung Display Co., however, the both aromatic rings should be the exactly the same, which prevent the efficient those nitrogen-containing six-membered phosphacycle derivatives synthesis.[12c] Romero-Nieto group accessed the six-membered phosphacycles via subsequent monolithiation on the aryl halide with $PhPCl_2$ and

Scheme □□ Synthesis of nitrogen-containing six-membered phosphacycles□



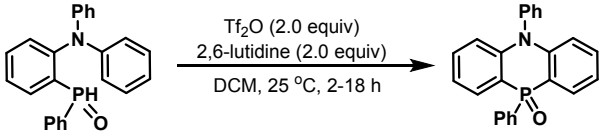
intramolecular Fridel-Crafts reaction，but none of heteroatom containing phosphacycles was synthesized.[11e] Chatani group achieved the Pd-catalyzed dibenzofused six-membered phosphacycle synthesis via C–P cleavage, however, only one

example of nitrogen-containing product was reported.[7] The two aromatic rings tethered with the nitrogen should contain bromide and phosphine functionalities, which may cause a synthetic challenge for preparation of starting material again. More importantly, photophysical properties of this phosphacycles hasn't been systematically investigated. Thereby, it would be great of interest of exploration the efficient synthesis and the examination of unexplored photophysical properties of the nitrogen-containing six-membered benzofuzed phosphacycles.

We recently disclosed the saddle-shaped N,N'-disubstituted-dihydrodibenzo[a,c]phenazines exhibiting the large Storks-shifted red emission due to the VIE (Vibration Induced Emission) Effect. It could be applied as function materials such as single molecule device, biomedical imaging and gelation process.[13] Along with the growing research interest on π-conjugated materials, we seek the possibility to change one of the nitrogen atom to phosphorus and explore the photophysical properties. To address the synthetic gap for six-membered nitrogen-containing benzofuzed phosphacycles, we propose the facile synthesis of the corresponding compound triggered by Tf_2O. Miura group conceived electrophilic phosphinations through the in situ formation of phosphenium cations which was generated with phosphine oxide and Tf_2O through both intermolecular and intramolecular manners to form phosphine-containing heterocycles.[14] Moreover, the Tf_2O promoted electrophilic phosphination was extended to activation of phosphonates for versatile synthesis of phosphonylated scaffolds.[15]

Herein, we report the synthesis of multi-substituted nitrogen-containing phosphacycles under metal-free conditions. (2-(Diphenylamino)phenyl)(phenyl)phosphine oxide □**a** was selected as the model substrate to test the feasibility of electrophilic phosphination, which could be readily prepared via a two-step synthetic sequence via Pd-catalyzed Buchwald–Hartwig amination and lithiation with dichloro(phenyl)phosphane electrophiles. We employed 2.0 equivalent Tf_2O to generate a phosphenium cation intermediate and 2.0 equiv 2,6-lutidine as the acid scavenger. The reaction proceeded in DCM at 25 °C for 2 hours to generate the phenophosphazinine, which was then oxidized by H_2O_2 (aq) to afford the desired phenophosphazinine oxides □**a** in 79% isolated yield (table 1, entry 1). Next, two other organic weak bases including Et_3N and pyridine were ex-

□able □□ □ptimization for the reaction conditions□



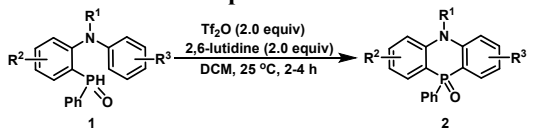
1a **2a**

Entry	Deviation from the standard conditions	Yield (%)[b]
1	none	79
2	Et_3N instead of 2,6-lutidine	59
3	pyridine instead of 2,6-lutidine	61
4	Toluene instead of DCM	53
5	DMF instead of DCM	65
6	1,4-dioxane instead of DCM	67
7	1.5 equiv Tf_2O and 2,6-lutidine instead of 2.0 equiv Tf_2O and 2,6-lutidine	62
8[c]	$Pd(OAc)_2$ instead of Tf_2O/2,6-lutidine	4
9[d]	Et_3B/O_2 instead of Tf_2O/2,6-lutidine	0

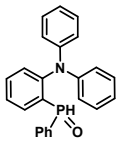
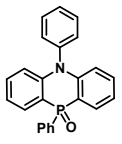
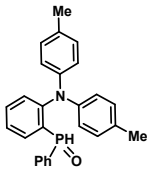
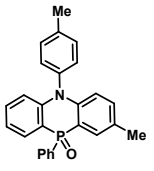
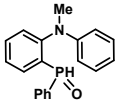
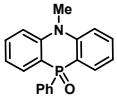
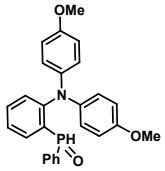
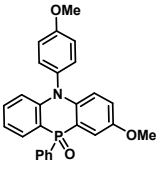
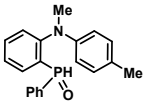
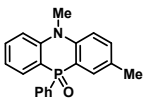
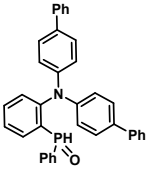
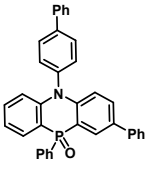
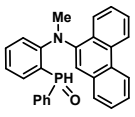
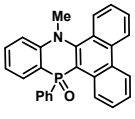
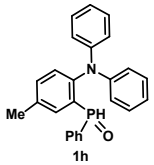
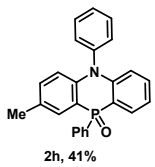
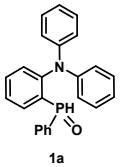
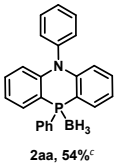
Standard conditions: □**a** (0.1 mmol), Tf_2O (2.0 equiv), 2,6-lutidine (2.0 equiv), DCM (1.0 mL), 25 °C, 2-18 h, then H_2O_2 (2.0 equiv). [b]Isolated yield. [c]$Pd(OAc)_2$ (5 mol%), THF (0.1 mL), 65 °C, 3 h. [d]Et_3B (2.1 equiv), O_2, MeOH (10 mL), 25 °C, 11 h.

amined which obtained a slightly lower isolated yield (entries 2 and 3). Solvent screening revealed that DCM delivered the best results (entries 4-6). Notably, 2.0 equivalence of both Tf_2O and 2,6-lutidine appeared to be crucial for high efficiency as the isolated yield dropped down to 62% when 1.5 equiv Tf_2O was employed (entry 7). We also tested two other reported protocols for benzofuzed phospholes synthesis: the desired □**a** was only obtained in 4% isolated yield with Pd-catalyzed intramolecular C–H phosphination condition, which clearly demonstrated the difficulty for seven-membered palladacycle intermediate formation presumably due to the disfavoured steric effect (entry 8).[5] Meanwhile, the radical strategy initiated by Et_3B/O_2 also failed to afford the desired product (entry 9).[3]

□able □□ Substrate Scope[a]□



1 **2**

Substrate	Product	Substrate	Product
 **1a**	 **2a, 79%**	 **1e**	 **2e, 75%**
 **1b**	 **2b, 73%**	 **1f**	 **2f, 63%**
 **1c**	 **2c, 60%**	 **1g**	 **2g 55%[b]**
 **1d**	 **2d, 75%[b]**	 **1h**	 **2h, 41%**
 **1a**	 **2aa, 54%[c]**		

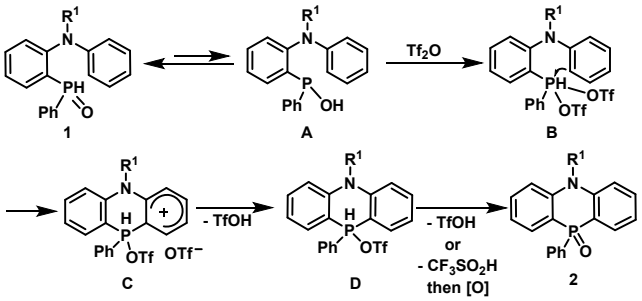
[a]Reaction conditions: □ (1.0 equiv), Tf_2O (2.0 equiv), 2,6-lutidine (2.0 equiv), DCM (0.1 M), 25 °C, then added H_2O_2 (2.0 equiv). Isolated yields are shown. [b]Tf_2O (4.0 equiv), 2,6-

lutidine (4.0 equiv). [c]standard condition followed by reduction with $NaBH_4$, reported herein is two-step isolated yield.

With the optimized conditions in hand, we then investigated the substrate scope for these six-membered nitrogen-containing benzofused phosphacycles synthesis (Table 2). The N-Methyl substituted phosphacycle □**b** could be isolated at 73% yield, which was previously synthesized[7]. The substrates bearing substitutions at the para-position of aromatic rings (4-MeC_6H_4, 4-$OMeC_6H_4$, 4-PhC_6H_4) worked well, delivering the corresponding products □**e**, □**f**, □**g** in moderate to good isolated yield. When the methyl group was introduced to the phenyl ring which is adjacent to the P atom, the desired product □**h** could also be obtained at 41% yield. To our delight, the sterically hindered phenanthrene tethered phosphine oxide □**d** was suitable for this protocol as the desired product □**d** was isolated in 75% yield, which paves the way for potential material studies and demonstrates the generality of this approach. Additionally, □**a** was converted to corresponding phosphine boranes □**aa** in 2 steps via the $NaBH_4$ reduction of phosphine oxide in 54% yield. The structure of phosphine oxide □**a** and phosphine borane □**aa** was confirmed by single-crystal X-ray diffraction.

The tentative reaction pathway is similar to reported literature as depicted in Scheme 2.[14d] First, the nitrogen-containing biarylphosphine oxide □ undergoes tautomerization to the corresponding phosphinic acid intermediate □. Then, Tf_2O activates the OH moiety of □ to generate the highly active electrophilic phosphenium cation equivalent **B**, which was readily trapped by the proximal aromatic ring to form intermediate □, followed by subsequent re-aromatization to deliver the desired dibenzophosphole □, which is finally oxidized by H_2O_2 to provide the desired product □.

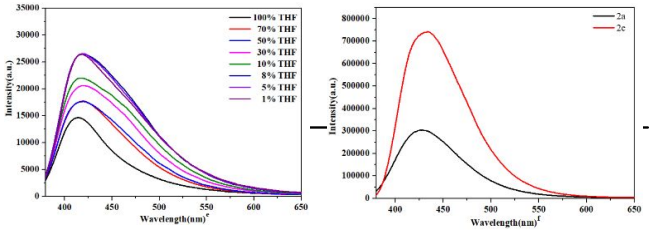
Scheme □□ Plausible path□ay□



The photophysical properties of compound □**a** and □**d** were examined through UV-vis absorption and fluorescence spectroscopy as shown in table 3. Although both compounds possess comparative emission wavelength, the introducing of phenanthrene group in phosphacycles significantly increase the absolute quantum yield either in CH_2Cl_2 solution or solid state. Relative fluorescence quantum yield of compound □**d** is 51.5%, while compound □**a** is 0.5%, which indicates that increasing the π–conjugated system would greatly impact on the quantum yields. The absolute fluorescence quantum yield of □**d** (15.1%) in neat film is also higher than □**a** (2.8%). In addition, we also test the fluorescence intensity in different solvent and realize that the fluorescence intensity increased gradually with the increase of water content (a poor solvent for □**a**), which may attribute to the aggregates in the solid state.[16]

□able □□ Photophysical data for the compound □a and □d□

	λ_{max}(nm)[a]	$\log_\varepsilon$(%)	λ_{em}(nm)[a]	Φ (%)[b]	λ_{em}(nm)[c]	Φ (%)[d]
2a	344	4.18	427	0.5	445	2.8
2d	372	3.78	433	51.5	457	15.1



[a]Measured in DCM. [b]Relative fluorescence quantum yield in DCM, relative to quinine sulfate (H_2SO_4, 0.1 M solution). [c]In neat film. [d]Absolute fluorescence quantum yield in neat film. [e]Fluorescent intensity of □**a** in water–tetrahydrofuran mixtures with different fractions of tetrahydrofuran. [f]Fluorescent intensity of □**a** and □**d** in same concentration.

Theoretical calculations on phospholes □**a** and □**d** were carried out to further investigate the photophysical properties with Gaussian 09 program (Figure 1). The HOMOs show obvious π bonding orbital in six-membered phosphacycles indicating the existence of the π-conjugated system. The HOMOs and LUMOs of molecule □**a** illustrate components of charge-transfer (CT) from nitrogen atom and N-phenyl to the phosphacycles π- conjugate system. The N-phenyl ring almost perpendicular to π-conjugate system to give a dihedral angle of 85°. The twisted intramolecular CT may increase nonradiative relaxation and results to low fluorescence quantum yield.[17] While in molecule □**d**, the CT of molecule □**d** is from nitrogen atom and benzene rings on one side to phenanthrene rings on the other because of the nonsymmetry and absence of phenyl ring, which may contribute the higher quantum yield. Meanwhile, the fluorescence oscillator strength of □**d** is higher than □**a**.

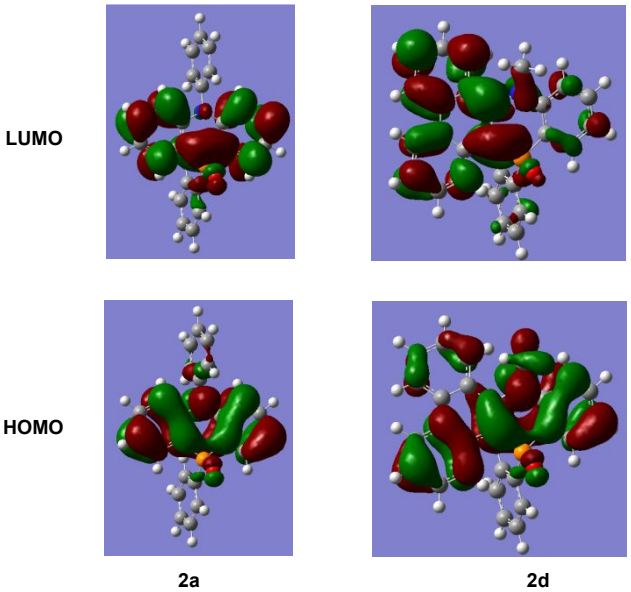


Figure □ Frontier orbitals of □**a**and □**d**(B3LYP/6-31G(d) level of theory).

In conclusion, we report the facile synthesis of nitrogen-containing six-membered benzofuzed phosphacycles. This Tf_2O-promoted electrophilic phosphinative cyclization reaction proceeds with broad substrate scope and overcomes implementation of organometallic reagents. This novel P-containing molecule possesses high quantum yields with introducing the phenanthrene group. Investigations aimed at realising further applications of this benzofuzed phophacycles is still ongoing and will be reported in due course.

Experimental section

□eneral □nformation

All reactions were carried out under nitrogen atmosphere and anhydrous conditions unless otherwise indicated. All manipulations of air-sensitive or moisture-sensitive compounds were performed in a glovebox under an atmosphere of nitrogen. Unless otherwise noted, all catalytic reactions were run in dried glassware. THF were distilled from sodium/benzophenone. DCM was distilled over CaH_2. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.20 mm Huanghai silica gel plates (HSGF 254) using UV light as the visualizing agent. All new compounds were characterized by means of ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR and HR-MS. NMR spectra were recorded using a Bruker AVANCE Ⅲ 400 MHz NMR spectrometer. The UV/Vis spectra were recorded on a Nicolet CARY 100 spectrophotometer. The fluorescence spectra were recorded on Horiba Fluoromax 4 and quantum yields were calculated relative to quinine sulfate (F = 0.577 in 0.2 N H2SO4). Absolute quantum yields were calculated by HAMAMATUS Quantaurus-QY C11347-11. High-resolution mass spectra (HRMS) were recorded on Agilent Technologies 6224 TOF LC/MS using ESI. Single crystal X-ray diffraction data was collected at 193(2) K for □**a** and □**aa** on a Bruker D8 Venture diffractometer. The geometry optimizations were performed using DFT calculations at B3LYP/6-31+G* using Gaussian 09. All ^{1}H NMR, ^{13}C NMR, ^{31}P NMR data are reported in δ units, parts per million (ppm), and using chloroform-d ($CDCl_3$) and DMSO-d_6 as the internal standards. ^{31}P NMR spectra were acquired without ^{1}H decoupling.

□eneral procedure □ for biarylphosphine oxide

To a -78 °C aryl bromide solution in THF (0.3 M) was slowly added ^{n}BuLi (1.1 equiv), and the resulting mixture was stirred at -78 ℃ for 1 h. PCl_2Ph (1.5 equiv) was then added dropwise by a syringe at -78 ℃. The reaction mixture was allowed to slowly warm to 25 ℃ and then stirred for 12 h. The reaction was quenched with water and extracted three times with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The desired product was isolated by column chromatography on silica gel.

□eneral procedure B for biarylphosphine oxide

To a 25 °C aryl bromide solution in THF (0.3 M) was slowly added ^{i}PrMgCl•LiCl(1.1 equiv, 1.3M in THF), and the resulting mixture was stirred at 90 ℃ for 3 h. The mixture was then cool to 25 °C, PCl_2Ph (2.0 equiv) was then added dropwise by a syringe at 25 ℃. The reaction mixture was heated to 90 ℃ and then stirred for 12 h. The reaction was quenched with water and extracted three times with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The desired product was isolated by column chromatography on silica gel.

(2-(diphenylamino)phenyl)(phenyl)phosphine oxide □□**a**□: General procedure A was followed on 2 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 1/1) afforded □**a** as a white solid (499.1 mg, 68%). mp = 258 °C; □$_f$ = 0.44 (PE/EtOAc = 1/1); □□ **NM**□ (400 MHz, $CDCl_3$): δ 8.11 (ddd, *J* = 13.2, 7.6, 1.2 Hz, 1H), 7.58 (d, J_{P-H} = 523.6 Hz, 1H), 7.55–7.45 (m, 4H), 7.42–7.35 (m, 3H), 7.15–7.11 (m, 4H), 7.06 (dd, *J* = 7.2, 5.2 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 2H), 6.72 (d, *J* = 7.6 Hz, 4H); □□□□□ **NM**□ (100 MHz, $CDCl_3$): δ 149.2 (d, *J* = 5.5 Hz), 147.7, 134.2 (d, *J* = 2.3 Hz), 134.2 (d, *J* = 6.8 Hz), 132.3 (d, *J* = 2.7 Hz), 132.2 (d, *J* = 102.9 Hz), 130.6 (d, *J* = 11.8 Hz), 129.8 (d, *J* = 7.5 Hz), 129.5 (d, *J* = 98.0 Hz), 129.3, 128.8 (d, *J* = 13.0 Hz), 126.1 (d, *J* = 11.0 Hz), 123.0, 122.7; □**P NM**□ (162 MHz, $CDCl_3$): δ 15.9 (d, J_{P-H} = 508.1 Hz); □□**MS** □**S**□ (m/z) [M+H]$^+$ calcd. for $C_{24}H_{21}NOP$ 370.1355; found: 370.1355.

(2-(methyl(phenyl)amino)phenyl)(phenyl)phosphine oxide □□**b**□: General procedure A was followed on 0.33 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 1/2) afforded □**b** as a colourless oil (18.6 mg, 20%). □$_f$ = 0.43 (PE/EtOAc = 1/2); □□ **NM**□ (400 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 12.4, 7.6 Hz, 1H), 7.92 (d, J_{P-H} = 501.2 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.53 (dd, *J* = 14.8, 7.2 Hz, 2H), 7.46 (dd, *J* = 13.2, 6.4 Hz, 2H), 7.37 (t, *J* = 6.4 Hz, 2H), 7.15 (dd, *J* = 7.6, 4.8 Hz, 1H), 7.10 (t, *J* = 8.0 Hz, 2H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.40 (d, *J* = 8.4 Hz, 2H), 2.86 (s, 3H); □□□□□ **NM**□ (100 MHz, $CDCl_3$): δ 151.3 (d, *J* = 5.6 Hz), 149.2, 135.0 (d, *J* = 1.1 Hz), 133.9 (d, *J* = 10.3 Hz), 132.1 (d, *J* = 94.5 Hz), 132.2 (d, *J* = 2.0 Hz), 130.4 (d, *J* = 11.9 Hz), 129.1, 128.8, 128.7 (d, *J* = 5.6 Hz), 127.4 (d, *J* = 11.8 Hz), 127.3 (d, *J* = 107.6 Hz), 118.9, 114.2, 40.3; □**P NM**□ (162 MHz, $CDCl_3$): δ 18.1 (d, J_{P-H} = 508.2 Hz); □□**MS** □**S**□ (m/z) [M+H]$^+$ calcd. for $C_{19}H_{19}NOP$ 308.1199; found: 308.1202.

(2-(methyl(p-tolyl)amino)phenyl)(phenyl)phosphine oxide (**c**): General procedure A was followed on 1.75 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 1/3) afforded **c** as a green oil (78.9 mg, 14%). R_f = 0.44 (PE/EtOAc = 1/2); ^{1}H NMR (400 MHz, DMSO-*d6*): δ 7.88 (dd, *J* = 12.8, 7.6, 1H), 7.83 (d, J_{P-H} = 498.8 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H),7.60–7.39 (m, 6H), 7.18 (m, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.30 (d, *J* = 8.4 Hz, 2H), 2.79 (s, 3H), 2.16 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): δ 151.5 (d, *J* = 5.3 Hz), 147.1, 134.9 (d, *J* = 1.5 Hz), 133.6 (d, *J* = 100.2 Hz), 133.0 (d, *J* = 4.9 Hz), 132.0 (d, *J* = 4.7 Hz), 130.0 (d, *J* = 11.9 Hz), 129.2, 128.7 (d, *J* = 12.7 Hz), 128.4 (d, *J* = 7.1 Hz), 127.6 (d, *J* = 118.0 Hz), 127.1, 127.0 (d, *J* = 11.5 Hz), 114.6, 40.3, 20.0; ^{31}P NMR (162 MHz, DMSO-*d6*): δ 15.3 (d, J_{P-H} = 498.7 Hz); HRMS (ESI) (m/z) [M+H]$^+$ calcd. for $C_{20}H_{21}NOP$ 322.1355; found: 322.1359.

(2-(methyl(phenanthren-9-yl)amino)phenyl)(phenyl)phosphine oxide (**d**): General procedure B was followed on 0.58 mmol scale and purification by flash column chromatography on silica gel (EtOAc) afforded **d** as a green oil (94.6 mg, 40%). R_f = 0.56 (EtOAc); ^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.89 (d, *J* = 8.4 Hz, 1H), 8.80 (d, *J* = 7.6 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 7.88–7.84 (m, 1H), 7.82–7.65 (m, 5H), 7.63–7.49 (m, 5H), 7.57 (d, J_{P-H} = 567.2 Hz, 1H), 7.47–7.35 (m, 2H), 7.25 (t, *J* = 6.8 Hz, 1H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): δ 148.8, 147.7, 133.1 (d, *J* = 2.7 Hz), 132.7, 131.9 (d, *J* = 94.6 Hz), 131.3 (d, *J* = 1.9 Hz), 131.0, 130.6, 130.4, 130.2 (d, *J* = 11.4 Hz), 129.7, 129.2, 129.0, 128.8, 128.7, 128.5 (d, *J* = 4.3 Hz), 127.9, 127.6 (d, *J* = 11.7 Hz), 127.2 (d, *J* = 7.9 Hz), 126.3 (d, *J* = 9.6 Hz), 126.3 (d, *J* = 99.6 Hz), 123.8, 123.1, 119.3 (d, *J* = 4.7 Hz), 44.9; ^{31}P NMR (162 MHz, DMSO-*d6*): δ 25.0 (d, J_{P-H} = 567.1 Hz).

(2-(di-p-tolylamino)phenyl)(phenyl)phosphine oxide (**e**): General procedure A was followed on 0.5 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 1/2) afforded **e** as a yellow solid (136.8 mg, 69%). mp = 165 °C; R_f = 0.46 (PE/EtOAc = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (dd, *J* = 12.0, 7.6 Hz, 1H), 7.93 (d, J_{P-H} = 557.2Hz, 1H), 7.78 (dd, *J* = 13.6, 7.6 Hz, 1H), 7.56–7.42 (m, 4H), 7.42–7.31 (m, 2H), 7.02 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 4H), 6.58 (d, *J* = 8.0 Hz, 4H), 2.24 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.7 (d, *J* = 6.3 Hz), 145.6, 134.1 (d, *J* = 3.8 Hz), 132.4, 132.2 (d, *J* = 1.5 Hz), 130.6 (d, *J* = 11.7 Hz), 129.9, 129.2 (d, *J* = 7.4 Hz), 128.9 (d, *J* = 8.6 Hz), 128.7 (d, *J* = 13.0 Hz), 127.6 (d, *J* = 115.1 Hz), 126.0 (d, *J* = 101.7 Hz), 125.5 (d, *J* = 10.6 Hz), 122.8, 20.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.4 (d, J_{P-H} = 511.7 Hz); HRMS (ESI) (m/z) [M+H]$^+$ Calcd for $C_{26}H_{25}NOP$ 398.1668; found: 398.1680.

(2-(bis(4-methoxyphenyl)amino)phenyl)(phenyl)phosphine oxide (**f**): General procedure A was followed on 0.32 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 1/3) afforded **f** as a green oil (69 mg, 54%). R_f = 0.32 (PE/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40– 7.98 (m, 1H), 7.89–7.15 (m, 8H), 6.97–6.91 (m, 2H), 6.82–6.35 (m, 7H), 3.72 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.5, 150.2 (d, *J* = 5.3 Hz), 141.7, 134.2 (d, *J* = 8.3 Hz), 132.4 (d, *J* = 2.9 Hz), 132.3 (d, *J* = 3.4 Hz), 130.9 (d, *J* = 97.4 Hz), 130.6 (d, *J* = 12.0 Hz), 128.7 (d, *J* = 12.6 Hz), 128.4 (d, *J* = 7.4 Hz), 125.9 (d, *J* = 108.6 Hz), 125.0 (d, *J* = 10.2 Hz), 124.2, 114.6, 55.4; ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.4 (d, J_{P-H} = 508.0 Hz); HRMS (ESI) (m/z) [M+H]$^+$ Calcd for $C_{26}H_{25}NO_3P$ 430.1567; found: 430.1573.

(2-(di([1,1'-biphenyl]-4-yl)amino)phenyl)(phenyl)phosphine oxide (**g**): General procedure A was followed on 2.7 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 1/3) afforded **g** as a yellow oil (422 mg, 30%). R_f = 0.52 (PE/EtOAc = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (dd, *J* = 12.4, 7.6 Hz, 1H), 7.75–7.74 (m, 3H), 7.73 (d, J_{P-H} =509.2 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.54–7.51 (m, 5H), 7.44–7.38 (m, 10H), 7.35–7.29 (m, 2H), 7.18 (dd, *J* = 8.0, 5.2 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.7, 140.3, 135.8, 135.4 (d, *J* = 3.8 Hz), 134.9 (d, *J* = 4.7 Hz), 134.4 (d, *J* = 12.3 Hz), 132.4 (d, *J* = 2.8 Hz), 131.6 (d, *J* = 103.6 Hz),130.6 (d, *J* = 12.0 Hz), 130.0 (d, *J* = 7.4 Hz), 128.9, 128.5 (d, *J* = 3.0 Hz), 128.3 (d, *J* = 86.0 Hz), 128.0, 127.1, 126.8, 126.5 (d, *J* = 11.0 Hz), 122.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.0 (d, J_{P-H} = 505.1 Hz); HRMS (ESI) (m/z) [M+H]$^+$: Calcd for $C_{36}H_{29}NOP$ 522.1981; found: 522.1990.

(2-(diphenylamino)-5-methylphenyl)(phenyl)phosphine oxide (**h**): General procedure A was followed on 2 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 1/3) afforded **h** as a white soild (256.8 mg, 33%). mp = 174 °C; R_f = 0.48 (PE/EtOAc = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 12.0 Hz, 1H), 7.60 (dd, *J* = 13.2, 6.4 Hz, 2H), δ 7.58 (d, J_{P-H} = 619.2 Hz,1H), 7.42–7.40 (m, 3H), 7.19 (t, *J* = 6.4 Hz, 4H), 7.12–6.93 (m, 4H), 6.80 (d, *J* = 7.2 Hz, 4H), 2.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.4, 146.3 (d, *J* = 10.7 Hz), 136.1 (d, *J* = 10.6 Hz), 134.9 (d, *J* = 1.1 Hz), 134.0 (d, *J* = 5.9 Hz), 132.1 (d, *J* = 1.5 Hz), 131.7 (d, *J* = 103.3 Hz), 130.3 (d, *J* = 11.9 Hz), 129.6 (d, *J* = 7.9 Hz), 129.0, 128.5 (d, *J* = 12.9 Hz), 122.5, 122.1, 121.8 (d, *J* = 109.3 Hz), 20.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.3 (d, J_{P-H} = 509.0 Hz); HRMS (ESI) (m/z) [M+H]$^+$ Calcd for $C_{25}H_{23}NOP$: 384.1512; found: 384.1513.

General procedure A for six-membered benzofuzed phosphacycles

To a solution of the biarylphosphine oxide in DCM (0.1 M) was added 2,6-lutidine (2.0 equiv) and Tf_2O (2.0 equiv). The reaction mixture was stirred at 25 ℃ for 2 h. The reaction was quenched with H_2O_2 (2.0 equiv) and washed with water. The resulting mixture was extracted three times with DCM. The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The desired product was isolated by column chromatography on silica gel.

General procedure B for six-membered benzofuzed phosphacycles

To a solution of the biarylphosphine oxide in DCM (0.1 M) was added 2,6-lutidine (4.0 equiv) and Tf_2O (4.0 equiv). The reaction mixture was stirred at 25 ℃ for 4 h. The reaction was quenched with H_2O_2 (2.0 equiv) and washed with water. The resulting mixture was extracted three times with DCM. The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The desired product was isolated by column chromatography on silica gel.

5,10-diphenyl-5H-phenophosphazinine 10-oxide (**a**): General procedure A was followed on 0.2 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 1/1) afforded **a** as a white solid (58.1 mg, 79%). R_f = 0.37 (PE/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.75 (m, 4H), 7.72 (t, *J* =7.6 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.51–7.43 (m, 3H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.30 (dt, *J* = 8.0, 1.2 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 2H), 6.52 (dd, *J* = 8.8, 6.0 Hz, 2H);

□□ **NM**□ (100 MHz, $CDCl_3$): δ 145.0 (d, *J* = 4.3 Hz), 140.9, 135.4 (d, *J* = 115.8 Hz), 132.4 (d, *J* = 1.0 Hz), 132.1 (d, *J* = 5.8 Hz), 131.9 (d, *J* = 10.4 Hz), 131.4, 131.4 (d, *J* = 2.8 Hz), 130.7, 129.2, 128.4 (d, *J* = 12.7 Hz), 121.2 (d, *J* = 10.8 Hz), 117.0 (d, *J* = 6.7 Hz), 113.8 (d, *J* = 102.5 Hz); □**P NM**□ (162 MHz, $CDCl_3$): δ 5.1; □□**MS** □**S**□ (m/z) [M+H]+ Calcd for $C_{24}H_{19}NOP$ 368.1199; found: 368.1199.

5-methyl-10-phenyl-5H-phenophosphazinine 10-oxide □□**b**□: General procedure A was followed on 0.19 mmol scale and purification by flash column chromatography on silica gel (EtOAc) afforded □**b** as a white solid (42.4 mg, 73%). R_f = 0.40 (EtOAc); □□ **NM**□ (400 MHz, $CDCl_3$): δ 7.73 (dd, *J* = 13.2, 8.4 Hz, 2H), 7.64–7.49 (m, 4H), 7.43 (td, *J* = 7.2, 1.2 Hz, 1H), 7.35 (td, *J* = 7.2, 2.8 Hz, 2H), 7.23 (dd, *J* = 8.4, 6.4 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 2H), 3.65 (s, 3H); □□□□ **NM**□ (100 MHz, $CDCl_3$): δ 145.5 (d, *J* = 4.2 Hz), 133.8 (d, *J* = 116.9 Hz), 132.9 (d, *J* = 1.6 Hz), 131.6 (d, *J* = 1.1 Hz), 131.4 (d, *J* = 9.9 Hz), 131.2 (d, *J* = 2.3 Hz), 128.4 (d, *J* = 10.8 Hz), 121.3 (d, *J* = 13.3 Hz), 115.4 (d, *J* = 103.6 Hz), 115.2 (d, *J* = 6.2 Hz), 36.8; □**P NM**□ (162 MHz, $CDCl_3$): δ 7.1; □□**MS** □**S**□ (m/z) [M+H]+ Calcd for $C_{19}H_{17}NOP$: 306.1042; found: 306.1049.

2,5-dimethyl-10-phenyl-5H-phenophosphazinine 10-oxide □□**c**□: General procedure A was followed on 0.14 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 1/3) afforded □**c** as a white solid (26.5 mg, 60%). mp = 145 °C; R_f = 0.26 (PE/EtOAc = 1/2); □□ **NM**□ (400 MHz, $CDCl_3$): δ 7.77 (ddd, *J* = 13.2, 7.6, 1.2 Hz, 1H), 7.67–7.51 (m, 4H), 7.48–7.42 (m, 1H), 7.40–7.35 (m, 3H), 7.22 (dd, *J* = 8.0, 6.4 Hz, 1H), 7.15 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.10 (dt, *J* = 7.2, 0.8 Hz, 1H), 3.66 (s, 3H), 2.31 (s, 3H); □□□□ **NM**□ (100 MHz, $CDCl_3$): δ 145.5 (d, *J* = 4.7 Hz), 143.5 (d, *J* = 4.7 Hz), 134.2 (d, *J* = 113.4 Hz), 133.8 (d, *J* = 1.2 Hz), 132.7 (d, *J* = 0.9 Hz), 131.4 (d, *J* = 2.5 Hz), 131.3 (d, *J* = 5.4 Hz), 131.2 (d, *J* = 10.5 Hz), 131.0 (d, *J* = 5.7 Hz), 128.6 (d, *J* = 11.5 Hz), 128.3 (d, *J* = 12.6 Hz), 120.9 (d, *J* = 10.9 Hz), 115.6 (d, *J* = 102.0 Hz), 115.5 (d, *J* = 102.1 Hz), 115.2 (d, *J* = 7.7 Hz), 114.9 (d, *J* = 7.2 Hz), 36.7, 20.2; □**P NM**□ (162 MHz, $CDCl_3$): δ 7.5; □□**MS** □**S**□ (m/z) [M+H]+: Calcd for $C_{20}H_{19}NOP$: 320.1199; found: 320.1205.

9-methyl-14-phenyl-9H-dibenzo[a,c]phenophosphazinine 14-oxide □□**d**□: General procedure B was followed on 0.18 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 1/3) afforded □**d** as a yellow solid (54.9 mg, 75%). mp = 123 °C; R_f = 0.35 (PE/EtOAc = 1/3); □□ **NM**□ (400 MHz, $CDCl_3$): δ 8.65 (d, *J* = 8.0 Hz, 1H), 8.54 (d, *J* = 7.6 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.78–7.63 (m, 4H), 7.53–7.45 (m, 4H), 7.36–7.31 (m, 3H), 7.09 (m, 1H), 3.73 (s, 3H); □□□□ **NM**□ (100 MHz, $CDCl_3$): δ 148.4 (d, *J* = 5.3 Hz), 139.4 (d, *J* = 97.1 Hz), 134.0 (d, *J* = 1.6 Hz), 132.6 (d, *J* = 1.4 Hz), 131.3 (d, *J* = 2.8 Hz), 131.0 (d, *J* = 4.5 Hz), 128.8, 128.5 (d, *J* = 12.5 Hz), 127.9, 127.7 (d, *J* = 8.1 Hz), 127.5, 127.4 (d, *J* = 0.9 Hz), 126.4 (d, *J* = 8.8 Hz), 126.3, 125.8, 123.7, 122.9–122.7 (m), 122.6, 118.6 (d, *J* = 5.4 Hz), 112.5 (d, *J* = 106.3 Hz), 112.4 (d, *J* = 106.5 Hz), 46.7; □**P NM**□ (162 MHz, $CDCl_3$): δ 7.9; □□**MS** □**S**□ (m/z) [M+H]+ Calcd for $C_{27}H_{21}NOP$: 406.1355; found: 406.1368.

2-methyl-10-phenyl-5-(p-tolyl)-5H-phenophosphazinine 10-oxide □□**e**□: General procedure A was followed on 0.2 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 1/3) afforded □**e** as a yellow solid (58.9 mg, 75%). R_f = 0.33 (PE/EtOAc = 1/3); □□ **NM**□ (400 MHz, $CDCl_3$): δ 7.76–7.68 (m, 3H), 7.53 (dd, *J* = 13.6, 1.2 Hz, 1H), 7.50–7.35 (m, 5H), 7.26–7.21 (m, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.07 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.50 (dd, *J* = 8.8, 6.4 Hz, 1H), 6.43 (dd, *J* = 8.8, 6.4 Hz, 1H), 2.50 (s, 3H), 2.18 (s, 3H); □□□□ **NM**□ (100 MHz, $CDCl_3$): δ 145.1 (d, *J* = 4.6 Hz), 143.1 (d, *J* = 4.3 Hz), 139.2, 138.3, 135.5 (d, *J* = 110.5 Hz), 133.8 (d, *J* = 1.5 Hz), 132.4 (d, *J* = 0.9 Hz), 132.1 (d, *J* = 6.0 Hz), 132.0, 131.9 (d, *J* = 10.6 Hz), 131.5 (d, *J* = 5.6 Hz), 131.4 (d, *J* = 2.4 Hz), 130.7 (d, *J* = 10.8 Hz), 130.3, 128.4 (d, *J* = 12.7 Hz), 120.9 (d, *J* = 10.7 Hz), 117.2 (d, *J* = 7.1 Hz), 116.9 (d, *J* = 6.7 Hz), 113.0 (d, *J* = 102.7 Hz), 113.0 (d, *J* = 101.1 Hz), 21.4, 20.3; □**P NM**□ (162 MHz, $CDCl_3$): δ 5.9; □□**MS** □**S**□ (m/z) [M+H]+: Calcd for $C_{26}H_{23}NOP$: 396.1512; found: 396.1523.

2-methoxy-5-(4-methoxyphenyl)-10-phenyl-5H-phenophosphazinine 10-oxide □□**f**□: General procedure A was followed on 0.17 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 1/3) afforded □**f** as a yellow soild (47.1 mg, 63%). R_f = 0.35 (PE/EtOAc = 1/2); □□ **NM**□ (400 MHz, $CDCl_3$): δ 7.72 (tdd, *J* = 13.2, 7.6, 2.0 Hz, 3H), 7.45–7.38 (m, 3H), 7.29–7.24 (m, 1H), 7.23 (t, *J* = 2.4 Hz, 1H), 7.20 (m, 2H), 7.19–7.13 (m, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.89 (dd, *J* = 9.6, 3.2 Hz, 1H), 6.57–6.46 (m, 2H), 3.91 (s, 3H), 3.70 (s, 3H); □□□□ **NM**□ (100 MHz, $CDCl_3$): δ 159.8, 153.9 (d, *J* = 12.6 Hz), 145.2 (d, *J* = 4.3 Hz), 139.9 (d, *J* = 4.2 Hz), 135.6 (d, *J* = 114.5 Hz), 133.6, 132.3 (d, *J* = 1.3 Hz), 131.9 (d, *J* = 5.8 Hz), 131.8 (d, *J* = 10.5 Hz), 131.7, 131.3 (d, *J* = 2.9 Hz), 128.4 (d, *J* = 12.7 Hz), 121.3 (d, *J* = 1.8 Hz), 120.7 (d, *J* = 10.8 Hz), 119.0 (d, *J* = 8.4 Hz), 116.8 (d, *J* = 6.9 Hz), 116.5, 113.9 (d, *J* = 101.2 Hz), 113.0 (d, *J* = 6.2 Hz), 112.6 (d, *J* = 103.3 Hz), 55.8, 55.7; □**P NM**□ (162 MHz, $CDCl_3$): δ 5.9; □□**MS** □**S**□ (m/z) [M+H]+: Calcd for $C_{26}H_{23}NO_3P$: 428.1410; found: 428.1420.

5-([1,1'-biphenyl]-4-yl)-2,10-diphenyl-5H-phenophosphazinine 10-oxide □□**g**□: General procedure B was followed on 0.17 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 1/3) afforded □**g** as a white solid (48.3 mg, 55%). R_f = 0.36 (PE/EtOAc = 1/3); □□ **NM**□ (400 MHz, $CDCl_3$): δ 8.01 (dd, *J* = 14.0, 2.0 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.87–7.70 (m, 5H), 7.65–7.42 (m, 11H), 7.41 – 7.31 (m, 3H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.70 (dd, *J* = 9.2, 6.0 Hz, 1H), 6.64 (dd, *J* = 8.4, 6.4 Hz, 1H); □□□□ **NM**□ (100 MHz, $CDCl_3$): δ 144.9 (d, *J* = 4.1 Hz), 144.3 (d, *J* = 4.5 Hz), 142.3, 139.9, 139.8, 139.5, 135.3 (d, *J* = 93.0 Hz), 134.1 (d, *J* = 9.9 Hz), 132.6 (d, *J* = 0.8 Hz), 132.3 (d, *J* = 4.8 Hz), 132.0 (d, *J* = 10.9 Hz), 131.5 (d, *J* = 1.1 Hz), 131.3, 131.0, 130.2 (d, *J* = 5.2 Hz), 130.1, 129.2, 128.9, 128.5 (d, *J* = 12.6 Hz), 128.2, 127.3, 127.2 (d, *J* = 2.8 Hz), 126.8, 121.4 (d, *J* = 10.1 Hz), 117.8 (d, *J* = 6.5 Hz), 117.2 (d, *J* = 6.4 Hz), 113.8 (d, *J* = 102.1 Hz), 113.7 (d, *J* = 102.1 Hz); □**P NM**□ (162 MHz, $CDCl_3$): δ 5.5; □□**MS** □**S**□ (m/z) [M+H]+ Calcd for $C_{36}H_{27}NOP$: 520.1825; found: 520.1833.

2-methyl-5,10-diphenyl-5H-phenophosphazinine 10-oxide □□**h**□: General procedure A was followed on 0.24 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 1/3) afforded □**h** as a yellow soild (36.4 mg, 41%). mp = 182 °C; R_f = 0.38 (PE/EtOAc = 1/3); □□ **NM**□ (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 13.2, 7.6 , 3H), 7.69 (t, *J* = 7.6 Hz, 2H), 7.62–7.58 (m, 1H), 7.55 (dd, *J* = 13.6, 1H), 7.49–7.39 (m, 3H), 7.36–7.30 (m, 2H), 7.29–7.22 (m, 1H), 7.09 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.46 (dd, *J* = 8.8, 6.0 Hz, 1H), 6.39 (dd, *J* = 8.8, 6.4 Hz, 1H), 2.24 (s, 3H); □□□□ **NM**□ (100 MHz, $CDCl_3$): δ 145.0 (d, *J* = 4.5 Hz), 143.0 (d, *J* = 4.2 Hz),

141.1, 135.6 (d, J = 112.6 Hz), 133.8 (d, J = 1.3 Hz), 132.4 (d, J = 1.0 Hz), 132.2 (d, J = 5.8 Hz), 132.0 (d, J = 10.3 Hz), 131.6 (d, J = 5.6 Hz), 131.4, 131.4 (d, J = 2.9 Hz), 130.9 (d, J = 11.3 Hz), 130.8, 129.2, 128.4 (d, J = 12.6 Hz), 121.0 (d, J = 10.7 Hz), 117.2 (d, J = 7.4 Hz), 116.9 (d, J = 6.5 Hz), 113.4 (d, J = 100.4 Hz), 112.3 (d, J = 96.3 Hz), 20.3. □**P NM**□ (162 MHz, $CDCl_3$): δ 5.5; □□**MS** □**S**□ (m/z) [M+H]$^+$ Calcd for $C_{25}H_{21}NOP$: 382.1355; found: 382.1354.

Synthesis of six-membered benzofuzed phosphacycles-boranes□ To a solution of the □**a** (36.7 mg, 0.1 mmol, 1.0 equiv) in tol (0.2 mL, 0.5 M) was added Oxalyl chloride (12.7 mg, 0.1 mmol, 1.0 equiv) in tol (0.2 mL, 0.5 M) and Tf_2O (4.0 equiv). The reaction mixture was stirred at 25 ℃ for 0.5 h. Sodium borohydride (8.0 mg, 0.21 mmol, 2.1 equiv) in diglyme (0.3 mL, 0.7 M) was added. The reaction mixture was stirred at 25 ℃ for 1 h. The reaction mixture was washed with water, dried over Na_2SO_4 and concentrated in vacuo. The desired product was isolated by column chromatography (PE/EtOAc = 10/1) on silica gel afforded □**aa** as a yellow solid (19.9 mg, 54%).R_f = 0.58 (PE/EtOAc = 10/1); □□ **NM**□ (400 MHz, $CDCl_3$): δ 8.01 (dd, J = 7.6, 1.6 Hz, 1H), 7.98 (dd, J = 7.6, 1.6 Hz, 1H). 7.65 (t, J = 7.6 Hz, 2H), 7.61–7.52 (m, 1H), 7.44–7.39 (m, 2H), 7.36–7.30 (m, 3H), 7.30–7.20 (m, 4H), 7.11 (tdd, J = 7.6, 1.6, 0.8 Hz, 2H), 6.49 (dd, J = 8.4, 3.6 Hz, 2H); □□□□□ **NM**□ (100 MHz, $CDCl_3$): δ 145.3 (d, J = 1.1 Hz), 140.9, 134.3 (d, J = 51.7 Hz), 133.3 (d, J = 13.5 Hz), 132.1 (d, J = 1.6 Hz), 131.3, 131.2 (d, J = 10.1 Hz), 131.0, 130.6 (d, J = 2.4 Hz), 129.2, 128.8 (d, J = 10.0 Hz), 122.1 (d, J = 11.7 Hz), 116.9 (d, J = 4.0 Hz), 108.7 (d, J = 60.8 Hz); □**P NM**□ (162 MHz, $CDCl_3$): δ -11.3; □□**MS** □**S**□ (m/z) [M-BH_3]$^+$: Calcd for $C_{24}H_{18}NP$: 351.1177; found: 351.1179.

Synthesis of □□□□-diphenyl-□□-phenophosphazinine □□-oxide □□a□ in □ mmol scale□ To a solution of the □**a** (369.0 mg, 1.0 mmol, 1.0 equiv) in DCM (10.0 mL, 0.1 M) was added 2,6-lutidine (241.3 mg, 2.0 mmol, 2.0 equiv) under N_2, then dropwise Tf_2O (564.3 mg, 2.0 mmol, 2.0 equiv) with syringe. The reaction mixture was stirred at 25 ℃ for 3 h. The reaction was quenched with H_2O_2 (227.0 mg, 2.0 mmol, 2.0 equiv) and washed with water. The resulting mixture was extracted three times with DCM. The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The desired product was isolated by column chromatography (PE/EtOAc = 1/3) on silica gel afforded □**a** as a white solid (290.1 mg, 79%).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Copies of NMR spectra (PDF)

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by the Youth 1000-Talent Plan Program, East China University of Science and Technology for startup funding, NSFC/China (21421004, 21702060), Shanghai Municipal Science and Technology Major Project (Grant No.2018SHZDZX03) and the Program of Introducing Talents of Discipline to Universities (B16017), and the Fundamental Research Funds for the Central Universities (WJ1814012). The authors thank Research Center of Analysis and Test of East China University of Science and Technology for the help on NMR analysis. Y.C. thanks Prof. Jianhua Su and Prof. Zhiyun Zhang for helpful discussion. The authors thank anonymous reviewer's comments for improving the manuscript.

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