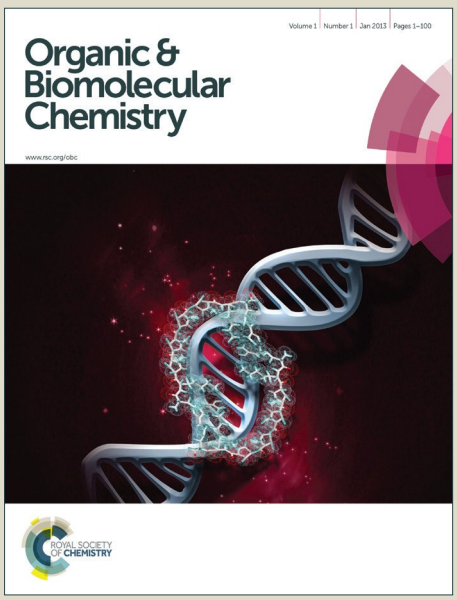
Organic & Biomolecular Chemistry

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/obc

Journal Name

COMMUNICATION

Lactone-fused cyclohexadiene as versatile platform for diversified synthesis of 5,6,5-tricyclic scaffolds

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

M. Shibuya,[a*] T. Sudoh,[a] T. Kawamura[a] and Y. Yamamoto[a*]

A lactone-fused cyclohexadiene, which can be readily prepared by the ruthenium(III)-catalyzed [2 + 2 + 2] cyclization of an enediyne, functioned as a versatile platform for the stereoselective synthesis of differently functionalized 5,6,5-tricyclic scaffolds.

The 5,6,5-tricyclic lactone scaffold has been found in natural products such as anticancer agent pleurotin,[1] diterpene glycoside farnesiaside,[2] and *seco*-prezizaane-type sesquiterpenes.[3] In particular, the last family consists of diversely oxygenated congeners, some of which display neurotrophic activity, such as jiadifenin, jiadifenolide, and jiadienoxolane A (Figure 1).[4,5] Owing to these attractive properties, continuous efforts have been devoted to the syntheses of these highly intriguing molecules.[6] Notably, some of the intermediates with structures simpler than the parent natural products exhibit more potent neurotrophic activities.[6a,b,h] This fact suggests that the diversified synthesis of relevant small molecules ultimately leads to the formation of a novel neurotrophic modulator. Herein, we report our study along this line on the facile access to differently functionalized 5,6,5-tricyclic lactone scaffolds using a lactone-fused cyclohexadiene as a versatile platform.

Generally, the basic 5,6,5-tricyclic lactone framework is constructed in a stepwise manner.[6] However, we envisaged that the transition-metal-catalyzed [2 + 2 + 2] cyclization of enediyne **1** possessing a propiolate moiety provides straightforward access to the desired lactone-fused cyclohexadiene platform **2**, which can be further transformed into diverse scaffolds (Scheme 1). To the best of our knowledge, the transition-metal-catalyzed [2 + 2 + 2] cyclization approach to 5,6,5-tricyclic lactone systems relevant to the abovementioned natural products has not been reported thus far.[7] To realize this strategically new approach to polycyclic lactone natural products, it would be highly beneficial to investigate the reactivity profile of lactone-fused cyclohexadiene **2**. Herein, we disclose the results of our study along this line on the synthesis of tricyclic lactone-fused cyclohexadienes and their reactivity and selectivity toward diverse transformations.

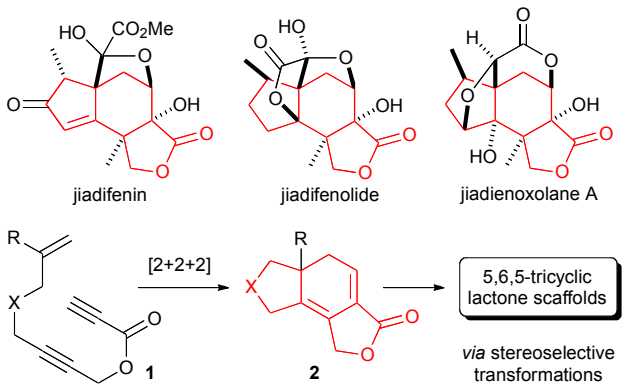
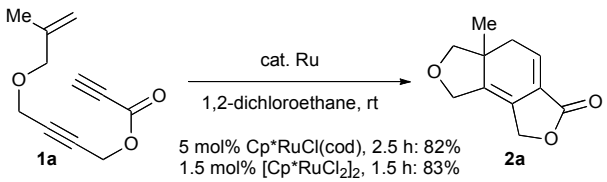


Figure 1 [2 + 2 + 2] cyclization approach to 5,6,5-tricyclic lactone scaffolds relevant to natural products.

To this aim, we investigated the synthesis of model compounds **2** with a tetrahydrofuran ring (X = O) because ether-tethered enediynes **1** (X = O) is readily prepared. In the presence of 5 mol% Cp*RuCl(cod) (Cp* = η^5-pentamethylcyclopentadienyl, cod = 1,5-cyclooctadiene), **1** (X = O, R = H) underwent cyclization even at room temperature in 1,2-dichloroethane. However, a complex mixture of products was formed due to extensive isomerizations of the cyclohexadiene moiety, resulting in detection of a trace amount of **2**. Thus, methallyl analog **1a** was subjected to the same reaction conditions to afford the desired cycloadduct **2a** as a sole product in 82% yield (Scheme 1).[8]



Scheme 1 Preparation of lactone-fused cyclohexadiene platform **2a**.

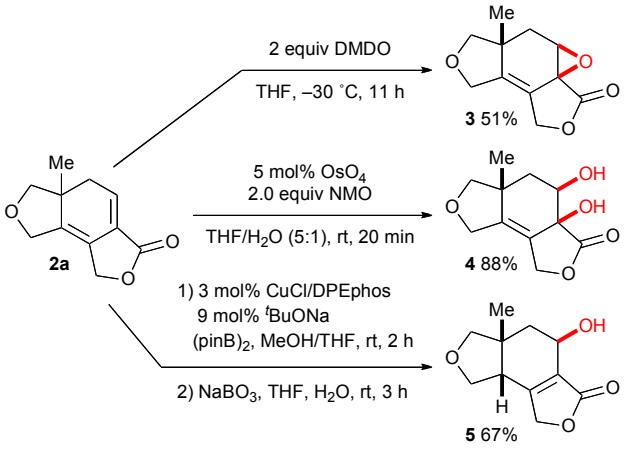
Previously, it was found that $[Cp^*RuCl_2]_2$, which is the precursor of Cp*RuCl(cod), effectively catalysed the cycloaddition of 1,6-diynes with 3,4-dihydrofuran.[8a] Therefore, the cyclization of **1a** was

[a] *Department of Basic Medicinal Sciences, Graduate School of Pharmaceutical Sciences, Nagoya University, Chikusa, Nagoya 464-8601, Japan. e-mail: yamamoto-yoshi@ps.nagoya-u.ac.jp, m-shibu@ps.nagoya-u.ac.jp*

† Electronic Supplementary Information (ESI) available: Experimental details, and ^{1}H and ^{13}C NMR charts for all products. See DOI: 10.1039/x0xx00000x

performed with 1.5 mol% (3 mol% Ru) $[Cp^*RuCl_2]_2$ at room temperature for 1.5 h, affording **2a** in 85% yield. Using this procedure, the cyclization of **1a** could be carried out in 1.9 g scale, affording **2a** in 88% yield.

Having obtained the desired platform **2a**, its transformation was investigated, with particular focus on the introduction of oxygen functionalities (Scheme 2). Thus, **2a** was treated with dimethyldioxirane (DMDO) in THF at –30 ˚C to selectively afford epoxide **3** in 51% yield. The osmium-catalyzed dihydroxylation of **2a** in aqueous THF at room temperature also afforded *cis* diol **4** in 88% yield. Furthermore, the copper-catalyzed conjugate borylation of **2a** was conducted according to the report by Yun and coworkers.[9] After the oxidation of the crude product with $NaBO_3$, hydroxybutenolide **5** was obtained in 67% yield as a result of concomitant alkene transposition. All these reactions proceeded regioselectively at the electron-deficient alkene in such a way that the epoxy and hydroxyl groups were introduced *cis* to the angular methyl substituent, as evidenced by X-ray crystallographic analyses.



Scheme 2 Transformation of platform **2a** via epoxidation, dihydroxylation, and conjugate borylation.

These reactions took place from the convex face of **2a** due to the axially oriented protons hampering the approach from the concave face (Figure 2). Moreover, the tetrasubstituted olefin moiety is rather unreactive because of steric congestion due to the angular methyl substituent, although electrophilic epoxidation and dihydroxylation are expected to occur more electron-rich olefin rather than electron-deficient olefin.

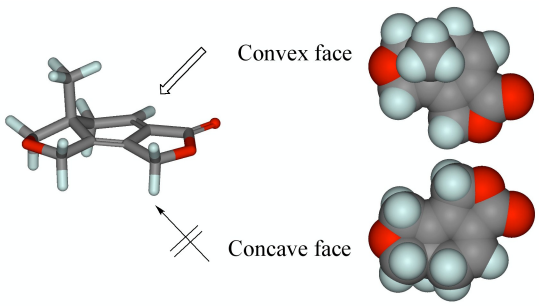
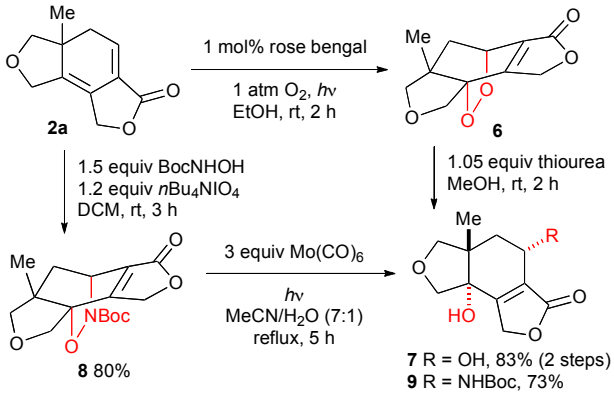


Figure 2 DFT-optimized structure of platform **2a**.

Next, the Diels–Alder (DA) reaction with singlet oxygen was examined, as shown in Scheme 3. In the presence of 1 mol % rose bengal, **2a** was irradiated in ethanol at room temperature under O_2, affording endoperoxide **6** as a single stereoisomer in 65% yield. Upon treatment with thiourea in methanol, the crude **6** was also directly converted to diol **7** in 83% overall yield. Previously, Jones and Snyder have reported the DA reaction of a related 5,6,5-tricyclic cyclohexadiene with singlet oxygen.[7f] In their study, the corresponding endoperoxide was obtained as a 13:1 diastereomeric mixture in 37% yield with 70% conversion. From the above observations, **2a** has distinctly high reactivity and stereoselectivity, although its 1,3-diene moiety is electronically deactivated by the lactone carbonyl group (*vide infra*). The DA reaction of **2a** with *tert*-butyl nitrosoformate, which was generated *in situ* by the oxidation of *N*-Boc hydroxylamine, also proceeded under mild conditions to selectively afford **8** in 80% yield as the sole product. The N–O bond cleavage of **8** using $Mo(CO)_6$ in refluxing aqueous acetonitrile under irradiation also afforded *cis* amino alcohol **9** in 73% yield. The stereochemistry of these hetero-DA reactions was unambiguously confirmed by the X-ray crystallographic analysis of **6** and **8**, revealing that the DA reaction occurs from the face opposite to the angular methyl substituent.



Scheme 3 Hetero-Diels–Alder reactions of platform **2a**.

As abovementioned, **2a** exhibited superior DA reactivity to the relevant tricyclic diene, which was previously used by the Snyder group,[7f] although **2a** must be deactivated by the electron-withdrawing carbonyl group. The facial selectivity opposite to those of other reactions presented in Scheme 2 is also intriguing. However, there has been no report on the detailed study disclosing the facial selectivity and structure-activity relationship of tricyclic cyclohexadienes. To investigate the DA reactivity in more detail, various 5,6,5-tricyclic compounds were prepared using the ruthenium-catalyzed cyclization and their DA reactivity toward *N*-phenyltriazolinedione (**10a**) and *N*-phenylmaleimide (**10b**) was compared (Figure 3). When **2a** was treated with **10a** in toluene at room temperature for 0.5 h, *endo*-cycloadduct **11aa** was obtained in 95% yield. The stereochemistry of **11aa** was unambiguously confirmed by X-ray crystallography. In contrast, the reaction with the less reactive dienophile **10b** required an elevated temperature: refluxing a solution of **2a** and **10b** in toluene for 6 h afforded **11ab** in 83% yield.

Cyclohexadienes **12a** and **12b**, which have no lactone carbonyl group, were prepared in high yields by treating the corresponding enediynes with the ruthenium catalyst (1.5 mol%) at room temperature. The cycloaddition of **12a** with **10a** and **10b** proceeded at room temperature for 0.5 h or in refluxing toluene for 6 h, affording the corresponding cycloadducts **13aa** and **13ab** in 92% and 76% yields, respectively. In striking contrast, the DA reaction of ester-substituted analog **12b** with **10a** took 1 h for completion, although **13ba** was obtained in a comparably high yield of 95%. Moreover, the reaction with less reactive dienophile **10b** was incomplete even after refluxing for 6 h, affording **13bb** in 7% yield along with the recovery of **12b** (78%). These results imply that **2a** is significantly superior to **12b** as the DA substrate, although both cyclohexadienes are deactivated by the conjugated carbonyl groups.

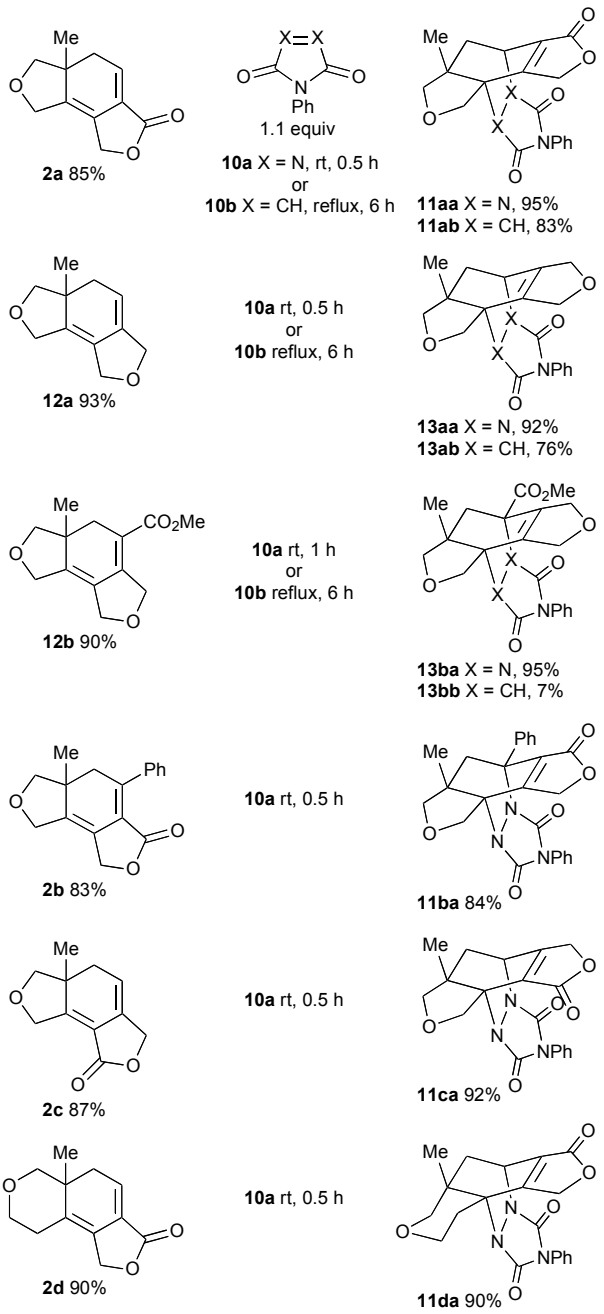


Figure 3 Preparation of cyclohexadienes **2a–d** and **12a,b**, and their Diels–Alder reactions.

To gain further insights into the selectivity and reactivity of the 5,6,5-tricyclic compounds for the DA reaction, DFT calculations were performed using the PCM (toluene) M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) method (see ESI for details). First, the activation energies of the four transition states (TSs) for the DA reactions of **2a** with maleimide (**10c**) as a model dienophile were estimated (Figure 4). As a result, the TSs for cycloaddition from the face opposite to the angular methyl substituent (**TS1** and **TS2**) were located 6.8 and 9.2 kcal/mol lower than the corresponding *syn* TSs (**TS3** and **TS4**), respectively. The most favorable *anti-endo* TS (**TS1**) was located 6.4 kcal/mol lower than the *anti-exo* TS (**TS2**). On the other hand, the *syn-endo* product was 1.8 kcal/mol more stable than the *anti-endo* product, indicating that the latter is a kinetic product. These results qualitatively agree with the experimentally observed product selectivity, with the exclusive formation of *anti-endo* products.

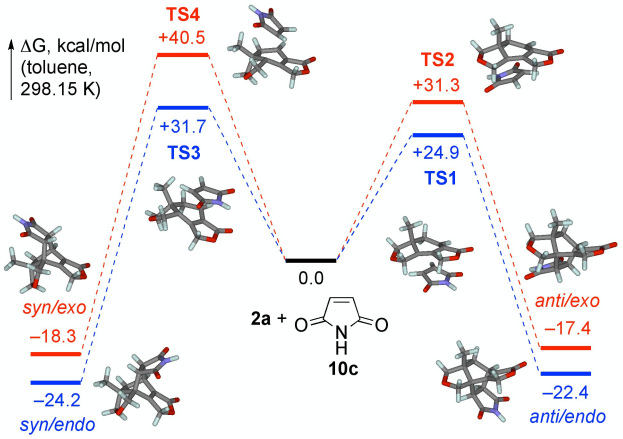


Figure 4 Reaction profile for Diels–Alder reaction of **2a** with **10c**.

Next, the free energies of activation and reaction ($\Delta G^{\ddagger}$ and ΔG_{rxn}), and the HOMO energies of **2a**, **12a**, and **12b** as well as other model lactones **2b** and **2c** were compared in terms of the *anti-endo* cycloaddition with **10c** (Table 1, for structures of **2b** and **2c**, see Figure 1). The HOMO energies of **2b** and **12a** (–8.1 and –8.3 eV, respectively) were higher than those of other cyclohexadienes (–8.8 to –8.6 eV). The smallest $\Delta G^{\ddagger}$ (24.4 kcal/mol) was estimated for **12a**. On the other hand, $\Delta G^{\ddagger}$ calculated for lactone-fused cyclohexadienes **2a** and **2c**, which have the lowest HOMO energies of –8.8 eV, were around 25 kcal/mol, values of which are only slightly higher than that for **12a**. The highest $\Delta G^{\ddagger}$ of 29.7 kcal/mol was calculated for lactone **2b**, which has a phenyl group similar to the relevant cyclohexadiene of Jones and Snyder.[7f] Moreover, a similarly high $\Delta G^{\ddagger}$ value of 28.9 kcal/mol was estimated for ester-substituted cyclohexadiene **12b**, although its HOMO energy (–8.6 eV) was 0.2 eV higher than those of **2a** and **2c**. Therefore, the DA reactivity trend cannot be explained only by the HOMO energy levels of these compounds. In addition, there was no correlation between ΔG_{rxn} and $\Delta G^{\ddagger}$.

Table 1 Calculated parameters for Diels–Alder reactions of **2a–d** and **12a,b** with **10c**.[a]

	HOMO	$\Delta G^{\ddagger}$	ΔG_{rxn}	$\Delta E^{\ddagger}_{act}$	$\Delta E^{\ddagger}_{dist,4e}$	$\Delta E^{\ddagger}_{dist,all}$
2a	–8.8	24.9	–22.4	5.7	21.2	28.5
2b	–8.1	29.7	–16.1	10.3	24.9	34.3
2c	–8.8	25.2	–21.1	6.3	21.0	28.7
2d	–8.7	24.5	–23.0	5.3	19.4	27.3
12a	–8.3	24.4	–20.6	4.5	23.3	31.4
12b	–8.6	28.9	–15.2	6.4	26.5	35.5

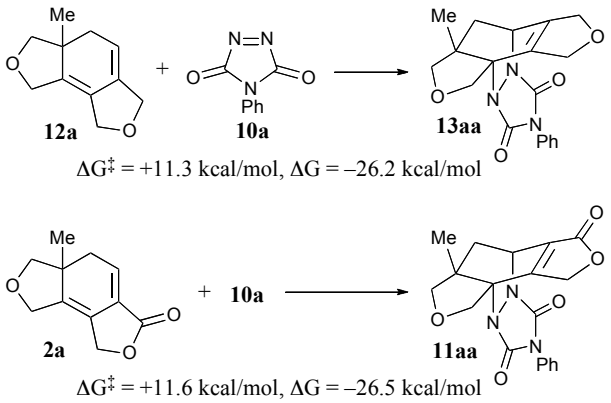
[a]HOMO and other energies are given in eV and kcal/mol, respectively.

Distortion analysis was applied to the DA reactions of the 5,6,5-tricycles to understand the structure–reactivity relationship. Houk's group has successfully introduced this method to estimate the degree of distortion in the TSs, which significantly contributes to the activation energy in the DA reactions involving strained cycloalkenes as dienophiles.[10] According to their study, each transition structure was separated into cyclohexadiene and dienophile fragments, and single-point energy calculations were performed for each fragment to obtain the distortion energies $\Delta E^{\ddagger}_{dist,4e}$ and $\Delta E^{\ddagger}_{dist,2e}$, respectively. The total distortion energy $\Delta E^{\ddagger}_{dist,all}$ is the sum of $\Delta E^{\ddagger}_{dist,4e}$ and $\Delta E^{\ddagger}_{dist,2e}$. The distortion energies of the diene fragment ($\Delta E^{\ddagger}_{dist,4e}$) ranged from 21.0 to 26.5 kcal/mol, while those of dienophile ($\Delta E^{\ddagger}_{dist,2e}$) ranged from 7.3 to 9.4 kcal/mol (Table S5 in ESI). From these values, the former significantly affects the reactivity trend.

Among 5,6,5-tricycles, **12a** without a conjugated carbonyl group exhibited the smallest $\Delta E^{\ddagger}_{act}$ (4.5 kcal/mol), while other lactone-fused cyclohexadienes **2a–c** exhibited larger $\Delta E^{\ddagger}_{act}$ values (5.7–10.3 kcal/mol). However, the $\Delta E^{\ddagger}_{dist,all}$ of **2a** and **2c** (28.5 and 28.7 kcal/mol, respectively) was smaller than that of **12a** (31.4 kcal/mol). Thus, the negative effect of a larger $\Delta E^{\ddagger}_{act}$ value is partially lessened by a smaller $\Delta E^{\ddagger}_{dist,all}$ value in the reactions of **2a** and **2c**. In good accordance with this analysis, $\Delta G^{\ddagger}$ for **2a** and **2c** were only slightly (0.5~0.8 kcal/mol) higher than that for **12a**. In contrast, the $\Delta E^{\ddagger}_{dist,all}$ of **12b** was the highest of all (35.5 kcal/mol), although its $\Delta E^{\ddagger}_{act}$ of 6.4 kcal/mol was comparable to those of **2a** and **2c**. Consequently, **12b** was expected to be a less efficient substrate as its $\Delta G^{\ddagger}$ (28.9 kcal/mol) was the second highest among others. This result is reasonable because the ester substituent of **12b** not only decreases the HOMO energy but also increases the distortion energy. Similarly, the phenyl substituent β to the carbonyl group in **2b** increased $\Delta E^{\ddagger}_{dist,all}$ by 5.8 kcal/mol compared with that of **2a**, and this high $\Delta E^{\ddagger}_{dist,all}$ surpasses the favorable HOMO energy. Accordingly, $\Delta G^{\ddagger}$ increased from 24.9 kcal/mol for **2a** to 29.7 kcal/mol for **2b**.

6,6,5-Tricyclic lactone **2d**, which bears a tetrahydropyran (THP) ring in place of the THF ring, was also analyzed. The $\Delta G^{\ddagger}$ value (24.5 kcal/mol) for **2d** was comparable to that for **12a** (24.4 kcal/mol) and this is ascribed mainly to the smallest distortion energy of the diene fragment ($\Delta E^{\ddagger}_{dist,4e}$ = 19.4 kcal/mol) as well as relatively small $\Delta E^{\ddagger}_{act}$ (5.3 kcal/mol). These results suggest that conformational constraint by the THF ring is the principal reason for the distortion energy for **2a**, **2c**, and **12a** and the fused lactone ring possibly relieves the distortion of the THF ring moiety in the TSs. Therefore, **2d** with less strained THP ring is superior to **2a** and **2c** as the diene substrate. Inversely, additional substituents on the cyclohexadiene moiety increase the distortion energy as evidenced by the significantly high $\Delta E^{\ddagger}_{dist,all}$ values for **2b** and **12b**.

To confirm the theoretically expected reactivity trend, cyclohexadienes **2b–d** were newly prepared in good yields by the Ru(III)-catalyzed cycloaddition and subjected to the DA reaction with triazolinedione **10a** (Table 1). The standard cyclization method was applied to the synthesis of **2c**, while **2b** and **2d** were obtained in high yields by performing cycloadditions with increased amounts of the catalyst at elevated temperatures (5 mol%, 80 ˚C or 10 mol%, 60 ˚C, respectively). The DA reactions of these cyclohexadienes with **10a** were performed in acetone at room temperature for 30 min to afford the corresponding cycloadducts **11ba**, **11ca**, and **11da** in high yields. To estimate the relative reactivity of the cyclohexadienes, a series of competition experiments were then performed. A 1:1:1 mixture of **2a**, **12a**, and **10a** was stirred in toluene at 0 ˚C for 1 h. The ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of the remaining substrates was **2a**:**12a** = 67:33 and that of products was **11aa**:**13aa** = 24:76. Therefore, the rate of DA reaction was approximately 3 times faster for **12a** than for **2a**. The difference in activation barriers inferred from this experiment was ca. 0.5 kcal/mol, which is similar to the calculated value by the DFT method (0.3 kcal/mol, Scheme 4).



Scheme 4 Calculated reaction parameters for Diels–Alder reactions of **2a** and **12a** with **10ab** in toluene at 273.15 K.

The competition reaction of **2a** and **2c** showed that the latter has slightly higher reactivity as the ratios of the remaining substrates and the DA adducts were **2a**:**2c** = 56:44 and **11aa**:**11ca** = 42:58, respectively. In contrast, the competition reactions of **2a** with **2b** or **12b** exclusively afforded **11aa**. Moreover, the competition reaction of **2a** and **2d** was similarly performed in acetone at 0 ˚C for 1 h. As a result, **2d** was found to be superior to **2a** as the ratio of the remaining substrates was **2a**:**2d** = 67:33 and that of products was **11aa**:**11da** = 30:70. Finally, the competition reaction of **2d** and **12a** revealed that the latter is still more reactive as the ratios of the remaining substrates and the DA adducts were **2d**:**12a** = 71:39 and **11da**:**13aa** = 34:66, respectively. From these results, the order of the reactivity was estimated as **12a** > **2d** > **2c** ≥ **2a** ≫ **2b**,**12b**. This reactivity trend is qualitatively consistent with that expected by computational results.

Conclusions

In conclusion, we synthesized lactone-fused cyclohexadiene **2a** in a gram scale by the Ru(III)-catalyzed [2 + 2 + 2] cyclization of enediyne **1a** containing propiolate and methallyl moieties. The versatility of **2a** as a synthetic platform was demonstrated by its regio- and stereoselective transformations to various 5,6,5-tricyclic lactone scaffolds with oxygen functional groups. Moreover, the exceptional selectivity and reactivity of **2a** were also revealed by a combination of computational and experimental investigations on the Diels–Alder reactions of a series of cyclohexadienes.

Acknowledgements

This work was partially supported by Grant-in-Aid for Scientific Research on Innovative Areas "Advanced Molecular Transformations by Organocatalysts" and Platform for Drug Discovery, Informatics, and Structural Life Sciences from the Ministry of education, Culture, Sports and Technology, Japan.

Notes and references

1 (*a*) W. J. Robbins, F. Kavanagh and A. Hervey, *Proc. Nat. Acad. Sci. U.S.A.*, 1947, **33**, 171; (*b*) J. Grandjean and R. Huls, *Tetrahedron Lett.*, 1974, 1893; (*c*) C. Cohen-Addad and J. Riondel, *Acta Cryst.*, 1981, **B37**, 1309.

2 (*a*) N. P. Sahu, K. Koike, S. Banerjee, B. Achari, Z. Jia and T. Nikaido, *Tetrahedron Lett.*, 1997, **38**, 8405; (*b*) K. Bhattacharyya, T. Kar, G. Bocelli, S. Banerjee and N. B. Mondal, *Acta Cryst.*, 2006, **E62**, o4007.

3 Y.-N. Liu, X.-H. Su, C.-H. Huo, X.-P. Zhang, Q.-W. Shi and Y.-C. Gu, *Chem. Biodiversity*, 2009, **6**, 963.

4 R. Yokoyama, J.-M. Huang, C.-S. Yang and Y. Fukuyama, *J. Nat. Prod.*, 2002, **65**, 527.

5 M. Kubo, C. Okada, J.-M. Huang, K. Harada, H. Hioki and Y. Fukuyama, *Org. Lett.*, 2009, **11**, 5190.

6 (*a*) Y. S. Cho, D. A. Carcache, Y. Tian, Y.-M. Li and S. J. Danishefsky, *J. Am. Chem. Soc.*, 2004, **126**, 14358; (*b*) D. A. Carcache, Y. S. Cho, Z. Hua, Y. Tian, Y.-M. Li and S. J. Danishefsky, *J. Am. Chem. Soc.*, 2006, **128**, 1016; (*c*) K. Harada, A. Imai, K. Uto, R. G. Carter, M. Kubo, H. Hioki and Y. Fukuyama, *Org. Lett.*, 2011, **13**, 988; (*d*) L. Trzoss, J. Xu, M. H. Lacoske, W. C. Mobley and E. A. Theodorakis, *Org. Lett.*, 2011, **13**, 4554; (*e*) J. Xu, L. Trzoss, W. K. Chang and E. A. Theodorakis, *Angew. Chem. Int. Ed.*, 2011, **50**, 3672; (*f*) Y. Yang, X. Fu, J. Chen and H. Zhai, *Angew. Chem. Int. Ed.*, 2012, **51**, 9825; (*g*) G. Mehta, H. M. Shinde and R. S. Kumaran, *Tetrahedron Lett.*, 2012, **53**, 4320; (*h*) L. Trzoss, J. Xu, M. H. Lacoske, W. C. Mobley and E. A. Theodorakis, *Chem. – Eur. J.*, 2013, **19**, 6398; (*i*) D. A. Siler, J. D. Mighion and E. J. Sorensen, *Angew. Chem. Int. Ed.*, 2014, **53**, 5332; (*j*) I. Paterson, M. Xuan and S. M. Dalby, *Angew. Chem. Int. Ed.*, 2014, **53**, 7286; (*k*) X. Cheng and G. C. Micalizio, *Org. Lett.*, 2014, **16**, 5144; (l) K. Harada, A. Imai, K. Uto, R. G. Carter, M. Kudo, H. Hioki and Y. Fukuyama, *Tetrahedron*, 2015, **71**, 2199.

7 For recent examples of the catalytic [2 + 2 + 2] cyclization of enediynes, see: (*a*) Y. Yamamoto, S. Kuwabara, Y. Ando, H. Nagata, H. Nishiyama and K. Itoh, *J. Org. Chem.*, 2004, **69**, 6697; (*b*) K. Tanaka, G. Nishida, H. Sagae and M. Hirano, *Synlett*, 2007, 1426; (*c*) T. Shibata, H. Kurokawa and K. Kanda, *J. Org. Chem.*, 2007, **72**, 6521; (*d*) A. L. Jones and J. K. Snyder, *J. Org. Chem.*, 2009, **74**, 2907; (*e*) A. Geny, S. Gaudrel, F. Slowinski, M. Amatore, G. Chouraqui, M. Malacria, C. Aubert and V. Gandon, *Adv. Synth. Catal.*, 2009, **351**, 271; (*f*) A. L. Jones and J. K. Snyder, *Org. Lett.*, 2010, **12**, 1592; (*g*) A. Dachs, A. Pla-Quintana, T. Parella, M. Solà, and A. Roglans, *Chem. – Eur. J.*, 2011, **17**, 14493; (*h*) S. Ventre, C. Simon, F. Rekhroukh, M. Malacria, M. Amatore, C. Aubert, and M. Petit, *Chem. – Eur. J.*, 2013, **19**, 5830.

8 (*a*) Y. Yamamoto, H. Kitahara, R. Ogawa, H. Kawaguchi, K. Tatsumi and K. Itoh, *J. Am. Chem. Soc.*, 2000, **122**, 4310; (*b*) Y. Yamamoto, T. Arakawa, R. Ogawa, and K. Itoh, *J. Am. Chem. Soc.*, 2003, **125**, 12143.

9 S. Mun, J.-E. Lee and J. Yun, *Org. Lett.*, 2006, **8**, 4887.

10 F. Liu, R. S. Paton, S. Kim, Y. Liang and K. N. Houk, *J. Am. Chem. Soc.*, 2013, **135**, 15642.