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RESEARCH ARTICLE

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Superacid-catalyzed Friedel–Crafts phosphination of 2-hydroxybiphenyls with phosphorus trichloride

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Abstract

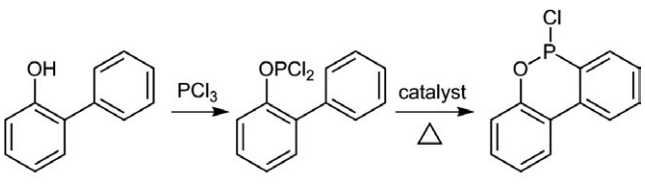
Cyclic phosphorus compounds, 6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin-6-oxide derivatives, were efficiently synthesized by the Friedel–Crafts reaction of 2-hydroxybiphenyls with phosphorus trichloride in the presence of superacids, especially trifluoromethanesulfonic acid (TfOH) as a catalyst. TfOH was investigated for the first time as an effective catalyst for the aromatic phosphination of 2-hydroxybiphenyls.

1 | INTRODUCTION

6*H*-Dibenz[*c*,*e*][1,2]oxaphosphorin ring derivatives (Fig. 1) are industrially significant compounds for the preparation of flame retardants, additives for polymerization processes, photoinitiators, stabilizers for polymers, and photographic materials.[1]

Numerous patents and literatures have been issued for the preparation and characterization of 6*H*-dibenz[*c*,*e*][1,2] oxaphosphorin ring system.[2,3] Their synthetic intermediate, 6-chloro-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin (**3a**) is generally synthesized by the reaction of 2-hydroxybiphenyl (**1a**) with phosphorus trichloride to give the intermediate **2a,**[4] followed by the Friedel–Crafts type reaction using Lewis acids, such as $ZnCl_2$, $AlCl_3$ and $FeCl_3$, as catalysts (Scheme 1).[3] However, in this preparation process of the cyclic phosphorus compound **3a**, the Lewis acid-catalyzed phosphination required elevated temperatures which in some case exceeded to a final temperature of >200°C and were not adequate for industrial processes.

However, various aryl dichlorophosphine have been prepared by the Friedel–Crafts reaction of aromatic hydrocarbons with phosphorus trichloride.[5,6] In the recent improvement of phosphination of aromatic compounds, the use of bismuth chloride and bismuth trifluoromethanesulfonate were revealed as efficient catalysts.[7] These observations promoted us to propose a suitable catalyst and an improvement in the syntheses of **3**. In this letter, we would like to report superacids[8] catalyzed phosphination of 2-hydroxybiphenyls with phosphorus trichloride to afford the corresponding **3** in good to excellent yields. Although various superacids have been found to catalyze nucleophilic addition of nitrogen, oxygen, and sulfur to olefins,[9] Friedel–Crafts acylation,[10] and Diels–Alder reaction,[11] to the best of our knowledge, no superacid-catalyzed phosphination of aromatic compounds has been hitherto described. As compared with the conventional Lewis acid-catalyzed reaction, the present method in the presence of superacid is characterized by mild reaction conditions and metal-free process.



SCHEME 1 Friedel–Crafts type phosphination reaction

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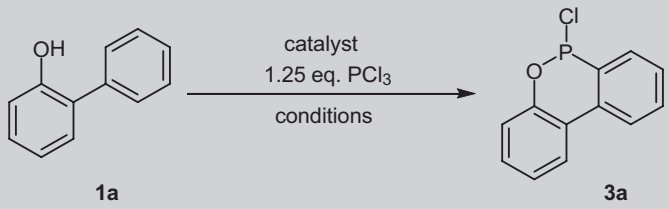
2 | RESULTS AND DISCUSSION

First, the Friedel–Crafts reaction of 2-hydroxybiphenyl (**1a**) was examined by a slightly modified literature procedure.[3e] Brief optimization of the reaction conditions was studied using **1a** (8.51 g, 50 mmol) and phosphorus trichloride (8.58 g, 62.5 mmol) in the presence of various acids as catalysts without solvent. The results are summarized in Table 1. In the presence of 1.5 mol% of $ZnCl_2$, the reaction was carried out at 150°C and the corresponding phosphorus compound **3a** was obtained in 92% yield (Table 1, entry 1). Lowering the reaction temperature to 120°C decreased the product yield (Table 1, entry 2). In the previous report,[7] $BiCl_3$ was shown as an effective catalyst for the aromatic phosphination of activated aromatic compounds compared to the use of commonly used $AlCl_3$. Next we chose $BiCl_3$ as a catalyst, however, only 14% of **3a** was obtained with considerable amount of starting materials (Table 1, entry 3). Use of metal triflates, such as $Zn(OTf)_2$, gave a comparable yield to that of $ZnCl_2$ (Table 1, entry 4). It is well-known that superacid, such as TfOH, efficiently catalyses the Friedel–Crafts acylation reaction of acyl chlorides with aromatic compounds. Thus, we tried to use TfOH as a catalyst in the Friedel–Crafts phosphination. Consequently, it was found that the reaction in the presence of TfOH could enhance the yield and reduce the reaction time effectively in the preparation of cyclic compounds (Table 1, entry 5). Moreover, it was revealed that other superacids, such as nonafluorobutane-1-sulfonic acid ($C_4F_9SO_3H$) and bis(trifluoromethane)sulfonimide (Tf_2NH), also gave **3a** in excellent yield, respectively (Table 1, entries 6 and 7). None of desired product was obtained in the case of simple Brønsted acids, such as sulfuric acid, methanesulfonic acid, and trifluoroacetic acid. (Table 1, entries 12, 13, and 14). Next, effects of the reaction temperature and catalyst loading were investigated. A decrease in the reaction temperature to 120°C, reduced both the reaction rate and the product yield. However, it is noteworthy that the yield was improved from 53% to 88% by carrying out the reaction for longer reaction times (Table 1, entries 8 and 9). In addition, only 0.15 mol % of the catalyst showed high catalytic activity (Table 1, entries 10 and 11).

To establish the generality of this method, the reactions of several 2-hydroxybiphenyls **1a–i** with phosphorus trichloride in the presence of TfOH were examined under the optimized conditions. 2-hydroxybiphenyls **1b–g** and **1i** were prepared according to a literature procedure, using cross-coupling reaction of the corresponding Grignard reagents with halophenols in the presence of palladium catalyst.[12] The chloro derivatives **3** can in principle be isolated as exemplified for

TABLE 1 Friedel–Crafts phosphination of 2-hydroxybiphenyl with phosphorus trichloride under various reaction conditions[a]



1a **3a**

Entry	Catalyst (mol%)	Temp. (°C)	Time (h)	Yield of 3a (%)[b]
1	$ZnCl_2$ (1.5)	150	8	92
2	$ZnCl_2$ (1.5)	120	10	12
3	$BiCl_3$ (1.5)	150	4	14
4	$Zn(OTf)_3$ (1.5)	150	8	90
5	TfOH (1.5)	150	4	95 (94)[c]
6	$C_4F_9SO_3H$ (1.5)	150	4	95
7	$(CF_3SO_2)_2NH$ (1.5)	150	4	94
8	TfOH (1.5)	120	4	53
9	TfOH (1.5)	120	8	88
10	TfOH (0.15)	150	6	80
11	TfOH (0.15)	180	6	89
12	H_2SO_4 (1.5)	150	4	0
13	$MeSO_3H$ (1.5)	150	4	0
14	CF_3CO_2H (1.5)	150	4	0

[a]All reactions were carried out by using 2-phenylphenol (50 mmol) with phosphorus trichloride (62.5 mmol) in the presence of various catalysts.
[b]Yield was determined by the HPLC analysis after hydrolysis of **3a**.
[c]Isolated yield of 6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin-6-oxide.

the compound **3a,**[3d] (after simple filtration and concentration of reaction mixture, chloro compound **3a** is obtained in considerable yield and purity. *6-chloro-6*H-*dibenz[*c,e*][1, 2] oxaphosphorin (***3a***)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.99–7.92 (m, 2 H), 7.69–7.55 (m, 2 H), 7.46–7.33 (m, 2 H), 7.28–7.18 (m, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 148.0 (d, J = 10.0 Hz), 132.8 (d, J = 36.7 Hz), 132.8, 131.3, 130.0 (d, J = 10.6 Hz), 129.2, 127.8 (d, J = 13.1 Hz), 124.8, 124.6, 123.9, 122.2 (d, J = 6.9 Hz), 121.0 (d, J = 2.5 Hz); ^{31}P NMR (109 MHz, $CDCl_3$): δ (ppm) 132.8; δ 132.18; ref. [3c]), however, because of their sensitivity to humidity,[3e] they were transformed to the stable oxides **4** after hydrolysis (Scheme 2). The results are shown in Table 2.

In the case of 2-hydroxybiphenyls bearing not only electron-releasing groups but also electron-withdrawing groups on the phenol ring, the compounds smoothly underwent to afford the corresponding phosphonated compounds **4** in fair to good yields. The presence of a substituted group on the aryl ring where electrophilic substitution occurs has no influence on the regioselectivity of the intramolecular cyclization, producing the corresponding products as the unseparable mixture of regioisomers (Table 2, entries 5).

Recently, bridged 6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin-6-oxide derivatives were developed and evaluated as frame retardant having high thermally stability.[13] Novel bridged derivatives **4j** was synthesized from compound **1j** [14] having two 2-hydroxybiphenyl units on the molecule and 3 equivalent of trichlorophosphine in 74% yield (Scheme 3).

In the case of the Friedel–Crafts acylation of acyl chlorides with aromatic compounds in the presence of TfOH, it is assumed that the triflic mixed anhydrides are generated in situ as acylating agents.[10b-d] Although we are unsure about exact structure of the active reaction species and the mechanistic details still remain ambiguous at present, it is conceivable that the aromatic phosphination of phenols with PCl_3 in the presence of TfOH proceeds through in situ generated $PCl_2(OTf)$, $P^+Cl_2 + TfO^-$ and/or ArO PCl (OTf), $ArOP^+Cl + TfO^-$ as active species. [5c]

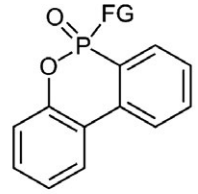
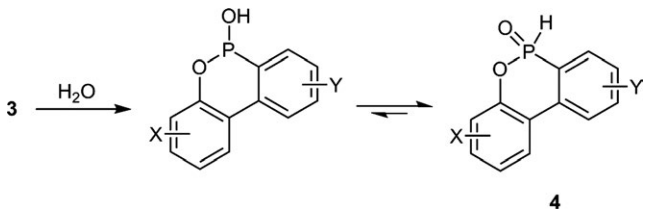


FIGURE 1 6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin ring derivatives.



SCHEME 2 The tautomeric equilibrium of 6*H*-dibenz[*c*,*e*][1,2] oxaphosphorin ring

3 | CONCLUSION

In summary, 6*H*-dibenz[c,e][1,2]oxaphosphorin-6-oxide derivatives were efficiently synthesized by the Friedel–Crafts reaction of 2-hydroxybiphenyls with phosphorus trichloride in the presence of super acids, especially TfOH as a catalyst. TfOH was investigated for the first time in the present results to prove to be an effective catalyst. Thus, it was revealed that the superacid is effective for the phosphination of 2-phenylbiphenyls.

Elucidation of the detailed reaction mechanism must await further study.

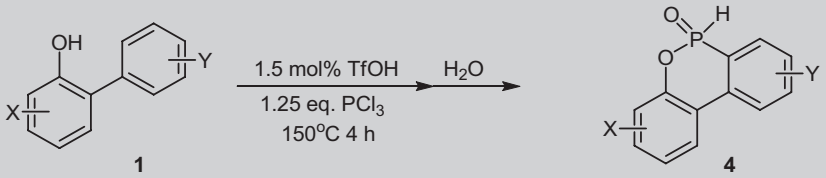
4 | EXPERIMENTAL

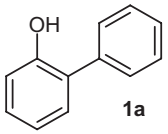
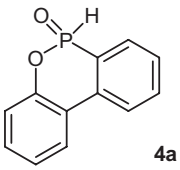
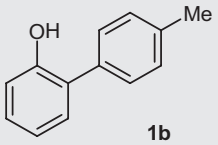
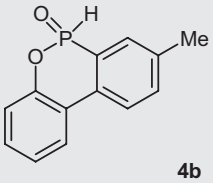
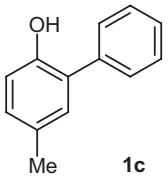
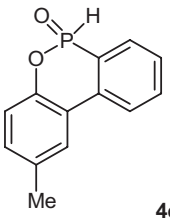
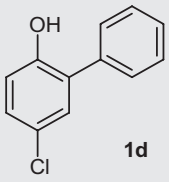
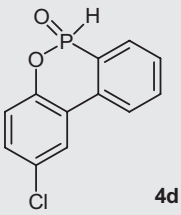
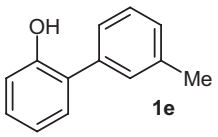
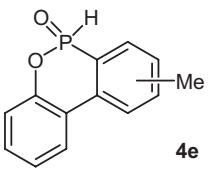
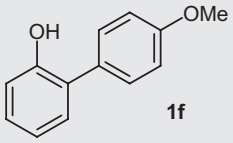
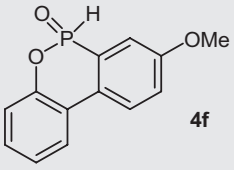
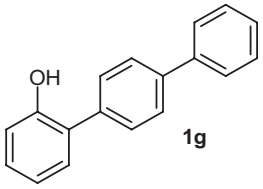
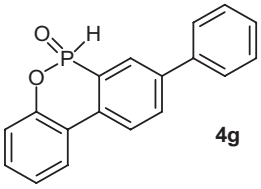
Melting points were determined with a Yanako MP-I3 instrument (Yanako, Kyoto, Japan) and were uncorrected. FT-IR spectra were recorded on a JASCO FT/IR-4100 instrument. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL JNM-AL300 (300 MHz, 75 MHz) instrument. Chemical shifts were reported in ppm on the δ scale relative to tetramethylsilane (0 ppm) and chloroform-d (77 ppm) as an internal standard, respectively. ^{31}P NMR spectra were obtained on a JEOL JNM-EX270 (109 MHz) or JEOL JNM-ECA600 (243 MHz) spectrometer with complete decoupling. Chemical shifts were reported in the scale relative to phosphoric acid (0 ppm). Mass spectra were measured on a Shimadzu LCMS-IT-TOF spectrometer.

4.1 | The representative procedure for the preparation of 6*H*-dibenz[*c*,*e*][1,2] oxaphosphorin-6-oxide (4a) is as follows

In a two-necked round-bottom flask equipped with a reflux condenser, 2-phenylphenol (8.51 g, 50 mmol) and trifluoromethanesulfonic acid (113 mg, 0.75 mmol) were put and heated to 150°C. Then, phosphorus trichloride (8.58 g, 62.5 mmol) was added dropwise to the mixture for ca. 30 min, so as to maintain a slow reflux of phosphorus trichloride with a simultaneous evolution of HCl. The reaction mixture was stirred for further 4 hours until no further HCl was evolved. After the excess of phosphorus trichloride was then distilled off, the reaction mixture including the chloro compound **3a** was then cooled to room temperature and dissolved in 20 mL of chloroform, followed by the insoluble orange solid was filtered off and washed with 20 mL of chloroform. To the filtrate, 10 mL of water was added dropwise (vigorous

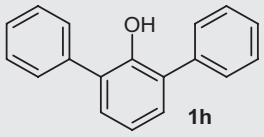
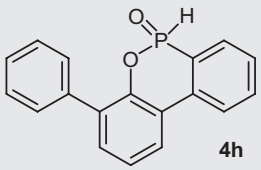
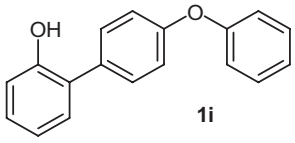
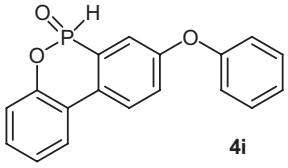
TABLE 2 Trifluoromethanesulfonic acid-catalyzed Friedel–Crafts phosphination of various 2-hydroxybiphenyls with phosphorus trichloride



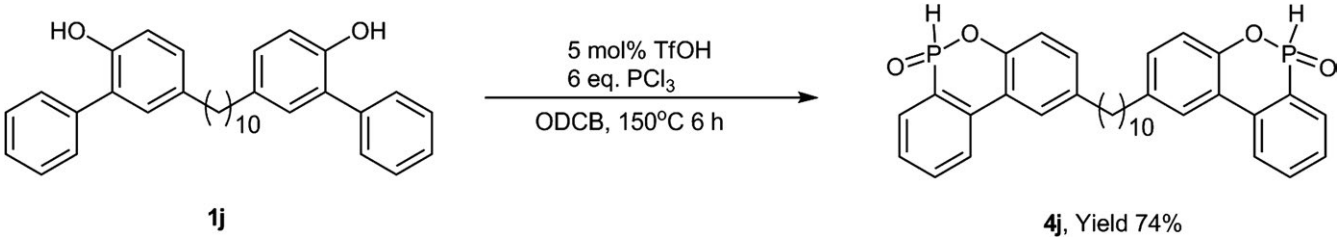
Entry	Substrate	Product	Yield (%)[d]
1[a]	 1a	 4a	94
2[b]	 1b	 4b	90
3[c]	 1c	 4c	81
4[c]	 1d	 4d	88
5[c]	 1e	 4e	90[e]
6[c]	 1f	 4f	75
7[c]	 1g	 4g	80

Continued

TABLE 2 Continued

Entry	Substrate	Product	Yield (%)[d]
8[c]	 1h	 4h	73
9[c]	 1i	 4i	81

[a]Reaction was carried out by using 2-hydroxybiphenyl (50 mmol) with phosphorus trichloride (62.5 mmol) at 150°C for 4 hours in the presence of 1.5 mol% of TfOH.
[b]Reactions were carried out by using 2-hydroxybiphenyls (10 mmol) with phosphorus trichloride (12.5 mmol) at 150°C for 4 hours in the presence of 1.5 mol% of TfOH.
[c]Reactions were carried out by using 2-hydroxybiphenyls (1 mmol) with phosphorus trichloride (1.5 mmol) at 150°C for 6 hours in the presence of 5.0 mol% of TfOH in 1,2-dichlorobenzene (3 mL).
[d]Isolated yield.
[e]The regioisomeric mixtures of the products were obtained with ca. 3:2.



SCHEME 3 Synthesis of bridged 6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin-6-oxide derivative

HCl formation) very carefully. After evaporation of the solvent under reduced pressure, residual water was removed by azeotropic distillation with toluene for 2 hours. The solution was concentrated and the residue dried under vacuum to give analytically pure **4a** in 10.1 g (94%) yield. Their derivatives **4** can be further purified by recrystallization or gel permission chromatography, if necessary.[2d–f,3d]

The intermediated chloro compound **3a**, *6-chloro-6H-dibenz[c,e][1, 2] oxaphosphorin*, is obtained after simple filtration and concentration of reaction mixture in considerable yield and purity. $_1$H NMR (300 MHz, CDC_{l3}): δ (ppm) 7.99–7.92 (m, 2 H), 7.69–7.55 (m, 2 H), 7.46–7.33 (m, 2 H), 7.28–7.18 (m, 2 H); $_{13}$C NMR (75.5 MHz, CDC_{l3}): δ (ppm) 148.0 (d, J = 10.0 Hz), 132.8 (d, J = 36.7 Hz), 132.8, 131.3, 130.0 (d, J = 10.6 Hz), 129.2, 127.8 (d, J = 13.1 Hz), 124.8, 124.6, 123.9, 122.2 (d, J = 6.9 Hz), 121.0 (d, J = 2.5 Hz); $_{31}$P NMR (109 MHz, CDC_{l3}): δ (ppm) 132.8; δ 132.18; ref. [3c].

4.1.1 | 6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin-6-oxide (4a)

White solid, 94% yield, mp 114–116°C; IR (KBr, cm^{-1}): ν 2384 (P-H), 1592, 1448, 1151, 1076; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.06 (d, 1H, J = 591.6 Hz), 7.99–7.86 (m, 3H), 7.78–7.72 (m, 1H), 7.59–7.51 (m, 1H). 7.44–7.38 (m, 1H) 7.32–7.26 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 148.2 (d, J = 8.7 Hz), 135.9 (d, J = 6.9 Hz), 134.1 (d, J = 2.5 Hz), 130.9, 130.6 (d, J = 12.5 Hz), 128.7 (d, J = 14.3 Hz), 125.2, 125.1, 124.0 (d, J = 9.9 Hz), 123.5 (d, J = 122.0 Hz), 122.0 (d, J = 12.5 Hz), 120.7 (d, J = 6.2 Hz); ^{31}P NMR (109 MHz, $CDCl_3$): δ (ppm) 15.13; DART-HRMS calcd for $C_{12}H_{10}O_2P$ $[M+H]^+$: 217.0413; found 217.0438.

4.1.2 | 8-Methyl-6*H*-dibenz[*c*,*e*][1,2] oxaphosphorin-6-oxide (4b)

White solid, 90% yield, mp 124–126°C; IR (KBr, cm^{-1}): ν 2431 (P-H), 1479, 1230, 917, 760; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.00 (d, J = 590.4 Hz, 1H), 7.99–7.85 (m, 2H), 7.66 (d, J = 15.0 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 5.7 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 147.8 (d, J = 8.7 Hz), 138.7 (d, J = 14.2 Hz), 134.8 (d, J = 2.5 Hz), 132.8 (d, J = 6.8 Hz), 130.5 (d, J = 12.4 Hz), 130.1, 124.8, 124.7, 122.2, 121.7 (d, J = 12.5 Hz), 120.2 (d, J = 6.2 Hz), 20.9; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 15.86; DART-HRMS calcd for $C_{13}H_{12}O_2P$ $[M+H]^+$: 231.0569; found 231.0563.

4.1.3 | 2-Methyl-6*H*-dibenz[*c*,*e*][1,2] oxaphosphorin-6-oxide (4c)

Pale yellow solid, 81% yield, mp 98–101°C; IR (KBr, cm^{-1}): ν 2409 (P-H), 1228, 1209, 903, 491; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.00 (d, J = 589.2 Hz, 1H), 7.99–7.85 (m, 2H), 7.78–7.68 (m, 2H), 7.58–7.51 (m, 1H), 7.28–7.12 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 146.0 (d, J = 8.7 Hz), 136.0 (d, J = 6.9 Hz), 134.6, 133.9 (d, J = 2.5 Hz), 131.5, 130.5 (d, J = 12.4 Hz), 128.4 (d, J = 14.3 Hz), 125.3, 123.8 (d, J = 9.4 Hz), 123.6 (d, J = 122.5 Hz), 121.6 (d, J = 12.4 Hz), 120.3 (d, J = 6.2 Hz), 20.94; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 15.76; DART-HRMS calcd for $C_{13}H_{12}O_2P$ $[M+H]^+$: 231.0569; found 231.0589.

4.1.4 | 2-Chloro-6*H*-dibenz[*c*,*e*][1,2] oxaphosphorin-6-oxide (4d)

White solid, 88% yield, mp 129–131°C; IR (KBr, cm^{-1}): ν 3068, 2371 (P-H), 1477, 1223, 903; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.06 (d, J = 602.7 Hz, 1H), 7.95–7.83 (m, 3H), 7.79–7.73 (m, 1H), 7.61–7.54 (m, 1H), 7.40–7.32 (m, 1H), 7.20 (d, J = 8.7 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 146.4 (d, J = 8.7 Hz), 134.5 (d, J = 6.9 Hz), 134.4 (d, J = 2.5 Hz), 130.8, 130.6, 130.6, 129.3 (d, J = 14.3 Hz), 125.0, 124.2 (d, J = 110.2 Hz), 124.0 (d, J = 9.9 Hz), 123.1 (d, J = 12.5 Hz), 121.9 (d, J = 6.2 Hz); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 15.18; DART-HRMS calcd for $C_{12}H_9ClO_2P$ $[M+H]^+$: 251.0023; found 251.0005.

4.1.5 | Mixture (ca. 3: 2) of 7-Methyl-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin-6-oxide and 9-Methyl-6*H*-dibenz[*c*,e][1,2] oxaphosphorin-6-oxide (4e)

White solid, 90% yield; IR (KBr, cm^{-1}): ν 2400 (P-H), 1606, 1488, 1456, 1440, 1228; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.46 (d, J = 600.3 Hz, 0.7H), 8.03 (d, J = 589.4 Hz, 0.3H), 7.94–7.74 (m, 2.3H), 7.6 (t, J = 7.5 Hz, 0.7H), 7.43–7.23 (m, 4H), 2.72 (s, 2.1H), 2.50 (s, 0.9H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 148.3 (d, J = 8.4 Hz), 147.8 (d, J = 8.7 Hz), 144.8 (d, J = 2.5 Hz), 140.7 (d, J = 12.3 Hz), 135.9 (d, J = 6.8 Hz), 135.6 (d, J = 4.9 Hz), 133.4 (d, J = 1.9 Hz), 130.8, 130.7, 130.5, 130.5, 130.4, 130.3, 129.5 (d, J = 14.9 Hz), 1258.4, 125.0 (d, J = 8.0 Hz), 124.9, 124.5 (d, J = 5.7 Hz), 121.8 (d, J = 12.5 Hz), 121.7 (d, J = 9.3 Hz), 120.6 (d, J = 6.3 Hz), 120.4 (d, J = 5.6 Hz), 22.2, 19.7 (d, J = 10.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 14.84; DART-HRMS calcd for $C_{13}H_{12}O_2P$ $[M+H]^+$: 231.0569; found 231.0593.

4.1.6 | 8-Methoxy-6*H*-dibenz[*c*,*e*][1,2] oxaphosphorin-6-oxide (4f)

White solid, 75% yield, mp 144–147°C; IR (KBr, cm^{-1}): ν 2370 (P-H), 1606, 1475, 1227, 1207; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.00 (d, J = 591.3 Hz, 1H), 7.99–7.70 (m, 2H), 7.40–7.25 (m, 2H), 7.23–7.15 (m, 3H), 385 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 159.4 (d, J = 17.4 Hz), 147.3 (d, J = 8.1 Hz), 129.5, 128.1 (d, J = 6.2 Hz), 125.6 (d, J = 11.9 Hz), 124.8, 124.3, 124.2 (d, J = 120.7 Hz), 121.7 (d, J = 33.6 Hz), 121.2 (d, J = 2.4 Hz), 120.1 (d, J = 6.3 Hz), 113.1 (d, J = 14.2 Hz), 55.5; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 15.76; DART-HRMS calcd for $C_{13}H_{12}O_3P$ $[M+H]^+$: 247.0519; found 247.0543.

4.1.7 | 8-Phenyl-6*H*-dibenz[*c*,*e*][1,2] oxaphosphorin-6-oxide (4 g)

White solid, 80% yield, mp 60–64°C; IR (KBr, cm^{-1}): ν 2370 (P-H), 1473, 1234, 1204, 957, 913; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.08 (d, J = 592.2 Hz, 1H), 8.15–7.80 (m, 4H), 7.70–7.60 (m, 2H), 7.55–7.35 (m, 4H), 7.30–7.21 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 148.1 (d, J = 8.1 Hz), 141.4 (d, J = 14.3 Hz), 138.6, 134.4 (d, J = 6.3 Hz), 132.4, 130.7, 129.0, 128.7 (d, J = 13.1 Hz), 128.3, 126.8, 125.1, 125.0, 124.4 (d, J = 10.6 Hz), 123.8 (d, J = 196.7 Hz), 121.7 (d, J = 11.8 Hz), 120.5 (d, J = 6.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 15.53. DART-HRMS calcd for $C_{18}H_{14}O_2P$ $[M+H]^+$: 293.0726; found 293.0751.

4.1.8 | 4-Phenyl-6*H*-dibenz[*c*,*e*][1,2] oxaphosphorin-6-oxide (4 h)

White solid, 73% yield, mp 157–159°C; IR (KBr, cm^{-1}): ν 2370 (P-H), 1410, 1229, 1211, 1189; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.97 (d, 1H, J = 593.7 Hz), 8.05–7.97 (m, 1H), 7.96–7.83 (m, 2H), 7.79–7.69 (m, 1H), 7.62–7.51 (m, 3H), 7.50–7.29 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 144.7 (d, J = 8.8 Hz), 136.4 136.0 (d, J = 6.3 Hz), 133.9 (d, J = 2.5 Hz), 133.8 (d, J = 5.6 Hz), 132.2, 130.2 (d, J = 13.7 Hz), 129.5, 128.5 (d, J = 14.3 Hz), 128.3, 127.7, 124.9, 124.5, 124.5, 123.6 (d, J = 115.1 Hz), 122.6 (d, J = 11.8 Hz); ^{31}P NMR (109 MHz, $CDCl_3$): δ (ppm) 14.50, ref. [3d] δ 14.5. DART-HRMS calcd for $C_{18}H_{14}O_2P$ $[M+H]^+$: 293.0726; found 293.0725.

4.1.9 | 8-Phenoxy-6*H*-dibenz[*c*,*e*][1,2] oxaphosphorin-6-oxide (4i)

White solid, 81% yield, mp 63–66°C; IR (KBr, cm^{-1}): ν 2367 (P-H), 1587, 1488, 1259, 1223, 757; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.97 (d, 1H, J = 595.2 Hz), 7.95–7.80 (m, 2H), 7.45–7.30 (m, 5H), 7.30–7.15 (m, 3H), 7.10–7.05 (m, 2H); ^{13}C

NMR (75.5 MHz, $CDCl_3$): δ (ppm) 158.1 (d, $J = 18.0$ Hz), 155.4, 147.6 (d, $J = 8.7$ Hz), 130.3, 130.0 (d, $J = 6.2$ Hz), 126.1 (d, $J = 11.2$ Hz), 125.1, 124.8 (d, $J = 119.4$ Hz), 124.7, 124.0 (d, $J = 3.1$ Hz), 121.7 (d, $J = 12.6$ Hz), 120.5 (d, $J = 6.3$ Hz), 119.9, 118.4 (d, $J = 13.7$ Hz); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 14.65. DART-HRMS calcd for $C_{13}H_{14}O_3P$ $[M+H]^+$: 309.0675; found 309.0702.

4.1.10 | 2,2′-(1,10-decanediyl)-bis(6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin-6-oxide) (4j)

White solid, 71% yield, mp 133–136°C; IR (KBr, cm^{-1}): ν 2923, 2361 (P-H), 1233, 1211, 910; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.99 (d, 1H, $J = 589.8$ Hz), 7.99–7.80 (m, 4H), 7.78–7.65 (m, 4H), 7.55–7.41 (m, 2H), 7.20–7.12 (m, 4H), 2.64 (d, $J = 7.8$ Hz, 4H), 1.626 (br, 4H), 1.31 (br, 12H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 145.9 (d, $J = 8.1$ Hz), 139.5, 135.8 (d, $J = 6.8$ Hz), 133.8 (d, $J = 2.5$ Hz), 130.1, 130.3 (d, $J = 12.5$ Hz), 128.2 (d, $J = 14.3$ Hz), 124.6, 123.7 (d, $J = 9.4$ Hz), 123.3 (d, $J = 122.5$ Hz), 121.4 (d, $J = 12.4$ Hz), 120.1 (d, $J = 6.9$ Hz), 35.3, 31.3, 29.4, 29.6, 29.0; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 15.67. DART-HRMS calcd for $C_{34}H_{37}O_4P_2$ $[M+H]^+$: 571.2167; found 571.2164.

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REFERENCES

[1] a) R. L. Fan, L. S. Wang, M. Y. Li, *J. Chem. Eng. Data* **2008**, *53*, 228; b) Y. L. Liu, *Polymer* **2001**, *42*, 3445; c) W. C. Shan, L. C. Hsuan, *Polymer* **1999**, *40*, 4387; d) C. H. Lin, C. S. Wang, *Polymer* **1869**, *2001*, 42; e) C. S. Wang, J. Y. Shieh, *Polymer* **1998**, *39*, 5819; f) Y. L. Liu, S. H. Tsai, *Polymer* **2002**, *43*, 5757.

[2] a) T. Saito, U S Pat 3 **1972**, *702*, 878; b) T. Saito, T. Hirayama, Y. Kohguchi, U S Pat 6 **2000**, *107*, 506; c) H.-J. Kleiner, U S Pat 5 **1995**, *391*, 798 and 5, 1996, 481, 017; d) P. Rathfelder, H. Rieckert, J. Dietrich, U S Pat 5 **1998**, *821*, 376; e) H. Takeuchi, M. Sato, S. Gyobu, U S Pat 6 **2001**, *245*, 880; f) H. J. Kleiner, U S Pat 5 **1996**, *481*, 17.

[3] a) K. A. Salmeia, S. Gaan, *Polym. Degrad. Stab.* **2015**, *113*, 119; b) E. A. Chernyshev, V. I. Aksenov, V. V. Ponmarev, S. A. Golubtsov, E. F. Bugerenko, *J. Gen. Chem.* **1972**, *42*, 88; c) T. K. Prakasha, R. O. Day, R. R. Holmes, *J. Am. Chem. Soc.* **1994**, *116*, 8095; d) S. D. Pastor, J. D. Spivack, L. P. Steinhuebel, *Phosphorus Sulfur* **1987**, *31*, 71; e) A. Qureshi, A. S. Hay, *J. Chem. Res. (m).* **1998**, 1601.

[4] H. Tolkmith, *J. Org. Chem.* **1958**, *23*, 1682.

[5] a) B. Buchner, L. B. Lockhart Jr, *J. Am. Chem. Soc.* **1951**, *73*, 755; b) I. Granoth, Y. Segall, A. Kalir, *J. Chem. Soc. Perkin Trans. I* **1973**, 1972; c) Z. W. Wang, L. S. Wang, *Green Chem.* **2003**, *5*, 737.

[6] J. Emsley, D. Hall, The Chemistry of Phosphorus, Harper and Row, London **1976**.

[7] F. Siméon, P. A. Jaffrés, D. Villemin, *Tetrahedron* **1998**, *54*, 10111.

[8] a) G. A. Olah, G. K. S. Prakash, J. Sommer, Superacids, John Wiley & Sons, New York **1985**; b) H. Yamamoto, K. Ishihara, Acid Catalysis in Modern Organic Synthesis, Wiley-VCH, Weinheim **2008**.

[9] a) B. Schlummer, J. F. Hartwig, *Org. Lett.* **2002**, *4*, 1471; b) T. C. Wabnitz, J. B. Spencer, *Org. Lett.* **2003**, *5*, 2141; c) Z. Li, J. Zhang, C. Brouwer, C. G. Yang, N. W. Reich, C. He, *Org. Lett.* **2006**, *8*, 4175; d) K. P. Kalbarczyk, S. T. Diver, *J. Org. Chem.* **2009**, *74*, 2193.

[10] a) F. Effenberger, F. Buckel, A. H. Maier, J. Schmider, *Synthesis* **2000**, *2000*, 1427; b) B. Hulin, M. Koreeda, *J. Org. Chem.* **1984**, *49*, 207; c) F. Effenberger, G. Epple, *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 299; d) F. Effenberger, E. Sohn, G. Epple, *Chem. Ber.* **1983**, *116*, 1195; e) J. P. Hwang, G. K. S. Prakash, G. A. Olah, *Tetrahedron* **2000**, *56*, 7199.

[11] D. Nakashima, H. Yamamoto, *Org. Lett.* **2005**, *7*, 1251.

[12] N. A. Bumagin, E. V. Luzikova, *J. Organomet. Chem.* **1997**, *532*, 271.

[13] A. Buczko, T. Stelzig, L. Bommer, D. Rentsch, M. Heneczkowski, S. Gaan, *Polym. Degrad. Stab.* **2014**, *107*, 158.

[14] A. Ciogli, A. D. Cort, F. Gasparrini, F. Lunazzi, L. Mandolini, A. Mazzanti, C. Pasquini, M. Pierini, L. Schiaffino, F. Mihan, *J. Org. Chem.* **2008**, *73*, 6108.

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