Zirconocene Complexes of Imines: General Synthesis, Structure, Reactivity, and in Situ Generation To Prepare Geometrically Pure Allylic Amines

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Abstract: A general method for the preparation of zirconocene complexes of imines has been developed. The X-ray crystal structure of the (trimethylsilyl)benzaldimine complex **2b** shows that these complexes should be viewed as metallaaziridenes due to significant π-donation from the zirconium center to the π^* orbitals of the coordinated imine. These complexes undergo a number of chemo-, regio-, and diastereoselective coupling reactions with unsaturated organic compounds to cleanly form metallacyclic compounds. In situ generation of the complexes followed by coupling with alkynes and hydrolysis affords a general route to geometrically pure allylic amines.

Unsaturated organic molecules bound to transition metals oftentimes manifest unique reactivity which differs greatly from that displayed in the free state.[2] Experimentally simple, general methods for the preparation of such complexes, from readily available starting materials, are required in order to fully probe the reactivity of such complexes. Additionally, the ready availability of these complexes enhances their utility as reagents and/or intermediates of use in organic synthesis. Of the methods used to prepare transition-metal complexes of unsaturated organic molecules, by far the most common is to add the free unsaturated organic species to a metal fragment.[2-4b] It is often advantageous, however, to begin with a saturated organic compound which can then be "dehydrogenated" while bound to the metal. We have recently reported several examples of such a synthetic tack.[5] Due to the importance of nitrogen-containing organic molecules in organic synthesis and the paucity of examples of structurally characterized examples of early transition-metal complexes of imines we endeavored to devise a general route to such complexes. We felt that the use of simple amines as the organic progenitor to such complexes would impart the greatest generality for their preparation and subsequent application to organic synthesis. The work of Bercaw,[6] Nugent,[7a] and Bradley[7b] provided precedent for such dehydrogenations of amines to form transition-metal complexes of imines.

As shown in Scheme I, treatment of zirconocene (methyl) chloride with lithium dibenzylamide produces intermediate **1a** which loses methane to form **2a** upon heating to 110 °C for several hours. Remarkably, **1b** loses methane rapidly at −10 °C to produce imine complex **2b** (L = THF). A similar rate of methane loss is seen from intermediate **1c** (R = R′ = Ph). We feel that this large rate difference observed for methane loss for **1b,c** compared to **1a** is due to reduced availability of the lone pairs on nitrogen in these complexes.[8] As shown in Scheme I, this route to imine complexes of zirconocene has proven extremely general. The starting primary amine, in THF, can be successively treated with 1 equiv of *n*-BuLi, 1 equiv of chlorotrimethylsilane, and another equivalent of *n*-BuLi to prepare the lithium trimethylsilylamide. This is added to a solution of zirconocene (methyl) chloride in THF at −78 °C, and the resulting solution is warmed (to room temperature for R′ = aromatic, to 40–50 °C for R′ = alkyl, H) and allowed to stir overnight. After purification, complexes **2b,d–f** have been isolated as THF or PMe_3 adducts in 43–59% yield, while **2c** was isolated in 79%. While complexes **2g,h** are not readily isolable in a pure state, they can be generated in ca. 75% yield as evidenced by their trapping with diphenylacetylene and 3-hexyne, respectively. It is important to note that, *although trimethylphosphine can aid in the isolation of many of these complexes, it is not needed for their generation or subsequent coupling reactions.*

Shown in Figure 1 is the X-ray crystal structure of **2b**, L = THF. The C–N bond distance of 1.41 Å is similar to that seen in the other structurally characterized early transition-metal complexes of imines.[9] This bond distance indicates that these complexes are best thought of as metallaaziridines and that a great deal of π-backbonding from the zirconocene fragment to the π^* orbitals of the imine moiety is occurring.

As is shown in Scheme II, these complexes participate in coupling reactions with an extremely wide group of unsaturated organic groups to cleanly form the corresponding air- and moisture-sensitive metallacycles. The typical reaction is performed by the addition of the unsaturated organic group to a benzene solution of the imine complex and allowed to stir at room temperature for less than 1 h. In most cases removal of the solvent in vacuo allows the isolation of the metallacycle as a solid or an oil in greater than 95% purity. The imine complex **2b** has been

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(2) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

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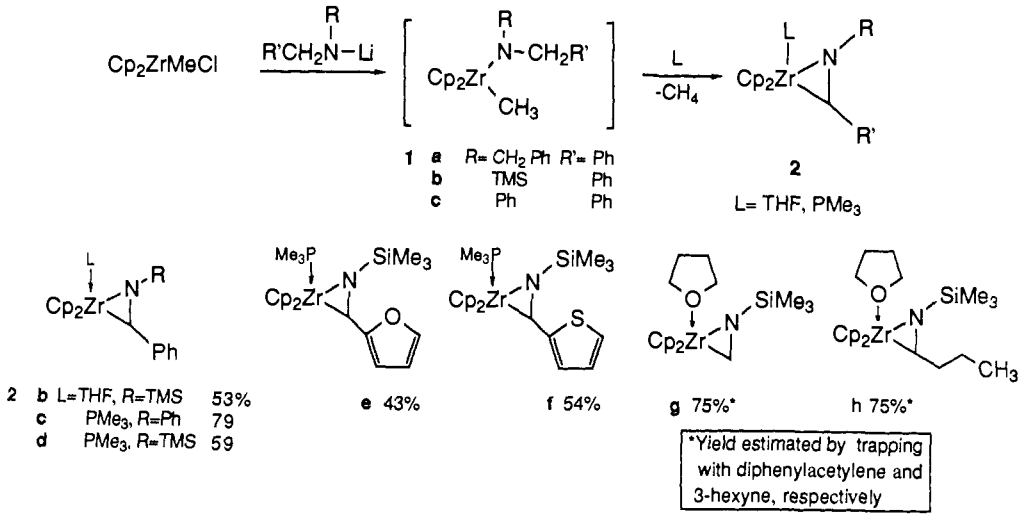
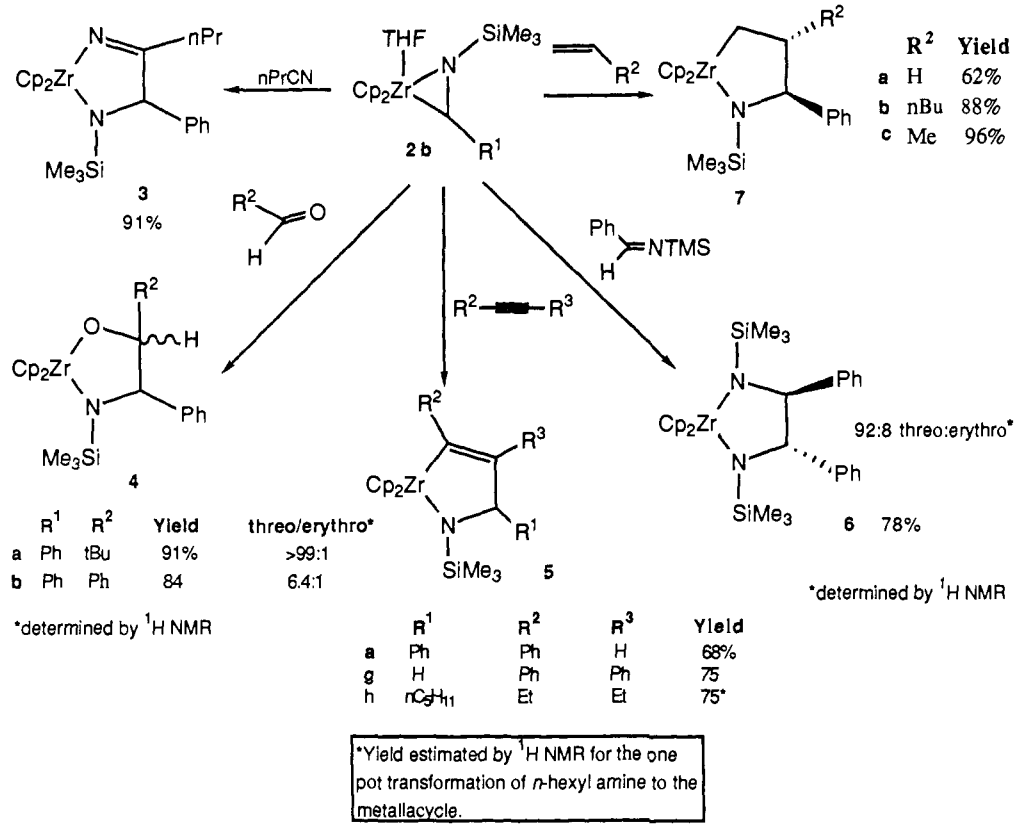
Scheme I



Scheme II

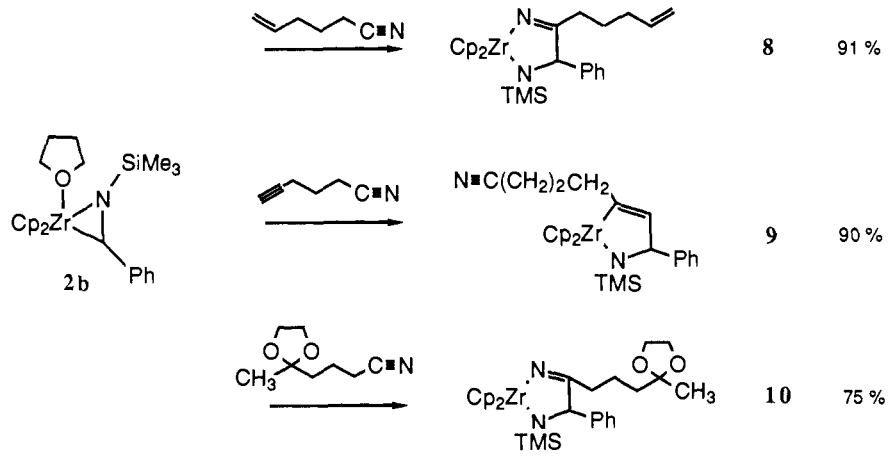


shown to couple in a diastereoselective fashion with aldehydes and imines to give metallacyclic products in a manner analogous to that recently reported by Pedersen.[4a,b] Unlike many of the other complexes which we have reported,[5b] coupling with 1 equiv of a terminal olefin proceeds in high yield in a regio- and diastereoselective manner. For example **2b** reacts with 1-hexene to give a 94:6 ratio of the metallacycle shown and the regioisomeric 3,5-disubstituted metallacycle(s) as evidenced by the fact that methanolysis of the resulting mixture gives a 16:1 ratio of a single diastereomer of 2-methyl-1-phenylhexylamine and 1-phenylheptylamine in an overall 85% yield. No evidence is seen for formation of the other diastereomeric 3,4-disubstituted metallacycle. Propene couples with **2b** to give a high yield of metallacycle **7c** as a single diastereomer.[4c] *This is synthetically equivalent to the regio- and diastereoselective addition of an α-amino carbanion to an unactivated terminal olefin.*

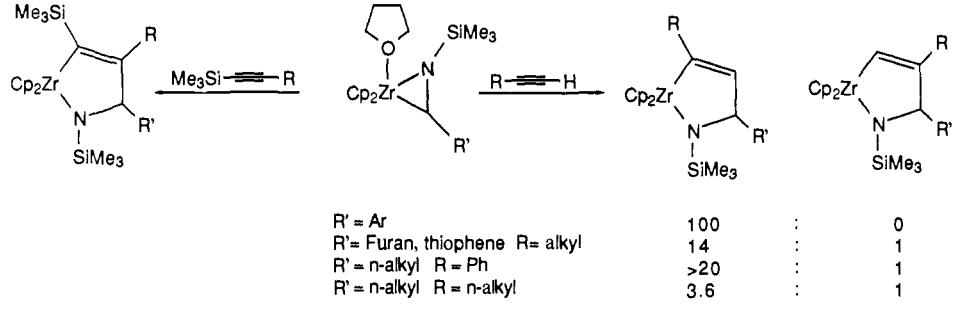
Although, these imine complexes are quite reactive, they also display interesting chemoselectivity as shown in Scheme III. Reaction of **2b** with 5-cyano-1-pentene gives the metallacycle derived solely from attack at the nitrile group in 91% isolated yield. In contrast, exposure of **2b** to 5-cyano-1-pentyne gives only the metallacycle resulting from reaction with the terminal alkyne moiety. While free carbonyl groups are incompatible with these reaction conditions (vide supra), conventional carbonyl-protecting groups pose no problems as is shown by the formation of metallacycle **10**.

The coupling reactions with alkynes are also of note. Unlike many related early transition-metal complexes,[3] these complexes undergo clean coupling reactions with both terminal alkynes and internal alkynes. The regiochemical outcome of the reactions was studied by the in situ generation of the imine complex, coupling with a terminal alkyne, subsequent methanolysis, and analysis of the organic products. As shown in Scheme IV, if the R′ substituent is an aromatic moiety, essentially only the 3,5-regioisomer is

Scheme III



Scheme IV



R' = Ar	100	:	0
R'= Furan, thiophene R= alkyl	14	:	1
R' = n-alkyl R = Ph	>20	:	1
R' = n-alkyl R = n-alkyl	3.6	:	1

formed regardless of the nature of R. If R = *n*-butyl and R′ = *n*-pentyl, a 3.6:1 ratio of the 3,5- and the 3,4-isomers is produced. If R′ = *n*-alkyl and R = phenyl, again, only the 3,5-regioisomer is formed. Coupling of a trialkylsilylalkyne gives only the regioisomer in which the trialkylsilyl group is situated adjacent to the zirconium, consistent with our observations in related systems.[10]

In order to demonstrate the synthetic utility of these imine complexes we have developed a general one-flask synthesis of allylic amines based on the in situ generation and subsequent reaction of zirconocene–imine complexes with both terminal and internal alkynes. *This procedure is synthetically equivalent to the addition of an α-amino carbanion to a geometrically stable (E)-vinyl cation* and is outlined in Scheme V. The lithium trimethylsilylalkylamide is added to a THF solution of zirconocene (methyl) chloride at −78 °C. The reaction mixture is warmed to 0 °C, and the alkyne is added. The mixture is warmed to room temperature (50 °C if R′ = alkyl) and allowed to stir overnight. Excess methanol is added to the reaction mixture to cleave the zirconium–carbon and zirconium–nitrogen bonds. After an organic workup, the crude product may be purified by chromatography to afford the geometrically pure[11] allylic amines in good yields based upon the starting amine as shown in Table I.

In summary, this constitutes the first general procedure for the dehydrogenation of an amine to form a metal complex of the corresponding imine. We have shown that this procedure works with a variety of amines and proceeds under extremely mild conditions. The imine complexes, once formed, undergo a number of chemo-, regio-, and diastereoselective coupling reactions. In situ generation of the complexes followed by coupling with alkynes provides a general method for the preparation of geometrically pure allylic amines. We are currently exploring the utility of these complexes as vehicles for the synthesis of a variety of heterocyclic and acyclic nitrogen-containing compounds.

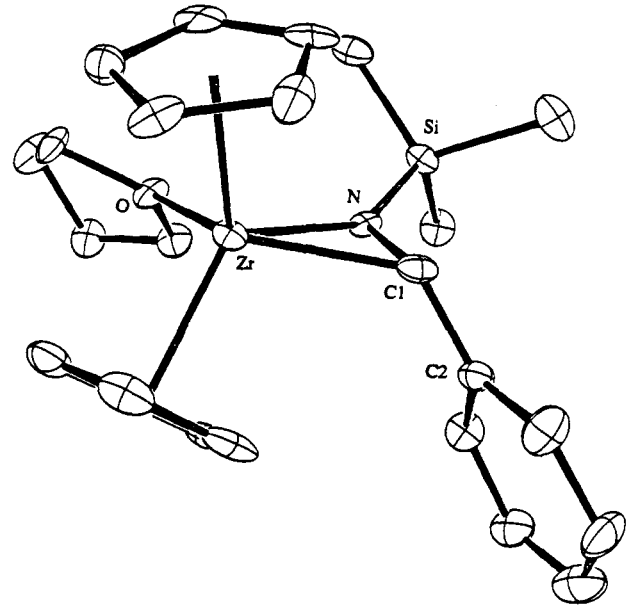


Figure 1. Molecular structure and selected bond lengths and bond angles of **2b** are as follows: Zr–Cl, 2.26 (1); Zr–N, 2.11 (1); Zr–O, 2.376 (9); Cl–C2, 1.48 (2); N–Cl, 1.41 (1); Si–N, 1.69 (1) Å; N–Zr–Cl 37.5 (4); N–Zr–O 80.7 (3); N–Cl–Zr, 65.5 (6); C2–Cl–Zr, 128.6 (8); Cl–N–Si, 125.3 (8); Cl–N–Zr, 77.0 (7); Si–N–Zr, 148.1 (6)°.

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(11) The geometry of the disubstituted allylic amines has been determined by the examination of the coupling constants of the HC=CH in the ^{1}H NMR spectra and are consistent with known values (Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, NY, 1981.) Hydrolysis of the zirconacycles to form disubstituted allylic amines was shown to proceed with retention of the stereochemistry of the carbon bond. Analogously the hydrolysis of zirconacycles leading to trisubstituted allylic amines is assumed to proceed with retention of stereochemistry of the carbon bond. sp^2-Hybridized carbon atoms bonded to zirconium have been shown to hydrolyze with retention of stereochemistry, (e.g., see: Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679. Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6422. Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788). Geometric purity was ascertained by examination of their ^{1}H, ^{13}C NMR spectra and by capillary GC and is estimated to be >98% in all cases.

Scheme V

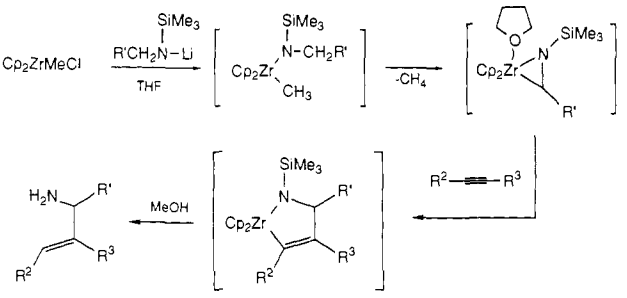
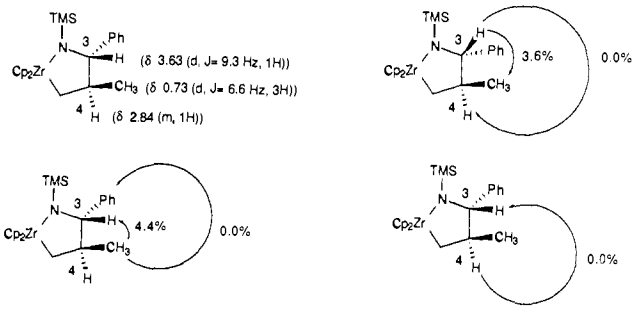


Chart I



Experimental Section

All reactions were conducted under a nitrogen or argon atmosphere by using standard schlenk techniques. Transfers and storage of air- or moisture-sensitive reagents were performed in a Vacuum Atmospheres Co. drybox. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker WM-250, Bruker WM-270, Varian XL-300, Varian XL-400, or a Varian VXR 500 Fourier transform spectrometer. All ^{13}C NMR and ^{31}P NMR spectra were proton decoupled unless otherwise indicated. Infrared (IR) spectra were recorded on an IBM IR/30S or a Mattson Cygnus Starlab 100 Fourier transform spectrometer. Gas chromatography analyses were performed on a Hewlett Packard Model 5890 GC with a 3392A integrator and FID detector by using a 25 m capillary column with crosslinked SE-30 as a stationary phase. Electron impact high resolution mass determinations (HRMS) were recorded on a Finnegan MAT System 8200. Elemental analyses were performed by Desert Analytics, Inc.; air-sensitive samples were sent in sealed ampules under argon.

Tetrahydrofuran, benzene, and diethyl ether were distilled from sodium/benzophenone ketyl. Hexane was deolefinated by stirring over H_2SO_4 followed by distillation from sodium/benzophenone ketyl. Chlorotrimethylsilane was purified by stirring over CaH_2 followed by vacuum transfer. Unless otherwise stated, preparative flash chromatography was performed on E.M. Science Kieselgel 60 (230-400 mesh). Chromatography was also performed on a Chromatotron, Model 7924T, Harrison Research CA. The chromatography plates were prepared with EM Science silica gel/$CaSO_4$, no. $60PF_{254}$. Unless otherwise stated, yields refer to isolated yields of compounds of greater than 95% purity as determined by capillary GC and ^1H NMR. Cp_2ZrCl_2 was purchased from Boulder Scientific Inc., Mead, CO. $Cp_2Zr(Me)Cl$[12] and the (trimethylsilyl)benzaldimine[13] were prepared by published procedures. 1-(3-Cyanopropyl)-1-methyl-2,5-dioxolane was synthesized by the following procedure: 5-oxohexanenitrile was dissolved in benzene, and ethylene glycol was added followed by *p*-toluenesulfonic acid. The flask was fitted with a Dean–Stark apparatus, and the mixture was refluxed until no water was collected. After a standard organic workup the crude product was distilled at reduced pressure. 5-Cyano-1-pentene was prepared by the following procedure: 5-bromo-1-pentene and KCN were heated at 100 °C in ethylene glycol for 2 h. After a standard organic workup, the crude product was distilled at reduced pressure. *tert*-Butyldimethylsilyl-protected 1-hexyne was prepared by the addition of 1 equiv of *n*-butyllithium to an ether solution of 1-hexyne at −78 °C. An ether solution of *tert*-butyldimethylsilyl chloride (1 equiv) was added to the reaction mixture and allowed to stir for 48 h. After a normal organic workup and distillation, the product was collected as a pale yellow liquid. Ethylene and propene were purchased from Matheson Gas Products and Aldrich Chemical Co., respectively, and both were used without further purification. Alkynes were purified before use by passage through a short column of neutral alumina (ICN Alumina N, Akt.I). All other reagents were available from commercial sources and were used without further purification.

The degree of diastereoselectivity of the reactions of the imine complex **2b** with pivaldehyde (**4a**) and benzaldehyde (**4b**) were determined by ^1H NMR. The sense of diastereoselectivity was determined by adding trichloromethyl chloroformate (diphosgene) to the metallacycles and examining the 5-*tert*-butyl-4-phenyl-2-oxazolidone and the 4,5-diphenyl-2-oxazolidone which were produced. In the case of the pivaldehyde, the ^1H NMR spectrum of the product was consistent with literature values for *trans*-5-*tert*-butyl-4-phenyl-2-oxazolidone and was inconsistent with literature values for the cis compound.[14] In the case of benzaldehyde, the white solid product (mp 160 °C) had a melting point corresponding to that of *trans*-4,5-diphenyl-2-oxazolidone (mp 161–162 °C, *cis*-4,5-diphenyl-2-oxazolidone mp 193–194 °C.)[15] The diastereoselectivity of the reaction of the imine complex with the (tetramethylsilyl)benzaldimine was determined by hydrolysis to form the 1,2-diamine and employing the method of Roskamp and Pedersen[4b] and by ^1H NMR.

Preparation of 1a. To a solution of dibenzylamine (3.16 g, 19.8 mmol) in THF (50 mL) at −78 °C was added *n*-butyllithium (12.6 mL of a 1.56 M solution, 19.7 mmol), and the solution was allowed to stir 10 min. This solution was added to a solution of zirconocene (methyl) chloride in THF (200 mL) at −78 °C and slowly warmed to 0 °C. Chlorotrimethylsilane (0.029 g, 0.27 mmol) was added, and the reaction mixture was allowed to warm to room temperature and allowed to stir for 30 min. The solvent was removed in vacuo, and benzene was added. The benzene solution was cannula filtered away from the lithium chloride. The benzene was removed in vacuo, ether was added and removed in vacuo to yield 8.25 g of a yellow solid 95% pure by ^1H NMR (91% isolated yield): ^1H NMR (250 MHz, C_6D_6) δ 0.34 (s, 3 H), 4.25 (s, 4 H), 5.78 (s, 10 H), 7.10–7.50 (m, 10 H).

Preparation of 2a. A solution of **1a** (2.16 g, 5.0 mmol) in benzene (10 mL) was placed into a Fischer–Porter bottle. Trimethylphosphine (0.46 g, 6.0 mmol) was added, and the reaction mixture was heated to 110 °C for 4 h. The solvent was evaporated to yield a semisolid which was shown to be a 3:1 mixture of the two regioisomers which differ by the orientation of the PMe_3 ligand (85% crude yield by ^1H NMR) (PMe_3 next to the nitrogen and PMe_3 next to the benzylic carbon). A portion of the product was purified by recrystallization from a THF/hexane mixture for analysis (>95% pure by ^1H NMR). Major isomer: ^1H NMR (300 MHz, C_6D_6) δ 0.62 (d, J = 6.3 Hz, 9 H), 2.20 (d, J = 2 Hz, 1 H), 4.1 (d, J = 12 Hz, 1 H), 4.50 (d, J = 12 Hz, 1 H), 5.34 (d, J = 2 Hz, 5 H), 5.37 (d, J = 2 Hz, 5 H), 6.85 (t, J = 9 Hz, 1 H), 7.01–7.20 (m, 6 H), 7.28 (t, J = 9 Hz, 2 H), 7.52 (d, J = 7 Hz, 1 H); ^{13}C NMR (100 MHz, C_6D_6) δ 15.79 (d, J_{CP} = 17.5 Hz), 57.30 (d, J_{CP} = 13.6 Hz), 66.26, 103.86, 106.89, 119.68, 126.29, 129.923, 143.71, 158.70 (d, J_{CP} = 8 Hz), 2 peaks obscured by solvent; IR (mixture of major and minor isomers) (KBr) (cm^{-1}) 3080, 3023, 2912, 2837, 2819, 2794, 1642, 1598, 1491, 1450, 1346, 1309, 1296, 1154, 1099, 948, 917, 791, 751, 744, 698, 645, 604, 569, 530. Minor isomer: ^1H NMR (300 MHz, C_6D_6) δ 0.89 (d, J = 6 Hz, 9 H), 2.8 (s, 1 H), 3.78 (d, J = 12 Hz, 1 H), 4.65 (d, J = 12 Hz, 1 H), 5.22 (d, J = 2 Hz, 5 H), 6.9–7.2 (m, 10 H), one Cp peak obscured by major isomer; ^{13}C NMR (100 MHz, C_6D_6) δ 16.27 (d, J_{CP} = 12 Hz), 120.23, 126.11, 126.42, 129.28, 141.61, 157.55, other peaks obscured by major isomer.

Preparation of 2b. To a solution of benzylamine (1.97 g, 18.4 mmol) in ether (20 mL) at 0 °C was added *n*-butyllithium (11.2 mL of a 1.64 M solution in hexane, 18.4 mmol), and the resulting suspension was allowed to stir for 5 min. Chlorotrimethylsilane (2.00 g, 18.4 mmol) was added, and the reaction mixture was allowed to stir for 5 min. *n*-Butyllithium (11.2 mL of a 1.64 M solution in hexane, 18.4 mmol) was added, and the reaction mixture was allowed to stir for an additional 5 min. This solution was transferred by cannula to a solution of zirconocene (methyl) chloride (5.00 g, 18.4 mmol) in THF (75 mL) at −78 °C, and the resulting solution was allowed to stir for 0.5 h, warmed to 0 °C, and allowed to stir for 3 h. The reaction mixture was then warmed to room temperature and allowed to stir for 6 h. The solvent was removed to yield a yellow solid. This was diluted with benzene (50 mL) and cannula-filtered to removed LiCl. The benzene was removed to yield a yellow solid which was washed with hexane (3 × 10 mL) and dried in vacuo to yield 4.55 g product (53%): ^1H NMR (300 MHz, C_6D_6) δ 0.21 (s, 9 H), 1.23 (m, 4 H), 3.39 (m, 4 H), 4.50 (br s, 1 H), 5.44 (br s, 5 H), 5.49 (br s, 5 H), 6.78 (br s, 2 H), 7.25–7.35 (br m, 3 H); ^{13}C NMR

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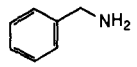
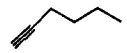
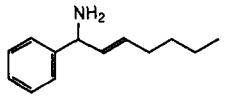
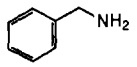
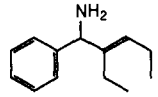
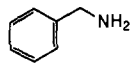
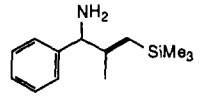
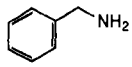
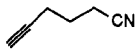
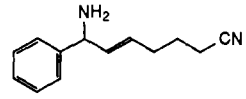
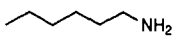
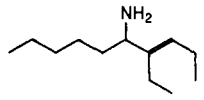
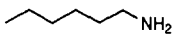
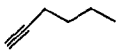
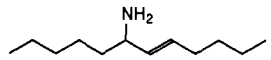
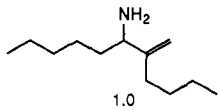
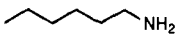
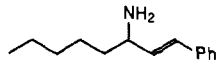
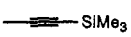
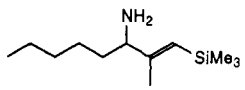
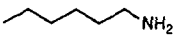
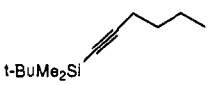
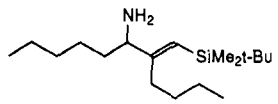
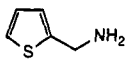
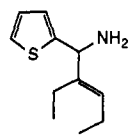
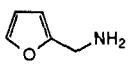
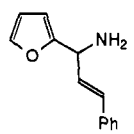
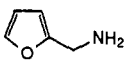
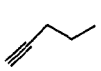
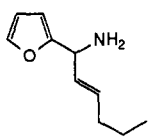
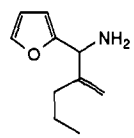
(15) Zimmerman, H. E.; Traxler, M. D. *J. Am. Chem. Soc.* **1957**, *79*, 1920.

Table I

	Amine	Alkyne	Product(s)	Isolated Yield(%)
1)				68
2)				68
3)				75
4)				48
5)				66
6)			 3.6  1.0	50
7)				58
8)				80
9)				68
10)				63
11)				62
12)			 14.0  1.0	63

(75 MHz, THF-d_8) δ 2.79, 26.37, 68.26, 71.09, 108.21, 109.38, 116.81, 120.85, 127.75, 159.81; IR (KBr) 3112, 3083, 3062, 3004, 2981, 2963, 2947, 2920, 2906, 2888, 2863, 2849, 1588, 1480, 1446, 1238, 1219, 1128, 1066, 1020, 915, 887, 866, 839, 828, 806, 790, 763, 748, 699, 670 cm^{-1}. Anal. Calcd for $C_{24}H_{33}N_1O_1Si_1Zr_1$: C, 61.22; H, 7.09; N, 2.97. Found: C, 61.09; H, 7.08; N, 3.03.

Preparation of 2c. To a solution of *N*-phenylbenzylamine (0.915 g, 5.0 mmol) in THF (15 mL) at 0 °C was added *n*-butyllithium (2.91 mL of a 1.71 M solution in hexane, 5.0 mmol), and the resulting suspension was allowed to stir for 5 min. Chlorotrimethylsilane (0.543 g, 5.0 mmol) was added, and the reaction mixture was allowed to stir for 5 min. *n*-Butyllithium (2.91 mL of a 1.71 M solution in hexane, 5.0 mmol) was

added, and the reaction mixture was allowed to stir for an additional 5 min. This solution was added to a solution of zirconocene (methyl) chloride (1.36 g, 5.0 mmol) in THF (25 mL) at −78 °C, and the resulting solution was allowed to stir for 0.5 h and warmed to room temperature, and the reaction mixture was allowed to stir overnight. The solvent was removed to yield a yellow solid. This was dissolved in benzene (20 mL) and cannula-filtered to remove LiCl. To the benzene solution was added trimethylphosphine (0.38 g, 5.0 mmol) and a yellow solid precipitated. The benzene was removed by cannula, and the yellow solid was washed with hexane and dried in vacuo to yield 1.90 g of product shown to be greater than 95% pure by ^{1}H NMR (79% isolated yield): ^{1}H NMR (300 MHz, THF-d_8) δ 1.31 (d, J = 6.3 Hz, 9 H), 2.47 (d, J = 3.3 Hz, 1 H), 5.63 (d, J = 1.8 Hz, 5 H), 5.75 (d, J = 2.1 Hz, 5 H), 6.30–6.38 (m, 2 H), 6.50–6.60 (m, 3 H), 6.80–7.00 (br m, 5 H); ^{13}C NMR (100 MHz, THF-d_8) δ 18.29 (d, J_{CP} = 18.2 Hz), 46.81 (d, J_{CP} = 14.6 Hz), 105.78, 107.62, 114.93, 117.41, 128.24, 129.02, 138.09, 155.83, 158.83; IR (KBr) 3097, 3086, 3068, 3044, 3031, 3020, 3006, 2984, 2975, 2968, 2911, 2904, 2813, 2797, 2780, 1951, 1918, 1908, 1825, 1814, 1734, 1719, 1710, 1588, 1486, 1468, 1352, 1337, 1283, 1273, 1209, 1166, 1007, 983, 961, 949, 827, 817, 804, 796, 768, 748, 721, 698, 684 cm^{-1}. Anal. Calcd for $C_{26}H_{30}NPZr$: C, 65.23; H, 6.32; N, 2.93. Found: C, 65.03; H, 6.44; N, 2.73.

Preparation of 2d. To a solution of benzylamine (0.536 g, 5.0 mmol) in ether (15 mL) at 0 °C (15 mL) was added *n*-butyllithium (2.91 mL of a 1.71 M solution in hexane, 5.0 mmol), and the resulting suspension was allowed to stir for 5 min. Chlorotrimethylsilane (0.543 g, 5.0 mmol) was added, and the reaction mixture was allowed to stir for 5 min. *n*-Butyllithium (2.91 mL of a 1.71 M solution in hexane, 5.0 mmol) was added, and the reaction mixture was allowed to stir for an additional 5 min. This solution was added to a solution of zirconocene (methyl) chloride (1.36 g, 5.0 mmol) in THF (25 mL) at −78 °C, the reaction mixture was allowed to stir 30 min and warmed to 0 °C, trimethylphosphine (0.38 g, 5.0 mmol) and added, and the reaction mixture was warmed to room temperature and allowed to stir overnight. The solvent was removed in vacuo to yield a yellow solid, that was dissolved in benzene (25 mL), cannula-filtered away from LiCl. The benzene was removed to yield a yellow solid which was washed with ether/hexane (1:10) and dried to yield 1.40 g of product shown to be greater than 95% pure by ^{1}H NMR (59% isolated yield): ^{1}H NMR (300 MHz, C_6D_6) δ 0.33 (s, 9 H), 0.62 (d, J = 6.3 Hz, 9 H), 2.77 (d, J = 3.3 Hz, 1 H), 5.36 (d, J = 2.7 H, 5 H), 5.43 (d, J = 1.8 Hz, 5 H), 6.80–6.95 (m, 2 H), 7.05–7.15 (m, 3 H); ^{13}C NMR (100 MHz, C_6D_6) δ 1.94, 15.5 (d, J_{CP} = 18.2 Hz), 56.1 (d, J_{CP} = 12.8 Hz), 104.42 107.06, 112.6, 115.70, 119.84, 121.46, 124.17, 158.13; ^{31}P NMR (121 MHz, C_6D_6) (external H_3PO_4 reference) δ −0.24; IR (KBr) 3110, 3098, 3085, 3077, 3068, 3051, 3028, 3012, 3007, 2991, 2987, 2981, 2949, 2924, 2909, 2899, 2821, 2787, 1597, 1585, 1563, 1556, 1491, 1477, 1446, 1384, 1350, 1283, 1249, 1233, 1227, 1167, 1149, 1067, 1013, 957, 862, 827, 811, 800, 757, 653, 527 cm^{-1}; HRMS, no M$^+$ peak was observed; calcd for $C_{20}H_{25}NSiZr\cdot[M - PMe_3]^+$ 397.0799, found 397.0799 ± 0.0012 amu.

Preparation of 2e. To a solution of furfurylamine (0.485 g, 5.0 mmol) in THF (20 mL) at −78 °C was added *n*-butyllithium (2.92 mL of a 1.71 M solution in hexane), and the solution was allowed to stir 5 min. Chlorotrimethylsilane (0.542 g, 5.0 mmol) was added and allowed to stir for an additional 5 min. To the reaction mixture was added *n*-BuLi (2.92 mL of a 1.71 M solution in hexane, 5.0 mmol) and the resulting solution was stirred for 5 min. This solution was added to a solution of Cp_2Zr-(Me)Cl (1.36 g, 5.0 mmol) in THF (30 mL) at −78 °C and allowed to stir for 5 min. The reaction mixture was allowed to warm to 0 °C, PMe_3 (0.380 g, 5.0 mmol) was added, and the reaction mixture was allowed to stir overnight. The solvent was removed, and the product was dissolved in benzene (20 mL) and filtered away from the LiCl. The benzene was removed to yield a solid which was washed (5 × ether/hexane 1:10), dried in vacuo to yield 1.05 g powder greater than 95% yield by ^{1}H NMR (43% isolated yield): ^{1}H NMR (300 MHz, C_6D_6) δ 0.32 (s, 9 H), 0.77 (d, J = 6.3 Hz, 9 H), 2.82 (d, J = 3.6 Hz, 1 H), 5.34 (d, J = 2.1 Hz, 5 H), 5.45 (d, J = 1.8 Hz, 5 H), 5.47 (m, 1 H), 6.25 (m, 1 H), 7.03 (br s, 1 H); ^{13}C NMR (100 MHz, C_6D_6) δ 1.78, 15.80 (d, J_{CP} = 20.1 Hz), 46.40 (d, J_{CP} = 16.4 Hz), 94.68, 104.51, 107.04, 111.38, 114.13, 134.94, 170.74; ^{31}P NMR (121 MHz, C_6D_6) (external H_3PO_4 reference) δ −1.08; IR (KBr) 3106, 2982, 2949, 2917, 2906, 2894, 2877, 2855, 2813, 1553, 1543, 1511, 1490, 1444, 1414, 1386, 1328, 1285, 1237, 1186, 1008, 999, 395, 854, 835, 807, 786, 752, 670, 521 cm^{-1}; HRMS, no M$^+$ peak was observed, calcd for $C_{18}H_{23}NOSiZr\cdot[M - PMe_3]^+$ 387.0592, found 387.0591 ± 0.0008 amu.

Preparation of 2f. The same basic procedure as described for the preparation of **2e** was used starting with thiophenemethylamine to yield 1.31 g of product shown to be greater than 95% pure by ^{1}H NMR (54% isolated yield): ^{1}H NMR (300 MHz, C_6D_6) δ 0.36 (s, 9 H), 0.70 (d, J = 6.3 Hz, 9 H), 3.02 (d, J = 2.7 Hz, 1 H), 5.32 (d, J = 2.1 Hz, 5 H), 5.54 (d, J = 1.8 Hz, 5 H), 5.95–6.00 m, 2 H), 6.78–6.80 (m, 1 H); ^{13}C NMR (75 MHz, C_6D_6) δ 2.22, 15.60 (d, J_{CP} = 17.3 Hz), 52.58 (d, J_{CP} = 12.7 Hz), 104.68, 107.62, 113.69, 114.15, 125.39, 126.49; ^{31}P NMR (121 MHz, C_6D_6) (external H_3PO_4 reference) δ 2.25; IR (KBr) 3098, 3053, 2979, 2968, 2950, 2911, 2907, 2891, 2871, 2840, 1503, 1426, 1362, 1284, 1238, 1227, 1209, 1183, 1178, 1058, 1020, 951, 896, 859, 801, 790, 728, 664 cm^{-1}; HRMS, no M$^+$ peak was observed, calcd for $C_{18}H_{23}NSSiZr\cdot[M - PM_3]^+$ 403.0363, found 403.0363 ± 0.0012 amu.

Preparation of 2g Trapped with Diphenylacetylene. To a suspension of methyl ammonium chloride (0.248 g, 3.68 mmol) in THF (20 mL) at −78 °C was added *n*-butyllithium (4.6 mL of a 1.60 M solution in hexane, 7.36 mmol), and the resulting suspension was allowed to stir for 5 min. Chlorotrimethylsilane (0.400 g, 3.68 mmol) was added, and the reaction mixture was allowed to stir for 5 min. *n*-Butyllithium (2.3 mL of a 1.60 M solution in hexane, 3.68 mmol) was added, and the reaction mixture was allowed to stir for 5 min. This solution was added to a solution of zirconocene (methyl) chloride (1.00 g, 3.68 mmol) in THF (20 mL) at −78 °C, and the resulting solution was allowed to stir for 5 min, warmed to room temperature, and allowed to stir for 5 more min. A solution of diphenylacetylene (0.655 g, 3.68 mmol) in THF (10 mL) was added, and the reaction mixture was stirred at room temperature overnight. The solvent was removed to yield an orange solid. The product was dissolved in benzene (25 mL) and cannula-filtered to remove LiCl. The benzene was removed in vacuo to yield an orange solid which was purified by recrystallization from hexane/ether (9:1) to yield 1.47 g of an orange solid (75%): ^{1}H NMR (300 MHz, C_6D_6) δ 0.22 (s, 9 H), 4.16 (s, 2 H), 6.25 (s, 10 H), 7.0–7.4 (m, 10 H); ^{13}C NMR (67.9 MHz, C_6D_6) δ 0.38, 51.75, 112.76, 123.39, 126.75, 127.02, 127.16, 127.84, 128.96, 131.20, 131.93, 143.12, 145.41, 148.54, 150.34, 186.43, one carbon obscured; IR (KBr) 3074, 3069, 3050, 2965, 2956, 2896, 2785, 2750, 1799, 1701, 1592, 1485, 1478, 1443, 1399, 1363, 1259, 1178, 1069, 1011, 959, 911, 861, 790, 696 cm^{-1}; HRMS, calcd for $C_{28}H_{31}NSiZr$ 499.1268, found 499.1268 ± 0.0014 amu.

Preparation of 2h Trapped with 3-Hexyne. To a solution of hexylamine (0.372 g, 3.68 mmol) in THF (20 mL) at −78 °C was added *n*-butyllithium (2.3 mL of a 1.60 M solution in hexane, 3.68 mmol), and the resulting suspension was allowed to stir for 5 min. Chlorotrimethylsilane (0.400 g, 3.68 mmol) was added and the reaction mixture was allowed to stir for 5 min. *n*-Butyllithium (2.3 mL of 1.6 M solution in hexane, 3.68 mmol) was added, and the reaction mixture was allowed to stir 5 min. This solution was added to a solution of zirconocene (methyl) chloride (1.00 g, 3.68 mmol) in THF (20 mL) at −78 °C, and the resulting solution was allowed to stir for 10 min. The reaction mixture was warmed to room temperature and allowed to stir for 15 min. 3-Hexyne (0.333 g, 4.05 mmol) was added, and the reaction mixture was heated at 50 °C overnight. The solvent was removed to yield 1.67 g of a yellow oil shown to be 80% pure by ^{1}H NMR (75% yield): ^{1}H NMR (300 MHz, C_6D_6) δ 0.04 (s, 9 H), 0.97 (t, J = 7.0 Hz, 3 H), 1.04 (t, J = 7.5 Hz, 3 H), 1.11 (t, J = 7.0 Hz, 3 H), 1.33 (m, 7 H), 1.68 (m, 3 H), 2.15 (6 lines, 7.0 Hz, 1 H), 2.42 (6 lines, J = 7.0 Hz, 1 H), 3.95 (br s, 1 H), 5.93 (s, 5 H), 6.09 (s, 5 H); ^{13}C NMR (67.9 MHz, C_6D_6) δ 2.23, 13.29, 14.34, 14.93, 22.83, 23.07, 23.38, 28.88, 32.81, 36.28, 59.59, 111.98, 112.24, 146.09, 188.92; IR (neat) 2955, 2928, 2895, 2869, 1568, 1456, 1448, 1369, 1245, 1048, 1014, 941, 888, 872, 852, 843, 833, 791, 745, 668 cm^{-1}; HRMS, calcd for $C_{25}H_{41}NSiZr$ 473.2051, found 473.2051 ± 0.0019 amu.

2b Coupled with Butyronitrile (3, Scheme II). To a solution of **2b** (0.469 g, 1.00 mmol) in benzene (10 mL) at room temperature was added butyronitrile (0.069 g, 1.00 mmol), and the solution was allowed to stir for 10 min. The solvent was removed to yield 0.450 g of a yellow solid shown to be greater than 95% pure by ^{1}H NMR (91% isolated yield): ^{1}H NMR (300 MHz, C_6D_6) δ −0.29 (s, 9 H), 0.88 (t, J = 6.9 Hz, 3 H), 1.50–1.80 (m, 4 H), 5.29 (s, 1 H), 6.13 (s, 5 H), 6.21 (s, 5 H), 7.09 (m, 1 H), 7.21 (t, J = 7.0 Hz, 2 H), 7.40 (d, J = 7.0 Hz, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 2.00, 14.09, 19.87, 39.07, 90.65, 113.47, 113.82, 127.21, 128.60, 128.92, 145.44, 179.14; IR (KBr) 3054, 3029, 2961, 2933, 2915, 2895, 2871, 2770, 1625, 1596, 1451, 1255, 1244, 1038, 1016, 933, 911, 895, 830, 796, 794, 791, 765, 701, 676, 614, 592 cm^{-1}; HRMS, calcd for $C_{24}H_{32}N_2SiZr$ 466.1377, found 466.1376 ± 0.0016 amu.

2b Coupled with 1,1,1-Trimethylacetaldehyde (4a, Scheme II). To a solution of **2b** (0.100 g, 0.213 mmol) in benzene (1 mL) at room temperature was added 1,1,1-trimethylacetaldehyde (0.018 g, 0.213 mmol), and the solution was allowed to stir for 10 min. The solvent was removed to yield a 0.099 g of a yellow solid shown to be 95% pure by ^{1}H NMR (91% isolated yield): ^{1}H NMR (300 MHz, C_6D_6) δ −0.29 (s, 9 H), 0.79 (s, 9 H), 4.64 (d, J = 8.4 Hz, 1 H), 5.14 (d, J = 8.4 Hz, 1 H), 6.19 (s, 10 H), 7.00–7.20 (m, 3 H), 7.40 (m, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 2.76, 27.47, 36.57, 82.19, 98.38, 113.83, 113.95, 127.47, 128.15, 130.04, 146.92. IR (KBr) (cm^{-1}) 3080, 2975, 2951, 2945, 2926, 2900, 2862, 1597, 1490, 1477, 1460, 1388, 1359, 1355, 1246, 1059, 1025, 1020, 1009, 705, 680, 663 cm^{-1}; HRMS, calcd for $C_{25}H_{35}NOSiZr$ 483.1531, found 483.1533 ± 0.002 amu.

2b Coupled with Benzaldehyde (4b, Scheme II). To a solution of **2b**

(0.100 g, 0.213 mmol) in benzene (1 mL) at room temperature was added benzaldehyde (0.022 g, 0.213 mmol), and the solution was allowed to stir for 10 min at room temperature. The solvent was removed to yield 0.095 g of a yellow solid shown to be a 5.5:1 ratio of two diastereomers, 95% pure by ^{1}H NMR (84% isolated yield). Major diastereomer: ^{1}H NMR (300 MHz, C_6D_6) δ −0.24 (s, 9 H), 5.02 (d, J = 8.7 Hz, 1 H), 5.79 (d, J = 8.7 Hz, 1 H), 6.24 (s, 5 H), 6.28 (s, 5 H), 6.95–7.20 (m, 10 H); ^{13}C NMR (75 MHz, C_6D_6) δ 2.99, 88.41, 93.42, 114.25, 126.86, 126.90, 127.58, 127.70, 127.89, 130.01, 144.38, 144.46; IR (KBr) 3080, 3063, 3026, 2952, 2857, 2811, 1491, 1451, 1442, 1259, 1243, 1042, 1024, 1022, 894, 837, 833, 795, 699 cm^{-1}; MS shows no M$^+$; HRMS, calcd for $C_{20}H_{25}NSiZr\cdot[M - C_7H_6O]^+$ 397.0799, found 397.0799 ± 0.0008 amu. Minor diastereomer: ^{1}H NMR (300 MHz, C_6D_6) δ −0.15 (s, 9 H), 5.32 (d, J = 6.0 Hz, 1 H), 5.45 (d, J = 6.0 Hz, 1 H), 6.16 (s, 5 H), 6.33 (s, 5 H), 6.90–7.20 (m, 10 H); ^{13}C NMR (75 MHz, C_6D_6) δ 2.00, 87.00, 113.47, nine carbons obscured.

2b Coupled with Phenylacetylene (5a, Scheme II). To a solution of benzylamine (3.15 g, 29.4 mmol) in ether (100 mL) at room temperature was added *n*-butyllithium (16.7 mL of a 1.71 M solution in hexane, 29.4 mmol), and the solution was allowed to stir 5 min. Chlorotrimethylsilane (3.15 g, 29.4 mmol) was added, and the reaction was allowed to stir 5 min. *n*-Butyllithium (16.7 mL of a 1.71 M solution in hexane, 29.4 mmol) was used, and the reaction was allowed to stir for an additional 5 min. This solution was added to a solution of $Cp_2Zr(Me)Cl$ (8.0 g, 29.4 mmol) in THF (150 mL) at −78 °C and allowed to stir 15 min. The reaction mixture was warmed to room temperature, phenylacetylene (3.0 g, 29.4 mmol) was added, and the solution was allowed to stir overnight. The solvent was removed, and residue was dissolved in benzene (50 mL), cannula-filtered and removed to yield a solid. This was washed with ether/hexane (1:10) to yield 10.0 g of solid product shown to be greater than 95% pure by ^{1}H NMR (68% isolated yield): ^{1}H NMR (300 MHz, C_6D_6) δ −0.25 (s, 9 H), 4.67 (d, J = 1.5 Hz, 1 H), 6.07 (s, 5 H), 6.11 (s, 5 H), 6.24 (d, J = 1.5 Hz, 1 H), 7.06–7.14 (m, 4 H), 7.21–7.24 (m, 4 H), 7.36–7.39 (m, 2 H); ^{13}C NMR (125 MHz, C_6D_6) δ 1.71, 63.00, 112.57, 113.16, 125.24, 126.45, 126.95, 128.36, 128.54, 128.84, 138.02, 148.08, 150.09, 186.96; IR (KBr) 3097, 3070, 3063, 3055, 3031, 2965, 2923, 2898, 2772, 1933, 1875, 1798, 1741, 1619, 1562, 1482, 1277, 1217, 1081, 953, 931 cm^{-1}. Anal. Calcd for $C_{28}H_{31}NSiZr$: C, 67.15; H, 6.24; N, 2.80. Found: C, 66.78; H, 6.38; N, 2.75.

2b Coupled with (Trimethylsilyl)benzaldimine (6, Scheme II). To a solution of **2b** (0.100 g, 0.213 mmol) in benzene (1 mL) was added (trimethylsilyl)benzaldimine (0.037 g, 0.213 mmol), and the solution was allowed to stir 10 min. The solvent was removed to yield 0.100 g of a yellow solid shown to be a mixture of two diastereomers in a 92:8 ratio. Products were greater than 95% pure by ^{1}H NMR (78% isolated yield). Major diastereomer: ^{1}H NMR (300 MHz, C_6D_6) δ −0.16 (s, 9 H), 4.75 (s, 2 H), 6.34 (s, 10 H), 6.90–7.05 (m, 10 H); ^{13}C NMR (75 MHz, C_6D_6) δ 3.98, 75.15, 113.95, 126.92, 127.45, 130.03, 144.95; IR (KBr) 3058, 3028, 2981, 2977, 2958, 2951, 2901, 2893, 2838, 1600, 1489, 1451, 1337, 1257, 1242, 1073, 1018, 986, 579, 496 cm^{-1}; MS shows no M$^+$ peak; HRMS, M$^+$ peak was not observed, calcd for $[M - C_7H_6O]^+$ 397.0799, found 397.0799 ± 0.0008 amu; minor diastereomer: ^{1}H NMR (300 MHz, C_6D_6) δ −0.10 (s, 9 H), 5.15 (s, 2 H), 6.30 (s 5 H), 6.48 (s, 5 H), other peaks obscured by major diastereomer; ^{13}C NMR (75 MHz, C_6D_6) δ −3.90, 76.0, 112.0, 127.0, 131.0, other peaks obscured by major diastereomer.

2b Coupled with Ethylene (7a, Scheme II). Imine complex was prepared in the same manner as described in the above experimental for the preparation of **2b** on a 7.5-mmol scale. The benzene filtrate solution of the imine complex was freeze-pump-thawed (one cycle) and charged with ethylene (1 atm). The reaction mixture was allowed to stir at room temperature for 30 min, and the solvent was removed to yield a solid product. This was washed with hexane to yield 2.64 g of yellow solid product shown to be 95% pure by ^{1}H NMR (62% isolated yield): ^{1}H NMR (300 MHz, C_6D_6) δ −0.22 (s, 9 H), 0.81–0.88 (m, 1 H), 2.02 (dt, J_1 = 12.8 Hz, J_2 = 4.8 Hz, 1 H), 2.50 (m, 1 H), 3.00–3.09 (m, 1 H), 4.38 (dd, J_1 = 6.3 Hz, J_2 = 3.0, 1 H), 5.92 (s, 5 H), 5.98 (s, 5 H), 7.29 (m, 3 H), 7.47 (m, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 1.63, 41.12, 41.38, 65.06, 111.71, 112.23, 126.11, 127.57, 127.88, 149.97; IR (KBr) 3120, 3106, 3100, 3084, 3020, 2937, 2910, 2849, 2634, 1950, 1812, 1689, 1625, 1444, 1404, 1335, 1321, 1223, 1050, 971, 906, 851 cm^{-1}. Anal. Calcd for $C_{22}H_{29}NSiZr$: C, 61.91; H, 6.85; N, 3.28. Found: C, 62.01; H, 6.98; N, 3.42.

2b Coupled with Hexene (7b, Scheme II). To a solution of **2b** (0.94 g, 2.0 mmol) in benzene (10 mL) at room temperature was added 1-hexene (0.210 g, 2.5 mmol), and the solution was allowed to stir 1 h. The solvent was removed to yield 0.92 g as a yellow oil shown to be 92% pure by ^{1}H NMR (88% yield): ^{1}H NMR (300 MHz, C_6D_6) δ −0.32 (s, 9 H), 0.86 (t, J = 6.9 Hz, 6 H), 1.24 (m, 7 H), 1.92 (dd, J_1 = 12.9 Hz, J_2 = 12.9 Hz, 1 H), 2.77 (m, 1 H), 3.72 (d, J = 10.8 Hz, 1 H), 5.95 (s, 5 H), 6.00 (s, 5 H), 7.07 (m, 2 H), 7.18 (m, 2 H), 7.31 (m, 1 H); ^{13}C NMR (75 MHz, C_6D_6) δ 2.48, 14.31, 23.18, 29.47, 38.05, 50.28, 52.27, 73.59, 112.17, 126.97, 128.21, 128.52, 129.48; IR (KBr) 3082, 3059, 3024, 2952, 2923, 2855, 2793, 1451, 1244, 884, 837, 876, 859, 844, 795, 770 cm^{-1}; HRMS, no M$^+$ peak was observed, $C_{20}H_{25}NSiZr\cdot[M - C_6H_{12}]^+$ 397.0799, found 397.0799 ± 0.0008 amu. Minor diastereomer peaks are obscured by the major diastereomer in the ^{1}H and ^{13}C NMR spectra.

2b Coupled with Hexene Hydrolysis Product (Scheme II). To a solution of **2b** (0.94 g, 2.0 mmol) in benzene (20 mL) at room temperature was added 1-hexene (0.25 g, 3.0 mmol), and the solution was allowed to stir at room temperature for 1 h. Methanol (2 mL) was added, and the reaction mixture was allowed to stir for 1 h. The solvent was removed (rotary evaporator) to yield a semisolid material. This was extracted into ether (25 mL), washed with water and brine, and dried ($MgSO_4$) to yield an oil. This was purified by flash chromatography (95 pentane:5 triethylamine) to yield 0.33 g of a pale yellow oil 98% pure by GC and ^{1}H NMR analyses (85% isolated yield). This consisted of the two regioisomers, 2-methyl-1-phenylhexylamine/1-phenylheptylamine in a 16:1 ratio as determined by ^{1}H NMR and GC analyses. Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.842 (t, J = 6.5 Hz, 3 H), 0.883 (d, J = 7.0 Hz, 3 H), 1.00–1.10 (m, 1 H), 1.20–1.32 (m, 5 H), 1.42 (br s, 2 H), 1.70 (m, 1 H), 3.77 (d, J = 7.0 Hz, 1 H), 7.28 (m, 5 H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 13.88 (q, J = 124 Hz), 14.72 (q, J = 124 Hz), 22.73 (t, J = 125 Hz), 29.44 (t, J = 126 Hz), 33.46 (t, J = 125 Hz), 40.23 (d, J = 126 Hz), 60.39 (d, J = 135 Hz), 126.49 (d, J = 158 Hz), 126.82 (d, J = 156 Hz), 128.02 (d, J = 158 Hz), 145.81 (s); IR (neat) 3379, 3323, 3083, 3062, 2958, 2929, 2872, 2858, 1943, 1889, 1816, 1810, 1615, 1602, 1585, 1492, 1466, 1452, 1377, 1028, 910, 873, 775, 761, 747, 734, 701, 643, 618; HRMS calcd for $C_{13}H_{21}N$ 191.1674, found 191.1674 ± 0.0008 amu. Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (t, J = 6 Hz) other peaks obscured by major isomer; ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.41, 26.31, 29.09, 31.59, 39.55, 56.11, 126.09, 125.6, 128.19, 146.74, one carbon obscured.

2b Coupled with Propene (7c, Scheme II). A solution of **2b** (0.47 g, 1.0 mmol) in benzene (20 mL) was freeze-pump-thawed (one cycle), warmed to room temperature, charged with propene (1 atm), and allowed to stir for 45 min. The solvent was removed to yield 0.430 g of an orange-yellow solid shown to be pure by ^{1}H NMR (96% isolated yield): ^{1}H NMR (300 MHz, C_6D_6) δ −0.37 (s, 9 H), 0.73 (d, J = 6 Hz, 3 H), 1.08 (dd, J_1 = 12 Hz, J_2 = 4 Hz, 1 H), 2.07 (dd, J_1 = 12 Hz, J_2 = 12 Hz, 1 H), 2.84 (m, 1 H), 3.62 (d, J = 9.3 Hz, 1 H), 5.29 (s, 5 H), 5.96 (s, 5 H), 7.10 (m, 1 H), 7.17 (m, 2 H), 7.30 (m, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 2.49, 25.31, 47.45, 53.96, 74.73, 112.07, 112.12, 126.9, 128.23, 129.25, 148.08; IR (KBr) 3082, 3059, 3025, 2951, 2894, 1448, 1246, 1016, 959, 895, 834, 793, 745, 700, 664, 654 cm^{-1}; HRMS, no M$^+$ peak was observed, calcd for $C_{20}H_{25}NSiZr$ $[M - C_3H_6]^+$ 397.0799, found 397.0800 ± 0.001 amu.

Determination of the Stereochemistry of 7c. A difference NOE experiment was performed on **7c** in which the benzylic proton in the 3 position of the metallacycle was irradiated and the methyl group in the 4 position of the metallacycle showed 3.6% NOE signal, whereas the proton in the 4 position shows no NOE and does not appear in the spectrum. Irradiation of the methyl group in the 4 position shows the benzylic proton in the 3 position of the metallacycle with 4.4% NOE signal, and no NOE signals are detected in the aryl region for the phenyl group. Irradiation of the proton in the 4 position of the metallacycle shows no NOE signal for the benzylic proton. These relationships define the ring to have the 3-phenyl and the 4-methyl group in a trans arrangement as shown below.

2b Coupled with 5-Cyano-1-pentene (8, Scheme III). To a solution of **2b** (0.47 g, 1.0 mmol) in benzene (10 mL) at room temperature was added 5-cyano-1-pentene (0.095 g, 1.0 mmol), and the solution was allowed to stir for 10 min. The solvent was removed to yield 0.46 g of an orange solid shown to be greater than 95% pure by ^{1}H NMR (91% isolated yield): ^{1}H NMR (300 MHz, C_6D_6) δ −0.29 (s, 9 H), 1.61–1.75 (m, 4 H), 1.95–1.98 (m, 2 H), 4.93 (dd, J_1 = 9.3 Hz, J_2 = 1.5 Hz, 1 H), 5.00 (dd, J_1 = 17.1 Hz, J_2 = 1.5 Hz, 1 H), 5.29 (s, 1 H), 5.69–5.82 (m, 1 H), 6.12 (s, 5 H), 6.20 (s, 5 H), 7.08 (m, 1 H), 7.20 (t, J = 7.5 Hz, 2 H), 7.40 (d, J = 7.5 Hz, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 1.98, 25.82, 34.11, 36.23, 90.58, 113.49, 113.84, 114.50, 127.25, 128.64, 128.92, 139.29, 145.39, 178.80; IR (KBr) 3072, 3063, 3024, 2944, 2885, 2858, 1625, 1596, 1488, 1450, 1254, 1243, 1014, 997, 927, 907, 860, 833, 797, 789, 750, 702, 687, 677, 641, 621, 616, 590 cm^{-1}; HRMS, calcd for $C_{26}H_{34}NSiZr$ 492.15343, found 492.1534 ± 0.0012 amu.

2b Coupled with 5-Cyano-1-pentyne (9, Scheme III). To a solution of **2b** (0.47 g, 1.0 mmol) in benzene (10 mL) at room temperature was added 5-cyano-1-pentyne (0.093 g, 1.0 mmol), and the solution was allowed to stir for 10 min. The solvent was removed to yield 0.45 g of an orange solid. This solid was washed with hexane and dried to yield 0.45 g of a yellow powder shown to be greater than 95% pure by ^{1}H

NMR (90% isolated yield): ^{1}H NMR (300 MHz, C_6D_6) δ −0.28 (s, 9 H), 1.22 (m, 2 H), 1.57 (m, 2 H), 2.01 (m, 2 H), 4.57 (m, 1 H), 5.63 (m, 1 H), 5.93 (s, 5 H), 6.03 (s, 5 H), 7.09 (t, J = 7.5 Hz, 1 H), 7.21 (t, J = 7.5 Hz, 2 H), 7.31 (d, J = 7.5 Hz, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 1.41, 16.66, 24.27, 38.84, 63.75, 112.34, 112.65, 119.85, 126.82, 128.43, 128.57, 135.34, 148.72, 187.65; IR (KBr) 3079, 3056, 3020, 2943, 2936, 2932, 2893, 2883, 2832, 2789, 2773, 2243, 1597, 1486, 1455, 1450, 1424, 1257, 1243, 1087, 1015, 1001, 975, 951, 930, 889, 872, 827, 803, 794, 778, 772, 765, 743, 705, 664 cm^{-1}; HRMS, calcd for $C_{26}H_{32}N_2SiZr$ 490.1378, found 490.1379 ± 0.0009 amu.

2b Coupled with 1-(3-Cyanopropyl)-1-methyl-2,5-dioxolane (10, Scheme III). To a solution of **2b** in benzene (10 mL) at room temperature was added 1-(3-cyanopropyl)-1-methyl-2,5-dioxolane (0.15 g, 1.0 mmol), and the solution was allowed to stir for 10 min. The solvent was removed to yield a yellow solid. This was washed with hexane to yield 0.44 g of a yellow solid shown to be 95% pure by ^{1}H NMR (75% isolated yield): ^{1}H NMR (300 MHz, C_6D_6) δ −0.28 (s, 9 H), 1.32 (s, 3 H), 1.60–1.90 (m, 6 H), 3.57 (s, 4 H), 5.31 (s, 1 H), 6.14 (s, 5 H), 6.20 (s, 5 H), 7.09 (t, J = 7.5 Hz, 1 H), 7.21 (t, J = 7.5 Hz, 2 H), 7.42 (d, J = 7.5 Hz, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 2.00, 21.19, 24.06, 37.06, 39.52, 64.54, 90.71, 110.28, 113.51, 113.85, 127.23, 128.62, 128.97, 145.45, 179.03; IR (KBr) 3027, 2977, 2950, 2925, 2886, 2781, 2769, 1633, 1596, 1489, 1451, 1376, 1253, 1239, 1221, 1205, 1104, 1064, 1037, 1017, 996, 948, 930, 915, 864, 851, 832, 815, 790, 787, 709, 697, 686, 674, 666, 615, 590, 474 cm^{-1}; HRMS, calcd for $C_{28}H_{38}N_2O_2SiZr$ 552.1745, found 552.1749 ± 0.0014 amu.

Product of the Coupling of Benzylamine with 1-Hexyne. (Example 1, Table I). To a solution of benzylamine (0.39 g, 3.7 mmol) in THF (20 mL) at −78 °C was added *n*-butyllithium (2.25 mL of a 1.63 M solution in hexane, 3.7 mmol), and the reaction mixture was allowed to stir for 15 min. Chlorotrimethylsilane (0.400 g, 3.7 mmol) was added, and the resulting solution was allowed to stir for 15 min. *n*-Butyllithium (2.25 mL of a 1.63 M solution in hexane, 3.7 mmol) was added, and the solution was allowed to stir for an additional 10 min. This solution was added to a solution of zirconocene (methyl) chloride (1.3 g, 4.8 mmol) in THF (20 mL) at −78 °C, and the reaction mixture was allowed to stir 15 min. The reaction mixture was warmed to 0 °C and allowed to stir for 5 min. To this was added 1-hexyne (0.33 g, 4.0 mmol), and the reaction mixture was allowed to stir 24 h. Methanol (3 mL) was added to the reaction mixture and allowed to stir 1 h at room temperature. The solvent was removed by rotary evaporation to yield an oil. This oil was diluted with ether, washed with water and brine, and dried over $MgSO_4$. The resulting oil was chromatographed (Chromatotron) using a hexane/triethylamine mixture (19:1) to produce 0.495 g of a pale yellow oil shown to be 96% pure by GC and ^{1}H NMR analyses (68% isolated yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.77 (t, J = 7.5 Hz, 3 H), 1.10–1.30 (m, 4 H), 1.39 (br s, 2 H), 1.95–1.98 (m, 2 H), 4.36 (d, J = 4.5 Hz, 1 H), 5.49–5.52 (m, 2 H), 7.05–7.25 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.85 (q, J = 123 Hz), 22.18 (t, J = 123 Hz), 37.31 (t, J = 123 Hz), 31.83 (t, J = 123 Hz), 57.81 (d, J = 137 Hz), 126.41 (d, J = 156 Hz), 126.80 (d, J = 160 Hz), 128.37 (d, J = 158 Hz), 130.31 (d, J = 154 Hz), 134.10 (d, J = 152 Hz), 145.32 (s); IR (neat) 3370, 3292, 3061, 3026, 2957, 2926, 2871, 1601, 1491, 1466, 1452, 1437, 1027, 968, 911, 862, 856, 853, 757, 699, 618 cm^{-1}; HRMS, calcd for $C_{13}H_{19}N$ 189.1517, found 189.1523 ± 0.0009 amu.

Product of the Reaction of Benzylamine Coupled with 3-Hexyne (Example 2, Table I). Experimental carried out the same as in example 1 except that 3-hexyne was used to yield 0.48 g of a pale yellow oil shown to be 98% pure by ^{1}H NMR and GC analyses (68% isolated yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (t, J = 7.6 Hz, 3 H), 1.00 (t, J = 7.0 Hz, 3 H), 1.44 (br s, 2 H), 1.71–1.82 (m, 1 H), 1.95–2.01 (m, 3 H), 4.45 (s, 1 H), 5.51 (t, J = 7.0 Hz, 1 H), 7.15–7.35 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.06, 14.49, 20.75, 21.55, 60.66, 126.48, 126.71, 126.97, 128.14, 143.37, 144.77; IR (neat) 3372, 3296, 3026, 2962, 2932, 2872, 1491, 1465, 862, 764, 731, 700, 635 cm^{-1}; HRMS, calcd for $C_{13}H_{19}N$ 189.1517, found 189.1517 ± 0.0004 amu.

Product of the Reaction of Benzylamine Coupled with 1-(Trimethylsilyl)propyne (Example 3, Table I). Experimental carried out the same as in example 1 except that 1-(trimethylsilyl)propyne was used to yield 0.613 g of product shown to be 98% pure by GC and ^{1}H NMR analyses (75% isolated yield). Regiochemistry was determined by the observation of ^{29}Si satellites in the ^{13}C spectrum at shifts of δ −0.03, 121.90: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 9 H), 1.49 (s, 2 H), 1.57 (s, 3 H), 4.32 (s, 1 H), 5.68 (s, 1 H), 7.10–7.25 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.03 (q, J = 118 Hz), 18.91 (q, J = 123 Hz), 64.01 (d, J = 134 Hz), 121.90 (d, J = 132 Hz), 127.00 (d, J = 180 Hz), 128.25 (d, J =176 Hz), 143.99 (s), 156.31 (s), one peak obscured; IR (neat) 3377, 3291, 3027, 2954, 2897, 1618, 1615, 1601, 1492, 1452, 1435, 1376, 1258, 1248, 871, 854, 836, 768, 761, 746, 700, 639, 631, 614 cm^{-1}; HRMS, calcd for $C_{13}H_{21}NSi$ 219.1443, found 219.1443 ± 0.0009 amu.

Product of the Reaction of Benzylamine Coupled with 5-Cyano-1-pentyne (Example 4, Table I). Same procedure as in experimental 1 except that 5-cyano-1-pentyne was used. Purified by column chromatography (pentane/ether/triethylamine, 15:5:1) to yield 0.365 g of a yellow oil shown to be 95% pure by GC and ^{1}H NMR analyses (48% isolated yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (br s, 2 H), 1.72 (five lines, J = 7.0 Hz, 2 H), 2.18 (q, J = 7.0 Hz, 2 H), 2.29 (t, J = 7.0 Hz, 2 H), 4.49 (d, J = 6.6 Hz, 1 H), 5.57 (dt, J_1 = 15.0 Hz, J_2 = 6.0 Hz, 1 H), 5.70 (dd, J_1 = 15.0 Hz, J_2 = 6.6 Hz, 1 H), 7.24 (m, 1 H), 7.31–7.32 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.31 (t, J = 133 Hz), 24.68 (t, J = 131 Hz), 30.76 (t, J = 130 Hz), 57.44 (d, J = 140 Hz), 119.45 (s), 126.38 (d, J = 155 Hz), 126.87 (d, J = 161 Hz), 127.11 (d, J = 150 Hz), 128.40 (d, J = 150 Hz), 136.25 (d, J = 154 Hz), 144.53 (s); IR (neat) 3375, 3365, 3296, 3061, 3027, 2940, 2894, 2851, 2245, 1601, 1491, 1453, 970, 762, 701 cm^{-1}; HRMS, calcd for $C_{13}H_{16}N_2$ 200.1313, found 200.1313 ± 0.0006 amu.

Product of the Reaction of Hexylamine Coupled with 3-Hexyne (Example 5, Table I). To a solution of hexylamine (0.372 g, 3.68 mmol) in THF (20 mL) at −78 °C was added *n*-butyllithium (2.20 mL of a 1.68 M solution in hexane, 3.68 mmol) and allowed to stir for 5 min. Chlorotrimethylsilane (0.400 g, 3.68 mmol) was added and allowed to stir for 5 min. *n*-Butyllithium (2.20 mL of a 1.68 M solution in hexane) was added and allowed to stir for an additional 5 min. This solution was added to a solution of $Cp_2Zr(Me)Cl$ (1.3 g, 3.68 mmol) in THF (20 mL) at −78 °C and allowed to stir for 5 min. The reaction mixture was allowed to warm to 0 °C; 3-hexyne (0.333 g, 3.68 mmol) was added and the reaction mixture was heated to 40 °C overnight. Methanol (2 mL) was added and the reaction mixture was allowed to stir for 1 h at room temperature. The solvent was removed (rotary evaporator) to yield a semisolid. This was extracted into ether (25 mL) washed with water, brine and dried over $MgSO_4$. The solvent was removed to yield an oil; purification by flash chromatography (pentane/ether, 19:1) gave 0.446 g of a pale yellow oil shown to be 98% pure by GC and ^{1}H NMR analyses, (66% isolated yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, J = 6.0 Hz, 3 H), 0.94–1.02 (m, 6 H), 1.26–1.50 (m, 10 H), 2.04 (m, 4 H), 3.20 (t, J = 6.0 Hz, 1 H), 5.23 (t, J = 7.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.88 14.36, 14.61, 20.38, 20.61, 22.50, 26.17, 31.79, 36.32, 57.82, 126.53, 144.06; IR (neat) 3381, 3316, 2961, 2930, 2872, 2859, 1635, 1617, 1466, 1376, 857, 810 cm^{-1}; HRMS, no M$^+$ peak was observed, calcd for $C_{12}H_{24}N$ $[M - H]^+$ 182.1908, found 182.1908 ± 0.0003 amu.

Products of the Reaction of Hexylamine Coupled with 1-Hexyne (Example 6, Table I). Same procedure as in example 5 except that 1-hexyne was used to give a mixture of two regioisomers which could be partially separated by flash chromatography (pentane/triethylamine, 19:1) as 0.339 g of a pale yellow oil shown to be greater than 95% pure by GC and ^{1}H NMR analyses (50% isolated yield). Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85–0.91 (m, 6 H), 1.28–1.38 (m, 14 H), 1.99 (m, 2 H), 3.20 (m, 1 H), 5.35 (dd, J_1 = 14 Hz, J_2 = 7.2 Hz, 1 H), 5.46 (dt, J_1 = 14 Hz, J_2 = 7.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.83, 13.95, 22.12, 22.58, 25.85, 31.53, 31.79, 31.91, 38.03, 53.89, 129.82, 135.30; ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.80 (q, J = 118 Hz), 31.80 (t, J = 125 Hz), 38.00 (t, J = 125 Hz), 53.80 (d, J = 134 Hz), 129.70 (d, J = 151 Hz), 135.20 (d, J = 148 Hz) (other peaks obscured); IR (neat) 3369, 3295, 2958, 2931, 2916, 2872, 2858, 1610, 1598, 1580, 1466, 1459, 1439, 1378, 1342, 968, 925, 888, 842, 823, 809 cm^{-1}; HRMS, calcd for $C_{12}H_{24}N$ $[M - H]^+$ 182.1908, found 182.1908 ± 0.0003 amu. Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88–0.94 (m, 6 H), 1.27–1.45 (m, 14 H), 1.93–2.09 (m, 2 H), 3.26 (t, J = 6.3 Hz, 1 H), 4.77 (d, J = 1.5 Hz, 1 H), 4.90 (s, 1 H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 13.97, 22.59, 22.65, 26.06, 30.46, 31.64, 31.92, 36.29, 56.95, 108.14, 154.02, one carbon obscured; ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.90 (q, J = 124 Hz), 22.67 (t, J = 123 Hz), 36.20 (t, J = 129 Hz), 56.90 (d, J = 137 Hz), 108.10 (t, J = 150 Hz), 154.00 (s) (other peaks obscured by major isomer); IR (neat) 3375, 3295, 3079, 2958, 2926, 2872, 2859, 1642, 1615, 1467, 1378, 1120, 892, 850, 822, 808, 784, 733, 729 cm^{-1}; HRMS, calcd for $C_{1H24}N$ $[M - H]^+$ 182.1908, found 182.1908 ± 0.0003 amu.

Product of the Reaction of Hexylamine Coupled with Phenylacetylene (Example 7, Table I). Same procedure as in example 5 except that phenylacetylene was used to give 0.426 g of a yellow oil which was shown to be 93% by GC and ^{1}H NMR analyses (58% isolated yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3 H), 1.32 (m, 6 H), 1.48 (m, 4 H), 3.45 (q, J = 6.3 Hz, 1 H), 6.14 (dd, J_1 = 16.0 Hz, J_2 = 7.0 Hz, 1 H), 6.46 (d, J = 16.0 Hz, 1 H), 7.21–7.39 (m, 5 H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 13.87 (q, J = 124 Hz), 22.50 (t, J = 124 Hz), 25.76 (t, J = 125 Hz), 31.79 (t, J = 124 Hz), 38.01 (t, J = 127 Hz), 54.07 (d, J = 134 Hz), 126.18 (d, J = 151 Hz), 127.03 (d, J = 153 Hz), 128.47 (d, J = 159 Hz), 128.70 (d, J = 147 Hz), 135.41 (d, J = 147 Hz), 137.33 (s); IR (neat) 3368, 3025, 2956, 2928, 2870, 2856, 1944, 1874, 1800,

1670, 1598, 1578, 1494, 1466, 1449, 1378, 965, 815, 748, 693 cm^{-1}; HRMS, calcd for $C_{14}H_{21}N$ 203.1674, found 203.1674 ± 0.0004 amu.

Product of the Reaction of Hexylamine Coupled with 1-(Trimethylsilyl)propyne (Example 8, Table I). Same procedure as in example 5 except that 1-(trimethylsilyl)propyne was used to give 0.627 g of a yellow oil shown to be greater than 98% pure by GC and ^1H NMR analyses (80% isolated yield). Regiochemistry was determined by the observation of ^{29}Si satellites in the ^{13}C NMR spectrum on peaks at δ −0.08 and 122.4: ^1H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 9 H), 0.82 (t, J = 7.0 Hz, 3 H), 1.22 (m, 10 H), 1.69 (d, J = 1.8 Hz, 3 H), 3.16 (t, J = 7.0 Hz, 1 H), 5.29 (s, 1 H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ −0.08 (q, J = 119 Hz), 13.90 (q, J = 124 Hz), 17.20 (q, J = 124 Hz), 22.50 (t, J = 124 Hz), 25.90 (t, J = 119 Hz), 31.80 (t, J = 128 Hz), 35.70 (t, J = 126 Hz), 61.10 (d, J = 132 Hz), 122.40 (d, J = 130 Hz), 158.10 (s); IR (neat) 3375, 3298, 2954, 2858, 1615, 1467, 1458, 1442, 1420, 1405, 1377, 1341, 1259, 1248, 926, 860, 847, 836, 790, 770, 689, 621, 615, 576 cm^{-1}; HRMS, calcd for $C_{11}H_{24}NSi$ $[M - CH_3]^+$ 198.1678, found 198.1674 ± 0.0007 amu.

Product of the Reaction of Hexylamine Coupled with 1-(*tert*-Butyldimethylsilyl)-1-hexyne (Example 9, Table I). Same procedure as in example 5 except that 1-*tert*-butyldimethylsilyl-1-hexyne was used to yield 0.768 g of a pale yellow oil shown to be 95% pure GC and ^1H NMR analyses (68% isolated yield). Regiochemistry was determined by the observation of ^{29}Si satellites in the ^{13}C NMR spectrum on peaks at δ −4.10 and 117.85: ^1H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 3 H), 0.07 (s, 3 H), 0.86 (m, 15 H), 1.25 (m, 13 H), 1.50 (m, 1 H), 2.00 (m, 1 H), 2.16 (m, 1 H), 3.25 (m, 1 H), 5.38 (s, 1 H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ −4.03, 13.94, 17.04, 22.61, 23.30, 26.12, 26.61, 31.97, 32.83, 34.63, 37.53, 57.69, 117.85, 165.03, one carbon obscured; ^{13}C NMR (67.9 MHz, $CDCl_3$) δ −4.10 (q, J = 110 Hz), 13.84 (q, J = 124 Hz), 16.90 (s), 26.50 (q, J = 124 Hz), 37.30 (t, J = 126 Hz), 57.50 (d, J = 134 Hz), 117.73 (d, J = 128 Hz), 164.80 (s), (other peaks obscured); IR (neat) 3374, 3297, 2955, 2933, 2928, 2857, 1612, 1468, 1464, 1388, 1378, 1361, 1248, 1007, 937, 836, 804, 778, 576 cm^{-1}; HRMS, calcd for $C_{18}H_{39}NSi$ 297.2851, found 297.2848 ± 0.0013 amu.

Product of the Reaction of 2-Thiophenemethylamine Coupled with 3-Hexyne (Example 10, Table I). To a solution of 2-thiophenemethylamine (0.416 g, 3.68 mmol) in THF (20 mL) at −78 °C was added *n*-butyllithium (2.30 mL of a 1.61 M solution in hexane, 3.68 mmol), and the solution was allowed to stir for 5 min. Chlorotrimethylsilane (0.400 g, 3.68 mmol) was added and allowed to stir for 5 min. *n*-Butyllithium (2.30 mL of 1.61 M solution in hexane, 3.68 mmol) was added, and the reaction mixture was allowed to stir an additional 5 min. This solution was added to a solution of $Cp_2Zr(Me)(Cl)$ (1.3 g, 4.78 mmol) in THF (20 mL) at −78 °C and allowed to stir for 5 min. The reaction mixture was warmed to 0 °C, 3-hexyne (0.333 g, 3.68 mmol) was added, and the reaction was allowed to warm to room temperature and stir overnight. Methanol (2 mL) was added and allowed to stir for 1 h at room temperature. The solvent was removed (rotary evaporator) to yield a semisolid. This was extracted into ether (25 mL), washed with water and brine, and dried over $MgSO_4$. The solvent was removed to yield an oil which was purified by flash chromatography (pentane/ether, 15:1) to yield 0.471 g of a yellow oil shown to be 96% pure by GC and ^1H NMR analyses (63% isolated yield): ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 3 H), 1.00 (t, J = 7.5 Hz, 3 H), 1.06 (s, 2 H), 1.90–2.30 (m, 4 H), 4.07 (s, 1 H), 5.51 (t, J = 7.0 Hz, 1 H), 6.87–6.89 (m, 2 H), 7.12 (d, J = 7.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.04, 14.15, 20.54, 20.87, 57.07, 123.21, 123.54, 126.10, 127.01, 143.11, 149.88; IR (neat) 3387, 3362, 2962, 2944, 2932, 2894, 2872, 1463, 1455, 1438, 1373, 1064, 851, 831, 813, 749, 696, 614, 570, 537, 524, 518, 513, 510, 508, 504 cm^{-1}; HRMS, calcd for $C_{11}H_{17}NS$ 195.1081, found 195.1081 ± 0.0003 amu.

Product of the Reaction of Furfurylamine Coupled with Phenylacetylene (Example 11, Table I). Same procedure as in example 10 except that furfurylamine and phenylacetylene were used to yield 0.476 g of a yellow oil shown to be 95% pure by GC and ^1H NMR analyses (62% isolated yield): ^1H NMR (300 MHz, $CDCl_3$) δ 1.61 (br s, 2 H), 4.64 (d, J = 7.0 Hz, 1 H), 6.14 (t, J = 1.8 Hz, 1 H), 6.27 (m, 2 H), 6.35 (dd, J_1 = 16.0 Hz, J_2 = 6.0 Hz, 1 H), 6.56 (d, J = 16.0 Hz, 1 H), 7.14–7.36 (m, 5 H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 51.60 (d, J = 137 Hz), 104.60 (d, J = 172 Hz), 109.90 (d, J = 172 Hz), 126.20 (d, J = 155 Hz), 127.20 (d, J = 160 Hz), 128.20 (d, J = 160 Hz), 130.00 (d, J = 155 Hz), 130.40 (d, J = 158 Hz), 136.40 (s), 141.20 (d, J = 200 Hz), 157.00 (s); IR (neat) 3371, 3305, 3295, 3144, 3114, 3105, 3058, 3025, 1617, 1611, 1577, 1502, 1448, 1311, 1224, 1172, 1146, 1071, 1028, 1009, 966, 921, 884, 823, 808, 739, 598, 544, 518, 506, 504, 500 cm^{-1}; HRMS, calcd for $C_{13}H_{13}NO$ 199.0997, found 199.0995 ± 0.0007 amu.

Products of the Reaction of Furfurylamine Coupled with 1-Pentyne (Example 12, Table I). Same procedure as in example 10 except that furfurylamine and 1-pentyne were used to yield 0.400 g of a yellow oil which was shown to be an inseparable mixture of the two possible regioisomeric allylic amines by ^1H NMR. Mixture is 97% pure by GC and ^1H NMR analyses (63% isolated yield). Major isomer: ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 7.0 Hz, 3 H), 1.41 (six lines, J = 7.0 Hz, 2 H), 1.57 (s, 2 H), 2.03 (dq, J_1 = 7.0 Hz, J_2 = 2.3 Hz, 2 H), 4.49 (d, J = 5.4 Hz, 1 H), 5.64–5.67 (m, 2 H), 6.11 (d, J = 3.0 Hz, 1 H), 6.28 (m, 1 H), 7.34 (d, J = 1.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.2 (q, J = 134 Hz), 21.3 (q, J = 134 Hz), 34.00 (t, J = 134 Hz), 51.7 (d, J = 135 Hz), 104.40 (d, J = 187 Hz), 109.8 (d, J = 187 Hz) 130.7 (d, J = 160 Hz), 131.6 (d, J = 187 Hz), 141.4 (d, J = 214 Hz), 157.9 (s); IR (mixture of isomers) (neat) 3378, 3346, 3325, 3269, 3010, 2931, 2910, 2872, 1600, 1595, 1504, 1464, 1438, 1379, 1175, 1147, 1072, 1008, 969, 927, 873, 734, 514 cm^{-1}; HRMS (mixture of isomers), calcd for $C_{10}H_{15}NO$ 165.1153, found 165.1153 ± 0.0006 amu. Minor isomer: ^1H NMR (300 MHz, $CDCl_3$) δ 1.90–2.00 (m, 2 H), 4.95 (s, 1 H), 5.10 (s, 1 H), 5.59 (m, 1 H), 5.71 (m, 1 H), 6.15 (m, 1 H), other peaks obscured by major isomer; ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.75, 21.00, 34.85, 54.64, 104.40, 105.26, 109.87, 141.33, 150.211, 157.827; ^{13}C NMR (75 MHz, $CDCl_3$) δ (other peaks obscured by major isomer peaks) 54.45 (d, J = 161 Hz), 105.53 (d, J = 184 Hz), 109.85 (t, J = 184 Hz), 150.30 (s), 157.75 (s).

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Supplementary Material Available: Crystallographic procedures and tables of crystal data and intramolecular distances and angles for **2b** (9 pages); table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.