DOI: 10.1002/chem.201201383

Azobenzene-Tethered Bis(Trityl Alcohol) as a Photoswitchable Cooperative Acid Catalyst for Morita–Baylis–Hillman Reactions

Tatsushi Imahori,*[a] Ryo Yamaguchi,[b] and Seiji Kurihara[b]

Manipulation of functions at the molecular level by external stimuli is a key controlling mechanism in nature, as exemplified by the allosteric control of enzymes. To realize advanced functions in man-made materials, various functional molecules whose functions can be controlled and operated by suitable stimuli have been developed.[1,2] Among them, photoswitchable catalysts are very attractive.[3] As well as being potentially clean, light can readily provide diverse non-invasive stimuli by selecting the wavelength, and this allows precise control of catalyst reactivities by light stimuli.[3] In the reactions promoted by the photoactivated catalysts, light stimuli are amplified in the catalytic cycle, and clean light energy is efficiently translated into chemical actions.[4] Photoswitchable catalysts are considered to hold great promise for realizing various advanced functions, such as a multi-catalyst system,[5] on account of their switching ability.[6] Despite such attractive features, however, relatively few developments have been made in the area of photoswitchable catalysts.[3] Although a few general photoswitchable catalysts have been reported in recent years,[7] the overall scope remains small. Herein, we report on a new photoswitchable acid catalyst, azobenzene-tethered bis(trityl alcohol).[8] This catalyst switches its catalytic activity as a cooperative acid based on the photoinduced dynamic molecular motion like a molecular machine.[1] A stimuli-responsive and highly efficient Morita–Baylis–Hillman (MBH) reaction has been demonstrated by using this photomechanical, new cooperative acid catalyst.

To develop useful and widely applicable photoswitchable catalysts, we focused our attention on bifunctional catalysts, whose activity is attributed to the cooperative function of two functional units. Bifunctional catalysts are an important class of catalyst in organic synthesis because they can demonstrate advanced catalyses on account of their multifunctionality.[9] The cooperative function mechanism of a bifunctional catalyst appears suitable for photoswitchable catalysts. Manipulating this cooperative function by using light stimuli can directly induce photoresponsivity. Then, we envisaged the incorporation of a photoresponsive core, which provides reversible dynamic molecular motion by photoisomerization, into the bifunctional catalyst (Figure 1). Because the positional relationships of the constituent functional units greatly affect the cooperative function of a bifunctional catalyst,[9] reversible photoisomerization of the photoresponsive core could be used to switch the catalyst reactivity by changing the spatial arrangement of the functional units.

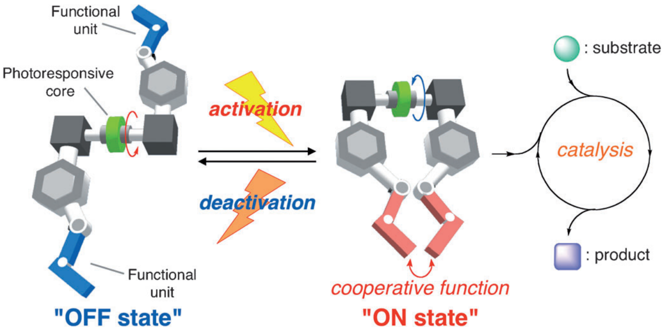


Figure 1. Concept of photoswitchable cooperative catalyst on the basis of photoinduced reversible dynamic molecular motion.

When we started to develop such a photomechanical cooperative catalyst, only a few related catalysts had been reported.[10] These previously reported catalysts[10a,b] are categorized as photoswitchable templates that perform the photomechanical cooperative function based on host–guest chemistry.[3] Thus, the scope of the applicable transformations was limited. We designed an azobenzene-tethered bis(trityl alcohol) **1** (Figure 2). Based on our ongoing studies of

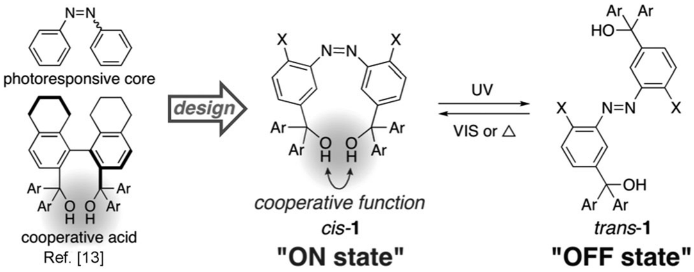


Figure 2. Design of the photoswitchable cooperative acid catalyst.

---

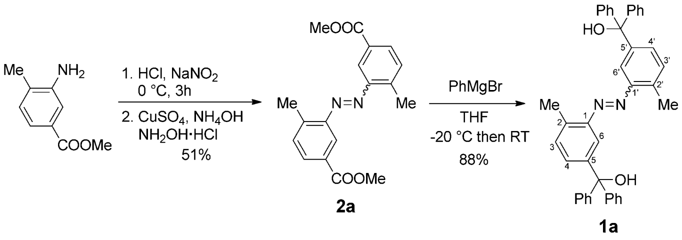
[a] Prof. Dr. T. Imahori
Priority Organization for Innovation and Excellence
Kumamoto University (Japan)
E-mail: imahori@kumamoto-u.ac.jp

[b] R. Yamaguchi, Prof. Dr. S. Kurihara
Department of Applied Chemistry and Biochemistry
and Graduate School of Science and Technology
Kumamoto University, 2-39-1 Kurokami, Chuo-ku
Kumamoto 860-8555 (Japan)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201201383.

azobenzene-based functional materials,[11] we selected azobenzene as the photoresponsive core. The distinct, reversible structural changes in the photoisomerization of azobenzene (*trans*/*cis*) should be beneficial for switching the arrangement of functional units as the core.[12] Bis(trityl alcohol), which can function as a cooperative acid catalyst (hydrogen-bonding catalyst),[13] was chosen as the functional units. We assumed that the *cis*-azobenzene form of **1** would locate its two acidic trityl alcohol units in proximity to each other in order to avoid the steric hindrance of substituent X (Figure 2), and then, their cooperative function, such as an intramolecular hydrogen bonding between the two hydroxyl groups to enhance the acidity of one trityl alcohol unit[13,14] or a certain proximity effect, could be induced. On the other hand, the separately placed two trityl alcohol units in *trans*-**1** could not induce the cooperative function. This photoswitchable cooperative function would demonstrate a photoswitchable catalyst activity. Very recently, Wang and Feringa reported an excellent photoswitchable bifunctional catalyst with a similar design concept that, remarkably, switches the stereochemistry, too, via thermal isomerization.[7b]

The designed catalyst **1a** (X = Me, Ar = Ph) was synthesized from commercially available methyl 3-amino-4-methylbenzoate (Scheme 1). The azobenzene core was first constructed according to the reported procedure via the formation of diazonium salt to afford diester **2**.[15] Then, two equivalents of PhMgBr were added to each methoxy carbonyl group to afford the desired bis(trityl alcohol) **1a**. The photoresponsive structural changes in **1a** were then evaluated through spectral studies. The changes in the UV/Vis absorption spectra of **1a** upon photoirradiation are shown in Figure 3 (a: UV light irradiation on the solution of **1a** (*trans*-**1a**/*cis*-**1a** = 93:7 (^{1}H NMR) in $CHCl_3$), b: subsequent visible light irradiation).[16] The photoresponsivity in the absorption spectra indicates reversible photoisomerization of the azobenzene core of **1a** between the *trans*- and *cis*-forms.[16,17]



Scheme 1. Synthesis of azobenzene-tethered bis(trityl alcohol) **1a**.

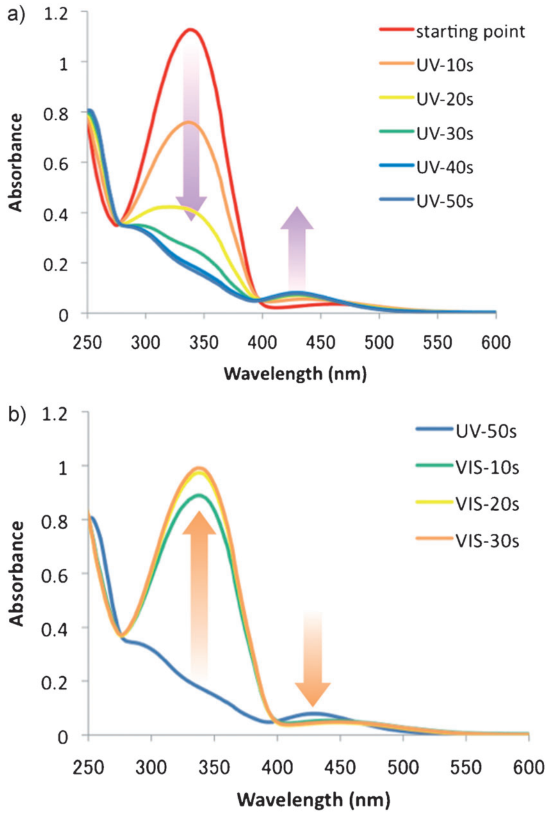


Figure 3. Changes in UV/Vis absorption spectra of **1a** upon photoirradiation in $CHCl_3$.

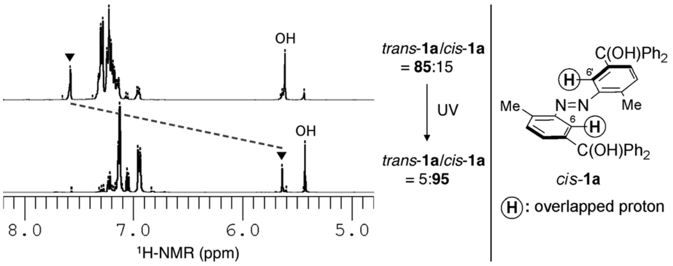
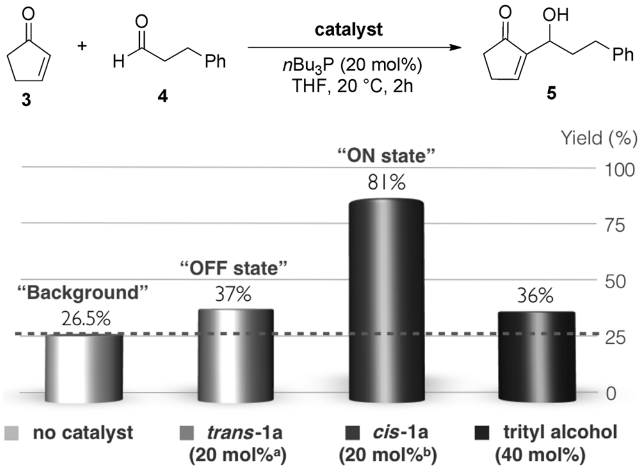


Figure 4. Changes in ^{1}H NMR spectrum upon photoisomerization in $[D_8]$THF and proposed structure of *cis*-azobenzene core of *cis*-**1a**.

The transition of **1a** was investigated in detail by ^{1}H NMR spectroscopy.[16] The irradiation of UV light (365 nm, 30 mW cm^2) on the solution of **1a** (*trans*/*cis* = 85:15 (^{1}H NMR), 1.0×10^{-1} M in $[D_8]$THF) induced a characteristic upfield shift of a doublet peak with a small coupling constant (Figure 4, ▼). This signal is assigned as the 6- and 6′-position protons of the azobenzene core (Scheme 1). Because the overlapped protons in the helical structure of *cis*-azobenzene are shown at higher field than normal aromatic protons in the ^{1}H NMR spectra owning to the shielding effect of the overlapping benzene ring,[7a,18] the observed upfield shift is attributed to photoisomerization of *trans*-**1a** to the *cis*-isomer which is overlapped at the 6- and 6′-positions (Figure 4). This spectrum of *cis*-**1a** supports the expected structure in which the two trityl alcohol units are located inside the *cis*-azobenzene nucleus (Figure 2). Other major isomers of *cis*-**1a** were not observed in the NMR spectrum. The composition of the *cis*-isomer increased with the irradiation of UV light and reached *trans*/*cis* = 5:95 at the photostationary state (after irradiation for 80 min). Then, the irradiation of visible light (> 420 nm, 361 mW cm^2) on the solution led to a reversal, and the *trans*-isomer recovered to *trans*/*cis* = 48:52 (saturated after irradiation for 60 min). The photoinduced reversible dynamic motion of **1a** was supported by these spectral analyses.[16] Additionally, the isomerization of *cis*-**1a** to the *trans*-isomer can be completed (*trans*/*cis* = >99:<1) via thermal isomerization (150 °C, 24 h).[16]

Having already investigated the photoresponsive reversible dynamic motion of the azobenzene-tethered bis(trityl alcohol) **1a**, we next investigated its ability as a photoswitchable cooperative acid catalyst. We first tried hetero Diels–Alder reaction that the related biaryl-tethered bis(trityl alcohol) catalysts can promote,[13] but neither *cis*- nor *trans*-**1a** notably accelerated the reaction. Instead, it was interestingly found that a catalytic amount of **1a** can promote the phosphine-catalyzed Morita–Baylis–Hillman (MBH) reaction in response to light stimuli (Figure 5). A trityl alcohol-catalyzed MBH reaction has never been reported previously.[19] Among the reported acid-catalyzed MBH reactions,[20] we chose the reaction of 2-cyclopenten-1-one (**3**) and 3-phenylpropanal (**4**) with 20 mol % of P*n*Bu$_3$ in THF at 20 °C for 2 h as the standard reaction conditions to evaluate the photoresponsive catalyst activity of **1a**. The reaction without **1a**, that is, the background reaction proceeded in 26.5 % yield. With 20 mol % of *trans*-**1a** (*trans*/*cis* = >99:<1 (^{1}H NMR)) prepared by the photo(visible light)- and thermal isomerizations, the reaction was accelerated slightly (37 % yield), but good catalytic activity was not obtained.[21] In contrast, *cis*-**1a** showed distinct acceleration of the MBH reaction. The reaction with 20 mol % of quasi-*cis*-**1a** (*trans*/*cis* = 5:95 (^{1}H NMR)) generated by UV-irradiation in THF provided product **5** in 78 % yield.[22] The result of extrapolation to 20 mol % of pure *cis*-**1a** indicated that, if pure *cis*-**1a** is used, the yield would increase to 81 %.[23] A clear photoswitchable catalyst activity was demonstrated.



a: *trans*-**1a** / *cis*-**1a** = >99 : <1, b: Extrapolated to *trans*-**1a** / *cis*-**1a** = 0 : 100

Figure 5. Photoswitchable catalyst activity of **1a** in MBH reaction.

Table 1. Evaluation of photoreswitchable catalyst activities of **1a**–**c**.

Catalyst [mol %, *trans*/*cis*]	Yield of **5** [%]	Acceleration [%]	TONA[a]	TONA$_{rel}$[b] (ON/OFF)
none	26.5	–	–	–
trans-**1a** (5, >99:<1)	26.8	0.3	0.06	–
quasi-*cis*-**1a** (5, 5:95)	51	24.5	4.9	**82**
cis-**1a** (5, 0:100)[c]	52.3	25.8	5.15	**85.9**
trans-**1b** (5, >99:1)	31	4.5	0.9	–
quasi-*cis*-**1b** (5, 15:85)	52	25.5	5.1	**5.7**
cis-**1a** (5, 0:100)[c]	55.7	29.2	5.8	**6.5**
quasi-*trans*-**1c** (3, >99:>1)	53	26.5	8.8	–
quasi-*cis*-**1c** (3, 15:85)	61	34.5	11	1.3

[a] TONA = Turnover number of the catalyst for the acceleration. These values were calculated from following equations: TONA = acceleration (%)/catalyst loading (mol %). [b] TONA$_{rel}$ (ON/OFF) = TONA$_{cis}$/TONA$_{trans}$ [c] Extrapolated to pure *cis*-catalyst.[23]

To evaluate the proposed photoswitchable cooperative function of the two trityl alcohol units in **1a**, we then investigated the catalyst activity of trityl alcohol (**6**), the functional unit of **1a** (Figure 5). The reaction with 40 mol % of **6**, the same amount of trityl alcohol units as in **1a**, afforded **5** in 36 % yield. This result suggests that the catalyst acitivity of *trans*-**1a** (37 %) is probably attributable to the independent function of the each trityl alcohol unit. Thus, the difference between the catalyst activities of the *cis*- and the *trans*-isomers of **1a** in the MBH reaction arises from additional acceleration effect(s) in *cis*-**1a** associated with the structure. A certain cooperative function of the two proximal trityl alcohol units in the *cis*-azobenzene form would provide the potent acceleration.[24]

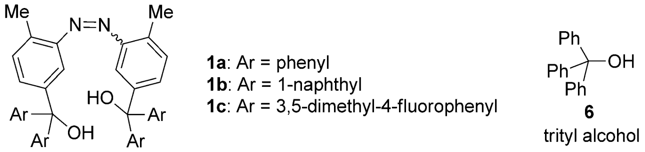
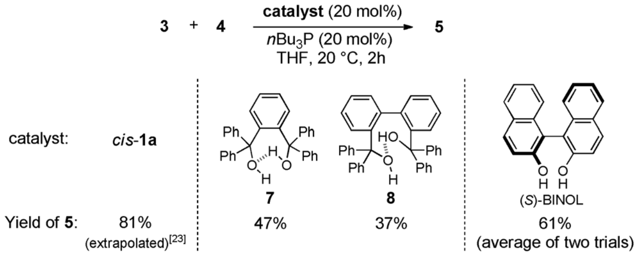


Figure 6. Structures of azobenzene-tethered bis(trityl alcohol) catalysts

The photoswitchable catalyst was modified by changing the aryl groups of the trityl alcohol units (Table 1, Figure 6). Azobenzene-tethered bis(trityl alcohol) derivatives **1b** (Ar = 1-naphthyl) and **1c** (Ar = 4-fluoro-3,5-dimethylphenyl) were prepared by adding appropriate aryl-metal reagents to diester **2**.[16] For **1b**, bulky 1-naphthyl group was selected to fix the two functional hydroxyl groups in the active *cis*-azobenzene form.[25] We expected that the fixation of the hydroxyl groups at suitable positions would induce potent catalyst activity. Furthermore, **1c** was designed to increase the acidity of the functional hydroxyl groups in order to enhance the cooperative function. An electron-withdrawing fluoro group was introduced to the aryl groups at the 4-positions for this purpose; in addition, two methyl groups were introduced at the 3,5-positions to lend bulkiness for fixation. The activities of these catalysts in the MBH reaction are summarized in Table 1. To accurately evaluate the switching abilities of the catalysts (**1a**–**c**), the reactions were performed with low loading of each catalyst under the standard conditions, and the results at an intermediate stage of the reaction were investigated.[26] An approximately *86*-fold difference in catalyst activity is expected between the ON- and the OFF-states of **1a** on the basis of each turnover number of the catalyst for the accelerations (TONA).[23] The 1-naphthyl-containing catalyst **1b** showed worse switching ability (ca. 6.5-fold) although the catalyst activity of the ON-state is slightly better than that of **1a**.[23] The catalyst **1c** induced greater accelerations of the MBH reaction. However, the switching ability was low because of the unexpectedly high catalyst activity of the OFF-state *trans*-isomer.[27] Consequently, **1a** achieved the best photoswitching ability.

Although the detailed photoswitchable cooperative function of the two trityl alcohol units in azobenzene-tethered bis(trityl alcohol) catalysts remains unclear at this stage of our investigations, some insights have been obtained. We first assumed the intramolecular hydrogen-bonding between the two hydroxyl groups to enhance the acidity of one trityl alcohol unit as the cooperative function,[14,28] which was proposed in the related biaryl-tethered bis(trityl alcohol) catalyst for hetero Diels–Alder reaction.[13] However, *cis*-**1a** did not function as a catalyst for the hetero Diels–Alder reaction. To estimate effect of the intramolecular hydrogen-bonding in azobenene-tethered bis(trityl alcohol) catalysts, we investigated catalyst activities of hydrogen-bonding bis(-trityl alcohol)s in the MBH reaction (Scheme 2). We chose bis(trityl alcohol) derivatives **7** and **8** as the hydrogen-bonding catalysts, in which or in whose close derivative the intramolecular hydrogen-bonding was observed.[29,30] The MBH reaction with 20 mol % of **7** proceeded in 47 % yield and a small acceleration (11 %) was observed from the reaction with 40 mol % of trityl alcohol (**6**, 36 % yield). But, **8** showed almost same catalyst activity as **6**. These results suggest that the intramolecular hydrogen bonding in bis(trityl alcohol) catalysts is not enough to gain potent catalyst activity in the MBH reaction like *cis*-**1a**. Other main cooperative function of the proximal two trityl alcohol units should exist in the *cis*-azobenene-tethered bis(trityl alcohol) catalysts. Further mechanistic studies to elucidate the photoswitchable catalyst activity of this new cooperative acid catalyst in greater detail are currently underway.



Scheme 2. Effect of the intramolecular hydrogen-bonding in bis(trityl alcohol) catalysts and comparison with (*S*)-BINOL.

Finally, we evaluated potential of the azobenzene-tethered bis(trityl alcohol) catalysts by comparing the catalyst activity with that of a representative organo acid catalyst for MBH reaction. We chose (*S*)-1,1′-bi(2-naphthol) ((*S*)-BINOL) as the standard of comparison.[20] When (*S*)-BINOL (20 mol %) was used under the standard conditions, the MBH reaction proceeded in 61 % yield (average of two trials, Scheme 2). Thus, *cis*-**1a** has more superior catalyst activity (81 %) than (*S*)-BINOL in the MBH reaction. A highly reactive novel organo acid catalyst for the MBH reaction has been developed by present photomechanical cooperative system.[19]

In summary, we have developed azobenzene-tethered bis(trityl alcohol) as a photoswitchable cooperative acid catalyst, which demonstrated photoswitchable catalyst activity in the MBH reaction.[8] The switching ability is based on the photoinduced reversible dynamic molecular motion of catalyst associated with the photoisomerization of the azobenzene core, and the differently arranged two trityl alcohol units on the resulting isomeric catalysts would switch the catalyst activity by changing their cooperative function. Some insights into the photoswitchable catalyst activity suggest a different cooperative function of the two trityl alcohol units than that of the related biaryl-tethered bis(trityl alcohol) catalysts.[13] Further modification and expansion of the scope of this photoswitchable, new cooperative acid catalyst as well as detailed mechanistic studies are currently underway. Furthermore, it should be noted that this new cooperative acid catalyst has demonstrated a new catalysis of MBH reaction and improved the efficiency. We believe that dynamic photomechanical catalysts can potentially demonstrate new reactivities, new efficiencies, and new reaction controls on the basis of the specific reaction field created by the photoinduced dynamic molecular motion. Our future studies will focus on developing smart chemical transformations using dynamic photomechanical catalysts, which open up new possibilities in organic synthesis.[5]

Acknowledgements

This work was supported by the Program of Institutional Reforms for Creating a Personnel Support System for Creative Young Researchers from Kumamoto University. This work was performed under the Cooperative Research Program: Network Joint Research Center for Materials and Devices (Institute for Materials Chemistry and Engineering, Kyushu University). We thank Prof. Ryo Irie (Kumamoto University), Prof. Masanobu Uchiyama (The University of Tokyo and RIKEN), Dr. Kazuto Takaishi (RIKEN), and Prof. Takuji Hatakeyama (Kyoto University) for their valuable comments and suggestions.

Keywords: acid catalysts · azo compounds · cooperative catalysts · Morita–Baylis–Hillman reaction · photochemistry

---

[1] a) *Molecular Switches* (Ed.: B. L. Feringa), Wiley-VCH, Weinheim, **2001**; b) V. Balzani, M. Venturi, A. Credi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, **2008**; c) E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem.* **2007**, *119*, 72–196; *Angew. Chem. Int. Ed.* **2007**, *46*, 72–191; d) O. Sato, J. Tao, Y.-Z. Zhang, *Angew. Chem.* **2007**, *119*, 2200–2236; *Angew. Chem. Int. Ed.* **2007**, *46*, 2152–2187; e) A. P. R. Johnston, G. K. Such, F. Caruso, *Angew. Chem.* **2010**, *122*, 2723–2725; *Angew. Chem. Int. Ed.* **2010**, *49*, 2664–2666; f) Special Issue: "Photochromism" M. Irie, *Chem. Rev.* **2000**, *100*, 1683–1890; g) I. Willner, S. Rubin, *Angew. Chem.* **1996**, *108*, 419–439; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 367–385; h) G. Mayer, A. Heckel, *Angew. Chem.* **2006**, *118*, 5020–5042; *Angew. Chem. Int. Ed.* **2006**, *45*, 4900–4921; i) P. Gorostiza, E. Y. Isacoff, *Science* **2008**, *322*, 395–399; j) K. Kinbara, T. Muraoka, T. Aida, *Org. Biomol. Chem.* **2008**, *6*, 1871–1876.

[2] For selected recent reports of stimuli-responsive functional materials, see: a) H. Maeda, Y. Bando, K. Shimomura, I. Yamada, M. Naito, K. Nobusawa, H. Tsumatori, T. Kawai, *J. Am. Chem. Soc.* **2011**, *133*, 9266–9269; b) J. Wang, L. Hou, W. R. Browne, B. L. Feringa, *J. Am. Chem. Soc.* **2011**, *133*, 8162–8164; c) E. Kim, D. Kim, H. Jung, J. Lee, S. Paul, N. Selvapalam, Y. Yang, N. Lim, C. G. Park, K. Kim, *Angew. Chem.* **2010**, *122*, 4507–4510; *Angew. Chem. Int. Ed.* **2010**, *49*, 4405–4408; d) H. J. Yoon, J. Kuwabara, J.-H. Kim, C. A. Mirkin, *Science* **2010**, *330*, 66–69; e) H. Komatsu, S. Matsumoto, S. Tamaru, K. Kaneko, M. Ikeda, I. Hamachi, *J. Am. Chem. Soc.* **2009**, *131*, 5580–5585; f) V. Blanco, A. Carlone, K. D. Hanni, D. A. Leigh, B. Lewandowski, *Angew. Chem.* **2012**, *124*, 5256–5259; *Angew. Chem. Int. Ed.* **2012**, *51*, 5166–5169.

[3] For reviews on photoswitchable catalysts, see: R. S. Stoll, S. Hecht, *Angew. Chem.* **2010**, *122*, 5176–5200; *Angew. Chem. Int. Ed.* **2010**, *49*, 5054–5075.

[4] A photoswitchable catalyst that switches the catalyst activity and/or reactivity in response to light stimuli is different from a photocatalyst in this point. The photocatalyst harvests and converts light into chemical energy, but it does not amplify light. For photocatalysts, see: a) V. N. Parmon, *Catal. Today* **1997**, *39*, 137–144; b) A. J. Esswein, D. G. Nocera, *Chem. Rev.* **2007**, *107*, 4022–4047; c) G. Palmisano, V. Augugliaro, M. Pagliaro, L. Palmisano, *Chem. Commun.* **2007**, 3425–3437.

[5] The potential of stimuli-responsive switchable catalysts for multicatalyst systems toward one-pot multistep synthesis has been mentioned, see: H. Birch, *Chemistry World*, *News*, 01 Oct. **2010**. See also ref. [2f].

[6] For applications of photoinduced catalysts, see: a) S. A. MacDonald, C. G. Willson, J. M. J. Fréchet, *Acc. Chem. Res.* **1994**, *27*, 151–158; b) D. Wang, K. Wurst, W. Knolle, U. Decker, L. Prager, S. Naumov, M. R. Buchmeiser, *Angew. Chem.* **2008**, *120*, 3311–3314; *Angew. Chem. Int. Ed.* **2008**, *47*, 3267–3270.

[7] a) M. V. Peters, R. S. Stoll, A. Kühn, S. Hecht, *Angew. Chem.* **2008**, *120*, 6056–6060; *Angew. Chem. Int. Ed.* **2008**, *47*, 5968–5972; b) J. Wang, B. L. Feringa, *Science* **2011**, *331*, 1429–1432; c) O. B. Berryman, A. C. Sather, A. Lledo, J. Rebek, Jr., *Angew. Chem.* **2011**, *123*, 9572–9575; *Angew. Chem. Int. Ed.* **2011**, *50*, 9400–9403.

[8] A part of the results of this communication were utilized in a patent application: Japanese patent application No. 2011-115326.

[9] a) *Bifunctional Molecular Catalysis* T. Ikariya, M. Shibasaki, *Top. Organomet. Chem.* **2011**, *37*, 1–210; b) P. I. Dalko, L. Moisan, *Angew. Chem.* **2004**, *116*, 5248–5286; *Angew. Chem. Int. Ed.* **2004**, *43*, 5138–5175; c) M. Shibasaki, M. Kanai, K.-I. Funabashi, *Chem. Commun.* **2002**, 1989–1999; d) T. Ooi, M. Takahashi, M. Yamada, E. Tayama, K. Omoto, K. Maruoka, *J. Am. Chem. Soc.* **2004**, *126*, 1150–1160. Our recent reports on bifunctional cooperative catalyst systems, see: e) C. H. Cheon, T. Imahori, H. Yamamoto, *Chem. Commun.* **2010**, *46*, 6980–6982; f) T. Imahori, H. Ojima, Y. Yoshimura, H. Takahata, *Chem. Eur. J.* **2008**, *14*, 10762–10771.

[10] For photoswitchable cooperative catalysts, see: a) F. Würthner, J. Rebek, Jr., *Angew. Chem.* **1995**, *107*, 503–505; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 446–448; b) R. Cacciapaglia, S. Di Stefano, L. Mandolini, *J. Am. Chem. Soc.* **2003**, *125*, 2224–2227. Although details of the catalyst activity are unclear, an azobenzene-tethered bis-copper complex with a similar cooperative function mechanism has been reported for photoswitchable DNA cleavage, see: c) H. Prakash, A. Shodai, H. Yasui, H. Sakurai, S. Hirota, *Inorg. Chem.* **2008**, *47*, 5045–5047. In addition, a photoswitchable cooperative catalyst that switches enantioselectivity has been developed, see: d) D. Sud, T. B. Norsten, N. R. Branda, *Angew. Chem.* **2005**, *117*, 2055–2057; *Angew. Chem. Int. Ed.* **2005**, *44*, 2019–2021.

[11] a) A. Kausar, H. Nagano, Y. Kuwahara, T. Ogata, S. Kurihara, *Chem. Eur. J.* **2011**, *17*, 508–515; b) A. Kausar, H. Nagano, T. Ogata, T. Nonaka, S. Kurihara, *Angew. Chem.* **2009**, *121*, 2178–2181; *Angew. Chem. Int. Ed.* **2009**, *48*, 2144–2147; c) Md. Z. Alam, T. Yoshioka, T. Ogata, T. Nonaka, S. Kurihara, *Chem. Eur. J.* **2007**, *13*, 2641–2647; d) T. Yoshioka, T. Ogata, T. Nonaka, M. Moritsugu, S.-N. Kim, S. Kurihara, *Ad. Mater.* **2005**, *17*, 1226–1229.

[12] The related photoswitchable templates also use azobenzene as the photoresponsive core, see refs. [10a,b].

[13] Biaryl-tethered bis(trityl alcohol)s were reported as a hydrogen-bonding catalyst for hetero Diels–Alder reactions, see; A. K. Unni, N. Takenaka, H. Yamamoto, V. H. Rawal, *J. Am. Chem. Soc.* **2005**, *127*, 1336–1337.

[14] Activation of a Brønsted acid by another Brønsted acid through hydrogen-bonding interaction is defined as a Brønsted acid-assisted Brønsted acid (BBA), which is a common activation method for Brønsted acid catalysts, see: H. Yamamoto, K. Futatsugi, *Angew. Chem.* **2005**, *117*, 1958–1977; *Angew. Chem. Int. Ed.* **2005**, *44*, 1924–1942. Actually, enhanced acidities of TADDOL (α,α,α′,α′-tetraaryl-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol) derivatives compared with the corresponding mono-methanols have been observed, see: P. Christ, A. G. Lindsay, S. S. Vormittag, J.-M. Neudörfl, A. Berkessel, A. C. O'Donogue, *Chem. Eur. J.* **2011**, *17*, 8524–8528.

[15] T. Kawasaki, M. Tokuhiro, N. Kimizuka, T. Kunitake, *J. Am. Chem. Soc.* **2001**, *123*, 6792–6800.

[16] Details are reported in the Supporting Information.

[17] *Photochromism: Molecules and Systems* (Eds.: H. Dürr, H. Bouas-Laurent), Elsevier, Amsterdam, **2003**.

[18] The overlapped protons in helicenes also show similar higher-field signals in ^{1}H NMR spectra, see: a) R. Irie, A. Tanoue, S. Urakawa, T. Imahori, K. Igawa, T. Matsumoto, K. Tomooka, S. Kikuta, T. Uchida, T. Katsuki, *Chem. Lett.* **2011**, *40*, 1343–1345; b) S. K. Collins, A. Grandbois, M. P. Vachon, J. Côté, *Angew. Chem.* **2006**, *118*, 2989–2992; *Angew. Chem. Int. Ed.* **2006**, *45*, 2923–2926; c) Y. Kitahara, K. Tanaka, *Chem. Commun.* **2002**, 932–933; d) H. Wynberg, M. B. Groen, H. Schadenberg, *J. Org. Chem.* **1971**, *36*, 2797–2809.

[19] The potential of trityl alcohol derivatives as a catalyst for MBH reaction will be reported in due course.

[20] a) Y. M. A. Yamada, S. Ikegami, *Tetrahedron Lett.* **2000**, *41*, 2165–2169; b) N. T. McDougal, S. E. Schaus, *J. Am. Chem. Soc.* **2003**, *125*, 12094–12095.

[21] The composition of isomers of the utilized *trans*-**1a** (*trans*-**1a**/*cis*-**1a** = >99:<1) would remain unchanged during the MBH reaction. Isomerization of *trans*-**1a** to the *cis*-isomer was not observed in the ^{1}H NMR spectrum in [D$_8$]THF at 20°C for 2 h. For details, see the Supporting Information.

[22] *cis*-**1a** would hardly isomerize to the *trans*-isomer during the MBH reaction. The composition of isomers of the utilized quasi-*cis*-**1a** changed only slightly in [D$_8$]THF at 20°C for 2 h (0 min: *trans*-**1a**/*cis*-**1a** = 3:97, 2 h: *trans*-**1a**/*cis*-**1a** = 3.3:96.7). For details, see the Supporting Information.

[23] The acceleration abilities of pure catalysts were approximately extrapolated on a pro-rate basis of the observed accelerations of the MBH reactions based on the composition of isomers of the utilized catalyst. For details, see the Supporting Information.

[24] Although we cannot rule out changes in the intrinsic acidity of the trityl alcohol units associated with the structural changes of the catalyst in the photoisomerization, ^{1}H NMR spectra of *cis*- and *trans*-**1a** showed similar chemical shifts of the hydroxyl groups (see the Supporting Information). Rather, *cis*-**1a** showed lower chemical shift

than the *trans*-isomer and weaker acidity was implied. Thus, the clear photoswitchable catalyst activity of **1a** would not be derived from the difference in the intrinsic acidy of the isomeric catalysts.

[25] a) A. N. Thadani, A. R. Stankovic, V. H. Rawal, *Pros. Natl. Acad. Soc.* **2004**, *101*, 5846–5850; b) Y. Huang, A. K. Unni, A. N. Thadani, V. H. Rawal, *Nature* **2003**, *424*, 146–146.

[26] Because the reaction slows down in the last stage, the catalyst activities of **1a**–**c** were investigated at the intermediate stage to obtain adequate switching abilities. In the initial stage, it is difficult to estimate the OFF-state activities.

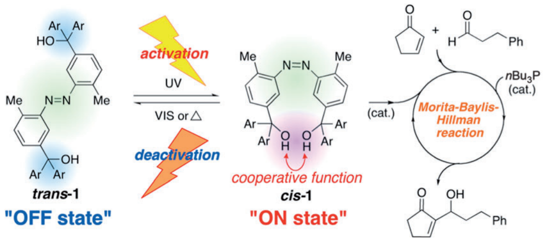
[27] The extrapolations to pure catalysts were not performed for **1c** because of the poor photoswitching ability in the acceleration of the MBH reaction.

[28] Although chemical shifts of the hydroxyl groups in the ^{1}H NMR spectra of *cis*-azobenzene catalysts did not support the enhanced acidity (see ref. [24] and the Supporting Information), the optimized structure of *cis*-**1a** by DFT calculations using the B3LYP/6–31G** basis set (Spartan 08 for Macintosh, Wavefunction) indicated the intramolecular hydrogen-bonding between the two hydroxyl groups. We assumed the transient intramolecular hydrogen-bonding. For details of DFT calculations, see the Supporting Information.

[29] For the intramolecular hydrogen-bonding in a close derivative of **7**, see; K. A. Carey, W. Clegg, M. R. J. Elsegood, B. T. Golding, H. Maskill, *Acta Crystallogr. E* **2003**, *59*, o263–o265.

[30] For the intramolecular hydrogen-bonding in **8**, see: F. Toda, A. Kai, R. Toyotaka, W.-H. Yip, T. C. W. Mak, *Chem. Lett.* **1989**, *18*, 1921–1924.

Received: April 24, 2012



Incorporation of an azobenzene core into tethered bis(trityl alcohol) allows the photoswitchable arrangement of the two trityl alcohol units through photoisomerization of azobenzene. The differently arranged trityl alcohol units change their cooperative function to reflect the positional relationships, and thus, the activity as a cooperative acid can be controlled by light stimuli (see figure).

Photoswitchable Catalysts

T. Imahori, R. Yamaguchi, S. Kurihara* .... ▮▮▮▮–▮▮▮▮

Azobenzene-Tethered Bis(Trityl Alcohol) as a Photoswitchable Cooperative Acid Catalyst for Morita–Baylis–Hillman Reactions