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Reaction of Bicyclic Zirconacyclopentenes with Aldehydes and a Potential Pathway to Condensed 5–7–6(Ar) Ring Systems

Nikola Topolovčan,[a] Illia Panov,[a] and Martin Kotora*[a]

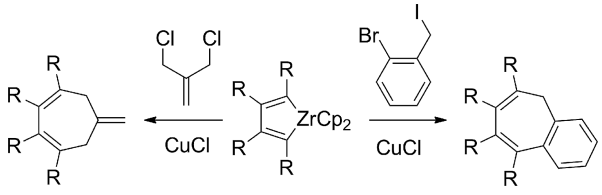
Dedicated to Professor Tamotsu Takahashi on the occasion of his 60th birthday

Keywords: Homogeneous catalysis / Zirconium / Metallacycles / Cyclization / Insertion / Fused-ring systems / Aldehydes

Bicyclic zirconacyclopentenes prepared by the reactions of 1,6- and 1,7-enynes with [Cp_2ZrBu_2] (Negishi reagent) reacted with a plethora of aldehydes (aryl, heteroaryl, alkyl, α,β-unsaturated) by chemo- and stereoselective insertion into the sp^3 C–Zr bond to give the corresponding oxazirconacycloheptenes. Subsequent hydrolysis or halogenolysis provided the corresponding alcohols **4** (31–74 % isolated yields) or halides **10** (35–50 % isolated yields). The oxazirconacycloheptenes prepared by the insertion of 2-iodobenzaldehyde were also subjected to intramolecular coupling in the presence of CuCl and additives, and compounds possessing the condensed 5–7–6(aryl) ring system were obtained in reasonable isolated yields (32–46 %). The same ring system was also prepared by the Pd-catalyzed coupling of dihalo derivatives **10** (38–42 % ^{1}H NMR yields). Moreover, the mechanism of the unproductive side-reaction leading to ketones during the reaction with CuCl was elucidated.

Introduction

Zirconacycles are a class of bis-nucleophiles that readily react with a number of electrophiles to provide a variety of differently substituted compounds and such processes have also been used for the formation of carbocyclic compounds.[1] Typical examples are the reactions of zirconacyclopentadienes with alkynes to give substituted benzenes,[2] with allyl and propargyl halides to form cyclohexadienes,[3] with *o*-dihaloarenes to yield naphthalenes,[4] and with *o*-di(halomethyl)arenes to form benzooctatrienes.[5] Zirconacycles also react with 3-iodoenones to form spirocyclic compounds.[6] Also worth mentioning are the reactions of zirconacyclopentanes and -cyclopentadienes with acyl halides[7] or aldehydes[8] to give five-membered ring compounds. As far as the formation of seven-membered ring compounds using zirconacycles is concerned, two methods have been reported: The reactions of zirconacyclopentadienes with bis-functional allyl halides[3a] and *o*-iodobenzyl bromides[9] to provide cycloheptadienes and benzocycloheptatrienes, respectively (Scheme 1). In this respect, an early example of the synthesis of tricyclic compounds based on carbene insertion into zirconacyclopentanes reported by Whitby and co-workers should also be acknowledged.[10]



Scheme 1. Formation of compounds with a cycloheptane scaffold from zirconacyclopentadienes.

Although the above-mentioned processes allows the preparation of a variety of carbocyclic compounds possessing five- to eight-membered rings, there are still other opportunities for developing new synthetic protocols. In particular, the synthesis of polycyclic compounds possessing seven-membered rings is of considerable synthetic interest because such compounds are often an important structural motif in natural and biologically active compounds.[11]

In principal, zirconacyclopentenes can react with aldehydes and other compounds possessing the carbonyl group in two ways. The reaction may proceed either by the extrusion of ethylene from the zirconacyclopentenes to form oxazirconacyclopentenes that yield allylic alcohols after hydrolysis[12] or by insertion into the sp^3 C–Zr bond to give oxazirconacycloheptenes, which upon hydrolysis give rise to pent-4-en-1-ols and derivatives thereof. As far as the latter pathway is concerned, it has been shown that monocyclic zirconacyclopentenes (along with one example of a bicyclic zirconacyclopentene) react with aromatic and aliphatic al-

[a] Department of Organic Chemistry, Faculty of Science, Charles University in Prague,
Hlavova 8, 128 43 Praha 2, Czech Republic
E-mail: martin.kotora@natur.cuni.cz
https://www.natur.cuni.cz/chemistry/orgchem/kotora?set_language=en

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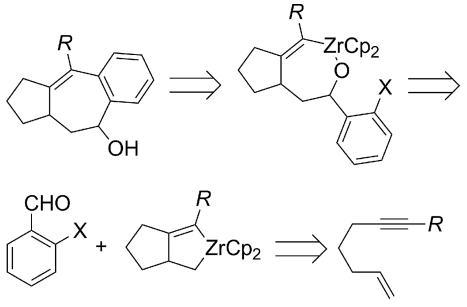
dehydes to form the corresponding oxazirconacycloheptenes, which, after hydrolysis, give the expected pent-4-en-1-ols.[13] The treatment of the intermediate oxazirconacycles with transition-metal salts (CuCl) and additional Lewis acids resulted in the formation of tetrahydrofurans[14] or homoallyl ketones.[15,16] Interestingly, the reactions of related titanacyclopentenes with aldehydes proceed exclusively by the insertion of the carbonyl group into the sp^2 C–Ti bond.[17] In this respect, it is worth noting that the reaction of the α-vinylzirconacyclopentene with aldehydes proceeds at the sp^2 C–Zr bond by an allylic rearrangement instead of by insertion into the sp^3 C–Zr bond to provide homoallenyl alcohols.[18]

Although the oxazirconacycloheptenes obtained by the insertion of aldehydes might be considered interesting intermediates for subsequent synthetic elaboration, their further reactions with carbon-based nucleophiles (alkyl, allyl, alkenyl, or aryl halides) have not yet been reported. In this respect, the sequential reaction of a bicyclic zirconacyclopentene, prepared by the oxidative dimerization of an enyne, with *o*-halobenzaldehydes, followed by the intramolecular coupling of the sp^2 C–Zr bond with an sp^2 C–halide bond in the pendant chain to provide a seven-membered ring compound, has not yet been explored. The retrosynthetic analysis of this reaction sequence is depicted in Scheme 2.



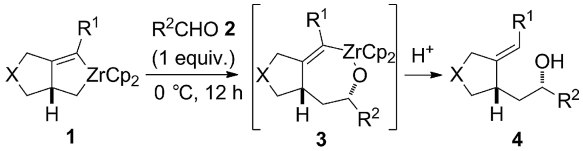
Scheme 2. Retrosynthetic analysis of seven-membered ring formation from enynes and *o*-halobenzaldehydes.

If such a reaction could be successfully accomplished, it would represent a new and synthetically straightforward approach to the synthesis of polycyclic condensed carbocycles possessing 6–7–6(aryl) and 5–7–6(aryl) ring systems[19] from simple and easily accessible building blocks such as enynes[20] and aromatic aldehydes. The 6–7–6(Ar) condensed ring structural motif is commonly found in natural compounds, for example, in members of the icetaxane family.[21] On the other hand, the 5–7–6(Ar) framework is rather rare and, to the best of our knowledge, has so far been identified in just one compound with the isodolastane skeleton.[22]

Results and Discussion

Insertion of Aldehydes into the sp^3 C–Zr Bond in Zirconacyclopentenes

Because there is a lack of information on the reactions of bicyclic zirconacyclopentenes with aldehydes, we initially decided to screen the reaction of the bicyclic zirconacyclopentene **1a** with variously substituted aromatic, heteroaromatic, α,β-unsaturated, and alkyl aldehydes followed by protonolysis (Scheme 3).



1a, R^1 = *p*Tol, X = CH_2
1b, R^1 = *n*Bu, X = CH_2
1c, R^1 = $(CH_2)_2$OTBDMS, X = CH_2
1d, R^1 = *n*Bu, X = $(CH_2)_2$
1e, R^1 = *p*Tol, X = BnN
1f, R^1 = Ph, X = BnN
R^2 = see Figure 1

Scheme 3. Reactions of **2** with **1** and subsequent protonolysis.

The reactions proceeded as expected, usually with the full conversion of the starting enyne, providing the corresponding alcohols **4** in sensible isolated yields at 0 °C (in some cases the reduced yields of the isolated compounds may be attributed to the purification of the products from side-products; Table 1, Figure 1). Interestingly, the *o*-substi-

Table 1. Results of the insertion of aldehydes **2** into **1a**.

Entry[a]	**2**	*T* [°C]	*dr* [a]	**4**	Yield [%][b]
1	**2a**	20	≈5.5:1	**4aa**	40 (61)
2	**2a**	0	≈5.5:1	**4aa**	35 (61)
3	**2b**	20	>20:1[c]	**4ab**	70
4	**2b**	0	>20:1[c]	**4ab**	55 (73)
5	**2c**	20	≈15:1	**4ac**	33
6	**2c**	0	≈15:1	**4ac**	57 (75)
7	**2d**	0	>20:1[c]	**4ad**	52 (77)
8	**2e**	0	>20:1[c]	**4ae**	70
9	**2f**	–10	>20:1[c]	**4af**	53
10	**2g**	20	>20:1[c]	**4ag**	31
11	**2g**	0	>20:1[c]	**4ag**	32 (46)
12	**2h**	0	>20:1[c]	**4ah**	62 (72)
13	**2i**	0	≈5.5:1	**4ai**	60
14	**2j**	0	>20:1[c]	**4aj**	74 (88)
15	**2k**	0	≈19:1	**4ak**	31 (51)
16	**2l**[d]	0	>20:1[c]	**4al**	62 (81)
17	**2m**	0	≈5.5:1	**4am**	62 (80)

[a] The *dr* value was determined by ^{1}H NMR spectroscopy. [b] Isolated yields. The ^{1}H NMR yields are given in parentheses. [c] The second diastereoisomer was not detected in the reaction mixture or after isolation. [d] 3 equiv. of **2l** were used.

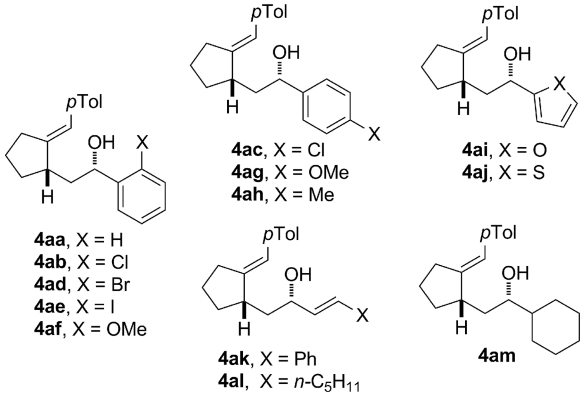


Figure 1. Alcohols **4** obtained by the insertion of aldehydes **2** into zirconacylopentene **1a**.

tuted benzaldehydes gave higher yields of the desired products. The reaction of **1a** with 4-pyridinecarbaldehyde was tested as well, but the reaction furnished an intractable reaction mixture in which the expected product could not be detected. The reactions of **1a** with aldehydes **2a**–**2c** and **2g** were also carried out at 20 °C for comparison (entries 1, 3, 5, and 10). In general, the higher reaction temperature did not affect the diastereoselective ratios, which are essentially the same as those at 0 °C, or the isolated yields of **4aa**–**4ac** and **4ag**. Nevertheless, greater amounts of unidentified side-products were observed. The generally high diastereoselectivity of the insertion process is worth noting. We assume that the aldehydes favored approach to the sp^3 C–Zr bond from the less sterically hindered side leading to the preferential formation of (*S**,*S**) diastereoisomers with >99% selectivity in most cases. On the other hand, it should be mentioned that the reactions with **2a**, **2c**, **2i**, **2k**, and **2m** gave lower diastereoselectivities (entries 1, 2, 5, 6, 13, 15, and 17).

The assumption regarding the formation of the (*S**,*S**) diastereoisomers was confirmed by theoretical calculations, which showed that the (*S**,*S**) diastereoisomer of zirconacyclopentene **3** ($R^1 = R^2 = Ph$) is 8 kJ mol^{-1} more stable than the (*S**,*R**) diastereoisomer (the optimized geometries and energies can be found in the Supporting Information).[23] The predicted relative stereochemistry of the products, that is, (*S**,*S**), was confirmed by a single-crystal X-ray analyses of **4fe** (Figure 2) and **4ed** (see the Supporting Information).

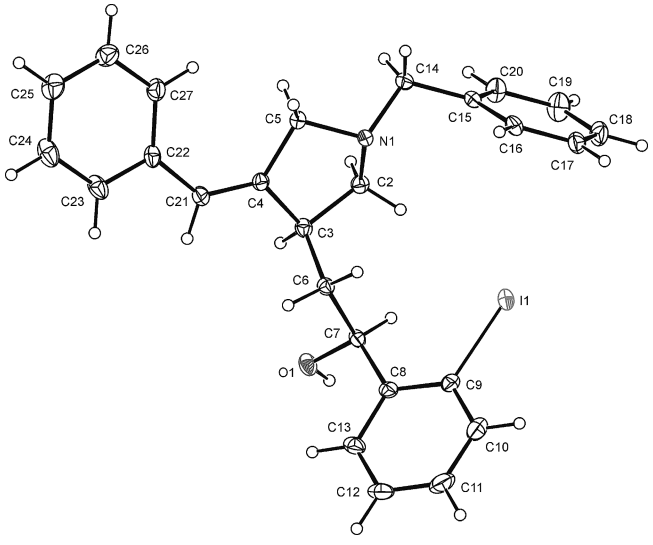
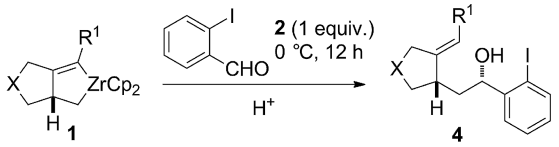


Figure 2. View of (*S**,*S**)-**4fe** with the atomic numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. Only the position of the iodine atom with 95% occupation is displayed.

The result of the insertion of *o*-iodobenzaldehyde (**2e**) into zirconacyclopentene **1a** prompted us to attempt insertions into bicyclic zirconacyclopentenes **1** possessing other structural features to assess the scope of the reaction (Table 2). The reaction of **1a** (entry 1) is also included for comparison with the reactions of the zirconacyclopentenes **1b**–**1f**. The insertion of **2e** into zirconacycle **1b** was initially carried out at 0 °C and gave the corresponding product **4be** in 60% yield; however, carrying out the reaction at 20 °C resulted in an improved yield of 84% (entries 2 and 3). Zirconacyclopentene **1c** bearing a hydroxylated side-chain reacted with **2e** uneventfully at 0 °C to give the desired product **4ce** in a good yield of 75% (entry 4). In an analogous manner, the insertion into the bicyclic zirconacyclopentene **1d** yielded the product **4de** in 86% yield (entry 5). Then the reaction of the zirconacyclopentene possessing a nitrogen atom (**1e**) was attempted with **2d** and **2e**; the reactions proceeded in both cases to furnish the corresponding insertion products **4ed** and **4ee** in isolated yields of 55 and 32% (entries 6 and 7), respectively. In a similar manner, the reaction of **1f** with **2e** gave **4fe** in 57% isolated yield (entry 8). In most cases the products were obtained with excellent diastereoselectivities.

Table 2. Insertion of *o*-iodobenzaldehyde (**2e**) into zirconacyclopentenes **1a**–**1f**.



4ae, R^1 = *p*Tol, X = CH_2 **4de**, R^1 = *n*Bu, X = $(CH_2)_2$
4be, R^1 = *n*Bu, X = CH_2 **4ee**, R^1 = *p*Tol, X = BnN
4ce, R^1 = $(CH_2)_2$OTBDMS, X = CH_2 **4fe**, R^1 = Ph, X = BnN

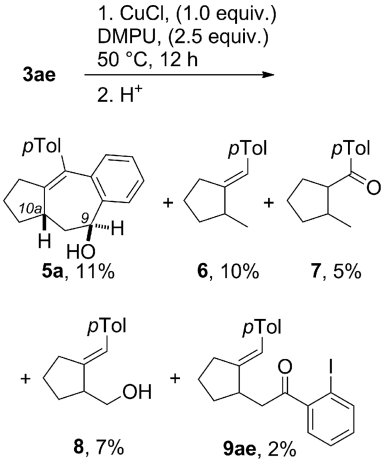
Entry[a]	1	*T* [°C]	*dr* [a]	Product	Yield [%][b]
1	**1a**	0	>20:1[c]	**4ae**	70
2	**1b**	0	>20:1[c]	**4be**	31 (60)
3	**1b**	20	>20:1[c]	**4be**	52 (84)
4	**1c**	0	>20:1[c]	**4ce**	53 (75)
5	**1d**	0	≈16:1	**4de**	63 (86)
6[d]	**1e**	0	>20:1[c]	**4ed**	55
7	**1e**	0	>20:1[c]	**4ee**	32 (54)
8	**1f**	0	>20:1[c]	**4fe**	57

[a] The *dr* value was determined by ^{1}H NMR spectroscopy. [b] Isolated yields. The ^{1}H NMR yields are given in parentheses. [c] The second diastereoisomer was not detected in the reaction mixture or after isolation. [d] The insertion reaction was carried out with *o*-bromobenzaldehyde (**2d**).

Insertion of Aldehydes Followed by Intramolecular Coupling

The high-yielding insertion of *o*-iodobenzaldehyde (**2e**) into the zirconacyclopentene **1a** (70%, Table 1, entry 8) prompted us to investigate an intramolecular cyclization based on the transmetallation of the sp^2 C–Zr bond with CuCl followed by subsequent reaction of the organocopper compound formed with the aryl iodide moiety in accordance with the previously successfully applied methodology.[3,4] The insertion of **2e** into **1a** was followed by the addition of CuCl (1 equiv.) and 1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone (DMPU; 2 equiv.) and the mixture was allowed to react at 50 °C for 12 h (Scheme 4). After acidic work-up, which showed almost full conversion of the starting material, the desired compound **5a** was isolated in

a rather low yield of 11% along with a number of other products, such as **6** (the product of hydrolysis of the parental zirconacyclopentene **1a**), the products of oxidation of the sp^2 (ketone **7**) and sp^3 C atoms (alcohol **8**; it is clear that these compounds must be formed by the oxidation of the corresponding C–metal bonds, but the origin of the oxidizing species is not clear at the moment), and, finally, the product of oxidation of the intermediate **3ae** (ketone **9ae**). Interestingly, the presence of unreacted alcohol **4ae**, the product of hydrolysis of oxazirconacycloheptene **3ae**, was not detected.



Scheme 4. Products formed in the reaction of oxazirconacycloheptene **3ae** with CuCl.

Because of this unsatisfactory and slightly puzzling result regarding the products formed, we decided to screen various reaction conditions to improve the yield of the desired tricyclic compound **5a** and to elucidate the course of the reaction. The reaction was performed again under the same reaction conditions and the subsequent analysis of the reaction mixture revealed that the desired compound **5a** was formed in 31% yield (Table 3, entry 1). (Fortunately, compound **5a** has the distinct multiplet in the region δ = 4.96–4.94 ppm that was not overlapped by other signals, which allowed us to monitor its presence in reaction mixtures.) The discrepancy in isolated yields between this result and the one above can be attributed to problems encountered during isolation. Increasing the amount of DMPU to 3 equiv. (entry 2) or the amount of CuCl (entry 3) did not have any effect on the overall yield of **5a**, with yields of 27 and 30%, respectively, obtained. However, a considerable improvement in yield (44%) was seen with Cu(*t*BuO) as the transmetallating agent (entry 4). The use of catalytic amounts of $[(PPh_3)_4Pd]$ in the absence of DMPU or a combination of a Pd–N-heterocyclic carbene complex (PEPPSI) and zinc chloride (instead of CuCl) did not result in better yields of **5a**, which in both cases were around 30% (entries 5 and 6). Interestingly, a combination of catalytic amounts of $[(PPh_3)_4Pd]$ and CuCl in the presence of DMPU and JohnPhos (**L1**) provided **5a** in 40% yield, as shown by ^{1}H NMR analysis (entry 7). It is worth noting that this is the first example of the use of CuCl in a catalytic amount in coupling reactions with aryl halides in zirconocene-based procedures. The use of a higher amount of CuCl and **L1** (entry 8) had only a marginal effect on the yield, with the desired compound **5a** being isolated in 46% yield. However, this was the best result obtained so far. Finally, bipyridine (**L2**) was used as an additive in the presence of catalytic amounts of $[(PPh_3)_4Pd]$ and CuCl (entry 9), or a stoichiometric amount of CuCl (entry 10) to provide **5a** in yields of 41 and 48%, respectively. These results, that is, the inability to improve the yield of **5a** as well as the isolation of various side-products in the initial experiment, indicated that perhaps the conversion of **3ae** into **5a** might be hampered by a hitherto unreported side-reaction. The reaction conditions of CuCl (1.1 equiv.), JohnPhos (1.25 equiv.), and $[(PPh_3)_4Pd]$ (5 mol-%) were also used for the cyclization of the insertion product **3fe**, which resulted in the formation of the tricyclic compound **5e** (Figure 3) in an isolated yield of 32%. As far as the formation of tetrahydrofuran derivatives observed by others[14] is concerned, we did not detect any such product.

Table 3. Intramolecular reaction of **3ae** to yield **5a** under various conditions.

Entry	Catalyst[a]	MX_n (amount [equiv.])	DMPU [equiv.]	Ligand[b] (amount [equiv.])	Yield [%][c]
1	–	CuCl (1)	2		19 (31)
2	–	CuCl (1)	3		10 (27)
3	–	CuCl (2)	2.5		10 (30)
4	–	CuO*t*Bu (1.5)			(44)
5	$[(PPh_3)_4Pd]$	CuCl (1)			(30)
6	PEPPSI	$ZnBr_2$ (1)	3		(30)
7	$[(PPh_3)_4Pd]$	CuCl (0.2)	2.5	**L1** (0.8)	(40)
8	$[(PPh_3)_4Pd]$	CuCl (1.5)	3	**L1** (4)	46[d]
9	$[(PPh_3)_4Pd]$	CuCl (0.2)		**L2** (0.4)	(41)
10	$[(PPh_3)_4Pd]$	CuCl (1)		**L2** (2)	32 (48)

[a] 5 mol-%. [b] **L1** = JohnPhos, **L2** = bipyridine. [c] ^{1}H NMR yield. The isolated yields are given in parentheses. [d] It was not possible to determine the yield in the reaction mixture by ^{1}H NMR analysis because of overlap with other signals.

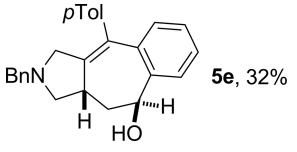
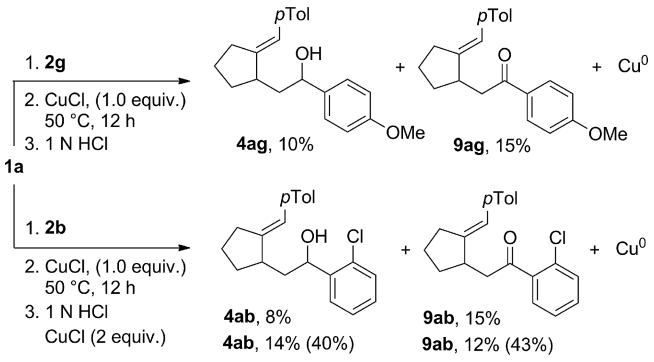


Figure 3. Structure of **5e**.

Reaction of 3 with CuCl

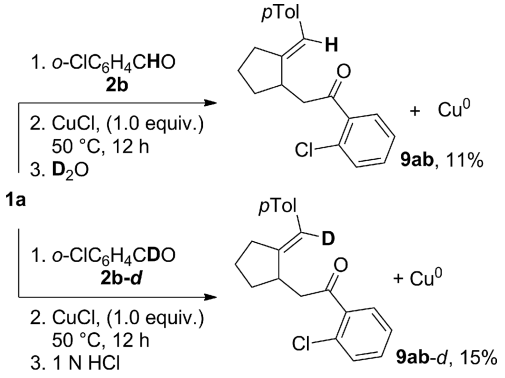
Our attention was attracted by the presence of oxidation products in the reaction of **1a** with *o*-iodobenzaldehyde (**2e**), namely ketone **9ae**, because its origin was rather puzzling. To elucidate its formation, oxazirconacycloheptenes **3ab** and **3ag**, formed by the insertion of **2b** and **2g** into **1a**, were heated with CuCl at 50 °C for 12 h followed by acidic work-up (Scheme 5). Along with the expected insertion products **4ab** and **4ag** isolated in yields of 10 and 8% and **6** obtained in a yield of around 10%, the isolated ketones

9ab and **9ag** were also isolated both in yields of 15%. In addition, the precipitation of metallic copper was observed during the course of the reaction. The presence of the ketones and metallic copper unequivocally indicated that an internal redox process must occur.



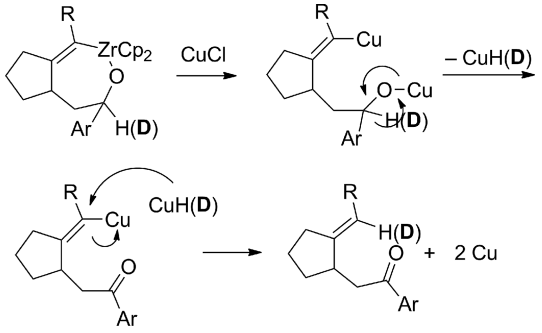
Scheme 5. Reactions of oxazirconacycloheptenes **3ag** and **3ab**, formed from **1a** and **2g**,**b**, with CuCl.

To gain further insight into the course of the reaction, the reaction of **1a** with **2b** was carried out again and quenched with D_2O (Scheme 6). Surprisingly, the incorporation of deuterium into the products was not observed and only ketone **9ab** was isolated in 11% yield. This indicated that the hydrogen atom at the sp^2 C must come from one of the reactants. To prove this assumption the reaction with deuteriated *o*-ClC_6H_4CDO (**2b**-*d*) was carried out. After work-up, deuteriated ketone **9ab**-*d* was isolated in 15% yield with >99% deuterium incorporation.



Scheme 6. Reaction of **1a** with *o*-chlorobenzaldehyde (**2b**) followed by quenching with H^+ or D^+.

These results indicated that an intermediate copper(I) compound formed by transmetallation with CuCl could be assumed to be the only culprit capable of such reactions. First, it has previously been reported that copper(I) alkoxides undergo β-hydrogen elimination to form ketones and copper(I) hydride.[24] Secondly, copper(I) hydride has been reported to react with organocopper compounds to provide reductive demetallation products and metallic copper.[25] A combination of the results obtained in this work and published reports has enabled us to propose the reaction mechanism in Scheme 7 to explain the formation of the major side-product (ketone **9**) during the reaction of oxazirconacycloheptenes with CuCl.

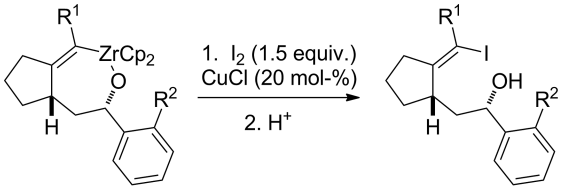


Scheme 7. Proposed mechanism for the formation of ketone **9**.

The first step is the transmetallation of the Zr–C and Zr–O bonds with CuCl giving rise to the corresponding bis-organocopper compound. Then β-hydrogen elimination ensues from the copper alkoxide to form CuH, which in turn reacts with the sp^2 C–Cu bond giving rise to the reduced product and metallic copper. Whether the last step proceeds through an ionic pathway or is a radical process at this point remains undecided.

Iodonolysis and Coupling

To circumvent this undesirable side-reaction, we decided to explore a different approach to the formation of the seven-membered ring. The plan was based on the formation of a diiodide by iodination of the formed oxazirconacycloheptene (Scheme 8). Four zirconacycloheptenes, **3ab**, **3ad**, **3ae**, and **3bd**, were prepared and subjected to iodonolysis in the presence of a catalytic amount of CuCl,[26] the corresponding dihalides **10a**–**10d** being obtained in isolated yields of 35, 41 (74% ^1H NMR yield), 50, and 41%, respectively.

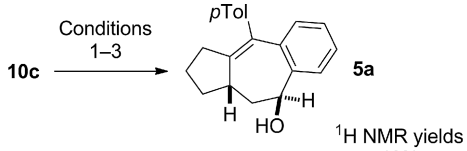


3ab, R^1 = *p*Tol, R^2 = Cl — **10a**, R^1 = *p*Tol, R^2 = Cl 35%
3ad, R^1 = *p*Tol, R^2 = Br — **10b**, R^1 = *p*Tol, R^2 = Br 41 (74%)
3ae, R^1 = *p*Tol, R^2 = I — **10c**, R^1 = *p*Tol, R^2 = I 50%
3bd, R^1 = *n*Bu, R^2 = Br — **10d**, R^1 = *n*Bu, R^2 = Br 41%

Scheme 8. Iodonolysis of oxazirconacyclopentenes **3**.

Finally, **10c** was subjected to a Pd-catalyzed homocoupling reaction in the presence of indium (Scheme 9).[27] Initially the reaction was performed by using Pd/C in the presence of 0.5 or 1 equiv. of indium metal. The reaction provided the corresponding tricyclic compound **5a** in a yield of

42 or 38%, respectively. The use of a combination $Pd(OAc)_2$ and JohnPhos in the presence of 1 equiv. of indium metal yielded **5a** in a similar yield of 41%.



	^{1}H NMR yields
1. Pd/C (10 wt.-%), In (0.5 equiv.)	42%
2. Pd/C (10 wt.-%), In (1 equiv.)	38%
3. $Pd(OAc)_2$ (2 mol-%), JohnPhos (2 mol-%)	41%

Scheme 9. Intramolecular homocoupling of **10c** to give **5a**.

Conclusions

We have shown that the insertion of aldehydes into the sp^3 C–Zr bond proceeds with a high efficiency and diastereoselectivity (in many cases >99%). In the case of the insertion of *o*-iodobenzaldehyde (**2e**), the oxazirconacycloheptene formed can undergo intramolecular coupling to yield compounds possessing the tricyclic condensed 5–7–6(aryl) ring system in moderate yields upon transmetallation of the remaining sp^2 C–Zr bond. The reaction is hampered by a side-reaction that produces ketones thereby diminishing the yields of the cyclized products. In this respect, it was also shown that dihalogenated intermediates, obtained by halogenolysis of the oxazirconacycloheptenes, could also be converted into tricyclic compounds.

Experimental Section

General Procedure for the Synthesis of Alcohols 4: *n*BuLi (1.6 M in hexanes, 1.25 mL, 2.00 mmol) was added dropwise within 5 min to a solution of bis(cyclopentadienyl)zirconium dichloride (0.292 g, 1.00 mmol) in dry THF (5 mL) cooled to –78 °C and the reaction mixture was stirred for 1 h at the same temperature. An enyne (1.00 mmol) was added and the reaction mixture was gradually warmed to 25 °C. After 3 h freshly distilled aldehyde (1.00 mmol) was added at 0 °C and the reaction mixture was stirred for 12 h. After warming to 25 °C, it was quenched with 1 N HCl (10 mL) and extracted with EtOAc (3× 20 mL). The combined organic phases were washed with a saturated solution of $NaHCO_3$ (20 mL), water (2× 20 mL), and brine (20 mL), dried with $MgSO_4$, and the solution was filtered and concentrated under reduced pressure. Purification of the residue by column chromatography provided the corresponding alcohol **4**.

(1*S)-2-[(1*S**,2*E*)-2-(4-Methylbenzylidene)cyclopentyl]-1-phenylethanol (4aa):** Column chromatography of the residue on silica gel (4:1 hexanes/EtOAc) yielded 0.116 g (40%) of the title compound as a yellow oil. R_f (4:1 hexanes/EtOAc) = 0.42. Major diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41–7.35 (m, 4 H), 7.30–7.27 (m, 1 H), 7.20–7.19 (m, 2 H), 7.12–7.10 (m, 2 H), 6.28–6.27 (m, 1 H), 4.86–4.82 (m, 1 H), 2.86–2.80 (m, 1 H), 2.69–2.64 (m, 1 H), 2.60–2.54 (m, 1 H), 2.33 (s, 3 H), 2.20–2.16 (m, 1 H), 2.04–2.00 (m, 1 H), 1.90–1.85 (m, 2 H), 1.71–1.65 (m, 2 H), 1.41–1.36 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.1, 145.3, 135.9, 135.4, 128.9, 128.5, 128.1, 127.5, 125.8, 120.6, 73.2, 44.7, 43.0, 31.9, 31.4, 24.8, 21.1 ppm. Minor diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.68–4.66 (m, 1 H) ppm; the remaining signals are overlapped by the signals of the major diastereoisomer. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 135.5, 128.4, 125.9 ppm; the remaining signals are overlapped by the signals of the major diastereoisomer. IR (KBr): $\tilde{\nu}_{max}$ = 3360, 3087, 3063, 3025, 2998, 2947, 2935, 2869, 1652, 1506, 1494, 1449, 1048, 869, 806, 752, 704 cm^{-1}. HRMS (TOF-ESI): calcd. for $C_{21}H_{24}ONa$ 315.17170 $[M + Na]^+$; found 315.17194.

(1*S)-1-(2-Chlorophenyl)-2-[(1*S**,2*E*)-2-(4-methylbenzylidene)cyclopentyl]ethanol (4ab):** Column chromatography of the residue on silica gel (4:1 hexanes/EtOAc) yielded 0.228 g (70%) of the title compound as a yellow oil. R_f (4:1 hexanes/EtOAc) = 0.38. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.66–7.64 (m, 1 H), 7.33–7.30 (m, 2 H), 7.21 (dd, *J* = 7.2, 1.2 Hz, 1 H), 7.20–7.18 (m, 2 H), 7.12–7.10 (m, 2 H), 6.26–6.25 (m, 1 H), 5.27–5.24 (m, 1 H), 2.95–2.90 (m, 1 H), 2.70–2.65 (m, 1 H), 2.62–2.55 (m, 1 H), 2.32 (s, 3 H), 2.11–2.06 (m, 1 H), 2.04 (d, *J* = 3.6 Hz, 1 H), 2.01–1.97 (m, 1 H), 1.93–1.87 (m, 1 H), 1.77–1.66 (m, 2 H), 1.56–1.50 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.1, 142.6, 135.8, 135.4, 131.4, 129.4, 128.8, 128.3, 128.0, 127.2, 126.7, 120.6, 69.5, 43.1, 43.0, 31.6, 31.3, 24.9, 21.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3404, 3066, 3016, 2950, 2872, 1706, 1449, 1048, 1036, 755 cm^{-1}. HRMS (TOF-ESI): calcd. for $C_{21}H_{23}OClNa$ 349.13271 $[M + Na]^+$; found 349.13296.

(1*S)-1-(4-Chlorophenyl)-2-[(1*S**,2*E*)-2-(4-methylbenzylidene)cyclopentyl]ethanol (4ac):** Column chromatography of the residue on silica gel (4:1 hexanes/EtOAc) yielded 0.178 g (57%) of the title compound as a yellow oil. R_f (4:1 hexanes/EtOAc) = 0.44. Major diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.33–7.32 (m, 4 H), 7.20–7.19 (m, 2 H), 7.13–7.12 (m, 2 H), 6.26–6.25 (m, 1 H), 4.81–4.80 (m, 1 H), 2.83–2.78 (m, 1 H), 2.70–2.64 (m, 1 H), 2.60–2.54 (m, 1 H), 2.33 (s, 3 H), 2.16–2.11 (m, 1 H), 2.07 (s, 1 H), 2.03–2.0 (m, 1 H), 1.91–1.83 (m, 1 H), 1.70–1.61 (m, 2 H), 1.40–1.33 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.9, 143.6, 135.6, 135.4, 133.0, 128.9, 128.6, 128.0, 127.1, 120.6, 72.4, 44.6, 42.9, 31.8, 31.4, 24.8, 21.1 ppm. Minor diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): the signals were overlapped by the signals of the major diastereoisomer. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.4, 142.9, 133.2, 128.7, 128.0, 127.5, 121.0, 77.2, 76.8, 72.8, 43.9, 42.9, 32.2, 30.9 ppm; the remaining signals are overlapped by the signals of the major diastereoisomer. IR (KBr): $\tilde{\nu}_{max}$ = 3363, 3019, 2947, 2866, 1649, 1509, 1491, 1093, 1057, 1018, 872, 830 cm^{-1}. HRMS (CI-TOF): calcd. for 326.1437 $[M + H]^+$; found 326.1436.

(1*S)-1-(2-Bromophenyl)-2-[(1*S**,2*E*)-2-(4-methylbenzylidene)cyclopentyl]ethanol (4ad):** Column chromatography of the residue on silica gel (5:1 hexanes/Et_2O) yielded 0.195 g (52%) of the title compound as a yellow oil. R_f (5:1 hexanes/Et_2O) = 0.17. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.65 (dd, *J* = 7.8, 1.8 Hz, 1 H), 7.51 (dd, *J* = 8.4, 1.2 Hz, 1 H), 7.36 (td, *J* = 7.8, 1.2 Hz, 1 H), 7.20–7.19 (m, 2 H), 7.15–7.10 (m, 3 H), 6.28–6.27 (m, 1 H), 5.21–5.19 (m, 1 H), 2.96–2.92 (m, 1 H), 2.70–2.64 (m, 1 H), 2.62–2.60 (m, 1 H), 2.32 (s, 3 H), 2.10–2.06 (m, 2 H), 2.00–1.94 (m, 1 H), 1.93–1.90 (m, 1 H), 1.80–1.74 (m, 1 H), 1.73–1.67 (m, 1 H), 1.60–1.54 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.2, 144.2, 135.9, 135.4, 132.7, 128.9, 128.7, 128.0, 127.8, 127.1, 121.6, 120.7, 71.8, 43.3, 43.2, 31.5, 31.3, 24.9, 21.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3395, 3063, 3022, 2953, 2869, 1706, 1512, 1464, 1437, 1024, 752 cm^{-1}. HRMS (CI-TOF): calcd. for $C_{21}H_{23}OBr$ 370.0932 $[M + H]^+$; found 370.0919.

(1*S)-1-(2-Iodophenyl)-2-[(1*S**,2*E*)-2-(4-methylbenzylidene)cyclopentyl]ethanol (4ae):** Column chromatography of the residue on silica gel (4:1 hexanes/EtOAc) yielded 0.292 g (70%) of the title compound as a yellow oil. R_f (4:1 hexanes/EtOAc) = 0.38. ^{1}H NMR

(600 MHz, $CDCl_3$): δ = 7.80 (dd, J = 7.8, 1.2 Hz, 1 H), 7.61 (dd, J = 7.8, 1.8 Hz, 1 H), 7.40 (td, J = 7.2, 0.6 Hz, 1 H), 7.20–7.18 (m, 2 H), 7.11–7.10 (m, 2 H), 6.97 (td, J = 7.8, 1.8 Hz, 1 H), 6.27–6.26 (m, 1 H), 5.03–5.00 (m, 1 H), 2.98–2.92 (m, 1 H), 2.70–2.64 (m, 1 H), 2.62–2.56 (m, 1 H), 2.32 (s, 3 H), 2.11–2.06 (m, 1 H), 2.05 (dd, J = 3.6, 1.2 Hz, 1 H), 1.94–1.89 (m, 2 H), 1.76–1.69 (m, 2 H), 1.67–1.60 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.1, 146.9, 139.3, 135.9, 135.4, 129.1, 128.9, 128.7, 128.1, 126.9, 120.7, 97.2, 76.4, 43.4, 43.2, 31.5, 31.4, 24.9, 21.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3398, 3049, 3016, 2947, 2866, 1700, 1509, 1461, 1434, 1195, 1057, 1009, 869, 809, 755 cm^{-1}. HRMS (TOF-ESI): calcd. for $C_{21}H_{23}OINa$ 441.06851 [M + Na]$^+$; found 441.0685.

(1*S)-1-(2-Methoxyphenyl)-2-[(1*S**,2*E*)-2-(4-methylbenzylidene)-cyclopentyl]ethanol (4af):** Column chromatography of the residue on silica gel (4:1 hexanes/EtOAc) yielded 0.171 g (53%) of the title compound as a yellow oil. R_f (4:1 hexanes/EtOAc) = 0.27. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35 (dd, J = 7.8, 1.8 Hz, 1 H), 7.26 (td, J = 8.4, 1.8 Hz, 1 H), 7.20–7.19 (m, 2 H), 7.12–7.11 (m, 2 H), 6.98 (td, J = 7.2, 0.6 Hz, 1 H), 6.89 (dd, J = 8.4, 0.6 Hz, 1 H), 6.27–6.26 (m, 1 H), 5.03–5.00 (m, 1 H), 3.86 (s, 3 H), 2.91–2.86 (m, 1 H), 2.70–2.64 (m, 1 H), 2.60–2.54 (m, 2 H), 2.32 (s, 3 H), 2.22–2.17 (m, 1 H), 2.08–2.03 (m, 1 H), 1.90–1.84 (m, 1 H), 1.72–1.63 (m, 2 H), 1.43–1.37 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 156.3, 149.6, 135.9, 135.2, 132.9, 128.8, 128.2, 128.0, 126.5, 120.7, 120.3, 110.4, 69.5, 55.2, 43.0, 42.5, 32.6, 31.6, 24.8, 21.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3563, 3404, 3019, 2995, 2944, 2860, 2833, 1598, 1586, 1509, 1494, 1464, 1437, 1287, 1236, 1051, 1030, 869, 809, 752 cm^{-1}. HRMS (TOF-ESI): calcd. for $C_{22}H_{26}O_2Na$ 345.18261 [M + Na]$^+$; found 345.18250.

(1*S)-1-(4-Methoxyphenyl)-2-[(1*S**,2*E*)-2-(4-methylbenzylidene)-cyclopentyl]ethanol (4ag):** Column chromatography of the residue on silica gel (4:1 hexanes/EtOAc) yielded 0.103 g (32%) of the title compound as a yellow oil. R_f (4:1 hexanes/EtOAc) = 0.24. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34–7.32 (m, 2 H), 7.20–7.19 (m, 2 H), 7.13–7.11 (m, 2 H), 6.91–6.90 (m, 2 H), 6.28–6.27 (m, 1 H), 4.80–4.78 (m, 1 H), 3.81 (s, 3 H), 2.82–2.77 (m, 1 H), 2.68–2.62 (m, 1 H), 2.60–2.53 (m, 1 H), 2.32 (s, 3 H), 2.20–2.16 (m, 1 H), 2.00–1.96 (m, 1 H), 1.90–1.84 (m, 1 H), 1.83–1.80 (m, 1 H), 1.69–1.64 (m, 2 H), 1.40–1.33 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.1, 149.2, 137.4, 135.9, 135.4, 128.9, 128.1, 127.1, 120.6, 113.9, 72.7, 55.3, 44.5, 43.1, 31.9, 31.3, 24.8, 21.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3354, 3019, 2995, 2947, 2935, 2863, 2836, 1610, 1509, 1245, 1174, 1039, 839 cm^{-1}. HRMS (TOF-ESI): calcd. for $C_{22}H_{26}O_2Na$ 345.18283 [M + Na]$^+$; found 345.18250.

(1*S)-2-[(1*S**,2*E*)-2-(4-Methylbenzylidene)cyclopentyl]-1-(*p*-tolyl)-ethanol (4ah):** Column chromatography of the residue on silica gel (5:1 hexanes/Et_2O) yielded 0.189 g (62%) of the title compound as a yellow solid. R_f (5:1 hexanes/Et_2O) = 0.24, m.p. 75.8–78.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.30–7.29 (m, 2 H), 7.20–7.17 (m, 4 H), 7.12–7.11 (m, 2 H), 6.28–6.26 (m, 1 H), 4.81–4.79 (m, 1 H), 2.84–2.79 (m, 1 H), 2.68–2.63 (m, 1 H), 2.60–2.53 (m, 1 H), 2.36 (s, 3 H), 2.33 (s, 3 H), 2.20–2.16 (m, 1 H), 2.04–1.98 (m, 1 H), 1.91–1.84 (m, 1 H), 1.82 (d, J = 6.0 Hz, 1 H), 1.70–1.63 (m, 2 H), 1.40–1.34 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.2, 142.3, 137.2, 135.9, 135.4, 129.2, 128.9, 128.1, 125.7, 120.6, 73.0, 44.5, 43.0, 31.9, 31.4, 24.8, 21.1, 21.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3357, 3019, 2944, 2866, 1512, 1446, 1051, 809 cm^{-1}. HRMS (CI-TOF): calcd. for $C_{22}H_{26}O$ 306.1984 [M + H]$^+$; found 306.1975.

(1*S)-1-(2-Furyl)-2-[(1*S**,2*E*)-2-(4-methylbenzylidene)cyclopentyl]-ethanol (4ai):** Column chromatography of the residue on silica gel (5:1 hexanes/Et_2O) yielded 0.169 g (60%) of the title compound as a yellow oil. R_f (5:1 hexanes/Et_2O) = 0.26. Major diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40 (dd, J = 1.8, 1.2 Hz, 1 H), 7.22–7.20 (m, 2 H), 7.14–7.12 (m, 2 H), 6.35–6.34 (m, 1 H), 6.30–6.28 (m, 2 H), 4.86–4.82 (m, 1 H), 2.83–2.78 (m, 1 H), 2.68–2.63 (m, 1 H), 2.61–2.52 (m, 1 H), 2.33 (s, 3 H), 2.28–2.34 (m, 1 H), 1.98–1.81 (m, 4 H), 1.70–1.60 (m, 1 H), 1.37–1.31 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 157.1, 148.9, 141.9, 135.8, 135.5, 128.9, 128.1, 120.8, 110.2, 105.7, 66.5, 42.6, 40.7, 31.6, 31.3, 24.8, 21.1 ppm. Minor diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.31–6.30 (m, 1 H) ppm; the remaining signals are overlapped by the signals of the major diastereoisomer. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 156.6, 148.4, 142.1, 135.7, 135.5, 128.1, 121.1, 110.2, 106.2, 66.7, 42.9, 40.6, 32.2, 30.9. ppm; the remaining signals are overlapped by the signals of the major diastereoisomer. IR (KBr): $\tilde{\nu}_{max}$ = 3333, 3159, 3147, 3120, 3093, 3019, 2947, 2866, 1509, 1449, 1431, 1156, 1066, 1045, 1009, 881, 869, 812, 734 cm^{-1}. HRMS (TOF-MS-CI): calcd. for $C_{19}H_{22}O_2$ 282.1620 [M + H]$^+$; found 282.1612.

(1*S)-2-[(1*S**,2*E*)-2-(4-Methylbenzylidene)cyclopentyl]-1-(2-thienyl)ethanol (4aj):** Column chromatography of the residue on silica gel (5:1 hexanes/Et_2O) yielded 0.220 g (74%) of the title compound as a yellow oil. R_f (5:1 hexanes/Et_2O) = 0.20. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.27–7.26 (m, 1 H), 7.22–7.20 (m, 2 H), 7.14–7.12 (m, 2 H), 7.03–7.02 (m, 1 H), 7.00–6.98 (dd, J = 5.4, 3.6 Hz, 1 H), 6.30–6.29 (m, 1 H), 5.10–5.07 (m, 1 H), 2.86–2.81 (m, 1 H), 2.68–2.63 (m, 1 H), 2.61–2.55 (m, 1 H), 2.33 (s, 3 H), 2.30–2.25 (m, 1 H), 2.02–1.97 (m, 2 H), 1.91–1.81 (m, 2 H), 1.71–1.64 (m, 1 H), 1.41–1.35 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.2, 148.8, 135.8, 135.5, 128.9, 128.0, 126.7, 124.5, 123.6, 120.8, 68.9, 44.7, 42.9, 31.7, 31.3, 24.8, 21.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3386, 3081, 3066, 3046, 3022, 2995, 2947, 2869, 1506, 1036, 701 cm^{-1}. HRMS (TOF-ESI): calcd. for $C_{19}H_{22}ONaS$ 321.12833 [M + Na]$^+$; found 321.12836.

(2*S,3*E*)-1-[(1*S**,2*E*)-2-(4-Methylbenzylidene)cyclopentyl]-4-phenylbut-3-en-2-ol (4ak):** Column chromatography of the residue on silica gel (5:1 hexanes/Et_2O) yielded 0.098 g (31%) of the title compound as a yellow oil. R_f (5:1 hexanes/Et_2O) = 0.16. Major diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41–7.40 (m, 2 H), 7.34–7.31 (m, 2 H), 7.25–7.23 (m, 1 H), 7.22–7.20 (m, 2 H), 7.13–7.12 (m, 2 H), 6.63 (d, J = 15.6 Hz, 1 H), 6.32–6.25 (m, 2 H), 4.47–4.42 (m, 1 H), 2.84–2.79 (m, 1 H), 2.69–2.63 (m, 1 H), 2.60–2.54 (m, 1 H), 2.33 (s, 3 H), 2.06–1.95 (m, 2 H), 1.91–1.85 (m, 1 H), 1.70–1.60 (m, 3 H), 1.42–1.36 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.2, 136.7, 135.8, 135.4, 132.9, 130.0, 128.9, 128.6, 128.1, 127.7, 126.5, 120.7, 71.6, 42.7, 42.6, 32.0, 31.4 24.8, 21.1 ppm. Minor diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.61 (d, J = 15.6 Hz, 1 H) ppm; the remaining signals are overlapped by the signals of the major diastereoisomer. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.8, 132.3, 130.8, 128.1, 127.7, 126.5, 121.0, 72.1, 42.9, 42.3, 32.3, 31.0, 24.9. ppm; the remaining signals are overlapped by the signals of the major diastereoisomer. IR (KBr): $\tilde{\nu}_{max}$ = 3348, 3078, 3022, 2947, 2863, 1652, 1509, 1494, 1446, 1069, 1048, 967, 872, 806, 749, 682 cm^{-1}. HRMS (CI-TOF): calcd. for $C_{23}H_{27}O$ 319.2062 [M + H]$^+$; found 319.2054.

(2*S,3*E*)-1-[(1*S**,2*E*)-2-(4-Methylbenzylidene)cyclopentyl]non-3-en-2-ol (4al):** Column chromatography of the residue on silica gel (5:1 hexanes/Et_2O) yielded 0.193 g (62%) of the title compound as a yellow oil. R_f (5:1 hexanes/Et_2O) = 0.20. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.20–7.19 (m, 2 H), 7.13–7.11 (m, 2 H), 6.26–6.25 (m, 1 H), 5.72–5.67 (m, 1 H), 5.56–5.52 (m, 1 H), 4.23–4.19 (m, 1 H), 2.77–2.72 (m, 1 H), 2.67–2.62 (m, 1 H), 2.60–2.53 (m, 1 H), 2.33 (s, 3 H), 2.04 (q, J = 7.4 Hz, 2 H), 2.00–1.95 (m, 1 H), 1.94–1.90 (m, 1 H), 1.88–1.83 (m, 1 H), 1.69–1.61 (m, 1 H), 1.51–1.47 (m, 2

H), 1.41–1.36 (m, 2 H), 1.34–1.26 (m, 5 H), 0.89 (t, J = 6.6 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.4, 135.9, 135.3, 133.4, 132.0, 128.9, 128.0, 120.5, 71.6, 42.7, 42.7, 32.2, 32.0, 31.4, 31.3, 28.9, 24.8, 22.5, 21.1, 14.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3354, 3084, 3019, 2956, 2923, 2866, 2857, 1512, 1470, 1455, 973, 869, 812 cm^{-1}. HRMS (TOF-MS-CI): calcd. for $C_{22}H_{32}O$ 312.2453 [M + H]$^+$; found 312.2458.

(1*S)-1-Cyclohexyl-2-[(1*S**,2*E*)-2-(4-methylbenzylidene)cyclopentyl]ethanol (4am):** Column chromatography of the residue on silica gel (5:1 hexanes/Et_2O) yielded 0.184 g (62%) of the title compound as a colorless solid, m.p. 62.5–64.0 °C. R_f (5:1 hexanes/Et_2O) = 0.21. Major diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.21–7.20 (m, 2 H), 7.13–7.12 (m, 2 H), 6.27–6.26 (m, 1 H), 3.50–3.47 (m, 1 H), 2.81–2.76 (m, 1 H), 2.70–2.63 (m, 1 H), 2.60–2.54 (m, 1 H), 2.33 (s, 3 H), 2.00–1.96 (m, 1 H), 1.88–1.83 (m, 2 H), 1.80–1.76 (m, 3 H), 1.73–1.61 (m, 3 H), 1.50–1.46 (m, 1 H), 1.45–1.40 (m, 1 H), 1.38–1.33 (m, 1 H), 1.30–1.21 (m, 3 H), 1.20–1.11 (m, 1 H), 1.10–1.01 (m, 2 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.8, 135.9, 135.3, 128.9, 128.0, 120.3, 74.6, 44.5, 42.8, 39.7, 31.7, 31.6, 29.1, 28.1, 26.6, 26.3, 26.2, 24.8, 21.1 ppm. Minor diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.30–6.29 (m, 1 H), 3.60–3.58 (m, 1 H) ppm; the remaining signals are overlapped by the signals of the major diastereoisomer. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.2, 135.8, 135.4, 128.1, 120.9, 74.8, 43.7, 43.6, 39.1, 32.6, 30.7, 29.5, 27.0, 26.5, 26.3, 24.7 ppm; the remaining signals are overlapped by the signals of the major diastereoisomer. IR (KBr): $\tilde{\nu}_{max}$ = 3431, 3386, 3087, 3052, 3025, 2998, 2920, 2851, 1512, 1440, 1425, 1404, 1042, 982, 875, 809 cm^{-1}. HRMS (TOF-MS-CI): calcd. for $C_{21}H_{30}O$ 298.2297 [M + H]$^+$; found 298.2292.

(1*S)-1-(2-Iodophenyl)-2-[(1*S**,2*E*)-2-pentylidenecyclopentyl]ethanol (4be):** Column chromatography of the residue on silica gel (5:1 hexanes/Et_2O) yielded 0.200 g (52%) of the title compound as a yellow oil. R_f (5:1 hexanes/Et_2O) = 0.32. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.78 (dd, J = 7.8, 1.2 Hz, 1 H), 7.57 (dd, J = 7.8, 1.8 Hz, 1 H), 7.39–7.36 (m, 1 H), 6.95 (td, J = 7.2, 1.8 Hz, 1 H), 5.21–5.18 (m, 1 H), 4.96 (dd, J = 10.2, 1.8 Hz, 1 H), 2.72–2.67 (m, 1 H), 2.34–2.29 (m, 1 H), 2.26–2.20 (m, 1 H), 2.09 (br. s, 1 H), 2.05–2.00 (m, 1 H), 1.98–1.94 (m, 2 H), 1.80–1.75 (m, 2 H), 1.64–1.48 (m, 3 H), 1.31–1.28 (m, 4 H), 0.90–0.87 (m, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 147.0, 146.3, 139.3, 129.0, 128.6, 126.8, 120.4, 97.2, 76.5, 43.2, 41.3, 32.4, 31.9, 29.1, 29.0, 24.1, 22.4, 14.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3357, 3058, 2953, 2869, 2854, 1461, 1434, 1060, 1012, 752 cm^{-1}. HRMS (CI-TOF): calcd. for $C_{18}H_{25}OI$ 384.0950 [M + H]$^+$; found 384.0940.

(1*S)-2-{(1*S**,2*E*)-2-[3-(*tert*-Butyldimethylsilyloxy)propylidene]-cyclopentyl}-1-(2-iodophenyl)ethanol (4ce):** Column chromatography of the residue on silica gel (10:1 hexanes/Et_2O) yielded 0.257 g (53%) of the title compound as a yellow oil. R_f (5:1 hexanes/Et_2O) = 0.24. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.78 (dd, J = 7.8, 1.2 Hz, 1 H), 7.56 (dd, J = 7.8, 1.8 Hz, 1 H), 7.37 (t, J = 7.2 Hz, 1 H), 6.95 (td, J = 7.8, 1.8 Hz, 1 H), 5.20–5.18 (m, 1 H), 4.97–4.94 (m, 1 H), 3.58 (t, J = 6.6 Hz, 2 H), 2.71–2.70 (m, 1 H), 2.36–2.32 (m, 1 H), 2.30–2.25 (m, 1 H), 2.21 (q, J = 7.8 Hz, 2 H), 2.09 (d, J = 3.6 Hz, 1 H), 2.05–2.00 (m, 1 H), 1.84–1.75 (m, 2 H), 1.64–1.58 (m, 2 H), 1.54–1.50 (m, 1 H), 0.87 (s, 9 H), 0.03 (s, 6 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.7, 147.0, 139.3, 129.0, 128.6, 126.8, 116.0, 97.2, 76.4, 63.0, 43.2, 41.5, 33.3, 32.3, 29.1, 26.0, 24.0, 18.4, –5.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3416, 2953, 2932, 2896, 2860, 2881, 1461, 1257, 1096, 1012, 836, 779, 752 cm^{-1}. HRMS (TOF-ESI): calcd. for $C_{22}H_{35}O_2INaSi$ 509.13427 [M + Na]$^+$; found 509.13432.

(1*S)-1-(2-Iodophenyl)-2-[(1*S**,2*E*)-2-(pentylidene)cyclohexyl]-ethanol (4de):** Column chromatography of the residue on silica gel (50:1–5:1 hexanes/Et_2O) yielded 0.250 g (63%) of the title compound as a yellow oil. R_f (5:1 hexanes/Et_2O) = 0.35. Major diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.80 (dd, J = 7.8, 1.2 Hz, 1 H), 7.54 (dd, J = 7.8, 1.2 Hz, 1 H), 7.37 (td, J = 7.2, 0.6 Hz, 1 H), 6.95 (td, J = 7.8, 1.8 Hz, 1 H), 5.25 (t, J = 7.2 Hz, 1 H), 4.94 (td, J = 9.6, 3.0 Hz, 1 H), 2.48–2.44 (m, 1 H), 2.37 (d, J = 2.4 Hz, 1 H), 2.25–2.16 (m, 2 H), 2.04–2.01 (m, 2 H), 1.85–1.74 (m, 3 H), 1.71–1.67 (m, 1 H), 1.65–1.60 (m, 1 H), 1.59–1.50 (m, 2 H), 1.46–1.39 (m, 1 H), 1.33–1.30 (m, 4 H), 0.91–0.98 (m, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 146.8, 142.9, 139.2, 128.9, 128.6, 126.9, 122.0, 97.4, 76.9, 42.6, 40.9, 33.4, 32.3, 28.1, 26.8, 26.4, 23.4, 22.4, 14.0 ppm. Minor diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.30 (t, J = 7.2 Hz, 1 H), 4.84 (td, J = 10.2, 3.0 Hz, 1 H), 2.56–2.52 (m, 1 H) ppm; the remaining signals are overlapped by the signals of the major diastereoisomer. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 140.3, 127.2, 123.2, 41.0, 40.3, 34.2, 32.5, 28.0, 25.7, 22.6, 22.4, 14.0 ppm; the remaining signals are overlapped by the signals of the major diastereoisomer. IR (KBr): $\tilde{\nu}_{max}$ = 3398, 3055, 2953, 2923, 2851, 1458, 1431, 1057, 1003, 758 cm^{-1}. HRMS (CI-TOF): calcd. for $C_{19}H_{26}OI$ 397.1028 [M + H]$^+$; found 397.1032.

(1*S)-2-[(4*S**,3*Z*)-*N*-Benzyl-3-(4-methylbenzylidene)pyrrolidin-4-yl]-1-(2-iodophenyl)ethanol (4ee):** Column chromatography of the residue on silica gel (2:1 hexanes/Et_2O) yielded 0.162 g (32%) of the title compound as a yellow oil. R_f (5:1 hexanes/Et_2O) = 0.13. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74 (dd, J = 7.8, 1.2 Hz, 1 H), 7.65 (dd, J = 7.8, 1.8 Hz, 1 H), 7.37–7.34 (m, 5 H), 7.30–7.28 (m, 1 H), 7.13–7.10 (m, 4 H), 6.92 (td, J = 7.2, 1.2 Hz, 1 H), 6.55–6.54 (m, 1 H), 4.90 (dd, J = 10.8, 1.2 Hz, 1 H), 4.04 (d, J = 15.0 Hz, 1 H), 3.96 (d, J = 13.2 Hz, 1 H), 3.64 (d, J = 12.6 Hz, 1 H), 3.15 (d, J = 9.6 Hz, 1 H), 2.68–2.65 (m, 1 H), 2.32 (s, 3 H), 2.20–2.16 (m, 1 H), 1.65–1.60 (m, 2 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 147.4, 140.4, 138.9, 137.3, 136.3, 134.5, 129.1, 128.8, 128.7, 128.6, 128.4, 128.0, 127.5, 127.4, 123.8, 97.2, 73.7, 60.4, 59.7, 58.0, 44.0, 42.6, 21.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3156, 3087, 3058, 3022, 2917, 2803, 1509, 1455, 1434, 1120, 1075, 1027, 1012, 896, 806, 752, 689 cm^{-1}. HRMS (TOF-ESI): calcd. for $C_{27}H_{29}ONI$ 510.12873 [M + H]$^+$; found 510.12883.

(1*S)-2-[(4*S**,3*Z*)-*N*-Benzyl-3-(4-methylbenzylidene)pyrrolidin-4-yl]-1-(2-bromophenyl)ethanol (4ed):** Column chromatography of the residue on silica gel (2:1 hexanes/Et_2O) yielded 0.253 g (55%) of the title compound as a yellow solid, m.p. 49.3–50.1 °C. R_f (2:1 hexanes/Et_2O) = 0.39. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 (dd, J = 7.2, 1.2 Hz, 1 H), 7.45 (dd, J = 7.8, 1.2 Hz, 1 H), 7.38–7.28 (m, 7 H), 7.14–7.12 (m, 2 H), 7.10–7.08 (m, 2 H), 7.07 (dd, J = 7.8, 1.8 Hz, 1 H), 6.48–6.47 (m, 1 H), 5.09 (d, J = 10.2 Hz, 1 H), 4.02 (d, J = 14.4 Hz, 1 H), 3.94 (d, J = 12.6 Hz, 1 H), 3.66 (d, J = 12.6 Hz, 1 H), 3.22–3.18 (m, 2 H), 3.13 (d, J = 9.6 Hz, 1 H), 2.67 (t, J = 7.2 Hz, 1 H), 2.33 (s, 3 H), 2.24–2.20 (m, 1 H), 1.69–1.65 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 144.7, 140.8, 137.4, 136.3, 134.7, 132.3, 129.2, 128.8, 128.7, 128.2, 127.9, 127.6, 127.5, 123.5, 121.5, 69.2, 60.5, 59.8, 58.1, 43.9, 42.6, 21.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3055, 3025, 3004, 2977, 2950, 2908, 2872, 2854, 2812, 2744, 1512, 1464, 1440, 1374, 1362, 1347, 1260, 1099, 800, 752, 707, 513 cm^{-1}. HRMS (FTMS-ESI): calcd. for $C_{27}H_{29}ONBr$ 462.14274 [M + H]$^+$; found 462.14270.

(1*S)-2-[(4*S**,3*Z*)-*N*-Benzyl-3-(benzylidene)pyrrolidin-4-yl]-1-(2-iodophenyl)ethanol (4fe):** Column chromatography of the residue on silica gel (2:1 hexanes/EtOAc) yielded 0.282 g (57%) of the title compound as a yellow solid, m.p. 55.7–57.0 °C. R_f (2:1 hexanes/Et_2O) = 0.40. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.75 (dd, J = 7.8, 1.2 Hz, 1 H), 7.65 (dd, J = 7.8, 1.2 Hz, 1 H), 7.38–7.28 (m, 8 H),

7.23–7.18 (m, 3 H), 6.20 (td, J = 7.8, 1.8 Hz, 1 H), 6.58 (s, 1 H), 4.92–4.90 (m, 1 H), 4.05 (d, J = 15 Hz, 1 H), 3.94 (d, J = 12.6 Hz, 1 H), 3.68 (d, J = 12.6 Hz, 1 H), 3.24–3.19 (m, 2 H), 3.14 (d, J = 9.0 Hz, 1 H), 2.68 (t, J = 7.8 Hz, 1 H), 2.22–2.18 (m, 1 H), 1.67–1.63 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 147.5, 141.6, 139.0, 137.4, 137.3, 128.9, 128.7, 128.6, 128.5, 128.4, 128.1, 127.5, 127.4, 126.5, 124.0, 97.2, 73.8, 60.4, 59.7, 58.1, 44.0, 42.8 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3084, 3058, 3025, 2938, 2902, 2806, 1494, 1455, 1437, 1117, 1078, 1015, 914, 755, 695 cm^{-1}. HRMS (CI-TOF): calcd. for $C_{26}H_{27}NOI$ 496.1137 $[M + H]^+$; found 496.1142.

General Procedure for the Synthesis of Iodinated Alcohols 10: *n*BuLi (1.6 M in hexanes, 1.25 mL, 2.00 mmol) was added dropwise within 5 min to a solution of bis(cyclopentadienyl)zirconium dichloride (0.292 g, 1.00 mmol) in dry THF (5 mL) cooled to –78 °C and the reaction mixture was stirred for 1 h at the same temperature. Enyne (1.00 mmol) was added and the reaction mixture was gradually warmed to 25 °C. After 3 h, freshly distilled aldehyde (1.00 mmol) was added at 0 °C and the reaction mixture stirred for 12 h. CuCl (0.018 g, 0.2 mmol) was then added followed by the addition of solid iodine (0.190 g, 1.5 mmol). After stirring at 25 °C for 24 h the reaction mixture was quenched with 1 N HCl (10 mL) and extracted with Et_2O (2 × 20 mL). The combined organic phases were washed with a saturated solution of Na_2SO_3 (20 mL), water (20 mL), and brine (30 mL), dried with $MgSO_4$, and the solution was filtered and concentrated under reduced pressure. Purification of residue by column chromatography yielded the corresponding iodinated alcohol.

(1*S)-1-(2-Chlorophenyl)-2-{(1*S**,2*Z*)-2-[iodo(4-tolyl)methylene]-cyclopentyl}ethanol (10a):** Column chromatography of the residue on silica gel (5:1 hexanes/Et_2O) yielded 0.161 g (35%) of the title compound as a colorless solid, m.p. 142.2–145.0 °C. R_f (5:1 hexanes/Et_2O) = 0.20. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.69 (d, J = 12 Hz, 1 H), 7.34–7.31 (m, 2 H), 7.21 (t, J = 12 Hz, 1 H), 7.15–7.14 (m, 2 H), 7.10–7.08 (m, 2 H), 5.25 (d, J = 10.2 Hz, 1 H), 3.17–3.14 (m, 1 H), 2.38–2.32 (m, 4 H), 2.30–2.24 (m, 1 H), 2.22–2.12 (m, 2 H), 2.03–1.98 (m, 1 H), 1.97–1.92 (m, 1 H), 1.90–1.83 (m, 1 H), 1.82–1.77 (m, 1 H), 1.75–1.71 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.5, 142.4, 141.6, 137.3, 131.3, 129.4, 128.8, 128.6, 128.3, 127.2, 126.9, 89.8, 69.5, 47.8, 41.0, 32.6, 30.0, 25.7, 21.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3569, 3461, 3060, 3040, 3019, 2956, 2941, 2887, 2866, 2839, 1509, 1467, 1443, 1048, 1036, 794, 770, 755 cm^{-1}. HRMS (TOF-ESI): calcd. for $C_{21}H_{22}OClI$ 452.0404 $[M + H]^+$; found 452.0403.

(1*S)-1-(2-Bromophenyl)-2-{(1*S**,2*Z*)-2-[iodo(4-tolyl)methylene]-cyclopentyl}ethanol (10b):** Column chromatography of the residue on silica gel (5:1 hexanes/Et_2O) yielded 0.203 g (41%) of the title compound as a yellow oil. R_f (5:1 hexanes/Et_2O) = 0.20. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70–7.68 (dd, J = 7.8, 1.8 Hz, 1 H), 7.52–7.50 (dd, J = 7.8, 1.2 Hz, 1 H), 7.38 (td, J = 7.8, 1.2 Hz, 1 H), 7.16–7.13 (m, 3 H), 7.10–7.08 (m, 2 H), 5.21–5.18 (m, 1 H), 3.18–3.14 (m, 1 H), 2.39–2.33 (m, 1 H), 2.32 (s, 3 H), 2.30–2.24 (m, 1 H), 2.18 (d, J = 4.8 Hz, 1 H), 2.12–2.08 (m, 1 H), 2.0–1.97 (m, 2 H), 1.91–1.84 (m, 1 H), 1.83–1.77 (m, 1 H), 1.76–1.71 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.5, 143.9, 141.6, 137.3, 132.6, 128.8, 128.7, 128.6, 127.8, 127.2, 121.4, 89.8, 71.7, 47.8, 41.0, 32.5, 29.9, 25.8, 21.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3578, 3455, 3052, 3016, 2956, 2944, 2866, 1464, 1440, 1054, 1039, 1021, 785, 770, 755 cm^{-1}. HRMS (TOF-ESI): calcd. for $C_{21}H_{22}OBrINa$ 518.97929 $[M + Na]^+$; found 518.97909.

(1*S)-1-(2-Iodophenyl)-2-{(1*S**,2*Z*)-2-[iodo(4-tolyl)methylene]-cyclopentyl}ethanol (10c):** Column chromatography of the residue on silica gel (5:1 hexanes/Et_2O) yielded 0.271 g (50%) of the title compound as a colorless solid, m.p. 111.6–112.4 °C. R_f (5:1 hexanes/Et_2O) = 0.20. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.80 (dd, J = 7.8, 1.2 Hz, 1 H), 7.65 (dd, J = 7.8, 1.8 Hz, 1 H), 7.40 (td, J = 7.8, 1.2 Hz, 1 H), 7.15–7.13 (m, 2 H), 7.10–7.08 (m, 2 H), 6.98 (td, J = 7.2, 1.8 Hz, 1 H), 5.03–5.00 (m, 1 H), 3.20–3.16 (m, 1 H), 2.40–2.34 (m, 1 H), 2.32 (s, 3 H), 2.30–2.24 (m, 1 H), 2.21 (d, J = 4.2 Hz, 1 H), 2.09–2.03 (m, 2 H), 2.00–1.94 (m, 1 H), 1.93–1.87 (m, 1 H), 1.84–1.78 (m, 1 H), 1.70 (td, J = 14.4, 2.4 Hz, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.5, 146.6, 141.6, 139.3, 137.3, 129.1, 128.8, 128.7, 128.5, 127.0, 96.9, 89.7, 76.1, 47.7, 41.0, 32.5, 29.9, 25.8, 21.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3560, 3443, 3049, 3019, 2950, 2914, 2872, 2833, 1461, 1437, 1057, 1042, 1006, 791, 770, 755 cm^{-1}. HRMS (TOF-ESI): calcd. for $C_{21}H_{22}OI$ 543.9760 $[M + H]^+$; found 543.9753.

(1*S)-1-(2-Bromophenyl)-2-[(1*S**,2*Z*)-2-(1-iodopentylidene)cyclopentyl]ethanol (10d):** Column chromatography of the residue on silica gel (5:1 hexanes/Et_2O) yielded 0.183 g (41%) of the title compound as a yellow oil. R_f (5:1 hexanes/Et_2O) = 0.30. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.64 (dd, J = 7.2, 1.2 Hz, 1 H), 7.49 (dd, J = 8.4, 1.2 Hz, 1 H), 7.35 (td, J = 8.4, 1.2 Hz, 1 H), 7.12 (td, J = 7.8, 1.8 Hz, 1 H), 5.13–5.11 (m, 1 H), 3.02–2.98 (m, 1 H), 2.44–2.32 (m, 4 H), 1.99–1.79 (m, 5 H), 1.63 (td, J = 14.4, 2.4 Hz, 1 H), 1.50–1.39 (m, 2 H), 1.31–1.24 (m, 2 H), 0.89 (t, J = 7.8 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 150.9, 143.9, 132.6, 128.6, 127.8, 127.2, 121.4, 97.8, 71.8, 47.8, 41.7, 40.6, 31.4, 30.8, 29.5, 25.3, 21.5, 14.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3452, 3055, 2953, 2929, 2869, 1706, 1467, 1437, 1060, 1045, 1024, 931, 755 cm^{-1}. HRMS (CI-TOF): calcd. for $C_{18}H_{23}OBrI$ 460.9977 $[M + H]^+$; found 460.9975.

A Typical Example of the Insertion/cyclization Reaction − Synthesis of (9*S,10a*S**)-4-(4-Tolyl)-1,2,3,9,10,10a-hexahydrobenzo[*f*]azulen-9-ol (5a):** (Table 3, entry 8). *n*BuLi (1.6 M in hexanes, 1.25 mL, 2.00 mmol) was added dropwise within 5 min to a solution of bis(cyclopentadienyl)zirconium dichloride (0.292 g, 1.00 mmol) in dry THF (5 mL) cooled to –78 °C and the reaction mixture was stirred for 1 h at the same temperature. Then **1a** (1.00 mmol, 0.184 g) was added and the reaction mixture was gradually warmed to 25 °C. After 3 h 2-iodobenzaldehyde (0.232 g, 1.00 mmol) was added at 0 °C and the reaction mixture was stirred for 12 h. Then it was cooled to –15 °C and CuCl (0.148 g, 1.50 mmol) was added. After stirring for 30 min JohnPhos (1.19 g, 4.00 mmol), [Pd(PPh_3)$_4$] (0.058 g, 0.05 mmol), and DMPU (0.360 mL, 3.00 mmol) were added and the reaction mixture was stirred at 50 °C for 12 h. After cooling to 25 °C, the reaction mixture was quenched with 1 N HCl (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with a saturated solution of $NaHCO_3$ (20 mL), water (2 × 20 mL), and brine (20 mL), dried with $MgSO_4$, and then the solution was filtered and concentrated under reduced pressure. Column chromatography of the residue on silica gel (6:1 hexanes/EtOAc) yielded 133 mg (46%) of the title compound as a yellow oil. R_f (6:1 hexanes/EtOAc) = 0.13. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70–7.69 (m, 1 H), 7.30–7.27 (m, 1 H), 7.19–7.16 (m, 1 H), 7.15–7.13 (m, 2 H), 7.10–7.08 (m, 2 H), 6.88 (dd, J = 7.2, 1.2 Hz, 1 H), 4.96–4.94 (m, 1 H), 2.68–2.63 (m, 1 H), 2.51–2.47 (m, 1 H), 2.43–2.40 (m, 2 H), 2.37 (s, 3 H), 2.25–2.18 (m, 1 H), 1.94 (br. s, 1 H), 1.88–1.82 (m, 1 H), 1.80–1.72 (m, 2 H), 1.57–1.51 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 147.3, 142.8, 140.5, 139.3, 136.0, 130.7, 129.4, 128.6, 128.4, 126.2, 126.2, 122.3, 70.4, 50.3, 39.4, 33.2, 32.8, 25.6, 21.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3330, 3058, 3019, 2935, 2860, 1706, 1509, 1443, 1069, 1039, 818, 761, 752 cm^{-1}. HRMS (CI-TOF): calcd. for $C_{21}H_{23}O$ 291.1749 $[M + H]^+$; found 291.1744.

(9*S,10a*S**)-2-Benzyl-4-phenyl-1,2,3,9,10,10a-hexahydrobenzo-[4,5]cyclohepta[1,2-*c*]pyrrol-9-ol (5e):** *n*BuLi (1.6 M in hexanes, 1.25 mL, 2.00 mmol) was added dropwise within 5 min to a solution of bis(cyclopentadienyl)zirconium dichloride (0.292 g, 1.00 mmol) in dry THF (5 mL) cooled to –78 °C and the reaction mixture was stirred for 1 h at the same temperature. Then **1f** (1.00 mmol, 0.261 g) was added and the reaction mixture was gradually warmed to 25 °C. After 3 h 2-iodobenzaldehyde (0.232 g, 1.00 mmol) was added at 0 °C and the reaction mixture was stirred for 12 h. Then it was cooled to –15 °C and CuCl (0.109 g, 1.10 mmol) was added. After stirring for 30 min JohnPhos (0.372 g, 1.25 mmol), $[Pd(PPh_3)_4]$ (0.058 g, 0.05 mmol), and DMPU (0.360 mL, 3.00 mmol) were added and the reaction mixture was stirred at 50 °C for 12 h. After cooling to 25 °C, the reaction mixture was quenched with brine (20 mL) and 1 N HCl (10 mL). Then a saturated solution of $NaHCO_3$ (40 mL) was added and reaction mixture was extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with water (2 × 20 mL) and brine (20 mL), dried with $MgSO_4$, and then the solution was filtered and concentrated under reduced pressure. Column chromatography of the residue on silica gel (2:1 hexanes/EtOAc) yielded 117 mg (32%) of the title compound as a yellow oil. R_f (2:1 hexanes/EtOAc) = 0.37. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.72–7.70 (m, 1 H), 7.36–7.35 (m, 2 H), 7.32–7.27 (m, 5 H), 7.25–7.22 (m, 2 H), 7.16 (td, J = 7.2, 1.2 Hz, 1 H), 7.13–7.11 (m, 2 H), 6.85 (dd, J = 7.8, 1.2 Hz, 1 H), 5.07–5.04 (m, 1 H), 3.78 (d, J = 12.6 Hz, 1 H), 3.67 (d, J = 14.4 Hz, 1 H), 3.57 (d, J = 13.2 Hz, 1 H), 3.28 (d, J = 14.4 Hz, 1 H), 2.75–2.68 (m, 2 H), 2.45–2.41 (m, 1 H), 2.37–2.35 (m, 1 H), 2.27–2.21 (m, H), 2.00 (v. br. s, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 143.4, 142.9, 141.2, 139.2, 138.8, 130.6, 129.1, 128.6, 128.5, 128.3, 128.0, 127.0, 126.7, 126.6, 126.3, 122.7, 70.0, 60.2, 59.6, 59.2, 50.1, 39.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3060, 3022, 2926, 2854, 2782, 2729, 1721, 1494, 1476, 1455, 1440, 1341, 1263, 1066, 1045, 776, 758, 701 cm^{-1}. HRMS (TOF-MS-CI): calcd. for $C_{26}H_{25}NO$ 367.1936 $[M + H]^+$; found 367.1939.

Supporting Information (see footnote on the first page of this article): Further experimental details, crystallographic data, and ^{1}H and ^{13}C spectra of all prepared compounds.

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