Enantiomer differentiation in intramolecular carbon—hydrogen insertion reactions of racemic secondary alkyl diazoacetates catalyzed by chiral dirhodium(II) carboxamidates*

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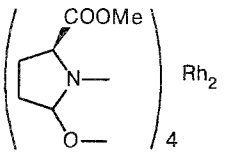
Highly efficient kinetic resolution of racemic secondary alkyl diazoacetates in intramolecular carbon-hydrogen insertion reactions has been achieved using chiral dirhodium(II) carboxamidates. Products formed from catalytic diazo decomposition of racemic 2-octyl diazoacetate and, separately, its (2*R*)- and (2*S*)-enantiomeric forms, as well as both *cis*- and *trans*-2-methylcyclohexyl diazoacetates, have been systematically evaluated. Enantioselectivities up to 99 % *ee* have been obtained for γ-lactone formation. β-Lactone production has been observed and, although minor with cyclohexyl diazoacetates, is the major insertion pathway for diazo decomposition of 2-octyl diazoacetate.

Key words: kinetic resolution, chiral dirhodium(II) carboxamidates, enantioselective carbon—hydrogen insertion, γ-lactone formation, diastereoselective carbon—hydrogen insertion.

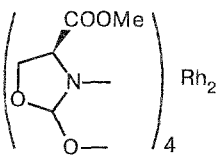
Exceptional enantiocontrol has been achieved in intramolecular CH insertion reactions of secondary alkyl diazoacetates catalyzed by chiral dirhodium(II) carboxamidates.[1] Enantiomeric excesses ≥94 % are generally associated with these transformations, and they are similarly characterized by a high level of diastereocontrol (up to 99 : 1).[2—4] Appropriate dirhodium(II) catalysts are those constructed from pyrrolidinone (**1**),[5] oxazolidinone (**2**),[6] or, for enhanced diastereoselection, 1-*N*-acylimidazolidinone (**3**)[2] ligands, all of which possess a methyl carboxylate group at the chiral center adjacent to the amide nitrogen.

Applications of enantioselective CH insertion transformations have thus far been limited to symmetric systems that undergo selective reactions at one of two prochiral C—H bonds.[1—8] Extensions of this methodology to racemic secondary alkyl diazoacetates where, optimally, the two reactant enantiomers form different enantiomerically enriched CH insertion products (kinetic resolution), have not been previously reported. We now describe results with representative racemic secondary alkyl diazoacetates that approach the ideal in kinetic resolution.



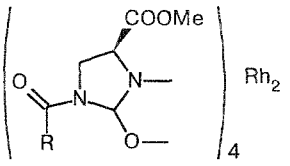
1

$Rh_2(5S\text{-MEPY})_4$



2

$Rh_2(4S\text{-MEOX})_4$



3

$Rh_2(4S\text{-MACIM})_4$

R = Me

Results and Discussion

rac-2-Octyl diazoacetate undergoes facile diazo decomposition in the presence of catalytic amounts of chiral dirhodium(II) carboxamidates. From reactions performed in refluxing dichloromethane four carbon—hydrogen insertion products have been isolated and identified (Scheme 1), including β-lactone **5** which is the major reaction product. As can be seen from results reported in Table 1, product yields and enantioselectivities are catalyst dependent. Although low for β-lactone formation with all dirhodium(II) catalysts, enantioselectivities are as high as 98 % *ee* for the production of γ-lactone **8**, which is formed by insertion into a primary C—H bond. β-Lactone products have been previously observed[9] but not generally as the major product.

* Dedicated to Academician of the RAS N. S. Zefirov (on his 60th birthday).

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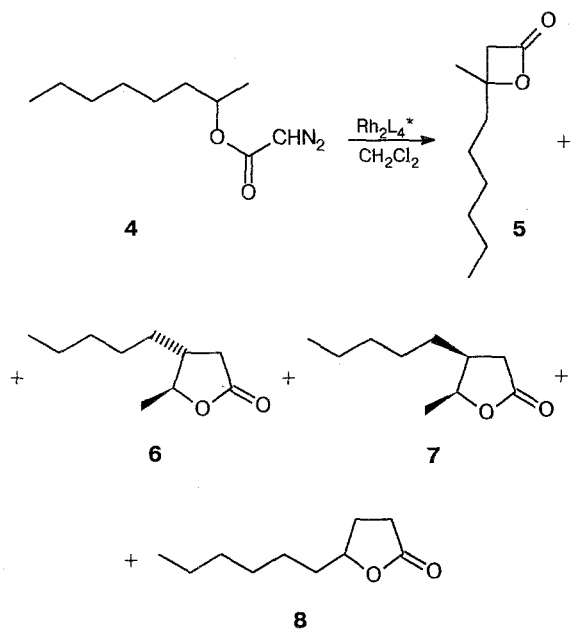
Scheme 1



Diastereoselectivity in these CH insertion reactions was separately determined by performing a similar set of catalytic reactions with optically pure (*R*)- and (*S*)-2-octyl diazoacetate, and these results are also reported in Table 1. Use of (*R*)- and (*S*)-catalyst with (*R*)-**4** or one catalyst configuration with both (*R*)-**4** and (*S*)-**4** shows obvious match/mismatch for the formation of individual products, and this is a primary requirement for kinetic resolution. For example, the formation of **7** from (*R*)-**4** with $Rh_2(5S\text{-MEPY})_4$ occurs in 6 % relative yield, whereas **7** is produced from (*R*)-**4** using $Rh_2(5R\text{-MEPY})_4$ in 42 % relative yield; these results predict a 76 % *ee* in the formation of **7** from *rac*-**4** with either $Rh_2(5S\text{-MEPY})_4$ or $Rh_2(5R\text{-MEPY})_4$. Similarly, use of $Rh_2(5R\text{-MEPY})_4$ for diazo decomposition of (*R*)-**4** and (*S*)-**4** provides **7** in 42 % and 7 % relative yield, respectively; the predicted enantioselectivity for the production of **7** from *rac*-**4** from these results is 72 % *ee*. The observed 74 % and 77 % *ee* for **7** from *rac*-**4** with $Rh_2(5S\text{-MEPY})_4$ and $Rh_2(5R\text{-MEPY})_4$, respectively, is within experimental error.

As expected from results obtained with cycloalkyl diazoacetates,[2] use of $Rh_2(4S\text{-MAClM})_4$ significantly enhances diastereoselection for γ-lactone formation from insertion into a secondary C—H bond of *rac*-**4**. Whereas the **7** : **6** ratio is (61—65) : (39—35) with either $Rh_2(MEPY)_4$ or $Rh_2(MEOX)_4$ catalysts, $Rh_2(4S\text{-MACIM})_4$ provides a 96 : 4 diasteromer ratio, and in contrast to results with other catalysts that possess the (*S*)-configuration, $Rh_2(4S\text{-MACIM})_4$ caused a reversal in the configuration of **7** from (4*S*,5*S*) to (4*R*,5*R*). Use of $Rh_2(4S\text{-MACIM})_4$ also leads to a reduction in the relative yield of **5** with a corresponding increase in the relative yield of **8**.

The carbon—hydrogen insertion reaction from diazo decomposition of racemic *trans*-2-methylcyclohexyl diazoacetate (**9**) catalyzed by chiral dirhodium(II) carboxamidates exhibited exceptional kinetic resolution. Four insertion products were isolated and identified (Scheme 2), and, in contrast to reaction of *rac*-**4**, β-lactone formation was a minor pathway. The two products that defined the major insertion reaction pathways with $Rh_2(MEPY)_4$ and $Rh_2(MEOX)_4$ catalysts, **10** and **11**, were formed with exceptional enantiocontrol (Table 2), reaching ≥95 % *ee* with the use of $Rh_2(4S\text{-MEOX})_4$. Products having the mirror image configuration of those formed from the use of the (*S*)-catalysts were obtained with $Rh_2(5R\text{-MEPY})_4$. Surprisingly, but consistent with results from reactions with *trans*-4-methylcyclohexyl diazoacetate,[2] $Rh_2(4S\text{-MACIM})_4$ formed **12** as the major

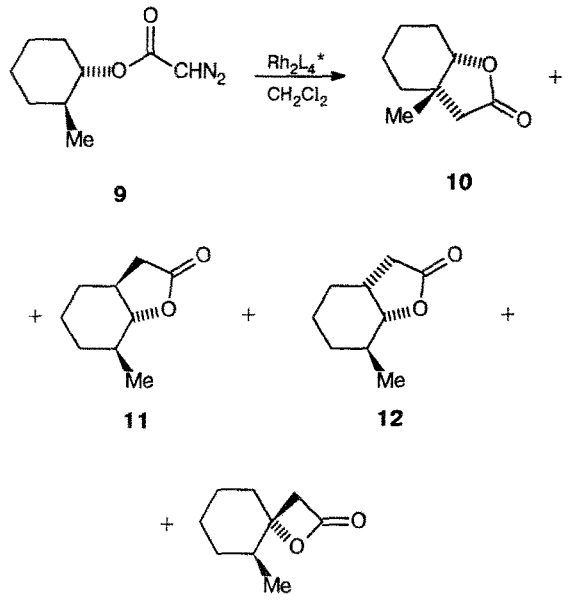
Table 1. Enantiomer differentiation and diastereoselectivity in intramolecular CH insertion reactions of 2-octyl diazoacetate catalyzed by chiral dirhodium(II) carboxamidates[a]

Diazo ester	Catalyst	Yield (%)[b]	Relative yield (%)				*ee* (%) (Configuration)[c]			
			5	**6**	**7**	**8**	**5**	**6**	**7**	**8**
***rac*-4**	$Rh_2(5S\text{-MEPY})_4$	50	49	17	27	7	16 (*R*)	6 (*R,S*)	74 (*S,S*)	88 (*R*)
	$Rh_2(5R\text{-MEPY})_4$	45	51	15	27	7	17 (*S*)	5 (*S,R*)	77 (*R,R*)	87 (*S*)
	$Rh_2(4S\text{-MEOX})_4$	59	72	8	15	5	10 (*R*)	51 (*R,S*)	88 (*S,S*)	93 (*R*)
	$Rh_2(4S\text{-MACIM})_4$	65	29	4	46	21	15 (*R*)	64 (*S,R*)	80 (*S,S*)	98 (*R*)
(*R*)-4[d]	$Rh_2(5S\text{-MEPY})_4$	59	66	14	6	14	(*S*)	(*R,R*)	(*R,R*)	(*R*)
	$Rh_2(5R\text{-MEPY})_4$	53	43	14	42	1	(*S*)	(*S,R*)	(*R,R*)	(*R*)
	$Rh_2(4S\text{-MEOX})_4$	59	83	4	3	10	(*S*)	(*S,R*)	(*R,R*)	(*R*)
	$Rh_2(4R\text{-MEOX})_4$	71	57	12	29	2	(*S*)	(*S,R*)	(*R,R*)	(*R*)
	$Rh_2(4S\text{-MACIM})_4$	58	39	7	10	44	(*S*)	(*S,R*)	(*R,R*)	(*R*)
(*S*)-4[d]	$Rh_2(5R\text{-MEPY})_4$	52	65	14	7	14	(*R*)	(*R,S*)	(*S,S*)	(*S*)
	$Rh_2(4R\text{-MEOX})_4$	53	85	4	2	9	(*R*)	(*R,S*)	(*S,S*)	(*S*)
	$Rh_2(4S\text{-MACIM})_4$	74	22	2	76	<1	(*R*)	(*R,S*)	(*S,S*)	(*S*)

[a] Reactions performed in refluxing CH_2Cl_2 with 1.0 mol. % catalyst. [b] Yield obtained after distillation. [c] Absolute configuration; for **6** and **7** (4-position and 5-position of dihydrofuran). [d] Products are optically pure.

reaction product, demonstrating the preference of this catalyst for construction of *cis*-ring fusions.

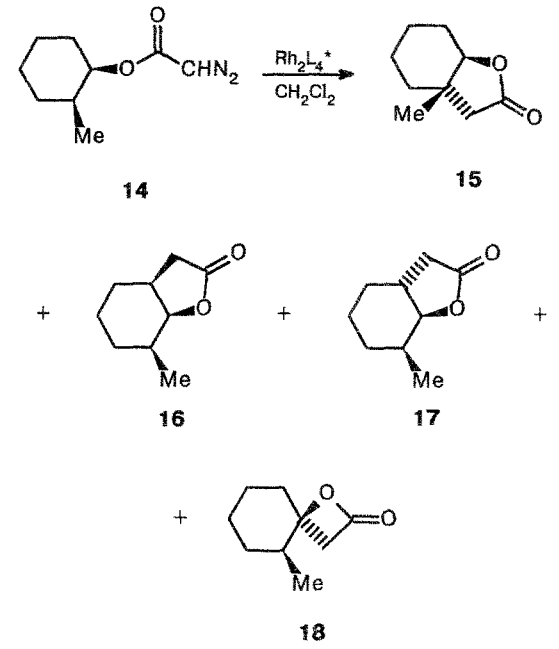
Scheme 2



Even higher levels of enantiocontrol were associated with catalytic diazo decomposition of racemic *cis*-2-methylcyclohexyl diazoacetate (**14**), whose insertion products were diastereomeric with those formed from **9** (Scheme 3). Kinetic resolution in this system was virtually complete with the use of $Rh_2(4S\text{-MEOX})_4$ (Table 3). Diastereoselectivity with the use of $Rh_2(4S\text{-MACIM})_4$ was consistent with that observed for insertion reactions of *cis*-4-methylcyclohexyl diazoacetate.[2]

The data presented for C—H insertion reactions of three racemic secondary diazoacetates clearly establish

Scheme 3



dirhodium(II) carboxamidate catalysts as exceptionally effective for kinetic resolution. Although enantiomer differentiation is pronounced with both acyclic and cyclic systems, the cyclohexyl systems exhibit greater enantiocontrol and regiocontrol. Accordingly, single enantiomers of the 2-methylcyclohexyl diazoacetates are expected to exhibit extraordinary diastereoselectivity for the formation of single products, and efforts are underway to evaluate this potential.

Experimental

^1H NMR (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Varian VXR-300 spectrometer from solutions in $CDCl_3$, and chemical shifts (δ) are reported in parts per million downfield from internal Me_4Si (TMS). Mass spectra were obtained using electron ionization at 70 eV on a

Table 2. Enantiomer differentiation in intramolecular CH insertion reactions of racemic *trans*-2-methylcyclohexyl diazoacetate[a]

Catalyst	Yield (%)[b]	Relative yield (%)				*ee* (%) [c]		
		10	**11**	**12**	**13**	**10**	**11**	**12**
$Rh_2(5S\text{-MEPY})_4$	65	49	40	9	2	80	93	78
$Rh_2(5R\text{-MEPY})_4$	57	47	41	9	3	79	93	82
$Rh_2(4S\text{-MEOX})_4$	75	39	50	6	5	96	95	79
$Rh_2(4S\text{-MACIM})_4$	57	18	19	51	12	87	49	86

[a] Reactions performed in refluxing CH_2Cl_2 with 1.0 mol. % catalyst.
[b] Yield obtained after distillation.
[c] Values for **13** were not determined.

Table 3. Enantiomer differentiation in intramolecular CH insertion reactions of racemic *cis*-2-methylcyclohexyl diazoacetate[a]

Catalyst	Yield (%)[b]	Relative yield (%)			*ee* (%) [c]		
		15	**16**	**17**	**18**	**15**	**16**
$Rh_2(5S\text{-MEPY})_4$	75	45	49	2	4	91	98
$Rh_2(5R\text{-MEPY})_4$	62	44	49	2	5	92	98
$Rh_2(4S\text{-MEOX})_4$	86	40	47	4	9	99	99
$Rh_2(4S\text{-MACIM})_4$	77	11	66	1	22	87	77

[a] Reactions performed in refluxing CH_2Cl_2 with 1.0 mol. % catalyst.
[b] Yield obtained after distillation.
[c] Values for **17** and **18** were not determined.

Hewlett Packard 5995 instrument. Infrared spectra were recorded either from a thin film on sodium chloride plates or from solutions as indicated, and absorptions are reported in wavenumbers from a Nicollet 550 FT-IR instrument. Elemental analyses were performed at Texas Analytical Laboratories, Inc.

Dichloromethane was distilled from calcium hydride prior to use in catalytic reactions.

2-Octyl diazoacetate (4). To a solution of (*R*)-2-octanol (4.59 g, 35.3 mmol) and triethylamine (0.18 g, 1.8 mmol) in 50 mL of dry THF cooled to 0 °C was added diketene (4.45 g, 53.0 mmol) over a period of 30 min. The resulting solution was stirred for 1 h at 0 °C and then for 12 h at room temperature. The solvent was then evaporated under reduced pressure, and the crude product was diluted with ether (100 mL), passed through a short plug of silica gel, and then distilled under reduced pressure (b.p. 116—119 °C at 0.6 Torr) to afford 7.28 g of a colorless liquid identified as 2-octyl acetoacetate (50.9 mmol, 96 % yield). ^{1}H NMR, δ: 4.96 (sex, J = 6.2 Hz, 1 H); 3.43 (s, 2 H); 2.27 (s, 3 H); 1.70—1.53 (m, 1 H); 1.52—1.42 (m, 1 H); 1.40—1.20 (m, 8 H); 1.24 (d, J = 6.2 Hz, 3 H); 0.88 (t, J = 6.4 Hz, 3 H); enol form at 5.02 (s, 1 H); 1.94 (s, 3 H). ^{13}C NMR, δ: 200.7, 166.8, 72.4, 50.5, 35.8, 31.7, 30.1, 29.1, 25.3, 22.6, 19.8, 14.0.

To a solution of the acetoacetate ester (3.58 g, 16.7 mmol) in dry acetonitrile (30 mL) was added triethylamine (1.69 g, 16.7 mmol) and then methanesulfonyl azide (2.43 g, 20.1 mmol).[10] The resulting solution was stirred for 4 h at room temperature, and then LiOH—H_2O (2.11 g, 50.2 mmol) in 43 mL of H_2O (5 % in H_2O) was added. This mixture was stirred for 5 h, then diluted with water (200 mL), and extracted three times with 50-mL portions of ether. The combined ether extract was washed twice with 150-mL portions of water and once with 150 mL of brine and then dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The crude diazo ester was passed through a short plug of silica gel (EtOAc—hexane, 1 : 1) and then distilled (b.p. 70—75 °C at 0.3 Torr) to yield 2.29 of a yellow liquid identified as (*R*)-2-octyl diazoacetate (11.5 mmol, 69 % yield); $[\alpha]_D^{22}$ —27.8° (*c* 1.45, $CHCl_3$). ^{1}H NMR, δ: 4.98 (sex, J = 6.1 Hz, 1 H); 4.71 (s, 1 H); 1.67—1.40 (m, 2 H); 1.40—1.20 (m, 8 H); 1.23 (d, J = 6.1 Hz, 3 H); 0.88 (t, J = 6.8 Hz, 3 H). ^{13}C NMR, δ: 166.7, 71.9, 46.3, 36.1, 31.8, 29.2, 25.4, 22.6, 20.2, 14.1. IR (film), ν/cm^{-1}: 2116 (C=NN); 1695 (C=O). Found (%): C, 60.68; H, 9.46; N, 14.01. $C_{10}H_{18}N_2O_2$. Calculated (%): C, 60.58; H, 9.15; N, 14.13. *rac*-**4** and (*S*)-**4** were prepared by the same procedure in 64 and 71 % overall yield, respectively; for (*S*)-**4**, $[\alpha]_D^{22}$ +27.7° (*c* 1.44, $CHCl_3$).

Catalytic diazodecomposition of 2-octyl diazoacetate. The diazo compound (0.198 g, 1.00 mmol) in 10 mL of anhydrous CH_2Cl_2 was added *via* syringe pump (1.0 mL h^{-1}) to a refluxing solution of dirhodium(II) catalyst (10 mmol, 1.0 mol %) in 20 mL of CH_2Cl_2. After refluxing for an additional hour, the reaction solution was filtered through a short plug of silica gel, and the solvent was removed under reduced pressure. The residue was analyzed by NMR and GC methods and then distilled (b.p. 80—85 °C at 0.2 Torr). The resulting colorless liquid was separated into its individual components by column chromatography on silica gel (hexane—EtOAc, 9 : 1) with elution in the order: **5**, **6**, and **7**. γ-Decanolactone **8** was identified by comparison with an authentic sample. Enantiomer separations were performed by GC with baseline resolution on 30-m Chiraldex B-PH (**5** and **6**) and G-TA (**7** and **8**) columns operated at 80 °C for 80 min and then programmed at 0.5 °C/min to 150 °C: **5**, 147.3 min (*R*-**5**) and 148.9 min (*S*-**5**); **6**, 177.7 min (4*R*,5*S*-**6**) and 180.1 min (4*S*,5*R*-**6**); **7**, 207.5 min (4*R*,5*R*-**7**) and 210.8 min (4*S*,5*S*-**7**); **8**, 193.9 min (*S*-**8**) and 196.8 min (*R*-**8**).

4-Methyl-4-(*n*-hexyl)-1-oxacyclobutan-2-one (5). $[\alpha]_D^{21}$ +4.8° (*c* 1.17, $CHCl_3$) from (*R*)-**4** with Rh_2(5*R*-MEPY)$_4$. ^{1}H NMR, δ: 3.19 (d, J = 16.1 Hz, 1 H); 3.10 (d, J = 16.1 Hz, 1 H); 1.92—1.74 (m, 2 H); 1.57 (s, 3 H); 1.45—1.24 (m, 8 H); 0.90 (t, J = 6.8 Hz, 3 H). ^{13}C NMR, δ: 168.3, 78.8, 47.5, 39.5, 31.7, 29.3, 24.34, 24.27, 22.6, 14.1. IR ($CHCl_3$), ν/cm^{-1}: 1814 (C=O). MS, *m/z* (I_{rel} (%)): 126 [M—CO_2] (7), 113 (7), 110 (7), 100 (67), 85 (30), 69 (43), 58 (57), 57 (42), 56 (100), 55 (66). Found (%): C, 70.43; H, 10.61. $C_{10}H_{18}O_2$. Calculated (%): C, 70.55; H, 10.65.

***trans*-Dihydro-5-methyl-4-(*n*-pentyl)-2(3*H*)-furanone (6).** $[\alpha]_D^{21}$ +66.6° (*c* 0.35, $CHCl_3$) from (*R*)-**4** with Rh_2(5*R*-MEPY)$_4$. ^{1}H NMR, δ: 4.21 (dq, J = 7.6, 6.2 Hz, 1 H); 2.68 (dd, J = 17.3, 8.2 Hz, 1 H); 2.21 (dd, J = 17.3, 9.6 Hz, 1 H); 2.13—1.99 (m, 1 H); 1.58—1.50 (m, 1 H); 1.40 (d, J = 6.2 Hz, 3 H); 1.39—1.24 (m, 7 H); 0.90 (t, J = 6.6 Hz, 3 H); stereochemical assignment consistent with analogous *trans*-disubstituted γ-lactones.[11—13] ^{13}C NMR, δ: 176.6, 82.3, 43.5, 35.6, 32.6, 31.8, 27.4, 22.6, 20.0, 14.1. IR ($CHCl_3$), ν/cm^{-1}: 1770 (C=O). MS, *m/z* (I_{rel} (%)): 155 [M—15] (3), 128 (5), 109 (6), 98 (64), 95 (14), 83 (12), 70 (85), 69 (46), 57 (27), 56 (100), 55 (86). For (**6** + **7**) found: C, 70.48; H, 10.69. $C_{10}H_{18}O_2$. Calculated (%): C, 70.55; H, 10.65.

***cis*-Dihydro-5-methyl-4-(*n*-pentyl)-2(3*H*)-furanone (7).** $[\alpha]_D^{21}$ +2.5° (*c* 0.52, $CHCl_3$) from (*R*)-**4** with Rh_2(5*R*-MEPY)$_4$. ^{1}H NMR, δ: 4.70 (quin, J = 6.6 Hz, 1 H); 2.56 (dd, J = 14.8, 7.8 Hz, 2 H); 2.56—2.48 (m, 1 H); 2.24 (dd, J = 14.8, 8.2 Hz, 1 H); 1.52—1.40 (m, 1 H); 1.39—1.23 (m, 7 H); 1.27 (d, J = 6.6 Hz, 3 H); 0.90 (t, J = 6.7 Hz, 3 H); stereochemical assignment consistent with analogous *cis*-disubstituted γ-lactones.[11—13] ^{13}C NMR, δ: 176.9, 79.5, 39.0, 33.9, 31.9, 28.7, 27.5, 22.6, 15.5, 14.1. IR ($CHCl_3$), ν/cm^{-1}: 1773 (C=O). MS, *m/z* (I_{rel} (%)): 170 [M] (1), 128 (7), 109 (6), 98 (70), 95 (12), 83 (14), 70 (86), 69 (43), 57 (30), 56 (100), 55 (86).

***trans*-2-Methylcyclohexyl diazoacetate (9).** A solution of *trans*-2-methylcyclohexanol (5.00 g, 43.8 mmol) and freshly distilled 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (6.18 g, 43.8 mmol) in xylene (20 mL) was heated with rapid stirring in a preheated oil bath at 150 °C for 30 min until the acetone that was produced had evaporated.[14] The xylene was removed by distillation, and the residue was purified by distillation (b.p. 90—95 °C at 0.05 Torr) to yield 7.29 g (40.6 mmol, 93 % yield) of *trans*-2-methylcyclohexyl acetoacetate as a colorless liquid. ^{1}H NMR, δ: 4.48 (dt, J = 4.3, 10.2, 1 H); 3.45 (s, 2 H); 2.27 (s, 3 H); 2.02—1.00 (m, 9 H); 0.91 (d, J = 6.5 Hz, 3 H); enol form at 4.98 (s, 1 H) and 1.95 (s, 3 H). Diazo transfer and deacylation were performed as described for **4** in 63 % isolated yield after chromatography on silica gel (hexane); yellow liquid, b.p. 75 °C at 0.2 Torr. ^{1}H NMR, δ: 4.72 (br s, 1 H); 4.49 (dt, J = 4.5, 10.1 Hz, 1 H); 2.06—1.96 (m, 1 H); 1.80—1.00 (m, 8 H); 0.91 (d, J = 6.5 Hz, 3 H). ^{13}C NMR, δ: 166.8, 79.1, 46.2, 37.5, 33.6, 32.1, 25.4, 24.8, 18.5. IR (film), ν/cm^{-1}: 2121 (C=NN); 1689 (C=O). Found (%): C, 59.40; H, 7.71; N, 15.42. $C_9H_{14}N_2O_2$. Calculated (%): C, 59.32; H, 7.74; N, 15.37.

Catalytic diazodecomposition of *trans*-2-methylcyclohexyl diazoacetate was performed according to the same procedure as for **4**, and reaction products were distilled (b.p. 80—85 °C

at 0.2 Torr). The resulting colorless liquid was separated into its individual components by column chromatography on silica gel (hexane—EtOAc, 20 : 1) with elution in the order **11**, **10**, and **12**. Enantiomer separations were performed by GC with baseline resolution on a 30-m Chiraldex B-PH column operated at 100 °C for 100 min and then programmed at 0.5°C/min to 150 °C: **10**, 152 min (minor) and 154 min (major); **11**, 143 min (major) and 147 min (minor); **12**, 164 min (minor) and 168 min (major) for reactions with $Rh_2(5S\text{-MEPY})_4$, $Rh_2(4S\text{-MEOX})_4$, and $Rh_2(4S\text{-MACIM})_4$. Compound **13** underwent thermal decomposition upon GC analysis.

***cis*-3a-Methylhexahydro-2(3*H*)-benzofuranone (10).** ^{1}H NMR, δ: 4.16 (t, J = 3.8 Hz, 1 H); 2.32 (s, 2 H); 2.03—1.92 (m, 1 H); 1.76—1.32 (m, 7 H); 1.17 (s, 3 H); stereochemical assignments were based on chemical shift data (CH—O, *cis, trans*) and coupling constants (J_{ae}(*cis*) ≈ 10 Hz, J_{aa}(*trans*) ≈ 4 Hz).[15] ^{13}C NMR, δ: 176.9, 84.2, 45.2, 33.2, 29.8, 25.8, 22.1, 21.0, 20.0. IR (film), ν/cm^{-1}: 1777 (C=O). MS, *m/z* (I_{rel} (%)): 154 [M] (4), 108 (12), 95 (16), 93 (15), 82 (100), 81 (21), 69 (27), 67 (47), 56 (33), 55 (48). For **(10+11+12)** found (%): C, 70.18; H, 9.03. $C_9H_{14}O_2$. Calculated (%): C, 70.10; H, 9.15.

7α-Methyl-(3aα,7aβ)-hexahydro-2(3*H*)-benzofuranone (11). ^{1}H NMR, δ: 3.44 (t, J = 10.4 Hz, 1 H); 2.52 (dd, J = 16.1, 6.2 Hz, 1 H); 2.23 (dd, J = 16.1, 13.0 Hz, 1 H); 2.05—1.20 (m, 8 H); 1.06 (d, J = 6.2 Hz, 3 H). ^{13}C NMR, δ: 176.7, 90.8, 44.3, 36.8, 36.2, 33.4, 28.3, 25.4, 18.6. IR (film), ν/cm^{-1}: 1777 (C=O). MS, *m/z* (I_{rel} (%)): 154 [M] (1), 97 (14), 95 (16), 82 (100), 81 (25), 68 (38), 67 (63), 55 (80), 54 (50).

7α-Methyl-(3aβ,7aβ)-hexahydro-2(3*H*)-benzofuranone (12). ^{1}H NMR, δ: 4.09 (dd, J = 7.6, 6.5 Hz, 1 H); 2.72—2.60 (m, 1 H); 2.45—2.30 (m, 2 H); 1.74—1.34 (m, 7 H); 1.05 (d, J = 6.6 Hz, 3 H). ^{13}C NMR, δ: 177.3, 85.4, 34.3, 33.5, 33.4, 29.8, 26.0, 19.5, 18.5. IR (film), ν/cm^{-1}: 1776 (C=O). MS, *m/z* (I_{rel} (%)): 154 [M], (4), 126 (15), 98 (18), 97 (27), 95 (28), 94 (39), 82 (53), 68 (30), 67 (29), 56 (24), 55 (100).

(1a,5β)-5-Methyl-1-oxaspiro[5.3]nonan-2-one (13). ^{1}H NMR, δ: 3.19 (d, J = 16.2 Hz, 1 H); 2.88 (d, J = 16.2 Hz, 1 H); 2.05—1.30 (m, 9 H); 1.01 (d, J = 6.8 Hz, 3 H). ^{13}C NMR, δ: 170.9, 80.2, 42.3, 37.3, 36.0, 31.0, 24.2, 23.8, 14.3. IR (film), ν/cm^{-1}: 1817 (C=O). MS, *m/z* (I_{rel} (%)): 154 [M] (5), 112 (46), 110 (29), 95 (48), 84 (46), 82 (26), 81 (51), 69 (46), 68 (100), 67 (86), 56 (50), 55 (79), 54 (29), 53 (43).

***cis*-2-Methylcyclohexyl diazoacetate (14)** was prepared in 73 % overall yield by the procedure described for the synthesis of **9**; yellow liquid, b.p. 75 °C at 0.2 Torr. ^{1}H NMR, δ: 5.04—5.00 (m, 1 H); 4.74 (br s, 1 H); 1.94—1.83 (m, 1 H); 1.80—1.60 (m, 2 H); 1.56—1.25 (m, 6 H); 0.89 (d, J = 6.9 Hz, 3 H). ^{13}C NMR, δ: 166.6, 74.5, 46.2, 34.8, 30.0, 29.4, 24.6, 21.0, 17.2. IR (film), ν/cm^{-1}: 2121 (C=NN), 1692 (C=O). Found (%): C, 59.26; H, 7.78; N, 15.25. $C_9H_{14}N_2O_2$. Calculated (%): C, 59.32; H, 7.74; N, 15.37.

Catalytic diazodecomposition of *cis*-2-methylcyclohexyl diazoacetate was performed according to the same procedure as for **4**, and reaction products were distilled (b.p. 80—85 °C at 0.2 Torr). The resulting colorless liquid was separated into its individual components by column chromatography on silica gel (hexane—EtOAc, 20 : 1) with elution in the order **18**, **15**, and **16**. Enantiomer separations were performed by GC with baseline resolution on a 30-m Chiraldex B-PH column operated at 100 °C for 100 min and then programmed at 0.3°C/min to 150 °C: **16**, 146 min (major) and 158 min (minor); **15**, 184 min (major) and 188 min (minor) for reactions with $Rh_2(5S\text{-MEPY})_4$, $Rh_2(4S\text{-MEOX})_4$, and $Rh_2(4S\text{-MACIM})_4$. Compound **18** underwent thermal decomposition upon GC analysis.

***trans*-3a-Methylhexahydro-2(3*H*)-benzofuranone (15).** ^{1}H NMR, δ: 3.89 (dd, J = 12.4, 3.8 Hz, 1 H); 2.29 (s, 2 H); 2.02—1.86 (m, 2 H); 1.82—1.30 (m, 6 H); 1.04 (s, 3 H). ^{13}C NMR, δ: 176.9, 86.7, 46.0, 41.2, 34.5, 24.2, 23.8, 20.7, 16.7. IR (film), ν/cm^{-1}: 1778 (C=O). MS, *m/z* (I_{rel} (%)): 154 [M] (2), 110 (14), 108 (12), 95 (16), 82 (100), 81 (19), 69 (35), 67 (80), 56 (39), 55 (49), 53 (21). For **(15 + 16)** found (%): C, 70.03; H, 9.19. $C_9H_{14}O_2$. Calculated (%): C, 70.10; H, 9.15.

7α-Methyl-(3aα,7aα)-hexahydro-2(3*H*)-benzofuranone (16). ^{1}H NMR, δ: 4.36 (dd, J = 4.0, 3.0 Hz, 1 H); 2.67 (dd, J = 16.7, 6.5 Hz, 1 H); 2.32 (dddd, J = 11.8, 6.5, 6.2, 4.0 Hz, 1 H); 2.19 (d, J = 16.7 Hz, 1 H); 1.78—1.61 (m, 3 H); 1.56—1.46 (m, 1 H); 1.34—1.17 (m, 2 H); 1.15—1.00 (m, 1 H); 1.12 (d, J = 6.9 Hz, 3 H). ^{13}C NMR, δ: 177.6, 83.6, 38.7, 35.7, 34.0, 27.5, 27.2, 23.9, 18.5. IR (film), ν/cm^{-1}: 1771 (C=O). MS, *m/z* (I_{rel} (%)): 154 [M] (5), 126 (21), 125 (19), 111 (14), 98 (25), 97 (43), 95 (65), 94 (62), 84 (20), 82 (85), 81 (30), 68 (48), 67 (53), 56 (41), 55 (100).

7β-Methyl-(3aα,7aβ)-hexahydro-2(3*H*)-benzofuranone (17) was assigned from its mass spectrum, *m/z* (I_{rel} (%)): 154 [M] (5), 126 (14), 125 (12), 111 (8), 98 (15), 97 (27), 95 (26), 94 (29), 84 (17), 82 (100), 81 (27), 68 (33), 67 (46), 56 (21), 55 (87). ^{1}H NMR, δ: 4.06 (dd, J = 10, 4 Hz) is consistent with this assignment.

(1α,5α)-5-Methyl-1-oxaspiro[5.3]nonan-2-one (18). ^{1}H NMR, δ: 3.28 (d, J = 16.2 Hz, 1 H); 2.94 (d, J = 16.2 Hz, 1 H); 2.07—1.96 (m, 1 H); 1.91—1.78 (m, 1 H); 1.75—1.30 (m, 7 H); 1.05 (d, J = 6.8 Hz, 3 H). ^{13}C NMR, δ: 168.8, 80.8, 45.8, 37.3, 35.2, 30.7, 23.5, 23.1, 13.9. IR (film), ν/cm^{-1}: 1818 (C=O). MS, *m/z* (I_{rel} (%)): 154 [M] (1), 112 (52), 111 (10), 110 (33), 95 (54), 84 (31), 82 (23), 81 (53), 69 (50), 68 (100), 67 (74), 56 (42), 55 (68), 53 (28).

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