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Communication

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AgPd Nanoparticles Deposited on $WO_{2.72}$ Nanorods as an Efficient Catalyst for One-Pot Conversion of Nitrophenol/ Nitroacetophenone into Benzoxazole/Quinazoline

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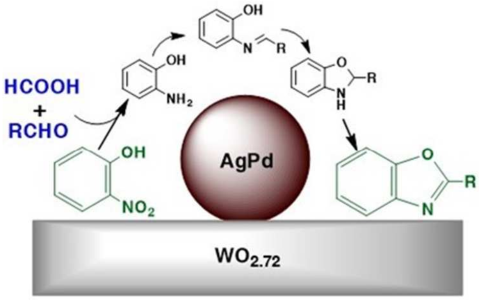
Supporting Information Placeholder

ABSTRACT: We report a seed-mediated growth of 2.3 nm AgPd nanoparticles (NPs) in the presence of 40 × 5 nm $WO_{2.72}$ nanorods (NRs) for the synthesis of AgPd/$WO_{2.72}$ composites. The strong interactions between AgPd NPs and $WO_{2.72}$ NRs make the composites, especially the $Ag_{48}Pd_{52}/WO_{2.72}$, catalytically active for dehydrogenation of formic acid (TOF = 1718 h^{-1} and E_a = 31 kJ/mol), and one-pot reactions of formic acid, 2-nitrophenol and aldehydes into benzoxazoles in near quantitative yields under mild conditions. The catalysis can also be extended to the one-pot reactions of ammonium formate, 2-nitroacetophenone and aldehyde for high yield syntheses of quinazolines. Our studies demonstrate a new catalyst design to achieve a green chemistry approach to one-pot reactions for the syntheses of benzoxazoles and quinazolines.

Developing an efficient and reusable catalyst for multi-step chemical reactions under environmentally benign conditions is a hierarchic goal in catalytic sciences. This has stimulated tremendous research efforts aiming to understand dimension- and structure-dependent catalysis as well as synergistic effects that can be employed within multiple catalyst systems to extend the catalytic power from one reaction to another. Despite the progress made in past computational and experimental studies, the catalysts developed thus far are often effective for one specific reaction. Recent demonstrations on the dehydrogenation of ammonia borane and hydrogenation of nitro- (RNO_2) or cyano-compounds (R-CN) to primary amines without using pure hydrogen provide an exciting potential for using well-designed nanoparticles (NPs) to catalyze tandem reactions.[1-6] Compared to ammonia borane, formic acid (FA) is environmentally greener and a less toxic choice as a hydrogen source for hydrogenation reactions. Pd-based NP catalysts have been the most attractive candidates explored to promote FA dehydrogenation ($HCOOH \rightarrow H_2 + CO_2$) over dehydration pathway ($HCOOH \rightarrow CO + H_2O$).[7-15] However, these catalysts are rarely reported for other tandem reactions, except for the two-step dehydrogenation of FA and hydrogenation of RNO_2 to RNH_2.[16-18]

In this communication, we report a new catalyst design based on AgPd alloy NPs and the defected perovskite-type $WO_{2.72}$ nanorods (NRs) for efficient one-pot FA dehydrogenation and conversion of nitrophenol/aldehyde to benzoxazole, as summarized in Scheme 1. In this composite catalyst structure, AgPd NPs act as the catalyst, which are then coupled strongly to the acid-stable and oxygen-deficient $WO_{2.72}$ NRs for strong interactions with reactants.[19-22] In the solvent mixture of dioxane/water (v/v 2/1), the $Ag_{48}Pd_{52}/WO_{2.72}$ composite catalyzes the dehydrogenation of FA, the hydrogenation of RNO_2 to RNH_2, the condensation between RNH_2 and aldehydes (RCHO) to form Schiff base intermediates (RNH=CR), and the intra-molecular nucleophilic addition within the Schiff base compounds followed by the dehydrogenation into benzoxazoles. Each reaction step gives nearly a quantitative yield of the related product. The $Ag_{48}Pd_{52}/WO_{2.72}$ catalysis can be readily extended to one-pot reactions comprising the dehydrogenation of ammonium formate (AF) and the conversion of 2-nitroacetophenone/aldehyde to quinazolines. The catalyst offers a green chemistry approach to high yield syntheses of benzoxazoles or quainazolines that are key components found in large molecules prepared for natural product and biomedical applications.[23-28]



Scheme 1. Schematic illustration of one-pot FA dehydrogenation and conversion of nitrophenol/aldehyde to benzoxazole catalyzed by AgPd/$WO_{2.72}$.

We prepared the $WO_{2.72}$ NRs by reacting WCl_4 with oleic acid (OA) and oleylamine (OAm) in 1-octadecene (ODE) at 280 °C for 10 h, as reported (supporting information, SI).[29] Figure S1 shows the transmission electron microscopy (TEM) image of the representative NRs with an average length of 40 nm and diameter of 5 nm. We also synthesized AgPd NPs by the co-reduction of silver(I) acetate (AgOAc) and palladium(II) acetylacetonate ($Pd(acac)_2$) at 180°C as described previously.[8] Figure S2 is the representative TEM image of the as-synthesized 2.3 nm $Ag_{48}Pd_{42}$ NPs. We tested self-assembly of the AgPd NPs and the $WO_{2.72}$ NRs but could only obtain a physical mixture of the two components without evidence of them being in strong coupling. To obtain the strongly coupled AgPd/$WO_{2.72}$ nanocomposites, we ran the same reaction leading to the synthesis of AgPd NPs but in the presence of $WO_{2.72}$ NRs (SI). The in-situ nucleation and growth of AgPd NPs along the $WO_{2.72}$ NRs ensures strong coupling between AgPd NPs and $WO_{2.72}$ NRs.[19, 30] The metal content of the AgPd and the molar ratios of the AgPd/$WO_{2.72}$ were controlled by the molar ratios of metal precursors, and the composition of the final products were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). From the controlled reaction, $Ag_{78}Pd_{22}/WO_{2.72}$, $Ag_{57}Pd_{43}/WO_{2.72}$, $Ag_{48}Pd_{52}/WO_{2.72}$, $Ag_{39}Pd_{61}/WO_{2.72}$ and $Ag_{20}Pd_{80}/WO_{2.72}$ were obtained with the final metal/metal oxide molar ratio at 3:5 (SI) and the $Ag_{48}Pd_{52}/WO_{2.72}$ composition was further supported by energy dispersive X-ray (EDX) spectroscopy (Figure S3). Figure 1 shows the representative TEM images of the $Ag_{48}Pd_{52}/WO_{2.72}$ obtained from the synthesis (SI). The 2.3 nm $Ag_{48}Pd_{52}$ NPs attach to $WO_{2.72}$ NRs. High-resolution TEM (HRTEM) of a single $WO_{2.72}$ NR shown in Figure 1C indicates that the $WO_{2.72}$ structure has an interfringe distance of 0.38 nm that is close to 0.378 nm of (010) interplanar distance of monoclinic $WO_{2.72}$ (JCPDS No. 65-1291). $Ag_{48}Pd_{52}$ NPs attached to the $WO_{2.72}$ NR have an average interfringe distance of 0.25 nm that is slightly larger than 0.23 nm measured from the as-synthesized $Ag_{48}Pd_{52}$ NPs (Figure 1C inset). X-ray diffraction (XRD) of the $Ag_{48}Pd_{52}/WO_{2.72}$, $Ag_{48}Pd_{52}$ and $WO_{2.72}$ structure (Figure S4) show a very weak diffraction pattern of the fcc structured $Ag_{48}Pd_{52}$ NPs due to their small size. After attaching to $WO_{2.72}$, the (111) diffraction peak of the $Ag_{48}Pd_{52}$ NPs shift to a lower diffraction angle, while the $WO_{2.72}$ NRs in the composite structure show no obvious diffraction peak change. The (111) peak shift of the AgPd NPs is similar to what was reported.[8] These HRTEM and XRD studies indicate that in the composite AgPd/$WO_{2.72}$ structure, AgPd NPs are in the alloy form and interactions between AgPd and $WO_{2.72}$ lead to more obvious changes to AgPd (lattice expansion) than to $WO_{2.72}$.

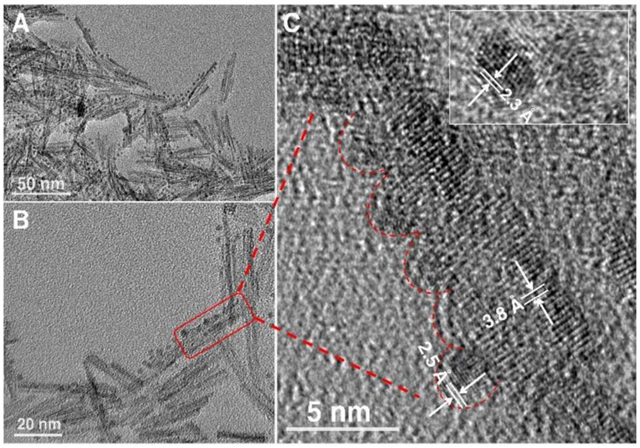
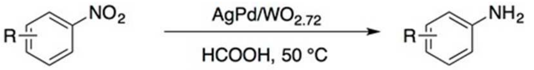


Figure 1. (**A-B**) TEM image of the $Ag_{48}Pd_{52}/WO_{2.72}$ nanocomposite in different scale bar; (**C**) HRTEM image of the $Ag_{48}Pd_{52}/WO_{2.72}$. Inset is the HRTEM image of the $Ag_{48}Pd_{52}$ NPs synthesized in the absence of $WO_{2.72}$.

We first studied catalytic properties of the AgPd/$WO_{2.72}$ for FA dehydrogenation reactions, similar to what was reported in the study of the AgPd/C systems.[8] From the FA dehydrogenation kinetics studied at 50°C (Figure S5), we concluded that our AgPd/$WO_{2.72}$ is generally more active than AgPd/C for the reaction. The most active catalyst in the AgPd/C system is $Ag_{42}Pd_{58}$/C while in the current $WO_{2.72}$-supported AgPd system, $Ag_{48}Pd_{52}/WO_{2.72}$ is the most active one (Figure S5&S6). With an initial TOF of 1718 h^{-1} and an activation energy of $E_a = 31$ kJ/mol, this $Ag_{48}Pd_{52}/WO_{2.72}$ is one of the most active heterogeneous catalysts ever reported.[10, 11, 13, 31-35] We also deposited the $Ag_{48}Pd_{52}$ NPs on C and found $Ag_{48}Pd_{52}$/C to be much less active than $Ag_{48}Pd_{52}/WO_{2.72}$ (Figure S7). The high activity of the $Ag_{48}Pd_{52}/WO_{2.72}$ is induced most likely by the presence of $WO_{2.72}$ and the strong binding between $Ag_{48}Pd_{52}$ and $WO_{2.72}$ as the defected $WO_{2.72}$ tends to absorb "H" to form $H_xWO_{2.72}$,[36-41] which should facilitate AgPd catalysis for the FA dehydrogenation reaction.

We tested the $Ag_{48}Pd_{52}/WO_{2.72}$ catalyst for the hydrogenation of R-NO_2 to R-NH_2 with FA as a hydrogen source at 50 °C. Nitrobenzene was chosen as a model substrate to obtain the optimum reaction conditions. After investigating the effects of solvents, catalyst loadings and FA amounts on this reaction (Table S1 and S2), we found that the reaction in the mixed solvent of dioxane + water (v/v 2/1) could be completed within 30 mins and the conversion yield (obtained by gas chromatography-mass spectrometry (GC-MS)) to aniline reached 98%. Following this reaction optimization, we studied the FA-induced hydrogenation of five additional RNO_2 molecules and summarize the results in Table 1. The $Ag_{48}Pd_{52}/WO_{2.72}$ catalyst is very effective in using FA to hydrogenate RNO_2 to RNH_2 with nearly quantitative conversion yield (by GC-MS) within 2 h.

Table 1. The $Ag_{48}Pd_{52}/WO_{2.72}$-catalyzed hydrogenation of Ar-NO_2 in the presence of FA. Reaction conditions: R-NO_2 (1 mmol), $Ag_{48}Pd_{52}/WO_{2.72}$ (3 mol%), dioxane (6 mL), H_2O (3 mL), FA (3 mmol), 50 °C.

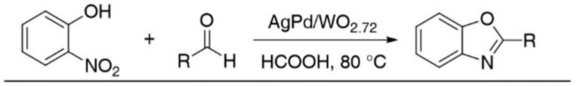


Entry	R	Time	Yield(%)	Entry	R	Time	Yield(%)
1	H	0.5	98	4	3-OH	2.0	94
2	2-Me	0.5	99	5	3-F	1.5	98
3	2-OH	1	98	6	3-CN	1.5	97

Next, we studied the $Ag_{48}Pd_{52}/WO_{2.72}$ catalyzed hydrogenation of RNO_2 and condensation of the resulting RNH_2 with RCHO. Under similar reaction conditions with addition of 1.2 mmol benzaldehyde, 1.5 h of reaction at 50 °C led to the formation of the Schiff base, diphenylmethanimine (conversion yield 98%).

We further studied the combined hydrogenation of 2-nitrophenol and subsequent condensation/cyclization with benzaldehyde to give benzoxazoles. Benzoxazoles are commonly synthesized by condensation of 2-substituted aminoaromatics with aldehydes or by coupling 2-substituted aminoaromatics with carboxylic acid derivatives.[42-47] Both methods are complicated by strongly acidic conditions, long reaction times, multiple reaction steps, and tedious work-up procedures. We studied the reaction in the presence of different Ag, Pd, and AgPd catalysts with different supports (Table S3) and reaction conditions (Table S4) and found $Ag_{48}Pd_{52}/WO_{2.72}$ to be the best catalyst, and 80 °C to be the optimal reaction temperature for the synthesis of 2-phenylbenzoxazole (99 % conversion yield). Using the $Ag_{48}Pd_{52}/WO_{2.72}$ catalyzed one-pot reactions, we prepared several different benzoxazoles as listed in Table 2. The nearly quantitative yields of the purified products indicate that the tandem reactions are insensitive to the electron-donating or election-withdrawing nature of the substitutes. The results from the one-pot reactions and two control experiments (Figure S8) show that the one-pot reactions follow the known reaction mechanisms,[48, 49] but the presence of $Ag_{48}Pd_{52}/WO_{2.72}$ makes the reactions proceed (Scheme S1) in much milder reaction conditions. Overall, compared with previous syntheses of benzoxazoles, the unique part of the current catalyst is that it catalyzes one-pot reactions into the benzoxazole products without the use of pure hydrogen and in environmentally benign conditions. Compared to any other catalyst reported,[48-54] $Ag_{48}Pd_{52}/WO_{2.72}$ is much more active and selective towards the formation of benzoxazole products due likely to the synergistic role of $WO_{2.72}$ in enriching the O-containing precursors around each AgPd NP and in facilitating AgPd-catalyzed dehydrogenation reactions *via* the $H_xWO_{2.72}$ intermediates. Detailed mechanistic studies are on the way.

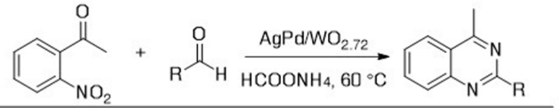
Table 2. $Ag_{48}Pd_{52}/WO_{2.72}$-catalyzed one-pot aromatization of 2-nitrophenol and various benzaldehydes. Reaction conditions: 2-nitrophenol (1 mmol), aromatic or aliphatic aldehyde (1.2 mmol), $Ag_{48}Pd_{52}/WO_{2.72}$ (3 mol%), dioxane (6 mL), water (3 mL) and formic acid (4 mmol), 8 h.



Entry	R	Yield(%)	Entry	R	Yield(%)
1	ph	99	4	4-F-ph	95
2	4-Me-ph	99	5	4-CN-ph	98
3	4-OMe-ph	99	6	cyclohexyl	83

The $Ag_{48}Pd_{52}/WO_{2.72}$ composite can also catalyze the dehydrogenation of ammonium formate (AF) for the one-pot synthesis of quinazolines. The $Ag_{48}Pd_{52}/WO_{2.72}$ catalyzed decomposition of AF (Figure S9&S10) provides the desired source of hydrogen and ammonia for next-step reactions. Using the formation of 4-methyl-2-phenylquinazoline as an example, we screened reaction conditions (Table S5) and chose 60 °C as the optimal reaction temperature. We investigated the aromatization of 2-nitroacetophenone with several representative aromatic or aliphatic aldehydes in the $Ag_{48}Pd_{52}/WO_{2.72}$ catalyzed one-pot reactions and list the results in Table 3. The one-pot reactions lead to the high yield formation of the corresponding quinazoline products. Furthermore, control experiments (Figure S11) corroborate what has been reported in the related organic reactions,[55, 56] and indicate that the formation of quinazoline follows a similar reaction mechanism as outlined in Scheme S3.

Table 3. $Ag_{48}Pd_{52}/WO_{2.72}$-catalyzed one-pot aromatization of 2-nitroacetophenone with various aldehydes. Reaction conditions: 2-nitroacetophenone (1 mmol), aromatic or aliphatic aldehyde (1.2 mmol), $Ag_{48}Pd_{52}/WO_{2.72}$ (4 mol%), dioxane (6 ml), water (3 ml) and ammonium formate (3 mmol), 6 h.



Entry	R	Yield(%)	Entry	R	Yield(%)
1	ph	99	4	4-F-ph	92
2	4-Me-ph	96	5	4-CN-ph	99
3	4-OMe-ph	93	6	cyclohexyl	88

Finally, we studied the stability of the $Ag_{48}Pd_{52}/WO_{2.72}$ catalyst in the one-pot reactions. Once the reaction was over, we precipitated the catalyst by adding a small amount of ethyl acetate for better catalyst isolation and purification (Figure S12). We separated and washed the catalyst with water/methanol, and re-used it in the one-pot reactions for the formation of 2-phenylbenzoxazole or 4-methyl-2-phenylquinazoline. In each case, after the 5th reaction-purification cycle, the catalyst showed no obvious loss in activity and the yield remained >92% (Figure S13). We characterized again the catalyst after the 5th reaction cycle for the synthesis of 2-phenylbenzoxazole and found that the catalyst had neither morphology nor structure change (Figure S14).

In conclusion, we report a convenient seed-mediated approach to synthesize the composite $AgPd/WO_{2.72}$. In this seed-mediated growth process, the in-situ nucleation/growth of AgPd NPs in the presence of $WO_{2.72}$ NRs stabilizes the AgPd NPs and enhances their interactions with the $WO_{2.72}$ NRs. The resultant lattice expansion of the AgPd NPs coupled with the synergistic effect from $WO_{2.72}$ make the composite, especially $Ag_{48}Pd_{52}/WO_{2.72}$, an excellent catalyst to promote one-pot reactions of formic acid, 2-nitrophenol and RCHO into benzoxazoles in near quantitative yields under mild conditions. In this one-pot high-yield synthesis of benzoxazole, the $Ag_{48}Pd_{52}/WO_{2.72}$ composite shows a unique capability to catalyze two dehydrogenations, one hydrogenation, one condensation and one cyclization reaction. The hydrogenation reaction proceeds without the use of pure hydrogen in dioxane/water (v/v 2/1) at temperatures below 80 °C. The $Ag_{48}Pd_{52}/WO_{2.72}$ catalysis can be further extended to one-pot reactions of ammonium formate, 2-nitroacetophenone and aldehyde for high-yield syntheses of quinazolines under 60 °C. Our studies demonstrate the design of a new catalyst to achieve a green chemistry approach to one-pot reactions for the syntheses of benzoxazoles or quinazolines that can be important for natural product and pharmaceutical applications in the future.

ASSOCIATED CONTENT

Materials and experimental methods, and supplementary figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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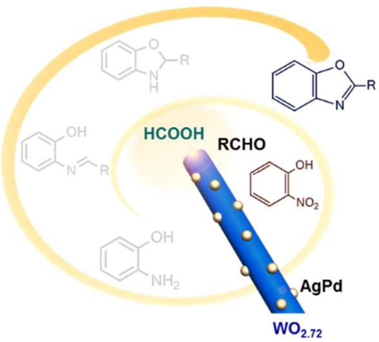
REFERENCES

(1) Shao, Z. H.; Fu, S. M.; Wei, M. F.; Zhou, S. L.; Liu, Q. *Angew. Chem. Int. Ed.* **2016**, *55*, 14653.
(2) Li, S. L.; Li, G.; Meng, W.; Du, H. F. *J. Am. Chem. Soc.* **2016**, *138*, 12956.
(3) Byun, S.; Song, Y.; Kim, B. M. *Acs. Appl. Mater. Inter.* **2016**, *8*, 14637.

(4) Goksu, H.; Ho, S. F.; Metin, O.; Korkmaz, K.; Garcia, A. M.; Gultekin, M. S.; Sun, S. H. *Acs. Catal.* **2014**, *4*, 1777.
(5) Goksu, H.; Can, H.; Sendil, K.; Gultekin, M. S.; Metin, O. *Appl Catal a-Gen* **2014**, *488*, 176.
(6) Vasilikogiannaki, E.; Gryparis, C.; Kotzabasaki, V.; Lykakis, I. N.; Stratakis, M. *Adv. Synth. Catal.* **2013**, *355*, 907.
(7) Marcinkowski, M. D.; Liu, J. L.; Murphy, C. J.; Liriano, M. L.; Wasio, N. A.; Lucci, F. R.; Flytzani-Stephanopoulos, M.; Sykes, E. C. H. *Acs. Catal.* **2017**, *7*, 413.
(8) Zhang, S.; Metin, O.; Su, D.; Sun, S. H. *Angew. Chem. Int. Ed.* **2013**, *52*, 3681.
(9) Tedsree, K.; Li, T.; Jones, S.; Chan, C. W. A.; Yu, K. M. K.; Bagot, P. A. J.; Marquis, E. A.; Smith, G. D. W.; Tsang, S. C. E. *Nat. Nanotechnol.* **2011**, *6*, 302.
(10) Bi, Q. Y.; Lin, J. D.; Liu, Y. M.; He, H. Y.; Huang, F. Q.; Cao, Y. *Angew. Chem. Int. Ed.* **2016**, *55*, 11849.
(11) Zhu, Q. L.; Tsumori, N.; Xu, Q. *J. Am. Chem. Soc.* **2015**, *137*, 11743.
(12) Chen, Y.; Zhu, Q. L.; Tsumori, N.; Xu, Q. *J. Am. Chem. Soc.* **2015**, *137*, 106.
(13) Jiang, K.; Xu, K.; Zou, S. Z.; Cai, W. B. *J. Am. Chem. Soc.* **2014**, *136*, 4861.
(14) Porter, N. S.; Wu, H.; Quan, Z. W.; Fang, J. Y. *Accounts. Chem. Res.* **2013**, *46*, 1867.
(15) Jones, S.; Qu, J.; Tedsree, K.; Gong, X. Q.; Tsang, S. C. E. *Angew. Chem. Int. Ed.* **2012**, *51*, 11275.
(16) Gilkey, M. J.; Xu, B. J. *Acs. Catal.* **2016**, *6*, 1420.
(17) Yu, L.; Zhang, Q.; Li, S. S.; Huang, J.; Liu, Y. M.; He, H. Y.; Cao, Y. *Chemsuschem* **2015**, *8*, 3029.
(18) Sorribes, I.; Wienhofer, G.; Vicent, C.; Junge, K.; Llusar, R.; Beller, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 7794.
(19) Lu, Y. Z.; Jiang, Y. Y.; Gao, X. H.; Wang, X. D.; Chen, W. *J. Am. Chem. Soc.* **2014**, *136*, 11687.
(20) Manthiram, K.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2012**, *134*, 3995.
(21) Park, K. W.; Ahn, K. S.; Nah, Y. C.; Choi, J. H.; Sung, Y. E. *J. Phys. Chem. B* **2003**, *107*, 4352.
(22) Lee, K.; Seo, W. S.; Park, J. T. *J. Am. Chem. Soc.* **2003**, *125*, 3408.
(23) Demmer, C. S.; Bunch, L. *Eur. J. Med. Chem.* **2015**, *97*, 778.
(24) Mor, M.; Rivara, S.; Pala, D.; Bedini, A.; Spadoni, G.; Tarzia, G. *Expert Opin. Ther. Pat.* **2010**, *20*, 1059.
(25) Neyts, J.; De Clercq, E.; Singha, R.; Chang, Y. H.; Das, A. R.; Chakraborty, S. K.; Hong, S. C.; Tsay, S. C.; Hsu, M. H.; Hwu, J. R. *J. Med. Chem.* **2009**, *52*, 1486.
(26) Taki, M.; Wolford, J. L.; O'Halloran, T. V. *J. Am. Chem. Soc.* **2004**, *126*, 712.
(27) Haugwitz, R. D.; Maurer, B. V.; Jacobs, G. A.; Narayanan, V. L.; Cruthers, L.; Szanto, J. *J. Med. Chem.* **1979**, *22*, 1113.
(28) Reiser, A.; Saunders, D.; Mijovic, M. V.; Bogie, J.; Bright, A.; Leyshon, L. J. *J. Am. Chem. Soc.* **1972**, *94*, 2414.
(29) Lou, X. W.; Zeng, H. C. *Inorg. Chem.* **2003**, *42*, 6169.
(30) Huang, Z. F.; Song, J. J.; Pan, L.; Zhang, X. W.; Wang, L.; Zou, J. J. *Adv. Mater.* **2015**, *27*, 5309.
(31) Zhu, Q. L.; Xu, Q. *Energ. Environ. Sci.* **2015**, *8*, 478.
(32) Bi, Q. Y.; Du, X. L.; Liu, Y. M.; Cao, Y.; He, H. Y.; Fan, K. N. *J. Am. Chem. Soc.* **2012**, *134*, 8926.
(33) Yang, X. C.; Pachfule, P.; Chen, Y.; Tsumori, N.; Xu, Q. *Chem. Commun.* **2016**, *52*, 4171.
(34) Karatas, Y.; Bulut, A.; Yurderi, M.; Ertas, I. E.; Alal, O.; Gulcan, M.; Celebi, M.; Kivrak, H.; Kaya, M.; Zahmakiran, M. *Appl. Catal. B-Environ.* **2016**, *180*, 586.
(35) Hu, C. Y.; Mu, X. L.; Fan, J. M.; Ma, H. B.; Zhao, X. J.; Chen, G. X.; Zhou, Z. Y.; Zheng, N. F. *Chemnanomat* **2016**, *2*, 28.
(36) Xi, Z.; Mendoza-Garcia, A.; Zhu, H.; Chi, M.; Su, D.; Erdosy, D. P.; Li, J.; Sun, S. *Green Energy & Environment* **2017**, DOI: 10.1016/j.gee.2017.01.001.
(37) Xi, Z.; Erdosy, D. P.; Mendoza-Garcia, A.; Duchesne, P. N.; Li, J.; Muzzio, M.; Li, Q.; Zhang, P.; Sun, S. *Nano. Lett.* **2017**, DOI: 10.1021/acs.nanolett.7b00870
(38) Zhou, Y.; Li, C.; Fu, J. X.; Yu, C. L.; Hu, X. C. *Rsc. Adv.* **2016**, *6*, 92852.
(39) Cong, S.; Yuan, Y. Y.; Chen, Z. G.; Hou, J. Y.; Yang, M.; Su, Y. L.; Zhang, Y. Y.; Li, L.; Li, Q. W.; Geng, F. X.; Zhao, Z. G. *Nat. Commun.* **2015**, *6*.
(40) Kuo, C. H.; Lamontagne, L. K.; Brodsky, C. N.; Chou, L. Y.; Zhuang, J.; Sneed, B. T.; Sheehan, M. K.; Tsung, C. K. *Chemsuschem* **2013**, *6*, 1993.
(41) Kibler, L. A.; El-Aziz, A. M.; Hoyer, R.; Kolb, D. M. *Angew. Chem. Int. Ed.* **2005**, *44*, 2080.
(42) Guru, M. M.; Ali, M. A.; Punniyamurthy, T. *Org. Lett.* **2011**, *13*, 1194.
(43) Evindar, G.; Batey, R. A. *J. Org. Chem.* **2006**, *71*, 1802.
(44) Perry, R. J.; Wilson, B. D.; Miller, R. J. *J. Org. Chem.* **1992**, *57*, 2883.
(45) Edwards, P. D.; Meyer, E. F.; Vijayalakshmi, J.; Tuthill, P. A.; Andisik, D. A.; Gomes, B.; Strimpler, A. *J. Am. Chem. Soc.* **1992**, *114*, 1854.
(46) Bunnett, J. F.; Hrutfiord, B. F. *J. Am. Chem. Soc.* **1961**, *83*, 1691.
(47) Hein, D. W.; Alheim, R. J.; Leavitt, J. J. *J. Am. Chem. Soc.* **1957**, *79*, 427.
(48) Wu, M. Y.; Hu, X.; Liu, J.; Liao, Y. F.; Deng, G. J. *Org. Lett.* **2012**, *14*, 2722.
(49) Tang, L.; Guo, X. F.; Yang, Y.; Zha, Z. G.; Wang, Z. Y. *Chem. Commun.* **2014**, *50*, 6145.
(50) Urzua, J. I.; Contreras, R.; Salas, C. O.; Tapia, R. A. *Rsc. Adv.* **2016**, *6*, 82401.
(51) Sarode, S. A.; Bhojane, J. M.; Nagarkar, J. M. *Tetrahedron Lett.* **2015**, *56*, 206.
(52) Khalafi-Nezhad, A.; Panahi, F. *Acs. Catal.* **2014**, *4*, 1686.
(53) Cao, X. X.; Cheng, X. F.; Bai, Y.; Liu, S. W.; Deng, G. J. *Green Chem.* **2014**, *16*, 4644.
(54) Jin, X. K.; Liu, Y. X.; Lu, Q. Q.; Yang, D. J.; Sun, J. K.; Qin, S. S.; Zhang, J. W.; Shen, J. X.; Chu, C. H.; Liu, R. H. *Org. Biomol. Chem.* **2013**, *11*, 3776.
(55) Tang, L.; Yang, Y.; Wen, L. X.; Zhang, S.; Zha, Z. G.; Wang, Z. Y. *Org. Chem. Front.* **2015**, *2*, 114-118.
(56) Tang, L.; Wang, P. F.; Fan, Y.; Yang, X. K.; Wan, C. F.; Zha, Z. G.; *ChemCatChem* **2016**, *8*, 3565-3569.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