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Advances in Photocatalysis: A Microreview of Visible Light Mediated Ruthenium and Iridium Catalyzed Organic Transformations

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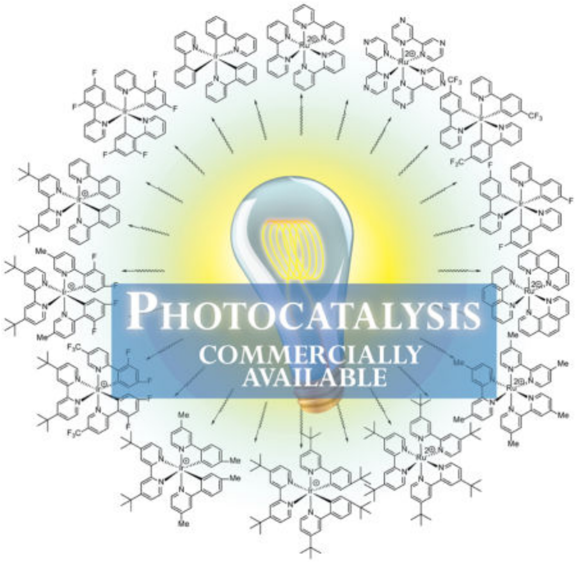
Abstract

Photocatalytic organic transformations utilizing ruthenium and iridium complexes have garnered significant attention due to the access they provide to new synthetic spaces through new reaction mechanisms. A survey of the photophysical data and the diversity of transformations that may be accomplished utilizing commercially available photocatalysts is contained herein.

Graphical Abstract



Keywords

Photocatalysis; photocatalysts; organic synthesis

[§]Authors contributed equally

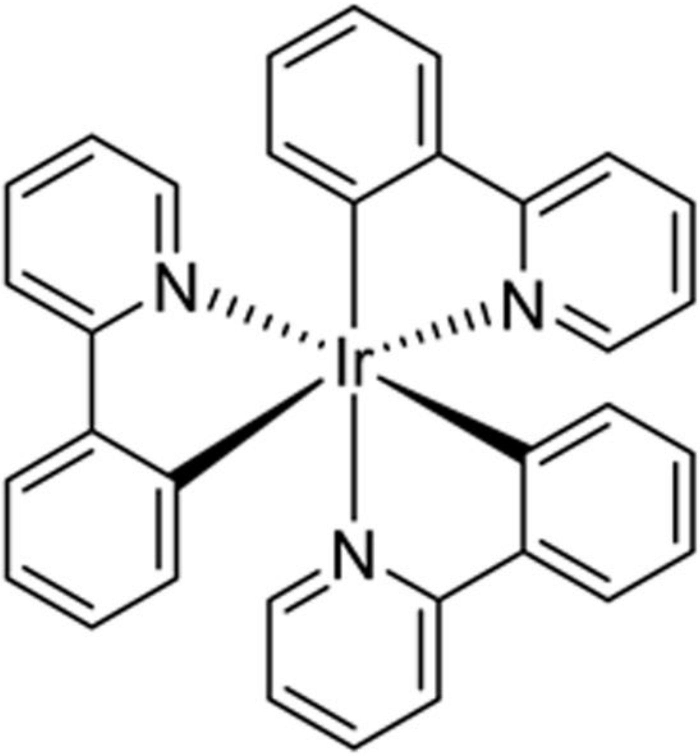
INTRODUCTION

Over the course of the preceding 30 years, there have been substantial developments utilizing cyclometalated ruthenium and iridum complexes in photochemistry.[1–4] Historically these complexes have been primarily employed in solar cells,[5] light emitting diodes (LEDs),[6] and as initiators in free radical polymerizations.[7] Both of the prototypical complexes, $Ru(bpy)_{32+}$ and $Ir(ppy)_3$ are d^6, coordinatively saturated, 18-electron complexes. When excited by visible light they undergo a metal-to-ligand-charge transfer (MLCT) from the highest occupied molecular orbital of the metal (HOMO) to the lowest unoccupied molecular orbital of the ligand (LUMO).[2,3] As a consequence, these complexes undergo both reductive and oxidative quenching pathways with relative ease,[2–4] which can be rationally applied in organic transformations.[8–12] Comparison of the potential of the photocatalyst to a substrate that may undergo a redox event can suggest the likelihood of an electron transfer event. However, caution should practiced because almost certainly the conditions under which the redox properties where determined are different than the reaction conditions and in addition may involve a nonreversible step. The former may affect the necessary potential and the latter can facilitate reactions that appear to have an underpotential.

While electron transfer serves as a means for these complexes to return to the ground state, this can also be accomplished by energy transfer to other molecules with orbitals of the appropriate energy level. Importantly, modification of the ligand scaffold provides many opportunities to tune the photophysical properties of these complexes as can be seen in surveys of the various ruthenium and iridium complexes found in current literature.[2–4] However, the number of complexes commercially available for use in catalysis is currently more limited. In this review, we will briefly discuss some of the electrochemical and photophysical properties of ruthenium and iridium photocatalysts which are commercially available[65] (Table 1) and highlight a select number of the diverse organic transformations enabled by each catalyst.

PHOTOCATALYST DETAILS

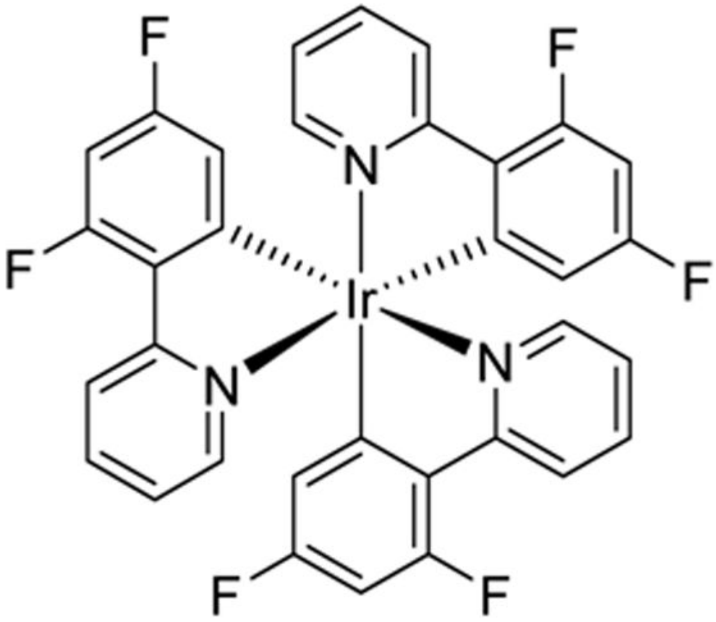
PHOTOCATALYST 1



fac-Ir(ppy)$_3$

There has been significant progress in α-C–H functionalization of amines in photocatalysis, including the arylation of tertiary amines by MacMillan and coworkers,[13] (Scheme 1a), the azoylation of aliphatic amines by our own lab[14] (Scheme 1b), and the C-H amidation of unfunctionlized indoles with hydroxyl amines by Yu and coworkers[15] (Scheme 1c), all of which use the prototypical catalyst **1**.

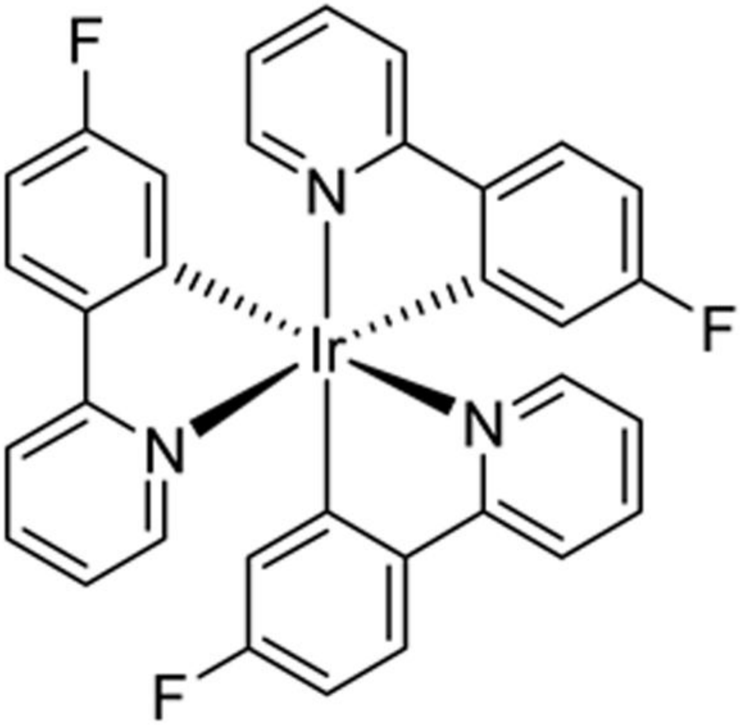
PHOTOCATALYST 2



fac-Ir(2′,4′-dF-ppy)$_3$

Lee and coworkers[38] utilized **2** to initiate a C–H imidation of hetereoarenes with *N*-chlorophthalimide. After initially investigating **1**, photocatalyst **2** proved to be the superior catalyst. The reaction likely proceeds through a *N*-radical intermediate initiated by electron transfer from excited **2**, which undergoes radical addition to the arene partner. The hexadienyl radical serves to reduce the catalyst leading to rearomatization (Scheme 2). The scope consists of various substituted arenes with modest yields and regioselectivity.

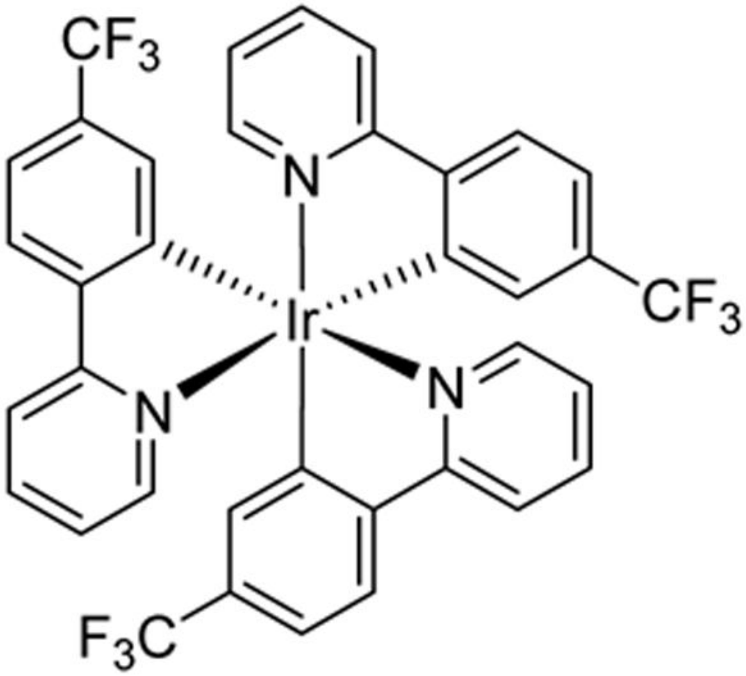
PHOTOCATALYST 3



fac-Ir(4′-F-ppy)$_3$

While current literature references are limited, and transformations that utilize photocatalyst **3** as an optimal catalyst are presently absent, it is noteworthy that the catalyst is being employed. Our group[1,39] has routinely used **3** in our standard catalyst screen, and likewise Ooi and coworkers[40] synthesized this catalyst in their asymmetric α-coupling of *N*-arylaminomethanes and used the photocatalyst in their optimization experiments. **3** is thus included in order to provide electrochemical and photophysical data.

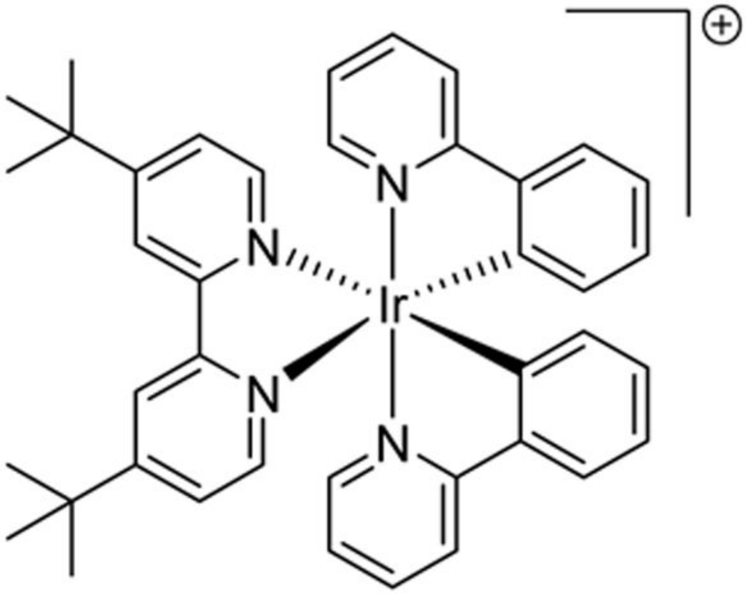
PHOTOCATALYST 4



fac-Ir(4′-CF_3-ppy)$_3$

Photocatalyst **4** is another photocatalyst that has now become commercially available but has yet to have been demonstrated to be an optimal catalyst in current organic transformations. Our group[1,41] has and will continue to employ **4** in our standard catalyst screens.

PHOTOCATALYST 5



$[Ir(ppy)_2\ (4,4'\text{-dtb-bpy})]PF_6$

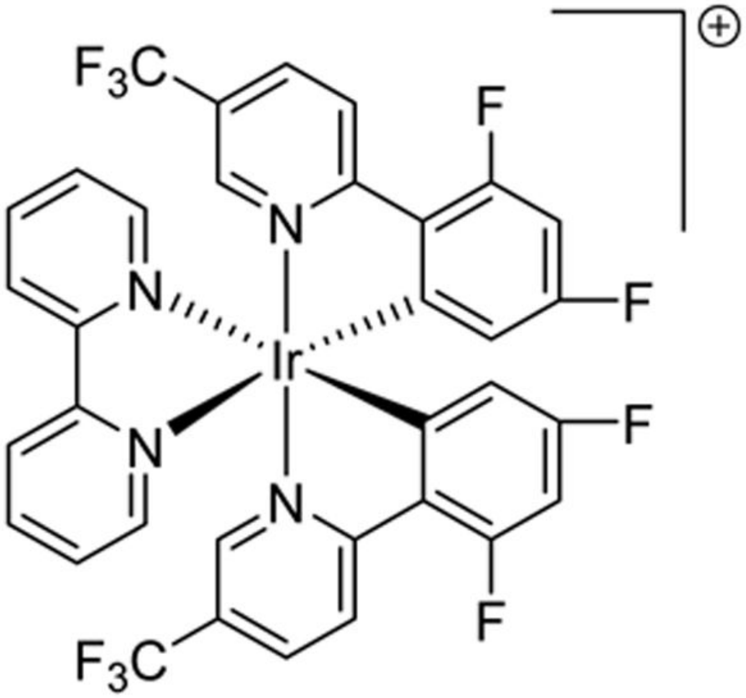
Advances have been made recently in photocatalytic biomass remediation. Stephenson and coworkers[42] utilized visible light and **5** in a photoflow reactor to degrade lignin biomass model substrates, in a two-step reaction sequence (not shown).

In 2015, Zheng[43] demonstrated that cyclobutylanilines could undergo a ring-opening [4+2] reaction with alkynes using **5**. They proposed that the reaction likely proceeds through a distonic radical cation. Excellent yields were achieved using various aliphatic cyclobutlyanilines and bicyclic amines (Scheme 3).

In 2013, Knowles and coworkers[44] used **5** in concert with Binol-derived phosphoric acid to perform an asymmetric azapinacol cyclization with excellent yields and enantiomeric excess (ee) (Scheme 4). Electron transfer to the ketone only occurred when it was protonated by the chiral acid, allowing the C–C formation to take place enantioselectively.

In 2015, Yu[45] reported a visible light mediated remote C–H chlorination of aliphatic and benzylic amines (Scheme 5a) using **5** which took advantage of the ease of *N*-chlorination to functionalize a distant and far less reactive C–H bond on the same molecule. The reaction likely takes place via a 1,5-atom transfer, which upon addition of NaOH provides the subsequent cyclization product. Yu went on to apply the methodology to the late stage functionalization of the antitumor drug (+)-dehydroabietyamine (Scheme 5b) to produce a chlorinated version of the pharmacophore.

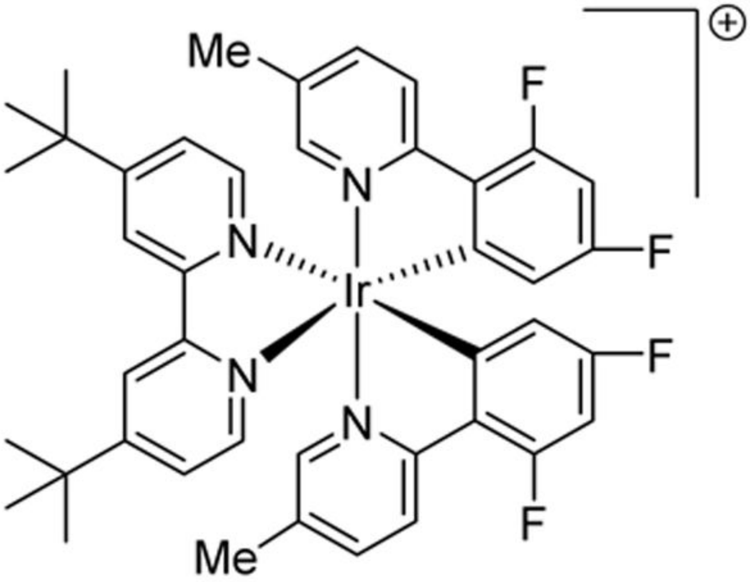
PHOTOCATALYST 6



[Ir(2′,4′-dF-5-CF3-ppy)$_2$(bpy)]PF$_6$

While photocatalysis has resulted in a number of enabling methods, there has also been a significant increase in the development and use of photocatalysis in concert with other transition-metal chemistry, which is just beginning to reveal new mechanistic possibilities. Molander[46] demonstrated a recent example of photocatalysis being used in concert with other transition-metal catalysis. The group demonstrated a single-electron transmetalation in organoboron cross-coupling using Ni(0). The traditional two-electron transmetallation cleaves the C–B bond hetereolytically, giving lower or no reactivity in regards to sp^3 hybridized carbons.[47] Molander and coworkers demonstrated that a photocatalytic single-electron transfer (SET) using **6** enables cleavage of the C–B bond to occur homolytically, effectively reversing the order of reactivity (sp^3>sp^2>sp) and correlates to radical stability.[48] A wide variety of aryl halide partners were shown to be compatible (Scheme 6a). Furthermore, it was demonstrated that stereoselectivity is possible with help of photoredox cross-coupling and a chiral ligand (Scheme 6b).

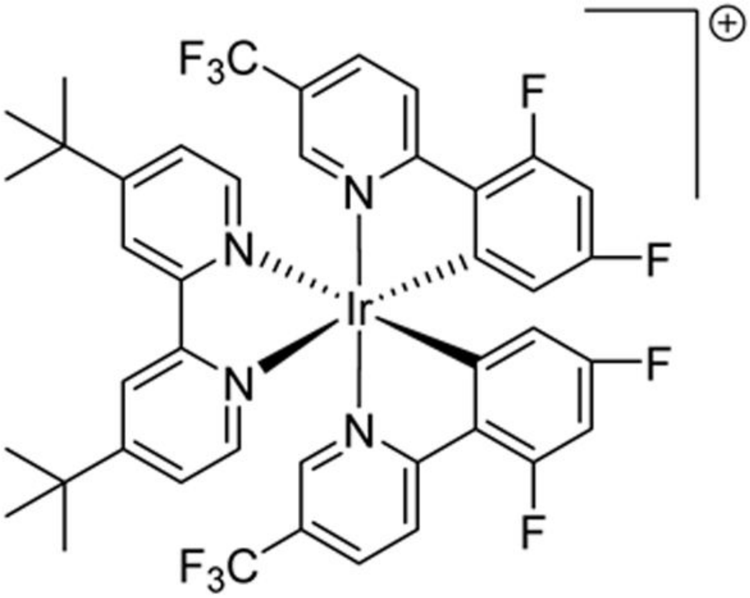
PHOTOCATALYST 7



[Ir(2′,4′-dF-5-me-ppy)$_2$ (4,4′-dtb-bpy)]PF$_6$

MacMillan et al. showed that *N*-aryl amines could undergo selective C–H vinylation utilizing vinyl sulfones and photocatalyst 7 in good yields and E:Z selectivity. The methodology could be extended to *N*-Boc α-amino acids as well (via decarboxylation), though a change to catalyst **5** was necessary (Scheme 7).[49]

PHOTOCATALYST 8



[Ir(2′,4′-dF-5-CF$_3$-ppy)$_2$(4,4′-dtb-bpy)]PF$_6$

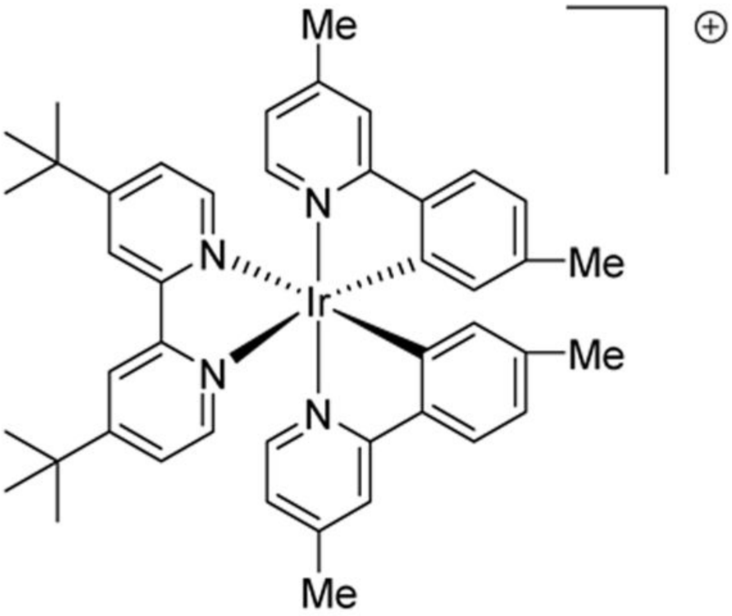
Photocatalysis has also been used in the derivatization of natural products into biologically interesting molecules in both early and late stages. In 2014, Stephenson utilized **8** to access a key intermediate via an oxidative ring fragmentation of (+)-catharanthine (**8a**) in a photoflow reactor early in the synthetic process (Scheme 8), presumably generating a transient cyclic iminium (**8b**) which underwent cyanation to produce the intermediate species (**8c**) in 96% yield, followed by acid mediated rearrangement to reach (−)-pseudotabersonine (**8d**) in 90% yield.[50]

DiRocco and coworkers demonstrated the efficacy of the same photocatalyst to perform late stage functionalization (LSF) by methylation, ethylation, or cyclopropylation of various complex medicinal and agrochemical molecules by visible light photocatalysis (Scheme 9).[51] Established methods such as Minisci’s persulfate mediated decarboxylation required high temperatures[52] and are often too harsh for large, complex molecules. While increases to the scope have been made,[53] DiRocco’s method to overcome these issues represents a significant advancement in LSF, in part, because the catalyst can help regulate the concentration of the reactive species.

In 2015, MacMillan showed that photocatalysts **7**[54] or **8**[55] could be combined synergistically with a $NiCl_2$•dtbbpy catalyst for the formation of olefins and aryl ketones (Scheme 10).

In 2008, Yoon demonstrated the [2+2] intramolecular cycloaddition took place via an electron transfer mechanism with catalytic amounts of **11,** vide infra**,** (Scheme 11a).[8] Then, in 2012, he also demonstrated that an energy transfer pathway could be used for substrates that were unlikely to undergo electron transfer (Scheme 11b). **8** was selected not only because the excited state oxidation potential cannot initialize radical cation cycloadditions, but also because the energy of the catalyst’s excited state is comparable to the triplet state energy of excited styrenes.[56]

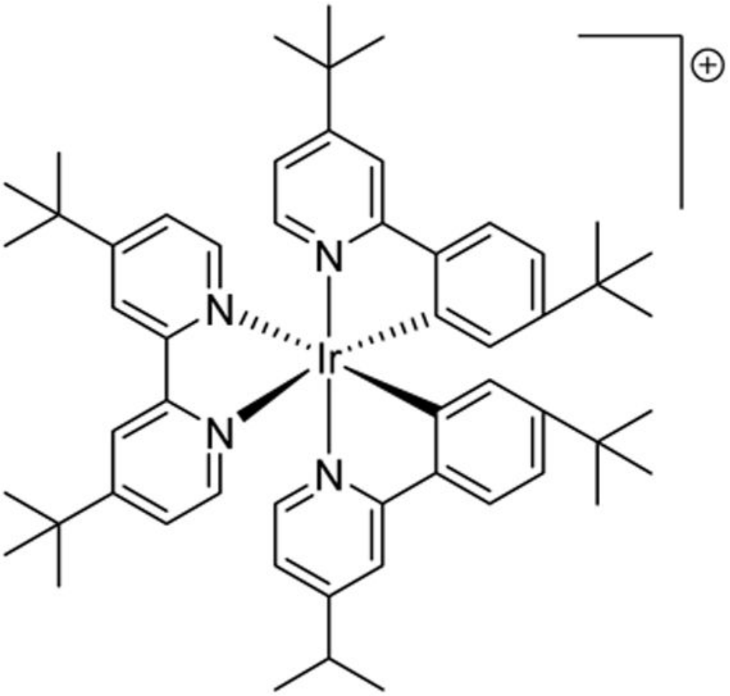
PHOTOCATALYST 9



[Ir(3,4′-dm-ppy)$_2$(4,4′-dtb-bpy)]PF$_6$

In 2014, MacMillan and coworkers reported a method that utilizes **9** to directly couple a Michael acceptor and an aldehyde at the β-position (Scheme 12a). The β-functionalization of the aldehydes (as opposed to α-functionalization) via any method has little precedence and demonstrates the enabling nature of photocatalysis. It also allows for intramolecular 5- or 6-exo-trig radical cyclizations onto aldehydes that are unsaturated and possess a terminal electron withdrawing group (Scheme 12b).[16]

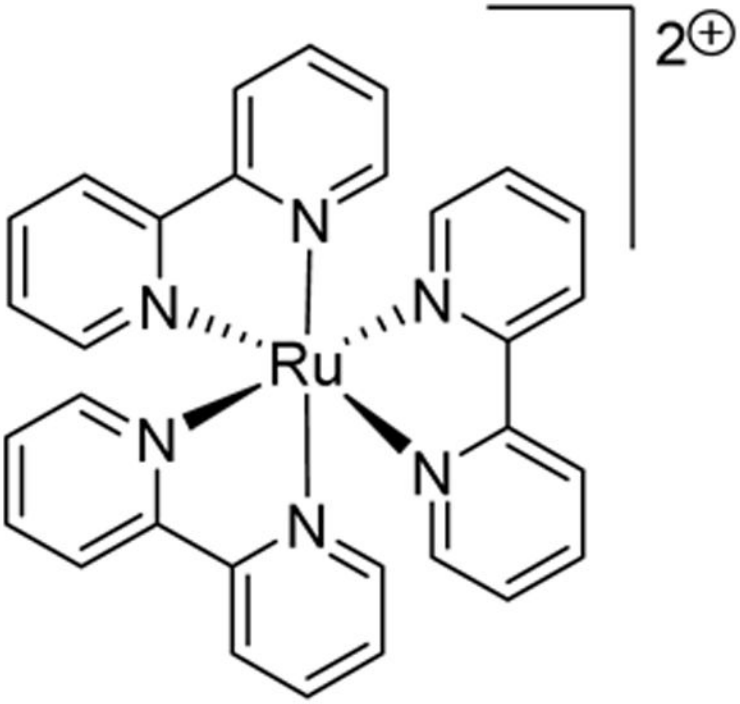
PHOTOCATALYST 10



[Ir(4,4′-dtb-ppy)2(3,4′-dtb-bpy)]PF_6

Current literature references for catalyst **10** are limited and it is included in order to provide electrochemical and photophysical data.

PHOTOCATALYST 11

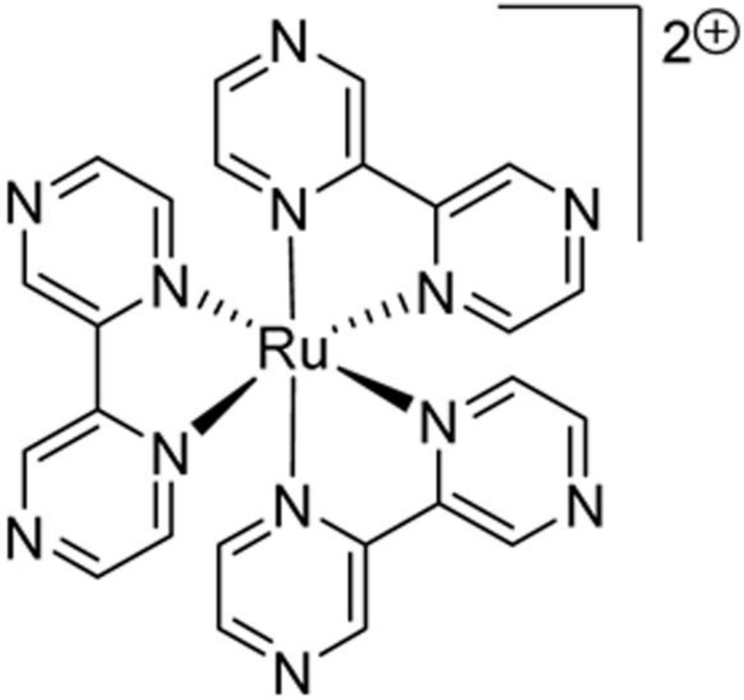


$[Ru(bpy)_3](PF_6)_2$

In another example of merging catalytic cycles of transition-metal catalysis and photocatalysis, Glorius and coworkers[57] merged gold catalysis and photocatalysis (Scheme 13), with oxidation of the gold complex by **11** during the reaction. Moderate to good yields of oxy- and amino arylated alkenes were realized using $[Ph_3PAu]NTf_2$ and vinyl alcohols.

Our group[58] has shown that visible light and **1** can facilitate (E) to (Z) isomerizations of substituted styrenes. Osawa's group[59] has also shown isomerizations of stilbene derivatives with photocatalyst **11**. Rueping[60] and coworkers produced an economical and practical two-phase photoflow setup using **11**, achieving quantitative yields of cis-stilbene on a 1.8 g scale (Scheme 14). The catalyst/DMF mixture and (E) stilbene/pentane was circulated through an illuminated glass microreactor. As the volatile (Z) stilbene was evaporated, the catalyst and the unreacted high boiling (E) stilbene were pumped back into system for further isomerization.

PHOTOCATALYST 12

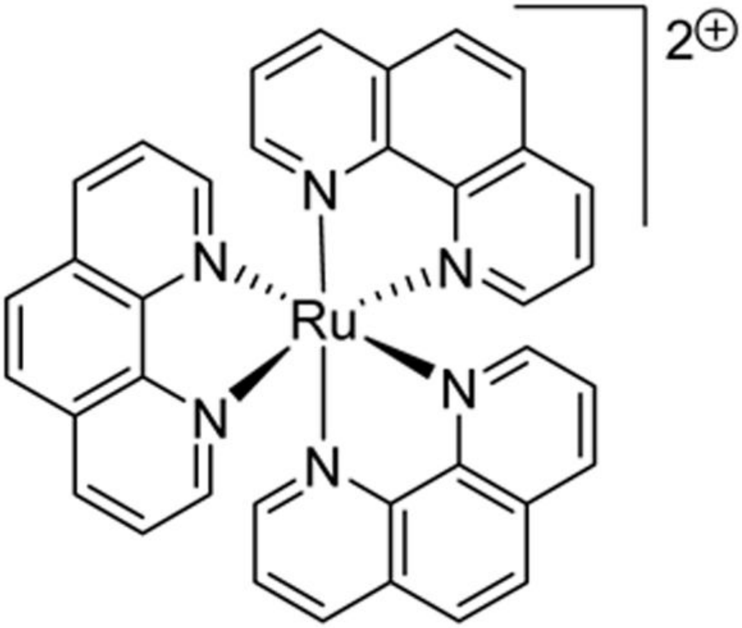


[Ru(bpz)$_3$](PF$_6$)$_2$

In 2012, Zheng and coworkers[61] utilized **12** for an intermolecular [3+2] cycloaddition of olefins with cyclopropylanilines, monocyclic, and bicyclic amines, giving good yields and diastereomeric ratios (Scheme 15).

In 2014, utilizing **12** with an external oxidant Yoon and cowokers[62] detailed an oxidative [3+2] cycloaddition of phenols with alkenes (Scheme 16a) which demonstrated a modular synthesis of dihyrobenzofurans. In the same year they developed a thio-ene “click” reaction of thiols with alkenes (Scheme 16b).[63]

PHOTOCATALYST 13

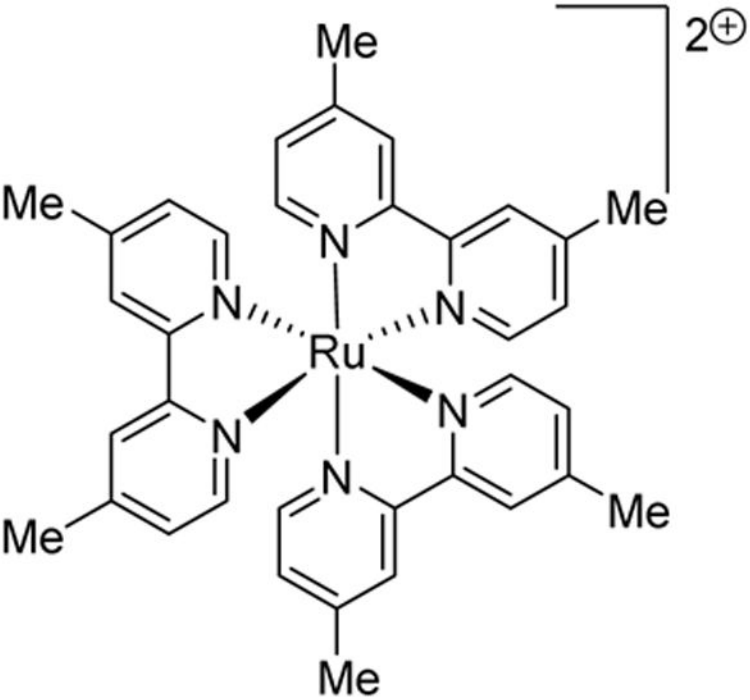


[Ru(phen)$_3$](PF$_6$)$_2$

In 2014, using **13**, Jung and Han reported a convenient method to trifluoromethylate and vicinally chlorinate both internal and terminal alkenes (Scheme 17). **1** gave similar conversion in initial screening.[64] In the same year, Cho and coworkers synthesized difunctionalized alkenes from alkynes using CF$_3$I.[65] In Cho's work, however, it was shown that a switch in catalyst from **13** to **1**, resulted in the hydrotrifluoromethylated product, albeit with poor E:Z selectivity (Scheme 18).

Dolbier and coworkers showed that with **13** and a trifluoromethylsulfonyl chloride, *N*-arylacrylamides could be cyclized through the trifluoromethyl radical to produce 3,3-disubstituted 2-oxoindoles (Scheme 19). The scope was expanded to include the use of the CF$_2$H radical, though it required a change of photocatalyst to **1**.[66]

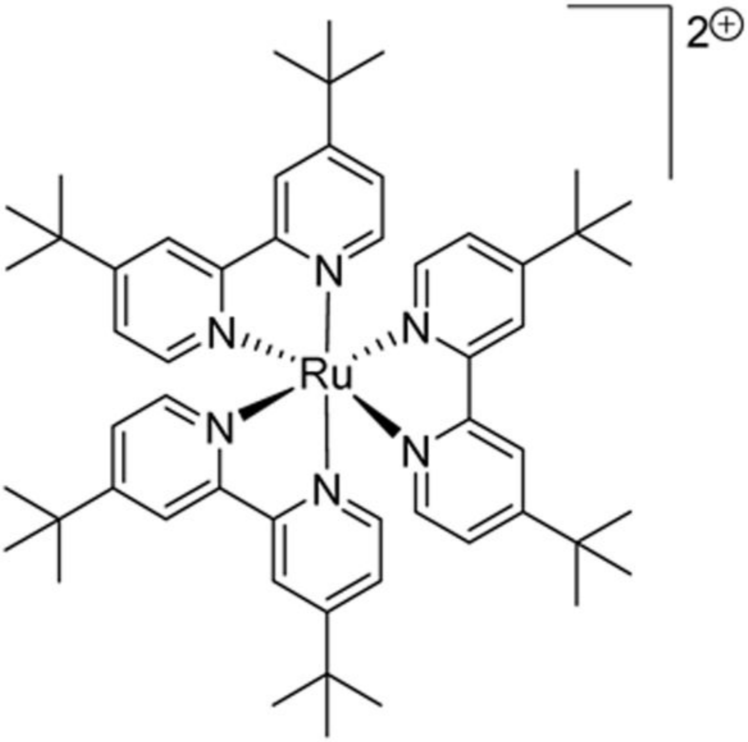
PHOTOCATALYST 14



$[Ru(4,4'\text{-dm-bpy})_3](PF_6)_2$

Investigating the radical mediated C-C bond formation between an α-glucosylbromide and methyl acrylate in 2011, Gagné et al. reported that while the common photocatalyst **11** accomplished the desired transformation, the rate was exceptionally slow. By changing the solvent and the catalyst to **14** (Scheme 20), the rates of conversion were enhanced.[67] In 2012, utilizing similar conditions, Gagné investigated the permeation of light into the reaction mixture using a photoflow reactor and also expanded the scope to include acroleins.

PHOTOCATALYST 15



[Ru(4,4′-dtb-bpy)$_3$](PF$_6$)$_2$

In 2014, Yoon and coworkers utilized the energy transfer mechanism of **15**. Following energy transfer, the substrate expelled the N_2 to produce a nitrene intermediate, which underwent subsequent intramolecular insertion to produce pyrroles in good yields (Scheme 21a). Similarly, photocatalyst **8** transformed ortho alkenylated aryl azides to provide access to substituted indoles (Scheme 21b). [24]

CONCLUSION

We have shown a handful of examples of the rapidly growing and diverse repertoire of reactions and collected electro- and photophysical data for a set of commercially available photocatalysts. We have shown some of the distinct mechanisms in which these catalysts can participate and based on this versatility, we expect to see new directions continue to emerge from this powerful new set of catalysts.

Acknowledgments

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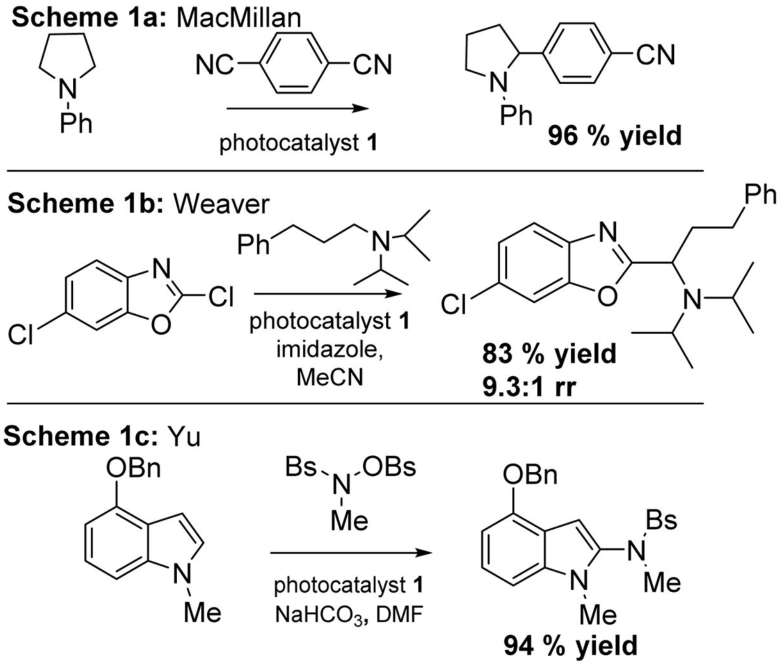
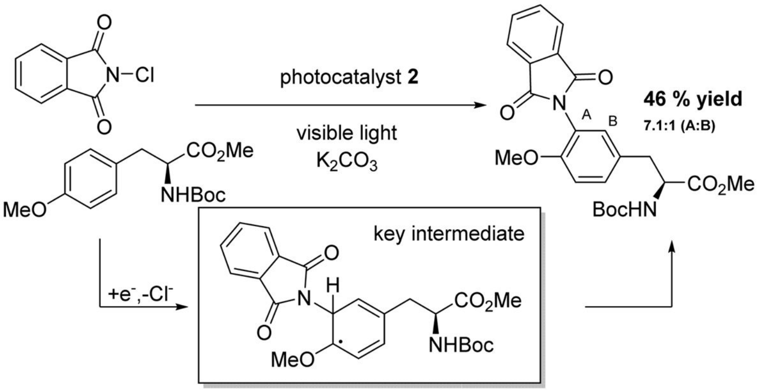
67. Andrews RS, Becker JJ, Gagné MR. Org Lett. 2011; 13:2406. [PubMed: 21473567]
68. These catalysts are commercially available from: (a) Aspira Scientific, Cat # 300895, Sigma-Aldrich, Cat # 688096, and many others, (b) Aspira Scientific, Cat # 300896, Sigma-Aldrich, Cat # 682594, (c) Aspira Scientific, Cat # 300997, (d) Aspira Scientific, Cat # 300998, (e) Aspira Scientific, Cat # 300897, Sigma-Aldrich, Cat # 747769, and many others, (f) Sigma-Aldrich, Cat # 804215, (g) Aspira Scientific, Cat # 300981, (h) Aspira Scientific, Cat # 300898, Strem Chemicals Inc., Cat # 77-0425, (i) Aspira Scientific, Cat # 300899 (j) Aspira Scientific, Cat # 300900, (k) Aspira Scientific, Cat # 300891, Sigma-Aldrich, Cat # 754730, (l) Aspira Scientific, Cat # 300892, Sigma-Aldrich, Cat # 747777, (m) Aspira Scientific, Cat # 300901, and many others, (n) Aspira Scientific, Cat # 300893, (o) Aspira Scientific, Cat # 300894

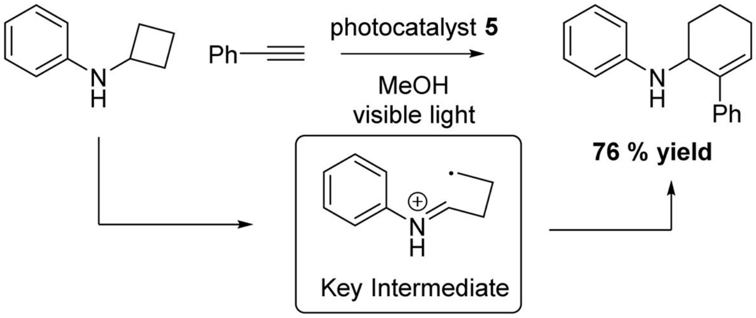

Scheme 1a: MacMillan
N
Ph
NC
CN
photocatalyst 1
96 % yield
Scheme 1b: Weaver
Cl
N
O
Cl
Ph
N
photocatalyst 1
imidazole,
MeCN
83 % yield
9.3:1 rr
Scheme 1c: Yu
OBn
N
Me
Bs
N
OBs
Me
photocatalyst 1
NaHCO3, DMF
94 % yield

Scheme 1.


N–Cl
CO2Me
NHBoc
MeO
photocatalyst 2
visible light
K2CO3
46 % yield
7.1:1 (A:B)
A
B
MeO
BocHN
CO2Me
+e-,-Cl-
key intermediate
H
N
CO2Me
NHBoc
MeO

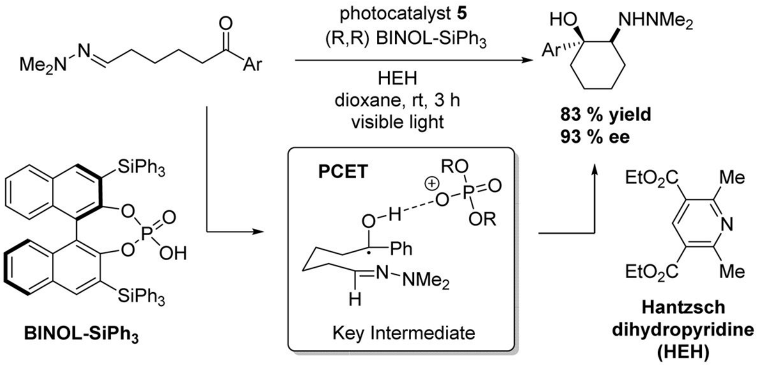
Scheme 2.

Lee



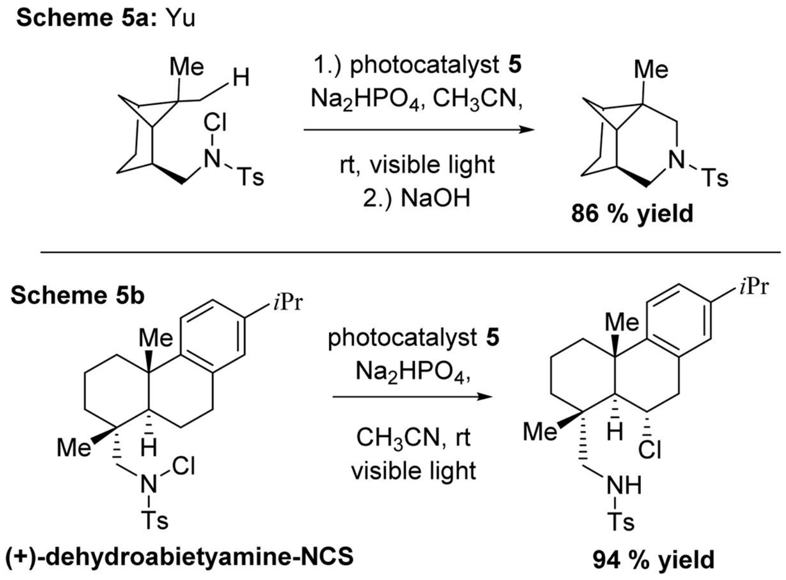
Scheme 3.

Zheng

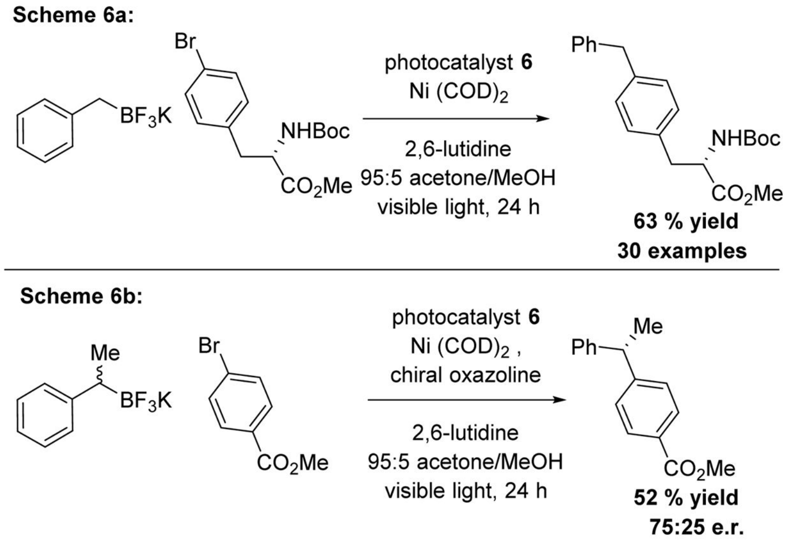


Scheme 4.

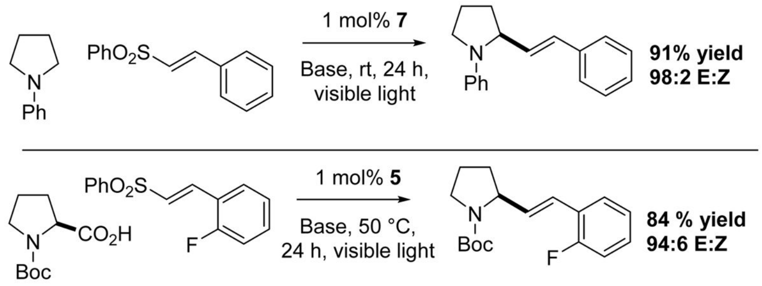
Knowles


Scheme 5a: Yu
Me
H
Cl
N
Ts
1.) photocatalyst 5
Na2HPO4, CH3CN,
rt, visible light
2.) NaOH
Me
N
Ts
86 % yield
Scheme 5b
iPr
Me
Me
H
N
Cl
Ts
(+)-dehydroabietyamine-NCS
photocatalyst 5
Na2HPO4,
CH3CN, rt
visible light
iPr
Me
Me
H
Cl
NH
Ts
94 % yield

Scheme 5.

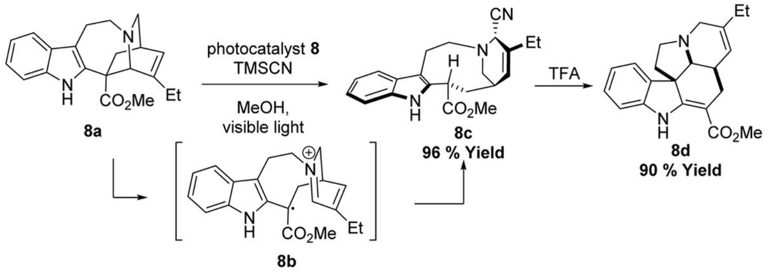

Scheme 6a:
Br
BF$_3$K
NHBoc
CO$_2$Me
photocatalyst 6
Ni (COD)$_2$
2,6-lutidine
95:5 acetone/MeOH
visible light, 24 h
Ph
NHBoc
CO$_2$Me
63 % yield
30 examples
Scheme 6b:
Me
BF$_3$K
Br
CO$_2$Me
photocatalyst 6
Ni (COD)$_2$,
chiral oxazoline
2,6-lutidine
95:5 acetone/MeOH
visible light, 24 h
Ph
Me
CO$_2$Me
52 % yield
75:25 e.r.

Scheme 6.



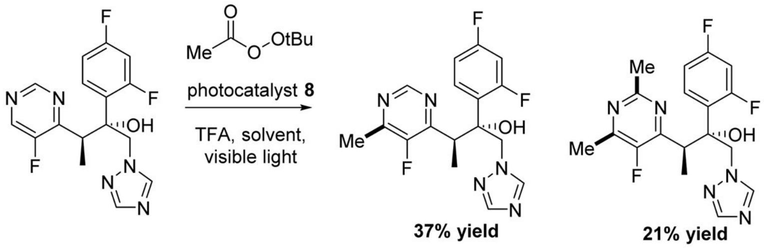
Scheme 7.

MacMillan



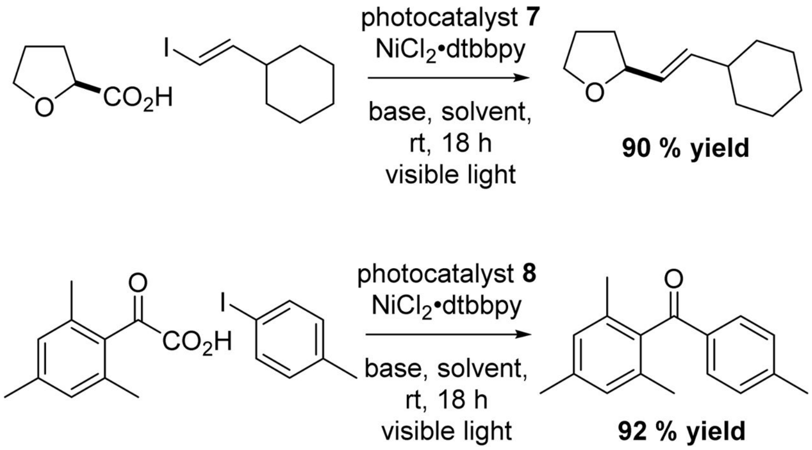
Scheme 8.

Stephenson

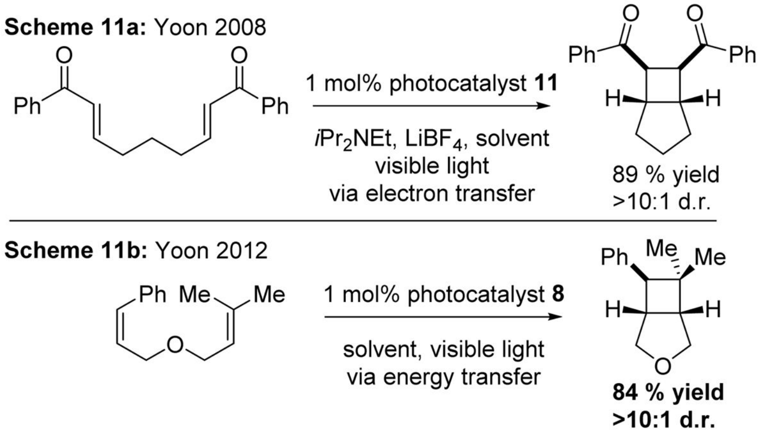


Scheme 9.

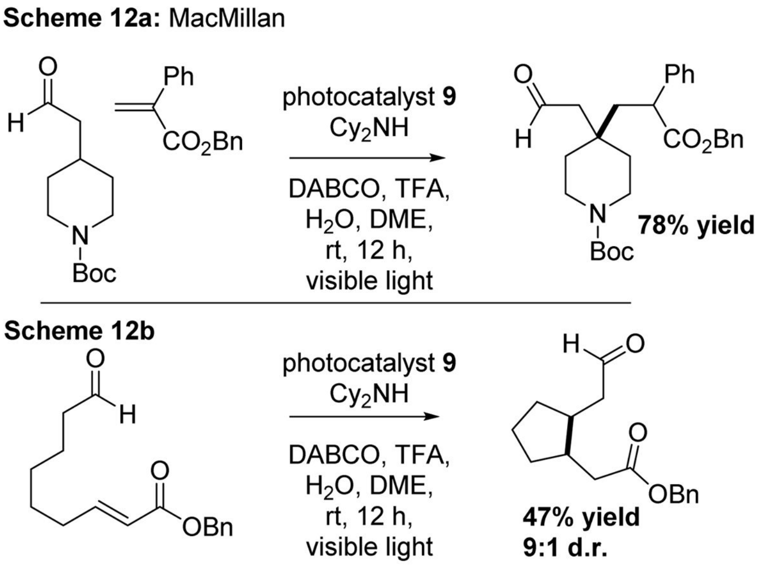
DiRocco



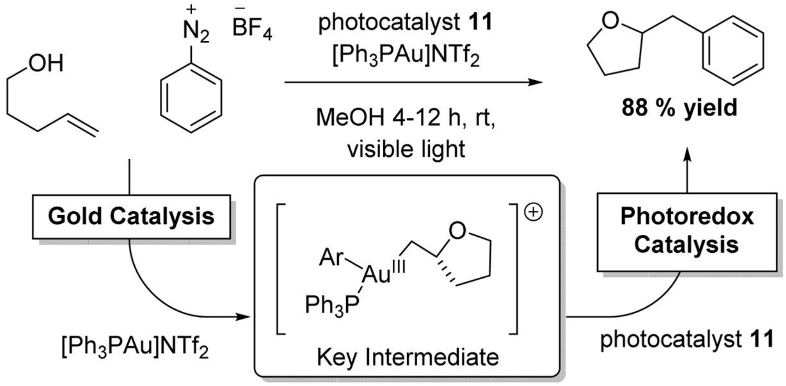
Scheme 10.
MacMillan


Scheme 11a: Yoon 2008
O
O
Ph
Ph
1 mol% photocatalyst 11
iPr2NEt, LiBF4, solvent
visible light
via electron transfer
O
O
Ph
Ph
H
H
89 % yield
>10:1 d.r.
Scheme 11b: Yoon 2012
Ph
Me
Me
O
1 mol% photocatalyst 8
solvent, visible light
via energy transfer
Ph
Me
Me
H
H
O
84 % yield
>10:1 d.r.

Scheme 11.

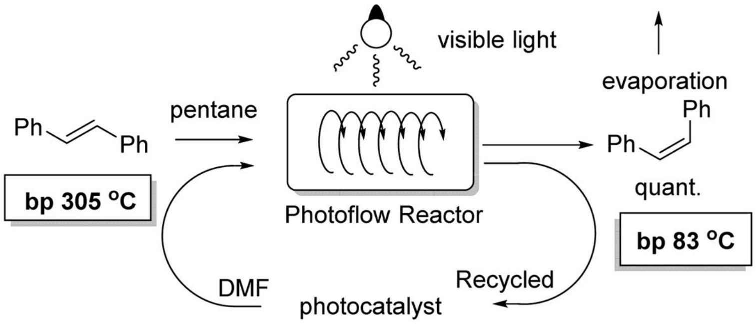

Scheme 12a: MacMillan
O
H
Ph
CO2Bn
N
Boc
photocatalyst 9
Cy2NH
DABCO, TFA,
H2O, DME,
rt, 12 h,
visible light
O
H
Ph
CO2Bn
N
Boc
78% yield
Scheme 12b
O
H
O
OBn
photocatalyst 9
Cy2NH
DABCO, TFA,
H2O, DME,
rt, 12 h,
visible light
H
O
O
OBn
47% yield
9:1 d.r.

Scheme 12.

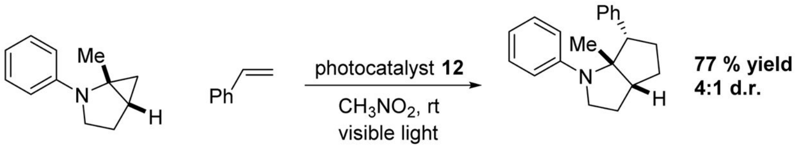


Scheme 13.

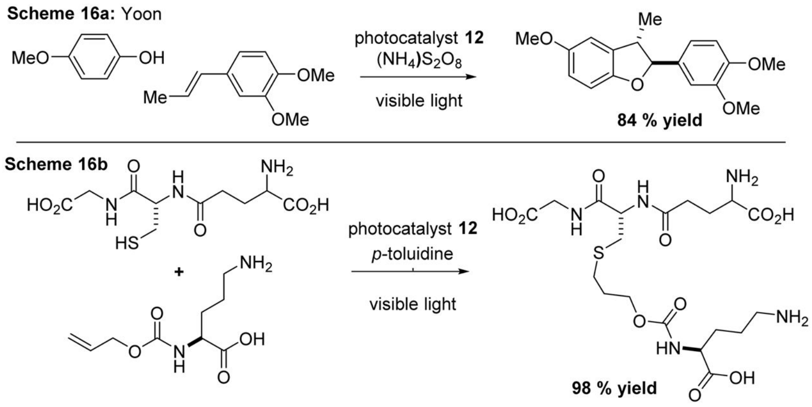
Glorius



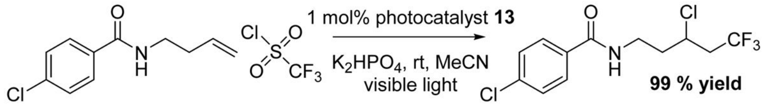
Scheme 14.
Rueping



Scheme 15.
Zheng

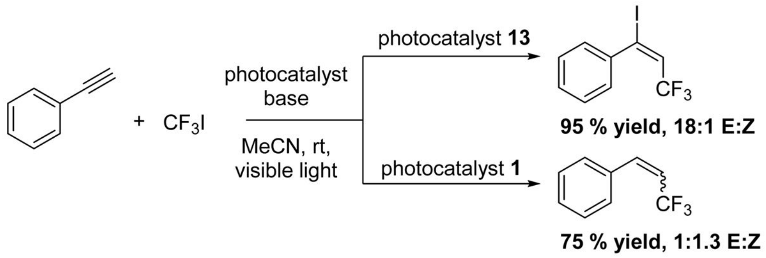

Scheme 16a: Yoon
MeO
OH
Me
OMe
OMe
photocatalyst 12
$(NH_4)S_2O_8$
visible light
MeO
Me
O
OMe
OMe
84 % yield
Scheme 16b
HO_2C
NH_2
CO_2H
HS
+
NH_2
OH
photocatalyst 12
p-toluidine
visible light
S
HN
NH_2
OH
98 % yield

Scheme 16.



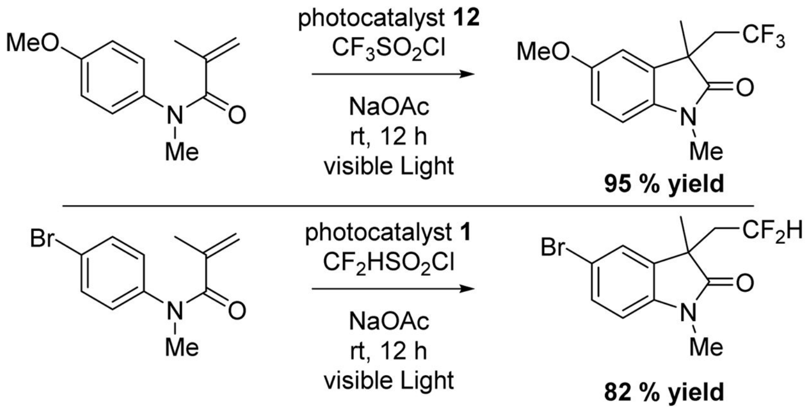
Scheme 17.

Jung & Han



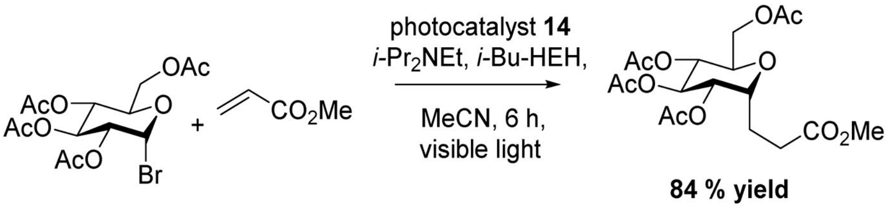
Scheme 18.

Cho

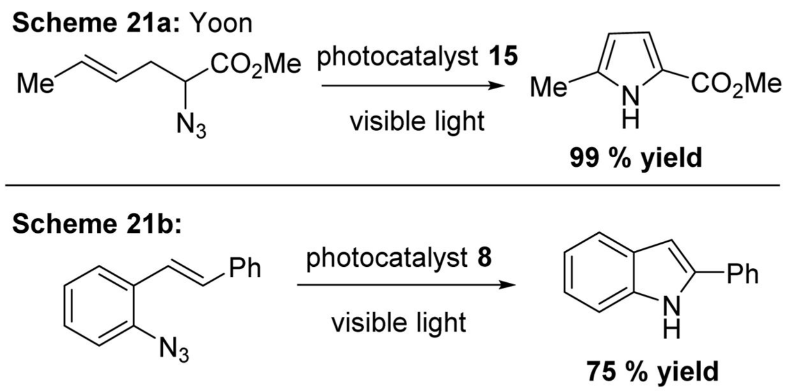


Scheme 19.

Dolbier



Scheme 20.
Gagné


Scheme 21a: Yoon
Me
CO2Me
N3
photocatalyst 15
visible light
Me
N
H
CO2Me
99 % yield
Scheme 21b:
Ph
N3
photocatalyst 8
visible light
N
H
Ph
75 % yield

Scheme 21.

TABLE 1

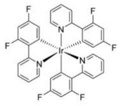
Photophysical properties of selected commercially available photocatalysts.[2,3,16–37,68] Potentials vs. saturated calomel electrode (SCE). *n/a*: information not available.

1

fac-Ir(ppy)$_3$

CAS 94928-86-6

$\lambda_{max\,(excitation)}$ nm	**$\lambda_{max\,(emission)}$ nm**
375	518
τ ns	**Emission kcal/mol**
1900	55.2
$E_{1/2\,Ox}$ V	**$E_{1/2\,Red}$ V**
0.78	-2.20
$E_{1/2\,(M+/M^*)}$ V	**$E_{1/2\,(M^*/M-)}$ V**
-1.73	0.31
E_{gap} eV	**Ref**
2.75	23, 24, 27, 68a

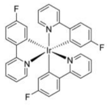


2

fac-Ir(2',4'-dF-ppy)$_3$

CAS 387859-70-3

$\lambda_{max\,(excitation)}$ nm	**$\lambda_{max\,(emission)}$ nm**
378	476
τ ns	**Emission kcal/mol**
1570	60.1
$E_{1/2\,Ox}$ V	**$E_{1/2\,Red}$ V**
0.935	-1.87
$E_{1/2\,(M+/M^*)}$ V	**$E_{1/2\,(M^*/M-)}$ V**
-1.28	0.36
E_{gap} eV	**Ref**
2.21	3, 24, 27, 34, 68b

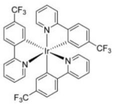


3

fac-Ir(4'-F-ppy)$_3$

CAS 370878-69-6

$\lambda_{max\,(excitation)}$ nm	**$\lambda_{max\,(emission)}$ nm**
380	488
τ ns	**Emission kcal/mol**
2040	58.6
$E_{1/2\,Ox}$ V	**$E_{1/2\,Red}$ V**
0.955	-2.18
$E_{1/2\,(M+/M^*)}$ V	**$E_{1/2\,(M^*/M-)}$ V**
-1.905	0.685
E_{gap} eV	**Ref**
2.86	24, 27, 68c

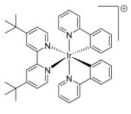


4

fac-Ir(4'-CF$_3$-ppy)$_3$

CAS 500295-52-3

$\lambda_{max\,(excitation)}$ nm	**$\lambda_{max\,(emission)}$ nm**
372	507
τ ns	**Emission kcal/mol**
2160	56.4
$E_{1/2\,Ox}$ V	**$E_{1/2\,Red}$ V**
1.065	-2.175
$E_{1/2\,(M+/M^*)}$ V	**$E_{1/2\,(M^*/M-)}$ V**
-1.695	0.59
E_{gap} eV	**Ref**
2.76	24, 27, 68d

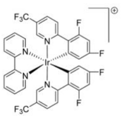


5

[Ir(ppy)$_2$(4,4'-dtb-bpy)]PF$_6$

CAS 676525-77-2

$\lambda_{max\,(excitation)}$ nm	**$\lambda_{max\,(emission)}$ nm**
410	581
τ ns	**Emission kcal/mol**
557	49.21
$E_{1/2\,Ox}$ V	**$E_{1/2\,Red}$ V**
1.21	-1.51
$E_{1/2\,(M+/M^*)}$ V	**$E_{1/2\,(M^*/M-)}$ V**
-0.96	0.66
E_{gap} eV	**Ref**
n/a	17, 18, 23, 68e

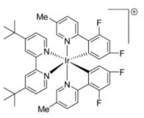


6

[Ir(2',4'-dF-5-CF$_3$-ppy)$_2$(bpy)]PF$_6$

CAS n/a

$\lambda_{max\,(excitation)}$ nm	**$\lambda_{max\,(emission)}$ nm**
405	473
τ ns	**TSE kcal/mol**
2280	60.4
$E_{1/2\,Ox}$ V	**$E_{1/2\,Red}$ V**
1.23	-1.23
$E_{1/2\,(M+/M^*)}$ V	**$E_{1/2\,(M^*/M-)}$ V**
-0.97	0.97
E_{gap} eV	**Ref**
2.20	3, 24, 37, 68f

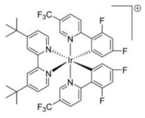


7

[Ir(2',4'-dF-5-me-ppy)$_2$(4,4'-dtb-bpy)]PF$_6$

CAS 1335047-34-1

$\lambda_{max\,(excitation)}$ nm	**$\lambda_{max\,(emission)}$ nm**
360	475
τ ns	**Emission kcal/mol**
1221	60.2
$E_{1/2\,Ox}$ V	**$E_{1/2\,Red}$ V**
1.51	-1.43
$E_{1/2\,(M+/M^*)}$ V	**$E_{1/2\,(M^*/M-)}$ V**
-0.92	0.97
E_{gap} eV	**Ref**
2.97	28, 29, 68g

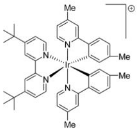


8

[Ir(2',4'-dF-5-CF$_3$-ppy)$_2$(4,4'-dtb-bpy)]PF$_6$

CAS 870987-63-6

$\lambda_{max\,(excitation)}$ nm	**$\lambda_{max\,(emission)}$ nm**
380	470
τ ns	**Emission kcal/mol**
2300	60.1
$E_{1/2\,Ox}$ V	**$E_{1/2\,Red}$ V**
1.69	-1.37
$E_{1/2\,(M+/M^*)}$ V	**$E_{1/2\,(M^*/M-)}$ V**
-0.89	1.21
E_{gap} eV	**Ref**
2.20	18, 23, 27, 68h

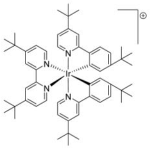


9

[Ir(3,4'-dm-ppy)$_2$(4,4'-dtb-bpy)]PF$_6$

CAS 1607469-49-7

$\lambda_{max\,(excitation)}$ nm	**$\lambda_{max\,(emission)}$ nm**
450	597
τ ns	**Emission kcal/mol**
n/a	47.89
$E_{1/2\,Ox}$ V	**$E_{1/2\,Red}$ V**
1.208	-1.524
$E_{1/2\,(M+/M^*)}$	**$E_{1/2\,(M^*/M-)}$**
-0.868	0.552
E_{gap} eV	**Ref**
2.076	16, 68i

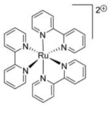


10

[Ir(4,4'-dtb-ppy)$_2$(3,4'-dtb-bpy)]PF$_6$

CAS 808142-80-5

$\lambda_{max\,(excitation)}$ nm	**$\lambda_{max\,(emission)}$ nm**
n/a	583
τ ns	**Emission kcal/mol**
444	49.04
$E_{1/2\,Ox}$ V	**$E_{1/2\,Red}$ V**
n/a	n/a
$E_{1/2\,(M+/M^*)}$ V	**$E_{1/2\,(M^*/M-)}$ V**
n/a	n/a
E_{gap} eV	**Ref**
n/a	18, 68j

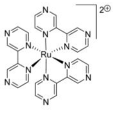


10

[Ru(bpy)$_3$](PF$_6$)$_2$

CAS 60804-74-2

$\lambda_{max\,(excitation)}$ nm	**$\lambda_{max\,(emission)}$ nm**
452	615
τ ns	**Emission kcal/mol**
1100	46.49
$E_{1/2\,Ox}$ V	**$E_{1/2\,Red}$ V**
1.29	-1.33
$E_{1/2\,(M+/M^*)}$ V	**$E_{1/2\,(M^*/M-)}$ V**
-0.81	0.77
E_{gap} eV	**Ref**
n/a	19, 23, 68k

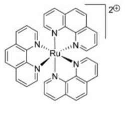


12

[Ru(bpz)$_3$](PF$_6$)$_2$

CAS 80907-56-8

$\lambda_{max\,(excitation)}$ nm	**$\lambda_{max\,(emission)}$ nm**
443	591
τ ns	**Emission kcal/mol**
740	48.38
$E_{1/2\,Ox}$ V	**$E_{1/2\,Red}$ V**
1.86	-0.80
$E_{1/2\,(M+/M^*)}$ V	**$E_{1/2\,(M^*/M-)}$ V**
-0.26	1.45
E_{gap} eV	**Ref**
n/a	21, 23, 68l

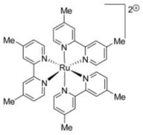


13

[Ru(phen)$_3$](PF$_6$)$_2$

CAS 28277-60-3

$\lambda_{max\,(excitation)}$ nm	**$\lambda_{max\,(emission)}$ nm**
447	610
τ ns	**Emission kcal/mol**
500	46.87
$E_{1/2\,Ox}$ V	**$E_{1/2\,Red}$ V**
1.26	-1.36
$E_{1/2\,(M+/M^*)}$ V	**$E_{1/2\,(M^*/M-)}$ V**
-0.87	0.82
E_{gap} eV	**Ref**
2.18	22, 23, 35, 68m

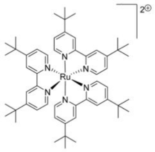


14

[Ru(4,4'-dm-bpy)$_3$](PF$_6$)$_2$

CAS 83605-44-1

$\lambda_{max\,(excitation)}$ nm	**$\lambda_{max\,(emission)}$ nm**
457	632
τ ns	**Emission kcal/mol**
875	45.32
$E_{1/2\,Ox}$ V	**$E_{1/2\,Red}$ V**
1.14	-1.43
$E_{1/2\,(M+/M^*)}$ V	**$E_{1/2\,(M^*/M-)}$ V**
n/a	0.22
E_{gap}	**Ref**
2.57	30, 31, 32, 36, 68n



15

[Ru(4,4'-dtb-bpy)$_3$](PF$_6$)$_2$

CAS 75777-87-6

$\lambda_{max\,(excitation)}$ nm	**$\lambda_{max\,(emission)}$ nm**
459	614
τ ns	**Emission kcal/mol**
990	46.56
$E_{1/2\,Ox}$ V	**$E_{1/2\,Red}$ V**
n/a	n/a
$E_{1/2\,(M+/M^*)}$ V	**$E_{1/2\,(M^*/M-)}$ V**
n/a	n/a
E_{gap}	**Ref**
n/a	18, 31, 32, 33, 68o