Kinetics and Mechanism of the Aminolysis of Diphenyl Phosphinic Chloride with Anilines

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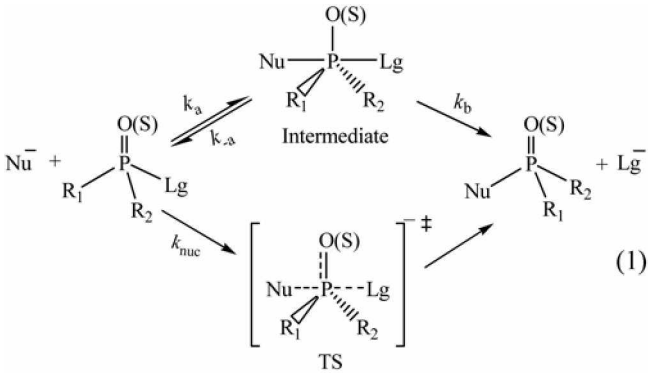
The aminolyses of diphenyl phosphinic chloride (**1**) with substituted anilines in acetonitrile at 55.0 °C are investigated kinetically. Large Hammett ρ_X (ρ_{nuc} = –4.78) and Brönsted β_X (β_{nuc} = 1.69) values suggest extensive bond formation in the transition state. The primary normal kinetic isotope effects (k_H/k_D = 1.42-1.82) involving deuterated aniline ($XC_6H_4ND_2$) nucleophiles indicate that hydrogen bonding results in partial deprotonation of the aniline nucleophile in the rate-limiting step. The faster rate of diphenyl phosphinic chloride (**1**) than diphenyl chlorophosphate (**2**) is rationalized by the large proportion of a frontside attack in the reaction of **1**. These results are consistent with a concerted mechanism involving a partial frontside nucleophilic attack through a hydrogen-bonded, four-center type transition state.

Key Words : Anilinolysis of diphenyl phosphinic chloride, Frontside nucleophilic attack, Deuterium kinetic isotope effect

Introduction

Nucleophilic substitution at a phosphoryl (P=O) or thiophosphoryl (P=S) center generally proceeds either through stepwise mechanism with a trigonal bipyramidal pentacoordinate (TBP-5C) intermediate (upper route) or an S_N2 mechanism with transition state (TS) (lower route), where the attacking and leaving groups occupy apical positions, *i.e.*, backside nucleophilic attack toward the leaving group.[1]

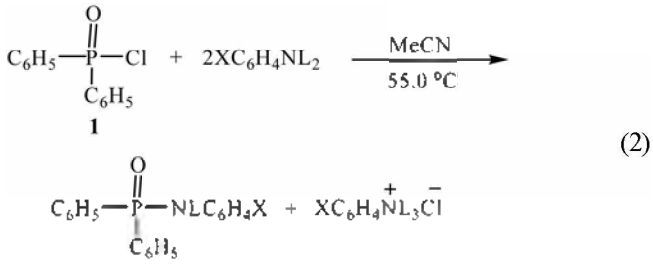


(1)

Stereochemical studies of the displacement of exocyclic groups at phosphorus from a variety of dioxaphosphorinane derivatives show that front- or back- side nucleophilic attack leads to retention or inversion of configuration depending on the nature of the nucleophile, leaving group, solvent, other ionic species present, and other heteroatoms in the six-membered ring.[2]

In previous work, we studied several phosphoryl and thiophosphoryl transfer reactions kinetically and theoretically.[3] The concerted mechanism with a frontside nucleophilic attack was proposed based on the ρ_X, β_X, β_Z and the especially large negative ρ_{XZ} (= –1.98) value for more basic phenolate groups (Z = 4-Cl, 3-Cl, and 3-CN) and less basic pyridines (X = 3-Cl, 3-CH_3CO, 4-CH_3CO, 3-CN, and 4-CN) in the reactions of Z-aryl bis(4-methoxyphenyl) phosphates, $(4\text{-}MeOC_6H_4O)_2P(=O)OC_6H_4Z$, with pyridines, XC_5H_4N, in acetonitrile.[3d] For the pyridinolysis of aryl phenyl isothiocyanophosphates, $(YC_6H_4O)(C_6H_5O)P(=O)NCS$, in acetonitrile, the biphasic Hammett ($\log k_2$ *vs.* σ_X) and Brönsted [$\log k_2$ *vs.* $pK_a(X)$] plots were interpreted as a frontside attack TS for more basic pyridines (X = 4-MeO, 4-Me, 3-Me, H, and 3-C_6H_5) and backside attack TS for less basic pyridines (X = 3-CH_3CO, 3-Cl, 4-CH_3CO, and 4-CN).[3e] The partial participation of a frontside nucleophilic attack concerted mechanism was proposed for the anilinolysis of aryl phenyl (and 4-chlorophenyl) chlorothiophosphates in acetonitrile.[3f]

To clarify the phosphoryl transfer mechanism, as well as to compare the reactivity of diphenyl chlorophosphate (**2**)[3a] and diphenyl chlorothiophosphate (**3**),[3f] here we investigate the aminolysis of diphenyl phosphinic chloride (**1**) with substituted anilines and deuterated anilines ($XC_6H_4NH_2$ and $XC_6H_4ND_2$) in acetonitrile at 55.0 °C.



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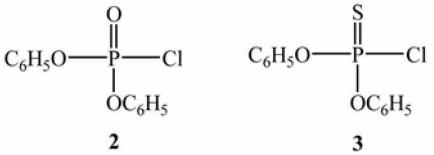


Table 1. Second-Order Rate Constants, k_H and k_D ($\times 10^4/M^{-1}s^{-1}$), of the Aminolysis of Diphenyl Phosphinic Chloride (**1**) with $XC_6H_4NH_2$ and $XC_6H_4ND_2$ in Acetonitrile at 55.0 °C

X	k_H [a]	k_D [b]	k_H/k_D
4-CH_3O	524 ± 14[c]	288 ± 7.9	1.82 ± 0.070
4-CH_3	156 ± 3.2	86.3 ± 1.4	1.81 ± 0.047
3-CH_3	33.7 ± 1.0	18.7 ± 0.56	1.80 ± 0.076
H	17.3 ± 0.54	9.69 ± 0.33	1.79 ± 0.082
3-CH_3O	3.13 ± 0.12	2.20 ± 0.11	1.42 ± 0.090
4-Cl	1.87 ± 0.077	1.32 ± 0.041	1.42 ± 0.073
3-Cl	0.476 ± 0.018	0.335 ± 0.012	1.42 ± 0.074

[a]Correlation coefficients (r) were better than 0.997. [b] r ≥ 0.997. [c]Standard deviation.

Results and Discussion

The second-order rate constants, k_H, for the reactions were obtained as the slope of k_{obsd} (pseudo-first-order rate constant) against aniline concentration, [An].

$$k_{obsd} = k_0 + k_H[An] \quad (3)$$

where the intercept, k_0, was negligible in all cases. No third-order kinetics were observed and no complications were found in the determination of k_{obsd}. The k_H values are summarized in Table 1, together with k_D values involving deuterated anilines ($XC_6H_4ND_2$).

The changes in rate observed by varying substituents in the nucleophiles were consistent with the nature of a typical nucleophilic substitution reaction, *i.e.*, the stronger the nucleophile, the faster the rate. Figure 1 shows the nonbonding orbital (NBO) charges and rate ratios of the anilinolysis of **1**, **2**, and **3**. The NBO charges of the reaction center P are 1.844 in **1** and 2.230 in **2**, which are consistent with the inductive effects of Ph (σ_I = 0.12)[5] and PhO (σ_I = 0.40)[5] ligands. Solely considering the positive charge of the reaction center P atom, the anilinolysis rate of **2** should be faster than that of **1**. However, the observed rate ratio of k_H (**1**)/k_H (**2**) = 1.9 is opposite to expectation, implying that the reaction rate does not depend only on the positive charge of the reaction center P.

Two phenyl groups are bonded to the reaction center P atom in **1**, while an intervening oxygen atom is located between the reaction center P and the phenyl group in **2**. As a result, the steric hindrance in **1** would be much larger than that in **2** when the nucleophile attacks opposite the Cl leaving group, *i.e.*, backside nucleophilic attack. This result strongly suggests that the reaction of **1** with anilines does not simply proceed by a backside nucleophilic attack. The slower rate of **3** (P=S system) than those of **1** and **2** (P=O system) is attributed to several causes, the so-called "thio effect", which is mainly the electronegativity difference between O and S.[1c,6]

The pK_a(X) values in H_2O are used to obtain the Brönsted β_X value as shown in Figure 2. The $\Delta pK_a = pK_a(MeCN) - pK_a(H_2O)$ values for structurally similar amines are nearly constant, so determination of β_X by plotting $\log k_H$(MeCN) against $pK_a(H_2O)$ is probably justified.[7] The magnitudes of Hammett ρ_X (−4.78) and Brönsted β_X (1.69) values are both large, suggesting extensive bond formation in the TS. The obtained β_X value is considerably larger than those of other phosphoryl and thiophosphoryl reactions in which the reactions proceed through a concerted mechanism. The β_X values of the reactions of (i) 4-nitrophenyl dimethyl phosphinothioate with phenoxides,[1c] (ii) 4-nitrophenyl diphenyl phosphate with phenoxides,[8] (iii) 4-nitrophenyl diphenyl

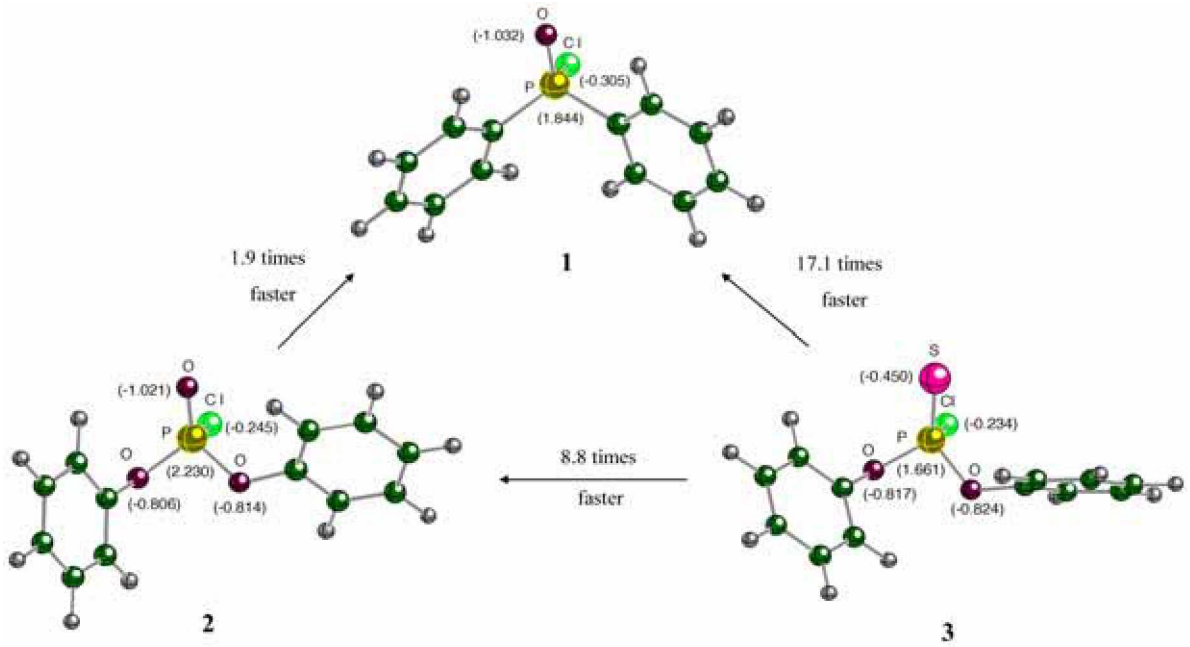


Figure 1. The B3LYP/6-311+G(d,p)[d] geometries and nonbonding orbital (NBO) charges of **1**, **2**,[3a] and **3**.[3f] The relative rate ratios are for unsubstituted aniline ($C_6H_5NH_2$).

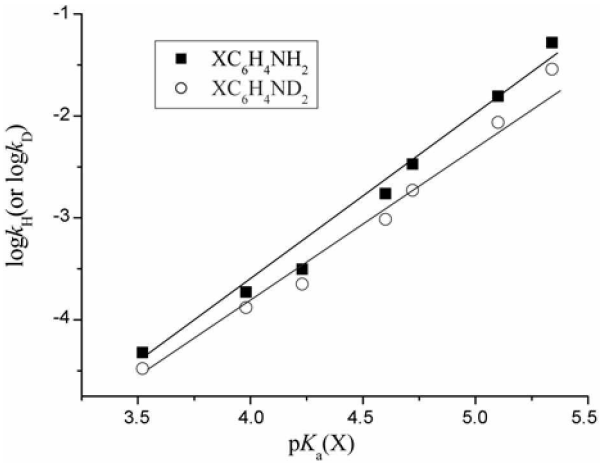
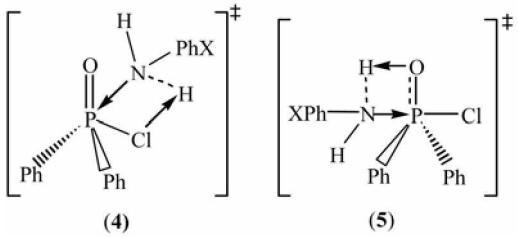


Figure 2. Brönsted plots of the aminolysis of diphenyl phosphinic chloride (**1**) with $XC_6H_4NH_2$ (■) and $XC_6H_4ND_2$ (○) in acetonitrile at 55.0 °C. The pK_a values of $XC_6H_4ND_2$ are assumed to be the same as the pK_a values of $XC_6H_4NH_2$ in water.

phosphinate with phenoxides.[9] (iv) isoquinolino-*N*-phosphonate with pyridines.[10] and (v) *O*,*O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate with phenoxides[6f] are 0.47, 0.53, 0.46, 0.15, and 0.49, respectively. The β_X (and ρ_X) values of the anilinolysis of **2** and **3** are 1.35 (and 3.74)[3a] and 1.36 (and 3.88),[3f] respectively, somewhat smaller than that of **1**. The especially large ρ_X and β_X values seem to be characteristic of the anilinolysis of **1**-**3**, with the Cl leaving group, in acetonitrile.

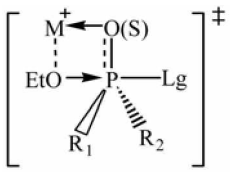
A backside nucleophilic attack concerted mechanism with a late, product-like TS in the anilinolysis of **2** was proposed based on large ρ_X (and β_X), large negative cross-interaction constant[11] (ρ_{XY} = −1.31, where X is the substituent of the nucleophile and Y is the substituent of the substrate), and the secondary inverse kinetic isotope effects (KIEs; k_H/k_D = 0.7-0.8) with deuterated aniline nucleophiles ($XC_6H_4ND_2$).[3a] In contrast, a partial frontside attack concerted mechanism through a hydrogen-bonded four-center type TS was suggested for the anilinolysis of **3** based on several reasons, mainly the primary KIEs, k_H/k_D = 1.1-1.3.[3f] The KIEs with deuterated anilines are summarized in Table 1 (see also Table 2). As observed in the anilinolysis of **3**, the k_H/k_D values of **1** are all greater than unity, k_H/k_D = 1.4-1.8, indicating that partial deprotonation of the aniline nucleophile occurs in the rate-limiting step by hydrogen bonding.

Two possible TS structures can be proposed: hydrogen bonding between the Cl leaving group and the hydrogen of the N-H(D) moiety (**4**) or between the polar oxygen in P=O and the hydrogen of the N-H(D) moiety in aniline (**5**).



(**4**) (**5**)

Buncel[12] and Um[13] reported a four-membered TS (**6**) in the ethanolysis of the phosphinates, paraxon and parathion, caused by alkali metal ions. In such a model, the catalytic effect increases with increasing positive charge density of M^+ ions. The catalytic effect of the M^+



(**6**)

ions is stronger in a P=O than in a P=S system, due to the polarizable S atom. Positive charge development on the hydrogen of the N-H moiety in the TS would be much smaller than that of M^+ ions, so hydrogen bonding involving the strong accepter P=O, TS **5**, is not feasible in the present work. Moreover, the secondary inverse KIE, k_H/k_D < 1, of the anilinolysis of **2** and primary normal KIE, k_H/k_D > 1, of the anilinolysis of **3** cannot be rationalized by TS **5**. Therefore, the possibility of TS **5** can be neglected in the present work.

When the aniline nucleophile attacks backside toward the Cl leaving group, the steric effect on the TS would be larger in **1** than in **3** due to the intervening oxygen atom between the reaction center P atom and phenyl group in **3** (see Figure 1). As a result, the proportion of frontside nucleophilic attack (TS **4**) would be greater in **1** than in **3**; therefore, the k_H/k_D values of **1** (1.42-1.82) are larger than those of **3** (1.11-1.27). The faster rate of **1** than **2** could be rationalized by the large proportion of frontside attack in the reaction of **1**, where steric hindrance does not play an important role.

The obtained KIEs would be the sum of the primary KIE, k_H/k_D > 1, due to partial deprotonation as shown in TS **4**, and the secondary inverse KIE, k_H/k_D < 1, due to steric hindrance that increases the out-of-plane bending vibrational frequencies of N-H(D) bonds in the TS for a backside attack.[16] As a result, the real primary KIE due to the hydrogen bond between the hydrogen of N-H(D) moiety and the Cl leaving group should be greater than the observed value.

When the frontside nucleophilic attack is major direction, greater deprotonation would occur with a greater bond formation, *i.e.*, the stronger nucleophile ($\partial\sigma_X$ < 0) leads to a

Table 2. The k_H ($\times 10^4/M^{-1}s^{-1}$), ρ_X, β_X, and k_H/k_D Values of the Reactions of $(Ph)_2P(O)Cl$ (**1**), $(PhO)_2P(O)Cl$ (**2**), and $(PhO)_2P(S)Cl$ (**3**) with X-Anilines in Acetonitrile at 55.0 °C

Substrate	k_H[a]	$-\rho_X$	β_X	k_H/k_D	ref.
1	17.3	4.78[d](4.56)[e]	1.69[f](1.62)[g]	1.42-1.82	This work
2	8.91	3.74	1.35	0.71-0.77[h]	3(a)
3	1.01	3.88	1.36	1.11-1.27[i]	3(f)

[a]When X = H. [b]The σ values were taken from ref. 14. [c]The pK_a values were taken from ref. 15. [d]Calculated from k_H values. Correlation coefficient (r) = 0.992. [e]Calculated from k_D values. r = 0.991. [f]Calculated from k_H values. r = 0.993. [g]Calculated from k_D values. r = 0.993. [h]0.77 for X = 4-CH_3O, 0.75 for X = H, and 0.71 for X = 4-Cl. [i]1.27 for X = 4-CH_3O, 1.20 for X = H, and 1.11 for X = 4-Cl.

greater hydrogen bond formation. Then the observed primary KIE, k_H/k_D values greater than unity, may be proportional to the degree of hydrogen bond formation and the expected sequence of the k_H/k_D values is X = 4-MeO > 4-Me > 3-Me > H >3-MeO > 4-Cl > 3-Cl. similar to the observed sequence. X = 4-MeO ≥ 4-Me ≥ 3-Me ≥ H > 3-MeO ≈ 4-Cl ≈ 3-Cl. The observed sequence of the k_H/k_D values in **3** shows the same tendency as in **1**. X = 4-MeO > H > 4-Cl (footnote of Table 2).[3f] When the backside nucleophilic attack is major direction. which leads to the secondary inverse KIEs, $k_H/k_D < 1$, more bond formation will result in smaller k_H/k_D value. The observed sequence of the k_H/k_D values in **2** is X = 4-MeO > H > 4-Cl, contrary to the expectations based on the backside nucleophilic attack (footnote of Table 2).[3a] When the front and back side attack is comparable, the substituent effects of X on the KIEs would be complicated. The discrepancy between the expected and obtained substituent effects of X on the KIEs may be due to the proportion of front and back side nucleophilic attack, *i.e.*, more frontside attack results in greater k_H/k_D value and more backside attack results in smaller k_H/k_D value.

The larger magnitudes of ρ_X and β_X values of **1** (–4.78 and 1.69, respectively) compared to **2** (–3.74 and 1.35, respectively) and **3** (–3.88 and 1.36, respectively) suggest that **1** has a later. more product-like TS than **2** and **3**. The magnitudes of ρ_X and β_X values of **1** (–4.56 and 1.62, respectively) with deuterated anilines ($XC_6H_4ND_2$) are somewhat smaller than those with anilines ($XC_6H_4NH_2$). suggesting less sensitivity to substituent effect of deuterated anilines than of anilines.

Summary

The reactions of diphenyl phosphinic chloride (**1**) with X-anilines were studied kinetically in acetonitrile at 55.0 °C. When substituents in the nucleophiles were varied, the rate changes were consistent with the nature of a typical nucleophilic substitution reaction. Structure-reactivity relationship between **1**, **2**, and **3** was discussed based on NBO charges and steric effects. The primary normal KIEs (k_H/k_D = 1.42-1.82) involving deuterated aniline ($XC_6H_4ND_2$) nucleophiles were obtained and were consistent with a partial frontside attack concerted mechanism through a hydrogen-bonded four-center type TS. The large magnitudes of ρ_X and β_X values of **1** (–4.78 and 1.69) suggest a late, product-like TS.

Experimental Section

Materials. Diphenyl phosphinic chloride, 98% (substrate), and HPLC grade acetonitrile (water content is less than 0.005%) were used for kinetic studies without further purification. Anilines were redistilled or recrystallized before use as previously described.[17] Deuterated anilines were prepared by heating anilines with D_2O at 85 °C for 72 h and. after numerous attempts, were more than 98% deuterated. as confirmed by ^{1}H-NMR.

Kinetics Measurement. Rates were measured conductometrically as described previously.[3] For the present work, [substrate] = 1×10^{-3} M and [An] = 0.03-0.15 M were used. We tried at least five concentrations of anilines. Pseudo-first-order rate constant values were the average of three runs, which were reproducible within ± 3%.

Product Analysis. Diphenyl phosphinic chloride was refluxed with excess anilines ($XC_6H_4NH_2$; X = 4-CH_3O. H.[3f] 4-Cl) for more than 15 half-lives at 55.0 °C in acetonitrile, as described.[3f] Analytical data of the products gave the following results:

$(C_6H_5)_2P(=O)NH-C_6H_4$-4-CH_3O.[18] Purple Solid; mp 142-144 °C; IR (nujol mull) 3375 (NH). 3124 (C-H, aromatic). 2724 (CH_3), 1511, 1378 (P-C_6H_5). 1463 (CH_3-O), 1242 (C-O-C. Ar). 737 cm^{-1} (P=O); ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.67 (3H, s. CH_3O), 6.88 (2H. d. J = 8.8 Hz), 7.01 (2H, d. J = 8.8 Hz). 7.48-7.54 (6H. m, benzene). 7.76-7.81 (4H. m, benzene). 8.00 (1H. d, J = 11.6 Hz, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 55.2 (CH_3O). 114.0-154.2 (C=C. aromatic); ^{31}P NMR (162 MHz. DMSO-d_6) δ 26.4 (1P. s, P=O); m/z. 323 (M^-); Anal. Calcd for $C_{19}H_{18}O_2NP$: C, 70.6; H. 5.6; N. 4.3. Found: C. 70.9; H, 5.9; N, 4.0.

$(C_6H_5)_2P(=O)NH-C_6H_5$.[3f,19] Yellowish Solid: mp 85-86 °C; IR (nujol mall) 3128 (NH), 3054. 1461. 1377, 725 cm^{-1} (P=O); ^{1}H NMR (400 MHz. $CDCl_3$) δ 5.2 (1H, d. J = 11.6 Hz. NH), 6.9 (1H, t, J = 7.6 Hz). 7.0 (2H. d, J = 7.6 Hz). 7.1 (2H. t, J = 7.6 Hz). 7.4 (4H. m), 7.5 (2H. m). 7.8-7.9 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.3-140.2 (C=C, aromatic); ^{31}P NMR (162 MHz. $CDCl_3$) δ 23.7 (s. 1P); m/z, 292 (M^-); Anal. Calcd for $C_{18}H_{16}ONP$: C, 73.7; H, 5.5; N, 4.8. Found: C, 73.7; H. 5.7; N. 4.5.

$(C_6H_5)_2P(=O)NH-C_6H_4$-4-Cl.[18b,20] Light-purple Solid: mp 180-182 °C; IR (nujol mull) 3179 (NH). 3089 (C-H, aromatic). 2723 (CH_3), 1594. 1378 (P-C_6H_4). 724 cm^{-1} (P=O); ^{1}H NMR (400 MHz. DMSO-d_6) δ 7.05 (2H. d, J = 8.8 Hz), 7.16 (2H, d, J = 8.8 Hz), 7.48-7.57 (6H. m. benzene), 7.75-7.80 (4H. m. benzene). 8.40 (1H. d, J = 11.6 Hz. NH); ^{13}C NMR (100 MHz. DMSO-d_6) δ 115.7-141.0 (C=C. aromatic); ^{31}P NMR (162 MHz. DMSO-d_6) δ 27.1 (1P. s. P=O); m/z. 327 (M^-); Anal. Calcd for $C_{18}H_{15}ONPCl$: C, 66.0; H. 4.6; N. 4.3. Found: C. 65.7; H. 4.7; N. 4.5.

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