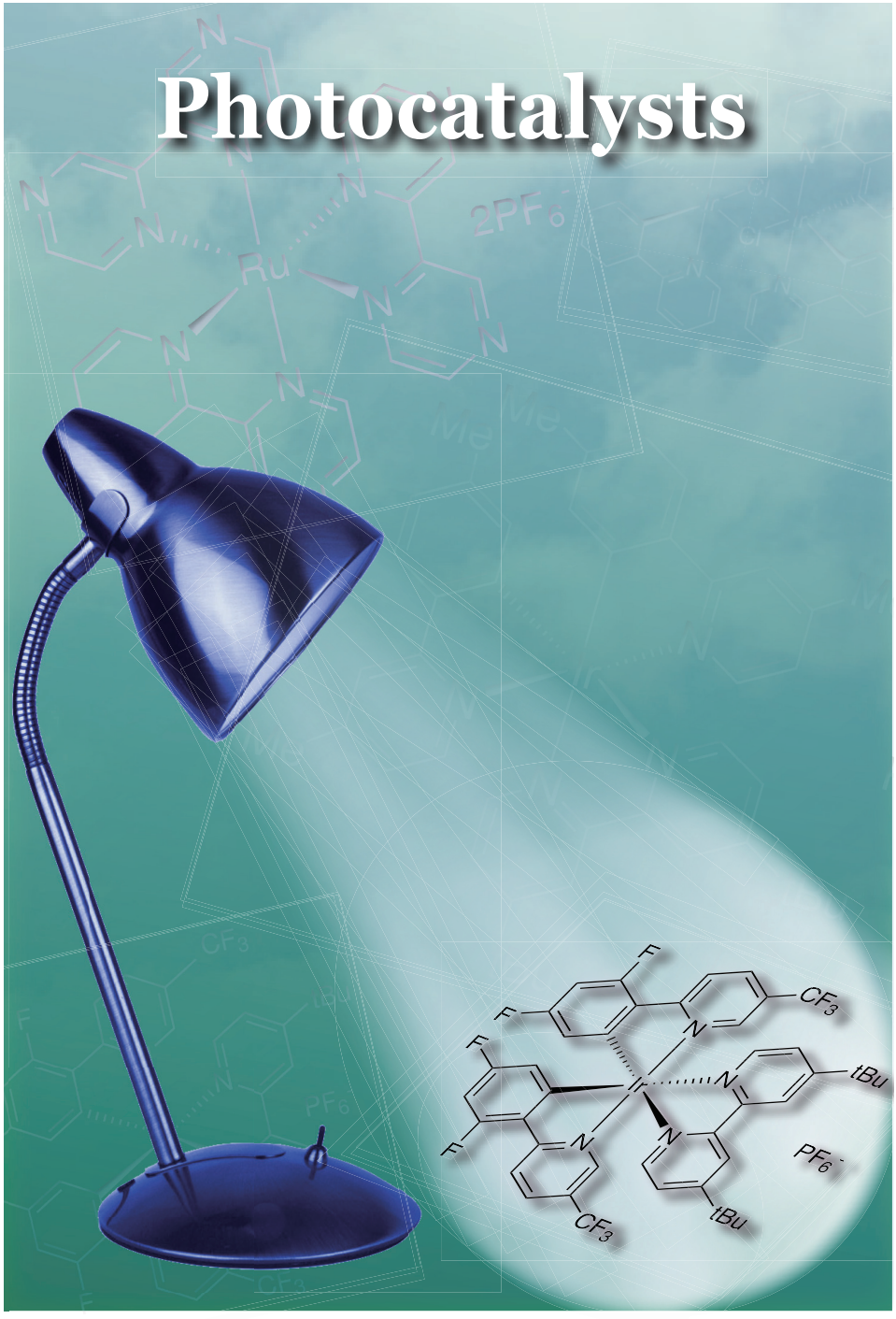
Photocatalysts



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Photocatalysts

Strem Chemicals has been providing fine chemicals for research and commercial production for over fifty years. In this booklet you will find our selection of photocatalysts, related kits for screening purposes, as well as ligands and precursors for photocatalyst synthesis. There have been interesting developments in photocatalysis in the past few decades. Many of these novel compounds have been applied to solar cell research, light emitting diode manufacturing (LED) and initiators for free radical polymerizations. Specifically, cyclometallated ruthenium and iridium complexes are the most prominent. Recently, these compounds have been successfully applied to catalytic transformations. These catalysts can also be utilized in challenging organic transformations in both bench-top and commercial scales.

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In addition, custom synthesis services are provided on a contract basis. For pharmaceutical applications, manufacturing is conducted under current Good Manufacturing Practices (cGMP) in FDA inspected kilo-lab suites. Complete documentation is available, including validation and stability studies. Active Drug Master Files (DMF's) are maintained in North America and Europe.

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- Biocatalysts
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- Carbon-Base Nanomaterials & Elemental Forms
- Catalysts & Ligands *Sold in Collaboration with Takasago*
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- PURATREM: High Purity Inorganics

Ephraim S. Honig, Ph.D., M.B.A
Chief Executive Officer

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Glossary of Terms

$[\alpha]_D$	.....	Specific rotation
AAS	.....	Atomic Absorption Standard
ACS	.....	Conforms to American Chemical Society specifications
air sensitive	.....	Product may chemically react with atmospheric oxygen or carbon dioxide at ambient conditions. Handle and store under an inert atmosphere of nitrogen or argon.
amp	.....	Ampouled
b.p.	.....	Boiling point in °C at 760mm, unless otherwise noted
d.	.....	Density
dec.	.....	Decomposes
elec. gr.	.....	Electronic Grade, suitable for electronic applications
f.p.	.....	Flash point in °F
gran.	.....	Granular
heat sensitive	.....	Product may chemically degrade if stored for prolonged periods of time at ambient temperatures or higher. Store at 5°C or lower.
hydrate	.....	Unspecified water content which may vary slightly from lot to lot
hygroscopic	.....	Product may absorb water if exposed to the atmosphere for prolonged periods of time (dependent on humidity and temperature). Handle and store under an inert atmosphere of nitrogen or argon.
light sensitive	.....	Product may chemically degrade if exposed to light
liq.	.....	Liquid
m.p.	.....	Melting point in °C
moisture sensitive	.....	Product may chemically react with water. Handle and store under an inert atmosphere of nitrogen or argon.
NMR grade		Suitable as a Nuclear Magnetic Resonance reference standard
optical grade	.....	For optical applications
pwdr.	.....	Powder
primary standard	.....	Used to prepare reference standards and standardize volumetric solutions
PURATREM	.....	Product has a minimum purity of 99.99% (metals basis)
purified	.....	A grade higher than technical, often used where there are no official standards
P. Vol.	.....	Pore volume
pyrophoric	.....	Product may spontaneously ignite if exposed to air at ambient conditions
reagent	.....	High purity material, generally used in the laboratory for detecting, measuring, examining or analyzing other substances
REO	.....	Rare Earth Oxides. Purity of a specific rare-earth metal expressed as a percentage of total rare-earths oxides.
SA	.....	Surface area
store cold	.....	Product should be stored at -18°C or 4°C, unless otherwise noted (see product details)
subl.	.....	Sublimes
superconductor grade	.....	A high purity, analyzed grade, suitable for preparing superconductors
tech. gr.	.....	Technical grade for general industrial use
TLC	.....	Suitable for Thin Layer Chromotography
v.p.	.....	Vapor pressure mm of Hg
xtl.	.....	Crystalline

About Purity

Chemical purity	.....	is reported after the chemical name, e.g. Ruthenium carbonyl, 99%
Metals purity	.....	is reported in parentheses with the respective element, e.g. Gallium (III) bromide, anhydrous, granular (99.999%-Ga) PURATREM where 100% minus the metal purity is equal to the maximum allowable percentage of trace metal impurity

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Iridium and Ruthenium Photocatalysts for Visible Light Photocatalysis in Organic Synthesis

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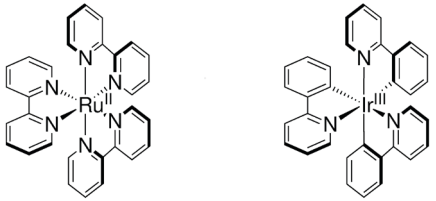
Introduction

Photoredox catalysis has, in the past decade, grown to become a commonly employed catalytic manifold for the construction of molecular complexity in unique and powerful ways.[1] In particular, C–C and C–heteroatom bond constructions have been enabled by the intermediacy of open-shell or electronically-excited intermediates generated by single-electron transfer (SET) or energy transfer (ET). The most fruitful catalyst frameworks to emerge have been those of homoleptic ruthenium and homo- and heteroleptic iridium polypyridyl complexes, of the $Ru(bpy)_3^{2+}$ (**Ru-1**) and $Ir(ppy)_3$ (**Ir-1**) framework, previously used in dye-sensitized solar cells,[2] as emitters in phosphorescent OLEDs,[3] photocatalysts in water splitting[4] and CO_2 reduction,[5] and in oxygen sensing[6] *(Figure 1)*. However, as more complex organic reactivity has been explored and developed, the use of functionalized ligands on the metal center has proven necessary.



$Ru(bpy)_3^{2+}$ **Ru-1** $Ir(ppy)_3$ **Ir-1**

Figure 1. *$Ru(bpy)_3^{2+}$ and $Ir(ppy)_3$,commonly employed photocatalysts*

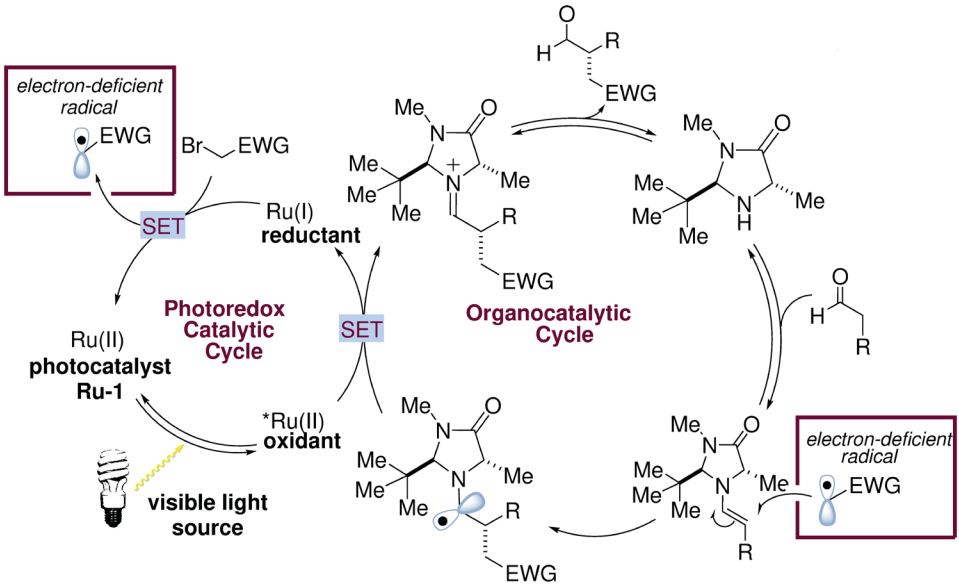
The use of specialized photocatalysts with rationally designed ligand scaffolds has become commonplace, as characteristics such as oxidizing or reducing power, excited state lifetime, and triplet excited state energy have been optimized for specific transformations or catalytic platforms. As such, robust synthetic methods for the rapid generation of differentially substituted ruthenium and iridium polypyridyl complexes have been developed, enabling a variety of synthetic transformations.

History of Photocatalysts in Other Applications

Previous to the use of ruthenium and iridium polypyridyl complexes as photocatalysts in synthetic organic chemistry, a rich literature had been developed for their use in other applications. Their ability to perform photo-initiated electron transfer enabled their use as photosensitizers in water splitting, and subsequent work demonstrated their utility in dye-sensitized solar cells. More relevantly, limited reports appear sporadically in the literature describing the use of $Ru(bpy)_3^{2+}$ as a photocatalyst in organic transformations prior to the current era. In 1981, Pac and coworkers demonstrated a photocatalytic reduction of electron-deficient olefins via neutral α-acyl radicals, using 1-benzyl-1,4-dihydronicotinamide (BANH) as the terminal reductant.[7] Similar transformations for the reduction of activated alkyl halides via the fragmentation of neutral alkyl radicals and halide anions have also been reported.[8] Additionally, some $Ru(bpy)_3^{2+}$-mediated net oxidative transformations had appeared in the literature prior to 2000.[9]

Ruthenium Photocatalysts

In 2008, we published an enantioselective α-alkylation of aldehydes using a combination of chiral amine organocatalysis and $Ru(bpy)_3^{2+}$ (**Ru-1**) photoredox catalysis (Scheme 1).[10] This transformation proceeded via initial quenching of the photocatalyst excited-state $*Ru(bpy)_3^{2+}$ by a sacrificial amount of enamine to generate the highly reducing $Ru(bpy)_3^{+}$ (not shown). Then, single-electron transfer (SET) from this Ru^{I} state to an alkyl bromide could induce fragmentation to afford bromide anion and a neutral electron-deficient radical. This electrophilic radical can add to a catalytically-generated enamine to forge the new C−C bond and generate an α-amino radical. Then, SET oxidation of this species could be accomplished by $*Ru(bpy)_3^{2+}$ to yield the product, after hydrolysis of the organocatalyst.



Scheme 1**. Catalytic cycle of enantioselective α-alkylation of aldehydes using **Ru-1

As such, the ruthenium photocatalyst could perform both SET oxidation and reduction in the same reaction, enabling a redox neutral, room-temperature, light-driven radical pathway. This mechanism was also extended in 2015 to accommodate bromoacetonitrile derivatives as the alkyl radical precursor,[11] and a representative scope of this general reaction manifold is shown in Table 1.

Concurrent with our publication the Yoon[12] group, followed shortly thereafter by the Stephenson[13] group, published different methodologies which similarly took advantage of the ability of the reduced $Ru(bpy)_3^{+}$ state to perform challenging single-electron reductions of organic substrates. These contemporaneous reports sparked the interest of the synthetic organic community in utilizing ruthenium photocatalysts to enable open-shell mechanistic pathways, leading to a rapid growth in the number of publications concerning synthetic organic photoredox catalysis.

Other ruthenium-based photocatalysts have also been successful for a variety of chemical transformations. Within our group, in particular, we accomplished the direct C–H trifluoromethylation of arenes with trifluoromethyl radical derived from reduction of triflyl chloride, CF_3SO_2Cl, mediated by

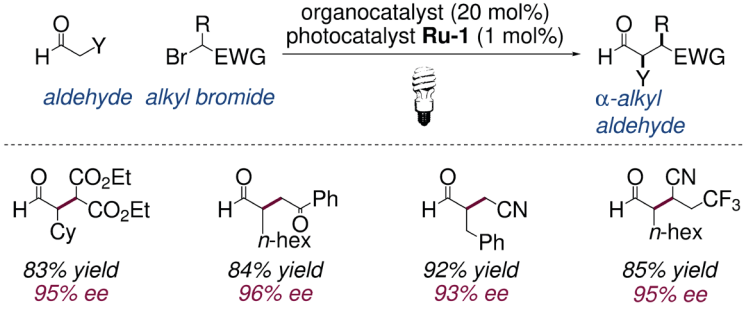


Table 1. *Representative scope of enantioselective α-alkylation of aldehydes using* ***Ru-1***

$Ru(phen)_3^{2+}$ (**Ru-2**) as photocatalyst (Table 2).[14] Here, the more reducing excited state $*Ru(phen)_3^{2+}$ can undergo SET with triflyl chloride, resulting in $\bullet CF_3$ addition to an aromatic ring. This radical addition pathway results in an incredibly broad scope of successful aromatic substrates, including numerous pharmaceutical compounds such as Lipitor (not shown).

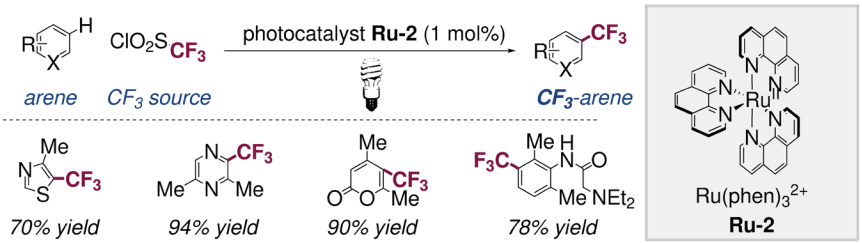


Table 2. *Direct trifluoromethylation of arenes with* CF_3SO_2Cl *using* ***Ru-2***

Other analogues of $Ru(bpy)_3^{2+}$ have demonstrated broad applicability in organic synthesis, including those shown in Table 3. In particular, $Ru(bpz)_3^{2+}$ (**Ru-3**) has been used by the Yoon group to accomplish radical cation-mediated [4+2] cycloadditions of electronically-mismatched dienes and dienophiles,[15]

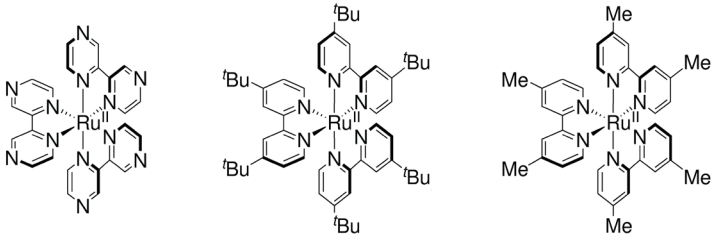
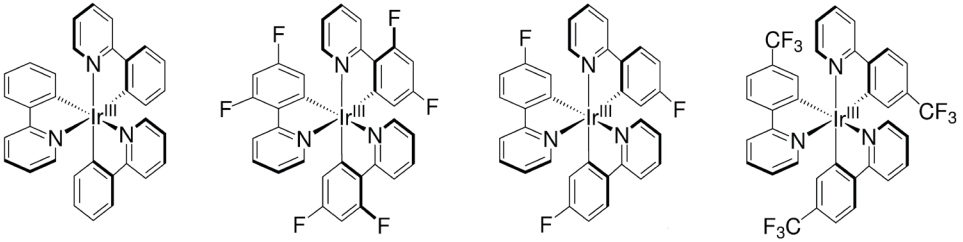


Table 3. *Other ruthenium trisbipyridyl photocatalysts*

while our group has used the same photocatalyst for the decarboxylative fluorination of certain alkyl carboxylic acids.[16] $Ru(dtbbpy)_3^{2+}$ (**Ru-4**) has also been used by Yoon and coworkers for the visible light sensitization of vinyl azides via energy transfer (ET) from the triplet excited state of the photocatalyst,[17] as well as by Rueping for the aerobic oxidation of benzylic alcohols to aldehydes and ketones.[18]

Homoleptic Iridium Photocatalysts

Owing to the ability to orthogonally manipulate the HOMO and LUMO energies of iridium polypyridyl complexes, a diverse suite of analogues of $Ir(ppy)_3$ have been developed for numerous uses in organic chemistry. In particular, homoleptic iridium photocatalysts, in which each ligand is the same cyclometalated phenylpyridine, have been utilized in transformations in which the excited photocatalyst performs a single-electron reduction of a substrate molecule, described as an oxidative quenching mechanism *(Table 4)*.

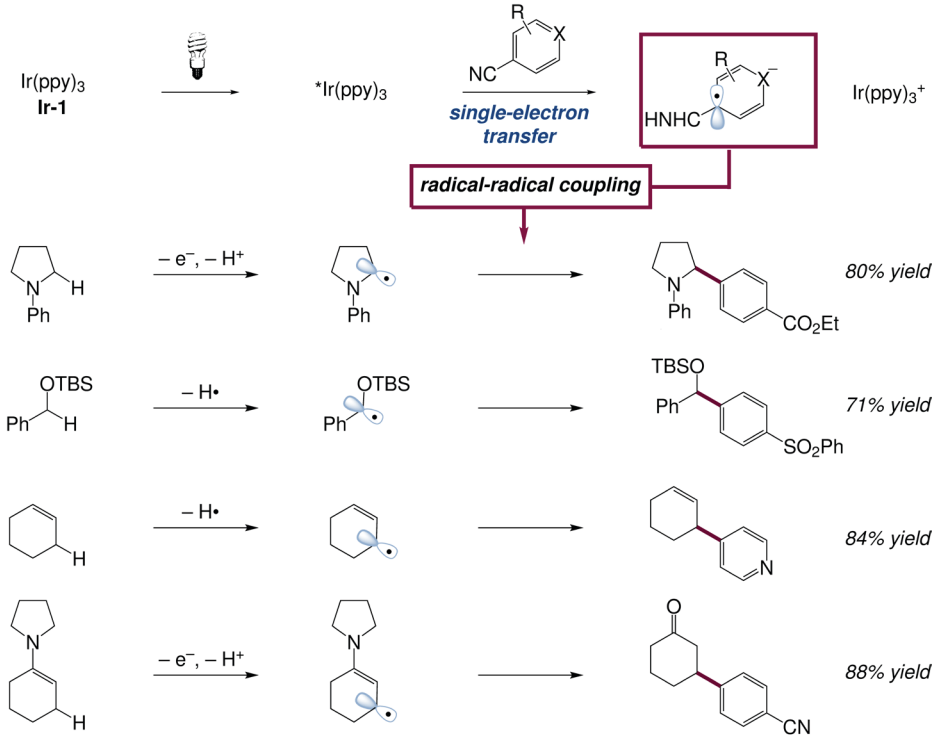


$Ir(ppy)_3$	$Ir(dFppy)_3$	$Ir(Fppy)_3$	$Ir(CF_3ppy)_3$
Ir-1	**Ir-2**	**Ir-3**	**Ir-4**

Table 4. *Homoleptic iridium photocatalysts*

The parent molecule, $Ir(ppy)_3$ (**Ir-1**), previously used as a phosphorescent emitter in PhOLEDs, has been utilized extensively within our group's research program for its ability to accomplish challenging excited state reductions. In particular, the SET reduction of electron-deficient cyanoarenes, such as 1,4-dicyanobenzene, by $*Ir(ppy)_3$ has enabled a number of radical-radical coupling reactions to generate arylated products via the intermediacy of persistent aryl radical anions (*Scheme 2*). In particular, our group has demonstrated the utility of this activation mode in the α-arylation of amines via oxidation/deprotonation;[19] α-arylation of benzylic ethers[20] and olefins[21] via thiyl radical-mediated hydrogen atom transfer; and β-arylation of carbonyls via enamine oxidation/deprotonation.[22] Our group also recently used **Ir-1** to enable the energy transfer-mediated esterification of aryl halides with carboxylic acids.[23]

Other homoleptic iridium photocatalysts, including those shown in Table 4, have been used in organic transformations by our group and others for their fine-tuned photophysical and electron-transfer properties. In particular, our group has used $Ir(dFppy)_3$ (**Ir-2**) as a highly competent complementary photocatalyst to $Ru(phen)_3^{2+}$ (**Ru-2**) in the arene C–H trifluoromethylation using triflyl chloride, while Alemán, Paton, and Smith have shown it to be an efficient photocatalyst for ET- induced radical cyclization reactions.[24] Meanwhile, the monofluorinated $Ir(Fppy)_3$ (**Ir-3**) has been shown to be an efficient photocatalyst for the asymmetric addition of α-amino radicals into imines by Ooi,[25] while the trifluoromethyl analogue, $Ir(CF_3ppy)_3$ (**Ir-4**) has been shown by Weaver to be efficient for defluorinative reactions of fluoroarenes.[26] These homoleptic iridium photocatalysts have received much attention for their ease of synthesis and broad applications.



Scheme 2. *Radical-radical coupling arylation reactions using* ***Ir-1***

Heteroleptic Iridium Photocatalysts

Cationic polypyridyl complexes of iridium(III), in which one of the phenylpyridine ligands is replaced by a bipyridine-type ligand, have been extensively used by synthetic organic chemists owing to the nearly complete orthogonality of the HOMO and LUMO, localized on the metal center and phenyl ring of the phenylpyridine, and bipyridine ligand, respectively. As such, the reducing and oxidizing power can be manipulated individually with minimal perturbation to the other.

Simple Heteroleptic Iridium Photocatalysts

Photocatalysts of the type $Ir(ppy)_2(N^N)^+$ have been exploited by our group and others for a variety of SET and ET-dependent transformations. The simplest heteroleptic iridium photocatalyst, $Ir(ppy)_2(bpy)^+$ (**Ir-5**) was recently used by our group in collaboration with Lee and coworkers as the ideal photocatalyst for an energy transfer-enabled metallaphotoredox sulfonamidation of aryl halides (Table 5).[27] In this case, the excited *Ir(III) state of the photocatalyst could directly transfer its triplet energy to a Ni(II) aryl sulfonamido complex, leading to a highly efficient reductive elimination.

Furthermore, the di-*tert*-butyl-substituted analogue, $Ir(ppy)_2(dtbbpy)^+$ (**Ir-6**) has been utilized extensively by our group for a variety of transformations, including aldehyde α-trifluoromethylation[28] and amine α-heteroarylation.[29] One particularly interesting use of this photocatalyst is in the radical-radical coupling of α-amino radicals formed by reduction of imines with other carbon-centered radicals formed through oxidation, such as enamine oxidation[30] and benzyl ether Hydrogen atom transfer (HAT).[31] In these cases, it is the fine-tuned oxidizing and reducing power of **Ir-6** that enables these transformations to work. Furthermore, **Ir-6** was found to be the ideal photocatalyst for the HAT-enabled spin-center shift-

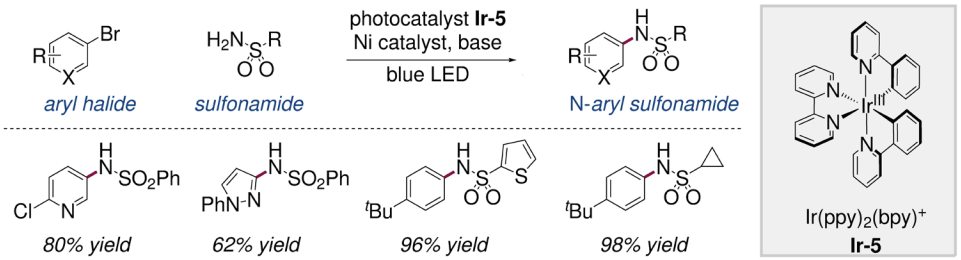


Table 5. *Energy transfer-mediated sulfonamidation of aryl halides using* ***Ir-5***

mediated alkylation of heteroarenes with simple alcohols.[32] In this transformation, the oxidized Ir(IV) state of the photocatalyst can oxidize a thiol catalyst, which can subsequently abstract a hydrogen atom from an alcohol substrate. The resultant nucleophilic radical can add to a protonated heteroarene, which, after spin-center shift, generates an electron-deficient benzylic radical, which can be reduced by the excited state of the photocatalyst. This mechanism enables a variety of heteroarenes to be directly alkylated using simple alcohols, as shown in Table 6.

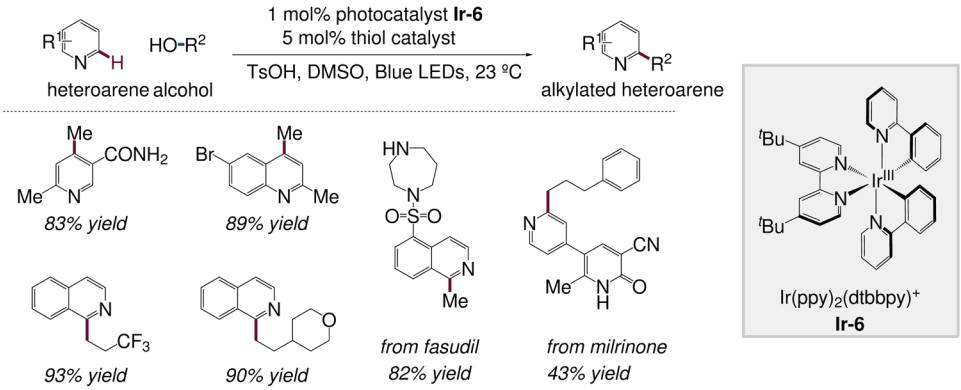


Table 6. *Direct alkylation of heteroarenes with alcohols using* ***Ir-6****.*

Further substitutions on the phenylpyridine ligand can be used to fine-tune reaction efficiency, as in the case the direct β-alkylation of aldehydes by addition of a catalytically-generated β-enaminyl radical to a Michael acceptor.[33] Indeed, as shown in Table 7, optimal yield of 80% could be obtained with **Ir-6**, while a diminished 56% yield was observed with $Ir(dtbppy)_2(dtbbpy)^+$ (**Ir-8**). However, a slight improvement in the yield to 84% yield could be obtained with $Ir(dmppy)_2(dtbbpy)^+$ (**Ir-7**), leading to the optimized general conditions. This example demonstrates the effect that fine-tuning of photocatalyst structure and electronics can have on the efficiency of a desired transformation, necessitating a broad understanding of photocatalyst structure-function relationship for photoredox-mediated organic transformations.

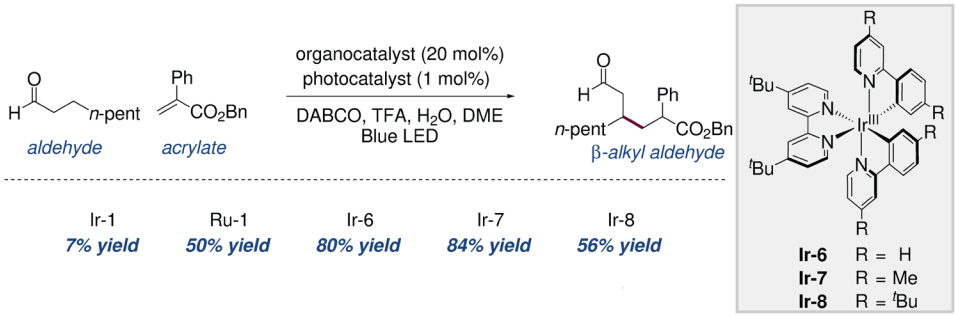
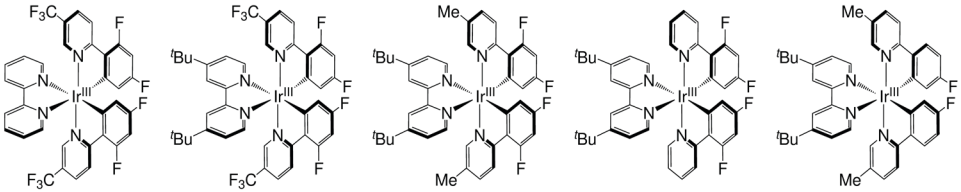


Table 7. *Direct β-alkylation of aldehydes via β-enaminyl radicals using* ***Ir-7***

Fluorinated Heteroleptic Iridium Photocatalysts

Owing to the orthogonal nature of the HOMO and LUMO of heteroleptic iridium photocatalysts, substitution of the phenyl ring of the phenylpyridine ligands can alter the HOMO energy level with minimal perturbation of the LUMO energy level, effectively shifting the oxidizing power without affecting the reducing power of the photocatalyst. Indeed, by substituting the phenylpyridine ligand with fluoro and trifluoromethyl groups, a number of more oxidizing photocatalysts can be prepared *(Table 8)*. These more strongly oxidizing photocatalysts are capable of performing SET oxidations on functionalities such as carboxylates, amine, trifluoroborates, and silicates, among others.



$Ir(dFCF_3ppy)_2(bpy)^+$	$Ir(dFCF_3ppy)_2(dtbbpy)^+$	$Ir(dFMeppy)_2(dtbbpy)^+$	$Ir(dFHppy)_2(dtbbpy)^+$	$Ir(FMeppy)_2(dtbbpy)^+$
Ir-9	**Ir-10**	**Ir-11**	**Ir-12**	**Ir-13**

Table 8. *Iridium photocatalysts bearing fluorinated phenylpyridine ligands*

In particular, $Ir(dFCF_3ppy)_2(dtbbpy)^+$ (**Ir-10**) has been used extensively within our group in combination with nickel catalysis, enabling a number of transformations such as decarboxylative arylation,[34] alkylation,[35] and vinylation,[36] as well as alkylation,[37] etherification,[38] and amination[39] of aryl halides, while $Ir(dFCF_3ppy)_2(bpy)^+$ (**Ir-9**) has been used by the Molander group for the SET-enabled transmetalation of trifluoroborates and silicates for similar cross-coupling reactions[40] and by the Knowles lab for alkene amidation via proton-coupled electron transfer.[41] As a representative example of the broad applicability of **Ir-10** in metallaphotoredox cross-couplings,[42] Table 9 displays the arylation[43] and alkylation[44] of hydridic C–H bonds via the merger of HAT and metallaphotoredox catalysis. Here, the oxidizing nature of the excited state of the photocatalyst enables oxidation of the quinuclidine HAT catalyst,[45] while the reducing nature of the Ir(II) state allows for initial reduction of the Ni(II) precatalyst to the required Ni(0) oxidation state, as well as catalytic turnover by reduction of Ni(I) to Ni(0).

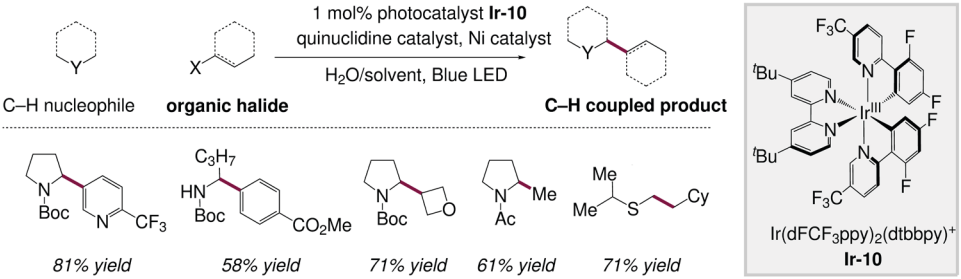
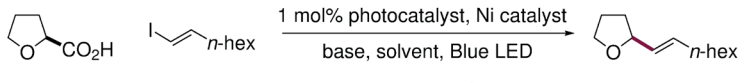


Table 9. *C–H arylation and alkylation via HAT metallaphotoredox catalysis using* ***Ir-10***

In some cases, however, the highly electron-deficient phenylpyridine ligand of **Ir-9** and **Ir-10** proves detrimental to the overall efficiency of the reaction, oftentimes owing to direct addition of intermediate carbon-centered radicals to the electrophilic arenes. In these cases, catalysts $Ir(dFMeppy)_2(dtbbpy)^+$ (**Ir-11**) and $Ir(dFHppy)_2(dtbbpy)^+$ (**Ir-12**) can oftentimes be used to restore the efficiency of the reaction. For example, our group has shown that the decarboxylative vinylation of carboxylic acids with vinyl halides can be accomplished via metallaphotoredox catalysis.[46] As shown in Table 10, however, the use of photocatalyst **Ir-10** required dilute conditions, with insoluble inorganic base and high nickel catalyst loadings for optimal efficiency. If the reaction was run under more concentrated conditions with soluble organic base and lower nickel loadings, however, the maximum efficiency achieved was 61%. Under these conditions, substantial alkylated photocatalyst could be observed in the crude reaction mixture, stemming from direct radical addition to electrophilic sites on the phenyl pyridine ligand. Simply by exchanging the trifluoromethyl group for a methyl group (i.e. using **Ir-11** in place of **Ir-10**) led to a dramatic increase to the fully optimized 92% yield, demonstrating the value of the less electron-deficient dFMeppy ligand scaffold. A similar dramatic improvement in yield was observed between **Ir-10** and **Ir-11** in our group's direct aldehyde C–H alkylation transformation[47] and Knowles's intermolecular anti-Markovnikov hydroamination,[48] while **Ir-12** proved to be the ideal photocatalyst in our double-decarboxylative metallaphotoredox coupling of alcohol-derived oxalate esters.[49]



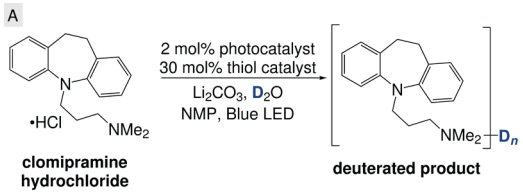
α-oxy acid **vinyl iodide** **allylic ether**

Ni loading	photocatalyst	base	solvent	time	yield
10 mol%	**Ir-10**	Cs_2CO_3	DMF (0.025 M)	72 h	83%
2 mol%	**Ir-10**	Cs_2CO_3	DMF (0.1 M)	18 h	22%
2 mol%	**Ir-10**	Cs_2CO_3	DMSO (0.1 M)	18 h	52%
2 mol%	**Ir-10**	DBU	DMSO (0.1 M)	18 h	61%
2 mol%	**Ir-11**	DBU	DMSO (0.1 M)	18 h	92%

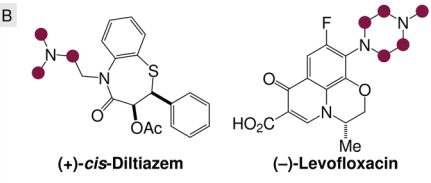
Table 10. *Superior decarboxylative vinylation of carboxylic acids using* ***Ir-11*** *vs.* ***Ir-10***

Furthermore, the slightly less-oxidizing $Ir(FMeppy)_2(dtbbpy)^+$ (**Ir-13**) has found application in our group in two distinct transformations. Indeed, **Ir-13** has been used for the enantioselective alkylation of aldehydes with simple olefins[50] and the direct isotopic labeling of pharmaceutical molecules by Hydrogen Isotope Exchange (HIE).[51] Indeed, as shown in Table 11A, **Ir-13** was vastly superior to **Ir-10**,

delivering 5.2 D/molecule with 0% unlabeled substrate, whereas **Ir-10** delivered only 4.2 D/molecule with 2.6% unlabeled material remaining. Indeed, as shown in part in Table 11B, a number of pharmaceutical molecules could be successfully deuterated and tritiated at positions adjacent to oxidizable amines via the intermediacy of α-amino radicals, using **Ir-13** as the photocatalyst.



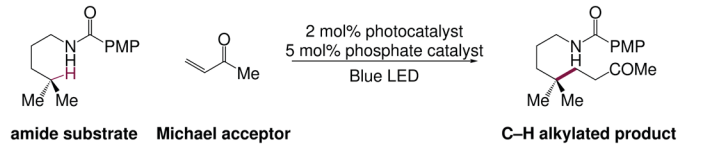
photocatalyst	D/molecule	unlabelled (%)	yield (%)
Ir-6	3.7	2.3	84
Ir-10	4.2	2.6	86
Ir-13	**5.2**	**0**	**85**

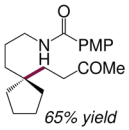
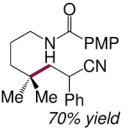
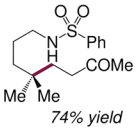


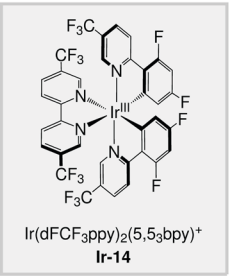
	(+)-*cis*-Diltiazem	(–)-Levofloxacin
D_2O	7.05 D/molecule 84% yield, 1.39 g	6.53 D/molecule 75% yield, 1.09 g
T_2O	34.5 Ci mmol^{-1} 28.4 mCi	22.5 Ci mmol^{-1} 14.0 mCi

Table 11. *Photoredox HIE deuteration and trititation of pharmaceutical compounds using* ***Ir-13***

In addition to derivatization of the phenylpyridine substituents to modulate the oxidizing power of the photocatalyst, as in the **Ir-10–Ir-13** series, modifications to the bipyridine backbone, as between **Ir-9** and **Ir-10**, can be extended even further, to Ir(dFCF$_3$ppy)$_2$(5,5'-dCF$_3$bpy) (**Ir-14**). Here, **Ir-14** has severely diminished reductive capability, as the reduced Ir(II) state reduction potential is $E_{1/2}^{red}$ (Ir^{III}/Ir^{II}) = –0.67 V while that of **Ir-10** is $E_{1/2}^{red}$ (Ir^{III}/Ir^{II}) = –1.37 V, both vs. SCE. Indeed, the difference in these photocatalysts enabled Knowles's catalytic alkylation of remote C–H bonds via proton-coupled electron transfer (PCET)-enabled amidyl radical HAT (*Table 12*).[52]



photocatalyst	yield	selected products
Ir-9	28%	 *65% yield*
Ir-10	10%	 *70% yield*
Ir-14	82%	 *74% yield*

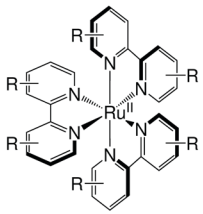


Ir(dFCF$_3$ppy)$_2$(5,5$_3$bpy)$^+$
Ir-14

Table 12*. PCET-enabled remote C–H alkylation via amidyl radical abstraction using* ***Ir-14***

Conclusions

In conclusion, the use of polypyridyl complexes of ruthenium and iridium as photocatalysts in organic transformations is a highly enabling mode of activating organic substrates towards SET and ET processes. The ability to use precisely tuned photocatalysts for the appropriate electrochemical potential or triplet energy requirement allows for the implementation of the ideal optimized reaction

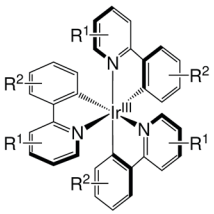


homoleptic Ru

$Ru(bpy)_3^{2+}$ (**Ru-1**)

enantioselective a-alkyaltion

arene trifluoromethylation

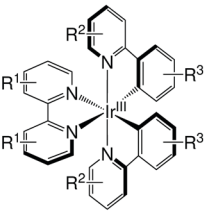


homoleptic Ir

$Ir(ppy)_3$ (**Ir-1**)

radical-radical coupling

ET-mediated Ni coupling



heteroleptic Ir

$Ir(dFCF_3ppy)_2(dtbbpy)^+$ (**Ir-10**)

arene alkylation

metallaphotoredox coupling

Table 13. *Representative Ru and Ir polypyridyl photocatalyst classes*

conditions. Photocatalysts of the type $Ru(N^N)_3^{2+}$, $Ir(C^N)_3$, and $Ir(C^N)_2(N^N)^+$ each have optimal uses in synthetic organic photocatalysis, as demonstrated by our group and others (*Table 13*). Indeed, by selecting the appropriate photocatalyst for the desired transformation, or extrapolating from known trends, optimal conditions can be developed. We anticipate that the implementation of the various photocatalysts described herein, and future iterations of these scaffolds, will greatly improve the scope of synthetic organic photocatalyzed transformations.

Acknowledgments

Financial support provided by the NIHGMS (RO1 GM103558).

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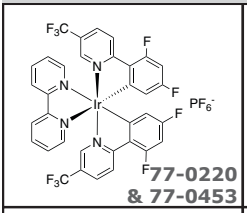
Photocatalysts - Quick Reference

Iridium Photocatalysts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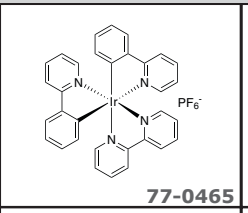
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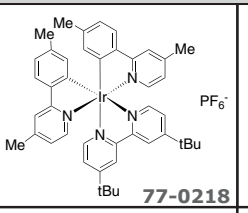
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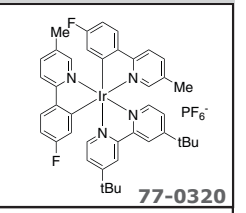
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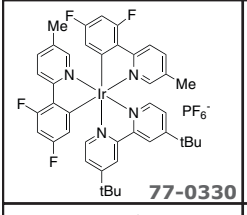
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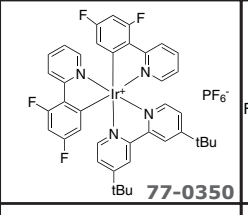
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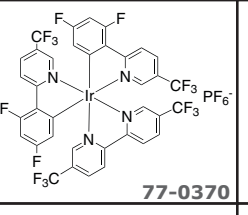
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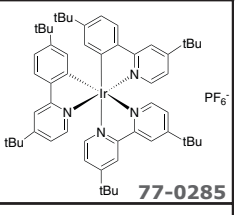
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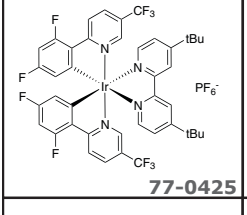
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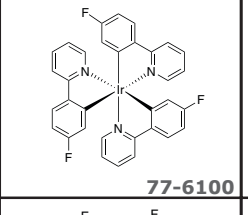
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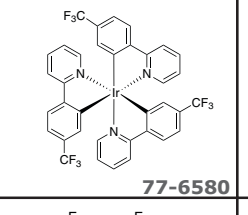
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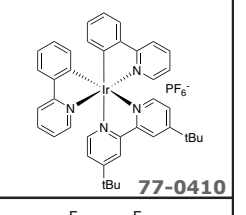
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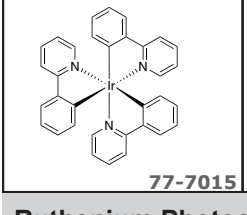
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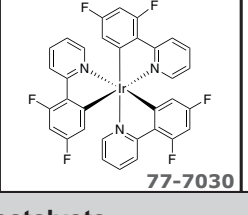
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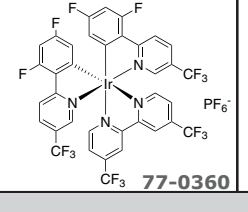
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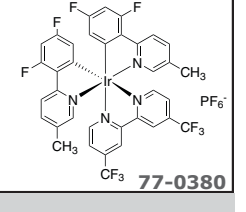
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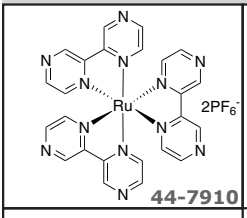
Ruthenium Photocatalysts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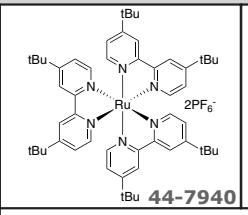
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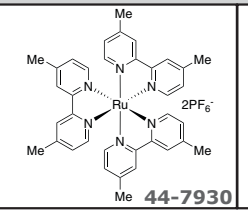
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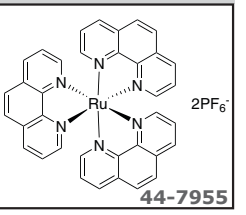
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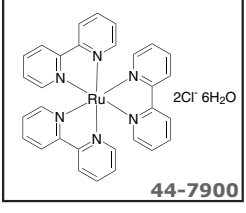
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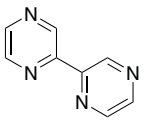
Photocatalysts - Quick Reference

Ligands for Photocatalyst Synthesis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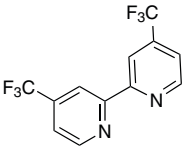
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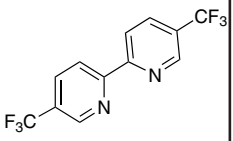
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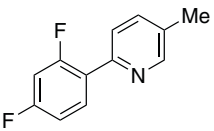
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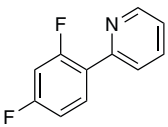
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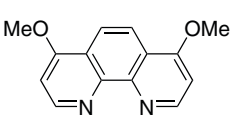
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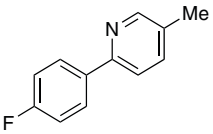
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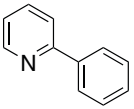
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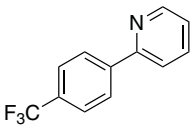
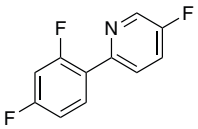

07-2625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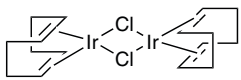
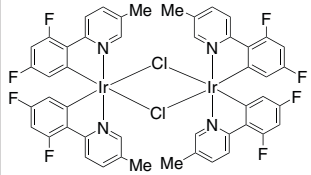
Precursors for Photocatalyst Synthesis


77-0400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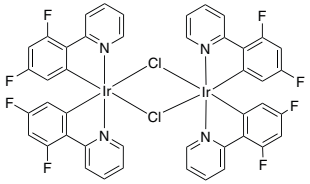
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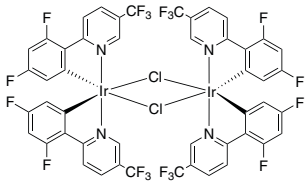
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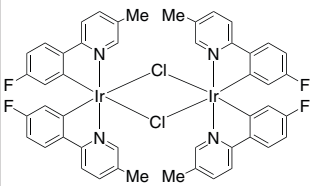
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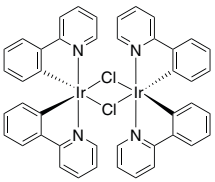
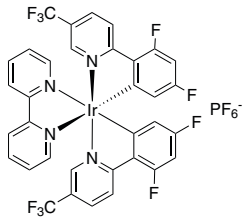

77-0455

IRIDIUM (Compounds)

77-0220 NEW

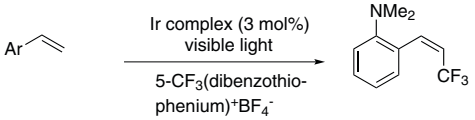
(2,2'-Bipyridine)bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-kN][phenyl-kC] iridium(III) hexafluorophosphate, 95%
(1092775-62-6)
$C_{34}H_{18}F_{16}IrN_4P$; FW: 1009.70; yellow pwdr.
air sensitive
Note: Photocatalyst



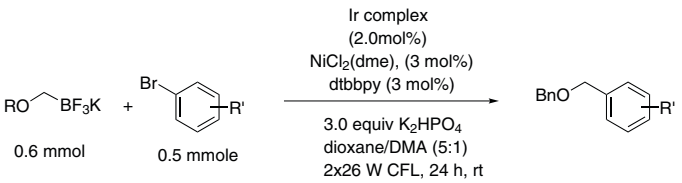
50mg
250mg

Technical Notes:

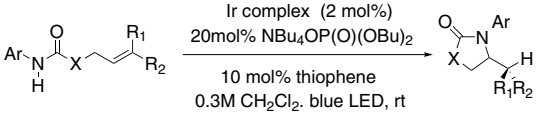
1. Photocatalyst used for the chemo-, regio, and stereoselective trifluoromethylation of styrene.
2. Photoredox catalyst used in cross-coupling: Ir/Ni dual catalysts for the synthesis of benzylic ethers.
3. Iridium complex used for catalytic olefin hydroamidation enabled by proton-coupled electron transfer.
4. Catalyst used for visible light photoredox cross-coupling of acyl chlorides with potassium alkoxymethyltrifluoroborates.
5. Iridium catalyst used in the photoredox/nickel dual catalytic cross-coupling of secondary alkyl β-trifluoroboratoketones and –esters with aryl bromides.
6. Photocatalyst used in the cross-coupling of trifluoroalkylboranes.



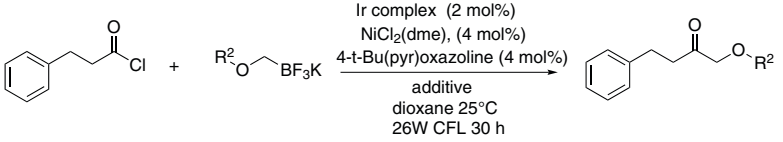
Tech. Note (1)
Ref. (1)



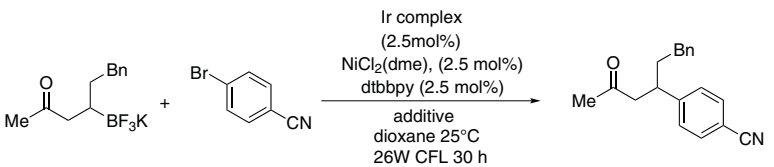
Tech. Note (2)
Ref. (2)



Tech. Note (3)
Ref. (3)



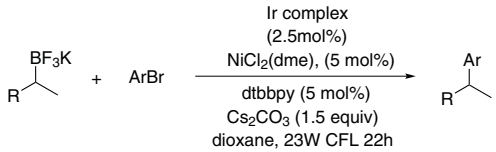
Tech. Note (4)
Ref. (4)



Tech. Note (5)
Ref. (5)

IRIDIUM (Compounds)

77-0220 **(2,2'-Bipyridine)bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-kN][phenyl-kC] iridium(III) hexafluorophosphate, 95%** *(1092775-62-6)*
(continued)



Tech. Note (6)
Ref. (6)

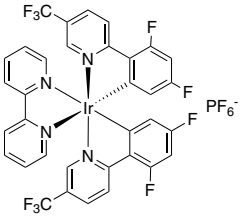
References:

1. *J. Org. Chem.*, **2014**, *79*, 10446.
2. *Org. Lett.*, **2015**, *17*, 3294.
3. *J. Am. Chem. Soc.*, **2015**, *137*, 13495.
4. *Org. Lett.*, **2016**, *18*, 732.
5. *Org. Lett.*, **2016**, *18*, 2994.
6. *Org. Lett.*, **2016**, *18*, 5760.

77-0453 **(2,2'-Bipyridine)bis[3,5-difluoro-2-[5-trifluoromethyl-2-pyridinyl-kN)phenyl-kC] iridium(III) hexafluorophosphate, 99%** *(1092775-62-6)*

NEW

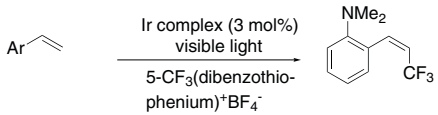
$[Ir(C_{10}H_8N_2)(C_{12}H_5F_5N)_2]$ PF_6; FW: 1009.70; yellow pwdr.
Note: Photocatalyst



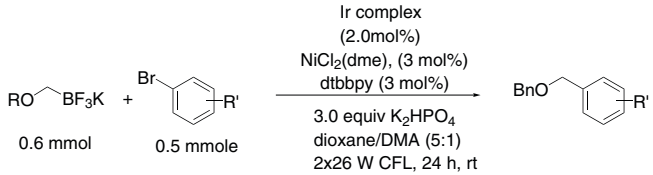
50mg
250mg

Technical Notes:

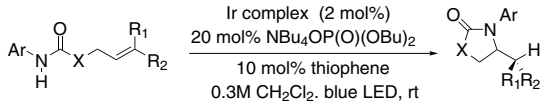
1. Catalyst used for the chemo-, regio, and stereoselective trifluoromethylation of styrene.
2. Photoredox catalyst used in cross-coupling: Ir/Ni dual catalysts for the synthesis of benzylic ethers.
3. Iridium complex used for catalytic olefin hydroamidation enabled by proton-coupled electron transfer.
4. Catalyst used for visible light photoredox cross-coupling of acyl chlorides with potassium alkoxymethyltrifluoroborates.
5. Iridium catalyst used in the photoredox/nickel dual catalytic cross-coupling of secondary alkyl β-trifluoroboratoketones and –esters with aryl bromides.
6. Photocatalyst used in the cross-coupling of trifluoroalkylboranes.



Tech. Note (1)
Ref. (1)



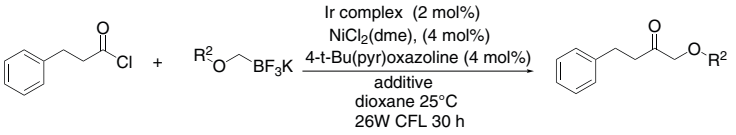
Tech. Note (2)
Ref. (2)



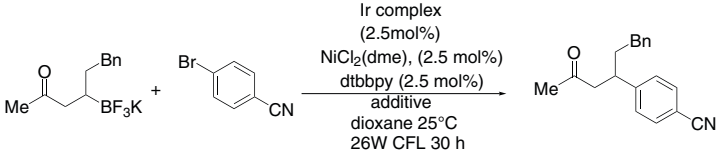
Tech. Note (3)
Ref. (3)

IRIDIUM (Compounds)

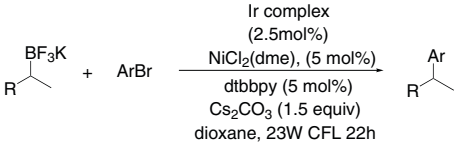
77-0453 **(2,2'-Bipyridine)bis[3,5-difluoro-2-[5-trifluoromethyl-2-pyridinyl-kN)phenyl-kC]iridium(III) hexafluorophosphate, 99%** *(1092775-62-6)*
(continued)



Tech. Note (4)
Ref. (4)



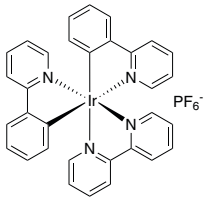
Tech. Note (5)
Ref. (5)



Tech. Note (6)
Ref. (6)

References:
1. *J. Org. Chem.*, **2014**, *79,* 10446.
2. *Org. Lett.*, **2015**, *17*, 3294.
3. *J. Am. Chem. Soc.*, **2015**, *137*, 13495.
4. *Org. Lett.,* **2016**, *18*, 732.
5. *Org. Lett.*, **2016**, *18*, 2994.
6. *Org. Lett.*, **2016**, *18*, 5760.

77-0465 **(2,2'-Bipyridine)bis[2-pyridinyl-kN)phenyl-kC] iridium(III) hexafluorophosphate, 99%**
NEW
(106294-60-4)
$[Ir(C_{10}H_8N_2)(C_{11}H_8N)_2]PF_6$; FW: 801.74;
yellow pwdr.
Note: Photocatalyst



100mg
500mg

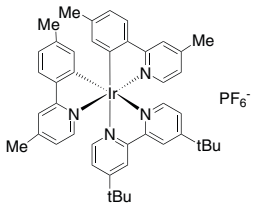
Technical Notes:
1. Catalyst used in the visible-light, photoredox-catalyzed synthesis of nitrones.
2. Catalyst used in light-mediated, direct arylation of arenes and heteroarenes.
3. Photoredox catalyst used in C-P bond formation reactions.

References:
1. *Org. Lett.,* **2014**, *16*, 2872.
2. *Chem. Lett.,* **2013**, *42*, 1203.
3. *Chem. Comm.,* **2011**, *47*, 8679.

IRIDIUM (Compounds)

77-0218 NEW

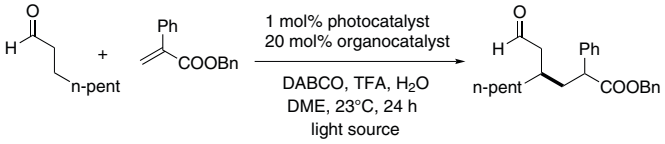
4,4'-Bis(t-butyl-2,2'-bipyridine]bis[5-methyl-2-(4-methyl-2-pyridinyl-kN)phenyl-kC]iridium hexafluorophosphate, 95% *(1607469-49-7)*
$C_{44}H_{48}F_6IrN_4P$; FW: 970.06; yellow pwdr.
air sensitive
Note: Photocatalyst



50mg
250mg

Technical Note:

1. Catalyst used for the direct β-alkylation of aldehydes via photoredox organocatalysis.



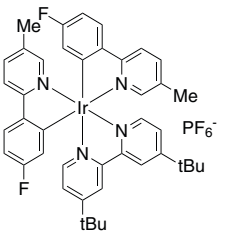
Tech. Note (1)
Ref. (1)

References:

1. *J. Am. Chem. Soc.*, **2014**, *136*, 6858.

77-0320 NEW

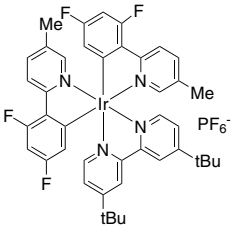
[4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine-κN,κN] bis[5-fluoro-2-(5-methyl-2-pyridinyl-κN)phenyl-κC] iridium hexafluorophosphate, 98% *(808142-88-3)*
$C_{42}H_{42}F_8IrN_4P$; FW: 977.98; yellow solid
air sensitive
Note: Photocatalyst



50mg
250mg

77-0330 NEW

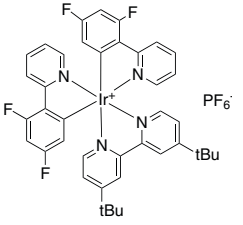
[4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine-κN,κN] bis[3,5-difluoro-2-(5-methyl-2-pyridinyl)phenyl] iridium hexafluorophosphate, 98% *(1335047-34-1)*
$C_{42}H_{40}F_{10}IrN_4P$; FW: 1013.96; yellow solid
air sensitive
Note: Photocatalyst



100mg
500mg

77-0350 NEW

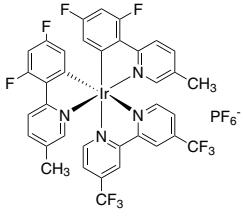
[4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine-κN,κN] bis[3,5-difluoro-2-(2-pyridinyl-κN)phenyl-κC]iridium hexafluorophosphate, 97% *(1072067-44-7)*
$C_{40}H_{36}F_{10}IrN_4P$; FW: 985.92; Yellow pwdr.
air sensitive
Note: Photocatalyst



100mg
500mg

77-0380 NEW

4,4'-Bis(trifluoromethyl)-2,2'-bipyridinebis[3,5-difluoro-2-[5-methyl-2-pyridinyl)phenyl] iridium(III) hexafluorophosphate
$C_{36}H_{22}F_{16}IrN_4P$; FW: 1037.77
air sensitive
Note: Photocatalyst

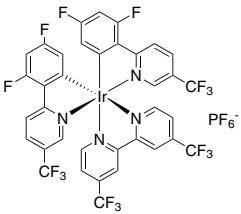


50mg
250mg

IRIDIUM (Compounds)

77-0360 NEW

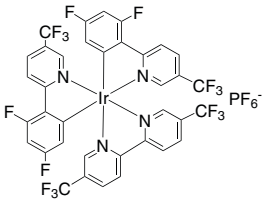
4,4'-Bis(trifluoromethyl)-2,2'-bipyridinebis[3,5-difluoro-2-[5-trifluoromethyl-2-pyridinyl)phenyl] iridium(III) hexafluorophosphate *(2030437-90-0)*
$C_{36}H_{16}F_{22}IrN_4P$; FW: 1145.69
air sensitive
Note: Photocatalyst



50mg
250mg

77-0370 NEW

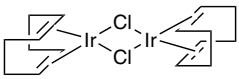
[5,5'-Bis(trifluoromethyl)-2,2'-bipyridine-κN,κN] bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-κN]phenyl]iridium hexafluorophosphate, 98%
(1973375-72-2)
$C_{36}H_{16}F_{22}IrN_4P$; FW: 1145.69; yellow solid
air sensitive
Note: Photocatalyst



50mg
250mg

77-0400

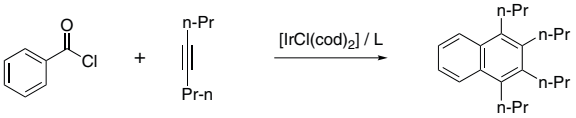
Chloro-1,5-cyclooctadiene iridium(I) dimer, 99%
(12112-67-3)
$[IrCl(C_8H_{12})]_2$; FW: 671.71; red to orange pwdr.; m.p. 190° dec.
Note: Precursor for Photocatalyst Synthesis



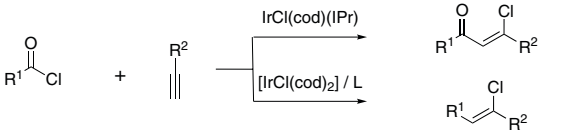
500mg
2g
10g

Technical Notes:

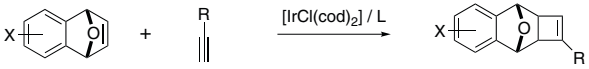
1. Precursor to catalysts for the asymmetric hydrogenation of tri- and tetrasubstituted olefins.
2. Precursor to catalyst for enantioselective reduction of imines.
3. Precursor to catalyst for allylic alkylation.
4. Precursor to catalyst for allylic amination and etherification.
5. Precursor to catalyst for the reaction of aroyl chlorides with internal alkynes to produce substituted naphthalenes and anthracenes.
6. Ir-catalyzed addition of acid chlorides to terminal alkynes.
7. Intramolecular hydroamination of unactivated alkenes with secondary alkyl- and arylamines.
8. Enantioselective [2+2] cycloaddition.
9. Silyl-directed, Ir-catalyzed ortho-borylation of arenes.
10. Ir-catalyzed cross-coupling of styrene derivatives with allylic carbonates.
11. Transfer hydrogenative C-C coupling



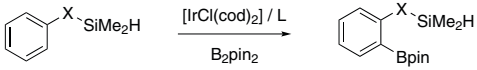
Tech. Note (5)
Ref. (5)



Tech. Note (6)
Ref. (6)



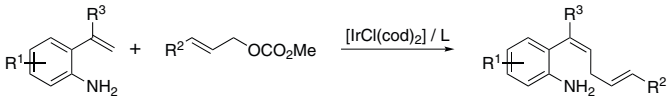
Tech. Note (8)
Ref. (8)



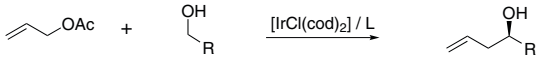
Tech. Note (9)
Ref. (9)

IRIDIUM (Compounds)

77-0400 **Chloro-1,5-cyclooctadiene iridium(I) dimer, 99%** *(12112-67-3)*
(continued)



Tech. Note (10)
Ref. (10)

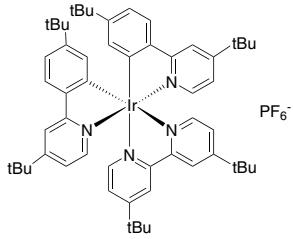


Tech. Note (11)
Ref. (11)

References:

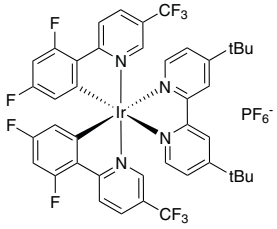
1. *Angew. Chem. Int. Ed.,* **1998**, *37*, 2897
2. *J. Am. Chem. Soc.,* **1999**, *121*, 6421
3. *J. Am. Chem. Soc.,* **1998**, *120*, 8647
4. *J. Am. Chem. Soc.,* **2003**, *125*, 14272
5. *J. Am. Chem. Soc.,* **2002**, *124*, 12680
6. *J. Am. Chem. Soc.,* **2009**, *131*, 6668
7. *J. Am. Chem. Soc.,* **2010**, *132*, 413
8. *Org. Lett.,* **2010**, *12*, 304
9. *J. Am. Chem. Soc.,* **2008**, *130*, 7534
10. *J. Am. Chem. Soc.,* **2009**, *131*, 8346
11. *(a) J. Am. Chem. Soc.,* **2008**, *130*, 6340, *(b) Angew, Chem, Int, Ed,* **2009**, *48*, 6313

77-0285 NEW
[4,4'-Di-t-butyl-2,2'-bipyridine][bis[5-(t-butyl)-2-[4-(t-butyl)-2-pyridinyl-kN] phenyl-kC]iridium(III) hexafluorophosphate, 95% *(808142-80-5)*
$C_{56}H_{72}F_6IrN_4P$; FW: 1138.38; yellow pwdr.
air sensitive
Note: Photocatalyst



50mg
250mg

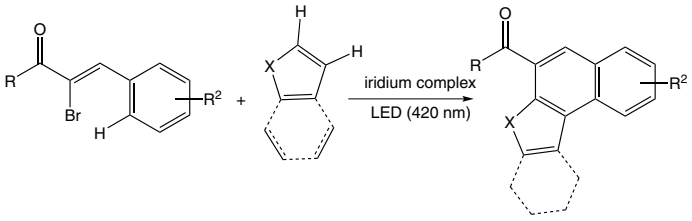
77-0425 NEW
(4,4'-Di-t-butyl-2,2'-bipyridine)bis[3,5-difluoro-2-[5-trifluoromethyl-2-pyridinyl-kN) phenyl-kC]iridium(III) hexafluorophosphate, 99% *(870987-63-6)*
$[Ir(C_{18}H_{24}N_2)(C_{12}H_5F_5N)_2]^+PF_6^-$; FW: 1121.91; yellow xtl.
Note: Photocatalyst



50mg
250mg
1g

Technical Notes:

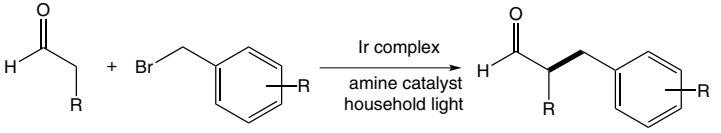
1. Visible light photoredox-catalyzed cascade cyclizations of α-bromochalcones or α-bromocinnamates with heteroarenes.
2. Enantioselective α-benzylation of aldehydes via photoredox organocatalysis..



Tech. Note (1)
Ref. (1)

IRIDIUM (Compounds)

77-0425 ***(continued)*** **(4,4'-Di-t-butyl-2,2'-bipyridine)bis[3,5-difluoro-2-[5-trifluoromethyl-2-pyridinyl-kN) phenyl-kC]iridium(III) hexafluorophosphate, 99%** *(870987-63-6)*



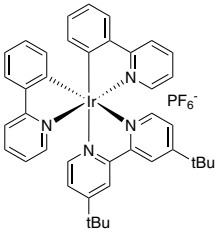
Tech. Note (2)
Ref. (2)

References:

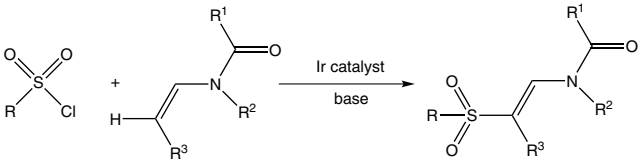
1. *Adv. Synth. Cat.,* **2014**, *356*, 557
2. *J. Amer. Chem. Soc.,* **2010**, *132*, 13600

77-0410 NEW **(4,4'-Di-t-butyl-2,2'-bipyridine)bis[2-(2-pyridinyl-kN)phenyl-kC]iridium(III) hexafluorophosphate, 99%** *(676525-77-2)*
$[Ir(C_{18}H_{24}N_2)(C_{11}H_8N)_2]^+PF_6^-$; FW: 913.95; yellow xtl.
Note: Photocatalyst

100mg
500mg



Technical Notes:
1. This Iridium catalyst is used in the synthesis of β-amidovinyl sulfones via visible-light photoredox catalysis.
2. Numerous uses of this photoredox catalyst are reported (see Ref. 2).



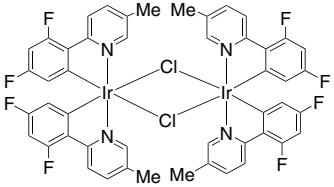
Tech. Note (1)
Ref. (1)

References:

1. *Adv. Synth. Cat.,* **2013**, *355*, 809
2. *Chem. Rev.,* **2013**, *113*, 5322, review

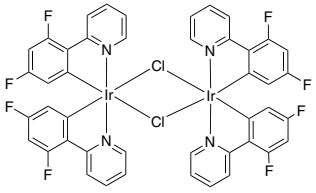
77-0345 NEW **Di-μ-chlorotetrakis[3,5-difluoro-2-(5-methyl-2-pyridinyl-κN)phenyl-κC] diiridium, 98%** *(1335047-33-0)*
$C_{48}H_{32}Cl_2F_8Ir_2N_4$; FW: 1272.11; yellow solid
Note: Precursor for Photocatalyst Synthesis

250mg
1g



77-0365 NEW **Di-μ-chlorotetrakis[3,5-difluoro-2-(2-pyridinyl-κN)phenyl-κC]diiridium, 98%** *(562824-27-5)*
$C_{44}H_{24}Cl_2F_8Ir_2N_4$; FW: 1216.05 ; yellow solid
air sensitive
Note: Precursor for Photocatalyst Synthesis

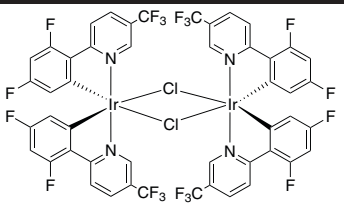
250mg
1g



IRIDIUM (Compounds)

77-0468 NEW

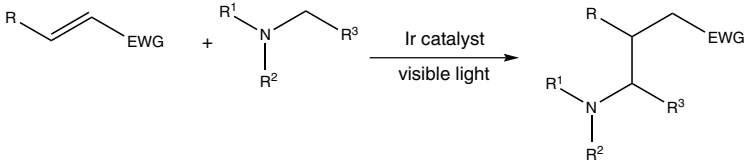
Di-μ-chlorotetrakis[3,5-difluoro-2-[5-trifluoromethyl-2-pyridinyl-kN)phenyl-kC] diiridium(III), 99% *(870987-64-7)*
$C_{48}H_{20}Cl_2F_{20}Ir_2N_4$; FW: 1488.01; yellow xtl.
Note: Precursor for Photocatalyst Synthesis



50mg
250mg

Technical Note:

1. Addition to electron–deficient alkenes using a photoredox catalyst.



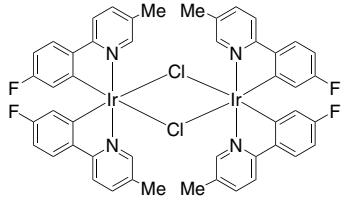
Tech. Note (1)
Ref. (1)

References:

1. *J. Am. Chem. Soc.*, **2012**, *134*, 3338.

77-0335 NEW

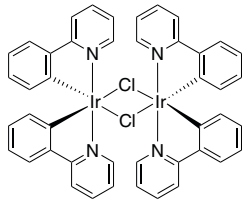
Di-μ-chlorotetrakis[5-fluoro-2-(5-methyl-2-pyridinyl-κN)phenyl-κC]diiridium, 98% *(808142-89-4)*
$C_{48}H_{36}Cl_2F_4Ir_2N_4$; FW: 1200.15; yellow solid
Note: Precursor for Photocatalyst Synthesis



250mg
1g

77-0455

Di-μ-chlorotetrakis[2-(2-pyridinyl-kN) phenyl-kC]diiridium(III), 99% *(603109-48-4)*
$C_{44}H_{32}Cl_2Ir_2N_4$; FW: 1072.09; yellow-green xtl.
Note: Precursor for Photocatalyst Synthesis



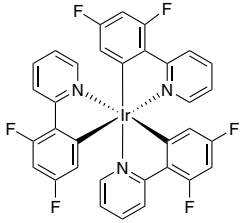
250mg
1g

Technical Note:

1. Iridium complex is a photoredox catalyst having numerous uses in electroluminescent materials and devices, organic light-emitting diodes, display devices and chemosensors.

77-7030 NEW

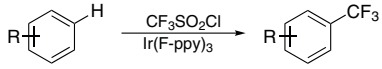
Tris[2-(2,4-difluorophenyl)pyridine] iridium(III), 95% *(387859-70-3)*
$C_{33}H_{18}F_6IrN_3$; FW: 762.72; yellow pwdr.
air sensitive
Note: Photocatalyst



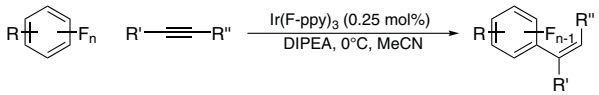
50mg
250mg

Technical Notes:

1. Photoredox catalysis for trifluoromethylation of arenes and heteroarenes.
2. Photocatalyst for C–F alkenylation coupling reactions between perfluoroarenes and alkynes.



Tech. Note (1)
Ref. (1)



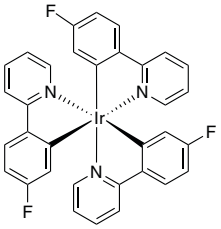
Tech. Note (2)
Ref. (2)

References:

1. *Nature*, **2011**, *480*, 224.
2. *Chem. Sci.*, **2016**, *7*, 6796.

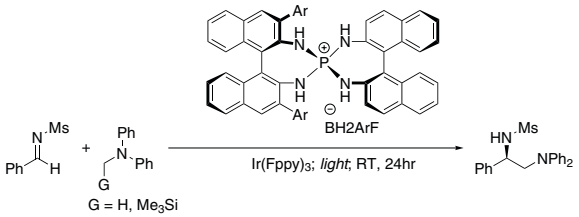
IRIDIUM (Compounds)

77-6100 **Tris[5-fluoro-2-(2-pyridinyl-kN)phenyl-kC] iridium(III), 95%** *(370878-69-6)*
NEW
$C_{33}H_{21}F_3IrN_3$; FW: 708.75; yellow pwdr.
air sensitive
Note: Photocatalyst
50mg
250mg

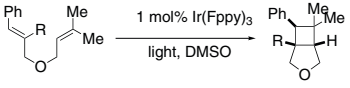


Technical Notes:

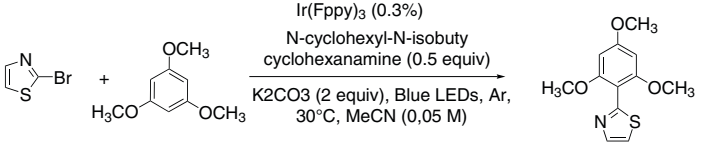
1. Photosensitizer for the enantioselective coupling reaction between (N-arylamino)methanes and (N-methanesulfonyl)-aldimines catalyzed by P-Spiro chiral (arylamino)phosphonium catalyst.
2. Photocatalyst for [2+2] styrene cycloadditions.
3. Photocatalyst for azoylation of trimethoxybenzene by via C−H functionalization.



Tech. Note (1)
Ref. (1)



Tech. Note (2)
Ref. (2)

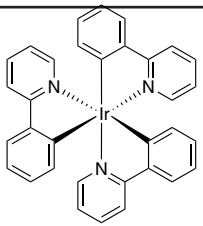


Tech. Note (3)
Ref. (3)

References:

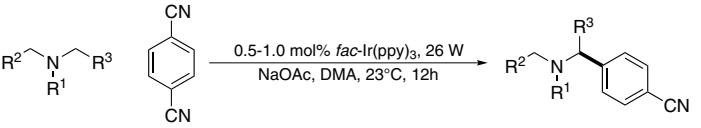
1. *J. Org. Chem.,* **2016**, *81*, 6953.
2. *Chem. Sci.,* **2016**, *7*, 6796.
3. *Org. Lett.,* **2016**, *18*, 3996.

77-7015 **Tris(2-phenylpyridinato-C2,N)iridium(III), 95%** *(94928-86-8)*
NEW
$C_{33}H_{24}IrN_3$; yellow pwdr.
air sensitive
Note: Photocatalyst
50mg
250mg



Technical Notes:

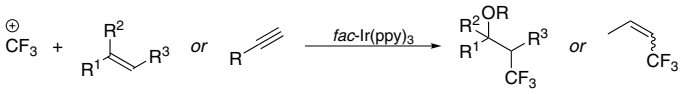
1. Photocatalyst for α-amino C–H arylation of cyano(hetero)arenes by tertiary amines
2. Photocatalyst for trifluoromethylation of alkenes and alkynes
3. Photocatalyst for reduction of alkyl, alkenyl, aryl iodides (a) and intramolecular reductive cyclizations (d)
4. Photocatalyst for organocatalyst assisted direct arylation of allylic sp^3 C–H bonds
5. Photocatalyst for the generation multifluorinated biaryls via functionalization of the C−F bond of a perfluoroarene and C−H bond of the other arene in the presence of amines
6. Photocatalyst for visible-light photoredox arylation of thiols with various aryl halides



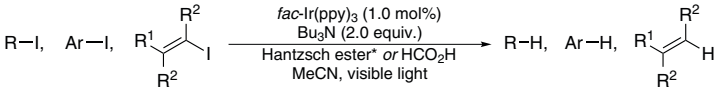
Tech. Note (1)
Ref. (1)

IRIDIUM (Compounds)

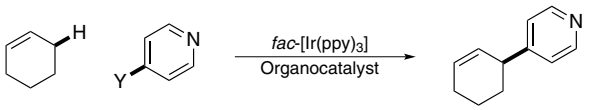
77-7015 **Tris(2-phenylpyridinato-C2,N)iridium(III), 95%** *(94928-86-8)*
(continued)



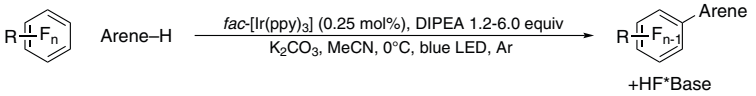
Tech. Note (2)
Ref. (2,3)



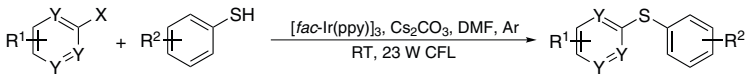
Tech. Note (3)
Ref. (4)



Tech. Note (4)
Ref. (5)



Tech. Note (5)
Ref. (6)



X=I, Br, Cl, F
Y=CH, N

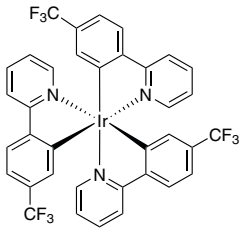
Tech. Note (6)
Ref. (7)

References:

1. *Science* **2011**, *334*, 1114
2. *Angew. Chem. Int. Ed.* **2012**, *51*, 9567
3. *Angew. Chem. Int. Ed.* **2014**, *53*, 539
4. *Nat. Chem.* **2012**, *4*, 854
5. *Nature* **2015** *519*, 74
6. *J. Am. Chem. Soc.* **2016**, *138*, 2520
7. *Angew. Chem. Int. Ed.* **2017**, *56*, 874

77-6580 NEW

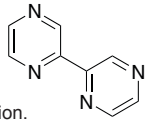
Tris[(2-(2-pyridinyl-kN)-5-(trifluoromethyl) phenyl-kC]iridium(III), 95% *(500295-52-3)*
$C_{36}H_{21}F_9IrN_3$; FW: 858.78; yellow solid
air sensitive
Note: Photocatalyst



50mg
250mg

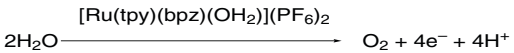
NITROGEN (Compounds)

07-0750 **2,2'-Bipyrazine, 95%** *(10199-00-5)* 250mg
NEW $C_8H_6N_4$; FW: 158.16; light-brown solid 1g
air sensitive
Note: Ligand for Photocatalyst Synthesis

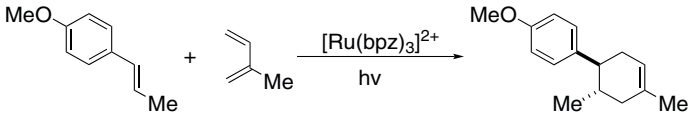


Technical Notes:

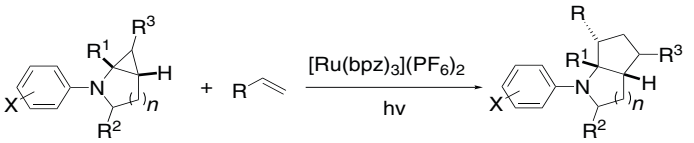
1. Ligand for the ruthenium- promoted catalytic water oxidation reaction.
2. Ligand for the ruthenium promoted photocatalytic Diels-Alder cycloaddition.
3. Ligand for the ruthenium photocatalyzed intermolecular [3+2] cycloaddition of cyclopropylamines with olefins.
4. Ligand for the ruthenium mediated photocatalytic reaction for the preparation of N-arylindoles.
5. Endoperoxide synthesis by photocatalytic aerobic [2+2+2] cycloadditions.
6. $[Ru(bpz)_3](PF_6)_2$ catalyzed anti-Markovnikov hydrothiolation of olefins with a variety of thiols.
7. $[Ru(bpz)_3](PF_6)_2$ catalyzed [3+2] photooxygenation of aryl cyclopropanes.
8. $[Ru(bpz)_3](PF_6)_2$ catalyzed intermolecular [3 + 2] annulation of cyclopropylanilines with alkynes.



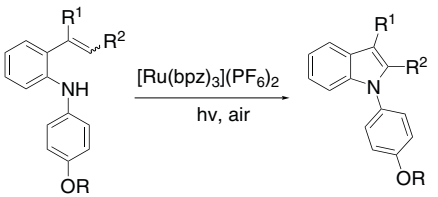
Tech. Note (1)
Ref. (1)



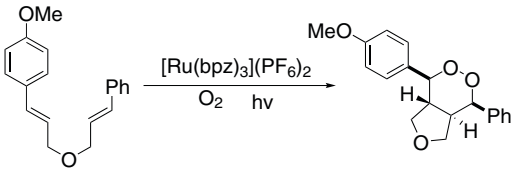
Tech. Note (2)
Ref. (2)



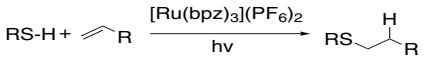
Tech. Note (3)
Ref. (3)



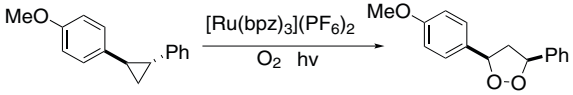
Tech. Note (4)
Ref. (4)



Tech. Note (5)
Ref. (5)



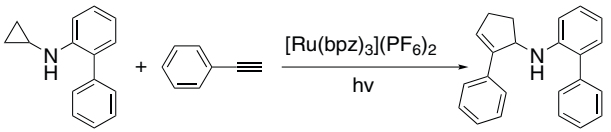
Tech. Note (6)
Ref. (6)



Tech. Note (7)
Ref. (7)

NITROGEN (Compounds)

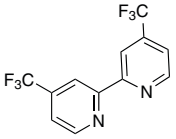
07-0750 **2,2'-Bipyrazine, 95%** *(10199-00-5)*
(continued)



Tech. Note (8)
Ref. (8)

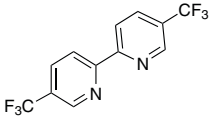
References:
1. *J. Am. Chem. Soc.*, **2008**, *130,* 16462.
2. *J. Am. Chem. Soc.*, **2011**, *133,* 19350.
3. *Angew. Chem. Int. Ed.,*., **2012**, *51,* 222.
4. *Angew. Chem. Int. Ed.,*., **2012**, *51,* 9562.
5. *Org. Lett.,*., **2012**, *14,* 1640.
6. *J. Org. Chem.,*., **2013**, *78,* 2046.
7. *Tetrahedron*, **2014**, *70*, 4270.
8. *Beilstein J. Org. Chem.,* , **2014**, *10*, 975.

07-1425 NEW
4,4'-Bis(trifluoromethyl)-2,2'-bipyridine, min. 95% *(142946-79-0)*
$C_{12}H_6F_6N_2$; FW: 292.17; off-white to light yellow pwdr.
air sensitive
Note: Ligand for Photocatalyst Synthesis



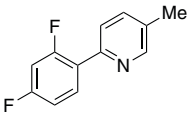
1g
5g

07-1430 NEW
5,5'-Bis(trifluoromethyl)-2,2'-bipyridine, min 97% *(142946-80-3)*
$C_{12}H_6F_6N_2$; FW: 292.17; White pwdr.
air sensitive
Note: Ligand for Photocatalyst Synthesis



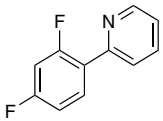
1g
5g

07-1280 NEW
2-(2,4-Difluorophenyl)-5-methylpyridine, 95% *(583052-21-5)*
$C_{12}H_9F_2N$; FW: 205.20; white solid
air sensitive
Note: Ligand for Photocatalyst Synthesis



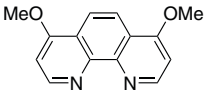
500mg
2g

07-1420 NEW
2-(2,4-Difluorophenyl)pyridine, min. 97% *(391604-55-0)*
$C_{11}H_7F_2N$; FW: 191.17; white solid
air sensitive
Note: Ligand for Photocatalyst Synthesis



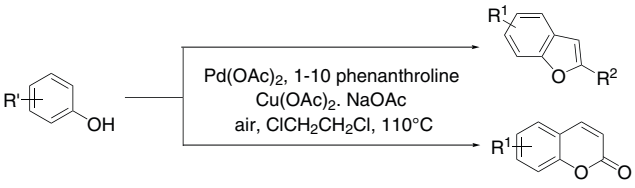
1g
5g

07-1923 NEW HAZ
4,7-Dimethoxy-1,10-phenanthroline, 98% *(92149-07-0)*
$C_{14}H_{10}N_2O_2$; FW: 238.24; white to off-white pwdr.;
m.p. 210-212°; d. 1.25
air sensitive
Note: Ligand for Photocatalyst Synthesis



250mg
1g

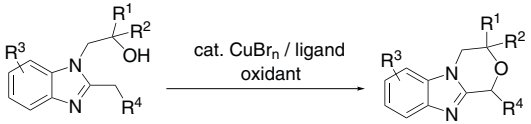
Technical Notes:
1. Palladium-catalyzed synthesis of benzofurans and coumarins from phenols and olefins.
2. Copper-catalyzed benzylic C(sp3)-H alkoxylation of heterocyclic compounds.
3. Synthesis of amides via copper-catalyzed amidation of aryl halides using isocyanides.
4. Iridium-catalyzed silylation of aryl C-H bonds.
5. Palladium-catalyzed intramolecular cyclization of nitroalkenes: synthesis of thienopyrroles.
6. A Copper-catalyzed N-alkynylation route to 2-substitued N-alkynyl pyrroles and their cyclization into pyrrolo[2,1-c]oxazin-1-ones



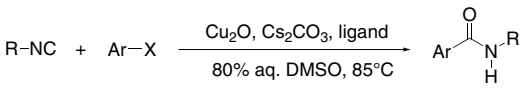
Tech. Note (1)
Ref. (1)

NITROGEN (Compounds)

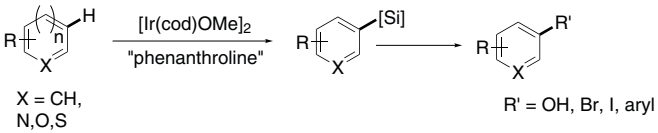
07-1923 **4,7-Dimethoxy-1,10-phenanthroline, 98%** *(92149-07-0)*
(continued)



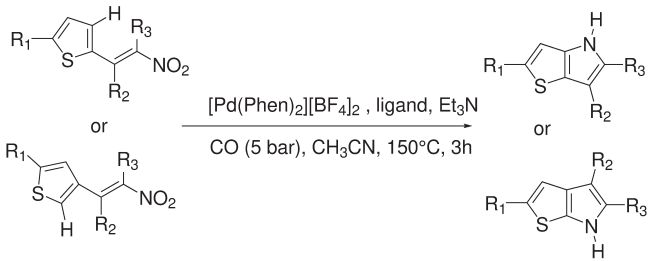
Tech. Note (2)
Ref. (2)



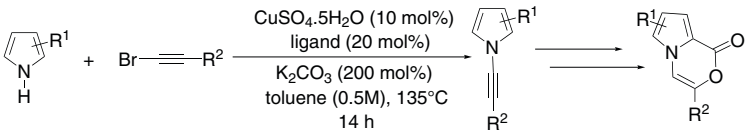
Tech. Note (3)
Ref. (3)



Tech. Note (4)
Ref. (4)



Tech. Note (5)
Ref. (5)

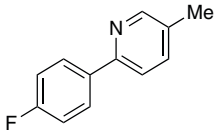


Tech. Note (6)
Ref. (6)

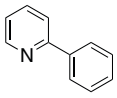
References:

1. *Angew. Chem. Int. Ed.*, **2013**, *52*, 12669.
2. *Organic & Biomolecular Chemistry,* **2014**, *12*, 2528.
3. *Tetrahedron Letts.*, **2014**, *55*, 4981.
4. *J. Am. Chem. Soc.*, **2015**, *137*, 592.
5. *European Journal of Organic Chemistry*, **2017**, *2017(14)*, 1902.
6. *Synthesis,* **2017**, *49*, 2544.

07-1410 **2-(4-Fluorophenyl)-5-methylpyridine, min. 97%** 1g
NEW *(85237-65-6)* 5g
$C_{12}H_{10}FN$; FW: 187.07; Off white pwdr.
air sensitive
Note: Ligand for Photocatalyst Synthesis



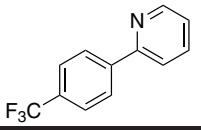
07-1780 **2-Phenylpyridine, 95%** *(1008-89-5)* 1g
NEW $C_{11}H_9N$; FW: 155.20; amber liquid; b.p. 268-270°; f.p. 230°; d. 1.086
air sensitive
Note: Ligand for Photocatalyst Synthesis



NITROGEN (Compounds)

07-2625 NEW — **2-[4-(Trifluoromethyl)phenyl]pyridine, 95%** *(203065-88-7)* — 1g

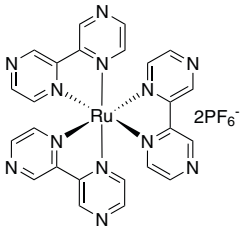
$C_{12}H_8F_3N$; FW: 223.19; white to yellow solid
air sensitive
Note: Ligand for Photocatalyst Synthesis



RUTHENIUM (Compounds)

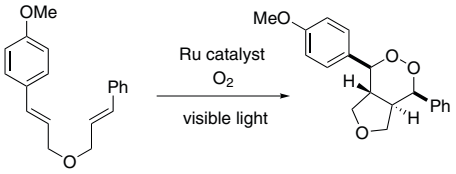
44-7910 NEW — **Tris(2,2'-bipyrazine)ruthenium(II) hexafluorophosphate, 95%** *(80907-56-8)* — 50mg, 250mg

$C_{24}H_{18}F_{12}N_{12}P_2Ru$; FW: 865.48; red pwdr.
air sensitive
Note: Photocatalyst.

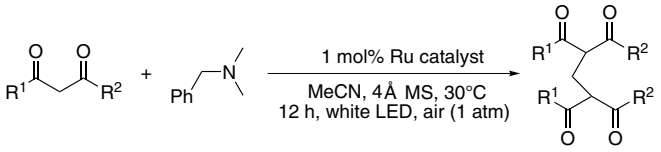


Technical Notes:

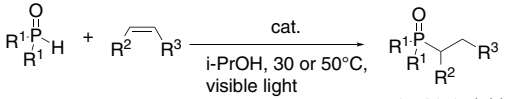
1. Endoperoxide synthesis by photocatalytic aerobic [2+2+2] cycloadditions.
2. Aerobic oxidation of a tertiary aliphatic amine under visible-light photocatalysis. Facile synthesis of methylene-bridged bis-1,3-dicarbonyl compounds.
3. Hydrophosphinylation of unactivated alkenes with secondary phosphine oxides under visible-light photocatalysis.
4. [3+2] Photooxygenation of aryl cyclopropanes via visible light photocatalysis.
5. Photocatalytic synthesis of dihydrobenzofurans by oxidative cycloaddition of phenols.



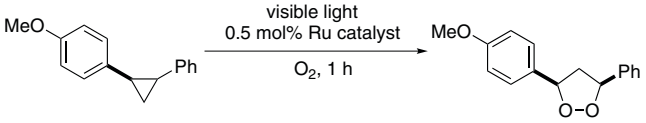
Tech. Note (1)
Ref. (1)



Tech. Note (2)
Ref. (2)



Tech. Note (3)
Ref. (3)



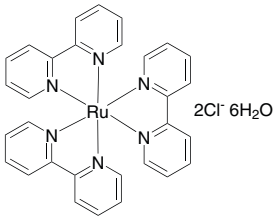
Tech. Note (4)
Ref. (4)

References:

1. *Org. Lett.*, **2012**, *14*, 1640.
2. *Chemistry – An Asian Journal*, **2012**, *7*, 2764.
3. *Green Chemistry*, **2013**, *15*, 1844.
4. *Advanced Synthesis & Catalysis*, **2014**, *356*, 2831.
5. *J. Am. Chem. Soc.*, **2015**, *137*, 5654.

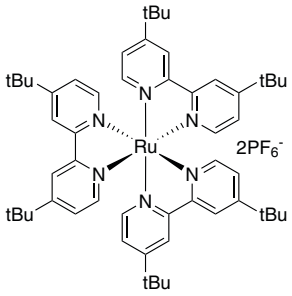
RUTHENIUM (Compounds)

44-7900 **Tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate, min. 98%** *(50525-27-4)*
$Ru(C_{10}H_8N_2)_3Cl_2 \cdot 6H_2O$; FW: 640.54 (748.63); orange to red xtl.
Note: Photocatalyst



250mg
1g
5g

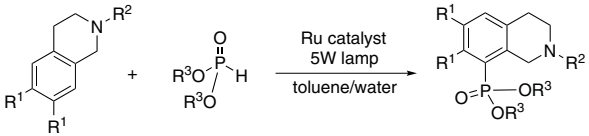
44-7940 NEW **Tris[4,4'-bis(t-butyl)-2,2'-bipyridine] ruthenium(II) hexafluorophosphate, 95%** *(75777-87-6)*
$C_{54}H_{72}F_{12}N_6RuP_2$; FW: 1196.19; red pwdr.
air sensitive
Note: Photocatalyst.



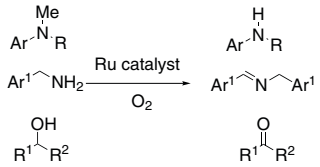
50mg
250mg

Technical Notes:

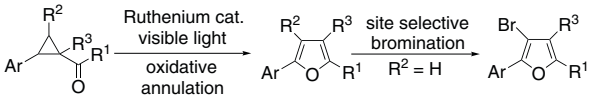
1. Photoredox catalysed C-P bond formation reactions – visible light mediated oxidative phosphonylations of amines.
2. Aerobic oxidation of a tertiary aliphatic amine under visible-light photocatalysis: facile synthesis of methylene-bridged bis-dicarbonyl compounds.
3. Photoredox catalysis as an efficient tool for the aerobic oxidation of amines and alcohols.
4. Visible-light induced, direct synthesis of polysubstituted furans from cyclopropyl ketones.



Tech. Note (1)
Ref. (1)



Tech. Note (2)
Ref. (2)



Tech. Note (3)
Ref. (3)

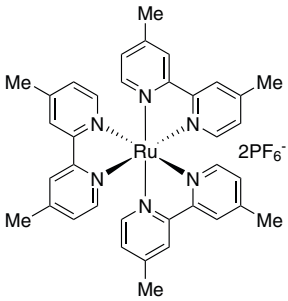
References:

1. *Chem. Commun.*, **2011**, *47*, 8679.
2. *Chemistry – An Asian Journal*, **2012,** *7*, 2764.
3. ACS Catalysis, **2012**, *2,* 2810.
4. *J. Org. Chem.*, **2016**, *81*, 7008.

RUTHENIUM (Compounds)

44-7930 NEW

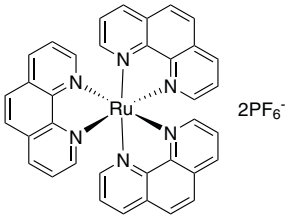
Tris(4,4'-dimethyl-2,2'-bipyridine) ruthenium(II) hexafluorophosphate, 95%, DMBPY *(83605-44-1)*
$C_{36}H_{36}F_{12}N_6RuP_2$; FW: 943.71; red pwdr.
air sensitive
Note: Photocatalyst.



50mg
250mg

44-7955 NEW

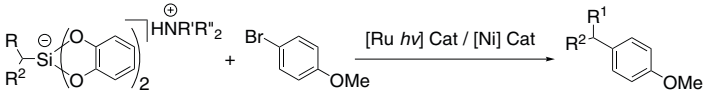
Tris(1,10-phenanthroline)ruthenium(II) hexafluorophosphate, 95% *(60804-75-3)*
$C_{36}H_{24}F_{12}N_6RuP_2$; FW: 931.62; red pwdr.
air sensitive
Note: Photocatalyst



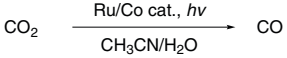
50mg
250mg

Technical Notes:

1. Photoredox catalyst for nickel assisted cross-coupling reactions of ammonium alkylsilicates with aryl bromides
2. A photosensitizer for cobalt catalyzed visible-light driven CO_2 - Reduction to CO in CH_3CN/H_2O Solution



Tech. Note (1)
Ref. (1)



Tech. Note (2)
Ref. (2)

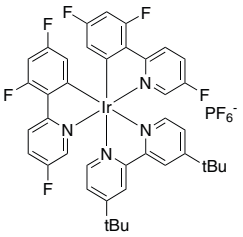
References:

1. *J. Am. Chem. Soc.*, **2016**, *138*, 475.
2. *Angew. Chem. Int. Ed.*, **2017**, *56*, 738.

COMING SOON...

77-0340 NEW

[4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine]bis[3, 5-difluoro-2-(5-fluoro-2-pyridinyl)phenyl]iridium hexafluorophosphate *(2042201-18-1)*
$C_{40}H_{34}F_{12}IrN_4P$; FW: 1021.89
air sensitive
Note: Photocatalyst

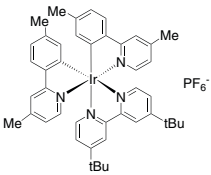


KITS - Iridium Photocatalyst Kit 1

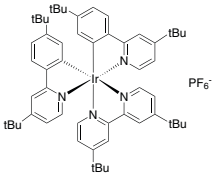
96-7780 **Iridium Photocatalyst Kit 1**

NEW

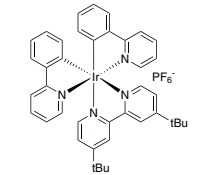
Components also available for individual sale.
Contains the following:



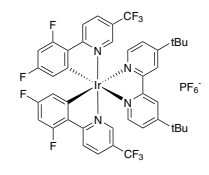
77-0218 50mg



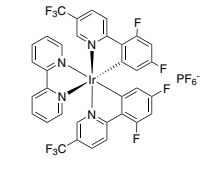
77-0285 50mg



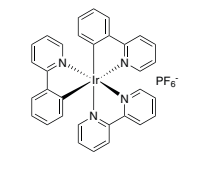
77-0410 100mg



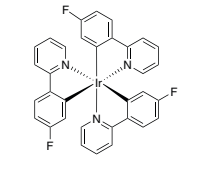
77-0425 50mg



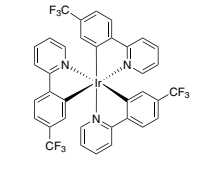
77-0453 50mg



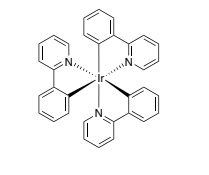
77-0465 100mg



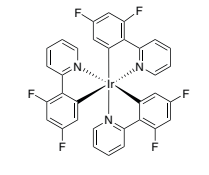
77-6100 50mg



77-6580 50mg



77-7015 50mg



77-7030 50mg

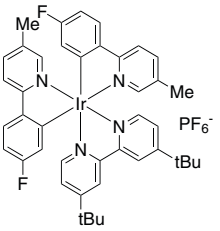
77-0218	4,4'-Bis(t-butyl-2,2'-bipyridine]bis[5-methyl-2-(4-methyl-2-pyridinyl-kN)phenyl-kC]iridium hexafluorophosphate, 95% *(1607469-49-7)*	50mg	See page 17
77-0285	[4,4'-Di-t-butyl-2,2'-bipyridine][bis[5-(t-butyl)-2-[4-(t-butyl)-2-pyridinyl-kN]phenyl-kC]iridium(III) hexafluorophosphate, 95% *(808142-80-5)*	50mg	See page 19
77-0410	(4,4'-Di-t-butyl-2,2'-bipyridine)bis[2-(2-pyridinyl-kN)phenyl-kC] iridium(III) hexafluorophosphate, 99% *(676525-77-2)*	100mg	See page 20
77-0425	(4,4'-Di-t-butyl-2,2'-bipyridine)bis[3,5-difluoro-2-[5-trifluoromethyl-2-pyridinyl-kN)phenyl-kC]iridium(III) hexafluorophosphate, 99% *(870987-63-6)*	50mg	See page 19
77-0453	(2,2'-Bipyridine)bis[3,5-difluoro-2-[5-trifluoromethyl-2-pyridinyl-kN)phenyl-kC]iridium(III) hexafluorophosphate, 99% *(1092775-62-6)*	50mg	See page 15
77-0465	(2,2'-Bipyridine)bis[2-pyridinyl-kN)phenyl-kC]iridium(III) hexafluorophosphate, 99% *(106294-60-4)*	100mg	See page 16
77-6100	Tris[5-fluoro-2-(2-pyridinyl-kN)phenyl-kC]iridium(III), 95% *(370878-69-6)*	50mg	See page 22
77-6580	Tris[(2-(2-pyridinyl-kN)-5-(trifluoromethyl)phenyl-kC] iridium(III), 95% *(500295-52-3)*	50mg	See page 23
77-7015	Tris(2-phenylpyridinato-C2,N)iridium(III), 95% *(94928-86-8)*	50mg	See page 22
77-7030	Tris[2-(2,4-difluorophenyl)pyridine]iridium(III), 95% *(387859-70-3)*	50mg	See page 21

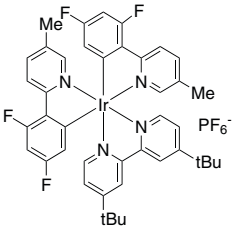
KITS - Iridium Photocatalyst Kit 2

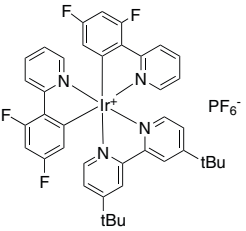
96-7790 **Iridium Photocatalyst Kit 2**

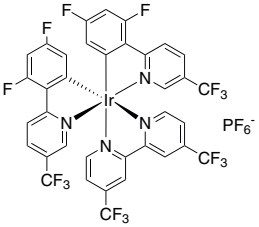
NEW

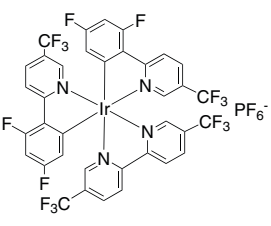
Components also available for individual sale.
Contains the following:

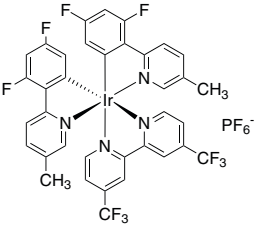

77-0320 50mg


77-0330 100mg


77-0350 100mg


77-0360 50mg


77-0370 50mg


77-0380 50mg

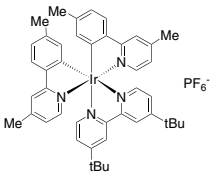
77-0320	[4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine-κN,κN] bis[5-fluoro-2-(5-methyl-2-pyridinyl-κN)phenyl-κC]iridium hexafluorophosphate, 98% *(808142-88-3)*	50mg	See page 17
77-0330	[4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine-κN,κN] bis[3,5-difluoro-2-(5-methyl-2-pyridinyl)phenyl] iridium hexafluorophosphate, 98% *(1335047-34-1)*	100mg	See page 17
77-0350	[4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine-κN,κN] bis[3,5-difluoro-2-(2-pyridinyl-κN)phenyl-κC]iridium hexafluorophosphate, 97% *(1072067-44-7)*	100mg	See page 17
77-0360	4,4'-Bis(trifluoromethyl)-2,2'-bipyridinebis[3,5-difluoro-2-[5-trifluoromethyl-2-pyridinyl)phenyl] iridium(III) hexafluorophosphate *(2030437-90-0)*	50mg	See page 18
77-0370	[5,5'-Bis(trifluoromethyl)-2,2'-bipyridine-κN,κN]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-κN]phenyl]iridium hexafluorophosphate, 98% *(1973375-72-2)*	50mg	See page 18
77-0380	4,4'-Bis(trifluoromethyl)-2,2'-bipyridinebis[3,5-difluoro-2-[5-methyl-2-pyridinyl)phenyl] iridium(III) hexafluorophosphate	50mg	See page 17

KITS - Iridium Photocatalyst Master Kit

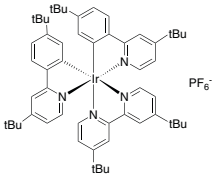
96-7795 **Iridium Photocatalyst Master Kit**

NEW

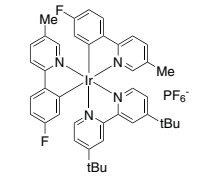
Components also available for individual sale.
Contains the following:



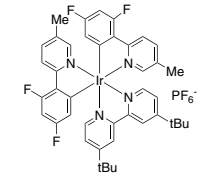
77-0218 50mg



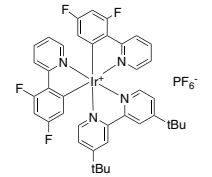
77-0285 50mg



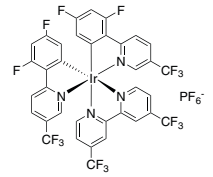
77-0320 50mg



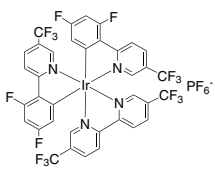
77-0330 100mg



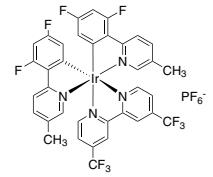
77-0350 100mg



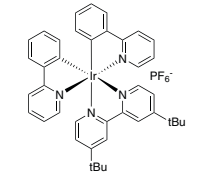
77-0360 50mg



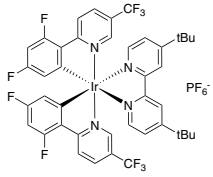
77-0370 50mg



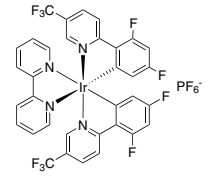
77-0380 50mg



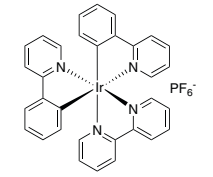
77-0410 100mg



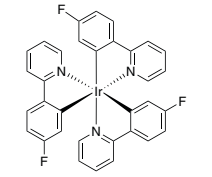
77-0425 50mg



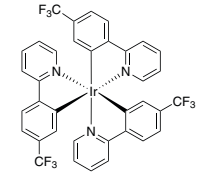
77-0453 50mg



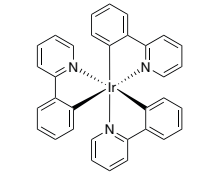
77-0465 100mg



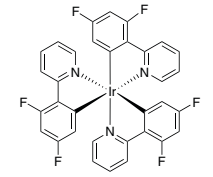
77-6100 50mg



77-6580 50mg



77-7015 50mg



77-7030 50mg

KITS - Iridium Photocatalyst Master Kit

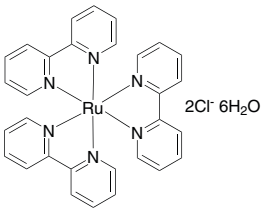
96-7795 *(continued)*	**Iridium Photocatalyst Master Kit**		
77-0218	4,4'-Bis(t-butyl-2,2'-bipyridine]bis[5-methyl-2-(4-methyl-2-pyridinyl-kN)phenyl-kC]iridium hexafluorophosphate, 95% *(1607469-49-7)*	50mg	See page 17
77-0285	[4,4'-Di-t-butyl-2,2'-bipyridine][bis[5-(t-butyl)-2-[4-(t-butyl)-2-pyridinyl-kN]phenyl-kC]iridium(III) hexafluorophosphate, 95% *(808142-80-5)*	50mg	See page 19
77-0320	[4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine-κN,κN] bis[5-fluoro-2-(5-methyl-2-pyridinyl-κN)phenyl-κC]iridium hexafluorophosphate, 98% *(808142-88-3)*	50mg	See page 17
77-0330	[4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine-κN,κN] bis[3,5-difluoro-2-(5-methyl-2-pyridinyl)phenyl] iridium hexafluorophosphate, 98% *(1335047-34-1)*	100mg	See page 17
77-0350	[4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine-κN,κN] bis[3,5-difluoro-2-(2-pyridinyl-κN)phenyl-κC]iridium hexafluorophosphate, 97% *(1072067-44-7)*	100mg	See page 17
77-0360	4,4'-Bis(trifluoromethyl)-2,2'-bipyridinebis[3,5-difluoro-2-[5-trifluoromethyl-2-pyridinyl)phenyl] iridium(III) hexafluorophosphate *(2030437-90-0)*	50mg	See page 18
77-0370	[5,5'-Bis(trifluoromethyl)-2,2'-bipyridine-κN,κN]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-κN]phenyl]iridium hexafluorophosphate, 98% *(1973375-72-2)*	50mg	See page 18
77-0380	4,4'-Bis(trifluoromethyl)-2,2'-bipyridinebis[3,5-difluoro-2-[5-methyl-2-pyridinyl)phenyl] iridium(III) hexafluorophosphate	50mg	See page 17
77-0410	(4,4'-Di-t-butyl-2,2'-bipyridine)bis[2-(2-pyridinyl-kN)phenyl-kC] iridium(III) hexafluorophosphate, 99% *(676525-77-2)*	100mg	See page 20
77-0425	(4,4'-Di-t-butyl-2,2'-bipyridine)bis[3,5-difluoro-2-[5-trifluoromethyl-2-pyridinyl-kN)phenyl-kC]iridium(III) hexafluorophosphate, 99% *(870987-63-6)*	50mg	See page 19
77-0453	(2,2'-Bipyridine)bis[3,5-difluoro-2-[5-trifluoromethyl-2-pyridinyl-kN)phenyl-kC]iridium(III) hexafluorophosphate, 99% *(1092775-62-6)*	50mg	See page 15
77-0465	(2,2'-Bipyridine)bis[2-pyridinyl-kN)phenyl-kC]iridium(III) hexafluorophosphate, 99% *(106294-60-4)*	100mg	See page 16
77-6100	Tris[5-fluoro-2-(2-pyridinyl-kN)phenyl-kC]iridium(III), 95% *(370878-69-6)*	50mg	See page 22
77-6580	Tris[(2-(2-pyridinyl-kN)-5-(trifluoromethyl)phenyl-kC] iridium(III), 95% *(500295-52-3)*	50mg	See page 23
77-7015	Tris(2-phenylpyridinato-C2,N)iridium(III), 95% *(94928-86-8)*	50mg	See page 22
77-7030	Tris[2-(2,4-difluorophenyl)pyridine]iridium(III), 95% *(387859-70-3)*	50mg	See page 21

KITS - Ruthenium Photocatalyst Kit

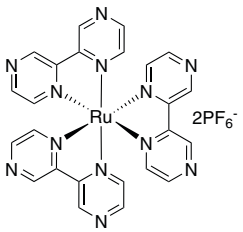
96-4450 **Ruthenium Photocatalyst Kit**

NEW

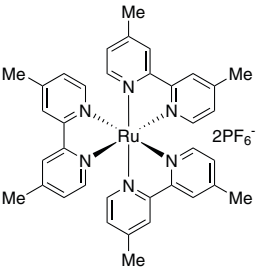
Components also available for individual sale.
Contains the following:



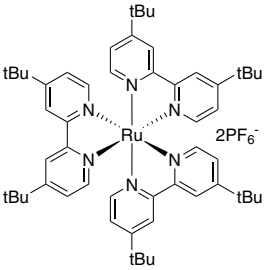
44-7900 250mg



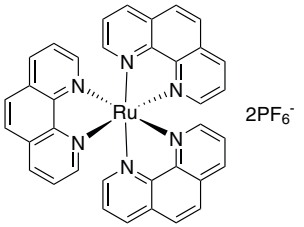
44-7910 50mg



44-7930 50mg



44-7940 50mg



44-7955 50mg

44-7900	Tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate, min. 98% *(50525-27-4)*	250mg	See page 28
44-7910	Tris(2,2'-bipyrazine)ruthenium(II) hexafluorophosphate, 95% *(80907-56-8)*	50mg	See page 27
44-7930	Tris(4,4'-dimethyl-2,2'-bipyridine)ruthenium(II) hexafluorophosphate, 95%, DMBPY *(83605-44-1)*	50mg	See page 29
44-7940	Tris[4,4'-bis(t-butyl)-2,2'-bipyridine]ruthenium(II) hexafluorophosphate, 95% *(75777-87-6)*	50mg	See page 28
44-7955	Tris(1,10-phenanthroline)ruthenium(II) hexafluorophosphate, 95% *(60804-75-3)*	50mg	See page 29

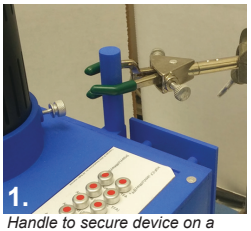
PHOTOCHEMICAL EQUIPMENT

98-7500 NEW

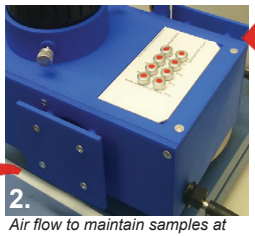
EvoluChem™ PhotoRedOx Box
Note: Sold in collaboration with HepatoChem

1 pc

The EvoluChem™ PhotoRedOx Box device is designed to facilitate photochemical experiments. This device is compatible with most vial formats (see related Photochemistry holders: 98-7600, 98-7650 or 98-7700). Its compact design allows for use with any stirring plate. A built-in fan keeps the reaction conditions at room temperature.



Handle to secure device on a stirring plate



Air flow to maintain samples at room temperature

Features

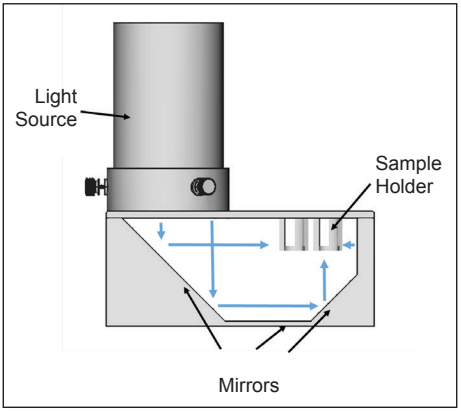
- Light source (See 98-7800)
- Photochemistry chamber to evenly distribute light
- Flexible vial formats
- Magnetic stirring on standard stirring plate
- Cooling by fan to maintain experiment at room temperature
- Pre-designed array of catalysts and reagents available

Benefits

- Easy set-up on a standard stiring plate
- Performs up to 32 reaction conditions simutaneously
- Individually sealed vials enable flexible study design
- Save your substrate using low scale reaction conditions
- Save time on optimization

Easy set-up and compact design (see images on left)

1. Handle to secure device on a stirring plate
2. Air flow to maintain samples at room temperature



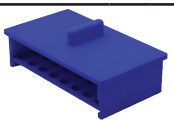
Unique Geometry to focus light on samples
EvoluChem™ PhotoRedOx Box is equpped with several mirrors that direct and distribute the light toward the samples. The geometry of the box enables parallel reaction with homogeneous light exposure.

Better Heat Management
The position of the light source on the side of the samples reduces the amount of heat directed to the samples. The embedded fan eliminates any remaining heat.

98-7600 NEW

EvoluChem™ PhotoRedOx Box Photochemistry Holder 32 x 0.3ml vials
Note: Sold in collaboration with HepatoChem

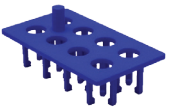
1 pc



98-7650 NEW

EvoluChem™ PhotoRedOx Box Photochemistry Holder 8 x 2ml vials
Note: Sold in collaboration with HepatoChem

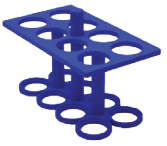
1 pc



98-7700 NEW

EvoluChem™ PhotoRedOx Box Photochemistry Holder 8 x 8ml vials
Note: Sold in collaboration with HepatoChem

1 pc



PHOTOCHEMICAL EQUIPMENT

98-7800 1 pc

NEW

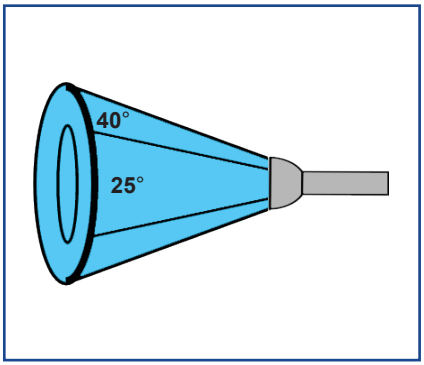
EvoluChem™ PhotoRedOx Box Light Source
Wavelength 450nm, Electric Power 18W
Note: Sold in collaboration with HepatoChem

The EvoluChem™ light source is designed specifically for photocatalytic chemistry applications. It fits the EvoluChem™ PhotoRedOx Box (98-7500) and is designed to irradiate all samples with maximum effieciency. The LED chips are selected for specific wavelengths.

General Specifications

Power Consumption	18W
Input Voltage	100-240 VAC
Beam Angle	25°
Wavelength Options	450nm
LED	Cree XPE

Light Power vs. Irradiance
Although the total power of LED light is important, it is essential to estimate the amount of light that actually goes on the sample. If the light is spread over a large area the density of light (irradiance) on sample will be little. Therefore we designed the EvoluChem™ LEDs to focus the light toward the samples at a 25° angle.



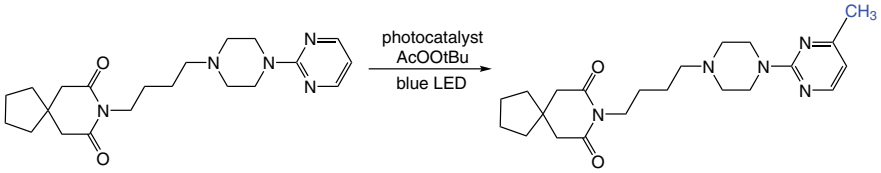
Focused Light Beam

Directly compatible with PhotoRedOx Box 98-7500

PHOTOCATALYST KITS - Compatible with PhotoRedOx Box

96-7510 **EvoluChem™ Photochemical Methylation Array Kit** 1 kit
NEW
Note: Sold in collaboration with HepatoChem

This kit and the PhotoRedOx Box (98-7500) work together seamlessly.



Reference: *Chem. Soc. Rev.*, **2016**, *45*, 546-576

Kit Protocol:

The typical protocol is performed in a 0.05 Mol/l concentration reaction condition using a substrate solution of four different solvents. Each sealed reaction vial contains 0.1 µmol of photocatalyst and 12.5 µmol of *tert*-butyl peracetate. Based on the concentration of the substrate stock solution and the volume added, the following reaction stoichiometry can be achieved with the standard photomethylation kit.

	77-0425	77-0410
50/50 Acetonitrile/TFA	5 equiv. tert-butyl peracetic acid	
Acetonitrile (10 equiv. TFA)		
Acetic acid (10 equiv. TFA)		
Acetic acid/H_2O (10 equiv. TFA)		

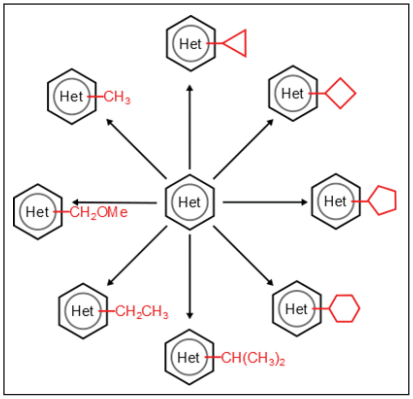
Kit contents:

Description	Quantity	Amount
(4,4'-Di-t-butyl-2,2'-bipyridine)bis[3,5-difluoro-2-[5-trifluoromethyl-2-pyridinyl-kN)phenyl-kC]iridium(III) hexafluorophosphate, 99% ***Item # 77-0425***	8 vials	0.1µmol/12.5 µmol
(4,4'-Di-t-butyl-2,2'-bipyridine)bis[2-(2-pyridinyl-kN)phenyl-kC] iridium(III) hexafluorophosphate, 99% ***Item # 77-0410***	8 vials	0.1µmol/12.5 µmol
50/50 Acetonitrile/ trifluoroacetic acid	1 vial	1 ml
Acetonitrile (10 equiv. trifluoracetic acid*)	1 vial	1 ml
Acetic acid (10 equiv. trifluoracetic acid*)	1 vial	1 ml
Acetic acid/water (10 equiv. trifluoracetic acid*)	1 vial	1 ml
Substrate stock vial 1	1 vial	--
Substrate stock vial 2	1 vial	--
Substrate stock vial 3	1 vial	--
Substrate stock vial 4	1 vial	--

PHOTOCATALYST KITS - Compatible with PhotoRedOx Box

96-7560 **EvoluChem™ Photocatalytic Alkylation Kit** 1 kit
NEW
Note: Sold in collaboration with HepatoChem

Product Overview:
The trifluoroborate alkylation reaction (Minisci reaction)[1] is a powerful late stage functionalization tool. Our kit allows convenient, one-step production of eight different analogues of a lead compound in mg quantities. Each reaction vial contains 75 µmol of trifluoroborate alkylation reagent (pre-weighed) and a stirring bar to react with 50 µmol of substrate. C-H functionalization will primarily occur on electron-deficient heteroarenes at one or several positions.



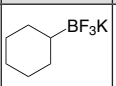
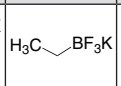
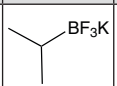
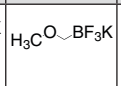
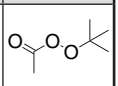
Kit Contents *(16 reaction vials total)*:

- 2 reaction vials of BF_3K reagents (75 µmol)
- 2 reaction vials of $K_2S_2O_8$ (100 µmol)
- 2 vials of photocatalysts
- 2 vials of TFA

Kit Protocol:

For each kit, 4mL of a 0.1 M solution of substrate (400 µmol total) in DMSO is prepared with 8.98 mg photocatalyst Ir(dF-CF_3-ppy)$_2$(dtbbpy) (77-0425) (8 µmol, 2 mol%) and trifluoroacetic acid (153 µL, 5 equiv) included. The solution is sparged with nitrogen. Each vial contains 27.0mg $K_2S_2O_8$ (100 µmol, 2 equiv.) and 1.5 equiv. BF_3K reagent (75 µmol) in 2ml vials equipped with a stir bar and Teflon septa. Alternatively for methylation, vials contain 39.9 µL of tert-butyl peracetate (TBPA). Vials are prepared under argon. 500µL of substrate solution is added via syringe and the vial is placed in PhotoRedOx Box (98-7500) equipped with light source. Reaction is stirred for 2-24 hr.

Photocatalytic Alkylation Reagents (2 Vials of each)

	cyclopropyl	cyclobutyl	cyclopentyl	cyclohexyl	ethyl	isopropyl	methoxy methyl	*t*-butyl peracetate
								
MW (g/mol)	147.98	162.00	176.03	190.06	135.97	149.99	151.97	132.16
CAS #	1065010-87-8	1065010-88-9	1040745-70-7	446065-11-8	44248-07-9	1041642-13-0	910251-11-5	107-71-1

References:
1. *Chem. Sci.*, **2017**, *8 (39)*, 3512-3522
2. *Chem. Soc. Rev.*, **2016**, *45*, 546-576

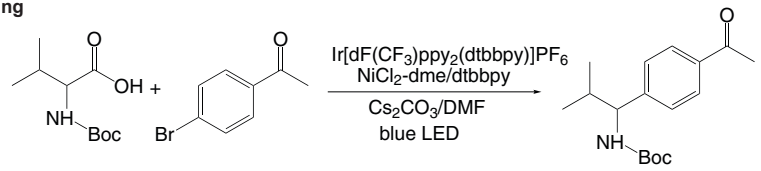
PHOTOCATALYST KITS - Compatible with PhotoRedOx Box

Iridium/Nickel Photoredox Kits

Photoredox chemistry has been reported in literature using a wide range of catalysts and reagents. However, often these reactions are highly substrate, solvent and base specific. In order to facilitate the screening of common photochemistry reactions, HepatoChem has released a series of kits combining common Iridium, Nickel, ligand and base combinations to achieve successful cross-coupling transformations.

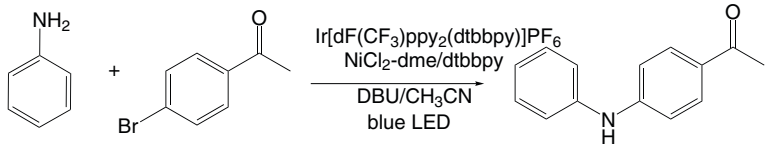
Ir/Ni catalysis versatility
Depending on the ligand, base and solvent, the Ir/Ni catalytic systems can perform different cross-coupling reaction.

C-C Coupling



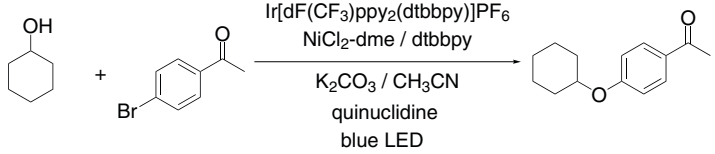
(Ref. 1)

C-N Coupling



(Ref. 2)

C-O Coupling



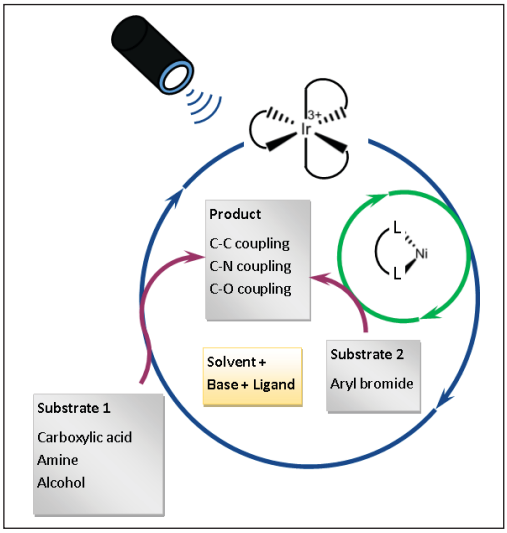
(Ref. 3)

Several Kits Available

Standard Protocol:
5 µmol of substrates in 100 µl solvent with Ir catalyst (2 mol %), $NiCl_2$•dme (10 mol %), ligand (10 mol %), and 3 equivalent of base.

Features:

- 0.3ml vial with crimp cap and stirring bar
- Specifically designed for photchemistry device
- Pre-weighed reagents and catalysts
- Temperature maintained at RT
- Pre-designed or custom arrays available
- Reagents are packaged under inert atmosphere



References

1. *Science* **2014**, *345*, 437-440
2. *Angew. Chemie*, **2016**, *55*, 13219-13223
3. *Nature* **2015**, *524*, 330-334

PHOTOCATALYST KITS - Compatible with PhotoRedOx Box

Iridium/Nickel Photoredox Kits *(continued)*

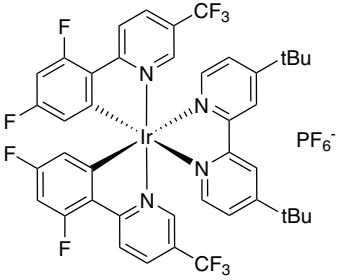
Results summary:
Selection of base and solvent is important to find the condition for appropriate coupling (5µmol per reaction/100µL scale)

Reaction Type	Substrates	Solvent	Base			
			Cs_2CO_3	K_3PO_4	DABCO	DBU
C-C coupling through decarboxylation	Boc-Val 4-bromoacetophenone	DMF	✓	✓		
C-N coupling (secondary amines)	Pyrolidine 4-bromoacetophenone	DMA			✓	
C-N couping (aromatic amine/secondary amine)	Indoline 4-bromoacetophenone	DMA		✓		
C-N coupling (aromatic amine)	Aniline 4-bromoacetophenone	ACN			✓	✓

96-7520 NEW — **EvoluChem™ Iridium/Nickel PhotoRedOx Base and Solvent Screening Kit 1** — 1 kit
Note: Sold in collaboration with HepatoChem

Kit Contents:
This kit contains 77-0425 (2 mol%), Ni/Ligand (10 mol%) and base (3 eq)

	Cs_2CO_3	K_3PO_4	K_2HPO_4	KOH	Li_2CO_3	K_2CO_3	DABCO	DBU
Solvent A	2 sets of 8 conditions with 8 different bases per kit (16 total vials) 5 µmol of substrates in 100 µl solvent 77-0425 (2 mol%), Ni/Ligand (10 mol%) and base (3 eq)							
Solvent B								



Iridium Catalyst: 77-0425

Suggested Solvents *(not included)*

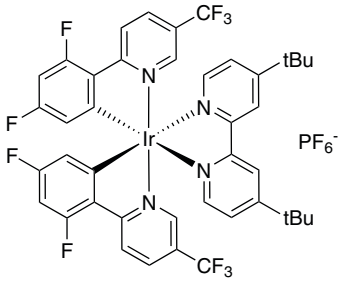
1. **ACN**
2. **DMF**
3. **DMA**
4. **DMSO**

PHOTOCATALYST KITS - Compatible with PhotoRedOx Box

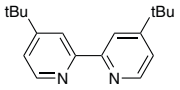
96-7530 **EvoluChem™ Iridium/Nickel PhotoRedOx Base and Ligand Screening Kit 2** 1 kit
NEW
Note: Sold in collaboration with HepatoChem

Kit Contents:
This kit contains 77-0425 (2 mol%) , Ni/Ligand (10 mol%) and base (3 eq)

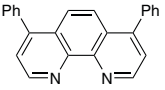
	Cs_2CO_3	K_3PO_4	K_2HPO_4	K_2CO_3
dtbbpy	2 sets of 16 conditions with 4 bases and 4 ligands per kit (32 total vials) 5 µmol of substrates in 100 µl solvent 77-0425 (2 mol%), Ni/Ligand (10 mol%) and base (3 eq)			
bphen				
$(MeO)_2$bpy				
biox				



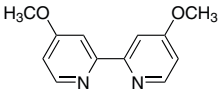
Iridium Catalyst: 77-0425



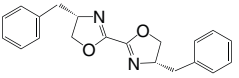
Nitrogen Ligand: dtbbpy



Nitrogen Ligand: bphen



Nitrogen Ligand: $(MeO)_2$bpy



Nitrogen Ligand: biox

96-7540 **EvoluChem™ Iridium/Nickel PhotoRedOx Base and Ligand Screening Kit 3** 1 kit
NEW
Note: Sold in collaboration with HepatoChem

Kit Contents:
This kit contains 77-0425 (2 mol%), Ni/Ligand (10 mol%) and base (3 eq)

	Cs_2CO_3	K_3PO_4	K_2HPO_4	K_2CO_3	DABCO	DBU
dtbbpy	2 sets of 24 conditions with 6 bases and 4 ligands per kit (48 total vials) 5 µmol of substrates in 100 µl solvent 77-0425 (2 mol%), Ni/Ligand (10 mol%) and base (3 eq)					
bphen						
$(MeO)_2$bpy						
biox						

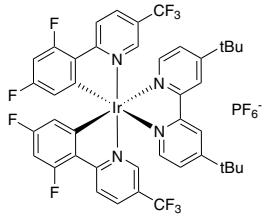
See catalyst and ligand structures with 96-7530.

PHOTOCATALYST KITS - Compatible with PhotoRedOx Box

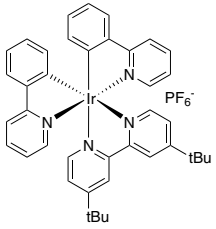
96-7550 **EvoluChem™ Iridium/Nickel PhotoRedOx Base and Iridium Catalyst Screening Kit** 1 kit
NEW
Note: Sold in collaboration with HepatoChem

Kit Contents:
This kit contains Ir catalyst (2 mol%), Ni/Ligand (10 mol%) and base (3 eq)

	Cs_2CO_3	CsF	DBU
77-0425	2 sets of 18 conditions with 3 bases and 6 Ir catalysts per kit (36 total vials) 5 µmol of substrates in 100 µl solvent Ir catalyst (2 mol%), Ni/Ligand (10 mol%) and base (3 eq)		
77-0410			
77-0453			
77-7030			
77-0218			
77-0330			



77-0425



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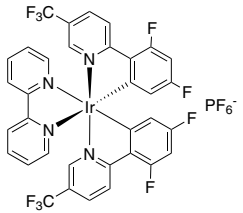

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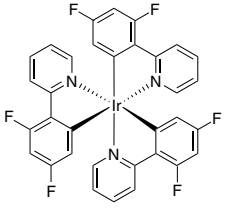

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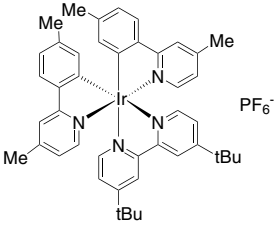

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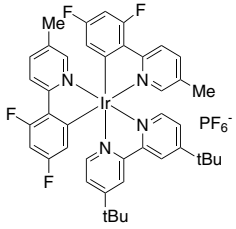

77-0330

96-7570 **EvoluChem™ Iridium/Nickel PhotoRedOx Base and Solvent Screening Kit 2 (C-O coupling)** 1 kit
NEW
Note: Sold in collaboration with HepatoChem

Kit Contents:
This kit contains 2 sets of 8 reaction conditions per kit (16 total vials) with 77-0425 (1 mol%), Ni/Ligand and quinuclidine

Condition 1	Condition 2	Condition 3	Condition 4	Condition 5	Condition 6	Condition 7	Condition 8
Cs_2CO_3 1.5 eq.	K_3PO_4 1.5 eq.	K_2CO_3 1.5 eq.	K_2CO_3 1.5 eq.	K_2CO_3 1.5 eq.	DABCO 1.5 eq.	Quinuclidine 1.5 eq.	No Base Control
$NiCl_2$-dme/ dtbbpy 5 mol%	$NiCl_2$-dme/ dtbbpy 5 mol%	$NiCl_2$-dme/ dtbbpy 5 mol%	$NiCl_2$-dme/ dtbbpy 2.5 mol%	$NiCl_2$-dme/ dtbbpy 1.25 mol%	$NiCl_2$-dme/ dtbbpy 5 mol%	$NiCl_2$-dme/ dtbbpy 5 mol%	$NiCl_2$-dme/ dtbbpy 5 mol%
Quinuclidine 10 mol%							
77-0425 1 mol%							

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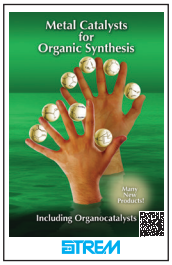

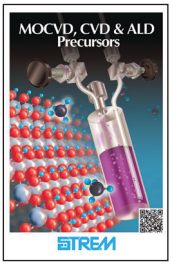

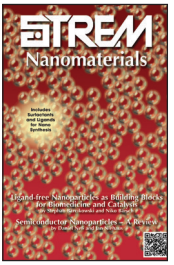

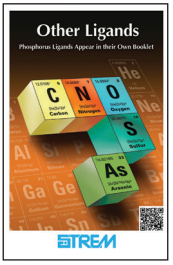

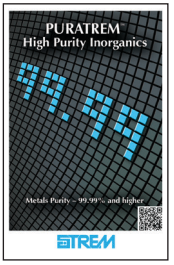

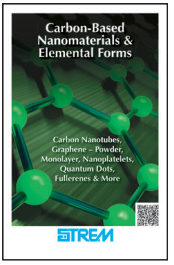

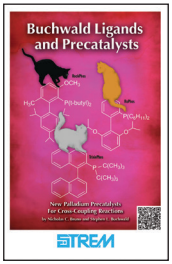

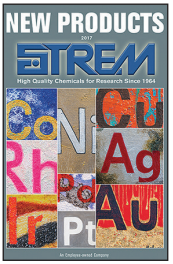

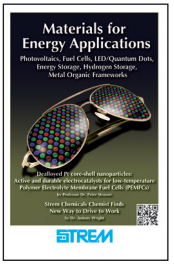

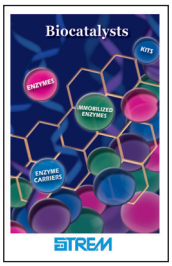

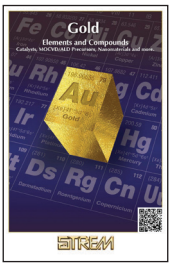

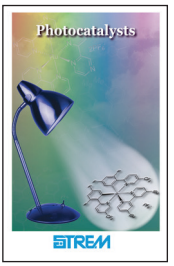

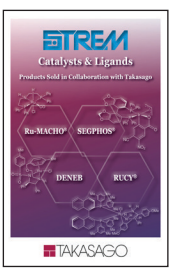

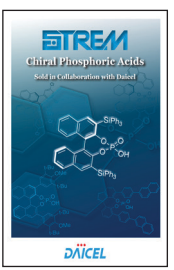

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