OL Organic Letters

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Ruthenium-Catalyzed Asymmetric *N*-Acyl Nitrene Transfer Reaction: Imidation of Sulfide

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Cite This: https://dx.doi.org/10.1021/acs.orglett.0c01373 Read Online

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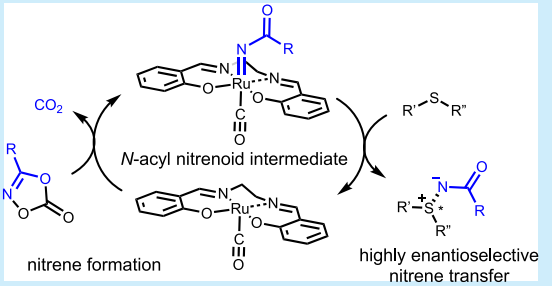
ABSTRACT: The asymmetric nitrene transfer reaction is a useful and strong tool for the construction of nitrogen functional groups such as *N*-sulfonyl amide and carbamic ester in a highly enantioselective manner. On the other hand, there is a substantial limitation in this filed: the transfer of *N*-acyl amide via the corresponding nitrene intermediates is still difficult because *N*-acyl nitrenes undergo undesired nitrene dimerization or Curtius rearrangement. Herein, we achieved highly enantioselective imidation of sulfides via catalytic *N*-acyl nitrene transfer with (OC)ruthenium−salen complex **2b** as the catalyst and 3-substituted 1,4,2-dioxazol-5-ones **1** as the nitrene source. Complex **2b** can decompose dioxazolones **1** to the desired *N*-acyl nitrene intermediates without any activation via heating or UV irradiation, or transfer generating nitrene intermediates to the sulfur atom of sulfides with good to excellent enantioselectivities (≤98% ee) without diazene and isocyanate contamination.

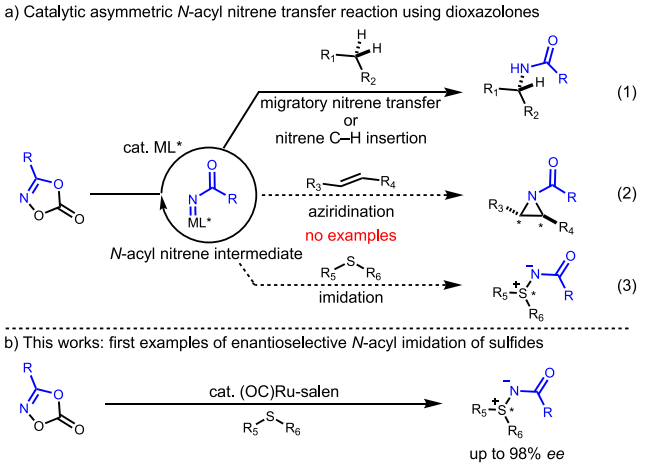


Nitrene transfer reactions such as imidation of heteroatoms,[1,2] aziridination of olefins,[3] and amination of C−H bonds[4] are useful and powerful tools for the synthesis of nitrogen-containing organic compounds, which are ubiquitous in biologically active compounds such as alkaloids and amides. Thus, these transformations have attracted continuing and growing interest, leading to the development of various powerful and useful methodologies in this field.[5] Today, the introduction of a nitrogen functional group can be readily performed in a highly site-selective, chemoselective, and enantioselective manner by using the appropriate catalyst and nitrene source. However, there is a substantial limitation in this field: the transfer of *N*-acyl amides via the corresponding nitrene intermediates is still difficult. Unfortunately, *N*-acyl nitrene species often undergo Curtius rearrangement and produce the corresponding isocyanates or related products under UV irradiation or thermal conditions.[6] Although catalytic *N*-acyl nitrene transfer reactions using azides have been reported, the product is contaminated with diazene derivatives as coproducts.[7] On the other hand, the reaction using metal(nitride) complexes as stoichiometric nitrene source affords the desired product in a chemo- and stereoselective manner.[8] These results indicate that *N*-acyl metal(nitrene), which can be obtained catalytically, would give the desired *N*-acyl-amidated products without the formation of isocyanates and diazenes as byproducts. Recently, Bolm and co-workers demonstrated the high utility of 3-substituted 1,2,4-dioxazol-5-ones **1** in the imidation of sulfides.[9,10] Thus, the imidation of sulfides and sulfoxides using dioxazolones **1** as the nitrene source proceeds successfully with complete chemoselectivity. Subsequently, Chang et al. reported a catalytic C−H amination using **1** as the nitrogen source.[11] In this reaction, a cationic (pentamethylcyclopentadienyl)rhodium complex induces the decomposition of **1** into the desired nitrene intermediate without any activation method such as heating or photoirradiation, and *N*-acyl amide groups are transferred to C−H bonds in a chemoselective and site-selective manner. After these findings had been published, the C−H amidation reaction based on the transition metal/dioxazolone **1** system has developed considerably, including asymmetric versions.[12−14]

However, the enantioselective *N*-acyl nitrene transfer reaction is still limited to the C−H amination (Scheme 1a).[15] This limitation could be overcome if the *N*-acyl nitrene group could be transferred to heteroatoms and/or olefins with chemo- and stereoselectivity, which would boost the applicability of nitrene transfer reactions in organic synthesis. Motivated by this, we were interested in the development of the catalytic asymmetric *N*-acyl nitrene transfer reactions. Herein, we describe highly chemo- and enantioselective *N*-acyl imidation of sulfides catalyzed by (OC)ruthenium−salen complexes **2** using dioxazolone **1** as the nitrene source (Scheme 1b).

Received: April 21, 2020

Scheme 1. Asymmetric *N*-Acyl Nitrene Transfer Reactions



Recently, we reported that (OC)ruthenium−salen complexes **2** are efficient catalysts in asymmetric nitrene transfer reactions such as imidation of sulfides, aziridination of olefins, and C−H aminations, using *N*-sulfonyl and *N*-alkoxycarbonyl azides as nitrene sources (Figure 1).[5c,16−18] These ruthenium-catalyzed nitrene transfer reactions using azides could be expected to prompt further development of *N*-acyl nitrene transfer reactions.

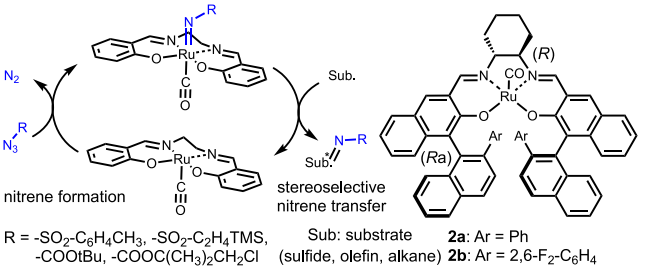
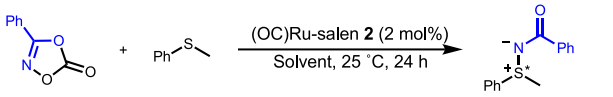


Figure 1. Cross-selective oxidative coupling between two different arenols.

We conducted the *N*-acyl imidation of methyl phenyl sulfide **3a** using ruthenium−salen complex **2a** as the catalyst (Table 1). No reaction was observed in the presence of *N*-benzoyl azide (entry 1). Fortunately, 3-phenyl-1,4,2-dioxazol-5-one **1a** gave the desired sulfide **4aa** with 84% ee in quantitative yield without any activation such as heating or photoirradiation (entry 2). Diazene and isocyanate derivatives were not observed under those conditions. Encouraged by these results, we conducted the *N*-acyl imidation of methyl phenyl sulfide **3a** using 3-phenyl-1,2,4-dioxazol-5-one **1a** as the nitrene precursor with a series of ruthenium complexes **2** as catalysts (Table 1, entries 2 and 3, and Table S1[19]). Complex **2b** showed the best enantioselectivity (95% ee) in tetrahydrofuran (THF) as the solvent. The imidation with te complex **2b**/dioxazolone **1a** system in nonpolar and less polar solvents proceeded with good to high enantioselectivities (entries 3−8). On the other hand, the reaction in methanol was sluggish (entry 9). Acetonitrile could be used as the solvent, albeit with reduced yield and enantioselectivity (entry 10). It was also possible to reduce the catalyst loading to 0.2 mol % in THF without affecting the chemical yield or the enantioselectivity (entries 11 and 12).

Table 1. Optimization of Imidation Using 3-Phenyl-1,4,2-dioxazolone as a Nitrene Source[a]



1a 3a 4aa

entry	catalyst	solvent	yield (%)[b]	ee (%)[c]
1[d]	**2a**	THF	NR[e]	–
2	**2a**	THF	>99	84
3	**2b**	THF	>99	95
4	**2b**	1,4-dioxane	>99	90
5	**2b**	Et_2O	73	81
6	**2b**	AcOEt	>99	93
7	**2b**	toluene	>99	90
8	**2b**	CH_2Cl_2	>99	94
9	**2b**	MeOH	trace	–
10	**2b**	CH_3CN	46	76
11[f]	**2b**	THF	>99	95
12[g]	**2b**	THF	88	97

[a]Reactions were carried out using **1a** (0.13 mmol) and **3a** (0.1 mmol) with ruthenium complex **2** (2 mol %) at 25 °C for 24 h, unless otherwise specified. [b]Isolated yield, based on sulfide **3**. [c]Determined by HPLC with a chiral stationary phase. [d]*N*-Benzoyl azide (0.13 mmol) was used as the nitrene source instead of **1a**. [e]No reaction was observed. [f]Carried out with **2b** (1 mol %) and 4 Å molecular sieves (20 mg) for 18 h. [g]Carried out on a 1.0 mmol scale with **2b** (0.2 mol %) and 4 Å molecular sieves (20 mg) for 24 h.

With the optimized conditions in hand, we conducted the asymmetric imidation using 3-substituted 1,2,4-dioxazolones **1** as nitrene precursors with methyl phenyl sulfide in the presence of complex **2b** as the catalyst (Table 2). The reaction of *para*- and *meta*-substituted 3-phenyl-1,2,4-dioxazolones **1b−k** gave better yields than the *ortho*-substituted derivatives **1l−o**, and high enantioselectivities were obtained in all cases (90−98% ee) (entries 1−14). In addition, 3-alkyl- and 3-alkenyl-1,2,4-dioxazolones **1p−u** could be also successfully applied as the nitrene source. 3-Methyl-, 3-pentyl-, and 3-(2-propyl)-dioxazolones **1p−r** gave desired products **4** with good enantioselectivity and moderate to high yields (entries 15−17, respectively). However, no reaction occurred when using dioxazolone **1s** as the nitrene source (entry 18). Furthermore, 3-(*E*)-propenyldioxazolones **1t** also produced the corresponding *N*-acyl sulfimides **4ta** with good enantioselectivities (entry 19).

We further examined the asymmetric sulfimidation of various sulfides **3** using the complex **2b**/3-phenyldioxazolone **1a** system (Scheme 2). In general, aryl methyl sulfides **3b−g** gave the desired products **4** with high enantioselectivities and high yields, irrespective of the electronic nature and position of the substituents. Ethyl phenyl sulfide **3j** and benzyl phenyl sulfide **3k** also underwent the *N*-acyl imidation with moderate stereoselectivities. Meanwhile, benzyl methyl sulfide **3l** gave an 89% ee, albeit sluggish. Fortunately, the chemical yield of **4al** was improved to 99% by using a 4 mol % catalyst loading. Dialkyl sulfides **3m−p** also gave the products with good to high enantioselectivities, and sterically hindered dialkyl sulfides such as methyl 2-propyl sulfide **3n** and methyl *tert*-butyl sulfide **3o** afforded yields better than those of the less hindered sulfides **3m** and **3p**. Ethyl propyl sulfide **3p** also gave the desired sulfimide **4ap** with acceptable enantioselectivity (75% ee).

https://dx.doi.org/10.1021/acs.orglett.0c01373
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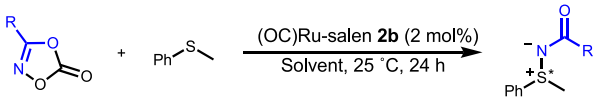
Table 2. Scope and Limitation of 3-Substituted 1,4,2-Dioxazolone 1[a]

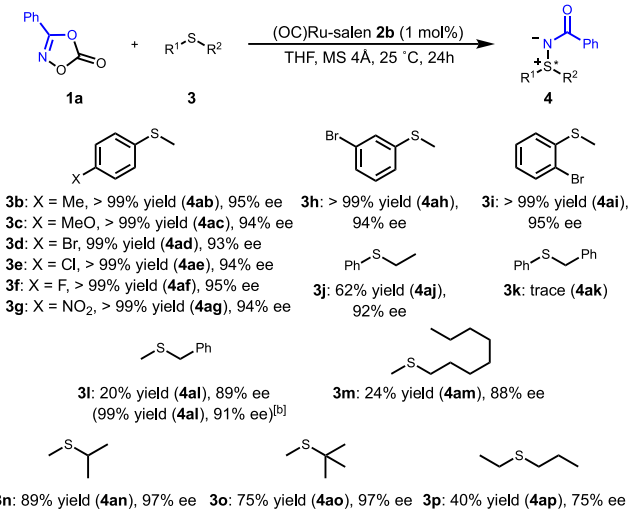


1 3a 4

entry	R	product	yield (%)[b]	ee (%)[c]
1	4-MeC_6H_4 (**1b**)	**4ba**	>99	96
2	4-$MeOC_6H_4$ (**1c**)	**4ca**	99	98
3	4-BrC_6H_4 (**1d**)	**4da**	99	95
4	4-ClC_6H_4 (**1e**)	**4ea**	93	94
5	4-FC_6H_4 (**1f**)	**4fa**	>99	93
6	4-$CF_3C_6H_4$ (**1g**)	**4ga**	51	91
7	3-MeC_6H_4 (**1h**)	**4ha**	>99	97
8	3-BrC_6H_4 (**1i**)	**4ia**	>99	92
9	3-ClC_6H_4 (**1j**)	**4ja**	>99	92
10	3-FC_6H_4 (**1k**)	**4ka**	98	93
11	2-MeC_6H_4 (**1l**)	**4la**	46	90
12	2-BrC_6H_4 (**1m**)	**4ma**	75	94
13	2-ClC_6H_4 (**1n**)	**4na**	86	94
14	2-FC_6H_4 (**1o**)	**4oa**	>99	95
15	Me (**1p**)	**4pa**	91	94 (*R*)[d]
16	*n*-pentyl (**1q**)	**4qa**	>99	93
17	*i*Pr (**1r**)	**4ra**	52	96
18	*t*Bu (**1s**)	**4sa**	NR	–
19	(*E*)-PhC═C- (**1t**)	**4ta**	94	94

[a]Unless otherwise specified, all reactions were carried out using **1** (0.13 mmol) and **3a** (0.1 mmol) with complex **2b** (1 mol %) and 4 Å molecular sieves (20 mg) in THF at 25 °C. [b]Isolated yield, based on methyl phenyl sulfide **3a**. [c]Determined by HPLC with a chiral stationary phase. [d]Determined by chiroptical comparison after **4pa** was converted into sulfoximine **6pa**.[20]

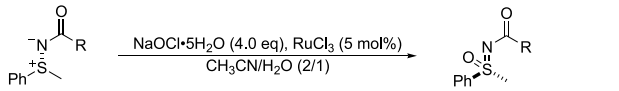
Scheme 2. Scope and Limitation of Sulfide 3[a]



[a]Unless otherwise specified, all reactions were carried out using **1a** (0.11 mmol) and **3** (0.1 mmol) with complex **2b** (1 mol %) at 25 °C in the presence of 4 Å molecular sieves. [b]Carried out with **2b** (4 mol %).

N-Acyl sulfimides **4aa** and **4pa** could be oxidized to sulfoximines **5aa** and **5pa**, respectively, in good yields without a decreasing enantiomeric ratio (Scheme 3).[21]

Scheme 3. Oxidation of Sulfimides 4 to Sulfoximines 5



R = Ph; **4aa** (98% *ee*)
R = Me; **4pa** (94% *ee*)

R = Ph; **5aa** (86%, 97% *ee*)
R = Me; **5pa** (40%, 95% *ee*, (*R*))

In conclusion, highly enantioselective *N*-acyl imidation of sulfide **3** was achieved by using dioxazolones **1** as the nitrene source in the presence of (OC)ruthenium−salen complex **2b** as the catalyst. It was thought that ruthenium complex **2b** decomposes various dioxazolones **1** to the corresponding *N*-acyl ruthenium(nitrene) intermediates without any activation such as heating and photoirradiation and produces the desired sulfimides **4** in an excellent enantio- and chemoselective manner. Fortunately, during these studies, undesired nitrene dimerization and Curtius rearrangement were not observed. Moreover, the reaction proceeded with a high yield even at a 0.2 mol % catalyst loading to give the corresponding products. Obtained sulfimides **4** could be transformed into the corresponding sulfoximines **5** with no erosion of the enantiomeric excess.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01373.

Optimization, experimental procedure, characterization data, HPLC conditions, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from JSPS KAKENHI Grant 18H04264 in Precisely Designed Catalysis with Customized Scaffolding and The International Institute for Carbon-Neutral Energy Research (WPI-I2CNER) from MEXT, Japan, is gratefully acknowledged.

■ REFERENCES

(1) For reviews of sulfimides, see: (a) Gilchrist, T. L.; Moody, C. J. The Chemistry of Sulfilimines. *Chem. Rev.* **1977**, *77*, 409−435. (b) Furukawa, N.; Oae, S. Sulfilimines. Synthetic Applications and Potential Utilizations. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 260−

https://dx.doi.org/10.1021/acs.orglett.0c01373
Org. Lett. XXXX, XXX, XXX−XXX

270. (c) Koval, I. V. Advances in the Chemistry of Sulfimides and Related Compounds. *Sulfur Rep.* **1993**, *14*, 149−215. (d) Taylor, P. C. Sulfimides (Sulfilimines): Applications in Stereoselective Synthesis. *Sulfur Rep.* **1999**, *21*, 241−280. (e) Bizet, V.; Hendriks, C. M. M.; Bolm, C. Sulfur Imidations: Access to Sulfimides and Sulfoximines. *Chem. Soc. Rev.* **2015**, *44*, 3378−3390.

(2) (a) Takada, H.; Nishibayashi, Y.; Ohe, K.; Uemura, S. Novel Asymmetric Catalytic Synthesis of Sulfimides. *Chem. Commun.* **1996**, 931−932. (b) Takada, H.; Nishibayashi, Y.; Ohe, K.; Uemura, S.; Baird, C. P.; Sparey, T. J.; Taylor, P. C. Catalytic Asymmetric Sulfimidation. *J. Org. Chem.* **1997**, *62*, 6512−6518. (c) Nishikori, H.; Ohta, C.; Oberlin, E.; Irie, R.; Katsuki, T. Mn-salen catalyzed nitrene transfer reaction: Enantioselective imidation of alkyl aryl sulfides. *Tetrahedron* **1999**, *55*, 13937−13946. (d) Wang, J.; Frings, M.; Bolm, C. Enantioselective Nitrene Transfer to Sulfides Catalyzed by a Chiral Iron Complex. *Angew. Chem., Int. Ed.* **2013**, *52*, 8661−8665.

(3) For reviews of aziridinations, see:(a) Sweeney, J. B. Synthesis of Aziridine. In *Aziridines and Epoxides in Organic Synthesis*; Yudin, A. K., Ed.; Wiley-VCH: Weinheim, Germany, 2006; pp 117−144. (b) Karila, D.; Dodd, R. H. Recent Progress in Iminoiodone-Mediated Aziridination of Olefins. *Curr. Org. Chem.* **2011**, *15*, 1507−1538. (c) Chang, J. W. W.; Ton, T. M. U.; Chan, P. W. H. Transition-Metal-Catalyzed Aminations and Aziridinations of C−H and C = C Bonds with Iminoiodinanes. *Chem. Rec.* **2011**, *11*, 331−357. (d) Scamp, R. J.; Rigoli, J. W.; Schomaker, J. M. Chemoselective Silver-Catalyzed Nitrene Insertion Reactions. *Pure Appl. Chem.* **2014**, *86*, 381−393. (e) Damiano, C.; Intrieri, D.; Gallo, E. Aziridination of Alkenes Promoted by Iron or Ruthenium Complexes. *Inorg. Chim. Acta* **2018**, *470*, 51−67.

(4) For reviews of C−H amination, see:(a) Dauban, P.; Dodd, R. H. Catalytic C−H Amination. In *Amino Group Chemistry: From Synthesis to the Life Science*; Ricci, A., Ed.; Wiley-VCH: Weinheim, Germany, 2008; pp 55−92. (b) Collet, F.; Dodd, R. H.; Dauban, P. Catalytic C−H Amination: Recent Progress and Future Directions. *Chem. Commun.* **2009**, 5061−5079. (c) Collet, F.; Lescot, C.; Dauban, P. Catalytic C−H Amination: the Stereoselectivity Issue. *Chem. Soc. Rev.* **2011**, *40*, 1926−1936. (d) Ramirez, T. A.; Zhao, B.; Shi, Y. Recent Advances in Transition Metal-Catalyzed sp^3 C−H Amination Adjacent to Double Bonds and Carbonyl Groups. *Chem. Soc. Rev.* **2012**, *41*, 931−942. (e) Roizen, J.; Harvey, M. E.; Du Bois, J. Metal-Catalyzed Nitrogen-Atom Transfer Methods for the Oxidation of Aliphatic C−H Bonds. *Acc. Chem. Res.* **2012**, *45*, 911−922. (f) Dequirez, G.; Pons, V.; Dauban, P. Nitrene Chemistry in Organic Synthesis: Still in Its Infancy? *Angew. Chem., Int. Ed.* **2012**, *51*, 7384−7395. (g) Gephart, R. T.; Warren, T. H. Copper-Catalyzed sp^3 C−H Amination. *Organometallics* **2012**, *31*, 7728−7752. (h) Hayashi, H.; Uchida, T. Nitrene Transfer Reactions for Asymmetric C−H Amination: Recent Development. *Eur. J. Org. Chem.* **2020**, *2020*, 909−916.

(5) For reviews of nitrene transfer reaction, see: (a) Fantauzzi, S.; Caselli, A.; Gallo, E. Nitrene Transfer Reactions Mediated by Metallo-Porphyrin Complexes. *Dalton Trans.* **2009**, 5434−5443. (b) Driver, T. G. Recent Advances in Transition Metal-Catalyzed *N*-Atom Transfer Reactions of Azides. *Org. Biomol. Chem.* **2010**, *8*, 3831−3846. (c) Uchida, T.; Katsuki, T. Asymmetric Nitrene Transfer Reactions: Sulfimidation, Aziridination and C−H Amination Using Azide Compounds as Nitrene Precursors. *Chem. Rec.* **2014**, *14*, 117−129. (d) Darses, B.; Rodrigues, R.; Neuville, L.; Mazurais, M.; Dauban, P. Transition Metal-Catalyzed Iodine(III)-Mediated Nitrene Transfer Reactions: Efficient Tools for Challenging Syntheses. *Chem. Commun.* **2017**, *53*, 493−508. (e) Alderson, J. M.; Corbin, J. R.; Schomaker, J. M. Tunable, Chemo- and Site-Selective Nitrene Transfer Reactions through the Rational Design of Silver(I) Catalysis. *Acc. Chem. Res.* **2017**, *50*, 2147−2158. (f) Shimbayashi, T.; Sasakura, K.; Eguchi, A.; Okamoto, K.; Ohe, K. Recent Progress on Cyclic Nitrenoid Precursors in Transition-Metal-Catalyzed Nitrene-Transfer Reactions. *Chem. - Eur. J.* **2018**, *25*, 3156−3180.

(6) (a) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. Organic Azides: An Exploding Diversity of a Unique Class of Compounds. *Angew. Chem., Int. Ed.* **2005**, *44*, 5188−5240. (b) Clayden, J.; Donnard, M.; Lefranc, J.; Tetlow, D. J. Quaternary Centres bearing Nitrogen (α-Tertiary amines) as Products of Molecular Rearrangements. *Chem. Commun.* **2011**, *47*, 4624−4636. (c) Sagandira, C. R.; Watts, P. Synthesis of Amines, Carbamates and Amides by Multi-Step Continuous Flow Synthesis. *Eur. J. Org. Chem.* **2017**, *2017*, 6554−6565. (d) Zhou, H.; Hong, J.; Huang, J.; Chen, Z. Highly Efficient Curtius Rearrangement Approach for the Synthesis of Unsymmetrical Sulfonimidoyl Ureas. *Asian J. Org. Chem.* **2017**, *6*, 817−820. (e) Li, W.-H.; Dong, L. Synthesis of 7-Azaindole Amidated Derivatives: An Efficient Usage of Acyl Azides as the Nitrogen Source. *Adv. Synth. Catal.* **2018**, *360*, 1104−1110.

(7) Bakhoda, A.; Jiang, Q.; Badiei, Y. M.; Bertke, J. A.; Cundari, T. R.; Warren, T. H. Copper-Catalyzed C(sp3)−H Amidation: Sterically Driven Primary and Secondary C−H Site-Selectivity. *Angew. Chem., Int. Ed.* **2019**, *58*, 3421−3425.

(8) (a) Groves, J. T.; Takahashi, T. Activation and Transfer of Nitrogen from a Nitridomanganese(V) Porphyrin Complex. The Aza Analog of Epoxidation. *J. Am. Chem. Soc.* **1983**, *105*, 2073−2074. (b) Du Bois, J.; Hong, J.; Carreira, E. M.; Day, M. W. Nitrogen Transfer from a Nitridomanganese(V) Complex: Amination of Silyl Enol Ethers. *J. Am. Chem. Soc.* **1996**, *118*, 915−916. (c) Minakata, S.; Ando, T.; Nishimura, M.; Ryu, I.; Komatsu, M. Novel Asymmetric and Stereospecific Aziridination of Alkenes with a Chiral Nitridomanganese Complex. *Angew. Chem., Int. Ed.* **1998**, *37*, 3392−3394. (d) Svenstrup, N.; Bøgevig, A.; Hazell, R. G.; Jørgensen, K. A. Enantioselective α-Amination of Ketones Mediated by Chiral Nitridomanganese(V) Complexes using Ammonia as the Terminal Nitrogen Source. *J. Chem. Soc., Perkin Trans. 1* **1999**, *1*, 1559−1566. (e) Ho, C.-M.; Lau, T.-C.; Kwong, H.-L.; Wong, W.-T. Activation of Manganese Nitrido Complexes by Brønsted and Lewis Acids. Crystal Structure and Asymmetric Alkene Aziridination of a Chiral Salen Manganese Nitrido Complex. *J. Chem. Soc., Dalton Trans.* **1999**, 2411−2414.

(9) Sauer, J.; Mayer, K. K. Thermolyse und Photolyse von 3-subtituierten Δ^2-1.4.2-Dioxazolinonen-(5), Δ^2-1.4.2-Dioxazolin-thionen-(5) und 4-substituierten Δ^3-1.2.5.3-thiadioxazolin-s-oxiden. *Tetrahedron Lett.* **1968**, *9*, 319−324.

(10) (a) Bizet, V.; Buglioni, L.; Bolm, C. Light-Induced Ruthenium-Catalyzed Nitrene Transfer Reactions: A Photochemical Approach towards *N*-Acyl Sulfimides and Suloximines. *Angew. Chem., Int. Ed.* **2014**, *53*, 5639−5642. (b) Bizet, V.; Bolm, C. Sulfur Imidations by Light-Induced Ruthenium-Catalyzed Nitrene Transfer Reactions. *Eur. J. Org. Chem.* **2015**, *2015*, 2854−2860.

(11) (a) Park, Y.; Park, K. T.; Kim, J. G.; Chang, S. Mechanistic Studies on the Rh(III)-Mediated Amido Transfer Process Leading to Robust C−H Amination with a New Type of Amidating Reagent. *J. Am. Chem. Soc.* **2015**, *137*, 4534−4562. (b) Park, J.; Chang, S. Comparative Catalytic Activity of Group 9 [Cp^*M^{III}] Complexes: Cobalt-Catalyzed C−H Amidation of Arenes with Dioxazolones as Amidating Reagents. *Angew. Chem., Int. Ed.* **2015**, *54*, 14103−14107. (c) Park, Y.; Heo, J.; Baik, M.-H.; Chang, S. Why is the Ir(III)-Mediated Amido Transfer Much Faster Than the Rh(III)-Mediated Reaction ? A Combined Experimental and Computational Study. *J. Am. Chem. Soc.* **2016**, *138*, 14020−14029. (d) Park, J.; Lee, J.; Chang, S. Iterative C−H Functionalization Leading to Multiple Amidations of Anilides. *Angew. Chem., Int. Ed.* **2017**, *56*, 4256−4260. (e) Hong, S. Y.; Park, Y.; Hwang, Y.; Kim, Y. B.; Baik, M.-H.; Chang, S. Selective Formation of γ-Lactams via C−H Amidation Enabled by Tailored Iridium Catalysts. *Science* **2018**, *359*, 1016−1021. (f) Jung, H.; Schrader, M.; Kim, D.; Baik, M.-H.; Park, Y.; Chang, S. Ligand Controlled Ir-Catalyzed Regiodivergent Oxyamination of Unactivated Alkenes. *J. Am. Chem. Soc.* **2019**, *141*, 15356−15366.

(12) (a) Wang, H.; Tang, G.; Li, X. Rhodium(III)-Catalyzed Amidation of Unactivated C(sp^3)−H Bonds. *Angew. Chem., Int. Ed.* **2015**, *54*, 13049−13052. (b) Liang, Y.; Liang, Y.-F.; Tang, C.; Yuan, Y.; Jiao, N. Cationic Cobalt(III)-Catalyzed Aryl and Alkenyl C−H Amidation: A Mild Protocol for the Modification of Purine Derivatives. *Chem. - Eur. J.* **2015**, *21*, 16395−16399. (c) Hermann,

https://dx.doi.org/10.1021/acs.orglett.0c01373
Org. Lett. XXXX, XXX, XXX−XXX

G. N.; Bolm, C. Mechanochemical Rhodium(III)-Catalyzed C−H Bond Amidation of Arenes with Dioxazolones under Solventless Conditions in a Ball Mill. *ACS Catal.* **2017**, *7*, 4592−4596. (d) Tan, P. W.; Mak, A. M.; Sullivan, M. B.; Dixon, D. J.; Seayad, J. Thioamide-Directed Cobalt(III)-Catalyzed Selective Amidation of C(sp^3)−H Bonds. *Angew. Chem., Int. Ed.* **2017**, *56*, 16550−16554. (e) Huang, D.-Y.; Yao, Q.-J.; Zhang, S.; Xu, X.-T.; Zhang, K.; Shi, B.-F. Amide-Directed Cobalt(III)-Catalyzed C−H Amidation of Ferrocenes. *Org. Lett.* **2019**, *21*, 951−954. (f) Lei, H.; Rovis, T. Ir-Catalyzed Intermolecular Branch-Selective Allylic C−H Amidation of Unactivated Terminal Olefins. *J. Am. Chem. Soc.* **2019**, *141*, 2268−2273. (g) Mi, X.; Feng, W.; Pi, C.; Cui, X. Iridium(III)-Catalyzed C−H Amidation of Nitrones with Dioxazolones. *J. Org. Chem.* **2019**, *84*, 5305−5312. (h) Knecht, T.; Mondal, S.; Ye, J.-H.; Das, M.; Glorius, F. Intermolecular, Branch-Selective, and Redox-Neutral Cp*Ir^{III}-Catalyzed Allylic C−H Amidation. *Angew. Chem., Int. Ed.* **2019**, *58*, 7117−7121. (i) Samanta, S.; Mondal, S.; Ghosh, D.; Hajra, A. Rhodium-Catalyzed Directed C−H Amidation of Imidazoheterocycles with Dioxazolones. *Org. Lett.* **2019**, *21*, 4905−4909. (j) Li, J.; Zhang, S.; Lonka, M. R.; Zhang, J.; Zou, H. Rhodium(III)-Catalyzed Cascade Reactions of Benzoic Acids with Dioxazolones: Discovery of 2,5-Substituted Benzoxazinones as AIE Molecules. *Chem. Commun.* **2019**, *55*, 11203−11206.

(13) (a) Fukagawa, S.; Kato, Y.; Tanaka, R.; Kojima, M.; Yoshino, T.; Matsunaga, S. Enantioselective C(sp3)−H Amidation of Thioamides Catalyzed by a Cobalt^{III}/Chiral Carboxylic Acid Hybrid System. *Angew. Chem., Int. Ed.* **2019**, *58*, 1153−1157. (b) Sekine, D.; Ikeda, K.; Fukagawa, S.; Kojima, M.; Yoshino, T.; Matsunaga, S. Chiral 2-Aryl Ferrocene Carboxylic Acids for the Catalytic Asymmetric C(sp^3)−H Activation of Thioamides. *Organometallics* **2019**, *38*, 3921−3926. (c) Fukagawa, S.; Kojima, M.; Yoshino, T.; Matsunaga, S. Catalytic Enantioselective Methylene C(sp^3)−H Amidation of 8-Alkylquinolines Using a Cp*Rh^{III}/Chiral Carboxylic Acid System. *Angew. Chem., Int. Ed.* **2019**, *58*, 18154−18158. (d) Xing, Q.; Chan, C.-M.; Yeung, Y.-W.; Yu, W.-Y. Ruthenum(II)-Catalyzed Enantioselective γ-Lactams Formation by Intermolecular C−H Amidation of 1,4,2-Dioxazol-5-ones. *J. Am. Chem. Soc.* **2019**, *141*, 3849−3849. (e) Liu, Y.-H.; Li, P.-X.; Yao, Q.-J.; Zhang, Z.-Z.; Huang, D.-Y.; Le, M. D.; Song, H.; Liu, L.; Shi, B.-F. Cp*Co(III)/MPAA-Catalyzed Enantioselective Amidation of Ferrocenes Directed by Thioamides under Mild Conditions. *Org. Lett.* **2019**, *21*, 1895−1899.

(14) (a) Park, Y.; Chang, S. Asymmetric Formation of γ-Lactams via C−H Amidation Enabled by Chiral Hydrogen-Bond-Donor Catalysts. *Nat. Catal.* **2019**, *2*, 219−227. (b) Wang, H.; Park, Y.; Bai, Z.; Chang, S.; He, G.; Chen, G. Iridium-Catalyzed Enantioselective C(sp^3)−H Amidation Controlled by Attractive Noncovalent Interactions. *J. Am. Chem. Soc.* **2019**, *141*, 7194−7201.

(15) van Vliet, K. M.; de Bruin, B. Dioxazolones: Stable Substrates for the Catalytic Transfer of Acyl Nitrenes. *ACS Catal.* **2020**, *10*, 4751−4769.

(16) (a) Murakami, M.; Uchida, T.; Katsuki, T. Ru(salen)-Catalyzed Asymmetric Sulfimidation using Arylsulfonyl Azide. *Tetrahedron Lett.* **2001**, *42*, 7071−7074. (b) Tamura, Y.; Uchida, T.; Katsuki, T. Highly Enantioselective (OC)Ru(salen)-Catalyzed Sulfimidation using *N*-Alkoxycarbonyl Azide as Nitrene Precursor. *Tetrahedron Lett.* **2003**, *44*, 3301−3303. (c) Uchida, T.; Tamura, Y.; Ohba, M.; Katsuki, T. Mechanism of Asymmetric Sulfimidation with *N*-Alkoxycarbonyl Azide in the Presence of (OC)Ru(salen) Complex. *Tetrahedron Lett.* **2003**, *44*, 7965−7968.

(17) (a) Omura, K.; Murakami, M.; Uchida, T.; Irie, R.; Katsuki, T. Enantioselective Aziridination and Amination using *p*-Toluenesulfonyl Azide in the Presence of Ru(salen)(CO) Complex. *Chem. Lett.* **2003**, *32*, 354−355. (b) Omura, K.; Uchida, T.; Irie, R.; Katsuki, T. Design of a Robust Ru(salen) Complex: Aziridination with Improved Turnover Number using *N*-Arylsulfonyl Azide as Precursors. *Chem. Commun.* **2004**, 2060−2061. (c) Fukunaga, Y.; Uchida, T.; Ito, Y.; Matsumoto, K.; Katsuki, T. Ru(CO)-salen-Catalyzed Synthesis of Enantiopure Aziridinyl Ketones and Formal Asymmetric Synthesis of (+)-PD 128907. *Org. Lett.* **2012**, *14*, 4658−4661. (d) Kim, C.; Uchida, T.; Katsuki, T. Asymmetric Olefin Aziridination using a Newly Designed Ru(CO)(salen) Complex as the Catalyst. *Chem. Commun.* **2012**, *48*, 7188−7190.

(18) Nishioka, Y.; Uchida, T.; Katsuki, T. Enantio- and Regioselective Intermolecular Benzylic and Allylic C−H Bond Amination. *Angew. Chem., Int. Ed.* **2013**, *52*, 1739−1742.

(19) Further optimizations of reaction conditions are described in the Supporting Information.

(20) Bolm, C.; Hackenberger, C. P. R.; Simić, O.; Verrucci, M.; Müller, D.; Bienewald, F. A Mild Synthetic Procedure for the Preparation of *N*-Alkylated Sulfoximines. *Synthesis* **2002**, *2002*, 879−887.

(21) Hendriks, C. M. M.; Lamers, P.; Engel, J.; Bolm, C. Sulfoxide-to-Sulfimine Conversions: Use of Modified Burgess-Type Regents. *Adv. Synth. Catal.* **2013**, *355*, 3363−3368.

https://dx.doi.org/10.1021/acs.orglett.0c01373
Org. Lett. XXXX, XXX, XXX−XXX