Visible light photoredox mediated C-C bond formation under metal-free condition

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**Visible Light Photoredox Mediated C-C Bond Formation under
Metal-Free Condition**

DAS MRINMOY

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2019

Visible Light Photoredox Mediated C-C Bond Formation under Metal-Free Condition

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological University in partial fulfilment of the requirement for the degree of Doctor of Philosophy

2019

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Authorship Attribution Statement

This thesis contains material from 1 paper published in the following peer-reviewed journal(s) where I was the first and/or corresponding author.

Chapter 2 is published as M. Das[†], M. D. Vu[†], Q. Zhang and X.-W. Liu. Metal-free visible light photoredox enables generation of carbyne equivalents via phosphonium ylide C-H activation. *Chemical Science* **10**, 1687-1691 (2019). DOI: 10.1039/C8sC04195D

The contributions of the co-authors are as follows:

- I did most of the synthetic experiments, including set-up of the reaction, optimization, substrate scope evaluation, product purification, characterization and prepared the supplementary information for the manuscript.
- Dr. Vu gave the initial idea and result, prepared the manuscript drafts and gave important ideas during mechanistic study.
- Dr. Zhang gave helpful inputs and discussion for our mechanistic studies.
- Prof. Xue-Wei Liu provided overall guidance for the project.
- All the laboratory work at the school of Physical and Mathematical Sciences.

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Abstract

Over the last decade, visible-light photoredox catalysis is rising as an important route for new chemical bond formation. The source of activation is visible-light which helps the reaction to occur in ambient temperature. In addition, due to the ability to tune the redox potential of other molecule, photoredox catalyst enables several challenging transformations easier. As a consequence, photoredox catalysts can facilitate many unfavourable electron transfer processes by diminishing the earlier reports and proceed the reaction through different pathways. Because of its usefulness towards organic synthesis the reports using this strategy is increasing gradually. Therefore, I intended to develop novel C-H activation strategies during my doctoral research work by employing organo-photoredox catalysis.

The first chapter of this thesis describes photoredox catalysis, photophysical properties and application towards organic chemistry. Subsequently, in the second chapter we have developed a metal-free C-C bond forming method which involves C-H activation of phosphonium ylides, followed by the addition of electron rich olefin. This work describes a novel strategy to generate carbyne equivalents from phosphonium ylides under photoredox condition. Finally, in the last chapter we have successfully introduced photocatalytic metal free method for the intermolecular radical-radical cross coupling involving ketyl radical to produce complex tertiary alcohols.

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Table of Contents

Abstract	1
Acknowledgements	2
Table of Contents	4
List of Abbreviations	6
Chapter 1 Introduction to visible-light photoredox catalysis and synthetic applications	8
1.1 Photophysical properties of photoredox catalysis	9
1.2 Working principles of visible-light photoredox catalysis	18
1.3 Visible-light photoredox catalysis: Application to organic synthesis	23
References	45
Chapter 2 Metal-free visible light photoredox enables generation of carbyne equivalents via phosphonium ylides C-H activation	55
2.1 Introduction	56
2.2 Results and discussion	58
2.3 Conclusions	65
2.4 Experimental section	66
References	98
Chapter 3 Metal-free Photoredox mediated ketone carbonyl alkylation for easy access to tertiary alcohols	102
3.1 Introduction	103
3.2 Results and discussion	108
3.3 Conclusions	114

3.4	Future work	114
3.5	Experimental section	115
	References	135
	List of Publications and conferences	138

List of Abbreviations

μL	microlitre	$\text{dF}(\text{CF}_3)\text{ppy}$	2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine
Acr^+	acridinium	DFT	density functional theory
ATRA	atom transfer radical addition	DIPEA	N-diisopropylethylamine
BDE	bond-dissociation energy	DMA	dimethylacetamide
Bn	benzyl	DMF	dimethylformamide
Boc	<i>tert</i> -butoxycarbonyl	DMSO	dimethyl sulfoxide
Bpy	2,2'-bipyridine	dr	diastereoisomeric ratio
Brs	broad singlet	dtbbpy	4,4'-di- <i>tert</i> butyl-2,2'-bipyridine
Bz	benzoyl	EDG	electron donating groups
Calc.	calculated	equiv	equivalents
CAN	cerium ammonium nitrate	Et	ethyl
CDCl_3	deuterated chloroform	EWG	electron withdrawing groups
Cod	1,5-cyclooctadiene	<i>fac</i> -	facial
d	doublet	FGI	functional group interconversion
DABCO	1,4-diazabicyclo-[2.2.2]-octane	HAT	hydrogen atom transfer
bda	dibenzylideneacetone	HFIP	1,1,1,3,3,3-hexafluoro isopropanol
DCE	1,2-dichloroethane	Hz	hertz
DCM	dichloromethane	IC	internal conversion
dd	doublet of doublets	ⁱ Pr	<i>iso</i> -propyl
DDQ	2,3-dichloro-5,6 dicyanobenzoquinone	ISC	intersystem crossing
LED	light emitting diode	ppy	2-phenylpyridine
M	mole per litre	PRC	polarity reversal catalyst

Me	methyl	s	singlet
MeCN	acetonitrile	SCE	saturated calomel electrode
MeOH	methanol	SET	single electron transfer
Mes	mesityl	t	triplet
mL	millilitre	^t Bu	<i>tert</i> -butyl
MLCT	metal to ligand charge transfer	TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
mmol	millimoles	TIPS	tri- <i>iso</i> -propylsilyl
mol%	mol percentage	TMS	trimethylsilyl
NHC	N-heterocyclic carbene	TMSCN	trimethylsilyl cyanide
PC	photocatalyst	TTET	triplet-triplet energy transfer
PCET	proton coupled electron transfer	Δ	reflux or heat
PET	photoinduced electron transfer	δ	chemical shift
Ph	phenyl		
Phen	1,10-phenanthroline		
PMB	<i>para</i> -methoxybenzyl		
PMP	<i>para</i> -methoxyphenyl		
ppm	part per million		

Chapter 1

Introduction to Visible-Light Photoredox Catalysis and - Synthetic Applications

Abstract: This part contains introduction to visible-light photoredox catalysis, photophysical theory of both transition metal and organic photosensitizer, classification with respect to the binding ligands and functional principle, including its numerous applications to organic synthesis.

1.1 Photophysical properties of photoredox catalysts

In catalysis field, the fundamental objective is to develop new modes of activation of small molecules. Over the last few years, plenty of attention has been gained by photoredox catalysis for the activation of organic molecules. The most frequently used photosensitizers are the polypyridyl complexes of ruthenium and iridium. Besides transition metals chromophores, there is an extensive range of organic chromophores which are also recognized because of its competence in photoinduced electron transfer (PET) process. The typical working principle of any photocatalyst consists of photoinduced excitation and relaxation pathways. The photochemical reactivity of any molecule is ultimately governed by its photophysical properties of the electronically excited state. Moreover, the photophysical consideration of a photosensitizer in both ground state and the excited state is essential towards its desired reactivity. A simplified state energy diagrams (**Fig. 1.1**) has been laid out through which photoredox catalysts' reactivity could be understood easily.¹

Fig. 1.1. Photophysical and photochemical process of photoredox catalysts

The photosensitizer absorbs photon upon light irradiation and an electron is promoted to the higher energy level from a ground state singlet (S_0) to singlet excited state (S_1). The future of

that excited singlet state (S_1) relies on both radiative and nonradiative process for decaying if we consider only photophysical pathways. The radiative transition involves, returning of excited S_1 to S_0 via light emission ($-h\nu$), known as fluorescence. Moreover, it can return to ground state S_0 following nonradiative transition that is termed as internal conversion (IC). S_1 has different option for decaying, for instances, proceeding towards spin forbidden state T_1 , known as intersystem crossing (ISC), which is a nonradiative spin forbidden pathway. This triplet state is long-lived, due to the spin forbidden $T_1 \rightarrow S_0$ transition and it returns to ground state by slow decaying radiative pathways, known as phosphorescence. Chemists have designed some special photosensitizers with the extended lifetime from nanosecond to millisecond regions. As a consequence, the excited states S_1 and T_1 can engaged in bimolecular reactions and go through either energy transfer (EnT) or electron transfer (ET) or both. The overall process starting from excitation to electron transfer process between excited state to ground state is known as photoinduced electron transfer (PET).

Photosensitizers can be categorized into three different groups depending on their structural diversity: transition metal complexes, organic dyes and semiconductor. The semiconductors are rarely used in organic synthesis, but they are extensively used in environmental aspects²⁻³ such as CO_2 reduction, pollutant degradation, water photolysis.

1.1.1 Transition metal photoredox catalysts

The most commonly used transition metal photocatalysts are consists of polypyridyl complexes of iridium (III) and ruthenium (II). Upon visible light irradiation, the photosensitizer absorbs photon and an electron is excited from the metal-centred t_{2g} orbitals to ligand-centred π^* orbital, known as metal-ligand charge transfer (MLCT).² This transition leads to an excited species, in which the metal has undergone single-electron oxidation and the ligand has been reduced (**Fig. 1.2**).⁴

Fig 1.2. Simplified MO diagram of $\text{Ru}(\text{bpy})_3^+$ photochemistry

The originally generated MLCT state suffers rapid intersystem crossing to produce lowest-energy and long-lived triplet MLCT state, which participates in the single-electron transfer process. The photoexcited species possess an exceptional property of being more oxidative and reductive in nature compared to its ground state species. The standard reduction potential is considered to quantify this phenomenon. For instances, the reduction potential of $\text{Ru}(\text{bpy})_3^{2+}$ photosensitizer for $E_{1/2}^{\text{III/II}}$ and $E_{1/2}^{\text{II/I}}$ are +1.29 V and -1.33 V (vs SCE) respectively.⁵ This shows that the reduction is thermodynamically unfavourable for $\text{Ru}(\text{II})$ to $\text{Ru}(\text{III})$ and $\text{Ru}(\text{I})$ to $\text{Ru}(\text{II})$. Simultaneously, excited species' reduction potential shows that they have much more electron donating and accepting ability respect to its ground state ($E_{1/2}^{\text{III}/*\text{II}} = -0.81 \text{ V}$ and $E_{1/2}^{\text{II}/*\text{I}} = +0.77 \text{ V vs SCE}$).⁶

Fig 1.3. Quenching pathways of transition metal photocatalyst

Therefore, this uniqueness of the excited photoredox catalyst $\text{Ru}(\text{bpy})_3^{2+}$ leads to the possibility of two pathways, one is oxidative quenching and alternative choice is reductive quenching (**Fig. 1.3**). In oxidative quenching, the excited $^*\text{Ru}(\text{bpy})_3^{2+}$ catalyst act as reducing agent. It can reduce electronically poor substances through single electron transfer (SET) to form a radical anion and the photocatalyst itself get oxidised to $\text{Ru}(\text{bpy})_3^{3+}$.

Fig 1.4. Examples of Homoleptic and heteroleptic complexes

The oxidised photocatalyst can act as a strong oxidising agent ($E_{1/2}^{\text{III/II}} = +1.29 \text{ V vs SCE}$). It can take an electron from electronically rich species for the generation of radical cation and come back to its ground state $\text{Ru}(\text{II})$. The commonly used oxidative quenchers are

aryldiazonium salts, dicyanobenzene, dinitrobenzene and viologen. During reductive quenching process the excited photocatalyst $^*\text{Ru}(\text{bpy})_3^{2+}$ accepts one electron from electron rich species to produce $\text{Ru}(\text{bpy})_3^+$. The reduced Ru(I) species serve as a strong reducing agent ($E_{1/2}^{\text{I/II}} = -1.33 \text{ V vs SCE}$), it donates electron to reductive quencher and returns to ground state Ru(II) completing the catalytic cycle. Tertiary amines are known as the most commonly used reductive quenchers. The redox potential of the photocatalytic cycle can be monitored by attaching different ligand to the metal centre.

Table 1.1. Photophysical properties of frequently used photocatalysts⁴

Photocatalyst	$E_{1/2}(\text{M}^+/\text{M}^*)$ vs SCE (V)	$E_{1/2}(\text{M}^*/\text{M}^-)$ vs SCE (V)	Excited state lifetime τ (ns)	Excitation λ_{max} (nm)
$\text{Ru}(\text{bpm})_3^{2+}$	-0.21	+0.99	131	454
$\text{Ru}(\text{bpz})_3^{2+}$	-0.26	+1.45	740	443
$\text{Ru}(\text{bpy})_3^{2+}$	-0.81	+0.77	1100	452
<i>fac</i> - $\text{Ir}(\text{ppy})_3$	-1.73	+0.31	1900	375
$\text{Ir}[(\text{dtbpy})(\text{ppy})_2]^+$	-0.96	+0.66	557	410
$\text{Ir}[\text{dFCF}_3(\text{ppy})]_2(\text{dtbpy})^+$	-0.89	+1.21	2300	380

In respect to the ligands used, the photocatalyst can be divided into two categories, homoleptic and heteroleptic complexes. $\text{Ru}(\text{bpy})_3^{2+}$, $\text{Ir}(\text{ppy})_3$ are in homoleptic categories because the metal centre is surrounded with the same ligands, while the heteroleptic ones are $[\text{Ir}(\text{ppy})_2(\text{dtbpy})]^+$ or $[\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbpy})]^+$, containing different ligand moieties (**Fig. 1.4**). In comparison with ruthenium, iridium can function as a better host for the accommodation of

a heteroleptic ligand system because of its larger spin-orbit coupling, which facilitates the MLCT efficiency. Therefore, most of the ruthenium complexes are homoleptic.

By substituting the ligand with different electronically rich substituents and electron withdrawing functional groups, reduction potential of the photocatalyst also can be tuned. It's obvious that anionic ligand 2-phenylpyridine (ppy) is the most reducing in nature with respect to neutral ligand 2,2'-bipyridine (bpy) due to its more electron donating ability. Whether the fluorine (-F) and trifluoromethyl (-CF₃) substitution to the ligands induces the oxidative nature to the photocatalyst due to their electron withdrawing ability (**Table 1.1**). Nowadays, chemists have been using other earth-abundant transition metal such as copper (Cu), iron (Fe), chromium (Cr) as a photocatalyst to lower the expense.⁷⁻⁸

1.1.2 Organic photoredox catalysts

Organic dyes also have been used in organic photoredox catalysis for many years.⁹ Due to the light absorbing ability, the organic dyes appear in different colours, and they have been used in dye industry. In the presence of visible light, a wide range of organic dyes can participate in photoinduced electron transfer (PET) process.^{1, 10} In comparison to transition metal photosensitizer, organo-photocatalysts are less expensive, readily available with minimum toxicity. In **Fig. 1.5** we will introduce different classes of organic photoredox catalysis which are widely used for organic transformation.

Fig 1.5. Commonly used organic photoredox catalysis

Organic dyes such as *p*-dicyanobezene and dicyanonaphthalene, 9,10-dicyanoanthracene belong to cyanoarene class, have relatively higher excited state energies and moderately high ground state reduction potential, which enables the cyanoarenes to oxidise substrates owing relatively higher oxidation potential exceeding +2.0 V.¹¹ Over the decades, probably xanthenes are the most commonly used organic photoredox catalyst.¹²⁻¹³ Rhodamine B, Fluorescein, Eosin Y, Rose Bengal are also representative of this category. Because of their balanced reduction potential, they have been broadly employed for redox transformation. Eosin Y was employed to oxidise benzyl bromide and benzyl alcohol which is named as Kornblum oxidation.¹⁴ It was also used for the deprotection of *p*-methoxybenzyl (PMB) group.¹⁵ Rhodamine B and Eosin Y also have been used for dehydrogenative coupling.¹⁶ DDQ is a well-known organic oxidant which is also used in many non-photochemical reactions at elevated temperature.¹⁷ It can oxidise many non-reactive substrates such as

benzene and enables its catalytic coupling. Fukuzumi and co-workers have developed a highly powerful oxidising organic dye, acridinium¹⁸ that has been used by Nicewicz group for anti-Markovnikov addition to inactivated alkenes through the oxidative addition to alkene¹⁹ and arene functionalisation²⁰.

Pyrylium deactivation

Acridinium deactivation

Scheme 1.1. Deactivation pathways of organophotoredox catalysts

Moreover, several strong reducing organic dyes have been reported such as electron rich derivatives of pyrenes and anthracenes. Their redox potential lies in the span of +2.0 V to +2.5 V. Therefore, they served as an excellent candidate for ketone reduction to generate ketyl radicals. Jamison has developed the direct synthesis of amino acids via CO_2 reduction

using *p*-triphenyl ($E^0 = +2.63$ V) which is a very strong reducing organic dyes.²¹ These reducing organic dyes could be used in organic transformation instead of iridium catalysts which are commonly employed for reduction.

Even though organic photoredox catalyst has facilitated us with a greener way to transform organic molecules, it renders significant disadvantages involving deactivation pathways, because of the involvement of harsh reaction conditions.¹ As a consequence, the catalyst loading for organic photoredox catalysis is higher respect to the transition metal catalysts. Moreover, acridinium and pyrylium dyes suffer the irreversible deactivation process either by reacting with strong nucleophile or they could undergo photoinduced electron transfer (PET) and subsequently quenched by oxygen to generate superoxide (O_2^-) or undergo radical-radical coupling to form dimer which can't participate in the catalytic cycle (**Scheme 1.1**).

1.2 Working principles of visible-light photoredox catalysis

1.2.1 Electron transfer mechanism

Photoinduced electron transfer (PET) is an excited state electron transfer process where a donor donates the excited electron to the acceptor. In recent decades, most of the photocatalytic reaction follows photoinduced electron transfer pathway. At their excited state, photocatalysts show excellent reducing and oxidising power which enables the versatile reaction design. Either by utilising cyclic voltammetry or theoretical calculation, reduction potential of the substrates can be quantified. Subsequently, by adjusting the reduction potential of the substrate or the photocatalysts, the reaction can be eased. For example, one can use Ir(ppy)₃ ($E = -2.19$ V vs SCE) to reduce benzophenone ($E = -2.0$ V vs SCE) through reductive quenching pathway to generate ketyl radical or can utilize other photocatalysts such as phenoxazine that possess comparable reduction potential. Therefore, the feasibility of the novel reaction pathways can be predicted by assuming the electron transfer steps.

Moreover, the quenching experiments could also show the responsible quenchers for photocatalyst and the electron transfer process, as discussed by Glorius,²² MacMillan and co-workers²³. Glorius has found the novel chemistry of triazole by mechanism-based luminescence screening.²⁴ The discovery of α -amine C_{sp3-H} arylation in 2011 by MacMillan, triggered a new era in photoredox catalysis.

1.2.2 Electron donor-acceptor (EDA) complexes

Sometimes, the control experiments affirm that there is no involvement of photoredox catalysts in the reaction mechanism. That happens when the substrates itself can absorb light and helps the electron transfer. Often, one of the fastest indications of formation of donor-acceptor complex is a noticeable colour change in the reaction mixture upon mixing of substrates. Kochi and co-workers²⁵ have described the mechanism of electron transfer in intermolecular charge-transfer complexes first in 2008 and recently it has been harnessed by Melchiorre²⁶⁻²⁷ and other

research group²⁸ to develop catalyst-free photocatalytic reaction using visible light. EDA complexes may form with either one of the substrates and the photocatalyst and absorb the photon in relatively lower energy than both of the reactants separately.

1.2.3 Energy transfer mechanism

Other than the electron transfer mechanism, another fundamental pathway for the decay of excited state of the photocatalysts is energy transfer. Upon irradiation by visible light, the photocatalyst excites from the ground state (S_0) to lowest energy singlet excited state (S_1) (**Fig 1.6**). After relaxing to long lived-triplet state (T_1) via intersystem crossing (ISC), the relatively higher energy photocatalyst facilitates to excite the lower energy substrate to the triplet (T_1) state relatively lower in energy via triplet-triplet energy transfer, which then participates in chemical transformation.

Fig 1.6. Triplet-triplet energy transfer from photosensitizer to substrate

The first instance of triplet-triplet energy transfer was, synthesis of quadricyclane through the transformation of substituted norbornadiene²⁹ using $\text{Ru}(\text{bpy})_3^{2+}$ as energy transfer catalyst (**Scheme 1.2a**). The triplet-triplet energy transfer from excited $^*\text{Ru}(\text{bpy})_3^{2+}$ photocatalyst to norbornadiene helps the norbornadiene to become lowest energy triplet state species which went through the rearrangement to form the quadricyclene. This transformation is not possible via electron transfer mechanism due to its higher potential barrier ($E_{1/2}^{0/-1} = -1.39 \text{ V vs SCE}$ and $E_{1/2}^{+1/0} = +1.82 \text{ V vs SCE}$). The redox potential of norbornadiene shows that oxidative or

reductive quenching by $^*\text{Ru}(\text{bpy})_3^{2+}$ is extremely disfavoured. In 2012, Yoon has developed [2+2] cycloaddition of styrene through triplet-triplet energy transfer (**Scheme 1.2b**).³⁰ They used styrene substrate ($E_{1/2}^{\text{red}} = +1.42 \text{ V vs SCE}$) which have relatively higher reduction potential than the working photocatalyst ($E_{1/2}^{*\text{III/II}} = +1.21 \text{ V vs SCE}$), thereby excluding SET involved radical pathway, reported by the same group previously. Instead of that, the excited triplet state energy (E_T) of both photocatalyst and the styrene substrate is almost similar ($E_T \approx 60 \text{ kcal/mol}$).³¹

Scheme 1.2. Examples of energy transfer mechanism reaction

Hence, this suggests the possibility of triplet-triplet energy transfer from the photocatalyst and triggers the transformation. Recently, MacMillan group also unfolded a direct coupling reaction between aryl halides and carboxylic acids (**Scheme 1.2c**).³² They have proved that energy transfer is the activation mode to form the desired coupling product instead of modulating the nickel catalysts oxidation states.

1.2.4 Hydrogen atom transfer mechanism

Hydrogen atom transfer is a key process in lots of C-H functionalisation process. Different bond strength plays a crucial role (thermodynamically) for this kind of activation mode. In

addition to the thermodynamic part for hydrogen atom transfer (HAT) activation, the kinetic consideration also plays an important role, that is polarity match between hydrogen atom acceptor radicals and substrate (Hydrogen atom donor). Electrophilic radicals (carboxyl,

Scheme 1.3. Hydrogen atom transfer via photoexcited Eosin Y

hydroxyl, thiyl) have preferred to generate carbon-centered radicals by abstracting a hydrogen atom from C-H bonds. Recently, Wu *et al.* have described, Eosin Y can act as HAT agent upon excitation by visible light (**Scheme 1.3**).³³ After irradiation by visible light, the photoexcited form of Eosin Y contains an electrophilic hydroxyl radical which helps the HAT process to proceed the reaction.

Fig 1.7. Example of Photoacid and Lewis acid catalysts

1.2.5 Photoacid and Lewis acid catalysis

Some organic chromophores which possess catalytic activity in their photoexcited state similar like acid catalysts, termed as photoacid catalysts (**Fig. 1.7**), was developed by Wyatt in 1976.³⁴ A few years back, Toshima et al. has reported photocatalytic glycosylation in presence of thiourea, where the excited thiourea gives a proton to facilitate the removal of leaving group.³⁵ In 2018, Wang and co-workers presented the synthesis of 2-deoxyglycosides via photoacid catalysis using Eosin Y as a photoacid catalyst from protected glycals.³⁶ Recently, Meggers group has succeeded to develop an iridium complex which is upon irradiation removes some labile ligands and possess the Lewis acid characteristic.³⁷

1.3 Visible-light photoredox catalysis: Application to organic synthesis

Having the above described mode of activation for photoredox catalysis, chemists have succeeded to expand a broad range of novel and useful methods for organic transformation through serendipitous reaction screen or designing the reactions intentionally. In the following part recently developed breakthrough applications to organic synthesis are being discussed.

1.3.1 Functional group interconversion

In organic synthesis, functional group interconversion has a vital role. After the evolution of visible-light photoredox catalysis, a huge amount of conventional methods are being replaced by its greener advantage.

1.3.1a Reductive transformation

In the late seventies, Kellogg's group have reported sulfonium salt reduction through photoredox condition by using Hantzsch ester as a reducing agent together with $\text{Ru}(\text{bpy})_3^{2+}$ (**Scheme 1.4**).³⁸ In presence of light the excited $^*\text{Ru}(\text{bpy})_3^{2+}$ helps to cleave C-S bond and produced radical *in situ*, which undergoes reduction by Hantzsch ester.

Scheme 1.4. Reduction of sulfones and sulfonium salts

In 1986, Ohno and co-workers have utilised Hantzsch ester for the desulfonylation of β -ketosulfones under visible-light condition.³⁹ Eosin Y also can act as reducing photocatalyst to promote desulfonylation under visible light.⁴⁰

In the early eighties, Tanaka⁴¹ and Fukuzumi⁴² (1990) have employed $\text{Ru}(\text{bpy})_3^{2+}$ to reduce the phenacyl bromide under photoredox condition (**Scheme 1.5**). Previously they have used benzyl

substituted dihydronicotinamide (BNAH) as a sacrificial reductant but later dihydromethylacridine has been used by Fukuzumi group. A seminal work has been reported by Kern and Sauvage (1987) which involves introduction of $\text{Cu}(\text{dap})_2\text{BF}_4$ as a photocatalyst.⁴³ Almost twenty years later, Stephenson and co-workers have developed reductive dehalogenation protocol⁴⁴, especially introducing unactivated iodide⁴⁵ as a substrate with $\text{Ir}(\text{ppy})_3$ photocatalyst which is relatively more reducing in nature. This was a breakthrough towards organotin-free dehalogenation method, that acquits us from the use of toxic tin substances.

Scheme 1.5. Reductive dehalogenation via SET

Moreover, the newly generated radical from dehalogenation can participate in radical cyclisation known as reductive cyclisation or atom transfer radical addition (ATRA).⁴⁶ Generally, in these reactions, tertiary amine Hünig's base or formic acid was used as sacrificial reductant instead of metal hydrides that makes the reaction condition more environment friendly. Willner group have reported the reduction of vicinal dibromides merging viologen catalysis with photoredox catalysis using a biphasic system ($\text{EtOAc/H}_2\text{O}$).⁴⁷ In 2015, Miyabe

and co-workers reported that Rhodamine B can help to accomplish the reductive dehalogenation to perform ATRA.⁴⁸ Similar kind of work was reported employing phenothiazine by de Alaniz (2015)⁴⁹, perelyne diimides (PDI) by Konig (2014)⁵⁰ and Eosin Y by Zeitler (2010)⁵¹.

Scheme 1.6. Nitrogen-containing functional group interconversion

Nitrogen functional group interconversion has a great impact on organic chemistry. After the emergence of visible-light photocatalysis, it has been extensively employed to reduce nitrogen-containing functional groups (**Scheme 1.6**). In 2004, Hirao *et al.* have developed the nitrobenzene reduction to aniline where hydrazine was used as a reductant.⁵² This is also can be achieved using Eosin Y, reported by Gazi in 2011⁵³. Liu has described a biocompatible reduction of azide to amines in presence of $\text{Ru}(\text{bpy})_3^{2+}$ which goes through aminyl radical.⁵⁴ Moreover, photoredox catalysis has been known to reduce hydrazine and hydrazide using $\text{Ru}(\text{bpz})_3^{2+}$ as a photocatalyst by Zheng.⁵⁵ Yadav and co-workers have described interconversion of aldoximes and amides to their corresponding nitriles in presence of Eosin Y with a catalytic amount of DMF.⁵⁶

1.3.1b Oxidative transformation

In organic synthesis, single-electron oxidation plays a crucial role in the interconversion of functional groups (**Scheme 1.7**). In 1984, Deronzier and Cano-Yelo reported benzyl alcohol oxidation using Ru-complex as a photocatalyst and aryl diazonium as an oxidant.⁵⁷

Scheme 1.7. Photoredox catalysed oxidative transformation

Recently, a metal-free aerobic alcohol oxidation method has been introduced by Das group, that features 9-florenone as a organophotoredox catalyst.⁵⁸ Jiao and co-workers have developed photoredox mediated aerobic oxidation of α -haloester to α -ketoester where pyridine derivative acts as an activator to haloester.⁵⁹ In 2012, Xiao and Jørgensen have described the use of molecular oxygen towards photocatalytic oxidation of aryl boronic acids to aryl alcohol.⁶⁰ In this reaction Ru(bpy)_3^{2+} has been used as a photocatalyst along with the reductant *N,N*-diisopropylethylamine (Hünig's base). Stephenson and co-workers have detailed the photoredox mediated deprotection of labile protecting group, such as *para*-methoxybenzyl

(PMB) using iridium complex as a photocatalyst⁶¹ which replaces the previously used stoichiometric oxidant DDQ, CAN.

Additionally, the photocatalytic interconversion of a hydroxyl group to halide was reported by Stephenson in 2012 which includes both primary and secondary alcohol (**Scheme 1.8**).⁶² This method had a great advantage compared to the previously reported procedure, which requires stoichiometric amount of triphenylphosphine along with halogen compounds (CBr_4 , I_2) that generates a hardly-separable waste phosphine oxide.⁶³

Scheme 1.8. Interconversion of alcohol to halide

In summary, photoredox catalysis has a great impact on the numerous functional group interconversion through either single-electron reduction or oxidation. The conversion of key functionalities like, azide, nitro, halide, aldoximes, alcohol and carboxylic acid has been developed successfully under photoredox condition.

1.3.2 Functionalisation of C-H bond

From decades, synthetic chemists have great interest in environmentally benign synthetic methods to form complex molecules. Instead of using pre-functional groups, C-H bond functionalisation is the best procedure to form the C-C or C-X bonds. In literature, there is an evolution of C-H bond activation methods from stoichiometric to catalytic reagents. However, still, it has been a challenging task for organic chemists to find milder activation mode to activate C-H bond selectively. On the rise of photoredox chemistry and previously reported HAT⁶⁴ process, the radical C-H functionalisation has brought a great advancement in organic synthesis.⁶⁵

Scheme 1.9. α -amine C_{sp^3} -H functionalisation

One of the most classic examples is α -amine C_{sp^3} -H activation achieved by Stephenson and co-workers.⁶⁶ Upon visible light irradiation, photocatalysts get excited and helps aliphatic amines to oxidise and produce a radical cation which is very prone towards either HAT or deprotonation with the help of either a hydrogen acceptor or base (**Scheme 1.9**). In the second pathways, the generating nucleophilic radical can be quenched by the involvement of electron-deficient olefins. In the former case, iminium ion is formed by HAT process which can undergo nucleophilic addition. Seminal kind of work i.e. α -amino radical generation has been detailed by several research group: Reiser⁶⁷, Yoon⁶⁸, Nishibayashi⁶⁹ and MacMillan⁷⁰.

In 2010, Stephenson has detailed photoredox mediated aza-Henry reaction where nitroalkane act as a carbanion to perform nucleophilic addition to iminium intermediate.⁷¹ Rueping have reported another two different carbon nucleophile such as enamine⁷² and later on copper acetylides⁷³. In 2012, Rovis *et al.* has described a cooperative mechanism between photoredox catalysis and N-heterocyclic carbene (NHC), in which they have achieved enantioselective acylation of amines.⁷⁴ In addition, MacMillan and co-workers have introduced another radical C_{sp^3} -H functionalisation via dual catalytic chemistry which consists enamine catalysis and photoredox catalysis.

Other than the amine C_{sp3}-H functionalisation, several functional groups with relatively higher oxidation potential such as ether, olefin and alcohol follow a similar pathway. Still, these precursors have few difficulties, but can be overcome by implying HAT catalyst, activated by visible light and photoredox catalysts *in situ* via SET. Different substituted thiols and quinuclidine belong to this category as developed by MacMillan (**Scheme 1.10**). Thiols are known as polarity reversal catalyst (PRC)⁷⁵ and it can efficiently accelerate the HAT process i.e. it has a kinetic effect towards C-H functionalisation. Due to the higher acidic nature of thiol than alcohol, deprotonation happens to generate thiolate which suffers single-electron oxidation by excited photocatalyst and form thiyl radical. This *in situ* generated thiyl radical is electrophilic in nature that helps to abstract hydrogen atom from organic molecules and yields a nucleophilic carbon centered radical. Recently, plenty of example of radical C-H functionalisation methods have been reported following this mechanism, for instances, allylic C_{sp3}-H arylation⁷⁶ and benzylic ether C_{sp3}-H functionalisation⁷⁷.

Though thiol makes the HAT process kinetically favoured, quinuclidine has several advantages over thiol. Firstly, the N-H bond is more stronger in quinuclidinium cation (BDE $\approx$ 100 kcal/mol)⁷⁸ whereas the S-H bond is comparatively weaker than the N-H bond (BDE $\approx$ 87-90 kcal/mol)⁷⁷ with respect to unactivated C_{sp3}-H which makes the process thermodynamically disfavoured. In contrast, quinuclidinium cation has an inherent electrophilic character and the strong bond energy helps the HAT process favourable both thermodynamically and kinetically.⁷⁹ In addition, thiol has a poisoning effect towards transition metal catalysts whereas quinuclidine does not show such activity which gives another precedence to dual catalytic coupling reaction, consists of transition metal catalysis and photoredox catalysis. In recent years, MacMillan and Liu have reported the use of quinuclidine for α -hydroxyl C_{sp3}-H activation⁷⁹ and aldehyde C_{sp2}-H functionalisation.⁸⁰

Scheme 1.10. Example of co-operative catalysis: thiol/quinuclidine HAT and photoredox catalysis

In 2016, Glorius group have shown that benzoate salts also can serve as a hydrogen atom acceptor in the presence of photocatalytic condition due to the high electrophilic nature of benzoate radical along with high O-H bond energy.

They have successfully achieved to functionalize unactivated tertiary C_{sp3}-H⁸¹ and aldehyde C_{sp2}-H⁸² bond consisting trifluoromethylthiol (-SCF₃) with ample productivity (**Scheme 1.11**).

Scheme 1.11. Benzoate salt as HAT catalyst

Later in the same year, Rovis⁸³ and Knowles⁸⁴ have described proton coupled electron transfer (PCET) pathway mediated *in situ* generation of amidyl radical independently. The radical species subsequently suffered intramolecular 1,5-hydrogen atom transfer (**Scheme 1.12**). This procedure has been extended to functionalise γ -C_{sp3}-H bond of substituted carboxylic acids.⁸⁵

Rovis

Knowles

Scheme 1.12. Selected example of amidyl radical for HAT ability

In 2016, Doyle *et al.* observed that *in situ* generated catalytic chlorine radical can act as a potential HAT catalyst during photoredox and nickel dual catalysis (**Scheme 1.13**).⁸⁶

Scheme 1.13. Chlorine radical as HAT catalyst

In organophotoredox catalysis, Fukuzumi *et al.* have developed the usage of acridinium organic dye for aerobic regioselective bromination of aromatic hydrocarbons.⁸⁷ Later C_{sp2}-H cyanation⁸⁸, amination²⁰ have been described by Nicewicz with using acridinium salts.

Fukuzumi

Nicewicz

Nicewicz Alexanian

Scheme 1.14. Acridinium catalysed C-H functionalisation

In 2018, Alexanian and Nicewicz have detailed a strategy for the functionalisation of aliphatic C_{sp3}-H bonds where phosphate salt shows its HAT ability in presence of photocatalytic condition.⁸⁹ Earlier this year, Li in collaboration with Nicewicz reported direct C_{sp2}-H fluorination of arenes using acridinium salt.⁹⁰

Scheme 1.15. Organocatalytic benzylic C_{sp3}-H fluorination and amination

Recently, Chen has developed a photocatalytic metal-free benzylic C_{sp3}-H fluorination using diarylketone as organic photocatalyst.⁹¹ In 2015, Pandey's group have demonstrated organocatalytic intramolecular dehydrogenative coupling between benzylic C_{sp3}-H and amine using dicyanoanthracene as a photocatalyst.⁹²

Scheme 1.16. Minsci type radical addition

Moreover, numerous methods have been developed through radical substitution for arene C_{sp2}-H functionalisation following Minisci type reaction (**Scheme 1.16**).⁹³ Iodonium salt, aryl halide,

acyl halide, alkyl halide, diazonium salt, sulfonyl chloride and boronic acids can serve as an excellent radical precursor via single-electron reduction in photocatalytic condition. Seminal kind of reactivity is observed for the carboxylic acids and trifluoroborate salt also. In presence of a base, deprotonation occurs that leads to the formation of carboxylate anion which is very prone to single-electron oxidation, followed by the decarboxylation generates desired alkyl or aryl radical.⁹⁴ In 2018, Phipps and co-workers have developed enantioselective Minisci-type radical addition to heteroarene by using chiral Brønsted acid and photoredox catalyst.⁹⁵

Fig 1.8. Various C-H bond functionalised by photoredox catalysis

Therefore, with milder reaction conditions and use of catalytic activators have enabled a large variety of C-H activation and functionalisation which have various applications towards synthetic chemistry (**Fig 1.8**).

1.3.3 Cooperative catalysis between transition metal and photoredox catalysis for coupling reaction

Over the past few decades, transition-metal catalysis for cross coupling reaction to form the C-C and C-heteroatom bond has been evolved quite widely. Especially, nickel catalysed coupling reactions have achieved to provide a large number of C-C bond forming protocols developed by different research groups (Negishi, Stille, Hiyama, Suzuki-Miyaura, Kumada and others).⁹⁶ Photoredox catalysts also can take part in synergistic chemistry with transition metal catalysts due to its capability to modulate the oxidation state of other substances through SET. Till now researchers have observed nickel (Ni), cobalt (Co), palladium (Pd), gold (Au), copper (Cu), chromium (Cr) can be merged with photoredox catalysts for the cross-coupling reaction.⁹⁷⁻¹⁰⁰

The coupling reactions governed by transition metal consists of three fundamental steps: firstly, oxidative addition then transmetalation, followed by reductive elimination. In the catalytic cycle, the oxidation state of the transition metal catalyst varies between M(II) to M(IV) or M(0) to M(II). With the development of photoredox catalysts which have an affinity towards radical, opens a new window of oxidation state variation M(I) to M(III) that have a great impact in coupling chemistry.

Fig 1.9. Comparison between metallaphotoredox catalysis and transition metal catalysed coupling reaction

1.3.3a Cooperative catalysis between metal photoredox and transition metal catalysis

In 2007, Akita and co-workers have developed photocatalyst and palladium mediated Sonogashira coupling under Xe-lamp irradiation.¹⁰¹ A few years later, Sanford has introduced C-H arylation using aryldiazonium salt in presence of both palladium catalyst and photoredox catalyst.¹⁰² They have also reported trifluoromethylation of boronic acids merging photoredox catalyst and copper catalyst under visible light irradiation.¹⁰³ Glorius group has achieved to combine gold catalysis with photoredox catalysis for oxyarylation and aminoarylation of alkene.²² Later Hashmi and co-workers have synthesized a gold complex that can act as a photoredox catalyst and helps C-C bond formation via cross-coupling reaction.¹⁰⁴ Seminal works have been reported by Toste using photoredox/gold catalysis¹⁰⁵, Rueping employing photoredox/palladium catalysis¹⁰⁶. In addition to the cooperative catalysis, a dual copper/photocatalytic Chan-Lam coupling between amines together with aryl boronic acids were discovered by Kobayashi.¹⁰⁷

In 2014, MacMillan was the first to introduce dual catalytic decarboxylative cross-coupling to form C_{sp3}-C_{sp2} bond by combining photoredox and nickel catalysis.¹⁰⁸ Single-electron transfer from photosensitizer to Ni(II) for the generation of Ni(I) species and oxidative addition of *in situ* generated radical are the key steps in this metallaphotoredox transformation. At first, they reported the use of aryl halide and later this method has been extended for vinyl halides¹⁰⁹ and alkyl halides¹¹⁰ (**Scheme 1.17**).

MacMillan *et al.* also have discovered a unique way to form C-X bond merging transition metal catalysis and photoredox catalysis, for instances, they have successfully achieved aryl ethers synthesis through C-O bond formation using nickel and photocatalyst (**Scheme 1.18**).¹¹¹ This reaction mechanism consists of a nickel alkoxide reductive elimination step.

Scheme 1.17. Metallaphotoredox decarboxylative cross-coupling

By conducting a series of studies Hillhouse has shown that the reductive elimination of Ni(II) alkoxide complexes don't occur in ambient or high temperature, the conversion requires less stable Ni(III) alkoxide complexes.¹¹²⁻¹¹³ Moreover, the computational studies show that reductive elimination process of Ni(II) alkoxide complexes is endothermic, in

Fig 1.10. Energy diagram of reductive elimination for metal alkoxide complexes¹¹¹

contrast, for Pd, Pt the elimination step is exothermic (**Fig 1.10**).¹¹⁴ The oxidation potential of employing photocatalyst is high enough for the generation of Ni(III) species and it's noteworthy that the photocatalysts' role is not only the Ni(II) oxidation but also it takes part in single-electron reduction of Ni(0) from Ni(I) for closing the cycle.

Scheme 1.18. Photoredox and metal catalysed C-heteroatom coupling

The discovery of this method has enacted a new era of C-X bond formation where the use of sacrificial oxidant or reductant is not required.

Previously reported C-N bond forming reaction by palladium or copper catalysis such as Buchwald-Hartwig amination and Ullmann reaction requires relatively higher (>100 °C) temperature. In 2016, MacMillan has succeeded in developing a cross-coupling reaction to form aryl C_{sp2}-N bond in ambient temperature by employing iridium photoredox catalysts along with ligand-free air-stable nickel catalysts (**Scheme 1.19**).¹¹⁵ The mechanistic rationale follows a similar pathway like cross-coupling between aryl bromide and alcohol. The reductive elimination step of Ni(III) amine complex is very sluggish. To facilitate the sluggish reaction rate, they have used small amount of the [Ir] catalyst (0.02 mol%). Seminal work has been reported by Johannes and co-workers with broadening of amine substrate scope to primary aryl amines.¹¹⁶

C-S cross-coupling has been explored comparatively lesser cases than the C-O and C-N bond because the thiol has a higher affinity towards transition metal and form a relatively stronger bond than the alkoxy or amine, which makes the C-S coupling challengeable. In the same year, Johannes *et al.* have overcome all those difficulties and developed a metallaphotoredox catalysed cross-coupling between aryl iodides and thiols to generate C_{sp2}-S bond by using nickel catalyst with photocatalyst.¹¹⁷

In this reaction radical addition to Ni(I) occurs first followed by the single electron oxidation, prior to the aryl iodide oxidative addition steps, that is the main difference from C-O and C-N bond forming coupling reaction. Additionally, Manolikakes has described a cross-coupling reaction with aryl iodides and sulfinic acids merging visible light photoredox catalyst and nickel catalyst.¹¹⁸ In 2015, Xiao and co-workers have a detailed C-P bond forming method utilising photoredox and nickel dual catalysis in ambient temperature.¹¹⁹

C-N bond formation

C-S bond formation

C-P bond formation

Scheme 1.19. Examples of C-X bond forming reaction by transition metal/photoredox dual catalysis

Therefore, for cooperative photoredox/nickel catalysis the *in situ* generated radical undergo radical addition to Ni(II) complex to form Ni(III) complex followed by thermodynamically favourable reductive elimination. A large variety of radical precursors was reported by different researchers. One early example of such functionalities is carboxylic acids introduced by MacMillan, which is abundant in natural products (**Scheme 1.20**). It can form carbon-centered radical through deprotonation followed by single-electron oxidation in presence of strong oxidising catalyst followed by decarboxylation. Several aryl, alkyl and vinyl halides are found to be potential coupling partner, making this dual catalytic method truly useful in synthetic

organic chemistry.¹⁰⁸ Moreover, other radical precursors and coupling partners have been synthesized, such as silicate^{120,121} (Molander and Fensterbank), Hantzsch ester derivative^{122,123} (Molander and Nishibayashi), trifluoroborate¹²⁴ (Molander) or alcohol functionalised oxalate ester¹²⁵ (MacMillan).

Scheme 1.20. Metallaphotoredox mediated C-C bond formation

In 2016, MacMillan and co-workers have discovered a triple catalytic cross-coupling reaction which contains photoredox catalysis, nickel catalysis and hydrogen atom transfer catalysis for the formation $\text{C}_{\text{sp}2}\text{-C}_{\text{sp}3}$ and $\text{C}_{\text{sp}3}\text{-C}_{\text{sp}3}$ bond.¹²⁶⁻¹²⁷ In this reaction the photocatalyst is not involved directly to activate the substrate and generate the radical, instead, it provides an activated hydrogen atom transfer species (quinuclidinium radical cation) which takes up a

hydrogen atom from the substrate and provides alkyl radical to be suffered addition to Ni(II) complex. Lei and co-workers have described metallaphotoredox mediated halide cross-coupling by the reductive generation of a radical fragment.¹²⁸ Seminal cross-electrophilic coupling has been reported by MacMillan where they have utilised organosilane to activate the bromide substrate.¹²⁹

1.3.3b Dual catalysis with organophotoredox and transition metal catalysts

Molander and co-workers have introduced dual catalysis by merging organophotoredox catalyst 4CzIPN and nickel catalyst using 1,4-dihydropyridines as radical precursor to couple with heteroaryl bromide (**Scheme 1.21**).¹²² The role of the organophotoredox catalysts is similar to transition metal photocatalysts. It helps the Ni(I) complex to convert Ni(0) by single-electron reduction which is prone to radical addition or oxidative addition. Later in 2017, Doyle and Rovis have reported enantioselective desymmetrisation of cyclic *meso*-anhydrides employing Ni catalyst and organophotoredox catalyst.¹³⁰ Earlier this year, a organophotoredox/nickel dual catalytic deaminative arylation has been described by Molander by employing Katritzky salt and aryl halides.¹³¹ Apart from that, this group have detailed the formation of non-classical arylation and acylation of carbohydrates to synthesize C-glycosides involving dual organophotoredox and nickel catalysis.¹³² In 2016, Zhang group have introduced a cross-coupling reaction to form C_{sp2}-C_{sp3} bond via decarboxylative arylation with aryl halide by merging organophotoredox and nickel catalyst.¹³³

Scheme 1.21. Organophotoredox/nickel dual catalysis

Therefore, the use of organophotoredox catalyst has a great advantage over metal photoredox catalysts. For example, the reaction condition became milder and inexpensive. However, the evaluation organophotoredox/transition metal dual catalysis has not been studied extensively due to the comparatively lower stability and they experienced several side reactions.

1.3.4 Photocatalytic organic transformation via electron donor-acceptor complex

The concept of donor-acceptor complex was introduced by Robert Mulliken more than 50 years ago and it was one of the greatest contributions to chemistry to have the idea of such molecular complexes.¹³⁴⁻¹³⁵ In 1991, Hall and co-workers have developed a cycloaddition reaction of vinyl carbazole and its dienophile partner which goes through an electron donor-acceptor (EDA) complex intermediate.¹³⁶ Later Kochi has detailed about the reactivity of EDA complexes and its mechanistic underpinnings.^{25, 137} The reactivity of the EDA complexes for organic

transformation was first reported by Melchiorre in 2013 (**Scheme 1.22**).¹³⁸ They have developed stereoselective α -alkylation of aldehydes by utilising chiral secondary amine under visible light irradiation. Initially, in this reaction, an enamine complex is generated with aldehyde and secondary amine which acts as an electron donor moiety.

Scheme 1.22. Photocatalytic α -alkylation of aldehyde via donor-acceptor complex

Upon addition of acceptor molecule produces a coloured intermediate known as donor-acceptor complex. In presence of light ($h\nu$) enamine donates an electron to acceptor and assists to dissociate the leaving group followed by the radical-radical coupling that provides the desired stereoselective product. To expand the EDA concept, they have demonstrated several examples of organic transformation, such as metal-free aromatic perfluoro alkylation²⁶, α -alkylation to cyclic ketone¹³⁹, γ -alkylation to enal¹⁴⁰⁻¹⁴¹. In 2017, Aggarwal group have developed photocatalytic decarboxylative borylation using *N*-hydroxyphthalimide ester as the photolabile protecting group and bis(catecholato)diboron as a boronating agent (**Scheme 1.23**).¹⁴²

In this case mixture of phthalimido ester and diboron acts donor-acceptor complex. Seminal work has been reported by the same research group by using dihydropyridine (DHP) as a

photolabile group.¹⁴³ They have also described the functionalisation of primary by deamination using 2,4,6-triphenylpyrylium as an activator.¹⁴⁴

Scheme 1.23. Decarboxylative borylation via EDA complex

Glorius *et al.* have used the similar activating group for deaminative borylation¹⁴⁵, deaminative addition to indole¹⁴⁶. Earlier this year, [5+1] annulation has been reported for the synthesis of fluoroalkyltriazene which involves the formation of EDA complex.¹⁴⁷ Nowadays, the use of EDA complexes has been gradually increasing because of its mild and catalyst-free condition.

In summary, the ability to regulate redox profile gives a great flexibility to photoredox catalysts to design the reaction. The dual catalysis consisting of transition metal and photoredox catalysts has advantages not only the generation of radical species but also the light-harvesting catalyst provides a unique environment in the reaction condition through which highly reactive oxidation state is easily accessible in the catalytic cycle. By implying the available catalytic manifolds, chemists can achieve many challenging organic transformations to form valuable building blocks which are currently not possible by reported methodologies.

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Chapter 2

Metal-Free Visible Light Photoredox Enables Generation of Carbyne Equivalents via Phosphonium Ylides C-H Activation

Abstract: Carbyne, an interesting synthetic intermediate, has recently been generated from hypervalent iodine precursors via photoredox catalysis. Given the underexplored chemistry of carbyne due to the paucity of carbyne sources, we are intrigued to discover a new source for this reactive species from classical reagents - phosphonium ylides. Our novel strategy employing phosphonium ylides in an olefin hydrocarbonation reaction features a facile approach for constructing carbon-carbon bond through a metal-free and benign reaction condition. Moreover, the hydrocarbonation products were delivered in highly regioselective manner.

2.1 Introduction

Conventionally, in organic structures, a carbon atom with lack of valences are categorized into 4 common classes, namely, carbocation, radical, carbene and carbanion. Since 1967, the interesting carbyne intermediate, which would belong to the 5th class, was discovered by Strausz in a decomposition reaction of diethyl mercurybisdiazoacetate.¹⁻³ This species contains 3 non-bonding electrons and appeared to be so reactive that its chemistry has not been widely established. Until earlier this year, Suero and co-workers reported a convenient access to diazomethyl radical, which is a direct equivalent to carbyne species, via the use of hypervalent iodine and photoredox chemistry (**Fig. 2.1a**).⁴ In line with our interest in utilizing ylides in single electron transfer processes, we propose that mono-substituted stabilized phosphonium ylides could undergo C-H activation to form ylide radicals, which would be a new synthetic equivalent of carbyne. In this article, we report the reaction between the ylides and activated olefins to form a hydrocarbonation-like product under that novel mechanism.

In recent years, olefins have been employed as a valuable synthon for synthesis due to their ubiquitous occurring in nature and chemical industry. Atom transfer radical addition (ATRA) reaction is a classical choice to forge new carbon-carbon bond from alkene. Seminal work done by Stephenson⁵, Reiser⁶⁻⁷, Melchiorre⁸, and Martin⁹ on photoredox catalysis together with Severin's work¹⁰⁻¹² on ruthenium catalysis has brought ATRA to a great advance. Liu's work on reductive olefin hydrocarbonation via nickel catalysis also offers a highly practical alternative for carbon-carbon bond formation from olefins.¹³ Additionally, since 2014, independent work done by Baran and Shenvi has revealed the possibility of radical formation from electron rich olefins via silane reduction with iron, manganese or cobalt catalysts.¹⁴⁻¹⁹ Furthermore, the new trend of methodology development using inactivated olefins as substrates for carbon-carbon bond formation has been blooming over the past few years thanks to great contribution from other groups.²⁰⁻²⁵

Fig. 2.1 Overview of reported carbyne chemistry, anti-Markovnikov HX addition, ylide chemistry and our strategy

With the rise of visible light photoredox catalysis,²⁶⁻²⁸ its application to functionalize alkenes was demonstrated by several groups. Nicewicz and co-workers pioneered on anti-Markovnikov addition of olefins by utilizing Acridinium photosensitizers since 2012 (**Fig. 2.1b**).²⁹⁻³² The catalyst's high oxidation potential ($> 2.0\text{V}$ vs SCE) suffices single electron oxidation process of several alkenes, leading to the attack of various nucleophiles such as alcohols³³, amines³⁴, carboxylate³⁵ and halides³⁶. The work was subsequently extended to olefin anti-Markovnikov hydration by Lei and co-workers.³⁷ Very recently, Huang *et al.* also demonstrated [4+2] cycloaddition of styrene using similar Acridinium photosensitizer.³⁸

Initially, we questioned whether the cationic radical intermediate resulted from olefin single electron oxidation would be vulnerable to a carbon nucleophile. In that case, a useful carbon-carbon bond formation could be developed. Our tremendous effort turned out unsuccessful while employing “hard” nucleophiles such as enolates or other organometallic reagents, presumably due to low stability of the organophotocatalyst under the reaction conditions. When we turned our attention to phosphonium ylides, the classical carbon nucleophiles,³⁹⁻⁴⁰ our initial trials achieved a remarkable success. In precedent literature, the attack of the ylides to electron deficient olefins was reported to form the new elongated ylide through trivial Michael type addition (**Fig. 2.1c**).⁴¹ In our reaction, with the carbyne radical involvement subsequently disclosed, the final product is no longer a phosphorane, due to phosphine cleavage via *in situ* reduction (**Fig. 2.1d**). To the best of our knowledge, there is only one recent example of the reaction between ester-stabilized ylides and olefin under photoredox condition, reported by Miura and Murakami.⁴² It was proposed that the formation of alkyl radical from the phosphonium salt using Iridium photocatalyst is the key step in the mechanistic pathway.

2.2 Results and discussion

Prime investigation with model substrate **2.1a** and **2.2a** revealed the successful carbon-carbon bond formation when using thiol as hydrogen atom transfer (HAT) catalyst and Hantzsch ester as hydride donor. A wide range of aromatic as well as aliphatic thiols was found to catalyse the reaction (**Entry 1-4**). Among them, thiophenol was chosen as the best catalyst due to its simplicity and high efficiency. Subsequently, some other hydride sources were evaluated in place of Hantzsch ester. However, diminished yields were obtained in all the cases (**Entry 5-8**). Solvent screening (see Supporting Document) showed that chlorinated non-polar solvent such as DCM or DCE is the best candidate.

Table 2.1 Selected results for condition optimisation

Entry	Thiol catalyst (10 mol%)	Hydride source (1.2 equiv)	Results ^a
1	T1	H1	57%
2	T2	H1	51%
3	T3	H1	20%
4	T4	H1	24%
5	T1	H2	NR.
6	-	H3	49%
7	T1	H4	ND.
8	T1	H5	ND.
9	-	H1	NR.
10	T1	-	NR.
11 ^b	T1	H1	NR.
12 ^c	T1	H1	NR.
13 ^d	T1	H1	63%

All reactions were carried out under inert atmosphere, with 0.1 mmol of **2.1a** and 0.3 mmol of **2.2a** in dry DCM (0.1 M). 9-Mesityl-10-methylacridinium tetrafluoroborate (5 mol%) was used as photosensitizer in all experiments. (a) Yields were determined from the crude reaction mixture by ¹H-NMR using 1,3,5-trimethoxybenzene as an internal standard. (b) without photosensitizer. (c) without light irradiation. (d) diluted concentration: 0.025M of **2.1a**, isolated yield was reported. NR. no reaction. ND. not determined, complex mixture.

The conversion of phosphonium ylide **2.1a** substrate was almost complete in the majority of trials and the frequent side product observed results from the reduction of **2.1a** to acetophenone.⁴³⁻⁴⁴ We were pleased to discover that further diluted reaction concentration slightly helps to improve the yield to desired product (**Entry 13**). Control experiments (**Entry 9-12**) reassured the necessity of all parameters in the optimized condition.

Fig. 2.2 Phosphonium ylide and olefin substrate evaluation. All reactions were carried out under inert atmosphere, with 0.1 mmol of the phosphonium ylides and 0.3 mmol of the corresponding alkenes in dry DCM (0.025 M). 9-Mesityl-10-methylacridinium tetrafluoroborate (5 mol%) was used as photosensitizer in all experiments. Isolated yields were reported. (a) 10 equivalents of alkenes were used instead. Isomeric ratio was determined by analysis of crude ¹H-NMR.

With the optimized reaction condition in hand, we proceeded to evaluate substrate scope of both olefins and phosphonium ylides (**Fig. 2.2**). Generally, in most of the examples, moderate to excellent yield was observed with absolute regioselectivity as determined by crude ¹H-NMR

(the linear form is predominant). Ester stabilized phosphonium ylides (**2.4-2.7**) worked slightly better than ketone counterparts (**2.8-2.23**). This is probably due to slow undesirable Wittig olefination of the expected product with the ylide starting materials. Aliphatic (**2.8-2.10** and **2.18-2.20**) and aromatic substituted ketone stabilized ylides (**2.11-2.17** and **2.21-2.23**) worked equally well. Electronic effect of substituent on the aromatic ring does not significantly affect reaction efficiency.

Fig 2.3 Stern-Volmer plot for fluorescence quenching of each component

In term of olefin substrates, *para*-substituted styrenes gave reasonably good yield despite electronic effect differences (**2.24-2.27**). Additionally, α - and β -disubstituted styrene showed positive reactivity, although low yield was obtained for β -isomer presumably due to steric effect (**2.30-2.33**). Cyclic alkene such as indene could be a viable substrate for the reaction as well (**2.28** and **2.29**). Not only styrene derivatives, but vinyl ether (**2.34** and **2.36**) and allylic trimethylsilane (**2.35**) could also work to some certain extent. Interestingly, terminal alkyne such as phenyl acetylene successfully

reacted, furnishing the formation of disubstituted alkene in decent yield with a mixture of (*Z*) and (*E*) isomers (**2.37**). It is worth to note that the alkene product in this case did not undergo further addition.

Fig 2.4 The fate of radical cation (A) resulted from single electron oxidation of phosphonium ylide

After measuring redox potential, we realized that ylide **2.1a** actually has considerably lower oxidation potential ($E_{\text{ox}} = 1.12\text{V}$ vs SCE) than the alkene partner **2.2a** ($E_{\text{ox}} = 1.97\text{V}$ vs SCE).⁴⁵ The results from fluorescence quenching plot (**Fig. 2.3**) also suggest that among all reaction components, ylide **2.1a** is the most efficient quencher. We therefore propose that **2.1a** might first undergo single electron oxidation by the excited photocatalyst, forming the cationic radical (A) (**Fig. 2.4**). This is in contrast with the mechanism from anti-Markovnikov addition for C-X bond formation by Nicewicz. The reactivity of intermediate (A) has not been reported to date.

We rationalize that it might undergo 3 different pathways (**Fig. 2.4**). Its cationic character could facilitate nucleophilic addition of alkene while its radical character could enable radical addition to alkene. Either pathway will result in a new radical cation intermediate with the ylide hydrogen intact. To our surprise, starting from deuterated ylide **1b**, the obtained hydrocarbonation product does not contain any deuterium (verified by NMR and MS). We hence postulate that the hydrogen in (**A**) is acidic and possibly undergoes a fast proton exchange with the medium. In other words, deprotonation of (**A**) leading to a neutral carbyne radical could happen. Further confirmation by trapping reaction with radical scavenger TEMPO showed the trace of unstable trapping product (**C**) in MS analysis of the reaction mixture.

[a]

[b]

Fig. 2.5 Other labelling experiments with deuterated Hantzsch esters and photoinduced reduction test on the phosphonium ylide

In addition, new peaks account for compound (**D**) was also observed in MS. This explains well for the formation of radical intermediate (**B**) which may undergo HAT process with TEMPO radical (MS peaks for (**D**) was not observed in the normal reaction without TEMPO). Together with the recent work done by Suero and co-workers,⁴ this constitutes one of the rare examples for the formation and reaction of carbyne intermediate equivalent.

Fig. 2.6 Our hypothesised mechanism

To gain more mechanistic insight, we have carried out other deuterium labelling experiments (**Fig. 2.5a**) using different deuterated Hantzsch esters. The results showed that deuterium only ends up at C₂ of product **24d**, in despite of its origin in the Hantzsch ester. This interesting phenomenon could explain that the source of hydrogen at C₄ is from thiol catalyst through HAT, and the deuterium incorporated to final product via reduction with Hantzsch ester, even though detail mechanism of the reduction is unclear. We also tested the probability of this photoinduced reduction between the Hantzsch ester and ylide **1b**, and complete reduction to acetophenone was observed after 12 hours (**Fig. 2.5b**).

With all the information gathered so far, we propose the mechanism for our hydrocarbonation protocol in figure **2.6**. The key step that determines regioselectivity of our protocol is the addition of carbyne radical (**A'**) to olefin. Linear chain isomer was obtained in all cases resulted from stability of secondary radical (**B**).

2.3 Conclusions

In conclusion, a benign method for the addition of phosphonium ylides to electron rich alkenes was developed. The reaction condition is completely metal-free, carrying out at room temperature, utilizing only visible light as activation source. Our reactions gave absolute predictable regioselectivity and synthetically useful yields. Preliminary studies suggest a novel mechanism involving the recently introduced carbyne radical intermediate. The outlook of this study would be the employment of phosphonium ylide as carbyne equivalent in multi-functionalization reactions.

2.4 Experimental section

2.4.1 General Information

All the reactions were carried out in oven-dried glassware under inert atmosphere. All the anhydrous solvents and commercially available chemicals were purchased and used without further purification. Thin layer chromatography (TLC) were performed on Merck 60 F254 precoated silica gel (0.2 mm thickness) to monitor the reactions. TLC were visualized through irradiation with UV light at 254 nm and/or by staining with p-anisaldehyde or basic solution of potassium permanganate. Flash column chromatography was performed to purify the products with distilled technical grade solvents using silica gel 60 (40-60 μ m). High resolution mass spectrometry was recorded on a Waters Q-ToF premierTM machine. ¹H and ¹³C-NMR spectra were recorded on Bruker 400MHz and 500MHz NMR spectrometers. For ¹H-NMR spectra, the chemical shifts are reported as δ in ppm (parts per million), calibrated to the peak of CHCl₃ residue (δ 7.26, singlet) and the coupling constants (J) are reported in Hz. Peak multiplicities are reported as follows: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublet); dt (doublet of triplet); m (multiplet). For ¹³C-NMR spectra the chemical shifts are also reported as δ in ppm (parts per million), calibrated to the peak of CHCl₃ residue (δ 77.00, triplet). All the reactions were irradiated with blue light using 34W Blue LEDs 150 made by Kessil.

2.4.2 Catalytic phosphonium ylide addition to electron rich alkenes

To an oven dried 8 ml vial was charged with 9-mesityl-10-methylacridinium tetrafluoroborate (5 mol %), Hantzsch ester (1.2 equiv.) and ylide substrate (0.1 mmol). The

mixture was dissolved in anhydrous DCM (0.025 M), followed by the addition of thiophenol (10 mol %) and alkene substrate (0.3 mmol). The reaction mixture was subsequently degassed by freeze-pump-thaw technique (three cycles). The reaction vial was then irradiated by using 34W Kessil Blue LEDs (10 cm distance to the light source) and the surroundings temperature was cooled by using USB powered cooling fan. After 12 hours, reaction mixture was concentrated and purified by flash column chromatography (ethyl acetate : hexane).

2.4.3 Synthesis of deuterated Hantzsch esters

1. 1-deuterated diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate

Compound **1** was synthesized according to the reported literature procedure.⁴⁶ In an oven dried round bottom flask, diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (0.25 g, 0.98 mmol) and CD₃OD (3 ml) were mixed and stirred overnight under argon atmosphere. The solvent was evaporated, and the desired compound was obtained as a pale green solid (0.24 g, 96%).

¹H NMR (400 MHz, CDCl₃): δ 4.16 (q, *J* = 7.2 Hz, 4H), 3.26 (s, 2H), 2.19 (s, 6H), 1.28 (t, *J* = 6.8 Hz, 6H).

2. 4,4-dideuterio-2,6-dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine

Compound **2** was synthesized according to the reported literature procedure.⁴⁷ An oven dried round bottom flask was charged with ethyl acetoacetate (1.6 ml, 12.48 mmol, 4 equiv.), d₂-paraformaldehyde (0.1 g, 3.12 mmol, 1 equiv.), ammonium acetate (0.48 g, 6.24 mmol, 2 equiv.) and water (6.5 ml), then the mixture was heated at 86 °C. After 3 hours, the reaction

mixture was allowed to cool down to room temperature and filtered. The precipitate was dried in vacuo to afford the desired compound as yellow solid (0.4 g, 50%).

¹H NMR (400 MHz, CDCl₃): δ 5.13 (s, 1H), 4.16 (q, *J* = 7.2 Hz, 4H), 2.19 (s, 6H), 1.28 (t, *J* = 6.8 Hz, 6H).

3. 1,4,4-trideuterio-2,6-dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine

Compound **3** was synthesized by following the reported literature procedure.⁴⁶ In an oven dried round bottom flask compound **2** (0.1g, 0.39 mmol) and CD₃OD (1 ml) were mixed and stirred for overnight under argon atmosphere. The solvent was evaporated, and the desired compound was obtained as a pale green solid (0.096 g, 97%).

¹H NMR (500 MHz, CDCl₃): δ 4.16 (q, *J* = 7.5 Hz, 4H), 2.19 (s, 6H), 1.28 (t, *J* = 7.0 Hz, 6H).

2.4.4 Solvent evaluation

Entry	Photocatalyst	Co-catalyst	Hydride Donor	Solvent (conc.)	NMR Yields
1	Mes-Acr-Me ⁺	PhSH	Hantzsch ester	DCM (0.1 M)	57%
2	Mes-Acr-Ph ⁺	PhSH	Hantzsch ester	DCM (0.1 M)	49%
3	Mes-Acr-Me ⁺	PhSH	Hantzsch ester	DCE (0.1 M)	10%
4	Mes-Acr-Me ⁺	PhSH	Hantzsch ester	CHCl ₃ (0.1 M)	54%
5	Mes-Acr-Me ⁺	PhSH	Hantzsch ester	MeCN (0.1 M)	-
6	Mes-Acr-Me ⁺	PhSH	Hantzsch ester	THF (0.1 M)	-
7	Mes-Acr-Me ⁺	PhSH	Hantzsch ester	Dioxane (0.1 M)	-
8	Mes-Acr-Me ⁺	PhSH	Hantzsch ester	DMSO (0.1 M)	-
9	Mes-Acr-Me ⁺	PhSH	Hantzsch ester	MeOH (0.1 M)	41%
10	Mes-Acr-Me ⁺	PhSH	Hantzsch ester	DME (0.1 M)	-
11	Mes-Acr-Me ⁺	PhSH	Hantsch ester	PhCF ₃ (0.1 M)	-

2.4.5 TEMPO Trapping Experiment

To an oven dried 8 ml vial was charged with 9-mesityl-10-methylacridinium tetrafluoroborate (1 equiv.), Hantzsch ester (1.2 equiv.), chloro substituted ylide substrate **1b** (0.05 mmol) and TEMPO (1.2 equiv.). The mixture was dissolved in anhydrous DCM (0.025 M), followed by the addition of thiophenol (5 mol%) and alkene substrate (0.3 mmol). The reaction mixture was subsequently degassed by freeze-pump-thaw technique (three cycles). The reaction vial was then irradiated by using 34W Kessil Blue LEDs (10 cm distance to the light source) and the surroundings temperature was cooled by using USB powered cooling fan. After 8 hrs the blue LEDs was turned off and the reaction mixture was taken for mass spectrometry analysis (using MeOH solvent, ESI method).

Fig. 2.7. Analysis of mass spectrum of the reaction mixture with TEMPO scavenger

Fig. 2.8. Comparison of mass spectra of the reaction mixture with and without TEMPO scavenger

2.4.6 Synthesis of Deuterium Labelled Ylide (1b)

Compound **1b** was synthesized according to the reported literature.⁴⁸ In an oven dried round bottom flask 2-bromo-4'-chloroacetophenone (0.5 g, 2.14 mmol) was dissolved in toluene (15 ml), then triphenylphosphine (0.56 g, 2.14 mmol) was added to it and stirred for overnight under argon atmosphere. The white phosphonium salt was filtered and washed with diethyl ether and dried under vacuum. Dried phosphonium salt was dissolved in $\text{D}_2\text{O}:\text{THF}$ (2:1) and heated at $50\text{ }^\circ\text{C}$ for 2 hours. Then the solution was cooled to room temperature and the solvent was evaporated in vacuum. Then the deuterated phosphonium salt was dissolved in $\text{D}_2\text{O}:\text{MeOH}$ (1:1) and 2 N NaOH solution was added dropwise and stirred for 10 minutes. The reaction mixture was extracted with DCM and the organic layer was extracted with saturated NaCl solution. Then the organic layer was dried with anhydrous sodium sulfate and evaporated to dryness. The desired compound **1b** was obtained as white solid.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.89 (d, $J = 8.05\text{ Hz}$, 2H), 7.72-7.68 (m, 6H), 7.58-7.55 (m, 3H), 7.49-7.46 (m, 6H), 7.30 (d, $J = 8.1\text{ Hz}$, 2H).

2.4.7 Fluorescence Quenching Studies

Fluorescence quenching studies were performed on RF-5301PC Spectro-fluorophotometer. The experiments were carried out by mixing a 5×10^{-4} M solution of 9-mesityl-10-phenylacridinium (Mes-Acr⁺-Me) tetrafluoroborate in degassed dichloromethane with various amount of quencher in quartz cuvette. All the solutions were irradiated at $\lambda = 455$ nm and the emission intensity at $\lambda = 504$ nm was observed. The samples were degassed first with nitrogen for 15 minutes then the emission spectrum of the sample was collected.

a. Stern-Volmer Quenching Studies with Alkene

Increasing amounts of alkene were added to a solution of 9-mesityl-10-phenylacridinium (Mes-Acr⁺-Me) tetrafluoroborate in dichloromethane. After each addition, the absorption and emission spectrum of the solution were recorded.

Fig. 2.9. Emission spectrum of Mes-Acr⁺-Me while changing the concentration of styrene

b. Stern-Volmer Quenching Studies with Ylide

Increasing amounts of alkene were added to a solution of 9-mesityl-10-phenylacridinium (Mes-Acr⁺-Me) tetrafluoroborate in dichloromethane. After each addition, the absorption and emission spectrum of the solution were recorded.

Fig. 2.10. Emission spectrum of Mes-Acr⁺-Me while changing the concentration of ylide **1b**

a. Stern-Volmer Quenching Studies with Hantzsch Ester

Increasing amounts of alkene were added to a solution of 9-mesityl10-phenylacridinium (Mes-Acr⁺-Me) tetrafluoroborate in dichloromethane. After each addition, the absorption and emission spectrum of the solution were recorded.

Fig. 2.11. Emission spectrum of Mes-Acr⁺-Me while changing the concentration of Hantzsch ester

b. Stern-Volmer Quenching Studies with Thiol

Increasing amounts of alkene were added to a solution of 9-mesityl10-phenylacridinium (Mes-Acr⁺-Me) tetrafluoroborate in dichloromethane. After each addition, the absorption and emission spectrum of the solution were recorded.

Fig. 2.12. Emission spectrum of Mes-Acr⁺-Me while changing the concentration of thiophenol

Fig. 2.13. Overall Stern-Volmer plot

2.4.8 Characterization of compounds

Compound 4.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), ethyl 2-(triphenyl-λ⁵-phosphaneylidene)acetate (34.8 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 μl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography gave compound 4 as a colourless oil (18.7 mg, 84%).

¹H-NMR (400 MHz, CDCl₃): δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 2.59 (t, *J* = 7.4 Hz, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.91 (quint, *J* = 7.7 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

¹³C-NMR (100 MHz, CDCl₃): δ 173.7, 158.0, 133.6, 129.5, 113.9, 60.3, 55.3, 34.3, 33.7, 26.9, 14.3.

HRMS: *m/z* for C₁₃H₁₈O₃ [M+H]⁺ calculated 223.1334, found 223.1335.

Spectra matches with reported literature.⁴⁹

Compound 5.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), *tert*-butyl 2-(triphenyl-λ⁵-phosphaneylidene)acetate (37.6 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 μl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **5** as a colourless oil (15.5 mg, 62%).

¹H-NMR (500 MHz, CDCl₃): δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.21 (t, *J* = 7.4 Hz, 2H), 1.86 (quint, *J* = 7.6 Hz, 2H), 1.44 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ 173.1, 158.0, 133.9, 129.5, 113.9, 80.2, 55.4, 35.0, 34.3, 28.2, 27.1.

HRMS: *m/z* for C₁₅H₂₂O₃ [M+H]⁺ calculated 251.1647, found 251.1641.

Spectra matches with reported literature.⁵⁰

Compound 6.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), benzyl 2-(triphenyl- λ^5 -phosphaneylidene)acetate (41.0 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **6** as a colourless oil (18.1 mg, 71%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.38-7.30 (m, 5H), 7.28-7.25 (m, 2H), 7.20-7.14 (m, 3H), 5.11 (s, 2H), 2.64 (t, $J = 7.4$ Hz, 2H), 2.38 (t, $J = 7.4$ Hz, 2H), 1.97 (quint, $J = 7.7$ Hz, 2H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 173.4, 141.4, 136.2, 128.7, 128.6, 128.5, 128.3, 126.1, 66.3, 35.2, 33.7, 26.6.

HRMS: m/z for $\text{C}_{17}\text{H}_{18}\text{O}_2$ $[\text{M}+\text{H}]^+$ calculated 255.1385, found 255.1384.

Spectra matches with reported literature.⁵¹

Compound 7.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), benzyl 2-(triphenyl- λ^5 -phosphaneylidene)acetate (41.0 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **7** as a colourless oil (22.2 mg, 78%).

¹H-NMR (400 MHz, CDCl₃): δ 7.38-7.30 (m, 5H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.11 (s, 2H), 3.78 (s, 3H), 2.58 (t, *J* = 7.4 Hz, 2H), 2.36 (t, *J* = 7.4 Hz, 2H), 1.94 (quint, *J* = 7.6 Hz, 2H).

¹³C-NMR (125 MHz, CDCl₃): δ 173.5, 158.0, 136.2, 133.5, 129.5, 128.7, 128.3, 113.9, 66.3, 55.4, 34.3, 33.7, 26.8.

HRMS: *m/z* for C₁₈H₂₀O₃ [M+H]⁺ calculated 285.1491, found 285.1494.

Compound 8.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 3,3-dimethyl-1-(triphenyl-λ⁵-phosphaneylidene)butan-2-one (36.0 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 μl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **8** as a colourless oil (9.8 mg, 48%).

¹H-NMR (500 MHz, CDCl₃): δ 7.29-7.26 (m, 2H), 7.19-7.16 (m, 3H), 2.60 (t, *J* = 7.4 Hz, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 1.89 (quint, *J* = 7.3 Hz, 2H), 1.11 (s, 9H).

¹³C-NMR (125 MHz, CDCl₃): δ 215.9, 142.0, 128.6, 128.4, 126.0, 44.2, 35.7, 35.3, 26.5, 25.5.

HRMS: *m/z* for C₁₄H₂₀O [M+H]⁺ calculated 205.1592, found 203.1590.

Spectra matches with reported literature.⁵²

Compound 9.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 3,3-

dimethyl-1-(triphenyl- λ^5 -phosphaneylidene)butan-2-one (36.0 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **9** as a colourless oil (13.8 mg, 59%).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.08 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 3.78 (s, 3H), 2.54 (t, J = 7.4 Hz, 2H), 2.48 (t, J = 7.1 Hz, 2H), 1.85 (quint, J = 7.3 Hz, 2H), 1.11 (s, 9H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 215.9, 157.9, 134.1, 129.4, 113.9, 55.4, 44.2, 35.7, 34.4, 26.5, 25.7.

HRMS: m/z for $\text{C}_{15}\text{H}_{22}\text{O}_2$ $[\text{M}+\text{H}]^+$ calculated 235.1698, found 235.1699.

Compound 10.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 3,3-dimethyl-1-(triphenyl- λ^5 -phosphaneylidene)butan-2-one (36.0 mg, 0.1 mmol, 1 equiv.) and 4-methylstyrene (39.5 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **10** as a colourless oil (10.7 mg, 49%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.09-7.05 (m, 4H), 2.56 (t, J = 7.4 Hz, 2H), 2.49 (t, J = 7.1 Hz, 2H), 2.31 (s, 3H), 1.87 (quint, J = 7.3 Hz, 2H), 1.11 (s, 9H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 215.9, 138.9, 135.4, 129.1, 128.4, 44.2, 35.8, 34.9, 26.5, 25.6, 21.1.

HRMS: m/z for $\text{C}_{15}\text{H}_{22}\text{O}$ $[\text{M}+\text{H}]^+$ calculated 219.1749, found 219.1751.

Compound 11.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **11** as a white solid (18.6 mg, 72%).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.85 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.21-7.19 (m, 3H), 2.94 (t, J = 7.2 Hz, 3H), 2.72 (t, J = 7.5 Hz, 2H), 2.08 (quint, J = 7.3 Hz, 2H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 198.9, 141.6, 169.5, 135.4, 129.5, 129.0, 128.6, 128.5, 126.1, 37.7, 35.2, 25.7.

HRMS: m/z for $\text{C}_{16}\text{H}_{15}\text{ClO}$ $[\text{M}+\text{H}]^+$ calculated 259.0890, found 259.0891.

Spectra matches with reported literature.⁵³

Compound 12.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and 4-methylstyrene (39.5 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs

for 12 hrs. Purification by flash column chromatography furnished compound **12** as a white solid (20.7 mg, 76%).

¹H-NMR (500 MHz, CDCl₃): δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.09 (s, 4H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.67 (t, *J* = 7.4 Hz, 2H), 2.32 (s, 3H), 2.05 (quint, *J* = 7.5 Hz, 2H).

¹³C-NMR (125 MHz, CDCl₃): δ 199.0, 139.4, 138.5, 135.6, 135.4, 129.5, 129.2, 128.9, 128.5, 37.7, 34.7, 25.8, 21.1.

HRMS: *m/z* for C₁₇H₁₇ClO [M+H]⁺ calculated 273.1046, found 273.1043.

Compound 13.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl-λ⁵-phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 μl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **13** as a white solid (24.8 mg, 86%).

¹H-NMR (500 MHz, CDCl₃): δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 2.92 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H), 2.03 (quint, *J* = 7.4 Hz, 2H).

¹³C-NMR (125 MHz, CDCl₃): δ 199.0, 158.0, 139.4, 135.4, 133.6, 129.6, 129.5, 128.9, 113.9, 55.3, 37.7, 34.3, 25.9.

HRMS: *m/z* for C₁₇H₁₇ClO₂ [M+H]⁺ calculated 289.0995, found 289.0998.

Compound 14.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and 4-chlorostyrene (36.0 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **14** as a colourless oil (16.4 mg, 56%).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.85 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.3 Hz, 2H), 2.92 (t, J = 7.2 Hz, 2H), 2.67 (t, J = 7.5 Hz, 2H), 2.04 (quint, J = 7.4 Hz, 2H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 198.7, 140.1, 139.6, 135.3, 129.9, 129.5, 129.0, 128.6, 37.5, 34.5, 25.5.

HRMS: m/z for $\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{O}$ $[\text{M}+\text{H}]^+$ calculated 293.0500, found 293.0502.

Compound 15.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(benzofuran-2-yl)-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (42.1 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **15** as a yellow solid (9.3 mg, 35%).

¹H-NMR (500 MHz, CDCl₃): δ 7.69 (d, *J* = 7.8 MHz, 1H), 7.57 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.48-7.44 (m, 2H), 7.32-7.28 (m, 3H), 7.22-7.19 (m, 3H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.12 (quint, *J* = 7.6 Hz, 2H).

¹³C-NMR (125 MHz, CDCl₃): δ 191.3, 155.7, 152.7, 141.6, 128.6, 128.5, 128.3, 127.1, 126.1, 124.0, 123.3, 112.7, 112.6, 38.2, 35.2, 25.7.

HRMS: *m/z* for C₁₈H₁₆O₂ [M+H]⁺ calculated 265.1229, found 265.1231.

Compound 16.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-fluorophenyl)-2-(triphenyl-λ⁵-phosphaneylidene)ethan-1-one (39.8 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 μl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **16** as a white solid (14.8 mg, 61%).

¹H-NMR (500 MHz, CDCl₃): δ 7.94 (t, *J* = 6.9 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.1 Hz, 3H), 7.11 (t, *J* = 8.4 Hz, 2H), 2.94 (t, *J* = 7.2 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.08 (quint, *J* = 7.4 Hz, 2H).

¹³C-NMR (125 MHz, CDCl₃): δ 198.6, 165.8 (d, *J*_{C,F} = 253.0 Hz), 141.7, 133.5, 130.7 (d, *J*_{C,F} = 9.0 Hz), 128.6 (t, *J*_{C,F} = 8.0 Hz), 126.1, 115.7 (d, *J*_{C,F} = 22.0 Hz), 37.7, 35.2, 25.7.

HRMS: *m/z* for C₁₆H₁₅FO [M+H]⁺ calculated 243.1185, found 243.1186.

Spectra matches with reported literature.⁵³

Compound 17.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-fluorophenyl)-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (39.8 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **16** as a white solid (17.7 mg, 65%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.95-7.92 (m, 2H), 7.11 (t, $J = 7.4$ Hz, 4H), 6.83 (d, $J = 8.6$ Hz, 2H), 3.79 (s, 3H), 2.93 (t, $J = 7.2$ Hz, 2H), 2.66 (t, $J = 7.3$ Hz, 2H), 2.04 (quint, $J = 6.9$ Hz, 2H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 198.7, 165.8 (d, $J_{\text{C,F}} = 253.0$ Hz), 158.0, 133.6 (d, $J_{\text{C,F}} = 15.0$ Hz), 130.7 (d, $J_{\text{C,F}} = 9.0$ Hz), 129.5, 115.7 (d, $J_{\text{C,F}} = 21.0$ Hz), 113.9, 55.4, 37.6, 34.3, 26.0.

HRMS: m/z for $\text{C}_{17}\text{H}_{17}\text{FO}_2$ $[\text{M}+\text{H}]^+$ calculated 273.1291, found 243.1288.

Compound 18.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(adamantan-1-yl)-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (43.9 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **18** as a colourless oil (17.5 mg, 62%).

¹H-NMR (500 MHz, CDCl₃): δ 7.29-7.26 (m, 2H), 7.19-7.16 (m, 3H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.45 (t, 7.2 Hz, 2H), 2.03 (br, 3H), 1.87 (quint, *J* = 7.3 Hz, 2H), 1.78-1.66 (m, 12 H).

¹³C-NMR (125 MHz, CDCl₃): δ 215.6, 142.0, 128.6, 128.4, 125.9, 46.4, 38.3, 36.7, 35.4, 35.3, 28.1, 25.2.

HRMS: *m/z* for C₂₀H₂₆O [M+H]⁺ calculated 283.2062, found 283.2063.

Compound 19.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(adamantan-1-yl)-2-(triphenyl-λ⁵-phosphaneylidene)ethan-1-one (43.9 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 μl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **19** as a colourless oil (18.8 mg, 60%).

¹H-NMR (400 MHz, CDCl₃): δ 7.08 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.53 (t, *J* = 7.4 Hz, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.02 (br, 3H), 1.87-1.65 (m, 14H).

¹³C-NMR (100 MHz, CDCl₃): δ 215.6, 157.9, 134.1, 129.4, 113.8, 55.4, 46.4, 38.4, 36.7, 35.2, 34.4, 28.1, 25.5.

HRMS: *m/z* for C₂₁H₂₈O₂ [M+H]⁺ calculated 313.2168, found 313.2170.

Compound 20.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-

(adamantan-1-yl)-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (43.9 mg, 0.1 mmol, 1 equiv.) and 4-methylstyrene (39.5 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **20** as a colourless oil (15.7 mg, 53%).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.09-7.05 (m, 4H), 2.55 (t, $J = 7.4$ Hz, 2H), 2.44 (t, $J = 7.1$ Hz, 2H), 2.31 (s, 3H), 2.02 (br, 3H), 1.85 (quint, $J = 7.3$ Hz, 2H), 1.78-1.66 (m, 12H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 215.6, 138.9, 135.3, 129.1, 128.4, 46.4, 38.4, 36.7, 35.3, 34.9, 28.1, 25.4, 21.1.

HRMS: m/z for $\text{C}_{21}\text{H}_{28}\text{O}$ $[\text{M}+\text{H}]^+$ calculated 297.2218, found 297.2221.

Compound 21.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-methoxyphenyl)-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (41.1 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **21** as a colourless oil (16.1 mg, 63%).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.90 (d, $J = 8.9$ Hz, 2H), 7.29 (t, $J = 7.6$ Hz, 2H), 7.21-7.18 (m, 3H), 6.91 (d, $J = 8.9$ Hz, 2H), 3.86 (s, 3H), 2.93 (t, $J = 7.2$ Hz, 2H), 2.71 (t, $J = 7.4$ Hz, 2H), 2.07 (quint, $J = 7.5$ Hz, 2H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 198.8, 163.5, 141.9, 130.4, 130.2, 128.6, 128.5, 126.0, 113.8, 55.5, 37.5, 35.4, 26.0.

HRMS: m/z for $\text{C}_{17}\text{H}_{18}\text{O}_2$ $[\text{M}+\text{H}]^+$ calculated 255.1385, found 255.1382.

Spectra matches with reported literature.⁵⁴⁻⁵⁵

Compound 22.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-methoxyphenyl)-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (41.1 mg, 0.1 mmol, 1 equiv.) and 4-methylstyrene (39.5 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **22** as a white solid (17.7 mg, 66%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.91 (d, J = 6.5 Hz, 2H), 7.10 (s, 4H), 6.91 (d, J = 8.9 Hz), 3.87 (s, 3H), 2.92 (t, J = 7.3 Hz, 2H), 2.67 (t, J = 7.3 Hz, 2H), 2.32 (s, 3H), 2.05 (quint, J = 7.5 Hz, 2H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 198.9, 163.4, 138.8, 135.4, 130.4, 130.3, 129.1, 128.5, 113.8, 55.5, 37.5, 34.9, 26.1, 21.1.

HRMS: m/z for $\text{C}_{18}\text{H}_{20}\text{O}_2$ $[\text{M}+\text{H}]^+$ calculated 269.1542, found 269.1535.

Compound 23.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-methoxyphenyl)-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (41.1 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **23** as a white solid (20.2 mg, 71%).

¹H-NMR (500 MHz, CDCl₃): δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.11 (d, *J* = 8.6, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H), 3.79 (s, 3H), 2.90 (t, *J* = 7.3 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H), 2.03 (quint, *J* = 7.5 Hz, 2H).

¹³C-NMR (125 MHz, CDCl₃): δ 198.9, 163.4, 157.9, 133.9, 130.4, 130.3, 129.5, 125.4, 113.9, 113.8, 55.5, 55.4, 37.4, 34.4, 26.3.

HRMS: *m/z* for C₁₈H₂₀O₃ [M+H]⁺ calculated 285.1491, found 285.1496.

Spectra matches with reported literature.⁷

Compound 24.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-phenyl-2-(triphenyl-λ⁵-phosphaneylidene)ethan-1-one (38.1 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 μl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **24** as a white solid (14.2 mg, 63%).

¹H-NMR (500 MHz, CDCl₃): δ 7.93 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.22-7.19 (m, 3H), 2.98 (t, *J* = 7.3 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.09 (quint, *J* = 7.5 Hz, 2H).

¹³C-NMR (125 MHz, CDCl₃): δ 200.2, 141.8, 137.1, 133.0, 128.6, 128.6, 128.5, 128.1, 126.0, 37.8, 35.3, 25.8.

HRMS: *m/z* for C₁₆H₁₆O [M+H]⁺ calculated 225.1274, found 225.1271.

Spectra matches with reported literature.⁵⁶

Compound 25.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-phenyl-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (38.1 mg, 0.1 mmol, 1 equiv.) and 4-methylstyrene (39.5 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **25** as a colourless oil (17.9 mg, 75%).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.92 (d, $J = 7.2$ Hz, 2H), 7.54 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.10 (s, 4H), 2.97 (t, $J = 7.3$ Hz, 2H), 2.68 (t, $J = 7.4$ Hz, 2H), 2.32 (s, 3H), 2.06 (quint, $J = 7.5$ Hz, 2H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 200.3, 138.7, 137.1, 135.5, 133.0, 129.2, 128.6, 128.5, 128.1, 37.8, 34.8, 25.9, 21.1.

HRMS: m/z for $\text{C}_{17}\text{H}_{18}\text{O}$ $[\text{M}+\text{H}]^+$ calculated 239.1430, found 239.1433.

Spectra matches with reported literature.⁵⁷

Compound 26.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-phenyl-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (38.1 mg, 0.1 mmol, 1 equiv.) and 4-acetoxystyrene (45.9 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12

hrs. Purification by flash column chromatography furnished compound **26** as a white solid (17.5 mg, 62%).

¹H-NMR (400 MHz, CDCl₃): δ 7.92 (d, *J* = 9.3 Hz, 2H), 7.55 (t, *J* = 9.1 Hz, 1H), 7.45 (t, *J* = 9.8 Hz, 2H), 7.20 (d, *J* = 10.4, 2H), 7.00 (d, *J* = 10.5 Hz, 2H), 2.98 (t, *J* = 9.0 Hz, 2H), 2.71 (t, *J* = 9.2 Hz, 2H), 2.29 (s, 3H), 2.07 (quint, *J* = 9.4 Hz, 2H).

¹³C-NMR (125 MHz, CDCl₃): δ 200.1, 169.8, 149.0, 139.4, 137.1, 133.1, 129.5, 128.7, 128.1, 121.5, 37.7, 34.6, 25.7, 21.2.

HRMS: *m/z* for C₁₈H₁₈O₃ [M+H]⁺ calculated 283.1334, found 283.1337.

Compound 27.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-phenyl-2-(triphenyl-λ⁵-phosphaneylidene)ethan-1-one (38.1 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 μl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **27** as a colourless oil (20.4 mg, 80%).

¹H-NMR (500 MHz, CDCl₃): δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.54 (t, *J* = 7.1 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.67 (t, 7.5 Hz, 2H), 2.04 (quint, *J* = 7.4 Hz, 2H).

¹³C-NMR (125 MHz, CDCl₃): δ 200.3, 157.9, 137.1, 133.8, 133.0, 129.5, 128.6, 128.1, 113.9, 55.3, 37.7, 34.4, 26.0.

HRMS: *m/z* for C₁₇H₁₈O₂ [M+H]⁺ calculated 255.1380, found 255.1381.

Spectra matches with reported literature.⁵⁸

Compound 28.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-phenyl-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (38.1 mg, 0.1 mmol, 1 equiv.) and indene (35.0 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **28** as a white solid (7.1 mg, 30%).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.97 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.20-7.14 (m, 4H), 3.24-3.16 (m, 4H), 3.13-3.07 (m, 1H), 2.67 (dd, J = 15.6, 6.6 Hz, 2H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 199.8, 142.9, 137.2, 133.1, 128.7, 128.1, 126.3, 124.6, 44.4, 39.3, 35.4.

HRMS: m/z for $\text{C}_{17}\text{H}_{16}\text{O}$ $[\text{M}+\text{H}]^+$ calculated 237.1274, found 237.1272.

Compound 29.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and indene (35.0 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **29** as a white solid (9.5 mg, 35%).

¹H-NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4, 2H), 7.25-7.13 (m, 4H), 3.22 (dd, *J* = 15.5, 7.5 Hz, 2H), 3.13 (d, *J* = 7.0 Hz, 2H), 3.10-3.03 (m, 1H), 2.65 (dd, *J* = 15.4, 6.5 Hz, 2H).

¹³C-NMR (125 MHz, CDCl₃): δ 198.6, 142.8, 139.6, 135.5, 129.6, 129.0, 126.4, 124.6, 44.4, 39.3, 35.3.

HRMS: *m/z* for C₁₇H₁₅ClO [M+H]⁺ calculated 271.0890, found 271.0884.

Compound 30.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-phenyl-2-(triphenyl-λ⁵-phosphaneylidene)ethan-1-one (38.1 mg, 0.1 mmol, 1 equiv.) and α-methylstyrene (39.0 μl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **30** as a colourless oil (16.7 mg, 70%).

¹H-NMR (500 MHz, CDCl₃): δ 7.85 (d, *J* = 7.7 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.3 Hz, 3H), 2.90-2.76 (m, 3H), 2.11-1.95 (m, 2H), 1.31 (d, *J* = 6.9 Hz, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ 200.5, 146.6, 137.0, 133.0, 128.6, 128.1, 127.2, 126.3, 39.6, 36.8, 32.6, 22.7.

HRMS: *m/z* for C₁₇H₁₈O [M+H]⁺ calculated 239.1430, found 239.1428.

Spectra matches with reported literature.⁵⁹

Compound 31.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-fluorophenyl)-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (39.8 mg, 0.1 mmol, 1 equiv.) and α -methylstyrene (39.0 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **31** as a colourless oil (12.3 mg, 48%).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.86 (t, J = 6.6 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.20 (d, J = 7.2 Hz, 3H), 7.07 (t, J = 8.4 Hz, 2H), 2.86-2.72 (m, 3H), 2.10-1.94 (m, 2H), 1.31 (d, J = 6.9 Hz, 3H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 198.8, 165.7 (d, $J_{\text{C,F}}$ = 253.0 Hz), 146.5, 133.5, 130.7 (d, $J_{\text{C,F}}$ = 9.0 Hz), 128.6, 127.2, 126.3, 115.7 (d, $J_{\text{C,F}}$ = 22.0 Hz), 39.6, 36.7, 32.6, 22.7.

HRMS: m/z for $\text{C}_{17}\text{H}_{17}\text{FO}$ $[\text{M}+\text{H}]^+$ calculated 257.1336, found 257.1337.

Compound 32.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and α -methylstyrene (39.0 μ l, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **32** as a colourless oil (17.7 mg, 65%).

¹H-NMR (500 MHz, CDCl₃): δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.20 (t, *J* = 7.7 Hz, 3H), 2.79-2.72 (m, 3H), 2.10-1.93 (m, 2H), 1.31 (d, *J* = 6.9 Hz, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ 199.2, 146.5, 139.4, 135.3, 129.5, 128.9, 128.6, 127.2, 126.4, 39.6, 39.7, 32.5, 22.7.

HRMS: *m/z* for C₁₇H₁₇ClO [M+H]⁺ calculated 273.1046, found 273.1045.

Compound 33.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl-λ⁵-phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and β-methylstyrene (38.9 μl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **33** as a colourless oil (5.7 mg, 21%).

¹H-NMR (500 MHz, CDCl₃): δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 6.3 Hz, 3H), 2.93 (dd, *J* = 16.0, 5.2 Hz, 1H), 2.73-2.56 (m, 3H), 2.50-2.41 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ 198.9, 140.4, 139.4, 135.7, 132.5, 129.6, 129.4, 128.9, 128.4, 126.2, 45.0, 43.4, 31.9, 29.8, 20.1.

HRMS: *m/z* for C₁₇H₁₇ClO [M+H]⁺ calculated 273.1046, found 273.1041.

Compound 34.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and 2-methoxypropene (47.9 μ l, 0.5 mmol, 5 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **34** as a colourless oil (13.2 mg, 58%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.91 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 3.43-3.36 (m, 1H), 3.29 (s, 3H), 3.06-3.00 (m, 2H), 1.99-1.79 (m, 2H), 1.18 (d, J = 6.1 Hz, 3H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 199.2, 139.4, 135.5, 129.6, 129.0, 75.9, 56.1, 34.3, 30.7, 19.1.

HRMS: m/z for $\text{C}_{12}\text{H}_{15}\text{ClO}_2$ $[\text{M}+\text{H}]^+$ calculated 227.0839, found 227.0840.

Compound 35.

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl- λ^5 -phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and allyltrimethylsilane (79.5 μ l, 0.5 mmol, 5 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **35** as a white solid (15.1 mg, 56%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.89 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 2.93 (t, J = 7.3 Hz, 2H), 1.74 (quint, J = 7.4 Hz, 2H), 1.42-1.34 (m, 2H), 0.53 (t, J = 8.5 Hz, 2H), -0.02 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ 199.4, 139.4, 135.5, 129.6, 129.0, 38.5, 28.2, 23.9, 16.7, -1.5.

HRMS: m/z for C₁₄H₂₁ClOSi [M+H]⁺ calculated 269.1128, found 269.1128.

Compound 36

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triethyl-λ⁵-phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and ethyl vinyl ether (47.9 μl, 0.5 mmol, 5 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **36** as a white solid (11.6 mg, 51%).

¹H-NMR (400 MHz, CDCl₃): δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 3.51-3.43 (m, 4H), 3.04 (t, *J* = 7.1 Hz, 2H), 2.00 (quint, *J* = 6.4 Hz, 2H), 1.17 (t, *J* = 6.9 Hz, 3H).

¹³C-NMR (100 MHz, CDCl₃): δ 199.0, 139.4, 135.5, 129.6, 128.9, 69.5, 66.2, 35.3, 24.4, 15.3.

HRMS: m/z for C₁₂H₁₅ClO₂ [M+H]⁺ calculated 227.0839, found 227.0834.

Compound 37.

White solid

Colourless oil

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl-λ⁵-phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and ethyl vinyl ether (32.9 μl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs

for 12 hrs. Purification by flash column chromatography furnished compound **37** as a mixture of two isomers (*Z* : *E* = 1.3 : 1, 40%).

¹H-NMR-*trans*- isomer (500 MHz, CDCl₃): δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.24-7.21 (m, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.44 (dt, *J* = 15.9, 6.6 Hz, 1H), 3.88 (dd, *J* = 6.7, 1.2 Hz, 2H).

¹³C-NMR-*trans*-isomer (125 MHz, CDCl₃): δ 196.9, 139.8, 136.9, 135.0, 133.9, 129.9, 129.1, 128.7, 127.7, 126.4, 122.2, 42.8.

¹H-NMR-*cis*- isomer (400 MHz, CDCl₃): δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.38-7.35 (m, 2H), 7.29-7.25 (m, 3H), 6.73 (d, *J* = 11.5 Hz, 1H), 6.02 (dt, *J* = 11.5, 7.1 Hz, 1H), 3.95 (dd, *J* = 7.0, 1.7 Hz, 2H).

¹³C-NMR-*cis*-isomer (100 MHz, CDCl₃): δ 196.8, 136.9, 134.9, 132.5, 129.8, 129.1, 128.7, 128.5, 127.3, 123.6, 38.4.

HRMS: *m/z* for C₁₆H₁₃ClO [M+H]⁺ calculated 257.0733, found 257.0735.

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Chapter 3

Metal-Free Photoredox Mediated Ketone Carbonyl Alkylation for Easy Access to Tertiary Alcohols

Abstract: The presence of quaternary carbon centres along with olefins invaluable organic building blocks makes tertiary alcohol an important objective in organic synthesis. However, traditional routes towards these syntheses have suffered many difficulties including undesired side products, decomposition of the alcohol product due to their vigorous reaction conditions. After the development of photoredox catalysis, the synthetic approach to these bulky alcohols has become easily accessible through its environmentally benign catalytic protocol. In this part, we have established a metal free procedure for intermolecular radical-radical cross coupling involving ketyl radical to produce complex tertiary alcohols in presence of light harvesting photocatalyst. Starting from naturally occurring feedstock starting materials beyond any pre-activation, makes this strategy much more superior towards industrial application.

3.1 Introduction

Tertiary alcohol moiety and their subordinate molecule consisting tertiary C-O bonds are very versatile building blocks in several agrochemicals, natural products and pharmaceuticals (**Fig. 3.1**), such as efavirenz (treatment for AIDS), flutriafol (fungicide), dicofol (pesticide).¹⁻² The conventional routes towards the synthesis of tertiary alcohol are utilising Barbier type reaction condition for carbonyl addition.³ In the past century several researchers have developed different methods to synthesize tertiary alcohol mainly by C-C bond formation involving organometallic reagents and ketones, for instances, organomagnesium (Grignard reagent), organolithium, organocopper, organoaluminium, organozinc and many others.⁴ However, the organometallic reagents are very pyrophoric and unstable upon exposure to air and they cause enolization of ketone substrate due to their high basic character. Furthermore, the use of organometallic reagent is not environmentally benign because of its demand in stoichiometric amounts. In addition, the nucleophilic attack to ketones is quite difficult due to its inherent steric hindrance, also the harsh condition leads to many undesired side products.⁴ Therefore, the synthesis of tertiary alcohol is still a very challenging work with high yield.

Fig. 3.1. Selected examples of naturally occurring and artificial tertiary alcohol

To overcome such challenges, several novel methodologies to produce tertiary alcohol have been reported in the last few years (**Scheme 3.1**). Such as transition metal (copper, nickel, palladium) catalysed reductive cross-coupling between carbonyl derivatives and halide compounds have been introduced.⁵ Moreover, different milder organometallic reagents have been evolved which can be used in aqueous condition, but the usage of the stoichiometric amount couldn't be overruled.^{4, 6-9}

Scheme 3.1. Schematic overview towards tertiary alcohol

Buchwald was the first to report metal catalysed reductive cross-coupling between alkene and ketone but it still needs stoichiometric metal catalyst which is toxic.¹⁰⁻¹¹ Then moving from conventional concepts of stoichiometric reagents to synthesize tertiary alcohol, Krische *et al.* have made a revolutionary discovery inventing reductive coupling between primary or secondary alcohol with olefin nucleophiles by using a catalytic amount of transition metal.¹² The similar concept of using olefin derived nucleophile has been adopted by Buchwald and Liu for their report of copper catalysed enantioselective addition to ketones.¹³ Li and co-workers have detailed ruthenium catalysed alkyl addition to carbonyl.¹⁴ They have utilised aldehyde as carbanion equivalents by converting its polarity using hydrazine (**Scheme 3.2**).

Krische **Buchwald & Liu** **Li** **Scheme 3.2.** Transition metal catalysed alkylation to carbonyls

Beyond the use of charge interaction pathway, people have been reinventing the carbonyl addition reaction by introducing radical concept (**Scheme 3.3**). In 2016, Chi *et al.* have developed organocatalysed reductive coupling between an activated ketone and electron-poor benzyl bromide by using *N*-heterocyclic carbene as a catalyst.¹⁵ This reaction follows a radical mechanism, at first, the activated complex of aldehyde and carbene helps the electron-poor halide to reduce by SET and followed by the debromination that generates the desired benzyl

Chi et al. **Glorius et al.** **Scheme 3.3.** Examples of radical carbonyl alkylation

radical which leads to the product by addition to carbonyl group. Earlier this year, Glorius group has discovered visible light photoredox mediated intermolecular radical addition to carbonyl compounds following hole catalysis.¹⁶ Samarium (II) iodide is known as a single electron reductant for decades. By employing this concept, ketyl radical can be obtained that can participate in C-C bond forming reaction.¹⁷⁻²²

From the last decade, visible-light photoredox catalysis is appearing as one of the best methods for organic transformation. On the rise of this concept, several research groups have developed photoinduced single electron reduction of carbonyl to ketyl radical intermediate which can undergo different transformation (**Scheme 3.4**).

Knowles *et al.*

Rueping *et al.*

Scheme 3.4. Photoredox mediated ketyl radical formation

Proton coupled electron transfer (PCET) approach was first introduced by Knowles, to obtain ketyl radicals intermediates, that can suffer intramolecular cyclisation with imine or olefins.²³⁻

²⁴ In 2015, Rueping group have successfully developed photoinduced single electron reduction of imine and carbonyl substrate.²⁵⁻²⁷ They have revealed that under the activation of ammonium cation act as a hole catalyst, the reduction potential of carbonyl compounds significantly

reduced which facilitates the single electron reduction of carbonyl substances in presence of a wide variety of photoredox catalysts.

In contrast to olefin addition to ketyl radical species, cross-coupling between ketyl radical and other radical is not described so often. The first successful attempt was done by Zhu for the synthesis of nitrogen heterocycles via intramolecular radical-radical cross-coupling.²⁸ Xiao *et al.* have reported intermolecular radical cross-coupling between ketyl radical and alkyl radicals stabilised by α -heteroatom (O,N).²⁹ Recently, this year König and co-workers have described intermolecular cross-coupling between allyl radical derived from allyl bromide and ketyl radical with the use of an excessive amount of reductant.³⁰

Fig. 3.2. Examples of C-H activation by photoredox and HAT catalysis

C-H functionalisation has become a highly important tool to synthesize organic molecule due to its minimal requisition of pre-functionalisation.³¹⁻³³ Macmillan group has reported several C-X and C-C bond forming reaction by developing photocatalytic transient radical generation through C-H bond activation (**Fig. 3.2**).³⁴⁻³⁸ We have questioned whether the reported transient radicals could couple with ketyl radicals to synthesise highly substituted tertiary alcohols and we have successfully developed the method using iridium photocatalyst, according to our conception with complete atom economy. Later we have realised that we can perform the reaction with organic photosensitizer which makes the reaction condition entirely metal-free. Therefore, our new strategy will be metal-free, highly atom economical and sacrificial reductant free, that leads to very mild reaction condition for tertiary alcohol synthesis.

3.2 Results and discussions

Table 3.1 Optimisation of ketone carbonyl alkylation reaction

Entry	HAT catalyst (20 mol%)	Additive (20 mol%)	Solvent (0.1 M)	Results ^a
1	HAT 1	-	Acetone	36%
2	HAT 2	-	Acetone	N.D.
3	HAT 3	K ₂ CO ₃	Acetone	70%
4	HAT 4	K ₂ CO ₃	Acetone	35%
5	HAT 3	K ₂ CO ₃	Acetone : DMA (1:1)	30%
6	HAT 3	K ₂ CO ₃	DMA	90%
7	HAT 3	K ₂ CO ₃	DMF	42%
8	HAT 3	K ₃ PO ₄	DMA	35%
9	HAT 3	LiBF ₄	DMA	32%
10	HAT 3	Li ₂ CO ₃	DMA	40%
11 ^b	HAT 3	K ₂ CO ₃	DMA	N.R.
12	-	K ₂ CO ₃	DMA	3.7
13 ^c	HAT 3	K ₂ CO ₃	DMA	N.R.

Reactions were performed under Ar atmosphere using benzophenone (0.2 mmol) and cyclohexene (1 mmol). ^a

isolated yield, ^b without photocatalyst, ^c reaction performed without any Blue LED. N.R. no reaction, N.D. not determined complex mixture.

We started our study by performing the reaction between benzophenone (**3.2**) as a model carbonyl substrate and cyclohexene (**3.3**) under various conditions (**Table 3.1**). Initially, we took same equivalent of the alkene with benzophenone, but the yield was not good. After examining a few conditions, the alkene loading was increased by five-folds, which assists to improve the chemical yield. Following our previous finding we first used potassium thioacetate (KSAc) as a hydrogen atom transfer (HAT) catalyst, however, the yield was poor (**Entry 1**). We employed several other thiol catalysts for HAT but triisopropylsilane thiol along with potassium carbonate (K_2CO_3) was the best of choices (**Entry 2, 3 & 4**). The use of protic solvent or presence of water gave rise to dimerise product of ketyl radical. Therefore, screening of solvents showed that dimethylacetamide (DMA) gives the highest chemical yield (85%) (**Entry 6**). The use of different alkali metal bases diminishes the yield significantly (**Entry 8, 9 & 10**). Our control experiments confirmed the necessity of all parameters for the reaction.

Therefore, having optimised condition in hand, we focused on synthesizing a library of substrates. Firstly, a wide variety of ketones has been applied in our reaction condition with cyclohexene coupling partner (**Fig. 3.3**). In case of diaryl ketones, the reaction provides good to excellent yield in spite of its steric congestion. However, the steric hindrance plays a key role in determining the yield which was observed for *ortho*-substituted ketone (**3.14**) whether its *meta*-counterpart gives comparatively very high yield (**3.13**). Electron withdrawing substituents such as fluorine (F), chlorine (Cl), trifluoromethyl ($-CF_3$) were expected to give the better yield because these substituents facilitate the single electron reduction process (**3.10, 3.11, 3.13**). Electron donating functionalities like methoxy ($-OMe$), amine ($-NH_2$) give moderate to good yield (**3.15, 3.16**). Despite their stabilising behaviour to ketyl radical intermediates, due to the electron donating ability they tend to increase the energy barrier for ketone reduction which causes the relatively lower yield. However, the reducing power of this

Fig. 3.3. Reactions were performed under Ar atmosphere, ketone (0.2 mmol) and cyclohexene (1 mmol) in dry DMA (0.1 M). 2.5 mol% 3,7-Di(4-biphenyl) 1-naphthalene was used as photosensitizer and 20 mol% of thiol and K_2CO_3 were used in all experiments. Yields were reported after purification by column chromatography. (a) reactions were carried out over 36 hrs.

organo-photocatalyst is so high that it can reduce -OMe substituted ketone easily and gives a very good yield.

Moreover, heteroaryl aryl ketones also performed as very good ketyl radical precursor and yielded moderately despite their electronic character (40%-70%). The unsymmetrical ketone

with one side heterocycle with electron poor (benzothiazole in **3.19**) and electron enriched (thiophene in **3.18**) substituent did not show different effects in reactivity. We have noticed when the substrate contains free -NH proton the yield is diminished significantly (**3.16**, **3.20**).

Fig. 3.4. Reactions were performed under Ar atmosphere, cyclohexene (0.2 mmol) and olefins (1 mmol) in dry DMA (0.1 M). 2.5 mol% 3,7-Di(4-biphenyl) 1-naphthalene was used as photosensitizer and 20 mol% of thiol and K₂CO₃ were used in all experiments. Yields were reported after purification by column chromatography.

We have found that the unsymmetrical ketones consist of an aryl and alkyl group that also can take part in the reaction and produces cross-radical coupling product with longer reaction time. Cyclic alkyl (**3.21**), linear alkyl (**3.23**) and as well as branched alkyl (**3.22**) worked similarly.

These examples significantly expand the variety of ketone substrate scope for the synthesis of tertiary alcohols.

In addition, it is worth to mention that not only the ketone substances, also the aldehyde substrate was used for radical generation and performed the radical-radical cross-coupling with its counterpart and found to be worked very well (**3.24**). The substrate scope expansion of aldehydes is ongoing in our lab.

Subsequently, next, we focused to broaden the substrate scope by employing a different variety of allylic systems (**Fig. 3.4**). Highly conjugated alkene substrate such as cycloheptatriene furnished excellent result (**3.27**), due to the higher stability of the radical species. As well as, the cycloalkenes with different ring sizes produced a very promising result, for example, *cis*-cyclooctene (**3.26**) and cycloheptene (**3.25**). Heterocyclic alkene, such as, dihydropyran, which has polarized double bond, provided the cross-coupling product in regioisomeric mixture because of the tendency of 1,3-allylic rearrangement of the transient allyl radical (**3.29**). Furthermore, we accomplished to widen the substrate scope towards acyclic internal and terminal alkenes for cross-radical coupling (**3.30, 3.31, 3.32**). To our delight, we were able to utilize free hydroxyl containing substrate for our coupling reaction with high yielding (**3.28**). Finally, naturally occurring alkene-containing organic scaffold, for example, γ -terpinene, α -pinene was employed to provide tertiary alcohol which gave moderate yield (**3.33, 3.34**).

A plausible overview of the mechanistic rationale for the ketone carbonyl alkylation is described in figure **3.5**. Upon irradiation by blue LED (400 nm), the light harvesting organocatalyst (**3.1**) get excited to its long-lived triplet excited state ($\tau = 480 \mu\text{s}$).³⁹ Owing very high reduction potential ($E = -1.90 \text{ V vs SCE}$)⁴⁰ the excited photocatalyst has the capability to reduce the ketone substrate by single electron transfer (SET) to give semi-persistent ketyl radical **3.5**

and the photocatalyst converts into an electron deficient radical cationic species, which suffers single electron reductive quenching by *in situ* generated thiolate to form thiyl radical.

Fig. 3.5. Plausible mechanism for ketone carbonyl alkylation

We assume that the role of HAT catalyst can be played by electrophilic thiyl radical, which is certainly capable to abstract hydrogen atom from the allylic C_{sp3}-H bonds (BDE for cyclohexene C-H_{allylic} = 83.2 kcal·mol⁻¹) and produce the transient radical **3.6**.⁴¹ Finally, the radical-radical cross-coupling between two radical species **3.5** and **3.6** provides the desired tertiary alcohol product.

3.3 Conclusion

In conclusion, we have successfully synthesized very challenging bulkier tertiary alcohols by alkylating the carbonyl group in completely metal-free conditions. The reactions progressed through an intermolecular radical cross-coupling between a transient alkyl radical, *in situ* originated from allyl substrate by HAT and a semi-persistent ketyl radical under visible light mediated organo-photoredox catalysis. A wide range of ketone and allyl substrate has been employed in the reaction condition and provides moderate to high yield with different functional group tolerance. One of our previous obstacles has been achieved by reducing aldehyde efficiently. Our approach diminishes the use of stoichiometric sacrificial reductant, expensive transition metal catalysts and the necessity of pre-functionalisation steps.

3.4 Future work

The broad substrate scope with using aldehyde as a ketyl precursor and activation of benzylic and other allylic C_{sp2}-H bonds are undergoing in our lab. Simultaneously, several experiments are being performed to understand the reaction mechanism properly.

During our literature study, we realised that the methods for enantioselective synthesis of tertiary alcohols were reported mostly by using either organometallic reagents or transition metal catalysis together with chiral additives. There is a limited report for photoredox catalysed enantioselective reduction of ketone or imine. The enantioselectivity was achieved by introducing chiral Brønsted acid in the reaction condition. Therefore, we assume that it is doable to synthesize the bulky tertiary alcohol through our method by utilising chiral Brønsted acid.

2.4 Experimental section

2.4.1 General Information

All the reactions were performed in oven-dried vials under inert atmosphere. Anhydrous solvents and commercially available chemicals were bought and used without purifying unless otherwise discussed. Thin layer chromatography (TLC) were performed on Merck 60 F254 precoated silica gel (0.2 mm thickness) to monitor the reactions. TLC were visualized through irradiation with UV light at 254 nm and/or by staining with phosphomolybdic acid or basic solution of potassium permanganate. Silica gel 60 (40-63 μm) was used for column chromatography. ^1H and ^{13}C -NMR spectra were recorded on Bruker 400MHz and 500MHz NMR spectrometers. For ^1H -NMR spectra, the chemical shifts are reported as δ in ppm (parts per million), calibrated to the peak of CHCl_3 residue (δ 7.26, singlet) and the coupling constants (J) are reported in Hz. Peak multiplicities are reported as follows: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublet); dt (doublet of triplet); m (multiplet). For ^{13}C -NMR spectra the chemical shifts are also reported as δ in ppm (parts per million), calibrated to the peak of CHCl_3 residue (δ 77.00, triplet). All the reactions were irradiated with blue light using 34W Blue LEDs 150 made by Kessil.

2.4.2 General procedure

3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%), ketone (0.2 mmol) and potassium carbonate (20 mol%) was mixed in an 8 ml vial in glovebox under Ar atmosphere. Then, DMA (2 mL), allylic substrate (5 equiv) and tri-isopropylsilanethiol (20 mol%) was added to it. Subsequently, it was brought outside of the glovebox and stirred using a magnetic stirrer for 12-36 h under irradiation by 34 W blue LED at room temperature. Then, the light was turned off and water was added to reaction mixture, then the organic layer was extracted by ethyl acetate. Subsequently, the product was purified by flash column chromatography by using Ethyl acetate/Hexane eluent.

2.4.3 Characterisation of compounds

Compound 3.8

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), benzophenone (36.4 mg, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.8 was obtained as white solid (47.6 mg, 90%).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.62-7.61 (m, 2H), 7.60-7.59 (m, 2H), 7.50-7.26 (m, 4H), 7.22-7.14 (m, 2H), 5.99-5.96 (m, 1H), 5.52-5.49 (m, 1H), 3.46-3.45 (m, 1H), 2.23 (s, 1H), 2.03-2.01 (m, 2H), 1.80-1.77 (m, 1H), 1.57-1.45 (m, 3H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 173.9, 158.0, 133.7, 129.8, 113.9, 60.5, 55.4, 34.3, 33.7, 27.0, 14.6.

Compound 3.9

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), 4-methylbenzophenone (39.2 mg, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue

LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.9 was obtained as colourless oil (45.6 mg, 82%).

Product was obtained as a mixture of 2 diastereomers.

¹H-NMR (400 MHz, CDCl₃): δ 7.58-7.56 (m, 1H), 7.47-7.445 (m, 2H), 7.35-7.24 (m, 3H), 7.23-7.06 (m, 3H), 5.96-5.93 (m, 1H), 5.52-5.49 (m, 1H), 3.43-3.40 (m, 1H), 2.28 (s, 3H), 2.16 (s, 1H), 2.05-2.01 (m, 2H), 1.77-1.72 (m, 1H), 1.52-1.42 (m, 3H).

¹³C-NMR (100 MHz, CDCl₃): δ 147.3, 145.8, 144.0, 142.7, 136.1, 135.5, 134.0, 133.5, 129.0, 129.2, 128.3, 128.0, 126.5, 126.5, 126.4, 126.2, 125.0, 125.4, 125.3, 79.5, 79.2, 43.8, 43.7, 25.3, 23.8, 23.8, 22.1, 20.9.

Compound 3.10

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), 4-fluorobenzophenone (40.0 mg, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μl, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μl, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.10 was obtained as colourless oil (49.6 mg, 88%).

Product was obtained as a mixture of 2 diastereomers.

¹H-NMR (400 MHz, CDCl₃): 7.57-7.52 (m, 2H), 7.44-7.40 (m, 2H), 7.33-7.15 (m, 3H), 7.00-6.91 (m, 2H), 5.98-5.94 (m, 1H), 5.47-5.44 (m, 1H), 3.41-3.38 (m, 1H), 2.20 (brs, 1H), 2.00-1.97 (m, 2H), 1.77-1.74 (m, 1H), 1.51-1.40 (m, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ 162.3 (d, J_{CF} = 245 Hz), 162.0 (d, J_{CF} = 244 Hz), 145.9, 144.8, 141.9 (d, J_{CF} = 3.5 Hz), 140.8 (d, J_{CF} = 3.2 Hz), 135.1, 133.9, 128.1, 127.7 (d, J_{CF} = 7.6 Hz),

126.9 (d, $J_{CF} = 7.5$ Hz), 126.5, 126.4, 126.1, 125.9, 125.7, 124.8, 115.2 (d, $J_{CF} = 26.8$ Hz), 115.0 (d, $J_{CF} = 26.7$ Hz), 78.8, 44.2, 44.0, 26.1, 24.8, 23.6, 22.0.

Compound 3.11

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), 4-chlorobenzophenone (43.3 mg, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.11 was obtained as white solid (41.8 mg, 70%).

Product was obtained as a mixture of 2 diastereomers.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.56-7.50 (m, 2H), 7.44-7.38 (m, 2H), 7.33-7.15 (m, 5H), 5.98-5.95 (m, 1H), 5.48-5.43 (m, 1H), 3.40-3.38 (m, 1H), 2.21 (brs, 1H), 2.00-1.98 (m, 2H), 1.76-1.74 (m, 1H), 1.47-1.39 (m, 3H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 144.9, 143.5, 134.6, 132.5, 128.5, 128.3, 127.0, 126.7, 126.2, 125.2, 78.7, 43.4, 25.0, 23.5, 21.8

Compound 3.12

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), 4,4'-dichlorobenzophenone (50.2 mg, 0.2 mmol, 1

equiv.), cyclohexene (101.3 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.12 was obtained as white solid (41.3 mg, 62%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.50 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 7.29-7.23 (m, 4H), 6.02-5.98 (m, 1H), 5.45-5.39 (m, 1H), 3.38-3.34 (m, 1H), 2.08 (s, 1H), 2.04-1.97 (m, 2H), 1.79-1.74 (m, 1H), 1.54-1.43 (m, 3H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 144.9, 143.5, 134.6, 132.5, 132.4, 128.5, 128.3, 127.0, 126.7, 125.2, 78.7, 43.4, 25.0, 23.5, 21.8

Compound 3.13

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), 3-(trifluoromethyl)benzophenone (50.0 mg, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.13 was obtained as colourless oil (53.2 mg, 80%).

Product was obtained as a mixture of 2 diastereomers.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.85-7.80 (m, 2H), 7.64-7.21 (m, 7H), 6.05-6.02 (m, 1H), 5.59-5.39 (m, 1H), 3.51-3.48 (m, 1H), 2.33 (brs, 1H), 2.05-2.02 (m, 2H), 1.81-1.78 (m, 1H), 1.57-1.46 (m, 3H).

^{13}C -NMR (100 MHz, CDCl_3): δ 147.9, 146.3, 145.9, 145.0, 133.9, 133.3, 131.4 (q, $J_{\text{C-F}} = 32$ Hz, $\text{C}_{\text{Ar-CF}_3}$), 129.3, 128.7, 128.6, 128.2, 128.1, 128.0, 126.8, 126.5, 125.7, 125.4, 125.6, 125.3, 122.7 (q, CF_3), 79.0, 78.9, 43.6, 43.4, 25.2, 25.0, 23.7, 23.4, 21.8, 21.7.

Compound 3.14

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), 2-(trifluoromethyl)benzophenone (50.0 mg, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μl , 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μl , 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.14 was obtained as colourless oil (32.6 mg, 49%).

Product was obtained as a mixture of 2 diastereomers.

^1H -NMR (400 MHz, CDCl_3): δ 7.85-7.19 (m, 9H), 6.05-6.02 (m, 1H), 5.55-5.43 (m, 1H), 3.56-3.38 (m, 1H), 2.52 (s, 1H), 2.07-2.03 (m, 2H), 1.82-1.79 (m, 1H), 1.56-1.48 (m, 3H).

^{13}C -NMR (100 MHz, CDCl_3): δ 148.3, 146.2, 145.9, 145.0, 135.5, 135.2, 131.2 (q, $J_{\text{C-F}} = 32$ Hz, $\text{C}_{\text{Ar-CF}_3}$), 129.3, 128.8, 128.6, 128.5, 128.1, 128.0, 126.8, 126.3, 125.7, 125.2, 125.1, 124.9, 122.7 (q, CF_3), 79.0, 78.7, 43.6, 43.2, 26.0, 25.3, 23.7, 23.4, 21.7, 21.7.

Compound 3.15

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), 4-methoxybenzophenone (42.4 mg, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.15 was obtained as colourless oil (43.5 mg, 74%).

Product was obtained as a mixture of 2 diastereomers.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.57 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 8.8 Hz, 1H), 7.44 (d, J = 7.5 Hz, 1H), 7.36 (d, J = 8.9 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.17 (t, J = 7.2 Hz, 0.5H), 7.14 (t, J = 7.3 Hz, 0.5H), 6.84 (d, J = 8.9 Hz, 1H), 6.80 (d, J = 8.9 Hz, 1H), 5.97-5.94 (m, 1H), 5.54-5.46 (m, 1H), 3.75 (s, 1.5H), 3.73 (s, 1.5H (isomer)), 3.39-3.37 (m, 1H), 2.19 (s, 0.5H), 2.17 (s, 0.5H), 2.00-1.98 (m, 2H), 1.76-1.74 (m, 1H), 1.50-1.40 (m, 3H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 158.0, 157.8, 146.7, 145.5, 139.0, 137.6, 133.3, 133.0, 128.2, 127.7, 127.5, 126.8, 126.6, 126.5, 126.2, 126.0, 125.7, 125.4, 113.3, 113.0, 79.17, 79.0, 55.1, 54.8, 43.6, 43.5, 25.2, 23.8, 22.0.

Compound 3.16

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), 4-aminobenzophenone (39.5 mg, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.16 was obtained as colourless oil (26.3 mg, 47%).

Product was obtained as a mixture of 2 diastereomers.

¹H-NMR (500 MHz, CDCl₃): δ 7.55 (d, *J* = 7.6, 1H), 7.42 (d, *J* = 7.6, 1H), 7.35-7.12 (m, 5H), 6.63 (d, *J* = 8.5 Hz, 1H), 6.59 (d, *J* = 9.0 Hz, 1H), 5.93-5.91 (m, 1H), 5.57-5.45 (m, 1H), 3.58 (brs, 2H), 3.36-3.33 (m, 1H), 2.13 (brs, 1H), 1.99-1.96 (m, 2H), 1.76-1.74 (m, 1H), 1.54-1.38 (m, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ 147.0, 145.9, 144.8, 144.5, 136.8, 135.7, 133.3, 133.0, 128.1, 127.7, 127.0, 126.5, 126.5, 126.3, 126.1, 125.8, 125.4, 114.4, 114.1, 79.2, 79.0, 43.7, 43.5, 25.3, 23.7, 22.0

Compound 3.17

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), 4-bromobenzophenone (52.2 mg, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μl, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μl, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.17 was obtained as colourless oil (51.5 mg, 75%).

Product was obtained as a mixture of 2 diastereomers.

¹H-NMR (500 MHz, CDCl₃): δ 7.59-7.52 (m, 2H), 7.47-7.39 (m, 2H), 7.34-7.15 (m, 5H), 5.99-5.96 (m, 1H), 5.47-5.43 (m, 1H), 3.50-3.47 (m, 1H), 2.23 (brs, 1H), 2.00-1.97 (m, 2H), 1.78-1.74 (m, 1H), 1.54-1.43 (m, 3H).

¹³C-NMR (100 MHz, CDCl₃): δ 145.1, 143.8, 134.7, 132.9, 129.0, 128.6, 127.1, 126.7, 126.5, 125.3, 78.7, 43.8, 25.6, 23.9, 22.0.

Compound 3.18

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), 2-benzoylthiophene (37.7 mg, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.18 was obtained as colourless oil (35.3 mg, 65%).

Product was obtained as a mixture of 2 diastereomers.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.63-6.91 (m, 8H), 6.09-6.04 (m, 0.5H), 5.96-5.90 (m, 0.5H (isomer)), 5.65-5.62 (m, 0.5H), 5.39-5.35 (m, 0.5H (isomer)), 3.37-3.25 (m, 1H), 2.62 (s, 0.5H), 2.40 (s, 0.5H (isomer)), 2.01-1.97 (m, 2H), 1.80-1.73 (m, 1H), 1.54-1.35 (m, 3H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 154.0, 152.1, 146.0, 145.1, 133.9, 133.5, 129.0, 128.7, 127.3, 127.0, 126.5, 126.3, 126.0, 125.8, 125.6, 125.0, 124.6, 124.3, 122.9, 80.6, 80.3, 47.4, 47.0, 26.3, 26.0, 24.2, 23.8, 22.3, 21.9.

Compound 3.19

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), 2-benzoylbenzothiazole (47.9 mg, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%)

and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.19 was obtained as mixture of white solid and colourless oil (45.0 mg, 70%).

Diastereomer 1 (colourless oil)

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 8.10 (d, $J = 8.1$ Hz, 1H), 7.84 (d, $J = 7.8$ Hz, 1H), 7.79-7.77 (m, 2H), 7.49-7.43 (m, 1H), 7.34-7.31 (m, 3H), 7.27-7.22 (m, 1H), 5.97-5.92 (m, 1H), 5.35 (dd, $J_1 = 2.1$ Hz, $J_2 = 9.9$ Hz, 1H), 3.70-3.64 (m, 1H), 3.38 (s, 1H), 1.99-1.96 (m, 2H), 1.77-1.72 (m, 1H), 1.54-1.36 (m, 3H).

$^{13}\text{C-NMR}$ (125 MHz; CDCl_3) δ 179.8, 153.5, 141.7, 135.8, 134.9, 128.3, 127.5, 125.8, 125.6, 125.5, 124.9, 123.4, 121.7, 80.9, 46.2, 25.5, 23.7, 21.6.

Diastereomer 2 (white solid)

$^1\text{H-NMR}$ (500 MHz; CDCl_3) δ 7.98 (d, $J = 8.2$ Hz, 1H), 7.86-7.81 (m, 3H), 7.47-7.28 (m, 5H), 6.08-6.02 (m, 1H), 5.48 (m, 1H), 3.78-3.72 (m, 1H), 3.42 (s, 1H), 2.01-1.97 (m, 2H), 1.79-1.73 (m, 1H), 1.57-1.39 (m, 3H).

$^{13}\text{C-NMR}$ (125 MHz; CDCl_3) δ 177.3, 153.1, 143.6, 135.5, 133.9, 128.4, 127.7, 126.0, 125.9, 125.4, 124.8, 123.0, 121.7, 80.9, 46.3, 25.2, 23.7, 21.9.

Compound 3.20

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), (1*H*-imidazol-2-yl)(phenyl)methanone (34.4 mg, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is

irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.20 was obtained as white solid (20.3 mg, 40%).

¹H-NMR (400 MHz, CDCl₃): δ 9.40 (br, 1H), 7.60-6.99 (m, 7H), 6.04-6.01 (m, 1H), 5.49-5.42 (m, 1H), 3.58-3.49 (m, 1H), 2.82 (brs, 1H), 1.98-1.95 (m, 2H), 1.78-1.74 (m, 1H), 1.54-1.43 (m, 3H).

¹³C-NMR (100 MHz, CDCl₃): δ 152.3, 142.7, 134.5, 128.2, 127.2, 126.4, 125.6, 77.8, 77.4, 45.3, 29.9, 25.4, 23.7, 21.7.

Compound 3.21

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), cyclohexyl phenyl ketone (37.6 mg, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μl, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μl, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 36 hrs. Column chromatography was performed for the purification of the desired product and compound 3.21 was obtained as colourless oil (36.3 mg, 67%).

Product was obtained as a mixture of 2 diastereomers.

¹H-NMR (400 MHz, CDCl₃): δ 7.43-7.20 (m, 5H), 5.92-5.81 and 5.16-5.14 (m, 2H), 3.07-2.90 (m, 1H), 2.03-0.45 (m, 17H)

¹³C-NMR (100 MHz, CDCl₃): δ 144.3, 142.8, 132.7, 131.7, 127.5, 127.4, 127.1, 126.8, 126.5, 126.3, 126.2, 126.0, 80.3, 80.1, 46.0, 44.7, 41.8, 40.9, 27.8, 27.7, 27.2, 27.0, 26.8, 26.7, 26.6, 26.5, 26.4, 26.3, 25.5, 25.2, 24.3, 23.0, 22.3, 21.9.

Compound 3.22

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), 2-methyl-1-phenyl-1-propanone (30.0 μ l, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 36 hrs. Column chromatography was performed for the purification of the desired product the product and compound 3.22 was obtained as colourless oil (28.1 mg, 61%).

Product was obtained as a mixture of 2 diastereomers.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.48-7.24 (m, 5H), 5.97-5.85 (m, 1.5H), 5.27-5.22 (m, 0.5H), 3.09-2.90 (m, 1H), 2.36-1.27 (m, 8H), 0.90-0.77 (m, 6H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 143.3, 142.5, 132.5, 131.7, 127.7, 127.6, 127.4, 127.2, 126.8, 126.5, 126.3, 126.2, 80.6, 42.3, 41.8, 34.9, 33.7, 25.3, 25.2, 24.5, 23.0, 22.3, 21.9, 17.62, 17.6, 16.9, 16.7.

Compound 3.23

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), acetophenone (23.6 μ l, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue

LEDs for 36 hrs. Column chromatography was performed for the purification of the desired product and compound 3.23 was obtained as colourless oil (20.2 mg, 50%).

Product was obtained as a mixture of 2 diastereomers.

¹H-NMR (500 MHz, CDCl₃): δ 7.48-7.24 (m, 5H), 5.97-5.85 (m, 1.5H), 5.27-5.22 (m, 0.5H), 3.09-2.90 (m, 1H), 2.36-1.27 (m, 8H), 1.35 (m, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ 143.4, 142.6, 132.4, 131.9, 127.7, 127.6, 127.3, 127.2, 126.9, 126.5, 126.3, 126.2, 80.6, 42.3, 41.8, 34.9, 33.7, 25.3, 25.2, 24.5, 23.0, 22.3, 21.9.

Compound 3.24

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), benzaldehyde (20.3 μl, 0.2 mmol, 1 equiv.), cyclohexene (101.3 μl, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μl, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12 hrs. Column chromatography was performed for the purification of the desired product and compound 3.24 was obtained as colourless oil (23.7 mg, 63%).

Product was obtained as a mixture of 2 diastereomers.

¹H-NMR (500 MHz, CDCl₃): δ 7.35-7.26 (m, 5H), 5.85-5.81 (m, 1.5H), 5.40-5.37 (m, 0.5H), 4.59-4.46 (m, 1H), 2.50-2.48 (m, 1H), 1.99-1.33 (m, 8H).

¹³C-NMR (125 MHz, CDCl₃): 143.5, 142.8, 131.6, 130.9, 129.7, 129.3, 128.5, 127.2, 126.7, 126.4, 126.3, 126.0, 79.8, 41.3, 40.5, 35.1, 34.0, 25.3, 24.3, 23.5, 22.7.

Compound 3.25

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), benzophenone (36.4 mg, 0.2 mmol, 1 equiv.), cycloheptene (116.7 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.25 was obtained as colourless oil (40.1 mg, 72%).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.58-7.54 (m, 4H), 7.35-7.29 (m, 4H), 7.20-7.17 (m, 2H), 5.91-5.85 (m, 1H), 5.67 (dd, $J_1 = 3.7$ Hz, $J_2 = 11.2$ Hz, 1H), 3.61-3.53 (m, 1H), 2.30 (brs, 1H), 2.29-2.22 (m, 2H), 2.02-1.26 (m, 6H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 147.2, 146.7, 134.0, 132.7, 128.3, 128.1, 126.5, 126.2, 126.0, 125.6, 81.2, 47.7, 31.0, 28.5, 28.2, 26.3

Compound 3.26

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), benzophenone (36.4 mg, 0.2 mmol, 1 equiv.), cyclooctene (130.3 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.26 was obtained as colourless oil (39.7 mg, 68%).

¹H-NMR (500 MHz, CDCl₃): δ 7.53-7.48 (m, 2H), 7.47-7.43 (m, 2H), 7.34-7.20 (m, 6H), 5.75-5.70 (m, 1H), 5.50-5.45 (m, 1H), 3.75-3.70 (m, 1H), 2.41-2.36 (m, 1H), 2.33 (brs, 1H), 2.25-2.19 (m, 1H), 1.80-1.31 (m, 8H).

¹³C-NMR (125 MHz, CDCl₃): δ 147.6, 146.9, 130.0, 129.9, 128.3, 128.0, 126.6, 126.2, 126.1, 125.8, 80.0, 44.2, 30.2, 29.5, 27.1, 26.9, 25.8.

Compound 3.27

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), benzophenone (36.4 mg, 0.2 mmol, 1 equiv.), cycloheptatriene (103.8 μl, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μl, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.27 was obtained as colourless oil (46.1 mg, 84%).

¹H-NMR (500 MHz, CDCl₃): δ 7.42-7.20 (m, 10H), 6.75-6.70 (m, 2H), 6.21-6.17 (m, 2H), 5.39-5.34 (m, 2H), 2.67-2.64 (m, 1H), 2.51 (brs, 1H).

¹³C-NMR (125 MHz, CDCl₃): δ 147.0, 131.1, 128.7, 127.3, 126.3, 125.0, 123.0, 78.9, 47.7.

Compound 3.28

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), benzophenone (36.4 mg, 0.2 mmol, 1 equiv.), 3-methyl-2-butene-1-ol (101.7 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.28 was obtained as colourless oil (39.8 mg, 74%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.60-7.12 (m, 10H), 5.39 (d, $J = 9.1$ Hz, 1H), 5.22 (d, $J = 9.1$ Hz, 1H), 3.20 (brs, 1H), 1.85 (brs, 1H), 1.62 (s, 3H), 1.40 (s, 3H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 146.2, 144.0, 138.7, 128.4, 128.1, 127.4, 126.9, 126.8, 126.4, 122.6, 80.5, 72.9, 26.0, 18.7.

Compound 3.29

Regio-isomer 1

Regio-isomer 2

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), benzophenone (36.4 mg, 0.2 mmol, 1 equiv.), 3,4-dihydro-2*H*-pyran (91.2 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.29 was obtained as colourless oil (44.2 mg, 83%).

Regio-isomer 1 (white solid).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.61-7.57 (m, 2H), 7.47-7.44 (m, 2H), 7.37-7.28 (m, 4H), 7.24-7.19 (m, 2H), 6.60 (dd, $J_1 = 6.5$ Hz, $J_2 = 1.8$ Hz, 1H), 4.48-4.45 (m, 1H), 4.15-4.10 (m, 1H),

3.90 (dt, $J_1 = 10.8$ Hz, $J_2 = 2.8$ Hz, 1H), 3.53-3.49 (m, 1H), 2.38 (brs, 1H), 1.92-1.88 (m, 1H), 1.52-1.48 (m, 1H).

^{13}C -NMR (125 MHz, CDCl_3): δ 149.2, 146.5, 144.8, 128.7, 128.3, 126.8, 126.4, 126.0, 125.5, 99.3, 78.6, 65.5, 38.7, 24.5.

Regio-isomer 2 (colourless oil)

^1H -NMR (500 MHz; CDCl_3) δ 7.57-7.56 (m, 2H), 7.50-7.47 (m, 2H), 7.34-7.28 (m, 4H), 7.25-7.20 (m, 2H), 6.02-5.98 (m, 1H), 5.43-5.38 (m, 1H), 5.11-5.09 (m, 1H), 4.13-4.08 (m, 1H), 3.83 (dt, $J_1 = 3.5$ Hz, $J_2 = 11.5$ Hz, 1H), 3.22 (brs, 1H), 2.43-2.37 (m, 1H), 1.96-1.89 (m, 1H).

^{13}C -NMR (125 MHz; CDCl_3) δ 145.9, 143.7, 128.1, 128.0, 127.7, 126.9, 126.7, 126.5, 126.1, 125.8, 80.1, 78.2, 64.9, 25.1.

Compound 3.30

Regio-isomer 1

Regio-isomer 2

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), benzophenone (36.4 mg, 0.2 mmol, 1 equiv.), *cis*-4-octene (116.7 μl , 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μl , 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.30 was obtained as colourless oil (38.3 mg, 65%).

Product was obtained as a mixture of regio-isomers.

^1H -NMR (500 MHz, CDCl_3): δ 7.51-7.13 (m, 10H), 5.53-5.41 (m, 1H), 5.20-5.17 (m, 1H), 3.11-2.99 (m, 1H), 2.43 (brs, 1H), 1.92-1.86 (m, 2H), 1.48-1.20 (m, 4H), 0.86-0.75 (m, 6H).

^{13}C -NMR (125 MHz, CDCl_3): δ 147.6, 146.3, 146.0, 136.6, 135.0, 128.7, 128.2, 127.9, 127.7, 126.9, 126.7, 126.5, 126.4, 126.3, 126.2, 126.1, 126.0, 80.3, 80.1, 53.2, 50.8, 34.8, 31.3, 25.9, 22.7, 21.9, 20.8, 14.1, 13.9, 13.4, 12.7.

Compound 3.31

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), benzophenone (36.4 mg, 0.2 mmol, 1 equiv.), allyl acetate (107.9 μl , 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μl , 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.31 was obtained as colourless oil (35.6 mg, 63%).

^1H -NMR (400 MHz, CDCl_3): δ 7.65-7.17 (m, 10H), 6.05 (d, J = 9.1 Hz, 1H), 5.92 (m, 1H), 5.36-5.23 (m, 2H), 3.25-3.20 (m, 1H), 2.09 (s, 3H).

^{13}C -NMR (100 MHz, CDCl_3): δ 171.0, 145.3, 143.7, 131.8, 129.7, 129.2, 128.4, 127.9, 126.8, 126.4, 121.1, 86.4, 70.3, 21.2.

Compound 3.32

Regio-isomer 1

Regio-isomer 2

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), benzophenone (36.4 mg, 0.2 mmol, 1 equiv.), 3-methyl-1-pentene (107.9 μl , 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%)

and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.32 was obtained as colourless oil (32 mg, 60%).

Product was obtained as a mixture of regio-isomers.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.53-7.20 (m, 10H), 5.10-5.01 (m, 1H), 3.08 (d, $J = 7.5$ Hz, 2H), 2.58 (brs, 1H), 2.17-1.97 (m, 2H), 1.69 (s, 3H), 1.00-0.93 (m, 3H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 147.6, 143.9, 143.5, 137.7, 132.6, 130.0, 128.5, 128.3, 128.1, 126.7, 126.5, 126.2, 118.1, 117.0, 77.7, 40.9, 40.5, 32.7, 25.4, 23.5, 16.5, 13.0, 12.8.

Compound 3.33

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), benzophenone (36.4 mg, 0.2 mmol, 1 equiv.), α -pinene (159 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.33 was obtained as colourless oil (37 mg, 58%).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.66 (d, $J = 7.5$ Hz, 2H), 7.45 (d, $J = 7.5$ Hz, 2H), 7.39-7.19 (m, 6H), 5.17-5.12 (m, 1H), 3.54-3.47 (m, 1H), 2.26 (s, 1H), 2.24-2.18 (m, 1H), 2.07-1.99 (m, 1H), 1.90-1.86 (m, 1H), 1.76 (s, 3H), 1.60 (brs, 1H), 1.22 (s, 3H), 0.93 (s, 3H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 151.8, 147.9, 146.0, 128.3, 127.9, 126.6, 126.3, 126.1, 125.8, 114.6, 80.2, 47.6, 47.2, 42.7, 42.3, 28.1, 26.3, 23.6, 20.8.

Compound 3.34

Regio-isomer 1

Regio-isomer 2

Following the general procedure, a mixture of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%, 0.005 mmol), benzophenone (36.4 mg, 0.2 mmol, 1 equiv.), γ -terpinene (159 μ l, 1 mmol, 5 equiv.), potassium carbonate (5.53 mg, 0.04 mmol, 20 mol%) and triisopropylsilane thiol (8.59 μ l, 0.04 mmol, 20 mol%) in DMA (2 ml) is irradiated by Blue LEDs for 12-16 hrs. Column chromatography was performed for the purification of the desired product and compound 3.34 was obtained as colourless oil (33.2 mg, 52%).

Product was obtained as a mixture of regio-isomers.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.66-7.20 (m, 10H), 5.79-5.37 (m, 2H), 4.03-3.96 (m, 1H), 2.82-2.54 (m, 4H), 2.25-2.21 (m, 1H), 1.72 (s, 3H), 1.15 (s, 3H), 0.97-0.93 (m, 6H), 0.85 (d, J = 7.0 Hz, 3H), 0.65 (d, J = 7.0 Hz, 3H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 147.1, 146.6, 146.3, 145.9, 144.3, 138.3, 133.1, 128.5, 128.0, 127.9, 127.8, 127.7, 126.9, 126.7, 126.6, 126.4, 126.3, 126.2, 126.1, 125.9, 122.0, 121.3, 118.8, 81.9, 80.6, 50.5, 48.8, 34.6, 33.2, 32.0, 28.7, 24.4, 23.7, 23.0, 21.7, 21.3, 20.1.

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List of Publications and Conferences

Publications

1. Direct Aldehyde Csp²-H Functionalization through Visible-Light-Mediated Photoredox Catalysis.
Chemistry-A European Journal, Volume 23, Issue 63, Pages 15899-15902
Authors: M.D. Vu, M. Das and Prof. X.-W. Liu^{*}
2. Metal-free Visible Light Photoredox Enables Generation of Carbyne Equivalents *via* Phosphonium Ylide C–H Activation.
Chemical Science, Volume 10, Issue 6, Pages 1687-1691
Authors: M. Das[†], M.D. Vu[†], Q. Zhang and Prof. X.-W. Liu^{*} ([†] the two authors contributed equally).
3. Visible Light Photoredox Enables Ketone Carbonyl Alkylation for Easy Access to Tertiary Alcohols.
ACS Catalysis, *Manuscript under revision*
Authors: M.D. Vu[†], M. Das[†], Z.-E. Ang, A. Guo and Prof. X.-W. Liu^{*} ([†] the two authors contributed equally).
4. Stereo- and Regioselective *O*-Glycosidic Bond Formation of 2-Nitroglycals *via* Superbase-Catalysis: An Elegant Approach to Access 2-Amino-2-deoxy-*O*-glycosides.
Manuscript in preparation
Authors: K. B. Pal^[a], A. Guo^[a], M. Das^[a], G. B^áti^[a], M. B. Chan-Park^[b], X.-W. Liu^{*[a]}
5. A Resplendent Approach to α -Stereoselective Bond Formation of Glucal *via* Iridium Catalyzed Ferrier-type *O*-Glycosylation.
Manuscript in preparation
Authors: K. B. Pal^{†[a]}, M. Das^{†[a]}, A. Guo^[a], J. D. Lee^[a], G. B^áti^[a], M. B. Chan-Park^[b], X.-W. Liu^{*[a]} ([†] the two authors contributed equally).
6. Organo-Photoredox Catalytic Stereoselective Synthesis of Tertiary Alcohols under Metal-Free Condition.
In progress
Authors: M. Das, M. D. Vu, J. D. Lee, K. B. Pal and Prof. X.-W. Liu^{*}

Conferences

1. 2nd Chemistry National Meeting Singapore (May 2019)

Presented on: Visible-light photoredox enables ketone carbonyl alkylation for easy access to tertiary alcohols.