Supporting Information

Visible-light-induced radical cyclization of N-allylbenzamide with CF3SO2Na to trifluoromethylated

dihydroisoquinolinones in water at room temperature

Long Zou,^a Pinhua Li*,^a Bin Wang,^a and Lei Wang,*,^{a,b}

^a Department of Chemistry, Huaibei Normal University, Huaibei, 235000, P. R. China Fax: (+86)-561-380-3602; phone: (+86)-561-380-6281; e-mail: *pphuali@126.com; leiwang@chnu.edu.cn*

^b State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, P. R. China

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 X-Ray single crystal diffraction analysis of 3s (CCDC: 1874460)



R(reflections) = 0.0612 (839)S = 0.859 wR2(reflections) = 0.1127 (2278) Npar = 172

2. Further optimization of the reaction conditions (TS1)

O N OMe		Ru(bpy ₎₃ Cl ₂ (mol%) TBHP (70% solution in H ₂ O)		O N_OMe	
1a	2a	Blue LED (450-455 n H ₂ O, air, room temp	m, 3 W)	CF ₃ 3a	
Entry	Ru(bpy) ₃ Cl ₂ (mol%)	TBHP (equiv)	Time (h)	Yield (%) ^b	
1	Ru(bpy) ₃ Cl ₂ (1.0 mol%)	TBHP (1.5 equiv)	24	63	
2	Ru(bpy) ₃ Cl ₂ (2.0 mol%)	TBHP (1.5 equiv)	24	89	
3	Ru(bpy) ₃ Cl ₂ (3.0 mol%)	TBHP (1.5 equiv)	24	88	
4	Ru(bpy) ₃ Cl ₂ (2.0 mol%)	TBHP (1.0 equiv)	24	65	
5	Ru(bpy) ₃ Cl ₂ (2.0 mol%)	TBHP (2.0 equiv)	24	87	
6	Ru(bpy) ₃ Cl ₂ (2.0 mol%)	TBHP (1.5 equiv)	24	75 ^c	
7	Ru(bpy) ₃ Cl ₂ (2.0 mol%)	TBHP (1.5 equiv)	24	87 ^d	
8	Ru(bpy) ₃ Cl ₂ (2.0 mol%)	TBHP (1.5 equiv)	18	83	
9	Ru(bpy) ₃ Cl ₂ (2.0 mol%)	TBHP (1.5 equiv)	30	86	
10	Ru(bpy) ₃ Cl ₂ (2.0 mol%)	TBHP (1.5 equiv)	24	87 ^e	
11	Ru(bpy) ₃ Cl ₂ (2.0 mol%)	TBHP (1.5 equiv)	24	NR ^f	
12	Ru(bpy) ₃ Cl ₂ (2.0 mol%)	_	24	NR	
13	_	TBHP (1.5 equiv)	24	NR	

Table S1 Further optimization of the reaction conditions^a

^{*a*} Reaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), Ru(bpy)₃Cl₂, TBHP (70% solution in H₂O), H₂O (2.0 mL) at room temperature under blue LED (450–455 nm, 3 W) irradiation in air. ^{*b*} Isolated yield. ^{*c*} **2a** (1.0 equiv) was used. ^{*d*} **2a** (3.0 equiv)

was used. ${}^{e}N_{2}$ atmosphere. ${}^{f}In$ the darkness. NR = no reaction.

3. Investigation of photocatalysts with light sources (TS2)

O N	,OMe + CF₃	Ph ₃ SO ₂ Na —	Photocatalyst (2.0 mol%) <u>3 W LED irradiation</u> TBHP (1.5 equiv)			
1a		2a	Π ₂ Ο, απ, π,	24 11	CF ₃	3a
Sield (000 bounded	380–385 nm	420–425 nm	450–455 nm	520–525 nm	530–535 nm	I _{max} nm
Acridine red	NR	NR	Trace	55	64	526
Ru(bpy) ₃ Cl ₂	Trace	59	89	NR	NR	452
Ru(phen) ₃ Cl ₂	Trace	55	46	NR	NR	422
Na ₂ -Eosin Y	NR	Trace	33	39	48	539
Fluorescein	NR	NR	27	54	59	528
Rhodamine B	NR	NR	Trace	Trace	Trace	553
Rose bengal	NR	NR	Trace	Trace	Trace	548

Table S2 Investigation of photocatalysts with light sources^a

^{*a*} Reaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), photocatalyst (2.0 mol%), TBHP (70% solution in H₂O, 1.5 equiv), H₂O (2.0 mL) at room temperature under LED irradiation (3 W) in air for 24 h. ^{*b*} Isolated yield. NR = no reaction.

4. Removal of *N*-protection groups from the substrates or products

4.1 Removal of *N*-Boc group from the corresponding substrate (1af)



Typical procedure for the deprotection of *N*-Boc-amide to amide: According the reported method (K.-I. Tanaka, S. Yoshifuji and Y. Nitta, *Chem. Pharm. Bull.*, 1988, **36**, 3125–3129), *tert*-butyl allyl(benzoyl)carbamate (**1af**, 1307 mg, 5.0 mmol) was dissolved in a mixture of CF₃CO₂H (TFA, 4.0 mL) and CH₂Cl₂ (DCM, 4.0 mL). The mixture was stirred at room temperature for 2 h and then evaporated under reduced pressure. The resulting residue was purified by recrystallization, yielding the pure product amide (**7**, 717 mg, 89% yield). *N*-Allylbenzamide (**6**). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ : 7.81–7.79 (m, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 6.90 (br, 1H), 5.94–5.84 (m, 1H), 5.21 (dd, *J*₁ = 17.2 Hz, *J*₂ = 0.8 Hz, 1H), 5.12 (d, *J* = 10.3 Hz, 1H), 4.03 (t, *J* = 5.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 167.5, 134.5, 134.3, 131.3, 128.4, 127.1, 116.2, 42.4.

4.2 Removal of *N*-Bn group from the corresponding substrate (1ag)



Typical procedure for the deprotection of *N*-Bn-amide to amide: According the reported method (L. Kuang, J. Zhou, S. Chen and K. Din, *Synthesis*, 2007, 3129–3134), to a solution of *N*-Bn-amide (**1ag**, 502.7 mg, 2.0 mmol) in CHCl₃ (10 mL),

NBS (5.0 mmol) were added at room temperature and the resulting mixture was stirred for 18 h. After the solvent was removed under reduced pressure, EtOAc (25 mL) and NaOH (aq. 1.0 mol/L, 10 mL) were added to the residue. The mixture was stirred for 10 min at room temperature, and then the organic layers were separated. The aqueous phase was extracted with EtOAc (3×10 mL) and the combined organic layers were washed with H₂O (2×10 mL), brine (1×10 mL) and dried over Na₂SO₄. The solvent was removed and the residue was purified by chromatography to yield the deprotection product (**6**, 261 mg, 81% yield).

4.3 Removal of *N*-MeO group from the product **3a**



Typical procedure for the deprotection of *N*-MeO-amide to amide: According the reported method (H. Zhong, D. Yang, S. Wang and J. Huang, *Chem. Commun.*, 2012, **48**, 3236–3238), NaH (1.50 mmol) was added into a stirred solution of 2-methoxy-4-(2,2,2-trifluoroethyl)-3,4-dihydroisoquinolin-1(2*H*)-one (**3a**, 130 mg, 0.50 mmol) in DMF (3.0 mL) and the resulting mixture was heated at 120 °C for 2 h. After the reaction was completed, the reaction mixture was allowed to cool down to room temperature, and H₂O (12.0 mL) was added, extracted with CH₂Cl₂ (3×10 mL). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel, providing the deprotection product **7** (86 mg, 75% yield). **4-(2,2,2-Trifluoroethyl)-3,4-dihydroisoquinolin-1(2***H***)-one (7**). White solid. ¹H NMR (400 MHz, CDCl₃) δ : 8.12 (d, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.54 (br, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.22–7.19 (m, 1H), 2.39–2.35 (m, 1H), 1.80–1.66 (m, 2H), 1.01 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 171.4, 135.3, 132.7, 132.6, 125.9 (q, *J* = 5.3 Hz), 124.8, 124.4, 124.1 (q, *J* = 271.2 Hz), 49.3, 39.5, 25.2. HRMS

(ESI) $([M + H]^+)$ Calcd For $C_{11}H_{10}F_3NO$: 229.0714, found: 229.0715.

5. ¹H and ¹³C and ¹⁹F NMR spectra of the products























































-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 ppm



















































