Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron Letters
Tetrahedron Letters 46 (2005) 4965–4969

Palladium-mediated synthesis of novel *meso*-chiral porphyrins: cobalt-catalyzed cyclopropanation

Ying Chen, Guang-Yao Gao and X. Peter Zhang*

Department of Chemistry, University of Tennessee, Room 614, Buehler Hall, Knoxville, TN 37996-1600, USA

Received 21 April 2005; revised 20 May 2005; accepted 20 May 2005
Available online 13 June 2005

Abstract—A series of novel *meso*-chiral porphyrins were effectively synthesized from reactions of 5,15-dibromo-10,20-diarylporphyrins with readily available chiral alcohols and amides via palladium-mediated C–N and C–O bond formations. Cobalt complexes of these chiral porphyrins were prepared and shown to be effective catalysts for cyclopropanation of styrene with ethyl diazoacetate under mild and practical conditions, affording the desired cyclopropane ester as a trans-dominant form in excellent yields. Due to orientation and flexibility of the chiral appendages, only low enantioselectivity was observed.

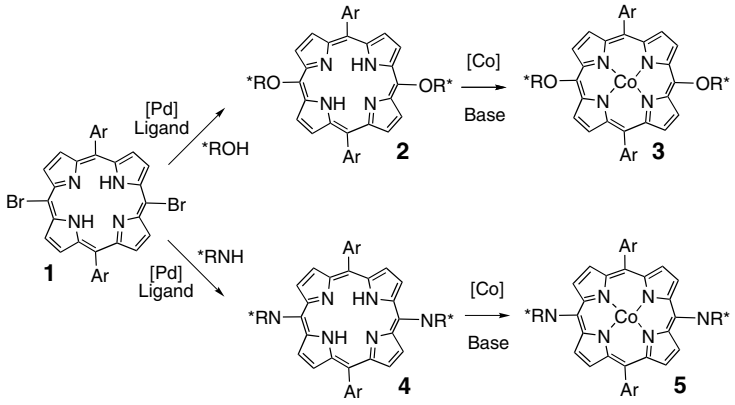
Biologically relevant chiral porphyrins have found a range of useful applications in several areas such as asymmetric catalysis, chiral recognition/sensing and enzymatic mimicry.[1] Several approaches have been described for the syntheses of chiral porphyrins.[2] Among them, covalent link of appropriate chiral building blocks to a preformed porphyrin synthon via peripheral functional groups is one of the most general and chirally economic approaches.[1,2] Established porphyrin synthons include *meso*-tetrakis(2-aminophenyl)-porphyrin,[3] *meso*-tetrakis(2,6-diaminophenyl)porphyrin,[4] *meso*-tetrakis(2,6-dihydroxyphenyl)porphyrin[5] and *meso*-tetrakis(2,6-dicarboxyphenyl)porphyrin,[6] which permit linkages of multiple chiral acids, amines or alcohols through amide or ester bond formation.[1,2] To enhance generality and practicality of chiral porphyrin synthesis, there is a need to develop alternative synthons that allow versatile and effective assembly of chiral porphyrins.

Based on metal-catalyzed carbon–heteroatom bond formations,[7] we have developed several general and efficient methods for the synthesis of heteroatom-substituted porphyrins from catalytic reactions of halogenated porphyrins with soft, non-organometallic nucleophiles.[8–11] For example, a general and efficient method has been developed for the synthesis of *meso*-arylamino- and alkylamino-substituted porphyrins from reactions of *meso*-bromoporphyrins with amines.[8a] Similar methodology can also be effectively applied to brominated diphenylporphyrins and tetraphenylporphyrins, leading to versatile synthesis of porphyrin derivatives bearing multiple arylamino and alkylamino groups.[8b] In addition, we described a convenient and general approach for the synthesis of *meso*-aryloxy- and alkoxy-substituted porphyrins from reactions with alcohols via palladium-catalyzed etheration.[8c] Subsequently, we reported a general synthetic method for *meso*-amidoporphyrins from reactions with amides via palladium-catalyzed amidation.[8d] Expanding the synthetic strategy to palladium-mediated carbon–sulfur bond formation, a versatile procedure has been recently developed for the synthesis of *meso*-arylsulfanyl- and alkylsulfanyl-substituted porphyrins from reactions of the corresponding bromoporphyrin precursors and thiols.[8e] These catalytic reactions can be performed in high yields under mild conditions and are suitable for a wide variety of amines, amides, alcohols and thiols, forming a variety of new functional porphyrins.[8]

Given that large numbers of chiral amines, amides, alcohols and thiols are readily available, our synthetic methodologies[8] would render halogenated porphyrins a new class of synthons for construction of chiral porphyrins. For example, we demonstrated previously

Keywords: Chiral porphyrins; Cobalt porphyrins; Cyclopropanation; Palladium-catalyzed; Cross-coupling; C–N bond formation; C–O bond formation.
* Corresponding author. Tel.: +1 865 974 3419; fax: +1 865 974 3454; e-mail: pzhang@utk.edu

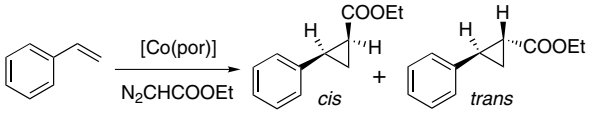
0040-4039/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2005.05.089



Scheme 1. Synthesis of *meso*-chiral porphyrins and their cobalt complexes.

that 5,10-bis(2′,6′-dibromophenyl)porphyrins are versatile synthons for modular construction of *ortho*-chiral porphyrins via palladium-catalyzed amidation reactions with chiral amides.[12] The quadruple carbon–nitrogen bond formation reactions can be accomplished in high yields with different chiral amide building blocks under mild conditions, forming a family of D_2-symmetric *ortho*-chiral porphyrins.[12] As a part of our program of metalloporphyrin-based atom/group transfer catalysis,[13] we also showed that cobalt(II) complexes of these *ortho*-chiral porphyrins are active catalysts for highly enantioselective and diastereoselective cyclopropanation.[12] To probe the relationship between porphyrin structure and reaction selectivity in asymmetric cyclopropanation, we expanded our efforts in chiral porphyrin synthesis to include *meso*-chiral porphyrins. We report herein effective synthesis of novel *meso*-chiral porphyrins from reactions of *meso*-dibromoporphyrins with chiral nucleophiles via palladium-catalyzed etheration[8c] and amidation[8d] (Scheme 1). The synthesis can be carried out under mild conditions, typically giving high yields, and is suitable to various porphyrin precursors with different chiral alcohols and amides. In this letter, we also describe the preparation of cobalt complexes of these chiral porphyrins (Scheme 1) and their application as catalysts for cyclopropanation of styrene with ethyl diazoacetate (EDA) (Scheme 2).

Four types of *meso*-dibromoporphyrin **1** bearing different *meso*-aryl groups (**1a**: Ar = phenyl; **1b**: Ar = 2,6-dimethylphenyl; **1c**: Ar = 2,4,5-trimethylphenyl; **1d**: Ar = 3,5-di-*tert*-butylphenyl), which were readily prepared in gram scale via selective bromination of 5,15-diarylporphyrins,[11b,e,f] were successfully coupled with several commercially available chiral alcohols and amides under palladium-catalyzed etheration[8c] and amidation[8d] conditions (Table 1), affording a series of novel *meso*-chiral porphyrins (Fig. 1). For example, the combination of $Pd_2(dba)_3$ and DPEphos could effect the double C–O coupling reactions of the secondary cyclic alcohol (+)-dihydrocholesterol with **1a**–**c** to form *meso*-chiral porphyrins **2a**–**c**, respectively, in 45–82% yields (Table 1, entries 1–4). The same catalytic system also doubly coupled the aromatic alcohol (+)-estrone with **1a** to produce *meso*-chiral porphyrin **2e** in 98%

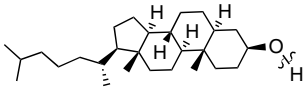
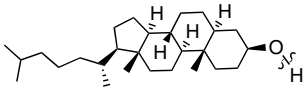
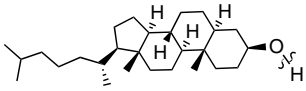
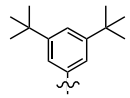
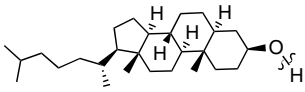
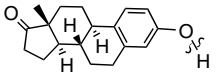
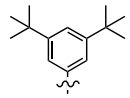
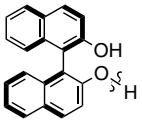
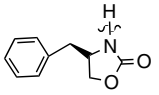
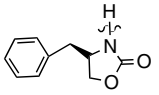
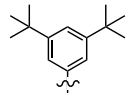
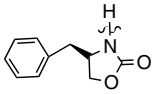


Scheme 2. Cyclopropanation of styrene by cobalt complexes of *meso*-chiral porphyrins.

yield (Table 1, entry 5). Only one set of resonances was observed in both ^1H and ^{13}C spectra of the products **2a**–**e**, suggesting that there is a free rotation around the O–C bond at ambient temperature in these *meso*-chiral porphyrins. When *R*-(+)-BINOL was used in an excess amount, the double etheration reaction with **1d** could be controlled to give *meso*-chiral porphyrin **2f** where only one of the two hydroxyl groups was reacted, although the yield was low (Table 1, entry 6). The observation of multiple ^1H NMR resonances for the *tert*-butyl groups suggests the product **2f** existed as a mixture of two atropisomers (α,α- and α,β-isomers), presumably due to increased rotation barrier around the O–C bond. Using Xantphos as a supporting ligand in combination with $Pd_2(dba)_3$, *meso*-dibromoporphyrin **1a**,**c** and **d** could be doubly amidated with chiral amide (*R*)-(+)-4-benzyl-2-oxazolidinone via C–N bond formation, producing *meso*-chiral porphyrin **4a**,**b** and **c**, respectively, in high yields (Table 1, entries 7–9). As evidenced by the two well-separated sets of ^1H NMR resonances in approximately equal intensities, the products **4a**–**c** all existed as a mixture of two atropisomers in nearly same amounts, resulting from a high rotation barrier around the bond between the porphyrin *meso*-carbon atom and the amide nitrogen atom. Attempts to separate these atropisomers have been unsuccessful.[14]

In our first step to explore the applications of these novel chiral porphyrins, *meso*-chiral porphyrin **2a**–**f** and **4a**–**c** were converted to their cobalt(II) complexes **3a**–**f** and **5a**–**c,** respectively (Scheme 1 and Fig. 1). The metallation reactions were performed either with $CoCl_2$ in THF in the presence of 2,6-lutidine or with $Co(OAc)_2$ in DMF at higher temperature. In all cases, the desired cobalt(II) porphyrins were obtained in high to excellent yields (Table 1).

Table 1. Synthetic conditions and yields for *meso*-chiral porphyrins and their cobalt complexes

Entry	Ar group of **1**	*ROH/*RNH	Coupling condition	Product: yield [a] (%)	Metallation condition	Product: yield[a] (%)
1			$Pd_2(dba)_3$/DPEphos/Cs_2CO_3 toluene/100 °C/17 h	**2a**: 45	$CoCl_2$/2,6-lutidine/THF 70 °C/15 h	**3a**: 71
2			$Pd_2(dba)_3$/DPEphos/Cs_2CO_3 toluene/100 °C/20 h	**2b**: 82	$CoCl_2$/2,6-lutidine/THF 70 °C/14 h	**3b**: 96
3			$Pd_2(dba)_3$/DPEphos/Cs_2CO_3 toluene/100 °C/20 h	**2c**: 80	$CoCl_2$/2,6-lutidine/THF 70 °C/14 h	**3c**: 88
4			$Pd_2(dba)_3$/DPEphos/Cs_2CO_3 toluene/100 °C/18 h	**2d**: 79	$CoCl_2$/2,6-lutidine/THF 70 °C/14 h	**3d**: 89
5			$Pd_2(dba)_3$/DPEphos/Cs_2CO_3 toluene/100 °C/40 h	**2e**: 98	$Co(OAc)\cdot 4H_2O$/DMF 160 °C/2 h	**3e**: 77
6			$Pd_2(dba)_3$/DPEphos/Cs_2CO_3 toluene/100 °C/20 h	**2f**: 35[b]	$CoCl_2$/2,6-lutidine/THF 70 °C/14 h	**3f**: 96[b]
7			$Pd_2(dba)_3$/Xantphos/Cs_2CO_3 THF/68 °C/22 h	**4a**: 62[b]	$CoCl_2$/2,6-lutidine/THF 70 °C/14 h	**5a**: 87[b]
8			$Pd_2(dba)_3$/Xantphos/Cs_2CO_3 THF/80 °C/20 h	**4b**: 72[b]	$CoCl_2$/2,6-lutidine/THF 70 °C/14 h	**5b**: 94[b]
9			$Pd_2(dba)_3$/Xantphos/Cs_2CO_3 THF/80 °C/22 h	**4c**: 79[b]	$CoCl_2$/2,6-lutidine/THF 70 °C/14 h	**5c**: 95[b]

[a] Yields represent isolated yields of >95% purity as determined by ^1H NMR.
[b] Products existed as a mixture of two atropisomers (α,α- and α,β-isomers) in approximately equal amounts.

In line with the recent findings by us[13d] and others,[15] cobalt(II) porphyrins **3a**–**f** and **5a**–**c** were found to be effective catalysts for cyclopropanation of alkenes as demonstrated with the reaction of styrene with EDA (Scheme 2 and Table 2).[16] Using 2 mol% catalysts, the cyclopropanation reactions could be successfully performed with styrene as the limiting reagent and required no slow-addition of EDA. The practical one-pot protocol could effectively operate at different temperatures (80, 23 or 0 °C). In all these cases, the desired cyclopropanes were produced in high to excellent yields with moderate trans-selectivities but low enantioselectivities (Table 2). Although all the enantioselectivities were low, statistically significant differences were observed for different *meso*-chiral porphyrins. For example, the secondary cyclic alcohol-substituted cobalt(II) porphyrins **3a**–**d** provide relatively higher enantioselectivities than the aromatic alcohol-substituted cobalt(II) porphyrin **3e** (Table 2, entries 1–9). While the R-(+)-BINOL-substituted cobalt(II) porphyrin **3f** gave the lowest enantioselectivities (Table 2, entries 10–11), the enantioselectivities of the amide-substituted cobalt(II) porphyrins **5a**–**c** were in-between others (Table 2, entries 12–17). As we reported previously,[12] cobalt(II) complexes of the D_2-symmetric *ortho*-chiral porphyrins proved as efficient catalysts for cyclopropanation with both high enantioselectivity and high diastereoselectivity. The favorable orientation and suitable rigidity of the chiral elements in the D_2-symmetric *ortho*-chiral porphyrins are attributed due to their high selectivities.[12] Similarly, the orientation and flexibility of the chiral appendages are likely responsible for the low enantioselectivities observed for these *meso*-chiral porphyrins. For complexes **3f** and **5a**–**c**, the existence of atropisomers certainly caused additional problems for obtaining high enantioselectivity.

In summary, the results demonstrated that *meso*-bromoporphyrins are a class of versatile synthons for effective construction of *meso*-chiral porphyrins via palladium-mediated C–N and C–O bond formation reactions. Considering the ready availability of large number of chiral alcohols, amines and amides, the new approach will allow the synthesis of different types of *meso*-chiral porphyrins that could find broad applications. For the specific application in asymmetric catalysis, we are

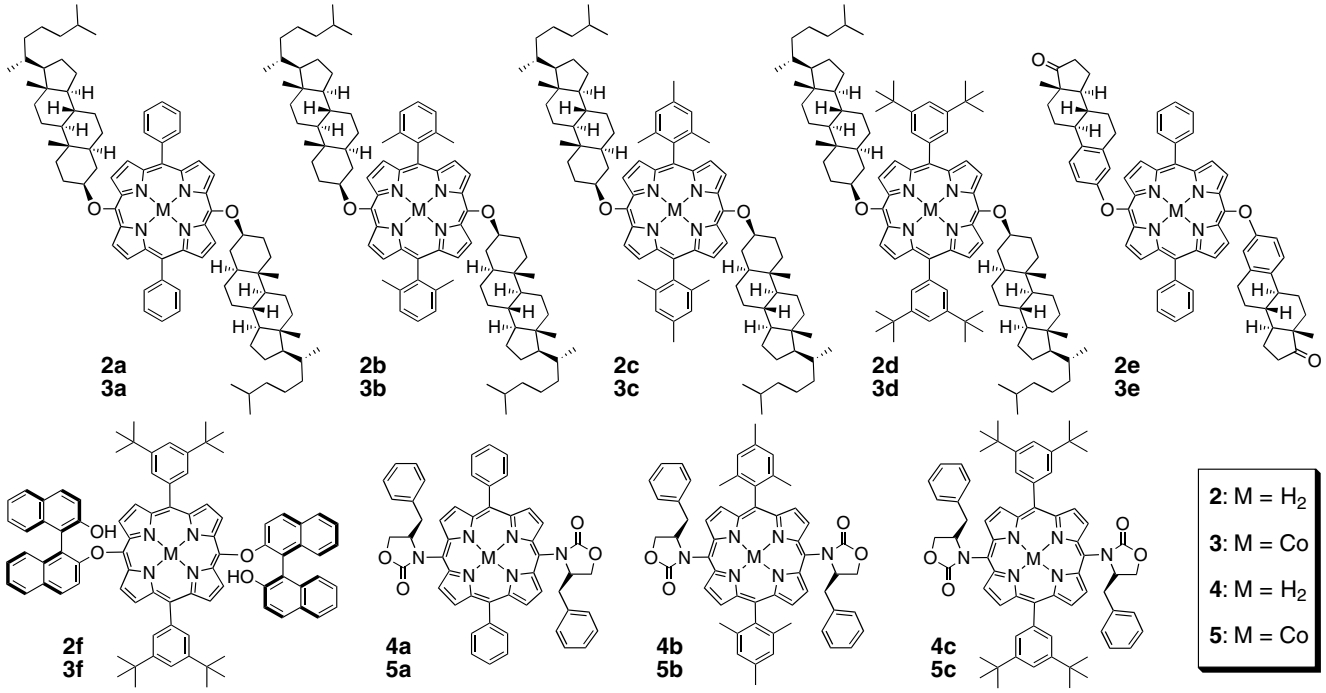


Figure 1. Cyclopropanation of styrene by cobalt complexes of *meso*-chiral porphyrins.

Table 2. Cyclopropanation of styrene with EDA catalyzed by cobalt complexes of *meso*-chiral porphyrins[a]

Entry	[co(por)][b]	Temp (°C)	Yield (%)[c]	cis:trans[c]	ee (%)[d]
1	**3a**	80	97	28:72	9(1)
2	**3a**	23	92	27:73	11(2)
3	**3a**	0	88	26:74	12(2)
4	**3b**	80	95	32:68	8(5)
5	**3c**	80	95	31:69	9(5)
6	**3d**	0	87	27:73	12(1)
7[e]	**3e**	80	99	32:68	1(1)
8	**3e**	23	98	30:70	4(1)
9[e]	**3e**	0	92	30:70	3(1)
10	**3f**	80	79	36:64	1(1)
11	**3f**	23	73	35:65	1(0)
12	**5a**	80	80	34:66	6(6)
13	**5a**	0	83	32:68	5(8)
14	**5b**	80	99	37:63	6(6)
15	**5c**	80	82	32:68	5(4)
16	**5c**	23	79	32:68	6(5)
17	**5c**	0	73	32:68	6(6)

[a] Reactions were carried out in toluene for 24 h under N_2 with 1.0 equiv of styrene, 1.2 equiv of EDA and 2 mol% [Co(por)]. Concentration: 0.5 mmol styrene/2 mL toluene.
[b] See Fig. 1 for structures.
[c] Determined by GC.
[d] Determined by chiral GC: trans (cis).
[e] Reaction time was 15 h.

currently in the process of designing and synthesizing new *meso*-chiral porphyrins that contain more rigid chiral appendages with desirable geometry and orientation for improving diastereoselectivity and enantioselectivity. This new generation of *meso*-chiral porphyrins should offer different electronic, steric and chiral environments from those of the *ortho*-chiral porphyrins that we described previously.[12]

Acknowledgement

We are grateful for financial support for this work from the UT Department of Chemistry, the UT Center of Excellence for Structural Biology (CESB), Oak Ridge Associated Universities (ORAU) for a Ralph E. Powe Junior Faculty Enhancement Award, Hereditary Disease Foundation (HDF) and High Q Foundation (HQF).

Supplementary data

Analytical data and ^{1}H NMR spectra of all new compounds (PDF). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.05.089.

References and notes

1. (a) Tani, F.; Matsu-ura, M.; Nakayama, S.; Naruta, Y. *Coord. Chem. Rev.* **2002**, *226*, 219; (b) Simonneaux, G.; Le Maux, P. *Coord. Chem. Rev.* **2002**, *228*, 43; (c) Collman, J. P.; Wang, Z. *Chemtracts* **1999**, *12*, 229; (d) Rose, E.; Lecas, A.; Quelquejeu, M.; Kossanyi, A.; Boitrel, B. *Coord. Chem. Rev.* **1998**, *178–180*, 1407; (e) Boschi, T. In *Metalloporphyrins Catalyzed Oxidations*; Montanari, F., Casella, L., Eds.; Kluwer Academic: Boston, 1994, pp 239–267; (f) Naruta, Y. In *Metalloporphyrins in Catalytic Oxidations*; Sheldon, R. A., Ed.; Marcel Dekker: New York, 1994, pp 241–259.
2. (a) Marchon, J.-C. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2003; Vol. 11, pp 75–132; (b) Rose, E.; Quelquejeu, M.; Pandian, R. P.; Lecas-Nawrocka, A.; Vilar, A.; Ricart, G.; Collman, J. P.; Wang, Z.; Straumanis, A. *Polyhedron* **2000**, *19*, 581; (c) Collman, J. P.;

Zhang, X. M.; Lee, V. J.; Uffelman, E. S.; Brauman, J. I. *Science* **1993**, *261*, 1404.
3. (a) Collman, J. P.; Gagne, R. R.; Reed, C. A.; Halbert, T. R.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 1427; (b) Leondiadis, L.; Momenteau, M. *J. Org. Chem.* **1989**, *54*, 6135; (c) Rose, E.; Quelquejeu, M.; Pochet, C.; Julien, N.; Kossanyi, A.; Hamon, L. *J. Org. Chem.* **1993**, *58*, 5030; (d) Rose, E.; Cardon-Pilotaz, A.; Quelquejeu, M.; Bernard, N.; Kossanyi, A.; Desmazieres, B. *J. Org. Chem.* **1995**, *60*, 3919; (e) Rose, E.; Ren, Q.-Z.; Andrioletti, B. *Chem. Eur. J.* **2004**, *10*, 224.
4. Rose, E.; Kossanyi, A.; Quelquejeu, M.; Soleilhavoup, M.; Duwavran, F.; Bernard, N.; Lecas, A. *J. Am. Chem. Soc.* **1996**, *118*, 1567.
5. (a) Collman, J. P.; Lee, V. J.; Zhang, X. M. *Inorg. Synth.* **1997**, *31*, 117; (b) Tsuchida, E.; Komatsu, T.; Hasegawa, E.; Nishide, H. *J. Chem. Soc., Dalton Trans.* **1990**, 2713.
6. Nakagawa, H.; Nagano, T.; Higuchi, T. *Org. Lett.* **2001**, *3*, 1805.
7. (a) Prim, D.; Andrioletti, B.; Rose-Munch, F.; Rose, E.; Couty, F. *Tetrahedron* **2004**, *60*, 3325; (b) Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5400; (c) Prim, D.; Campagne, J. M.; Joseph, D.; Andrioletti, B. *Tetrahedron* **2002**, *58*, 2041; (d) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131; (e) Hartwig, J. F. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley-Interscience: New York, 2002, p 1051; (f) Auffrant, A.; Prim, D.; Rose-Munch, F.; Rose, E.; Vaissermann, J. *Organometallics* **2002**, *21*, 3500; (g) Yang, B. H.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125; (h) Wolfe, J. P.; Wagaw, S.; Marcoux, J. F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805; (i) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2047; (j) Hartwig, J. F. *Synlett* **1997**, 329.
8. (a) Chen, Y.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 4432; (b) Gao, G.-Y.; Chen, Y.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 6215; (c) Gao, G.-Y.; Colvin, A. J.; Chen, Y.; Zhang, X. P. *Org. Lett.* **2003**, *5*, 3261; (d) Gao, G.-Y.; Chen, Y.; Zhang, X. P. *Org. Lett.* **2004**, *6*, 1837; (e) Gao, G.-Y.; Colvin, A. J.; Chen, Y.; Zhang, X. P. *J. Org. Chem.* **2004**, *69*, 8886.
9. (a) For contributions from others on porphyrin synthesis via palladium-catalyzed C–N bond formation, see: Khan, M. M.; Ali, H.; van Lier, J. E. *Tetrahedron Lett.* **2001**, *42*, 1615; (b) Takanami, T.; Hayashi, M.; Hino, F.; Suda, K. *Tetrahedron Lett.* **2003**, *44*, 7353.
10. For a review on porphyrin synthesis via metal-mediated C–C bond formation, see: Sharman, W. M.; Van Lier, J. E. *J. Porphyrins Phthalocyanines* **2000**, *4*, 441–453.
11. (a) For selective examples that applied Suzuki and Stille cross-coupling reactions for porphyrin synthesis via C–C bond formation, see: DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 2513; (b) DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Org. Chem.* **1993**, *58*, 5983; (c) Hyslop, A. G.; Kellett, M. A.; Iovine, P. M.; Therien, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 12676; (d) Liu, C.-J.; Yu, W.-Y.; Peng, S.-M.; Mak, T. C. W.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1998**, 1805; (e) Shi, X.; Amin, R.; Liebeskind, L. S. *J. Org. Chem.* **2000**, *65*, 1650; (f) Shanmugathasan, S.; Johnson, C. K.; Edwards, C.; Matthews, E. K.; Dolphin, D.; Boyle, R. W. *J. Porphyrins Phthalocyanines* **2000**, *4*, 228; (g) Iovine, P. M.; Kellett, M. A.; Redmore, N. P.; Therien, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 8717; (h) Deng, Y.; Chang, C. K.; Nocera, D. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1066; (i) Chng, L. L.; Chang, C. J.; Nocera, D. G. *J. Org. Chem.* **2003**, *68*, 4075.
12. Chen, Y.; Fields, K. B.; Zhang, X. P. *J. Am. Chem. Soc.* **2004**, *126*, 14718.
13. (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) Vyas, R.; Gao, G.-Y.; Harden, J. D.; Zhang, X. P. *Org. Lett.* **2004**, *6*, 1907.
14. The same or similar R_f values were obtained for two atropisomers using different solvent systems.
15. Penoni, A.; Wanke, R.; Tollari, S.; Gallo, E.; Musella, D.; Ragaini, F.; Demartin, F.; Cenini, S. *Eur. J. Inorg. Chem.* **2003**, 1452.
16. (a) For selected recent examples on metal-catalyzed cyclopropanation, see: Ferrand, Y.; Le Maux, P.; Simonneaux, G. *Org. Lett.* **2004**, *6*, 3211; (b) Berkessel, A.; Kaiser, P.; Lex, J. *Chem. Eur. J.* **2003**, *9*, 4746; (c) Zhang, J. L.; Chan, P. W. H.; Che, C. M. *Tetrahedron Lett.* **2003**, *44*, 8733; (d) Che, C.-M.; Huang, J.-S. *Coord. Chem. Rev.* **2002**, *231*, 151; (e) Du, G.; Andrioletti, B.; Rose, E.; Woo, L. K. *Organometallics* **2002**, *21*, 4490; (f) Niimi, T.; Uchida, T.; Irie, R.; Katsuki, T. *Adv. Synth. Catal.* **2001**, *343*, 79; (g) Ikeno, T.; Sato, M.; Sekino, H.; Nishizuka, A.; Yamada, T. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2139; (h) Gross, Z.; Galili, N.; Simkhovich, L. *Tetrahedron Lett.* **1999**, *40*, 1571; (i) Bartley, D. W.; Kodadek, T. *J. Am. Chem. Soc.* **1993**, *115*, 1656.