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PAPER
Jason B. Benedict *et al.*
The role of atropisomers on the photo-reactivity and fatigue of diarylethene-based metal–organic frameworks

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ARTICLE

Hydrotalcite-Supported Palladium Nanoparticles as Catalyst for the Hydroarylation of Carbon-Carbon Multiple Bond

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Palladium nanoparticles supported on Mg/Ca hydrotalcites catalyze the hydroarylation reaction of different alkynes and alkenes with aryl iodides under air in MeCN. The reaction of tertiary propargylic alcohols (**1**) with aryl iodides (**2**) yields, stereoselectively, γ,γ-diarylallylic alcohols (**3**) in moderate to high yields and high selectivity. Also, the HT/Pd hydroarylation reaction with aryl iodides was attempted on norbornene and α,β-unsaturated ketones affording, respectively, exo-aryl bicyclo[2.2.1]heptanes and β-aryl ketones in moderate to high yields. All the reactions described benefit from using an heterogeneous catalyst with evident advantages in term or reaction purification and recyclability of the catalyst.

Introduction

In recent years, great focus has been devoted by academic and industrial research groups to the development of sustainable chemistry.[1] Because of their great importance, carbon-carbon cross-coupling reactions are among the most widely studied synthetic transformations. In particular, transition-metal catalyzed couplings have become a reliable and indispensable tool for the synthesis of fine chemicals and pharmaceuticals.[2] Homogeneous catalysts based on simple or sophisticated palladium-complexes resulted the catalysts of choice in many applications.[3] However, most of the highly active catalytic systems use homogeneous palladium species with air-sensitive, expensive and environmentally unfriendly phosphine ligands. Consequently, alternative catalysts[4] are emerging as a more sustainable alternative to conventional homogenous catalysts by taking advantage of their interesting properties, such as high surface area and high catalytic activity.[5] Also, immobilization of catalytically active palladium species on heterogeneous supports has drawn significant interest.[6] Different materials such as silica,[7] alumina,[8] graphene,[9] modified graphene,[10] graphene oxide,[11] reduced graphene oxide,[12] carbon/other-carbon-based materials[13] zeolites,[14] metal-organic frameworks,[15] and other were used as effective supports. Applications of palladium nanocatalysis are growing in importance in organic synthesis.[16] In this field hydrotalcite-supported palladium catalysts have been developed for the Suzuki-Miyaura-,[17,18a] Heck-,[17f,18] Sonogashira-, and Stille-type[17f] coupling reactions of aryl halides. Hydrotalcite-supported Pd-Au nanocatalysts were also found to be efficient heterogeneous catalysts for Ulmann homocoupling reactions of aryl bromides or chlorides at low-temperature.[19] Moreover, Pd nanoparticles on hydrotalcite have been explored for selective reduction of carbon-carbon multiple bonds.[20] Strategies for the controllable characterization and functionalities of Pd/hydrotalcite catalysts have been reported.[21] Since the initial disclosure by Cacchi and co-workers,[22] the palladium-catalyzed hydroarylation of carbon-carbon multiple bonds with aryl halides has been well-exploited[23] and widely used in natural products synthesis.[24] Hydrotalcite docked Rh-phosphines complexes showed good catalytic activity in the hydroarylation of alkynes[25] and 2-cyclohexen-1-one[26] with aryl boronic acids. However, to the best of our knowledge, there is no report available on the hydrotalcite-supported phosphine-free palladium nanoparticles as catalysts for the hydroarylation of carbon-carbon multiple bond with aryl halides. Considering that boronic acids usually were produced from aryl halides, their replacement with these latter derivative is attractive for industrial synthetic transformations. Moreover, it is highly desirable the application of palladium nanocatalysts as a valuable alternative to the use of the more conventional air-sensitive homogeneous palladium complexes in the hydroarylative process.

In this article, we report that the readily available HT-$PdCl_2$ and HT-Pd are very effective catalysts for the hydroarylation of alkynes/alkenes with aryl iodides under air. The catalytic process is not completely heterogeneous; rather, the reaction involves substantial homogeneous catalysis.

Results and discussion

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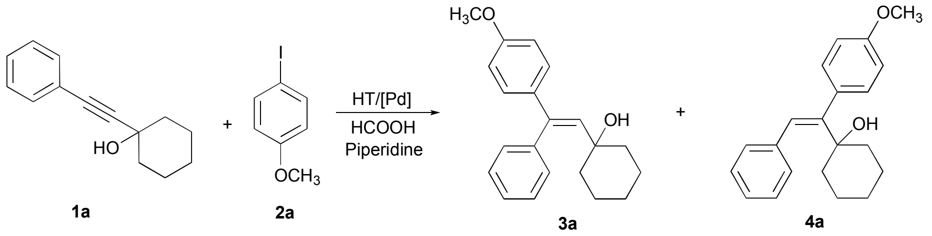
Our study started by choosing the reaction of 1-(phenylethynyl)cyclohexan-1-ol **1a** with 4-iodoanisole **2a** in the presence of hydrotalcite-supported palladium nanoparticles as a model system to explore the suitability of phosphine-free palladium nanocatalysts for the hydroarylation of unsaturated organic scaffolds (Table 1).

Table 1. Optimization of the reaction conditions of HT-Pd-catalyzed hydroarylation of propargylic alcohol **1a** with 4-Iodoanisole **2a**



Entry	HT-Pd	Solvent	Temp/time (°C/h)	Overall Yield (%)	Isomeric Ratio **3a/4a**
1	HT-Pd Mg/Al = 2/1	DMF	100/17	45	94:6
2	HT-Pd Mg/Al = 2/1	EtOH/H_2O (1/1)	120/24	--	--
3	HT-Pd Mg/Al = 2/1	CH_3CN	80/7	84	92:8
4	HT-Pd Mg/Al = 3/1	CH_3CN	80/16	93	93:7
5	HT-$PdCl_2$ Mg/Al = 2/1	CH_3CN	80/8	92	95:5

It was previously reported that arylethynyl, dialkyl carbinols **1** in the presence of the tri- or dialkylammonium formate/$Pd(OAc)_2[P(Ph_3)]_2$ can provide a convenient approach to the regioselective formation of γ,γ-diaryl allylic alcohols **3**. The isomeric β,γ-diaryl allilic alcohols **4** were isolated in only 5-10% yield.[27] The reaction was highly stereoselective leading to the *syn* addition product.[28] Steric and coordinating effects played a major role in controlling the regioselectivity. In general, other reaction parameters such as solvents, the presence or the absence as well as the features of ligands, the nature of the C_{sp2}-donor were found to influence the regiochemical outcome of the hydroarylation of unsymmetrical alkynes.[29] Indeed the palladium-catalyzed hydroarylation of propargylic alcohols provided better results in room temperature ionic liquids than in molecular solvents in terms of regioselectivity and/or reactivity.[30] Accordingly, the key role of the solvent also in the HT-palladium catalyzed hydroarylation of **1a** with **2a** is highlighted in entries 1-3 of Table 1. The reaction was carried out in the presence of 1.0 mol % of Pd, 2.4 eq. of the aryl iodide **2a**, 2.64 eq. of HCOOH and 3.4 eq. of piperidine. By contrast with the results observed in the $Pd(OAc)_2P(Ph_2)_2$ catalyzed reaction under homogeneous conditions,[27] DMF resulted a poor one in the presence of HT-Pd nanocaltalyst. In our study of the influence of the solvent simultaneously with that of the temperature, we failed to obtain the hydroarylation product with hydroxylated solvent which have been reported to be beneficial for the HT-Pd catalyzed Suzuki-Miyaura couplings.[17] The solvent of choice resulted CH_3CN which accomplished the formation of the desired **3a** in higher yield at a lower temperature (Table 1, entry 3). The HT-Pd catalyst with Mg/Al ratio of 3/1 showed slightly higher activity than that with Mg/Al of 2/1 (Table 1, entry 4), though the differences were not substantial. A good performance was also observed with the HT-$PdCl_2$ (Mg/Al = 2/1) catalyst that very likely is prone to undergo fast conversion in HT-Pd under the reaction conditions. Catalyst recycling tests were conducted. After the reaction, catalyst HT-Pd (Mg/Al = 1/2) was isolated by filtration, washed, and dried at a low pressure for reuse. No significant loss of activity was observed after two re-uses (Table 2).

Table 2. HT-Pd (Mg/Al = 2/1) catalyst recycling in the hydroarylation reaction of **1a** with **2a**

1st run [overall yield (%)]	2nd run [overall yield (%)]	3rd run [overall yield (%)]
84	84	84

To establish unambiguously whether the reaction proceeds exclusively on the heterogeneous surface, in the homogeneous phase or partly on the heterogeneous surface/homogeneous phase, the reaction of **1a** with **2a** in CH_3CN at 80 °C in the presence of HT-Pd or HT-$PdCl_2$ was stopped at a low conversion level, and while the reaction mixture was still hot,

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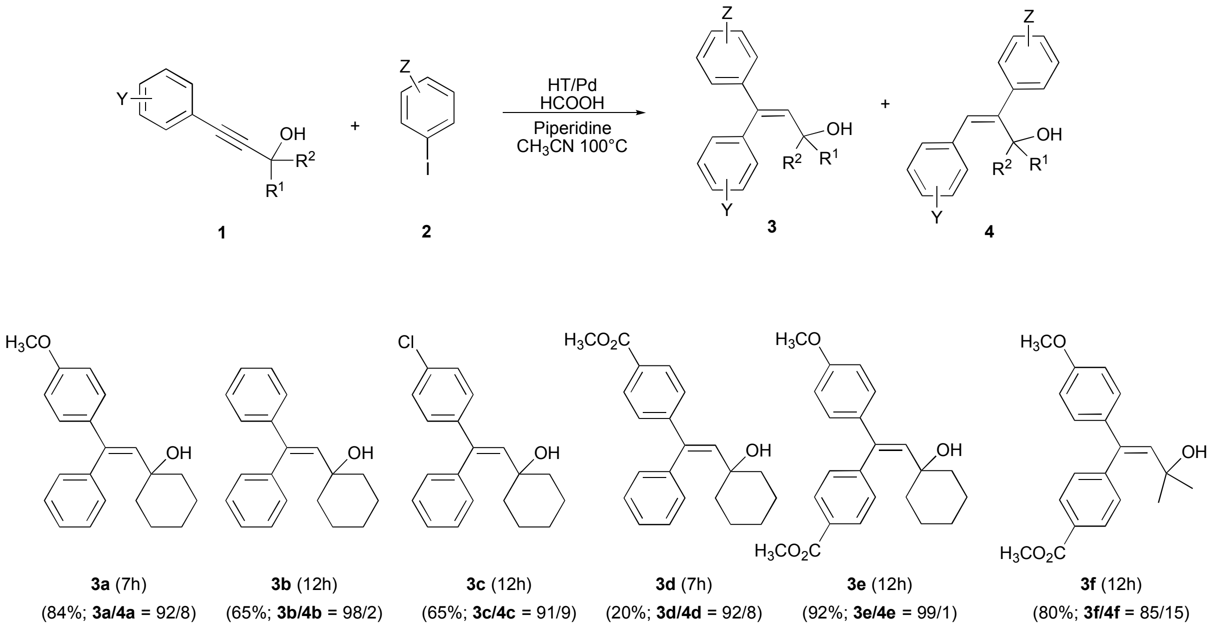
the catalyst was rapidly filtered, and the reaction was allowed to proceed overnight. The results obtained, under these conditions, revealed that the filtrate was catalytically active and the reaction continued in the absence of the HT-palladium catalyst. This indicates that partial leaching of Pd from the solid catalyst to the solution should involve substantial homogeneous catalysis. Nevertheless, HT-Pd catalyst could be reused and is able to remain catalytically active in the hydroarylation reaction albeit subject to leaching. Very likely, cooling the reaction mass causes fast deposition of nanoparticles onto the hydrotalcite support, achieving the efficient recycle of the catalyst.

On the basis of the above studies, the hydroarylation reaction was extended to other propargylic alcohols and aryl iodides. According to previous findings[28,30] and related reactions,[31] tertiary propargylic alcohols gave, as the main product, the γ,γ-diarylallylic alcohols **3** containing the new carbon-carbon bond close to the aryl substituent of the starting alkyne as consequence of the prevailing of the directing effect of the tertiary hydroxyl group (Scheme 1). The isomeric β,γ-diarylallylic alcohols were obtained only in 1-15 % yield. Variable amounts of the starting alkyne **1** were recovered. Hydroarylation products were obtained in similar yields with those observed by carrying out the reaction in the presence of homogeneous palladium catalysts. Aryl iodides bearing strong withdrawing substituents are prone to undergo, under the above mentioned reaction conditions, faster reduction of the C-I bond[32] than the carbopalladation step leading to the formation of the corresponding allylic alcohol.

With the secondary propargylic alcohol and the less branched primary propargylic alcohol, according to the results observed under homogeneous conditions, a worsening of the regioselectivity occurs. Furthermore, with the secondary propargylic alcohol **1g**, in addition to the isomeric alcohol **4g**, a *E*/*Z* mixture of the α,β-unsaturated ketone **5** was isolated in significant yield. The formation of this latter derivative can be accounted by assuming that the β-elimination of HPdI species is faster than the iodide formate exchange in the intermediate **A.** The subsequent isomerization of the resultant allenyl alcohol generates **5**. A reversion of the regioselective outcome prevailed with the less branched primary propargylic alcohol **1h**. In this case, the phenyl group of the starting alkyne, rather than the hydroxyl group, apparently directs the regioselective addition of the arylpalladium iodide over the C-C triple bond (Scheme 2).

The formation of the diarylacetylene derivatives was also previously reported to occur by reacting aryl iodides with trimethylsilylacetylenes in the presence of an excess of sodium methoxide under refluxing methanol by using $Pd(PPh_3)_4$ as the catalyst.[33] As expected, the formation of the trisubstituted alkene **7** occurred in good yield by reacting the diphenylacetylene **6** with the 4-iodotoluene **2f** under the present reaction conditions (Scheme 3).[34]



Scheme 1. HT/Pd catalyzed hydroarylation of tertiary propargylic alcohols with aryl iodides.

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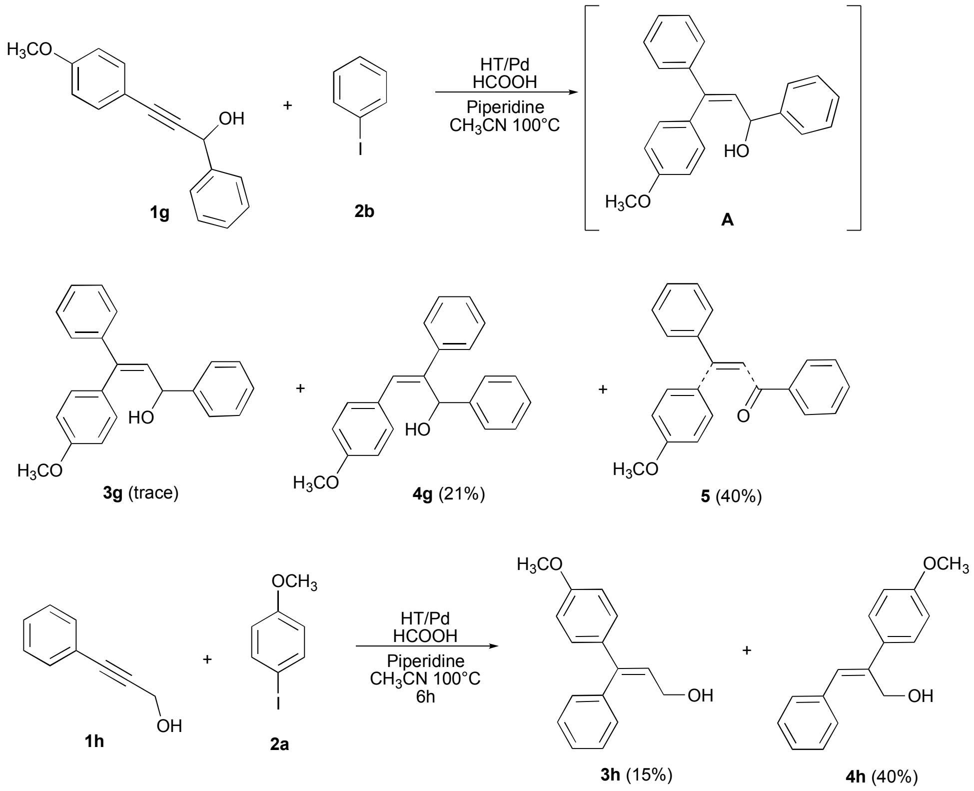
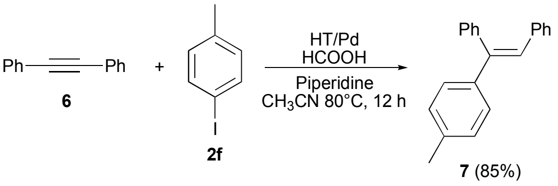


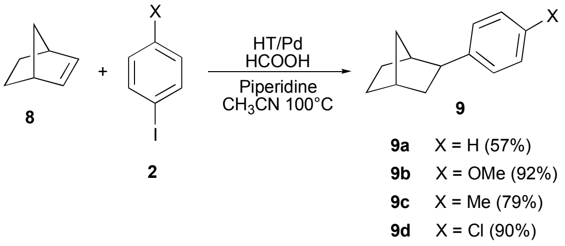
Scheme 2. HT-Pd catalyzed hydroarylation of secondary and primary propargylic alcohols with aryl iodides.

The palladium catalyzed hydroarylation of norbornenes with aryl halides,[35] triflates,[36] and arenediazonium salts[37] has proved to be an effective method for the synthesis of bicyclo[2.2.1]heptanes and related compounds with an aryl substituent in the exo- position.[38]



Scheme 3. HT-Pd Catalyzed Hydroarylation of Diphenylacetylene **6** with 4-Iodotoluene **2f**.

It has been used in the total synthesis of the potent nonopiate analgesic alkaloid epibatedine,[39] a compound isolated from the skin of the Ecuadorian frog, Epipedobates tricolor, as well as in different approaches to its analogues.[40] Enantioselective hydroarylations of norbornene derivatives have also been described.[41] We envisaged that the use of palladium naoparticles as alternative catalysts would widen significantly its synthetic scope. Indeed, the HT-Pd catalyzed hydroarylation of norbornene with aryl iodides resulted a very effective procedure leading stereoselectively to the targed adducts (Scheme 4).



Scheme 4. HT-Pd Catalyzed Hydroarylation of Norbornenes **8** with Aryl Iodides **2**.

The significant interest towards the development of practical approach to the conjugate addition type reaction of aryl iodides with α,β-unsaturated ketones,[42] encouraged our exploration of the HT-Pd catalyzed version. The HT-Pd catalytic activity is comparable with that of $Pd(OAc)_2$[42b] and Pd-NHC catalysts (Scheme 5).[42c]

Conclusions

In conclusions, we have developed a new methodology for the palladium catalysed hydroarylation reaction of carbon-carbon multiple bonds. The method implies the use of hydrotalcite-supported palladium nanoparticles with all the evident advantages derived by the use of a heterogeneous catalyst.

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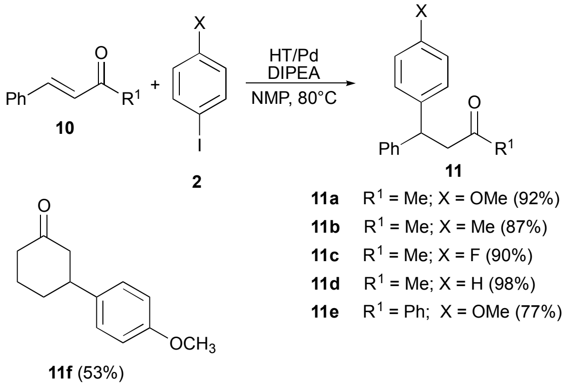

Scheme 5. HT-Pd Catalyzed Hydroarylation of α,β-Unsaturated Ketones **10** with Aryl Iodides **2**.

Reaction yields and selectivity are, in general, very goods. The methods is very versatile and the reaction can be carried out on primary, secondary and tertiary propargyl alcohols, diphenylacetilene, norbornene and α,β-unsaturated carbonyl compounds.

Experimental

General

All commercially available reagents were used without further purification unless otherwise stated. Reactions were monitored by analytical thin-layer chromatography (TLC) using silica gel 60 F254 precoated glass plates (0.25 mm thickness) and visualized using UV light, iodide, and vanillin reagent. Flash column chromatography was performed on a silica gel (230–400 mesh). ^{1}H NMR and ^{13}C NMR were recorded on a 400 MHz nuclear magnetic resonance spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR).

Synthesis of HT/Pd (Mg/Al 2:1) and HT/Pd (Mg/Al 3:1)

HT were prepared according to ref.17b (Mg/Al2:1) and ref.43 HT/Pd (palladium content 1.0%$_{w/w}$)was obtained according to ref.17b using $PdCl_2$ as palladium source.

General Procedure for the Hydroarylation Reaction

To a stirred solution of aryl iodide (2.54mmol) and piperidine (3.57 mmol) in MeCN (2 mL) were added propargylic alcohol (1.0 mmol), HT/Pd(0) (20 mg) and formic acid (2.77 mmol). The mixture was stirred at 80° C for the required time, then the mixture was filtered on celite with AcOEt and concentrated. The residue was purified by flash chromatography.

Conflicts of interest

There are no conflicts of interest to declare

References

1 R. A. Sheldon, *Green Chem.* **2017**, *19*, 18.
2 A. O. King, N. Yasuda, Palladium-catalyzed Cross-Coupling Reactions in the Synthesis of Pharmaceuticals. In *Organometallics in Process Chemistry*, Larsen, R. D. Ed.; Springer: Berlin, Germany, 2004; pp. 205.
3 *(a)* C. C. C. J. Seechurn, M. O. Kitching, T. J. Colcot, V. Snieckus, *Angew. Chem. Int. Ed.* **2012,** *51*, 5062. *(b)* J. Magano, J. R. Dunetz, *Chem. Rev.* **2011,** *111*, 2177.
4 V. Polshettiwar, R. S. Varma, *Green Chem.* **2010**, *12*, 743.
5 V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J. M. Basset, *Chem. Rev.* **2011**, *111*, 3036.
6 *(a)* J. C. Park, E. Heo, A. Kim, M. Kim, K. H. Park, H. Song, *J. Phys. Chem. C* **2011**, *115*, 15772; *(b)* J. Zhi, D. Song, Z. Li, X. Lei, A. Hu, *Chem. Commun.* **2011**, *47*, 10707.
7 *(a)* X. Chen, Y. Hou, H. Wang, Y. Cao, J. He, *J. Phys. Chem. C* **2008**, *112*, 8172; *(b)* B. Cornelio, G. A. Rance, M. Laronze-Cochard, A. Fontana, J. Sapi, A. N. Khlobystov, *J. Mater. Chem. A* **2013**, *1*, 8737.
8 *(a)* A. M. S. Hossain, A. Balbín, R. S. Erami, S. Prashar, M. Fajardo, S. Gómez-Ruiz, *Inorg. Chim. Acta* **2017**, *455*, 645; *(b)* A. P. Kumar, B. P. Kumar, A. B. V. K. Kumar, B. T. Huy, Y. -I. Lee, *Appl. Surface Sci.* **2013**, *265*, 500.
9 *(a)* M. Gómez-Martínez, E. Buxaderas, I. M. Pastor, D. A. Alonso, *J. Mol. Catal. A: Chem.* **2015**, 404–405, 1; *(b)* A. R. Siamaki, A. E. R. S. Khder, V. Abdelsayed, M. S. El-Shall, B. F. Gupton, *J. Catal.* **2011**, *279*, 1.
10 *(a)* S. K. Movahed, R. Esmatpoursalmani, A. Bazgir, *RSC Adv.* **2014**, 4, 14586; *(b)* H. Joshi, K. N. Sharma, A. K. Sharma, A. K. Singh, *Nanoscale* **2014**, *6*, 4588.
11 S.-I. Yamamoto, H. Kinoshita, H. Hashimoto, Y. Nishina, *Nanoscale* **2014**, 6, 6501.
12 J. Lin, T. Mei, M. Lv, C. Zhang, Z. Zhao, X. Wang, *RSC Adv.* **2014**, *4*, 29563.
13 *(a)* T. Hattori, A. Tsubone, Y. Sawama, Y. Monguchi, H. Sajiki, *Catalysts* **2015**, *5*, 18. *(b)* A. Corma, H. Garcia, A. Leyva, *Appl. Catal. A* **2002**, *236*, 179; *(c)* K. Okumura, T. Tomiyama, S. Okuda, H. Yoshida, M. Niwa, *J. Catal.* **2010**, *273*, 156.
14 *(a)* F. X. L. Xamena, A. Abad, A. Corma, H.Garcia, *J. Catal.* **2007**, *250*, 294; *(b)* H. Choudhary, S. Nishimura, K. Ebitani, *J. Mater. Chem. A* **2014**, *2*, 18687; *(c)* A. Dhakshinamoorthy, A. M. Asiri, H. Garcia, *Chem. Soc. Rev.* **2015**, *44*, 1922.
15 *(a)* C. Ornelas, J. Diallo, A. K. Ruiz, D. Astruc, *Adv. Synth. Catal.* **2009**, *351*, 2147; *(b)* M. Lamblin, L. Nassar-Hardy, J.-C. Hierso, E. Fouquet, F.-X. Felpin, *Adv. Synth. Catal.* **2010**, *352*, 33.
16 R. S. Erami, D. Díaz-García, S. Prashar, A. Rodríguez-Diéguez, M. Fajardo, M. Amirnasr, S. Gómez-Ruiz, *Catalysts* **2017**, *7*, 76.
17 *(a)* H. Choudhary, J. Jia, S. Nishimura, K. Ebitani, *Asian J. Org. Chem.* **2017**, *6*, 274; *(b)* M. I. Burrueco, M. Mora, C. Jiménez-Sanchidrián, J. R. Ruiz, *Applied Catalysis A: General* **2014**, *485*, 196; *(c)* M. Mora, C. Jiménez-Sanchidrián, J. R. Ruiz, *J. Mol. Catal. A: Chemical* **2008**, *285*, 79; *(d)* M. Mora, C. Jiménez-Sanchidrián, J. R. Ruiz, *J. Colloid and Interface Sience* **2006**, *302*, 568; *(e)* C. Jiménez-Sanchidrián, M. Mora, J. R. Ruiz, *Catal. Comm.* **2006**, *7*, 1025; *(f)* B. M. Choudary, S. Madhi, N. S. Chowdari, M. L. Kantam, B. Sreedhar, *J. Am. Chem. Soc.* **2002**, *124*, 14127; *(g)* B. Van Vaerenbergh, K. De Vlieger, K. Claeys, G. Vanhoutte, J. De Clercq, P. Vermeir, A. Verberckmoes, *Appl. Catal. A-Gen.* **2018**, *550*, 236.
18 *(a)* M. Martínez, R. Ocampo, L. A. Rios, A. Ramírez, O. Giraldo, *J. Braz. Chem. Soc.* **2011**, *22*, 2322; *(b)* H. Zhou, G. L. Zhuo, X. Z. Jiang, *J. Mol. Catal. A: Chemical* **2006**, *248*, 26; *(c)* T. H. Bennur, A. Ramani, R. Bal, B. M. Chanda, S. Sivasanker, *Catal. Comm.* **2002**, *3*, 493.
19 J. Wang, A. Xu, M. Jia, S. Bai, X. Cheng, B. Zhaorigetu, *New J. Chem.,* **2017**, *41*, 1905.

View Article Online
DOI: 10.1039/C7NJ04046F

20 *(a)* Y. He, J. Fan, J. Feng, C. Luo, P. Yang, D. Li, *J. Catal.* **2015**, *331*, 118; *(b)* M. Lakshimi Kantam, T. Parsharamulu, S. V. J. Manorama, *Mol. Catal. A: Chemical* **2012**, *365*, 115.

21 *(a)* Z. Wu, Q. Zhu, C. Shen, T. Tan, *ACS Omega* **2016**, *1*, 498; *(b)* D. Naresh, V. P. Kumar, M. Harisekhar, N. Nagarju, B. Putrakumar, K. V. R. Chary, *Applied Surface Science* **2014**, *314*, 199.

22 *(a)* S. Cacchi, A. Arcadi, *J. Org. Chem.* **1983**, *48*, 4236; *(b)* A. Amorese, A. Arcadi, E. Bernocchi, S. Cacchi, S. Cerrini, W. Fedeli, G. Ortar, *Tetrahedron* **1989**, *45*, 813; *(c)* S. Cacchi, *Pure Appl. Chem.* **1990**, 62, 713; *(d)* A. Arcadi, S. Cacchi, G. Fabrizi, F. Marinelli, P. Pace, *Tetrahedron* **1996**, *52*,6983.

23 (a) S. Raoufmoghaddam, S. Mannathan, A. J. Minnaard, J. G. de Vries, J. N. H. Reek, *Chem. Eur. J.* **2015**, *21*, 18811; (b) A. L. Gottumukkala, J. G. de Vries, A. J. Minnaard, *Chem. Eur. J.* **2011**, *17*, 3091.

24 For selected examples, see: *(a)* S. Diethelm, E. M. Carreira, *J. Am. Chem. Soc.* **2013**, *135*, 8500; *(b)* J. Chen, J. Xie, D. Bao, S. Liu, Q. Zhou, *Org. Lett.* **2012**, *14*, 2714; *(c)* P. Gao, S. P. Cook, *Org. Lett.* **2012**, *14*, 3340; *(d)* R. Peng, M. S. Van Nieuwenhze, *Org. Lett.* **2012**, *14*, 1962; *(e)* A. B. Dounay, P. G. Humphreys, L. E. Overman, A. D. Wrobleski, *J. Am. Chem. Soc.* **2008**, *130*, 5368; *(f)* Z. Li, E. B. Watkins, H. Liu, A. G. Chittiboyina, P. B. Carvalho, M. A. Avery, *J. Org. Chem.* **2008**, *73*, 7764; *(g)* M. Ichikawa, M. Takahashi, S. Aoyagi, C. Kibayashi, *J. Am. Chem. Soc.* **2004**, *126*, 16553; *(h)* B. M. Trost, O. R. Thiel, H.-C. Tsui, *J. Am. Chem. Soc.* **2002**, *124*, 11616; *(i)* K. Lee, , J. K. Cha, *J. Am. Chem. Soc.* **2001**, *123*, 5590; *(j)* D. Solé, J. Bonjoch, S. García-Rubio, E. Peidrl, J. Bosch, *Angew. Chem. Int. Ed.* **1999**, *38*, 395; *(k)* B. M. Trost, F. D. Toste, *J. Am. Chem. Soc.* **1999**, *121*, 3543; *(l)* S. C. Clayton, A. C. Regan, *Tetrahedron Lett.* **1993**, *34*, 7493; *(m)* B. Schmidt, H. M. R. Hoffmann, *Tetrahedron* **1991**, *47*, 9357.

25 F. Neaţu, M. Ciobanu, L. E. Ştoflea, L. Frunză, V. I, Părvulescu, V. Michelet, *Catalysis Today* **2015**, *247*, 155.

26 F. Neaţu, M. Besnea, V. G. Komvokis, J.-P. Genêt, V. Michelet, K. S. Triantafyllidis, V. I. Părvulescu, *Catalysis Today* **2008**, *139*, 161.

27 A. Arcadi, S. Cacchi, F.Marinelli *Tetrahedron* **1985**, *41*, 5121.

28 A. Arcadi, S. Cacchi, S. Iannelli, F. Marinelli, M. Nardelli, *Gazz. Chim. It.* **1986**, *116*, 725.

29 L. H. Hay, T. M. Koenig, F. O. Ginah, J. D. Copp, D. Mitchell, *J. Org. Chem.* **1998**, *63*, 5050.

30 S. Cacchi, G. Fabrizi, A. Goggiamani *J. Mol. Catal. A: Chemical* **2004**, *214*, 57.

31 *(a)* A. Arcadi, S. Cacchi, G. Fabrizi, F. Marinelli, P. Pace, *Eur. J. Org. Chem.* **1999**, 3305; *(b)* A. Arcadi, E. Bernocchi, A. Burini, S. Cacchi, F. Marinelli, B. Pietroni, *Tetrahedron Lett.* **1989**, *30*, 3465; *(c)* A. Arcadi, E. Bernocchi, A. Burini, S. Cacchi, F. Marinelli, B. Pietroni, *Tetrahedron* **1988**, *44*, 481.

32 N. A. Cortese, R. F. Heck, *J. Org. Chem.* **1977**, *42*, 3491.

33 M.-J. Wu, L.-M. Wei, C.-F. Lin, S.-P. Leou, L.-L. Wei, *Tetrahedron* **2001**, *57*, 7839.

34 S. Cacchi, M. Felici, B. Pietroni, *Tetrahedron Lett.* **1984**, 3137.

35 *(a)* A. Arcadi, F. Marinelli, E. Bernocchi, S. Cacchi, G. Ortar, *J. Organomet. Chem.* **1989**, *368*, 249. *(b)* R. C. Larock, P. L. Johnson, *Chem. Commun.* **1989**, 1368.

36 P. Mayo, W. Tam, Tetrahedron **2002**, 58, 9527.

37 G. Bartolo, S. Cacchi, G. Fabrizi, A. Goggiamani, *Synlett* **2008**, 2508.

38 A. Wållberg, G. Magnusson, *Tetrahedron* **2000**, *56*, 8533.

39 S. C. Clayton, A. C. Regan, *Tetrahedron Lett.* **1993**, *34*, 7493.

40 *(a)* F. I. Carroll, L. E. Brieaddy, H. A. Navarro, M. I. Damaj, B. R. Martin, *J. Med. Chem.* **2005**, *48*, 7491; *(b)* A. Kasyan, C. Wagner, M. E. Maier, *Tetrahedron* **1998**, *54*, 8047; *(c)* D. Bai, R. Xu, G. Chu, X. Zhu, *J. Org. Chem.* **1996**, 61, 4600.

41 (a) H. Brunner, K. Kramler, *Synthesis* **1991**, 1121; (b) S. Sakuraba, K. Awano, K. Achiwa, *Synlett* **1994**, 291; (c) S. Sakuraba, T. Okada, T. Morimoto, K. Achiwa, *Chem. Pharm. Bull.* **1995**, *43*, 927; (d) X.-Y. Wu, H.-D. Xu, Q.-L. Zhoua, A. S. C. Chan, *Tetrahedron: Asymmetry* **2000**, *11*, 1255; (e) X.-Y. Wu, H.-D. Xu, F.-Y. Tang, Q.-L. Zhou, *Tetrahedron: Asymmetry* **2001**, *12*, 2565.

42 *(a)* S. Mannathan, S. Raoufmoghaddam, J. N. H. Reek, J. G. de Vries, A. J. Minnaard, *ChemCatChem.* **2017**, *9*, 551; *(b)* Mannathan, S.; Raoufmoghaddam, S.; Reek, J. N. H.; de Vries J. G.; Minnaard, A. J. *ChemCatChem.* **2015**, *7*, 3923; *(c)* S. Raoufmoghaddam, S. Mannathan, A. Minnaard, J. G. de Vries, J. N. H. Reek, *Chem. Eur. J.* **2015**, *21*, 18811; A. L. Gottumukkala, J. G. de Vries, A. Minnaard, *Chem. Eur. J.* **2011**, *17*, 3091; *(d)* A. Amorese, A. Arcadi, E. Bernocchi, S. Cacchi, S. Cerrini, M. Fedeli, G. Ortar, *Tetrahedron* **1989**, *45*, 813; (e) S.; Cacchi, A. Arcadi, *J. Org. Chem.* **1983**, *48*, 4236.

43 Qi. Tao, Y. Zhang, X. Zhang, P. Yuan, H. He, *J. Solid State Chem.* **2006**, 179, 3, 708.

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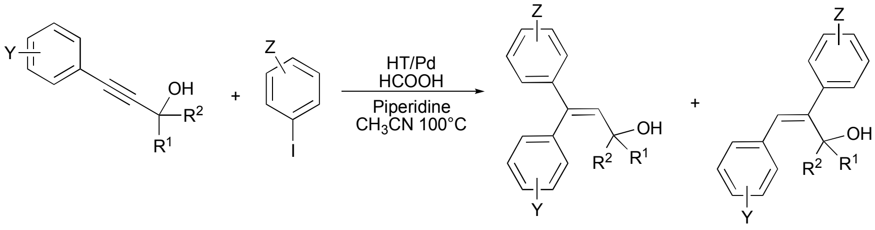
Hydrotalcite-Supported Palladium Nanoparticles as Catalyst for the Hydroarylation of Carbon-Carbon Multiple Bond



Palladium nanoparticles supported on hydrotalcites catalyze the hydroarylation reaction of Carbon-Carbon Multiple Bond.