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Synthesis of iridium complexes with novel planar chiral chelating imidazolylidene ligands

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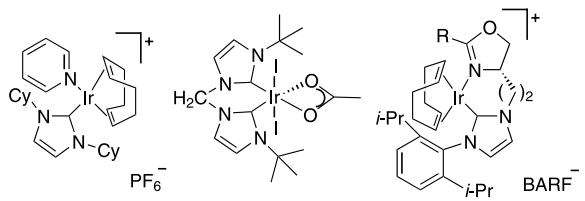
Abstract—New planar chiral imidazolium salts such as (S_p)-1-[4-(4,4-dimethyl-4,5-dihydrooxazolyl)[2.2]paracyclophane-12-ylmethyl]-3-methyl imidazolium bromide (S_p)-**8a** have been synthesized starting from enantiopure 4,12-dibromo[2.2]paracyclophane (S_p)-**4**. Deprotonation of these salts followed by reaction with $[Ir(COD)Cl]_2$ yielded chelating iridium imidazolylidene complexes **9a**–**c**, which were applied in asymmetric hydrogenations of alkenes. The solid state structure of (S_p)-**9c** was determined by single-crystal X-ray structure analysis.

1. Introduction

Since the early reports on metal complexes bearing *N*-heterocyclic carbene (NHC) ligands by Öfele[1a] and Wanzlick[1b] in 1968 and the first isolation of free NHCs by Arduengo in 1991,[2] much progress has been made with respect to the synthesis and the catalytic applications of NHCs and their metal complexes.[3,4] Hence, they now represent a significant alternative to phosphine ligands in homogenous catalysis. In particular, NHC complexes of ruthenium have become very popular in olefin metathesis and exhibit superior properties to the analogous phosphine ligands.[5]

Only recently have transition metal NHC complexes been applied in the catalytic hydrogenations of alkenes and transfer hydrogenations of ketones. Nolan et al. have prepared saturated and unsaturated iridium NHC complexes such as **1**, which are similar to Crabtree's catalyst.[6] The synthesis and application of complexes of type **2** bearing chelating biscarbene ligands has been reported by Crabtree, Faller and Peris.[7]



1 **2** **3**: R = Adamantyl

However, only a few examples are known to date directly relating to the application of chiral NHC ligands in asymmetric catalysis. First, Herrmann and, shortly after, Enders reported enantioselective hydrosilylations using rhodium NHC complexes.[8] The application of chiral ruthenium NHC complexes in asymmetric olefin metathesis was demonstrated by Grubbs and Hoveyda.[9] Other examples include the use of silver NHC complexes in the conjugate addition of diethylzinc to unsaturated ketones,[10] and the application of chiral triazonium salts as catalysts in the enantioselective benzoin condensation and *Stetter* reaction.[11] Asymmetric hydrogenations were reported by Burgess et al.[12] They successfully applied iridium complex **3** bearing a chiral chelating imidazolylidene ligand in catalyzed hydrogenations of unfunctionalized alkenes giving products with up to 99% ee in 98% yield.

Recently, we reported on the synthesis of the first planar chiral carbene and metal complexes thereof.[13] In this case, the planar chirality of the molecules originated from a ferrocene backbone. We have now extended those studies and focused our attention on syntheses of planar chiral *pseudo-ortho*-disubstituted [2.2]paracyclophanes[14] with imidazolylidenyl and oxazolinyl substituents. Furthermore, we have investigated applications of the corresponding iridium carbene complexes in catalyzed asymmetric olefin hydrogenations.

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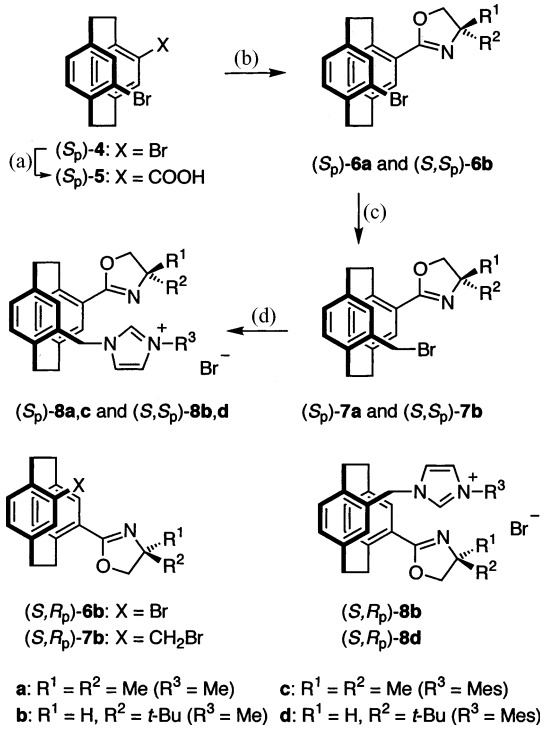
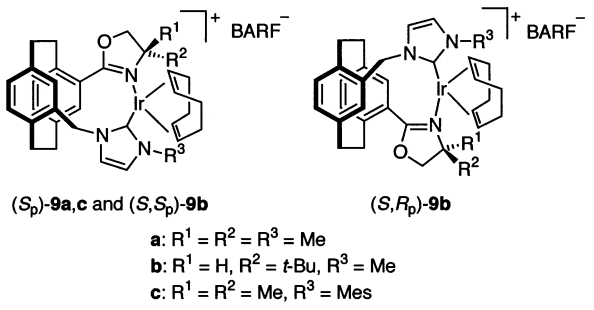
2. Results and discussion

The syntheses of the desired compounds started from enantiopure 4,12-dibromo[2.2]paracyclophane (S_p)-**4**.[14,15] Following a standard protocol for the synthesis of oxazolines as described by Pelter,[16] (S_p)-**4** was treated with 1 equiv. of *n*-BuLi, and the resulting carbanion was trapped with carbon dioxide affording carboxylic acid (S_p)-**5** in 87% yield (Scheme 1). [2.2]Paracyclophanes (S_p)-**6a** and (S,S_p)-**6b** bearing a bromo and an oxazolinyl substituent in the 4 and 12 positions, respectively, were then obtained from (S_p)-**5** by sequential formation of the acid chloride, its treatment with the appropriate amino alcohol and subsequent oxazoline formation by ring closure (80–87% overall yields). Metallation of (S_p)-**6a** and (S,S_p)-**6b** with *t*-BuLi followed by reaction with CO_2 gave the corresponding lithium carboxylates which were reduced with $LiAlH_4$. The resulting alcohols were then reacted with pyridine/PBr_3 to afford methyl bromides (S_p)-**7a** and (S,S_p)-**7b**, respectively (for details see Scheme 1). Upon heating of mixtures of (S_p)-**7a** or (S,S_p)-**7b** and imidazoles[17] in DMF, the desired imidazolium salts (S_p)-**8a**,**c** and (S,S_p)-**8b**,**d** were obtained in yields ranging from 50 to 97%. The diastereomeric products (S,R_p)-**6b**, (S,R_p)-**7b**, (S,R_p)-**8b** and (S,R_p)-**8d** were prepared by the same reaction sequence starting from the R_p-enantiomer of **4**.



Scheme 1. *Reagents and conditions*: (a) *n*-BuLi, THF, −78°C, CO_2, 87% yield. (b) i. $SOCl_2$; ii. NEt_3, amino alcohol, CH_2Cl_2; iii. $SOCl_2$, NaOH, 80–87% yield. (c) i. *t*-BuLi, THF, −78°C, CO_2; ii. $LiAlH_4$, 52–73% yield; iii. PBr_3, pyridine, THF, 69–93% yield. (d) Imidazoles, DMF, 80°C, 50–97% yield.

Next, we focused on the preparation of iridium complexes **9**. For their syntheses imidazolium salts **8** were treated with KO*t*-Bu in THF, and subsequent reactions of the in situ formed carbenes with $[Ir(COD)Cl]_2$ followed by anion exchange with NaBARF[18] afforded complexes **9a**–**c** in yields of 48–74%. The BARF counterion was chosen, since it had previously been shown to be superior over other bulky counterions such as PF_6^-. Interestingly, only (S_p)-**8a**, (S,S_p)-**8b**, (S_p)-**8c**, and (S,R_p)-**8b** reacted well (to give (S_p)-**9a**, (S,S_p)-**9b**, (S_p)-**9c**, and (S,R_p)-**9b**, respectively), whereas no products were obtained from (S,S_p)-**8d** and (S,R_p)-**8d**. Presumably, the combination of the two bulky substituents at both donor sites of the latter [2.2]paracyclophanes (at the carbene a mesityl and at the oxazoline group a *tert*-butyl substituent) inhibited complex formation due to steric crowding.



Complexes **9a**–**c** are bright yellow, air-stable solids. The NMR spectra are consistent with the proposed chelating structures. The proton NMR spectra exhibit pronounced chemical shifts for the two *ortho* protons (5-H and 13-H) of the [2.2]paracyclophane rings, which show low- and high-field absorptions at $\delta = 9.4$–9.6 and 4.6–5.4 ppm, respectively. In the ^{13}C NMR spectra the signals for the coordinated carbenes appear at $\delta = 176$–178 ppm. Final structural proof was obtained by single-crystal X-ray analysis of complex (S_p)-**9c** (Fig. 1). Suitable crystals were obtained from a solvent mixture

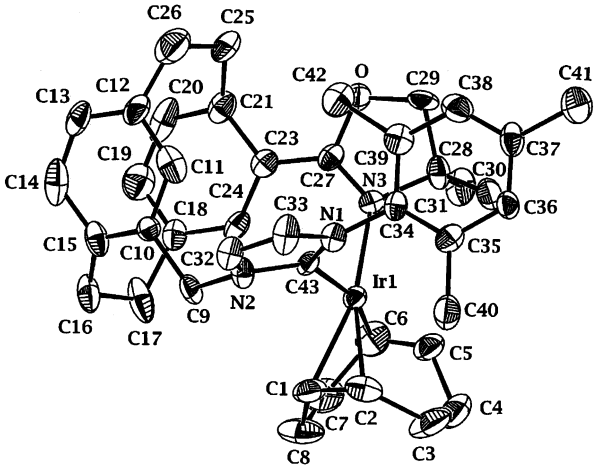


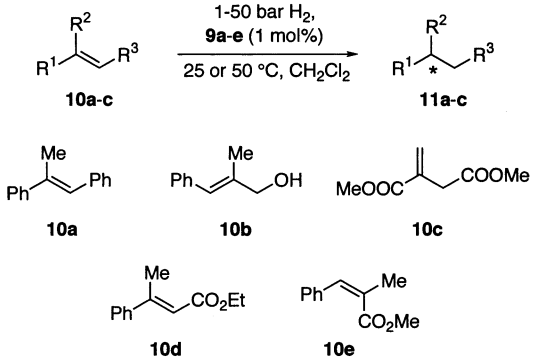
Figure 1. The structure of (S_p)-**9c** in the solid state. The anion has been omitted for clarity. The ellipsoids have been plotted at the 30% probability level. [Ir1–C43: 2.05(1), Ir1–C1: 2.12(2), Ir1–C2: 2.14(2), Ir1–C5: 2.23(1), Ir1–C6: 2.17(2), Ir1–N3: 2.137(9), C1=C2: 1.34(2), C5=C6: 1.37(2) Å].

of EtOH, CH_2Cl_2 and Et_2O. The solid state structure showed a significant steric crowding around the metal core, which might be the reason for the unavailability of defined structures of (S,S_p)-**9b** and (S,R_p)-**9b**.

The iridium complexes were then tested as chiral catalysts in the asymmetric hydrogenation of alkenes.[19,20] Although at room temperature their activities were rather low (at a catalyst loading of 1 mol%), all complexes except one, (S_p)-**9a**, led to optically active products **11** (Table 1). Interestingly, the most promising results with respect to enantioselectivity were achieved with planar chiral (S_p)-**9c**, which proved superior to its analoges (S,S_p)-**9b** and (S,R_p)-**9b** having additional stereogenic centers at the oxazolinyl groups. At 25°C (and 50 bar of hydrogen pressure), the conversions in the hydrogenation of *trans*-α-methyl stilbene **10a** did not exceed 35% affording the product with 28% ee at best using (S_p)-**9c** as catalyst. The performance of diastereomeric complexes (S,S_p)-**9b** and (S,R_p)-**9b** was almost equal, leading to lower yields and reduced enantioselectivities (12 and 11% ee, respectively) under comparable conditions (Table 1, entries 2 and 3). In all cases, the (*R*)-enantiomer of the product was predominantly formed. Apparently, cooperative effects between the stereogenic elements[21] in the diastereomeric complexes (S,S_p)-**9b** and (S,R_p)-**9b** leading to matched/mismatched combinations played only a minor role as indicated by the insignificant variation in conversion and ee in catalyses with those complexes (Table 1, entry 2 versus entry 3). At 50°C the conversion of **10a** increased up to 76%, however, now the enantioselectivity was lower as compared to the room temperature experiments. The same trend was observed in the hydrogenation of allylic alcohol **10b** (Table 1, entry 5). The best result was achieved in the hydrogenation of dimethyl itaconate **10c** using (S_p)-**9c** as catalyst. In this case, full conversion was even observed at room temperature applying the relatively low hydrogen pressure of 10 bar. Reducing the latter further to 1 bar resulted in a lower conversion of the substrate, but at the same time, the ee of the product increased to 46% (Table 1, entry 8). At 25°C and under 50 bar of hydrogen monoesters **10d** and **10e** afforded the corresponding saturated products with 38 and 21% ee, respectively (Table 1, entries 9 and 10).

On the basis of these results, we conclude that the steric properties of the substituents on both the imidazole as well as the oxazoline ring play an important role in the activity of the catalyst. For example, in contrast to its *N*-mesityl analogue (S_p)-**9c**, the *N*-methyl complex (S_p)-**9a** showed no activity at all in the room temperature hydrogenation of **10a** (Table 1, entries 1 and 4). When

Table 1. Asymmetric hydrogenations with various Ir complexes **9** as catalysts[a]



Entry	Substrate	Catalyst	p(H_2) (bar)	T (°C)	Conversion (%)[b]	Ee (%)[c]
1	**10a**	(S_p)-**9a**	50[d]	25/50	–/40	–/0
2	**10a**	(S,S_p)-**9b**	50[d]	25/50	17/61	12/4 (*R*)
3	**10a**	(S,R_p)-**9b**	50[d]	25/50	15/59	11/10 (*R*)
4	**10a**	(S_p)-**9c**	50[d]	25/50	35/76	28/15 (*R*)
5	**10b**	(S_p)-**9c**	50[d]	25/50	25/100	11/4[e]
6	**10c**	(S_p)-**9c**	50[f]	25	100	9 (*R*)
7	**10c**	(S_p)-**9c**	10[d]	25	100	13 (*R*)
8	**10c**	(S_p)-**9c**	1[g]	25	46	46 (*R*)
9	**10d**	(S_p)-**9c**	50[d]	25	99	38 (*R*)
10	**10e**	(S_p)-**9c**	50[d]	25	100	21 (*R*)

[a] See Section 3 for reaction details.
[b] Determined by ^{1}H NMR; conversions at 25°C/50°C.
[c] Determined by HPLC using a chiral column; the absolute configurations were assigned by comparison of the HPLC retention times with literature values; ee's at 25°C/50°C.
[d] Reaction time: 6–24 h.
[e] Absolute configuration not determined.
[f] Reaction time: 2 h.
[g] Reaction time: 48 h.

complexes (S,S_p)-**9b** and (S,R_p)-**9b** were used as catalysts, product formation was observed, and in these cases we attribute the catalytic activity to the presence of the sterically bulky *tert*-butyl groups on the oxazolinyl substituents. Unfortunately, complexes bearing a combination of an *N*-mesityl on the imidazole and a *tert*-butyl group on the oxazoline moiety could not be prepared. However, since we expect promising catalytic activities from those complexes, attempts to synthesize these compounds will be pursued further.

In summary, we have synthesized new iridium imidazolylidine complexes with planar chiral [2.2]paracyclophanes as ligands. They have been applied as catalysts in the asymmetric hydrogenations of alkenes giving enantiomerically enriched products with up to 46% ee. Studies towards improvements of activity and stereoselectivity are currently on-going in our laboratories.

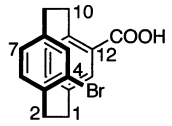
3. Experimental

3.1. General information

pseudo-ortho-Dibromo[2.2]paracyclophane[15] and 1-mesitylimidazole[17] were prepared according to published procedures. (*S*)-*t*-Leucinol was prepared from (*S*)-*t*-leucine (obtained as a gift from Degussa). The following reagents and solvents are commercially available and were used as received: 2-amino-2-methylpropan-1-ol (Aldrich), *n*-BuLi (1.6 M in *n*-hexane, Merck-Schuchardt), *t*-BuLi (1.48 M in pentane, Merck-Schuchardt), KO*t*-Bu (1 M, Aldrich), 1-methylimidazole (Aldrich), anhydrous DMF (Aldrich). $[Ir(COD)Cl]_2$ was obtained as a gift from OMG. THF was distilled under nitrogen from sodium benzophenone ketyl and CH_2Cl_2 from calcium hydride prior to use. All reactions were performed under an inert atmosphere of argon using standard Schlenk techniques. The NMR spectra were recorded on a Varian Mercury 300 (^{1}H NMR at 300 MHz; ^{13}C NMR at 75 MHz), a Varian Inova 400 (^{1}H NMR at 400 MHz; ^{13}C NMR at 100 MHz; ^{19}F NMR at 376 MHz), or Varian Unity 500 (^{1}H NMR at 500 MHz; ^{13}C NMR at 125 MHz; ^{11}B NMR at 160 MHz) spectrometer. Chemical shifts are given in ppm with internal referencing to TMS (^{1}H NMR), external $CFCl_3$ (^{19}F NMR), external $BF_3{\cdot}OEt_2$ (^{11}B NMR) or the solvent peaks (^{1}H, ^{13}C NMR). Assignments are based on 2D NMR experiments. IR spectra were measured on a Perkin–Elmer 1760 FT spectrometer, mass spectra were obtained by using a Varian MAT 212 (EI, ESI, APCI) and a Finnigan MAT 95 (SIMS-FAB) spectrometer. Only fragments containing the isotopes of the highest abundance are listed. Elemental analyses were carried out at the Institut für Organische Chemie der RWTH Aachen on a Heraeus CHNO-Rapid apparatus. Melting points were measured with a Büchi B-540 melting point determination apparatus. Optical rotations were measured on a Perkin–Elmer 241 polarmeter.

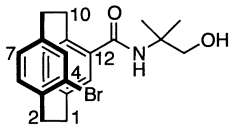
3.2. Synthesis of (S_p)-4-bromo-12-(4,4-dimethyl-4,5-dihydrooxazolyl)[2.2]paracyclophane (S_p)-6a

3.2.1. (S_p)-4-Bromo-12-carboxy[2.2]paracyclophane (S_p)-5.



(S_p)-*pseudo-ortho*-Dibromo[2.2]paracyclophane (S_p)-**4** (10.0 g, 27.3 mmol) was placed in a Schlenk flask under an argon atmosphere and dissolved in anhydrous THF (120 mL). After cooling to −78°C in a dry ice/acetone bath, a solution of *n*-BuLi in pentane (20.0 mL, 32.0 mmol) was added slowly. The reaction mixture was stirred at −78°C for 1 h, and subsequently carbon dioxide was bubbled through it for 30 min. The solution was then allowed to slowly warm to room temperature, acidified with 5 M HCl to pH 1–2, and extracted with dichloromethane (3×100 mL). The combined organic extracts were washed with 10 M NaOH (4×100 mL). After acidification of the aqueous layers to pH 1–2 with concentrated HCl and extraction with dichloromethane (3×100 mL), the combined organic phase was dried ($MgSO_4$) and concentrated to give 7.90 g of (S_p)-4-bromo-12-carboxy[2.2]paracyclophane (S_p)-**5** as a white solid (87% yield). The product can be recrystallized from glacial acetic acid. Mp 228–229°C; $[\alpha]_D^{25}=+141$ (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.74–2.89 (m, 3H, CH_2), 2.98–3.08 (m, 3H, CH_2), 3.23 (ddd, 1H, $J=13.0$, 8.7, 2.9 Hz, CH_2), 3.91–3.97 (m, 1H, CH_2), 6.44 (d, 1H, $J=1.6$ Hz, 5-*H*), 6.54 (d, 1H, $J=7.7$ Hz, *Aryl*-C*H*), 6.62–6.65 (m, 2H, *Aryl*-C*H*), 6.68 (dd, 1H, $J=8.0$, 2.0 Hz, 15-*H*), 7.58 (d, 1H, $J=1.9$ Hz, 13-*H*), 12.51 Hz (bs, 1H, COO*H*); ^{13}C NMR (100 MHz, DMSO-d_6) δ 32.8, 34.3, 35.7, 36.1 (*C*H$_2$), 126.6 (q*C*), 131.3 (*C*-13), 131.5 (q*C*), 132.2 (*C*H), 135.4 (*C*-5), 136.0, 136.6, 137.3 (*C*H), 139.1, 139.6, 142.2, 142.6 (q*C*), 168.6 (*C*=O); IR (KBr) $\tilde{\nu}$ 1679, 1297, 1273 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 332 (31), 330 (34, M$^+$), 185 (100), 184 (44), 183 (99), 182 (35), 148 (57), 103 (24), 91 (19), 77 (25). Anal. calcd for $C_{17}H_{15}BrO_2$: C, 61.65; H, 4.56. Found: C, 61.85; H, 4.75.

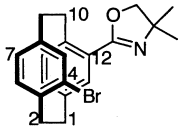
3.2.2. (S_p)-4-Bromo-*N*-(1-hydroxy-2-methyl-2-propyl)-[2.2]paracyclophane-12-carboxamide.



(S_p)-4-Bromo-12-carboxy[2.2]paracyclophane (S_p)-**5** (7.4 g, 22.3 mmol) was stirred in thionyl chloride at 60°C for 4 h. After evaporation of $SOCl_2$ in vacuo, remaining traces of it were removed by destillation with small portions of toluene (3×5 mL). The residue was dissolved in anhydrous CH_2Cl_2 (20 mL) and cooled to 0°C. A solution of 2-amino-2-methyl-

propan-1-ol (4.2 mL, 44.0 mmol) and NEt_3 (6.1 mL, 44.1 mmol) in CH_2Cl_2 (30 mL) was added over 1 h while maintaining the temperature at 0°C. The reaction mixture was allowed to warm to room temperature and stirred over night. The solution was diluted with dichloromethane (50 mL) and washed with aqueous $NaHCO_3$ (2×80 mL) and brine (80 mL). The organic phase was concentrated and the residue purified by column chromatography on silica gel (hexane:ethyl acetate, 7:3) to give 7.88 g (88% yield) of (S_p)-4-bromo-*N*-(1-hydroxy-2-methyl-2-propyl)[2.2]paracyclophane-12-carboxamide as a white, crystalline solid. Mp 152–154°C; $[\alpha]_D^{25}=+63$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 3H, C*H*$_3$), 1.48 (s, 3H, C*H*$_3$), 2.77–2.87 (m, 2H, C*H*$_2$), 2.96–3.06 (m, 2H, C*H*$_2$), 3.07–3.18 (m, 2H, C*H*$_2$), 3.44 (ddd, 1H, *J*=9.3, 2.6 Hz, C*H*$_2$), 3.68–3.79 (m, 3H, C*H*$_2$OH, C*H*$_2$), 4.85 (bs, 1H, O*H*), 6.08 (bs, 1H, N*H*), 6.52 (d, 1H, *J*=7.7 Hz, *Aryl*-C*H*), 6.56–6.61 (m, 3H, *Aryl*-C*H*), 6.80 (d, 1H, *J*=1.6 Hz, 5-*H*), 7.17 (d, 1H, *J*=1.7 Hz, 13-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 25.2 (*C*H$_3$), 32.9, 34.8, 34.9, 36.0 (*C*H$_2$), 57.0 (*C*(CH$_3$)$_2$), 71.3 (*C*H$_2$OH), 126.6 (q*C*), 126.9 (*C*-13), 131.8 (*C*H), 135.0 (*C*-5), 135.2 (*C*H), 135.4 (q*C*), 135.6, 136.3 (*C*H), 138.8, 139.8, 139.8, 142.4 (q*C*), 170.0 (*C*=O); IR (KBr) $\tilde{\nu}$ 3254, 3162, 3068, 2981, 2964, 2934, 2858, 1630, 1568, 1548, 1348, 1067 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 403 (20), 401 (20, M^+), 332 (18), 330 (20), 219 (29), 148 (10), 147 (100), 146 (12), 131 (32), 103 (22), 77 (16). Anal. calcd for $C_{21}H_{24}BrNO_2$: C, 62.69; H, 6.01; N, 3.48. Found: C, 62.39; H, 5.79; N, 3.22.

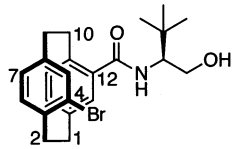
3.2.3. (S_p)-4-Bromo-12-(4,4-dimethyl-4,5-dihydrooxazolyl)[2.2]paracyclophane (S_p)-6a.



(S_p)-4-Bromo-*N*-(1-hydroxy-2-methyl-2-propyl)[2.2]-paracyclophane-12-carboxamide (7.65 g, 19.0 mmol) was stirred in thionyl chloride at room temperature for 4 h. After concentration of the reaction mixture in vacuo at 40°C, the residue was dissolved in CH_2Cl_2 (200 mL) and stirred with a solution of sodium hydroxide (10%, 200 mL) over night. After phase separation, the organic layer was washed with brine (50 mL), dried ($MgSO_4$) and evaporated to yield 7.26 g (99% yield) of (S_p)-4-bromo-12-(4,4-dimethyl-4,5-dihydrooxazolyl)-[2.2]paracyclophane (S_p)-**6a** as a pale orange solid. No by-product was detectable by NMR spectroscopy. An analytical pure sample of (S_p)-**6a** was obtained by recrystallization from methanol. Mp 104–106°C; $[\alpha]_D^{25}=+81$ (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 3H, C*H*$_3$), 1.46 (s, 3H, C*H*$_3$), 2.74–2.82 (m, 2H, C*H*$_2$), 2.94–3.10 (m, 3H, C*H*$_2$), 3.15–3.23 (m, 1H, C*H*$_2$), 3.45 (ddd, 1H, *J*=13.2, 10.1 Hz, 1.7 Hz, C*H*$_2$), 4.03 (d, 1H, *J*=7.9 Hz, OC*H*$_2$), 4.12 (d, 1H, *J*=8.0 Hz, OC*H*$_2$), 4.24 (ddd, 1H, *J*=12.3, 9.9, 1.3 Hz, C*H*$_2$), 6.46 (d, 1H, *J*=7.7 Hz, *Aryl*-C*H*), 6.53–6.60 (m, 3H, *Aryl*-C*H*), 6.62 (d, 1H, *J*=1.4 Hz, 5-*H*), 7.65 (d, 1H, *J*=1.3 Hz, 13-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.8, 28.9 (*C*H$_3$), 33.0, 34.2, 36.1, 36.4 (*C*H$_2$), 68.1 (*C*(CH$_3$)$_2$), 78.6 (OCH$_2$), 126.8, 128.6 (q*C*), 130.6 (*C*-13), 131.5, 135.1, 135.2, 135.3, 135.9 (*C*H), 139.0, 139.4, 140.7, 142.3 (q*C*), 161.9 (*C*=N); IR (KBr) $\tilde{\nu}$ 2961, 2929, 2898, 1627, 1303, 1192 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 385 (22), 383 (26, M^+), 202 (15), 201 (100), 146 (11), 103 (10). Anal. calcd for $C_{21}H_{22}BrNO$: C, 65.63; H, 5.77; N, 3.64. Found: C, 65.81; H, 5.84; N, 3.58.

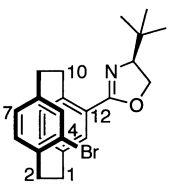
3.3. Synthesis of (S,S_p)-4-bromo-12-(4-*tert*-butyl-4,5-dihydrooxazolyl)[2.2]paracyclophane (S,S_p)-6b

3.3.1. (S,S_p)-4-Bromo-*N*-(1-hydroxy-3-dimethyl-2-butyl)-[2.2]paracyclophane-12-carboxamide.



This compound was prepared by the method described for (S_p)-4-bromo-*N*-(1-hydroxy-2-methyl-2-propyl)-[2.2]paracyclophane-12-carboxamide using (S_p)-4-bromo-12-carboxy-[2.2]paracyclophane (S_p)-**5** (5.0 g, 15.1 mmol), $SOCl_2$ (10 mL), CH_2Cl_2 (30 mL), NEt_3 (4.2 mL, 30.1 mmol), and (*S*)-*t*-leucinol (3.5 g, 29.9 mmol). Purification by column chromatography on silica gel (EtOAc:hexane, 1:2 to 2:1) yielded 5.26 g (81%) of the title compound as a white solid. Mp 150–152°C; $[\alpha]_D^{25}=+70$ (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.09 (s, 9H, C*H*$_3$), 2.64 (bs, 1H, O*H*), 2.74–2.88 (m, 2H, C*H*$_2$), 2.97–3.20 (m, 4H, C*H*$_2$), 3.45 (ddd, 1H, *J*=13.2, 9.2, 2.3 Hz, C*H*$_2$), 3.59 (dd, 1H, *J*=11.1, 7.8 Hz, C*H*$_2$OH), 3.72 (ddd, 1H, *J*=12.2, 10.2, 2.0 Hz, C*H*$_2$), 3.90 (dd, 1H, *J*=11.2, 3.3 Hz, C*H*$_2$OH), 4.04 (ddd, 1H, *J*=9.3, 7.8, 3.5 Hz, C*H*t Bu), 5.99 (bd, 1H, *J*=9.2 Hz, N*H*), 6.51 (d, 1H, *J*=7.7 Hz, *Aryl*-C*H*), 6.56–6.60 (m, 3H, *Aryl*-C*H*), 6.79 (d, 1H, *J*=1.8 Hz, 5-*H*), 7.28 (d, 1H, *J*=1.3 Hz, 13-*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.7 (3C, C(*C*H$_3$)$_3$), 32.9, 34.4, 34.9, 35.1, 36.1 (*C*(CH$_3$)$_3$, *C*H$_2$), 60.0 (*C*Ht Bu), 63.6 (*C*H$_2$OH), 127.0 (*C*-13), 131.5 (*C*H), 134.8 (q*C*), 134.9 (*C*-5), 135.6, 135.7, 136.1 (*C*H), 138.8, 139.8, 140.0, 142.5 (q*C*), 170.2 (*C*=O); IR (KBr) $\tilde{\nu}$ 3424, 3329, 2962, 2929, 2866, 1659, 1623, 1513, 1477, 1085 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%): 432 (11), 431 (48), 430 (12), 429 (M^+, 47), 374 (11), 372 (11), 355 (11), 332 (46), 330 (45), 315 (18), 313 (16), 248 (16), 247 (100), 147 (87), 146 (12), 132 (14), 131 (87), 104 (11), 103 (44). Anal. calcd for $C_{23}H_{28}BrNO_2$: C, 64.19; H, 6.56; N, 3.25. Found: C, 64.30; H, 6.24; N, 3.15.

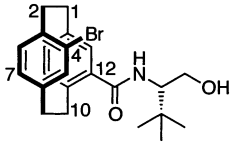
3.3.2. (S,S_p)-4-Bromo-12-(4-*tert*-butyl-4,5-dihydrooxazolyl)[2.2]paracyclophane (S,S_p)-6b.



This compound was prepared by the same procedure as described for (S_p)-**6a** using (S,S_p)-4-bromo-*N*-(1-hydroxy-3-dimethyl-2-butyl)-[2.2]paracyclophane-12-carboxamide (5.0 g, 11.6 mmol) and $SOCl_2$ (40 mL). The product was obtained as a pale yellow solid (4.76 g, 99% yield). No by-product was detectable by NMR spectroscopy. The compound can be recrystallized from methanol. Mp 103–105°C; $[\alpha]_D^{25}=+7$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (s, 9H, CH_3), 2.75–2.87 (m, 2H, CH_2), 3.02–3.12 (m, 3H, CH_2), 3.14–3.22 (m, 1H, CH_2), 3.46 (ddd, 1H, $J=13.2$, 9.9, 1.4 Hz, CH_2), 4.07 (dd, 1H, $J=10.0$, 9.0 Hz, OCH_2), 4.19 (t, 1H, $J=8.6$ Hz, CH*t*Bu), 4.28 (dd, 1H, $J=10.3$, 8.3 Hz, OCH_2), 4.31–4.37 (m, 1H, CH_2), 6.49 (d, 1H, $J=8.0$ Hz, *Aryl*-CH), 6.54–6.62 (m, 4H, *Aryl*-CH), 7.61 (bs, 1H, 13-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8 (3C, C(CH_3)$_3$), 32.9, 34.0 (CH_2), 34.6 (*C*(CH$_3$)$_3$), 35.9, 36.1 (CH_2), 67.9 (OCH_2), 77.4 (CH*t*Bu), 126.9, 128.2 (q*C*), 130.0 (*C*-13), 131.5, 135.1, 135.3, 135.5, 135.8 (CH), 139.0, 139.3, 140.8, 142.3 (q*C*), 162.9 (*C*=N). IR (KBr) $\tilde{\nu}$ 2956, 2928, 2866, 1638, 1047, 1031, 984 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 413 (38), 411 (M$^+$, 36), 230 (17), 229 (100), 147 (11). Anal. calcd for $C_{23}H_{26}BrNO$: C, 66.99; H, 6.36; N, 3.40. Found: C, 66.77; H, 6.49; N, 3.29.

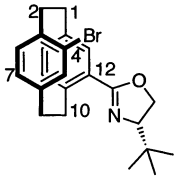
3.4. Synthesis of (S,R_p)-4-bromo-12-(4-*tert*-4,5-dihydrooxazolyl)[2.2]paracyclophane (S,R_p)-6b

3.4.1. (S,R_p)-4-Bromo-*N*-(1-hydroxy-3-dimethyl-2-butyl)-[2.2]paracyclophane-12-carboxamide.



This compound was prepared by the method described for (S_p)-4-bromo-*N*-(1-hydroxy-2-methyl-2-propyl)-[2.2]paracyclophane-12-carboxamide using (R_p)-4-bromo-12-carboxy-[2.2]paracyclophane (R_p)-**5** (5.6 g, 16.9 mmol), $SOCl_2$ (12 mL), CH_2Cl_2 (40 mL), NEt_3 (4.8 mL, 34.4 mmol), and (*S*)-*t*-leucinol (4.0 g, 34.1 mmol). The title compound was obtained as a white solid in 88% yield (6.44 g) after purification on silica gel (EtOAc:hexane, 1:1). Mp 146°C; $[\alpha]_D^{25}=-53$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 9H, CH_3), 2.78–2.89 (m, 3H, CH_2, OH), 3.00–3.04 (m, 2H, CH_2), 3.11–3.20 (m, 2H, CH_2), 3.45 (ddd, 1H, $J=13.2$, 9.1, 2.5 Hz, CH_2), 3.82–3.89 (m, 1H, CH_2OH), 3.85 (ddd, 1H, $J=12.5$, 8.7, 3.9 Hz, CH_2), 4.07–4.15 (m, 2H, CH_2OH, CH*t*Bu), 6.32 (bd, 1H, $J=9.4$ Hz, NH), 6.53 (d, 1H, $J=7.9$ Hz, *Aryl*-CH), 6.57–6.61 (m, 2H, *Aryl*-CH), 6.64 (d, 1H, $J=8.0$ Hz, *Aryl*-CH) 6.94 (d, 1H, $J=1.3$ Hz, 5-*H*), 7.24 (d, 1H, $J=1.6$ Hz, 13-*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5 (3C, C(CH_3)$_3$), 32.9 (CH_2), 34.1 (*C*(CH$_3$)$_3$), 34.6 (CH_2), 34.9 (CH_2), 36.0 (CH_2), 60.3 (CH*t*Bu), 63.7 (CH_2OH), 126.3 (*C*-13), 126.4 (q*C*), 131.9 (CH), 135.2 (*C*-5), 135.3, 135.4 (CH), 136.1 (q*C*), 136.5 (CH), 138.7, 139.7, 140.1, 142.8 (q*C*), 170.1 (*C*=O). IR (KBr) $\tilde{\nu}$ 3305, 2935, 1638, 1536 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 431 (40), 429 (M$^+$, 44), 374 (15), 372 (16), 332 (52), 330 (50), 315 (15), 313 (13), 248 (14), 247 (99), 147 (99), 146 (10), 132 (13), 131 (100), 103 (50). Anal. calcd for $C_{23}H_{28}BrNO_2$: C, 64.19; H, 6.56; N, 3.25. Found: C, 64.44; H, 6.53; N, 3.11.

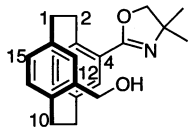
3.4.2. (S,R_p)-4-Bromo-12-(4-*tert*-4,5-dihydrooxazolyl)-[2.2]paracyclophane (S,R_p)-6b.



This compound was prepared by the same procedure as described for (S_p)-**6a** using (S,R_p)-4-bromo-*N*-(1-hydroxy-3-dimethyl-2-butyl)-[2.2]paracyclophane-12-carboxamide (6.2 g, 14.4 mmol) and $SOCl_2$ (50 mL). The product was obtained as a pale yellow solid (5.86 g, 99% yield). No by-product was detectable by NMR spectroscopy. The compound can be recrystallized from methanol. Mp 60–62°C; $[\alpha]_D^{25}=-110$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.02 (s, 9H, C(CH_3)$_3$), 2.72–2.84 (m, 2H, CH_2), 2.93–3.10 (m, 3H, CH_2), 3.14–3.24 (m, 1H, CH_2), 3.45 (ddd, 1H, $J=13.1$, 9.9, 1.6 Hz, CH_2), 4.05–4.20 (m, 3H, CH_2, OCH_2, CH*t*Bu), 4.33 (dd, 1H, $J=9.7$, 7.9 Hz, OCH_2), 6.47 (d, 1H, $J=7.7$ Hz, *Aryl*-CH), 6.53–6.60 (m, 3H, *Aryl*-CH), 6.66 (d, 1H, $J=1.4$ Hz, 5-*H*), 7.66 (bs, 1H, 13-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.5 (3C, C(CH_3)$_3$), 32.9, 34.3 (CH_2), 34.4 (*C*(CH$_3$)$_3$), 36.2, 36.4 (CH_2), 68.4 (OCH_2), 76.9 (CH*t*Bu), 126.9, 128.3 (q*C*), 130.5 (*C*-13), 131.4, 135.1, 135.2 (CH), 135.3 (*C*-5), 135.8 (CH), 139.0, 139.4, 140.5, 142.3 (q*C*), 163.4 (*C*=N); IR (KBr) $\tilde{\nu}$ 2932, 2866, 1645, 1477, 1048, 1031, 980 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 413 (26), 411 (M$^+$, 26), 230 (15), 229 (100), 147 (12). Anal. calcd for $C_{23}H_{26}BrNO$: C, 66.99; H, 6.36; N, 3.40. Found: C, 66.79; H, 6.20; N, 3.29.

3.5. Synthesis of (S_p)-4-bromomethyl-12-(4,4-dimethyl-4,5-dihydrooxazolyl)[2.2]paracyclophane (S_p)-7a

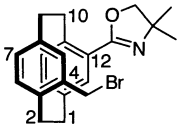
3.5.1. (S_p)-4-(4,4-Dimethyl-4,5-dihydrooxazolyl)-12-hydroxymethyl[2.2]paracyclophane.



At −78°C a solution of oxazoline (S_p)-**6a** (5.2 g, mmol) in THF (100 mL) was treated slowly with a solution of *t*-BuLi in pentane (20.0 mL, 29.6 mmol). After stirring for 1 h at this temperature, carbon dioxide was bubbled through the reaction mixture for 30 min (at −78°C). After warming slowly to room temperature, the reaction mixture was carefully degassed by means of a super sonic bath, and then $LiAlH_4$ (1.0 g, 27.1 mmol) was added at 0°C. The mixture was stirred at room temperature over

night. Then, it was treated with aqueous HCl (5 M) until a pH of ~4 was reached. After phase separation, the aqueous layer was extracted with dichloromethane (3×40 mL). The combined organic phase was dried ($MgSO_4$), concentrated, and the remaining residue was purified by column chromatography on silica gel (hexane:ethyl acetate, 2:1) to give 3.33 g of (S_p)-4-(4,4-dimethyl-4,5-dihydrooxazolyl)-12-hydroxymethyl[2.2]paracyclophane (73% yield) as a white solid. Mp 121–122°C; $[\alpha]_D^{25}=+107$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.38 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 2.78–2.91 (m, 3H, CH_2), 3.06–3.16 (m, 3H, CH_2), 3.27 (ddd, 1H, $J=12.8$, 9.8, 3.1 Hz, CH_2), 3.63–3.68 (m, 1H, CH_2), 4.14 (d, 1H, $J=8.2$ Hz, OCH_2), 4.19 (d, 1H, $J=7.9$ Hz, OCH_2), 4.54 (d, 1H, $J=15.3$ Hz, CH_2OH), 4.68 (d, 1H $J=15.0$ Hz, CH_2OH), 5.90 (bs, 1H, O*H*), 6.42 (d, 1H, $J=7.6$ Hz, 16-*H*), 6.46 (dd, 1H $J=7.7$, 1.6 Hz, 15-*H*), 6.56 (d, 1H, $J=7.6$ Hz, 7-*H*), 6.61 (dd, 1H, $J=7.9$, 1.8 Hz, 8-*H*), 6.80 (bs, 1H, 13-*H*), 7.19 (d, 1H, $J=1.9$ Hz, 5-*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.2, 28.3 (*C*H$_3$), 32.2, 33.3, 34.4, 34.7 (*C*H$_2$), 63.0 (*C*H$_2$OH), 66.8 (*C*(CH$_3$)$_2$), 79.9 (O*C*H$_2$), 127.3 (*C*-13), 128.8 (q*C*), 130.5 (*C*-5), 131.2 (*C*-15), 134.1 (*C*-16), 135.3 (*C*-8), 135.5 (*C*-7), 135.8, 139.5, 139.7, 139.7, 140.5 (q*C*), 165.4 (*C*=N); IR (KBr) $\tilde{\nu}$ 3254, 2963, 2925, 2898, 2852, 1642, 1420, 1307, 1188, 1070, 1046, 966, 652 cm^{-1}; MS (70 eV) *m*/*z* (%) 336 (12), 335 (56, M$^+$), 202 (23), 201 (100). Anal. calcd for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.80; H, 7.56; N, 4.13.

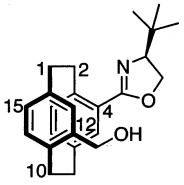
3.5.2. (S_p)-4-Bromomethyl-12-(4,4-dimethyl-4,5-dihydrooxazolyl)[2.2]paracyclophane (S_p)-7a.



A solution of (S_p)-4-(4,4-dimethyl-4,5-dihydrooxazolyl)-12-hydroxymethyl[2.2]paracyclophane (2.69 g, 8.0 mmol) and pyridine (0.32 mL, 4.0 mmol) in THF (120 mL) was treated with PBr_3 (0.76 mL, 8.0 mmol) at 0°C. A white, cloudy precipitate immediately formed. The reaction mixture was stirred at room temperature over night and then washed with an ice-cold, saturated $NaHCO_3$ (60 mL) solution. The aqueous phase was extracted with dichloromethane (3×50 mL). The combined organic phases were dried ($MgSO_4$), concentrated and the residue was purified using a short silica gel column and hexane:ethyl acetate (4:1) as the eluent. Thus, 2.98 g (93% yield) of (S_p)-**7a** was obtained as a white solid. Mp 70–72°C; $[\alpha]_D^{25}=+14$ (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 2.76–2.82 (m, 1H, CH_2), 2.86–2.93 (m, 2H, CH_2), 2.97–3.03 (m, 1H, CH_2), 3.08–3.13 (m, 1H, CH_2), 3.15–3.20 (m, 1H, CH_2), 3.47 (ddd, 1H, $J=13.8$, 10.3, 1.6 Hz, CH_2), 4.06 (d, 1H, $J=7.9$ Hz, OCH_2), 4.14 (d, 1H, $J=7.9$ Hz, OCH_2), 4.18 (ddd, 1H, $J=12.1$, 10.1, 1.5 Hz, CH_2), 4.32 (d, 1H, $J=10.1$ Hz, CH_2Br), 4.51 (d, 1H $J=10.4$ Hz, CH_2Br), 6.42 (d, 1H, $J=1.2$ Hz, 5-*H*), 6.48 (d, 1H, $J=7.9$ Hz, 8-*H*), 6.52 (dd, 1H $J=7.8$, 1.7 Hz, 7-*H*), 6.56 (d, 1H, $J=7.9$ Hz, 16-*H*), 6.60 (dd, 1H, $J=8.0$, 1.9 Hz, 15-*H*), 7.11 (bs, 1H, 13-*H*), ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.3, 28.4 (*C*H$_3$), 32.9 (*C*H$_2$), 33.2 (*C*H$_2$Br), 33.8, 34.1 (*C*H$_2$), 35.6 (*C*H$_2$), 67.5 (*C*(CH$_3$)$_2$), 78.6 (O*C*H$_2$), 128.4 (q*C*), 131.3 (*C*-13), 133.1 (*C*-5), 133.2 (*C*-7), 135.0 (*C*-15), 135.4 (*C*-8), 136.2 (*C*-16), 136.9, 137.8, 139.2, 140.6, 140.8 (q*C*), 162.1 (*C*=N); IR (KBr) $\tilde{\nu}$ 2957, 2930, 2859, 1630, 1587, 1300, 1195, 1039, 986, 622 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 399 (36), 397 (34, M$^+$), 318 (29), 202 (17), 201 (100), 200 (13), 146 (12), 117 (13), 115 (15). Anal. calcd for $C_{22}H_{24}BrNO$: C, 66.33; H, 6.07; N, 3.52. Found: C, 66.17; H, 6.26; N, 3.38.

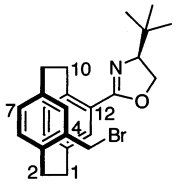
3.6. Synthesis of (S,S_p)-4-bromomethyl-12-(4-*tert*-butyl-4,5-dihydrooxazolyl)[2.2]paracyclophane (S,S_p)-7b

3.6.1. (S,S_p)-4-(4-*tert*-Butyl-4,5-dihydrooxazolyl)-12-hydroxymethyl[2.2]paracyclophane.



This compound was prepared by the method described for (S_p)-4-(4,4-dimethyl-4,5-dihydrooxazolyl)-12-hydroxymethyl[2.2]paracyclophane using (S,S_p)-**6b** (4.12 g, 10.0 mmol), *t*-BuLi (15 mL, 22.5 mmol), THF (220 mL) and $LiAlH_4$ (0.8 g, 21.3 mmol). Purification by column chromatography (pentane:ethyl acetate, 4:1) gave 2.42 g (66%) of the title compound as a white solid. Mp 89–90°C; $[\alpha]_D^{25}=+74$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (s, 9H, CH_3), 2.76–2.95 (m, 3H, CH_2), 3.04–3.19 (m, 3H, CH_2), 3.28 (ddd, 1H, $J=12.5$, 9.2, 3.3 Hz, CH_2), 3.56–3.66 (m, 1H, CH_2), 4.16 (dd, 1H, $J=10.2$, 7.3 Hz, C*H*t Bu), 4.27 (dd, 1H, $J=8.6$, 7.3 Hz, OCH_2), 4.43 (dd, 1H, $J=10.1$, 8.8 Hz, OCH_2), 4.53 (bd, 1H, $J=15.6$ Hz, CH_2OH), 4.68 (bd, 1H, $J=15.1$ Hz, CH_2OH), 5.99 (bs, 1H, CH$_2$O*H*), 6.41 (d, 1H, $J=7.9$ Hz, 16-*H*), 6.46 (dd, 1H, $J=7.7$, 1.8 Hz, 15-*H*), 6.56 (d, 1H, $J=7.6$ Hz, 8-*H*), 6.60 (dd, 1H, $J=7.9$, 1.9 Hz, 7-*H*), 6.75 (s, 1H, 13-*H*), 7.23 (d, 1H, $J=2.0$ Hz, 5-*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.2 (3C, C(*C*H$_3$)$_3$), 32.6, 33.7 (*C*H$_2$), 34.6 (*C*(CH$_3$)$_3$), 34.7, 35.0 (*C*H$_2$), 63.4 (*C*H$_2$OH), 69.9 (O*C*H$_2$), 75.1 (C*H*t Bu), 127.7 (*C*H), 129.1 (q*C*), 130.5, 131.4, 134.2, 135.7, 135.8 (*C*H), 136.1, 139.8, 140.0, 140.1, 140.9 (q*C*), 167.0 (*C*=N); IR (KBr) $\tilde{\nu}$ 2949, 2864, 1637, 1480, 1044 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 364 (18), 363 (M$^+$, 68), 306 (11), 230 (32), 229 (100), 228 (12), 147 (13), 131 (11), 105 (10). Anal. calcd for $C_{24}H_{29}NO_2$: C, 79.30; H, 8.04; N, 3.85. Found: C, 79.36; H, 8.11; N, 3.76.

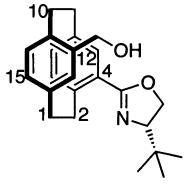
3.6.2. (S,S_p)-4-Bromomethyl-12-(4-*tert*-butyl-4,5-dihydrooxazolyl)[2.2]paracyclophane (S,S_p)-7b.



This compound was prepared by the same procedure as described for (S_p)-**7a** using (S,S_p)-4-(4-*tert*-butyl-4,5-dihydrooxazolyl) - 12 - hydroxymethyl[2.2]paracyclophane (2.17 g, 6.0 mmol), THF (100 mL), PBr_3 (0.57 mL, 6.0 mmol), and pyridine (0.24 mL, 3.0 mmol). The product was purified by chromatography using a short column (silica gel; pentane:Et_2O, 9:1) to give **7b** as a white solid (1.76 g, 69% yield). Mp 164–166°C; $[\alpha]_D^{25} = -26$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (s, 9H, CH_3), 2.83–2.92 (m, 3H, CH_2), 2.94–3.10 (m, 2H, CH_2), 3.16–3.22 (m, 1H, CH_2), 3.47 (ddd, 1H, J = 13.1, 10.2, 1.7 Hz, CH_2), 4.09 (dd, 1H, J = 10.2, 8.3 Hz, CH*t*Bu), 4.19–4.26 (m, 2H, CH_2, OCH_2), 4.26 (d, 1H, J = 10.2 Hz, CH_2Br), 4.31 (dd, 1H, J = 10.2, 8.5 Hz, OCH_2), 4.48 (d, 1H, J = 10.1 Hz, CH_2Br), 6.40 (bs, 1H, 5-H), 6.50 (d, 1H, J = 7.7 Hz, 8-H), 6.52–6.54 (m, 1H, 7-H), 6.55 (d, 1H, J = 7.7 Hz, 16-H), 6.58 (dd, 1H, J = 7.7, 1.7 Hz, 15-H), 7.08 (bs, 1H, 13-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.7 (3C, C(CH_3)$_3$), 33.3 (CH_2), 33.6 (CH_2Br), 34.2, 34.3 (CH_2), 34.7 (C(CH$_3$)$_3$), 35.3 (CH_2), 68.3 (OCH_2), 76.8 (CH*t*Bu), 128.5 (qC), 131.1 (C-13), 133.5 (CH), 133.6 (C-5), 135.4, 135.5, 136.4 (CH), 137.2, 138.2, 139.4, 140.8, 141.0 (qC), 163.3 (C=N). IR (KBr) $\tilde{\nu}$ 2957, 2929, 2895, 2864, 1638 cm^{-1}; MS (EI, 70 eV) m/z (%) 428 (12), 427 (49), 426 (12), 425 (M$^+$, 48), 347 (10), 346 (42), 229 (100), 228 (13), 117 (14), 115 (13).

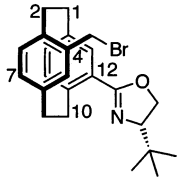
3.7. Synthesis of (S,R_p)-4-bromomethyl-12-(4-*tert*-butyl-4,5-dihydrooxazolyl)[2.2]paracyclophane (S,R_p)-7b

3.7.1. (S,R_p)-4-(4-*tert*-Butyl-4,5-dihydrooxazolyl)-12-hydroxymethyl[2.2]paracyclophane.



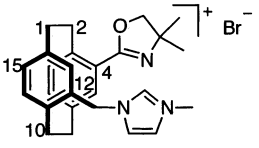
This compound was prepared by the method described for (S_p)-4-(4,4-dimethyl-4,5-dihydrooxazolyl)-12-hydroxymethyl[2.2]paracyclophane using (S,R_p)-**6b** (5.2 g, 12.6 mmol), *t*-BuLi (19 mL, 28.5 mmol), THF (350 mL) and $LiAlH_4$ (1.1 g, 29.2 mmol). After purification by column chromatography on silica gel (hexane:EtOAc, 5:1), the title compound was obtained as a white solid (2.37 g, 52% yield). Mp 80°C; $[\alpha]_D^{25} = -79$ (c 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (s, 9H, CH_3), 2.79–2.87 (m, 1H, CH_2), 2.91–3.09 (m, 3H, CH_2), 3.11–3.18 (m, 2H, CH_2), 3.26–3.33 (m, 1H, CH_2), 3.40–3.47 (m, 1H, CH_2), 4.06 (t, 1H, J = 10.2 Hz, CH*t*Bu), 4.24 (t, 1H, J = 9.4 Hz, OCH_2), 4.40 (t, 1H, J = 9.5 Hz, OCH_2), 4.55 (d, 1H, J = 15.4 Hz, CH_2OH), 4.68 (d, 1H, J = 15.4 Hz, CH_2OH), 5.84 (bs, 1H, CH$_2$OH), 6.45 (d, 1H, J = 7.7 Hz, 16-H), 6.50 (d, 1H, J = 7.7 Hz, 15-H), 6.55 (d, 1H, J = 7.7 Hz, 8-H), 6.58 (dd, 1H, J = 7.7, 1.3 Hz, 7-H), 6.80 (s, 1H, 13-H), 7.15 (s, 1H, 5-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.7 (3C, C(CH_3)$_3$), 32.6, 33.6 (CH_2), 34.0 (C(CH$_3$)$_3$), 34.2, 35.0 (CH_2), 63.7 (CH_2OH), 69.8 (OCH_2), 76.5 (CH*t*Bu), 128.1 (C-13), 129.2 (qC), 130.1 (C-5), 131.4 (C-16), 134.1 (C-15), 135.5 (C-8), 135.9 (C-7), 136.2, 139.5, 139.8, 139.9, 141.0 (qC), 167.5 (C=N); IR (KBr) $\tilde{\nu}$ 2942, 2866, 1638, 964 cm^{-1}; MS (EI, 70 eV) m/z (%) 364 (17), 363 (M$^+$, 68), 306 (11), 230 (24), 229 (100), 228 (11), 147 (10). Anal. calcd for $C_{24}H_{29}NO_2$: C, 79.30; H, 8.04; N, 3.85. Found: C, 78.98; H, 8.31; N, 3.65.

3.7.2. (S,R_p)-4-Bromomethyl-12-(4-*tert*-butyl-4,5-dihydrooxazolyl)[2.2]paracyclophane (S,R_p)-7b.



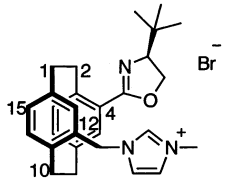
This compound was prepared by the same procedure as described for (S_p)-**7a** using (S,R_p)-4-(4-*tert*-butyl-4,5-dihydrooxazolyl)-12-hydroxymethyl[2.2]paracyclophane (1.95 g, 5.4 mmol), CH_2Cl_2 (60 mL), PBr_3 (0.51 mL, 5.4 mmol), and pyridine (0.43 mL, 5.3 mmol). The product was obtained as a white solid (1.59 g, 70% yield) after purification using a short column (silica gel; pentane:Et_2O, 4:1). Mp 75–76°C; $[\alpha]_D^{25} = -52$ (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.04 (s, 9H, CH_3), 2.77–3.10 (m, 5H, CH_2), 3.12–3.23 (m, 1H, CH_2), 3.43–3.51 (m, 1H, CH_2), 3.99 (ddd, 1H, J = 12.0, 9.8, 2.3 Hz, CH_2), 4.08 (dd, 1H, J = 9.9, 8.7 Hz, CH*t*Bu), 4.16 (t, 1H, J = 8.4 Hz, OCH_2), 4.36 (d, 1H, J = 10.1 Hz, CH_2Br), 4.33 (dd, 1H, J = 9.8, 8.0 Hz, OCH_2), 4.47 (d, 1H, J = 10.2 Hz, CH_2Br), 6.47–6.53 (m, 4H, *Aryl*-CH) 6.58 (dd, 1H, J = 7.9, 1.8 Hz, 15-H), 7.06 (d, 1H, J = 2.0 Hz, 13-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.6 (3C, C(CH_3)$_3$), 33.3 (CH_2), 33.4 (CH_2Br), 34.2 (CH_2), 34.3 (C(CH$_3$)$_3$), 34.4, 35.7 (CH_2), 68.6 (OCH_2), 76.9 (CH*t*Bu), 128.9 (qC), 131.2 (C-13), 133.4, 133.5 (CH), 135.1 (C-15), 135.5, 136.2 (CH), 137.2, 138.0. 139.4, 140.7, 140.9 (qC), 163.8 (C=N); IR (KBr) $\tilde{\nu}$ 2950, 2900, 2862, 1648, 1071, 977 cm^{-1}; MS (EI, 70 eV) m/z (%) 427 (38), 425 (M$^+$, 40), 346 (35), 230 (16), 229 (100), 228 (12), 117 (12), 115 (10). Anal. calcd for $C_{24}H_{28}BrNO$: C, 67.61; H, 6.62; N, 3.29. Found: C, 67.70; H, 6.79; N, 3.13.

3.8. Synthesis of (S_p)-1-{4-(4,4-dimethyl-4,5-dihydrooxazolyl)[2.2]paracyclophane-12-yl-methyl}-3-methyl imidazolium bromide (S_p)-8a



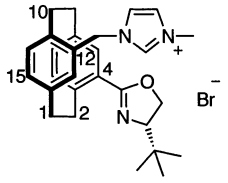
A solution of methyl bromide (S_p)-**7a** (0.77 g, 1.93 mmol) and 1-methylimidazole (0.24 mL, 3.0 mmol) in DMF (5 mL) was stirred at 80°C for 48 h. After cooling to room temperature, diethyl ether was added. Purification of the precipitate by column chromatography on silica gel (CH_2Cl_2:MeOH, 95:5 to 90:10), treatment of the residue with benzene, and drying in vacuo at elevated temperature yielded 0.73 g of the title compound (79% yield) as a white, hygroscopic powder. Mp 110–113°C; $[\alpha]_D^{25}=+67$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 2.78–2.92 (m, 3H, CH_2), 3.09–3.27 (m, 3H, CH_2), 3.42–3.49 (m, 1H, CH_2), 4.06 (s, 3H, NCH_3), 4.07 (d, 1H, $J=8.2$ Hz, OCH_2), 4.11–4.17 (m, 1H, CH_2), 4.24 (d, 1H, $J=8.2$ Hz, OCH_2), 5.04 (d, 1H, $J=14.5$ Hz, CH_2N), 5.63 (d, 1H, $J=14.5$ Hz, CH_2N), 6.50 (d, 1H, $J=1.4$ Hz, 13-*H*), 6.53–6.62 (m, 4H, *Aryl*-C*H*), 7.02 (t, 1H, $J=1.8$ Hz, NC*H*=CH), 7.11 (d, 1H, $J=1.7$ Hz, 5-*H*), 7.53 (t, 1H, $J=1.7$ Hz, NC*H*=CH), 10.30 (s, 1H, NC*H*N); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.8, 28.9 (*C*H_3), 33.5, 34.3, 34.4, 35.6 (*C*H_2), 37.1 (*C*H_3), 52.2 (*C*H_2N), 68.1 (*C*(CH$_3$)$_2$), 78.9 (O*C*H$_2$), 121.8 (N*C*H=CH), 123.8 (N*C*H=CH), 129.3 (q*C*), 131.3 (*C*-5), 131.9 (q*C*), 133.4, 134.4, 135.0, 136.0, 136.2 (*C*H), 137.3 (N*C*HN), 138.9, 139.5, 140.6, 141.5 (q*C*), 162.2 (*C*=N); IR (KBr) $\tilde{\nu}$ 3031, 2927, 2861, 1637, 1590, 1565, 1302, 1161, 1040, 682, 619 cm^{-1}; MS (SIMS-FAB, pos) *m*/*z* (%) 401 (28), 400 (100, M$^+$), 318 (41); MS (SIMS-FAB, neg) *m*/*z* (%) 81 (99), 79 (100).

3.9. Synthesis of (S,S_p)-1-{4-(4-*tert*-butyl-4,5-dihydrooxazolyl)[2.2]paracyclophane-12-yl-methyl}-3-methyl imidazolium bromide (S,S_p)-8b



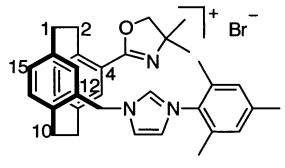
This compound was prepared by the method described for (S_p)-**8a** using (S,S_p)-**7b** (0.8 g, 1.9 mmol), 1-methylimidazole (0.3 mL, 3.8 mmol), and DMF (4 mL). The precipitate was treated several times with diethyl ether in a super sonic bath and dried in vacuo at elevated temperature to give 0.8 g (83% yield) of the title compound as a white solid. Mp 185–188°C; $[\alpha]_D^{25}=+43$ (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 9H, C(CH_3)$_3$), 2.85–3.00 (m, 4H, CH_2), 3.06–3.12 (m, 1H, CH_2), 3.15–3.25 (m, 2H, CH_2), 4.07 (s, 3H, NCH_3), 4.04–4.16 (m, 2H, CH_2, *CH*t Bu), 4.32 (t, 1H, $J=8.4$ Hz, OCH_2), 4.43 (t, 1H, $J=9.5$ Hz, OCH_2), 5.05 (d, 1H, $J=14.8$ Hz, CH_2N), 5.63 (d, 1H, $J=14.6$ Hz, CH_2N), 6.41 (s, 1H, 13-*H*), 6.57–6.65 (m, 4H, *Aryl*-C*H*), 7.06 (s, 1H, NC*H*=CH), 7.21 (s, 1H, 5-*H*), 7.53 (s, 1H, NC*H*=CH), 10.23 (s, 1H, NC*H*N); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.6 (3C, C(CH_3)$_3$), 33.5, 34.3, 34.4, 34.7, 35.1 (CH_2, *C*(CH$_3$)$_3$), 37.2 (NCH_3), 52.0 (CH_2N), 68.9 (OCH_2), 76.4 (*C*H t Bu), 122.0, 123.8 (N*C*H=CH), 128.8 (q*C*), 131.0 (*C*-5), 132.2 (q*C*), 133.1 (*C*-13), 134.2, 135.5, 135.8, 136.3 (*C*H), 137.4 (N*C*HN), 139.6, 138.9, 140.7, 141.5 (q*C*), 163.9 (*C*=N); IR (KBr) $\tilde{\nu}$ 2952, 2864, 1638, 1571, 1165 cm^{-1}; MS (SIMS-FAB, pos) *m*/*z* (%) 429 (25), 428 (100, M$^+$), 426 (15), 347 (11), 346 (51); MS (SIMS-FAB, neg) *m*/*z* (%) 81 (93), 79 (100). Anal. calcd for $C_{28}H_{34}BrN_3O\cdot H_2O$: C, 63.87; H, 6.89; N, 7.98. Found: C, 63.83; H, 7.22; N, 8.11.

3.10. Synthesis of (S,R_p)-1-{4-(4-*tert*-butyl-4,5-dihydrooxazolyl)[2.2]paracyclophane-12-yl-methyl}-3-methyl imidazolium bromide (S,R_p)-8b



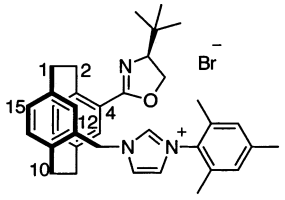
This compound was prepared by the same procedure as described for (S_p)-**8a** using (S,R_p)-**7b** (0.5 g, 1.2 mmol), 1-methylimidazole (0.19 mL, 2.4 mmol), and DMF (1 mL). After purification of the precipitate by column chromatography on silica gel (CH_2Cl_2:MeOH, 95:5 to 90:10) and drying in vacuo at elevated temperature, the product was obtained as a white solid (0.56 g, 93% yield). Mp 136–138°C; $[\alpha]_D^{25}=-91$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 9H, C(CH_3)$_3$), 2.83–2.91 (m, 2H, CH_2), 2.95–3.02 (m, 1H, CH_2), 3.05–3.11 (m, 1H, CH_2), 3.15–3.21 (m, 1H, CH_2), 3.23–3.31 (m, 1H, CH_2), 3.45–3.53 (m, 1H, CH_2), 4.01 (ddd, 1H, $J=12.3$, 10.2, 2.0 Hz, CH_2), 4.05 (s, 3H, NCH_3), 4.11–4.18 (m, 2H, *CH*t Bu, OCH_2), 4.42–4.48 (m, 1H, OCH_2), 4.99 (d, 1H, $J=14.3$ Hz, CH_2N), 5.63 (d, 1H, $J=14.3$ Hz, CH_2N), 6.54–6.64 (m, 5H, *Aryl*-C*H*), 6.95 (t, 1H, $J=1.7$ Hz, NC*H*=CH), 7.07 (d, 1H, $J=1.7$ Hz, 5-*H*), 7.58 (t, 1H, $J=1.7$ Hz, NC*H*=CH), 10.31 (s, 1H, NC*H*N); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.4 (3C, C(*C*H$_3$)$_3$), 33.4, 34.0, 34.1, 34.2, 35.2 (*C*H$_2$, *C*(CH$_3$)$_3$), 37.0 (NCH_3), 52.2 (*C*H$_2$N), 68.5 (OCH_2), 76.9 (*C*H t Bu), 121.6, 124.0 (N*C*H=CH), 129.1 (q*C*), 131.3 (*C*-5), 131.9 (q*C*), 133.8, 134.6, 135.1, 136.0, 136.1 (*C*H), 137.1 (N*C*HN), 139.1, 139.7, 140.6, 141.6 (q*C*), 163.6 (*C*=N); IR (KBr) $\tilde{\nu}$ 3030, 2952, 2865, 1642, 1570, 1163 cm^{-1}; MS (SIMS-FAB, pos) *m*/*z* (%) 429 (30), 428 (100, M$^+$), 426 (26), 347 (11), 346 (48), 344 (13); MS (SIMS-FAB, neg) *m*/*z* (%) 81 (96), 79 (100). Anal. calcd for $C_{28}H_{34}BrN_3O\cdot 0.5H_2O$: C, 64.99; H, 6.82; N, 8.12. Found: C, 64.59; H, 7.00; N, 8.00.

3.11. Synthesis of (S_p)-1-{4-(4,4-dimethyl-4,5-dihydrooxazolyl)[2.2]paracyclophane-12-yl-methyl}-3-(2,4,6-trimethylphenyl) imidazolium bromide (S_p)-8c



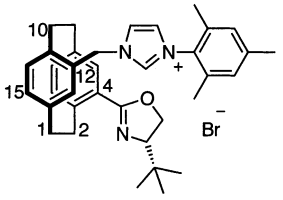
This compound was prepared by the same procedure as described for (S_p)-**8a** using methyl bromide (S_p)-**7a** (1.2 g, 3.0 mmol), 1-mesitylimidazole (0.84 g, 4.5 mmol) and DMF (5 mL). The precipitate was treated several times with diethyl ether in a super sonic bath and dried in vacuo at elevated temperature to give 1.71 g (97% yield) of the title compound as a white solid. Mp 268°C; $[\alpha]_D^{25}=+63$ (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 2.02 (s, 3H, *Mesityl*-CH_3), 2.05 (s, 3H, *Mesityl*-CH_3), 2.30 (s, 3H, *Mesityl*-CH_3), 2.82–2.96 (m, 3H, CH_2), 3.10–3.17 (m, 2H, CH_2), 3.48–3.54 (m, 1H, CH_2), 3.59–3.65 (m, 1H, CH_2), 4.05 (d, 1H, $J=8.2$ Hz, OCH_2), 4.16–4.21 (m, 1H, CH_2), 4.26 (d, 1H, $J=8.3$ Hz, OCH_2), 5.17 (d, 1H, $J=14.6$ Hz, CH_2N), 6.27 (d, 1H, $J=14.5$ Hz, CH_2N), 6.55–6.64 (m, 5H, *Aryl*-C*H*), 6.95 (s, 2H, *Mesityl*-C*H*), 7.18 (bs, 2H, NC*H*=CH, 5-*H*), 7.35 (t, 1H, $J=1.7$ Hz, NC*H*=CH), 10.49 (s, 1H, NC*H*N); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.6, 17.7, 21.0 (*Mesityl*-CH_3), 28.3, 28.6 (CH_3), 33.0 (CH_2), 34.0 (2C, CH_2), 35.2 (CH_2), 52.6 (CH_2N), 67.7 (C(CH$_3$)$_2$), 78.5 (OCH_2), 122.5 (NCH=CH), 123.0 (NCH=CH), 128.9 (q*C*), 129.6 (2C, *Mesityl*-C*H*), 130.5 (q*C*), 131.3 (*C*-5), 132.0 (q*C*), 133.2 (*C*H), 133.9, 134.0 (q*C*), 134.1, 134.7, 135.6, 135.8 (*C*H), 137.5 (N*C*HN), 139.1, 139.6, 140.1, 140.9, 141.1 (q*C*), 161.8 (*C*=N); IR (KBr) $\tilde{\nu}$ 2967, 2917, 1631, 1208, 1045 cm^{-1}. MS (ESI, pos) *m*/*z* (%) 505 (29), 504 (100, M$^+$), 318 (10); MS (ESI, neg) *m*/*z* (%) 81 (96), 79 (100). Anal. calcd for $C_{34}H_{38}BrN_3O\cdot0.5\,H_2O$: C, 68.80; H, 6.62; N, 7.08. Found: C, 68.47; H, 6.81, N, 7.40.

3.12. Synthesis of (S,S_p)-3-{4-(4-*tert*-butyl-4,5-dihydrooxazolyl)[2.2]paracyclophane-12-yl-methyl}-1-(2,4,6-trimethylphenyl) imidazolium bromide (S,S_p)-8d



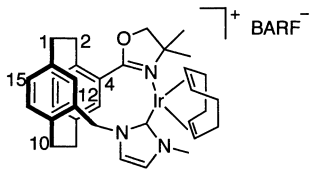
This compound was prepared by the same procedure as described for (S_p)-**8a** using (S,S_p)-**7b** (0.7 g, 1.64 mmol), 1-mesitylimidazole (0.46 g, 2.47 mmol), and DMF (4 mL). After addition of diethyl ether, treatment of the precipitate with the same solvent in a super sonic bath, and drying in vacuo at elevated temperature, the product was obtained as a white solid (0.94 g, 94%). Mp 270–271°C (dec); $[\alpha]_D^{25}=+29$ (*c* 0.6, CHCl)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (s, 9H, C(CH_3)$_3$), 2.03 (s, 3H, *Mesityl*-CH_3), 2.08 (s, 3H, *Mesityl*-CH_3), 2.32 (s, 3H, *Mesityl*-CH_3), 2.83–2.95 (m, 3H, CH_2), 3.09–3.18 (m, 2H, CH_2), 3.42–3.48 (m, 1H, CH_2), 3.60–3.66 (m, 1H, CH_2), 3.90 (bt, 1H, $J=9.0$ Hz, C*H*t Bu), 4.11–4.16 (m, 1H, CH_2), 4.25–4.35 (m, 2H, OCH_2), 5.15 (d, 1H, $J=15.1$ Hz, CH_2N), 6.31 (d, 1H, $J=15.1$ Hz, CH_2N), 6.34 (s, 1H, 13-*H*), 6.57–6.65 (m, 4H, *Aryl*-C*H*), 6.98 (s, 2H, *Mesityl*-C*H*), 7.23 (s, 1H, NC*H*=CH), 7.29 (s, 1H, 5-*H*), 7.43 (s, 1H, NC*H*=CH), 10.44 (s, 1H, NC*H*N); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1 (2C, *Mesityl*-CH_3), 21.4 (*Mesityl*-CH_3), 26.5 (3C, C(CH_3)$_3$), 33.5, 34.2, 34.5, 34.6, 35.1 (CH_2, C(CH$_3$)$_3$), 52.8 (CH_2N), 68.7 (OCH_2), 76.4 (C*H*t Bu), 123.3, 123.4 (NCH=CH), 128.8 (q*C*), 129.9, 130.1 (*Mesityl*-C*H*), 130.9 (q*C*), 131.0 (*C*-5), 132.3 (*C*-13), 132.7 (q*C*), 134.0 (*C*H), 134.4, 134.6 (q*C*), 135.5, 135.9, 136.1 (*C*H), 138.3 (N*C*HN), 139.3, 140.1, 140.4, 141.2, 141.4 (q*C*), 164.0 (*C*=N); IR (KBr) $\tilde{\nu}$ 2950, 2921, 1640, 1204 cm^{-1}; MS (SIMS-FAB, pos) *m*/*z* (%) 533 (40), 532 (100, M$^+$), 346 (21); MS (SIMS-FAB, neg) *m*/*z* (%) 81 (97), 79 (100). Anal. calcd for $C_{36}H_{42}BrN_3O\cdot0.25H_2O$: C, 70.06; H, 6.94; N, 6.81. Found: C, 69.92; H, 7.02; N, 6.89.

3.13. Synthesis of (S,R_p)-3-{4-(4-*tert*-butyl-4,5-dihydrooxazolyl)[2.2]paracyclophane-12-yl-methyl}-1-(2,4,6-trimethylphenyl) imidazolium bromide (S,R_p)-8d



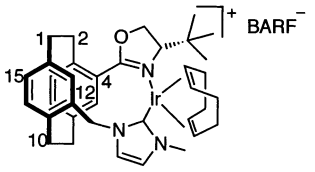
This compound was prepared by the same procedure as described for (S_p)-**8a** using (S,R_p)-**7b** (0.7 g, 1.64 mmol), 1-mesitylimidazole (0.46 g, 2.47 mmol), and DMF (2 mL). After addition of diethyl ether, treatment of the precipitate with diethyl ether and pentane in a super sonic bath, and drying in vacuo at elevated temperature, the product was obtained as a white solid (0.85 g, 85% yield). Mp 151–154°C (dec); $[\alpha]_D^{25}=-87$ (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (s, 9H, C(CH_3)$_3$), 2.00 (s, 3H, *Mesityl*-CH_3), 2.02 (s, 3H, *Mesityl*-CH_3), 2.27 (s, 3H, *Mesityl*-CH_3), 2.80–2.87 (m, 2H, CH_2), 2.97–3.16 (m, 3H, CH_2), 3.47–3.54 (m, 1H, CH_2), 3.61–3.67 (m, 1H, CH_2), 4.02 (ddd, 1H, $J=12.4$, 10.2, 2.7 Hz, CH_2), 4.07–4.13 (m, 2H, C*H*t Bu, OCH_2), 4.37–4.44 (m, 1H, OCH_2), 5.17 (d, 1H, $J=14.6$ Hz, CH_2N), 6.22 (d, 1H, $J=14.5$ Hz, CH_2N), 6.51–6.63 (m, 4H, *Aryl*-C*H*), 6.67 (bs, 1H, 13-*H*), 6.92 (s, 2H, *Mesityl*-C*H*), 7.06 (bs, 1H, NC*H*=CH), 7.11 (bs, 1H, 5-*H*), 7.19 (bs, 1H, NC*H*=CH), 10.50 (s, 1H, NC*H*N); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1 (2C, *Mesityl*-CH_3), 21.4 (*Mesityl*-CH_3), 26.6 (3C, C(CH_3)$_3$), 33.5, 34.1, 34.2, 34.5, 35.4 (CH_2, C(CH$_3$)$_3$), 52.9 (CH_2N), 68.4 (OCH_2), 77.3 (C*H*t Bu), 122.4, 123.1 (NCH=CH), 129.3 (q*C*), 130.0 (2C, *Mesityl*-C*H*), 130.9 (q*C*), 131.7 (*C*-5), 132.4 (q*C*), 133.9 (*C*-13), 134.6 (*C*H), 134.2, 134.4 (q*C*), 135.0, 135.8, 136.0 (*C*H), 138.0 (N*C*HN), 139.7, 140.1, 140.3, 141.4, 141.7 (q*C*), 163.4 (*C*=N); IR (KBr) $\tilde{\nu}$ 2950, 2865, 1641, 1198; MS (SIMS-FAB, pos) *m*/*z* (%) 533 (35), 532 (M$^+$, 100), 346 (16); MS (SIMS-FAB, neg) *m*/*z* (%) 81 (97), 79 (100). Anal. calcd for $C_{36}H_{42}BrN_3O\cdot0.75H_2O$: C, 69.05, H, 7.00; N, 6.71. Found: C, 69.09; H, 6.76; N, 6.72.

3.14. Synthesis of (S_p)-(η⁴-1,5-cyclooctadiene){1-[4-(4,4-dimethyl-4,5-dihydrooxazolyl)[2.2]paracyclophane-12-yl-methyl]-3-methylimidazolin-2-ylidene}iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (S_p)-9a



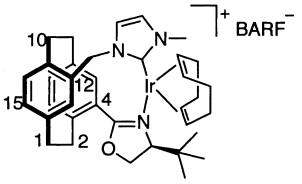
To a suspension of imidazolium salt (S_p)-**8a** (0.192 g, 0.4 mmol) and $[Ir(COD)Cl]_2$ (0.134 g, 0.2 mmol) in THF (10 mL) was added at room temperature a solution of KO*t*-Bu in THF (0.6 mL, 0.6 mmol) via syringe. The resulting mixture was heated to 60°C for 18 h. After cooling to room temperature, the volatiles were removed in vacuo. NaBARF (0.54 g, 0.6 mmol), degassed water (10 mL) and dichloromethane (15 mL) were added, and the mixture was stirred vigorously for 20 h. After phase separation, the aqueous layer was washed with CH_2Cl_2 (3×10 mL). The combined organic layers were dried ($MgSO_4$), evaporated and the residue was purified by column chromatography using a short silica gel column and CH_2Cl_2:pentane (1:1 to 7:3) as the eluent. Complex (S_p)-**9a** was isolated as a bright yellow solid in 59% yield (0.371 g). Mp 221–222°C; $[\alpha]_D^{25}=-15$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (s, 3H, CH_3), 1.53–1.62 (m, 1H, *COD*-CH_2), 1.68–1.75 (m, 1H, *COD*-CH_2), 1.77–1.83 (m, 1H, *COD*-CH_2), 1.95–2.00 (m, 1H, *COD*-CH_2), 1.97 (s, 3H, CH_3), 2.07–2.16 (m, 1H, *COD*-CH_2), 2.30–2.42 (m, 4H, CH_2, *COD*-CH_2), 2.70 (ddd, 1H, $J=13.7$, 9.2 Hz, CH_2), 2.88 (ddd, 1H, $J=13.5$, 10.7, 6.9 Hz, CH_2), 3.11 (dd, 1H, $J=13.4$, 9.2 Hz, *CH*$_2$), 3.17–3.40 (m, 5H, CH_2, *COD*-C*H*), 3.75–3.80 (m, 1H, *COD*-C*H*), 3.80 (d, 1H, $J=8.5$ Hz, OCH_2), 3.81–3.86 (m, 1H, CH_2), 4.04 (s, 3H, NCH_3), 4.20–4.25 (m, 1H, *COD*-C*H*), 4.27 (d, 1H, $J=8.5$ Hz, OCH_2), 5.10 (d, 1H, $J=17.0$ Hz, CH_2N), 5.35 (bs, 1H, 13-*H*), 5.90 (d, 1H, $J=17.0$ Hz, CH_2N), 6.47 (d, 1H, $J=7.7$ Hz, 16-*H*), 6.54 (dd, 1H, $J=7.7$, 1.1 Hz, 15-*H*), 6.64 (d, 1H, $J=7.7$ Hz, 8-*H*), 6.67–6.69 (m, 1H, 7-*H*), 6.68 (d, 1H, $J=1.9$ Hz, NC*H*=CH), 6.84 (d, 1H, $J=1.9$ Hz, NC*H*=CH), 7.45 (s, 4H, *BARF*-C*H*), 7.65 (t, 8H, $J=2.4$ Hz, *BARF*-C*H*), 9.59 (d, 1H, $J=1.6$ Hz, 5-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.9, 27.2 (*C*H$_3$), 28.3, 29.6 (*COD*-*C*H$_2$), 32.0, 32.4, 33.4, 33.5, 35.7 (*C*H$_2$, *COD*-*C*H$_2$), 38.5 (NC*H*$_3$), 38.8 (*C*H$_2$), 52.9 (*C*H$_2$N), 60.8, 63.0 (*COD*-*C*H), 72.3 (*C*(CH$_3$)$_2$), 78.9 (O*C*H$_2$), 86.9, 87.5 (*COD*-*C*H), 117.7 (m, 4C, *BARF*-*C*H), 123.1, 123.9 (N*C*H=CH), 124.8 (q, 8C, $J_{FC}=272.1$ Hz, *C*F$_3$), 125.0 (q*C*), 127.0 (*C*-13), 129.1 (q, 8C, $J_{FC}=32.8$ Hz, *C*CF$_3$), 131.3 (*C*-16), 132.2 (*C*-5), 135.0 (b, 8C, *BARF*-*C*H), 135.1 (*C*-15), 136.3 (q*C*), 136.8 (*C*-8), 138.0 (*C*-7), 139.3, 141.0, 144.0 (q*C*), 161.9 (q, 4C, $J_{CB}=49.8$ Hz, B*C*), 167.4 (C=N), 176.0 (N*C*N); ^{19}F NMR (376 MHz, $CDCl_3$) δ 62.8 (s); IR (KBr) $\tilde{\nu}$ 1564, 1356, 1279, 1127, 896, 714, 682, 672 cm^{-1}; MS (SIMS-FAB, pos) *m*/*z* (%) 700 (100, M$^+$), 590 (45), 400 (10), 318 (12), 197 (27); MS (SIMS-FAB, neg) *m*/*z* (%) 863 (100, M$^-$). Anal. calcd for $C_{66}H_{53}BF_{24}IrN_3O$: C, 50.71; H, 3.42; N, 2.69. Found: C, 50.71; H, 3.74; N, 2.56.

3.15. Synthesis of (S,S_p)-(η⁴-1,5-cyclooctadiene){1-[4-(4-*tert*-butyl-4,5-dihydrooxazolyl)[2.2]paracyclophane-12-yl-methyl]-3-methylimidazolin-2-ylidene}iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (S,S_p)-9b



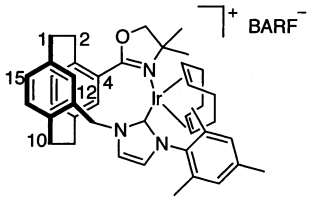
This compound was prepared by the same procedure described for **9a** using imidazolium salt (S,S_p)-**8b** (0.203 g, 0.4 mmol), $[Ir(COD)Cl]_2$ (0.134 g, 0.2 mmol), KO*t*-Bu (0.6 mL, 0.6 mmol) and NaBARF (0.54 g, 0.6 mmol). After purification using a short silica gel column (CH_2Cl_2:pentane, 7:3), complex (S,S_p)-**9b** was obtained as a bright yellow solid (0.306 g, 48% yield). Mp 193–195°C; $[\alpha]_D^{25}=+78$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 9H, C(CH_3)$_3$), 1.19–1.28 (m, 1H, *COD*-CH_2), 1.34–1.44 (m, 1H, *COD*-CH_2), 1.95–2.06 (m, 2H, *COD*-CH_2), 2.23–2.30 (m, 2H, *COD*-CH_2), 2.32–2.52 (m, 2H, CH_2, *COD*-CH_2), 2.54–2.68 (m, 2H, CH_2, *COD*-CH_2), 2.86–2.93 (m, 1H, CH_2), 3.07–3.12 (m, 1H, CH_2), 3.20–3.33 (m, 2H, CH_2, *COD*-C*H*), 3.35–3.39 (m, 2H, CH_2), 3.44–3.48 (m, 1H, *COD*-C*H*), 3.78–3.83 (m, 1H, CH_2), 3.85 (dd, 1H, $J=10.6$, 6.5 Hz, C*H*t*B*u), 4.04 (s, 3H, NCH_3), 4.22 (t, 1H, $J=10.1$ Hz, CH_2O), 4.34–4.38 (m, 1H, *COD*-C*H*), 4.41–4.47 (m, 1H, *COD*-C*H*), 4.48 (dd, 1H, $J=9.6$, 6.3 Hz, CH_2O), 5.08 (d, 1H, $J=17.0$ Hz, CH_2N), 5.13 (s, 1H, 13-*H*), 5.96 (d, 1H, $J=17.0$ Hz, CH_2N), 6.45 (d, 1H, $J=7.6$ Hz, 16-*H*), 6.54 (bd, 1H, $J=8.0$ Hz, 15-*H*), 6.62 (d, 1H, $J=7.9$ Hz, 8-*H*), 6.65 (d, 1H, $J=1.9$ Hz, NC*H*=CH), 6.71 (dd, 1H, $J=8.0$, 1.7 Hz, 7-*H*), 6.80 (d, 1H, $J=2.2$ Hz, NC*H*=CH), 7.45 (s, 4H, *BARF*-C*H*), 7.65 (bs, 8H, *BARF*-C*H*), 10.27 (d, 1H, $J=1.7$ Hz, 5-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.2 (*COD*-*C*H$_2$), 28.2 (3C, C(*C*H$_3$)$_3$), 29.2, 31.2, 32.3, 33.1, 34.2, 35.3, 36.6 (*C*H$_2$, *COD*-*C*H$_2$, *C*(CH$_3$)$_3$), 38.6 (NC*H*$_3$), 40.8 (*C*H$_2$), 53.2 (*C*H$_2$N), 57.7, 61.9 (*COD*-*C*H), 69.1 (O*C*H$_2$), 78.4 (*C*H*t*B*u*), 86.5, 87.3 (*COD*-*C*H), 117.7 (m, 4C, *BARF*-*C*H), 123.1, 124.0 (N*C*H=CH), 124.8 (q, 8C, $J_{FC}=272.1$ Hz, *C*F$_3$), 124.3 (q*C*), 126.9 (*C*-13), 129.1 (q, 8C, $J_{FC}=32.3$ Hz, *C*CF$_3$), 131.3 (*C*-15), 135.0 (b, 8C, *BARF*-*C*H), 135.2 (*C*-5), 135.3 (*C*-16), 135.6, 136.1 (q*C*), 137.8 (*C*-7), 138.7 (*C*-8), 139.3, 141.5, 145.7 (q*C*), 161.9 (q, 4C, $J_{CB}=49.9$ Hz, B*C*), 170.6 (C=N), 174.2 (N*C*N); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.8 (s); IR (KBr) $\tilde{\nu}$ 1356, 1280, 1127 cm^{-1}; MS (SIMS-FAB, pos) *m*/*z* (%) 728 (100, M$^+$), 618 (25), 428 (11), 197 (10); MS (SIMS-FAB, neg) *m*/*z* (%) 863 (100, M$^-$). Anal. calcd for $C_{68}H_{57}BF_{24}IrN_3O$: C, 51.33; H, 3.61; N, 2.64. Found: C, 51.23; H, 3.58; N, 2.56.

3.16. Synthesis of (S,R_p)-(η⁴-1,5-Cyclooctadiene){1-[4-(4-*tert*-butyl-4,5-dihydrooxazolyl)[2.2]paracyclophane-12-yl-methyl]-3-methylimidazolin-2-ylidene}iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (S,R_p)-9b



This compound was prepared by the method described for **9a** using imidazolium salt (S,R_p)-**8b** (0.203 g, 0.4 mmol), $[Ir(COD)Cl]_2$ (0.134 g, 0.2 mmol), KO*t*-Bu (0.6 mL, 0.6 mmol) and NaBARF (0.54 g, 0.6 mmol). After column chromatography on silica gel (CH_2Cl_2:pentane, 7:3), complex (S,R_p)-**9b** was obtained as a bright yellow solid (0.440 g, 69% yield). Mp 180–183°C; $[\alpha]_D = +26$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (s, 9H, C(CH_3)$_3$), 1.36–1.46 (m, 1H, *COD*-CH_2), 1.50–1.58 (m, 1H, *COD*-CH_2), 1.87–1.92 (m, 2H, *COD*-CH_2), 2.06–2.15 (m, 1H, *COD*-CH_2), 2.32–2.43 (m, 2H, CH_2, *COD*-CH_2), 2.45–2.54 (m, 1H, *COD*-CH_2), 2.67–2.74 (m, 1H, CH_2), 2.86–2.95 (m, 2H, CH_2), 2.99–3.06 (m, 3H, CH_2), 3.22–3.32 (m, 3H, CH_2, *COD*-CH), 3.34–3.40 (m, 1H, CH_2), 3.78–3.82 (m, 1H, *COD*-CH), 3.92 (s, 3H, NCH_3), 4.08 (t, 1H, J=9.6 Hz, CH*t*Bu), 4.18 (d, 1H, J=9.3 Hz, CH_2O), 4.23 (d, 1H, J=10.2 Hz, CH_2O), 4.27–4.31 (m, 1H, *COD*-CH), 5.02 (d, 1H, J=16.8 Hz, CH_2N), 5.15 (s, 1H, 13-*H*), 5.87 (d, 1H, J=16.7 Hz, CH_2N), 6.48 (bd, 1H, J=7.7 Hz, 7-*H*), 6.54 (d, 1H, J=7.9 Hz, 8-*H*), 6.57–6.59 (m, 2H, NC*H*=CH, 16-*H*), 6.63 (bd, 1H, J=7.7 Hz, 15-*H*), 6.80 (d, 1H, J=1.9 Hz, NC*H*=CH), 7.45 (s, 4H, *BARF*-C*H*), 7.65 (bs, 8H, *BARF*-C*H*), 9.33 (s, 1H, 5-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.4 (3C, C(CH_3)$_3$), 27.7, 30.3, 31.4 (*COD*-CH_2), 32.3 (CH_2), 33.0, 33.5, 33.8 (CH_2, *COD*-CH_2, $C(CH_3)_3$), 34.7, 34.8 (CH_2), 39.3 (NCH_3), 53.0 (CH_2N), 60.2, 60.8 (*COD*-CH), 68.9 (OCH_2), 79.5 (CH*t*Bu), 83.6, 85.8 (*COD*-CH), 117.7 (m, 4C, *BARF*-CH), 122.4 (NCH=CH), 124.8 (q, 8C, J_{FC}= 272.6 Hz, CF_3), 125.1 (NCH=CH), 125.6 (qC), 127.4 (C-5), 128.7 (C-13), 129.1 (q, 8C, J_{FC}=30.9 Hz, CCF_3), 131.3 (C-15), 133.9 (C-16), 135.0 (b, 8C, *BARF*-CH), 135.3 (qC), 136.2 (C-8), 136.8 (qC), 138.1 (2C, C-7, qC), 140.5, 142.5 (qC), 161.9 (q, 4C, J_{CB}=49.6 Hz, BC), 169.9 (C=N), 175.7 (NCN); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.8 (s); IR (KBr) $\tilde{\nu}$ 1356, 1279, 1129 cm^{-1}; MS (SIMS-FAB, pos) m/z (%) 729 (100, M$^+$+H), 619 (14), 197 (14); MS (SIMS-FAB, neg) m/z (%) 864 (100, M$^-$+H). Anal. calcd for $C_{68}H_{57}BF_{24}IrN_3O$: C, 51.33; H, 3.61; N, 2.64. Found: C, 51.16; H, 3.71; N, 2.42.

3.17. Synthesis of (S_p)-(η⁴-1,5-cyclooctadiene){1-[4-(4,4-dimethyl-4,5-dihydrooxazolyl)[2.2]paracyclophane-12-yl-methyl]-3-(2,4,6-trimethylphenyl)imidazolin-2-ylidene}-iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (S_p)-9c



This compound was prepared by the method described for (S_p)-**9a** using imidazolium salt (S_p)-**8c** (0.234 g, 0.4 mmol), $[Ir(COD)Cl]_2$ (0.134 g, 0.2 mmol), KO*t*-Bu (0.6 mL, 0.6 mmol) and NaBARF (0.54 g, 0.6 mmol). After column chromatography on silica gel (CH_2Cl_2:pentane, 1:1 to 2:1), complex (S_p)-**9c** was obtained as a bright yellow solid in 74% yield (0.494 g). Mp 172–173°C; $[\alpha]_D^{25} = +89$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.64 (s, 3H, CH_3), 0.84 (s, 3H, CH_3), 1.18–1.27 (m, 1H, *COD*-CH_2), 1.41–1.50 (m, 1H, *COD*-CH_2), 1.84–1.92 (m, 1H, *COD*-CH_2), 1.90 (s, 3H, *Mesityl*-CH_3), 2.14–2.23 (m, 2H, *COD*-CH_2), 2.23 (s, 3H, *Mesityl*-CH_3), 2.26–2.37 (m, 2H, *COD*-CH_2), 2.34 (s, 3H, *Mesityl*-CH_3), 2.62–2.72 (m, 1H, *COD*-CH_2), 2.78–2.82 (m, 2H, CH_2), 2.99 (ddd, 1H, J=14.1, 11.6, 5.3 Hz, CH_2), 3.11–3.22 (m, 4H, CH_2, *COD*-CH), 3.26–3.38 (m, 2H, CH_2), 3.48 (t, 1H, J=6.5 Hz, *COD*-CH), 3.65 (d, 1H, J=8.5 Hz, OCH_2), 3.89 (d, 1H, J=8.5 Hz, OCH_2), 4.33 (q, 1H, J=7.6 Hz, *COD*-CH) 4.46 (t, 1H, J=7.0 Hz, *COD*-CH) 4.61 (s, 1H, 13-*H*), 5.21 (d, 1H, J=16.2 Hz, CH_2N), 6.02 (d, 1H, J=16.2 Hz, CH_2N), 6.40 (dd, 1H, J=7.9, 1.6 Hz, 7-*H*), 6.45 (d, 1H, J=7.7 Hz, 8-*H*), 6.61 (d, 1H, J=7.7 Hz, 16-*H*), 6.66 (dd, 1H, J=7.6, 1.5 Hz, 15-*H*), 6.73 (d, 1H, J=1.9 Hz, NC*H*=CH), 6.75 (d, 1H, J=1.9 Hz, NC*H*=CH), 6.89 (s, 1H, *Mesityl*-C*H*), 7.08 (s, 1H, *Mesityl*-C*H*), 7.44 (s, 4H, *BARF*-C*H*), 7.64 (t, 8H, J=2.2 Hz, *BARF*-C*H*), 9.41 (d, 1H, J=1.6 Hz, 5-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.3, 19.2, 21.1 (*Mesityl*-CH_3), 21.8 (CH_3), 26.5 (*COD*-CH_2), 27.9 (CH_3), 29.3 (*COD*-CH_2), 32.4 (2C, CH_2, *COD*-CH_2), 32.5, 33.7, 34.5 (CH_2), 35.2 (*COD*-CH_2), 54.3 (CH_2N), 62.6, 62.9 (*COD*-CH), 72.0 ($C(CH_3)_2$), 78.6 (OCH_2), 81.2, 82.3 (*COD*-CH), 117.6 (m, 4C, *BARF*-CH), 123.3 (NCH=CH), 125.1 (qC), 124.8 (q, 8C, J_{FC}=272.1 Hz, CF_3), 126.0 (NCH=8CH), 128.8 (C-13), 129.1 (q, 8C, J_{FC}=30.5 Hz, CCF_3), 129.3 (C-5), 129.8, 131.1 (*Mesityl*-CH), 131.8 (C-16), 133.2 (C-15), 135.0 (b, 8C, *BARF*-CH), 135.5, 135.7, 135.9, 136.0, 136.1 (qC), 136.2 (C-8), 137.8 (qC), 139.0 (C-7), 140.3, 141.2, 144.3 (qC), 161.8 (q, 4C, J_{CB}=49.8 Hz, BC), 171.1 (C=N), 178.3 (NCN); ^{11}B NMR (160 MHz, $CDCl_3$) δ 4.29 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ 62.8 (s); IR (KBr) $\tilde{\nu}$ 1559, 1355, 1279, 1126, 888, 713, 682, 671 cm^{-1}; MS (APCI, pos) m/z (%) 804 (100, M$^+$), 694 (59); (APCI, neg) m/z (%) 863 (100, M$^-$). Anal. calcd for $C_{74}H_{61}BF_{24}IrN_3O$: C, 53.31; H, 3.69; N, 2.52. Found: C, 52.96; H, 3.96; N, 2.33.

3.18. Crystal structure analysis of (S_p)-9c

Suitable crystals of (S_p)-**9c** have been obtained from a mixture of EtOH, CH_2Cl_2, and Et_2O at 25°C. The compound crystallizes in orthorhombic space group $P2_12_12_1$ (19) with one formula unit ($C_{74}H_{61}BF_{24}N_3OIr$) in the asymmetric unit. The cell constants are a= 15.422(2), b=18.973(2), c=24.548(3) Å. A cell volume of V=7182.8(15) Å^3, Z=4, and M_r=1667.31, amount to a calculated density of r_{cal}=1.542. A total number of 53665 reflections (–20<h<20, –25<k<25, –23<l<32,

$\lambda_{max}=28.3°$) have been collected at room temperature on a Bruker SMART APEX diffractometer employing graphite-monochromated MoK_α radiation ($\lambda=0.71073$ Å). Data have been corrected for Lorentz-, polarization and absorption effects ($\mu=1.967$ mm^{-1}).[22a] The structure has been solved by direct methods as implemented in the Xtal3.7 set of crystallographic routines,[22b] employing GENSIN[22c] for the generation of structure invariant relation ships and GENTAN[22d] for the general tangent phasing procedure. 12529 observed reflections ($F>4\sigma(F)$) have been included in the final full-matrix least squares refinement on F involving 705 parameters and converging at r (r_w) = 0.082(0.088, $w=1/[\sigma^2(F)+0.0004F^2]$) a residual electron density of −1.98/+2.27e Å^{-3}, and a goodness of fit of $S=2.326$. All hydrogen atoms have been calculated in idealized positions. Their equivalent displacement parameters have been fixed at 1.5 U of the relevant heavy atom prior to final refinement where all hydrogen parameters have been kept constant. The representation is Figure 1 in an ORTEP plot.[22e,f]

The CF_3 groups of the anion are severely disordered. For six groups the disorder could be split into two components with equal occupation parameters and all CF_3 substituents have isotropically been refined as rigid groups. Moreover, a slight disorder of the COD ligand is reflected by the relatively large displacement parameters of C3, C4, C7, and C8 and the apparently shortened C3–C4 and C7–C8 bonds. No attempts have been made to resolve this disorder.

3.19. Procedure for the hydrogenation of substrates 10a–e and analyses of products 11a–e

Substrate **10**, iridium complex **9**, and dichloromethane (1 mL) were added to a small tube containing a magnetic stirring bar, which was then placed in 100 mL autoclave. The autoclave was sealed and pressurized to 10–50 bar of hydrogen. One sequence of experiments was carried out at 50°C using a heating mantle. After stirring for several hours at the appropriate temperature, the reactor was vented. Reaction times were not optimized. If necessary, it was cooled to room temperature before venting. Hydrogenations at ambient pressure were carried out in a Schlenk tube using a ballon. The tube containing the catalyst and the substrate was evacuated and refilled with hydrogen gas several times before adding the solvent.

The reaction mixture was diluted with pentane and passed through a short silica gel plug using hexane:ethyl acetate (3:1) as the eluent. After evaporation of the solvents, the conversion and the ee was determined by ^{1}H NMR and HPLC using a chiral column, respectively. **11a**: Daicel Chiracel OJ column, 254 nm, 20°C, 0.5 mL min^{-1}, *n*-heptane:2-propanol, 99:1, retention times (in min) = 15.5 (*R*), 25.7 (*S*), 29.5 (starting material).[20a] **11b**: Daicel Chiralcel OD-H column, 254 nm, 40°C, 0.5 mL min^{-1}, *n*-heptane:2-propanol, 95:5, retention times (in min) = 15.2, 16.9, 19.2 (starting material).[20a] **11c**: Daicel Chiracel OD-H column, 215 nm, 20°C, 0.5 mL min^{-1}, *n*-heptane:2-propanol, 96:4, retention times (in min) = 13.7 (*R*), 18.9 (starting material), 21.6 (*S*).[23] **11d**: Daicel Chiracel OB-H column, 254 nm, 20°C, 0.5 mL min^{-1}, *n*-heptane:2-propanol, 99.5:0.5, retention times (in min) = 17.1 (*R*), 19.5 (*S*).[20a] **11e**: Daicel Chiracel OD-H column, 254 nm, 20°C, 0.5 mL min^{-1}, *n*-heptane:2-propanol, 99.5:0.5, retention times (in min) = 21.5 (*R*), 25.4 (*S*).[24]

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