A New Planar Chiral Bipyridine-Ligand: Pyrid-2-yl[2](1,4)benzeno[2](5,8)quinolino-phane

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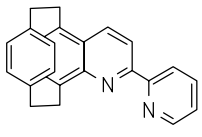
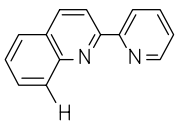
Abstract. The synthesis of the new planar chiral heterocyclic nitrogen ligand pyrid-2-yl[2](1,4)benzeno[2](5,8)quinolino-phane (**1)** with [2.2]paracyclophane-skeleton is described. The enantiomeric resolution is achieved by HPLC. The CD-spectra of **1** and of its chiral quinoline precursor are recorded. The enantiomerically pure title compound **1** is used in copper-catalyzed asymmetric cyclopropanation of styrene and in asymmetric iridium-catalyzed transfer-hydrogenation of acetophenone.

In recent years, homogeneous asymmetric catalysis with metal complexes has been a very fast developing field of research [1]. Most of the organic reactions in which prostereogenic compounds can be used, are now feasible under metal-complex-catalysis. The ligands used in these reactions, for the most part, possess phosphorous donor groups as coordination sites. Nitrogen ligands, not as numerous as their phosphorous counterparts, find more and more interest in the last few years, too [2]. Planar chirality generated by making use of the unique [2.2]paracyclophane skeleton, however, is very rare both in the field of phosphorous and nitrogen ligands [3]. Recently, we reported the synthesis and enantiomeric resolution of the first planar chiral 2,2'-bipyridine with [2.2]paracyclophane skeleton (**8**) and its use in asymmetric catalytic reactions [4].

To find out more about the opportunities, which this new lead structure for the design of chiral ligands offers, we now synthesized pyrid-2-yl[2](1,4)benzeno-[2](5,8)quinolinophane (**1**), a planar chiral analogue of 2-(pyrid-2'-yl)quinoline [5] (**2**).



1



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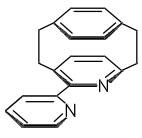

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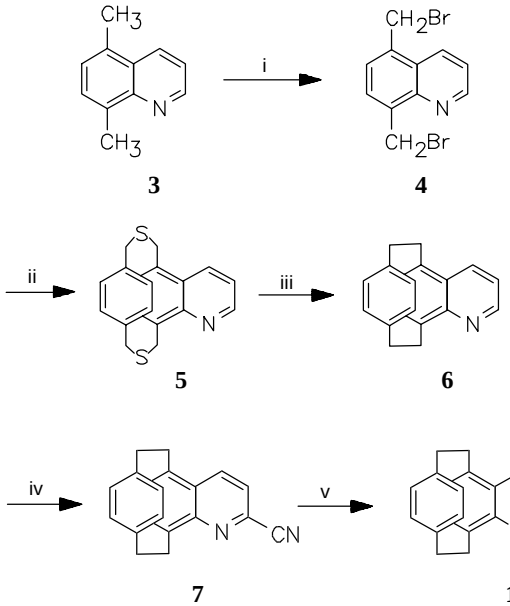
The synthesis of **1** proceeded *via* the NBS-bromination of 5,8-dimethylquinoline [6] (**3**) leading to the dibromide **4**. Cyclisation of **4** under high-dilution conditions with 1,4-bis(mercaptomethyl)benzene generated the new dithiaphane **5**, which was irradiated by UV (Hg, 180 W) in a thiophilic solvent ($P(OMe)_3$). By cyanation [7] of the reaction product, the planar chiral [2](1,4) benzeno[2](5,8)quinolinophane **6**, which has not been described in literature before, we obtained the nitrile **7**. With this key-compound in hand, we could synthesize the hitherto unknown title compound **1** in a one-step-procedure, by cobalt-catalyzed cyclisation with acetylene (Bönnemann-reaction) [8].



Scheme 1 Reagents and conditions: i, NBS, CCl_4, reflux, 7 h, 38%; ii, sol. A: **4** in EtOH, sol. B: 1,4-bis(mercaptomethyl)benzene (1 equiv.), KO*t*-Bu (2.3 equiv.) in EtOH (85%); Cs_2CO_3 in reaction mixture, reflux, 16h, 40%; iii, $P(OMe)_3$, hν (Hg, 180 W), r.t., 18h, 71%; iv, MCPBA (2 equiv.), CH_2Cl_2, r.t., 20h, then *N*,*N*-dimethylcarbamoyl chloride (1.3 equiv.), TMSCN (1.3 equiv.), CH_2Cl_2, r.t., 16h, 70%; v, cyclopentadienyl-1,5-cyclooctadiene-cobalt (4 equiv.), C_2H_2 (1.5 bar), toluene, 120 °C, 20 h, 36%.

  1436-9966/99/3410X-445 $ 17.50 + .50/0

The enantiomers of **1** and **6** were separated (baseline separation) by HPLC on a Daicel Chiralcel OD semi-preparative column (10 × 250 mm; **1**: ethanol, 1.5 mL/min, R_t = 25 and 32 min; **6**: *n*-hexane/ethanol = 95/5 v/v, 1.5 mL/min, R_t = 28 and 31 min). The resulting CD-spectra of the pure enantiomers are shown in Fig. 1

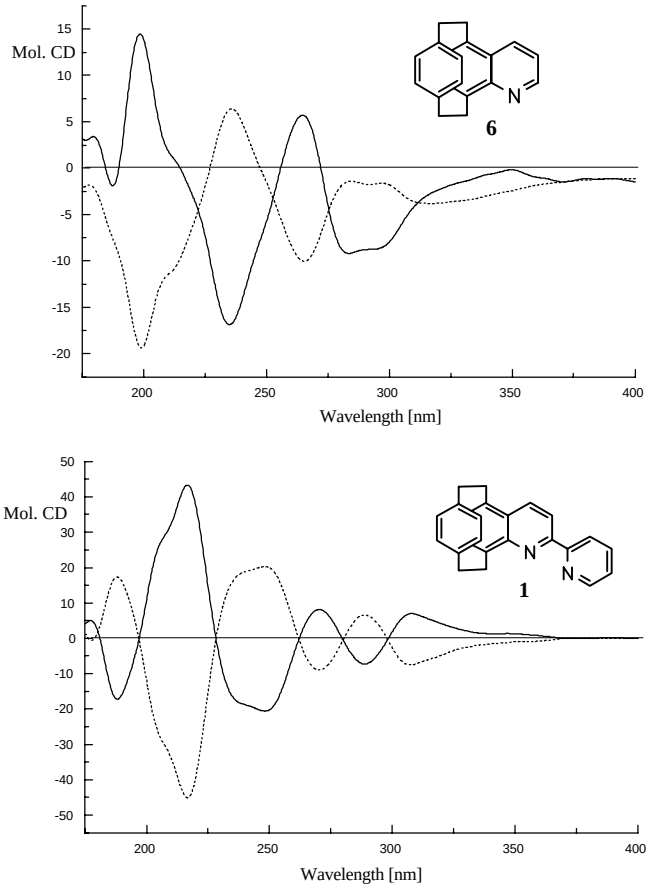


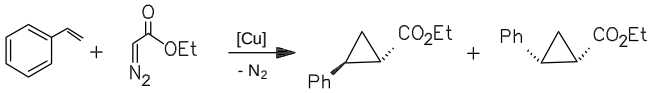
Figure 1 The circular dichroism spectra of the new planar chiral quinolinophanes **1** and **6**.

To test the effectiveness of **1** concerning asymmetric catalysis and to compare with ligand **8** we published earlier [4], we used **1** as chiral ligand in copper-catalyzed cyclopropanation of styrene with ethyl diazoacetate and iridium-catalyzed transfer-hydrogenation of acetophenone with 2-propanol. The results are summarized in tables 1 and 2.

As shown in table 2, the ligand **1** is practically inactive towards transfer-hydrogenation when performed at room temperature. This corresponds to the behaviour of many other ligands used in this reaction [9]. When the reaction mixture is heated to 80 °C, however, the reaction is strongly accelerated and must be stopped early enough, in order to produce some enantiomeric excess.

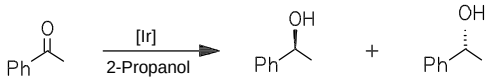
This is the difference between **1** and **8**: Ligand **8**, in which the π–π-interaction, typical for [2.2](1,4)phanes, directly influences the 2,2'-bipyridine-structure, shows a good activity towards transfer-hydrogenation even at room temperature. This finding could prove to be useful for the design of future ligands. Based upon the ligands **1** and **8**, which have proved the usefulness of our concept to combine the [2.2]paracyclophane- with the 2,2'-bipyridine-structure, it seems well worth now to optimize these new ligands by further substitution.

Table 1 Results of the asymmetric cyclopropanation with ligand **1**; for comparison, the results of ligand **8** are shown as well.



ligand	*trans*/*cis*-ratio	ee (%) *trans*	ee (%) *cis*
1	2.0 : 1	26	26
8	1.9 : 1	10	23

Table 2 Results of the asymmetric transfer hydrogenation with ligand **1**. The different temperature-dependence of ligands **1** and **8** is apparent.



ligand	reaction time (h), temperature	1-phenylethanol (%)	*ee* (%)
1	2, r.t.	8	–
	1, (80 °C)	93	23
	2, (80 °C)	97	20
	4, (80 °C)	97	18
8	2, r.t.	49	25
	4, r.t.	70	31
	16, r.t.	91	31

Experimental

5,8-Bis(bromomethyl)quinoline (**4**)

5,8-Dimethylquinoline (5.00 g, 0.032 mol) was dissolved in tetrachloromethane (120 mL). NBS (11.4 g, 0.064 mol) and benzoylperoxide (50 mg) were added, and the mixture was kept under reflux for 7 h. After cooling to r.t., the reaction mixture was washed with saturated $KHCO_3$-solution (50 mL each, 3×) and water (50 mL each, 4×). The organic layer was dried (Na_2SO_4), and the solvent was evaporated. The product was isolated by column chromatography (SiO_2; CH_2Cl_2; R_f = 0.8). A colourless solid was obtained (3.73 g, 38%) melting at 143 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 4.87 (s, 2H, C$\underline{H}_2$Br), 5.2 (s, 2H, C$\underline{H}_2$Br), 7.54 (d, J = 7.2 Hz, 1H, arom.), 7.56 (dd, J = 4.1 and 8.6 Hz, 1H, arom.), 7.76 (d, J = 7.2 Hz, 1H, arom.), 8.48 (dd, J = 1.6 and 8.6 Hz, 1H, arom.),

9.05 (dd, *J* = 1.6 and 4.2 Hz, 1H, arom.). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ/ppm = 29.67, 30.22 (CH_2Br), 122.06, 126.92, 128.11, 130.44, 132.82, 134.97, 138.0, 146.53, 150.3 (arom. C). – EI-MS 317, 315, 313 (3, 6, 3, $M^{\oplus}$), 236, 234 (82, 82, $[M-Br]^{\oplus}$), 155 (100, $[M-2Br]^{\oplus}$), 127 (14, $[M-2CH_2Br]^{\oplus}$);

2,15-Dithia[3](1,4)benzeno[3](5,8)quinolinophane (**5**)

Solution A: 1.58 g (5 mmol) of **4** in EtOH (270 mL); solution B: 0.86 g (5 mmol) of 1,4-bis(mercaptomethyl)benzene and 1.25 g (11 mmol) of potassium *tert*-butylate (KO*t*-Bu) in a mixture of EtOH and water (250 mL EtOH, 20 mL H_2O). Both solutions were dropped simultanously into a 2L-flask containing EtOH (1L) and Cs_2CO_3 (0.20 g). After that, the mixture was kept under reflux for 16 h, and then the solvent was evaporated *in vacuo* . The residue was dissolved in CH_2Cl_2 (150 mL), filtered and purified by column chromatography (SiO_2, CH_2Cl_2, R_f = 0.4). A colourless solid melting at 168 °C was obtained (0.65 g, 40%). – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 3.7–3.9 (m, 5H, C$\underline{H}_2$), 4.03 (d, *J* = 14.82 Hz, 1H, C$\underline{H}_2$), 4.27 (d, *J* = 14.75 Hz, 1H, C$\underline{H}_2$), 5.12 (d, *J* = 14.97 Hz, 1H, C$\underline{H}_2$), 6.09 (dd, *J* = 1.27 and 8.00 Hz, 1H, arom.), 6.18 (dd, *J* = 1.27 and 8.00 Hz, 1H, arom.), 6.84 (d, *J* = 7.12 Hz, 1H, arom.), 6.85 (d, *J* = 7.12 Hz, 1H, arom.), 7.01 (dd, *J* = 1.70 and 7.87 Hz, 1H, arom.), 7.18 (d, *J* = 7.29 Hz, 1H, arom.), 7.45 (dd, *J* = 4.25 and 8.45 Hz, 1H, arom.), 8.38 (dd, *J* = 1.80 and 8.42 Hz, 1H, arom.), 8.95 (dd, *J* = 1.80 and 4.25 Hz, 1H, arom.). – ^{13}C NMR (62.86 MHz, $CDCl_3$): δ/ppm = 33.22, 35.78, 38.14 (CH_2), 120.02, 126.28, 127.97, 128.34, 128.44, 128.61, 128.80, 130.33, 132.28, 132.37, 134.74, 134.93, 136.42, 146.91, 148.45 (arom. C). – GC-MS R_t = 11.86 min, *m/z* = 323. – EI-MS 325, 324, 323 (10, 21, 96, $M^{\oplus}$), 221, 220, 219 (8, 16, 95 $[M-C_8H_8]^{\oplus}$), 187, 186 (27, 41 $[M-C_8H_8S]^{\oplus}$), 156, 154 (100, 8 $[M-C_8H_8S_2]^{\oplus}$);

$C_{19}H_{17}NS_2$	Calcd.: C 70.55	H 5.30	N 4.33	S 19.82
(323.5)	Found: C 69.94	H 5.27	N 4.14	S 19.68.

[2](1,4)Benzeno[2](5,8)quinolinophane (**6**)

The sulfide **5** (0.87 g, 2.7 mmol) was suspended in $P(OMe)_3$ (300 mL) and irradiated with UV (Hg, 180 W) at r.t. for 18 h. The trimethyl phosphite was removed *in vacuo*, and **6** was isolated from the yellowish residue by flash chromatography (SiO_2; CH_2Cl_2/acetone = 10/1 v/v; R_f = 0.83). A colourless solid was obtained (0.5 g, 71 %), *m.p*. 125 °C. Enantiomeric resolution: Daicel Chiralcel OD semipreparative column, 10 × 250 mm (*n*-hexane/ethanol = 95/5 v/v, 1.5 mL/min, R_t = 28 and 31 min). – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 2.8 (m, 1H; C$\underline{H}_2$), 2.95-3.15 (m, 5H; C$\underline{H}_2$), 3.7 (m, 1H; C$\underline{H}_2$), 4.25 (m, 1H; C$\underline{H}_2$), 5.48 (d, *J* = 7.89 Hz, 1H, arom.), 5.65 (d, *J* = 7.89 Hz, 1H, arom.), 6.45 (s, 1H, arom.), 6.80 (d, *J* = 7.21 Hz, 1H, arom.), 6.98 (d, *J* = 7.21 Hz, 1H, arom.), 7.30 (dd, *J* = 4.24 and 8.33 Hz, 1H, arom.), 7.93 (dd, *J* = 1.72 and 8.33 Hz, 1H, arom.), 8.85 (dd, *J* = 1.69 and 4.25 Hz, 1H, arom.). – ^{13}C NMR (62.86 MHz, $CDCl_3$): δ/ppm = 31.76, 32.26, 34.56 (CH_2), 120.10, 127.13, 128.70, 130.40, 131.20, 132.26, 132.72, 132.81, 133.40, 137.59, 137.65, 138.27, 139.51, 147.68, 149.50 (arom. C). – GC-MS R_t = 9.43 min, *m/z* = 259. – HRMS ($C_{19}H_{17}N$); cald. 259.1361, found 259.1358;

$C_{19}H_{17}N$	Calcd.: C 87.99	H 6.61	N 5.40	
(259.4)	Found: [10]	[10]	N 5.24 [10].	

[2](1,4)Benzeno[2](5,8)quinolinophane-N-oxide

Compound **6** (0.20 g, 0.77 mmol) was dissolved in CH_2Cl_2 (15 mL) and *meta*-chloroperbenzoic acid (MCPBA) (0.3 g, 1.75 mmol) was added slowly. The reaction mixture was stirred at r.t. for 20 h. Then it was diluted with CH_2Cl_2 (10 mL), washed with 5% NaOH solution (12 mL each, 5×) and brine (12 mL each, 2×) and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue used without further purification.

2-Cyano[2](1,4)benzeno[2](5,8)quinolinophane (**7**)

To a solution of [2](1,4)benzeno-[2](5,8)quinolinophane-*N*-oxide (0.11 g, 0.41 mmol) in CH_2Cl_2 (10 mL) was slowly added *N*,*N*-dimethylcarbamoyl chloride (59 mg, 0.55 mmol) in CH_2Cl_2 (1 mL). After stirring for 30 min at r.t., TMSCN (60 mg, 0.6 mmol) in CH_2Cl_2 (1 mL) was added, and stirring was continued for 16 h. The reaction mixture was extracted with aq. $NaHCO_3$ (10 mL) and CH_2Cl_2 (20 mL each, 4×). The organic layer was washed with brine (30 mL each, 2×), dried over Na_2SO_4 and freed from the solvent *in vacuo*. **7** was isolated by column chromatography (SiO_2; CH_2Cl_2; R_f = 0.7) as a colourless solid melting at 117 °C (81 mg, 70%). – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 2.75 (m, 1H; C$\underline{H}_2$), 2.90–3.1 (m, 5H; C$\underline{H}_2$), 3.65 (m, 1H; C$\underline{H}_2$), 4.20 (m, 1H; C$\underline{H}_2$), 5.38 (dd, *J* = 1.48 and 8.37 Hz, 1H, arom.), 5.52 (dd, *J* = 1.48 and 8.12 Hz, 1H, arom.), 6.42 (s, 2H, arom.), 6.87 (d, *J* = 7.39 Hz, 1H, arom.), 6.99 (d, *J* = 7.14 Hz, 1H, arom.), 7.57 (d, *J* = 8.37 Hz, 1H, arom.), 8.00 (d, *J* = 8.37 Hz, 1H, arom.). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ/ppm = 31.26, 32.15, 34.44 (CH_2), 118.24, 122.67, 127.91, 129.26, 130.64, 130.93, 132.24, 132.90, 133.38, 133.91, 134.73, 137.59, 137.61, 139.36, 139.68, 149.82 (arom. C). – GC-MS R_t = 10.68 min, *m/z* = 284. – HRMS ($C_{20}H_{16}N_2$); calcd. 284.1315, found 284.1314;

$C_{20}H_{16}N_2$	Calcd.: C 84.48	H 5.67	N 9.85	
(284.4)	Found: C 83.92	H 5.13	N 9.62.	

2-Pyridyl[2](1,4)benzeno[2](5,8)quinolinophane (**1**)

An autoclave was charged with a solution of **7** (0.25 g, 0.88 mmol) and cyclopentadienyl-1,5-cyclooctadiene-cobalt (0.5 g, 2.2 mmol) in toluene (200 mL). The mixture was stirred at 120 °C under an acetylene pressure of 1.5 bar for 20 h, during which the acetylene pressure was kept constant. After cooling to r.t. the solvent was evaporated *in vacuo*, the residue dissolved in CH_2Cl_2 (75 mL), filtered (celite) and washed with water (30 mL). The solution was dried over Na_2SO_4 and purified by flash chromatography (SiO_2; CH_2Cl_2/MeOH/NH_3 = 100/10/1 v/v/v) . From this raw product **1** was isolated by column chromatography (SiO_2; CH_2Cl_2/MeOH = 100/1 v/v; R_f = 0.3) to obtain colourless crystals melting at 204 °C (107 mg, 36%). Enantiomeric resolution : Daicel Chiralcel OD semipreparative column, 10 × 250 mm (ethanol, 1.5 mL/min, R_t = 25 and 32 min). – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 2.83–2.95 (m, 1H; C$\underline{H}_2$), 3.00–3.20 (m, 5H; C$\underline{H}_2$), 3.70–3.82 (m, 1H; C$\underline{H}_2$), 4.35–4.50 (m, 1H; C$\underline{H}_2$), 5.55 (d, *J* = 7.83 Hz, 1H, arom.), 5.59 (d, *J* = 7.82 Hz, 1H, arom.), 6.48 (s, 2H, arom.), 6.82 (d, *J* = 7.04 Hz, 1H, arom.), 6.99 (d, *J* = 7.05 Hz, 1H, arom.), 7.40 (ddd, *J* = 1.18, 4.64 and 7.83 Hz, 1H, arom., Py.), 7.95 (ddd (pt), *J* = 1.57, 7.82 and 7.63 Hz, 1H, arom., Py.), 8.09 (d, *J* = 9.00 Hz, 1H, arom.),

8.56 (d, J = 8.61 Hz, 1H, arom.), 8.76–8.80 (m, 2H, arom., Py.). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ/ppm = 31.77, 32.22, 34.53, 34.82 (CH_2), 117.52, 121.81, 123.98, 127.52, 128.78, 130.37, 131.59, 132.18, 132.57, 133.46, 133.75, 137.56, 137.58, 137.64, 138.82, 139.39, 148.63, 148.93, 152.38, 156.41 (arom. C). – GC-MS R_t = 14.36 min, m/z = 336; HRMS ($C_{24}H_{20}N_2$): calcd. 336.1614, found 336.1620;

$C_{24}H_{20}N_2$	Calcd.: C 81.64	H 6.85	N 7.32
(336.4)	Found:		N 7.45 [10].

Copper(I)-catalyzed Cyclopropanation of Styrene with Compound 1

$Cu(OTf)_2$ (3.6 mg, 0.01 mmol) and **1** (6.7 mg, 0.02 mmol) were dissolved in CH_2Cl_2 (1 mL). After stirring for 30 min. the solution was filtered. Styrene (88 µL, 0.77 mmol) and phenylhydrazine (2 µL,0.02 mmol) were added, resulting in a deep blue solution. A solution of ethyl diazoacetate (88 µl, 0.84 mmol) in CH_2Cl_2(1 mL) was added dropwise over a period of 5 h. The reaction was then stirred for 15 hours at r. t.. Purification was achieved by flash chromatography (SiO_2; pentane/Et_2O = 10/1 v/v). To check the results of the asymmetric catalysis reaction, a GC-system with the following columns was used (Restek Rtx-1701, 30 m × 0.25 mm, 0.25 µm, 0.6 bar H_2, injector: 220 °C, detector: 320 °C temperature programme: 120–140 °C, 1 °C per min.; t_R = 14.5 min (*cis*-product), t_R = 16.9 min (trans-product). Chrompack β-CD-permethylated, 25 m × 0.25 mm, 0.5 bar, Injector: 200 °C, Detector: 300 °C. Temperature program: 90 –120 °C, 0.3 °C per min.; t_R = 68.6/**71.9** min (*cis*-product: *1S*, *2R*/***1R***, ***2S***), t_R = **75.5**/77.1 min (*trans*-product: ***1R***, ***2R***/*1S*, *2S*)). In the reaction 30% of the *trans*-product was formed with 26% *ee* (*1R*, *2R*) and 15% of the *cis*-product with 26% *ee* (*1R*, *2S*). This corresponds to a *trans/cis*- ratio of 66 : 33 or 2.0 : 1.

Transfer-Hydrogenation using [Ir(1)] as Catalyst

1 (7.1 mg, 0.021 mmol) and $[IrCODCl]_2$ (5.9 mg, 0.009 mmol) were placed in a sealed tube which was flushed with argon. After addition of isopropanol (4.5 mL) the resulting mixture was stirred for 1 h. The resulting orange solution was degassed. A 0.08M solution of sodium isopropylate in isopropanol (1.65 mL, 0.13 mmol) was added followed by the addition of acetophenone (103 µL, 0.9 mmol). The reaction mixture was degassed once again, and the tube was sealed. The reaction mixture was stirred at room temperature for 3 h, then 4 h at 80 °C. For GC-analysis an aliqout was taken and filtered through a small pad of basic alumina. (Macherey-Nagel LIPODEX A, 25 m × 0.25 mm, 0.5 bar, injector: 200 °C, detector: 300 °C. Temperature program: 60–90°C, 1°C pro min.; t_R = 15.3 min (acetophenone), t_R = 22.6 min (*S*-(–)-1-phenylethanol), t_R = 23.3 min (*R*-(+)-1-phenylethanol)). After 2 h at r.t., only 8% of 1-phenylethanol were formed. After 1 h at 80 °C, 93% 1-phenylethanol with 23% *ee*, after 2h at 80 °C 97% 1-phenylethanol with 20% ee and after 4h at 80 °C 97% 1-phenylethanol with 18% *ee* (*R*-(+)-enantiomer) were formed.

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[10] The values for carbon and hydrogen were generally obtained too – an effect known in literature for some types of compounds – although the purity of the substances has been proven unambigously by spectroscopic methods.

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