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Regioselective Synthesis of 2,3,4- or 2,3,5-Trisubstituted Pyrroles via [3,3] or [1,3] Rearrangements of *O*-Vinyl Oximes

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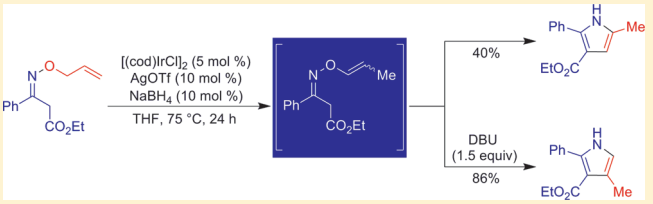
Supporting Information

ABSTRACT: The regioselective synthesis of 2,3,4- or 2,3,5-trisubstituted pyrroles has been achieved via [3,3] and [1,3] sigmatropic rearrangements of *O*-vinyl oximes, respectively. Iridium-catalyzed isomerization of easily prepared *O*-allyl oximes enables rapid access to *O*-vinyl oximes. The regioselectivity of pyrrole formation can be controlled by either the identity of the α-substituent or through the addition of an amine base. When enolization is favored, a [3,3] rearrangement followed by a Paal-Knorr cyclization provides a 2,3,4-trisubstituted pyrrole; when enolization is disfavored, a [1,3] rearrangement occurs prior to enolization to produce a 2,3,5-trisubstituted pyrrole after cyclization. Optimization and scope of the *O*-allyl oxime isomerization and subsequent pyrrole formation are discussed and mechanistic pathways are proposed. Conditions are provided for selecting either the [3,3] rearrangement or the [1,3] rearrangement product with β-ester *O*-allyl oxime substrates.



INTRODUCTION

The regioselective synthesis of substituted pyrroles is an important synthetic problem due to the prevalence of these structures in biologically active compounds and new materials.[1,2] A variety of methods have been developed and evaluated for the synthesis of substituted pyrroles[3] including the Paal−Knorr reaction,[4] the Piloty−Robinson synthesis,[5] 1,3-dipolar cycloadditions,[6] Hantzsch coupling reactions,[7] Buchwald−Hartwig coupling reactions,[8] metal-catalyzed cyclization,[9] C−H bond amination,[10] aza-Claisen rearrangements,[11] and substitution of the preformed heterocycle.[12−14] Although many of these methods provide efficient access to specific types of pyrroles, the development of complementary access to two different types of substitution patterns from the same starting material with a simple change in reaction conditions provides an appealing alternative for efficient library synthesis.

[3,3] Sigmatropic rearrangements, such as the Claisen and Fisher−indole reactions, are powerful methods for forming new carbon−carbon bonds.[15] [1,3] Rearrangements are less often observed for allyl vinyl ethers but have recently been studied and applied to diastereoselective ring contractions.[16−18] An underutilized example of a [3,3] rearrangement is the transformation of *O*-vinyl oximes to pyrroles. Trofimov and co-workers have shown that oximes can be added to acetylenes under strongly basic conditions to form *O*-vinyl oximes that rearrange to 1,4-imino carbonyl compounds and then participate in a Paal−Knorr cyclization and condensation sequence.[19,20] This transformation is an intriguing alternative approach to the synthesis of pyrroles because it uses the Paal−Knorr reaction sequence without requiring the synthesis of 1,4-dicarbonyl compounds. Unfortunately, the Trofimov reaction is limited in scope and efficiency. The strongly basic conditions limit functional group compatibility and the use of substituted alkynes is rare and gives regioisomeric mixtures of products in low yields (Scheme 1).[21] [1,3] Rearrangements of isoxazoles have been used as precursors to aziridines and azomethine ylides (Scheme 1);[22,23] however, to the best of our knowledge, the [1,3] rearrangement of *O*-vinyl oximes has not previously been reported as a method to access pyrrole precursors.

Recently, we developed a mild alkene isomerization method for the facile preparation of *O*-vinyl oximes from easily accessible *O*-allyl oximes.[24,25] A catalytic mixture of $[(cod)IrCl]_2$ (5 mol %), AgOTf (10 mol %), and $NaBH_4$ or $LiAlH_4$ (10 mol %) provided optimal results for this transformation in THF at 25 °C (Scheme 2).[26−28] The isomerization was shown to be tolerant of a variety of acetophenone derivatives with both electron-donating and electron-withdrawing substituents on the aryl ring, as well as alkyl, aryl, and ester substituents at the α-position. Only *E*-oxime isomers were isolated as 2:1mixtures of *Z*/*E* vinyl isomers in good yield. Dialkyl ketone-derived *O*-allyl oximes were also tolerated under the isomerization conditions but provided mixtures of oxime isomers as well as vinyl isomers.

Using our isomerization method, we have now broadened the range of pyrroles that can be accessed using sigmatropic reactions by developing single-flask procedures for the direct conversion of easily prepared *O*-allyl oximes to either 2,3,4- or 2,3,5-trisubstituted pyrroles via [3,3] or [1,3] rearrangements of *O*-vinyl oxime intermediates, respectively. Here we report the scope of the

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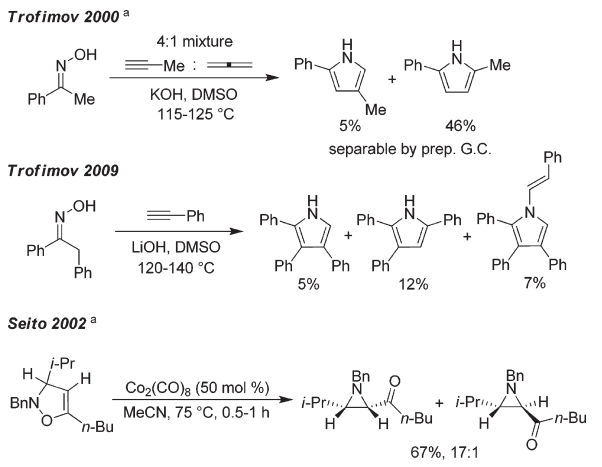
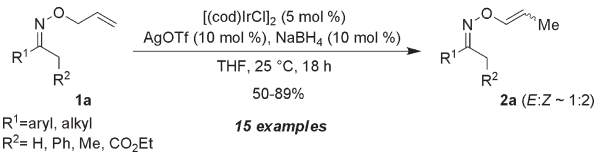
Scheme 1. Examples of [3,3] and [1,3] Rearrangements of *O*-Vinyl Oximes

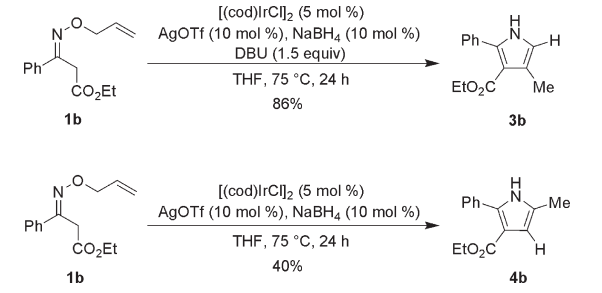


[a] Representative example.

Scheme 2. Synthesis of *O*-Vinyl Oximes via Isomerization of *O*-Allyl Oximes



Scheme 3. This work—Regioselective Synthesis of Trisubstituted Pyrroles from *O*-Allyl Oximes

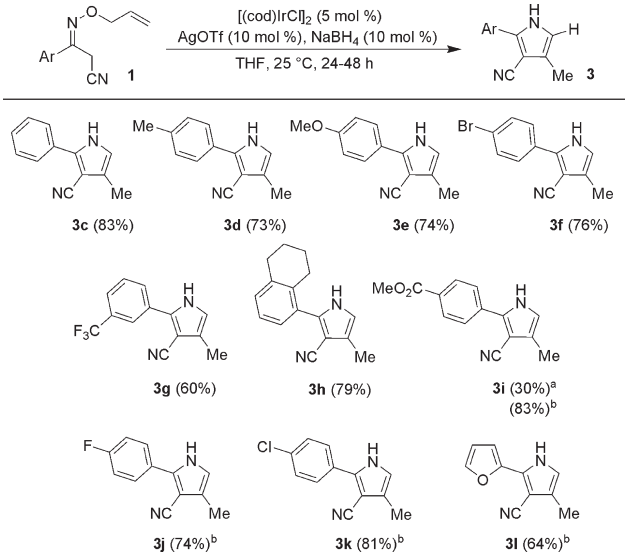


O-allyl oxime isomerization and pyrrole synthesis as well as the factors that control the mechanistic pathway for pyrrole formation. The overall method provides a simple, regioselective, and functional group tolerant synthesis of 2,5-disubstituted pyrroles and 2,3,4- or 2,3,5-trisubstituted pyrroles in two- or three steps from commercially available ketones and allyl hydroxylamine (Scheme 3).

RESULTS AND DISCUSSION

Regioselective Preparation of 2,3,4- and 2,3,5-Trisubstituted Pyrroles. While investigating the scope of our iridium-catalyzed isomerization conditions for the conversion of *O*-allyl oximes to *O*-vinyl oximes, the transformation was tested for α-cyano *O*-allyl oximes **1c**—**i**. Surprisingly, these isomerizations

Scheme 4. Isomerization and Conversion of α-Cyano-Substituted *O*-Allyl Oximes to Pyrroles



[a] No byproducts were observed that corresponded to reduction of the ester substituent. [b] Reactions were run at 50 °C.

provided the corresponding 2,3,4-trisubstituted pyrroles **3c**—**i** in good yield (Scheme 4).[29,30] The conversion of α-cyano *O*-allyl oximes to pyrroles at ambient temperature under the isomerization conditions was in contrast to the isolation of the corresponding *O*-vinyl oximes that occurred when unsubstituted, α-alkyl- or α-aryl-substituted, and *β*-ester *O*-allyl oximes were subjected to the same isomerization conditions.[24] Both electron-rich- and electron-poor aryl substituents were tolerated for the 3-cyanopyrrole synthesis and heating the reaction mixture to 50 °C further expanded the scope of the transformation to include other halide substituents and furanyl ketone-derived oximes (**1j**—**l**).[31] The elevated reaction temperature also increased the yield of the conversion of **1i** to **3i**. These data suggested that [3,3] rearrangements and subsequent Paal—Knorr cyclizations are particularly facile for α-cyano *O*-vinyl oximes and are tolerated under the iridium-catalyzed isomerization conditions.[32] The *O*-vinyl oxime intermediates required in this reaction sequence could not be isolated or purified but could be observed by ^{1}H NMR spectroscopy by taking aliquots of the reaction mixture at 25 °C at time points less than 18 h. The transformations shown in Scheme 4 signified an expansion in the scope of the isomerization method, showed that 3-cyano pyrroles could be efficiently synthesized in two steps from commercially available starting materials, and provided initial evidence that *O*-vinyl oximes could be converted to pyrroles under mild conditions with appropriate substitution patterns.

To determine if isolated *O*-vinyl oximes without cyano substituents could be converted to pyrroles via an analogous [3,3] rearrangement and Paal—Knorr cyclization, *p*-methoxy acetophenone *O*-allyl oxime **2a** was heated to 75 °C in THF for 18 h. As shown in Table 1 (entry 1), 2,5-disubstituted pyrrole **4a** was isolated from the reaction mixture and 4-methylpyrrole **3a** was not observed. The regiochemistry of the product was assigned by a ^{1}H—^{1}H NOE experiment and was surprising due to its complementary relationship to pyrroles **1c**—**l** which were generated from α-cyano *O*-allyl oximes (Scheme 4).[29,33] The synthesis of **4a** from **2a** was optimized and the thermal

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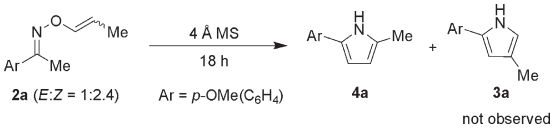
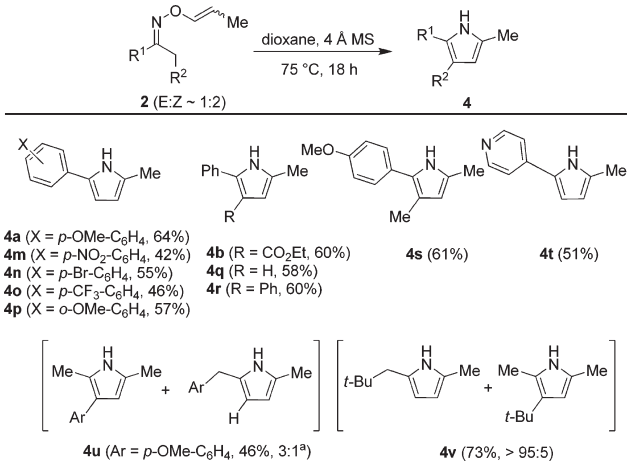
Table 1. Optimization of the Conversion of *O*-Vinyl Oximes to 5-Methylpyrroles



entry	solvent	conc (M)	T (°C)	**4a** (%, yield)
1	THF	0.13	75	33
2	benzene	0.13	75	43
3	MeCN	0.13	75	47
4	dioxane	0.13	75	67
5	*i*-PrOAc	0.13	75	59
6	dioxane	0.27	75	60
7	dioxane	0.07	75	64
8	dioxane	0.13	55	60
9	dioxane	0.13	100	64

Scheme 5. Thermal Conversion of *O*-Vinyl Oximes to 5-Methylpyrroles

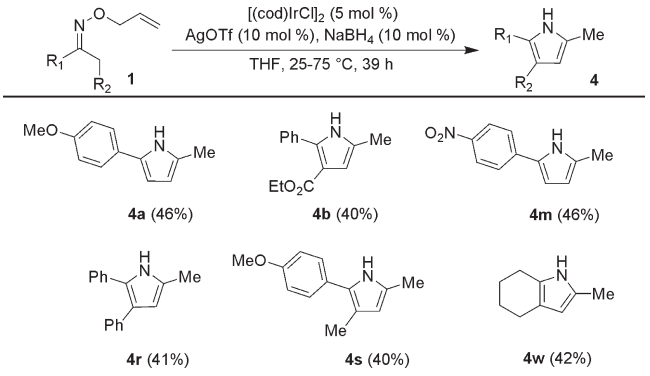


[a] Regioselectivity ratio.

transformation was shown to provide **4a** in good yield when run in dioxane (Table 1, entry 4).[34] The transformation was also more efficient at lower concentrations and the temperature of the rearrangement seemed to only affect reaction time and not reaction efficiency (Table 1, entries 4, 6−9).

The conversion of *O*-vinyl oximes **2** to 5-methylpyrroles **4** was further investigated for a variety of *O*-vinyl oximes using the optimized conditions determined for **2a**. As shown in Scheme 5, the corresponding 2,5-disubstituted and 2,3,5-trisubstituted pyrroles **4b** and **4m**−**v** were isolated from these thermal transformations in moderate to good yield.[33,34] The regiochemistry of the products matched that of **4a**, and the corresponding 4-methylpyrroles **3** were not observed.[29] Both electron-donating- and electron-withdrawing groups were tolerated on the aryl ring of the acetophenone-derived substrates and alkyl-, aryl- and ester groups were tolerated at the α-position. Dialkyl *O*-vinyl oxime **2u** provided a chemoselective mixture of pyrroles due to

Scheme 6. Single-Flask Process for the Conversion of *O*-Allyl Oximes to 5-Methylpyrroles



the two potential sites for enolization for this substrate. Pyrrole **4v** was isolated as a single isomer due to unfavorable steric interactions that would arise from enolization at the neopentyl position of **2v**.

The difference in regioselectivity observed for the tandem, iridium-catalyzed isomerization and pyrrole formation of α-cyano *O*-allyl oximes (Scheme 4) and the metal-free, thermal rearrangement and pyrrole formation observed for *O*-vinyl oximes lacking α-cyano substitution (Scheme 5) prompted an investigation of the direct conversion of unsubstituted, α-alkyl- or α-aryl-substituted, and β-ester *O*-allyl oximes to pyrroles in the presence of the iridium-isomerization catalyst. As shown in Scheme 6, when *O*-allyl oximes **1** were exposed to isomerization conditions and heated to 75 °C, 2,3,5-trisubstituted pyrroles **4** were isolated from the corresponding reaction mixtures with yields equal to the cumulative yield of the two-step procedure.[30,33] An advantage to the single flask process was that it expanded the scope of the isomerization reaction by facilitating the slow isomerization of **1w** and allowing the direct conversion of this compound to pyrrole **4w**. Comparison of the single flask process to the two-step procedure indicated that the presence of the iridium catalyst was not responsible for the regioselective difference between the pyrrole syntheses using α-cyano-substituted *O*-allyl oximes (Scheme 4) and those using unsubstituted, α-alkyl or α-aryl-substituted, and β-ester *O*-allyl oximes (Schemes 5 and 6).

Mechanistic Analysis of Substituent Effects on the Regioselectivity of Pyrrole Formation. The formation of 2,3,5-trisubstituted pyrroles **4**, from either *O*-vinyl oximes **2** (Scheme 5) or *O*-allyl oximes **1** (Scheme 6) cannot occur via a [3,3] rearrangement and Paal−Knorr cyclization as proposed for α-cyano substrates that provide 2,3,4-trisubstituted pyrroles **3** (Schemes 4 and 7).[35] To better understand the origin of the regioselectivity of this process and to propose a mechanism for the synthesis of **4**, the thermal transformation of *O*-vinyl oxime **2s** was monitored by ^{1}H and ^{13}C NMR spectroscopy to observe potential reactive intermediates. Surprisingly, after 2.5 h of heating at 75 °C, **2s** had undergone a [1,3] rearrangement and complete conversion to aldehyde **5s** (Scheme 8). Continued heating and the addition of molecular sieves to the reaction mixture led to the further conversion of aldehyde **5s** to pyrrole **4s**. These observations suggested that pyrrole formation was occurring via an initial [1,3] rearrangement followed by tautomerization and cyclization by nucleophilic attack of the enamine at the aldehyde (Scheme 7). In order to prove the

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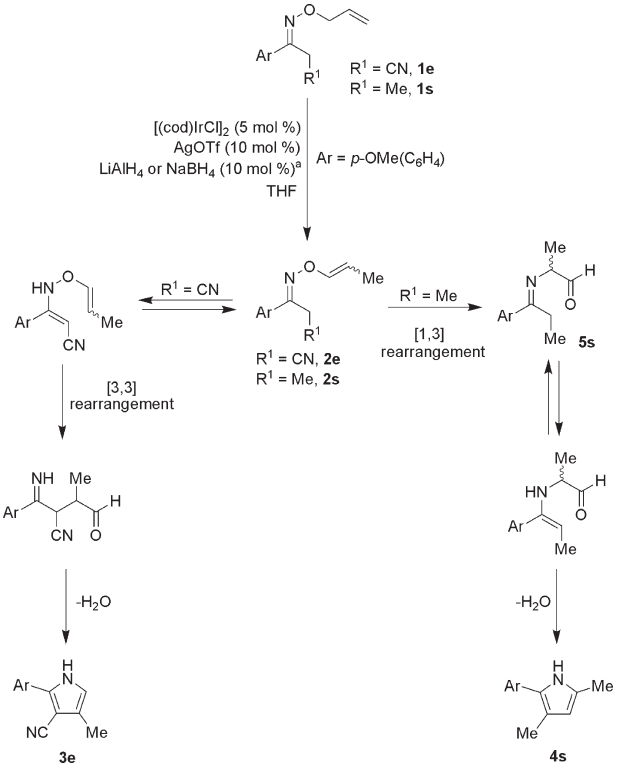
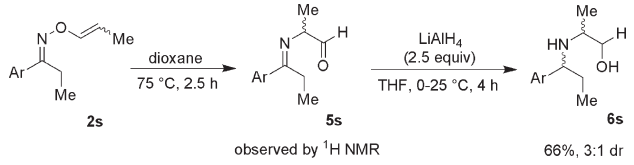
Scheme 7. Proposed Mechanism for 4- and 5-Methylpyrrole Formation via *O*-Vinyl Oxime [3,3] and [1,3] Rearrangements



[a] $NaBH_4$ was used when R^1 = CN. $LiAlH_4$ was used when R^1 = Me.

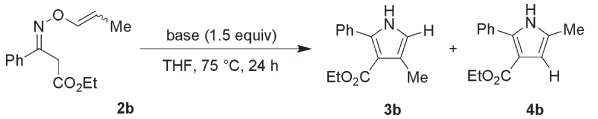
Scheme 8. Observation, Derivatization, and Isolation of an *O*-Vinyl Oxime [1,3] Rearrangement Product



identity of the aldehyde intermediate **5s**, *O*-vinyl oxime **2s** was once again heated for 2.5 h at 75 °C and then treated with $LiAlH_4$.[36] After workup and purification, the corresponding amino alcohol **6s** was isolated as a diastereotopic mixture (Scheme 8). A potential explanation for the deviation in the sigmatropic rearrangement reactivity between transient α-cyano *O*-vinyl oximes and the *O*-vinyl oxime substrates and intermediates shown in Schemes 5 and 6 is the potential for enolization.[37] When enolization is facile for *O*-vinyl oximes, as it is for α-cyano substrates, the reaction proceeds via a [3,3] rearrangement and Paal–Knorr cyclization to give 4-methylpyrroles **3**; when enolization is less favored the [1,3] rearrangement is faster than tautomerization and pyrrole formation occurs by attack of the enamine on the tethered aldehyde (Scheme 7).

Effect of a Basic Additive on the Regioselectivity of Pyrrole Formation. The apparent dependence of the regioselectivity of the conversion of *O*-vinyl oximes to pyrroles on the enolizability of the substrate prompted our investigation of basic reaction conditions to promote the formation of 2,3,4-trisubstituted pyrroles with less

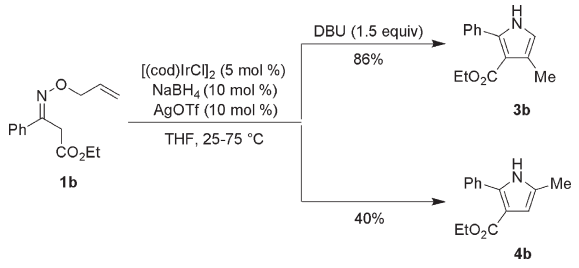
Table 2. Optimization of Basic Additives for the Formation of Pyrrole 3b



entry	base	%, yield[a]	3j:4j[b]
1	NEt_3	58	50:50
2	**DBU**	**88**	**86:14**
3	DABCO	72	84:16
4	imidazole	69	50:50
5	DMAP	64	66:33
6	Cs_2CO_3	62	66:33
7	KO-*t*-Bu	18	50:50
8	KH	14	66:33
9	KHMDS	30	25:75

[a] Determined by ^{1}H NMR spectroscopy with CH_2Br_2 as a reference. [b] Determined by ^{1}H NMR spectroscopy.

Scheme 9. Single-Flask, Regioselective Procedures for the Synthesis of Pyrroles 3b and 4b



electron-withdrawing substituents at the α-position of the oxime. β-Ester *O*-vinyl oxime **2b** was chosen for this study due to the intermediate acidity of this substrate in comparison to α-cyano-substituted *O*-allyl oxime **1c** and α-aryl-substituted *O*-vinyl oxime **2r**.[37] When a THF solution of **2b** was heated in the presence of triethylamine, a 1:1 mixture of 4-methylpyrrole **3b** and 5-methylpyrrole **4b** was obtained (Table 2, entry 1). This mixture indicated a change in mechanism based on reaction conditions and provided access to the new regioisomer **3b**. Following this initial result, several amine bases were tested as additives for the transformation, and DBU was identified as the optimal reagent for the selective formation of 2,3,4-trisubstituted pyrrole **3b** (entry 2). Carbonate, *tert*-butoxide, hydride, and disilazane salts were also evaluated and compared to DBU, but only poorly selective regioisomeric mixtures of **3b** and **4b** were produced in low yield.[38]

A single-flask process incorporating the iridium-catalyzed alkene isomerization and the use of DBU to control the regioselectivity of pyrrole formation was shown to be viable for the conversion of *O*-allyl oxime **1b** to 4-methylpyrrole **3b** (Scheme 9). This procedure avoids the isolation of *O*-vinyl oxime intermediate **2b** and gives a higher overall yield of **3b** (86%) than the cumulative yield of the two-step process (51%). The transformation of **1b** to **3b** is in contrast to the single-flask procedure for the conversion of **1b** to 5-methylpyrrole **4b** which occurs under neutral conditions in significantly lower yield. Comparison of the reactions illustrated in Scheme 9 describes

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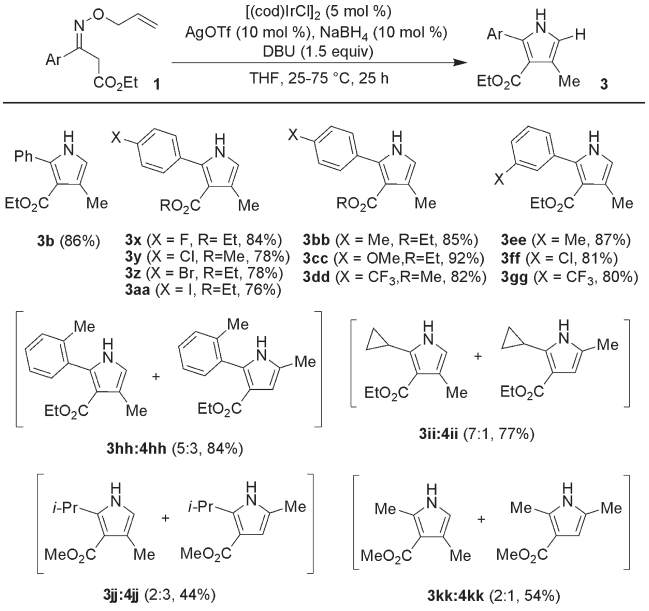
Scheme 10. Scope of Isomerization and [3,3] Rearrangement of β-Ester *O*-Allyl Oximes

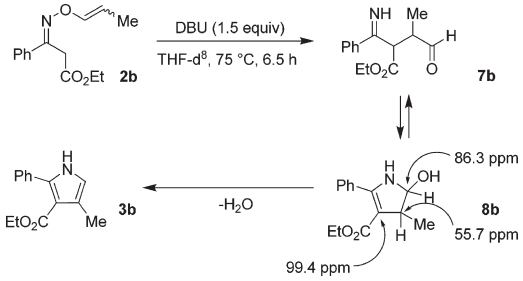


how the regioselectivity of the pyrrole synthesis can be controlled by the presence or the absence of DBU and how a single substrate can be easily manipulated to selectively produce two different pyrrole regioisomers.

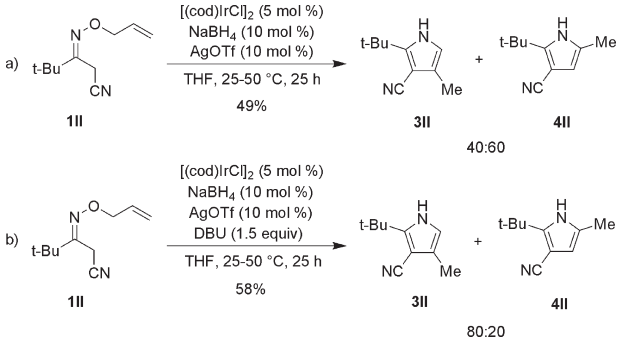
The scope of the β-ester *O*-allyl oxime isomerization and pyrrole synthesis in the presence of DBU was investigated to determine the tolerance of the method as well as the steric and electronic substituent effects on the regioselectivity of pyrrole formation (Scheme 10). A variety of β-ester acetophenone derivatives were tested, and halide, methoxy-, trifluoromethyl-, and alkyl groups were shown to be tolerated at both the *para*- and *meta*-positions of the aryl ring, providing exclusively 4-methylpyrroles **3x**−**kk** in good to excellent yield. In contrast, methyl substitution at the *ortho*-position of the aryl group dramatically decreased the regioselectivity of the transformation and provided a mixture of pyrroles **3hh** and **4hh**. Destabilizing steric interactions involved in tautomerization of the *o*-methyl *O*-vinyl oxime intermediate **2hh** may be responsible for decreasing the amount of product formed by the proposed [3,3] rearrangement. Alkyl-substituted β-ketoester oximes **1ii**−**kk** were also tolerated for the isomerization and pyrrole formation sequence but similarly gave regioisomeric mixtures of pyrroles. The decreased regioselectivity observed for these substrates may be caused by a decreased electronic preference for tautomerization due to lack of resonance stabilization. The preference for 4-methylpyrrole formation observed for cyclopropyl β-ester *O*-allyl oxime **1ii** is noteworthy but difficult to explain. Overall, the results illustrated in Scheme 10 support the proposed mechanistic and regioselectivity dependence of pyrrole formation on oxime tautomerization and suggest that the use of DBU to favor [3,3] rearrangement and 4-methylpyrrole formation for acetophenone-derived β-ester *O*-allyl oximes is general.

In order to observe the reactive intermediates involved in the conversion of *O*-vinyl oxime **2b** to 4-methylpyrrole **3b**, the transformation was monitored by ^{1}H and ^{13}C NMR spectroscopy. After 6.5 h of heating a THF-d_8 solution of **2b** and DBU at 75 °C, a new major product was observed with a small amount of

Scheme 11. Observation of *N,O*-Acetal Intermediate from [3,3] Rearrangement



Scheme 12. Effect of DBU on the Regioisomeric Ratio of 3ll:4ll



starting material **2b** and pyrrole **3b** (Scheme 11). Additional heating for 14 h resulted in the disappearance of the observed intermediate and conversion to **3b**. New methine resonances in the ^{1}H NMR spectrum between 4.5 and 6.0 ppm and carbon resonances at 86.3 and 55.7 ppm suggested that the intermediate was *N,O*-acetal **8b**. These chemical shifts are analogous to NMR data reported for similar cyclic *N,O*-acetals and do not match **2b** or **3b**.[39] Imino aldehyde **7b** was eliminated as a potential structure due to the lack of an aldehydic resonance in both the ^{1}H and ^{13}C NMR spectra.

The generality of the use of DBU as an additive to favor the [3,3] rearrangement of *O*-vinyl oximes over [1,3] rearrangement was further tested for *tert*-butyl-substituted cyano *O*-allyl oxime **1ll** and deoxybenzoin-derived substrate **1r**. As illustrated in Scheme 12a, when *O*-allyl oxime **1ll** is subjected to the iridium-catalyzed isomerization conditions under neutral conditions a mixture of regioisomeric pyrroles **3ll**:**4ll** (40:60) is observed. This deviation in regioselectivity in comparison to the other α-cyano *O*-allyl oxime substrates illustrated in Scheme 4 may be due to a decreased energetic preference for tautomerization due to a lack of resonance stabilization in analogy to isomeric mixtures obtained for β-ester oximes with alkyl substituents. To facilitate tautomerization and favor the [3,3] rearrangement, DBU was added to an isomerization reaction mixture with **1ll** (Scheme 12b). Although 4-methylpyrrole **3ll** was not isolated exclusively, the addition of DBU changed the ratio of **3ll**:**4ll** from 40:60 in favor of 2,3,5-trisubstituted pyrrole **4ll** to 80:20 in favor of 2,3,4-trisubstituted pyrrole **3ll**. The pK_a limits for the use of DBU to favor enolization and the [3,3] rearrangement of *O*-vinyl oximes were further evaluated with deoxybenzoin-derived

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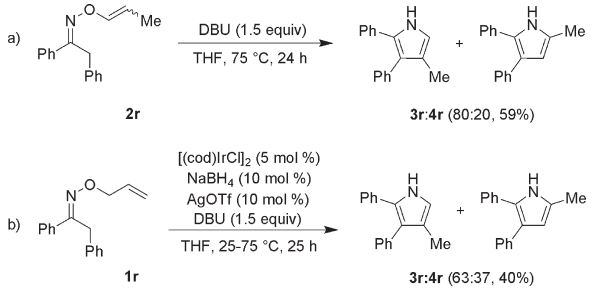
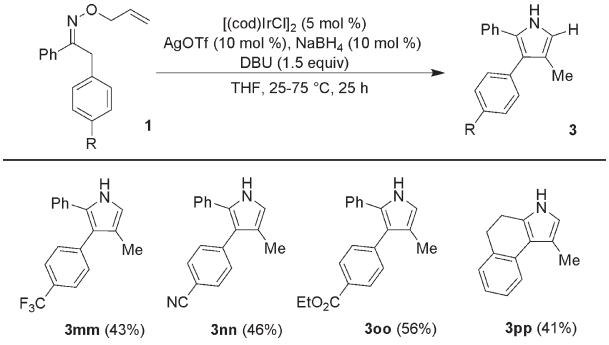
Scheme 13. Effect of DBU on the Rearrangement and Cyclization of Deoxybenzoin-Derived Substrates



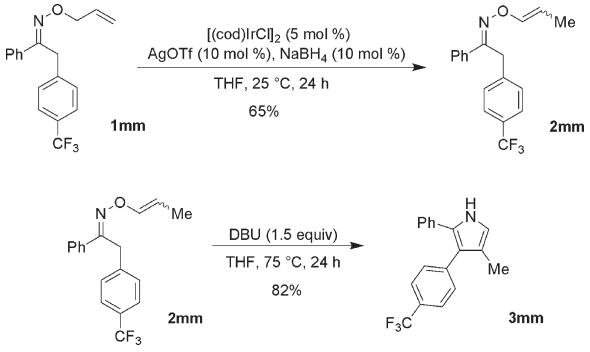
Scheme 14. Effect of Aryl Substituents with Electron-Withdrawing Groups on the Ratio of 3:4



O-vinyl oxime **2r**. When this substrate was heated in the absence of DBU, only the 5-methylpyrrole **4r** was observed (Scheme 5). In contrast, when **2r** was heated in the presence of DBU, a 80:20 mixture of the corresponding 4-methyl- and 5-methylpyrroles **3r** and **4r** was isolated (Scheme 13a). The corresponding single-flask isomerization and pyrrole formation procedure was also tested but provided a less selective product ratio in lower yield (Scheme 13b). These results showed that the use of DBU to favor the [3,3] rearrangement of *O*-vinyl oxime intermediates was not limited to β-ester oxime substrates.

To further facilitate the regioselective preparation of diaryl pyrroles such as **3r**, deoxybenzoin-derived substrates with electron-withdrawing substituents on the α-aryl group were prepared and evaluated. These substrates were chosen to test our hypothesis that the amount of competing [1,3] rearrangement product **4** could be suppressed if enolization was electronically favored. When *O*-allyl oximes **1mm**−**oo** were subjected to the isomerization and pyrrole formation reaction conditions, the 4-methylpyrrole products **3mm**−**oo** were isolated exclusively (Scheme 14). These results further supported our mechanistic proposal that the regioisomeric preference is determined by the enolizability of the substrate. The moderate yields observed for these transformations are due to an inefficient alkene isomerization as described by the analogous two-step procedure illustrated in Scheme 15. β-Tetralone-derived *O*-allyl oxime **1pp** was also tested and similarly gave a single regioisomeric product, albeit without increased acidity at α-position due to substitution.

Scheme 15. Two-Step Procedure for the Synthesis of 4-Methylpyrrole 3mm



CONCLUSION

In summary, we have developed mild procedures for the isomerization of easily accessible *O*-allyl oximes to *O*-vinyl oximes and the efficient transformation of *O*-vinyl oximes to either 2,3,4- or 2,3,5-trisubstituted pyrroles. The regioselectivity of pyrrole formation can be controlled by favoring or disfavoring oxime tautomerization with substituent effects and reaction conditions. The use of electron-withdrawing substituents at the α-position of the oxime and the addition of DBU to the reaction mixture favor enolization, a [3,3] rearrangement of the *O*-vinyl oxime intermediate, and formation of 2,3,4-trisubstituted pyrroles. In contrast, electron-donating or electronically neutral substituents at the α-position of the oxime and the lack of an amine base disfavor enolization, allowing a [1,3] rearrangement of the *O*-vinyl oxime intermediate to occur prior to tautomerization, cyclization, and elimination to provide 2,3,5-trisubstituted pyrroles. These procedures provide a facile entry to an uncommon synthetic intermediate and highlight the utility of *O*-vinyl oximes with a simple, regiospecific, and functional group tolerant preparation of either 2,3,4- or 2,3,5-trisubstituted pyrroles in two steps from the same commercially available starting materials.

EXPERIMENTAL SECTION

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 500 MHz spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectra were acquired on an LTQ FT spectrometer and were obtained by peak matching. Melting points are reported uncorrected. Analytical thin-layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on 60 Å (40 − 60 μm) mesh silica gel (SiO_2). All reactions were carried out under an atmosphere of nitrogen in glassware that had been oven-dried. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. THF was dried by filtration through alumina according to the procedure of Grubbs.[40] Acetonitrile, isopropyl acetate, benzene, dioxane, dichloroethane, DBU, and THF-d_8 were distilled over CaH_2 and degassed prior to use in the glovebox. Metal salts were stored in a nitrogen atmosphere drybox. *O*-Allyl oximes **1a**, **1b**, **1d**−**f**, **1i**, and **1m**−**w** and *O*-vinyl oximes **2a**,**b** and **2m**−**v** were prepared by previously reported procedures.[24]

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General Procedure for the Synthesis of *O*-Allyl Oximes 1[25]. A 100 mL round-bottom flask (rbf) was charged with 1 equiv of allylhydroxylamine hydrochloride salt, 1 equiv of NaOAc, and ~40 mL of MeOH. The resulting slurry was allowed to stir at 25 °C for 30 min. At this time, 1 equiv of the corresponding ketone was added to the slurry over a 5 min time period. Regardless of their physical state, ketones were weighed into scintillation vials, mixed with 15 mL of MeOH, and added as solutions with a syringe. The reaction mixtures were then allowed to stir at 25 °C for 12−24 h or heated to 60 °C for 24 h. At this time, 30 mL of water were added to the flask and a white precipitate appeared. The mixture was then transferred to a separatory funnel and mixed with an additional 20 mL of water and 40 mL of MTBE or CH_2Cl_2. The water layer was extracted with 3 × 15 mL of MTBE or CH_2Cl_2 and the organic layer was extracted with 2 × 20 mL of water and 1 × 20 mL of brine. The organic layers were then combined, dried over $MgSO_4$, and filtered. Solvent was separated from the product under vacuum on a rotary evaporator. Allyl oxime **1** was then transferred to a scintillation vial and all remaining volatiles were removed on a high vacuum line. No further purification of the products was required in most cases. For condensation reactions that did not go to completion, the remaining starting material was separated by flash chromatography using a solvent gradient of 2% TEA/hexanes−10% EtOAc/2% TEA/hexanes.

O-Allyl Oxime ***1c***. Allyl hydroxylamine hydrochloride (0.601 g, 5.49 mmol) was treated with NaOAc (0.675 g, 8.23 mmol) and benzoylacetonitrile (0.716 g, 4.93 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 12 h. After workup, **1c** was isolated as a clear, colorless oil (0.810 g, 82%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67−7.65 (m, 2H), 7.39−7.36 (m, 3H), 6.09−7.06 (m, 1H), 5.38 (dd, J = 17.0, 1.0 Hz, 1H), 5.29 (dd, J = 10.5, 1.0 Hz, 1H), 4.79 (d, J = 5.5 Hz, 2H), 3.81 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 133.5, 133.3, 130.2, 128.9, 126.2, 118.4, 115.0, 76.0, 15.3; IR (thin film) 2926, 2252, 1604, 1445, 1415, 1341, 1020, 930, 759, 691, 532 cm^{-1}; HRMS (ESI) m/z calcd for $C_{12}H_{13}N_2O$ $(M + H)^+$ 201.1028, found 201.1027. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

O-Allyl Oxime ***1g***. Allyl hydroxylamine hydrochloride (0.539 g, 4.92 mmol) was treated with NaOAc (0.443 g, 5.28 mmol) and 3-trifluoromethylbenzoyl acetonitrile (0.868 g, 4.07 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 12 h. After workup and purification by flash chromatography (5% EtOAc/2% TEA/hexanes), **1g** was isolated as a clear, colorless oil (1.02 g, 94%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.69 (d, J = 7.5 Hz, 1H), 7.56 (m, 1H), 6.08−6.02 (m, 1H), 5.39 (dd, J = 19.0, 1.0 Hz, 1H), 5.30 (dd, J = 10.5, 1.0 Hz, 1H), 4.82 (d, J = 6.0 Hz, 2H), 3.84 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 134.2, 133.3, 131.6 (d, J_{C-F} = 32.5 Hz), 129.6, 129.5, 126.9, 123.9 (q, J_{C-F} = 270 Hz), 123.2, 119.0, 114.7, 76.6, 15.3; IR (thin film) 2900, 2251, 1616, 1424, 1304, 1278, 1125, 1021, 930, 800 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{12}F_3N_2O$ $(M + H)^+$ 269.0902, found 269.0904. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

Allyl Oxime ***1h***. Allyl hydroxylamine hydrochloride (0.663 g, 6.05 mmol) was treated with NaOAc (0.745 g, 9.08 mmol) and 5,6,7,8-tetrahydro-2-napthoyl acetonitrile (1.09 g, 5.47 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 12 h. After workup, **1h** was isolated as a clear, colorless oil (1.17 g, 84%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36−7.32 (m, 2H), 7.11−7.10 (m, 1H), 6.09−6.03 (m, 1H), 5.37 (d, J = 17.5 Hz, 1H), 5.27 (d, J = 10.5 Hz, 1H), 4.77 (d, J = 5.5 Hz, 2H), 3.78 (s, 2H), 2.80−2.78 (m, 4H), 1.81−1.80 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 139.8, 137.8, 133.6, 130.4, 129.6, 126.8, 123.2, 118.2, 115.2, 75.9, 29.5, 29.3, 23.0, 22.9, 15.3; IR (thin film) 2926, 2859, 2250, 1650, 1424, 1330, 1021, 927, 852, 703 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{19}N_2O$ $(M + H)^+$ 255.1497, found 255.1496. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

O-Allyl Oxime ***1j***. Allyl hydroxylamine hydrochloride (0.682 g, 6.22 mmol) was treated with NaOAc (0.562 g, 6.85 mmol) and 4-fluorobenzoylacetonitrile (1.02 g, 6.25 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 12 h. After workup, **1j** was isolated as a clear, colorless oil (1.06 g, 78%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66−7.63 (m, 2H), 7.13−7.09 (m, 2H), 6.07−6.02 (m, 1H), 5.37 (dd, J = 17.0, 1.0 Hz, 1H), 5.27 (dd, J = 10.5, 1.0 Hz, 1H), 4.77 (d, J = 5.5 Hz, 2H), 3.80 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9 (d, J_{C-F} = 248.8 Hz), 145.5, 133.4, 129.4, 128.2, 118.5, 116.1, 114.9, 76.1, 15.2; IR (thin film) 2930, 2257, 1602, 1511, 1417, 1233, 1161, 1022, 931, 835 cm^{-1}; HRMS (ESI) m/z calcd for $C_{12}H_{12}FN_2O$ $(M + H)^+$ 219.0934, found 219.0933. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

O-Allyl Oxime ***1k***. Allyl hydroxylamine hydrochloride (0.539 g, 4.92 mmol) was treated with NaOAc (0.412 g, 5.02 mmol) and 4-chlorobenzoylacetonitrile (0.818 g, 4.56 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 12 h. After workup, **1k** was isolated as a clear, colorless oil (0.843 g, 79%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60−7.59 (m, 2H), 7.40−7.38 (m, 2H), 6.07−6.01 (m, 1H), 5.36 (dd, J = 20.0, 1.0 Hz, 1H), 5.29 (dd, J = 10.5, 1.0 Hz, 1H), 4.78 (d, J = 6.0 Hz, 2H), 3.79 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 145.5, 133.3, 131.6, 129.1, 127.4, 118.6, 114.8, 76.2, 15.1; IR (thin film) 2950, 2250, 1600, 1490, 1412, 1327, 1092, 1009, 930, 829 cm^{-1}; HRMS (ESI) m/z calcd for $C_{12}H_{12}ClN_2O$ $(M + H)^+$ 235.0638, found 235.0640. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

O-Allyl Oxime Ether ***1l***. Allyl hydroxylamine hydrochloride (0.405 g, 3.70 mmol) was treated with NaOAc (0.334 g, 4.07 mmol) and 2-furoylacetonitrile (0.500 g, 3.70 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 12 h. After workup and flash chromatography (2% TEA/hexanes−5% EtOAc/2% TEA/hexanes), **1l** was isolated as a clear, colorless oil (0.530 g, 75%, *E*:*Z* = 1:2): ^{1}H NMR of *E*-imine isomer (500 MHz, $CDCl_3$) δ 7.55−7.54 (m, 1H), 6.84−6.83 (m, 1H), 6.53−6.52 (m, 1H), 6.10−6.04 (m, 1H), 5.40 (dd, J = 17.5, 1.5 Hz, 1H), 5.30 (dd, J = 10.5, 1.5 Hz, 1H), 4.79 (m, 2H), 3.76 (s, 2H); ^{13}C NMR of *E*-imine isomer (125 MHz, $CDCl_3$) δ 147.2, 144.6, 139.2, 133.2, 118.6, 114.7, 112.0, 111.1, 76.3, 14.6; ^{1}H NMR of *Z*-imine isomer (500 MHz, $CDCl_3$) δ 7.54−7.53 (m, 1H), 7.42−7.41 (m, 1H), 6.59−6.58 (m, 1H), 6.10−6.04 (m, 1H), 5.38 (dd, J = 17.5, 1.5 Hz, 1H), 5.30 (dd, J = 10.5, 1.5 Hz, 1H), 4.79 (m, 2H), 3.73 (s, 2H); ^{13}C NMR of *Z*-imine isomer (125 MHz, $CDCl_3$) δ 143.8, 143.4, 137.3, 133.5, 119.0, 118.4, 115.8, 112.7, 76.5, 20.9; IR (thin film) 2932, 2255, 1602, 1482, 1411, 1161, 999, 935, 896, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{10}H_{11}N_2O_2$ $(M + H)^+$ 191.0822, found 191.0821.

O-Allyl Oxime ***1x***. Allylhydroxylamine hydrochloride (0.625 g, 5.70 mmol) was treated with NaOAc (0.468 g, 5.70 mmol) and ethyl (4-fluorobenzoyl) acetate (1.00 g, 4.76 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 12 h. After workup, **1x** was isolated as a clear colorless liquid (1.08 g, 86%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64−7.61 (m, 2H), 7.07−7.04 (m, 2H), 6.04−5.98 (m, 1H), 5.32 (dd, J = 17.5, 1.5 Hz, 1H), 5.22 (dd, J = 10.5, 1.5 Hz, 1H), 4.71 (d, J = 5.5 Hz, 2H), 4.15 (q, J = 7.0 Hz, 2H), 3.76 (s, 2H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 163.5 (d, J_{C-F}= 247.5 Hz), 150.6, 134.0, 131.6, 128.2, 117.4, 115.6, 75.3, 61.2, 33.4, 14.1; IR (thin film) 3080, 2983, 2927, 2869, 1733, 1602, 1510, 1021, 922, 837 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{17}NO_3F$ $(M + H)^+$ 266.1192, found 266.1194. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

O-Allyl Oxime ***1y***. Allylhydroxylamine hydrochloride (0.624 g, 5.70 mmol) was treated with NaOAc (0.468 g, 5.70 mmol) and methyl 4-chlorobenzoyl acetate (1.01 g, 4.75 mmol). The reaction flask was

then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup, **1y** was isolated as a clear colorless liquid (1.15 g, 91%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59−7.57 (m, 2H), 7.35−7.33 (m, 2H), 6.03−5.98 (m, 1H), 5.31 (dd, J = 17.5, 1.5 Hz, 1H), 5.22 (dd, J = 10.5, 1.5 Hz, 1H), 4.72 (d, J = 5.5 Hz, 2H), 3.77 (s, 2H), 3.68 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 150.3, 135.5, 134.0, 133.7, 128.8, 127.5, 117.6, 75.5, 52.3, 32.8; IR (thin film) 3077, 2951, 2869, 1737, 1602, 1493, 1026, 921, 831, 706 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{13}H_{15}NO_3Cl$ $(M + H)^+$ 268.0740, found 268.0740. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

O-Allyl Oxime ***1z***. Allylhydroxylamine hydrochloride (0.485 g, 4.43 mmol) was treated with NaOAc (0.363 g, 4.42 mmol) and ethyl 4-bromobenzoyl acetate (1.00 g, 3.69 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup, **1z** was isolated as a clear colorless liquid (0.916 g, 76%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53−7.48 (m, 4H), 6.03−5.98 (m, 1H), 5.32 (dd, J = 17.5, 1.5 Hz, 1H), 5.22 (dd, J = 10.5, 1.5 Hz, 1H), 4.72 (d, J = 5.5 Hz, 2H), 4.14 (q, J = 7.5 Hz, 2H), 3.75 (s, 2H), 1.21 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 150.6, 134.3, 133.9, 131.7, 127.8, 123.7, 117.5, 75.5, 61.2, 33.1, 14.1; IR (thin film) 3080, 2981, 2930, 2869, 1733, 1602, 1488, 1021, 920, 829, 525 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{17}NO_3Br$ $(M + H)^+$ 326.0392, found 326.0395. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

O-Allyl Oxime ***1aa***. Allylhydroxylamine hydrochloride (0.413 g, 3.77 mmol) was treated with NaOAc (0.309 g, 3.77 mmol) and ethyl 4-iodobenzoyl acetate (1.00 g, 3.14 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup, **1aa** was isolated as a clear colorless liquid (0.874 g, 75%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70−7.69 (m, 2H), 7.38−7.37 (m, 2H), 6.04−5.96 (m, 1H), 5.32 (dd, J = 17.5, 1.5 Hz, 1H), 5.22 (dd, J = 10.5, 1.5 Hz, 1H), 4.71 (d, J = 5.5 Hz, 2H), 4.13 (q, J = 7.0 Hz, 2H), 3.74 (s, 2H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 150.7, 137.7, 134.9, 133.9, 127.9, 117.5, 95.6, 75.5, 61.2, 33.0, 14.1; IR (thin film) 3079, 2980, 2931, 2869, 1731, 1601, 1486, 1020, 919, 826, 524 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{17}NO_3I$ $(M + H)^+$ 374.0253, found 374.0257. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

O-Allyl Oxime ***1bb***. Allylhydroxylamine hydrochloride (0.637 g, 5.81 mmol) was treated with NaOAc (0.477 g, 5.81 mmol) and ethyl 4-methylbenzoyl acetate (1.00 g, 4.85 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup, **1bb** was isolated as a clear colorless liquid (1.20 g, 95%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55−7.53 (m, 2H), 7.19−7.17 (m, 2H), 6.05−5.99 (m, 1H), 5.33 (dd, J = 17.5, 1.5 Hz, 1H), 5.22 (dd, J = 10.5, 1.5 Hz, 1H), 4.71 (d, J = 5.5 Hz, 2H), 4.14 (q, J = 7.0 Hz, 2H), 3.77 (s, 2H), 2.36 (s, 3H), 1.22 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 151.5, 139.4, 134.2, 132.6, 129.2, 126.2, 117.2, 75.2, 61.1, 33.4, 21.3, 14.1; IR (thin film) 3082, 3031, 2982, 2922, 2869, 1734, 1614, 1157, 1022, 919, 817 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{20}NO_3$ $(M + H)^+$ 262.1443, found 262.1441. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

O-Allyl Oxime ***1cc***. Allylhydroxylamine hydrochloride (0.526 g, 4.80 mmol) was treated with NaOAc (0.393 g, 4.79 mmol) and ethyl 3-(4-methoxyphenyl)-3-oxopropionate (0.889 g, 4.00 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup, **1cc** was isolated as a clear colorless liquid (1.10 g, 99%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60−7.58 (m, 2H), 6.90−6.88 (m, 2H), 6.04−5.98 (m, 1H), 5.31 (dd, J = 17.5, 1.5 Hz, 1H), 5.21 (dd, J = 10.5, 1.5 Hz, 1H), 4.70 (d, J = 5.5 Hz, 2H), 4.14 (q, J = 7.0 Hz, 2H), 3.82 (s, 3H), 3.75 (s, 2H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 160.6, 151.1, 134.2, 128.0, 127.6, 117.2, 113.9, 75.1, 61.1, 55.3, 33.4, 14.1; IR (thin film) 2979, 2934, 2871, 2837, 1731, 1608, 1247, 1173, 1023, 915, 833 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{15}H_{20}NO_4$ $(M + H)^+$ 278.1392, found 278.1395. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

O-Allyl Oxime ***1dd***. Allylhydroxylamine hydrochloride (0.394 g, 3.60 mmol) was treated with NaOAc (0.295 g, 3.60 mmol) and methyl 4-trifluoromethylbenzoyl acetate (0.738 g, 3.00 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup, **1dd** was isolated as a clear colorless liquid (0.839 g, 93%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77−7.76 (m, 2H), 7.63−7.61 (m, 2H), 6.05−5.98 (m, 1H), 5.33 (dd, J = 17.0, 1.5 Hz, 1H), 5.24 (dd, J = 10.5, 1.5 Hz, 1H), 4.74 (d, J = 5.5 Hz, 2H), 3.81 (s, 2H), 3.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 150.1, 138.7, 133.8, 131.1 (q, J_{FC} = 32.5 Hz), 126.5, 125.5, 123.9 (d, J_{FC} = 271.2 Hz), 117.7, 75.7, 52.3, 32.7; IR (thin film) 2994, 2956, 2926, 1740, 1606, 1256, 1163, 1010, 925, 844 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{14}H_{15}NO_3F_3$ $(M + H)^+$ 302.1004, found 302.1001. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

O-Allyl Oxime ***1ee***. Allylhydroxylamine hydrochloride (0.637 g, 5.81 mmol) was treated with NaOAc (0.477 g, 5.81 mmol) and ethyl 3-methylbenzoyl acetate (1.00 g, 4.85 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup, **1ee** was isolated as a clear colorless liquid (1.01 g, 80%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.42−7.41 (m, 1H), 7.27−7.25 (m, 1H), 7.19−7.18 (m, 1H), 6.05−5.99 (m, 1H), 5.33 (dd, J = 17.5, 1.5 Hz, 1H), 5.22 (dd, J = 10.5, 1.5 Hz, 1H), 4.72 (d, J = 5.5 Hz, 2H), 4.15 (q, J = 7.0 Hz, 2H), 3.77 (s, 2H), 2.37 (s, 3H), 1.22 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 151.8, 138.2, 135.4, 134.1, 130.2, 128.4, 126.9, 123.5, 117.3, 75.3, 61.1, 33.6, 21.5, 14.1; IR (thin film) 2982, 2920, 2864, 1733, 1602, 1255, 1158, 1021, 926, 786, 692 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{15}H_{20}NO_3$ $(M + H)^+$ 262.1443, found 262.1444. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

O-Allyl Oxime ***1ff***. Allylhydroxylamine hydrochloride (0.580 g, 5.29 mmol) was treated with NaOAc (0.434 g, 5.29 mmol) and ethyl (3-chlorobenzoyl) acetate (1.00 g, 4.42 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup, **1ff** was isolated as a clear colorless liquid (1.13 g, 91%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.51−7.48 (m, 1H), 7.35−7.28 (m, 2H), 6.05−5.98 (m, 1H), 5.33 (dd, J = 17.5, 1.5 Hz, 1H), 5.22 (dd, J = 10.5, 1.5 Hz, 1H), 4.73 (d, J = 5.5 Hz, 2H), 4.15 (q, J = 7.0 Hz, 2H), 3.75 (s, 2H), 1.22 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 150.4, 137.2, 134.6, 133.9, 129.8, 129.4, 126.4, 124.4, 117.6, 75.5, 61.2, 33.2, 14.1; IR (thin film) 3078, 2981, 2932, 2872, 1735, 1603, 1161, 1022, 922, 786, 684 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{17}NO_3Cl$ $(M + H)^+$ 282.0897, found 282.0896. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

O-Allyl Oxime ***1gg***. Allylhydroxylamine hydrochloride (0.505 g, 4.61 mmol) was treated with NaOAc (0.378 g, 4.61 mmol) and ethyl (3-trifluoromethylbenzoyl) acetate (1.00 g, 3.84 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup, **1gg** was isolated as a clear colorless liquid (1.04 g, 86%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.82−7.81 (m, 1H), 7.63−7.61 (m, 1H), 7.51−7.48 (m, 1H), 6.05−5.99 (m, 1H), 5.33 (dd, J = 17.5, 1.5 Hz, 1H), 5.23 (dd, J = 10.5, 1.5 Hz, 1H), 4.75 (d, J = 5.5 Hz, 2H), 4.15 (q, J = 7.0 Hz, 2H), 3.80 (s, 2H), 1.22 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 150.3, 136.2, 133.8, 131.0 (q, J_{FC} = 32.5 Hz), 129.5, 129.1, 125.9, 124.0 (d, J_{FC} = 271.2 Hz), 123.1, 117.7, 75.6, 61.3, 33.2, 14.0; IR (thin film) 2988, 2933, 2871, 1735, 1616, 1249, 1163, 1022, 923, 696 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{17}NO_3F_3$ $(M + H)^+$ 316.1161, found 316.1160. The ^{1}H NMR spectrum showed that <10% of the product mixture was the Z-oxime isomer.

O-Allyl Oxime ***1hh***. Allylhydroxylamine hydrochloride (0.637 g, 5.81 mmol) was treated with NaOAc (0.477 g, 5.81 mmol) and ethyl 2-methylbenzoyl acetate (1.00 g, 4.85 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup, **1hh** was isolated as a clear colorless liquid (1.07 g, 84%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29−7.19 (m, 4H), 6.04−5.98 (m, 1H), 5.33 (dd, J = 17.0, 1.5 Hz, 1H), 5.23 (dd, J = 10.5, 1.5 Hz, 1H), 4.69 (d, J = 5.5 Hz, 2H), 4.11 (q, J = 7.0 Hz, 2H), 3.67 (s, 2H), 2.41 (s, 3H), 1.20 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 153.1, 136.4, 135.7, 134.2, 130.8, 128.8, 128.6, 125.8, 117.3, 75.0, 61.0, 36.6, 20.2, 14.0; IR (thin film) 3068, 3030, 2980, 2927, 2870, 1735, 1601, 1156, 1019, 921, 757 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{15}H_{20}NO_3$ $(M + H)^+$ 262.1443, found 262.1439. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

O-Allyl Oxime ***1ii***. Allylhydroxylamine hydrochloride (0.842 g, 7.69 mmol) was treated with NaOAc (0.630 g, 7.68 mmol) and ethyl-3-cyclopropyl-3-oxopropionate (1.00 g, 6.40 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup, **1ii** was isolated as a clear colorless liquid (1.22 g, 90%, *E*:*Z* = 5:1): ^{1}H NMR of *E*-imine isomer (500 MHz, $CDCl_3$) δ 5.95−5.89 (m, 1H), 5.23 (dd, J = 17.0, 1.5 Hz, 1H), 5.15 (dd, J = 10.5, 1.5 Hz, 1H), 4.51 (d, J = 5.5 Hz, 2H), 4.13 (q, J = 7.0 Hz, 2H), 3.17 (s, 2H), 1.63−1.58 (m, 1H), 1.24 (t, J = 7.0 Hz, 3H), 0.75 (d, J = 1.0 Hz, 4H); ^{13}C NMR of *E*-imine isomer (125 MHz, $CDCl_3$) δ 168.9, 154.6, 134.3, 116.9, 74.5, 60.9, 33.4, 14.6, 14.1, 5.0; ^{1}H NMR of Z-imine isomer (500 MHz, $CDCl_3$) δ 6.03−5.96 (m, 1H), 5.29 (dd, J = 17.0, 1.5 Hz, 1H), 5.19 (dd, J = 10.5, 1.5 Hz, 1H), 4.59 (d, J = 5.5 Hz, 2H), 4.13 (q, J = 7.0 Hz, 2H), 2.90 (s, 2H), 2.34−2.28 (m, 1H), 1.24 (t, J = 7.0 Hz, 3H), 0.86 (d, J = 1.0 Hz, 2H), 0.70 (d, J = 1.0 Hz, 2H); ^{13}C NMR of *Z*-imine isomer (125 MHz, $CDCl_3$) δ 169.7, 155.4, 134.4, 117.1, 74.7, 61.1, 35.9, 14.1, 9.6, 5.1; IR (thin film) 3084, 3002, 2983, 2920, 2871, 1735, 1251, 1156, 1024, 922 cm^{-1}; HRMS (ESI) m/z calcd for $C_{11}H_{18}NO_3$ $(M + H)^+$ 212.1287, found 212.1286.

O-Allyl Oxime ***1jj***. Allylhydroxylamine hydrochloride (0.526 g, 4.80 mmol) was treated with NaOAc (0.394 g, 4.80 mmol) and methyl 4-methyl-3-oxovalerate (0.623 g, 4.32 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup, **1jj** was isolated as a clear colorless liquid (0.605 g, 70%, *E*:*Z* = 3:1). ^{1}H NMR of *E*-imine isomer (500 MHz, $CDCl_3$) δ 5.96−5.88 (m, 1H), 5.23 (d, J = 17.0 Hz, 1H), 5.15 (d, J = 10.5 Hz, 1H), 4.51 (d, J = 5.5 Hz, 2H), 3.69 (s, 3H), 3.23 (s, 2H), 2.61−2.56 (m, 1H), 1.10 (d, J = 7.0 Hz, 6H); ^{13}C NMR of *E*-imine isomer (125 MHz, $CDCl_3$) δ 169.6, 158.0, 134.3, 116.8, 74.4, 52.0, 33.7, 32.3, 19.6; ^{1}H NMR of Z-imine isomer (500 MHz, $CDCl_3$) δ 6.00−5.95 (m, 1H), 5.27 (d, J = 17.0 Hz, 1H), 5.20 (d, J = 10.5 Hz, 1H), 4.55 (d, J = 5.5 Hz, 2H), 3.70 (s, 3H), 3.35−3.30 (m, 1H), 3.17 (s, 2H), 1.06 (d, J = 7.0 Hz, 6H); ^{13}C NMR of *Z*-imine isomer (125 MHz, $CDCl_3$) δ 170.5, 159.2, 134.4, 117.0, 74.6, 52.1, 36.7, 72.4, 18.8; IR (thin film) 3018, 3002, 2968, 2933, 2871, 1739, 1259, 1160, 1028, 919 cm^{-1}; HRMS (ESI) m/z calcd for $C_{10}H_{18}NO_3$ $(M + H)^+$ 200.1287, found 200.1285.

O-Allyl Oxime ***1kk***. Allylhydroxylamine hydrochloride (0.606 g, 5.53 mmol) was treated with NaOAc (0.454 g, 5.53 mmol) and methyl acetoacetate (0.581 g, 5.00 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup, **1kk** was isolated as a clear colorless liquid (0.674 g, 79%, *E*:*Z* = 1:1): ^{1}H NMR of *E*-imine isomer (500 MHz, $CDCl_3$) δ 5.99−5.93 (m, 1H), 5.26 (dd, J = 17.5, 1.5 Hz, 1H), 5.18 (dd, J = 10.5, 1.5 Hz,1H), 4.56 (d, J = 5.5 Hz, 2H), 3.71 (s, 3H), 3.22 (s, 2H), 1.94 (s, 3H); ^{13}C NMR of *E*-imine isomer (125 MHz, $CDCl_3$) δ 170.1, 151.6, 134.3, 117.2, 74.6, 52.1, 41.2, 14.6; ^{1}H NMR of Z-imine isomer (500 MHz, $CDCl_3$) δ 5.99−5.93 (m, 1H), 5.28 (dd, J = 17.5, 1.5 Hz, 1H), 5.20 (dd, J = 10.5, 1.5 Hz, 1H), 4.54 (d, J = 5.5 Hz, 2H), 3.70 (s, 3H), 3.36 (s, 2H), 1.97 (s, 3H); ^{13}C NMR of *Z*-imine isomer (125 MHz, $CDCl_3$) δ 169.3, 150.5, 134.3, 117.0, 74.4, 41.2, 35.2, 20.6; IR (thin film) 3079, 2989, 2952, 2920, 2866, 1737, 1434, 1164, 1023, 922 cm^{-1}; HRMS (ESI) m/z calcd for $C_8H_{14}NO_3$ $(M + H)^+$ 172.0974, found 172.0974.

O-Allyl Oxime ***1ll***. Allyl hydroxylamine hydrochloride (0.241 g, 2.20 mmol) was treated with NaOAc (0.246 g, 3.00 mmol) and 4,4-dimethyl-3-oxopentanenitrile (0.257 g, 2.05 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 12 h. After workup and flash chromatography (2% EtOAc/2% TEA/hexanes), **1ll** was isolated as a clear, colorless oil (0.305 g, 83%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.00−5.94 (m, 1H), 5.29 (dd, J = 17.0, 1.0 Hz, 1H), 5.18 (dd, J = 10.5, 1.0 Hz, 1H), 4.60 (d, J = 6.0 Hz, 2H), 3.25 (s, 2H), 1.15 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 133.8, 117.6, 115.5, 75.1, 37.3, 27.3, 13.4; IR (thin film) 2969, 2871, 2251, 1720, 1480, 1366, 1122, 1021, 924, 849 cm^{-1}; HRMS (ESI) m/z calcd for $C_{10}H_{17}N_2O$ $(M + H)^+$ 181.1341, found 181.1340. The ^{1}H NMR spectrum showed that <10% of the product mixture was the *Z*-oxime isomer.

O-Allyl Oxime ***1mm***. Allyl hydroxylamine hydrochloride (0.082 g, 0.75 mmol) was treated with NaOAc (0.92 mg, 1.1 mmol) and ketone **9mm** (0.198 g, 0.750 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup and flash chromatography (2% TEA/hexanes−2% EtOAc/2%TEA/hexanes), **1mm** was isolated as a clear, colorless oil (0.163 g, 68%, *E*:*Z* = 3:1): ^{1}H NMR of *E*-imine isomer (500 MHz, $CDCl_3$) δ 7.98−7.94 (m, 2H), 7.66−7.64 (m, 2H), 7.35−7.28 (m, 5H), 6.08−6.00 (m, 1H), 5.32 (d, J = 18.0 Hz, 1H), 5.24 (d, J = 10.5 Hz, 1H), 4.76 (d, J = 5.5 Hz, 2H), 4.22 (s, 2H); ^{13}C NMR of *E*-imine isomer (125 MHz, $CDCl_3$) δ 155.4, 141.0, 135.3, 134.4, 134.2, 129.6, 128.9, 128.8, 128.2, 126.4, 117.8, 75.4, 32.9 (the CF_3 resonance was not observed due to ^{19}F splitting); ^{1}H NMR of *Z*-imine isomer (500 MHz, $CDCl_3$) δ 7.98−7.94 (m, 2H), 7.66−7.64 (m, 2H), 7.35−7.28 (m, 5H), 6.08−6.00 (m, 1H), 5.32 (d, J = 18.0 Hz, 1H), 5.24 (d, J = 10.5 Hz, 1H), 4.63 (d, J = 5.5 Hz, 2H), 3.91 (s, 2H); ^{13}C NMR of *Z*-imine isomer (125 MHz, $CDCl_3$) δ 155.4, 141.0, 135.3, 134.4, 134.2, 129.6, 128.9, 128.8, 128.2, 125.4, 117.2, 75.0, 41.5 (the CF_3 resonance was not observed due to ^{19}F splitting); IR (thin film) 3067, 2920, 1681, 1616, 1321, 1109, 1066, 1017, 923, 692 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{18}H_{16}F_3NO$ $(M+H)^+$ 320.1262, found 320.1255.

Ketone ***9 mm***:[41]. Ketone **9 mm** was prepared via a cross coupling reaction between acetophenone and 4-trifluoromethyl iodobenzene.[42] In an inert atmosphere glovebox, a 25 mL round-bottom flask was charged with $Pd(dba)_2$ (0.045 g, 0.078 mmol) and dppf (0.052 g, 0.094 mmol). To the flask, 6 mL of THF were added and allowed to stir for 5 min before the addition of NaO*t*-Bu (0.211 g, 2.20 mmol). The remaining solids were washed from the sides of the flask with 4 mL of THF. The flask was then removed from the glovebox and placed under an atmosphere of N_2 with a needle. While stirring, 4-iodobenzotrifluoride (0.271 g, 1.00 mmol) was added to the catalyst mixture, followed by acetophenone (0.120 g, 1.00 mmol). The reaction flask was then attached to a reflux condenser and the reaction mixture was heated to 75 °C for 2.5 h. The crude product was dry loaded on to silica and purified by flash chromatography (2% TEA/hexanes −10% EtOAc/2% TEA/hexanes) to afford **9mm** as a white solid (0.229 g, 76%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02−7.99 (m, 2H), 7.61−7.58 (m, 3H), 7.51−7.47 (m, 2H), 7.40−7.38 (m, 2H), 4.36 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.7, 164.0, 137.4 (d, J_{C-F} = 271 Hz), 133.5, 130.0, 129.9, 129.2, 128.8, 128.5, 125.6, 45.1; IR (thin film) 3057, 2912, 1675, 1594, 1327, 1112, 994, 870, 754, 687 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{11}OF_3$ $(M + H)^+$ 265.0840, found 265.0843; mp 130−132 °C.

O-Allyl Oxime Ether ***1nn***. Allyl hydroxylamine hydrochloride (0.61 g, 0.57 mmol) was treated with NaOAc (0.62 g, 0.76 mmol) and ketone **9nn** (0.11 g, 0.50 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup and flash chromatography (2% TEA/hexanes−5% EtOAc/2%TEA/hexanes), **1nn** was isolated as a clear, colorless oil (0.11 g, 79%, *E*:*Z* = 3:1): ^{1}H NMR of *E*-imine isomer (500 MHz, $CDCl_3$) δ 7.62−7.60 (m, 2H),

7.55−7.52 (m, 2H), 7.35−7.28 (m, 5H), 6.05−5.99 (m, 1H), 5.30 (d, J = 16.0 Hz, 1H), 5.23 (d, J = 11.5 Hz, 1H), 4.74 (d, J = 6.0 Hz, 2H), 4.21 (s, 2H); ^{13}C NMR of *E*-imine isomer (125 MHz, $CDCl_3$) δ 117.8, 75.4, 32.9; ^{1}H NMR of *Z*-imine isomer (500 MHz, $CDCl_3$) δ 7.62−7.60 (m, 2H), 7.55−7.52 (m, 2H), 7.35−7.28 (m, 5H), 6.05−5.99 (m, 1H), 5.30 (d, J = 16.0 Hz, 1H), 5.23 (d, J = 11.5 Hz, 1H), 4.13 (d, J = 5.5 Hz, 2H), 3.91 (s, 2H); ^{13}C NMR of *Z*-imine isomer (125 MHz, $CDCl_3$) δ 117.3, 75.1, 41.8; IR (thin film) 3060, 2923, 2865, 2227, 1607, 1502, 1444, 1020, 922, 694 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{16}N_2O$ $(M + H)^+$ 277.1341, found 277.1345.

Ketone ***9nn***[43]. Ketone **9nn** was prepared via a cross-coupling reaction between acetophenone and 4-cyano iodobenzene.[42] In an inert atmosphere glovebox, a 25 mL round-bottom flask was charged with $Pd(dba)_2$ (0.087 g, 0.150 mmol) and dppf (0.099 g, 0.18 mmol). To the flask, 6 mL of THF were added and allowed to stir for 5 min before the addition of NaO-*t*-Bu (0.211 g, 2.20 mmol). The remaining solids were washed from the sides of the flask with 4 mL of THF. The flask was then removed from the glovebox and placed under an atmosphere of N_2 with a needle. While stirring, 4-iodobenzotrifluoride (0.462 g, 2.02 mmol) was added to the catalyst mixture, followed by acetophenone (0.240 g, 2.0 mmol). The reaction flask was then attached to a reflux condenser and the reaction mixture was heated to 75 °C for 2.5 h. The crude product was dry loaded on to silica and purified by flash chromatography (2% TEA/hexanes−10% EtOAc/2% TEA/hexanes) to afford **9nn** as a white solid (0.238 g, 53%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01−7.99 (m, 2H), 7.63−7.59 (m, 3H), 7.51−7.48 (m, 2H), 7.38−7.36 (m, 2H), 4.36 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.2, 140.0, 136.2, 133.7, 132.3, 130.6, 128.9, 128.5, 118.8, 111.0, 45.2, 166.4, 139.7, 139.7, 136.4, 133.4, 129.9, 129.6, 129.2, 128.8, 128.6, 60.3, 45.4, 14.4; IR (thin film) 3063, 2897, 2223, 1686, 1605, 1447, 1338, 1219, 999, 683 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{11}NO$ $(M + H)^+$ 222.0919, found 222.0919.

O-Allyl Oxime ***1oo***. Allyl hydroxylamine hydrochloride (0.128 g, 1.17 mmol) was treated with NaOAc (0.131 g, 1.60 mmol) and ketone **9oo** (0.285 g, 1.06 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup and flash chromatography (2% TEA/hexanes−5% EtOAc/2%TEA/hexanes), **1oo** was isolated as a clear, colorless oil (0.271 g, 79%, *E*:*Z* = 3:1): ^{1}H NMR of *E*-imine isomer (500 MHz, $CDCl_3$) δ 7.98−7.94 (m, 2H), 7.66−7.64 (m, 1H), 7.35−7.28 (m, 6H), 6.09−6.02 (m, 1H), 5.34 (dd, J = 17.5, 1.5 Hz, 1H), 5.25 (dd, J = 10.5, 1.5 Hz, 1H), 4.78 (d, J = 5.5 Hz, 2H), 4.36 (q, J = 7.0 Hz, 2H), 4.24 (s, 2H), 1.38 (t, J = 7.0 Hz, 3H); ^{13}C NMR of *E*-imine isomer (125 MHz, $CDCl_3$) δ 166.5, 155.6, 142.2, 134.3, 133.5, 133.3, 130.2, 128.9, 126.2, 118.4, 115.0, 117.6, 75.3, 60.8, 32.9, 14.4; ^{1}H NMR of *Z*-imine isomer (500 MHz, $CDCl_3$) δ 7.98−7.94 (m, 2H), 7.66−7.64 (m, 1H), 7.35−7.28 (m, 6H), 6.09−6.02 (m, 1H), 5.34 (dd, J = 17.5, 1.5 Hz, 1H), 5.25 (dd, J = 10.5, 1.5 Hz, 1H), 4.65 (d, J = 5.5 Hz, 2H), 4.36 (q, J = 7 Hz, 2H), 3.92 (s, 2H), 1.38 (t, J = 7 Hz, 3H); ^{13}C NMR of *Z*-imine isomer (125 MHz, $CDCl_3$) δ 166.5, 155.6, 142.2, 134.5, 133.5, 133.3, 130.2, 128.9, 126.2, 118.4, 117.2, 75.0, 60.9, 41.8, 14.4; IR (thin film) 2980, 2919, 1714, 1611, 1415, 1272, 1102, 1020, 918, 693 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{21}NO_3$ $(M + H)^+$ 324.1600, found 324.1599.

Ketone ***9oo***[44]. Ketone **9oo** was prepared via a cross-coupling reaction between acetophenone and 4-(ethyl ester) iodobenzene.[42] In an inert atmosphere glovebox, a 25 mL round-bottom flask was charged with $Pd(dba)_2$ (0.0863 g, 0.150 mmol) and dppf (0.0998 g, 0.179 mmol). To the flask, 6 mL of THF were added and allowed to stir for 5 min before the addition of NaO-*t*-Bu (0.288 g, 3.00 mmol). The remaining solids were washed from the sides of the flask with 4 mL of THF. The flask was then removed from the glovebox and placed under an atmosphere of N_2 with a needle. While stirring, ethyl 4-iodobenzoate (0.553 g, 2.00 mmol) was added to the catalyst mixture, followed by acetophenone (0.240 g, 2.0 mmol). The reaction flask was then attached to a reflux condenser, and the reaction mixture was heated to 75 °C for 2.5 h. The crude product was dry loaded on to silica and purified by flash chromatography (2% TEA/hexanes−10% EtOAc/2% TEA/hexanes) to afford **9oo** as a white solid (0.285 g, 53%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02−7.99 (m, 4H), 7.59−7.56 (m, 1H), 7.49−7.44 (m, 2H), 7.35−7.33 (m, 2H), 4.36 (q, J = 7.0 Hz, 2H), 4.35 (s, 2H), 1.38 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.8, 166.4, 139.7, 139.7, 136.4, 133.4, 129.9, 129.6, 129.2, 128.8, 128.6, 60.3, 45.4, 14.4; IR (thin film) 3053, 2982, 2884, 1707, 1683, 1610, 1449, 1104, 997, 755 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{17}H_{16}O_3$ $(M + H)^+$ 269.1178, found 269.1178; mp 88−90 °C.

O-Allyl Oxime ***1pp***. Allylhydroxylamine hydrochloride (0.899 g, 8.21 mmol) was treated with NaOAc (0.673 g, 8.20 mmol) and β-tetralone (1.00 g, 6.84 mmol). The reaction flask was then attached to a reflux condenser and allowed to stir at 60 °C for 24 h. After workup and flash chromatography (2% TEA/hexanes), **1pp** was isolated as a light orange liquid (1.25 g, 91%, *E*:*Z* = 1:1): ^{1}H NMR of *E*-imine isomer (500 MHz, $CDCl_3$) δ 7.22−7.15 (m, 4H), 6.10−5.99 (m, 1H), 5.36 (dd, J = 17.0, 1.5 Hz, 1H), 5.22 (dd, J = 10.5, 1.5 Hz, 1H), 4.58 (d, J = 5.5 Hz, 2H), 3.54 (s, 2H), 2.85 (t, J = 7.0 Hz, 2H), 2.72 (t, J = 7.0 Hz, 2H); ^{13}C NMR of *E*-imine isomer (125 MHz, $CDCl_3$) δ 158.7, 138.4, 134.6, 133.4, 128.9, 127.6, 126.7, 126.6, 117.3, 74.6, 35.1, 29.1, 27.7; ^{1}H NMR of Z-imine isomer (500 MHz, $CDCl_3$) δ 7.22−7.15 (m, 4H), 6.10−5.99 (m, 1H), 5.32 (dd, J = 17.0, 1.5 Hz, 1H), 5.26 (dd, J = 10.5, 1.5 Hz, 1H), 4.64 (d, J = 5.5 Hz, 2H), 3.83 (s, 2H), 2.91 (t, J = 7.0 Hz, 2H), 2.59 (t, J = 7.0 Hz, 2H); ^{13}C NMR of *Z*-imine isomer (125 MHz, $CDCl_3$) δ 158.1, 137.1, 135.0, 134.7, 128.2, 127.3, 126.6, 126.2, 117.1, 74.5, 35.1, 29.4, 24.9; IR (thin film) 3020, 2921, 2907, 2861, 2847, 1641, 1419, 1032, 912, 741 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{16}NO$ $(M + H)^+$ 202.1232, found 202.1230.

General Procedure for the Synthesis of Pyrroles 3c−l (Scheme 4). In an inert atmosphere drybox, a 20 mL scintillation vial was charged with 0.5 equiv of $[(cod)IrCl]_2$, 1 equiv of AgOTf, 1 equiv of $NaBH_4$, and 3 mL of THF. This mixture was then allowed to stir at 25 °C for 20 min. *O*-Allyl oxime **1** (10 equiv) was mixed with 2 mL of THF in a small vial. The oxime solution was then transferred to the scintillation vial containing the 10 mol % iridium mixture. For pyrroles **3c**−**i**, the reaction mixture was then allowed to stir at 25 °C for 24−48 h. For pyrroles **3i**−**l**, the reaction mixture was then transferred to a Teflon-sealed, conical vial and allowed to stir at 25 °C for 18 h. The vial was then removed from the glovebox and heated to 50 °C for 24 h in an aluminum block. After the indicated reaction times, an aliquot was removed from the reaction mixture and checked by ^{1}H NMR spectroscopy to determine if the transformation had gone to completion. The reaction mixture was then dry-loaded on to silica gel and **3** was purified by flash chromatography (2% TEA/hexanes −40% EtOAc/2% TEA/hexanes).

Pyrrole ***3c***[45]. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1c** (0.122 g, 0.609 mmol) was then added to the catalyst mixture, and the reaction mixture was allowed to stir for 48 h. After flash chromatography (2% TEA/hexanes −40% EtOAc/2% TEA/hexanes), **3c** was isolated as a light yellow solid (0.092 g, 83%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (br s, 1H), 7.69−7.67 (m, 2H), 7.45−7.41 (m, 2H), 7.37−7.33 (m, 1H), 6.60 (m, 1H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 130.1, 129.2, 128.5, 125.5, 124.2, 117.4, 116.8, 91.6, 10.7; IR (thin film) 3214, 3042, 2920, 2218, 1584, 1468, 1098, 763, 694, 623 cm^{-1}; HRMS (ESI) m/z calcd for $C_{12}H_{11}N_2$ $(M + H)^+$ 183.0922, found 183.0920; mp 120−122 °C.

Pyrrole ***3d***[24]. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1d** (0.126 g, 0.588 mmol) was then added to the catalyst mixture, and the complete reaction mixture was allowed to stir for 24 h. After flash

chromatography (2% TEA/hexanes −40% EtOAc/2% TEA/hexanes), **3d** was isolated as light yellow solid (0.0847 g, 73%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (br s, 1H), 7.58−7.56 (m, 2H), 7.23−7.21 (m, 2H), 6.57 (s, 1H), 2.37 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.6, 129.9, 127.3, 125.4, 124.0, 117.7, 116.5, 91.0, 21.3, 10.7; IR (thin film) 3429, 3295, 3027, 2941, 2917, 2857, 2206, 1641, 1536, 820, 771 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{13}N_2$ $(M + H)^+$ 197.1079, found 197.1076; mp 135−137 °C.

Pyrrole ***3e***[24]. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (16.8 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1e** (0.147 g, 0.638 mmol) was then added to the catalyst mixture, and the complete reaction mixture was allowed to stir for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3e** was isolated as light yellow solid (0.101 g, 74%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (br s, 1H), 7.61−7.59 (m, 2H), 6.93−6.91 (m, 2H), 6.54 (s, 1H), 3.82 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 138.9, 127.0, 123.7, 122.9, 117.9, 116.2, 114.6, 90.4, 55.4, 10.7; IR (thin film) 3288, 3133, 3108, 2917, 2840, 2206, 1613, 1536, 1251, 820, 727 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{13}N_2O$ $(M + H)^+$ 213.1028, found 213.1026; mp 114−116 °C.

Pyrrole ***3f***[24]. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime ether **1f** (0.168 g, 0.602 mmol) was then added to the catalyst mixture, and the complete reaction mixture was allowed to stir for 48 h. After flash chromatography (2% TEA/hexanes −40% EtOAc/2% TEA/hexanes), **3f** was isolated as light yellow solid (0.120 g, 76%): ^{1}H NMR (500 MHz, CD_3OD) δ 7.64−7.62 (m, 2H), 7.60−7.58 (m, 2H), 6.68 (s, 1H), 2.18 (s, 3H) the NH peak did not appear in the ^{1}H NMR spectrum; ^{13}C NMR (125 MHz, CD_3OD) δ 136.9, 131.8, 129.6, 126.8, 123.5, 121.5, 117.8, 117.1, 90.3, 9.2; IR (thin film) 3284, 3133, 2921, 2860, 2218, 1523, 824, 771, 706 cm^{-1}; HRMS (ESI) m/z calcd for $C_{12}H_{10}N_2Br$ $(M + H)^+$ 261.0027, found 261.0023; mp 212−215 °C.

Pyrrole ***3g***. The catalyst mixture was synthesized by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (16.8 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1g** (0.180 g, 0.671 mmol) was then added to the catalyst mixture, and the reaction mixture was allowed to stir for 36 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3g** was isolated as an light yellow solid (0.101 g, 60%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (br s, 1H), 7.96−7.94 (m, 1H), 7.81 (s, 1H), 7.63−7.57 (m, 2H), 6.67 (s, 1H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 130.8, 130.0, 129.0, 125.1, 124.8, 121.9, 117.5, 116.6, 93.0, 10.7 (the CF_3 and aryl *C*-CF_3 resonances were not observed due to ^{19}F-splitting and low solubility in $CDCl_3$); IR (thin film) 3265, 2930, 2222, 1587, 1522, 1469, 1314, 1168, 1109, 803 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{13}H_{10}N_2F_3$ $(M + H)^+$ 251.0796, found 251.0797; mp 178−180 °C.

Pyrrole ***3h***. The catalyst mixture was synthesized by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.00225 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1h** (0.122 g, 0.480 mmol) was then added to the catalyst mixture, and the reaction mixture was allowed to stir for 36 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3h** was isolated as a light yellow solid (0.0895 g, 79%): ^{1}H NMR (500 MHz, $CDCl_3$) 8.37 (br s, 1H), 7.40−7.38 (m, 1H), 7.35 (s, 1H), 7.14−7.12 (m, 1H), 6.56 (s, 1H), 2.80−2.79 (m, 4H), 2.22 (s, 3H), 1.83−1.80 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 138.1, 138.0, 130.0, 127.3, 126.1, 124.1, 122.7, 117.3, 116.1, 91.3, 29.4, 29.3, 23.0 (2C, coincidental CH_2), 10.7; IR (thin film) 3268, 2917, 2852, 2217, 1736, 1580, 1467, 1106, 826, 713 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{19}N_2O$ $(M + H)^+$ 237.1392, found 237.1391; mp 174−176 °C.

Pyrrole ***3i***[24]. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime ether **1i** (0.328 g, 1.27 mmol) was then added to the catalyst mixture, and the complete reaction mixture was allowed to stir for 36 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3i** was isolated as light yellow solid (0.0916 g, 30%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (br s, 1H), 8.07−8.05 (m, 2H), 7.76−7.74 (m, 2H), 6.67 (s, 1H), 3.93 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 136.8, 134.1, 130.5, 129.6, 125.1, 125.0, 117.9, 117.0, 92.9, 52.3, 10.7; IR (thin film) 3251, 3035, 2954, 2926, 2214, 1714, 1613, 1580, 1271, 857, 727 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{13}N_2O_2$ $(M + H)^+$ 241.0977, found 241.0969; mp 198−200 °C.

Pyrrole ***3i*** *at 50 °C*[24]. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1i** (0.173 g, 0.671 mmol) was then added to the catalyst mixture and the reaction was allowed to stir for 18 h at 25 °C and then 24 h at 50 °C. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3i** was isolated as light yellow solid (0.134 g, 83%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (br s, 1H), 8.07−8.05 (m, 2H), 7.76−7.74 (m, 2H), 6.67 (s, 1H), 3.93 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 136.8, 134.1, 130.5, 129.6, 125.1, 125.0, 117.9, 117.0, 92.9, 52.3, 10.7; IR (thin film) 3251, 3035, 2954, 2926, 2214, 1714, 1613, 1580, 1271, 857, 727 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{13}N_2O_2$ $(M + H)^+$ 241.0977, found 241.0969; mp 198−200 °C.

Pyrrole ***3j***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1j** (0.153 mg, 0.701 mmol) was then added to the catalyst mixture, and the reaction was allowed to stir for 18 h at 25 °C and then 24 h at 50 °C. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3j** was isolated as a light yellow solid (0.103 g, 74%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (br s, 1H), 7.65−7.62 (m, 2H), 7.16−7.12 (m, 2H), 6.60 (m, 1H), 2.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7 (d, J_{C-F} = 247.5 Hz),154.8, 136.7, 134.5, 129.0, 128.4, 126.1, 117.3, 75.1, 12.8; IR (thin film) 3262, 2929, 2850, 2208, 1606, 1528, 1495, 1229, 1092, 822, cm^{-1}; HRMS (ESI) m/z calcd for $C_{12}H_{10}FN_2$ $(M + H)^+$ 201.0828, found 201.0831; mp 124−126 °C.

Pyrrole ***3k***. The catalyst mixture was synthesized by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1k** (0.182 g, 0.777 mmol) was then added to the catalyst mixture, and the reaction mixture was allowed to stir for 18 h and then heated at 50 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3k** was isolated as a light yellow solid (0.136 g, 81%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (br s, 1H), 7.62−7.58 (m, 2H), 7.42−7.40 (m, 2H), 6.62 (m, 1H), 2.23 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2, 134.5, 129.5, 128.5, 127.1, 126.7, 124.5, 117.0, 92.2, 10.7; IR (thin film) 3252, 2917, 2852, 2215, 1646, 1457, 1083, 948, 820, 709 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{12}H_9ClN_2$ $(M + H)^+$ 217.0533, found 217.0534; mp 177−179 °C.

Pyrrole ***3l***. The catalyst mixture was synthesized by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1l** (0.129 g, 0.678 mmol) was then added to the catalyst mixture, and the reaction mixture was allowed to stir at 25 °C for 18 h and then at 50 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3l** was isolated as a light yellow solid (0.0742 g, 64%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (br s, 1H), 7.40 (s, 1H), 6.91−6.90 (m, 1H), 6.54 (s, 1H), 6.50−6.49 (m, 1H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 141.7, 130.2, 123.5, 116.5, 116.2, 112.1, 107.0, 90.0, 10.6; IR (thin film) 3265, 2925, 2214, 1614, 1561, 1441, 1092, 1017, 887, 733 cm^{-1}; HRMS (ESI) m/z calcd for $C_{10}H_9N_2O$ $(M+H)^+$ 173.0715, found 173.0715; mp 102−104 °C.

General Procedure for the Synthesis of Pyrroles 4a,b and 4m−v (Scheme 5). A 10 mL reaction flask with a Teflon stopper was flushed with N_2 and charged with 1 equiv of **2** dissolved in 4 mL of dioxane (dried over CaH_2 and isolated by vacuum transfer) and ∼15 4 Å molecular sieves. The flask was then sealed and heated to 75 °C for 18 h. The reaction mixture was then dry-loaded onto ∼2 mL of silica gel. The crude product was purified by flash chromatography using a solvent gradient (2% TEA/hexanes−20% EtOAc/2% TEA/hexanes). The fractions containing **3** were combined, and the solvent was removed under vacuum using a rotary evaporator. The product was then transferred to a scintillation vial and all remaining volatiles were removed under high vacuum.

Pyrrole ***4a***[46]. Vinyl oxime ether **2a** (117 mg, 0.570 mmol) was dissolved in dioxane with 4 Å molecular sieves and heated at 75 °C for 18 h. After workup and purification, **4a** was isolated as a light yellow solid (68.3 mg, 64%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (br s, 1H), 7.37−7.35 (m, 2H), 6.90−6.89 (m, 2H), 6.28 (s, 1H), 5.93 (s, 1H), 3.82 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.9, 130.9, 128.4, 126.2, 124.8, 114.3, 107.7, 105.0, 55.4, 13.2; IR (thin film) 3437, 3395, 3050, 2920, 2835, 1616, 1590, 1245, 822, 764 cm^{-1}; HRMS (ESI) m/z calcd for $C_{12}H_{14}NO$ $(M + H)^+$ 188.1075, found 188.1079; mp 126−129 °C.

Pyrrole ***4b***[47]. Vinyl oxime ether **2b** (130 mg, 0.524 mmol) was dissolved in dioxane with 4 Å molecular sieves and heated at 75 °C for 24 h. After workup and column chromatography, **4b** was isolated as a light yellow amphorous solid (72 mg, 60%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (br s, 1H), 7.56−7.54 (m, 2H), 7.37−7.30 (m, 3H), 6.38 (s, 1H), 4.16 (q, J = 7.0 Hz, 2H), 2.24 (s, 3H), 1.23 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 136.1, 132.3, 128.9, 128.0, 127.9, 127.8, 112.0, 109.5, 59.6, 14.3, 12.7; IR (thin film) 3292, 3028, 2980, 2925, 1666, 1593, 1528, 1222, 814, 762 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{16}NO_2$ $(M + H)^+$ 230.1181, found 230.1179.

Pyrrole ***4m***. Vinyl oxime ether **2m** (132 mg, 0.599 mmol) was dissolved in dioxane with 4 ÅÅ molecular sieves and heated at 75 °C for 18 h. After workup and purification, **4m** was isolated as a light yellow oil (51 mg, 42%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (bs, 1H), 7.83 (d, J = 9 Hz, 2H), 7.50 (d, J = 9 Hz, 2H), 6.63 (s, 1H), 6.04 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 138.9, 132.6, 128.6, 124.8, 122.7, 110.6, 109.7, 13.5; IR (thin film) 3361, 2919, 1597, 1512, 1495, 1321, 1265, 1220, 1109, 1045, 850, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{11}H_{10}N_2O_2$ $(M + H)^+$ 203.0821, found 203.0822.

Pyrrole ***4n***[48]. Vinyl oxime ether **2n** (227 mg, 0.897 mmol) was dissolved in dioxane with 4 Å molecular sieves and heated at 75 °C for 18 h. After workup and purification, **4n** was isolated as a light yellow solid (117 mg, 55%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (br s, 1H), 7.46−7.44 (m, 2H), 7.30−7.28 (m, 2H), 6.39 (s, 1H), 5.96 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.9, 129.7, 124.8, 119.0, 108.3, 106.8, 13.2 (two quaternary carbons were not visible even with high signal-to-noise); IR (thin film) 3385, 2919, 2848, 1606, 1503, 827, 768, 662 cm^{-1}; HRMS (ESI) m/z calcd for $C_{11}H_{11}NBr$ $(M)^+$ 236.0075, found 236.0073; mp 102−105 °C.

Pyrrole ***4o***[48]. Vinyl oxime ether **2o** (130 mg, 0.535 mmol) was dissolved in dioxane with 4 Å molecular sieves and heated at 75 °C for 24 h. After workup and purification, **4o** was isolated as a light yellow solid (55.5 mg, 46%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (br s, 1H), 7.58−7.56 (m, 2H), 7.50−7.48 (m, 2H), 6.52 (s, 1H), 6.00 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.1, 130.6, 129.3, 127.1 (q, J_{C-F} = 33 Hz), 126.6 (q, J_{C-F} = 270 Hz), 125.9, 123.0, 108.6, 108.1, 13.2; IR (thin film) 3395, 1616, 1528, 1480, 1326, 1105, 832, 777 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{12}H_{11}NF_3$ $(M + H)^+$ 226.0844, found 226.0836; mp 130−132 °C.

Pyrrole ***4p***. Vinyl oxime ether **2p** (95.5 mg, 0.465 mmol) was dissolved in dioxane with 4 Å molecular sieves and heated at 75 °C for 18 h. After workup and purfication, **4p** was isolated as a light yellow oil (49.3 mg, 57%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (br s, 1H), 7.65−7.64 (m, 1H), 7.15−7.12 (m, 1H), 7.01−6.95 (m, 2H), 6.53 (s, 1H), 5.97 (s, 1H), 3.97 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 128.4, 127.9, 126.2, 126.1, 121.4, 111.6, 106.8, 106.5, 55.7, 13.4 (one quaternary carbon was not visible even with high signal-to-noise); IR (thin film) 3450, 3104, 3064, 2958, 2917, 1589, 1507, 1231, 816, 743 cm^{-1}; HRMS (ESI) m/z calcd for $C_{12}H_{14}NO$ $(M + H)^+$ 188.1075, found 188.1078.

Pyrrole ***4q***[49]. Vinyl oxime ether **2q** (143 mg, 0.817 mmol) was dissolved in dioxane with 4 Å molecular sieves and heated at 75 °C for 18 h. After workup and purification, **4q** was isolated as a light yellow solid (75.1 mg, 58%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (br s, 1H), 7.46−7.44 (m, 2H), 7.38−7.34 (m, 2H), 7.21−7.17 (m, 1H), 6.43 (s, 1H), 5.98 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.0, 130.8, 129.1, 128.9, 125.7, 123.4, 108.0, 106.2, 13.2; IR (thin film) 3437, 3395, 3050, 2913, 2861, 1606, 1587, 1251, 893, 741 cm^{-1}; HRMS (ESI) m/z calcd for $C_{11}H_{12}N$ $(M + H)^+$ 158.0970, found 158.0968; mp 85−88 °C.

Pyrrole ***4r***[50]. Vinyl oxime ether **2r** (145 mg, 0.579 mmol) was dissolved in dioxane with 4 Å molecular sieves and heated at 75 °C for 18 h. After workup and column chromatography, **4r** was isolated as a light yellow amorphous solid (81.4 mg, 60%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (br s, 1H), 7.38−7.18 (m, 10H), 6.12 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.8, 133.6, 128.6, 128.5, 128.4, 128.3, 127.3, 126.9, 126.4, 125.6, 122.3, 109.0, 13.0; IR (thin film) 3414, 3056, 3020, 2916, 1596, 1499, 1076, 803, 744 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{16}N$ $(M + H)^+$ 234.1283, found 234.1272.

Pyrrole ***4s***[51]. Vinyl oxime ether **2s** (141 mg, 0.641 mmol) was dissolved in dioxane with 4 Å molecular sieves and heated at 75 °C for 18 h. After workup and column chromatography, **4s** was isolated as a light yellow oil (78.2 mg, 61%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (br s, 1H), 7.33−7.31 (m, 2H), 6.95−6.93 (m, 2H), 5.82 (s, 1H), 3.84 (s, 3H), 2.29 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7, 127.5, 126.8, 126.7, 126.7, 115.3, 114.1, 109.9, 55.3, 13.0, 12.3; IR (thin film) 3395, 3304, 2937, 2835, 1606, 1567, 1239, 819, 764 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{13}H_{16}NO$ $(M + H)^+$ 202.1232, found 202.1240.

Pyrrole ***4t***[52]. Vinyl oxime ether **2t** (197 mg, 1.120 mmol) was dissolved in dioxane with 4 Å molecular sieves and heated at 75 °C for 24 h. After workup and column chromatography, **4t** was isolated as a light yellow solid (90.0 mg, 51%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89−8.74 (br s, 1H), 8.49−8.48 (m, 2H), 7.30−7.29 (m, 2H), 6.64 (s, 1H), 6.01 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.1, 139.6, 131.8, 127.7, 117.2, 109.6, 109.0, 13.3; IR (thin film) 3196, 3128, 2930, 2852, 1603, 1587, 819, 780 cm^{-1}; HRMS (ESI) m/z calcd for $C_{10}H_{11}N_2$ $(M + H)^+$ 159.0922, found 159.0915; mp 210−213 °C.

Pyrrole ***4u (Minor)***. Vinyl oxime ether **2u** (122 mg, 0.557 mmol) was dissolved in dioxane with 4 Å molecular sieves and heated at 75 °C for 24 h. After workup and purification, **4u (minor)** was isolated as a light yellow oil (13 mg, 12%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (br s, 1H), 7.15−7.13 (m, 2H), 6.86−6.85 (m, 2H), 5.83 (s, 1H), 5.78 (s, 1H), 3.87 (s, 2H), 3.80 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 131.8, 129.8, 129.7, 126.9, 114.0, 106.3, 105.7, 55.3, 33.3, 13.1; IR (thin film) 3365, 3055, 2994, 2966, 2935, 1600, 1508, 1262, 816, 731 cm^{-1}; HRMS (EI) m/z calcd for $C_{13}H_{15}NO$ $(M)^+$ 201.1154, found 201.1156.

Pyrrole ***4u (Major)***. Vinyl oxime ether **2u** (122 mg, 0.557 mmol) was dissolved in dioxane with 4 Å molecular sieves and heated at 75 °C for 24 h. After workup and column chromatography, **4u (major)** was isolated as a light yellow oil (38 mg, 34%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (br s, 1H), 7.36−7.34 (m, 2H), 6.96−6.94 (m, 2H), 5.99 (s, 1H), 3.85 (s, 3H), 2.36 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 130.0, 128.6, 125.7, 121.8, 120.6, 113.8, 106.3, 55.3, 12.9, 12.5; IR (thin film) 3437, 3369, 3055, 2935, 2911, 2838, 1608, 1532, 1267, 832, 731 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{16}NO$ $(M + H)^+$ 202.1232, found 202.1230.

Pyrrole ***4v***. Vinyl oxime ether **2v** (40.0 mg, 0.236 mmol) was dissolved in dioxane with 4 Å molecular sieves and heated at 75 °C for 24 h. After workup and column chromatography, **4v** was isolated as a light yellow oil (26 mg, 73%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (br s, 1H), 5.79−5.76 (m, 2H), 2.41 (s, 2H), 2.25 (s, 3H), 0.96 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 128.9, 125.8, 107.4, 105.7, 42.6, 31.6, 28.2, 13.1; IR (thin film) 3373, 1949, 2906, 2864, 1653, 1593, 1508, 1476, 1390, 1357, 1236, 1039 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{10}H_{18}N$ $(M + H)^+$ 152.1439, found 152.1432.

General Procedure for the Synthesis of Pyrroles 4a, 4b, 4m, 4r, 4s, and 4w (Scheme 6). The general procedure used for the preparation of **2** was used to prepare the reaction mixtures. After 24 h at 25 °C, the reaction mixtures were transferred to 10 mL Teflon-sealed reaction flasks, charged with ∼15 4 Å molecular sieves, and heated to 75 °C for 15 h. The reaction mixtures were then transferred to scintillation vials and dry-loaded on ∼3 mL of silica gel. The product was then purified by flash chromatography as described in the general procedure for the synthesis of **4a**, **4b**, and **4m**−**v** (Scheme 5). The mass balance for these transformations is assumed to be highly colored polymeric pyrrole materials that were observed to remain coordinated to the silica gel.

Pyrrole ***4a***[46]. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0665 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1a** (0.133 g, 0.649 mmol) was then added to the catalyst mixture, and the complete reaction mixture was allowed to stir for 24 h and then transferred to a Teflon-sealed reaction flask and heated to 75 °C for 15 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **4a** was isolated as light yellow solid (0.0562 g, 46%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (br s, 1H), 7.37−7.35 (m, 2H), 6.90−6.89 (m, 2H), 6.28 (s, 1H), 5.93 (s, 1H), 3.82 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.9, 130.9, 128.4, 126.2, 124.8, 114.3, 107.7, 105.0, 55.4, 13.2; IR (thin film) 3437, 3395, 3050, 2920, 2835, 1616, 1590, 1245, 822, 764 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{12}H_{14}NO$ $(M + H)^+$ 188.1075, found 188.1079; mp 126−129 °C.

Pyrrole ***4b***[47]. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1b** (0.128 mg, 0.518 mmol) was then added to the catalyst mixture, and the complete reaction mixture was allowed to stir for 24 h and then transferred to a Teflon-sealed reaction flask and heated to 75 °C for 15 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **4b** was isolated as light yellow oil (0.0478 g, 40%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (br s, 1H), 7.56−7.54 (m, 2H), 7.37−7.30 (m, 3H), 6.38 (s, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 2.24 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 136.1, 132.3, 128.9, 128.0, 127.9, 127.8, 112.0, 109.5, 59.6, 14.3, 12.7; IR (thin film) 3292, 3028, 2980, 2925, 1666, 1593, 1528, 1222, 814, 762 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{16}NO_2$ $(M + H)^+$ 230.1181, found 230.1179.

Pyrrole ***4m***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.045 g, 0.067 mmol), AgOTf (0.034 g, 0.13 mmol), and $NaBH_4$ (0.005 g, 0.13 mmol) in THF for 15 min. Allyl oxime **1m** (0.290 g, 1.32 mmol) was then added to the catalyst mixture, and the complete reaction mixture was allowed to stir for 24 h and then transferred to a Teflon-sealed reaction flask and heated to 75 °C for 15 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **4m** was isolated as light yellow oil (0.107 g, 40%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (bs, 1H), 7.83 (d, *J* = 9 Hz, 2H), 7.50 (d, *J* = 9 Hz, 2H), 6.63 (s, 1H), 6.04 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 138.9, 132.6, 128.6, 124.8, 122.7, 110.6, 109.7, 13.5; IR (thin film) 3361, 2919, 1597, 1512, 1495, 1321, 1265, 1220, 1109, 1045, 850, 750 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{11}H_{10}N_2O_2$ $(M + H)^+$ 203.0821, found 203.0822.

Pyrrole ***4r***[50]. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.654 mmol), and $NaBH_4$ (0.0025 g, 0.66 mmol) in THF for 15 min. Allyl oxime **1r** (0.138 g, 0.550 mmol) was then added to the catalyst mixture, and the complete reaction mixture was allowed to stir for 24 h and then transferred to a Teflon-sealed reaction flask and heated to 75 °C for 15 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **4r** was isolated as light yellow amphorous solid (0.052 g, 41%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (br s, 1H), 7.38−7.18 (m, 10H), 6.12 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.8, 133.6, 128.6, 128.5, 128.4, 128.3, 127.3, 126.9, 126.4, 125.6, 122.3, 109.0, 13.0; IR (thin film) 3414, 3056, 3020, 2916, 1596, 1499, 1076, 803, 744 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{16}N$ $(M + H)^+$ 234.1283, found 234.1272.

Pyrrole ***4s***[51]. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime ether **1s** (0.130 g, 0.594 mmol) was then added to the catalyst mixture, and the complete reaction mixture was allowed to stir for 24 h and then transferred to a Teflon-sealed reaction flask and heated to 75 °C for 15 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **4s** was isolated as light yellow oil (0.0478 g, 40%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (br s, 1H), 7.33−7.31 (m, 2H), 6.95−6.93 (m, 2H), 5.82 (s, 1H), 3.84 (s, 3H), 2.29 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7, 127.5, 126.8, 126.7, 126.7, 115.3, 114.1, 109.9, 55.3, 13.0, 12.3; IR (thin film) 3395, 3304, 2937, 2835, 1606, 1567, 1239, 819, 764 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{13}H_{16}NO$ $(M + H)^+$ 202.1232, found 202.1240.

Pyrrole ***4w***[53]. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime ether **1w** (0.120 g, 0.78 mmol) was then added to the catalyst mixture and the complete reaction mixture was allowed to stir for 24 h and then transferred to a Teflon-sealed reaction flask and heated to 75 °C for 15 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **4w** was isolated as light yellow oil (0.044 g, 42%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (br s, 1H), 5.65 (s, 1H), 2.46−2.54 (m, 4H), 2.24 (s, 3H), 1.73−1.83 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 125.8, 125.4, 117.0, 105.1, 23.9, 23.6, 22.9, 22.7, 13.0; IR (thin film) 3294, 3206, 2926, 2855, 1632, 1443, 864 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_9H_{14}N$ $(M + H)^+$ 136.1, found 136.1.

General Procedure for the Synthesis of Pyrroles 3b, 3x−kk, and 3mm−pp (Schemes 10 and 14). In an inert atmosphere drybox, a 20 mL scintillation vial was charged with 0.5 equiv of $[(cod)IrCl]_2$, 1 equiv of AgOTf, 1 equiv of $NaBH_4$, and 3 mL of THF. This mixture was then allowed to stir at 25 °C for 20 min. *O*-Allyl oxime **1** (10 equiv) was mixed with 2 mL of THF in a small vial. The oxime solution was then transferred to the scintillation vial containing the 10 mol % iridium mixture, and DBU (10 equiv) was added after the substrate. The reaction mixture was then transferred to a Teflon-sealed, conical vial and allowed to stir at 25 °C for 1 h. The vial was then removed from the glovebox and heated to 75 °C for 24 h in an aluminum block. The reaction mixture was then dry-loaded on to silica gel and **3** was purified by flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes).

Pyrrole ***3b***[54]. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1b** (0.165 g, 0.667 mmol) was then added to the catalyst mixture, followed by DBU (0.145 g, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3b** was isolated as light yellow solid (0.132 g, 86%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (br s, 1H), 7.43−7.40 (m, 2H), 7.04−7.01 (m, 2H), 6.50 (s, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 2.30 (s, 3H), 1.21 (t, *J* = 7.0 Hz,

3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 137.6, 133.1, 129.1, 128.9, 127.9, 122.5, 116.8, 111.3, 59.4, 14.1, 12.6; IR (thin film) 3301, 2981, 2925, 2857, 1670, 1432, 1284, 1137, 1081, 759 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{16}NO_2$ $(M + H)^+$ 230.1181, found 230.1183; mp 90−92 °C.

Pyrrole ***3b*** *from* ***2b***:[54]. *O*-Vinyl oxime **2b** (0.127 g, 0.512 mmol) was dissolved in 3 mL of THF and mixture with DBU (0.112 g, 0.952 mmol). The reaction mixture was then transferred to a Teflon-sealed reaction flask at allowed to heat at 75 °C for 24 h. After column chromatography, **3b** was isolated as a light yellow solid (0.105 g, 89%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (br s, 1H), 7.43−7.40 (m, 2H), 7.04−7.01 (m, 2H), 6.50 (s, 1H), 4.14 (q, J = 7.0 Hz, 2H), 2.30 (s, 3H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 137.6, 133.1, 129.1, 128.9, 127.9, 122.5, 116.8, 111.3, 59.4, 14.1, 12.6.

Pyrrole ***3x***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1x** (0.177 g, 0.668 mmol) was then added to the catalyst mixture, followed by DBU (0.145 g, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3x** was isolated as light yellow solid (0.139 g, 84%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (br s, 1H), 7.43−7.40 (m, 2H), 7.04−7.01 (m, 2H), 6.51 (s, 1H), 4.14 (q, J = 7.0 Hz, 2H), 2.29 (s, 3H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 162.5 (d, J_{C-F} = 246.3 Hz), 136.7, 130.9, 129.1, 122.5, 116.7, 114.9, 111.3, 59.5, 14.2, 12.6; IR (thin film) 3300, 2985, 2926, 2920, 2858, 1665, 1443, 1277, 1082, 822 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{15}NO_2F$ $(M + H)^+$ 248.1087, found 248.1091; mp 77−82 °C.

Pyrrole ***3y***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1y** (0.178 g, 0.665 mmol) was then added to the catalyst mixture followed by DBU (0.145 g, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes −40% EtOAc/2% TEA/hexanes), **3y** was isolated as light yellow solid (0.130 g, 78%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (br s, 1H), 7.40−7.38 (m, 2H), 7.34−7.32 (m, 2H), 6.55 (s, 1H), 3.69 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 136.4, 134.0, 131.4, 130.2, 128.3, 122.8, 117.0, 111.4, 50.7, 12.6; IR (thin film) 3316, 2980, 2944, 2920, 1660, 1442, 1284, 1081, 831, 715 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{13}NO_2Cl$ $(M + H)^+$ 250.0635, found 250.0639; mp 118−122 °C.

Pyrrole ***3z***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1z** (0.217 g, 0.665 mmol) was then added to the catalyst mixture followed by DBU (0.145 g, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3z** was isolated as light yellow solid (159 mg, 78%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (br s, 1H), 7.49−7.47 (m, 2H), 7.35−7.32 (m, 2H), 6.55 (s, 1H), 4.16 (q, J = 7.0 Hz, 2H), 2.29 (s, 3H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 136.2, 131.9, 131.1, 130.6, 122.8, 122.1, 117.0, 111.7, 59.6, 14.2, 12.6; IR (thin film) 3297, 2985, 2923, 2858, 1674, 1443, 1284, 1076, 826, 520 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{15}NO_2Br$ $(M + H)^+$ 308.0286, found 308.0288; mp 111−115 °C.

Pyrrole ***3aa***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1aa** (0.248 g, 0.666 mmol) was then added to the catalyst mixture followed by DBU (0.145 g, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3aa** was isolated as light yellow solid (0.179 g, 76%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (br s, 1H), 7.68−7.66 (m, 2H), 7.20−7.19 (m, 2H), 6.53 (s, 1H), 4.16 (q, J = 7.0 Hz, 2H), 2.29 (s, 3H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 137.1, 136.3, 132.4, 130.8, 122.8, 117.1, 111.7, 93.8, 59.6, 14.2, 12.7; IR (thin film) 3356, 3022, 2970, 2944, 1670, 1432, 1284, 1095, 861, 537 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{15}NO_2I$ $(M + H)^+$ 356.0148, found 356.0148; mp 116−122 °C.

Pyrrole ***3bb***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1bb** (0.175 g, 0.670 mmol) was then added to the catalyst mixture followed by DBU (0.145 g, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3bb** was isolated as light yellow solid (0.138 g, 85%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (br s, 1H), 7.38−7.36 (m, 2H), 7.18−7.17 (m, 2H), 6.51 (s, 1H), 4.16 (q, J = 7.0 Hz, 2H), 2.38 (s, 3H), 2.30 (s, 3H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 137.9, 137.8, 130.1, 128.9, 128.7, 122.4, 116.4, 111.1, 59.4, 21.3, 14.2, 12.7; IR (thin film) 3314, 2988, 2952, 2926, 2900, 1665, 1443, 1291, 1082, 826 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{18}NO_2$ $(M + H)^+$ 244.1338, found 244.1337; mp 85−90 °C.

Pyrrole ***3cc***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1cc** (0.184 g, 0.663 mmol) was then added to the catalyst mixture followed by DBU (0.145 g, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3cc** was isolated as light yellow solid (0.158 g, 92%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (br s, 1H), 7.39−7.37 (m, 2H), 6.87−6.85 (m, 2H), 6.46 (s, 1H), 4.13 (q, J = 7.0 Hz, 2H), 3.82 (s, 3H), 2.29 (s, 3H), 1.20 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 159.4, 137.7, 130.3, 125.6, 122.3, 116.4, 113.4, 110.8, 59.4, 55.3, 14.2, 12.7; IR (thin film) 3309, 3014, 2982, 2945, 2839, 1663, 1440, 1237, 1137, 833 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{18}NO_3$ $(M + H)^+$ 260.1287, found 260.1287; mp 73−76 °C.

Pyrrole ***3dd***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1dd** (0.200 g, 0.664 mmol) was then added to the catalyst mixture followed by DBU (0.145 g, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3dd** was isolated as light yellow solid (154 mg, 82%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (br s, 1H), 7.60−7.58 (m, 2H), 7.55−7.53 (m, 2H), 6.54 (s, 1H), 3.68 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 136.4, 135.9, 129.5 (d, J_{C-F} = 32.5 Hz), 129.2, 125.0, 124.1 (q, J_{C-F} = 270 Hz), 123.0, 117.7, 111.9, 50.8, 12.5; IR (thin film) 3286, 2992, 2959, 2920, 1655, 1615, 1445, 1156, 1086, 848 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{13}NO_2F_3$ $(M + H)^+$ 284.0898, found 284.0897; mp 134−137 °C.

Pyrrole ***3ee***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (22.5 mg, 0.0335 mmol), AgOTf (16.8 mg, 0.065 mmol), and $NaBH_4$ (2.5 mg, 0.066 mmol) in THF for 15 min. Allyl oxime **1ee** (174 mg, 0.666 mmol) was then added to the catalyst mixture followed by DBU (145 mg, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3ee** was isolated as light yellow oil (141 mg, 87%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (br s, 1H), 7.26−7.23 (m, 3H), 7.15−7.13 (m, 1H), 6.46 (s, 1H), 4.13 (q, J = 7.0 Hz, 2H), 2.35 (s, 3H), 2.31 (s, 3H), 1.20 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 137.8, 137.4, 133.0, 129.7, 128.6, 127.9, 127.8, 126.2, 116.7, 111.1, 59.4, 21.4, 14.1, 12.6; IR

(thin film) 3315, 3029, 2976, 2924, 2864, 1671, 1164, 1087, 781, 698 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{18}NO_2$ $(M + H)^+$ 244.1338, found 244.1339.

Pyrrole ***3ff***[55]. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.065 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1ff** (0.189 g, 0.671 mmol) was then added to the catalyst mixture followed by DBU (0.145 g, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3ff** was isolated as light yellow solid (0.144 g, 81%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (br s, 1H), 7.43 (s, 1H), 7.31−7.24 (m, 3H), 6.49 (s, 1H), 4.12 (q, J = 7.0 Hz, 2H), 2.28 (s, 3H), 1.20 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 135.8, 134.7, 133.7, 129.2, 129.1, 127.8, 127.2, 122.8, 117.4, 111.6, 59.6, 14.1, 12.6; IR (thin film) 3283, 2998, 2965, 2930, 2897, 1670, 1168, 10876, 774, 695 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{15}NO_2Cl$ $(M + H)^+$ 264.0791, found 264.0791; mp 77−82 °C.

Pyrrole ***3gg***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **3gg** (0.209 g, 0.663 mmol) was then added to the catalyst mixture followed by DBU (0.145 g, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3gg** was isolated as light yellow solid (0.157 g, 80%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (br s, 1H), 7.72 (s, 1H), 7.64−7.63 (m, 1H), 7.57−7.56 (m, 1H), 7.47−7.44 (m, 1H), 6.55 (s, 1H), 4.12 (q, J = 7.0 Hz, 2H), 2.29 (s, 3H), 1.15 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 135.6, 133.8, 132.4, 130.3 (d, J_{C-F} = 32.5 Hz), 128.4, 126.2 (q, J_{C-F} = 270 Hz), 126.0, 124.5, 123.0, 117.4, 112.0, 59.6, 14.0, 12.5; IR (thin film) 3303, 2956, 2933, 2907, 1654, 1613, 1430, 1161, 1069, 700 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{15}NO_2F_3$ $(M + H)^+$ 298.1055, found 298.1055; mp 62−65 °C.

Pyrrole Mixture ***3hh*:*4hh***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1hh** (0.174 g, 0.666 mmol) was then added to the catalyst mixture followed by DBU (0.145 g, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), pyrrole mixture **3hh**:**4hh** was isolated as light yellow oil (0.136 g, 84%). The ratio of **3hh**:**4hh** was 5:3, and the ratio was determined by the relative ^{1}H integrations of the pyrrole methine resonances: ^{1}H NMR of **3hh** (500 MHz, $CDCl_3$) δ 8.21 (br s, 1H), 7.29−7.16 (m, 4H), 6.51 (s, 1H), 4.00 (q, J = 7.0 Hz, 2H), 2.32 (s, 3H), 2.16 (s, 3H), 1.00 (t, J = 7.0 Hz, 3H); ^{13}C NMR of **3hh** (125 MHz, $CDCl_3$) δ 165.6, 137.8, 133.6, 130.2, 129.7, 128.3, 127.2, 125.1, 121.6, 116.0, 112.4, 59.0, 19.9, 13.9, 12.4; ^{1}H NMR of **4hh** (500 MHz, $CDCl_3$) δ 8.21 (br s, 1H), 7.29−7.16 (m, 4H), 6.35 (s, 1H), 4.00 (q, J = 7.0 Hz, 2H), 2.25 (s, 3H), 2.20 (s, 3H), 1.08 (t, J = 7.0 Hz, 3H); ^{13}C NMR of **4hh** (125 MHz, $CDCl_3$) δ 165.0, 137.2, 135.5, 132.9, 130.2, 129.7, 128.3, 125.1, 121.6, 113.4, 108.0, 59.3, 19.9, 14.1, 12.7; IR (thin film) 3314, 3062, 3024, 2977, 2926, 1667, 1439, 1283, 1078, 759 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{18}NO_2$ $(M + H)^+$ 244.1338, found 244.1336.

Pyrrole Mixture ***3ii*:*4ii***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1ii** (0.140 g, 0.663 mmol) was then added to the catalyst mixture followed by DBU (0.145 g, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), pyrrole mixture **3ii**:**4ii** was isolated as light yellow oil (0.099 g, 77%). The ratio of **3ii**:**4ii** was 7:1, and the ratio was determined by the relative ^{1}H integrations of the pyrrole methine resonances: ^{1}H NMR of **3ii** (500 MHz, $CDCl_3$) δ 8.03 (br s, 1H), 6.29 (s, 1H), 4.28 (q, J = 7.5 Hz, 2H), 2.58−2.51 (m, 1H), 2.22 (s, 3H), 1.35 (t, J = 7.5 Hz, 3H), 0.95 (dd, J = 8.5, 1.5 Hz, 2H), 0.66 (dd, J = 5.5, 1.5 Hz, 2H); ^{13}C NMR of **3ii** (125 MHz, $CDCl_3$) δ 166.5, 140.7, 121.8, 113.9, 111.8, 59.1, 14.5, 12.7, 9.1, 7.2; ^{1}H NMR of **4ii** (500 MHz, $CDCl_3$) δ 7.94 (br s, 1H), 6.20 (s, 1H), 4.28 (q, J = 7.5 Hz, 2H),), 2.58−2.51 (m, 1H), 2.17 (s, 3H), 1.35 (t, J = 7.5 Hz, 3H), 0.95 (dd, J = 8.5, 1.5 Hz, 2H), 0.66 (dd, J = 5.5, 1.5 Hz, 2H); ^{13}C NMR of **4ii** (125 MHz, $CDCl_3$) δ 165.9, 139.4, 125.2, 112.5, 107.9, 59.3, 14.5, 12.7, 8.5, 7.5; IR (thin film) 3326, 2982, 2956, 2907, 2861, 1665, 1445, 1242, 1076, 786 cm^{-1}; HRMS (ESI) m/z calcd for $C_{11}H_{16}NO_2$ $(M + H)^+$ 194.1179, found 194.1179.

Pyrrole Mixture ***3jj*:*4jj***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (22.5 mg, 0.0335 mmol), AgOTf (16.8 mg, 0.065 mmol), and $NaBH_4$ (2.5 mg, 0.066 mmol) in THF for 15 min. Allyl oxime ether **1jj** (133 mg, 0.667 mmol) was then added to the catalyst mixture followed by DBU (145 mg, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After column chromatography, pyrrole mixture **3jj**:**4jj** was isolated as light yellow oil (53.2 mg, 44%). The ratio of **3jj**:**4jj** was 2:3, and the ratio was determined by the relative ^{1}H integrations of the pyrrole methine resonances: ^{1}H NMR of pyrrole **3jj** (500 MHz, $CDCl_3$) δ 8.18 (br s, 1H), 6.38 (s, 1H), 3.82−3.74 (m, 1H), 3.81 (s, 3H), 2.23 (s, 3H), 1.25 (d, J = 7.0 Hz, 3H); ^{13}C NMR of pyrrole **3jj** (125 MHz, $CDCl_3$) δ 166.6, 145.9, 121.4, 114.3, 109.7, 50.4, 26.3, 22.0, 12.7; ^{1}H NMR of pyrrole **4jj** (500 MHz, $CDCl_3$) δ 8.09 (br s, 1H), 6.18 (s, 1H), 3.82−3.74 (m, 1H), 3.77 (s, 3H), 2.21 (s, 3H), 1.25 (d, J = 7.0 Hz, 3H); ^{13}C NMR of pyrrole **4jj** (125 MHz, $CDCl_3$) δ 165.9, 144.5, 125.4, 109.7, 107.5, 50.6, 25.9, 22.1, 12.7; IR (thin film) 3339, 2970, 2954, 2932, 2874, 1671, 1620, 1448, 1240, 1082, 781 cm^{-1}; HRMS (ESI) m/z calcd for $C_{10}H_{16}NO_2$ $(M + H)^+$ 182.1181, found 182.1183.

Pyrrole mixture ***3kk*:*4kk***[56,57]. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1kk** (0.108 g, 0.633 mmol) was then added to the catalyst mixture followed by DBU (0.145 g, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 20 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), pyrrole mixture **3kk**:**4kk** was isolated as light yellow solid (0.106 g, 54%). The ratio of **3kk**:**4kk** was 2:1, and the ratio was determined by the relative ^{1}H integrations of the pyrrole methine resonances: ^{1}H NMR of **3kk** (500 MHz, $CDCl_3$) δ 8.29 (br s, 1H), 6.35 (s, 1H), 3.81 (s, 3H), 2.47 (s, 3H), 2.23 (s, 3H); ^{13}C NMR of **3kk** (125 MHz, $CDCl_3$) δ 166.9, 136.1, 121.5, 114.4, 110.6, 50.5, 14.1, 12.6; ^{1}H NMR of **4kk** (500 MHz, $CDCl_3$) δ 8.29 (br s, 1H), 6.18 (s, 1H), 3.78 (s, 3H), 2.47 (s, 3H), 2.18 (s, 3H); ^{13}C NMR of **4kk** (125 MHz, $CDCl_3$) δ 166.4, 134.5, 125.8, 111.2, 107.4, 50.7, 13.1, 12.6; IR (thin film) 3298, 3020, 3002, 2922, 2853, 1665, 1444, 1222, 1088, 781 cm^{-1}; HRMS (ESI) m/z calcd for $C_8H_{12}NO_2$ $(M + H)^+$ 154.0868, found 154.0868; mp 68−73 °C.

Pyrrole ***3mm***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime ether **1mm** (0.213 g, 0.667 mmol) was then added to the catalyst mixture. DBU (0.132 g, 0.873 mmol) was added to the complete reaction mixture and the complete reaction mixture was allowed to stir at 25 °C for 1 h and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3mm** was isolated as light yellow solid (0.0858 g, 43%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (br s, 1H), 7.60−7.58 (m, 2H), 7.40−7.39 (m, 2H), 7.29−7.27 (m, 2H), 7.25−7.20 (m, 3H), 6.74 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 132.9, 130.5, 129.5, 128.7, 127.8, 127.1, 126.7, 125.1, 124.6 (q, J_{C-F} = 270 Hz), 120.8, 119.5, 116.7, 11.0; IR (thin film)

3401, 2949, 2926, 2864, 1698, 1616, 1322, 1164, 1066, 694 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{15}NF_3$ $(M + H)^+$ 302.1157, found 302.1159; mp 72−75 °C.

Pyrrole ***3nn***. *O*-Vinyl oxime **2nn** (0.109, 0.342 mmol) was treated with DBU (0.078 mg, 0.51 mmol), and the reaction mixture was allowed to stir for 18 h at 75 °C. After workup and column chromatography, **3nn** was isolated as a yellow solid (0.0847 g, 82%): ^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (br s, 1H), 7.60−7.58 (m, 2H), 7.40−7.39 (m, 2H), 7.29−7.27 (m, 2H), 7.25−7.20 (m, 3H), 6.74 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 132.9, 130.5, 129.5, 128.7, 127.8, 127.1, 126.7, 125.1, 124.6 (q, J_{C-F}= 270 Hz), 120.8, 119.5, 116.7, 11.0; IR (thin film) 3401, 2949, 2926, 2864, 1698, 1616, 1322, 1164, 1066, 694 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{15}NF_3$ $(M + H)^+$ 302.1157, found 302.1159; mp 72−75 °C.

Pyrrole ***3nn***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0135 g, 0.0201 mmol), AgOTf (0.0101 g, 0.0393 mmol), and $NaBH_4$ (0.0015 g, 0.040 mmol) in THF for 15 min. Allyl oxime ether **1nn** (0.110 g, 0.398 mmol) was then added to the catalyst mixture. DBU (0.079 g, 0.524 mmol) was added to the complete reaction mixture, and the complete reaction mixture was allowed to stir at 25 °C for 1 h and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3nn** was isolated as light yellow solid (0.0465 g, 46%): ^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (br s, 1H), 7.58−7.57 (m, 2H), 7.35−7.34 (m, 2H), 7.29−7.26 (m, 2H), 7.24−7.18 (m, 3H), 6.74 (s, 1H), 2.11 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6, 132.6, 132.0, 130.8, 129.9, 128.8, 127.3, 127.0, 120.3, 119.5, 119.3, 117.0, 109.2, 11.1; IR (thin film) 3332, 2973, 2929, 2893, 2861, 2227, 1603, 1174, 1002, 841 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{18}H_{15}N_2$ $(M + H)^+$ 259.1235, found 259.1230; mp 185−188 °C.

Pyrrole ***3oo***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0135 g, 0.0201 mmol), AgOTf (0.010.1 g, 0.0398 mmol), and $NaBH_4$ (0.0015 g, 0.040 mmol) in THF for 15 min. Allyl oxime ether **1oo** (0.127 g, 0.390 mmol) was then added to the catalyst mixture. DBU (0.079 g, 0.524 mmol) was added to the complete reaction mixture and the complete reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3oo** was isolated as light orange oil (0.0684 g, 56%): ^1H NMR (500 MHz, $CDCl_3$) δ 8.23 (br s, 1H), 8.01−7.99 (m, 2H), 7.35−7.33 (m, 2H), 7.26−7.23 (m, 2H), 7.20−7.19 (m, 3H), 6.73 (s, 1H), 4.38 (q, J = 7.0 Hz, 2H), 2.12 (s, 3H), 1.40 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 141.4, 133.0, 130.2, 129.5, 129.4, 128.7, 127.8, 127.1, 126.6, 121.2, 119.5, 116.7, 60.8, 11.4, 11.1; IR (thin film) 3336, 2983, 2915, 2877, 2848, 1737, 1607, 1372, 1044, 847 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{20}NO_2$ $(M + H)^+$ 306.1494, found 306.1492.

Pyrrole ***3pp***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime ether **1pp** (0.129 g, 0.642 mmol) was then added to the catalyst mixture. DBU (0.132 g, 0.873 mmol) was added to the complete reaction mixture, and the complete reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3pp** was isolated as a yellow oil (0.0476 g, 41%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.72 (br s, 1H), 7.57−7.56 (m, 1H), 7.23−7.18 (m, 2H), 7.05−7.02 (m, 1H), 6.46 (s, 1H), 2.98 (t, J = 7.5 Hz, 2H), 2.77 (t, J = 7.5 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.6, 133.8, 130.2, 128.1, 126.7, 124.0, 122.1, 116.6, 115.9, 115.1, 30.4, 22.1, 13.0; IR (thin film) 3358, 3007, 2928, 2917, 2902, 2886, 1603, 1184, 1024, 745 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{14}N$ $(M + H)^+$ 184.1126, found 184.1125.

Synthesis of Pyrrole Mixtures 3ll:4ll and 3rr:4rr (Schemes 12 and 13). *Pyrrole Mixture* ***3aa:4aa*** *(2:3).* The catalyst mixture was synthesized by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime **1aa** (0.147 g, 0.816 mmol) was then added to the catalyst mixture and the reaction mixture was allowed to stir at 25 °C for 18 h then at 50 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3aa**:**4aa** was isolated as a light yellow oil (0.0639 g, 49%). The ratio of **3aa**:**4aa** was 2:3, and the ratio was determined by the relative ^1H integrations of the pyrrole methine resonances: ^1H NMR of **3aa** (500 MHz, $CDCl_3$) δ 8.38 (br s, 1H), 6.35 (s, 1H), 2.13 (s, 3H), 1.41 (s, 9H); ^{13}C NMR of **3aa** (125 MHz, $CDCl_3$) δ 149.0, 123.1, 117.9, 113.5, 89.3, 32.8, 29.6, 10.6; ^1H NMR of **4aa** (500 MHz, $CDCl_3$) δ 8.38 (br s, 1H), 6.01 (s, 1H), 2.21 (s, 3H), 1.41 (s, 9H); ^{13}C NMR of **4aa** (125 MHz, $CDCl_3$) δ 148.3, 126.1, 118.7, 109.8, 87.2, 32.8, 29.9, 12.5; IR (thin film) 3275, 2968, 2868, 2210, 1594, 1444, 1367, 1267, 804, 756 cm^{-1}; HRMS (ESI) m/z calcd for $C_{10}H_{15}N_2$ $(M + H)^+$ 163.1235, found 163.1234.

Pyrrole Mixture ***3ll:4ll*** *(3:1) Synthesized with DBU.* The catalyst mixture was synthesized by mixing $[(cod)IrCl]_2$ (0.0230 g, 0.0343 mmol), AgOTf (0.013 g, 0.051 mmol), and $NaBH_4$ (0.0025 g, 0.065 mmol) in THF for 15 min. Allyl oxime **1ll** (0.142 g, 0.787 mmol) was then added to the catalyst mixture followed by DBU (0.179 g, 1.18 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 50 °C for 18 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), **3ll**:**4ll** was isolated as a light yellow oil (0.0744 g, 58%). The ratio of **3ll**:**4ll** was 3:1 and the ratio was determined by the relative ^1H integrations of the pyrrole methine resonances: ^1H NMR of **3ll** (500 MHz, $CDCl_3$) δ 8.38 (br s, 1H), 6.35 (s, 1H), 2.13 (s, 3H), 1.41 (s, 9H); ^{13}C NMR of **3ll** (125 MHz, $CDCl_3$) δ 149.0, 123.1, 117.9, 113.5, 89.3, 32.8, 29.6, 10.6; ^1H NMR of **4ll** (500 MHz, $CDCl_3$) δ 8.38 (br s, 1H), 6.01 (s, 1H), 2.21 (s, 3H), 1.41 (s, 9H); ^{13}C NMR of **4ll** (125 MHz, $CDCl_3$) δ 148.3, 126.1, 118.7, 109.8, 87.2, 32.8, 29.9, 12.5.

Pyrrole Mixture ***3r:4r*** *(5:3).* The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0225 g, 0.0335 mmol), AgOTf (0.0168 g, 0.0654 mmol), and $NaBH_4$ (0.0025 g, 0.066 mmol) in THF for 15 min. Allyl oxime ether **1r** (0.168 g, 0.668 mmol) was then added to the catalyst mixture, followed by DBU (0.145 g, 0.952 mmol). The reaction mixture was allowed to stir for 1 h at 25 °C and then heated to 75 °C for 24 h. After flash chromatography (2% TEA/hexanes−40% EtOAc/2% TEA/hexanes), a mixture of **3r** and **4r** was isolated as light orange oil (0.062 g, 40%). The ratio of **3r**:**4r** was 5:3 and the ratio was determined by the relative ^1H integrations of the pyrrole methine resonances: ^1H NMR of **3r** (500 MHz, $CDCl_3$) δ 8.07 (br s, 1H), 7.40−7.17 (m, 10H), 6.73 (s, 1H), 2.13 (s, 3H); ^{13}C NMR of **3r** (125 MHz, $CDCl_3$) δ 136.4, 133.4, 130.5, 128.6, 128.4, 128.3, 127.4, 126.9, 126.5, 126.3, 126.0, 116.4, 11.1; ^1H NMR of **4r** (500 MHz, $CDCl_3$) δ 7.94 (br s, 1H), 7.40−7.17 (m, 10H), 6.14 (s, 1H), 2.37 (s, 3H); ^{13}C NMR of **4r** (125 MHz, $CDCl_3$) δ 137.0, 133.7, 128.7, 128.6, 128.3, 128.2, 127.4, 126.9, 126.3, 125.7, 122.3, 109.1, 13.1; IR (thin film) 3414, 3056, 3020, 2916, 2897, 1596, 1499, 1076, 803, 744 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{16}N$ $(M + H)^+$ 234.1283, found 234.1278.

Pyrrole Mixture ***3r:4r*** *(4:1) from* ***2r***. *O*-Vinyl oxime **2r** (0.0904 g, 0.360 mmol) was dissolved in 3 mL of THF and mixed with DBU (0.0822 g, 0.540 mmol). The reaction mixture was then transferred to a Teflon-sealed reaction flask at allowed to heat at 75 °C for 24 h. After column chromatography, pyrrole mixture **3r**:**4r** was isolated as a light yellow oil (0.0493 g, 59%). The ratio of **3r**:**4r** was 4:1 and the ratio was determined by the relative ^1H integrations of the pyrrole methine resonances. ^1H NMR of **3r** (500 MHz, $CDCl_3$) δ 8.07 (br s, 1H), 7.40−7.17 (m, 10H), 6.73 (s, 1H), 2.13 (s, 3H); ^{13}C NMR of **3r** (125 MHz, $CDCl_3$) δ 136.4, 133.4, 130.5, 128.6, 128.4, 128.3, 127.4, 126.9, 126.5, 126.3, 126.0, 116.4, 11.1; ^1H NMR of **4r** (500 MHz, $CDCl_3$) δ 7.94 (br s, 1H), 7.40−7.17 (m, 10H), 6.14 (s, 1H), 2.37 (s, 3H); ^{13}C NMR of **4r** (125 MHz, $CDCl_3$) δ 137.0, 133.7, 128.7, 128.6, 128.3, 128.2, 127.4, 126.9, 126.3, 125.7, 122.3, 109.1, 13.1.

Preparation of O-Vinyl Oxime ***2mm***. The catalyst mixture was prepared by mixing $[(cod)IrCl]_2$ (0.0164 g, 0.0244 mmol), AgOTf

(0.011 g, 0.043 mmol), and $NaBH_4$ (0.0018 g, 0.047 mmol) in THF for 15 min. Allyl oxime ether **1mm** (0.166 g, 0.520 mmol) was then added to the catalyst mixture, and the reaction mixture was allowed to stir for 24 h. After flash chromatography (2% TEA/hexanes−2% EtOAc/2% TEA/hexanes), **2mm** was isolated as a light yellow oil (0.109 g, 65%): ^{1}H NMR of *E*-imine, *Z*-vinyl isomer (500 MHz, $CDCl_3$) δ 7.70−7.68 (m, 1H), 7.56−7.53 (m, 2H), 7.39−7.34 (m, 6H), 6.98 (m, 1H), 4.58 (q, J = 7.0 Hz, 1H), 4.30 (s, 2H), 1.62 (dd, J = 7.0, 1.5 Hz, 3H); ^{13}C NMR of *E*-imine, *Z*-vinyl isomer (125 MHz, $CDCl_3$) δ 157.1, 146.8, 140.5, 134.6, 129.9, 128.8, 128.7, 128.6, 128.2, 126.7, 125.6, 100.3, 33.2, 9.5. ^{1}H NMR of *E*-imine, *E*-vinyl isomer (500 MHz, $CDCl_3$) δ 7.70−7.68 (m, 1H), 7.56−7.53 (m, 2H), 7.39−7.34 (m, 6H), 6.94 (m, 1H), 5.28 (q, J = 5.5 Hz, 1H), 4.26 (s, 2H), 1.67 (dd, J = 6.5, 1.5 Hz, 3H); ^{13}C NMR of *E*-imine, *Z*-vinyl isomer (125 MHz, $CDCl_3$) δ 157.1, 147.3, 140.5, 134.6, 129.9, 128.8, 128.7, 128.6, 128.2, 126.7, 125.6, 99.7, 33.0,12.3. ^{1}H NMR of *Z*-imine, *Z*-vinyl isomer (500 MHz, $CDCl_3$) δ 7.70−7.68 (m, 1H), 7.56−7.53 (m, 2H), 7.39−7.34 (m, 6H), 6.86 (m, 1H), 4.48 (q, J = 6.5 Hz, 1H), 3.96 (s, 2H), 1.50 (dd, J = 7.0, 1.5 Hz, 3H); ^{13}C NMR of *Z*-imine, *Z*-vinyl isomer (125 MHz, $CDCl_3$) δ 156.9, 147.3, 140.5, 134.6, 129.9, 128.8, 128.7, 128.6, 128.2, 126.7, 125.6, 101.5, 41.2,12.3. The Z-imine, *E*-vinyl isomer was difficult to distinguish from the other isomers but specific resonances for the vinyl group were observed at 5.20 and 4.5 ppm.

*Observation of [1,3] Rearrangement Product **5s** and Isolation of Amino Alcohol **6s***. A 10 mL Teflon-sealed flask was charged with **2s** (0.1081 g, 0.493 mmol) and 4 mL of dioxane. The flask was then stoppered and heated to 75 °C for 2.5 h. At this time, an aliquot was removed from the flask and checked by ^{1}H NMR spectroscopy which showed that **2s** had been completely converted into aldehyde **5s**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.79 (d, J = 9.0 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 2.71 (q, J = 7.5 Hz, 2H), 2.62 (q, J = 7.5 Hz, 1H), 1.39 (d, J = 7.0 Hz, 3H), 1.12 (t, J = 7.5 Hz, 3H). Compound **5s** was not isolated or purified. The crude solution of **5s** was transferred to a 25 mL round-bottom flask containing a slurry of $LiAlH_4$ (0.039 g, 1.03 mmol) in 10 mL of THF. The reaction mixture was then allowed to stir for 4 h. At this time, the reaction mixture was diluted with 20 mL of MTBE and slowly quenched with water. The reaction mixture was then extracted with 3 × 20 mL of 1 M $HCl_{(aq)}$, neutralized with 1 M $NaOH_{(aq)}$, and extracted with 3 × 15 mL of MTBE, and volatiles were removed under reduced pressure to give **6s** as a light yellow oil (0.0728 g, 66%): ^{1}H NMR of major diastereomer (500 MHz, $CDCl_3$) δ 7.19−7.17 (m, 2H), 6.87−6.86 (m, 2H), 3.79 (s, 3H), 3.60 (dd, J = 8.0, 6.0 Hz, 1H), 3.37 (dd, J = 10.5, 4.5 Hz, 1H), 3.13 (dd, J = 10.5, 8.0 Hz, 1H), 2.56−2.53 (m, 1H), 1.69−1.60 (m, 2H), 0.99 (d, J = 6.0 Hz, 3H), 0.79 (t, J = 7.5 Hz, 3H); ^{13}C NMR of major diasteromer (125 MHz, $CDCl_3$) δ 158.7, 135.9, 128.3, 113.8, 66.6, 61.2, 55.2, 51.3, 31.9, 16.8, 10.9; ^{1}H NMR of minor diastereomer (500 MHz, $CDCl_3$) δ 7.16−7.14 (m, 2H), 6.87−6.86 (m, 2H), 3.80 (s, 3H), 3.57 (dd, J = 10.5, 4.0 Hz, 1H), 3.48 (dd, J = 7.5, 6.5 Hz, 1H), 3.16 (dd, J = 10.5, 5.5 Hz, 1H), 3.17−3.14 (m, 1H), 1.77−1.72 (m, 1H), 1.59−1.53 (m, 1H), 0.94 (d, J = 6.5 Hz, 3H), 0.80 (t, J = 7.5 Hz, 3H); ^{13}C NMR of minor diasteromer (125 MHz, $CDCl_3$) δ 158.6, 136.7, 127.9, 113.8, 64.6, 61.6, 55.3, 51.4, 30.9, 18.6, 10.9; IR (thin film) 3294, 3191, 2959, 2929, 2871, 2834, 1610, 1510, 1245, 1035, 828 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{23}N_2O$ $(M + H)^+$ 223.1810, found 223.1814.

*Observation of N,O-Acetal **8b***. In order to observe an intermediate on the reaction pathway between **2b** and **3b**, the reaction was monitored by ^{1}H NMR spectroscopy. *O*-Vinyl oxime **2b** (0.072 g, 0.29 mmol) was dissolved in 0.5 mL of THF-d_8 and mixed with DBU (0.066 g, 0.44 mmol). The reaction mixture was then transferred to a J. Young tube and heated for 6.5 h at 75 °C. At this time, the major product in solution appeared to be *N,O*-acetal intermediate **8b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58−6.52 (m, 2H), 7.45−5.32 (m, 3H), 5.08 (m, 1H), 4.11−4.01 (m, 2H), 2.94−2.87 (m, 1H), 1.71 (d, J = 8.0 Hz, 3H), 1.17−1.05 (m, 3H), the O−H resonance was not observed. This assignment was supported by a ^{13}C NMR spectrum and comparison to other similar compounds reported in the literature: ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 154.1, 144.9, 131.5, 127.3, 126.1, 99.4, 86.3, 58.4, 55.4, 15.9, 13.5. The ^{13}C NMR chemical shift observed for the *N,O*-acetal carbon (86.3 ppm) and the sp^2 carbons of the dihydropyrrole (99.4 ppm and 154.1 ppm) match other similar structures in the literature and do not match **2b**, **3b**, **4b**, **5b**, or the expected resonances for **7b**.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures, expanded optimization tables, and compound characterization data. This information is available free of charge via the Internet at http://pubs.acs.org.

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