Solvent-free solid acid-catalyzed nucleophilic substitution of propargylic alcohols: a green approach for the synthesis of 1,4-diynes†

Tao Wang, Rui-da Ma, Liu Liu and Zhuang-ping Zhan*

Received 17th May 2010, Accepted 2nd July 2010
DOI: 10.1039/c0gc00117a

Acid-treated K10 montmorillonite (H-K10 mont) exhibited an outstanding catalytic activity in the nucleophilic substitution of propargylic alcohols with alkynylsilanes. The reactions were carried out under solvent-free conditions, and the solid catalyst was reusable with retention of its high activity. This method provides a green and rapid route to 1,4-diynes.

The nucleophilic substitution of propargylic alcohols has turned into an important organic transformation, as it provides facile and expeditious routes to a wide range of propargylic products.[1,2] Although substantial attention has been paid to this field in the past decade, many studies have been restricted to the development of metal-catalyzed homogeneous transformations,[2a–f] and at the same time, very few reports on the preparation of synthetically valuable 1,4-diynes *via* sp–sp^3 C–C bond formation currently exist.[3] Jung *et al.* reported a propargylic substitution reaction between terminal TMS-alkynes and propargyl halides in the presence of a fluoride source and a catalytic amount of copper iodide to prepare 1,4-diynes in good yields under mild conditions.[4] Takai and co-workers recently demonstrated a rhenium-catalyzed smooth substitution of propargyl alcohols with an alkynylsilane. It was proposed that this reaction proceeded *via* propargylic cations as intermediates.[5] Cohen carried out an $InCl_3$-catalyzed nucleophilic substitution of a propargylic alcohol with an alkynylsilane to afford a 1,4-diyne, which was subsequently transformed into bioactive Nyasol.[6] Yadav *et al.* described an efficient procedure for the alkynylation of aryl propargyl alcohols with alkynylsilanes using molecular iodine as the catalyst.[7] However, more extensive use of these approaches is confined to some extent by virtue of the high price of the complex metallic catalysts and the harmfulness of halogen-containing solvents to the environment. Thus, it is still highly attractive to develop efficient, economical and environmentally benign methodologies for the synthesis of 1,4-diynes *via* a propargylic substitution protocol.

Heterogeneous catalysis is of great importance in a variety of chemical processes,[8,9] and the corresponding solid acid catalysts based on commercially available K-10 montmorillonite (K10 mont) have recently received much attention due to their unique properties, such as their cation exchange ability in the interlayer, expansible interlayer space and tunable acidity.[10] Furthermore, the application of K10 mont in liquid-phase organic synthesis allows facile catalyst separation and reutilization, providing environmentally benign or green processes compared with homogeneous acids. Recently, Patti *et al.* reported that K10 mont, on treatment by acid before use, exhibits significant enhancements in its catalytic activity.[11] This discovery indicates the promising application value of acid-treated K10 mont in organic synthesis. However, to the best of our knowledge, no report of further studies in this field currently exists.

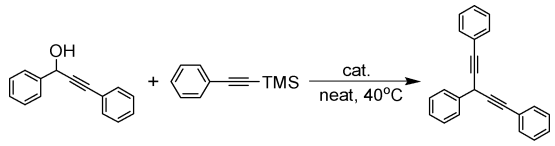
Herein, as a result of developments in the propargylic substitution reaction by our group,[12] an acid-treated K10 mont-catalyzed synthesis of 1,4-diynes from propargylic alcohols and terminal TMS-alkynes under solvent-free conditions is reported.[13] Not only did the acid-treated K10 mont display a higher catalytic activity than virgin K10 mont, but the catalyst could be easily separated and reused. Also, this is the first clay-catalyzed sp–sp^3 C–C coupling reaction carried out under solvent-free conditions.

In our initial study, propargylic alcohol **1a** was treated with trimethyl(phenylethynyl)silane (**2a**) using commercial virgin K10 as the catalyst under solvent-free conditions (Table 1). Unfortunately, the desired product, **3aa**, was obtained in only 48% yield (Table 1, entry 1). On the basis of the structural characteristics of montmorillonite, we reasoned that such an unsatisfactory yield was probably due to the inadequacy of the exchangeable protons in the catalyst. Thus, we hypothesized that the catalytic efficiency of K10 mont could be enhanced on the condition that the charge compensating cations in the hydrate interlayer were further exchanged for H^+. To test our hypothesis, K10 mont was treated with different concentrations of hydrochloric acid under various conditions, whose catalytic efficacy was subsequently examined (Table 1). We were pleased to find that K10 mont treated with 1 M HCl at 80 °C exhibited an excellent catalytic performance and dramatically increased the yield of the expected product (Table 1, entry 4). However, increasing the concentration of HCl to 5 M for the treatment of K10 mont failed to exhibit any further improvement in yield (Table 1, entry 5). To test whether Brønsted acids such as HCl, *p*-toluenesulfonic acid and TfOH also possessed similar high catalytic activities to acid-treated K10 mont, this transformation was also performed using these strong acids as catalysts under the same reaction conditions. However, the results shown in Table 1 indicate that their catalytic efficiency was rather lower than that of acid-treated K10 mont, whose structural characteristics probably played a crucial role in the reaction. The optimization results show that the employment of

Department of Chemistry, College of Chemistry and Chemical Engineering, and State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen, 361005, Fujian, P. R. China. E-mail: zpzhan@xmu.edu.cn; Fax: +86 (592) 2180318; Tel: +86 (592) 2180318

† Electronic Supplementary Information (ESI) available: Experimental and spectral data of compounds **3aa**–**3bc**. Copies of ^{1}H and ^{13}C NMR spectra of new compounds. See DOI: 10.1039/c0gc00117a

Table 1 Nucleophilic substitution of propargylic alcohol **1a** with alkynylsilane **2a** using various acid catalysts[a]



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

Entry	Catalyst	Acid amount / mmol g^{-1} [b]	Time	Yield (%)[c]
1	K10 mont	0.25	45 min	48
2	A	0.73	35 min	54
3	B	0.86	35 min	67
4	**C**	**0.98**	**25 min**	**89**
5	D	1.03	25 min	88
6	HCl[d]	—	24 h	Trace
7	*p*-TsOH·H_2O[d]	—	24 h	Trace
8	TfOH[d]	—	24 h	37
9	(none)	—	24 h	0[e]

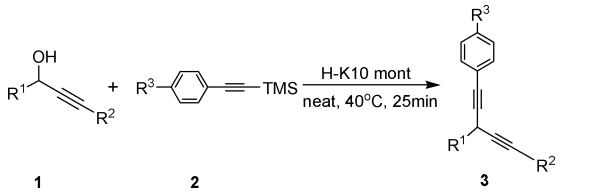
[a] Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), catalyst (20 wt% of **1a**), solvent-free, 40 °C. A: H-K10 mont (K10 mont treated with 0.1 M HCl at 20 °C). B: H-K10 mont (K10 mont treated with 1 M HCl at 20 °C). C: H-K10 mont (K10 mont treated with 1 M HCl at 80 °C). D: H-K10 mont (K10 mont treated with 5 M HCl at 80 °C). [b] Determined by NH_3-TPD. [c] Isolated yields. [d] 0.1 mmol. [e] Starting material was recovered.

K10 mont treated with 1M HCl at 80 °C is reasonably efficient for this nucleophilic substitution of propargylic alcohols with alkynylsilanes.

Next, with the optimized reaction conditions in hand, the generality of this novel H-K10 mont-catalyzed nucleophilic substitution was examined (Table 2).[14] To our delight, we found this transformation to be very general for a wide range of propargylic alcohols and alkynylsilanes. The employment of propargylic alcohol **1b**, bearing an alkyl chain at the terminal position of the acetylene moiety, smoothly afforded the desired product, **3ba**, under mild conditions (Table 2, entry 2). Also, as expected, 1,4-diynes **3ea** and **3eb** were obtained from propargylic alcohol **1e** in 82 and 81% yields, respectively, and no ring-opening of the cyclopropyl groups was observed (Table 2, entries 5 and 13). When R^2 was replaced by an unsaturated alkyl group, the reaction also led to the formation of the desired 1,4-diyne in good yield (Table 2, entry 4).

Interestingly, propargylic alcohols **1c** and **1g–1i**, containing an alkynylsilane moiety, all gave the corresponding products retaining their TMS groups (Table 2, entries 3, 7–9). Among them, **1g** possessing an electron-donating group in the aryl ring (R^1 = 4-MeO-Ph), reacted smoothly, affording **3ga** in good yield (Table 2, entry 7). Substrates **1h** and **1i**, bearing an electron-withdrawing group, were also successfully employed in the substitution reaction to give the corresponding products **3ha** and **3ia** in good yields of 83 and 82%, respectively (Table 2, entries 8 and 9). Unfortunately, propargylic alcohol **1j**, bearing a 4-methoxycarbonylphenyl group, failed to give any of the desired product, even after a prolonged reaction time (Table 2, entry 10), perhaps because of the strong electron-withdrawing effect of the methoxycarbonyl group. The above results indicate that the substitution may occur *via* an S_N1 mechanism, in which a propargylic cation intermediate is formed, whose instability clearly makes the nucleophilic substitution less favorable.

Table 2 H-K10 mont-catalyzed nucleophilic substitution of propargylic alcohols with alkynylsilanes[a]



1 **2** **3**

Entry	R^1; R^2	R^3	Product	Yield (%)[b]
1	**1a**: Ph; Ph	**2a**: H	**3aa**	89
2	**1b**: Ph; *n*-Bu	**2a**: H	**3ba**	81
3	**1c**: Ph; TMS	**2a**: H	**3ca**	85
4	**1d**: Ph; 1-cyclohexenyl	**2a**: H	**3da**	86
5	**1e**: Ph; cyclopropyl	**2a**: H	**3ea**	82
6	**1f**: Ph; H	**2a**: H	**3fa**	81
7	**1g**: 4-MeO-Ph; TMS	**2a**: H	**3ga**	87
8	**1h**: 4-Cl-Ph; TMS	**2a**: H	**3ha**	83
9	**1i**: 4-Br-Ph; TMS	**2a**: H	**3ia**	82
10	**1j**: 4-COOMe-Ph; *n*-Bu	**2a**: H	**3ja**	n. r.[c]
11	**1k**: 1-naphthyl; H	**2a**: H	**3ka**	85
12	**1a**: Ph; Ph	**2b**: Br	**3ab**	83
13	**1e**: Ph; cyclopropyl	**2b**: Br	**3eb**	81
14	**1f**: Ph; H	**2b**: Br	**3fb**	80
15	**1a**: Ph; Ph	**2c**: MeO	**3ac**	89
16	**1b**: Ph; *n*-Bu	**2c**: MeO	**3bc**	82

[a] Reaction conditions: **1** (1 mmol), **2** (1 mmol), H-K10 mont (20 wt% of **1**), 40 °C, 25 min. [b] Isolated yields. [c] n. r. = No reaction. Reaction time was 24 h.

The reaction was not limited to substrates bearing internal alkyne groups. For example, propargylic alcohols **1f** and **1k**, with terminal alkyne groups, afforded the corresponding 1,4-diynes in high yields under the same conditions (Table 2, entries 6, 11 and 14). Additionally, fused aromatic propargylic alcohol **1k** readily underwent this nucleophilic substitution (Table 2, entry 11).

We next turned to investigating the scope of alkynylsilane **2**. Gratifyingly, both electron-rich and electron-poor alkynylsilanes reacted smoothly with propargylic alcohols, affording the desired 1,4-diynes in good yields (Table 2, entries 12–16). It should be noted that halogenated aromatic substrates, which may participate in transition metal-catalyzed cross-coupling reactions, survive the reaction conditions, allowing subsequent elaboration of the products.

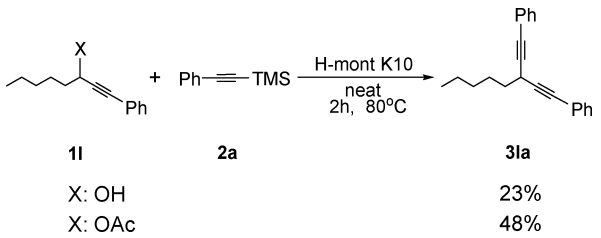
Nucleophilic substitution of alkyl-substituted propargylic alcohols (R^1 = alkyl) with alkynylsilanes has generally been considered difficult to achieve, perhaps because of the instability of the propargylic cation intermediates.[5–7] However, we were delighted to find that alkyl-substituted propargylic alcohol **1l** participated in the H-K10 mont-catalyzed nucleophilic substitution as well (Scheme 1). Treatment of **1l** with alkynylsilane **2a** in the presence of H-K10 mont led to the formation of **3la**, albeit in low yield. In contrast, replacing propargylic alcohol with propargylic acetate increased the yield of **3la** to 48%.

As a further demonstration of the advantages of this novel propargylic substitution, we studied the catalytic efficacy of the catalyst after the reaction. We found that H-K10 mont could be easily separated from the reaction system and continued to exhibit good catalytic efficiency, even in the seventh recycling experiment (Table 3).

Table 3 Re-use of the H-K10 mont catalyst for the substitution of **1a** with **2a**[a]

Recycle number	Fresh	1st	2nd	3rd	4th	5th	6th	7th
Isolated yield (%)	89	89	87	88	87	88	87	87

[a] Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), H-K10 mont (20 wt% of **1a**), 40 °C.



Scheme 1 Nucleophilic substitution of alkyl-substituted propargylic alcohol and acetate.

As HCl, *p*-toluenesulfonic acid and TfOH showed much lower activities than H-K10 mont (Table 1), we supposed that the specific structure of H-K10 mont was likely to play a pivotal role in this transformation. To further test whether the reactions took place at the surface of the catalyst or were homogeneously catalyzed by leached protons, we carried out a Sheldon test.[15] Gratifyingly, the result was totally in accordance with our hypothesis; the H-K10 mont-catalyzed nucleophilic substitution was demonstrated to be a heterogeneous reaction.†

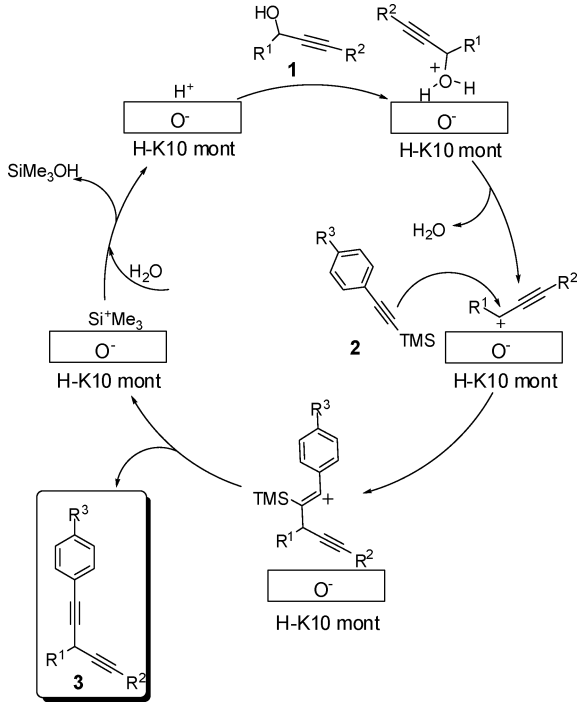
A possible mechanism for the H-K10 mont-catalyzed nucleophilic substitution reaction is proposed in Scheme 2. According to the catalytic path, propargylic alcohol **1** is first protonated by a H^+ site to give a propargylic cation intermediate. The silicate layers are capable of acting as delocalized counteranions to stabilize cationic intermediates, on which subsequent nucleophilic attack of alkynylsilane **2** generates an alkenyl cationic intermediate stabilized by both the phenyl ring and the silyl group.[16] The trimethylsilyl group is then eliminated to give the desired 1,4-diyne. Finally, the H^+ active site is regenerated by hydration so as to enter into the next catalytic cycle.

In summary, we have developed the H-K10 mont-catalyzed nucleophilic substitution of propargylic alcohols with alkynylsilanes, providing a green and rather facile approach to 1,4-diynes. Besides the mild and solvent-free reaction conditions, the solid catalyst can be easily separated and reused at least seven times without any appreciable loss in its catalytic efficiency, which gives it great potential for large-scale applications. Furthermore, this substitution reaction has good functionality tolerance, and the scope of substrates is broad. Further studies on the application of this methodology are in progress in our laboratories.

Experimental

Acid treatment procedure

A mixture of K10 mont (10 g) and hydrochloric acid (200 ml) was stirred at a chosen temperature for 6 h. The slurry obtained was filtered and washed with de-ionized water until no Cl^- could be detected by a silver nitrate test. The clay was then dried at 110 °C to afford acid-treated K10 mont as a white-gray powder.



Scheme 2 A proposed mechanism of the H-K10 mont-catalyzed nucleophilic substitution.

General procedure for the alkynylation of propargylic alcohols

A mixture of propargylic alcohol (1 mmol), alkynylsilane (1 mmol) and H-K10 mont (20 wt% of propargylic alcohol) was stirred at 40 °C in a round-bottomed flask. When the reaction was complete (monitored by TLC), the product was dissolved in ethyl acetate and separated from the catalyst by filtration. The solvent was removed under reduced pressure, and then the residue further purified by silica gel column chromatography (petroleum ether) to afford the 1,4-diyne. The recovered catalyst could be reused after drying at 110 °C for 1 h.

Acknowledgements

This research was financially supported by the National Natural Science Foundation of China (no. 20772098).

Notes and references

1 For recent reviews, see: (*a*) N. Ljungdahl and N. Kann, *Angew. Chem., Int. Ed.*, 2009, **48**, 642–644; (*b*) Y. Miyake, S. Uemura and Y. Nishibayashi, *ChemCatChem*, 2009, **1**, 342–356; (*c*) R. J. Detz, H. Hiemstra and J. H. van Maarseveen, *Eur. J. Org. Chem.*, 2009, 6263–6276.

2 For selected examples, see: (*a*) B. D. Sherry, A. T. Radosevich and F. D. Toste, *J. Am. Chem. Soc.*, 2003, **125**, 6076–6077; (*b*) M. Georgy, V. Boucard and J.-M. Campagne, *J. Am. Chem. Soc.*, 2005, **127**, 14180–14181; (*c*) H. Matsuzawa, Y. Miyake and Y. Nishibayashi, *Angew. Chem., Int. Ed.*, 2007, **46**, 6488–6491; (*d*) H. Qin, N. Yamagiwa, S. Matsunaga and M. Shibasaki, *Angew. Chem., Int. Ed.*, 2007, **46**, 409–413; (*e*) M. Yoshimatsu, T. Yamamoto, A. Sawa, T. Kato, G. Tanabe and O. Muraoka, *Org. Lett.*, 2009, **11**, 2952–2955; (*f*) X. Zhang, W. T. Teo and P. W. H. Chan, *Org. Lett.*, 2009, **11**, 4990–4993; (*g*) Y.-L. Liu, L. Liu, Y.-L. Wang, Y.-C. Han, D. Wang and Y.-J.

Chen, *Green Chem.*, 2008, **10**, 635–640; (*h*) R. Sanz, D. Miguel, A. Martínez, J. M. Álvarez-Gutiérrez and F. Rodríguez, *Org. Lett.*, 2007, **9**, 727–730; (*i*) R. Sanz, A. Martínez, J. M. Álvarez-Gutiérrez and F. Rodríguez, *Eur. J. Org. Chem.*, 2006, 1383–1386.

3 For some uses of 1,4-diynes, see: (*a*) A. Voss, M. Reinhart, S. Sankarappa and H. Sprecher, *J. Biol. Chem.*, 1991, **266**, 19995–20000; (*b*) J. Rokach, Y. Guindon, R. N. Young, J. Adams and J. G. Atkinson, *Total Synth. Nat. Prod.*, 1988, **7**, 141–273 and references cited therein; (*c*) S. Banerjee, E. Barnea and A. L. Odom, *Organometallics*, 2008, **27**, 1005–1014; (*d*) V. Lavallo, G. D. Frey, B. Donnadieu, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2008, **47**, 5224–5228; (*e*) B. Ramanathan, A. J. Keith, D. Armstrong and A. L. Odom, *Org. Lett.*, 2004, **6**, 2957–2960.

4 F. Montel, R. Beaudegnies, J. Kessabi, B. Martin, E. muller, S. Wendeborn and P. M. J. Jung, *Org. Lett.*, 2006, **8**, 1905–1908.

5 Y. Kuninobu, E. Ishii and K. Takai, *Angew. Chem., Int. Ed.*, 2007, **46**, 3296–3299.

6 I. Cohen, *US Pat.*, US 2009/0312274 A1, 2009.

7 J. S. Yadav, B. V. Subba Reddy, N. Thrimurtulu, N. Mallikarjuna Reddy and A. R. Prasad, *Tetrahedron Lett.*, 2008, **49**, 2031–2033.

8 For recent reviews, see: (*a*) D. S. Su, J. Zhang, B. Frank, A. Thomas, X. Wang, J. Paraknowitsch and R. Schlögl, *ChemSusChem*, 2010, **3**, 169–180; (*b*) M. Lamblin, L. Nassar-Hardy, J.-C. Hierso, E. Fouquet and F.-X. Felpin, *Adv. Synth. Catal.*, 2010, **352**, 33–79; (*c*) K. Fang, D. Li, M. Lin, M. Xiang, W. Wei and Y. Sun, *Catal. Today*, 2009, **147**, 133–138; (*d*) J. A. Melero, J. Iglesias and G. Morales, *Green Chem.*, 2009, **11**, 1285–1308; (*e*) D. P. Debecker, E. M. Gaigneaux and G. Busca, *Chem.–Eur. J.*, 2009, **15**, 3920–3935; (*f*) S. Shylesh, V. Schünemann and W. R. Thiel, *Angew. Chem., Int. Ed.*, 2010, **49**, 3428–3459.

9 For selected examples, see: (*a*) T. Zeng, W.-W. Chen, C. M. Cirtiu, A. Moores, G. Song and C.-J. Li, *Green Chem.*, 2010, **12**, 570–573; (*b*) R. Skouta, R. S. Varma and C.-J. Li, *Green Chem.*, 2005, **7**, 571–575; (*c*) M. S. Holm, S. Saravanamurugan and E. Taarning, *Science*, 2010, **328**, 602–605; (*d*) J.-M. Yan, X.-B. Zhang, T. Akita, M. Haruta and Q. Xu, *J. Am. Chem. Soc.*, 2010, **132**, 5326–5327; (*e*) K. Motokura, S. Matsunaga, A. Miyaji, Y. Sakamoto and T. Baba, *Org. Lett.*, 2010, **12**, 1508–1511; (*f*) D.-H. Lee, M. Choi, B.-W. Yu, R. Ryoo, A. Taher, S. Hossain and M.-J. Jin, *Adv. Synth. Catal.*, 2009, **351**, 2912–2920; (*g*) M. Rueping, E. Sugiono, A. Steck and T. Theissmann, *Adv. Synth. Catal.*, 2010, **352**, 281–287.

10 For selected examples, see: (*a*) F. Nowrouzi, A. N. Thadani and R. A. Batey, *Org. Lett.*, 2009, **11**, 2631–2634; (*b*) M. R. Dintzner, Y. A. Mondjinou and B. Unger, *Tetrahedron Lett.*, 2009, **50**, 6639–6641; (*c*) J.-M. Lu and M. Shi, *Tetrahedron*, 2007, **63**, 7545–7549; (*d*) P. J. Wallis, K. J. Booth, A. F. Patti and J. L. Scott, *Green Chem.*, 2006, **8**, 333–337; (*e*) J. Azizian, A. R. Karimi, Z. Kazemizadeh, A. A. Mohammadi and M. R. Mohammadizadeh, *J. Org. Chem.*, 2005, **70**, 1471–1473; (*f*) B. P. Bandgar, S. S. Pandit and V. S. Sadavarte, *Green Chem.*, 2001, **3**, 247–249.

11 P. J. Wallis, W. P. Gates, A. F. Patti, J. L. Scott and E. Teoh, *Green Chem.*, 2007, **9**, 980–986.

12 (*a*) Z.-P. Zhan, J.-L. Yu, H.-J. Liu, Y.-Y. Cui, R.-F. Yang, W.-Z. Yang and J.-P. Li, *J. Org. Chem.*, 2006, **71**, 8298–8301; (*b*) Z.-P. Zhan, X.-B. Cai, S.-P. Wang, J.-L. Yu, H.-J. Liu and Y.-Y. Cui, *J. Org. Chem.*, 2007, **72**, 9838–9841; (*c*) X.-T. Liu, L. Huang, F.-J. Zheng and Z.-P. Zhan, *Adv. Synth. Catal.*, 2008, **350**, 2778–2788; (*d*) Y.-M. Pan, F.-J. Zheng, H.-X. Lin and Z.-P. Zhan, *J. Org. Chem.*, 2009, **74**, 3148–3151.

13 Solvent-free reactions have attracted tremendous attention. For selected examples, see: (*a*) P. D. Macleod, Z. Li and C.-J. Li, *Tetrahedron*, 2010, **66**, 1045–1050; (*b*) W.-W. Chen, R. V. Nguyen and C.-J. Li, *Tetrahedron Lett.*, 2009, **50**, 2895–2898; (*c*) P. D. MacLeod, Z. Li, J. Feng and C.-J. Li, *Tetrahedron Lett.*, 2006, **47**, 6791–6794; (*d*) J. Zhang, Z. Wang, Y. Wang, C. Wan, X. Zheng and Z. Wang, *Green Chem.*, 2009, **11**, 1973–1978; (*e*) D. Wang, J. Li, N. Li, T. Gao, S. Hou and B. Chen, *Green Chem.*, 2010, **12**, 45–48; (*f*) V. Declerck, P. Nun, J. Martinez and F. Lamaty, *Angew. Chem., Int. Ed.*, 2009, **48**, 9318–9321; (*g*) R. B. Bedford, C. J. Charlotte and R. L. Webster, *Chem. Commun.*, 2010, **46**, 3095–3097; (*h*) B. Bradshaw, G. Etxebarría-Jardi, J. Bonjoch, S. F. Viózquez, G. Guillena and C. Nájera, *Adv. Synth. Catal.*, 2009, **351**, 2482–2490.

14 As discussed above, K10 mont treated with 1 M HCl at 80 °C is the most appropriate catalyst for this reaction. From here onwards, "H-K10 mont" refers to K10 montmorillonite treated with 1 M HCl at 80 °C.

15 This idea was proposed by one of the referees and we consider it an effective supplement to our work. We are grateful to the referee. For the Sheldon test, see: H. E. B. Lempers and R. A. Sheldon, *J. Catal.*, 1998, **175**, 62–69.

16 Inspired by one of the referees, we examined the substitution of propargylic alcohol with some other alkynyl nucleophiles, including terminal alkynes and terminal TMS-substituted aliphatic alkynes. Unfortunately, our attempt to insert these nucleophiles into propargylic alcohol failed (see the ESI, Table S1†). However, the unsatisfactory results provided indirect proof for the proposed mechanism: aryl and TMS groups in the nucleophiles seem essential for the reaction due to their well-known ability to stabilize this alkenyl cationic intermediate. Several α-phenyl-β-silyl-substituted vinyl cations have been characterized, see: (*a*) H.-U. Siehl and F.-P. Kaufmann, *J. Am. Chem. Soc.*, 1992, **114**, 4937–4939; (*b*) T. Müller, R. Meyer, D. Lennartz and H.-U. Siehl, *Angew. Chem., Int. Ed.*, 2000, **39**, 3074–3077.