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C−H Bond Functionalization of Benzoic Acid: Catalytic Synthesis of 2-Hydroxy-6*H*-benzo[*c*]chromen-6-ones Using $(Cp^*IrCl_2)_2$

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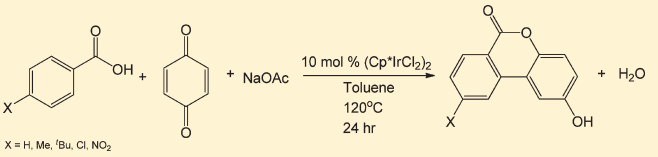
ABSTRACT: Catalytic H/D exchange reactions of benzene and benzoic acid with deuterated solvents have been studied using $(Cp^*IrCl_2)_2$. A 1:1 mixture of D_2O/CD_3OD produced the highest turnover numbers for benzene. High levels of deuterium incorporation into benzoic acid were observed only when sodium acetate was added to the reaction mixture. Attempts at producing hydroxybenzoic acid by catalytic C−H functionalization of benzoic acid with benzoquinone were unsuccessful. Instead, 2-hydroxy-6*H*-benzo[*c*]chromen-6-one was isolated as the major product. An array of substituted benzoic acids was analyzed for this functionalization reaction. Preliminary mechanistic studies indicate that the benzochromenones are formed by C−H bond activation of benzoic acid followed by insertion of benzoquinone into the iridium−carbon bond.



INTRODUCTION

As current fuel supplies continue to diminish, the need for alternative fuel sources becomes increasingly apparent. One pathway currently being examined is C−H bond activation and functionalization of natural gas, primarily CH_4.[1,2] The first transition metal promoted C−H bond activation was reported by Chatt et al. in 1965.[3] Many transition metal C−H bond activation catalysts have been reported since.[1,4−15]

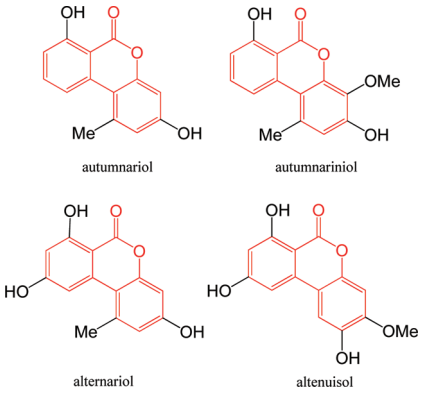
Despite the vast amount of literature on transition metal catalyzed C−H bond activation, as generally demonstrated by H/D exchange studies, strategies for the insertion of a functionality in the new metal−carbon bond once a C−H bond has been cleaved (C−H functionalization) have been less successful. The majority of catalytic C−H bond functionalization reactions center around activation using either rhodium or palladium.[7,16−19] Given the prominence of iridium catalysts in the C−H bond activation literature, the development of catalytic methods for C−H bond functionalization using iridium complexes is highly desirable.[19−29]

We herein report the C−H bond activation of benzene and benzoic acid by $(Cp^*IrCl_2)_2$ resulting in H/D exchange with deuterated solvents. In addition, C−H bond functionalization of benzoic acid with benzoquinone using $(Cp^*IrCl_2)_2$ produced a series of benzo[*c*]chromen-6-ones.

Benzo[*c*]chromen-6-ones (dibenzo[*b*,*d*]pyran-6-ones) have been found in numerous natural products, including citrus fruits, herbs, and vegetables.[30] These compounds act as progesterone receptor agonists[31,32] and endothelial cell growth inhibitors.[33] Among known natural 6*H*-benzo[*c*]chromen-6-ones are autumnariol, autumnariniol, alternariol, and altenuisol (Chart 1).[34−37]

There are several known pathways to synthesize benzochromenones. Langer and co-workers developed a series of predominantly organic pathways for the synthesis of these complexes; however these reactions generally require highly functionalized starting materials and often have low yields.[38−43] Metal-catalyzed processes have significantly higher yields, but also require strategically functionalized starting materials.[44−47] For example, Vishnumurthy et al. recently reported the one-step synthesis of benzochromenones; however, the reaction proceeds by a Suzuki−Miyaura cross-coupling of *o*-hydroxylarylboronic acids and bromoarylcarboxylates.[46] A similar pathway using *o*-amidoarylboronic acids and bromoaryl ethers was reported by Snieckus and co-workers (Scheme 1).[44]

Chart 1. Natural 6*H*-Benzo[*c*]chromen-6-ones



In this paper, we report a new reaction for the synthesis of benzochromenone that proceeds by two steps. First, C−H bond activation of the benzoic acid occurs, resulting in the formation of an iridium metallacycle. Second, C−H bond functionalization occurs by insertion of the benzoquinone into the metal carbon bond of the metallacycle. Due to the rare nature of reactions involving C−H bond activation and functionalization utilizing electrophilic iridium catalysts, the catalytic synthesis of benzochromenones by C−H bond functionalization of benzoic acid

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Scheme 1

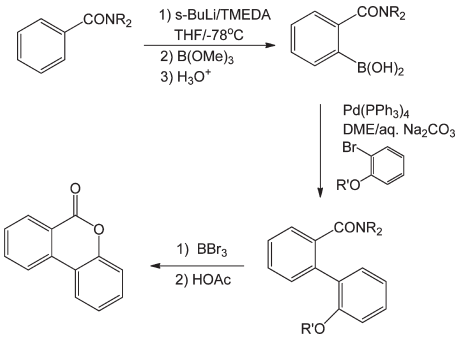

Table 1. Catalytic H/D Exchange of Benzene Using $(Cp^*IrCl_2)_2$ in Deuterated Solvents

$C_6H_6 \xrightarrow[150^oC,\ 24\ hr]{2\ mol\ \%\ (Cp^*IrCl_2)_2} C_6H_{6-n}D_n$

entry	solvent[a]	TON[b]
1	CD_3OD	1(1)
2	1:1 CD_3OD/D_2O	86(3)
3	TFA-d_1	4(3)

[a] Conditions: $(Cp^*IrCl_2)_2$ (2 mol %, 0.025 mmol), benzene (111 μL, 1.25 mmol), solvent (25 mmol); 150 °C for 24 h. Numbers represent an average of three runs with standard deviations in parentheses. [b] TON calculated by GC MS assay.[49,50]

with $(Cp^*IrCl_2)_2$ is an elegant example of the capabilities of these catalysts. We demonstrate that, in addition to activating arene C−H bonds, Cp*Ir complexes can be used for further functionalization of C−H bonds.

RESULTS

As recently reported by our group, several Cp*Ir(NHC) complexes catalyze H/D exchange between an arene and various deuterated solvents.[48] The catalytic H/D exchange reactions by these iridium complexes reflect their propensity to activate aromatic C−H bonds. Similarly, the complex $(Cp^*IrCl_2)_2$, **1**, catalyzes H/D exchange of benzene with deuterated solvents as shown in Table 1. In accordance with our previous findings, there is a large solvent dependence, with a 1:1 mix of CD_3OD and D_2O producing the highest turnover numbers (TON).

Catalytic H/D exchange studies were also performed using benzoic acid as the substrate. However, when the reaction was performed in either CD_3OD or toluene-d_8, the distribution of benzoic acid isotopologues indicated that predominantly benzoic acid-d_0 was observed in the GC-MS spectrum and that minimum deuterium incorporation occurred (Table 2).

Table 2. H/D Exchange of Benzoic Acid Using $(Cp^*IrCl_2)_2$ and NaOAc with Deuterated Solvents

$C_6H_5COOH \xrightarrow[120^oC,\ 24\ hr]{10\ mol\ \%\ [Ir]} C_6(H/D)_5COO(H/D)$

		CD_3OD solvent[a]		toluene-d_8 solvent[b]	
entry	isotopologue	$(Cp^*IrCl_2)_2$	$(Cp^*IrCl_2)_2$/NaOAc	$(Cp^*IrCl_2)_2$	$(Cp^*IrCl_2)_2$/NaOAc
1	% benzoic acid-d_0[c]	77(6)	8(4)	83(3)	4(1)
2	% benzoic acid-d_1	20(4)	29(8)	15(3)	15(4)
3	% benzoic acid-d_2	3(1)	44(2)	1(1)	33(2)
4	% benzoic acid-d_3	0	17(9)	0	31(3)
5	% benzoic acid-d_4	0	3(2)	0	14(3)
6	% benzoic acid-d_5	0	0	0	3(1)
7	% benzoic acid-d_6	0	0	0	0

[a] Conditions: $(Cp^*IrCl_2)_2$ (10 mol %, 0.025 mmol), NaOAc (when added, 10 mol %, 0.025 mmol), benzoic acid (0.25 mmol), CD_3OD (25 mmol); 120 °C for 24 h. Numbers represent an average of three runs with standard deviations in parentheses. [b] Conditions: $(Cp^*IrCl_2)_2$ (10 mol %, 0.025 mmol), NaOAC (when added, 10 mol %, 0.025 mmol), benzoic acid (0.25 mmol), toluene-d_8 (8.33 mmol); 120 °C for 24 h. Numbers represent an average of three runs with standard deviations in parentheses. [c] % Benzoic acid-d_n calculated by GC-MS relative to total benzoic acid intensity

The influence of sodium acetate as an additive was also investigated. Previous reports by Jones and co-workers indicated that the presence of sodium acetate enhances the rate of C−H bond activation of phenyl imines by $(Cp^*IrCl_2)_2$.[6] When catalytic quantities of $(Cp^*IrCl_2)_2$ were reacted with benzoic acid in deuterated solvents in the presence of NaOAc, higher isotopologues of benzoic acid were observed when compared to the reactions run without NaOAc (Table 2). For the reaction in CD_3OD, benzoic acid-d_2 was produced in the highest relative percent yield when NaOAc was added to the reaction mixture. When the reaction was performed in toluene-d_8, both benzoic acid-d_2 and benzoic acid-d_3 were observed in high concentrations with the addition of NaOAc.

C−H bond functionalization was then investigated using $(Cp^*IrCl_2)_2$ as the catalyst and benzoic acid as the substrate. Yu et al. reported the catalytic synthesis of hydroxybenzoic acid using benzoic acid as the substrate and benzoquinone as the oxygen atom transfer reagent.[51] Percent yields as high as 82% were observed when 10 mol % $Pd(OAc)_2$ was used as the catalyst.

However, the reaction of benzoic acid, benzoquinone, and sodium acetate in the presence of stoichiometric amounts of $(Cp^*IrCl_2)_2$ in air did not produce the desired hydroxybenzoic acid. Instead, 2-hydroxy-6*H*-benzo[*c*]chromen-6-one was isolated (Scheme 2).

An initial study of the substrate scope indicated a high functional group tolerance at the *para* position of the benzoic

Scheme 2

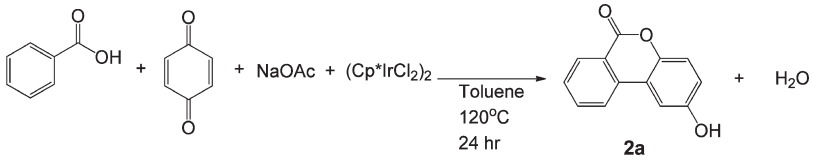

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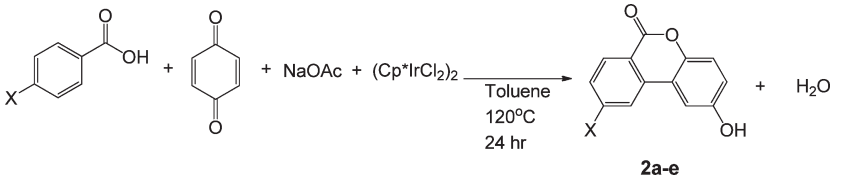
Table 3. Yields of Benzochromenone Formation by Reaction with Various Benzoic Acid Derivatives

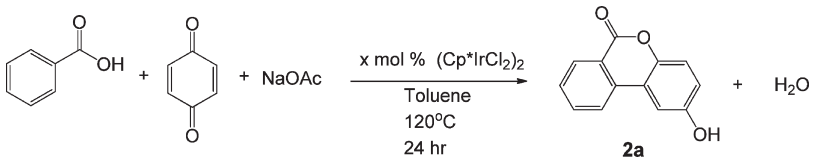


2a-e

compound	X	percent yield[a]
2a	H	98(63)
2b	Me	90(60)
2c	^{t}Bu	66(34)
2d	Cl	57(36)
2e	NO_2	64(20)

[a] Percent yield of benzochromenone by crude NMR versus an internal DSS standard. Numbers in parentheses are isolated yields.

Table 4. Percent Yield, TON, and Percent Conversion for Various Catalyst Loadings



2a

	catalyst loading (mol %)			
	2%	5%	7.5%	10%
% yield[a]	24(3)	31(1)	35(5)	83(2)
TON[a]	12(2)	6(1)	5(1)	9(1)
% conversion[b]	63(10)	81(1)	82(3)	82(1)

[a] Determined by crude NMR versus an internal DSS standard. Average of three runs. Numbers in parentheses are standard deviations. [b] Conversion of benzoquinone as determined by crude NMR versus an internal DSS standard. Average of three runs. Numbers in parentheses are standard deviations.

acid (Table 3). Benzochromenone formation was observed for both electron-withdrawing and electron-donating substituents.

Catalyst loading studies using benzoic acid as the substrate indicated that the highest yields were obtained with 10% catalyst loading (Table 4). The percent conversions of benzoquinone were anomalously high for 2, 5, and 7.5% catalyst loading relative to the percent yield. Percent yields for all substrates using a 10% catalyst loading along with percent conversions of benzoquinone are reported in Table 5.

DISCUSSION

The H/D exchange studies of benzoic acid suggest that sodium acetate is involved in the formation of the active catalyst. Under the same conditions as in Scheme 2, a variety of other bases were examined in the absence of NaOAc, including pyridine, triethylamine, and aniline. No product formation was observed with these other bases, indicating that sodium acetate is not merely acting as a base in the reactions. We believe that the starting iridium complex $(Cp^*IrCl_2)_2$, **1**, is the catalyst precursor to the active catalyst $Cp^*Ir(OAc)^+$, **3**, for the synthesis of benzochromenones, identical to the formation of **3** that was observed by Jones and co-workers in the reaction with phenyl imines (Scheme 3).[6]

We propose that benzoic acid consumption proceeds by both O−H bond activation of the acid moiety and *ortho* C−H bond activation to produce an iridium metallacycle (Scheme 4). The metallacycle has not been observed by NMR, even when the reaction is performed in the absence of benzoquinone. A similar iridium metallacycle was proposed by Satoh et al. as an intermediate in the catalytic coupling of benzoic acids with alkynes.[52]

Reaction of $(Cp^*IrCl_2)_2$ with 2,6-dimethylbenzoic acid and benzoquinone in the presence of NaOAc did not produce the analogous benzochromenone; however consumption of the acid was still observed. This suggests that although O−H bond activation may have occurred, a C−H bond activation at the *ortho* position of benzoic acid is required for product formation.

The role of benzoquinone was also studied. It was first postulated that benzoquinone acted only as an oxidant. However, reactions in which benzoquinone was replaced with various other oxidants, including dioxygen, potassium chromate, and hydrogen peroxide, did not produce the desired benzochromenone. In addition, catalytic reactions in which benzoquinone and an additional oxidant were used did not exhibit an increased yield of benzochromenone, indicating that a sacrificial oxidant is not necessary for conversion. Reactions using hydroquinone instead of benzoquinone did not lead to any product formation, suggesting that reduction of the benzoquinone occurs after incorporation into the metal fragment.

On the basis of initial results, we propose a general catalytic cycle as shown in Scheme 5. The first half of the cycle consists of

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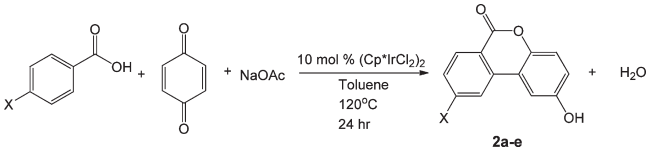
Table 5. Percent Yield and Percent Conversion for the Catalytic Reaction with Benzoic Acid Derivatives[a]

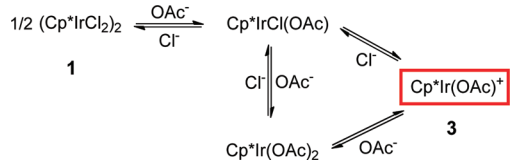


2a-e

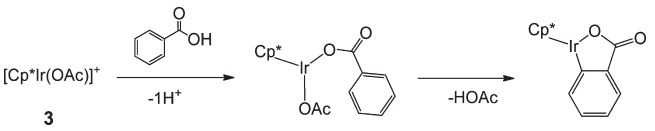
compound	X	percent yield[b]	percent conversion[c]
2a	H	83%	100%
2b	Me	86%	100%
2c	^{t}Bu	58%	100%
2d	Cl	23%	96%
2e	NO_2	33%	93%

[a] Conditions: $(Cp^*IrCl_2)_2$ (10 mol %, 0.038 mmol), benzoquinone (0.380 mmol), substrate (0.380 mmol), NaOAc (0.380 mmol) in toluene; 120 °C for 24 h. [b] Percent yield of benzochromenone as determined by crude NMR versus an internal DSS standard. [c] Percent conversion of benzoquinone as determined by crude NMR versus an internal DSS standard.

Scheme 3



Scheme 4



the formation of an iridium metallacycle by *ortho* C−H bond activation of the benzoic acid. Attempts at isolating this metallacycle were unsuccessful, which is consistent with previous literature attempts.[6,52] Functionalization of the carbon occurs by insertion of the benzoquinone into the iridium−carbon bond, followed by intramolecular reduction of the benzoquinone fragment and elimination of the benzochromenone.

Several control reactions have been performed to ensure that the catalyst is necessary for benzochromenone production. Reaction of benzoic acid, benzoquinone, and NaOAc in toluene in the absence of catalyst did not lead to benzochromenone production. To rule out an acid-assisted organic coupling reaction, benzoic acid and benzoquinone were combined in acetic acid and heated at 120 °C for 24 h. No benzochromenone formation was observed. Similar results were obtained for the reaction in hydrochloric acid.

The mechanism for the elimination of the benzochromenone has not been thoroughly studied. However, a proposed mechanism is shown in Scheme 6. Intramolecular proton transfer results in aromatization of the benzoquinone ring. Protonation of the benzoate oxygen followed by rotation about the aryl−aryl bond allows for synthesis of 2-hydroxy-6*H*-benzo[*c*]chromen-6-one. The benzoquinone acts not only as a substrate but also as an intramolecular oxidant to regenerate the active catalyst.

The discrepancy between the high percent conversions of benzoquinone compared with the moderate percent yields as demonstrated in Table 5 indicates that there is a nonproductive side reaction involving benzoquinone. Amouri et al. reported a series of studies on the binding of hydroquinone with $[Cp^*Ir(Solvent)][BF_4]_2$.[53,54] In these studies, η^6-binding of the hydroquinone was observed. Reaction with two equivalents of base provided the η^4-bound benzoquinone adduct along with the reduction of the oxidation state of the metal from (III) to (I). Subsequently, reaction of the Cp*Ir-benzoquinone complex with two equivalents of acid reproduces the hydroquinone adduct (Scheme 7). As we previously noted, reaction of benzoic acid and $(Cp^*IrCl_2)_2$/NaOAc in the presence of hydroquinone does not lead to benzochromenone production. We conclude that our active catalyst binds benzoquinone competitively with benzoic acid and converts a portion of the benzoquinone to hydroquinone in a nonproductive side reaction. This is supported by the observation of hydroquinone in the crude benzochromenone NMR spectra.

CONCLUSIONS

Catalytic H/D exchange of benzene and benzoic acid with deuterated solvents was achieved using the readily synthesized catalyst $(Cp^*IrCl_2)_2$. Reaction of this catalyst with benzoic acid and benzoquinone results in the formation of 2-hydroxy-6*H*-benzo[*c*]chromen-6-one. The reaction is a rare example of C−H functionalization with an electrophilic Ir(III) catalyst and involves two important steps, C−H activation of benzoic acid and C−H functionalization to produce benzochromenone. Further mechanistic studies are currently underway.

EXPERIMENTAL SECTION

General Procedures. Unless otherwise noted, reagents and solvents were used as received from commercial suppliers. $(Cp^*IrCl_2)_2$ was prepared according to a known procedure.[55] ^{1}H and ^{13}C NMR spectra were recorded at room temperature on either a Varian 300 MHz or a Varian 400 MHz NMR. H/D exchange experiments were analyzed using an Agilent Technologies GCMS 5975 instrument. H/D turnover numbers were calculated using a worksheet reported by Sanford.[49,50] FT-IR spectra were obtained from KBr thin films on a JASCO FT/IR 4100 infrared spectrometer. HRMS were recorded using electrospray ionization (ESI) on an Agilent Technologies 6210 LC-TOF mass spectrometer.

General Procedure for H/D Exchange of Benzene. $(Cp^*IrCl_2)_2$ (20 mg, 0.025 mmol), 50 equiv of benzene (111 μL, 1.25 mmol), and solvent (25 mmol) were combined in a screw-cap NMR tube and heated to 150 °C for 24 h. The reaction mixture was cooled to room temperature and filtered through Celite. The Celite plug was washed with CH_2Cl_2. The resulting solution was then analyzed by GC-MS.

Procedure for H/D Exchange of Benzene in 1:1 CD_3OD/D_2O. $(Cp^*IrCl_2)_2$ (20 mg, 0.025 mmol), 50 equiv of benzene (111 μL, 1.25 mmol), 500 equiv of CD_3OD (507 μL, 12.5 mmol), and 500 equiv of D_2O (226 μL, 12.5 mmol) were combined in a screw-cap NMR tube and heated to 150 °C for 24 h. The reaction mixture was cooled to room temperature, and Na_2SO_4 was added to remove D_2O. The resulting solution was filtered through Celite, and the Celite plug was washed with CH_2Cl_2. The solution was then analyzed by GC-MS.

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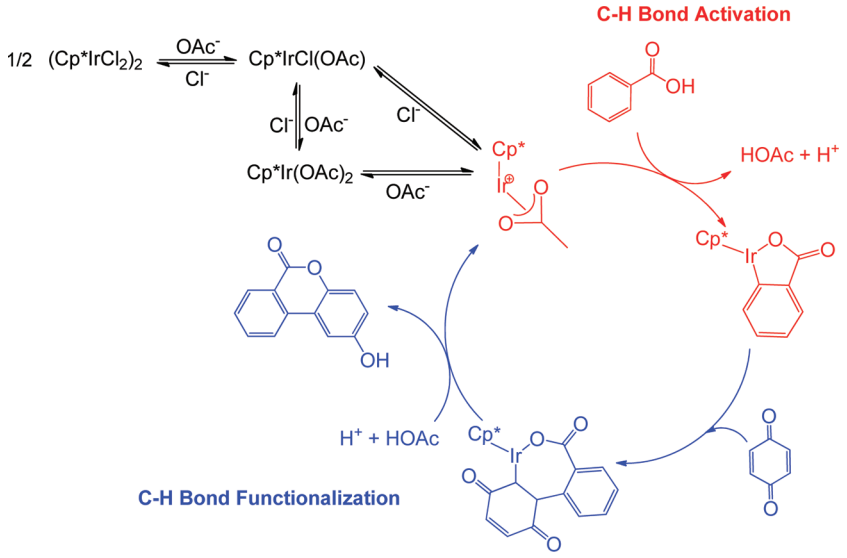
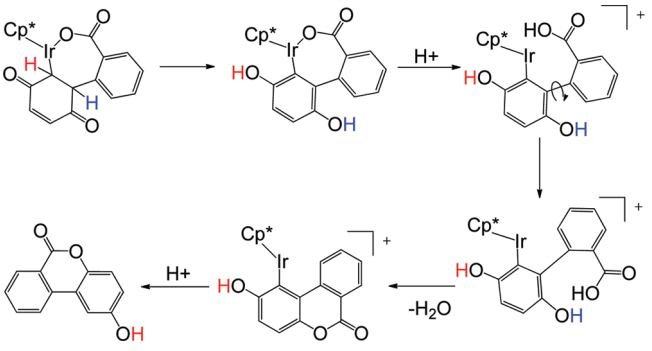
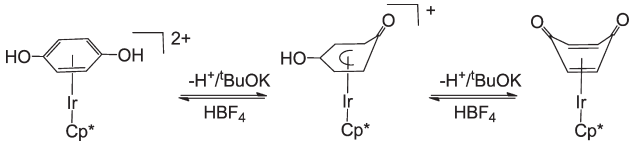
Scheme 5



Scheme 6



Scheme 7



Procedure for H/D Exchange of Benzoic Acid in CD_3OD. $(Cp^*IrCl_2)_2$ (20 mg, 0.025 mmol), benzoic acid (31 mg, 0.025 mmol), and CD_3OD (1015 μL, 25 mmol) were combined in a screw-cap NMR tube and heated at 120 °C for 24 h. The reaction mixture was cooled to room temperature and filtered through Celite. The Celite plug was washed with CH_2Cl_2. The solution was then analyzed by GC-MS.

Procedure for H/D Exchange of Benzoic Acid in CD_3OD with NaOAc Additive. The procedure above was followed, but 1 equiv of NaOAc (2 mg, 0.025 mmol) was added to the reaction mixture prior to heating.

Procedure for H/D Exchange of Benzoic Acid in Toluene-d_8. $(Cp^*IrCl_2)_2$ (20 mg, 0.025 mmol), benzoic acid (31 mg, 0.025 mmol), and toluene-d_8 (885 μL, 8.33 mmol) were combined in a screw-cap NMR tube and heated at 120 °C for 24 h. The reaction mixture was cooled to room temperature and filtered through Celite. The Celite plug was washed with CH_2Cl_2. The solution was then analyzed by GC-MS.

Procedure for H/D Exchange of Benzoic Acid in Toluene-d_8 with NaOAc Additive. The procedure above was followed, but 1 equiv of NaOAc (2 mg, 0.025 mmol) was added to the reaction mixture prior to heating.

General Procedure for Stoichiometric Benzochromenone Synthesis. $(Cp^*IrCl_2)_2$ (60 mg, 0.075 mmol), benzoquinone (16 mg, 0.150 mmol), sodium acetate (12 mg, 0.150 mmol), and acid (0.150 mmol) were combined in a storage tube with 10 mL of toluene. The solution was heated to 120 °C for 24 h. The solution was cooled to 0 °C, and 5 equiv of a 1:1 acetic anhydride/18 M sulfuric acid mixture was added to decompose the catalyst. After stirring at room temperature for 14 h, the solvent was removed *in vacuo*. Chromatography on silica with a 2:2:1 mixture of CH_2Cl_2/hexanes/EtOAc produced a white powder.

2-Hydroxy-6H-benzo[c]chromen-6-one, ***2a***. Yield: 63%. ^{1}H NMR (400 MHz, CD_3OD): δ 8.31 (dd, 1H, J = 8.2, 1.2 Hz, Ar-H), 8.19 (d, 1H, J = 8.4 Hz, Ar-H), 7.90 (dt, 1H, J = 7.7, 1.2 Hz, Ar-H), 7.64 (dt, 1H, J = 8.4, 1.2 Hz, Ar-H), 7.56 (d, 1H, J = 2.7 Hz, Ar-H), 7.22 (d, 1H, J = 8.8 Hz, Ar-H), 6.99 (dd, 1H, J = 9.0 Hz, 2.8 Hz, Ar-H). ^{13}C NMR (400 MHz, CD_3OD): δ 162.0, 154.7, 144.7, 135.2, 135.1, 130.0, 128.9, 122.1, 120.0, 118.7, 118.3, 118.2, 107.8. IR (KBr, cm^{-1}): ν 3400 (br, OH), 1698 (s, C=O). HRMS (ESI): calcd for $C_{13}H_8O_3$ $[M]^+$ 213.0546; found 213.0546.

2-Hydroxy-9-methyl-6H-benzo[c]chromen-6-one, ***2b***. Yield: 60%. ^{1}H NMR (300 MHz, CD_3OD): δ 8.11 (d, 1H, J = 8.1 Hz, Ar-H), 7.90 (s, 1H, Ar-H), 7.43 (d, 1H, J = 2.7 Hz, Ar-H), 7.39 (dd, 1H, J = 8.4, 1.8 Hz, Ar-H), 7.14 (d, 1H, J = 8.7 Hz, Ar-H), 6.93 (dd, 1H, J = 9.0, 2.7 Hz, Ar-H), 2.52 (s, 3H, Me). IR (KBr, cm^{-1}): ν 3323 (br, OH), 1693 (s, C=O). HRMS (ESI): calcd for $C_{14}H_{10}O_3$ $[M]^+$ 227.0709; found 227.0703.

9-(tert-Butyl)-2-hydroxy-6H-benzo[c]chromen-6-one, ***2c***. Yield: 34%. ^{1}H NMR (300 MHz, AcOD-d_7): δ 8.34 (d, 1H, J = 8.4 Hz, Ar-H), 8.16 (s, 1H, Ar-H), 7.73 (d, 1H, J = 8.4 Hz, Ar-H), 7.67 (d, 1H, J = 2.7 Hz, Ar-H), 7.26 (d, 1H, J = 9.0 Hz, Ar-H), 7.05 (dd, 1H, J = 8.7, 3.0 Hz, Ar−H), 1.55 (s, 9H, ^{t}Bu). IR (KBr, cm^{-1}): ν 3199 (br, OH), 1686 (s, C=O). HRMS (ESI): calcd for $C_{17}H_{16}O_3$ $[M]^+$ 269.1174; found 269.1172.

9-Chloro-2-hydroxy-6H-benzo[c]chromen-6-one, ***2d***. Yield: 36%. ^{1}H NMR (300 MHz, CD_3OD): δ 8.27 (d, 1H, J = 8.5 Hz, Ar-H),

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8.18 (d, 1H, J = 2.0 Hz, Ar-H), 7.59 (dd, 1H, J = 8.5, 2.0 Hz, Ar-H), 7.47 (d, 1H, J = 2.8 Hz, Ar-H), 7.21 (d, 1H, J = 8.9 Hz, Ar-H), 7.01 (dd, 1H, J = 8.9, 2.8 Hz, Ar-H). IR (KBr, cm^{-1}): ν 3391 (br, OH), 1693 (s, C═O). HRMS (ESI): calcd for $C_{13}H_7ClO_3$ $[M]^+$ 247.016; found 247.0156.

2-Hydroxy-9-nitro-6H-benzo[c]chromen-6-one, ***2e***. Yield: 20%. ^1H NMR (300 MHz, CD_2Cl_2): δ 8.91 (d, 1H, J = 2.1 Hz, Ar-H), 8.53 (s, 1H, J = 8.7 Hz, Ar-H), 8.33 (dd, 1H, J = 8.7, 2.2 Hz, Ar-H), 7.56 (d, 1H, J = 2.7 Hz, Ar-H), 7.27 (d, 1H, J = 8.9 Hz, Ar-H), 7.07 (dd, 1H, J = 8.9, 2.7 Hz, Ar-H). IR (KBr, cm^{-1}): ν 3350 (br, OH), 1690 (s, C═O), 1533 (s, NO).

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