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Visible Light-Mediated Metal-Free Synthesis of Vinyl Sulfones from Aryl Sulfinates

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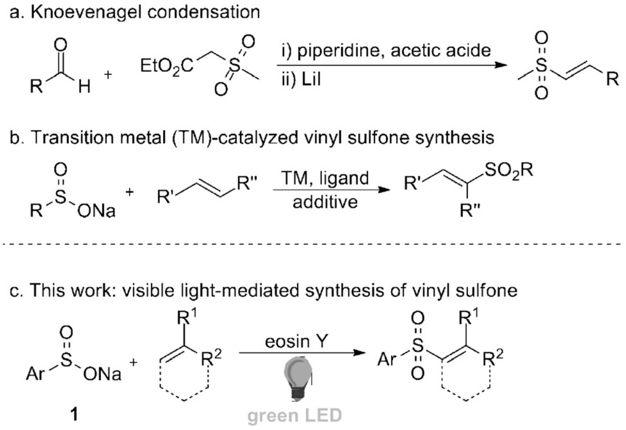
Abstract: Visible light and eosin Y catalyze the synthesis of vinyl sulfones from aryl sulfinates and alkenes by a photoredox process. The reaction scope is broad in aryl sulfinates and alkenes and the general and simple procedure provides a metal-free alternative for the synthesis of synthetically valuable vinyl sulfones.

Keywords: aryl sulfinates; metal-free conditions; photocatalysis; vinyl sulfones; visible light

Vinyl sulfones are used in synthetic organic transformations as intermediates and reagents.[1] A recent example is the photoredox-mediated vinylation by vinyl sulfones.[2] They are of biological importance[3] as inhibitors for different enzymes, for example, cysteine proteases,[4] protein tyrosine phosphatases,[5] and sortases.[6]

Classic vinyl sulfone preparations are based on the Knoevenagel condensation (Scheme 1, a),[7] and the Horner–Emmons reaction.[8] Alternative methods are transition metal [e.g., Pd, Cu] catalyzed reactions of vinyl tosylates with aryl sulfinates,[9] alkenes or alkynes with sodium sulfinates (Scheme 1, b),[10] and alkynes with arylsulfinic acids.[11] In 2011, Taniguchi developed a copper-catalyzed aerobic system for the synthesis of alkenyl sulfones from alkenes or alkynes with sodium sulfonates.[12] Lei et al. reported an iodide-catalyzed alkenylation reaction with sodium sulfinates or sulfonyl hydrazides and olefins yielding vinyl sulfones.[13] In 2013, Yu et al. described a visible-light photoredox-catalyzed protocol for the synthesis of β-amidovinyl sulfones from enamides with sulfonyl chlorides.[14] They used $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ and synthesized exclusively β-amidovinyl sulfones with sulfonyl chlorides as sulfonylation reagents.



Scheme 1. Different vinyl sulfone syntheses.

The use of sodium salts of sulfinic acid as sulfonylation reagents has gained much attention in recent years.[9,10,12,13,15] Sodium sulfinates are stable, easy to handle and readily available from their corresponding sulfonyl chlorides. A recent example of an ionic reaction is the addition of aryl sulfinates to 3-halooxindoles.[16] Under oxidative conditions sodium and zinc sulfinates serve as radical precursors.[17] Stephenson et al. generated sulfinyl radicals *via* reduction of sulfonyl chlorides.[18] In 2013, Nicewicz et al. reported the hydrotrifluoromethylation of styrenes by single electron oxidation of sodium trifluoromethanesulfinate by *N*-methyl-9-mesitylacridinium as the photoredox catalyst.[19] We report here the visible light-mediated, metal-free synthesis of vinyl sulfones from aryl sulfinates with olefins using green light, the organic dye eosin Y as photocatalyst and nitrobenzene as the terminal oxidant (Scheme 1, c).

The conditions were optimized by irradiating a reaction mixture of sodium benzenesulfinate (**1a**), styrene (**2a**), the photocatalyst and nitrobenzene with visible light. All reactions were performed at 40 °C to dissolve all starting materials and different catalysts, solvents and irradiation times were investigated.

The product yield using $[Ru(bpy)_3]Cl_2$ (**A**) as photocatalyst strongly depends on the solvent. Dipolar

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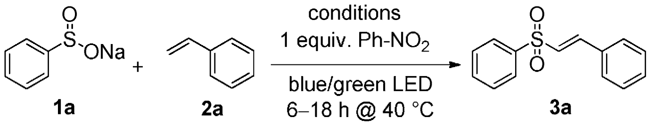
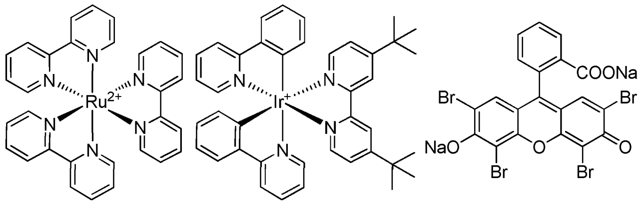
Table 1. Optimization of the reaction conditions.



1a + **2a** → **3a**



A: Ru(bpy)$_3$Cl$_2$ · 6 H$_2$O B: [Ir(ppy)$_2$(dtb-bpy)]PF$_6$ C: Eosin Y

Entry	Cat (mol%)	hν [nm]	Solvent	*t* [h]	Yield [%][a]
1	**A** (5)	455	DMF	6	26
2	–	455	DMF	6	6
3	**A** (5)	–	DMF	6	–
4	–	–	DMF	6	–
5	**A** (5)	455	DMF/H_2O (3:1)	6	58
6	**A** (5)	455	EtOH	6	59
7	**B** (2)	455	EtOH	6	59
8	**C** (10)	535	EtOH	6	43
9	**C (10)**	**535**	**EtOH**	**18**	**73[b]**
10	–	535	EtOH	18	–
11	**C** (10)	535	EtOH	18	55[c]

[a] Determined by GC analysis with naphthalene as internal standard.

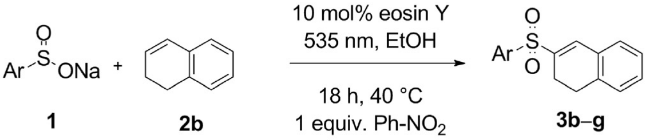
[b] *General reaction conditions 1*: **1a** (0.50 mmol, 3 equiv.), **2a** (0.17 mmol, 1 equiv.), Ph-NO$_2$ (0.17 mmol, 1 equiv.) and **C** (10 mol%) in EtOH was irradiated with green light for 18 h.

[c] N_2: degassed by three freeze-pump-thaw cycles.

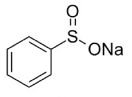
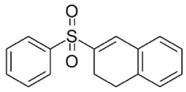
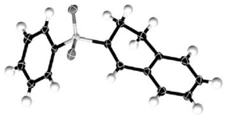
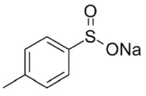
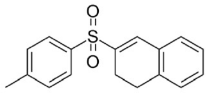
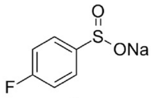
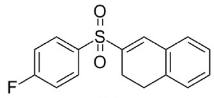
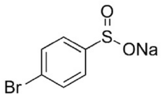
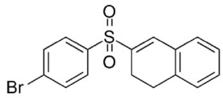
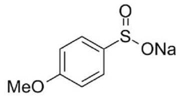
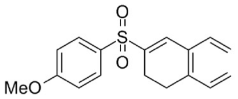
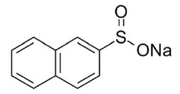
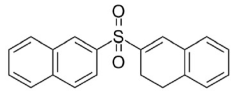
aprotic solvents, such as DMF, DMSO, NMP and CH_3CN led to low or even no yields. The yield in DMF was 26% of **3a** (Table 1, entry 1), which did not increase with more catalyst. The control experiment in DMF without catalyst led to 6% product formation by a background reaction. Without light or without catalyst and light no product is formed. The yields increased in protic solvents. A mixture of DMF/H_2O (3:1) led to 58% yield (Table 1, entry 5), but ethanol was selected as the optimal solvent due to its low toxicity and a product yield of 59% (Table 1, entry 6). Both metal complexes [Ru(bpy)$_3$]Cl$_2$ (**A**) and [Ir(p-py)$_2$(dtb-bpy)]PF$_6$ (**B**) (5 and 2 mol%, respectively) gave under these conditions identical amounts of **3a** (59%, Table 1, entries 6 and 7), while the commercially available organic dye eosin Y (**C**) (10 mol%) gave 43% after 6 h irradiation time (Table 1, entry 8). However, extending the irradiation time to 18 h increased the yield of **3a** to 73% (Table 1, entry 9). The control experiment without catalyst and green light (535 nm) irradiation showed no product formation at all after 18 h (Table 1, entry 10). Reaction under exclusion of oxygen gave a yield of 55% after 18 h (Table 1, entry 11), but the yield in air was significantly higher (73%, Table 1, entry 9), because atmospheric oxygen may serve as an additional terminal oxidant.

Using these conditions, the scope of the reaction of 1,2-dihydronaphthalene (**2b**) with different sodium aryl sulfinates **1**, eosin Y (**C**) and ethanol was explored. As depicted in Table 2 all expected products **3b–g** were obtained in moderate to excellent yields. The best result of 99% for **3b** was obtained for the

Table 2. Scope of aryl sulfinates.[a]



1 + **2b** → **3b–g**

Entry	1	Product	Yield [%][b]
1	 **1a**	 **3b** 	99
2	 **1b**	 **3c**	79
3	 **1c**	 **3d**	79
4	 **1d**	 **3e**	74
5	 **1e**	 **3f**	51
6	 **1f**	 **3g**	88

[a] *General reaction conditions 1:* **1a–f** (0.50 mmol, 3 equiv.), **2b** (0.17 mmol, 1 equiv.), Ph-NO$_2$ (0.17 mmol, 1 equiv.) and **C** (10 mol%) in EtOH was irradiated with green light for 18 h.

[b] Isolated yield after purification on SiO_2.

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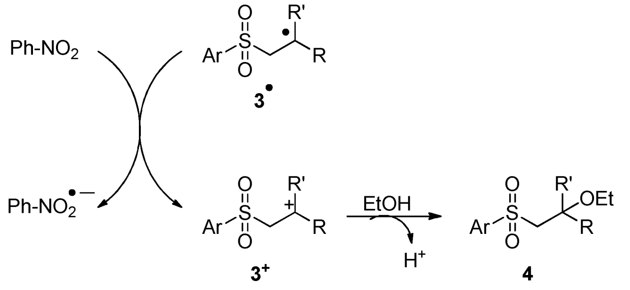


Scheme 2. Formation of the by-product **4** by nucleophilic attack of the solvent ethanol.

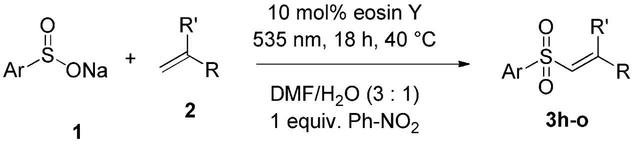
unsubstituted sodium benzenesulfinate (**1a**) (Table 2, Entry 1). The structure of product **3b** was confirmed by X-ray single crystal analysis. An electron donating methyl or an electron-withdrawing bromide substituent in the *para* position to the sulfinate and even the bulky naphthalene group were tolerated with yields of 74–88% (Table 2, entries 2, 3, 4 and 6). The bromide substituent allows further synthetic modifications of the products. A lower yield of 51% (Table 2, entry 5) was obtained from reaction with a methoxy-substituted aryl sulfinate.

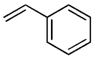
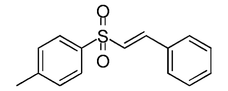
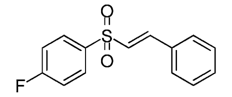
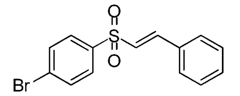
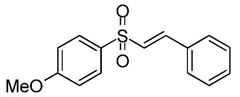
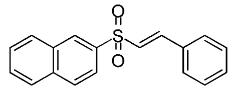
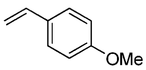
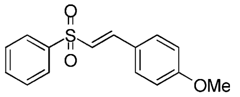
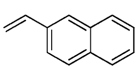
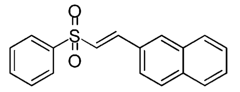
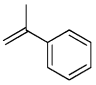
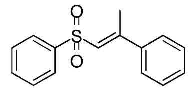
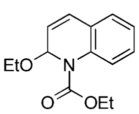
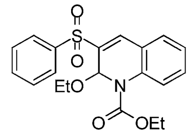
After establishing the scope of sodium aryl sulfinates, the olefin **2** was varied. As vinyl derivatives yield by-product **4** (see the Supporting Information) resulting from the reaction of the carbenium ion **3**$^+$ intermediate and the solvent ethanol, the solvent mixture DMF/H$_2$O was used for the reactions of vinyl derivatives with **1** (Scheme 2).

Styrene (**2a**) was reacted with aryl sulfinates **1b–f**. Electron-donating and electron-withdrawing substituents in the *para* position, and the bulky naphthalene moiety were tolerated and afforded moderate to good product yields of 54–76% (Table 3, entries 1, 2, 3 and 5). The reaction with **1e** gave again a lower yield (46%, Table 3, entry 4), while 1-ethenyl-4-methoxybenzene (**2c**) led to product **3m** (Table 3, entry 6) in 90%. The methoxy group increases the electron density at the double bond, which may facilitate the attack of the aryl sulfinate radical. α-Methylstyrene (**2e**) and *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ, **2f**)[20] gave only 19% and 11% of the coupling products **3o** and **3p** (Table 3, entries 8 and 9), respectively. Analysis of the reaction mixture of **2e** by GC/MS revealed incomplete conversion of the starting material and the formation of isopropylbenzene.

The proposed mechanism of the photocatalytic vinyl sulfone synthesis using eosin Y is shown in Scheme 3. The cycle is initiated by excitation of the photocatalyst **PC**, which is reductively quenched by the aryl sulfinate **1** giving an oxygen centered radical **1′**$^{\bullet}$ resonating with the corresponding sulfur-centered aryl sulfinate radical **1**$^{\bullet}$.[21] Radical **1**$^{\bullet}$ attacks the double bond of **2** to form intermediate **3**$^{\bullet}$. Nitrobenzene reoxidizes the photocatalyst and its radical anion abstracts an H atom of **3**$^{\bullet}$ to give the vinyl sulfone **3**.

Table 3. Scope of alkenes.[b]



Entry	1	2	Product	Yield [%][b]
1	**1b**	 **2a**	 **3h**	74
2	**1c**		 **3i**	54
3	**1d**		 **3j**	66
4	**1e**		 **3k**	46
5	**1f**		 **3l**	76
6	**1a**	 **2c**	 **3m**	90
7		 **2d**	 **3n**	44
8		 **2e**	 **3o**	19 (57)[c]
9[d]		 **2f**	 **3p**	11

[a] *General reaction conditions 2:* **1a–f** (0.50 mmol, 3 equiv.), **2a**, **c–e** (0.17 mmol, 1 equiv.), Ph-NO$_2$ (0.17 mmol, 1 equiv.) and **C** (10 mol%) in DMF/H$_2$O (3:1) was irradiated with green light for 18 h.

[b] Isolated yield after purification on SiO$_2$.

[c] Yield based on starting material conversion.

[d] Ethanol as solvent instead of DMF/H$_2$O (3:1).

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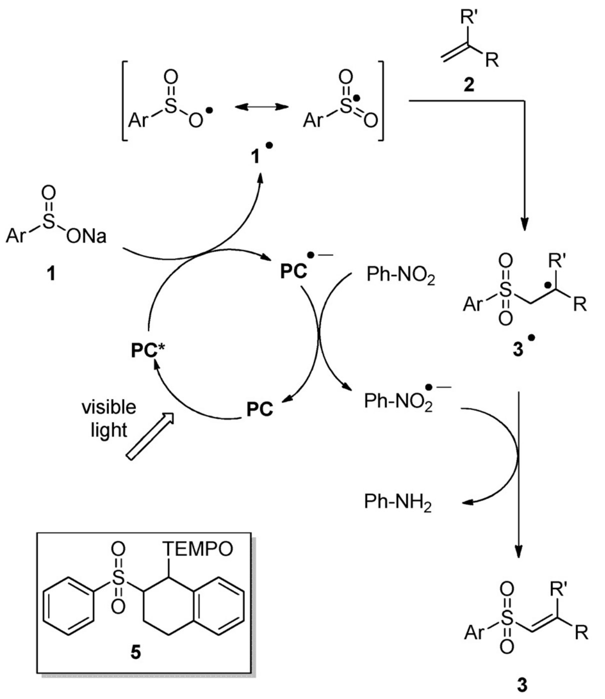

Scheme 3. Proposed mechanism for the visible light-mediated metal-free synthesis of vinyl sulfones **3** and TEMPO-trapped reaction intermediate **5**.

TEMPO addition to the reaction mixture of **1a**, **2b**, eosin Y and nitrobenzene stops the vinyl sulfone synthesis and the TEMPO addition product **5** (Scheme 3) was detected, supporting that the photoreaction proceeds *via* a radical pathway (see the Supporting Information). The oxidation potential of sodium benzenesulfinate (**1a**) was determined by cyclic voltammetry as −0.37 V *vs.* SCE (see the Supporting Information).[22] Therefore, **1a** is easily oxidized and able to donate an electron to the excited photocatalyst. In the case of eosin Y the oxidative quenching cycle is thermodynamically possible and a mechanistic alternative in which nitrobenzene acts as an oxidant for the photocatalyst.[23] A more detailed mechanistic discussion is provided in the Supporting Information.

In conclusion, vinyl sulfones were obtained from aryl sulfinates and alkenes by metal-free photoredox catalysis with green light. The reaction uses the organic dye eosin Y as photoredox catalyst and allows the conversion of a variety of aryl sulfinates and alkenes with functional group tolerance. A plausible reaction mechanism was proposed and is supported by spectroscopic and electrochemical investigations, and TEMPO-trapped intermediates.

Experimental Section

For full experimental data see the Supporting Information.

General Procedure for the Preparation of Sodium Aryl Sulfinates

Compounds were prepared according to literature procedures.[24] Sodium sulfite (2.50 g, 0.02 mol, 2 equiv.), sodium bicarbonate (1.68 g, 0.02 mol, 2 equiv.) and the corresponding aryl sulfonyl chloride (0.01 mmol, 1 equiv.) were dissolved in distilled water (9.6 mL). The reaction mixture was stirred for 4 h at 80 °C. After cooling to room temperature the water was removed by lyophilization overnight. The white residue was extracted with ethanol (25 mL) to obtain the desired aryl sulfinate as white crystalline powder.

Sodium 4-fluorobenzenesulfinate (1c): ^{1}H NMR (400 MHz, D_2O): $\delta_H = 7.26$ (t, $J = 8.9$ Hz, 2H), 7.63–7.70 (m, 2H); ^{13}C NMR (101 MHz, D_2O): $\delta_C = 115.7$ (d, +), 125.7 (d, $^3J_{C,F} = 9.0$ Hz, +), 149.5 (d, $^4J_{C,F} = 2.9$ Hz, C_q), 163.6 (d, $^1J_{C,F} = 264.4$ Hz, C_q); ^{19}F NMR (376 MHz, D_2O): $\delta_H = -111.2$ (s); MS (ESI): $m/z = 158.9814$ $[M-Na]^-$, calcd. for $C_6H_4FO_2S$: 158.9921.

General Reaction Conditions for the Photocatalytic Vinyl Sulfone Synthesis

A 5-mL crimp-cap vial was charged with the aryl sulfinate **1** (0.50 mmol, 3 equiv.), the respective olefin **2** (0.17 mmol, 1 equiv.), nitrobenzene (17.1 μL, 0.17 mmol, 1 equiv.), photocatalyst **PC** (5 or 10 mol%) and a stirring bar. Solvent (2 mL) was added *via* syringe and the vessel was capped to prevent evaporation. The reaction mixture was stirred and irradiated using blue LEDs (455 nm) or green LEDs (535 nm) for 6 or 18 h at 40 °C. The progress could be monitored by GC analysis and GC/MS analysis using naphthalene as internal standard.

The reaction mixture was diluted with water (5 mL) and extracted with EtOAc (3×5 mL). The combined organic layers were dried over $MgSO_4$, and the solvents were removed under reduced pressure. Evaporation of volatiles led to the crude product. Purification of the crude product was performed by automated flash column chromategraphy (PE/EtOAc, 25% EtOAc) yielding the corresponding vinyl sulfone **3** as yellowish oil.

3-(Benzenesulfonyl)-1,2-dihydronaphthalene (3b): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.50$ (dt, $J = 8.3$, 1.3 Hz, 2H), 2.86 (t, $J = 8.3$ Hz, 2H), 7.10–7.16 (m, 1H), 7.20–7.31 (m, 3H), 7.51–7.57 (m, 2H), 7.58–7.64 (m, 2H), 7.91–7.96 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta_C = 21.8$ (−), 27.6 (−), 127.2 (+), 127.9 (+), 128.0 (+), 129.1 (+), 129.3 (+), 130.6 (+), 131.0 (C_q), 133.4 (+), 135.3 (+), 135.6 (C_q), 138.3 (C_q), 139.7 (C_q); HR-MS (ESI): $m/z = 271.0790$ $[M+H]^+$, calcd. for $C_{16}H_{15}O_2S$: 271.0787.

TEMPO Trapping of Radical Reaction Intermediates

To a 5-mL crimp-cap vial were added **1a** (82.1 mg, 0.50 mmol, 3 equiv.), **2b** (21.8 μL, 0.17 mmol, 1 equiv.), nitrobenzene (17.1 μL, 0.17 mmol, 1 equiv.), **C** (108 mg, 100 mol%), TEMPO (32.6 mg, 0.21 mmol, 1.25 equiv.) and a stirring bar. EtOH (2 mL) was added *via* syringe and the vessel was capped to prevent evaporation. The reaction mixture was stirred and irradiated using green LEDs (535 nm) for 18 h at 40 °C. After the irradiation the reaction mixture was submitted to mass spectrometry (LC-MS) without any further work-up. *TEMPO adduct* **5**. MS (ESI): $m/z = 428.2262$ $[M+H]^+$, calcd. for $C_{25}H_{34}NO_3S$:428.2254.

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References

[1] a) K. Oh, *Org. Lett.* **2007**, *9*, 2973–2975; b) F. Hof, A. Schütz, C. Fäh, S. Meyer, D. Bur, J. Liu, D. E. Goldberg, F. Diederich, *Angew. Chem.* **2006**, *118*, 2193–2196; *Angew. Chem. Int. Ed.* **2006**, *45*, 2138–2141; c) G. Pandey, K. N. Tiwari, V. G. Puranik, *Org. Lett.* **2008**, *10*, 3611–3614; d) M. N. Noshi, A. El-awa, E. Torres, P. L. Fuchs, *J. Am. Chem. Soc.* **2007**, *129*, 11242–11247; e) O. Arjona, R. Menchaca, J. Plumet, *Org. Lett.* **2001**, *3*, 107–109; f) D. J. Wardrop, J. Fritz, *Org. Lett.* **2006**, *8*, 3659–3662; g) D. Enders, S. F. Müller, G. Raabe, J. Runsink, *Eur. J. Org. Chem.* **2000**, *2000*, 879–892; h) P. Mauleón, I. Alonso, M. R. Rivero, J. C. Carretero, *J. Org. Chem.* **2007**, *72*, 9924–9935; i) S. Sulzer-Mossé, A. Alexakis, J. Mareda, G. Bollot, G. Bernardinelli, Y. Filinchuk, *Chem. Eur. J.* **2009**, *15*, 3204–3220; j) H. Kumamoto, K. Deguchi, T. Wagata, Y. Furuya, Y. Odanaka, Y. Kitade, H. Tanaka, *Tetrahedron* **2009**, *65*, 8007–8013; k) T. Nishimura, Y. Takiguchi, T. Hayashi, *J. Am. Chem. Soc.* **2012**, *134*, 9086–9089; l) J.-N. Desrosiers, W. S. Bechara, A. B. Charette, *Org. Lett.* **2008**, *10*, 2315–2318; m) J.-N. Desrosiers, A. B. Charette, *Angew. Chem.* **2007**, *119*, 6059–6061; *Angew. Chem. Int. Ed.* **2007**, *46*, 5955–5957; n) D. Ravelli, S. Montanaro, M. Zema, M. Fagnoni, A. Albini, *Adv. Synth. Catal.* **2011**, *353*, 3295–3300.

[2] A. Noble, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2014**, *136*, 11602–11605.

[3] a) D. C. Meadows, T. Sanchez, N. Neamati, T. W. North, J. Gervay-Hague, *Bioorg. Med. Chem.* **2007**, *15*, 1127–1137; b) I. D. Kerr, J. H. Lee, C. J. Farady, R. Marion, M. Rickert, M. Sajid, K. C. Pandey, C. R. Caffrey, J. Legac, E. Hansell, J. H. McKerrow, C. S. Craik, P. J. Rosenthal, L. S. Brinen, *J. Biol. Chem.* **2009**, *284*, 25697–25703; c) R. López, M. Zalacain, C. Palomo, *Chem. Eur. J.* **2011**, *17*, 2450–2457; d) R. Cancio, R. Silvestri, R. Ragno, M. Artico, G. De Martino, G. La Regina, E. Crespan, S. Zanoli, U. Hubscher, S. Spadari, G. Maga, *Antimicrob. Agents Chemother.* **2005**, *49*, 4546–4554.

[4] a) R. Ettari, E. Nizi, M. E. Di Francesco, M.-A. Dude, G. Pradel, R. Vičík, T. Schirmeister, N. Micale, S. Grasso, M. Zappalà, *J. Med. Chem.* **2008**, *51*, 988–996; b) J. J. Reddick, J. Cheng, W. R. Roush, *Org. Lett.* **2003**, *5*, 1967–1970; c) J. T. Palmer, D. Rasnick, J. L. Klaus, D. Bromme, *J. Med. Chem.* **1995**, *38*, 3193–3196.

[5] S. Liu, B. Zhou, H. Yang, Y. He, Z.-X. Jiang, S. Kumar, L. Wu, Z.-Y. Zhang, *J. Am. Chem. Soc.* **2008**, *130*, 8251–8260.

[6] B. A. Frankel, M. Bentley, R. G. Kruger, D. G. McCafferty, *J. Am. Chem. Soc.* **2004**, *126*, 3404–3405.

[7] a) S. Chodroff, W. F. Whitmore, *J. Am. Chem. Soc.* **1950**, *72*, 1073–1076; b) D. A. R. Happer, B. E. Steenson, *Synthesis* **1980**, 806–807.

[8] I. C. Popoff, J. L. Dever, G. R. Leader, *J. Org. Chem.* **1969**, *34*, 1128–1130.

[9] D. C. Reeves, S. Rodriguez, H. Lee, N. Haddad, D. Krishnamurthy, C. H. Senanayake, *Tetrahedron Lett.* **2009**, *50*, 2870–2873.

[10] N. Taniguchi, *Tetrahedron* **2014**, *70*, 1984–1990.

[11] W. Wei, J. Li, D. Yang, J. Wen, Y. Jiao, J. You, H. Wang, *Org. Biomol. Chem.* **2014**, *12*, 1861.

[12] N. Taniguchi, *Synlett* **2011**, *2011*, 1308–1312.

[13] S. Tang, Y. Wu, W. Liao, R. Bai, C. Liu, A. Lei, *Chem. Commun.* **2014**, *50*, 4496–4499.

[14] H. Jiang, X. Chen, Y. Zhang, S. Yu, *Adv. Synth. Catal.* **2013**, *355*, 809–813.

[15] a) R. Chawla, A. K. Singh, L. D. S. Yadav, *Eur. J. Org. Chem.* **2014**, *2014*, 2032–2036; b) B. Das, M. Lingaiah, K. Damodar, N. Bhunia, *Synthesis* **2011**, 2941–2944; c) Y. Xu, X. Tang, W. Hu, W. Wu, H. Jiang, *Green Chem.* **2014**, *16*, 3720–3723; d) V. Nair, A. Augustine, T. D. Suja, *Synthesis* **2002**, 2259–2265.

[16] J. Zuo, Z.-J. Wu, J.-Q. Zhao, M.-Q. Zhou, X.-Y. Xu, X.-M. Zhang, W.-C. Yuan, *J. Org. Chem.* **2015**, *80*, 634–640.

[17] a) Y. Fujiwara, J. A. Dixon, F. O'Hara, E. D. Funder, D. D. Dixon, R. A. Rodriguez, R. D. Baxter, B. Herlé, N. Sach, M. R. Collins, Y. Ishihara, P. S. Baran, *Nature* **2012**, *492*, 95–99; b) Y. Fujiwara, J. A. Dixon, R. A. Rodriguez, R. D. Baxter, D. D. Dixon, M. R. Collins, D. G. Blackmond, P. S. Baran, *J. Am. Chem. Soc.* **2012**, *134*, 1494–1497; c) F. O'Hara, D. G. Blackmond, P. S. Baran, *J. Am. Chem. Soc.* **2013**, *135*, 12122–12134.

[18] C.-J. Wallentin, J. D. Nguyen, P. Finkbeiner, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2012**, *134*, 8875–8884.

[19] D. J. Wilger, N. J. Gesmundo, D. A. Nicewicz, *Chem. Sci.* **2013**, *4*, 3160.

[20] a) A. D. Crocker, D. L. Cameron, *Clin. Exp. Pharmacol. Physiol.* **1989**, *16*, 545–548; b) T. Der-Ghazarian, A. Gutierrez, F. A. Varela, M. S. Herbert, L. R. Amodeo, S. Charntikov, C. A. Crawford, S. A. McDougall, *Neuroscience* **2012**, *226*, 427–440.

[21] Q. Lu, J. Zhang, F. Wei, Y. Qi, H. Wang, Z. Liu, A. Lei, *Angew. Chem.* **2013**, *125*, 7297–7300; *Angew. Chem. Int. Ed.* **2013**, *52*, 7156–7159.

[22] V. V. Pavlishchuk, A. W. Addison, *Inorg. Chim. Acta* **2000**, *298*, 97–102.

[23] D. P. Hari, B. König, *Chem. Commun.* **2014**, *50*, 6688.

[24] a) J. Liu, X. Zhou, H. Rao, F. Xiao, C.-J. Li, G.-J. Deng, *Chem. Eur. J.* **2011**, *17*, 7996–7999; b) L. K. Liu, Y. Chi, K.-Y. Jen, *J. Org. Chem.* **1980**, *45*, 406–410.

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