Orange-red fluorescent Cinnolino[2,3-f]phenanthridin-9-ium salts by palladium(II)-catalyzed C-H bond activation of 2-azobiaryls and alkenes

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The Preparation of Cyclopentadienyl [*o*-(phenylazo)phenyl]nickel

ortho C–H bond cleavage

Kleiman, J. P.; Dubeck, M. *J. Am. Chem. Soc.* **1963**, 85, 1544.

The Tautomerism of Arene and Ditertiary Phosphine Complexes of Ruthenium(0), and the Preparation of New Types of Hydrido-complexes of Ruthenium(II)

Oxidative addition

(a) Chatt, J.; Watson, H. W. *J. Chem. Soc.* **1962**, 2545.

(b) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843.

Ruthenium-Catalyzed Reaction

$\text{H}_2\text{Ru}(\text{CO})_2\text{L}_2$ and $\text{Ru}(\text{CO})_2\text{L}_3$ [L = PPh_3] are found to catalyse the reaction of a variety of aromatic ketones with olefins.

An Overview of Functionalization on the Biarylamine System Through C-H Bond Activation

Scheme 1. Representative studies of directing-group-assisted *N*-free and substituted biarylamine for functionalization through C-H activation. **(a)** Pd (II), X = Ts, acrylates **(b)** Pd (II), X = Ac **(c)** Pd (II), X = Ac, acrylates **(d)** Pd (II), X = Ts, C₆₀ **(e)** Pd (II), X = H, aryl iodides **(f)** Pd (II), X = Ts, CO **(g)** Pd (II), X = H, diphenyl acetylene **(h)** Pd (II), X = Ac, diphenyl acetylene **(i)** Pd (II), X = Ts, dienes **(j)** Pd (II), X = iminoquinone, acrylates **(k)** Pd (II), X = Ac, substituted olefins.

Transition metal-catalyzed C2'-H functionalization of *o*-arylanilines

(c) This work
concept

Raju, S.; Hsiao, H.-C.; Thirupathi, S.; Chen, P.-L.; Chuang, S.-C. *Adv. Synth. Catal.* **2019**, 361, 683-689.

Orange-Red Fluorescent Polycyclic Cinnolino[2,3-f]phenanthridin-9-ium Salts by Palladium(II)-Catalyzed C–H Bond Activation

stoichiometric and catalytic approach

present work

catalytic approach

Optimization studies for the alkenylation/cyclization of 2-azobiaryls with n-butyl acrylate^[a]

Entry	Catalyst (10 mol %)	Co-oxidant (3.0 equiv)	Solvent (1.0 mL)	Yield [%] ^[b] 4ab:5ab
1	Pd(OAc) ₂	CuCl ₂	TFE	68:0
2	Pd(OAc) ₂	CuF ₂	TFE	65:0
3	Pd(OAc) ₂	CuBr ₂	TFE	55:0
4	Pd(OAc) ₂	Cu(BF ₄) ₂ ·6H ₂ O	TFE	15:0
5	Pd(OAc) ₂	PivOH	TFE	15:45
6 ^c	Pd(OAc) ₂	O ₂ /NaBF ₄	TFE	20:trace
7	PdCl ₂	CuCl ₂	TFE	60:0
8	Pd(PPh ₃) ₄	CuCl ₂	TFE	45:0
9	-	CuCl ₂	TFE	trace:0
10	Pd(OAc) ₂	CuCl ₂	<i>t</i> -amyl-OH	trace:0
11	Pd(OAc) ₂	CuCl ₂	DMF	0:0
12	Pd(OAc) ₂	CuCl ₂	DCM	0:0
13 ^d	Pd(OAc) ₂	CuCl ₂	TFE	45:0

Orange-Red Fluorescent Polycyclic Cinnolino[2,3-f]phenanthridin-9-ium Salts

Control experiment

Proposed Mechanism

a) Absorption (1.0×10^{-5} M), b) fluorescence (1.0×10^{-5} M) and c) fluorescence lifetime spectra of 4ad, 4ab, 4ah, 4aj and 4bf.

Conclusion

- We have successfully developed a new, mild, efficient and unprecedented Pd(II)/Cu(II)/Ag(I)/TFE system for the synthesis of orange-red fluorescent 15*H*-cinnolino[2,3-*f*]phenanthridin-9-ium-10-ide and cinnolino[2,3-*f*]phenanthridin-9-ium salts and their derivatives from substituted 2-azobiaryls and various alkenes in one pot.
- This functionalization involves a C-H ortho-olefination, followed by an intramolecular aza-Michael addition process, a step- and atom-economical approach.
- After three decades, we here find a promising method for the synthesis of cinnolino[2,3-*f*]phenanthridin-9-ium salts using azobenzenes with alkenes under palladium catalysis through C-H bond activation.
- Due to the unique emission properties, we believe that these salts can be useful in solution-processed orange-red based OLED materials and the detailed mechanistic investigations of this catalytic reaction are in progress.

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