WebLog Journal of Molecular and Cellular Biology

Research Article
Published: 01 Sep, 2025

Theoretical Investigation on Lewis/Brønsted Acid Catalyzed Modulation of BCB Reactive Site in Synthesis of Spirocyclic and Bicyclic Framework

*Dr. Nan Lu**

College of Chemistry and Material Science, Shandong Agricultural University, Taian 271018, P. R. China



Abstract

Our DFT calculation provided the first theoretical investigation on Lewis/Brønsted acids-catalyzed syntheses of bicyclo[2.1.1]hexane and spirocyclic compound from disubstituted BCB and ester-activated quinone. For [2π + 2σ] cycloaddition with $Ni(OTf)_2$, BCB was activated as nucleophile to attack quinone initially. Then bicyclic product was achieved via cyclization. For (3 + 2) cycloaddition with DTBP, the dehydrogenation of BCB and aromatization of quinone is promoted owing to enhanced acidity of DTBP. The activation of BCB via hydrogen bonding between DTBP forms ion pair through intramolecular bridgehead bond cleavage. The nucleophilic addition of enolized BCB happens followed by deprotonation mediated by DTBP anion and aromatizes to cyclobutene. Another spirocyclic product was yielded via ester exchange along with recovered DTBP and CH_4 release. The nucleophilic attack and ester exchange are rate-limiting for $Ni(OTf)_2$-catalyzed [2π + 2σ] and DTBP-catalyzed (3 + 2) cycloaddition.

Keywords: Bicyclo[1.1.0]butane; Lewis/Brønsted acid; (3 + 2) cycloaddition; [2π + 2σ] cycloaddition; Quinone

Introduction

As aromatic bioisostere with drug-like properties, the bicyclo[1.1.0]-butanes (BCBs) can function as effective fragments to assemble rigid three-dimensional scaffolds in recent studies. For example, Tsien reported three-dimensional saturated C(sp3)-rich bioisosteres for benzene [1]. Bellotti discovered strain-release photocatalysis [2]. Yang explored asymmetric synthesis of chiral caged hydrocarbons as arenes bioisosteres [3]. Xiao researched advance and application for bicyclo[1.1.0]butane transformation [4]. Many efforts have focused on radical pathway of BCBs owing to π-character of strained central C–C bond such as [2π + 2σ] cycloaddition in synthesis of bicyclo[2.1.1]hexanes and bicyclo[1.1.0]butyl radical cation [5-7]. In addition, BCBs can serve as 1,3-dipoles, either electrophiles or nucleophiles in Palladium-catalyzed decarboxylative (4 + 3) cycloaddition of bicyclobutane with 2-alkylidenetrimethylene carbonate leading to 2-oxabicyclo[4.1.1]octanes and Ti-catalyzed formal [2π + 2σ] cycloaddition of bicyclo[1.1.0]butanes with 2-azadienes to access aminobicyclo[2.1.1]hexanes [8-10]. In this field, diverse reactivity of BCBs enables them ideal architectures applying in divergent annulation.

Recently, various BCBs have been utilized in divergent synthesis as a widely adopted strategy. Major achievements are Hu's synthesis of diverse polycyclic molecules using quinones catalyzed by Lewis acid, Zhang's regio- and diastereoselective cascade reaction to gem-difluorinated carbocyclic ring and Wang's switchable, structure-dependent alder-ene/[2π + 2σ] cycloaddition with α-ketoesters enabled by Palladium catalysis [11-13]. Although Leitch group developed azabicyclo[3.1.0]hexanes and cyclobutenyl amines employing different imines as coupling partner, tedious substrate preparation limits divergent syntheses [14-16]. It is attractive to construct various molecular frameworks from single substrate. Yu researched diverse synthesis of arene-fused [n.1.1]-bridged molecules via rearrangement reaction [17]. Tian discovered substrate-regulated divergent addition of N-sulfonyl ketimines to bicyclo[1.1.0]butanes enabled by photoinduced energy transfer [18]. Feng group reported Pd-catalyzed ligand-controlled switchable hetero-(5 + 3)/enantioselective [2σ+2σ] cycloaddition with vinyl oxirane [19]. Glorius demonstrated solvent-dependent divergent cyclization between 1,2- or 2,3-reactive sites [20].

In addition, Zheng explored synthesis of azabicyclo[3.1.1]heptene with vinyl azide [21]. Hong

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Correspondence:

Dr. Nan Lu, College of Chemistry and Material Science, Shandong Agricultural University, Taian 271018, P. R. China, E-mail: lun@sdau.edu.cn

Received Date: *23 Aug 2025*

Accepted Date: *29 Aug 2025*

Published Date: *01 Sep 2025*

Citation:

Nan Lu. Theoretical Investigation on Lewis/Brønsted Acid Catalyzed Modulation of BCB Reactive Site in Synthesis of Spirocyclic and Bicyclic Framework. WebLog J Mol Cell Biol. wjmcb.2025.i0101. https://doi.org/10.5281/zenodo.17092177

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realized divergent enantioselective access to chiral compound from α,β-unsaturated ketone [22]. There are also condition-controlled divergent annulation of dioxopyrrolidine and synthesis of bridged sulfur heterocycle via enantioselective (4 + 3)/thia-(3 + 2) cycloaddition of bicyclobutane and enaminothione [23, 24]. A great breakthrough was Xu's divergent syntheses of spirocyclic and bicyclic frameworks from disubstituted BCB and ester-activated quinone substrates [25]. Although desired modulation of BCB reactive site was obtained, how bicyclo[2.1.1]hexane was selective by Lewis acids-promoted [2π + 2σ] cycloaddition? Why spirocyclic compound was favored by (3 + 2) cycloaddition of Brønsted acids which suppressed bicyclic? What's the origin of selectivity during precise control and expansion of BCB reactivity profile?

Computational Details

The geometry was optimized with Gaussian 09 package at B3LYP/BSI level [26, 27]. The mixed basis set was denoted as BSI with LanL2DZ for Ni, 6-31G(d) for non-metal atoms [28-32]. Different singlet, multiplet states were clarified with B3LYP approach including Becke's three-parameter hybrid functional with Lee–Yang–Parr correction [33, 34]. Harmonic frequency calculations were carried out at B3LYP/BSI level to gain thermodynamic corrections and zero-point vibrational energy (ZPVE) at 298 K, 1 atm for each structure in toluene. Using integral equation formalism polarizable continuum model (IEFPCM), the solvation-corrected free energies were obtained at B3LYP/6-311++G(d,p) (LanL2DZ for Ni) level on B3LYP/BSI-optimized geometries with Truhlar's "density" solvation model [35-37].

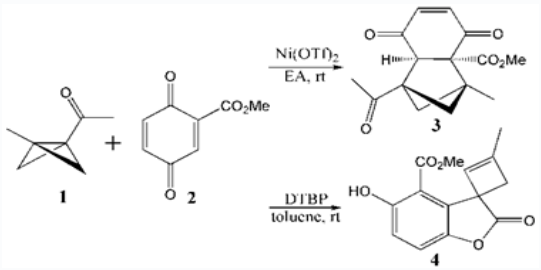
To characterize bonding orbital interactions and electronic properties, NBO procedure was performed with Natural bond orbital (NBO3.1) [38, 39]. Using Multiwfn_3.7_dev package [40], the wave function analysis was provided together by research on frontier molecular orbital (FMO).

Results and Discussion

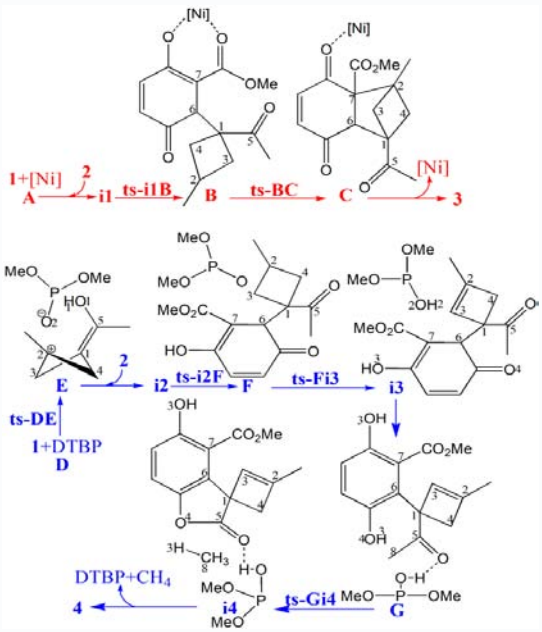
The mechanism was explored for switching Lewis/Brønsted acids-catalyzed syntheses of bicyclo[2.1.1]hexane **3** and spirocyclic compound **4** from disubstituted BCB **1** and ester-activated quinone **2** (Scheme 1). Shown by Scheme 2, $Ni(OTf)_2$ and DTBP was selected as Lewis and Brønsted acids. Under the influence of Lewis acid $Ni(OTf)_2$, **1** was activated forming **A** as nucleophile to attack **2** also activated by $Ni(OTf)_2$ generating intermediate **B**. Subsequently, **B** undergoes cyclization to complete [2π + 2σ] cycloaddition yielding final bicyclic product **3** (red arrow). On the other with enhanced acidity, Brønsted acid DTBP is positive for promoting dehydrogenation of BCB and aromatization of quinone. The activation of **1** by DTBP in (3 + 2) cycloaddition forms **D** via hydrogen bonding. Then ion pair **E** was given through cleavage of intramolecular bridgehead bond. The nucleophilic addition of enolized **1** to **2** affords intermediate **F**, which undergoes deprotonation mediated by DTBP anion and aromatizes to cyclobutene **G**. At last, the ester exchange of **G** delivers another spirocyclic product **4** along with release of CH_4 molecule and recovered DTBP (blue arrow) (Schemes 1 and 2).

$Ni(OTf)_2$-catalyzed [2π + 2σ] cycloaddition

1 was initially activated by $Ni(OTf)_2$ as Lewis acid forming stable complex **A** with greatly reduced relative energy (-101.5 kcal mol^{-1}). The first step is nucleophilic attack of **A** to **2** also under the influence of $Ni(OTf)_2$ from starting point intermediate **i1** (black dash line of Figure 1a). Via **ts-i1B**, the activation energy is 20.4 kcal mol^{-1} endothermic by 18.0 kcal mol^{-1} producing reactive complex **B**. The transition vector corresponds to noticable bonding of C1 to C6 and cooperative breaking of bridged link C1-C2, elongation of C6-C7 from double to single (1.99, 1.74, 1.43 Å) (Figure S1a). Once step 1 is accomplishd, the bridged ring of **1** is bonded to **2** in forms of formal four-membered ring in **B**.



Scheme 1: Switching Lewis/Brønsted acids-catalyzed syntheses of bicyclo[2.1.1]hexane **3** and spirocyclic compound **4** from disubstituted BCB **1** and ester-activated quinone **2**.



Scheme 2: Proposed reaction mechanism of $Ni(OTf)_2$/DTBP-catalyzed syntheses of **3** and **4** from BCB-quinone substrates **1** and **2**. TS is named according to the two intermediates it connects.

Subsequently in step 2, the cyclization from **B** undergoes via **ts-BC** with activation energy of 3.1 kcal mol^{-1} generating complex **C** exothermic by -22.3 kcal mol^{-1}. The transition vector is simple just about linkage of C2···C7 (2.68 Å), which enables two new five-membered ring in final bicyclic product **3**. Therefore, the [2π + 2σ] cycloaddition is completed with recovered Lewis acid $Ni(OTf)_2$. Comparatively, the nucleophilic attack in step 1 is rate-limiting with medium barrier. The whole process is favorable owing to step 2 of $Ni(OTf)_2$-catalyzed [2π + 2σ] cycloaddition (Table 1) (Figure 1).

DTBP-activated BCB, Nucleophilic attack/deprotonation/aromatization/ester exchange

On the other hand, DTBP functions as Brønsted acid with enhanced acidity thus favorable for dehydrogenation of BCB and aromatization of quinone. In alternative(3 + 2) cycloaddition, **1** is activated by DTBP via hydrogen bonding to form **D** as starting point

Table 1: The activation energy of all steps.

TS	$\Delta G^{\neq}_{gas}$	$\Delta G^{\neq}_{sol}$
ts-i1B	24.5	20.4
ts-BC	4.7	3.1
ts-DE	15.7	14.9
ts-i2F	4.8	4.6
ts-Fi3	20.3	18.2
ts-Gi4	30.6	28.8

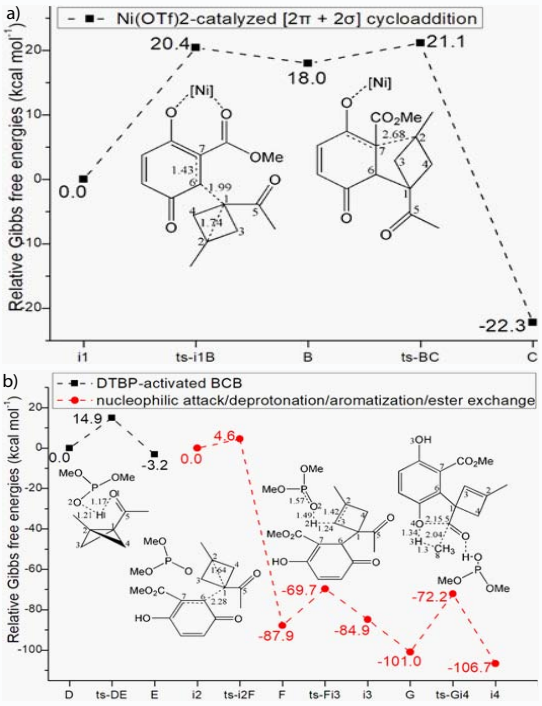


Figure 1: Relative free energy in solvent phase from complex (a) **i1** (b) **D**, **i2**.

of step 1, which proceeds via **ts-DE** with activation energy of 14.9 kcal mol^{-1} exothermic by -3.2 kcal mol^{-1} leading to ion pair intermediate **E**. The cleavage of intramolecular bridgehead bond is shown by the transition vector, which contains donation of proton from DTBP to carbonyl of **1** O2···H1···O1 (1.21, 1.17 Å). The positive charge is located on C2 in resultant **E**.

The step 2 is also nucleophilic addition of **1** to **2** similar with $Ni(OTf)_2$-catalyzed case yet involving decreased barrier of 4.6 kcal mol^{-1} and released energy huge to be -87.9 kcal mol^{-1}. An intermediate **i2** binding enolized **1** and **2** is taken as new starting point of next three steps. Via **ts-i2F**, the transition vector comprises breaking down of C1···C2 and bonding of C1···C6 as single one (1.64, 2.28 Å) (Figure S1b). The resulting **F** here is much more stable than aforementioned counterpart **B**. Furthermore, the structures later are also on lower potential energy surfaces. This is supposed by activation of enolized **1** for the whole process revealing high efficiency of DTBP.

Mediated by DTBP anion, **F** undergoes deprotonation in step 3 via **ts-Fi3** with activation energy of 18.2 kcal mol^{-1} yielding cyclobutene intermediate **i3** with relative energy of -84.9 kcal mol^{-1}. The transition vector is complex illustrating one proton on C3 taken away by DTBP anion C3···H2···O2 and strengthened C3···C2 from single to double one (1.24, 1.49, 1.42 Å) (Figure S1c). Via aromatization of **i3**, another cyclobutene complex **G** is afforded with enhanced stability from H bonding between recovered DTBP and carbonyl.

At last, the ester exchange of **G** occurs in step 4 via **ts-Gi4** with increased activation energy of 28.8 kcal mol^{-1} exothermic by -106.7 kcal mol^{-1} giving **i4**. The transition vector reveals a series of detailed atomic motion including hydroxyl losing hydrogen, methyl breaking off from carbonyl, and oxygen attacking carbonyl to form cyclic lactones via O4···H3, C5···C8 breakage and simultaneous O4···C5 connection. H3···C8 is consequently bonded as CH_4 molecule (1.34, 2.04, 2.15, 1.30 Å) (Figure S1d). *After the release of* CH_4 and recovered DTBP, another spirocyclic product **4** is obtained from **i4**. Undoubtedly, this ester exchange of step 4 is determined to be rate-limiting for DTBP-catalyzed (3 + 2) cycloaddition.

Conclusions

The theoretical investigation was provided on switching Lewis/Brønsted acids-catalyzed syntheses of bicyclo[2.1.1]hexane and spirocyclic compound from disubstituted BCB and ester-activated quinone. For [2π + 2σ] cycloaddition under the influence of $Ni(OTf)_2$, BCB was activated as nucleophile to attack quinone initially. Then bicyclic product was achieved via cyclization. On the other hand, for DTBP-catalyzed (3 + 2) cycloaddition, the dehydrogenation of BCB and aromatization of quinone is promoted by enhanced acidity of DTBP. The activation of BCB via hydrogen bonding with DTBP forms ion pair through cleavage of intramolecular bridgehead bond. The nucleophilic addition of enolized BCB happens followed by deprotonation mediated by DTBP anion and aromatizes to cyclobutene. Another spirocyclic product was yielded via ester exchange along with recovered DTBP and CH_4 release. The nucleophilic attack and ester exchange are rate-limiting for $Ni(OTf)_2$-catalyzed [2π + 2σ] and DTBP-catalyzed (3 + 2) cycloaddition.

Electronic Supplementary Material

Supplementary data available: [Computation information and cartesian coordinates of stationary points; Calculated relative energies for the ZPE-corrected Gibbs free energies (ΔG_{gas}), and Gibbs free energies (ΔG_{sol}) for all species in solution phase at 298 K.]

Author contributions: Conceptualization, Nan Lu; Methodology, Nan Lu; Software, Nan Lu; Validation, Nan Lu; Formal Analysis, Nan Lu; Investigation, Nan Lu; Resources, Nan Lu; Data Curation, Nan Lu; Writing-Original Draft Preparation, Nan Lu; Writing-Review & Editing, Nan Lu; Visualization, Nan Lu; Supervision, Nan Lu; Project Administration, Nan Lu. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by Key Laboratory of Agricultural Film Application of Ministry of Agriculture and Rural Affairs, P.R. China.

Conflict of interest: The authors declare no conflict of interest.

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