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Article

Stereoselective 1,3-Cyclotelomerization of Butadiene with Dienophiles under Nickel Catalysis

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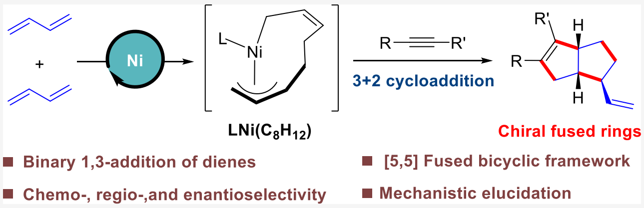

ABSTRACT: The discovery of new chemoselectivity with readily accessible chemicals is important to expand the reaction space for modern chemistry. For dienes and dienophiles, most people will naturally use them to carry out the classic Diels−Alder reaction to construct six-membered cyclic compounds. Here, we demonstrated a chemoselective coupling of butadiene with dienophiles through stereoselective 1,3-cyclotelomerization. By utilizing robust Ni/IPr catalysis, valuable bicyclic products were created with high regio- and chemoselectivities under mild conditions. Asymmetric cyclotelomerization enabled by the chiral NHC ligand was also performed, generating enantioenriched bicyclic compounds. The reaction mechanism was also investigated via experiments and density functional theory (DFT) calculations, which indicate that the reaction might start with oxidative cyclometalation between two molecules of 1,3-diene and Ni(0) species, followed by a [3 + 2]-cycloaddition between nickelacycle and dienophile. The products can undergo a variety of intricate transformations, which emphasizes the potential applications of this strategy. It is hoped that the discovery of this protocol will further inspire people to rethink classic organic reactions.

■ INTRODUCTION

It has always been a permanent pursuit among organic chemists to develop efficient catalytic systems and realize structurally diverse synthetic reactions, starting from simple raw materials. For example, 1,3-butadiene serves as a crucial C4 synthon in synthetic chemistry, and chemists have shown significant interest in its selective functionalizations.[1−7] The Frontier Orbit Theory (FOT) provides an explanation for these transformations, as they are governed by the principles of symmetry matching and energy proximity. The interaction of butadiene with its reaction partner (X = Y or X−Y) in 1,2- or 1,4-addition reactions is well-established, leading to cycloaddition and linear conjugate addition products, respectively (Figure 1A).[4,8−11] However, the potential for achieving new transformations with unconventional selectivity (e.g., 1,3-addition) remains less explored (Figure 1A).

Taking catalytic cycloadditions of dienes as examples, although many elegant and divergent approaches have been developed, their general pattern still follows the traditional 1,2 or 1,4-addition model (Figure 1B).[12−15] When you have dienophiles, most people will naturally use them to carry out the classic Diels−Alder reaction (1,4-addition) to construct six-membered cyclic compounds.[16−20] Using ruthenium(II) complexes as photosensitizers, the Yoon group realized a [2 + 2] cycloaddition between 2′-hydroxychalcone and conjugated dienes via 1,2-addition in the presence of Lewis acids.[21] Under a transition metal-catalyzed system, butadiene underwent 1,4-addition to generate eight-membered cyclic olefins.[22] Conversely, 1,2-addition predominated under a photocatalytic system, resulting in the formation of cyclobutane products.[23]

Taking advantage of the unique structure and reactivity of 1,3-diene, its cyclotelomerization provided a nice approach to construct more complicated molecules in one step. Through a mixed 1,4/1,2-addition, our group successfully achieved asymmetric heteroarylative cyclotelomerization of isoprene in the presence of Ni catalysis.[24] Using alkynes as reactants for binary 1,4-addition, the Thomel group accomplished the catalytic cyclotelomerization of 1,3-butadiene to afford ten-membered cycloalkenes with the Ni/PR$_3$ system.[25] All of these cycloadditions can make only single rings with even carbon numbers (4, 6, 8, and 10). Exploring the feasibility of the creation of double rings with odd carbon numbers will require the discovery of a new reaction model.

In 1975, Hagihara et al. reported a stoichiometric cyclization of the *p*-benzoquinone-palladium complex with butadiene to give an interesting tricyclic product.[26] Ten years later, Jolly and Raspel uncovered an unusual 1,3-addition between alkyne and ally fragments of the palladium complex to deliver cyclopentene-substituted η^3-allylpalladium species.[27] Unfortunately, such an important discovery has completely vanished into historical oblivion after that and no catalytic approach has been developed up to now. The discovery of a catalytic protocol,

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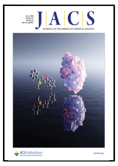

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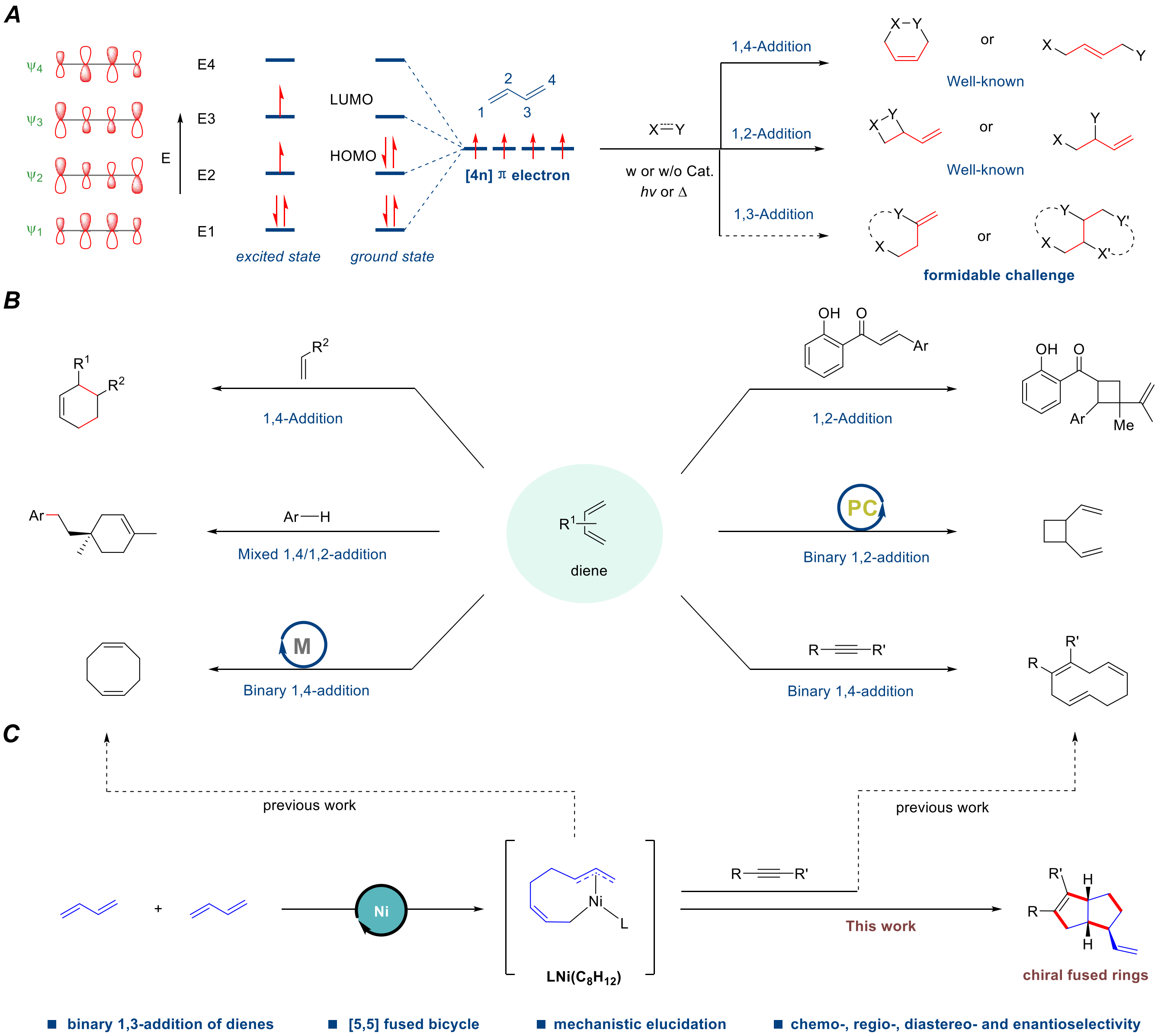


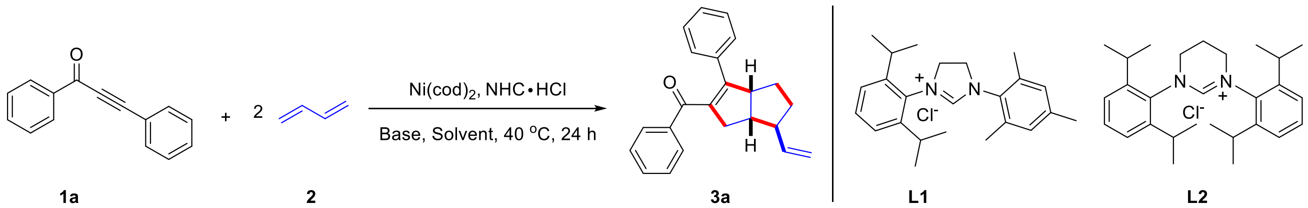
Figure 1. Catalytic telomerization of butadiene. (A) π-Molecular orbitals of 1,3-butadiene and its representative reactions. (B) Intrinsic 1,4- or 1,2-addition tendency of dienes in telomerization. (C) This work: stereoselective 1,3-cyclotelomerization of butadiene with dienophiles under Ni catalysis.

especially an asymmetric catalysis, to access these chiral polycycles would be very valuable for revitalizing telomerization chemistry. Based on our long-standing interest in the functionalizations of 1,3-dienes,[24,28−31] we wonder if we can discover a new chemoselective catalytic coupling of dienes and dienophiles by regulating the reactivity of nickelacycle (Figure 1C). We envision that oxidative cyclometalation between two molecules of 1,3-diene and Ni(0) catalyst gives the LNi(C_8H_{12}) complex, which then proceeds through intermolecular annulation with alkyne to deliver a unique chiral [5,5] bicycle. Obviously, there are many challenges associated with this proposal. For example, (1) the competitive coordination of the alkyne substrate with the Ni(0) catalyst may result in alkyne oligomerization;[32] (2) the direct reductive elimination of the LNi(C_8H_{12}) complex would give 1,3-diene dimerization product;[4] (3) how to switch the chemoselectivity from cyclodecatriene product to the [5,5] fused ring?[25,33,34] and (4) the simultaneous control of diastereo- and enantioselectivity of the obtained bicyclic product. By addressing these challenges, we herein developed an efficient 1,3-cyclotelomerization of butadiene with dienophiles under nickel/NHC catalysis with high chemo-, regio-, and enantioselectivities (Figure 1C). It features a formal binary 1,3-addition of dienes with high atom and step economy, providing an important complement to known precedents for the reaction of diene with dienophiles.

■ RESULTS AND DISCUSSION

Reaction Optimization. To verify our hypothesis, ynone (**1a**) and 1,3-butadiene (**2a**) were initially selected as model substrates (Table 1). In the presence of Ni(cod)$_2$, IPr·HCl and ^{t}BuOK in toluene at 40 °C, the reaction resulted in bicyclic product **3a** in 33% yield (entry 1). Interestingly, the reactivity showed significant improvement when polar aprotic solvents such as DMF or NMP were used, while the use of DCE as a

Table 1. Optimization for 1,3-Cyclotelomerization of Butadiene with Ynone[a]



1a **2** **3a** **L1** **L2**

entry	ligand	base	solvent	**3a** (%)	recovery of **1a** (%)
1	IPr·HCl	^{t}BuOK	toluene	33	33
2	IPr·HCl	^{t}BuOK	dioxane	53	14
3	IPr·HCl	^{t}BuOK	DCE	N.D.	87
4	IPr·HCl	^{t}BuOK	^{t}BuOH	55	N.D.
5	IPr·HCl	^{t}BuOK	DMF	70	N.D.
6	IPr·HCl	^{t}BuOK	NMP	72	N.D.
7	SIPr·HCl	^{t}BuOK	NMP	71	N.D.
8	IMes·HCl	^{t}BuOK	NMP	57	7
9	SIMes·BF_4^-	^{t}BuOK	NMP	29	34
10	**L1**	^{t}BuOK	NMP	58	8
11	**L2**	^{t}BuOK	NMP	50	N.D.
12	IPr·HCl	^{t}BuONa	NMP	76	N.D.
13	IPr·HCl	^{t}BuOLi	NMP	67	N.D.
14	IPr·HCl	EtOK	NMP	72	N.D.
15	IPr·HCl	MeONa	NMP	72	N.D.
16	**IPr**		**NMP**	**79 (76)**[b]	**N.D.**

[a]Conditions: **1a** (0.10 mmol), **2** (0.50 mmol), Ni(cod)$_2$ (10 mol %), NHC (10 mol %), base (20 mol %), solvent (0.4 mL), 40 °C, 24 h. Yields were determined by GC-FID analysis of crude mixture with mesitylene as the internal standard. [b]Isolated yield. N.D. = not detected.

solvent severely hindered the reaction (entries 1−6). Evaluation of NHC ligands revealed that IPr·HCl exhibited a superior performance in terms of yield (entries 6−11). Dissociation of carbene ligands usually requires the addition of a base, thus different bases were then examined and ^{t}BuOK was identified as the most effective base, providing **3a** with 72% yield (entry 12). It should be noted that the ynone **1a** underwent undesired self-dimerization or trimerization easily, especially at an elevated temperature, resulting in complete conversion of **1a**. Encouragingly, the free IPr ligand can increase the yield of **3a** to 79% in the absence of an additional base (entry 16).

Substrate Scope. With the optimized conditions in hand, we sought to investigate the substrate scope for the 1,3-cyclotelomerization of butadiene with ynones under Ni/NHC catalysis (Figure 2). When unsubstituted **1a** was subjected to the standard conditions, bicyclic product **3a** was obtained in an isolated yield of 76%. Both electron-donating (**3a**−**3c**) and electron-withdrawing substituents (**3d**−**3g**) at the *para* position of the phenyl group Ar^1 were well-tolerated, resulting in products with yields ranging from 38% to 76% and excellent diastereoselectivities. Chemically sensitive but useful groups such as Cl and Br were also compatible. Substituents at the *meta* and *ortho* positions of the phenyl motif (Ar^1) demonstrated good compatibility (**3h** and **3i**). Notably, naphthyl-, furyl-, and thienyl-substituted ynones were viable substrates, efficiently yielding the bicyclic products (**3j**−**3l**). Moreover, the *para* position of Ar^2 was investigated with both electron-donating and electron-withdrawing substituents. All candidates smoothly reacted with butadiene, affording the corresponding products in good yields and excellent selectivities (**3m**−**3s**). Substituents such as F and Cl at the *meta* position were compatible with the reaction, affording products **3t** and **3u** in good yields, respectively. The 3-thienyl-derived substrate was also amenable to the protocol, albeit with a decreased yield due to the propensity of homodimerization or trimerization (**3v**). To this end, substrates with steric bulk in the phenyl group were selected. For instance, 3,5-dimethyl and 2,4,6-trimethyl phenyl groups provided the optimal balance, yielding products in decent yields (**3w**−**3aa**, **3dd**−**3gg**). Additionally, 3,5-dimethoxy and 3,5-dichloro phenyl groups were applicable, resulting in products with yields of 77% and 38%, respectively (**3bb** and **3cc**). We speculated that the decreased yield of **3cc** could be attributed to the electron-deficient nature of the ynone substrate, which might promote alkyne self-oligomerization. Unfortunately, when replacing the aryl ring with an alkyl substituent in the ynone substrates, the reactions failed to deliver the corresponding products (for unsuccessful substrates, see Supporting Information, page S21). The stereo configuration of products **3e** (CCDC: 2321680), **3s** (CCDC: 2321686), and **3ee** (CCDC: 2321773) was further confirmed by X-ray crystallographic analysis.

To expand the application range of substrates, an investigation into the scope of the enones was conducted (Figure 3). Previously, we reported a hydrobivinylation reaction between enone and 1,3-butadiene catalyzed by Ni(0)/PCy$_3$, which yielded a diene product.[29] By modifying the reaction conditions and replacing PCy$_3$ with IPr, we found that enones could also undergo cyclotelomerization with 1,3-butadiene. The reaction for enones could be performed well with a mixed solvent (DMF/^{i}PrOH = 4/1). A wide range of *para*-substituted phenyl enones demonstrated successful application in this method with moderate diastereoselectivity, irrespective of their electronic factors (**5a**−**5g**). Moreover, 3-Cl or 2-Me on the phenyl ring of the Ar^2 group proved compatible with the current process, yielding **5h** and **5i** in 60% and 71%

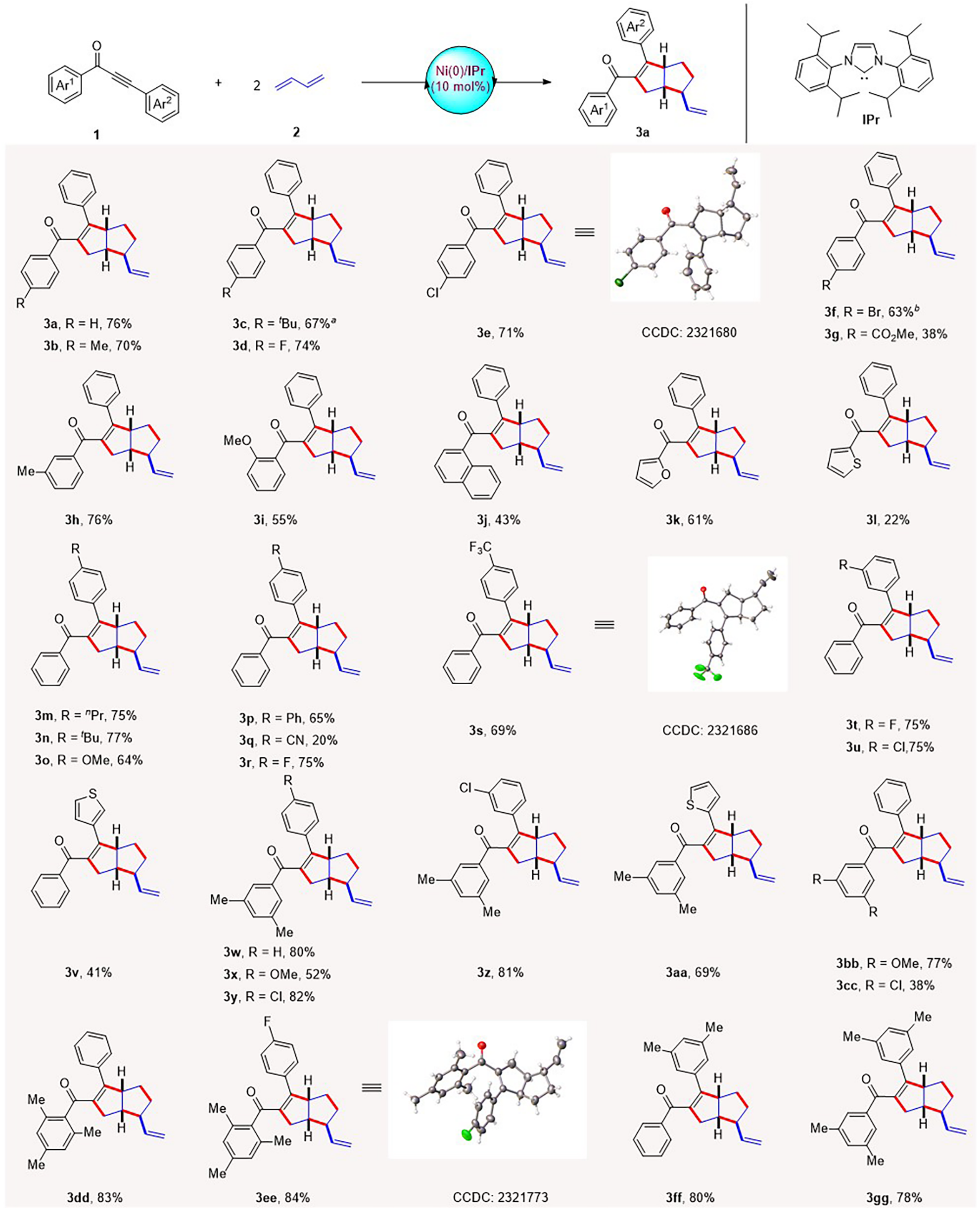


Figure 2. Substrate scope of ynones. Conditions: **1** (0.20 mmol), **2** (1.0 mmol), Ni(cod)$_2$ (10 mol %), IPr (10 mol %), NMP (0.8 mL), 40 °C, 24 h. Isolated yields were given in all cases. All the dr of products were >20/1. [a]48 h. [b]Ni(cod)$_2$ (15 mol %), IPr (15 mol %).

yield, respectively. Substituting the phenyl group with naphthyl or furyl still resulted in good yields for products **5j** and **5k**. However, the enone substrate bearing a hydroxyl group was not amenable to this protocol. The 3-pyridyl-substituted enone also only afforded diastereoisomers in 14% total yield (by ^{1}H NMR) with a 1.7:1 dr, accompanied by some inseparable

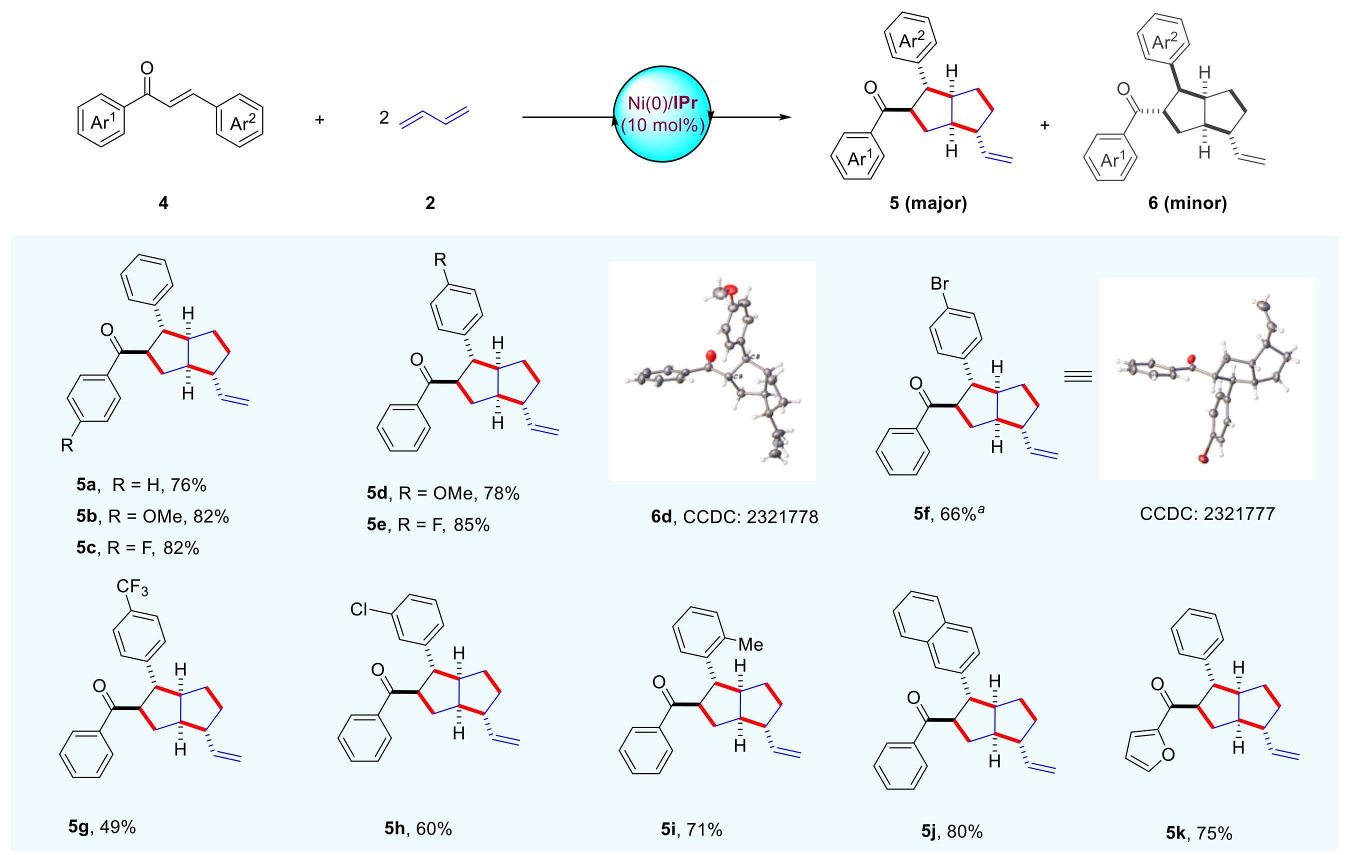
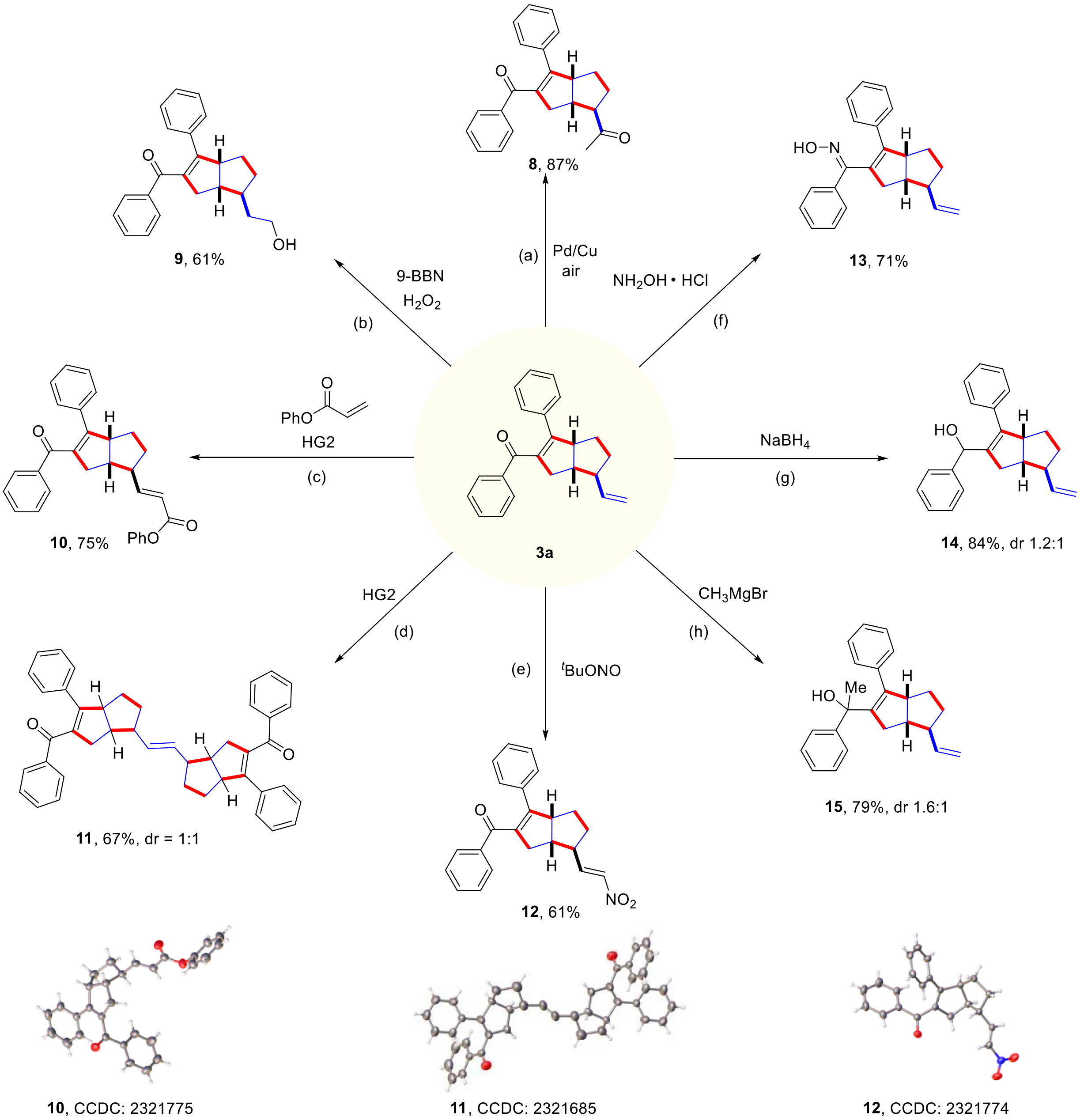


Figure 3. Substrate scopes of enones. Conditions: **4** (0.20 mmol), **2** (1.0 mmol), Ni(cod)$_2$ (10 mol %), IPr (10 mol %), DMF/^{i}PrOH (4/1, 0.5 mL), 50 °C, 24 h. Isolated yields were given in all cases. All the *dr* of **5** is between 3:1 and 4:1. ^{a}*i*-PrOH (0.5 mL), Ni(cod)$_2$ (15 mol %), IPr (15 mol %).

impurities (for unsuccessful substrates, see Supporting Information, page S21). The stereo configuration of products **6d** and **5f** was further confirmed by X-ray crystallographic analysis.

To showcase the synthetic utility of this protocol, various transformations were performed (Figure 4). First, the product **3a** underwent a Wacker-type oxidation at the terminal C=C bond under Pd/Cu catalysis, resulting in the formation of ketone **8** in 87% yield.[35] Furthermore, the hydroboration reaction of **3a** with 9-BBN, followed by oxidation with H_2O_2, smoothly provided alcohol **9** in a 61% yield. Using HG2 as the catalyst, the olefin metathesis of **3a** and phenyl acrylate yielded compound **10** at room temperature.[36] In the absence of an external alkene, an olefin metathesis of two molecules of **3a** at 70 °C provided compound **11** in 67% yield. Notably, the nitration of **3a** with ^{t}BuONO and TEMPO exhibited excellent *E*-selectivity, leading to the desired product **12** in 61% yield.[37] Subsequently, attention shifted toward functionalizing the ketone moiety. The condensation of **3a** with hydroxylamine resulted in the formation of oxime **13** in 71% yield.[38] Moreover, in the presence of $NaBH_4$, a chemoselective hydrogenation of **3a** occurred, providing alcohol **14** in good yield.[39] Additionally, the ketone motif underwent nucleophilic addition with MeMgBr, leading to the formation of tertiary alcohol **15** in 79% yield.[39] The structures of compounds **10**, **11**, and **12** were further confirmed through single-crystal X-ray crystallography (CCDC: 2321775, 2321685, and 2321774, respectively).

Substrate Scope for the Asymmetric 1,3-Cyclotelomerization of Butadiene with Ynones. Encouraged by the ligand effect in the Ni-catalyzed asymmetric catalytic reaction with NHC ligands,[24,40−44] we hypothesized that an asymmetric Ni-catalyzed 1,3-cyclotelomerization of butadiene with dienophiles could be achieved with bulky chiral NHC ligands. Through the optimization of the reaction conditions, good yields with excellent enantioselectivities could be achieved with chiral NHC **L10** as the optimal ligand (Figure 5A, for details, see Tables S1−S3). The undesired self-oligomerization of ynone easily occurred at 40 °C. Lowering the reaction temperature to 30 °C can slow this side reaction, resulting in an improved yield of **3dd** (73% yield, 99% ee). In addition, a linear relationship was observed by the nonlinear effect experiment, indicating that one ligand may coordinate with one nickel atom to form the active catalyst (Figure 5B). This innovative protocol exhibited good compatibility with various functional groups present in ynones (**3a**−**3ee**, Figure 5C). Ynones with electron-donating or electron-withdrawing groups on the phenyl moiety were suitable substrates, regardless of the position, affording the desired products with moderate to good yields (31−86%) and excellent enantioselectivities (93−99% ee). The reaction displayed the same remarkable diastereoselectivities as the racemic reaction (Figures 2 and 6). Importantly, heterocyclic ynones (**3k**, **3aa**) also underwent the process with high enantioselectivities. Ynones with significant steric hindrance were particularly favorable, providing the desired chiral bicyclic products in high yields and enantiomeric excess (**3w**−**3ee**). The absolute configuration of the chiral fused ring (**3dd**) was determined through X-ray crystallography (CCDC: 2321630).



10, CCDC: 2321775 **11**, CCDC: 2321685 **12**, CCDC: 2321774

Figure 4. Synthetic transformations. Conditions: (a) **3a** (0.10 mmol), $PdCl_2$ (15 mol %), CuCl (1.5 equiv), DMF/H_2O, air, 40 °C, 60 h; (b) **3a** (0.10 mmol), 9-BBN (0.10 mmol), 0 °C-rt, 12 h, then NaOH, H_2O_2, rt, 3 h; (c) **3a** (0.10 mmol), phenyl acrylate (0.15 mmol), HG2 (5 mol %), DCM, 40 °C, 24 h; (d) **3a** (0.10 mmol), HG2 (5 mol %), DCM, 70 °C, 48 h; (e) **3a** (0.10 mmol), ^{t}BuONO (0.20 mmol), TEMPO (0.04 mmol), dioxane, 90 °C, 12 h; (f) **3a** (0.10 mmol), $NH_2OH\cdot HCl$ (0.15 mmol), pyridine (0.25 mmol), EtOH, 60 °C, 40 h; (g) **3a** (0.10 mmol), $NaBH_4$ (0.30 mmol), MeOH, 0−40 °C, 3 h; and (h) **3a** (0.20 mmol), CH_3MgBr (0.60 mmol), THF, −78−60 °C, 40 h.

Mechanistic Investigations. To elucidate the mechanism, kinetic experiments were conducted by using model substrates under standard conditions (Figure 6A). Notably, we found that the operating procedure of this cyclotelomerization had an important impact on the reaction rate. The reaction protocol, which involved prestirring $Ni(cod)_2$, IPr, and 1,3-butadiene in NMP for 15 min prior to the addition of alkyne **1a** (procedure I), was much faster than that subjecting the 1,3-butadiene and alkyne **1a** simultaneously into $(IPr)Ni(cod)_2$ solution (procedure II). Moreover, we also observed that this cyclization reaction proceeded rapidly in the first 10 min upon the addition of alkyne **1a** (procedure I) and then slowed down along with time. The reaction between alkyne **1a** and butadiene **2** with a stoichiometric amount of (IPr)Ni(cod) proceeded very fast with procedure I (Figure 6B). Therefore, we speculated that this cyclotelomerization reaction first went through an oxidative cyclometalation between (IPr)Ni(0) and two molecules of 1,3-diene to form a nickelacycle species and then reacted with the alkyne substrate to deliver the corresponding bicyclic product. If the 1,3-diene and alkyne were added to the reaction system simultaneously, the competitive coordinated ability of alkyne would impede the formation of required nickelacycle. To further testify our hypothesis, we synthesized the $IPrNi(C_8H_{12})$ complex from IPr, $Ni(cod)_2$ and 1,3-butadiene (Figure 6C).[45] To our delight, such nickelacycle reacted with alkyne **1a** very smoothly, giving

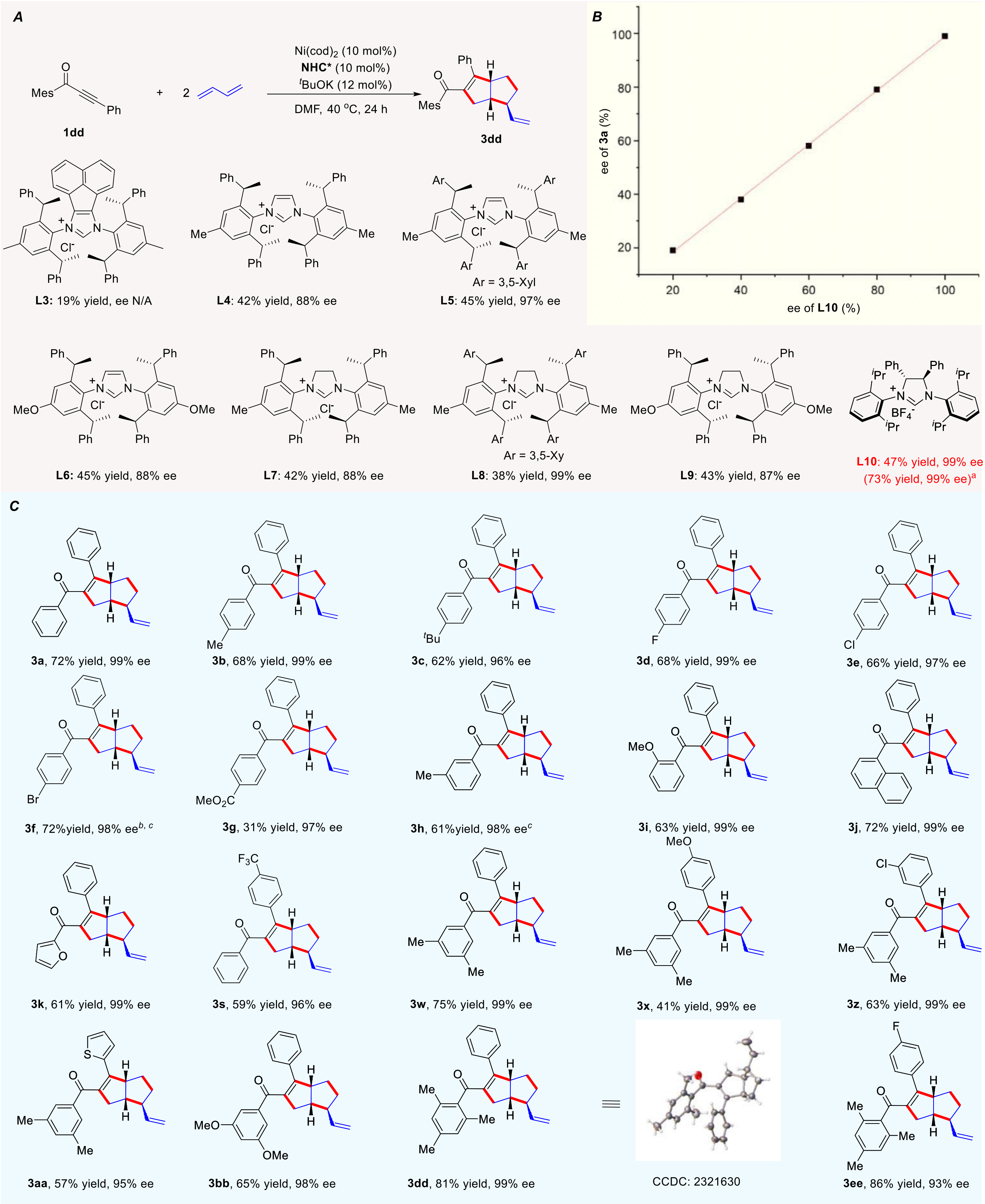


Figure 5. (A) Optimization of chiral NHC ligands. Conditions: **1** (0.10 mmol), **2** (0.5 mmol), Ni(cod)$_2$ (10 mol %), chiral NHC (10 mol %), ^{t}BuOK (20 mol %), DMF (0.4 mL), 40 °C, 24 h. (B) Nonlinear effect study. (C) The substrate scope for enantioselective 1,3-cyclotelomerization of butadiene with ynones. Conditions: **1** (0.20 mmol), **2** (1.0 mmol), Ni(cod)$_2$ (10 mol %), **L10** (10 mol %), ^{t}BuOK (12 mol %), DMF (0.8 mL), 30 °C, 24 h. Isolated yields were given in all cases. Enantioselectivities were determined by chiral HPLC analysis. ^{a}30 °C, ^{t}BuOK (12 mol %). ^{b}48 h. ^{c}Ni(cod)$_2$ (15 mol %), **L10** (15 mol %).

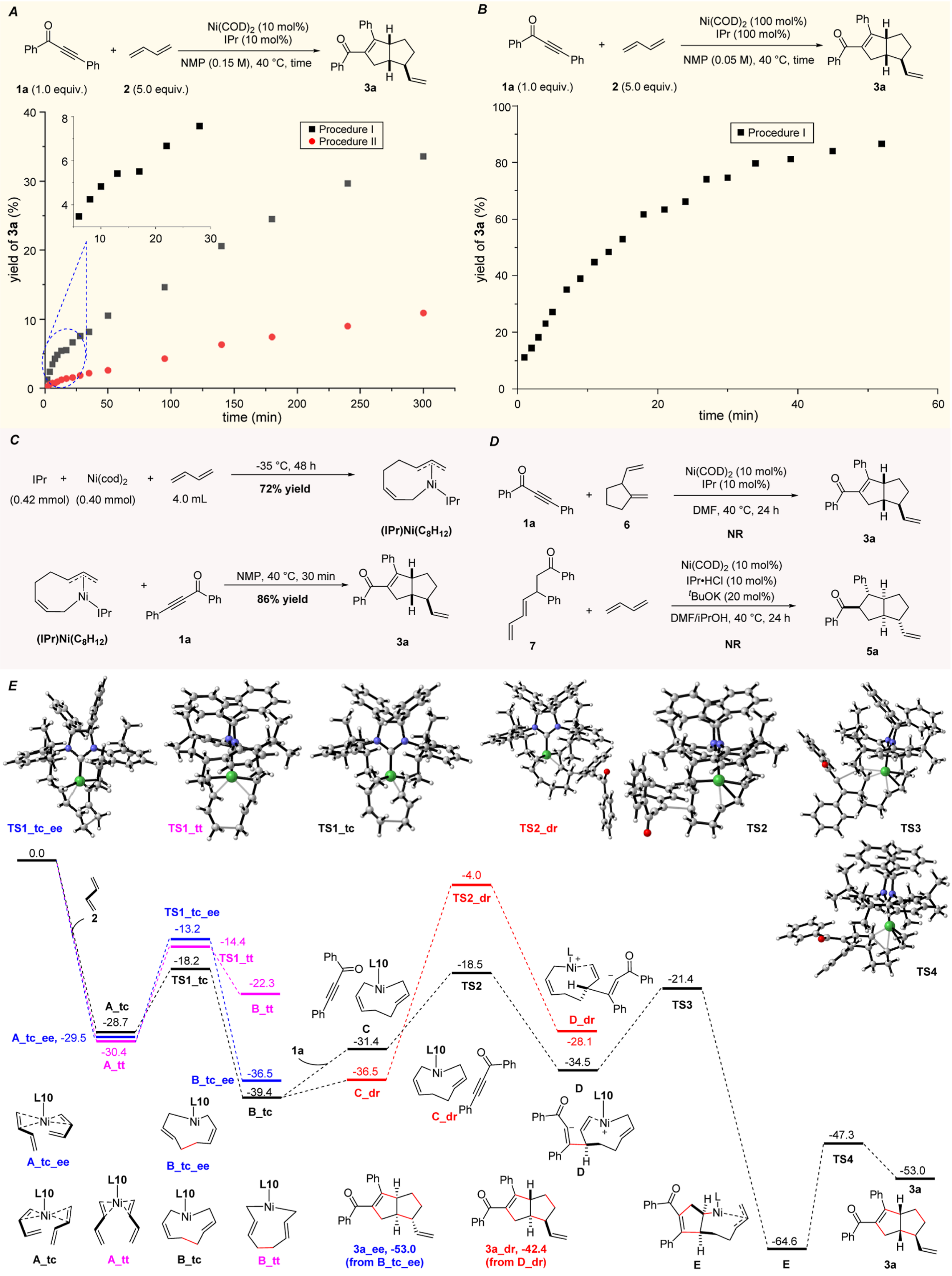


Figure 6. Mechanistic experiments and the proposed mechanism. (A) Kinetic experiments. (B) Reaction profile with stoichiometric Ni (procedure I). (C) Synthesis and transformation of (IPr)Ni(C$_8$H$_{12}$). (D) Control experiments. (E) DFT calculations on the proposed reaction pathways.

desired product **3a** in good yield within 1 h (Figure 6C). To exclude other possible pathways, control experiments were performed (Figure 6D). Under standard conditions, the reaction of five-membered dimerized intermediate **6** and alkyne **1a** did not give any desired product **3a**. Using our previously reported hydrobivinylation protocol,[29] the diene **7** was synthesized from the reaction of enone **4** with 1,3-butadiene under Ni catalysis. However, the imaginary intermediate **7** also could not react with 1,3-butadiene to form desired product **5a**.

To further probe the mechanism and understand the origin of its enantio- and diastereoselectivity of this Ni-catalyzed cyclotelomerization, density functional theory (DFT) calculations were performed on a model reaction with ynone **1a** and 1,3-butadiene. When the chiral NHC ligand **L10** is used, (**L10**)Ni(0) can activate two molecules of 1,3-butadiene **2** by alkene coordination, forming intermediate **A_tc** and its enantiomer **A_tc_ee** in the s-trans, -cis conformation or intermediate **A_tt** in the s-trans, -trans conformation. Followed by the oxidative cyclometalation, bis-π-allyl nickelacycle **B_tc** is generated preferably through transition state **TS1_tc** with a lower free-energy barrier (10.5 kcal/mol), than transition state **TS1_tc_ee** leading to the enantiomeric product **3a_ee** (from intermediate **B_tc_ee**, see Supporting Information for more details). Meanwhile, calculations indicate that the formation of **B_tt** has a higher free energy (16.0 kcal/mol for **TS1_tt**) than that of **B_tc**. Then, charge-transfer (CT) complex **Int C** or its diastereoisomer **Int C_dr** may be formed between electron-rich nickelacycle **B_tc** and electron-poor ynone **1a**. Although **Int C** entails a higher energy barrier than **Int C_dr** by 5.1 kcal/mol, the transition state **TS2** forming the desirable product **3a** is much favored by exhibiting a lower free-energy barrier of 12.9 kcal/mol than **TS2_dr**. The latter requires a very higher barrier (32.5 kcal/mol), thus making the diastereoselective product **3a_dr** (from intermediate **D_dr**) unfavorable at 40 °C. Once the intermediate **D** is produced, nickelacycle **E** can be obtained feasibly by means of transition state **TS3** ($\Delta G^{\ddagger}$ = 13.1 kcal/mol). After a final reductive elimination, product **3a** is successfully furnished through **TS4** ($\Delta G^{\ddagger}$ = 17.3 kcal/mol).

■ CONCLUSIONS

In summary, an unconventional 1,3-cyclotelomerization reaction of butadiene with α,β-unsaturated ketones has been successfully developed under nickel catalysis by using the IPr ligand. Employing the chiral NHC ligand **L10**, an asymmetric cyclotelomerization system was established, enabling the synthesis of chiral bicyclic products in good yields with excellent enantioselectivities. Mechanistic experiments and related DFT calculations showed that the reaction might proceed through an oxidative cyclometalation between two molecules of 1,3-diene and Ni(0) species first, followed by a [3 + 2]-cycloaddition between nickelacycle and dienophile. The synthetic utility of the bicyclic products was demonstrated through various transformations. This protocol introduces a new strategy for diversifying the telomerization of butadiene. Ongoing research in our laboratory focuses on further studying and applying the nickel-catalyzed asymmetric 1,3-cyclotelomerization reaction with chiral NHC ligands.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.5c06414.

Experimental procedures, characterization data, and NMR spectra (PDF)

Accession Codes

Deposition Numbers 2321630, 2321680, 2321685−2321686, 2321773−2321775, and 2321777−2321778 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Author Contributions

Q.-A.C. conceived and supervised the project. Q.-A.C., Y.L., and D.-W.J. designed the experiments. Y.L., D.-W.J., L.-M.Z., X.-T.L., H.L., and T.-T.S. performed the experiments and analyzed the data. All authors discussed the results and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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