Syntheses and X-Ray Crystal Structures of Tricyclic Ketones Containing *Trans*-Fused Azabicyclo[3.3.0]octane Units

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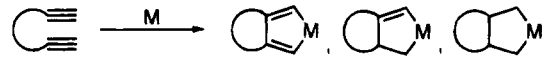
Tricyclic ketones containing the *trans*-fused 3-azabicyclo[3.3.0]octane framework were prepared from the reactions of dienes and Cp_2ZrBu_2, followed by treatment with carbon monoxide. The structures were confirmed by X-ray analysis.

Introduction

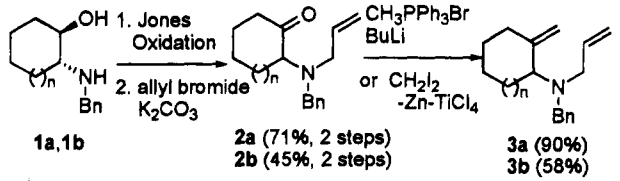
Metalacycles formed from dienes, enynes, and diynes are useful intermediates for the synthesis of cyclic compounds such as cyclopentanoids, nitrogen heterocycles, and oxygen heterocycles. Interestingly, rather strained molecules can be obtained from these metalacycles. Though the ring junction of a 5,5-ring system is usually *cis* and syntheses of *trans*-fused bicyclo[3.3.0]-octanes are few,[1] *trans*-fused 5,5-ring systems containing transition metals can be prepared from dienes and transition metals. The reaction of 1,6-heptadiene with nickelacyclopentane resulted in the evolution of ethylene.[2] Protonolysis of the reaction mixture gave the *trans*- and *cis*-dimethylcyclopentanes in a ratio of 2.7 to 1, in 96% yield. The insertion of carbon monoxide into the bicyclic nickelacycles afforded *trans*-fused bicyclo[3.3.0]-octan-3-one in 19% yield along with the *cis*-fused product in 2.6% yield. The stereochemistry of these products was confirmed by comparison with literature characterization data.[3] In the reaction of 1,6-heptadiene with titanocene, the *cis*- and the *trans*-fused 5,5-ring titanacycles were obtained. Carbonylation of these titanacycles afforded *cis*- and *trans*-fused bicyclo[3.3.0]octanones in 74 and 18% yields, respectively.[4] Recent reports of the zirconium-promoted cyclization also described the preparation of the *trans*-fused zirconacycle from 1,6-heptadiene.[5] The insertion of carbon monoxide into the zirconacycle gave the *trans*-fused bicyclo[3.3.0]octane skeleton. However, in these cases, the stereochemistry of the *trans*-fused[3.3.0]-octane unit was not confirmed by X-ray analysis. We wish to report the syntheses and the X-ray crystal structure determination of the *trans*-fused azabicyclo-[3.3.0]octane unit.

Scheme 1



M : Ti, Zr, Cr, Mo, Co, Ni, Pd, etc.

Scheme 2[a]



[a] **1a**, $n = 1$; **1b**, $n = 0$.

Syntheses of the Azabicyclo[7.3.0.0^{4,9}]dodecane and Azabicyclo[6.3.0.0^{4,8}]undecane Skeletons. During the course of our study of zirconium-promoted enyne or diene cyclizations, we found that highly stereocontrolled perhydroindole derivatives could be prepared in a one-pot reaction, and the total synthesis of (−)-dendrobine was achieved by this method.[6] This procedure was extended to the synthesis of azabicyclo[7.3.0.0^{4,9}]-dodecane and azabicyclo[6.3.0.0^{4,8}]undecane, from the exomethylenes **3a** and **3b**. The starting materials were prepared as shown in Scheme 2. The amino alcohols **1a** and **1b**[7] were converted to ketones by Jones oxidation and then treated with allyl bromide to give the ketones **2a** and **2b**. Methylenation *via* a Wittig reaction of Nozaki–Lombardo reaction[8] afforded the exomethylenes **3a** and **3b**.

When a THF solution of **3a** and Cp_2ZrBu_2, prepared from Cp_2ZrCl_2 and BuLi,[9] was stirred at room temperature and then treated with 10% HCl, the perhydroindole derivative was obtained in 82% yield as an inseparable mixture of **6a** and **6b**. The NMR spectrum of the mixture revealed a ratio of **6a** to **6b** of 1.9 to 1. To determine the stereochemistry of these products, hydrogenolysis was effected, followed by treatment with TsCl and K_2CO_3 to afford the tosyl amides **8a** and **8b** in 59 and 29% yields,

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Scheme 3

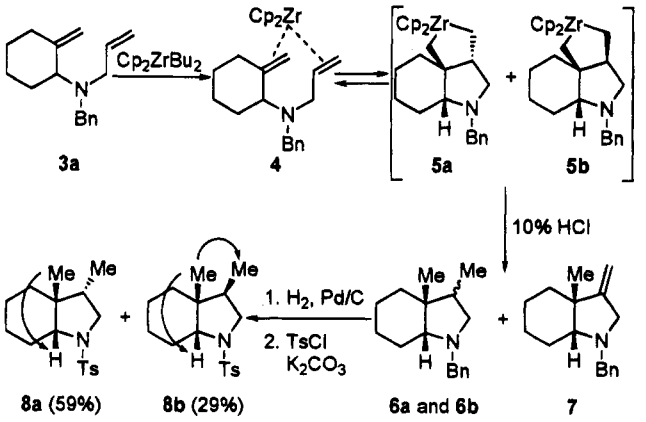
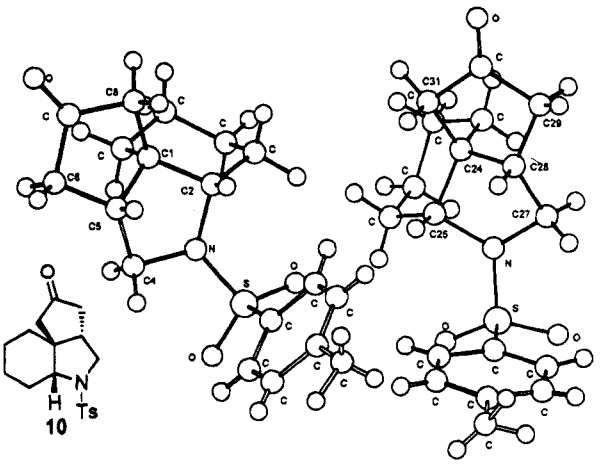


Table 1. Reaction of 3a with Cp_2ZrBr_2

			yield (%)		
run	temp, °C	time (h)	**6**	**7**	**6a:6b**
1	rt	1.3	82	–	1.9:1
2	0	18	90	–	2.1:1
3	rt	18	90	–	1.8:1
4	60	1	91	–	1.2:1
5	60	6	52	28	1:2
6	60	12	62	38	1:2

respectively. NOE experiments indicated that the ring junctions of the 6,5-ring systems of these compounds were *cis*. It was also apparent that the ring junction methyl group of the major product **8a** was *trans* to the methyl group on the five-membered ring, and that of the minor product **8b** was *cis* to the methyl group on the five-membered ring. These results suggest that two zirconacycles exist as intermediates, and that the stereochemistry of the zirconacycle of the major product is **5a** as shown in Scheme 3. Thus, the next question is whether or not the zirconacycle **5a** is in a state of equilibrium with **5b**. To determine this point, the reaction was carried out under various conditions, with the results shown in Table 1.

At the lowest reaction temperature, the yield of **6a** was slightly higher (Table 1, run 2). At a higher reaction temperature (run 4) and with a longer reaction time (run 5), the amount of **6b** increased relative to **6a**, though the β-hydride elimination product **7** was produced. This indicates that the *trans*-fused zirconacycle **5a** is in a state of equilibrium with the *cis*-fused zirconacycle **5b** *via* the zirconocene-coordinated diene. The stereochemistry of the carbonylated product was scrutinized since the *trans*-fused bicyclo[3.3.0]octanones are highly strained compounds and the *trans*-fused zirconacycle **5a** is in equilibrium with the *cis*-fused zirconacycle **5b**. The insertion of carbon monoxide into the zirconacycle **5** proceeded smoothly at room temperature and was followed by treatment with I_2[10] to give the tricyclic ketones **9a** and **9b** in 36 and 18% yields, respectively. The structures of these compounds were confirmed from IR and other spectral data. One of them should have the *trans*-fused azabicyclo[3.3.0]octane skeleton. To determine the stereochemistry, an X-ray analysis was carried out. Hydrogenolysis of the major product **9a** was followed by treatment with TsCl to give the tosyl amide **10**, in 73% yield, as a colorless crystal. The result of the X-ray analysis of **10** is shown in Figure 1.[11] The bond angles of C(5)—C(1)—C(8), C(2)—C(1)—C(8), C(4)—C(5)—C(6), and C(2)—C(1)—C(5) are 101.0°, 122.4°, 128.5°, and 99.8°, respectively. The bond distances of C(1)—C(2), C(4)—C(5), and C(5)—C(6) are 1.526, 1.513, and 1.516 Å, respectively. It is apparent that the ring junction of the 5,5-ring system is *trans*. To our knowledge, this is the first example of the stereochemistry of a compound with a *trans*-configuration between the two five-membered rings being confirmed by X-ray analysis.[14] Thus, the ring junction of the 5,5-ring system of the minor product **9b** is *cis*.[12] This indicates that the hydrolysis products **6a** and **6b**, and the carbonylated products **9a** and **9b**, were obtained from the corresponding zirconacycles **5a** and **5b**, respectively.

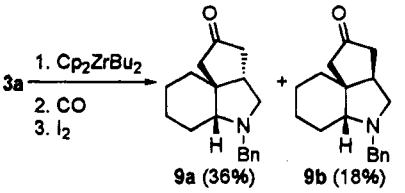


Bond distances (Å):
C(1)-C(2), 1.526(4); C(1)-C(5), 1.531(4); C(1)-C(8), 1.531(4); C(4)-C(5), 1.513(4); C(5)-C(6), 1.516(5); C(24)-C(25), 1.535(4); C(24)-C(28), 1.530(4); C(24)-C(31), 1.529(4); C(27)-C(28), 1.513(4); C(28)-C(29), 1.515(4)

Bond angles (°):
C(2)-C(1)-C(5), 99.8(2); C(2)-C(1)-C(8), 122.4(2); C(5)-C(1)-C(8), 101.0(2); C(1)-C(5)-C(4), 103.9(2); C(1)-C(5)-C(6), 104.0(3); C(4)-C(5)-C(6), 128.5(3); C(25)-C(24)-C(28), 100.3(2); C(25)-C(24)-C(31), 122.5(2); C(28)-C(24)-C(31), 100.7(2); C(24)-C(28)-C(27), 103.2(2); C(24)-C(28)-C(29), 104.7(2); C(27)-C(28)-C(29), 127.4(2)

Figure 1. A perspective view of **10**.

Scheme 4



(10) Hydrolysis of the intermediary zirconium complex with 10% HCl afforded the desired carbonylated products **13a** and **13b** in 26 and 8% yields, respectively. See ref Swanson, D. R.; Rousset, C. R.; Negishi, E. *J. Org. Chem.* **1989**, *54*, 3521.

(11) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 2EZ, UK.

(12) The heat of formation of *trans*-fused azabicyclo[7.3.0.$0^{4,8}$]-dodecanone (**9a**) is −14.6 kcal/mol calculated by MOPAC (PM3), and that of the *cis*-fused product **9b** is −36.1 kcal/mol. MOPAC Ver. 5.00 (QCPE No. 445), Stewart, J. J. P. *QCPE Bull.* **1989**, *9*, 10. Hirano, T. *JCPE Newsletter* **1989**, *1* (2), 36. Revised as Ver. 5.01 by J. Toyoda for Apple Macintosh.

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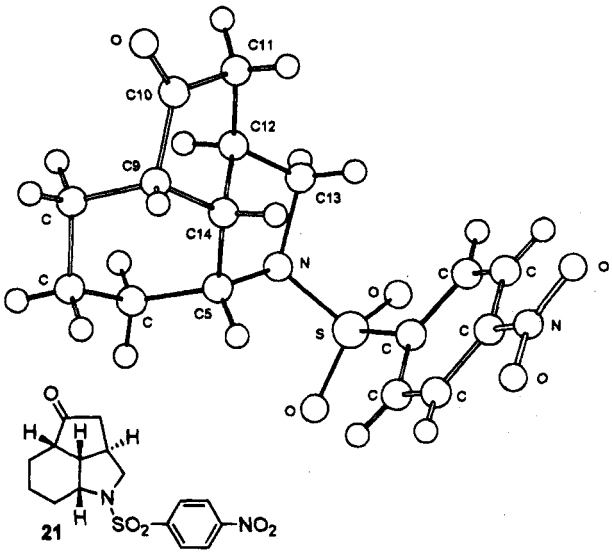
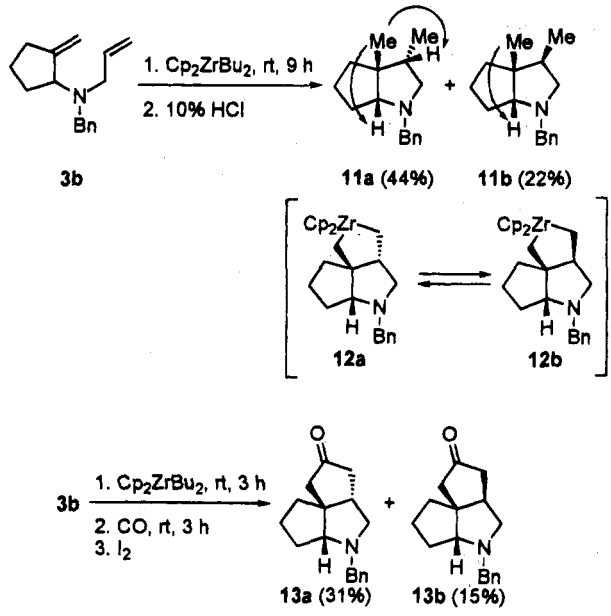
(14) After we submitted this paper, the result of the X-ray analysis of the compound having a *trans*-fused oxabicyclo[3.3.0]octane unit was reported. Clive, D. L.; Cole, D. C.; Tao, Y. *J. Org. Chem.* **1994**, *59*, 1396.



Bond distances (Å):
C(5)-C(14), 1.512(3); C(9)-C(14), 1.512(4); C(11)-C(12), 1.517(4); C(12)-C(13), 1.512(4); C(12)-C(14), 1.531(4)
Bond angles (°):
C(5)-C(14)-C(9), 123.6(2); C(5)-C(14)-C(12), 102.8(2); C(9)-C(14)-C(12), 103.6(2); C(13)-C(12)-C(14), 102.0(2); C(11)-C(12)-C(14), 101.4(2); C(11)-C(12)-C(13), 127.2(2)

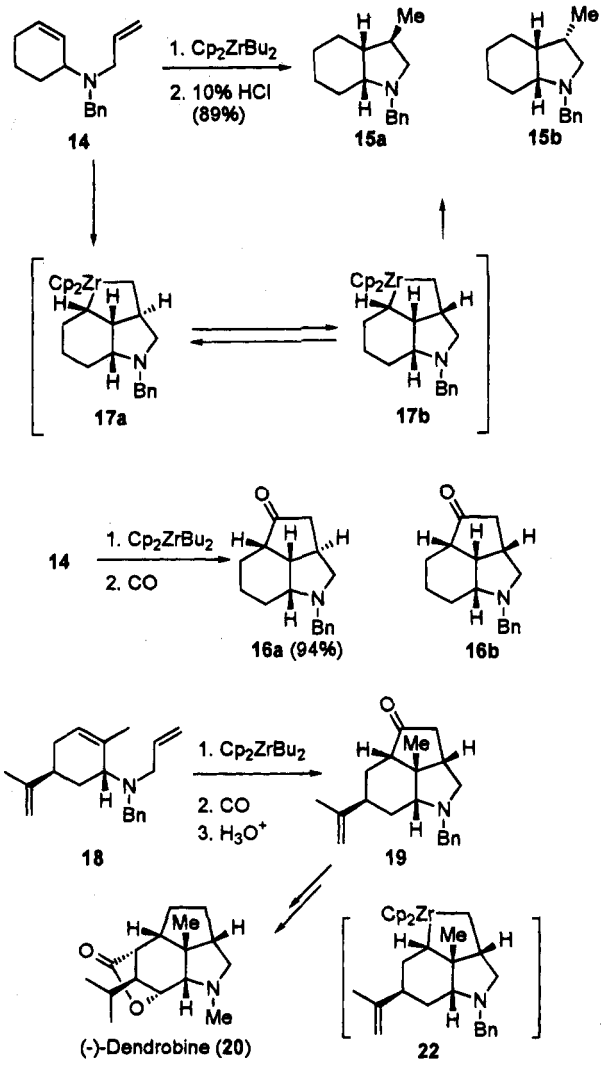
Figure 2. A perspective view of **21**.

Scheme 5



Subsequently, the diene **3b** was treated with Cp_2ZrBu_2, followed by treatment with 10% HCl, to give the fused five-five membered heterocycles **11a** and **11b** in 44 and 22% yields, respectively. NOE experiments indicate that the ring junctions of **11a** and **11b** are *cis* and that the methyl group on the ring junction of the major product **11a** is *trans* to the methyl group on the five-membered ring. Thus, the stereochemistry of the zirconacycles of the major product would be **12a** as shown in Scheme 5. The insertion of carbon monoxide into the zirconacycles, **12a** and **12b**, followed by treatment with I_2 afforded the tricyclic ketones, **13a** and **13b**, in 31 and 15% yields, respectively. These structures were confirmed by spectral data. On the basis of the above results, the major product **13a** must possess the *trans*-fused azabicyclo[3.3.0]octane unit because the ring junctions of the hydrolysis products **11a** and **11b** are *cis*.

Scheme 6



Synthesis of the Azabicyclo[6.2.1.$0^{4,11}$]undecane Skeleton. We have previously reported the synthesis of the perhydroindole derivative **15b** and tricyclic ketone **16b** from the diene **14**, using zirconium-promoted reductive cyclization.[6] Namely, when the diene **14** was treated with a stoichiometric amount of Cp_2ZrBu_2, followed by treatment with 10% HCl, the perhydroindole derivative **15b** was obtained in 89% yield as the sole product. The insertion of carbon monoxide into the zirconacycle **17** afforded the tricyclic ketone **16b** in high yield (94%). We could not determine the stereochemistry of the hydrolysis product, nor that of the tricyclic ketone, by NOE experiments. However, we have synthesized (−)-dendrobine (**20**) from the tricyclic ketone **19**, which was prepared by the reaction of the diene **18** with Cp_2ZrBu_2, followed by treatment with carbon monoxide.[6] On the basis of the dendrobine synthesis results, we concluded that the stereochemistry of the tricyclic ketone was as shown in **16b** in Scheme 6, because all of the ring junctions of **19** were evidently *cis*. On the other hand, the aforementioned *trans*-fused bicyclo[3.3.0]octane skeleton could be easily obtained by zirconium-promoted reductive cyclization. Thus, we reinvestigated the stereochemistry of these compounds.

We tried to confirm the structure of the tricyclic ketone

16 by X-ray analysis. Hydrogenolysis of the tricyclic ketone with 10% palladium on charcoal in MeOH gave the debenzylation product, which was followed by treatment with *p*-nitrobenzenesulfonyl chloride in the presence of DMAP (dimethylaminopyridine) and pyridine, to afford the *p*-nitrobenzenesulfonamide **21** as a colorless crystalline product. The X-ray analysis of compound **21** was carried out and the result is shown in Figure 2.[11] The bond angles of C(5)—C(14)—C(9) and C(11)—C(12)—C(13) are 123.6° and 127.2°, respectively, and the bond distance of C(12)—C(14) is 1.531 Å. Evidently, the ring junction protons of the 6,5-ring system of **21** are *cis* and those of the 5,5-ring system are *trans*. The results indicate that the carbonylated product **16a** is derived from the zirconacycle **17a**. Thus the structures of the hydrolysis product and the carbonylation product, prepared from the diene **14** and Cp_2ZrBu_2, were confirmed to be **15a** and **16a**. The production of the *cis*-fused zirconacycle **22** from the reaction of **18** with Cp_2ZrBu_2 would be due to the steric congestion caused by the methyl group on the cyclohexene ring.

This study has shown that compounds possessing the strained *trans*-fused 3-azabicyclo[3.3.0]octane unit can be obtained using zirconium-promoted cyclization. The stereochemistry of the products is consistent with that of the intermediate zirconacycles.

Experimental Section

All manipulations were performed under an argon atmosphere. Solvents were distilled under an argon atmosphere from sodium benzophenone (THF) or CaH_2 (CH_2Cl_2). All other reagents and solvents were purified when necessary using standard procedures. Column chromatography was performed on silica gel 60 (70–230 mesh, 60 Å) and flash chromatography was performed on silica gel 60 (230–400 mesh, 60 Å) using the indicated solvent.

***trans*-2-(*N*-Benzylamino)cyclohexanol (1a).** To a suspension of Al_2O_3 (7.5 g)[7] in Et_2O (8.0 mL) was added benzylamine (0.31 mL, 2.80 mmol) at 0 °C. After stirring the mixture for 5 min at rt, cyclohexene oxide (0.1 mL, 1.02 mmol) was added and the mixture was stirred rt for 19.5 h. To the suspension was added MeOH (30 mL) at 0 °C and the reaction mixture was stirred at rt for a further 4 h. After Al_2O_3 was filtered off, the solvent was removed under vacuum and the residue was purified by column chromatography on Al_2O_3 (AcOEt–hexane, 1:4, 1:2, 1:1) to afford 176 mg (84%) of **1a** as colorless crystals: mp 70.0–71.0 °C[13] (recryst from AcOEt–hexane); IR (neat) 3296, 3104 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 0.80–2.60 (m, 11 H), 3.00–3.55 (m, 1 H), 3.64 (d, J = 12.9 Hz, 1 H), 3.90 (d, J = 12.9 Hz, 1 H), 7.10–7.40 (m, 5 H); MS (EI, *m/z*) 205 (M^+), 114, 106, 91 (bp), 77; HRMS (EI, *m/z*) for $C_{13}H_{19}NO$, calcd 205.1467, found 205.1473. Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 75.91; H, 9.44; N, 6.61.

***trans*-2-(*N*-Benzylamino)cyclopentanol (1b).** To a stirred suspension of Al_2O_3 (25 g)[7] in Et_2O (30 mL) was added benzylamine (1.02 mL, 9.33 mmol) at 0 °C. After stirring the mixture for 10 min at rt, cyclopentene oxide (0.30 mL, 3.44 mmol) was added at 0 °C and the reaction mixture was stirred at rt for 14 h. To the suspension was added MeOH (30 mL) at 0 °C and the reaction mixture was stirred at rt for a further 4 h. After Al_2O_3 was filtered off, the solvent was removed under vacuo and the residue was purified by column chromatography on Al_2O_3 (AcOEt–hexane, 1:2, 1:1, 2:1, 3:2, 4:1) to afford 282 mg (43%) of **1b** as a colorless oil: IR (neat) 3291 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.06–2.10 (m, 8 H), 2.84 (dd, J = 5.1, 14.1 Hz, 1 H), 3.70 (d, J = 13.0 Hz, 1 H), 3.76 (d, J = 13.0 Hz, 1 H), 3.74–4.00 (m, 1 H), 7.30 (m, 5 H); MS (EI, *m/z*) 191 (M^+), 106, 100, 91 (bp); HRMS (EI, *m/z*) for $C_{12}H_{17}NO$, calcd 191.1310, found 191.1314. Anal. Calcd for $C_{12}H_{17}NO$: C, 75.36; H, 8.96; N, 7.32. Found: C, 75.58; H, 9.17; N, 7.15.

2-(*N*-Allyl-*N*-benzylamino)cyclohexanone (2a). To a stirred solution of **1a** (100.0 mg, 0.49 mmol) in acetone (4.0 mL) was added a solution of Jones reagent (0.98 mL) at 0 °C and the solution was stirred at rt for 23.5 h. To the solution was added *i*-PrOH (1.0 mL) at 0 °C and the resultant solution was stirred at rt for 10 min. After the mixture was filtered through Celite, the solvent was removed. To the residue in CH_3CN (4.0 mL) containing K_2CO_3 (135 mg, 0.98 mmol) was added allyl bromide (0.064 mL, 0.74 mmol) at 0 °C. After stirring the mixture at rt for 46 h, saturated $NaHCO_3$ solution (1.0 mL) was added and the mixture was diluted with AcOEt. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (AcOEt–hexane, 1:4) to afford 84.6 mg (71%, 2 steps) of **2a** as a colorless oil: IR (neat) 1713 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.30–2.52 (m, 8 H), 2.94–3.50 (m, 3 H), 3.60 (d, J = 14.8 Hz, 1 H), 3.84 (d, J = 14.8 Hz, 1 H), 4.95 (ddd, J = 1.4, 2.6, 9.3 Hz, 1 H), 5.06 (ddd, J = 1.4, 2.6, 15.5 Hz, 1 H), 5.72 (dddd, J = 5.8, 6.2, 9.3, 15.5 Hz, 1 H), 7.00–7.40 (m, 5 H); MS (EI, *m/z*) 243 (M^+), 215, 146, 91 (bp); HRMS (EI, *m/z*) for $C_{16}H_{21}NO$, calcd 243.1623, found 243.1643. Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found: C, 78.70; H, 8.98; N, 5.66.

2-(*N*-Allyl-*N*-benzylamino)cyclopentanone (2b). To a stirred solution of **1b** (50 mg, 0.26 mmol) in acetone (2.0 mL) was added Jones reagent (0.5 mL) at 0 °C and the solution was stirred at rt for 15 h. To the solution was added *i*-PrOH (0.5 mL) at 0 °C and the resultant solution was stirred at rt for 10 min. After the mixture was filtered through Celite, the solvent was removed. To the residue in CH_3CN (2.0 mL) containing K_2CO_3 (71.9 mg, 0.52 mmol) was added allyl bromide (0.034 mL, 0.39 mmol) at 0 °C. After stirring at rt for 24 h, saturated $NaHCO_3$ solution (1.0 mL) was added and the mixture was diluted with AcOEt. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (AcOEt–hexane, 1:4) to afford 26.9 mg (45% two steps) of **2b** as a colorless oil: IR (neat) 1742 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.20–2.40 (m, 6 H), 2.98–3.40 (m, 3 H), 3.58 (d, J = 14.0 Hz, 1 H), 3.80 (d, J = 14.0 Hz, 1 H), 5.00–5.30 (m, 2 H), 5.84 (m, 1 H), 7.30 (m, 5 H); MS (EI, *m/z*) 229 (M^+), 201, 146, 91 (bp); HRMS (EI, *m/z*) for $C_{15}H_{19}NO$, calcd 229.1467, found 229.1441. Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.31; H, 8.53; N, 6.00.

1-(*N*-Allyl-*N*-benzylamino)-2-methylenecyclohexane (3a). To a stirred solution of $CH_3P^+Ph_3Br^-$ (250 mg, 0.70 mmol) in THF (3.0 mL) was added dropwise *n*-BuLi (1.64 M solution in hexane, 0.32 mL, 0.53 mmol) at −78 °C and the solution was stirred at 0 °C for 40 min. To the solution was added **2a** (84.6 mg, 0.35 mmol) at −78 °C and the reaction mixture was allowed to warm to rt. After stirring the mixture for 1 h, saturated $NaHCO_3$ solution (1.0 mL) was added and the mixture was diluted with AcOEt. The aqueous layer was separated, and and the organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (AcOEt–hexane, 1:10) to afford 76.0 mg (90%) of **3a** as a colorless oil: IR (neat) 1645 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.26–2.16 (m, 7 H), 2.27–2.45 (m, 1 H), 3.09 (dd, J = 6.6, 15.5 Hz, 1 H), 3.13 (m, 1 H), 3.22 (dddd, J = 1.1, 1.8, 5.5, 15.5 Hz, 1 H), 3.63 (d, J = 14.7 Hz, 1 H), 3.77 (d, J = 14.7 Hz, 1 H), 4.76 (d, J = 1.1 Hz, 1 H), 4.96 (d, J = 1.1 Hz, 1 H), 5.09 (ddd, J = 1.1, 1.8, 9.5 Hz, 1 H), 5.14 (ddd, J = 1.1, 1.8, 16.8 Hz, 1 H), 5.89 (dddd, J = 5.5, 6.6, 9.5, 16.8 Hz, 1 H), 7.17–7.38 (m, 5 H); MS (EI, *m/z*) 241 (M^+), 226, 200, 164, 149, 146, 122, 108, 105, 95, 91 (bp), 77, 55, 41; HRMS (EI, *m/z*) for $C_{17}H_{23}N$, calcd 241.1831, found 241.1817. Anal. Calcd for $C_{17}H_{23}N$: C, 84.59; H, 9.60; N, 5.80. Found: C, 84.48; H, 9.47; N, 5.83.

1-(*N*-Allyl-*N*-benzylamino)-2-methylenecyclopentane (3b). To a suspension of Zn (1.0 g, 15.4 mmol) in THF (14 mL) was added CH_2I_2 (0.69 mL, 8.55 mmol) at 0 °C. After stirring the mixture for 30 min at 0 °C, to the suspension was addeded $TiCl_4$ (1.0 M solution in CH_2Cl_2, 1.88 mL, 1.88 mmol) at −30 °C. After stirring the mixture at rt for 30 min, **2b** (393 mg, 1.71 mmol) in THF (1.0 mL) was added at 0 °C and the reaction mixture was stirred at rt. After 30 min, ether was

added and saturated $NaHCO_3$ solution (10 mL) was added to the solution at 0 °C. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (AcOEt–hexane, 1:40) to afford 224 mg (58%) of **3b** as a colorless oil: IR (neat) 1655, 1642 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.20–1.80 (m, 4 H), 2.28 (m, 2 H), 2.84 (dd, J = 3.4, 14.2 Hz, 1 H), 3.24 (m, 1 H), 3.30 (d, J = 13.6 Hz, 1 H), 3.60 (m, 1 H), 3.86 (d, J = 13.6 Hz, 1 H), 5.00–5.38 (m, 2 H), 5.80 (m, 1 H), 7.30 (m, 5 H); MS (EI, m/z) 227 (M^+), 199, 186, 146, 136, 91 (bp); HRMS (EI, m/z) for $C_{16}H_{21}N$, calcd 227.1674, found 227.1653. Anal. Calcd for its picrate $C_{22}H_{24}N_4O_7$: C, 57.89; H, 5.30; N, 12.27. Found: C, 57.85; H, 5.32; N, 12.15; mp of picrate 103.0–104.0 °C.

General Procedure for Preparing Zirconacycles. According to Negishi's procedure,[9] to a stirred suspension of Cp_2ZrCl_2 (0.26 mmol) in THF (0.5 mL) was added dropwise BuLi (1.60 M solution in hexane, 0.31 mL, 0.5 mmol) at −78 °C. After stirring the mixture for 1 h at −78 °C, diene (0.2 mmol) in THF (1.0 mL) was added. The solution was allowed to warm to rt and stirred for 1.5 h to give the zirconacycle.

(3*S,3a*R**,7a*R**)-1-Benzyl-3,3a-dimethylperhydroindole (6a), (3*R**,3a*R**,7a*R**)-1-Benzyl-3,3a-dimethylperhydroindole (6b), and (3a*R**,7a*R**)-1-Benzyl-3a-methyl-3-methyleneperhydroindole (7).** To a stirred solution of zirconacycle **5**, which was prepared from Cp_2ZrCl_2 (46.8 mg, 0.16 mmol), BuLi (1.63 M solution in hexane, 0.19 mL, 0.31 mmol), and **3a** (30.1 mg, 0.12 mmol) in THF (1.5 mL), was added 10% HCl (1.0 mL) at 0 °C and the solution was stirred for 30 min. The resultant solution was diluted with AcOEt and basified with K_2CO_3. The aqueous layer was separated, and the organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (AcOEt–hexane 1:10) to afford 6.0 mg (21%) of **6a**, 12.1 mg (41%) of **6b**, and 11.4 mg (38%) of **7** as colorless oils. **6a** and **6b**: IR (neat) 1603 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.72 (d, J = 7.0 Hz, 1 H), 0.77 (d, J = 7.0 Hz, 2 H), 0.90 (s, 2 H), 0.92 (s, 1 H), 0.99–1.81 (m, 28/3 H), 2.22 (dd, J = 3.3, 4.0 Hz, 2/3 H), 2.33 (dd, J = 2.9, 2.9 Hz, 1/3 H), 2.43 (dd, J = 9.9, 9.9 Hz, 1/3 H), 2.60 (dd, J = 9.5, 9.9 Hz, 1/3 H), 3.12 (d, J = 13.6 Hz, 2/3 H), 3.15 (dd, J = 7.3, 7.3 Hz, 2/3 H), 3.19 (d, J = 13.9 Hz, 1/3 H), 3.96 (br.d, J = 13.6, 13.9 Hz, 1 H), 7.14–7.33 (m, 5 H); MS (EI, m/z) 243 (M^+), 228, 152, 91 (bp); HRMS (EI, m/z) for $C_{17}H_{25}N$, calcd 243.1987, found 243.1962. Anal. Calcd for $C_{17}H_{25}N$: C, 83.89; H, 10.35; N, 5.75. Found: C, 83.90; H, 10.46; N, 5.80. **7**: IR (neat) ν_{max} 1661 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.70–1.80 (m, 9 H), 1.06 (s, 3 H), 2.17 (br s, 1 H), 2.75 (dd, J = 2.3, 14.5 Hz, 1 H), 2.98 (d, J = 13.2 Hz, 1 H), 3.54 (dd, J = 1.4, 14.5 Hz, 1 H), 4.01 (d, J = 13.2 Hz, 1 H), 4.59 (dd, J = 1.4, 2.3 Hz, 2 H), 7.10–7.20 (m, 5 H); MS (EI, m/z) 241 (M^+), 226, 150, 91 (bp), 77; HRMS (EI, m/z) for $C_{17}H_{23}N$, calcd 241.1831, found 241.1819.

(3*S,3a*R**,7a*R**)-3,3a-Dimethyl-1-tosylperhydroindole (8a) and (3*R**,3a*R**,7a*R**)-3,3a-Dimethyl-1-tosylperhydroindole (8b).** A suspension of **6a** and **6b** (81.5 mg, 0.33 mmol) and 10% Pd on charcoal (81.7 mg) in AcOH (6.0 mL) was stirred at rt for 3 h under an atmosphere of hydrogen. After the catalyst was filtered off, the solvent was removed. To the residue in CH_2Cl_2 (6.0 mL) containing K_2CO_3 (912 mg, 6.6 mmol) was added tosyl chloride (629 mg, 3.3 mmol) at 0 °C. After stirring at rt for 8.5 h, to the suspension was added H_2O (1.0 mL) at 0 °C and the resultant mixture was diluted with AcOEt. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (AcOEt–hexane, 1:10, 1:4) and preparative TLC (AcOEt–hexane, 1:40) to afford 59.3 mg (59%) of **8a** and 29.6 mg (29%) of **8b** as colorless crystals. **8a**: IR (KBr) 1335, 1159 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.74 (d, J = 7.0 Hz, 3 H), 0.86 (s, 3 H), 1.11–1.70 (m, 8 H), 2.43 (s, 3 H), 2.50–2.54 (m, 1 H), 2.85 (br.s, 1 H), 3.11 (dd, J = 11.1, 11.1 Hz, 1 H), 3.51 (dd, J = 8.4, 11.1 Hz, 1 H), 7.31 (d, J = 8.2 Hz, 2 H), 7.69 (d, J = 8.2 Hz, 2 H); MS (EI, m/z) 307 (M^+), 292, 278, 155, 152 (bp), 91; HRMS (EI, m/z) for $C_{17}H_{25}NO_2S$, calcd 307.1606, found 307.1582. **8b**: IR (KBr) 1342, 1161 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.33 (s, 3 H), 0.70 (d, J = 6.6 Hz, 3 H), 1.10–1.63 (m, 7 H), 2.02 (m, 1 H), 2.29 (ddq, J = 6.6, 8.1, 9.5 Hz, 1 H), 2.42 (s, 3 H), 2.79 (dd, J = 9.5, 9.5 Hz, 1 H), 3.32 (dd, J = 6.2, 9.9 Hz, 1 H), 3.56 (dd, J = 8.1, 9.5 Hz, 1 H), 7.29 (d, J = 8.1 Hz, 2 H), 7.72 (d, J = 8.1 Hz, 2 H); MS (EI, m/z) 307 (M^+), 292, 278, 155, 152 (bp), 91; HRMS (EI, m/z) for $C_{17}H_{25}NO_2S$, calcd 307.1606, found 307.1594.

(1*S,4*R**,9*S**)-3-Benzyl-3-azatricyclo[7.3.0.0^{4,9}]dodecan-11-one (9a) and (1*R**,4*R**,9*S**)-3-Benzyl-3-azatricyclo[7.3.0.0^{4,9}]dodecan-11-one (9b).** A solution of zirconacycle (**5**), which was prepared from Cp_2ZrCl_2 (46.8 mg, 0.0.16 mmol), BuLi (1.62 M solution in hexane, 0.19 mL, 0.30 mmol) and **3a** (30.4 mg, 0.13 mmol) in THF (1.5 mL), was stirred at rt for 3 h under an atmosphere of carbon monoxide. To the solution was added I_2 (101 mg, 0.39 mmol) in THF (1.0 mL) at −78 °C and the solution was stirred at rt for 30 min. To the solution was added 10% $Na_2S_2O_3$ (1.0 mL), and the mixture was basified with K_2CO_3 and diluted with AcOEt. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (AcOEt–hexane, 1:20, 1:10, 1:5) to afford a mixture of **9a** and **9b**. The mixture was further purified by TLC (CH_2Cl_2– hexane, 1:40) to afford 12.6 mg (36%) of **9a** and 6.3 mg (18%) of **9b** as colorless oils. **9a**: IR (neat) 1748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (m, 1 H), 1.21 (m, 1 H), 1.37–1.49 (m, 2 H), 1.62 (m, 1 H), 1.68–1.80 (m, 2 H), 1.90 (m, 1 H), 1.91 (d, J = 16.7 Hz, 1 H), 2.03 (dd, J = 2.2, 9.1 Hz, 1 H), 2.09 (ddd, J = 2.2, 7.9, 10.8 Hz, 1 H), 2.14 (d, J = 9.1 Hz, 1 H), 2.33 (d, J = 16.7 Hz, 1 H), 2.64 (dd, J = 7.9, 10.8 Hz, 1 H), 2.83 (br.s, 1 H), 3.01 (dd, J = 10.8. 10.8 Hz, 1 H), 3.58 (d, J = 14.2 Hz, 1 H), 4.06 (d, J = 14.2 Hz, 1 H), 7.20–7.40 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 219.70, 141.09, 128.20, 128.05, 126.57, 65.55, 58.14, 51.24, 48.87, 48.67, 48.61, 37.69, 26.34, 22.62, 20.69; MS (EI, m/z) 269 (M^+), 268, 241, 178, 91 (bp); HRMS (EI, m/z) for $C_{18}H_{23}NO$, calcd 269.1780, found 269.1801. **9b**: IR (neat) 1740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.25–1.38 (m, 1 H), 1.39–1.73 (m, 5 H), 1.76–1.92 (m, 2 H), 2.04 (dd, J = 5.6, 18.8 Hz, 1 H), 2.11 (d, J = 18.9 Hz, 1 H), 2.12 (dd, J = 4.7, 9.7 Hz, 1 H), 2.33 (dddd, J = 4.7, 5.6, 8.8, 10.1 Hz, 1 H), 2.37 (dd, J = 4.1, 5.0 Hz, 1 H), 2.53 (d, J = 18.9 Hz, 1 H), 2.56 (dd, J = 10.1, 18.8 Hz, 1 H), 3.25 (d, J = 13.1 Hz, 1 H), 3.32 (dd, J = 8.8, 9.7 Hz, 1 H), 3.96 (d, J = 13.1 Hz, 1 H), 7.20–7.35 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 219.46, 139.78, 128.40, 128.22, 126.77, 65.82, 60.06, 56.73, 49.21, 49.21, 45.67, 42.01, 35.43, 23.56, 23.50, 20.81; MS (EI, m/z) 269 (M^+), 241, 226, 178, 91 (bp); HRMS (EI, m/z) for $C_{18}H_{23}NO$, calcd 269.1780, found 269.1770. Anal. Calcd for $C_{18}H_{23}NO$: C, 80.25; H, 8.61; N, 5.20. Found: C, 80.28; H, 8.70; N, 5.02.

(1*S,4*R**,9*S**)-3-Tosyl-3-azatricyclo[7.3.0.0^{4,9}]dodecan-11-one (10).** A suspension of **9a** (12.7 mg, 0.047 mmol) and 10% Pd on charcoal (12.7 mg) in AcOH (2.0 mL) was stirred at rt for 3 h under an atmosphere of hydrogen. After the catalyst was filtered off, the solvent was removed. The residue was dissolved in CH_2Cl_2 (2.0 mL) containing K_2CO_3 (66.3 mg, 0.48 mmol), and tosyl chloride (45.8 mg, 0.24 mmol) was added at 0 °C. After stirring at rt for 20 h, 10% HCl (1.0 mL) was added at 0 °C and the mixture was extracted with AcOEt. The organic layer was washed with saturated $NaHCO_3$ solution and with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (AcOEt–hexane, 1:2) to afford 11.4 mg (73%, two steps) of **10** as a colorless crystal: mp 119–120 °C (recryst from Et_2O); IR (KBr) 1746, 1333, 1157 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.00–1.65 (m, 7 H), 1.73 (m, 1 H), 1.77 (dd, J = 2.4, 16.6 Hz, 1 H), 1.97–2.18 (m, 2 H), 2.31 (d, J = 16.6 Hz, 1 H), 2.44 (s, 3 H), 2.70 (m, 1 H), 3.14 (br.s, 1 H), 3.44 (dd, J = 10.8, 10.8 Hz, 1 H), 3.75 (dd, J = 7.6, 10.8 Hz, 1 H), 7.33 (d, J = 8.3 Hz, 2 H), 7.73 (d, J = 8.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.44, 143.51, 134.58, 129.77, 128.31, 64.21, 49.21, 48.68, 48.06, 47.64, 36.83, 27.78, 26.19, 21.78, 21.53, 20.15; MS (EI, m/z) 333 (M^+), 178 (bp), 155, 91. HRMS (EI, m/z) for $C_{18}H_{23}NO_3S$, calcd 333.1399, found 333.1413. Anal. Calcd for $C_{18}H_{23}NO_3S$: C, 64.84; H, 6.95; N, 4.20. Found: C, 64.56; H, 6.93; N, 4.20.

(1*R,4*S**,5*R**)-*N*-Benzyl-4,5-dimethyl-2-azabicyclo[3.3.0]-octane (11a) and (1*R**,4*R**,5*R**)-*N*-Benzyl-4,5-dimethyl-2-azabicyclo[3.3.0]octane (11b).** To a stirred solution of zirconacycle **12**, which was prepared from Cp_2ZrCl_2 (49.7 mg, 0.17 mmol), BuLi (1.63 M solution in hexane, 0.20 mL, 0.33 mmol), and **3b** (30.0 mg, 0.13 mmol) in THF (1.5 mL), was added 10% HCl (1.0 mL) at 0 °C and the solution was stirred for 30 min. The resultant solution was diluted with AcOEt and basified with K_2CO_3. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (AcOEt–hexane 1:4) to afford 13.2 mg (44%) of **11a** and 6.6 mg (22%) of **11b** as colorless oils. **11a**: IR (neat) 1604 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.91 (d, J = 7.0 Hz, 3 H), 1.05 (s, 3 H), 1.53–1.78 (m, 6 H), 1.89 (ddd, J = 7.0, 8.8, 9.5 Hz, 1 H), 2.77 (dd, J = 4.0, 5.0 Hz, 1 H), 3.43 (d, J = 13.6 Hz, 1 H), 3.81 (d, J = 13.6 Hz, 1 H), 7.31 (m, 5 H); MS (EI, *m/z*) 229 (M^+), 214, 152, 138, 91 (bp); HRMS (EI, *m/z*) for $C_{16}H_{23}N$, calcd 229.1831, found 229.1822. Anal. Calcd for $C_{16}H_{23}N$: C, 83.78; H, 10.11; N, 6.11. Found: C, 83.86; H, 10.13; N, 5.93. **11b**: IR (neat) 1604 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.86 (d, J = 6.6 Hz, 3 H), 0.91 (s, 3 H), 1.04–1.97 (m, 8 H), 2.47 (m, 1 H), 2.79 (m, 1 H), 3.34 (d, J = 13.0 Hz, 1 H), 3.79 (d, J = 13.0 Hz, 1 H), 7.30 (m, 5 H); MS (EI, *m/z*) 229 (M^+), 214, 152, 138, 91 (bp); HRMS (EI, *m/z*) for $C_{16}H_{23}N$, calcd 229.1831, found 229.1832. Anal. Calcd for $C_{16}H_{23}N$: C, 83.78; H, 10.11; N, 6.11. Found: C, 83.81; H, 10.23; N, 5.88.

(4*R,4*S**,8*S**)-2-Benzyl-2-azatricyclo[6.3.0.0^{4,8}]undecan-6-one (13a) and (4*R**,4*R**,8*S**)-2-Benzyl-2-azatricyclo-[6.3.0.0^{4,8}]undecan-6-one (13b).** A solution of zirconacycle **12**, which was prepared from Cp_2ZrCl_2 (50.3 mg, 0.17 mmol), BuLi (1.62 M solution in hexane, 0.20 mL, 0.33 mmol), and **3b** (29.5 mg, 0.13 mmol) in THF (1.5 mL), was stirred at rt for 3 h under an atmosphere of carbon monoxide. To the solution was added I_2 (111 mg, 0.44 mmol) in THF (1.0 mL) at −78 °C and the solution was stirred at rt for 30 min. To the solution was added 10% $Na_2S_2O_3$ (1.0 mL), and the mixture was basified with K_2CO_3 and diluted with AcOEt. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (AcOEt–hexane, 1:4, 1:2) to afford 10.2 mg (31%) of **13a** and 5.0 mg (15%) of **13b** as colorless oils: **13a**: IR (neat) 1746 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.00–2.00 (m, 6 H), 2.00–2.30 (m, 4 H), 2.40 (m, 1 H), 2.78 (dd, J = 7.2, 9.7 Hz, 1 H), 2.91 (dd, J = 9.7, 11.0 Hz, 1 H), 3.81 (d, J = 13.8 Hz, 1 H), 3.95 (d, J = 13.8 Hz, 1 H), 7.20–7.40 (m, 5 H); MS (EI, *m/z*) 255 (M^+), 227, 199, 178, 164, 91 (bp), 77; HRMS (EI, *m/z*) for $C_{17}H_{21}NO$, calcd 255.1623, found 255.1683. Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.80; H, 8.40; N, 5.41. **13b**: IR (neat) 1742 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.10–2.15 (m, 8 H), 2.15–2.55 (m, 4 H), 2.77 (d, J = 6.1 Hz, 1 H), 2.96 (d, J = 6.2, 9.1 Hz, 1 H), 3.31 (d, J = 13.4 Hz, 1 H), 3.79 (d, J = 13.4 Hz, 1 H), 7.15–7.30 (m, 5 H); MS (EI, *m/z*) 255 (M^+), 227, 199, 178, 164, 91 (bp), 77; HRMS (EI, *m/z*) for $C_{17}H_{21}NO$, calcd 255.1623, found 255.1633. Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.92; H, 8.48; N, 5.36.

(1*R,4*S**,8*R**,11*S**)-3-Benzyl-3-azatricyclo[6.2.1.0^{4,11}]-undecan-9-one (16a).** A solution of zirconacycle **17**, which was prepared from Cp_2ZrCl_2 (84.6 mg, 0.29 mmol), BuLi (1.62 M solution in hexane, 0.34 mL, 0.55 mmol), and **14** (49.6 mg, 0.22 mmol) in THF (1.5 mL), was stirred at rt for 17.5 h under an atmosphere of carbon monoxide. To the solution was added at 0 °C 10% HCl (1.0 mL), and the solution was stirred at rt for 2 h. The mixture was diluted with AcOEt and basified with saturated $NaHCO_3$. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (AcOEt–hexane, 1:5) to afford 52.9 mg (94%) of **16a** as an oil: IR (neat) 1740 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.02–1.30 (m, 3 H), 1.48–1.84 (m, 3 H), 2.02 (dd, J = 13.2, 16.0 Hz, 1 H), 2.09 (ddd, J = 7.8, 7.8, 12.0 Hz, 1 H), 2.39 (dd, J = 2.5, 7.9 Hz, 1 H), 2.44 (dd, J = 2.5, 16.0 Hz, 1 H), 2.42–2.63 (m, 2 H), 2.91 (ddd, J = 7.8, 7.8, 9.5 Hz, 1 H), 3.30 (dd, J = 4.8, 7.9 Hz, 1 H), 3.84 (d, J = 13.2 Hz, 1 H), 3.94 (d, J = 13.2 Hz, 1 H), 7.17–7.38 (m, 5 H); MS (EI, *m/z*) 255 (M^+), 178, 164, 91 (bp); HRMS (EI, *m/z*) for $C_{17}H_{21}NO$, calcd 255.1623, found 255.1600. Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 80.06; H, 8.40; N, 5.53.

(1*R,4*S**,8*R**,11*S**)-3-(*p*-Nitrobenzenesulfonyl)-3-azatricyclo[6.2.1.0^{4,11}]undecan-9-one (21).** A suspension of **16a** (315.4 mg, 1.24 mmol) and 10% Pd on charcoal (302.1 mg) in MeOH (12 mL) was stirred at rt for 8 h under an atmosphere of hydrogen. After the catalyst was filtered off, the solvent was removed. The residue was dissolved in CH_2Cl_2 (10 mL) containing pyridine (0.46 ml, 4.96 mmol) and *N*,*N*-dimethylaminopyridine (178.0 mg, 1.24 mmol), and *p*-nitrobenzenesulfonyl chloride (630.0 mg, 2.48 mmol) was added at 0 °C. After stirring at rt for 9.5 h, H_2O (2.0 mL) was added at 0 °C and the resultant mixture was diluted with AcOEt. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (AcOEt–hexane, 1:2) to afford 41.5 mg (10%) of **21** as colorless crystals: mp 215.5–218.0 °C (recryst from AcOEt–hexane); IR (KBr) 1740, 1525, 1345, 1160 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.03–1.89 (m, 6 H), 2.00 (dd, J = 13.0, 15.9 Hz, 1 H), 2.16–2.31 (m, 1 H), 2.41–2.71 (m, 3 H), 2.90 (dd, J = 8.1, 10.9 Hz, 1 H), 3.88 (ddd, J = 7.2, 7.2, 9.8 Hz, 1 H), 3.89 (dd, J = 5.7, 8.1 Hz, 1 H), 8.06 (d, J = 8.9 Hz, 2 H), 8.39 (d, J = 8.9 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.70, 140.27, 128.79, 128.11, 126.83, 60.50, 57.63, 56.99, 49.18, 46.45, 42.91, 39.39, 31.31, 23.30, 22.15; MS (EI, *m/z*) 350 (M^+), 220, 186, 164, 41 (bp); HRMS (EI, *m/z*) for $C_{16}H_{18}O_5N_2S$, calcd 350.0937, found 350.0942. Anal. Calcd for $C_{16}H_{18}O_5N_2S$: C, 54.85; H, 5.18; N, 7.99; S, 9.15. Found: C, 54.60; H, 5.22; N, 7.79; S, 9.18.