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COMMUNICATION

Unusual Phosphine Oxidation: New Triazolopyridyl-Quinolyl Phosphine Oxide Fluorescent Dyes

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3-(2-Pyridyl)-[1,2,3]triazolo[1,5-*a*]quinolylphosphines suffer an unusual phosphine oxidation due to its special geometry that allows a σ -donation of the nitrogen (N1) lone pair to phosphorus. This family of compounds behaves as strong fluorophores with high quantum yields.

The chemistry of [1,2,3]triazolo[1,5-*a*]pyridines **1** or [1,2,3]triazolo [1,5-*a*]quinolines **2** have been reported as a powerful tool in synthetic chemistry (Figure 1).¹⁻⁵ Position 7 in triazolopyridine **1** and 9 in triazoloquinoline **2** can be easily functionalized by means of regioselective lithiation and subsequent trapping with an electrophile.

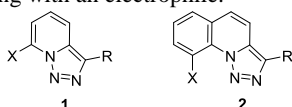
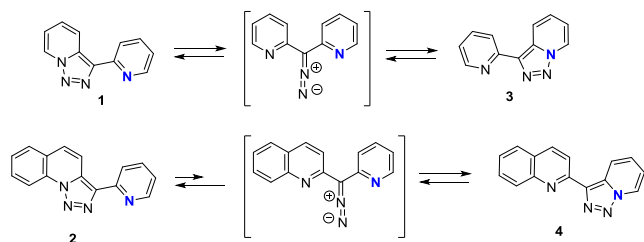


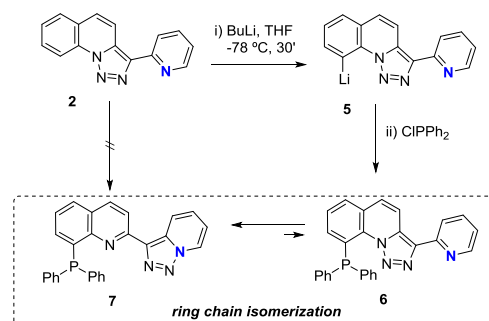
Figure 1.

These systems are in equilibrium with a diazo compound (see Scheme 1).^{6,7} When substituted at position C3 with a pyridyl ring (R = 2-pyridyl), the intermediate diazo compound can undergo cyclization to the five membered ringsystem via two possible nitrogen atoms giving the equilibria **1** \rightleftharpoons **3** or **2** \rightleftharpoons **4**, respectively (Scheme 1). This equilibrium, known as ring-chain isomerization, is controlled by the different substituents (X), either by electronic effects in compound **1**,⁶ or electronic and steric effects in compound **2**.⁷

Scheme 1: Ring-chain isomerization in **1** and **2**.

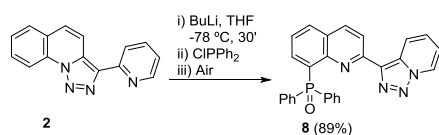
In the framework of our work on triazolopyridines and -quinolines we have studied several applications based on this particular and intriguing ring-chain isomerization including the preparation of fluorescent dyes,⁸ tridentate ligands,⁹ and phosphines based on scaffold **1** (X = PPh₂, PCy₂, P^tPr₂...) as efficient sensors for the electronic profile of phosphines.¹⁰ Furthermore, heterocyclic phosphines represent an unique and efficient family of ligands for homogeneous transition metal-mediated catalysis.¹¹

Following these studies, we become interested in the preparation of phosphine derivatives based on the triazoloquinoline scaffold **2** in order to evaluate the influence of steric and electronic properties of phosphorus in the ring-chain equilibrium. Scheme 2 illustrates our approach towards the phosphine derivative. Regioselective lithiation of **2** gives intermediate **5** which upon treatment with ClPPh₂ should afford phosphine **6**. However, according to our previous studies,⁷ bulky substituents, like a PPh₂-group, should isomerize to a tridentate structure **7** via the ring-chain isomerization.

Scheme 2: Scheduled preparation of **7** by means of ring chain isomerization.

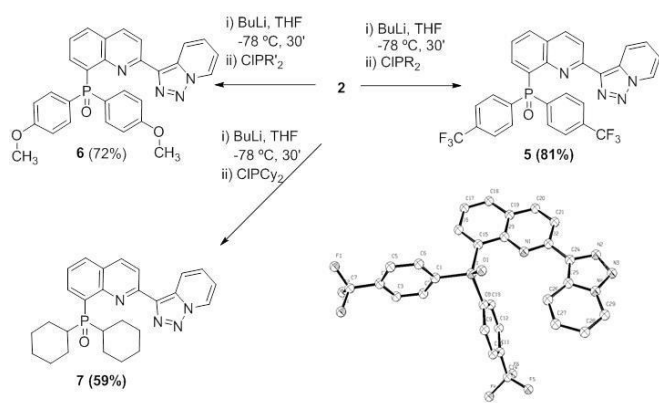
However, when performing the reaction, compound **7** was never observed. In contrast, the corresponding fluorescent phosphine oxide **8** has been obtained in an excellent 89% yield (Scheme 3). Then we prepared a large family of triazolopyridine derivatives bearing different phosphines (*i.e.* **1** with X = P(Ar, Alk)₂). In no case a similar sensitivity towards oxidation has been observed.^{10,12}

It is well known that aromatic tertiary phosphines are air stable, and those bearing deficient heteroaromatic rings (like in the case of triazoloquinoline) should be even more stable towards oxidation.¹³



Scheme 3: Obtention of compound **8**.

Next, due to this uncommon behavior the electronic nature of the ClPR_2 reagent has been modified. When the electron-deficient ($p\text{-CF}_3\text{-Ph}$) $_2\text{PCl}$ has been used phosphine oxide **9** was once again obtained in high yield (81%). We were able to obtain suitable single crystals and perform X-ray diffraction studies which confirmed the presence of a phosphine oxide on a tridentate structure (Scheme 4).



Scheme 4: Preparation of compounds **9**, **10** and **11**. ORTEP view of compound **9**. R = $p\text{-CF}_3\text{-Ph}$, R' = $p\text{-H}_3\text{CO-Ph}$.

Employing similar conditions, now with more electron-rich phosphines, the corresponding phosphine oxide were isolated in moderate yields. With a *para*-methoxyphenyl group, compound **10** has been obtained in 72% yield, and with cyclohexyl phosphine compound **11** in 59% (Scheme 4). The NMR spectra of the ring-chain isomerized compounds **8-11** show the characteristic coupling constants for H7 ($J = 7$ Hz) and H4 ($J = 9$ Hz) of triazolopyridines (Figure 2).^{6a,7}

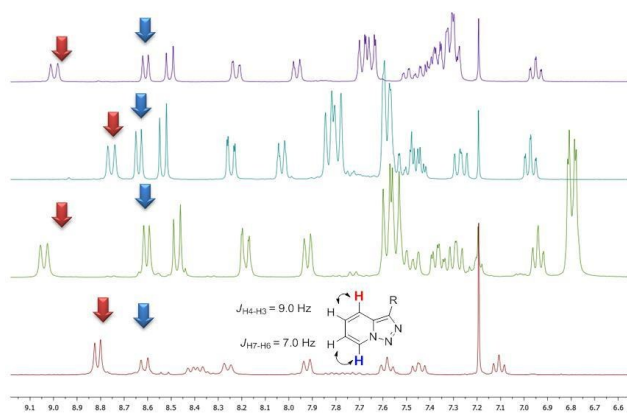
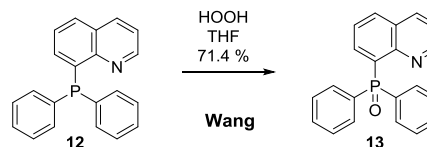


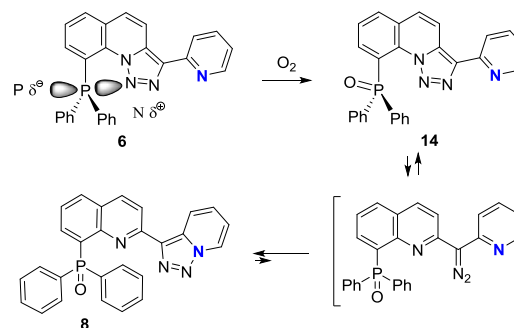
Figure 2: $^1\text{H-NMR}$ spectra (aromatic domain) of **8**, **9**, **10** and **11** (from top to bottom).

$^{31}\text{P-NMR}$ also indicates the presence of a phosphine oxide for all derivatives ($^{31}\text{P NMR}$: **8**: $\delta = 31.9$ ppm, **9**: $\delta = 28.0$ ppm, **10**: $\delta = 30.6$ ppm and **11**: $\delta = 48.1$). These values are within the range of phosphine oxides. Noteworthy, the oxidation of arylphosphines require in general oxidants and normally it does not take place under atmospheric conditions. Wang *et al.* reported the oxidation of phosphine **12** employing excess H_2O_2 as oxidant leading to **13** in 72% yield (Scheme 5).¹⁴ The structure of compound **12** resembles the non-oxidized triazoloquinoline derivatives (**7**). However, in our case air (introduced during the work up) induced rapid oxidation of the formed phosphines.



Scheme 5: Wang methodology for the oxidation of compound **12**.

To explain why the spontaneous oxidation in the case of 3-(2-pyridyl)-9-triazoloquinolylphosphines occurs, we suppose that isomers **6** have a particular geometry in which a preferential conformation with σ -donation of the nitrogen (N1) lone pair towards phosphorus becomes possible. This leads to an increased electron-density at phosphorus and makes it more susceptible for oxidation towards oxide **14**. Next, ring-chain isomerization to structure **8** happens (Scheme 6).



Scheme 6: Proposed mechanism for the formation of **8**.

This feature has been employed by Verkade,¹⁵ for the preparation of extremely basic (electron-rich phosphorus) compounds presenting high sensitivity towards molecular oxygen in contrast to air stable triphenylphosphine.

Heterocyclic P-N ligands and their corresponding oxides have significant applications in catalysis and as chemosensors.¹⁴ Therefore, we studied the fluorescence properties of these novel compounds. In the past we have reported on triazolopyridine and triazoloquinoline derivatives as excellent chemosensors but moderate quantum yields.⁷⁻⁹ However, any of our previous triazolopyridyl phosphine derivatives gave significant emission.¹⁰ The corresponding measured emission properties of compounds **8-11** are reported in Table 1. Surprisingly, all of them exhibited intense emission upon irradiation at its higher absorption band.

Table 1: λ_{exc} and λ_{em} in nm.

Entry	Compound	λ_{exc} (nm)	λ_{emi} (nm)	Quantum yield ^a ϕ_F
1	1	359	411	0.01
2	2	358	397	0.13
3	8	376	423	0.54
4	9	380	427	0.60
5	10	375	419	0.48
6	11	369	404	0.34

a) Quantum yield: ratio of the number of emitted photons to the number of absorbed photons. Solutions were prepared $5 \cdot 10^{-5}$ M in ethanol. Quantum yield was determined with a Hamamatsu-PHA equipment.

Compounds **8-10** have high quantum yields (Table 1 entry 3, 4 and 5) when compared with parent compounds **1** or **2**. Another tendency is that electron-donating substituents on the aromatic phosphine substituent induce a hypsochromic shift of 4 nm (comparing **8**: 423 nm with **10**: 419 nm), and more electron-rich systems like **11** present a higher shift (19 nm for **11**). The electron-withdrawing trifluoromethyl group in **9** induces a more significant opposed effect (bathochromic shift) of 4 nm. In Figure 3, the emission spectra are presented as well as a picture of the emission of compounds **11** (left) and **10** (right).

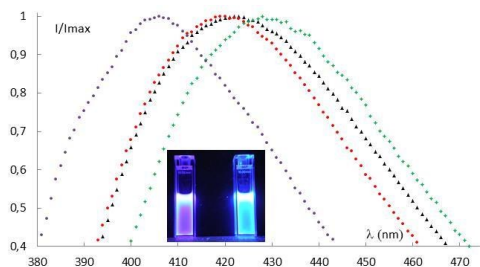


Figure 3: Normalized maximum emission spectra for compounds **8** (black), **9** (green), **10** (red) and **11** (violet). Inset compounds **11** and **10** (10^{-5} M in ethanol)

In order to analyse the viability as sensors for metals we first studied the luminescent behaviour of the compounds in presence of Zn(II) and Cu(II).⁹ While no changes were observed for Zn(II), Cu(II) induced a quenching of the fluorescence (Figure 4) of all compounds.¹⁶ Among them, **10** and **11** have the highest binding constants (Table 2) experimenting a complete quenching upon the addition of two equivalents of copper solution.

Table 2: Binding constants¹⁷ with copper.

	8	9	10	11
logK	4.05(1)	4.56(8)	4.836(8)	5.016(8)

Solutions of compounds **8-11** were prepared $5 \cdot 10^{-5}$ M in ethanol (2 mL sample), $[Cu^{2+}]$ 0.00494 M in water. Values in parenthesis are standard deviations in the last significant figure,

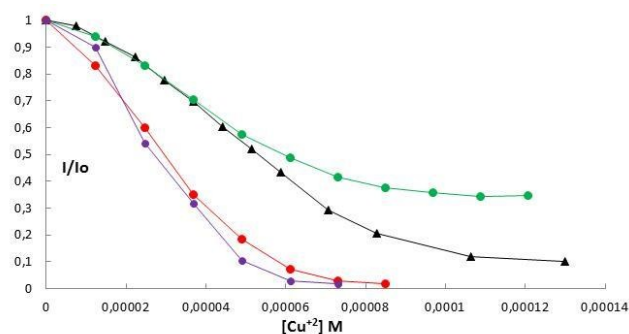


Figure 4: Normalized maximum emission quenching spectra upon the addition of Cu^{2+} (0.004945 M in water) for compounds **8** (black), **9** (green), **10** (red) and **11** (violet) $5 \cdot 10^{-5}$ M in ethanol.

Moreover, a more exhaustive study was performed with **11** to find out if the fluorescence response was selective for copper.¹⁸ Figure 5 shows the normalized emission intensities after the addition of Zn(II), Co(II), Ni(II), Cu(II), Mn(II), Pb(II), Cd(II), Ag(I), Fe(II) and Fe(III) solutions to an ethanolic solution of **11**. Complete fluorescence quenching is exclusively observed with Cu(II) (blue columns); addition of 3 equivalents of the other metal ions tested (black columns) does not produce any change. However, it is important to remark that in almost all cases the presence of 3 eq. of the other metal ions does not disturb the quenching when copper(II) is subsequently added (red columns). Only Fe(II) and Fe(III) do present interference. Finally, the addition of aqueous ammonia to solutions of **11** with 3 equivalents of Cu(II) avoids the quenching (by copper ammonia complexation, green column) See figures S14-S24 for full spectra.

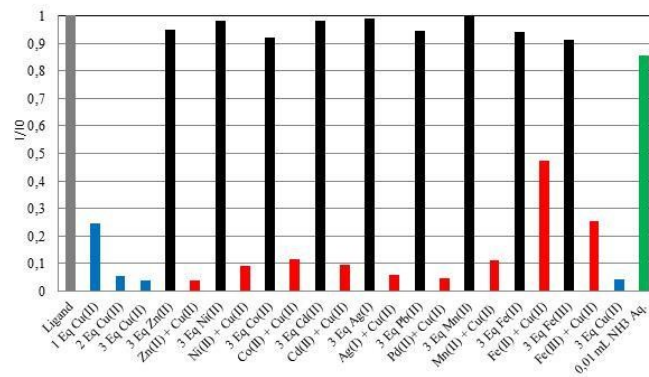


Figure 5: Normalized emission quenching spectra (404 nm) of ligand **11** ($5 \cdot 10^{-5}$ M in ethanol) upon the addition of different metals (black lines) for compound **11** (3 mL $2.98 \cdot 10^{-5}$ M, grey). Copper tests are reported in blue, Mixed (3 Eq. of M^{n+} + 3 Eq. of $Cu(II)$) are reported in red, and ammonia ligand displacement in green.

Conclusions

We have reported on a spontaneous oxidation of pyridyltriazoloquinolyl phosphines affording strong fluorophores able to sense copper with high binding constants. This oxidation can be rationalized by means of a hypervalent phosphorus atom that can be present due a particular conformational arrangement

which increases the electron density at phosphorus. The electron enriched phosphorus atom becomes highly air sensitive and oxidizes spontaneously. Next, a ring-chain isomerization provides the fluorescent compounds. These compounds have been shown as good copper sensors. Compound **11** has been studied more in detail and has shown high selectivity for copper even in presence of other transition metals.

Experimental

3-(Pyridin-2-yl)-[1,2,3]triazolo[1,5-*a*]quinolone 2 was synthesized as described.⁷

General procedure for the preparation of compounds 8-11. At -78 °C, butyllithium (1.6 mL, 2.2 mmol, 1.1 eq) in hexanes (1.5M) was added dropwise to a solution of 3-(pyridin-2-yl)-[1,2,3]triazolo[1,5-*a*]quinoline **2** (0.5 g, 2.0 mmol, 1.0 eq.) in tetrahydrofuran (50 mL). The mixture was kept for 30 min at -78 °C before a solution of the corresponding Ar₂PCl (2.3 mmol, 1.2 eq) in tetrahydrofuran (1 mL) was added and allowed to reach 25 °C (1 h). Then a saturated aqueous solution of ammonium chloride (20 mL) was added. The resulting mixture was extracted with dichloromethane (3×10 mL). The organic extracts were combined, washed with brine (10 mL), dried over sodium sulphate, filtered, and concentrated. Sonication with ethyl acetate (40 mL, 1 minute) provided the phosphine oxides **8-11**.

2-([1,2,3]Triazolo[1,5-*a*]pyridin-3-yl)-8-(diphenylphosphoryl)quinoline 8. Yellow powder (0.8 g, 89%). mp 241 °C decomp. ¹H NMR (300 MHz, CDCl₃): δ = 9.06 (d, *J* = 8.9 Hz, 1H), 8.68 (d, *J* = 6.9 Hz, 1H), 8.57 (d, *J* = 8.7 Hz, 1H), 8.29 (dd, *J* = 8.7, 1.1 Hz, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.8-7.7 (m, 4H), 7.6-7.3 (m, 9H), 7.02 (ddd, *J* = 6.8, 6.8, 0.7 Hz, 1H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 152.1 (C), 148.8 (d, *J* = 4.4 Hz, C), 137.3 (d, *J* = 10.5 Hz, CH), 137.0 (d, *J* = 21.0 Hz, C), 136.9 (CH), 133.9 (C) 133.0 (d, *J* = 2.7 Hz, CH), 132.7 (d, *J* = 20.6 Hz, 2C), 132.0 (d, *J* = 9.9 Hz, 4CH), 131.5 (d, *J* = 2.9 Hz, 2CH), 130.8 (d, *J* = 1.4 Hz, C) 128.4 (d, *J* = 12.3 Hz, 4CH), 127.7 (d, *J* = 7.1 Hz, C), 127.1 (CH), 125.0 (d, *J* = 13.7 Hz, CH), 124.7 (CH), 122.6 (CH), 119.9 (CH), 116.3 (CH). ³¹P NMR (161 MHz, CDCl₃): δ = 31.0 (PO). MS (EI): *m/z* (%) = 446(10), 418(52), 417(100), 340(19). HRMS ESI-[TOF] for C₂₇H₁₉N₄OP: calcd. 446.1296; found 446.1300.

2-([1,2,3]Triazolo[1,5-*a*]pyridin-3-yl)-8-bis(4-trifluoromethylphenyl)phosphoryl)quinoline 9. Yellow powder (0.5 g, 81%). mp 247–250 °C decomp. ¹H NMR (300 MHz, CDCl₃): δ = 8.75 (d, *J* = 8.9 Hz, 1H), 8.64 (d, *J* = 7.0 Hz, 1H), 8.53 (d, *J* = 8.7 Hz, 1H), 8.25 (dd, *J* = 8.7, 1.5 Hz, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 11.7 Hz, 2H), 7.80 (d, *J* = 11.8 Hz, 2H), 7.62-7.54 (m, 4H), 7.55-7.41 (m, 2H), 7.27 (dd, *J* = 8.9, 6.8 Hz, 1H), 6.97 (dt, *J* = 6.8, 6.8, 1.1 Hz, 1H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 152.6 (C), 148.7 (d, *J* = 4.4 Hz, C), 137.9 (C), 137.3 (d, *J* = 10.5 Hz, CH), 137.0 (d, *J* = 1.0 Hz, CH), 136.9 (d, *J* = 30.0 Hz, C), 136.5 (C), 133.93 (CH), 133.9 (CH), 133.7 (qd, *J* = 30.4, 30.4, 30.4, 1.1 Hz, 2×C), 132.7 (C), 132.4 (d, *J* = 10.2 Hz, 4×CH), 127.7 (d, *J* = 7.4 Hz, 2×C), 127.6 (C), 127.3 (CH), 127.4 (q, *J* = 280.1 Hz, 2×C), 125.4 (dq, *J* = 11.1, 3.7, 3.7, 3.7 Hz, 4×CH), 125.1 (CH), 121.7 (CH), 120.5 (CH), 116.4 (CH). ³¹P NMR (161 MHz, CDCl₃): δ = 28.0 (PO). MS (EI): *m/z* (%) = 582(12), 555(43), 554(100), 553(80), 533(47), 409(33), 355(50), 338(38). HRMS ESI-[TOF] for C₂₉H₁₇F₆N₄OP: calcd. 582.1044; found 582.1048.

2-([1,2,3]Triazolo[1,5-*a*]pyridin-3-yl)-8-bis(4-methoxyphenyl)phosphoryl)quinoline 10: Pale colourless needles (0.4 g, 72%). mp 260 °C decomp. ¹H NMR (300 MHz, CDCl₃): δ = 9.11 (d, *J* = 8.9 Hz, 1H), 8.67 (d, *J* = 7.0 Hz, 1H), 8.54 (d, *J* = 8.7 Hz, 1H), 8.25 (dd, *J* = 8.7, 1.2 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.69-7.58 (m, 4H), 7.59-7.49 (m, 1H), 7.43 (dt, *J* = 7.7, 7.4, 2.3 Hz, 1H), 7.35 (dd, *J* = 8.3, 7.2 Hz, 1H), 7.00 (t, *J* = 6.8, 6.8 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.0 Hz, 4H), 3.75 (s, 6H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 162.0 (d, *J* = 2.8 Hz, 2×C), 152.1 (C), 150.0 (d, *J* = 4.4 Hz, C), 137.4 (C), 137.2 (d, *J* = 10.5 Hz, CH), 136.7 (CH), 133.8 (d, *J* = 11.3 Hz, 4×CH), 132.8 (d, *J* = 2.6 Hz, CH), 131.8 (C), 130.4 (C), 127.6 (d, *J* = 7.0 Hz, 2×C), 127.1 (CH), 125.7 (C), 125.0 (d, *J* = 13.7 Hz, CH), 124.7

(CH), 124.2 (C), 122.8 (CH), 119.7 (CH), 116.4 (CH), 113.9 (d, *J* = 13.4 Hz, 4×C), 55.2 (s, 2C). ³¹P NMR (161 MHz, CDCl₃): δ = 30.6 (PO). MS (EI): *m/z* (%) = 506(12), 478(37), 477(100), 462(22). HRMS ESI-[TOF] for C₂₉H₂₃N₄O₃P: calcd. 506.1508; found 506.1504.

2-([1,2,3]Triazolo[1,5-*a*]pyridin-3-yl)-8-(dicyclohexylphosphoryl)quinoline 11: Pale yellow needles (0.3 g, 59%). mp 235 °C decomp. ¹H NMR (300 MHz, CDCl₃): δ = 8.88 (app d, *J* = 7.2 Hz, 2H), 8.68 (d, *J* = 8.5 Hz, 1H), 8.46 (dd, *J* = 11.8, 6.8 Hz, 1H), 8.32 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.65 (t, *J* = 7.4, 7.4 Hz, 1H), 7.51 (dd, *J* = 8.6, 7.0 Hz, 1H), 7.17 (t, *J* = 6.8, 6.8 Hz, 1H), 2.9-2.7 (m, 2H), 2.4-2.2 (m, 2H), 1.9-0.8 (m, 18H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 151.7 (C), 147.6 (C), 137.9 (d, *J* = 5.6 Hz, CH), 137.7 (d, *J* = 2.2 Hz, CH), 137.6 (d, *J* = 20.1 Hz, C), 137.5 (C), 131.9 (d, *J* = 1.5 Hz, CH), 131.8 (C), 127.3 (d, *J* = 7.2 Hz, C), 126.8 (d, *J* = 0.8 Hz, CH), 125.9 (CH), 125.7 (d, *J* = 10.2 Hz, CH), 119.9 (CH), 119.9 (CH), 116.1 (CH), 38.2 (d, *J* = 67.1 Hz, 2×CH), 26.7 (d, *J* = 3.5 Hz, 2×CH₂), 26.6 (2×CH₂), 26.0 (d, *J* = 3.6 Hz, 2×CH₂), 25.7 (4×CH₂). ³¹P NMR (161 MHz, CDCl₃): δ = 48.1 (PO). MS (EI): *m/z* (%) = 458(39), 430(47), 376(31), 348(30), 347(30), 301(22), 267(100), 266(30), 265(45), 219(36), 218(29). HRMS ESI-[TOF] for C₂₉H₃₁N₄OP: calcd. 458.2235; found 458.2229.

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Electronic Supplementary Information (ESI) available: General conditions, details of the synthesis, NMR spectroscopic data, crystallographic data for CCDC 1031770 and fluorescence titrations. DOI: 10.1039/c000000x/

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