JOC*Note*

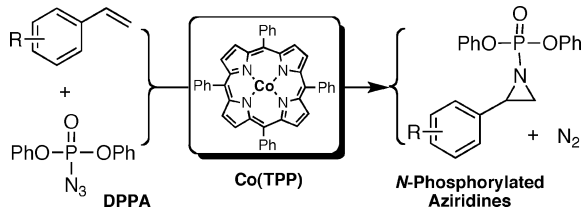
Cobalt-Catalyzed Aziridination with Diphenylphosphoryl Azide (DPPA): Direct Synthesis of *N*-Phosphorus-Substituted Aziridines from Alkenes

Guang-Yao Gao, Jess E. Jones, Renu Vyas, Jeremiah D. Harden, and X. Peter Zhang*

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600

pzhang@utk.edu

Received May 3, 2006



A new catalytic aziridination system that consists of cobalt(II) tetraphenylporphyrin [Co(TPP)] as the catalyst and diphenylphosphoryl azide (DPPA) as the nitrene source has been developed. The cobalt-based catalytic system allows direct synthesis of *N*-phosphorus-substituted aziridines from alkenes with dinitrogen as the byproduct. Cobalt ion seems essential to the catalytic aziridination with DPPA as no or only trace amounts of the desired products were observed with other metal complexes of tetraphenylporphyrin.

Aziridines, the smallest nitrogen-containing heterocyclic compounds, have received considerable research interests because of their fundamental and practical importance.[1] In addition to being an important motif in many biologically and pharmaceutically interesting compounds, aziridines are notably known as a class of versatile synthons for preparation of functionalized amines. Of known synthetic strategies, catalytic nitrene transfer from a suitable nitrene source to alkene substrates by transition metal complexes is considered the most attractive approach for the construction of the three-membered ring structures.[2] Compared to the considerable advances in analogous epoxidation and cyclopropanation reactions, catalytic aziridination is much less developed, presumably due to the lack of suitable nitrene sources. [*N*-(*p*-Toluenesulfonyl)imino]phenyliodinane (PhI═NTs) has been extensively used as the primary nitrene source for metal-catalyzed aziridination.[3] While notable results have been obtained with PhI═NTs in several metal-catalyzed systems,[4] the nitrene source suffers from several drawbacks: commercial unavailability, costly synthesis, short shelf life, insolubility in common solvents, and generation of PhI as a byproduct.[5] To this end, recent efforts have been made to develop alternative nitrene sources that can be used in metal-catalyzed aziridination, including chloramine-T,[6] bromamine-T,[7] and tosyl azide.[8]

Supported by different ligands, complexes of several transition metals, including Mn, Fe, Cu, Ru, and Rh, have been demonstrated to catalyze aziridination of alkenes with these nitrene sources.[1−9] Most of these catalytic systems lead to the formation of *N*-sulfonylated aziridines. Different from *N*-sulfonylated aziridines in which the deprotection of *N*-sulfonyl groups normally requires harsh conditions,[10] *N*-phosphorylated and *N*-phosphinylated aziridines offer advantages as synthetic building blocks since the phosphoryl and phosphinyl groups bring suitable activation to the aziridine ring and can be easily deprotected.[11−13] Although several methods are available for the preparation of *N*-phosphorus-substituted aziridines,[11,12] their direct synthesis from alkenes via transition-metal-catalyzed aziridination has not been developed.[14]

Attracted by their unique ligand environments and metal coordination modes,[15] we[16,17] and others[18,19] have been interested in developing metalloporphyrin-based catalytic systems for

(1) (a) Hu, X. E. *Tetrahedron* **2004**, *60*, 2701. (b) Sweeney, J. B. *Chem. Soc. Rev.* **2002**, *31*, 247. (c) Zwanenburg, B.; ten Holte, P. *Top. Curr. Chem.* **2001**, *216*, 93. (d) McCoull, W.; Davis, F. A. *Synthesis* **2000**, 1347. (e) Tanner, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 599.

(2) (a) Muller, P.; Fruit, C. *Chem. Rev.* **2003**, *103*, 2905. (b) Jacobsen, E. N. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; Vol. 2, p 607. (c) Osborn, H. M. I.; Sweeney, J. *Tetrahedron: Asymmetry* **1997**, *8*, 1693.

(3) (a) Dauban, P.; Dodd, R. H. *Synlett* **2003**, 1571. (b) Koser, G. F. *Top. Curr. Chem.* **2003**, *224*, 137. (c) Yamada, Y.; Yamamoto, T.; Okawara, M. *Chem. Lett.* **1975**, 361.

(4) For selected examples of metal-catalyzed aziridination with PhI═NTs, see: (a) Li, Z.; Conser, K. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1993**, *115*, 5326. (b) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2742. (c) Vedernikov, A.; Caulton, K. G. *Org. Lett.* **2003**, *5*, 2591.

(5) For the use of in situ formed iminoiodanes under oxidative conditions, see: (a) Yu, X.-Q.; Huang, J.-S.; Zhou, X.-G.; Che, C.-M. *Org. Lett.* **2000**, *2*, 2233. (b) Dauban, P.; Saniere, L.; Tarrade, A.; Dodd, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 7707. (c) Guthikonda, K.; Du Bois, J. *J. Am. Chem. Soc.* **2002**, *124*, 13672.

(6) (a) Simkhovich, L.; Gross, Z. *Tetrahedron Lett.* **2001**, *42*, 8089. (b) Albone, D. P.; Aujla, P. S.; Taylor, P. C.; Challenger, S.; Derrick, A. M. *J. Org. Chem.* **1998**, *63*, 9569.

(7) (a) Chanda, B. M.; Vyas, R.; Bedekar, A. V. *J. Org. Chem.* **2001**, *66*, 30. (b) Antunes, A. M. M.; Marto, S. J. M.; Branco, P. S.; Prabhakar, S.; Lobo, A. M. *Chem. Commun.* **2001**, 405.

(8) (a) Omura, K.; Murakami, M.; Uchida, T.; Irie, R.; Katsuki, T. *Chem. Lett.* **2003**, 354. (b) Omura, K.; Uchida, T.; Irie, R.; Katsuki, T. *Chem. Commun.* **2004**, 2060.

(9) For a recent Ag-based aziridination system, see: Cui, Y.; He, C. *J. Am. Chem. Soc.* **2003**, *125*, 16202.

(10) (a) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley-Interscience: New York, 1991; p 379. (b) Alonso, D. A.; Anderson, P. G. *J. Org. Chem.* **1998**, *63*, 9455.

(11) (a) Hu, X. E. *Tetrahedron Lett.* **2002**, *43*, 5315. (b) Hu, X. E.; Kim, N. K.; Ledoussal, B.; Colson, A.-O. *Tetrahedron Lett.* **2002**, *43*, 4289. (c) Osowska-Pacewicka, K.; Zwierzak, A. *Synth. Commun.* **1998**, *28*, 1127. (d) Gajda, T.; Napieraj, A.; Osowska-Pacewicka, K.; Zwierzak, A. *Tetrahedron* **1997**, *53*, 4935. (e) Osowska-Pacewicka, K.; Zwierzak, A. *Synthesis* **1996**, 333. (f) Osowska-Pacewicka, K.; Zwierzak, A. *Pol. J. Chem.* **1994**, *68*, 1263.

(12) (a) Sweeney, J. B.; Cantrill, A. A. *Tetrahedron* **2003**, *59*, 3677. (b) Cantrill, A. A.; Osborn, H. M. I.; Sweeney, J. B. *Tetrahedron* **1998**, *54*, 2181. (c) Osborn, H. M. I.; Sweeney, J. B.; Howson, W. *Tetrahedron Lett.* **1994**, *35*, 2739. (d) Osborn, H. M. I.; Sweeney, J. B.; Howson, B. *Synlett* **1994**, 145.

(13) For examples of biomedical applications of *N*-phosphorus-substituted aziridines, see: (a) Perlman, M. E.; Bardos, T. J. *J. Org. Chem.* **1988**, *53*, 1761. (b) Borkovec, A. B.; Woods, C. W.; Brown, R. T. *J. Med. Chem.* **1966**, *9*, 522.

(14) A *N*-phosphorylated aziridine was recently synthesized in 33% yield via Rh-catalyzed aziridination. See ref 5c.

10.1021/jo0609226 CCC: $33.50
Published on Web 07/21/2006

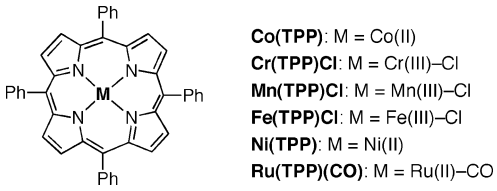


FIGURE 1. Structures of several common metal complexes of tetraphenylporphyrin.

SCHEME 1. Aziridination of Alkenes with DPPA Catalyzed by Cobalt(II) Tetraphenylporphyrin Complex

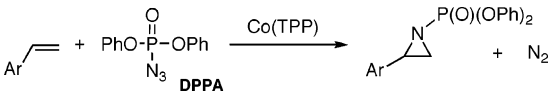
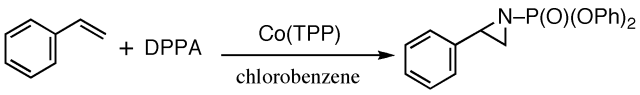


TABLE 1. Aziridination of Styrene with DPPA by Cobalt(II) Tetraphenylporphyrin Complex under Various Conditions[a]

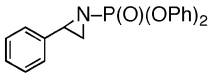
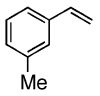
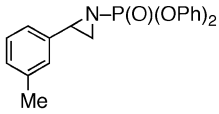
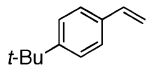
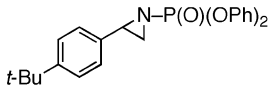
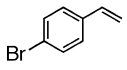
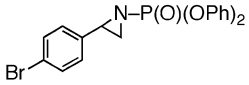
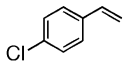
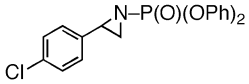
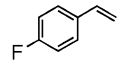
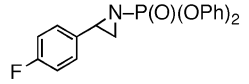
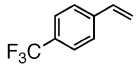
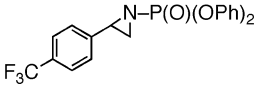
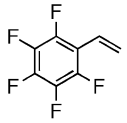
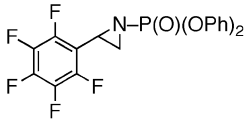
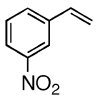
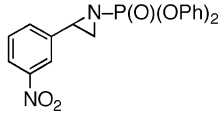
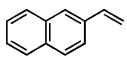
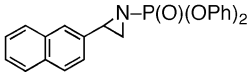


entry	cat (mol %)	S:A[b]	additv (mol %)	temp (°C)	time (h)	yield (%)[c]
1	10	1:2	none (0)	100	17	0
2	10	3:1	none (0)	100	17	32
3	10	5:1	none (0)	100	17	50
4	10	10:1	none (0)	100	17	33
5	10	5:1	none (0)	100	40	29
6	10	5:1	none (0)	120	17	54
7	10	5:1	none (0)	120	7	17
8	10	5:1	none (0)	120	40	0
9	10	5:1	none (0)	80	17	19
10	10	5:1	none (0)	80	46	56
11	5	5:1	none (0)	100	17	20
12	5	5:1	none (0)	120	17	27
13	10	5:1	DMAP (10)	100	17	0
14	10	5:1	DMAP (10)	80	17	0
15	10	5:1	DMAP (10)	100	6	0
16	10	5:1	THF (100)	100	17	35
17	10	5:1	CH_3CN (100)	100	17	43
18	10	5:1	Ph_3P (10)	100	17	42

[a] Reactions were carried out in chlorobenzene under N_2 in the presence of 5 Å molecular sieves using Co(TPP) as the catalyst with or without additives. Concentration: [DPPA] = 0.1 M. [b] Mole ratio of styrene to DPPA. [c] Isolated yields.

aziridination. Previously, we reported that iron and cobalt porphyrins can effectively catalyze aziridination reactions of a wide variety of alkenes with bromamine-T as an alternative nitrene source.[16] We reveal herein that cobalt(II) porphyrin complex Co(TPP) (Figure 1) can catalyze aziridination of alkenes using diphenylphosphoryl azide (DPPA) as a convenient new nitrene source,[20] leading to the formation of *N*-phosphorylated aziridines with dinitrogen as the byproduct (Scheme 1). To the best of our knowledge, this represents one of the few catalytic aziridination systems that use cobalt-based catalysts[16,21] or that employ azides as nitrene sources.[8,22]

TABLE 2. Aziridination of Styrene Derivatives with DPPA Catalyzed by Cobalt(II) Tetraphenylporphyrin Complex[a]

entry	substrate	product	yield (%)[b]
1			50
2			64
3			43
4			54
5			52
6			45
7			60
8			36
9			68
10			24

[a] Reactions were carried out overnight at 100 °C in chlorobenzene under N_2 in the presence of 5 Å molecular sieves using 10 mol % of Co(TPP). Concentration: [DPPA] = 0.1 M; alkene:DPPA = 5:1. [b] Isolated yields.

To explore the possibility of DPPA as an effective nitrene source, we initially carried out systematic studies on aziridination of styrene as a model reaction using different metalloporphyrins as potential catalysts under various conditions. Among porphyrin complexes of different metal ions that were evaluated, cobalt ion seems essential to successful aziridination of styrene with

(15) Kadish, K. M., Smith, K. M., Guilard, R., Eds. *The Porphyrin Handbook*; Academic Press: San Diego, CA, 2000−2003; Vols. 1−20.

(16) (a) Vyas, R.; Gao, G.-Y.; Harden, J. D.; Zhang, X. P. *Org. Lett.* **2004**, *6*, 1907. (b) Gao, G.-Y.; Harden, J. D.; Zhang, X. P. *Org. Lett.* **2005**, *7*, 3191.

(17) For our recent efforts on metalloporphyrin-catalyzed analogous carbene transfer reactions, see: (a) Chen, Y.; Huang, L.; Ranade, M. A.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 3714. (b) Chen, Y.; Huang, L.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 5925. (c) Chen, Y.; Huang, L.; Zhang, X. P. *Org. Lett.* **2003**, *5*, 2493. (d) Huang, L.; Chen, Y.; Gao, G.-Y.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 8179. (e) Lee, M.-Y.; Chen, Y.; Zhang, X. P. *Organometallics* **2003**, *22*, 4905. (f) Chen, Y.; Zhang, X. P. *J. Org. Chem.* **2004**, *69*, 2431. (g) Chen, Y.; Fields, K. B.; Zhang, X. P. *J. Am. Chem. Soc.* **2004**, *126*, 14178. (h) Chen, Y.; Gao, G.-Y.; Zhang, X. P. *Tetrahedron Lett.* **2005**, *46*, 4965. (i) Chen, Y.; Zhang, X. P. *Synthesis* **2006**, 1697.

(18) Metalloporphyrins represent the first transition metal complexes for catalyzing aziridination. See: (a) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073. (b) Mansuy, D.; Mahy, J.-P.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1161.

(19) (a) Mahy, J.-P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1517. (b) Lai, T.-S.; Kwong, H.-L.; Che, C.-M.; Peng, S.-M. *Chem. Commun.* **1997**, 2373. (c) Simonato, J.-P.; Pecaut, J.; Scheidt, W. R.; Marchon, J.-C. *Chem. Commun.* **1997**, 989. (d) Au, S.-M.; Huang, J.-S.; Yu, W.-Y.; Fung, W.-H.; Che, C.-M. *J. Am. Chem. Soc.* **1999**, *121*, 9120. (e) Liang, J.-L.; Huang, J.-S.; Yu, X.-Q.; Zhu, N.; Che, C.-M. *Chem.—Eur. J.* **2002**, *8*, 1563.

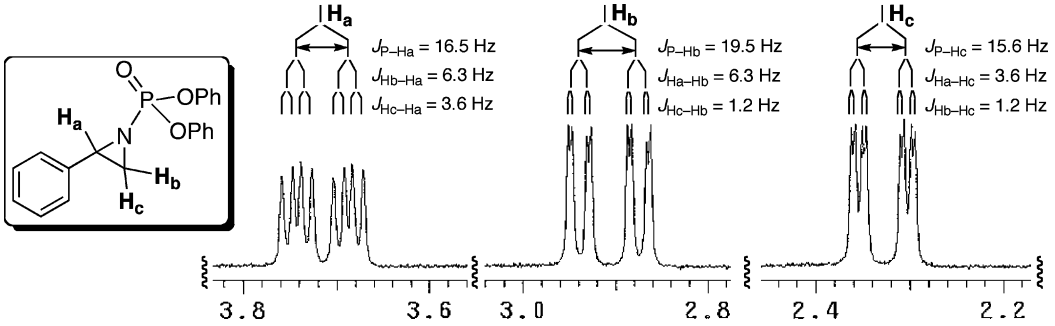


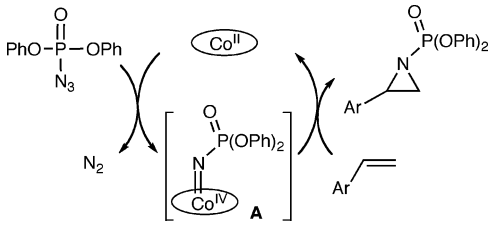
FIGURE 2. Characteristic ^{1}H NMR splitting peak pattern of aziridine-ring hydrogens of *N*-phosphorylated aziridines.

DPPA. While Co(TPP) could catalyze the formation of the desired product (Table 1), employment of other metalloporphyrins, including Cr(TPP)Cl, Mn(TPP)Cl, Fe(TPP)Cl, Ni(TPP), and Ru(TPP)(CO) (Figure 1), produced only trace amounts of the *N*-phosphorylated aziridine. It should be noted that no aziridines were observed without a catalyst. Strong solvent effects were also noticed for the aziridination process. Of common solvents used, chlorobenzene appeared the solvent of choice for the reaction, forming the desired *N*-phosphorylated aziridine as the major product. Uses of other solvents, including acetonitrile, dichloromethane, dimethylformamide, tetrahydrofuran, and toluene, gave little or no amount of the desired product.

As summarized in Table 1, a styrene to DPPA ratio of 5:1 gave the best result for the Co(TPP)-catalyzed aziridination in chlorobenzene. An increase or decrease in the ratio lowered the yield of the desired product (entries 1−4). Although the catalytic reaction could proceed with a nearly complete conversion of DPPA overnight at 100 °C, the *N*-phosphorylated aziridine was isolated in only 50% yield (entry 3) due to formation of some unidentified side products during reaction (and possibly during product isolation with silica gels). While a slight increase in yield was obtained at a higher temperature (entry 6), prolonged heating resulted in a yield reduction (entries 5 and 8). A reduced yield was also observed at a shorter reaction time (entry 7) or at a lower reaction temperature (entry 9). However, a reaction that was carried out at lower temperature for longer time gave the desired product in an improved yield (entry 10). Reduction in catalyst loadings dropped the yields for overnight reactions (entries 11 and 12). A negative additive effect was observed for the catalytic process. Addition of a small amount of DMAP completely shut down the reaction (entries 13−15). The negative effect was reduced with weaker coordinative additives, such as Ph_3P, THF, and CH_3CN (entries 16−18). As aforementioned, no desired products were observed when the reactions were performed with THF or CH_3CN as the solvent. Block of coordination sites of cobalt center by the potentially coordinative additives might be responsible for the observed negative effects.

The substrate scope of the Co(TPP)-based aziridination with DPPA was then investigated with different alkenes. The results

SCHEME 2. Proposed Aziridination Mechanism with DPPA by Cobalt(II) Tetraphenylporphyrin Complex



of a series of styrene derivatives are summarized in Table 2. Under the above-mentioned typical reaction conditions, *m*-methylstyrene was a better substrate than styrene, while aziridination of *p-tert*-butyl styrene gave a slightly lower yield (entries 1−3). The Co-based aziridination system appeared equally suitable to styrene derivatives having electron-withdrawing substituents, such as halogen and trifluoromethyl groups (entries 4−7). Even the highly electron-deficient pentafluorostyrene could be aziridinated with DPPA, albeit in lower yields (entry 8).[23] While a low yield was obtained for the aziridination of 2-vinylnaphthalene (entry 10), the reaction of *m*-nitrostyrene produced the desired *N*-phosphorylated aziridine in the highest yield (entry 9). All the aziridination products were isolated in high purity and characterized by ^{1}H, ^{13}C, and ^{31}P NMR, FT-IR, and high-resolution MS spectroscopy. As exemplified with the *N*-phosphorylated aziridine from styrene (Figure 2), each of the three aziridine-ring hydrogens exhibits a characteristic doublet of doublet of doublets (ddd) peak pattern in the ^{1}H NMR spectrum between 2.2 and 3.8 ppm, which results from the coupling among the three hydrogens that was further split by the phosphorus atom.

The catalytic aziridination by Co(TPP) with DPPA can be assumed to proceed via a mechanism similar to that proposed for other metalloporphyrin-based systems with PhI═NTs.[16,18,19] As proposed in Scheme 2, this mechanism requires, however, the involvement of a cobalt−nitrene intermediate **A**, which has not been known previously. More experimental work is obviously necessary before there is further discussion of the reaction mechanism for this new catalytic process.

In summary, we have demonstrated the first application of the common reagent DPPA as a new nitrene source for catalytic aziridination by Co(TPP), forming synthetically valuable *N*-phosphorylated aziridines directly from the corresponding

(20) The commercially available, low cost diphenylphosphoryl azide is a stable and distillable liquid that has been widely used in various organic syntheses. For selected examples, see: (a) Shioiri, T.; Ninomiya, K.; Yamada, S. *J. Am. Chem. Soc.* **1972**, *94*, 6203. (b) Yamada, S.; Ikota, N.; Shioiri, T.; Tachibana, S. *J. Am. Chem. Soc.* **1975**, *97*, 7174. (c) Lai, B.; Pramanik, B. N.; Manhas, M. S. Bose, A. K. *Tetrahedron Lett.* **1977**, 1977. (d) Qian, L.; Sun, Z.; Deffo, T.; Mertes, K. B. *Tetrahedron Lett.* **1990**, *45*, 6469.

(21) Under microwave conditions, $CoCl_2$ was shown to catalyze aziridination of styrene with bromamine-T to form the desired aziridine in 56% yield. See ref 7a.

(22) For cobalt porphyrin-mediated amination with aryl azides, see: Ragaini, F.; Penoni, A.; Gallo, E.; Tollari, S.; Gotti, C. L.; Lapadula, M.; Mangioni, E.; Cenini, S. *Chem.—Eur. J.* **2003**, *9*, 249.

(23) To the best of our knowledge, the only other example of aziridination of pentafluorostyrene was previously reported by us with a cobalt porphyrin/bromamine-T catalytic system. See ref 16b.

alkenes. Considering its low cost, commercial availability, and high stability, DPPA and related phosphoryl azides may find broad applications in metal-catalyzed aziridination and other nitrene-transfer processes. In addition to our ongoing efforts to understand the mechanism of the Co-catalyzed aziridination, further improvement of its catalytic efficiency and the development of its asymmetric variant are in progress in our laboratory.

Experimental Section

(2-Phenylaziridin-1-yl)phosphonic acid diphenyl ester (Table 2, entry 1) was synthesized from the reaction of styrene with DPPA and obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27−7.00 (m, 15H), 3.63 (ddd, 1H, J = 16.5, 6.3, 3.6 Hz), 2.82 (ddd, 1H, J = 19.5, 6.3, 1.2 Hz), 2.24 (ddd, 1H, J = 15.6, 3.6, 1.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.7, 129.6, 128.5, 128.1, 126.2, 125.2, 120.5, 120.4, 120.3, 39.0, 38.9, 35.0, 34.9. ^{31}P NMR (121 MHz, $CDCl_3$): δ 6.11 (s). FT-IR (film, cm^{-1}): 1590, 1191, 941, 669. HRMS-EI ([M]$^+$) for $C_{20}H_{18}NO_3P$, calcd 351.1024, found 351.1022.

(2-*m*-Tolylaziridin-1-yl)phosphonic acid diphenyl ester (Table 2, entry 2) was synthesized from the reaction of *m*-methylstyrene with DPPA and obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28−6.95 (m, 14H), 3.61 (ddd, 1H, J = 16.5, 6.0, 3.3 Hz), 2.80 (dd, 1H, J = 19.2, 6.0 Hz), 2.22 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.7, 129.6, 128.8, 128.3, 126.8, 125.2, 123.4, 120.5, 120.4, 120.3, 39.0, 38.9, 34.9, 34.8, 21.3. ^{31}P NMR (121 MHz, $CDCl_3$): δ 6.19 (s). FT-IR (film, cm^{-1}): 1711, 1585, 1482, 1190, 1010, 932, 762. HRMS-EI ([M]$^+$) for $C_{21}H_{20}NO_3P$, calcd 365.1181, found 365.1174.

[2-(*p*-*tert*-Butylphenyl)aziridin-1-yl]phosphonic acid diphenyl ester (Table 2, entry 3) was synthesized from the reaction of *p*-*tert*-butylstyrene with DPPA and obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28−7.00 (m, 14H), 3.62 (ddd, 1H, J = 16.5, 6.0, 3.6 Hz), 2.80 (ddd, 1H, J = 19.8, 6.6, 1.2 Hz), 2.24 (ddd, 1H, J = 15.3, 3.6, 1.2 Hz), 1.24 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.7, 129.6, 125.9, 125.4, 125.2, 120.5, 120.4, 120.3, 38.9, 38.8, 34.9, 34.8, 34.5, 31.3. ^{31}P NMR (121 MHz, $CDCl_3$): δ 6.24 (s). FT-IR (film, cm^{-1}): 1592, 1490, 1193, 943, 773, 689. HRMS-EI ([M]$^+$) for $C_{24}H_{26}NO_3P$, calcd 407.1650, found 407.1658.

[2-(*p*-Bromophenyl)aziridin-1-yl]phosphonic acid diphenyl ester (Table 2, entry 4) was synthesized from the reaction of *p*-bromostyrene with DPPA and obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (d, 2H, J = 8.4 Hz), 7.28−7.07 (m, 10H), 7.01 (d, 2H, J = 8.4 Hz), 3.57 (ddd, 1H, J = 16.2, 6.0, 3.3 Hz), 2.80 (ddd, 1H, J = 18.9, 6.0, 1.2 Hz), 2.19 (ddd, 1H, J = 15.3, 3.3, 1.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.7, 129.6, 127.9, 125.3, 120.4, 120.3, 120.3, 38.3, 38.2, 35.0, 34.9. ^{31}P NMR (121 MHz, $CDCl_3$): δ 5.76 (s). FT-IR (film, cm^{-1}): 1591, 1489, 1283, 1192, 1163, 1072, 1006, 945, 827, 774. HRMS-EI ([M]$^+$) for $C_{20}H_{17}BrNO_3P$, calcd 429.0129, found 429.0127.

[2-(*p*-Chlorophenyl)aziridin-1-yl]phosphonic acid diphenyl ester (Table 2, entry 5) was synthesized from the reaction of *p*-chlorostyrene with DPPA and obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28−7.07 (m, 14H), 3.57 (ddd, 1H, J = 16.2, 6.0, 3.3 Hz), 2.80 (ddd, 1H, J = 19.2, 6.0, 1.2 Hz), 2.19 (ddd, 1H, J = 15.3, 3.3, 1.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.7, 129.6, 128.6, 127.5, 125.3, 120.4, 120.3, 120.2, 38.3, 38.2, 35.0, 34.9. ^{31}P NMR (121 MHz, $CDCl_3$): δ 5.79 (s). FT-IR (film, cm^{-1}): 1592, 1490, 1193, 943, 773, 689. HRMS-EI ([M]$^+$) for $C_{20}H_{17}ClNO_3P$, calcd 385.0635, found 385.0629.

[2-(*p*-Fluorophenyl)aziridin-1-yl]phosphonic acid diphenyl ester (Table 2, entry 6) was synthesized from the reaction of *p*-fluorostyrene with DPPA and obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28−7.04 (m, 12H), 6.92 (t, 2H, J = 8.7 Hz), 3.59 (ddd, 1H, J = 16.5, 6.0, 3.6 Hz), 2.80 (ddd, 1H, J = 19.5, 6.3, 1.2 Hz), 2.19 (ddd, 1H, J = 15.0, 3.3, 0.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.7, 129.6, 127.8, 127.7, 125.3, 120.4, 120.3, 120.2, 115.6, 115.3, 38.3, 38.2, 35.0, 34.9. ^{31}P NMR (121 MHz, $CDCl_3$): δ 5.96 (s). FT-IR (film, cm^{-1}): 1592, 1490, 1224, 1192, 932, 835, 689. HRMS-EI ([M]$^+$) for $C_{20}H_{17}FNO_3P$, calcd 369.0930, found 369.0946.

[2-(*p*-Trifluoromethylphenyl)aziridin-1-yl]phosphonic acid diphenyl ester (Table 2, entry 7) was synthesized from the reaction of *p*-trifluoromethylstyrene with DPPA and obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, 2H, J = 7.80 Hz), 7.26 (d, 2H, J = 7.5 Hz), 7.23−7.04 (m, 10H), 3.65 (ddd, 1H, J = 16.2, 6.0, 3.6 Hz), 2.84 (dd, 1H, J = 19.2, 6.3 Hz), 2.22 (dd, 1H, J = 15.3, 3.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.8, 129.7, 126.5, 125.5, 125.4, 125.3, 120.3, 120.3, 120.2, 38.3, 38.2, 35.0, 35.0. ^{31}P NMR (121 MHz, $CDCl_3$): δ 5.63 (s).^{19}F NMR (280 MHz, $CDCl_3$): δ −62.95. FT-IR (film, cm^{-1}): 1621, 1592, 1490, 1326, 1193, 1165, 1068, 1005, 947, 904, 774, 689. HRMS-EI ([M]$^+$) for $C_{21}H_{17}F_3NO_3P$, calcd 419.0898, found 419.0894.

(2-Pentafluorophenylaziridin-1-yl)phosphonic acid diphenyl ester (Table 2, entry 8) was synthesized from the reaction of pentafluorostyrene with DPPA and obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29−7.07 (m, 10H), 3.71 (ddd, 1H, J = 16.5, 6.3, 3.6 Hz), 2.86 (dd, 1H, J = 18.9, 6.3 Hz), 2.76 (dd, 1H, J = 15.6, 3.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.8, 129.7, 125.4, 125.3, 120.2, 120.1, 120.0, 30.9, 30.0. ^{31}P NMR (121 MHz, $CDCl_3$): δ 5.35 (s). ^{19}F NMR (280 MHz, $CDCl_3$): δ −140, −152, −160. FT-IR (film, cm^{-1}): 1687, 1520, 1476, 1176, 980. HRMS-EI ([M]$^+$) for $C_{20}H_{13}F_5NO_3P$, calcd 441.0553, found 441.0559.

[2-(*m*-Nitrophenyl)aziridin-1-yl]phosphonic acid diphenyl ester (Table 2, entry 9) was synthesized from the reaction of *m*-nitrostyrene with DPPA and obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (dd, 1H, J = 8.1, 0.9 Hz), 7.98 (br s, 1H), 7.49−7.04 (m, 10H), 3.70 (ddd, 1H, J = 16.2, 6.0, 3.3 Hz), 2.89 (dd, 1H, J = 18.6, 6.0 Hz), 2.25 (dd, 1H, J = 15.3, 3.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.3, 129.8, 129.7, 129.5, 125.4, 123.0, 121.1, 120.3, 120.2, 37.9, 37.8. ^{31}P NMR (121 MHz, $CDCl_3$): δ 5.27 (s). FT-IR (film, cm^{-1}): 1591, 1531, 1488, 1350, 1190, 950. HRMS-EI ([M − H]$^+$) for $C_{20}H_{17}N_2O_5P$, calcd 395.0797, found 395.0789.

[2-(2-Naphthalenyl)aziridin-1-yl]phosphonic acid diphenyl ester (Table 2, entry 10) was synthesized from the reaction of 2-vinylnaphthalene with DPPA and obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77−7.64 (m, 4H), 7.42−7.39 (m, 2H), 7.28−7.05 (m, 10H), 3.80 (ddd, 1H, J = 16.5, 6.0, 3.6 Hz), 2.89 (ddd, 1H, J = 19.2, 6.0, 1.2 Hz), 2.34 (ddd, 1H, J = 15.3, 3.3, 1.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.7, 129.6, 128.3, 127.7, 127.7, 126.3, 126.1, 125.8, 125.2, 123.4, 120.5, 120.4, 120.3, 39.2, 34.9. ^{31}P NMR (121 MHz, $CDCl_3$): δ 6.13 (s). FT-IR (film, cm^{-1}): 1593, 1489, 1193, 936, 689. HRMS-EI ([M]$^+$) for $C_{24}H_{20}NO_3P$, calcd 401.1181, found 401.1183.

Acknowledgment. We are grateful for financial support of this work from the University of Tennessee for Startup Funds, Oak Ridge Associated Universities (ORAU) for a Powe Junior Faculty Award, American Chemical Society (ACS) for a PRF-AC grant, National Science Foundation (NSF) for a CAREER Award, and a RSEC grant.

Supporting Information Available: ^{1}H NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0609226