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Stereoselective synthesis of hexahydroindoles and octahydrocyclohepta-[*b*]pyrroles via gold(I)-catalyzed intramolecular 1,4-hydroamination of cyclic 1,3-dienes

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ABSTRACT

The gold(I)-catalyzed intramolecular hydroamination of cyclohexa-1,3-dienes bearing an arylsulfonamide at the C-5 position proceeds in a 1,4-addition manner to afford hexahydroindole derivatives in a diastereoselective fashion and in good yields, whereas octahydrocyclohepta[*b*]pyrrole derivatives can be obtained from seven-membered ring substrates under the same reaction conditions. Coordination of the gold(I) species to the 1,3-diene at the double bond adjacent to the arylsulfonamide tether gave an η^2-alkene gold complex. The anti-attack of the sulfonamide to the η^2-alkene gold complex at the terminal position of the 1,3-diene resulted in the formation of the fused bicyclic ring with a newly formed Au–C bond at the allylic position. Allylic rearrangement of the η^1-allylgold complex followed by protodemetalation provided the fused heterobicyclic skeletons and regenerated the catalyst.

1. Introduction

The hexahydroindole and octahydrocyclohepta[*b*]pyrrole ring skeletons are present in numerous natural products of biological interest.[1,2] Because the availability of these building blocks could greatly facilitate the elaboration of more complex target molecules, the design of expedient synthetic routes to such intermediates has been actively pursued. Recently, transition metal-promoted intramolecular hydroamination of C–C multiple bonds has been a convenient process for the synthesis of nitrogen heterocycles. Metals such as Hg(II),[3] Ag(I),[4] Pd(0 or II),[5] and Au(I or III)[6] as well as organolanthanides[7] were used for intramolecular cyclization of aminoallenes, whereas in the case of cyclization of aminoalkenes and alkynes the reactions were performed using alkali metals,[8] rare earth metals,[9] early transition metals,[9b,10] and late transition metals.[9b,11] However, only few examples are known for hydroamination of dienes. Hartwig and co-workers reported palladium- and nickel-catalyzed intermolecular hydroamination reactions of 1,3-dienes with amines,[12] while Shibasaki and co-workers reported the bismuth-catalyzed intermolecular hydroamination of 1,3-dienes with amides.[13] Recently, Au(I) and Au(III) complexes have emerged as efficient catalysts for intermolecular hydroamination of 1,3-dienes with benzyl carbamates or sulfonamides to produce allylic amines.[14] It has been shown that coordination of electrophilic gold(I) complexes to the 1,3-diene group at the less substituted double bond of the diene afforded an η^2-alkene gold complex. Attack of the *N*-nucleophile at the internal position of the alkene ligand generated an Au–C bond. Proton transfer from NH_2 group to the carbon atom provided allylic amines. Concerning the gold-catalyzed hydroamination of dienes, the intermolecular reaction is well-known in comparison with the intramolecular reaction.[14] Herein, we report for the first time that the gold(I)-catalyzed intramolecular hydroamination of cyclic 1,3-dienes containing an arylsulfonamide tether at C-5 proceeds in a 1,4-addition manner in refluxing toluene to afford hexahydroindole and octahydrocyclohepta[*b*]pyrrole ring systems in a diastereoselective fashion and in high yields.

2. Results and discussion

2.1. Synthesis of cyclic 1,3-dienes bearing an arylsulfonamide tether at C-5

The requisite cyclohexadienic sulfonamides **1a–f** were prepared by addition of lithium diphenylacetonitrile to the (η^5-cyclohexadienyl)tricarbonyliron cation salt in THF according to literature

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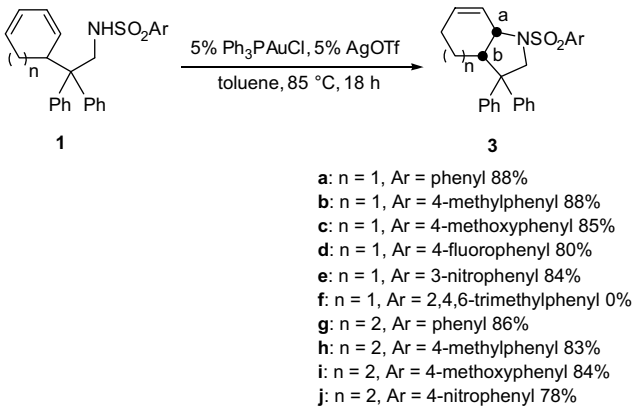
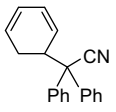


Scheme 1. Intramolecular gold(I)-catalyzed hydroamination of cyclohexa-1,3-dienes.

procedures.[15] Decomplexation of the resulting complex with cerium ammonium nitrate (CAN) in acetone at 0 °C afforded 2-(cyclohexa-2,4-dienyl)-2,2-diphenylacetonitrile **2**. Treatment of **2** with lithium aluminumhydride followed by reaction with corresponding arylsulfonyl chlorides furnished **1a–f** in 72–88% overall yields. The seven-membered ring substrates **1g–k** were prepared in good yields (78–87%) starting from addition of lithium diphenylacetonitrile to the (η^5-cycloheptadienyl)-tricarbonyliron cation salt following the same procedure as described above for synthesis of **1a–f**.



2.2. Synthesis of hexahydroindoles via gold(I)-catalyzed intramolecular 1,4-hydroamination of cyclohexa-1,3-dienes

Our study of intramolecular gold(I)-catalyzed hydroamination of cyclohexa-1,3-dienes began with compound **1a** (Scheme 1). Treatment of **1a** with 5 mol % of Ph_3PAuCl/AgOTf in toluene at 85 °C for 18 h produced 2,3,3a,4,5,7a-hexahydro-3,3-diphenyl-1-tosyl-1*H*-indole (**3a**) in 88% isolated yield (Scheme 1). The 1,4-addition product of the relative stereochemistry as depicted was obtained as a single diastereomer, which is derived from addition of the arylsulfonamide and proton across the conjugated diene. The cis stereochemistry of **3a** was determined by ^{1}H NMR spectroscopy, with assignments deriving from coupling constants. The proton at δ 4.16 as a triplet, J=4.6 Hz was assigned to H_a. The coupling constant of H_a–H_b (J_{ab}) of 4.6 Hz agrees with the coupling constants for similar cis hydrogens compared to the 10–12 Hz observed when these protons are trans.[16] The structure elucidation of **3a** was further accomplished by X-ray diffraction analysis. The *syn* relative stereochemistry between two hydrogen atoms at fused carbon centers further supports the proposed reaction path suggested for the formation of the hexahydroindole **3a** (vide infra). It is important to mention that similar *cis* hexahydroindole rings were available by palladium-catalyzed intramolecular 1,4-oxyamidation of cyclic 1,3-dienes.[17] The reaction pathway leading to **3a** was suggested as follows (Fig. 1). In the known experimental work $Ph_3PAuOTf$ was proposed as the catalytically reactive species, which is generated in situ from Ph_3PAuCl and AgOTf in toluene.[14c] Coordination of the gold(I) species to **1a** at the double bond adjacent to the arylsulfonamide tether gave an η^2-alkene gold complex **4** (Fig. 1). Attack of the arylsulfonamide from the opposite face of the gold center at the terminal position of the diene would generate the η^1-allylgold intermediate **5a** with the newly formed carbon–nitrogen bond. The cis relative stereochemistry of the two fused protons at the ring juncture of **5a** was fixed by arylsulfonamide moiety aligned with the face of the cyclic diene in which the tethering chain resides. Allylic isomerization of **5a** led to **5b**. The triflate-assisted tautomerization of **5b** gave **5c**, as suggested in the literature.[14b,c] Proton transfer from either NH (**5b**) or OH (**5c**) to the carbon atom followed by recoordination of the remaining double bond to the gold center afforded the η^2-alkene gold intermediate **5d**. Replacement of the double bond of **5d** with triflate produced the hexahydroindole derivative **3a** and regenerated the reactive species $Ph_3PAuOTf$ in the catalytic cycle. It must be mentioned that the current result is contrast to the regioselectivity of gold-catalyzed intermolecular addition of *N*-nucleophiles to 1,3-dienes.[14a] In

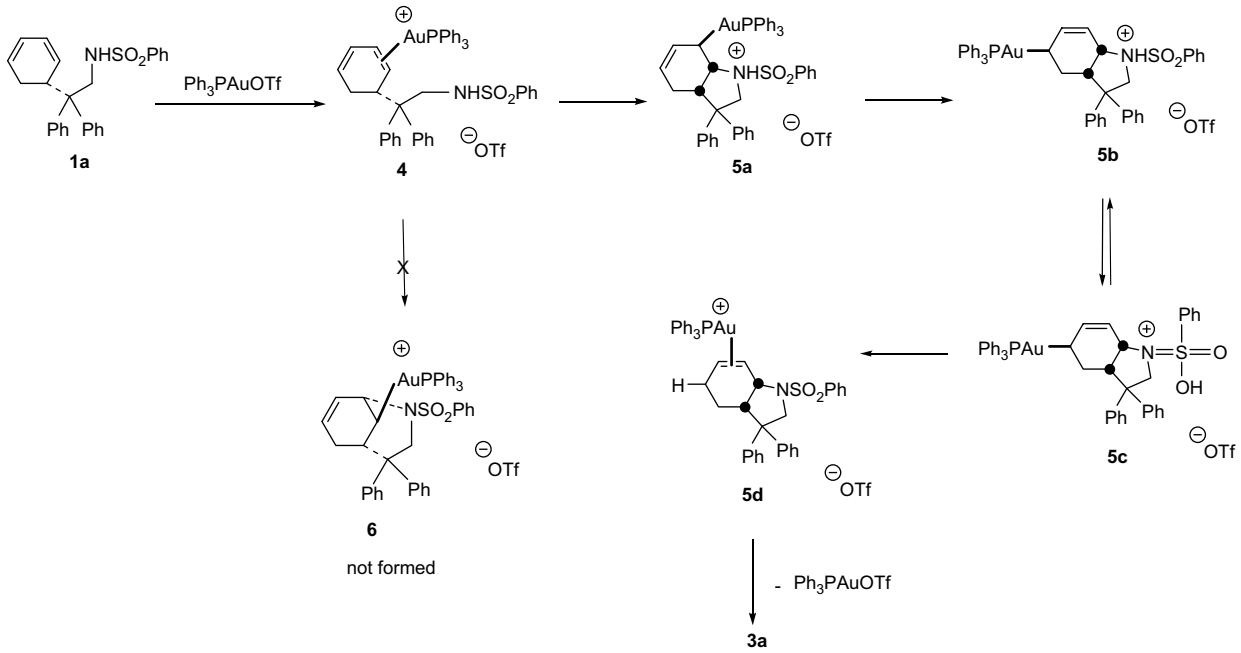
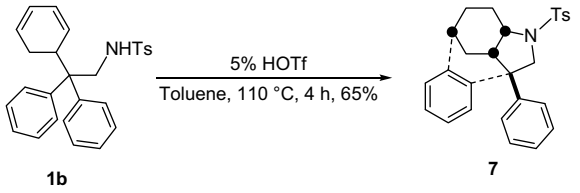
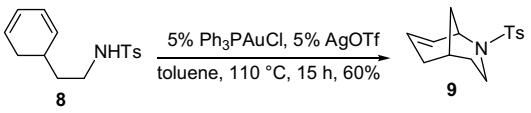


Figure 1. A plausible reaction path for the formation of hexahydroindole **3a**.



Scheme 2. Intramolecular HOTf-catalyzed hydroamination of **1b**.



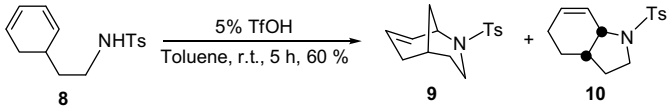
Scheme 3. Intramolecular gold(I)-catalyzed 1,2-hydroamination of **8**.

general, gold-catalyzed intermolecular addition of *N*-nucleophiles, such as carbamates and sulfonamides occurred at the internal position of 1,3-dienes to give 1,2-hydroamination products. Therefore, it is reasonable to state that the arylsulfonamide may add initially to the transient intermediate **4** at the internal position of the diene to produce the steric congested bridged bicyclic skeleton **6**. The nucleophile reversed and added at the terminal position of the diene to generate the thermally more stable fused bicyclic intermediate **5a**. The transient intermediate **5a** led to the hexahydroindole derivative **3a** as stated above.

It is also known that TfOH-catalyzed hydroamination of alkenes and 1,3-dienes to afford amine products in good yields.[18] Thus, TfOH generated from sulfonamide and AgOTf may catalyze the hydroamination of cyclohexadienic sulfonamide **1** to afford hexahydroindole **3** (Scheme 1). To examine this possibility, cyclohexadienic sulfonamide **1b** was treated with TfOH in refluxing toluene for 4 h. The nitrogen heterotricyclic compound **7** was isolated in 65% yield (Scheme 2). The product of the relative stereochemistry as depicted was obtained as a single diastereomer, which is derived from hydroamination and hydroarylation of the conjugated diene. The structure elucidation of **7** was established by X-ray diffraction analysis.

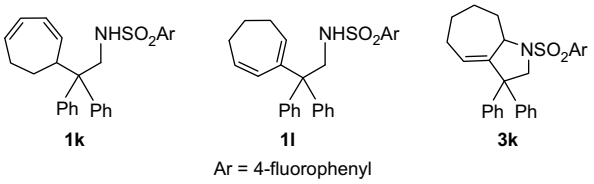
In order to examine the scope and limitation of the intramolecular 1,4-hydroamination, the parent compound **8** was treated with 5 mol% of $Ph_3PAuCl/AgOTf$ in refluxing toluene for 15 h to generate 2-toluenesulfonyl-2-azabicyclo[3.3.1]non-7-ene (**9**) in 60% isolated yield (Scheme 3). The morphan derivative **9**[19] was resulted from addition of the sulfonamide at the internal position of the cyclohexadiene ring and is consistent with the regioselectivity of gold-catalyzed intermolecular addition of *N*-nucleophiles to 1,3-dienes.[14] However, two phenyl groups presenting on the tether of intermediate **6** (Fig. 1) may increase steric congestion of the bridged skeleton, the sulfonamide reverses and adds at the terminal position of the diene to afford hexahydroindole derivatives. Moreover, treatment of the cyclohexadienic sulfonamide **8** with TfOH in toluene at room temperature for 5 h produce both 1,2-hydroamination product **9** and 1,4-hydroamination product **10**[17c] in a ratio of 1:1 and in 60% total isolated yield (Scheme 4).

Results of gold(I)-catalyzed intramolecular 1,4-hydroamination of cyclohexa-1,3-dienes **1a–f** are listed in Scheme 1. The relative



Scheme 4. Intramolecular TfOH-catalyzed 1,2- and 1,4-hydroamination of **8**.

stereochemistry of cycloaddition products **3a–e** was assigned as the same all-*syn* relationship between two fused protons on the basis of their close chemical shift values and similar coupling patterns of the fused protons in their ^1H NMR spectra. Furthermore, the structure elucidations of hexahydroindole derivatives **3a–e** were accomplished by X-ray diffraction analysis. Electron-neutral and -rich phenylsulfonamides were proven to be good substrates, as the yields of desired hexahydroindole products **3a–c** ranged from 85% to 88% (Scheme 1). In addition, the substrate with a fluoro atom, for example, **1d**, did not inhibit the catalytic activity of the gold species, as evidenced by a good yield of the cyclized product **3d** (80%, Scheme 1). An electron-withdrawing group on the benzene ring also provided the desired product. For example, substrate **1e**, possessing a *meta* nitro group at the phenyl ring, was effective and afforded **3e** in 84% isolated yield. However, substrate **1f**, bearing three methyl groups at the phenyl ring, failed to give any cyclized products. Compound **1f** was recovered quantitatively after treatment of **1f** with the catalytic species in refluxing toluene for 2 days. The failure of cyclization may be due to the steric hindrance of the two *ortho* methyl groups at the phenyl ring.



2.3. Synthesis of octahydrocylohepta[*b*]pyrroles via gold(I)-catalyzed intramolecular 1,4-hydroamination of cyclohepta-1,3-dienes

The chemistry can be applied to synthesis of octahydrocyclohepta[*b*]pyrroles from seven-membered ring substrates. As shown in Scheme 1, cycloheptadienic arylsulfonamides **1g–j** underwent 1,4-hydroamination using the same reaction protocols to provide octahydrocyclohepta[*b*]pyrrole derivatives **3g–j**, respectively, as the only stereoisomer in each case and in good yields (78–86%). NOESY (nuclear Overhauser enhancement spectroscopy) experiments provided the initial evidence for support of all-*syn* relationship between two hydrogen atoms at the fused carbons of **3g–j**. The structure elucidations of **3g–j** were further confirmed by X-ray diffraction analysis.

Interestingly, substrate **1k**, possessing a *para* fluoro atom at the phenyl ring, generated the octahydrocyclohepta[*b*]pyrrole derivative **3k** in 82% yield under the same reaction conditions. Compound **1k** may undergo double bond rearrangement assisted by the catalytic gold species to give **1l**, which underwent gold(I)-catalyzed 1,4-hydroamination as those found for **3g–j** to produce the octahydrocyclohepta[*b*]pyrrole derivative **3k**. The structure of **3k** was proved by X-ray diffraction analysis.

3. Conclusions

In conclusion, a gold(I)-catalyzed intramolecular regio- and stereoselective hydroamination of cyclic dienes containing a germinal diphenyl group has been successfully developed. Intramolecular addition of the arylsulfonamide occurred at the terminal position of the cyclohexa-1,3-diene in the presence of a catalytic amount of $Ph_3PAuCl/AgOTf$ to generate an η^1-allylgold intermediate. Allylic rearrangement of the η^1-allylgold species followed by triflate-assisted proton transfer followed by replacement

of the double bond of the η^2-alkene gold intermediate with triflate afforded hexahydroindoles. Under the same reaction conditions, intramolecular 1,4-hydroamination of cycloheptadienic arylsulfonamides furnished octahydrocyclohepta[*b*]pyrroles in high stereoselective fashion and in good yields. Hydroamination of the parent cyclohexadienic sulfonamide without a germinal diphenyl group proceeds in a 1,2-addition fashion to afford a bridged azabicyclic ring system.

4. Experimental section

4.1. General experimental information

All reactions were conducted in oven-dried glassware under a nitrogen atmosphere unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. Toluene was predried by molecular sieves and then by passing through an Al_2O_3 column.[20] Flash column chromatography, following the method of Still, was carried out with E. Merck silica gel (Kieselgel 60, 230–400 mesh) using the indicated solvents.[21] ^{1}H nuclear magnetic resonance (NMR) spectra were obtained with Bruker-AC 400 (400 MHz) and 500 (500 MHz) spectrometers. The chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or $CDCl_3$ (7.26 ppm) as internal standard. ^{13}C NMR spectra were recorded with Bruker-AC 400 (100 MHz) and 500 (125 MHz) spectrometers with $CDCl_3$ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer. Mass spectra were acquired on a JEOL JMS-D 100 spectrometer at an ionization potential of 70 eV and were reported as mass/charge (*m*/*e*) with percent relative abundance. High-resolution mass spectra were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer at the Department of Chemistry, Central Instrument Center, Taichung, Taiwan.

4.2. Representative procedure for gold(I)-catalyzed intramolecular 1,4-hydroamination of cyclic-1,3-dienes

To an oven-dried 50 mL round-bottom flask equipped with a stirrer bar and capped with a rubber septa were added cyclohexa-1,3-diene sulfonamide **1a** (415.5 mg, 1.0 mmol) and AgOTf (12.5 mg, 0.05 mmol). The apparatus was evacuated (oil pump) and filled with nitrogen three times. To the reaction mixture was then added via syringe Ph_3PAuCl (24.7 mg, 0.05 mmol) in 20 mL of toluene. The resulting mixture was stirred at 80 °C until all **1a** was consumed (typically 18 h). The reaction mixture was filtered through a bed of Celite. The filtrate was concentrated in vacuo to give the crude mixture.

*4.2.1. (±)-(3aS,8aR)-3,3-Diphenyl-1-(phenylsulfonyl)-1,3,3a,4,5,7a-hexahydro-1H-indole (**3a**)*

The crude mixture obtained from intramolecular 1,4-hydramination of **1a** (415.5 mg, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10– 30% ethyl acetate/hexanes) to give **3a** (370 mg, 0.89 mmol, 89%) as a yellow solid: mp 172–174 °C; IR (CH_2Cl_2) 3433, 2093, 1638, 1445, 1341, 1160 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J*=7.5 Hz, 2H), 7.34 (t, *J*=7.5 Hz, 1H), 7.23–7.18 (m, 4H), 7.13–7.10 (m, 3H), 7.04–6.99 (m, 5H), 6.21 (dt, *J*=9.9, 2.0 Hz, 1H), 5.97–5.95 (m, 1H), 4.35 (q, *J*=10.8 Hz, 2H), 4.16 (t, *J*=4.6 Hz, 1H), 3.09 (dt, *J*=12.8, 4.5 Hz, 1H), 2.02–1.89 (m, 2H), 1.43–1.39 (m, 1H), 1.19 (qd, *J*=12.7, 5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.74, 143.45, 138.38, 131.99, 130.55, 128.60, 128.58, 128.45, 127.43, 126.90, 126.58, 126.41, 126.20, 126.05, 56.73, 56.62, 56.02, 43.80, 24.31, 21.65; MS (EI) *m*/*z* (rel intensity) 415.1 (M^+, 58), 274.1 (87), 248.1 (100), 205.1 (59), 193.1 (87), 178.0 (68), 167.0 (92), 165.0 (74), 115.0 (82), 91.0 (85), 77.0 (79); HRMS (EI) *m*/*z* calcd for $C_{26}H_{25}NO_2S$ 415.1606, found 415.1601. Crystals suitable for X-ray diffraction analysis were grown from methylenechloride and hexanes.

*4.2.2. (±)-(3aS,8aR)-3,3-Diphenyl-1-(4-methylphenylsulfonyl)-1,3,3a,4,5,7a-hexahydro-1H-indole (**3b**)*

The crude mixture obtained from intramolecular 1,4-hydramination of **1b** (429.6 mg, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10–30% ethyl acetate/hexanes) to give **3b** (378 mg, 0.88 mmol, 88%) as a yellow solid: mp 188–190 °C; IR (CH_2Cl_2) 3432, 2372, 2092, 1654, 1340, 1159 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J*=8.1 Hz, 2H), 7.20 (t, *J*=8.1 Hz, 2H), 7.13–6.94 (m, 10H), 6.23–6.20 (m, 1H), 5.96 (m, 1H), 4.39 (d, *J*=10.8 Hz, 1H), 4.26 (d, *J*=10.8 Hz, 1H), 4.14 (br s, 1H), 3.08 (dt, *J*=12.6, 4.4 Hz, 1H), 2.31 (s, 3H), 2.02–1.85 (m, 2H), 1.40–1.37 (m, 1H), 1.28–1.15 (m, 1H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 144.86, 143.57, 142.47, 134.98, 130.39, 129.23, 128.47, 128.42, 127.40, 126.88, 126.66, 126.29, 126.14, 125.81, 56.73, 56.66, 56.02, 43.62, 24.32, 21.65, 21.38; MS (EI) *m*/*z* (rel intensity) 429.0 (M^+, 69), 274.1 (67), 246.1 (49), 245.0 (40), 193.0 (70), 180.0 (38), 167.0 (64), 165.0 (38), 115.0 (42), 91.0 (100); HRMS (EI) *m*/*z* calcd for $C_{27}H_{27}NO_2S$ 429.1763, found 429.1765. Crystals suitable for X-ray diffraction analysis were grown from methylenechloride and hexanes.

*4.2.3. (±)-(3aS,8aR)-3,3-Diphenyl-1-(4-methoxyphenylsulfonyl)-1,3,3a,4,5,7a-hexahydro-1H-indole (**3c**)*

The crude mixture obtained from intramolecular 1,4-hydramination of **1c** (445.6 mg, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10–30% ethyl acetate/hexanes) to give **3c** (380 mg, 0.85 mmol, 85%) as a yellow solid: mp 195–197 °C; IR (CH_2Cl_2) 3422, 3090, 1654, 1498, 1339, 1257, 1154 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J*=8.8 Hz, 2H), 7.21 (t, *J*=7.4 Hz, 2H), 7.14–7.07 (m, 3H), 7.05–6.98 (m, 5H), 6.63 (d, *J*=8.8 Hz, 2H), 6.22–6.19 (m, 1H), 5.97–5.95 (m, 1H), 4.40 (d, *J*=10.8 Hz, 1H), 4.25 (d, *J*=10.8 Hz, 1H), 4.14 (t, *J*=4.7 Hz, 1H), 3.81 (s, 3H), 3.08 (dt, *J*=12.6, 4.6 Hz, 1H),1.98–1.89 (m, 2H), 1.41–1.37 (m, 1H), 1.27–1.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.21, 145.00, 143.61, 130.35, 129.85, 128.93, 128.54, 128.43, 127.43, 126.73, 126.37, 126.16, 126.10, 113.81, 56.74, 56.06, 55.39, 43.68, 24.33, 21.69; MS (EI) *m*/*z* (rel intensity) 445.2 (M^+, 100), 274.2 (83), 246.2 (49), 193.1 (72), 171.0 (43), 167.1 (82), 165.1 (54), 115.1 (55), 91.1 (71), 77.0 (54); HRMS (EI) *m*/*z* calcd for $C_{27}H_{27}NO_3S$ 445.1711, found 445.1717. Crystals suitable for X-ray diffraction analysis were grown from methylenechloride and hexanes.

*4.2.4. (±)-(3aS,8aR)-3,3-Diphenyl-1-(4-fluorophenylsulfonyl)-1,3,3a,4,5,7a-hexahydro-1H-indole (**3d**)*

The crude mixture obtained from intramolecular 1,4-hydramination of **1d** (433.5 mg, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10–30% ethyl acetate/hexanes) to give **3d** (347 mg, 0.80 mmol, 80%) as a yellow solid: mp 189–193 °C; IR (CH_2Cl_2) 3429, 2360, 2104, 1642, 1592, 1492, 1164 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J*=8.6, 5.2 Hz, 2H), 7.21 (t, *J*=7.5 Hz, 2H), 7.14–6.99 (m, 8H), 6.82 (t, *J*=8.6 Hz, 2H), 6.19 (m, 1H,), 6.01–5.99 (m, 1H), 4.42 (d, *J*=10.9 Hz, 1H), 4.26 (d, *J*=10.9 Hz, 1H), 4.15 (m, 1H), 3.13–3.09 (m, 1H), 2.06–1.91 (m, 2H), 1.39–1.36 (m, 1H), 1.19 (qd, *J*=12. 6, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.81, 163.29, 144.76, 143.33, 134.17, 134.14, 130.70, 129.48, 129.39, 128.61, 128.50, 127.31, 126.67, 126.30, 126.25, 126.07, 115.86, 115.64, 56.89, 56.75, 56.13, 43.63, 24.34, 21.71; MS (EI) *m*/*z* (rel intensity) 433.2 (M^+, 46), 274.2 (66), 243.1 (57), 205.1 (60), 180.1 (34), 167.1 (87), 165.1 (96), 159.0 (59), 95.0 (100), 91.1 (53); HRMS (EI) *m*/*z* calcd for $C_{26}H_{24}NO_2SF$ 433.1511, found 433.1508. Crystals suitable for X-ray diffraction analysis were grown from methylenechloride and hexanes.

*4.2.5. (±)-(3aS,8aR)-3,3-Diphenyl-1-(3-nitrophenylsulfonyl)-1,3,3a,4,5,7a-hexahydro-1H-indole (**3e**)*

The crude mixture obtained from intramolecular 1,4-hydramination of **1e** (460.5 mg, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10–30% ethyl acetate/hexanes) to give **3e** (387 mg, 0.84 mmol, 84%) as a yellow solid: mp 202–204 °C; IR (CH_2Cl_2) 3433, 2091, 1735, 1637, 1528, 1350 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (t, J=1.8 Hz, 1H), 8.16–8.14 (m, 1H), 7.88 (d, J=7.8 Hz, 1H), 7.41 (t, J=8.0 Hz, 1H), 7.22 (t, J=7.3 Hz, 2H), 7.12 (t, J=7.4 Hz, 1H), 7.03 (d, J=7.4 Hz, 2H), 6.96 (d, J=7.3 Hz, 2H), 6.93–6.84 (m, 3H), 6.28–6.24 (m, 1H), 6.08–6.04 (m, 1H), 4.49 (d, J=14.4 Hz, 1H), 4.29–4.24 (m, 2H), 3.13 (dt, J=13.5, 4.2 Hz, 1H), 2.11–2.07 (m, 1H), 2.01–1.93 (m, 1H), 1.36–1.33 (m, 1H), 1.16 (qd, J=12.8, 5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.96, 144.38, 142.85, 139.93, 132.38, 131.15, 129.50, 128.54, 128.48, 127.08, 126.57, 126.50, 126.31, 125.77, 121.97, 57.22, 56.90, 56.26, 43.33, 24.24, 21.75; MS (EI) m/z (rel intensity) 460.0 (M^+, 25), 274.1 (96), 245.0 (84), 193.0 (51), 180.0 (52), 178.0 (50), 167.0 (100), 165.0 (99), 122.0 (58), 115.0 (61), 91.0 (63); HRMS (EI) m/z calcd for $C_{26}H_{24}N_2O_4S$ 460.1457, found 460.1461. Crystals suitable for X-ray diffraction analysis were grown from methylenechloride and hexanes.

*4.2.6. (±)-(3aS,8aR)-3,3-Diphenyl-1-(phenylsulfonyl)-1,2,3,3a,4,5,6,8a-octahydrocyclohepta[b]pyrrole (**3g**)*

The crude mixture obtained from intramolecular 1,4-hydramination of **1g** (429.2 mg, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10–30% ethyl acetate/hexanes) to give **3g** (370 mg, 0.86 mmol, 86%) as a yellow solid: mp 174–176 °C; IR (CH_2Cl_2) 2093, 1638 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J=7.4 Hz, 2H), 7.62–7.58 (m, 1H), 7.54–7.50 (m, 2H), 7.26–7.16 (m, 8H), 7.04 (d, J=7.0 Hz, 2H), 5.65 (dt, J=10.9, 3.0 Hz, 1H), 5.27–5.21 (m, 1H), 4.62 (br d, J=9.4 Hz, 1H), 4.41 (d, J=9.7 Hz, 1H), 3.12 (d, J=9.7 Hz, 1H), 2.84 (td, J=11.1, 4.4 Hz, 1H), 2.19–2.11 (m, 1H), 2.03–1.94 (m, 1H), 1.79–1.73 (m, 1H), 1.58–1.47 (m, 2H), 1.09–0.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.45, 143.20, 135.86, 132.85, 131.80, 129.69, 129.10, 128.39, 127.89, 127.31, 126.99, 126.67, 126.48, 124.85, 61.00, 60.16, 55.22, 48.98, 26.62, 24.94, 21.13; MS (EI) m/z (rel intensity) 429.3 (M^+, 13), 336.2 (14), 260.2 (19), 194.1 (19), 193.1 (100), 178.1 (13), 167.1 (19), 115.1 (20), 91.1 (18), 77.0 (21); HRMS (EI) m/z calcd for $C_{27}H_{27}NO_2S$ 429.1749, found 429.1756. Crystals suitable for X-ray diffraction analysis were grown from ethyl acetate and hexanes.

*4.2.7. (±)-(3aS,8aR)-3,3-Diphenyl-1-(4-methylsulfonyl)-1,2,3,3a,4,5,6,8a-octahydrocyclohepta[b]pyrrole (**3h**)*

The crude mixture obtained from intramolecular 1,4-hydramination of **1h** (443.2 mg, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10–30% ethyl acetate/hexanes) to give **3h** (368 mg, 0.83 mmol, 83%) as a yellow solid: mp 173–175 °C, IR (CH_2Cl_2) 3088, 3059, 2861, 2104, 1638, 1599, 1495, 1477, 1445, 1346, 1163 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J=8.2 Hz, 2H), 7.35–7.15 (m, 10H), 7.04 (d, J=8.0 Hz, 2H), 5.65 (ddd, J=10.8, 3.52, 2.64 Hz, 1H), 5.26–5.20 (m, 1H), 4.59 (br.d, J=9.9 Hz, 1H), 4.38 (d, J=9.7 Hz, 1H), 3.09 (d, J=9.7 Hz, 1H), 3.83 (ddd, J=10.2, 12.1, 4.6 Hz, 1H), 2.42 (s, 3H), 2.18–2.12 (m, 1H), 2.01–1.95 (m, 1H), 1.77–1.72 (m, 1H), 1.56–1.41 (m, 2H), 1.08–0.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.51, 143.60, 143.26, 132.82, 131.95, 129.99, 129.70, 129.68, 128.72, 128.34, 127.91, 127.55, 127.27, 126.98, 126.59, 126.41, 124.71, 60.97, 60.07, 55.19, 48.89, 26.57, 24.96, 21.50, 21.12; MS (EI) m/z (rel intensity) 443.1 (M^+, 29), 379.2 (26), 378.1 (17), 350.0 (19), 288.1 (79), 178.0 (21), 165.0 (20), 101.1 (24), 91.0 (61), 86.1 (100); HRMS (EI) m/z calcd for $C_{28}H_{29}NO_2S$ 443.1919, found 443.1917. Crystals suitable for X-ray diffraction analysis were grown from ethyl acetate and hexanes.

*4.2.8. (±)-(3aS,8aR)-3,3-Diphenyl-1-(4-methoxysulfonyl)-1,2,3,3a,4,5,6,8a-octahydrocyclohepta[b]pyrrole (**3i**)*

The crude mixture obtained from intramolecular 1,4-hydramination of **1i** (459.2 mg, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10–30% ethyl acetate/hexanes) to give **3i** (386 mg, 0.84 mmol, 84%) as a yellow solid: mp 152–154 °C; IR (CH_2Cl_2) 2943, 2066, 1637, 1596, 1497, 1444, 1345, 1261, 1159, 1026, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J=6.8 Hz, 2H), 7.25–7.13 (m, 8H), 7.05 (d, J=10.7 Hz, 2H), 6.96 (d, J=8.8 Hz, 2H), 5.64 (ddd, J=10.9, 3.6, 2.6 Hz, 1H), 5.26–5.19 (m, 1H), 4.58 (d, J=9.8 Hz, 1H), 4.38 (d, J=9.7 Hz, 1H), 3.86 (s, 3H), 3.10 (d, J=9.7 Hz, 1H), 2.84 (ddd, J=12.2, 10.2, 4.4 Hz, 1H), 2.18–2.12 (m, 1H), 2.00–1.94 (m, 1H), 1.78–1.72 (m, 1H), 1.57–1.50 (m, 2H), 1.05–1.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.99, 145.52, 143.28, 131.99, 129.96, 129.68, 128.34, 127.46, 127.25, 126.97, 126.59, 126.39, 124.70, 114.22, 61.00, 60.02, 55.51, 55.19, 48.86, 26.56, 24.95, 21.11; MS (EI) m/z (rel intensity) 459.3 (M^+, 41), 395.3 (26), 366.2 (29), 288.2 (100), 261.2 (14), 205.1 (12), 193.1 (30), 180.1 (29), 171.0 (44), 91.1 (40); HRMS (EI) m/z calcd for $C_{28}H_{29}NO_3S$ 459.1863, found 459.1868. Crystals suitable for X-ray diffraction analysis were grown from ethyl acetate and hexanes.

*4.2.9. (±)-(3aS,8aR)-3,3-Diphenyl-1-(4-nitrophenylsulfonyl)-1,2,3,3a,4,5,6,8a-octahydrocyclohepta[b]pyrrole (**3j**)*

The crude mixture obtained from intramolecular 1,4-hydramination of **1j** (474.2 mg, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10–30% ethyl acetate/hexanes) to give **3j** (370 mg, 0.78 mmol, 78%) as a yellow solid: mp 234–237 °C; IR (CH_2Cl_2) 2092, 1654, 1499, 1458, 1350, 1165 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J=8.8 Hz, 2H), 7.97 (d, J=8.8 Hz, 2H), 7.26–7.02 (m, 10H), 5.66 (ddd, J=11.0, 3.5, 2.5 Hz, 1H), 5.33–5.27 (m, 1H), 4.62 (br d, J=9.1 Hz, 1H), 4.44 (d, J=9.9 Hz, 1H), 3.21 (d, J=9.9 Hz, 1H), 3.12–3.09 (m, 1H), 2.92 (ddd, J=11.9, 9.7, 4.1 Hz, 1H), 2.20–2.14 (m, 1H), 2.03–1.98 (m, 1H), 1.76–1.71 (m, 1H), 1.53–1.49 (m, 1H), 1.41 (t, J=7.2 Hz, 1H), 1.15–1.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.19, 144.99, 142.91, 141.89, 130.96, 129.29, 128.93, 128.54, 127.58, 126.90, 126.68, 125.65, 124.33, 60.95, 60.75, 55.44, 48.89, 26.44, 24.73, 21.37; MS (EI) m/z (rel intensity) 474.1 (M^+, 15), 409.1 (24), 381.0 (25), 288.1 (100), 210.1 (19), 180.0 (27), 178.0 (34), 167.0 (27), 165.0 (37), 91.0 (40); HRMS (EI) m/z calcd for $C_{27}H_{26}N_2O_4S$ 474.1613, found 474.1622. Crystals suitable for X-ray diffraction analysis were grown from ethyl acetate and hexanes.

*4.2.10. Azatricyclic compound (**7**)*

To a solution of **1b** (429 mg, 1.0 mmol) in 30 ml of toluene was added 0.005 ml of HOTf. The mixture was refluxed under a nitrogen untill no **1b** was detected on TLC (ca. 4 h). Removal of the solvent on rotary evaporator gave the crude mixture. The crude mixture was purified by flash column chromatography (silica gel, gradient elution: 10–20% ethyl acetate/hexanes) to give **7** (270 mg, 0.63 mmol, 65%) as a white solid: mp 209–211 °C; IR (CH_2Cl_2) 2930, 2863, 1598, 1343, 1155, 1104 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J=8.1 Hz, 2H), 7.34 (d, J=8.1 Hz, 2H), 7.23–7.18 (m, 2H), 7.15–7.09 (m, 3H), 7.08–7.05 (m, 1H), 7.00–6.97 (m, 1H), 6.75–6.71 (m, 2H), 4.42 (d, J=11.3 Hz, 1H), 4.23 (dt, J=9.8, 7.4 Hz, 1H), 4.04 (d, J=11.3 Hz, 1H), 2.97 (m, 1H), 2.45 (s, 3H), 2.30–2.24 (m, 1H), 1.90–1.84 (m, 1H), 1.75–1.71 (m, 1H), 1.70–1.57 (m, 3H), 1.14–1.02 (m, 1H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 147.64, 143.28, 142.69, 140.17, 136.90, 129.89, 129.73, 128.09, 127.87, 127.65, 127.34, 126.95, 126.82, 126.09, 62.63, 60.37, 54.62, 49.43, 33.13, 30.51, 24.91, 24.63, 21.50; MS (EI) m/z (rel intensity) 429.3 (M^+, 20), 274.2 (88), 247.2 (59), 246.2 (30), 245.2 (30), 217.1 (53), 205.1 (30), 203.1 (30), 202.1 (31), 91.0 (100); HRMS (EI) m/z calcd for $C_{27}H_{27}NO_2S$ 429.1764, found 429.1763. Anal. Calcd for $C_{27}H_{27}NO_2S$: C, 75.49; H, 6.34; N, 3.26; S, 7.46. Found: C, 75.19; H, 6.15; N, 3.26; S, 7.74. Crystals suitable for X-ray diffraction analysis were grown from methylenechloride and hexanes.

*4.2.11. 2-Toluenesulfonyl-2-azabicyclo[3.3.1]non-7-ene (**9**)*

The crude mixture obtained from the gold-catalyzed intramolecular 1,4-hydramination of **8** (277 mg, 1 mmol) was purified by flash column chromatography (silica gel, gradient elution: 5–10% ethyl acetate/hexanes) to give **9** (167 mg, 0.6 mmol, 60%) as a light yellow oil: IR (CH_2Cl_2) 3026, 2937, 1598, 1344, 1159, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J=8.1 Hz, 2H), 7.27 (d, J=8.1 Hz, 2H), 5.88 (dt, J=9.65, 3.16 Hz, 1H), 5.22 (m, 1H), 4.39 (m, 1H), 3.60 (dd, J=12.2, 5.6 Hz, 1H), 2.95 (td, J=12.8, 3.3 Hz, 1H), 2.41 (s, 3H), 2.33–2.25 (m, 1H), 2.08 (m, 1H), 1.87–1.78 (m, 3H), 1.71–1.66 (m, 1H), 1.53–1.49 (m, 1H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 142.85, 137.36, 133.43, 129.45, 127.09, 122.37, 46.84, 38.48, 32.19, 31.24, 30.93, 24.16, 21.40; MS (EI) m/z (rel intensity) 277.1 (M^+, 44), 269.0 (8), 255.0 (5), 243.5 (16), 236.1 (100), 234.1 (27), 231.0 (38), 223.1 (27); HRMS (EI) m/z calcd for $C_{15}H_{19}NO_2S$ 277.1135, found 277.1133.

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Supplementary data

^1H and ^{13}C NMR spectra of compounds **3a**–**e**, **3g**–**k**, and **7** and X-ray crystallographic information files for compounds **3a**–**e**, **3g**–**k**, and **7** are provided, Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2009.04.064.

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