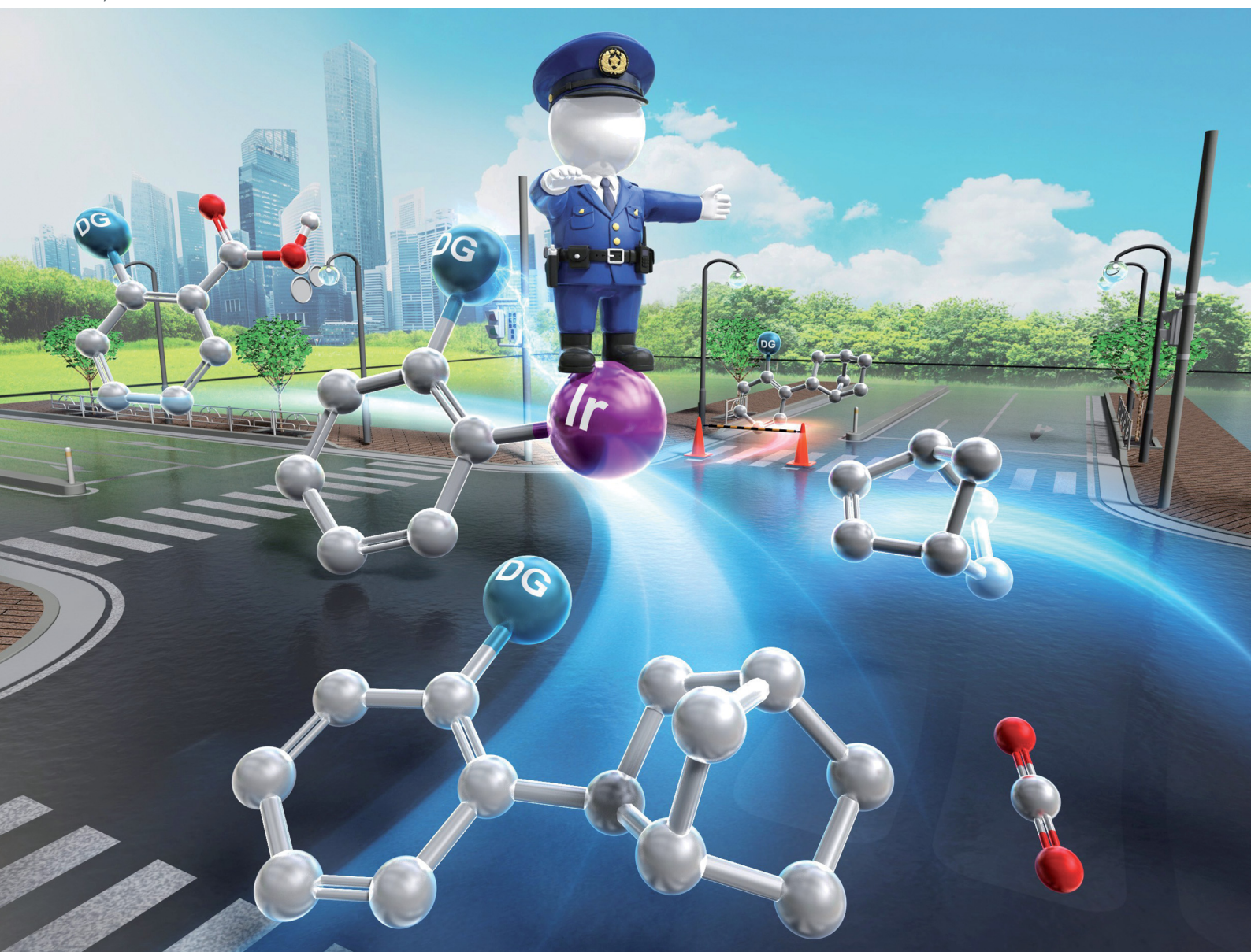


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Cationic iridium-catalyzed enantioselective decarboxylative aryl addition of aromatic carboxylic acids to bicyclic alkenes

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Decarboxylative functionalization is an environmentally benign approach that enables the formation of new chemical bonds while emitting only CO₂ as a byproduct. Herein, we report an asymmetric aryl addition to bicyclic alkenes involving the decarboxylation of aromatic carboxylic acids. The cationic iridium/*S*-Me-BIPAM catalyst system is effective in this reaction, enabling the enantioselective construction of chiral aryl-substituted bicyclo[2.2.1]heptane cores (up to 85% yield and up to 99% ee).

The chiral bicyclo[2.2.1] framework is an attractive structural motif and a prevalent substructure found in bioactive molecules such as SPK-601,¹ AMG 221,² setrobuvir, and sordarins (Fig. 1).³

In addition, a chiral phosphine compound containing a bicyclo[2.2.1] moiety has also been employed as a chiral ligand in asymmetric synthesis.⁴ Consequently, substantial effort has been devoted to the development of various synthetic methodologies for the construction of these frameworks.⁵ In particular, in view of the pharmacological relevance of chiral aryl-substituted bicyclo[2.2.1]heptane derivatives,⁶ considerable attention has been directed toward the development of asymmetric arylation that provides direct access to these scaffolds *via* metal catalysis. Methods employing reactive reagents such as organometallic compounds⁷ or (pseudo)halides⁸ have been reported. Approaches based on the direct transformation of

moieties that are ubiquitously present in organic molecules also provide an alternative entry to asymmetric arylation.^{9,10} Alongside catalytic asymmetric directed C(sp²)-H addition established by Hartwig¹¹ and our group¹² (Scheme 1a), the enantioselective *ipso*-transformation of ubiquitous carbonyl moieties represents an attractive strategy. In 2022, we reported that chiral cationic iridium catalysts could generate aryl-metal species *via* C-C bond activation through decarbonylation of aldehydes (Scheme 1b).^{13,14} These species enabled enantioselective decarbonylative aryl addition to bicyclic alkenes, constructing optically active bicyclo[2.2.1] skeletons. Our process represents the first highly enantioselective decarbonylative aryl addition to C-C double bonds; however, it has the potential drawback of catalyst deactivation through coordination of the generated CO. Thus, this reaction typically requires a high catalyst loading (at least 10 mol%), high temperatures, and long reaction times. To address these issues, we turned our attention to the decarboxylation of carboxylic acids and found that a cationic iridium complex with a chiral diphosphine ligand exhibited excellent catalytic activity for the decarboxylation of aromatic carboxylic acids.¹⁵ Aromatic carboxylic acids are abundant in nature and readily available as chemical feedstocks, and therefore have been widely utilized in conventional organic transformations as well as catalytic decarboxylative functionalization. Among the various methods, decarboxylative

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[†] These authors contributed equally to this work.

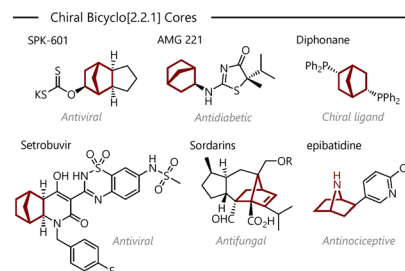
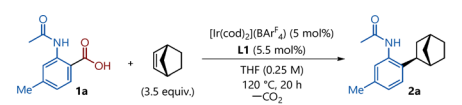


Fig. 1 Selected molecules, including the bicyclo[2.2.1] core.



aryl addition reactions of aromatic carboxylic acids represent an environmentally benign and attractive approach that does not require organometallic reagents and does not generate strongly coordinating gases. However, asymmetric variants of decarboxylative aryl addition have not been reported to date.^{16–19} Herein, we report a cationic iridium-catalyzed asymmetric aryl addition to bicyclic alkenes *via* C–C bond activation through decarboxylation (Scheme 1c).

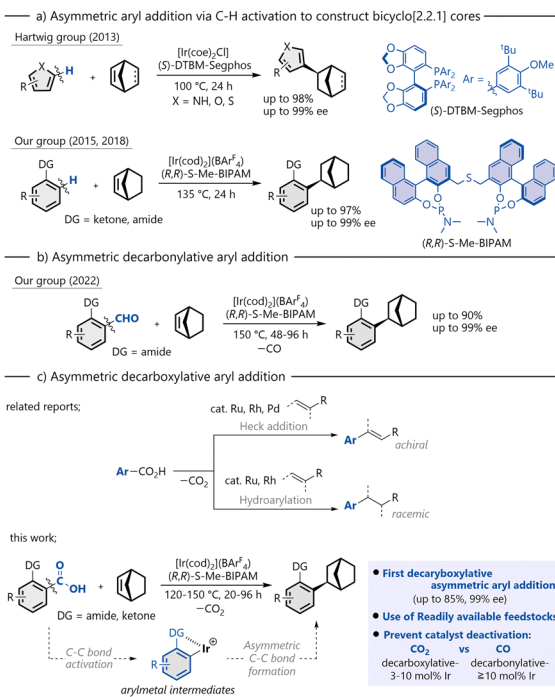
Our investigation started using carboxylic acid **1a**, as the model substrate, with 2-norbornene over $[\text{Ir}(\text{cod})_2](\text{BAR}^{\text{F}}_4)$ (5 mol%, cod = 1,5-cyclooctadiene, BAR^{F}_4 = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) and (R,R) -S-Me-BIPAM (5.5 mol%) in tetrahydrofuran (THF) at 120 °C in a sealed tube for 20 h under an N_2 atmosphere, to give the desired adduct in 82% yield with 99% ee (Table 1, entry 1). The counterion strongly affects the decarboxylation process, presumably because enhanced Lewis acidity plays a crucial role in facilitating decarboxylation. Using $[\text{Ir}(\text{cod})_2](\text{OTf})$ or $[\text{Ir}(\text{cod})\text{Cl}]_2$ as precursors did not give the desired product (entries 2 and 3). When $[\text{Ir}(\text{cod})_2](\text{OTf})$ was employed, only the decarboxylation product was obtained in 13% yield, whereas $[\text{Ir}(\text{cod})\text{Cl}]_2$ did not promote the decarboxylation. Reactions with (R,R) -Me-BIPAM, (R,R) -BINAP, (R) -SEGPHOS, and (S,S) -CHIRAPHOS afforded the products in low yields and enantioselectivities (entries 4–7). The reaction was performed with 3 mol% catalyst loading, and the desired product **2a** was obtained in 81% yield and 98% ee (entry 8). The iridium source and phosphine ligand are essential for reactivity (entries 9 and 10). Next, the scope of the reaction was explored by examining the functional groups on

Table 1 Reaction optimization^a


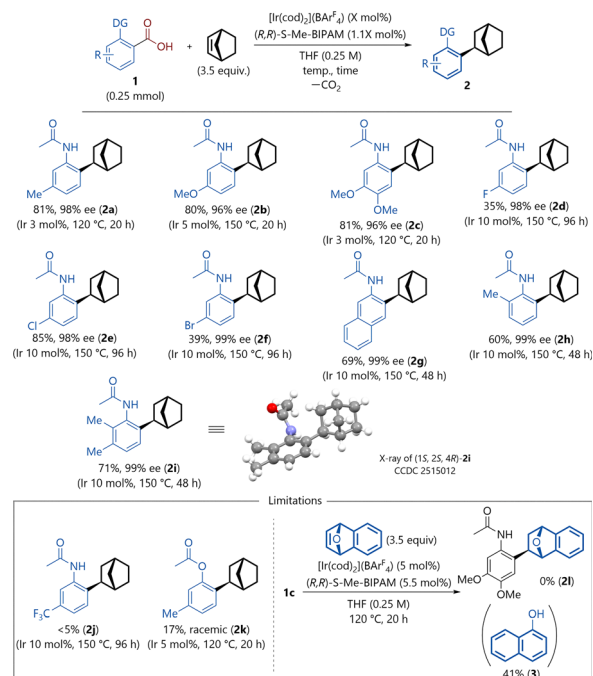
Entry	Deviation from above	Yield ^b (%)	ee ^c
1	None	82	99%
2	$[\text{Ir}(\text{cod})_2](\text{OTf})$	0	—
3	$[\text{Ir}(\text{cod})\text{Cl}]_2$ (2.5 mol%)	0	—
4	(R,R) -Me-BIPAM (L2)	20	92%
5	(R) -BINAP (L3)	10	n.d.
6	(R) -SEGPHOS (L4)	57	28%
7	(S,S) -CHIRAPHOS (L5)	72	0%
8	Ir/ligand (3 mol%)	81	98%
9	No $[\text{Ir}(\text{cod})_2](\text{BAR}^{\text{F}}_4)$	0	—
10	No ligand	Trace	n.d.

^a Reactions were run on a 0.25 mmol scale. ^b Isolated yields. ^c Enantiomeric excess (ee) was determined by HPLC analysis with a chiral stationary phase. n.d. denotes not determined.

the aromatic ring of the carboxylic acids under the optimized conditions (Scheme 2). A substituent on aromatic carboxylic acid **1** significantly influenced the reactivity. Electron-donating substituents at the 4- or 5-position of the substrates were well tolerated (**2a–2c**). In contrast, when aromatic carboxylic acids bearing electron-withdrawing groups such as fluoro (**1d**) or bromo groups (**1f**) were used, the yields decreased, with the exception of the chloro group (**1e**), while enantioselectivities of



Scheme 1 (a) Asymmetric aryl addition *via* C–H activation to construct bicyclo[2.2.1] cores. (b) Asymmetric decarboxylative aryl addition. (c) Asymmetric decarboxylative aryl addition.



Scheme 2 Scope of aromatic carboxylic acids **1**.



over 90% ee were maintained. 3-Acetamido-2-naphthoic acid (**1g**) reacted by using 10 mol% of catalyst at 150 °C for 48 h, affording the product **2g** in 69% yield with 99% ee. The presence of a methyl group at the 3-position of the aryl backbone (**1h**, **1i**) had a negative effect on the reactivity, giving products **2h** (60%, 99% ee) and **2i** (71%, 99% ee), respectively, by using 10 mol% of catalyst at 150 °C for 48 h.

In addition, the absolute configuration of (1*S*, 2*S*, 4*R*)-**2i** was confirmed by X-ray crystallographic analysis. Substrate **1j**, which bears a CF₃ group at the 4-position, was unsuccessful. The reaction in the presence of an ester group at the 2-position gave the racemic product **2k** in a diminished yield. The reaction of substrate **1c** with oxa-benzonorbornadiene gave no desired addition product; instead, 1-naphthol **3** was obtained in 41% yield *via* the catalytic isomerization of bicycloalkene.²⁰ Having identified the optimal reaction conditions, we investigated the reactions of aromatic carboxylic acids bearing ketone moieties (Scheme 3). Our previous studies on the decarboxylation of aromatic carboxylic acids showed that the 2-thienylcarbonyl group is a suitable directing group for the reaction, affording the desired arene product in high yield (81%).¹⁵ The first attempt was carried out using 3-(5-methylthiophene-2-carbonyl)-2-naphthoic acid (**1m**) and 2-norbornene, in the presence of 5 mol% Ir precursor and 5.5 mol% BIPAM ligand in THF at 150 °C. However, the desired adduct (**2m**) was obtained in only 9% yield after 20 h with the formation of undesired regioisomeric side products (see the SI for details). To suppress the formation of side products *via* C–H activation, a methyl group was introduced at the 4-position of the thiophene ring. Substrate bearing 4,5-dimethyl groups on the thiophene ring (**1n**) afforded the desired product (**2n**) in moderate yield with high enantioselectivity (36% yield, 98% ee). Next, the effects of bicyclic alkenes were explored. In the case of benzonorbornadiene, the reaction resulted in the formation of the desired product (**2o**) in improved yield with excellent enantioselectivity (58% yield, 99% ee). Based on the experimental observations and our previous studies, a plausible catalytic cycle for the reaction is proposed, as shown in Fig. 2a. Initially, the decarboxylation generates aryl–iridium hydride intermediates ($\delta_{\text{H}} -14.5$, see the SI for details). Subsequently,

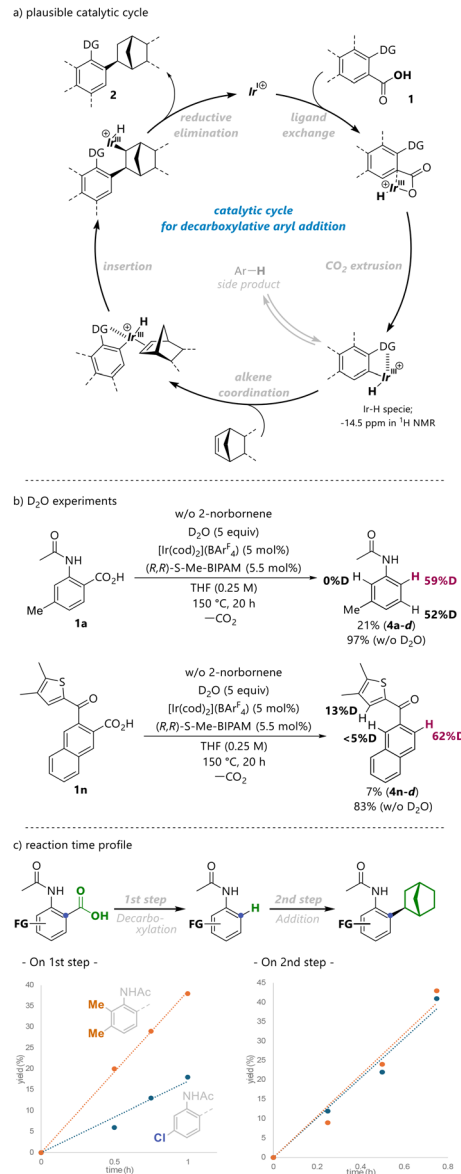
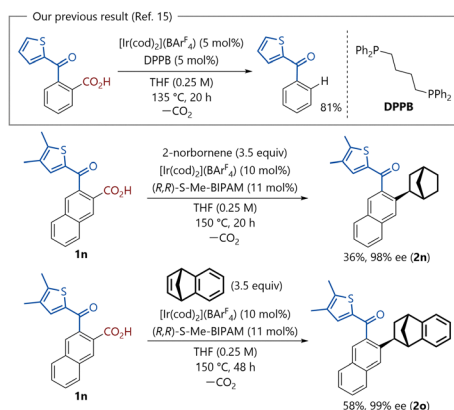


Fig. 2 (a) Plausible catalytic cycle. (b) D₂O experiments. (c) Reaction time profile.

the alkene inserts into the aryl–iridium bond to form an alkyl–iridium species. Finally, the cationic Ir^I active species are generated from the alkyl iridium complex *via* reductive elimination.

To gain further insight into the reaction mechanism, we performed D₂O experiments to determine the site of activation by the catalyst (Fig. 2b). This catalytic system for decarboxylation was not effective in the presence of H₂O or D₂O, but predominant incorporation of a deuterium label at the *ipso* position was observed in the products (**4a-d** and **4n-d**) (see the SI for details). In the amide product (**4a-d**), deuteration at the adjacent position was also observed.

In addition, the reaction time profiles were investigated (Fig. 2c). This reaction proceeds *via* decarboxylation followed by addition. Therefore, we compared the initial rates for each step using substrates with electron-donating and electron-withdrawing groups. As a result, the decarboxylation was



Scheme 3 Scope of aromatic carboxylic acids bearing a ketone moiety.



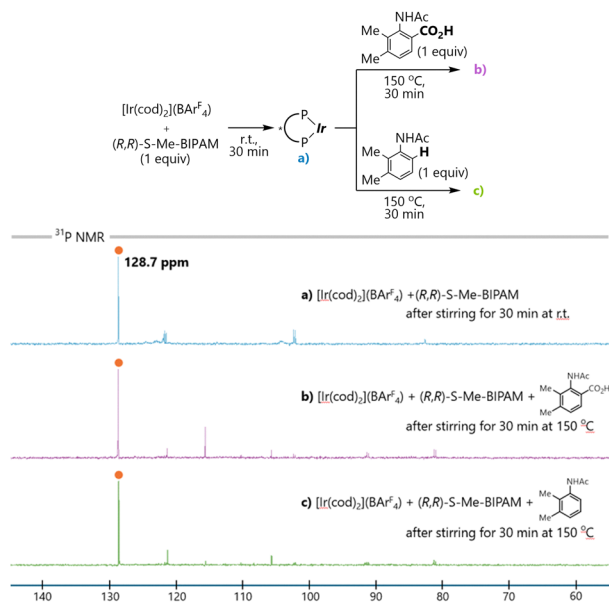


Fig. 3 ^{31}P NMR spectra in THF-d_8 (160 MHz).

accelerated in the presence of electron-donating groups, whereas no significant rate difference was observed for the addition step. This suggests that the CO_2 extrusion process accompanied by carbon-carbon bond activation is facilitated by electron-donating groups and is likely involved in the rate-determining step. Next, ^{31}P NMR was recorded before and after decarboxylation. For the active complex prepared from $[\text{Ir}(\text{cod})_2](\text{BARF}_4)$ and S-Me-BIPAM, a major peak was observed at 128.7 ppm (Fig. 3a), and no peak shift was observed even after decarboxylation (Fig. 3b). The peak position remained unchanged even in the presence of acetanilide, where reversible C-H activation proceeds (Fig. 3c). These results indicate that CO_2 generated by the decarboxylation does not affect the catalyst structure, and hence its reactivity.

In conclusion, we have developed the first asymmetric decarboxylative aryl addition of aromatic carboxylic acids directed by anilide or ketone moieties, with excellent enantioselectivity (up to 99% ee). Although the reaction is limited to the use of carbon bridged bicyclic alkenes, our findings provide a new synthetic strategy for constructing chiral carbon-carbon bonds using metal catalysis. Furthermore, ongoing efforts are focused on elucidating the origins of enantioselectivity and extending this catalytic protocol to challenging molecular transformations.

All authors contributed to the writing of this manuscript and have approved the final submitted version.

Conflicts of interest

The authors declare no conflicts of interest.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: experimental details, NMR spectra of the new compounds

and X-ray crystallographic data. See DOI: <https://doi.org/10.1039/d6cc00389c>.

CCDC 2515012 contains the supplementary crystallographic data for this paper.²¹

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