Journal Name

ChemComm

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Gold-Catalyzed 1,2-Acyloxy Migration/Intramolecular Cyclopropanation/Ring Enlargement Cascade: Syntheses of Medium-Sized Heterocycles

Yin-Wei Sun,† Xiang-Ying Tang‡* Min Shi†,‡*

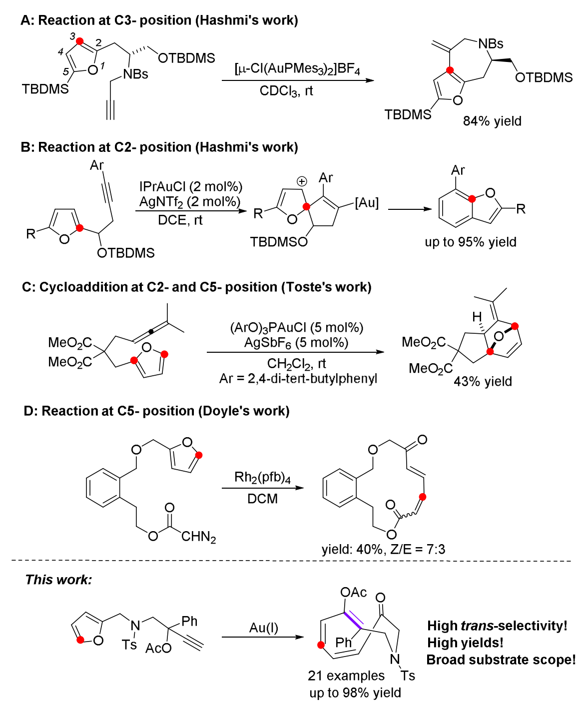
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The synthesis of medium-sized heterocycles possessing a trans double bond is still a challenge. Herein, a gold(I)-catalyzed 1,2-acyloxy migration/intramolecular cyclopropanation/ring enlargement cascade reaction of furans has been developed, providing a highly efficient access to ten- and eleven-membered heterocycles with broad substrate scope under mild reaction conditions. The reaction outcome features high chemoselectivity at the C5-position of furan. Moreover, a trans-double bond was embodied into the medium ring system.

Medium-sized heterocycles possessing *trans* double bonds are prevalent structure in a large number of biologically active natural products, for example Herbarumin, Abyssomicin and Madangamine.[1] However, efficient synthetic access to install such ring systems remains a big challenge.[2] Thus far, very limited methods have been accomplished. The ring-closing metathesis (RCM) is the most versatile and efficient method to construct *cis*-C-C double bonds, but there are only a few examples for the synthesis of cyclic *trans*-alkenes.[3,4] The Yamaguchi macrolactonization offers another excellent solution, however, stoichiometric chloride and base are required.[5] In recent years, gold catalysis has witnessed intensive advancements.[6] Alternatively, gold catalyzed cycloadditions and cycloisomerizations have served as a powerful tool-box to build medium ring systems.[7] For example, She's group has developed a facile protocol to construct medium-sized ring catalyzed by gold(I) catalysis.[7e] Nevertheless, formation of *cis*-alkenes is still unavoidable. Thus, the development of a new strategy with atom efficiency and practical simplicity to construct medium sized heterocycles, especially those with *trans* double bonds, is still highly demanded.

† *Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, and 130 MeiLong Road, Shanghai 200237, People's Republic of China.*
‡ *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, P. R. China. E-mail: siocxiangying@mail.sioc.ac.cn; mshi@mail.sioc.ac.cn.*
† Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data of new compounds, and CCDC 973301, 996019, 966978, 972417, 1401380, 1406576 and 997457. See DOI: 10.1039/b000000x/

Furan rings are valuable five-membered aromatic heterocycles due to the unique diversity of their chemical transformations under gold catalysis. The intramolecular reactions of furan are particularly attractive due to its versatile reactivities in the presence of gold(I) complex, providing easy access to heterocycles.[8] Accordingly, there are several types of intramolecular reactions of furan with other functional groups: nucleophilic attack from C3- or C2-position[9d] of furan (Scheme 1, A and B),[9] and cycloaddition taking place at both C2- and C5-positions (Scheme 1, C) under gold catalysis.[10]



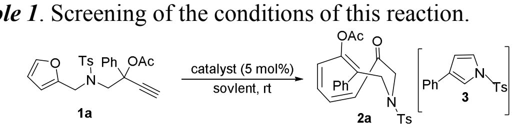
Scheme 1. Different reaction patterns on furan ring.

Surprisingly, reactions specifically occur at furan's C5-position are extremely rare. As reported by Doyle, the tandem cyclopropanation and ring-opening process gave a 14-membered ring compound as a *Z*/*E* isomeric mixture in only 40% yield (Scheme 1, D).[11] Herein, we reported an intramolecular reaction of furan-ring at C5-position under gold catalysis, affording ten or eleven-membered heterocycles with a *trans*-double bond in high chemoselectivity and regioselectivity in up to 98% yield.

Gold-catalyzed 1,2-acyloxy migration of propargylic esters to form a gold vinyl carbenoid species has been widely reported.[12-14] It is well known that such electrophilc carbenes can readily accept nucleophilic attack. We thus envisage that if the chain between furan and carbene center is long enough, the reaction of gold carbene with furan would take place at C5-position, and the only challenge may rely on the competitive reaction which takes place at the alkene part of vinly gold carbene.

Initially, the ester **1a** was selected as substrate to screen the reaction conditions (Table 1). Pleasingly, using IPrAuCl/$AgSbF_6$ as catalyst, **2a**[15] was isolated in 30% yield, along 3-phenyl-1-tosyl-1H-pyrrole **3**[15,16] in 31% yield (entry 1). Among various phosphine ligands, $Me_4{}^tBuXphos$ turned out to be the most effective with 70% isolated yield of **2a** (Table 1, entries 2 and 3). $Me_4{}^tBuXphosAu(MeCN)OTf$ was chosen as the best catalyst, affording **2a** in 91% yield (Table 1, entry 4). We were pleased to find that if cut the loading of catalyst to 2.5 mol% and 1 mol%, **2a** was isolated in 95% and 96% yields, respectively (entries 5 and 6) (see Table SI-1 for more information).

Table 1. Screening of the conditions of this reaction.

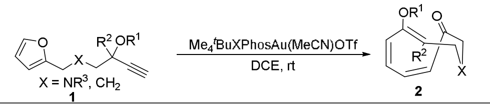


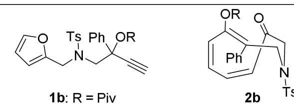
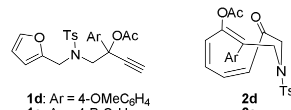
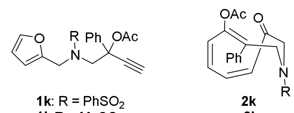
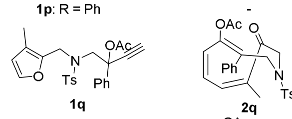
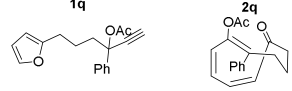
entry[a]	catalyst	solvent	yield (%)[b]
1[c]	IPrAuCl/$AgSbF_6$	DCE	30
2	$^tBuXPhosAu(MeCN)SbF_6$	DCE	58
3	$Me_4{}^tBuXPhosAu(MeCN)SbF_6$	DCE	70
4	$Me_4{}^tBuXPhosAu(MeCN)OTf$	DCE	91
5[d]	$Me_4{}^tBuXPhosAu(MeCN)OTf$	DCE	95
6[e]	***$Me_4{}^tBuXPhosAu(MeCN)OTf$***	***DCE***	***96***

[a] The reaction was carried out on a 0.1 mmol scale in solvents (1.0 mL). [b] Isolated yield. [c] 3-phenyl-1-tosyl-1*H*-pyrrole **3** was found under this condition. [d] 2.5 mol% of Au catalyst was added. [e] 1 mol% Au of catalyst was added.

With the optimized reaction conditions in hand, we set out to define the scope of this cascade reaction (Table 2). Other propargyl esters (OPiv and OBz) were suitable for this cyclization, with the formation of **2b** and **2c** in 72% and 81% yields, respectively (Table 2, entries 1 and 2). It was found that R^2 could be various aryl rings. When either electron-withdrawing or electron-donor groups were introduced on the benzene ring of R^2, the reactions proceeded smoothly to give the corresponding products **2d**-**2h** in moderate to excellent yields (Table 2, entries 3-7). When R^2 were 1-naphthalenyl and 2-chlorophenyl groups, the reactions produced the desired products **2i** and **2j** in 20% and 45% yields, and the relatively low yields were probably due to the increased steric hindrance (Table 2, entries 8 and 9). Other sulfonyl groups (R^3), such as $PhSO_2$, Ms, 2-$ClC_6H_4SO_2$, Bs and 2-$MeC_6H_4SO_2$ were well tolerated under the standard reaction conditions, furnishing **2k-2o** in 81-94% yields (Table 2, entries 10-14). However, treatment of N-phenyl group (R^3) protected substrate under gold catalysis, the reaction became complex, presumably due to this phenyl ring could also take part in the reaction as that of furan ring (Table 2, entry 15). When substrate **1q** with Me group on its C3-position of furan ring was employed, the reaction gave product **2q** in 96% yield successfully (Table 2, entry 16). Notably, when all carbon chain tethered substrate, such as **1r**, was treated under the standard reaction conditions, the reaction worked very well to give ten-membered rings **2r** in 82% yield (Table 2, entry 17).

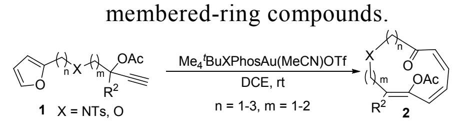
Table 2. Gold-catalyzed reaction for formation of ten-membered rings.

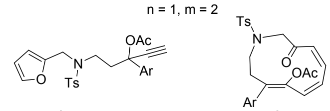
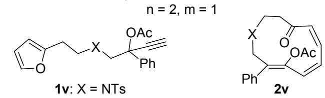
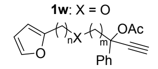


entry[a]	substrate	product	yield (%)[b]
			
1	**1b**: R = Piv	**2b**	72
2	**1c**: R = Bz	**2c**	81
			
3	**1d**: Ar = 4-$OMeC_6H_4$	**2d**	56
4	**1e**: Ar = 4-BrC_6H_4	**2e**	88
5	**1f**: Ar = 3-BrC_6H_4	**2f**	91
6	**1g**: Ar = 4-MeC_6H_4	**2g**	83
7	**1h**: Ar = 3,4-$Cl_2C_6H_3$	**2h**	81
8	**1i**: Ar = 1-Naphthyl	**2i**	20
9	**1j**: Ar = 2-ClC_6H_4	**2j**	45
			
10	**1k**: R = $PhSO_2$	**2k**	91
11	**1l**: R = $MeSO_2$	**2l**	81
12	**1m**: R = 2-$ClC_6H_4SO_2$	**2m**	89
13	**1n**: R = Bs	**2n**	93
14	**1o**: R = 2-$MeC_6H_4SO_2$	**2o**	94
15	**1p**: R = Ph	-	complex
			
16	**1q**	**2q**	96
			
17	**1r**	**2r**	82

[a] The reaction was carried out on a 0.2 mmol scale with 2.5 mol% catalyst in solvent (2.0 mL). [b] Isolated yield.

Table 3. Gold-catalyzed reaction for construction of eleven-membered-ring compounds.

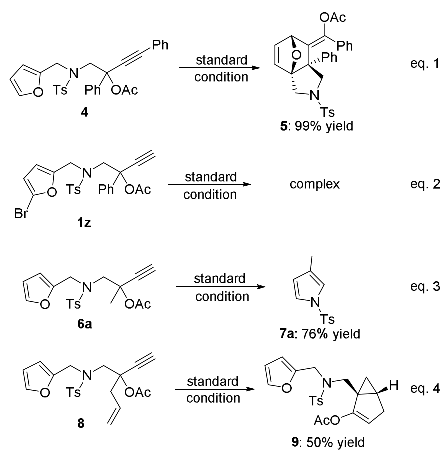


entry	substrates	products	yield (%)[b]
	n = 1, m = 2		
			
1	**1s**: Ar = Ph	**2s**	98
2	**1t**: Ar = 4-MeC_6H_4	**2t**	98
3	**1u**: Ar = 4-BrC_6H_4	**2u**	80
	n = 2, m = 1		
			
4	**1v**: X = NTs	**2v**	97
5	**1w**: X = O	**2w**	78
			
6[c]	**1x**: n = 2, m = 2 **1y**: n = 3, m = 1	-	complex

[a] The reaction was carried out on a 0.2 mmol scale with 2.5 mol% catalyst in solvent (2.0 mL). [b] Isolated yield. [c] Both reaction became complexed.

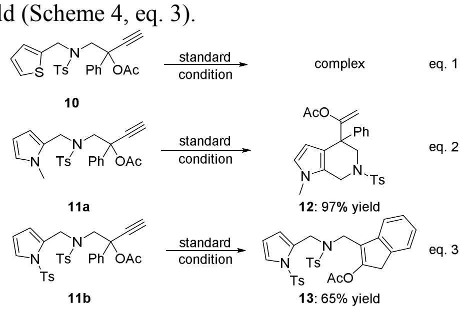
Moreover, the reaction could also be extended to synthesize eleven-membered-ring system. As shown in Table 3, for substrates **1s**-**1u**, in which n = 1, m = 2, the reactions gave the corresponding eleven-membered heterocycles **2s**-**2u** in 80-98% yields (Table 3, entries 1-3). [15] While, when n = 2, m = 1, the reactions of **1v** and **1w** went on smoothly to furnish the desired products **2v** and **2w** in 78% and 97% yields, respectively (Table 3, entries 4 and 5). The nitrogen tether could also be replaced by oxygen; as for substrate **1u**, the corresponding eleven-membered cyclic ether was obtained in 78% yield (Table 3, entry 5). The reaction failed in the syntheses of twelve-membered cyclic amines; as for substrates **1x** and **1y** with longer chain, the reactions gave complex product mixtures (Table 3, entry 6).

To further define the substrate scope of this reaction, some different types of substrates were synthesized and new reaction patterns were observed (Scheme 3).[17] As for non-terminal propargyl ester **4**, a formal [4 + 2] cycloaddition reaction took place to form oxo-bridged bicyclic compound **5**[17] in 99% yield (Scheme 3, eq. 1). When furan **1z** with its C5-position being blocked by Br atom was employed as substrate, the reaction became complex (Scheme 3, eq. 2). When R^2 was replaced by alkyl (Me) groups, fragmentation was observed and 3-methyl pyrrole was obtained in 76% yield (Scheme 3, eq. 3 and more information is included in Table SI-2). Interestingly, if R^2 was an allyl group, the reaction of **8** delivered **9** in 50% yield via cyclopropanation (Scheme 3, eq. 4).[13c,13h] The structure of **9** was assigned by ^{1}H NMR, ^{13}C NMR and 2D NMR spectroscopic experiments (see SI for the details). These results suggested that the terminal alkyne and aryl substituent of R^2 were two critical factors for the desired ring synthesis.



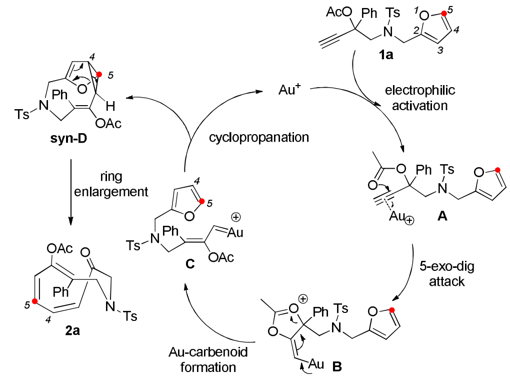
Scheme 3. Other products were observed using different substrates.

Then we tried to use other heterocyclic substrates. When using thiophene derivative **10** as substrate, the reaction became complex (Scheme 4, eq. 1). As for N-Me pyrrole **11a**, a Friedel-Crafts reaction gave product **12**[15] in 97% yield (Scheme 4, eq. 2). If using N-Ts pyrrole **11b** as substrate, **13**[15] was obtained in 65% yield (Scheme 4, eq. 3).



Scheme 4. Gold-catalyzed reaction using other heterocyclic substrates.

A mechanistic proposal is proposed in Scheme 5. Gold(I) catalyst activation of triple bond in **1a** gives □complex **A**, which undergoes a 5-exo-dig attack to the activated triple bond results in intermediate **B**. Subsequent 1,2-acyloxy migration delivers gold carbene intermediate **C**.[12] Following a cyclopropanation at C4- and C5-positions of furan delivers intermediate **syn-D** and regenerates the catalyst.[11] The steric hindrance of aryl groups in intermediate **C** may cause the cyclopropanation exclusively taking place at C4- and C5-positions. Finally, the ring opening process of **syn-D** provides the desired product **2a**.



Scheme 5. Proposed Mechanisms.

In conclusion, we have developed a highly efficient procedure for the formation of ten and eleven-membered carbo- and heterocycles by gold-catalyzed cascade reaction. The appropriate distance from furan ring and the carbene center may be the key to form these medium-sized ring systems. We believe that this transformation will provide new insights into gold catalyzed intramolecular cyclization reactions and new future of furan's reaction.

Acknowledgement: 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] For selected examples, see: (a) G. V. M. Sharma, K. L. Reddy, *Tetrahedron: Asymmetry,* **2006**, *17*, 3197; (b) F. Bihelovic, R. N. Saicic, *Angew. Chem. Int. Ed.,* **2012**, *51*, 5687; (c) J. S. Yadav, S. Avuluri, S. S. Kattela, S. Das, *Eur. J. Org. Chem.,* **2013**, 6967; (d) R. Ballette, M. Pérez, S. Proto, M. Amat, J. Bosch, *Angew. Chem. Int. Ed.,* **2014**, *53*, 6202.

[2] M. Isobe, A. Hamajima, *Nat. Prod. Rep.,* **2010**, *27*, 1204.

[3] For recent reviews, see: (a) R. H. Grubbs, S. Chang, *Tetrahedron,* **1998**, *54*, 4413; (b) S. P. Nolan, H. Clavier, *Chem. Soc. Rev.,* **2010**, *39*, 3305.

[4] For recent RCM reaction in total syntheses, see: (a) I. Volchkov, L. Daesung, *J. Am. Chem. Soc.,* **2013**, *135*, 5324; (b) H. Park, H.-K. Lee, T.-L. Choi, *J. Am. Chem. Soc.,* **2013**, *135*, 10769; (c) F. Horeischi, N. Biber, B. Plietker, *J. Am. Chem. Soc.,* **2014**, *136*, 4026; (d) H. Zhang, E. C. Yu, S. Torker, R. R. Schrock, A. H. Hoveyda, *J. Am. Chem. Soc.,* **2014**, *136*, 16493; (e) P. N. Carlsen, T. J. Mann, A. H. Hoveyda, A. J. Frontier, *Angew. Chem. Int. Ed.,* **2014**, *53*, 9334.

[5] For recent Yamaguchi macrolactonization in total syntheses, see: (a) S. M. Dalby, J. Goodwin-Tindall, I. Paterson, *Angew. Chem. Int. Ed.,* **2013**, *52*, 6517; (b) J. S. Clark, F. Romiti, *Angew. Chem. Int. Ed.,* **2013**, *52*, 10072; (c) B. M. Trost, C. E. Stivala, K. L. Hull, A. Huang, D. R. Fandrick, *J. Am. Chem. Soc.,* **2014**, *136*, 88.

[6] For selected reviews on gold catalysis, see: (a) S. Sengupta, X. Shi, *ChemCatChem,* **2010**, *2*, 609; (b) A. Corma, A. Leyva-Pérez, M. J. Sabater, *Chem. Rev.,* **2011**, *111*, 1657; (c) N. Krause, C. Winter, *Chem. Rev.,* **2011**, *111*, 1994; (d) M. Bandini, *Chem. Soc. Rev.,* **2011**, *40*, 1358; (e) M. Rudolph, A. S. K. Hashmi, *Chem. Soc. Rev.,* **2012**, *41*, 2448; (f) B.-L. Lu, L. Dai, M. Shi, *Chem. Soc. Rev.,* **2012**, *41*, 3318; (g) D.-H. Zhang, X.-Y. Tang, M. Shi, *Acc. Chem. Res.,* **2013**, *47*, 913; (h) A. S. K.

Hashmi, *Acc. Chem. Res.,* **2014**, *47*, 864; (i) W. Yang, A. S. K. Hashmi, *Chem. Soc. Rev.,* **2014**, *43*, 2941; (j) Y.-M. Wang, A. D. Lackner, F. D. Toste, *Acc. Chem. Res.,* **2014**, *47*, 889; (k) C. Obradors, A. M. Echavarren, *Acc. Chem. Res.,* **2014**, *47*, 902; (l) L. Fensterbank, M. Malacria, *Acc. Chem. Res.,* **2014**, *47*, 953.

[7] (a) C. Ferrer, A. M. Echavarren, *Angew. Chem. Int. Ed.,* **2006**, *45*, 1105; (b) C. Ferrer, C. H. M. Amijs, A. M. Echavarren, *Chem. Eur. J.,* **2007**, *13*, 1358; (c) H.-H. Liao, R.-S. Liu, *Chem. Commun.,* **2011**, *47*, 1339; (d) L. Zhang, L. Chang, H. Hu, H. Wang, Z.-J. Yao, S. Wang, *Chem. Eur. J.,* **2014**, *20*, 2925; (e) C. Zhao, X. Xie, S. Duan, H. Li, R. Fang, X. She, *Angew. Chem. Int. Ed.,* **2014**, *53*, 10789.

[8] For furan reactions catalyzed by gold(I) complex, see: (a) A. S. K. Hashmi, T. M. Frost, J. W. Bats, *J. Am. Chem. Soc.,* **2000**, *122*, 11553; (b) Y. Chen, W. Yan, N. G. Akhmedov, X. Shi, *Org. Lett.,* **2010**, *12*, 344; (c) A. S. K. Hashmi, *Pure Appl. Chem.,* **2010**, *82*, 1517; (d) A. S. K. Hashmi, M. Woelfle, F. Ata, W. Frey, F. Rominger, *Synthesis,* **2010**, *13*, 2297; (e) M. S. Hadfield, A.-L. Lee, *Chem. Commum.,* **2011**, *47*, 1333; (f) Y. Chen, G. Li, Y. Liu, *Adv. Synth. Catal.,* **2011**, *353*, 392; (g) Y. Chen, Y. Liu, *J. Org. Chem.,* **2011**, *76*, 5274; (h) A. S. K. Hashmi, W. Yang, F. Rominger, *Angew. Chem. Int. Ed.,* **2011**, *50*, 5762; (i) C. Wang, Y. Chen, X. Xie, J. Liu, Y. Liu, *J. Org. Chem.,* **2012**, *77*, 1915; (j) A. S. K. Hashmi, M. Ghanbari, M. Rudolph, F. Rominger, *Chem. Eur. J.,* **2012**, *18*, 8113; (k) A. S. K. Hashimi, T. Häffner, W. Yang, S. Pankajakshan, S. Schäfer, L. Schultes, F. Roninger, W. Frey, *Chem. Eur. J.,* **2012**, *18*, 10480; (l) A. S. K. Hashmi, J. Hofmann, S. Shi, A. Schütz, M. Rudolph, C. Lothschütz, M. Wieteck, M. Bührle, M. Wölfle, F. Rominger, *Chem. Eur. J.,* **2013**, *19*, 382; (m) N. Huguet, D. Lebœuf, A. M. Echavarren, *Chem. Eur. J.,* **2013**, *19*, 6581; (n) Z. Dong, C.-H. Liu, Y. Wang, M. Lin, Z.-X. Yu, *Angew. Chem. Int. Ed.,* **2013**, *52*, 14157; (o) D. Lebœuf, M. Gaydou, Y. Wang, A. M. Echavarren, *Org. Chem. Front.,* **2014**, *1*, 759; (p) N. Sun, X. Xie, Y. Liu, *Chem. Eur. J.,* **2014**, *20*, 7514; (q) Y. Chen, L. Wang, N. Sun, X. Xie, X. Zhao, H. Chen, Y. Li, Y. Liu, *Chem. Eur. J.,* **2014**, *20*, 12015; (r) C. Wang, X. Xie, J. Liu, Y. Liu, Y. Li, *Chem. Eur. J.,* **2015**, *21*, 559.

[9] (a) A. S. K. Hashmi, P. Haufe, C. Schmid, A. Rivas Nass, W. Frey, *Chem. Eur. J.,* **2006**, *12*, 5376; (b) A. S. K. Hashmi, M. Rudolph, J. Huck, W. Frey, J. W. Bats, M. Hamzić, *Angew. Chem. Int. Ed.,* **2009**, *48*, 5848; (c) A. S. K. Hashmi, S. Pankajakshan, M. Rudolph, E. Enns, T. Bander, F. Rominger, W. Frey, *Adv. Synth. Catal.,* **2009**, *351*, 2855; (d) A. S. K. Hashmi, W. Yang, F. Rominger, *Angew. Chem. Int. Ed.,* **2011**, *50*, 5762.

[10] (a) P. Mauleón, R. M. Zeldin, A. Z. González, F. D. Toste, *J. Am. Chem. Soc.,* **2009**, *131*, 6348; (b) I. Alonso, B. Trillo, F. López, S. Montserrat, G. Ujaque, L. Castedo, A. Lledós, J. L. Mascareñas, *J. Am. Chem. Soc.,* **2009**, *131*, 13020; (c) P. Mauleon, *ChemCatChem,* **2013**, *5*, 2149; (d) M. E. Muratore, A. Homs, C. Obradors, A. M. Echavarren, *Chem. Asian. J.,* **2014**, 9, 3066; (e) B. W. Gung, R. C. Conyers, J. Wonser, *Synlett,* **2013**, *24*, 1238.

[11] M. P. Doyle, B. J. Chapman, W. Hu, C. S. Peterson, *Org. Lett.,* **1999**, *1*, 1327.

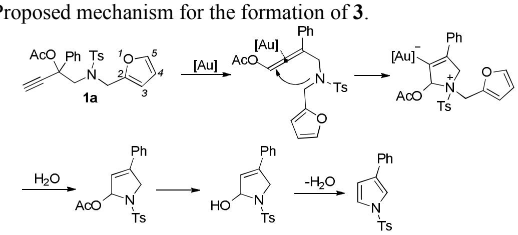
[12] For recent reviews of propargyl esters catalyzed by gold(I) complex, see: (a) C. Bruneau, *Angew. Chem. Int. Ed.,* **2005**, *44*, 2328; (b) N. Marion, S. P. Nolan, *Angew. Chem. Int. Ed.,* **2007**, *46*, 2750; (c) S. Wang, G. Zhang, L. Zhang, *Synlett,* **2010**, 692; (d) X.-Z. Shu, D. Shu, C. M. Schienebeck, W. Tang, *Chem. Soc. Rev.,* **2012**, *41*, 7698; (e) R. K. Shiroodi, V. Gevorgyan, *Chem. Soc. Rev.,* **2013**, *42*, 4991; (f) D. Qian, J. Zhang, *Chem. Soc. Rev.,* **2015**, *44*, 677.

[13] (a) X, Shi, D. J. Gorin, F. D. Toste, *J. Am. Chem. Soc.,* **2005**, *127*, 5802; (b) M. J. Johansson, D. J. Gorin, S. T. Staben, F. D. Toste, *J. Am. Chem. Soc.,* **2005**, *127*, 18002; (c) N. Marion, P. de Frémont, G. Lemière, E. D. Stevens, E. L. Fensterbank, M. Malacria, S. P. Nolan, *Chem. Commun.,* **2006**, 2048; (d) C. A. Witham, P. Mauleón, N. D. Shapiro, B. D. Sherry, F. D. Toste, *J. Am. Chem. Soc.,* **2007**, *129*, 5838; (e) G. Li, G. Zhang, L. Zhang, *J. Am. Chem. Soc.,* **2008**, *130*, 3740; (f) X. Moreau, J.-P. Goddard, M. Bernard, G. Lemière, J. M. López-Romero, E. Mainetti, N. Marion, V. Mouriès, S. Thorimbert, L. Fensterbank, M. Malacria, *Adv. Synth. Catal.,* **2008**, *350*, 43; (g) A. Correa, N. Marion, L. Fensterbank, M. Malacria, S. P. Nolan, L. Cavallo, *Angew. Chem. Int. Ed.,* **2008**, *47*, 718; (h) N. Marion, G. Lemière, A. Correa, C. Costabile, R. S. Ramón, X. Moreau, P. de Frémont, R. Dahmane, A. Hours, D. Lesage, J.-C. Tabet, J.-P. Goddard, V. Gandon, L. Cavallo, L. Fensterbank, M. Malacria, S. P. Nolan, *Chem. Eur. J.,* **2009**, *15*, 3243; (i) I. D. G. Watson, S. Ritter, F. D. Toste, *J. Am. Chem. Soc.,* **2009**, *131*, 2056; (j) M. Uemura, I. D. G. Watson, M. Katsukawa, F. D. Toste, *J. Am. Chem. Soc.,* **2009**, *131*, 3463; (k) Y. Peng, L. Cui, G. Zhang, L. Zhang, *J. Am. Chem. Soc.,* **2009**, *131*, 5062; (l) W. Rao, M. J. Koh, D. Li, H. Hirao, P. W. H. Chan, *J. Am. Chem. Soc.,* **2013**, *135*, 7926; (m) W. Rao, P. W. H. Chan, *Chem. Eur. J.,* **2014**, *20*, 713; (n) W. Rao, S. N. Berry, P. W. H. Chan, *Chem. Eur. J.,* **2014**, *20*, 13174.

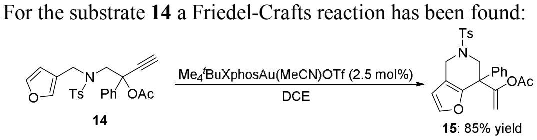
[14] (a) V. Mamane, T. Gress, H. Krause, A. Fürstner, *J. Am. Chem. Soc.,* **2004**, *126*, 8654; (b) C. H. M. Amijs, V. López-Carrillo, A. M. Echavarren, *Org. Lett.,* **2007**, *9*, 4021; (c) F.-D. Boyer, X. L. Goff, I. Hanna, *J. Org. Chem.,* **2008**, *73*, 5163; (d) D. Garayalde, E. Gómez-Bengoa, X. Huang, A. Goeke, C. Nevado, *J. Am. Chem. Soc.,* **2010**, *132*, 4720; (e) D. Garayalde, K. Krüger, C. Nevado, *Angew. Chem. Int. Ed.,* **2011**, *50*, 911; (f) T. Kusakabe, K. Kato, *Tetrahedron,* **2011**, *67*, 1511; (g) C. A. Sperger, J. E. Tungen, A. Fiksdahl, *Eur. J. Org. Chem.,* **2011**, 3719; (h) G. Wang, Y. Zou, Z. Li, Q. Wang, A. Goeke, *J. Org. Chem.,* **2011**, *76*, 5825; (i) V. V. Pagar, A. M. Jadhav, R.-S. Liu, *J. Am. Chem. Soc.,* **2011**, *133*, 20728; (j) R. C. Conyers, B. W. Gung, *Chem. Eur. J.,* **2013**, *19*, 654; (k) C. H. Oh, J. H. Kim, B. K. Oh, J. R. Park, J. H. Lee, *Chem. Eur. J.,* **2013**, *19*, 2592; (l) N. Iqbal, C. A. Sperger, A. Fiksdahl, *Eur. J. Org. Chem.,* **2013**, 907; (m) T. Lauterbach, S. Gatzweiler, P. Nösel, M. Rudolph, F. Rominger, A. S. K. Hashmi, *Adv. Synth. Catal.,* **2013**, *355*, 2481; (n) C. H. Oh, J. H. Kim, L. Piao, J. Yu, S. Y. Kim, *Chem. Eur. J.,* **2013**, *19*, 10501; (o) J. Liu, M. Chen, L. Zhang, Y. Liu, *Chem. Eur. J.,* **2015**, *21*, 1009.

[15] The structures of **2a**, **3**, **2s**, **5**, **12**, **13** and **15** were determined by X-ray analyses.

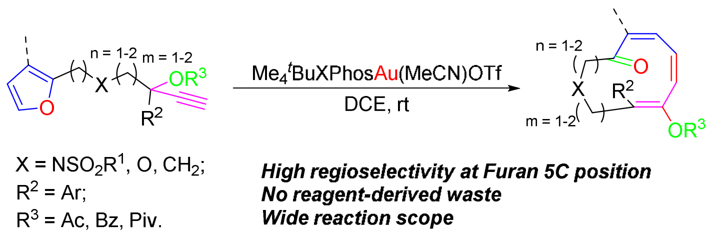
[16] Proposed mechanism for the formation of **3**.



[17] For the substrate **14** a Friedel-Crafts reaction has been found:



Gold-Catalyzed 1,2-Acyloxy Migration/Intramolecular Cyclopropanation/Ring Enlargement Cascade: Syntheses of Medium-Sized Heterocycles



Gold catalyzed 1,2-acyloxy migration/intramolecular cyclopropanation/ring enlargement cascade of furan substrates provides a new highly efficient procedure for the formation of ten and eleven-membered ring compounds. A new transformation type of intermolecular furan compounds catalyzed by gold catalyst was reported.

Yin-Wei Sun,[†] Xiang-Ying Tang,[‡]* Min Shi[†,‡]*