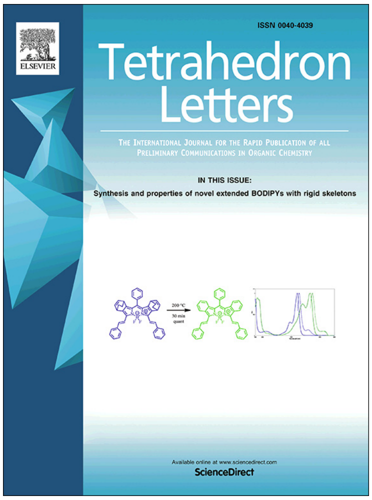


Hydroarylation of alkynes and alkenes through alumina-sulfuric acid catalyzed regioselective C-C bond formation

Amit Pramanik, Avishek Ghatak, Sagar Khan, Sanjay Bhar

PII: S0040-4039(19)30207-2
DOI: https://doi.org/10.1016/j.tetlet.2019.03.006
Reference: TETL 50647

To appear in: *Tetrahedron Letters*

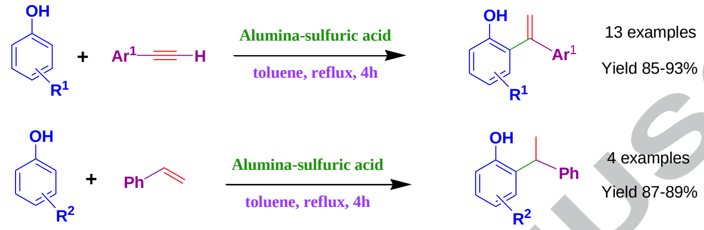
Received Date: 4 January 2019
Revised Date: 27 February 2019
Accepted Date: 3 March 2019

Please cite this article as: Pramanik, A., Ghatak, A., Khan, S., Bhar, S., Hydroarylation of alkynes and alkenes through alumina-sulfuric acid catalyzed regioselective C-C bond formation, *Tetrahedron Letters* (2019), doi: https://doi.org/10.1016/j.tetlet.2019.03.006

Graphical Abstract

Hydroarylation of alkynes and alkenes through alumina-sulfuric acid catalyzed regioselective C-C bond formation

Amit Pramanik, Avishek Ghatak, Sagar Khan and Sanjay Bhar*



Tetrahedron Letters
journal homepage: www.elsevier.com

Hydroarylation of alkynes and alkenes through alumina-sulfuric acid catalyzed regioselective C-C bond formation

Amit Pramanik,[a] Avishek Ghatak,[b] Sagar Khan[c] and Sanjay Bhar[c,*]

[a] *Department of Chemistry, Taki Government College, Taki, North 24 Pgs, Pin-743 429, India*
[b] *Department of Chemistry, Dr. A.P.J Abdul Kalam Govt. College, Newtown, Kolkata- 700156, India*
[c] *Department of Chemistry, Organic Chemistry Section, Jadavpur University, Kolkata- 700 032, India*
e-mail: sanjaybharin@yahoo.com; sanjay.bhar@jadavpuruniversity.in

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Catalysis
Regioselection
supported reagents/reactions
Sulfuric acid and derivatives

ABSTRACT

A highly atom-efficient synthetic protocol for hydroarylation of terminal-aryl alkynes and styrene through the regioselective C-C bond formation via the electrophilic addition of naphthols and substituted phenols has been developed using alumina-sulfuric acid as a heterogeneous supported solid acid catalyst. This methodology shows excellent regioselectivity and affords the desired product in good to excellent yield. The heterogeneous catalyst can also be recycled efficiently without much loss of activity.

1. Introduction

Catalytic hydroarylation of alkenes and acetylenes is one of the fascinating and useful tools for C-C bond forming reaction as they lead to the construction of the core structure of a number of biologically active compounds such as isocombretastatin A-4 (*iso* CA-4),[1] avrainvilleol, haplopappin, papaverine, and phenprocoumone (Figure 1).[2] Diarylmethanes are widely used for the preparation of fluorenyl-based electroactive and photoactive oligomers and polymers.[3] In addition, these 1,1-disubstituted alkenes are frequently used as key starting materials in the synthesis of fine chemicals,[4a-4c] agrochemicals,[4d] polymers,[5] and pharmaceutically important compounds.[6]

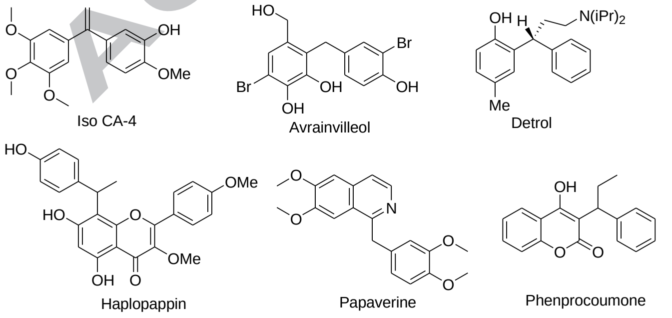


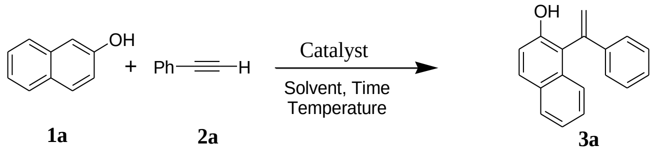
Figure1: Some important biologically active 1,1- diarylalkenes and 1,1-diarylalkanes

The Friedel-Crafts reaction[7] and hydroarylation[8-9] of olefins and alkynes are commonly employed for the construction of the aforesaid molecular frameworks. In recent times, various metal-promoted hydroarylation protocols of alkenes and alkynes have been reported using $SnCl_4/Bu_3N$ in acetonitrile,[8a] Y-type zeolite (HSZ-360) in 1,2-dichlorobenzene,[8b] $FeCl_3$ in DCM,[8c] $Bi(OTf)_3$ in cyclohexane,[8d] $GaCl_3$ in toluene,[8e] different bimetallic catalysts like Fe-Al-MCM-41 in cyclohexane,[8f] Fe-Al-KIT-5 in cyclohexane,[8g] iron containing mesoporous aluminosilicate,[8h] $In(OTf)_3$ under microwave irradiation[8i] as well as organometallic complexes like Ir(I) diphosphine complexes,[9a] $Re_2(CO)_{10}$ in toluene[9b] and many others. Most of the aforesaid reagents suffer from one or more drawbacks like lower selectivity, over-alkylation, large amount of salt formation, moisture-sensitivity, toxicity, involvement of metals, prolonged reaction time and utilization of toxic organic solvents. Although iron catalysts are comparatively less toxic but they often require long reaction time, activating groups and protection and de-protection steps.[10] Therefore, development of a cost-effective, operationally simple, eco-compatible transition metal-free efficient catalytic system for the hydroarylation reaction is of great demand in the perspective of present environmental scenario.

In recent years, organic reactions using heterogeneous acid catalysts have gained much interest[11] and often found as better alternatives than the similar conventional homogeneous protocols[12] because of cost effectiveness, operational simplicity, reusability and environmental benefits. Alumina–sulfuric acid[13] has been reported in recent past but not exploited much in organic synthesis. As a part of our ongoing research programme to unravel novel catalytic attributes of alumina-sulfuric acid,[14] we disclose herein a convenient protocol for the synthesis of novel 1,1-diarylalkene and 1,1-diarylalkane moieties from naphthols and differently substituted phenols with a wide substrate scope using alumina-sulfuric acid as an easily accessible, heterogeneous and reusable transition metal-free solid acid catalyst.

2. Results and discussion

When 2-naphthol **1a** (1.5 mmol) was treated with phenylacetylene **2a** (1 mmol) in a specified solvent in the presence of alumina-sulfuric acid under ambient atmosphere, hydroarylated product **3a** was obtained (Scheme 1). The reaction was carried out with different solvents, temperatures and catalysts to obtain the optimum condition. The results are summarised in Table 1.



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

Scheme 1. Reaction between 2-naphthol and phenylacetylene

There was no reaction either at room temperature or at elevated temperature (120 °C) in the absence of any catalyst, the unreacted substrates were isolated intact (Table 1, entries 1 and 2). When alumina-sulfuric acid was used as a catalyst at room temperature, a trace amount of product was isolated after 20h (Table 1, entry 3). But when the reaction was carried out at 80°C the yield of the isolated product **3a** was increased to 67% (Table 1, entry 4). Extent of conversion and isolated yield of the product were further improved when the reaction was carried out under reflux (120°C) (Table 1, entries 5 and 6). This reaction was extremely sluggish in protic polar solvents (ethanol and water, Table 1, entries 7 and 8) as well as aprotic polar solvents (DMF and DMSO, Table 1, entries 9 and 10) even under reflux. It also failed in DCM, CH_3CN and $MeNO_2$ at ambient temperature but occurred at refluxing condition albeit with moderate conversions (Table 1, entries 11–16). Thus, toluene, an aromatic non-polar solvent, has come out as the best choice as a medium for this reaction.

In order to establish the catalytic efficacy of the alumina-sulfuric acid, the coupling reaction between **1a** and **2a** was carried out using a wide variety of catalysts in toluene at 120 °C. HY-zeolite and neutral alumina failed to afford the hydroarylated product **3a** (Table 1, entries 17–18). Although a little amount of conversion of **2a** was noted in the presence of conc. H_2SO_4 (Table 1, entry 19) but the desired product **3a** could not be isolated probably due to acid-catalyzed polymerization the **2a** and **3a**. Even conc. H_2SO_4 supported on neutral Al_2O_3 (Table 1, entry 20) could not promote the reaction to a satisfactory level. Some other silica gel-supported acids (Table 1, entries 21–23) afforded **3a** in poor yields due to various side reactions like polyalkylation and polymeric decomposition. Only $NaHSO_4 – SiO_2$ afforded 59% of **3a** (Table 1, entry 23). The reaction between **1a** and **2a** totally failed to produce any product in the presence of chlorosulfonic acid alone without alumina support. Thus the importance alumina-sulfuric acid as an effective supported Bronsted acid catalyst for this hydroarylation reaction in terms of stability and catalytic activity was firmly established.

The effect of catalyst loading was also studied (Table 2), where the optimum amount of alumina-sulfuric acid (with H^+ concentration of $3x10^{-4}$ molgm^{-1} of the support[14b]) was found to be 100 mg per 1 mmol of **2a**. Highest conversion of **2a** and maximum yield of **3a** were achieved using **1a** and **2a** in the molar ratio of 1.5:1. Therefore, optimum condition for the present protocol has been laid down in Scheme 2.

Table 1. Optimization of reaction condition

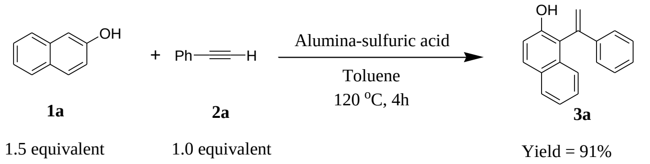
Entry[a]	Catalyst	Solvent	Temp. (°C)	Time (h)	Conversion of **2a**[b] (%)	Yield of **3a**[c] (%)
1	None	Toluene	rt	10	0	NR[d]
2	None	Toluene	120	10	0	NR[d]
3	Alumina–sulfuric acid	Toluene	rt	20	0	trace
4	Alumina–sulfuric acid	Toluene	80	8	75	67
5	Alumina–sulfuric acid	Toluene	120	3	79	69
6	Alumina–sulfuric acid	Toluene	120	4	100	91
7	Alumina–sulfuric acid	EtOH	80	10	5	LR[d]
8	Alumina–sulfuric acid	H_2O	100	10	9	LR[d]
9	Alumina–sulfuric acid	DMF	153	10	7	LR[d]
10	Alumina–sulfuric acid	DMSO	189	10	10	LR[d]
11	Alumina–sulfuric acid	MeCN	rt	10	0	NR[d]
12	Alumina–sulfuric acid	DCM	rt	10	0	NR[d]
13	Alumina–sulfuric acid	CH_3NO_2	rt	10	0	NR[d]
14	Alumina–sulfuric acid	MeCN	82	10	5	LR[d]
15	Alumina–sulfuric acid	DCM	52	10	53	30
16	Alumina–sulfuric acid	CH_3NO_2	80	10	29	15
17	HY Zeolite	Toluene	120	4	0	NR[d]
18	Neutral Al_2O_3	Toluene	120	4	0	NR[d]
19	Conc. H_2SO_4	Toluene	120	4	95	--[e]
20	Conc. H_2SO_4 on Al_2O_3	Toluene	120	4	50	6
21	$HClO_4 – SiO_2$	Toluene	120	4	33.5	26
22	PPA – SiO_2	Toluene	120	4	13.7	7
23	$NaHSO_4 – SiO_2$	Toluene	120	4	72.9	59

[a] Reaction condition: 2-naphthol **1a** (1.5 mmol), phenylacetylene **2a** (1 mmol), catalyst (100 mg), solvents (5 ml). [b] Percentage of conversion of phenylacetylene **2a** was calculated by ^1H NMR (300 MHz). [c] Isolated yield of the product. [d] unreacted substrates were isolated almost exclusively.
[e] the polymerized materials.

Table 2. Effect of the catalyst loading towards the model reaction

Entry[a]	Amount of catalyst (mg)	Isolated yield (%)
1	50	63
2	75	74
3	100	91
4	150	90

[a] Reactions condition: **1a** (1.5 mmol), **2a** (1 mmol), and alumina-sulfuric acid in dry toluene at 120°C.



Scheme 2. Optimized reaction between 2-naphthol (**1a**) and phenylacetylene (**2a**) (Reactions condition: **1a** (1.5 mmol), **2a** (1 mmol), and alumina-sulfuric acid (100 mg).

After each cycle, the reaction mixture was cooled to ambient temperature, and the catalyst was separated by simple filtration. Recovered catalyst was successively washed with toluene, ethanol and dried at 130ºC for 1 h. The catalyst was recycled successively up to eight runs without significant loss of its catalytic activity (Figure 2). Thus the alumina-sulfuric acid has been found to be more effective and efficient compared to many recently reported laboriously prepared catalysts, for example, sulfonic acid functionalized hyperbranched poly (ether sulfone) [SHBPES] grafted on carbon black[15] in terms of operational simplicity and recyclability.

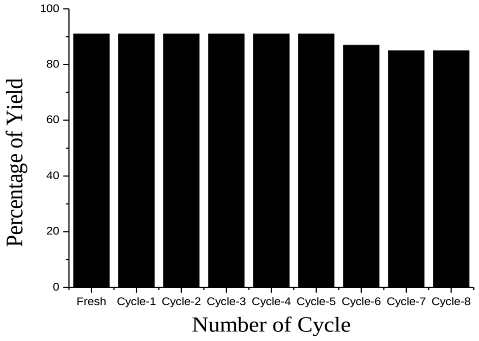


Figure 2. Recycling of the alumina-sulfuric acid

The comparative profile of the atom composition (Table 3) obtained from the EDX spectra (Supporting information) of freshly prepared and recycled alumina-sulfuric acid provided further support to substantiate the efficacy and recyclability of the present catalyst. Extremely marginal loss of sulphur from the supported catalyst during the reaction and recycling process was noted. So it can be concluded that sulphur containing -SO_3H moiety remained covalently anchored and firmly immobilized with the alumina support throughout the entire process.

Table 3. Comparative profile of the atom compositions according to EDX measurements

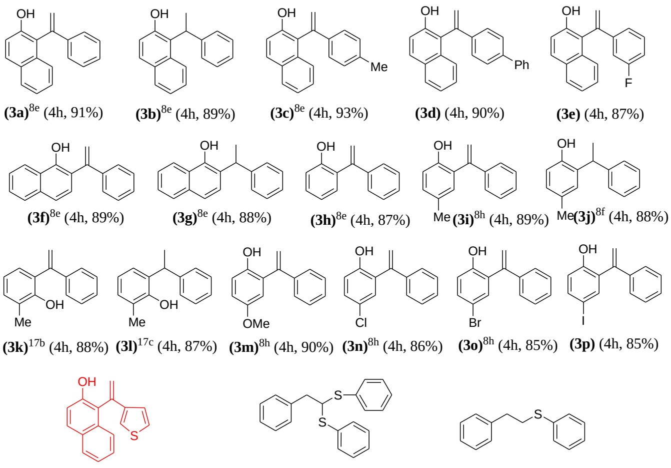
Support	Element	Weight%	Atomic%	Total
Alumina – sulfuric acid (freshly prepared)	O K	54.69	67.14	100.0
	Al K	44.20	32.18	
	S K	1.11	0.68	
Alumina – sulfuric acid (after first recycling)	O K	54.66	67.16	100.0
	Al K	44.23	32.16	
	S K	1.11	0.68	
Alumina – sulfuric acid (after recycling five times)	O K	54.69	67.14	100.0
	Al K	44.20	32.18	
	S K	1.11	0.68	
Alumina – sulfuric acid (after recycling six times)	O K	54.18	66.53	100.0
	Al K	44.73	32.81	
	S K	1.09	0.66	
Alumina – sulfuric acid (after recycling eight times)	O K	54.07	66.13	100.0
	Al K	44.91	33.22	
	S K	1.02	0.65	
Neutral alumina	O K	54.62	67.00	100.0
	Al K	45.37	33.00	
	S K	0.01	0.00	

The heterogeneity of the catalyst was established with the help of "hot filtration method" as depicted by Lempers and Sheldon.[16] β-Naphthol and phenylacetylene were taken for this experiment. When 37% conversion of the substrate was noted after 1h, catalyst was taken out by simple filtration under hot condition to avoid re-adsorption of leached sulphur (if any) at room temperature on the catalyst surface. The "catalyst free" filtrate was then kept under optimized reaction conditions. After 18 h, further progress of the reaction was not observed at all. Hence, the heterogeneity of the catalyst was conclusively proved.

The said reactions are highly atom-efficient (atom economy 100%) and generate no by-product as the waste. The present method involves alumina-sulfuric acid as an efficient and recyclable catalyst and toluene as the reaction medium, which has greater acceptance than many aromatic and other conventional organic solvents in terms of safety and environmental issues. Thus the present method bodes for eco-compatibility in terms of atom-economy, reaction medium, minimal waste generation and maximum utilization of renewable resources through efficient recovery and recycling of both the catalyst as well as the solvent.

In order to explore the scope and limitation of the present protocol, a wide variety of naphthols **1a**–**1b** and phenols **1c**–**1k** were reacted with substituted arylacetylenes and styrene under optimized reaction condition (Scheme 2) in order to obtain the hydroarylated products **3**, as listed below.

Compounds prepared by the alumina-sulfuric acid-catalyzed protocol



(3a)[8e] (4h, 91%) **(3b)**[8e] (4h, 89%) **(3c)**[8e] (4h, 93%) **(3d)** (4h, 90%) **(3e)** (4h, 87%)

(3f)[8e] (4h, 89%) **(3g)**[8e] (4h, 88%) **(3h)**[8e] (4h, 87%) **(3i)**[8h] (4h, 89%) **(3j)**[8f] (4h, 88%)

(3k)[17b] (4h, 88%) **(3l)**[17c] (4h, 87%) **(3m)**[8h] (4h, 90%) **(3n)**[8h] (4h, 86%) **(3o)**[8h] (4h, 85%) **(3p)** (4h, 85%)

(3q)[17d] (4h, 86%) **(3r)**[17a] (3h, 89%) **(3s)**[17e](3h, 88%)

[a] Isolated yield of the purified product fully characterized spectroscopically

Hydroarylation of 2-naphthol **1a** and 1-naphthol **1b** with differently substituted arylacetylenes moieties **2a**, **2c-2e** and styrene **2b** furnished the desired products **3a-3g** in good to excellent yield, where regioselectivity was governed in accordance to the fixation of double bonds in the naphthol moieties. Interesting regioselectivity was observed in case of phenol. In spite of the availability of both *ortho-* and *para-*positions, the reaction took place exclusively at the sterically more demanding *ortho*-position with >98% of conversion and the product **3h** was obtained with 87% of yield. *para*-Substituted phenol **1d** reacted with **2a** and **2b** to produce the expected *ortho*-arylated products **3i** and **3j** with 89% and 88% of yields respectively. Exclusive *ortho*-arylation occured in 2-methylphenol (**1e**) where sterically more accessible *para*-position was left unaffected and the corresponding products **3k** and **3l** were obtained with 88% and 87% yields respectively. When two electron-donating groups, namely, OH and OMe were present mutually at *para*-positions in the substrate **1f**, **2a** reacted exclusively at the *ortho*-position with respect to the OH group and **3m** was produced with 90% of yield. Similar trends were also observed with halogen-substituted phenols (**1g-1i**) and the products (**3n-3p**) were obtained with good yield without affecting the substituents. 3-Ethynylthiophene (**2c)** (with electron-rich heterocycle) reacted smoothly with **1a** to produce **3q** in 86% yield but 2-ethynylpyridine (**2d**) (with electron-deficient heterocycle) failed to react with **1a** under the present protocol. The *ortho*-disubstituted-*para*-unsubstituted substrate, namely, 2, 6-dimethoxyphenol **1j** failed to react with **2a** even after prolonged reaction (10h). Thus, the exclusive *ortho*-selectivity of the present protocol was convincingly established. A plausible reaction pathway has been speculated (Figure 3). Presumably, the reaction was initiated by the initial polarization of the carbon-carbon multiple bond by the protic hydrogen of alumina-sulfuric acid with the development of incipient electron-deficiency at the α–carbon (**A**). This seemed to be crucial because no conversion was noted with the alkyne **2d** with electron-withdrawing heterocyclic moiety. Subsequent intermolecular reaction of **A** with phenolic compounds might occur through a six-membered cyclic transition state involving the phenolic-OH moiety leading to **B** with exclusive *ortho*-substitution, followed by aromatization through tautomerization. The exact mechanism of the present protocol is neither unambiguously nor conclusively established.

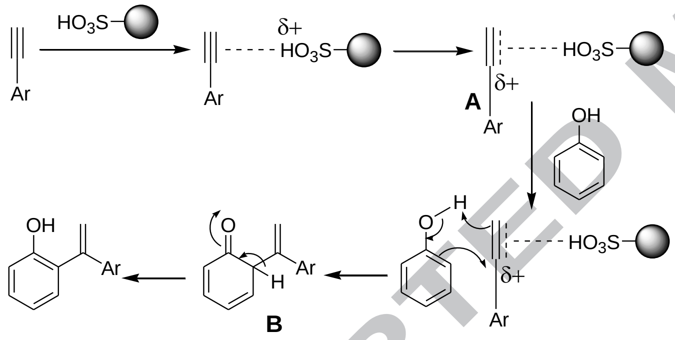


Figure 3: Speculated reaction pathway

Unlike phenols, thiophenol **1k** reacted with both phenylacetylene **2a** and styrene **2b** under the present reaction condition but did not afford to the hydroarylated products, rather nucleophilic addition across the multiple bonds took place to produce the *bis*- and *mono*-S-alkylated products **3r** and **3s** with 89% and 88% yields respectively. This observation was in accordance to the HSAB (Hard Soft Acid Base) principle, where sulphur atom of **1k**, being a relatively softer nucleophile, preferentially reacted with the C-2 (relatively softer electrophilic centre) of both **2a** and **2b**. As a result, **2a** initially produced the *mono*-S-alkylated product through nucleophilic addition of **1k** across the acetylenic linkage which on further nucleophilic addition with the second molecule of **1k** yielded the *bis*-S-alkylated product **3r**. Similarly, **2b** afforded the *mono*-S-alkylated product **3s**. Alumina-mediated thia-Michael reactions between thiols and conjugated enones as well as ynones have earlier literature precedence.[18] It is important to note that the site-selectivity with reference to the nucleophile as well as the arylalkyne/arylalkene in the nucleophilic addition reaction (**3r** and **3s**) is totally opposite in comparison to the earlier observations (**3a** – **3q**).

3. Conclusion

In summary, we have developed a highly regioselective, atom efficient, environmentally benign transition metal-free synthetic protocol using alumina-sulfuric acid as a reusable heterogeneous solid acid catalyst for the hydroarylation of arylacetylenes and styrene with differently substituted phenols and naphthols to prepare a series of important 1,1-diarylalkenes and 1,1-diarylalkanes within a reasonable reaction time. There was no occurrence of any by-product due to polyalkylation, dimerization and polymerization of styrene and phenylacetylenes as well as the hydroarylated products.

Acknowledgements

Infrastructural support from DST-FIST programme and financial assistance from DST-PURSE-programme and UGC-CAS-II programme in Chemistry at Jadavpur University are gratefully acknowledged. The authors express sincere gratitude to Ms. S. Nandy and Dr. K. K. Chattopadhyay of Jadavpur University, Mr. N. Dutta and Mr. A. K. Ghosh of Indian Association for the Cultivation of Science and Ms. P. Das of Indian Institute of Chemical Biology for necessary assistance.

References and notes

1. (a) Corma, A. *Chem. Rev.* **1997**, *97*, 2373-2420.
2. (a) Hamze, A.; Veau, D.; Provot, O.; Brion, J. D.; Alami, M. *J. Org. Chem*. **2009**, *74*, 1337-1340. (b) Hamze, A.; Giraud, A.; Messaoudi, S.; Provot, O.; Peyrat, F. J.; Bignon, J.; Liu, J. M.; Bakala, J. W.; Thoret, S.; Dubois, J.; Brion, J. D.; Alami, M. *Chem. Med. Chem*. **2009**, *4*, 1912-1924. (c) Messaoudi, S.; Treguier, B.; Hamze, A.; Provot, O.; Peyrat, J-F.; Losada, J. R. D.; Liu, J-M.; Bignon, J.; Wdzieczak-Bakala, J.; Thoret, S.; Dubois, J.;Brion, J-D.; Alami, M. *J. Med. Chem*. **2009**, *52*, 4538-4542. (d) Treguier, B.; Hamze, A.; Provot, O.; Bignon, J.; Alami, M. *Tetrahedron Lett*. **2009**, *50*, 6549-6552 (e) Alami, M., Messaoudi, S.; Hamze, A.; Provot, O.; Brion, J-D.; Liu, J-M.; Bignon, J.; Bakala, J. U. S. Patent, 0160228A1, 2011.
3. (a) Skabara, P. J.; Serebryako, I. M.; Perepichka, I. F.; *Synth. Met*. **1999**, *102*, 1336-1337. (b) Khan, M. S.; Al-Mandhary, M. R. A.; Al-Suti, M. K.; Ahrens, B.; Mahon, M. F.; Male, L.; Raithby, P. R.; Boothby, C. E.; Kohler, A. *J. Chem. Soc., Dalton Trans*. **2003**, 74-84. (c) Jacob, J.; Oldridge, L.; Zhang, J.Y.; Gaal, M.; List, E. J. W.; Grimsdale, A. C.; Mullen, K. *Curr. Appl. Phys*. **2004**, *4*, 339-342.
4. (a) Yuki, H.; Okamoto, Y.; Sadamoto, K. *Bull. Chem. Soc. Jpn.* **1969,** *42*, 1754-1755. (b) Brady, W. T.; Giang, Y. F. *J. Org. Chem.* **1985,** *50*, 5177-5179. (c) D'Auria, M.; Esposito, V.; Mauriello, G. *Tetrahedron* **1996,** *52*, 14253-14272. (d) Robert, J. R.; Volgas, G. C.; Delashmit, P. T. US Patent 0262061A1, 2008.
5. (a) Meyer, N.; Delaite, C.; Hurtrez, G.; Dumas, P. *Polymer* **2002,** *43*, 7133-7139. (b) Viala, S.; Tauer, K.; Antonietti, M.; Krüger, R.-P.; Bremser, W. *Polymer* **2002,** *43*, 7231-7241. (c) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009,** *109*, 897-1091.
6. (a) Evans, D.; Cracknell, M. E.; Saunders, J. C.; Smith, C. E.; Williamson, W. R. N.; Dawson, W.; Sweatman, W. J. F. *J. Med. Chem.* **1987,** *30*, 1321-1327. (b) Botteghi, C.; Corrias, T.; Marchetti, M.; Paganelli, S.; Piccolo, O. *Org. Process Res. Dev.* **2002,** *6*, 379-383.
7. (a) Koenigs, *Ber*. **1890**, *23*, 3145. (b) Stoermer and Kippe, *Ber*. **1903**, *26*, 4012. (c) Calloway, N. O. *Chem. Rev.* **1935,** *17,* 327-392 (d) Olah, G. A. *In Friedel-Crafts Chemistry*; Wiley: New York, 1973. (e) Olah, G. A.; Krishnamurti, R.; Prakash, G. K. S. *In Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991, *3*, 293. (g) Bandini, M.; Melloni, A.; Ronchi, A. U. *Angew. Chem., Int. Ed*. **2004**, *43*, 550-556.
8. (a) Yamaguchi, M.; Hayashi, A.; Hirama, M. *J. Am. Chem. Soc*. **1995**, *117*, 1151-1152. (b) Sartori, G.; Bigi, F.; Pastorio, A.; Porta, C.; Arienti, A.; Maggi, R.; Moretti, N.; Gnappi, G. *Tetrahedron Lett*. **1995**, *36*, 9177-9180. (c) Kischel, J.; Jovel, I.; Mertins, K.; Zapf, A.; Beller, M. *Org. Lett*. **2006**, *8*, 19-22. (d) Rueping, M.;

Nachtsheim, B. J.; Scheidt, T. *Org. Lett*. **2006**, *8*, 3717-3719. (e) Yadav, J. S.; Reddy, B. V. S.; Sengupta, S.; Biswas, S. K. *Synthesis* **2009**, 1301-1304. (f) Haldar, S.; Koner, S. *J. Org. Chem*. **2010**, *75*, 6005-6008. (g) Varghese, S.; Nagarajan, S.; Benzigar, M. R.; Mano, A.; Alothman, Z. A.; Raj, G. A. G.; Vinu, A. *Tetrahedron Lett*. **2012**, *53*, 1485-1489. (h) Haldar, S.; Koner, S. *Beilstein J. Org. Chem*. **2013**, *9*, 49-55. (i) Rao, V. K.; Kaswan, P.; Parang, K.; Kumar, A. *Org. Biomol. Chem*. **2015**, *13*, 11072-11077.

9. (a) Dorta, R.; Togni, A. *Chem. Commun*. **2003**, 760-761. (b) Kuninobu, Y.; Matsuki, T.; Takai, K. *J. Am. Chem. Soc*. **2009**, *131*, 9914-9915.
10. (a) Jia, C. G.; Lu, W. T.; Oyamada, J.; Kitamura, T.; Matsuda, K.; Irie, M.; Fujiwara, Y. *J. Am. Chem. Soc*. **2000**, *122*, 7252-7263. (b) Bolm, C.; Legros, J.; Paih, J. L.; Zani, L. *Chem. Rev*. **2004**, *104*, 6217-6254. (c) Jovel, I.; Mertins, K.; Kischel, J.; Zapf, A.; Beller, M. *Angew. Chem. Int. Ed*. **2005**, *44*, 3913-3917. (d) Chu, C. M.; Huang, W. J.; Liu, J. T.; Yao, C. F. *Tetrahedron Lett*. **2007**, *48*, 6881-6885. (e) Gao, K.; Yoshikai, N. *J. Am. Chem. Soc*. **2011**, *133*, 400-402.
11. (a) Jiang, H.; Yang, C.; Li, C.; Fu, H.; Chem, H.; Li, R.; Li, X. *Angew. Chem. Int. Ed*. **2008**, *47*, 9240-9244. (b) Jeganathan, M.; Dhakshinamoorthy, A.; Pitchumani, K. *Tetrahedron Lett*. **2014**, *55*, 1616 – 1620. (c) Molinari, V.; Giordano, C.; Antonietti, M.; Esposito, D. *J. Am. Chem. Soc*. **2014**, *136*, 1758–1761. (d) Mandi, U.; Pramanik, M.; Singha Roy, A.; Salam, N.; Bhaumik, A.; Islam, M. *RSC Adv*. **2014**, *4*, 15431-15440. (e) Tsubogo, T.; Oyamada, H.; Kobayashi, S. *Nature*, **2015**, *520*, 329-332. (f) Hajjami, M.; Tahmasbi, B. *RSC Adv*. **2015**, *5*, 59194-59203. (g) Munnik, P.; de Jongh, P. E.; de Jong, K. P. *Chem. Rev*. **2015**, *115*, 6687–6718. (h) Braun, M.; Antonietti, M. *Green Chem*. **2017**, *19*, 3813-3819. (i) Zhao, J.; Jin, R. *Nanotoday*, **2018**, *18*, 86-102. (j) Dey, S. K.; Dietrich, D.; Wegner, S.; Gil-Hernandez, B.; Harmalkar, S. S.; Amadeu, N. S.; Janiak. C. *Chem. Select* **2018**, *3*, 1365 – 1370. (k) Arora, N., Mehta, A., Mishra, A., Basu, S. *Appl. Clay Sc*. **2018**, *151*, 1–9.
12. (a) Khorasandi, Z.; Khosropour, A. R.; Mirkhani, V.; Baltork, I. M.; Moghadam, M.; Tangestaninejad, S. *Tetrahedron Lett.* **2011**, *52*, 1213-1216. (b) Zhong, F.; Wang, Y.; Han, X.; Huang, K-W.; Lu, Y. *Org.Lett*. **2011**, *13*, 1310-1313. (c) Hajipour, A. R.; Nazemzadeh, S. H.; Mohammadsaleh, F. *Tetrahedron Lett*. **2014**, *55*, 654 – 656. (d) Schroder, K.; Matyjaszewski, K.; Noonan, K. J. T.; Mathers, R. T. *Green Chem*. **2014**, *16*, 1673 – 1686. (e) Deepa, A. K.; Dhepe, P. L. *RSC Adv*. **2014**, *4*, 12625 – 12629.
13. (a) Hashem, S.; Saravani, H.; Hasseimi, M. *J. Chem. Res*. **2005**, *29***,** 488-491. (b) Saravani, H.; Hasseimi, M.; Hashem, S. *J. Chem. Res*. **2006**, *30***,** 205-208.
14. (a) Saha, M.; Bhar, S. *Green Chem. Lett. Rev*. **2011**, *4***,** 137-142. (b) Pramanik, A.; Bhar, S. *Catal. Commum*. **2012**, *20***,** 17-24. (c) Pramanik, A.; Roy, R.; Khan, S.; Ghatak, A.; Bhar, S. *Tetrahedron Lett.* **2014**, *55*, 1771-1777.
15. Nabae, Y.; Liang, J.; Huang, X.; Hayakawa, T.; Kakimoto, M. *Green Chem*., **2014**, *16*, 3596-3602.
16. Lempers, H. E. B.; Sheldon, R. A. *J. Catal*. **1998**, *175*, 62-69.
17. (a) Nuyken, O.; Siebzehnruebl, F. *Phosphorus Sulfur and the Related Elements* **1988**, *35*, 47-53. (b) Wang, X.; Guram, A.; Caille, S.; Hu, J.; Preston, JP.; Ronk, M.; Walker, S. *Org. Lett.* **2011**, *13*, 1881-1883 (c) Lanke, S. R.; Qureshi, Z. S.; Patil, A. B.; Patil, D. S.; Bhanage, B. M. *Green Chem. Lett. Rev*. **2012**, *1*, 1-12. (d) Duarah, G.; Kaishap, P. P.; Sarma, B.; Gogoi, S. *Chem. Eur. J.* **2018**, *24*, 10196-10200. (e) Tyson, E. L.; Ament, M. S.; Yoon, T. P. *J. Org. Chem*. **2013**, *78*, 2046-2050.
18. (a) Ranu, B. C.; Bhar, S. *Tetrahedron* **1992**, *48*, 1327-1332. (b) Ranu, B. C.; Bhar, S.; Chakraborty, R. *J. Org. Chem*. **1992**, *57*, 7349-7352.

Supplementary Material

Representative experimental procedure, EDX spectra of alumina-sulfuric acid and the spectral data of the hydroarylated compounds have been furnished as Supporting information.

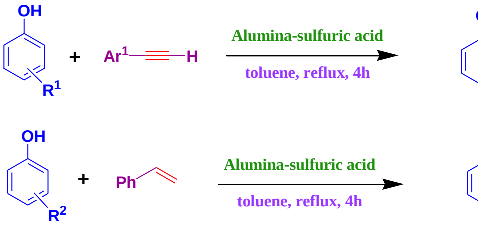
Title: Hydroarylation of alkynes and alkenes through alumina-sulfuric acid catalyzed regioselective C-C bond formation

Authors: Amit Pramanik, Avishek Ghatak, Sagar Khan and Sanjay Bhar*

Highlights

- regioselective C-C bond formation
- recyclable heterogeneous supported solid acid catalyst
- no occurrence of any by-product
- minimal waste generation
- eco-compatibility

Graphical Abstract



Hydroarylation of alkynes and alkenes through alumina-sulfuric acid catalyzed regioselective C-C bond formation

Amit Pramanik, Avishek Ghatak, Sagar Khan and Sanjay Bhar*
* Corresponding author. Tel.: +918697179547; e-mail: sanjaybharin@yahoo.com, sanjay.bhar@jadavpuruniversity.in