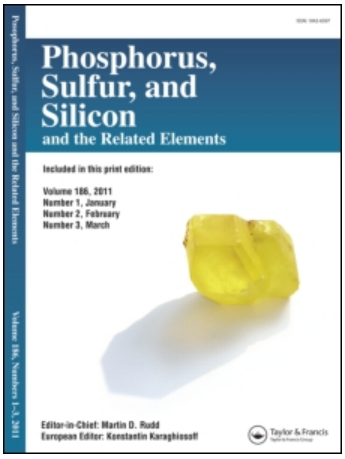

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SYNTHESIS OF NEW BENZOSUBSTITUTED DIOXAPHOSPHONINES CONTAINING QUINOXALINE SUBUNIT

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A simple and efficient synthesis of previously unknown benzosubstituted dioxaphosphonines containing a quinoxaline subunit is described. Reasonably good yields of the products, mild reaction conditions, and convenient work-up are the advantages of this method. The procedure does not require any catalyst or activator and can be efficiently achieved via dianion cyclization. All the synthesized compounds have been characterized by satisfactory elemental analyses and spectral (IR, ^{1}H, ^{13}C, ^{31}P NMR, and mass) studies.

Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.

Keywords Aldimine coupling; dianion cyclization; phosphorus heterocycles; quinoxaline; Schiff base

INTRODUCTION

Organophosphorus[1] compounds continue to be popular targets due to their ubiquity in biological systems[2] and their potential to serve as novel pharmaceutical,[3] agricultural,[4] and chemical agents.[5] The formation of a phosphorus–oxygen bond is one of the most fundamental and important processes for producing useful natural and unnatural compounds in organic synthesis. Quinoxalines have been found to show a wide range of biological activities,[6] such as antiviral, anti-inflammatory, antiprotozoal, anthelmintic, anticancer, antimalarial, antidepressant, and anti-HIV activity.[7] These benzoheterocycles are useful intermediates in organic synthesis, and they can be important structural components in combinatorial drug discovery libraries.[8] Among the various methods available for the synthesis of substituted quinoxalines,[9] we have used the cyanide mediated aldimine coupling reaction[10] to convert the starting Schiff base to quinoxaline derivatives. To the best of our

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knowledge, no example of a quinoxaline-fused, benzosubstituted, nine-membered phosphorus heterocycle has been reported. In continuation of our previous reports on the synthesis of heterocycles via dianion chemistry,[11,12] in this article we report some well-defined examples of dioxaphosphonines containing a quinoxaline subunit via dianion cyclization with the aim that they may have high biological activities and opto-electronic properties.

RESULTS AND DISCUSSION

The adopted strategy for the synthesis of dioxaphosphonines depends on the condensation between o-phenylenediamine and the appropriate aldehydes, to give the corresponding Schiff base (**1**) followed by aldimine coupling[10] to give a 2,3-disubstituted quinoxaline (**2**). Alternatively, quinoxaline **2b** has also been synthesized by microwave irradiation using cyanide as a catalyst in DMF. The reaction was completed in 10 min at 90°C. The crude product was recrystallized from dichloromethane to afford **2b** in good yield (78%). The structures of compounds **2a** and **2b** were established by comparing their spectral data with the literature values.[10] We initially aimed to form a quinoxaline moiety into dibasic Schiff base ligands fused with two benzene units, which was confirmed by the disappearance of a peak for azomethine protons in their ^{1}H NMR spectrum that was present in salophen Schiff base ligands at 8.63 ppm in **1a** and at 8.62 ppm in **1b**. The reaction of quinoxalines (**2**) with sodium in dry isopropanol or with triethyl amine in dry toluene generated the corresponding dianion **A**. The reaction of dianion **A** with the appropriate phosphorus(V) and phosphorus(III) dielectrophiles afforded the nine-membered phosphorus heterocycles

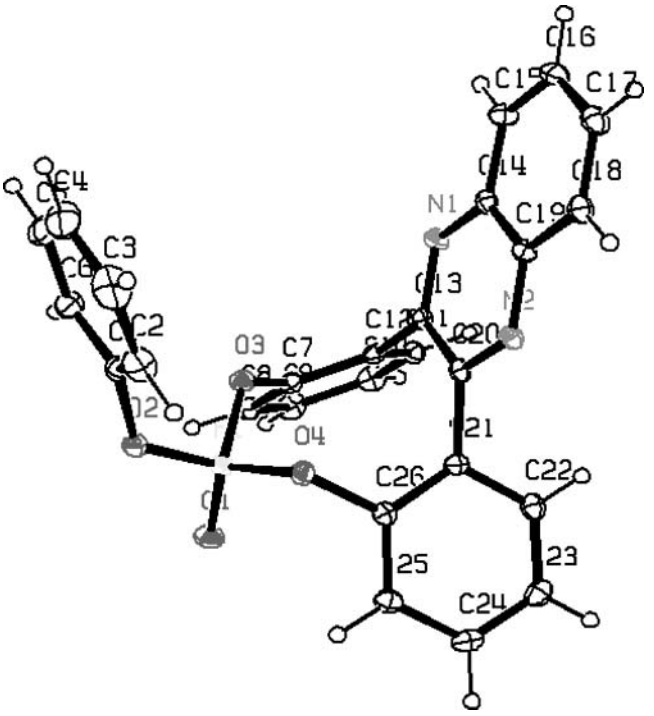
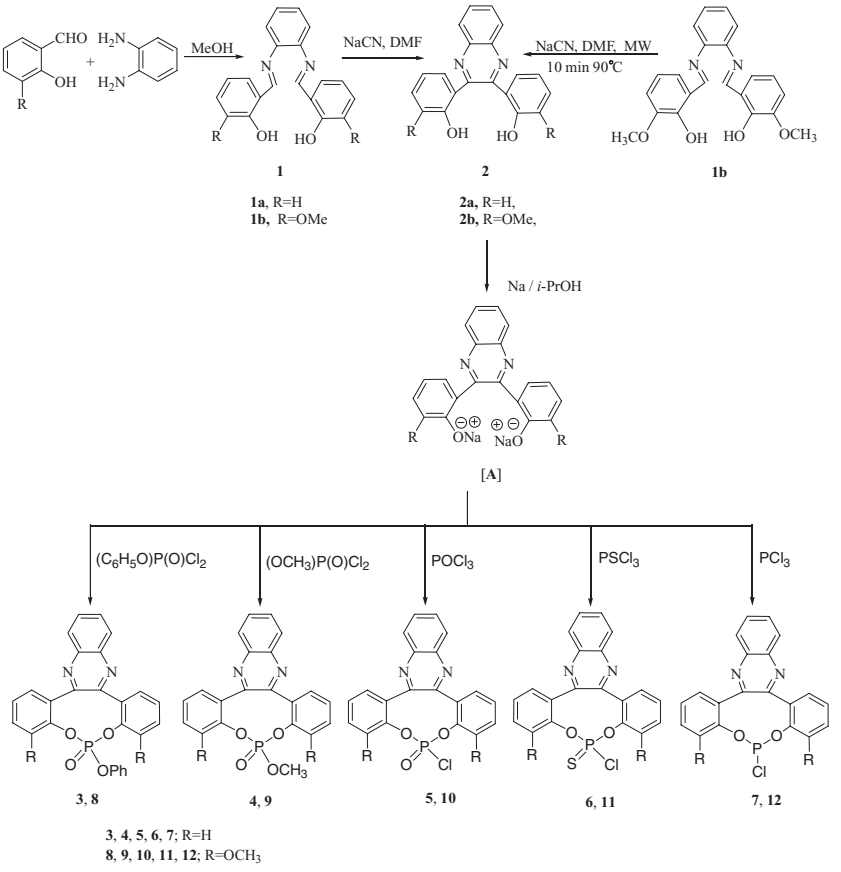


Figure 1 The ORTEP drawing of **3**.

3–12. The reaction proceeds via intermolecular cyclization of the dianion **A** with the phosphorus dielectrophiles. The beauty of the reaction procedure lies in the in situ formation of a remote dianion followed by cyclization so that the multistep reaction sequence occurs in one pot. The synthetic route to novel phosphorus heterocycles is outlined in Scheme 1.



Scheme 1 Synthesis of ligands and phosphorus heterocycles.

^{1}H NMR spectra of all the compounds (**3–12**) indicate the absence of phenolic protons, which was also supported by the absence of characteristic υ (OH) bands in their IR spectra. The proton signals were unambiguously assigned on the basis of their multiplicity, position, and intensity in the ^{1}H NMR spectra. ^{13}C NMR exhibits new signals at 50.3 and 50.7 ppm for methoxy carbons attached to phosphorus in compounds **4** and **9**. The formation of P—O bonds was suggested by the appearance of new bands in the region 1195–1289, 1010–1060, and 950–1000 cm^{-1}, which may be assigned to P=O, P—O—C, and P—O—Ar stretching bands, respectively. ^{31}P NMR spectra of **3–12** show phosphorus resonance signals in the region −10.5 to 32.6 ppm, which supports the insertion of phosphorus in the synthesized compounds. The P—Cl band appears in between 550–500 cm^{-1}, and P=S appears in the region 710–670 cm^{-1}. The mass spectra of these compounds displayed molecular ion peaks at appropriate *m/z* values.

Table I Crystal structure and data refinement parameters

Compound	**3**
Empirical formula	$C_{26}\ H_{17}\ N_2\ O_4\ P$
Formula weight	452.39
Crystal system/space group	Monoclinic/P21/n
a/Å	15.3750(7)
b/Å	9.0273(3)
c/Å	16.9486(3)
α/°	90°
β/°	116.872(3)°
γ/°	90°
V/Å^3	2098.36(14)
Z	4
D_{calc} (g/cm^3)	1.432
μ (mm^{-1})	0.169
Crystal size (mm)	0.28 × 0.21 × 0.18 mm
Color/shape	Golden yellow, block
Temp (K)	150
Theta range for collection	0.954, 0.970
Reflections collected	3672
Goodness of fit on F^2	0.999
Final R indices [$I > 2\sigma(I)$]	0.046(2556)
R indices (all data)	0.1155(3672)

Dibenzodioxaphosphoninoquinoxaline-6-oxide **3** was purified by crystallization from isopropanol, and its structure was confirmed by single crystal X-ray diffraction analysis (Figure 1, Table I).[13] The various crystal stabilizing factors, i.e., intermolecular hydrogen bonding and short contacts, present in the molecule are N(1)···H(22)C(22) = 2.57Å, N(2)···H(10)C(10) = 2.60Å, N(2)···H(18)C(18) = 2.67Å, O(1)···H(6)C(6) = 2.63Å, O(1)···H(25)C(25) = 2.48Å, O(2)···H(8)C(8) = 2.59Å, C(4)H(4)···Cg(C(24)) = 3.88Å, C(15)H(15)···Cg(C(11)) = 3.61 Å, Cg(C(14))···Cg(C(16)) = 3.62 Å. These contacts and interactions provide a rigid 3D arrangement to the molecule. Packing diagrams are shown in Figures S1 and S2 (Supplemental Materials, available online). The structures proposed for these new compounds are consistent with the data obtained from their IR, ^{1}H, ^{13}C, ^{31}P NMR, and mass spectrometry. A supplemental file of bond lengths and angles is included (Tables S1 and S2, available online).

In order to gain an insight into the possible use of the synthesized compounds as opto-electronic devices, the first excited state energies (S_1) and oscillator strength (f) of some compounds are reported (Table II). It is observed that compounds have first excited singlet energy in the visible range exhibiting possibility of fluorescence and phosphorescence, suggesting that such compounds could be used as opto-electronic devices.

Table II First excited state energies (S^1) and oscillator strength (f) of compounds

Compound No.	**2a**	**2b**	**3**	**7**	**8**	**12**
(S^1) eV	410	445	367	444	371	369
(f)	0.06	0.01	0.01	0.01	0.01	0.01

CONCLUSIONS

In summary, an efficient and convenient method for the synthesis of nine-membered benzo-substituted phosphorus heterocycles containing quinoxaline moiety has been established. It is noteworthy that the procedure does not require any catalyst and can be efficiently achieved via dianion cyclization. Also, their first excited state singlet energy values infer reasonable assumption that such compounds may be used as opto-electronic devices, since they would fluoresce in the visible region. So, this article makes a useful contribution in the field of the interesting family of dioxaphosphonine scaffolds.

EXPERIMENTAL

All the chemicals were obtained from Sigma-Aldrich, Merck, Fluka, and Lancaster, and are used as such without further purification. All solvents (AR or extra pure grade) used for spectroscopic and other physical studies were further purified by methods in the literature.[14] All operations were performed under a nitrogen atmosphere using standard glassware. Microwave study was done in a Discover BenchMate System, Make CEM, USA. IR spectra were recorded as KBr discs on a Jasco FT/IR-5300 spectrophotometer. NMR (^{1}H, ^{13}C, and ^{31}P) spectra were recorded on a JEOL AL 300 FT NMR spectrometer using $CDCl_3$ as solvent. All chemical shifts were reported in parts per million (δ) relative to TMS as an internal standard in $CDCl_3$. Mass spectra were recorded at 70 eV ionizing voltage on a JEOL-D300 MS instrument. Combustion analyses were performed on a CE-440 elemental analyzer from Exeter Analytical, Inc. Single crystal X-ray study was performed on an Oxford Diffraction XCalibur-S from National Single Crystal X-ray Diffraction Laboratory, IIT Powai, Bombay, India.

Synthesis of 2,3-Di(2-hydroxyphenyl)quinoxaline (2a)

N,N′-Bis(salicylidene)-*o*-phenylenediamine[10] **1a** (2.00g, 6.3 mmol), NaCN (0.124 g, 2.5 mmol), and DMF (27.5 mL) were stirred in a 100 mL round bottom flask for 48 h at room temperature. After completion of the reaction (monitored by TLC), the reaction mixture was poured onto ice-cold water. The resulting yellow solid was filtered, dissolved in dichloromethane (DCM), and washed with water. The organic layer was dried over anhydrous sodium sulfate and evaporated in vacuo to give 2,3-di(2-hydroxyphenyl)quinoxaline **2a** (1.66 g, 83.8%) as yellow powder; mp 184–186°C; IR (KBr): $\nu = 3510, 1450\ cm^{-1}$;^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.69$–6.65 (m, 2H, ArH), 7.15–7.11 (m, 2H, ArH), 7.28–7.25 (m, 4H, ArH), 7.83–7.78 (m, 2H, ArH), 8.08–8.02 (m, 2H, ArH), 9.91 (s, 2H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 157.1, 151.7, 137.9, 132.2, 131.8, 131.0, 127.9, 120.7, 119.3, 118.6$; MS (ESI) m/z: 315 $[M+H]^+$; Anal. Calcd for $C_{20}H_{14}N_2O_2$ (314.34): C, 76.42; H, 4.49; N, 8.91%, Found: C, 76.51; H, 4.39; N, 8.79%.

Synthesis of 2,3-Di(2-hydroxy-3-methoxyphenyl)quinoxaline (2b)

Method A. N,N′-Bis(*o*-vanillidene)-*o*-phenylenediamine[10] **1b** (2.00g, 5.3 mmol), NaCN (0.145 g, 2.9 mmol), and DMF (27.5 mL) were stirred in a 100 mL round bottom flask for 98 h at 60°C. After completion of the reaction (monitored by TLC), the reaction mixture was poured onto ice-cold water. The resulting yellow solid was filtered, dissolved in DCM,

and washed with water. The organic layer was dried over anhydrous sodium sulfate and evaporated in vacuo to give crude product, which was further purified by recrystallization in methanol to obtain **2b** (1.22 g, 61%), mp 213–215°C.

Method B. Compound 2,3-di(2-hydroxy-3-methoxyphenyl)quinoxaline **2b** has also been synthesized under microwave irradiation. A mixture of N,N′-bis(*o*-vanillidene)-*o*-phenylenediamine **1b** (1.00 g, 2.6 mmol) and NaCN (0.068 g, 1.4 mmol) in DMF (10 mL) was irradiated in a microwave oven for 10 min. After completion of the reaction (monitored by TLC), reaction mixture was poured onto ice-cold water and extracted using DCM. The organic layer was washed with water, dried over anhydrous sodium sulfate, and evaporated in vacuo to obtain **2b** (0.408 g, 78%); mp 214–216°C; IR (KBr) ν 3519, 1464 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.86$ (s, 6H, OCH_3), 6.66–6.61 (t, 2H, $J = 8.0$ Hz, ArH), 6.88–6.82 (m, 4H, ArH), 7.73–7.70 (m, 2H, ArH), 8.02–7.99 (m, 2H, ArH), 9.99 (s, 2H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 152.1$, 148.3, 146.5, 138.9, 130.6, 128.3, 122.9, 122.5, 119.0, 112.8, 56.3; MS (ESI) m/z: 375 $[M+H]^+$; Anal. Calcd for $C_{22}H_{18}N_2O_4$ (374.39): C, 70.58; H, 4.85; N, 7.48%, Found: C, 70.35; H, 4.81; N, 7.62%.

6-Phenoxydibenzo[3,4:8,9][1,3,2]dioxaphosphonino-[6,7-*b*]quinoxaline-6-oxide (3)

2,3-Di(2-hydroxyphenyl)quinoxaline **2a** (0.314 g, 1 mmol) dissolved in dry isopropanol (50 mL) was added to a solution of sodium isopropoxide (generated from 0.046g Na and 2 mL dry isopropanol) in dry isopropanol (10 mL) at −4°C. The reaction mixture was stirred for 4 h at the same temperature. After complete consumption of **2a**, phenyl dichlorophosphate (0.15 mL, 1 mmol) dissolved in dry isopropanol (2 mL) was added slowly at −20°C, and the reaction mixture was stirred for 30 min. The reaction mixture was further stirred at room temperature for 4 h. The precipitate that formed was filtered on a sintered glass crucible (G4), and the solvent was evaporated under reduced pressure. The resulting solid was washed with diethyl ether and recrystallized from isopropanol to give the yellow colored compound, **3** (0.29 g, 64%); IR (KBr): $\nu = 1642$, 1612, 1252, 1181, 978 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.18$–6.74 (m, 17H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 151.8$, 147.6, 147.5, 141.2, 130.7, 129.6, 129.4, 129.0, 126.1, 125.3, 122.2, 121.9, 119.8, 119.7; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = -18.5$; MS (ESI) m/z: 453 $[M+H]^+$; Anal. Calcd for $C_{26}H_{17}N_2O_4P$ (452.40): C, 69.03; H, 3.79; N, 6.19%, Found: C, 69.23; H, 3.91; N, 6.05%.

6-Methoxydibenzo[3,4:8,9][1,3,2]dioxaphosphonino-[6,7-*b*]quinoxaline-6-oxide (4)

Following the procedure described above, 2,3-di(2-hydroxyphenyl)quinoxaline (**2a**) (0.314 g, 1 mmol) and methyl dichlorophosphate (0.1 mL, 1 mmol) afforded **4** (0.265 g, 68%); IR (KBr): $\nu = 1638$, 1602, 1259, 1175, 988 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta =$ 3.82 (s, 3H, $POCH_3$), 8.25–7.17 (m, 12H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 152.6$, 147.1, 146.5, 141.2, 131.6, 129.1, 129.0, 126.1, 122.2, 119.7, 50.3; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = -21.7$; MS (ESI) m/z: 391 $[M+H]^+$; Anal. Calcd for $C_{21}H_{15}N_2O_4P$ (390.33): C, 64.62; H, 3.87; N, 7.18%, Found: C, 64.42; H, 3.49; N, 6.91%.

6-Chlorodibenzo[3,4:8,9][1,3,2]dioxaphosphonino[6,7-*b*]-quinoxaline-6-oxide (5)

Following the procedure described above, 2,3-di(2-hydroxyphenyl)quinoxaline (**2a**) (0.314 g, 1 mmol) and $POCl_3$ (0.1 mL, 1 mmol) gave **5** (0.24 g, 61%); IR (KBr): $\nu = 1634$, 1598, 1273, 1190, 966 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.32–6.77$ (m, 12H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 153.6$, 146.1, 145.5, 143.2, 130.6, 129.9, 129.0, 126.1, 121.2, 117.7; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = -17.8$; MS (ESI) m/z: 395 $[M+H]^+$; Anal. Calcd for $C_{20}H_{12}ClN_2O_3P$ (394.75): C, 60.85; H, 3.06; N, 7.10%, Found: C, 61.08; H, 3.31; N, 6.92%.

6-Chlorodibenzo[3,4:8,9][1,3,2]dioxaphosphonino[6,7-*b*]-quinoxaline-6-sulfide (6)

Following the procedure described above for the preparation of **5**, 2,3-di(2-hydroxyphenyl) quinoxaline (**2a**) (0.314 g, 1 mmol) and $PSCl_3$ (0.1 mL, 1 mmol) afforded **6** (0.258 g, 63%); IR (KBr): $\nu = 1642$, 1612, 1188, 978, 692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.05–6.69$ (m, 12H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 152.4$, 146.3, 144.9, 142.8, 130.2, 129.4, 128.8, 126.3, 121.7, 117.1; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = -14.6$; MS (ESI) m/z: 411 $[M]^+$; Anal. Calcd for $C_{20}H_{12}ClN_2O_2PS$ (410.81): C, 58.47; H, 2.94; N, 6.82%, Found: C, 58.65; H, 3.15; N, 6.61%.

6-Chlorodibenzo[3,4:8,9]dioxaphosphonino[6,7-*b*]quinoxaline (7)

Following the procedure described above for the preparation of **5**, 2,3-di(2-hydroxyphenyl) quinoxaline (**2a**) (0.314 g, 1 mmol) and PCl_3 (0.09 mL, 1 mmol) yielded **7** (0.245 g, 65%); IR (KBr): $\nu = 1637$, 1596, 1177, 992 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.22–6.67$ (m, 12H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 152.9$, 145.8, 145.3, 144.0, 131.3, 129.1, 128.4, 125.1, 121.5, 117.9; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 29.8$; MS (ESI) m/z: 380 $[M+H]^+$; Anal. Calcd for $C_{20}H_{12}ClN_2O_2P$ (378.75): C, 63.42; H, 3.19; N, 7.40%, Found: C, 63.61; H, 3.43; N, 7.21%.

6-Phenoxydiaryl[3,4:8,9][1,3,2]dioxaphosphonino[6,7-*b*]-quinoxaline-6-oxide (8)

To a stirred solution of 2,3-di(2-hydroxy-3-methoxyphenyl) quinoxaline **2b** (0.374 g, 1 mmol) in dry toluene (10 mL), triethyl amine (0.3 mL) was added slowly, and stirring was continued for 1 h. A solution of phenyl dichlorophosphate (0.15 mL, 1 mmol) in toluene (1 mL) was added to reaction mixture and was refluxed for 4 h. The solvent was evaporated in vacuo, and the residue was dissolved in DCM. The organic layer was washed with water followed by brine and dried over anhydrous $MgSO_4$. The solvent was evaporated to give crude product, which was crystallized from ethanol to afford **8** (0.348 g, 68%); IR (KBr): $\nu = 1638$, 1604, 1260, 1176, 965 cm^{-1};^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.88$ (s, 6H, OCH_3), 8.18–6.81 (m, 15H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 152.2$, 147.2, 147.1, 140.6, 131.1, 129.8, 122.7, 122.3, 121.9, 120.3, 119.7, 118.2, 117.5, 57.1; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = -17.6$; MS (ESI) m/z: 513 $[M+H]^+$; Anal. Calcd for $C_{28}H_{21}N_2O_6P$ (512.45): C, 65.63; H, 4.13; N, 5.47%, Found: C, 65.91; H, 4.33; N, 5.61%.

6-Methoxydiaryl[3,4:8,9][1,3,2]dioxaphosphonino[6,7-*b*]-quinoxaline-6-oxide (9)

Following the procedure described above for the preparation of **8**, 2,3-di(2-hydroxy-3-methoxyphenyl)quinoxaline (**2b**) (0.374 g, 1 mmol) and methyl dichlorophosphate (0.1 mL, 1 mmol) gave **9** (0.306 g, 68%); IR (KBr): ν = 1647, 1603, 1264, 1182, 948 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 6H, OCH_3), 3.93 (s, 3H, $POCH_3$), 8.19–6.77 (m, 10H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.2, 147.8, 147.1, 142.2, 131.1, 129.8, 121.9, 121.7, 120.1, 119.3, 57.5, 50.7; ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = −9.8; MS (ESI) m/z: 451 $[M+H]^+$; Anal. Calcd for $C_{23}H_{19}N_2O_6P$ (450.38): C, 61.34; H, 4.25; N, 6.22%, Found: C, 61.52; H, 4.33; N, 6.12%.

6-Chlorodiaryl[3,4:8,9][1,3,2]dioxaphosphonino[6,7-*b*]-quinoxaline-6-oxide (10)

Following the procedure described above for the preparation of **8**, 2,3-di(2-hydroxy-3-methoxyphenyl)quinoxaline (**2b**) (0.374 g, 1 mmol) and $POCl_3$ (0.1 mL, 1 mmol) afforded **10** (0.299 g, 65.9%); IR (KBr): ν = 1637, 1592, 1276, 1194, 973 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 6H, OCH_3), 8.23–6.85 (m, 10H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.8, 147.6, 147.5, 141.2, 130.7, 129.6, 122.2, 121.9, 119.8, 119.7, 57.3; ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = -10.4; MS (ESI) m/z: 456 $[M+H]^+$; Anal. Calcd for $C_{22}H_{16}ClN_2O_5P$ (454.80): C, 58.10; H, 3.55; N, 6.16%, Found: C, 58.45; H, 3.69; N, 5.98%.

6-Chlorodiaryl[3,4:8,9][1,3,2]dioxaphosphonino[6,7-*b*]-quinoxaline-6-sulfide (11)

Following the procedure described above for the preparation of **8**, 2,3-di(2-hydroxy-3-methoxyphenyl)quinoxaline (**2b**) (0.374 g, 1 mmol) and $PSCl_3$ (0.1 mL, 1 mmol) gave **11** (0.296 g, 63%); IR (KBr): ν = 1632, 1602, 1178, 988, 678 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 6H, OCH_3), 8.26–6.76 (m, 10H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.1, 147.2, 146.9, 141.2, 131.3, 128.8, 122.9, 121.3, 120.1, 119.5, 57.5; ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = −16.6; MS (ESI) m/z: 472 $[M+H]^+$; Anal. Calcd for $C_{22}H_{16}ClN_2O_4PS$ (470.87): C, 56.12; H, 3.42; N, 5.95%, Found: C, 56.40; H, 3.61; N, 5.72%.

6-Chlorodiaryl[3,4:8,9]dioxaphosphonino[6,7-*b*]quinoxaline (12)

Following the procedure described above for the preparation of **8**, 2,3-di(2-hydroxy-3-methoxyphenyl)quinoxaline (**2b**) (0.374 g, 1 mmol) and PCl_3 (0.09 mL, 1 mmol) yielded **12** (0.262 g, 60%); IR (KBr): ν = 1633, 1593, 1179, 964 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 6H, OCH_3), 8.29–6.62 (m, 10H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.6, 147.5, 146.2, 140.2, 132.3, 127.8, 122.6, 121.3, 120.6, 119.1, 58.1; ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 32.6; MS (ESI) m/z: 440 $[M+H]^+$; Anal. Calcd for $C_{22}H_{16}ClN_2O_4P$ (438.80): C, 60.22; H, 3.68; N, 6.38%, Found: C, 60.41; H, 3.79; N, 6.52%.

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13. Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication

number CCDC 703302. Copies of the data can be obtained free of charge upon an application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk or at www.ccdc.cam.ac.uk/conts/retrieving.html].

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