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Intramolecular C−N Bond Formation Reactions Catalyzed by Ruthenium Porphyrins: Amidation of Sulfamate Esters and Aziridination of Unsaturated Sulfonamides

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Ruthenium porphyrins [Ru(F_{20}-TPP)(CO)] (F_{20}-TPP = 5,10,15,20-tetrakis(pentafluorophenyl)-porphyrinato dianion) and [Ru(Por*)(CO)] (Por* = 5,10,15,20-tetrakis[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl]porphyrinato dianion) catalyzed intramolecular amidation of sulfamate esters *p*-X-$C_6H_4(CH_2)_2OSO_2NH_2$ (X = Cl, Me, MeO), $XC_6H_4(CH_2)_3OSO_2NH_2$ (X = *p*-F, *p*-MeO, *m*-MeO), and $Ar(CH_2)_2OSO_2NH_2$ (Ar = naphthalen-1-yl, naphthalen-2-yl) with PhI-$(OAc)_2$ to afford the corresponding cyclic sulfamidates in up to 89% yield with up to 100% substrate conversion; up to 88% ee was attained in the asymmetric intramolecular amidation catalyzed by [Ru(Por*)(CO)]. Reaction of [Ru(F_{20}-TPP)(CO)] with PhI=$NSO_2OCH_2CCl_3$ (prepared by treating the sulfamate ester $Cl_3CCH_2OSO_2NH_2$ with PhI$(OAc)_2$) afforded a bis(imido)ruthenium(VI) porphyrin, [Ru^{VI}(F_{20}-TPP)($NSO_2OCH_2CCl_3$)$_2$], in 60% yield. A mechanism involving reactive imido ruthenium porphyrin intermediate was proposed for the ruthenium porphyrin-catalyzed intramolecular amidation of sulfamate esters. Complex [Ru(F_{20}-TPP)(CO)] is an active catalyst for intramolecular aziridination of unsaturated sulfonamides with PhI$(OAc)_2$, producing corresponding bicyclic aziridines in up to 87% yield with up to 100% substrate conversion and high turnover (up to 2014).

Introduction

Intramolecular C−N bond formation reactions mediated by transition-metal complexes provide a convenient access to cyclic amines/amides or bicyclic aziridines. An important type of such reactions involves iodine(III) compounds PhI=NSO_2R, PhI=O, or commercially available PhI$(OAc)_2$ and possibly occurs via intramolecular nitrogen atom transfer from putative metal imido (or nitrene) species to saturated C−H bonds or alkene double bonds.[1−5] This hitherto includes the intramolecular amidation of sulfonamides,[1,2a] carbamates,[4a] and sulfamate esters[4b,5a] and intramolecular aziridination of unsaturated sulfonamides[2b,3a−c,5b,c] and sulfamate esters[3d,4c] in the presence of manganese,[1] iron,[1] copper,[3] ruthenium,[5a] and dirhodium[2,4,5b,c] catalysts (routes I−VI in Scheme 1). The intramolecular amidation and aziridination reactions of sulfonamides were first studied by Breslow,[1] Müller,[2b] and co-workers, respectively, by preconversion of sulfonamide substrates into respective PhI=NSO_2R compounds through reaction with PhI$(OAc)_2$ (routes I and IV). Du Bois and co-workers[4a,b] realized direct intramolecular amidation with PhI$(OAc)_2$ by employing carbamate and sulfamate ester substrates and dirhodium catalysts (route II), like our earlier intermolecular PhI-$(OAc)_2$-amidation of sulfonamides catalyzed by ruthenium and manganese complexes.[6] Dodd and co-workers reported the intramolecular aziridination or amidation of unsaturated sulfonamides/sulfamate esters with

(1) Breslow, R.; Gellman, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 6728.
(2) (a) Müller, P. In *Advances in Catalytic Processes, Vol. 2, Asymmetric Catalysis*; Doyle, M. P., Ed.; JAI Press: Greenwich, 1997; p 113. (b) Müller, P.; Baud, C.; Jacquier, Y. *Can. J. Chem.* **1998**, *76*, 738. (c) Müller, P.; Fruit, C. *Chem. Rev.* **2003**, *103*, 2905.
(3) (a) Dauban, P.; Dodd, R. H. *Org. Lett.* **2000**, *2*, 2327. (b) Dauban, P.; Dodd, R. H. *Tetrahedron Lett.* **2001**, *42*, 1037. (c) Dauban, P.; Sanière, L.; Tarrade, A.; Dodd, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 7707. (d) Duran, F.; Leman, L.; Ghini, A.; Burton, G.; Dauban, P.; Dodd, R. H. *Org. Lett.* **2002**, *4*, 2481. (e) Dauban, P.; Dodd, R. H. *Synlett* **2003**, 1571.
(4) (a) Espino, C. G.; Du Bois, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 598. (b) Espino, C. G.; Wehn, P. M.; Chow, J.; Du Bois, J. *J. Am. Chem. Soc.* **2001**, *123*, 6935. (c) Guthikonda, K.; Du Bois, J. *J. Am. Chem. Soc.* **2002**, *124*, 13672.
(5) (a) Liang, J.-L.; Yuan, S.-X.; Huang, J.-S.; Yu, W.-Y.; Che, C.-M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3465. (b) Liang, J.-L.; Yuan, S.-X.; Chan, P. W. H.; Che, C.-M. *Org. Lett.* **2002**, *4*, 4507. (c) Liang, J.-L.; Yuan, S.-X.; Chan, P. W. H.; Che, C.-M. *Tetrahedron Lett.* **2003**, *44*, 5917.
(6) (a) Yu, X.-Q.; Huang, J.-S.; Zhou, X.-G.; Che, C.-M. *Org. Lett.* **2000**, *2*, 2233. (b) Au, S.-M.; Huang, J.-S.; Che, C.-M.; Yu, W.-Y. *J. Org. Chem.* **2000**, *65*, 7858.

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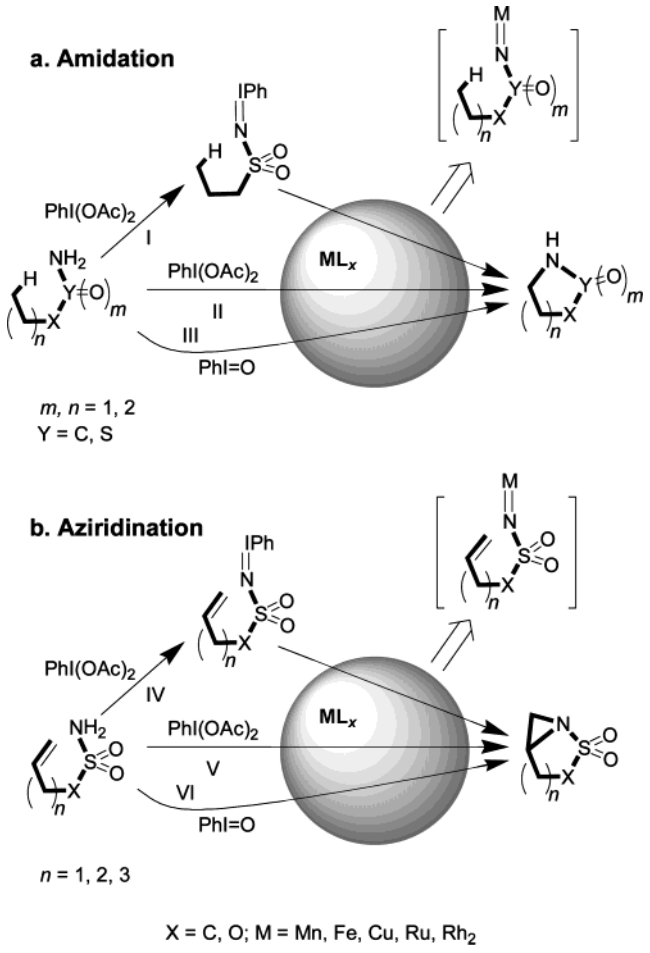
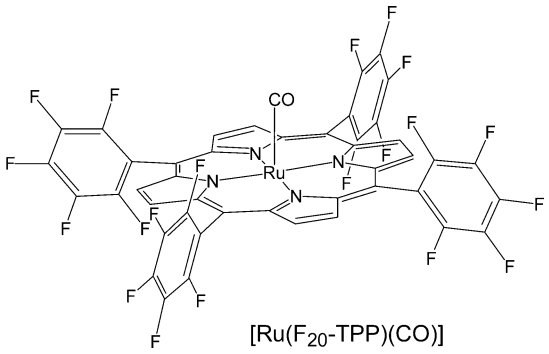
SCHEME 1. Schematic Diagram Depicting the Metal-Catalyzed Intramolecular Amidation and Aziridination with Iodine(III) Compounds (Only the Key Moiety of the Substrate Is Shown)



PhI═O in the presence of copper catalysts (routes III and VI).[3b−d] Recently, we communicated highly diastereo- and enantioselective intramolecular $PhI(OAc)_2$-amidation of sulfamate esters catalyzed by ruthenium porphyrins[5a] (route II) and intramolecular $PhI(OAc)_2$-aziridination of unsaturated sulfonamides catalyzed by dirhodium complexes[5b,c] (route V). We now report here extensive investigations on the ruthenium porphyrin-catalyzed intramolecular $PhI(OAc)_2$-amidation of sulfamate esters and the first intramolecular $PhI(OAc)_2$-aziridination of unsaturated sulfonamides catalyzed by a ruthenium porphyrin (route V); the latter is so far the only example of metalloporphyrin-catalyzed intramolecular aziridination reactions.

Results and Discussion

Intramolecular Amidation of Sulfamate Esters Catalyzed by Achiral Ruthenium Porphyrins. As shown in Scheme 1, intramolecular amidation of sulfamate esters (X/Y/*m* = O/S/2 in Scheme 1a) with $PhI(OAc)_2$ in the presence of metal catalysts affords cyclic sulfamidates, which are versatile reagents in organic synthesis[4b,7] (for example, as useful precursors for preparing amino acids,[7a,d,e] carbohydrates,[7b] and glycopeptides[7f]). Our previous work[5a] on ruthenium porphyrin-catalyzed intramolecular amidation of sulfamate esters was initially conducted for the reaction of sulfamate indan-2-yl ester (**1a**) with $PhI(OAc)_2$ in dichloromethane containing 1.5 mol % of [Ru(F_{20}-TPP)(CO)]. This reaction gave the corresponding cyclic sulfamidate (**2a**) in 52% yield (entry 1 in Table 1) with virtually complete *cis*-selectivity. Subsequent examination of the reactions between **1a** and $PhI(OAc)_2$ in the presence of [Ru(F_{20}-TPP)(CO)] under various conditions (see entries 1−12 in Table 1) revealed that the [Ru(F_{20}-TPP)(CO)]-catalyzed amidation of **1a** would best be performed in dichloromethane at 40 °C in the presence of additive Al_2O_3. Under these conditions, other



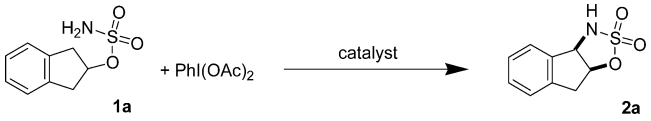
ruthenium porphyrins, [Ru(TPP)(CO)], [Ru(TMP)(CO)], and [Ru(OEP)(CO)], could also catalyze the intramolecular amidation of **1a** but gave **2a** in substantially lower yields (cf. entries 10, 13−15 in Table 1). Non-porphyrin ruthenium complexes (1*R*,2*R*)-[Ru(Br_4salen)(PPh_3)$_2$] and [Ru(pybox-ip)Cl_2(CH_2═CH_2)] and the iron and manganese porphyrins [Fe(F_{20}-TPP)Cl] and [Mn(F_{20}-TPP)Cl] were also examined and found to be inferior to [Ru(F_{20}-TPP)(CO)] as a catalyst for this intramolecular amidation process (cf. entries 10, 16−19 in Table 1). The intramolecular $PhI(OAc)_2$-amidation of a sulfamate ester catalyzed by [Ru(F_{20}-TPP)(CO)] has been extended to substrates **1b**−**f** (Chart 1) at a catalyst/substrate/$PhI(OAc)_2$/Al_2O_3 molar ratio of 0.015:1:2:2.5, affording cyclic sulfamidates **2b**−**f** in 56−88% yields with virtually complete *cis*-selectivity for **2e**,**f**.[5a]

To further expand the scope of the [Ru(F_{20}-TPP)(CO)]-catalyzed intramolecular amidation and inspect the effect of substituents, we prepared a series of new sulfamate esters **1g**−**o** and examined their reactions with $PhI(OAc)_2$ in the presence of [Ru(F_{20}-TPP)(CO)] under the same conditions as for **1b**−**f**. The results are summarized in Table 2.

It is evident that sulfamate esters **1g**−**n** are good substrates for the [Ru(F_{20}-TPP)(CO)]-catalyzed intramolecular amidation. These catalytic intramolecular C−N bond formation reactions produced cyclic sulfami-

(7) (a) Baldwin, J. E.; Spivey, A. C.; Schofield, C. J. *Tetrahedron: Asymmetry* **1990**, *1*, 881. (b) Aguilera, B.; Fernández-Mayotalas, A. *Chem. Commun.* **1996**, 127. (c) Corral, C.; Lissavetzky, J.; Manzanares, I.; Darias, V.; Expósito-Orta, M. A.; Conde, J. A. M.; Sánchez-Mateo, C. C. *Bioorg. Med. Chem.* **1999**, *7*, 1349. (d) Wei, L.; Lubell, W. D. *Can. J. Chem.* **2001**, *79*, 94. (e) Nicolaou, K. C.; Huang, X.; Snyder, S. A.; Rao, P. B.; Bella, M.; Reddy, M. V. *Angew. Chem., Int. Ed.* **2002**, *41*, 834. (f) Cohen, S. B.; Halcomb, R. L. *J. Am. Chem. Soc.* **2002**, *124*, 2534. (g) Posakony, J. J.; Grierson, J. R.; Tewson, T. J. *J. Org. Chem.* **2002**, *67*, 5164. (h) Williams, A. J.; Chakthong, S.; Gray, D.; Lawrence, R. M.; Gallagher, T. *Org. Lett.* **2003**, *5*, 811. (i) Meléndez, R. E.; Lubell, W. D. *Tetrahedron* **2003**, *59*, 2581.

TABLE 1. Intramolecular Amidation of Sulfamate Indan-2-yl Ester (1a) with $PhI(OAc)_2$ Catalyzed by Ruthenium Porphyrins and Related Metal Complexes[a]

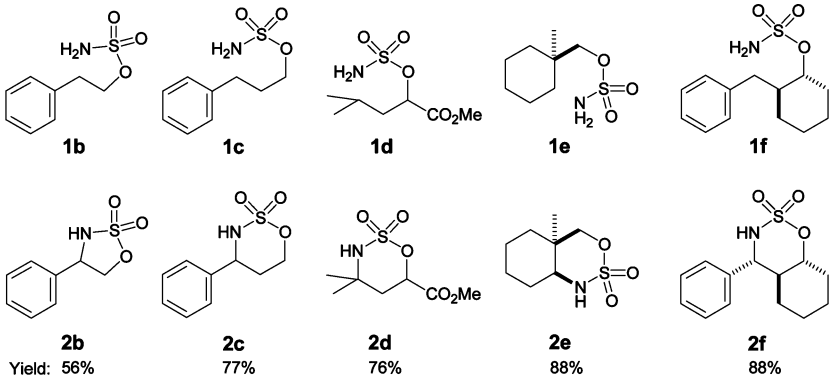


1a **2a**

entry	catalyst	additive	solvent	yield[b] (%)
1	[Ru(F_{20}-TPP)(CO)]		CH_2Cl_2	52
2	[Ru(F_{20}-TPP)(CO)]	MgO	CH_2Cl_2	58
3	[Ru(F_{20}-TPP)(CO)]	MgO	CH_3CN	11
4	[Ru(F_{20}-TPP)(CO)]	MgO	C_6H_6	58
5	[Ru(F_{20}-TPP)(CO)]	MgO	$ClCH_2CH_2Cl$	37
6	[Ru(F_{20}-TPP)(CO)]	ZnO	CH_2Cl_2	58
7	[Ru(F_{20}-TPP)(CO)]	K_2CO_3	CH_2Cl_2	30
8	[Ru(F_{20}-TPP)(CO)]	NaOH	CH_2Cl_2	10
9	[Ru(F_{20}-TPP)(CO)]	2,6-Cl_2py	CH_2Cl_2	30
10	[Ru(F_{20}-TPP)(CO)]	Al_2O_3	CH_2Cl_2	61
11[c]	[Ru(F_{20}-TPP)(CO)]	Al_2O_3	CH_2Cl_2	66
12[d]	[Ru(F_{20}-TPP)(CO)]	Al_2O_3	CH_2Cl_2	34
13	[Ru(TPP)(CO)][e]	Al_2O_3	CH_2Cl_2	30
14	[Ru(TMP)(CO)][f]	Al_2O_3	CH_2Cl_2	42
15	[Ru(OEP)(CO)][g]	Al_2O_3	CH_2Cl_2	12
16	[Mn(F_{20}-TPP)Cl]	Al_2O_3	CH_2Cl_2	40
17	[Fe(F_{20}-TPP)Cl]	Al_2O_3	CH_2Cl_2	34
18[h]	(1*R*,2*R*)-[Ru(Br_4salen)(PPh_3)$_2$][i]	Al_2O_3	CH_2Cl_2	10
19[j]	[Ru(pybox-ip)Cl_2(CH_2=CH_2)][k]	Al_2O_3	CH_2Cl_2	33

[a] All reactions were performed at 40 °C for 2 h with a catalyst/**1a**/$PhI(OAc)_2$/additive molar ratio of 0.015:1:2:2.5 (unless otherwise denoted). [b] Isolated yield based on the amount of starting **1a**. [c] 5 mol % of **1** was added. [d] At room temperature. [e] TPP = 5,10,15,20-tetraphenylporphyrinato dianion. [f] TMP = 5,10,15,20-tetramesitylporphyrinato dianion. [g] OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion. [h] 12.5 mol % of catalyst was used, with **2a** obtained in 8% ee. [i] Br_4salen = 1,2-bis(3,5-dibromo-2-hydroxybenzylideneamino)-cyclohexane dianion. [j] 12.5 mol % of catalyst was used, with **2a** obtained in 9% ee. [k] pybox-ip = bis(2-oxazolin-2-yl)pyridine.

CHART 1



1b **1c** **1d** **1e** **1f**

2b Yield: 56% **2c** 77% **2d** 76% **2e** 88% **2f** 88%

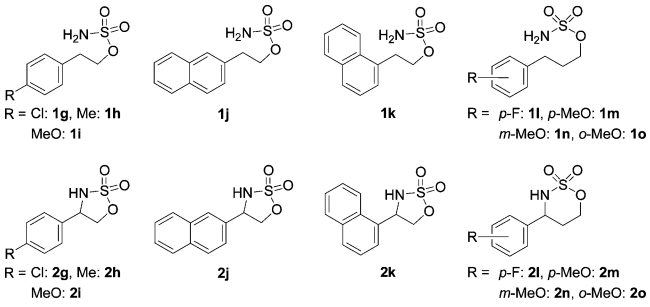
dates **2g**−**n** in 63−87% yields, with a regioselectivity similar to that observed for previously reported analogues.[4b,5a] The intramolecular amidation of **1h**,**i**,**l**−**n** proceeded with excellent substrate conversions of 92−100%.

Inspection of entries 7−9 in Table 2 reveals that the position of the substituent on sulfamate ester substrate can affect the efficiency of the intramolecular amidation process. On going from *p*-MeO-$C_6H_4(CH_2)_3OSO_2NH_2$ (**1m**) to *m*-MeO-$C_6H_4(CH_2)_3OSO_2NH_2$ (**1n**), the yield of the resulting cyclic sulfamidate drops from 85% to 63% (entries 7 and 8). Strikingly, for *o*-MeO-$C_6H_4(CH_2)_3OSO_2NH_2$ (**1o**), no cyclic sulfamidate **2o** was detected in the reaction mixture (the substrate largely remained unreacted). We attribute such a decrease in intramolecular amidation efficiency along **1m** → **1n** → **1o** to the increase in steric interaction in the active amidation species (see below).

Competitive intramolecular amidation of *p*-X-$C_6H_4(CH_2)_2OSO_2NH_2$ (X = Br, Cl (**1g**), H (**1b**), Me (**1h**), and OMe (**1i**)) catalyzed by [Ru(F_{20}-TPP)(CO)] (see the Experimental Section) gave $\log(k_X/k_H)$ values of 0.137 (X = MeO), 0.036 (X = Me), −0.040 (X = Br), and −0.041 (X = Cl), indicating that electron-donating substituents accelerate, whereas electron-withdrawing substituents slow, the intramolecular amidation reactions. Fitting the $\log(k_X/k_H)$ values with Hammett constants σ_p^+ resulted in a linearity with $R = 0.99$ and $\rho = -0.19 \pm 0.01$. The $\log(k_X/k_H)$ vs σ_p^+ plot is shown in Figure 1.

Asymmetric Intramolecular Amidation of Sulfamate Esters Catalyzed by Chiral Ruthenium Porphyrin. Metal-catalyzed enantioselective intramolecular amidation of sulfamate esters is an attractive method for the synthesis of optically active cyclic sulfamidates. Du Bois and co-workers reported the synthesis of optically pure cyclic sulfamidates from optically pure sulfamate

TABLE 2. Intramolecular Amidation of Sulfamate Esters 1g−o with $PhI(OAc)_2$ in the Presence of Al_2O_3 Catalyzed by [Ru(F_{20}-TPP)(CO)][a]



entry	substrate	product	conversion (%)	yield[b] (%)
1	**1g**	**2g**	88	69
2	**1h**	**2h**	99	68
3	**1i**	**2i**	100	76
4	**1j**	**2j**	70	87
5	**1k**	**2k**	81	68
6	**1l**	**2l**	100	81
7	**1m**	**2m**	100	85
8	**1n**	**2n**	92	63
9	**1o**	**2o**	10	not detectable

[a] Reaction conditions: CH_2Cl_2, 40 °C, 2 h, catalyst/substrate/$PhI(OAc)_2/Al_2O_3$ molar ratio = 0.015:1:2:2.5. [b] Isolated yield based on the amount of consumed substrate.

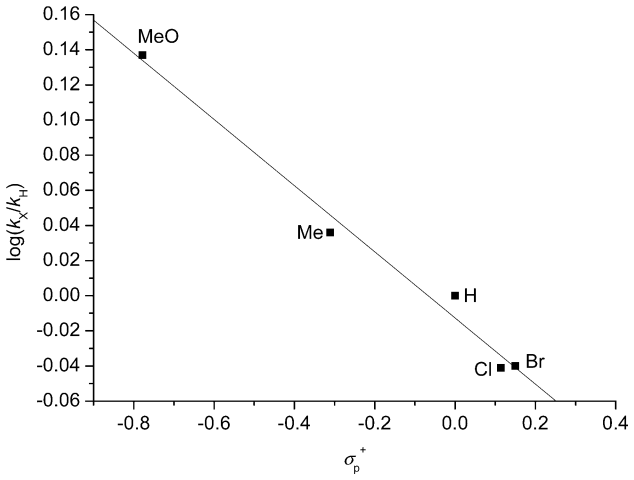


FIGURE 1. $\log(k_X/k_H)$ vs σ_p^+ plot for the [Ru(F_{20}-TPP)(CO)]-catalyzed intramolecular amidation of *para*-substituted sulfamate esters *p*-X-$C_6H_4(CH_2)_2OSO_2NH_2$ with $PhI(OAc)_2$.

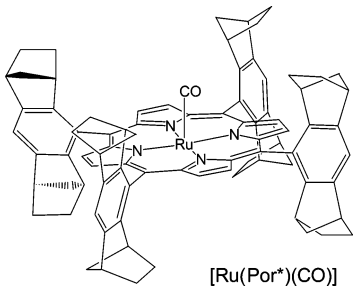
esters through dirhodium-catalyzed intramolecular amidation with $PhI(OAc)_2$,[4b] which has found great utility in the synthesis of natural products manzacidins A and C.[8] Our previous work[5a] realized the first metal-catalyzed enantioselective intramolecular amidation of *prochiral* sulfamate esters by employing chiral ruthenium porphyrin [Ru(Por*)(CO)] as a catalyst. The [Ru(Por*)(CO)]-catalyzed $PhI(OAc)_2$-intramolecular amidation of **1a−c** and *p*-X-$C_6H_4(CH_2)_2OSO_2NH_2$ (X = F, Br) resulted in highest enantiocontrol in benzene at 5 °C with a catalyst/substrate/$PhI(OAc)_2/Al_2O_3$ molar ratio of 0.1:1:1.4:2.5, affording, within 8 h, the corresponding optically active cyclic sulfamidates in 20−48% yields and 82−87% ee, with virtually complete *cis*-selectivity for **1a**.[5a] These ee values are much higher than that observed for the chiral non-porphyrin ruthenium catalyst (1*R*,2*R*)-[Ru(Br_4salen)-(PPh_3)$_2$] (<10%, see entry 18 in Table 1).

(8) Wehn, P. M.; Du Bois, J. *J. Am. Chem. Soc.* **2002**, *124*, 12950.

TABLE 3. Asymmetric Intramolecular Amidation of Sulfamate Esters with $PhI(OAc)_2$ in the Presence of Al_2O_3 Catalyzed by [Ru(Por*)(CO)][a]

entry	substrate	product	conversion (%)	yield[b] (%)	ee[c] (%)
1	**1f**	**2f**	79	82	87
2	**1g**	**2g**	60	72	77
3	**1h**	**2h**	68	89	83
4	**1i**	**2i**	91	75	88[d]
5	**1j**	**2j**	60	73	86
6	**1k**	**2k**	58	74	83[d]
7	**1l**	**2l**	58	78	86
8	**1m**	**2m**	65	82	85
9	**1n**	**2n**	59	70	84
10	**1o**	**2o**	<5	not detectable	

[a] Reaction conditions: benzene, 5 °C, 8 h, catalyst/substrate/$PhI(OAc)_2/Al_2O_3$ molar ratio = 0.1:1:1.4:2.5. [b] Isolated yield based on the amount of consumed substrate. [c] Determined by HPLC using chiral OD column. [d] Determined by HPLC using chiral OJ column.



We have now extended the [Ru(Por*)(CO)]-catalyzed asymmetric intramolecular $PhI(OAc)_2$-amidation of sulfamate ester to substrates **1f−o**. Again, **1o** is an unreactive substrate, as in the intramolecular amidation catalyzed by [Ru(F_{20}-TPP)(CO)] described above. The reactions of **1f−n** with $PhI(OAc)_2$ in the presence of [Ru(Por*)(CO)], under the same conditions as for substrates **1a−c**, gave respective optically active cyclic sulfamidates **2f−n** in 70−89% yields and 77−88% ee, with virtually complete *cis*-selectivity for **1f** (see Table 3).

Note that [Ru(Por*)(CO)] is a less active catalyst than [Ru(F_{20}-TPP)(CO)] for the intramolecular amidation of sulfamate esters.[5a] Considerably higher catalyst loading (10 vs 1.5 mol %) was required to obtain the cyclic sulfamidates in significant yields.

The ee values observed for substrate series *p*-X-$C_6H_4(CH_2)_2OSO_2NH_2$ (X = Br,[5a] H: **1b**,[5a] F,[5a] Me: **1h**, OMe: **1i**; ee = 83−88%) or *p*-X-$C_6H_4(CH_2)_3OSO_2NH_2$ (X = H: **1c**,[5a] F: **1l**, OMe: **1m**; ee = 84−86%) are similar, indicating that these para-substituents have insignificant or little effect on the enantioselectivity of the intramolecular amidation reactions. As a matter of fact, all the optically active cyclic sulfamidates **2f−n** in Table 3 except **2g** were obtained with similar ee values (83−88%). The highest enantioselectivity (88% ee) attained in this work is for the intramolecular amidation of **1i** (entry 4 in Table 3), which, to our knowledge, is also the highest enantiocontrol so far achieved for metal-catalyzed asymmetric intramolecular amidation of saturated C−H bonds utilizing iodine(III) compounds.

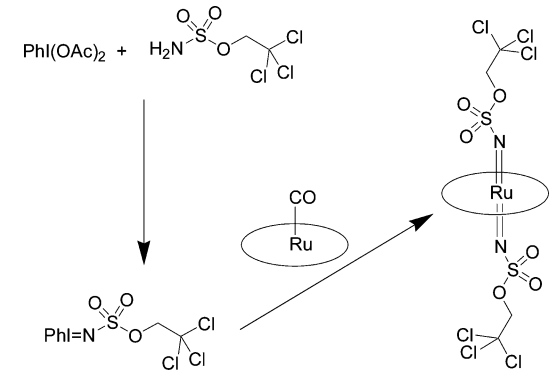
On the Mechanism of Intramolecular Amidation of Sulfamate Esters Catalyzed by Ruthenium Porphyrins. Although metal-catalyzed intramolecular C−N bond formation reactions depicted in Scheme 1 are usually proposed to involve metal imido (or nitrene) intermediates (like their intermolecular analogues[9]), there has been no report in which a reactive metal imido (or nitrene) species is isolated or directly observed for such catalytic intramolecular reactions.

The intramolecular $PhI(OAc)_2$-amidation of sulfamate esters $ROSO_2NH_2$ catalyzed by metal complexes might involve in situ generation of $PhI{=}NSO_2OR$, since the reactions between $PhI(OAc)_2$ and RSO_2NH_2 are well documented as a general method for preparation of stable $PhI{=}NSO_2R$ compounds.[10] Previously, we isolated $PhI{=}NSO_2O$-indan-2-yl by treating $PhI(OAc)_2$ with sulfamate ester **1a**.[5a] We also examined the intramolecular amidation of $PhI{=}NSO_2O$-indan-2-yl in the presence of catalyst [Ru(Por*)(CO)], which gave optically active cyclic sulfamidate **2a** in comparable yield and ee to those obtained for the asymmetric intramolecular amidation of **1a** with $PhI(OAc)_2$ catalyzed by the same ruthenium porphyrin.[5a]

We speculate that reaction of the in situ formed $PhI{=}NSO_2OR$ with [Ru(F_{20}-TPP)(CO)] and [Ru(Por*)(CO)] would afford the bis(imido)ruthenium(VI) species [Ru^{VI}(Por)$(NSO_2OR)_2$] (Por = F_{20}-TPP, Por*), like the reactions between [Ru(Por)(CO)] (Por = TPP, OEP, Por*, etc.) and $PhI{=}NSO_2$-*p*-$C_6H_4CH_3$ to give isolable [Ru^{VI}(Por)$(NSO_2$-*p*-$C_6H_4CH_3)_2$] in previous works.[9e,h] However, attempts to isolate [Ru^{VI}(F_{20}-TPP)$(NSO_2OR)_2$] and [Ru^{VI}(Por*)$(NSO_2OR)_2$] from the foregoing [Ru(F_{20}-TPP)(CO)]- and [Ru(Por*)(CO)]-catalyzed intramolecular amidation of **1a**−**n** were not successful. This could be due to the presence of reactive β- or γ-C−H bonds in the corresponding imido groups, which cause degradation of the imido species through, for example, intramolecular amidation reactions.

Thus, we prepared $PhI{=}NSO_2OCH_2CCl_3$ from reaction of $PhI(OAc)_2$ with the sulfamate ester $Cl_3CCH_2OSO_2NH_2$. Interestingly, subsequent treatment of $PhI{=}NSO_2OCH_2CCl_3$ with [Ru(F_{20}-TPP)(CO)] according to a procedure similar to that for preparation of [Ru^{VI}(TPP)$(NSO_2$-*p*-$C_6H_4CH_3)_2$][9e] did give [Ru^{VI}(F_{20}-TPP)$(NSO_2OCH_2CCl_3)_2$] (Scheme 2), which was isolated in 60% yield and identified by ^{1}H NMR, IR, UV−vis spectroscopy, and mass spectrometry, together with elemental analyses (see the Experimental Section). This is the first isolated metal imido complex derived from a sulfamate ester, whose formation signifies the intermediacy of bis(imido)ruthenium(VI) porphyrins in the intramolecular amidation of sulfamate esters with $PhI(OAc)_2$ catalyzed by ruthenium porphyrins.

SCHEME 2. Synthesis of Bis(imido)ruthenium(VI) Porphyrin [Ru^{VI}(F_{20}-TPP)$(NSO_2OCH_2CCl_3)_2$]



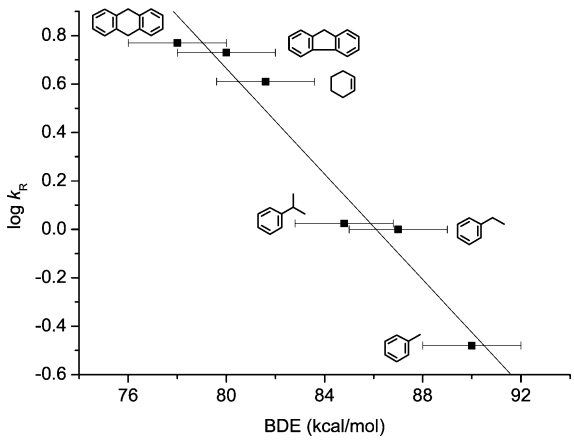


FIGURE 2. Correlation between relative amidation rates (log k_R) and C−H bond dissociation energies (BDE) for the intermolecular amidation of hydrocarbons with "$PhI(OAc)_2 + NH_2SO_2$-*p*-$C_6H_4NO_2$" catalyzed by [Ru(F_{20}-TPP)(CO)].

Our previous mechanistic studies[9e] on the intermolecular amidation of saturated C−H bonds by [Ru^{VI}(TPP)$(NSO_2$-*p*-$C_6H_4CH_3)_2$] supported a mechanism that features hydrogen atom abstraction by the bis(imido) complex to give a carboradical and an amido ruthenium porphyrin intermediate. Scavenging of the carboradical by the amido ruthenium porphyrin results in formation of the amidation product.

Examination of the intermolecular amidation of a variety of hydrocarbons, including 9,10-dihydroanthracene, fluorene, cyclohexene, cumene, ethylbenzene, and toluene, with "$PhI(OAc)_2 + NH_2SO_2$-*p*-$C_6H_4NO_2$" catalyzed by [Ru(F_{20}-TPP)(CO)] revealed that the relative amidation rates of these hydrocarbons (measured through competitive amidation reactions, see the Experimental Section) correlate with the C−H bond dissociation energies (Figure 2), like the C−H bond oxidations by [$(bpy)_2$(py)$Ru^{IV}O$]$^{2+}$.[11] This further supports the hydrogen atom abstraction mechanism of the ruthenium porphyrin-mediated intermolecular amidation reactions.

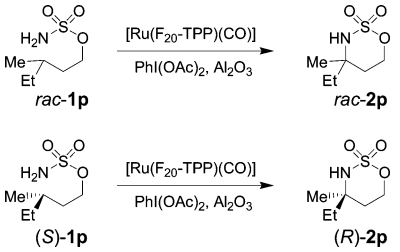
We propose that the intramolecular amidation of sulfamate esters with $PhI(OAc)_2$ catalyzed by ruthenium porphyrins also occurs by hydrogen atom abstraction. To gain further insight into the mechanism of such reactions, we examined the reactions of racemic and enantiopure sulfamate 3-methylpentyl ester (*rac*- and (*S*)-**1p**)

(9) For mechanistic studies on intermolecular C−N bond formation reactions with $PhI{=}NSO_2R$ catalyzed by metal complexes, see: (a) Mahy, J.-P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1517. (b) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2742. (c) Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5889. (d) Nägeli, I.; Baud, C.; Bernardinelli, G.; Jacquier, Y.; Moran, M.; Müller, P. *Helv. Chim. Acta* **1997**, *80*, 1087. (e) Au, S.-M.; Huang, J.-S.; Yu, W.-Y.; Fung, W.-H.; Che, C.-M. *J. Am. Chem. Soc.* **1999**, *121*, 9120. (f) Brandt, P.; Sodergren, M. J.; Andersson, P. G.; Norrby, P. O. *J. Am. Chem. Soc.* **2000**, *122*, 8013. (g) Gillespie, K. M.; Crust, E. J.; Deeth, R. J.; Scott, P. *Chem. Commun.* **2001**, 785. (h) Liang, J.-L.; Huang, J.-S.; Yu, X.-Q.; Zhu, N.; Che, C.-M. *Chem. Eur. J.* **2002**, *8*, 1563.

(10) (a) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123. (b) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523.

(11) Bryant, J. R.; Mayer, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 10351.

SCHEME 3. Intramolecular Amidation of Sulfamate 3-Methylpentyl Ester with PhI(OAc)$_2$ Catalyzed by [Ru(F$_{20}$-TPP)(CO)].



with PhI(OAc)$_2$ in the presence of [Ru(F$_{20}$-TPP)(CO)] and Al_2O_3 under the same conditions as for **1g**−**o**. These reactions afforded the corresponding cyclic sulfamidate **2p** in 72% yield (Scheme 3). For the amidation of (*S*)-**1p**, only a single enantiomer of **2p** was detected, whose absolute configuration is identical to that observed by using catalyst [$Rh_2(CH_3CO_2)_4$], as revealed by the ^{1}H NMR spectra of the products in the presence of europium tris(3-(heptafluoropropylhydroxymethylene)-(+)-camphorate) (see Figure S1 in the Supporting Information). The other enantiomer of **2p**, if any, should account for <5% of the total amount of the two enantiomers (estimated from the sensitivity of the NMR instrument). Since the intramolecular PhI(OAc)$_2$-amidation of (*S*)-**1p** catalyzed by [$Rh_2(CH_3CO_2)_4$] is stereospecific,[4b] the same intramolecular amidation catalyzed by [Ru(F$_{20}$-TPP)(CO)] should occur in a similar manner with no or little racemization. This could indicate that the carboradical species resulting from the hydrogen atom abstraction in the ruthenium porphyrin-catalyzed intramolecular amidation is too short-lived to undergo configuration inversion. Alternatively, one can consider the intramolecular amidation as a concerted process. If such is the case, a nonsynchronous concerted mechanism bearing significant hydrogen atom abstraction character and involving short-lived or partially developed carboradical species seems more reasonable, given the fact that the intermolecular amidation with "PhI(OAc)$_2$ + NH_2SO_2-*p*-$C_6H_4NO_2$" catalyzed by [Ru(F$_{20}$-TPP)(CO)] most probably occurs by a hydrogen atom abstraction.

Irrespective of whether the ruthenium porphyrin-catalyzed intramolecular amidation of sulfamate esters proceeds by a hydrogen atom abstraction or a concerted mechanism, we could rationalize the virtually complete *cis*-selectivity previously observed in the [Ru(F$_{20}$-TPP)(CO)]-catalyzed intramolecular amidation of **1e**,[5a] which contrasts with a 8:1 (*cis*/*trans*) *cis*-selectivity in the dirhodium-catalyzed counterpart.[4b] Figure 3a shows a simplified model structure of the proposed imido intermediate in the former intramolecular amidation system. The positional parameters of the F$_{20}$-TPP ligand and the geometry of the Ru−N−S moieties were taken from the X-ray crystal structure of bis(imido)osmium(VI) porphyrin [Os^{VI}(F$_{20}$-TPP)(NSO_2-*p*-$C_6H_4CH_3$)$_2$].[12] The geometry of the imido groups was based on the model structure of **1e** built in CS Chem3D Pro 4.0 with MM2 energy minimization. Inspection of the model structure in Figure 3a by employing the Chem3D program revealed that the C−H_a bond can well approach the imido nitrogen atom, through a combination of internal rotations about the C−C, C−O, O−S, and S−N bonds in the imido group, to form a three-centered transition state, whereas the C−H_b bond always points away from the imido nitrogen atom during any combinations of the internal rotations. This could explain why the *trans* cyclic sulfamidate was not obtained from the corresponding intramolecular amidation.

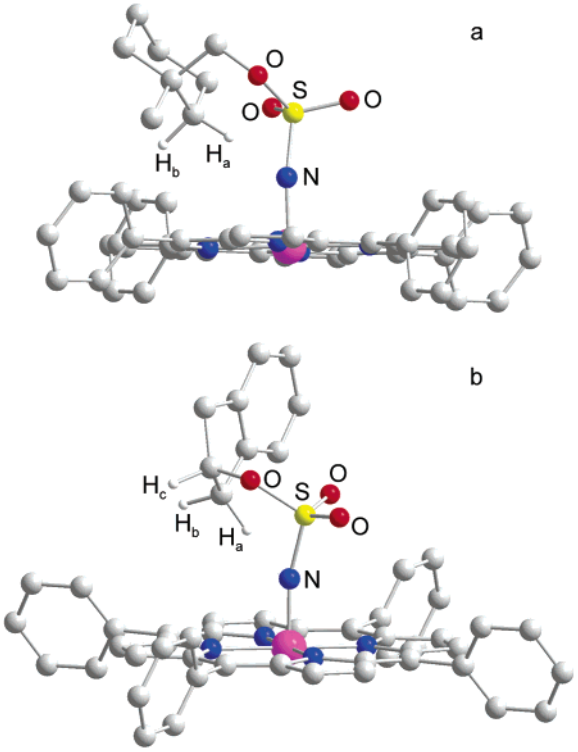


FIGURE 3. Simplified model structures of the proposed bis(imido) intermediates [Ru^{VI}(F$_{20}$-TPP)(NSO_2OR)$_2$] in the intramolecular PhI(OAc)$_2$-amidation of (a) **1e** and (b) **1a** catalyzed by [Ru(F$_{20}$-TPP)(CO)]. Only one of the two imido groups and key hydrogen atoms are shown. The fluoro substituents on the *meso*-phenyl groups of F$_{20}$-TPP are omitted for clarity.

Similar rationalization is also applicable for the virtually complete *cis*-selectivity in the intramolecular amidation of **1a** catalyzed by [Ru(F$_{20}$-TPP)(CO)] or [Ru(Por*)(CO)] (see Figure 3b). The situation for **1f** is somewhat different. Modeling studies showed that the benzylic C−H bond that results in *trans* cyclic sulfamidate does not always point away from the imido nitrogen atom during the internal rotations; however, the steric interactions between the phenyl, cyclohexyl, and $-OSO_2$ moieties prevent this C−H bond to closely approach the nitrogen atom to reach the three-centered transition state.

For substrate series **1m** → **1n** → **1o** with [Ru(F$_{20}$-TPP)(CO)] as a catalyst, we observed increased steric interaction between the imido group and the F$_{20}$-TPP *meso*-pentafluorophenyl groups in the proposed imido intermediates. In the case of **1o**, the steric interaction between the oxygen atom of the *o*-methoxy group and the benzylic hydrogen atoms, coupled with the steric interaction between the phenyl group and the porphyrin ligand, renders it hard for the benzylic C−H bonds to approach the imido nitrogen atom to reach the three-centered transition state. This could account for the above-mentioned decreased intramolecular amidation efficiency along **1m** → **1n** and the ineffectiveness of catalyst [Ru-

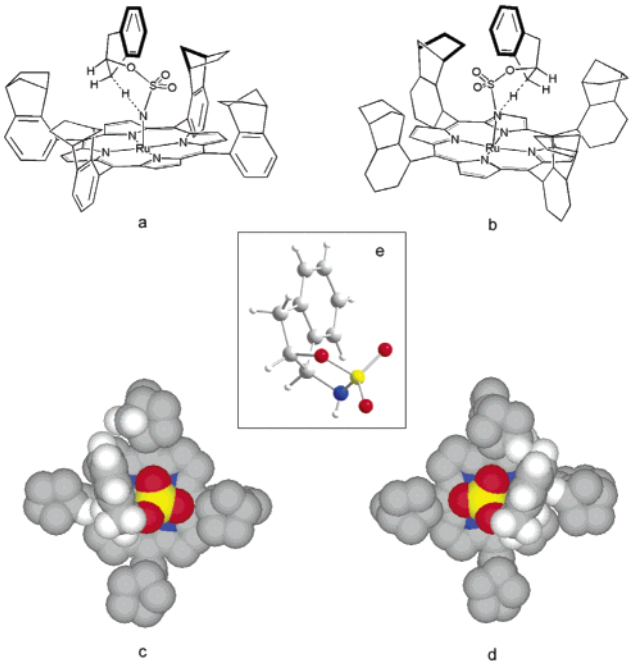
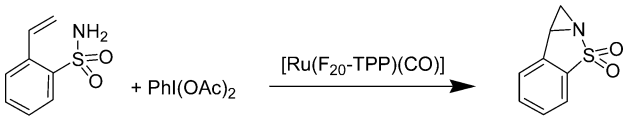


FIGURE 4. Schematic structures of the key transition states proposed for the asymmetric intramolecular $PhI(OAc)_2$-amidation of **1a** catalyzed by [Ru(Por*)(CO)]. The transition states in (a) and (b) result in formation of (1*R*,2*S*)-**2a** and (1*S*,2*R*)-**2a**, respectively. Space-filling representations for these transition states are depicted in (c) for (a) and in (d) for (b). The X-ray crystal structure of the predominant enantiomer in the optically active **2a** obtained from the [Ru(Por*)(CO)]-catalyzed asymmetric intramolecular amidation of **1a** is shown in (e). For clarity, only one imido group and the norbornane moieties at the same side as the imido group are shown. The key hydrogen atoms are indicated in (a)−(d) to facilitate evaluation of the configuration or steric hindrance.

(F_{20}-TPP)(CO)] in catalyzing intramolecular amidation of **1o** with $PhI(OAc)_2$.

To rationalize the enantioselectivity in the asymmetric intramolecular amidation reactions of **1a**,**f**−**n**, it is necessary to know the absolute configuration of the predominant enantiomers of the optically active cyclic sulfamidates **2a**,**f**−**n**, which was found to be (1*R*,2*S*) for **2a** by X-ray crystal structure analysis[5a] (so far we have not been able to determine such configurations in other cases). By taking the positional parameters of Por* in the X-ray crystal structure of [Ru(Por*)(CO)(L)],[9h] we built a model structure for the proposed intermediate [Ru^{VI}(Por*)-(NSO_2O-indan-2-yl)$_2$] in the same manner as for its F_{20}-TPP analogue. Figure 4 shows the model structures of the symmetric three-centered transition states typical for the hydrogen atom abstraction mechanism (the unsymmetric three-centered transition states typical for a concerted mechanism are not shown, which result in a similar rationalization to that described below). Examination of the model structures revealed that the transition state corresponding to (1*R*,2*S*)-**2a** (Figure 4a) encounters little steric interaction between the imido group and the porphyrin ligand, whereas significant steric interaction persists in the transition state corresponding to (1*S*,2*R*)-**2a** (Figure 4b), as is evident from the space-filling models depicted in parts c and d, respectively, of Figure 4. This can be rationalized by the fact that the imido phenyl group points to the smaller methano-bridge in Figure 4a and to the bulkier ethano-bridge in Figure 4b, thus leading to the observed preferential formation of (1*R*,2*S*)-**2a** in the [Ru(Por*)(CO)]-catalyzed intramolecular amidation of **1a**.

TABLE 4. Intramolecular Aziridination of 2-Vinyl-benzenesulfonamide (3a) with $PhI(OAc)_2$ Catalyzed by [Ru(F_{20}-TPP)(CO)][a]



entry	equiv of $PhI(OAc)_2$	additive[b]	solvent	*T* (°C) (reaction time (h))	conv (%)	yield[c] (%)
1	1.5	MgO	CH_2Cl_2	rt (12)	90	61
2	1.5	MgO	C_6H_6	rt (12)	72	68
3	1.5	MgO	CH_3CN	rt (12)	18	10
4	1.5	K_2CO_3	CH_2Cl_2	rt (12)	95	54
5	1.5	Al_2O_3	CH_2Cl_2	rt (12)	93	63
6	1.5	Al_2O_3	CH_2Cl_2	40 (3)	92	68
7	2	Al_2O_3	CH_2Cl_2	40 (3)	98	53
8	1.1	Al_2O_3	CH_2Cl_2	40 (3)	82	54

[a] Catalyst loading: 2 mol % (relative to **3a**). [b] 2.5 equiv. [c] Isolated yield based on the amount of consumed substrate.

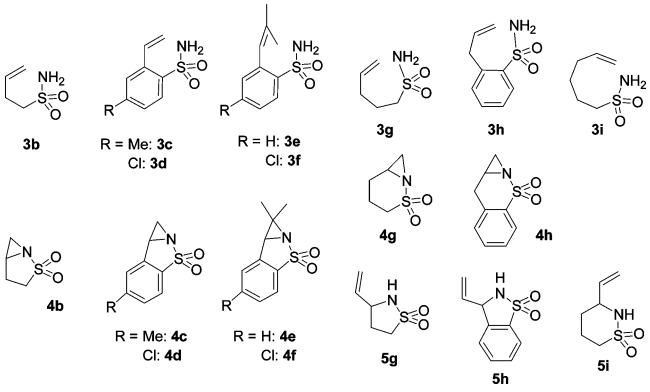
Intramolecular Aziridination of Unsaturated Sulfonamides Catalyzed by Ruthenium Porphyrins. Intramolecular aziridination of unsaturated sulfonamides involving iodine(III) compounds catalyzed by metal complexes is so far confined to dirhodium[2b,5b,c] and copper catalysts.[3a−c] The lack of metalloporphyrin catalysts for such transformation is somewhat surprising in view of the well-documented intermolecular aziridination reactions with $PhI{=}NSO_2R$ catalyzed by iron, manganese,[13] and ruthenium porphyrins.[6a,9h]

Following our recent work on dirhodium-catalyzed intramolecular aziridination of unsaturated sulfonamides with $PhI(OAc)_2$, which affords bicyclic aziridines in up to 98% yield with up to 100% substrate conversion,[5b,c] we studied the reaction between 2-vinylbenzenesulfonamide (**3a**) and $PhI(OAc)_2$ in the presence of 2 mol % of [Ru(F_{20}-TPP)(CO)] and observed formation of the corresponding bicyclic aziridine (**4a**). Table 4 shows the results obtained for this reaction under various conditions.

As shown in Table 4, the [Ru(F_{20}-TPP)(CO)]-catalyzed intramolecular $PhI(OAc)_2$-aziridination of **3a** at room temperature for 12 h, with MgO as an additive at a $PhI(OAc)_2$/**3a** molar ratio of 1.5:1, resulted in 90% conversion and 61% yield in dichloromethane (entry 1), a solvent superior to benzene and acetonitrile for this reaction in terms of substrate conversion (cf. entries 1−3). Changing the additive to K_2CO_3 or Al_2O_3 increased the conversion to 95 and 93%, respectively (entries 4 and 5), and Al_2O_3 is a better additive than K_2CO_3 in terms of product yield. The reaction occurred more rapidly when the temperature was raised to 40 °C, with 92% conversion and 68% yield obtained within 3 h (entry 6). However, increasing and decreasing the $PhI(OAc)_2$/**3a** molar ratio both led to a significant drop in the yield of **4a** (cf. entries 6−8).

A series of other unsaturated sulfonamides, **3b**−**h** (see Table 5), also underwent similar intramolecular aziridination. When the reactions were conducted in dichloromethane at 40 °C for 3 h, with substrate/$PhI(OAc)_2$/

TABLE 5. Intramolecular Aziridination of Various Unsaturated Sulfonamides with $PhI(OAc)_2$ in the Presence of Al_2O_3 Catalyzed by [Ru(F_{20}-TPP)(CO)][a]



entry	substrate	product	conversion (%)	yield[b] (%)
1	**3b**	**4b**	100	87
2	**3c**	**4c**	90	73
3	**3d**	**4d**	95	87
4	**3e**	**4e**	88	82
5	**3f**	**4f**	85	79
6	**3g**	**4g** + **5g**	100	28 (**4g**), 45 (**5g**)
7	**3h**	**4h** + **5h**	100	41 (**4h**), 25 (**5h**)
8	**3i**	**5i**	100	55

[a] Reaction conditions: CH_2Cl_2, 40 °C, 3 h, catalyst/substrate/$PhI(OAc)_2/Al_2O_3$ molar ratio = 0.02:1:1.5:2.5. [b] Isolated yield based on the amount of consumed substrate.

Al_2O_3 molar ratio of 1:1.5:2.5, we obtained the corresponding cyclic aziridines **4b**−**h** in 28−87% yields with 85−100% conversions (entries 1−7, Table 5).

The intramolecular aziridination of **3d** catalyzed by [Ru(F_{20}-TPP)(CO)] resulted in 95% conversion with 87% yield (entry 3, Table 5); both are higher than those catalyzed by dirhodium complexes (up to 81 and 74%, respectively).[5b,c] For substrates **3a**−**c**,**e**,**f**, the corresponding products **4a**−**c**,**e**,**f** were obtained in 68−87% yields (entry 6 in Table 4 and entries 1, 2, 4, and 5 in Table 5), which are lower than those observed for the dirhodium-catalyzed counterparts (80−97%).[5b,c]

Unsaturated sulfonamides **3g**,**h** have allylic or benzylic C−H bonds that could undergo intramolecular amidation to form five-membered cyclic sulfonamides **5g**,**h** in a manner analogous to that of metal-catalyzed intramolecular amidation of sulfamate esters containing β-C−H bonds.[4b,5a] However, such intramolecular amidation of **3g**,**h** has not been observed by employing copper[3a,c] and dirhodium catalysts.[5b,c] It is surprising that, in the presence of catalyst [Ru(F_{20}-TPP)(CO)], the reactions between **3g**,**h** with $PhI(OAc)_2$ gave **5g**,**h** in 45 and 25% yields, respectively, with the intramolecular aziridination products formed in 28 (**4g**) and 41% (**4h**) yields. While this indicates a decreased selectivity of catalyst [Ru(F_{20}-TPP)(CO)] for the intramolecular aziridination of **3g**,**h**, it reflects a higher catalytic activity of the ruthenium porphyrin for intramolecular amidation of related sulfonamides.

For unsaturated sulfonamide **3i** (see Table 5), whose allylic C−H bonds could be amidated intramolecularly to give six-membered cyclic sulfonamide **5i**, no intramolecular aziridination product was obtained; the product identified was **5i**. This is similar to the analogous copper-[3a,c] or dirhodium-catalyzed[5b,c] reactions, except that the yield of **5i** from the [Ru(F_{20}-TPP)(CO)]-catalyzed reaction (55%, entry 8 in Table 5) is substantially lower than that in the [$Rh_2(OAc)_4$]-catalyzed one (90%).[5b]

In an effort to develop an asymmetric version of the intramolecular aziridination of sulfonamides, we examined the reaction between **3a** and $PhI(OAc)_2$ in the presence of catalyst [Ru(Por*)(CO)] under the same conditions as denoted in Table 5. This reaction resulted in 43% conversion, affording **4a** in 65% yield and 9% ee, an enantioselectivity much lower than that in the [Ru(Por*)(CO)]-catalyzed intramolecular amidation of sulfamate esters with $PhI(OAc)_2$. Good enantioselectivity (up to 76% ee) in asymmetric intramolecular aziridination of sulfonamides with $PhI(OAc)_2$ has been attained in our recent work by employing chiral dirhodium catalysts.[5c]

Earlier, we found that [Ru(F_{20}-TPP)(CO)] is a robust catalyst for intramolecular amidation of saturated C−H bonds, exhibiting up to >300 turnovers in $PhI(OAc)_2$-amidation of **1e** to form **2e**.[5a] Remarkably, when the [Ru(F_{20}-TPP)(CO)]-catalyzed intramolecular aziridination of **3e** was performed in dichloromethane at 40 °C for 36 h at a low catalyst loading (catalyst/substrate/$PhI(OAc)_2$/Al_2O_3 molar ratio = 1:5000:6500:12500), the cyclic aziridine **4e** was obtained in 53% yield with 76% conversion, corresponding to a turnover number of 2014. This turnover number is substantially higher than those (up to 1375) observed for the intramolecular aziridination reactions catalyzed by copper[3a,c] and dirhodium complexes.[5b,c]

Conclusions

Ruthenium porphyrins are active catalysts for intramolecular C−N bond formation reactions. The intramolecular amidation of sulfamate esters with $PhI(OAc)_2$ catalyzed by [Ru(F_{20}-TPP)(CO)] and [Ru(Por*)(CO)] affords cyclic sulfamidates with excellent diastereoselectivity, good-to-high enantioselectivity (for the latter catalyst), and is applicable to a wide variety of sulfamate ester substrates. These ruthenium-catalyzed reactions probably involve bis(imido)ruthenium(VI) porphyrin intermediates, whose conversion to cyclic sulfamidates might occur by intramolecular hydrogen atom abstraction. The intramolecular aziridination of unsaturated sulfonamides with $PhI(OAc)_2$ catalyzed by [Ru(F_{20}-TPP)(CO)] features good-to-high product yields with up to complete substrate conversion and unprecedentedly high turnovers, creating a precedent for efficient intramolecular aziridination catalyzed by metalloporphyrins.

Experimental Section

Preparation of Sulfamate Esters 1g−o. These compounds were prepared from respective alcohols according to a procedure similar to that reported by Du Bois and co-workers.[4b]

1g. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.28 (m, 2H), 7.16 (m, 2H), 4.77 (s, 2H), 4.37 (t, J = 6.8 Hz, 2H), 3.02 (t, J = 6.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 135.3, 133.3, 130.7, 129.2, 71.4, 34.9. HRMS: calcd for $C_8H_{10}ClNO_3S$ 235.0070, found 235.0067.

1h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.12 (m, 4H), 4.66 (s, 2H), 4.37 (t, J = 7.0 Hz, 2H), 3.01 (t, J = 7.0 Hz, 2H); 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.0, 133.7, 129.7, 129.9, 72.0, 35.2, 21.4. HRMS: calcd for $C_9H_{13}NO_3S$ 215.0616, found 215.0615.

1i. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.14 (m, 2H), 6.85 (m, 2H), 4.62 (s, 2H), 4.36 (t, J = 7.0 Hz, 2H), 3.79 (s, 3H), 2.99 (t,

J = 7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 158.6, 130.0, 128.4, 114.1, 71.8, 55.3, 34.4. HRMS: calcd for $C_9H_{13}NO_4S$ 231.0565, found 231.0560.

1j. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (m, 3H), 7.69 (s, 1H), 7.47 (m, 2H), 7.32 (d, J = 8.1 Hz, 1H), 4.63 (s, 2H), 4.49 (t, J = 6.9 Hz, 2H), 3.21 (t, J = 6.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 134.2, 133.8, 132.8, 128.7, 128.0, 127.9, 127.8, 127.4, 126.7, 126.2, 71.8, 35.8. HRMS: calcd for $C_{12}H_{13}NO_3S$ 251.0616, found 251.0601.

1k. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.01 (d, J = 7.4 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.77(m, 1H), 7.53 (m, 2H), 7.41 (m, 2H), 4.53 (m, 4H), 3.54 (t, J = 7.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 134.2, 132.1, 129.4, 128.3, 127.7, 126.8, 126.2, 125.9, 123.5, 118.5, 71.1, 32.7. HRMS: calcd for $C_{12}H_{13}NO_3S$ 251.0616, found 251.0616.

1l. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.14 (m, 2H), 6.98 (m, 2H), 4.89 (s, 2H), 4.20 (t, J = 6.3 Hz, 2H), 2.72 (t, J = 7.4 Hz, 2H), 2.04 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 161.6 (d, J_{C-F} = 242.5 Hz), 136.0, 129.8, 115.3, 70.3, 30.7, 30.4. HRMS: calcd for $C_9H_{12}FNO_3S$ 233.0522, found 233.0517.

1m. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.11 (m, 2H), 6.83 (m, 2H), 4.82 (s, 2H), 4.19 (t, J = 6.3 Hz, 2H), 3.79 (s, 3H), 2.69 (t, J = 7.3 Hz, 2H), 2.04 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.1, 132.4, 129.4, 114.0, 70.5, 55.3, 30.6, 30.5. HRMS: calcd for $C_{10}H_{15}NO_4S$ 245.0722, found 245.0720.

1n. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.21 (t, J = 7.4 Hz, 1H), 6.76 (m, 3H), 4.75 (s, 2H), 4.09 (t, J = 6.6 Hz, 2H), 3.80 (s, 3H), 2.67 (t, J = 8.0 Hz, 2H), 1.96 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.8, 142.0, 129.5, 120.9, 114.4, 111.5, 70.5, 55.2, 31.6, 30.2. HRMS: calcd for $C_{10}H_{15}NO_4S$ 245.0722, found 245.0723.

1o. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.21 (m, 1H), 7.12 (d, J = 7.3 Hz, 1H), 6.87 (m, 2H), 4.89 (s, 2H), 4.20 (t, J = 6.4 Hz, 2H), 3.81 (s, 3H), 2.73 (t, J = 7.3 Hz, 2H), 2.03 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.8, 130.4, 129.2, 127.9, 120.8, 110.8, 71.5, 55.6, 29.0, 26.7. HRMS: calcd for $C_{10}H_{15}NO_4S$ 245.0722, found 245.0721.

Typical Procedure for Intramolecular Amidation of Sulfamate Esters Catalyzed by [Ru(F_{20}-TPP)(CO)]. Dichloromethane (1.5 mL) was added via syringe into a Schlenk flask containing sulfamate ester (0.18 mmol), $PhI(OAc)_2$ (0.36 mmol), catalyst (0.0027), Al_2O_3 (0.45 mmol), and molecular sieves (4 Å, 50 mg) under an argon atmosphere. The mixture was stirred at 40 °C for 2 h, diluted with dichloromethane (5 mL) after cooling to room temperature, and filtered through Celite. The residue on Celite was washed with dichloromethane (2 × 5 mL). Evaporation of the combined filtrates under reduced pressure followed by chromatography on silica gel column with dichloromethane as eluent afforded cyclic sulfamidate as a white solid.

Typical Procedure for Asymmetric Intramolecular Amidation of Sulfamate Esters Catalyzed by [Ru(Por*)(CO)]. This procedure is the same as that for catalyst [Ru(F_{20}-TPP)(CO)] except that 0.25 mmol of $PhI(OAc)_2$ and 0.018 mmol of catalyst [Ru(Por*)(CO)] (rather than [Ru(F_{20}-TPP)(CO)]) was used and the reaction was conducted in benzene at 5 °C for 8 h.

2g. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.38 (m, 4H), 5.06 (m, 1H), 4.89 (d, J = 5.7 Hz, 1H), 4.84 (t, J = 7.0 Hz, 1H), 4.40 (t, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 135.9, 134.5, 130.0, 128.4, 74.9, 59.3. HRMS: calcd for $C_8H_8ClNO_3S$ 232.9913, found 232.9922.

2h. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.26 (m, 4H), 5.05 (m, 1H), 4.81 (m, 1H), 4.70 (d, J = 6.2 Hz, 1H), 4.44 (t, J = 8.8 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 139.7, 132.1, 130.1, 126.6, 75.1, 59.5, 21.1. HRMS: calcd for $C_9H_{11}NO_3S$ 213.0460, found 213.0453.

2i. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.34 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.5 Hz, 2H), 5.02 (m, 1H), 4.78 (t, J = 6.8 Hz, 1H), 4.69 (d, J = 6.4 Hz, 1H), 4.44 (t, J = 8.7 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.9, 129.4, 128.5, 115.1, 75.5, 59.7, 55.9. HRMS: calcd for $C_9H_{11}NO_4S$ 229.0409, found 229.0406.

2j. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.88 (m, 4H), 7.51 (m, 3H), 5.26 (m, 1H), 4.91 (t, J = 8.6 Hz, 1H), 4.82 (m, 1H), 4.55 (t, J = 8.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 134.0, 133.5, 132.9, 130.1, 128.4, 128.2, 127.5, 127.4, 126.8, 123.7, 75.1, 60.2. HRMS: calcd for $C_{12}H_{11}NO_3S$ 249.0460, found 249.0454.

2k. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.92 (m, 3H), 7.76 (d, J = 7.2 Hz, 1H), 7.58 (m, 3H), 5.84 (m, 1H), 5.06 (m, 1H), 4.93 (d, J = 6.7 Hz, 1H), 4.59 (t, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 133.9, 130.8, 130.3, 129.9, 129.4, 127.3, 126.4, 125.6, 123.9, 123.8, 74.3, 56.4. HRMS: calcd for $C_{12}H_{11}NO_3S$ 249.0460, found 249.0460.

2l. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.34 (m, 2H), 7.10 (m, 2H), 4.85 (m, 2H), 4.65 (m, 1H), 4.35 (d, J = 9.3 Hz, 1H), 2.22 (m, 1H), 2.01 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.8 (d, J_{C-F} = 247.0 Hz), 133.8, 128.4, 116.1, 71.7, 58.3, 30.1. HRMS: calcd for $C_9H_{10}FNO_3S$ 231.0365, found 231.0365.

2m. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.27 (m, 2H), 6.91 (m, 2H), 4.81 (m, 2H), 4.65 (m, 1H), 4.25 (d, J = 9.3 Hz, 1H), 3.81 (s, 3H), 2.25 (m, 1H), 1.99 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 159.9, 130.1, 127.6, 114.5, 71.8, 58.4, 55.3, 30.1. HRMS: calcd for $C_{10}H_{13}NO_4S$ 243.0565, found 243.0567.

2n. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.32 (m, 1H), 6.91 (m, 3H), 4.85 (m, 2H), 4.67 (m, 1H), 4.32 (d, J = 9.3 Hz, 1H), 3.82 (s, 3H), 2.23 (m, 1H), 2.04 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.2, 139.5, 130.2, 118.2, 114.3, 112.1, 71.8, 58.8, 55.4, 30.2. HRMS: calcd for $C_{10}H_{13}NO_4S$ 243.0565, found 243.0571.

Typical Procedure for Competitive Intramolecular Amidation of *para*-Substituted Sulfamate Ester *p*-X-$C_6H_4(CH_2)_2OSO_2NH_2$ (X = MeO, Me, Cl, Br) vs $C_6H_5(CH_2)_2OSO_2NH_2$ Catalyzed by [Ru(F_{20}-TPP)(CO)]. To a mixture of *p*-X-$C_6H_4(CH_2)_2OSO_2NH_2$ (1 mmol), $C_6H_5(CH_2)_2OSO_2NH_2$ (1 mmol), [Ru(F_{20}-TPP)(CO)] (0.015 mmol), and Al_2O_3 (0.6 mmol) in dichloromethane (10 mL) was added $PhI(OAc)_2$ (0.5 mmol). The mixture was stirred at room temperature under argon for 3 h, followed by filtration through Celite. Chromatography on silica gel with dichloromethane as eluent gave a mixture of two cyclic sulfamidate products (corresponding to the intramolecular amidation of *p*-X-$C_6H_4(CH_2)_2OSO_2NH_2$ and $C_6H_5(CH_2)_2OSO_2NH_2$, respectively). The molar ratio of these two products was determined by ^{1}H NMR and was taken as the relative rate k_X/k_H.

Typical Procedure for Competitive Intermolecular Amidation of Hydrocarbons with "$PhI(OAc)_2$ + NH_2SO_2-*p*-$C_6H_4NO_2$" Catalyzed by [Ru(F_{20}-TPP)(CO)]. $PhI(OAc)_2$ (0.5 mmol) was added to a dichloromethane solution containing ethylbenzene (1 mmol), another hydrocarbon (1 mmol), NH_2SO_2-*p*-$C_6H_4NO_2$ (0.5 mmol), 1,4-dichlorobenzene (1 mmol) (as the internal standard), and [Ru(F_{20}-TPP)(CO)] (0.02 mmol). The reaction mixture was stirred at room temperature for 3 h. The amounts of ethylbenzene and the other hydrocarbon before and after the reaction were determined by GC. The ratio between the consumed moles of the other hydrocarbon and ethylbenzene was taken as the relative rate k_R.

Typical Procedure for Intramolecular Aziridination of Unsaturated Sulfonamides Catalyzed by [Ru(F_{20}-TPP)(CO)]. This procedure is the same as that for the [Ru(F_{20}-TPP)(CO)]-catalyzed intramolecular amidation of sulfamate esters except that 0.2 mmol of unsaturated sulfonamide (instead of sulfamate ester), 0.3 mmol of $PhI(OAc)_2$, 0.004 mmol of catalyst, and 0.5 mmol of Al_2O_3 were used, and the mixture was stirred for 3 h (affording cyclic sulfonamide rather than sulfamidate).

5g. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.86 (m, 1H), 5.32 (m, 2H), 4.21 (s, 1H), 4.16 (t, J = 6.7 Hz, 1H), 3.18 (m, 2H), 2.58 (m, 1H), 2.23 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 136.8, 117.9, 57.2, 47.6, 29.9. HRMS: calcd for $C_5H_9NO_2S$ 147.0354, found 147.0347.

5h. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.80 (d, J = 7.4 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 5.85 (m, 1H), 5.56 (d, J = 16.9 Hz, 1H), 5.41 (d, J = 9.9 Hz, 1H), 5.14 (m, 1H), 4.80 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 159.2, 138.7, 135.4, 133.6, 130.0, 125.3, 121.7, 120.5, 60.6. HRMS: calcd for $C_9H_9NO_2S$ 195.0354, found 195.0344.

Preparation of PhI=NSO$_2$OCH$_2$CCl$_3$. This compound was prepared from reaction of $PhI(OAc)_2$ with $CCl_3CH_2OSO_2NH_2$ in the presence of KOH according to the procedure reported by Dodd and Dauban for preparation of PhI=$NSO_2(CH_2)_2SiMe_3$.[14] ^{1}H NMR (CD_3OD, 300 MHz): δ = 8.05 (d, J = 7.8 Hz, 2H), 7.60 (m, 3H), 4.57 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 137.8, 135.3, 130.6, 127.8, 78.9, 78.8. HRMS: calcd for $C_8H_7Cl_3INO_3S$ 428.8257, found 428.8245.

Synthesis of Bis(imido)ruthenium(VI) Porphyrin [Ru^{VI}(F$_{20}$-TPP)(NSO$_2$OCH$_2$CCl$_3$)$_2$]. A mixture of [Ru(F_{20}-TPP)(CO)] (0.05 mmol) and PhI=$NSO_2OCH_2CCl_3$ (0.2 mmol) in dichloromethane (8 mL) was stirred at room temperature under argon for 5 min. The mixture was then evaporated to dryness in vacuo followed by chromatography on a short column of neutral alumina (active grade II) with dichloromethane as eluent. The first red band was collected and the solvent was removed in vacuo. Recrystallization from dichloromethane−hexane afforded the desired product in 60% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.14 (s, 8H), 1.26 (s, 4H). IR (KBr pellet, cm^{-1}): 1022 ("oxidation state marker" band[9e]). UV−vis (CH_2Cl_2) λ_{max} (log ϵ) = 409 (5.21), 527 (4.19). ESI MS: m/z 1526 (M^+). Anal. Calcd for $C_{48}H_{12}Cl_6F_{20}N_6O_6S_2Ru\cdot 3C_6H_{14}$: C, 44.41; H, 3.05; N, 4.71. Found: C, 44.64; H, 2.43; N, 4.40.

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Supporting Information Available: General experimental methods, Figure S1, ^{13}C NMR spectra of **1g**−**o**, **2g**−**n**, **5g**,**h**, and PhI=$NSO_2OCH_2CCl_3$, and HPLC spectra of racemic and optically active **2g**−**n**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Li, Y.; Huang, J.-S.; Zhou, Z.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2001**, *123*, 4843.

(13) (a) Mansuy, D.; Mahy, J.-P.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1161. (b) Mahy, J.-P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1517.

(14) Dauban, P.; Dodd, R. H. *J. Org. Chem.* **1999**, *64*, 5304.