Organic & Biomolecular Chemistry

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Org. Biomol. Chem.*, 2024, **22**, 3209

Received 8th February 2024,
Accepted 22nd March 2024

DOI: 10.1039/d4ob00205a

rsc.li/obc

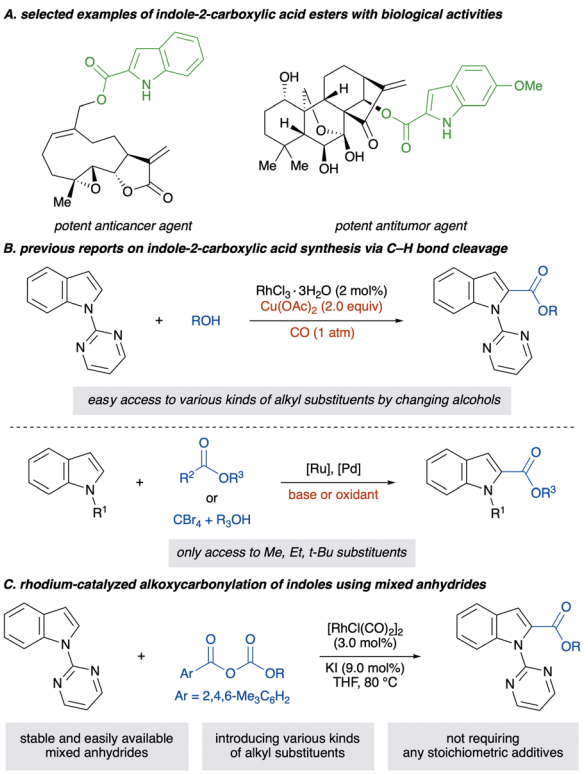
Rhodium-catalysed additive-free alkoxycarbonylation of indoles: 2,4,6-trimethylbenzoic acid-based carbonate anhydrides as a versatile alkoxycarboxyl source†

Hirotsugu Suzuki, *[a] Yuki Ito,[b] Kentaro Yabe,[b] Yosuke Takemura[b] and Takanori Matsuda *[b]

We report a CO-free approach to indole-2-carboxylic esters: rhodium-catalysed C(2)-alkoxycarbonylation of indoles with 2,4,6-trimethylbenzoic acid-based carbonate anhydrides. Selective C–O bond cleavage of the anhydrides facilitates the introduction of various alkoxycarbonyl groups. Control experiments suggest that merging a rhodium catalyst and KI promotes the *in situ* formation of the RhI species.

Indole-2-carboxylic acid esters and their derivatives are prevalent structural motifs in numerous biologically active compounds and pharmaceuticals and serve as versatile intermediates in organic synthesis (Scheme 1A).[1–4] Given their structural importance, diverse synthetic methods toward indole-2-carboxylic acid esters have been developed. For instance, an intramolecular or intermolecular cyclisation forming a pyrrole ring is essential for synthesising these esters.[5–14] However, the requisite multi-step synthesis to prepare prefunctionalised starting materials can consume substantial resources and time, posing significant drawbacks for practical applications. As an alternative, transition-metal-catalysed C(2)–H carbonylation of indoles has been explored as an atom- and step-economical approach for synthesising these molecules.[15,16] Among them, carbon monoxide (CO) serves as a cost-effective and readily available C1 carbonyl source (Scheme 1B).[17,18] However, its toxicity and inflammability restrict its utility, demanding special handling techniques and equipment. Moreover, the alkoxycarbonylation using CO requires a stoichiometric amount of an oxidant such as a copper salt, diminishing the atom economy of the reaction and complicating reaction operation. Therefore, the development of a complementary carbonyl source is highly desirable for enhancing safety and synthetic efficiency. Additionally, in recent decades, investigation of CO surrogates has become a crucial point of focus in C–H carbonylation reactions of arenes.[19,20] Consequently, exploring safe, easy-to-handle and CO-free C(2)–H alkoxycarbonylations of indoles is warranted.

The investigation on carboxylating reagents has garnered considerable attention in the past decade for their environmentally benign CO-free process, resulting in various reagents, such as azodicarboxylates,[21–28] chloroformates,[29–31] oxaziri-



Scheme 1 Previous C(2)–H alkoxycarbonylations of indoles and this work.

[a]*Tenure-Track Program for Innovative Research, University of Fukui, 3-9-1 Bunkyo, Fukui-shi, Fukui 910-8507, Japan. E-mail: h-suzuki@u-fukui.ac.jp*
[b]*Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan. E-mail: mtd@rs.tus.ac.jp*

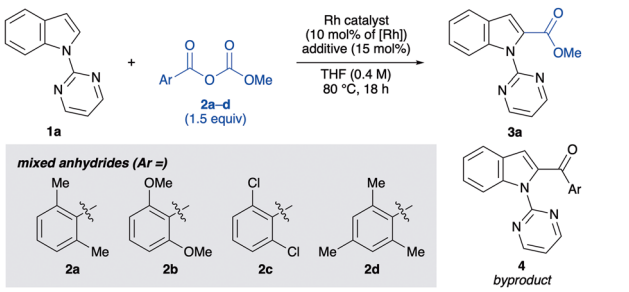
†Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d4ob00205a

dines,[32] glyoxylates,[33] α-keto esters,[34] dicarbonates,[35–38] formates,[39] potassium oxalates,[40] carbazates,[41–43] bromodifluoroacetates[44] and tetrabromomethanes[45–48] (Scheme 1B). However, these reactions necessitate the use of stoichiometric amounts of additives, such as oxidants and bases, and alkoxycarbonylations without any stoichiometric additives have rarely been reported.[32,36–38] Furthermore, introduced substituents on alkoxycarbonyl moieties are restricted to simple alkyl chains such as methyl, ethyl and *tert*-butyl groups, likely due to the structural limitations of available carboxylating reagents, even though the structure of the ester moiety crucially affects biological activities.[2,3]

Recently, Dong *et al.* reported the palladium-catalysed Catellani reaction using a novel carbonate anhydride as a carboxylating reagent.[49,50] Inspired by these reports[49,50] and our previous studies,[36–38,51,52] we hypothesised that rhodium carboxylate species possessing various alkoxycarbonyl groups could be generated by the selective C–O bond cleavage of a carbonate anhydride, thereby promoting C(2)-selective C–H activation of indoles without any stoichiometric additives. The key challenges, however, are (1) how to control C–O bond cleavage due to unsymmetrical anhydrides possessing the two weak C–O bonds and (2) how to promote selective C–H activation by rhodium carboxylate species in the absence of an oxidant and a base. Herein, we report a rhodium-catalysed alkoxycarbonylation of indoles with mixed carbonate anhydrides without stoichiometric amounts of additives, yielding indole-2-carboxylic acid esters with various ester substituents (Scheme 1C). The easily accessible and stable mixed carbonate anhydrides make alkoxycarbonylation more straightforward and operationally simple.

Our study commenced by investigating the C(2)-selective alkoxycarbonylation of 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) with the mixed carbonate anhydride **2** in the presence of $[RhCl(CO)_2]_2$ (5.0 mol%, 10 mol% Rh) and potassium iodide (KI, 15 mol%) in THF at 80 °C (Table 1). After 18 h, the desired indole-2-carboxylic acid ester **3a** was obtained in 78% yield from the mixed carbonate anhydride **2a**, synthesised from 2,6-dimethylbenzoic acid and methyl chloroformate in a single step. However, a small amount of 2-aroylindole **4** was also formed as a byproduct (entry 1). Encouraged by this result, other mixed carbonate anhydrides derived from 2,6-disubstituted benzoic acids were examined. The yield of **3a** was further improved using **2d** (entry 4), although other mixed anhydrides gave lower yields (entries 2 and 3). Employing methyl chloroformate instead of **2** resulted in no product formation, indicating the importance of the carboxylate moiety for C–H bond activation (entry 5). Among the iodide sources examined, KI was found to be optimal, affording **3a** in 89% yield(entries 4 *vs.* 6–8). Only $[RhCl(CO)_2]_2$ exhibited catalytic activity, and other rhodium(I) complexes were found to be ineffective (entries 9–12). Moreover, this alkoxycarbonylation reaction was not affected by atmospheric air conditions (entry 13). On the other hand, adding a small amount of water decreased both the yield and the chemoselectivity, probably due to the decomposition of **2d** by water (entry 14). Lowering

Table 1 Optimisation of reaction conditions[a]



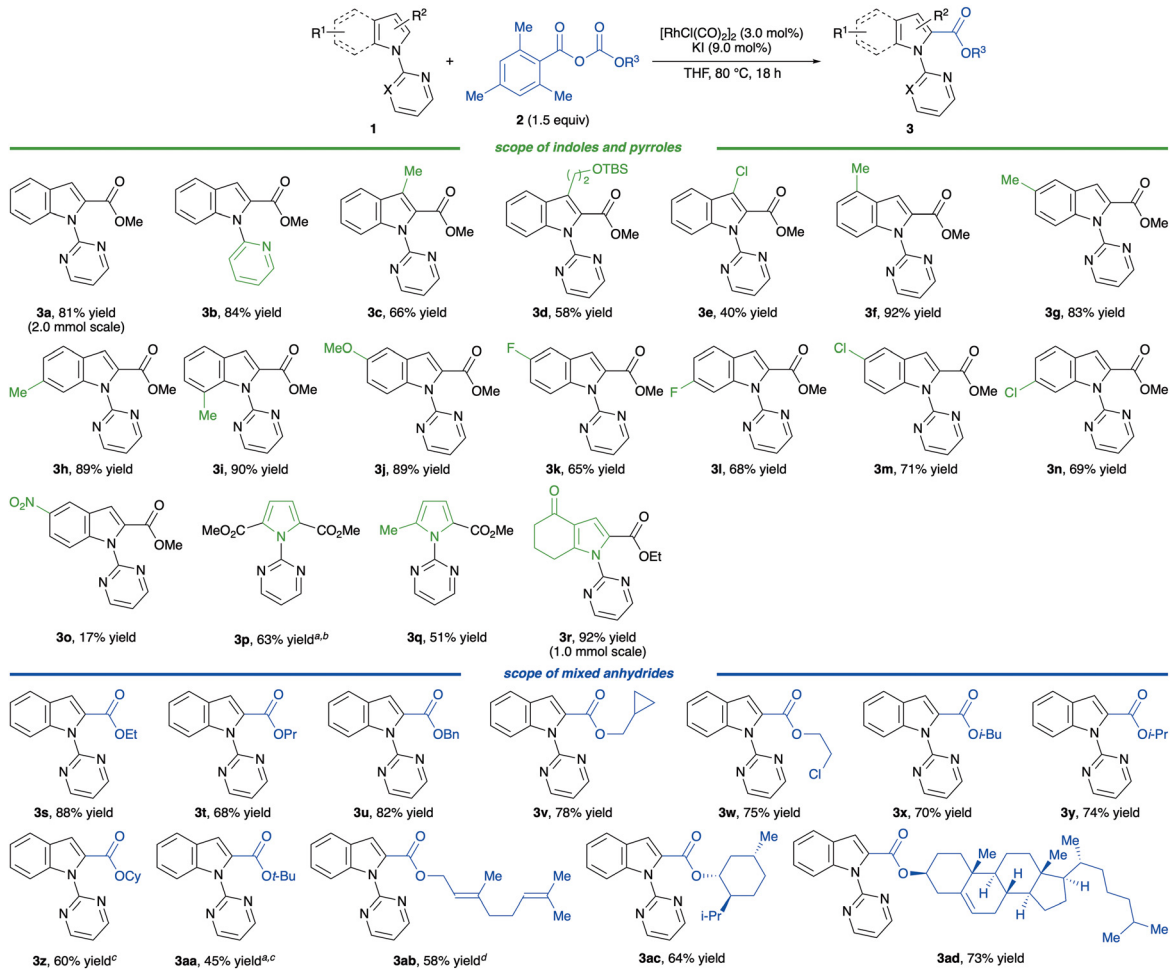
Entry	Anhydride	Additive	Rh catalyst	Yield of **3**[b] (%)	**3** : **4**
1	**2a**	KI	$[RhCl(CO)_2]_2$	78	8.7 : 1
2	**2b**	KI	$[RhCl(CO)_2]_2$	87	12 : 1
3	**2c**	KI	$[RhCl(CO)_2]_2$	70	>20 : 1
4	**2d**	KI	$[RhCl(CO)_2]_2$	89	15 : 1
5[c]	—	KI	$[RhCl(CO)_2]_2$	0	—
6	**2d**	NaI	$[RhCl(CO)_2]_2$	81	9.0 : 1
7	**2d**	LiI	$[RhCl(CO)_2]_2$	25	1 : 2.0
8	**2d**	TBAI	$[RhCl(CO)_2]_2$	0	—
9	**2d**	KI	$[RhCl(cod)]_2$	Trace	—
10	**2d**	KI	$[RhCl(nbd)]_2$	0	—
11	**2d**	KI	$RhCl(PPh_3)_3$	Trace	—
12	**2d**	KI	$RhCl(CO)(PPh_3)_2$	Trace	—
13[d]	**2d**	KI	$[RhCl(CO)_2]_2$	90	13 : 1
14[e]	**2d**	KI	$[RhCl(CO)_2]_2$	52	7.4 : 1
15[f]	**2d**	KI	$[RhCl(CO)_2]_2$	91 (87)	>20 : 1
16	**2d**	KI	—	0	—
17	**2d**	—	$[RhCl(CO)_2]_2$	50	5.0 : 1

[a] Reaction conditions: **1a** (0.30 mmol), **2** (0.45 mmol), Rh catalyst (10 mol% of [Rh]) and additive (15 mol%) in THF (0.75 mL) at 80 °C for 18 h under an Ar atmosphere. [b] Yields were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. Value in parentheses indicates isolated yields. [c] Methyl chloroformate was used instead of **2**. [d] The reaction was performed under an air atmosphere. [e] 2.0 equivalents of H_2O were added. [f] $[RhCl(CO)_2]_2$ (3.0 mol%) and KI (9.0 mol%) were used. TBAI: tetrabutylammonium iodide; cod: 1,5-cyclooctadiene; and nbd: 2,5-norbornadiene.

the catalyst loading to 3.0 mol% gave a comparable yield of **3a** while suppressing byproduct formation (entry 15). Control experiments revealed that $[RhCl(CO)_2]_2$ is crucial for the reaction to proceed, and the addition of KI significantly improved the yield and chemoselectivity (entries 16 and 17). Therefore, the additive is considered to assist the formation of RhI species by exchanging halogen ions *in situ*.

With the optimised reaction conditions in hand, we examined the generality of the alkoxycarbonylation (Scheme 2). Initially, we tested the model reaction on a large scale.

Subjecting 2 mmol of **2a** to the optimised reaction conditions gave indole **3a** in 81% yield. A pyridyl directing group could function in this reaction, affording **3b** in 84% yield. Introducing a substituent at the 3-position of indoles resulted in a slight decline in the reactivity; however, products **3c–e** were still obtained in 40–66% yields. Notably, a 3-chloroindole, which did not provide any product in previous CO-mediated alkoxycarbonylations,[17] furnished the corresponding ester **3e** in 40% yield. A methyl group on the benzenoid moiety did not

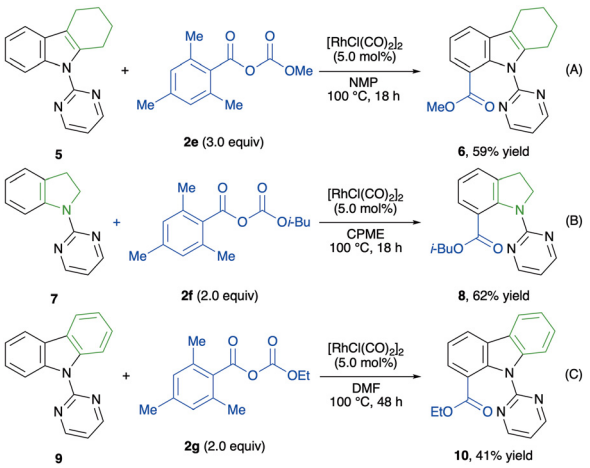


Scheme 2 Substrate scope. Reaction conditions: **1** (0.30 mmol), **2** (0.45 mmol), $[RhCl(CO)_2]_2$ (3.0 mol%), and KI (9.0 mol%) in THF (0.75 mL) at 80 °C for 18 h under an Ar atmosphere. [a] $[RhCl(CO)_2]_2$ (5.0 mol%) and KI (15 mol%) were used. [b] 4.0 equivalents of **2** were used. [c] 2.0 equivalents of **2** were used. [d] The reaction was conducted with 1.2 equivalents of **2** at 100 °C.

affect the yield, affording the desired esters **3f–i** in 83–92% yields. An electron-rich indole bearing a methoxy group at the 5-position was well tolerated (**3j**). In contrast, indoles attached with a weak electron-withdrawing group slightly decreased the yields but still yielded **3k–n** in 65–71% yields; thus, the yield of a nitro-substituted indole **3o** was insufficient. The results indicated that this alkoxycarbonylation was likely to be sensitive to the electronic properties of indoles. Pyrrole substrates were also good coupling partners, affording products **3p–r** in 51–92% yields.

We then tested the effect of a substituent on the ester group. Linear alkyl groups, such as ethyl, propyl, benzyl, cyclopropylmethyl, 2-chloroethyl and isobutyl groups, gave the esters **3s–x** without compromising on reactivity and selectivity. Moreover, a mixed carbonate anhydride possessing an α-branched alkyl group such as isopropyl and cyclohexyl groups also produced **3y** and **3z** in 74 and 60% yields, respectively. A more sterically hindered *tert*-butyl group diminished the yield of **3aa** to 45% due to the formation of a significant amount of the undesired product **4**. To demonstrate the broad applicability of this reaction, mixed carbonate anhydrides possessing a natural product moiety, geraniol, menthol and cholesterol, were tested, and fortunately, all reacted smoothly to afford products **3ab–ad** in 58–73% yields. Thus, these results indicate that this alkoxycarbonylation demonstrates good functional group tolerance and potential for late-stage functionalisation.

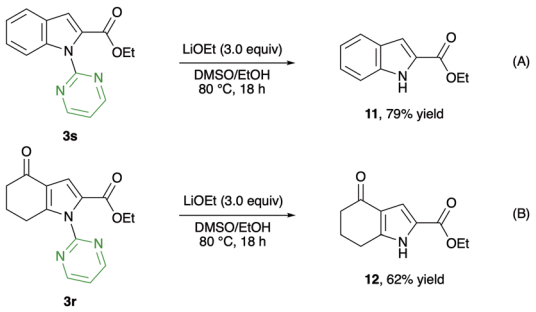
Taking into account the importance of indole-7-carboxylic acid esters and their derivatives in pharmaceutical science,[53–55] we next investigated the C(7)-alkoxycarbonylation of indole derivatives (Scheme 3). Unfortunately, applying the standard reaction conditions to 2-substituted indole **5** did not afford the desired alkoxycarbonylated indole **6**. Interestingly, omitting KI from the conditions enhanced the reactivity, furnishing product **6** in 59% yield (Scheme 3A). Encouraged by this result, alkoxycarbonylations of indoline **7** and carbazole **9** were tested, and both reactions afforded the corresponding products (Scheme 3B and C). Thus, our protocol was extended to functionalise benzenoid moieties, proving the versatility of this methodology for a site-selective alkoxycarbonylation of indoles.



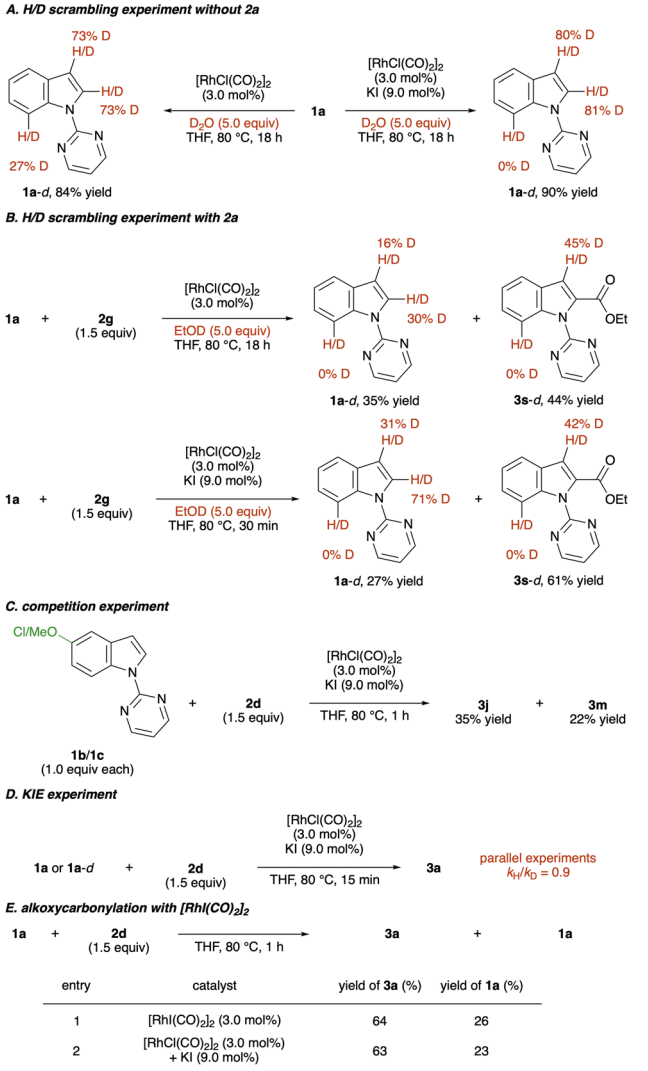
Scheme 3 C(7)-alkoxycarbonylations of indoles and their derivatives.

To demonstrate the utility of this alkoxycarbonylation, further transformation of the products was examined (Scheme 4). Subjecting indole-2-carboxylic acid ester **3s** to the basic reaction conditions enabled the smooth deprotection of the pyrimidyl directing group, providing the unprotected product **11** in 79% yield (Scheme 4A). Similarly, the *N*-pyrimidyl pyrrole **3r** underwent deprotection to afford the free NH-pyrrole **12** in 62% yield (Scheme 4B). These transformations indicate the possibility of further application of this methodology to the synthesis of biologically active molecules.

To elucidate the reaction mechanism, several control experiments were conducted (Scheme 5). Initially, H/D scrambling experiments were performed by adding 5.0 equivalents of D_2O to the reaction of **1a**; over 80% deuterium incorporation at the C(2) and C(3) positions occurred, indicating the reversibility of the C–H activation step (Scheme 5A, right). Interestingly, removing KI from the reaction conditions promoted C(7)–H activation, which was not observed in a $[RhCl(CO)_2]_2$ and KI system (Scheme 5A, left). This reactivity difference might explain the result of the C(7)-alkoxycarbonylation of an indole and its derivatives. Deuterium incorporation of **1a** was also observed even when **2a** was employed with EtOD (Scheme 5B). Next, a competition experiment was conducted by reacting electron-rich and -deficient indoles with mixed anhydride **2a**



Scheme 4 Deprotection of the pyrimidyl directing group.



entry	catalyst	yield of **3a** (%)	yield of **1a** (%)
1	$[RhI(CO)_2]_2$ (3.0 mol%)	64	26
2	$[RhCl(CO)_2]_2$ (3.0 mol%) + KI (9.0 mol%)	63	23

Scheme 5 Mechanistic investigations.

in the same vessel (Scheme 5C). A larger amount of **3j** was formed than **3m**, implying that the C–H activation step could proceed *via* an electrophilic mechanism. In addition, kinetic isotope effect experiments were conducted (Scheme 5D). Parallel experiments showed a KIE of 0.9, indicating that the rate-determining step is not involved in the C–H activation step. Finally, we synthesised $[RhI(CO)_2]_2$ to confirm the active catalyst species.[56] When $[RhI(CO)_2]_2$ was employed in the reaction of indole **1a** with anhydride **2d**, **3a** was formed in a yield comparable to that obtained under the optimised reaction conditions (Scheme 5E). Therefore, we assume the active species of this transformation is $[RhI(CO)_2]_2$.

Based on the mechanistic investigations and previous reports on rhodium-catalysed C–H functionalisation with anhydrides,[36–38,51,52] we propose the reaction mechanism for the C(2)-alkoxycarbonylation of indoles, as depicted in Fig. 1. First, an anion exchange between $[RhCl(CO)_2]_2$ and KI yields the catalytically active $[RhI(CO)_2]_2$. Then, selective C–O bond

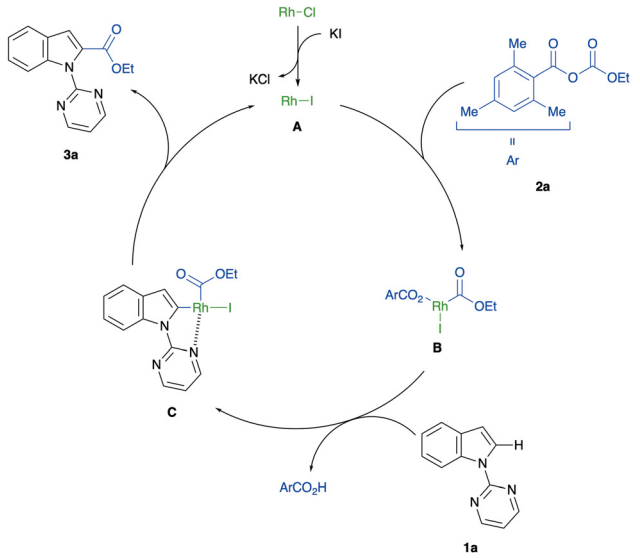


Fig. 1 Plausible reaction mechanism.

cleavage of mixed carbonate anhydride **2a**, controlled by the steric hindrance of a mesityl group, generates the rhodium carboxylate **B**. A subsequent pyrimidyl-directed C–H bond activation, which might proceed by an electrophilic mechanism, gives the five-membered rhodacycle intermediate **C**. Finally, reductive elimination of **C** leads to the formation of the indole-2-carboxylic acid ester **3a** and the regeneration of the RhI species **A**.

Conclusions

In conclusion, we have developed a concise synthesis of indole-2-carboxylic acid esters using 2,4,6-trimethylbenzoic acid-based carbonate anhydrides as carboxylating reagents. Preliminary mechanistic investigations revealed that [RhI$(CO)_2$] generated from [RhCl$(CO)_2$] and KI accelerates the C(2)–H bond cleavage of an indole while suppressing the undesired C(7)–H bond cleavage. The C(2)-alkoxycarbonylation of indoles proceeds selectively to afford the indole-2-carboxylic acid esters in up to 92% isolated yield. Removing KI from the standard reaction conditions enables the C(7)-alkoxycarbonylation of 2-substituted indole derivatives, indoline and carbazole, by facilitating C(7)–H bond cleavage. We anticipate that this novel alkoxycarbonylation using mixed anhydrides will open a new avenue for C–H alkoxycarbonylation with CO surrogates and expand the scope of this field.

Author contributions

Conceptualisation: H. S.; supervision: H. S. and T. M.; investigation: Y. I., K. Y., and Y. T.; resources: T. M.; writing – original draft: H. S.; and writing – review and editing: H. S. and T. M.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by JSPS KAKENHI (grant numbers JP23K13743 and JP21K05061).

References

1 M. Ishikura, T. Abe, T. Choshi and S. Hibino, *Nat. Prod. Rep.*, 2013, **30**, 694–752.
2 S. Bommagani, J. Ponder, N. R. Penthala, V. Janganati, C. T. Jordan, M. J. Borrelli and P. A. Crooks, *Eur. J. Med. Chem.*, 2017, **136**, 393–405.
3 Q.-K. Shen, H. Deng, S.-B. Wang, Y.-S. Tian and Z.-S. Quan, *Eur. J. Med. Chem.*, 2019, **177**, 15–31.
4 G. Cui, F. Lai, X. Wang, X. Chen and B. Xu, *Eur. J. Med. Chem.*, 2020, **188**, 111985.
5 C. Barberis, T. D. Gordon, C. Thomas, X. Zhang and K. P. Cusack, *Tetrahedron Lett.*, 2005, **46**, 8877–8880.
6 B. J. Stokes, H. Dong, B. E. Leslie, A. L. Pumphrey and T. G. Driver, *J. Am. Chem. Soc.*, 2007, **129**, 7500–7501.
7 A. G. O'Brien, F. Lévesque and P. H. Seeberger, *Chem. Commun.*, 2011, **47**, 2688–2690.
8 C. Bolm and J. Bonnamour, *Org. Lett.*, 2011, **13**, 2012–2014.
9 Z. Zhu, J. Yuan, Y. Zhou, Y. Qin, J. Xu and Y. Peng, *Eur. J. Org. Chem.*, 2014, 511–514.
10 X. Xiao, T.-Q. Chen, J. Ren, W.-D. Chen and B.-B. Zeng, *Tetrahedron Lett.*, 2014, **55**, 2056–2060.
11 D. Formenti, F. Ferretti and F. Ragaini, *ChemCatChem*, 2018, **10**, 148–152.
12 A. Baykal and B. A. Plietker, *Eur. J. Org. Chem.*, 2020, 1145–1147.
13 M. A. Gouad, F. Ferretti, D. Formenti, F. Milani and F. Ragaini, *Eur. J. Org. Chem.*, 2021, 4876–4894.
14 M. A. Fouad, F. Ferretti and F. Ragaini, *J. Org. Chem.*, 2023, **88**, 5108–5117.
15 M. Bandini and A. Eichholzer, *Angew. Chem., Int. Ed.*, 2009, **48**, 9608–9644.
16 R. A. Jagtap and B. Punji, *Asian J. Org. Chem.*, 2020, **9**, 326–342.
17 K. Zhao, R. Du, B. Wang, J. Liu, C. Xia and L. Yang, *ACS Catal.*, 2019, **9**, 5545–5551.
18 R. Du, K. Zhao, J. Liu, F. Han, C. Xia and L. Yang, *Org. Lett.*, 2019, **21**, 6418–6422.
19 K. Mondal, P. Halder, G. Gopalan, P. Sasikumar, K. V. Radhakrishnan and P. Das, *Org. Biomol. Chem.*, 2019, **17**, 5212–5222.
20 Z. Chen, L.-C. Wang and X.-F. Wu, *Chem. Commun.*, 2020, **56**, 6016–6030.
21 W.-Y. Yu, W. N. Sit, K.-M. Lai, Z. Zhou and A. S. C. Chan, *J. Am. Chem. Soc.*, 2008, **130**, 3304–3306.

22 Y. Huang, G. Li, J. Huang and J. You, *Org. Chem. Front.*, 2014, **1**, 347–350.
23 N. Xu, D. Li, Y. Zhang and L. Wang, *Org. Biomol. Chem.*, 2015, **13**, 9083–9092.
24 R. Sang, Y. Zheng, H. Zhang, X. Wu, Q. Wang, L. Hai and Y. Wu, *Org. Chem. Front.*, 2018, **5**, 648–652.
25 M. Usman, X.-W. Zhang, D. Wu, Z.-H. Guan and W.-B. Liu, *Org. Chem. Front.*, 2019, **6**, 1905–1928.
26 J. Ni, J. Li, Z. Fan and A. Zhang, *Org. Lett.*, 2016, **18**, 5960–5963.
27 T. T. Nguyen, L. Grigorjeva and O. Daugulis, *Chem. Commun.*, 2017, **53**, 5136–5138.
28 F. Ling, C. Ai, Y. Lv and W. Zhong, *Adv. Synth. Catal.*, 2017, **359**, 3707–3712.
29 T. Kochi, S. Urano, H. Seki, E. Mizushima, M. Sato and F. Kakiuchi, *J. Am. Chem. Soc.*, 2009, **131**, 2792–2793.
30 G. Liao, H.-M. Chen and B.-F. Shi, *Chem. Commun.*, 2018, **54**, 10859–10862.
31 Y. Shi, F. Yang and Y. Wu, *Org. Biomol. Chem.*, 2020, **18**, 4628–4637.
32 X. Peng, Y. Zhu, T. A. Ramirez, B. Zhao and Y. Shi, *Org. Lett.*, 2011, **13**, 5244–5247.
33 S. Wang, Z. Yang, J. Liu, K. Xie, A. Wang, X. Chen and Z. Tan, *Chem. Commun.*, 2012, **48**, 9924–9926.
34 W. Zhou, P. Li, Y. Zhang and L. Wang, *Adv. Synth. Catal.*, 2013, **355**, 2343–2352.
35 X. Hong, H. Wang, B. Liu and B. Xu, *Chem. Commun.*, 2014, **50**, 14129–14132.
36 H. Suzuki, Y. Liao, Y. Kawai and T. Matsuda, *Eur. J. Org. Chem.*, 2021, 4938–4942.
37 H. Suzuki, F. Sasamori and T. Matsuda, *Org. Lett.*, 2022, **24**, 1141–1145.
38 H. Suzuki, Y. Ito and T. Matsuda, *Chem. Lett.*, 2022, **51**, 775–777.
39 J. Wu, J. Lan, S. Guo and J. You, *Org. Lett.*, 2014, **16**, 5862–5865.
40 Z.-Y. Li and G.-W. Wang, *Org. Lett.*, 2015, **17**, 4866–4869.
41 Y. Gao, W. Lu, P. Liu and P. Sun, *J. Org. Chem.*, 2016, **81**, 2482–2487.
42 L.-Y. Xie, S. Peng, T.-G. Fan, Y.-F. Liu, M. Sun, L.-L. Jiang, X.-X. Wang, Z. Cao and W.-M. He, *Sci. China: Chem.*, 2019, **62**, 4660–4464.
43 G. R. Y. Kumar and N. S. Begum, *Eur. J. Org. Chem.*, 2020, 4698–4704.
44 N. Tao, J. Wang, C. Yuan, R. Zeng and Y.-S. Zhao, *Org. Lett.*, 2019, **21**, 8607–8610.
45 Q.-Q. Yang, M. Marchini, W.-J. Xiao, P. Ceroni and M. Bandini, *Chem. – Eur. J.*, 2015, **21**, 18052–18056.
46 C. Sen, T. Sahoo, H. Singh, E. Suresh and S. C. Ghosh, *J. Org. Chem.*, 2019, **84**, 9869–9896.
47 T. Sahoo, C. Sen, H. Singh, E. Suresh and S. C. Ghosh, *Adv. Synth. Catal.*, 2019, **361**, 3950–3957.
48 S. Kumar, S. Pradhan, S. Roy, P. B. De and T. Punniyamurthy, *J. Org. Chem.*, 2019, **84**, 10481–10489.
49 J. Wang, L. Zhang, Z. Dong and G. Dong, *Chem*, 2016, **1**, 581–591.
50 Z. Dong, J. Wang, Z. Ren and G. Dong, *Angew. Chem., Int. Ed.*, 2015, **54**, 12664–12668.
51 H. Suzuki, Y. Kawai, Y. Takemura and T. Matsuda, *Org. Biomol. Chem.*, 2022, **20**, 2808–2812.
52 H. Suzuki, Y. Takemura and T. Matsuda, *Synlett*, 2023, **34**, 1894–1898.
53 D. D. Miller, P. Bamborough, J. A. Christopher, I. R. Baldwin, A. C. Champigny, G. J. Cutler, J. K. Kerns, T. Longstaff, G. W. Mellor, J. V. Morey, M. A. Morse, H. Nie, W. L. Rumsey and J. J. Taggart, *Bioorg. Med. Chem. Lett.*, 2011, **21**, 2255–2258.
54 J. K. Kerns, J. Busch-Petersen, W. Fu, J. C. Boehm, H. Nie, M. Muratore, A. Bullion, G. Lin, H. Li, R. Davis, X. Lin, A. S. Lakdawala, R. Cousins, R. Field, J. Payne, D. D. Miller, P. Bamborough, J. A. Christopher, I. Baldwin, R. R. Osborn, J. Yonchuk, E. Webb and W. L. Rumsey, *ACS Med. Chem. Lett.*, 2018, **9**, 1164–1169.
55 F. L. Gonzalez, S. R. Wisniewski, K. Katipally, J. M. Stevens, V. Rosso, B. Mack and T. M. Razler, *Org. Process Res. Dev.*, 2019, **23**, 1143–1151.
56 D. H. Nguyen, N. Lassauque, S. Vendier, S. Mallet-Ladeira, C. L. Berre, P. Serp and P. Kalck, *Eur. J. Inorg. Chem.*, 2014, 326–336.