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## Visible-Light-Induced Thiotrifluoromethylation of Terminal Alkenes with Sodium Triflinate and Benzenesulfonothioates

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An unconventional reductive quenching cycle was developed to realize the visible-light-induced thiotrifluoromethylation of terminal alkenes.  $CF_3SO_2Na$  was used as an easy handled  $CF_3$  radical source to afford the desired products in moderate to good yields. Mild reaction conditions and broad substrate scope featured this transformation.

Due to its high efficiency in the preparation of polyfunctionalized compounds and valuable building blocks for natural and biologically active compounds, the difunctionalization of alkenes, which involves the installation of two functional groups across a double bond, has received increasing attention in organic synthesis.<sup>1</sup> Meanwhile, it is well-known that the introduction of trifluoromethyl group  $(CF_3)$ can significantly alter the physical, chemical, and biological properties of the parent compounds.<sup>2</sup> Thus, the difunctionalization of alkenes along with the formation of a new C-CF<sub>3</sub> bond has become an important area and much effort has been devoted into it with the aim of developing novel and efficient methods.<sup>3</sup>

Recently, the visible light induced photocatalysis using photocatalysts to activate organic molecules has been established as a powerful strategy for triggering new chemical reactions in organic synthesis with a host of attractive features, such as mild and environmentally benign reaction conditions, excellent functional group tolerance, and high reactivity.<sup>4</sup> By applying this ideal protocol, photoredox-catalyzed difunctionalization of alkenes along with the formation of a  $C-CF_3$  bond has been extensively studied and great progress has been achieved including halotrifluoromethylation,<sup>5</sup> oxytrifluoromethylation,<sup>6</sup> aminotrifluoromethylation,<sup>7</sup> carbotrifluoromethylation<sup>8</sup> and thiotrifluoromethylation

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Scheme 1. Visible-Light-Induced Difunctionalization of Alkenes Involving the Formation of C-CF<sub>3</sub> Bonds.

(Scheme 1) <sup>5d, 9</sup> with CF<sub>3</sub>I, CF<sub>3</sub>SO<sub>2</sub>Cl, Umemoto's reagent or Togni's reagents as a CF<sub>3</sub> radical source. Despite the success of these reactions, some issues still get on with these reagents such as the difficult handling of CF<sub>3</sub>I (gas), the corrosive and volatile property of CF<sub>3</sub>SO<sub>2</sub>Cl and the high cost of Umemoto's reagent and Togni's reagents. Therefore, a convenient, easyhandling and cheaper CF<sub>3</sub> radical source is highly desirable.

Consideration from the aspect of mechanism, all of these photoredox-catalyzed alkene difunctionalizations involving construction of a C-CF<sub>3</sub> bond experienced an oxidative quenching cycle, e.g. a nucleophile was needed to attack the newly generated carbocation to finish the cycle (Scheme 2, left, red cycle). We envisage that if a reductive quenching cycle is possible by selecting appropriate CF<sub>3</sub> radical source, electrophile and photoredox catalyst, the product that couldn't be accessible through oxidative quenching cycle might be obtained (Scheme 2, right, blue cycle). Herein, we report the visible-light-induced thiotrifluoromethylation of terminal alkenes with sodium triflinate (CF<sub>3</sub>SO<sub>2</sub>Na, Langlois reagent, white solid) as an easy handled CF<sub>3</sub> radical source and benzen sulfonothioates as a sulfur source. This transformation is believed to undergo a reductive quenching cycle.

To achieve our goal of photoredox-catalyzed alkene

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difunctionalizations along with the formation of a C-CF<sub>3</sub> bond through a reductive quenching cycle, two challenges should be overcome. Firstly, the oxidation potential of excited state of photoredox catalyst should be high enough to oxidize  $CF_3SO_2Na$  ( $E_{ox}$  = 1.05 V vs. SCE,  $CF_3SO_2K$ ) into  $CF_3$  radical,<sup>10</sup> more importantly, the reduced form of photoredox catalyst should have robust reducing power to reduce the carbon radical generated from the addition of CF<sub>3</sub> radical on alkene into carbanion. According to the redox property of  $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6 [E_{1/2}red (*Ir^{III}/Ir^{II}) = +1.21 V, E_{1/2}red$  $(Ir^{III}/Ir^{II}) = -1.37$  V vs. SCE], it would meet the requirements of these two aspects.<sup>11</sup> Secondly, in order to avoid the competitive protonation reaction, choosing an appropriate electrophile with enough reactivity toward the carbanion intermediate is critically important. Benzenesulfonothioates are electrophiles of this kind, they are easily attacked by a nucleophile due to the good leaving property of benzenesulphinate, with the  $pK_a$  of phenylsulfinic acid being 2.76. 12

Under this context, we chose allylbenzene (1a), S-phenyl benzenesulfonothioate (2a), CF<sub>3</sub>SO<sub>2</sub>Na as the model substrates and Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> as photoredox catalyst to conduct our initial studies (Table 1). To our delight, thiotrifluoromethylation product (3aa) was obtained in 76% isolated yield after irradiating a reaction mixture composed of 1a (0.2 mmol), 2a (0.3 mmol), CF<sub>3</sub>SO<sub>2</sub>Na (0.3 mmol) and Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbpy)PF<sub>6</sub> (1) (2.5 mol%) in anhydrous CH<sub>3</sub>CN for 18 h (Table 1, entry 1). It should be noted that no protonation byproduct was detected by GC-MS under this reaction conditions.  $Ir[dF(CF_3)ppy]_2(bpy)(PF_6)$  (2) could also promote the reaction yet with somewhat lower yield (entry 2). Further screening of solvents revealed that CH<sub>3</sub>CN was still the best choice (entry 1, 3-8), using other solvents not only led to the decrease in yields but also increased the amount of protonation byproduct. Control experiments found that light and photoredox catalyst were essential for the reactions, the reaction did not proceed either without irradiation (entry 9) or in the absence of the photocatalyst (entry 10).

With the optimized conditions in hand, we set out to explore the substrate scope of the reaction with a range of different terminal alkenes (Table 2). It was demonstrated that this reaction showed good functional group compatibility.

Table 1. Optimization of Thiotrifluoromethylation of Terminal Alkenes.<sup>a</sup> DOI: 10.1039/C7.CC03520A

$\sim$	<i>\</i>	т		т.		photocataly (2.5 mol%)	st	
		I	2a 2a		CF3502Na-	5 W blue LED solvent (0.1	D, rt M) 3	SPh aa
	entry		photocatalys	t <sup>e</sup>	solvent	time	yield <sup>b</sup> (%)	
	1		1		CH <sub>3</sub> CN	18 h	90 (76 <sup>d</sup>	 ?)
	2		2		CH <sub>3</sub> CN	18 h	64	
	3		1		dioxane	18 h	81	
	4		1		toluene	18 h	trace	
	5		1		DCM	18 h	43	
	6		1		THF	18 h	14	
	7		1		DMF	18 h	63	
	8		1		DMSO	18 h	61	
	9 <sup>d</sup>		1		CH <sub>3</sub> CN	18 h	_	
	10				CH <sub>3</sub> CN	18 h	_	

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), CF<sub>3</sub>SO<sub>2</sub>Na (0.3 mmol), photocatalyst (2.5 mol%), solvent (2 mL), rt. <sup>*b*</sup> GC yield. <sup>*c*</sup> Isolated yield. <sup>*d*</sup> No light. <sup>*c*</sup> **1**: Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)(PF<sub>6</sub>), **2**: Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(bpy)(PF<sub>6</sub>).

Simple terminal alkenes (**3aa-3fa**) exhibited robust reactivity in this transformation and all of the corresponding products were obtained in good yields. Notably, the synthetic useful epoxide group was well compatible in the reaction (**3ag**). Phenyl allyl ethers were competent candidates in the reactions, and they were smoothly thiotrifluoromethylated in 50-61% yields with different para-substituted groups such as -Me, - OMe, -F, -Cl, -Br, -CH<sub>2</sub>CN and -NHCOMe (**3ha-3oa**), however, 2-(allyloxy)-1,3dimethylbenzene and 2-(allyloxy)naphthalene gave inferior results (**3pa**, **3qa**) probably owing to the steric hindrance and low reactivity. (But-3-en-1-yloxy)benzene, 1-(vinyloxy)butane and but-3-en-1-yl(p-tolyl)sulfane could also give the desired products in moderate yields (**3ra-3ta**). It should be noted that terminal alkene with a -OH group could successfully undergo **Table 2. Scope of the Terminal Alkenes.** 



Reaction conditions: 1 (0.2 mmol), 2a (0.3 mmol), CF\_3SO\_2Na (0.3 mmol), photocatalyst (2.5 mol%), CH\_3CN (2 mL), rt, 18 h.

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thiotrifluoromethylation without formation of the protonation side product (**3ua**). In addition, 1-phenylpent-4-en-1-one could give the desired products in 65% yields (**3va**). Moreover, the nitrogen-containing groups such as phthaloyl and carbazolyl were also well tolerated in the reaction, and the desired products were obtained in moderate to good yields (**3wa-3ya**). In the case of carboxylic ester, sulfonate and 4-(but-3-en-1yloxy)-2H-chromen-2-one, the corresponding desired products were obtained in moderate to good yields (**3za-3§a**).

We next examined the substrate scope of this transformation with respect to different benzenesulfonothioates (Table 3). It was found that a variety of S-aryl benzenesulfonothioates could be used to participate this visible-light-induced thiotrifluoromethylation of in terminal alkenes. Generally, functional groups such as -Me, -OMe, -F, -Cl, -Br could be well tolerated to give the desired products in moderate to good yields without the influence of the position of functional groups (3ab-3ae, 3ag-3ai). Moreover, benzenesulfonothioates with sensitive group -NO<sub>2</sub> and pyridyl could also give the products in satisfied yields (3af, 3aj). However, for S-alkyl benzenesulfonothioates, the reactions became unreactive (3ak-3am) probably due to the weak eletrophilicity of S-alkyl benzenesulfonothioates. Several experiments were conducted to gain insight into the mechanism of the reaction (Scheme 3). When radical scavenger (BHT or TEMPO) was added, the reaction was totally Table 3. Scope of the Benznenesulfonothioates.



Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol),  $CF_3SO_2Na$  (0.3 mmol), photocatalyst (2.5 mol%),  $CH_3CN$  (2 mL), rt, 18 h.

suppressed (eq 1), which suggested that a SET pathway was involved in this transformation. Next when ethene-1,1diyldibenzene was added to the reaction under the standard conditions, radical addition elimination product **4a** and radical addition protonation product **4b** were afforded in overall 42% yield (eq 2), this radical-trapping experiment clarified the formation of CF<sub>3</sub> radical in this thiotrifluoromethylation process. It was reported that disulphide could be attacked by a radical to form a C-S bond, <sup>13</sup> however, when 1, 2-diphenyldisulfane was added to the our system instead of **2a**, only trace amount of **3aa** was detected by GC-MS (eq 3). This result demonstrated that the next step which followed CF<sub>3</sub> radical attack should be a carboanion involved reaction. The quantum yield for the reaction of **1a**, **2a** and CF<sub>3</sub>SO<sub>2</sub>Na under standard conditions was also measured according to the reported procedure (for details, see Supporting Information), <sup>14</sup> its value was  $\Phi = 0.142$ , which indicated that radical chain process was theoretically ruled out in this visible-light-induced thiotrifluoromethylation of terminal alkenes. All of these results confirmed our hypothesis that this visible-light-induced thiotrifluoromethylation of terminal alkenes with CF<sub>3</sub>SO<sub>2</sub>Na and benzenesulfonothioates undergoes a reductive quenching cycle.



Scheme 3. Experimental Probes on Reaction Mechanism

Gratifyingly, the reaction could be readily scaled up without loss of its efficiency, 296 mg (50% yield) of thiotrifluoromethylation product 3aa was obtained in 2 mmol scale (Scheme 4, eq 1). The practicability of the reaction was further demonstrated by applying it into the modification of (-)-Borneol derivative 18 and estrone derivative 18, the desired thiotrifluoromethylaed products 3ßa and 3&a were obtained in 44% and 41% yield respectively (Scheme 4, eq 2 and 3). The products of this thiotrifluoromethylation reaction could also be transformed into its sulphone derivatives under mild condition. As an example, 5a was obtained in 84% yield (Scheme 4, eq 4).

In summary, a novel visible-light-induced thiotrifluoromethylation of terminal alkenes with sodium triflinate and benzenesulfonothioates has been developed. The mechanistic studies suggested that this reaction undergoes an untraditional reductive quenching cycle.  $CF_3SO_2Na$  was used as an easy-handled and cheaper  $CF_3$  radical



make this transformation valuable and practical in organic synthesis.

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### Notes and references

- 1 For selected reviews on the alkene difunctionalization, see: (a) A. K. Yudin, In Catalyzed Carbon-Heteroatom Bond Formation; Wiley-VCH: Weinheim, 2010; pp 119-135; (b) K. Muñiz, Chem. Soc. Rev., 2004, 33, 166; (c) K. H. Jensen and M. S. Sigman, Org. Biomol. Chem., 2008, 6, 4083; (d) F. Cardona and A. Goti, Nat. Chem., 2009, 1, 269; (e) R. I. McDonald, G. Liu and S. S. Stahl, Chem. Rev.; 2011, 111, 2981; (f) J. P. Wolfe, Angew. Chem., Int. Ed., 2012, 51, 10224; (g) G. Liu, Org. Biomol. Chem., 2012, 10, 6243; (h) S. R. Chemler and M. T. Bovino, ACS Catal., 2013, 3, 1076; (i) Y. Shimizu and M. Kanai, Tetrahedron Lett., 2014, 55, 3727; For recent alkene difunctionalization examples, see: (j) X. Sun, X. Li, S. Song, Y. Zhu, Y.-F. Liang and N. Jiao, J. Am. Chem. Soc., 2015, 137, 6059; (k) R. Zhu and S. L. Buchwald, J. Am. Chem. Soc., 2015, 137, 8069; (I) K. Zhang, H. Wang, J. Zheng, L. Yu and H. Ding, Chem. Commun., 2015, 51, 6399; (m) N. Wang, L. Li, Z.-L. Li, N.-Y. Yang, Z. Guo, H.-X. Zhang and X.-Y. Liu, Org. Lett., 2016, 18, 6026; (n) K. Yang and Q. Song, Org. Lett., 2016, 18, 5460; (o) B. N. Hemric, K. Shen and Q. Wang, J. Am. Chem. Soc., 2016, 138, 5813; (p) Z. Wu, R. Ren and C. Zhu, Angew. Chem., Int. Ed., 2016, 55, 10821; (q) S. M. Banik, J. W. Medley and E. N. Jacobsen, J. Am. Chem. Soc., 2016, 138, 5000; (r) J. Xu, X. Yu and Q. Song, Org. Lett., 2017, 19, 980; (s) Z. Wu, D. Wang, Y. Liu, L. Huan and C. Zhu, J. Am. Chem. Soc., 2017, 139, 1388; (t) J. D. Griffin, C. L. Cavanaugh and D. A. Nicewicz, Angew. Chem., Int. Ed., 2017, 56, 2097; (u) D. Wang, F. Wang, P. Chen, Z. Lin and G. Liu, Angew. Chem., Int. Ed., 2017, 56, 2054.
- 2 (a) P. Kirsch, Modern Fluoroorganic Chemistry: Synthesis Reactivity Applications; Wiley-VCH: Weinheim, Germany, 2004. (b) I. Ojima, Fluorine in Medicinal Chemistry and Chemical Biology; Wiley-Blackwell: Chichester, U.K., 2009. (c) B. E. Smart, Chem. Rev., 1996, 96, 1555. (d) S. Purser, P. R. Moore, S. Swallow and V. Gouverneur, Chem. Soc. Rev., 2008, 37, 320. (e) J. Wang, M. Sánchez-Roselló, J. L. Aceña, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok and H. Liu, Chem. Rev., 2014, 114, 2432.
- 3 (a) C. Alonso, E. M. de Marigorta, G. Rubiales and F. Palacios, Chem. Rev., 2015, 115, 1847; (b) J. Xu, Y. Fu, D.-F. Luo, Y.-Y. Jiang, B. Xiao, Z.-J. Liu, T.-J. Gong and L. Liu, J. Am. Chem. Soc., 2011, 133, 15300; (c) H. Egami, R. Shimizu and M. Sodeoka, Tetrahedron Lett., 2012, 53, 5503; (d) C. Feng and T.-P. Loh, Chem. Sci., 2012, 3, 3458; (e) Y. Li and A. Studer, Angew. Chem., Int. Ed., 2012, 51, 8221; (f) L. Zhu, G. Wang, Q. Guo, Z. Xu, D. Zhang and R. Wang, Org. Lett., 2014, 16, 5390; (g) B. Yang, X.-H. Xu and F.-L. Qing, Org. Lett., 2015, 17, 1906; (h) Y. Yang, Y. Liu, Y. Jiang, Y. Zhang and D. A. Vicic, J. Org. Chem., 2015, 80, 6639; (i) M. Fu, L. Chen, Y. Jiang, Z.-X. Jiang and Z. Yang, Org. Lett., 2016, 18, 348; (j) J.-Y. Guo, R.-X. Wu, J.-K. Jin and S.-K. Tian, Org. Lett., 2016, 18, 3850; (k) M. Fu, L. Chen, Y. Jiang, Z.-X. Jiang and Z. Yang, Org. Lett., 2016, 18, 348; (I) F. Wang, D. Wang, X. Wan, L. Wu, P. Chen and G. Liu, J. Am. Chem. Soc., 2016, 138, 15547; (m) Z.-Q. Liu and D. Liu J. Org. Chem., 2017, 82, 1649; (n) S. Zhou, T. Song, H. Chen, Z. Liu, H.

Shen and C. Li, Org. Lett., 2017, **19**, 698; (o) L. Wu, F. Wang, X. Wan, D. Wang, P. Chen and G. Liu, J. <u>Am. 164699/326302917</u>, **139**, 2904.

- For selected reviews on photocatalysis, see: (a) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322; (b) D. Ravelli, S. Protti and M. Fagnoni, *Chem. Rev.*, 2016, **116**, 9850; (c) N. A. Romero and D. A. Nicewicz, *Chem. Rev.*, 2016, **116**, 10075; (d) K. L. Skubi, T. R. Blum and T. P. Yoon, *Chem. Rev.*, 2016, **116**, 10035; (e) M. N. Hopkinson, A. Tlahuext-Aca and F. Glorius, *Acc. Chem. Res.*, 2016, **49**, 2261; (f) D. Staveness, I. Bosque and C. R. J. Stephenson, *Acc. Chem. Res.*, 2016, **49**, 2295; (g) T. Chatterjee, N. Iqbal, Y. You and E. J. Cho, *Acc. Chem. Res.*, 2016, **49**, 2307; (i) A. Arora and J. D. Weaver, *Acc. Chem. Res.*, 2016, **49**, 2273; (j) T. Koike and M. Akita, *Acc. Chem. Res.*, 2016, **49**, 1937; (k) M. Majek and A. J. von Wangelin, *Acc. Chem. Res.*, 2016, **49**, 2316.
- 5 (a) J. D. Nguyen, J. W. Tucker, M. D. Konieczynska and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2011, **133**, 4160; (b) C.-J. Wallentin, J. D. Nguyen, P. Finkbeiner and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2012, **134**, 8875; (c) S. H. Oh, Y. R. Malpani, N. Ha, Y.-S. Jung and S. B. Han, *Org. Lett.*, 2014, **16**, 1310; (d) D. B. Bagal, G. Kachkovskyi, M. Knorn, T. Rawner, B. M. Bhanage and O. Reiser, *Angew. Chem., Int. Ed.*, 2015, **54**, 6999.
- (a) Y. Yasu, T. Koike and M. Akita, Angew. Chem., Int. Ed., 2012, 51, 9567; (b) E. Kim, S. Choi, H. Kim and E. J. Cho, Chem. Eur. J., 2013, 19, 6209; (c) Y. Yasu, Y. Arai, R. Tomita, T. Koike and M. Akita, Org. Lett., 2014, 16, 780; (d) N. Noto, K. Miyazawa, T. Koike and M. Akita, Org. Lett., 2015, 17, 3710; (e) Q.-H. Deng, J.-R. Chen, Q. Wei, Q.-Q. Zhao, L.-Q., Lua and W.-J. Xiao, Chem. Commun., 2015, 51, 3537; (f) L. Jarrige, A. Carboni, G. Dagousset, G. Levitre, E. Magnier and G. Masson, Org. Lett., 2016, 18, 2906.
- 7 (a) Y. Yasu, T. Koike and M. Akita, *Org. Lett.*, 2013, **15**, 2136;
  (b) Q. Wei, J.-R. Chen, X.-Q. Hu, X.-C. Yang, B. Lu and W.-J. Xiao, *Org. Lett.*, 2015, **17**, 4464.
- 8 (a) P. Xu, J. Xie, Q. Xue, C. Pan, Y. Cheng and C. Zhu, *Chem. Eur. J.* 2013, **19**, 14039; (b) L. Zheng, C. Yang, Z. Xu, F. Gao and W. Xia, *J. Org. Chem.* 2015, **80**, 5730; (c) F. Gao, C. Yang, G.-L. Gao, L. Zheng and W. Xia, *J. Org. Chem.* 2015, **80**, 5730.
- 9 T. Rawner, M. Knorn, E. Lutsker, A. Hossain and O. Reiser, J. Org. Chem., 2016, 81, 7139.
- J.-B. Tommasino, A. Brondex, M. Médebielle, M. Thomalla, B. R. Langlois and T. Billard, Synlett, 2002, 13, 1697.
- (a) M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, Jr., G. G. Malliaras and S. Bernhard, *Chem. Mater.*, 2005, **17**, 5712; (b) L. Zhu, L.-S. Wang, B. Li, B. Fu, C.-P. Zhang and W. Li, *Chem. Commun.*, 2016, **52**, 6371.
- 12 W. Wang, X. Peng, F. Wei, C.-H. Tung and Z. Xu, Angew. Chem., Int. Ed., 2016, **55**, 649.
- (a) M. Teders, A. Gómez-Suárez, L. Pitzer, M. N. Hopkinson and F. Glorius, *Angew. Chem., Int. Ed.*, 2017, **56**, 902; (b) P.-F. Wang, X.-Q. Wang, J.-J. Dai, Y.-S. Feng and H.-J. Xu, *Org. Lett.*, 2014, **16**, 4586; (c) X. Zhu, X. Xie, P. Li, J. Guo and L. Wang, *Org. Lett.*, 2016, **18**, 1546; (d) W.-J. Wang, X.-J. Liu and X.-C. Wang, *ChemistrySelect* 2017, **2**, 1140.
- 14 (a) M. A. Cismesia and T. P. Yoon, *Chem. Sci.* 2015, 6, 5426. (b)
  X. Huang, R. D. Webster, K. Harms and E. Meggers, *J. Am. Chem. Soc.* 2016, 138, 12636. (c) Y. Zhao, B. Huang, C. Yang,
  B. Li, B. Gou, and W. Xia, *ACS Catal.* 2017, 7, 2446. (d) *The exploration of supramolecular systems and nanostructures by photochemical techniques*, Lecture notes in Chemistry, vol 78, P74-95. ed. P. Ceroni, Springer Dordrecht Heidelberg London New York, 2012.

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