First attempts at differential diastereoselection in catalytic reactions of *N*-chirally substituted dirhodium(II) tetrakis[methyl 2-oxoimidazolidine-4(*S*)-carboxylates] with diazoacetates

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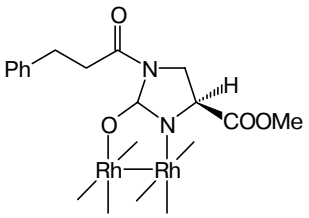
Chiral attachments on 2-oxoimidazolidine-4(*S*)-carboxylate ligands for dirhodium(II) can provide differential diastereoselection in catalytic reactions of diazo compounds. The synthesis of these heterocyclic ligands from the readily available amino acid asparagine is reported. Reactions with diazoacetates offering intramolecular carbon—hydrogen insertion provide evaluative data that demonstrate differential diastereoselection. Surprisingly, placement of a carbonyl group within the chiral attachment removes enantiocontrol from the catalyst, presumably because of intramolecular ylide formation.

Key words: chiral dirhodium(II) catalysts, catalysis, *N*-acylimidazolidinone-carboxylates, asymmetric carbon—hydrogen insertion, metal carbene reactions.

Chiral dirhodium(II) carboxamidates have proven to be remarkably effective catalysts for asymmetric metal carbene transformations.[1—4] High enantiocontrol has been demonstrated in intramolecular cyclopropanation and carbon—hydrogen insertion reactions. The catalyst that offers the greatest advantage for enantioselectivity and regioselectivity in carbon—hydrogen insertion reactions is dirhodium(II) tetrakis[methyl *N*-(3-phenylpropanoyl)-2-oxoimidazolidine-4(*S*)-carboxylate] (**1**).[5,6] Here the placement of the *N*-acyl group provides a fixed geometry for the carbonyl oxygen that is *anti* to the carbonyl oxygen at the ring 2-position. Accordingly, the methylene groups adjacent to and the one removed from the carbonyl are positioned conformationally in a predictable fashion so that, proceeding down the chain, the phenyl group sits over the volume of space that is expected to encompass the carbene transformations that take place at the axial coordination site of dirhodium. If E = COOMe, a particularly relevant depiction of the face of this catalyst is **2**, where A is the *N*-acyl attachment. Now, if instead of 3-phenylpropanoyl, a chiral attachment is used, two orientations of the attachment are possible — one depicting movement of the attachment in opposition to the ester functionality (**3a**) and the other in the same direction as the ester functionality (**3b**).

To determine the viability of this approach, we have synthesized selected chiral imidazolidinone ligands, constructed the corresponding catalysts, and tested these catalysts against selected metal carbene transformations.



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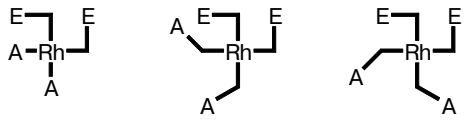

2 **3a** **3b**

Results and Discussion

Chiral imidazolidinone ligands were prepared from *N*-Z-protected L-asparagine **4** *via* the Hofmann reaction, esterification, acylation and then deprotection (Scheme 1; substituents R are decoded in Scheme 3).[6]

Improved procedures for the syntheses of **5** and **6** are given in Experimental. Three structurally different imidazolidinones **7a—c** were prepared by procedures that varied with the structure of R (see Scheme 1).

Methyl 1-[(*l* and *d*)-menthoxyacetyl]-2-oxoimidazolidine-4(*S*)-carboxylates (**7a,b**) were prepared from compound **6** and acyl chlorides **8a,b** by the standard acylation-deprotection procedure *via* the intermediate Z-protected derivatives **9a,b** (the sequence of transfor-

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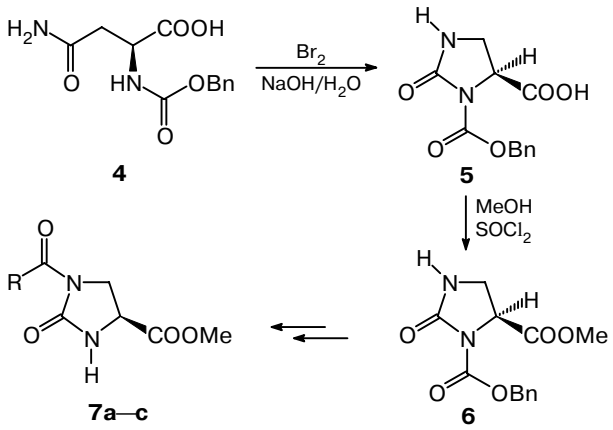
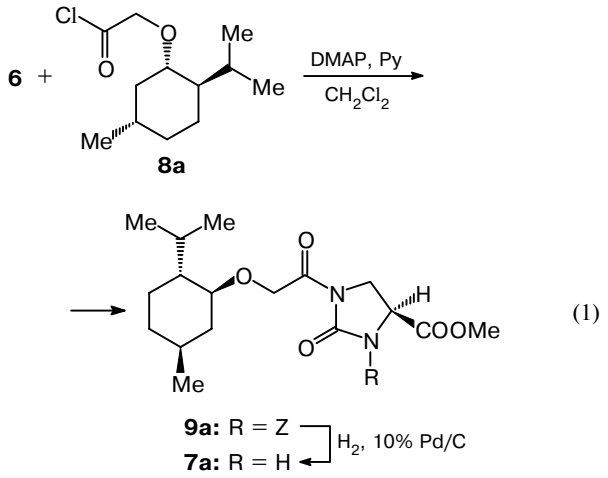
Scheme 1



mations is shown for the synthesis of ester **7a**, (reaction (1)).[6,7]

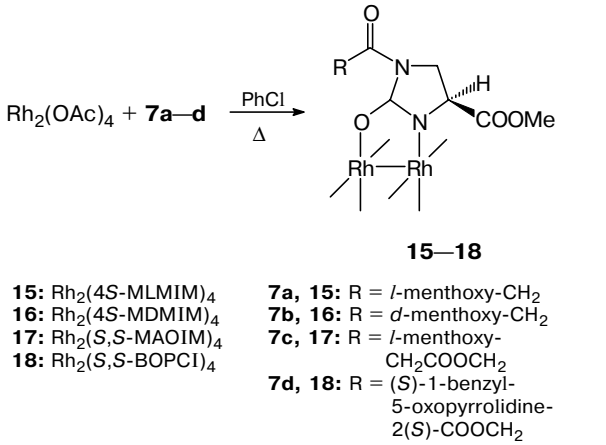


The analogous (Scheme 2) methyl 1-(*l*-menthoxyacetoxyacetyl]-2-oxoimidazolidine-4(*S*)-carboxylate (**7c**) utilized a bromoacetyl intermediate **10** and Z-protected derivative **13** to good effect.

A similar construction was used to prepare the prolinate derivative **7d** through Z-protected precursor **14**. Interestingly, despite our best efforts, **7a** could not be prepared from **10** by direct displacement with either menthol or its corresponding alkoxide.

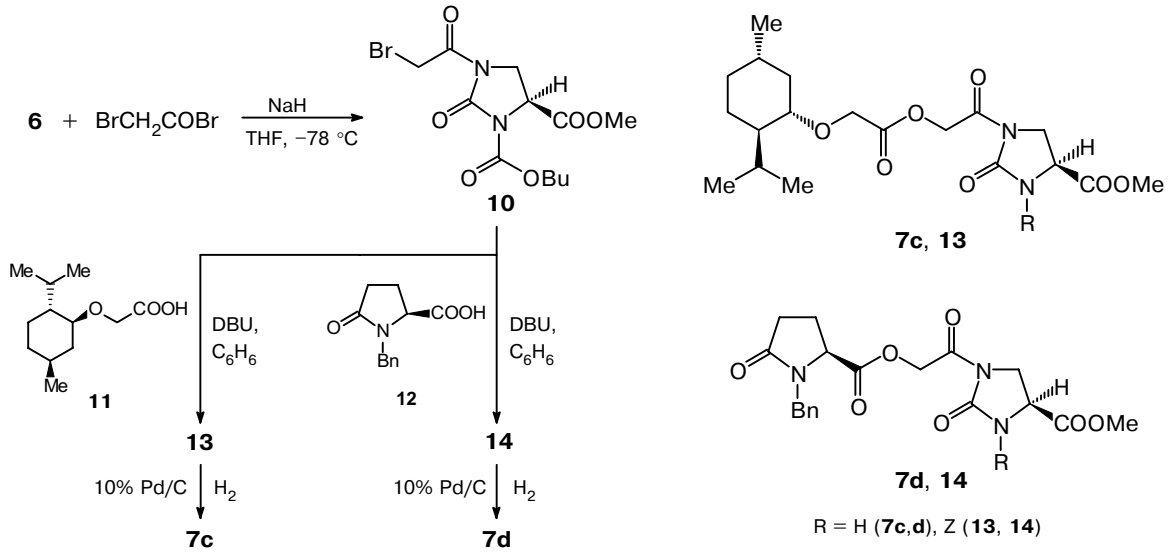
The dirhodium(II) derivatives **15—18** containing imidazolidinones **7a—d** as ligands were prepared from dirhodium(II) acetate by the standard acetate displacement reactions (Scheme 3), and each was characterized spectroscopically. Several transformations were used to test the viability of these catalysts.

Scheme 3

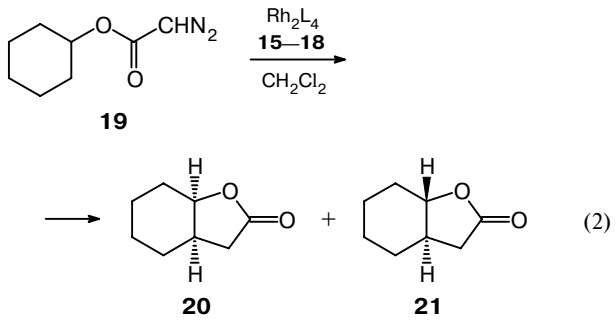


With cyclohexyl diazoacetate (**19**), which offers an estimate of diastereoselectivity as well as enantioselectivity

Scheme 2



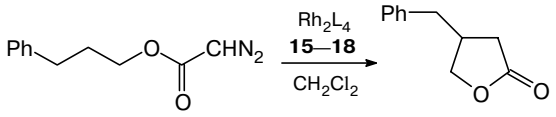
(reaction (2)),[8] remarkable differences were observed with catalysts **15**—**18**.



(2)

Here there is a demonstrable difference between **15** and **16** in their stereochemical influence on selectivity, with **16** showing a significant enhancement in enantiocontrol (Table 1). Unlike this, no substantial difference was observed for the stereochemical behavior of complexes **17** and **18**.

With 3-phenylpropyl diazoacetate,[10] carbon—hydrogen insertion gave one product (reaction (3)). Enantioselectivity in this case was enhanced with **15** (82% *ee*) but diminished with **16** (27% *ee*) and was virtually absent (10% *ee*) with **18**.



(3)

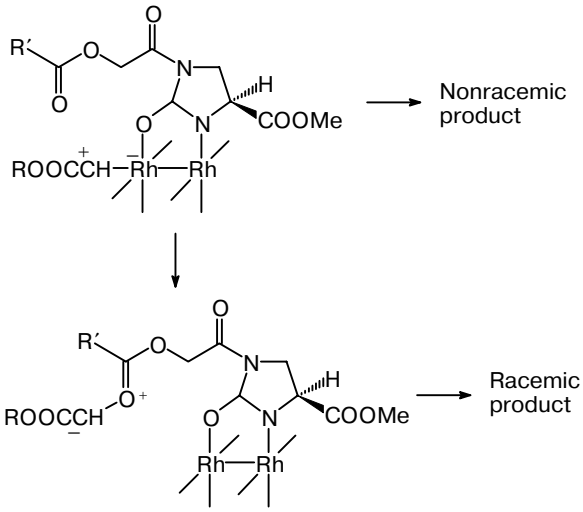
The outcome of these preliminary results demonstrates that remote chiral attachments on a carboxamidate ligand to dirhodium can and do have a significant influence on enantiocontrol. With diastereoisomers **15** and **16** virtually opposite influences are observed in the outcomes of reactions (2) and (3). In contrast, both **17** and **18** appear to have destroyed any significant enantiocontrol, and we believe this is due to carbonyl ylide formation (Scheme 4).[11,12]

Table 1. Diastereoselectivity and enantioselectivity in carbon—hydrogen insertion reactions from diazo decomposition of cyclohexyl diazoacetate **19** [a]

Catalyst	Yield (%)[b] **20** + **21**	Ratio **20** : **21**	*ee* (%)	
			20	**21**
$Rh_2(OAc)_4$	14	46 : 54	—	—
Rh_2(4*S*-MLMIM) (**15**)	64	81 : 19	53	16
Rh_2(4*S*-MDMIM)$_4$ (**16**)	33	91 : 9	>99	67
Rh_2(*S*,*S*-MAOIM)$_4$ (**17**)	53	76 : 24	0	—[c]
Rh_2(*S*,*S*-BOPCI)$_4$ (**18**)	80	54 : 46	6	10

[a] Reactions were performed as previously described (Refs. 8 and 9).
[b] Yield after chromatographic separation of the catalyst.
[c] Not determined.

Scheme 4



Efforts are underway to further develop diastereomer-directed enantiocontrol in catalytic metal carbene reactions and to determine structure/selectivity relationships.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini spectrometer (300 and 75 MHz, respectively). Mass spectra were obtained on a Finnigan spectrometer.

3-Benzyloxycarbonyl-2-oxoimidazolidine-4(*S*)-carboxylic acid (5). A 250 mL round bottom flask was charged with dry sodium hydroxide (9.32 g, 232.9 mmol) and 200 mL of distilled water and cooled to 0 °C. Over a period of 30 min, dry bromine (3.9 mL, 78.1 mmol) was added *via* addition funnel to yield a pale yellow solution. To this was added *N*-benzyloxycarbonyl-L-asparagine (20 g, 75.1 mmol) over 2 min. The resulting colorless solution was heated at 55 °C for 3 h. After cooling, the clear solution was washed with Et_2O (2×20 mL) and then acidified to pH 2 with 6 *M* HCl which precipitated a white solid. After cooling overnight, the solid was collected and dried under vacuum to yield 18.3 g of **5** (92% yield). ^{1}H NMR (DMSO-d_6), δ: 3.16—3.27 (m, 1 H); 3.59—3.72 (m, 1 H); 4.70 (dd, 1 H, J = 10.1 Hz, J = 2.8 Hz); 5.20 (s, 2 H); 7.32—7.41 (m, 5 H); 7.59 (s, 1 H).

Methyl 3-benzyloxycarbonyl-2-oxoimidazolidine-4(*S*)-carboxylate (6). To a rapidly stirred suspension of carboxylic acid **5** (4.40 g, 16.6 mmol) in MeOH (50 mL) was added dropwise $SOCl_2$ (0.98 g, 8.3 mmol) at ~20 °C, and the mixture was stirred for ~15 h. The solvent was removed under reduced pressure and the residual white powder was dissolved in boiling AcOEt (130 mL). After cooling to ~20 °C, the solution was washed with 5% aqueous $NaHCO_3$ (35 mL) and concentrated under reduced pressure to yield **6** (4.59 g) as a white solid with m.p. 140 °C, $[\alpha]_D^{25}$ −68.1 (*c* 0.36, CH_2Cl_2). ^{1}H NMR ($CDCl_3$), δ: 3.35—3.46 (m, 1 H); 3.66 (s, 3 H); 3.65—3.80 (m, 2 H); 4.75 (dd, 1 H, J = 10.1 Hz, J = 3.5 Hz); 5.26 (dd, 2 H, J = 12.2 Hz, J = 3.5 Hz); 6.69 (s, 1 H); 7.25—7.40 (m, 5 H).

Methyl 3-benzyloxycarbonyl-1-(*l*-menthoxyacetyl)-2-oxoimidazolidine-4(*S*)-carboxylate (9a). To a stirred solution

of methyl carboxylate **6** (4.00 g, 14.4 mmol), DMAP (0.264 mg, 2.17 mmol), and anhydrous Py (1.69 g, 21.6 mmol) in anhydrous CH_2Cl_2 (35 mL) at 0 °C under nitrogen was added dropwise *l*-menthoxyacetyl chloride (**8a**) (6.72 g, 28.9 mmol). The reaction mixture was then heated at reflux for 24 h. The reaction mixture was then cooled and washed with saturated aqueous NaCl (2×40 mL), 1% aqueous HCl (3×40 mL), saturated aqueous Na_2CO_3 (3×40 mL) and H_2O (2×40 mL). The organic layer was dried (anhydrous $MgSO_4$), filtered, and concentrated under reduced pressure to give a pale yellow solid that was purified by silica gel column chromatography (eluent AcOEt—hexanes, 1 : 2) to give 4.17 g (61%) of the desired product **9a** as a white crystalline solid, which was dried under vacuum with m.p. 139—140 °C, $[\alpha]_D^{26.5}$ −71.0 (*c* 0.60, CH_2Cl_2). ^{1}H ($CDCl_3$), δ: 0.79 (d, 3 H, *J* = 6.8 Hz); 0.87—1.04 (m, 9 H); 1.32 (m, 2 H); 1.63 (m, 2 H); 2.08 (m, 1 H); 2.29 (m, 1 H); 3.19 (dt, 1 H, *J* = 10.5 Hz, *J* = 3.9 Hz); 3.72 (s, 3 H); 3.86—4.02 (m, 2 H); 4.64, 4.78 (AB, 2 H, *J* = 18.3 Hz); 4.74 (dd, 1 H, *J* = 9.9 Hz, *J* = 3.8 Hz); 5.26, 5.36 (AB, 2 H, *J* = 12.2 Hz); 7.35—7.38 (m, 5 H). ^{13}C NMR ($CDCl_3$), δ: 16.1, 20.9, 22.1, 23.1, 25.4, 31.4, 34.3, 39.7, 41.6, 47.8, 52.8, 53.1, 68.9, 80.0, 128.2, 128.5, 128.6, 134.4, 149.1, 150.6, 169.3, 170.9. MS (FAB^+, in mixture matrix), *m/z* (I_{rel} (%)): 475 $[M + H]^+$ (15), 949 $[2 M + H]^+$ (1).

Methyl 1-(*l*-menthoxyacetyl)-2-oxoimidazolidine-4(*S*)-carboxylate (4*S*-MLMIMH) (7a). A solution of methyl carboxylate **9a** (4.17 g, 8.79 mmol) in AcOEt (250 mL) containing 10% Pd/C (0.250 g) was shaken in a Parr hydrogenator under H_2 (35 Torr) until hydrogen uptake ceased (about 6 h) and TLC indicated 100% conversion. The Pd/C catalyst was removed by filtration through a Celite plug, and the filtrate was concentrated to give a yellow powder that was purified by column chromatography on silica gel (eluent AcOEt—hexanes, 1 : 1, R_f 0.14) to yield 2.81 g (94%) of a white powder with 105—106 °C, $[\alpha]_D^{22.0}$ −44.0 (*c* 0.60, CH_2Cl_2). Found (%): C, 60.28; H, 8.25; N, 7.74. Calculated (%): C, 59.98; H, 8.29; N, 8.23. ^{1}H NMR ($CDCl_3$), δ: 0.79 (d, 3 H, *J* = 6.8 Hz); 0.91 (m, 9 H); 1.31 (m, 2 H); 1.62 (m, 2 H); 2.10 (m, 1 H); 2.31 (m, 1 H); 3.19 (dt, 1 H, *J* = 10.5 Hz, *J* = 4.1 Hz); 3.82 (s, 3 H); 4.12, 4.18 (AB, 2 H, *J* = 12.0 Hz); 4.33 (m, 1 H); 4.61, 4.73 (AB, 2 H, *J* = 17.8 Hz); 5.40 (s, 1 H). ^{13}C NMR ($CDCl_3$), δ: 16.2, 20.9, 22.2, 23.2, 25.3, 31.4, 34.3, 39.8, 44.5, 47.9, 50.3, 53.0, 68.0, 79.9, 155.3, 170.6, 170.7. MS (FAB^+, in mixture matrix), *m/z* ($I_{отн}$ (%)): 341 $[M + H]^+$ (41), 681 $[2 M + H]^+$ (4).

Dirhodium(II) tetrakis[methyl 1-(*l*-menthoxyacetyl)-2-oxoimidazolidine-4(*S*)-carboxylate], Rh_2(4*S*-MLMIM)$_4$ (15). Rhodium(II) acetate (0.265 g, 0.60 mmol), methyl carboxylate **7a** (2.03 g, 5.96 mmol), and 20 mL of anhydrous PhCl were mixed in a round bottom flask fitted with a Soxhlet extraction apparatus into which was placed a thimble containing an oven-dried mixture of two parts Na_2CO_3 and one part sand. The resulting blue-green solution was heated at reflux under nitrogen for about 22 h. The progress of ligand displacement was followed by HPLC (μ-Bondapak-CN column, MeOH—MeCN, 92 : 2, flow rate 1.5 mL min^{-1}). The initial $Rh_2(OAc)_4$ band disappeared and was replaced by several bands with longer retention times (t_r). After 22 h one principal band (t_r = 6.3 min), in addition to that for the ligand (t_r = 2.0 min), was observed. The resulting blue solution was cooled to ~20 °C, and the solvent was evaporated under reduced pressure. The residue was dissolved in a minimal volume of MeOH and gray decomposition products were removed by filtration. The filtrate was chromatographed on a column with Bakerbond Cyano 40 μm prep LC packing eluting with MeOH. The first slightly brown band containing excess of ligand (0.990 g) was removed. The following two purple bands were collected and concentrated under reduced pressure. The first purple band contained the title compound (1.12 g), which was recrystallized from MeOH—MeCN. A second recrystallization yielded pure purple crystals. The yield of recrystallized purple crystals of **15** 0.645 g (65%), $[\alpha]_D^{21.7}$ −287.9 (*c* 0.51, MeCN). ^{1}H NMR, δ: 0.83 (m, 12 H); 0.93 (m, 36 H); 1.32 (m, 8 H); 1.65 (m, 8 H); 2.17 (m, 4 H); 2.32 (m, 4 H); 2.38 (s, 6 H); 3.24 (m, 4 H); 3.62 (s, 6 H); 3.78 (s, 6 H); 3.88—4.12 (br.s, 12 H); 4.55 (br.s, 8 H). ^{13}C NMR ($CDCl_3$), δ: 2.22, 16.1, 21.0, 22.2, 22.3, 23.1, 25.3, 31.4, 31.5, 34.3, 40.1, 46.2, 46.5, 48.3, 48.5, 51.8, 52.4, 59.5, 59.9, 67.4, 67.5, 79.4, 79.5, 115.3, 164.6, 168.6, 168.8, 172.4, 172.9. The second purple band contained an unidentified side product (0.121 g) presumed to be the [3,1]-isomer.[6]

***d*-Menthoxyacetyl chloride (8b).** In a 100-mL round-bottomed flask was placed $SOCl_2$ (60.8 g, 511 mmol), and to it was added, during the course of 30 min *d*-menthoxyacetic acid (10.0 g, 46.7 mmol) by using a dropping funnel. When all the acid had been added, the dropping funnel was washed with 15 mL of $ClCH_2CH_2Cl$, and the combined reaction mixture was heated at gentle reflux for 5 h during which time it turned slightly yellow. After the reaction was complete, the excess of thionyl chloride was removed by distillation. The ^{1}H NMR spectrum revealed that the solution contained 93% *d*-menthoxyacetyl chloride **8b** and 7% *d*-menthoxyacetic acid. ^{1}H NMR ($CDCl_3$), δ: 0.79 (d, 3 H, *J* = 6.8 Hz); 0.95 (m, 9 H); 1.32 (m, 2 H); 1.65 (m, 2 H); 2.04 (m, 1 H); 2.26 (m, 1 H); 3.23 (dt, 1 H, *J* = 10.5 Hz, *J* = 4.4 Hz); 4.44, 4.48 (AB, 2 H, *J* = 18.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 16.1, 21.0, 22.2, 23.1, 25.3, 31.4, 34.2, 39.8, 48.1, 73.9, 80.8, 172.2.

Methyl 3-benzyloxycarbonyl-1-(*d*-menthoxyacetyl)-2-oxoimidazolidine-4(*S*)-carboxylate (9b). To a stirred solution of methyl carboxylate **6** (5.00 g, 18.0 mmol), DMAP (0.329 g, 2.71 mmol), and anhydrous Py (2.10 g, 26.9 mmol) in anhydrous CH_2Cl_2 (40 mL) at 0 °C under nitrogen was added dropwise chloride **8b** (10.1 g, 43.4 mmol) dissolved in CH_2Cl_2. The reaction mixture was then heated at reflux for 24 h. The reaction mixture was then cooled and washed with saturated aqueous NaCl (2×50 mL), 1% aqueous HCl (3×50 mL), saturated aqueous Na_2CO_3 (3×50 mL), and H_2O (2×50 mL). The organic layer was dried (anhydrous $MgSO_4$), filtered, and concentrated under reduced pressure to give a brown oil that was purified by silica gel column chromatography (eluent AcOEt—hexanes, 1 : 2) to give 5.52 g (65%) of the desired product **9b** as a white crystalline solid which was dried under vacuum, m.p. 49—50 °C, $[\alpha]_D^{23.5}$ +26.7 (*c* 0.55, CH_2Cl_2). ^{1}H NMR ($CDCl_3$), δ: 0.79 (d, 3 H, *J* = 6.8 Hz); 0.86—0.99 (m, 9 H); 1.36 (m, 2 H); 1.63 (m, 2 H); 2.07 (m, 1 H); 2.29 (m, 1 H); 3.20 (dt, 1 H, *J* = 10.6 Hz, *J* = 4.1 Hz); 3.73 (s, 3 H); 3.87—4.09 (m, 2 H); 4.64, 4.78 (AB, 2 H, *J* = 18.3 Hz); 4.75 (dd, 1 H, *J* = 10.2 Hz, *J* = 3.8 Hz); 5.26, 5.36 (AB, 2 H, *J* = 12.2 Hz); 7.34—7.41 (m, 5 H). ^{13}C NMR ($CDCl_3$), δ: 16.2, 20.9, 22.2, 23.2, 25.5, 31.5, 34.3, 39.9, 41.7, 47.9, 53.0, 53.2, 68.6, 69.1, 80.2, 128.3, 128.6, 128.7, 134.5, 149.2, 150.7, 169.3, 170.1. MS (FAB^+, in mixture matrix), *m/z* (I_{rel} (%)): 475 $[M + H]^+$ (12); 949 $[2 M + H]^+$ (1).

Methyl 1-(*d*-menthoxyacetyl)-2-oxoimidazolidine-4(*S*)-carboxylate (4*S*-MDMIMH) (7b). A solution of ester **9b** (5.52 g, 11.6 mmol) containing 10% Pd/C (0.330 g) in AcOEt (300 mL) was shaken in a Parr hydrogenator under H_2 until hydrogen uptake ceased (about 6 h) and TLC indicated 100% conversion. The Pd/C catalyst was removed by filtration through a Celite plug, and the filtrate was concentrated to give a yellow powder that was purified by column chromatography on silica

gel (eluent AcOEt—hexanes, 1 : 1, R_f 0.24) to yield 0.377 g (95%) of product **7b** as a white powder with m.p. 76—77 °C, $[\alpha]_D^{23.5}$ +92.3 (*c* 0.64, CH_2Cl_2). ^{1}H NMR ($CDCl_3$), δ: 0.79 (d, 3 H, *J* = 6.8 Hz); 0.93 (m, 9 H); 1.29 (m, 2 H); 1.64 (m, 2 H); 2.08 (m, 1 H); 2.29 (m, 1 H); 3.20 (dt, 1 H, *J* = 10.5 Hz, *J* = 3.9 Hz); 3.81 (s, 3 H); 4.08, 4.14 (AB, 2 H, *J* = 11.7 Hz); 4.39 (m, 1 H); 4.61, 4.73 (AB, 2 H, *J* = 17.8 Hz); 6.86 (s, 1 H). ^{13}C NMR ($CDCl_3$), δ: 15.9, 20.6, 21.9, 22.9, 25.1, 31.1, 34.0, 39.6, 44.2, 47.6, 50.1, 52.6, 67.8, 79.7, 155.2, 170.0, 170.4. MS (FAB$^+$, in mixture matrix), *m/z* (I_{rel} (%)): 341 [M + H]$^+$ (25); 681 [2 M + H]$^+$ (2).

Dirhodium(II) tetrakis[methyl 1-(*d*-menthoxyacetyl)-2-oxoimidazolidine-4(*S*)-carboxylate], Rh_2(4*S*-MDMIM)$_4$ (16). Rhodium(II) acetate (0.301 g, 0.68 mmol), methyl carboxylate **7d** (1.64 g, 4.83 mmol), and 20 mL of anhydrous PhCl were mixed in a round bottom flask fitted with a Soxhlet extraction apparatus into which was placed a thimble containing an oven dried mixture of two parts Na_2CO_3 and one part sand. The resulting blue-green solution was heated at reflux under nitrogen for about 48 h. The progress of ligand displacement was followed by HPLC (μ-Bondapak-CN column, eluent MeOH—MeCN, 99 : 1, flow 1.5 mL min^{-1}). The initial $Rh_2(OAc)_4$ band disappeared and was replaced by several bands with longer retention times. After 48 h one principal band (t_r = 5.9 min), in addition to that for the ligand (t_r = 1.6 min) was observed. The resulting blue solution was cooled to ~20 °C, and the solvent was evaporated under reduced pressure. The residue was dissolved in minimal volume of MeOH and gray decomposition products were removed by filtration. The filtrate was chromatographed on a column with Bakerbond Cyano 40 μm prep LC packing eluting with MeOH. The first slightly brown band containing excess of ligand was removed. The following purple band was collected and concentrated under reduced pressure. The residue (0.97 g) contained the title compound and a considerable amount of ligand. A second purification on a column with Bakerbond Cyano 40 μm prep LC packing eluting with MeOH gave 0.68 g (60%) of the desired complex **16**. ^{1}H NMR ($CDCl_3$), δ: 0.80 (d, 12 H, *J* = 6.6 Hz); 0.92 (m, 36 H); 1.32 (m, 8 H); 1.65 (m, 8 H); 2.14 (m, 4 H); 2.29 (m, 4 H); 3.19 (m, 4 H); 3.61 (s, 6 H); 3.78 (s, 6 H); 3.91—4.15 (m, 12 H); 4.53 (m, 8 H). ^{13}C NMR ($CDCl_3$), δ: 16.3, 21.1, 22.4, 23.1, 25.4, 31.6, 34.4, 40.3, 46.3, 46.6, 48.4, 52.0, 59.5, 60.2, 67.9, 79.9, 164.8, 168.6, 172.4, 172.9.

Methyl 3-benzyloxycarbonyl-1-bromoacetyl-2-oxoimidazolidine-4(*S*)-carboxylate (10). To a mixture of methyl carboxylate **6** (4.95 g, 17.8 mmol) and anhydrous THF (75 mL) under inert atmosphere was added NaH (0.427 g, 17.8 mmol). After effervescence ceased, the solution was cooled to −78 °C and bromoacetyl bromide (7.19 g, 35.6 mmol) was added. After stirring for 30 min at −78 °C, the reaction was allowed to warm to ~20 °C during ~15 h. Solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2 (200 mL). The pale white solution was washed with H_2O (100 mL), brine (100 mL) and concentrated under reduced pressure. Purification by silica gel column chromatography (eluent AcOEt—hexanes, 1 : 1, R_f 0.25) gave the title compound **10** (6.24 g) as a white solid in 87% yield with m.p. 110—112 °C, $[\alpha]_D^{19}$ −20.9 (*c* 1.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ: 3.80 (s, 3 H); 3.89 (dd, 1 H, *J* = 11.1 Hz, *J* = 3.3 Hz); 4.09 (dd, 1 H, *J* = 11.1 Hz, *J* = 10.2 Hz); 4.57 (dd, 2 H, *J* = 4.8 Hz, *J* = 12.9 Hz); 7.41 (m, 5 H); 4.78 (dd, 1 H, *J* = 10.5 Hz, *J* = 3.6 Hz); 5.31 (s, 2 H). ^{13}C NMR ($CDCl_3$), δ: 28.3 (t), 43.3 (t), 51.3 (q), 53.2 (d), 68.7 (t), 128.3 (d), 128.6 (d), 128.7 (d), 134.4 (s), 149.9 (s), 150.0 (s), 166.1 (s), 168.6 (s).

Methyl 3-benzyloxycarbonyl-1-(*l*-menthoxyacetoxyacetyl)-2-oxoimidazolidine-4(*S*)-carboxylate (13). A clear solution of (+)-menthoxyacetic acid (**11**) (0.27 g, 1.25 mmol) and DBU (0.2 mL, 1.4 mmol) was prepared in benzene. After addition of bromide **10** (0.5 g, 1.25 mmol), the mixture was heated at reflux for 1 h. Upon cooling, DBU salts precipitated and the benzene solution was decanted. The solvent was removed under reduced pressure yielding the title compound **13** as a white solid (100% yield). ^{1}H NMR ($CDCl_3$), δ: 0.70—0.95 (m, 13 H); 1.20—1.34 (m, 1 H); 1.54—1.64 (m, 2 H); 2.04 (d, 1 H); 2.24 (dq, 1 H); 3.16 (dt, 1 H); 3.70 (s, 3 H); 3.8—4.0 (dd, 2 H); 4.19 (d, 2 H); 4.68 (dd, 1 H); 5.22 (s, 2 H); 5.12—5.39 (dd, 2 H); 7.23—7.39 (m, 5 H). ^{13}C NMR ($CDCl_3$), δ: 20.8, 22.1, 23.0, 25.2, 31.3, 34.2, 39.6, 44.0, 47.8, 47.9, 50.6, 53.1, 63.2, 65.2, 68.8, 80.0, 128.0, 128.1, 128.2, 128.4, 128.5, 128.6, 134.4, 149.2, 150.4, 167.1, 168.6, 170.1.

Methyl 1-(*l*-menthoxyacetoxyacetyl)-2-oxoimidazolidine-4(*S*)-carboxylate (7c). A solution of methyl carboxylate **13** (1.25 g, 2.4 mmol) in AcOEt containing a small scoop of 10% Pd/C was shaken in a Parr hydrogenator under H_2 (2.38 atm) until TLC indicated 100% conversion. The Pd/C catalyst was removed by filtration through a Celite plug, washed with CH_2Cl_2, and the filtrate was concentrated under reduced pressure and purified by silica gel column chromatography (eluent AcOEt—hexanes, 3 : 1) yielding the ligand **7c** (0.56 g, 60%). ^{1}H NMR ($CDCl_3$), δ: 0.79—1.02 (m, 13 H); 1.20—1.38 (m, 2 H); 1.60—1.70 (m, 2 H); 2.11 (d, 1 H); 2.32 (dq, 1 H); 3.21 (dt, 1 H); 3.53 (dd, 1 H); 3.80 (s, 3 H); 3.80—3.91 (m, 1 H); 4.24 (d, 2 H); 4.85 (dd, 1 H); 5.18—5.47 (dd, 2 H); 6.08 (s, 1 H). ^{13}C ($CDCl_3$), δ: 16.2, 20.9, 22.2, 23.2, 25.3, 31.4, 34.3, 39.8, 41.3, 48.1, 53.1, 54.3, 63.1, 65.4, 80.1, 155.5, 166.9, 169.4, 170.4.

Dirhodium(II) tetrakis[methyl 1-*l*-(menthoxyacetoxyacetyl)-2-oxoimidazolidine-4(*S*)-carboxylate], Rh_2(*S,S*-MAOIM)$_4$ (17). The title compound was prepared by a standard procedure using $Rh_2(OAc)_4$ (0.105 g, 0.24 mmol) and ligand **7c** (0.538 g, 1.44 mmol) in PhCl. After purification on a column with Bakerbond Cyano 40 μm prep LC packing eluting with MeOH, complex **17** (95 mg, 22%) was isolated as a purple solid. ^{13}C ($CDCl_3$), δ: 16.1, 20.9, 22.2, 23.1, 25.4, 31.4, 34.3, 39.8, 48.0, 60.3, 65.5, 75.1, 75.7, 80.5, 80.8, 106.0, 108.5, 109.3, 170.4. MS (FAB$^+$), *m/z*: 1796 [M + H]$^+$.

Methyl 3-benzyloxycarbonyl-1-[(1-benzyl-5-oxopyrrolidine-2(*S*)-carbonyloxy)acetyl]-2-oxoimidazolidine-4(*S*)-carboxylate (14). A clear solution of 1-benzyl-5-oxopyrrolidine-2(*S*)-carboxylic acid (**12**) (2.29 g, 10.4 mmol) and DBU (1.58 g, 10.4 mmol) was prepared in benzene. After addition of **10** (3.50 g, 8.7 mmol), the mixture was stirred at reflux for 1 h. Upon cooling, DBU salts precipitated and the benzene solution was decanted. The solvent was removed under reduced pressure and the product purified by silica gel column chromatography (eluent AcOEt—hexanes, 1 : 1, R_f 0.20) to give the title compound **14** (2.42 g, 51%) as a white solid, $[\alpha]_D^{19}$ −36 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ: 2.27 (m, 2 H); 2.54 (m, 2 H); 3.80 (s, 3 H); 4.09 (m, 4 H); 4.77 (dd, 1 H, *J* = 10.2 Hz, *J* = 3.3 Hz); 5.12 (d, 1 H, *J* = 15 Hz); 5.15 (d, 1 H, *J* = 17.1 Hz); 5.31 (s, 2 H); 5.40 (d, 1 H, *J* = 17.4 Hz); 7.38 (m, 10 H). ^{13}C NMR ($CDCl_3$), δ: 22.7 (t), 29.5 (t), 44.1 (t), 45.3 (t), 50.6 (q), 53.3 (d), 58.3 (d), 63.7 (t), 69.1 (t), 127.7 (d), 128.3 (d), 128.5 (d), 128.6 (d), 128.8 (d), 134.3 (s), 135.6 (s), 149.2 (s), 150.4 (s), 166.8 (s), 168.5 (s), 171.2 (s), 175.3 (s). MS (FAB$^+$), *m/z*: 538 [M + H]$^+$.

Methyl 1-[(1-benzyl-5-oxopyrrolidine-2(*S*)-carbonyloxy)acetyl]-2-oxoimidazolidine-4(*S*)-carboxylate (7d). A solution of methyl carboxylate **14** (1.47 g, 2.7 mmol) in AcOEt

(75 mL) containing 10% Pd/C (39 mg) was shaken in a Parr hydrogenator under H_2 (2.38 atm) until TLC indicated 100% conversion. The Pd/C catalyst was removed by filtration through a Celite plug, washed with CH_2Cl_2, and the filtrate was concentrated under reduced pressure to give the product **7d** (1.08 g) as a white solid. Purification by silica gel column chromatography (AcOEt, R_f 0.38) yielded the ligand **7d** (0.85 g, 79%), $[\alpha]_D^{20}$ −58 (*c* 1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ: 2.41 (m, 4 H); 3.55 (dd, 1 H, *J* = 9.9 Hz); 3.80 (s, 3 H); 4.09 (m, 3 H); 4.85 (dd, 1 H, *J* = 10.2 Hz, *J* = 3.3 Hz); 5.14 (d, 1 H, *J* = 16.5 Hz); 5.43 (d, 1 H, *J* = 17.1 Hz); 5.90 (br.s, 1 H); 7.33 (m, 5 H). ^{13}C NMR ($CDCl_3$), δ: 22.7 (t), 29.5 (t), 41.3 (t), 45.3 (t), 53.1 (q), 54.2 (d), 58.3 (d), 63.5 (t), 127.7 (d), 128.5 (d), 128.6 (d), 128.7 (d), 135.7 (s), 155.3 (s), 166.5 (s), 169.3 (s), 171.4 (s), 175.3 (s). MS (FAB^+), *m/z*: 404 $[M + H]^+$.

Dirhodium(II) tetrakis{methyl 1-[(1-benzyl-5-oxopyrrolidine-2(*S*)-carbonyloxy)acetyl]-2-oxoimidazolidine-4(*S*)-carboxylate]}, Rh_2(*S*,*S*-BOPCI)$_4$ (18). The title compound was prepared by a standard procedure using $Rh_2(OAc)_4$ (0.183 g, 0.41 mmol) and ligand **7d** (1.34 g, 3.32 mmol) in 10 mL of anhydrous PhCl. After purification on a column with Bakerbond Cyano 40 μm prep LC packing eluting with MeOH, complex **18** (0.409 g, 55%) was isolated as a purple solid, $[\alpha]_D^{23}$ −88 (*c* 0.78, MeCN). ^{1}H NMR ($CDCl_3$), δ: 2.26 (br.m, 17 H); 2.88 (m, 4 H); 3.73 (br.s, 14 H); 4.00 (m, 6 H); 4.30 (m, 3 H); 4.72 (br.s, 4 H); 5.14 (br.dd, 10 H); 7.30 (m, 20 H). ^{13}C NMR ($CDCl_3$), δ: 22.8, 29.5, 49.4, 52.6, 55.7, 58.5, 128.3, 128.7, 152.1. MS (FAB^+), *m/z*: 1816 $[M + H]^+$, 1837 $[M + Na]^+$. Found (HRMS): *m/z* 1814.4804. $C_{16}H_{80}N_{12}O_{28}Rh_2$. Calculated: 1814.33.

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