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C_{70} as a Photocatalyst for Oxidation of Secondary Benzylamines to Imines

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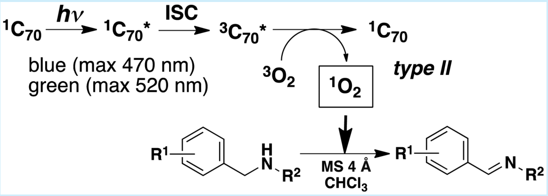
Supporting Information

ABSTRACT: Photosensitive C_{70} was used for the catalytic oxidation of benzylamines to the corresponding imines. The advantages of using C_{70} compared to C_{60} or other commonly used photosensitizers such as tetraphenylporphyrin (TPP) are (1) faster reaction rates, especially under lower energy of light sources, (2) clean reactions with simple workup without chromatography, and (3) lower catalyst loadings. The reactions were suitable for various benzylamine derivatives. Subsequent nucleophilic additions to the imines were successfully carried out on substituted products. Quenching experiments in the presence of DABCO and benzoquinone implicate the involvement of the singlet oxygen ($^1O_2$) and the superoxide radical anion ($O_2^{\bullet-}$) as important reactive species in the oxidation.



The remarkable photosensitivity of fullerenes such as C_{60} and C_{70} has been widely known for decades and has been applied in photovoltaic materials and photodynamic therapy (PDT) agents. In the case of the former, the electron-donating or -accepting properties of fullerenes, which can be induced by photoirradiation, is utilized. In the case of the latter, photo-induced generation of reactive oxygen species (ROSs) such as $^1O_2$[1,2] and $O_2^{\bullet-}$[3] produced, respectively, via energy transfer (type II reaction) and electron transfer (type I reaction) is a key phenomenon. Importantly, the quantum yields of both type I and II reactions are quantitiative,[4] and therefore, many PDT studies using fullerenes were reported, influenced by an initial report on photo DNA-cleavage with C_{60}[5] using water-soluble fullerene materials.[6] Alternatively, the use of fullerenes as organic reagents such as a catalyst for oxidation has been studied for decades. These studies include the oxidation of olefins,[7] phenols,[8] and sulfides.[9]

Imines are important intermediates in the synthesis of bioactive compounds,[10] and there is a high demand for useful synthetic methods for the production of imines.[11−13] Reported methods for the conversion of amines to imines include the use of (1) stoichiometric oxidants such as *N-tert*-butylphenylsulfinimidoyl chloride[14] and *o*-iodoxybenzoic acid (IBX)[15,16] and (2) metal catalysts in the presence of oxidants[10,17−23] or molecular oxygen.[17,24−26] Quinone- and catechol-based aerobic oxidations of amines were also found to be efficient.[27−29] These methods provide sufficient yields but often require harsh reaction conditions, stoichiometric oxidizing reagents, or other additives.

Recently, the use of photosensitizers has emerged as a promising method for the conversion of amines to imines. Photocatalysts such as organic dyes[30,31] and transition-metal complexes[30,32,33] have been explored for various organic transformations. Specifically, recent reports on the oxidation of amines using $^1O_2$ generated from photosensitizers such as porphyrin derivatives[34−36] and gold catalysts have received a great attention.[37] Che and co-workers used tetraphenylporphyrin (TPP) as a catalyst for the photooxidation of amines to imines, which were directly subjected to a subsequent Ugi reaction.[34] The same group also reported an organogold(III) complex for the oxidation of benzylamines to imines, including the oxidative cyanation of tertiary amines.[37] König and co-workers used porphycene in photooxidation reactions of primary and secondary amines to provide the corresponding imines and aldehydes.[35] Recent work by Seeberger and co-workers described the photooxidation of amines and subsequent nucleophilic addition with TPP using continuous-flow photoreactor techniques.[36,38]

In this study, we used C_{60} and C_{70} as photocatalysts for the oxidation of benzylamines to imines. Although the price of fullerenes is now comparable to other photosensitizers such as TPP, the application of fullerenes for such a reaction has not been previously explored. While the initial trials with C_{60} were not as efficient when compared to the commonly used photosensitizer TPP, the use of C_{70} provided a very effective reaction even with lower catalyst loadings. In addition, under lower light energy (blue LED), nucleophilic addition to the imines can be successfully carried out in the same reaction flask to provide a substitution at the benzylic position. Due to the low solubility of C_{70}, the workup of the reactions is very simple and requires only the removal of C_{70} by precipitation to provide imines as a single product. The reaction was successfully applied to various benzylamines as substrates.

As an initial trial for the oxidation of benzylamines to imines, 1,2,3,4-tetrahydroisoquinoline **1** was used as a substrate in the presence of C_{60} (99.95%, MTR Ltd.) as a photocatalyst under white light irradiation by a tungsten lamp. The reaction rates were compared in the several different solvents as listed in Table

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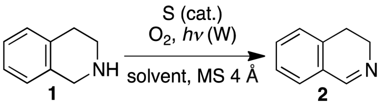
Table 1. Photoinduced Oxidation of Amine 1 in the Presence of Photosensitizer (C_{60}, TPP or C_{70}) and under White Light Irradiation[a]



run	catalyst		O_2[b]	light[c]	solvents	reaction time ($t_{1/2}$) [h][d]	NMR yield [%][e]
	S	mol %					
1	C_{60}	1.0	satd.	+	$CHCl_3$	7 (3.5)	>99
2	C_{60}	1.0	satd.	+	CH_2Cl_2	13 (6.3)	>99
3	C_{60}	1.0	satd.	+	THF	28 (15)	>99
4	C_{60}	1.0	satd.	+	CH_3CN	>40 (N.D.)	<10
5	C_{60}	0.1	satd.	+	$CHCl_3$	21 (11)	>99
6	C_{60}	0.05	satd.	+	$CHCl_3$	>53 (44)	56
7	C_{60}	0.01	satd.	+	$CHCl_3$	>53 (N.D.)	20
8	C_{60}	0.1	satd.	–(Δ)[f]	$CHCl_3$	>19 (N.D.)	N.R.
9	C_{60}	0.1	air	+	$CHCl_3$	>19 (18)	53
10	–	–	satd.	+	$CHCl_3$	>19 (N.D.)	<6
11	C_{60}-adduct[g]	0.1	satd.	+	$CHCl_3$	15(7)	>99
12	TPP	0.1	satd.	+	$CHCl_3$	5 (2.4)	>99
13	C_{70}	0.1	satd.	+	$CHCl_3$	5 (2.4)	>99
14	C_{70}	0.05	satd.	+	$CHCl_3$	8.5 (4.2)	>99
15	C_{70}	0.01	satd.	+	$CHCl_3$	28 (13)	>99

[a] Amine **1** (50 mg, 0.38 mmol) was subjected in the reaction with 5 mL of solvent. [b] Satd: oxygen was saturated by bubbling (about 11.5 mM of O_2 in $CHCl_3$). Air: reaction mixture was exposed to the air by using an open flask (about 2.1 mM of O_2 in $CHCl_3$). [c] A 200 W tungsten lamp (white light) at a distance of 20 cm (20000–20500 lx). [d] The time required for completion (with no detectable **1** by NMR) and the time for 50% conversion from **1** to **2** ($t_{1/2}$). N.D.: not determined. [e] Obtained from the integration of ^1H NMR spectra of the reaction mixture. N.R.: no reaction with starting material recovery. [f] Without light and under a thermal condition (40 °C). [g] C_{60}-mono-Bingel derivative (structure is provided in Figure S14, SI).

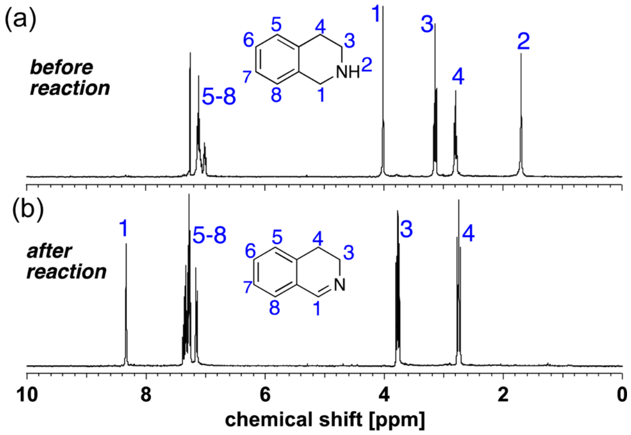


Figure 1. ^1H NMR spectra of the starting material **1** (a) and the crude extract of the reaction mixture (b) after white light irradiation with 0.1 mol % of C_{60} for 21 h in $CHCl_3$ at room temperature.

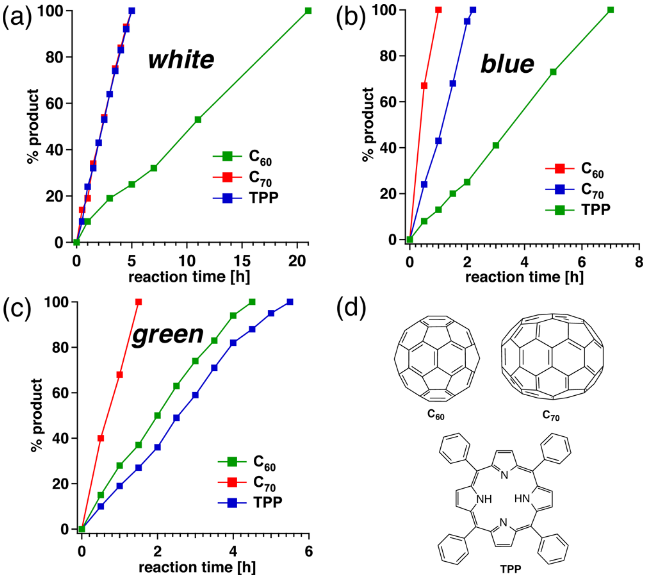


Figure 2. Reaction process of oxidation under (a) white tungsten lamp (200 W, 20000–20500 lx), (b) blue diode (emission maximum: 470 nm, 14000–14500 lx), (c) green diode (emission maximum: 520 nm, 73000–74000 lx). (d) Structures of the photosensitizers. The reactions were carried out using 0.1 mol % of photosensitizer and 50 mg (0.38 mmol) of amine **1** in $CHCl_3$. The value of % product was estimated by ^1H NMR spectra integration.

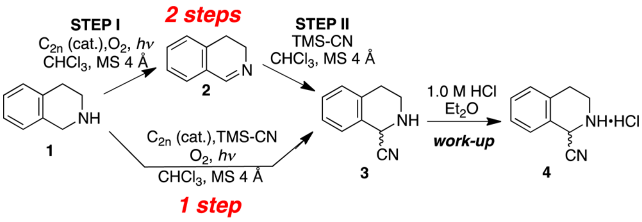
1 (runs 1–4), and these studies revealed that $CHCl_3$ was the most efficient solvent. This solvent effect may be partially related to the lifetime of the $^1O_2$ in each solvent (250 ± 10, 91 ± 10, 30 ± 10, and 54 μs for $CHCl_3$, CH_2Cl_2, THF, and CH_3CN, respectively[39,40]). The very slow reaction in CH_3CN (run 4) was presumably due to the low solubility of C_{60} in this polar solvent. A similar situation was observed in the reaction of the more soluble C_{60}–Bingel adduct (SI, Figure S14), in which a slightly faster reaction rate was shown compared to the less soluble pristine C_{60} (runs 5, 11). None or only trace product generation was observed in the absence of C_{60} or light (runs 8, 10). The saturated oxygen concentration was advantageous than the ambient condition with open flask (run 9).

Importantly, the oxidation of **1** with C_{60} proceeded in a clean manner to show a single product **2** in the crude extract (Figure 1) after a simple workup of precipitation of C_{60} fraction by MeOH and subsequent Celite filtration. However, the reaction efficiency was not sufficient when compared with TPP, a commonly used photosensitizer (runs 5, 12).As an alternative, we used C_{70} (99.5%, MTR Ltd.) as a catalyst, which has stronger absorbance of visible light (Figure S25) and a longer triplet state ($^3C_{70}$*) lifetime than C_{60} or TPP. As expected, the reaction with C_{70} was much faster than the one with C_{60} and almost the same as the one with TPP (runs 5, 12, 13 and Figure 2a). Importantly, we could lower the catalyst loading of C_{70} to 0.01 mol % and still complete the oxidation in a practical reaction time (28 h, run 15).

Based on the promising results of using C_{70} under white light above, along with the fact that C_{70} has absorbance in longer wavelength region, which has less risk of decomposition of the compounds involved in the reaction, we used commercially available, inexpensive diode lamps for irradiation. We compared the reaction rates in the presence of C_{60}, C_{70}, and TPP. As a result, under both blue (max: 470 nm, Figure 2b) and green (max: 520 nm, Figure 2c) LED lights, the reaction with C_{70} proceeded faster than those with either TPP or C_{60}, indicating the advantage in the use of C_{70} as a photocatalyst. In addition, under green light, the reaction of C_{60} was faster than that of TPP, despite the fact that the absorbance of TPP at around 520 nm is much higher than the one of C_{60} (Figure S25). This is presumably because the quantum yields in $^1O_2$ generation from photoexcited fullerenes are quite high (0.96 ± 0.04 for C_{60}[1] and 0.81 ± 0.15 for C_{70}[2] in benzene at 532 nm) compared to the one from TPP (0.62 ± 0.20 in benzene at 532 nm).[41]

Based on the above results for the efficient oxidation with C_{70}, we simultaneously carried out amine oxidation and nucleophilic addition (Table 2). An initial attempt of this one-step protocol using 0.1 mol % of C_{60} and white light resulted only in the generation of imine **2**, presumably due to the decomposition of **3** by white light irradiation (run 4). This was overcome by a one-pot/two-step protocol (run 1) involving an initial step of photooxidation with 1 mol % of C_{60} under white light and the subsequent second step of nucleophile addition in dark to provide **4** in 65% yield. By switching the photocatalyst to C_{70}, the yield by a one-pot/two-step protocol was improved to 71% (white light, run 2) and 75% (blue light, run 3) with shorter reaction times and lower catalyst loading. Furthermore, using C_{70} (0.1 mol %), the one-pot/one-step protocol was successfully achieved to provide **4** in good yield with shorter reaction intervals, especially under blue light irradiation (runs 5, 6).

Table 2. Combination of Amine Oxidation and Nucleophilic Addition[a]



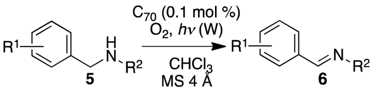
	two-step conditions						
	step I (light)			step II (dark)			
run	S (mol %)	hν	time [h]	TMS-CN [equiv]	time [h]	NMR yield of **3**[b] [%]	yield of **4**[c] [%]
1	C_{60} (1.0)	W	15	2.0	1.5	73	65
2	C_{70} (0.1)	W	7	1.5	4	>99	71
3	C_{70} (0.1)	B	2	1.5	4	>99	75

	one-step conditions (light)					
run	S (mol %)	hν	TMS-CN [equiv]	time [h]	NMR yield of **3**[b] [%]	yield of **4**[c] [%]
4	C_{60} (0.1)	W	1.5	45	<5	N.D.[d]
5	C_{70} (0.1)	W	1.5	10	>99	74
6	C_{70} (0.1)	B	1.5	3	>99	76

[a] Reactions were carried out using amine **1** (133 mg, 1.0 mmol). [b] The NMR yield was obtained by NMR integration. [c] Obtained yields of **4** by one-time precipitation in HCl/Et_2O. [d] Imine **2** was observed after slight generation of **3** in the reaction process by NMR (Figure S27).

The C_{70}-catalyzed photooxidation was applied to various benzylamines **5a**–**i** with substituents on the aromatic ring in the presence of C_{70} (0.1 mol %) under white light. As a result, all reactions provided the corresponding imines in good yields (>90%) within 20 h. There was no significant effect of substituents with electron-donating groups (Me and OMe, Table 3, runs 2, 3) or electron-withdrawing groups (F, Cl, and CF_3, runs 4, 5, and 8) in the *para*-position on the reaction rate. The *ortho*- and *meta*-substitution had a slight effect to diminish the reaction rate (runs 6, 7, 9), presumably due to steric hindrance. These results are very similar to recent reports by Seeberger and co-workers,[38] where TPP is used as a photocatalyst, and indicate (1) that C_{70} itself does not have any influence in the selectivity of amine oxidation and (2) that oxidation is suitable for various kinds of benzylamine derivatives. In addition, when an aliphatic amine (e.g., piperidine) was used as a substrate, no imine formation was observed as a limitation of this amine oxidation reaction. Benzylamine oxidation works better presumably due to the stable benzylic radical formation as an important intermediate to provide imine.

Table 3. Photoinduced Oxidation of Benzylamine Derivatives Catalyzed by C_{70}

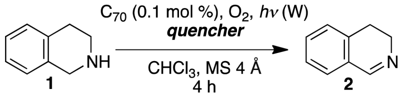


	substrate **5**				
run		R^1	R^2	reaction time [h]	yield[a] [%]
1	**5a**	H	Bn	7	97
2	**5b**	*p*-Me	*p*-MeBn	9	95
3	**5c**	*p*-OMe	*p*-OMeBn	6.5	92
4	**5d**	*p*-F	*p*-FBn	8	93
5	**5e**	*p*-Cl	*p*-ClBn	6	97
6	**5f**	*o*-Cl	*o*-ClBn	15	90
7	**5g**	*m*-Cl	*m*-ClBn	8	95
8	**5h**	*p*-CF_3	*p*-CF_3Bn	10	95
9	**5i**	*m*-CF_3	*m*-CF_3Bn	20	91

[a] Isolated yields.

In order to elucidate aspects of the reaction mechanism, the photooxidations were carried out in the presence of ROS quenchers. In a detailed examination previously reported by the groups of Seeberger[38] and Baciocchi,[42] two possible mechanisms were proposed for the $^1O_2$-mediated oxidation of amines. Both start from initial coordination of $^1O_2$ to amine nitrogen to cause an exciplex formation followed by the generation of benzylic radical through either (1) single-electron transfer to provide amine radical cation and $O_2^{\bullet -}$ and subsequent deprotonation at the benzyl position or (2) direct hydrogen abstraction. Since we used a photosensitizer with a higher oxidation potential as compared to TPP, it was important to clarify what kind of ROS is involved as reactive species in the current oxidation reaction. We used DABCO and benzoquinone as quenchers of $^1O_2$ and $O_2^{\bullet -}$, respectively. In addition, anthracene was added as a competitive substrate for oxidation by $^1O_2$ (cycloaddition). As shown in Table 4, significant suppression of the oxidation reaction was observed in the presence of DABCO (run 1) with a linear correlation in Stern–Volmer plotting (Figure S96), which

Table 4. Effects of ROS Quenchers on Oxidation[a]



run	quencher (equiv to amine)	solvent	reaction time [h]	NMR yield[b] [%]
1	DABCO (1.0)	$CHCl_3$	4	7
2	anthracene (1.0)	$CHCl_3$	4	85
3	benzoquinone (0.1)[c]	$CHCl_3$	4	25
4		$CHCl_3$	4	>99

[a] All reactions were carried out with amine **1** (15 mg, 0.11 mmol). [b] Observed by ^1H NMR of crude mixture. [c] Reaction was carried out in the presence of smaller amounts of quencher to avoid complex side reactions observed in the presence of larger amounts of benzoquinone.

indicates that $^1O_2$ is an important reactive species involved in the oxidation. In addition, a moderate decrease of yield was observed in the presence of anthracene (run 2). On the other hand, a slower reaction was also observed in the presence of benzoquinone (run 3) indicating the involvement of $O_2^{\bullet-}$, which is probably generated by the electron transfer from an amine to $^1O_2$. The detailed investigation of the mechanism is still in progress.

Finally, the reaction was carried out on a larger scale to test the recovery of catalyst C_{70}. As described above, separation of C_{70} from reaction mixture is easily done by precipitation from MeOH. In a reaction of **1** (2.0 g) using 12.6 mg (0.1 mol %) of C_{70} (9 h under blue light), 10.1 mg of the C_{70} fraction was recovered, which was subjected to a recycled reaction with **1** (2.0 g) to provide 97% yield in 10 h reaction time under blue light. The recovered C_{70} fraction contained substantial amounts of C_{70} mono- and diepoxides as detected by HPLC and MALDI-TOF-MS (Figures S101, S102).[43] By thermal treatment (reflux in *o*-dichlorobenzene for 17 h), most of the C_{70} epoxides were easily converted back to underivatized C_{70} as indicated by both HPLC and MALDI-TOF-MS (Figures S103, S104).

In conclusion, we successfully developed a clean and efficient oxidation of benzylamines with a simple workup process. Due to the efficiency of C_{70} as a photosensitizer, we achieved lower catalyst loading and provided a high yield of the products. This photoexcited C_{70}-mediated oxidation reaction is also applicable to many benzylamine derivatives and is suitable for simultaneous nucleophilic additions. Easy recovery of C_{70} fraction, which can be converted by simple thermal treatment to C_{70}, enabled the recycling of the C_{70} catalyst.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03194.

> Syntheses of amines; detail of photoinduced oxidation reaction; oxidation−nucleophile addition with full spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11.

(2) Arbogast, J. W.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, *113*, 8886.

(3) Yamakoshi, Y.; Umezawa, N.; Ryu, A.; Arakane, K.; Miyata, N.; Goda, Y.; Masumizu, T.; Nagano, T. *J. Am. Chem. Soc.* **2003**, *125*, 12803.

(4) Nagano, T.; Arakane, K.; Ryu, A.; Masunaga, T.; Shinmoto, K.; Mashiko, S.; Hirobe, M. *Chem. Pharm. Bull.* **1994**, *42*, 2291.

(5) Tokuyama, H.; Yamago, S.; Nakamura, E.; Shiraki, T.; Sugiura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 7918.

(6) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, 807.

(7) Tokuyama, H.; Nakamura, E. *J. Org. Chem.* **1994**, *59*, 1135.

(8) Jensen, A. W.; Daniels, C. *J. Org. Chem.* **2003**, *68*, 207.

(9) Latassa, D.; Enger, O.; Thilgen, C.; Habicher, T.; Offermanns, H.; Diederich, F. *J. Mater. Chem.* **2002**, *12*, 1993.

(10) Murahashi, S. I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2443.

(11) Adams, J. P.; Robertson, G. *Contemp. Org. Synth.* **1997**, *4*, 183.

(12) Martin, S. F. *Pure Appl. Chem.* **2009**, *81*, 195.

(13) Kobayashi, S.; Mori, Y.; Fossey, J. S.; Salter, M. M. *Chem. Rev.* **2011**, *111*, 2626.

(14) Mukaiyama, T.; Kawana, A.; Fukuda, Y.; Matsuo, J. *Chem. Lett.* **2001**, 390.

(15) Nicolaou, K. C.; Mathison, C. J. N.; Montagnon, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 4077.

(16) Nicolaou, K. C.; Mathison, C. J. N.; Montagnon, T. *J. Am. Chem. Soc.* **2004**, *126*, 5192.

(17) Largeron, M. *Eur. J. Org. Chem.* **2013**, *2013*, 5225.

(18) Zhang, E.; Tian, H.; Xu, S.; Yu, X.; Xu, Q. *Org. Lett.* **2013**, *15*, 2704.

(19) Chu, G. B.; Li, C. B. *Org. Biomol. Chem.* **2010**, *8*, 4716.

(20) Hu, Z.; Kerton, F. M. *Org. Biomol. Chem.* **2012**, *10*, 1618.

(21) Sonobe, T.; Oisaki, K.; Kanai, M. *Chem. Sci.* **2012**, *3*, 3249.

(22) Choi, H.; Doyle, M. P. *Chem. Commun.* **2007**, 745.

(23) Ell, A. H.; Samec, J. S.; Brasse, C.; Backvall, J. E. *Chem. Commun.* **2002**, 1144.

(24) Lang, X. J.; Ma, W. H.; Chen, C. C.; Ji, H. W.; Zhao, J. C. *Acc. Chem. Res.* **2014**, *47*, 355.

(25) Patil, R. D.; Adimurthy, S. *Adv. Synth. Catal.* **2011**, *353*, 1695.

(26) Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 1480.

(27) Wendlandt, A. E.; Stahl, S. S. *J. Am. Chem. Soc.* **2014**, *136*, 506.

(28) Yuan, H.; Yoo, W. J.; Miyamura, H.; Kobayashi, S. *J. Am. Chem. Soc.* **2012**, *134*, 13970.

(29) Wendlandt, A. E.; Stahl, S. S. *Org. Lett.* **2012**, *14*, 2850.

(30) Girard, S. A.; Knauber, T.; Li, C. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 74.

(31) Nicewicz, D. A.; Nguyen, T. M. *ACS Catal.* **2014**, *4*, 355.

(32) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322.

(33) Yoon, T. P.; Ischay, M. A.; Du, J. *Nat. Chem.* **2010**, *2*, 527.

(34) Jiang, G.; Chen, J.; Huang, J. S.; Che, C. M. *Org. Lett.* **2009**, *11*, 4568.

(35) Berlicka, A.; König, B. *Photochem. Photobiol. Sci.* **2010**, *9*, 1359.

(36) Ushakov, D. B.; Gilmore, K.; Kopetzki, D.; McQuade, D. T.; Seeberger, P. H. *Angew. Chem., Int. Ed.* **2014**, *53*, 557.

(37) To, W. P.; Tong, G. S.; Lu, W.; Ma, C.; Liu, J.; Chow, A. L.; Che, C. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 2654.

(38) Ushakov, D. B.; Plutschack, M. B.; Gilmore, K.; Seeberger, P. H. *Chem. - Eur. J.* **2015**, *21*, 6528.

(39) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423.

(40) Salokhiddinov, K. I.; Gurinovich, G. P.; Byteva, I. M. *J. Appl. Spectrosc.* **1981**, *34*, 561.

(41) Schmidt, R.; Afshari, E. *J. Phys. Chem.* **1990**, *94*, 4377.

(42) Baciocchi, E.; Del Giacco, T.; Lanzalunga, O.; Lapi, A. *J. Org. Chem.* **2007**, *72*, 9582.

(43) A trace amount of an amine adduct of C_{70} produced by nucleophilic addition was observed in the reaction mixture, but it was minor compared to the C_{70} epoxides.