Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supplementary Information

Kinetics and mechanism of the anilinolyses of aryl dimethyl, methyl phenyl and diphenyl phosphinates

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Substrates

Substituted phenyl dimethyl, methyl phenyl, and diphenyl phosphinates were prepared by reacting dimethyl, methyl phenyl, and diphenyl phosphinic chlorides with phenols in the presence of triethyl amine in acetonitrile at room temperature, respectively. Finally the products were isolated by solvent evaporation under reduced pressure, after filtration, and the products passed through column chromatography (50% ethyl acetate and n-hexane) for purification. Analytical data of the products gave the following results:

$Me_2P(=O)OPh$-4-Me.[1-3] White solid, mp 58-60 °C; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.059, 7.060, 7.081, 7.102, 7.123, 7.124 (4H, m, aromatic), 1.588, 1.590, 1.624, 1.625 (6H, m, methyl), 2.303 (3H, s, methyl); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.443, 120.481, 130.260, 134.459, 148.407 (C=C, m, aromatic), 115.182, 16.130, 20.670 (C=C, s, methyl); ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.295 (1P, s); Mass, m/z, 184 (M^+), Anal. Calcd for $C_9H_{13}O_2P$: C, 58.69; H, 7.11; Found: C, 58.63; H, 7.30.

$Me_2P(=O)OPh$.[3-6] White solid, mp 40-42 °C; ^{1}H NMR (400MHz, $CDCl_3$) δ 6.795, 6.797, 6.818, 7.109, 7.114, 7.128, 7.130, 7.148, 7.152, 7.163, 7.177, 7.229, 7.295, 7.314, 7.717 (5H, m, aromatic), 1.533, 1.570, 1.585, 1.611, 1.612, 1.620, 1.636, 1.670, 1.672 (6H, m, methyl); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.395, 119.185, 124.840, 129.206, 129.737, 157.125 (C=C, m, aromatic), 120.633-120.678 (C=C, aromatic, d, J = 4.5 Hz), 150.469-150.552 (C=C, aromatic,d, J = 8.3 Hz); 156.129, 16.077 (C=C, s, methyl); ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.924 (1P, s); Mass, m/z, 169 (M^+); Anal. Calcd for $C_8H_{11}O_2P$: C, 56.47; H, 6.52; Found: C, 56.25; H, 6.42.

$Me_2P(=O)OPh$-4-NO_2.[1,3,7] White crystal, mp 88-90 °C; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.256, 7.378, 7.401, 8.223, 8.224, 8.246 (4H, m, phenyl), 1.696, 1.731 (6H, m, methyl); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.592 (C=C, s, aromatic), 121.065-121.110 (C=C, aromatic, d, J = 4.5 Hz), 125.840, 126.166 (C=C, s, aromatic); ^{31}P NMR (162 MHz, $CDCl_3$) δ 60.463 (1P, s); Mass, m/z, 215 (M^+); Anal. Calcd for $C_8H_{10}NO_4P$: C, 44.66; H, 4.68; N, 6.51. Found: C, 44.34; H, 4.86; N, 6.65.

MePhP(=O)OPh-4-Me.[9-11] White solid, mp 70-72 °C, ^{1}H NMR (400MHz, $CDCl_3$) δ 7.014, 7.256, 7.468, 7.482, 7.523, 7.839, 7.849, 7.853, 7.870 (9H, m, aromatic), 2.247 (3H, s, methyl), 1.807-1.843 (3H, d, J = 14.4 Hz, methyl); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.352-120.398 (C=C, aromatic, d, J = 4.6 Hz), 128.398, 128.668, 130.093, 131.260, 131.366, 132.496, 134.148, 148.460 (C=C, m, aromatic), 20.647 (C=C, s, methyl), 15.455, 16.471 (C=C, s, methyl); ^{31}P NMR (162 MHz, $CDCl_3$) δ 46.800 (1P, s); Mass, m/z, 246 (M^+); Anal. Calcd for $C_{14}H_{15}O_2P$: C, 68.29; H, 6.14; Found: C, 68.02; H, 6.17.

MePhP(=O)OPh.[5,6,9,10,12,13] White crystal, mp 60-62 °C, ^{1}H NMR (400MHz, $CDCl_3$) δ 7.051, 7.088, 7.116, 7.210, 7.449, 7.454, 7.544, 7.823, 7.873 (10H, m, aromatic), 1.831-1.867 (3H, d, J = 14.4 Hz, methyl); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.602-120.648 (C=C, aromatic, d, J = 4.6 Hz), 124.628, 128.698, 129.615, 130.184, 131.207, 131.306, 131.480, 132.579, 132.610, 150.734 (C=C, m, aromatic), 15.417, 16.433 (C=C, s, methyl); ^{31}P NMR (162 MHz, $CDCl_3$) δ 47.478 (1P, s); Mass, m/z, 232 (M^+); Anal. Calcd for $C_{13}H_{13}O_2P$: C, 67.24; H, 5.64; Found: C, 67.42; H, 5.87.

MePhP(=O)OPh-4-NO_2.[9,12] Light-yellowish liquid, ^{1}H NMR (400MHz, $CDCl_3$) δ 7.255, 7.298, 7.531, 7.827, 7.841, 7.859, 8.116, 8.122, 8.139 (9H, m, aromatic), 1.428-1.414 (3H, d, J = 5.6 Hz, methyl); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.012−121.065 (C=C, aromatic, d, J = 4.6 Hz), 125.628, 126.151, 128.971, 129.100, 131.169, 131.276, 133.315 (C=C, m, aromatic), 15.773, 16.789, 17.426 (C=C, s, methyl); ^{31}P NMR (162 MHz, $CDCl_3$) δ 49.983 (1P, s); Mass, m/z, 277 (M^+); Anal. Calcd for $C_{13}H_{12}NO_4P$: C, 56.32; H, 4.36; N, 5.05. Found: C, 56.53; H, 4.38; N, 4.88.

Ph_2P(=O)OPh-4-Me.[15-17] White solid, mp 122-124 °C, ^{1}H NMR (400MHz, $CDCl_3$) δ 7.025, 7.062, 7.064, 7.445, 7.455, 7.473, 7.504, 7.508, 7.856, 7.877, 7.891, 7.908 (14H, m, aromatic), 2.244 (3H, s, methyl); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.405-120.451 (C=C, aromatic, d, J = 4.6 Hz), 128.463, 128.592, 130.070, 131.768, 131.867, 132.322, 132.352 (C=C, m, aromatic), 20.655 (C=C, s, methyl); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.548 (1P, s); Mass, m/z, 308 (M^+); Anal. Calcd for $C_{19}H_{17}O_2P$: C, 74.02; H, 5.56. Found: C, 73.88; H, 5.67.

Ph_2P(=O)OPh.[18-21] White solid, mp 132-134 °C, ^{1}H NMR (400MHz, $CDCl_3$) δ 7.070, 7.182, 7.185, 7.200, 7.202, 7.203, 7.436, 7.454, 7.457, 7.463, , 7.532, 7.862, 7.894, 7.915, 7.918 (15H, m, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.716, 124.567, 128.516, 128.645, 129.631, 131.761, 131.867, 132.405 (C=C, m, aromatic); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.714 (1P, s); Mass, m/z, 294 (M^+); Anal. Calcd for $C_{18}H_{15}O_2P$: C, 73.46; H, 5.14. Found: C, 73.26; H, 5.28.

$Ph_2P(=O)OPh\text{-}4\text{-}NO_2$.[17,22-24] White solid, mp 100-102 °C, ^{1}H NMR (400MHz, $CDCl_3$) δ 7.357, 7.380, 7.496, 7.505, 7.515, 7.526, 7.570, 7.589, 7.593, 7.854, 7.878, 7.910, 8.131, 8.155 (14H, m, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.156-121.209 (C=C, aromatic, d, J = 5.3 Hz), 125.636, 126.083 (C=C, s, aromatic), 128.835-128.971 (C=C, aromatic, d, J = 13.6 Hz), 131.624−131.730 (C=C, aromatic, d, J = 10.6 Hz), 133.095-133.125 (C=C, aromatic, d, J = 3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.3 (1P, s); Mass, m/z, 339 (M^+); Anal. Calcd for $C_{18}H_{14}NO_4P$: C, 63.72; H, 4.16; N, 4.13. Found: C, 63.48; H, 3.99; N, 3.89.

Product Analysis. $Me_2P(=O)PhO\text{-}4\text{-}NO_2$, $MePhP(=O)PhO\text{-}4\text{-}NO_2$, and $Ph_2P(=O)PhO\text{-}4\text{-}NO_2$ were reacted with excess $4\text{-}MePhNH_2$, $4\text{-}MeOPhNH_2$ and $PhNH_2$ for more than 15 half-lives at 60.0 ^{o}C in DMSO, respectively. The 4-methyl, 4-methoxy, and anilinium chloride salts were separated by filtration. Analytical and spectroscopic data of the products gave the following results:

$Me_2P(=O)NHPh\text{-}4\text{-}Me$.[8] Brown solid, mp 172-174 °C; ^{1}H NMR (400MHz, $CDCl_3$) δ 1.62-1.70 (6H, m, CH_3), 2.23-2.27 (3H, d, J = 16.0 Hz, CH_3), 4.84-4.86 (1H, d, J = 8.0 Hz, NH), 6.61-7.26 (4H, m, phenyl); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.3-17.2 (CH_3, s), 20.6 (CH_3, s), 115.2, 119.2, 119.3, 129.7, 130.0, 131.8, 37.7 (C=C, aromatic); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.9-40.0 (1P, d, J = 16.2 Hz, P=S); Mass, m/z, 183 (M^+); Anal. Calcd for $C_9H_{14}NOP$: C, 59.1; H, 7.7; N, 7.8; Found: C, 59.0; H, 7.7; N, 7.7.

$MePhP(=O)NHPh\text{-}4\text{-}OMe$. [8,14] Purple gummy solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77, 1.80 (3H, s, CH_3), -

3.72 (3H, s, OCH_3), 4.96 (1H, d, J = 8.4 Hz, NH), 6.73 (d, J = 8.8 Hz, 2H, phenyl), 6.96 (2H, d, J = 8.8 Hz, phenyl), 7.47 (2H, t, J = 8.8 Hz, phenyl), 7.52 (1H, d, J = 8.8 Hz, phenyl), 7.86 (2H, d, J = 8.8 Hz, phenyl); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.2−17.1 (CH_3, s), 55.5 (OCH_3), 114.6, 115.4, 120.6, 121.2, 128.3, 131.5, 132.1, 133.1, 155.2 (C=C, aromatic); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.9 (s, 1P, P=O); m/z 261 (M^+); Anal. Calcd for $C_{14}H_{16}NO_2P$: C, 64.4; H, 6.2; N, 5.4. Found: C, 64.3; H, 6.2; N, 5.4.

$Ph_2P(=O)NHPh$.[24-26] Yellowish Solid; mp 85-86 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.2 (1H, d, J = 11.6Hz, NH), 6.9 (1H, d, J = 7.6 Hz), 7.0 (2H, d, J = 7.6 Hz), 7.1 (2H, d, 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 118.331, 120.716, 124.567, 128.516, 128.645, 129.631, 131.761, 131.867, 140.213 (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.

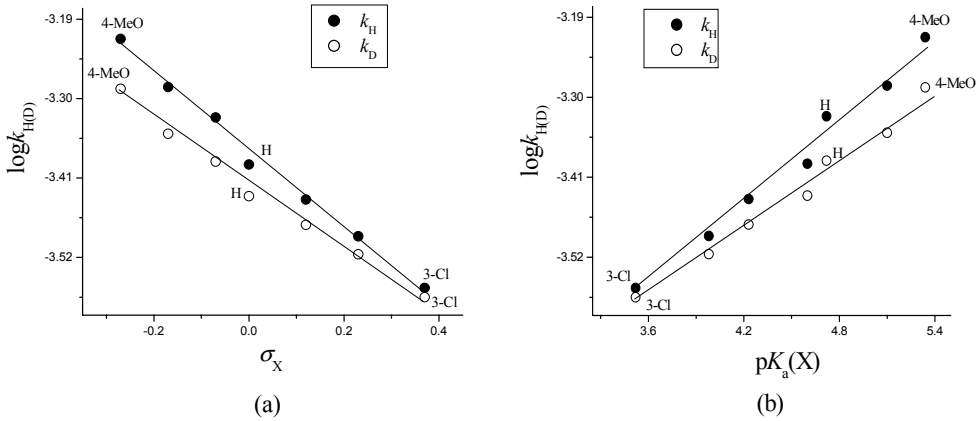

Fig. S1 The Hammett (a) and Brönsted (b) plots of the aminolysis of $Me_2P(=O)OPh$-4-NO_2 with $XPhNH_2$ (●) and $XPhND_2$ (○) in DMSO at 60.0 ºC.

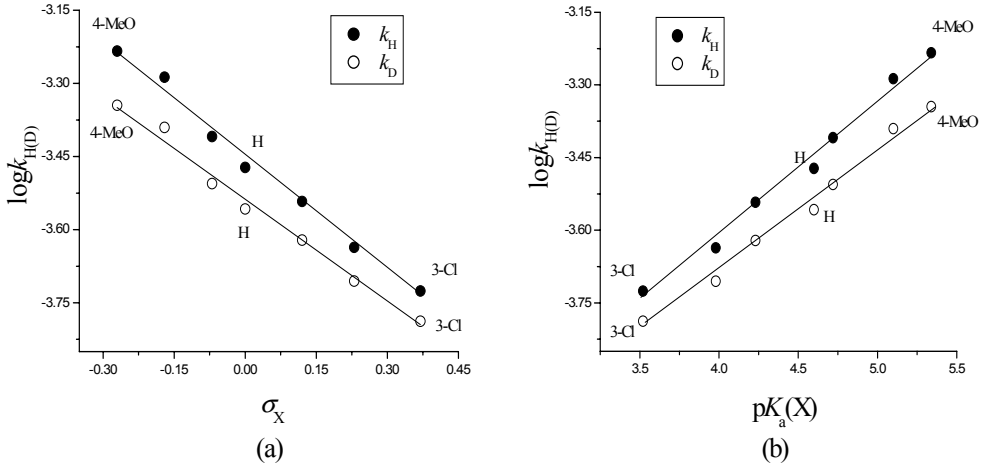

Fig. S2 The Hammett (a) and Brönsted (b) plots of the aminolysis of MePhP(=O)OPh-4-NO_2 with $XPhNH_2$ (●) and $XPhND_2$ (○) in DMSO at 60.0 ºC.

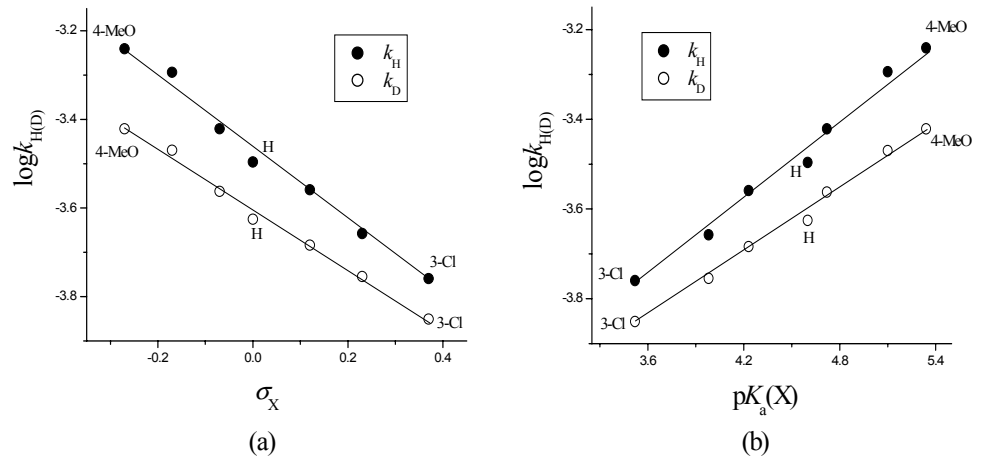

Fig. S3 The Hammett (a) and Brönsted (b) plots of the aminolysis of Ph_2P(=O)OPh-4-NO_2 with $XPhNH_2$ (●) and $XPhND_2$ (○) in DMSO at 60.0 ºC.

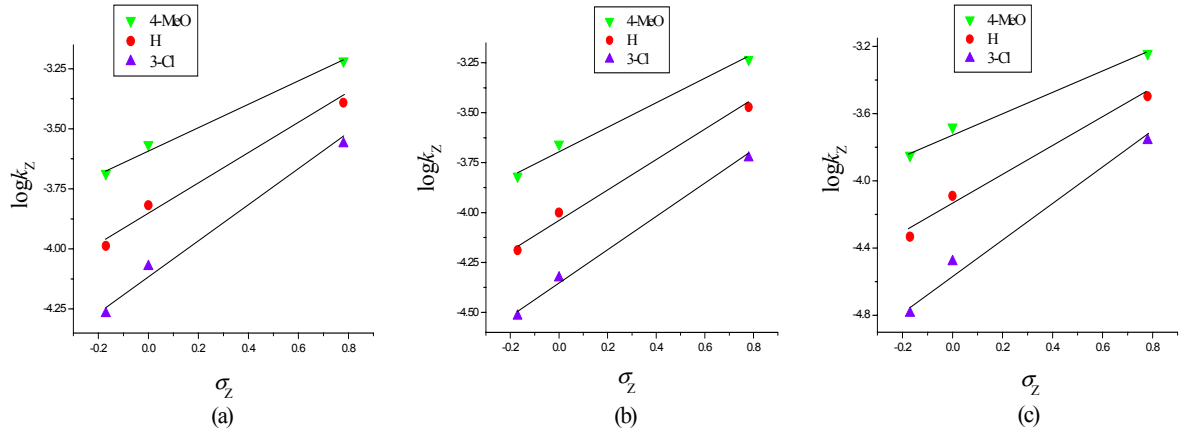

Fig. S4 The Hammett plots a, b, and c by plotting logk_H vs σ_Z for the reactions of $Me_2P(=O)OPhZ$, $MePhP(=O)OPhZ$, and $Ph_2P(=O)OPhZ$, respectively, with $XPhNH_2$ in DMSO at 60.0 °C.

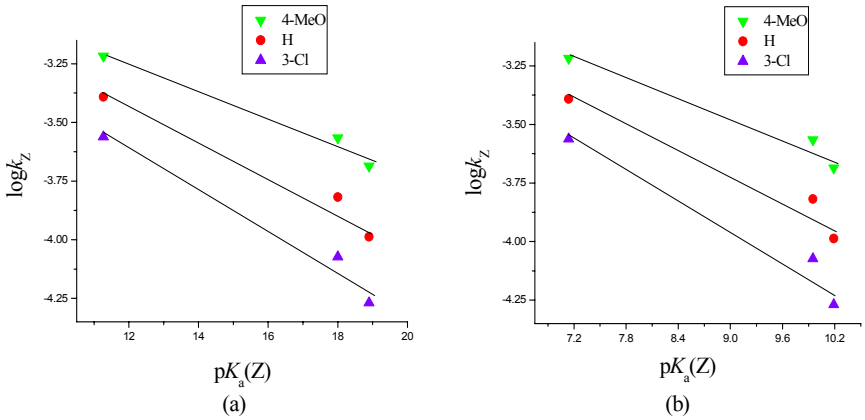

Fig. S5 The Brönsted (a) for logk_H vs pK_a(Z) (in DMSO) and (b) for logk_H vs pK_a(Z) (in water) plots of the aminolysis of $Me_2P(=O)OPhZ$ with $XPhNH_2$ in DMSO at 60.0 ºC.

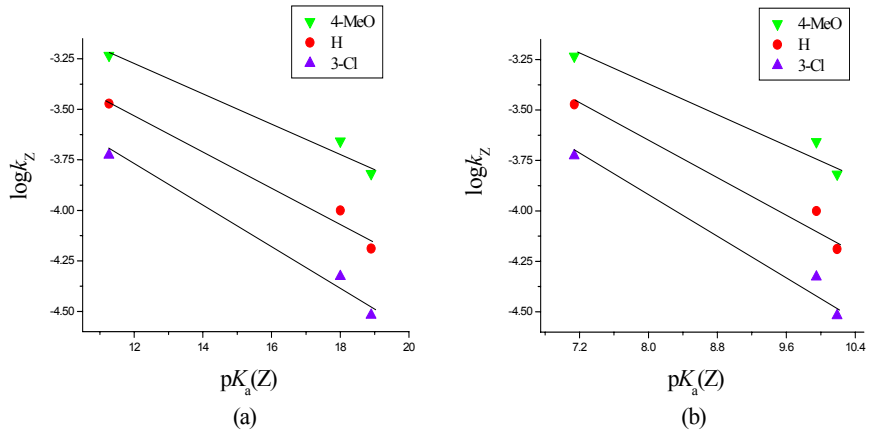

Fig. S6 The Brönsted (a) for logk_H vs pK_a(Z) (in DMSO) and (b) for logk_H vs pK_a(Z) (in water) plots of the aminolysis of (Me)(Ph)P(=O)(OPhZ) with $XPhNH_2$ in DMSO at 60.0 ºC.

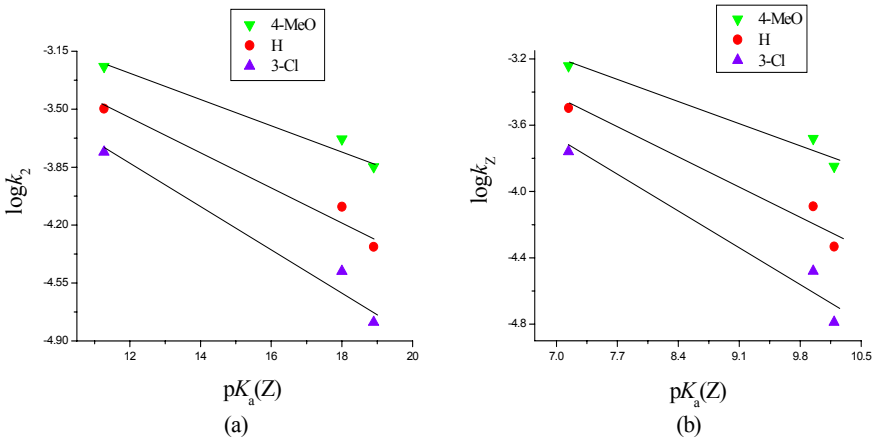

Fig. S7 The Brönsted (a) for logk_H vs pK_a(Z) (in DMSO) and (b) for logk_H vs pK_a(Z) (in water) plots of the aminolysis of $(Ph)_2P(=O)(OPhZ)$ with $XPhNH_2$ in DMSO at 60.0 ºC.

References

(1) E. Buncel, K. G. Albright and I. Onyido, *Org. Biomol. Chem.*, 2004, **2**, 601.

(2) E. J. Dunn, J. G. Purdon, R. A. B. Bannard, K. Albright and E. Buncel, *Can. J. Chem.*, 1988, **66**, 3137.

(3) K. T, Douglas and A. Williams, *J. Chem. Soc.*, *Perkin Trans. 2*, 1976, 515.

(4) S. Trippett and P. J. Whittle, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1220.

(5) S. A. Bone, S. Trippett and P. J. Whittle, *J. Chem. Soc., Perkin Trans. 1*, 1977, 437.

(6) M. J. P. Harger, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1505.

(7) M. E. U. Hoque, D N. K.ey, C. K. Kim, B. S. Lee and H. W. Lee, *Org. Biomol. Chem.*, 2007, **5**, 3944.

(8) N. K. Dey, M. E. U. Hoque, C. K. Kim, B. S. Lee and H. W. Lee, *J. Phys. Org. Chem.*, 2009, **22**, 425.

(9) I. Onyido, K.Albright and E. Buncel, *Org. Biomol. Chem.*, 2005, **3**, 1468.

(10) G. Baccolini and C. Boga, *Tetrahedron Lett.*, 2001, **42**, 6121.

(11) J.-F. Gal, I. Koppel, R. Kurg and P.-C. Maria, *In. J. Quantum Chem.*, 1996, **59**, 409.

(12) Y. Li, S. D. Aubert, E. G. Maes and F. M. Raushel, *J. Am. Chem. Soc.*, 2004, **126**, 8888.

(13) D. I. Phillips, I. Szele and F. H. Westheimer, *J. Am. Chem. Soc.*, 1976, **98**, 184.

(14) M. J. P. Harger, *J. Chem. Soc*., *Perkin Trans. 1*, 1979, 1294.

(15) A. Williams and R. A. Naylor, *J. Chem. Soc. B, Physical Organic*, 1971, 1967.

(16) P. Haake, D. R. McCoy, W. Okamura, S. R. Alpha, S.-Y. Wong, D. A. Tyssee, J. P. McNeal and R. D. Cook, *Tetrahedron Lett.*, 1968, **50**, 5243.

(17) S. Hoz, E. J. Dunn, E. Buncel, R. A. B. Bannard and J. G. Purdon, *Phosphorus and Sulfur and the Related Elements*, 1985, **24**, 321.

(18) I.-H. Um, J. E. Park and Y.-H. Shin, *Org. Biomol. Chem.*, 2007, **5**, 3539.

(19) M. Aresta, A. Dibenedetto and E. Quaranta, *Tetrahedron*, 1998, **54**, 14145.

(20) A. Blasko, C. A. Bunton, Y. S. Hong, M. M. Mhala, J. R. Moffatt and S. Wright, *J. Phys. Org. Chem.*, 1991, **4**, 618.

(21) L. Horner and R. Gehring, *Phosphorus and Sulfur and the Related Elements*, 1981, **11**, 157.

(22) J.-K. Limb, S.-E. Jeon, S.-E. Lee and I.-H. Um, *Bull. Korean. Chem. Soc.*, 2002, **23**, 1263.

(23) R. M. Tarkka and E. Buncel, *J. Am. Chem. Soc.*, 1995, **117**, 1503.

(24) A. Williams, K. T. Douglas and J. S. Loran, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1010.

(25) M. E. U. Hoque and H. W. Lee, *Bull. Korean Chem. Soc.*, 2007, **28**, 936.

(26) M. E. U. Hoque, S. Dey, A. K. Guha, C. K. Kim, B. S. Lee and H. W. Lee, *J. Org. Chem.*, 2007, **72**, 5493.