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Chiral [Bis(olefin)amine]rhodium(I) Complexes – Transfer Hydrogenation in Ethanol

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*B*is(*o*lefin)*a*mines (*boa*s) are a new class of ligands for the synthesis of transition metal complexes, which can be used in various homogeneous catalytic reactions. A simple straightforward coupling reaction between 5*H*-dibenzo[*a*,*d*]-cycloheptен-5-yl chloride (tropCl) and primary amines allows the synthesis of various chiral *boa*s. Birch reduction of phenylalanine gives (2*S*)-2-amino-3-cyclohexa-1,4-dien-1-yl propanoate, which is used for the synthesis of the bis(olefin)-amine methyl (2*S*)-3-(cyclohexa-1,4-dienyl)-2-(5*H*-dibenzo-[*a*,*d*]cycloheptен-5-yl-amino)propionate. Coupling between cyclohex-3-en-1-ylamine with tropCl gives *N*-(cyclohex-3′-en-1′-yl)-5*H*-dibenzo[*a*,*d*]cycloheptен-5-ylamine, which was separated into its enantiomers. Bicyclic cyclohexenylamine derivatives like bicyclo[2.2.2]oct-5-en-2-ylamine and 2-(methoxycarbonyl)bicyclo[2.2.1]hept-5-en-3-ylamine were likewise coupled with tropCl to give chiral bis(olefin)amines. Alternatively, 5*H*-dibenzo[*a*,*d*]cycloheptен-5-ylamine (trop-NH_2) can react with cyclohexenyl ketones to give prochiral bis(olefin)imines, which were reduced to the corresponding bis(olefin)amines. With $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ or $[Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4]$, a complexation of these compounds was achieved leading to chiral rhodium complexes of the type [Rh(*boa*)-(CO)]OTf or [Rh(*boa*)(PR_3)]OTf. The complexes have a strongly distorted saw-horse-type structure (determined by X-ray diffraction studies) and were tested in transfer hydrogenations with ethanol/2-propanol as hydrogen donor. Only complexes with tightly bound olefinic binding sites and a pronounced saw-horse-type structure give significant activities. Furthermore, a phosphane ligand in *trans* position to the coordinated amine function has a positive impact of the catalysts performance. None of the investigated catalysts gave an impressive enantiomeric excess (*ee* < 60 %) in the transfer hydrogenation of acetophenone.

Introduction

Asymmetric transfer hydrogenation has been the subject of intense research during the last two decades. Transfer hydrogenation is safer, cheaper and simpler than most other methods of ketone reduction. It avoids the use of highly flammable and/or reactive reagents like $LiAlH_4$, silanes, H_2, and no high-pressure equipment is needed. The use of a sacrificial alcohol is environmentally sound since it produces only benign byproducts, which are easily removed. Highly active and selective catalysts are available today.[1] 2-Propanol or formic acid/triethylamine mixtures as reductants in combination with (arene)ruthenium(II) or (cyclopentadienyl)rhodium(III) complexes as catalysts are the most popular choices so far.[2]

Ethanol is a renewable resource, which has been used successfully as hydrogen donor in transfer hydrogenation by our group.[3] The cationic d^8-Rh^I complex of bis(5*H*-dibenzo[*a*,*d*]cycloheptен-5-yl)amine [$trop_2NH$ (**1**) with trop referring to the trivial name "*trop*ylidenyl" for 5*H*-dibenzo[*a*,*d*]cycloheptен-5-yl] [$Rh(trop_2NH)(PPh_3)$]OTf (**2**) is a very efficient catalyst precursor for this reaction (see Scheme 1), and remarkable activities (TOF_{50} = 500000 for acetophenone) were achieved. In this reaction, ethanol is converted into ethyl acetate by reaction (1).

$$2\ R_2C{=}O + 2\ EtOH \rightarrow 2\ R_2HCOH + MeCOOEt \quad (1)$$

Importantly, reaction (1) is exothermic and practically irreversible, whereas conventional transfer hydrogenation in 2-propanol is more or less thermoneutral and therefore reversible. Consequently, the transfer hydrogenation in ethanol proceeds at high substrate concentrations (2 M or higher), which are impossible to achieve in 2-propanol. Recently, we showed that the same catalyst precursors **2a**–**c** efficiently promote the dehydrogenative coupling of alcohols with water or amines to give carboxylic acids or amides.[4] In these papers, propositions for the mechanisms of these reactions are discussed in detail. It is suggested that the catalysts precursors like **2a**–**c** are initially deprotonated to the corresponding rhodium amide complexes [$Rh(trop_2N)(PR_3)$], which operate according to the Noyori–Morris mechanism: The alcohol is hydrogen-bonded to the

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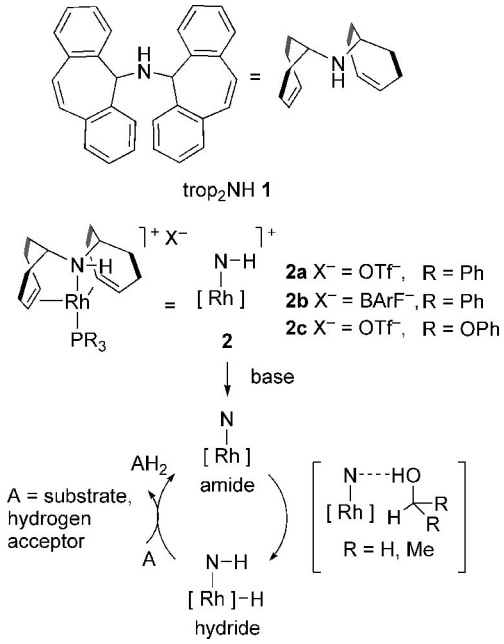


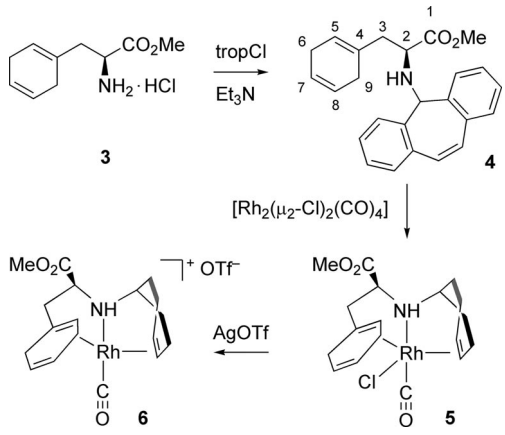
Scheme 1. $Trop_2NH$ (**1**), [Rh($trop_2NH$)(PPh_3)]OTf (**2**) and proposed catalytic cycle. The benzo groups of the trop units in the ligand are omitted for clarity and only denoted by bold lines in this and all subsequent schemes. OTf^- = trifluoromethanesulfonate anion, $BArF^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion.

amide nitrogen atom, dehydrogenated to give an amino hydrido complex [RhH($trop_2NH$)(PR_3)], which in turn reduces the ketone. The transfer hydrogenation of imines with formic acid as hydrogen donor is likewise an irreversible reaction (liberation of CO_2), and it was demonstrated that this feature improves the enatioselectivity of the reaction.[5] Thus, we became interested in extending our transfer hydrogenation method in ethanol into an enantioselective variant by using chiral bis(olefin)amine ligands. In this paper, we report several approaches for the syntheses of new chiral bis(olefin)amine ligands. Complexes with these new ligands were tested in catalysis, and their ability to induce asymmetry in transfer hydrogenation was studied.

Results and Discussion

Phenylalanine as Ligand Building Block

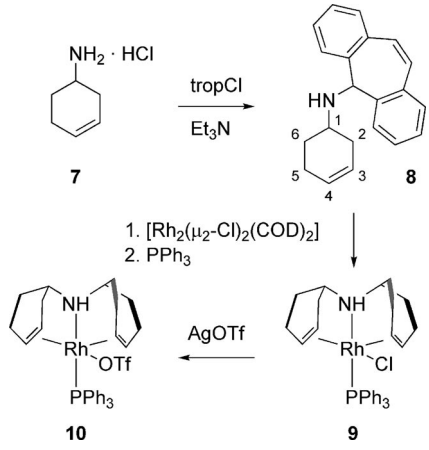
Methyl (2*S*)-2-amino-3-cyclohexa-1,4-dien-1-yl propanoate (**3**) is readily available from L-phenylalanine by Birch reduction and subsequent esterification.[6] Addition of a trop moiety to yield methyl (2*S*)-3-(cyclohexa-1,4-dienyl)-2-(5*H*-dibenzo[*a*,*d*]cycloheptен-5-yl-amino)propionate (**4**) is straightforward and shown in Scheme 2. Complexation of ligand **4** mandated the right choice of a rhodium precursor complex. Only [$Rh_2(\mu_2\text{-}Cl)_2(CO)_4$] reacted cleanly with **4** to give [Rh(Cl)(**4**)(CO)] (**5**). Other precursors, including for example [$Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4$], gave no clean product. The chloride **5** was quantitatively converted into the cationic triflate complex [Rh(**4**)(CO)]OTf (**6**) by addition of 1 equiv. of silver triflate. All attempts to replace the carbonyl ligand by another ligand in this complex were unsuccessful. If a strongly binding ligand like triphenylphosphane was added to **5** or **6**, displacement of the ligand **4** was observed instead.



Scheme 2. Synthesis of **4** and the rhodium complexes **5**, **6**. Numbers given in ligand **4** are the labeling key for the NMR spectroscopic data of compounds **3**–**6**.

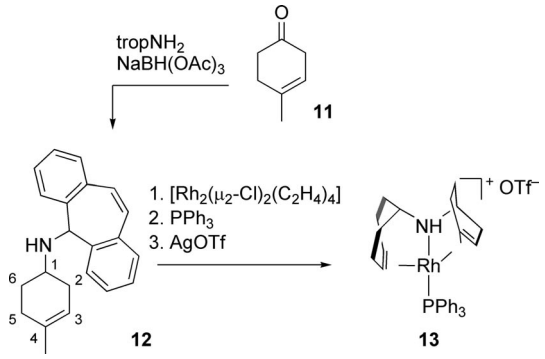
Cyclohex-3-en-1-ylamine as Ligand

A chiral bis(olefin)amine ligand resembling the $trop_2NH$ is simply obtained by replacing one dibenzo[*a*,*d*]cycloheptен-5-yl moiety by a suitable cycloheptenyl group. However, cycloheptenyl moieties are rather difficult to synthesize, whereas cyclohexenyl moieties are relatively easy to access by Diels–Alder reactions, Birch reductions and other synthetic methods. Starting from cyclohex-3-en-1-ylamine hydrochloride (**7**),[7] *N*-cyclohex-3′-en-1′-yl-5*H*-dibenzo[*a*,*d*]cycloheptен-5-ylamine (**8**) was obtained by addition of a trop moiety in good yield (see Scheme 3). Subsequently, the two enantiomers of **8** were successfully separated on a preparative chiral HPLC column.

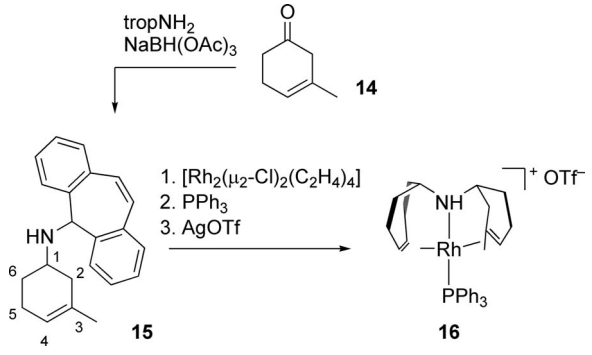


Scheme 3. Synthesis of ligand **8** and complexes **9**, **10**. Numbers given in ligand **8** are the labelling key for the NMR spectroscopic data of compounds **8**–**10**.

Rhodium complexes of **8** were easily obtained by applying the established protocol already used for ligand **1**.[3] Reaction with $[Rh_2(\mu_2\text{-}Cl)_2(cod)_2]$ and addition of triphenylphosphane gave [Rh(Cl)(**8**)(PPh_3)] (**9**). The chloride is readily abstracted with silver triflate, and [Rh(OTf)(**8**)(PPh_3)] (**10**) is obtained. 4-Methylcyclohex-3-en-1-one (**11**) and 3-methylcyclohex-3-en-1-one (**14**) are readily available by Birch reduction of 3- or 4-methylanisole, respectively.[8] The ligands **12** and **15** were obtained by reductive amination of **11** and **14** with $tropNH_2$ by using $NaBH(OAc)_3$ (see Schemes 4 and 5).[9] Reaction of **12** with $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ afforded an insoluble precipitate, which was treated with PPh_3 and subsequently silver triflate to give [Rh(OTf)(**12**)(PPh_3)] (**13**) (Scheme 4).



Scheme 4. Synthesis of ligand **12** and complex **13**. Numbers given in ligand **12** are the labeling key for the NMR spectroscopic data of compounds **12** and **13**.



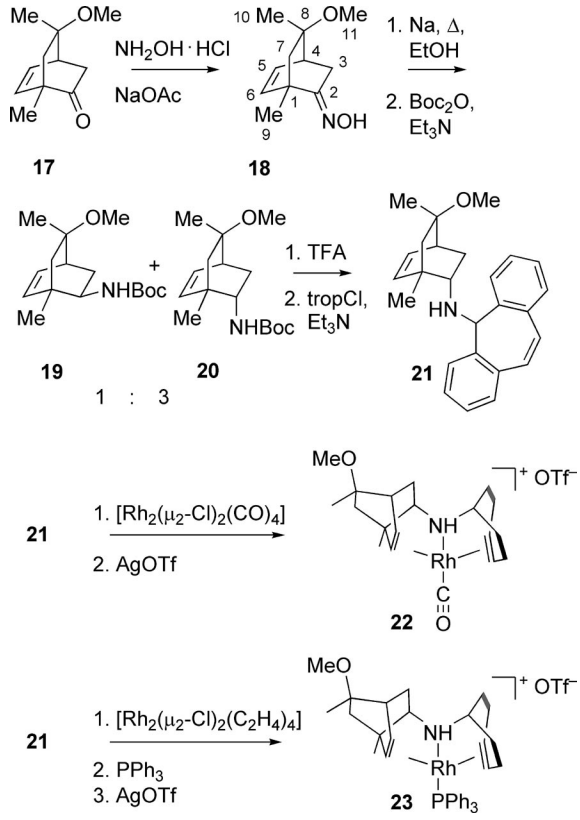
Scheme 5. Synthesis of ligand **15** and complex **16**. Numbers given in ligand **15** are the labeling key for the NMR spectroscopic data of compounds **15** and **16**.

Heating of ligand **15** in toluene with $[Rh_2(\mu_2\text{-}Cl)_2(COD_2)]$ gave an insoluble precipitate, which was treated with PPh_3 and silver triflate to give [Rh(**15**)(PPh_3)]OTf (**16**).

The resolution of ligands **12** and **15** into the pure enantiomers was not attempted due to their disappointing performance in transfer hydrogenation (vide infra).

Unsaturated Bicyclic Amines

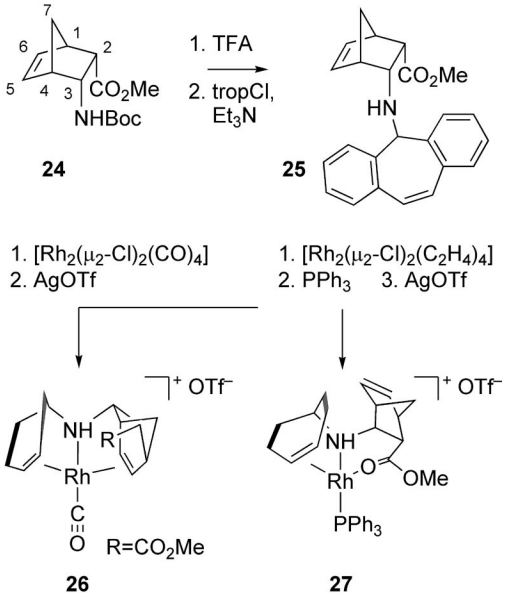
In order to avoid problems arising from ligands capable of coordination from two different sides, we envisioned bicyclic cyclohexenylamines as building block for chiral bis(olefin)amine ligands. Inspired by the chiral bicyclo[2.2.2]-octa-2,5-diene successfully used by Carreira et al. in conjugate additions of boronic acids,[10] the synthesis of a new bicyclo[2.2.2]oct-5-en-2-ylamine was initiated. Starting from the natural product (*R*)-carvone, the ketone (1*S*,4*S*,8*R*)-8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-one (**17**) is readily available.[11] The latter was treated with hydroxylamine hydrochloride to afford the corresponding oxime **18**. Subsequently, the oxime **18** was reduced by sodium/ethanol in refluxing toluene to give the desired bicyclo[2.2.2]oct-5-en-2-ylamines (not shown in Scheme 6) as diastereoisomers in excess. Separation of these diastereoisomers was possible by flash chromatography using Boc as protecting group for the free amines, and the *tert*-butyl bicyclo[2.2.2]oct-5-en-2-ylcarbamates **19** and **20** were obtained. After deprotection, the reaction with tropCl to the final ligand **21** was straightforward (see Scheme 6).



Scheme 6. Synthesis of ligand **21** and complexes **22**, **23**. Numbers given in ligand **18** are the labeling key for the NMR spectroscopic data of compounds **17**–**23**.

Ligand **21** did not react readily with $[Rh_2(\mu_2\text{-}Cl)_2(COD)_2]$, but with $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ or $[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ complexes **22** and **23**, respectively, were obtained.

Finally, ligand **25** containing a bicyclo[2.2.1]hept-5-en-2-yl moiety was prepared as shown in Scheme 7. The starting material methyl (2*S*3*R*)-3-[(*tert*-butoxycarbonyl)amino]bicyclo[2.2.1]hept-5-ene-2-carboxylate (**24**) was synthesized by a quinidine-mediated stereoselective anhydride opening as described by Bolm et al.[12]



Scheme 7. Synthesis of ligand **25** from **24** and complexes **26**, **27**. Numbers given in ligand **24** are the labeling key for the NMR spectroscopic data of compounds **24**–**27**.

Deprotection of **24** by trifluoroacetic acid (TFA) and addition of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl chloride (trop-Cl) gave methyl (2*S*3*R*)-3-(5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylamino)bicyclo[2.2.1]hept-5-ene-2-carboxylate (**25**) in a straightforward reaction (see Scheme 7). Similar to **21**, ligand **25** reacted readily with $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ and $[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ to yield complexes **26** and **27**, respectively.

The chlorido complexes of **12**, **15**, **21** and **25** were not isolated and the chloride was abstracted in situ with silver triflate to give the corresponding triflate complexes in very good yields (>80%). The physical properties (X-ray diffraction data obtained with single crystals and NMR spectroscopic data) are briefly discussed after the next section discussing the catalytic performances. They prove the structural assignments made to all complexes shown in Schemes 2, 3, 4, 5, 6, and 7.

Transfer Hydrogenation

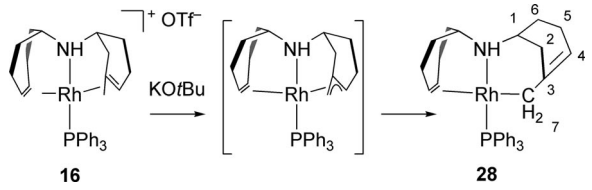
All catalysts were tested in transfer hydrogenation in acetophenone to yield (*R*)- and/or (*S*)-1-phenylethanol by using 2-propanol and ethanol as hydrogen donors. The results are presented in Table 1. The best results obtained with complex **2b** described earlier are given for comparison (Entries 1, 2).[3] Complex **10** containing a cyclohexenyl group was the best catalyst precursor in terms of activity either with ethanol or 2-propanol. A moderate enantiomeric excess (*ee*) was also obtained, even at high conversions (Table 1, Entries 5–7). Turnover numbers of up to 400000 were observed at a substrate/catalyst ratio S/C = 10^6 after 48 h, but no enantiomeric excess (*ee*) was observable under these conditions (see Entry 6). Surprisingly, the comparable complexes **13** and **16** were almost inactive in the reaction studied (Entries 8, 9). Obviously, the additional methyl substituent at the cyclohexenyl olefin entity has a large effect on the catalyst's activity. This effect may be either purely steric, or the deprotonation of the amine precursor complexes **13** or **16** did not give the corresponding catalytically active amide complexes but yields catalytically inactive allyl complexes. Indeed, in a previous paper we could show that in a related complex deprotonation of a C=Ctrop-bonded methyl group does occur leading to a fully characterized η^3-bonded allyl complex.[13] Although we could not isolate the deprotonation product of **16** here, the NMR spectroscopic data obtained of a solution containing **16** and KO*t*Bu clearly indicates that a proton is abstracted form the methyl group (Scheme 8). However, the rigid structure of the bis(olefin)amine ligand forestalls the formation of an η^3-allyl complex, and an η^1-allyl binding mode is observed instead as the NMR spectroscopic data of the H_2C^7 group suggests [$\delta(^{13}C)$ = 59.8 (m, 1 C, CH_2^7); $\delta(^1H)$ = 4.45 (m, 2 H, CH_2^{allyl})].

The best enantiomeric excess (*ee* 58%) was obtained with complex **6** containing the phenylalanine-derived ligand **4** (Entry 4). However, the complex is comparatively less active. The complexes obtained from ligands based on unsaturated bicyclic amines performed all disappointingly. Except for complex **27** (Entries 13, 14), which contains an un-

Table 1. Transfer hydrogenation of acetophenone with complexes of chiral tripodal bis(olefin)amine ligands (S/C denotes the substrate/catalyst ratio).

Entry	Catalyst	Solvent	S/C	t [h]	Conversion [%]	*ee* [%]
1	[Rh(trop$_2$NH)(PPh$_3$)]OTF (**2b**)	EtOH[a]	10^6	48	90	–
2	[Rh(trop$_2$NH)(PPh$_3$)]OTF (**2b**)	EtOH[a]	100000	1	99	–
3	[Rh(**4**)(CO)]OTf (**6**)	EtOH[a]	1000	0.8	83	30
4	[Rh(**4**)(CO)]OTf (**6**)	*i*PrOH[b]	1000	1.5	75	58
5	[Rh(**8**)(PPh$_3$)]OTf (**10**)	EtOH[a]	10000	0.1	96	33
6	[Rh(**8**)(PPh$_3$)]OTf (**10**)	EtOH[a]	10^6	48	40	0
7	[Rh(**8**)(PPh$_3$)]OTf (**10**)	*i*PrOH[b]	10000	0.25	91	44
8	[Rh(**12**)(PPh$_3$)]OTf (**13**)	EtOH, *i*PrOH[a,b]	100	1.2	<1	–
9	[Rh(**15**)(PPh$_3$)]OTf (**16**)	EtOH, *i*PrOH[a,b]	100	1.2	5	–
10	[Rh(**21**)(CO)]OTf (**22**)	EtOH, *i*PrOH[a,b]	100	1.2	0	–
11	[Rh(**21**)(PPh$_3$)]OTf (**23**)	EtOH, *i*PrOH[a,b]	100	1.2	<1	0
12	[Rh(**25**)(CO)]OTf (**26**)	EtOH, *i*PrOH[a,b]	100	1.2	<1	0
13	[Rh(**25**)(PPh$_3$)]OTf (**27**)	EtOH[a]	100	1.2	66	42
14	[Rh(**25**)(PPh$_3$)]OTf (**27**)	*i*PrOH[b]	100	2	46	45

[a] Acetophenone 2 M in EtOH, 1 mol-% KO*t*Bu. [b] Acetophenone 0.5 M in *i*PrOH, 1 mol-% KO*t*Bu.



Scheme 8. Allyl complex **28** from **16**. Numbers given in complex **28** are the labeling key for its NMR spectroscopic data.

usually bound ligand coordinating via the CO group of its ester moiety (see Scheme 7 and below), no or only insignificant activities were found (Entries 10–12). A small solvent effect on the *ee* was found for ethanol vs. 2-propanol. Against our hope, lower *ee* values are systematically obtained if ethanol is used as hydrogen donor when compared to reactions with 2-propanol. The reason for this poorer performance is not clear, but it may be that the higher dipole moment of ethanol lowers the energy difference between the two diastereoisomeric transition states leading to lower *ee* values.

X-ray Diffraction Studies

The structures of complexes **5**, **10**, **13**, **16** and **23** were determined by X-ray diffraction studies with suitable single crystals; the results are displayed in Figures 1, 2, 3, 4, and 5, respectively. Selected bond lengths and angles of these structures are given in Table 2. For comparison, the data of **2b**,**c** are also listed. Crystal data and refinement details are given in Table 5. The chlorido complex **5** and the triflato complex **10** crystallized with trigonal-bipyramidal structures. Complexes **13**, **16** and **23** adopt "saw-horse"-type structures similar to those observed for **2b** and **2c**.[3] Saw-horse (SH) structures may be viewed as trigonal pyramids with one missing ligand in the equatorial plane. In contrast to classical planar tetracoordinated 16-electron complexes, this feature makes SH complexes Lewis-acidic. In all structures the olefin ligands – the π-acceptors – are in the equatorial plane, and the two axial positions are occupied by the σ-donors, the amino group of the respective ligands and the phosphorus center of the additional phosphane ligand. Because of its extended π-system the trop ligand [comparable to a (*Z*)-stilbene] is a superior π-accepting olefin with a rigid concave structure. It is always in close contact to the metal atom as indicated by the distance between Rh and the centroid of the C4=C5$_{trop}$ bond, ct1. This distance is always shorter than the distance between Rh and the centroid ct2 of the other olefinic group CA=CB (see Table 2).[14] Only in **10** does the cyclohexenyl moiety of ligand **8** bind as well as the trop moiety. Due to steric reasons, the higher substituted olefinic non-trop units in ligands **4**, **12** and **15** bind more weakly. Furthermore, a rather unsymmetrical coordination mode is observed, that is, the distances to the highest substituted olefinic carbon centers are generally significantly longer (see Table 2), especially in **5** (Rh–CA) and **13** (Rh–CB). The longest Rh–ct2 bond [2.193(5) Å] was found for structure **5** (see Table 2), and indeed ligand **4** coordinates rather weakly and is easily displaced by strong donor ligands like phosphanes (vide supra). On the other hand, the range of Rh–ct1 distances previously found in the cationic complexes **2b** and **2c** is significantly shorter [2.040(3)–2.133(5) Å].[3,4]

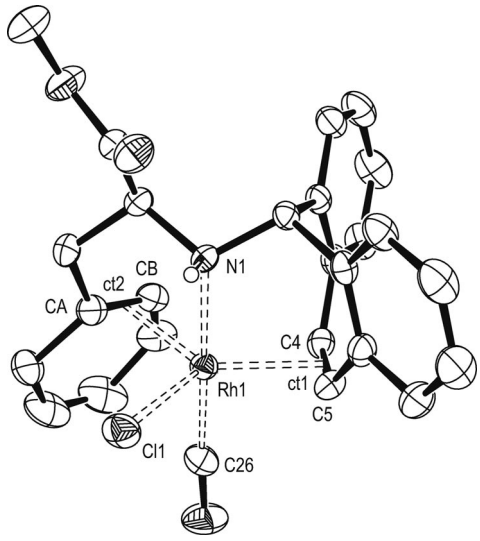


Figure 1. ORTEP plot (at 30% ellipsoid probability) of structure **5**. Carbon-bound hydrogen atoms and one solvent molecule are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid CA=CB): Rh1–N1 2.151(3), Rh1–C26 1.867(4), Rh1–Cl 2.526(3), Rh1–ct1 2.074(4), Rh1–ct2 2.193(5), Rh1–C4 2.176(5), Rh1–C5 2.212(5), Rh1–CA 2.321(5), Rh1–CB 2.282(5), C4=C5 1.430(6), CA=CB 1.396(7); N1–Rh1–C26 174.28(12), ct1–Rh1–ct2 129.18(18).

The ct1–Rh–ct2 angles of the trigonal-bipyramidal structures **5** [129.2(2)°] and **10** [135.1(1)°] are about 10–15° smaller than the ct1–Rh–ct2 angles found for the saw-horse structures **2b**,**c** [144.7(4)°, 145.5(5)], **13** [144.0(1)°] and **16** [143.6(1)°]. Interestingly, the ct1–Rh–ct2 angle of structure **23** [153.2(2)°] is 10° larger than the ct1–Rh–ct2 angles in **2b**,**c**, **13** and **16**, giving structure **23** a more planar character. This is due to the rigid nature of the bicyclo[2.2.2]octa-2,5-diene moiety. Whereas the angle N1–Rh–L (L = ligand *trans* to N1) is close to 180° for most structures, this angle is compressed to 162.8(1)° and 168.8(1)° in complexes **13** and **16**, respectively, due to the steric influence of the methyl group on the cyclohexenyl moiety. The two olefinic groups, C4=C5$_{trop}$ and CA=CB, do not coordinate in a parallel fashion to the metal center but deviate by the tilt angle θ form planarity (θ measures the interplanar angle of the Rh,C4,C5 and Rh,CA,CB planes; see Table 2). For structures **2b**,**c**, **5**, **10**, **13** and **16** the values for θ vary from 5 to 12°. Most distorted is clearly the structure **23** (θ = 21.1°; see also Figure 5), again likely due to the rigidity of the bicyclo[2.2.2]octa-2,5-diene moiety.

An interesting aspect of structure **10** is the hydrogen bond between one of the oxygen atoms of the triflate anion and the amine NH group. The N1–O2 distance of

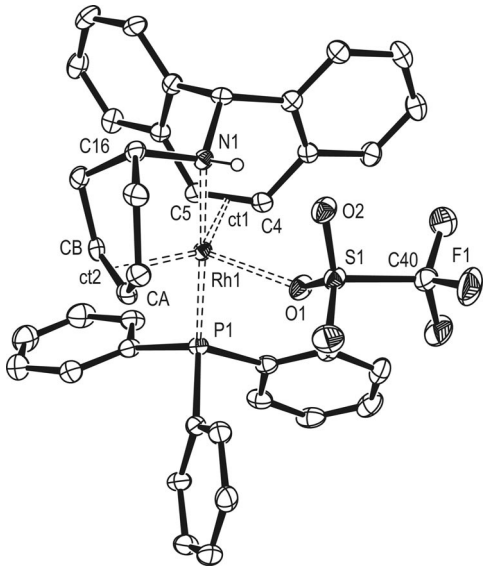


Figure 2. ORTEP plot (at 30% ellipsoid probability) of structure **10**. Carbon-bonded hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid CA=CB): Rh1–N1 2.135(3), Rh1–P1 2.075(4), Rh1–O1 2.347(3), Rh1–ct1 2.053(4), Rh1–ct2 2.075(4), Rh1–C4 2.182(4), Rh1–C5 2.161(4), Rh1–CA 2.210(4), Rh–CB 2.168(4), C4=C5 1.418(6), CA=CB 1.395(6), N1–O2 3.094(8); N1–Rh1–P1 177.62(9), ct1–Rh1–ct2 135.05(14).

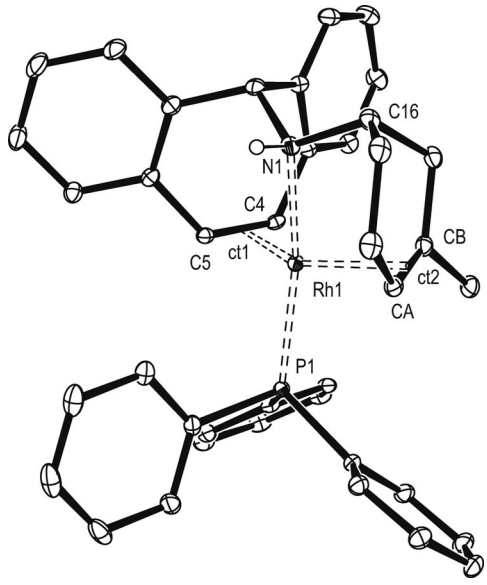


Figure 4. ORTEP plot (at 30% ellipsoid probability) of structure **16**. The noncoordinated anion, two thf molecules and carbon-bonded hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid CA=CB): Rh1–N1 2.1199(22), Rh1–P1 2.2815(7), Rh1–ct1 2.045(3), Rh1–ct2 2.128(3), Rh1–C4 2.151(3), Rh1–C5 2.177(3), Rh1–CA 2.230(3), Rh–CB 2.2450(3), C4=C5 1.418(4), CA=CB 1.385(4); N1–Rh1–P1 168.79(7), ct1–Rh1–ct2 143.59(11).

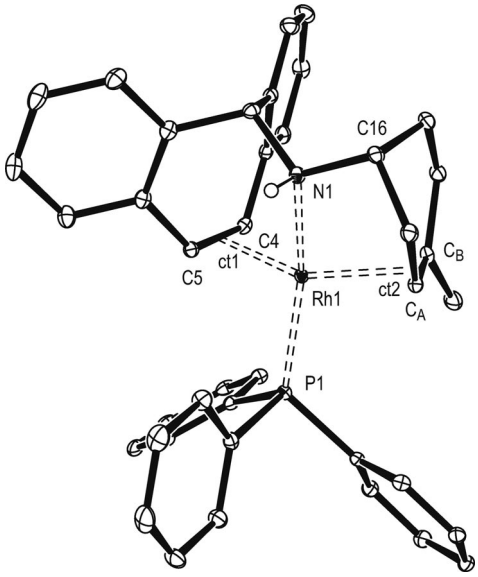


Figure 3. ORTEP plot (at 30% ellipsoid probability) of structure **13**. The noncoordinated anion and carbon-bonded hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid CA=CB): Rh1–N1 2.1069(15), Rh1–P1 2.2772(4), Rh1–ct1 2.026(2), Rh1–ct2 2.165(2), Rh1–C4 2.1277(17), Rh1–C5 2.1663(17), Rh1–CA 2.2129(17), Rh–CB 2.3317(18), C4=C5 1.420(3), CA=CB 1.383(3); N1–Rh1–P1 162.84(5), ct1–Rh1–ct2 143.98(7).

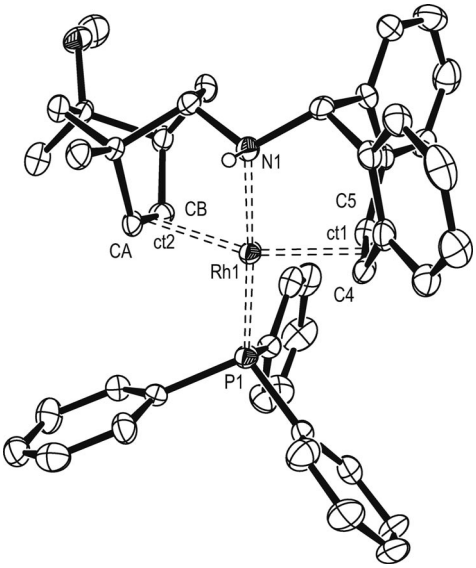


Figure 5. ORTEP plot (at 30% ellipsoid probability) of structure **23**. Carbon-bonded hydrogen atoms and the disordered triflate anion are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid CA=CB): Rh1–N1 2.114(4), Rh1–P1 2.2762(15), Rh1–ct1 2.073(5), Rh1–ct2 2.153(5), Rh1–C4 2.168(5), Rh1–C5 2.215(5), Rh1–CA 2.203(4), Rh–CB 2.320(6), C4=C5 1.418(8), CA=CB 1.393(7); N1–Rh1–P1 176.58(12), ct1–Rh1–ct2 153.22(21).

3.094(8) Å is in the typical range of a strong N–H–O hydrogen interaction. Remarkably, in both structures, **13** and **16**, the methyl group on the olefin is oriented away from the open side of the complex to the back of the saw-horse structure. In this position its influence on the stereochemical outcome of the catalytic reaction is very limited. We assume, however, that the energy difference between the two possible diastereoisomers is small. Specifically under basic

Table 2. Selected bond lengths [Å] and angles [°] from X-ray diffraction studies of [bis(olefin)amine]rhodium complexes.

Entry	Compound	Rh–ct1	Rh–C4	Rh–C5	Rh-ct2	Rh–CA	Rh–CB	ct1–Rh–ct2	N1–Rh–L[a]	θ
1	[Rh(trop$_2$NH)(PPh$_3$)]BArF (**2b**)	2.040(3)	2.180(2)	2.201(2)	2.075(3)	2.241(1)	2.247(2)	144.7(4)	173.1(2)	4.7(1)
2	[Rh(trop$_2$NH)(P(OPh)$_3$)]OTf (**2c**)	2.074(4)	2.191(2)	2.193(3)	2.133(5)	2.195(4)	2.189(4)	145.5(5)	170.1(4)	10.1(1)
3	[Rh(Cl)(**4**)(CO)] (**5**)	2.074(4)	2.176(5)	2.212(5)	2.193(5)	2.321(5)	2.282(5)	129.2(2)	174.3(1)	13.7(1)
4	[Rh(**8**)(PPh$_3$)]OTf (**10**)	2.053(4)	2.182(4)	2.161(4)	2.075(4)	2.210(4)	2.168(4)	135.1(1)	177.6(1)	10.6(1)
5	[Rh(**12**)(PPh$_3$)]OTf (**13**)	2.026(2)	2.128(2)	2.166(2)	2.165(2)	2.213(2)	2.332(2)	144.0(1)	162.8(1)	11.4(1)
6	[Rh(**15**)(PPh$_3$)]OTf (**16**)	2.045(3)	2.151(3)	2.177(3)	2.128(3)	2.230(3)	2.245(3)	143.6(1)	168.8(1)	12.3(1)
7	[Rh(**21**)(PPh$_3$)]OTf (**23**)	2.073(5)	2.168(5)	2.215(5)	2.153(5)	2.203(4)	2.320(6)	153.2(2)	176.6(1)	21.1(1)

[a] L = ligand *trans* to N1.

conditions, where the deprotonated forms, the amide or allyl complexes, are present in the reaction equilibria, inversion at the nitrogen atom and metal center can occur. In order to assign the relative stereochemistries observed in the solid-state structures of **10**, **13**, and **16** (see Table 3), the coordinated double bond is considered as a metallacyclopropane and its carbon atoms treated as pseudo-tetrahedral centers.[15] The configuration of the highest substituted carbon atom is then determined relative to the carbon atom in α-position to the nitrogen atom.

Table 3. Stereochemical assignment of **10**, **13** and **16**.

Compound	Relative stereochemistry[a]
[Rh(**8**)(PPh$_3$)]OTf (**10**)	*lk,like* $(S,S)/(R,R)^{C16,C19}$
[Rh(**12**)(PPh$_3$)]OTf (**13**)	*ul, unlike* $(R,S)/(S,R)^{C16,C20}$
[Rh(**15**)(PPh$_3$)]OTf (**16**)	*lk, like* $(S,S)/(R,R)^{C16,C19}$

[a] The superscripts correspond to the labels in the crystal structures.

NMR Spectroscopic Data

The coordination shifts $\Delta\delta = \delta_{free\ ligand} - \delta_{complex}$ of the resonances of the olefinic ^{13}C nuclei correlate well with the strength of the metal–olefin back bonding.[16] These data are listed in Table 4 for the complexes synthesized here (**6**, **10**, **13**, **16**, **22**, **23**, **26**, **27**, and **28**) in comparison with those of **2a**–**c**. An increasing positive $\Delta\delta$ value indicates a shift to lower frequency and increasingly tight metal–olefin interaction.

Table 4. Olefinic ^{13}C NMR coordination shift differences ($\Delta\delta$) of rhodium complexes.

Entry	Compound	$\Delta\delta$ C4	$\Delta\delta$ C5	$\Delta\delta$ CA	$\Delta\delta$ CB
1	[Rh(trop$_2$NH)(PPh$_3$)]OTf (**2a**)	57	57	–	–
2	[Rh(trop$_2$NH)(PPh3)]BArF (**2b**)	50	40	–	–
3	[Rh(trop$_2$NH)(P(OPh)$_3$)]OTf (**2c**)	50	50	–	–
4	[Rh(**4**)(CO)]OTf (**6**)	64	64	29	37
5	[Rh(**8**)(PPh$_3$)]OTf (**10**)	57	57	50	33
6	[Rh(**12**)(PPh$_3$)]OTf (**13**)	57	49	27	14
7	[Rh(**15**)(PPh$_3$)]OTf (**16**)	60	49	36	14
8	[Rh(**21**)(CO)]OTf (**22**)	51	51	36	36
9	[Rh(**21**)(PPh$_3$)]OTf (**23**)	49	44	33	27
10	[Rh(**25**)(CO)]OTf (**26**)	72	73	16	8
11	[Rh(**25**)(PPh$_3$)]OTf (**27**)	67	71	–0.6	–2.5
12	[Rh(**15**-H)(PPh$_3$)] (**28**)	3.5	3.5	–24	–36

The coordination shift differences confirm the trends in rhodium–olefin bond strengths deduced from the structural data of **5**, **10** and **23**. Short Rh–ct distances indicate tighter binding and remarkably in all complexes the trop moiety has the largest $\Delta\delta$ value. Clearly, the special structural preorganization and the superior π-accepting character make the trop unit an especially tightly bonded olefin ligand. Furthermore, the $\Delta\delta$ value of the two olefinic binding sites compensate each other: A small $\Delta\delta$ value of the CA=CB unit is counterbalanced by a large $\Delta\delta$ value of the $C{=}C_{trop}$ unit.

In good agreement with observations from the crystal structures, the cyclohexenyl moiety in **8** has the largest $\Delta\delta$ value of all non-trop moieties and therefore binds most strongly to the metal cation. The methyl-substituted cyclohexenyl moieties in ligands **12** and **15** bind less tightly to the rhodium cation. Not surprisingly, the doubly substituted olefinic carbon atoms of **4**, **12** and **15** have a significantly lower $\Delta\delta$ value in agreement with the observed longer C–Rh distances in the crystal structures. Ligands **12** and **15** show an especially small $\Delta\delta$ value (albeit not reflected in the Rh–ct2 distances), and the methyl-substituted cyclohexenyl moiety appears to be a weaker ligand. Based on $\Delta\delta$, ligand **4** seems to bind only slightly weaker than ligand **21** in the respective carbonyl complexes. As mentioned above, ligand **4** is readily displaced from complex **5** or **6** when a strong ligand like triphenylphosphane is added. For the complexes with the ligands **21** and **25** this is not observed, the carbonyl complexes **22** and **26** do not react immediately with triphenylphosphane, and starting from $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$, the triphenylphosphane complexes **23** and **27** are readily obtained. Due to its steric demand and its weak bonding, ligand **4** is only compatible with small additional ligands like CO (see Figure 1). The olefin moiety, CA=CB, in ligand **25** is an even weaker ligand for rhodium(I) than the one in ligand **21**, most likely because the methyl carboxylate moiety in **25** is sterically too demanding. Consequently, the $\Delta\delta$ value for the carbonyl complex **26** is quite small. Most remarkably, when the CO ligand in **26** is replaced by PPh_3, a de-coordination of the CA=CB moiety occurs, which is clearly indicated by the negative $\Delta\delta$ value observed for complex **27**. The carbonyl group of the ester moiety binds to the metal center instead, as is confirmed by NOESY NMR experiments. In the η^1-allyl complex **28** $\Delta\delta$ is small for the trop moiety. More importantly, CA and CB have a very large negative $\Delta\delta$ value as expected for an η^1-allyl complex.

Conclusions

The most successful ligand is clearly the bis(olefin)amine ligand **8**. The precursor complex **10** showed the best catalytic activity (up to 44% *ee* in short reaction times at S/C = 10000, Table 1, Entries 5–7). This is not much different from the previously obtained results with the bis(trop)-amine ligand, $trop_2NH$ (Table 1, Entries 1, 2).[3] The structure of **10** is very similar to **2a**–**c**, and the access to the rhodium center is sterically not blocked. The moderate *ee* values found with this precatalyst indicate that the energy difference between the two diastereoisomeric transition states is small. This is not surprising considering its structure (Figure 2). Complex **5** was found to be catalytically active, but lower reaction rates were observed (up to 58% *ee* at S/C = 1000, Table 1, Entries 3, 4). The electron-withdrawing CO ligand is likely responsible for that, and we do not exclude the possibility that the CO group itself interacts with the basic components in the reaction mixture (alcoholates), which would evidently lower the concentration of the intermediates in the catalytic cycle. The ligand **4** on this complex is rather flexible, which explains the observed moderate *ee* values. Complexes **13** and **16** of ligands bearing methyl-substituted cyclohexenyl moieties as well as complexes **22**, **23** and **26** of the ligands derived from unsaturated bicyclic amines showed only minimal activity in transfer hydrogenation. The second olefin moiety of these ligands is a weakly binding ligand and sterically demanding. We have evidence that the methyl group in the cyclohexenyl ligands **12** and **15** is easily deprotonated. The formation of catalytically inactive allyl complexes in deprotonation/protonation equilibria under the conditions employed for transfer hydrogenation not unexpectedly lowers the catalytic activity.[17] Furthermore, the methyl group on the CA=CB binding site in **13** and **16** is, at least in the solid state, oriented to the "wrong side" and in this position would only have a minor influence on the stereochemical outcome of the transfer hydrogenation. Interestingly, the triphenylphosphane complex **27** with the cyclohexenyl moiety not coordinated served as precursor to a mediocre catalyst, which is, however, more active for transfer hydrogenations than **23** (see Table 1, Entries 13, 14). The reason for that is unclear, but possibly the reaction proceeds by another mechanism than the one depicted in Scheme 1, which is assumed to be operative with the amides derived from complexes **2a**–**c**.

Our results indicate that very active transfer hydrogenation catalysts with rhodium(I) and a bis(olefin)amine ligand can be obtained with C=C binding sites firmly bound to the metal center. In addition, a phosphane ligand in one of the axial positions opposite to the NH function has a positive impact on the catalyst's performance. As a consequence, trigonal-bipyramid (TP) or saw-horse (SH) type structures result, which we believe are crucial for high activities. Note, that a related complex, where a TP or SH structure is impeded by steric constraints in the ligand backbone and a planar structure is enforced, is inactive.[18]

Of the four bis(olefin)amine ligand types studied here for asymmetric transfer hydrogenation, the cyclohexenyl moiety is the most promising. However, methyl substitution at the C=C binding sites must be avoided. As a result, complex **10** performed well and proved to be a notably stable catalyst. Turnover numbers of up to 400000 were observed at S/C = 10^6 after 48 h. The more substituted bicyclic amines turned out to be problematic for the catalytic reaction, most likely because they are too rigid and perhaps also sterically to demanding.

Experimental Section

General Techniques: All manipulations of air- or moisture-sensitive compounds were performed in flame-dried flasks under argon by using a standard vacuum line. Air-sensitive compounds were stored and weighted in a glovebox (M Braun: lab master 130 or 150B-G). Reactions in small quantities were performed within a glovebox.

Chemicals: Solvents were distilled under argon from sodium/benzophenone (thf, diethyl ether), sodium/benzophenone/tetraglyme (*n*-hexane, dme) or calcium hydride (dcm). The following organic compounds and metal precursors were prepared according to literature methods: tropCl,[19] $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$,[20] $[Rh_2(\mu_2\text{-}Cl)_2(COD)_2]$,[21] $[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$,[22] (2*S*)-2-amino-3-cyclohexa-1,4-dien-1-yl propanoate (**3**),[6] cyclohex-3-en-1-ylamine hydrochloride (**7**),[7] $tropNH_2$,[23] 4-methylcyclohex-3-en-1-one (**11**) and 3-methylcyclohex-3-en-1-one (**14**),[8] (1*S*,4*S*,8*R*)-8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-one (**17**).[11]

Physical and Analytical Measurements: NMR spectra were recorded with Bruker Avance 700, 500, 400 and 300 spectrometers. The chemical shifts (δ) are measured according to IUPAC[24] and expressed in ppm relative to tms, $CFCl_3$, H_3PO_4, and $Rh(acac)_3$ for ^1H, ^2H, ^{13}C, ^{19}F, ^{31}P and ^{103}Rh respectively. Coupling constants *J* are given in Hertz [Hz] as absolute values, unless specifically stated. The multiplicity of the signals is indicated as s, d, t, q, or m for singlets, doublets, triplets, quartets, or multiplets, respectively. The abbreviation br. is given for broadened signals. Quaternary carbon atoms are indicated as C^{quart}, aromatic units as CH^{ar} and CH^{ar} when not noted otherwise. The small numbers in Schemes 2, 3, 4, 5, 6, and 7 indicate the detailed numbering key for the NMR spectroscopic data of the corresponding compounds. The olefinic protons and carbon atoms of the $C{=}C^{trop}$ unit in the central seven-membered ring are indicated as CH^{olefin} and CH^{olefin}. The benzylic protons and carbon atom in the central seven-membered ring are indicated as CH^{benzyl} and CH^{benzyl}. The seven-membered ring in the trop unit can adopt two conformations, which are, if they can be distinguished in the NMR spectra, listed separately as *exo* and *endo* conformers. IR spectra were recorded with a Perkin–Elmer Spectrum 2000 FT-IR-Raman spectrometer with KBr beam splitter (range 500–4000 cm^{-1}). For solid compounds the ATR technique was applied. The absorption bands are described as follows: very strong (vs), strong (s), medium (m), weak (w), or broad (br.). Optical rotation was measured at 589 nm (Na/Hal) and room temperature (22 °C) with a Perkin–Elmer 341 polarimeter by using a 10 cm cell and a concentration of 1 mg/1 mL (c = 1.0) in the given solvent where not stated otherwise. Gas chromatography was performed with a Hewlett Packard HP 6890 Series GC system equipped with an EPC split splitless injector, H_2 as carrier gas and a flame ionization detector. Experimental details of the separation into pure enantiomers for **8** is given below, in the experimental part of the compound. High-resolution MALDI MS was measured by the mass spectroscopy service of ETH Zürich. Elemental analyses were

Table 5. Crystal data and summary of data collection and refinement details for **5**, **10**, **13**, **16** and **23**.

	5	**10**	**13**	**16**	**23**
Empirical formula	$C_{26}H_{24}ClNO_3Rh{\cdot}CH_2Cl_2$	$C_{40}H_{36}F_3NO_3PRhS{\cdot}CH_2Cl_2$	$C_{41}H_{38}F_3NO_3PRhS$	$C_{44}H_{46}F_3NO_3PRhS{\cdot}2C_2H_4O$	$C_{45}H_{44}F_3NO_4PRhS$
Formula mass	621.75	886.56	815.90	959.90	885.76
T [K]	298(2)	200(2)	100(2)	100(2)	293(2)
Crystal system	monoclinic	triclinic	tetragonal	monoclinic	orthorhombic
Space group	$P2(1)$	$P\bar{1}$	$I41/a$	$P21/c$	$P2(1)2(1)2(1)$
a [Å]	8.909(10)	10.5178(9)	37.1992(6)	16.1780(12)	9.5792(5)
b [Å]	15.030(17)	14.1050(12)	37.1992(6)	13.5047(10)	18.372(4)
c [Å]	10.475(11)	14.5010(12)	10.3140(3)	20.9085(15)	24.792(8)
α [°]	90	64.3720(10)	90	90	90
β [°]	94.50(2)	82.892(2)	90	104.1330(10)	90
γ [°]	90	78.926(2)	90	90	90
V [Å^3]	1398(3)	1901.5(3)	14272.3(5)	4429.8(6)	4363.3(16)
Z	2	2	16	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.477	1.548	1.518	1.439	1.349
Crystal size [mm]	0.29 × 0.29 × 0.12	0.48 × 0.23 × 0.07	0.28 × 0.19 × 0.15	0.26 × 0.23 × 0.10	0.27 × 0.24 × 0.11
$2\theta_{max}$ [°]	56.04	52.76	56.60	56.62	68.84
N_{tot}	11361	17067	72422	44796	43321
N (R_{int})	5919 (0.0190)	7744 (0.0459)	8868 (0.0441)	10990 (0.0333)	17012 (0.0846)
Final R indices	R_1 = 0.0303,	R_1 = 0.0516,	R_1 = 0.0310,	R_1 = 0.0475,	R_1 = 0.0501,
[$I > 2\sigma(I)$]	wR_2 = 0.0783	wR_2 = 0.1019	wR_2 = 0.0724	wR_2 = 0.1193	wR_2 = 0.1428
R indices	R_1 = 0.0352,	R_1 = 0.0616,	R_1 = 0.0346,	R_1 = 0.0546,	R_1 = 0.1534,
(all data)	wR_2 = 0.0812	wR_2 = 0.1067	wR_2 = 0.0742	wR_2 = 0.1242	wR_2 = 0.1500

performed by the microanalytical laboratory of the ETH Zürich. X-ray diffraction was measured with an Oxford XCalibur or a Bruker SMART Apex diffractometer with CCD area detector. Structures were refined by direct methods against full matrix (versus F^2) using Bruker AXS SHELXTL 6.14 sofware. Details are listed in Table 5. CCDC-718261 (**5**), -718097 (**10**), -723520 (**13**), -723657 (**16**) and -718036 (**23**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Catalysis. Ethanol: A 2 M solution of the substrate in dry ethanol was prepared in a Schlenk tube under argon. The catalyst was added as solid under a stream of argon. Then 1 mol-% KO*t*Bu was added under a stream of argon. The reaction was monitored by NMR spectroscopy by taking samples periodically. **2-Propanol:** A 0.5 M solution of the substrate in dry 2-propanol was prepared in a Schlenk tube under argon. The catalyst was added either as solid or as solution in thf or 2-propanol. For low catalyst loadings (>0.1 mol-%) the solution was degassed by three pump-freeze-thaw cycles. Then 1 mol-% of the base (K_2CO_3 or KO*t*Bu) was added under a stream of argon. The reaction was monitored by NMR spectroscopy or GC by taking samples periodically. **Separation of (*R*)-, (*S*)-1-Phenylethanol and Acetophenone:** Column: Machery & Nagel Lipodex E (25 m × 0.32 mm × 0.25 μm), carrier gas: H_2, temperature: 1 min 70 °C then 1 °C/min to 110 °C, H_2 pressure: 0.50 bar, retention times: acetophenone: 26.0 min, (*S*)-1-phenylethanol 31.0 min, (*S*)-1-phenylethanol 31.7 min.

Methyl (2*S*)-3-(Cyclohexa-1,4-dienyl)-2-(5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylamino)propionate (4): Methyl (2*S*)-2-amino-3-cyclohexa-1,4-dien-1-ylpropanoate (**3**) (7.0 g, 32 mmol, 1 equiv.) was suspended in dcm (100 mL), and triethylamine (9 mL, 64 mmol, 2 equiv.) was added. After stirring for 30 min, tropCl (7.3 g, 32 mmol, 1 equiv.) was added. Stirring was continued for 2 h, and the reaction mixture was washed with water (3 × 100 mL) and dried with $MgSO_4$. The solvent was removed in vacuo yielding a yellow oil. The product was purified by flash chromatography (ethyl acetate/*n*-hexane, 1:4). Yield: 93%, 11 g, 30 mmol as off-white solid. M.p. 68–71 °C. $[\alpha]_D^{22}$ = –45.3 (c = 0.1, CH_2Cl_2). *endo*/*exo* = 9:1. *endo* conformer: ^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.87 (dt, $^2J_{HH}$ = 22.0, $^3J_{HH}$ = 8.0 Hz, 1 H, CH_2^6), 2.15 (dd, $^2J_{HH}$ = 13.3, $^3J_{HH}$ = 10.8 Hz, 1 H, CH_2^3), 2.23 (dd, $^2J_{HH}$ = 13.3, $^3J_{HH}$ = 3.6 Hz, 1 H, CH_2^3), 2.25 (m, 1 H, CH_2^6), 2.59 (br., 1 H, N*H*), 2.71 (m, 2 H, CH_2^9), 2.99 (dd, $^3J_{HH}$ = 10.7, $^3J_{HH}$ = 4.6 Hz, 1 H, CH^2), 3.73 (s, 3 H, OCH_3), 4.88 (s, 1 H, CH^{benzyl}), 5.39 (br. s, 1 H, CH^5), 5.61 (m, 1 H, CH^8), 5.73 (m, 1 H, CH^7), 6.95 (d, $^3J_{HH}$ = 11.9 Hz, 1 H, CH^{olefin}), 6.99 (d, $^3J_{HH}$ = 11.9 Hz, 1 H, CH^{olefin}), 7.27–7.40 (m, 7 H, CH^{ar}), 7.46 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, CH^{ar}) ppm. ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$): δ = 26.9 (s, 1 C, CH_2^9), 27.7 (s, 1 C, CH_2^6), 41.1 (s, 1 C, CH_2^3), 51.8 (s, 1 C, OCH_3), 55.2 (s, 1 C, CH^2), 67.5 (s, 1 C, CH^{benzyl}), 123.3 (s, 1 C, CH^5), 123.6 (s, 1 C, CH^7), 124.1 (s, 1 C, CH^8), 127.1 (s, 1 C, CH^{ar}), 127.2 (s, 1 C, CH^{ar}), 128.2 (s, 1 C, CH^{ar}), 129.0 (s, 1 C, CH^{ar}), 129.4 (s, 1 C, CH^{ar}), 129.8 (s, 1 C, CH^{ar}), 129.9 (s, 1 C, CH^{ar}), 130.1 (s, 1 C, CH^{ar}), 130.2 (s, 1 C, CH^{olefin}), 130.4 (s, 1 C, C^4), 130.5 (s, 1 C, CH^{olefin}), 133.5 (s, 1 C, C^{quart}), 133.5 (s, 1 C, C^{quart}), 139.0 (s, 1 C, C^{quart}), 139.4 (s, 1 C, C^{quart}), 174.7 (s, 1 C, C^1) ppm. *exo* conformer: ^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.87 (m, 1 H, CH_2^6), 2.27 (m, 1 H, CH_2^6), 2.47 (m, 1 H, CH_2^3), 2.52 (m, 1 H, CH_2^3), 2.59 (s, 1 H, N*H*), 2.71 (m, 1 H, CH_2^9), 2.78 (m, 1 H, CH_2^9), 3.58 (m, 1 H, CH^2), 3.62 (s, 3 H, OCH_3), 4.06 (s, 1 H, CH^{benzyl}), 5.67 (br. s, 1 H, CH^5), 5.76 (m, 2 H, CH^{7,8}), 7.21 (m, 2 H, CH^{olefin}), 7.35 (m, 6 H, CH^{ar}), 7.63 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, CH^{ar}), 7.69 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, CH^{ar}) ppm. ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$): δ = 27.0 (s, 1 C, CH_2^6), 29.4 (s, 1 C, CH_2^9), 42.3 (s, 1 C, CH_2^3), 51.6 (s, 1 C, CH^2), 57.9 (s, 1 C, OCH_3), 58.8 (s, 1 C, CH^{benzyl}), 121.6 (s, 1 C, CH^{ar}), 122.6 (s, 1 C, CH^{ar}), 122.6 (s, 1 C, CH^5), 124.0 (s, 1 C, CH^7) 124.1 (s, 1 C, CH^8), 125.6 (s, 1 C, CH^{ar}), 125.6 (s, 1 C, CH^{ar}), 127.6 (s, 1 C, CH^{ar}), 127.7 (s, 1 C, CH^{ar}), 128.5 (s, 1 C, CH^{ar}), 128.6 (s, 1 C, CH^{ar}), 131.0 (s, 1 C, CH^{olefin}), 131.1 (s, 1 C, CH^{olefin}), 131.2 (s, 1 C, C^4), 133.5 (s, 1 C, C^{quart}), 134.1 (s, 1 C, C^{quart}), 139.3 (s, 1 C, C^{quart}), 140.2 (s, 1 C, C^{quart}), 175.6 (s, 1 C, C^1) ppm. ATR IR: $\tilde{\nu}$ = 3301 (w, NH), 3027 (w, CH), 2820 (w, CH), 1736 (s, CO), 1493 (w), 1464 (w), 1431 (w), 1359 (w), 1328 (w), 1286 (m), 1269 (m), 1212 (s), 1201 (m), 1189 (m), 1170 (s), 1151 (m), 1098 (m), 1080 (m), 1031 (s), 984 (m), 963 (m), 878 (m), 833 (m), 803 (s), 772 (s), 763 (m), 736 (s), 722 (m), 702 (m), 684 (m), 668 (s) cm^{-1}. $C_{25}H_{25}NO_2$ (371.47): calcd. C 80.83, H 6.78, N 3.77; found C 80.67, H 6.84, N 3.79.

[Rh(Cl)(CO)(4)] (5): $[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ (200 mg, 0.51 mmol, 1 equiv.) was dissolved in thf (1 mL) under argon, and **4** (420 mg, 1.3 mmol, 2.2 equiv.) was added. The solution was stirred for 2 h and layered with *n*-hexane. A yellow, air-stable, crystalline material was obtained. Yield: 86%, 449 mg, 0.88 mmol. M.p. 108–111 °C (dec). $[\alpha]_D^{22}$ = –108.0 (*c* = 0.1, CH_2Cl_2). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 2.50 (dd, $^2J_{HH}$ = 15.4, $^3J_{HH}$ = 3.2 Hz, 1 H, CH_2^3), 2.67 (m, 1 H, CH_2^6), 2.70 (t, $^2J_{HH}$ = 14.5 Hz, 1 H, CH_2^3), 2.80 (m, 1 H, CH_2^9) 2.87 (m, 1 H, CH_2^9), 2.93 (td, $^2J_{HH}$ = 13.0, $^3J_{HH}$ = 4.0 Hz, 1 H, CH^2), 3.42 (m, 1 H, CH_2^6), 3.87 (s, 3 H, OCH_3), 3.92 (br. s, 1 H, CH^5), 4.45 (s, 1 H, N*H*), 4.46 (s, 1 H, CH^{benzyl}), 5.25 (dd, $^3J_{HH}$ = 9.2, $^2J_{RhH}$ = 2.1 Hz, 1 H, CH^{olefin}), 5.28 (dd, $^3J_{HH}$ = 9.0, $^2J_{RhH}$ = 2.00 Hz, 1 H, CH^{olefin}), 5.74 (dd, $^3J_{HH}$ = 7.3, $^3J_{HH}$ = 2.8 Hz, 1 H, CH^7) 5.84 (dd, $^3J_{HH}$ = 10.0, $^3J_{HH}$ = 2.1 Hz, 1 H, CH^8), 7.22 (t, $^3J_{HH}$ = 6.4 Hz, 2 H, CH^{ar}), 7.28 (td, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.2 Hz, 1 H, CH^{ar}), 7.33 (td, $^3J_{HH}$ = 7.5, $^3J_{HH}$ = 1.2 Hz, 1 H, CH^{ar}), 7.40 (dt, $^3J_{HH}$ = 7.5, $^3J_{HH}$ = 1.2 Hz, 1 H, CH^{ar}), 7.45 (td, $^3J_{HH}$ = 7.6, $^3J_{HH}$ = 1.2 Hz, 1 H, CH^{ar}), 7.64 (t, $^3J_{HH}$ = 6.6 Hz, 2 H, CH^{ar}) ppm. ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$): δ = 29.6 (s, 1 C, CH_2^9), 30.9 (s, 1 C, CH_2^6), 38.2 (s, 1 C, CH_2^3), 53.1 (s, 1 C, OCH_3), 56.6 (s, 1 C, CH^2), 61.1 (d, $^1J_{RhC}$ = 11.3 Hz, 1 C, CH^{olefin}), 63.7 (d, $^1J_{RhC}$ = 8.6 Hz, 1 C, CH^{olefin}), 66.7 (s, 1 C, CH^{benzyl}), 78.7 (d, $^1J_{RhC}$ = 8.6 Hz, 1 C, CH^5), 98.0 (d, $^1J_{RhC}$ = 4.8 Hz, 1 C, C^4), 123.4 (s, 1 C, CH^7), 125.8 (s, 1 C, CH^8), 126.6 (s, 1 C, CH^{ar}), 126.8 (s, 1 C, CH^{ar}), 127.8 (s, 1 C, CH^{ar}), 128.7 (s, 1 C, CH^{ar}), 129.2 (s, 1 C, CH^{ar}), 129.3 (s, 1 C, CH^{ar}), 129.6 (s, 1 C, CH^{ar}), 129.8 (s, 1 C, CH^{ar}), 133.4 (s, 1 C, C^{quart}), 134.4 (s, 1 C, C^{quart}), 137.6 (s, 1 C, C^{quart}), 138.1 (d, $^2J_{RhC}$ = 1.3 Hz, 1 C, C^{quart}), 171.1 (s, 1 C, C^1), 186.2 (*d*, $^1J_{RhH}$ = 64.1 Hz, 1 C, CO) ppm. ATR IR: $\tilde{\nu}$ = 3170 (w, NH), 3043 (w, CH), 2899 (w, CH), 2032 (m, CO), 1738 (s, CO), 1602 (w), 1490 (m), 1471 (m), 1432 (m), 1397 (w), 1360 (m), 1348 (m), 1329 (m), 1269 (m), 1248 (m), 1217 (s), 1191 (m), 1163 (m), 1098 (m), 1075 (w), 1056 (m), 1034.36 (s), 1009 (m), 978 (m), 946 (m), 922 (m), 905 (m), 894 (m), 868 (m), 843 (m), 818 (w), 773 (s), 763 (s), 747 (m), 712 (m), 660 (m) cm^{-1}. $C_{26}H_{25}ClNO_3Rh$ (537.84): calcd. C 58.06, H 4.68, N 2.60; found C 57.92, H 4.72, N 2.61.

[Rh(CO)(4)]OTf (6): [Rh(Cl)(CO)(**4**)] (**5**) (421 mg, 0.83 mmol, 1 equiv.) and AgOTf (223 mg, 0.91 mmol, 1.1 equiv.) were dissolved in dcm (20 mL). The reaction mixture was stirred for 12 h and then filtered through Celite. The yellow dcm solution was concentrated to 5 mL under reduced pressure. The solution was layered with hexane, and the product was obtained as air-sensitive yellow powder. Yield: 89%, 478 mg, 0.73 mmol. M.p. 162–165 °C (dec). $[\alpha]_D^{22}$ = –143.7 (*c* = 0.1, CH_2Cl_2). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 2.53 (dd, $^2J_{HH}$ = 15.6, $^3J_{HH}$ = 13.4 Hz, 1 H, CH_2^3), 2.67 (m, 1 H, CH_2^3), 2.72 (m, 2 H, CH_2^9), 2.73 (m, 1 H, CH_2^6), 3.11 (dt, $^3J_{HH}$ = 12.5, $^3J_{HH}$ = 3.7 Hz, 1 H, CH^2), 3.26 (m, 1 H, CH_2^6), 3.90 (s, 3 H, OCH_3), 4.47 (br., 1 H, N*H*), 4.48 (br., 1 H, 1 H, CH^5), 4.65 (s, 1 H, CH^{benzyl}), 5.47 (dd, $^3J_{HH}$ = 9.0, $^2J_{RhH}$ = 1.0 Hz, 1 H, CH^{olefin}), 5.76 (dd, $^3J_{HH}$ = 9.0, $^2J_{RhH}$ = 2.8 Hz, 1 H, CH^{olefin}), 5.80 (m, 1 H, CH^7), 5.92 (m, 1 H, CH^8), 7.29 (dt, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.8 Hz, 2 H, CH^{ar}), 7.36 (td, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.1 Hz, 1 H, CH^{ar}) 7.42–7.49 (m, 3 H, CH^{ar}) 7.67 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, CH^{ar}) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ = 30.4 (s, 1 C, CH_2^9), 31.0 (s, 1 C, CH_2^6), 38.4 (s, 1 C, CH_2^3), 53.7 (s, 1 C, OCH_3), 57.3 (s, 1 C, CH^2), 67.4 (s, 1 C, CH^{benzyl}), 67.5 (m, 1 C, CH^{olefin}), 67.5 (m, 1 C, CH^{olefin}), 85.4 (m, 1 C, CH^5), 102.3 (m, 1 C, C^4), 120.4 (q, $^1J_{CF}$ = 320.1 Hz, 1 C, CF_3), 123.8 (s, 1 C, CH^7), 126.1 (s, 1 C, CH^8), 127.9 (s, 1 C, CH^{ar}), 128.1 (s, 1 C, CH^{ar}), 128.4 (s, 1 C, CH^{ar}), 129.2 (s, 1 C, CH^{ar}), 129.7 (s, 1 C, CH^{ar}), 130.5 (s, 1 C, CH^{ar}), 130.6 (s, 1 C, CH^{ar}), 130.7 (s, 1 C, CH^{ar}), 134.7 (s, 1 C, C^{quart}) 134.7 (d, $^2J_{RhC}$ = 1.4 Hz, 1 C, C^{quart}) 136.1 (s, 1 C, C^{quart}), 137.0 (d, $^2J_{RhC}$ = 1.9 Hz, 1 C, C^{quart}), 170.9 (s, 1 C, C^1), 185.8 (d, $^1J_{RhC}$ = 65.7 Hz, 1 C, C*O*) ppm. ^{103}Rh NMR (15.8 MHz, CD_2Cl_2): δ = –7201 ppm. ATR IR: $\tilde{\nu}$ = 3170 (w, NH), 2899 (w, CH), 2032 (m, CO), 1737 (s, CO), 1602 (w), 1491 (w), 1471 (w), 1432 (m), 1397 (w), 1361 (w), 1329 (m), 1309 (m), 1275 (m), 1248 (m), 1207 (s), 1159 (m), 1098 (m), 1057 (m), 1034 (s), 978 (m), 946 (w), 921 (m), 905 (m), 867 (m), 844 (w), 818 (w), 773 (s), 761 (s), 711 (m), 660 (m) cm^{-1}. $C_{27}H_{25}F_3NO_6RhS{\cdot}thf_{0.4}$ (713.96): calcd. C 52.15, H 4.66, N 1.96; found C 52.11, H 4.71, N 1.90.

***N*-(Cyclohex-3′-en-1′-yl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylamine (8):** Cyclohex-3-en-1-ylamine hydrochloride (**7**) (1 g, 7.48 mmol, 1 equiv.) was suspended in dry dcm (20 mL). Triethylamine (8 mL, 57 mmol, 7 equiv.) was added and the mixture cooled to 0 °C; tropCl (1.86 g, 8.23 mmol, 1.1 equiv.) was added and the mixture stirred overnight. A white solid precipitated. The organic phase was washed with a saturated $NaHCO_3$ solution and dried with Na_2SO_4. The product was purified by flash chromatography on silica gel with dcm. Yield: 69%, 1.48 g, 5.15 mmol.

Analytical HPLC: Separation of enantiomers was successful with an Agilent 1100 series HPLC using a Chiralcel OJ column, *n*-hexane/2-propanol (80:20), 1 mL/min. Retention time: enantiomer A: 18.3 min, enantiomer B: 26.7 min.

Preparative HPLC: The product (50 mg) was separated by preparative HPLC [Gilson (306 pump, 156 UV/Vis detector, automatic sample collector), Diacel Chiralcel OJ column, *n*-hexane/2-propanol (85:15), 15 mL/min]. Retention time: enantiomer A: 18.3 min, enantiomer B: 29.7 min. Enantiomeric purity was checked by analytical HPLC; it was >99% for both enantiomers. Yield of the separation: enantiomer A: 44%, 22 mg, enantiomer B: 32%, 17 mg, both as colorless oils. In order to obtain reasonable amounts of enantiomeric purity, the separation was repeated several times. M.p. 88 °C. Enantiomer A: $[\alpha]_D^{22}$ = +37.8 (*c* = 0.1, CH_2Cl_2). Enantiomer B: $[\alpha]_D^{22}$ = –38.0 (*c* = 0.1, CH_2Cl_2). *endo*/*exo* (9:1). *endo* conformer: ^{1}H NMR (400 MHz, $CDCl_3$, 223K): δ = 1.2–1.5 (m, 1 H, CH_2), 1.7–2.2 (m, 4 H, CH_2), 2.3–2.5 (m, 1 H, CH_2), 2.83 (br. s, 1 H, N*H*), 4.36 (s, 1 H, C*H*NH), 5.03 (s, 1 H, CH^{benzyl}), 5.56 (m, 2 H, C^3 and C^4), 7.09 (s, 2 H, CH^{olefin}), 7.2–7.7 (m, 8 H, CH^{ar}) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 223K): δ = 25.1 (s, 1 C, CH_2), 29.3 (s, 1 C, CH_2), 32.4 (s, 1 C, CH_2), 49.5 (s, 1 C, CHNH), 65.4 (s, 1 C, CH^{benzyl}), 125.5 (s, 1 C, CH^3), 127.5 (s, 1 C, CH^4), 127.6 (s, 1 C, CH^{ar}), 127.6 (s, 1 C, CH^{ar}), 129.4 (s, 1 C, CH^{ar}), 129.5 (s, 1 C, CH^{ar}), 130.0 (s, 1 C, CH^{ar}), 130.0 (s, 1 C, CH^{ar}), 130.5 (s, 1 C, CH^{ar}) 130.5 (s, 1 C, CH^{ar}), 131.0 (s, 2 C, CH^{olefin}), 133.3 (s, 1 C, C^{quart}), 133.4 (s, 1 C, C^{quart}), 139.7 (s, 1 C, C^{quart}), 139.9 (s, 1 C, C^{quart}) ppm. *exo* conformer: ^{1}H NMR (400 MHz, $CDCl_3$, 223K): δ = 1.2–1.5 (m, 1 H, CH_2), 1.7–2.2 (m, 4 H, CH_2), 2.3–2.5 (m, 1 H, CH_2), 2.83 (br. s, 1 H, N*H*), 4.36 (s, 1 H, C*H*NH), 5.06 (s, 1 H, CH^{benzyl}), 5.63 (m, 2 H, CH^{olefin}), 7.19 (s, 2 H, CH^{olefin}), 7.2–7.7 (m, 8 H, CH^{ar}) ppm. MS (EI): *m*/*z* (%) = 54.1 (40), 79.1 (15), 81.1 (15), 165.0 (20) 191.1 (100) [trop$^+$], 287.2 (8) [M$^+$]. ATR IR: $\tilde{\nu}$ = 3022 (w), 2914 (w), 2817 (w), 1653 (w), 1483 (w), 1449 (w), 1432 (w), 1389 (w), 1355 (w), 1265 (w), 1199 (w), 1155 (w), 1127 (w), 1101 (m), 1038 (m), 953 (w), 931 (w), 873 (m), 853 (w), 835 (m), 797 (s), 768 (m), 748 (s), 733 (s), 696 (m), 654 (m), 636 (m), 606 (m) cm^{-1}. $C_{21}H_{21}N$ (287.40): calcd. C 87.48, H 7.36, N 4.87; found C 87.48, H 7.41, N 4.84.

[Rh(Cl)(8)(PPh$_3$)] (9): $[Rh_2(\mu_2\text{-}Cl)_2(COD)_2]$ (380 mg, 0.77 mmol, 1 equiv.) and **8** (446 mg, 1.55 mmol, 2.02 equiv.) were dissolved in dcm (5 mL) under argon. Over the course of 72 h a red solid precipitated. The mother liquor was decanted and the solid dried in high vacuum to yield a very insoluble substance assumed to be the (crude) dimer $[Rh_2(\mu_2\text{-}Cl)_2(\mathbf{8})_2]$ (605 mg, 1.42 mmol, 0.92 equiv.). To a suspension of $[Rh_2(\mu_2\text{-}Cl)_2(\mathbf{8})_2]$ (605 mg, 0.7 mmol, 1 equiv.)

in dcm (4 mL) PPh_3 (390 mg, 1.48 mmol, 2.1 equiv.) was added, and an orange solution formed after 10 min. Addition of *n*-hexane precipitated the orange-red, air-stable product complex [Rh(Cl)(cyhtropNH)(PPh_3)], which was isolated by filtration followed by drying under vacuum. Yield: 84%, 893 mg, 1.3 mmol. M.p. >230 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.38 (m, 1 H, C*H*^{6}), 0.46 (m, 1 H, C*H*^{2}), 0.90 (m, 1 H, C*H*^{2}), 1.00 (m, 1 H, N*H*), 1.19 (m, 1 H, C*H*^{6}), 2.16 (m, 1 H, C*H*^{1}), 2.2 (m, 1 H, C*H*^{5}), 2.3 (m, 1 H, C*H*^{5}), 4.06 (m, 1 H, C*H*^{benzyl}), 4.70 (t, J = 8.5 Hz, 1 H, C*H*^{olefin}), 4.75 (m, 1 H, C*H*$_4$), 4.95 (m, 1 H, C*H*$_3$), 5.50 (m, 1 H, C*H*^{olefin}), 6.10–6.20 (m, 3 H, C*H*^{ar}), 6.86–7.38 (m, 15 H, C*H*^{ar}), 7.60–8.04 (m, 5 H, C*H*^{ar}) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 20.1 (d, J = 8.3 Hz, 1 C, *C*H^5), 28.1 (s, 1 C, *C*H^6), 29.4 (d, J = 3.6 Hz 1 C, *C*H ^{2}), 60.0 (d, J = 2.7 Hz, 1 C, *C*H^1), 65.8 (dd, J = 8.2, J = 5.9 Hz, 1 C, *C*H^{olefin}), 67.3 (dd, J = 8.7, J = 6.9 Hz, 1 C, *C*H^4), 69.5 (dd, J = 20.8, J = 9.4 Hz, 1 C, *C*H^{olefin}), 71.1 (dd, J = 16.0, J = 9.1 Hz,1 C, *C*H^3), 71.6 (s, 1 C, CH^{benzyl}), 123.9–140.2 (m, 30 C, *C*H^{ar} and *C*^{quart}) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 10.6 (d, $^1J_{RhP}$ = 112.6 Hz) ppm. ATR IR: $\tilde{\nu}$ = 3220 (w), 3045 (w), 2837 (w), 2360 (w), 2160 (w), 1977 (w), 1597 (w), 1470 (w), 1433 (m), 1090 (m), 977 (w), 876 (w), 750 (s), 696 (s), 621 (m) cm^{-1}. $C_{39}H_{36}ClNPRh\cdot(CH_2Cl_2)_{0.2}$ (688.04): calcd. C 66.78, H 5.20, N 1.99; found C 67.20, H 5.29, N 1.99.

[Rh(8)(PPh_3)]OTf (10): [Rh(Cl)(**8**)(PPh_3)] (**9**) (315 mg, 0.46 mmol, 1 equiv.) and AgOTf (124 mg, 0.48 mmol, 1.05 equiv.) were suspended in dcm (5 mL) and stirred under argon for 12 h. The solution was filtered through Celite. The solution was concentrated and layered with *n*-hexane, yielding orange-red crystals of the product. Yield: 90%, 112 mg, 0.13 mmol as air-stable orange solid. M.p. 218–224 °C (dec.). Enantiomer A: $[\alpha]_D^{22}$ = –49.8 (c = 0.1, CH_2Cl_2), Enantiomer B: $[\alpha]_D^{22}$ = 52.0 (c = 0.1, CH_2Cl_2). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.61 (d, J = 13.9 Hz, 1 H, C*H*^{2}), 0.74 (d, J = 15.7 Hz, 1 H, C*H*^{2}), 1.68–1.75 (m, 1 H, C*H*^{5}), 2.12 (t, J = 12.5 Hz, 1 H, C*H*^{5}), 2.38 (t, J = 13.9 Hz, 1 H, C*H*^{6}), 2.87–3.00 (m, 1 H, C*H*^{6}), 3.08 (s, 1 H, C*H*^{1}), 4.23 (br. s, 1 H, C*H*^{4}), 4.64 (d, $^3J_{PH}$ = 4.0 Hz, 1 H, N*H*), 4.89 (d, J = 8.8 Hz, 1 H, C*H*^{olefin}), 4.96 (d, J = 7.3 Hz, 1 H, C*H*^{3}), 5.03 (d, J = 8.8 Hz, 1 H, C*H*^{benzyl}), 5.82 (dt, $^3J_{HH}$ = 9.2, $^2J_{RhH}$ = 3.5 Hz, 1 H, C*H*^{olefin}), 7.42–7.62 (m, 8 H, C*H*^{ar}), 7.47–7.62 (m, 9 H, C*H*^{ar}), 7.63–7.76 (m, 6 H, C*H*^{ar}) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ = 19.0 (s, 1 C, *C*H^6), 27.6 (s, 1 C, *C*H^5), 34.4 (s, 1 C, *C*H^2), 57.3 (d, $^3J_{PC}$ = 2.7 Hz, 1 C, CH^1), 71.1 (s, 1 C, *C*H^{benzyl}), 73.9 (d, $^1J_{RhC}$ = 7.6 Hz, 1 C, *C*H^{olefin}), 74.1 (d, $^1J_{RhC}$ = 14.0 Hz, 1 C, *C*H^{olefin}), 77.1 (d, $^1J_{RhC}$ = 7.3 Hz, 1 C, CH^4), 92.8 (d, $^1J_{RhC}$ = 12.2 Hz, 1 C, CH^3), 120.4 (q, $^1J_{CF}$ = 320.7 Hz, 1 C, *C*F$_3$), 126.7 (s, 1 C, *C*H^{ar}), 126.9 (s, 1 C, *C*H^{ar}), 127.2 (s, 1 C, *C*H^{ar}), 127.6 (s, 1 C, *C*H^{ar}), 128.7 (d, J = 9.7 Hz, 6 C, *C*H^{ar}), 128.6 (s, 1 C, *C*H^{ar}), 129.1 (s, 1 C, *C*H^{ar}), 129.5 (d, J = 46.3 Hz, 3 C, *C*^{quart}), 129.3 (s, 1 C, *C*H^{ar}), 129.6 (s, 1 C, *C*H^{ar}), 130.8 (d, J = 2.4 Hz, 3 C, *C*H^{ar}), 134.0 (d, J = 9.7 Hz, 6 C, *C*H^{ar}), 134.3 (s, 1 C, *C*^{quart}), 135.9 (d, J = 1.5 Hz, 1 C, *C*^{quart}), 137.1 (s, 1 C, *C*^{quart}), 137.5 (d, J = 2.4 Hz, 1 C, *C*^{quart}) ppm. ^{19}F NMR (183 MHz, CD_2Cl_2) δ = –78.1 (s) ppm. ^{31}P{^{1}H} NMR (203 MHz, CD_2Cl_2): δ = 39.7 (d, $^1J_{RhP}$ = 140.9 Hz) ppm. ^{103}Rh NMR (15.8 MHz, CD_2Cl_2): δ = –6898 (d, $^1J_{RhP}$ = 140.9 Hz) ppm. ATR IR: $\tilde{\nu}$ = 3220 (w), 3045 (w), 2929 (w), 2837 (w), 1597 (w), 1482 (m), 1470 (m), 1433 (m), 1416 (w), 1349 (w), 1314 (w), 1261 (w), 1223 (w), 1191 (w), 1158 (w), 1120 (w), 1090 (m), 1070 (w), 1058 (w), 1026 (w), 996 (w), 976 (w), 910 (w), 875 (w), 857 (w), 778 (w), 749 (s), 695 (s,6 46 w), 621 (m), 579 (w), 556 (w) cm^{-1}. $C_{40}H_{36}F_3NO_3PRhS\cdot(CH_2Cl_2)_{0.7}$ (861.11): calcd. C 56.76, H 4.38, N 1.63; found C 56.81, H 4.37, N 1.58.

***N*-(4-Methylcyclohex-3′-en-1′-yl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylamine (12):** 4-Methylcyclohex-3-en-1-one (**11**) (1.27 g, 11.6 mmol, 1 equiv.) and $tropNH_2$ (2.39 g, 11.6 mmol, 1 equiv.) were dissolved in dry dcm (10 mL). $NaBH(OAc)_3$ (3.42 g, 16.1 mmol, 1.4 equiv.) was added and the turbid solution stirred for 12 h. The reaction was quenched by addition of a saturated aqueous $NaHCO_3$ solution (20 mL). The organic phase was separated and the aqueous phase extracted twice with dcm (10 mL). The organic phase was dried with Na_2SO_4. The product was purified by flash chromatography on silica gel (ethyl acetate/*n*-hexane, 1:4). Yield: 89%, 3.12 g, 10.28 mmol as colorless oil. *endo*/*exo* = 7:3. *endo* conformer: ^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.38–1.42 (m, 1 H, C$H_2^{5\text{ or }6}$), 1.60 (s, 3 H, CH_3), 1.70–1.75 (m, 1 H, CH_2^2), 1.75–1.80 (m, 1 H, C$H_2^{5\text{ or }6}$), 1.86–2.00 (m, 1 H, C$H_2^{5\text{ or }6}$), 1.89 (br. s, 1 H, N*H*), 1.79–2.05 (m, 1 H, C$H_2^{5\text{ or }6}$), 2.09 (d, $^2J_{HH}$ = 16.5 Hz, 1 H, CH_2^2), 2.21 (m, 1 H, C*H*^{1}), 5.04 (s, 1 H, C*H*^{benzyl}), 5.25 (s, 1 H, C*H*^{3}), 7.07 (m, 2 H, C*H*^{olefin}), 7.20–7.47 (m, 8 H, C*H*^{ar}) ppm. ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$): δ = 23.3 (s, 1 C, *C*H$_3$), 29.3 (s, 1 C, *C*H$_2^{5\text{ or }6}$), 29.4 (s, 1 C, *C*H$_2^{5\text{ or }6}$), 32.4 (s, 1 C, *C*H$_2^2$), 49.6 (s, 1 C, *C*H^1), 66.1 (s, 1 C, *C*H^{benzyl}), 119.2 (s, 1 C, *C*H^3), 126.9 (s, 1 C, *C*H^{ar}), 126.9 (s, 1 C, *C*H^{ar}), 128.7 (s, 1 C, *C*H^{ar}), 128.7 (s, 1 C, *C*H^{ar}), 129.4 (s, 2 C, *C*H^{ar}), 130.0 (s, 1 C, *C*H^{ar}), 130.0 (s, 1 C, *C*H^{ar}), 130.5 (s, 1 C, *C*H^{olefin}), 130.5 (s, 1 C, *C*H^{olefin}), 133.2 (s, 1 C, *C*^{quart}), 133.3 (s, 1 C, *C*^{quart}), 133.8 (s, 1 C, *C*^{4}), 140.1 (s, 1 C, *C*^{quart}), 140.1 (s, 1 C, *C*^{quart}) ppm. *exo* conformer ^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.55 (m, 1 H, C$H_2^{5,6}$), 1.65 (s, 3 H, CH_3), 1.69–2.22 (m, 5 H, C$H_2^{2,5,6}$ + N*H*), 2.37 (d, J = 16.5 Hz, 1 H, CH_2^2), 2.87 (m, 1 H, C*H*^{1}), 4.38 (s, 1 H, C*H*^{benzyl}), 5.33 (s, 1 H, C*H*^{3}), 7.20 (s, 2 H, CH^{olefin}), 7.36 (m, 6 H, C*H*^{ar}), 7.68 (dd, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 2.8 Hz, 2 H, C*H*^{ar}) ppm. ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$): δ = 23.4 (s, 1 C, *C*H$_3$), 29.4 (s, 1 C, *C*H$_2^{5\text{ or }6}$), 29.5 (s, 1 C, *C*H$_2^{5\text{ or }6}$), 33.0 (s, 1 C, *C*H$_2^2$), 49.9 (s, 1 C, *C*H^1), 57.0 (s, 1 C, *C*H^{benzyl}), 119.4 (s, 1 C, *C*H^3), 122.4 (s, 1 C, *C*H^{ar}), 122.4 (s, 1 C, *C*H^{ar}), 125.5 (s, 2 C, *C*H^{ar}), 127.6 (s, 1 C, *C*H^{ar}), 127.6 (s, 1 C, *C*H^{ar}), 128.5 (s, 2 C, *C*H^{ar}), 131.1 (s, 1 C, *C*H^{olefin}), 131.2 (s, 1 C, CH^{olefin}), 133.9 (s, 1 C, *C*^{quart}), 133.9 (s, 1 C, *C*^{quart}), 134.1 (s, 1 C, *C*^{4}), 140.7 (s, 1 C, *C*^{quart}), 140.8 (s, 1 C, *C*^{quart}) ppm. ATR IR: $\tilde{\nu}$ = 3013 (w, CH), 2911 (w, CH), 2831 (w,, CH), 1598 (w), 1483 (w), 1437 (m), 1375 (w), 1312 (w), 1262 (m), 1201 (w), 1159 (w), 1098 (m), 1037 (m), 967 (w), 946 (w), 914 (w), 875 (w), 833 (m), 796 (s), 767 (s), 739 (s), 698 (m), 670 (m), 633 (m), 609 (m) cm^{-1}. HRMS (MALDI, 3-HPA): found (calcd.) for $[C_{22}H_{23}N + H]^+$ 302.1908 (302.1909). $C_{22}H_{23}N$ (301.42): calcd. C 74.76, H 7.67, N 2.77; found C 74.81, H 7.61, N 2.72.

[Rh(12)PPh_3]OTf (13): 12 (250 mg, 0.83 mmol, 2.2 equiv.) was dissolved in thf (2 mL), and [Rh$_2$(μ_2-Cl)$_2$(C_2H_4)$_4$] (147 mg, 0.38 mmol, 1 equiv.) was added. Evolution of C_2H_4 and formation of a precipitate were observed. After standing for 36 h, the precipitate was filtered off and dried for a short time. It is a very insoluble orange powder of the composition [Rh$_2$(μ_2-Cl)$_2$(**12**)$_2$] (312 mg, 0.35 mmol, 0.95 equiv.). The orange powder was suspended in thf (5 mL) and PPh_3 (197 mg, 0.75 mmol, 2 equiv.) added. After stirring for 30 min, a clear orange solution was obtained. AgOTf (193 mg, 0.75 mmol, 2 equiv.) was added. The suspension was stirred for 2 h, then the thf was removed under reduced pressure and the residue dissolved in dcm. The solution was filtered through Celite and concentrated to 2 mL. The red solution was layered with *n*-hexane yielding the product as red microcrystalline powder, which was filtered off and dried. Overall yield: 516 mg, 84%, 0.63 mmol. M.p. 210–220 °C (dec). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.86 (m, 2 H, CH_2^6), 1.43 (s, 3 H, CH_3), 1.46 (td, $^2J_{HH}$ = $^3J_{HH}$ = 13.0, $^3J_{HH}$ = 3.0 Hz, 1 H, CH_2^5), 1.54 (td, $^2J_{HH}$ = $^3J_{HH}$ = 13.0, $^3J_{HH}$ = 3.0 Hz, 1 H, CH_2^5), 2.29 (d, $^2J_{HH}$ = 15.9 Hz, 1 H, CH_2^2), 2.85 (dd, $^2J_{HH}$ = 15.9, $^3J_{HH}$ = 1.5 Hz, 1 H, CH_2^2), 3.55 (s, 1 H, C*H*^{1}), 4.55 (dd, $^3J_{HH}$ = 8.7, $^2J_{RhH}$ = 2.9 Hz, 1 H, C*H*^{olefin}), 4.84 (s, 1 H, C*H*^{3}), 5.13 (d, $^4J_{PH}$ = 8.2 Hz, 1 H, C*H*^{benzyl}), 5.23 (d, $^3J_{PH}$ = 4.9 Hz, 1 H, NH), 5.66 (dt, $^3J_{HH}$ = 8.6, $^2J_{RhH}$ = $^3J_{PH}$ = 2.8 Hz, 1 H, C*H*^{olefin}),

7.02 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, C*H*^{ar}), 7.17–7.23 (m, 2 H, C*H*^{ar}), 7.27 (t, *J* = 7.5 Hz, 1 H, C*H*^{ar}), 7.34–7.39 (m, 3 H, C*H*^{ar}), 7.48–7.57 (m, 10 H, C*H*^{ar}), 7.60–7.64 (m, 6 H, C*H*^{ar}) ppm. $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ = 23.2 (s, 1 C, *C*H$_2^5$), 30.5 (s, 1 C, *C*H$_2^6$), 30.8 (s, 1 C, *C*H$_3$), 34.1 (s, 1 C, *C*H$_2^2$), 54.8 (s, 1 C, *C*H^1), 68.5 (s, 1 C, *C*H^{benzyl}), 73.9 (d, $^1J_{RhC}$ = 8.2 Hz, 1 C, *C*H^{olefin}), 82.0 (d, $^1J_{RhC}$ = 15.5 Hz, 1 C, *C*H^{olefin}), 92.7 (d, *J* = 5.9 Hz, 1 C, *C*H^3), 120.9 (q, $^1J_{CF}$ = 320.3 Hz, 1 C, *C*F$_3$), 119.9 (d, *J* = 10.5 Hz, 1 C, *C*^{4}), 126.9 (s, 1 C, *C*H^{ar}), 128.4 (s, 1 C, *C*H^{ar}), 128.5 (s, 1 C, *C*H^{ar}), 128.8 (s, 2 C, *C*H^{ar}), 129.0 (s, 1 C, *C*H^{ar}), 129.2 (s, 1 C, *C*H^{ar}), 129.5 (d, *J* = 10.1 Hz, 6 C, *C*H^{ar}), 129.7 (s, 1 C, *C*H^{ar}), 130.6 (d, *J* = 43.9 Hz, 3 C, *C*^{quart}), 131.4 (d, *J* = 2.3 Hz, 3 C, *C*H^{ar}), 134.5 (d, *J* = 10.5 Hz, 6 C, *C*H^{ar}), 135.5 (s, 1 C, *C*^{quart}), 136.2 (d, 1 C, *C*^{quart}), 137.8 (d, *J* = 1.8 Hz, 1 C, *C*^{quart}), 138.4 (d, *J* = 2.3 Hz, 1 C, *C*^{quart}) ppm. $^{31}P\{^1H\}$ NMR (283 MHz, $CDCl_3$): δ = 35.24 (d, $^1J_{RhP}$ = 153.6 Hz) ppm. ^1H, ^{103}Rh NMR (22.1 MHz, $CDCl_3$): δ = –6958 (d, $^1J_{RhP}$ = 153.6 Hz) ppm. ATR IR: $\tilde{\nu}$ = 3150 (w, NH), 2938 (w, CH), 1588 (w), 1486 (m), 1435 (m), 1373 (w), 1331 (w), 1279 (s), 1253 (s), 1241 (s), 1222 (s), 1158 (s), 1146 (s), 1096 (m), 1070 (m), 1027 (vs), 999 (m), 937 (w), 888 (m), 878 (m), 836 (w), 809 (w), 754 (s), 741 (s), 718 (m), 699 (s), 690 (s), 634 (vs), 611 (m) cm^{-1}. $C_{41}H_{38}F_3NO_3PRhS\cdot(CH_2Cl_2)_{0.3}$ (841.17): calcd. C 58.97, H 4.63, N 1.67; found C 58.75, H 4.61, N 1.66.

***N*-(4-Methylcyclohex-3′-en-1′-yl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylamine (15):** 3-Methylcyclohex-3-en-1-one (**14**) (0.85 g, 7.7 mmol, 1 equiv.) and tropNH$_2$ (1.59 g, 7.7 mmol, 1 equiv.) were dissolved in dry dcm (10 mL). $NaBH(OAc)_3$ (2.3 g, 10.8 mmol, 1.4 equiv.) was added and the turbid solution stirred for 12 h. The reaction was quenched by addition of a saturated aqueous $NaHCO_3$ solution (20 mL). The organic phase was separated and the aqueous phase extracted twice with dcm (20 mL) The organic phase was dried with Na_2SO_4. The product was purified by flash chromatography on silica gel (ethyl acetate/*n*-hexane, 1:4). Yield: 71%,1.67 g, 10.28 mmol as colorless oil. *endo*/*exo* = 3:2. *endo* conformer: ^1H NMR (700 MHz, $CDCl_3$): δ = 1.30–2.10 (m, 6 H, C*H*$_2^{2,5\text{ and }6}$), 1.64 (s, 3 H, C*H*$_3$), 2.76 (m, 1 H, C*H*^{1}), 5.05 (s, 1 H, C*H*^{benzyl}), 5.18 (s, 1 H, C*H*^{4}), 7.09 (m, 2 H, C*H*^{olefin}), 7.35 (m, 8 H, C*H*^{ar}) ppm. $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ = 20.4 (s, 1 C, *C*H$_2^5$), 23.8 (s, 1 C, *C*H$_3$), 29.2 (s, 1 C, *C*H$_2^{2\text{ or }6}$), 30.2 (s, 1 C, *C*H$_2^{2\text{ or }6}$), 50.2 (s, 1 C, *C*H^1) 66.7 (s, 1 C, *C*H^{benzyl}), 123.9 (s, 1 C, *C*H^4), 126.9 (s, 1 C, *C*H^{ar}), 128.5 (s, 2 C, *C*H^{ar}), 128.7 (s, 1 C, *C*H^{ar}), 129.5 (s, 1 C, *C*H^{ar}) 129.6 (s, 1 C, *C*H^{ar}) 130.0 (s, 1 C, *C*H^{ar}) 130.0 (s, 1 C, *C*H^{ar}), 130.5 (s, 1 C, *C*H^{olefin}), 130.6 (s, 1 C, *C*H^{olefin}), 133.4 (s, 1 C, *C*^{quart}), 133.4 (s, 1 C, *C*^{quart}), 136.1 (s, 1 C, *C*^{3}), 140.2 (s, 1 C, *C*^{quart}), 140.4 (s, 1 C, *C*^{quart}) ppm. *exo* conformer: ^1H NMR (700 MHz, $CDCl_3$): δ = 1.30–2.10 (m, 6 H, C*H*$_2^{2,5\text{ and }6}$), 1.74 (s, 3 H, C*H*$_3$), 3.25 (s, 1 H, C*H*^{1}), 4.42 (s, 1 H, CH^{benzyl}), 5.66 (s, 1 H, C*H*^{4}), 7.22 (s, 2 H, C*H*^{olefin}), 7.37 (m, 6 H, C*H*^{ar}), 7.74 (t, $^3J_{HH}$ = 7.0 Hz, 2 H, C*H*^{ar}) ppm. $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ = 20.6 (s, 1 C, *C*H$_2^5$), 23.8 (s, 1 C, *C*H$_3$), 29.6 (s, 1 C, *C*H$_2^{2\text{ or }6}$), 30.4 (s, 1 C, *C*H$_2^{2\text{ or }6}$), 50.4 (s, 1 C, *C*H^1), 57.2 (s, 1 C, *C*H^{benzyl}), 122.5 (s, 1 C, *C*H^{ar}), 122.6 (s, 1 C, *C*H^{ar}), 124.7 (s, 1 C, *C*H^4), 125.5 (s, 2 C, *C*H^{ar}), 126.9 (s, 1 C, *C*H^{ar}), 127.6 (s, 1 C, *C*H^{ar}), 127.6 (s, 1 C, *C*H^{ar}), 128.5 (s, 1 C, *C*H^{ar}), 131.1 (s, 1 C, *C*H^{olefin}), 131.2 (s, 1 C, *C*H^{olefin}), 133.9 (s, 1 C, *C*^{quart}), 134.0 (s, 1 C, *C*^{quart}), 136.3 (s, 1 C, C^4), 140.6 (s, 1 C, *C*^{quart}), 140.8 (s, 1 C, *C*^{quart}) ppm. ATR IR: $\tilde{\nu}$ = 2922 (m, CH), 1671 (w), 1597 (w), 1560 (w), 1483 (m), 1439 (m), 1376 (m), 1344 (w), 1315 (w), 1264 (w), 1201 (w), 1157 (w), 1124 (w), 1090 (s), 1037 (m), 967 (w), 946 (w), 891 (m), 874 (m), 831 (m), 796 (s), 767 (s), 738 (s), 651 (m), 635 (m), 623 (m) cm^{-1}. HRMS (MALDI, 3-HPA): found (calcd.) for $[C_{22}H_{23}N + H]^+$ 302.1907 (302.1909). $C_{22}H_{23}N$ (301.42): calcd. C 74.76, H 7.67, N 2.77; found C 74.80, H 7.60, N 2.82.

[Rh(15)PPh$_3$]OTf (16): 15 (150 mg, 0.5 mmol, 2.2 equiv.) and $[Rh_2(\mu_2\text{-}Cl)_2(COD)_2]$ (112 mg, 0.23 mmol, 1 equiv.) were dissolved in toluene (4 mL) in a Schlenk bomb. The resulting solution was heated at 100 °C for 48 h, whereby an orange precipitate formed. The solution was left to cool to room temperature, then the precipitate was filtered off and dried under vacuum, affording a very insoluble orange powder of the composition $[Rh_2(\mu_2\text{-}Cl)_2(\mathbf{15})_2]$ (167 mg, 0.19 mmol, 0.84 equiv.). This orange powder was suspended in thf (3 mL) and PPh_3 (118 mg, 0.45 mmol, 2 equiv.) added. Over the course of 1 h, a clear orange solution formed. AgOTf (116 mg, 0.45 mmol, 2 equiv.) was added and the resulting suspension stirred for 5 h. Then the solvent was removed under reduced pressure and the residue dissolved in dcm. The solution was filtered through Celite and concentrated to 2 mL. The solution was layered with *n*-hexane, the precipitated product filtered off and dried. Yield: 265 mg, 72%, 0.33 mmol. M.p. 180–200 °C (dec). ^1H NMR (700 MHz, CD_2Cl_2): δ = 0.86 (d, $^2J_{HH}$ = 15.6 Hz, 1 H, C*H*$_2^2$), 0.93 (d, $^2J_{HH}$ = 15.6 Hz, 1 H, C*H*$_2^2$), 1.45 (s, 3 H, C*H*$_3$), 1.56 (dtd, $^2J_{HH}$ = 14.5, $^3J_{HH}$ = 9.8, $^3J_{HH}$ = 2.1 Hz, 1 H, C*H*$_2^6$), 2.19 (m, 1 H, C*H*$_2^6$), 2.49 (ddd, $^2J_{HH}$ = 18.9, $^3J_{HH}$ = 9.5, $^3J_{HH}$ = 4.0 Hz, 1 H, C*H*$_2^5$), 2.79 (ddd, $^2J_{HH}$ = 18.8, $^3J_{HH}$ = 9.6, $^3J_{HH}$ = 9.5 Hz, 1 H), 3.33 (s, 1 H, C*H*^{1}), 4.31 (d, $^3J_{PH}$ = 4.0 Hz, 1 H, N*H*), 4.37 (dd, $^3J_{HH}$ = 8.9, $^2J_{RhH}$ = 2.8 Hz, 1 H, C*H*^{olefin}), 4.65 (t, $^2J_{RhH}$ = $^3J_{PH}$ = 4.1 Hz, 1 H, C*H*^{4}), 5.23 (d, $^4J_{PH}$ = 8.5 Hz, 1 H, C*H*^{benzyl}), 5.69 (dt, $^3J_{HH}$ = 8.9, $^2J_{RhH}$ = $^3J_{PH}$ = 3.2 Hz, 1 H, C*H*^{olefin}), 7.17 (dd, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.7 Hz, 1 H, C*H*^{ar}), 7.34 (d, $^3J_{HH}$ = 4.0 Hz, 2 H, C*H*^{ar}), 7.37–7.43 (m, 3 H, C*H*^{ar}), 7.48–7.51 (m, 1 H, C*H*^{ar}), 7.55 (dd, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 2.0 Hz, 1 H, C*H*^{ar}), 7.57–7.61 (m, 6 H, C*H*^{ar}), 7.62–7.68 (m, 9 H, C*H*^{ar}) ppm. $^{13}C\{^1H\}$ NMR (176 MHz, CD_2Cl_2): δ = 20.4 (s, 1 C, *C*H$_2^5$), 26.5 (s, 1 C, *C*H$_2^6$), 29.2 (s, 1 C, *C*H$_3$), 42.6 (s, 1 C, *C*H$_2^2$), 57.3 (s, 1 C, *C*H^1), 70.4 (s, 1 C, *C*H^{benzyl}), 71.1 (d, $^1J_{RhC}$ = 7.8 Hz, 1 C, *C*H^{olefin}), 82.2 (d, $^1J_{RhC}$ = 15.0 Hz, 1 C, *C*H^{olefin}), 88.7 (d, $^1J_{RhC}$ = 5.9 Hz, 1 C, *C*H^4), 120.9 (q, $^1J_{CF}$ = 321.3 Hz, 1 C, *C*F$_3$), 122.6 (d, *J* = 10.2 Hz, 1 C, *C*^{3}), 127.3 (s, 1 C, *C*H^{ar}), 127.6 (s, 1 C, *C*H^{ar}), 128.4 (s, 1, *C*H^{ar}), 128.6 (s, 1, *C*H^{ar}), 129.0 (s, 2 C, *C*H^{ar}) 129.1 (d, *J* = 9.7 Hz, 6 C, *C*H^{ar}), 129.1 (s, 1 C, *C*H^{ar}), 129.2 (s, 1, *C*H^{ar}), 129.6 (d, *J* = 20.7 Hz, 3 C, *C*^{quart}), 131.3 (d, *J* = 2.4 Hz, 3 C, *C*H^{ar}), 134.4 (d, *J* = 10.2 Hz, 6 C, *C*H^{ar}), 134.5 (s, 1 C, *C*^{quart}), 136.2 (s, 1 C, *C*^{quart}), 136.2 (s, 1 C, *C*^{quart}), 137.6 (d, *J* = 2.4 Hz, 1 C, *C*^{quart}) ppm. $^{31}P\{^1H\}$ NMR (283 MHz, CD_2Cl_2): δ = 35.9 (d, $^1J_{RhP}$ = 152.6 Hz) ppm. ^1H, ^{103}Rh NMR (22.1 MHz, CD_2Cl_2): δ = –7027 (d, $^1J_{RhP}$ = 152.6 Hz) ppm. ATR IR: $\tilde{\nu}$ = 3141 (w,, NH), 2894 (w), 1602 (w), 1479 (w), 1434 (w), 1373 (w), 1282 (m), 1253 (m), 1222 (m), 1151 (m), 1095 (m), 1064 (m), 1030 (s), 998 (m), 961 (w), 909 (w), 840 (w), 811 (w), 775 (w), 743 (m), 696 (s), 635 (s) cm^{-1}. $C_{41}H_{38}F_3NO_3PRhS\cdot(CH_2Cl_2)$ (900.62): calcd. C 56.01, H 4.48, N 1.56; found C 55.46, H 4.45, N 1.54.

(1*S*,4*S*,8*R*)-8-Methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-one Oxime (18): (1*S*,4*S*,8*R*)-8-Methoxy-1,8-dimethylbicyclo-[2.2.2]oct-5-en-2-one (**17**) (1.63 g, 9.0 mmol, 1 equiv.), sodium acetate (1.48 g, 18 mmol, 2 equiv.) and hydroxylamine hydrochloride (1.57 g, 22.6 mmol, 2.5 equiv.) were suspended in methanol (50 mL). The mixture was heated at reflux for 6 h, the solvent removed under reduced pressure and the residue dissolved in diethyl ether (50 mL), which was washed with a saturated $NaHCO_3$ solution and dried with Na_2SO_4. The solvent was removed under reduced pressure and the crude product recrystallized from *n*-hexane. Yield: 95%, 1.668 g, 8.6 mmol. M.p. 104 °C. $[\alpha]_D^{22}$ = –454.8 (*c* = 0.1, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.21 (s, 3 H, C*H*$_3^{10}$), 1.31 (s, 3 H, C*H*$_3^9$), 1.37 (d, $^2J_{HH}$ = 13.2 Hz, 1 H, C*H*$_2^7$), 1.73 (d, $^2J_{HH}$ = 13.2 Hz, 1 H, C*H*$_2^7$), 2.05 (dd, $^2J_{HH}$ = 18.3, $^3J_{HH}$ = 3.4 Hz, 1 H, C*H*$_2^3$), 2.83 (dd, $^2J_{HH}$ = 18.3, $^3J_{HH}$ = 2.5 Hz, 1 H, C*H*$_2^3$), 2.86 (m, 1 H, C*H*^{4}), 3.19 (s, 3 H, OC*H*$_3^{11}$), 5.92 (d, $^3J_{HH}$ = 8.1 Hz, 1 H,

C*H*^{6}), 6.35 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, C*H*^{5}), 9.14 (s, 1 H, O*H*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 19.2 (s, 1 C, *C*H$_3$^{9}), 24.8 (s, 1 C, *C*H$_3$^{10}), 25.9 (s, 1 C, CH$_2$^{3}), 40.3 (s, 1 C, *C*H^4), 41.6 (s, 1 C, *C*^{1}), 47.8 (s, 1 C, CH$_2$^{7}), 49.6 (s, 1 C, OCH$_3$^{11}), 78.6 (s, 1 C, *C*^{8}), 134.7 (s, 1 C, *C*H^5), 136.2 (s, 1 C, *C*H^6), 163.8 (s, 1 C, *C*^{2}) ppm. ATR IR: $\tilde{\nu}$ = 3257 (w), 3140 (w), 3038 (w), 2965 (m), 2928 (m), 2827 (w), 2161 (w), 1682 (w), 1614 (w), 1435 (m), 1372 (m), 1338 (w), 1321 (w), 1284 (m), 1252 (m), 1188 (m), 1164 (m), 1152 (m), 1129 (w), 1096 (w), 1072 (m), 1059 (m), 1020 (w), 992 (w), 931 (s), 913 (s), 888 (m), 848 (m), 812 (m), 758 (m), 722 (s), 675 (m), 646 (m) cm^{-1}. $C_{11}H_{17}NO_2$ (195.26): calcd. C 67.66, H 8.78, N 7.19; found C 67.62, H 8.78, N 7.17.

***tert*-Butyl (1*S*,2*R*,4*S*,8*R*)-(8-Methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-yl)carbamate (19) and *tert*-Butyl (1*S*,2*S*,4*S*,8*R*)-(8-Methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-yl)carbamate (20):** Sodium (2.4 g, 103 mmol, 20 equiv.) was suspended in dry toluene (100 mL) in a three-neck round-bottomed flask equipped with a large stir bar, an efficient reflux condenser with an argon inlet and a dropping funnel charged with a solution of (1*S*,4*S*,8*R*)-8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-one oxime (**18**) (1 g, 5.15 mmol, 1 equiv.) in toluene (50 mL). The toluene was refluxed until a fine suspension of sodium was obtained. Then the solution of the oxime was added dropwise over 15 min. The reaction mixture was refluxed for another 15 min and dry ethanol (20 mL) added carefully to the hot solution until all the sodium had reacted. The solution was cooled in an ice bath and acidified with 4 M HCl (27 mL). All volatiles were removed under reduced pressure and the solid dissolved in as little water as possible. The aqueous phase was extracted with *n*-hexane to remove impurities and then basified with sodium hydroxide. The crude amine was extracted with diethyl ether (5 × 20 mL) and the organic phase dried with pulverized potassium hydroxide. The solvent was removed under reduced pressure. Attention: the amine is quite volatile and should not be dried under high vacuum. It can be purified by column chromatography (SiO_2; dcm/ethanol, 5:1) but the yield obtained was poor. Therefore, the amine was protected with a Boc group, which simplified the isolation. Crude (1*S*,2*RS*,4*S*,8*R*)-8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-ylamine (790 mg, 4.36 mmol, 85%) was dissolved in dry dcm (8 mL), and triethylamine (0.8 mL, 5.7 mmol, 1.3 equiv.) and di-*tert*-butyl dicarbonate (1050 mg, 4.8 mmol, 1.1 equiv.) were added. The mixture was stirred overnight. The organic phase was washed with an aqueous solution of sodium carbonate and dried with Na_2SO_4. The diastereoisomers were separated by chromatography on silica gel (*n*-hexane/ethyl acetate, 10:1) and dried under high vacuum. The compounds did not absorb well the UV detection light, and stains (ninhydrin, anisaldehyde) were used. **20**: R_f = 0.32. Yield: 61%, 748 mg, 2.66 mmol as white solid. **19**: R_f = 0.43. Yield: 29%, 355 mg, 1.26 mmol as colorless oil. Yield combined: 90%, 1103 mg, 3.92 mmol. **20**: M.p. 73 °C. $[\alpha]_D^{22}$ = –76.3 (*c* = 0.1, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.77 (dt, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 2.90 Hz, 1 H, CH$_2$^{7}), 1.11 (s, 3 H, CH$_3$^{10}), 1.14 (s, 3 H, CH$_3$^{9}), 1.17 (d, $^2J_{HH}$ = 13.6 Hz, 1 H, C*H*^{7}), 1.45 (s, 9 H, CH$_3$^{14}), 1.52 (d, $^2J_{HH}$ = 13.6 Hz, 1 H, C*H*^{7}), 2.54 (dt, $^3J_{HH}$ = 6.0, $^3J_{HH}$ = 2.9 Hz, 1 H, C*H*^{4}), 2.65 (ddd, $^2J_{HH}$ = 13.5, $^3J_{HH}$ = 10.0, $^3J_{HH}$ = 2.9 Hz, 1 H, CH$_2$^{3}), 3.18 (s, 3 H, OCH$_3$^{11}), 3.75 (ddd, $^3J_{HH}$ = 10.0, $^3J_{HH}$ = 9.5, $^3J_{HH}$ = 2.9 Hz, 1 H, C*H*^{2}), 4.20 (d, $^3J_{HH}$ = 9.5 Hz, 1 H, N*H*), 5.82 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, C*H*^{6}), 6.35 (dd, $^3J_{HH}$ = 8.0, $^3J_{HH}$ = 6.2 Hz, 1 H, C*H*^{5}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 21.8 (s, 1 C, *C*H$_3$^{9}), 25.0 (s, 1 C, *C*H$_3$^{10}), 28.9 (s, 3 C, *C*H$_3$^{14}), 33.0 (s, 1 C, *C*H$_2$^{3}), 40.5 (s, 1 C, *C*^{1}), 40.5 (s, 1 C, *C*H^4), 47.8 (s, 1 C, CH$_2$^{7}), 50.0 (s, 1 C, OCH$_3$^{11}), 53.2 (s, 1 C, *C*H^2), 79.1 (s, 1 C, *C*^{1}), 79.2 (s, 1 C, *C*^{8}), 135.6 (s, 1 C, *C*H^5), 136.1 (s, 1 C, *C*H^6), 156.1 (s, 1 C, *C*^{12}) ppm. ATR IR: $\tilde{\nu}$ = 3315 (m, NH), 3044 (w, CH), 2964 (m, CH), 2933 (m, CH), 2826 (w), 1682 (s, C=O), 1529 (s, C=C), 1454 (m), 1390 (m), 1377 (m), 1365 (m), 1330 (m), 1287 (m), 1270 (m), 1248 (m), 1214 (m), 1171 (s), 1129 (m), 1103 (m), 1076 (m), 1060 (s), 1051 (s), 1030 (m), 1003 (m), 975 (m), 955 (w), 926 (w), 901 (m), 879 (m), 836 (m), 786 (m), 755 (m), 744 (s), 722 (s), 674 (m), 644 (m), 613 (m) cm^{-1}. $C_{16}H_{27}NO_3$ (281.39): calcd. C 68.29, H 9.67, N 4.98; found C 68.26, H 9.61, N 4.91. **19**: $[\alpha]_D^{22}$ = –96.9 (*c* = 0.1, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.04 (dd, $^2J_{HH}$ = 13.6, *J* = 1.8 Hz, 1 H, CH$_2$^{7}), 1.08 (s, 3 H, CH$_3$^{9}), 1.14 (s, 3 H, CH$_3$^{10}), 1.47 (s, 9 H, CH$_3$^{14}), 1.52 (dt, $^2J_{HH}$ = 13.6, $^3J_{HH}$ = 2.9 Hz, 1 H, CH$_2$^{3}), 1.69 (d, $^2J_{HH}$ = 13.6 Hz, 1 H, CH$_2$^{7}), 1.76 (ddd, $^2J_{HH}$ = 13.5, $^3J_{HH}$ = 11.0, $^3J_{HH}$ = 2.9 Hz, 1 H, CH$_2$^{3}), 2.57 (dt, $^3J_{HH}$ = 7.2, $^3J_{HH}$ = 2.9 Hz, 1 H, C*H*^{4}), 3.22 (s, 3 H, OCH$_3$^{11}), 3.56 (ddd, $^3J_{HH}$ = 10.0, $^3J_{HH}$ = 9.5, $^3J_{HH}$ = 2.9 Hz, 1 H, C*H*^{2}), 4.92 (d, $^3J_{HH}$ = 9.5 Hz, 1 H, N*H*), 5.98 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, C*H*^{6}), 6.24 (dd, $^3J_{HH}$ = 8.0, $^3J_{HH}$ = 7.2 Hz, 1 H, C*H*^{5}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 21.9 (s, 1 C, *C*H$_3$^{9}), 25.1 (s, 1 C, *C*H$_3$^{10}), 28.9 (s, 3 C, *C*H$_3$^{14}), 31.3 (s, 1 C, *C*H$_2$^{3}), 39.4 (s, 1 C, *C*H^4), 40.1 (s, 1 C, *C*^{1}), 44.5 (s, 1 C, *C*H$_2$^{7}), 49.9 (s, 1 C, OCH$_3$^{11}), 50.3 (s, 1 C, *C*H^2), 79.1 (s, 1 C, *C*^{8}), 79.2 (s, 1 C, *C*^{13}), 134.1 (s, 1 C, *C*H^5), 139.7 (s, 1 C, *C*H^6), 156.5 (s, 1 C, *C*^{13}) ppm. ATR IR: $\tilde{\nu}$ = 3438 (w, NH), 2966 (w, CH), 2932 (w, CH), 2870 (w), 2826 (w), 1715 (s, C=O), 1497 (s, C=C), 1453 (m), 1390 (m), 1364 (m), 1322 (m), 1298 (m), 1284 (m), 1248 (m), 1209 (m), 1166 (s), 1124 (m), 1097 (m), 1065 (m), 1044 (m), 1029 (m), 992 (w), 968 (w), 931 (w), 889 (m), 844 (m), 776 (w), 760 (w), 699 (s), 677 (m) cm^{-1}.

(1′*S*,2′*S*,4′*S*,8′*S*)-8′-Methoxy-1′,8′-dimethylbicyclo[2.2.2]oct-5′-en-2′-yl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylamine (21): *tert*-Butyl (1*S*,2*S*,4*S*,8*S*)-(8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-yl)-carbamate (**20**) (300 mg, 1.07 mmol, 1 equiv.) was dissolved in dcm (2 mL) and the solution cooled to 0 °C. Trifluoroacetic acid (0.25 mL, 3.2 mmol, 3 equiv.) was added dropwise and the reaction mixture stirred at room temperature for 4 h. The reaction was monitored by TLC. Water (5 mL) was added and the reaction mixture neutralized with K_2CO_3 until no further CO_2 was evolved. The aqueous phase was extracted five times with dcm (5 mL) and the organic phase dried with potassium carbonate. The solvent was removed under reduced pressure to yield the deprotected amine. The amine (170 mg, 0.94 mmol, 87%) was dissolved in dcm (5 mL) and triethylamine (0.65 mL, 4.7 mmol, 5 equiv.) added. The solution was cooled with an ice bath, and tropCl (319 mg, 1.41 mmol, 1.5 equiv.) was added. The reaction mixture was stirred for 6 h. The organic phase was washed with aqueous sodium carbonate and the organic phase dried with Na_2SO_4. The product was chromatographed on silica gel with dcm containing 1–5% ethanol, starting with 1%. After drying for a long time, a colorless solid, still containing some residual solvent, was obtained. Yield: 87%, 302 mg, 0.81 mmol. M.p. 58 °C. $[\alpha]_D^{22}$ = +0.4 (*c* = 0.1, CH_2Cl_2). *endo*/*exo* = 9:1. *endo* conformer: ^1H NMR (700 MHz, $CDCl_3$): δ = 0.91 (dt, $^2J_{HH}$ = 11.6, $^3J_{HH}$ = 2.9 Hz, 1 H, CH$_2$^{3}), 0.95 (s, 3 H, CH$_3$^{9}), 0.99 (d, $^2J_{HH}$ = 13.1 Hz, 1 H, CH$_2$^{7}), 1.05 (s, 3 H, CH$_3$^{10}), 1.14 (d, $^2J_{HH}$ = 13.1 Hz, 1 H, CH$_2$^{7}), 2.12 (ddd, $^3J_{HH}$ = 10.1, $^3J_{HH}$ = 2.9, $^3J_{HH}$ = 2.0 Hz, 1 H, CH$_2$^{2}), 2.15 (ddd, $^2J_{HH}$ = 10.0, $^3J_{HH}$ = 9.0, $^3J_{HH}$ = 2.9 Hz, 1 H, CH$_2$^{3}), 2.50 (dt, $^3J_{HH}$ = 7.0, $^3J_{HH}$ = 2.9 Hz, 1 H, C*H*^{4}), 3.10 (s, 3 H, OCH$_3$^{11}), 4.83 (s, 1 H, C*H*^{benzyl}), 5.73 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, C*H*^{6}), 6.18 (dd, $^3J_{HH}$ = 7.9, $^3J_{HH}$ = 7.0 Hz, 1 H, C*H*^{5}), 7.03 (s, 2 H, C*H*^{olefin}), 7.15–7.45 (m, 7 H, C*H*^{ar}), 7.54 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, C*H*^{ar}) ppm. $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ = 21.7 (s, 1 C, *C*H$_3$^{9}), 24.6 (s, 1 C, *C*H$_3$^{10}), 31.7 (s, 1 C, *C*H$_2$^{3}), 39.6 (s, 1 C, *C*H^4), 39.7 (s, 1 C, *C*^{1}), 48.7 (s, 1 C, *C*H$_2$^{7}), 49.4 (s, 1 C, OCH$_3$), 57.7 (s, 1 C, *C*H^2), 66.9 (s, 1 C, *C*H^{benzyl}), 79.0 (s, 1 C, *C*^{8}), 121.8 (s, 1 C, CH^{ar}), 130.4 (s, 1 C, CH^{olefin}), 130.6 (s, 1 C, CH^{olefin}), 132.6 (s, 1 C, *C*H^5), 136.6 (s, 1 C, *C*H^6), 125–134 (11 C, *C*H^{ar} and

C^{quart}) ppm. *exo* conformer: ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.87 (dt, $^2J_{HH}$ = 12.8, $^3J_{HH}$ = 2.9 Hz, 1 H, CH_2^3), 1.12 (s, 3 H, CH_3^{10}), 1.24 (d, $^2J_{HH}$ = 13.4 Hz, 1 H, CH_2^7), 1.39 (d, $^2J_{HH}$ = 13.4 Hz, 1 H, CH_2^7), 1.60 (s, 3 H, CH_3^9), 2.26 (ddd, $^2J_{HH}$ = 12.7, $^3J_{HH}$ = 8.3, $^3J_{HH}$ = 2.1 Hz, 1 H, CH_2^3), 2.54 (dt, $^3J_{HH}$ = 7.0, $^3J_{HH}$ = 2.9 Hz, 1 H, CH^4), 2.78 (dt, $^3J_{HH}$ = 7.5, $^3J_{HH}$ = 2.9 Hz, 1 H, CH^2), 3.11 (s, 3 H, OCH_3^{11}), 4.18 (s, 1 H, CH^{benzyl}), 6.04 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, CH^6), 6.31 (dd, $^3J_{HH}$ = 7.9, $^3J_{HH}$ = 7.0 Hz, 1 H, CH^5), 7.15 (d, $^3J_{HH}$ = 11.6 Hz, 1 H, CH^{olefin}) 7.19 (d, $^3J_{HH}$ = 11.6 Hz, 1 H, CH^{olefin}), 7.2–7.45 (m, 7 H, CH^{ar}), 7.85 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, CH^{ar}) ppm. ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$): δ = 22.7 (s, 1 C, CH_3^9), 24.5 (s, 1 C, CH_3^{10}), 31.4 (s, 1 C, CH_2^3), 39.7 (s, 1 C, CH^4), 40.4 (s, 1 C, C^1), 48.8 (s, 1 C, CH_2^7), 49.4 (s, 1 C, OCH_3^{11}), 56.2 (s, 1 C, CH^{benzyl}), 57.4 (s, 1 C, CH^2), 79.0 (s, 1 C, C^8), 123.7 (s, 1, CH^{ar}), 130.6 (s, 1 C, CH^{olefin}), 131.3 (s, 1 C, CH^{olefin}), 134.3 (s, 1 C, CH^5), 136.5 (s, 1 C, CH^6), 125–134 (11 C, CH^{ar} and C^{quart}) ppm. ATR IR: $\tilde{\nu}$ = 3017 (w), 2924 (m), 2823 (w), 1671 (w), 1597 (w), 1484 (w), 1440 (m), 1366 (m), 1334 (w), 1243 (w), 1199 (w), 1157 (m), 1143 (m), 1102 (m), 1070 (m), 1038 (m), 995 (w), 945 (w), 892 (w), 876 (w), 861 (w), 845 (m), 795 (s), 764 (s), 736 (m), 724 (s), 678 (m), 641 (m) cm^{-1}. HRMS (MALDI, 3-HPA): found (calcd.) for $[C_{26}H_{29}NO + H]^+$ 370.2161 (370.2165). $C_{26}H_{29}NO$ (371.51): calcd. C 84.06, H 7.87, N 3.77; found C 83.91, H 7.97, N 3.64.

[Rh(21)(CO)]OTf (22): $[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ (21 mg, 0.05 mmol, 1 equiv.) was dissolved in thf (1 mL), and **21** (40 mg, 0.11 mmol, 2 equiv.) was added. After 1 h, AgOTf (31 mg, 0.12 mmol, 2 equiv.) was added. The solvent was removed under reduced pressure and the residue dissolved in dcm (2 mL), filtered through Celite and the solvet removed under reduced pressure. The complex was recrystallized from thf/*n*-hexane giving a yellow, air-sensitive, crystalline material. Yield: 68%, 48 mg, 0.07 mmol. M.p. 198 °C (dec.). $[\alpha]_D^{22}$ = –20.4 (c = 0.1, CH_2Cl_2). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = –0.06 (dd, $^2J_{HH}$ = 14.9, $^3J_{HH}$ = 4.9 Hz, 1 H, CH_2^3), 1.24 (s, 3 H, CH_3^{10}), 1.29 (s, 3 H, CH_3^9), 1.30 (d, $^2J_{HH}$ = 14.0 Hz, 1 H, CH_2^7), 1.61 (dd, $^2J_{HH}$ = 14.0, $^3J_{HH}$ = 7.9 Hz, 1 H, CH_2^3), 1.67 (d, $^2J_{HH}$ = 14.0 Hz, 1 H, CH_2^7), 2.20 (t, $^3J_{HH}$ = 5.3 Hz, 1 H, CH^4), 3.02 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, CH^2), 3.06 (s, 3 H, OCH_3^{11}), 3.49 (s, 1 H, NH), 4.96 (s, 1 H, CH^{benzyl}), 5.47 (d, $^3J_{HH}$ = 6.7 Hz, 1 H, CH^6), 6.24 (d, $^3J_{HH}$ = 8.83 Hz, 1 H, CH^{olefin}), 6.43 (ddd, $^3J_{HH}$ = 6.7, $^3J_{HH}$ = 5.3, $^1J_{RhH}$ = 3.2 Hz, 1 H, CH^5), 6.64 (dd, $^3J_{HH}$ = 9.1, $^1J_{RhH}$ = 3.3 Hz, 1 H, CH^{olefin}), 7.34 (dd, $^3J_{HH}$ = 7.3, $^3J_{HH}$ = 1.5 Hz, 1 H, CH^{ar}), 7.40–7.50 (m, 5 H, CH^{ar}), 7.67 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, CH^{ar}) ppm. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 22.1 (s, 1 C, CH_3^9), 23.9 (s, 1 C, CH_3^{10}), 24.4 (d, $^3J_{RhC}$ = 1.8 Hz, 1 C, CH_2^3), 39.0 (s, 1 C, CH^4), 43.5 (s, 1 C, CH_2^7), 43.6 (s, 1 C, C^1), 50.0 (s, 1 C, OCH_3^{11}), 68.9 (s, 1 C, CH^{benzyl}), 69.4 (s, 1 C, CH^2), 79.4 (d, $^1J_{RhC}$ = 6.4 Hz, 1 C, CH^{olefin}), 79.8 (d, $^1J_{RhC}$ = 7.8 Hz, 1 C, CH^{olefin}), 79.9 (s, 1 C, C^8), 98.7 (d, $^1J_{RhC}$ = 11.4 Hz, 1 C, CH^5), 100.7 (d, $^1J_{RhC}$ = 6.4 Hz, 1 C, CH^6), 120.8 (q, $^1J_{CF}$ = 320.3 Hz, 1 C, CF_3), 127.7 (s, 1 C, CH^{ar}), 128.6 (s, 1 C, CH^{ar}), 128.6 (s, 1 C, CH^{ar}), 128.9 (s, 1 C, CH^{ar}), 129.0 (s, 1 C, CH^{ar}), 129.7 (s, 1 C, CH^{ar}), 129.8 (s, 1 C, CH^{ar}), 131.3 (s, 1 C, CH^{ar}), 135.3 (d, $^2J_{RhC}$ = 2.3 Hz, 1 C, C^{quart}), 135.4 (s, 1 C, C^{quart}), 136.2 (s, 1 C, C^{quart}), 138.0 (d, $^2J_{RhC}$ = 1.8 Hz, 1 C, C^{quart}), 185.5 (d, $^1J_{RhC}$ = 63.5 Hz, 1 C, CO) ppm. ^{103}Rh NMR (12.6 MHz, CD_2Cl_2): δ = –7569 (s) ppm. ATR IR: $\tilde{\nu}$ = 3234 (w, NH), 2961 (w, CH), 2882 (w, CH), 2036 (m, CO), 1465 (w), 1389 (w), 1371 (w), 1326 (w), 1294 (m), 1283 (s), 1231 (s), 1218 (s), 1156 (s), 1103 (m), 1059 (m), 1023 (s), 992 (m), 953 (w), 895 (w), 880 (w), 864 (w), 847 (w), 817 (w), 778 (w), 752 (m), 743 (w), 706 (w), 689 (w), 666 (w), 633 (s), 609 (w) cm^{-1}. $C_{28}H_{29}F_3NO_5RhS{\cdot}thf_{0.2}$ (665.92): calcd. C 51.94, H 4.63, N 2.10; found C 52.02, H 4.67, N 2.09.

[Rh(21)(PPh$_3$)]OTf (23): $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ (26.2 mg, 0.07 mmol, 1 equiv.) was dissolved in thf (1 mL) under argon and **21** (50 mg, 0.13 mmol, 2 equiv.) added. After 1 h, PPh_3 (35.3 mg, 0.13 mmol, 2 equiv.) was added. After another 1 h, AgOTf (38 mg, 0.15 mmol, 2.2 equiv.) was added. The solvent was removed under reduced pressure, the residue was dissolved in dcm (2 mL) and filtered through Celite. The complex was crystallized from dcm/*n*-hexane to give an air-stable orange powder. Yield: 60%, 71 mg, 0.08 mmol, not optimized. M.p. 220–222 °C (dec.). $[\alpha]_D^{22}$ = 76.6 (c = 0.1, CH_2Cl_2). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.04 (dd, J = 14.7, 4.4 Hz, 1 H, CH_2^3), 0.77 (s, 3 H, CH_3^{10}) 1.01 (d, J = 13.6 Hz, 1 H, CH_2^7), 1.25 (s, 3 H, CH_3^9), 1.62 (d, J = 13.9 Hz, 1 H, CH_2^7), 1.70 (dd, J = 14.5, 7.9 Hz, 1 H, CH_2^3), 2.22 (t, J = 4.8 Hz, 1 H, CH^4), 3.02 (s, 3 H, OCH_3^{11}), 3.18 (t, J = 7.2 Hz, 1 H, CH^2), 3.44 (d, J = 3.7 Hz, 1 H, NH), 4.58 (d, J = 6.2 Hz, 1 H, CH^6), 5.09 (d, J = 8.5 Hz, 1 H, CH^{olefin}), 5.16 (d, J = 8.1 Hz, 1 H, CH^{benzyl}), 5.80 (d, J = 8.8 Hz, 1 H, CH^{olefin}), 5.96 (s, 1 H, CH^5), 7.13 (d, J = 7.7 Hz, 1 H, CH^{ar}), 7.35–7.45 (m, 5 H, CH^{ar}), 7.52 (t, J = 7.89 Hz, 2 H, CH^{ar}), 7.60–7.90 (m, 9 H, CH^{ar}), 7.71–7.91 (m, 6 H, CH^{ar}) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ = 22.5 (s, 1 C, CH_3^9), 23.8 (s, 1 C, CH_3^{10}), 26.1 (s, 1 C, CH_2^3), 40.5 (s, 1 C, CH^4), 43.2 (s, 1 C, CH_2^7), 50.0 (s, 1 C, OCH_3^{11}), 68.8 (s, 1 C, CH^{benzyl}), 70.3 (s, 1 C, CH^2), 79.4 (d, J = 4 Hz, C^1), 82.5 (d, J = 7.08 Hz, 1 C, CH^{olefin}), 87.2 (d, J = 11.7 Hz, 1 C, CH^{olefin}), 103.3 (d, J = 7.1 Hz, 1 C, CH^6), 107.6 (d, J = 12.6 Hz, 1 C, CH^5), 128.1 (s, 1 C, CH^{ar}), 128.5 (s, 1 C, CH^{ar}), 129.0 (s, 1 C, CH^{ar}), 129.1 (s, 1 C, CH^{ar}), 129.4 (s, 1 C, CH^{ar}), 129.4 (s, 1 C, CH^{ar}), 129.5 (d, J = 9.8 Hz, 6 C, CH^{ar}), 129.6 (s, 1 C, CH^{ar}), 130.0 (d, J = 19.4 Hz, 3 C, C^{quart}), 131.9 (d, J = 2.2 Hz, 3 C, CH^{ar}), 131.9 (s, 1 C, CH^{ar}), 134.5 (d, J = 10.2 Hz, 6 C, CH^{ar}), 135.7 (s, 1 C, C^{quart}), 136.3 (s, 1 C, C^{quart}), 136.4 (s, 1 C, C^{quart}), 137.4 (s, 1 C, C^{quart}) ppm. ^{31}P{^{1}H} NMR (203 MHz, CD_2Cl_2): δ = 42.7 (d, $^1J_{RhP}$ = 140.5 Hz) ppm. ^{103}Rh NMR (15.8 MHz, CD_2Cl_2): δ = 789 (d, $^1J_{RhP}$ = 140.5 Hz) ppm. ATR IR: $\tilde{\nu}$ = 3514 (w), 3220 (w), 2949 (w), 1630 (w), 1479 (w), 1455 (w), 1439 (m), 1374 (w), 1281 (w), 1248 (m 1227 m), 1156 (m), 1103 (m), 1093 (m), 1071 (m), 1060 (m), 1032 (s), 1013 (m), 988 (m), 950 (m), 892 (w), 880 (w), 863 (w), 846 (w), 814 (w), 781 (m), 756 (s), 746 (s), 704 (s), 697 (s), 638 (s) cm^{-1}. $C_{45}H_{44}F_3NO_4PRhS{\cdot}(CH_2Cl_2)_{0.2}$ (902.76): calcd. C 60.14, H 4.96, N 1.55; found C 60.27, H 5.06, N 1.53.

Methyl (2*S*3*R*)-3-[(*tert*-Butoxycarbonyl)amino]bicyclo[2.2.1]hept-5-ene-2-carboxylate (24): The compound was synthesized according to an established literature procedure by using *tert*-butyl alcohol; a colorless solid was obtained.[12] M.p. 44 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.38 (d, $^2J_{HH}$ = 8.9 Hz, 1 H, CH_2^7), 1.44 (s, 9 H, CH_3), 1.51 (d, $^2J_{HH}$ = 9.2 Hz, 1 H, CH_2^7), 3.08 (m, 1 H, CH^4), 3.11 (m, 1 H, CH^1), 3.24 (dd, $^3J_{HH}$ = 9.0, $^3J_{HH}$ = 2.3 Hz, 1 H, CH^2), 3.64 (s, 3 H, OCH_3^9), 4.61 (td, $^3J_{HH}$ = 10, $^3J_{HH}$ = 2.9 Hz, 1 H, CH^3), 4.88 (d, $^3J_{HH}$ = 9.2 Hz, 1 H, NH), 6.20 (dd, $^3J_{HH}$ = 5.5, $^3J_{HH}$ = 3.0 Hz, 1 H, CH^5), 6.46 (dd, $^3J_{HH}$ = 5.8, $^3J_{HH}$ = 3.1 Hz, 1 H, CH^6) ppm. ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$): δ = 28.4 (s, 3 C, CH_3^{12}), 46.4 (s, 1 C, CH^1), 47.2 (s, 1 C, CH^4), 47.6 (s, 1 C, CH_2^7), 48.9 (s, 1 C, CH^2), 51.5 (s, 1 C, OCH_3^9), 53.8 (s, 1 C, CH^3), 79.1 (s, 1 C, C^{11}), 133.0 (s, 1 C, CH^5), 138.5 (s, 1 C, CH^6), 155.5 (s, 1 C, C^{10}), 173.2 (s, 1 C, C^8) ppm. ATR IR: $\tilde{\nu}$ = 3409 (w, NH), 2978 (w), 2954 (w), 2878 (w), 1709 (s, C=O), 1501 (s, C=C) 1449 m), 1437 (m), 1390 (m), 1356 (s), 1338 (m), 1300 (m), 1259 (m), 1240 (m), 1220 (m), 1207 (m), 1160 (s), 1120 (m), 1090 (m), 1072 (m), 1056 (s), 1031 (s), 1015 (m), 984 (m), 963 (m), 945 (m), 916 (m), 879 (m), 858 (m), 844 (m), 825 (m), 789 (m), 776 (m), 721 (m), 679 (m) cm^{-1}. $C_{14}H_{21}NO_4$ (267.32): calcd. C 62.90, H 7.92, N 5.24; found C 62.63, H 8.06, N 5.24.

Methyl (2*S*3*R*)-3-(5*H*-Dibenzo[*a*,*d*]cyclohepten-5-ylamino)bicyclo-[2.2.1]hept-5-ene-2-carboxylate (25): Methyl 3-[(*tert*-butoxycarbonyl)amino]bicyclo[2.2.1]hept-5-ene-2-carboxylate (**24**) (270 mg,

1.01 mmol, 1 equiv.) was dissolved in dcm (5 mL) and the solution cooled to 0 °C. Trifluoroacetic acid (0.23 mL, 3.0 mmol, 3 equiv.) was added dropwise and the reaction mixture stirred at room temperature for 4 h. The reaction was monitored by TLC. Water (5 mL) was added and the reaction mixture neutralized with K_2CO_3 until no further CO_2 was evolved. Next, the aqueous phase was extracted five times with dcm (5 mL) and the organic phase dried with powdered K_2CO_3. The solvent was removed under reduced pressure to yield the deprotected amine. The amine (110 mg, 0.66 mmol, 65%) was dissolved in dry dcm (5 mL) and triethylamine (0.45 mL, 3.3 mmol, 5 equiv.) added. The solution was cooled with an ice bath, and tropCl (223 mg, 0.99 mmol, 1.5 equiv.) was added. The reaction mixture was stirred for 6 h. The organic phase was washed with aqueous sodium carbonate and the organic phase dried with Na_2SO_4. The product was chromatographed on silica gel (dcm/EtOH, 99:1). An oil was obtained, which solidified to an off-white solid, still containing small amounts of residual solvent after drying under high vacuum. Yield: 85%, 202 mg, 0.56 mmol. M.p. 127 °C. $[\alpha]_D^{22}$ = –25.3 (c = 0.1, CH_2Cl_2). *endo*/*exo* = 1:2. *endo* conformer: ^{1}H NMR (700 MHz, C_6D_6): δ = 0.80 (d, $^2J_{HH}$ = 8.9 Hz, 1 H, CH_2^7), 1.31 (d, $^2J_{HH}$ = 8.9 Hz, 1 H, CH_2^7), 2.42 (s, 1 H, N*H*), 2.66 (m, 1 H, CH_1), 2.84 (s, 1 H, CH_4), 2.87 (dd, $^3J_{HH}$ = 9.5, $^3J_{HH}$ = 3.4 Hz, 1 H, CH^2), 3.37 (s, 3 H, OCH_3^9), 3.37 (m, 1 H, CH^3), 4.95 (s, 1 H, CH^{benzyl}), 6.05 (dd, $^3J_{HH}$ = 5.7, $^3J_{HH}$ = 2.9 Hz, 1 H, CH^5), 6.61 (dd, $^3J_{HH}$ = 5.5, $^3J_{HH}$ = 2.8 Hz, 1 H, CH^6), 6.94 (m, 2 H, CH^{olefin}), 7.15–7.45 (m, 8 H, CH^{ar}) ppm. ^{13}C{^{1}H} NMR (176 MHz, C_6D_6): δ = 45.4 (s, 1 C, CH^4), 46.4 (s, 1 C, CH^1), 46.8 (s, 1 C, CH_2^7) 50.0 (s, 1 C, CH^2), 50.5 (s, 1 C, OCH_3^9), 60.1 (s, 1 C, CH^4), 68.99 (s, 1 C, CH^{benzyl}), 126.7 (s, 1 C, CH^{ar}), 126.9 (s, 1 C, CH^{ar}), 128.3 (s, 1 C, CH^{ar}), 128.4 (s, 1 C, CH^{ar}), 129.4 (s, 1 C, CH^{ar}), 129.4 (s, 1 C, CH^{ar}), 130.0 (s, 1 C, CH^{ar}), 130.1 (s, 1 C, CH^{ar}), 130.3 (s, 1 C, CH^{ar}), 130.8 (s, 1 C, CH^{ar}), 132.7 (s, 1 C, CH^5), 134.0 (s, 1 C, C^{quart}), 134.1 (s, 1 C, C^{quart}), 137.4 (s, 1 C, CH^6), 140.4 (s, 1 C, C^{quart}), 141.1 (s, 1 C, C^{quart}), 172.4 (s, 1 C, C^8) ppm. *exo* conformer: ^{1}H NMR (700 MHz, C_6D_6): δ = 0.77 (d, $^2J_{HH}$ = 8.5 Hz, 1 H, CH_2^7), 1.29 (d, $^2J_{HH}$ = 8.5 Hz, 1 H, CH_2^7), 2.57 (d, $^3J_{HH}$ = 11.9 Hz, 1 H, N*H*), 2.84 (m, 1 H, CH^1), 2.89 (m, 1 H, CH^4), 3.07 (dd, $^3J_{HH}$ = 9.5, $^3J_{HH}$ = 3.4 Hz, 1 H, CH^2), 3.50 (s, 3 H, OCH_3^9), 3.82 (ddd, $^3J_{HH}$ = 12.0, $^3J_{HH}$ = 9.5, $^3J_{HH}$ = 3.5 Hz, 1 H, CH^3), 4.45 (s, 1 H, CH^{benzyl}), 6.07 (dd, $^3J_{HH}$ = 5.5, $^3J_{HH}$ = 3.1 Hz, 1 H, CH^5), 6.64 (dd, $^3J_{HH}$ = 5.5, $^3J_{HH}$ = 3.1 Hz, 1 H, CH^6), 7.14 (m, 2 H, CH^{olefin}), 7.10–7.45 (m, 6, CH^{ar}), 7.97 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, CH^{ar}), 8.07 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, CH^{ar}) ppm. ^{13}C{^{1}H} NMR (176 MHz, C_6D_6): δ = 46.0 (s, 1 C, CH^4), 46.2 (s, 1 C, CH^1) 47.5 (s, 1 C, CH_2^7), 49.5 (s, 1 C, CH^2), 50.7 (s, 1 C, OCH_3^9), 58.8 (s, 1 C, CH^{benzyl}), 60.4 (s, 1 C, CH^3), 122.5 (s, 1 C, CH^{ar}), 123.1 (s, 1 C, CH^{ar}), 125.6 (s, 1 C, CH^{olefin}), 125.7 (s, 1 C, CH^{ar}), 127.7 (s, 1 C, CH^{ar}), 128.1 (s, 1 C, CH^{ar}), 128.8 (s, 1 C, CH^{ar}), 128.9 (s, 1 C, CH^{ar}), 131.1 (s, 1 C, CH^{olefin}), 131.2 (s, 1 C, CH^{ar}), 132.4 (s, 1 C, CH^5), 134.1 (s, 1 C, C^{quart}), 134.1 (s, 1 C, C^{quart}), 138.5 (s, 1 C, CH^6), 140.4 (s, 1 C, C^{quart}), 141.1 (s, 1 C, C^{quart}), 173.1 (s, 1 C, C^8) ppm. ATR IR: $\tilde{\nu}$ = 2967 (w), 2945 (w), 1723 (s), 1597 (w), 1562 (w), 1482 (w), 1467 (w), 1450 (m), 1433 (m), 1364 (m), 1340 (m), 1298 (w), 1248 (m), 1192 (m), 1172 (m), 1155 (m), 1130 (w), 1113 (m), 1067 (w), 1037 (w), 963 (m), 935 (w), 913 (w), 897 (w), 887 (w), 862 (w), 846 (w), 835 (w), 816 (w), 794 (m), 777 (m), 762 (s), 749 (s), 734 (s), 714 (m), 702 (s), 674 (m), 635 (m), 610 (m) cm^{-1}. HRMS (MALDI, 3-HPA): found (calcd.) for $[C_{24}H_{23}O_2N + H]^+$ 358.1798 (358.1802). $C_{24}H_{23}NO_2$ (357.44): calcd. C 80.64, H 6.49, N 3.92; found C 80.75, H 6.38, N 3.81.

[Rh(25)(CO)]OTf (26): $[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ (16.8 mg, 0.04 mmol, 1 equiv.) was dissolved in thf (1 mL) under argon and **25** (31 mg, 0.09 mmol, 2 equiv.) added. After 1 h, AgOTf (22.3 mg, 0.09 mmol, 2 equiv.) was added. The thf was removed under reduced pressure and the residue dissolved in dcm (2 mL), filtered through Celite and the dcm removed under reduced pressure. The complex was recrystallized from thf/*n*-hexane to give a yellow, air-sensitive powder. Yield: 64%, 36 mg, 0.06 mmol. M.p. 218–224 °C (dec.). $[\alpha]_D^{22}$ = –50.1 (c = 0.1, CH_2Cl_2). ^{1}H NMR (700 MHz, CD_2Cl_2): δ = 1.76 (d, $^3J_{HH}$ = 9.8 Hz, 1 H, CH_2^7), 1.94 (d, $^3J_{HH}$ = 9.8 Hz, 1 H, CH_2^7), 2.32 (s, 1 H, CH^4), 3.13 (s, 1 H, CH^1), 3.70 (dd, $^3J_{HH}$ = 8.5, $^3J_{HH}$ = 3.05 Hz, 1 H, CH^2), 3.92 (s, 3 H, OCH_3), 4.03 (ddd, $^3J_{HH}$ = 8.5, $^3J_{HH}$ = 3.4, $^3J_{HH}$ = 1.2 Hz, 1 H, CH^3), 4.94 (dd, $^3J_{HH}$ = 8.5, $^2J_{RhH}$ = 2.1 Hz, 1 H, CH^{olefin}), 4.99 (s, 1 H, N*H*), 5.07 (s, 1 H, CH^{benzyl}), 5.27 (dd, $^3J_{HH}$ = 8.7, $^2J_{RhH}$ = 2.6 Hz, 1 H, CH^{olefin}), 6.34 (t, $^3J_{HH}$ = 4.4 Hz, 1 H, CH^6), 7.39 (td, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.3 Hz, 1 H, CH^{ar}), 7.42 (td, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.5 Hz, 1 H, CH^{ar}), 7.35–7.50 (m, 4 H, CH^{ar}), 7.67 (m, 1 H, CH^{ar}), 7.69 (dd, $^3J_{HH}$ = 7.5, 1.07 Hz, 1 H, CH^{ar}), 7.76 (m, 1 H, CH^5) ppm. ^{13}C{^{1}H} NMR (176 MHz, CD_2Cl_2): δ = 46.2 (s, 1 C, CH^1) 46.3 (s, 1 C, CH^4), 51.0 (s, 1 C, CH^2), 53.2 (s, 1 C, CH^7), 54.0 (d, $^1J_{RhC}$ = 14.2 Hz, 1 H, CH^{olefin}), 54.9 (s, 1 C, OCH_3), 58.5 (d, $^1J_{RhC}$ = 15.4 Hz, 1 C, CH^{olefin}), 67.8 (s, 1 C, CH^{benzyl}), 69.0 (s, 1 C, CH^3), 122.3 (s, 1 C, CH^6), 124.9 (s, 1 C, CH^5), 127.3 (s, 1 C, CH^{ar}), 128.2 (s, 1 C, CH^{ar}), 128.7 (s, 1 C, CH^{ar}), 128.9 (s, 1 C, CH^{ar}), 129.1 (s, 1 C, CH^{ar}), 129.3 (s, 1 C, CH^{ar}), 129.4 (s, 1 C, CH^{ar}), 129.5 (s, 1 C, CH^{ar}), 134.9 (d, J = 1.8 Hz, 1 C, C^{quart}), 136.3 (s, 1 C, C^{quart}), 136.8 (d, J = 1.8 Hz, 1 C, C^{quart}), 136.9 (d, J = 1.8 Hz, 1 C, C^{quart}), 181.0 (s, 1 C, C^{quart}), 184.0 (d, $^1J_{RhC}$ = 64.8 Hz, 1 C, CO) ppm. ^{103}Rh NMR (22.1 MHz, CD_2Cl_2): δ = –7348 (s) ppm. ATR IR: $\tilde{\nu}$ = 3125 (w, NH), 2957 (w, CH), 2052 (m, CO), 2038 (m, CO), 1645 (m, C=O), 1492 (w), 1448 (m), 1385 (m), 1373 (m), 1327 (w), 1264 (s), 1222 (s), 1190 (m), 1151 (s), 1092 (m), 1077 (m), 1047 (m), 1028 (s), 960 (w), 927 (m), 910 (m), 893 (m), 868 (w), 841 (w), 831 (w), 814 (w), 778 (w), 770 (m), 759 (s), 751 (w), 733 (m), 721 (m), 683 (w), 635 (s), 617 (m), 605 (m) cm^{-1}. $C_{26}H_{23}F_3NO_6RhS\cdot(C_4H_8O)_{0.4}$ (666.27): calcd. C 49.75, H 3.96, N 2.10; found C 49.83, H 3.99, N 2.09.

[Rh(25)(PPh$_3$)]OTf (27): $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ (27.2 mg, 0.07 mmol, 1 equiv.) was dissolved in thf (1 mL) under argon and **25** (50 mg, 0.14 mmol, 2 equiv.) added. After 1 h, PPh_3 (36.7 mg, 0.14 mmol, 2 equiv.) was added. The reaction mixture was stirred for an additional 1 h before AgOTf (40 mg, 0.15, 2.2 equiv.) was added. The solvent was removed under reduced pressure and the residue dissolved in dcm (2 mL), filtered through Celite and the solvent removed under reduced pressure. Recrystallization from dcm/*n*-hexane gave the desired complex. Yield: 52%, 64 mg, 0.07 mmol, not optimized. M.p. >230 °C (dec.). $[\alpha]_D^{22}$ = –2.1 (c = 0.1, CH_2Cl_2). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.35 (d, J = 9.4 Hz, 1 H, CH_2^7), 1.69 (d, J = 9.8 Hz, 1 H, CH_2^7), 2.79 (m, 1 H, N*H*), 3.15 (s, 3 H, OCH_3), 3.24 (dd, J = 8.5, 3.5 Hz, 1 H, CH^2), 3.26 (s, 1 H, CH^1), 3.44 (ddd, J = 12.5, 9.0, 3.2 Hz, 1 H, CH^3), 3.59 (s, 1 H, CH^4), 3.67 (ddd, J = 8.4, 4.0, 1.7 Hz, 1 H, CH^{olefin}), 4.09 (ddd, J = 8.3, 4.0, 2.0 Hz, 1 H) 5.06 (d, J = 6.70 Hz, 1 H, CH^{olefin}), 6.37 (dd, J = 5.48, 2.74 Hz, 1 H, CH^5), 6.43 (dd, J = 5.78, 2.43 Hz, 1 H, CH^6), 7.35–7.65 (m, 17 H, CH^{ar}), 7.70–7.80 (m, 6 H, CH^{ar}) ppm. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 45.2 (d, J = 1.8 Hz, 1 C, CH^4), 45.5 (s, 1 C, CH^1), 46.3 (s, 1 C, CH_2^7), 50.0 (s, 1 C, CH^2), 55.6 (s, 1 C, OCH_3), 58.3 (d, J = 16.9 Hz, 1 C, CH^{olefin}), 60.4 (d, J = 18.0 Hz, 1 C, CH^{olefin}), 60.3 (s, 1 C, CH^3), 66.0 (s, 1 C, CH^{benzyl}), 127.9 (s, 1 C, CH^{ar}), 128.1 (s, 1 C, CH^{ar}), 129.3 (d, $^2J_{PC}$ = 10.1 Hz, 6 C, CH^{ar}), 129.5 (s, 1 C, CH^{ar}), 129.7 (d, $^1J_{PC}$ = 29.2 Hz, 3 C, C^{quart}), 129.7 (s, 1 C, CH^{ar}), 130.0 (s, 1 C, CH^{ar}), 130.1 (s, 2 C, CH^{ar}), 130.1 (s, 1 C, CH^{ar}), 131.6 (d, $^4J_{PC}$ = 2.3 Hz, 3 C, CH^{ar}), 133.0 (s, 1 C, CH^5), 133.6 (s, 1 C, C^{quart}), 134.4 (d, $^3J_{PC}$ = 11.4 Hz, 6 C, CH^{ar}), 136.2 (s, 1 C, C^{quart}), 138.4 (d, J =

1.8 Hz, 1 C, C^{quart}), 139.7 (d, J = 2.3 Hz, 1 C, C^{quart}), 141.0 (s, 1 C, CH^{6}), 182.1 (s, 1 C, C^{quart}) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2): δ = 45.5 (d, $^{1}J_{RhP}$ = 162.5 Hz) ppm. ^{103}Rh NMR (12.6 MHz, CD_2Cl_2): δ = –7472 (d, $^{1}J_{RhP}$ = 162.5 Hz) ppm. ATR IR: $\tilde{\nu}$ = 3125 (m), 1977 (w), 1629 (m), 1573 (w), 1473 (w), 1453 (w), 1436 (m), 1356 (m), 1301 (m), 1282 (m), 1249 (m), 1224 (m), 1183 (w), 1142 (m), 1094 (m), 1058 (m), 1028 (m), 999 (m), 935 (w), 915 (m), 897 (w), 867 (w), 842 (w), 827 (w), 810 (w), 776 (w), 769 (m), 761 (m), 747 (m), 726 (m), 707 (m), 697 (m), 635 (s), 607 (m) cm^{-1}. $C_{43}H_{38}F_3NO_5PRhS\cdot(CH_2Cl_2)_{0.3}$ (897.19): calcd. C 57.97, H 4.34, N 1.56; found C 58.29, H 4.40, N 1.56.

[Rh(15-H)(PPh$_3$)] (28): [Rh(**15**)(PPh$_3$)]OTf (**16**) (50 mg, 6 μm, 1 equiv.) was suspended in thf (2 mL) and treated with KO*t*Bu (6.8 mg, 6 μm, 1 equiv.). A color change from green to red was observed. The solution was stirred further for 30 min. The solvent was removed under reduced pressure, the resulting oil dissolved in toluene and filtered through Celite. Addition of *n*-hexane precipitated part of the product, which was analyzed by NMR spectroscopy. Yield: 50%, 25 mg 3 μm. ^{31}P NMR indicates that the product contains 10% of an unknown impurity. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.01 (m, 2 H, CH_2^{5}), 1.19 (m, 1 H, CH^{1}), 1.24 (m, 2 H, CH_2^{2}), 2.20 (m, 2 H, CH_2^{6}), 4.45 (m, 2 H, CH_2^{allyl}), 6.03 (s, 1 H, CH^{benzyl}), 6.48 (d, $^{3}J_{HH}$ = 7.34 Hz, 2 H, CH^{olefin}), 6.82 (s, 1 H, N*H*), 6.95–7.16 (m, 17 H, CH^{ar}), 7.26–7.38 (m, 9 H, CHar and CH^{4}) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): δ = 22.5 (s, 1 C, CH_2^{5}), 24.3 (s, 1 C, CH_2^{2}), 28.9 (s, 1 C, CH_2^{6}), 30.1 (s, 1 C, CH^{1}), 59.8 (m, 1 C, CH_2^{7}), 71.9 (s, 1 C, CH^{benzyl}), 122–145 (30 C, CH^{ar} and C^{quart}), 127.5 (s, 2 C, CH^{olefin}), 148.5 (s, 1 C, CH^{4}), 166.6 (s, 1 C, CH^{3}) ppm. $^{31}P\{^{1}H\}$ NMR (283 MHz, CD_2Cl_2): δ = 40.8 (d, $^{1}J_{RhP}$ = 155.3 Hz) ppm. ^{1}H, ^{103}Rh NMR (15.8 MHz, CD_2Cl_2): δ = –8690 (d, $^{1}J_{RhP}$ = 155.3 Hz) ppm.

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