# *Notes*

## Reactivities of Novel [Hydroxy(tosyloxy)iodo]arenes and [Hydroxy(phosphoryloxy)iodo]arenes for α-Tosyloxylation and α-Phosphoryloxylation of Ketones

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**Abstract:** Novel [hydroxy(tosyloxy)iodo]arenes bearing 2-thienyl, 3-thienyl, *N*-tosyl-4-pyrazolyl, 3-trifluoromethylphenyl, and 3,5-bis(trifluoromethy)phenyl as an aromatic group, and [hydroxy(phosphoryloxy)iodo]arenes bearing *N*-tosyl-4-pyrazolyl, 3-trifluoromethylphenyl, and 3,5-bis(trifluoromethy)phenyl as an aromatic group, were prepared. α-Tosyloxylation and α-phosphoryloxylation of ketones with these compounds were carried out, respectively. Their reactivities were compared with that of the parent [hydroxy(tosyloxy)iodo]benzene and [hydroxy(phosphoryloxy)iodo]benzene, respectively, and consequently [hydroxy(tosyloxy)iodo]arenes and [hydroxy(phosphoryloxy)iodo]arenes bearing 3-trifluoromethylphenyl and 3,5-bis(trifluoromethy)phenyl as an aromatic group showed the best reactivity. These new compounds can be used as powerful α-tosyloxylation and α-phosphoryloxylation reagents, instead of the parent [hydroxy(tosyloxy)iodo]benzene and [hydroxy(phosphoryloxy)iodo]benzene.

Recently, extensive study on hypervalent iodine compounds such as (diacetoxyiodo)benzene, [bis(trifluoroacetoxy)iodo]benzene, [hydroxy(tosyloxy)iodo]benzene, etc., has been carried out and their use for organic synthesis has been reported.[1] Among them, [hydroxy(tosyloxy)iodo]benzene (Koser's reagent) is a useful reagent for α-tosyloxylation of ketones which are the precursors for the construction of heterocyclic compounds such as thiazoles, selenazoles, oxazoles, imidazoles, pyrazoles, benzofurans, and lactones, and for the formation of alkynyl phenyl iodonium tosylate.[2] However, to our knowledge, detailed study on the preparation of [hydroxy(tosyloxy)iodo]arenes bearing other aromatics instead of a phenyl group and their synthetic uses have been rather limited.[3] Thus, we planned to prepare novel [hydroxy(tosyloxy)iodo]arenes and [hydroxy(phosphoryloxy)iodo]arenes and compare their reactivities for α-tosyloxylation and α-phosphoryloxylation[4] of ketones with those of [hydroxy(tosyloxy)iodo]benzene and [hydroxy(phosphoryloxy)iodo]benzene, respectively. Two types of aromatics, $\pi$-excess aromatics (thienyl) and $\pi$-deficient aromatics (pyrazolyl, trifluoromethylphenyl, and bis(trifluoromethyl)phenyl), i.e., 2-thienyl (**2**), 3-thienyl (**3**), *N*-tosyl-4-pyrazolyl (**4**), 3-trifluoromethylphenyl (**5**), and 3,5-bis(trifluoromethy)phenyl (**6**), were prepared by treatment of the corresponding iodoarenes with sodium perborate or peracetic acid in acetic acid, and subsequent treatment with *p*-toluenesulfonic acid or diphenylphosphoric acid as shown in Figure 1. The conversion of (diacetoxyiodo)arenes to [hydroxy(tosyloxy)iodo]arenes in acetonitrile proceeded smoothly to give compounds **2A**−**6A** in quite good yields.

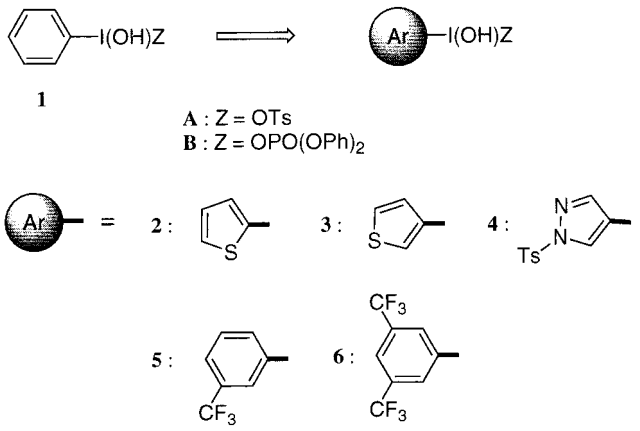


**Figure 1.** Novel [hydroxy(tosyloxy)iodo]arenes and [hydroxy(phosphoryloxy)iodo]arenes.

At first, the α-tosyloxylation of acetophenone with compounds **2A**−**6A** was carried out under the same

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(2) (a) Koser, G. F.; Wettach, R. H.; Troup, J. M.; Frenz, B. A. *J. Org. Chem*. **1976**, *41*, 3609. (b) Koser, G. F.; Wettach, R. H. *J. Org. Chem*. **1977**, *42*, 1476. (c) Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem*. **1982**, *47*, 2487. (d) Moriarty, R. M.; Penmasta, R.; Awasthi, A. K.; Epa, W. R.; Prakash, I. *J. Org. Chem*. **1989**, *54*, 1101. (e) Moriarty, R. M.; Vaid, R. K.; Hopkins, T. E.; Vaid, B. K.; Prakash, O. *Tetrahedron Lett*. **1990**, *31*, 201. (f) Moriarty, R. M.; Vaid, B. K.; Duncan, M. P.; Levy, S. G.; Prakash, O.; Goyal, S. *Synthesis* **1992**, 845. (g) Tuncay, A.; Dustman, J. A.; Fisher, G.; Tuncay, C. I. *Tetrahedron Lett*. **1992**, *33*, 7647. (h) Prakash, O.; Goyal, S. *Synthesis* **1992**, 629. (i) Prakash, O.; Saini, N.; Sharma, P. K. *Synlett* **1994**, 221. (j) Prakash, O.; Saini, N.; Sharma, P. K. *Heterocycles* **1994**, *38*, 409. (k) Lee, J. C.; Choi, Ju-H. *Synlett* **2001**, 234.

(3) Ligand exchange reaction of [hydroxy(tosyloxy)iodo]benzene with *p*-iodoarenes (Cl, Br, I, $CH_3$, $NO_2$, Ph) to form para-substituted [hydroxy(tosyloxy)iodo]benzene: Koser, G. F.; Wettach, R. H.; Smith, C. S. *J. Org. Chem*. **1980**, *45*, 1544. Preparation of [hydroxy(tosyloxy)iodo]pentafluorobenzene and formation of iodonium species: Moriarty, R. M.; Penmasta, R.; Prakash, I. *Tetrahedron Lett*. **1987**, *28*, 877.

(4) Koser, G. F.; Lodaya, J. S.; Ray, D. G., III; Kokil, P. B. *J. Am. Chem. Soc*. **1988**, *110*, 2987.

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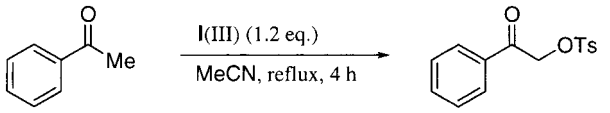
**Table 1. α-Tosyloxylatin of Acetophenone**




| I(III) | 1A | 2A | 3A | 4A | 5A | 6A |
|---|---|---|---|---|---|---|
| yields (%) | 93 | 38 | 60 | (93)[a] | 98 | 96 |

[a] Reagent **4A** was prepared in situ.

conditions, and the reactivity was compared with that of the parent compound **1A** as shown in Table 1.

The results indicate that compounds **2A** and **3A** did not work effectively, while compounds **1A**, **4A**, **5A**, and **6A** showed good reactivities with, especially compounds **5A** and **6A** showing the best reactivity. Thus, $\pi$-excess aromatics retarded the α-tosyloxylation of the ketone. This result came from the fact that the enol tautomer of ketone is the reactive species for α-tosyloxylation of ketone, and its nucleophilic attack to the hypervalent iodine atoms of [hydroxy(tosyloxy)iodo]arenes is the second key step.[1c] Compound **4A** was prepared in situ and used for α-tosyloxylation without purification, because protonation of the pyrazole nitrogen by *p*-toluenesulfonic acid in the preparation of compounds **4A** with *N*-tosyl-4-[(diacetoxy)iodo]pyrazole[5] and *p*-toluenesulfonic acid occurred partly, and its purification was difficult. In other ketone derivatives, compounds **5A** and **6A** showed again the best reactivity among the other [hydroxy(tosyloxy)iodo]arenes, as shown in Table 2.

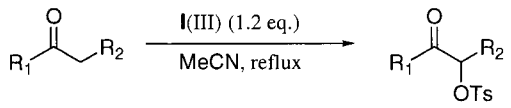
α-Phosphoryloxylation of acetophenone with compounds **2B**−**6B** was carried out, and the reactivity was compared again with that of the parent compound **1B** as shown in Table 3. Since compounds **2B**−**6B** are viscous oils and their isolation as a pure state was difficult, these compounds were used for the α-phosphoryloxylation of ketones without isolation. α-Phosphoryloxylation of acetophenone with compounds **1B**, **4B**, **5B**, and **6B** with the in-situ method proceeded effectively. However, when α-phosphoryloxylation of other ketones with compounds **1B**, **4B**, **5B**, and **6B** was carried out, compounds **5B** and **6B** gave the corresponding α-phosphoryloxyketones in better yields than those with compounds **1B** and **4B** as shown in Table 4.

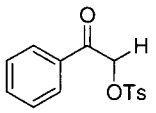
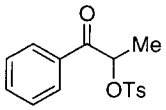
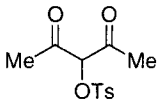
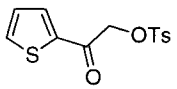
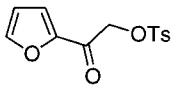
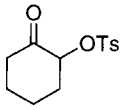
In conclusion, novel [hydroxy(tosyloxy)iodo]arenes **2A**−**6A** were prepared, and [hydroxy(phosphoryloxy)iodo]-arenes **2B**−**6B** were prepared in situ, and α-tosyloxylation and α-phosphoryloxylation of ketones with these compounds were carried out, respectively. When their reactivities were compared with those of the parent compounds **1A** and **1B**, respectively, compounds **5A** and **6A**, and compounds **5B** and **6B**, showed the best reactivity. These new hypervalent iodine compounds can be used as powerful α-tosyloxylation and α-phosphoryloxylation reagents, instead of the parent compounds **1A** and **1B**.

## Experimental Section

**General**. $^1$H NMR spectra were recorded on 400 and 500 MHz spectrometers, $^{13}$C NMR spectra were recorded on 100 and 125 MHz spectrometers, and $^{31}$P NMR spectra were recorded on 500 MHz spectrometer. $^1$H NMR and $^{13}$C NMR chemical shifts and $^{31}$P NMR chemical shifts are expressed in ppm downfield from TMS and 85% $H_3PO_4$ in $\delta$ units, respectively. *J*-Values are given in hertz. In the $^{13}$C NMR spectra, p, s, t, and q means primary, secondary, tertiary, and quaternary. Melting points were determined on an electrothermal apparatus in open capillary tubes and are uncorrected. Wakogel C-200 and Silica Gel 50 (Merck) were used for column chromatography, Kieselgel 60 F254 (Merck) was used for TLC, and Wakogel B-5F was used for preparative TLC.

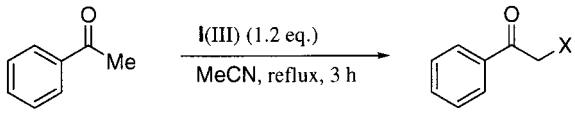
**Table 2. α-Tosyloxylation of Ketones**




| Entry | Products | Time (h) | Yields (%) 1A | 4A | 5A | 6A |
|---|---|---|---|---|---|---|
| 1 |  | 4 | 93 | (93)[a)] | 98 | 96 |
| 2 |  | 6 | 76 | (86)[a)] | 84 | 96 |
| 3 |  | 0.5[b)] | 73 | (90)[a)] | 90 | 96 |
| 4 |  | 18 | 81 | (81)[a)] | 84 | 90 |
| 5 |  | 8 | 55 | (70)[a)] | 67 | 82 |
| 6 |  | 1.5[c)] | 50 | (42)[a)] | 60 | 70 |

[a] Reagent **4A** was prepared in situ. [b] Solvent: $CHCl_3$ at rt. [c] Solvent: $CHCl_3$ at 30 °C.

**Table 3. α-Phosphoryloxylation of Acetophenone**



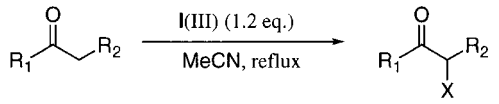

| I(III) | 1B | 2B | 3B | 4B | 5B | 6B |
|---|---|---|---|---|---|---|
| yields (%) | 74 (90)[a] | 63[a] | 86[a] | 89[a] | 97[a] | 97[a] |

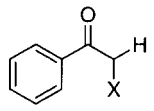
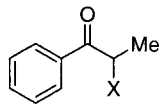
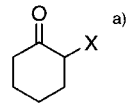
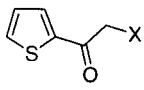
[a] Reagent was prepared in situ. [b] α-Acetoxyacetophenone was formed in 9% yield as a byproduct.

**General Procedure for the Preparation of [Hydroxy-(tosyloxy)iodo]arene.** A suspension of (diacetoxyiodo)arene (1 mmol) in acetonitrile (2 mL) was added to a solution of *p*-toluenesulfonic acid monohydrate (2 mmol) in acetonitrile (2 mL) under an argon atmosphere and stirred for 1 h at room temperature. After the reaction, the reaction mixture was filtered, and the solid was washed with diethyl ether or acetonitrile.

(5) Togo, H.; Nabana, T.; Yamaguchi, K. *J. Org. Chem*. **2000**, *65*, 8391.

**Table 4. α-Phosphoryloxylation of Ketones**




| Entry | Products | Time (h) | Yields (%) 1B | 4B[b)] | 5B[b)] | 6B[b)] |
|---|---|---|---|---|---|---|
| 1 |  | 3 | 74 (90)[b)] | 89[c)] | 97 | 97 |
| 2 |  | 6 | 60 (65)[b)] | 45[d)] | 80[e)] | 84[e)] |
| 3 |  a) | 5.5 | 55 (57)[b)] | 52 | 60 | 69 |
| 4 |  | 30 | 50 | 48 | 87[f)] | 91[f)] |

[a] Solvent: $CHCl_3$ at rt. [b] Reagent was prepared in situ. [c] α-Acetoxyacetophenone was obtained in 9% yield as a byproduct. [d] α-Acetoxypropiophenone was obtained in 24% yield as a byproduct. [e] Reaction time was 4 h. [f] Reaction time was 6.5 h.

**2-[Hydroxy(tosyloxy)iodo]thiophene 2A.** Compound **2A** slowly decomposed when it was dried by vacuum pump for elemental analysis; 100% yield; mp 65−68 °C (decomp); IR (KBr) 560, 700, 1130, 1190, and 3620 $cm^{-1}$; $^1H$ NMR ($CDCl_3$ + 3 drops of $CF_3CO_2H$) $\delta$ = 2.43 (3H, s), 7.24 (1H, dd, $J$ = 5.3 and 3.9 Hz), 7.30 (2H, d, $J$ = 8.2 Hz), 7.69 (2H, d, $J$ = 8.2 Hz), 7.80 (1H, dd, $J$ = 5.3 and 1.4 Hz), 8.04 (1H, dd, $J$ = 3.9 and 1.4 Hz).

**3-[Hydroxy(tosyloxy)iodo]thiophene 3A:** 87% yield; mp 120−123 °C (decomp.); IR (KBr) 560, 700, 1130, 1190, and 3630 $cm^{-1}$; $^1H$ NMR ($CDCl_3$ + 3 drops of $CF_3CO_2H$) $\delta$ = 2.45 (3H, s), 7.32 (2H, d, $J$ = 8.1 Hz), 7.60 (1H, dd, $J$ = 5.3 and 3.0 Hz), 7.66 (1H, dd, $J$ = 5.3 and 1.2 Hz), 7.69 (2H, d, $J$ = 8.1 Hz), 8.37 (1H, dd, $J$ = 3.0 and 1.2 Hz). Anal. Calcd for $C_{11}H_{11}IO_4S_2$: C 33.18; H 2.78. Found: C 33.16; H 2.77.

***N*-Tosyl-4-[hydroxy(tosyloxy)iodo]pyrazole 4A**: 100% yield; mp 118−121 °C (decomp); IR (KBr) 820, 1050, 1200, 1310, 1340, and 3450 $cm^{-1}$; $^1H$ NMR ($CDCl_3$ + 3 drops of $CF_3CO_2H$) $\delta$ = 2.45 (3H, s), 2.48 (3H, s), 7.34 (2H, d, $J$ = 8.2 Hz), 7.43 (2H, d, $J$ = 8.3 Hz), 7.71 (2H, d, $J$ = 8.2 Hz), 7.96 (2H, d, $J$ = 8.3 Hz). 8.21 (1H, s), 8.82 (1H, s). Anal. Calcd for $C_{17}H_{17}N_2IO_6S_2$: C 38.07; H 3.19; N 5.22. Found: C 37.65; H 3.51; N 5.12.

**3-Trifluoromethyl-1-[hydroxy(tosyloxy)iodo]benzene 5A:** 91% yield; mp 158−162 °C (decomp); IR (KBr) 690, 800, 1185, 1320, and 3450 $cm^{-1}$; $^1H$ NMR ($CDCl_3$ + 3 drops of $CF_3CO_2H$) $\delta$ = 2.44 (3H, s), 7.31 (2H, d, $J$ = 7.7 Hz), 7.70 (2H, d, $J$ = 7.7 Hz), 7.78 (1H, t, $J$ = 8.0 Hz), 8.00 (1H, d, $J$ = 8.0 Hz), 8.41 (1H, d, $J$ = 8.0 Hz), 8.42 (1H, s). Anal. Calcd for $C_{14}H_{12}F_3IO_4S$: C 36.54; H, 2.63. Found: C, 36.49; H, 2.44.

**3,5-Bis(trifluoromethyl)-1-[hydroxy(tosyloxy)iodo]benzene 6A**: 100% yield; mp 89−91 °C (decomp); IR (KBr) 700, 820, 1190, 1350, and 3400 $cm^{-1}$;$^1H$ NMR ($CDCl_3$) $\delta$ = 2.34 (3H, s), 7.09 (2H, d, $J$ = 8.0 Hz), 7.48 (2H, d, $J$ = 8.0 Hz), 7.89 (1H, s), 8.61 (2H, s). Anal. Calcd for $C_{15}H_{11}F_6IO_4S$: C, 34.11; H, 2.10. Found: C, 34.19; H, 1.86.

**Typical Procedure for α-Tosyloxylation of Acetophenone**. To a solution of acetophenone (1 mmol) in acetonitrile (6 mL) was added 3-trifluoromethyl-1-[hydroxy(tosyloxy)iodo]benzene (1.2 mmol). The mixture was refluxed for 4 h under an argon atmosphere. Then the reaction mixture was poured into water and extracted with chloroform twice. The combined organic layer was dried over $Na_2SO_4$. After filtration, the solvent was evaporated under reduced pressure, and the residue was purified by preparative TLC on silica gel (eluent: hexane/ethyl acetate = 3/1) to give 284 mg of α-tosyloxyacetophenone in 98% yield.

**Typical Procedure for α-Tosyloxylation of Acetophenone (in situ reaction)**. To a solution of *p*-toluenesulfonic acid monohydrate (2.4 mmol) in acetonitrile (6 mL) was added *N*-tosyl-4-[(diacetoxy)iodo]pyrazole (1.2 mmol). The mixture was stirred for 1 h at room temperature. After the reaction, the mixture was evaporated under reduced pressure. Then a solution of acetophenone (1 mmol) in acetonitrile (6 mL) was added to the residue, and the mixture was refluxed for 4 h under an argon atmosphere. Then the reaction mixture was poured into water and extracted with chloroform twice. The combined organic layer was dried over $Na_2SO_4$. After filtration, the solvent was evaporated under reduced pressure, and the residue was purified by preparative TLC on silica gel (eluent: hexane/ethyl acetate = 3/1) to give 270 mg of α-tosyloxyacetophenone in 93% yield.

**α-Tosyloxyacetophenone**: mp 90 °C (lit.[2c] mp 90−91 °C); IR (KBr) 1715, 1360, 1180, 820, 750, 680 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 2.45 (s, 3H), 5.27 (s, 2H), 7.35 (d, $J$ = 8.5 Hz, 2H), 7.47 (t, $J$ = 8.2 Hz, 2H), 7.61 (t, $J$ = 8.2 Hz, 1H), 7.84 (d, $J$ = 8.5 Hz, 2H), 7.85 (d, $J$ = 8.2 Hz, 2H).

**α-Tosyloxypropiophenone**: mp 68 °C (lit.[2c] mp 68−69 °C); IR (KBr) 1700, 1370, 1170, 830, 760, 660 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 1.60 (d, $J$ = 7.0 Hz, 3H), 2.41 (s, 3H), 5.79 (q, $J$ = 7.0 Hz, 1H), 7.29 (d, $J$ = 8.0 Hz, 2H), 7.46 (t, $J$ = 8.0 Hz, 2H), 7.60 (t, $J$ = 8.0 Hz, 1H), 7.75 (d, $J$ = 8.0 Hz, 2H), 7.88 (d, $J$ = 8.0 Hz, 2H).

**α-Tosyloxycyclohexanone**: mp 72 °C (lit.[2c] mp 74−76 °C); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 1.64−2.60 (m, 6H), 2.44 (s, 3H), 4.90 (dd, $J$ = 10.8, 5.9 Hz, 1H), 7.34 (d, $J$ = 8.0 Hz, 2H), 7.84 (d, $J$ = 8.0 Hz, 2H).

**α-Tosyloxy-2,4-pentadione**: mainly enol tautomer; mp 82 °C (lit.[2c] mp 82 − 83 °C); IR (KBr) 3060, 1600, 1370, 1200, 1180, 800 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 1.96 (s, 6H), 2.49 (s, 3H), 7.40 (d, $J$ = 8.1 Hz, 2H), 7.83 (d, $J$ = 8.1 Hz, 2H), 14.80 (s, 1H).

**(Tosyloxy)methyl 2-Thienyl Ketone**: mp 92 − 93 °C (lit.[2d] mp 94 − 96 °C); IR (KBr) 1685, 1370, 1180, 730 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 2.45 (s, 3H), 5.09 (s, 2H), 7.16 (dd, $J$ = 5.0, 3.9 Hz, 1H). 7.35 (d, $J$ = 8.1 Hz, 2H), 7.73 (dd, $J$ = 5.0, 1.0 Hz, 1H), 7.79 (dd, $J$ = 3.9, 1.0 Hz, 1H), 7.85 (d, $J$ = 8.1 Hz, 2H).

**(Tosyloxy)methyl 2-Furanyl Ketone:** mp 63 − 64 °C (lit.[2c] mp 65−67 °C); IR (KBr) 1695, 1370, 1170, 810, 750 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 2.45 (s, 3H), 5.09 (s, 2H), 6.58 (dd, $J$ = 3.7, 1.7 Hz, 1H). 7.33 (dd, $J$ = 3.7, 0.7 Hz, 1H), 7.36 (d, $J$ = 8.2 Hz, 2H), 7.61 (dd, $J$ = 1.7, 0.7 Hz, 1H), 7.86 (d, $J$ = 8.2 Hz, 2H).

**Typical Procedure for α-Phosphoryloxylation of Acetophenone (in situ reaction).** To a solution of diphenylphosphoric acid (2.4 mmol) and $H_2O$ (2.4 mmol) in acetonitrile (3 mL) was added 3-trifluoromethyl-1-(diacetoxyiodo)benzene (1.2 mmol). The mixture was stirred for 1 h at room temperature. After the reaction, the mixture was evaporated under reduced pressure. Then a solution of acetophenone (1 mmol) in acetonitrile (3 mL) was added to the residue, and the mixture was refluxed for 3 h under an argon atmosphere. Then the reaction mixture was poured into water and extracted with chloroform twice. The combined organic layer was dried over $Na_2SO_4$. After filtration, the solvent was evaporated under reduced pressure, and the residue was purified by preparative TLC on silica gel (eluent: hexane/ethyl acetate = 4/1) to give 357 mg of α-(diphenylphosphoryloxy)acetophenone in 97% yield.

**α-(Diphenylphosphoryloxy)acetophenone:** oil; IR (neat) 700, 760, 1270, and 1710 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ = 5.45 (2H, d, $J_{H-P}$ = 9.9 Hz), 7.16−7.37 (10H, m), 7.42−7.49 (2H, m), 7.56−7.62 (1H, m), 7.86−7.89 (2H, m); $^{13}C$ NMR ($CDCl_3$) $\delta$ = 69.9 (s, $J_{C-P}$ = 6 Hz), 120.2 (t, $J_{C-P}$ = 5 Hz), 125.5 (t), 127.8 (t), 128.9 (t), 129.8 (t), 133.7 (q), 134.1 (t), 150.4 (q, $J_{C-P}$ = 7 Hz), 190.8 (q); $^{31}P$ NMR ($CDCl_3$) $\delta$ = −12.98; HRMS (FAB) Found $m/z$ = 369.0912, Calcd for $C_{20}H_{18}O_5P$ M + 1 = 369.0814.

**α-(Diphenylphosphoryloxy)cyclohexanone:** oil; IR (neat) 690, 770, 1285, and 1740 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ = 1.57−2.03

(5H, m), 2.28−2.36 (2H, m), 2.52−2.56 (1H, m), 4.96−5.03 (1H, m), 7.14−7.36 (10H, m); $^{13}$C NMR ($CDCl_3$) $\delta$ = 23.3 (s), 26.8 (s), 34.9 (s, $J_{C-P}$ = 4 Hz), 40.4 (s), 81.4 (t, $J_{C-P}$ = 7 Hz), 120.2 (t, $J_{C-P}$ = 5 Hz), 120.3 (t, $J_{C-P}$ = 5 Hz), 125.2 (t), 125.4 (t), 129.6 (t, $J_{C-P}$ = 9 Hz), 129.7 (t, $J_{C-P}$ = 9 Hz), 150.3 (q, $J_{C-P}$ = 7 Hz), 150.5 (q, $J_{C-P}$ = 7 Hz), 203.7 (q); $^{31}$P NMR ($CDCl_3$) $\delta$ = −13.07; HRMS (FAB) Found $m/z$ = 347.1054, Calcd for $C_{18}H_{20}O_5P$ M + 1 = 347.0970.

**α-(Diphenylphosphoryloxy)propiophenone:** oil; IR (neat) 690, 770, 1280, and 1700 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ = 1.61 (3H, d, $J$ = 6.8 Hz), 5.91 (1H, qd, $J$ = 6.8 Hz, $J_{H-P}$ = 6.7 Hz), 7.13−7.37 (10H, m), 7.42−7.46 (2H, m), 7.53−7.60 (1H, m), 7.91−7.93 (2H, m); $^{13}$C NMR ($CDCl_3$) $\delta$ = 19.3 (p, $J_{C-P}$ = 5 Hz), 76.4 (t, $J_{C-P}$ = 6 Hz), 115.3 (t), 120.2 (t, $J_{C-P}$ = 5 Hz), 125.5 (t, $J_{C-P}$ = 6 Hz), 128.8 (t, $J_{C-P}$ = 3 Hz), 129.5 (q), 129.7 (t, $J_{C-P}$ = 11 Hz), 133.7 (t), 150.3 (q), 195.2 (q); $^{31}$P NMR ($CDCl_3$) $\delta$ = −12.98; HRMS (FAB) Found $m/z$ = 383.1014, Calcd for $C_{21}H_{20}O_5P$ M + 1 = 383.0970.

**α-(Diphenylphosphoryloxy)-2-acetylthiophene:** oil; IR (neat) 690, 730, 760, 780, 1290, and 1680 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ = 5.31 (2H, d, $J_{H-P}$ = 9.7 Hz), 7.13 (1H, dd, $J$ = 4.8 and 3.9 Hz), 7.17−7.23 (2H, m), 7.25−7.30 (4H, m), 7.33−7.37 (4H, m), 7.71 (1H, dd, $J$ = 4.8 and 1.0 Hz), 7.73 (1H, dd, $J$ = 3.9 and 1.0 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ = 69.6 (s, $J_{C-P}$ = 6 Hz),120.2 (t, $J_{C-P}$ = 5 Hz), 125.6 (t), 128.4 (t), 129.9 (t), 132.5 (t), 134.8 (t), 139.9 (q), 150.4 (q, $J_{C-P}$ = 7 Hz), 184.1 (q); $^{31}$P NMR ($CDCl_3$) $\delta$ = −12.26; HRMS (FAB) Found $m/z$ = 375.0428, Calcd for $C_{18}H_{16}SPO_5$ M + 1 = 375.0378.

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**Supporting Information Available:** Copies of $^1$H NMR spectra for compounds **2A**−**6A** and all α-tosyloxyketones and α-phosphoryloxy ketones. This material is available free of charge via the Internet at http://pubs.acs.org.

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