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Cite this: *Org. Chem. Front.*, 2025, **12**, 808

Catalytic haloallylation/Zr-mediated dienyne cyclization/isomerization sequence for tailored cyclopentadiene substitution†

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Received 28th October 2024,
Accepted 22nd November 2024

DOI: 10.1039/d4qo02020k

rsc.li/frontiers-organic

The chemical properties and reactivity of cyclopentadienes (Cp) originate from the number and nature of attached functionalities. Even a slight change in their molecular architecture dramatically affects their application in organic synthesis and the performance of the respective Cp complexes in catalytic transformations. Thus, the current demand for multisubstituted cyclopentadienes requires a strategic design, allowing substituents to be installed around the Cp ring to fine-tune its reactivity profile. Herein, we present a five-step synthetic sequence that allows site-selective positioning of diverse functional groups that are otherwise difficult to attach with current methods. A judicious choice of stereoelectronically defined internal alkynes enabled regioselective bromoallylation, resulting in 1-bromo-1,4-dienes bearing three functionalities that will be part of the target Cp. Continued substitution-enrichment through the Sonogashira coupling firstly gave ornamented dienynes that upon Zr-mediated cyclization afforded a series of cyclopentenes. Finally, an acid-catalyzed *exo*-to-*endo* double bond isomerization concluded the controlled allocation of functionalities and gave a series of tetrasubstituted cyclopentadienes. Additionally, the transformability of the organozirconium intermediate enables the synthesis of bicyclic cyclopentadienes.

Introduction

The discovery of ferrocene in 1951[1] triggered the accelerated evolution of research on related metallocenes and half-sandwich complexes that resulted in the identification of a synergistic relationship between the stereoelectronic nature of a Cp complex and the number of substituents on the pentacyclic ligand.[2] This culminated in the build-up of fundamental knowledge and expansion of the corpus of work on the chemistry of cyclopentadienes as ligands and as synthons in organic synthesis.[3] The more profound understanding of how substitution affects the reactivity or stability of cyclopentadienes has fuelled the design and development of synthetic methods allowing their customized molecular decoration.[4] Increased stability of pentamethyl cyclopentadiene (Cp*) compared to the unsubstituted parent cyclopentadiene is a nice illustration of how the installation of functionalities around the Cp ring can adjust its chemical properties.[5] A well-defined geometry of the chiral pocket can also be fine-tuned with additional substituents on the Cp ring, resulting in enhanced performance of respective chiral catalysts.[6] Since the synthetic repertoire leading to multifunctionalized cyclopentadienes is limited and new findings emerge daily, the progress of organometallic chemistry depends on the availability of a reliable synthetic tool that would allow controllable positioning of functional groups around the cyclopentadiene scaffold. In turn, this could unlock the dormant potential of diversely decorated multisubstituted cyclopentadienes as synthons in organic synthesis and as ligands in coordination chemistry. The two most challenging aspects in synthesizing multifunctional cyclopentadienes are control of the site-selective substitution and installation of chemically disparate functionalities, especially aryl and heteroaryl groups. For example, sequential bisalkylation of cyclopentadienide gives a regioisomeric mixture of 1,2- and 1,3-disubstituted cyclopentadienes or multisubstituted derivatives as a result of overalkylation.[7] Another example of the inability to control the site-selective substitution is the arylation of cyclopentadienide with perfluorotoluene, resulting in regioisomeric mixtures.[8] Alternative pathways to synthesize multiarylated cyclopentadienes have been developed, but the limited scope remains an issue.[9] In addition, the recently introduced Co-catalyzed C–C bond activation of cyclopropenes leads to tetrasubstituted cyclopentadienes bearing all four different substituents but again, only in a small number of

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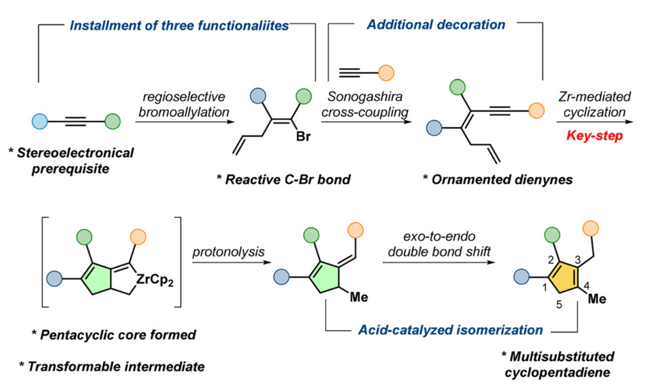
†Electronic supplementary information (ESI) available: Experimental details, compound characterization data, NMR spectra and computational details. See DOI: **https://doi.org/10.1039/d4qo02020k**

examples.[10] To tackle this problem, we designed a five-step protocol that allows controllable decoration of the Cp ring based on cyclization of pre-assembled dienyne to avoid positional regioisomer formation (Scheme 1). In our approach, site-selectivity was achieved by two distinct transformations at different stages of the synthetic sequence. In the first step, through regioselective *syn*-bromoallylation of electronically uneven internal alkynes, it is possible to control the positional installation of different functionalities representing a 1,2,4-substitution pattern in the targeted cyclopentadiene. The added value of this transformation is the formation of a reactive carbon–halogen bond used in the Sonogashira coupling for the introduction of additional substituents. In the key step, cyclization of decorated dienyne by Negishi's reagent, a pentacyclic core of cyclopentadiene is formed within the bicyclic zirconacyclopentene intermediate. Its protonolysis affords cyclopentene with an *exo*-cyclic double bond that under acidic conditions easily transforms into an *endo*-cyclic double bond, thus affording the targeted cyclopentadiene. The transformable nature of the zirconacycle also allows its *in situ* conversion to more complex structures. Considering the number of options that this protocol offers, it could easily serve as a blueprint for the customized synthesis of the targeted cyclopentadienes for diverse applications in organic synthesis and organometallic catalysis.

The bottom-line strength of the proposed methodology is the full control over the positioning of each substituent during the synthetic sequence. Since the location of three substituents of the final molecule is already defined in the first step, it is crucial to control the regioselective outcome of the bromoallylation process. Distinct stereoelectronic properties of specifically designed internal alkynes are used to dictate the positioning of 1,2,4-substituents. The presumable mechanism of the haloallylation of internal alkynes comprises the addition of halogen and palladium atoms across the triple bond as the first step.[11] This allows a high level of regioselectivity in two ways: (i) through the polarization effect and (ii) chelation *via* heteroatoms in the pendant side chain.[12] Because of the uneven charge distribution of the components of the catalyst and the uneven electron density of the triple bond, the bromide would connect to the electrophilic atom of the triple bond while the palladium atom would be attacked by the nucleophilic carbon atom. Depending on the direction of polarization of the triple bond, it is possible to control the relative position of the allyl group and bromine atom which would result in a controlled 1,2,4-substitution pattern. On the other hand, the presence of heteroatoms in the pendant side chain of specifically designed internal alkynes induces chelation that overcomes the polarization effect and coordinates the palladium atom to the opposite side of the triple bond through the vinylpalladium intermediate, resulting in the directed bromoallylation and consequentially in regioselective substitution (Scheme 2).

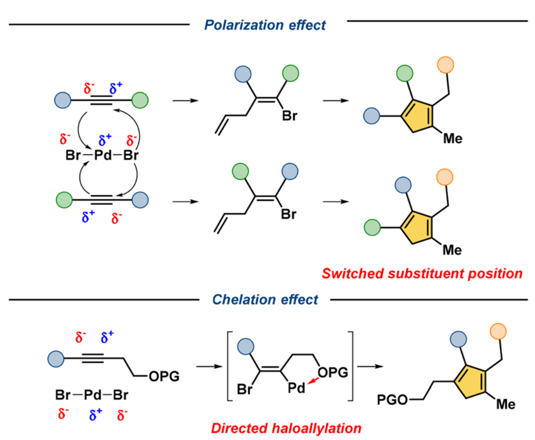


Scheme 1 Proposed synthetic route to multisubstituted cyclopentadienes.

Results and discussion

We used these features to control the site-selective placement of different functional groups around the Cp ring of multisubstituted cyclopentadienes. By taking advantage of knowing which internal alkynes undergo regioselective bromoallylation giving just one *syn*-regioisomer, we prepared a series of 1-bromo-1,4-dienes with defined positions of different functionalities (Fig. 1). Bromodienes **2a**–**2d** are a result of bromoallylation of tolanes directed by the polarization effect, while chelation through an oxygen atom of the protecting group defined the regioselective outcome in bromodienes **2e** and **2f**.

Since the proposed methodology involves the unexplored possibility of Zr-mediated cyclization of dienynes bearing decorated and preassembled functionalities, we prepared a list of non-conjugated dienynes through the Sonogashira coupling of 1-bromo-1,4-dienes **2** and diverse terminal acetylenes (Fig. 2).[13] The choice of coupling partners dictates the chemical diversity and position of respective substituents in the final cyclopentadienes. Thus, coupling of bromodiene **2a** with aryl, alkyl, and TMS-acetylenes (dienynes **3a**–**3n**) will eventually result in tetrasubstituted Cp bearing two identical functionalities at positions 1 and 2. The coupling of phenylacetylene



Scheme 2 Polarization and chelation effect in bromoallylation of alkynes.

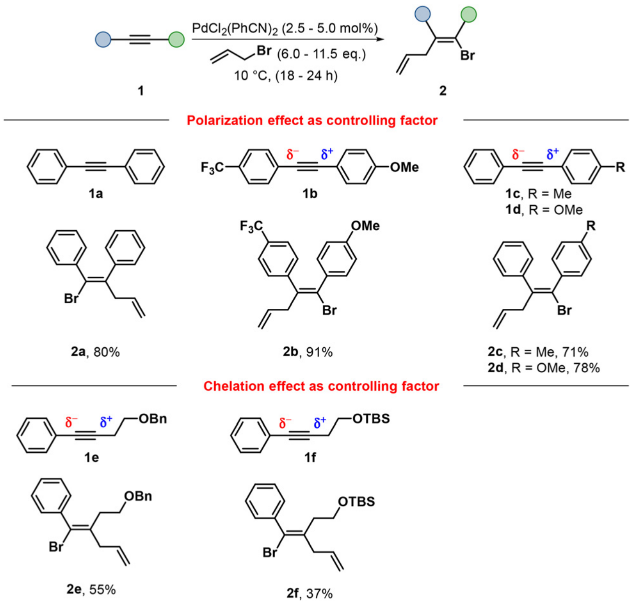


Fig. 1 Bromoallylation of internal alkynes (polarization and chelation effect).

with bromodienes (**2b**–**2d**) derived from unsymmetrically substituted tolanes gave dienynes (**3o**–**3r**) that can be transformed into cyclopentadienes decorated with four different functionalities. Finally, the Sonogashira reaction with chelation products **2e** and **2f** afforded dienynes **3s** and **3t** that would upon sequential transformation give cyclopentadienes with aryl and three alkyl groups.

A low-valent zirconium-mediated cyclization of alkenes, alkynes, dienes, or diynes is highly efficient in transforming simple linear building blocks into their annulated derivatives. This approach provides structurally diverse target molecules depending on the structural features of the olefinic starting material and has been used previously to prepare various substituted cyclopentadienes.[14] Furthermore, a reactive C–Zr bond of the zirconacyclometallated intermediate enables further build-up of molecular complexity as exemplified in a variety of transformations.[15] Although the cyclization of non-conjugated enynes using low-valent organozirconium species is well explored, the same transformation of dienynes is unknown. Thus, we applied the standard cyclization protocol using Negishi's reagent and were delighted to find that cyclization of

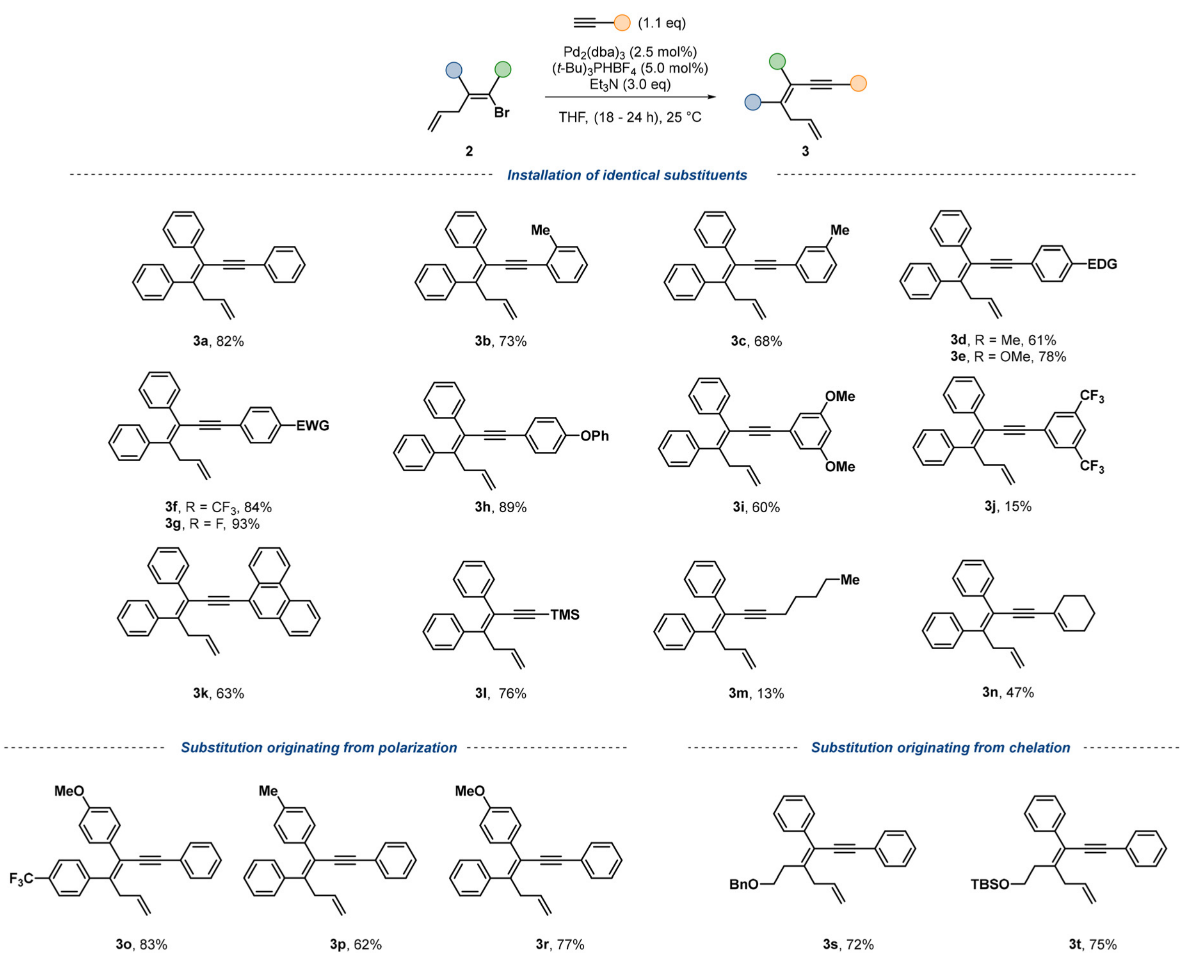


Fig. 2 Substrate scope of dienynes **3**.

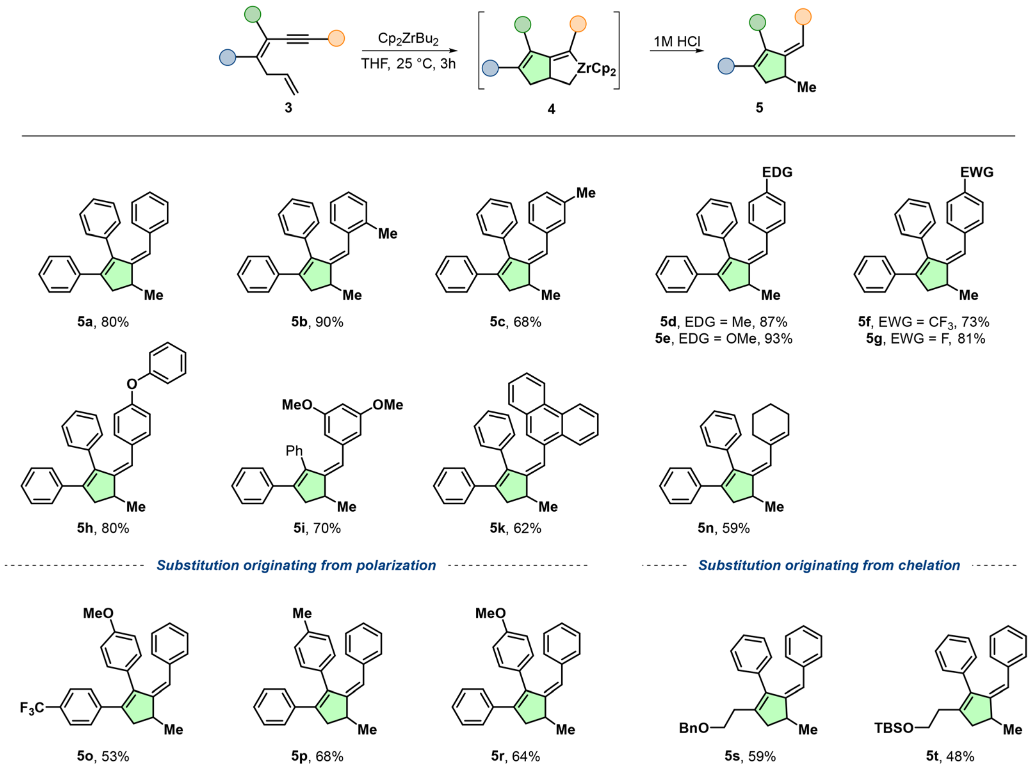


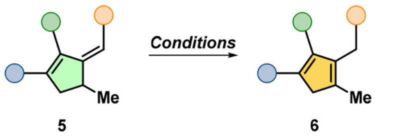
Fig. 3 Substrate scope of pentacycles **5**.

3a followed by acidic quenching gave the corresponding pentacycle **5a** in a high 80% isolated yield (Fig. 3). It should be mentioned that quenching the reaction mixture using 1 N HCl did not induce the *exo*-to-*endo* double bond isomerization to give cyclopentadiene **6a** even after prolonged exposure to acidic conditions (4 days). Following this result, we continued with the investigation of the substrate scope firstly by allocation of the methyl group around the aromatic ring in dienynes **3b–3d** that had a marginal effect on the isolated yields of pentacycles **5b–5d**. The different electron charge distributions caused by the presence of either *para*-positioned electron-withdrawing or electron-donating groups seem to slightly influence the effectiveness of the cyclization process as **5e** and **5h** were isolated in comparable yields to **5f** and **5g**. Reductive dimerization proceeds nicely with a disubstituted aryl ring in **3i** to give **5i** bearing methoxy groups, while product **5j** (di-CF_3) was not isolated. A lower yield of **5k** suggests the sensitivity of the reaction to steric factors. An acetylenic portion of dienynes **3l** and **3m** substituted with TMS and an aliphatic chain did not tolerate the reaction conditions while cyclization of **3n** bearing a cyclohexenyl functionality proceeded but not as effectively compared to aromatic substituents. So far, all these isolated products would eventually give Cp with three different substituents because of the identical functionalities at the internal double bond. On the other hand, the cyclization of dienynes obtained through the polarization effect gave pentacycles **5o–5r** upon acidic work-up while the chelation effect that extends to dienynes **3s** and **3t** afforded their cyclized counterparts **5s** and **5t**. It is highly important to emphasize that even though the conversion of dienynes to zirconacycle intermediates **4** and the corresponding pentacycles **5** proceeds with high efficiency, their purification using column chromatography resulted in a low yield when using silica gel. However, the isolated yield increased dramatically when using alumina (*e.g.* 32% on silica *vs.* 80% on alumina for **5a**). The same trend was observed in all other cases. Additionally, a highly important observation was that during the NMR analysis, unintentional acidity of deuterated chloroform induced the isomerization. This could easily lead to the false impression that acidic quenching yields cyclopentadiene **6**. For this reason, all NMR samples were dissolved in deuterated dichloromethane and the obtained spectra undoubtedly confirm the sole formation of cyclopentenes **5**.

Given the fact that the prolonged exposure of **5a** to acidic conditions did not induce the formation of cyclopentadiene, it is evident that a stronger initiator of double bond isomerization is required. Thus, a series of experiments was performed for the obtention of the most efficient reaction conditions (Table 1). Several catalysts were tested and *p*-TsOH outperformed others in terms of conversion and reaction time (entries 1–5). Furthermore, double bond isomerization was the most effective in dichloromethane (entries 6–9) while catalyst loading, as expected, had a big influence on the isolated yield of cyclopentadiene **6a**.

The obtained conditions were then employed in the *exo*-to-*endo* double-bond isomerization of remaining pentacycles **5**,

Table 1 Screening of conditions for *exo*-to-*endo* double bond isomerization



Entry	Catalyst	Solvent	mol%	*t*/min	Yield/%
1	*p*-TsOH	DCM	10.0	10	86
2	BzOH	DCM	10.0	o/n	65
3	PPA	DCM	10.0	10	69
4	TFA	DCM	10.0	o/n	33
5	MsOH	DCM	10.0	5	60
6	*p*-TsOH	MeCN	10.0	15	41
7	*p*-TsOH	Toluene	10.0	o/n	24
8	*p*-TsOH	$CHCl_3$	10.0	10	52
9	*p*-TsOH	1,2-DCE	10.0	120	41
10	*p*-TsOH	DCM	5.0	60	60
11	*p*-TsOH	DCM	2.5	o/n	31
12[a]	*p*-TsOH	DCM	1.0	120	71

Reactions were performed on a 0.2 mmol scale of **5** in 2.0 mL of solvent at 25 °C. [a] Reaction performed on a 0.4 mmol scale.

resulting in the successful formation of cyclopentadienes **6**. Interestingly, *exo*-to-*endo* isomerization was also accompanied by acid-induced isomerization of an exocyclic double bond, resulting in **5′** products that are difficult to separate from cyclopentadienes **6** using standard column chromatography. Structures **5a′** and **5e′** were confirmed by 2D NMR analysis (see the ESI†) and all other stereoisomers were assigned accordingly (Fig. 4). Despite this issue, the major event in the acid-catalyzed double bond isomerization is the *exo*-to-*endo* double bond shift. The exocyclic bonds in **5a–5e** shifted easily to form the corresponding cyclopentadienes **6a–6e** in high yields with a comparable ratio of regioisomeric mixtures. Interestingly, the presence of electron-withdrawing groups in **5f** and **5g** had a detrimental effect on the isomerization process. While isomerization of **5h** to **6h** proceeded uneventfully, lower yields of **6i** and **6k** suggest the strong electronic and steric impact on the effectiveness of the reaction. As expected, isomerization of **5n** gave a complex reaction mixture most probably because of the additional double bond prone to isomerization under acidic conditions. Double bond isomerization in preassembled pentacycles **5o–5r** afforded the corresponding tetrasubstituted

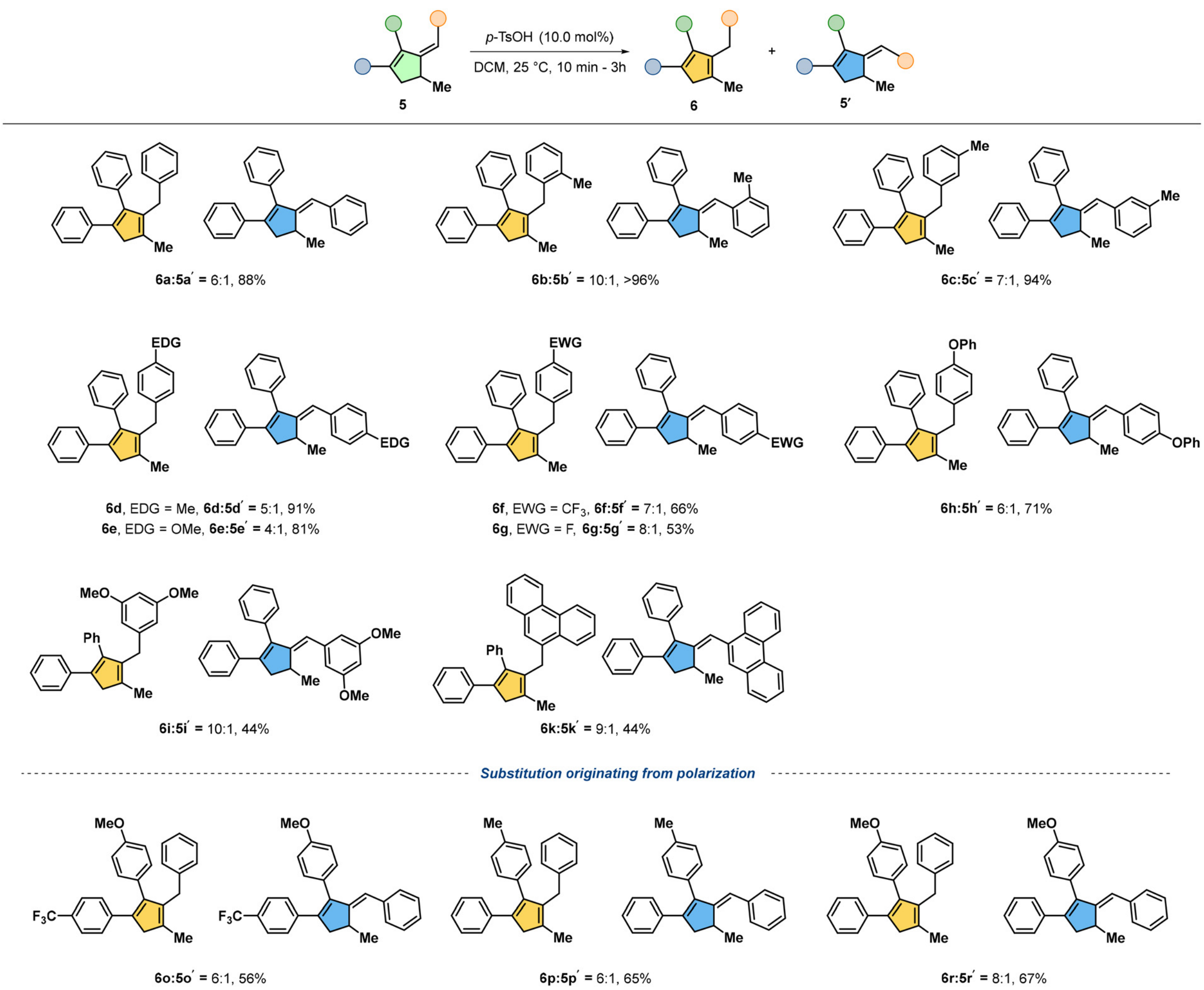
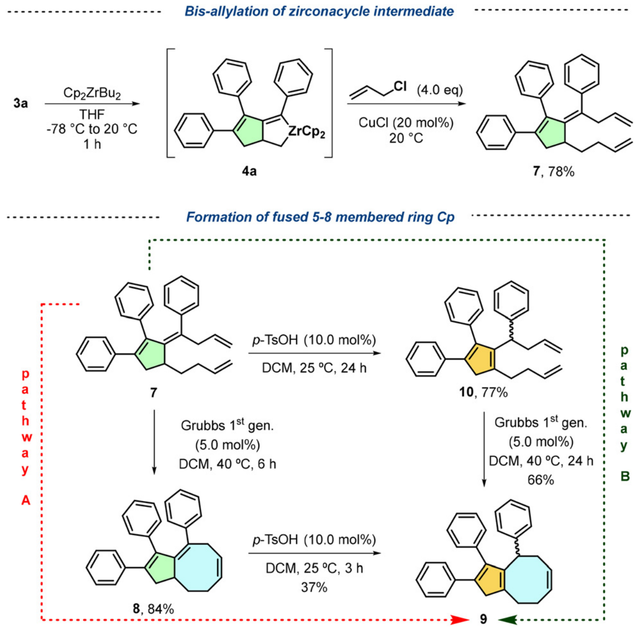


Fig. 4 Substrate scope of cyclopentadienes **6**.

cyclopentadienes **6o–6r** bearing all four different substituents. Attempts to finalize the series of cyclopentadienes that would be the result of the initial control of the substitution pattern through the chelation effect were unsuccessful under the used reaction conditions. In both cases, cyclization of **5s** and **5t** gave a complex reaction mixture with unidentified products. The same was observed even with weaker acids such as phenylphosphinic acid and hexafluoro-2-propanol. Again, all of the products (except **6e**) were isolated on alumina since dramatically lower yields were obtained when using silica gel even though the NMR analysis of the crude reaction mixture showed clean conversion to cyclopentadiene (37% on silica *vs.* 88% on alumina for **6a**). Although unstable on silica gel, the cyclopentadiene mixture **6a**/**5a′** stored as neat or as a solution in CD_2Cl_2 at −20 and 25 °C showed no significant decomposition and the product ratio remained constant even after several weeks.

We believe that the formation of products **5′** could be attributed to their relative stability compared to isomers **5** and **6**. Thus, we performed DFT calculations for geometry optimization to shed light on the energy difference between the three isomers (Fig. 5). As expected, cyclopentadiene **6a** has the lowest Gibbs free energy while **5a** (ΔG = 6.08 kcal mol^{-1}) has the highest Gibbs free energy. The calculated small difference in stability (ΔG = 2.20 kcal mol^{-1}) between **5a′** and **6** suggests the equilibrium between the two isomers that could reason for the formation and isolation of products **5′**.

Besides resulting in an alternative synthetic approach toward tetrasubstituted cyclopentadienes, the additional valuable aspect of the proposed methodology lies in the nucleophilic nature of the C–Zr bond of the zirconacyclopentene intermediate and its ability to undergo selective transformation with various types of electrophiles. Structural modification of the metallocene intermediate possessing a pentacyclic core provides a base for a significant degree of build-up of molecular complexity of the tailored cyclopentadienes. We explored it in the synthesis of fused eight-membered ring Cp, an interesting molecular architecture structurally related to the ligand recently used in iron-catalyzed propylene functionalization.[16] Thus, Zr-mediated cyclization of **3a** gave its zirconacyclic intermediate **4a** that upon transmetallation with a copper(I) salt and the subsequent nucleophilic substitution with allyl chlor-



Scheme 3 Extension of the developed method.

ide gave the corresponding bis-allylated precursor **7** (Scheme 3).[17] The presence of two terminal olefins allows for ring-closing metathesis (RCM) into the cyclooctene motif. Firstly, the bis-allylated product **7** was cyclized into the eight-membered ring **8** in a quite satisfactory 84% isolated yield, but even though the target cyclopentadiene **9** was obtained, the isomerization step was not so efficient (pathway A). Thus, in pathway B, the acid-catalyzed isomerization of **7** gave cyclopentadiene **10** that smoothly cyclized into the 8-membered ring with almost doubled isolated yield. The synthesis of bicyclic cyclopentadiene **9** is just a fraction of transformative possibilities that would result in specifically tailored cyclopentadienes.

Conclusion

In conclusion, we introduced an unexplored synthetic method towards multisubstituted cyclopentadienes with emphasis on the site-selective installation of diverse chemical functionalities and the possibility for molecular decoration enabled by the reactive organozirconium intermediate. A five-step sequence takes advantage of the electronic and steric features of internal alkynes to induce the regioselective attachment of two juxtapositioned substituents. The following Sonogashira coupling allows subsequent decoration of the Cp ring, while in the key step, Zr-mediated cyclization of preassembled dienynes yields the pentacyclic core. The synthetic sequence ends with the acid-catalyzed *exo*-to-*endo* double bond isomerization, yielding several multisubstituted cyclopentadienes. High functional group tolerance combined with the transformable nature of the zirconacycle as a vital intermediate giving ornamented cyclopentadienes paves the way for future exploratory studies involving this valuable structural motif.

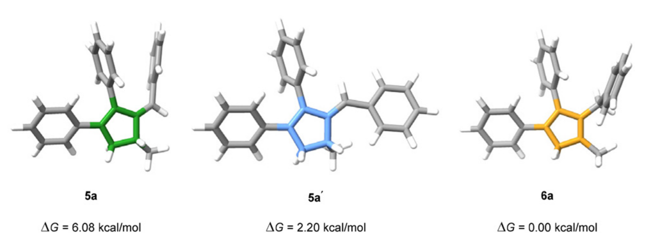


Fig. 5 Optimized structures of compounds **5a**, **5a′**, and **6a** and relative Gibbs free energies in DCM solvent. The most stable isomer **6a** taken as a reference, B3LYP-D3/6-311+G(2d,p) level of theory, SMD model for solvent.

Author contributions

N. T. was responsible for conceptualization, funding acquisition, and writing the original draft. M. G. performed the experiments while I. N.-F. performed the DFT calculations.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the European Union – NextGenerationEU (NPOO.C3.2.R2-I1.06.0022). The authors thank Dr Krunoslav Užarević and Dr Katarina Lisac (Division of Physical Chemistry, RBI) for the IR measurements and Dr Ana Čikoš (NMR Centre, RBI) for the help with NMR analyses.

References

1 T. J. Kealy and P. L. Pauson, A New Type of Organo-Iron Compound, *Nature*, 1951, **168**, 1039–1040.
2 (*a*) W. J. Evans, Tutorial on the Role of Cyclopentadienyl Ligands in the Discovery of Molecular Complexes of the Rare-Earth and Actinide Metals in New Oxidation States, *Organometallics*, 2016, **35**, 3088–3100, references therein. (*b*) A. Vander Weide and D. E. Prokopchuk, Cyclopentadienyl ring activation in organometallic chemistry and catalysis, *Nat. Rev. Chem.*, 2023, **7**, 561–572.
3 *Metallocenes in Regio- and Stereoselective Synthesis*, ed. M. Hapke and M. Kotora, Springer, Berlin, Heidelberg, 2024, vol. 74.
4 A. Frei, Synthetic Routes towards Multifunctional Cyclopentadienes, *Chem. – Eur. J.*, 2019, **25**, 7074–7090.
5 R. B. King and M. B. Bisnette, Organometallic Chemistry of the Transition Metals XXI*. Some π-Pentamethylcyclopentadienyl Derivatives of Various Transition Metals, *J. Organomet. Chem.*, 1967, **8**, 287–297.
6 (*a*) J. Mas-Roselló, A. G. Herraiz, B. Audic, A. Laverny and N. Cramer, Chiral Cyclopentadienyl Ligands: Design, Syntheses, and Applications in Asymmetric Catalysis, *Angew. Chem., Int. Ed.*, 2021, **60**, 13198–13224; (*b*) Y. Sun and N. Cramer, Tailored trisubstituted chiral Cp^xRh^{III} catalysts for kinetic resolutions of phosphinic amides, *Chem. Sci.*, 2018, **9**, 2981–2985.
7 S. Mclean and P. Haynes, Substitution in the cyclopentadienide anion series: Methylation of the cyclopentadienide and methylcyclopentadienide anions, *Tetrahedron*, 1965, **21**, 2313–2327.
8 P. A. Deck, B. D. McCauley and C. Slebodnick, Transition metal cyclopentadienyl complexes bearing perfluoro-4-tolyl substituents, *J. Organomet. Chem.*, 2006, **691**, 1973–1983.
9 Y. Gisbert, P. S. Marqués, C. Baccini, S. Abid, N. Saffon-Merceron, G. Rapenne and C. Kammerer, Copper-catalysed perarylation of cyclopentadiene: synthesis of hexaarylcyclopentadienes, *Chem. Sci.*, 2024, **15**, 9127–9137.
10 T. Zeng, Y. Li, R. Wang and J. Zhu, Temperature-Dependent Divergent Cyclopentadiene Synthesis through Cobalt-Catalyzed C–C Activation of Cyclopropenes, *Org. Lett.*, 2024, **26**, 3413–3418.
11 (*a*) K. Kaneda, T. Uchiyama, Y. Fujiwara, T. Imanaka and S. Teranishi, Selective Codimerization of Acetylenes and Allyl Halides Catalyzed by Palladium Complexes, *J. Org. Chem.*, 1979, **44**, 55–63; (*b*) K. Kaneda, F. Kawamoto, Y. Fujiwara, T. Imanaka and S. Teranishi, Codimerization of Acetylenes and Allyl Halides by Pd-benzonitrile Complexes, *Tetrahedron Lett.*, 1974, **15**, 1067–1070; (*c*) K. Kaneda, H. Kobayashi, Y. Fujiwara, T. Imanaka and S. Teranishi, Selective Linear Cotrimerization of Acetylene and Allyl Halides Catalyzed by Palladium Acetate and Lithium Halides, *Tetrahedron Lett.*, 1975, **16**, 2833–2836.
12 N. Topolovčan, S. Hara, I. Císařová, Z. Tošner and M. Kotora, A Study of Polarization and Directing Effects of Unsymmetrical Alkynes Using Regioselective Pd-Catalyzed Bromoallylation, *Eur. J. Org. Chem.*, 2020, 234–240.
13 M. Vician, *Master's thesis, Synthesis of 1,2-disubstituted cyclopentadienes and their application in syntheses of metallocenes*, Charles University in Prague, Czechia, 2018.
14 (*a*) T. Takahashi, Z. Xi, M. Kotora, C. Xi and K. Nakajima, Preparation of 1,2,3-Trisubstituted Cyclopentadienes and Tetrahydroindene Derivatives from Zirconacyclopentenes, *Tetrahedron Lett.*, 1996, **37**, 7521–7524; (*b*) C. Zhao, P. Li, X. Cao and Z. Xi, Lewis Acid Mediated Reactions of Zirconacyclopentadienes with Aldehydes: One-Pot Synthetic Route to Indene and Cyclopentadiene Derivatives from Aldehydes and Benzyne or Alkynes, *Chem. – Eur. J.*, 2002, **8**, 4292–4298; (*c*) W. Geng, C. Wang, J. Guang, W. Hao, W.-X. Zhang and Z. Xi, 1,2,3,4-Tetrasubstituted Cyclopentadienes and Their Applications for Metallocenes: Efficient Synthesis through Zirconocene- and CuCl-Mediated Intermolecular Coupling of Two Alkynes and One Diiodomethane, *Chem. – Eur. J.*, 2013, **19**, 8657–8664; (*d*) C. Wang, G.-L. Mao, Z.-H. Wang and Z. Xi, Facile Synthesis of Multiply Substituted Cyclopentadienes and Conjugated Dienals through Reactions between 1,4-Dilithio-1,3-dienes and Carboxylic Acid Derivatives Including Acyl Chlorides, Anhydrides, and DMF, *Eur. J. Org. Chem.*, 2007, 1267–1273; Z. Xi and P. Li, Deoxygenative Cycloaddition of Aldehydes with Alkynes Mediated by $AlCl_3$ and Zirconium: Formation of Cyclopentadiene Derivatives, *Angew. Chem., Int. Ed.*, 2000, **39**, 2950–2952.
15 *Titanium and zirconium in organic synthesis*, ed. I. Marek, Wiley-VCH, Weinheim, 2002.

16 R. Wang, Y. Wang, R. Ding, P. B. Staub, C. Z. Zhao, P. Liu and Y.-M. Wang, Designed Iron Catalysts for Allylic C-H Functionalization of Propylene and Simple Olefins, *Angew. Chem., Int. Ed.*, 2023, **62**, e202216309.

17 N. Topolovčan, I. Panov and M. Kotora, Bisallylation of Zirconacyclopentenes and Ring-Closing Metathesis: A Route to Eight-Membered-Ring Compounds, *Synlett*, 2016, 432–436.