Articles

Discrimination of Enantiofaces and Stereoselective Electrophilic Addition Reactions for η^2-Pyrrole Complexes

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A series of asymmetric *N*-substituted pyrroles (**1**−**7**) has been synthesized from amino acid derivatives and complexed to the pentaammineosmium(II) fragment. Many of these pyrrole complexes (**8**−**14**) show a thermodynamic preference for one coordination diastereomer according to their NMR spectra (−5 to −20 °C). This stereoselective coordination results in stereoselective electrophilic addition at the uncoordinated β carbon (C3) when the complexes are treated with trifluoromethanesulfonic acid (HOTf), methyl triflate, or dimethoxymethane. These stereoselective reactions at C3 are a direct result of differentiation of the pyrrole enantiofaces.

Introduction

Through the formation of stable π complexes, transition metals have been used to activate arenes toward otherwise inaccessible reactions for more than forty years.[1] In recent years, this strategy has been extended to aromatic heterocycles, with particular attention being given to pyrrole and furan.[2] Specifically, the π-base pentaammineosmium(II) forms thermally stable η^2-complexes with these heterocycles. These complexes undergo reactions that have no organic parallel. Electrophilic addition at the β carbon of osmium-bound pyrrole results in 3*H*-pyrrolium complexes that can be subsequently treated with nucleophiles to generate 2- or 3-pyrrolines.[3,4] The nucleophilic nature of the uncoordinated β carbon has also been exploited to generate functionalized indoles.[5,6] Osmium coordination has also been used to promote dipolar cycloaddition reactions with pyrroles.[7] This methodology has been used in the generation of a number of new bicyclic alkaloids,[8,9] some of which show promising biological activity.[10] Despite the breadth of new transformations for pyrrole made available through this methodology, every reaction reported to date for an η^2-pyrrole complex has yielded racemic products. Binding the $\{Os(NH_3)_5\}^{2+}$ fragment (abbreviated as [Os]) to pyrrole in an η^2 fashion results in a chiral complex (Figure 1); however, the metal readily undergoes both intrafacial (ring-walk) and interfacial (face-flip) linkage isomerizations at 20 °C that interconvert the enantiomers.[11]

For arenes, there are both transition metal-based and nontransition metal-based dearomatization methodologies that employ chiral auxiliaries in order to achieve high stereocontrol. Examples include nucleophilic addition to η^6-arene complexes[12] of chromium[13−17] and manganese[18−20] and the use of chiral oxazolines[21] or alcohols[22] in the dearomatization of naphthalenes. Relevant to the present study, η^6-arenes have been

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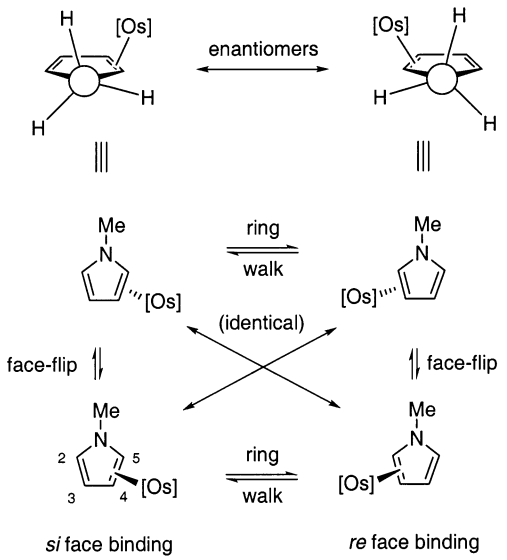
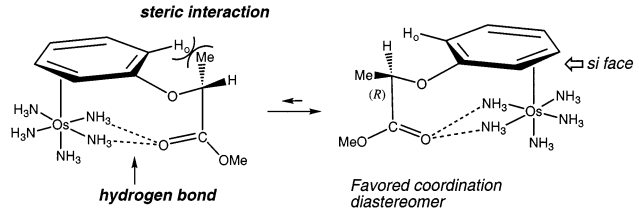


Figure 1. Racemization of the pentaammineosmium(II) η^2-pyrrole complex via intrafacial isomerization (ring-walk) or interfacial isomerization (face-flip).

decorated with chiral auxiliaries bearing a heteroatom at the benzylic position in order to induce stereoselective binding of the metal fragment.[23−33] Recently, this concept has been extended to η^2-bound arene complexes. The [Os]-promoted dearomatization of phenyl ethers derived from a nonracemic lactate has been shown to afford stereodefined cyclohexenes and cyclohexenones.[34,35] The (*R*)-lactate auxiliary stereoselectively induced binding of the osmium to the *si* face of the phenyl ether, which resulted in high stereocontrol of subsequent reactions with the unbound portion of the molecule. Using a similar strategy, stereoselective reactions could be performed on η^2-*N*-alkylated pyrrole complexes.



Results

The highly stereoselective coordination found with [Os]-phenyl ether complexes depends on both a hydrogen-bonding interaction between the lactate carbonyl group and the acidic ammine ligands[36] and a steric interaction between the unbound ortho proton (H_O) and the methyl group of the auxiliary. The asymmetric carbon of the lactate lies in the arene plane, away from the metal, which results in an increased steric interaction upon binding the *re* face. In the case of pyrrole, however, because an alkyl substituent of a pyrrole nitrogen has no π interactions with the heterocycle, the asymmetric carbon is not expected to be held in the heterocycle plane. Thus, in addition to a hydrogen-bonding interaction with R_2, a successful strategy for stereospecific coordination would require a steric interaction directly between R_1 of the chiral auxiliary and the pentaammineosmium fragment (Figure 2).[34]

A series of asymmetric pyrroles (**1**−**7**) was synthesized from the amino acids L-alanine, L-valine, and L-*tert*-leucine (Scheme 1). The methyl ester derivatives (**1**, **3**, and **6**) were synthesized from the condensation of the amino acid with 2,5-dimethoxytetrahydrofuran in acetic acid at 80 °C[37] and subsequent esterification in methanol. The alcohol derivatives (**4**, **7**) were generated upon hydride reduction of the corresponding ester, and the ether derivatives (**2**, **5**) were accessed by deprotonation of the alcohol followed by treatment with dimethyl sulfate.

Complexes **8**, **10**, and **13** were synthesized by reducing $[Os(NH_3)_5(OTf)](OTf)_2$ with Zn/Hg in a MeOH solution of the respective ester precursors **1**, **3**, and **6**. Complexes **9**, **11**, **12**, and **14** were isolated after $[Os(NH_3)_5(OTf)](OTf)_2$ was reduced with Mg^0 in DMA in the presence of the appropriate alcohol or ether derivative (Table 1). Isolated yields for **8**−**14** range from 78 to 98% (Table 1) with an estimated purity of >90% (^{1}H NMR, ^{13}C NMR, COSY, HSQC, nOe, CV (combustion analysis where possible)). To observe the pyrrole protons for the complexes, their ^{1}H NMR spectra had to be recorded at a temperature at which intrafacial linkage isomerization (i.e., ring-walk) was suppressed to the point that individual isomers could be resolved.[11] The ^{1}H NMR spectra for **8**−**14** revealed the presence of two diastereomers for each metal complex (Table 1). With the exception of complex **8**, which displays no selectivity at −20 °C, the major diastereomer for all the complexes has the osmium bound to the *si* face of the pyrrole. Stereochemical assignments were made on the basis of 1D nOe experiments. Irradiation of the methine proton H_A (Figure 2) at the temperature indicated in Table 1 resulted in enhancement (typically ∼10% nOe) of H_5, while irradiation of a selected proton(s) from R_1 showed enhancement of H_2.

Two trends emerge regarding the nature of R_1 and R_2 with the coordination diastereoselectivity (dr). When $R_2 = CO_2Me$ the ratio of *si* face:*re* face binding increases with the steric bulk of R_1 (i.e., dr for Me (**8**) < *i*-Pr (**10**)

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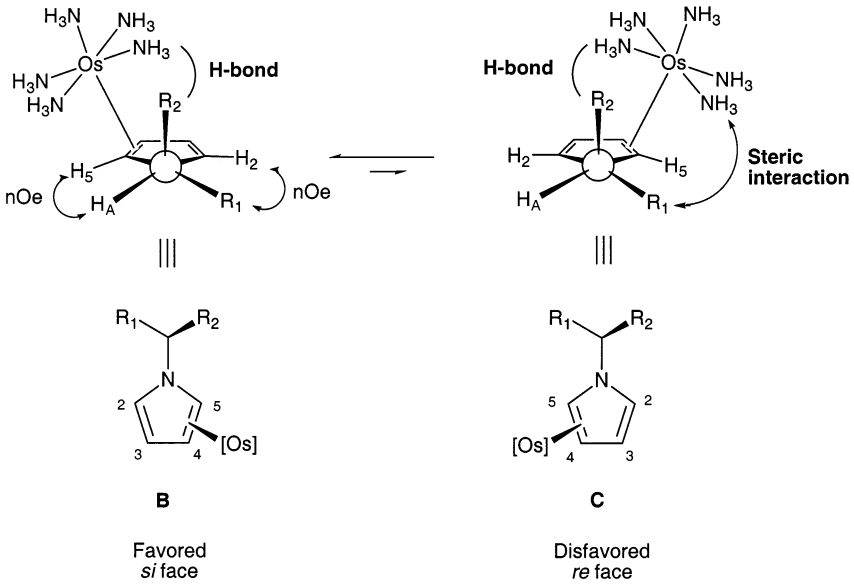


Figure 2. Differentiation of pyrrole enantiofaces using a chiral substituent with a hydrogen bond acceptor.

Scheme 1. Synthetic Route to Asymmetric Pyrroles

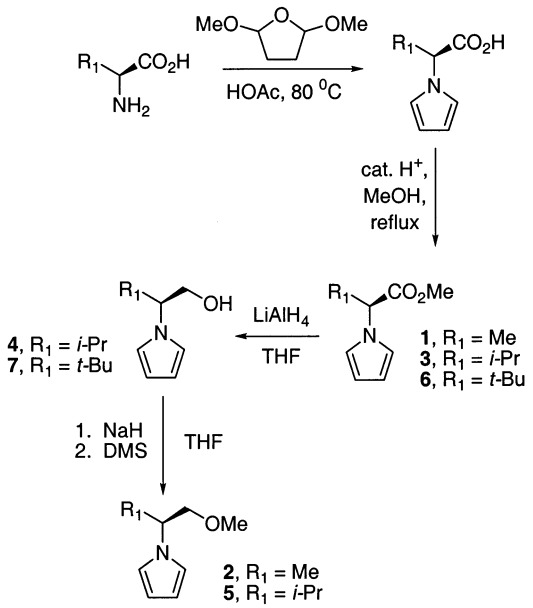
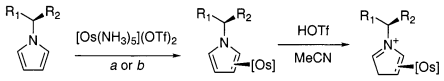


Table 1. Ratios of Coordination Diastereomers and β-Protonated Diastereomers



B	R_1	R_2	dr	T (°C)	% Yield	D	dr	T (°C)	% Yield
8	Me	CO_2Me	1 : 1	-20	81	**15**	1 : 1 1 : 1	20 -40	88
9	Me	CH_2OMe	4 : 1	-9	90	**16**	6 : 1 6 : 1	20 -40	99
10	*i*-Pr	CO_2Me	2 : 1	-20	92	**17**	5 : 1 6 : 1	20 -40	96
11	*i*-Pr	CH_2OH	7 : 1	-10	98	**18**	8 : 1 10 : 1	20 -40	95
12	*i*-Pr	CH_2OMe	16 : 1	-15	89	**19**	14 : 1 28 : 1	20 -40	97
13	*t*-Bu	CO_2Me	6 : 1	-5	78	**20**	24 : 1 32 : 1	20 -40	93
14	*t*-Bu	CH_2OH	>20 : 1	-5	88	**21**	>50 : 1 >50 : 1	20 -40	92

[a] Mg^0, DMAc (for **9**, **11**, **12**, and **14**). [b] Zn/Hg, MeOH (for **8**, **10**, and **13**).

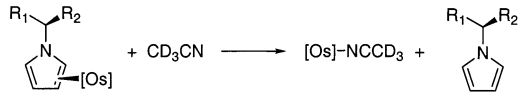
< *t*-Bu (**13**)). When R_1 = *i*-Pr and R_2 is changed from methyl ester (**10**) to alcohol (**11**) to methoxy methyl ether (**12**), the diastereomeric ratio also increases.

To gauge the effectiveness of the putative hydrogen bond between R_2 and the ammine ligand set for complexes **10**−**12**, $t_{1/2}$ measurements were recorded for the substitution of the asymmetric pyrrole (**3**−**5**) by CD_3CN (Table 2). Compared to the half-life of the *N*-methylpyrrole complex (i.e., when $R_1 = R_2 = H$), the asymmetric pyrrole complexes were found to have longer half-lives despite their increased steric bulk. In the cases of **10** and **11**, the rate constant (determined assuming first-order or pseudo-first-order kinetics) is a factor of 3 less than that for the *N*-methylpyrrole complex. The ether derivative **12**, which displays the highest coordination selectivity, has the shortest substitution half-life.

Solvents that typically disrupt H-bonds, such as DMF-d_7 and DMSO-d_6, were found to significantly compromise the coordination diastereoselectivity for asymmetric phenyl ether complexes of pentaammineosmium(II).[35] However, when complexes **11** and **12** were dissolved in DMF-d_7 and their ^1H NMR spectra were recorded at the temperature indicated in Table 1, their diastereomeric equilibria were unaffected.

Upon treatment with an acetonitrile solution of triflic acid, the asymmetric pyrrole complexes (**B**) undergo protonation at the β carbon to form 3*H*-pyrrolium complexes (**D**) with yields ranging from 88 to 99% (Table 1). These complexes display a characteristic singlet in their ^1H NMR spectra near δ 9 and a signal in the ^{13}C NMR spectra near δ 175 that correspond to the iminium proton and carbon, respectively. Other characteristic signals in the ^1H NMR spectra of **15**−**21** include a doublet of doublets at δ 2.7 and a doublet at δ 3.0 corresponding to the diastereotopic methylene protons at C3 of the ring. The geminal coupling constant between these two protons is typically 27 Hz. The stereochemistry of the major diastereomer (*si* face

Table 2. Half-Life Measurements for the Substitution of Asymmetirc Pyrroles by CD_3CN



B A

Cpd.	R_1	R_2	k (s^{-1})	$t_{1/2}$ (h)
N-Me	H	H	2.8×10^{-6}	69
10	*i*-Pr	CO_2Me	8.4×10^{-7}	229
11	*i*-Pr	CH_2OH	9.3×10^{-7}	207
12	*i*-Pr	CH_2OMe	1.6×10^{-6}	120

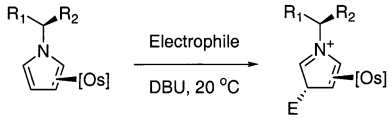
binding) was confirmed by 1D NOE experiments. As with the deprotonated precursors (**B**), the 3*H*-pyrrolium complexes (**D**) show strong NOE interactions between the iminium proton (H2) and a selected proton resonance-(s) from R_1, consistent with *si* face protonation.

With the exception of complex **20**, the diastereomeric ratios for the 3*H*-pyrrolium species are comparable to those of their pyrrole precursors (**B**). Complexes that display low coordination stereoselectivity, such as complex **8**, afford products with low coordination stereoselectivity, while those with high coordination stereoselectivity, such as complex **14**, result in 3*H*-pyrrolium complexes with high coordination stereoselectivity. Complex **20** has a dr of 24:1 at 20 °C, significantly higher than that observed for its unprotonated precursor (**13**). For all the complexes save **8**, performing the protonation at −40 °C can further enhance the diastereomeric ratio. In fact, for the protonation of complex **12**, the selectivity doubles from 14:1 to 28:1.

At 20 °C, the diastereomeric ratios for the isolated β-protonated complexes **D** are identical by ^{1}H NMR integrations to those observed in situ in CD_3CN. Furthermore, generating complex **19** in situ and observing it over a period of 9 days revealed no alteration of its diastereomeric ratio and no decomposition of the complex. These observations are particularly significant considering that [Os]-phenyl ether complexes with lactate auxiliaries underwent racemization over a period of hours in the presence of triflic acid.[35] In the presence of the weak acid, anilinium triflate, complex **21** initially protonates at C3 to yield a 16:1 ratio of diastereomers. However, after 90 min, the more stable 2*H*-pyrrolium isomer appears as a 1:1 mixture of diastereomers. Despite the observation that the 3*H*-pyrrolium species almost entirely tautomerizes to the 2*H*-pyrrolium over a period of 24 h, the ratio of β-protonated diastereomers remains constant (16:1) throughout the reaction. This confirms that the thermodynamic diastereomeric ratio was the same as that formed under kinetic control.

Compounds **9** and **12** react with methyl triflate (MeOTf) at C3 to generate compounds **22** and **23**, respectively (Table 3). These complexes show diastereomeric ratios similar to those of their β-protonated counterparts, **16** and **19** (Table 1). These β-methylated complexes show characteristic iminium signals in their ^{1}H and ^{13}C NMR spectra similar to those of their protonated analogues as well as the appearance of a

Table 3. Addition of Carbon Electrophiles



B I

B	R_1	R_2	dr	T (°C)	I	E	dr
9	Me	CH_2OMe	4 : 1	-9	**22**[a]	Me	5 : 1
					24[b]	OMe	6 : 1
12	*i*-Pr	CH_2OMe	16 : 1	-15	**23**[a]	Me	12 : 1
					25[b]	OMe	12 : 1
					26[c]	O OMe	12 : 1

[a] MeOTF in DME. [b] Dimethoxymethane and TBSOTf in MeCN. [c] Methyl acrylate and TBSOTf in MeCN. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

doublet (3H) at δ 1.62 (correlated to a ^{13}C NMR signal at δ 14.7) corresponding to the newly attached methyl group. Both **9** and **12** also add dimethoxymethane in the presence of *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf) to yield methoxymethyl pyrrolium complexes **24** and **25**. Iminium signals and a singlet at δ 3.32 that corresponds to the protons of the methoxy group are present in the ^{1}H NMR spectra. Two additional carbon resonances in the ^{13}C NMR spectra of these two complexes confirm the addition of the methoxymethylene group. Under Lewis acidic conditions, compound **12** also undergoes a Michael addition with methyl acrylate at C3 to generate **26** with a dr of 12:1. This complex was characterized by two downfield resonances in the ^{13}C NMR at δ 174.0 and 172.5 corresponding to the iminium carbon and the C=O from the ester. Characteristic resonances in the ^{1}H NMR spectrum include a singlet (3H) at δ 3.69 corresponding to the ester methoxy group as well as new methylene proton resonances. In all cases, ^{1}H−^{1}H coupling data confirm that the alkyl group has added anti to the metal.

Discussion

One of the most important outcomes of [Os]-mediated reactions of aromatic molecules is the excellent stereochemical control of addition to the ring carbons relative to the metal.[2] However, because the metal has equal accessibility to both enantiofaces of the ring, the challenge of inducing asymmetry does not lie in the discrimination of enantiofaces by the incoming electrophile but rather by the metal itself. Thus, in principle, a pyrrole bearing a chiral auxiliary may be used to set the absolute stereochemistry of multiple carbons.

The two features of the chiral auxiliary that were initially considered to be essential for a significant energetic difference between the pyrrole enantiofaces were a hydrogen bond acceptor (R_2) and a large steric difference between R_1 and H_A (**B** and **C** in Figure 2).

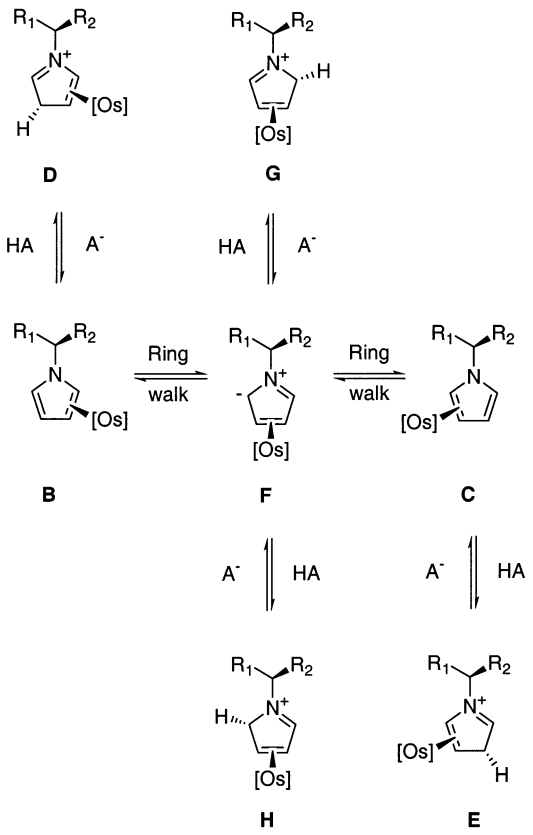
This latter facet is in contrast to the steric profile of the related phenyl ether/lactate system (vide supra), which depended on a steric interaction between the ortho proton of the aromatic ring and the chiral auxiliary to provide good stereocontrol. The combination of R_1 = Me and R_2 = CO_2Me was sufficient to provide a high diastereomeric ratio for the phenyl ether complex. However, the exact same substituents for pyrrole (complex **9**) were completely ineffective in providing differentiation of the enantiofaces even though the stereogenic center was actually *closer* to the ring and to the metal in the case of the heterocycle.

While the stereospecificity seen with the lactate-derived phenyl ether systems was compromised by hydrogen bond disrupting solvents such as DMSO or DMF,[35] the present system appears to be immune to such effects. When dissolved in DMF-d_7, complexes **11** and **12** displayed no alteration to their diastereomeric ratios. However, half-life studies of pyrrole displacement by CD_3CN support the notion that a hydrogen bond is present (Table 2). Interestingly, the hydrogen-bond acceptor substitutent (R_2) that provided the greatest control for the phenyl ether system was an ester, while for the pyrrole system, the ester group offered the poorest differentiation (vide supra).

Upon protonation at C3, complexes **15**−**21** maintain their diastereomeric ratios even under prolonged acid exposure at 20 °C. Indeed, the diastereomeric ratio of **19** in solution does not change, even under conditions where **19** is known to tautomerize to its more stable 2*H*-pyrrolium form. This observation indicates that the two diastereomers of **19**, at least at 20 °C, have reached equilibrium. Thus, for the formation of 3*H*-pyrrolium **19**, the kinetic diastereomeric ratio is virtually identical to the thermodynamic ratio at 20 °C (an earlier study confirmed that protonation in acetonitrile is irreversible in the absence of a moderate base).[3,4]

The proposed mechanism for tautomerization from a 3*H*- to a 2*H*-pyrrolium complex involves deprotonation, intrafacial isomerization, and re-protonation of the azomethine ylide **F** (Scheme 2).[7] This species can protonate at either C2 or C5 to form a 1:1 mixture of **G** and **H**. In contrast to diastereomers **B** and **C**, the metal is sufficiently far away from the chiral auxiliary in the 3,4-η^2 isomer **F** that it no longer can impact the diastereomer ratio.

Scheme 2. Tautomerization Pathways



Conclusion

The present study demonstrates for the first time a chiral auxiliary influencing the metal coordination and subsequent organic reactions for a π-bound aromatic heterocycle. However, the present system is not likely to be practical as a methodology for the preparation of alkaloids. Although amino acid esters have been cleaved from secondary amines either by mild oxidation with MCPBA[38] or by a sequence of steps involving a Curtius rearrangement,[39] the cleavage of the chiral auxiliary is not trivial, and the relative cost of osmium is high. The present system was chosen because of the ease in preparation of the pyrroles from amino acids. It has been demonstrated that a chiral substituent with the right characteristics can direct the stereoselective binding of osmium to pyrrole, which can then lead to stereoselective carbon−carbon bond formation. A more practical approach would be to build asymmetry into the metal/ligand system to influence binding to a single enantioface. It has been demonstrated that the fragment {TpRe(CO)(MeIm)} binds *N*-methylpyrrole with a 7:1 ratio of coordination diastereomers,[40] and the scope of this chemistry is currently under investigation.

Experimental Section

General Methods. NMR spectra were obtained on a 500 MHz Varian INOVA spectrometer unless otherwise noted. All chemical shifts are reported in ppm and are referenced to tetramethylsilane (TMS) utilizing residual ^{1}H or ^{13}C signals of the deuterated solvents as an internal standard. Coupling constants (*J*) are reported in hertz (Hz). Electrochemical experiments were performed under a dinitrogen atmosphere using a PAR model 362 potentiostat driven by a PAR model 175 universal programmer. Cyclic voltammograms (CV) were recorded (Kipp and Zonen BD90 XY recorder) at 100 mV/s (25 °C) in a standard three-electrode cell from +1.7 to −1.7 V with a glassy carbon working electrode, acetonitrile (CH_3CN) solvent, and tetrabutylammonium hexafluorophosphate (TBAH) electrolyte. All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2}$ = −780 mV) or ferrocene ($E_{1/2}$ = 550 mV) as an internal standard. Elemental analysis (EA) was performed with a Perkin-Elmer 2400 Series II CHNS/O analyzer. All synthetic reactions with osmium were performed under a dinitrogen atmosphere in a drybox. Acetonitrile and hexanes were purged with nitrogen and purified by passage through a column

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packed with activated alumina.[41] Other solvents were used as received from Fisher Chemicals. Deuterated solvents were used as received from Cambridge Isotopes. Before complexation to the pentaammineosmium(II) fragment, the asymmetric pyrroles that were isolated as liquids were purified by reduced pressure distillation. Dimethoxymethane, TBSOTf, and methyl acrylate were each purified with basic alumina before use. Without careful drying, alkylation reactions were contaminated by protonation products. Other reagents were used as received.

Determination of Rate Constants in Table 2. Compound **12** was dissolved in CD_3CN, and the solution was observed by ^1H NMR. Over time, the pyrrole ligand is substituted by CD_3CN and proton resonances that correspond to the unbound pyrrole, **5**, begin to appear. The integrations of the methine proton attached to the asymmetric carbon as well as the ring protons of both the bound (**12**) and unbound pyrrole (**5**) were used to estimate the relative concentrations of those species as a function of time. The linear plot of $\ln([\mathbf{12}]_t/[\mathbf{12}]_i)$ versus time provides the rate constant (negative slope).

1-(2-Methoxy-1-methylethyl)-1*H*-pyrrole (2). The same procedure for the synthesis of **5** (vide infra) was employed using 2-pyrrol-1-ylpropan-1-ol (6.70 g, 0.054 mol) to afford 3.08 g (41%) of a colorless liquid. ^1H NMR (300 MHz, $CDCl_3$, 21 °C): δ 6.82 (2H, dd, J = 2.1, α-H's), 6.24 (2H, dd, J = 2.1, β-H's), 4.32 (1H, ddq, ^3J = 6.6, 6.6, 6.6, CH), 3.60 (2H, m, OCH_2), 3.38 (3H, s, OCH_3), 1.55 (3H, d, ^3J = 6.9, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 21 °C): δ 118.7 (α-C's), 107.6 (β-C's), 77.0 (CH), 58.8 (OCH_3), 54.5 (OCH_2), 18.1 (CH_3).

3-Methyl-2-pyrrol-1-ylbutan-1-ol (4). 3-Methyl-2-pyrrol-1-ylbutyric acid methyl ester (**3**) (14.01 g, 0.077 mol) was slowly dripped into a THF (300 mL) suspension of $LiAlH_4$ (4.53 g, 0.119 mol) under N_2. After 2 h of stirring, the THF was evaporated under reduced pressure. Diethyl ether (200 mL) was added to the resulting white residue. The system was cooled to 0 °C, and 100 mL of 1:1 concentrated HCl/H_2O was added. The ether layer was thrice washed with 50 mL of H_2O and then dried over Na_2SO_4. The Na_2SO_4 was then filtered away, and the ether was removed under reduced pressure. The resulting liquid was subjected to reduced pressure distillation to afford 11.10 g (94%) of a colorless liquid. ^1H NMR (300 MHz, $CDCl_3$, 21 °C): δ 6.67 (2H, dd, J = 2.1, α-H's), 6.15 (2H, dd, J = 2.1, β-H's), 3.84 (1H, dd, ^2J = 11.7, ^3J = 4.0, 1/2-OCH_2), 3.76 (1H, dd, ^2J = 11.7, ^3J = 8.4, 1/2-OCH_2), 3.55 (1H, ddd, ^3J = 8.9, 8.8, 4.0, CH), 2.00 (1H, d of sextet, ^3J = 9.0, 6.7, *i*-Pr CH), 1.92 (1H, s, OH), 1.00 (3H, d, ^3J = 6.6, *i*-Pr CH_3), 0.73 (3H, d, ^3J = 6.6, *i*-Pr CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 21 °C): δ 119.6 (α-C's), 107.9 (β-C's), 68.5 (CH), 63.9 (OCH_2), 30.6 (*i*-Pr CH), 19.9 (*i*-Pr CH_3), 19.3 (*i*-Pr CH_3).

1-(1-Methoxymethyl-2-methylpropyl)-1*H*-pyrrole (5).[42] 3-Methyl-2-pyrrol-1-ylbutan-1-ol (**4**) (1.50 g, 9.79 mmol) was added dropwise to a THF (50 mL) suspension of NaH (258 mg, 10.77 mmol) under N_2. Dimethyl sulfate (1.23 g, 9.79 mmol) was added dropwise, and the mixture was stirred for 2 h and then allowed to reflux for 24 h. The THF was then evaporated under reduced pressure, and the mixture was taken up again in diethyl ether (100 mL) and 100 mL of 1:1 concentrated HCl/H_2O. The aqueous layer was then thrice washed with 75 mL of Et_2O. The ethereal extracts were then dried over Na_2SO_4 and filtered through a 1 cm silica plug. The ether was then removed under reduced pressure, and the resulting oil was subjected to reduced pressure distillation to afford 1.50 g (91%) of a colorless liquid. ^1H NMR (300 MHz, $CDCl_3$, 21 °C): δ 6.70 (2H, dd, J = 2.1, α-H's), 6.14 (2H, dd, J = 2.1, β-H's), 3.65 (3H, m, CH and OCH_2), 3.30 (3H, s, OCH_3), 2.13 (1H, d of sextet, ^3J = 6.7, 5.1, *i*-Pr CH), 1.00 (3H, d, ^3J = 6.8, *i*-Pr CH_3), 0.73 (3H, d, ^3J = 6.4, *i*-Pr CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 21 °C): δ 120.0 (α-C's), 107.4 (β-C's), 73.8 (CH), 66.1 (OCH_2), 59.1 (OCH_3), 30.9 (*i*-Pr CH), 20.0 (*i*-Pr CH_3), 19.3 (*i*-Pr CH_3).

3,3-Dimethyl-2-pyrrol-1-ylbutyric Acid Methyl Ester (6). A glacial acetic acid solution (175 mL) of L-*tert*-leucine (11.11 g, 0.084 mol) and NaOAc (7.02 g, 0.086 mol) was heated to 80 °C. 2,5-Dimethoxytetrahydofuran (11.60 g, 0.87 mol) was added dropwise, and the mixture was stirred for 1 h. The acetic acid was then distilled under reduced pressure, and the mixture was taken up again in 400 mL of 1:1 CH_2Cl_2/H_2O. The aqueous layer was thrice washed with 50 mL of CH_2Cl_2. The CH_2Cl_2 extracts were combined, and the solvent was removed under reduced pressure. The resulting brown residue was taken up again in MeOH (300 mL) and refluxed for 24 h after the addition of concentrated H_2SO_4 (10 mL). The methanol was removed under reduced pressure, and then the brown residue was taken up in CH_2Cl_2 (250 mL) and filtered through 1 cm of silica. The CH_2Cl_2 was then removed under reduced pressure. The resulting brown oil was subjected to reduced pressure distillation to afford 9.00 g (54%) of a white solid. ^1H NMR (300 MHz, $CDCl_3$, 21 °C): δ 6.87 (2H, dd, J = 2.0, α-H's), 6.15 (2H, dd, J = 2.0, β-H's), 4.39 (1H, s, CH), 3.73 (3H, s, OCH_3), 1.02 (9H, s, *t*-Bu CH_3's). ^{13}C NMR (75 MHz. $CDCl_3$, 21 °C): δ 169.9 (C═O), 122.0 (α-C's), 107.6 (β-C's), 70.8 (CH), 51.8 (OCH_3), 35.8 (*t*-Bu C), 26.8 (*t*-Bu CH_3's).

3,3-Dimethyl-2-pyrrol-1-ylbutan-1-ol (7). The same procedure for the synthesis of **4** was employed using **6** (4.48 g, 0.023 mol) to afford 2.48 g (65%) of a white solid. ^1H NMR (300 MHz, $CDCl_3$, 21 °C): δ 6.66 (2H, dd, J = 2.1, α-H's), 6.15 (2H, dd, J = 2.1, β-H's), 3.91 (2H, m, OCH_2), 3.70 (1H, dd, ^3J = 8.7, 5.4, CH), 1.77 (1H, s, OH), 0.92 (9H, s, *t*-Bu CH_3's). ^{13}C NMR (75 MHz, $CDCl_3$, 21 °C): δ 120.6 (α-C's), 107.7 (β-C's), 71.6 (CH), 61.4 (OCH_2), 34.3 (*t*-Bu C), 27.3 (*t*-Bu CH_3's).

[Os(NH$_3$)$_5$(4,5-η^2-(2-pyrrol-1-ylpropionic acid methyl ester))](OTf)$_2$ (8). A methanolic solution (520 mg, 16.24 mmol) of 2-pyrrol-1-ylpropionic acid methyl ester (**1**) (295 mg, 1.92 mmol) and $[Os(NH_3)_5(OTf)](OTf)_2$ (251 mg, 0.35 mmol) was treated with a Zn/Hg amalgam (650 mg). After 2 h of stirring, the resulting green slurry was diluted with ∼1 g of DME and filtered through a 30 mL medium-porosity frit. The filtrate was twice washed with 20 mL of 1:1 CH_2Cl_2/Et_2O, and the solvent was decanted. The leftover yellow-brown solid was taken up in ∼5 mL of CH_3CN, precipitated into 75 mL of 2:1 Et_2O/CH_2Cl_2, filtered through a 60 mL fine-porosity firt, washed with 2 × 10 mL of CH_2Cl_2, washed with 3 × 10 mL of Et_2O, and dried in vacuo to afford a yellow solid (204 mg, 81%) with a diastereomeric ratio of 1:1 by ^1H NMR integrations. CV (CH_3CN, TBAH, 100 mV/s): $E_{1/2}$ = 130 mV (NHE). ^1H NMR (500 MHz, CD_3CN, −15 °C): δ 6.56/6.49 (1H, d, ^3J = 2.6, α-unbound), 6.30/6.28 (1H, d, ^3J = 3.8, α-bound), 5.62/5.60 (1H, dd, ^3J = 2.6, 2.6, β-unbound), 5.09/5.08 (1H, m, β-bound), 4.75/4.57 (1H, q, ^3J = 7.4, CH), 3.95/3.92 (3H, s, *trans*-NH_3), 3.69/3.68 (3H, s, OCH_3), 2.85/2.83 (12H, s, *cis*-NH_3), 1.56/1.53 (3H, d, ^3J = 7.4, CH_3). ^{13}C NMR (125 MHz, CD_3CN, −15 °C): δ 176.7/176.1 (C═O), 129.1/125.7 (α-unbound), 122.7 and 120.1 (OTf), 107.8/106.8 (β-unbound), 80.6/76.6 (α-bound), 58.1/57.6 (CH), 56.2/55.3 (β-bound), 53.4/53.2 (OCH_3), 19.1/16.3 (CH_3).

[Os(NH$_3$)$_5$(4,5-η^2-(1-(2-methoxy-1-methylethyl)-1*H*-pyrrole))](OTf)$_2$ (9). A DMA solution (1140 mg, 13.08 mmol) of 1-(2-methoxy-1-methylethyl)-1*H*-pyrrole (**2**) (472 mg, 3.39 mmol) and $[Os(NH_3)_5(OTf)](OTf)_2$ (473 mg, 0.65 mmol) was treated with activated Mg^0 (1048 mg, 43.12 mmol). After 3 h and 30 min of vigorous stirring, the resulting brown slurry was diluted with ∼1 g of DME and filtered through a 30 mL medium-porosity frit. The filtrate was washed with 10 mL of 1:1 Et_2O/hexanes, then twice washed with 15 mL of 1:1:1 CH_2Cl_2/Et_2O/hexanes with the solvent being decanted. The leftover brown solid was taken up in CH_3CN, precipitated in 50 mL of 1:1 CH_2Cl_2/Et_2O, filtered through a 60 mL fine-porosity frit, washed with 2 × 20 mL of 1:1 CH_2Cl_2/Et_2O, and dried in vacuo

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to afford a bright yellow solid (421 mg, 90%) with a diastereomeric ratio of 6:1 by ^{1}H NMR (71% de). CV (CH_3CN, TBAH, 100 mV/s): $E_{1/2}$ = 140 mV (NHE). ^{1}H NMR (500 MHz, CD_3CN, −9 °C): δ 6.69 (1H, d, ^3J = 2.5, α-unbound), 6.33 (1H, d, ^3J = 4.0, α-bound), 5.53 (1H, dd, ^3J = 3.0, 3.0, β-unbound), 5.11 (1H, dd, ^3J = 3.5, 3.5, β-bound), 3.92 (1H, dq, ^3J = 7.0, 7.0, CH), 3.86 (3H, br s, *trans*-NH_3), 3.45 (2H, m, OCH_2), 3.26 (3H, s, OCH_3), 2.77 (12H, br s, *cis*-NH_3), 1.18 (3H, d, ^3J = 6.5, CH_3). ^{13}C NMR (125 MHz, CD_3CN, −9 °C): δ 123.2 (α-unbound), 105.8 (β-unbound), 81.1 (α-bound), 76.8 (OCH_2), 58.6 (CH), 56.2 (OCH_3), 56.0 (β-bound), 19.5 (CH_3).

[Os(NH$_3$)$_5$(4,5-η^2-(3-Methyl-2-pyrrol-1-ylbutyric acid methyl ester))](OTf)$_2$ (10). A sandalwood solution of 3-methyl-2-pyrrol-1-ylbutyric acid methyl ester (**3**) (902 mg, 5.14 mmol), $[Os(NH_3)_5(OTf)](OTf)_2$ (700 mg, 0.97 mmol), and methanol (1396 mg, 43.61 mmol) was treated with a Zn/Hg amalgam (1778 mg). After 40 min of vigorous stirring, the resulting brown slurry was diluted with DME (1 mL) and filtered through a 30 mL coarse-porosity frit into a 1:1 solution (400 mL) of Et_2O/hexanes. The yellow precipitate was filtered through a 150 mL fine-porosity frit, washed with ether (2 × 10 mL), and dried in vacuo to afford a yellow solid (669 mg, 92%) with a diastereomeric ratio of 1.88:1.00 by ^{1}H NMR (30% de). CV (CH_3CN, TBAH, 100 mV/s): $E_{1/2}$ = 230 mV (NHE). ^{1}H NMR (500 MHz, CD_3CN, −20 °C): major diastereomer = δ 6.62 (1H, d, ^3J = 2.9, α-unbound), 6.40 (1H, d, ^3J = 4.0, α-bound), 5.60 (1H, dd, ^3J = 2.9, 2.6, β-unbound), 5.12 (1H, dd, ^3J = 4.0, 2.6, β-bound), 4.10 (1H, d, ^3J = 9.5, CH), 3.91 (3H, br s, *trans*-NH_3), 3.68 (3H, s, OCH_3), 2.78 (12H, br s, *cis*-NH_3), 2.32 (1H, d of 7-et, ^3J = 9.5, 6.6, *i*-Pr CH), 0.92 (3H, d, ^3J = 6.6, *i*-Pr CH_3), 0.80 (3H, d, ^3J = 7.0, *i*-Pr CH_3); minor diastereomer = δ 6.49 (1H, d, ^3J = 2.6, α-unbound), 6.36 (1H, d, ^3J = 3.7, α-bound), 5.58 (1H, dd, ^3J = 2.9, 2.6, β-unbound), 5.08 (1H, dd, ^3J = 3.7, 2.6, β-bound), 4.13 (1H, d, ^3J = 11.0, CH), 3.94 (3H, br s, *trans*-NH_3), 3.69 (3H, s, OCH_3), 2.82 (12H, br s, *cis*-NH_3), 2.44 (1H, d of 7-et, ^3J = 11.0, 6.6, *i*-Pr CH), 0.95 (3H, d, ^3J = 6.6, *i*-Pr CH_3), 0.78 (3H, d, ^3J = 6.6 *i*-Pr CH_3). ^{13}C NMR (125 MHz, CD_3CN, −20 °C): major diastereomer = δ 174.5 (C═O), 126.0 (α-unbound), 108.1 (β-unbound), 82.2 (α-bound), 69.2 (CH), 55.8 (β-bound), 53.8 (OCH_3), 33.9 (*i*-Pr CH), 20.3 (*i*-Pr CH_3), 19.2 (*i*-Pr CH_3); minor diastereomer = δ 176.2 (C═O), 131.8 (α-unbound), 107.0 (β-unbound), 76.2 (α-bound), 69.7 (CH), 56.7 (β-bound), 53.6 (OCH_3), 30.5 (*i*-Pr CH), 20.0 (*i*-Pr CH_3), 19.9 (*i*-Pr CH_3).

[Os(NH$_3$)$_5$(4,5-η^2-(3-Methyl-2-pyrrol-1-ylbutan-1-ol))](OTf)$_2$ (11). A DMA solution (1103 mg, 12.66 mmol) of 3-methyl-2-pyrrol-1-ylbutan-1-ol (**4**) (578 mg, 3.77 mmol) and $[Os(NH_3)_5(OTf)](OTf)_2$ (464 mg, 0.642 mmol) was treated with activated Mg^0 (962 mg, 39.58 mmol). After 4 h of vigorous stirring, the resulting brown slurry was diluted with 1 g of DME and precipitated through a 30 mL medium-porosity frit, after which the solvent was removed under reduced pressure. The resulting brown oil was then diluted with 10 mL of 1:1 Et_2O/hexanes and swirled, and the solvent was decanted. The oil was then redissolved in 2 mL of CH_2Cl_2, and 10 mL of 1:1 Et_2O/hexanes was added, which produced a yellow precipitate, which was filtered through a 15 mL medium-porosity frit, washed with 2 × 10 mL of CH_2Cl_2 and 2 × 10 mL of Et_2O, and dried in vacuo to afford a yellow solid (456 mg, 98%) with a diastereomeric ratio of 10:1 by ^{1}H NMR (82% de). CV (CH_3CN, TBAH, 100 mV/s): $E_{1/2}$ = 110 mV (NHE). ^{1}H NMR (500 MHz, CD_3CN, −10 °C): δ 6.66 (1H, d, ^3J = 3.0, α-unbound), 6.41 (1H, d, ^3J = 4.5, α-bound), 5.53 (1H, dd, ^3J = 2.5, 2.5, β-unbound), 5.12 (1H, dd, ^3J = 3.5, 3.5, β-bound), 3.92 (2H, m, 1/2-OCH_2 + CH), 3.80 (3H, br s, *trans*-NH_3), 3.54 (1H, m, 1/2-OCH_2), 2.82 (12H, br s, *cis*-NH_3), 1.75 (1H, d of 7-et, ^3J = 9.0, 6.5, *i*-Pr H), 0.91 (3H, d, ^3J = 6.5, *i*-Pr CH_3), 0.68 (3H, d, ^3J = 6.5, *i*-Pr CH_3). ^{13}C NMR (125 MHz, CD_3CN, −10 °C): δ 123.4 (α-unbound), 105.6 (β-unbound), 82.9 (α-bound), 68.4 (CH), 63.4 (OCH_2), 56.1 (β-bound), 34.5 (*i*-Pr H), 20.5 (*i*-Pr CH_3), 19.6 (*i*-Pr CH_3). Anal. Calcd. for $C_{11}H_{30}N_6O_7S_2F_6Os$: C, 18.18; H, 4.16; N, 11.56. Found: C, 17.91; H, 4.14; N, 11.20.

[Os(NH$_3$)$_5$(4,5-η^2-(1-(1-methoxymethyl-2-methylpropyl)-1*H*-pyrrole))](OTf)$_2$ (12). A DMA solution (1209 mg, 13.87 mmol) of 1-(1-methoxymethyl-2-methylpropyl)-1*H*-pyrrole (**5**) (615 mg, 3.67 mmol) and $[Os(NH_3)_5(OTf)](OTf)_2$ (480 mg, 0.644 mmol) was treated with activated Mg^0 (894 mg, 36.79 mmol). After 1 h and 40 min of vigorous stirring, the resulting brown slurry was diluted with ∼1 g of DME and filtered through a 30 mL coarse-porosity frit followed by solvent removal under reduced pressure. The resulting brown oil was twice washed with 10 mL of 1:1 Et_2O/hexanes, redissolved in ∼2 mL of DME, precipitated into 100 mL of 9:1 Et_2O/CH_2Cl_2, filtered through a 30 mL medium-porosity frit, washed twice with 5 mL of CH_2Cl_2, washed twice with 5 mL of Et_2O, and dried in vacuo to afford a yellow solid (436 mg, 89%) with a diastereomeric ratio of 16:1 by ^{1}H NMR (88% de). CV (CH_3CN, TBAH, 100 mV/s): $E_{1/2}$ = 130 mV (NHE). ^{1}H NMR (500 MHz, CD_3CN, −10 °C): δ 6.64 (1H, d, ^3J = 3.0, α-unbound), 6.41 (1H, d, ^3J = 4.0, α-bound), 5.527 (1H, dd, ^3J = 3.0, 3.0, β-unbound), 5.12 (1H, dd, ^3J = 3.5, 3.5, β-bound), 3.88 (3H, br s, *trans*-NH_3), 3.68 (1H, m, 1/2-OCH_2) 3.48 (2H, m, 1/2-OCH_2 + CH), 3.26 (3H, s, OCH_3), 2.80 (12H, br s, *cis*-NH_3) 1.773 (1H, d of 7-et, ^3J = 8.5, 6.5, *i*-Pr H), 0.91 (3H, d, ^3J = 6.5, *i*-Pr CH_3), 0.68 (3H, d, ^3J = 7.0, *i*-Pr CH_3). ^{13}C NMR (125 MHz, CD_3CN, −10 °C): δ 123.2 (α-unbound), 105.6 (β-unbound), 82.8 (α-bound), 74.3 (OCH_2), 66.7 (CH), 58.5 (OCH_3), 55.9 (β-bound), 34.5 (*i*-Pr CH), 20.4 (*i*-Pr CH_3), 19.4 (*i*-Pr CH_3). Anal. Calcd for $C_{12}H_{32}N_6O_7S_2F_6Os$: C, 19.45; H, 4.35; N, 11.34. Found: C, 19.02; H, 4.03; N, 11.35.

[Os(NH$_3$)$_5$(4,5-η^2-(3,3-Dimethyl-2-pyrrol-1-ylbutyric acid methyl ester))](OTf)$_2$ (13). A tan solution of 3,3-dimethyl-2-pyrrol-1-ylbutyric acid methyl ester (**6**) (387 mg, 1.98 mmol), $[Os(NH_3)_5(OTf)](OTf)_2$ (293 mg, 0.405 mmol), and methanol (1019 mg, 31.8 mmol) was treated with a Zn/Hg amalgam (1148 mg). After 50 min of vigorous stirring, the resulting lime green solution was diluted with DME (1 mL) and filtered through a 30 mL coarse-porosity frit into 200 mL of stirring ether. The precipitate was filtered through a 60 mL medium-porosity frit, washed with 3 × 10 mL of ether, and dried in vacuo to afford a lime green solid (244 mg, 78%) with a diastereomeric ratio of 6:1 by ^{1}H NMR. CV (CH_3CN, TBAH, 100 mV/s): $E_{1/2}$ = 190 mV (NHE). ^{1}H NMR (500 MHz, CD_3CN, 0 °C): δ 6.75 (1H, d, ^3J = 1.8, α-unbound), 6.43 (1H, d, ^3J = 2.4, α-bound), 5.56 (1H, dd, ^3J = 1.8, 1.8, β-unbound), 5.12 (1H, dd, ^3J = 1.8, 1.8, β-bound), 4.37 (1H, s, CH), 3.88 (3H, br s, *trans*-NH_3), 3.67 (3H, s, OCH_3), 2.77 (12H, br s, *cis*-NH_3), 1.02 (9H, s, *t*-Bu CH_3's). ^{13}C NMR (125 MHz, CD_3CN, 0 °C): δ 172.9 (C═O), 127.4 (α-unbound), 106.5 (β-unbound), 82.0 (α-bound), 70.6 (CH), 55.4 (β-bound), 52.8 (OCH_3), 38.3 (*t*-Bu C), 27.3 (*t*-Bu CH_3's).

[Os(NH$_3$)$_5$(4,5-η^2-(3,3-dimethyl-2-pyrrol-1-ylbutan-1-ol))](OTf)$_2$ (14). A DMA solution (822 mg, 9.44 mmol) of 3,3-dimethyl-2-pyrrol-1-ylbutan-1-ol (**7**) (423 mg, 2.52 mmol) and $[Os(NH_3)_5(OTf)](OTf)_2$ (323 mg, 0.45 mmol) was treated with activated Mg^0 (867 mg, 35.6 mmol). After 3 h of vigorous stirring, the resulting brown slurry was diluted with ∼1 mL of DME and filtered through a 30 mL coarse-porosity frit. The solvent was removed under reduced pressure, and the resulting brown oil was washed with 3 × 10 mL of Et_2O and then decanted. The oil was then redissolved in ∼2 mL of CH_3CN, precipitated into 100 mL of 10:1 Et_2O/CH_2Cl_2, filtered through a 60 mL fine-porosity frit, washed with 3 × 10 mL of Et_2O, and dried in vacuo to afford a tan solid (292 mg, 88%) with a diastereomeric ratio of >20:1 by ^{1}H NMR (98% de). CV (CH_3CN, TBAH, 100 mV/s): $E_{1/2}$ = 110 mV (NHE). ^{1}H NMR (500 MHz, CD_3CN, −10 °C): δ 6.73 (1H, d, ^3J = 3.0, α-unbound), 6.48 (1H, d, ^3J = 4.5, α-bound), 5.46 (1H, dd, ^3J = 2.75, ^3J = 3.0, β-unbound), 5.14 (1H, dd, ^3J = 3.5, ^3J = 3.5, β-bound), 3.99 (1H, d, ^3J = 8.0, 1/2-OCH_2), 3.80 (3H, br s, *trans*-NH_3), 3.69 (1H, d, ^3J = 8.0, CH), 3.68 (1H, s, 1/2-OCH_2) 2.85 (12H,

br s, *cis*-NH_3), 0.89 (9H, s, *t*-Bu-CH_3's). ^{13}C NMR (125 MHz, CD_3CN, −10 °C): δ 124.2 (α-unbound), 103.9 (β-unbound), 82.6 (α-bound), 70.6 (CH), 61.4 (OCH_2), 56.2 (β-bound), 37.3 (*t*-Bu-C), 27.3 (*t*-Bu-CH_3's).

[Os(NH_3)$_5$(4,5-η^2-(1-(1-methoxycarbonylethyl)-3*H*-pyrrolium))](OTf)$_3$ (15). The same procedure was used for the protonation of all [Os]-bound asymmetric pyrroles, and a sample experimental is listed below. [Os(NH_3)$_5$(4,5-η^2-(2-pyrrol-1-ylpropionic acid methyl ester))](OTf)$_2$ (**8**) (76 mg, 0.10 mmol) was dissolved in CH_3CN (∼1 mL), cooled to −40 °C, and treated with a −40 °C acetonitrile solution (∼1 mL) of triflic acid (64 mg, 0.43). After 5 min of swirling, the red reaction mixture was added to 75 mL of stirring Et_2O, filtered through a 30 mL medium-porosity frit, washed with 3 × 10 mL of Et_2O, and dried in vacuo to afford a pink solid (81 mg, 88%) with a diastereomeric ratio of 1:1 by ^1H NMR (0% de). The same procedure repeated at room temperature afforded a diastereomeric ratio of 1:1 by ^1H NMR (0% de). ^1H NMR (500 MHz, CD_3CN, 21 °C): δ 8.95/8.90 (1H, s, iminium), 6.44/6.41 (1H, d, ^3J = 4.5, α-bound), 5.16/5.14 (1H, q, ^3J = 6.9, CH), 4.81/4.80 (1H, m, β-bound), 4.44/4.44 (3H, s, *trans*-NH_3), 3.81/3.80 (3H, s, OCH_3), 3.27/3.26 (12H, s, *cis*-NH_3), 2.92/2.92 (1H, d, ^2J = 26.6, 1/2-CH_2), 2.75/2.75 (1H, dd, ^2J = 26.3, ^3J = 5.8, 1/2-CH_2), 1.77/1.76 (3H, d, ^3J = 7.0). ^{13}C NMR (125 MHz, CD_3CN, 21 °C): δ 177.4/177.3 (C═O), 170.9/170.4 (iminium), 76.3/73.4 (α-bound), 63.0/62.4 (CH), 54.8/54.5 (OCH_3), 44.5/43.7 (CH_2), 42.3/41.9 (β-bound), 19.0/16.0 (CH_3).

[Os(NH_3)$_5$(4,5-η^2-(1-(2-methoxy-1-methylethyl-3*H*-pyrrolium))](OTf)$_3$ (16). A pink solid was afforded (99%) with a diastereomeric ratio of 6:1 by ^1H NMR (71% de). The same procedure repeated at room temperature afforded the same diastereomeric ratio by ^1H NMR. CV (CH_3CN, TBAH, 100 mV/s): $E_{p,a}$ = 1.32 V (NHE). ^1H NMR (500 MHz, CD_3CN, 22 °C): δ 8.84 (1H, s, iminium), 6.46 (1H, d, ^3J = 4.5, α-bound), 4.71 (1H, dd, ^3J = 5.5, 5.5, β-bound), 4.44 (3H, br s, *trans*-NH_3), 4.43 (1H, m, CH), 3.79 (1H, dd, ^2J = 10.5, ^3J = 11.0, 1/2-OCH_2), 3.72 (1H, dd, ^2J = 10.5, ^3J = 3.5, 1/2-OCH_2), 3.31 (3H, s, OCH_3), 3.24 (12H, br s, *cis*-NH_3), 2.92 (1H, d, ^2J = 26.5, 1/2-CH_2), 2.70 (1H, dd, ^2J = 26.5, ^3J = 6.0, 1/2-CH_2), 1.43 (3H, d, ^3J = 6.5, CH_3). ^{13}C NMR (125 MHz, CD_3CN, 22 °C): δ 172.0 (iminium), 76.0 (α-bound), 74.4 (OCH_2), 61.8 (CH), 59.3 (OCH_3), 43.7 (CH_2), 42.0 (β-bound), 18.4 (CH_3).

[Os(NH_3)$_5$(4,5-η^2-(1-(1-methoxycarbonyl-2-methylpropyl)-3*H*-pyrrolium))](OTf)$_3$ (17). A pink solid was afforded (96%) with a diastereomeric ratio of 6:1 by ^1H NMR (71% de). The same procedure repeated at room temperature afforded a diastereomeric ratio of 5:1 by ^1H NMR (67% de). CV (CH_3CN, TBAH, 100 mV/s): $E_{p,a}$ = 1.40 V (NHE). ^1H NMR (500 MHz, CD_3CN, 22 °C): δ 8.87 (1H, s, iminium), 6.46 (1H, d, ^3J = 4.4, α-bound), 5.02 (1H, d, ^3J = 6.0, CH), 4.80 (1H, dd, ^3J = 4.6, 4.6, β-bound), 4.45 (3H, br s, *trans*-NH_3), 3.84 (3H, s, CH_3), 3.27 (12H, br s, *cis*-NH_3), 3.01 (1H, d, ^2J = 26.4, 1/2-CH_2), 2.88 (1H, dd, ^2J = 26.7, ^3J = 5.7, 1/2-CH_2), 2.67 (1H, m, *i*-Pr CH), 1.14 and 1.03 (each 3H, d, ^3J = 6.5, *i*-Pr CH_3's). ^{13}C NMR (125 MHz, CD_3CN, 22 °C): δ 177.0 (iminium), 169.6 (C═O), 78.5 (α-bound), 71.4 (CH), 55.2 (OCH_3), 45.2 (CH_2), 41.7 (β-bound), 33.8 (*i*-Pr CH), 19.2 and 17.9 (*i*-Pr CH_3's).

[Os(NH_3)$_5$(4,5-η^2-(1-(1-hydroxymethyl-2-methylpropyl)-3H-pyrrolium))](OTf)$_3$ (18). A pink solid was afforded (95%) with a diastereomeric ratio of 10:1 by ^1H NMR (82% de). The same procedure repeated at room temperature afforded a diastereomeric ratio of 8:1 by ^1H NMR (78% de). CV (CH_3CN, TBAH, 100 mV/s): $E_{p,a}$ = 1.34 V (NHE). ^1H NMR (500 MHz, CD_3CN, 22 °C): δ 8.83 (1H, s, iminium), 6.46 (1H, d, ^3J = 4.4, α-bound), 4.75 (1H, dd, ^3J = 5.5, ^3J = 5.5, β-bound), 4.44 (3H, br s, *trans*-NH_3), 4.15 (2H, m, CH + 1/2-OCH_2), 3.90 (1H, m, 1/2-OCH_2), 3.30 (12H, br s, *cis*-NH_3), 3.03 (1H, d, ^2J = 26.4, 1/2-CH_2), 2.65 (1H, dd, ^2J = 26.4, ^3J = 6.2, 1/2-CH_2), 2.02 (1H, m, *i*-Pr CH), 1.05 (3H, d, ^3J = 6.6, *i*-Pr CH_3), 1.04 (3H, d, ^3J = 6.6, *i*-Pr CH_3). ^{13}C NMR (125 MHz, CD_3CN, 22 °C): δ 171.2 (iminium), 78.8 (α-bound), 73.9 (CH), 63.5 (OCH_2), 44.3 (CH_2), 42.2 (β-bound), 34.1 (*i*-Pr CH), 20.0 (*i*-Pr CH_3), 19.6 (*i*-Pr CH_3). Anal. Calcd for $C_{12}H_{31}N_6O_{10}S_3F_9Os$: C, 16.44; H, 3.56; N, 9.58. Found: C, 16.14; H, 3.47; N, 9.28.

[Os(NH_3)$_5$(4,5-η^2-(1-(1-methoxymethyl-2-methylpropyl)-3*H*-pyrrolium))](OTf)$_3$ (19). A pink solid was afforded (97%) with a diastereomeric ratio of 28:1 by ^1H NMR (93% de). The same procedure repeated at room temperature afforded a diastereomeric ratio of 14:1 by ^1H NMR (87% de). CV (CH_3CN, TBAH, 100 mV/s): $E_{p,a}$ = 1.37 V (NHE). ^1H NMR (500 MHz, CD_3CN, 22 °C): δ 8.81 (1H, s, iminium), 6.43 (1H, d, ^3J = 4.2, α-bound), 4.72 (1H, dd, ^3J = 5.6, 5.6, β-bound), 4.47 (3H, br s, *trans*-NH_3), 4.20 (1H, ddd, ^3J = 11.5, 8.0, 3.8, CH), 3.86 (1H, dd, ^2J = 10.9, ^3J = 3.8, 1/2-OCH_2), 3.81 (1H dd, ^2J = 10.6, ^3J = 11.2, 1/2-OCH_2), 3.31 (3H, s, OCH_3), 3.24 (12H, br s, *cis*-NH_3), 3.02 (1H, d, ^2J = 26.6, 1/2-CH_2), 2.77 (1H, dd, ^2J = 26.6, ^3J = 6.1, 1/2-CH_2), 2.03 (1H, 8-et, ^3J = 6.7, *i*-Pr CH), 1.03 (6H, d, ^3J = 6.7, *i*-Pr CH_3's). ^{13}C NMR (125 MHz, CD_3CN, 22 °C): δ 172.3 (iminium), 78.5 (α-bound), 73.1 (OCH_2), 71.8 (CH), 59.9 (OCH_3), 44.3 (CH_2), 42.1 (β-bound), 34.2 (*i*-Pr CH), 20.0 (*i*-Pr CH_3), 19.5 (*i*-Pr CH_3).

[Os(NH_3)$_5$(4,5-η^2-(1-(1-methoxycarbonyl-2,2-dimethylpropyl)-3*H*-pyrrolium))](OTf)$_3$ (20). A pink solid was afforded (93%) with a diastereomeric ratio of 32:1 by ^1H NMR (94% de). The same procedure repeated at room temperature afforded a diastereomeric ratio of 24:1 by ^1H NMR (92% de). CV (CH_3CN, TBAH, 100 mV/s): $E_{p,a}$ = 1.57 V (NHE). ^1H NMR (500 MHz, CD_3CN, 22 °C): δ 8.98 (1H, s, iminium), 6.53 (1H, d, ^3J = 4.5, α-bound), 4.96 (1H, s, CH), 4.78 (1H, dd, ^3J = 5.0, 5.0, β-bound), 4.46 (3H, br s, *trans*-NH_3), 3.85 (3H, s, OCH_3), 3.26 (12H, br s, *cis*-NH_3), 3.04 (1H, d, ^2J = 27.0, 1/2-CH_2), 2.91 (1H, dd, ^2J = 27.0, ^3J = 6.0, 1/2-CH_2), 1.18 (9H, s, *t*-Bu CH_3's). ^{13}C NMR (125 MHz, CD_3CN, 22 °C): δ 176.3 (iminium), 169.0 (C═O), 79.2 (α-bound), 73.8 (CH), 55.1 (OCH_3), 45.2 (CH_2), 41.1 (β-bound), 38.6 (*t*-Bu C), 26.8 (*t*-Bu CH_3's). Anal. Calcd for $C_{14}H_{33}N_6O_{11}S_3F_9Os$: C, 18.30; H, 3.62; N, 9.14. Found: C, 17.83; H, 3.45; N, 9.36.

[Os(NH_3)$_5$(4,5-η^2-(1-(1-hydroxymethyl-2,2-dimethylpropyl)-3*H*-pyrrolium))](OTf)$_3$ (21). A pink solid was afforded (92%) with a diastereomeric ratio >50:1 by ^1H NMR (>96% de). The same procedure repeated at room temperature afforded the same diastereomeric ratio. ^1H NMR (500 MHz, CD_3CN, 22 °C): δ 8.79 (1H, s, iminium), 6.48 (1H, d, ^3J = 4.5, α-bound), 4.71 (1H, dd, ^3J = 6.1, 5.1; β-bound), 4.44 (3H, br s, *trans*-NH_3), 4.37 (1H, dd, ^3J = 3.2, 2.2; OH), 4.22 (1H, dd, ^3J = 11.5, 3.2; CH), 4.16 (1H, m, 1/2-OCH_2), 3.92 (1H, m, 1/2-OCH_2), 3.30 (12H, br s, *cis*-NH_3), 3.09 (1H, d, ^2J = 26.3, 1/2-CH_2), 2.82 (1H, dd, ^2J = 26.0, ^3J = 6.1, 1/2-CH_2), 1.06 (9H, s, *t*-Bu CH_3's). ^{13}C NMR (125 MHz, CD_3CN, 22 °C): δ 170.5 (iminium), 78.9 (α-bound), 75.9 (CH), 61.4 (OCH_2), 43.9 (CH_2), 41.1 (β-bound), 35.9 (*t*-Bu C), 26.4 (*t*-Bu CH_3's).

[Os(NH_3)$_5$(4,5-η^2-1-(2-methoxymethyl-1-methylethyl)-3-methyl-3*H*-pyrrolium)](OTf)$_3$ (22). A dimethoxyethane solution (∼1 mL) of methyl triflate (86 mg, 0.52 mmol) was added to a dimethoxyethane solution (∼1 mL) of [Os(NH_3)$_5$(4,5-η^2-(1-(2-methoxymethyl-1-methylethyl)-1*H*-pyrrole))](OTf)$_2$ (**9**) (104 mg, 0.15 mmol) and DBU (67 mg, 0.44 mmol). After 1 h of stirring, the resulting red slurry was added to a stirring solution of 2:1 Et_2O/CH_2Cl_2 (75 mL), filtered through a 30 mL medium-porosity frit, and dried in vacuo to afford 106 mg (83%) of a pink solid with a diastereomeric ratio of 5:1 by ^1H NMR integrations (67% de). ^1H NMR (300 MHz, CD_3CN, 22 °C): δ 8.84 (1H, s, iminium), 6.42 (1H, d, ^3J = 4.5, α-bound), 4.57 (1H, d, ^3J = 4.5, β-bound), 4.45 (3H, br s, *trans*-NH_3), 4.41 (1H, m, CH), 3.74 (2H, m, OCH_2), 3.32 (3H, s, OCH_3), 3.26 (12H, br s, *cis*-NH_3), 3.03 (1H, q, ^3J = 6.5, CH), 1.60 (3H, d, ^3J = 6.5, CH_3), 1.45 (3H, d, ^3J = 7.2, CH_3). ^{13}C NMR (125 MHz, CD_3CN, 22 °C): δ 174.0 (iminium), 77.4, 74.2, 61.6, 59.3, 50.2, 49.5, 18.5, 14.6.

[Os(NH_3)$_5$(4,5-η^2-1-(1-methoxymethyl-2-methylpropyl)-3-methyl-3*H*-pyrrolium)](OTf)$_3$ (23). A dimethoxyethane solution (∼1 mL) of methyl triflate (44 mg, 0.27 mmol) was

added to a dimethoxyethane solution (~1 mL) of $[Os(NH_3)_5(4,5\text{-}\eta^2\text{-}(1\text{-}(1\text{-methoxymethyl-2-methylpropyl})\text{-}1H\text{-pyrrole}))](OTf)_2$ (**12**) (41 mg, 0.06 mmol) and DBU (8 mg, 0.05 mmol). After 1 h of stirring, the resulting red slurry was added to a stirring solution of 2:1 Et_2O/CH_2Cl_2 (75 mL), filtered through a 15 mL fine-porosity frit, and dried in vacuo to afford 45 mg (90%) of a pink solid with a diastereomeric ratio of 11:1 by ^1H NMR integrations (83% de). ^1H NMR (500 MHz, CD_3CN, 22 °C): δ 8.84 (1H, s, iminium), 6.40 (1H, d, $^3J = 4.5$, α-bound), 4.60 (1H, d, $^3J = 4.5$, β-bound), 4.49 (3H, br s, *trans*-NH_3), 4.19 (1H, ddd, $^3J = 11.5$, 8.0, 3.5, CH), 3.87 (1H, dd, $^2J = 10.9$, $^3J = 3.5$, 1/2-OCH_2), 3.79 (1H, dd, $^2J = 10.9$, $^3J = 11.2$, 1/2-OCH_2), 3.32 (3H, s, OCH_3), 3.28 (12H, br s, *cis*-NH_3), 3.12 (1H, q, $^3J = 7.7$, CH), 2.05 (1H, dqq, $^3J = 7.7$, 6.7, 6.7, *i*-Pr CH), 1.63 (3H, d, $^3J = 7.5$, CH_3), 1.04 (6H, d, $^3J = 6.5$, *i*-Pr CH_3's). ^{13}C NMR (125 MHz, CD_3CN, 22 °C): δ 173.8 (iminium), 123.0 and 120.4 (triflates), 76.0 (α-bound), 72.4 (OCH_2), 70.8 (CH), 59.3 (OCH_3), 49.7 (β-bound), 49.4 (CH), 33.4 (*i*-Pr CH), 19.3 and 18.8 (*i*-Pr CH_3's), 14.9 (CH_3).

$[Os(NH_3)_5(4,5\text{-}\eta^2\text{-}3\text{-methoxymethyl-1-(2-methoxy-1-methylethyl)-}3H\text{-pyrrolium})](OTf)_3$ (24). The same procedure employed for **25** afforded a purple solid (87%) with a diastereomeric ratio of 5:1 by ^1H NMR (67% de). ^1H NMR (500 MHz, CD_3CN, 22 °C): δ 8.92 (1H, s, iminium), 6.45 (1H, d, $^3J = 4.5$, α-bound), 4.63 (1H, d, $^3J = 4.8$, β-bound), 4.49 (3H, br s, *trans*-NH_3), 4.45 (1H, m, CH), 4.10 (1H, dd, $^2J = 9.6$, $^3J = 5.1$, 1/2-OCH_2), 3.87 (1H, dd, $^2J = 9.6$, $^3J = 5.4$, 1/2-OCH_2), 3.79 (1H, m, 1/2-OCH_2), 3.72 (1H, m, 1/2-OCH_2), 3.37 (3H, s, OCH_3), 3.32 (3H, s, OCH_3), 3.28 (12H, br s, *cis*-NH_3), 3.19 (1H, dd, $^3J = 5.1$ and 5.1, CH), 1.43 (3H, d, $^3J = 7.0$, CH_3). ^{13}C NMR (125 MHz, CD_3CN, 22 °C): δ 172.2 (iminium), 76.5, 75.2, 74.3, 60.2, 59.7, 59.2, 43.1, 37.6, 18.9 (CH_3).

$[Os(NH_3)_5(4,5\text{-}\eta^2\text{-}3\text{-methoxymethyl-1-(1-methoxymethyl-2-methylpropyl)-}3H\text{-pyrrolium})](OTf)_3$ (25). An acetonitrile solution (~1 mL) of TBSOTf (45 mg, 0.17 mmol) was added to an acetonitrile solution (~3 mL) of $[Os(NH_3)_5(4,5\text{-}\eta^2\text{-}(1\text{-}(1\text{-methoxymethyl-2-methylpropyl})\text{-}1H\text{-pyrrole}))](OTf)_2$ (**12**) (58 mg, 0.078 mmol), dimethoxymethane (113 mg, 1.48 mmol), and DBU (11 mg, 0.72 mmol). After 15 min of stirring the purple solution was added to 75 mL of 2:1 Et_2O/CH_2Cl_2, filtered through a 15 mL fine-porosity frit, washed with 15 mL of the same solvent combination, and dried in vacuo to afford a purple solid (67 mg, 96%) with a diastereomeric ratio of 12:1 by ^1H NMR (86% de). ^1H NMR (500 MHz, CD_3CN, 22 °C): δ 8.86 (1H, s, iminium), 6.42 (1H, d, $^3J = 4.2$, α-bound), 4.67 (1H, d, $^3J = 4.8$, β-bound), 4.50 (3H, br s, *trans*-NH_3), 4.21 (1H, dd, $^2J = 9.6$, $^3J = 4.2$, 1/2-OCH_2), 4.20 (1H, m, CH), 3.91 (1H, dd, $^2J = 9.6$, $^3J = 4.5$, 1/2-OCH_2), 3.83 (2H, m, OCH_2), 3.36 (3H, s, OCH_3), 3.32 (3H, s, OCH_3), 3.29 (12H, br s, *cis*-NH_3), 3.23 (1H, dd, $^3J = 4.5$ and 4.5, CH), 2.03 (1H, m, *i*-Pr CH), 1.06 and 1.05 (each 3H, d, $^3J = 6.8$, *i*-Pr CH_3's). ^{13}C NMR (125 MHz, CD_3CN, 22 °C): δ 172.1 (iminium), 123.0 and 120.5 (OTf), 76.7, 72.6, 71.4, 70.5, 59.4, 59.3, 56.3, 45.7, 33.4, 19.2, and 18.2 (*i*-Pr CH_3's).

$[Os(NH_3)_5(4,5\text{-}\eta^2\text{-}3\text{-(2-methoxycarbonylethyl)-1-(1-methoxymethyl-2-methylpropyl)-}3H\text{-pyrrolium})](OTf)_3$ (26). An acetonitrile solution (~1 mL) of TBSOTf (19 mg, 0.72 mmol) was added to an acetonitrile solution of $[Os(NH_3)_5(4,5\text{-}\eta^2\text{-}(1\text{-}(1\text{-methoxymethyl-2-methylpropyl})\text{-}1H\text{-pyrrole}))](OTf)_2$ (**12**) (58 mg, 0.078 mmol), methyl acrylate (23 mg, 0.27 mmol), and DBU (11 mg, 0.72 mmol). After 15 min of stirring, MeOH (102 mg, 3.18 mmol) was added and the reaction mixture stirred for an additional 5 min. The purple solution was then added to 75 mL of 2:1 Et_2O/CH_2Cl_2, filtered through a 15 mL fine-porosity frit, washed with 15 mL of the same solvent combination, and dried in vacuo to afford a purple solid (25 mg, 76%) with a diastereomeric ratio of 13:1 by ^1H NMR (86% de). ^1H NMR (500 MHz, CD_3CN, 22 °C): δ 8.84 (1H, s, iminium), 6.42 (1H, d, $^3J = 4.8$, α-bound), 4.64 (1H, d, $^3J = 4.8$, β-bound), 4.49 (3H, br s, *trans*-NH_3), 4.17 (1H, ddd, $^3J = 10.9$, 7.7, 3.5; CH), 3.87 (1H, m, 1/2-OCH_2), 3.78 (1H, m, 1/2-OCH_2), 3.69 (3H, s, OCH_3-ester), 3.32 (3H, s, OCH_3-ether), 3.28 (12H, br s, *cis*-NH_3), 3.03 (1H, dd, $^3J = 7.7$ and 7.4, CH), 2.68 (2H, dd, $^3J = 7.4$ and 7.0, CH_2), 2.27 (1H, m, 1/2-CH_2), 2.15 (1H, m, 1/2-CH_2), 2.05 (1H, m, *i*-Pr CH), 1.07 and 1.05 (each 3H, d, $^3J = 6.9$, *i*-Pr CH_3's). ^{13}C NMR (125 MHz, CD_3CN, 22 °C): δ 174.0, 172.5, 123.1, and 120.6 (OTf), 76.0, 72.5, 71.2, 59.3, 54.3, 52.5, 47.5, 33.6, 31.8, 25.7, 19.3, and 19.1 (*i*-Pr CH_3's).

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Supporting Information Available: NMR spectra of new compounds prepared. This material is available free of charge via the Internet at http://pubs.acs.org.

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