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Visible Light Accelerated Vinyl C-H Arylation in Pd-Catalysis: Application in the Synthesis of *ortho* Tetra-substituted Vinylarene Atropisomers

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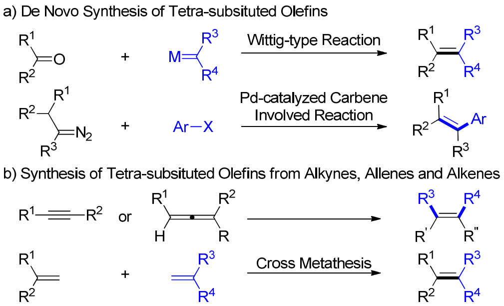
Dedication ((optional))

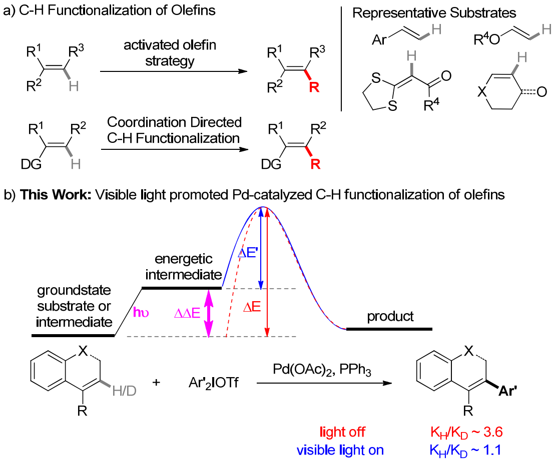
Abstract: A visible light accelerated C-H functionalization reaction in palladium-catalyzed arylation of vinyl arenes with diaryliodonium salts is reported in the absence of additional photosensitizer. The kinetic isotope effect (k_H/k_D) was changed from 3.6 (under darkness) to 1.1 with irradiated by visible light, which indicated that the C-H functionalization step was the rate determining step under darkness and significantly accelerated by the irradiation of visible light. Finally the synthesis of *ortho* tetra-substituted vinylarene atropisomers with high enantiospecificity was realized via this protocol.

The synthesis of *tetra*-substituted olefins is gaining much attention in synthetic organic chemistry since there are important applications in chemistry, medicinal chemistry and life science. However, their synthesis are of great challenges not only because of the highly steric congestion of four substituents, but also the difficulties in control of the stereochemistry. Some approaches have been applied in the construction of tetra-substituted olefins. De novo synthesis via Wittig-type reaction[1] and palladium-catalyzed Heck reaction, carbene-involved reaction[2] invariably suffered either its low reactivity or poor stereoselectivity (Scheme 1a). Functionalization of alkynes[3] and 2,3-allenals[4] is a very useful protocol for the synthesis of stereodefined tetra-substituted olefins (Scheme 1b). Cross-metathesis of alkenes is a feasible method for construction of fully-substituted alkenes, which, however, is usually limited to the intramolecular reaction for construction of cyclic compounds.[5]

Direct functionalization of vinyl C-H is a robust method for the construction of poly-substituted alkenes.[6] Two strategies were usually employed in the previous studies in this area. The first is the use of activated olefins, such as styrenes, vinyl ethers (esters), enamines, α-oxoketene dithioacetates (Scheme 2a).[7] The second frequently used strategy is coordination-directed C-H functionalization.[8] Albeit these great successes, the synthesis of tetra-substituted olefins via these strategies is still challenging, such as limited directing groups or poor chemical selectivity (vinyl vs. allylic C-H bonds). Recently, organic syntheses reap huge fruit from visible light-promoted reactions.[9] Till now an army of visible light-promoted C-H functionalization were developed.[10] We reasoned that irradiation of a ground-state substrate or intermediate would give a higher energetic species. As a result, the activation energy of the reaction was lowered by $\Delta\Delta E$ (Scheme 2b).[11,12] Herein we report our efforts in direct vinyl C-H arylation via the photo and palladium synergistic catalysis.



Scheme 1. Approaches for the Synthesis of Tetrasubstituted Olefins.



Scheme 2. Approaches for Vinyl C-H Functionalization.

During the research on the Pd-catalyzed arylation reaction of substrate **1a** with diphenyliodonium salt,[13] we serendipitously found that the reaction proceeded much fast in day time than in the night. Further investigation indicated that irradiation with visible light significantly accelerated the reaction rate, and indeed all subsequent optimizations were conducted under the irradiation of 36 W lamp. Survey the palladium source found that $Pd(OAc)_2$ was better than $PdCl_2$ or $Pd_2(dba)_3$ (Table 1, entries 1-3). In the absence of $NaHCO_3$, the reaction did proceed albeit with a relative lower conversion (entry 4). Bidentate ligand dppp

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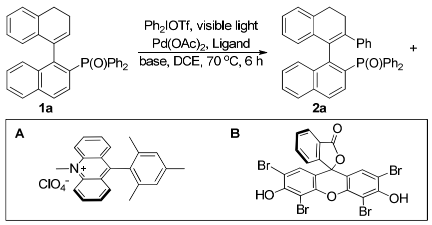
completely inhibited the reaction, while (4-FC$_6$H$_4$)$_3$P produced a considerable amount of side product, which was identified as aromatized compound **3a** (entries 5-6). Organic base Et$_3$N or strong base *t*BuOLi produced inferior results (entries 7-8). Surprisingly, upon the addition of photosensitizers, such as **A**, **B** and Ru(bipy)$_3$Cl$_2$, the efficiency of this transformation somehow decreased (entries 9-11). In the absence of palladium source, no conversion was observed either in the presence of Ru(bipy)$_2$(PF$_6$)$_2$ or in the absence of photosensitizer.

Table 1. Reaction Condition Optimization[a]



Entry	ligand	Base	Additive (5 mol%)	Yield of **2a**/%	Yield of **3a**/%
1[b]	PPh$_3$	NaHCO$_3$	-	37 (43)	-
2[c]	PPh$_3$	NaHCO$_3$	-	30 (66)	-
3	PPh$_3$	NaHCO$_3$	-	91	-
4	PPh$_3$	-	-	72 (78)	-
5	dppp	NaHCO$_3$	-	-	-
6	(4-FC$_6$H$_4$)$_3$P	NaHCO$_3$	-	61	22
7	PPh$_3$	Et$_3$N	-	-	-
8	PPh$_3$	*t*BuOLi	-	<5	-
9	PPh$_3$	NaHCO$_3$	**A**	14	35
10	PPh$_3$	NaHCO$_3$	**B**	47	-
11	PPh$_3$	NaHCO$_3$	Ru(bipy)$_3$Cl$_2$	-	-

[a] The reactions were performed with **1a** (0.10 mmol), Ph$_2$IOTf (1.1 equiv), Pd(OAc)$_2$ (5 mol%), ligand (5 mol%), and base (1.1 equiv) in dichloroethane at 70 °C under the irradiation of 36W light bulb. The numbers in parentheses are the conversions. [b] Pd$_2$(dba)$_3$ was used. [c] PdCl$_2$ was used.

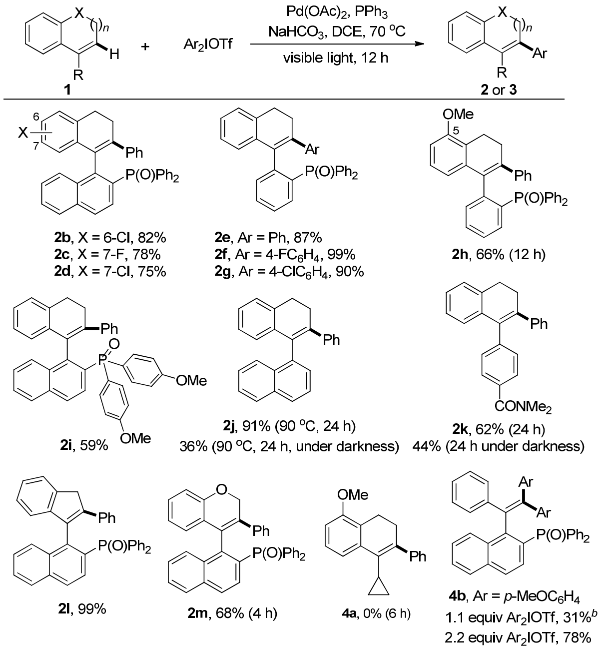
The investigation of wavelength effect was also performed by the use of a parallel reactor irradiated from the bottom of the Schlenk tube (Table 2). All the different wavelength light we used was able to promote the reaction (5 watts for 6 h). However white (300-850 nm) and green (530 nm) light gave the highest efficiency (entries 1-6), though it was surprise to find that **1a**, Ph$_2$IOTf, or palladium catalyst have no absorption at the region of wavelength larger than 500 nm in UV-Vis spectra [see the Supporting Information (SI) for details]. The reaction with white and green light irradiation could give 67% and 38% yield, respectively, even decreasing the irradiation power to 1 watt and quenched the reaction after 1 h (entries 7-9).

Table 2. Wavelength Effect Investigation[a]

entry	wavelength /nm	power/W	time/h	yield/%	
				2a	**3a**
1	300-850	5	6	93	--
2	365	5	6	69	17
3	400-405	5	6	51	10
4	465	5	6	73	11
5	530	5	6	95	--
6	700	5	6	31	--
7	300-850	1	1	67	--
8	365	1	1	15	--
9	530	1	1	38	--

[a] The reactions were performed with **1a** (0.10 mmol), Ph$_2$IOTf (1.1 equiv), Pd(OAc)$_2$ (5 mol%), PPh$_3$ (5 mol%), and NaHCO$_3$ (1.1 equiv) in DCE at 70 °C.

Table 3. Substrate Scope



[a] The reactions were performed with **1** (0.10 mmol), Ar$_2$IOTf (1.1 equiv), Pd(OAc)$_2$ (5 mol%), PPh$_3$ (5 mol%), and NaHCO$_3$ (1.1 equiv) in dichloroethane at 70 °C under the irradiation of 36W light bulb. [b] A small amount of mono-arylation product (~3%) was detected.

Subsequently, the generality of this reaction was investigated under optimized conditions. The 3,4-dihydronaphthalene moiety could be elaborated with halides (Table 3, **2b-d**), methoxyl group (**2h**). The diaryliodonium was compatible with halogen substituents (**2f-g**), however currently the *ortho*-substituted diaryliodoniums were not suitable arylation reagents (See SI). The phosphine oxide was not indispensable: **2j** and **2k** were isolated in 91% and 62%, respectively, at a slight elevated temperature or prolonged reaction time. Compounds **2j** and **2k** were isolated in 36% and 44% under darkness, indicating that they were less depend on the irradiation than the corresponding phosphine oxides. The reactions with indene derivative also provided satisfactory results (**2l**), and reaction of the 2*H*-chromene analogue completed within 4 h albeit with a dropped yield (**2m**). Replacing the aryl rings by a cyclopropyl group resulted poor reactivity of the substrate, and no desired arylated product **4a** was detected. Disappointedly, these results gave no

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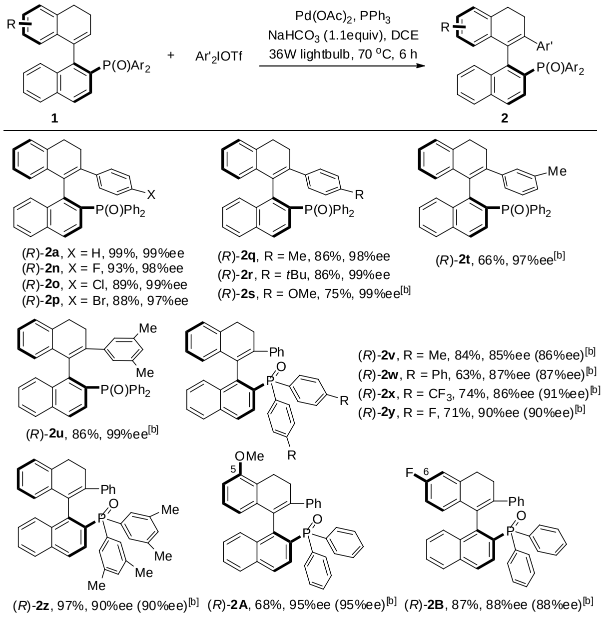
information regarding the possibility of radical pathway. The use of acyclic substrate, diarylation product **4b** was formed predominantly even with only 1.1 equiv of diaryliodonium salt.

Recently, we developed a protocol for synthesis optically active vinylarene atropisomers.[14] However, it was found that the flexibility of the cyclohexene ring leads to these molecules have a relatively lower rotation barrier than the corresponding biaryl compounds. Studies on the thermal stability of axial chirality found that the half-life of optically pure **1a** is around 40 h at 80 °C, and E_a is 28.7 kcal mol^{-1} (See SI). To gain high chirality retention the reaction temperature is better to be performed below 80 °C. Remarkably, this visible light-promoted vinyl C-H arylation provided an ideal method for the functionalization of these compounds. Thus, the synthesis of *ortho*-tetrasubstituted vinylarene atropisomers was probed and in all the cases high chirality retention was observed (Table 4). Electron-rich substituents on the diaryliodonium salt diminished the reaction rates (Table 4, compare **2s**, **2t** with **2a**, **2n**-**p**). No conspicuous effect on the enantioselectivity was found for the identity of the phosphine oxide and substituents on dihydronaphthalene moiety (**2u**-**2B**).

Table 4. Synthesis of *ortho*-Tetrasubstituted Atropisomers



[a] The reaction was conducted at 0.10 mmol scale of **1**. The ee values of starting materials are 99% unless stated otherwise. [b] Reaction time is 12 h. The ee values in parentheses refer to starting materials.

Primary kinetic studies found the first-order dependence of the reaction rate on the concentration of Pd(OAc)$_2$, while zeroth order dependence on Ph$_2$IOTf (Figure 1a).[15] Switching the catalyst-ligand ratio from 1:1 to 1:2 increased the initial rate, while the rate slightly decreased by further addition of PPh$_3$ (Figure 1b). With alternating periods of irradiation or darkness, very slow reaction rate was observed at dark stage, which excluded a radical chain reaction process (Figure 1c). Under darkness, it got less than 10% conversion after being stirred at 70 °C for 24 h (see SI).

Benzene radical cation signals in 1,2-dichloroethane solution was detected by the EPR analysis, which might be generated from phenyl radical. The experimental signal well matched the simulated results (Figure 1d). Experimentally, the addition of radical scavengers galvinoxyl and TEMPO, partially inhibited the reaction, and galvinoxyl was a more effective inhibitor (Scheme 3). The isotope effect was around 1.1 with irradiation while the reaction showed a typical primary isotope effect (k_H/k_D~3.6) under darkness. It means that the C-H functionalization step is rate determining step under darkness, which could be immensely accelerated by visible light irradiation to become a fast step.

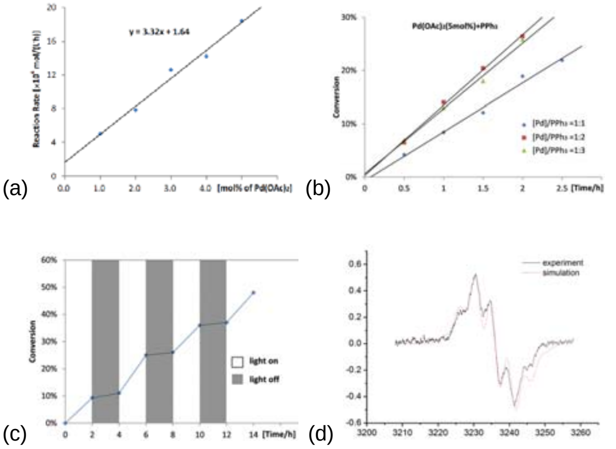
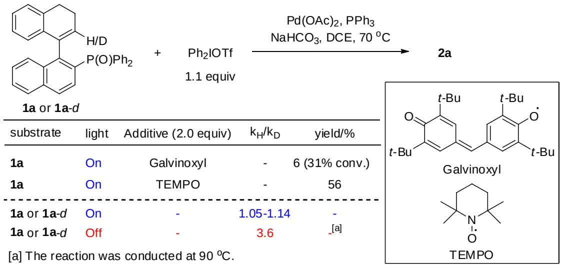


Figure 1. (a) Initial rate vs [Pd(OAc)$_2$]; (b) Conversion vs Time at different ratio of Pd/PPh$_3$. (c) Irradiation control experiments. (d) Experimental and simulated EPR spectra for the reaction mixture at room temperature. Microwave frequency: 9074.603 MHz; Microwave power: 2.0 mW.



substrate	light	Additive (2.0 equiv)	k_H/k_D	yield/%
1a	On	Galvinoxyl	-	6 (31% conv.)
1a	On	TEMPO	-	56
1a or **1a**-*d*	On	-	1.05-1.14	-
1a or **1a**-*d*	Off	-	3.6	-[a]

[a] The reaction was conducted at 90 °C.

Scheme 3. Control Experiments

Bringing together these experimental results, as well as the DFT calculation, a plausible radical-involved catalytic cycle was proposed in Scheme 4,[16] albeit the energy transfer process could not be ruled out. The irradiation of Ph$_2$IOTf gave excited [Ph$_2$IOTf]*, which split to two radical species **I** and **II**.[17] DFT calculation revealed that the homolysis of Ph$_2$I$^+$ is a highly endothermic process, which, however could be readily overcome by absorbing visible light (See SI for details). Radical addition of

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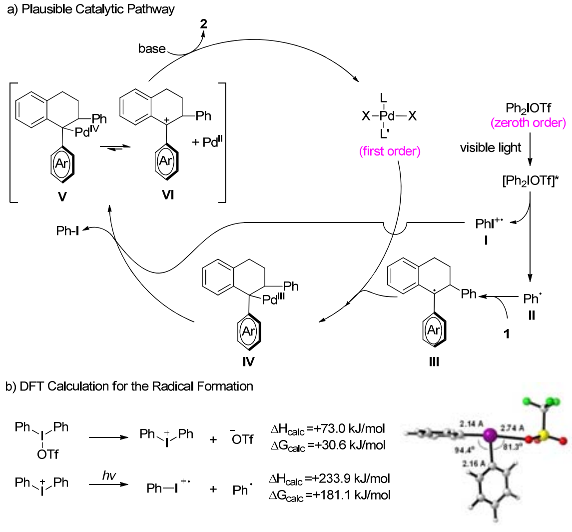
II to **1** would afford **III**, which might associate with catalyst Pd^{II} to give a new palladium species **IV**. The oxidation of **IV** by **I** through single-electron-transfer gave PhI and **V**, which showed significant carbon cation character by DFT calculation and readily formed benzylic cation **VI** and Pd(II). The formation of PhI was unambiguously confirmed by GC-Mass with the comparison of authentic iodobenzene. Finally, **V** would give the olefin product **2** via base-mediated elimination (See SI for details). It is fair to state that under darkness, the C-H functionalization step was the rate determining step, while the irradiation of visible light changed the reaction pathway and C-H functionalization became a fast step.



Scheme 4. Plausible Catalytic Cycle.

In conclusion, we report a visible light promoted C-H functionalization reaction in palladium-catalyzed arylation of vinyl arenes, where no photosensitizer is required. The rate determining step (C-H functionalization step) was accelerated to be a fast step via the irradiation of visible light, which confirmed by the change of kinetic isotope effect (k_H/k_D) from ~3.6 (darkness) to ~1.1 (irradiation). Remarkably, this method enabled the efficient synthesis of *ortho* tetra-substituted vinylarene atropisomers under mild conditions with high enantiospecificity.

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Keywords: palladium • visible light • C-H functionalization • isotope effect • atropisomer

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[15] For convenience, compound **2A** was selected in kinetic studies because of its relatively lower reaction rate.

[16] The true catalytic cycle might be complicated since UV-Vis spectra has no absorption at 530 nm, while 530 nm light was one of the most efficient light sources.

[17] a) J. V. Crivello, J. L. Lee, *J. Polym. Sci.: Part A: Polym. Chem.,* **1989**, *27*, 3951; b)J. L. Dektar, N. P. Hacker, *J. Org. Chem.* **1990**, *55*, 639; c) A. Shirai, H. Kubo, E. Takahashi, *J. Photopolym. Sci. Technol.* **2002**, *15*, 29; d) S. R. Neufeldt, M. S. Sanford, *Adv. Synth. Catal.* **2012**, *354*, 3517.

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Layout 2:

COMMUNICATION

Palladium-catalyzed vinyl C-H functionalization with diaryliodonium was promoted by the irradiation of visible light. Under darkness the C-H activation step is the rate determining step, and kinetic isotope effect (KIE) is around 3.6. With the aid of visible light, the C-H activation step was significantly accelerated and KIE was changed to 1.1.

Jia Feng, Bin Li, Julong Jiang, Mingkai Zhang, Wenbai Ouyang, Chunyu Li, Yao Fu and Zhenhua Gu**

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Visible Light Accelerated Vinyl C-H Arylation in Pd-Catalysis: Application in the Synthesis of *ortho* Tetra-substituted Vinylarene Atropisomers

Accepted Article

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