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Debenzylative Sulfonylation of Tertiary Benzylamines Promoted by Visible Light

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An efficient, general, inexpensive, and environmentally friendly photosynthesis of sulfonamides via visible light promoted debenzylative sulfonylation of tertiary benzylamines is described. Compared to the traditional S–N coupling reactions, which are promoted by oxidative C–N bond cleavage of symmetrical tertiary alkylamines, this strategy provides a selective C–N bond cleavage protocol and avoids the use of transition-metal, explosive oxidants, and ligands.

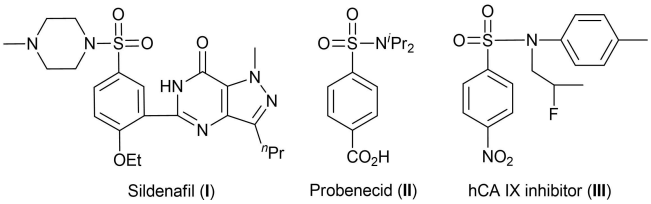


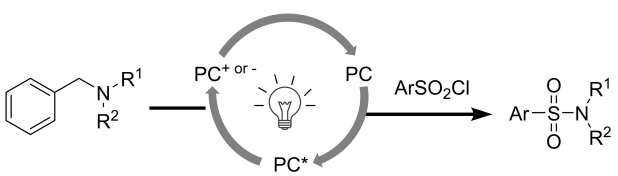
Figure 1. Selected drugs and bioactive compounds encompassing a tertiary sulfonamide moiety.

The tertiary sulfonamide structural motif represents a fundamental class of compounds that play a pivotal role in both synthetic[1] and medicinal chemistry.[2] For examples (Figure 1), Sildenafil (**I**) is a potent and selective inhibitor of type 5 cGMP phosphodiesterase.[3] Probenecid (**II**) is an uricosuric agent used for the treatment of hyperuricemia associated with gout and gouty arthritis.[4] Compound (**III**) was observed strong selectivity toward tumor-associated inhibitors of human carbonic anhydrases hCA IX.[5] The classic tertiary sulfonamide synthesis method is the coupling reaction between a secondary amine and a sulfonyl chloride.[6] Other methods including the metal-catalyzed N-alkylation/arylation of secondary sulfonamides,[7] oxidative coupling reactions between sulfonyl hydrazides and secondary amines,[8] oxidative coupling reactions between sulfinate salts and amines,[9] and the electrochemical oxidative coupling of amines with thiols,[10] etc. are continually developed. Although these procedures are effective in a way, limitations such as the employments of expensive and toxic metal catalysts, explosive oxidants, and air-sensitive secondary amines are still involved in these procedures.

Tertiary alkylamines are readily available amine species and are commonly more stable than their primary and secondary siblings. However, these compounds, due to the absence of active N–H groups as well as the tough C–N bonds,[11] are rarely employed as the feedstock in organic syntheses. Recently, with the quick developments on C–H[12] and C–N[13] bonds activation of tertiary amines, the synthetic application of tertiary alkylamines, commonly with C–N bond cleavage, have attracted extensive attention. However, previous investigations mainly focused on transition-metal catalytic processes which are largely limited to symmetric tertiary alkylamines.[14] Thus, a selective transitional metal-free catalysis for C–N bond dissociation of tertiary aliphatic amines is still in highly desirable.

In recent years, photochemical rebuild of chemical bond has achieved impetus in organic synthesis. In this scenario, we recently demonstrated that the adjacent functional groups presented at aliphatic tertiary amines have significant effects on C–N bond activation and future dissociation.[15] In view that benzylamine is frequently used as a nitrogen source in many natural products syntheses where the benzyl group, being an amine protecting group,[16] could be selectively removed via a variety of methods including palladium-catalyzed hydrogenolysis,[17] lithium base,[18] bromo radical,[19] or metals in protic solvents,[20] together with our recent achievements on radical C–N bond cleavage of tertiary aliphatic amines,[15] we thus envision that the benzylic C–N bonds in tertiary benzylamines could be cleaved via a visible light induced, oxidative pathway.

Taking advantage of our experiences in tertiary alkylamine sulfonylation, sulfonyl chlorides were again selected as the electrophile to evaluate the efficiency of our photopromoted debenzylation protocol (Scheme 1). At the outset of the research, the reaction of tosyl chloride (**1a**) and N,N-dimethylbenzylamine (**2a**) was selected as a model to explore the optimal reaction conditions, including the bases, photocatalysts,



Scheme 1. Visible-light-mediated debenzylative sulfonylation of tertiary benzylamines.

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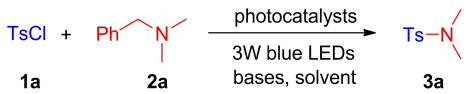
and solvents under air and irradiation with visible light using a 3 W blue LED bulb. At first, $Ru(bpy)_3Cl_2$, a powerful metal photosensitizer that succeeds in many photoredox reactions, was checked and failed to promote such as a coupling reaction (Table 1, entry 1). To our delight, when the reaction was proceeded in the presence of 2 mol% of Eosin Y in MeCN under a 3 W blue LED irradiation, sulfonamide **3a** was indeed produced in 33% yield. Further screening of photosensitizers suggested that methyl violet was the best choice, affording **3a** in 85% isolated yield (entries 2–5). Obviously, the photosensitizer played a crucial role to initiate this debenzylative coupling reaction as shown in entry 6, without the presence of a photosensitizer, no reaction occurred (entry 6). Then a variety of bases, including inorganic bases, i.e. anhydrous Na_2CO_3, K_2CO_3, Cs_2CO_3, and organic bases such as pyridine, triethylamine, N-methylmorpholine (NMM), and N-methylpiperidine (NMP) were validated, and the results revealed that none of these bases was superior to CaH_2 (entries 7–13). A screen of solvents showed that the debenzylative cross-coupling of **1a** and **2a** could be performed in CH_2Cl_2 (82%), toluene (66%), but could not be carried out in THF (n.r.) and 1,4-dioxane (n.r.). Thus acetonitrile was chosen to be the optimal reaction media.

Table 1. Screening of the Reaction Conditions.[a,b]

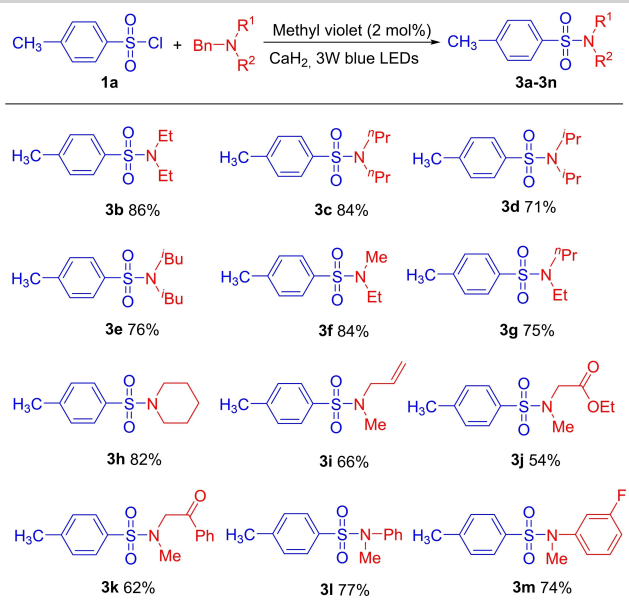


1a **2a** **3a**

Entry	Photocatalyst	Base	Solvent	**3a** Yield [%]
1	$Ru(bpy)_3Cl_2$	CaH_2	MeCN	trace
2	Eosin Y	CaH_2	MeCN	33
3	Alizarine yellow R	CaH_2	MeCN	54
4	Solvent red 49	CaH_2	MeCN	21
5	Methyl violet	CaH_2	MeCN	85
6	–	CaH_2	MeCN	N.r.
7	Methyl violet	Na_2CO_3	MeCN	35
8	Methyl violet	K_2CO_3	MeCN	42
9	Methyl violet	Cs_2CO_3	MeCN	48
10	Methyl violet	pyridine	MeCN	72
11	Methyl violet	Et_3N	MeCN	60
12	Methyl violet	NMM	MeCN	78
13	Methyl violet	NMP	CH_2Cl_2	82
14	Methyl violet	CaH_2	Toluene	66
15	Methyl violet	CaH_2	THF	N.r.[c]
16	Methyl violet	CaH_2	1,4-dioxane	N.r.

[a] Reaction conditions: TsCl **1a** (0.5 mmol), N,N-dimethylbenzylamine **2a** (0.75 mmol), photocatalyst (0.01 mmol), base (1.0 mmol), for CaH_2 (100 mg), solvent (4 mL), r.t., 24 h; [b] Isolated yields based on N,N-dimethylbenzylamine **2a**. [c] N.r. = No reaction.

Table 2. Scope of Tertiary Benzylamines.[a,b]



[a] A mixture of **1a** (0.5 mmol), benzylamine (0.75 mmol), methyl violet (0.01 mmol) and CaH_2 (100 mg) in MeCN (4 mL) under air irradiation using 3 W blue LEDs at room temperature for 24 h. [b] Isolated yields.

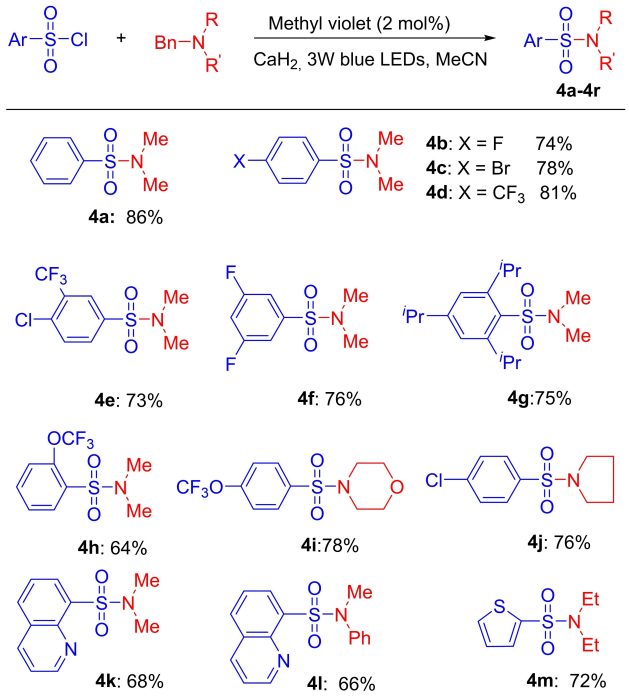
Having the optimal reaction conditions in hand (Table 1, entry 5), the scope of tertiary benzylamines for this transformation was examined with TsCl (**1a**) (Table 2). First, N,N-diethylbenzylamine, and N,N-di-*n*-propylbenzylamine proceeded this reaction quite well and yielded the desired sulfonamide products **3b** (86%) and **3c** (84%) in high yield. The sterically hindered branched tertiary benzylamines such as N,N-diisopropylbenzylamine and N,N-diisobutylbenzylamine could participate in this transformation with slightly lower yields of products obtained, indicating the broad feasibility of this approach. Other dialkylbenzylamines screened, i.e. N-methyl-N-ethylbenzylamine, N-ethyl-N-propylbenzylamine, and N-benzylpiperidine participated in this transformation very well and yielded the corresponding sulfonamides in high yields (**3f**–**3h**). This process could tolerate a variety of functional groups such as allyl, ester, and ketone (**3i**–**3k**), which provided the possibility for further functionalization. Finally, N-benzyl-N-methylanilines were also investigated under the standard conditions, affording the desired products in 74–77% yields (**3l** and **3m**).

Next, we sought to examine the scope with respect to various sulfonyl chlorides (Table 3). Aromatic sulfonyl chlorides bearing both electron-withdrawing and electron-donating substituents readily underwent the desired debenzylative coupling reactions, providing sulfonamides in good to high yields (**4a**–**4j**). Functional groups, including halogens (F, Cl, Br), trifluoromethyl, trifluoromethoxyl were well tolerated and transferred into desired products (**4b**–**i**, 64–81% yields). Fortunately, the highly steric hindered aromatic sulfonyl chloride i.e. 2,4,6-trimethylbenzenesulfonyl chloride could also participate this transformation to yield the desired sulfonamides (**4g**) in moderate yield. Heterocyclic sulfonyl chlorides represented with 8-quinolinesulfonyl chloride and 2-thiophenesulfonyl chloride readily underwent this debenzylative coupling reactions to form desired sulfonamide products in moderate to good yields (Table 3, **4k**–**4m**).

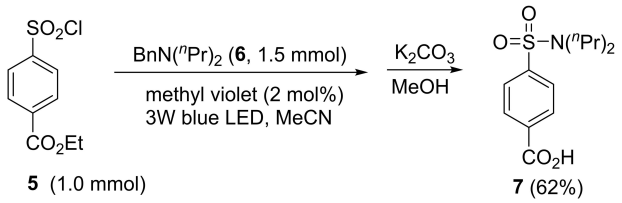
The efficiency of the present reaction system was further highlighted by the synthesis of probenecid (**7**), a well-established drug for the treatment of gout (Scheme 2). Thus ethyl 4-(chlorosulfonyl)benzoate **5** completed conversion of N,N-di-*n*-propylbenzylamine (1.0 mmol) within 24 h to afford, after in situ alcoholysis, compound **7** in 62% isolated yield.

To gain insights into the origination of radical species involved in this debenzylative sulfonylation reaction, a series of

Table 3. Scope of Various Sulfonyl Chlorides.[a,b]

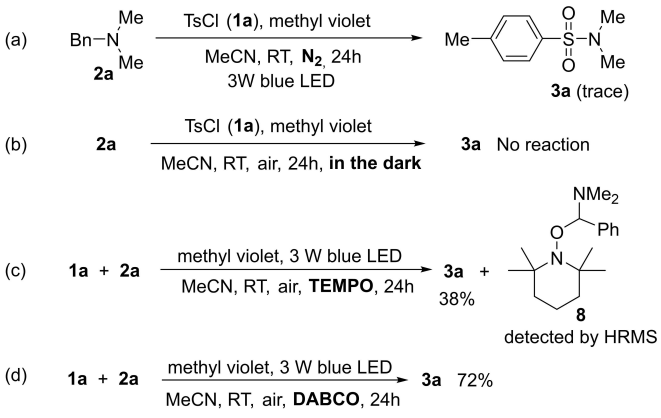


[a] A mixture of sulfonyl chloride (0.5 mmol), benzylamine (0.75 mmol), and 2.0 mmol of CaH_2 in MeCN (4 mL) under air irradiation using 3 W blue LEDs at room temperature for 24 h. [b] Isolated yields.



Scheme 2. Synthesis of probenecid.

control experiments were then carried out (Scheme 3). At first, when the reaction of **1a** with **2a** was carried out under N_2, the desired product **3a** was not detected (Scheme 3, (a)), indicating that the reaction might involve an aerobic oxidative cross-coupling. When the reaction was conducted in the dark, no reaction occurred (Scheme 3, (b)), suggesting that visible light is an indispensable reaction factor for this transformation. When the radical scavenger TEMPO (2,2,6,6-tetramethylpiperidine N-oxyl) (2 equiv.) was employed under standard conditions, the reaction was largely suppressed and adduct **8** was detected by HRMS, indicating the existence of an N,N-dimethylbenzylamine radical in the reaction system (Scheme 3c). In order to check if a reactive singlet oxygen species were formed in our photo-promoted oxidative cross-coupling reaction system, a singlet oxygen quencher,[21] 1,4-diazabicyclo[2.2.2]octane (DABCO), was added to the above-mentioned reaction system and that proceeded smoothly to produce **3a** in 72% isolated yield, indicating that $^1O_2$ is not generated from O_2 under our reaction conditions. (Scheme 3d). The "light/dark" experiments showed that the desired product **3a** formed only under continuous irradiation, thus excluding the possibility of a radical chain propagation in our reaction system (Figure 2). To further probe the nature of the radical species formed during the reaction, electron paramagnetic resonance (EPR) studies were next performed (Figure 3). 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was introduced as a spin-trap, as it is known to react with short-living radicals to furnish more stable and EPR detectable nitroxide radicals.[22] After irradiation for 30 s under blue LEDs at room temperature, a quadruple EPR signal (g = 2.01), which might be ascribed to peroxide radical, was observed in the mixture of photocatalyst with TsCl **1a**, N,N-dimethylbenzylamine **2a**, indicating that peroxide radical was generated therein. To verify if a charge-transfer complex, which has been frequently observed in our previously reported reaction systems,[15] relates to sulfonyl chlorides and aliphatic tertiary amine, a UV-Vis experiment was then carried out. The UV-Vis spectroscopic measurements of the combination of **1a** and **2a** in MeCN showed that weak absorption bands ranging from 300 and 400 nm appeared (Figure 4), demonstrating the formation



Scheme 3. Control experiments.

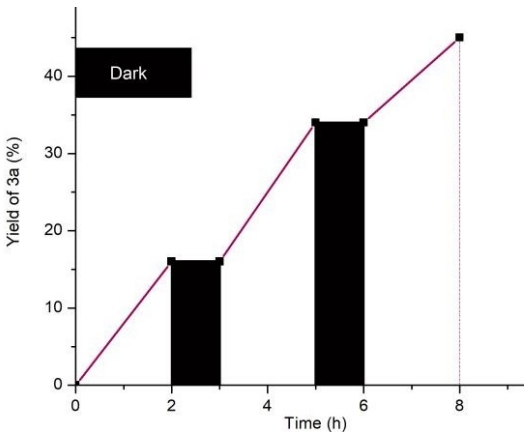


Figure 2. "Light/dark" experiments over time.

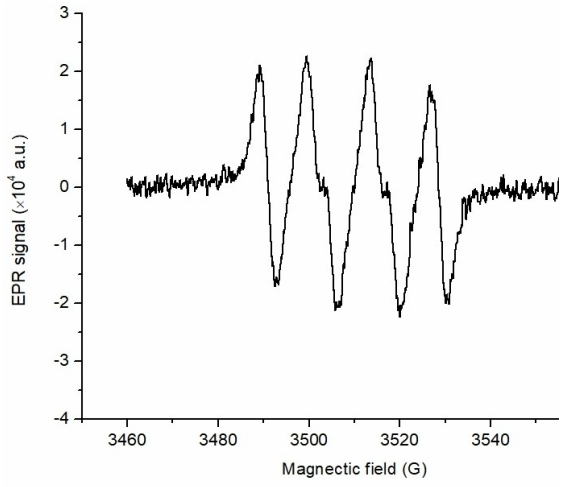


Figure 3. EPR spectra generated as follows: TsCl **1a** (0.1 mmol), methyl violet (2 mol%) and N,N-dimethylbenzylamine **2a** (0.1 mmol) in MeCN were stirred at room temperature under 3 W blue LED irradiation. After 30 s, the mixture was directly measured by EPR.

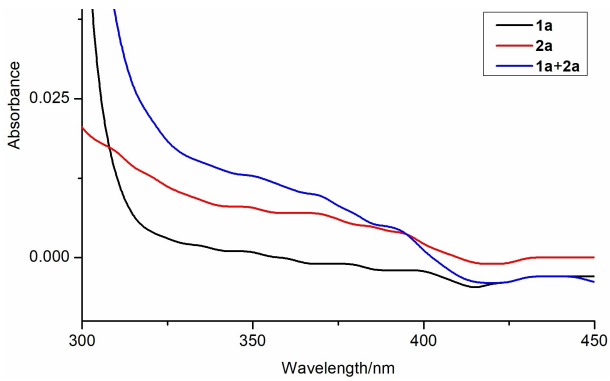
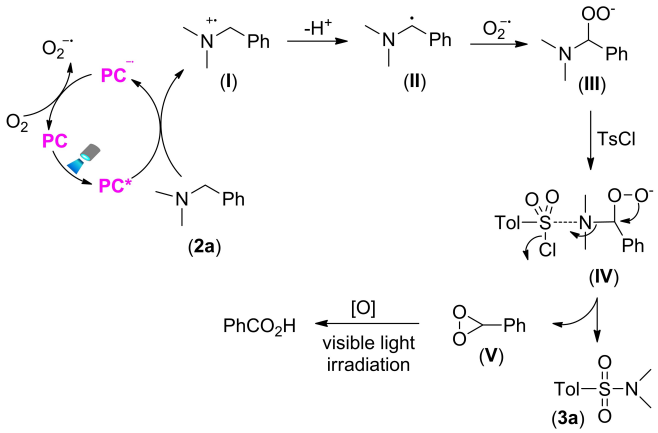


Figure 4. UV-Vis absorption spectra of **1a** (TsCl, 0.2 mM), **2a** (N,N-dimethylbenzylamine 0.2 mM), and their mixture (**1a** + **2a**, 0.2 mM) in MeCN.

of the charge-transfer complex by the reaction between amine and sulfonyl chloride which may play a role in the oxidative C–N bond cleavage of aliphatic tertiary benzylamines.

On the basis of the above-mentioned results and related documents on oxidative radical C–N bond cleavages,[23] a plausible radical mechanism of this photopromoted oxidative coupling protocols, which was exemplified by the reactions of **1a** and **2a** for the formations of **3a** is depicted in Scheme 4. Upon visible light irradiation, photocatalyst (PC) was excited (PC*) and was reductively quenched with N,N-dimethylbenzylamine (**2a**) to $PC^{\bullet-}$, concomitantly, a nitrogen-centered radical cation (**I**) was generated.[24] The reduced catalyst ($PC^{\bullet-}$) was then oxidized by dioxygen to its normal state and generated a reactive perhydroxyl radical anion ($HO_2^{\bullet-}$). The carbon-centered radical (**II**), generated from radical cation (**I**) via hydronium ion extrusion, cross-coupled with the perhydroxyl radical anion ($HO_2^{\bullet-}$) to produce the peroxide **III**. Subsequently, a charge-transfer complex (**IV**) between sulfonyl chloride **1a** and intermediate **III** was formed to facilitate C–N bond cleavage



Scheme 4. Proposed reaction mechanism.

of tertiary benzylamine **2a**. Sulfonamide **3a** was thus formed and an unstable 3-phenyldioxirane intermediate **V** was generated simultaneously. Intermediate **V** could be further oxidized to benzoic acid under photocatalysis.[25] The existence of benzoic acid was verified in our ^{13}C NMR analysis of the reaction mixture.

In summary, we have developed a new photochemical C–N bond cleavage protocol of tertiary benzylamines. Compared with existing literature methods to C–N bond cleavage protocols, the present approach demonstrates several attractive features, including using air as the ideal and green oxidant, photocatalysis, high efficiency, and simple operation.

Experimental Section

General synthetic procedure: To a 10 mL Schlenk-tube equipped with a stirring bar, sulfonyl chlorides (0.5 mmol), tertiary benzylamines (0.75 mmol), methyl violet (4 mg, 2 mmol%), and MeCN (4 mL) were added. After stirred and irradiated with a 3 W blue LED for 24 hours at room temperature, the reaction mixtures were quenched with aqueous $NaHCO_3$ solution and was then dissolved in ethyl acetate (10 mL), washed successively with water (2× 10 mL), and then brine (10 mL). The aqueous phase was further extracted from ethyl acetate (10 mL) and washed as previously. The organic phase was combined, dried over $MgSO_4$, and concentrated. Purification by silica gel column chromatography gave the desired products.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Debenzylation · Photocatalysis · Organic photocatalysts · Sulfonamide · Synthetic methods

[1] a) S. Mondal, S. Malakar, *Tetrahedron* **2020**, *76*, 131662–131689; b) T. C. Das, S. A. Quadri, M. Farooqui, *Chem. Biol. Interface* **2018**, *8*, 194–204; c) A. Scozzafava, T. Owa, A. Mastrolorenzo, C. T. Supuran, *Curr. Med. Chem.* **2003**, *10*, 925–953.
[2] a) J. M. Dorn, M. Alpern, C. McNulty, G. W. Volcheck, *Curr. Allergy Asthma Rep.* **2018**, *18*, 38–47; b) F. A. Khan, S. Mushtaq, S. Naz, U. Farooq, A. Zaidi, S. M. Bukhari, A. Rauf, M. S. Mubarak, *Curr. Org. Chem.* **2018**, *22*, 818–830; c) R. N. Dash, A. K. Moharana, B. B. Subudhi, *Curr. Org. Chem.* **2020**, *24*, 1018–1041.
[3] N. K. Terrett, A. S. Bell, D. Brown, P. Ellis, *Bioorg. Med. Chem. Lett.* **1996**, *6*, 1819–1824.
[4] a) M. H. Cheng, S.-J. Kim, *Biomol. Therap.* **2020**, *28*, 104–109; b) W. Silverman, S. Locovei, G. Dahl, *Am. J. Physiol. Cell Physiol.* **2008**, *295*, C761-C767.
[5] a) B. Metayer, A. Mingot, D. Vullo, C. T. Supuran, S. Thibaudeau, *Chem. Commun.* **2013**, *49*, 6015–6017.
[6] A. Gioiello, E. Rosatelli, M. Teofrasti, P. Filipponi, R. Pellicciari, *ACS Comb. Sci.* **2013**, *15*, 235–239.
[7] a) X. Liu, K. Tong, A. H. Zhang, R. X. Tan, S. Yu, *Org. Chem. Front.* **2017**, *4*, 1354–1357; b) B. G. Reed-Berendt, L. C. Morrill, *J. Org. Chem.* **2019**, *84*, 3715–3724; c) Z. Li, H. Zhang, S. Yu, *Org. Lett.* **2019**, *21*, 4754–4758; d) K. Tong, X. Liu, Y. Zhang, S. Yu, *Chem. Eur. J.* **2016**, *22*, 15669–15673.
[8] a) S. Chung, J. Kim, *Tetrahedron Lett.* **2019**, *60*, 792–795; b) S. K. R. Parumala, R. K. Peddinti, *Tetrahedron Lett.* **2016**, *57*, 1232–1235; c) S. Yotphan, L. Sumunnee, D. Beukeaw, C. Buathongjan, V. Reutrakul, *Org. Biomol. Chem.* **2016**, *14*, 590–597.
[9] a) A. S. Tsai, J. M. Curto, B. N. Rocke, A.-M. R. Dechert-Schmitt, G. K. Ingle, V. Mascitti, *Org. Lett.* **2016**, *18*, 508–511; b) P. Kin, T. Lo, Y. Chen, M. C. Willis, *ACS Catal.* **2019**, *9*, 10668–10673.
[10] G. Laudadio, E. Barmpoutsis, C. Schotten, L. Struik, S. Govaerts, D. L. Browne, T. Noël, *J. Am. Chem. Soc.* **2019**, *141*, 5664–5668.
[11] S. J. Blanksby, G. B. Ellison, *Acc. Chem. Res.* **2003**, *36*, 255–263.
[12] a) W. Chen, L. Ma, A. Paul, D. Seidel, *Nat. Chem.* **2018**, *10*, 165–169; b) R. Shang, L. Ilies, E. Nakamura, *Chem. Rev.* **2017**, *117*, 9086–9139; c) S. A. Girard, T. Knauber, C.-J. Li, *Angew. Chem. Int. Ed.* **2014**, *53*, 74–100; *Angew. Chem.* **2014**, *126*, 76–103.
[13] a) K. Ouyang, W. Hao, W.-X. Zhang, Z. Xi, *Chem. Rev.* **2015**, *115*, 12045–12090; b) T. Wang, N. Jiao, *Acc. Chem. Res.* **2014**, *47*, 1137–1145; c) J. Luo, W.-T. Wei, *Adv. Synth. Catal.* **2018**, *360*, 2076–2086; d) Z. X. Wang, B. Yang, *Org. Biomol. Chem.* **2020**, *18*, 1057–1072; e) J. Bariwal, E. V. der Eycken, *Chem. Soc. Rev.* **2013**, *42*, 9283–9303.
[14] O. I. Afanasyev, E. A. Kuchuk, K. M. Muratov, G. L. Denisov, D. Chusov, *Eur. J. Org. Chem.* **2021**, *2021*, 543–586.
[15] a) Y. Fu, C.-Z. Shi, Q.-S. Xu, Z. Du, C. Huo, *Green Chem.* **2020**, *22*, 2264–2269; b) Y. Fu, Q.-S. Xu, C.-Z. Shi, Z. Du, C. Xiao, *Adv. Synth. Catal.* **2018**, *360*, 3502–3506; c) Y. Fu, Q.-S. Xu, Q.-Z.u Li, M.-P. Li, C.-Z. Shi, Z. Du, *ChemistryOpen* **2019**, *8*, 127–131.
[16] a) A. Ricci, *Modern Amination Methods*, Wiley-VCH, New York, **2000**; b) P. G. M. Wuts, T. W. Greene, *Greene's Protective Groups in Organic Synthesis*; Wiley-Interscience: Hoboken, **2007**, 4th ed.
[17] a) A. David, M. A. Vannice, *J. Catal.* **2006**, *237*, 349–358; b) M. Seki, *Synthesis* **2014**, *46*, 3249–3255; c) V. Pandarus, F. Béland, R. Ciriminna, M. Pagliaro, *ChemCatChem* **2011**, *3*, 1146–1150.
[18] H. Suzuki, A. Tsukuda, M. Kondo, M. Aizawa, Y. Senoo, M. Nakajima, T. Watanabe, Y. Yokoyama, Y. Murakami, *Tetrahedron Lett.* **1995**, *36*, 1671–1672.
[19] K. Moriyama, Y. Nakamura, H. Togo, *Org. Lett.* **2014**, *16*, 3812–3815.
[20] a) S. N. N. Babu, G. R. Srinivasa, D. C. Santhosh, D. C. Gowda, *J. Chem. Res.* **2004**, 66–67; b) C. Behloul, M. Benlahrech, F. Foubelo, C. Nájera, M. Yus, *Synthesis* **2018**, *50*, 3430–3435.
[21] a) T. Keshari, V. K. Yadav, V. P. Srivastava, L. D. S. Yadav, *Green Chem.* **2014**, *16*, 3986–3992; b) C. Ouannes, T. Wilson, *J. Am. Chem. Soc.* **1968**, *90*, 6527–6528; c) J.-G. Sun, H. Yang, P. Li, B. Zhang, *Org. Lett.* **2016**, *18*, 5114–5117.
[22] J. M. Fontmorin, R. C. Burgos Castillo, W. Z. Tang, M. Sillanpää, *Water Res.* **2016**, *99*, 24–32.
[23] a) Y. Zhang, W. Schilling, D. Riemer, Shoubhik Das, *Nature Protocols* **2020**, *15*, 822–839; b) W. Schilling, Y. Zhang, D. Riemer, S. Das, *Chem. Eur. J.* **2020**, *26*, 390–395; c) Y. Zhang, W. Schilling, S. Das, *ChemSusChem* **2019**, *12*, 2898–2910; d) J. Kollmann, Y. Zhang, W. Schilling, T. Zhang, D. Riemer, S. Das, *Green Chem.* **2019**, *21*, 1916–1920; e) D. Riemer, W. Schilling, A. Goetz, Y. Zhang, S. Gehrke, I. Tkach, O. Hollóczki, S. Das, *ACS Catal.* **2018**, *8*, 11679–11687; f) *ACS Catal.* **2018**, *8*, 6659–6664; g) J. He, G. Chen, B. Zhang, Y. Li, J.-R. Chen, W.-J. Xiao, F. Liu, C. Li, *Chem.* **2020**, *6*, 1149–1159; h) R. J. Griffiths, W. C. Kong, S. A. Richards, G. A. Burley, M. C. Willis, E. P. A. Talbot, *Chem. Sci.* **2018**, *9*, 2295–2300; i) J. Chen, X. Han, L. Mei, J. Liu, K. Du, T. Cao, Q. Li, *RSC Adv.* **2019**, *9*, 31212–31216; j) C. J. Legacy, M. H. Emmert, *Synlett* **2016**, *27*, 1893–1897.
[24] N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075–10166.
[25] W. Subhan, P. Rempala, R. S. Sheridan, *J. Am. Chem. Soc.* **1998**, *120*, 11528–11529.

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