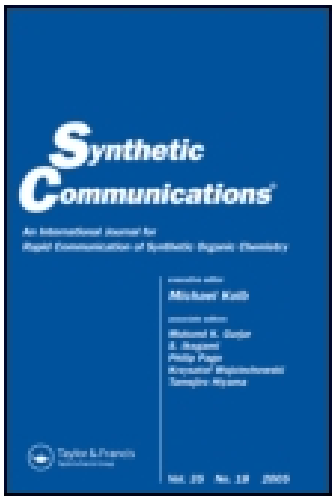

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A Study of the Aryl-Aryl Coupling Reactions of $(4\text{-}X\text{-}C_6H_4)Ph_2P{=}O$

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A Study of the Aryl–Aryl Coupling Reactions of (4-X-C_6H_4)Ph_2P═O

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ABSTRACT

The Suzuki coupling reactions of (4-X-Ph)Ph_2P═O, where X = bromide or triflate, with a series of boronic acids were studied using tetrakis-(triphenylphosphino) palladium or palladium acetate as the catalyst. The boronic acids utilized were phenyl, *p*-tolyl, 3-methoxy, 4-methoxy, and 4-acetyl. Yields of the corresponding biphenyl analogues ranged from 50 to 95%. Palladium acetate provided products free of triphenylphosphine contamination, and required significantly shorter reaction times for complete reaction (2 to 4 hours vs. 12 to 24 hours, respectively) than when tetrakis-(triphenylphosphino) palladium was used. The methodology was applied to *bis*(4-F-Ph)(4-OTf-Ph)P═O to afford, in excellent yield (99%), a biphenyl-based AB_2 monomer precursor for dendritic and hyperbranched poly(arylene ether phosphine oxide)s.

Key Words: Triarylphosphine oxides; Coupling; Biphenyl.

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INTRODUCTION

During the course of a project involving the synthesis of hyperbranched poly(arylene ether phosphine oxide)s from unsymmetrically substituted triarylphosphine oxides **1a**, **1b**, and **1c** (Fig. 1), the need arose to prepare the corresponding biphenyl analogues. Polymerization reactions of **1a**, **1b**, and **1c** using nucleophilic aromatic substitution conditions (K_2CO_3, NMP, reflux) afforded hyperbranched poly(polyarylene ether phosphine oxide)s, HB PAEPOs, with limited molecular weights ($<$15,000 g/mol) and broad molecular weight distributions (2.5–3.5).[1] One potential reason for the observed molecular weights may have been the presence of intramolecular cyclization reactions. Two approaches to eliminate or decrease the possibility of intramolecular cyclization are polymerization reactions in the presence of core molecules[2–5] and the use of more rigid monomers. Polymerization reactions of **1a**, **1b**, and **1c** in the presence of a variety of core molecules has led to HB PAEPOs with controlled molecular weights and molecular weight distributions as low as 1.25.[6]

An alternative method for eliminating or minimizing intramolecular cyclization during the polymerization reactions is the use of more rigid, biphenyl-substituted monomers. Monomers **1a**, **1b**, and **1c** are prepared using standard Grignard chemistry and chlorophosphines, however the starting materials that would be needed to prepare the desired biphenyl derivatives are not readily available and thus, the biphenyl derivatives need to be prepared via an alternate route. Coupling reactions of aryl halides with diphenylphosphine oxide have been utilized to prepare triarylphosphine oxide derivatives in good yield.[7–10] Unfortunately, *bis*-(4-fluorophenyl)phenylphosphine oxide is not commercially available and the use of 4-bromo-4′methoxybiphenyl is cost prohibitive. Therefore, a more cost efficient route to the desired biphenyl monomers using derivatives of **1a**, **1b**, and **1c** as the starting materials has been explored. A number of synthetic methodologies exist for aryl–aryl coupling, but we have chosen to explore the most widely utilized method, the Suzuki coupling reactions.[11,12]

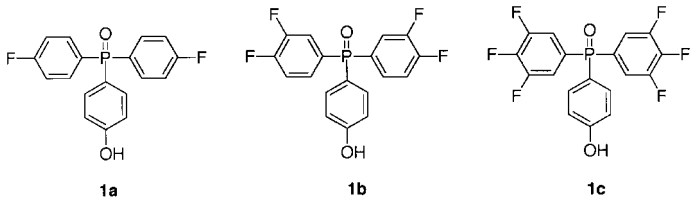

Figure 1. AB_2 monomers, **1a**, **1b**, and **1c**, utilized to prepare hyperbranched poly(arylene ether phosphine oxide)s via nucleophilic aromatic substitution reactions.

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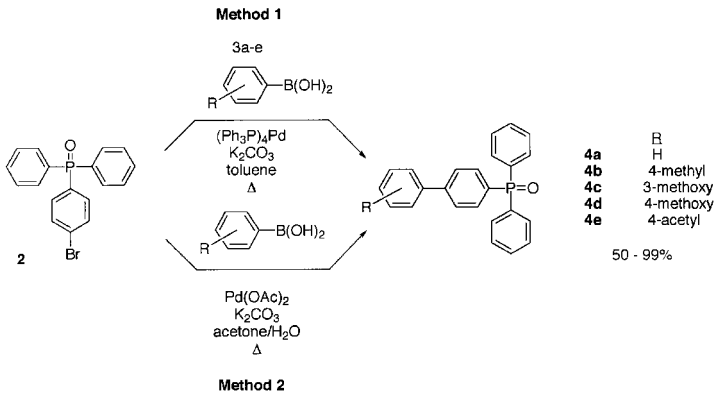
Aryl–aryl coupling reactions of triarylphosphine oxide derivatives are not well known. McGrath et al. have prepared linear poly(arylene phosphine oxide)s via the nickel catalyzed coupling reaction of bis-(4-chlorophenyl)-phenylphosphine oxide.[13] During the course of our investigation we became aware of work by Xiao et al. in which the Suzuki coupling of (2-Br-Ph)Ph_2P=O with a variety of boronic acids using tetrakis(triphenylphosphino) palladium was studied as a means to prepare bulky, triarylphosphine ligands.[14] Similar work has been reported by Buchwald et al. for the preparation of binaphthyl based phosphine ligands.[15] This paper will describe our efforts to develop and apply a synthetic strategy to prepare biphenyl substituted triarylphosphine oxides for subsequent use as monomers for HB PAEPOs.

RESULTS AND DISCUSSION

Initial screening reactions have been performed using (4-bromophenyl)-diphenylphosphine oxide, **2**, a variety of aryl boronic acids, **3a–e**, and tetrakis(triphenylphosphino)palladium, $(Ph_3P)_4Pd$, in toluene as shown in Sch. 1 (Method 1). The yields are listed in Table 1. While the reactions using $(Ph_3P)_4Pd$ have provided the desired biaryl derivatives in reasonably good yields, 50–89%, removal of the residual triphenylphosphine from the catalyst has proven difficult. "Phosphine-free" palladium catalyzed aryl–aryl coupling reactions using palladium acetate, $Pd(OAc)_2$ have been reported by a number of research groups with the key advantage being the absence of Ph_3P impurities at the conclusion of the reaction.[16–19] Application of $Pd(OAc)_2$



Scheme 1.

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Table 1. Results from Suzuki Coupling Reaction of **2** using tetrakis(triphenylphosphino)palladium or palladium acetate.

Boronic acid	Solvent	Catalyst	Product	% yield (GC/MS)
3a	Toluene	$(Ph_3P)_4Pd$	**4a**	60
3b	Toluene	$(Ph_3P)_4Pd$	**4b**	89
3c	Toluene	$(Ph_3P)_4Pd$	**4c**	50
3e	Toluene	$(Ph_3P)_4Pd$	**4e**	70
3a	Acetone/H_2O	$Pd(OAc)_2$	**4a**	95
3b	Acetone/H_2O	$Pd(OAc)_2$	**4b**	97
3c	Acetone/H_2O	$Pd(OAc)_2$	**4c**	92
3d	Acetone/H_2O	$Pd(OAc)_2$	**4d**	95

conditions (Sch. 1, Method 2) to aryl coupling reactions of **2** with a number of aryl boronic acids has provided the desired biphenyl compounds in excellent yields, 92–97%, free of triphenylphosphine impurities. Reaction times using $Pd(OAc)_2$ have also decreased significantly. For example, a typical reaction with $(Ph_3P)_4Pd$ requires from 12–24 hours to reach completion whereas those with $Pd(OAc)_2$ are complete within 2–4 hours. Purification of the desired products is afforded by recrystallization or column chromatography as necessary. Confirmation of the desired structures has been provided by ^1H and ^{13}C NMR spectroscopy, GC/MS, and either elemental analysis or high resolution MS as necessary.

In order to apply the $Pd(OAc)_2$ protocol to the synthesis of biphenyl AB_2 monomers, the appropriate starting material, (4-bromophenyl)-*bis*-(4-fluorophenyl)phenylphosphine oxide, was needed. Since its synthesis proved elusive, an alternative route was explored. Suzuki coupling reactions with aryl triflates are well known and the synthesis of triflates from phenols, in our case **1a**, **1b**, and **1c**, is straightforward.

Therefore, to test the feasibility of aryl coupling reactions with triarylphosphine oxide-based triflate derivatives, (4-OTf-Ph)$Ph_2P{=}O$, **6**, was prepared according to the route shown in Sch. 2. Treatment of (4-hydroxyphenyl)diphenylphosphine oxide, **5**, with an excess of triflic anhydride in dichloromethane afforded the triflate derivative, **6**, in excellent yield. Unreacted starting material, **5**, was removed by dissolving the reaction product mixture in toluene and filtering off the toluene insoluble starting material. Subsequent removal of the toluene under reduced pressure and drying in vacuo afforded **6** as yellow, analytically pure crystals.

As shown in Sch. 2 coupling reactions with **6** and a number of arylboronic acids, **3a**, **3d**, and **3e**, were performed in toluene at 90°C using $(Ph_3P)_4Pd$ (Method 1b). The corresponding biphenyl derivatives, **4a**, **4d**, and **4e**, were

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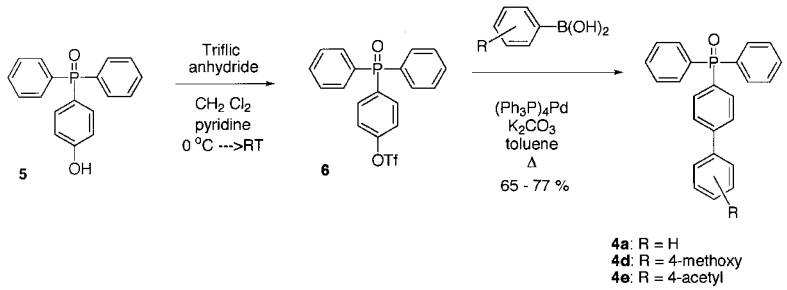

Scheme 2.

afforded in good yields (Table 2). Comparison of spectral data and GC/MS data of **4a**, **4d**, and **4e** prepared from the triflate derivate, **6**, with those prepared from the bromide derivate, **2**, confirmed their identity.

The synthetic methodology developed with model compound **6** was then applied to prepare the desired AB_2 monomer precursor, **8** (Sch. 3). Reaction of **1a** with an excess of triflic anhydride provided the corresponding triflate derivative, **7**, in 90% yield after workup. Coupling of **7** with **3b** using the conditions of Method 1b provided the desired biphenyl derivative, **8**, in 99% yield after workup (Sch. 3). Characterization by ^1H and ^{13}C NMR spectroscopy as well GC/MS and elemental analysis confirmed the structure of **8**. Deprotection of the phenol group in **8** to provide the corresponding AB_2 monomer and subsequent polymerization to prepare a HB PAEPO is currently being investigated.

A general route to biphenyl substituted triarylphosphine oxides via the use of Suzuki coupling of either bromo or trifluorosulfonyl derivatives of triphenylphosphine oxide and arylboronic acids has been developed. Reactions using $Pd(OAc)_2$ with the bromo derivative, **2**, provided the desired biphenyl analogues, **4a–d**, in excellent yields (92–97%) free of triphenylphosphine impurities. Reactions using $(Ph_3P)_4Pd$ with **2** and **6** provided the corresponding biphenyl derivatives, **4a–e**, in good yields, 50 to 89%. The

Table 2. Results from Suzuki Coupling Reactions of the triarylphosphine oxide triflate derivative, **6**.

Boronic acid	Solvent	Catalyst	Product	% yield (GC/MS)
3a	Toluene	$(Ph_3P)_4Pd$	**4a**	77
3d	Toluene	$(Ph_3P)_4Pd$	**4d**	70
3e	Toluene	$(Ph_3P)_4Pd$	**4e**	65

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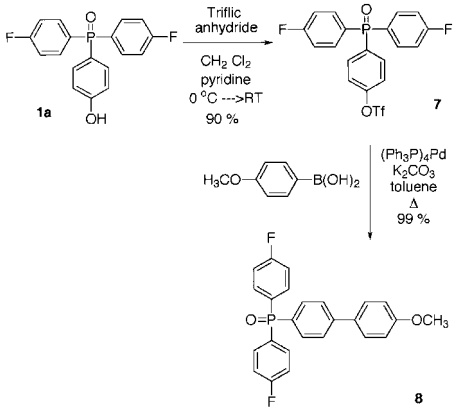

Scheme 3.

methodology has been applied to prepare an AB_2 monomer precursor, **8**, in excellent yield (99%). The polymerization and subsequent property studies of the HB PAEPO prepared from **8** will be described elsewhere.

EXPERIMENTAL

Materials

All reactions were performed under a nitrogen atmosphere and all transfers were done using syringes or cannula as necessary. The boronic acids were purchased from the Aldrich Chemical Co. and used as received. Tetrakis(triphenylphosphino) palladium and palladium acetate were purchased from the Aldrich Chemical Co. and used as received. Toluene was dried over and distilled from sodium/benzophenone prior to use. Both 4-bromophenyldiphenylphosphine oxide[20] and bis(4-fluorophenyl)-4-hydroxyphenylphosphine oxide[1] were synthesized according to literature procedures.

^1H, ^{13}C, and ^{31}P NMR spectra were obtained using a Bruker Avance DMX 300 MHz instrument operating at 300, 75.5, and 121.5 MHz, respectively. Samples were dissolved in $CDCl_3$. Elemental analyses were obtained from Midwest Microlabs, Inc., Indianapolis, IN. High-resolution mass spectra were obtained at the Campus Chemical Instrumentation Center—Mass Spectrometry and Proteomics Facility at Ohio State University.

(4-Tolyphenyl)diphenylphosphine oxide, 4b. **Method 1**. A 25 mL RB flask was charged with 0.40 g (1.12 mmol) of **2**, 0.22 g (1.624 mmol) of

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4-tolyboronic acid, 0.44 g of K_2CO_3, 5 mL of nitrogen sparged toluene, and 1 mol% $Pd(PPh_3P)_4$. The mixture was heated to 90°C overnight at which point GC/MS analysis showed the presence of unreacted **2**. An additional 0.05 g (0.37 mmol) of 4-tolyboronic acid were added and the mixture was heated for 24 hours further. GC/MS analysis showed complete conversion of **2** to **4b**. Additional toluene, 5 mL, was added and the organic layer was washed 3 times with 10 mL of distilled water, followed by drying over $MgSO_4$. Removal of the solvent under reduced pressure afforded the desired compound as a white powder. The identity of **4b** was confirmed via comparison of its analytical data with the analytical data obtained for **4b** from Method 2 below.

Method 2. A method similar to that first reported by Novak et al. was utilized for $Pd(OAc)_2$ catalyzed reactions.[16] A 25 mL Schlenk flask was charged with 0.40 g (1.12 mmol) of **2**, 0.18 g (1.32 mmol) of 4-tolyphenylboronic acid, and 3.0 mL of reagent grade acetone. In separate Schlenk flasks were placed 0.38 g of K_2CO_3 in 3.0 mL of distilled water and 1 mol% $Pd(OAc)_2$ in acetone, respectively. The contents of the Schlenk flasks were subjected to three freeze-pump-thaw cycles, back-filled with nitrogen, and combined. The reaction mixture was heated to 60°C for 2 hours at which point an additional 10% of the boronic acid was added followed by heating for an additional 4 hours. The layers were separated and the organic layer was diluted with toluene (~10 mL), washed with brine and dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by recrystallization from ethanol/water afforded 0.40 g (99%) of **4b** as white crystals (m.p. = 159–161°C). ^{1}H NMR ($CDCl_3$, δ): 2.42 (s, 3 H), 7.28 (m, 2 H), 7.46–7.58 (m, 8 H), 7.66–7.80 (m, 8 H); ^{13}C NMR ($CDCl_3$, δ): 21.5 (s), 127.3 (d), 127.5 (s), 128.9 (d) 130.1 (s), 131.2 (d), 132.5 (d), 133.0 (d), 133.4 (d), 137.4 (s), 138.6 (s) 145.0 (d). Elem. Anal. Calc'd for $C_{25}H_{21}OP$: C, 81.50%, H, 5.75%. Found: C, 81.44%, H, 5.86%.

4-Biphenyldiphenylphosphine oxide, 4a. 95% yield; preparation of **4a** from 0.40 g (1.12 mmol) of **2** using Method 2 gave 0.39 g (98%) of **4a**. ^{1}H NMR ($CDCl_3$, δ): 7.52 (m), 7.59 (m), 7.67 (m); ^{13}C NMR ($CDCl_3$, δ): 127.6 (d), 127.7 (s), 128.6 (s), 129.0 (d), 129.4 (s), 131.5 (d), 132.4 (d), 132.5 (d), 133.1 (d), 134.1, (d), 140.3 (s), 145.2 (d). HRMS: molecular mass + sodium m/z, calc. For $C_{24}H_{19}OPNa$ 377.1071, found 377.1088.

4-(3′-Methoxy)biphenyldiphenylphosphine oxide, 4c. 92% yield; ^{1}H NMR ($CDCl_3$, δ): 3.87 (s, 3 H), 6.95 (d, 1 H), 7.20 (m, 2 H), 7.40 (t, 1 H), 7.55 (m, 6 H), 7.74 (m, 8 H); ^{13}C NMR ($CDCl_3$, δ): 55.8 (s), 113.5 (s), 113.9 (s), 120.2 (s), 127.7 (d), 129.0 (d), 130.4 (s), 131.5 (d), 132.4 (d), 132.5 (d), 132.8 (d), 141.8 (s), 145.1 (d), 160.3 (s). HRMS: molecular mass + sodium m/z, calc. For $C_{25}H_{21}OPNa$ 407.1177, found 407.1158.

4-(4′-Methoxy)biphenyldiphenylphosphine oxide, 4d. 95% yield; (m.p. = 146–150°C). ^{1}H NMR ($CDCl_3$, δ): 3.87 (s, 3 H), 7.00 (d, 2 H),

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7.47–7.58 (m, 8 H), 7.65–7.76 (m, 8 H); ^{13}C NMR ($CDCl_3$, δ): 55.8 (s), 114.8 (s), 127.1 (d), 128.8 (d), 129.1 (s), 130.5 (d), 132.2 (d), 132.5 (d), 132.6 (s), 132.9 (d), 133.0 (d), 144.8 (d), 160.3 (s). HRMS: molecular mass + sodium m/z, calc. For $C_{25}H_{21}OPNa$ 407.1177, found 407.1158.

4-(4′-Acetyl)biphenyldiphenylphosphine oxide, 4e. 70% yield; (m.p. = 201–203°C) ^{1}H NMR ($CDCl_3$, δ): 2.64 (s, 3 H), 7.48–7.57 (m, 6 H), 7.69–7.82 (m, 10 H), 8.05 (d, 2 H); ^{13}C NMR ($CDCl_3$, δ): 27.1 (s), 127.1 (d), 127.9 (s), 129.0 (d), 129.4 (s), 132.2 (d), 132.5 (d), 132.6 (d), 132.7 (d), 132.9 (d), 137.0 (s), 143.8 (d), 144.8 (s), 198.0 (s). Elem. Anal. Calc'd for $C_{26}H_{21}O_2P$: C, 78.78%, H, 5.34%. Found: C, 78.00%, H, 5.54%.

(4-Trifluoromethylsulfonylphenyl)diphenylphosphine oxide, 6. An oven-dried RB flask was charged with 3.37 g (11.5 mmol) of **5**, 45 mL of CH_2Cl_2, and 2.3 mL of pyridine. The flask was immersed in an ice bath (0°C) and a solution of 1.95 mL (11.6 mmol) of triflic anhydride dissolved in 10 mL of CH_2Cl_2 was added drop-wise. The resulting cloudy mixture was allowed to warm to room temperature and subsequently stirred overnight. The mixture was filtered and the CH_2Cl_2 solution was poured slowly into an excess of ice water. The layers were separated and the aqueous layer was washed twice with 10 mL of CH_2Cl_2. The organic layers were combined and dried over $MgSO_4$. Removal of the solvent under reduced pressure afforded a mixture of **5** and **6** that was separated by dissolution of **6** in toluene leaving behind insoluble **5**. Removal of the toluene afforded 3.61 g (74%) of **6** as yellow crystals (m.p. = 120–124°C). ^{1}H NMR ($CDCl_3$, δ): 7.39 (dd, 2 H), 7.51 (m, 4 H), 7.59 (m, 2 H), 7.67 (m, 4 H), 7.79 (dd, 2 H); ^{13}C NMR ($CDCl_3$, δ): 122.0 (d), 129.3 (d), 131.8 (d), 132.5 (d), 132.9 (d), 133.8 (d), 134.8 (d), 152.3 (d). Elem. Anal. Calc'd for $C_{19}H_{14}F_3O_4P$: C, 53.53%, H, 3.31%. Found: C, 53.57%, H, 3.71%.

***bis*-(4-Fluorophenyl)-(4-trifluoromethylsulfonylphenyl)phosphine oxide, 7**. The synthesis of **7** was carried out as described for **6** starting with 2.55 g (7.73 mmol) of **1a** to provide 3.21 g (90%) of **7** as yellow crystals (m.p. = 96.5–99°C). ^{1}H NMR ($CDCl_3$, δ): 7.20 (dt, 4 H), 7.41 (dd, 2 H), 7.67 (m, 4 H), 7.78 (dd, 4 H); ^{13}C NMR ($CDCl_3$, δ): 116.7 (dd), 122.2 (d), 127.2 (dd), 133.6 (d), 134.1 (dd), 134.8 (d), 152.5 (d), 165.8 (dd), 167.3 (d). HRMS: molecular mass + sodium m/z, calc. For $C_{19}H_{12}F_5O_4PNa$ 485.0012, found 485.0016.

***bis*-(4-Fluorophenyl)-(4-methoxybiphenyl)phosphine oxide, 8**. An oven dried RB flask was charged with 0.5 g (1.10 mmol) of **7**, 0.25 g (mmol) of *p*-methoxy phenyl boronic acid, 0.5 g of potassium carbonate, 15 mg of Pd(0) tetrakis triphenyl phosphine and 5.0 mL of sparged toluene. The reaction mixture was heated to reflux for 16 hours at which point the solution was slowly poured into 150 mL distilled water. The layers were separated and the aqueous layer was extracted three times with 35 mL of chloroform. The chloroform layers were combined, washed three times with

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distilled water (3 × 40 mL), dried over $MgSO_4$ and the solvent was removed under reduced pressure to afford **8** (99%) as white crystals (m.p. 149–150°C). ^{1}H NMR ($CDCl_3$, δ): 3.87 (s, 3 H), 7.01 (d, 2 H), 7.20 (m, 4 H), 7.57 (d, 2 H), 7.71 (m, 8 H); ^{13}C NMR ($CDCl_3$, δ): 55.8 (s), 116.5 (m), 127.2 (d), 130.9 (s), 132.8 (d), 134.9 (m), 45.0 (d), 160.4 (s), 163.9 (d), 167.3 (d); ^{31}P NMR ($CDCl_3$, δ): 28.70 (s). Elem. Anal. Calc'd for $C_{25}H_{19}F_2O_2P$: C, 71.43%, H, 4.56%. Found: C, 71.61%, H, 4.61%.

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