

# *Supporting Information*

## **Cp\*Ir(III)-Catalyzed C–H/O–H Functionalization of Salicylaldehydes for the Synthesis of Chromones at Room Temperature**

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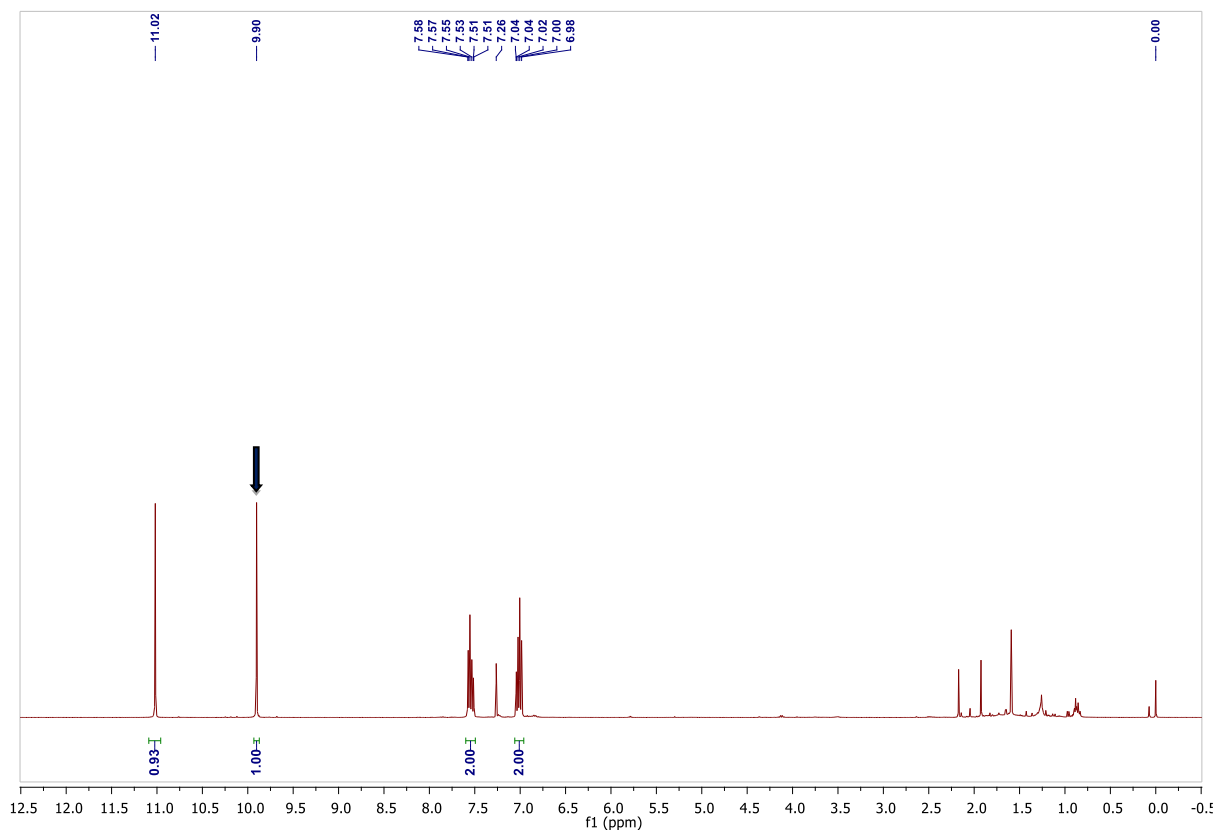
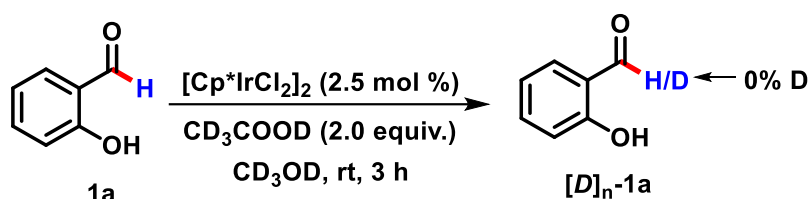
(<sup>φ</sup>Both the authors contributed equally to this work)

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## 1. H/D Exchange Experiment (Scheme 5a)

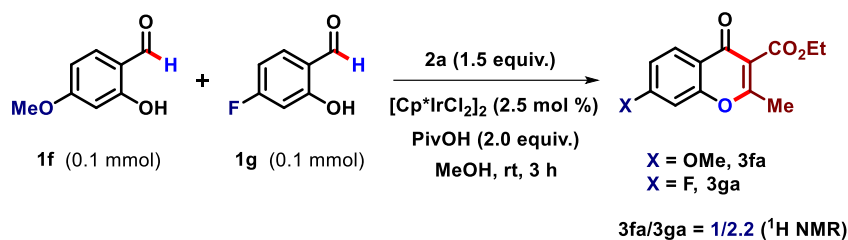
### Iridium-Catalyzed H/D Exchange in salicylaldehyde **1a** with CD<sub>3</sub>COOD

To a dried screw capped vial with a spinvane triangular-shaped Teflon stirbar were added salicylaldehyde **1a** (12.2 mg, 0.10 mmol), [Cp\*IrCl<sub>2</sub>]<sub>2</sub> (2.0 mg, 2.5 mol %), CD<sub>3</sub>COOD (2.0 equiv) and CD<sub>3</sub>OD (0.6 mL). The reaction mixture was stirred at room temperature for 3 h, filtered through a pad of celite and the celite pad was washed with CHCl<sub>3</sub> (10 mL × 2). The solvent was removed under reduced pressure and the extents of deuterium incorporation was measured by <sup>1</sup>H NMR analysis of the crude mixture (Figure S1).

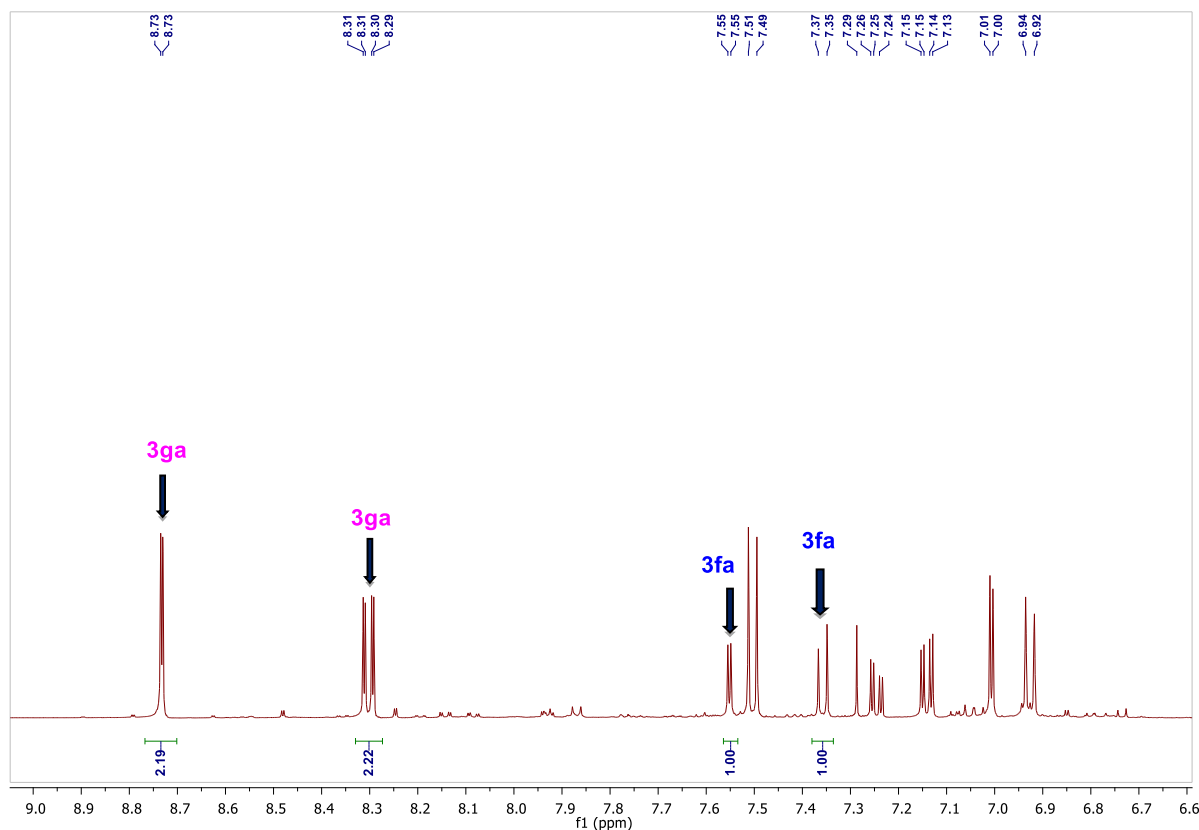


**Figure S1.** Crude <sup>1</sup>H NMR for H/D exchange experiment of **1a** with CD<sub>3</sub>COOD in absence of **2a**.

## 2. Intermolecular Competitive Experiment (Scheme 5b)



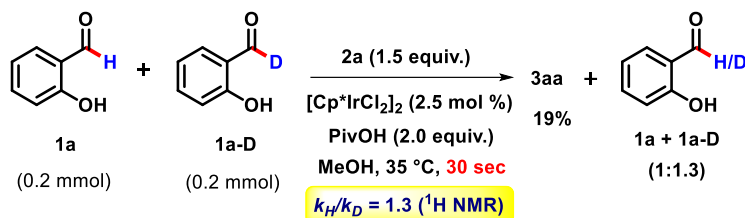
To a dried screw capped vial with a spinvane triangular-shaped Teflon stirbar were added **1f** (15.2 mg, 0.10 mmol), **1g** (14.0 mg, 0.10 mmol), ethyl diazoacetate **2a** (23.4 mg, 0.15 mmol),  $[\text{Cp}^*\text{IrCl}_2]_2$  (2.0 mg, 2.5 mol %), PivOH (20.4 mg, 2.0 equiv.), and MeOH (0.6 mL) under air atmosphere. The reaction mixture was stirred at room temperature for 3 h, filtered through a pad of celite and then the celite pad was washed with  $\text{CHCl}_3$  (10 mL  $\times$  2). The combined organic layers were removed under reduced pressure. The solvent was evaporated under reduced pressure and dried under vacuo. The crude  $^1\text{H NMR}$  was recorded to determine the ratio of the products **3fa** and **3ga** (Figure S2).



**Figure S2.** Crude  $^1\text{H NMR}$  for intermolecular competitive experiment between **1f** and **1g**.

### 3. Intermolecular Kinetic Isotope Effect Experiments (Scheme 5c)

#### (A) Competitive reaction



To a dried screw capped vial with a spinvane triangular-shaped Teflon stirbar were added **1a** (24.4 mg, 0.20 mmol), **1a-D** (24.6 mg, 0.20 mmol), ethyl diazoacetoacetate **2a** (46.8 mg, 0.3 mmol),  $[\text{Cp}^*\text{IrCl}_2]_2$  (4.0 mg, 2.5 mol %), PivOH (40.4 mg, 2.0 equiv.), and MeOH (1.2 mL) under air atmosphere. The reaction mixture was stirred at room temperature for 30 sec and immediately diluted with HPLC Hexane (15 mL) and transferred to 25 mL round bottom flask. The solvent was evaporated and the residue was purified by column chromatography to afford the desired **3aa** (9 mg, 19%) and unreacted mixture of **1a** and **1a-D** in 1:1.3 ratio as determined by  $^1\text{H}$  NMR ( $k_H/k_D = 1.34$ ) (Figure S3).

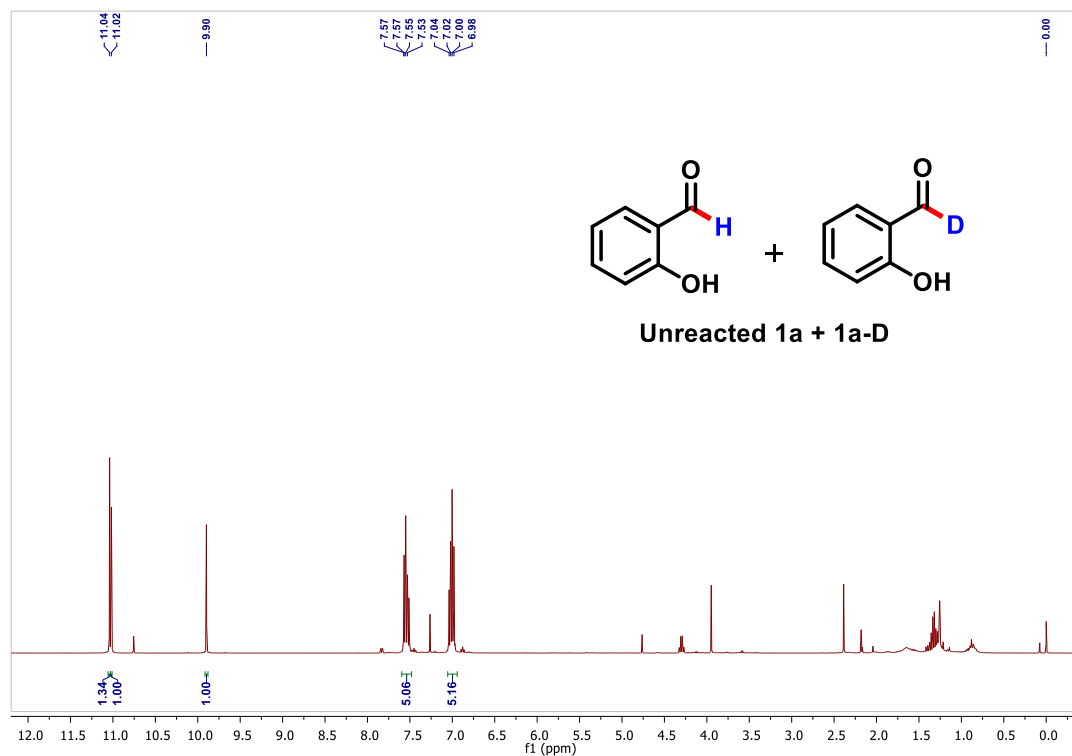
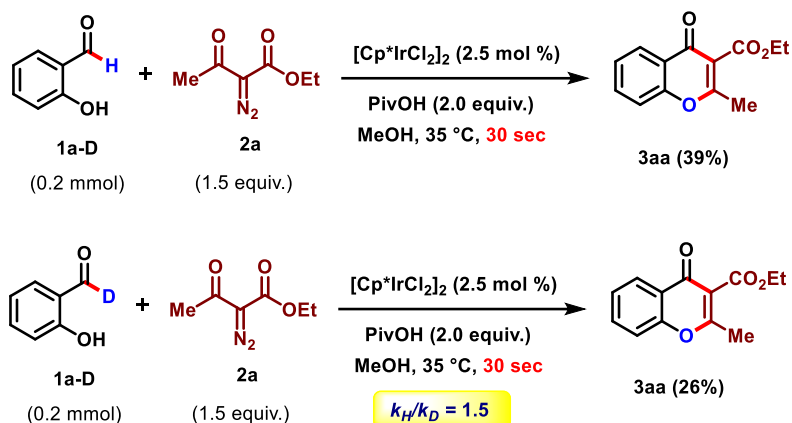


Figure S3.  $^1\text{H}$  NMR for unreacted **1a** and **1a-D** from Intermolecular KIE Study.

**(B) Parallel reactions**



To a dried two separate screw capped vial with a spinvane triangular-shaped Teflon stirbar were added **1a** (24.4 mg, 0.20 mmol) and **1a-D** (24.6 mg, 0.20 mmol). Then in each vial were added ethyl diazoacetate **2a** (46.8 mg, 0.3 mmol),  $[\text{Cp}^*\text{IrCl}_2]_2$  (4.0 mg, 2.5 mol %), PivOH (40.4 mg, 2.0 equiv.) and MeOH (1.2 mL) under air atmosphere. Both the reaction mixtures were stirred at room temperature for 30 sec and immediately diluted with HPLC Hexane (15 mL) and transferred to two different 25 mL round bottom flasks. The solvent was evaporated and the residues were purified separately by column chromatography. The reaction with **1a** afforded the desired **3aa** in 38% yield (18.0 mg) and the reaction with **1a-D** afforded the desired **3aa** in 26% yield (12.0 mg). **KIE = 1.5**

# *Appendix I*

**Spectral Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR of Compounds  
Obtained in this study**

