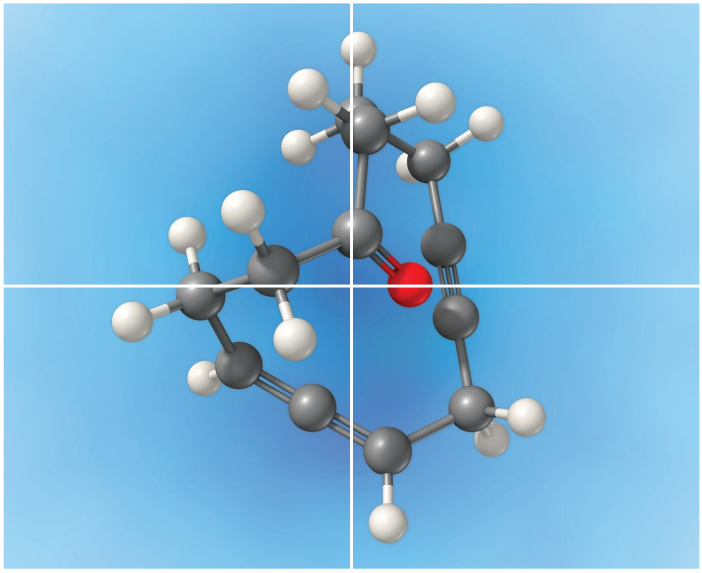
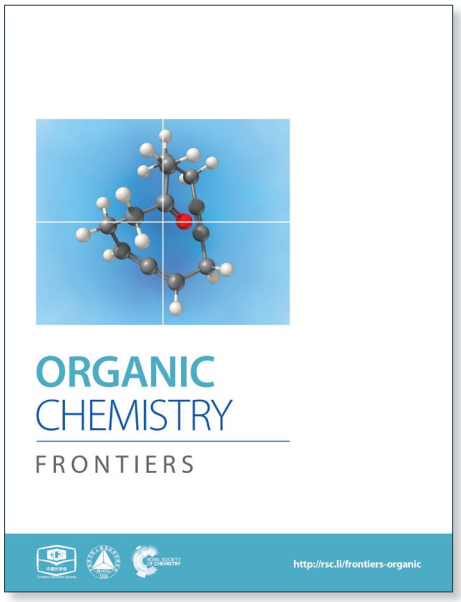
ORGANIC CHEMISTRY

FRONTIERS



Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Palladium-catalyzed intramolecular rearrangement of vinylidenecyclopropanes through C-C bond activation

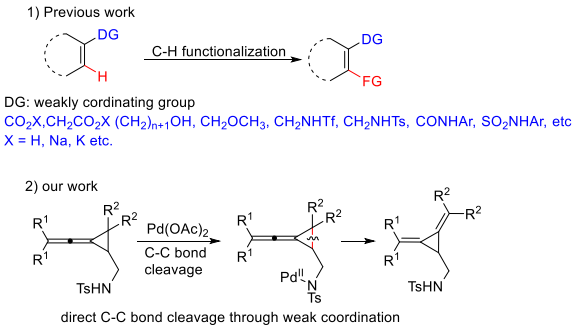
Dong Pan, Gen-Qiang Chen, Xiang-Ying Tang and Min Shi*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Vinylidenecyclopropanes bearing sulfonamide can undergo a novel intramolecular rearrangement to give the corresponding functionalized dimethylenecyclopropanes in moderate to good yields in the presence of $Pd(OAc)_2$ in toluene upon heating through C-C bond activation based on weak coordination of sulfonamide directing group. The reaction pathway can be changed for phenyl substituted vinylidenecyclopropane, giving another type of dimethylenecyclopropane in methanol in the presence of K_2CO_3 under reflux.

The use of coordinating moieties as directing groups for the C-H bond activation has become a powerful established method to enhance reactivity and regioselectivity.[1] In this very active research arena, weak coordination as a powerful means for developing broadly useful C-H functionalization reactions has attracted much attention.[2] For example, the group of Yu as well as other research groups have utilized carboxylic acids,[3] alcohols,[4] amides,[5] sulfonamides,[6] *N*-methoxy amides,[7] etc as weakly coordinating functional groups[8] for a series of efficient metal-catalyzed C-H functionalizations (Scheme 1). Beside C-H bond activations, several examples of C-C bond activation with the coordinating moieties as directing groups have been also reported recently.[9] However, to the best of our knowledge, the C-C bond activation through a weak-coordination approach has been seldom reported thus far. Methylenecyclopropanes (MCPs) and vinylidenecyclopropanes (VDCPs) are both highly strained but readily accessible and adequately reactive molecules which can serve as useful building blocks in organic synthesis.[10] They can undergo a variety of ring-opening reactions because the release of cyclopropyl ring strain can provide a thermodynamic driving force for reactions and the π-character of the bonds within the cyclopropane can afford the kinetic opportunity to initiate the unleashing of the strain.[11] During our ongoing investigation on the ring-opening reactions on the MCPs and VDCPs in the presence of metal catalysts, we found a new C-C bond activation mode of VDCPs bearing a weakly coordinating



Scheme 1. C-H and C-C Bond Cleavages through Weak Coordination

group in the presence of $Pd(OAc)_2$ under mild conditions (Scheme 1). Herein, we wish to report the details.

The starting materials sulfonamide-tethered vinylidene-cyclopropanes (VDCPs) **1** were prepared according to the previously reported procedure[12] and these functionalized VDCPs were utilized as substrates for the further transformation in the presence of Pd catalysts.

The initial examination on the intramolecular rearrangement of VDCPs **1** was carried out upon heating **1a** in toluene at 60 °C in the presence of $Pd(OAc)_2$ (10 mol %) and PPh_3 (20 mol%) as the ligand under argon atmosphere. However, complex product mixtures were obtained after 10 h (Table 1, entry 1). In the absence of PPh_3 ligand, the rearranged product **2a** was formed in 76% isolated yield (91% NMR yield) (Table 1, entry 2). Its structure was determined by X-ray diffraction and its ORTEP drawing is shown in Figure 1.[13]

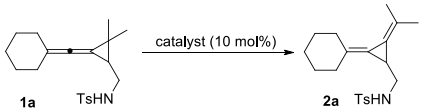
Then we studied other Pd catalysts such as Pd/C, $Pd(\eta^3\text{-}C_3H_5)Cl$, $Pd(OAc)_2(Py)_2$, $Pd(PhCN)_2Cl_2$, $PdCl_2(PPh_3)_2$, $Pd(dppf)(OTf)_2$, $Pd(dppf)Cl_2$, $PdCl_2$ and $(2,2'\text{-biPy})Pd(OAc)_2$ and the results are summarized in Table 1. We found that the reaction almost did not give the desired product cleanly using these Pd catalysts in toluene, suggesting that $Pd(OAc)_2$ is the best Pd catalyst for this reaction (Table 1, entries 3-11). Using $Pd(OAc)_2$ as the catalyst, the addition of Bu_4NCl or $PhEt_3NCl$ completely stopped the reaction (Table 1, entries 12-13). The use of $Pd(TFA)_2$ as the catalyst gave **2a** in 30% yield in toluene at 80 °C under otherwise identical conditions (Table 1, entry 14). Other transition metal catalysts such as $AuCl_3$, $Rh_2(OAc)_2$ and $PtCl_2$ produced complex product mixtures (Table 1, entries 15-17). No

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, P. R. China. E-mail: mshi@mail.sioc.ac.cn.

† Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data of new compounds, and CCDC 958985 and 1031145. See DOI: 10.1039/b000000x/

reaction occurred using $Cu(OAc)_2$ (10 mol%) as the catalyst (Table 1, entry 18). The examination of solvent effects revealed that toluene, CH_2Cl_2 and Et_2O were better than THF, DCE (1,2-dichloroethane) and MeCN (Table 1, entries 19-23) since upon heating in DCE (1.2-dichloroethane) or MeCN at 60 °C afforded **2a** in 73% or 62% NMR yield, respectively (Table 1, entries 22 and 23). All these results indicated that toluene is best suited to this reaction. The effect of temperature has been also examined in toluene. Upon heating at 80 °C gave **2a** in 91% NMR yield (76% isolated yield) which is exactly the same as that at 60 °C (Table 1, entry 2 and entry 25). Reducing the employed amount of $Pd(OAc)_2$ to 5 mol% produced **2a** in 83% yield under otherwise identical conditions (Table 2, entry 26) and increasing the reaction temperature up to 100 °C reduced the yield of **2a** to 57% yield in the presence of 5 mol% $Pd(OAc)_2$ (Table 1, entry 27). Furthermore, this reaction should be carried out under argon atmosphere and anhydrous conditions since under oxygen atmosphere or in the presence of water also reduced the yield of **2a** (Table 1, entries 28 and 29). The use of stoichiometric amount of $Pd(OAc)_2$ gave a complex product mixture (Table 1, entry 30). All these examinations revealed that this reaction should be carried out at 80 °C in toluene in the presence of 10 mol% $Pd(OAc)_2$.

Table 1. Optimization of the Reaction Conditions for the Rearrangement of Vinylidenecyclopropane **1a**



entry[a]	catalyst	additive	solvent	t (h)	T (°C)	yield (%)[b]
1	$Pd(OAc)_2/PPh_3$[c]	-	toluene	5	60	complex
2	$Pd(OAc)_2$	-	toluene	8	60	91 (76)[d]
3	Pd/C	-	toluene	5	60	N. R.
4	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	-	toluene	5	60	-[i]
5	$Pd(OAc)_2(Py)_2$	-	toluene	5	60	-[i]
6	$Pd(PhCN)_2Cl_2$	-	toluene	5	60	-[i]
7	$PdCl_2(PPh_3)_2$	-	toluene	5	60	-[i]
8	Pd(dppf)$(OTf)_2$	-	toluene	5	60	-[i]
9	Pd(dppf)Cl_2	-	toluene	5	60	-[i]
10	$PdCl_2$	-	toluene	5	60	-[i]
11	(2,2'-bipy)$Pd(OAc)_2$	-	toluene	5	60	-[i]
12	$Pd(OAc)_2$[e]	Bu_4NCl	toluene	10	60	N. R.
13	$Pd(OAc)_2$[e]	$PhEt_3NCl$	toluene	10	60	N. R.
14	$Pd(TFA)_2$	-	toluene	10	80	30
15	$AuCl_3$	-	toluene	10	80	-[i]
16	$Rh_2(OAc)_2$	-	toluene	10	80	-[i]
17	$PtCl_2$	-	toluene	10	80	-[i]
18	$Cu(OAc)_2$	-	toluene	10	80	N. R.
19	$Pd(OAc)_2$	-	THF	24	rt	70
20	$Pd(OAc)_2$	-	Et_2O	24	rt	83
21	$Pd(OAc)_2$	-	CH_2Cl_2	24	rt	85
22	$Pd(OAc)_2$	-	DCE	10	60	73
23	$Pd(OAc)_2$	-	MeCN	10	60	62
24	$Pd(OAc)_2$	-	toluene	24	rt	85
25	$Pd(OAc)_2$	-	toluene	8	80	91 (76)[d]
26[f]	$Pd(OAc)_2$	-	toluene	8	80	83
27[f]	$Pd(OAc)_2$	-	toluene	8	100	57
28	$Pd(OAc)_2$	O_2	toluene	8	60	45
29[g]	$Pd(OAc)_2$	H_2O	toluene	8	80	72
30[h]	$Pd(OAc)_2$	-	toluene	8	60	-[i]

[a] The reaction conditions: catalyst (10 mol%), 0.1 M in solvent unless otherwise specificed. [b] The yield was determined by ^1H NMR spectroscopic data using 1,3,5-trimethoxybenzene as an internal standard. [c] The ligand PPh_3 (20 mol%) was added. [d] Isolated yields. [e] The quaternary ammonium salts were added with 20 mol%. [f] With catalyst (5 mol%). [g] With H_2O (50 mol%). [h] Stoichiometric amount of catalyst was used. [i] The reactions gave complex product mixtures.

With the identification of the best reaction conditions, we next turned our efforts to investigate the scope and limitations of these intramolecular rearrangement and the results are summarized in Table 2. A variety of VDCPs **1** bearing different sulfonamide substituents have been tested and the corresponding products **2b-2g** were obtained in moderate to good yields without the observation of significant electronic effects (Table 2). Substrate

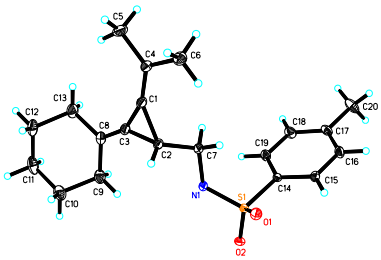
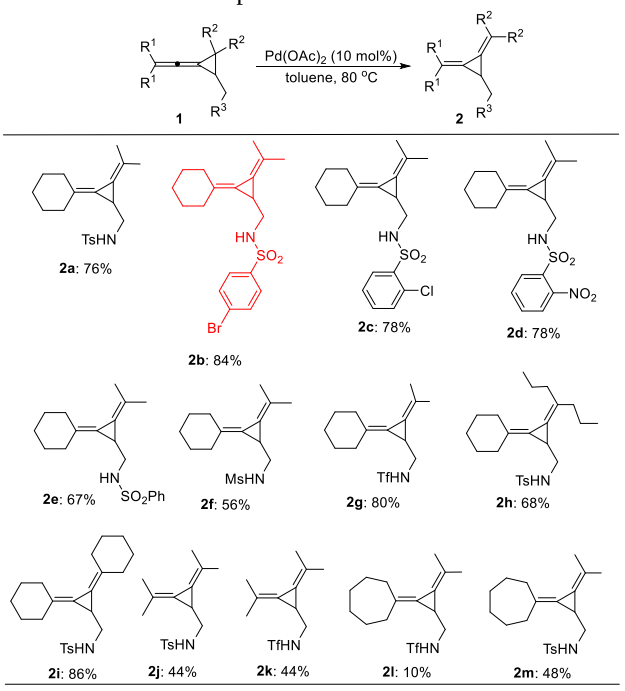


Figure 1. X-ray Crystal Structure of **2a**

2g having strongly electron-withdrawing trifluoro-methylsulfonamide (R^3 = triflamide) was also tolerated, affording the corresponding product **2g** in 80% yield. A range of different substituents at cyclopropane or allene moiety of **1** have been also tested, giving the desired products **2h-2m** in 10-86% yields. As for substrate **1l** having a cycloheptyl substituent (R^1 and R^1) and a triflamide functional group, the corresponding product **2l** was obtained in 10% yield presumably due to the instability of this product at 80 °C.

Table 2. Substrate Scope[a]

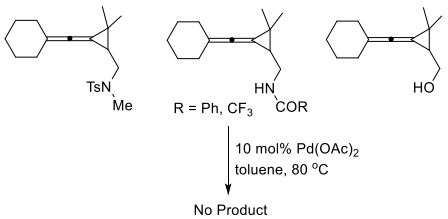


[a] Reaction conditions: VDCP **1** (0.2 mmol), $Pd(OAc)_2$ (0.02 mmol), toluene (2 mL). Isolated yields.

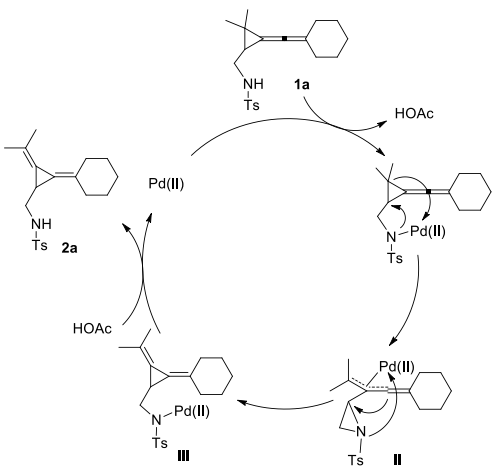
The control experiment shown in Scheme 2 indicated that when the substituent R^3 was a fully substituted sulfonamide

group, carbonamides or a free hydroxyl group, none of the desired product could be formed, suggesting that the sulfonamide group (R^3) is essential for this reaction.

A plausible reaction mechanism is depicted as below using **1a** as a substrate model on the basis of previous literature and the control experiments (Scheme 3). Since R^3 should be a sulfonamide group with a N-H moiety, it may work as a weak-coordinating group for Pd(II) to give intermediate **I**,[5,6] which subsequently undergoes ring-opening upon intramolecular attacking of NTs moiety to afford the corresponding allylic Pd intermediate **II** along with the formation of an aziridine. Then, the central carbon of previous allene moiety attacks onto the aziridine to afford intermediate **III**. The protonation of **III** produces the thermodynamically stable product **2a**. The N-H group in sulfonamide is important in proton exchange with $Pd(OAc)_2$ to incorporate the Pd(II) species into the directing group as shown in Scheme 3. The use of Pd(0) catalyst such as Pd_2dba_3 and $Pd(PPh_3)_4$ as catalysts gave complex product mixtures, rendering that this is a Pd(II) catalyzed process.

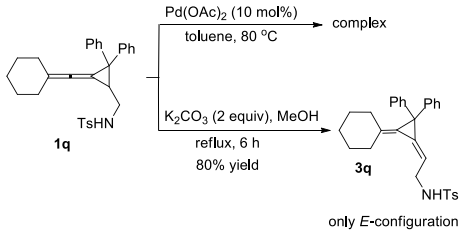


Scheme 2. The Control Experiments



Scheme 3. A Plausible Mechanism for the Formation of **2a**

Interestingly, substrate **1q**, bearing two phenyl groups at cyclopropane (R^2 = phenyl group), produced a complex mixture under the standard conditions. However, upon heating **1q** in methanol in the presence of K_2CO_3 (2 equiv) afforded another rearranged product **3q** in 80% as *E*-configuration (Scheme 4). Its structure was determined by X-ray diffraction and its ORTEP drawing is shown in Figure 2.[14] As comparison, compound **1a** was also subjected to the basic conditions, but none of the similar product was afforded.



Scheme 4. The Rearrangement of **1q** under Basic Condition

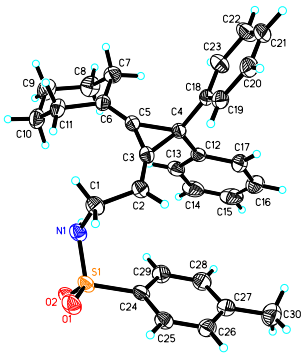
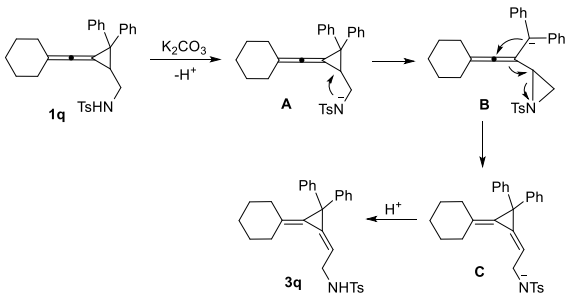


Figure 2. X-ray Crystal Structure of **3q**



Scheme 5. A Plausible Mechanism for the Formation of **3q**

A mechanistic explanation for the intramolecular rearrangement of **1q** in the presence of K_2CO_3 has been proposed in Scheme 5. Firstly, deprotonation of **1q** by K_2CO_3 gives anionic intermediate **A**, which undergoes intramolecular nucleophilic attack onto the cyclopropane affords anionic aziridine intermediate **B** accompanied by a ring-opening process. Then, a nucleophilic attack onto the central carbon of allene takes place along with the migration of double bond, leading to the aziridine ring-opening intermediate **C**. Protonation of intermediate **C** gives the corresponding product **3q**. The different reaction outcome on phenyl substituted substrate **1q** may be due to the stabilization of the anionic intermediate by the phenyl group.

In summary, we have developed a novel C-C bond activation mode of functionalized vinylidenecyclopropanes using a simple and weakly coordinating sulfonamide directing group. Different reaction pathways have been observed when R^2 was a phenyl group. The reaction mechanism has also been discussed on the basis of the control experiment and previous results. Further work is underway to elucidate further mechanistic details of these reactions and to understand their

scope and limitations in our laboratory.

We are grateful for the financial support from the National Basic Research Program of China (973)-2015CB856603, and the National Natural Science Foundation of China (20472096, 21372241, 21361140350, 20672127, 21421091, 21372250, 21121062, 21302203 and 20732008).

Notes and references

(1) (a) X.-X. Guo, D.-W. Gu, Z. Wu and W. Zhang, *Chem. Rev.*, 2015, **115**, 1622; (b) H. Huang, X. Ji, W. Wu and H. Jiang, *Chem. Soc. Rev.*, 2015, **44**, 1155; (c) M.-L. Louillat and F. W. Patureau, *Chem. Soc. Rev.*, 2014, **43**, 901; (d) D. G. Musaev, T. M. Figg and A. L. Kaledin, *Chem. Soc. Rev.*, 2014, **43**, 5009; (e) J. Xie, C. Pan, A. Abdukader and C. Zhu, *Chem. Soc. Rev.*, 2014, **43**, 5245; (f) F. Zhang and D. R. Spring, *Chem. Soc. Rev.*, 2014, **43**, 6906; (g) B.-J. Li and Z.-J. Shi, *Chem. Soc. Rev.*, 2012, **41**, 5588; (h) J. Wencel-Delord, T. Droege, F. Liu and F. Glorius, *Chem. Soc. Rev.*, 2011, **40**, 4740; (i) D. Balcells, E. Clot and O. Eisenstein, *Chem. Rev.*, 2010, **110**, 749; (j) E. M. Beck and M. J. Gaunt, *Top. Curr. Chem.*, 2010, **292**, 85; (k) D. A. Colby, R. G. Bergman and J. A. Ellman, *Chem. Rev.*, 2010, **110**, 624; (l) R. Jazzar, J. Hitce, A. Renaudat, J. Sofack-Kreutzer and O. Baudoin, *Chem. Eur. J.*, 2010, **16**, 2654; (m) T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010, **110**, 1147; (n) X. Chen, K. M. Engle, D.-H. Wang and J.-Q. Yu, *Angew. Chem., Int. Ed.*, 2009, **48**, 5094; (o) O. Daugulis, H.-Q. Do and D. Shabashov, *Acc. Chem. Res.*, 2009, **42**, 1074; (p) R. Giri, B.-F. Shi, K. M. Engle, N. Maugel and J.-Q. Yu, *Chem. Soc. Rev.*, 2009, **38**, 3242; (q) P. Thansandote and M. Lautens, *Chem. Eur. J.*, 2009, **15**, 5874; (r) D. Alberico, M. E. Scott and M. Lautens, *Chem. Rev.*, 2007, **107**, 174; (s) E. M. Beccalli, G. Broggini, M. Martinelli and S. Sottocornola, *Chem. Rev.*, 2007, **107**, 5318; (t) L.-C. Campeau, D. R. Stuart and K. Fagnou, *Aldrichimica Acta*, 2007, **40**, 35.

(2) (a) L. Ackermann, *Acc. Chem. Res.*, 2014, **47**, 281; (b) S. De Sarkar, W. Liu, S. I. Kozhushkov and L. Ackermann, *Adv. Synth. Catal.*, 2014, **356**, 1461; (c) Y. Rao, *Synlett*, 2013, **24**, 2472; (d) K. M. Engle, T.-S. Mei, M. Wasa and J.-Q. Yu, *Acc. Chem. Res.*, 2012, **45**, 788; (e) L. Ackermann, *Chem. Rev.*, 2011, **111**, 1315.

(3) (a) S. Ma, G. Villa, P. S. Thuy-Boun, A. Homs and J.-Q. Yu, *Angew. Chem., Int. Ed.*, 2014, **53**, 734; (b) P. S. Thuy-Boun, G. Villa, D. Dang, P. Richardson, S. Su and J.-Q. Yu, *J. Am. Chem. Soc.*, 2013, **135**, 17508; (c) K. M. Engle, P. S. Thuy-Boun, M. Dang and J.-Q. Yu, *J. Am. Chem. Soc.*, 2011, **133**, 18183.

(4) (a) Y. Lu, D.-H. Wang, K. M. Engle and J.-Q. Yu, *J. Am. Chem. Soc.*, 2010, **132**, 5916; (b) X. Wang, Y. Lu, H.-X. Dai and J.-Q. Yu, *J. Am. Chem. Soc.*, 2010, **132**, 12203.

(5) (a) X.-C. Wang, W. Gong, L.-Z. Fang, R.-Y. Zhu, S. Li, K. M. Engle and J.-Q. Yu, *Nature*, 2015, **519**, 334; (b) G. He, Y. Zhao, S. Zhang, C. Lu and G. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 3; (c) X.-G. Zhang, H.-X. Dai, M. Wasa and J.-Q. Yu, *J. Am. Chem. Soc.*, 2012, **134**, 11948.

(6) (a) C. Feng, D. Feng and T.-P. Loh, *Chem. Commun.*, 2015, **51**, 342; (b) C. Feng, D. Feng, Y. Luo and T.-P. Loh, *Org. Lett.*, 2014, **16**, 5956; (c) K. S. L. Chan, M. Wasa, X. Wang and J.-Q. Yu, *Angew. Chem., Int. Ed.*, 2011, **50**, 9081; (d) H.-X. Dai, A. F. Stepan, M. S. Plummer, Y.-H. Zhang and J.-Q. Yu, *J. Am. Chem. Soc.*, 2011, **133**, 7222.

(7) (a) Y.-J. Liu, H. Xu, W.-J. Kong, M. Shang, H.-X. Dai and J.-Q. Yu, *Nature*, 2014, **515**, 389; (b) D.-H.Wang, M. Wasa, R. Giri and J.-Q. Yu, *J. Am. Chem. Soc.*, 2008, **130**, 7190.

(8) (a) B. E. Haines and D. G. Musaev, *ACS Catal.*, 2015, **5**, 830; (b) G. Li, L. Wan, G. Zhang, D. Leow, J. Spangler and J.-Q. Yu, *J. Am. Chem. Soc.*, 2015; (c) W. Yang, S. Ye, D. Fanning, T. Coon, Y. Schmidt, P. Krenitsky, D. Stamos and J.-Q. Yu, *Angew. Chem., Int. Ed.*, 2015, **54**, 2501; (d) J. Kim and S. Chang, *Angew. Chem., Int. Ed.*, 2014, **53**, 2203; (e) S. Li, G. Chen, C.-G. Feng, W. Gong and J.-Q. Yu, *J. Am. Chem. Soc.*, 2014, **136**, 5267; (f) X. Sun, G. Shan, Y. Sun and Y. Rao, *Angew. Chem., Int. Ed.*, 2013, **52**, 4440; (g) X.-C. Wang, Y. Hu, S. Bonacorsi, Y. Hong, R. Burrell and J.-Q. Yu, *J. Am. Chem. Soc.*, 2013, **135**, 10326; (h) Z. Ren, F. Mo and G. Dong, *J. Am. Chem. Soc.*, 2012, **134**, 16991; (i) P. E. Zhichkin, S. G. Krasutsky and R. Krishnamoorthy, *Synlett*, 2010, 3039.

(9) (a) R. Zeng and G. Dong, *J. Am. Chem. Soc.*, 2015, **137**, 1408; (b) A. Dermenci, J. W. Coe and G. Dong, *Org. Chem. Front.*, 2014, **1**, 567; (c) A. Korotvicka, D. Necas and M. Kotora, *Curr. Org. Chem.*, 2012, **16**, 1170; (d) K. Ruhland, *Eur. J. Org. Chem.*, 2012, **2012**, 2683; (e) M. Murakami and T. Matsuda, *Chem. Commun.*, 2011, **47**, 1100; (f) T. Seiser, T. Saget, D. N. Tran and N. Cramer, *Angew. Chem., Int. Ed.*, 2011, **50**, 7740; (g) C.-H. Jun and J.-W. Park, *Top. Organomet. Chem.*, 2007, **24**, 117; (h) D. Necas and M. Kotora, *Curr. Org. Chem.*, 2007, **11**, 1566; (i) T. Kondo and T.-a. Mitsudo, *Chem. Lett.*, 2005, **34**, 1462; (j) C.-H. Jun, *Chem. Soc. Rev.*, 2004, **33**, 610; (k) M. E. van der Boom and D. Milstein, *Chem. Rev.*, 2003, **103**, 1759; (l) C. Perthuisot, B. L. Edelbach, D. L. Zubris, N. Simhai, C. N. Iverson, C. Muller, T. Satoh and W. D. Jones, *J. Mol. Catal. A: Chem.*, 2002, **189**, 157; (m) L. Giannini, S. Dovesi, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Angew. Chem., Int. Ed.*, 1999, **38**, 807; (n) M. Murakami and Y. Ito, *Top. Organomet. Chem.*, 1999, **3**, 97; (o) M. Gozin, A. Weisman, Y. Ben-David and D. Milstein, *Nature*, 1993, **364**, 699; (p) R. H. Crabtree, *Chem. Rev.*, 1985, **85**, 245.

(10) (a) A. Brandi, S. Cicchi, F. M. Cordero and A. Goti, *Chem. Rev.*, 2014, **114**, 7317; (b) D.-H. Zhang, X.-Y. Tang and M. Shi, *Acc. Chem. Res.*, 2014, **47**, 913; (c) M. Shi, J.-M. Lu, Y. Wei and L.-X. Shao, *Acc. Chem. Res.*, 2012, **45**, 641; (d) Y. Yamamoto, *Chem. Rev.*, 2012, **112**, 4736; (e) L. Yu and R. Guo, *Org. Prep. Proced. Int.*, 2011, **43**, 209; (f) A. Masarwa and I. Marek, *Chem. Eur. J.*, 2010, **16**, 9712; (g) M. Shi, L.-X. Shao, J.-M. Lu, Y. Wei, K. Mizuno and H. Maeda, *Chem. Rev.*, 2010, **110**, 5883; (h) M. Rubin, M. Rubina and V. Gevorgyan, *Chem. Rev.*, 2007, **107**, 3117; (i) I. Nakamura and Y. Yamamoto, *Adv. Synth. Catal.*, 2002, **344**, 111.

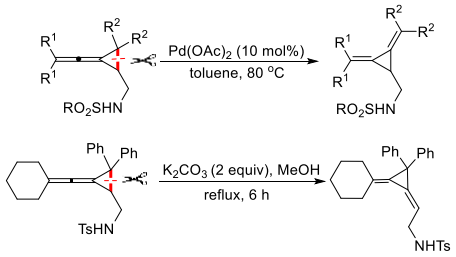
(11) (a) B. Mueller, T. Bally, R. Pappas and F. Williams, *J. Am. Chem. Soc.*, 2010, **132**, 14649; (b) A. De Meijere, S. Blechert and editors, *NATO Advanced Science Institutes Series, Series C Mathematical and Physical Sciences, Vol. 273: Strain and Its Implications in Organic Chemistry*, Kluwer Academic Publ., 1989; (c) A. De Meijere, *Top. Curr. Chem.*, 1988, **144**, 217.

(12) (a) B.-L. Lu, Y. Wei and M. Shi, *Organometallics*, 2012, **31**, 4601; (b) B.-L. Lu and M. Shi, *Eur. J. Org. Chem.*, 2011, 243; (c) B.-L. Lu and M. Shi, *Angew. Chem., Int. Ed.*, 2011, **50**, 12027; (d) B.-L. Lu, Y. Wei and M. Shi, *Chem. Eur. J.*, 2010, **16**, 10975.

(13) The CIF data of **2a** have been deposited in CCDC 958985 (see Supporting Information).

(14) The CIF data of **3q** have been deposited in CCDC 1031145 (see Supporting Information).

Palladium-catalyzed intramolecular rearrangement of vinylidenecyclopropanes through C-C bond activation



Intramolecular rearrangement of vinylidenecyclopropanes to dimethylenecyclopropanes through C-C bond activation has been developed.

Dong Pan, Gen-Qiang Chen, Xiang-Ying Tang and Min Shi*