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Design, Synthesis, and Structural Analysis of Binaphthyl-Based Chiral Benzindenes

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Correspondence: Nikola Topolovčan (ntopolov@irb.hr)**Received:** 4 December 2025 | **Revised:** 7 April 2026 | **Accepted:** 16 April 2026**Keywords:** axial chirality | benzindene | binaphthyl unit | embedded chirality | ring closing metathesis

ABSTRACT

Chiral benzindenes are an unexplored structural motif in the realm of organic synthesis. This is a result of a lack of synthetic protocols for constructing these compounds in which chirality does not arise from additional chiral substituents. This work introduces an unprecedented route toward chiral benzindenes as a new potential structural motif for further exploratory studies. Starting from readily available (*R*)-BINOL, the convergent synthesis over 9 steps culminated in benzindene with embedded chirality into the binaphthyl framework. The synthetic challenges associated with structural decoration are addressed and evaluated, while DFT and NMR structural analysis of the prepared chiral benzindene revealed its molecular characteristics.

1 | Introduction

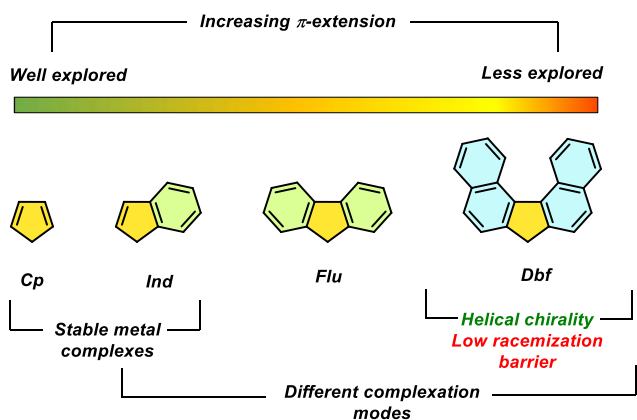
The significance of the cyclopentadiene structural motif in organic chemistry and synthesis has inspired exploratory studies of its derivatives that feature extended and conjugated π -systems. Extending one side of cyclopentadiene with a benzene ring results in indenenes and benzindenes, whereas symmetrical two-sided extension gives fluorenes and dibenzofluorenes (Figure 1a). Attachment of more benzene rings to the latter constructs helical structures based on the cyclopentaphenanthrene. The omnipresence of these structures, especially in metal-catalyzed and mediated transformations, is rooted in their ability to stabilize the respective organometallic complex, to transfer chirality in the case of chiral complexes, and to allow shorter routes toward complex molecules, with the C-H functionalizations being a notable application. The current corpus of work provides clear evidence for the importance of these structures and their impact on the production of both chiral and achiral molecules. The synergistic relationship between the metal's properties, its oxidation state, and the associated ligand, all combined in one catalyst, reflects on its efficiency in inducing a desired event. While the choice of the metal is determined by the mechanistic nature of the specific transformation, selecting the

appropriate ligand is much more complicated, as distinct ligands can lead to different reaction outcomes, which is highly important, especially in stereoselective transformations. Thus, engineering the original class of ligands is a prerequisite for the discovery of new reactivity that could raise unexplored possibilities in modern organic synthesis. Chiral cyclopentadienes, where chirality stems from the chiral backbone, are, by no doubt, one of the most explored ligands that revived, shaped, and revolutionized the field of transition-metal catalysis over the last several decades [1, 2]. One of the most explored chiral frameworks in Cp-metal complexes is binaphthyl (Figure 1b) [3], while other chiral units, such as spiroindane [4, 5], have also been successfully applied in stereoselective transformations. On the other hand, indenyl ligands, as their benzannulated analogs, are getting more attention, especially because of the simple synthetic routes allowing their fast deployment across a range of diverse reactions [6–16]. Indenyl ligands display unique properties, including the indenyl effect, which influences both the kinetics and stability of the relevant catalysts [17, 18]. The chirality of these ligands originates from the chiral substituent attached to the indenyl core, or, as recently exemplified, the indenyl group could be embedded into the helical framework [15]. For these reasons, undoubtedly, in the near future, we will witness an

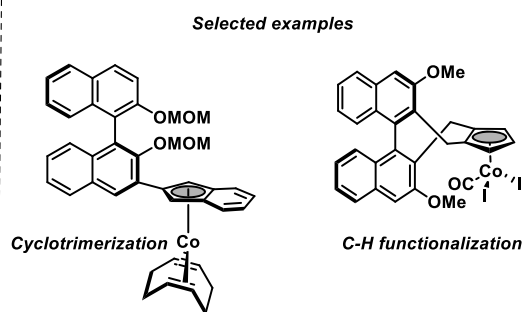
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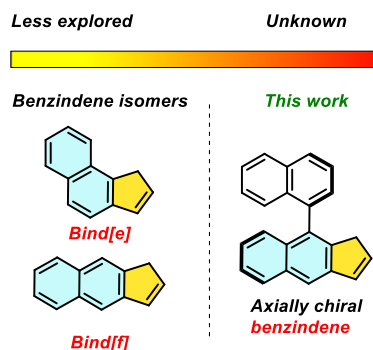
(a) Cyclopentadiene and its benzannulated derivatives



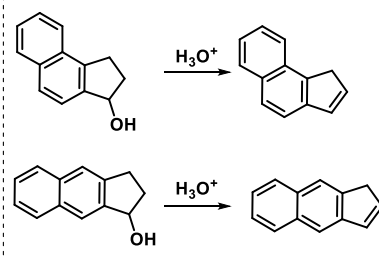
(b) Binaphthyl-based chiral catalysts



(c) Different types of benzindenes



(d) Typical synthetic route to benzindenes



(e) Our work

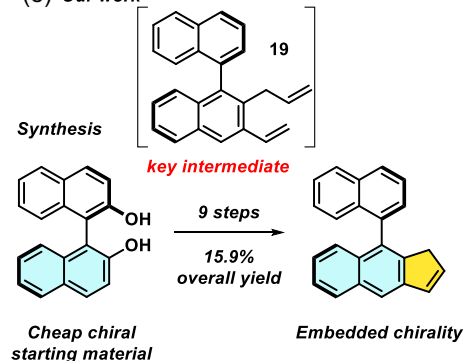


FIGURE 1 | a) Known and less explored cyclopentadiene-based ligands for transition metal complexation, b) common chiral backbone, c) two types of benzindenes, d) common synthetic route to benzindenes, e) our approach to axially chiral benzindene.

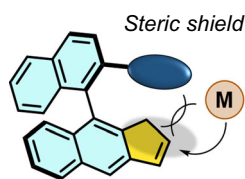
extensive application of these ligands in diverse transformations, as demonstrated by the forward momentum these ligands have gained. Moving to the higher homologs, two-sided π -extension of the Cp unit provides quite rare fluorenyl ligands, or their hydrogenated derivatives, where only a few incorporate a chiral element [8, 19]. A promising type of benzannulated ligand is the dibenzofluorenyl structure, which is the smallest fused aromatic capable of adopting helical chirality. In the 2000's there were attempts to prepare the Dbf-based chiral metal complexes, but the low racemization barrier of the deprotonated ligand prevents their employment as chiral ligands [20, 21]. All of the mentioned ligand structures are either widely present in contemporary organic synthesis or have a potential for future applications, but, despite the current state-of-the-art, it is compulsory to constantly refill the existing pool of potential chiral ligands with either structurally modified versions of the known ligands or with one having a completely new structural motif. While fine-tuning known ligands and understanding the effect of structural changes on mechanistic and kinetic behavior is extremely important in designing more efficient catalysts, the introduction of a unique class of ligands paves the way for new catalytic transformations.

For that reason, and guided by perspectives on future trends in homogeneous transition-metal catalysis, we provide insight into the design and synthesis of binaphthyl-based axially chiral benzindenes (BIND) as a new class of potential ligands, so far unexplored in organic synthesis (Figure 1e). There are two isomers of

benzindene with respect to the position of fused rings—angular named benz[e]indene and linear named benz[f]indene, where both structures have unique properties and distinct applications in organic synthesis (Figure 1c). Syntheses of each of the isomers are scattered, and examples include photolysis of substituted diazocyclopentadienes [22], [4 + 2] cycloreversion [23], Diels–Alder reaction between isobenzofuran and cyclopentadiene [24], and Pd-catalyzed [3 + 2] annulation between alkynes and alkylidene-cyclopropanes [25], as more unique synthetic strategies while more general approaches include acid-mediated dehydration of naphthalene-fused cyclopentanols (Figure 1d) [26–28]. The main drive for our interest in this type of structural motif is its scarcity in chemical literature, with only a handful of known examples of benzindenes being employed as ligands in transition metal complexation. These include complexation of benzindenes to rhodium [29], zirconium [30], ruthenium [31], and molybdenum [32]. Furthermore, to the best of our knowledge, chiral versions of these ligands have not been previously described, thus giving us an unprecedented opportunity to explore the rational design and synthetic challenges in constructing these molecules. One issue is the absence of C_2 -symmetry, where, because of the two diastereotopic faces, the trajectory for the metal to attach to the benzindenyl ligand could, in principle, originate from either side of the ligand. This scenario would result in a mixture of two distinct metal complexes that would likely be challenging to separate. To avoid this complication, it would be necessary to obstruct one side of the ligand by adding a steric barrier (Figure 2).

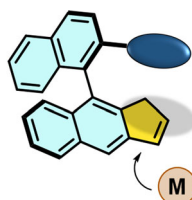
Selective complexation induced by the C2-substitution

Top-side approach



Less favorable trajectory

Bottom-side approach



More favorable trajectory

FIGURE 2 | Representation of the C2-positioned steric shield.

2 | Results and Discussion

In light of the allowable modifications at the C2-position and known benzindenyl-type complexes, we opted to add a methyl group to block one diastereotopic side in the potential formation of BIND-Mn complexes. To gain a clearer understanding of the geometry associated with the steric shield in substituted Mn-complexes, DFT calculations were carried out, and relative Gibbs free energies were compared (Figure 3). In the case of methylated **BIND-Mn-1a** and **BIND-Mn-1a'** complexes, there is a slight preference for the bottom-side approach of the metal, while the opposite situation is in the case of C2-H complexes, where the top-side approach should be less sterically obstructed (**BIND-Mn-1a/BIND-Mn-1a'**, $\Delta G = 0.72 \text{ kcal mol}^{-1}$). Despite a rather small energy difference between each diastereoisomer

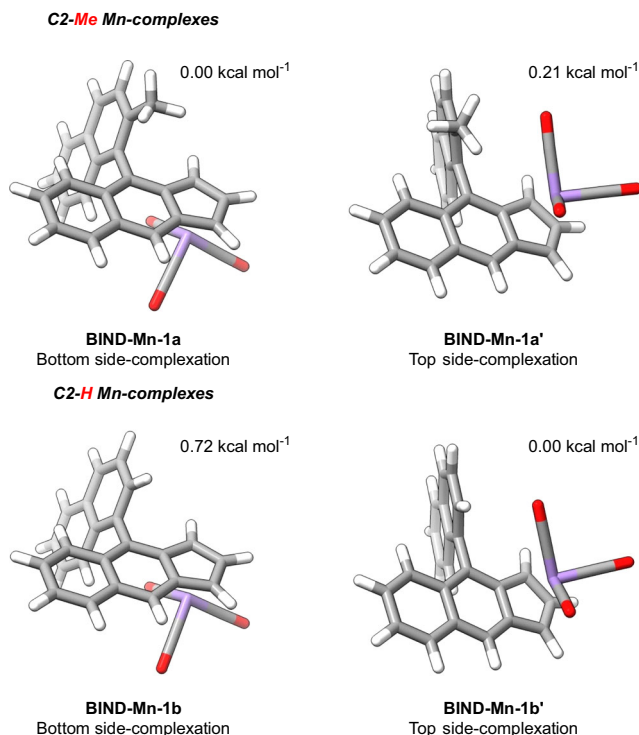


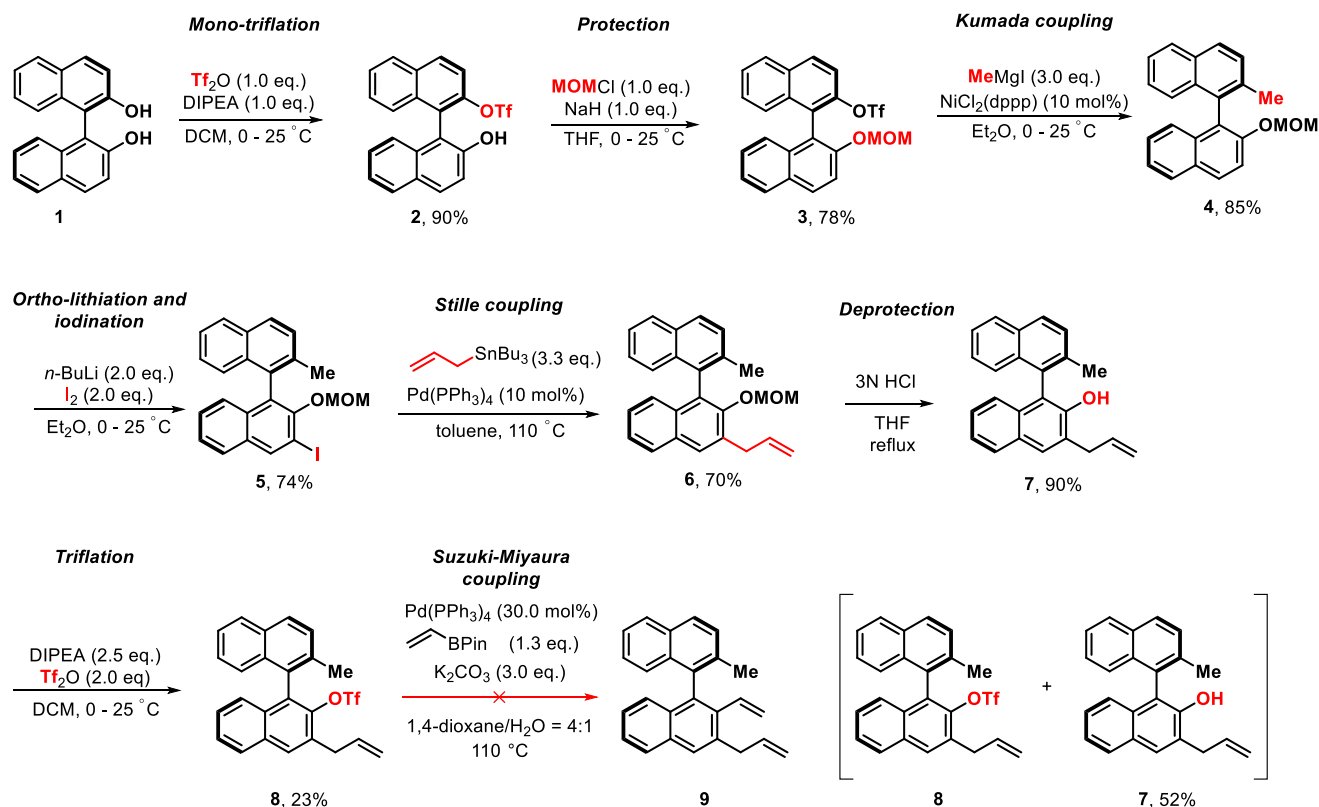
FIGURE 3 | Optimized structures of Mn-complexes and relative Gibbs energies (in kcal mol^{-1}) compared to the more stable isomer. B3LYP-D3/def2-TZVPD level of theory.

pair, we set out to explore the synthetic route to non-substituted and C2-methylated benzindenes.

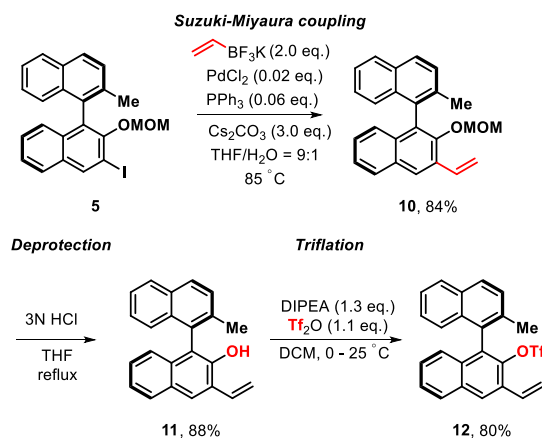
Dissecting the envisioned target molecule into its synthetic components resulted in a blueprint where the target molecule could be reached in nine convergent steps. Along the proposed synthetic pathway, we identified allyl/vinyl benzene **19** (shown in Figure 1e) as a key intermediate that, upon ring-closing metathesis (RCM), would yield the benzindene motif. An inspiration for this approach arose from the established protocol for converting phenols into functionalized indenenes [33]. As the envisioned benzindene incorporates an axially chiral binaphthyl backbone, an obvious starting point was readily available, enantiomerically pure (*R*)-BINOL, which possesses the necessary phenolic motif. Arguably, synthetic strategies for constructing a separately benz[*f*]indene component that would be later coupled with the naphthyl component could be more straightforward. Still, the requirement for chiral separation would ultimately result in losing half of the product, making this approach less desirable.

The synthetic effort began with the monotriflation of commercially available (*R*)-BINOL (Scheme 1). Protection of just one hydroxyl group in **2** as a triflate ester allowed the selective transformation of each hydroxyl group of the starting material. The remaining hydroxyl group was converted into the MOM-ether **3**, while through Kumada coupling, the methyl group as a steric shield was installed at the C2-position of the naphthyl ring in **4**. The directed ortho metalation, enabled by the MOM-protecting group, followed by an iodine quench, yielded the aryl iodide **5** in a 74% isolated yield. It has to be noted that the same transformation with methoxy ether was not so effective and never gave the targeted coupling partner in more than 40% isolated yield. With intermediate **5** in our hands, we envisioned first the installation of the allyl moiety at the C3-position, followed by the deprotection of the MOM group to get the free hydroxy group. Next, its conversion to the triflate again would set the stage for the installation of the vinyl group to form the intermediate for the ring-closing metathesis.

As planned, the allylation of the aryl iodide **5** under Stille coupling conditions gave the intermediate **6** in 70% isolated yield, which was uneventfully deprotected to release the free hydroxyl group in **7** for the subsequent triflation. The triflation itself afforded the intermediate **8** in rather modest yield of 23%, already suggesting a possible steric issue imposed by the methyl group at the C2-position. Indeed, the attempted vinylation did not result in the expected product **9**, but only the starting material was isolated together with the hydrolytic product **7**. As Suzuki–Miyaura coupling conditions usually require water, this led to the hydrolysis of the triflate ester rather than coupling with vinyl borate. All our attempts to circumvent this issue were not successful (for all the details, please see Supporting Information), so we had to adopt another strategy (Scheme 2). Thus, we planned to switch the order of the coupling procedures: first install the vinyl group at the C3-position, then perform the water-free Stille coupling to install the allyl group at the C2-position. In this way, the Suzuki–Miyaura coupling could be performed on the MOM-protected hydroxyl group that should remain intact under these coupling conditions, thus leaving the opportunity to install the allyl group in the later stage. Thus, vinylation of the aryl iodide **5** under Suzuki–Miyaura coupling conditions gave the C3-vinylated product **10** in 84% isolated yield. Removal of the MOM group in **11** again proceeded without any issues, and its subsequent triflation



SCHEME 1 | First approach—Synthetic pathway based on the allylation/vinylation strategy.



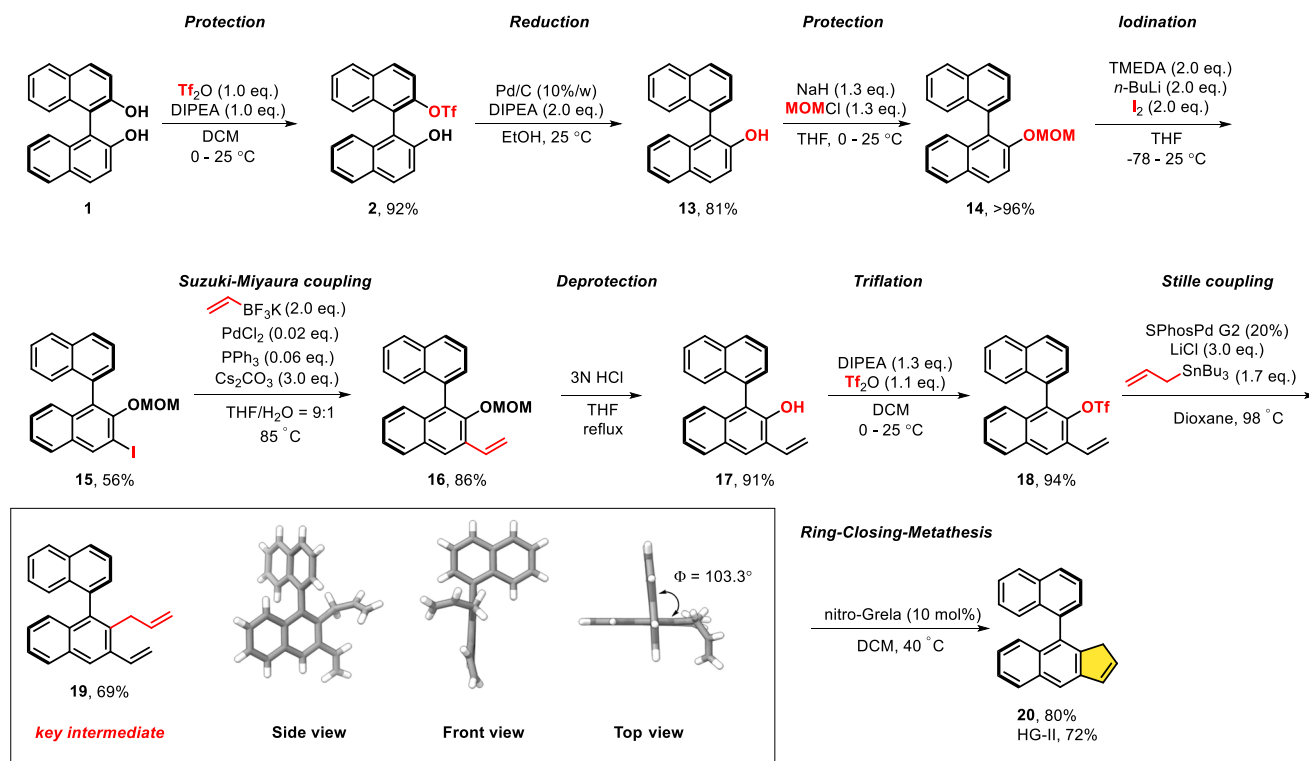
SCHEME 2 | Second approach—Synthetic pathway based on the vinylation/allylation strategy.

this time gave the triflate coupling partner **12** in 80% isolated yield. But, again, all our attempts (for more details, please see Supporting Information) to install the allyl group were not fruitful. It seems that the steric crowding imposed by the C2-positioned methyl group prevents the activation of the triflate ester, as only the starting material was isolated back in all cases.

Since the formation of benzindenyl ligands possessing a steric shield remains a synthetic challenge, we switched to the synthesis of the unsheltered variation (Scheme 3). To achieve this, we had to modify the synthetic plan by eliminating one of the hydroxyl groups from the (*R*)-BINOL at the outset of the synthetic pathway. Thus, we started with the monotriflation of one of the hydroxyl groups that gave the product **2** in 90% isolated

yield. Palladium-catalyzed reduction resulted in the clean removal of one of the hydroxyl groups in **13**, which, in the end, would remove any steric hindrance imposed by the substituent at the C2-position. The next two steps: protection of the remaining hydroxyl group as a MOM-ether in **14**, followed by the DoM/iodination, gave the aryl iodide **15**. From here, we had two options to continue with the assembly of the RCM precursor: i) vinylation/allylation or ii) allylation/vinylation strategy. Based on the previous results, and the efficiency of each step, we decided to first install the vinyl group using Suzuki-Miyaura coupling conditions that afforded the vinylated product **16** in high 86% isolated yield. Removal of the MOM-protection in **17** and the activation of the hydroxyl group as a triflate gave the intermediate **18** in 94% isolated yield. With this intermediate in hand, the endgame of the synthesis involved installation of the allyl group at the C2-position with concomitant RCM. The Stille cross-coupling conditions using the SPhos Pd G2 precatalyst and allylstannane gave the desired product **19** in 69% isolated yield. Its structure was unambiguously confirmed by single-crystal X-ray analysis [34] showing that the configurational integrity remained preserved during the synthesis, and no racemization event occurred even in reactions requiring elevated temperatures. Finally, the formation of the benzindenyl portion of the targeted structure was achieved through the RCM using nitro-Grela catalyst, giving the product **20** in 80% isolated yield. Besides the nitro-modified Ru carbene, the Hoveyda-Grubbs 2nd generation catalyst also smoothly catalyzed the RCM process to give the final product with comparable efficiency.

Although benzindene **20** was isolated as a solid material, we were unsuccessful in obtaining suitable crystals for X-ray analysis. Nonetheless, 2D NMR analysis together with the optimized



SCHEME 3 | Third approach—Synthetic pathway leading to the benzindene **20**.

molecular structure unambiguously confirmed its structural features (Figure 4). The NOESY NMR analysis showed a contact signal between one of the benzyl hydrogen atoms (H-25) and the hydrogen atom (H-2) at the naphthyl unit. This signal reveals that there is no double bond racemization occurring during the RCM or during subsequent column chromatography purification.

With chiral benzindene **20** in hand, we attempted the synthesis of its Mn-complexes to evaluate the initial hypothesis of two-folded complexation depending on the trajectory of the incoming metal.

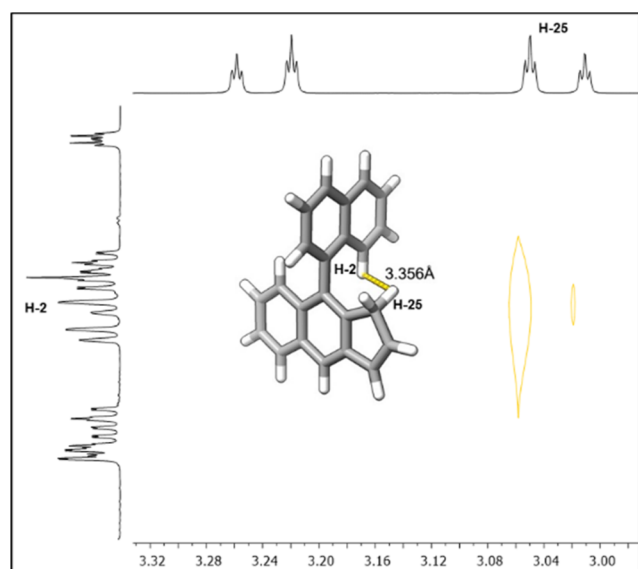


FIGURE 4 | Part of the NOESY spectrum of **20** and the optimized structure. B3LYP-D3/def2-TZVPD level of theory.

Previous literature protocols for the complexation of benzindenes required *n*-BuLi for deprotonation, followed by reaction with an appropriate metal reagent. In our hands, these protocols and others, employing a stronger base (*sec*-BuLi and *t*-BuLi) did not give the desired Mn-complexes. In all cases, for unknown reasons, we obtained complex reaction mixtures from which we could not isolate or even observe the formation of the desired product. In addition, attempts to form other metal complexes were unfortunately unfruitful as well (for more details, please see Supporting Information). The inability to form the envisioned metal complex suggests either high steric hindrance imposed by the naphthyl moiety, where the complexation does not occur, or haptotropic rearrangement, followed by decomplexation takes place. In general, the benz[*f*]indenyl complexes are less stable than their angular analogs, as it was exemplified in the synthesis of linear and angular titanium-complexes [35].

3 | Conclusion

Despite this stumbling block, in summary, the synthesis of an unprecedented chiral benzindenyl framework was achieved in 9 steps with 15.9% overall yield starting from cheap (*R*)-BINOL. The key step involves an RCM of a vinyl/allyl precursor, for which X-ray analysis confirmed the retained *R*-configuration throughout the synthetic sequence. The challenges in constructing C2-substituted analogs were addressed together with issues regarding the formation of the manganese complex of the prepared chiral benzindene. Considering that the stability of the chiral benzindenyl complexes could depend on the nature of a metal, currently, we are exploring other possibilities to prepare stable complexes that would enable more thorough structural analysis.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.