

Zirconium-Mediated Intramolecular Coupling of Terminal Alkynes and Their Subsequent Carbonylation: Novel Synthesis of Seven- and Eight-Membered Heterocycles

José Barluenga,* Roberto Sanz, and Francisco J. Fañanás

Dedicated to Professor Dieter Seebach on the occasion of his 60th birthday

Abstract: The development of a new method for the intramolecular coupling of terminal alkynes and for the synthesis of seven- and eight-membered benzoheterocycles is reported. The key steps involve the generation of zirconocene–alkyne complexes from 2-bromoalkenes and the subsequent intramolecular carbometalation of olefins or acetylides. The 8-unsubstituted zirconabicyclopentenes were carbonylated to afford unexpected products and allow access to polyfunctionalized molecules from simple starting materials.

Keywords

benzazocines · benzazepines ·
carbonylations · cyclizations ·
zirconium

Introduction

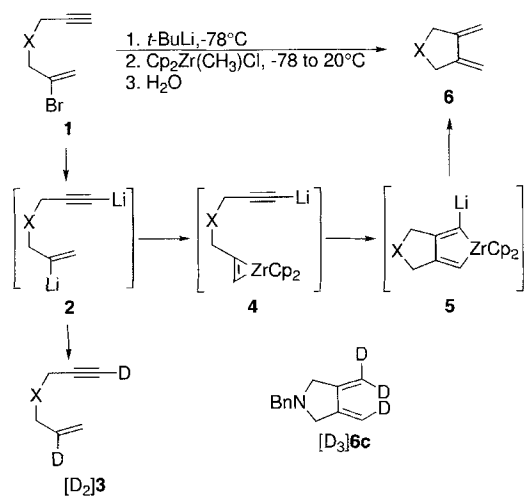
The reductive coupling of two unsaturated molecules by the use of low-valent metals from the two extremes of the transition series (Ni, Ti, Zr) is a very useful synthetic method.^[1] The unsaturated substrates undergo a formal reductive coupling, and the intermediate metallacycle can then be transformed into a variety of interesting products.^[2] In the last few years, organozirconium compounds have been developed into useful reagents and intermediates for organic synthesis, and transformations mediated by them have gained increasing recognition as a powerful means for achieving reaction selectivity.^[3] In particular, the cyclization of enynes and diynes, using a zirconocene equivalent prepared from zirconocene dichloride and butyllithium,^[4] affords zirconabicycles which are fairly stable. Treatment of these metallabicycles with protons, halogens,^[5] isocyanides,^[6] or oxygen^[7] produces mono- and bicyclic organic compounds with high regio- and stereoselectivity. Electrophilic cleavage with various main-group halides affords a number of unusual heterocycles.^[8] Of special interest is the direct and facile generation of conjugated bicyclic enones by carbonylation of these intermediates.^[2c, 4] This method provides an easy way of synthesizing cyclopentenone skeletons from simple starting materials through a formal [2 + 2 + 1] process. It has been successfully used as the key step in the synthesis of several natural products.^[9] Despite the large number of carbocycles that have been obtained in this

way, few nitrogen heterocycles have been synthesized.^[10] However, a major restriction of these reactions is that substrates containing terminal alkynes cannot be used, presumably owing to the ready oxidative addition of the electron-rich metallocene to the acidic acetylene hydrogen.^[11] Moreover, this type of direct cyclization reaction has a critical limitation for the ring size.^[12] While a convenient zirconium-mediated preparation of five or six-membered ring compounds from nonconjugated dienes, enynes, or diynes has been described,^[2a, c] only one example^[11] of the formation of a seven-membered ring from 2,9-undecadiyne and another of an eight-membered ring derivatives^[13] from stereodefined 1,4,6,9-decatetraenes have been reported. To the best of our knowledge, only five and six-membered^[14] *N*-heterocycles have been formed so far by means of a reductive coupling promoted by a metallocene. Moreover, seven- and eight-membered nitrogenated heterocycles possess potent biological activity and are attractive synthetic targets.^[15] On the other hand, the formation of metallocene η^2 -alkene,^[16] -heteroalkene,^[17] -alkyne,^[18] -aryne^[19] or allene^[20] complexes by a β -hydrogen activation process followed by the insertion of unactivated unsaturated molecules is an effective method of producing zirconacyclopentanoids, which may then undergo subsequent reaction. We have recently reported the regioselective zirconium-mediated insertion of alkynes, alkenes, and electron-rich alkenes in a η^2 -prop-2-ynylamine zirconocene complex.^[21] We now report on the first zirconium-promoted intramolecular coupling of terminal alkynes, as well as their carbonylation and subsequent reaction with electrophiles to form a new type of zirconabicyclopentenes.^[22] A new method of synthesizing seven- and eight-membered *N*-heterocycles has also been developed based on this methodology.

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Results and Discussion

Intramolecular coupling of terminal alkynes: Treatment of 2-bromoallylalkynyl compounds **1a-c**^[23] with 2 equiv^[24] of *tert*-butyllithium in diethyl ether at -78°C gave the dianions **2**, which were characterized by deuterolysis to give dideuterated compounds $[\text{D}_2]\mathbf{3}$. Their reaction with bis(cyclopentadienyl)zirconium methyl chloride at temperatures ranging between -78 and 20°C afforded, after the addition of water, the exocyclic dienes **6** in good yields (Scheme 1 and Table 1). The



Scheme 1. Intramolecular cyclization of terminal alkynes.

Table 1. Cyclization of terminal alkynes **1** to give products **6**.

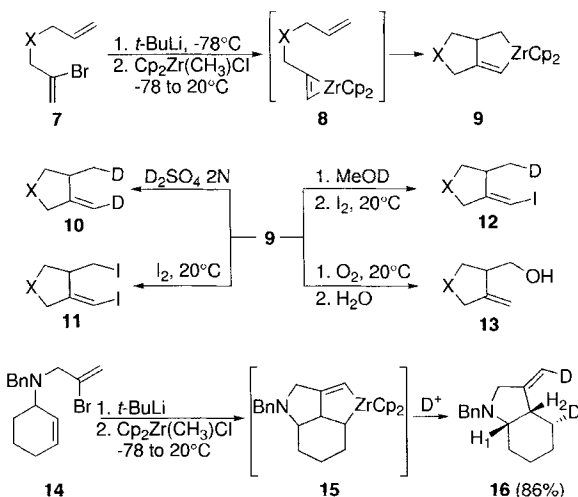
Starting material	X	Exocyclic Diene	Yield (%) [a]
1a	9-Flu [b]	6a	65
1b	PhN	6b	73
1c	PhCH ₂ N	6c	71
1c	PhCH ₂ N	$[\text{D}_3]\mathbf{6c}$	70

[a] Isolated yield based on the starting material **1**. [b] 9-Flu = 9-fluorenyl.

formation of these compounds can be understood by assuming an intramolecular insertion of the acetylide moiety into the zirconacycloprenes **4** leading to zirconacyclopentadienes **5**, which generate **6** on hydrolysis. In the case of **1c**, workup of the reaction mixture with deuterated sulfuric acid gave the trideuterated pyrrolidine $[\text{D}_3]\mathbf{6c}$, the structure of which was confirmed by ¹H NMR and MS. The key step in the reaction seems to be an insertion of the acetylide instead of nucleophilic attack to generate a zirconate,^[25] presumably prevented by the geometry of the triple bond. As far as we know, this is the first example of intramolecular coupling of terminal alkynes mediated by zirconium.

On the other hand, treatment of allyl-2-bromoallyl substrates **7** with *t*BuLi and then with bis(cyclopentadienyl)zirconium methyl chloride, under the same reaction conditions as described above, led to zirconabicyclopentenes **9**, by intramolecular carbometalation of the double bond by the zirconacycloprenes **8**. These represent a novel type of zirconabicyclopentene, although the 8-substituted homologues are known.^[2c] Complex

9b has been isolated and spectroscopically characterized. However, we found that it was not necessary to isolate any organometallic intermediates. Compounds **9** were chemically characterized by deuterolysis, iodolysis and oxidation to give pyrrolidines and fluorenyl derivatives **10-13** in good yields. In this context, the reaction of the cyclohexenyl amine **14** gave perhydroindole **16** as a single isomer by the deuterolysis of the tricyclic intermediate **15**. The NOE observed between protons H₁ and H₂ of **16** indicates a *cis* ring-junction and, in agreement with the literature,^[2c, 10d] the deuterium in the cyclohexenyl moiety must be *trans* to the ring junction protons. This result shows that high regio- and stereoselectivity are possible with this reaction. The results obtained are summarized in Scheme 2 and Table 2.



Scheme 2. Synthesis of 8-unsubstituted zirconabicyclopentenes and reaction with electrophiles.

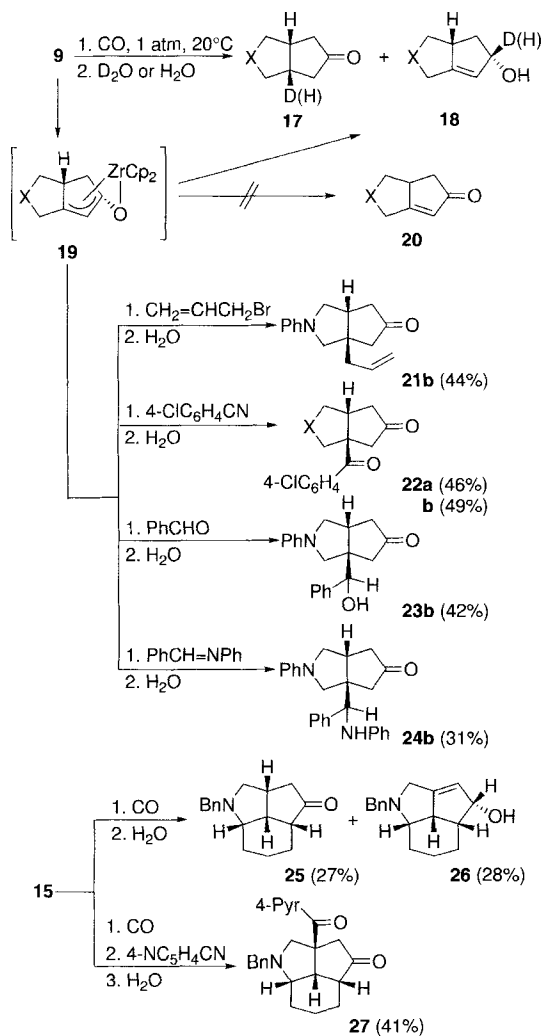
Table 2. Cyclization of allyl-2-bromoallyl substrates **7** and subsequent reaction with electrophiles to afford products **10-13**.

Starting material	X	Electrophile	Product	Yield (%) [a]
7a	9-Flu [b]	D ₂ SO ₄	10a	78
7a	9-Flu [b]	O ₂	13a	59
7b	PhN	D ₂ SO ₄	10b	87
7b	PhN	I ₂	11b	78
7b	PhN	MeOD/I ₂	12b	79
7b	PhN	O ₂	13b	60
7c	PhCH ₂ N	D ₂ SO ₄	10c	83
7c	PhCH ₂ N	I ₂	11c	77
7d	<i>c</i> -C ₆ H ₁₁ N	D ₂ SO ₄	10d	75
7d	<i>c</i> -C ₆ H ₁₁ N	O ₂	13d	56
7e	4-ClC ₆ H ₄ N	D ₂ SO ₄	10e	81

[a] Isolated yield based on the starting material **7**. [b] 9-Flu = 9-fluorenyl.

Carbonylation of zirconacycles and subsequent reaction with electrophiles: In order to test the reactivity of these new zirconabicyclopentenes **9** with carbon monoxide, a solution of these compounds in diethyl ether was stirred under a CO atmosphere at room temperature for 40 minutes and then quenched with deuterium oxide or water to give the unexpected saturated cyclopentanones **17** and allylic alcohols **18**. It is important to note that the expected cyclopentenones **20**, which are the usual carbonylation products of similar zirconacycles,^[2c, 9] were not obtained. The struc-

tures of compounds **17** and **18** were determined by their spectroscopic data and their stereochemistry was confirmed by NOE experiments on the non-deuterated products **18a** and **18b**. The insertion of CO into zirconabicycles **9** can be understood by assuming first that a π -allyl complex **19**^[10b] is produced by rearrangement of the previously formed η^2 -ketone complex.^[26] The formation of a strong metal–oxygen bond in the intermediate ketone complex has been invoked to explain the occurrence of the coupling of an alkyl and an acyl ligand to yield a ketone complexed to the metallocene moiety.^[27] The formation of **17** and **18** can be understood by the hydrolysis of complexes **19** with the zirconocene unit finishing at the bridge carbon or at the carbon nearest the oxygen (Scheme 3 and Table 3). We surmised



Scheme 3. Carbonylation of 8-unsubstituted zirconabicyclopentenes and reaction with electrophiles.

that the **17**:**18** ratio would increase if more basic amines were used, and tested our hypothesis on different aromatic amines in order to correlate their basicity with the ratio of products after carbonylation. However, the results were contradictory, and in some cases not even reproducible. Nevertheless, we found that reaction with benzylamines only gave small amounts of allylic alcohols, which were the major products when aromatic amines were used.

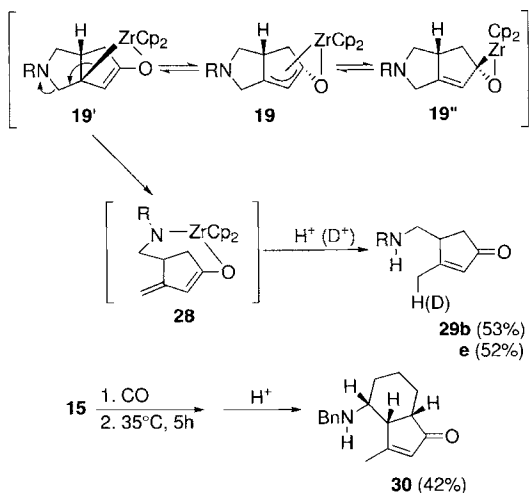
Table 3. Carbonylation and subsequent hydrolysis of zirconacycles **9** to ketones **17** and alcohols **18**.

Zirconacycles	X	Products (ratio)	Yield (%) [a]
9a	9-Flu [b]	17a + 18a (1:1)	65
9b	PhN	17b + 18b (1:4)	63
9b	PhN	17b + 18b (1:4) [c]	61
9c	PhCH ₂ N	17c [c,d]	59
9e	4-ClC ₆ H ₄ N	17e + 18e (1:3) [c]	62
9f	4-MeOC ₆ H ₄ N	17f + 18f (1:4) [c]	64

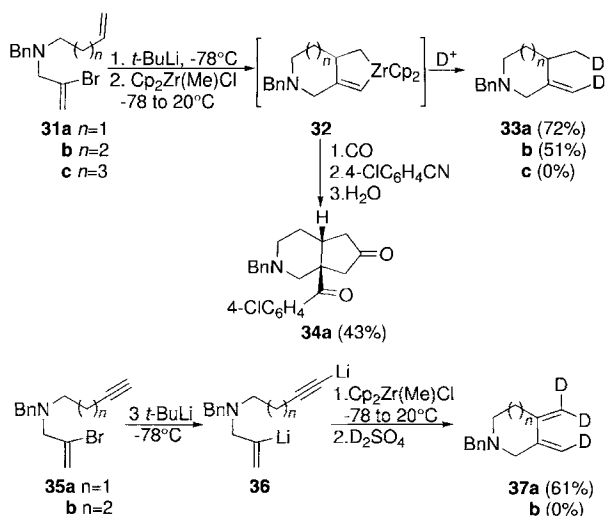
[a] Isolated yield based on the starting material **7**. [b] 9-Flu = 9-fluorenyl. [c] Quenched with D₂O. [d] Only small amounts of **18c** were detected in the crude reaction mixture.

Since it is well established that π -allylzirconium compounds react with carbonyl compounds^[28] and nitriles,^[29] we tested its reaction with several electrophiles (allyl bromide, 4-chlorobenzonitrile, benzaldehyde, and benzylideneaniline), assuming a π -allyl intermediate complex. After hydrolysis and purification, 1-substituted-bicyclo[3.3.0]octanones **21b–24b** and **22a** were obtained in moderate yields of ca. 40–50% based on the starting amine **7b** and fluorenyl derivative **7a**^[30] (Scheme 3). The structure of all the compounds was determined by their spectroscopic data. Moreover, we have assigned their stereochemistry on the basis of NOE experiments on **23b** and **24b**, which indicated a *cis* ring junction. In the case of the reaction with benzaldehyde and benzylideneaniline, in which a new chiral center is generated, a mixture of diastereoisomers is obtained. In the same way, treatment of **15** with carbon monoxide and subsequent hydrolysis afforded tricyclic cyclopentanone **25** and tricyclic allylic alcohol **26**. Their stereochemistry was assigned on the basis of previous results and NOE experiments on **26**. When 4-cyanopyridine was used as electrophile, diketone **27** was obtained as a single isomer. The difference in the carbonylation behavior of **9**, with respect to analogous systems described in the literature, might be due to the lack of substituents at C8; this would favor the formation of a π -allyl complex instead of a β -hydrogen abstraction process that would afford the bicyclic enones. Another fact which supports the existence of a π -allyl complex as an intermediate after carbonylation is their subsequent reaction to give monocyclic ketones **29** in the absence of electrophiles. This reaction could be accelerated by refluxing it in ether for several hours. The formation of **29** can be understood by considering the hydrolysis and tautomerization of **28**, generated by a β -elimination process in **19'**, one of the two η^1 -allyl complexes of **19**. Although this kind of process is well documented for β -oxygenated compounds,^[10a,27] only one example of deallylation reaction has been reported for a zirconocene complex containing a β -nitrogen.^[10c] Bicyclic pentenone **30** is obtained from **15** in an analogous manner (Scheme 4).

Synthesis of six- and seven-membered heterocycles: In order to extend this methodology to the formation of *N*-heterocycles with large rings, *N*-benzyl-*N*-(2-bromoallyl)amines **31a–c** were synthesized by conventional routes. Metallacycle formation under standard conditions proceeded as expected for $n = 1$ and 2. Piperidine **33a** and perhydroazepine **33b** were obtained in moderate yields after deuteration. However, the reaction failed for $n = 3$ and the azocine derivative **33c** was not detected. We be-

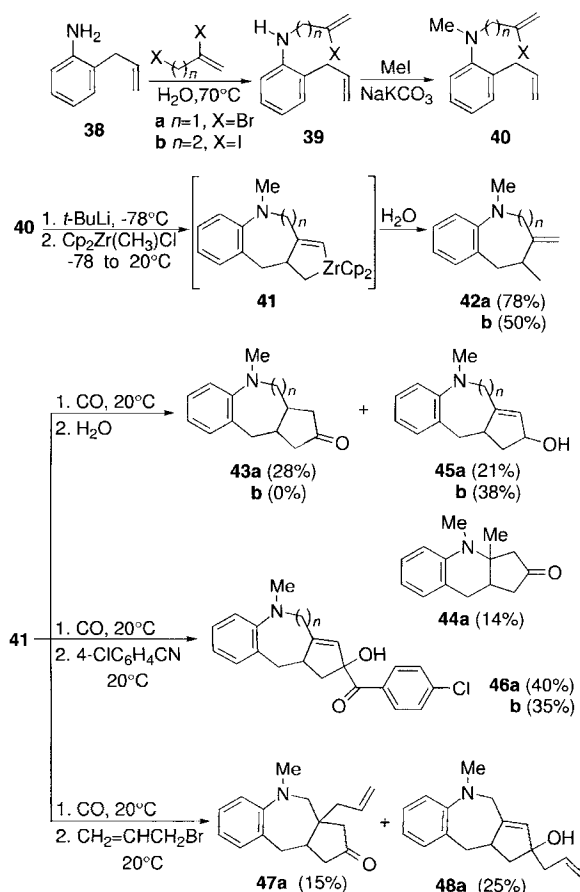
Scheme 4. Evolution of π -allylzirconium intermediates.

lieve that the reaction fails because the double bond in **31c** is too far away to coordinate with the intermediate η^2 -prop-2-ynylamine zirconocene complex, so that intermolecular insertion of isobutylene, generated in the lithiation step, is preferred. As far as we know, **33b** is the first seven-membered heterocycle synthesized by a zirconium-mediated coupling reaction. Treatment of zirconabicyclic **32a** with carbon monoxide (1 atm) and subsequent addition of 4-chlorobenzonitrile produced diketone **34a** as a single isomer. The structure of **34a** was assigned in analogy with the results above. In the same way, we prepared *N*-(2-bromoallyl)amines **35a,b** with a terminal triple bond to test this extension of the reaction. Treatment with 3 equiv of *t*BuLi at $-78^\circ C$ produced the dianions **36**, which were characterized by deuterolysis. A solution of bis(cyclopentadienyl)zirconium methyl chloride was then added, the mixture was allowed to warm up to room temperature and was stirred for eight hours. Cleavage of the zirconacycle with deuterated sulfuric acid gave trideuterated piperidine **37a** in 61% yield (based on **35a**). On the other hand, azepine derivative **37b** was not obtained, probably because of an intramolecular interaction between the acetylide and the metallic center, instead of formation of the alkyne–zirconocene complex (Scheme 5).



Scheme 5. Zirconium-promoted synthesis of pyridine and azepine derivatives.

Synthesis of seven- and eight-membered benzoheterocycles: Since the formation of eight-membered rings from 1,9-dienes^[12] or 1,9-diyne^[11] was not favorable, and only one example has been reported from stereodefined 1,4,6,9-decatetraenes,^[13] we then turned our attention to substrates in which the double bond approaches the bromoalkene moiety more closely. The starting material, *o*-allylaniline (**38**), was prepared by heating a solution of commercially available *N*-allylaniline in 2*N* sulfuric acid at $165^\circ C$ for two hours.^[13] Amine **38** was 2-bromoallylated or 3-iodohomoallylated in water with 2,3-dibromopropene or 2,4-diodobutene to give secondary amines **39a** and **b**, respectively. These were methylated with methyl iodide and NaKCO₃ in refluxing DMF to give tertiary amines **40a,b**. These were successfully converted to their corresponding metallacycles **41** by reacting the anion, generated with *t*-butyllithium in ether, with bis(cyclopentadienyl)zirconium methyl chloride. For the formation of **41b** the mixture needs to be refluxed in ether. This demonstrates that the relative position of the nitrogen exerts an influence on the β -hydrogen abstraction process. Compounds **41** were characterized by hydrolysis to give benzazepine and benzazocine derivatives **42a** and **42b** after standard purification by silica gel chromatography (Scheme 6). To the best of our knowledge, **42b** is the first eight-membered heterocycle to be synthesized by zirconium-mediated coupling. We thought that we could use our methodology (carbonylation and reaction with electrophiles) to build up some 1-benzazepine and 1-benzazocine derivatives. Therefore, the atmosphere of the vessel with



Scheme 6. Synthesis of benzazepine and benzazocine derivatives by zirconium-mediated intramolecular coupling.

the zirconium-containing compounds **41** was changed from N₂ to CO at room temperature, the solution was stirred for 30 min and subsequently hydrolyzed. This gave the 6-7-5 and 6-8-5 fused-ring ketone **43a** along with ketone **44a**, and alcohols **45a** and **45b**, the latter as a mixture of diastereoisomers. The formation of **44a** could be accounted for by assuming a β -elimination process in the π -allylzirconium intermediate generated after carbonylation (see Scheme 4), followed by an intramolecular Michael addition of the amine to the cyclopentenone moiety. Treatment of **41a,b** with 4-chlorobenzonitrile and subsequent carbonylation produced, almost exclusively, allylic alcohols **46a,b** and in both cases only one diastereoisomer was detected. However, the reaction of **41a** with CO and allyl bromide generated cyclopentanone **47a** as single diastereoisomer and allylic alcohol **48a** as a mixture of diastereoisomers (Scheme 6). While high diastereoselectivity is shown in the formation of five and six-membered cycles, we found here that a mixture of diastereoisomers is generated in some cases. The seven- and eight-membered rings are thought to permit the zirconocene unit more freedom to position itself at the same or the opposite side to the hydrogen-ring junction. Although a mixture of diastereoisomers is formed in some cases, this synthesis allows the generation of functionalized derivatives of benzazepines and benzazocines in a one-pot procedure from really available starting materials.

Conclusions

The work described here represents the first zirconium-mediated intramolecular coupling of terminal alkynes. The possibility of using one equivalent of terminal enyne allows the formation of 8-unsubstituted zirconabicyclopentenes. Their carbonylation and subsequent reaction with electrophiles represents a new behavior. These intermediates cannot be obtained by treatment of terminal enynes or diynes with "zirconocene" or "titanocene". This methodology has been extended to the formation of six-, seven-, and eight-membered ring heterocycles. Moreover, simple substrates are used as starting materials, and it is a one-pot synthesis.

Experimental Section

General techniques: All reactions involving organometallic reagents were carried out under an atmosphere of dry N₂ using standard Schlenk techniques and oven-dried glassware and syringes. All common reagents and solvents were obtained from commercial suppliers and used without further purification unless otherwise indicated. [Cp₂ZrCl₂] was purchased from Aldrich and [Cp₂Zr(Me)Cl] was prepared according to a published procedure.¹³² BuLi was used as a 2.5 M solution in hexane. *t*BuLi was used as a 1.7 M solution in pentane. THF and Et₂O were distilled from sodium benzophenone ketyl under N₂ immediately prior to use. Hexane, AcOEt, methanol, allyl bromide, and benzaldehyde were distilled before use. *N*-Benzylideneaniline was prepared by refluxing in toluene a mixture of benzaldehyde and aniline in the presence of a catalytic amount of *p*-toluenesulfonic acid in a system equipped with a Dean-Stark trap; 2,4-diiodobutene was obtained by treating 4-iodo-1-butene with NaI, Me₃SiCl, and H₂O in acetonitrile;¹³³ 2-cyclohexenyl bromide was synthesized by refluxing a mixture of cyclohexene and NBS in CCl₄ in the presence of a catalytic amount of benzoyl peroxide. TLC was performed on Al-backed plates coated with silica gel 60 with F₂₅₄ indicator (Scharlau). Flash column chromatography was carried out on silica gel 60, 230–240 mesh (SDS). Melting points were obtained on a Büchi-Tottoli

apparatus with open capillary tubes and are uncorrected. ¹H NMR (200, 300 MHz) and ¹³C NMR (50.5, 75.5 MHz) spectra were measured on Bruker AC-200 and AC-300 instruments, respectively, with TMS ($\delta = 0.0$, ¹H NMR) or CDCl₃ ($\delta = 76.95$, ¹³C NMR) as the internal standard. Chemical shifts are reported relative to TMS in CDCl₃. Homonuclear decoupling experiments served to assign coupling constants. Carbon multiplicities were assigned by DEPT techniques. Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV on a HP 5987A instrument, and the intensities are reported as a percentage relative to the base peak after the corresponding *m/z* value. High-resolution mass spectra (HRMS) were determined on a Finnigan MAT 95 spectrometer. Infrared (IR) spectra were recorded on a Unicam Matteson 3000 FTIR and only the most significant IR absorptions are given. Elemental analyses were performed with a Perkin Elmer analyzer.

Dianions 2 and diduterio compounds [D₂]3—General procedure: *tert*-Butyllithium (4 mmol) was added dropwise to a -78°C stirred solution of the corresponding 2-bromoallyl substrate **1** (2 mmol) in dry Et₂O (10 mL). After stirring at -78°C for 60 min, the dianions were formed and then were treated with D₂O and extracted with AcOEt (3 \times 20 mL). The combined organic layer was washed with saturated aq. NaHCO₃ (20 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude diduterated compounds were isolated without further purification as yellow oils.

9-(2-Deuterioallyl)-9-(3-deuteriopropargyl)fluorene ([D₂]3a): The reaction was performed as described in the general procedure with **1a** (0.64 g, 2 mmol) and *t*BuLi (3.6 mL, 6 mmol). Isolated yield: 96% (0.47 g); ¹H NMR (200 MHz, CDCl₃, 25°C, TMS): $\delta = 7.9\text{--}7.4$ (m, 8H, ArH), 5.0 (s, 1H, C=CHH), 4.9 (s, 1H, C=CHH), 3.0 (s, 2H, CH₂CD), 2.8 (s, 2H, CH₂C), ¹³C NMR (50.5 MHz, CDCl₃, 25°C): $\delta = 148.7, 140.1, 127.4, 126.9, 123.6, 119.7$ (ArC), 132.9 (t, *J*_{CD} = 23.5 Hz, =CD), 117.8 (=CH₂), 80.7 (=C), 69.6 (=CD), 51.7 (CCH₂), 41.1 (CH₂C=), 28.9 (CH₂C=); HRMS (EI) calcd for C₁₉H₁₄D₂: 246.1377, found 246.1377.

***N*-Benzyl-3-deuterio-*N*-(2-deuterioallyl)propargylamine ([D₂]3c):** Amine **1c** (0.53 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol). Isolated yield: 96% (0.36 g); ¹H NMR (200 MHz, CDCl₃, 25°C, TMS): $\delta = 7.5\text{--}7.3$ (m, 5H, ArH), 5.4 (s, 1H, CD=CHH), 5.2 (s, 1H, CD=CHH), 3.7 (s, 2H, ArCH₂N), 3.4 (s, 2H, NCH₂CD), 3.2 (s, 2H, NCH₂C); ¹³C NMR (50.5 MHz, CDCl₃, 25°C): $\delta = 138.4, 128.9, 128.1, 127.0$ (ArC), 135.0 (t, *J*_{CD} = 23.2 Hz, =CD), 117.8 (=CH₂), 77.8 (=C), 57.0, 56.3, 41.0 (3NCH₂); LRMS (70 eV, EI): *m/z* (%) = 187 (17) [*M*⁺], 186 (17), 159 (28), 110 (21), 96 (24), 92 (16), 91 (100).

General procedure for the preparation of exocyclic dienes 6: To a stirred solution of bis(cyclopentadienyl)zirconium methyl chloride (0.57 g, 2.1 mmol) in Et₂O (20 mL) was added a solution of dianion **2** (2 mmol) at -78°C under N₂, generated from substrates **1** (2 mmol) and 2 equiv *t*BuLi. After stirring for 1 h at this temperature, the mixture was allowed to warm to RT and was stirred for an additional 4 h. The reaction was quenched with H₂O or with 2N deuterated sulfuric acid, filtered through Celite, and extracted with AcOEt (3 \times 20 mL). The combined organic phases were dried (Na₂SO₄) and the solvents removed. The residue was purified by column chromatography to give compounds **6**.

3,4-Dimethylenespiro[cyclopentane-1,9'-(9H)fluorene] (6a): Fluorene derivative **1a** (0.64 g, 2 mmol) was treated with *t*BuLi (3.6 mL, 6 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 50:1). Yield: 0.32 g (65%) of diene **6a**. *R*_f = 0.35 (hexane/AcOEt 50:1); ¹H NMR (200 MHz, CDCl₃, 25°C, TMS): $\delta = 7.8\text{--}7.3$ (m, 8H, ArH), 5.7 (s, 2H, 2C=CHH), 5.1 (s, 2H, 2C=CHH), 3.0 (s, 4H, 2CH₂); ¹³C NMR (50.5 MHz, CDCl₃, 25°C): $\delta = 151.1, 147.4, 139.5, 127.3, 127.1, 122.7, 119.6$ (ArC and C=CH₂), 105.4 (=CH₂), 53.6 (CCH₂), 45.9 (CCH₂); HRMS (EI) calcd for C₁₉H₁₆: 244.1252, found 244.1259.

3,4-Dimethylene-1-phenylpyrrolidine (6b): Amine **1b** (0.50 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 25:1). Yield: 0.25 g (73%) of diene **6b**. *R*_f = 0.28 (hexane/AcOEt 15:1); ¹H NMR (200 MHz, CDCl₃, 25°C, TMS): $\delta = 7.4\text{--}6.7$ (m, 5H, ArH), 5.7–5.6 (m, 2H, 2C=CHH), 5.2 (s, 2H, 2C=CHH), 4.3–4.2 (m, 4H,

2CH₂N); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 147.2, 143.0, 129.1, 116.6, 112.0 (ArC and C=CH₂), 104.4 (=CH₂), 53.5 (CH₂N); LRMS (70 eV, EI): *m/z* (%) = 171 (82) [M⁺], 170 (40), 156 (17), 144 (73), 143 (26), 132 (23), 131 (29), 130 (82), 117 (24), 115 (27), 105 (36), 104 (89), 77 (100); HRMS (EI) calcd for C₁₂H₁₃N: 171.1048, found 171.1044.

1-Benzyl-3,4-dimethylenepyrrolidine (6c): Amine 1c (0.53 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 7:1). Yield: 0.26 g (71%) of diene 6c. *R_f* = 0.29 (hexane/AcOEt 5:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.4–7.2 (m, 5H, ArH), 5.5–5.4 (m, 2H, 2C=CHH), 4.9 (s, 2H, 2C=CHH), 3.7 (s, 2H, ArCH₂N), 3.4–3.3 (m, 4H, 2NCH₂C); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 144.4, 138.3, 128.6, 128.1, 126.9 (ArC and C=CH₂), 103.1 (=CH₂), 60.4, 59.7 (2CH₂N); LRMS (70 eV, EI): *m/z* (%) = 185 (56) [M⁺], 184 (67), 94 (42), 91 (100); HRMS (EI) calcd for C₁₃H₁₅N: 185.1204, found 185.1212.

1-Benzyl-3-(*E*)-deuteriomethylene-4-dideuteriomethylenepyrrolidine (D₃)6c): Amine 1c (0.53 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); the cleavage of the reaction was carried out with 2N D₂SO₄; the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 7:1). Yield: 0.25 g (70%) of diene [D₃]6c. ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.4–7.2 (m, 5H, ArH), 4.9 (s, 1H, C=CHD), 3.7 (s, 2H, ArCH₂N), 3.4 (s, 4H, 2NCH₂C); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 144.4, 144.3, 138.4, 128.7, 128.2, 127.0 (ArC and 2C=), 102.9 (t, *J*_{CD} = 24.3 Hz, CD and CD₂), 60.5, 59.7 (2CH₂N); LRMS (70 eV, EI): *m/z* (%) = 188 (66) [M⁺], 187 (72), 97 (46), 91 (100); HRMS (EI) calcd for C₁₃H₁₂D₃N: 188.1383, found 188.1386.

General procedure for the preparation of zirconabicyclopentenes 9 and their reactions with electrophiles:

Compounds 10–13: *tert*-Butyllithium (4 mmol) at –78 °C was added to a solution of the appropriate substrate 7^[30, 34] (2 mmol) in Et₂O (10 mL). After the mixture had been stirred at this temperature for 1 h, it was added to a solution of bis(cyclopentadienyl)zirconium methyl chloride (0.57 g, 2.1 mmol) in Et₂O (20 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 1 h. The cold bath was then removed, and the mixture was stirred at RT for 3 h. To the zirconium-containing metallacycles 9 were added different electrophiles: deuterated sulfuric acid (20 °C, 1 h), iodine (2.5 equiv, 20 °C, 4 h), MeOD (1.5 equiv, 20 °C, 1 h), and iodine (1.2 equiv, 20 °C, 2 h), dry O₂ (0 °C, 1 h). After addition of aq. NaHCO₃, the mixture was filtered through Celite and extracted with AcOEt (3 × 20 mL) and aq. Na₂S₂O₃. The organic layer was collected, washed with aq. NaHCO₃, dried over Na₂SO₄, and filtered. The solvents were removed by rotary evaporation and the products were isolated by flash chromatography as oils or solids.

7,7-Bis(cyclopentadienyl)-3-phenyl-3-aza-7-zircona-1(8)-bicyclo[3.3.0]octene (9b): Amine 7b (0.50 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol). After evaporation of the solvents, benzene (20 mL) was added, and LiCl filtered off. The filtrate was evaporated to dryness. Yield: 0.74 g (95%) of 9b. ¹³C NMR (50.5 MHz, C₆D₆, 25 °C): δ = 169.7 (=CH), 149.1, 142.6, 130.2, 116.7, 113.1 (ArC and C=CH), 112.1, 111.0 (Cp), 62.3, 57.3 (2CH₂N), 38.3 (CH), 36.5 (CH₂Zr).

3-(*E*)-Deuteriomethyl-4-deuteriomethylenespiro[cyclopentane-1,9'-fluorene] (10a): Fluorene derivative 7a (0.65 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); after the addition of D₂SO₄ and the extractive workup, the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 50:1). Yield: 0.38 g (78%) of 10a. M.p. 127–129 °C (hexane); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.9–7.3 (m, 8H, ArH), 5.2–5.1 (m, 1H, C=CHD), 3.4–3.2 (m, 1H, CH), 3.1 (dt, *J* = 16.4, 2.2 Hz, 1H, CHHC=), 2.8 (d, *J* = 16.4 Hz, 1H, CHHC=), 2.2 (dd, *J* = 13.0, 8.0 Hz, 1H, CHHC=), 2.1 (dd, *J* = 13.0, 10.8 Hz, 1H, CHHC=), 1.4 (d, *J* = 6.7 Hz, 2H, CH₂D); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 156.8, 153.3, 151.6, 139.7, 139.2, 127.3, 127.2, 126.9, 126.8, 123.1, 122.6, 119.6, 119.5 (ArC and C=CHD), 105.6 (t, *J*_{CD} = 24.3 Hz, CHD), 55.3 (CH₂), 47.9, 44.9 (2CH₂), 38.2 (CH), 19.3 (t, *J*_{CD} = 19.4 Hz, CH₂D); LRMS (70 eV, EI): *m/z* (%) = 248 (89) [M⁺], 233 (27), 232 (49), 219 (34), 218 (100), 217 (33), 216 (30), 204 (82), 203 (90), 202 (23), 179 (32), 178 (90), 165 (35); HRMS (EI) calcd for C₁₉H₁₆D₂: 248.1534, found 248.1537; anal. calcd C 91.88, H/D 8.12; found C 91.96, H/D 7.99.

3-Deuteriomethyl-4-(*E*)-deuteriomethylene-1-phenylpyrrolidine (10b): Amine 7b (0.50 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); after the addition of D₂SO₄ and the extractive workup, the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 25:1). Yield: 0.30 g (87%) of 10b. M.p. 63–65 °C (hexane/CHCl₃); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.4–6.7 (m, 5H, ArH), 5.2–5.1 (m, 1H, C=CHD), 4.2 (dd, *J* = 13.7, 1.9 Hz, 1H, NCHHC=), 4.0 (dd, *J* = 13.7, 1.6 Hz, 1H, NCHHC=), 3.8–3.7 (m, 1H, NCHHC=), 3.1–2.9 (m, 2H, NCHHC= and CH), 1.4–1.3 (m, 2H, CH₂D); ¹³C NMR (75.5 MHz, CDCl₃, 25 °C): δ = 151.4, 147.8, 129.0, 116.1, 111.8 (ArC and C=CHD), 104.3 (t, *J*_{CD} = 23.5 Hz, CHD), 55.1, 53.1 (2CH₂N), 37.1 (CH), 16.3 (t, *J*_{CD} = 19.6 Hz, CH₂D); LRMS (70 eV, EI): *m/z* (%) = 175 (74) [M⁺], 174 (96), 173 (31), 159 (100), 131 (46), 105 (35), 104 (49), 77 (58); HRMS (EI) calcd for C₁₂H₁₃D₂N: 175.1330; found 175.1328; anal. calcd C 82.23, H/D 9.78, N 7.99, found C 82.30, H/D 9.63, N 8.06.

1-Benzyl-3-deuteriomethyl-4-(*E*)-deuteriomethylenepyrrolidine (10c): Amine 7c (0.53 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); after the addition of D₂SO₄ and the extractive workup, the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 7:1). Yield: 0.31 g (83%) of 10c. *R_f* = 0.24 (hexane/AcOEt 5:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.4–7.3 (m, 5H, ArH), 5.0–4.9 (m, 1H, C=CHD), 3.7 (d, *J* = 18.1 Hz, 1H, ArCHHN), 3.6 (d, *J* = 18.1 Hz, 1H, ArCHHN), 3.5 (d, *J* = 13.1 Hz, 1H, NCHHC=), 3.1–3.0 (m, 2H, NCHHC= and NCHHC=), 2.9–2.7 (m, 1H, CH), 2.2 (dd, *J* = 8.6, 8.3 Hz, 1H, NCHHC=), 1.2–1.1 (m, 2H, CH₂D). ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 153.7, 138.8, 128.6, 128.1, 126.8 (ArC and C=CH₂), 103.4 (t, *J*_{CD} = 23.5 Hz, CHD), 62.1, 60.5, 59.3 (3CH₂N), 37.3 (CH), 17.3 (t, *J*_{CD} = 19.7 Hz, CH₂D); HRMS (EI) calcd for C₁₂H₁₅D₂N: 189.1486, found 189.1483.

1-Cyclohexyl-3-deuteriomethyl-4-(*E*)-deuteriomethylenepyrrolidine (10d): Amine 7d (0.52 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); after the addition of D₂SO₄ and the extractive workup, the resulting crude product was purified by silica gel chromatography (AcOEt/MeOH 1:1). Yield: 0.27 g (75%) of 10d. *R_f* = 0.39 (AcOEt/MeOH 1:1); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 4.9–4.8 (m, 1H, C=CHD), 3.6 (d, *J* = 13.8 Hz, 1H, NCHHC=), 3.2 (dd, *J* = 8.2, 7.7 Hz, 1H, NCHHC=), 3.0 (dt, *J* = 13.8, 2.2 Hz, 1H, NCHHC=), 2.8–2.6 (m, 1H, CH), 2.0–1.6 (m, 8H, NCH, NCHHC= and 3CH₂ cyclohexyl), 1.3–1.1 (m, 6H, CH₂D and 2CH₂ cyclohexyl); ¹³C NMR (75.5 MHz, CDCl₃, 25 °C): δ = 153.5 (C=CHD), 103.2 (t, *J*_{CD} = 23.5 Hz, CHD), 63.7 (CHN), 59.7, 57.4 (2CH₂N), 36.9 (CH), 31.6, 31.5, 25.9, 24.9, 24.8 (5CH₂ cyclohexyl), 16.9 (t, *J*_{CD} = 19.4 Hz, CH₂D); LRMS (70 eV, EI): *m/z* (%) = 181 (11) [M⁺], 138 (100), 137 (15), 124 (10); HRMS (EI) calcd for C₁₂H₁₉D₂N: 181.1799, found 181.1804.

1-(4-Chlorophenyl)-3-deuteriomethyl-4-(*E*)-deuteriomethylenepyrrolidine (10e): Amine 7e (0.57 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); after the addition of D₂SO₄ and the extractive workup, the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 25:1). Yield: 0.34 g (81%) of 10e. M.p. 74–76 °C (hexane/CHCl₃); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.2 (d, *J* = 8.9 Hz, 2H, ArH), 6.5 (d, *J* = 8.9 Hz, 2H, ArH), 5.1–5.0 (m, 1H, C=CHD), 4.1 (d, *J* = 13.6 Hz, 1H, NCHHC=), 3.9 (d, *J* = 13.6 Hz, 1H, NCHHC=), 3.6 (t, *J* = 7.3 Hz, 1H, NCHHC=), 3.0–2.8 (m, 2H, NCHHC= and CH), 1.3–1.2 (m, 2H, CH₂D); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 150.9, 146.2, 128.7, 120.7, 112.8 (ArC and C=CHD), 104.5 (t, *J*_{CD} = 23.6 Hz, CHD), 55.1, 53.1 (2CH₂N), 37.0 (CH), 16.1 (t, *J*_{CD} = 19.4 Hz, CH₂D); HRMS (EI) calcd for C₁₂H₁₂D₂ClN: 209.0940, found 209.0929; anal. calcd C 68.73, H/D 7.69, N 6.68; found C 68.69, H/D 7.52, N 6.73.

3-Iodomethyl-4-(*E*)-iodomethylene-1-phenylpyrrolidine (11b): Amine 7b (0.50 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); after the addition of I₂ (1.27 g, 5 mmol) and the extractive workup, the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 25:1). Yield: 0.66 g (78%) of 11b. *R_f* = 0.27 (hexane/AcOEt 20:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.3–6.6 (m, 5H, ArH), 6.3 (s, 1H, CHI), 4.2 (d, *J* = 14.2 Hz, 1H, NCHHC=), 3.8 (d, *J* = 14.2 Hz, 1H, NCHHC=), 3.7 (d, *J* = 9.9 Hz, 1H, NCHHC=), 3.5 (d, *J* = 7.7 Hz, 2H, CH₂I), 3.4–3.3 (m, 1H, CH), 3.3 (dd, *J* = 10.3, 9.9 Hz, 1H, NCHHC=); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 150.4, 147.4, 129.1,

117.4, 112.5 (ArC and C=CHI), 73.3 (CHI), 53.7, 53.3 (2CH₂N), 49.5 (CH), 7.1 (CH₂I); LRMS (70 eV, EI): *m/z* (%) = 425 (96) [*M*⁺], 298 (70), 193 (32), 186 (34), 171 (73), 170 (89), 156 (40), 144 (32), 104 (62), 77 (100), 66 (66); HRMS (EI) calcd for C₁₂H₁₃I₂N: 424.9131; found 424.9131.

1-Benzyl-3-iodomethyl-4-(E)-iodomethylenepyrrolidine (11c): Amine **7c** (0.53 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); after the addition of I₂ (1.27 g, 5 mmol) and the extractive workup, the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 20:1). Yield: 0.67 g (77%) of **11c**. *R_f* = 0.24 (hexane/AcOEt 15:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.3–7.2 (m, 5H, ArH), 6.2–6.1 (m, 1H, CHI), 3.7 (d, *J* = 12.9 Hz, 1H, ArCHHN), 3.6 (d, *J* = 12.9 Hz, 1H, ArCHHN), 3.6 (dd, *J* = 9.5, 3.0 Hz, 1H, NCHHC), 3.4 (d, *J* = 13.4 Hz, 1H, NCHHC), 3.4 (dd, *J* = 10.7, 9.5 Hz, 1H, NCHHC), 3.1 (dd, *J* = 13.4, 1.7 Hz, 1H, NCHHC), 3.1–3.0 (m, 1H, CH), 3.0–2.9 (m, 2H, CH₂I); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 151.7, 137.3, 128.6, 128.3, 127.3 (ArC and C=CHI), 72.2 (CHI), 60.0, 59.7, 59.5 (3CH₂N), 49.1 (CH), 7.3 (CH₂I); HRMS (EI) calcd for C₁₃H₁₅I₂N: 438.9294, found 438.9294.

3-Deuteriomethyl-4-(E)-iodomethylene-1-phenylpyrrolidine (12b): Amine **7b** (0.50 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); after the addition of MeOD (0.1 g, 3 mmol) the suspension was stirred at 20 °C for 1 h and then I₂ (0.6 g, 2.4 mmol) was added. After the extractive workup, the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 25:1). Yield: 0.47 g (79%) of **12b**. *R_f* = 0.34 (hexane/AcOEt 15:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.3–6.6 (m, 5H, ArH), 6.1 (dd, *J* = 1.9, 1.6 Hz, 1H, CHI), 4.2 (dd, *J* = 14.0, 1.9 Hz, 1H, NCHHC), 3.8 (dd, *J* = 14.0, 1.6 Hz, 1H, NCHHC), 3.5 (dd, *J* = 9.0, 6.7 Hz, 1H, NCHHC), 3.3 (dd, *J* = 9.0, 1.6 Hz, 1H, NCHHC), 3.2–3.0 (m, 1H, CH), 1.3 (d, *J* = 7.0 Hz, 2H, CH₂D); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 153.6, 147.7, 129.0, 116.6, 112.0 (ArC and C=CHI), 69.4 (CHI), 54.5, 52.9 (2CH₂N), 40.9 (CH), 18.1 (t, *J*_{CD} = 19.4 Hz, CH₂D); HRMS (EI) calcd for C₁₂H₁₃DIN: 300.0234, found 300.0234.

3-Hydroxymethyl-4-methylenespiro[cyclopentane-1,9'-(9H)fluorene] (13a): Fluorene derivative **7a** (0.65 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); dry O₂ was bubbled through the mixture for 1 h. After extractive workup, the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 4:1). Yield: 0.31 g (59%) of **13a**. M.p. 148–150 °C (hexane/CHCl₃); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.7–7.2 (m, 8H, ArH), 5.25–5.15 (m, 2H, =CH₂), 3.9–3.8 (m, 2H, CH₂O), 3.3–3.2 (m, 1H, CH), 3.1 (dd, *J* = 15.9, 2.6 Hz, 1H, CHHC=), 2.5 (d, *J* = 15.9 Hz, 1H, CHHC=), 2.3 (dd, *J* = 12.9, 10.1 Hz, 1H, CHHC=), 2.1 (dd, *J* = 12.9, 8.2 Hz, 1H, CHHC=); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 152.9, 152.5, 150.3, 139.9, 139.1, 127.4, 127.2, 127.1, 127.0, 123.0, 122.5, 119.7, 119.6 (ArC and C=CH₂), 108.3 (=CH₂), 65.8 (CH₂O), 55.5 (CCH₂), 46.0 (CH), 45.6, 41.7 (2CH₂); IR (KBr): $\tilde{\nu}$ = 3300 cm⁻¹ (O–H); HRMS (EI) calcd for C₁₉H₁₈O: 262.1357, found 262.1354; anal. calcd C 86.99, H 6.92; found C 86.87, H 6.95.

3-Hydroxymethyl-4-methylene-1-phenylpyrrolidine (13b): Amine **7b** (0.50 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); dry O₂ was bubbled through the mixture for 1 h. After extractive workup, the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 2:1). Yield: 0.23 g (60%) of **13b**. *R_f* = 0.28 (hexane/AcOEt 2:1); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.3–6.6 (m, 5H, ArH), 5.2 (dd, *J* = 4.0, 1.7 Hz, 1H, =CHH), 5.1 (dd, *J* = 4.0, 2.2 Hz, 1H, =CHH), 4.0 (dd, *J* = 14.0, 1.7 Hz, 1H, NCHHC), 3.9 (dd, *J* = 14.0, 2.2 Hz, 1H, NCHHC), 3.7 (d, *J* = 6.5 Hz, 2H, CH₂O), 3.5 (dd, *J* = 9.5, 7.7 Hz, 1H, NCHHC), 3.4 (dd, *J* = 9.5, 4.3 Hz, 1H, NCHHC), 3.1–3.0 (m, 1H, CH), 2.2 (brs, 1H, OH); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 147.8, 147.0, 129.1, 116.7, 112.3 (ArC and C=CH₂), 107.3 (=CH₂), 64.3 (CH₂O), 52.9, 50.7 (2CH₂N), 45.4 (CH); IR (neat): $\tilde{\nu}$ = 3370 cm⁻¹ (O–H); HRMS (EI) calcd for C₁₂H₁₅NO: 189.1153; found 189.1149.

1-Cyclohexyl-3-hydroxymethyl-4-methylenepyrrolidine (13d): Amine **7d** (0.52 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); dry O₂ was bubbled through the mixture for 1 h. After extractive workup, the resulting crude product was purified by silica gel chromatography (AcOEt/MeOH 1:1). Yield: 0.22 g (56%) of **13d**. *R_f* = 0.31 (AcOEt/MeOH 1:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 5.0 (s,

1H, =CHH), 4.9 (s, 1H, =CHH), 4.1 (brs, 1H, OH), 3.8–3.5 (m, 2H, CH₂O), 3.3 (d, *J* = 13.5 Hz, 1H, NCHHC), 3.1 (d, *J* = 13.5 Hz, 1H, NCHHC), 2.9–2.7 (m, 4H, NCH, NCH₂CH and CHCO), 2.1–1.1 (m, 10H, 5CH₂ cyclohexyl); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 148.9 (C=CH₂), 105.8 (=CH₂), 66.1 (CH₂O), 63.0 (CHN), 57.1, 55.4 (2CH₂N), 44.4 (CH), 31.2, 25.8, 24.6 (5CH₂ cyclohexyl); IR (neat): $\tilde{\nu}$ = 3360 cm⁻¹ (O–H); LRMS (70 eV, EI): *m/z* (%) = 195 (13) [*M*⁺], 153 (36), 152 (100); HRMS (EI) calcd for C₁₂H₂₁NO: 195.1623, found 195.1633.

N-Benzyl-N-(2-bromoallyl)-2-cyclohexenylamine (14): To a stirred suspension of *N*-benzyl-2-bromoallylamine (3.8 g, 17 mmol) and K₂CO₃ (2.6 g, 18.7 mmol) in CH₂Cl₂ (50 mL) at 0 °C was added 2-cyclohexenylbromide (3.0 g, 18.7 mmol). The mixture was stirred at RT for 2 d and then H₂O was added to the suspension. The aqueous layer was extracted with CH₂Cl₂, and the combined organic layer was washed with NaHCO₃ and dried over Na₂SO₄. After evaporation of the solvent (15 mm Hg), the residue was purified by column chromatography (hexane/AcOEt 30:1). Yield: 4.4 g (85%) of **14** as a colorless oil. *R_f* = 0.33 (hexane/AcOEt 20:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.5–7.3 (m, 5H, ArH), 6.1 (s, 1H, BrC=CHH), 6.0–5.8 (m, 2H, CH=CH), 5.6 (s, 1H, BrC=CHH), 3.9 (d, *J* = 14.3 Hz, 1H, ArCHHN), 3.7 (d, *J* = 14.3 Hz, 1H, ArCHHN), 3.5–3.3 (m, 3H, NCH and NCH₂C), 2.1–1.3 (m, 6H, 3CH₂ ring); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 139.8, 133.6, 130.4, 129.9, 128.3, 128.0 (ArC, CBr, and CH=CH), 117.0 (=CH₂), 57.9, 53.7 (2CH₂N), 54.7 (CHN), 25.1, 23.5, 21.6 (3CH₂ cyclohexenyl); LRMS (70 eV, EI): *m/z* (%) = 307 (3) [*M*⁺ + 1], 305 (3) [*M*⁺ – 1], 279 (10), 277 (11), 198 (61), 91 (100), 79 (13), 65 (15); HRMS (EI) calcd for C₁₆H₂₀BrN: 305.0779, found 305.0786.

(3aS*,4R*,7aS*)-1-Benzyl-4-deuterio-3-(E)-deuteriomethylenepyrrolidine (16): To a solution of **14** (0.61 g, 2 mmol) in Et₂O (10 mL) at –78 °C under a N₂ atmosphere was added *t*BuLi (2.4 mL, 4 mmol), and the solution was stirred at –78 °C for 1 h. This solution was added dropwise to a solution of bis(cyclopentadienyl)zirconium methyl chloride (0.57 g, 2.1 mmol) in Et₂O (20 mL) at –78 °C; stirring was continued for an additional 3 h at RT and 2N D₂SO₄ was added. The mixture was diluted with AcOEt, filtered through Celite, washed with NaHCO₃ and dried over Na₂SO₄. The solvent was removed (rotary evaporator) to yield an oil. Pure **16** was obtained by flash chromatography (hexane/AcOEt 10:1) as a colorless oil. *R_f* = 0.45 (hexane/AcOEt 7:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.5–7.3 (m, 5H, ArH), 4.85–4.8 (m, 1H, =CHD), 4.1 (d, *J* = 13.4 Hz, 1H, ArCHHN), 3.6 (d, *J* = 14.3 Hz, 1H, NCHHC), 3.3 (d, *J* = 13.4 Hz, 1H, ArCHHN), 3.0 (dd, *J* = 14.3, 1.9 Hz, 1H, NCHHC), 2.82–2.75 (m, 1H, NCH), 2.67–2.59 (m, 1H, CHC=), 1.8–1.4 (m, 7H, 3CH₂ ring and CHD); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 151.8, 139.7, 128.3, 128.0, 126.5 (ArC and C=CHD), 102.5 (t, *J*_{CD} = 23.7 Hz, =CHD), 62.2 (CHN), 57.6, 56.6 (2CH₂N), 43.8 (CHC=), 28.0 (t, *J*_{CD} = 19.7 Hz, CHD), 24.5, 24.0, 21.1 (3CH₂ cyclohexyl); HRMS (EI) calcd for C₁₆H₁₉D₂N: 229.1799, found 229.1792.

Ketones 17 and bicyclic alcohols 18—General procedure: A stream of CO was bubbled through the stirred solution of zirconacycle **9** for 40 min. After addition of H₂O or D₂O the mixture was stirred 15 min followed by addition of saturated aqueous NaHCO₃. The mixture reaction was filtered through Celite and extracted with AcOEt (3 × 20 mL). The extract was washed with aq. NaHCO₃ and the combined organic extracts were dried (Na₂SO₄), concentrated, and chromatographed on silica gel. Elution with hexane/AcOEt mixtures gave pure saturated ketones **17** and allylic alcohols **18** as oils or white solids.

cis-Spiro[bicyclo[3.3.0]octane-3,9'-(9H)fluorene]-7-one (17a): Fluorene derivative **7a** (0.65 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of H₂O and extractive workup, the resulting crude product (1:1 mixture of **17a** and **18a**) was purified by silica gel chromatography (hexane/AcOEt 5:1). Yield: 0.18 g (33%) of **17a**. M.p. 236–238 °C (hexane/CHCl₃); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.8–7.3 (m, 8H, ArH), 3.4–3.3 (m, 2H, 2CH), 2.7 (dd, *J* = 19.4, 9.5 Hz, 2H, 2CHCO), 2.4–2.2 (m, 4H, 2CHCO and 2CCHHC), 2.1 (dd, *J* = 13.7, 8.2 Hz, 2H, 2CCHHC); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 220.0 (CO), 153.4, 150.4, 139.7, 127.5, 127.3, 127.1, 127.0, 123.0, 122.4, 119.7, 119.6 (ArC), 59.4 (CCH₂), 46.4, 44.8 (4CH₂), 39.9 (2CH); IR (KBr): $\tilde{\nu}$ = 1730 cm⁻¹ (C=O); HRMS (EI) calcd for C₂₀H₁₈O: 274.1358, found 274.1355; anal. calcd C 87.56, H 6.61; found C 87.40, H 6.70.

cis-Spiro[1(8)-bicyclo[3.3.0]octene-3,9'-(9H)fluorene]-7-ol (18a): Yield: 0.18 g (33%). M.p. 183–185 °C (hexane/CHCl₃); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.7–7.3 (m, 8H, ArH), 5.6 (s, 1H, =CH), 5.3–5.2 (m, 1H, CHO), 3.5–3.4 (m, 1H, CH), 2.9–2.8 (m, 3H, CCH₂C and CHHCO), 2.2 (dd, *J* = 12.5, 8.1 Hz, 1H, CCHHCH), 2.0 (brs, 1H, OH), 1.9 (dd, *J* = 12.5, 10.8 Hz, 1H, CCHHCH), 1.5 (dt, *J* = 12.5, 7.8 Hz, 1H, CHHCO); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 154.7, 154.2, 153.5, 139.1, 127.7, 127.5, 126.9, 123.6, 122.9, 122.8, 119.6, 119.4 ArC and C=CH), 82.8 (CHO), 59.0 (CCH₂), 50.1 (CH), 46.3, 44.3, 38.1 (3 CH₂); IR (KBr): ν̄ = 3225 cm⁻¹ (O–H); HRMS (EI) calcd for C₂₂H₁₈O: 274.1358, found 274.1354; anal. calcd C 87.56, H 6.61; found C 87.45, H 6.69.

cis-3-Phenyl-3-azabicyclo[3.3.0]octan-7-one (17b): Amine **7b** (0.50 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of H₂O and extractive workup the resulting crude product (1:4 mixture of **17b** and **18b**) was purified by silica gel chromatography (hexane/AcOEt 3:1). Yield: 0.05 g (13%) of **17b**. M.p. 78–80 °C (hexane/CHCl₃); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.3–6.5 (m, 5H, ArH), 3.6 (dd, *J* = 9.6, 7.0 Hz, 2H, 2NCHH), 3.2 (dd, *J* = 9.6, 3.8 Hz, 2H, 2NCHH), 3.2–3.0 (m, 2H, 2CH), 2.6 (dd, *J* = 19.4, 7.9 Hz, 2H, 2CHHCO), 2.3 (dd, *J* = 19.4, 4.1 Hz, 2H, 2CHHCO); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 218.3 (CO), 147.4, 129.0, 116.1, 111.8 (ArC), 52.9 (2 CH₂N), 42.8 (2 CH₂CO), 38.9 (2 CH); IR (KBr): ν̄ = 1730 cm⁻¹ (C=O); HRMS (EI) calcd for C₁₃H₁₅NO: 201.1154, found 201.1154; anal. calcd C 77.58, H 7.51, N 6.96; found C 77.44, H 7.55, N 6.98.

cis-3-Phenyl-3-aza-1(8)-bicyclo[3.3.0]octen-7-ol (18b): Yield: 0.20 g (50%). M.p. 126–128 °C (hexane/CHCl₃); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.3–6.6 (m, 5H, ArH), 5.6 (s, 1H, =CH), 5.3–5.1 (m, 1H, CHO), 4.0 (d, *J* = 13.6 Hz, 1H, NCHHC=), 3.8 (d, *J* = 13.6 Hz, 1H, NCHHC=), 3.7 (t, *J* = 8.2 Hz, 1H, NCHHCH), 3.3–3.1 (m, 1H, CH), 2.9–2.7 (m, 2H, NCHHCH and CHHCO), 2.2 (brs, 1H, OH), 1.4 (dt, *J* = 12.4, 7.9 Hz, 1H, CHHCO); ¹³C NMR (75.5 MHz, CDCl₃, 25 °C): δ = 148.9, 147.5, 129.1, 123.9, 116.0, 111.5 (ArC and C=CH), 82.5 (CHO), 53.1, 46.9 (2 CH₂N), 47.4 (CH), 41.8 (CH₂CO); IR (KBr): ν̄ = 3300 cm⁻¹ (O–H); HRMS (EI) calcd for C₁₃H₁₅NO: 201.1154, found 201.1157; anal. calcd C 77.58, H 7.51, N 6.96; found C 77.46, H 7.57, N 6.92.

cis-1-Deuterio-3-phenyl-3-azabicyclo[3.3.0]octan-7-one ([D]17b): Amine **7b** (0.50 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of D₂O and extractive workup the resulting crude product (1:4 mixture of [D]17b and [D]18b) was purified by silica gel chromatography (hexane/AcOEt 3:1). Yield: 0.05 g (14%) of [D]17b. ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.3–6.6 (m, 5H, ArH), 3.7–3.6 (m, 2H, 2NCHH), 3.3–3.2 (m, 2H, 2NCHHCH), 3.1–3.0 (m, 1H, CH), 2.6–2.5 (m, 2H, 2CHHCO), 2.3–2.2 (m, 2H, 2CHHCO); ¹³C NMR (75.5 MHz, CDCl₃, 25 °C): δ = 218.4 (CO), 147.4, 129.1, 116.2, 111.9 (ArC), 53.0, 52.9 (2 CH₂N), 42.9, 42.8 (2 CH₂CO), 39.0, 38.9 (CH and CD); LRMS (70 eV, EI): *m/z* (%) = 202 (79) [M⁺], 201 (67), 119 (36), 91 (100), 77 (31).

cis-7-Deuterio-3-phenyl-3-aza-1(8)-bicyclo[3.3.0]octen-7-ol ([D]18b): Yield: 0.19 g (49%). ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.3–6.5 (m, 5H, ArH), 5.6 (s, 1H, =CH), 4.0 (d, *J* = 13.6 Hz, 1H, NCHHC=), 3.8 (d, *J* = 13.6 Hz, 1H, NCHHC=), 3.7 (t, *J* = 8.6 Hz, 1H, NCHHCH), 3.3–3.1 (m, 1H, CH), 2.8 (dd, *J* = 8.9, 8.6 Hz, 1H, NCHHCH), 2.7 (dd, *J* = 12.4, 7.2 Hz, 1H, CHHCO), 1.4 (dd, *J* = 12.4, 8.2 Hz, 1H, CHHCO); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 148.5, 147.5, 129.1, 123.8, 116.0, 111.5 (ArC and C=CH), 81.8 (t, *J*_{CD} = 22.2 Hz, CDO), 53.0, 46.8 (2 CH₂N), 47.2 (CH), 41.4 (CH₂CO); LRMS (70 eV, EI): *m/z* (%) = 202 (93) [M⁺], 201 (25), 157 (20), 156 (55), 149 (44), 106 (100), 105 (32), 104 (40), 80 (50), 78 (21), 77 (56).

cis-3-Benzyl-1-deuterio-3-azabicyclo[3.3.0]octan-7-one ([D]17c): Amine **7c** (0.53 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of D₂O and extractive workup, the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 1:1). Yield: 0.25 g (59%) of [D]17c. *R_f* = 0.14 (hexane/AcOEt 1:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.3–7.2 (m, 5H, ArH), 3.6 (s, 2H, ArCH₂N), 2.9–2.8 (m, 1H, CH), 2.7–2.4 (m, 6H, 2NCH₂C and 2CHHCO), 2.2 (dd, *J* = 19.1, 2.6 Hz, 2H, 2CHHCO); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 219.9

(CO), 138.9, 128.4, 128.1, 126.8 (ArC), 61.7, 61.6, 59.3 (3 CH₂N), 44.4, 44.3 (2 CH₂CO), 37.4, 37.3 (CH and CD); IR (neat): ν̄ = 1740 cm⁻¹ (C=O); LRMS (70 eV, EI): *m/z* (%) = 216 (27) [M⁺], 215 (26), 139 (29), 125 (44), 92 (28), 91 (100); HRMS (EI) calcd for C₁₄H₁₇NO: 216.1373, found 216.1377.

cis-3-(4-Chlorophenyl)-1-deuterio-3-azabicyclo[3.3.0]octan-7-one ([D]17e): Amine **7e** (0.57 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of D₂O and extractive workup, the resulting crude product (1:3 mixture of [D]17e and [D]18e) was purified by silica gel chromatography (hexane/AcOEt 3:1). Yield: 0.07 g (15%) of [D]17e. M.p. 109–111 °C (hexane/CHCl₃); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.2 (d, *J* = 9.2 Hz, 2H, ArH), 6.5 (d, *J* = 9.2 Hz, 2H, ArH), 3.6–3.5 (m, 2H, 2NCHHCH), 3.2–3.1 (m, 3H, 2NCHHCH and CH), 2.6–2.5 (m, 2H, 2CHHCO), 2.3–2.2 (m, 2H, 2CHHCO); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 218.1 (CO), 146.0, 128.8, 121.0, 112.9 (ArC), 53.2 (2 CH₂N), 42.8 (2 CH₂CO), 39.0, 38.9 (CH and CD); IR (KBr): ν̄ = 1740 cm⁻¹ (C=O); HRMS (EI) calcd for C₁₃H₁₃DClNO: 236.0826, found 236.0816; anal. calcd C 65.96, H/D 6.39, N 5.92; found C 66.03, H/D 6.28, N 5.95.

cis-3-(4-Chlorophenyl)-7-deuterio-3-aza-1(8)-bicyclo[3.3.0]octen-7-ol ([D]18e): Yield: 0.22 g (47%). M.p. 160–162 °C; ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.2 (d, *J* = 9.2 Hz, 2H, ArH), 6.5 (d, *J* = 9.2 Hz, 2H, ArH), 5.6 (s, 1H, =CH), 3.9 (d, *J* = 13.7 Hz, 1H, NCHHC=), 3.8 (d, *J* = 13.7 Hz, 1H, NCHHC=), 3.7 (t, *J* = 8.3 Hz, 1H, NCHHCH), 3.3–3.1 (m, 1H, CH), 2.8 (dd, *J* = 8.9, 8.3 Hz, 1H, NCHHCH), 2.7 (dd, *J* = 12.4, 7.3 Hz, 1H, CHHCO), 1.9 (brs, 1H, OH), 1.4 (dd, *J* = 12.4, 8.5 Hz, 1H, CHHCO); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 148.3, 146.1, 129.1, 128.8, 124.1, 112.5 (ArC and C=CH), 81.9 (t, *J*_{CD} = 22.5 Hz, CDO), 53.2, 47.0 (2 CH₂N), 47.3 (CH), 41.5 (CH₂CO); IR (KBr): ν̄ = 3300 cm⁻¹ (O–H); LRMS (70 eV, EI): *m/z* (%) = 238 (36) [M⁺ + 2], 236 (100) [M⁺], 218 (34), 190 (47), 141 (26), 140 (67), 139 (57), 138 (56), 111 (46), 80 (52); HRMS (EI) calcd for C₁₃H₁₃DClNO: 236.0826, found 236.0824; anal. calcd C 65.96, H/D 6.39, N 5.92; found C 66.04, H/D 6.26, N 5.97.

cis-1-Deuterio-3-(4-methoxyphenyl)-3-azabicyclo[3.3.0]octan-7-one ([D]17f): Amine **7f** (0.56 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of D₂O and extractive workup the resulting crude product (1:4 mixture of [D]17f and [D]18f) was purified by silica gel chromatography (hexane/AcOEt 3:1). Yield: 0.06 g (13%) of [D]17f. M.p. 81–83 °C (hexane/CHCl₃); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 6.9 (d, *J* = 9.2 Hz, 2H, ArH), 6.5 (d, *J* = 9.2 Hz, 2H, ArH), 3.8 (s, 3H, CH₃), 3.6–3.5 (m, 2H, 2NCHH), 3.2–3.1 (m, 2H, 2NCHH), 3.1–3.0 (m, 1H, CH), 2.6–2.5 (m, 2H, 2CHHCO), 2.3–2.2 (m, 2H, 2CHHCO); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 218.7 (CO), 151.2, 142.5, 114.8, 113.0 (ArC), 55.8 (CH₃), 54.0 (2 CH₂N), 43.2 (2 CH₂CO), 38.8 (CH), 38.8 (t, *J*_{CD} = 5.0 Hz, CD); IR (KBr): 1740 cm⁻¹ (C=O); LRMS (70 eV, EI): *m/z* (%) = 232 (95) [M⁺], 231 (50), 218 (47), 217 (100), 216 (35), 134 (28), 121 (50); HRMS (EI) calcd for C₁₄H₁₆DNO₂: 232.1322, found 232.1330; anal. calcd C 72.39, H/D 7.81, N 6.03; found C 72.45, H/D 7.70, N 6.05.

cis-7-Deuterio-3-(4-methoxyphenyl)-3-aza-1(8)-bicyclo[3.3.0]octen-7-ol ([D]18f): Yield: 0.24 g (51%). M.p. 129–131 °C (hexane/CHCl₃); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 6.9 (d, *J* = 8.9 Hz, 2H, ArH), 6.5 (d, *J* = 8.9 Hz, 2H, ArH), 5.6 (s, 1H, =CH), 3.9 (d, *J* = 13.7 Hz, 1H, NCHHC=), 3.8 (s, 3H, CH₃), 3.7 (d, *J* = 13.7 Hz, 1H, NCHHC=), 3.6 (t, *J* = 7.9 Hz, 1H, NCHHCH), 3.2–3.1 (m, 1H, CH), 2.7–2.6 (m, 2H, NCHHCH and CHHCO), 1.4 (dd, *J* = 12.3, 8.5 Hz, 1H, CHHCO); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 150.8, 148.6, 142.5, 123.6, 114.8, 112.3 (ArC and C=CH), 81.7 (t, *J*_{CD} = 19.8 Hz, CDO), 55.7 (CH₃), 53.4, 47.4 (2 CH₂N), 47.3 (CH), 41.2 (CH₂CO); LRMS (70 eV, EI): *m/z* (%) = 232 (93) [M⁺], 231 (50), 218 (37), 217 (100), 216 (34), 134 (26), 121 (45); HRMS (EI) calcd for C₁₄H₁₆DNO₂: 232.1322, found 232.1324; anal. calcd C 72.39, H/D 7.81, N 6.03; found C 72.47, H/D 7.66, N 6.08.

Reaction of 19 with electrophiles—General procedure: A solution of zirconacycle **9** was stirred at RT for 40 min under one atm CO. Then, a slight excess of different electrophiles (allyl bromide, 4-chlorobenzonitrile, benzaldehyde, and benzylideneaniline) was added. Alternatively, the electrophiles could be added before the introduction of CO. The suspension was stirred overnight and then aqueous NaHCO₃ was added. The resultant mixture was filtered

through Celite, extracted with AcOEt (3 × 20 mL), and dried over Na₂SO₄. After removal of the solvent (15 mm Hg), the residue was purified by flash column chromatography to afford functionalized bicyclopentanones **21–24**.

cis-1-Allyl-3-phenyl-3-azabicyclo[3.3.0]octan-7-one (21b): Amine **7b** (0.50 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol). Carbon monoxide was bubbled through the mixture for 40 min. After the addition of allyl bromide (0.36 g, 3 mmol), the mixture was stirred overnight. Hydrolysis and extractive workup afforded the crude product, which was purified by silica gel chromatography (hexane/AcOEt 7:1). Yield: 0.21 g (44%) of **21b**. *R*_f = 0.34 (hexane/AcOEt 5:1); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.3–6.6 (m, 5H, ArH), 5.9–5.8 (m, 1H, =CH), 5.2–5.1 (m, 2H, =CH₂), 3.7 (dd, *J* = 9.9, 7.3 Hz, 1H, NCHHC), 3.4 (d, *J* = 9.7 Hz, 1H, NCHHC), 3.3 (d, *J* = 9.7 Hz, 1H, NCHHC), 3.2 (dd, *J* = 9.9, 4.7 Hz, 1H, NCHHC), 2.8–2.7 (m, 1H, CH), 2.6 (dd, *J* = 18.9, 8.2 Hz, 1H, CHCHCO), 2.4–2.3 (m, 4H, CH₂CH= and CCH₂CO), 2.2 (dd, *J* = 18.9, 13.7 Hz, 1H, CHCHCO); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 217.2 (CO), 147.2, 129.0, 116.1, 111.6 (ArC), 133.5 (CH=CH₂), 118.8 (CH=CH₂), 56.8, 53.1 (2CH₂N), 49.2 (CCH), 47.2, 43.1, 42.0 (2CH₂CO and CH₂CH=), 43.3 (CH); IR (neat): ν̄ = 1740 cm⁻¹ (C=O); HRMS (EI) calcd for C₁₆H₁₉NO: 241.1466, found 241.1473.

cis-1-(4-Chlorobenzoyl)spiro[bicyclo[3.3.0]octane-3,9'-(9H)fluorene]-7-one (22a): Fluorene derivative **7a** (0.65 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol). Carbon monoxide was bubbled through the mixture for 40 min. After the addition of 4-chlorobenzonitrile (0.29 g, 2.1 mmol), the mixture was stirred overnight. Hydrolysis and extractive workup afforded the crude product, which was purified by silica gel chromatography (hexane/AcOEt 7:1). Yield: 0.38 g (46%) of **22a**. M.p. 162–164 °C (hexane/CHCl₃); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.8–7.2 (m, 12H, ArH), 4.3 (dt, *J* = 12.0, 8.2 Hz, 1H, CH), 3.2 (d, *J* = 19.4 Hz, 1H, CCHCO), 3.0 (d, *J* = 19.4 Hz, 1H, CCHCO), 2.9 (d, *J* = 14.6 Hz, 1H, CCHHC), 2.8 (d, *J* = 14.6 Hz, 1H, CCHHC), 2.7 (dd, *J* = 18.9, 8.2 Hz, 1H, CHCHCO), 2.4 (d, *J* = 18.9 Hz, 1H, CHCHCO), 2.2–2.1 (m, 2H, CCH₂CH); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 216.2 (CH₂CO), 200.1 (ArCO), 152.8, 149.8, 139.7, 139.4, 138.7, 131.3, 131.0, 128.7, 127.7, 127.5, 127.2, 123.2, 122.3, 119.7 (ArC), 60.6, 58.6 (2CCH₂), 52.0, 51.1, 45.7, 43.0 (4CH₂), 43.4 (CH); IR (KBr): ν̄ = 1735 (C=O), 1675 (C=O) cm⁻¹; HRMS (EI) calcd for C₂₇H₂₁ClO₂: 412.1230, found 412.1224; anal. calcd C 78.54, H 5.13; found C 78.46, H 5.15.

cis-1-(4-Chlorobenzoyl)-3-phenyl-3-azabicyclo[3.3.0]octan-7-one (22b): Amine **7b** (0.50 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol). Carbon monoxide was bubbled through the mixture for 40 min. After the addition of 4-chlorobenzonitrile (0.29 g, 2.1 mmol), the mixture was stirred overnight. Hydrolysis and extractive workup afforded the crude product, which was purified by silica gel chromatography (hexane/AcOEt 5:1). Yield: 0.33 g (49%) of **22b**. M.p. 118–120 °C (hexane/CHCl₃); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.9–6.6 (m, 9H, ArH), 3.9 (d, *J* = 10.2 Hz, 1H, NCHHC), 3.8–3.7 (m, 2H, CH and NCHHC), 3.7 (d, *J* = 10.2 Hz, 1H, NCHHC), 3.2 (dd, *J* = 12.7, 9.2 Hz, 1H, NCHHC), 3.0 (d, *J* = 19.0 Hz, 1H, CCHCO), 2.8 (d, *J* = 19.0 Hz, 1H, CCHCO), 2.7 (dd, *J* = 19.1, 7.0 Hz, 1H, CHCHCO), 2.4 (dd, *J* = 19.1, 4.5 Hz, 1H, CHCHCO); ¹³C NMR (75.5 MHz, CDCl₃, 25 °C): δ = 214.5 (CH₂CO), 198.4 (ArCO), 146.8, 139.7, 132.1, 130.4, 129.1, 129.0, 117.2, 112.4 (ArC), 59.4 (CCH₂), 57.6, 52.9, 47.8, 42.5 (4CH₂), 41.6 (CH); IR (KBr): ν̄ = 1740 (C=O), 1680 (C=O) cm⁻¹; HRMS (EI) calcd for C₂₀H₁₈ClNO₂: 339.1026, found 339.1022; anal. calcd C 70.69, H 5.34, N 4.12; found C 70.56, H 5.37, N 4.11.

cis-3-Phenyl-1-phenylhydroxymethyl-3-azabicyclo[3.3.0]octan-7-one (23b): Amine **7b** (0.50 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol). Carbon monoxide was bubbled through the mixture for 40 min. After the addition of benzaldehyde (0.23 g, 2.2 mmol), the mixture was stirred overnight. Hydrolysis and extractive workup afforded the crude product (a 4:1 mixture of diastereoisomers), which was purified by silica gel chromatography (hexane/AcOEt 4:1). Yield: 0.26 g (42%) of **23b**. Major diastereoisomer: *R*_f = 0.26 (hexane/AcOEt 2:1); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.5–6.5 (m, 10H, ArH), 4.7 (s, 1H, CHO), 3.7 (d, *J* = 9.9 Hz, 1H, NCHHC), 3.6 (t, *J* = 9.9 Hz, 1H, NCHHC), 3.3 (d, *J* = 9.9 Hz, 1H, NCHHC), 3.1 (dd, *J* = 9.9, 5.6 Hz, 1H, NCHHC), 3.0–2.8 (m, 2H, CH and OH), 2.7 (d, *J* = 18.9 Hz, 1H,

CCHCO), 2.2 (d, *J* = 18.9 Hz, 1H, CCHCO), 2.1–2.0 (m, 2H, CHCH₂CO); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 217.7 (C=O), 147.3, 140.6, 129.0, 128.3, 128.2, 127.0, 116.3, 111.9 (ArC), 77.3 (CHO), 56.1, 54.1 (2CH₂N), 54.8 (CCH₂), 44.5, 43.0 (2CH₂CO), 39.9 (CH); IR (neat): ν̄ = 3450 (O–H), 1735 (C=O) cm⁻¹; HRMS (EI) calcd for C₂₀H₂₁NO₂: 307.1559, found 307.1564.

cis-3-Phenyl-1-[phenyl-(*N*-phenylamino)methyl]-3-azabicyclo[3.3.0]octan-7-one (24b): Amine **7b** (0.50 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol). Carbon monoxide was bubbled through the mixture for 40 min. After the addition of benzyldeneaniline (0.38 g, 2.1 mmol), the mixture was stirred overnight. Hydrolysis and extractive workup afforded the crude product (a 5:1 mixture of diastereoisomers), which was purified by silica gel chromatography (hexane/AcOEt 5:1). Yield: 0.23 g (31%) of **24b**. Major diastereoisomer: *R*_f = 0.35 (hexane/AcOEt 3:1); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.4–6.5 (m, 15H, ArH), 4.5 (s, 1H, CHN), 4.5 (brs, 1H, NH), 3.9 (dd, *J* = 9.9, 8.2 Hz, 1H, NCHHC), 3.8 (d, *J* = 10.3 Hz, 1H, NCHHC), 3.4 (dd, *J* = 10.3, 2.1 Hz, 1H, NCHHC), 3.2 (dd, *J* = 9.9, 5.2 Hz, 1H, NCHHC), 3.1–3.0 (m, 1H, CH), 2.8 (d, *J* = 18.7 Hz, 1H, CCHCO), 2.3 (d, *J* = 18.7 Hz, 1H, CCHCO), 2.1–2.0 (m, 2H, CHCH₂CO); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 215.9 (CO), 147.1, 146.3, 139.4, 129.2, 129.1, 128.8, 128.0, 127.6, 117.8, 117.0, 113.4, 112.3 (ArC), 63.3 (CHN), 56.9, 54.4, 44.7, 43.3, 41.8; LRMS (70 eV, EI): *m/z* (%) = 382 (8) [*M*⁺], 182 (100), 106 (25), 77 (22).

Carbonylation of zirconatrimethylcyclopropane 15: *tert*-Butyllithium (2.4 mL, 4 mmol) was added *t*BuLi (2.4 mL, 4 mmol) to a suspension of **14** (0.61 g, 2 mmol) in Et₂O (10 mL) at –78 °C. The reaction mixture was stirred for 1 h and then was transferred by cannula into a solution of bis(cyclopentadienyl)zirconium methyl chloride (0.57 g, 2.1 mmol) in Et₂O (20 mL) at –78 °C. The mixture was stirred at RT for 3 h. The N₂ in the reaction vessel containing a solution of **15** was evacuated. CO was bubbled through the mixture over 40 min and then the reaction was quenched with aqueous NaHCO₃, filtered through Celite, and extracted with AcOEt (3 × 20 mL). The organic layer was washed with brine and dried over Na₂SO₄. Removal of the solvent in vacuo and subsequent column chromatography gave a 1:1 mixture of **25** and **26**.

(1*S,4*R**,8*S**,11*R**)-3-Benzyl-3-azatricyclo[6.2.1.0⁴]undecan-9-one (25)**: Yield: 0.14 g (27%). M.p. 74–76 °C (hexane/CHCl₃); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.4–7.2 (m, 5H, ArH), 4.0 (d, *J* = 13.7 Hz, 1H, ArCHHN), 3.0–2.9 (m, 1H, CHCN), 2.9 (d, *J* = 13.7 Hz, 1H, ArCHHN), 2.6 (d, *J* = 8.9 Hz, 1H, NCHH), 2.7–2.5 (m, 2H, CHCH₂N and CHCO), 2.4–2.2 (m, 2H, NCH and CHCO), 2.15 (dd, *J* = 8.9, 5.2 Hz, 1H, NCHH), 2.0 (d, *J* = 15.6 Hz, 1H, CHCO), 2.1–1.2 (m, 6H, 3CH₂ ring); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 216.7 (CO), 139.5, 128.1, 128.0, 126.5 (ArC), 62.8, 56.0 (2CH₂N), 61.8 (CHN), 45.1, 40.9, 32.0 (3CH), 44.7 (CH₂CO), 25.4, 22.7, 16.0 (3CH₂ cyclohexyl); IR (neat): ν̄ = 1735 cm⁻¹ (C=O) HRMS (EI) calcd for C₁₇H₂₁NO: 255.1623, found 255.1627; anal. calcd C 79.96, H 8.29, N 5.49; found C 79.83, H 8.31, N 5.47.

(4*R,8*S**,9*S**,11*R**)-3-Benzyl-3-aza-1(10)-tricyclo[6.2.1.0⁴]undecan-9-one (26)**: Yield: 0.14 g (28%). M.p. 88–90 °C (hexane/CHCl₃); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.4–7.2 (m, 5H, ArH), 5.3 (s, 1H, =CH), 5.1–5.0 (m, 1H, CHO), 3.9 (d, *J* = 12.8 Hz, 1H, ArCHHN), 3.7 (d, *J* = 12.8 Hz, 1H, ArCHHN), 3.5 (d, *J* = 5.5 Hz, 1H, NCHH), 3.4–3.1 (m, 3H, NCHH, NCH and OH), 3.1–3.0 (m, 1H, CHCN), 2.7–2.6 (m, 1H, CHCO), 1.7–0.9 (m, 6H, 3CH₂ ring); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 146.8, 138.0, 128.6, 128.2, 127.1, 121.7 (ArC and C=CH), 83.6 (CHO), 57.9 (CHN), 55.4, 49.1 (2CH₂N), 50.4, 44.4 (2CH), 22.6, 20.8 (3CH₂ cyclohexyl); IR (neat): ν̄ = 3485 cm⁻¹ (O–H); HRMS (EI) calcd for C₁₇H₂₁NO: 255.1623, found 255.1620; anal. calcd C 79.96, H 8.29, N 5.49; found C 79.88, H 8.33, N 5.52.

(1*S,4*R**,8*S**,11*R**)-3-Benzyl-1-(4-pyridinyl)-3-azatricyclo[6.2.1.0⁴]undecan-9-one (27)**: To a solution of **15** was added 4-cyanopyridine (0.22 g, 2.1 mmol) and then CO was bubbled through the mixture over 40 min. The reaction was stirred overnight, then hydrolyzed with aq. NaHCO₃. After filtering through Celite and extracting with AcOEt (3 × 20 mL) the solvent was removed at low pressure and the residue purified by flash chromatography (hexane/AcOEt 2:1). Yield: 0.3 g (41%) of **27**. *R*_f = 0.26 (hexane/AcOEt 1:1). ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 8.7–7.2 (m, 9H, ArH), 4.0 (d, *J* = 13.7 Hz, 1H, ArCHHN), 3.6 (dd, *J* = 10.7,

6.7 Hz, 1H, *CHCHN*), 3.1 (d, $J = 9.2$ Hz, 1H, *NCHH*), 2.9 (d, $J = 13.7$ Hz, 1H, *ArCHHN*), 2.8 (dd, $J = 17.5, 2.2$ Hz, 1H, *CHCO*), 2.6–2.5 (m, 2H, *CHN* and *CHCO*), 2.5 (d, $J = 17.5$ Hz, 1H, *CHCO*); 2.3 (d, $J = 9.2$ Hz, 1H, *NCHH*), 2.3–1.3 (m, 6H, 3CH₂ ring); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 212.3$ (CH₂CO), 201.3 (ArCO), 150.4, 142.3, 138.3, 128.2, 127.8, 126.8, 121.2 (ArC), 65.9, 55.4 (2CH₂N), 61.1 (CHN), 55.3 (CCH), 48.8 (CH₂CO), 44.7, 44.0 (2CH), 24.9, 22.2, 15.5 (3CH₂ cyclohexyl); IR (neat): $\tilde{\nu} = 1740$ (C=O), 1690 (C=O) cm⁻¹; HRMS (EI) calcd for C₂₃H₂₄N₂O₂: 360.1838, found 360.1829.

Evolution of π -allylzirconium intermediates to cyclopentenones **29 and **30**:** A solution of zirconacycles **9** or **15** were stirred under CO (40 min) in the absence of electrophiles. The mixture was refluxed for 5 h and then H₂O or D₂O was added. The mixture was filtered through Celite and extracted with AcOEt (3 × 20 mL). The organic layer was washed with brine and dried over Na₂SO₄. The solvent was removed and the residue was purified by column chromatography.

3-Methyl-4-phenylaminomethyl-2-cyclopentenone (29b): Amine **7b** (0.50 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After refluxing for 5 h, the mixture was hydrolyzed and extractive workup afforded the crude product which was purified by silica gel chromatography (hexane/AcOEt 2:1). Yield: 0.21 g (53%) of **29b**. $R_f = 0.34$ (hexane/AcOEt 1:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.3$ –6.6 (m, 5H, ArH), 6.0 (s, 1H, =CH), 3.7 (brs, 1H, NH), 3.5 (dd, $J = 14.8, 7.3$ Hz, 1H, *NCHH*), 3.2–3.1 (m, 2H, *NCHH* and CH), 2.6 (dd, $J = 18.5, 5.8$ Hz, 1H, *CHCO*), 2.3 (dd, $J = 18.5, 1.3$ Hz, 1H, *CHCO*), 2.2 (s, 3H, CH₃); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 208.0$ (CO), 178.5 (C=CH), 147.5, 129.1, 117.6, 112.6 (ArC), 132.2 (C=CH), 45.4 (CH₂N), 43.8 (CH), 40.1 (CH₂CO), 17.4 (CH₃); IR (neat): $\tilde{\nu} = 3370$ (N–H), 1680 (C=O) cm⁻¹; HRMS (EI) calcd for C₁₃H₁₅NO: 201.1154, found 201.1159.

4-(4-Chlorophenylaminomethyl)-3-deuteriomethyl-2-cyclopentenone (29e): Amine **7e** (0.57 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After refluxing for 5 h the mixture was treated with deuterium oxide and extractive workup afforded the crude product which was purified by silica gel chromatography (hexane/AcOEt 2:1). Yield: 0.25 g (52%) of **29e**. $R_f = 0.37$ (hexane/AcOEt 1:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.1$ (d, $J = 8.9$ Hz, 2H, ArH), 6.5 (d, $J = 8.9$ Hz, 2H, ArH), 6.0 (s, 1H, =CH), 3.7 (brs, 1H, NH), 3.4 (dd, $J = 14.8, 7.1$ Hz, 1H, *NCHH*), 3.2–3.1 (m, 2H, *NCHH* and CH), 2.6 (dd, $J = 18.5, 6.2$ Hz, 1H, *CHCO*), 2.3 (dd, $J = 18.5, 1.7$ Hz, 1H, *CHCO*), 2.1 (s, 2H, CH₂D); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 207.8$ (CO), 178.2 (C=CH), 146.2, 128.9, 122.1, 113.7 (ArC), 132.3 (C=CH), 45.4 (CH₂N), 43.7 (CH), 40.1 (CH₂CO), 17.1 (t, $J_{CD} = 19.6$ Hz, CH₂D); IR (neat): $\tilde{\nu} = 3370$ (N–H), 1685 (C=O) cm⁻¹; HRMS (EI) calcd for C₁₃H₁₃DCINO: 236.0826, found 236.0825.

(1S*,2R*,6S*)-2-Benzylamino-9-methyl-8(9)-bicyclo[4.3.0]nonen-7-one (30): Amine **14** (0.61 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. The mixture was refluxed for 5 h the mixture and then hydrolyzed. Extractive workup afforded the crude product, which was purified by silica gel chromatography (hexane/AcOEt 2:1). Yield: 0.21 g (42%) of **30**. $R_f = 0.41$ (hexane/AcOEt 1:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.4$ –7.2 (m, 5H, ArH), 6.0 (s, 1H, =CH), 3.8 (d, $J = 13.4$ Hz, 1H, *ArCHHN*), 3.7 (d, $J = 13.4$ Hz, 1H, *ArCHHN*), 3.2–3.15 (m, 1H, CHN), 3.0 (dd, $J = 6.4, 5.7$ Hz, 1H, *CHCHN*), 2.5–2.4 (m, 1H, CHCO), 2.2 (s, 3H, CH₃), 2.1–1.2 (m, 7H, NH and 3CH₂ ring); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 210.8$ (CO), 177.9 (C=CH), 140.3, 128.2, 127.8, 126.8 (ArC), 131.8 (C=CH), 52.0 (CHN), 51.2 (CH₂N), 47.9, 46.2 (2CH), 24.9, 21.4, 16.6 (3CH₂ cyclohexyl), 18.9 (CH₃); IR (neat): $\tilde{\nu} = 3300$ (N–H), 1695 (C=O) cm⁻¹; HRMS (EI) calcd for C₁₇H₂₁NO: 255.1623, found 255.1627.

General procedure for the synthesis of *N*-benzyl-*N*-(2-bromoallyl)amines **31 and **35**:** *N*-Benzyl-*N*-(2-bromoallyl)amine (5.58 g, 20 mmol), haloalkene (10 mmol) (4-bromo-1-butene, 5-bromo-1-pentene, 4-iodo-1-butyne, or 5-iodo-1-pentyne), and H₂O (100 mL) were placed in a flask. The mixtures were stirred for 2 d at 70 °C, cooled and poured into a separating funnel containing AcOEt (30 mL). The organic layers were collected, washed with water and brine, dried over Na₂SO₄, and filtered. The solvents were removed and the

residue purified by flash column chromatography to give **31 a,b** and **35 a,b** as colorless oils.

***N*-Benzyl-*N*-(2-bromoallyl)-3-butenylamine (31a):** The reaction was performed as described in the general procedure with 4-bromo-1-butene (1.35 g, 10 mmol). After extractive workup, the crude product was purified by silica gel chromatography (hexane/AcOEt 20:1). Yield: 1.86 g (67%) of **31a**. $R_f = 0.39$ (hexane/AcOEt 15:1); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.4$ –7.2 (m, 5H, ArH), 6.0 (s, 1H, BrC=CHH), 5.9–5.8 (m, 1H, CH=C), 5.6 (s, 1H, BrC=CHH), 5.1–5.0 (m, 2H, CH=CH₂), 3.7 (s, 2H, ArCH₂N), 3.3 (s, 2H, NCH₂C), 2.6 (dt, $J = 7.3, 2.2$ Hz, 2H, NCH₂CH₂), 2.3–2.25 (m, 2H, CH₂CH=), ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 138.9, 132.1, 128.6, 128.1, 126.6$ (ArC and CBr), 136.4 (CH=CH₂), 117.8, 115.5 (2=CH₂), 61.8, 57.5, 52.6 (3CH₂N), 31.4 (CH₂CH); HRMS (EI) calcd for C₁₄H₁₇BrN (M⁺ – 1): 278.0544, found 278.0541.

***N*-Benzyl-*N*-(2-bromoallyl)-4-pentenylamine (31b):** The reaction was performed as described in the general procedure with 5-bromo-1-pentene (1.49 g, 10 mmol). After extractive workup, the crude product was purified by silica gel chromatography (hexane/AcOEt 20:1). Yield: 1.70 g (58%) of **31b**. $R_f = 0.41$ (hexane/AcOEt 15:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.4$ –7.3 (m, 5H, ArH), 6.0 (s, 1H, BrC=CHH), 5.9–5.7 (m, 1H, CH=C), 5.6 (s, 1H, BrC=CHH), 5.1–4.9 (m, 2H, CH=CH₂), 3.7 (s, 2H, ArCH₂N), 3.3 (s, 2H, NCH₂C), 2.5 (dd, $J = 7.3, 7.0$ Hz, 2H, NCH₂CH₂), 2.2–2.1 (m, 2H, CH₂CH=), 1.7–1.6 (m, 2H, NCH₂CH₂); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 139.0, 132.3, 128.5, 128.0, 126.6$ (ArC and CBr), 138.4 (CH=CH₂), 117.8, 114.4 (2=CH₂), 62.0, 57.8, 52.5 (3CH₂N), 31.2, 26.2 (CH₂CH₂C=); HRMS (EI) calcd for C₁₅H₂₀BrN: 293.0779, found 293.0769.

***N*-Benzyl-*N*-(2-bromoallyl)-3-butenylamine (35a):** The reaction was performed as described in the general procedure with 4-iodo-1-butyne (1.80 g, 10 mmol). After extractive workup, the crude product was purified by silica gel chromatography (hexane/AcOEt 20:1). Yield: 1.62 g (68%) of **35a**. $R_f = 0.25$ (hexane/AcOEt 15:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.4$ –7.3 (m, 5H, ArH), 6.0 (s, 1H, BrC=CHH), 5.6 (s, 1H, BrC=CHH), 3.7 (s, 2H, ArCH₂N), 3.4 (s, 2H, NCH₂C), 2.8 (dd, $J = 7.7, 7.3$ Hz, 2H, NCH₂CH₂), 2.45–2.4 (m, 2H, CH₂C≡), 2.0 (t, $J = 2.6$ Hz, 1H, ≡CH); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 138.6, 131.7, 128.5, 128.1, 126.9$ (ArC and CBr), 118.1 (=CH₂), 82.6 (≡CH), 69.2 (≡C), 61.8, 57.4, 51.8 (3CH₂N), 17.1 (CH₂C≡); HRMS (EI) calcd for C₁₁H₁₃BrN (M⁺ – C₃H₃): 238.0231, found 238.0219.

***N*-Benzyl-*N*-(2-bromoallyl)-4-pentenylamine (35b):** The reaction was performed as described in the general procedure with 5-iodo-1-pentyne (1.94 g, 10 mmol). After extractive workup, the crude product was purified by silica gel chromatography (hexane/AcOEt 20:1). Yield: 1.74 g (69%) of **35b**. $R_f = 0.26$ (hexane/AcOEt 15:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.4$ –7.3 (m, 5H, ArH), 5.9 (s, 1H, BrC=CHH), 5.6 (s, 1H, BrC=CHH), 3.6 (s, 2H, ArCH₂N), 3.3 (s, 2H, NCH₂C), 2.6 (t, $J = 6.9$ Hz, 2H, NCH₂CH₂), 2.3–2.2 (m, 2H, NCH₂CH₂), 1.9 (t, $J = 2.6$ Hz, 1H, ≡CH), 1.8–1.7 (m, 2H, CH₂C≡); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 138.7, 132.1, 128.6, 128.0, 126.8$ (ArC and CBr), 118.1 (=CH₂), 84.1 (≡CH), 68.3 (≡C), 61.9, 57.7, 51.7 (3CH₂N), 26.1, 16.0 (CH₂CH₂C≡).

Formation of six- and seven-membered heterocycles (33, 34, and 37)—General procedure: 2-Bromoallyl amines **31** or **35** (2 mmol) were treated with *t*BuLi (4 mmol for **31** and 6 mmol for **35**) at –78 °C in Et₂O. The corresponding anions were added to a solution of bis(cyclopentadienyl)zirconium methyl chloride (0.57 g, 2.1 mmol) in Et₂O at –78 °C. The reaction mixtures were allowed to reach RT and then were quenched with deuterated sulfuric acid to afford products **33** and **37**, or were treated with CO and 4-chlorobenzonitrile to afford diketone **34**.

1-Benzyl-4-deuteriomethyl-3-(*E*)-deuteriomethylenepiperidine (33a): Amine **31a** (0.56 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); after the addition of D₂SO₄ and the extractive workup, the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 5:1). Yield: 0.29 g (72%) of **33a**. $R_f = 0.32$ (hexane/AcOEt 3:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.4$ –7.3 (m, 5H, ArH), 4.85–4.75 (m, 1H, =CH), 3.6 (s, 2H, ArCH₂N), 3.3 (dd, $J = 11.8, 1.7$ Hz, 1H, *CHHC*=), 3.0–2.9 (m, 1H, *NCHHCH*), 2.7 (d,

$J = 11.8$ Hz, 1H, CHHC=), 2.2 (dt, $J = 11.4$, 3.2 Hz, 1H, NCHHCH₂), 2.15–2.05 (m, 1H, CH), 1.8–1.7 (m, 1H, CHHCH), 1.5–1.3 (m, 1H, CHHCH), 1.15–1.05 (m, 2H, CH₂D); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 148.8$, 138.0, 129.1, 128.0, 126.8 (ArC and C=CHD), 106.7 (t, $J_{CD} = 23.9$ Hz, C=CHD), 62.7, 60.7, 53.2 (3CH₂N), 35.3 (CH), 34.4 (CH₂CH), 17.3 (t, $J_{CD} = 19.2$ Hz, CH₂D); HRMS (EI) calcd for C₁₄H₁₇D₂N: 203.1643, found 203.1638.

1-Benzyl-4-deuteriomethyl-3-(E)-deuteriomethylenepiperhydroazepine (33b): Amine **31b** (0.59 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); after the addition of D₂SO₄ and the extractive workup, the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 7:1). Yield: 0.22 g (51%) of **33b**. $R_f = 0.33$ (hexane/AcOEt 4:1); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.4$ –7.2 (m, 5H, ArH), 4.8 (s, 1H, =CH), 3.7 (d, $J = 13.3$ Hz, 1H, ArCHHN), 3.6 (d, $J = 13.3$ Hz, 1H, ArCHHN), 3.3 (d, $J = 13.8$ Hz, 1H, CHHC=), 3.2 (d, $J = 13.8$ Hz, 1H, CHHC=), 2.8 (dt, $J = 12.9$, 4.7 Hz, 1H, NCHHCH₂), 2.65–2.55 (m, 1H, CH), 2.55–2.45 (m, 1H, NCHHCH₂), 1.9–1.8 (m, 1H, CHHCH), 1.65–1.55 (m, 2H, CH₂CH₂CH₂), 1.35–1.25 (m, 1H, CHHCH), 1.15–1.0 (m, 2H, CH₂D); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 152.8$, 139.7, 128.8, 128.0, 126.7 (ArC and C=CHD), 111.2 (t, $J_{CD} = 23.5$ Hz, C=CHD), 60.9, 59.7, 55.6 (3CH₂N), 38.1 (CH), 36.3, 26.9 (CH₂CH₂CH), 21.5 (t, $J_{CD} = 19.9$ Hz, CH₂D); HRMS (EI) calcd for C₁₅H₁₉D₂N: 217.1800, found 217.1791.

cis-3-Benzyl-1-(4-chlorobenzoyl)-3-azabicyclo[4.3.0]nonan-8-one (34a): Amine **31a** (0.56 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of 4-chlorobenzonitrile (0.29 g, 2.1 mmol), the mixture was stirred overnight. Hydrolysis and extractive workup afforded the crude product, which was purified by silica gel chromatography (hexane/AcOEt 5:1). Yield: 0.32 g (43%) of **34a**. M.p. 143–145 °C (hexane/CHCl₃); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.5$ –6.9 (m, 9H, ArH), 3.5 (d, $J = 13.0$ Hz, 1H, ArCHHN), 3.3–3.2 (m, 1H, CH), 3.12 (d, $J = 13.0$ Hz, 1H, ArCHHN), 3.08 (d, $J = 12.4$ Hz, 1H, NCHHC), 2.7–2.6 (m, 1H, NCHHCH₂), 2.6 (d, $J = 18.1$ Hz, 1H, CCHHCO), 2.5 (d, $J = 18.1$ Hz, 1H, CCHHCO), 2.4–2.3 (m, 3H, CHCH₂CO and NCHHCH₂), 2.2 (d, $J = 12.4$ Hz, 1H, NCHHC), 2.2–2.0 (m, 1H, NCH₂CHH), 1.6 (dq, $J = 13.6$, 3.5 Hz, 1H, NCH₂CHH); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 214.7$ (CH₂CO), 202.1 (ArCO), 137.9, 137.1, 134.7, 129.3, 128.4, 128.3, 127.8, 126.7 (ArC), 62.7, 56.0, 49.4 (3CH₂N), 53.8 (CCH), 46.9, 39.5 (2CH₂CO), 33.8 (CH), 24.8 (CH₂CH₂N); IR (neat): $\tilde{\nu} = 1750$ (C=O), 1665 (C=O) cm⁻¹; HRMS (EI) calcd for C₂₂H₂₂ClNO: 367.1344, found 367.1342; anal. calcd C 71.83, H 6.03, N 3.81; found C 71.69, H 5.99, N 3.77.

1-Benzyl-3-(E)-deuteriomethylene-4-dideuteriomethylenepiperidine (37a): Amine **35a** (0.48 g, 2 mmol) was treated with *t*BuLi (3.6 mL, 6 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); after the addition of D₂SO₄ and the extractive workup, the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 7:1). Yield: 0.25 g (61%) of **37a**. $R_f = 0.36$ (hexane/AcOEt 5:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.4$ –7.3 (m, 5H, ArH), 4.8 (s, 1H, =CH), 3.6 (s, 2H, ArCH₂N), 3.1 (s, 2H, NCH₂C=), 2.6 (t, $J = 5.7$ Hz, 2H, NCH₂CH₂), 2.4 (t, $J = 5.7$ Hz, 2H, NCH₂CH₂); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 145.4$, 144.6, 138.1, 129.0, 128.1, 127.0 (ArC and 2C=), 109.4 (t, $J_{CD} = 23.5$ Hz, CD and CD₂), 62.2, 59.8, 53.2 (3CH₂N), 33.4 (CH₂C); HRMS (EI) calcd for C₁₄H₁₄D₃N: 202.1549, found 202.1546.

General procedure for the synthesis of *o*-allylanilines 39 and 40: *o*-Allylaniline^[31] (2.7 g, 20 mmol), 2,3-dibromopropene or 2,4-diiodobutene (10 mmol), and water (100 mL) were placed in a flask. The mixture was heated at 70 °C overnight, made basic, extracted with AcOEt, and dried over Na₂SO₄. The solvents were removed (15 mm Hg) and the residue purified by column chromatography to afford anilines **39**. To a flask were added **39** (10 mmol), methyl iodide (2.13 g, 15 mmol), NaKCO₃ (1.85 g, 15 mmol), and DMF (30 mL). The mixture was refluxed for 3 h, allowed to cool to RT, and then poured into a separating funnel containing AcOEt and water. The organic layer was collected, washed with water and brine, and dried over Na₂SO₄, and the solvents were then removed. The tertiary amines **40** were isolated by column chromatography.

2-Allyl-N-(3-iodo-3-butenyl)aniline (39b): The reaction was performed as described in the general procedure with 2,4-diiodobutene (3.08 g, 10 mmol).

After extractive workup, the crude product was purified by silica gel chromatography (hexane/AcOEt 30:1). Yield: 2.03 g (65%) of **39b**. Isolated yield: 65%. $R_f = 0.28$ (hexane/AcOEt 20:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.2$ –6.7 (m, 4H, ArH), 6.2 (s, 1H, IC=CHH), 6.0–5.9 (m, 1H, CH=CH₂), 5.9 (s, 1H, IC=CHH), 5.2–5.1 (m, 2H, CH=CH₂), 3.8 (brs, 1H, NH), 3.4–3.3 (m, 2H, NCH₂), 2.7 (dd, $J = 6.5$, 6.0 Hz, 2H, CH₂Cl); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 145.5$, 135.6, 129.7, 127.5, 123.5, 117.1, 110.3, 108.7 (ArC, =Cl, and CH=CH₂), 127.6 (CH₂=Cl), 116.2 (CH₂=Cl), 44.2, 42.1, 36.4 (3CH₂); LRMS (70 eV, EI): m/z (%) = 313 (4) [M⁺], 146 (100), 131 (21), 130 (33), 118 (34), 117 (20), 91 (23).

2-Allyl-N-(2-bromoallyl)-N-methylaniline (40a): The reaction was performed as described in the general procedure with 2,3-dibromopropene (2.0 g, 10 mmol) followed by addition of methyl iodide (2.13 g, 15 mmol). After extractive workup, the crude product was purified by silica gel chromatography (hexane/AcOEt 25:1). Yield: 2.0 g (77%) of **40a**. Isolated yield: 77%. $R_f = 0.40$ (hexane/AcOEt 15:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.3$ –7.1 (m, 4H, ArH), 6.2–6.0 (m, 1H, CH=CH₂), 6.1 (s, 1H, BrC=CHH), 5.7 (s, 1H, BrC=CHH), 5.3–5.2 (m, 2H, CH=CH₂), 3.8 (s, 2H, NCH₂C), 3.7 (d, $J = 6.7$ Hz, 2H, CH₂CH=), 2.8 (s, 3H, NCH₃); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 151.0$, 137.7, 135.1, 131.3, 130.3, 126.8, 123.8, 120.7 (ArC, =CBr, and CH=CH₂), 117.8, 115.5 (2=CH₂), 65.1 (CH₂N), 41.4 (CH₃), 34.8 (CH₂CH); HRMS (EI) calcd for C₁₃H₁₆BrN: 265.0466, found 265.0452.

2-Allyl-N-(3-iodo-3-butenyl)-N-methylaniline (40b): The reaction was performed as described in the general procedure with **39b** (3.13 g, 10 mmol) and methyl iodide (2.13 g, 15 mmol). After extractive workup, the crude product was purified by silica gel chromatography (hexane/AcOEt 25:1). Yield: 2.62 g (80%) of **40b**. Isolated yield: 80%. $R_f = 0.42$ (hexane/AcOEt 15:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.3$ –7.1 (m, 4H, ArH), 6.1–5.9 (m, 1H, CH=CH₂), 6.0 (s, 1H, IC=CHH), 5.8 (s, 1H, IC=CHH), 5.2–5.1 (m, 2H, CH=CH₂), 3.5 (d, $J = 6.4$ Hz, 2H, CH₂CH=), 3.2 (dd, $J = 7.6$, 7.0 Hz, 2H, NCH₂), 2.7 (s, 3H, NCH₃), 2.6 (dd, $J = 7.6$, 7.0 Hz, 2H, CH₂Cl); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 150.8$, 137.7, 135.7, 130.1, 126.7, 123.7, 120.9, 109.1 (ArC, =Cl, and CH=CH₂), 126.4 (CH₂=Cl), 115.6 (CH₂=CH), 55.7 (CH₂N), 43.3 (CH₃), 43.2, 34.8 (2CH₂C); HRMS (EI) calcd for C₁₄H₁₈IN: 327.0484, found 327.0496.

Synthesis of benzoheterocycles 42–48—General procedure: Compound **40a** (0.53 g, 2 mmol) or **40b** (0.65 g, 2 mmol) in Et₂O was placed in a Schlenk flask. Addition of *t*BuLi (4 mmol) at –78 °C generated the corresponding anions. The resulting solution was stirred at –78 °C for 30 min and was then added to a solution of bis(cyclopentadienyl)zirconium methyl chloride (0.57 g, 2.1 mmol) at –78 °C. The mixture was stirred at this temperature for 1 h, then allowed to warm to RT and, in the case of formation of **41b**, the reaction was heated to 35 °C for an additional 1 h. The hydrolysis of the intermediate zirconatrimethyls generated benzazepine and benzazocine derivatives **42a** and **42b** by filtration through Celite, extraction with AcOEt (3 × 20 mL), washing with aq. NaHCO₃, drying over Na₂SO₄ and column chromatography. The carbonylation of **41a,b** at 20 °C, under CO (1 atm), in the presence of different electrophiles (water, 4-chlorobenzonitrile, and allyl bromide) allowed the isolation, after standard treatment, of benzoheterocycles **42–48**.

2,3,4,5-Tetrahydro-1,4-dimethyl-3-methylene-1H-1-benzazepine (42a): Amine **40a** (0.53 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); after the addition of H₂O and the extractive workup, the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 20:1). Yield: 0.29 g (78%) of **42a**. $R_f = 0.32$ (hexane/AcOEt 15:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.3$ –6.9 (m, 4H, ArH), 4.8 (s, 2H, =CH₂), 3.9 (d, $J = 12.5$ Hz, 1H, NCHH), 3.4 (d, $J = 12.5$ Hz, 1H, NCHH), 2.9 (s, 3H, NCH₃), 2.85 (dd, $J = 13.3$, 5.2 Hz, 1H, CHHCH), 2.8 (dd, $J = 13.3$, 8.6 Hz, 1H, CHHCH), 2.7–2.6 (m, 1H, CH), 1.2 (d, $J = 6.3$ Hz, 3H, CH₃CH); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): $\delta = 150.7$, 150.4, 133.2, 129.6, 126.6, 120.6, 116.5 (ArC and C=CH₂), 112.8 (=CH₂), 60.9 (CH₂N), 41.5, 37.9 (CH₃N and CH), 40.1 (CH₂CH), 20.1 (CH₃CH); HRMS (EI) calcd for C₁₃H₁₇N: 187.1361, found 187.1361.

1,2,3,4,5,6-Hexahydro-1,5-dimethyl-4-methylene-1-benzazocine (42b): Amine **40b** (0.65 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and

[Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); after the addition of H₂O and the extractive workup, the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 40:1). Yield: 0.20 g (50%) of **42b**. *R*_f = 0.25 (hexane/AcOEt 30:1); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.3–7.0 (m, 4H, ArH), 4.8 (s, 1H, =C(H)H), 4.7 (s, 1H, =CHH), 2.95–2.85 (m, 2H, NCH₂), 2.8 (s, 3H, NCH₃), 2.8–2.7 (m, 2H, CH₂CH), 2.6–2.5 (m, 1H, CH), 2.0 (ddd, *J* = 13.8, 9.0, 3.9 Hz, 1H, CHHC=), 1.8 (ddd, *J* = 13.8, 6.4, 3.9 Hz, 1H, CHHC=), 1.1 (d, *J* = 6.9 Hz, 3H, CH₃CH); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 154.7, 151.1, 138.7, 130.4, 127.1, 124.1, 121.0 (ArC and C=CH₂), 110.0 (=CH₂), 63.1 (CH₂N), 44.4, 43.9 (CH₃N and CH), 38.3, 31.6 (2 CH₂C), 19.8 (CH₃CH); HRMS (EI) calcd for C₁₄H₁₉N: 201.1518, found 201.1526.

3,3,4,4,5,10,10 a-Hexahydro-5-methylbenzo[b]cyclopent[e]azepin-2(1H)-one (43a) and **2,3,3,4,4,9,9 a-hexahydro-3,4,4-dimethyl-1H-cyclopent[b]quinolin-2-one (44a)**: Amine **40a** (0.53 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of H₂O and extractive workup the resulting crude product (2:1:1.5 mixture of **43a**, **44a**, and **45a**) was purified by silica gel chromatography (hexane/AcOEt 5:1). Yield: 0.18 g (42%) of a 2:1 mixture of **43a** and **44a**. *R*_f = 0.29 (hexane/AcOEt 3:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.3–6.6 (m, 8H, ArH), 3.2–2.8 (m, 5H, NCH₂, NCH₂CH and C(H)HCH), 2.9 (s, 3H, NCH₃, major isom.), 2.8 (s, 3H, NCH₃, minor isom.), 2.7–2.0 (m, 12H, CHHCH, CCH₂CH and 2 × CH₂CO), 1.4 (s, 3H, CCH₃, minor isom.); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 218.2 (CO, major isom.), 215.7 (CO, minor isom.), 151.8, 144.6, 130.4, 130.2, 128.9, 127.2, 126.9, 120.4, 119.5, 116.4, 115.2, 111.0 (ArC), 61.3, 56.8, 51.3, 43.4, 42.0, 41.3, 41.2, 40.9, 38.5, 36.4, 35.6, 32.0, 27.2, 22.3; IR (neat): ν̄ = 1740 cm⁻¹ (C=O); HRMS (EI) calcd for C₁₄H₁₇NO: 215.1310, found 215.1305.

1,2,4,5,10,10 a-Hexahydro-2-hydroxy-5-methylbenzo[b]cyclopent[e]azepine (45a): Yield: 0.09 g (21%). M.p. 97–99 °C (hexane/CHCl₃); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.2–6.9 (m, 4H, ArH), 5.5 (s, 1H, =CH), 4.7–4.6 (m, 1H, CHO), 3.6 (d, *J* = 12.9 Hz, 1H, NCHH), 3.5 (d, *J* = 12.9 Hz, 1H, NCHH), 3.1 (dd, *J* = 12.9, 4.7 Hz, 1H, CHHCH), 2.9 (s, 3H, NCH₃), 2.75–2.65 (m, 2H, CH and CHHCHO), 2.55 (dd, *J* = 12.9, 5.8 Hz, 1H, CHHCH), 1.8 (brs, 1H, OH), 1.4–1.3 (m, 1H, CHHCHO); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 151.2, 145.9, 134.2, 131.4, 129.8, 127.0, 121.8, 117.6 (ArC and C=CH), 75.6 (CHO), 57.5 (CH₂N), 42.4, 42.0 (CH₃N and CH), 41.6, 38.7 (2 CH₂C); IR (neat): ν̄ = 3355 cm⁻¹ (O–H) HRMS (EI) calcd for C₁₄H₁₇NO: 215.1310, found 215.1305; anal. calcd C 78.10, H 7.96, N 6.51; found C 78.01, H 7.98, N 6.49.

2,4,5,6,11,11 a-Hexahydro-2-hydroxy-6-methyl-1H-benzo[b]cyclopent[e]azepine (45b): Amine **40b** (0.65 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of H₂O and extractive workup the resulting crude product (5:1 mixture of diastereoisomers) was purified by silica gel chromatography (hexane/AcOEt 3:1). Yield: 0.17 g (38%) of **45b**. Major diastereoisomer. *R*_f = 0.19 (hexane/AcOEt 2:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.3–7.1 (m, 4H, ArH), 5.5 (s, 1H, =CH), 4.85–4.8 (m, 1H, CHO), 3.0–2.8 (m, 3H, NCH₂ and CH), 2.7 (s, 3H, NCH₃), 2.7–2.6 (m, 2H, CCH₂CH), 2.3 (d, *J* = 13.7 Hz, 1H, CHHC=), 2.1–2.0 (m, 2H, CHHCHO and CHHC=), 1.8 (brs, 1H, OH), 1.5 (dt, *J* = 13.3, 4.3 Hz, 1H, CHHCHO); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 153.5, 150.1, 139.9, 129.6, 128.7, 127.4, 125.0, 121.7 (ArC and C=CH), 76.0 (CHO), 61.2 (CH₂N), 49.6, 43.8 (CH₃N and CH), 42.4, 38.8, 28.6 (3 CH₂C); IR (neat): ν̄ = 3345 cm⁻¹ (O–H); HRMS (EI) calcd for C₁₅H₁₉NO: 229.1467, found 229.1473.

2-(4-Chlorobenzoyl)-1,2,4,5,10,10 a-hexahydro-2-hydroxy-5-methylbenzo[b]cyclopent[e]azepine (46a): Amine **40a** (0.53 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min in the presence of 4-chlorobenzonitrile (0.29 g, 2.1 mmol) and the mixture was stirred overnight. Hydrolysis and extractive workup afforded the crude product which was purified by silica gel chromatography (hexane/AcOEt 5:1). Yield: 0.28 g (40%) of **46a**. *R*_f = 0.30 (hexane/AcOEt 3:1); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.4–7.0 (m, 8H, ArH), 5.6 (s, 1H, =CH), 4.6 (brs, 1H, OH), 4.1 (d, *J* = 12.5 Hz, 1H, NCHH), 3.6 (d, *J* = 12.5 Hz, 1H, NCHH), 3.6–3.5 (m, 1H, CH), 3.5 (dd, *J* = 11.2, 6.9 Hz, 1H, CCHHCH), 2.9 (s, 3H, CH₃), 2.4 (d, *J* = 11.2 Hz, 1H, CCHHCH), 2.3–2.1 (m, 2H, CH₂C); ¹³C NMR (50.5 MHz, CDCl₃,

25 °C): δ = 200.2 (C=O), 150.5, 150.3, 139.3, 133.1, 131.6, 131.5, 130.7, 130.1, 128.4, 127.5, 122.1, 118.3 (ArC and C=CH), 86.6 (CO), 57.8 (CH₂N), 45.5, 34.9 (2 CH₂C), 42.5, 41.2 (CH₃N and CH); IR (neat): ν̄ = 3450 (O–H), 1670 (C=O) cm⁻¹; HRMS (EI) calcd for C₂₁H₂₀ClNO₂: 353.1183, found 353.1179.

2-(4-Chlorobenzoyl)-2,4,5,6,11,11 a-hexahydro-2-hydroxy-6-methyl-1H-benzo[b]cyclopent[e]azepine (46b): Amine **40b** (0.65 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min in the presence of 4-chlorobenzonitrile (0.29 g, 2.1 mmol) and the mixture was stirred overnight. Hydrolysis and extractive workup afforded the crude product which was purified by silica gel chromatography (hexane/AcOEt 7:1). Yield: 0.26 g (35%) of **46b**. *R*_f = 0.22 (hexane/AcOEt 5:1); ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 8.2–7.1 (m, 8H, ArH), 5.6 (s, 1H, =CH), 4.7 (brs, 1H, OH), 3.3–3.2 (m, 1H, CH), 3.1 (d, *J* = 12.0 Hz, 1H, CCHHCH), 3.1–3.0 (m, 1H, NCHH), 2.9 (s, 3H, CH₃), 2.9–2.8 (m, 1H, NCHH), 2.75 (dd, *J* = 12.0, 4.2 Hz, 1H, CCHHCH), 2.5–2.4 (m, 2H, CHHC= and CHHCO), 2.3 (dd, *J* = 14.2, 6.2 Hz, 1H, CHHCO), 1.7 (dt, *J* = 13.3, 4.7 Hz, 1H, CHHC=); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 201.0 (C=O), 155.7, 150.4, 139.6, 138.7, 132.0, 131.8, 129.9, 129.1, 128.4, 127.9, 125.2, 121.7 (ArC and C=CH), 87.6 (CO), 60.8 (CH₂N), 49.6, 44.0 (CH₃N and CH), 45.8, 37.3, 28.8 (3 CH₂C); IR (neat): ν̄ = 3450 (O–H), 1670 (C=O) cm⁻¹; HRMS (EI) calcd for C₂₂H₂₂ClNO₂: 367.1339, found 367.1348.

3a-Allyl-3,3,4,4,5,10,10 a-hexahydro-5-methylbenzo[b]cyclopent[e]azepin-2(1H)-one (47a): Amine **40a** (0.53 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [Cp₂Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min in the presence of allyl bromide (0.36 g, 3 mmol) and the mixture was stirred overnight. Hydrolysis and extractive workup afforded the crude product (1:1.7 mixture of **47a** and **48a**), which was purified by silica gel chromatography (hexane/AcOEt 5:1). Yield: 0.08 g (15%) of **47a**. *R*_f = 0.47 (hexane/AcOEt 2:1); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.2–6.8 (m, 4H, ArH), 5.9–5.8 (m, 1H, =CH), 5.2–5.15 (m, 2H, =CH₂), 3.3 (d, *J* = 15.0 Hz, 1H, NCHH), 3.0 (d, *J* = 14.2 Hz, 1H, CCHHCO), 2.8 (s, 3H, CH₃), 2.8–2.3 (m, 7H, NCHH, CCHHCO, CH, CCH₂CH, CHHCHO and CHHC=), 2.1–2.0 (m, 1H, CHHC=), 2.0 (dd, *J* = 18.5, 10.0 Hz, 1H, CHHCHO); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 216.8 (CO), 152.0, 134.2, 131.9, 128.2, 127.2, 120.6, 114.7 (ArC and CH=CH₂), 118.6 (CH₂=CH), 61.1 (CH₂N), 48.2, 40.9, 40.8, 34.1 (4 CH₂C), 45.7 (CCH), 42.1, 40.0 (CH₃N and CH); IR (neat): ν̄ = 1740 cm⁻¹ (C=O); HRMS (EI) calcd for C₁₇H₂₁NO: 255.1623, found 255.1621.

2-Allyl-1,2,4,5,10,10 a-hexahydro-2-hydroxy-5-methylbenzo[b]cyclopent[e]azepine (48a): Yield: 0.13 g (25%) mixture of diastereoisomers 2:1. *R*_f = 0.25 (hexane/AcOEt 2:1). ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 7.3–7.0 (m, 8H, ArH), 5.9–5.7 (m, 2H, CH=CH₂), 5.5 (s, 1H, C=CH, minor diast.), 5.4 (s, 1H, C=CH, major diast.), 5.2–5.0 (m, 4H, CH=CH₂), 3.6–3.5 (m, 4H, NCH₂), 3.15–3.05 (m, 2H, CCHHCH), 2.9 (s, 6H, CH₃), 2.75–2.65 (m, 2H, CH), 2.6–2.4 (m, 4H, CCHHCH and CHHCO), 2.4–2.3 (m, 4H, CH₂CH=), 1.7–1.6 (m, 3H, OH and CHCO, minor diast.), 1.6 (dd, *J* = 13.2, 7.2 Hz, 1H, CHHCO, major diast.); ¹³C NMR (50.5 MHz, CDCl₃, 25 °C): δ = 151.4, 148.0, 145.4, 134.2, 133.9, 133.5, 132.2, 129.9, 129.7, 127.1, 121.9, 117.7, 117.5 (ArC, CH=CH₂ and C=CH), 118.3 (CH₂=CH, minor diast.), 118.1 (CH₂=CH, major diast.), 82.9 (CO, minor diast.), 82.8 (CO, major diast.), 58.0 (CH₂N, minor diast.), 57.6 (CH₂N, major diast.), 45.8, 44.5, 38.6 (3 CH₂C, major diast.), 45.4, 45.0, 38.3 (3 CH₂C, minor diast.), 42.6, 42.5, 42.1 (CH₃N and CHCH₂); HRMS (EI) calcd for C₁₇H₂₁NO: 255.1623, found 255.1615.

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