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Zirconium Complexes Supported by Imidazolones: Synthesis, Characterization, and Application of Precatalysts for the Hydroamination of Aminoalkenes

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Dimeric zirconium benzyl and amide complexes supported by an imidazolone framework have been successfully synthesized and fully characterized. The amide complexes were found to be effective catalysts for intramolecular hydroamination of primary and secondary amines.

Hydroamination has emerged as an atom-economical and one-step strategy for constructing nitrogen-containing molecules via functionalization of an N−H bond across a carbon−carbon unsaturation.[1] Eliciting significant interest among chemists over the years, the advantages of hydroamination have led to exploitation of much of the periodic table in an effort to improve the effectiveness and complexity of this process.[2−4] Over the past decade, the application of group 4 transition metal to intramolecular hydroamination of C−C multiple bonds with primary amines has arisen as one such alternative, with the additional benefit of commercial availability, low cost, and low toxicity.[5]

Previously, we reported the isolation of a zirconium complex bearing a unique η^2(N,C) imidazolyl carbene moiety resulting from the C−N cleavage of an amino-linked nitrogen heterocyclic carbene.[6] Interestingly, such imidazolyl carbene moieties have been implicated as intermediate species for scandium-, yttrium-, and uranium-mediated ring opening of imidazole rings.[7] Unfortunately, having a highly reactive imidazolyl carbene moiety in a metal complex may circumvent the stability of the complex that is important to the catalytic application. To eliminate the chemical promiscuity of the imidazolyl carbene group, while maintaining the desired imidazole scaffold, we have turned our attention to imidazolones, which are easily assembled five-membered heterocyclic molecules containing N and O binding sites. The imidazolones are known to

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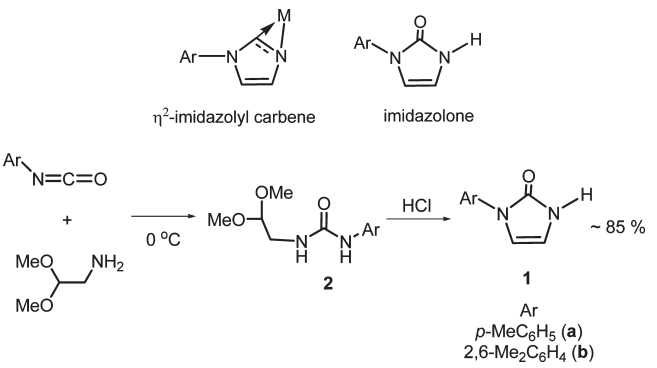
Scheme 1



manifest a broad range of biological activities,[8] but they are rarely employed as ligands for modulating the transition-metal reactivities.[9] With this in mind, we have sought to prepare the first example of zirconium complexes supported by an imidazolone ligand. In this contribution, we report the characterization of imidazolonated benzyl and amide zirconium complexes and an examination of their catalytic activity toward intramolecular hydroamination.

Result and Discussion

The preparation of imidazolone **1** was carried out in accord with a previous report by Joule et al., as shown in Scheme 1.[10] The 4-methylphenyl and 2,6-dimethylphenyl isocyanates were each reacted with acetaldehyde dimethyl acetal to give the corresponding urea **2**. Cyclization upon treatment of acid affords the imidazolones **1**. Imidazolone **1a** reacts readily with $Zr(CH_2Ph)_4$ in ether to furnish compound **3a** in moderate yield (Scheme 2). The ^1H NMR spectroscopic features of **3a** display a new singlet integrating to three protons at 2.31 ppm for the tolyl group of the imidazolone ligand and a broad peak for the benzyl moieties at 2.33 ppm integrating to a sum of six protons. Similar attempts were carried out to prepare an analogous compound of **3b** using ligand **1b**, but multiple products complicated the isolation of the pure product.[11] A single-crystal X-ray diffraction study was undertaken to determine the connectivity in **3a**. The structure model of **3a** in Figure 1 demonstrates a noncentrosymmetric dimer, with each zirconium atom bearing two η^1-benzyl groups, one η^2 benzyl group, and two bridging imidazolone ligands with a μ-N−C−O binding site, consistent with the solution NMR analysis. On the basis of a search of the Cambridge Structural Database,[12] we believe that compound **3a** represents the first isolated zirconium complex supported by imidazolonates (Figure 1). Both the C−O (O(1)−C(8) = 1.292(5) Å and O(2)−C(18) = 1.297(5) Å) and the C−N bonds

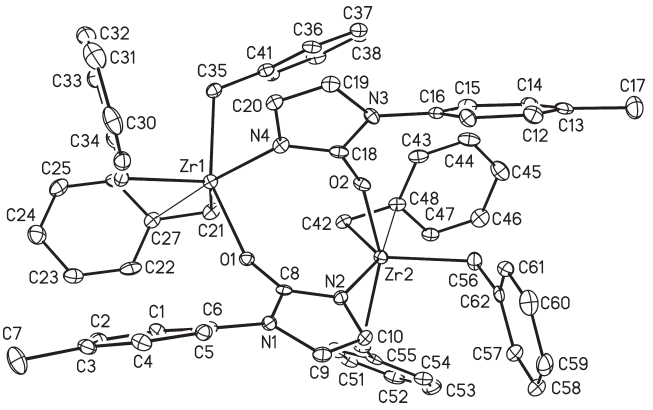
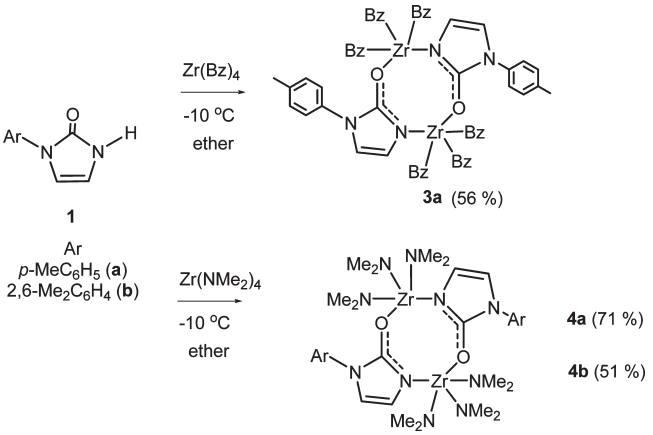


Figure 1. Molecular diagram of **3a** with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms have been omitted for clarity.

Scheme 2



(N(2)−C(8) = 1.327(5) Å and N(4)−C(18) = 1.334 (5) Å) lie between single- and double-bond distances, implying some electronic conjugation over the O−C−N moiety in the bridging imidazolone ring.[13] The Zr−N distances of 2.263(4) and 2.267(3) Å in **3a** are considered to be at the longer range of an anionic Zr−N amido bond,[14] but the Zr−O distances of 2.072(3) and 2.058(3) Å are shorter than those observed in other Zr(VI) amidate and ureate complexes (∼2.2−2.3 Å).[14a,15] Alternatively, the synthesis of imidazolone zirconium amide complexes **4** is straightforward. The addition of 1 equiv of **1a** or **1b** to an ether solution of $Zr(NMe_2)_4$ furnishes the pale yellow solid **4**. Like **3a**, **4b** exhibits a dimeric structure containing two bridging imidazolones (Figure 2). The π-donor character of the amido ligands in **4b** gives rise to a strong trans effect on the imidazolonate ligand, as witnessed by the slightly elongated bond distance of Zr−N (2.3635(19) Å) and Zr−O (2.1202(15) Å) in comparison with compound **3a** (vide supra).

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(11) We encountered problems with isolating and fully characterizing the product from the reaction of **1b** and $Zr(Bz)_4$. However, a single-crystal X-ray analysis for the crystal structure of **3b** was obtained (Figure S2; see the Supporting Information).

(12) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380–388.

(13) (a) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G. *J. Chem. Soc., Perkin Trans.* **1987**, S1. (b) Wu, Z. Z.; Zhou, X. G.; Zhang, W.; Xu, Z.; You, X. Z.; Huang, X. Y. *J. Chem. Soc., Chem. Commun.* **1994**, 813.

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(15) Leitch, D. C.; Beard, J. D.; Thomson, R. K.; Wright, V. A.; Patrick, B. O.; Schafer, L. L. *Eur. J. Inorg. Chem.* **2009**, 2691–2701.

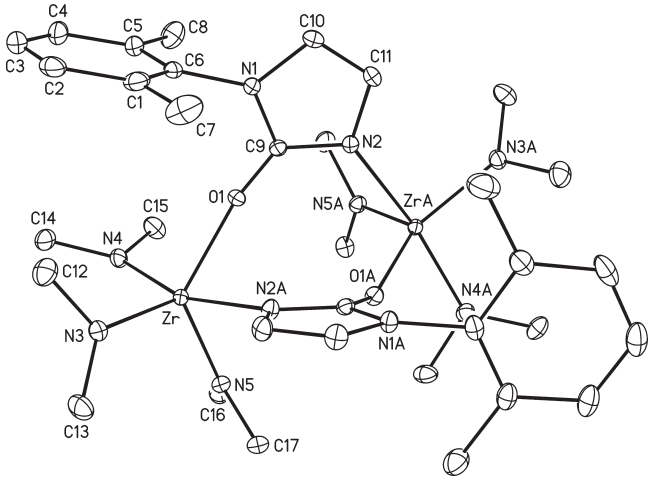
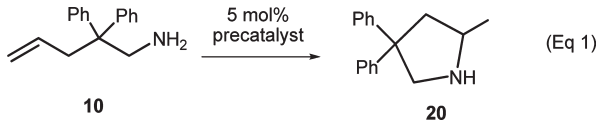


Figure 2. Molecular diagram of **4b** with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms have been omitted for clarity.

Table 1. Intramolecular Hydroamination and Condition Optimization



10 **20**

entry	precatalyst	temp (°C)	time (h)[a]	yield (%)[b]
1	**3a**	70	24	0
2	**4a**	70	7.5	>95
3	**4b**	70	4.5	>95
4	$Zr(NMe_2)_4$	70	7	>95
5	**4b**	130	0.25	>95

[a] Time for >99% conversion in toluene-d_8. [b] Yield determined by ^{1}H NMR spectroscopy on the basis of an internal standard.

Hydroamination catalysis with high-oxidation-state early transition metals has received a considerable amount of attention, particularly the intramolecular hydroamination of aminoalkenes. Preliminary screening experiments were undertaken to determine the viability of complexes **3**, **4a**, and **4b**, as precatalysts for the intramolecular hydroamination of 2,2-diphenyl-4-pentenylamine (**10**) substrate (eq 1). Tests were conducted on the substrate with a loading of 5 mol % of catalyst precursor and substrate and monitored at 70 °C by NMR spectroscopy. As seen in Table 1, the benzyl complex **3a** shows no catalytic activity (entry 1) even after prolonged heating for 24 h. When the reaction was performed in the presence of either amide complex, the substrate **10** underwent a successful cyclization process to **20** (entries 2 and 3), with precatalyst **4b** being found to be the most active. It was reported that a corresponding starting reagent such as $Zr(NMe_2)_4$ could also mediate an intramolecular hydroamination process.[16,17] Therefore, the possibility of the residual $Zr(NMe_2)_4$ mediating the reaction should not be ruled out. To verify such a notion, a separate experiment containing 5% mol of $Zr(NMe_2)_4$ was conducted. The results indicated that indeed compound **4b** is superior to $Zr(NMe_2)_4$ (entry 4), as the latter requires a longer period of time (7 h) to achieve a full conversion under similar reaction conditions. To our delight, the conversion time of **10** can be successfully shortened to 0.25 h by increasing the temperature to 130 °C (entry 5).

Having an optimized result in hand, the generality of the cyclization process was then extended with various aminoalkene substrates (Table 2). The results indicate that substrates with larger geminal disubstituents react very efficiently, achieving a 95% yield in around 1 h (entries 1−3 and 6, Table 2). When the size of the geminal group is reduced to less bulky methyl groups (**13**), a much longer reaction time is required to increased (24 h) to attain a good yield of the cyclic product **23** (entry 4). Nevertheless, transformation of the aminoalkene **14** (entry 5, Table 2) containing only one geminal aryl group proceeded with a higher conversion rate in 4 h in comparison to substrate **13**. In general, diastereoselectivity is considered to be moderate for substrates **12** (entry 3) and **14** (entry 5) with cis isomers as major products.

Very interestingly, **4b** exhibits significant reactivity toward the cyclization of secondary aminoalkenes of **16** and **17**, facilitating the formation of products **26** and **27**, respectively, in high yield (entries 7 and 8). The reactivity of a secondary aminoalkene was established by the emergence of characteristic singlet peaks at 2.07 ppm ($N(CH_3)$) and 1.11 ppm ($CH-CH_3$) for product **26** in proton NMR analysis. This reactivity is in contrast with the case for previously reported highly active Ti and Zr hydroamination systems exhibiting a lack of reactivity with secondary amines, which is usually attributed to an inability to form the imido species with the secondary amine.[18] There are only limited examples of neutral group 4 metal catalysts mediated the cyclization of secondary aminoalkenes.[5l,19] Although still speculative at this juncture, this result may interpreted as **4b** invoking uncommon catalytic behavior for the group 4 early transition metal, operating upon reactivity of σ-bond insertion. Such an operating mechanism is quite common in the trivalent lanthanide system.[20] Nevertheless, the several intriguing mechanistic possibilities of the [2 + 2] cycloaddition/imido route have not been excluded yet. Finally, it is worth mentioning that the cyclization reactions of aminoalkenes can also proceed as effectively as with compound **4b** by just adding catalytic equal amounts of imidazolones and $Zr(NMe_2)_4$ in situ. For example, a full conversion of substrate **10** can be achieved within 20 min upon mixing 5 mol % of Zr amide and imidazolone **2b** in situ. From a synthetic perspective, the combined imidazolone ligand/zirconium catalysts represent a unique fast-track manifold for tuning the modularity without resorting to the laborious effort of preparing and purifying the metal−ligand complexes prior to screening and tuning.

Conclusion

In summary, zirconium benzyl and amide complexes supported by imidazolones have been successfully synthesized and characterized. The amide complexes (**4**) show good catalytic activity for intramolecular hydroamination of primary and more importantly, secondary amines. Additional reactions, as

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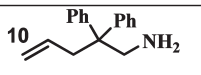
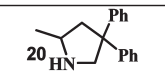
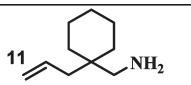
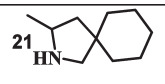
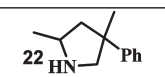
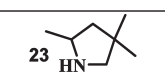
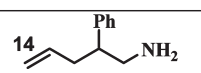
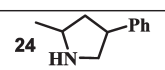
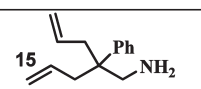
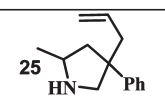
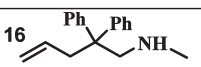
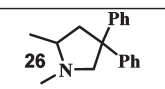
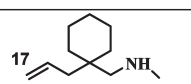
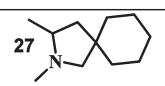
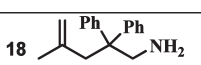
(17) Bexrud, J. A.; Beard, J. D.; Leitch, D. C.; Schafer, L. L. *Org. Lett*. **2005**, *7*, 1959–1962.
(18) (a) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc*. **1992**, *114*, 1708. (b) Baranger, A. M.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc*. **1993**, *115*, 2753. (c) Johnson, J. S.; Bergman, R. G. *J. Am. Chem. Soc*. **2001**, *123*, 2923.
(19) (a) Stubbert, B. D.; Marks, T. J. *J. Am. Chem. Soc*. **2007**, *129*, 6149–6167.
(20) (a) Hong, S.; Marks, T. J. *Acc. Chem. Res*. **2004**, *37*, 673. (b) Gagne, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc*. **1992**, *114*, 275.

Table 2. Hydroamination of Various Aminoalkenes with Compound 4b[a]

Entry	Aminoalkene	Product	% mol	Time(hour)[b]	Yield(%)[c]
1			5	0.25	>95 (95)
2			5	1.5	>95 (86)
3			5	1.5	93 (87)[d] cis/trans:4/1[e]
4			10	24	79
5			10	4	82 (61)[d] cis/trans:7/3[e]
6			5	0.75	>95 (91)[d] cis/trans:3/2[e]
7			10	19	88
8			10	24	86
9			5	3	87

[a] The reaction was conducted at 130 °C. [b] Time for > 99% conversion in toluene-d_8. [c] Yield determined by ^{1}H NMR spectroscopy on the basis of the internal standard; values in brackets are isolated yields. [d] Isolated yield based on the corresponding benzoylamide product from the derivatization of pyrrolidine with benzonyl chloride prior to isolation. [e] Diastereomeric ratio determined by ^{1}H NMR.

well as detailed kinetic and mechanistic investigations, are underway to gain more insight into the catalytic system.

Experimental Section

General Procedure. All air-sensitive manipulations were performed under an atmosphere of nitrogen using Schlenk techniques and/or a glovebox. Toluene, hexane, THF, and ether were purified by passage through a column of activated alumina using a solvent purification system purchased from Innovative Technology, Inc. Deuterated benzene and toluene were dried by vacuum transfer from activated molecular sieves. $Zr(NMe_2)_4$ was purchased from Aldrich Chemical Co. and used without further purification. ^{1}H and ^{13}C NMR spectra were run on Bruker 300, 400, and 500 MHz spectrometers using the residual proton of the deuterated solvent for reference. The preparation of imidazolone ligands **1a**.**b** was carried out on the basis of previous reports.[10] Aminoalkenes of the substrates 2,2-diphenyl-4-penten-1-amine (**10**),[21] (1-allylcyclohexyl)methylamine (**11**),[22] 2-methyl-2-phenyl-4-pentenylamine (**12**),[23] 2,2-dimethyl-4-pentenylamine (**13**),[24] 2-phenyl-4-pentenylamine (**14**),[23] 2-allyl-2-phenyl-4-pentenylamine (**15**),[5c] *N*-methyl-2,2-diphenyl-4-pentenylamine (**16**),[2g] (1-allylcyclohexyl)-*N*-methyl-methylamine (**17**),[23] 4-methyl-2,2-diphenyl-4-pentenylamine (**18**),[2g] and 2,2-diphenylhex-4-en-1-amine (**19**)[20b] were synthesized according to according to previous literature methods. Hydroamination products of **20**−**29** are known compounds and their NMR spectroscopic data were compared to the literature data.[2g,5c,20b,21−24]

Synthesis of [Zr(CH$_2$Ph)$_3$(1-(*p*-tolyl)-1*H*-imidazol-2-olate)]$_2$ (3a). In a 20 mL screw-capped vial equipped with a magnetic stir bar was added $Zr(CH_2Ph)_4$[25] (131 mg, 0.287 mmol) in 2 mL of an ether solution containing **1a** (50 mg, 0.287 mmol) at −10 °C. The mixture was reacted for 30 min at room temperature, during which time a yellow precipitate was formed. Then, the solvent was evaporated to dryness. The yellow solid was washed with iced ether and dried in vacuo. The product was further purified by recrystallization from CH_2Cl_2/hexane solution (3:1 volume) at −20 °C. Yield: 56% (86 mg). ^{1}H NMR (CD_2Cl_2, 500 MHz, −10 °C): 7.29−7.21 (m, 10H, Ar-*H*), 7.18−7.12 (m, 9H, Ar-*H*), 6.39 (s, 1H, C*H*), 4.50 (s, 1H, C*H*), 2.33 (s, 6H, CH_2Ph), 2.31 (s, 3H, ArCH_3). ^{13}C NMR (CD_2Cl_2, 125 MHz, −10 °C): 155.2 (NCN), 138.6 (*Ar*), 138.3 (*Ar*), 133.5 (*Ar*), 130.1 (*Ar*-H), 129.3 (*Ar*-H), 128.5 (*Ar*-H),

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125.5 (*Ar*-H), 124.4 (*Ar*-H), 120.8 (*C*H), 114.0 (*C*H), 54.4 (*C*H_2-Ph), 21.1 (Ar*C*H_3). Anal. Calcd for $C_{62}H_{60}N_4O_2Zr_2$: C, 69.23; H, 5.62; N, 5.21. Found: C, 68.92; H, 5.71; N, 5.12.

Synthesis of [Zr(NMe$_2$)$_3$(1-(4-methylphenyl)-1*H*-imidazol-2-olate)] (4a). To a solution of $Zr(NMe_2)_4$ (153 mg, 0.574 mmol) in ether (2 mL) was slowly added 1-(tolyl)-2-imidazolone (100 mg, 0.574 mmol) which was dissolved in 5 mL of ether at −10 °C. After the mixture was stirred for 10 min, it was warmed to room temperature. The solution was removed in vacuo to afford a pale yellow foamy compound. The compound was washed with *n*-hexane. The combined solution was concentrated to give a pale yellow solid compound. Yield: 71% (160 mg). ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): 7.32 (d, $^3J_{H-H}$ = 8 Hz, 2H, Ar-*H*), 6.97 (d, $^3J_{H-H}$ = 8 Hz, 2H, Ar-*H*), 6.45 (s, 1H, C*H*), 6.22 (s, 1H, C*H*), 3.13 (s, 18H, N*Me*$_2$), 2.02 (s, 3H, ArCH_3). ^{13}C NMR (C_6D_6, 100 MHz, 25 °C): 156.9 (N*C*N), 135.8 (*Ar*), 134.7 (*Ar*), 129.6 (*Ar*-H), 129.4 (*Ar*-H), 122.7 (*C*H), 112.7 (*C*H), 44.8 (N*Me*$_2$), 20.8 (Ar*C*H_3).

Synthesis of [Zr(NMe$_2$)$_3$(1-(2,6-dimethylphenyl)-1*H*-imidazol-2-olate)] (4b). To a solution of $Zr(NMe_2)_4$ (141 mg, 0.531 mmol) in ether (2 mL) was slowly added 1-(2,6-dimethylphenyl)-2-imidazolone (100 mg, 0.531 mmol) in 5 mL of ether at −10 °C. After the mixture was stirred for 30 min, it was warmed slowly to room temperature. The solvent was removed in vacuo to afford a yellow solid compound. The product was further purified by recrystallization from an ether solution at −20 °C. Yield: 51% (111 mg). ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): 6.97−6.87 (m, 3H, Ar-*H*), 6.32 (*s*, 1H, C*H*), 5.80 (*s*, 1H, C*H*), 3.04 (*s*, 18H, NCH_3), 1.99 (*s*, 6H, CH_3). ^{13}C NMR (C_6D_6, 100 MHz, 25 °C): 156.9 (N*C*N), 137 (*Ar*), 135.5 (*Ar*), 128.7 (*Ar*-H), 128.4 (*Ar*-H), 121.3 (*C*H), 112.6 (*C*H), 43.6 (N*Me*$_2$), 17.9 (Ar*C*H_3). Anal. Calcd for $C_{34}H_{58}N_{10}O_2Zr_2$: C, 49.72; H, 7.12; N, 17.05. Found: C, 49.03; H, 7.10; N, 16.54.

General Procedure for NMR-Scale Catalytic Intramolecular Hydroamination Reactions. In a drybox, the appropriate aminoalkenes (0.500 mmol) and catalyst **4b** (20.6 mg, 0.025 mmol) with the internal standard 1,3,5-trimethoxybenzene (16.8 mg, 0.04 mmol) were dissolved in deuterated toluene (1 mL), and the solution was loaded into a J. Young NMR tube. The tube was heated to 130 °C and was monitored by ^{1}H NMR spectroscopy for the disappearance of the olefinic peaks of the substrate relative to the internal standard. The yield of the reaction is based on the average value of two conducted experiments.

General Procedure for Isolated Yield of the Catalytic Intramolecular Hydroamination Reaction for Derivatization of Pyrrolidine with Benzonyl Chloride. The method of the catalysis is similar to the aforementioned NMR-scale method with the following few exceptions (Table 2, entries 3, 5, and 6). After the reaction mixture was heated to 130 °C for the appropriate time, it was cooled to room temperature. NEt_3 (3 equiv), benzoyl chloride (∼1.1 equiv), and dichloromethane (5.0 mL) were added to the reaction mixture and stirred at room temperature overnight. Then the solution was diluted with ether (25 mL) and washed with a saturated aqueous NH_4Cl solution. The organic solution was isolated and concentrated under vacuum. The residual product was further purified and isolated by flash chromatography.

Single-Crystal X-ray Characterization. Crystallographic data and refinement details for **3a**,**b** and **4b** are included in the Supporting Information, Tables S1−S3. Crystals were mounted using viscous oil or epoxy adhesive onto glass fibers and cooled to the data collection temperature. Data were collected using a Nonius Kappa CCD diffractometer (Mo Kα = 0.710 73 Å). Multiscan absorption corrections were employed. Unit cell parameters were obtained from 60 data frames, 0.3° ω, from three different sections of the Ewald sphere. Systematic absences are consistent with $P2_1$ and $P2_1/m$ for **3a**, *Cc* and *C*2/*c* for **4b**, and, uniquely, *Pnna* for **3b**. Solution in the centrosymmetric space group option, *C*2/*c*, for **4b** yielded chemically reasonable and computationally stable results of refinement. An exhaustive exploration of the centrosymmetric space group option in **3a** yielded bizarre results and was abandoned. The solution in $P2_1$ for **3a** was inspected with ADDSYM in Platon,[26] which did not report any overlooked symmetry. The Flack parameter in **3a** refined to nil, indicating the true hand of the data had been determined correctly. The structures were solved by direct methods and refined using the least-squares method on F^2. The compound molecules exhibit molecular, and for **3b** and **4b** also crystallographic, 2-fold symmetry. Structures **3a**,**b** each display cocrystallized methylene chloride solvent: one per compound molecule in **3a** and two per compound molecule in **3b** (one symmetry unique). The solvent molecule in **3b** was located disordered in two positions with a refined 86/14 refined site occupancy ratio. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Structure factors and anomalous dispersion coefficients are contained in the SHELXTL 6.12 program library.[27]

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Supporting Information Available: Text, figures, tables, and CIF files giving details on the preparation and characterization of ligands **1a**,**b** and crystallographic data for **3a**,**b** and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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