OL | Organic Letters

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

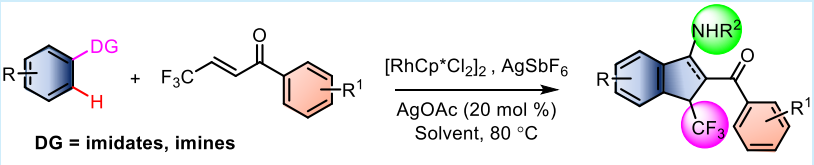
pubs.acs.org/OrgLett

Rh(III)-Catalyzed [3 + 2] Annulation via C−H Activation: Direct Access to Trifluoromethyl-Substituted Indenamines and Aminoindanes

Bharatkumar Chaudhary, Prashant Auti, Suchita Dattatray Shinde, Prasanna Anjaneyulu Yakkala, Deepesh Giri, and Satyasheel Sharma*

Department of Medicinal Chemistry, National Institute of Pharmaceutical Education and Research - Ahmedabad, Gandhinagar, Gujarat 382355, India

Supporting Information



ABSTRACT: The rhodium(III)-catalyzed direct C−H addition and annulation of benzimidates and aldimines with *β*-(trifluoromethyl)-*α*,*β*-unsaturated ketones is described. This protocol provides the facile and efficient formation of various trifluoromethyl-containing indenamines or aminoindanes in moderate to high yields.

Indenes and indanes are very important carbocyclic derivatives that are found in various natural products and pharmaceutically active molecules.[1] Moreover, they find application in organometallics and material science.[2] In particular, aminoindene/indane derivatives have shown important biological activities,[3] such as glutamate receptor antagonist, calcium antagonist, and anti-Parkinson. In addition, trifluoromethyl-containing indane acts as a selective CB2 ligand (Figure 1).[4]

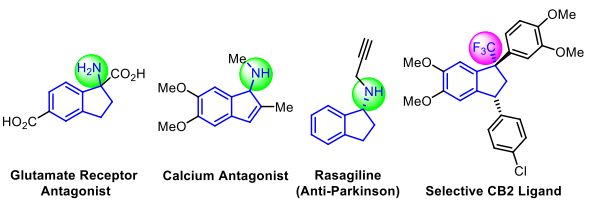


Figure 1. Selected examples of bioactive aminoindanes and (trifluoromethyl)indanes.

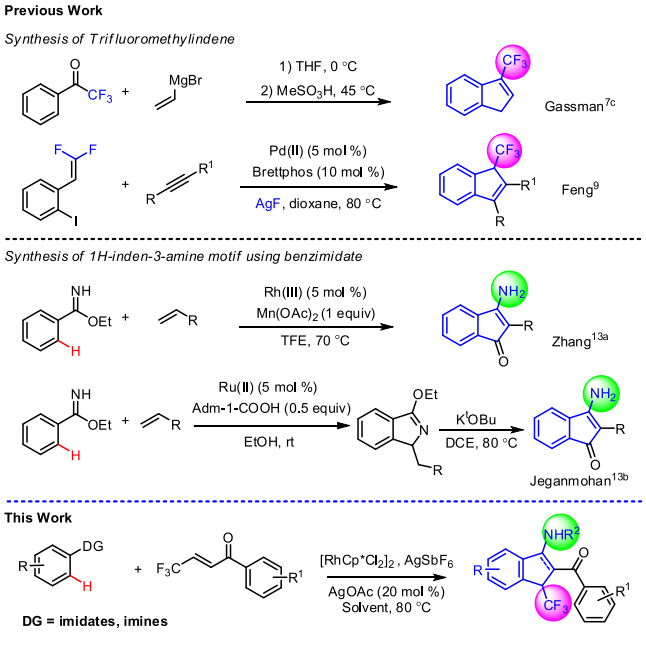
Introduction of perfluoroalkyl groups brings stimulating changes in the electronics of the parent molecule; in addition, incorporation of a trifluoromethyl group into the bioactive molecules can have a variety of overall positive effects, such as making them more selective, potent, highly efficacious, or easier to administer.[5] Despite many synthetic advances for the synthesis of indene derivatives,[6] the synthetic approach for 1-(trifluoromethyl)-1*H*-indenes is scarcely reported.[7] For example, it can be synthesized by nucleophilic trifluoromethylation of indenones or by using Grignard reagents with 2,2,2-trifluoroacetophenone followed by intramolecular cyclization[7c] or by using intramolecular cyclization of trifluoromethyl-containing enones and allyl alcohols.[8] Recently, Feng and co-workers have demonstrated Pd-catalyzed [3 + 2] annulation of (2,2-difluorovinyl)-2-iodoarenes with internal alkynes triggered by a fluoride nucleophilic addition to produce 1-(trifluoromethyl)-1*H*-indenes (Scheme1).[9] Thus, development of an efficient, straightforward route to the 1-(trifluoromethyl)-1*H*-indenes framework is highly desired.

Transition-metal-catalyzed C−H annulation reactions have been of considerable interest for the synthesis of various heterocycles and carbocycles of biological and material importance.[10] To this end, various indanes/indenes derivatives have been synthesized using C−H annulation reactions,[11] particularly aminoindane derivatives.[12] However, synthesis of 1*H*-inden-3-amines has been scarcely reported using a C−H activation strategy; for example, in 2005, Kuninobu and Takai described the first synthesis of 1*H*-inden-3-amine derivatives using a C−H annulation strategy with aromatic aldimines and internal alkynes under Re(I) catalysis.[12a] The construction of a 1*H*-inden-3-amine motif from the cross coupling of benzimidate with alkene was recently reported by Zhang[13a] under Rh(III) catalysis and Jeganmohan[13b] under Ru(II) catalysis. Both groups have reported the synthesis of 3-aminoindenone as shown in Scheme 1. In addition, transition-metal-catalyzed C−H annulation with a benzimidate directing group has been utilized for the construction of diverse heterocycles recently.[14] *To the best of our knowledge, there is no report for the construction of 1-(trifluoromethyl)-1H-inden-3-amine scaffolds.* We herein report the first synthesis of trifluoromethyl-containing 1*H*-inden-3-amines under Rh(III) catalysis involving the C−H annulation

Received: February 26, 2019

DOI: 10.1021/acs.orglett.9b00720
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 1

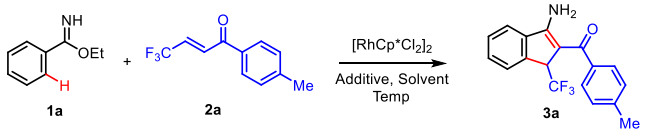


between benzimidates and β-(trifluoromethyl)-α,β-unsaturated ketones.

Our investigation was initiated by examining the coupling of benzimidate (**1a**) and trifluoromethyl α,β-unsaturated ketone (**2a**) under rhodium catalysis (Table 1). To our delight, the cationic rhodium complex, derived from $[Cp^*RhCl_2]_2$ (2.5 mol %) and $AgSbF_6$ (10 mol %), was found to promote the coupling of **1a** and **2a** in 1,2-dichloroethane (DCE) at 80 °C for 24 h to afford the corresponding derivative of 1-(trifluoromethyl)-1*H*-inden-3-amine **3a** in 40% yield (Table 1, entry 1). Screening of additives showed that the combination of $AgSbF_6$ and AgOAc was the most effective in this catalytic reaction to afford our desired product **3a** in 54% yield (Table 1, entries 2–6). However, the AcOH as additive was found to be less effective (Table 1, entry 7). Lowering the loading of AgOAc to 20 mol % gives a similar yield of **3a** (Table 1, entry 8). The effect of solvents was then investigated (Table 1, entries 9–15); it was found that DCE, ethyl acetate, toluene, and *t*-BuOH provided similar yields. Being more green and cheaper, EtOAc was the choice of solvent for further investigation. Further, an increase in catalyst loading to 4 mol % provided the desired compound **3a** in 80% yield. Further, without AgOAc, the reaction did proceed with a slightly decreased yield (Table 1, entry 17); however, a trace amount of product was observed in the absence of $AgSbF_6$ (Table 1, entry 18).

With the optimized C–H annulation conditions in hand, various trifluoromethyl α,β-unsaturated ketones (**2a–p**) were selected to realize this coupling with benzimidate (**1a**). As depicted in Scheme 2, both electron-donating and electron-withdrawing substituents at the *para*- and *meta*-positions in the aryl ring of CF_3-enone (**2a–i**) underwent smooth coupling to furnish the corresponding product (**3a–i**) in good yields. In the case of *ortho*-substituted enones, only moderate yields were obtained (**3j–m**), presumably because of the steric bulk. Other useful substrates such as 2,4-dichlorophenyl enones, piperonyl enones, and thiophene enones also underwent the C–H annulation reaction to give the corresponding 1-(trifluoromethyl)-1*H*-inden-3-amines (**3n–p**) in moderate to good yields.

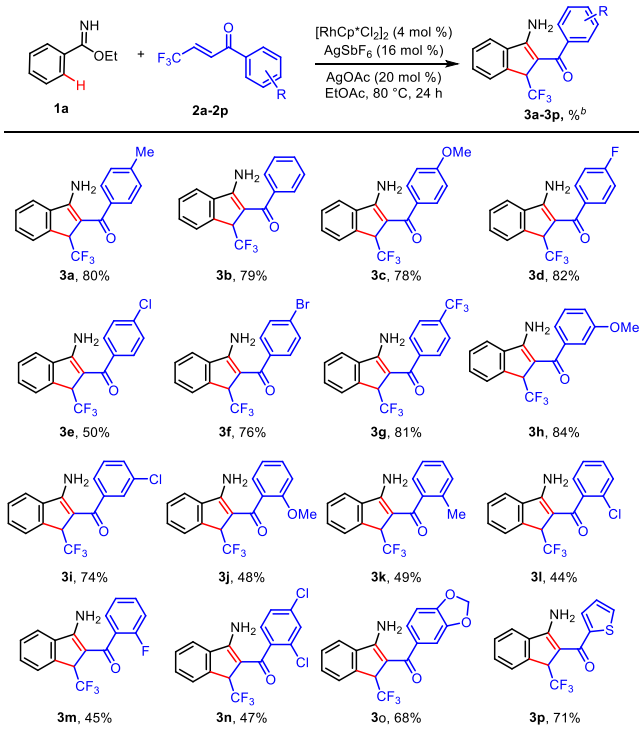
Table 1. Selected Optimization for Reaction Conditions[a]



entry	additive (mol %)	solvent	yield[b] (%)
1	$AgSbF_6$ (10)	DCE	40
2	$AgSbF_6$ (10) + AgOAc (50)	DCE	54
3	$AgSbF_6$ (10) + NaOAc (50)	DCE	31
4	$AgSbF_6$ (10) + CsOAc (50)	DCE	35
5	$AgSbF_6$ (10) + $Cu(OAc)_2$ (50)	DCE	50
6	$AgSbF_6$ (10) + AgOTf (50)	DCE	trace
7	$AgSbF_6$ (10) + AcOH (50)	DCE	22
8	$AgSbF_6$ (10) + AgOAc (20)	DCE	55
9	$AgSbF_6$ (10) + AgOAc (20)	EtOH	50
10	$AgSbF_6$ (10) + AgOAc (20)	THF	44
11	$AgSbF_6$ (10) + AgOAc (20)	toluene	54
12	$AgSbF_6$ (10) + AgOAc (20)	TFE	47
13	$AgSbF_6$ (10) + AgOAc (20)	EtOAc	57
14	$AgSbF_6$ (10) + AgOAc (20)	H_2O	NR
15	$AgSbF_6$ (16) + AgOAc (20)	*t*-BuOH	54
16[c]	**$AgSbF_6$ (16) + AgOAc (20)**	**EtOAc**	**80**
17[c]	$AgSbF_6$ (16)	EtOAc	74
18[c]	AgOAc (20)	EtOAc	trace

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), additive (quantity noted, mol %), solvent (1 mL) at 80 °C for 24 h under air in reaction tubes. [b]Isolated yield by column chromatography. [c]$[RhCp^*Cl_2]_2$ (4 mol %) was used.

Scheme 2. Scope of β-CF_3-enones[a]

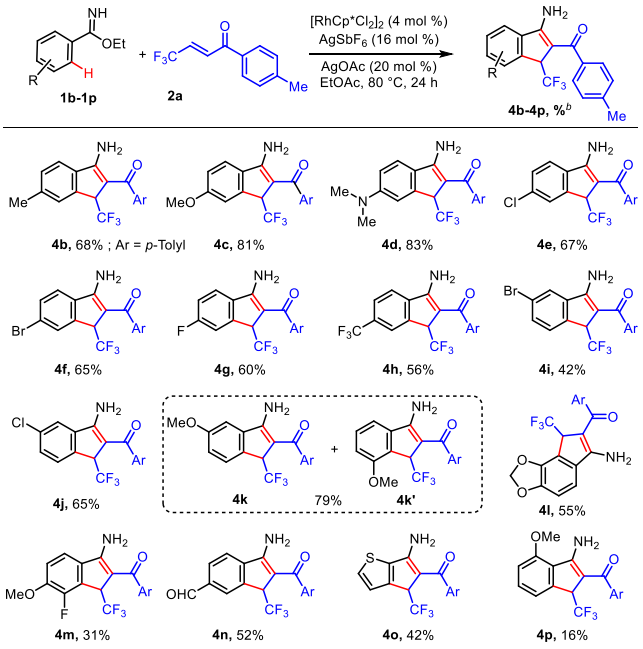


[a]Reaction conditions: **1a** (0.3 mmol), **2a-2p** (0.2 mmol), $[RhCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), AgOAc (20 mol %), EtOAc (1 mL) at 80 °C for 24 h under air in reaction tubes. [b]Isolated yield by column chromatography.

DOI: 10.1021/acs.orglett.9b00720
Org. Lett. XXXX, XXX, XXX–XXX

Furthermore, the generality and compatibility of this coupling reaction with a variety of benzimidates (**1b−p**) were investigated under the optimized conditions (Scheme 3).

Scheme 3. Scope of Benzimidates[a]

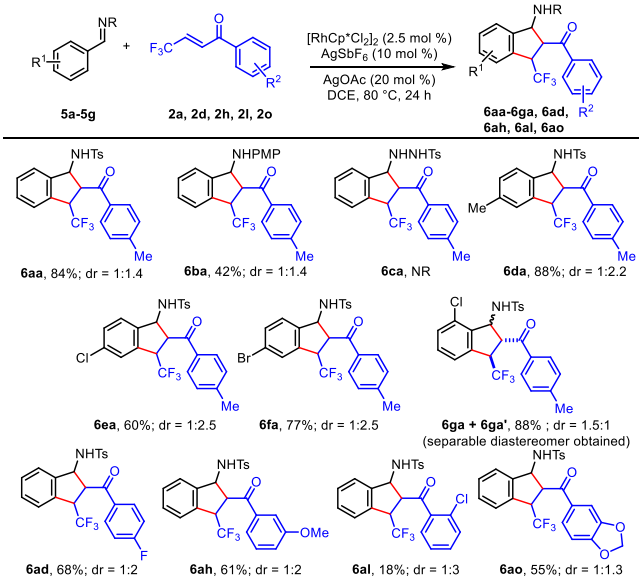


[a]Reaction conditions: **1b−p** (0.3 mmol), **2a** (0.2 mmol), $[RhCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), AgOAc (20 mol %), EtOAc (1 mL) at 80 °C for 24 h under air in reaction tubes. [b]Isolated yield by column chromatography.

Electron-donating (Me, OMe, NMe_2) or electron-withdrawing groups (F, Br, Cl, and CF_3) at the *meta*- or *para*-positions of benzimidates were found to undergo the C−H annulation reaction in moderate to good yield. Notably, with *m*-OMe benzimidate (**1k**), an inseparable regioisomeric mixture of CF_3-indenamine products (**4k** and **4k′**) in a combined yield of 79% was obtained, and **4k** was found to be the major compound based on the NOE data (see the Supporting Information). Furthermore, 3,4-disubstituted benzimidates **1l** and **1m** provided only one regioisomer of **4l** and **4m** in 55% and 31% yield, respectively. We were delighted to see that an aldehyde group in benzimidate (**1n**) was compatible during the reaction, furnishing the formyl product **4n** in 52% yield. It is noteworthy that 2-thienyl imidate (**1o**) was also found to couple with CF_3-enone (**2a**) providing an access to the CF_3-containing fused five membered thiophene product (**4o**) in moderate yield. *Ortho*-substituted benzimidate **1p** afforded the corresponding product **4p**, albeit in low yield.

Diastereodivergent spiroannulation of cyclic *N*-sulfonyl or *N*-acyl ketimines with *β*-CF_3-substituted enones under Rh catalysis has been reported by Li and co-workers.[15] However, the scope of acyclic aldimines with *β*-CF_3-substituted enones was not yet explored. Thus, having established the C−H annulation of benzimidates for 1-(trifluoromethyl)-1*H*-inden-3-amines synthesis, we set out to investigate the feasibility of C−H annulation of aldimines using a similar protocol. Initial screening of tosylaldimine (**5a**) was carried out under otherwise identical conditions. Unfortunately, no reaction was observed due to the degradation of aldimine in ethyl acetate. Further changing the solvent from ethyl acetate to DCE provided the desired coupling reaction to produce the aminoindane derivative **6aa** in 84% yield as shown in Scheme 4. Other aldimine directing groups such as,

Scheme 4. Synthesis of C3-Trifluoromethylindanes[a]



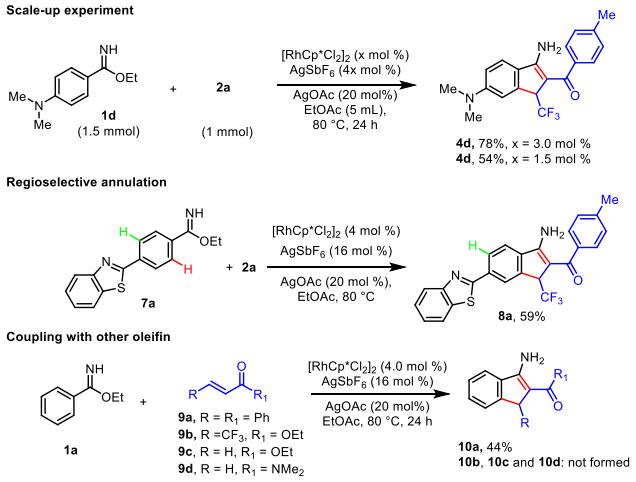
[a]Reaction conditions: **5a−g** (0.2 mmol), **2** (0.2 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), AgOAc (20 mol %), and DCE (1 mL) under air at 80 °C for 24 h in reaction tubes. [b]Isolated yield by column chromatography.

N-*p*-methoxyphenyl aldimine (**5b**) did provide the corresponding product **6ba** in 42% yield. However, tosylhydrazone (**5c**) did not deliver the desired coupling reaction. Further, we have carried out coupling of few selected substituted tosylimines (**5d−g**) and *β*-CF_3-enones (**2a**, **2d**, **2h**, **2l**, and **2o**). The corresponding 3-(trifluoromethyl)-1-aminoindanes were obtained in moderate to good yield. Notably, 2-chloro-substituted *β*-CF_3-enone provided the desired product, albeit in low yield. It is to be noted that in all the CF_3-aminoindanes mixtures of inseparable diastereomers were obtained. At this stage, we could not find any appropriate conditions for higher diastereoselectivity (see selective optimization table in the Supporting Information), which was observed with cyclic ketimines by Li and co-workers.[15] This could be attributed to the use of sterically bulky cyclic ketimines for the formation of distereoselective spiroindane derivatives in previous reports.

Next, we carried out the scaleup experiment of **1d** with **2a** under 3 mol % and 1.5 mol % of Rh(III) catalyst; to our delight, 3 mol % of Rh (III) catalyst provided the corresponding product **4d** in 78% yield, but with 1.5 mol % of Rh(III) the yield drops to 54% (Scheme 5). Further, we investigated the intramolecular regioselectivity of the two *ortho*-C−H bonds of the imidate and benzthiazole directing group of compound **7a** under optimal reaction conditions. We were delighted to see the formation of regioselective C−H annulations with an imidate directing group to afford CF_3-indenamine product **8a** in 59% yield. This outcome of regioselectivity could be attributed to the strong coordinating capability of the imidate moiety. In addition, when the reactions of a few other olefins (**9a−d**) with **1a** were carried out, chalcone (**9a**) did provide the corresponding compound (**10a**) in 44% yield. However, the enoates (**9b** and **9c**) and N,N-dimethylacrylamide (**9d**) did not undergo the desired coupling under our optimized conditions.

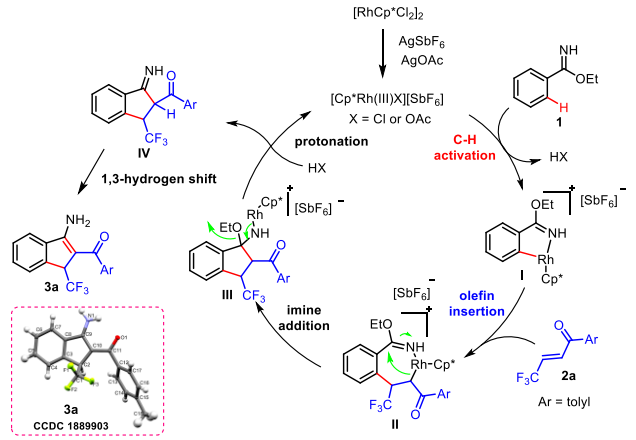
DOI: 10.1021/acs.orglett.9b00720
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 5. Scale-up and Synthetic Utility



On the basis of the previous literature[12] and our own understanding, a plausible mechanistic pathway is depicted in Scheme 6. In the presence of $AgSbF_6$, cationic [Cp*Rh(III)] is

Scheme 6. Plausible Reaction Mechanism



generated in situ as the active catalyst, which coordinates to imine and subsequently undergoes C−H activation to generate rhodacycle **I**. Further coordination and migratory insertion of β-CF_3-enones **2a** takes place to afford rhodacycle intermediate **II**. The Rh−C bond of the intermediate **II** may undergo intramolecular imine addition to a provide rhodium complex **III**, which on protonation regenerates the active Rh(III) catalyst and simultaneously gives the intermediate (**IV**), which on subsequent 1,3-hydrogen shift affords the CF_3-indenamine product **3**.

In conclusion, we have developed a [3 + 2] annulation reaction of benzimidate substrates and β-CF_3-enones via a rhodium-catalyzed C−H activation strategy affording interesting 1-(trifluoromethyl)-1*H*-inden-3-amine derivatives in good to high yields. Furthermore, the coupling reaction is also applicable to aldimines to produce trifluoromethylated aminoindanes. We believe that all of these synthesized indenamines and aminoindanes with a CF_3 moiety might be of great interest to the medicinal chemist.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00720.

Experimental procedures, characterization data, and ^1H and ^{13}C NMR spectra for all compounds (PDF)

Accession Codes

CCDC 1889903 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sharma.satyasheel@gmail.com.

ORCID

Bharatkumar Chaudhary: 0000-0001-6182-1273

Satyasheel Sharma: 0000-0002-4983-1572

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by Department of Science and Technology (DST) INSPIRE faculty award [DST/INSPIRE/04/2016/000414]. We also thank the Department of Pharmaceutical, Ministry of Chemicals and Fertilizers, India, and NIPER-Ahmedabad for providing the necessary support.

■ REFERENCES

(1) For a review, see: (a) Ahmed, N. Synthetic Advances in the Indane Natural Product Scaffolds as Drug Candidates: A Review. In *Studies in Natural Products Chemistry*; Atta-Ur-Rahman, Ed.; Elsevier, 2016; Vol. *51*, pp 383−484. For selected examples, see: (b) Gardelli, C.; Wada, H.; Ray, A.; Caffrey, M.; Llinas, A.; Shamovsky, I.; Tholander, J.; Larsson, J.; Sivars, U.; Hultin, L.; Andersson, U.; Sanganee, H. J.; Stenvall, K.; Leidvik, B.; Gedda, K.; Jinton, L.; Landergren, M. R.; Karabelas, K. *J. Med. Chem.* **2018**, *61*, 5974−5987. (c) Barlow, J. W.; Walsh, J. *Eur. J. Med. Chem.* **2010**, *45*, 25−37. (d) Liedtke, A. J.; Crews, B. C.; Daniel, C. M.; Blobaum, A. L.; Kingsley, P. J.; Ghebreselasie, K.; Marnett, L. J. *J. Med. Chem.* **2012**, *55*, 2287−2300. (e) Clegg, N. J.; Paruthiyil, S.; Leitman, D. C.; Scanlan, T. S. *J. Med. Chem.* **2005**, *48*, 5989−6003.

(2) For indane derivatives, see, for example: (a) Morales, A. R.; Frazer, A.; Woodward, A. W.; Ahn-White, H.-Y.; Fonari, A.; Tongwa, P.; Timofeeva, T.; Belfield, K. D. *J. Org. Chem.* **2013**, *78*, 1014−1025. (b) Acikbas, Y.; Capan, R.; Namli, H.; Turhan, O.; Stanciu, G. A. *J. Optoelectron. Adv. Mater.* **2007**, *9*, 56−59. For indene derivatives, see, for example: (c) Tao, R.; Umeyama, T.; Higashino, T.; Koganezawa, T.; Imahori, H. *ACS Appl. Mater. Interfaces* **2015**, *7*, 16676−16685. (d) Dang, J.-S.; Wang, W.-W.; Zhao, X.; Nagase, S. *Org. Lett.* **2014**, *16*, 170−173. (e) Li, Y. *Acc. Chem. Res.* **2012**, *45*, 723−733. (f) He, Y.; Chen, H.-Y.; Hou, J.; Li, Y. *J. Am. Chem. Soc.* **2010**, *132*, 1377−2382. (g) Yang, J.; Lakshmikantham, M. V.; Cava, M. P.; Lorcy, D.; Bethelot, J. R. *J. Org. Chem.* **2000**, *65*, 6739−6742.

(3) (a) Bertolini, G.; Vecchietti, V.; Mabilia, M.; Santangelo, F. *Eur. J. Med. Chem.* **1992**, *27*, 663−672. (b) Chazalette, C.; Masereel, B.; Rolin, S.; Supuran, C. T. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 5781−5786. (c) Thiry, A.; Ledecq, M.; Masereel, B. *J. Med. Chem.* **2006**, *49*, 2743−2749. (d) Walsh, J. J.; Barlow, J. W. *Eur. J. Med. Chem.* **2008**, *43*, 2891−2900. (e) Barlow, J. W.; Walsh, J. *Eur. J. Med. Chem.* **2010**, *45*, 25−37.

DOI: 10.1021/acs.orglett.9b00720
Org. Lett. XXXX, XXX, XXX−XXX

(f) Ugliarolo, E. A.; Cavallaro, L. V.; Moglioni, A. G. *Bioorg. Med. Chem.* **2012**, *20*, 5986−5991.
(4) Iakovenko, R. O.; Kazakova, A. N.; Muzalevskiy, V. M.; Ivanov, A. Y.; Boyarskaya, I. A.; Chicca, A.; Petrucci, V.; Gertsch, J.; Krasavin, M.; Starova, G. L.; Zolotarev, A. A.; Avdontceva, M. S.; Nenajdenko, V. G.; Vasilyev, A. V. *Org. Biomol. Chem.* **2015**, *13*, 8827−8842.
(5) For selected reviews, see: (a) Meanwell, N. A. *J. Med. Chem.* **2018**, *61*, 5822−5880. (b) Zhou, Y.; Wang, J.; Gu, Z.; Wang, S.; Zhu, W.; Aceña, J. L.; Soloshonok, V. A.; Izawa, K.; Liu, H. *Chem. Rev.* **2016**, *116*, 422−518. (c) Zhu, W.; Wang, J.; Wang, S.; Gu, Z.; Aceña, J. L.; Izawa, K.; Liu, H.; Soloshonok, V. A. *J. Fluorine Chem.* **2014**, *167*, 37−54. (d) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37*, 320−330.
(6) Gabriele, B.; Mancuso, R.; Veltri, L. *Chem. - Eur. J.* **2016**, *22*, 5056−5094.
(7) (a) Billard, T.; Bruns, S.; Langlois, B. R. *Org. Lett.* **2000**, *2*, 2101−2103. (b) Allen, A. D.; Fujio, M.; Mohammed, N.; Tidwell, T.; Tsuji, Y. *J. Org. Chem.* **1997**, *62*, 246−252. (c) Gassman, P. G.; Ray, J. A.; Wenthold, P. G.; Mickelson, J. W. *J. Org. Chem.* **1991**, *56*, 5143−5146.
(8) (a) Martynov, M. Y.; Iakovenko, R. O.; Kazakova, A. N.; Boyarskaya, I. A.; Vasilyev, A. V. *Org. Biomol. Chem.* **2017**, *15*, 2541−2550. (b) Iakovenko, R. O.; Kazakova, A. N.; Boyarskaya, I. A.; Gurzhiy, V. V.; Avdontceva, M. S.; Panikorovsky, T. L.; Muzalevskiy, V. M.; Nenajdenko, V. G.; Vasilyev, A. V. *Eur. J. Org. Chem.* **2017**, *2017*, 5632−5643. (c) Boreux, A.; Lonca, G. H.; Riant, O.; Gagosz, F. *Org. Lett.* **2016**, *18*, 5162−5165. (d) Ghavtadze, N.; Fröhlich, R.; Würthwein, E.-U. *J. Org. Chem.* **2009**, *74*, 4584−4591. (e) Radix-Large, S.; Kucharski, S.; Langlois, B. R. *Synthesis* **2004**, *3*, 456−465.
(9) Tang, H.-J.; Zhang, Y.-F.; Jiang, Y.-W.; Feng, C. *Org. Lett.* **2018**, *20*, 5190−5193.
(10) For selected reviews on the annulation reaction involving the C−H functionalization, see: (a) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624−655. (b) Patureau, F. W.; Wencel-Delord, J.; Glorius, F. *Aldrichimica Acta* **2012**, *45*, 31−41. (c) Kuninobu, Y. *Synlett* **2018**, *29*, 2093−2107. (d) Ackermann, L. *Acc. Chem. Res.* **2014**, *47*, 281−295. (e) De Sarkar, S.; Liu, W.; Kozhushkov, S. I.; Ackermann, L. *Adv. Synth. Catal.* **2014**, *356*, 1461−1480. (f) Guo, X.-X.; Gu, D.-W.; Wu, Z.; Zhang, W. *Chem. Rev.* **2015**, *115*, 1622−1651. (g) Song, R.-J.; Liu, Y.; Xie, Y.-X.; Li, J.-H. *Synthesis* **2015**, *47*, 1195−1209. (h) Liu, L.; Zhang, J. *Chem. Soc. Rev.* **2016**, *45*, 506−516. (i) Gulias, M.; Mascarenas, J. L. *Angew. Chem., Int. Ed.* **2016**, *55*, 11000−11019. (j) Lauder, K.; Toscani, A.; Scalacci, N.; Castagnolo, D. *Chem. Rev.* **2017**, *117*, 14091−14200. (k) Wang, Z.; Xie, P.; Xia, Y. *Chin. Chem. Lett.* **2018**, *29*, 47−53. (l) Tang, X.; Wu, W.; Zeng, W.; Jiang, H. *Acc. Chem. Res.* **2018**, *51*, 1092−1105. (m) Cao, Z.-Y.; Zhou, F.; Zhou, J. *Acc. Chem. Res.* **2018**, *51*, 1443−1454.
(11) For indane/indenes, see: (a) Kuninobu, Y.; Nishina, Y.; Shouho, M.; Takai, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2766−2768. (b) Qi, Z.; Wang, M.; Li, X. *Org. Lett.* **2013**, *15*, 5440−5443. (c) Dong, L.; Qu, C.; Huang, J.; Zhang, W.; Zhang, Q.; Deng, J. *Chem. - Eur. J.* **2013**, *19*, 16537−16540. (d) Huang, J.; Song, Q.; Zhu, Y.; Qin, L.; Qian, Z.; Dong, L. *Chem. - Eur. J.* **2014**, *20*, 16882−16886. (e) Liu, H.; Li, J.; Xiong, M.; Jiang, J.; Wang, J. *J. Org. Chem.* **2016**, *81*, 6093−6099.
(12) For aminoindane/indenenamine, see: (a) Kuninobu, Y.; Kawata, A.; Takai, K. *J. Am. Chem. Soc.* **2005**, *127*, 13498−13499. (b) Kuninobu, Y.; Tokunaga, Y.; Kawata, A.; Takai, K. *J. Am. Chem. Soc.* **2006**, *128*, 202−209. (c) Kuninobu, Y.; Yu, P.; Takai, K. R. *Org. Lett.* **2010**, *12*, 4274−4276. (d) Sun, Z.; Chen, S. P.; Zhao, P. *Chem. - Eur. J.* **2010**, *16*, 2619−2627. (e) Tran, D. N.; Cramer, N. *Angew. Chem., Int. Ed.* **2010**, *49*, 8181−8184. (f) Tran, D. N.; Cramer, N. *Angew. Chem., Int. Ed.* **2011**, *50*, 11098−11102. (g) Zhao, P.; Wang, F.; Han, K. L.; Li, X. W. *Org. Lett.* **2012**, *14*, 5506−5509. (h) Zhang, J.; Ugrinov, A.; Zhao, P. *Angew. Chem., Int. Ed.* **2013**, *52*, 6681−6684. (i) Tran, D. N.; Cramer, N. *Angew. Chem., Int. Ed.* **2013**, *52*, 10630−10634. (j) Chen, Y.; Wang, F.; Zhen, W.; Li, X. *Adv. Synth.Catal.* **2013**, *355*, 353−359. (k) Hung, C. H.; Gandeepan, P.; Cheng, C. H. *ChemCatChem* **2014**, *6*, 2692−2697. (l) Zhou, X.; Yu, S.; Qi, Z.; Li, X. *Sci. China: Chem.* **2015**, *58*, 1297−1301. (m) Liu, W. P.; Zell, D.; John, M.; Ackermann, L. *Angew. Chem., Int. Ed.* **2015**, *54*, 4092−4096. (n) Han, S. H.; Mishra, N. K.; Jeon, M.; Kim, S.; Kim, H. S.; Jung, S.-Y.; Jung, Y. H.; Ku, J.-M.; Kim, I. S. *Adv. Synth. Catal.* **2017**, *359*, 3900−3904. (o) Nagamoto, M.; Sakamoto, K.; Nishimura, T. *Adv. Synth. Catal.* **2018**, *360*, 791−795.
(13) (a) Lv, N.; Chen, Z.; Liu, Y.; Liu, Z.; Zhang, Y. *Org. Lett.* **2017**, *19*, 2588−2591. (b) Manikandan, R.; Tamizmani, M.; Jeganmohan, M. *Org. Lett.* **2017**, *19*, 6678−6681.
(14) (a) Yu, D. G.; Suri, M.; Glorius, F. *J. Am. Chem. Soc.* **2013**, *135*, 8802−8805. (b) Wang, J.; Zha, S.; Chen, K.; Zhang, F.; Song, C.; Zhu, J. *Org. Lett.* **2016**, *18*, 2062−2065. (c) Wang, H.; Li, L.; Yu, S.; Li, Y.; Li, X. *Org. Lett.* **2016**, *18*, 2914−2917. (d) Lv, N.; Liu, Y.; Xiong, C.; Liu, Z.; Zhang, Y. *Org. Lett.* **2017**, *19*, 4640−4643. (e) Wang, H.; Lorion, M. M.; Ackermann, L. *ACS Catal.* **2017**, *7*, 3430−3433. (f) Wu, X.; Xiong, H.; Sun, S.; Cheng, J. *Org. Lett.* **2018**, *20*, 1396−1399. (g) Anukumar, A.; Tamizmani, M.; Jeganmohan, M. *J. Org. Chem.* **2018**, *83*, 8567−8580.
(15) Liu, B.; Hu, P.; Zhang, Y.; Li, Y.; Bai, D.; Li, X. *Org. Lett.* **2017**, *19*, 5402−5405.

DOI: 10.1021/acs.orglett.9b00720
Org. Lett. XXXX, XXX, XXX−XXX