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A Highly Reusable Rhodium Catalyst-Organic Framework for the Intramolecular Cycloisomerization of 1,6-Enynes

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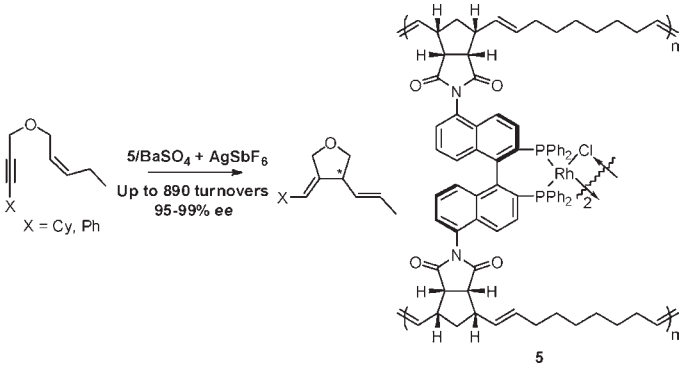
ABSTRACT



The intramolecular cycloisomerization of 1,6-enynes in 95−99% *ee* is reported using an immobilized Rh catalyst-organic framework synthesized from alternating ring-opening metathesis polymerization (altROMP) assembly. The framework was reused up to seven times, and it was used in high turnover number (TON) batch reactions. The catalyst provided the highest TONs to date (up to 890) for the cycloisomerizations, with catalyst loadings ranging from 0.2 to 0.06 mol %.

We report a highly reusable, immobilized, catalyst-organic framework for the intramolecular cycloisomerization of 1,6-enynes. The Rh-catalyzed cycloisomerization of 1,6-enynes, discovered by Zhang et al. in 2000,[1] is an extremely versatile C−C bond-forming reaction that has produced a wide range of furans, lactones, lactams, cyclopentanes, and cyclopentanones.[2,3] These products have numerous pharmaceutical applications and, remarkably, are almost exclusively produced in >99% *ee* by cycloisomerization.[4] Most reports of Rh-catalyzed cycloisomerizations utilize 10 mol % $[Rh(BINAP)]^+$ (BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) as the homogeneous catalyst, with 20 mol % $AgSbF_6$ as an activator, in dichloroethane (DCE) solvent. In fact, most examples of nontandem enantioselective cycloisomerizations occur with 5−10 mol % of chiral catalyst regardless of the

(1) (a) Cao, P.; Wang, B.; Zhang, X. *J. Am. Chem. Soc.* **2000**, *122*, 6490. (b) Cao, P.; Zhang, X. *Angew. Chem., Int. Ed.* **2000**, *39*, 4104.

(2) For recent reviews, see: (a) Michelet, V.; Toullec, P. Y.; Genêt, J.-P. *Angew. Chem., Int. Ed.* **2008**, *47*, 4268. (b) Zhang, Z.; Zhu, G.; Tong, X.; Wang, F.; Xie, X.; Wang, J.; Jiang, L. *Curr. Org. Chem.* **2006**, *10*, 1457. (c) *Modern Rhodium-Catalyzed Organic Reactions*; Evans, P. A., Ed.; Wiley-VCH: Weinheim, Germany, 2005.

(3) (a) Lei, A.; Waldkirch, J. P.; He, M.; Zhang, X. *Angew. Chem., Int. Ed.* **2002**, *41*, 4526. (b) Lei, A.; He, M.; Wu, S.; Zhang, X. *Angew. Chem., Int. Ed.* **2002**, *41*, 3457. (c) Hashmi, A. S. K.; Haufe, P.; Nass, A. R. *Adv. Synth. Catal.* **2003**, *345*, 1237. (d) Lei, A.; He, M.; Zhang, X. *J. Am. Chem. Soc.* **2003**, *125*, 11472. (e) Tong, X.; Zhang, Z.; Zhang, X. *J. Am. Chem. Soc.* **2003**, *125*, 6370. (f) Tong, X.; Li, D.; Zhang, Z.; Zhang, X. *J. Am. Chem. Soc.* **2004**, *126*, 7601. (g) Hashmi, A. S. K.; Haufe, P.; Nass, A. R.; Bats, J. W. *Adv. Synth. Catal.* **2004**, *346*, 421. (h) Mikami, K.; Kataoka, S.; Yusa, Y.; Aikawa, K. *Org. Lett.* **2004**, *6*, 3699. (i) Mikami, K.; Kataoka, S.; Aikawa, K. *Org. Lett.* **2005**, *7*, 5777. (j) Mikami, K.; Kataoka, S.; Wakabayashi, K.; Aikawa, K. *Tetrahedron Lett.* **2006**, *47*, 6361. (k) Liu, F.; Liu, Q.; He, M.; Zhang, X.; Lei, A. *Org. Biomol. Chem.* **2007**, *5*, 3531. (l) Nishimura, T.; Kawamoto, T.; Nagaosa, M.; Kumamoto, H.; Hayashi, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 1638. (m) Wang, J.; Xie, X.; Ma, F.; Peng, Z.; Zhang, L.; Zhang, Z. *Tetrahedron* **2010**, *66*, 4212. (n) Kim, S. Y.; Chung, Y. K. *J. Org. Chem.* **2010**, *75*, 1281.

(4) (a) Lei, A.; He, M.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 8198. (b) He, M.; Lei, A.; Zhang, X. *Tetrahedron Lett.* **2005**, *46*, 1823. (c) Nicolaou, K. C.; Edmonds, D. J.; Li, A.; Tria, G. S. *Angew. Chem., Int. Ed.* **2007**, *46*, 3942. (d) Nicolaou, K. C.; Li, A.; Ellery, S. P.; Edmonds, D. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 6293.

(5) Zhang et al. have reported lower loadings of $[Rh(BINAP)]^+$ (as low as 0.4 mol%) in the nontandem cycloisomerization of the methyl enyne (X = Me). For more information, see ref 3b.

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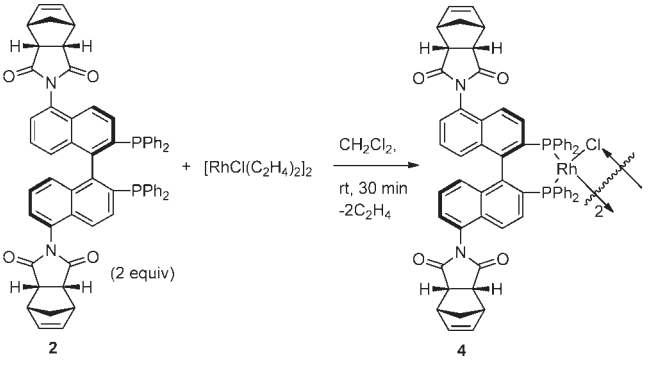
metal.[2,5] Some tandem reactions, however, occur with lower loadings of catalyst presumably because product inhibition and isomerization are avoided.[2a,4a] These relatively high loadings of catalyst and additives narrow the industrial applications of these systems. We reasoned that immobilization of the catalyst would provide higher turnover numbers (TONs) by allowing catalyst reuse, thereby avoiding product inhibition and isomerization that may occur during high TON homogeneous reactions. Further, the use of a heterogeneous catalyst would allow for a wide range of solvents as the solvent would no longer be required to dissolve the catalyst.

Two general approaches to separate the catalyst and reactant phases in enantioselective catalysis are the use of multiphase solvent mixtures (e.g., aqueous/organic,[6] supercritical CO_2,[7] fluorous catalysts and solvents,[8] and ionic liquids[9]) and catalyst immobilization. Homogeneous catalysts are immobilized through noncovalent and covalent interactions with a support. The noncovalent interactions[10] include electrostatic attractions between ionic catalysts and supports, physisorption onto the support, hydrogen bonding, and encapsulation within the support. Covalent immobilization techniques[11] include the formation of metal−support bonds and formation of bonds between a modified ligand and an inorganic or organic support. Copolymerization of modified catalyst ligands or grafting modified ligands onto polymeric supports is often carried out by incorporating the ligand into the support first, followed by metalating the incorporated ligand. The result is often incomplete metalation of the ligand-polymer support and poor mass transport at the active sites, leading to low catalyst activity and poor reusability. The direct polymerization of metal-containing monomers (MCM) ensures that ligand-containing sites on the polymer are metalated,[12] but mass transport at the active sites must still be addressed. We recently reported[13] an alternating ring-opening metathesis polymerization (altROMP) between *trans*-Ru(**2**)Cl_2Py_2 (**1**, where **2** = (*R*)-5,5′-dinorimido-BINAP[14]) and *cis*-cyclooctene (COE) using $RuCl_2(=CHPh)(PCy_3)_2$ (**3**) as a catalyst to assemble a catalyst-organic framework cross-linked with **1**.[15,16] This Ru-based catalyst-organic framework was reused for an enantioselective ketone hydrogenation with high TONs per run (≥1000) for 25 runs before loss in activity occurred. More than 35 reuses were carried out without loss in enantioselectivity or detectable leaching of Ru. We now report the preparation of a Rh-BINAP-containing catalyst-organic framework and its reuse as a catalyst for the enantioselective cycloisomerization of 1,6-enynes.

We synthesized the chloro-bridged Rh complex $[RhCl(\mathbf{2})]_2$ (**4**) by reacting **2** with $[RhCl(C_2H_4)_2]_2$ in CH_2Cl_2.[17,18] **4** was used immediately for altROMP without isolation to avoid its decomposition.



We found that **4** readily underwent altROMP assembly with COE and **3** (**3**/**4**/COE = 1:10:120, 40 °C, 24 h, CH_2Cl_2)

(6) (a) Dwars, T.; Oehme, G. *Adv. Synth. Catal.* **2002**, *344*, 239. (b) Joó, F. *Acc. Chem. Res.* **2002**, *35*, 738. (c) Pinault, N.; Bruce, D. W. *Coord. Chem. Rev.* **2003**, *241*, 1.

(7) Gordon, C. M.; Leitner, W. Homogeneous Catalysis in Supercritical Solvents as a Special Unit Operation. In *Multiphase Homogeneous Catalysis*; Cornils, B., Herrmann, W. A., Vogt, D., Horvath, I., Olivier-Bourbigon, H., Leitner, W., Mecking, S., Eds.; Wiley-VCH: Weinheim, Germany, 2005.

(8) (a) *Handbook of Fluorous Chemistry*; Gladysz, J. A., Curran, D. P., Horváth, I., Eds.; Wiley-VCH: Weinheim, Germany, 2004. (b) de Wolf, E.; van Koten, G.; Deelman, B.-J. *Chem. Soc. Rev.* **1999**, *28*, 37. (c) Horváth, I. T. *Acc. Chem. Res.* **1998**, *31*, 641.

(9) (a) Welton, T. *Coord. Chem. Rev.* **2004**, *248*, 2459. (b) Sheldon, R. *Chem. Commun.* **2001**, 2399. (c) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772.

(10) For recent reviews, see: (a) Fraile, J. M.; García, J. I.; Mayoral, J. A. *Chem. Rev.* **2009**, *109*, 360. (b) Heitbaum, M.; Glorius, F.; Escher, I. *Angew. Chem., Int. Ed.* **2006**, *45*, 4732. (c) McMorn, P.; Hutchings, G. J. *Chem. Soc. Rev.* **2004**, *33*, 108. (d) Zhao, X. S.; Bao, X. Y.; Guo, W.; Lee, F. Y. *Mater. Today* **2006**, *9*, 32.

(11) For recent reviews, see: (a) Dioos, B. M. L.; Vankelecom, I. F. J.; Jacobs, P. A. *Adv. Synth. Catal.* **2006**, *348*, 1413. (b) Leadbeater, N. E.; Marco, M. *Chem. Rev.* **2002**, *102*, 3217. (c) Fan, Q.-H.; Li, Y.-M.; Chan, A. S. C. *Chem. Rev.* **2002**, *102*, 3385. (d) Wang, Z.; Chen, G.; Ding, K. *Chem. Rev.* **2009**, *109*, 322. (e) Ding, K.; Wang, Z.; Wang, X.; Liang, Y.; Wang, X. *Chem.—Eur. J.* **2006**, *12*, 5188. For MOFs, see:(f) Liu, Y.; Xuan, W.; Cui, Y. *Adv. Mater.* **2010**, *22*, 4112. (g) Corma, A.; García, H.; Llabrés i Xamena, F. X. *Chem. Rev.* **2010**, *110*, 4606. (h) Ma, L.; Abney, C.; Lin, W. B. *Chem. Soc. Rev.* **2009**, *38*, 1248.

(12) Mastrorilli, P.; Nobile, C. F. *Coord. Chem. Rev.* **2004**, *248*, 377.

(13) Ralph, C. K.; Bergens, S. H. *Organometallics* **2007**, *26*, 1571.

(14) **2** was prepared in one step from the known diamine precursor. See: (a) Okano, T. K. H.; Akutagawa, S.; Kiji, J.; Konishi, H.; Fukuyama, K.; Shimano, Y. U.S. Patent 4,705,895, 1987. (b) Berthod, M.; Mignani, G.; Woodward, G.; Lemaire, M. *Chem. Rev.* **2005**, *105*, 1801.

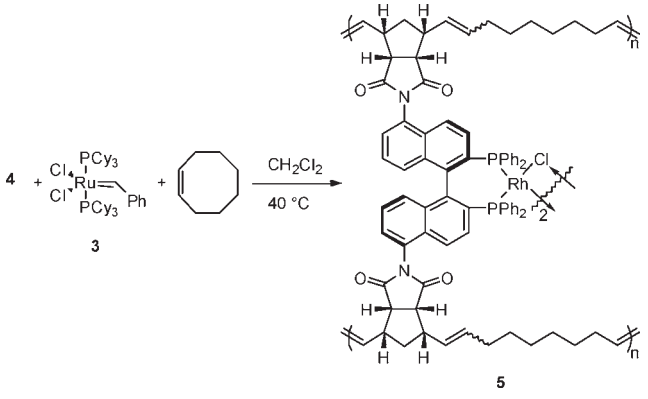
(15) For examples of BINAP-containing polymers, see: (a) ter Halle, R.; Colasson, B.; Schulz, E.; Spagnol, M.; Lemaire, M. *Tetrahedron Lett.* **2000**, *41*, 643. (b) Saluzzo, C.; Lamouille, T.; Le Guyader, F.; Lemaire, M. *Tetrahedron: Asymmetry* **2002**, *13*, 1141. (c) Fan, Q. H.; Ren, C. Y.; Yeung, C. H.; Hu, W. H.; Chan, A. S. C. *J. Am. Chem. Soc.* **1999**, *121*, 7407. (d) Fan, Q. H.; Wang, R.; Chan, A. S. C. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 1867. (e) Fan, Q. H.; Deng, G. J.; Lin, C. C.; Chan, A. S. C. *Tetrahedron: Asymmetry* **2001**, *12*, 1241. (f) Pu, L. *Chem.—Eur. J.* **1999**, *5*, 2227. (g) Yu, H. B.; Hu, Q. S.; Pu, L. *Tetrahedron Lett.* **2000**, *41*, 1681. (h) Framery, E.; Andrioletti, B.; Lemaire, M. *Tetrahedron: Asymmetry* **2010**, *21*, 1110. (i) Saluzzo, C.; Lemaire, M. *Adv. Synth. Catal.* **2002**, *344*, 915. (j) Hu, A.; Ngo, H. L.; Lin, W. B. *J. Am. Chem. Soc.* **2003**, *125*, 11490. (k) *Org. Lett.* **2004**, *6*, 2937. (l) Wang, P.; Liu, X.; Yang, J.; Yang, Y.; Zhang, L.; Yang, Q.; Li, C. *J. Mater. Chem.* **2009**, *19*, 8009. (m) Guerreiro, P.; Ratovelomanana-Vidal, V.; Genêt, J.-P.; Dellis, P. *Tetrahedron Lett.* **2001**, *42*, 3423.

(16) For examples of use of ROMP to prepare polymeric catalysts, see: (a) Chen, B.; Sleiman, H. F. *Macromolecules* **2004**, *37*, 5866. (b) Fuchter, M. J.; Hoffman, B. M.; Barrett, A. G. M. *J. Org. Chem.* **2006**, *71*, 724. (c) Sankaran, N. B.; Rys, A. Z.; Nassif, R.; Nayak, M. K.; Metera, K.; Chen, B.; Bazzi, H. S.; Sleiman, H. F. *Macromolecules* **2010**, *43*, 5530. (d) Carlisle, J. R.; Wang, X.-Y.; Weck, M. *Macromolecules* **2005**, *38*, 9000. (e) Dragutan, V.; Dragutan, I.; Fischer, H. *J. Inorg. Organomet. Polym.* **2008**, *18*, 18. (f) Dragutan, V.; Dragutan, I.; Fischer, H. *J. Inorg. Organomet. Polym.* **2008**, *18*, 311.

(17) Tokunaga, N.; Yoshida, K.; Hayashi, T. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5445.

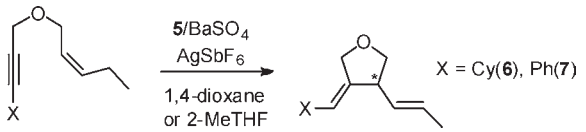
(18) **2** is initially formed as a mixture of three NMR distinct diastereomeric atropisomers that differ in the rotameric orientations of the norimido groups about the arene−nitrogen bonds. However **2** precipitated from 90 °C solutions of toluene as one C_2 dissymmetric diastereomeric atropisomer, which was then used in the synthesis of **4**. See ref 13 for more details.

to form the catalyst-organic framework **5**. We found that ROMP of **4** did not readily occur in the absence of COE, likely because of steric crowding around the *endo* norimido groups. We believe that altROMP with COE proceeds by reaction between a norimido group in **4** and **3** to form a Ru-alkylidene that is too crowded to react with another molecule of **4**. Instead, this alkylidene reacts with COE to insert a C_8 spacer and form a less crowded Ru-alkylidene group that reacts with **4** and so on. The difference in ring strain and steric crowding between the olefin groups in **4** and COE results in the altROMP assembly. ^{1}H NMR spectra recorded *in situ* showed that the ratio of COE to norimido unit consumed during the altROMP of **4** was ~1.7:1. We previously reported that the corresponding ratio for the altROMP of the Ru-MCM **1** and COE was 1:1.[13] We attribute this difference to the dimeric nature of **4**; specifically, the bent orientation of the chloro bridges in **4** engenders more steric crowding upon the norimido groups in **4** than in **1**. The norimido groups in **4** are thereby of lower net reactivity toward altROMP than those in **1**, resulting in incorporation of a higher number of COE spacers into the catalyst-organic framework **5**. ^{1}H NMR spectroscopy showed that no free norimido groups remained at the end of the altROMP and that a mixture of *cis*- and *trans*-olefin groups was present in the framework.



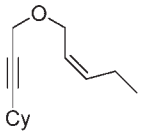
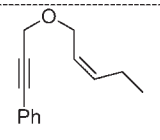
The ^{31}P NMR spectrum of **5** consisted of a broad signal centered on the chemical shift for the dimer **4**, showing that the electronic environment of the Rh centers was not significantly altered by the altROMP assembly. We note that, unlike the catalyst-organic framework containing **1**, framework **5** is doubly cross-linked by norimido-BINAP groups and by the chloro-bridged Rh centers. The framework **5** was deposited as a thin film onto $BaSO_4$ to provide mechanical stability and to aid mass transport during catalysis.

The intramolecular cycloisomerization of 1,6-enynes **6** and **7** was used to evaluate **5**. To our knowledge, the cycloisomerization of 1,6-enyne **6** has not been reported.



The reported homogeneous cycloisomerization of phenyl enyne **7** occurs with 10 mol % $[Rh(BINAP)]^+$, 20 mol % $AgSbF_6$ in DCE at room temperature (TON = 10).[3c] The first cycloisomerization of **7** over **5**/$BaSO_4$ was carried out with 5 mol % Rh, 10 mol % $AgSbF_6$ in 1,4-dioxane at 60 °C and was complete in 99% yield and in 99% *ee* after 3 h. Significantly, the catalyst-organic framework **5**/$BaSO_4$ was isolated and reused for four additional runs (five total) with loadings of **7**/Rh = 100:1 for each run, without additional $AgSbF_6$ (Table 1). Although it was necessary to increase time and temperature for each run, a total TON of 380 was obtained in 99% *ee*. The cyclohexyl enyne **6** was more active toward **5**/$BaSO_4$. After the first run over **5**/$BaSO_4$ (5 mol % Rh, 10 mol % $AgSbF_6$ in 1,4-dioxane at 60 °C for 3 h), six more reuses with loadings of **6**/Rh = 100:1 (50–65 °C, and > 98% yield/run) were carried out to give a total TON of 620 in > 95% *ee* (minor enantiomer not detected by NMR shift reagent).

Table 1. Reuse Results for the Cycloisomerization of **6**[a,b] and **7**[a,c]

substrate	run	temp (°C)	time (h)	% yield	% ee
 **6**	1	60	3	99	>95
	2	50	18	99	>95
	3	50	22.5	99	>95
	4	65	26	99	>95
	5	65	19.5	99	>95
	6	65	24	99	>95
	7	65	24	99	>95
 **7**	1	60	3	99	>99
	2	70	42	96	>99
	3	70	48	91	>99
	4	80	70	97	>99
	5	92	46	53	>99

[a] Run 1 was carried out in 0.1 M solutions of **6** and **7** respectively in 1,4-dioxane under the following conditions: Sub/Ag/Rh = 20/2/1, 60 °C. All subsequent runs were carried out in 0.2 M solutions of **6** and **7** respectively without any additional $AgSbF_6$ added under the following conditions: Sub/Rh = 100/1. [b] % *ee* determined by NMR shift reagent. [c] % *ee* determined by chiral GC.

For a comparison, we attempted the homogeneous cycloisomerization of cyclohexyl enyne **6** with 2.5 mol % $[RhCl(BINAP)]_2$, 10 mol % $AgSbF_6$ in 1,4-dioxane at 40 °C. The reaction was complete after 2 h (TON = 10) to give a complex mixture that likely formed by isomerization of the product. The same reaction carried out in DCE (5 mol % $[RhCl(COD)]_2$, 10 mol % (*R*)-BINAP, 20 mol % $AgSbF_6$) was complete after 5 min (TON = 10) at room temperature to also give a complex mixture of isomerized products. To our knowledge, these are the first enantioselective catalytic reactions in which the immobilized catalyst provides higher TONs and is more selective than the parent, homogeneous catalyst.

Table 2 summarizes the results from high loading batch reactions without reuse in 1,4-dioxane and in 2-MeTHF with $AgSbF_6$/Rh = 5:1 at 70 °C. These cycloisomerizations were best carried out by allowing $AgSbF_6$ and

Table 2. Batch Reactivity Results of the Cycloisomerization of **6**[a,b] and **7**[a,c]

entry	sub	solvent	loading (sub/Ag/Rh)	time (h)	TON	% ee
1[b]	**6**	dioxane	1000/5/1	2	200	>95
				45	800	>95
2[b]	**6**	MeTHF	1000/5/1	4	630	>95
3[b]	**6**	MeTHF	500/5/1	2	500	>95
4[c]	**7**	dioxane	500/5/1	23	480	>99
5[c]	**7**	MeTHF	1600/5/1	20	890	>99

[a] All runs were carried out at 70 °C. [b] % *ee* determined by NMR shift reagent. [c] % *ee* determined by chiral GC.

5/$BaSO_4$ to react for 30 min at 40 °C to aid framework swelling and chloride abstraction prior to introduction of substrate. The cycloisomerization of the cyclohexyl enyne **6** was faster in 2-MeTHF, giving a TON of 500 after 2 h compared to 200 after 2 h in 1,4-dioxane (entries 1 and 3). The total TON (800 vs 630, entries 1 and 2), however, was greater in 1,4-dioxane. These differences likely result from the lower coordinating ability of 2-MeTHF compared to 1,4-dioxane. The phenyl enyne **7** reacted to give a TON of 480 in 1,4-dioxane (entry 4) and 890 in 2-MeTHF (entry 5). To our knowledge, these are the highest reported TONs for any cycloisomerization. The % *ee*'s were the same in both solvents.

Zhang reported the elegant tandem cycloisomerization of **8** to form the α-methylene-γ-butyrolactone **9**, which can be converted in two steps into (+)-pilocarpine.[4a] (+)-Pilocarpine is a leading pharmaceutical in the treatment of narrow- or wide-angle glaucoma as well as Sjögren syndrome.[19] Using **5**/$BaSO_4$ (1 mol % Rh) in one batch, we obtained 100% conversion and 99% yield for the cycloisomerization of **8** in 1,4-dioxane at 70 °C (Table 3, entry 1). At 0.33 mol % Rh, the reaction was 90% complete after 24 h and 100% complete after 48 h with 5% isomerization byproducts (entry 2). The catalyst **5**/$BaSO_4$ was also active in 2-MeTHF but gave a mixture of products likely resulting from isomerization.

(19) (a) Ramos-Casals, M.; Tzioufas, A. G.; Stone, J. H.; Sisó, A.; Bosch, X. *JAMA* **2010**, *304*, 452. (b) Diestelhorst, M.; Nordmann, J.-P.; Toris, C. B. *Surv. Ophthalmol. (Suppl. 1)* **2002**, *47*, S155. (c) Worthen, D. M.; Zimmerman, T. J.; Wind, C. A. *Invest. Ophthalmol.* **1974**, *13*, 296. (d) Nusair, S.; Rubinow, A. *Semin. Arthritis Rheum.* **1999**, *28*, 360.

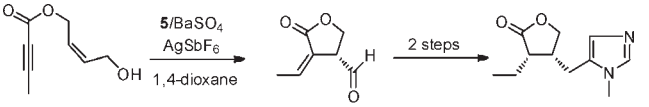


Table 3. Results of the Cycloisomerization of **8**

entry	loading (sub/Ag/Rh)	time (h)	TON	% ee
1[a]	100/5/1	2.5	99	>99
2[a]	300/5/1	48	285	>99

[a] Both runs were carried out at 70 °C in 0.9 mL of 1,4-dioxanes. % *ee* was determined by chiral GC.

We have presented the altROMP assembly of the $BaSO_4$ supported catalyst-organic framework **5** and its high activity toward the cycloisomerization of 1,6-enynes. The immobilized catalyst provided higher TONs and, in some cases, was more selective than the parent, homogeneous systems. The higher TONs and selectivity are rare, if not unique, in the field. Their possible origins include support ($BaSO_4$) effects, catalyst-framework interactions, and encapsulation phenomena. Current research is focused upon optimizing the structure of the catalyst-organic framework **5** and optimizing reaction conditions for cycloisomerization and other reactions, as well as investigating the origins of its activity and selectivity through controlled structural modifications and extensive characterization.

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Supporting Information Available. Text and figures giving experimental procedures for substrates, ligand, and catalyst-organic framework preparation and use. This material is available free of charge via the Internet at http://pubs.acs.org.