Zirconium-Mediated Intramolecular Coupling Reactions of Unsaturated Anilines. Diastereoselective Synthesis of Azetidines

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Imine complexes of zirconocene, generated by a β-hydrogen abstraction process, which possess a carbon−carbon multiple bond, undergo inter- or intramolecular carbometalation to afford 1,4-cyclohexanediamine or cycloalkylaniline derivatives depending on the relative position of the unsaturated moiety with respect to the imine complex. A new diastereoselective synthesis of azetidines has been developed by treatment of azazirconacyclopentanes with iodine.

Introduction

Zirconocene η^2-imine complexes (zirconaziridines) are useful carbometalating reagents for unactivated alkenes and alkynes.[1] The formation of these complexes has been achieved by different routes. The C−H activation from methylzirconocene amides[1,2] is the most used method, and this reaction is thought to proceed by a concerted cyclometalation *via* a four-membered transition state.[3] The second way to obtain azazirconacyclopropanes is the treatment of imines,[4] or their derivatives,[5] with 1 equiv of zirconocene in a ligand-exchange reaction. A more special method is the rearrangement of cyclic (iminoacyl)-zirconocene complexes generated by the insertion of phenyl isocyanide into bicyclic zirconabicyclopentanes[6] or zirconabicyclopentenes.[7] In addition, treatment of a η^2-iminosilaacyl complex with $LiEt_3BH$ gives silyl-substituted azazirconacyclopropanes.[8] These imine complexes have been trapped with alkenes, alkynes, allenes, and carbonyl compounds and recently with isocyanates[9] to give azazirconacycles, which afford elaborated amine derivatives upon protic workup. Remarkably, the formation of allylic amines was rendered asymmetric by replacement of zirconocene dichloride by a chiral equivalent and further insertion of alkynes in the imine complexes.[10] As far as we know, in all the examples reported in the literature, organic products were obtained free from the metal by treatment of the complex with a proton source,[11] and further productive elaborations of the resulting azazirconacyclopentanoids have not yet been developed. Otherwise, when the C−H activation route was applied to allylic amines, 1-azadiene complexes of zirconocene[12] were obtained by rearrangement of the initially formed η^2-imine complexes. In this context, we have recently reported[13] the synthesis of 4-substituted 1-aza-1,3-dienes from simple allylic amines by oxidation of the azazirconacyclopentene intermediates. However, η^2-imine complexes, generated by C−H abstraction of unsaturated amines other than allyl amines, have not been described, and only two examples of bicyclization of unsaturated imines promoted by zirconocene[5] or diisopropoxy(η^2-propene)titanium have been reported.[14]

On the other hand, although azetidines are an important class of four-membered heterocyclic compounds, no natural products or industrial processes provide a source of them as starting materials for synthesis.[15] The most important method of azetidine synthesis is cyclization of open-chain compounds by formation of the C−N bond.[16] A few azetidines have been obtained by cycloaddition methods[17] and occasionally by rearrangement of larger rings.[18]

In the present paper, we report the inter- or intramolecular coupling reactions of η^2-imine zirconocene complexes bearing a carbon−carbon triple or double bond to afford 1,4-cyclohexanediamine or cycloalkylaniline derivatives depending on the relative position of the unsaturated moiety with respect to the imine complex.

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1997.

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(8) (a) Honda, T.; Satoh, S.; Mori, M. *Organometallics* **1995**, *14*, 1548. (b) Honda, T.; Mori, M. *J. Org. Chem.* **1996**, *61*, 1196.

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(16) Synthesis of *N*-arylazetidines: (a) Bird, R.; Knipe, A. C.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1215. (b) Gogte, V. N.; Kulkarni, S. B.; Tilak, B. D. *Tetrahedron Lett.* **1973**, 1867. (c) Tilak, B. D.; Gogte, V. N. *Heterocycles* **1977**, *7*, 1339.

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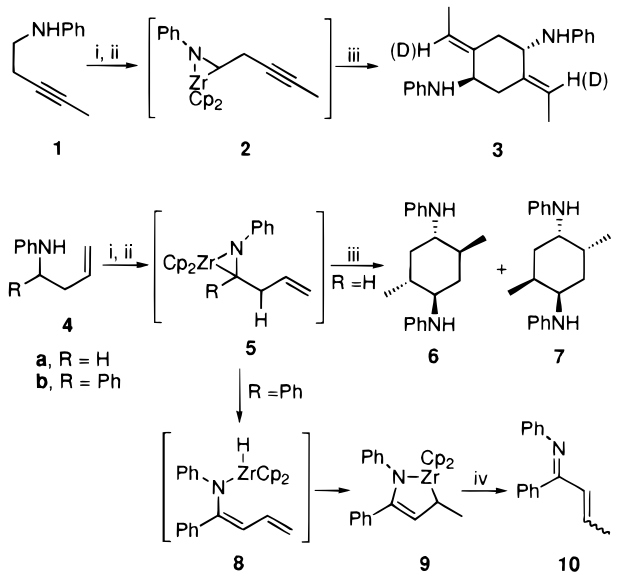
Scheme 1[a]



[a] Reagents and conditions: (i) *n*-BuLi, −40 °C; (ii) $Cp_2Zr(Me)Cl$, −78 to 67 °C; (iii) H_2SO_4 (D_2SO_4), 20 °C; (iv) O_2, 20 °C.

We also describe a simple and straightforward synthesis of azetidines by treatment of azazirconacyclopentanes with iodine, which could be seen as a formal [2 + 2] cycloaddition between alkenes and imines.

Results and Discussion

Imine Complexes from Homoallyl- and Homopropargylanilines. Successive treatment of *N*-(3-pentynyl)aniline (**1**) in THF with 1 equiv of butyllithium at −40 °C and zirconocene methyl chloride at temperatures ranging between −78 and 20 °C followed by refluxing (67 °C) for 3 h led, after hydrolysis or deuteriolysis and further purification, to the 1,4-cyclohexanediamine derivatives **3** as a single diastereoisomer in 41% yield (Scheme 1). When the reaction was carried out with *N*-(3-butenyl)aniline (**4a**) under the same reaction conditions, the diastereoisomeric 1,4-cyclohexanediamines, **6** and **7**, were isolated as a 1:1 mixture in 57% yield after column chromatography. The structure of both diastereoisomers was determined on the basis of their spectroscopic data. Compound **6** has all the substituents in equatorial position and, although the other isomer could not be obtained in a pure form, the stereochemistry shown in Scheme 1 could be assigned to it. However, starting from *N*-(1-phenyl-3-butenyl)aniline (**4b**), no intermolecular coupling occurred and the azazirconacyclopentene **9** was detected by NMR. Oxidation of this intermediate, according to our previously reported methodology,[13] afforded the 1-aza-1,3-diene **10** as a mixture of diastereoisomers (Scheme 1). It is important to note that these ketimines are not easy to obtain since the treatment of α,β-unsaturated ketones with primary amines affords Michael addition products.[19]

The diastereoselective formation of diamine **3** is interpreted by considering the intermolecular approach of two previously formed zirconocene η^2-imine complexes **2** outlined as **I** in Figure 1, which leads, after hydrolysis, to the cyclohexane derivative **3** with both phenylamino

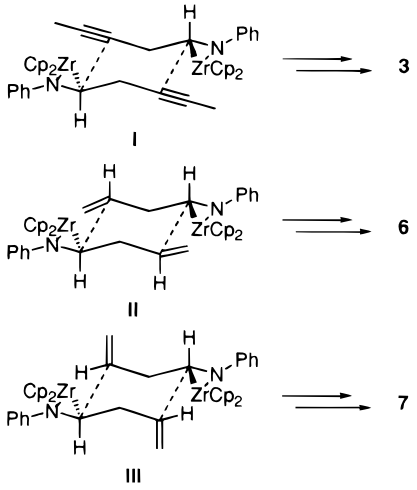


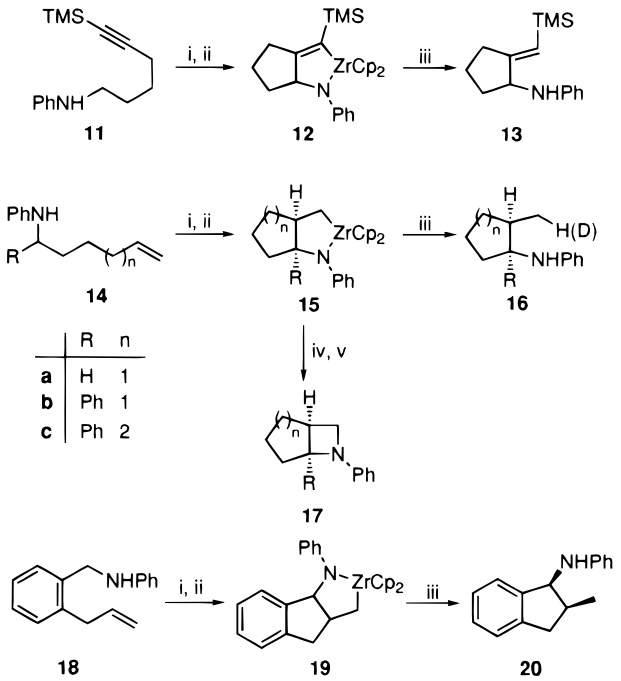
Figure 1.

moieties in pseudoequatorial position. Likewise, the formation of diastereoisomers **6** and **7** starting from homoallylaniline **4a** can be explained by assuming the intermolecular approach of the zirconocene η^2-imine complex **5a** according to the two possibilities outlined as **II** and **III** in Figure 1, which furnishes the symmetric cyclohexanediamine derivative **6**, with all the susbstituents in equatorial position, and **7**, having the two amino groups in equatorial and the two methyl groups in axial positions. However, the different behavior of **4a** and **4b** could be understood if we assume that the dimerization of η^2-imine complexes **5** is very sensitive to steric effects. When the α-position to the nitrogen is substituted the intermolecular reaction is not allowed. In this case, β-hydride transfer to the metal from the unstabilized η^2-imine complex occurs to generate the amidezirconocene hydride **8**. This complex undergoes an intramolecular hydrozirconation giving rise to **9** (Scheme 1). Whitby et al. have reported the formation of an (η^3-1-azaallyl)zirconocene hydride from zirconocene η^2-imine complexes in the absence of a trap.[3]

Imine Complexes from Hexenyl- and Heptenylamines. Reaction of a THF solution of *N*-[6-(trimethylsilyl)-5-hexynyl]aniline (**11**) with butyllithium at −40 °C followed by treatment with zirconocene methyl chloride at −78 °C yielded the azazirconacyclopentene **12** upon warming to room temperature and further refluxing (67 °C) for 3 h. The zirconacycle **12** was characterized by hydrolysis to the corresponding *N*-cyclopentylaniline derivative **13**, which was isolated in 79% yield. The same procedure was then applied to 5-hexenylanilines **14a**,**b**. Insertion of the double bonds in the zirconaziridines readily proceeded to generate the corresponding zirconabicycles **15a**,**b**, which were characterized by deuteriolysis or hydrolysis. *N*-Cyclopentylaniline derivatives **16a** and **16b** were isolated in 78 and 83% yield, respectively, after purification. The formation of six-membered rings under the same reaction conditions was also possible starting from *N*-(1-phenyl-6-heptenyl)aniline (**14c**). In this case, *N*-cyclohexylaniline derivative **16c** was obtained in 78% yield. A noteworthy fact is that the coupling of ketimine complexes from amines **14b**,**c** provides a convenient method for the synthesis of cycloalkylamines with stereoselective formation of a new quaternary center (**16b**,**c**). In this context, the treatment of *N*-(2-allylbenzyl)aniline (**18**) under the reaction conditions described above afforded azazirconatricyclopentane **19**, which yielded *N*-indanylaniline derivative **20** in 82%

(19) Dayagi, S.; Degani, Y. In *The Chemistry of the Carbon−Nitrogen Double Bond*; Patai, S., Ed.; John Wiley and Sons: New York, 1970; Chapter 2.

Scheme 2[a]



[a] Reagents and conditions: (i) *n*-BuLi, −40 °C; (ii) $Cp_2Zr(Me)Cl$, −78 to 67 °C; (iii) H_2SO_4 (D_2SO_4), 20 °C; (iv) I_2, 20 °C; (v) K_2CO_3, H_2O, 60 °C.

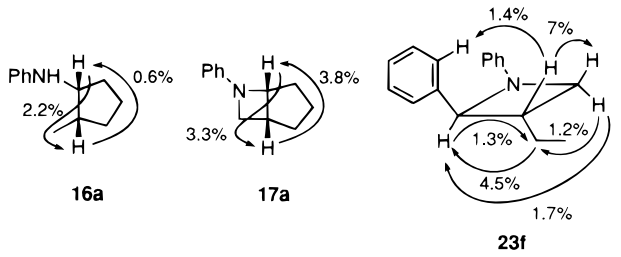


Figure 2.

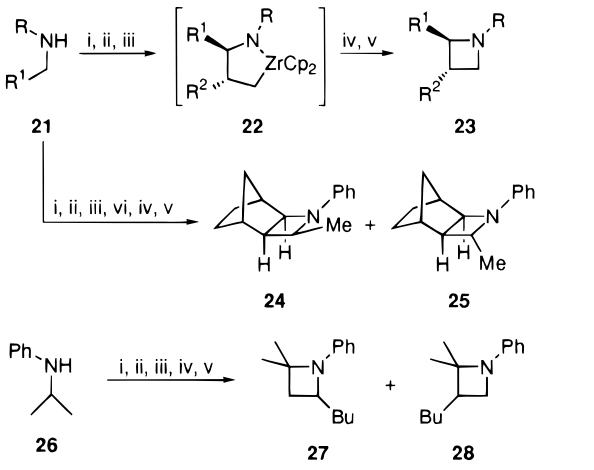
yield after hydrolysis and silica gel chromatography (Scheme 2). In contrast with the results reported in the literature[14] for the nondiastereoselective titanium-mediated bicyclization of olefinic imines, we have obtained only the *cis* diastereoisomer in all cases, probably because of the successive formation of the imine complex and the alkene insertion. This was supported by NOE experiments on **16** and **20**. Results on aniline **16a** are given in Figure 2.

In order to extend the synthetic utility of this kind of azazirconacycles, a solution of **15a** was treated with 2 equiv of iodine at room temperature. The basic workup afforded a mixture of the bicyclic azetidine **17a** and the corresponding iodide precursor. Warming the mixture in an aqueous solution of K_2CO_3 for several hours led to a complete consumption of the open product and allowed the isolation of **17a** in 68% yield (Scheme 2). Again, only the *cis* diastereoisomer was obtained as shown by NOE experiments on **17a** (Figure 2).

When the reaction with iodine was applied to **15c**, the corresponding azetidine **17c** was detected in the crude but 1-phenylcyclohexene was isolated after silica gel chromatography, probably due to a retro [2 + 2] cycloaddition.

Synthesis of Azetidines. Since azetidines are heterocyclic compounds of great interest,[20] the development

Scheme 3[a]



[a] Reagents and conditions: (i) *n*-BuLi, −40 °C; (ii) $Cp_2Zr(Me)Cl$, −78 to 0 °C; (iii) $R^2CH{=}CH_2$ (R^2 = Et, ^{n}Bu, $(CH_2)_4I$, $CH_2N(Me)Ph$, CH_2TMS), 0−67 °C; (iv) I_2, 20 °C; (v) K_2CO_3, H_2O, 60 °C; (vi) norbornene, 0−67 °C.

Table 1. Preparation of Azetidines 23−25, 27, and 28 from Zirconium-Mediated Intermolecular Coupling of Amines 21 or 26 and Terminal Alkenes

starting amine	R	R^1	alkene $R^2CH{=}CH_2$	product	yield[a] (%)
21a	Ph	Me	Bu	**23a**	82
21a	Ph	Me	$(CH_2)_4I$	**23b**	73
21a	Ph	Me	$CH_2N(Me)Ph$	**23c**	79
21b	Ph	Pr	Bu	**23d**	77
21b	Ph	Pr	CH_2TMS	**23e**	76
21c	Ph	Ph	Et	**23f**	68
21c	Ph	Ph	Bu	**23g**	72
21c	Ph	Ph	$(CH_2)_4I$	**23h**	62
21d	4-MeC_6H_4	Me	Bu	**23i**	80
21e	4-$MeOC_6H_4$	Me	Bu	**23j**	78
21a	Ph	Me	Norbornene	**24** + **25**[b]	55 + 27
26			Bu	**27**/**28**	69

[a] Isolated yield based on the starting amine **21** or **26**. [b] Easily separated by flash column chromatography.

of convenient routes to their synthesis is important. The regio- and diastereoselective coupling of *N*-aryl and *N*-silylzirconaziridines with terminal alkenes has been reported.[1] This reaction is synthetically equivalent to the regio- and diastereoselective addition of an α-amino carbanion to an unactivated terminal olefin. However, few synthetic applications of this interesting reaction have been reported.[21] The successive treatment of amines **21** with butyllithium at −40 °C and zirconocene methyl chloride at temperatures ranging between −78 and 0 °C and further addition of the corresponding terminal alkene afforded azazirconacyclopentane derivatives **22** upon warming to room temperature for R^1 = Ph (67 °C for R^1 = alkyl). Intermediates **22** were *in situ* treated first with iodine to cleave the zirconium−carbon bond and then with aqueous potassium carbonate, furnishing azetidines **23** in good yield (Scheme 3 and Table 1). The relative configuration of the substituents in the ring was expected to be *trans* on the basis of previously reported carbo-

(20) Two different syntheses of diastereo- and enantiomerically pure azetidines have been recently reported by our group: (a) Barluenga, J.; Fernández-Marí, F.; Viado, A.-L.; Aguilar, E.; Olano, B. *J. Org. Chem.* **1996**, *61*, 5659. (b) Barluenga, J.; Baragaña, B.; Concellón, J. M. *J. Org. Chem.* **1997**, in press.

(21) A convergent synthesis of five- to seven-membered-ring *N*-heterocycles has been reported: Harris, M. C. J.; Whitby, R. J.; Blagg, J. *Tetrahedron Lett.* **1995**, *36*, 4287.

metalation of alkenes by zirconaziridines[1] and it was further supported by NOE experiments. Figure 2 shows the results for azetidine **23f**.

As shown in Scheme 3, several kinds of terminal olefines could be used. It is interesting to note that when 6-iodo-1-hexene was used, the imine complex selectively attacked the alkene rather than the alkyl iodide. Moreover, further ring closure of the corresponding diiodide led chemoselectively to the formation of the four-membered ring instead of the corresponding azepine derivative.

However, when norbornene was used as unsaturated substrate, two diastereoisomeric azetidines **24** and **25** in a 2:1 ratio were isolated, whose stereochemistry was assigned on the basis of NOE experiments. In order to test the scope of this transformation with respect to the starting amine, we tried the reaction with *N*-isopropylaniline **26** in the same reaction conditions as described above. In this case, two regioisomeric azetidines **27** and **28** were isolated as a 1.2:1 mixture. The insertion of the alkene was not regioselective, probably due to the steric hindrance of the two methyl groups in the imine complex, avoiding the R group of the olefin to accommodate, as well as in the other cases, at the β-position of the azazirconacycle (Scheme 3).

In conclusion, we have described the inter- or intramolecular insertion reactions of unsaturated aromatic imine complexes. The outcome of this process depends on the relative position of the carbon−carbon multiple bond with respect to the imine complex. Moreover, we have developed a useful and diastereoselective synthesis of azetidines that expands the synthetic applications of azazirconacycles. This reaction could be seen as a formal regio- and diastereoselective [2 + 2] cycloaddition between an imine and an alkene that is usually difficult to carry out and occurs only in the presence of substituents that impart a high degree of polarization.

Experimental Section

General Methods. Solvents were dried according to established protocols by distillation under nitrogen from an appropriate drying agent. Thus, THF was distilled from sodium/benzophenone ketyl. Solvents used in extraction and purification were distilled prior to use.

Compounds were visualized on analytical thin-layer chromatograms (TLC) by UV light (254 nm) or iodine. Silica gel (230−400 mesh) was used for flash chromatography. NMR spectra were recorded at 400, 300, and 200 MHz for proton frequency and 100, 75, and 50 MHz for carbon frequency using the DEPT pulse sequence. IR spectra were recorded as neat samples. Elemental analyses were performed by the Microanalytical laboratory, Universidad de Oviedo. Mass Spectra were usually carried out by electron impact at 70 eV. Only the most significant IR absortions and the molecular ions and/or base peaks in MS are given. Melting points are uncorrected.

Reactions requiring an inert atmosphere were conducted under dry nitrogen, and the glassware was oven dried, evacuated, and purged with nitrogen. Temperatures are reported as bath temperatures.

Zirconocene dichloride, aniline, benzaldehyde, 4-bromo-1-butene, allyl bromide, 6-bromo-1-hexene, 5-hexynol, iodine, ethyl bromide, butyl bromide, isopropyl bromide, norbornene, 1-hexene, 1-butene, and allyltrimethylsilane were purchased from Aldrich or Acros and were used without further purification. *n*-BuLi was used as a 2.5 M solution in hexane. $Cp_2Zr(Me)Cl$ was prepared according to a published procedure.[22] *N*-Benzylideneaniline was prepared by refluxing in toluene a mixture of benzaldehyde and aniline in presence of a catalytic amount of *p*-toluenesulfonic acid in a system equipped with a Dean−Stark trap; 5-hexynol and 3-pentynol were tosylated with *p*-toluenesulfonic chloride and KOH in Et_2O;[23] secondary starting amines **1**, **4a**, **11**, **14a**, **21**, and **26** were prepared by warming 2 equiv of the primary arylamine with the corresponding bromide, iodide, or tosylate in water; amines **4b** and **14b**,**c** were synthesized by reaction of benzylideneaniline with the corresponding Grignard reagent in THF. Amine **18** was synthesized by treatment of the dianion generated from *N*-benzylaniline with *n*-BuLi in the presence of TMEDA[24] with 0.5 equiv of CuCN and further addition of allyl chloride.

Preparation of Cyclohexyldiamines 3, 6, and 7. General Procedure. A solution of the starting amine **1** or **4a** (2 mmol) in 10 mL of THF was treated with *n*-BuLi (2 mmol) at −40 °C. The reaction was stirred for 30 min and then was added to a solution of $Cp_2Zr(Me)Cl$ (0.57 g, 2.1 mmol) in 10 mL of THF at −78 °C. The mixture was stirred for 30 min and then the bath was removed, allowing the reaction to achieve room temperature for several hours. The resulting solution was refluxed in THF for 3 h, cooled to 0 °C, and treated with H_2SO_4 (2 N) or D_2SO_4 (2 N). The solvents were removed at reduced pressure, and the residue was dissolved in ethyl acetate (3 × 20 mL) and filtered through Celite. Extraction with ethyl acetate and saturated $NaHCO_3$ aqueous solution afforded the organic layer, which was dried over Na_2SO_4 and filtered. Solvents were removed under reduced pressure, and the crude residue was chromatographed on silica gel.

(1*R*,4*S*)-2,5-Bis[(*E*)-1-deuterioethylidene]-*N*,*N*′-diphenyl-1,4-cyclohexanediamine (3D): R_f = 0.26 (Hex:AcOEt, 15:1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.2−6.6 (m, 10 H), 4.0−3.8 (m, 4 H), 2.6 (dd, J = 14.3, 2.6 Hz, 2 H), 2.3 (dd, J = 14.3, 7.0 Hz, 2 H), 1.6 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.6, 137.5, 129.3, 120.4, 120.1, 119.8, 117.8, 114.2, 53.6, 30.8, 13.1; HRMS calcd for $C_{22}H_{24}D_2N_2$ 320.2221, found 320.2212.

(1*R*,4*S*)-2,5-Bis[(*E*)-ethylidene]-*N*,*N*′-diphenyl-1,4-cyclohexanediamine (3): R_f = 0.26 (Hex:AcOEt, 15:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.1−6.6 (m, 10 H), 5.5 (q, J = 6.9 Hz, 2 H), 3.9−3.7 (m, 4 H), 2.6 (dd, J = 14.4, 2.6 Hz, 2 H), 2.3 (dd, J = 14.4, 7.4 Hz, 2 H), 1.5 (d, J = 6.9 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 147.6, 137.6, 129.3, 120.4, 117.8, 114.2, 53.6, 30.8, 13.2; HRMS calcd for $C_{22}H_{26}N_2$ 318.2096, found 318.2084. Anal. Calcd for $C_{22}H_{26}N_2$: C, 82.97; H, 8.23; N, 8.80. Found: C, 82.74; H, 8.32; N, 8.69.

(1*R*,2*R*,4*S*,5*S*)-2,5-Dimethyl-*N*,*N*′-diphenyl-1,4-cyclohexanediamine (6): R_f = 0.24 (Hex:AcOEt, 10:1); mp 144−146 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.3−6.6 (m, 10 H), 3.5 (s broad, 2 H), 3.1 (dt, J = 10.6, 3.7 Hz, 2 H), 2.3 (td, J = 7.4, 3.6 Hz, 2 H), 1.6−1.5 (m, 2 H), 1.1 (d, J = 6.6 Hz, 6 H), 1.1−1.0 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 147.9, 129.2, 116.7, 112.8, 57.3, 41.3, 38.1, 19.0; IR (neat) 3410, 1600 cm^{-1}; HRMS calcd for $C_{20}H_{26}N_2$ 294.2096, found 294.2098. Anal. Calcd for $C_{20}H_{26}N_2$: C, 81.59; H, 8.90; N, 9.51. Found: C, 81.32; H, 8.75; N, 9.21.

(1*R*,2*S*,4*S*,5*R*)-2,5-Dimethyl-*N*,*N*′-diphenyl-1,4-cyclohexanediamine (7): R_f = 0.20 (Hex:AcOEt, 7:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.3−6.6 (m, 10 H), 3.5 (s broad, 2 H), 3.1 (dt, J = 10.6, 3.7 Hz, 2 H), 2.3 (td, J = 7.4, 3.6 Hz, 2 H), 1.6−1.5 (m, 2 H), 1.1 (d, J = 6.6 Hz, 6 H), 1.1−1.0 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 147.5, 129.3, 116.8, 112.7, 52.6, 34.0, 33.2, 18.7; IR (neat) 3410, 1600 cm^{-1}; HRMS calcd for $C_{20}H_{26}N_2$ 294.2096, found 294.2104.

1,2-Diphenyl-1-azapenta-1,3-diene (10). *N*-(1-Phenyl-3-butenyl)aniline (0.45 g, 2 mmol) in THF (10 mL) was cooled to −40 °C and *n*-BuLi (2 mmol) added. The solution was stirred for 30 min, and then it was added to a solution of $Cp_2Zr(Me)Cl$ (0.57 g, 2.1 mmol) in THF (10 mL) at −78 °C. The mixture was warmed to room temperature, and stirring was continued for 3 h. Dry oxygen was bubbled through the solution at 20 °C for 1 h. The solvents were removed at

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reduced pressure, and the residue was dissolved in ethyl acetate and filtered through Celite. After the addition of a saturated aqueous solution of $NaHCO_3$, the organic product was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography over silica gel (15:1, hexane: ethyl acetate) provided 0.3 g (68% yield) of azadiene **10** as a mixture of diastereoisomers: R_f = 0.35 (Hex:AcOEt, 10:1); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.0−6.6 (m, 10 H), 6.4−6.0 (m, 2 H), 2.0, 1.95 and 1.8 (3d, J = 6.4, 7.0, 4.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 168.7, 166.9, 150.9, 150.5, 144.8, 141.0, 140.4, 139.3, 135.5, 132.4, 129.4, 128.9, 128.6, 128.3, 128.1, 127.9, 127.6, 127.3, 125.5, 123.2, 122.8, 120.8, 120.1, 18.5, 18.4; IR (neat) 1670, 1645 cm^{-1}; HRMS calcd for $C_{16}H_{15}N$ 221.1204, found 221.1213. Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.55; H, 6.92; N, 6.05.

Preparation of Cycloalkylanilines 13, 16, and 20. To a stirred solution of the amines **11**, **14**, or **18** (2 mmol) in THF (10 mL) was added *n*-BuLi (2 mmol) at −40 °C. The resulting mixture was stirred at this temperature for 30 min and then added to a solution of $Cp_2Zr(Me)Cl$ (0.57 g, 2.1 mmol) in THF (10 mL) at −78 °C. The reaction mixture was stirred for 30 min while the temperature reached room temperature (warmed to 67 °C for **11** and **14a**), and stirring was continued for 3 h. After the mixture was quenched with H_2O or D_2O, the solvents were removed in vacuo and the residue was dissolved in ethyl acetate and then filtered through a short pad of Celite. The filtrate was dried over Na_2SO_4 and concentrated at reduced pressure. Purification by flash chromatography on silica gel afforded the corresponding cycloalkylanilines **13**, **16**, and **20**.

***N*-{2-[(*E*)-(Trimethylsilyl)methylene]cyclopentyl}aniline (13):** R_f = 0.32 (Hex:AcOEt, 20:1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.2−6.6 (m, 5 H), 5.6 (dd, J = 4.7, 2.15 Hz, 1 H), 4.1 (dd, J = 7.3, 6.9 Hz, 1 H), 3.4 (s broad, 1 H), 2.5−1.4 (m, 6 H), 0.1 (s, 9 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 162.3, 148.0, 129.1, 119.3, 116.8, 112.7, 59.7, 33.1, 30.9, 22.3, −0.5; IR (neat) 3415, 1600 cm^{-1}; HRMS calcd for $C_{15}H_{23}NSi$: 245.1600, found 245.1596.

***cis*-*N*-(2-Methylcyclopentyl)aniline (16a):** R_f = 0.33 (Hex:AcOEt, 25:1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.2−6.6 (m, 5 H), 3.8−3.7 (m, 1 H), 3.7 (s broad, 1 H), 2.4−2.3 (m, 1 H), 2.1−1.4 (m, 6 H), 0.9 (d, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.1, 129.1, 116.5, 112.8, 57.0, 35.6, 31.8, 31.4, 21.1, 14.2; IR (neat) 3410, 1600 cm^{-1}; HRMS calcd for $C_{12}H_{17}N$ 175.1361, found 175.1353.

(1*R,2*S**)-*N*-[2-(Deuteriomethyl)-1-phenylcyclopentyl]aniline (16b):** R_f = 0.39 (Hex:AcOEt, 20:1); mp 86−88 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.6−6.5 (m, 10 H), 4.1 (s broad, 1 H), 2.7−1.6 (m, 7 H), 1.0 (d, J = 6.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 145.5, 144.5, 128.5, 128.1, 126.1, 125.9, 116.5, 115.2, 67.5, 49.3, 35.1, 31.8, 21.8, 12.2, 11.9, 11.5; IR (neat) 3440, 1600 cm^{-1}; HRMS calcd for $C_{18}H_{20}DN$ 252.1737, found 252.1727. Anal. Calcd for $C_{18}H_{20}DN$: C, 85.66; H/D, 8.79; N, 5.55. Found: C, 85.28; H/D, 8.56; N, 5.25.

(1*R,2*S**)-[2-(Deuteriomethyl)-1-phenylcyclohexyl]aniline (16c):** R_f = 0.42 (Hex:AcOEt, 15:1); mp 57−59 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.6−6.5 (m, 10 H), 4.0 (s broad, 1 H), 2.7 (dd, J = 13.7, 2.0 Hz, 1 H), 2.1−1.4 (m, 8 H), 0.8−0.7 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 145.4, 145.2, 128.4, 127.8, 127.0, 126.0, 116.7, 115.7, 61.0, 43.8, 30.9, 30.7, 26.0, 21.2, 15.7, 15.4, 15.0; IR (neat) 3430, 1600 cm^{-1}; HRMS calcd for $C_{19}H_{22}DN$ 266.1893, found 266.1895. Anal. Calcd for $C_{19}H_{22}DN$: C, 85.66; H/D, 9.08; N, 5.26. Found: C, 85.26; H/D, 8.79; N, 5.13.

***cis*-2-Methyl-*N*-phenyl-1-indanamine (20):** R_f = 0.30 (Hex:AcOEt, 15:1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.4−6.7 (m, 9 H), 5.1 (d, J = 6.5 Hz, 1 H), 4.0 (s broad, 1 H), 3.15 (dd, J = 15.5, 6.9 Hz, 1 H), 3.1−2.9 (m, 1 H), 2.7 (dd, J = 15.5, 2.15 Hz, 1 H), 0.9 (d, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 147.8, 143.2, 141.8, 129.2, 127.6, 126.5, 125.0, 124.0, 117.1, 112.8, 60.5, 38.3, 36.9, 14.3; IR (neat) 3405, 1600 cm^{-1}; HRMS calcd for $C_{16}H_{17}N$ 223.1361, found 223.1359. Anal. Calcd for $C_{16}H_{17}N$: C, 86.06; H, 7.67; N, 6.27. Found: C, 86.21; H, 7.52; N, 6.13.

Preparation of Azetidines 17, 23−25, 27, and 28. General Procedure. To a solution of the corresponding secondary amine **14a**, **21**, or **26** (2 mmol) in THF (10 mL) was added *n*-BuLi (2 mmol) at −40 °C. The mixture was stirred for 30 min at this temperature and then added to a solution of $Cp_2Zr(Me)Cl$ (2.1 mmol) in THF (10 mL) at −78 °C. The mixture was stirred while the temperature reached 0 °C, and then the corresponding terminal alkene (2.1 mmol) was added. The mixture was refluxed (67 °C) for 4 h to give a bright red solution. After the mixture was cooled to room temperature, iodine (4 mmol) was added and the red color rapidly discharged. After the mixture was stirred for 1 h at room temperature, an aqueous solution of K_2CO_3 was added, and the reaction mixture was warmed at 60 °C overnight. The mixture was poured into water (50 mL), and the organic products were extracted in ethyl acetate (3 × 20 mL). The combined extracts were washed with aqueous $Na_2S_2O_3$, and then with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, and filtered. The solvents were removed by rotatory evaporation, and the products were isolated by flash column chromatography. Isolated yields of *N*-arylazetidines are reported in Table 1.

***cis*-6-Phenyl-6-azabicyclo[3.2.0]heptane (17a):** R_f = 0.32 (Hex:AcOEt. 15:1); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.4−6.5 (m, 5 H), 4.6 (dd, J = 5.4, 5.1 Hz, 1 H), 4.0 (dd, J = 7.9, 7.3 Hz, 1 H), 3.6 (dd, J = 7.3, 3.5 Hz, 1 H), 3.2−3.0 (m, 1 H), 2.2−1.4 (m, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 149.5, 128.8, 115.8, 110.1, 68.9, 55.0, 34.1, 32.0, 30.6, 24.1. Anal. Calcd for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.08. Found: C, 82.88; H, 8.81; N, 8.05.

***trans*-3-Butyl-2-methyl-1-phenylazetidine (23a):** R_f = 0.37 (Hex:AcOEt, 15:1); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.3−6.6 (m, 5 H), 4.1 (t, J = 7.2 Hz, 1 H), 3.7 (quint, J = 6.2 Hz, 1 H), 3.2 (dd, J = 7.2, 7.0 Hz, 1 H), 2.5−2.3 (m, 1 H), 1.6−1.3 (m, 6 H), 1.5 (d, J = 6.2 Hz, 3 H), 1.0−0.9 (m, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.4, 128.7, 117.3, 111.6, 66.4, 55.8, 39.2, 33.5, 29.1, 22.5, 22.3, 13.9; IR (neat) 1600 cm^{-1}; HRMS calcd for $C_{14}H_{21}N$ 203.1674, found 203.1662. Anal. Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41; N, 6.89. Found: C, 82.76; H, 10.32; N, 6.61.

***trans*-3-(4-Iodobutyl)-2-methyl-1-phenylazetidine (23b):** R_f = 0.31 (Hex:AcOEt, 15:1); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.3−6.6 (m, 5 H), 4.1 (t, J = 7.3 Hz, 1 H), 3.8−3.7 (m, 1 H), 3.3−3.2 (m, 3 H), 2.4−2.3 (m, 1 H), 1.9−1.8 (m, 2 H), 1.6−1.3 (m, 4 H), 1.5 (d, J = 6.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.2, 128.7, 117.5, 111.7, 66.4, 55.7, 38.9, 33.0, 32.6, 27.7, 22.3, 6.8; IR (neat) 1600 cm^{-1}. Anal. Calcd for $C_{14}H_{20}IN$: C, 51.08; H, 6.12; N, 4.25. Found: C, 50.82; H, 6.21; N, 4.19.

***trans*-2-Methyl-3-[(*N*-methyl-*N*-phenylamino)methyl]-1-phenylazetidine (23c):** R_f = 0.40 (Hex:AcOEt, 5:1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.3−6.6 (m, 10 H), 4.1 (t, J = 6.9 Hz, 1 H), 3.9−3.8 (m, 1 H), 3.6 (dd, J = 14.6, 7.0 Hz, 1 H), 3.5 (dd, J = 14.6, 6.9 Hz, 1 H), 3.4 (t, J = 7.3 Hz, 1 H), 3.0 (s, 3 H), 2.9−2.7 (m, 1 H), 1.5 (dd, J = 6.0, 1.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.1, 149.1, 129.1, 128.8, 117.8, 116.7, 112.5, 111.8, 64.8, 55.5, 54.2, 38.7, 37.4, 21.9; IR (neat) 1600 cm^{-1}; HRMS calcd for $C_{18}H_{22}N_2$ 266.1783, found 266.1783.

***trans*-3-Butyl-1-phenyl-2-propylazetidine (23d):** R_f = 0.39 (Hex:AcOEt, 15:1); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.3−6.5 (m, 5 H), 4.1 (dd, J = 7.4, 7.2 Hz, 1 H), 3.7−3.6 (m, 1 H), 3.2 (dd, J = 7.1, 6.7 Hz, 1 H), 2.5−2.3 (m, 1 H), 2.0−1.2 (m, 10 H), 1.0 and 0.9 (2t, J = 7.1 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.4, 128.7, 117.1, 111.5, 70.4, 56.1, 38.6, 37.4, 34.4, 29.2, 22.5, 18.2, 14.3, 13.9; IR (neat) 1600 cm^{-1}; HRMS calcd for $C_{16}H_{25}N$ 231.1987, found 231.1983. Anal. Calcd for $C_{16}H_{25}N$: C, 83.06; H, 10.89; N, 6.05. Found: C, 82.79; H, 10.95; N, 6.08.

***trans*-1-Phenyl-2-propyl-3-[(trimethylsilyl)methyl]azetidine (23e):** R_f = 0.42 (Hex:AcOEt, 15:1); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.3−6.5 (m, 5 H), 4.1 (dd, J = 7.3, 7.0 Hz, 1 H), 3.7−3.6 (m, 1 H), 3.1 (dd, J = 7.3, 7.0 Hz, 1 H), 2.6−2.4 (m, 1 H), 2.1−1.7 (m, 2 H), 1.6−1.4 (m, 2 H), 1.0 (t, J = 7.0 Hz, 3 H), 1.0−0.7 (m, 2 H), 0.0 (s, 9 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.7, 128.7, 117.3, 111.9, 74.0, 58.2, 38.7, 34.1, 22.9, 18.0, 14.4, −1.3; IR (neat) 1600 cm^{-1}; HRMS calcd for $C_{16}H_{27}NSi$ 261.1913, found 261.1913.

***trans*-3-Ethyl-1,2-diphenylazetidine (23f):** R_f = 0.41 (Hex:AcOEt, 15:1); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.6−6.5 (m, 10 H), 4.6 (d, J = 6.7 Hz, 1H), 4.2 (t, J = 7.2 Hz, 1 H), 3.4 (dd, J = 7.2, 7.0 Hz, 1 H), 2.7−2.5 (m, 1 H), 1.9−1.6 (m, 2 H), 0.9

(t, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.0, 143.1, 128.7, 128.6, 127.2, 125.9, 117.7, 112.0, 73.6, 55.2, 43.6, 26.8, 11.3; HRMS calcd for $C_{17}H_{19}N$ 237.1520, found 237.1518.

***trans*-3-Butyl-1,2-diphenylazetidine (23g):** R_f = 0.42 (Hex:AcOEt, 15:1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.6−6.5 (m, 10 H), 4.6 (d, J = 6.5 Hz, 1 H), 4.3 (t, J = 7.3 Hz, 1 H), 3.5 (dd, J = 7.3, 6.9 Hz, 1 H), 2.8−2.6 (m, 1 H), 1.9−1.4 (m, 6 H), 1.0 (t, J = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.0, 143.0, 128.7, 128.5, 127.2, 125.9, 117.7, 112.0, 73.8, 55.6, 42.1, 33.5, 29.1, 22.5, 13.9; IR (neat) 1600 cm^{-1}; HRMS calcd for $C_{19}H_{23}N$ 265.1830, found 265.1819. Anal. Calcd for $C_{19}H_{23}N$: C, 85.99; H, 8.73; N, 5.28. Found: C, 85.75; H, 8.59; N, 5.35.

***trans*-3-(4-Iodobutyl)-1,2-diphenylazetidine (23h):** R_f = 0.34 (Hex:AcOEt, 15:1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.5−6.4 (m, 10 H), 4.5 (d, J = 6.4 Hz, 1 H), 4.2 (t, J = 7.3 Hz, 1 H), 3.4 (dd, J = 7.3, 6.9 Hz, 1 H), 3.2 (t, J = 6.9 Hz, 2 H), 2.7−2.6 (m, 1 H), 1.8−1.3 (m, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 151.8, 142.7, 128.8, 128.6, 127.4, 125.9, 117.9, 112.1, 73.8, 55.4, 41.8, 33.0, 32.6, 27.8, 6.7; IR (neat) 1600 cm^{-1}; HRMS calcd for $C_{19}H_{22}IN$ 391.0797, found 391.0815.

***trans*-3-Butyl-2-methyl-1-(4-methylphenyl)azetidine (23i):** R_f = 0.38 (Hex:AcOEt, 15:1); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.05 (d, J = 8.4 Hz, 2 H), 6.5 (d, J = 8.4 Hz, 2 H), 4.1 (dd, J = 7.3, 7.0 Hz, 1 H), 3.7−3.6 (m, 1 H), 3.2 (dd, J = 7.3, 7.0 Hz, 1 H), 2.4−2.3 (m, 1 H), 2.3 (s, 3 H), 1.6−1.5 (m, 2H), 1.5 (d, J = 6.1 Hz, 3 H), 1.4−1.2 (m, 4 H), 1.0−0.9 (m, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 150.6, 129.3, 126.6, 111.9, 66.8, 56.3, 39.4, 33.5, 29.2, 22.5, 22.4, 20.3, 13.9; IR (neat) 1620 cm^{-1}; HRMS calcd for $C_{15}H_{23}N$ 217.1830, found 217.1817. Anal. Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.44. Found: C, 82.95; H, 10.55; N, 6.35.

***trans*-3-Butyl-1-(4-methoxyphenyl)-2-methylazetidine (23j):** R_f = 0.33 (Hex:AcOEt, 10:1); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.8 (d, J = 7.6 Hz, 2 H), 6.5 (d, J = 7.6 Hz, 2 H), 4.05 (dd, J = 7.3, 7.0 Hz, 1 H), 3.8 (s, 3 H), 3.65−3.5 (m, 1 H), 3.15 (dd, J = 7.3, 7.0 Hz, 1 H), 2.4−2.3 (m, 1 H), 1.6−1.4 (m, 2 H), 1.5 (d, J = 6.1 Hz, 3 H), 1.4−1.2 (m, 4 H), 1.0−0.9 (m, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.1, 147.2, 114.5, 112.9, 67.0, 56.6, 55.5, 39.4, 33.4, 29.2, 22.5, 22.4, 13.9; HRMS calcd for $C_{15}H_{23}NO$ 233.1780, found 233.1793.

(1*R,2*S**,4*R**,5*S**,6*S**)-4-Methyl-3-phenyl-3-azatricyclo[4.2.1.0^{2,5}]nonane (24):** R_f = 0.38 (Hex:AcOEt, 15:1); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.3−6.6 (m, 5 H), 4.15−4.1 (m, 1 H), 3.85−3.75 (m, 1 H), 3.3−3.1 (m, 1 H), 2.45 and 2.1 (2s, 2 H), 1.95−1.3 (m, 6 H), 1.3 (d, J = 6.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.2, 129.0, 116.6, 112.4, 60.6, 52.7, 45.0, 38.8, 37.1, 33.8, 29.4, 27.9, 20.2; IR (neat) 1600 cm^{-1}; HRMS calcd for $C_{15}H_{19}N$ 213.1518, found 213.1512.

(1*R,2*S**,4*S**,5*S**,6*S**)-4-Methyl-3-phenyl-3-azatricyclo[4.2.1.0^{2,5}]nonane (25):** R_f = 0.27 (Hex:AcOEt, 15:1); mp 80−82 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.3−6.6 (m, 5 H), 4.3 (d, J = 7.3 Hz, 1 H), 3.4−3.3 (m, 2 H), 2.85 and 2.35 (2s, 2 H), 2.0 (d, J = 9.2 Hz, 1 H), 1.6−1.2 (m, 8 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.5, 128.9, 116.8, 113.5, 55.8, 53.0, 50.0, 40.2, 39.3, 34.9, 31.1, 28.1, 19.5; HRMS calcd for $C_{15}H_{19}N$ 213.1518, found 213.1517. Anal. Calcd for $C_{15}H_{19}N$: C, 84.46; H, 8.98; N, 6.56. Found: C, 84.28; H, 8.95; N, 6.46.

4-Butyl-2,2-dimethyl-1-phenylazetidine (27) and 3-Butyl-2,2-dimethyl-1-phenylazetidine (28): Mixture of regioisomers 1.2:1; R_f = 0.38 (Hex:AcOEt, 15:1); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.3−6.6 (m, 10 H), 3.95 (dq, J = 7.7, 3.4 Hz, 1 H), 3.90 (dd, J = 7.8, 6.7 Hz, 1 H), 3.35 (dd, J = 7.1, 6.7 Hz, 1 H), 2.45 (m, 1 H), 2.25 (dd, J = 10.3, 8.3 Hz, 1 H), 2.10 (m, 1 H), 2.0 (dd, J = 10.3, 7.3 Hz, 1 H), 1.7 (s, 6 H), 1.6 (s, 6 H), 1.8−1.3 (m, 11 H), 1.1 (m, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 148.8, 148.7, 128.6, 117.2, 116.8, 113.4, 112.9, 67.9, 63.0, 56.6, 51.9, 41.5, 38.3, 35.6, 31.5, 29.8, 28.8, 28.7, 26.9, 23.1, 22.7, 19.0, 14.1, 14.0; IR (neat) 1600 cm^{-1}; HRMS calcd for $C_{15}H_{23}N$ 217.1831, found 217.1820.

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Supporting Information Available: ^{13}C-NMR spectra of **3**, **6**, **7**, **10**, **13**, **16**, **17**, **20**, and **23**−**28** are given (24 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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