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Erythrosine B catalyzed visible-light photoredox arylation-cyclization of *N*-alkyl-*N*-aryl-2-(trifluoromethyl)acrylamides to 3-(trifluoromethyl)indolin-2-one derivatives

Zsombor Gonda, Ferenc Béke, Orsolya Tischler, Milán Petró, Zoltán Novák,* Balázs L. Tóth*

Abstract: 3-Trifluoromethyl-indoline-2-one derivatives were prepared in a visible-light photocatalytic transformation of acrylamides. The arylation-ring closure was initiated by light induced aryl radical generation from aryl diazonium salts with the utilization of erythrosine B as a novel organic photocatalyst.

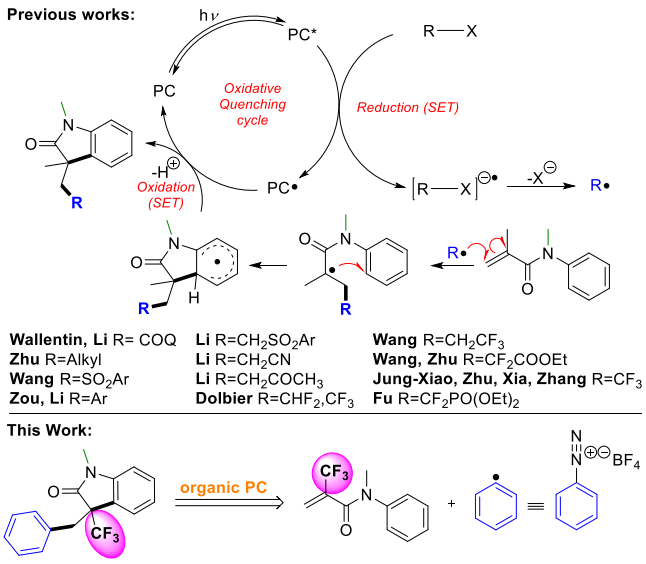
Introduction

In the last decade the photoredox catalysis evolved rapidly. There are numerous published transformations which uses the energy of visible light irradiation to cleave chemical bonds.[1] In a photocatalytic reaction colored photosensitizer dyes act as catalysts and after the absorption of appropriate wavelength of a photon instantaneously an excited state takes place. As the result of the relaxation charge transfer (CT) occurs which lead to generate reactive radicals in single electron transfer (SET) fashion. The library of these photocatalyst dye molecules are wide and truly diverse.[2] However, it can be concluded, Ir and Ru based complexes are prevalent, but the use of organic sensitizer molecules is a less developed part of this field. The photocatalytically generated radicals can recombine resulting a radical coupling, or attack on a substrate initiating a radical cascade, which leads to the formation of cyclized product in easily feasible way.[3]

The indolin-2-one core structure units can be formed by cyclization reactions of *N*-aryl acrylamide compounds. These ring closing reactions were well investigated and several methodology have already been developed such as transition metal catalyzed Heck-like coupling,[4] Suzuki-type reactions,[5] oxidative palladium catalyzed cyclizations,[6] oxidative cyclizations[7] and intramolecular radical ring closure initiated electrochemically,[8] with chemical initiators[9] (e.g. AIBN, TBHP, Bu_3SnH, Langlois' salt) or by UV and visible light.[10] Remarkably, there are significant examples for Ir and Ru photocatalyzed cyclization reactions of *N*-aryl acrylamide derivatives to oxazolines, benzoxazines,[11] 3,4-disubstituted dihydroquinolinones,[12,13] 1-azaspiro[4.5]decanes[13] and indolin-2-ones[14-20,22-25]. Various radical species can be used for the construction of the target indolin-2-one derivatives via the cyclization path (Scheme 1). In the existing methods, radicals for the initial step were originated from carboxylic anhydrides,[14] carboxylic acids,[15] iodonium salts,[13b, 16] arenediazonium salts,[17] solvents such as dichloromethane[17b] acetonitrile,[17c] or acetone,[17c] (phenylsulfonyl)methyl bromide[18] or arylsulfinic acids.[19] However, the cyclization takes place also by photocatalyzed dehalogenation of *o*-iodophenylacrylamides or bromodifluoroacetamides.[20]

The fluorinated functional groups have significant impact on medicinal and agricultural chemistry due to their electronic properties, metabolic stability and their effect on lipophilicity.[21] In this field the application of trifluoromethyl group is extensively investigated.[22]

According to general interest, the presence of fluorine functionalized groups appeared also in the chemistry of indolin-2-one derivatives. Based on radical photoredox cyclization reactions significant synthetic methods were developed to install fluorine into these cyclic organic compounds, therefore ethyl 2,2-difluoroacetyl,[23] diethyl (trifluoromethyl)phosphonyl,[24] 2,2,2-trifluoroethyl[25] or di- and trifluoromethyl group were introduced.[26]



Scheme 1. Photoredox catalyzed cyclization of *N*-aryl acrylamides to indolin-2-one structures.

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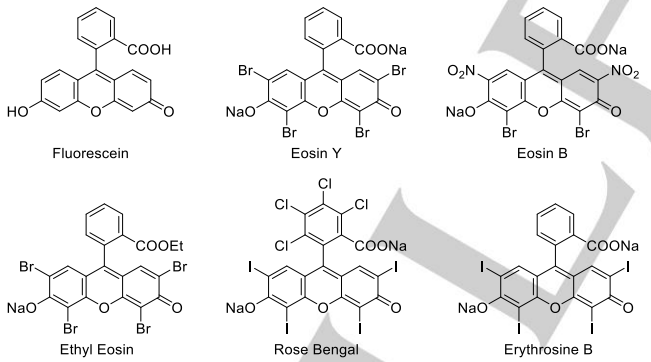
In our research, we aimed to prepare trifluoromethylated oxindole derivatives in the radical cyclization reaction in which the fluoroalkyl group attaches directly to the heterocyclic system.

To achieve the synthesis of the target heterocycle we aimed to utilize transition-metal-free photoredox catalytic conditions. The utilization of widely available structurally diverse organic photocatalysts could make the procedure more economic and environmentally benign.[27] Beside the utilization of transition metal based photoredox systems for the ring closure of acrylates,[14-18,20,23-26] organic photosensitizer (eosin Y) catalyzed cyclizations of *N*-aryl acrylamides were developed by Wang and coworkers.[19]

Herein we report a novel erythrosine B organic photosensitizer catalyzed cyclization reaction of *N*-aryl-2-(trifluoromethyl)-acrylamides to access new *N*-3-(trifluoromethyl)indolin-2-one derivatives. In our transformation, aryldiazonium tetrafluoroborate salts serve as radical aryl source. The reduction potentials of arenediazonium salts are very close to 0 V, which means the formation of aryl radicals are not energy demanding procedures, therefore it is easily feasible.[28] This is one of their advantages, which ease their use in synthetic applications and in photoredox transformations.

Erythrosine B is a member of the xanthene dye family, its structure derivable from fluorescein or eosin substances (Scheme 2). It is widely used as food colorant (E127, FD&C Red No. 3) or painting ink, but the chemical application remained within a narrow band such as photodegradation,[29] photodynamic therapy experiments[30] photoinitiated radical polymerization,[31] photodehydrogenation[32] and used as triplet sensitizer for *cis-trans* isomerization of alkenes.[33]



Scheme 2. Members of xanthene dye family used as photosensitizers such as fluoresceine and its substituted derivatives, eosin Y and erythrosine B.

Results and Discussion

At the beginning of the optimization of the reaction we used the most frequently applied conditions for our model reaction.[17] We studied the arylation-cyclization reaction of *N*-methyl-*N*-phenyl-2-(trifluoromethyl)acrylamide and 4-fluorophenyl-diazonium tetrafluoroborate, which serves as excellent aryl radical source under inert (argon atmosphere) photocatalytic conditions (Table 1). In dimethyl sulfoxide (DMSO) without irradiation, in absence of catalyst we did not observed the formation of any product (Table 1. Entry 1). Visible-light irradiation without any catalyst did not result the formation of the desired product (Entry 2). Although, it is important to mention, that 10% of the starting acrylamide was decomposed but no product was identified. In the presence of 5 mol% tetraacetylriboflavin or acrydine yellow the heterocycle formation took place in 25% and 18% yield (determined by calibrated GC-FID analysis, Entries 3 and 4) respectively under blue LEDs (Light Emitting Diodes) irradiation. Eosin B as photocatalyst gave similar results when blue or green light was used for the activation (Entries 5 and 6). Ethyl eosin gave slightly higher GC yields both in DMSO and MeOH for the cyclized product but the efficiency remained between 27-36% independently from the type of light source (Entries 7-9). During the optimization studies with other photocatalyst we recognized that the temperature has significant influence on the efficiency of the transformation (*vide infra*). With the use of LEDs without external cooling the reaction temperature was 45 °C, due to the heat generation. However, significant reduction of the temperature to -50 °C had beneficial effect on the yield and it was revealed, that the ethyl eosin photocatalyzed reaction in methanol under green light irradiation can convert quickly the starting *N*-aryl-2-(trifluoromethyl)acrylamide into arylated 3-(trifluoromethyl)-indolin-2-one derivative in 77% of GC yield (Entry 10). Replacement of the light source to blue LEDs resulted lower 46% yield at -50 °C (Entry 11). In searching the most efficient sensitizer we found that among the tested photocatalysts erythrosine B was superior for the transformation. As a reference for the study of this photocatalyst, the reaction was carried out in the absence of light and the reaction did not work (Entry 12). First, the reaction mixture of starting materials and 5 mol% of erythrosine B in DMSO solvent was irradiated by CFL (Compact Fluorescent Light bulb) and we observed 49% yield at 25 °C (Entry 13). When green LEDs were used for the reaction the product was formed in 33% GC yield after 2 hours (Entry 14). Changing the light source from green to blue LEDs resulted higher 43% GC yield of the oxindole derivative. Considering the properties of aryldiazonium salts, it is important to exclude or suppress their thermal decomposition reactions. Therefore, we carried out the green and blue light irradiated reactions in a wider temperature range between 45 °C and -50 °C (Entry 15-19). We found that decreasing the reaction temperature results in higher yields of the product, and the best result, 89% GC yield of the cyclic product was obtained at -50 °C under blue light irradiation after 2 hours reaction time (Entry 19). To compare the light sources, we carried out the reaction at -50 °C using green LEDs, but the reaction afforded the desired product only in 31% GC yield demonstrating the necessity of blue light (Entry 20). Additionally, during the optimization studies we demonstrated the importance of the inert reaction atmosphere. Changing the argon atmosphere to oxygen for the same reaction gave no product (Entry 21). It is easy to understand, since the oxygen is triplet in ground state, which allows to enter into the radical photocatalytic quenching cycle and thereby inhibit the reaction and the formation of the desired product. After finding the suitable catalyst and the optimal reaction temperature we tested further solvents for the transformation such as DMF, ethanol, hexane, THF but these solvents were not suitable in this arylation-cyclization reaction (Entries 21-24).

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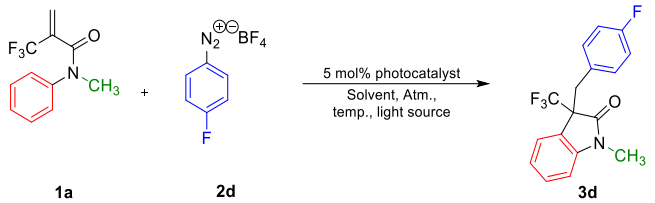
Table 1. Optimization study for photoredox 4-fluorophenylation-cyclization of *N*-methyl-*N*-phenyl-2-(trifluoromethyl)acrylamide.[a]



1a **2d** **3d**

Entry	Photocatalyst	Light Source	Solvent	T/°C	GC yield %[d]
1	-	dark	DMSO	25	0
2	-	23W CFL[b]	DMSO	25	0
3	Tetraacetyl-riboflavin	blue LEDs[c]	MeOH	45	25
4	Acrydine yellow	blue LEDs[c]	MeOH	45	18
5	Eosin B	blue LEDs[c]	MeOH	45	4
6	Eosin B	green LEDs[c]	MeOH	45	23
7	Ethyl eosin	blue LEDs[c]	MeOH	45	30
8	Ethyl eosin	green LEDs[c]	MeOH	45	36
9	Ethyl eosin	green LEDs[c]	DMSO	45	27
10	Ethyl eosin	green LEDs[c]	MeOH	-50	77
11	Ethyl eosin	blue LEDs[c]	MeOH	-50	46
12	Erythrosine B	dark	DMSO	25	0
13	Erythrosine B	23W CFL[b]	DMSO	25	49
14	Erythrosine B	green LEDs[c]	DMSO	45	33
15	Erythrosine B	blue LEDs[c]	MeOH	45	43
16	Erythrosine B	blue LEDs[c]	MeOH	25	44
17	Erythrosine B	blue LEDs[c]	MeOH	-20	53
18	**Erythrosine B**	**blue LEDs[c]**	**MeOH**	**-50**	**89**
19	Erythrosine B	green LEDs[c]	MeOH	-50	31
20	Erythrosine B	blue LEDs[c]	MeOH	-50	0[e]
21	Erythrosine B	blue LEDs[c]	DMF	-50	33
22	Erythrosine B	blue LEDs[c]	EtOH	-50	19
23	Erythrosine B	blue LEDs[c]	Hexane	-50	3
24	Erythrosine B	blue LEDs[c]	THF	-50	0

[a] General conditions: 0.005 mmol photocatalyst, 0.1 mmol *N*-methyl-*N*-phenyl-2-(trifluoromethyl)acrylamide, 0.25 mmol 4-fluorophenydiazonium tetrafluoroborate, 1.2 mL solvent, argon atmosphere. [b] CFL = Compact Fluorescent Light Bulb, [c] Green (520-530 nm) LEDs or blue (460-470 nm) LEDs. [d] Calibrated GC yield after 2 h. [e] O_2 atmosphere.

As a confirmation for the photoinitiation, the reaction was followed by *in situ* time-resolved infrared spectroscopy (IR). The photoredox reaction between *N*-methyl-*N*-phenyl-2-(trifluoromethyl)acrylamide (**1a**) and 4- fluorobenzenediazonium tetrafluoroborate (**2d**) catalyzed by erythrosine B (5 mol%) was performed in methanol. Dark and irradiated time periods (by 23 W CFL bulb) were alternated and the intensity changes of the carbonyl band of the product (located at 1717 cm^{-1}) was measured. The product formation was initiated by irradiation and was paused when the light was switched off. The temperature of the irradiated periods was between 26-28 °C while in the dark periods it was 24 °C (Figure 1). The cyclization in methanol was slower compared to DMSO (see Supporting Information), yet it reached completion after 6 hours. Therefore, *in situ* IR-monitoring demonstrated that the formation of the product occurs only under light irradiation, while in the absence of light the transformation stopped.

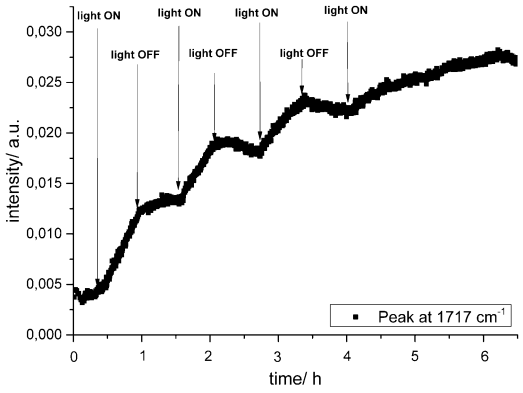


Figure 1. Evolution of peak 1717 cm^{-1} referring to the characteristic carbonyl band of 3-(4-fluorobenzyl)-1-methyl-3-(trifluoromethyl)indolin-2-one in a MeOH solution recorded by ReactIR.

As the result of our optimization studies we determined the most efficient condition for the synthesis of the 3-trifluoromethyl-2-oxindole derivatives through the photoredox catalyzed ring closure. Thus, we explored the substrate scope of the methodology in MeOH at -50 °C under argon atmosphere in the presence of 5 mol% erythrosine B photocatalyst under blue light irradiation by LEDs. The trifluoromethylated acrylamide **1a** was reacted with various diazonium salts under the optimized conditions (Table 1. Entry 18).

The reaction with phenyldiazonium salt provided the oxindole product **3a** in 41% yield. Reactions with aryldiazonium salts substituted with electron donating groups, such as methyl and methoxy, on the aromatic ring in *para* position afforded the desired products **3b** and **3c** in 83% and 38% yield, respectively. Halogenated aryldiazonium salts were also suitable reactants for the arylation-cyclization reaction. The presence of bromo, chloro and fluoro functions on the aromatic ring in *para* positions tolerated well the reaction conditions and the desired heterocycles (**3d**-**3f**) were obtained in good yields (70-80%).

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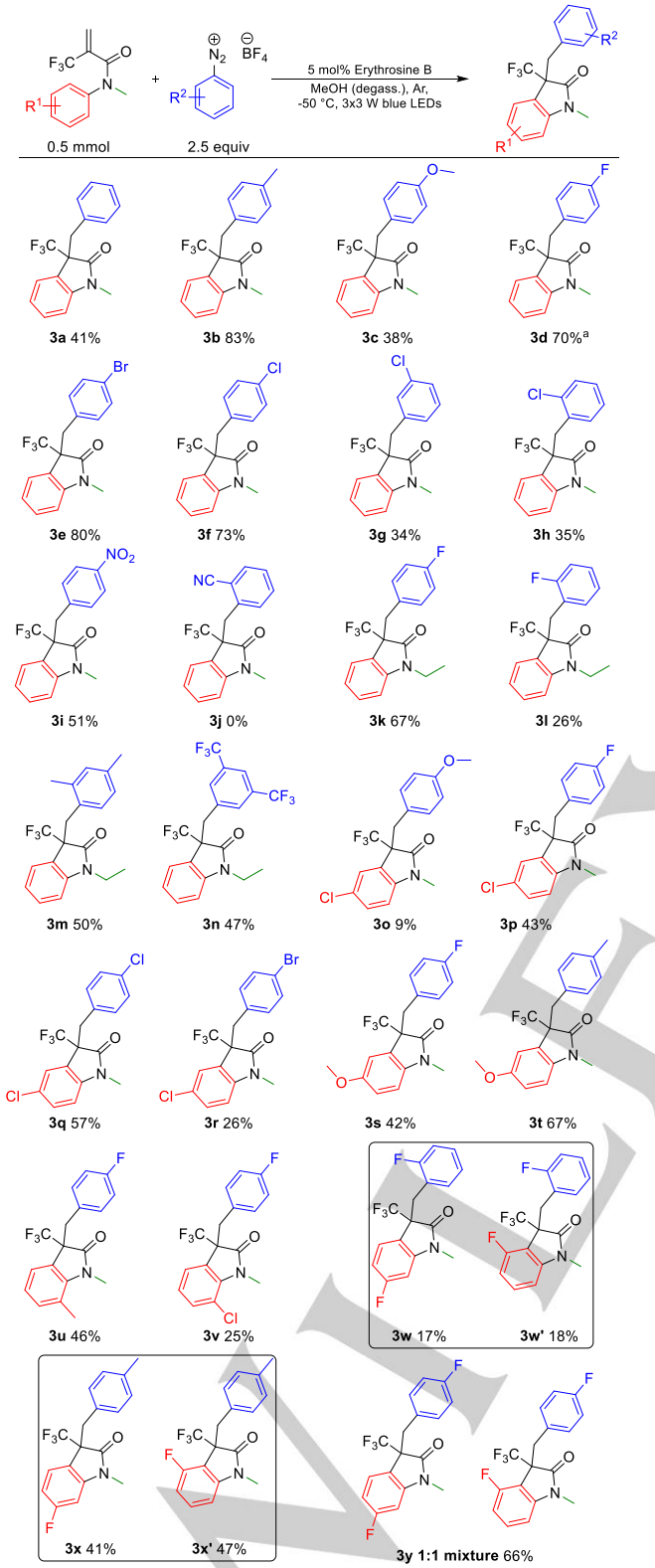

Scheme 3. Scope and limitations of the cyclization. Reaction conditions: erythrosine B (0.025 mmol, 5 mol%). *N*-alkyl-*N*-aryl-2-(trifluoromethyl)-acrylamide (0.5 mmol), aryldiazonium tetrafluoroborate (1.25 mmol, 2.5 equiv), 6 mL degassed methanol, 3x3 W blue (460-470 nm) Epistar power LEDs, -50 °C, 4-6 hours. Isolated yields. [a] Started from 1 mmol acrylamide.

When the chlorine atom was in *meta* and *ortho* position the appropriate products **3g** and **3h** was obtained in relatively lower yields (34% and 35% respectively). The reaction carried out with 4-nitrophenyldiazonium salt provided the oxindole derivative **3i** in 51% yield, demonstrating the applicability of electron deficient reaction partners. In contrast, electron withdrawing nitrile group in *ortho* position had deleterious effect on the transformation and the desired product **3j** was not formed. Further transformations were performed on the *N*-ethyl derivative of the acrylamide (**1b**) and similar reactivity pattern was observed when different diazonium salts were applied. Both the *para* and *ortho* fluorophenyl-diazonium salt provided the appropriate product **3k** and **3l** in 67% and 26% yield, respectively. The dimethylphenyl derivative was isolated in 50% yield, while the utilization of electron deficient bis(trifluoromethyl)phenyldiazonium salt in the transformation enabled the access of the appropriate oxindole **3n** in 47% yield. The ring closure was successfully achieved in the reaction of chloro- substituted aryl acrylamide and methoxy-, fluoro-, chloro- and bromophenyldiazonium salts, and the halide substituted heterocycles (**3o-r**) were obtained in 9-57% yields. The reaction was repeated under the developed photocatalytic conditions with electron rich 4-methoxyphenylacrylamide. The reaction of this substrate both with *para* fluorophenyl- and *para* tolyldiazonium salt provided the appropriate oxindole derivatives **3s** and **3t** in 42% and 67% yields, respectively. Phenylacrilamides with methyl and chloro substituents in *ortho* position to the amide function on the phenyl ring were also subjected to the transformation and the expected indolinones **3u** and **3v** were obtained in 46% and 25% yield. Reactions between the *meta*-fluoro substituted acrylamide and various aryldiazonium salts afforded two regioisomers. Reaction with 2-fluorophenyl diazonium salt afforded regioisomers **3w** and **3w'** in 1:1 ratio, which were separated and obtained in 17% and 18 % yields. The appropriate regioisomers were isolated in higher yields when 4-methylphenyldiazonium salt was used for the same substrate. In this case the isomers were formed also in 1:1 ratio but each product was obtained in higher yield (41% and 47% for **3x** and **3x'**). Unfortunately, the appropriate heterocyclic products of the reaction of 4-fluorophenyldiazonium salt and the *meta* substituted fluorophenyl-acrylamide were isolated as 1:1 mixture of the regioisomers in 66% yield.

Conclusions

In conclusion, we have developed a novel method for visible-light photoredox arylation-cyclization of *N*-alkyl-*N*-aryl-2-(trifluoromethyl)acrylamides resulting 3-(trifluoromethyl)indolin-2-one derivatives. The aryl radicals were generated from aryldiazonium tetrafluoroborate salts. In this reaction erythrosine B was used as novel organic photocatalyst. The photocatalytic transformation was carried out at -50 °C, irradiation by blue light LEDs, and the reaction was followed by *in situ* time-resolved infrared spectroscopy at room temperature. With the utilization of the optimized reaction conditions, wide variety of 3-(trifluoromethyl)indolin-2-one compounds were synthesized.

Experimental Section

A 20 mL septum-screw-cap vial was charged with erythrosine B (0.025 mmol, 5 mol%). *N*-alkyl-*N*-aryl-2-(trifluoromethyl)acrylamide (0.5 mmol), aryldiazonium tetrafluoroborate (1.25 mmol, 2.5 equiv) and equipped with stirring bar. The atmosphere was evacuated and backfilled with argon (repeated 3 times). 6 mL degassed methanol was added by syringe through the septa. 3x3 W blue (460-470 nm) or green (520-530 nm) Epistar Power LEDs and wires were insulated and the light sources were wrapped around the vessel. The reaction vessel and LEDs were placed into -50 °C cryostated isopropyl alcohol cooling bath. The reaction mixture was homogenized for 5 minutes then the lights were switched on and the mixture was stirred for 4-6 hours. The mixture was quenched with water, ad extracted with diethyl ether. The organic phase was collected and extracted 2 times with saturated $NaHCO_3$ solution, followed by brine then dried over $MgSO_4$ and evaporated in rotary evaporator. The crude product was purified by flash column chromatography (hexane/ethyl acetate).

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Keywords: erythrosine B • photoredox catalysis • arylation-cyclization • arenediazonium salts • trifluoromethyl group

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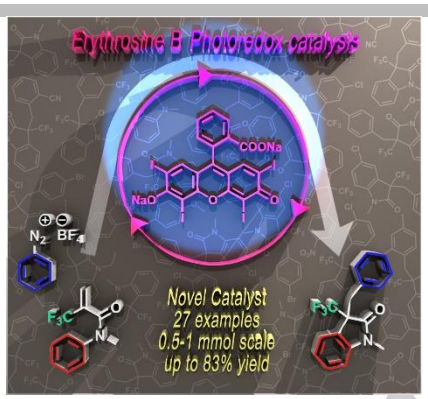
3-Trifluoromethyl-indoline-2-one derivatives were prepared in a visible light photocatalytic transformation of acrylamides. The arylation-ring closure was initiated by light induced aryl radical generation from aryl diazonium salts with the utilization of erythrosine B as novel organic photocatalyst.



Organic Dye

Zsombor Gonda, Ferenc Béke, Orsolya Tischler, Milán Petró, Zoltán Novák Balázs L. Tóth**

Page No. – Page No.

Erythrosine B catalyzed visible-light photoredox arylation-cyclization of N-alkyl-N-aryl-2-(trifluoromethyl)acrylamides to 3-(trifluoromethyl)indolin-2-one derivatives