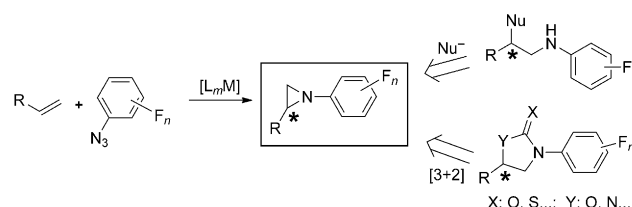


Effective Synthesis of Chiral *N*-Fluoroaryl Aziridines through Enantioselective Aziridination of Alkenes with Fluoroaryl Azides**

Li-Mei Jin, Xue Xu, Hongjian Lu, Xin Cui, Lukasz Wojtas, and X. Peter Zhang*

Catalytic aziridination of alkenes with nitrene sources through “C2+N1” addition represents a general approach for the direct synthesis of aziridines, the smallest three-membered N-heterocycles.^[1] The enantioselective version of this catalytic process allows for efficient access to chiral nonracemic aziridines, which are versatile synthetic intermediates in asymmetric synthesis.^[1,2] Several classes of transition-metal-based chiral catalysts, such as Mn, Fe, Cu, Rh, and Co complexes, are effective in catalyzing asymmetric olefin aziridination with different nitrene sources.^[1,3] Besides iminoiodanes and haloamines, organic azides, which enjoy several advantages, have been actively pursued as alternative nitrene sources for metal-catalyzed aziridination.^[3] While sulfonyl and phosphoryl azides have been effectively employed for metal-catalyzed asymmetric aziridination,^[4] catalytic processes based on the use of other types of azides, such as aryl azides, are less developed. In addition to generating environmentally friendly nitrogen gas as the only by-product, the asymmetric catalytic aziridination with readily available aryl azides provides an attractive approach for the synthesis of valuable *N*-aryl aziridines through direct introduction of *N*-aryl groups concurrently with the ring formation.^[5,6] This method would avoid two additional steps of deprotection and *N*-arylation when other types of nitrene sources such as sulfonyl azides are used for preparing *N*-aryl aziridines.^[7] However, few catalytic systems are effective for the asymmetric olefin aziridination with aryl azides.^[4d,6]

Fluoroaryl azides, which can be easily prepared from commercially available fluoroanilines, are a class of common aryl azides that have not been previously employed in catalytic aziridination of alkenes.^[8] A catalytic process for the asymmetric aziridination with fluoroaryl azides would be particularly attractive as the resulting enantioenriched *N*-fluoroaryl aziridines could serve as effective chiral synthons for the preparation of chiral fluoroarylamine-containing compounds through various ring-opening and ring-expansion transformations (Scheme 1).^[2] Chiral fluoroarylamine derivatives are useful in pharmaceutical and other important



Scheme 1. Synthesis and transformations of *N*-fluoroaryl aziridines.

applications.^[9] To date, only a few metal complexes, including Ru, Co, and Fe complexes, have been reported to catalyze the aziridination of alkenes with aryl azides.^[4d,6] None of them involved the use of fluoroaryl azides as nitrene sources. These existing catalytic aziridination systems typically required the use of excess olefins and relatively high reaction temperatures (70–90 °C) to achieve satisfactory yields. Furthermore, the majority of these systems are non-asymmetric; the issue of enantioselectivity is not addressed. To the best of our knowledge, the only example of asymmetric aziridination with aryl azides was that of α -methylstyrene with 4-nitrophenyl azide catalyzed by a Ru-based chiral catalyst, giving the product in only 10% enantiomeric excess and in 35% yield.^[10] It is evident that asymmetric olefin aziridination with aryl azides, including fluoroaryl azides, is an unsolved problem and faces formidable challenges in both reactivity and enantioselectivity.

As stable metalloradicals with a well-defined open-shell doublet d^7 electronic structure, cobalt(II) complexes of D_2 -symmetric chiral amidoporphyrins, [Co(D_2 -Por*)], are effective catalysts for the asymmetric aziridination of various olefin substrates with different classes of nitrene sources, particularly with sulfonyl and phosphoryl azides.^[4a,b] Results from computational and experimental studies suggest a distinctive metalloradical mechanism for the Co^{II}-catalyzed aziridination, involving an unprecedented Co^{III}-nitrene radical intermediate and a stepwise radical addition–substitution pathway.^[11] In addition to serving as rigid spacers to support and orient the chiral environments toward the cobalt center, the amide units of the D_2 -symmetric amidoporphyrins were shown to also function as potential donors to engage in hydrogen-bonding interaction with acceptors located at the nitrene moiety in the Co^{III}-nitrene radical intermediate,^[12,13] thus lowering the energy barrier of the transition state and accelerating the reaction rate.^[11a] Given that the fluorine atom in organic fluorides can act as a potential hydrogen-bond acceptor,^[14] we hypothesized the possibility of a similar hydrogen-bonding interaction in the corresponding Co^{III}-nitrene radical intermediate from activation of fluoroaryl azides (Figure 1). Depending on the number of fluorine atoms

[*] Dr. L. M. Jin, Dr. X. Xu, Dr. H. Lu, Dr. X. Cui, Dr. L. Wojtas, Prof. Dr. X. P. Zhang
Department of Chemistry, University of South Florida
Tampa, FL 33620-5250 (USA)
E-mail: xpzhang@usf.edu
Homepage: <http://chemistry.usf.edu/faculty/zhang/>

[**] We are grateful for financial support by NSF (CHE-1152767) and NIH (R01-GM098777). We thank the Advanced Photon Source at Argonne National Lab, Chicago, IL for the measurement of the X-ray structure of porphyrin P3.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201209599>.

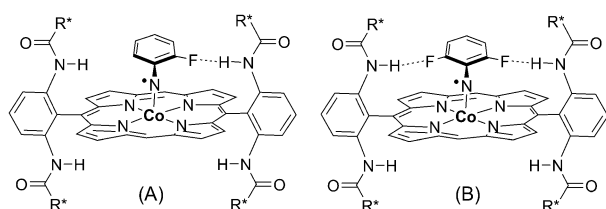


Figure 1. Hydrogen-bonding in postulated nitrene radical complex.

in the *ortho* position in fluoroaryl azides, formation of single (Figure 1 A) or double (Figure 1 B) N–H...F hydrogen bonds between the amide N–H elements of amidoporphyrins and the F atoms in *ortho* position of fluoroaryl groups would be attainable. On the basis of this hypothesis, we embarked on a research project to study the catalytic asymmetric olefin aziridination with fluoroaryl azides by [Co(*D*₂-Por*)].

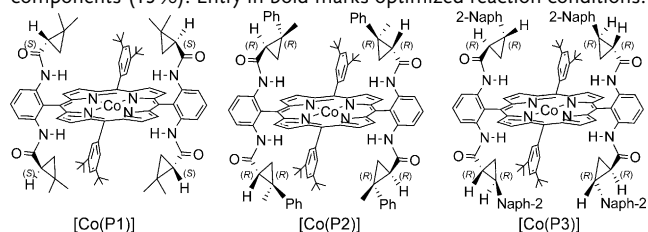
As an outcome of this effort, we report herein a highly effective catalytic system that is based on a new generation of chiral Co^{II} metalloradical catalysts for asymmetric aziridination of alkenes with fluoroaryl azides. The Co^{II}-catalyzed aziridination is suitable for a wide range of aromatic olefins and fluoroaryl azides, producing the corresponding *N*-fluoroaryl aziridines in high yields with excellent enantioselectivities. In addition to tolerating a wide variety of fluoroaryl azides as nitrene sources, the new metalloradical aziridination process features a practical protocol that operates at room temperature without the need of excess olefin, generating N₂ as the only by-product.

At the outset of our studies, we evaluated the catalytic capability of different *D*₂-symmetric chiral amidoporphyrins [Co(*D*₂-Por*)] in the aziridination of styrene (**1a**) with 2-fluorophenyl azide (**2a**; Table 1). Catalyzed by [Co(P1)] (2 mol %; P1 = 3,5-di-*tert*-butyl-ChenPhyrin),^[15] the reaction in benzene went smoothly even at room temperature, and afforded the desired aziridine product in 50% yield and 47% *ee* (Table 1, entry 1). Subsequent experiments showed that [Co(TPP)] (TPP = 5,10,15,20-tetraphenylporphyrin) was an ineffective catalyst for the reaction under the same conditions (Table 1, entry 2). The notable difference in catalytic capability between [Co(P1)] and [Co(TPP)] is in line with our assumption about the possible role of N–H...F hydrogen-bonding interaction in activating the fluoroaryl azide (Figure 1 A). Further studies showed that 2,4,6-trifluorophenyl azide (**2b**) also effectively aziridinated styrene under [Co(P1)] catalysis, affording the corresponding aziridine in 95% yield and 66% *ee* (Table 1, entry 3). The observed improvement in reactivity and stereoselectivity with azide **2b**, which contains two F atoms in *ortho* position, is ascribed to the potential formation of the double N–H...F hydrogen bonds in the postulated Co^{III}–nitrene radical intermediate (Figure 1 B). Further improvement in enantioselectivity was achieved for aziridination of styrene with azide **2b** when [Co(P2)] (P2 = 3,5-di-*tert*-butyl-QingPhyrin), a second-generation metalloradical catalyst that was previously shown to be highly effective for asymmetric intramolecular cyclopropanation,^[16] was employed as a catalyst, reaching 73% *ee* and the same high yield (Table 1, entry 4). Successive studies resulted in the design and synthesis of a new *D*₂-symmetric

Table 1: Enantioselective aziridination by different [Co(*D*₂-Por*)].^[a]

Entry	Catalyst	Ar	Solvent	Yield [%] ^[b]	<i>ee</i> [%] ^[c]
1 ^[d]	[Co(P1)]	<i>o</i> -FC ₆ H ₄ (2a)	PhH	50 ^[e]	–47
2 ^[d]	[Co(TPP)]	<i>o</i> -FC ₆ H ₄ (2a)	PhH	trace	–
3 ^[d]	[Co(P1)]	2,4,6-F ₃ C ₆ H ₂ (2b)	PhH	95	–66
4 ^[d]	[Co(P2)]	2,4,6-F ₃ C ₆ H ₂ (2b)	PhH	95	73
5	[Co(P3)]	2,4,6-F ₃ C ₆ H ₂ (2b)	PhH	94	90
6	[Co(P3)]	2,4,6-F ₃ C ₆ H ₂ (2b)	PhCl	80	91
7	[Co(P3)]	2,4,6-F₃C₆H₂ (2b)	PhF	94	92
8	[Co(P3)]	2,4,6-F ₃ C ₆ H ₂ (2b)	hexane	72	90
9	–	2,4,6-F ₃ C ₆ H ₂ (2b)	PhH	NR	–

[a] Carried out with olefin (**1**, 0.2 M), azide (1.2 equiv), and [Co(*D*₂-Por*)] (1 mol %). [b] Yields of isolated products. [c] Determined by HPLC on a chiral stationary phase. [d] 2 mol % catalyst loading. [e] Yield determined by ¹⁹F NMR spectroscopy. Product mixture contained **2a** (10%), azo fluorobenzene (15%), fluoroaniline (10%), and unknown components (15%). Entry in bold marks optimized reaction conditions.



chiral amidoporphyrin 3,5-di-*tert*-butyl-Xu(2'-Naph)Phyrin (P3),^[17] whose Co^{II} complex [Co(P3)] was shown to be the optimal catalyst for the process, giving the desired product in 94% yield and 90% *ee* even with only 1 mol % of catalyst loading (Table 1, entry 5). Among various solvents that were screened, fluorobenzene was found to be the solvent of choice, giving the aziridine product in high yield (94%) and excellent enantioselectivity (92% *ee*) at room temperature (Table 1, entries 5–8). As expected, control experiments in the absence of a catalyst gave no reaction (Table 1, entry 9).

Under the optimized reaction conditions, we then used the aziridination of styrene as a model reaction to investigate the scope and limitation of fluoroaryl azides as nitrene sources (Table 2). As in the case of aryl azide **2b**, which has two F atoms in *ortho* position (Table 1), the use of the new metalloradical catalyst, [Co(P3)], also led to significant improvement in enantioselectivity for the aziridination reaction with aryl azide **2a**, which contains one F atom in *ortho* position (Table 2, entry 1 versus Table 1, entry 1). The [Co(P3)]-based catalytic aziridination system could effectively employ other mono-*ortho*-fluoro-substituted aryl azides as nitrene sources, as demonstrated by the use of 2,4,5-trifluorophenyl azide (**2c**) (Table 2, entry 2). In addition to azide **2b**, various other di-*ortho*-fluoro-substituted aryl azides, including 2,6-difluoro-, 2,3,5,6-tetrafluoro-, and pentafluorophenyl azides (**2d–f**), were shown to be highly effective nitrene sources for the Co^{II}-based aziridination process, yielding the corresponding aziridines in high yields with excellent enantioselectivities (Table 2, entries 3–5). Presumably as a result of additional N–H...F hydrogen-bonding interactions in the postulated Co^{III}–nitrene radical intermedi-

Table 2: [Co(P3)]-catalyzed enantioselective aziridination of styrene with various fluoroaryl azides.^[a,b,c]

entry 1: ^[e] 3 aa ; 52 % yield, 75 % ee	entry 2: 3 ac ; 64 % yield, 80 % ee	entry 3: ^[d] 3 ad ; 80 % yield, 96 % ee
entry 4: 3 ae ; 95 % yield, 89 % ee	entry 5: 3 af ; 99 % yield, 92 % ee	entry 6: 3 ag ; 96 % yield, 90 % ee
entry 7: 3 ah ; 95 % yield, 80 % ee	entry 8: 3 ai ; 99 % yield, 68 % ee	entry 9: 3 aj ; no reaction

See Table 1 for footnotes [a], [b], [c], and [e]. [d] Determined by X-ray diffraction.

ate (Figure 1), di-*ortho*-fluoro-substituted aryl azides were found to be more selective and effective aziridinating agents than mono-*ortho*-fluoro-substituted aryl azides. Similarly, 4-tetrafluoropyridinyl azide (**2g**) was found to be equally effective in the aziridination of styrene, without complication from potential coordination of the pyridine unit to [Co(P3)] (Table 2, entry 6). Reactions with *para*-substituted fluoroaryl azides, such as 4-bromotetrafluorophenyl azide (**2h**) and 4-trifluoromethyltetrafluorophenyl azide (**2i**), produced the desired products in excellent yields, albeit with slightly lower enantioselectivities (Table 2, entries 7 and 8). It is worth noting that 3,4,5-trifluorophenyl azide (**2j**), which contains three F atoms but none of them in *ortho* position, gave no reaction under the same conditions (Table 2, entry 9), again suggesting the important role the N–H...F hydrogen bond plays in the Co^{II}-based metalloradical aziridination process (Figure 1).^[18]

The [Co(P3)]-catalyzed asymmetric aziridination was found to be suitable for a wide range of aromatic olefins with varied electronic and steric properties, as shown for 2,4,6-trifluorophenyl azide (**2b**) and pentafluorophenyl azide (**2f**) as representative fluoroaryl azides (Table 3).^[19] Similar to styrene, styrene derivatives with electron-donating substituents at various positions, including Me, *t*Bu, and MeO groups at the *para*, *meta*, and *ortho* positions, could be aziridinated smoothly to form the corresponding *N*-fluoroaryl aziridines in high yields and enantioselectivity (Table 3, entries 1–8). In addition, enantioenriched *N*-fluoroaryl aziridines could be readily formed from aziridination reactions of electron-deficient styrenes, such as *para*-CF₃- and *para*-CO₂Me-substituted styrenes (Table 3, entries 9–11). Moreover, [Co(P3)] could effect aziridination of various halogenated styrenes, such as fluorostyrenes and bromostyrenes, producing the corresponding aziridines with high enantiomeric excesses (Table 3, entries 12–16). The Co^{II}-based asymmetric aziridination could also be successfully applied to

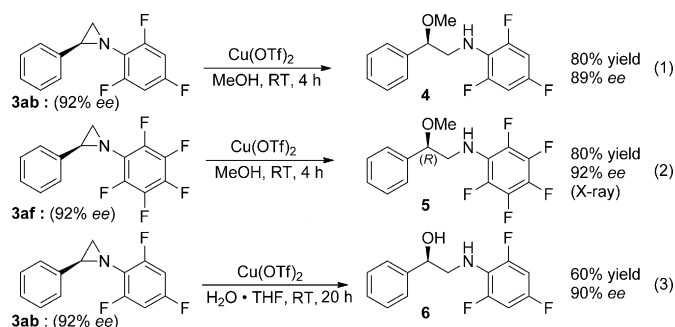
Table 3: Enantioselective aziridination of different combinations of olefins with azides catalyzed by [Co(P3)].^[a,b,c]

entry 1: 3 ab ; 99 % yield, 94 % ee	entry 2: 3 af ; 99 % yield, 92 % ee	entry 3: 3 bf ; 99 % yield, 96 % ee
entry 4: 3 cb ; 99 % yield, 92 % ee	entry 5: 3 cf ; 95 % yield, 94 % ee	entry 6: 3 df ; 99 % yield, 87 % ee
entry 7: 3 eb ; 85 % yield, 92 % ee	entry 8: 3 fb ; 99 % yield, 87 % ee	entry 9: 3 gb ; 77 % yield, 92 % ee
entry 10: ^[d] 3 gf ; 91 % yield, 85 % ee	entry 11: 3 hb ; 80 % yield, 92 % ee	entry 12: 3 ib ; 93 % yield, 95 % ee
entry 13: ^[d] 3 if ; 90 % yield, 91 % ee	entry 14: ^[d] 3 jb ; 81 % yield, 92 % ee	entry 15: 3 kb ; 82 % yield, 93 % ee
entry 16: 3 kf ; 95 % yield, 89 % ee	entry 17: 3 lb ; 80 % yield, 90 % ee	entry 18: 3 lf ; 73 % yield, 98 % ee
entry 19: 3 mb ; 74 % yield, 86 % ee	entry 20: 3 nf ; 90 % yield, 85 % ee	entry 21: 3 ob ; 80 % yield, 96 % ee

See Table 1 for footnotes [a], [b], and [c]. [d] Determined by X-ray diffraction.

extended aromatic olefins, including 2-vinylnaphthalene and sterically demanding 1-vinylnaphthalene and 9-vinylanthracene (Table 3, entries 17–20). Notably, heteroaromatic alkenes such as Boc-protected 3-vinylindole could also be aziridinated with fluoroaryl azides to generate the desired aziridindole **3ob** in high yield and excellent enantioselectivity (Table 3, entry 21).

The demonstrated asymmetric olefin aziridination with fluoroaryl azides by catalysis with Co^{II}-based metalloradical provides a practical method to access *N*-fluoroaryl-containing chiral compounds in high enantiomeric purity, which may find applications in asymmetric synthesis and pharmaceuticals.^[9] An initial exploration of further transformations of these chiral *N*-fluoroaryl aziridines showed that the aziridine ring could be readily opened in the presence of a Lewis acid without apparent loss of the enantiomeric purity [Scheme 2, Eqs. (1)–(3)].^[20] For instance, *N*-fluoroaryl-containing chiral aziridines **3ab** and **3af** readily underwent ring-opening reactions with MeOH in the presence of Cu(OTf)₂, thus



Scheme 2. Nucleophilic ring-opening of *N*-fluoroaryl aziridines.

generating chiral β -methoxy amine derivatives **4** and **5**, respectively, in high yields and with high optical purity [Eqs. (1) and (2)]. X-ray structural analysis showed the absolute configuration of the carbon stereocenter in product **5** to be (*R*) (see the Supporting Information), thus indicating an S_N2 -type ring-opening reaction at the original (*S*)-chiral center in **3af**. More significantly, even water could function as a nucleophile for the highly stereoselective ring-opening process, as demonstrated for the ring opening of chiral aziridine **3ab**, which resulted in the direct formation of chiral vicinal amino alcohol **6** [Eq. (3)].

In summary, we have demonstrated that the metalloradical [Co(P3)] is an efficient catalyst for the highly enantioselective aziridination of alkenes with fluoroaryl azides. This Co^{II}-based process represents the first catalytic system for asymmetric olefin aziridination with aryl azides as the nitrene source. Among other attributes, the metalloradical aziridination can be performed at room temperature using olefin as the limiting reagent without the need of any additives, thus generating nitrogen gas as the only by-product. The resulting optically pure *N*-fluoroaryl aziridines should find useful applications in asymmetric synthesis. Efforts are underway to employ fluoroaryl azides as effective nitrene sources for the development of other catalytic nitrene-transfer processes through Co^{II}-based metalloradical catalysis.

Received: November 30, 2012

Revised: February 17, 2013

Published online: April 15, 2013

Keywords: aziridines · aryl azides · asymmetric catalysis · cobalt · porphyrins

- [1] For reviews, see: a) P. Müller, C. Fruit, *Chem. Rev.* **2003**, *103*, 2905; b) H. Pellissier, *Tetrahedron* **2010**, *66*, 1509; c) T. G. Driver, *Org. Biomol. Chem.* **2010**, *8*, 3831; d) J. W. W. Chang, T. M. U. Ton, P. W. H. Chan, *Chem. Rev.* **2011**, *11*, 331.
- [2] For reviews, see: a) T. Ibuka, *Chem. Soc. Rev.* **1998**, *27*, 145; b) J. B. Sweeney, *Chem. Soc. Rev.* **2002**, *31*, 247; c) A. K. Yudin, *Acc. Chem. Res.* **2006**, *39*, 194; d) P. Lu, *Tetrahedron* **2010**, *66*, 2549; e) S. Stanković, M. D'Hooghe, S. Catak, H. Eum, M. Waroquier, V. Van Speybroeck, N. De Kimpe, H.-J. Ha, *Chem. Soc. Rev.* **2012**, *41*, 643; f) S. Florio, R. Luisi, *Chem. Rev.* **2010**, *110*, 5128; g) X. E. Hu, *Tetrahedron* **2004**, *60*, 2701; h) G. S. Singh, M. D'Hooghe, N. De Kimpe, *Chem. Rev.* **2007**, *107*, 2080.

- [3] For reviews, see: a) T. Katsuki, *Chem. Lett.* **2005**, *34*, 1304; b) S. Bräse, C. Gil, K. Knepper, V. Zimmermann, *Angew. Chem.* **2005**, *117*, 5320; *Angew. Chem. Int. Ed.* **2005**, *44*, 5188; c) S. Fantauzzi, A. Caselli, E. Gallo, *Dalton Trans.* **2009**, 5434; d) H. Lu, X. P. Zhang, *Chem. Soc. Rev.* **2011**, *40*, 1899.
- [4] For selected recent examples, see: a) V. Subbarayan, J. V. Ruppel, S. Zhu, J. A. Perman, X. P. Zhang, *Chem. Commun.* **2009**, 4266; b) J. E. Jones, J. V. Ruppel, G.-Y. Gao, T. M. Moore, X. P. Zhang, *J. Org. Chem.* **2008**, *73*, 7260; c) C. Kim, T. Uchida, T. Katsuki, *Chem. Commun.* **2012**, 48, 7188; d) L. Liang, H. Lv, Y. Yu, P. Wang, J.-L. Zhang, *Dalton Trans.* **2012**, *41*, 1457.
- [5] N. Jung, S. Bräse, *Angew. Chem.* **2012**, *124*, 5632; *Angew. Chem. Int. Ed.* **2012**, *51*, 5538.
- [6] a) S. Fantauzzi, E. Gallo, A. Caselli, F. Ragaini, P. Macchi, N. Casati, S. Cenini, *Organometallics* **2005**, *24*, 4710; b) S. Fantauzzi, E. Gallo, A. Caselli, C. Piangiolino, F. Ragaini, S. Cenini, *Eur. J. Org. Chem.* **2007**, 6053; c) A. Caselli, E. Gallo, S. Fantauzzi, S. Morlacchi, F. Ragaini, S. Cenini, *Eur. J. Inorg. Chem.* **2008**, 3009; d) Y. Liu, C.-M. Che, *Chem. Eur. J.* **2010**, *16*, 10494; e) S. A. Cramer, D. M. Jenkins, *J. Am. Chem. Soc.* **2011**, *133*, 19342; f) D. M. Jenkins, *Synlett* **2012**, 1267.
- [7] a) M. Sasaki, S. Dalili, A. K. Yudin, *J. Org. Chem.* **2003**, *68*, 2045; b) D. A. Alonso, P. G. Andersson, *J. Org. Chem.* **1998**, *63*, 9455; c) S. C. Bergmeier, P. P. Seth, *Tetrahedron Lett.* **1999**, *40*, 6181.
- [8] For selected examples of noncatalytic aziridination with fluoroaryl azides under thermal or photolytic conditions, see: a) R. A. Abramovitch, S. R. Challand, Y. Yamada, *J. Org. Chem.* **1975**, *40*, 1541; b) J. F. W. Keana, S. X. Cai, *J. Org. Chem.* **1990**, *55*, 3640; c) N. Soundararajan, M. S. Platz, *J. Org. Chem.* **1990**, *55*, 2034; d) K. G. Pinney, J. A. Katzenellenbogen, *J. Org. Chem.* **1991**, *56*, 3125; e) M. Yan, S. X. Cai, J. F. W. Keana, *J. Org. Chem.* **1994**, *59*, 5951.
- [9] For reviews, see: a) S. Purser, P. R. Moore, S. Swallow, V. Gouverneur, *Chem. Soc. Rev.* **2008**, *37*, 320; b) H. Amii, K. Uneyama, *Chem. Rev.* **2009**, *109*, 2119; c) K. C. K. Swamy, N. N. B. Kumar, E. Balaraman, K. V. P. P. Kumar, *Chem. Rev.* **2009**, *109*, 2551; d) D. Antonow, D. E. Thurston, *Chem. Rev.* **2011**, *111*, 2815; e) J. R. Barrio, N. Satyamurthy, S.-C. Huang, A. Petrič, G. W. Small, V. Kepe, *Acc. Chem. Res.* **2009**, *42*, 842; f) S. M. Ametamey, M. Honer, P. A. Schubiger, *Chem. Rev.* **2008**, *108*, 1501.
- [10] A. Caselli, E. Gallo, F. Ragaini, F. Ricatto, G. Abbiati, S. Cenini, *Inorg. Chim. Acta* **2006**, *359*, 2924.
- [11] For studies on the radical mechanism of aziridination involving Co^{III}-nitrene radical intermediates, see: a) A. I. Olivios Suarez, H. Jiang, X. P. Zhang, B. de Bruin, *Dalton Trans.* **2011**, *40*, 5697; b) K. H. Hopmann, A. Ghosh, *ACS Catal.* **2011**, *1*, 597; for related DFT studies on the radical mechanism of [Co(Por)]-catalyzed C–H amination, see: c) V. Lyaskovskyy, A. I. O. Suarez, H. Lu, H. Jiang, X. P. Zhang, B. de Bruin, *J. Am. Chem. Soc.* **2011**, *133*, 12264; for studies on the similar radical mechanism of cyclopropanation involving Co^{III}-carbene radical intermediates, see: d) W. I. Dzik, X. Xu, X. P. Zhang, J. N. H. Reek, B. de Bruin, *J. Am. Chem. Soc.* **2010**, *132*, 10891; e) J. L. Belof, C. R. Cioce, X. Xu, X. P. Zhang, B. Space, H. L. Woodcock, *Organometallics* **2011**, *30*, 2739; f) H. Lu, W. I. Dzik, X. Xu, L. Wojtas, B. de Bruin, X. P. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 8518.
- [12] J. V. Ruppel, J. E. Jones, C. A. Huff, R. M. Kamble, Y. Chen, X. P. Zhang, *Org. Lett.* **2008**, *10*, 1995.
- [13] H. Lu, H. Jiang, L. Wojtas, X. P. Zhang, *Angew. Chem.* **2010**, *122*, 10390; *Angew. Chem. Int. Ed.* **2010**, *49*, 10192.
- [14] a) I. Alkorta, I. Rozas, J. Elguero, *J. Fluorine Chem.* **2000**, *101*, 233; b) J. A. K. Howard, V. J. Hoy, D. O'Hagan, G. T. Smith, *Tetrahedron* **1996**, *52*, 12613; c) H.-J. Schneider, *Chem. Sci.* **2012**, *3*, 1381.

- [15] Y. Chen, K. B. Fields, X. P. Zhang, *J. Am. Chem. Soc.* **2004**, *126*, 14718.
- [16] X. Xu, H. Lu, J. V. Ruppel, X. Cui, S. Lopez de Mesa, L. Wojtas, X. P. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 15292.
- [17] Chiral porphyrin P3 was developed using an iterative approach based on Co^{II}-catalyzed asymmetric cyclopropanation.^[16] For details on its synthesis and X-ray crystal structure, see the Supporting Information.
- [18] a) No reactions were observed with phenyl azide and 2,6-dichlorophenyl azide; b) an inverse kinetic isotope effect was observed with deuterated catalyst.
- [19] The current catalytic system was found to be ineffective for disubstituted alkenes. For substrates that contain secondary and allylic C–H bonds, catalytic C–H amination was observed instead of olefin aziridination.
- [20] a) M. K. Ghorai, K. Das, D. Shukla, *J. Org. Chem.* **2007**, *72*, 5859. Preliminary results showed the possibility of further transformations of these polyfluorinated aryl groups by S_NAr reactions, see related references: b) M. Bella, S. Koppelgaard, K. A. Jørgensen, *J. Am. Chem. Soc.* **2005**, *127*, 3670; c) L. Qin, C. Sheridan, J. Gao, *Org. Lett.* **2012**, *14*, 528; d) A. Rolfe, T. B. Samarakoon, P. R. Hanson, *Org. Lett.* **2010**, *12*, 1216.