Photoinduced Hydroarylation and Cyclization of Alkenes with Luminescent Platinum(II) Complexes

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Abstract: Photoinduced hydroarylation of alkenes is an appealing synthetic strategy for arene functionalization. Herein, we demonstrated that aryl radicals generated from electron-deficient aryl chlorides/bromides could be trapped by an array of terminal/internal aryl alkenes in the presence of [Pt(O^N^C^N)] under visible-light (410 nm) irradiation, affording anti-Markonikov hydroarylated compounds in up to 95% yield. Besides, a protocol for [Pt(O^N^C^N)]-catalyzed intramolecular photocyclization of acrylanilides to give structurally diverse 3,4-dihydroquinolinones has been developed.

Introduction

Photoinduced hydroarylation of alkenes constitutes an appealing method of C(sp²)–C(sp³) bond formation reactions for arene/alkene functionalization,[1] which complements the conventional reductive Heck coupling reactions.[2] Because of the distinct mechanistic pathway, for intermolecular reactions, the former approach, typically operating through radical addition coupling, is highly anti-Markonikov selective while the latter usually shows less satisfactory regioselectivity for non-directing group bearing or sterically/electronically unbiased alkenes and could be complicated by the competing Heck reactions. The key step of photoredox hydroarylation reactions involves the generation of reactive aryl radical via single electron reduction in the presence of a photocatalyst, which is subsequently intercepted by an alkene coupling partner.[3] While aryl radicals are often derived from pre-functionalized aryl substrates with redox active groups such as aryl diazonium salts and diaryliodonium salts,[4,5] examples of direct use of aryl chlorides/bromides as radical precursor, despite their broad commercial availability, are scarce, presumably due to their highly negative reduction potentials and high C(sp²)–Cl/C(sp²)–Br bond dissociation energies.[6] In this regard, König and co-workers demonstrated the reductive activation of Ar–Br and Ar–Cl bonds by photoexcited radical anion of *N,N*-bis(2,6-

diisopropylphenyl)perylene-3,4,9,10-bis(dicarboximide) (PDI)[7] or by harnessing a photosensitization-initiated reductive activation strategy using [Ru(bpy)₃]²⁺ photosensitizer with pyrene as photoreductant[8] for C–H arylation reactions (Scheme 1a). Jui[3d,e]
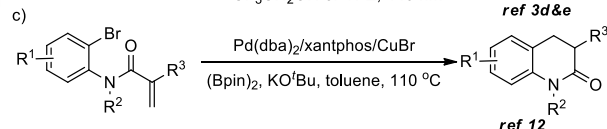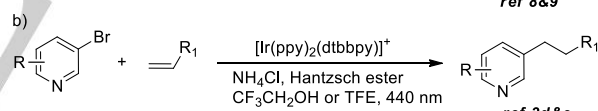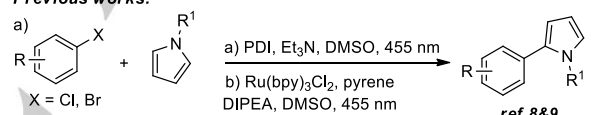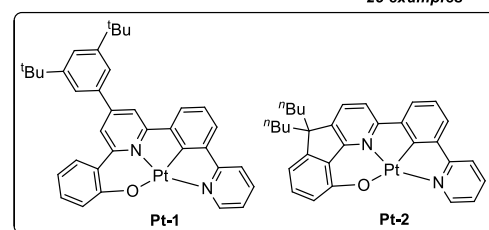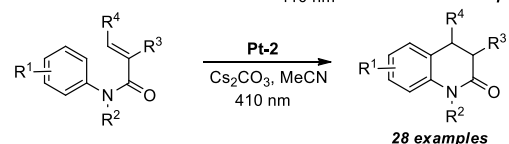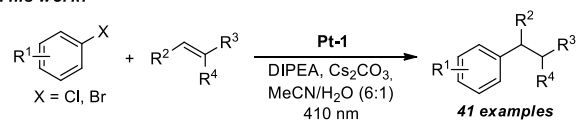
Scheme 1. Thermal and photoinduced inter- and intramolecular hyrdoarylation reactions and chemical structures of **Pt-1** and **Pt-2**.

recently reported that highly anti-Markonikov selective intermolecular hydropyridylation of alkenes could be achieved with bromopyridines using an iridium(III) photocatalyst and Hantzsch ester as sacrificial reductant (Scheme 1b).

Apart from single electron transfer radical pathway, energy transfer is also a viable mechanism for intramolecular photoinduced hydroarylation of alkenes. As examples, 3,4-dihydroquinolinones, a group of medicinally bioactive compounds,[9] could be synthesized via 6π-photocyclization of acrylanilides,[10] though a high-energy UV irradiation of 300–350 nm is necessary.[11] A recent work by Song and co-workers[12] showed that this intramolecular cyclization could be accomplished by a thermal Cu/Pd cooperative catalysis (Scheme 1c).

Luminescent platinum(II) complexes represent an emerging new class of photosensitizers and photocatalysts for light-induced organic transformations.[13] Because of substantial intraligand and relatively small metal-to-ligand charge transfer character, the emissive triplet excited states of tetradentate Pt(II) complexes, commonly assigned as ^{3}MLCT/^{3}IL in nature, generally display a longer lifetime than that of conventional luminescent Ru(II) and Ir(III) complexes,[14] which could facilitate bimolecular photochemical processes. Besides, the planar coordination geometry of Pt(II) complexes with vacant axial coordination sites allows for inner sphere substrate binding and trapping of radical intermediate(s) via Pt-C/Pt-X (X = halogen)/Pt-H bond formation,[13d,15] thereby giving rise to opportunities for new photo-catalysis. We previously reported that long-lived powerful photo-reductants could be generated from phosphorescent tetradentate platinum(II)-NHC complexes which could be used for photo-induced reductive debromination of aryl bromides.[16] Herein, we describe the use of two tetradentate [Pt(O^N^C^N)] complexes, **Pt-1** and **Pt-2**, as photocatalyst to achieve (i) aryl halides C–X (X = Cl, Br) bond reductive activation to produce aryl radicals, which could be trapped by terminal/internal aryl alkenes to afford various anti-Markonikov hydroarylated compounds, and (ii) photocyclization of triplet-sensitized acrylanilides to give 3,4-dihydroquinolinones at room temperature under visible-light irradiation of 410 nm (Scheme 1). Control experiments revealed the superior efficiency of these Pt-catalyzed reactions over those of [Ru(bpy)₃]²⁺ and [Ir(ppy)₃] photocatalysts (Table S1 and S2).

Results and Discussion

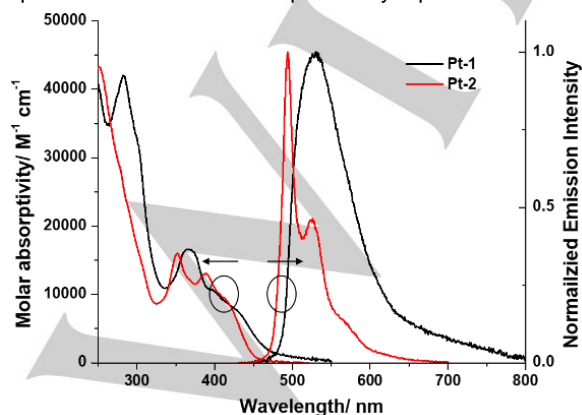Complexes **Pt-1** and **Pt-2** were previously reported as efficient

Figure 1. Electronic absorption and emission spectra of **Pt-1** (black) and **Pt-2** (red) in CH₃CN.

phosphorescent OLED emitters.[17] Their synthesis and characterizations are detailed in Supporting Information. These complexes show strong absorption band at 400–450 nm in CH₃CN with absorptivities of ca. 1 × 10⁴ M⁻¹ cm⁻¹, attributed to an admixture of ¹MLCT (¹[5dπ (Pt →π* (O^N^C^N)]) and ¹ILCT (¹[π (phenolate) → π* (N^C^N)]) transitions (Fig. 1). They exhibit strong phosphorescence in deaerated CH₃CN solution at room temperature with emission quantum yield of 48% and 50%, respectively. **Pt-1** displays a broad emission band at 532 nm with an emission lifetime of 3.2 μs coming from a mixed ³MLCT/³ILCT excited state while the vibronic-structured emission of **Pt-2** with maxima at 494, 526 and 564 nm with an emission lifetime of 15.0 μs is attributed to ³LC excited state (Fig. 1).[17] The triplet energies of **Pt-1** and **Pt-2** estimated from the emission onset are 2.57 and 2.63 eV, respectively. In cyclic voltammogram (CV), **Pt-1** exhibits a pair of quasi-reversible oxidation and reduction couples with $E_{1/2}$ = +0.43 and −1.78 V vs SCE, respectively, in MeCN (Fig. S2). These redox processes become irreversible in MeCN/H₂O (6:1) (Fig. S2). For **Pt-2**, both the first oxidation and reduction in MeCN/CH₂Cl₂ (9:1, v/v) solution are irreversible, occurring at E_{pa} = +0.83 and E_{pc} = −1.92 V vs SCE (Fig. S3). On the basis of spectroscopic and electrochemical data, the excited state redox potentials, E(Pt*/Pt⁻)/E(Pt⁺/Pt*), for **Pt-1** and **Pt-2** are estimated to be +0.79/–2.14 and +0.71/–1.80 V vs SCE, respectively. Thus, both Pt* and Pt⁻ states of **Pt-1** and **Pt-2** are strong one-electron reductant.
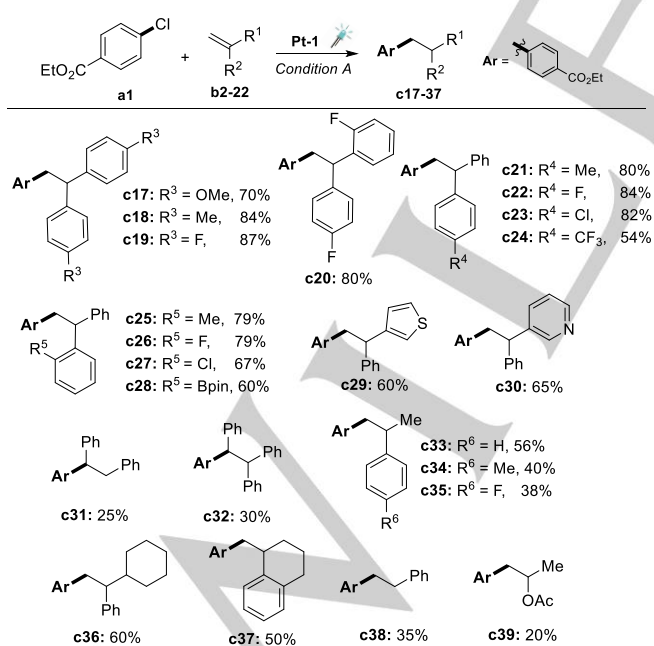
We started our investigation of hydroarylation reaction by LED irradiation (410 nm) of a mixture of ethyl 4-chlorobenzoate (**a1**)
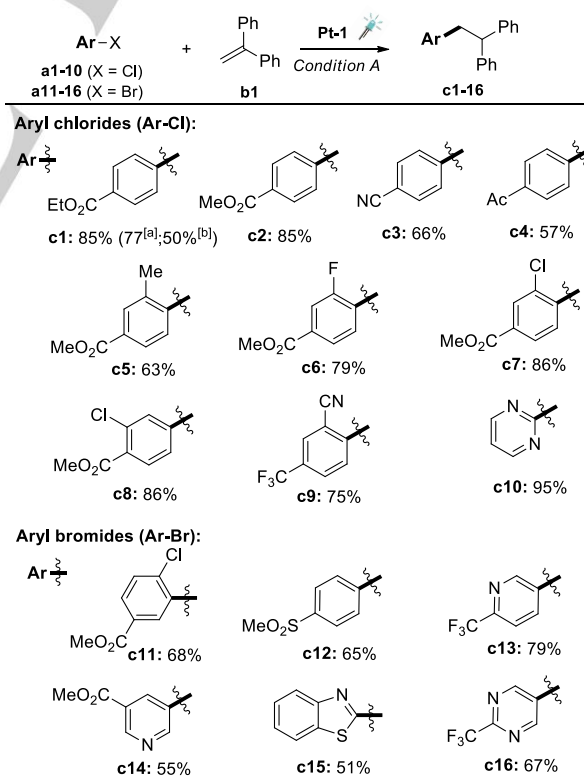
Scheme 2. Condition A: **Pt-1** (1 mol%), (hetero)aryl halide (0.2 mmol), alkene (0.6 mmol), Cs₂CO₃ (0.4 mmol), ᶦPr₂NEt (0.24 mmol) in 6 mL of CH₃CN/H₂O (6:1, v/v), under argon, irradiated by 410 nm LEDs (3 W x 4) for 10 h, isolated yields. [a] Using **Pt-1** (1 mol%), **a1** (1 mmol) and **b1** (1.2 mmol) in 10 mL of CH₃CN/H₂O. [b] Using **Pt-1** (0.5 mol%) **a1** (2 mmol) and **b1** (2.4 mmol) in 10 mL of CH₃CN/H₂O.
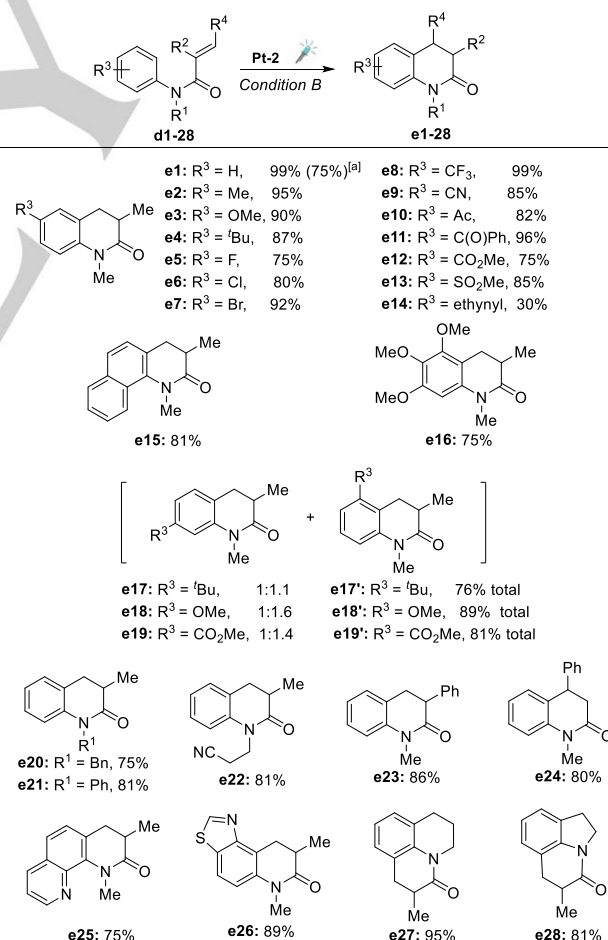
and 1,1-diphenylethylene (**b1**), complex **Pt-1**, a base additive, and a sacrificial electron donor (Table S1). In the presence of **Pt-1** (1 mol%), cesium carbonate (2 equiv) and a slight excess of diisopropylethylamine (*i*Pr₂NEt) in acetonitrile at room temperature, the reaction afforded product **c1** in 35% yield based on 37% conversion of **a1** (Table S1, entry 1). Several inorganic bases, including K_2CO_3, Na_2CO_3 and K_3PO_4, were further tested and none of them showed better effects than that of Cs_2CO_3. (Table S1, entries 2–4). Product **c1** was not obtained in the absence of a base. As for solvent, acetonitrile (CH_3CN) was found to be superior to dimethyl formamide (DMF), methanol (MeOH), tetrahydrofuran (THF) and 1, 2-dichloroethane (DCE) (Table S1, entries 6–9). Simliar to Zeitler's work,[18] the presence of water showed a dramatically positive impact and the best ratio of CH_3CN/H_2O was 6:1, in which **c1** was obtained in 87% yield (Table S1, entry 11). Control experiments confirmed the necessity of Pt complex and light irradiation. Finally, the optimal result was obtained with **Pt-1** (1 mol%), 0.2 mmol of aryl chloride, 2.0 equiv of Cs_2CO_3, and 1.2 equiv of *i*Pr₂NEt in 6 mL mixed solvent of CH_3CN/H_2O (6:1, *v/v*) (*Condition A*). With the optimized conditions in hand, a variety of aryl chlorides (**a1**–**10**) was investigated with 1,1-diphenylethylene (**b1**) as the coupling partner (Scheme 2).Generally, the reaction is compatible with various aryl chlorides, including cyano, ketone, ester, alkyl, halo, and trifluoromethyl substitution, affording the corresponding products in moderate to good yields (**c1**–**9**). Methyl/ethyl 4-chlorobenzoates with electron-withdrawing -F or -Cl groups gave better yields than that with electron-donating -Me group (**c6**, **c7** vs **c5**). Interestingly, methyl 3,4-dichloro benzoate and methyl 2,4-dichlorobenzoate underwent regioselective alkylation at the *para* position to methoxycarbonyl group and gave products **c7** and **c8**, respectively. This protocol also worked well for heterocyclic

substrate, 2-chloropyrimidine, and afforded product **c10** in 95% yield. Besides aryl chlorides, some common aryl bromides were tested under the standard conditions. The reaction afforded **c11** in 68% yield as major alkylation product when methyl 3-bromo-4-chlorobenzoate was used, suggesting that the cleavage of C–Br bond preferentially occurred. Sulfonyl substituted alkane **c12** was readily accessible with 65% yield. The reactions of pyridyl-containing substrates with **b1** proceeded smoothly, affording the coupling products **c13** and **c14** in 79% and 55% yields, respectively. Furthermore, 2-bromobenzothiazole and 5-bromopyrimidine gave **c15** and **c16** in moderate yields.

Then we turned our attention to the investigation of alkene substrates. 1,1-Diarylethylenes bearing various substituents such as Me, OMe, F, Cl, CF₃ and Bpin were subjected to the standard conditions in the presence of **a1** to give 1,1-diarylalkanes **c17–28** in 25-87% yields (Scheme 3). The diarylalkenes with both electron-donating and -withdrawing groups could undergo the reaction smoothly with similar product yield. Except for **c24**, where the reaction afforded the corresponding product in 54% yield, all other products were obtained in yields up to 87%. In addition, diversely unsymmetric *ortho*-substituted alkenes were efficiently converted to the desired products. Notably, alkenes containing heterocyclic moieties including 3-thiophene and 3-pyridine were tolerated in this

Scheme 3. *Condition A*: **Pt-1** (1 mol%), aryl halide (0.2 mmol), alkene (0.6 mmol), Cs_2CO_3 (0.4 mmol), *i*Pr₂NEt (0.24 mmol) in 6 mL of CH_3CN/H_2O (6:1, *v/v*), under argon, irradiated by 410 nm LEDs (3 W x 4) for 10 h, isolated yields.

Scheme 4. *Condition B*: **Pt-2** (1.0 mol%), alkene (0.1 mmol), Cs_2CO_3 (0.2 mmol), in 2.0 mL of CH_3CN, under argon, irradiated by 410 nm LEDs (3 W x 4) for 10 h, isolated yields. [a] Using **d1** (5 mmol), Cs_2CO_3 (1 mmol) and **Pt-2** (0.2 mol%) in 10 mL of CH_3CN.

reaction, affording the desired alkylated products **c29** and **c30** in moderate yields. This protocol was also applicable to 1,2-di- and tri-substituted alkenes (**c31** & **c32**), alkylaryl alkenes (**c33–37**), styrene (**c38**) and isopropenyl acetate (**c39**), albeit with lower product yields (20–60%). In general, the hydroarylation reaction exhibited good anti-Markonikov regioselectivity in all cases that C–C bond formation occurred at the terminal carbon atom of the terminal alkenes.

With respect to photoinduced intramolecular cyclization of alkenes, the initial optimal conditions for the cyclization utilized **Pt-2** as photocatalyst and *N*-methyl-*N*-phenylmethacrylamide (**d1**) as model substrate at room temperature in MeCN (Table S2). The reaction gave the cyclization product **e1** in 10% yield under light irradiation for 10 h. It is found that the addition of Cs_2CO_3 as additive could dramatically improve the product yield and afford **e1** almost quantitatively (Table S2). Control experiments revealed that both catalyst **Pt-2** and LEDs irradiation were necessary for the cyclization. Consequently, the optimal conditions were found to be 1 mol% catalyst **Pt-2**, 0.1 mmol of alkene, 2.0 equiv of Cs_2CO_3 in CH_3CN (2 mL) under LEDs irradiation (410 nm) for 10 h (*Condition B*). Next we focused on the cyclization allowing the conversion of alkenes **d** into 3,4-dihydroquinolinones **e** (Scheme 4). A wide range of acrylamides proceeded very well, regardless of the substitution pattern. Acrylamides with functional groups on the aromatic ring, for instance, alkyl, methoxy, cyano, halo, trifluoromethyl, naphthyl, alkynyl, ester, sulfonyl and ketone, were compatible to the standard conditions, leading to the corresponding products in 30-96% yields. The alkenes bearing *meta* substituents exhibited good reactivity as well and delivered the mixture of **e17**–**19** and **e17'**–**19'**, albeit with low regioselectivity. Replacement of methyl group on nitrogen atom of acrylamide by other alkyl and aromatic substituents resulted in an insignificant impact on the reaction efficiency (**e20**–**22**). Substrate with a phenyl group at the α and β position of alkene **d23**–**24** also afforded products **e23**–**24** in 86% and 80% yields, respectively. Heteroaromatic substrates, such as quinoline, benzothiazole, 1,2,3,4-tetrahydroquinoline, and indoline, could be readily to the desired products **e25**–**28** in 75-95% yields.

To demonstrate the synthetic utility of the as-developed Pt-catalyzed protocols, scaled-up reactions for the photo-induced hydroarylation of alkene and cyclization of acrylanilide have been performed. Light (410 nm) irradiation of the reaction mixtures containing 1-2 mmol of **a1** as limiting substrate and 1.2–2.4 mmol of **b1** in the presence of 0.5-1 mol% of **Pt-1** for 24 h afforded **c1** in 50-77% yields (Scheme 2). Similarly, photo-cyclization of **d1** catalyzed by **Pt-2** (0.2 mol%) could proceed smoothly on a 5 mmol scale in 24 h and **e1** was obtained in 75% yield (Scheme 4). These protocols were also applied in the modification of three complex organic compounds (Scheme 5). Aryl chlorides bearing (+)-menthol (**f1**) and pregnenolone motifs (**g1**) reacted with diaryl alkene **b1** to afford the corresponding products **f2** and **g2** in 60 and 66% yields, respectively. In addition, with optimized cyclization condition (*Condition B*), alkene **d18** was directly transferred to **e18** in one step, which could be further transformed into atypical schizophrenia drug (±)-SIPI 6360 according to a reported protocol.[19]

To probe the mechanism of these two types of photocatalytic reactions, emission quenching, nano-second time-resolved absorption spectroscopy (ns-TA), electron paramagnetic resonance (EPR) and CV measurements were conducted. The emission of **Pt-1** could be quenched by both DIPEA and 1,1-
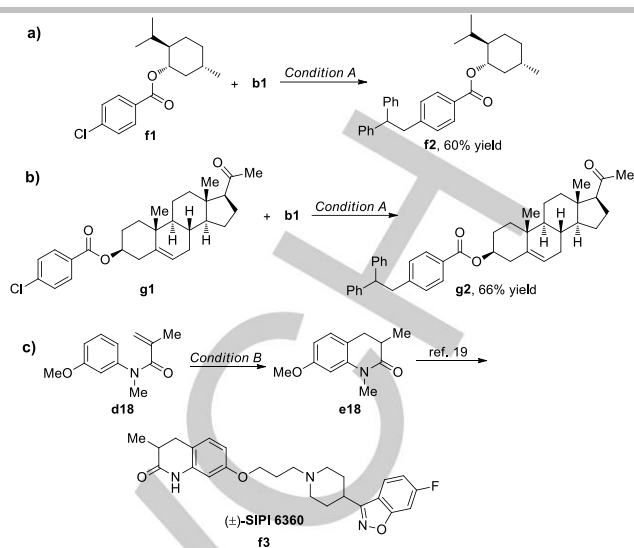
Scheme 5. Synthesis of (a) **f2**, (b) **g2** and (c) (±)-SIPI 6360 (**f3**).

diphenylethene with quenching rate constant of 7.1×10^7 and 8.1×10^8 M^{-1} s^{-1}, respectively, but not by ethyl 4-chlorobenzoate. In the presence of DIPEA (12 mM), the ns-TA signals of **Pt-1** at 335, 390 and 440–800 nm decayed with a shortened time constant from 2.4 to 0.8 μs and a long-lived species showing absorption features at 330, 430 and 690 nm was developed, which persisted over 50 μs (Fig. 2). As **Pt-1*** is capable of oxidizing DIPEA ($E(Pt^*/Pt^-) = +0.79$ V; $E(DIPEA^{+/0}) = +0.64$ V *vs* SCE in CH_3CN) (Fig. S6), the observed new species in ns-TA is assigned as the reduced **Pt-1** (**Pt-1·⁻**). Conversely, the emission quenching of **Pt-1*** by 1,1-diphenylethene is due to energy-transfer because (i) 1,1-diphenylethene is redox inactive within the solvent window (Fig. S5) and (ii) no new species was generated in the ns-TA experiment of **Pt-1** and 1,1-diphenylethene (Fig. S8). Low temperature X-band EPR experiment (100K) of a frozen CH_3CN/H_2O (6:1, v/v) solution of **Pt-1** and DIPEA obtained by light (410 nm) irradiation of the solution for 1.5 h at room temperature revealed a sharp signal at g ~2.0 comprising of three lines spanning a field range of ~100 G (Fig. S16), which is reminiscent of the nearly isotropic signals of the reported [Pt(II)(N^N)]·⁻ and [Pt(II)(O^O)]·⁻ species,[20] and could be approximately fitted using the parameters: $g_1 = 2.0042$, $g_2 = 2.0035$ and $g_3 = 2.0021$ ($g_{iso} = 2.0033$), $A_{1,Pt} = 30$ G, $A_{2,Pt} = 40$ G, $A_{3,Pt} = 80$ G ($A_{iso,Pt} = 54$ G) and $A_{1,N} = 4$ G, $A_{2,N} = 6$ G, $A_{3,N} = 8$ G ($A_{iso,N} = 6$ G). The g and A values
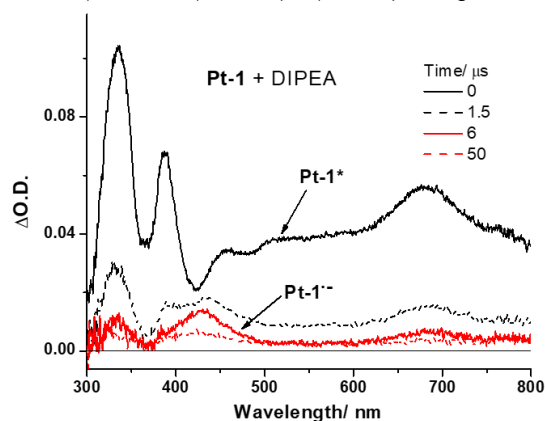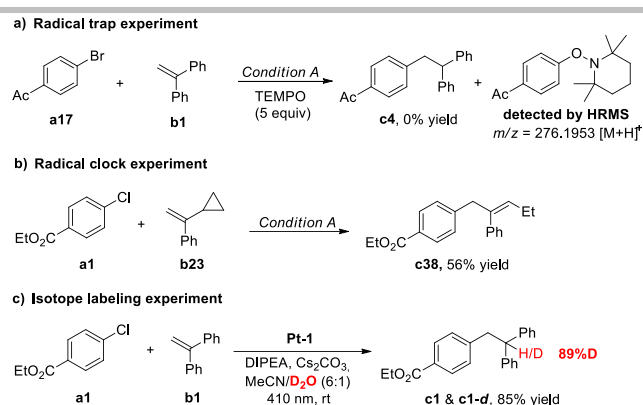

Figure 2. (a) Nanosecond time-resolved absorption difference spectra of **Pt-1** (40 μM) in the presence of DIPEA (12 mM) in degassed CH_3CN/H_2O (*v/v* = 6:1).

a) Radical trap experiment

b) Radical clock experiment

c) Isotope labeling experiment

Scheme 6. Mechanistic studies of **Pt-1**-catalyzed photoinduced hydroarylation reactions.

are well comparable to those of the [Pt(II)(N^N)]⁻ species.[20,21] This EPR signal could be quenched upon addition of ethyl 4-chlorobenzoate (**a1**) following an extended period of light irradiation (Fig. S19). The **Pt-1**⁻ species generated electrochemically in CV at –1.78 V *vs* SCE could react with **a1** (E_{red} = –2.01 V *vs* SCE) in CH_3CN/H_2O as revealed by the catalytic current with an E_{onset} of –1.69 V in the presence of the latter in excess (Fig. S7). The presence of water facilitates this reduction by stabilizing the LUMO of ethyl 4-chlorobenzoate by 0.11 V (Fig. S4). The involvement of aryl radical in the reaction under *Condition A* is substantiated by (i) the radical trap experiment that the aryl-TEMPO adduct was observed in HRMS (m/z = 276.1953 [M+H]⁺) from the reaction mixture of TEMPO (5 equiv) and 4'-bromoacetophenone (**a17**) (Scheme 6a) and (ii) the radical clock experiment in which a ring-open *E*-alkene product (**c38**) was obtained as a major product in 56% yield (Scheme 6b). The isotope labelling experiment of **a1** and **b1** using $MeCN/D_2O$ (6:1) as solvent resulted in a high ratio of deuterated hydroarlyation product (**c1**:**c1-*d*** = 11:89) (Scheme 6c), suggesting the formation of a benzylic anion intermediate in the catalytic cycle. Thus, the photoinduced hydroarylation reaction begins with single electron transfer (SET) from DIPEA to **Pt-1*** to give **Pt-1**⁻ (Scheme 7). The **Pt-1**⁻ species then reacts with aryl halide to restore to **Pt-1** and afford a reactive aryl radical after a reductive Ar–Cl/Br bond scission, which is subsequently trapped by the alkene (**b**) furnishing a tertiary benzylic radical intermediate with greatest electronic stabilization. This radical addition step is conceived to be the key mechanistic step that confers high regioselectivity for anti-Markonikov addition products. Since
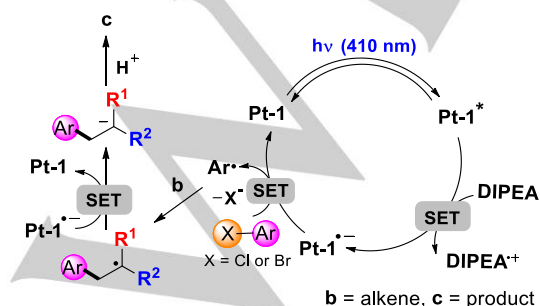
relevant tertiary benzylic radicals were reported to have E_{red} of *ca.* –1.35 V *vs* SCE in MeCN from previous studies,[22] it is expected that the third SET that generates the respective benzylic carbanion should derive from **Pt-1**⁻ (E(Pt/Pt⁻) = –1.78 V *vs* SCE). Although SET from **Pt-1*** (E(Pt⁺/Pt*) = –2.14 V *vs* SCE) is more thermodynamically feasible, the insufficient reducing power of DIPEA to reduce the oxidized **Pt-1** (**Pt-1**⁺; E(Pt⁺/Pt) = +0.43 V *vs* SCE) back to **Pt-1** does not favour this pathway. Finally, alkylation product **c** is formed after protonation of the benzylic carbanion.

As for the intramolecular cyclization reaction, the emission quenching rate constant of **Pt-2** by acrylanilide substrate **d1** was found to be 1.4×10^6 M⁻¹ s⁻¹. Because **d1** is electrochemically inactive from –2.2 to +1.5 V *vs* SCE in MeCN, neither reductive nor oxidative electron transfer quenching of **Pt-2*** by **d1** is deemed feasible. Previous mechanistic studies established that photocyclization of related acrylanilides in the presence of a triplet sensitizer could be triggered by triplet-triplet energy-transfer (TTEnT) followed by a cascade of radical ring closure of the diradicaloids and hydrogen migration.[11] The triplet energy of **d1**, determined from 77 K phosphorescence, is about 2.82 eV (Figure S12)[12b] and the presumed TTEnT process from **Pt-2*** to **d1** is, therefore, endergonic by *ca.* 0.2 eV (4.61 kcal mol⁻¹). Such an uphill EnT event could be made possible by thermal population of the higher vibrational/rotational levels of the triplet state of the photosensitizer. A recent work by Guldi and Glorius demonstrated an efficient [2+2]-photocycloaddition of benzothiophene involving an endergonic TTEnT step of 5.77 kcal mol⁻¹ from an Ir(III)-photosensitizer to benzothiophene.[23] It is conceived that similar photo-coupled-thermal activated TTEnT mechanism between **Pt-2*** and **d1** could also be operative. Addition of TEMPO as triplet quencher inhibited the reaction and the starting materials were recovered, lending support to an EnT mechanism. Despite the small k_q, the extended triplet excited state lifetime of **Pt-2** (15.0 µs) results in a practical quenching fraction (η_q) of **Pt-2*** by **d1** of 51.2% (η_q = $k_q\tau_0$[quencher]/(1+$k_q\tau_0$[quencher])) under the experimental conditions that effectively generates ³**d1*** per photoexcitation. From energy consideration, an exergonic reverse TTEnT event from ³**d1*** to **Pt-2** with a considerably higher rate constant than the forward TTEnT would be more favorable. Thus, the possibility of occurrence of a reversible EnT dynamics leading to a diminished ³**d1*** population cannot be excluded.[23b] In this scenario, the ensuing radical ring closure step has to be much faster than the reverse TTEnT process and/or irreversible to drive the productive reaction forward. The results from deuterium-labeling and kinetic isotopic effect studies confirmed an intramolecular [1,5]-H shift, which is non-rate limiting, to take place and afford photoproduct **e1**. Based on the above findings/considerations and established mechanistic studies,[11] a plausible mechanism for photocyclization of acrylanilides mediated by **Pt-2** is proposed and depicted in Scheme 8.
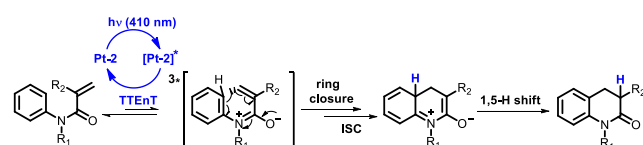
Scheme 8. Proposed reaction pathway for photocyclization of acrylanilides catalyzed by **Pt-2**.

Scheme 7. Proposed reaction pathway for hydroarylation catalyzed by **Pt-1**.

Conclusion

In summary, we described efficient visible-light (410 nm) [Pt(O^N^C^N)] photocatalysis that realized (i) reductive coupling of aryl chlorides/bromides with terminal/internal aryl alkenes to give anti-Markonikov hydroarylated compounds *via* aryl radical intermediacy and (ii) cyclization of acrylanilidines to access a variety of 3,4-dihydroquinolinones.

Acknowledgements

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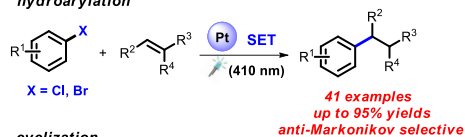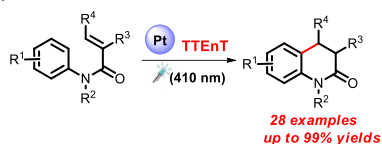
In the presence of luminescent [Pt(O^N^C^N)] complexes under visible light (410 nm) irradiation, aryl radicals derived from reductive aryl–chloride/bromide bond cleavage were trapped by aryl alkenes and afforded a series of anti-Markonikov hydroarylated compounds. Besides, a protocol for [Pt(O^N^C^N)]-catalyzed intramolecular photocyclization of acrylanilides to give structurally diverse 3,4-dihydroquinolinones has been developed.