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Cerium(IV)-Promoted Phosphinoylation-Nitratation of Alkenes

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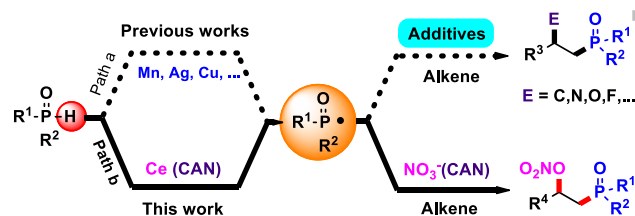
Abstract. A Cerium(IV)-promoted phosphinoylation-nitratation of alkenes is established under mild conditions. In this process, Ceric ammonium nitrate (CAN) acts as a cheap phosphorus-radical initiator, as well as a nitrate donor. Various β -nitrooxyphosphonates are delivered in high yield in a one-pot manner.

Keywords: phosphorylation; nitratation; difunctionalization; β -nitrooxyphosphonates; radicals

Organophosphorus compounds have broad applications in pharmaceutical and material sciences, and in phosphine-containing ligands due to their significant biological and chemical properties.^[1] Consequently, the development of concise and efficient strategies for C-P bond construction is a continuous research hotspot in organic chemistry.^[2] In the past few years, P-radical involved difunctionalization of alkenes has become a powerful protocol for C-P and C-E bond formation. Considerable effort has been devoted to expanding the substrate scope and identifying variants of this methodology.^[3,4] In these previous works, Mn, Ag and Cu salts are the most commonly used initiators to generate P(O)-radical (Scheme 1, Path a) and they exhibit high efficiency in most transformations. However, the limited metal scope restricts the development of P-radical chemistry. Thus, the introduction of alternative metal salts or initiating systems is still highly desirable. In this paper, we introduce a Ce(IV) salt as the initiator of P(O)-radical formation to trigger a new alkene phosphinoylation-nitratation transformation (Scheme 1, Path b).

Phosphinoyl and nitrooxy are functional groups commonly found in biologically active compounds. Molecules bearing both phosphinoyl and nitrooxy groups are extensively used in life and material science.^[5] At the same time, nitrate esters are crucial for high-energy materials,^[6] industrial fields,^[7] biomedical science,^[8] and drug synthesis.^[9] The

nitration of alcohols^[10] and nucleophilic substitution of halohydrocarbons^[11] as two traditional synthetic strategies are still the most common pathways to install nitrooxy groups. Although a few new methods have been established in recent years,^[12] the synthetic means to introduce nitrate esters are still limited. Herein, we describe the first example of Ce(IV)-promoted phosphinoylation-nitratation of alkenes. In our process, Ceric ammonium nitrate (CAN) acts as both a cheap initiator to generate P(O)-radical, as well as a nitrate donor. The highly effective utilization of CAN makes this process both materially and atomically economic. Furthermore, Ce(IV) is rarely reported to initiate the P(O)-radical generation, which provides an alternative approach in P-radical chemistry.

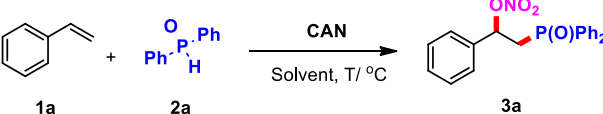


Scheme 1. P(O)-radical based difunctionalizations of alkenes.

Initially, our study was began with styrene (**1a**) and diphenylphosphine oxide (**2a**) in the presence of 1.5 equiv. of CAN ((NH₄)₂Ce(NO₃)₆) in 1,4-dioxane at 60 °C under an argon atmosphere (Table 1, entry 1). Gratifyingly, the phosphinoylation-nitratation product (**3a**) was obtained in 40% yield. Motivated by this result, we further optimized the reaction conditions. Firstly, when we reversed the ratio of **1a** to **2a**, the yield was improved to 48% (Table 1, entry 2). Next, it was a pleasure to find that by increasing the amount of **1a**, the yield was gradually increased to 66% (Table 1, entries 3-4). However, there was no further increase when 3 equiv. of **1a** was used (Table 1, entry 5). The reaction temperature screening showed that lowering the temperature to 40 °C lead to a higher

yield (Table 1, entries 6-8), but a further decrease temperature reduced the yield (Table 1, entry 9). Various solvents were surveyed next, and 1,4-dioxane remained the best choice (Table 1, entries 10-12). Remarkably, when increasing the loading of CAN to 2.0 equiv., the phosphinoylation-nitration proceeded cleanly, and product **3a** was isolated in 86% yield (Table 1, entry 13). Neither a reduction nor a further increase in the amount of CAN both resulted in higher yields (Table 1, entries 14 and 15). Additionally, when the reaction was performed in air, the desired product **3a** was obtained in only 40% yield (Table 1, entry 16). Moreover, we employed other nitrates instead of CAN (Table 1, entries 17 and 18). When using $\text{Cu}(\text{NO}_3)_2$, no products were detected. Using $\text{Fe}(\text{NO}_3)_3$ can result in the generation of **3a** in 25% yield. After a series of detailed investigations, the reaction conditions were eventually optimized as in Table 1, entry 13: 2.5 equiv of **1a** and 1.0 equiv of **2a** with 2.0 equiv of CAN in the presence of 2.0 mL of 1,4-dioxane at 40 °C under an argon atmosphere.

Table 1. Selected reaction condition optimizations ^[a,b]

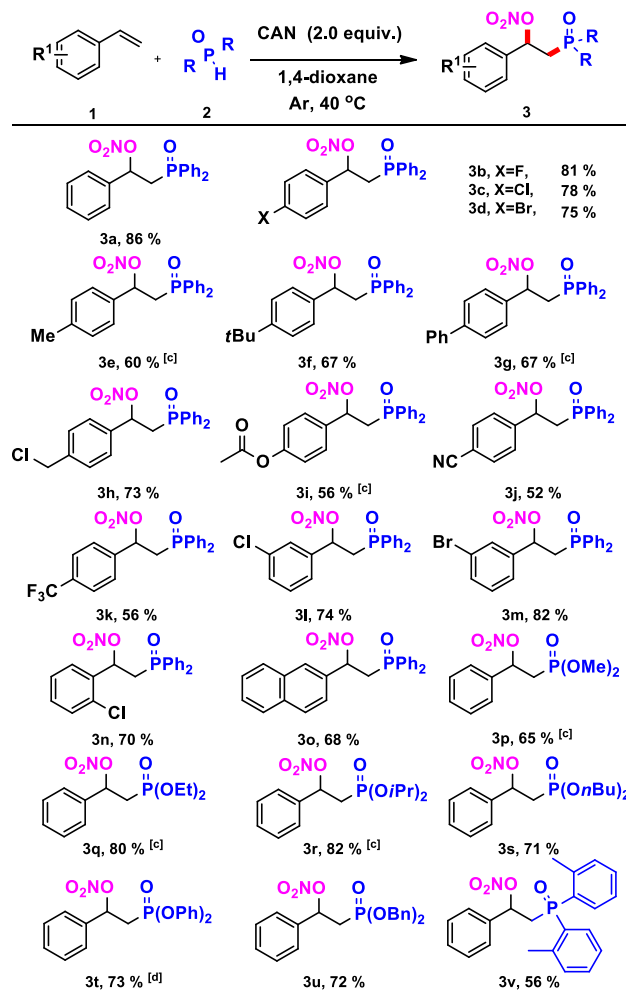


Entry	CAN (equiv.)	1a / 2a	Solvent	T / °C	Yield (%)
1	1.5	1.0 : 1.5	1,4-dioxane	60	40
2	1.5	1.5 : 1.0	1,4-dioxane	60	48
3	1.5	2.0 : 1.0	1,4-dioxane	60	54
4	1.5	2.5 : 1.0	1,4-dioxane	60	66
5	1.5	3.0 : 1.0	1,4-dioxane	60	63
6	1.5	2.5 : 1.0	1,4-dioxane	70	44
7	1.5	2.5 : 1.0	1,4-dioxane	50	68
8	1.5	2.5 : 1.0	1,4-dioxane	40	75
9	1.5	2.5 : 1.0	1,4-dioxane	30	70
10	1.5	2.5 : 1.0	THF	40	32
11	1.5	2.5 : 1.0	DCM	40	26
12	1.5	2.5 : 1.0	DMSO	40	trace
13	2.0	2.5 : 1.0	1,4-dioxane	40	86
14	1.0	2.5 : 1.0	1,4-dioxane	40	55
15	2.5	2.5 : 1.0	1,4-dioxane	40	66
16 ^[c]	2.0	2.5 : 1.0	1,4-dioxane	40	40
17 ^[d]	2.0	2.5 : 1.0	1,4-dioxane	40	n.r.
18 ^[e]	2.0	2.5 : 1.0	1,4-dioxane	40	25

^[a] Reaction condition: **1a** (0.5 mmol), **2a** (0.2 mmol), CAN (0.4 mmol), solvent (2.0 mL), stirred at 40 °C under an argon atmosphere for 12h. ^[b] Isolated yield. ^[c] The reaction was performed in air. ^[d] Using $\text{Cu}(\text{NO}_3)_2$ instead of CAN. ^[e] Using $\text{Fe}(\text{NO}_3)_3$ instead of CAN.

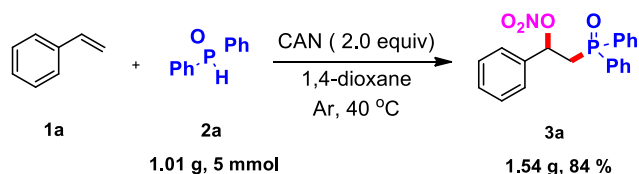
With the best conditions in hand, the substrate scope of the reaction was then investigated and the results are listed in Table 2. Firstly, we examined various substituted styrenes with different substituents located on the *para*-position. The corresponding products were obtained in moderate to good yields, including different halogens (**3b** – **3d**), alkyl or aryl (**3e** – **3h**), ester (**3i**), cyano (**3j**) and trifluoromethyl (**3k**) groups. Remarkably, styrenes bearing substitution on *meta* or *ortho* positions achieved good yields (**3l** – **3n**). Moreover, when we expanded the aromatic system to naphthalene, the reaction proceeded smoothly and the corresponding product (**3o**) was formed in moderate yield. To our delight, when the P(O)-H reagent was changed to dimethyl phosphonate (**2b**), the corresponding product (**3p**) was also formed. Encouraged by this result, different P(O)-H reagents were tested. Among them, diethyl phosphonate (**2c**), diisopropyl phosphonate (**2d**), dibutyl phosphonate (**2e**), diphenyl phosphonate (**2f**), and dibenzyl phosphonate (**2g**) were converted into the corresponding products **3q**, **3r**, **3s**, **3t**, and **3u** with good yields. Additionally, di-*o*-tolylphosphine oxide (**2h**) produced the desired product **3v** in moderate yield. Nevertheless, when alkylalkenes were employed as substrates, hydrophosphination products were detected instead of the phosphinoylation-nitration products.

Table 2. Substrate scope ^[a,b]



[a] Conditions: **1** (0.5 mmol), **2** (0.2 mmol), CAN (0.4 mmol), 1,4-dioxane (2.0 mL), stirred at 40 °C under an argon atmosphere for 12h. [b] Isolated yield. [c] CAN (0.3 mmol). [d] CAN (0.6 mmol).

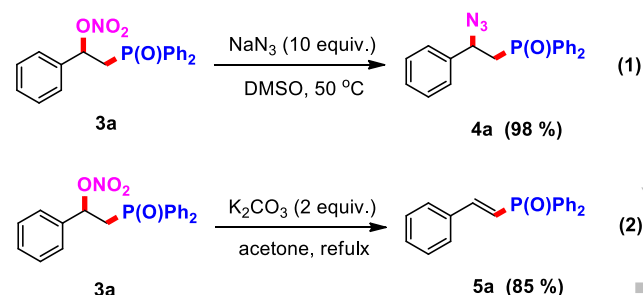
To show the potential applications of this protocol, a gram-scale reaction was carried out. For example, when diphenylphosphine oxide (**2a**, 5 mmol) was employed in a gram-scale reaction under the standard reaction conditions, 1.54 g of the desired product **3a** was obtained in 84% yield (Scheme 2). This result indicated that the phosphinylation-nitration process can be effectively scaled up with similar efficiency.



Scheme 2. Gram-scale preparation of **3a**.

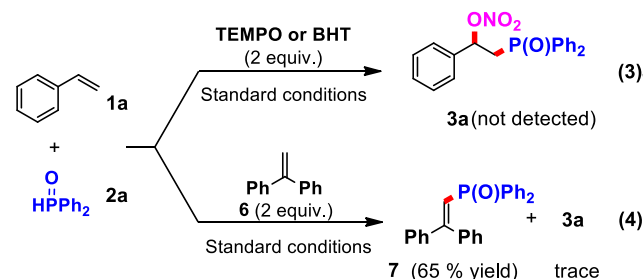
To further demonstrate the utility of this reaction in organic synthesis, the transformation of the nitrooxy group on the products were investigated (Scheme 3). When we used NaN_3 as a nucleophile, the nitrooxy

group smoothly transformed into an azide group, and the corresponding product was obtained in an almost quantitative yield (Scheme 3, Eq 1). The product **4a** can act as a precursor to a potential N-P ligand. Moreover, in the presence of 2 equiv. of K_2CO_3 in acetone, **3a** underwent an elimination reaction to generate the corresponding trans-alkenylphosphine oxide **5a** in good yield (Scheme 3, Eq 2).



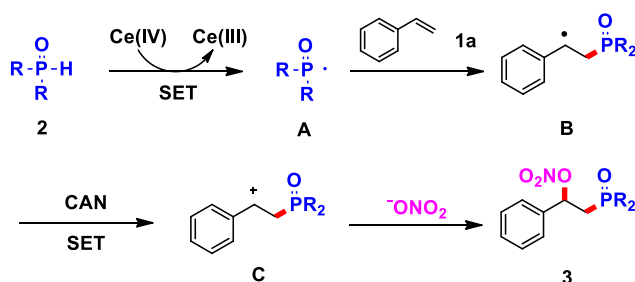
Scheme 3. Transformations of the nitrooxy group.

To gain insight into the mechanism of this transformation, several control experiments were carried out (Scheme 4). Firstly, addition of 2.0 equiv. of 2,2,6,6-tetramethyl-1-piperdinyloxy (TEMPO) or 2,6-di-*tert*-butyl-*p*-cresol (BHT) as the radical scavengers completely suppressed the phosphinylation-nitration process (Scheme 4, Eq 3). Furthermore, addition of 1, 1-diphenylethylene (**6**) in to the reaction system led to a competing reaction, yielding the alkenyl diphenylphosphine oxide **7** in 65 % yield (Scheme 4, Eq 4). These results suggested that a $[\text{R}_2\text{P(O)}]$ radical may be involved in this reaction.



Scheme 4. Control experiments.

Based on the above results and previous reports, we propose a plausible pathway for this phosphinylation-nitration process (Scheme 5). Initially, the P-radical **A** is generated from phosphorus reagents (**2**) through a single electron transfer (SET) with Ce(IV). Then, the addition of P(O)-radical **A** to **1a** generates a benzylic radical intermediate **B**. Subsequently, the benzylic-cation type **C** is formed via the second SET process from **B**. Finally, after along with the attack of nitrate, the desired product **3a** is formed. In this pathway, CAN acts as an oxidant as well as a nitrate-source.



Scheme 5. Plausible mechanistic pathway.

In conclusion, we have developed a convenient Ce(IV)-promoted phosphinoylation-nitration of alkenes under mild conditions. CAN was used as a cheap P(O)-radical initiator providing an important supplement to phosphorus radical chemistry. Furthermore, the highly effective utilization of CAN conferred this process with both high material and atom economy. This method can be easily adapted to large-scale preparations. Additional studies on the reaction mechanism and synthetic applications are underway in our laboratory.

Experimental Section

To a Schlenk tube was added diphenylphosphine oxide **2a** (0.2 mmol), $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (0.4 mmol) before being charged with argon three times. Then, anhydrous 1, 4-dioxane (2.0 mL) and styrene **1a** (0.5 mmol) were added via syringe. The mixture was allowed to stir at 40 °C in an oil bath overnight. At the completion of the reaction, the reaction mixture was cooled to room temperature, and the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to afford the product 2-(diphenylphosphoryl)-1-phenylethyl nitrate **3a**.

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References

- [1] a) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351-3378; b) M. N. Birkholz, Z. Freixa, P. W. N. M. van Leeuwen, *Chem. Soc. Rev.* **2009**, *38*, 1099-1118; c) L. Kollar, G. Keglevich, *Chem. Rev.* **2010**, *110*, 4257-4302; d) J. J. Feng, X. F. Chen, M. Shi, W. L. Duan, *J. Am. Chem. Soc.*, **2010**, *132*, 5562-5563; e) M. M. Pereira, M. J. Calvete, R. M. Carrilho, A. R. Abreu, *Chem. Soc. Rev.* **2013**, *42*, 6990-7027; f) S. Monge, G. David, *Phosphorus-Based Polymers from Synthesis to Applications*; (The Royal Society of Chemistry: Cambridge, **2014**); g) W. Feng, X. Y. Teo, W. N. P. Ramanujulu, M. D. Liang, D. Huang, P. K. Moore, L. W. Deng, B. W. Dymock, *J. Med. Chem.* **2015**, *58*, 6456-6480; h) L. Duan, H. Yang, Y. Shi, Y. Hou, Y. Zhu, Z. Gui, Y. Hu, *Ind. Eng. Chem. Res.* **2016**, *55*, 10218-10225; i) L. Lu, X. Qian, Z. Zeng, S. Yang, G. Shao, H. Wang, J. Jin, X. Xu, *J. Appl. Polym. Sci.* **2017**, *134*, 45105-45113.
- [2] Selected reviews on C-P bond formation: a) A. L. Schwan, *Chem. Soc. Rev.* **2004**, *33*, 218-224; b) S. Vander Jeught, C. V. Stevens, *Chem. Rev.* **2009**, *109*, 2672-2702; c) F. M. J. Tappe, V. T. Trepohl, M. Oestreich, *Synthesis* **2010**, 3037-3062; d) D. Zhao, R. Wang, *Chem. Soc. Rev.* **2012**, *41*, 2095-2108; e) Y. M. Li, S. D. Yang, *Synlett* **2013**, *24*, 1739-1744; f) Q. Xu, Y. B. Zhou, C. Q. Zhao, S. F. Yin, L. B. Han, *Mini Rev. Med. Chem.* **2013**, *13*, 824-835; g) H. Yorimitsu, *Beilstein J. Org. Chem.* **2013**, *9*, 1269-1277; h) J. L. Montchamp, *Acc. Chem. Res.* **2014**, *47*, 77-87; i) J. L. Montchamp, *Topics in Current Chemistry* 361, Phosphorus Chemistry II, Synthetic Methods; Springer International Publishing, **2015**; j) H. Zhang, X. Y. Zhang, D. Q. Dong, Z. L. Wang, *RSC Adv.* **2015**, *5*, 52824-52831; k) Y. H. Budnikova, T. V. Gryaznova, V. V. Grinenko, Y. B. Dudkina, M. N. Khrizanforov, *Pure Appl. Chem.* **2017**, *89*, 311-330; l) J. Yang, J. Xiao, Y. B. Zhou, T. Q. Chen, S. F. Yin, L. B. Han, *Chin. J. Org. Chem.* **2017**, *37*, 1055-1068.
- [3] Selected reviews on P-radical involved reactions: a) O. Delacroix, A. C. Gaumont, *Curr. Org. Chem.* **2005**, *9*, 1851-1882; b) S. Marque, P. Tordo, *Top. Curr. Chem.* **2005**, *250*, 43-76; c) D. Leca, L. Fensterbank, E. Lacote, M. Malacria, *Chem. Soc. Rev.* **2005**, *34*, 858-865; d) I. Wauters, W. Debrouwer, C. V. Stevens, *Beilstein J. Org. Chem.* **2014**, *10*, 1064-1096; e) V. Rodriguez-Ruiz, R. Carlino, S. Bezenine-Lafollée, R. Gil, D. Prim, E. Schulz, J. Hannedouche, *Dalton Trans.* **2015**, *44*, 12029-12059; f) Z. Li, F. Fan, Z. Zhang, Y. Xiao, D. Liu, Z. Q. Liu, *RSC Adv.* **2015**, *5*, 27853-27856; g) X. Q. Pan, J. P. Zou, W. B. Yi, W. Zhang, *Tetrahedron* **2015**, *71*, 7481-7529; h) H. Yi, D. Yang, Y. Luo, C. W. Pao, J. F. Lee, A. Lei, *Organometallics*, **2016**, *35*, 1426-1429; i) V. Quint, L. Noël-Duchesneau, E. Lagadic, F. Morlet-Savary, J. Lalevée, A. C. Gaumont, S. Lakhdar, *Synthesis* **2017**, *49*, 3444-3452; j) T. Taniguchi, *Synthesis* **2017**, *49*, 3511-3534; k) G. C. Fang, X. F. Cong, G. Zanon, Q. Liu, X. H. Bi, *Adv. Synth. Catal.* **2017**, *359*, 1422-1502; l) Y. Z. Gao, G. Tang, Y. F. Zhao, *Phosphorus, Sulfur Silicon Relat. Elem.* **2017**, *192*, 589-596.
- [4] Selected recent papers on P-radical involved difunctionalization of alkenes: a) W. Wei, J. X. Ji, *Angew. Chem., Int. Ed.* **2011**, *50*, 9097-9099; b) T. Taniguchi, A. Idota, S. I. Yokoyama, H. Ishibashi, *Tetrahedron Lett.* **2011**, *52*, 4768-4770; c) Y. M. Li, M. Sun, H. L. Wang, Q. P. Tian, S. D. Yang, *Angew. Chem. Int. Ed.* **2013**, *52*, 3972-3976; d) C. W. Zhang, Z. D. Li, L. Zhu, L. M. Yu, Z. T. Wang, C. Z. Li, *J. Am. Chem. Soc.* **2013**, *135*, 14082-14085; e) Y. Gao, J. Wu, J. Xu, P. Zhang, G. Tang, Y. Zhao, *RSC Adv.* **2014**, *4*, 51776-51779; f) W. Kong, E. Merino, C. Nevado, *Angew. Chem. Int. Ed.* **2014**, *53*, 5078-5082; g) S. F. Zhou, D. P. Li, K. Liu, J. P. Zou, O. T. Asekun, *J. Org. Chem.* **2015**, *80*, 1214-1220; h) V. Gutierrez, E. Mascaró, F. Alonso, Y. Moglie, G. Radivoy, *RSC Adv.* **2015**, *5*, 65739-65744; i) V. Richard, H. C. Fisher, J. L.

- Montchamp, *Tetrahedron Lett.* **2015**, *56*, 3197-3199; j) Y. Gao, X. Li, J. Xu, Y. Wu, W. Chen, G. Tang, Y. Zhao, *Chem. Commun.* **2015**, *51*, 1605-1607; k) H. Y. Zhang, L. L. Mao, B. Yang, S. D. Yang, *Chem. Commun.* **2015**, *51*, 4101-4104; l) J. Xu, X. Li, Y. Gao, L. Zhang, W. Chen, H. Fang, G. Tang, Y. Zhao, *Chem. Commun.* **2015**, *51*, 11240-11243; m) G. Y. Zhang, C. K. Li, D. P. Li, R. S. Zeng, A. Shoberu, J. P. Zou, *Tetrahedron* **2016**, *72*, 2972-2978; n) M. S. Li, Q. Zhang, D. Y. Hua, W. W. Zhong, M. Cheng, J. X. Ji, W. Wei, *Tetrahedron Lett.* **2016**, *57*, 2642-2646; o) J. Zhao, P. Li, X. Li, C. Xia, F. Li, *Chem. Commun.* **2016**, *52*, 3661-3664; p) C. X. Li, D. S. Tu, R. Yao, H. Yan, C. S. Lu, *Org. Lett.* **2016**, *18*, 4928-4931; q) H. Zhang, Z. Gu, Z. Li, C. Pan, W. Li, H. Hu, C. Zhu, *J. Org. Chem.* **2016**, *81*, 2122-2127; r) J. Zheng, Y. Zhang, D. Wang, S. Cui, *Org. Lett.* **2016**, *18*, 1768-1771; s) J. A. Li, P. Z. Zhang, K. Liu, A. Shoberu, J. P. Zou, W. Zhang, *Org. Lett.* **2017**, *19*, 4704-4706; t) P. Z. Zhang, L. Zhang, J. A. Li, A. Shoberu, J. P. Zou, W. Zhang, *Org. Lett.* **2017**, *19*, 5537-5540; u) D. Yi, Q. Fu, S. Y. Chen, M. Gao, L. Yang, Z. J. Zhang, W. Liang, Q. Zhang, J. X. Ji, W. Wei, *Tetrahedron Lett.* **2017**, *58*, 2058-2061; v) Z. K. Tao, C. K. Li, P. Z. Zhang, A. Shoberu, J. P. Zou, W. Zhang, *J. Org. Chem.* **2018**, *83*, 2418-2424.
- [5] a) R. I. Yurchenko, L. P. Peresyphkina, V. A. Andryushchenko, *Zhurnal Obshchei Khimii* **1995**, *65*, 961-964; b) E. A. Romanenko, E. E. Lavrova, R. I. Yurchenko, O. M. Voitsekhovskaya, *Teoreticheskaya Eksperimental'naya Khimiya* **1991**, *27*, 123-126; c) O. Moncea, M. A. Gunawan, D. Poinsot, H. Cattey, J. Becker, R. I. Yurchenko, E. D. Butova, H. Hausmann, M. Šekutor, A. A. Fokin, J. Hierso, P. R. Schreiner, *J. Org. Chem.* **2016**, *81*, 8759-8769.
- [6] a) D. Srinivas, V. D. Ghule, *RSC Adv.* **2016**, *6*, 7712-7716; b) D. Trache, A. F. Tarchoun, *J. Mater. Sci.* **2018**, *53*, 100-123.
- [7] a) Y. X. Gao, W. Xu, D. F. Zhu, L. Chen, Y. Y. Fu, Q. G. He, H. M. Cao, J. G. Cheng, *J. Mater. Chem. A* **2015**, *3*, 4820-4826; (b) E. Sisco, T. P. Forbes, *Talanta* **2016**, *150*, 177-183.
- [8] a) P. G. Wang, M. Xian, X. P. Tang, X. J. Wu, Z. Wen, T. W. Cai, A. J. Janczuk, *Chem. Rev.* **2002**, *102*, 1091-1134; b) T. W. Myers, C. J. Snyder, D. E. Chavez, R. J. Scharff, J. M. Veauthier, *Chem.-Eur. J.* **2016**, *22*, 10590-10596.
- [9] S. K. Kuttly, N. Barraud, A. Pham, G. Iskander, S. A. Rice, D. S. Black, N. Kumar, *J. Med. Chem.* **2013**, *56*, 9517-9529.
- [10] a) W. J. Fleming, E. J. Rowe, D. B. Meyers, *J. Am. Pharm. Assoc. (1912-1977)*, **1958**, *47*, 368-370; b) D. E. Chavez, M. A. Hiskey, D. L. Naud, D. Parrish, *Angew. Chem. Int. Ed.* **2008**, *47*, 8307-8309.
- [11] a) W. D. Emmons, A. F. Ferris, I. G. Marks, K. W. McLean, *J. Am. Chem. Soc.* **1953**, *75*, 4078-4079; b) A. K. Shaikh, G. Varvounis, *Org. Lett.* **2014**, *16*, 1478-1481.
- [12] a) V. Nair, A. Augustine, S. B. Panicker, T. D. Suja, S. Mathai, *Res. Chem. Intermed.* **2003**, *29*, 213-226; b) R. M. A. Pinto, J. A. R. Salvador, C. Le Roux, *Tetrahedron* **2007**, *63*, 9221-9228; c) T. Graham, H. C. M. Jones, N. T. Jui, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2008**, *130*, 16494-16495; d) S. Kamijo, Y. Amaoka, M. Inoue, *Tetrahedron Lett.* **2011**, *52*, 4654-4657; e) J. Z. Ni, J. Ozawa, K. Oisakia, M. Kanai, *Org. Biomol. Chem.* **2016**, *14*, 4378-4381; f) X. W. Zhang, Z. F. Xiao, Y. J. Zhuang, M. M. Wang, Y. B. Kang, *Adv. Synth. Catal.* **2016**, *358*, 1942-1945; g) X. D. Yang, Y. She, Y. Chong, H. C. Zhai, H. Zhu, B. H. Chen, G. S. Huang, R. L. Yan, *Adv. Synth. Catal.* **2016**, *358*, 3130-3134.

COMMUNICATION

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