

Anilinolysis of Diethyl Isothiocyanophosphate in Acetonitrile[†]

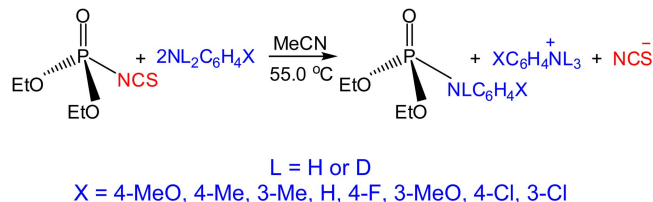
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To extend the kinetic studies on the phosphoryl transfer reactions involving a leaving group of isothiocyanate,¹ the nucleophilic substitution reactions of diethyl isothiocyanophosphate (**1**) with substituted anilines (XC₆H₄NH₂) and deuterated anilines (XC₆H₄ND₂) are investigated kinetically in acetonitrile (MeCN) at 55.0 ± 0.1 °C (Scheme 1). The kinetic studies on the anilinolysis involving a leaving group of isothiocyanate are the first work in this lab. The purpose of this work is to gain further information into the leaving group ability, deuterium kinetic isotope effects (DKIEs), and mechanism for phosphoryl transfer reactions, as well as to compare with the previous kinetic results of the anilinolysis of diethyl chlorophosphate [**2**: (EtO)₂P(=O)Cl] involving a leaving group of chloride.²



Scheme 1. The anilinolysis of diethyl isothiocyanophosphate (**1**) in MeCN at 55.0 °C.

Results and Discussion

The observed pseudo-first-order rate constants (k_{obsd}) were found to follow Eq. (1) for all the reactions under pseudo-first-order conditions with a large excess of aniline nucleophile. The k_0 values were negligible ($k_0 \approx 0$) in MeCN. The second-order rate constants ($k_{\text{H(D)}}$) were determined with at least five concentrations of anilines. The linear plots of Eq. (1) suggest that there are no base-catalysis or noticeable side reactions and that the overall reaction is described by Scheme 1.

$$k_{\text{obsd}} = k_0 + k_{\text{H(D)}} [\text{XC}_6\text{H}_4\text{NH}_2(\text{D}_2)] \quad (1)$$

The k_{H} and k_{D} values with X-anilines and deuterated X-anilines, respectively, are summarized in Table 1, together with the DKIEs ($k_{\text{H}}/k_{\text{D}}$), and Hammett $\rho_{\text{X(H and D)}}$ and Brønsted $\beta_{\text{X(H and D)}}$ selectivity parameters. The $\text{p}K_{\text{a}}(\text{X})$ values of the

Table 1. The Second-Order Rate Constants ($k_{\text{H(D)}} \times 10^4/\text{M}^{-1} \text{s}^{-1}$), Selectivity Parameters (ρ_{X} and β_{X}),^a and DKIEs ($k_{\text{H}}/k_{\text{D}}$) of the Reactions of Diethyl Isothiocyanophosphate (**1**) with XC₆H₄NH₂(D₂) in MeCN at 55.0 °C

X	$k_{\text{H}} \times 10^4$	$k_{\text{D}} \times 10^4$	$k_{\text{H}}/k_{\text{D}}$
4-MeO	122 ± 1 ^b	165 ± 3	0.739 ± 0.001 ^k
4-Me	47.7 ± 0.1	56.9 ± 0.1	0.838 ± 0.002
3-Me	17.1 ± 0.1	20.1 ± 0.5	0.851 ± 0.022
H	8.54 ± 0.02	9.78 ± 0.02	0.873 ± 0.003
4-F	21.7 ± 0.5	30.6 ± 0.1	0.709 ± 0.016
3-MeO	14.7 ± 0.1	17.8 ± 0.1	0.826 ± 0.007
4-Cl	6.80 ± 0.04	5.94 ± 0.04	1.15 ± 0.01
3-Cl	2.82 ± 0.01	1.79 ± 0.02	1.58 ± 0.02
$-\rho_{\text{X(H and D)}}$	4.30 ± 0.01 ^c	4.55 ± 0.01 ^g	
$\beta_{\text{X(H and D)}}$	1.45 ± 0.06 ^d	1.53 ± 0.07 ^h	
$-\rho_{\text{X(H and D)}}$	2.87 ± 0.01 ^e	4.00 ± 0.02 ⁱ	
$\beta_{\text{X(H and D)}}$	0.92 ± 0.06 ^f	1.28 ± 0.09 ^j	

^aThe σ values were taken from ref. 5. The $\text{p}K_{\text{a}}$ values of X-anilines in water were taken from ref. 6. ^bStandard deviation. ^cCorrelation coefficient, $r = 0.999$. ^d $r = 0.995$. ^e $r = 0.999$. ^f $r = 0.992$. ^g $r = 0.999$. ^h $r = 0.994$. ⁱ $r = 0.999$. ^j $r = 0.992$. ^kStandard error $\{= 1/k_{\text{D}}[(\Delta k_{\text{H}})^2 + (k_{\text{H}}/k_{\text{D}})^2 \times (\Delta k_{\text{D}})^2]\}^{1/2}$ from ref. 7.

X-anilines in water were used to obtain the Brønsted β_{X} values in MeCN, and this procedure was justified experimentally and theoretically.³ The values of $\text{p}K_{\text{a}}(\text{X})$ and σ_{X} of the deuterated X-anilines are assumed to be identical to those of the X-anilines. Perrin and coworkers reported that the basicities of β -deuterated analogs of benzylamine, *N,N*-dimethylaniline and methylamine increase roughly by 0.02 $\text{p}K_{\text{a}}$ units per deuterium, and that these effects are additive.⁴ Thus, the $\text{p}K_{\text{a}}(\text{X})$ values of deuterated X-anilines may be slightly greater than those of X-anilines, however, the difference is too small to be taken into account.

The anilinolysis rates are not consistent with a typical nucleophilic substitution reaction. The rate becomes slower with a weaker nucleophile for X = (4-MeO, 4-Me, 3-Me, H). However, the rate with X = 4-F is unusually 2.5 and 3.1 times faster than with X = H for aniline and deuterated aniline, respectively, in spite of greater basicity of aniline compared to 4-fluoroaniline. After a break region, the rate again becomes slower with a weaker nucleophile for X = (4-F, 3-MeO, 4-Cl, 3-Cl). Thus, both the Hammett (Fig. 1; $\log k_{\text{H(D)}} \text{ vs } \sigma_{\text{X}}$) and Brønsted [Fig. 2; $\log k_{\text{H(D)}} \text{ vs } \text{p}K_{\text{a}}(\text{X})$] plots for substituent X variations in the nucleophiles exhibit the

[†]This paper is to commemorate Professor Kook Joe Shin's honourable retirement.

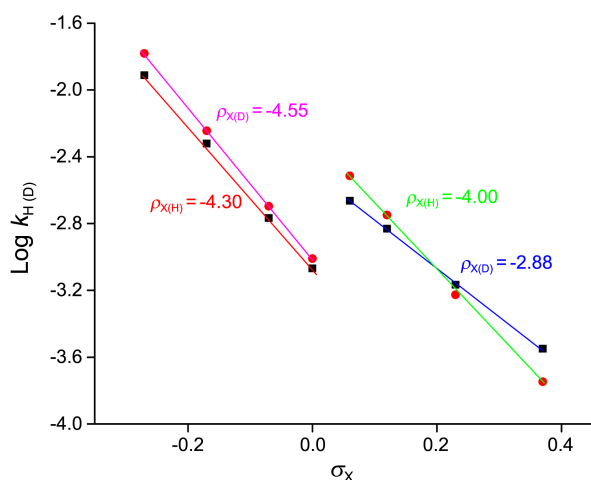


Figure 1. The Hammett plots ($\log k_{H(D)}$ vs σ_X) of the reactions of diethyl isothiocyanophosphate (**1**) with $\text{XC}_6\text{H}_4\text{NH}_2(\text{D}_2)$ in MeCN at 55.0 °C.

two discrete slopes with a break region between $X = \text{H}$ and 4-F, giving $\rho_{X(\text{H})} = -4.30$ and -2.84 ($\rho_{X(\text{D})} = -4.55$ and -4.00), and $\beta_{X(\text{H})} = 1.45$ and 0.92 ($\beta_{X(\text{D})} = 1.53$ and 1.28) with the strongly and weakly basic anilines, respectively. The magnitudes of selectivity parameters with the strongly basic anilines are greater than those with the weakly basic anilines. These kinetic results suggest a change of the reaction mechanism from the strongly to weakly basic anilines.

The DKIEs with the strongly basic anilines ($X = 4\text{-MeO}$, 4-Me, 3-Me, H) are secondary inverse ($k_{\text{H}}/k_{\text{D}} < 1$) and the values of DKIEs invariably increase as the nucleophile becomes weaker: from $X = 4\text{-MeO}$ ($k_{\text{H}}/k_{\text{D}} = 0.74$), via 4-Me ($k_{\text{H}}/k_{\text{D}} = 0.84$) and 3-Me ($k_{\text{H}}/k_{\text{D}} = 0.85$), to H ($k_{\text{H}}/k_{\text{D}} = 0.87$). The DKIEs with the weakly basic anilines ($X = 4\text{-F}$, 3-MeO, 4-Cl, 3-Cl) are secondary inverse ($k_{\text{H}}/k_{\text{D}} < 1$) with $X = 4\text{-F}$ ($k_{\text{H}}/k_{\text{D}} = 0.71$; remarkably small) and 3-MeO ($k_{\text{H}}/k_{\text{D}} = 0.83$) while primary normal ($k_{\text{H}}/k_{\text{D}} > 1$) with $X = 4\text{-Cl}$ ($k_{\text{H}}/k_{\text{D}} = 1.15$) and 3-Cl ($k_{\text{H}}/k_{\text{D}} = 1.58$; remarkably large), and the values of DKIEs invariably increase as the nucleophile becomes weaker. The substituent effects on DKIEs, the wide spectrum of $k_{\text{H}}/k_{\text{D}} = 0.71\text{--}1.58$, are surprising.⁸ Note that the values of DKIEs show the break region between $X = \text{H}$ and 4-F: $k_{\text{H}}/k_{\text{D}}(\text{X}) = 0.74(4\text{-MeO}) < 0.84(4\text{-Me}) < 0.85(3\text{-Me}) < 0.87(\text{H}) > 0.71(4\text{-F}) < 0.83(3\text{-MeO}) < 1.15(4\text{-Cl}) < 1.58(3\text{-Cl})$. These also suggest a change of the reaction mechanism from the strongly to weakly basic anilines.

The second-order rate constants (k_{H}) with unsubstituted aniline, natural bond order (NBO) charges at the reaction center P atom [B3LYP/6-311+G(d,p) level of theory] in the gas phase,⁹ Brønsted coefficients ($\beta_{X(\text{H})}$), and DKIEs ($k_{\text{H}}/k_{\text{D}}$)

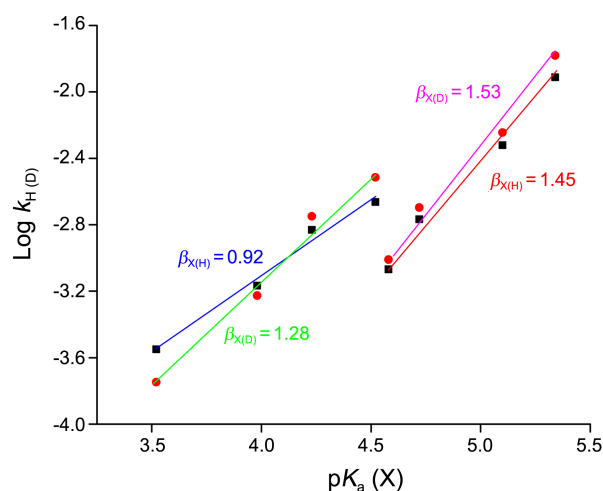


Figure 2. The Brønsted plots [$\log k_{H(D)}$ vs $\text{p}K_{\text{a}}(\text{X})$] of the reactions of diethyl isothiocyanophosphate (**1**) with $\text{XC}_6\text{H}_4\text{NH}_2(\text{D}_2)$ in MeCN at 55.0 °C.

of the reactions of **1** and **2** with $\text{XC}_6\text{H}_4\text{NH}_2(\text{D}_2)$ in MeCN at 55.0 °C are summarized in Table 2. The ratio of $k(\mathbf{2})/k(\mathbf{1}) = 3.3$ indicates that the leaving group mobility of chloride (Cl^-) is greater than that of isothiocyanate (NCS^-). In other words, chloride is a better leaving group compared to isothiocyanate. The magnitude of the NBO charge at the reaction center P atom does not play any role to determine the leaving group mobility. The anilinolysis of **2** involving a chloride leaving group yielded linear free energy relationship for substituent X variations in the nucleophiles and the DKIEs of **2** are secondary inverse ($k_{\text{H}}/k_{\text{D}} = 0.71\text{--}0.92$), invariably increasing with a stronger nucleophile in contrast to the present work of **1**.²

The DKIEs are one of the strong tools to clarify the reaction mechanism. The DKIEs have provided a useful means to determine the transition state (TS) structures in the nucleophilic substitution reactions, and how the reactants, especially through changes in substituents, alter the TS structures. Incorporation of deuterium in the nucleophile has an advantage in that the α -DKIEs reflect only the degree of bond formation. The DKIEs can only be secondary inverse ($k_{\text{H}}/k_{\text{D}} < 1.0$) in a normal $\text{S}_{\text{N}}2$ reaction, since the N–H(D) vibrational frequencies invariably increase upon going to the TS because of an increase in steric congestion in the bond-making process.¹⁰ The greater the degree of the steric congestion in the TS, the value of $k_{\text{H}}/k_{\text{D}}$ becomes smaller. In contrast, when partial deprotonation of the aniline occurs in a rate-limiting step by hydrogen bonding, the $k_{\text{H}}/k_{\text{D}}$ values are greater than unity, primary normal ($k_{\text{H}}/k_{\text{D}} > 1.0$).¹¹ The greater the extent of the hydrogen bond, the value of $k_{\text{H}}/k_{\text{D}}$

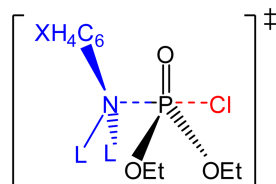
Table 2. Summary of the Second-Order Rate Constants ($k_{\text{H}} \times 10^3/\text{M}^{-1} \text{ s}^{-1}$) with $\text{C}_6\text{H}_5\text{NH}_2$, NBO Charges at the Reaction Center P Atom, Brønsted Coefficients ($\beta_{X(\text{H})}$), and DKIEs ($k_{\text{H}}/k_{\text{D}}$) for the Reactions of **1** and **2** with $\text{XC}_6\text{H}_4\text{NH}_2(\text{D}_2)$ in MeCN at 55.0 °C

Substrate	$k_{\text{H}} \times 10^3^a$	Charge at P	$\beta_{X(\text{H})}$	$k_{\text{H}}/k_{\text{D}}$
1 : $(\text{EtO})_2\text{P}(=\text{O})\text{NCS}$	0.854	2.454	1.45/0.92 ^b	0.74–0.87/0.71–1.58 ^b
2 : $(\text{EtO})_2\text{P}(=\text{O})\text{Cl}$	2.82	2.236	1.06	0.71–0.92

^aThe values with unsubstituted aniline. ^bStrongly/weakly basic anilines.

becomes greater.

The authors accordingly proposed that the anilinolysis of **2** proceeds through a concerted mechanism with a dominant backside nucleophilic attack TSb on the basis of the good leaving group of chloride and secondary inverse DKIEs of $k_H/k_D = 0.71$ - 0.92 .

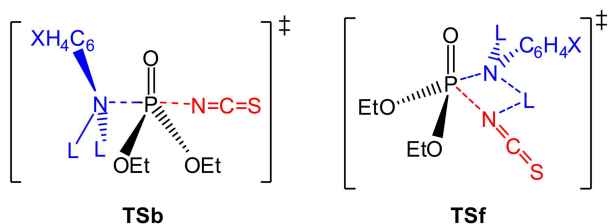


L = H or D

Backside attack TSb

In the present work of **1**, the authors propose a predominant backside attack TSb (Scheme 2) with the strongly basic anilines (X = 4-MeO, 4-Me, 3-Me, H) based on the secondary inverse DKIEs ($k_H/k_D = 0.74$ - 0.87), and the TS variation from a dominant backside attack TSb with more basic anilines (X = 4-F, 3-MeO) to a dominant frontside attack involving a hydrogen-bonded, four-center-type TSf (Scheme 2) with less basic anilines (X = 4-Cl, 3-Cl) on the basis of the secondary inverse DKIEs ($k_H/k_D = 0.71$ and 0.83) with X = (4-F and 3-MeO) and primary normal DKIEs ($k_H/k_D = 1.15$ and 1.58) with X = (4-Cl and 3-Cl). It should be noted that the real primary normal DKIE due to the hydrogen bond between the hydrogen of the N-H(D) moiety and the nitrogen atom in the NCS⁻ leaving group should be greater than the observed value since the observed DKIEs would be the sum of: (i) the primary normal DKIE, $k_H/k_D > 1$, because of the partial deprotonation of one of the two N-H(D) bonds in the TSf for a frontside attack; (ii) the secondary inverse DKIE, $k_H/k_D < 1$, because of the steric hindrance that increases the out-of-plane bending vibrational frequencies of the other N-H(D) bond in TSf for a frontside attack; (iii) lowering the k_H/k_D value because of the nonlinear and unsymmetrical structure of N...H(D)...NCS in TSf; and finally (iv) lowering the k_H/k_D value because of heavy atom (N in the nucleophile and N in the leaving group) contribution to the reaction-coordinate motion.

As mentioned earlier, chloride should be a far better leaving group than isothiocyanate. The change of the leaving group from chloride to that of a poor leaving ability, iso-



Scheme 2. Backside attack TSb and frontside attack involving a hydrogen-bonded, four-center-type TSf (L = H or D).

Table 3. Activation Parameters for the Reactions of Diethyl Isothiocyanophosphate (**1**) with Aniline (C₆H₅NH₂) in MeCN

$t/^\circ\text{C}$	$k_H \times 10^4/\text{M}^{-1}\text{s}^{-1}$	$\Delta H^\ddagger/\text{kcal mol}^{-1}$	$-\Delta S^\ddagger/\text{cal mol}^{-1}\text{K}^{-1}$
45.0	5.80 ± 0.01		
55.0	8.54 ± 0.02	6.9	52
65.0	11.8 ± 0.1		

thiocyanate, can cause a change in mechanism from a concerted to a stepwise process with a rate-limiting breakdown of the trigonal bipyramidal pentacoordinate (TBP-5C) intermediate. This is in accord with the well established trend of the mechanistic change depending on the leaving group ability: the lower the leaving ability of the leaving group, the greater is the tendency for a stepwise mechanism with a rate-limiting expulsion of the leaving group from the intermediate.¹² The change in mechanism from a concerted to a stepwise reaction has been shown to occur by varying the strength of the nucleophile and leaving group in the neutral phosphoryl transfer reactions.¹³ The concerted path becomes more likely to be followed with less basic nucleophiles and with stronger leaving group. For very basic nucleophiles and poor leaving groups, a stepwise path is favored.¹³ Thus, the authors propose a concerted S_N2 mechanism (or a stepwise mechanism with a rate-limiting bond formation step) with the weakly basic anilines and a stepwise mechanism with a rate-limiting leaving group departure from the TBP-5C intermediate with the strongly basic anilines. The greater values of $\beta_{X(H)} = 1.45$ and $\beta_{X(D)} = 1.53$ with the strongly basic anilines compared to those ($\beta_{X(H)} = 0.92$ and $\beta_{X(D)} = 1.28$) with the weakly basic anilines are consistent with the proposed mechanism.

Activation parameters, enthalpy and entropy of activation, are determined for the anilinolysis (with C₆H₅NH₂) of **1** in Table 3. The enthalpy of activation is relatively low (6.9 kcal mol^{-1}) and entropy of activation is relatively large negative values ($52\text{ cal mol}^{-1}\text{K}^{-1}$). The relatively low of activation enthalpy and large negative value of activation entropy are typical for the aminolyses of P=O systems.

In summary, the kinetic studies on the reactions of diethyl isothiocyanophosphate (**1**) with substituted anilines (XC₆H₄NH₂) and deuterated anilines (XC₆H₄ND₂) have been carried out in MeCN at 55.0 °C. The Hammett and Brønsted plots for substituent X variations in the nucleophiles exhibit the two discrete slopes with a break region between X = H and 4-F. The obtained DKIEs (k_H/k_D) are secondary inverse ($k_H/k_D = 0.74$ - 0.87) with the strongly basic anilines while secondary and primary normal ($k_H/k_D = 0.71$ - 1.58) with the weakly basic anilines. A stepwise mechanism with a rate-limiting leaving group departure from the TBP-5C intermediate involving a backside attack is proposed for the strongly basic anilines, and a concerted S_N2 mechanism (or a stepwise mechanism with a rate-limiting bond formation step) through both backside TSb and frontside attack involving a hydrogen-bonded, four-center-type TSf is proposed for the weakly basic anilines.

Experimental Section

Materials. The substrate of diethyl isothiocyanophosphate was synthesized as previously described.^{1,14} HPLC grade acetonitrile (water content is less than 0.005%) was used for kinetic studies without further purification. Anilines were redistilled or recrystallized before use as previously described.^{1,2} Deuterated anilines were synthesized by heating anilines and deuterium oxide (99.9 atom %D) and one drop of HCl as catalyst at 85 °C for 72 hours, and after numerous attempts, anilines were deuterated more than 98%, as confirmed by ¹H NMR.

Kinetic Procedure. Rates were measured conductometrically at 55.0 °C. The conductivity bridge used in this work was a self-made computer automated A/D converter conductivity bridge. Pseudo-first-order rate constants, k_{obsd} were measured by curve fitting analysis in origin program with a large excess of anilines, [substrate] = 5×10^{-3} M and [X-aniline] = 0.1-0.3 M. The second-order rate constants, $k_{\text{H(D)}}$, were obtained from the slope of a plot of k_{obsd} vs. [X-aniline] with five concentrations of anilines. The pseudo-first-order rate constant values (k_{obsd}) were the average of at least three runs that were reproducible within $\pm 3\%$.

Product Analysis. Diethyl isothiocyanophosphate was reacted with excess aniline for more than 15 half-lives at 55.0 °C in MeCN. Acetonitrile was evaporated under reduced pressure. The product mixture was treated with ether by a work-up process with dilute HCl and dried over anhydrous MgSO₄. Then the product was isolated through column chromatography (60% ethyl acetate/*n*-hexane) and then dried under reduced pressure. The analytical and spectroscopic data of the product gave the following results (see Supporting Information including activation parameters).

(C₂H₅O)₂P(=O)NHC₆H₅. White solid crystal, mp 92.0-93.0 °C; ¹H-NMR (400 MHz, MeCN-*d*₃) δ 1.20-1.31 (aliphatic, 6H, m), 3.98-4.12 (aliphatic, 4H, m), 6.06 (aliphatic, 1H, s), 6.91-6.96 (aromatic, 1H, m), 7.03-7.05 (aromatic, 2H, m), 7.22-7.26 (aromatic, 2H, m); ¹³C-NMR (100 MHz, MeCN-*d*₃) δ 16.49 (aliphatic, 2C, s), 63.60 (aliphatic, 2C, s), 118.38-130.20 (aromatic, 6C, m); ³¹P-NMR (162 MHz, MeCN-*d*₃) δ 12.46 (P=O, 1P, s); GC-MS for C₁₀H₁₆NO₃P (EI, *m/z*) 229 (M⁺).

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8. In general, the changes of the DKIEs of ($k_{\text{H}}/k_{\text{D}}$) with substituent X variations are in the range of 0.1-0.5 for the anilinolyses of P=O and P=S systems. The change of the DKIEs of ($k_{\text{H}}/k_{\text{D}}$) = 1.58-0.71 = 0.87 of the present work is surprising: the largest change of ($k_{\text{H}}/k_{\text{D}}$) = 1.94-0.88 = 1.06, second largest change of ($k_{\text{H}}/k_{\text{D}}$) = 1.30-0.37 = 0.93, and the third largest change of ($k_{\text{H}}/k_{\text{D}}$) = 1.34-0.44 = 0.90 are observed for the anilinolyses of 1,2-phenylene phosphorochloridate [C₆H₄OOP(=O)Cl], *O*-aryl methyl [Me(YC₆H₄O)P(=S)Cl] and *O*-aryl phenyl [Ph(YC₆H₄O)P(=S)Cl] phosphonochloridothioates, respectively. (a) Barai, H. R.; Lee, H. W. *Bull. Korean Chem. Soc.* 2011, 32, 4185. (b) Hoque, M. E. U.; Guha, A. K.; Kim, C. K.; Lee, B. S.; Lee, H. W. *Org. Biomol. Chem.* 2009, 7, 2919. (c) Adhikary, K. K.; Lumbiny, B. J.; Dey, S.; Lee, H. W. *Bull. Korean Chem. Soc.* 2011, 32, 2628.
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