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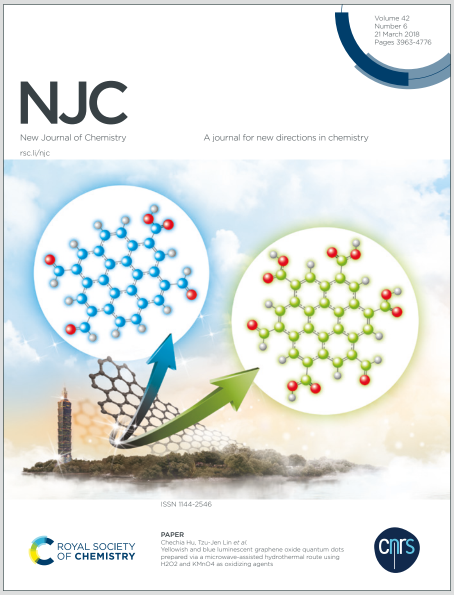

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Visible Light Assisted Oxidations of Organic Compounds by Iridium(III)dipyrrinato Complexes

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Abstract

Photo-assisted oxidation of organic compounds is a greener and more sustainable approach, which utilizes a very small amount of photocatalyst and visible light or sunlight. Ir(III) cyclometalated complexes have been explored extensively for photocatalytic applications in the past. Alternatively, Ir(III)dipyrrinato complexes can be employed for photocatalysis as they have attractive optical properties with high singlet oxygen generation ability. An efficient protocol for the photocatalytic aerobic oxidations of amines and sulfides by utilizing only 0.05 mol% Ir(III)dipyrrinato complexes is reported. The reactions complete in 2 hours, providing imines and sulfoxides, in excellent yields. Additionally, a methodology for the hydroxylation of aryl boronic acids using 0.05 mol% Ir(III)dipyrrinato catalyst is reported. These methods displayed excellent substrate tolerance and offered an effective strategy for synthesizing a diverse range of functionalized imines, sulfoxides and phenols in highly efficient manner that validates the versatility of Ir(III)dipyrrinato complexes as photocatalysts for various organic transformations. Notably, these photochemical transformations require only a minimal catalyst loading of 0.05 mol% for these reactions, which demonstrates their exceptional cost-effectiveness.

Keywords: Photocatalysis, Benzylamine coupling, Sulfoxidation, Hydroxylation of boronic acid

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Introduction

The oxidation of organic compounds plays an important role in organic synthesis. Compounds such as imine, phenol and sulfoxide are very important classes of compounds. In the case of imines, it is a key intermediate to synthesize many fine chemicals, dyes and pharmaceutical drugs.[1,2] The condensation between primary amine and carbonyl compounds leads to the formation of imine, but the high reactivity of carbonyl compounds leads to the formation of unwanted products. Phenols are frequently occurring scaffolds in biologically active compounds such as natural products and pharmaceuticals.[3] Along with that, it is also a key intermediate in organic synthesis.[4,5] Phenols are traditionally synthesized through nucleophilic aromatic substitution on aryl halides containing electron-withdrawing groups, as well as by the hydrolysis of arene diazonium salts. However, this method has very poor functional group tolerance, which leads to limited substrate scope.[6] In the case of sulfoxide, it is a crucial intermediate in organic synthesis[7–10] and is also present in many pharmaceutical drugs, such as *Omeprazole, Modafinil, Sulindac, Sulforaphane* and *Fipronil.*[1,11,12] Traditionally, strong oxidizing agents are needed for sulfoxidation, such as *m*-CPBA,[13,14] 2-iodobenzoic acid (IBX),[15] or Oxone[16] in many cases, high temperatures and high reaction time are also required. These harsh conditions result in the over-oxidation of sulfide to sulfone.

Above mentioned issues necessitate the development of efficient, sustainable and selective oxidation strategies. In recent years, visible-light assisted photocatalysis has emerged as an efficient and environmentally benign approach for the synthesis of fine chemicals. [17–20] Given its high natural abundance and clean energy profile, visible-light-driven photocatalysis offers a promising alternative to traditional oxidation methods. [12,17,21–28] Molecular oxygen (O_2) is a widely available and environmentally friendly oxidant that has been employed in oxidative photocatalytic

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transformations, including the oxidative coupling of benzylamines to imines,[25,29–31] oxidation of sulfides to sulfoxides,[22,24,26–28,32] and oxidative hydroxylation of boronic acids to phenols.[23,33–37] However, challenges such as high catalyst loading and long reaction times often limit the practical applicability of these methodologies.

Metal-dipyrrinato complexes have recently garnered significant attention as efficient photocatalysts due to their high absorption coefficients in the visible region and long-lived triplet excited states, making them excellent photosensitizers.[38,39] In this work, we have utilized previously reported three *meso*-substituted Ir(III)dipyrrinato complexes and investigated their catalytic efficiency for a number of photocatalytic reactions for the first time. These complexes have a high absorption coefficient in visible light and high singlet oxygen quantum yield. We demonstrated the photocatalytic application of Ir(III)dipyrrinato complexes using only 0.05 mole % catalytic loading for the oxidative coupling of benzylamine to imine, conversion of sulfide to sulfoxide and oxidative hydroxylation of boronic acids to phenol.

Results and Discussions

In this work, three Ir(III)dipyrrinato complexes (**Ir1-Ir3**) (as shown in Figure 1**)** containing electron donating and electron-withdrawing moieties at the C-5 position of the dipyrrin ligand

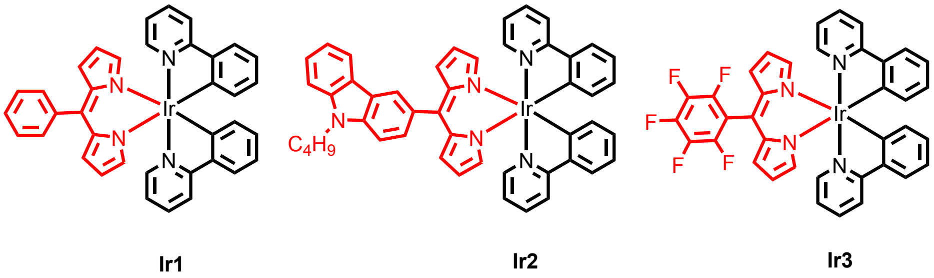

Figure 1: Structures of Ir(III)dipyrrinato complexes

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(Phenyl, *N*-butylcarbazole and pentafluorophenyl groups) were prepared as per the reported method and employed for photocatalytic applications.[40,41]

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Singlet oxygen generation

In the case of photocatalytic oxidation, molecular oxygen plays a crucial role as an oxidant. The generation of singlet oxygen became very important because it acts as one of the reagents in the reaction. Therefore, there is a significant demand for catalysts with exceptional singlet oxygen generation capability. A singlet oxygen generation experiment was conducted to determine the singlet oxygen quantum yields of Ir(III)dipyrrinato complexes (**Ir1**, **Ir2** and **Ir3**) by following the standard protocol[42] using Rose Bengal[43] as reference in methanol solvent.

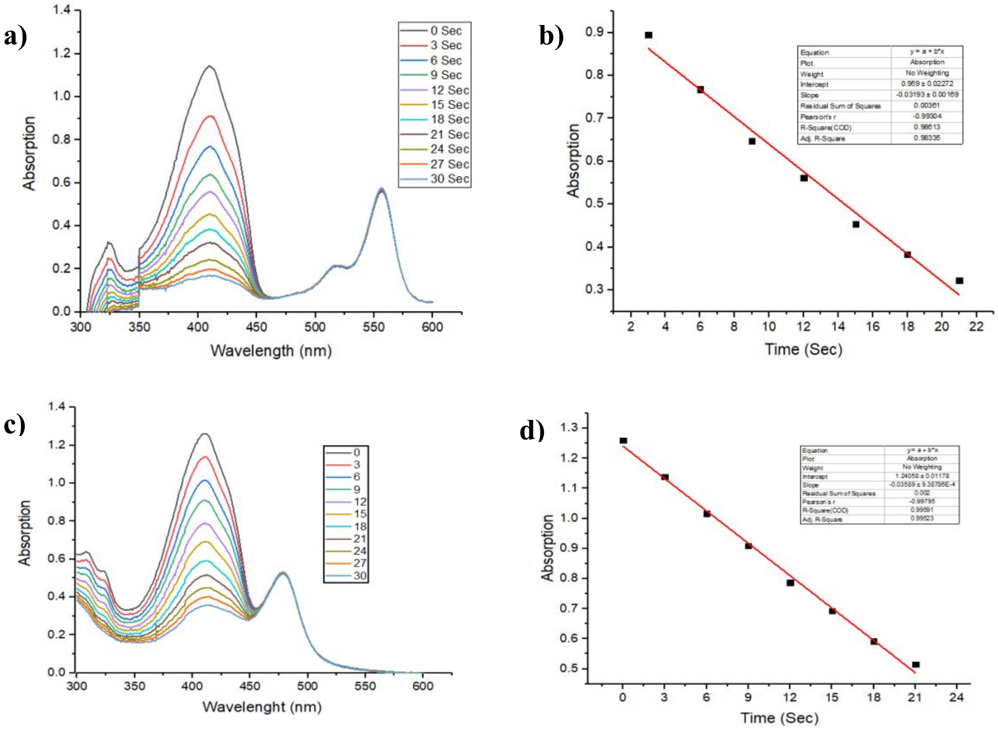


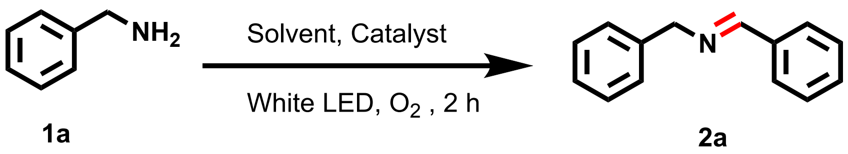
Figure 2: Singlet oxygen generation experiment, absorbance spectra of: (a) Rose Bengal and (c) **Ir 3** complex upon irradiation of light (λ = 300–600 nm); rate of decrease of absorbance of DPBF at 411 nm by: (b) Rose Bengal and (d) **Ir 3** complex.

Figure 2 shows plots of the **Ir3** complex's singlet oxygen generation assay, whereas data for the **Ir1** and **Ir2** complexes can be found in the supplementary information (Figure S1). The figures showed that **Ir3** produced a singlet oxygen quantum yield of 90 %, while for **Ir1** and **Ir2** complexes it was 87 % and 81 %, respectively.

Photo-oxidative benzylamine coupling

The excellent singlet oxygen quantum yield of these Ir(III)dipyrrinato complexes encouraged us to utilize them as photosensitizers for various photo-oxidation reactions. At first, we tested them for the photo-oxidative benzylamine coupling reaction and reaction optimization results are summarized in Table 1.

Table 1: Optimization of reaction conditions for photo-oxidative benzylamine coupling [a]



Entry	Light	Solvent	Catalyst	% Yield[b]
1	White	ACN	**Ir 3**	97
2	White	ACN	**Ir 2**	64
3	White	ACN	**Ir 1**	84
4	Sunlight	ACN	**Ir 3**	97
5	White	MeOH	**Ir 3**	23
6	White	Hexane	**Ir 3**	25
7	White	THF	**Ir 3**	32
8	White	Chloroform	**Ir 3**	54
9[c]	White	ACN	-	3
10[d]	-	ACN	**Ir 3**	2

[a]Reaction conditions: Benzylamine (1 mmol), Solvent 4 mL, catalyst (0.05 mol %), irradiation of white light (24W, 96 mW/cm^2) for 2h under O_2 rt. [b]Yield was calculated by ^{1}H-NMR using 1,3,5 trimethylbenzene (1 mmol) as an internal standard. [c & d] Time of reaction 12 h

When white light was used as the excitation source in acetonitrile (ACN), **Ir3** exhibited the highest catalytic efficiency, afforded **2a** in 97% yield (entry 1). Under the same conditions, **Ir1** and **Ir2** demonstrated moderate activity, yielding the desired product in 84% and 64%, respectively

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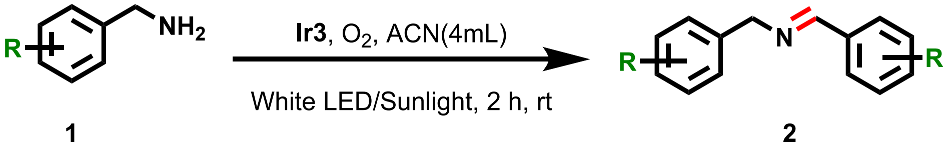
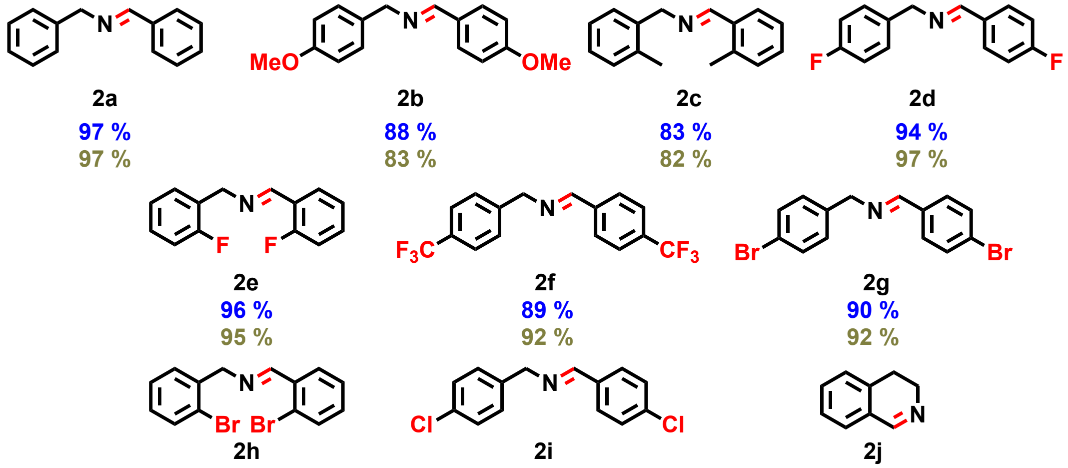
(entries 2 and 3). The reaction proceeded efficiently under natural sunlight, with a 97% yield (entry 4). The solvent effect was further explored using **Ir3** as the photocatalyst under white light. When methanol (MeOH) and hexane were used as the solvent, the reaction yield dropped significantly to 23% and 25%, respectively (entries 5 and 6). Tetrahydrofuran (THF) and chloroform exhibited slightly improved performance, affording yields of 32% and 54%, respectively (entries 7 and 8). The control experiments further confirmed the necessity of both the photocatalyst and light source. In the absence of a catalyst and light, the reaction in ACN afforded the product only in 3% and 2% yield, respectively (entries 9 and 10).



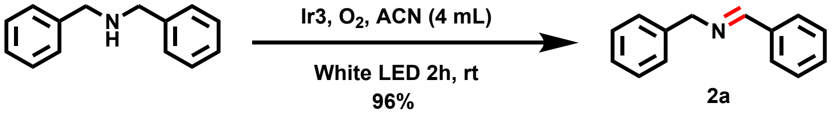
Scheme 1: Substrate scope of the benzylamine coupling[a]



	2a	2b	2c	2d
White LED	97 %	88 %	83 %	94 %
Sun Light	97 %	83 %	82 %	97 %

	2e	2f	2g
White LED	96 %	89 %	90 %
Sun Light	95 %	92 %	92 %

	2h	2i	2j
White LED	59 %	92 %	67 %
Sun Light	61 %	94 %	65 %



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[a] Reaction conditions: Benzylamine (1 mmol), **Ir3** (0.05 mol %), solvent ACN 4 mL, irradiation with white light (24 W, 96 mW/cm^2)/sunlight under O_2 at rt for 2 h.

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These optimization reactions suggest that **Ir3** works best for photo-oxidative benzylamine coupling reaction, in the presence of white LED or sunlight and ACN solvent. A variety of substrate scopes were examined by utilizing the optimized reaction conditions (Scheme 1). In the case of unsubstituted benzylamine, the product (**2a**) yield was 97% under both white LED and sunlight. Electron-donating substituents, such as *para*-methoxy and *ortho*-methyl groups, were also well tolerated and gave us **2b** and **2c** products with very good yields in both sunlight and white light. In contrast, fluorine derivatives exhibited excellent conversion, including *para*-fluoro (**2d**, 94% / 97%), *ortho*-fluoro (**2e**, 96% / 95%) and trifluoromethyl (**2f**, 89% / 92%), indicating strong compatibility with the reaction conditions. While *para*-substituted bromine (**2g**, 90% / 92%) and chlorine (**2h**, 92% / 94%) derivatives of benzylamine also yielded high conversions. However, *ortho*-substituted bromobenzylamine showed a decrease in reactivity, yielding the product **2i**, only 59% under white LED and 61% under sunlight, likely due to steric hindrance. However, in the case of secondary amine, dibenzylamine gave us **2a** with 96 % yield and 1,2,3,4-tetrahydroisoquinoline also gave the desired imine product **2j** with 67% and 65% yield in both white LED and sunlight, respectively.

Sulfoxidation

In the case of photocatalytic sulfoxidation, the influence of different parameters, such as catalyst, solvent and different light, was investigated to achieve high selectivity and conversion. For the optimization, methylphenyl sulfide (1 mmol, **3a**) was selected as the model substrate to assess the efficiency of the oxidation process. In all cases, molecular oxygen (O_2) was purged in the reaction mixture for 15 minutes and placed under O_2 atmosphere to ensure a sufficient oxygen supply for the catalytic transformation. The effect of different solvents and catalysts on the photocatalytic sulfoxidation of methylphenyl sulfide was systematically investigated (Table 2).

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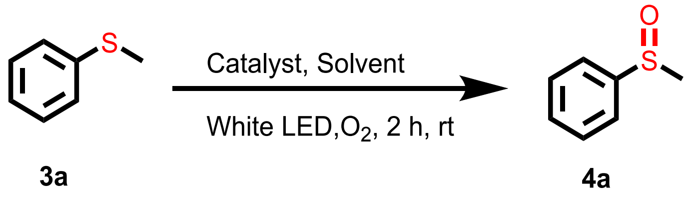
Table 2. Catalyst and solvent optimization [a]



Entry	Solvent	Catalyst	% Yield
1	MeOH 8 ml	**Ir 1**	76
2	MeOH 8 ml	**Ir 2**	67
3	MeOH 8 ml	**Ir 3**	98
4	MeOH 4 ml	**Ir 3**	64
5	EtOH 8 ml	**Ir 3**	94
6	THF 8 ml	**Ir 3**	12
7	DMF 8 ml	**Ir 3**	17
8	ACN 8 ml	**Ir 3**	58
9[c]	MeOH 8ml	**Ir 3**	2
10[d]	MeOH 8ml	**-**	4

[a] Reaction conditions**:** Methylphenyl sulfide (1 mmol), Catalyst (0.05 mol %), irradiation with white light (24 W, 96 mW/cm^2) under O_2 at rt [b] Yield was calculated by ^{1}H-NMR using 1,3,5 trimethylbenzene (1 mmol) as an internal standard, [c] No light reaction time 12 h., [d] No catalyst reaction time 12 h.

Initially, methanol (MeOH) was used as the solvent to assess the catalytic performance of various Ir(III)dipyrrinato photocatalysts. Among them, **Ir3** exhibited the highest efficiency, affording the sulfoxide product in 98% yield (entry 2). **Ir1** and **Ir2** demonstrated moderate activity, yielding the product in 76% and 67%, respectively (entries 1 and 3). Subsequently, the effect of solvent variation was explored using **Ir3** as the photocatalyst. When the volume of MeOH was reduced to 4 mL, the product yield decreased to 64% (entry 4). Switching to ethanol (EtOH) as the solvent resulted in a slightly lower yield of 94% (entry 5), while the use of tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) led to significantly lower conversions, affording the products in 12% and 17% yields, respectively (entries 6 and 7). Acetonitrile (ACN) demonstrated moderate efficiency, yielding 58% of the desired product (entry 8). In the absence of light and catalyst, only 2% and 4% yield were observed

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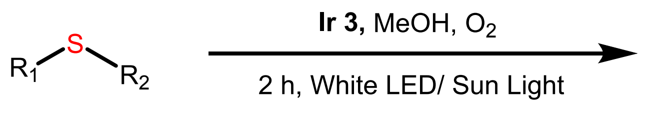

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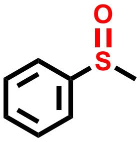
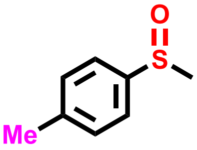
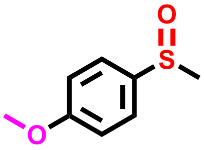
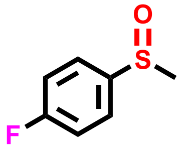
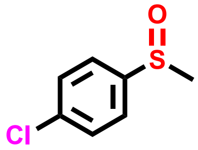
Scheme 2: Substrate scope for sulfoxidation reaction[a]



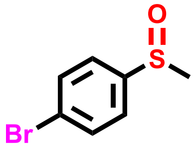


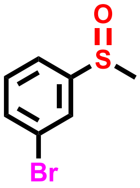


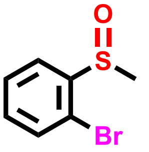


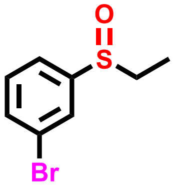


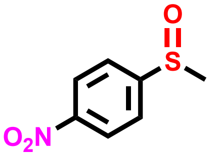
	4a	**4b**	**4c**	**4d**	**4e**
White light	**98 %**	**97 %**	**94%**	**78%**	**88 %**
Sun light	**96%**	**97%**	**95 %**	**77%**	**90%**



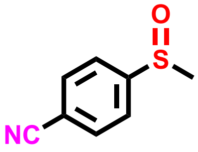


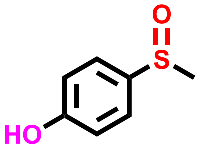


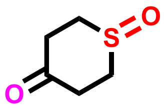


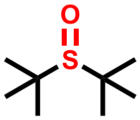


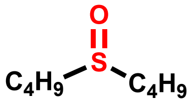
	4f	**4g**	**4h**	**4i**	**4j**
White light	**83 %**	**76 %**	**64 %**	**73 %**	**38%**
Sun light	**87 %**	**75%**	**65%**	**74%**	**39%**



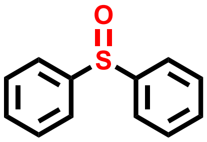


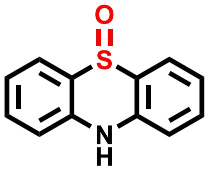


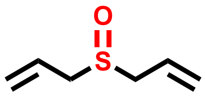


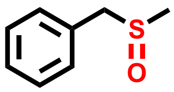


	4k	**4l**	**4m**	**4n**	**4o**
White light	**43%**	**78%**	**83 %**	**57 %**	**86 %**
Sun light	**46%**	**77%**	**82 %**	**55 %**	**83 %**









	4p	**4q**	**4r**	**4s**
White light	**18 %**	**41 %**	**84 %**	**94 %**
Sun light	**20 %**	**44 %**	**81 %**	**92 %**

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[a] Reaction conditions**:** sulfide (1 mmol), **Ir3** Catalyst (0.05 mol %), solvent MeOH 8 mL, irradiation of white light (24 W, 96 mW/cm^2)/sunlight under O_2 at rt for 2 h.

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respectively, confirming the necessity of light and photocatalyst for effective oxidation (entries 9 and 10). The light optimization (Table S1) suggested that white LED and sunlight work best for sulfoxidation reactions. These optimization results indicate that **Ir3** is most effective for sulfoxidation reactions, when exposed to white LED light or sunlight in methanol.

The substrate scope of the photocatalytic sulfoxidation reaction was explored using various substituted thioanisole derivatives under optimized reaction conditions (Scheme 2). The reaction proceeded efficiently for substrates having electron-donating groups, such as methyl (**4b**, 97% / 97%) and methoxy (**4c**, 83% / 87%), yielding high conversion under white light and sunlight. Similarly, substrates containing halogen substituents, including fluorine (**4d**, 94% / 95%), chlorine (**4e**, 78% / 77%) and bromine (**4f**, 88% / 90%), demonstrated good to excellent yields, indicating that halogenated substrates are well tolerated in the reaction. While, the yield of *meta*-substituted (**4g,** 76% / 75% & **4i,** 73% / 74%) and *ortho*-substituted (**4h,** 64% / 65%) bromine was less compared to *para*-substituted (**4f**, 88% / 90%) bromine, indicating a negative effect of steric hindrance on product yields. In contrast, substrates with electron-withdrawing groups, such as nitro (**4j**, 38% / 39%) and cyano (**4k**, 43% / 46%), exhibited lower yields. Diverse functional groups such as hydroxy-substituted compounds and heterocyclic sulfoxide also gave good yields (**4l**, 77% / 78%) and (**4m**, 82% / 83%), respectively, in both sunlight and white light. The alkyl-substituted sulfides, including tert-butyl (**4n**, 57% / 55%) and n-butyl (**4o**, 86% / 83%), also demonstrated efficient photo-oxidation. Where biphenyl thioether produced **4p** with a yield of only 18% in white light and 20% in sunlight, also indicating steric hindrance effects. In the case of phenothiazine, the product (**4q**) yield was only 41% and 47% in white light and sunlight, respectively. Also, diallylsulfane produces **4r** and benzyl(methyl)sulfane produces **4s** with excellent yields. In all cases, comparable yields were obtained under both white light and sunlight irradiation.

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Table 3: Inhibition experiments in the presence of various scavengers.[a]

Entry	Scavengers[c]	Inhibited Species	% Yield[b] (Sulfoxidation)	% Yield[b] (Benzylamine Coupling)
1	KI	$PC^{+\bullet}$ (h^+)	36	6
2	NaN_3	$^1O_2$	10	11
3	Benzoquinone	$O_2^{\bullet -}$	9	34
4[d]	1,4-dimethoxy-benzene	Thioether cationic radical	65	-
5	Isopropanol	•OH	94	93

[a]Reaction conditions**:** Methylphenyl sulfide/ Benzylamine (1.0 mmol), **Ir3** (0.05 mol %), MeOH/ACN 8/4 mL, irradiation with white light (24 W, 96 mW/cm^2) under O_2 at rt for 2 h, [b] ^{1}H-NMR yields, [c]scavengers (1.0 mmol), [d]Only used in sulfoxidation reaction.

To understand the reaction mechanism, inhibition experiments were conducted (Table 3) in the case of KI, which is an inhibitor of h^+ ($PC^{+\bullet}$).[24] The yield of sulfoxidation and benzylamine coupling reactions decreased to 36% and 6%, respectively (entry 1), which indicates that h^+ ($PC^{+\bullet}$) is responsible for the product formation in both cases. Where in the presence of NaN_3 and benzoquinone, which act as scavenger of singlet oxygen ($^1O_2$) [44] and peroxide radical ($O_2^{\bullet -}$), [45] respectively (entries 1 and 2), also shows a significant decrease in the yield of both products. Suggesting that singlet oxygen ($^1O_2$) and peroxide radical ($O_2^{\bullet -}$) both were involved in product formation.[45] The presence of thioether cationic radicals is also confirmed by 1,4-dimethoxy-benzene.[44] Where no significant change in yield was observed in the presence of isopropanol, which suggests no involvement of hydroxyl radical (•OH) in the reaction mechanism.[46] With the help of these inhibition experiments, the following mechanism was proposed (Figure 3), which indicates that the reaction follows both energy and electron transfer mechanisms. In the case of energy transfer, when light falls on the catalyst, it gets excited to a singlet excited state **Ir3***(S1) and then through ISC, got converted to a triplet excited state **Ir3***(T_1). The triplet excited state **Ir3***(T_1) reacts with O_2 and forms singlet oxygen ($^1O_2$); when this $^1O_2$ reacts with benzylamine and

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intermediate benzaldehyde is generated then it reacts with another benzylamine to form the desired photocoupled imine product.

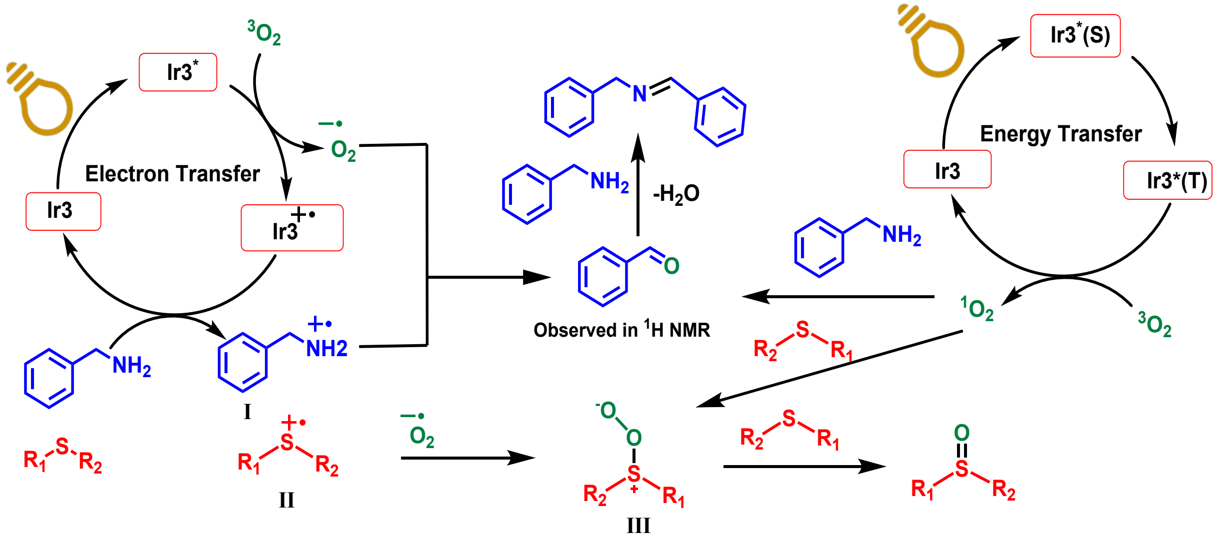

Figure 3. Proposed mechanisms for visible light-induced oxidation of sulfides and oxidative benzylamine coupling using **Ir3** as a photosensitizer (PS) through both electron transfer and energy transfer.

In the case of electron transfer, the excited state of the photocatalyst (**Ir3***) donates an electron to oxygen to generate oxygen anionic radical ($O_2^{-\cdot}$) and **Ir3*** gets oxidised to **Ir3**$^{+\cdot}$ which, upon reaction with benzylamine, generates an intermediate **I** and returns to its ground state (**Ir 3**). The intermediate **I** react with $O_2^{-\cdot}$ and generate benzaldehyde. Then, benzaldehyde reacts with another benzylamine to form the desired imine. In the case of sulfoxidation, energy transfer and electron transfer mechanisms follow the same cycle till singlet oxygen ($^1O_2$) or oxygen anionic radical ($O_2^{-\cdot}$) is generated. After that, singlet oxygen ($^1O_2$) and oxygen anionic radical ($O_2^{-\cdot}$) react with thioether and intermediate **II**, respectively, which generates an intermediate **III**. Then, another molecule of thioether reacts with aldehyde to form the desired sulfoxide.

Aerobic Hydroxylation of Boronic Acids

Apart from benzylamine coupling and sulfoxidation, the aerobic hydroxylation of boronic acid was also catalysed by the Ir(III)dipyrrinato catalyst system. In this reaction, phenylboronic acid is

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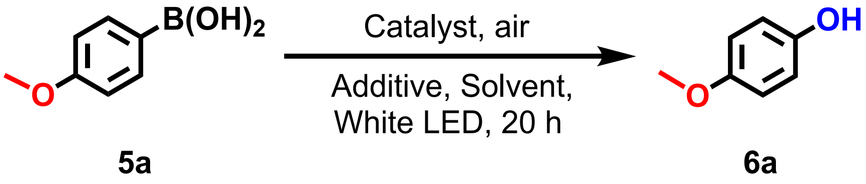
converted into phenol in the presence of light, an additive that acts as a sacrificial electron transfer reagent and catalyst in open air only.

Table 4: Optimization of reaction condition for aerobic hydroxylation of boronic acid[a]



Entry	Catalyst	Additive	Solvent	% Yield[b]
1	**Ir1**	Diethyl amine	ACN	75
2	**Ir2**	Diethyl amine	ACN	48
3	**Ir3**	Diethyl amine	ACN	98
4	**Ir3**	TEA	ACN	93
5	**Ir3**	DIPA	ACN	47
6	**Ir3**	Triphenyl amine	ACN	32
7	**Ir3**	Diethyl amine	MeOH	76
8	**Ir3**	Diethyl amine	DMSO	5
9	**Ir3**	Diethyl amine	Toluene	83
10	**Ir3**	Diethyl amine	$CHCl_3$	96
11	**Ir3**	Diethyl amine	H_2O	17
12	No cat	Diethyl amine	ACN	-
13	**Ir3**	-	ACN	3
14[c]	**Ir3**	Diethyl amine	ACN	2

[a]Reaction conditions: (4-methoxyphenyl)boronic acid (0.5 mmol), catalyst (0.05 mol %), additive (1 mmol), solvent 4 mL, irradiation with white light (24 W, 96 mW/cm^2) in the open air at rt for 20 h, [b]Isolated from column chromatography, [c]No light.

The influence of various additives and solvents on the photocatalytic aerobic hydroxylation of boronic acid was systematically investigated using different Ir(III)dipyrrinato photocatalysts (Table 4). When diethyl amine was used as an additive in acetonitrile (ACN), **Ir3** exhibited the highest catalytic efficiency, affording product **6a** with 98% yield (entry 3). Under the same conditions, **Ir1** and **Ir2** demonstrated 75% and 48% product yield, respectively (entries 1 and 2). The role of different additives was further explored using **Ir3** in ACN. Triethylamine (TEA) facilitated the reaction efficiently, yielding 93% (entry 4), whereas diisopropylamine (DIPA) and triphenylamine led to significantly lower yields of 47% and 32%, respectively (entries 5 and 6).

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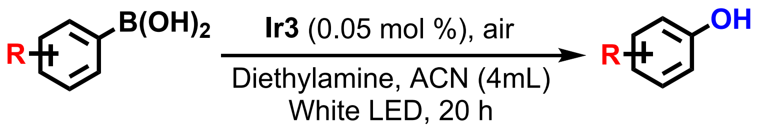
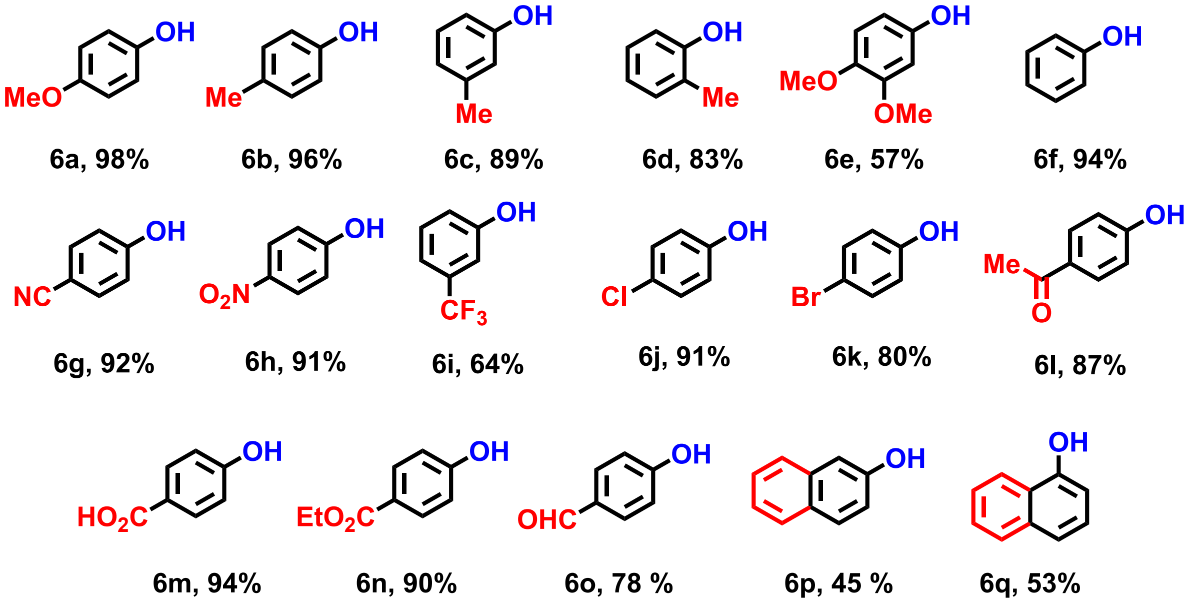
The effect of solvent was also examined using **Ir3** with diethyl amine as the additive. While the reaction proceeded efficiently in methanol (MeOH) and toluene, affording the product in 76% and 83% yields, respectively (entries 7 and 9), in the case of dimethyl sulfoxide (DMSO), only 5% of product yield was observed (entry 8). Notably, when chloroform ($CHCl_3$) was employed, an excellent yield of 96% was obtained (entry 10). When water is used for the reaction, the yield of the reaction decreases to 17% (entry 11). Notably, in the absence of a photocatalyst, no product formation was observed (entry 12), while without additive or without light, negligible product was observed (entries 13 and 14), which confirms that a catalyst, additive and white light are much needed for the reaction.



Scheme 3. Substrate scope for the aerobic hydroxylation of boronic acid[a]



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[a] Reaction condition: Boronic acid (0.5 mmol), catalyst **Ir3** (0.05 mol %), Diethylamine (1 mmol), ACN 4 mL, irradiation with white light (24 W, 96 mW/cm^2) in open air at rt for 20 h.

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These findings established that **Ir3** as a photocatalyst, diethyl amine as an additive and ACN as a solvent in the presence of white LED work best for the photocatalytic aerobic hydroxylation of boronic acid reaction.

The substrate scope of the photocatalytic hydroxylation of aryl boronic acids was investigated under optimized conditions (Scheme 3). Electron-donating substituents, such as methoxy (**6a**, 98%) and methyl (**6b**, 96%), exhibited excellent yields, while in the case of *meta* (**6c**) and *ortho* (**6d**), methyl-substituted groups also showed good conversion with 89% and 83% yield respectively. In contrast, the dimethoxy-substituted derivative (**6e**) showed 57% yield only. In case of, phenylboronic acid produced phenol (**6f**) with a 94% yield. Electron-withdrawing substituents such as Nitrile (**6g**, 94%), nitro (**6h**, 92%) and trifluoromethyl (**6i**, 64%) groups were well tolerated and gave good to excellent yield, while halogen, including chloro (**6j**, 91%) and bromo (**6k**, 80%), maintained high reactivity. Functionalized substrates with ketone (**6l**, 87%), carboxylic acid (6**m**, 94%), ethyl ester (**6n**, 90%) and aldehyde (**6o**, 78%), demonstrated excellent reactivity. While extended aromatic systems, such as naphthol (**6p**, 45%) and phenanthrene-derived hydroxylation product (**6q**, 53%), resulted in moderate yields. Overall, the results demonstrate the broad functional group tolerance of the photocatalytic hydroxylation system, making it a versatile approach for the selective hydroxylation of aryl boronic acids.

In the past, Ir or Ru cyclometalated complexes were employed for similar reactions. In Table 5 the results from this work are compared with the previously reported catalysts. It is clear that previous systems used a higher amount of catalyst loading (0.25-2 mol%) whereas Ir(III)dipyrrinato catalyst works very well at lower catalytic loading (0.05 mol%) with reduced reaction time.

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Table 5: Comparison between various catalytic systems with the current catalyst.

Ref	Reaction	Catalyst	Catalytic loading	Time	Maximum Yield%
32	Benzylamine coupling	Ir(III) based catalyst	0.25 mol%	5 h	92 %
26	Sulfoxidation	Rose Bengal $Ru(bpy)_3^{2+}$ $Ir(ppy)_3$	2 mol% 2 mol% 2 mol%	6-48 h 24 h 24 h	99% 50% -
29	Sulfoxidation	Ir(III) based catalyst	0.5 mol%	4 h	98 %
37	Hydroxylation of aryl boronic acids	$Ir(ppy)_3$	2 mol%	84 h	90%
		$Ru(bpy)_3^{2+}$	2 mol%	26 h	96%
36	Hydroxylation of aryl boronic acids	Ir(III) based catalyst	2 mol%	5-12 h	95%
This work	Benzylamine coupling	**Ir3**	0.05 mol%	2 h	97%
	Sulfoxidation	**Ir3**	0.05 mol%	2 h	98%
	Hydroxylation of aryl boronic acids	**Ir3**	0.05 mol%	20 h	98%

Conclusion

In summary, Ir(III)dipyrrinato complexes have proven to be highly efficient photocatalysts for aerobic oxidation reactions, including the photo-oxidative benzylamine coupling, oxidation of sulfides to sulfoxides and the hydroxylation of aryl boronic acids. These reactions proceed with excellent yields within a short reaction time, showcasing the high reactivity and efficiency of these complexes. The exceptional singlet oxygen generation quantum yields, long-lived triplet excited states and strong visible-light absorption make these complexes particularly well-suited for photochemical applications. Furthermore, the remarkably low catalyst loading of only 0.05 mol% compared to other catalytic systems highlights their cost-effectiveness and sustainability. The broad substrate tolerance and versatility of these systems provide an effective strategy for synthesizing diverse functionalized organic molecules.

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Experimental Section

General procedure for photocatalytic benzylamines coupling reaction:

Benzylamine (1 mmol) and the Ir(III)dipyrrinato catalyst (0.05 mol%) were dissolved in acetonitrile and placed in a 10 mL borosilicate round-bottom flask. The solution was periodically saturated with oxygen by slow purging with a long needle every hour. The reaction mixture was stirred at room temperature and irradiated using a Smartchem Synth Photoreactor (24W, White LED) for 2 hours. The reaction progress was monitored via ^{1}H NMR. Upon completion, the product was purified using basic silica gel column chromatography with hexane/ethyl acetate as the eluent and subsequently characterized by ^{1}H and ^{13}C NMR spectroscopy using a Bruker Avance-500 MHz spectrometer.

General procedure for sulfoxidation reaction:

Sulfide (1 mmol) and Ir(III)dipyrrinato catalyst (0.05 mol%) were dissolved in methanol and placed in a 25 mL borosilicate round-bottom flask. To ensure oxygen saturation, the solution was gently purged with oxygen using a long needle every hour for 15–20 minutes. The reaction mixture was stirred at room temperature while being irradiated with a Smartchem Synth Photoreactor (24W, White LED) for 2 hours. After completion, the product was purified using silica gel column chromatography with a hexane/ethyl acetate/methanol eluent system. The purified compound was then characterized by ^{1}H and ^{13}C NMR spectroscopy using a Bruker Avance-500 MHz spectrometer.

General procedure for photocatalytic aerobic hydroxylation of boronic acid:

Boronic acid (0.5 mmol), additive (1 mmol) and the Ir(III)dipyrrinato catalyst (0.05 mol%) were dissolved in 4 mL acetonitrile and placed in a 10 mL borosilicate round-bottom flask in open air. The reaction mixture was stirred at room temperature and irradiated using a Smartchem Synth

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Photoreactor (24W, White LED) for 20 hours. The reaction progress was monitored via thin-layered chromatography. Upon completion, the product was purified using basic silica gel column chromatography with hexane/ethyl acetate as the eluent and subsequently characterized by ^{1}H and ^{13}C NMR spectroscopy using a Bruker Avance-500 MHz spectrometer.

Conflicts of interest

No conflict of interest.

Supporting Information

Characterization data such as ^{1}H NMR, ^{13}C NMR and ^{19}F-NMR of selected compounds are available. Singlet oxygen generation plots for **Ir1** and **Ir2** are also available in Supporting Information.

Acknowledgments

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Data Availability Statement

All data will be made available on request and the supporting data have been included as per of the ESI