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Nickel-catalyzed arylative telomerization of isoprene

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Developing new transformations of bulky chemicals is an important approach to expand the reaction boundary of current chemistry. Instead of traditional hydroarylation of dienes, we herein demonstrate a nickel-catalyzed arylative telomerization of isoprene with high chemo- and regioselectivities. By utilizing a bulky mono-phosphine ligand, a range of structurally diverse aryl substituted terpenes are created efficiently under redox-neutral conditions. Preliminary mechanistic studies suggest this telomerization proceeds through an oxidative cyclometallation of isoprene with Ni(0) species followed by arylation with organoboron reagents. Beyond enabling efficient isoprene transformation, this work also provides a supplementary approach for the monoterpenoids synthesis.

In the traditional functionalization of alkenes[1–3], one alkene could react with functionalized reagents to form the desired functionalization product (Fig. 1a). Sometimes, undesired coupling products from two functionalized reagents were also observed. Taking advantage of different properties of alkenes and functional reagents (R^1-X and R^2-Y), the selective formations of functionalization product of alkenes over undesired side product have been well developed in the presence of catalyst. In the contrast, a telomerization that functional reagents react with the two or more molecules of alkene could create more complicated molecules (Fig. 1a). However, due to the intrinsic chemoselectivity challenge, controllable telomerization for the formation of specific telomer has been less developed[4,5].

Hydroarylation of olefins[6–8], the installation of a hydrogen atom and an aryl group onto alkenes, offers a straightforward method to construct C(sp^2)-C(sp^3) bonds. In 2018, Zhou and co-workers reported the hydroarylation of alkenes under redox-neutral conditions[9,10], which enabled the generation of active catalyst species Ni-H by the reaction of methanol and Ni(0). After that, various nickel-catalyzed hydroarylations of alkenes or 1,3-dienes with arylboron reagents have been developed by Mei[11], Zhao[12], Zhu[13], Meek[14], Wang[15], and Engle et al.[16,17]. Wang[18] and Lundgren[19] et al. switched the commonly observed 4,3-hydroarylation of 1,3-dienes to 1,4-hydroarylation with thermodynamically less stable *Z*-stereoselectivity (Fig. 1b). However, these systems always provided hydroarylation products. Arylative telomerization of alkenes, especially unsymmetric 1,3-dienes, is highly appealing but is still in its infancy.

As an easily available bulk chemical, isoprene is an attractive precursor for the synthesis of terpenes and terpenoids[20–22]. Keim, Hidai, Beller, Finn, Réau, Navarro, and Carbó et al.[23–31]. developed acyclic telomerizations of isoprene with strong nucleophiles. Our group also presented geranylation of oxindole[32]. However, achieving non-nucleophilic telomerization poses a significant challenge. Recently, Leyva-Pérez et al.[33] reported Pd-catalyzed telomerization reaction of dienes with aryl boronic derivatives, giving aryl-substituted 1,6- and 1,7-dienes. Nevertheless, the method lacked control over regioselectivity, leading to the production of regioisomer mixtures. Compared with Pd[5,23–35], the utilization of Ni catalyst in diene telomerization is relatively uncommon, despite its cost-effectiveness[36–40]. In 1976, Klein et al. reported Ni-catalyzed telomerization of isoprene with methacrylic ester[36]. In 1988, Hoberg et al. developed a nickel(0)-catalyzed telomerization of butadiene and CO_2[38,39]. In 2022, our group presented Ni-catalyzed asymmetric heteroarylative cyclotelomerization of isoprene[40]. Encouraged by hydroarylation of 1,3-dienes and our biomimetic transformations of isoprene[41–46], we imagined developing an arylative telomerization of isoprene using arylboron reagents. To realize this proposal, we had to address the following challenges: First, the direct hydroarylation of isoprene with organoboron compounds is relatively easier than telomerization. Second, isoprene is an unsymmetric diene for regioselective functionalization, the telomerization

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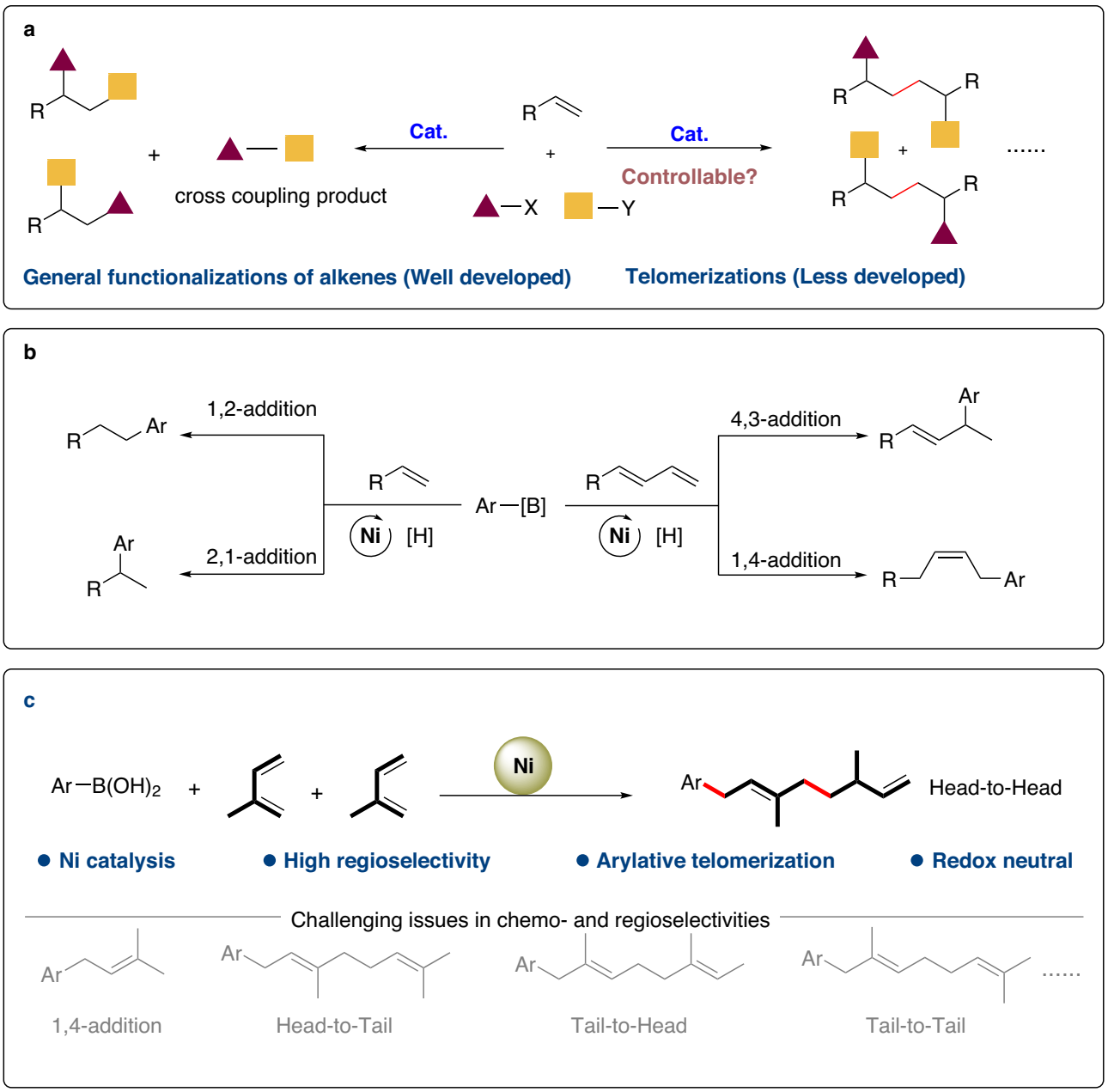

Fig. 1 | Transition-metal-catalyzed arylative telomerization of isoprene. a General functionalizations of alkenes and telomerization. **b** Ni-catalyzed arylation of alkenes and dienes with organoboron compounds. **c** This work: Ni(0)-catalyzed arylative telomerization of isoprene.

can theoretically generate up to >150 isomers[32]. Thus, the arylative telomerization of isoprene with high chemo- and regioselectivity is a daunting task.

By addressing those challenges, we herein show an efficient Ni-catalyzed arylative telomerization of isoprene (Fig. 1c). The protocol generates a series of linear monoterpene derivatives with up to 99% yield and >20:1 regioselectivities. It also provides an efficient strategy for expanding the chemical space of monoterpenoids by creating an unnatural structure.

Results

Reaction optimization

Initially, phenylboronic acid **1a** was chosen as model substrate for the investigation of arylative telomerization of isoprene **2a** (Table 1). Promising but low chemo- and regioselective hydroarylation (**3a** and **4a**) and arylative telomerization (**5a**–**8a**) of isoprene were observed with the use of $Ni(COD)_2$, PPh_3, DABCO, and ^{i}PrOH (entry 1). The subsequent evaluation on the substituent effect on PPh_3 suggested that bulkier and electron richer ligand facilitated the formation of arylative telomerization products **5a** and **6a** with high yields and decent regioselectivities (entries 2–5). The dimethoxy substituted mono-phosphine ligand **L5** gave the telomerization product **5a** in 85% yield and **6a** in 4% yield (entry 6). Then 2,6-$(OEt)_2$ and 2,6-$(O^{i}Pr)_2$ substituted triaryl phosphines **L6** and **L7** that were more steric hindrance and electron-richer than **L5** were designed and synthesized. To our delight, the head-to-head configuration product **5a** was obtained in 96% yield, accompanied by small amount of tail-to-head isomer **6a** using **L6** as the ligand (entry 7). When using **L7**, arylative telomerization of isoprene also be promoted with good yield but lower regioselectivity (entry 8). PCy_3 also gave **5a** in 80% yield, although the regioselectivity is slightly reduced (entry 9). The yield of **5a** was significantly decreased when using X-Phos (entry 10). Monophosphines bearing bulky alkyl groups in the ortho position of phenyl like **L8** and **L9**, gave no good results (entries 11–12).

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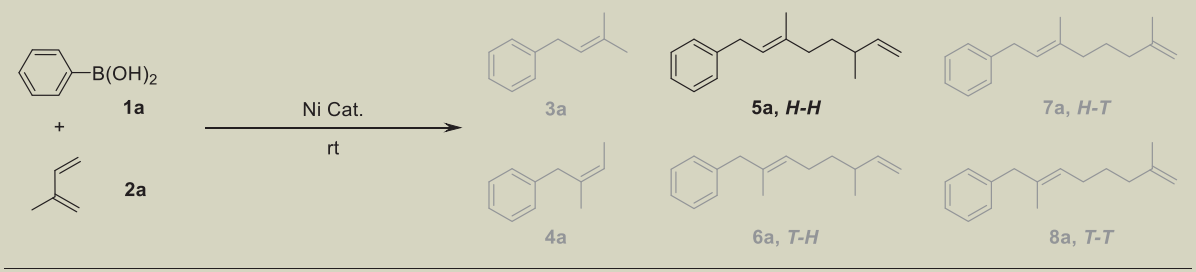
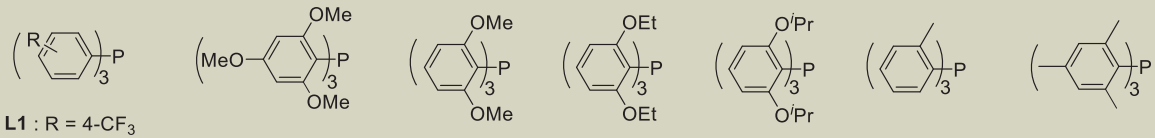
Table 1 | Optimization of reaction conditions[a]





Entry	Ligand	Solvent	3a (%)	4a (%)	5a (%)	6a (%)	7a + 8a (%)
1	PPh_3	1,4-Dioxane	7	1	13	16	18
2	**L1**	1,4-Dioxane	14	3	0	0	19
3	**L2**	1,4-Dioxane	7	1	16	14	12
4	**L3**	1,4-Dioxane	0	0	78	13	6
5	**L4**	1,4-Dioxane	0	0	90	7	1
6	**L5**	1,4-Dioxane	0	0	85	4	0
7	**L6**	1,4-Dioxane	0	0	96	4	0
8	**L7**	1,4-Dioxane	0	0	86	10	3
9	PCy_3	1,4-Dioxane	2	0	80	7	0
10	X-Phos	1,4-Dioxane	33	8	20	13	4
11	**L8**	1,4-Dioxane	7	2	8	10	4
12	**L9**	1,4-Dioxane	0	0	0	0	0
13[b]	**L6**	1,4-Dioxane	16	4	42	1	0
14[c]	**L6**	1,4-Dioxane	9	3	76	2	0
15	**L6**	THF	7	2	63	2	0
16	**L6**	^{i}PrOH	11	4	51	1	0
17	**L6**	MeOH	43	3	0	0	0

[a]Standard condition: **1a** (0.20 mmol), **2a** (0.80 mmol), $Ni(COD)_2$ (5 mol%), ligand (5 mol%), DABCO (0.5 equiv.), ^{i}PrOH (2.0 equiv.), 1,4-dioxane (1.0 mL), rt, 18 h. Yields and selectivities were determined by GC-FID analysis of crude mixtures with mesitylene as the internal standard.

[b]NEt_3 instead of DABCO.

[c]**2a** (0.40 mmol).

The promoting effect of other strong or hindered base like DBU, ^{t}BuONa, MeONa, NEt_3, and DIPEA is not as good as DABCO (entry 13 and Supplementary Table 3). When the amount of isoprene was reduced to 2 equiv., the telomerization product **5a** was generated with 76% yield and accompanied by a small amount of hydroarylation products **3a** and **4a** (entry 14). Ni(II) precursor was not suitable for this telomerization (Supplementary Table 1, entries 2–6). Increasing the reaction temperature or changing the concentration had adverse effects on the reaction (Supplementary Table 1, entries 9–12). Lower selectivities and yields on the formation of **5a** were observed when the solvent was changed from 1,4-dioxane to THF or ^{i}PrOH (entries 15–16 vs entry 7). No telomerization was observed when the solvent was changed to MeOH (entry 17). Using nonpolar solvent Toluene and ^{n}Hexane, the yield of **5a** significantly decreased and hydroarylation was observed (Supplementary Table 1, entries 13–14). Increasing the amount of ligand to 10 mol% led to the decrease of yield and regioselectivities (Supplementary Table 2, entries 1–8). When compared with Pd[33], the use of a Ni catalyst in the arylative telomerization of isoprene offers a more cost-effective and milder approach, featuring high chemo- and regioselectivities. Even though it requires five times the amount of Ni compared to Pd (with Pd being used at 1 mol%), when 2.5 mol% of $Ni(COD)_2$/**L6** were employed, the yield of **5a** could still reach 71% (Supplementary Table 1, entry 7).

Substrate scope

With the optimized conditions in hand, the generality of arylboronic acids was subsequently tested (Fig. 2). The phenylboronic acid **1a** was converted to the desired product **5a** in 97% isolated yield and >20:1 *rr*. The stereo configuration of product **5a** was determined as single *E*-type via two-dimensional nuclear magnetic resonance (NOESY) spectroscopy (Please see Supplementary Information, Page S42). Similarly, phenylboronic acids with different substituents (-Me, -^{t}Bu or -Ph) in the *para* position (**5b**–**5d**), could all be well adapted to the reaction process with high yields (92–99%) and good regioselectivities (18:1 to >20:1). It should be highlighted that *o*-methyl phenylboronic acid with large steric hindrance also worked smoothly under the standard conditions, giving the desired product **5e** in 83% yield. In addition, 3-Me substituted phenylboronic acid showed good performance on both reactivity and selectivity (**5f**). It was showed that the phenylboronic acids with -OMe group offered the products in high yields (**5g, 5i**), although the latter was accompanied by a small amount of ***T-H*** isomer. The arylboronic acid with naphthyl instead of phenyl also reacted smoothly in excellent yield (97%) under the current condition (**5h**). It was worth noting that -F, -Cl, and -Br group on the phenyl ring were all well tolerated to generate the corresponding telomerization products with 63–99% yields and high regioselectivities (**5j**–**5m**, 18:1 to >20:1). Electron-withdrawing groups (-Ac, $-CF_3$, $-SO_2Me$, and $-CO_2Me$) substituted phenylboronic acids were suitable substrates as well (**5n**–**5q**). The cyano group (**5r**) was also compatible with the process to provide the corresponding product in moderated yield (64%) and 7:1 *rr*, although that was accompanied by 1,4-addition product with 31% yield. It is speculated that the inability of 4-nitrophenylboronic acid to telomers may have been caused by its weak oxidizing properties.

Under optimized conditions, a variety of heteroaryl boron acids reacted efficiently. Furyl and benzofurylboronic acids were suitable substrates to generate the corresponding telomerization products with 29–67% yield and high regioselectivities (**5s, 5t**-**5u**, 17:1 to >20:1). Unfortunately, the 3-pridyl and 3-quinoline boronic acids were not suitable substrates (**5v**-**5w**). It may be due to the strong coordination of the nitrogen lead to the deactivation of the Ni catalyst. In light of this, we tried to use *N*-Boc-2-pyrrole- and *N*-Boc-2-indole-6-boronic acids as substrates (**5x, 5y**), the telomerization products were obtained with high yields (71-78%) and regioselectivities (18:1 to >20:1). Interestingly, the coupling of 4,4′-biphenyldiboronic acid (**1z**) with isoprene could incorporate two C10 blocks simultaneously to give product (**5z**) with 72% yield and 13:1 *rr*. To demonstrate the generality and potential utilization of this method in drug discovery, the telomerization of drug-like molecules was subsequently performed. The arylboronic acids from Naproxen and Estrone reacted with isoprene smoothly and gave the desired telomerized products in good yields (Fig. 2, **5aa** and **5ab**).

The substrate scope regarding terpenes was further explored with **1d** as model substrate (Fig. 3a). Monoterpenes, such as myrcene (**2b**), proceeded smoothly to deliver the telomer product **9b** with 98% yield and >20:1 *rr*. The derivatives of myrcene (**2c**–**2e**), substituted by -epoxy, -methoxy, and -acetoxy groups, could also be tolerated with 39–70% yields and good regioselectivities. Sesquiterpene *β*-farnesene **2f** reacted with 4-biphenylboronic acid **1d** smoothly, resulting in **9f** at 49% yield and 13:1 *rr*. Phytadiene (**2g**), derived from chlorophyll, was a suitable coupling partner and the expected product **9g** was formed with 75% yield and 10:1 *rr*. Not only isoprene-like dienes, but also butadiene was applicable in this protocol, giving the aryl-substituted 1,6-dienes (**9h**) with 95% yield. However, the 1,3-cyclohexadiene was found to be an unsuitable substrate. In addition to arylboronic acids, arylboroxines, arylboronic esters, and boranes could also be used as arylation reagent in this Ni-catalyzed arylative telomerization (Please see Supplementary Information for details, Supplementary Fig. 1).

The telomerization products of isoprene could be used as key building blocks in the synthesis of a series of terpenoids (Fig. 3b). Epoxidation of **5a** by *m*-CPBA occurred exclusively at the internal C = C bond and delivered epoxide **11a** in 98% yield (1:1 *dr*). A Wacker-type oxidation of **5a** under Pd/Cu catalysis took place at the terminal C = C bond and produced ketone **11b** in 61% yield. After hydroboration with 9-BBN, a further oxidation by $NaBO_3{\cdot}4H_2O$ could proceed smoothly to furnish alcohol **11c** in 65% yield. On the other hand, diaryl products **11d** and **11d′** could also be accessed from **5a** through Heck reaction with PhI in the presence of Pd catalysis (63% yield, 4:1 *rr*). Furthermore, with the help of Ni(0) and NHC (IPr) ligand, heteroaromatic rings such as *N*-methyl benzimidazole and benzofuran could also be introduced onto monoterpenoids **5a**, respectively (**11e, 11f**). Using prenyl borates as C5 block, a Pd-catalyzed Suzuki reaction underwent smoothly to deliver sesquiterpene derivative **11g** in 54% yield. Besides, diterpene compound **11h** could be obtained by a Pd-catalyzed Heck coupling reaction from **5l** with linalool.

Mechanistic investigations

Corresponding control experiments were carried out to shed light on mechanistic insight (Fig. 4a). No conversion was observed in the absence of $Ni(COD)_2$, indicating its indispensable role (entry 2). Only hydroarylation of isoprene was formed without **L6** (Fig. 4a, entry 3). This result supports that large hindered mono-phosphine ligand's ability to effectively promote the arylative telomerization of isoprene. Notably, desired telomerization product **5a** was generated in only 10% yield in the absence of DABCO. This result showed DABCO was an important additive to facilitate the reaction (Fig. 4a, entry 4). The yield of **5a** was decreased to 88% in the absence of isopropanol, indicating its slight promoting effect on the telomerization. When isopropanol was replaced by MeOH, EtOH, or H_2O, the yield of **5a** was reduced and hydroarylation products increased obviously (Supplementary Table 4).

In order to detect potential intermediates for this reaction, the linear dimerization of isoprene was examined. The dimer **12** or **13** from isoprene were not observed under standard condition without boronic acid according to ^{1}H NMR analysis (Please see Supplementary Information for details, Supplementary Fig. 7). Then, the mixture of dimer **12** and **13** (**12:13** = 7:1) was synthesized according to the reported method (Please see Supplementary Information for details, Supplementary Fig. 6)[47]. When the dimers (**12** and **13**) instead of **2a** was added into the reaction, it failed to generate the desired product (Fig. 4b).

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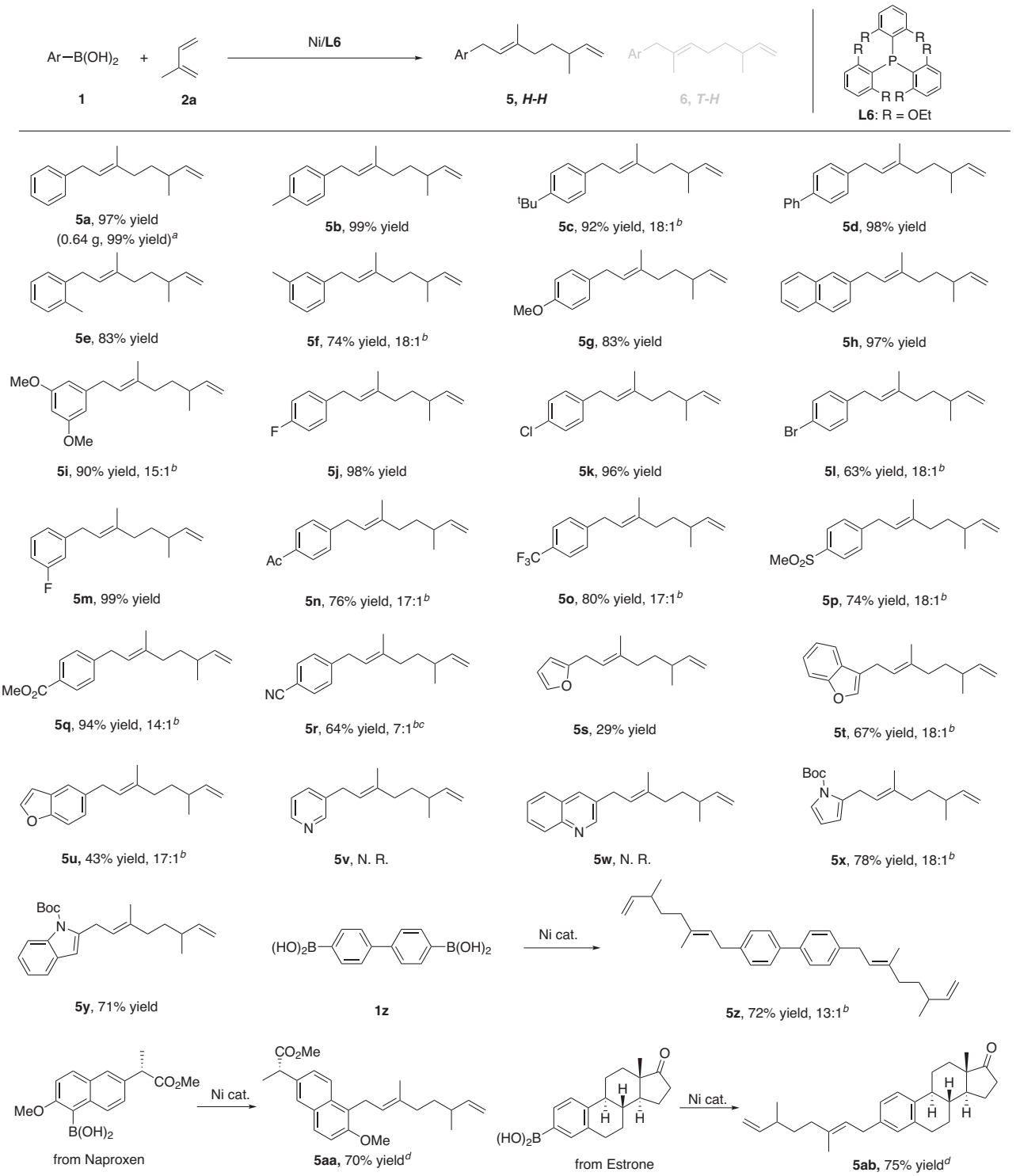

Fig. 2 | Substrate scope for arylboronic acid 1. Conditions: **1** (0.20 mmol), **2a** (0.80 mmol), $Ni(COD)_2$ (5 mol%), **L6** (5 mol%), DABCO (0.5 equiv.), ^{i}PrOH (2.0 equiv.), 1,4-dioxane (1.0 mL), rt, 18 h. Selectivities were determined by ^{1}H NMR analysis. [a]**1a** (3.0 mmol), **2a** (12 mmol). [b]Minor product is ***T-H*** product, combined yield of **5** and **6** was given. [c]Yield was determined by ^{1}H NMR analysis, combined yield of **5r** and **6r** was given. [d]**1** (0.10 mmol), **2a** (0.40 mmol).

These results indicate that no linear dimerization intermediates were formed in this arylative telomerization.

No Ni-H species was observed by ^{1}H NMR at 0 °C (Please see Supplementary Information, Supplementary Figs. 20 and 21). Using ^{i}PrOD(d_8) (2 eq.) instead of ^{i}PrOH, deuterium-labeled experiments showed that 56% of deuterium was observed on tertiary carbon of the obtained product ***5a-d*** (Fig. 4c). The result can be interpreted as a hydrogen-deuterium exchange occurring between the ^{i}PrOD and $PhB(OH)_2$. But when boroxin **1a'** and D_2O (2 eq.) were added instead of boronic acid and ^{i}PrOH into the reaction, the target product ***5a-d*** was yielded with 95% of deuterium on the tertiary carbon. These results suggest a protonation from H_2O which was generated by dehydration trimerization of phenylboronic acid was involved in this telomerization. When PhBneop **1x** and ^{i}PrOD(d_8) instead of boronic acid and

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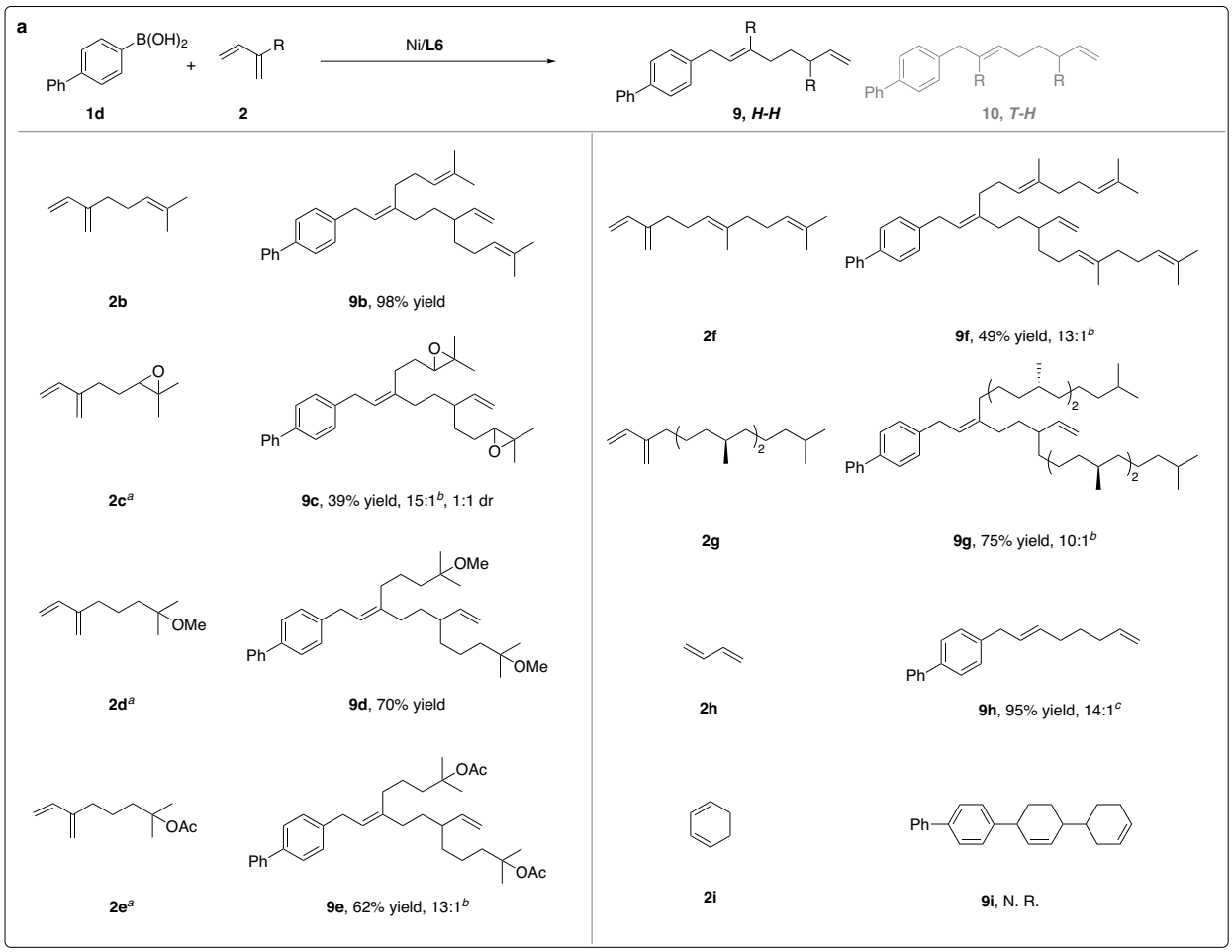

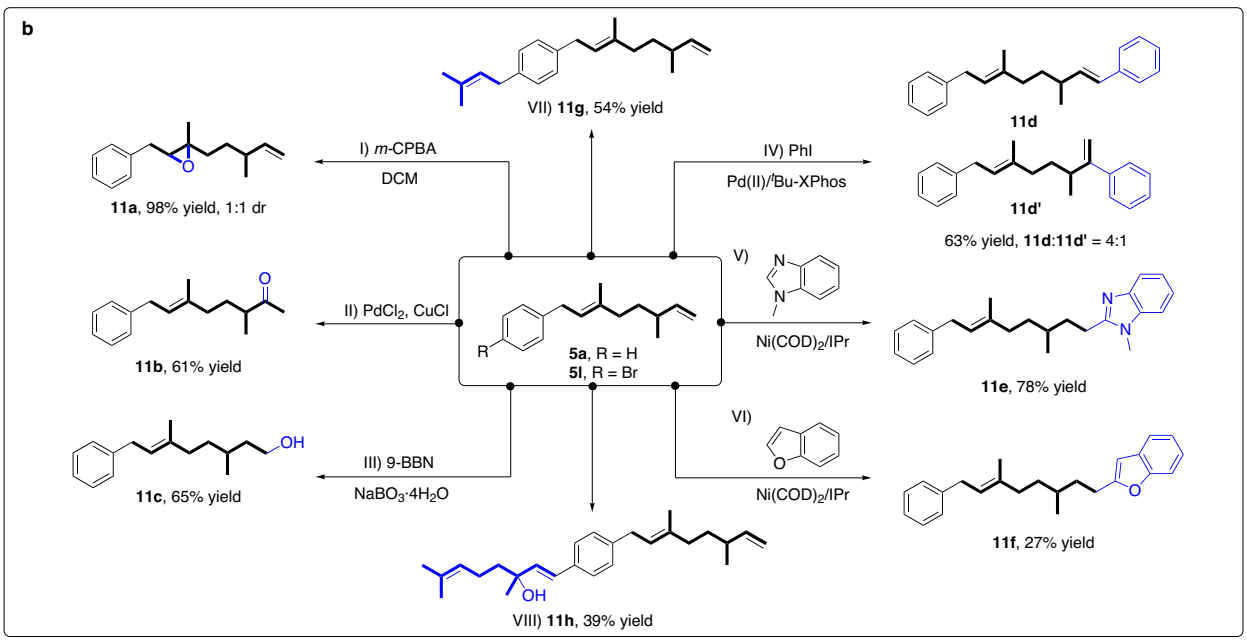

Fig. 3 | The scope of dienes and transformations of telomers. a The scope of dienes. **b** The transformations of telomers **5a** and **5l**. Conditions: **1d** (0.20 mmol), **2** (0.80 mmol), $Ni(COD)_2$ (5 mol%), **L6** (5 mol%), DABCO (0.5 equiv.), ^{i}PrOH (2.0 equiv.), 1,4-dioxane (1.0 mL), rt, 18 h. Regioselectivity and diastereoselectivity (dr) was determined by ^{1}H NMR analysis. [a]**2** (0.40 mmol). [b]Minor product is ***T-H*** product, combined yield of **9** and **10** was given. [c]Minor product is branched product, combined yield was given.

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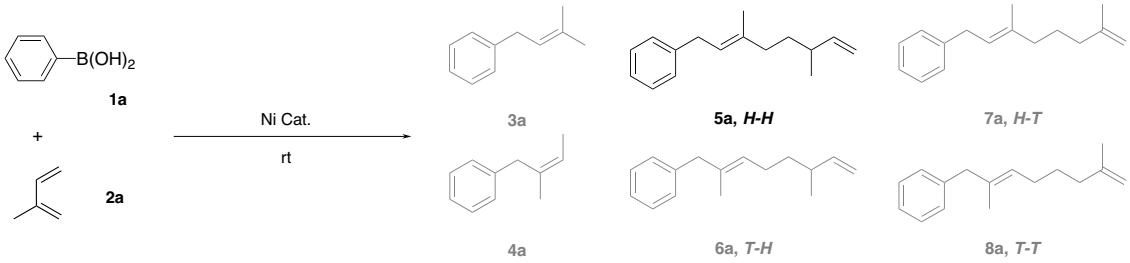
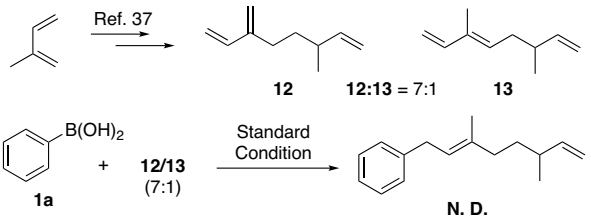
a



Entry	Deviation from standard conditions	**3a** (%)	**4a** (%)	**5a** (%)	**6a** (%)	**7a+8a** (%)
1	none	0	0	96	4	0
2	without $Ni(COD)_2$	0	0	0	0	0
3	without **L6**	44	14	0	0	0
4	without DABCO	5	1	10	0	0

Conditions: **1a** (0.20 mmol), **2a** (0.80 mmol), $Ni(COD)_2$ (5 mol%), **L6** (5 mol%), DABCO (0.5 equiv.), ^{i}PrOH (2.0 equiv.), 1,4-dioxane (1.0 mL). Yields and selectivities were determined by GC-FID analysis of crude mixture with mesitylene as the internal standard.

b



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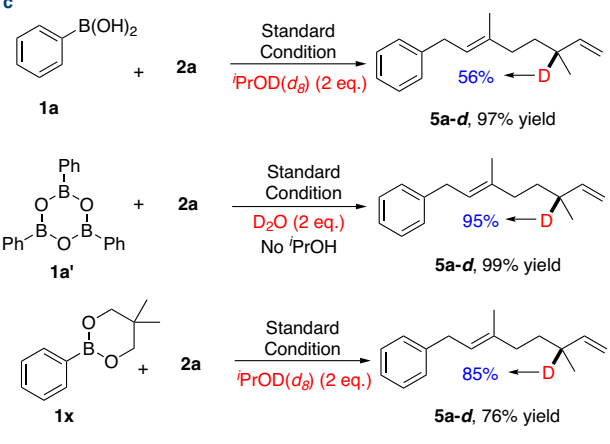

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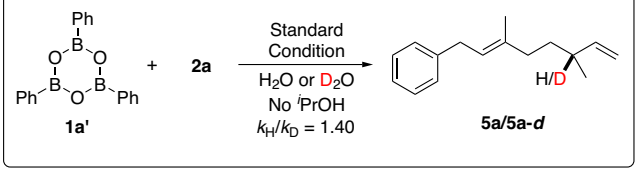

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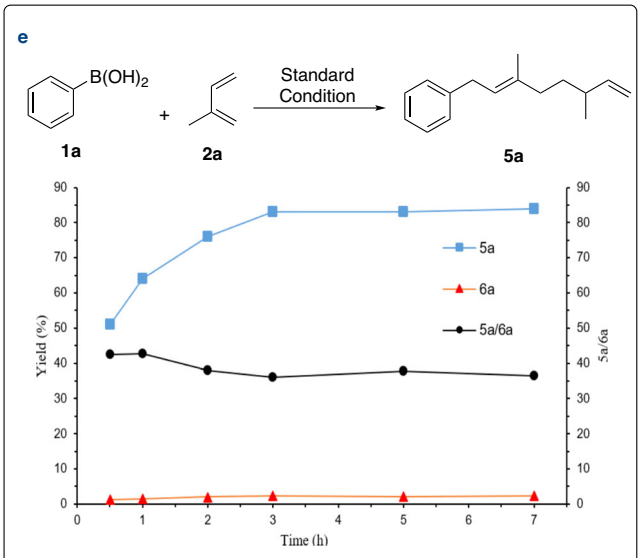

Fig. 4 | Mechanistic studies. a Control experiments. **b** Linear dimerization of isoprene. **c** Isotopic labelling studies. **d** Kinetic isotope effect (KIE) experiment. **e** Kinetic studies.

^{i}PrOH were added into the reaction, the target product **5a-*d*** was yielded with higher deuterium (85%) than $PhB(OH)_2$ **1a** because there is no active hydrogen atom in **1x**. The isotopic labelling study of PhBneop supports that protonation from ^{i}PrOH could be involved in this telomerization in the absence of water. Moreover, a kinetic isotope effect (KIE) experiment using H_2O and D_2O ($k_H/k_D = 1.40$) suggested that protonation was less likely to be the rate-determining step (Fig. 4d). Then, kinetic studies were further executed to reveal the reaction process (Fig. 4e). The yields of the stereoisomers **5a** and **6a** increased over time, but their corresponding ratio (**5a**/**6a**) remained constant during the reaction. These results demonstrate that no isomerization is engaged under the investigated conditions.

Next, we turned our attention to understanding the role of DABCO. The ^{11}B NMR studies of control experiments were performed to confirm the interaction between organoborons and DABCO. A significant upfield shift was observed in ^{11}B NMR due to the interaction of boronic acid **1a** and DABCO (Please see Supplementary Information for details, Supplementary Figs. 10 and 11). However, there is no two signals observed by the variable temperature experiments. It is probably attributed to the quickly tautomerism

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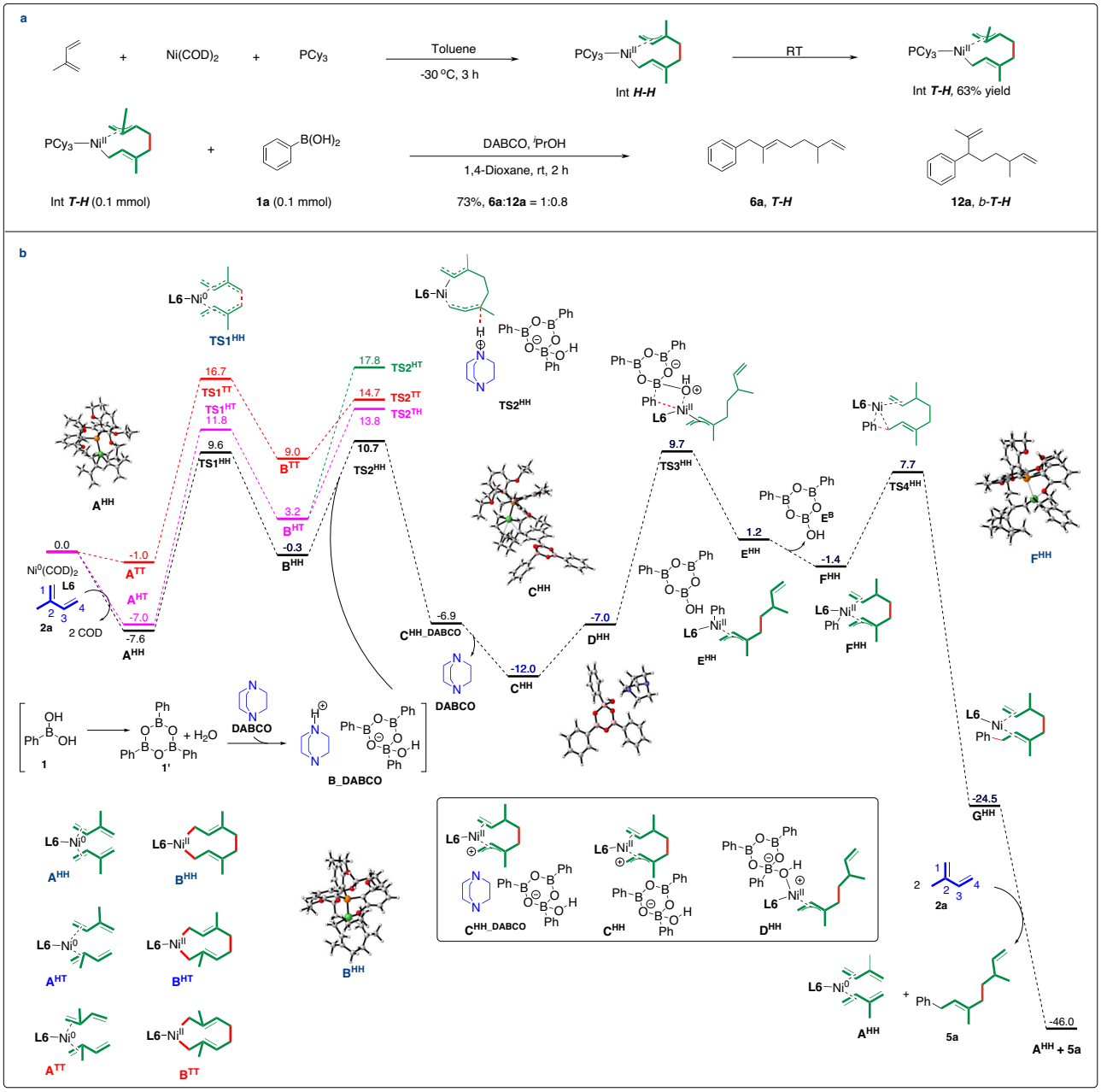

Fig. 5 | The capture of intermediate and reaction energy profiles. a The capture and transformation of Ni(II) species. **b** Reaction energy profiles for the arylative telomerization of isoprene.

equilibrium of the adduct **I**. When the temperature is below 0 °C, the adduct **I** precipitated due to solubility issues, thus no obvious signal was observed in ^{11}B NMR spectra (Please see Supplementary Information for details, Supplementary Fig. 12). No chemical shift was observed in the reaction of PhBpin with DABCO (Supplementary Fig. 13). Based on previous reports[31,32,48–50], a nickelacycle species was synthesized from Ni(COD)$_2$, PCy$_3$ and isoprene in Toluene. A quick rearrangement of Int ***H-H*** occurred to give Int ***T-H*** at room temperature. The stoichiometric transformation of Int ***T-H*** with **1a** gave the ***T-H*** telomers **6a** and **12a** with 73% yield (**6a:12a** = 1:0.8) (Fig. 5a). This result suggests Int ***H-H*** and ***T-H*** can be the intermediates for the telomerization of isoprene.

To further examine the validity of proposed mechanism, a density functional theory calculation of telomerization was performed (Fig. 5b, please see Supplementary Information and Supplementary Data 1 for details). Computational results showed that Ni^0 could coordinate with two molecules of isoprene **2a** in the presence of **L6**, generating three potential complexes (**A^{HH}**, **A^{HT}**, and **A^{TT}**) through different coordinations. The complexes **A^{HH}** and **A^{HT}** are more stable than **A^{TT}**, obviously. Through transition state **TS1^{HH}** ($\Delta G_1^{\ddagger}$ = 17.2 kcal mol^{-1}), the oxidative cyclometallation occurs to generate thermodynamically more stable nickelacycle **B^{HH}**. In contrast, kinetically unfavorable cyclometallation of **A^{HT}** and **A^{TT}** need to overcome higher free energy barriers, 18.8 kcal mol^{-1} (via **TS1^{HT}**) and 17.7 kcal mol^{-1} (via **TS1^{TT}**), respectively. Meanwhile, the adduct **I**, resulting from DABCO and PhB(OH)$_2$, can act as a proton source. Protonation of the intermediate **B^{HH}** with the adduct **I** gives the cationic Ni(II) intermediate **C^{HH_DABCO}**. The release of DABCO from **C^{HH_DABCO}** generates complex **C^{HH}**. A subsequent transmetalation of **C^{HH}** occurs to deliver Ar-Ni(II) species **E^{HH}**, which is proposed as rate limiting step ($\Delta\Delta G^{\ddagger}$ = 21.7 kcal/mol). Then, a recoordination of C = C generates stable 18e intermediate **F^{HH}**. Finally, a reductive elimination of **F^{HH}** delivers the intermediate **G^{HH}**, which is

subsequently displaced by **2a** to release product **5a** and regenerate the catalytically active $\mathbf{A}^{\mathbf{HH}}$ species.

Discussion

In conclusion, a practical strategy has been developed for arylative telomerization of isoprene with organoboron compounds under Ni catalysis. The using of bulky mono-phosphine ligand not only promotes the nickel catalysis arylative telomerization of isoprene but also tackles the challenge of simultaneous control of the chemo- and regioselectivities in this protocol. Various structurally diverse 1,3-dienes and organoboron compounds were well tolerated to support further derivatizations and potential application. Meanwhile, preliminary mechanistic studies support the proposed catalytic pathways. Moreover, this protocol provides a practical strategy for the creation of unnatural aryl-substituted monoterpenoids. It is anticipated that this protocol will arouse widespread interest among researchers in terpene transformations and serve as an efficient method for terpenoid synthesis.

Methods

General procedures for arylative telomerization of isoprene

In glove box, a sealed tube was charged with **1** (0.20 mmol), **2** (0.80 mmol), $Ni(COD)_2$ (2.8 mg, 5 mol%), **L6** (5.3 mg, 5 mol%), DABCO (11.2 mg, 0.5 equiv.), ^{i}PrOH (31 µL, 2.0 equiv.), and anhydrous 1,4-dioxane (1.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at room temperature for 18 h. Upon completion, the mixture was filtered through a short pad of celite, concentrated in vacuo, and purified by silica chromatography to afford the products.

Data availability

The authors declare that the data supporting the findings of this study, including experimental details and compound characterization, are available within the article and its Supplementary Information files. All data are also available from the corresponding author upon request.

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Author contributions

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

Competing interests

The authors declare no competing interests.

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