A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition GDCh Chemie

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Accepted Article

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201808892
Angew. Chem. 10.1002/ange.201808892

Link to VoR: http://dx.doi.org/10.1002/anie.201808892
http://dx.doi.org/10.1002/ange.201808892

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10.1002/anie.201808892

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Revisiting Arene C(sp^2)–H Amidation via Intramolecular Transfer of Iridium Nitrenoids: Evidence for a Spirocyclization Pathway

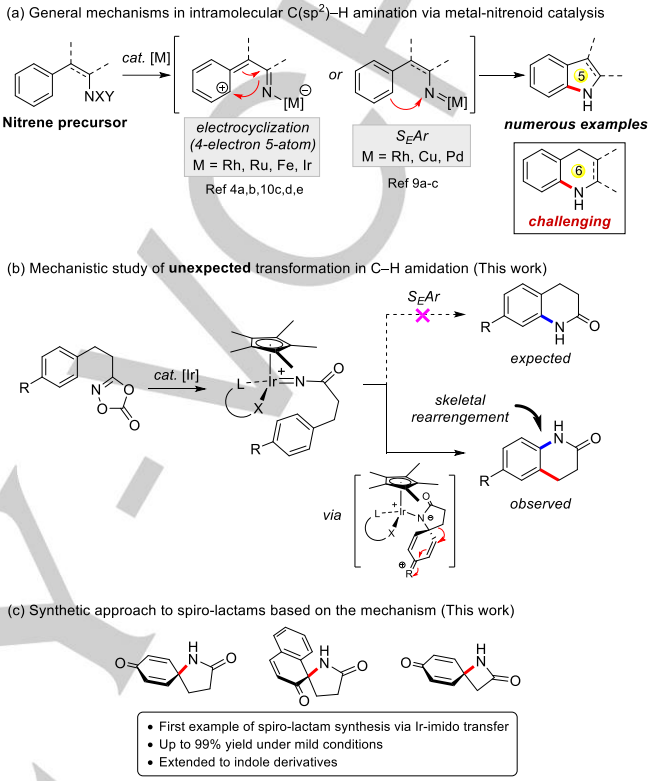
Yeongyu Hwang,[a,b,+] Yoonsu Park,[a,b,+] Yeong Bum Kim,[a,b] Dongwook Kim,[b,a] and Sukbok Chang[b,a,*]

Abstract: Two mechanistic pathways, i.e. electrocyclization and electrophilic aromatic substitution, are operative in most of intramolecular C–H amination reactions via metal nitrenoid catalysis. We now report an alternative mechanistic scaffold that benzo-fused δ-lactams can be obtained selectively. Integrated experimental and computational analysis revealed that the reaction proceeds via a key spirocyclization step followed by a skeletal rearrangement. Based on this mechanistic insight, a new synthetic route to spiro-lactams has been developed.

The development of selective C–H oxidation is of great interest in the synthetic and medicinal chemistry.[1] In the nitrogen-atom transfer reactions,[2] the success is frequently dependent on leveraging highly reactive metal-nitrenoid intermediate to the desired transformation with effective suppression of decomposition pathways. While a number of elegant methods have been developed with several amino precursors including nitrogen ylides,[3] organic azides,[4] and hydroxylamines,[5] construction of unprotected cyclic amides has been a remaining challenge due to the uncontrollable decomposition of carbonylnitrene intermediates to isocyanates via the Curtius-type rearrangement.[6] In this regard, our group recently demonstrated that cyclopentadienyl (Cp*)-based iridium catalysts can prevent such a side pathway, thus facilitating the C(sp^3)–H functionalization via a closed-shell pathway.[7]

We initially hypothesized that aromatic C(sp^2)–H amidation might be viable because singlet nitrenoid species could be engaged in a two-electron process. Indeed, two mechanistic working modes are widely accepted in the aromatic amination reactions (Scheme 1a). Driver and co-workers proposed a 4-electron-5-atom electrocyclization pathway in the dirhodium-catalyzed cyclization of aryl or styryl azides,[4a,b] which exclusively gives 5-membered aza-heterocycles.[8] Another pathway includes an electrophilic aromatic substitution (S_EAr), mainly enabled by electron-rich substituents on the arene moiety.[9] The Falck group reported an unique example that offers 6-membered heterocycles with compelling evidence on the S_EAr mechanism.[5b]

While we briefly communicated the viability of aromatic C–H amidation with Cp*Ir(III) catalysts in our recent report,[7] generality of the reaction was not explored in detail and consequently, the origin on the efficiency and selectivity was barely understood. Describe herein is a detailed analysis on the arene C–H amidation, where a new mechanistic insight is elucidated.



Scheme 1. Identification of a spirocyclization pathway in iridium-catalyzed C–H amidation enables the construction of spiro-lactam scaffold.

When a substrate bearing reactive sp^2 C–H bonds was subjected to the amidation conditions, to our surprise, a δ-lactam product was obtained selectively with unexpected *skeletal rearrangement* (Scheme 1b), suggesting that the operating mode is different from the conventionally accepted pathways. Indeed, our experimental and theoretical analysis revealed that a tandem process of spirocyclization and subsequent structural rearrangement via C–C bond migration is operative. Based on this mechanistic insight, a preparative method for unprotected spiro-lactams is now established (Scheme 1c), representing the first example of utilizing the metal-nitrenoid catalysis.

We commenced our study by subjecting a dioxazolone substrate **1** to the C–H amidation conditions with expectation of the formation of **2** via the widely-accepted S_EAr pathway (Scheme 2). However, no cyclization product was formed with the iridium catalyst **Ir1** that was the most effective for the aliphatic *sp^3* C–H amidation leading to 5-memberd lactams.[7] This result led us to screen an additional array of catalysts for the *sp^2* C–H amidation. Pleasingly, we observed that *κ^2-N,O* chelators exhibited significant improvement in reactivity (**Ir2** to **Ir5**). In particular, a catalyst bearing 8-alkoxyquinoline ligand (**Ir5**) was notable, and, moreover, the introduction of two chloro groups at the C5,7-position in the same ligand skeleton (**Ir6**) resulted in even higher catalytic reactivity in hexafluoro-2-propanol (HFIP) solvent.

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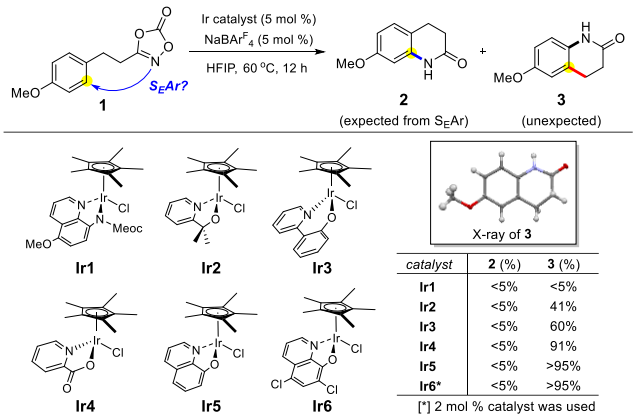
To our surprise, a careful analysis of the obtained product including single crystal XRD indicated that it is an isomeric 6-membered lactam (**3**) rather than the expected one (**2**).[16] This result suggested that the present cyclization proceeds via a pathway that is distinct to the S_EAr route.[5b,9] This unexpected outcome led us to pursue the mechanistic understanding with subsequent investigations on the substrate scope and synthetic applications. It is noteworthy that the facile formation of 6-membered azacyclic compounds has been regarded as a challenge in the metal-nitrenoid transfer chemistry.[4a,b,9,10]



catalyst	2 (%)	3 (%)
Ir1	<5%	<5%
Ir2	<5%	41%
Ir3	<5%	60%
Ir4	<5%	91%
Ir5	<5%	>95%
Ir6*	<5%	>95%

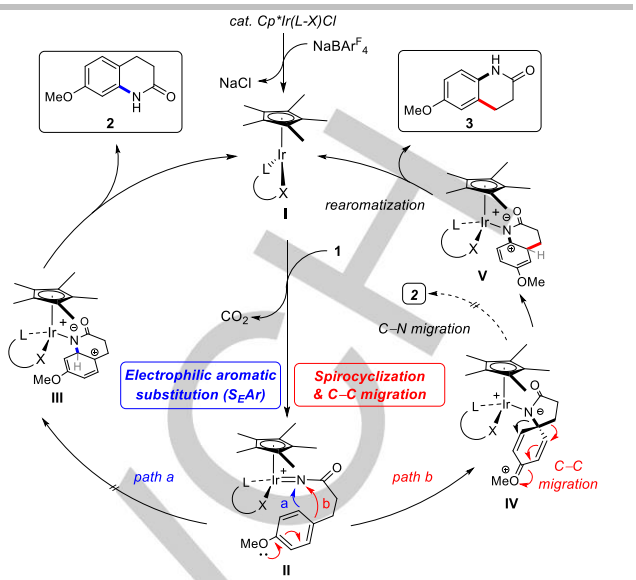
[*] 2 mol % catalyst was used

Scheme 2. Catalyst optimization and key observations. Reaction conditions: **1** (0.05 mmol), Ir catalyst (5 mol %), and $NaBAr^F_4$ (5 mol %) in HFIP (0.6 mL). NMR yields of the crude reaction mixture are shown.

To rationalize the unexpected regioselectivity observed in the initial experiment, several mechanistic scenarios were taken into account (Scheme 3). Upon the generation of a key Ir-nitrenoid intermediate (**II**),[7] the S_EAr mechanism can be firstly considered (path a), but it will give only a lactam product **2** that was not detected in the experiment. Another generally-accepted pathway involving electrocyclization (Scheme 1a) is also less likely, since the required π-conjugation is not allowed in this substrate.[4a,b,8,10e] Because the obtained product **3** shows a skeletal rearrangement in the pre-existing (phenyl-alkyl) C–C bond (migrated from *para*- to OMe in **1** to *meta*- in product **3**), we proposed an alternative pathway that can furnish this unexpected isomer.

Inspired by a *metal-free* amination utilizing nitrenium ions to give *N*-protected spiro-lactams or cyclic amides,[11] we supposed a pathway involving iridium-mediated spirocyclization of **II** at the electron-rich *ipso*-carbon to generate a spiro-amido intermediate **IV**. Subsequent ring-expansion via either C–N or C–C bond migration followed by rearomatization would provide lactam **2** or **3**, respectively (Scheme 3, right side). Of note, a resultant product from the C–N bond migration will be **2**, which is the same compound that can be obtained from the direct S_EAr. Given that only **3** was exclusively obtained without detecting **2**, we speculated that the C–C migration will be favored over the C–N rearrangement under the present iridium catalytic conditions.

To validate the mechanistic hypothesis, reaction energy profiles for each working mode were evaluated by DFT calculations. After forming a catalyst-substrate adduct **I'**, oxidative decarboxylation requires 20.8 kcal/mol of activation energy to generate Ir-nitrenoid species **II**. While **II** may traverse **II-TS1** via direct S_EAr pathway with 9.7 kcal/mol of barrier (dashed lines), spirocyclization pathway (**II-TS2**) to spiro-amido intermediate **IV** is kinetically more accessible in 5.3 kcal/mol (bold line).



Scheme 3. Possible mechanisms to account for the unexpected rearrangement.

Spiro-lactam moiety in complex **IV** may subsequently undergo two distinctive skeletal rearrangements via either C–C (red line) or C–N (blue line) bond cleavage. TS calculations revealed that the C–C migration is kinetically favored over the C–N bond cleavage (0.93 kcal/mol). Furthermore, more importantly, the C–N migration is thermodynamically uphill process, whereas the C–C rearrangement gives more stable intermediate. The C–N migrated complex **III**, which is the same intermediate via S_EAr pathway, is less stable than its former complex **IV** by 9.3 kcal/mol, thus making this interconversion reversible. As soon as **III** is formed, the reverse reaction to **IV** would proceed through **IV-TS$_{CN}$** with only 10.0 kcal/mol of barrier. In sharp contrast, the C–C migrated complex **V** is more stable than **IV** by 4.3 kcal/mol, and will give the experimentally-observed product **3** via subsequent decoordination/aromatization. This notable thermodynamic difference would be mainly due to direct stabilization of generating carbocation by migrated nitrogen atom in complex **V**.[12] The computational analysis pinpointed that the stability of migration intermediates are important in the selective structural rearrangement.

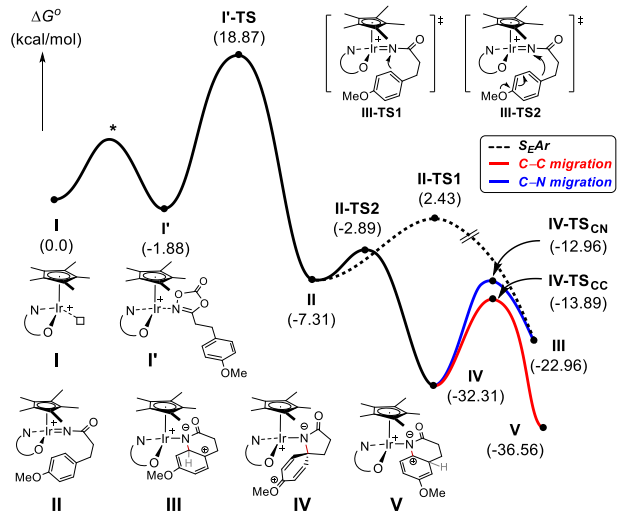


Figure 1. Reaction Energy Profiles for potential mechanisms at M06/SDD+6-311+G**/PCM(dichloromethane)//B3LYP/Lanl2dz+6-31G** level of theory.

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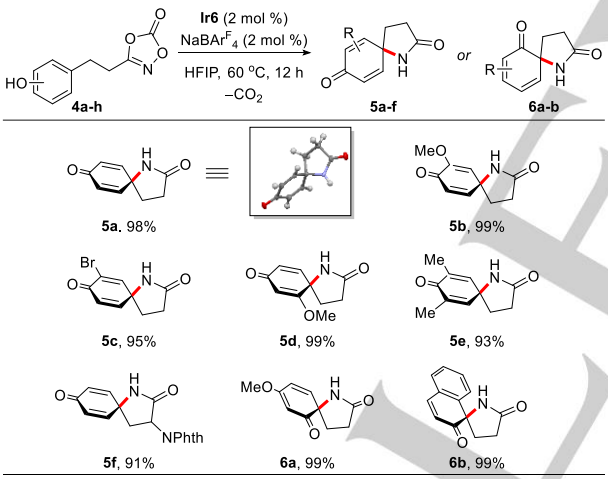
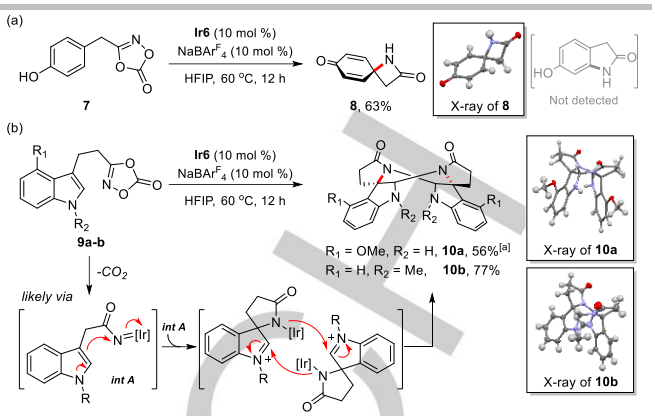
The intermediacy of complex **IV** in the computational study led us to attempt to isolate the putative spiro-lactam compound, which itself is also of synthetic and medicinal interest.[13] We envisaged that a dioxazolone substrate bearing *para*-hydroxyl in lieu of methoxy group will allow the formation of aza-spirodienone product based on the proposed pathway. To our delight, a targeted spiro-lactam product **5a** could be isolated in excellent yield by using 2 mol % of **Ir6** (Scheme 4). The structure of **5a** was confirmed by X-ray crystallographic analysis.[16] Again, this result is fully consistent with our mechanistic proposal on the spiro-lactam intermediacy (**IV** in Scheme 3).

To see the generality of this reaction, a range of substrates having additional substituents were further examined under the optimal catalytic conditions. The dearomative spirocyclization took place in a highly efficient manner with phenol-based dioxazolones with MeO- or Br groups (**5b** and **5c**, respectively). Derivatives having the same substituent at a different position (**4d**) or bearing multiple substituents (**4e**) also underwent the cyclization smoothly. A substrate prepared from *N*-protected tyrosine was facile for the current cyclization to afford **5f** in 91% yield. Significantly, reactions of *ortho*-phenol or *ortho*-naphthol substrates were quantitative to give the corresponding spiro-lactams **6a** and **6b**, respectively. To our best knowledge, it represents the first synthetic approach to spiro-lactams via a metal-nitrenoid transfer process.[14] Importantly, free amides can be directly accessed by our protocols, while most of classical approaches require specific *N*-protecting groups.[11a,b]

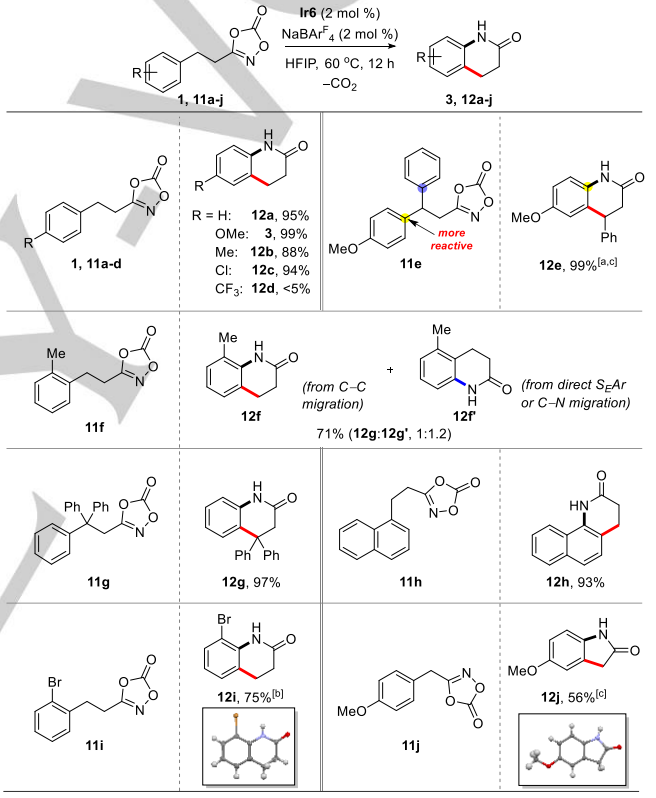


Scheme 4. Substrate scope of dearomative spirocyclization reaction. Reaction conditions: substrate (0.1 mmol), Ir catalyst (2 mol %), and NaBAr$^F_4$ (2 mol %) in HFIP (1.2 mL).

The present procedure was further extended to the formation of 4-membered spiro-lactams (Scheme 5a). Indeed, we were pleased to observe that the highly strained spiro-β-lactam **8** with 10 mol % of the catalyst. Of note, a 5-membered cyclic amide that can be formed via a direct S_EAr pathway was not detected in the present reaction. The current procedure was found to be successfully applied to the reaction of indole derivatives (Scheme 5b). In this case, highly condensed dispiro-indoline products were isolated under the identical conditions (**10a**–**b**), and their structures were confirmed by X-ray crystallographic analysis.[16] These structurally unique compounds are likely formed via an analogous dearomative spirocyclization followed by dimerization of the resultant intermediate, although the dimerization mechanism is remained elusive at the present stage.



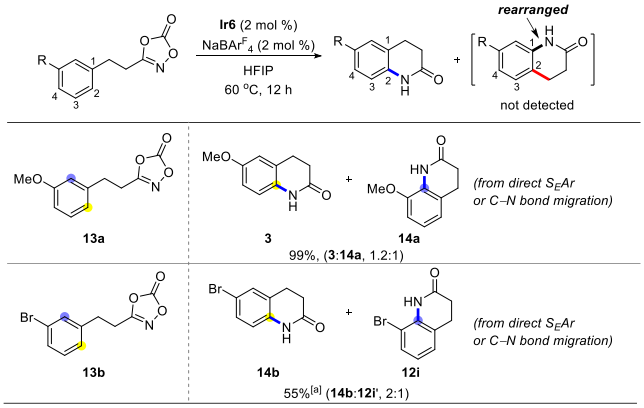
Scheme 5. Extension to β-lactam and dispiro-indoline synthesis. Reaction conditions: substrate (0.1 mmol), Ir catalyst (10 mol %), and NaBAr$^F_4$ (10 mol %) in HFIP (1.2 mL). [a] $C_6H_5CF_3$ was used as a solvent.



Scheme 6. Substrate scope of benzo-fused δ-lactams with skeletal rearrangements. Reaction conditions: substrate (0.1 mmol), Ir catalyst (2 mol %), and NaBAr$^F_4$ (2 mol %) in HFIP (1.2 mL). [a] CH_2Cl_2 was used as a solvent. [b] 5 Mol % catalyst was used. [c] 10 Mol % of catalyst was used.

Having well understood the details on the amidation pathways, scope of the substrates bearing substituents other than a hydroxyl group was next investigated (Scheme 6). Various phenyl substituents, such as alkoxy, alkyl, and halide groups, were all compatible, and provided corresponding benzo-fused δ-lactams via the analogous tandem process of spirocyclization and following the C–C bond migration (**12a**–**12c**). However, the reaction with CF_3 substituent (**11d**) was not successful, possibly due to its electronic property. The cyclization was found to be selective in that a more electron-rich phenyl was reacted exclusively (**12e**). On the other hand, when a methyl group is substituted at the *ortho*-position, the cyclization gave a mixture of two isomeric products **12f** and **12f'** (1:1.2), suggesting that competing pathways (direct S_EAr or C–N bond migration) might

be simultaneously operative in a specific type of substrates (*vide infra*). A sterically congested substrate having triphenyl moiety underwent the cyclization without difficulty leading to **12g** in excellent yield. Naphthylethyl dioxazolone was also efficiently amidated to afford tricyclic dihydroquinolinone (**12h**). Reaction of *ortho*-bromo-substituted phenylethyl dioxazolone proceeded in satisfactory yield (**12i**). Significantly, an analogous pathway is likely operative in a 5-membered cyclization of **11j**, and a skeletal-rearranged indolinone product **12j** was obtained in moderate yield. It needs to be emphasized that this result is consistent with the observation of the 4-membered spirocyclization (**7** in Scheme 5a).



Scheme 7. Substrates scope without skeletal rearrangement. Reaction conditions: substrate (0.1 mmol), Ir catalyst (2 mol %), and NaBAr$^F_4$ (2 mol %) in HFIP (1.2 mL). [a] 5 Mol % of catalyst was used.

On the other hand, a certain type of substrates was shown to give benzolactams without a skeletal rearrangement (Scheme 7). For example, a *meta*-methoxy-substituted phenylethyl dioxazolone (**13a**) was cyclized quantitatively to give two regioisomers **3** and **14a** (1.2:1). These products can be formed via either direct S_EAr pathway or a tandem process of spiro-cyclization and following C–N bond migration. Likewise, bromo-substituted substrate **13b** showed a similar product distribution pattern (**14b** and **12i**). Although, at the current stage, we are unable to distinguish which pathway is mainly operative for these substrates, computational analysis with substrate **13a** revealed that S_EAr path is a bit more favorable than the spirocyclization.[15]

In conclusion, we have elucidated the mechanistic details of iridium-catalyzed arene C–H amidation. Experimental and computational analysis revealed that the reaction proceeds via a tandem process of spirocyclization and following C–C bond migration instead of widely accepted pathways. Based on the mechanistic findings, a highly efficient Ir-catalyzed synthetic route to spiro-lactams and benzolactams is now developed for the first time. This preparative process is anticipated to find its utility in synthetic and medicinal chemistry.

Acknowledgements

This research was supported by the Institute for Basic Science (IBS-R010- D1). Single crystal x-ray diffraction experiments of compound **3**, **8**, and **10a** were performed at the BL2D-SMC in Pohang Accelerator Laboratory with synchrotron radiation.

Keywords: C–H amidation • spiro-lactams • skeletal rearrangement • iridium catalysis

[1] For selected reviews on the C–H functionalization, see: a) H. M. L. Davies, J, R. Manning, *Nature* **2008**, *451*, 417; b) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev*. **2010**, *110*, 624; c) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev*. **2012**, *112*, 5879; d) K. M. Engle, T.-S. Mei, M. Wasa, J.-Q. Yu, *Acc. Chem. Res.* **2012**, *45*, 788; e) J. F. Hartwig, *Acc. Chem. Res*. **2012**, *45*, 864; f) S. R. Neufeldt, M. S. Sanford, *Acc. Chem. Res.* **2012**, *45*, 936; g) G. Y. Song, F. Wang, X. W. Li, *Chem. Soc. Rev*. **2012**, *41*, 3651; h) N. Kuhl, N. Schroder, F. Glorius, *Adv. Synth. Catal*. **2014**, *356*, 1443; i) O. Daugulis, J. Roane, L. D. Tran, *Acc. Chem. Res.* **2015**, *48*, 1053; j) C. Borie, L. Ackermann, M. Nechab, *Chem. Soc. Rev*. **2016**, *45*, 1368; k) T. Gensch, M. N. Hopkinson, F. Glorius, J. Wencel-Delord, *Chem. Soc. Rev.* **2016**, *45*, 2900.

[2] For selected reviews on the C–H amination, see: a) A. Armstrong, J. C. Collins, *Angew. Chem. Int. Ed*. **2010**, *49*, 2282; *Angew. Chem*. **2010**, *122*, 2332; b) J. L. Roizen, M. E. Harvey, J. Du Bois, *Acc. Chem. Res.* **2012**, *45*, 911; c) G. Dequirez, V. Pons, P. Dauban, *Angew. Chem. Int. Ed.* **2012**, *51*, 7384; *Angew. Chem.* **2012**, *124*, 7498; d) M.-L. Louillat, F. W. Patureau, *Chem. Soc. Rev*. **2014**, 43, 901; e) J. Jiao, K. Murakami, K. Itami, *ACS Catal.* **2016**, *6*, 610; f) Y. Park, Y. Kim, S. Chang, *Chem. Rev.* **2017**, *117*, 9247; g) N. Sauermann, T. H. Meyer, Y. Qiu, L. Ackermann, *ACS Catal.* **2018**, *8*, 7086.

[3] a) X.-Q. Yu, J.-S. Huang, X.-G. Zhou, C.-M. Che, *Org. Lett.* **2000**, *2*, 2233; b) S. M. Paradine, J. R. Griffin, J. Zhao, A. L. Petronico, S. M. Miller, M. C. White, *Nat. Chem.* **2015**, 7, 987; c) N. D. Chiappini, J. B. C. Mack, J. Du Bois, *Angew. Chem. Int. Ed.* **2018**, 57, 4956; *Angew. Chem.* **2018**, *130*, 5050.

[4] a) B. J. Stokes, H. Dong, B. E. Leslie, A. L. Pumphrey, T. G. Driver, *J. Am. Chem. Soc.* **2007**, *129*, 7500; b) M. Shen, B. E. Leslie, T. G. Driver, *Angew. Chem. Int. Ed*. **2008**, *47*, 5056; *Angew. Chem.* **2008**, *120*, 5134; c) Q. Nguyen, K. Sun, T. G. Driver, *J. Am. Chem. Soc.* **2012**, *134*, 7262; d) E. T. Hennessy, T. A. Betley, *Science* **2013**, *340*, 591; e) C. K. Prier, R. K. Zhang, A. R. Buller, S. Brinkmann-Chen, F. H. Arnold, *Nat. Chem*. **2017**, *9*, 629.

[5] a) A. John, J. Byun, K. M. Nicholas, *Chem. Commun*. **2013**, *49*, 10965; b) M. P. Paudyal, A. M. Adebesin, S. R. Burt, D. H. Ess, Z. Ma, L. Kürti, J. R. Falck, *Science* **2016**, *353*, 1144.

[6] a) E. F. V. Scriven, K. Turnbull, *Chem. Rev*. **1988**, *88*, 297; b) S. Bräse, C. Gil, K. Knepper, V. Zimmermann, *Angew. Chem. Int. Ed*. **2005**, *44*, 5188; *Angew. Chem.* **2005**, *117*, 5320; c) D. Li, T. Wu, K. Liang, C. Xia, *Org. Lett*. **2016**, *18*, 2228.

[7] S. Y. Hong, Y. Park, Y. Hwang, Y. B. Kim, M.-H. Baik, S. Chang, *Science* **2018**, *359*, 1016.

[8] B. J. Stokes, K. J. Richert, T. G. Driver, *J. Org. Chem*. **2009**, *74*, 6442.

[9] a) G. Brasche, S. Buchwald, *Angew. Chem. Int. Ed*. **2008**, *47*, 1932; *Angew. Chem*. **2008**, *120*, 1958; b) S. Chiba, L. Zhang, S. Sanjaya, G. Y. Ang, *Tetrahedron* **2010**, *66*, 5692; c) R. Singh, K. Nagesh, M. Parameshwar, *ACS Catal*. **2016**, *6*, 6520.

[10] For selected examples of the five-membered ring synthesis via outer-sphere pathway, see: a) K. Isomura, K. Uto, H. Taniguchi, *J. Chem. Soc., Chem. Commun*. **1977**, 664; b) S. Chiba, G. Hattori, K. Narasaka, *Chem. Lett.* **2007**, *36*, 52; c) W. G. Shou, J. Li, T. Guo, Z. Lin, G. Jia, *Organometallics* **2009**, *28*, 6847; d) I. T. Alt, B. Plietker, *Angew. Chem. Int. Ed*. **2016**, *55*, 1519; *Angew. Chem*. **2016**, *128*, 1542; e) S. K. Das, S. Roy, H. Khatua, B. Chattopadhyay, *J. Am. Chem. Soc*. **2018**, *140*, 8429.

[11] a) S. A. Glover, A. Goosen, C. V. McClei, J. L. Schoonraad, *Tetrahedron* **1987**, *43*, 2577; b) M. Kawase, T. Kitamura, Y. Kikugawa, *J. Org. Chem*. **1989**, *54*, 3394; c) D. Liang, W. Yu, N. Nguyen, J. R. Deschamps, G. H. Imler, Y. Li, A. D. MacKerell, Jr., C. Jiang, F. Xue, *J. Org. Chem*. **2017**, *82*, 3589.

[12] a) V. P. Vitullo, E. A. Logue, *J. Org. Chem*. **1972**, *37*, 3339; b) J. N. Marx, J. C. Argyle, L. R. Norman, *J. Am. Chem. Soc*. **1974**, *96*, 2121; c) A. Fischer, G. N. Henderson, *J. Chem. Soc., Chem. Commun*. **1979**, 279.

[13] a) D. J. Wardrop, A. Basak, *Org. Lett*. **2001**, *3*, 1053; b) D. J. Wardrop, M. S. Burge, W. Zhang, J. A. Ortı´z, *Tetrahedron Lett.* **2003**, *44*, 2587.

[14] For selected examples of the electrophilic nitrogen triggered C–N bond forming dearomatization, see: a) K. Tanaka, Y. Mori, K. Narasaka, *Chem. Lett*. **2004**, *33*, 26; b) J. J. Farndon, X. Ma, J. F. Bower, *J. Am. Chem. Soc*. **2017**, *139*, 14005; c) X. Ma, J. J. Farndon, T. A. Young, N. Fey, J. F. Bower, *Angew. Chem. Int. Ed*. **2017**, *56,* 14531; *Angew. Chem*. **2017**, *129*, 14723.

[15] See the Supporting Information for details

[16] CCDC 1859413 (**3**), 1859414 (**5a**), 1859411 (**8**), 1859416 (**10a**), 1859415 (**10b**), 1859410 (**12i**), and 1859412 (**12j**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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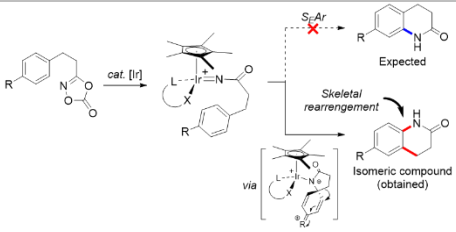

A tandem process of spirocyclization and subsequent skeletal rarrangement was elucidated as a working mode in the Ir-catalzyed arene C(sp^2)–H amidation of phenylalkyl dioxazolones. This mechanistic insight led us to develop an Ir-catalzyed efficient and selective synthetic route to spiro-lactams and benzolactams.

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