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The Synthesis of *Pseudo-Geminal*, *Pseudo-Ortho* and *Ortho* Hydroxy-oxazolinyl[2.2]paracyclophanes for Use as Ligands in Asymmetric Catalysis

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Abstract: Synthetic routes to *pseudo-geminal*, *pseudo-ortho* and *ortho* hydroxy-oxazolinyl-[2.2]paracyclophanes (and the diastereoisomers of each) for use as N,O ligands in asymmetric catalysis have been devised. The substitution pattern was found to have a strong effect on the rate and enantioselectivity of the formed catalyst in the addition of diethylzinc to benzaldehyde.

Keywords: asymmetric catalysis; organozinc compounds; oxazolines; paracyclophanes

Introduction

The planar chirality of substituted [2.2]paracyclophanes was first exploited for asymmetric catalysis in 1997. In this, 4,12-bis(diphenylphosphino)-[2.2]paracyclophane (PHANEPHOS) was the ligand of an organopalladium catalyst efficient at promoting asymmetric hydrogenation.[1] Since then, [2.2]paracyclophanes with a large variety of substituents have found application as chiral ligands.[2,3] All studies on bis-substituted [2.2]paracyclophanes to date, however, focus on only one of several possible substitution patterns available for a chelating ligand. We recently addressed this issue by showing that *pseudo-geminal*,[4] *pseudo-ortho* and *ortho* oxazolinyl-phosphinyl-[2.2]paracyclophanes are synthetically accessible and that the organometallic catalysts formed from them exhibit different enantioselectivities and activities.[5] Before this, the closest published research into the effect of differing substitution patterns was that reported by Rozenberg and Hopf. It involved the synthesis of *iso*-FHPC,[6] the *pseudo-geminal* analogue of 5-formyl-4-hydroxy[2.2]paracyclophane (FHPC),[7–10] an established precursor to [2.2]paracyclophane Schiff bases, salens[11] and hydroxyamines[12,13] which have been used in the asymmetric addition of diorganozinc reagents to aldehydes,[14,15] sulfoxidation[16] and trimethylsilylcyanation of benzaldehyde.[17,18] However, to the best of our knowledge, the conversion of *iso*-FHPC into similar compounds and their use in asymmetric catalysis has not yet been published.

We would now like to report the synthesis and brief testing of the full set of aromatic hydroxy-oxazolinyl substituted [2.2]paracyclophanes for use as chelating N,O ligands (Figure 1). All compounds were easily obtained from intermediates on the route to the previously described P,N compounds.[5] In this paper, only a brief description of the method used to set up the substitution pattern of these intermediates will be given. Their conversion to the phenols will be described in detail.

Results and Discussion

Synthesis of *Pseudo-Geminal* Isomers

The *pseudo-geminal* substitution pattern was established by directed bromination of oxazoline **4** (Scheme 1),[19,20] a technique discovered many years ago by Reich and Cram.[21] The resulting bromides **5** were converted to the phenols **1** by lithiation, quenching with $B(OMe)_3$ and oxidation with basic H_2O_2. This technique is based on the optimum synthesis of 4-hydroxy[2.2]paracyclophane described by Hopf and Krohn.[22] With our compounds, an improvement in yield was obtained by carrying out the reaction in a solvent mixture of Et_2O:THF (3:1) instead of pure Et_2O. The effect was largely due to the low solubility of the starting compounds in Et_2O, in particular diastereoisomer **5b**, the yield from which improved from 14 to 71%.

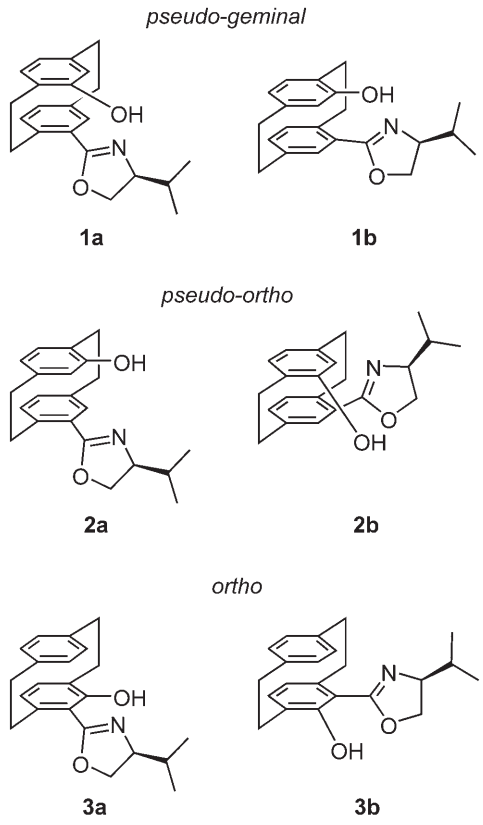
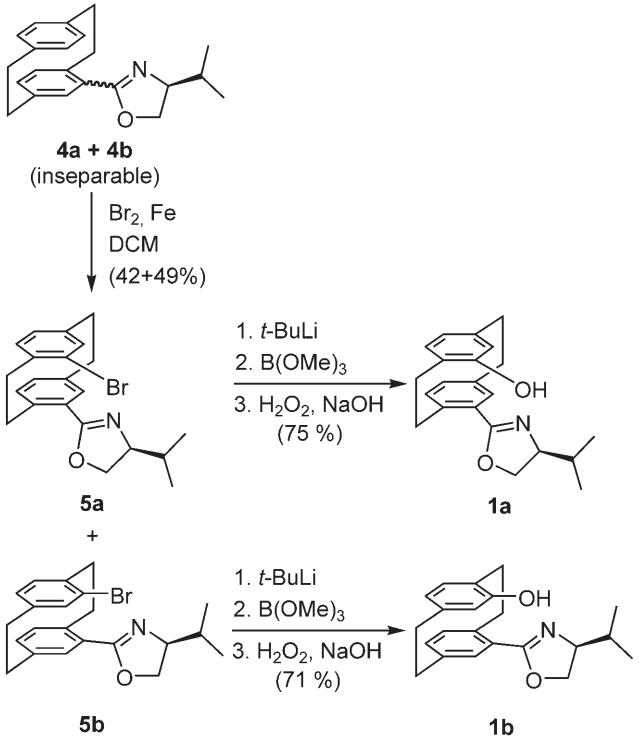


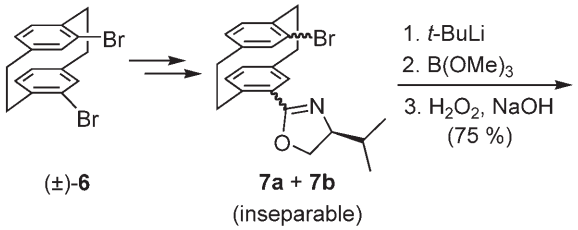
Figure 1. Regio- and diastereoisomers of aryl-substituted [2.2]paracyclophanes for use as N,O ligands.

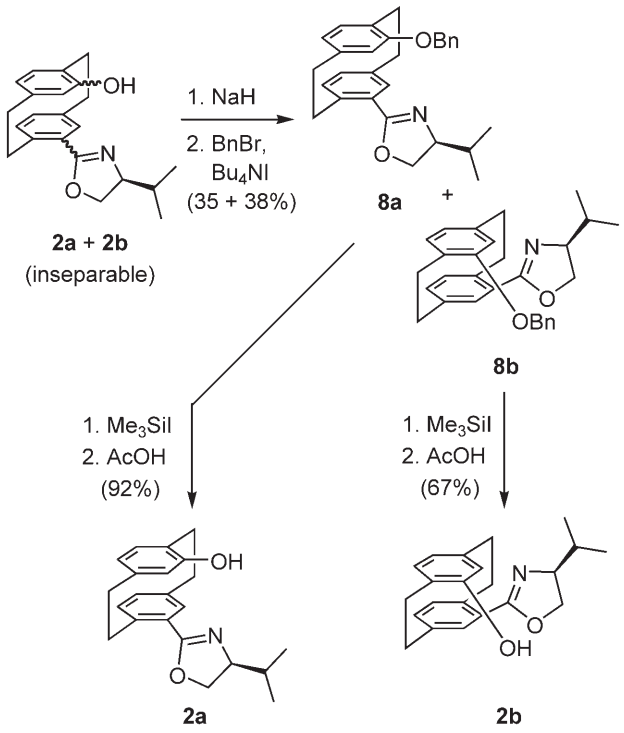


Scheme 1. Synthesis of *pseudo-geminal* hydroxy-oxazolinyl-[2.2]paracyclophanes.

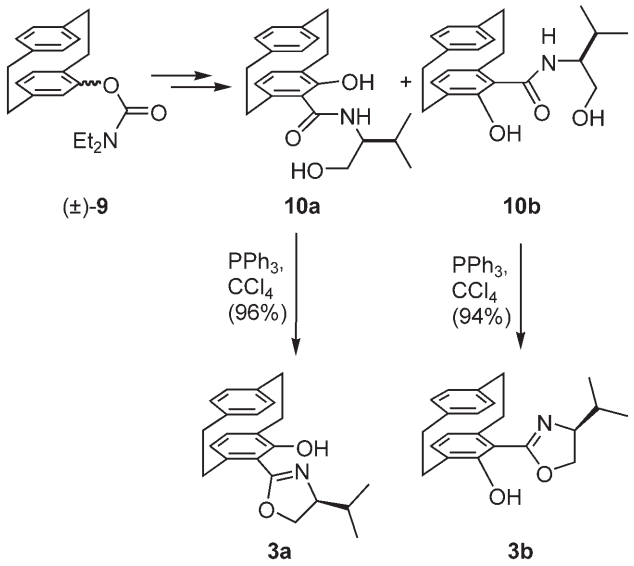
Synthesis of *Pseudo-Ortho* Isomers

The *pseudo-ortho* substitution pattern was easily achieved by starting from the known dibromide **6** (Scheme 2).[23–25] Racemic **6** was converted to the inseparable mixture of diastereomeric bromo-oxazolinyl[2.2]paracyclophanes **7** as previously described.[5] These were converted to the phenols in the same way as the *pseudo-geminal* analogues, above. Unfortunately, these diastereoisomers were also inseparable by chromatography. The phenols were therefore converted to the benzyl ethers **8**,[26] whose retention factors on silica (petroleum ether:Et_2O, 19:1) were sufficiently different to allow their separation. After separation, their reconversion to the phenols by hydrogenation using a Pd/C catalyst was unsuccessful. Hence, they were treated with Me_3SiI to form *in situ* the siloxane, which was hydrolyzed by reaction with AcOH.[27] The absolute stereochemistry of the pure hydroxy-oxazolinyl[2.2]paracyclophanes **2a** and **2b** was assigned by synthesis of **2a** from enantiopure dibromide (R_p)-(−)-**6**.[5]





Scheme 2. Synthesis of *pseudo-ortho* hydroxy-oxazolinyl-[2.2]paracyclophanes.



Scheme 3. Synthesis of *ortho* hydroxy-oxazolinyl[2.2]paracyclophanes.

Synthesis of *Ortho* Isomers

As described in our previous paper, attempts to *ortho*-lithiate oxazolinyl[2.2]paracyclophane and quench with Ph_2PCl were fruitless, so a starting material **9**, possessing a highly *ortho*-directing group, diethyl carbamate,[8,28] was used to set up the *ortho*-substitution pattern (Scheme 3).[5] The hydroxy-oxazolinyl-[2.2]paracyclophanes **3** were easily obtained from intermediate amides **10** by cyclization under Bryce's conditions.[29]

Use in Asymmetric Addition of Diethylzinc to Benzaldehyde

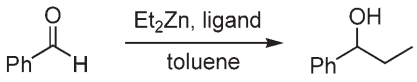
Several [2.2]paracyclophane N,O ligands have been described in the literature. As well as those derived from FHPC, mentioned in the introduction, many similar ketimines and amines have been synthesized and used for the diorganozinc addition to aldehydes[30–34] and imines.[35] Of closest analogy to our compounds, are the *pseudo-geminal* dimethyl-/diphenylhydroxymethyl-oxazolinyl[2.2]paracyclophanes developed by Hou, which led to *ee*s of up to 98% when used as ligands in the addition of diethylzinc to benzaldehyde.[20,36,37] It was therefore decided that this well-established reaction would be a discerning test of our ligands (Table 1). Both the highest *ee* and reaction rate were realized by *pseudo-geminal* ligand **1b** (entry 2). Interestingly, the lowest *ee* was given by its diastereoisomer **1a** (entry 1). Since these compounds have the oxazoline and hydroxy groups in the same relationship to each other, this shows how important their position on the [2.2]paracyclophane scaffold is. The effect of the position of the bulk of the [2.2]paracyclophane was also of great importance to the selectivity of the *ortho* ligands **3a** and **3b**, the diastereoisomers of which exhibited opposite enantioselectivities. These results show that it is not the stereochemistry of the oxazoline R group alone which determines the enantioselectivity of the catalytic reaction. As might be expected, the difference in selectivity between the *pseudo-ortho* diastereoisomers was low. This is thought to be due to the similarity between the [2.2]paracyclophane steric bulk each side of the site of metal complexation.

Optimization of the system was effected by synthesis (Scheme 4) and use of the *tert*-butyl analogue, **13**, of the best ligand **1b**. This improved the *ee* of the product phenylpropanol from 78% to 87% *ee* (Table 1, entry 7).

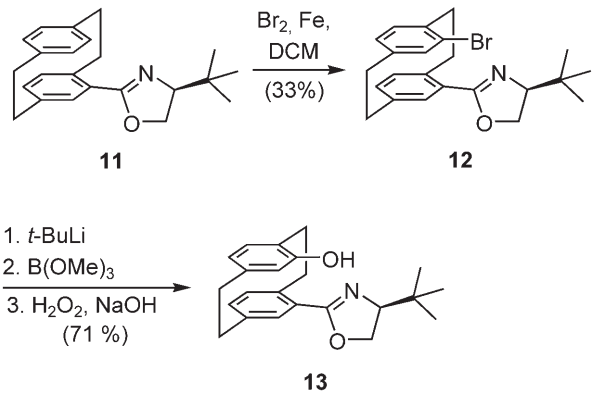
Conclusions

All aryl-substituted positional and diastereoisomers of hydroxy-oxazolinyl[2.2]paracyclophanes are synthetically accessible. When used as ligands in the addition of diethylzinc to benzaldehyde, they give widely different rates and enantioselectivities indicating that when [2.2]paracyclophanes are to be used as ligands,

Table 1. Asymmetric addition of diethylzinc to benzaldehyde.



Entry	Substitution pattern	Ligand	Oxazoline substituent	Time [h]	Yield [%]	*ee* [%]
1	*Pseudo-geminal*	**1a**	*i*-Pr	24	93	11 (*S*)
2	*Pseudo-geminal*	**1b**	*i*-Pr	2	78	78 (*R*)
3	*Pseudo-ortho*	**2a**	*i*-Pr	24	74	35 (*S*)
4	*Pseudo-ortho*	**2b**	*i*-Pr	4	96	51 (*S*)
5	*Ortho*	**3a**	*i*-Pr	24	79	62 (*S*)
6	*Ortho*	**3b**	*i*-Pr	48	72	44 (*R*)
7	*Pseudo-geminal*	**13**	*t*-Bu	4	93	87 (*R*)



Scheme 4. Synthesis of *pseudo-geminal tert*-butyl analogue **13**.

it is worth testing each positional isomer during optimization of the system. In the *pseudo-geminal* and *ortho* cases, the position of the bulk of the [2.2]paracyclophane was of utmost importance in determining the outcome of the catalysis, but not so in the *pseudo-ortho* case. In the diethylzinc addition to benzaldehyde, the *pseudo-geminal* (S,S_p) isomer was most selective.

Experimental Section

General Remarks

All air-sensitive manipulations were carried out under an inert atmosphere of argon. Toluene, THF and Et_2O for reactions were distilled, under nitrogen, from sodium/benzophenone ketyl radical. DCM for reactions was distilled, under nitrogen, from CaH_2. Et_2O, pentane, petroleum ether, DCM and EtOAc for column chromatography were distilled before use. Flash column chromatography was carried out using silica gel (bead size 40–63 μm). Analytical thin layer chromatography (TLC) was performed using precoated aluminium-backed plates (silica gel 60 F_{254}) and visualized with UV radiation at 254 nm, or by staining with a solution of potassium permanganate (3 g), K_2CO_3 (20 g) and NaOH (5%, 5 mL) in water (300 mL). ^1H and ^{13}C NMRspectra were recorded on a Varian Gemini 300 or Varian Inova 400 spectrometer and are reported as follows: chemical shift (ppm), [number of protons, multiplicity, coupling constant J (Hz), assignment (where possible)]. Where assignments have been made, they were done using DEPT, COSY and HETCOR experiments. IR spectra were measured on a Perkin–Elmer PE 1760 FT instrument as KBr pellets, neat (in the case of liquid compounds) or in $CHCl_3$ solution; absorptions are given in wave numbers (cm^{-1}). MS were carried out on a Varian MAT 212 or Finnigan MAT 95 spectrometer using EI. HR-MS were carried out on a Varian MAT 95 spectrometer. Optical rotation measurements were conducted at room temperature with a Perkin–Elmer PE 241 polarimeter at a wavelength of 589 nm. HPLC measurements were performed on a Dionex HPLC system (previously Gynkothek) with autosampler Gina 50, UV-detector UVD 170S, degasser DG 503 and gradient pump M480G.

Oxazolines **4**, bromides **5** and **7** and amides **10** were synthesized as previously described.[5] Dibromide **6**[25] was synthesized according to the literature and resolved by preparative chiral HPLC analysis (OD column, 55 mm ID, *n*-hexane/*i*-PrOH [95:5], flow rate = 30 mL min^{-1}, 2 bar, $t_{R\text{-}(-)}$ = 17 min, $t_{S\text{-}(+)}$ = 23 min), (Chiralcel OD column, *n*-hexane/*i*-PrOH [95:5], flow rate = 1 mL min^{-1}, $t_{R\text{-}(-)}$ = 5.9 min, $t_{S\text{-}(+)}$ = 7.5 min). Diethyl carbamate **9**[8] and *tert*-butyl-oxazoline **11**[38] were synthesized according to published procedures.

(−)-(S,4S_p,13R_p)-4-Hydroxy-13-(4-isopropyloxazolin-2-yl)[2.2]paracyclophane (1a)

t-BuLi (1.8 M solution in *n*-pentane, 2.0 mL, 3.59 mmol) was added dropwise to a solution of bromide **4a** (0.57 g, 1.43 mmol) in a mixture of Et_2O (12.5 mL) and THF (3.7 mL) at −78 °C to give an orange solution. After stirring for 2 h, $B(OMe)_3$ (0.24 mL, 2.14 mmol) was added dropwise. The solution was allowed to warm to room temperature and stirred for 21 h. Aqueous NaOH solution (0.5 M, 0.7 mL, 0.36 mmol) followed by aqueous H_2O_2 solution (30% w/v, 0.6 mL, 5.36 mmol) were added and the mixture stirred for 3.5 h. Saturated NH_4Cl solution was added and the mixture shaken vigorously. The aqueous layer was separated and extracted with DCM (20 mL) and EtOAc (20 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated. Flash column chromatography, gradient elution (pentane: EtOAc, 19:1 to 9:1 to 8:2) gave the title compound as a pale yellow solid; yield: 0.36 g (75%); R_f (petroleum ether: EtOAc, 8:2): 0.15; mp 91.5–92.5 °C; $[\alpha]_D^{20}$: −165 (*c* 1.15, $CHCl_3$); ^1H NMR (300 MHz): δ = 6.87 (1H, d, J = 2.0 Hz, H-12), 6.51 (1H, dd, J = 7.9, 2.0 Hz, H-16), 6.40 (1H, d, J = 7.7 Hz, H-8), 6.38 (1H, d, J = 7.9 Hz, H-15), 6.21 (1H, dd, J = 7.7, 1.7 Hz, H-7), 5.80 (1H, d, J = 1.7 Hz, H-5), 4.38 (1H, m, OC*H*H), 4.07 (2H, m, NC*H*, OCH*H*), 3.62 (1H, ddd, J = 12.9, 9.9, 4.5 Hz), 3.48 (1H, ddd, J = 12.9, 10.1, 2.5 Hz), 3.06–2.84 (5H, m), 2.66 (1H, ddd, J = 12.9, 10.4, 4.5 Hz), 1.83 [1H, m, C*H*(CH_3)$_2$], 1.07 (3H, d, J = 6.7 Hz, CH_3), 0.95 (3H, d, J = 6.7 Hz, CH_3); ^{13}C NMR (75 MHz): δ = 166.9, 156.3, 141.1, 140.0, 138.9, 135.4 (2 C, s), 134.6, 132.4, 128.1, 126.7, 125.4, 124.7, 72.6 (N*C*H), 70.9 (O*C*H$_2$), 34.8, 34.6, 32.8 [*C*H(CH_3)$_2$], 32.4, 31.1, 19.2 (*C*H$_3$), 18.4 (*C*H$_3$); IR ($CHCl_3$): ν_{max} = 1640 cm^{-1} (C=N); MS (EI): *m/z* (%) = 336 (29), 335 (M^+, 100), 320 (M^+−Me, 8), 292 (M^+−*i*-Pr, 18), 217 (7), 216 (51), 215 [$CH_2C_6H_4$(oxazoline)CH_2^+, 92], 214 (38), 172 (13), 159 (14), 147 (11), 131 (20), 130 (9), 121 (12), 120 (11), 103 (12), 91 (14); HR-MS: *m/z* = 335.1885, $C_{22}H_{25}NO_2$ requires 335.1885.

(+)-(S,4R_p,13S_p)-4-Hydroxy-13-(4-isopropyloxazolin-2-yl)[2.2]paracyclophane (1b)

Treatment of bromide **4b** (0.91 g, 2.28 mmol) according to the procedure for the synthesis of **1a** gave the title compound as a pale yellow solid; yield: 0.54 g (71%); R_f (petroleum ether:EtOAc, 8:2): 0.25; mp 108.5–110.0 °C; $[\alpha]_D^{20}$: +91 (*c* 1.23, $CHCl_3$); ^1H NMR (300 MHz): δ = 7.00 (1H, d, J = 1.9 Hz, H-12), 6.52 (1H, dd, J = 8.0, 1.9 Hz, H-16), 6.42 (1H, d, J = 7.7 Hz, H-8), 6.39 (1H, d, J = 8.0 Hz, H-15), 6.23 (1H, dd, J = 7.7, 1.5 Hz, H-7), 5.73 (1H, d, J = 1.5 Hz, H-5), 4.33

(1H, m, OC*H*H), 4.08 (2H, m, NC*H*, OCH*H*), 3.87 (1H, ddd, $J=13.4$, 9.9, 4.9 Hz), 3.50 (1H, ddd, $J=13.4$, 9.9, 2.7 Hz), 3.06–2.84 (5H, m), 2.65 (1H, ddd, $J=13.1$, 10.4, 4.9 Hz), 1.90 [1H, m, C*H*$(CH_3)_2$], 1.05 (3H, d, $J=6.7$ Hz, CH_3), 0.94 (3H, d, $J=6.7$ Hz, CH_3); ^{13}C NMR (75 MHz): $\delta=165.9$, 155.7, 140.9, 140.3, 138.3, 135.4, 134.7, 134.5, 132.2, 127.0, 126.1, 124.6, 123.1, 71.6 (N*C*H), 69.8 (O*C*H$_2$), 34.5, 34.3, 32.5 [*C*H$(CH_3)_2$], 32.2, 30.8, 18.7 (*C*H$_3$), 17.8 (*C*H$_3$); IR (KBr): $\nu_{max}=1629$ cm^{-1} (C=N); MS (EI): *m/z* (%) = 336 (27), 335 (M^+, 100), 320 (M^+-Me, 7), 292 (M^+-i-Pr, 15), 217 (5), 216 (39), 215 [$CH_2C_6H_4$(oxazoline)CH_2^+, 65], 214 (27), 172 (8), 159 (10), 147 (7), 131 (11), 130 (4), 121 (8), 120 (6), 103 (6), 91 (5); HR-MS: *m/z* = 335.1885, $C_{22}H_{25}NO_2$ requires 335.1885.

(+)-(*S*,4*R*$_p$,12*R*$_p$)- and (−)-(*S*,4*S*$_p$,12*S*$_p$)-4-Hydroxy-12-(4-isopropyloxazolin-2-yl)[2.2]paracyclophane (2a and 2b)

Treatment of the diastereomeric mixture of bromides **7** (1.69 g, 4.25 mmol) according to the procedure for the synthesis of **1a** gave an inseparable mixture of the title compounds as a white solid; yield: 0.89 g (63%).

(+)-(*S*,4*R*$_p$,12*R*$_p$)-4-Benzyloxy-12-(4-isopropyloxazolin-2-yl)[2.2]paracyclophane (8a)

A solution of the diastereomeric mixture of phenols **2a** and **2b** (0.80 g, 2.38 mmol) in DMF (6.1 mL) was added dropwise to NaH (55% w/w suspension in mineral oil, 0.11 g, 2.59 mmol) in DMF (4.2 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 1 h. It was then cooled to 0 °C and BnBr (0.34 mL, 2.83 mmol) was added followed by Bu_4NI. After warming to room temperature, the mixture was stirred for 2 h. Water (15 mL) and DCM (20 mL) were added and the mixture shaken vigorously. The organic phase was then separated, washed with brine (15 mL), dried over Na_2SO_4, filtered and concentrated. Flash column chromatography, gradient elution (petroleum ether:EtOAc, 19:1 to 14:1 to 9:1) gave the title compound as a colourless oil; yield: 0.35 g (35%); R_f (petroleum ether:EtOAc, 9:1): 0.49; $[\alpha]_D^{20}$: +19 (*c* 1.10, $CHCl_3$); ^{1}H NMR (400 MHz): $\delta=7.52$ (2H, m, *Ph*), 7.44–7.32 (4H, m, *Ph*, H-13), 6.54 (1H, d, $J=8.0$ Hz, H-16), 6.49 (1H, dd, $J=8.0$, 1.1 Hz, H-15), 6.47 (1H, d, $J=7.7$ Hz, H-8), 6.31 (1H, br. d, $J=7.7$ Hz, H-7), 5.98 (1H, br. s, H-5), 5.33 (1H, d, $J=11.0$ Hz, C*H*HPh), 4.67 (1H, d, $J=11.0$ Hz, CH*H*Ph), 4.36 (1H, m, OC*H*H), 4.16–4.03 (3H, m, NC*H*, OCH*H*, C*H*HCH$_2$), 3.49 (1H, ddd, $J=13.2$, 8.2, 1.9 Hz), 3.12–3.01 (3H, m), 2.93 (1H, ddd, $J=12.9$, 9.9, 6.9 Hz), 2.80 (1H, ddd, $J=12.6$, 10.2, 6.9 Hz), 2.57 (1H, ddd, $J=12.9$, 9.9, 7.4 Hz), 1.85 [1H, m, C*H*$(CH_3)_2$], 1.07 (3H, d, $J=6.8$ Hz, CH_3), 0.97 (3H, d, $J=6.8$ Hz, CH_3); ^{13}C NMR (100 MHz): $\delta=163.6$, 156.7, 142.5, 140.1, 139.8, 137.7, 135.5, 135.2, 134.7, 129.9, 128.4 (2 C, s), 127.7, 127.6 (2 C, s), 127.6, 127.4, 123.7, 115.5, 73.3 (N*C*H), 69.6 (O*C*H$_2$), 68.3 (*C*H$_2$Ph), 35.7, 34.7, 33.4, 33.2 [*C*H$(CH_3)_2$], 32.2, 19.4 (*C*H$_3$), 18.7 (*C*H$_3$); IR ($CHCl_3$): $\nu_{max}=1639$ cm^{-1} (C=N); MS (EI): *m/z* (%) = 426 (36), 425 (M^+, 100), 382 (M^+-i-Pr, 10), 334 (20), 318 (5), 306 (6), 248 (5), 216 (13), 215 [$CH_2C_6H_4$(oxazoline)CH_2^+, 65], 214 (20), 91 (24); HR-MS: *m/z* = 425.2355, $C_{29}H_{31}NO_2$ requires 425.2355.

(−)-(*S*,4*S*$_p$,12*S*$_p$)-4-Benzyloxy-12-(4-isopropyloxazolin-2-yl)[2.2]paracyclophane (8b)

Further elution gave the title compound as a white solid; yield: 0.39 g (38%); R_f (petroleum ether:EtOAc, 9:1): 0.43; mp 103.5–105.0 °C; $[\alpha]_D^{20}$: −112 (*c* 0.91, $CHCl_3$); ^{1}H NMR (400 MHz): $\delta=7.46$ (2H, m, *Ph*), 7.38–7.27 (4H, m, *Ph*, H-13), 6.49 (1H, d, $J=8.0$ Hz, H-16), 6.42 (1H, dd, $J=8.0$, 1.7 Hz, H-15), 6.40 (1H, d, $J=7.7$ Hz, H-8), 6.25 (1H, dd, $J=7.7$, 1.4 Hz, H-7), 5.82 (1H, d, $J=1.4$ Hz, H-5), 5.14 (1H, d, $J=11.0$ Hz, C*H*HPh), 4.58 (1H, dd, $J=11.0$, CH*H*Ph), 4.29 (1H, m, OC*H*H), 4.21 (1H, ddd, $J=12.1$, 9.6, 1.4 Hz), 4.08–3.98 (2H, m, NC*H*, OCH*H*), 3.41 (1H, ddd, $J=12.9$, 8.8, 2.2 Hz), 3.00 (3H, m), 2.90 (1H, ddd, $J=12.6$, 9.6, 6.9 Hz), 2.75 (1H, ddd, $J=12.4$, 10.2, 6.9 Hz), 2.50 (1H, ddd, $J=13.2$, 10.2, 7.4 Hz), 1.82 [1H, m, C*H*$(CH_3)_2$], 1.06 (3H, d, $J=6.9$ Hz, CH_3), 0.97 (3H, d, $J=6.6$ Hz, CH_3); ^{13}C NMR (100 MHz): $\delta=162.8$, 156.5, 142.3, 139.91, 139.89, 137.5, 135.5, 135.1, 134.5, 129.8, 128.3 (2 C, s), 127.51 (2 C, s), 127.46, 127.4, 127.2, 123.6, 115.3, 73.0 (N*C*H), 69.2 (O*C*H$_2$), 68.1 (*C*H$_2$Ph), 35.5, 34.4, 33.4 [*C*H$(CH_3)_2$], 33.2, 32.0, 19.1 (*C*H$_3$), 18.8 (*C*H$_3$); IR (KBr): $\nu_{max}=1640$ cm^{-1} (C=N); MS (EI): *m/z* (%) = 426 (36), 425 (M^+, 100), 382 (M^+-i-Pr, 10), 334 (19), 318 (5), 306 (5), 248 (4), 216 (11), 215 [$CH_2C_6H_4$(oxazoline)CH_2^+, 55], 214 (17), 91 (23); HR-MS: *m/z* = 425.2355, $C_{29}H_{31}NO_2$ requires 425.2355.

(+)-(*S*,4*R*$_p$,12*R*$_p$)-4-Hydroxy-12-(4-isopropyloxazolin-2-yl)[2.2]paracyclophane (2a)

Me_3SiI (0.21 mL, 1.45 mmol) was added to a solution of benzyloxyparacyclophane **8a** (0.33 g, 0.73 mmol) in DCM (6.5 mL). The resulting mixture was stirred for 19 h. TLC showed incomplete conversion so an extra equivalent of Me_3SiI (0.10 mL, 0.73 mmol) was added and the mixture stirred for a further 18 h. The reaction was quenched with MeOH (0.15 mL, 3.63 mmol), evaporated and dried under vacuum. The residue was dissolved in EtOAc (6.5 mL), aqueous AcOH solution (10% w/v, 4.4 mL, 7.25 mmol) was added and the mixture stirred rapidly for 6 h. Saturated aqueous $NaHCO_3$ solution (10 mL) was added and the mixture shaken vigorously. The aqueous phase was separated and extracted with EtOAc (3×10 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated. Flash column chromatography, gradient elution (petroleum ether:EtOAc, 8:2 to 6:4) gave the title compound as a pale orange solid; yield: 0.22 g, 92%); R_f (petroleum ether:EtOAc, 8:2): 0.21; mp 40.0–42.0 °C; $[\alpha]_D^{20}$: +2 (*c* 1.57, $CHCl_3$); ^{1}H NMR (400 MHz): $\delta=7.43$ (1H, d, $J=1.9$ Hz, H-13), 6.57 (1H, d, $J=7.8$ Hz, H-16), 6.49 (1H, dd, $J=7.8$, 1.9 Hz, H-15), 6.43 (1H, d, $J=7.7$ Hz, H-8), 6.27 (1H, dd, $J=7.7$, 1.5 Hz, H-7), 5.97 (1H, d, $J=1.5$ Hz, H-5), 4.48 (1H, dd, $J=9.6$, 8.2 Hz, OC*H*H), 4.18 (1H, t, $J=8.8$ Hz, OCH*H*), 4.08 (1H, m, NC*H*), 3.48 (1H, ddd, $J=13.1$, 10.2, 3.9 Hz), 3.26 (1H, ddd, $J=13.5$, 9.9, 5.3 Hz), 3.19 (1H, ddd, $J=12.9$, 10.2, 3.9 Hz), 3.02 (1H, ddd, $J=13.5$, 10.2, 3.3 Hz), 2.98–2.86 (2H, m), 2.78 (1H, ddd, $J=13.2$, 10.2, 5.3 Hz), 2.61 (1H, ddd, $J=13.1$, 10.4, 4.1 Hz), 1.94 [1H, m, C*H*$(CH_3)_2$], 1.15 (3H, d, $J=6.9$ Hz, CH_3), 1.03 (3H, d, $J=6.6$ Hz, CH_3); ^{13}C NMR (100 MHz): $\delta=167.7$, 154.8, 141.2, 140.2, 138.8, 136.0, 134.1, 133.8, 129.0, 128.7, 127.8, 125.4, 120.1, 72.0 (N*C*H), 71.1 (O*C*H$_2$), 34.8, 34.0, 33.6, 32.9 [*C*H$(CH_3)_2$], 30.0, 19.5 (*C*H$_3$), 18.6 (*C*H$_3$); IR ($CHCl_3$): $\nu_{max}=1634$ cm^{-1} (C=

N); MS (EI) *m/z* (%) = 336 (26), 335 (M^+, 100), 320 (M^+−Me, 3), 292 (M^+−*i*-Pr, 10), 217 (10), 216 (68), 215 [$CH_2C_6H_4$(oxazoline)CH_2^+, 80], 214 (18), 159 (8), 147 (7), 131 (11); HRMS: *m/z* = 335.1884, $C_{22}H_{25}NO_2$ requires 335.1885.

(−)-(*S*,4*S*$_p$,12*S*$_p$)-4-Hydroxy-12-(4-isopropyloxazolin-2-yl)[2.2]paracyclophane (2b)

Treatment of benzyloxyparacyclophane **8b** (0.38 g, 0.82 mmol) according to the procedure for the synthesis of **2a** gave the title compound as a pale orange solid; yield: 0.18 g (67%); R_f (petroleum ether:EtOAc, 8:2): 0.20; mp 48.0–50.0 °C; $[\alpha]_D^{20}$: −44 (*c* 1.34, $CHCl_3$); ^{1}H NMR (400 MHz): δ = 7.47 (1H, d, *J* = 1.7 Hz, H-13), 6.57 (1H, d, *J* = 8.0 Hz, H-16), 6.49 (1H, dd, *J* = 8.0, 1.4 Hz, H-15), 6.42 (1H, d, *J* = 7.7 Hz, H-8), 6.27 (1H, dd, *J* = 7.7, 1.4 Hz, H-7), 5.88 (1H, d, *J* = 1.4 Hz, H-5), 4.47 (1H, m, OC*H*H), 4.19 (2H, m, OCH*H*, NC*H*), 3.48 (1H, ddd, *J* = 12.9, 10.2, 3.8 Hz), 3.38 (1H, m), 3.19 (1H, ddd, *J* = 12.9, 10.2, 4.1 Hz), 2.99 (1H, ddd, *J* = 13.5, 10.2, 3.6 Hz), 2.96–2.86 (2H, m), 2.79 (1H, m), 2.61 (1H, ddd, *J* = 13.2, 10.7, 4.1 Hz), 1.87 [1H, m, C*H*(CH_3)$_2$], 1.05 (3H, d, *J* = 6.6 Hz, C*H*$_3$), 0.98 (3H, d, *J* = 6.6 Hz, C*H*$_3$); ^{13}C NMR (100 MHz): δ = 167.3, 154.9, 141.3, 140.3, 139.1, 135.9, 134.1, 133.9, 129.1, 128.7, 127.7, 125.2, 120.1, 71.2 (N*C*H), 70.8 (O*C*H$_2$), 34.8, 34.0, 33.7, 33.0 [*C*H(CH_3)$_2$], 30.1, 18.6 (*C*H$_3$), 18.3 (*C*H$_3$); IR ($CHCl_3$): ν_{max} = 1632 cm^{-1} (C=N); MS (EI): *m/z* (%) = 336 (27), 335 (M^+, 100), 320 (M^+−Me, 3), 292 (M^+−*i*-Pr, 9), 217 (10), 216 (66), 215 [$CH_2C_6H_4$(oxazoline)CH_2^+, 81], 214 (15), 159 (7), 147 (6), 131 (12); HR-MS: *m/z* = 335.1885, $C_{22}H_{25}NO_2$ requires 335.1885.

(−)-(*S*,4*S*$_p$,5*R*$_p$)-4-Hydroxy-5-(4-isopropyloxazolin-2-yl)[2.2]paracyclophane (3a)

Amide **10a** (0.99 g, 2.81 mmol), PPh_3 (2.02 g, 7.72 mmol), CCl_4 (0.75 mL, 7.72 mmol) and Et_3N (1.08 mL, 7.72 mmol) were dissolved in MeCN (59 mL) and the solution was stirred for 28 h. DCM (175 mL) was then added and the solution washed with brine (2 × 130 mL), dried over Na_2SO_4, filtered and concentrated. Flash column chromatography (pentane:EtOAc, 9:1) gave the title compound as a white solid; yield: 0.91 g (96%); R_f (petroleum ether:EtOAc, 8:2): 0.67; mp 123.5–125.0 °C; $[\alpha]_D^{20}$: −286 (*c* 0.95, $CHCl_3$); ^{1}H NMR (400 MHz): δ = 13.34 (1H, br. s, O*H*), 6.87 (1H, dd, *J* = 7.7, 1.7 Hz), 6.56 (1H, dd, *J* = 7.7, 1.7 Hz), 6.49 (1H, d, *J* = 7.7 Hz, H-8), 6.40 (1H, dd, *J* = 7.7, 1.7 Hz), 6.30 (1H, dd, *J* = 7.7, 1.7 Hz), 6.21 (1H, d, *J* = 7.7 Hz, H-7), 4.38 (1H, t, *J* = 8.5 Hz, OC*H*H), 4.11 (1H, t, *J* = 8.5 Hz, OCH*H*), 4.03 (1H, m, NC*H*), 3.86 (1H, m), 3.47 (1H, ddd, *J* = 12.9, 10.2, 2.8 Hz), 3.12 (2H, m), 3.00 (1H, ddd, *J* = 12.6, 10.7, 2.5 Hz), 2.70 (2H, m), 2.59 (1H, ddd, *J* = 13.2, 10.7, 5.2 Hz), 1.88 [1H, m, C*H*(CH_3)$_2$], 1.17 (3H, d, *J* = 6.6 Hz, C*H*$_3$), 1.06 (3H, d, *J* = 6.9 Hz, C*H*$_3$); ^{13}C NMR (100 MHz): δ = 166.5, 159.8, 141.8, 139.6, 138.2, 136.8, 133.2, 131.7, 129.8, 127.6, 126.8, 125.6, 111.8, 70.0 (N*C*H), 69.8 (O*C*H$_2$), 36.3, 35.0, 33.8, 33.3 [*C*H(CH_3)$_2$], 30.5, 19.2 (*C*H$_3$), 19.1 (*C*H$_3$); IR (KBr): ν_{max} = 1612 cm^{-1} (C=N); MS (EI): *m/z* (%) = 336 (14), 335 (M^+, 52), 292 (M^+−*i*-Pr, 1), 232 (17), 231 [$CH_2C_6H_4$(oxazoline)(OH)CH_2^+, 100], 188 (9), 162 (4), 146 (6), 104 ($CH_2C_6H_4CH_2^+$, 12); HR-MS: *m/z* = 335.1885, $C_{22}H_{25}NO_2$ requires 335.1885.

(+)-(*S*,4*R*$_p$,5*S*$_p$)-4-Hydroxy-5-(4-isopropyloxazolin-2-yl)[2.2]paracyclophane (3b)

Treatment of amide **10b** (0.76 g, 2.14 mmol) according to the procedure for the synthesis of **3a** gave the title compound as white solid; yield: 0.68 g (94%); R_f (petroleum ether:EtOAc, 8:2): 0.75; mp 96.0–98.0 °C; $[\alpha]_D^{20}$: +251 (*c* 1.28, $CHCl_3$); ^{1}H NMR (300 MHz): δ = 13.36 (1H, br. s, O*H*), 6.90 (1H, dd, *J* = 7.9, 1.7 Hz), 6.56 (1H, dd, *J* = 7.9, 1.7 Hz), 6.50 (1H, d, *J* = 7.7 Hz, H-8), 6.40 (1H, dd, *J* = 7.9, 1.7 Hz), 6.29 (1H, dd, *J* = 7.9, 1.7 Hz), 6.22 (1H, d, *J* = 7.7 Hz, H-7), 4.43 (1H, dd, *J* = 8.7, 7.5 Hz, OC*H*H), 4.15 (1H, m, NC*H*), 4.08 (1H, t, *J* = 7.5 Hz, OCH*H*), 3.87 (1H, m), 3.47 (1H, ddd, *J* = 13.1, 10.1, 2.7 Hz), 3.13 (2H, m), 3.00 (1H, ddd, *J* = 12.9, 10.4, 2.7 Hz), 2.71 (2H, m), 2.60 (1H, ddd, *J* = 13.1, 10.6, 5.2 Hz), 1.74 [1H, m, C*H*(CH_3)$_2$], 0.97 (3H, d, *J* = 6.7 Hz, C*H*$_3$), 0.92 (3H, d, *J* = 6.7 Hz, C*H*$_3$); ^{13}C NMR (75 MHz): δ = 166.5, 159.9, 142.1, 139.7, 138.3, 137.0, 133.3, 131.8, 130.0, 127.7, 127.1, 125.7, 111.8, 70.0 (N*C*H), 69.6 (O*C*H$_2$), 36.2, 35.0, 33.7, 33.0 [*C*H(CH_3)$_2$], 30.5, 18.5 (*C*H$_3$), 18.4 (*C*H$_3$); IR ($CHCl_3$): ν_{max} = 1612 cm^{-1} (C=N); MS (EI): *m/z* (%) = 336 (14), 335 (M^+, 51), 292 (M^+−*i*-Pr, 1), 232 (16), 231 [$CH_2C_6H_4$(oxazoline)(OH)CH_2^+, 100], 216 (6), 188 (9), 162 (4), 146 (6), 104 ($CH_2C_6H_4CH_2^+$, 9); HRMS: *m/z* = 335.1886, $C_{22}H_{25}NO_2$ requires 335.1885.

(−)-(*S*,4*R*$_p$,13*S*$_p$)-4-Bromo-13-(4-*tert*-butyloxazolin-2-yl)[2.2]paracyclophane (12)

A solution (2 mL) of bromine (0.14 mL, 2.71 mmol) in DCM (29 mL) was added to iron powder (15 mg, 0.26 mmol) and stirred in the dark for 40 min. To this, a solution of oxazoline **11** (0.75 g, 2.26 mmol) in DCM (44 mL) was added. The mixture was then heated to reflux and the remaining bromine solution added dropwise. Reflux was continued for 15 h after which time the mixture was washed with saturated aqueous $NaHCO_3$ solution (2 × 60 mL) and brine (60 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (petroleum ether:EtOAc, 9:1) gave first the starting material (0.29 g, 38%) and then the title compound as a white solid; yield: 0.31 g (33%); R_f (petroleum ether:EtOAc, 8:2): 0.24; mp 163.0–164.0 °C; $[\alpha]_D^{20}$: −98 (*c* 0.93, $CHCl_3$); ^{1}H NMR (300 MHz): δ = 7.18 (1H, d, *J* = 1.5 Hz, H-12), 6.61–6.50 (5H, m), 4.47 (1H, ddd, *J* = 13.4, 10.4, 4.7 Hz, H-1a), 4.36 (1H, dd, *J* = 10.1, 8.5 Hz, OC*H*H), 4.17 (1H, t, *J* = 8.5 Hz, OCH*H*), 4.00 (1H, m, NC*H*), 3.51 (1H, ddd, *J* = 13.1, 9.9, 3.2 Hz, H-2a), 3.11–2.96 (5H, m), 2.91 (1H, ddd, *J* = 13.1, 10.4, 4.5 Hz, H-2b), 1.04 [9H, s, C(C*H*$_3$)$_3$]; ^{13}C NMR (75 MHz): δ = 163.7 (*C*=N), 141.1, 140.1, 138.9, 138.3, 136.1, 136.0, 134.8, 134.6, 132.0 (C-12), 131.2, 126.9, 126.7, 76.6 (N*C*H), 67.8 (O*C*H$_2$), 35.6 (C-2), 34.8, 34.4, 34.2 [*C*(CH_3)$_3$], 32.9 (C-1), 26.6 [C(*C*H$_3$)$_3$]; IR (KBr): ν_{max} = 1637 cm^{-1} (C=N); MS (EI): *m/z* (%) = 414 (5), 413 (M^+, 23), 412 (12), 411 (M^+, 29), 398 (M^+−Me, 2), 396 (M^+−Me, 3), 356 (M^+−*t*-Bu, 11), 355 (10), 354 (M^+−*t*-Bu, 14), 230 (15), 229 [$CH_2C_6H_3$(oxazoline)CH_2^+, 100], 228 (14), 172 (10), 147 (7); anal. found: C 67.21, H 6.44, N 3.23; $C_{23}H_{26}BrNO$ requires: C 66.99, H 6.35, N 3.40.

(+)-(*S*,4R_p,13S_p)-4-Hydroxy-13-(4-*tert*-butyloxazolin-2-yl)[2.2]paracyclophane (13)

Treatment of bromide **12** (0.29 g, 0.71 mmol) according to the procedure for the synthesis of **1a** gave the title compound as a white solid; yield: 0.19 g (77%); R_f (petroleum ether:DCM:EtOAc, 5:3:2): 0.37; mp 134.0–135.5 °C; $[\alpha]_D^{20}$: +108 (*c* 0.99, $CHCl_3$); ^{1}H NMR (400 MHz): δ = 6.94 (1H, d, *J* = 1.8 Hz, H-12), 6.75 (1H, br. s, O*H*), 6.56 (1H, dd, *J* = 7.9, 1.8 Hz, H-16), 6.46 (1H, d, *J* = 7.7 Hz, H-8), 6.44 (1H, d, *J* = 7.9 Hz, H-15), 6.29 (1H, dd, *J* = 7.7, 1.8 Hz, H-7), 5.79 (1H, d, *J* = 1.8 Hz, H-5), 4.38 (1H, dd, *J* = 10.2, 8.8 Hz, OC*H*H), 4.24 (1H, br. t, *J* = 8.8 Hz, OCH*H*), 4.09 (1H, dd, *J* = 10.2, 7.7 Hz, NC*H*), 3.75 (1H, ddd, *J* = 13.2, 10.0, 5.2 Hz, H-1a), 3.51 (1H, ddd, *J* = 13.2, 10.0, 2.5 Hz, H-2a), 3.10–2.93 (5H, m), 2.67 (1H, ddd, *J* = 13.2, 10.4, 5.2 Hz, H-2b), 1.02 [9H, s, C(*CH*$_3$)$_3$]; ^{13}C NMR (100 MHz): δ = 166.3, 155.8, 141.0, 140.0, 138.5, 135.4 (C-15), 135.0 (C-16), 134.6 (C-8), 132.2 (C-12), 127.8, 126.9, 125.1 (C-7), 124.3 (C-5), 75.6 (N*C*H), 69.1 (O*C*H$_2$), 34.9, 34.6, 34.2 [*C*(CH$_3$)$_3$], 32.1 (C-1), 31.5 (C-2), 26.0 [C(*C*H$_3$)$_3$)]; IR (KBr): ν_{max} = 1633 cm^{-1} (C=N); MS (EI): *m/z* (%) = 350 (23), 349 (M$^+$, 100), 334 (M$^+$−Me, 8), 293 (12), 292 (M$^+$−*t*-Bu, 36), 231 (32), 230 (48), 229 [CH$_2$C$_6$H$_4$(oxazoline)CH$_2^+$, 76], 228 (33), 173 (12), 172 (20), 159 (6), 147 (16), 131 (8), 130 (13), 121 (12), 120 (11), 103 (7), 91 (6); HR-MS: *m/z* = 349.2041, $C_{23}H_{27}NO_2$ requires 349.2042.

Procedure for the Addition of Diethylzinc to Benzaldehyde[36]

The appropriate phenol (0.025 mmol) was dissolved in toluene (2.0 mL) and diethylzinc (1.0 M solution in heptane, 1.10 mL, 1.10 mmol) was added. The mixture was stirred for 20 min and then benzaldehyde was added. The reaction was monitored by TLC [R_f (petroleum ether:EtOAc, 8:2): benzaldehyde 0.53, product 0.32] until complete. Aqueous HCl (1 M, 5 mL) was then added and the mixture shaken vigorously. The aqueous phase was separated and extracted with DCM (2×10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (pentane:Et$_2$O, 8:2) gave 1-phenyl-1-propanol as a colourless oil. The *ee* was determined by HPLC analysis [(Chiralcel OB column, heptane:*i*-PrOH, 100:0.5), flow rate = 1.0 mL min^{-1}, t_S = 17.5 min, t_R = 21.6 min].

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