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Supporting Information

Photoredox Allylation Reactions Mediated by Bismuth in Aqueous Conditions

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## **General Methods and Synthesis**

All commercial chemicals and dry solvents were purchased from Sigma Aldrich, Alfa Aesar or TCI Chemicals. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Inova 400 NMR instrument with a 5 mm probe. All chemical shifts are referenced using deuterated solvent signals. GC-MS spectra were obtained by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection; they are reported as: m/z (rel. intensity).

Flash chromatography purifications were carried out using VWR or Merck silica gel (40-63 µm particle size). Thin-layer chromatography was performed on Merck 60 F254 plates.

Reaction mixture was irradiated with Kessil® PR160L@456 nm.<sup>[1]</sup>

Aldehydes **11**,<sup>[2]</sup> **1n**,<sup>[3]</sup> **1v**,<sup>[4]</sup> **1w-x**,<sup>[5]</sup> **1z**,<sup>[6]</sup> photocatalyst **3CzCIIPN**<sup>[7]</sup> and Hantzsch ester<sup>[8]</sup> were prepared according to literature procedures.

#### General procedure for photoredox bismuth-catalyzed allylation of aldehydes.



A dry 10 mL Schlenk tube, equipped with a Rotaflo stopcock, magnetic stirring bar and an argon supply tube, was subjected to three vacuum-argon cycles and then it was first charged with all the solids – i.e. Bi(OTf)<sub>3</sub> (0.02 mmol, 13 mg, 10 mol%), 3CzCIIPN (0.01 mmol, 6 mg, 5 mol%), Hantzsch ester (0.4 mmol, 100 mg, 2 equiv.) and, if solid, the aldehyde (0.2 mmol) – followed by EtOH (1.5 mL) and water (1.5 mL). Then, allyl bromide **2** (0.6 mmol, 73 mg, 52  $\mu$ L, 3 equiv.) and, if liquid, the aldehyde (0.2 mmol) were added. The reaction was irradiated under vigorous stirring for 16 or 72 h. After that the reaction was quenched with water (approx. 4 mL) and extracted with AcOEt (4 x 5 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The crude was subject of flash column chromatography (SiO<sub>2</sub>) to afford the products **3** in the stated yields. For aldehydes **1k,o,q** if the reaction was conducted for 72 h, the major final product was the corresponding ethyl ether (**5k,o,q**, See Table S4).

**Preparative scale reaction**: The reaction was performed on 1 mmol of aldehyde **1a** (140 mg) following the general procedure irradiating with Kessil® PR160L@456 nm for 72 hours. Reagent amounts: Bi(OTf)<sub>3</sub> (0.08 mmol, 52.5 mg, 8 mol%), 3CzCIIPN (0.03 mmol, 20 mg, 3 mol%), Hantzsch ester (2 mmol, 500 mg, 2 equiv.), allyl bromide (03 mmol, 260  $\mu$ L, 3 equiv.) in EtOH (7.5 mL) and water (7.5 mL) mixture. Product **3a** was obtained in 77% yield (0.77 mmol, 140 mg) after flash chromatographic purification (DCM).

(3a): yellowish oil, 74% (0.15 mmol, 27 mg). The general procedure (16 h) was applied using **1a** (0.2 mmol, 28 mg) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

(**3b**): brown oil, 65% (0.13 mmol, 22 mg). The general procedure (72 h) was applied using freshly distilled **1b** (0.2 mmol, 21  $\mu$ L) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[10]</sup>

(**3c**): brown oil, 66% (0.13 mmol, 29 mg). The general procedure (72 h) was applied using freshly distilled **1c** (0.2 mmol, 27  $\mu$ L) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

 $(\mathbf{3d})$ : brown oil, 74% (0.15 mmol, 27 mg). The general procedure (16 h) was applied using freshly distilled **1d** (0.2 mmol, 22 µL) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

(**3e**): yellowish oil, 94% (0.19 mmol, 28 mg). The general procedure (72 h) was applied using freshly distilled **1e** (0.2 mmol, 20  $\mu$ L) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

(**3f**): yellowish oil, 81% (0.16 mmol, 32 mg). The general procedure (16 h) was applied using **1f** (0.2 mmol, 31 mg) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

(**3g**): yellowish oil, 79% (0.16 mmol, 32 mg). The general procedure (72 h) was applied using freshly distilled **1g** (0.2 mmol, 33  $\mu$ L) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>



(**3h**): brown oil, 62% (0.12 mmol, 28 mg). The general procedure (16 h) was applied using **1h** (0.2 mmol, 36 mg) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were

in agreement with those reported in literature.<sup>[9]</sup>

(**3i**): brown oil, 79% (0.16 mmol, 28 mg). The general procedure (16 h) was applied using freshly distilled **1i** (0.2 mmol, 24 μL) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[11]</sup>

(**3j**): brown oil, 74% (0.15 mmol, 26 mg). The general procedure (16 h) was applied using freshly distilled **1j** (0.2 mmol, 24 μL) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[11]</sup>

 $^{OH}_{MeO}$  (**3k**): brown oil, 34% (0.07 mmol, 12 mg). The general procedure (16 h) was applied using freshly distilled **1k** (0.2 mmol, 24 µL) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

(**3I**): brown oil, 65% (0.13 mmol, 25 mg). The general procedure (16 h) was applied using previously synthesized **1I** (0.2 mmol, 30 mg) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

(**3m**): brown oil, 61% (0.12 mmol, 21 mg). The general procedure (16 h) was applied using **1m** (0.2 mmol, 26 mg) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

(**3n**): brown oil, 61% (0.12 mmol, 25 mg). The general procedure (16 h) was applied using previously synthesized **1n** (0.2 mmol, 33 mg) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

(**3o**): yellow oil, 33% (0.07 mmol, 10 mg). The general procedure (16 h) was applied using freshly distilled **1o** (0.2 mmol, 19  $\mu$ L) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[11]</sup>

(3p): brown oil, 66% (0.13 mmol, 20 mg). The general procedure (16 h) was applied using freshly distilled **1p** (0.2 mmol, 18 µL) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

(3q): yellow oil, 60% (0.12 mmol, 28 mg). The general procedure (16 h) was applied using 1q (0.2 mmol, 38 mg) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

 $\stackrel{OH}{\bigvee_8}$  (**3r**): brown oil, 68% (0.14 mmol, 27 mg). The general procedure (72 h) was applied using freshly distilled **1r** (0.2 mmol, 38 µL) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[12]</sup>

(**3s**): brown oil, 56% (0.11 mmol 18 mg). The general procedure (72 h) was applied using freshly distilled **1s** (0.2 mmol, 23 μL) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[13]</sup>

 $^{\text{Ph}}$  (3t): brown oil, 85% (0.17 mmol, 30 mg). The general procedure was applied using freshly distilled 1t (0.2 mmol, 26 µL) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

(3u): brown oil, 58% (0.12 mmol, 18 mg). The general procedure was applied using freshly distilled **1u** (0.2 mmol, 24 µL) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

 $_{BnO}$  (**3v**): brown oil, 68% (0.14 mmol, 20 mg). The general procedure was applied using previously synthesized **1v** (0.2 mmol, 36 mg) as aldehyde. Flash chromatography (0–2 % EtOAc in DCM) afforded a mixture of Hantzsch ester's pyridine and **3v**. Starting from this mixture, the title compound was isolated by flash column chromatography (30 % Et<sub>2</sub>O in CyH). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

Cbz OH HN

(**3w**): brown oil, 74% (0.15 mmol, 37 mg). The general procedure was applied using previously synthesized **1w** (0.2 mmol, 41 mg) as aldehyde. The title

compound was isolated by flash column chromatography (0–5 % EtOAc in DCM until Hantzsch ester's pyridine was recovered, then 2 % MeOH in DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

 $_{HN}^{Boc OH}$  (3x): brown oil, 70% (0.14 mmol, 30 mg). The general procedure was applied using previously synthesized 1x (0.2 mmol, 35 mg) as aldehyde. Flash chromatography (0–2 % EtOAc in DCM) afforded a mixture of Hantzsch ester's pyridine and 3x. Starting from this mixture, the title compound was isolated by flash column chromatography (30–50 % Et<sub>2</sub>O in CyH). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

(3y): brown oil, 80% (0.16 mmol, 29 mg). The general procedure was applied using **1y** (0.2 mmol, 33 µL) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9]</sup>

(**3z**): brown oil, 80% (0.16 mmol, 29 mg). The general procedure was applied using previously synthesized **1z** (0.2 mmol, 41 mg) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[14]</sup>

(**3aa**): (*syn:anti* dr of 2:1) yellow oil, 70% (0.14 mmol, 25 mg). The general procedure was applied using freshly distilled **1aa** (0.2 mmol, 27 μL) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9,15]</sup>

 $^{\text{Ph}}$  (3ab): the product was isolated as mixture of *E*:*Z* isomers (3:2) as brown oil, 70% (0.14 mmol, 24 mg). The general procedure was applied using freshly distilled 1ab (0.2 mmol, 25 µL) as aldehyde. The title compound was isolated by flash column chromatography (DCM). Spectroscopic data were in agreement with those reported in literature.<sup>[9,16]</sup>

(**5k**): yellow oil, 36% (0.07 mmol, 15 mg). The general procedure (72 h) was applied using freshly distilled **1k** (0.2 mmol, 24  $\mu$ L) as aldehyde. The title

OEt

MeO

compound was isolated by flash column chromatography (DCM). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 7.24 - 7.19$  (m, 2H), 6.90 - 6.84 (m, 2H), 5.82 - 5.69 (m, 1H), 5.07 - 4.96 (m, 2H), 4.21 (t, J = 6.5 Hz, 1H), 3.81 (s, 3H), 3.41 - 3.25 (m, 2H), 2.62 - 2.52 (m, 1H), 2.42 - 2.32 (m, 1H), 1.16 (t, J = 6.9 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 159.1$ , 135.3, 134.6, 128.0 (2C), 116.7, 113.8 (2C), 81.5, 64.0, 55.4, 42.7, 15.4; ESI-MS m/z = 207.1 [M+H]<sup>+</sup>.

## **Results and discussion**

#### Screening of reaction conditions

Table S1. Screening of reaction solvent.

0 J	× .	Bi(OTf) <sub>3,</sub> 10 mol% 3CzClIPN, 5 mol%	OH ∧ ⊥ ∧	OH R		
R 1a,h (0.1 mmol)	+ Br <b>2a</b> , 3 equiv.	SOLVENT [1a] = 0.05 M, Blue LEDs, rt, 16h Hantzsch ester, 2 equiv.	R 3a,h	+ R	OH 4a,h	
Entry <sup>[a]</sup>	R	Solvent	Conv. (%) <sup>[b]</sup>	<b>3a,h</b> (%) <sup>[c]</sup>	3a,h:4a,h (%) <sup>[c]</sup>	
1	CI	THF:H <sub>2</sub> O (9:1)	96	30	31:69	
2	CI	THF:H <sub>2</sub> O (1:1)	97	51	52:48	
3	CI	DMF:H <sub>2</sub> O (1:1)	53	48	85:15	
4	CI	MeCN:H <sub>2</sub> O (1:1)	81	45	56:44	
5	CI	MeOH:H <sub>2</sub> O (1:1)	>99	79	79:21	
6	CI	DMSO:H <sub>2</sub> O (1:1)	98	66	68:32	
7	CI	EtOH:H <sub>2</sub> O (1:1)	>99	83(74)	83:17	
8	CI	EtOH	90	62	69:31	
9	CI	H <sub>2</sub> O	92	50	55:45	
10	Ph	MeOH:H <sub>2</sub> O (1:1)	57	54	94:6	
11	Ph	EtOH:H <sub>2</sub> O (1:1)	94	88	94:6	

[a] All the reactions were carried out under irradiation with Kessil® 40W blue LED. [b] Conversions were measured by <sup>1</sup>H-NMR. Isolated yields after chromatographic purification is reported in parenthesis. [c] Yield% of the allylated product **(3a,h)** determined by <sup>1</sup>H-NMR. [d] Ratio% of allylated product **(3a,h)** and pinacol coupling **(4a,h)**. The d.r. for **(4a,h)**.is ca 1:1 for all the reactions.

Table S2. Screening of allylating reagent.



[a] All the reactions were carried out under irradiation with Kessil® 40W blue LED. [b] Conversions were measured by <sup>1</sup>H-NMR. Isolated yields after chromatographic purification is reported in parenthesis. [c] Yield% of the allylated product **(3a)** determined by <sup>1</sup>H-NMR. [d] Ratio% of allylated product **(3a)** and pinacol coupling **(4a)**. The d.r. for **(4a)**.is ca 1:1 for all the reactions.

 $\label{eq:constraint} \textbf{Table S3.} Screening of the type and amount of bismuth salt.$ 

CI 1a (0.1 mr	O + Br 2a, 3 equiv.	<b>[Bi]</b> , X m 3CzClIPN, 5 <b>SOLVENT</b> , [1a] Blue LEDs, Hantzsch ester	ol% 5 mol%   = 0.05 M, rt, 16h Cl ~ r, 2 equiv.	ОН За	+ Cl	OH OH 4a
Entry <sup>[a]</sup>	Solvent	[Bi]	[Bi] mol%	Conv. (%) <sup>[b]</sup>	<b>3a</b> (%) <sup>[c]</sup>	3a:4a (%) <sup>[c]</sup>
1	EtOH:H <sub>2</sub> O (1:1)	Bi(OTf) <sub>3</sub>	10	>99	83(74)	83:17
2	MeOH:H <sub>2</sub> O (1:1)	Bi(OTf) <sub>3</sub>	10	>99	79	79:21
3	MeOH:H <sub>2</sub> O (1:1)	Bi(OTf) <sub>3</sub>	5	>99	78	78:22
4	MeOH:H <sub>2</sub> O (1:1)	Bi(OTf) <sub>3</sub>	2	>99	68	58:42
5	EtOH:H <sub>2</sub> O (1:1)	BiCl <sub>3</sub>	10	50	50	>99:1
6	EtOH:H <sub>2</sub> O (1:1)	BiBr <sub>3</sub>	10	>99	87	87:13
7	EtOH:H <sub>2</sub> O (1:1)	BiBr <sub>3</sub>	5	82	77	87:13
8	EtOH:H <sub>2</sub> O (1:1)	BiBr <sub>3</sub>	2	68	59	79:11

[a] All the reactions were carried out under irradiation with Kessil® 40W blue LED. [b] Conversions were measured by <sup>1</sup>H-NMR. Isolated yields after chromatographic purification is reported in parenthesis. [c] Yield% of the allylated product **(3a)** determined by <sup>1</sup>H-NMR. [d] Ratio% of allylated product **(3a)** and pinacol coupling **(4a)**. The d.r. for **(4a)**.is ca 1:1 for all the reactions.

Table S4. Reaction time influence on the reaction outcome for substrates 1k,o,p.

0	N	Bi(OTf) <sub>3,</sub> 10 mol% 3CzCIIPN, 5 mol%	он Д		OEt ↓
R´ + 1k,o,q	Br 2a, 3 equiv.	EtOH:H <sub>2</sub> O 1:1 [ <b>1a</b> ] = 0.05 M, Blue LEDs, rt, 16 or 72h	R <sup>∕</sup> ∕∕ ∕∕ ∕∕ ∕∕ ∕∕ ∕∕ ∕∕ ∕∕ ∕∕ ∕∕ ∕∕ ∕∕ ∕	+	R <sup>7</sup> ~>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
(0.2 mmol)		Hantzsch ester, 2 equiv.			

Entry <sup>[a]</sup>	R	Time	Conv. (%) <sup>[b]</sup>	<b>3:5</b> (%) <sup>[b]</sup>	<b>3</b> (%) <sup>[c]</sup>	5 (%) <sup>[c]</sup>
1	1k	16 h	51	92:8	34	n.d. <sup>[d]</sup>
2	1k	72 h	51	21:79	n.d. <sup>[d]</sup>	36
3	10	16 h	50	>99:1	33	n.d. <sup>[d]</sup>
4	10	72 h	69	53:47	n.d. <sup>[d]</sup>	n.d. <sup>[d]</sup>
5	1q	16 h	70	86:14	60	n.d. <sup>[d]</sup>
6	1q	72 h	82	>1:99	n.d. <sup>[d]</sup>	n.d. <sup>[d]</sup>

[a] All the reactions were carried out under irradiation with Kessil® 40W blue LED. [b] Determined by <sup>1</sup>H-NMR. [c] Isolated yields after chromatographic purification. [d] Not determined.

Table S5. Test of the species responsible for the generation of 5k starting from 3k.



[a] Pyridinium was obtained by acidic treatment (HCl 1M in Et<sub>2</sub>O) of oxidized Hantzsch ester (i.e. its pyridinic form, recovered after chromatographic purifications of compounds **3**), followed by solvent evaporation. [b] Determined by <sup>1</sup>H-NMR.

#### **Unreactive substrates**

Figure S1. Unreactive or unreactive substrates tested in the bismuth catalyzed photoredox allyation.



#### Photoredox reaction performed with substituted allyl bromides

Table S6. Result obtained with crotyl and prenyl bromides.



[a] All the reactions were carried out under irradiation with Kessil® 40W blue LED.

[b] Determined by <sup>1</sup>H-NMR. [c] Relative configuration was assigned by comparison

of <sup>1</sup>H-NMR signals with literature data, see ref.17.

Different substituted allyl bromides were tested in the bismuth catalyzed photoredox allylation of aldehyde **1f**. Cinnamyl bromide gave a low conversion and a complex mixture of alcohol and ether isomers (result not reported). In the reaction with crotyl and prenyl

bromides branched products were exclusively formed with poor conversion and good diastereoselectivity in favour of the *syn* product.

#### Effect of radical inhibitor on reaction outcome



The reaction was performed following the general procedure but adding TEMPO (0.02 mmol, 3 mg). NMR analyses performed on the reaction mixture after work-up revealed the complete conversion of the aldehyde to afford mainly the allylated product **3a**, with almost negligible (5 %) amount of **4a**. As a matter of fact, TEMPO behaves as a radical scavenger, hampering radical pathways, including those involved in the generation of **4a** (pinacol coupling via ketyl radical).

#### **Photochemical Investigations**

Figure S2. Absorption (blue solid line) and emission spectrum (red line) recorded on a solution of 3CzCIIPN in air-equilibrated ethanol at r.t.;  $\lambda_{ex}$ = 400 nm. The excitation spectrum taken on a diluted solution is shown as the blue dotted line;  $\lambda_{em}$ = 550 nm.



Figure S3. A: absorption spectra of solutions of 3CzCIIPN in air-equilibrated ethanol (blue line) obtained upon addition of increasing amounts of bismuth(III) triflate (up to ca. 14 mM, red line). B: fluorescence emission spectra of 3CzCIIPN obtained from the same solutions at  $\lambda_{ex}$ =400 nm.



Figure S4. A: absorption spectra of solutions of 3CzCIIPN in air-equilibrated ethanol (blue line) obtained upon addition of increasing amounts of allyl bromide (up to ca. 95 mM, red line). B: fluorescence emission spectra of 3CzCIIPN obtained from the same solutions at  $\lambda_{ex}$ =400 nm. Inset: Stern-Volmer diagram relative to the emission intensities at  $\lambda_{em}$ =550 nm (since no quenching is detected, the quenching constant is not determined).



Figure S5. A: absorption spectra of solutions of 3CzCIIPN in air-equilibrated ethanol (blue line) obtained upon addition of increasing amounts of 4chlorobenzaldehyde (CI-BA, up to ca. 26 mM, red line). B: fluorescence emission spectra of 3CzCIIPN obtained from the same solutions at  $\lambda_{ex}$ =400 nm. Inset: Stern-Volmer diagram relative to the emission intensities at  $\lambda_{em}$ =550.



Figure S6. A: absorption spectra of solutions of 3CzCIIPN in air-equilibrated ethanol (blue line) obtained upon addition of increasing amounts of Hantzsch's ester (HE, up to ca. 10 mM, red line). B: fluorescence emission spectra of 3CzCIIPN obtained from the same solutions at  $\lambda_{ex}$ =465 nm. Inset: Stern-Volmer diagram relative to the emission intensities at  $\lambda_{em}$ =550 nm.



Figure S7. Emission decays obtained from 3CzCIIPN in air-equilibrated ethanol (blue dots) and from the same solution upon addition of Hantzsch's ester (HE, 1.7 mM, green dots). The monoexponential fitting curves are also shown (red and orange lines, respectively).



# Copies of NMR spectra































































































































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