



HAL
open science

Light-Triggered Nickel-Catalyzed Azide–Alkyne Cycloaddition for the Preparation of 1,5-Disubstituted 1,2,3-Triazoles

Baptiste Abadie, Axel Almansa, Ouchan He, Stéphane Massip, Florian
Molton, Carole Duboc, Jean-marc Vincent

► **To cite this version:**

Baptiste Abadie, Axel Almansa, Ouchan He, Stéphane Massip, Florian Molton, et al.. Light-Triggered Nickel-Catalyzed Azide–Alkyne Cycloaddition for the Preparation of 1,5-Disubstituted 1,2,3-Triazoles. *Advanced Synthesis and Catalysis*, 2022, 364 (24), pp.4266-4270. 10.1002/adsc.202201026 . hal-04269254

HAL Id: hal-04269254

<https://hal.science/hal-04269254>

Submitted on 3 Nov 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Light-Triggered Ni-Catalyzed Azide-Alkyne Cycloaddition for the Preparation of 1,5-Disubstituted 1,2,3-Triazoles

Baptiste Abadie,^a Axel Almansa,^a Ouchan He,^a Stéphane Massip,^b Florian Molton,^c Carole Duboc,^c and Jean-Marc Vincent^{a,*}


^a Univ. Bordeaux, CNRS, Bordeaux INP, ISM, UMR 5255, F-33400 Talence, France

E-Mail: jean-marc.vincent@u-bordeaux.fr

^b Univ Bordeaux, CNRS, INSERM, IECB, UAR 3033, F-33600 Pessac, France

^c Département de Chimie Moléculaire (DCM) CNRS UMR 5250, Univ. Grenoble Alpes, F-38000 Grenoble, France.

Received: ((will be filled in by the editorial staff))

 Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/adsc.201#####>. ((Please delete if not appropriate))

Abstract. When irradiated by UVA, a Ni(II) precatalyst integrating a benzophenone chromophore in its structure catalyzes the regioselective cycloaddition of alkynes and azides to produce 1,5-disubstituted 1,2,3-triazoles with 1,5:1,4 regioisomer ratios ranging from 1.7:1 to > 20:1. Speciation and reactivity studies revealed that the reaction most likely proceeds through a Ni(I)/Ni(III) catalytic cycle.

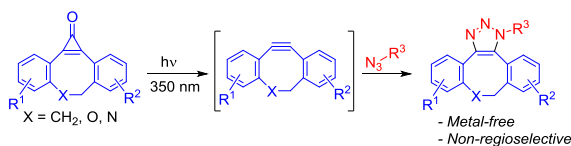
Keywords: Benzophenone; Click chemistry; Nickel; Photocatalysis; Triazole

These last 15 years, light-triggered click reactions have emerged as powerful tools to achieve ligation processes under mild conditions and with spatio-temporal control, a key feature for application in photopatterning processes.^[1] In this field, the development of light-triggered strain-promoted azide-alkyne cycloaddition (SPAAC)^[2] and Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC)^[3] has received particular interest. Light-induced SPAAC induced by light relies on the unmasking of the click-active dibenzocyclooctynes by irradiation at 350 nm of cyclopropenone precursors (Scheme 1). Such metal-free process is of particular interest for cellular or RNA labelling,^[2a,b] but also to derivatize/pattern materials.^[2c-g] Since the first report of König and coworkers in 2006, numerous light-triggered CuAAC have been developed (Scheme 1).^[3] They all rely on a photoinduced electron transfer (PET) process to a Cu(II) precatalyst to generate the catalytically active Cu(I) species. The PET is achieved using mainly three strategies, namely direct irradiation in the charge transfer band of a Cu(II)-X bond, photogeneration of reducing radicals from sacrificial photocleavable compounds or from triplet excited states of photosensitizers such as aromatic ketones.

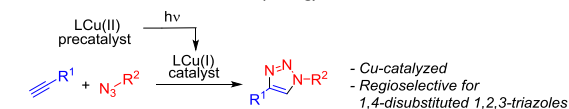
Although Ru(II)-based catalysts,^[4] Cp*RuCl(PPh₃)₂, Cp*RuCl(COD) or [Cp*RuCl]₄, to name a few, have proven to be potent in preparing

1,5-disubstituted triazoles regioselectively,^[5] a light-triggered process has not yet been reported for such key transformation. In the research area of nickel catalysis, seminal works by the groups of Louie and Ogoshi have established Ni(0)-catalyzed cycloaddition implying alkynes to afford heterocycles.^[6] In 2017, Hong and *coll.* reported that the combination of Cp₂Ni (10 mol%) and the Xantphos ligand catalyzed the NiAAC with 1,5:1,4 regioselectivities ranging from 3.2:1 to 99:1.^[7] Mechanistic studies supported a Ni(0)/Ni(II) catalytic cycle, with the *in situ* generation of the reactive Ni(0) species being explained by the dissociation of Cp radical-driven by the Xantphos coordination. Interestingly, in their optimization study the authors noted that employing bathocuproine (BCP) as ligand led to a significant reactivity, with the reaction between benzyl azide and phenylacetylene leading to the 1,5-disubstituted triazole **3a** in 33% yield and a satisfactory 1,5:1,4 regioisomer ratio of 11:1, compared to 94% and 15.7:1 with the Xantphos ligand.

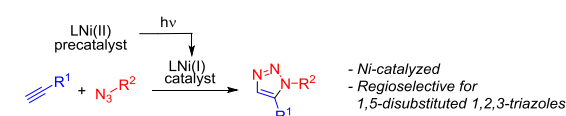
Photolabile SPAAC: since 2009 (Popik, Boons)



Photolabile CuAAC: since 2006 (König)



Photolabile NiAAC: this work



Scheme 1. Light-triggered azide-alkynes cycloadditions.

Inspired by these results and in continuation of our interest in the development of photolabile click catalysts,^[3d,j,l] we report herein a light-triggered Ni-catalyzed process for the synthesis of 1,5-disubstituted 1,2,3-triazoles.

The photoreducible Ni(II) precatalyst [(BCP)Ni(II)(BPCO₂)₂] **1** (BPCO₂ = 3-benzoylbenzoate), which integrates a benzophenone (BP) photosensitizer necessary to trigger a highly effective PET to the metal ion (Fig. 1), was prepared by reacting BPCO₂Na (2 equiv.) with NiSO₄ (1 equiv.) and BCP (1 equiv.) in refluxing ethanol. The X-ray structure of **1** revealed that the coordination sphere has a distorted octahedral geometry around the Ni(II) ion coordinated by one BCP and two bidentate BPCO₂ ligands.^[8] The same procedure was employed to prepare the complex [(BCP)Ni(PhCO₂)] **2**, a close structural analog of **1** which does not possess the benzophenone chromophore. Complex **2** was prepared to evaluate the impact of the BP photosensitizer on the Ni(II) photoreduction efficiency and catalytic activity.

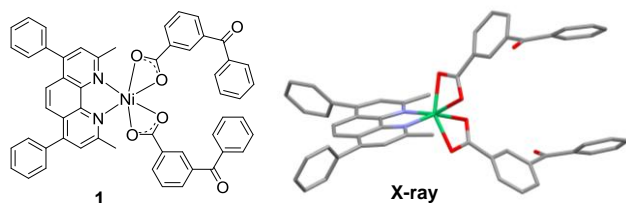


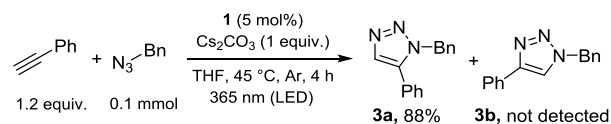
Figure 1. Schematic representation and crystal structure of **1** (Hydrogen atoms and disorder have been omitted for clarity).

As shown in Table 1, under the optimized conditions the benchmark reaction between **1** (5 mol%), phenylacetylene, benzyl azide and Cs₂CO₃ leads, after 4 h of irradiation at 365 nm, to the 1,5-disubstituted triazole **3a** in 88% yield and a regioselectivity > 20:1, **3b** being not detectable by ¹H NMR on the crude reaction mixture. Irradiation at 450 nm leads to **3a** in a low 20% yield (entry 2). In the absence of light, no reaction occurs, even when heating the reaction mixture at 50 °C, i.e. slightly above the temperature measured under irradiation (entry 3). Without the base, only 30% of **3a** is obtained (entry 4). Reactions conducted under air or O₂ atmospheres are strongly inhibited, as expected for a process involving low-valent Ni(0) or Ni(I) as catalytic species (entries 5-6). A yield of 24% was obtained by reducing the precatalyst loading to 2 mol% (entry 7). Finally, THF was found to be the optimal solvent (entries 8-12).

The scope of the reaction was then evaluated (Scheme 2). The reaction of benzyl azides with aromatic alkynes leads to the 1,5 triazoles **3a-9a** in 34-88% yields and 1,5:1:4 regioisomer ratios > 20:1. The presence of electron-donating/-withdrawing groups on the phenyl rings leads to a significant decrease in the yields. Interestingly, the involvement

of the chromophoric 1-ethynyl pyrene did not hamper the photoactivation of the precatalyst, the triazole **10a** being obtained in 57% yield and > 20:1 regioselectivity. The reaction of benzyl azide with benzyl propargyl ether leads to **11a** in 34% yield and

Table 1. Reaction optimization.



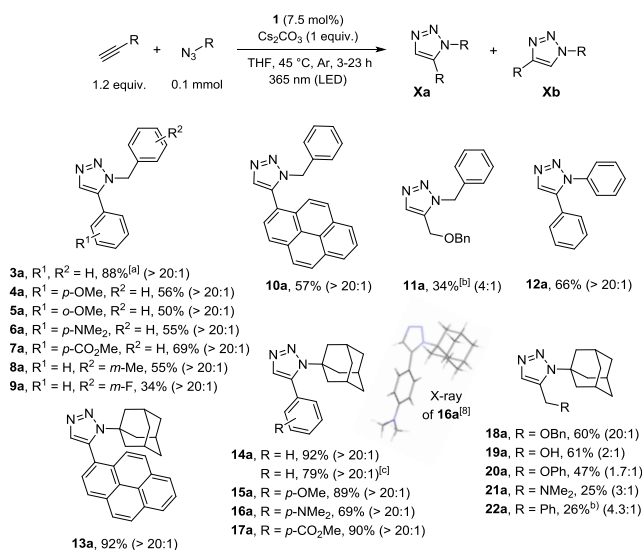
entry	Change from above conditions	yield 3a (%) ^[b]
1	none ^[a]	88
2	450 nm instead of 365 nm, 7 h	20
3	no light, ^[c] 7 h	0
4	no Cs ₂ CO ₃ , 7 h	30
5	under air (1 atm), 7 h	26
6	under O ₂ (1 atm), ^[d] 7 h	6
7	2 mol% of 1 , 7 h	24
8	H ₂ O instead of THF, 7 h	6
9	MeOH instead of THF, 7 h	26
10	DMF instead of THF, 7 h	32
11	DCM instead of THF, 7 h	traces
12	toluene instead of THF, 7 h	61

^[a] Reaction conditions: Alkyne (0.12 mmol), azide (0.1 mmol), **1** (7.5 mol%), Cs₂CO₃ (0.1 mmol), THF (3 mL), Ar (bubbling 10 min), stirring, irradiation at 365 nm (LED) for 4 h (the temperature of the solution reaches 45 °C); The 88% yield is the average of three reactions. ^[b] Isolated yields. ^[c] Tube embedded in aluminum foil and heated at 50 °C. ^[d] Bubbling of O₂ for 10 min then O₂ balloon.

4:1 regioselectivity. The reaction of phenyl acetylene and phenyl azide afforded the triazole **12a** in 66% yield and > 20:1 regioselectivity. Surprisingly, no triazole is formed from phenyl azides bearing a nitro, methyl, cyano or methoxy group in the para position. Degradation was observed for the first two azides, while the last two remained intact. Reaction of 1-azidoadamantane with aromatic azides afforded the 1,5-disubstituted triazoles **13a-17a** in 69-92% yields and > 20:1 regioselectivities. The X-ray structure of **16a** was solved confirming the 1,5-disubstitution.^[8] The triazole **14a** could be isolated in 79% yield on a 0.5 mmol scale. The reaction between benzyl propargyl ether and 1-azidoamantane afforded **18a** in 60% yield and > 20:1 selectivity. Using phenyl propargyl ether and propargyl alcohol, the triazoles **19a** and **20a** were obtained in 61% yield with 2:1 selectivity and 47% yield with 1.7:1 selectivity, respectively. Finally, N,N-dimethylpropargylamine and 3-phenyl-1-acetylene lead to the triazoles **21a** and **22a** in 25% yield with 3:1 selectivity and 26% with 4.3:1 selectivity, respectively. Note that **11a** and **22a** were obtained as mixtures with **11b** and **22b** as they could not be separated from the 1,4 regioisomers by silica gel column chromatography.

Preliminary mechanistic studies have been conducted, especially to determine whether the catalytic cycle occurs through Ni(0)/Ni(II) or

Ni(I)/Ni(III) species. Recently, Hong and *coll.* reported a combined experimental/theoretical mechanistic study for the NiAAC involving the Cp₂Ni(II)/Xantphos precatalytic system.^[7] According to their study, the first step of the reaction proceeds by oxidative addition of the alkyne onto the



Scheme 2. Scope of the light-triggered NiAAC. In parenthesis the 1,5:1,4 regioisomer ratios determined on the crude by ¹H NMR. ^[a] 1 at 5 mol%. ^[b] Isolated as a 4:1 mixture of the 1,5 and 1,4 regioisomers. ^[c] 0.5 mmol scale.

(Xantphos)Ni(0) catalyst to form a (Xantphos)Ni(II)-cyclopropene intermediate. Recent mechanistic studies in the field of dual photoredox/Ni-catalyzed aryl-heteroatom cross-couplings have revealed that the reactions most often proceed through “dark” Ni(I)/Ni(III) catalytic cycles.^[9] We thus wondered whether the BCP ligand, which exhibits similar electronic/structural properties to the 2,2'-bipyridine ligands commonly employed in cross-couplings, could not favour a Ni(I)/Ni(III) cycle. To test this hypothesis, we first investigated by UV-vis spectroscopy the speciation of the reduced species which formed upon photolysis of **1** in THF vs CH₃CN/THF (Figure 2). In a previous work Nocera and coworkers demonstrated that photolysis of [(BCP)Ni(II)Cl₂] in THF (> 305 nm) in the presence of 2 equiv. of 2,6-lutidine and 2 equiv. of exogenous BCP leads to [(BCP)₂Ni(0)], while photolysis in CH₃CN leads to [(BCP)₂Ni(I)Cl] exclusively.^[10] These two species exhibited characteristic intense electronic absorption bands centered at around 560 nm, 920 nm, and 1100 nm for [(BCP)₂Ni(0)], and at 480 nm and 680 nm for [(BCP)₂Ni(I)Cl]. It was shown that in THF the disproportionation of [(BCP)₂Ni(I)Cl] into [(BCP)₂Ni(0)] is promoted by chloride anions, while in CH₃CN [(BCP)₂Ni(I)Cl] is stable. It was also shown that the reduction of Ni(II) to Ni(I) is mediated by the singlet excited state of the exogenous BCP ligand, which transfers a H atom (HAT) from the THF to afford the BCP-H radical as

the reducing species. As observed by Nocera and coworkers, the photolysis of **1** in THF (Figure 2a) leads to the fast formation of [(BCP)₂Ni(0)], while in CH₃CN/THF (6/1 ratio; a small amount of THF is necessary to solubilize **1**) the exclusive formation of [(BCP)₂Ni(I)]⁺ is observed (Figure 2a).^[11,12] The formation of a S=1/2 Ni(I) species was confirmed by EPR spectroscopy (see SI).

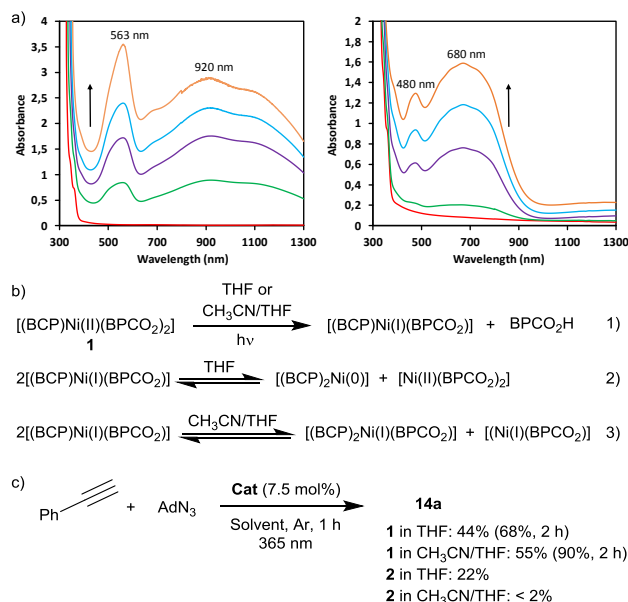
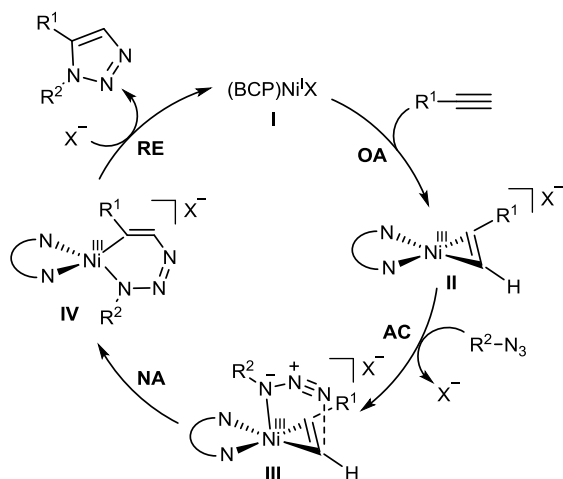


Figure 2. a) UV-vis follow-up of the photolysis of **1** revealing the formation of [(BCP)₂Ni(0)] in THF (left spectra) while [(BCP)₂Ni(I)]⁺ forms in CH₃CN/THF (6/1 ratio, right spectra). Photolysis were conducted using a 365 nm Luzchem LEDi-7UV lamp (set at 25% intensity, 2 cm from the cuvette) on solutions of **1** (0.5 mM, 3 mL) degassed by Ar bubbling (15 min). Spectra recorded at t = 0 (lower spectrum), 10, 15, 20, 30 min of irradiation for THF, and t = 0 (lower spectrum), 20, 30, 40, 50 min of irradiation for CH₃CN/THF (6/1 vol. ratio). b) Speciation of **1** when photolyzed in THF and CH₃CN/THF. c) NiAAC in THF vs CH₃CN/THF.

When the photolysis is conducted from complex **2**, in which the 3-benzoylbenzoate ion is replaced by a benzoate ion, no change in the UV-vis spectrum was noticed, showing that the Ni(II) to Ni(I) reduction is mainly driven by the BP triplet excited state (Figure 2, eq 1). Once formed, [(BCP)Ni(I)(BPCO₂)] either disproportionates in THF to generate [(BCP)₂Ni(0)] and [Ni(II)(BPCO₂)₂] (eq 2), or undergoes ligand exchange in CH₃CN/THF to afford [(BCP)₂Ni(I)(BPCO₂)] and [Ni(I)(BPCO₂)] (eq 3). We then compared the catalytic activity of **1** in the reaction between phenyl acetylene and 1-azidoadamantane in THF vs CH₃CN/THF, which was found to be significantly higher in CH₃CN/THF (Figure 2c). Combining this result with the fact that only Ni(I) but not Ni(0) is observed upon photolysis of **1** in CH₃CN/THF, strongly suggests that

[(BCP)Ni(I)(BPCO₂)], the primary reduced species expected to form both in THF and CH₃CN/THF, is the catalytic species. Interestingly, complex **2** with the benzoate counterion is unreactive in CH₃CN/THF, while a significant reactivity was observed in THF suggesting that a Ni(II) to Ni(I) reduction process mediated by the BCP excited state might be operant in this solvent in conjunction with the BP-driven process.^[10]



Scheme 3. a) Proposed Ni catalytic cycle according to our results and mechanistic studies of references 5c and 7 (OA = Oxidative Addition, AC = Azide Coordination, NA = Nucleophilic Addition, RE = Reductive Elimination).

The mechanism shown in Scheme 3 is proposed based on the present speciation study and extensive mechanistic reports conducted on RuAAC^[5c] and NiAAC.^[7] Oxidative addition of [(BCP)Ni(I)(BPCO₂)] **I** to the alkyne forms the (BCP)Ni(III)-cyclopropene intermediate **II**. Coordination of the azide by the internal N atom gives intermediate **III** stabilized by the interaction between the most nucleophilic carbon of the nickelacycle and the most electrophilic N atom of the azide. Nucleophilic attack of the nickelacycle on the terminal N atom affords the 6-membered ring nickelacycle **IV** which undergoes reductive elimination to afford the 1,5 triazole and regenerate the [(BCP)Ni(I)] catalyst.

To conclude, we succeeded in developing a light-triggered azide-alkyne cycloaddition for the synthesis of 1,5-disubstituted 1,2,3-triazoles. The process exploits the ability of the Ni(II) precatalyst **1** bearing the BCP ligand and benzoyl benzoate counterions to be effectively photoreduced under UVA irradiation in H atom donating solvents. Remarkably, in many cases the 1,4 isomers were not detected in the crude mixtures which is key for application, the two regioisomers being often very difficult to separate. Some limitations were nevertheless noticed, in particular when employing non-bulky aliphatic alkynes as substrates. Preliminary mechanistic studies

that focused on the precatalyst activation step suggest [(BCP)Ni(I)X] as the catalytic species, contrasting with the Cp₂Ni(II)/Xantphos precatalytic system for which a Ni(0)/Ni(II) catalytic cycle has been proposed.

Experimental Section

General procedure for the light-triggered NiAAC. In a test tube protected from light by aluminum foil, equipped with a magnetic stirrer, complex **1** (0.0075 mmol, 6.5 mg), Cs₂CO₃ (1 eq, 32.7 mg), the azide (1 eq, 0.1 mmol) and the alkyne (1.2 eq, 0.12 mmol) were dissolved in freshly distilled THF (3 mL) and sonicated for 1 minute. The tube was then capped with a rubber septum, and the reaction medium was deaerated by gentle argon bubbling for 10 minutes. The reaction was initiated by irradiating the tube at 365 nm with the Luzchem® illuminator setup. After stirring under irradiation at room temperature for 3-23 h, THF was removed under reduced pressure, and the crude mixture was purified by column chromatography over silica gel.

Acknowledgements

The Agence Nationale de la Recherche (LightNing project no. ANR-18-CE07-0037-01), the University of Bordeaux and the CNRS are gratefully acknowledged for their financial support.

References

- [1] a) B. D. Fairbanks, L. J. Macdougall, S. Mavila, J. Sinha, B. E. Kirkpatrick, K. S. Anseth, C. N. Bowman, *Chem. Rev.* **2021**, *121*, 6915–6990; b) G. S. Kumar, Q. Lin, *Chem. Rev.* **2021**, *121*, 6991–7031; c) M. A. Tasdelen, Y. Yagci, *Angew. Chem. Int. Ed.* **2013**, *52*, 5930–5938.
- [2] Selected examples: a) A. A. Poloukhine, N. E. Mbua, M. A. Wolfert, G.-J. Boons, V. V. Popik, *J. Am. Chem. Soc.* **2009**, *131*, 15769–15776; b) S. Nainar, M. Kubota, C. McNitt, C. Tran, V. V. Popik, R. C Spitale, *J. Am. Chem. Soc.* **2017**, *139*, 8090–8093; c) S. V. Orski, A. A. Poloukhine, S. Arumugam, L. Mao, V. V. Popik, J. Locklin, *J. Am. Chem. Soc.* **2010**, *132*, 11024–11026; d) C. D. McNitt, H. Cheng, S. Ullrich, V. V. Popik, M. Bjerknes, *J. Am. Chem. Soc.* **2017**, *139*, 14029–14032; e) M. Bjerknes, H. Cheng, C. D. McNitt, V. V. Popik, *Bioconjug. Chem.* **2017**, *28*, 1560–1565; f) W. Luo, S. M. Legge, J. Luo, F. Lagugné-Labarthe, M. S. Workentin, *Langmuir* **2020**, *36*, 1014–1022; g) S. Arumugam, V. V. Popik, *J. Org. Chem.* **2014**, *79*, 2702–2708; h) L. Sun, Y. Gai, C. D. McNitt, J. Sun, X. Zhang, W. Xing, Z. Li, V. V. Popik, D. Zeng, *J. Org. Chem.* **2020**, *85*, 5771–5777.
- [3] Selected examples: a) S. C. Ritter, B. König, *Chem. Commun.* **2006**, 4694–4696; b) B. J. Adzima, Y. Tao, C. J. Kloxin, C. A. DeForest, K. S. Anseth, C. N. Bowman, *Nat. Chem.* **2011**, *3*, 256–259; c) M. A. Tasdelen, Y. Yagci, *Tetrahedron Lett.* **2010**, *51*, 6945–6947; d) L. Harmand, S. Cadet, B. Kauffmann, L. Scarpantonio, P. Batat, G. Jonusauskas, N. D. McClenaghan, D. Lastécouères, J.-M. Vincent, *Angew. Chem. Int. Ed.*

- 2012, *51*, 7137–7141; e) M. A. Tasdelen, G. Yilmaz, B. Iskin, Y. Yagci, *Macromolecules* **2012**, *45*, 56–61; f) T. Gong, B. J. Adzima, N. H. Baker, C. N. Bowman, *Adv. Mater.* **2013**, *25*, 2024–2028; g) T. Gong, B. J. Adzima and C. N. Bowman, *Chem. Commun.* **2013**, *49*, 7950–7952; h) B. Sandmann, B. Happ, J. Vitz, M. D. Hager, P. Burtscher, N. Moszner, U. S. Schubert, *Polym. Chem.* **2013**, *4*, 3938–3942; i) Y. Yagci, M. A. Tasdelen, S. Jockusch, *Polymer*, **2014**, *55*, 3468–3474; j) R. Beniazza, R. Lambert, L. Harmand, F. Molton, C. Duboc, S. Denisov, G. Jonusauskas, N. D. McClenaghan, D. Lastécouères, J.-M. Vincent, *Chem. Eur. J.* **2014**, *20*, 13181–13187; k) J. Bae, K. Baek, D. Yuan, W. Kim, K. Kim, H.-C. Zhou, J. Park, *Chem. Commun.* **2017**, *53*, 9250–9253; l) O. Jennah, R. Beniazza, C. Lozach, D. Jardel, F. Molton, C. Duboc, T. Buffeteau, A. El Kadib, D. Lastécouères, M. Lahcini, J.-M. Vincent, *Adv. Synth. Catal.* **2018**, *360*, 4615–4624.
- [4] J. R. Johansson, T. Beke-Somfai, A. S. Stålsmeden, N. Kann, *Chem. Rev.* **2016**, *116*, 14726–14768.
- [5] Selected examples: a) L. Zhang, X. Chen, P. Xue, H. H. Y. Sun, I. D. Williams, K. B. Sharpless, V. V. Fokin, G. Jia, *J. Am. Chem. Soc.* **2005**, *127*, 15998–15999; b) L. K. Rasmussen, B. C. Boren, V. V. Fokin, *Org. Lett.* **2007**, *9*, 5337–5339; c) B. C. Boren, S. Narayan, L. K. Rasmussen, L. Zhang, H. Zhao, Z. Lin, G. Jia, V. V. Fokin, *J. Am. Chem. Soc.* **2008**, *130*, 8923–8930.
- [6] a) A. Thakur, J. Louie, *Acc. Chem. Res.* **2015**, *48*, 2354–2365; b) Y. Hoshimoto, T. Ohata, Y. Sasaoka, M. Ohashi, S. Ogoshi, *J. Am. Chem. Soc.* **2014**, *136*, 15877–15880.
- [7] a) W. G. Kim, M. E. Kang, J. B. Lee, M. H. Jeon, S. Lee, J. Lee, B. Choi, P. M. S. D. Cal, S. Kang, J.-M. Kee, G. J. L. Bernardes, J.-U. Rohde, W. Choe, S. Y. Hong, *J. Am. Chem. Soc.* **2017**, *139*, 12121–12124; b) W. G. Kim, S.-Y. Baek, S. Y. Jeong, D. Nam, J. H. Jeon, W. Choe, M.-H. Baik, S. Y. Hong, *Org. Biomol. Chem.* **2020**, *18*, 3374–3381.
- [8] CCDC-2171019 (**1**) and CCDC-2216129 (**16a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.
- [9] a) I. Kalvet, Q. Guo, G. J. Tizzard, F. Schoenebeck, *ACS Catal.* **2017**, *7*, 2126–2132; b) R. Sun, Y. Qin, S. Ruccolo, C. Schnedermann, C. Costentin, D. G. Nocera, *J. Am. Chem. Soc.* **2019**, *141*, 89–93; c) N. A. Till, L. Tian, Z. Dong, G. D. Scholes, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2020**, *142*, 15830–15841; d) R. Sun, Y. Qin, D. G. Nocera, *Angew. Chem. Int. Ed.* **2020**, *59*, 9527–9533; e) N. A. Till, S. Oh, D. W. C. MacMillan, M. J. Bird, *J. Am. Chem. Soc.* **2021**, *143*, 9332–9337; f) Y. Qin, R. Sun, N. P. Gianoulis, D. G. Nocera, *J. Am. Chem. Soc.* **2021**, *143*, 2005–2015; g) H. Ren, G.-F. Li, B. Zhu, X.-D. Lv, L.-S. Yao, X.-L. Wang, Z.-M. Su, W. Guan, *ACS Catal.* **2019**, *9*, 3858–3865; h) S. I. Ting, W. L. Williams, A. G. Doyle, *J. Am. Chem. Soc.* **2022**, *144*, 5575–5582; (i) H. Na, L. M. Mirica, *Nat. Commun.*, **2022**, *13*, 1313.
- [10] D. C. Powers, B. L. Anderson, D. G. Nocera, *J. Am. Chem. Soc.* **2013**, *135*, 18876–18883.
- [11] We suspect that the carboxylate counterions, that are coordinating anions like chloride ions, promote the disproportionation in THF.
- [12] The UV-vis spectra we obtained are superimposable to those described by Nocera and coworkers in ref. 10.

Title Text

Adv. Synth. Catal. Year, Volume, Page – Page

TOC Graphic

Author(s), Corresponding Author(s)*

