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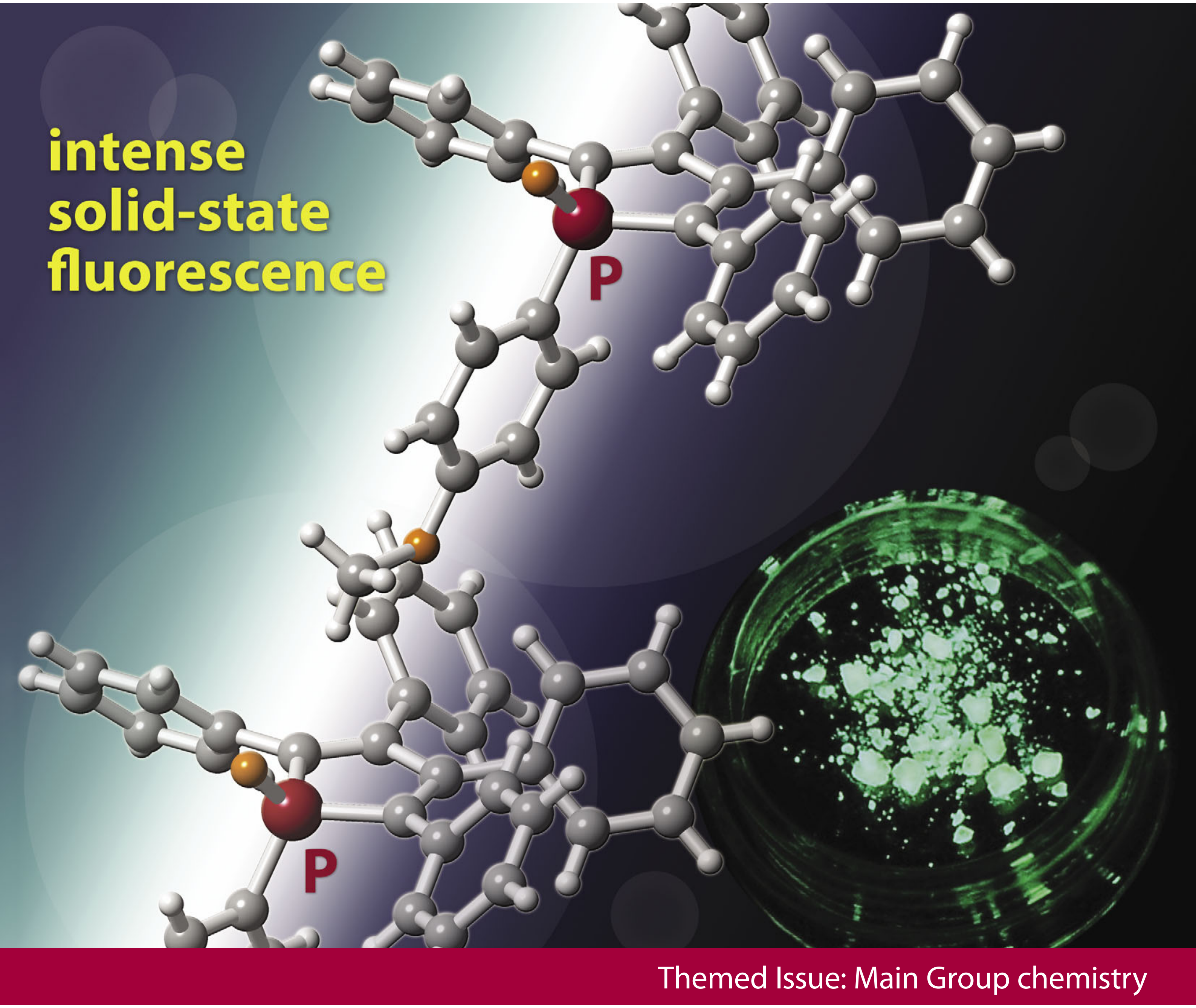

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LETTER
Shigehiro Yamaguchi *et al.*
Intense fluorescence of
1-aryl-2,3,4,5-tetraphenylphosphole
oxides in the crystalline state

Intense fluorescence of 1-aryl-2,3,4,5-tetraphenylphosphole oxides in the crystalline state†‡§

Aiko Fukazawa, Yasunori Ichihashi and Shigehiro Yamaguchi*

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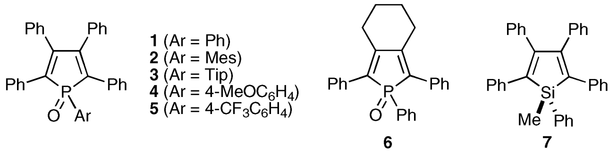
A series of 2,3,4,5-tetraphenylphosphole oxides with various aryl groups on the phosphorus atoms were synthesized and their fluorescence properties in the crystalline state were investigated. Some of these compounds showed an intense fluorescence with the quantum yields of 0.75–0.91. These intense emissions are attributable not only to the restricted rotation of the peripheral phenyl rings, but also to the long intermolecular distances between the adjacent molecules in the crystal packing.

π-Conjugated molecules are undoubtedly key components in the field of organic electronics. Their solid-state fluorescence properties are of particular importance for optoelectronic applications, such as organic LEDs and organic lasers. While there are many π-conjugated molecules that exhibit an intense fluorescence in a dilute solution, their fluorescence is usually substantially quenched in the solid state.[1] So far, several approaches to gain an intense solid-state emission have been reported, such as dendritic substituent protection,[2] cross dipole stacking,[3] aggregation-induced emission,[4–6] enhanced intramolecular charge transfer transition,[7] and *J*-aggregate formation.[8]

Meanwhile, the incorporation of the main group elements into a π-conjugated framework is a powerful strategy to develop new π-electron materials with intriguing properties.[9] Phosphole, a heavier analogue of pyrrole, has especially attracted attention due to its unique electronic structure, *i.e.*, its weak aromaticity and low-lying LUMO.[10] One fascinating feature of the phospholes is the chemical functionalization diversity on the phosphorus atom, which significantly affects the optical and electrochemical properties. A variety of phosphole-containing π-conjugated compounds have been synthesized and their interesting properties have been revealed. For example, Réau and co-workers reported the photo- and electroluminescences of the 2,5-diarylphospholes, including the phosphole sulfide derivatives and gold complexes.[11] Recently, an enhanced fluorescence of the dendritic phosphole derivatives was also demonstrated.[12] However, the fundamental photophysical properties of the phosphole derivatives, in particular, the detailed fluorescence properties in the solid state have not been fully clarified, despite their high potentials as light emitting materials.

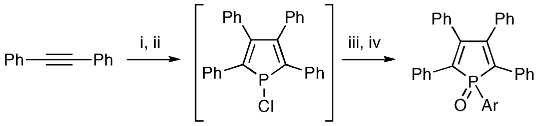
Among the various phosphole derivatives, we now focused our attention on the oxidized derivatives, *i.e.*, the phosphole oxides, because of their narrower HOMO–LUMO gap and their higher chemical stability compared to the σ^3, λ^3-phospholes. In addition, we chose the peripherally all-phenyl-substituted phosphole skeleton, taking into account the similarity to a highly emissive silicon analogue. Recently, Tang and co-workers extensively studied the intense solid-state fluorescence of the 2,3,4,5-tetraphenylsiloles, in which the restricted motion of the peripheral phenyl groups plays a crucial role in attaining an enhanced emission upon aggregation.[4,6] We now report the crystalline-state fluorescence properties of a series of 1-aryl-2,3,4,5-tetraphenylphosphole oxides, which include the all-phenylated **1**, bulky aryl (mesityl and 2,4,6-triisopropylphenyl)-substituted **2** and **3**, and electronically different aryl (p-MeOC$_6$H$_4$ and p-CF$_3$C$_6$H$_4$)-substituted **4** and **5** (Fig. 1). We explored the origin of their intense solid-state emission based on a study of their structure–property relationships.

A series of 1-aryl-2,3,4,5-tetraphenylphosphole oxides **2–5** were prepared by the modified procedure of the previously reported phosphole synthesis, as shown in Scheme 1.[13] Thus, an excess amount of PCl$_3$ was added to a frozen solution of the *in situ*-generated 1,4-dilithio-1,2,3,4-tetraphenylbutadiene at



6 **7**

Fig. 1 Structures of peripherally phenylated phosphole oxides and related compounds.



2 (Ar = Mes) 30%
3 (Ar = Tip) 3%
4 (Ar = 4-MeOC$_6$H$_4$) 44%
5 (Ar = 4-CF$_3$C$_6$H$_4$) 19%

Scheme 1 *Reagents and conditions*: (i) Li, Et$_2$O, rt; (ii) PCl$_3$, −196 °C then rt; (iii) ArLi (MesLi for **2**, TipLi for **3**, 4-MeOC$_6$H$_4$Li for **4**, and 4-CF$_3$C$_6$H$_4$Li for **5**), THF, 0 °C then rt; (iv) 30% H$_2$O$_2$ aq. for **2**, **3**, and **4**, and *m*CPBA for **5**, 0 °C then rt. Mes = 2,4,6-trimethylphenyl; Tip = 2,4,6-triisopropylphenyl.

Department of Chemistry, Graduate School of Science, Nagoya University, Furo, Chikusa, Nagoya, 464-8602, Japan. E-mail: yamaguchi.shigehiro@b.mbox.nagoya-u.ac.jp; Fax: +81 52 789 5947; Tel: +81 52 789 2291

† Dedicated to the late Professor Pascal Le Floch.

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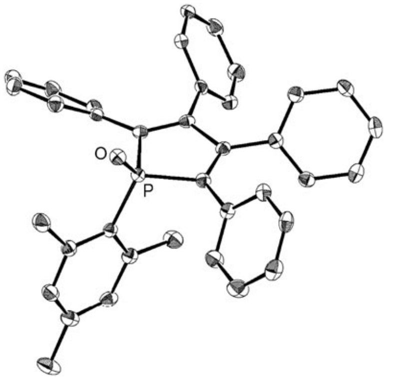

Fig. 2 ORTEP drawing of compound **2** (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.

−196 °C, then the mixture was gradually warmed to room temperature. The produced *P*-chlorophosphole intermediate was subsequently reacted with the corresponding aryllithiums and H_2O_2 or *m*CPBA to produce the 1-aryl-substituted phosphole oxides **2**, **3**, **4** and **5** in 30, 3, 44 and 19% yields, respectively. The low yield for **3** is likely due to the steric hindrance of the Tip group. The pentaphenylphosphole oxide **1** was synthesized according to the literature.[14] All compounds were unequivocally characterized by NMR spectroscopies and finally by X-ray crystallography (see ESI§). As a representative example, an ORTEP drawing of **2** is shown in Fig. 2, which reveals the propeller-like arrangement of the peripheral phenyl rings. In all the compounds, no significant intermolecular π-stacking interaction was observed, except for **4**, in which a slipped π-stacking between the phenyl rings of the molecules adjacent to each other was observed.

The photophysical data for the phosphole oxides **1–5** both in solution (THF) and in the crystalline state are summarized in Table 1. All the compounds have sufficient photo-stability and no decomposition was observed during the measurements.

In solution, the series of compounds **1–5** showed almost identical absorption spectra, indicating that the *P*-aryl groups do not affect the transition energy for the absorption. In contrast, in the fluorescence spectra, their fluorescence maximum wavelengths (λ_{em}) varied in the range of 509–528 nm depending on the *P*-aryl groups. As the aryl group became bulkier from **1** to **3**, the fluorescence band shifted to a shorter wavelength with a decrease in the Stokes shift from 6600 cm^{-1} for **1** to 6000 cm^{-1} for **3**. This may be simply due to the less effective π conjugation in the 2,5-diarylphosphole moiety in the excited state, caused by the restricted conformational change from the Franck–Condon state due to the bulkier aryl group on the phosphorus atom. As for the electronic effect, as the aryl group became more electron-withdrawing, the λ_{em} shifted to a longer wavelength. This may be attributed to the enhanced charge transfer nature in the excited state by the change in the electron-accepting character of the phosphole oxide moiety.

Table 1 Photophysical data for 1-aryl-2,3,4,5-tetraphenylphosphole oxides and their related compounds

	Solution[a]			Crystal		
Compound	λ_{abs}/nm	log ε	λ_{em}/nm	λ_{em}/nm	Φ_F[c]	τ_s/ns[d]
1	387	3.92	520[b]	538	0.49	5.0
2	389	3.85	517	509	0.91	10.6
3	391	3.90	509	520	0.75	10.0
4	388	3.91	517	508	0.91	10.7
5	389	3.89	528	535	0.25	3.1
6	370[e]	3.93[e]	505[e]	538	0.33	2.6
7	363[f,g]	—	371[f,g]	471	0.76	0.74/5.7

[a] In THF. [b] The relative fluorescence quantum yield determined with quinine sulfate as a standard was 0.00056. [c] Absolute quantum yield determined by a calibrated integrating sphere system equipped with a multichannel spectrometer. [d] All the decay profiles were fitted reasonably well using a single exponential function except for **7**. [e] Ref. 12*b*. [f] In cyclohexane. [g] Ref. 6.

Although compounds **1–5** showed only a faint fluorescence in solution, all of them exhibited an intense yellowish green or yellow fluorescence in the crystalline state. We evaluated their fluorescence quantum yields (Φ_F) in the crystalline state using a calibrated integrating sphere system equipped with a multichannel spectrometer (Hamamatsu C9920-02). Since a slight size dependence of the Φ_F was observed,[15] we adopted the highest value as the inherent value for the Φ_F of the compound. Significant enhancements in the Φ_F from solution to the crystalline state were observed. For instance, the all-phenylated **1** has the Φ_F value of 0.49 in the crystalline state, which is *ca.* 880 times higher than that in the THF solution (Φ_F = 0.00056). This enhancement in Φ_F may be mainly attributed to the suppression of rotation of the phenyl rings at the 3,4-positions in the solid state (*vide infra*), as has already been well discussed for the peripherally phenylated silole derivatives.[4,6] It is worth noting that the all-phenylated **1** has a higher Φ_F in the crystalline state than the 3,4-dialkylated analogue **6** (Φ_F = 0.33). This comparison demonstrates the benefit of the peripherally phenylated structure for attaining the intense solid-state fluorescence.[11,12]

The noteworthy issue is the substituent effects of the *P*-aryl groups on the λ_{em} and Φ_F in the crystalline state. Not only the bulkier aryl-substituted derivatives **2** and **3**, but also the electron-donating *p*-$MeOC_6H_4$-substituted **4** exhibited significantly intense fluorescences with the Φ_F values of 0.91, 0.75, and 0.91, respectively, whereas the all-phenylated **1** and the electron-withdrawing *p*-$CF_3C_6H_4$-substituted **5** showed a moderately intense fluorescence. This fact clearly demonstrates that the fluorescence efficiency in the solid state is not simply dependent on the degree of the steric congestion in the molecule or the electronic effects of the substituents. Notably, while the moderately emissive compounds **1** and **5** showed a considerably red-shifted fluorescence in the crystalline state compared to those in solution, the highly emissive compounds, particularly **2** and **4**, showed a blue-shifted λ_{em}. This trend suggests that the intermolecular interaction in the excited state is another important factor to determine the fluorescence efficiency in the solid state.

To gain a deeper insight into the excited state dynamics in the crystalline state, we conducted the fluorescence lifetime (τ_s) measurement using several crystals of each sample. The highly emissive compounds **2**, **3**, and **4** have longer fluorescence lifetimes than the less emissive compounds **1** and **5**. Fig. 3 shows a comparison of the radiative (k_r) and non-radiative (k_{nr}) decay rate constants, calculated from Φ_F and τ_s, for a

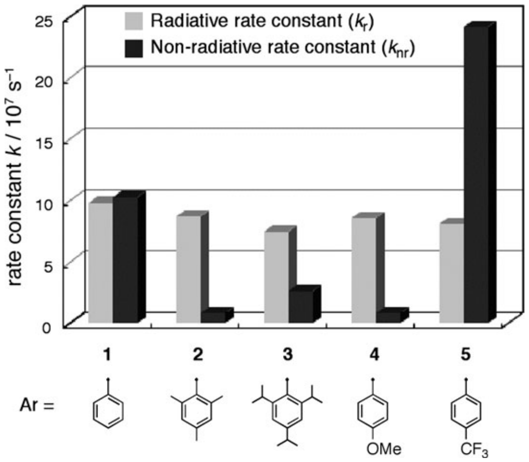

Fig. 3 Comparison of radiative (k_r) and non-radiative (k_{nr}) decay rate constants among the various phosphole oxides in the crystalline state. Rate constants were calculated with Φ_F and τ_s according to the formula of $k_r = \Phi_F/\tau_s$ and $k_{nr} = (1 - \Phi_F)/\tau_s$.

series of the phosphole oxides. Whereas the k_r values are comparable to one another for all the compounds (7.4–9.8×10^7 s^{-1}), the k_{nr} values of the highly emissive **2**, **3**, and **4** were significantly lower compared to those of **1** and **5** (8.2×10^6 s^{-1}, 2.6×10^7 s^{-1}, 8.1×10^6 s^{-1} for **2**, **3**, and **4**, and 1.0×10^8 s^{-1}, 2.4×10^8 s^{-1} for **1** and **5**, respectively). Thus, the high Φ_F values for compounds **2**, **3**, and **4** are attributable to the suppression of the non-radiative decay processes.

To elucidate the origin of the difference in Φ_F in the crystalline state among compounds **1–5**, we evaluated the fluorescent properties in a polymer matrix, the data of which are summarized in Table 2. All the phosphole oxides **1–5** dispersed in a poly(methyl methacrylate) (PMMA) matrix exhibited intense emissions. This fact demonstrates that not the intermolecular interaction, but the restricted rotation of the peripheral phenyl rings in the solid state may be a primary factor for their high Φ_F values. However, it should be also noted that, in contrast to the observed significant substituent effects on both λ_{em} and Φ_F in the crystalline state, almost identical fluorescent properties were observed for all the compounds in the polymer matrix. Namely, the Φ_F values of **1–5** were comparable (Φ_F = 0.41–0.56). Moreover, the λ_{em} values (507–511 nm) were comparable to one another and all blue-shifted when compared to those in solution. These facts revealed that the difference in Φ_F in the crystalline state among compounds **1–5** should be attributed not to such an intramolecular effect as the restricted rotation of the peripheral phenyl groups, but to another effect. We assumed that the difference in the packing mode might be an important factor. To examine the effect of the packing structure, we focused on the intermolecular P···P distances (d) between the closest adjacent phosphole rings in the crystal structures as an index. Fig. 4 shows a plot of the Φ_F values as a function of the P···P distances. Notably, a rough correlation between the P···P distance and Φ_F was observed, that is, the Φ_F becomes higher as d increases. These results suggest that the longer d, *i.e.*, less spatial proximity, may be an important factor for a more efficient suppression of the intermolecular excited state energy migration, resulting in the suppression of the non-radiative decay process and thus an enhancement in Φ_F.

Table 2 Photophysical data for compounds **1–5** in a polymer matrix[a]

Compound	λ_{em}/nm	Φ_F[b]
1	508	0.41
2	507	0.48
3	507	0.56
4	507	0.42
5	511	0.42

[a] 1 wt% in PMMA. [b] Absolute quantum yield determined by a calibrated integrating sphere system.

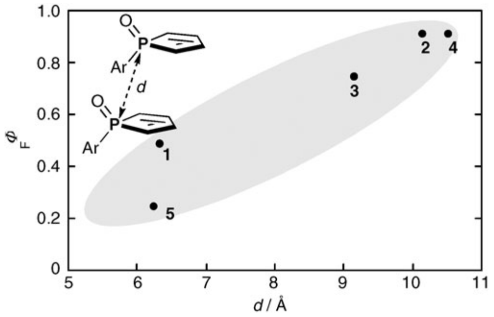

Fig. 4 A plot of the fluorescence quantum yield Φ_F as a function of the intermolecular P···P distance d in the crystalline state.

In summary, the 2,3,4,5-tetraphenylphosphole oxides with various aryl groups on the phosphorus atoms exhibited intense fluorescences in the crystalline state. While the enhanced fluorescence compared to those in solution is mainly due to the restricted rotation of the peripheral phenyl groups, whether they can show a significantly intense solid-state emission or not is highly dependent on the packing mode in the crystal structure. Some of the phosphole compounds indeed showed very high fluorescence quantum yields of 0.75–0.91. Notably, these values are comparable or even higher when compared to that of a silole analogue, 1,2,3,4,5-pentaphenyl-1-methylsilole **7** (Φ_F = 0.76).[6,16] These results well demonstrate the high potentials of the phosphole oxide derivatives as a new class of the light emitting materials for organic electronics.

Experimental

1-Mesityl-2,3,4,5-tetraphenyl-1*H*-phosphole-1-oxide (2): typical procedure for the preparation of 1-aryl-2,3,4,5-tetraphenylphosphole oxides

To a suspension of lithium (granular, 139 mg, 20 mmol) in dry Et$_2$O (20 mL) was added diphenylacetylene (3.74 g, 21 mmol) at room temperature. After stirring for 23 h, the reaction mixture was cooled to −196 °C with liquid N$_2$. After complete freeze of this mixture, PCl$_3$ (3.5 mL, 40 mmol) was added. The reaction mixture was allowed to warm to ambient temperature and stirred for 24 h. After removal of Et$_2$O and the remaining PCl$_3$ under reduced pressure, dry THF (10 mL) was added and the mixture was cooled to 0 °C. Mesityllithium prepared *in situ* from bromomesitylene (1.99 g, 10 mmol) and *t*-BuLi (1.57 M solution in pentane, 12.8 mL, 20 mmol) in dry THF (10 mL) at −78 °C was added dropwise at 0 °C and the mixture was allowed to warm to ambient temperature. After stirring for 24 h, H_2O_2 aq. (30%, 4.5 mL) was added at 0 °C and the resulting mixture was allowed to warm to ambient temperature again. After stirring for 18 h, the reaction was quenched by the addition of Na_2SO_3 aq. (10%, 50 mL) at 0 °C. After removal of THF under reduced pressure, Na_2SO_3 aq. (10%, 150 mL) was added and the organic layer separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water and brine, and dried over Na_2SO_4. After concentration of the organic layer, the residual crude product was purified by column chromatography (PSQ100B, 20/1 CH_2Cl_2/AcOEt, R_f = 0.27) to afford 1.57 g of **2** (3.0 mmol, 30% yield) as yellowish green solids: mp 192–193 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.26 (s, 3H), 2.70–2.82 (br, 6H), 6.88–6.90 (m, 6H), 7.04–7.17 (m, 16H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 50.60. HRMS calcd for $C_{37}H_{31}OP$: 522.2113. Found: 522.2115.

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