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, e] 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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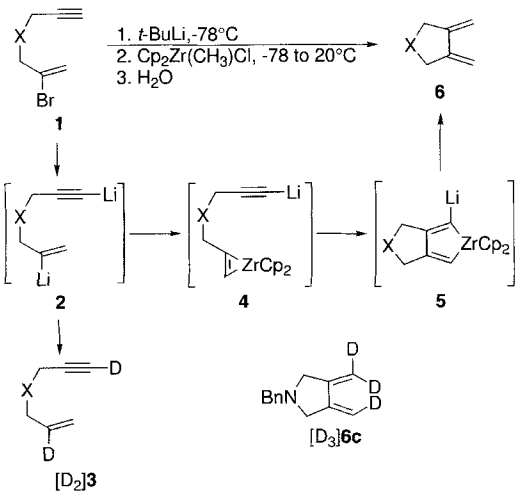
Results and Discussion

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 [D_2]**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.

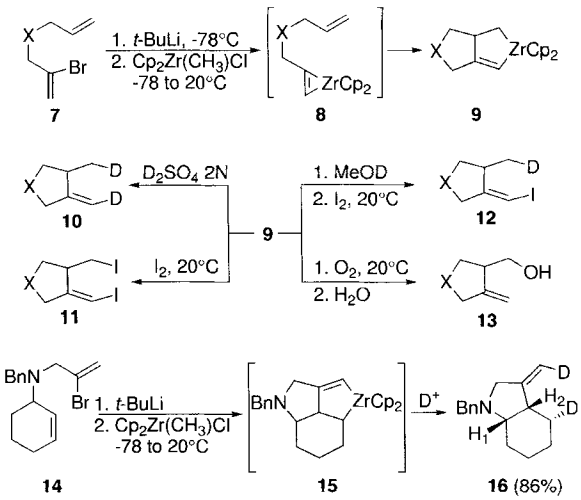
Table 1. Cyclization of terminal alkynes **1** to give products **6**.

Starting material	X	Exocyclic Diene	Yield (%) [a]
1a	9-Flu [b]	**6a**	65
1b	PhN	**6b**	73
1c	$PhCH_2N$	**6c**	71
1c	$PhCH_2N$	[D_3]**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 zirconacyclopropenes **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 [D_3]**6c**, the structure of which was confirmed by ^{1}H 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 zirconacyclopropenes **8**. These represent a novel type of zirconabicycle, 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, iodonolysis 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 H_1 and H_2 of **16** indicates a *cis* ring-junction and, in agreement with the literature,[2c, 10d] the deuterium in the cyclohexyl 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.

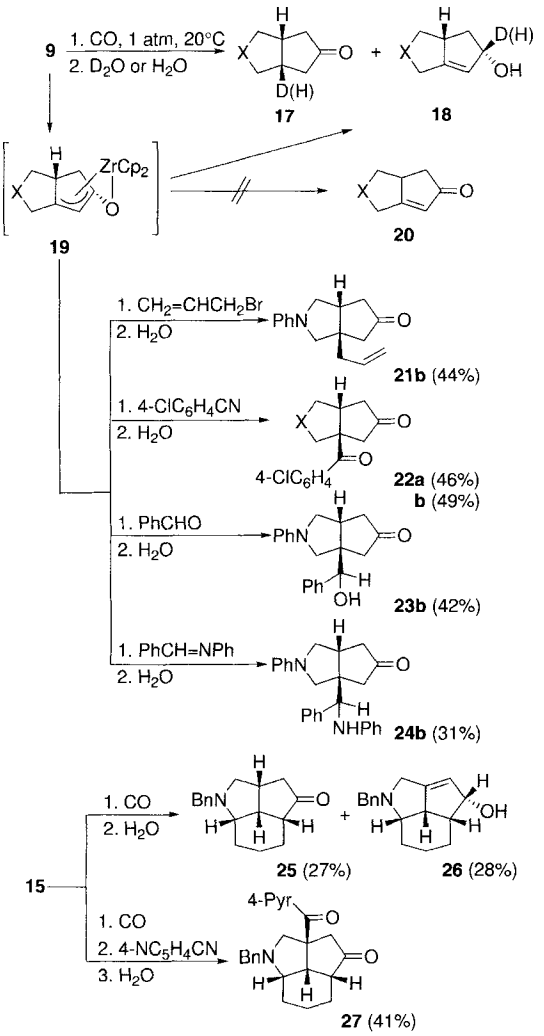
Table 2. Cyclization of allyl-2-bromoallyl substrates **7** and subsequent reaction with electrophiles to afford products **10–13**.

Starting material	X	Electrophile	Product	Yield (%) [a]
7a	9-Flu [b]	D_2SO_4	**10a**	78
7a	9-Flu [b]	O_2	**13a**	59
7b	PhN	D_2SO_4	**10b**	87
7b	PhN	I_2	**11b**	78
7b	PhN	MeOD/I_2	**12b**	79
7b	PhN	O_2	**13b**	60
7c	$PhCH_2N$	D_2SO_4	**10c**	83
7c	$PhCH_2N$	I_2	**11c**	77
7d	c-$C_6H_{11}N$	D_2SO_4	**10d**	75
7d	c-$C_6H_{11}N$	O_2	**13d**	56
7e	4-ClC_6H_4N	D_2SO_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 zirconabicycles **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	$PhCH_2N$	**17c** [c,d]	59
9e	4-ClC_6H_4N	**17e**+**18e** (1:3) [c]	62
9f	4-$MeOC_6H_4N$	**17f**+**18f** (1:4) [c]	64

[a] Isolated yield based on the starting material **7**. [b] 9-Flu = 9-fluorenyl. [c] Quenched with D_2O. [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 deuterolysis. However, the reaction failed for $n = 3$ and the azocine derivative **33c** was not detected. We be-

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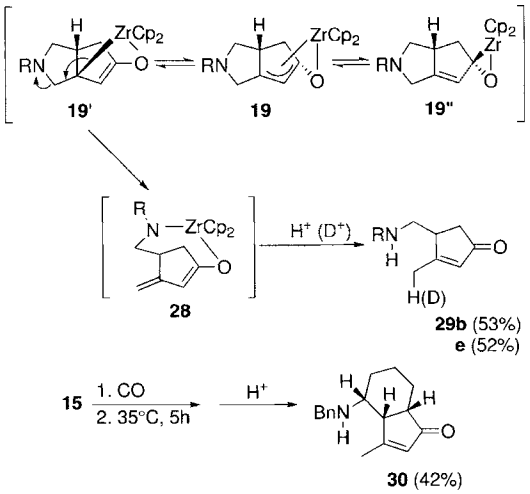
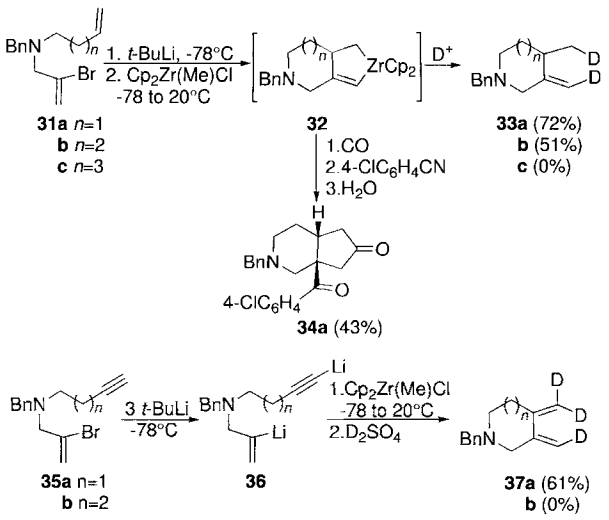


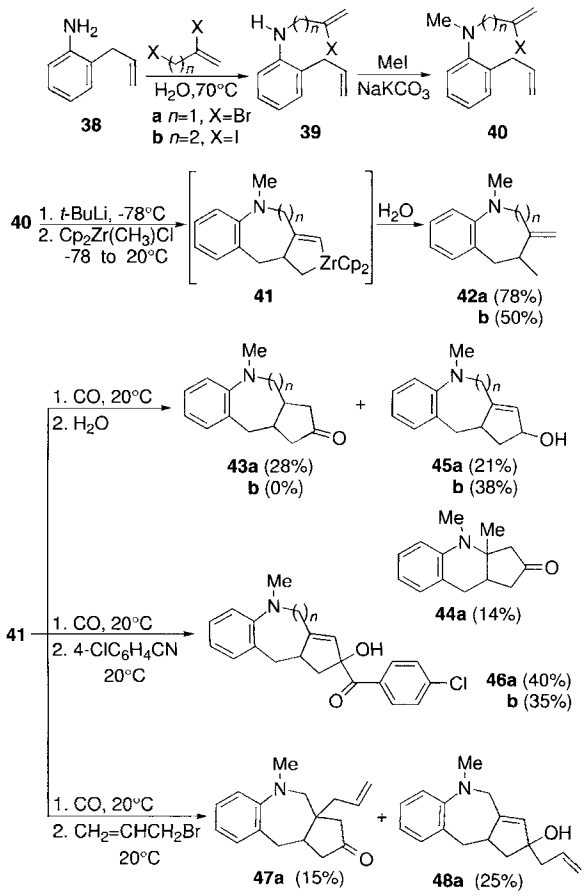
Scheme 4. Evolution of π-allylzirconium intermediates.

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 zirconabicycle **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 °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-diynes[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 °C for two hours.[31] Amine **38** was 2-bromoallylated or 3-iodohomoallylated in water with 2,3-dibromopropene or 2,4-diiodobutene to give secondary amines **39a** and **b**, respectively. These were methylated with methyl iodide and $NaKCO_3$ in refluxing DMF to give tertiary amines **40a,b**. These were successfully converted to their corresponding metallatricycles **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 N_2 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 diasteroselectivity 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 N_2 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. [Cp_2ZrCl_2] was purchased from Aldrich and [$Cp_2Zr(Me)Cl$] was prepared according to a published procedure.[32] 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 Et_2O were distilled from sodium benzophenone ketyl under N_2 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-butyne with NaI, Me_3SiCl, and H_2O in acetonitrile;[33] 2-cyclohexenyl bromide was synthesized by refluxing a mixture of cyclohexene and NBS in CCl_4 in the presence of a catalytic amount of benzoyl peroxide. TLC was performed on Al-backed plates coated with silica gel 60 with F_{254} 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. ^{1}H NMR (200, 300 MHz) and ^{13}C NMR (50.5, 75.5 MHz) spectra were measured on Bruker AC-200 and AC-300 instruments, respectively, with TMS ($\delta = 0.0$, ^{1}H NMR) or $CDCl_3$ ($\delta = 76.95$, ^{13}C NMR) as the internal standard. Chemical shifts are reported relative to TMS in $CDCl_3$. 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 MAT95 spectrometer. Infrared (IR) spectra were recorded on a Unicam Mattason 3000 FTIR and only the most significant IR absorptions are given. Elemental analyses were performed with a Perkin Elmer analyzer.

Dianions 2 and dideuterio compounds [D_2]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 Et_2O (10 mL). After stirring at −78 °C for 60 min, the dianions were formed and then were treated with D_2O and extracted with AcOEt (3 × 20 mL). The combined organic layer was washed with saturated aq. $NaHCO_3$ (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude dideuterated compounds were isolated without further purification as yellow oils.

9-(2-Deuterioallyl)-9-(3-deuteriopropargyl)fluorene ([D_2]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); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.9$–7.4 (m, 8H, ArH), 5.0 (s, 1H, C=C*H*H), 4.9 (s, 1H, C=CH*H*), 3.0 (s, 2H, CH_2CD), 2.8 (s, 2H, CH_2C); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 (=CH_2), 80.7 (≡C), 69.6 (≡CD), 51.7 (CCH_2), 41.1 (CH_2C=), 28.9 (CH_2C≡); HRMS (EI) calcd for $C_{19}H_{14}D_2$: 246.1377, found 246.1377.

***N*-Benzyl-3-deuterio-*N*-(2-deuterioallyl)propargylamine ([D_2]3c)**: Amine **1c** (0.53 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol). Isolated yield: 96% (0.36 g); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.5$–7.3 (m, 5H, ArH), 5.4 (s, 1H, CD=C*H*H), 5.2 (s, 1H, CD=CH*H*), 3.7 (s, 2H, $ArCH_2N$), 3.4 (s, 2H, NCH_2CD), 3.2 (s, 2H, NCH_2C); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): $\delta = 138.4$, 128.9, 128.1, 127.0 (ArC), 135.0 (t, $J_{CD} = 23.2$ Hz, =CD), 117.8 (=CH_2), 77.8 (≡C), 57.0, 56.3, 41.0 (3NCH_2); 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 Et_2O (20 mL) was added a solution of dianion **2** (2 mmol) at −78 °C under N_2, 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 H_2O or with 2 N deuterated sulfuric acid, filtered through Celite, and extracted with AcOEt (3 × 20 mL). The combined organic phases were dried (Na_2SO_4) and the solvents removed. The residue was purified by column chromatography to give compounds **6**.

3,4-Dimethylenespiro[cyclopentane-1,9′-(9*H*)fluorene] (6a): Fluorene derivative **1a** (0.64 g, 2 mmol) was treated with *t*BuLi (3.6 mL, 6 mmol) and [$Cp_2Zr(Me)Cl$] (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); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.8$–7.3 (m, 8H, ArH), 5.7 (s, 2H, 2C=C*H*H), 5.1 (s, 2H, 2C=CH*H*), 3.0 (s, 4H, $2CH_2$); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): $\delta = 151.1$, 147.4, 139.5, 127.3, 127.1, 122.7, 119.6 (ArC and C=CH_2), 105.4 (=CH_2), 53.6 (CCH_2), 45.9 (CCH_2); HRMS (EI) calcd for $C_{19}H_{16}$: 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 [$Cp_2Zr(Me)Cl$] (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); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.4$–6.7 (m, 5H, ArH), 5.7–5.6 (m, 2H, 2C=C*H*H), 5.2 (s, 2H, 2C=CH*H*), 4.3–4.2 (m, 4H,

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2 CH_2N); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 147.2, 143.0, 129.1, 116.6, 112.0 (ArC and C=CH_2), 104.4 (=CH_2), 53.5 (CH_2N); 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 $C_{12}H_{13}N$: 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 [$Cp_2Zr(Me)Cl$] (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, $CDCl_3$, 25 °C, TMS): δ = 7.4–7.2 (m, 5H, ArH), 5.5–5.4 (m, 2H, 2C=C*H*H), 4.9 (s, 2H, 2C=CH*H*), 3.7 (s, 2H, ArCH_2N), 3.4–3.3 (m, 4H, 2NCH_2C); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 144.4, 138.3, 128.6, 128.1, 126.9 (ArC and C=CH_2), 103.1 (=CH_2), 60.4, 59.7 (2CH_2N); LRMS (70 eV, EI): m/z (%) = 185 (56) [M^+] 184 (67), 94 (42), 91 (100); HRMS (EI) calcd for $C_{13}H_{15}N$: 185.1204, found 185.1212.

1-Benzyl-3-(*E*)-deuteriomethylene-4-dideuteriomethylenepyrrolidine ([D_3]6c): Amine **1c** (0.53 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); the cleavage of the reaction was carried out with 2N D_2SO_4; the resulting crude product was purified by silica gel chromatography (hexane/AcOEt 7:1). Yield: 0.25 g (70%) of diene [D_3]**6c**. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.4–7.2 (m, 5H, ArH), 4.9 (s, 1H, C=CHD), 3.7 (s, 2H, ArCH_2N), 3.4 (s, 4H, 2NCH_2C); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 CD_2), 60.5, 59.7 (2CH_2N); LRMS (70 eV, EI): m/z (%) = 188 (66) [M^+], 187 (72), 97 (46), 91 (100); HRMS (EI) calcd for $C_{13}H_{12}D_3N$: 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 Et_2O (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 Et_2O (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 O_2 (0 °C, 1 h). After addition of aq. $NaHCO_3$, the mixture was filtered through Celite and extracted with AcOEt (3 × 20 mL) and aq. $Na_2S_2O_3$. The organic layer was collected, washed with aq. $NaHCO_3$, dried over Na_2SO_4, 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 [$Cp_2Zr(Me)Cl$] (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**. ^{13}C NMR (50.5 MHz, C_6D_6, 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 (2CH_2N), 38.3 (CH), 36.5 (CH_2Zr).

3-(*E*)-Deuteriomethyl-4-deuteriomethylenespiro[cyclopentane-1,9′-(9*H*)fluorene] (10a): Fluorene derivative **7a** (0.65 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); after the addition of D_2SO_4 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, $CDCl_3$, 25 °C, TMS): δ = 7.9–7.3 (m, 8H, ArH), 5.2–5.1 (m, 1H, C=C*H*D), 3.4–3.2 (m, 1H, CH), 3.1 (dt, J = 16.4, 2.2 Hz, 1H, C*H*HC=), 2.8 (d, J = 16.4 Hz, 1H, CH*H*C=), 2.2 (dd, J = 13.0, 8.0 Hz, 1H, C*H*HCH), 2.1 (dd, J = 13.0, 10.8 Hz, 1H, CH*H*CH), 1.4 (d, J = 6.7 Hz, 2H, CH_2D); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 (CCH_2), 47.9, 44.9 (2CH_2), 38.2 (CH), 19.3 (t, J_{CD} = 19.4 Hz, CH_2D); 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 $C_{19}H_{16}D_2$: 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 [$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); after the addition of D_2SO_4 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/$CHCl_3$); ^1H NMR (300 MHZ, $CDCl_3$, 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, NC*H*HC=), 4.0 (dd, J = 13.7, 1.6 Hz, 1H, NCH*H*C=), 3.8–3.7 (m, 1H, NC*H*HCH), 3.1–2.9 (m, 2H, NCH*H*CH and CH), 1.4–1.3 (m, 2H, CH_2D); ^{13}C NMR (75.5 MHz, $CDCl_3$, 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 (2CH_2N), 37.1 (CH), 16.3 (t, J_{CD} = 19.6 Hz, CH_2D); 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 $C_{12}H_{13}D_2N$: 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 [$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); after the addition of D_2SO_4 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, $CDCl_3$, 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, ArC*H*HN), 3.6 (d, J = 18.1 Hz, 1H, ArCH*H*N), 3.5 (d, J = 13.1 Hz, 1H, NC*H*HC=), 3.1–3.0 (m, 2H, NCH*H*C= and NC*H*HCH), 2.9–2.7 (m, 1H, CH), 2.2 (dd, J = 8.6, 8.3 Hz, 1H, NCH*H*CH), 1.2–1.1 (m, 2H, CH_2D). ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 153.7, 138.8, 128.6, 128.1, 126.8 (ArC and C=CH_2), 103.4 (t, J_{CD} = 23.5 Hz, CHD), 62.1, 60.5, 59.3 (3CH_2N), 37.3 (CH), 17.3 (t, J_{CD} = 19.7 Hz, CH_2D); HRMS (EI) calcd for $C_{12}H_{15}D_2N$: 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 [$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); after the addition of D_2SO_4 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, $CDCl_3$, 25 °C, TMS): δ = 4.9–4.8 (m, 1H, C=C*H*D), 3.6 (d, J = 13.8 Hz, 1H, NC*H*HC=), 3.2 (dd, J = 8.2, 7.7 Hz, 1H, NC*H*HCH), 3.0 (dt, J = 13.8, 2.2 Hz, 1H, NCH*H*C=), 2.8–2.6 (m, 1H, CH), 2.0–1.6 (m, 8H, NCH, NCH*H*CH and 3CH_2 cyclohexyl), 1.3–1.1 (m, 6H, CH_2D and 2CH_2 cyclohexyl); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 153.5 (C=CHD), 103.2 (t, J_{CD} = 23.5 Hz, CHD), 63.7 (CHN), 59.7, 57.4 (2CH_2N), 36.9 (CH), 31.6, 31.5, 25.9, 24.9, 24.8 (5CH_2 cyclohexyl), 16.9 (t, J_{CD} = 19.4 Hz, CH_2D); LRMS (70 eV, EI): m/z (%) = 181 (11) [M^+], 138 (100), 137 (15), 124 (10); HRMS (EI) calcd for $C_{12}H_{19}D_2N$: 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 [$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); after the addition of D_2SO_4 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/$CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, 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, NC*H*HC=), 3.9 (d, J = 13.6 Hz, 1H NCH*H*C=), 3.6 (t, J = 7.3 Hz, 1H, NC*H*HCH), 3.0–2.8 (m, 2H, NCH*H*CH and CH), 1.3–1.2 (m, 2H, CH_2D); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 (2CH_2N), 37.0 (CH), 16.1 (t, J_{CD} = 19.4 Hz, CH_2D); HRMS (EI) calcd for $C_{12}H_{12}D_2ClN$: 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 [$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); after the addition of I_2 (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, $CDCl_3$, 25 °C, TMS): δ = 7.3–6.6 (m, 5H, ArH), 6.3 (s, 1H, CHI), 4.2 (d, J = 14.2 Hz, 1H, NC*H*HC), 3.8 (d, J = 14.2 Hz, 1H, NCH*H*C), 3.7 (d, J = 9.9 Hz, 1H, NC*H*HCH), 3.5 (d, J = 7.7 Hz, 2H, CH_2I), 3.4–3.3 (m, 1H, CH), 3.3 (dd, J = 10.3, 9.9 Hz, 1H, NCH*H*CH); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 150.4, 147.4, 129.1,

117.4, 112.5 (ArC and *C*=CHI), 73.3 (CHI), 53.7, 53.3 ($2CH_2N$), 49.5 (CH), 7.1 (CH_2I); 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 $C_{12}H_{13}I_2N$: 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 [$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); after the addition of I_2 (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); ^{1}H NMR (200 MHz, $CDCl_3$, 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, ArC*H*HN), 3.6 (d, J = 12.9 Hz, 1H, ArCH*H*N), 3.6 (dd, J = 9.5, 3.0 Hz, 1H, NC*H*HCH), 3.4 (d, J = 13.4 Hz, 1H, NC*H*HC), 3.4 (dd, J = 10.7, 9.5 Hz, 1H, NCH-*H*CH), 3.1 (dd, J = 13.4, 1.7 Hz, 1H, NCH*H*C), 3.1–3.0 (m, 1H, CH), 3.0–2.9 (m, 2H, CH_2I); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 ($3CH_2N$), 49.1 (CH), 7.3 (CH_2I); HRMS (EI) calcd for $C_{13}H_{15}I_2N$: 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 [$Cp_2Zr(Me)Cl$] (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 I_2 (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); ^{1}H NMR (200 MHz, $CDCl_3$, 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, NC*H*HC), 3.8 (dd, J = 14.0, 1.6 Hz, 1H, NCH*H*C), 3.5 (dd, J = 9.0, 6.7 Hz, 1H, NC*H*HCH), 3.3 (dd, J = 9.0, 1.6 Hz, 1H, NCH-*H*CH), 3.2–3.0 (m, 1H, CH), 1.3 (d, J = 7.0 Hz, 2H, CH_2D); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 153.6, 147.7, 129.0, 116.6, 112.0 (ArC and *C*=CHI), 69.4 (CHI), 54.5, 52.9 ($2CH_2N$), 40.9 (CH), 18.1 (t, J_{CD} = 19.4 Hz, CH_2D); HRMS (EI) calcd for $C_{12}H_{13}DIN$: 300.0234, found 300.0234.

3-Hydroxymethyl-4-methylenespiro[cyclopentane-1,9′-(9*H*)fluorene] (13a): Fluorene derivative **7a** (0.65 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); dry O_2 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/$CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.7–7.2 (m, 8H, ArH), 5.25–5.15 (m, 2H, $=CH_2$), 3.9–3.8 (m, 2H, CH_2O), 3.3–3.2 (m, 1H, CH), 3.1 (dd, J = 15.9, 2.6 Hz, 1H, C*H*HC=), 2.5 (d, J = 15.9 Hz, 1H, CH*H*C=), 2.3 (dd, J = 12.9, 10.1 Hz, 1H, C*H*HCH), 2.1 (dd, J = 12.9, 8.2 Hz, 1H, CH*H*CH); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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*=CH_2), 108.3 (=CH_2), 65.8 (CH_2O), 55.5 (*C*CH_2), 46.0 (CH), 45.6, 41.7 ($2CH_2$); IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1} (O–H); HRMS (EI) calcd for $C_{19}H_{18}O$: 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 [$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); dry O_2 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); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.3–6.6 (m, 5H, ArH), 5.2 (dd, J = 4.0, 1.7 Hz, 1H, =C*H*H), 5.1 (dd, J = 4.0, 2.2 Hz, 1H, =CH*H*), 4.0 (dd, J = 14.0, 1.7 Hz, 1H, NC*H*HC), 3.9 (dd, J = 14.0, 2.2 Hz, 1H, NCH*H*C), 3.7 (d, J = 6.5 Hz, 2H, CH_2O), 3.5 (dd, J = 9.5, 7.7 Hz, 1H, NC*H*HCH), 3.4 (dd, J = 9.5, 4.3 Hz, 1H, NCH*H*CH), 3.1–3.0 (m, 1H, CH), 2.2 (brs, 1H, OH); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 147.8, 147.0, 129.1, 116.7, 112.3 (ArC and *C*=CH_2), 107.3 (=CH_2), 64.3 (CH_2O), 52.9, 50.7 ($2CH_2N$), 45.4 (CH); IR (neat): $\tilde{\nu}$ = 3370 cm^{-1} (O–H); HRMS (EI) calcd for $C_{12}H_{15}NO$: 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 [$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); dry O_2 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); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.0 (s, 1H, =C*H*H), 4.9 (s, 1H, =CH*H*), 4.1 (brs, 1H, OH), 3.8–3.5 (m, 2H, CH_2O), 3.3 (d, J = 13.5 Hz, 1H, NC*H*HC), 3.1 (d, J = 13.5 Hz, 1H, NCH-*H*C), 2.9–2.7 (m, 4H, NCH, NCH_2CH and CHCO), 2.1–1.1 (m, 10H, $5CH_2$ cyclohexyl); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 148.9 (*C*=CH_2), 105.8 (=CH_2), 66.1 (CH_2O), 63.0 (CHN), 57.1, 55.4 ($2CH_2N$), 44.4 (CH), 31.2, 25.8, 24.6 ($5CH_2$ 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 $C_{12}H_{21}NO$: 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 K_2CO_3 (2.6 g, 18.7 mmol) in CH_2Cl_2 (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 H_2O was added to the suspension. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layer was washed with $NaHCO_3$ and dried over Na_2SO_4. 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); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.5–7.3 (m, 5H, ArH), 6.1 (s, 1H, BrC=C*H*H), 6.0–5.8 (m, 2H, CH=CH), 5.6 (s, 1H, BrC=CH*H*), 3.9 (d, J = 14.3 Hz, 1H, ArC*H*HN), 3.7 (d, J = 14.3 Hz, 1H, ArCH*H*N), 3.5–3.3 (m, 3H, NCH and NCH_2C), 2.1–1.3 (m, 6H, $3CH_2$ ring); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 139.8, 133.6, 130.4, 129.9, 128.3, 128.0, 126.6 (ArC, CBr, and CH=CH), 117.0 (=CH_2), 57.9, 53.7 ($2CH_2N$), 54.7 (CHN), 25.1, 23.5, 21.6 ($3CH_2$ 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 $C_{16}H_{20}BrN$: 305.0779, found 305.0786.

(3a*S,4*R**,7a*S**)-1-Benzyl-4-deuterio-3-(*E*)-deuteriomethyleneperhydroindole (16)**: To a solution of **14** (0.61 g, 2 mmol) in Et_2O (10 mL) at −78 °C under a N_2 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 Et_2O (20 mL) at −78 °C; stirring was continued for an additional 3 h at RT and 2N D_2SO_4 was added. The mixture was diluted with AcOEt, filtered through Celite, washed with $NaHCO_3$ and dried over Na_2SO_4. 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); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.5–7.3 (m, 5H, ArH), 4.85–4.8 (m, 1H, =C*H*D), 4.1 (d, J = 13.4 Hz, 1H, ArC*H*HN), 3.6 (d, J = 14.3 Hz, 1H, NC*H*HC), 3.3 (d, J = 13.4 Hz, 1H, ArCH*H*N), 3.0 (dd, J = 14.3, 1.9 Hz, 1H, NCH*H*C), 2.82–2.75 (m, 1H, NCH), 2.67–2.59 (m, 1H, CHC=), 1.8–1.4 (m, 7H, $3CH_2$ ring and CHD); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 ($2CH_2N$), 43.8 (*C*HC=), 28.0 (t, J_{CD} = 19.7 Hz, CHD), 24.5, 24.0, 21.1 ($3CH_2$ cyclohexyl); HRMS (EI) calcd for $C_{16}H_{19}D_2N$: 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 H_2O or D_2O the mixture was stirred 15 min followed by addition of saturated aqueous $NaHCO_3$. The mixture reaction was filtered through Celite and extracted with AcOEt (3 × 20 mL). The extract was washed with aq. $NaHCO_3$ and the combined organic extracts were dried (Na_2SO_4), 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′-(9*H*)fluorene]-7-one (17a)**: Fluorene derivative **7a** (0.65 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of H_2O 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/$CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, 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, 2C*H*HCO), 2.4–2.2 (m, 4H, 2CH*H*CO and 2CC*H*HCH), 2.1 (dd, J = 13.7, 8.2 Hz, 2H, 2CCH*H*CH); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 (*C*CH_2), 46.4, 44.8 ($4CH_2$), 39.9 (2CH); IR (KBr): $\tilde{\nu}$ = 1730 cm^{-1} (C=O); HRMS (EI) calcd for $C_{20}H_{18}O$: 274.1358, found 274.1355; anal. calcd C 87.56, H 6.61; found C 87.40, H 6.70.

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***cis*-Spiro[1(8)-bicyclo[3.3.0]octene-3,9′-(9*H*)fluorene]-7-ol (18a)**: Yield: 0.18 g (33%). M.p. 183–185 °C (hexane/$CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 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, CCH_2C and C*H*HCO), 2.2 (dd, J = 12.5, 8.1 Hz, 1H, CC*H*HCH), 2.0 (brs, 1H, OH), 1.9 (dd, J = 12.5, 10.8 Hz, 1H, CCH*H*CH), 1.5 (dt, J = 12.5, 7.8 Hz, 1H, CH*H*CO); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 (CCH_2), 50.1 (CH), 46.3, 44.3, 38.1 ($3CH_2$); IR (KBr): $\tilde{\nu}$ = 3225 cm^{-1} (O–H); HRMS (EI) calcd for $C_{20}H_{18}O$: 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 [Cp_2Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of H_2O 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/$CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.3–6.5 (m, 5H, ArH), 3.6 (dd, J = 9.6, 7.0 Hz, 2H, 2NC*H*H), 3.2 (dd, J = 9.6, 3.8 Hz, 2H, 2NCH*H*), 3.2–3.0 (m, 2H, 2CH), 2.6 (dd, J = 19.4, 7.9 Hz, 2H, 2C*H*HCO), 2.3 (dd, J = 19.4, 4.1 Hz, 2H, 2CH*H*CO); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 218.3 (CO), 147.4, 129.0, 116.1, 111.8 (ArC), 52.9 ($2CH_2N$), 42.8 ($2CH_2CO$), 38.9 (2CH); IR (KBr): $\tilde{\nu}$ = 1730 cm^{-1} (C=O); HRMS (EI) calcd for $C_{13}H_{15}NO$: 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/$CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 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, NC*H*HC=), 3.8 (d, J = 13.6 Hz, 1H, NCH*H*C=), 3.7 (t, J = 8.2 Hz, 1H, NC*H*HCH), 3.3–3.1 (m, 1H, CH), 2.9–2.7 (m, 2H, NCH*H*CH and C*H*HCO), 2.2 (brs, 1H, OH), 1.4 (dt, J = 12.4, 7.9 Hz, 1H, CH*H*CO); ^{13}C NMR (75.5 MHz, $CDCl_3$, 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 ($2CH_2N$), 47.4 (CH), 41.8 (CH_2CO); IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1} (O–H); HRMS (EI) calcd for $C_{13}H_{15}NO$: 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 [Cp_2Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of D_2O 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**. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.3–6.6 (m, 5H, ArH), 3.7–3.6 (m, 2H, 2NC*H*H), 3.3–3.2 (m, 2H, 2NCH*H*C), 3.1–3.0 (m, 1H, CH), 2.6–2.5 (m, 2H, 2C*H*HCO), 2.3–2.2 (m, 2H, 2CH*H*CO); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 218.4 (CO), 147.4, 129.1, 116.2, 111.9 (ArC), 53.0, 52.9 ($2CH_2N$), 42.9, 42.8 ($2CH_2CO$), 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%); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.3–6.5 (m, 5H, ArH), 5.6 (s, 1H, =CH), 4.0 (d, J = 13.6 Hz, 1H, NC*H*HC=), 3.8 (d, J = 13.6 Hz, 1H, NCH*H*C=), 3.7 (t, J = 8.6 Hz, 1H, NC*H*HCH), 3.3–3.1 (m, 1H, CH), 2.8 (dd, J = 8.9, 8.6 Hz, 1H, NCH*H*CH), 2.7 (dd, J = 12.4, 7.2 Hz, 1H, C*H*HCO), 1.4 (dd, J = 12.4, 8.2 Hz, 1H, CH*H*CO); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 ($2CH_2N$), 47.2 (CH), 41.4 (CH_2CO); 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 [Cp_2Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of D_2O 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); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.3–7.2 (m, 5H, ArH), 3.6 (s, 2H, ArC*H*$_2$N), 2.9–2.8 (m, 1H, CH), 2.7–2.4 (m, 6H, $2NCH_2C$ and 2C*H*HCO), 2.2 (dd, J = 19.1, 2.6 Hz, 2H, 2CH*H*CO); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 219.9 (CO), 138.9, 128.4, 128.1, 126.8 (ArC), 61.7, 61.6, 59.3 ($3CH_2N$), 44.4, 44.3 ($2CH_2CO$), 37.4, 37.3 (CH and CD); IR (neat): $\tilde{\nu}$ = 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 $C_{14}H_{17}NO$: 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 [Cp_2Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of D_2O 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/$CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$, 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, 2NC*H*HC), 3.2–3.1 (m, 3H, 2NCH*H*C and CH), 2.6–2.5 (m, 2H, 2C*H*HCO), 2.3–2.2 (m, 2H, 2CH*H*CO); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 218.1 (CO), 146.0, 128.8, 121.0, 112.9 (ArC), 53.2 ($2CH_2N$), 42.8 ($2CH_2CO$), 39.0, 38.9 (CH and CD); IR (KBr): $\tilde{\nu}$ = 1740 cm^{-1} (C=O); HRMS (EI) calcd for $C_{13}H_{13}DClNO$: 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; ^{1}H NMR (200 MHz, $CDCl_3$, 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, NC*H*HC=), 3.8 (d, J = 13.7 Hz, 1H, NCH*H*C=), 3.7 (t, J = 8.3 Hz, 1H, NC*H*HCH), 3.3–3.1 (m, 1H, CH), 2.8 (dd, J = 8.9, 8.3 Hz, 1H, NCH*H*CH), 2.7 (dd, J = 12.4, 7.3 Hz, 1H, C*H*HCO), 1.9 (brs, 1H, OH), 1.4 (dd, J = 12.4, 8.5 Hz, 1H, CH*H*CO); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 ($2CH_2N$), 47.3 (CH), 41.5 (CH_2CO); IR (KBr): $\tilde{\nu}$ = 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 $C_{13}H_{13}DClNO$: 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 [Cp_2Zr(Me)Cl] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of D_2O 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/$CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, 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, CH_3), 3.6–3.5 (m, 2H, 2NC*H*H), 3.2–3.1 (m, 2H, 2NCH*H*), 3.1–3.0 (m, 1H, CH), 2.6–2.5 (m, 2H, 2C*H*HCO), 2.3–2.2 (m, 2H, 2CH*H*CO); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 218.7 (CO), 151.2, 142.5, 114.8, 113.0 (ArC), 55.8 (CH_3), 54.0 ($2CH_2N$), 43.2 ($2CH_2CO$), 38.82 (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 $C_{14}H_{16}DNO_2$: 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/$CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$, 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, NC*H*HC=), 3.8 (s, 3H, CH_3), 3.7 (d, J = 13.7 Hz, 1H, NCH*H*C=), 3.6 (t, J = 7.9 Hz, 1H, NC*H*HCH), 3.2–3.1 (m, 1H, CH), 2.7–2.6 (m, 2H, NCH*H*CH and C*H*HCO), 1.4 (dd, J = 12.3, 8.5 Hz, 1H, CH*H*CO); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 (CH_3), 53.4, 47.4 ($2CH_2N$), 47.3 (CH), 41.2 (CH_2CO); 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 $C_{14}H_{16}DNO_2$: 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 $NaHCO_3$ was added. The resultant mixture was filtered

through Celite, extracted with AcOEt (3 × 20 mL), and dried over Na_2SO_4. 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 $[Cp_2Zr(Me)Cl]$ (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); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.3–6.6 (m, 5H, ArH), 5.9–5.8 (m, 1H, =CH), 5.2–5.1 (m, 2H, $=CH_2$), 3.7 (dd, J = 9.9, 7.3 Hz, 1H, NC*H*HCH), 3.4 (d, J = 9.7 Hz, 1H, NC*H*HC), 3.3 (d, J = 9.7 Hz, 1H, NCH*H*C), 3.2 (dd, J = 9.9, 4.7 Hz, 1H, NCH*H*CH), 2.8–2.7 (m, 1H, CH), 2.6 (dd, J = 18.9, 8.2 Hz, 1H, CHC*H*HCO), 2.4–2.3 (m, 4H, $CH_2CH=$ and CCH_2CO), 2.2 (dd, J = 18.9, 13.7 Hz, 1H, CHCH*H*CO); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 217.2 (CO), 147.2, 129.0, 116.1, 111.6 (ArC), 133.5 ($CH=CH_2$), 118.8 ($CH=CH_2$), 56.8, 53.1 ($2CH_2N$), 49.2 (*C*CH), 47.2, 43.1, 42.0 ($2CH_2CO$ and $CH_2CH=$), 43.3 (CH); IR (neat): $\tilde{\nu}$ = 1740 cm^{-1} (C=O); HRMS (EI) calcd for $C_{16}H_{19}NO$: 241.1466, found 241.1473.

***cis*-1-(4-Chlorobenzoyl)spiro[bicyclo[3.3.0]octane-3,9′-(9*H*)fluorene]-7-one (22a)**: Fluorene derivative **7a** (0.65 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and $[Cp_2Zr(Me)Cl]$ (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/$CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 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, CC*H*HCO), 3.0 (d, J = 19.4 Hz, 1H, CCH*H*CO), 2.9 (d, J = 14.6 Hz, 1H, CC*H*HC), 2.8 (d, J = 14.6 Hz, 1H, CCH*H*C), 2.7 (dd, J = 18.9, 8.2 Hz, 1H, CHC*H*HCO), 2.4 (d, J = 18.9 Hz, 1H, CHCH*H*CO), 2.2–2.1 (m, 2H, CCH_2CH); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 216.2 (CH_2CO), 200.1 (Ar*C*O), 152.8, 149.8, 139.7, 139.4, 138.7, 131.3, 131.0, 128.7, 127.7, 127.6, 127.5, 127.2, 123.2, 122.3, 119.7 (ArC), 60.6, 58.6 ($2CCH_2$), 52.0, 51.1, 45.7, 43.0 ($4CH_2$), 43.4 (CH); IR (KBr): $\tilde{\nu}$ = 1735 (C=O), 1675 (C=O) cm^{-1}; HRMS (EI) calcd for $C_{27}H_{21}ClO_2$: 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 $[Cp_2Zr(Me)Cl]$ (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/$CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.9–6.6 (m, 9H, ArH), 3.9 (d, J = 10.2 Hz, 1H, NC*H*HC), 3.8–3.7 (m, 2H, CH and NC*H*HCH), 3.7(d, J = 10.2 Hz, 1H, NCH*H*C), 3.2 (dd, J = 12.7, 9.2 Hz, 1H, NCH*H*CH), 3.0 (d, J = 19.0 Hz, 1H, CC*H*HCO), 2.8 (d, J = 19.0 Hz, 1H, CCH*H*CO), 2.7 (dd, J = 19.1, 7.0 Hz, 1H, CHC*H*HCO), 2.4 (dd, J = 19.1, 4.5 Hz, 1H, CHCH*H*CO); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 214.5 (CH_2CO), 198.4 (Ar*C*O), 146.8, 139.7, 132.1, 130.4, 129.1, 129.0, 117.2, 112.4 (ArC), 59.4 (CCH_2), 57.6, 52.9, 47.8, 42.5 ($4CH_2$), 41.6 (CH); IR (KBr): $\tilde{\nu}$ = 1740 (C=O), 1680 (C=O) cm^{-1}; HRMS (EI) calcd for $C_{20}H_{18}ClNO_2$: 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 $[Cp_2Zr(Me)Cl]$ (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); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.5–6.5 (m, 10H, ArH), 4.7 (s, 1H, CHO), 3.7 (d, J = 9.9 Hz, 1H, NC*H*HC), 3.6 (t, J = 9.9 Hz, 1H, NC*H*HCH), 3.3 (d, J = 9.9 Hz, 1H, NCH*H*C), 3.1 (dd, J = 9.9, 5.6 Hz, 1H, NCH*H*CH), 3.0–2.8 (m, 2H, CH and OH), 2.7 (d, J = 18.9 Hz, 1H, CC*H*HCO), 2.2 (d, J = 18.9 Hz, 1H, CCH*H*CO), 2.1–2.0 (m, 2H, $CHCH_2CO$); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 ($2CH_2N$), 54.8 (CCH_2), 44.5, 43.0 ($2CH_2CO$), 39.9 (CH); IR (neat): $\tilde{\nu}$ = 3450 (O–H), 1735 (C=O) cm^{-1}; HRMS (EI) calcd for $C_{20}H_{21}NO_2$: 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 $[Cp_2Zr(Me)Cl]$ (0.57 g, 2.1 mmol). Carbon monoxide was bubbled through the mixture for 40 min. After the addition of benzylideneaniline (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); ^{1}H NMR (300 MHz, $CDCl_3$, 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, NC*H*HCH), 3.8 (d, J = 10.3 Hz, 1H, NC*H*HC), 3.4 (dd, J = 10.3, 2.1 Hz, 1H, NCH*H*C), 3.2 (dd, J = 9.9, 5.2 Hz, 1H, NCH*H*CH), 3.1–3.0 (m, 1H, CH), 2.8 (d, J = 18.7 Hz, 1H, CC*H*HCO), 2.3 (d, J = 18.7 Hz, 1H, CCH*H*CO), 2.1–2.0 (m, 2H, $CHCH_2CO$); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 zirconatricycle 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 Et_2O (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 Et_2O (20 mL) at −78 °C. The mixture was stirred at RT for 3 h. The N_2 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 $NaHCO_3$, filtered through Celite, and extracted with AcOEt (3 × 20 mL). The organic layer was washed with brine and dried over Na_2SO_4. 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[6.2.1.0^{4,11}]undecan-9-one (25)**: Yield: 0.14 g (27%). M.p. 74–76 °C (hexane/$CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.4–7.2 (m, 5H, ArH), 4.0 (d, J = 13.7 Hz, 1H, ArC*H*HN), 3.0–2.9 (m, 1H, C*H*CHN), 2.9 (d, J = 13.7 Hz, 1H, ArCH*H*N), 2.6 (d, J = 8.9 Hz, 1H, NC*H*H), 2.7–2.5 (m, 2H, $CHCH_2N$ and C*H*HCO), 2.4–2.2 (m, 2H, NCH and C*H*CO), 2.15 (dd, J = 8.9, 5.2 Hz, 1H, NCH*H*), 2.0 (d, J = 15.6 Hz, 1H, CH*H*CO), 2.1–1.2 (m, 6H, $3CH_2$ ring); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 216.7 (CO), 139.5, 128.1, 128.0, 126.5 (ArC), 62.8, 56.0 ($2CH_2N$), 61.8 (CHN), 45.1, 40.9, 32.0 (3CH), 44.7 (CH_2CO), 25.4, 22.7, 16.0 ($3CH_2$ cyclohexyl); IR (neat): $\tilde{\nu}$ = 1735 cm^{-1} (C=O) HRMS (EI) calcd for $C_{17}H_{21}NO$: 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[6.2.1.0^{4,11}]undecen-9-ol (26)**: Yield: 0.14 g (28%). M.p. 88–90 °C (hexane/$CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 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, ArC*H*HN), 3.7 (d, J = 12.8 Hz, 1H, ArCH*H*N), 3.5 (d, J = 5.5 Hz, 1H, NC*H*H), 3.4–3.1 (m, 3H, NCH*H*, NCH and OH), 3.1–3.0 (m, 1H, C*H*CHN), 2.7–2.6 (m, 1H, C*H*CO), 1.7–0.9 (m, 6H, $3CH_2$ ring); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 ($2CH_2N$), 50.4, 44.4 (2CH), 22.6, 20.8 ($3CH_2$ cyclohexyl); IR (neat): $\tilde{\nu}$ = 3485 cm^{-1} (O–H); HRMS (EI) calcd for $C_{17}H_{21}NO$: 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-pyridinecarbonyl)-3-azatricyclo-[6.2.1.0^{4,11}]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. $NaHCO_3$. 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). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.7–7.2 (m, 9H, ArH), 4.0 (d, J = 13.7 Hz, 1H, ArC*H*HN), 3.6 (dd, J = 10.7,

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6.7 Hz, 1H, C*H*CHN), 3.1 (d, $J = 9.2$ Hz, 1H, NC*H*H), 2.9 (d, $J = 13.7$ Hz, 1H, ArCH*H*N), 2.8 (dd, $J = 17.5$, 2.2 Hz, 1H, C*H*HCO), 2.6–2.5 (m, 2H, CHN and CHCO), 2.5 (d, $J = 17.5$ Hz, 1H, CH*H*CO); 2.3 (d, $J = 9.2$ Hz, 1H, NCH*H*), 2.3–1.3 (m, 6H, $3CH_2$ ring); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): $\delta = 212.3$ (CH_2CO), 201.3 (Ar*C*O), 150.4, 142.3, 138.3, 128.2, 127.8, 126.8, 121.2 (ArC), 65.9, 55.4 ($2CH_2N$), 61.1 (CHN), 55.3 (*C*CH), 48.8 (CH_2CO), 44.7, 44.0 (2CH), 24.9, 22.2, 15.5 ($3CH_2$ cyclohexyl); IR (neat): $\tilde{\nu} = 1740$ (C=O), 1690 (C=O) cm^{-1}; HRMS (EI) calcd for $C_{23}H_{24}N_2O_2$: 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 H_2O or D_2O 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 Na_2SO_4. 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 [$Cp_2Zr(Me)Cl$] (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, $CDCl_3$, 25 °C, TMS): $\delta = 7.3–6.6$ (m, 5H, ArH), 6.0 (s, 1H, =CH), 3.7 (br s, 1H, NH), 3.5 (dd, $J = 14.8$, 7.3 Hz, 1H, NC*H*H), 3.2–3.1 (m, 2H, NCH*H* and CH), 2.6 (dd, $J = 18.5$, 5.8 Hz, 1H, C*H*HCO), 2.3 (dd, $J = 18.5$, 1.3 Hz, 1H, CH*H*CO), 2.2 (s, 3H, CH_3); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 (CH_2N), 43.8 (CH), 40.1 (CH_2CO), 17.4 (CH_3); IR (neat): $\tilde{\nu} = 3370$ (N–H), 1680 (C=O) cm^{-1}; HRMS (EI) calcd for $C_{13}H_{15}NO$: 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 [$Cp_2Zr(Me)Cl$] (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, $CDCl_3$, 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 (br s, 1H, NH), 3.4 (dd, $J = 14.8$, 7.1 Hz, 1H, NC*H*H), 3.2–3.1 (m, 2H, NCH*H* and CH), 2.6 (dd, $J = 18.5$, 6.2 Hz, 1H, C*H*HCO), 2.3 (dd, $J = 18.5$, 1.7 Hz, 1H, CH*H*CO), 2.1 (s, 2H, CH_2D); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 (CH_2N), 43.7 (CH), 40.1 (CH_2CO), 17.1 (t, $J_{CD} = 19.6$ Hz, CH_2D); IR (neat): $\tilde{\nu} = 3370$ (N–H), 1685 (C=O) cm^{-1}; HRMS (EI) calcd for $C_{13}H_{13}DClNO$: 236.0826, found 236.0825.

(1*S,2*R**,6*S**)-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 [$Cp_2Zr(Me)Cl$] (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, $CDCl_3$, 25 °C, TMS): $\delta = 7.4–7.2$ (m, 5H, ArH), 6.0 (s, 1H, =CH), 3.8 (d, $J = 13.4$ Hz, 1H, ArC*H*HN), 3.7 (d, $J = 13.4$ Hz, 1H, ArCH*H*N), 3.2–3.15 (m, 1H, CHN), 3.0 (dd, $J = 6.4$, 5.7 Hz, 1H, C*H*CHN), 2.5–2.4 (m, 1H, CHCO), 2.2 (s, 3H, CH_3), 2.1–1.2 (m, 7H, NH and $3CH_2$ ring); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 (CH_2N), 47.9, 46.2 (2CH), 24.9, 21.4, 16.6 ($3CH_2$ cyclohexyl), 18.9 (CH_3); IR (neat): $\tilde{\nu} = 3300$ (N–H), 1695 (C=O) cm^{-1}; HRMS (EI) calcd for $C_{17}H_{21}NO$: 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 H_2O (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 Na_2SO_4, and filtered. The solvents were removed and the residue purified by flash column chromatography to give **31a,b** and **35a,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, $CDCl_3$, 25 °C, TMS): $\delta = 7.4–7.2$ (m, 5H, ArH), 6.0 (s, 1H, BrC=C*H*H), 5.9–5.8 (m, 1H, CH=C), 5.6 (s, 1H, BrC=CH*H*), 5.1–5.0 (m, 2H, CH=CH_2), 3.7 (s, 2H, ArCH_2N), 3.3 (s, 2H, NCH_2C), 2.6 (dt, $J = 7.3$, 2.2 Hz, 2H, NCH_2CH_2), 2.3–2.25 (m, 2H, CH_2CH=); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): $\delta = 138.9$, 132.1, 128.6, 128.1, 126.6 (ArC and CBr), 136.4 (*C*H=CH$_2$), 117.8, 115.5 (2=*C*H$_2$), 61.8, 57.5, 52.6 (3CH_2N), 31.4 (*C*H$_2$CH); HRMS (EI) calcd for $C_{14}H_{17}BrN$ ($M^+ - 1$): 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, $CDCl_3$, 25 °C, TMS): $\delta = 7.4–7.3$ (m, 5H, ArH), 6.0 (s, 1H, BrC=C*H*H), 5.9–5.7 (m, 1H, CH=C), 5.6 (s, 1H, BrC=CH*H*), 5.1–4.9 (m, 2H, CH=CH_2), 3.7 (s, 2H, ArCH_2N), 3.3 (s, 2H, NCH_2C), 2.5 (dd, $J = 7.3$, 7.0 Hz, 2H, NCH_2CH$_2$), 2.2–2.1 (m, 2H, CH_2CH=), 1.7–1.6 (m, 2H, NCH$_2$CH_2); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): $\delta = 139.0$, 132.3, 128.5, 128.0, 126.6 (ArC and CBr), 138.4 (*C*H=CH$_2$), 117.8, 114.4 (2=*C*H$_2$), 62.0, 57.8, 52.5 (3CH_2N), 31.2, 26.2 (*C*H$_2$CH$_2$C=); HRMS (EI) calcd for $C_{15}H_{20}BrN$: 293.0779, found 293.0769.

***N*-Benzyl-*N*-(2-bromoallyl)-3-butynylamine (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, $CDCl_3$, 25 °C, TMS): $\delta = 7.4–7.3$ (m, 5H, ArH), 6.0 (s, 1H, BrC=C*H*H), 5.6 (s, 1H, BrC=CH*H*), 3.7 (s, 2H, ArCH_2N), 3.4 (s, 2H, NCH_2C), 2.8 (dd, $J = 7.7$, 7.3 Hz, 2H, NCH_2CH$_2$), 2.45–2.4 (m, 2H, CH$_2$C≡), 2.0 (t, $J = 2.6$ Hz, 1H, ≡CH); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): $\delta = 138.6$, 131.7, 128.5, 128.1, 126.9 (ArC and CBr), 118.1 (=CH$_2$), 82.6 (≡CH), 69.2 (≡C), 61.8, 57.4, 51.8 (3CH_2N), 17.1 (*C*H$_2$C≡); HRMS (EI) calcd for $C_{11}H_{13}BrN$ ($M^+ - C_3H_3$): 238.0231, found 238.0219.

***N*-Benzyl-*N*-(2-bromoallyl)-4-pentynylamine (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, $CDCl_3$, 25 °C, TMS): $\delta = 7.4–7.3$ (m, 5H, ArH), 5.9 (s, 1H, BrC=C*H*H), 5.6 (s, 1H, BrC=CH*H*), 3.6 (s, 2H, ArCH_2N), 3.3 (s, 2H, NCH_2C), 2.6 (t, $J = 6.9$ Hz, 2H, NCH_2CH$_2$), 2.3–2.2 (m, 2H, NCH$_2$CH_2), 1.9 (t, $J = 2.6$ Hz, 1H, ≡CH), 1.8–1.7 (m, 2H, CH$_2$C≡); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): $\delta = 138.7$, 132.1, 128.6, 128.0, 126.8 (ArC and CBr), 118.1 (=CH$_2$), 84.1 (≡CH), 68.3 (≡C), 61.9, 57.7, 51.7 (3CH_2N), 26.1, 16.0 (*C*H$_2$CH$_2$C≡).

Formation of six- and seven-membered heterocycles (33, 34, and 37)—General procedure: 2-Bromoallylamines **31** or **35** (2 mmol) were treated with *t*BuLi (4 mmol for **31** and 6 mmol for **35**) at −78 °C in Et_2O. The corresponding anions were added to a solution of bis(cyclopentadienyl)zirconium methyl chloride (0.57 g, 2.1 mmol) in Et_2O 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 [$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); after the addition of D_2SO_4 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, $CDCl_3$, 25 °C, TMS): $\delta = 7.4$ 7.3 (m, 5H, ArH), 4.85–4.75 (m, 1H, =CH), 3.6 (s, 2H, ArCH_2N), 3.3 (dd, $J = 11.8$, 1.7 Hz, 1H, C*H*HC=), 3.0–2.9 (m, 1H, NC*H*HCH$_2$), 2.7 (d,

$J = 11.8$ Hz, 1H, CH*H*C=), 2.2 (dt, $J = 11.4$, 3.2 Hz, 1H, NCH*H*CH_2), 2.15–2.05 (m, 1H, CH), 1.8–1.7 (m, 1H, C*H*HCH), 1.5–1.3 (m, 1H, CH*H*CH), 1.15–1.05 (m, 2H, CH_2D); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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=*C*HD), 62.7, 60.7, 53.2 ($3CH_2N$), 35.3 (CH), 34.4 (CH_2CH), 17.3 (t, $J_{CD} = 19.2$ Hz, CH_2D); HRMS (EI) calcd for $C_{14}H_{17}D_2N$: 203.1643, found 203.1638.

1-Benzyl-4-deuteriomethyl-3-(*E*)-deuteriomethyleneperhydroazepine (33b): Amine **31b** (0.59 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and $[Cp_2Zr(Me)Cl]$ (0.57 g, 2.1 mmol); after the addition of D_2SO_4 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, $CDCl_3$, 25 °C, TMS): $\delta = 7.4–7.2$ (m, 5H, ArH), 4.8 (s, 1H, =CH), 3.7 (d, $J = 13.3$ Hz, 1H, ArC*H*HN), 3.6 (d, $J = 13.3$ Hz, 1H, ArCH*H*N), 3.3 (d, $J = 13.8$ Hz, 1H, C*H*HC=), 3.2 (d, $J = 13.8$ Hz, 1H, CH*H*C=), 2.8 (dt, $J = 12.9$, 4.7 Hz, 1H, NC*H*HCH_2), 2.65–2.55 (m, 1H, CH), 2.55–2.45 (m, 1H, NCH*H*CH_2), 1.9–1.8 (m, 1H, C*H*HCH), 1.65–1.55 (m, 2H, $CH_2CH_2CH_2$), 1.35–1.25 (m, 1H, CH*H*CH), 1.15–1.0 (m, 2H, CH_2D); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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=*C*HD), 60.9, 59.7, 55.6 ($3CH_2N$), 38.1 (CH), 36.3, 26.9 (CH_2CH_2CH), 21.5 (t, $J_{CD} = 19.9$ Hz, CH_2D); HRMS (EI) calcd for $C_{15}H_{19}D_2N$: 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 $[Cp_2Zr(Me)Cl]$ (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/$CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.5–6.9$ (m, 9H, ArH), 3.5 (d, $J = 13.0$ Hz, 1H, ArC*H*HN), 3.3–3.2 (m, 1H, CH), 3.12 (d, $J = 13.0$ Hz, 1H, ArCH*H*N), 3.08 (d, $J = 12.4$ Hz, 1H, NC*H*HC), 2.7–2.6 (m, 1H, NC*H*HCH_2), 2.6 (d, $J = 18.1$ Hz, 1H, CC*H*HCO), 2.5 (d, $J = 18.1$ Hz, 1H, CCH*H*CO), 2.4–2.3 (m, 3H, $CHCH_2CO$ and NCH*H*CH_2), 2.2 (d, $J = 12.4$ Hz, 1H, NCH*H*C), 2.2–2.0 (m, 1H, NCH_2CHH), 1.6 (dq, $J = 13.6$, 3.5 Hz, 1H, NCH_2CH*H*); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): $\delta = 214.7$ (CH_2CO), 202.1 (Ar*C*O), 137.9, 137.1, 134.7, 129.3, 128.4, 128.3, 127.8, 126.7 (ArC), 62.7, 56.0, 49.4 ($3CH_2N$), 53.8 (*C*CH), 46.9, 39.5 ($2CH_2CO$), 33.8 (CH), 24.8 (CH_2CH_2N); IR (neat): $\tilde{\nu} = 1750$ (C=O), 1665 (C=O) cm^{-1}; HRMS (EI) calcd for $C_{22}H_{22}ClNO_2$: 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 $[Cp_2Zr(Me)Cl]$ (0.57 g, 2.1 mmol); after the addition of D_2SO_4 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, $CDCl_3$, 25 °C, TMS): $\delta = 7.4–7.3$ (m, 5H, ArH), 4.8 (s, 1H, =CH), 3.6 (s, 2H, $ArCH_2N$), 3.1 (s, 2H, NCH_2C=), 2.6 (t, $J = 5.7$ Hz, 2H, NCH_2CH_2), 2.4 (t, $J = 5.7$ Hz, 2H, NCH_2CH_2); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 CD_2), 62.2, 59.8, 53.2 ($3CH_2N$), 33.4 (CH_2C); HRMS (EI) calcd for $C_{14}H_{14}D_3N$: 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 Na_2SO_4. 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), $NaKCO_3$ (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 Na_2SO_4, 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, $CDCl_3$, 25 °C, TMS): $\delta = 7.2–6.7$ (m, 4H, ArH), 6.2 (s, 1H, IC=C*H*H), 6.0–5.9 (m, 1H, C*H*=CH_2), 5.9 (s, 1H, IC=CH*H*), 5.2–5.1 (m, 2H, CH=C*H*$_2$), 3.8 (brs, 1H, NH), 3.4–3.3 (m, 2H, NCH_2), 2.7 (dd, $J = 6.5$, 6.0 Hz, 2H, CH_2Cl); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): $\delta = 145.5$, 135.6, 129.7, 127.5, 123.5, 117.1, 110.3, 108.7 (ArC, =CI, and *C*H=CH_2), 127.6 (CH_2=CI), 116.2 (CH_2=CH), 44.2, 42.1, 36.4 ($3CH_2$); 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, $CDCl_3$, 25 °C, TMS): $\delta = 7.3–7.1$ (m, 4H, ArH), 6.2–6.0 (m, 1H, C*H*=CH_2), 6.1 (s, 1H, BrC=C*H*H), 5.7 (s, 1H, BrC=CH*H*), 5.3–5.2 (m, 2H, CH=C*H*$_2$), 3.8 (s, 2H, NC*H*$_2$C), 3.7 (d, $J = 6.7$ Hz, 2H, C*H*$_2$CH=), 2.8 (s, 3H, NCH_3); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): $\delta = 151.0$, 137.7, 135.1, 131.3, 130.3, 126.8, 123.8, 120.7 (ArC, =CBr, and *C*H=CH_2), 117.8, 115.5 (2=CH_2), 65.1 (CH_2N), 41.4 (CH_3), 34.8 (CH_2CH); HRMS (EI) calcd for $C_{13}H_{16}BrN$: 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, $CDCl_3$, 25 °C, TMS): $\delta = 7.3–7.1$ (m, 4H, ArH), 6.1–5.9 (m, 1H, C*H*=CH_2), 6.0 (s, 1H, IC=C*H*H), 5.8 (s, 1H, IC=CH*H*), 5.2–5.1 (m, 2H, CH=C*H*$_2$), 3.5 (d, $J = 6.4$ Hz, 2H, C*H*$_2$CH=), 3.2 (dd, $J = 7.6$, 7.0 Hz, 2H, NCH_2), 2.7 (s, 3H, NCH_3), 2.6 (dd, $J = 7.6$, 7.0 Hz, 2H, CH_2Cl); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): $\delta = 150.8$, 137.7, 135.7, 130.1, 126.7, 123.7, 120.9, 109.1 (ArC, =CI, and *C*H=CH_2), 126.4 (CH_2=CI), 115.6 (CH_2=CH), 55.7 (CH_2N), 43.3 (CH_3), 43.2, 34.8 ($2CH_2C$); HRMS (EI) calcd for $C_{14}H_{18}IN$: 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 Et_2O 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 zirconatricycles **41** generated benzazepine and benzazocine derivatives **42a** and **42b** by filtration through Celite, extraction with AcOEt (3 × 20 mL), washing with aq. $NaHCO_3$, drying over Na_2SO_4 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 benzoheterotricycles **42–48**.

2,3,4,5-Tetrahydro-1,4-dimethyl-3-methylene-1*H*-1-benzazepine (42a): Amine **40a** (0.53 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and $[Cp_2Zr(Me)Cl]$ (0.57 g, 2.1 mmol); after the addition of H_2O 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, $CDCl_3$, 25 °C, TMS): $\delta = 7.3–6.9$ (m, 4H, ArH), 4.8 (s, 2H, $=CH_2$), 3.9 (d, $J = 12.5$ Hz, 1H, NC*H*H), 3.4 (d, $J = 12.5$ Hz, 1H, NCH*H*), 2.9 (s, 3H, NCH_3), 2.85 (dd, $J = 13.3$, 5.2 Hz, 1H, C*H*HCH), 2.8 (dd, $J = 13.3$, 8.6 Hz, 1H, CH*H*CH), 2.7–2.6 (m, 1H, CH), 1.2 (d, $J = 6.3$ Hz, 3H, CH_3CH); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): $\delta = 150.7$, 150.4, 133.2, 129.6, 126.6, 120.6, 116.5 (ArC and *C*=CH_2), 112.8 (=CH_2), 60.9 (CH_2N), 41.5, 37.9 (CH_3N and CH), 40.1 (CH_2CH), 20.1 (CH_3CH); HRMS (EI) calcd for $C_{13}H_{17}N$: 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

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[$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); after the addition of H_2O 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, $CDCl_3$, 25 °C, TMS): δ = 7.3–7.0 (m, 4H, ArH), 4.8 (s, 1H, =C*H*H), 4.7 (s, 1H, =CH*H*), 2.95–2.85 (m, 2H, NCH_2), 2.8 (s, 3H, NCH_3), 2.8–2.7 (m, 2H, CH_2CH), 2.6–2.5 (m, 1H, CH), 2.0 (ddd, J = 13.8, 9.0, 3.9 Hz, 1H, C*H*HC=), 1.8 (ddd, J = 13.8, 6.4, 3.9 Hz, 1H, CH*H*C=), 1.1 (d, J = 6.9 Hz, 3H, CH_3CH); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 154.7, 151.1, 138.7, 130.4, 127.1, 124.1, 121.0 (ArC and C=CH_2), 110.0 (=CH_2), 63.1 (CH_2N), 44.4, 43.9 (CH_3N and CH), 38.3, 31.6 (2CH_2C), 19.8 (CH_3CH); HRMS (EI) calcd for $C_{14}H_{19}N$: 201.1518, found 201.1526.

3,3a,4,5,10,10a-Hexahydro-5-methylbenzo[*b*]cyclopent[*e*]azepin-2(1*H*)-one (43a) and **2,3,3a,4,9,9a-hexahydro-3a,4-dimethyl-1*H*-cyclopent[b]quinolin-2-one (44a)**: Amine **40a** (0.53 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of H_2O 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, $CDCl_3$, 25 °C, TMS): δ = 7.3–6.6 (m, 8H, ArH), 3.2–2.8 (m, 5H, NCH_2, NCH_2CH and C*H*HCH), 2.9 (s, 3H, NCH_3, major isom.), 2.8 (s, 3H, NCH_3, minor isom.), 2.7–2.0 (m, 12H, CH*H*CH, CCH_2CH and 2×CH_2CO), 1.4 (s, 3H, CCH_3, minor isom.); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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): $\tilde{\nu}$ = 1740 cm^{-1} (C=O); HRMS (EI) calcd for $C_{14}H_{17}NO$: 215.1310, found 215.1305.

1,2,4,5,10,10a-Hexahydro-2-hydroxy-5-methylbenzo[*b*]cyclopent[*e*]azepine (45a): Yield: 0.09 g (21%). M.p. 97–99 °C (hexane/$CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 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, NC*H*H), 3.5 (d, J = 12.9 Hz, 1H, NCH*H*), 3.1 (dd, J = 12.9, 4.7 Hz, 1H, C*H*HCH), 2.9 (s, 3H, NCH_3), 2.75–2.65 (m, 2H, CH and C*H*HCHO), 2.55 (dd, J = 12.9, 5.8 Hz, 1H, CH*H*CH), 1.8 (brs, 1H, OH), 1.4–1.3 (m, 1H, CH*H*CHO); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 (CH_2N), 42.4, 42.0 (CH_3N and CH), 41.6, 38.7 (2CH_2C); IR (neat): $\tilde{\nu}$ = 3355 cm^{-1} (O–H) HRMS (EI) calcd for $C_{14}H_{17}NO$: 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.

2,4,5,6,11,11a-Hexahydro-2-hydroxy-6-methyl-1*H*-benzo[*b*]cyclopent-[*e*]azocine (45b): Amine **40b** (0.65 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [$Cp_2Zr(Me)Cl$] (0.57 g, 2.1 mmol); CO was bubbled through the mixture for 40 min. After the addition of H_2O 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, $CDCl_3$, 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, NCH_2 and CH), 2.7 (s, 3H, NCH_3), 2.7–2.6 (m, 2H, CCH_2CH), 2.3 (d, J = 13.7 Hz, 1H, C*H*HC=), 2.1–2.0 (m, 2H, C*H*HCHO and CH*H*C=), 1.8 (brs, 1H, OH), 1.5 (dt, J = 13.3, 4.3 Hz, 1H, CH*H*CHO); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 (CH_2N), 49.6, 43.8 (CH_3N and CH), 42.4, 38.8, 28.6 (3CH_2C); IR (neat): $\tilde{\nu}$ = 3345 cm^{-1} (O–H); HRMS (EI) calcd for $C_{15}H_{19}NO$: 229.1467, found 229.1473.

2-(4-Chlorobenzoyl)-1,2,4,5,10,10a-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 [$Cp_2Zr(Me)Cl$] (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, $CDCl_3$, 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, NC*H*H), 3.6 (d, J = 12.5 Hz, 1H, NCH*H*), 3.6–3.5 (m, 1H, CH), 3.5 (dd, J = 11.2, 6.9 Hz, 1H, CC*H*HCH), 2.9 (s, 3H, CH_3), 2.4 (d, J = 11.2 Hz, 1H, CCH*H*CH), 2.3–2.1 (m, 2H, CH_2CO); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 (CH_2N), 45.5, 34.9 (2CH_2C), 42.5, 41.2 (CH_3N and CH); IR (neat): $\tilde{\nu}$ = 3450 (O–H), 1670 (C=O) cm^{-1}; HRMS (EI) calcd for $C_{21}H_{20}ClNO_2$: 353.1183, found 353.1179.

2-(4-Chlorobenzoyl)-2,4,5,6,11,11a-hexahydro-2-hydroxy-6-methyl-1*H*-benzo[*b*]cyclopent[*e*]azocine (46b): Amine **40b** (0.65 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [$Cp_2Zr(Me)Cl$] (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, $CDCl_3$, 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, CC*H*HCH), 3.1–3.0 (m, 1H, NC*H*H), 2.9 (s, 3H, CH_3), 2.9–2.8 (m, 1H, NCH*H*), 2.75 (dd, J = 12.0, 4.2 Hz, 1H, CCH*H*CH), 2.5–2.4 (m, 2H, C*H*HC= and C*H*HCO), 2.3 (dd, J = 14.2, 6.2 Hz, 1H, CH*H*CO), 1.7 (dt, J = 13.3, 4.7 Hz, 1H, CH*H*C=); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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 (CH_2N), 49.6, 44.0 (CH_3N and CH), 45.8, 37.3, 28.8 (3CH_2C); IR (neat): $\tilde{\nu}$ = 3450 (O–H), 1670 (C=O) cm^{-1}; HRMS (EI) calcd for $C_{22}H_{22}ClNO_2$: 367.1339, found 367.1348.

3a-Allyl-3,3a,4,5,10,10a-hexahydro-5-methylbenzo[*b*]cyclopent[*e*]azepin-2(1*H*)-one (47a): Amine **40a** (0.53 g, 2 mmol) was treated with *t*BuLi (2.4 mL, 4 mmol) and [$Cp_2Zr(Me)Cl$] (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, $CDCl_3$, 25 °C, TMS): δ = 7.2–6.8 (m, 4H, ArH), 5.9–5.8 (m, 1H, =CH), 5.2–5.15 (m, 2H, =CH_2), 3.3 (d, J = 15.0 Hz, 1H, NC*H*H), 3.0 (d, J = 14.2 Hz, 1H, CC*H*HCO), 2.8 (s, 3H, CH_3), 2.8–2.3 (m, 7H, NCH*H*, CCH*H*CO, CH, CCH_2CH, CHC*H*HCO and C*H*HC=), 2.1–2.0 (m, 1H, CH*H*C=), 2.0 (dd, J = 18.5, 10.0 Hz, 1H, CHCH*H*CO); ^{13}C NMR (50.5 MHz, $CDCl_3$, 25 °C): δ = 216.8 (CO), 152.0, 134.2, 131.9, 128.2, 127.2, 120.6, 114.7 (ArC and CH=CH_2), 118.6 (CH_2=CH), 61.1 (CH_2N), 48.2, 40.9, 40.8, 34.1 (4CH_2C), 45.7 (CCH), 42.1, 40.0 (CH_3N and CH); IR (neat): $\tilde{\nu}$ = 1740 cm^{-1} (C=O); HRMS (EI) calcd for $C_{17}H_{21}NO$: 255.1623, found 255.1621.

2-Allyl-1,2,4,5,10,10a-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, $CDCl_3$, 25 °C, TMS): δ = 7.3–7.0 (m, 8H, ArH), 5.9–5.7 (m, 2H, CH=CH_2), 5.5 (s, 1H, C=CH, minor diast.), 5.4 (s, 1H, C=CH, major diast.), 5.2–5.0 (m, 4H, CH=CH_2), 3.6–3.5 (m, 4H, NCH_2), 3.15–3.05 (m, 2H, CC*H*HCH), 2.9 (s, 6H, CH_3), 2.75–2.65 (m, 2H, CH), 2.6–2.4 (m, 4H, CCH*H*CH and C*H*HCO), 2.4–2.3 (m, 4H, CH_2CH=), 1.7–1.6 (m, 3H, OH and CH*H*CO, minor diast.), 1.6 (dd, J = 13.2, 7.2 Hz, 1H, CH*H*CO, major diast.); ^{13}C NMR (50.5 MHz, $CDCl_3$, 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=CH_2 and C=CH), 118.3 (CH_2=CH, minor diast.), 118.1 (CH_2=CH, major diast.), 82.9 (CO, minor diast.), 82.8 (CO, major diast.), 58.0 (CH_2N, minor diast.), 57.6 (CH_2N, major diast.), 45.8, 44.5, 38.6 (3CH_2C, major diast.), 45.4, 45.0, 38.3 (3CH_2C, minor diast.), 42.6, 42.5, 42.1 (CH_3N and $CHCH_2$); HRMS (EI) calcd for $C_{17}H_{21}NO$: 255.1623, found 255.1615.

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